



Research paper

Structural and textural analysis of the precursor of Laponite synthesis: Enhanced hydrogen adsorption in a clay material

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ABSTRACT

This study focuses on a precursor of the synthesis of Laponite, named pre-Laponite. Pre-Laponite shares similar molecular formula and structure with Laponite, but it exhibits reduced long-range order. N₂ adsorption isotherms reveal that both materials possess comparable BET (N₂) specific surface areas and micropore-dominated textures consistent with slit-shaped pores. Notably, the study demonstrates a 1.4-fold improvement in hydrogen uptake for pre-Laponite compared to Laponite at −196 °C and 1 bar, pointing to new opportunities for designing clay-based materials for hydrogen storage application.

1. Introduction

Clay minerals play a significant role in everyday life (Bergaya and Lagaly, 2006), from their use in gas barrier property enhancement in polymer/clay nanocomposites (Cui et al., 2015) to the containment of hazardous waste storage (Jalal et al., 2021), to cosmetics (Sarruf et al., 2024), paints (Buyondo et al., 2022), building materials (Shubbar et al., 2019), or biomaterials design (Dawson and Oreffo, 2013; Tomás et al., 2018). Clay minerals form a distinct realm in which these minerals interact widely with their environment, possessing the ability to absorb, release, and incorporate a wide variety of ions or molecules, making them versatile materials for various applications. However, one field of application for which clays have received little attention is hydrogen storage.

Hydrogen is the carbon-free fuel par excellence because its combustion, or its use in fuel cells, emits only water. At present, the limiting point to a massive deployment of technologies using hydrogen for energy purposes is its storage. Solid-state hydrogen storage being a

safe procedure, sorption technologies are among the most thoroughly explored. Investigations focus on specific materials, such as zeolites, activated carbons and MOFs (Metal Organic Frameworks) (Bastos-Neto et al., 2012) or metal hydrides (Sakintuna et al., 2007). Much of the current research into hydrogen storage has focused on the stringent requirements of mobile applications, so clay minerals have often been overlooked due to their intrinsic (relatively large) weight, resulting in a modest gravimetric storage capacity i.e. the mass of hydrogen stored per total mass of the material. Consequently, studies in the literature on hydrogen storage in clay minerals are sparse, which will be discussed later (Gil et al., 2009; Didier et al., 2012; Edge et al., 2014; Mondelli et al., 2015; Alver, 2017, 2018; Ziemiański and Derkowski, 2022; Masci et al., 2024; Masoudi et al., 2025; Yang and Jin, 2025). However, large-scale land-based storage for industrial or domestic applications are much more flexible on the low weight condition, and a cheap "green" and stable material, able at storing a large quantity of hydrogen might remain interesting even with a relatively low gravimetric capacity. In

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this context, clay minerals, with their unique properties such as high surface area, low cost, and favorable environmental safety profiles, present an interesting option worthy of further investigation.

Clay minerals are silicate materials, which can have either a tubular shape or a layered structure, the latter resulting from the stacking of individual layers. Among layered clay minerals, smectites are particularly promising because of their large surface area and swelling behavior (Ferrage, 2016). Their structural framework features a TOT layer, comprising two sheets of tetrahedral silicates (T) that sandwich a central sheet of metal octahedra (O). There are two types of octahedral sheets depending on the valency of the metal cation: the dioctahedral type, where two-thirds of the octahedral sites are occupied by trivalent atoms, and the trioctahedral type, where all sites are occupied by divalent atoms. Hectorite (Zhang et al., 2019) is a representative 2:1 trioctahedral smectite mineral, where octahedra centers are occupied by Mg and Li, the partial substitution of Li^+ for Mg^{2+} inducing a negative charge on the basal faces, which is compensated by Na^+ cations in the interlayer space. Hectorite deposits are rare in nature and contain various impurities. However, synthetic pure hectorite, named Laponite, can be easily produced under hydrothermal process (Neumann, 1977), either in laboratory or by industry where it is marketed under the name of Laponite®.

This article focuses on pre-Laponite, the sol-gel precursor of the synthesis of Laponite, which – to the best of our knowledge – has never been studied up to now. This study is motivated by our experimental observation, that pre-Laponite exhibits a 1.4-fold higher hydrogen mass uptake at -196°C and 1 bar compared to Laponite. This considerable difference came as a surprise and the objective of this paper is to characterize the structural and textural properties of pre-Laponite compared to Laponite, as it provides the foundation for further analyses of its hydrogen sorption.

2. Materials and methods

2.1. Synthesis protocol

The synthesis of Laponite follows the hydrothermal synthesis protocol proposed in Barbara Neumann's patent (Neumann, 1977).

Initially, 0.72 mol of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.09 mol of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ are dissolved in 85 mL of D_2O (solution 1).² This solution is added to 0.07 mol of Na_2CO_3 in 60 mL of D_2O (solution 2), leading to the precipitation of MgCO_3 . Subsequently, 0.121 mol of Si is introduced from a commercial aqueous sodium silicate solution (29% SiO_2 and 8.8% Na_2O) in 25 mL of D_2O (solution 3), resulting in Si precipitation. Each addition occurs under gentle stirring (100 rpm) with a magnetic stirrer for at least 30 min in a nitrogen atmosphere to minimize H-D exchange.

The resulting mixture is boiled under reflux at atmospheric pressure for 1 h, then rapidly cooled in an ice bath. The precipitate is separated by centrifugation (8000 rpm, 5 min, $\approx 10\,000 \times g$, JA-14 fixed-angle rotor), washed three times with D_2O , and freeze-dried to obtain a powder referred as pre-Laponite hereafter.

The Laponite sample is obtained from the pre-Laponite dispersion prior to the freeze-drying step. The dispersion is treated at 207°C and 17 bar for 5.5 h before it undergoes the same drying procedure. Based on the amounts of precursors, the nominal formula of Laponite is $[\text{Si}_8][\text{Mg}_{4.8}\text{Li}_{1.2}]\text{Na}_{1.2}\text{O}_{20}(\text{OD})_4$.

² D_2O was used instead of H_2O , as samples were also prepared to be studied by neutron scattering. Indeed, deuterated samples are preferred to minimize incoherent neutron scattering. The neutron scattering study will be published elsewhere. Although similar conclusions can be reached for hydrogenated and deuterated samples, we chose here to present deuterated samples as a reference for our neutron scattering investigations.

2.2. Inductively coupled plasma atomic emission spectroscopy

Chemical analysis of both Laponite and pre-Laponite was performed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) Varian 720ES instrument. 50 mg of powdered clay were dispersed in 45 g of Milli-Q water. The dispersion was sonicated at ambient temperature: for Laponite, 1 min of sonication was applied; for pre-Laponite, the dispersion was left to rest for 24 h and then sonicated for 1 h to ensure full dispersion. Both materials form stable colloidal dispersions in water. No visible precipitation was observed after ultrasonication, allowing direct ICP-AES analysis. Due to the high concentrations of Si and Mg in the resulting supernatant, samples were diluted by factors of 2, 5, 10, 20, and up to 1000. Analysis durations ranged from 15 to 90 s per sample, followed by a washing period of 30 to 90 s. For each element, at least two distinct wavelengths were used: 279.5, 280.3, and 285 nm for Mg; 568.8 and 589 nm for Na; 185, 212.4, 250.7, 251.4, 252.8, and 288.2 nm for Si. Finally, the measured intensities were compared to a calibration curve, which was generated from a series of known standard solutions containing the elements of interest.

2.3. X-ray Raman scattering

X-ray Raman scattering in the hard X-ray range has proven to be a valuable technique for characterizing light elements, enabling bulk-sensitive analysis under ambient conditions without requiring vacuum environments (Bergmann et al., 2002). Experiment was performed at the GALAXIES beamline of Synchrotron SOLEIL (Ablett et al., 2019). The samples were in the form of pellets, obtained by pressing powders under 5 tons. The sample, crystal analyzers, and the detector were all positioned on the circumference of a 1-meter diameter Rowland circle, ensuring precise focusing and an energy resolution of 1 eV. The backward-scattering spectrometer consists of 40 spherically bent Si(110) crystals, each with a diameter of 100 mm, achieving an energy resolution of 1 eV at the incident energy of 9697 eV. The two-dimensional detector allows one to separate the contributions from each of the 40 analyzers and calibrate them independently. The energy transfer spectrum is then summed over all analyzers to improve statistical accuracy. For each absorption edge of each sample, a scan of approximately 40 eV is performed with steps of 0.25 eV. The signal corresponding to the different edges overlaps with Compton scattering, which is subtracted by fitting a linear baseline to the pre-edge region, under the assumption that the slope remains constant over the 40 eV energy range of the scan. All measurements were performed at ambient conditions of pressure and temperature.

2.4. X-ray scattering

X-ray scattering (XRS) measurements were carried out on a two-circle powder diffractometer equipped with silicon-strip linear detectors (Mythen2, Dectris) on the CRISTAL beamline at synchrotron SOLEIL. The monochromatic X-ray beam with a wavelength of $\lambda = 0.53144 \text{ \AA}$ was extracted from the U20 undulator beam by means of a Si (111) double crystals monochromator. Synchrotron radiation is linearly polarized in the plane of the storage ring, so no polarization correction is required for measurements carried out in the vertical plane as it is the case with the 2-circle goniometer. Samples were placed in 1 mm glass capillaries and heated at 150°C for 6 h to remove water, then the capillaries were sealed. Powder diagrams were measured for about 20 min per sample while the samples were rotating. They extend over the Q wave-vector range from 0.1 to $20 \text{ \AA}^{-1}$.

Such large Q -range makes possible a pair distribution function (PDF) analysis. The PDF, $G(r)$, gives the scaled probability of finding two atoms in a material a distance r apart, the scaling factor being proportional to the product of their numbers of electrons (Farrow and Billinge, 2009). It was obtained using PDFgetX3 software (Juhás et al.,

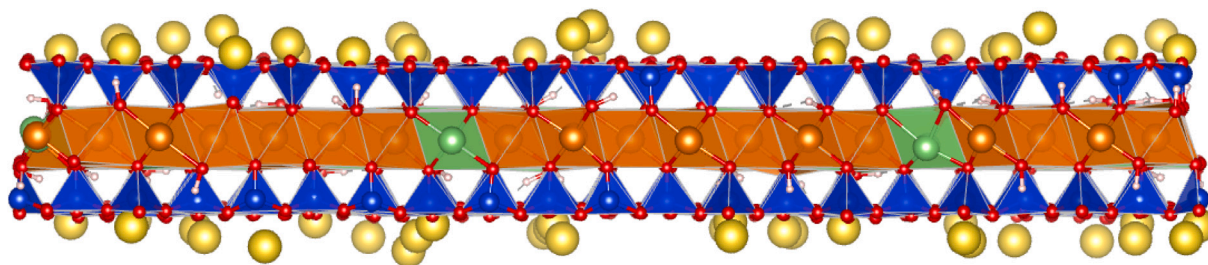


Fig. 1. Atomic structure of a single TOT layer of Laponite after optimization of atomic positions. Silicon atoms are represented in blue, magnesium ones in orange, lithium ones in green, oxygen ones in red, hydrogen ones above and below the layer are in pink and sodium ones in yellow. SiO_4 tetrahedra are represented in blue, MgO_6 and LiO_6 octahedra are in orange and green, respectively.

2013), with a finite upper limit of $Q_{\text{max}} = 14.8 \text{ \AA}^{-1}$, beyond which the signal-to-noise ratio was deteriorated (Khoder et al., 2020).

The scattering data were also compared to calculated diagrams. In order to make this comparison, measured XRS intensities were corrected from background using Eq. (1).

$$I_s(Q) = \frac{I_m(Q) - I_{Sn}(Q)}{T_s T_c} - \frac{I_c(Q) - I_{Sn}(Q)}{T_c} \quad (1)$$

where $I_s(Q)$ is the corrected intensity, $I_m(Q)$ is the measured intensity (sample + capillary), $I_{Sn}(Q)$ is the intensity measured with a 1 mm diameter tin wire used as an absorber in place of the sample, I_c is the intensity from the empty capillary, and T_s and T_c are the transmissions of the sample and the empty capillary, respectively.

2.5. Numerical simulations

The optimization of the atomic positions in a Laponite layer was performed for an isolated Laponite layer with the nominal composition $[\text{Si}_8][\text{Mg}_{4.8}\text{Li}_{1.2}]\text{Na}_{1.2}\text{O}_{20}(\text{OH})_{20}$ thanks to Molecular Dynamics (MD) simulations, where the clayFF force-field was used to calculate the interactions between atoms (Cygan et al., 2004). Half of the Na^+ ions were positioned above the layer, while the other half were placed below it. The layer was constructed with 50 rectangular centered unit cells with $a = 5.26 \text{ \AA}$ and $b = a\sqrt{3}$, within a rectangle of area $10a \times 5b$. A $25 \text{ \AA}$ gap is added above and below the clay layer so that the impact of interaction with the image boxes on the layer structure can be disregarded. Equilibration of the structure was carried out using the LAMMPS molecular dynamics software (Thompson et al., 2022), starting with an NVT ensemble at 1000 K to enhance cation mobility and facilitate system equilibration. This was followed by an anisotropic NPT ensemble at 1 bar along the x and y directions to achieve structural relaxation and stabilization. After optimization, the simulated layer had dimensions of $A = 52.608 \text{ \AA}$ and $B = 45.606 \text{ \AA}$ (see Fig. 1).

The samples being in powder form, X-ray scattering diagrams were calculated using the Debye formula (Debye, 1915), given by Eq. (2), calculations being performed on a laptop and speed up thanks to highly parallel calculation on GPUs. Neverov (2017).

$$I(Q) \propto \sum_{i,j} f_i(Q)f_j(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}} \quad (2)$$

where $I(Q)$ is the calculated intensity, $f_i(Q)$ and $f_j(Q)$ are the atomic form factors of atoms i and j , respectively, and r_{ij} denotes the inter-atomic distance.

A home made program was used for the calculations of X-ray scattering diagrams. Hydrogen atoms were replaced by deuterium ones. Laponite particles are reported in the literature to have, at first approximation, a circular shape with a diameter of approximately 30 nm (Avery and Ramsay, 1986; Mouchid et al., 1995). This morphology was used as a basis for constructing the particles used for the calculations. To generate layers in the form of disks of radius R , the rectangular layer was repeated with periods A and B on a surface larger than that of the disk, then the atoms located in the circle of radius R

centered on this extended layer were selected. The number of layers, as well as the interlayer distance, are chosen in the program. To account for the random stacking of the layers, the XRS intensity is calculated for $N = 100$ particles with random in-plane shifts, from 0 to a and from 0 to b along the two unit cell vectors, and with random orientations in each layer plane. Resolution convolution was not carried out because the resolution function on the CRISTAL line at SOLEIL gives much finer peaks than those observed experimentally.

2.6. Nuclear magnetic resonance

Solid-state Nuclear Magnetic Resonance (NMR) experiments were performed using a Bruker AV700 spectrometer with a ^{29}Si Magic Angle Spinning (MAS) / Cross Polarisation (CP)-MAS setup, operating at a spinning speed of 10 kHz. The relaxation delay was set to 60 s for MAS and 3 s for CP-MAS, with 1024 scans for MAS and 2048 scans for CP-MAS. The contact time in the CP-MAS experiment was 1 ms. DSS (3-(Trimethylsilyl)propane-1-sulfonic acid) was used for power calibration and as a reference, with a chemical shift of 1.67 ppm relative to tetramethylsilane.

2.7. X-ray Absorption Near Edge Spectroscopy

X-ray Absorption Near Edge Spectroscopy (XANES) was performed at the LUCIA beamline at Synchrotron SOLEIL (Vantelon et al., 2016). The X-ray beam was monochromatized with a potassium titanyl phosphate KTP (011) double crystal monochromator. Approximately 40 mg of the sample was mixed with 4 mg of cellulose powder and pressed under 2 tons to form pellets with a diameter of 1 cm, which were then mounted on a copper plate holder using carbon tape. The Mg and Si K-edge spectra were acquired under primary vacuum conditions over energy ranges of 1280–1400 eV for Mg and 1800–1920 eV for Si. For the Si K-edge, the following energy steps were used: 2 eV (1800–1840 eV), 0.2 eV (1840.2–1850 eV), 0.5 eV (1850.5–1860 eV), and 1 eV (1861–1920 eV). For the Mg K-edge, the step sizes were: 2 eV (1280–1304 eV), 0.2 eV (1304.2–1325 eV), 0.5 eV (1325.5–1340 eV), 1 eV (1341–1390 eV), and 2 eV (1392–1400 eV). A counting time of 2 s per point was used for all measurements. XANES data were collected in fluorescence mode on a 60 mm² mono-element silicon drift detector (Bruker AXS), corrected for self-absorption, and normalized by fitting the pre-edge and post-edge regions, using the Athena software (Ravel and Newville, 2005).

2.8. Adsorption isotherms

Nitrogen and hydrogen adsorption isotherm experiments were conducted at $-196 \text{ }^\circ\text{C}$ using a volumetric gas sorption instrument, ASAP 2020 PLUS, from Micromeritics Instruments®. Prior to the experiments, approximately 200 mg of the powdered samples were degassed at $150 \text{ }^\circ\text{C}$ for 6 h under secondary vacuum (4×10^{-3} mbar) to remove adsorbed water. The specific surface area was determined from N_2

isotherms using the Brunauer–Emmett–Teller (BET) method in the pressure range $0.05 \leq P/P_0 \leq 0.2$, with a nitrogen cross-sectional area of 0.162 nm^2 (Ismail, 1990). The density functional theory (DFT) and non-localized density functional theory (NLDFT) methods, based on high-resolution adsorption isotherms, provide a reasonably reliable approach for analysis of pore size/volume throughout the entire nanopore range (Rouquerol et al., 2013; Landers et al., 2013; Thommes and Cychosz, 2014). Calculations were made for slit-pores geometry using the NLDFT model.

The N_2 adsorption measurement consisted of 50 steps for adsorption and 40 steps for desorption, while the H_2 adsorption was measured in 25 steps, ranging from 10^{-6} to 0.01 bar in 6 steps, and from 0.01 to 1 bar in 19 steps, followed by 10 desorption steps. H_2 adsorption measurements are reliable to within $\pm 0.01 \text{ wt\% H}_2$ at 1 bar, as confirmed by reproducibility tests on commercial Laponite (LapRD). To minimize the dead volume of the sample cell, non-porous glass filler rods were used, with the dead volume assessed using helium gas (purity 99.99%) prior to each measurement.

3. Results and discussion

3.1. Pre-laponite: a novel pathway for enhanced hydrogen adsorption

Previous studies of H_2 adsorption in clays have focused on smectites, such as montmorillonite (Gil et al., 2009; Didier et al., 2012; Mondelli et al., 2015; Alver, 2017, 2018; Masoudi et al., 2025; Yang and Jin, 2025), Laponite (Edge et al., 2014) and saponite (Masci et al., 2024). Most of these studies concern adsorption under high pressure (Mondelli et al., 2015; Alver, 2017, 2018; Ziemiański and Derkowski, 2022; Masci et al., 2024; Masoudi et al., 2025; Yang and Jin, 2025), of interest for land-based H_2 storage applications. The possibility of modulating the interlayer space in smectites, through cation exchange or by controlling their degree of hydration, makes them particularly valuable for gas storage (Edge et al., 2014; Ziemiański and Derkowski, 2022; Masci et al., 2024). In this article, where we consider H_2 adsorption values at -196°C and 1 bar for Laponite and pre-Laponite, it is interesting to list the values obtained under the same temperature and pressure conditions in the literature. One finds $0.23 \text{ wt\% H}_2$ in sparingly hydrated laponite with calcium ions in the interlayer (Ca-Laponite) (Edge et al., 2014) and $0.02 \text{ wt\%}$ in saponite with sodium ions in the interlayer (Na-saponite) (Masci et al., 2024).

H_2 isotherm at -196°C (Fig. 2) demonstrates a 1.4-fold increase in H_2 uptake in pre-Laponite compared to Laponite at 1 bar, with uptake values of $(0.44 \pm 0.01) \text{ wt\%}$ in pre-Laponite and $(0.32 \pm 0.01) \text{ wt\%}$ in Laponite. A similar effect has been recently reported on a gel precursor of saponite, with an increased H_2 uptake for the gel precursor (Masci et al., 2024). But the absolute value of the H_2 uptake at -196°C and 1 bar is larger in pre-Laponite than in the saponite gel precursor ($0.44 \text{ wt\%}$ compared to $0.19 \text{ wt\%}$). Moreover, the hydrogen uptake in Na-pre-Laponite is approximately twice the one in sparingly hydrated Ca-Laponite and more than ten times larger than the one in Na-saponite, so that pre-Laponite appears to present rather large hydrogen adsorption at -196°C and 1 bar. It motivates the detailed textural and structural studies on pre-Laponite presented in this article.

3.2. Chemical analysis

Based on the amounts of precursors used in the synthesis, the chemical formula of the Laponite sample synthesized here should be $[\text{Si}_{4.8}][\text{Mg}_{4.8}\text{Li}_{1.2}]\text{Na}_{1.2}\text{O}_{20}(\text{OD})_{20}$. The corresponding nominal ratios between Si and Mg, and Si and Na, are presented in Table 1. These ratios were confirmed by ICP-AES analysis. For both Laponite and pre-Laponite samples, the measured ratios are consistent with the nominal values derived from the ideal structural formula of Laponite. As the amount of sodium is directly related to that of lithium, sodium compensating the negative charge resulting from the substitution of magnesium by lithium, one can infer that the amount of lithium is the same in both samples.

Table 1

Ratios between the amounts of different elements for pre-Laponite and Laponite, as deduced from ICP-AES measurements.

	[Si]:[Mg]	[Si]:[Na]
Laponite	1.8	7.8
pre-Laponite	1.6	5.5
Nominal values	1.67	6.67

Table 2

Laponite and pre-Laponite structural characteristics based on the analysis of XRS diagrams; n_c is the number of stacked layers and c is the period perpendicularly to the layers plane.

Sample	Layer diameter (nm)	n_c	c [Å]
Laponite	8.3	3	9.7
pre-Laponite	2.8	2	9.9

3.3. Structural analysis

Powder XRS diagrams of Laponite and pre-Laponite are shown in Fig. 3(a) up to Q equal to 6 Å^{-1} . The intense and relatively broad scattering features are related to Laponite or pre-Laponite. Additional narrow peaks are due to parasitic phases, but their small intensities ensure that they are only present in trace amounts. Laponite and pre-Laponite XRS diagrams can be fully indexed based on the structure of Laponite, with a rectangular unit cell in the plane with parameters $a \approx 5.26 \text{ Å}$ and $b \approx 9.11 \text{ Å}$ and a period c perpendicular to the layers, relative to their stacking (see Karmous et al., 2011 and references therein). Some hk or $00l$ values are reported in Fig. 3. The hk bands appear strongly asymmetric, except for the (33,06) one, showing large in-plane disorder between the stacked layers (Jones, 1949; Lanson, 2011; Karmous et al., 2011). The (33,06) band can be used for distinguishing between dioctahedral and trioctahedral smectites (Moore and Reynolds, 1989). Its maximum giving a real space distance of about 1.53 Å for both Laponite and pre-Laponite, the trioctahedral character of Laponite is confirmed and that of pre-Laponite can be inferred from this. From the position of the 003 peak, one finds $c \approx 9.7 \text{ Å}$ for Laponite and $c \approx 9.9 \text{ Å}$ for pre-Laponite. The 001 peak is surprisingly difficult to measure, as shown in Fig. 3(b), and may be masked by strong scattering at small angles due to the porosity of the material. The width of the 00 l peaks or the slope of the rising edges of the hk band Bousige et al. (2012) give the out-of-plane and the in-plane correlation lengths. The 003 peak being larger in pre-Laponite compared to Laponite and the slope of the 02,11 or of the 20,12 rising edges being smaller, it follows that correlation lengths are smaller in pre-Laponite.

Calculations of XRS diagrams have been made based on the layer structure obtained from MD simulations, varying the radius R of the layers, the period c perpendicular to them and the number of stacked layers. Random stacking of the layers, with no in-plane correlation between them, was assumed. Although this is a simplifying assumption (Karmous et al., 2011), rather good agreement with experimental data was obtained. Fig. 4(a) presents the experimental and calculated XRS diagrams, highlighting the best-fit results. Based on the fitting of the rising edge of the 20,13 band, the diameter of Laponite layers is found to be equal to about 8.3 nm while that of a pre-Laponite layer is approx. 2.8 nm . In fact, XRS data do not give access to the size of the layers but to the size over which the scattering is coherent. In principle, the layers may be larger with defects, which restrict their coherence surface. We find here that the coherence surface for Laponite sheets, is equal to 54 nm^2 , nine times larger than for pre-Laponite sheets (6 nm^2). The mean number of stacked layers is deduced from the width of the 003 peak: it is found to be 3 in Laponite and 2 in pre-Laponite. The results of the fits are summarized in Table 2.

To examine the atomic structure within Laponite and pre-Laponite samples, PDF analysis is shown in Fig. 4(b). The PDF diagrams reveal

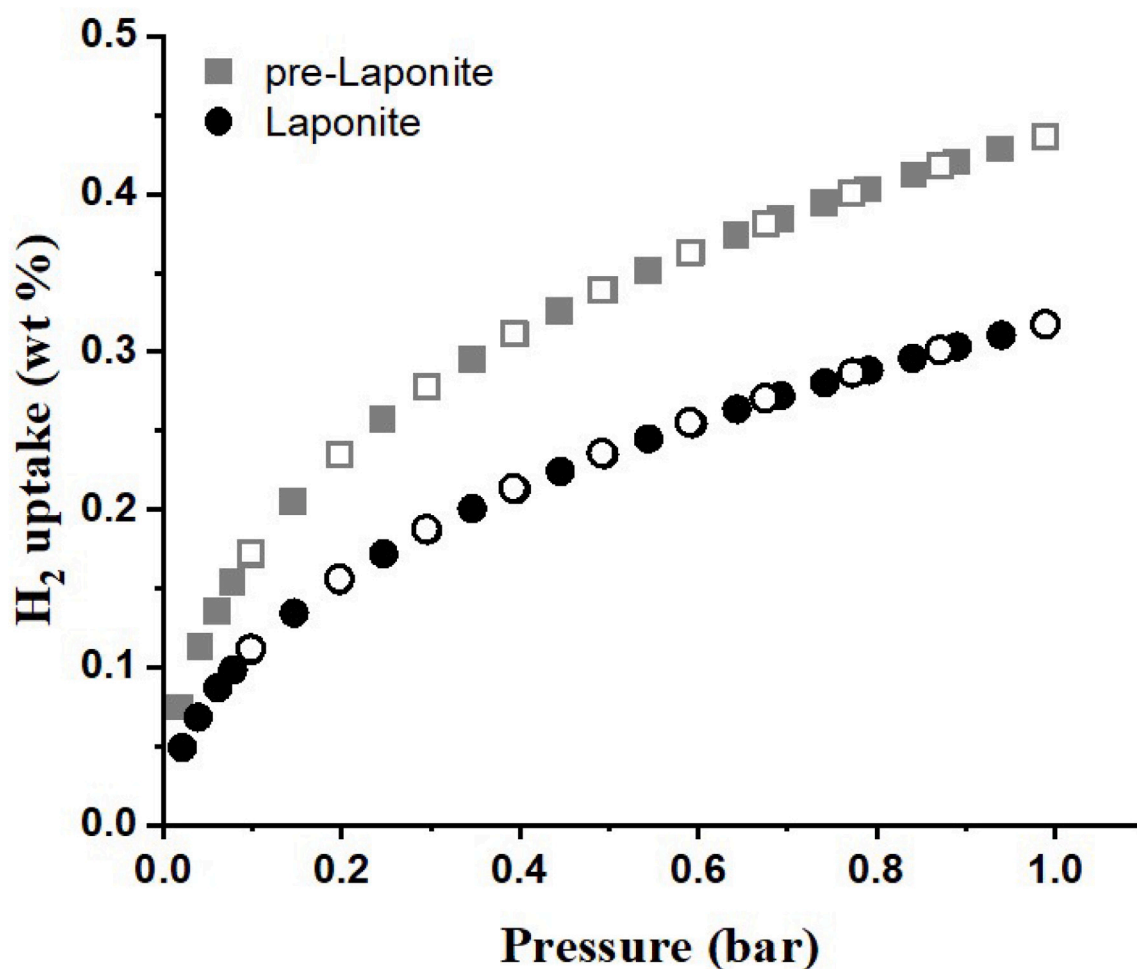


Fig. 2. H_2 adsorption (filled symbols) and desorption (open symbols) isotherms for pre-Laponite (squares, gray) and Laponite (circles, black) measured at -196°C .

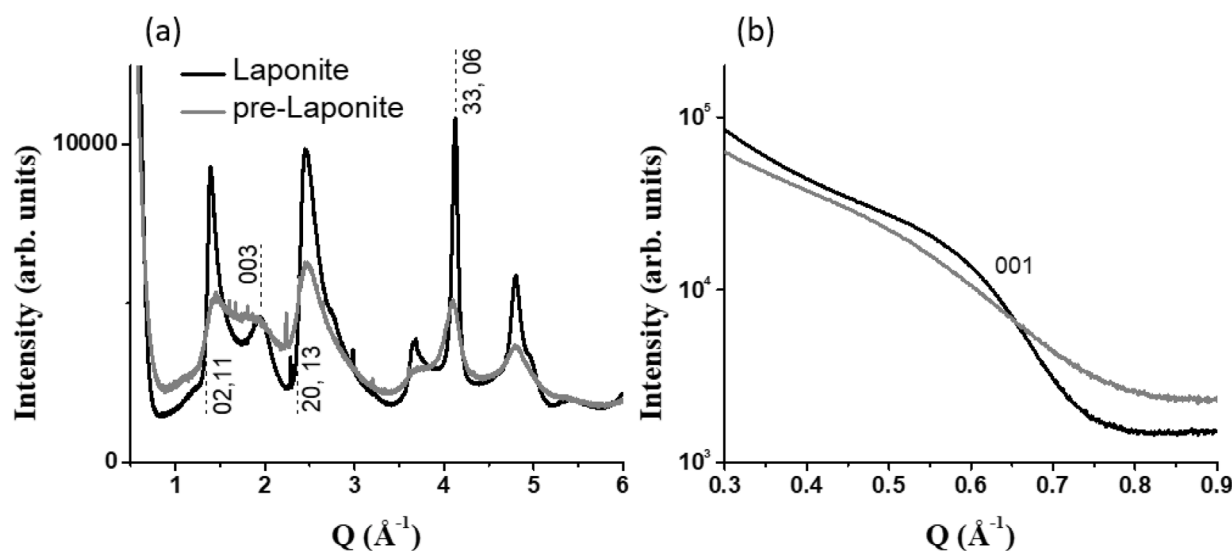


Fig. 3. (a) XRS diagrams of Laponite and pre-Laponite powder samples, with Miller indices of some scattering features indicated by vertical dotted lines, (b) magnified low-Q region.

similar pair distributions over a broad range of interatomic distances for both samples, indicating similar atomic arrangements. However, the stronger decay of the PDF amplitude in pre-Laponite compared to Laponite, from low- to high-distances, indicates a smaller coherent

domain size, in agreement with the conclusions drawn from the analysis of the XRS diagrams in reciprocal space. ^{29}Si NMR offers a more detailed investigation of the local tetrahedral silicon environments. Direct excitation spectra for both pre-Laponite (a) and Laponite (b) are

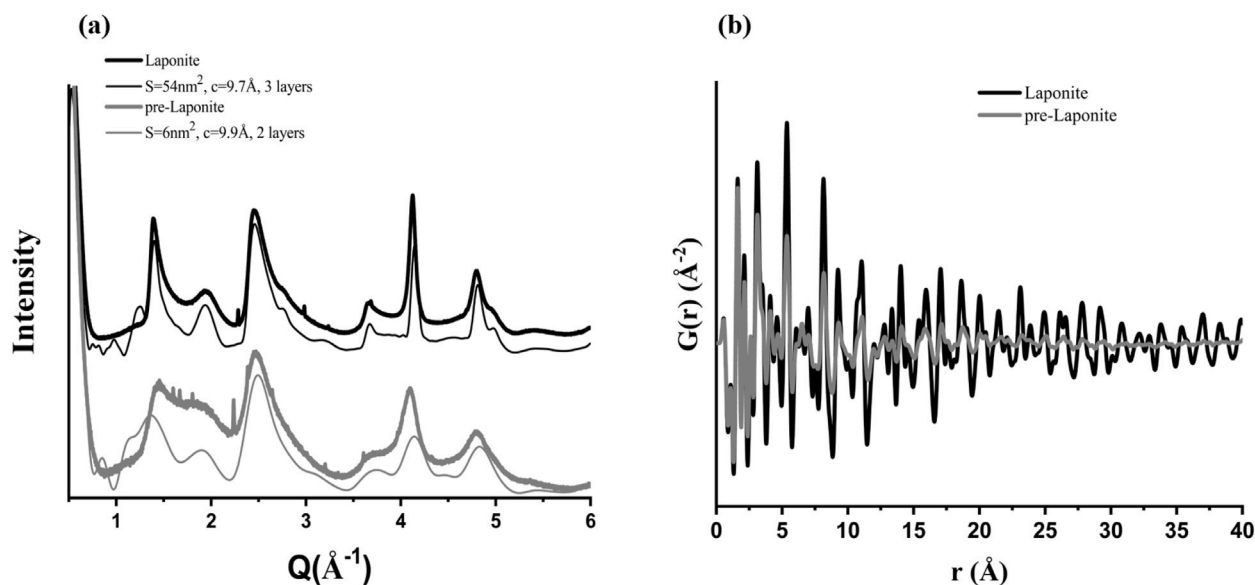


Fig. 4. (a) Experimental and calculated XRS diagrams for Laponite and pre-Laponite powders, (b) Pair distribution functions for Laponite and pre-Laponite, as deduced from experimental scattering data, with $Q_{\min} = 0.3 \text{ \AA}^{-1}$ and a $Q_{\max} = 14.8 \text{ \AA}^{-1}$.

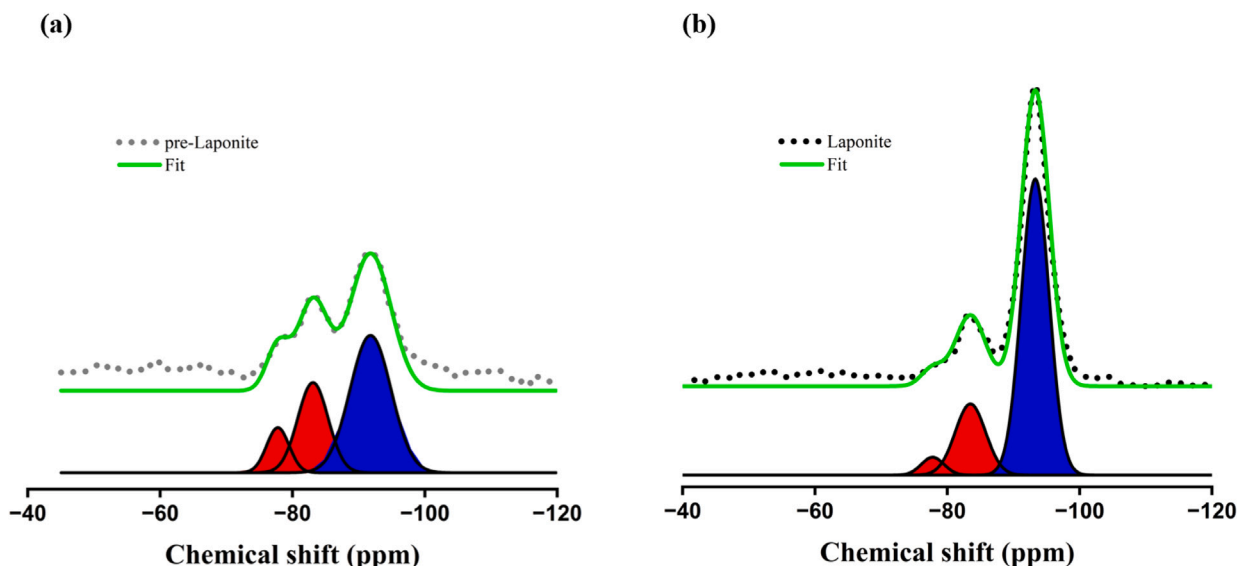


Fig. 5. ^{29}Si MAS NMR spectra of (a) pre-Laponite and (b) Laponite. The experimental data are shown as black dotted points, with the green line representing the sum of the three fitted gaussian components. The spectra have been vertically offset for clarity.

shown in Fig. 5, with the data fitted using three Gaussian functions, interpreted based on the number of SiO_4 tetrahedra connected via bridging oxygen atoms.

The most intense peak situated at -93.3 ppm for Laponite and -91.8 ppm for pre-Laponite is assigned to the two-dimensional silicate (Q^3) lattice. The corresponding signal is observed at -95.3 ppm for the natural counterpart of Laponite, hectorite (Mandair et al., 1990). Moreover, additional signal of lower intensity is observed at -83.3 ppm . This peak is attributed to Q^2 sites present at the edges of the silicate sheets (Negrete et al., 2004; Pálková et al., 2010), but it can also result from defects in the plane of the silicate lattice. Furthermore, a shoulder is observed at -77.8 ppm , which can be attributed to the $Q^{2'}$ site, corresponding to $\text{Si}(\text{OLi})(\text{OSi})_2\text{OH}$. The peaks assignment is further supported by the enhanced Q^2 signal through H-to-Si cross-polarization (Fig. 6).

The main difference between the two samples arises from the $\text{tot}Q^2/Q^3$ area ratio in Fig. 5 ($\text{tot}Q^2$ referring to the sum of the areas

below Q^2 and $Q^{2'}$ peaks). Pre-Laponite ($\text{tot}Q^2/Q^3 = 0.7$) shows a higher ratio compared to Laponite ($\text{tot}Q^2/Q^3 = 0.3$). If one assumes that Q^2 and $Q^{2'}$ sites stem from the edges, this ratio is indicative of the edge over surface ratio and a reduced layer size is inferred in pre-Laponite. If the Q^2 and $Q^{2'}$ sites are also representative of defects in the silicate lattice, one can only conclude that pre-Laponite is more defective than Laponite. Whatever it is, the NMR results are in agreement with XRS analysis which showed a reduced surface of coherence for pre-Laponite compared to Laponite.

Fig. 7(a) presents the Mg K-edge XANES spectra for Laponite and pre-Laponite samples. The XANES spectra for the Mg K-edge of Laponite and pre-Laponite exhibit similar absorption features, characterized by a triplet located at 1310 (A) , 1314 (B) , and 1318 (C) eV along with a distinct feature at 1324 (D) eV and a broad peak around 1331 (E) eV. In addition, a shoulder at 1315 eV is observed (marked by an asterisk). Peaks A and C are well defined and have comparable intensities that are characteristic of 2:1 trioctahedral smectites as reported by Inoue et al.

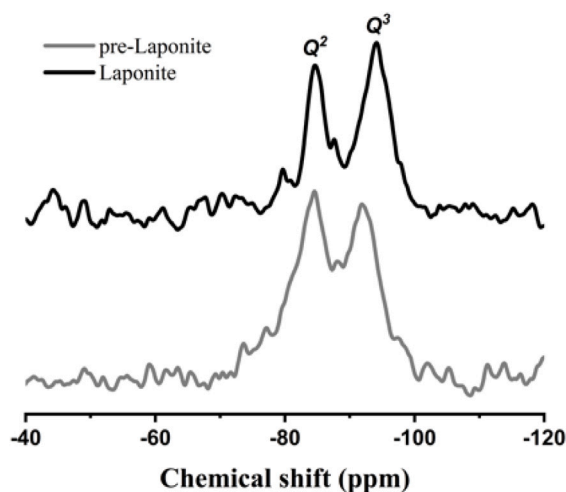


Fig. 6. CPMAS NMR spectra of Laponite and pre-Laponite. Spectra are translated vertically for the sake of clarity.

(2023). Furthermore, the peak D can only be found in trioctahedral smectites (Inoue et al., 2023), confirming that both samples consist of a trioctahedral layer and not a dioctahedral one.

Measurements performed at the Si K-edge spectra for Laponite and pre-Laponite are shown in 7(b). The white band A' in the Si K-edge spectra corresponds to the transition of Si 1s electrons to the 3p states (Li et al., 1995). Both Laponite and pre-Laponite exhibit similar spectra at the silicon K-edge, corroborating that they share a comparable local Si environment at the atomic level. However, the more defined post-edge features (C', D', and E') in Laponite suggest a higher degree of homogeneity in the Si environment compared to pre-Laponite. This can be attributed to the possible reduced size of layer sheets and/or the possible presence of defects in pre-Laponite. The Si atoms in pre-Laponite experience a larger deviation from the average environment than in Laponite.

Inelastic X-ray Raman scattering measurements were also performed to quantify the amount of magnesium and silicon in the Laponite and pre-Laponite powders. They are reported in Fig. 8. The same scaling factor of 1.45 was applied to all pre-Laponite spectra to enable a direct comparison with the Laponite spectra. This correction accounts

for differences in the probed sample volume and possibly in pellets densities between the pre-Laponite and Laponite measurements. In Fig. 8(a), the Mg $L_{2,3}$ absorption edge is clearly visible. Due to the small energy separation (less than 1 eV) between the L_2 and L_3 edges and the limited experimental resolution of 1 eV, the two edges appear unresolved. It is noteworthy that the Li K edge lies approximately 5 eV above the Mg $L_{2,3}$ edge. However, attempts to detect the Li K edge under identical conditions using a lithium-rich, magnesium-free reference sample yielded no measurable signal. This supports the attribution of the observed spectral features primarily to Mg. This assignment is further corroborated by the similarity to Mg $L_{2,3}$ edge electron energy loss spectroscopy (EELS) spectra reported in the literature (Jiang et al., 2008). Fig. 8(b) shows two distinct features: one below 100 eV and another with a peak at 108 eV. The former is attributed to the Mg L_1 edge, based on its shape and energy correspondence with simulated X-ray absorption spectra (Restaino et al., 2024). The latter feature corresponds to the Si $L_{2,3}$ edge and exhibits spectral characteristics consistent with those previously reported in the literature (Gaultois and Grosnevor, 2012), notably a pronounced white line at ~ 108 eV accompanied by a pre-edge shoulder at lower energy, not resolved within our experimental limits. In Fig. 8(c), the Si L_1 edge is shown. Within experimental uncertainty, primarily arising from statistical noise, the spectra for Laponite and pre-Laponite are indistinguishable in Figs. 8(a), (b) and (c). It follows that the Mg to Si ratio is identical in both materials, in agreement with the ICP-AES measurements.

3.4. Textural properties

Nitrogen adsorption-desorption isotherms of Laponite (black) and pre-Laponite (gray) are presented in Fig. 9. Based on the IUPAC (International Union of Pure and Applied Chemistry) classification (Sing, 1985), at first glance, pre-Laponite exhibits a nearly reversible type II isotherm, with a gradual increase in nitrogen uptake at high pressures, characteristic of a non porous or macroporous material (pore size > 50 nm). However, it is noticeable that there is significant uptake at low relative pressures (< 0.01 bar), suggesting the presence of microporosity (pore size < 2 nm). For Laponite, the adsorption isotherm primarily follows a Type I isotherm, characterized by the steep uptake at low pressures, indicative of microporosity. A slight increase in adsorption at higher pressures may reveal mesoporous contributions (2 nm < pore size < 50 nm).

Hysteresis, generally associated with capillary condensation, occurs when the pore size exceeds a certain critical width and is always

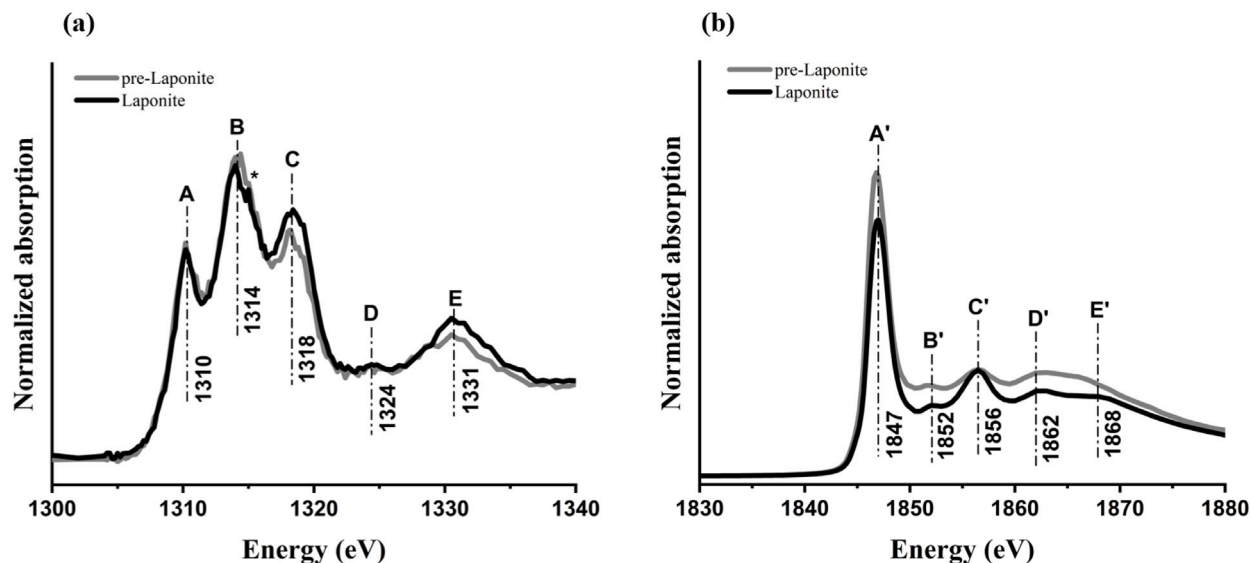


Fig. 7. (a) Mg K-edge, (b) Si K-edge of pre-Laponite and Laponite powders.

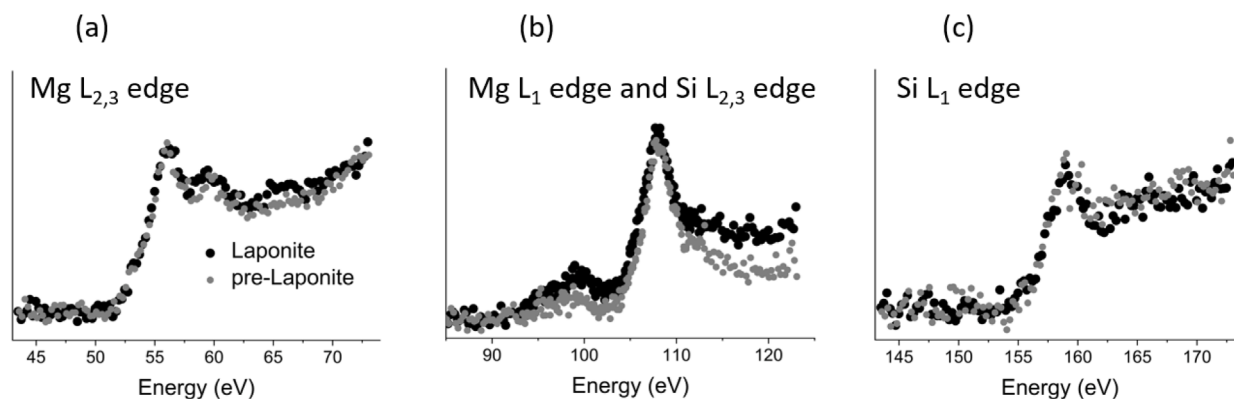


Fig. 8. X-ray Raman scattering intensities over three energy windows.

Table 3

Textural properties of Laponite and pre-Laponite. S_{BET} is the total specific surface area calculated using the BET method. C_{BET} parameter is the BET constant, reflecting the strength of adsorbate–adsorbent interactions. S_{ext} is the external surface area (calculated as the difference between BET and micropore surface area). $S_{\mu\text{p}}$ and $V_{\mu\text{p}}$ represent the micropore surface area and micropore volume, respectively, both determined using the NLDFT method, considering pores up to 2 nm in width.

Samples	S_{BET} [m ² /g]	C_{BET}	S_{ext} [m ² /g]	$S_{\mu\text{p}}$ [m ² /g]	$V_{\mu\text{p}}$ [cm ³ /g]	N ₂ uptake at $p/p^0 = 10^{-5}$ [mmol/g]
Laponite	466	720	128	338	0.12	0.80
pre-Laponite	468	1650	140	328	0.13	1.48

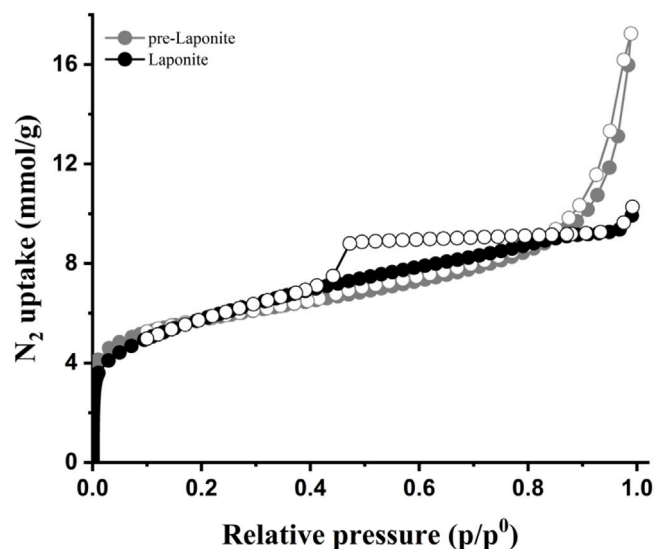


Fig. 9. N₂ adsorption (full circles) and desorption (empty circles) isotherms for pre-Laponite and Laponite measured at $-196\text{ }^{\circ}\text{C}$. Both samples were degassed at $150\text{ }^{\circ}\text{C}$ for 6 h under secondary vacuum.

observed in pores larger than 4 nm (Lowell et al., 2012; Landers et al., 2013). The hysteresis loop in Fig. 9 resembles types H3 and H4 for pre-Laponite and Laponite, respectively, indicating the presence of slit-shaped and narrower slit-shaped pores in non-rigid aggregates (Lowell et al., 2012).

The total specific surface area was calculated using the BET method, while the micropore surface area and pore volume were determined using the NLDFT method. These values are presented in Table 3, which shows that both samples have similar total surface areas of approximately 466–468 m²/g. Furthermore, the textural properties indicate that both Laponite and pre-Laponite exhibit micropore-dominated structures, with comparable micropore areas and volumes.

Despite these textural similarities, H₂ uptake is 1.4 times larger in pre-Laponite than in Laponite at $-196\text{ }^{\circ}\text{C}$ and 1 bar, which may appear surprising. A detailed neutron scattering study has been undertaken to understand this result, which goes beyond the scope of this article. Nevertheless, tentative scenarios could be built on the following remarks. On the one hand, the BET analysis revealed a markedly higher C parameter for pre-Laponite (more than twice that of Laponite), as reported in Table 3, which can be viewed in parallel with the smaller coherence sizes in pre-Laponite and with the previously reported NMR results. On the other hand, it can be observed in Table 3 that at low relative pressure ($p/p^0 = 10^{-5}$), pre-Laponite adsorbs almost twice as much nitrogen as Laponite. This suggests the presence of a higher proportion of small pores in pre-Laponite. Unfortunately, it was not possible to reach lower pressures; therefore, this “ultra”-microporosity could not be investigated in greater detail. Here, the reader should have in mind that conclusions drawn from N₂ isotherm will be based on indirect evidences. One should also underline that surface area measurements were made with nitrogen and not with hydrogen. H₂ adsorption could be enhanced within the interlayer space, facilitated by the slightly larger interlayer spacing in pre-Laponite than in Laponite (9.9 Å vs 9.7 Å). We thus propose that the enhanced H₂ adsorption could be linked to the presence of adequate micropores, as indicated by the low-pressure behavior of the N₂ isotherm or related to the slightly larger inter-layer space in pre-Laponite. But one cannot rule out the influence of a modification of the adsorbate–adsorbent interactions associated with the presence of in-plane defects and/or a higher edge-to-surface ratio in pre-Laponite (Rouquerol et al., 2014).

4. Conclusion

The study of pre-Laponite, a precursor of the synthesis of Laponite, whose chemical and physical characteristics were unknown, leads to a somehow surprising conclusion. The chemical and structural investigations reported in this paper, namely ICP-AES, X-ray Raman scattering, X-ray scattering, Nuclear Magnetic Resonance, and XANES, all indicate that pre-Laponite is (i) not an amorphous nor ill-defined compound as could be expected for a precursor of synthesis, (ii) has a chemical formula identical to that of Laponite and (iii) shares the same trioctahedral structure. The main differences between Laponite and

pre-Laponite are restricted to the following: (i) pre-Laponite coherence surface is significantly smaller and the stacking of the layers is reduced in pre-Laponite, (ii) the distance between the layers centers is also slightly larger in pre-Laponite (9.9 Å vs 9.7 Å). From the textural point of view, both Laponite and pre-Laponite exhibit micropore-dominated structures, as shown from the N₂ adsorption isotherms. This result is of interest in the context of hydrogen storage using clay minerals. This article lays the foundations for the understanding of hydrogen storage by pre-Laponite, by determining its structural and chemical characteristics.

CRedit authorship contribution statement

Mohammad AbdelSater: Writing – original draft, Investigation, Formal analysis, Data curation. **Martine Lanson:** Writing – review & editing, Data curation. **Valérie Magnin:** Writing – review & editing, Data curation. **Erwan Paineau:** Writing – review & editing. **Cristina Coelho:** Writing – review & editing, Data curation. **Delphine Vantelon:** Writing – review & editing, Data curation. **Erik Elkaim:** Writing – review & editing, Data curation. **Jean-Pascal Rueff:** Writing – review & editing, Data curation. **Victor Balédent:** Writing – review & editing, Data curation. **Marie-Vanessa Coulet:** Writing – review & editing, Formal analysis. **Virginie Marry:** Writing – review & editing, Data curation. **Lorella Masci:** Writing – review & editing. **Laurent Truche:** Writing – review & editing. **Stéphane Rols:** Writing – review & editing, Formal analysis. **Pascale Launois:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Pascale Launois reports financial support was provided by French National Research Agency. If there are other authors, they 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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Data availability

Data will be made available on request.

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