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To cite this article: N Fong *et al* 2011 *J. Phys.: Conf. Ser.* **262** 012022

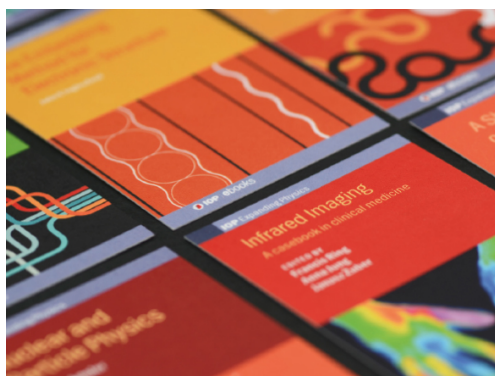
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## Clay particles - potential of positron annihilation lifetime spectroscopy (PALS) for studying interlayer spacing

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**Abstract.** Characterisation of clays is generally achieved by traditional methods, such as X-ray diffraction (XRD) and transmission electron microscopy (TEM). However, clays are often difficult to characterise due to lack of long-range order, thus these tools are not always reliable. Because interlayer spacing in clays can be adjusted to house molecules, there is growing interest to use these materials for drug delivery. Positron annihilation lifetime spectroscopy (PALS) was examined as an alternative tool to characterise a series of well-known clays. XRD of two layered double hydroxides; MgAl-LDH and MgGd-LDH, natural hectorite, fluoromica and laponite, and their PALS spectra were compared. XRD data was used to calculate the interlayer d- spacing in these materials and results show a decrease in interlayer spacing as the heavy metal ions are substituted for those of large ionic radii. Similar results were obtained for PALS data. This preliminary study suggests PALS has potential as a routine tool for characterising clay particles. Further work will examine the sensitivity and reliability of PALS to percent of metal doping and hydration in clay microstructure.

### 1. Introduction

Natural and synthetic clay nanoparticles are currently used in a range of applications such as cosmetics and pharmaceuticals [1]. In addition to having properties such as high aspect ratios, natural abundance and/or ease of manufacture, clay nanoparticles may be chemically manipulated to afford properties tailored for specific applications. One significant application that has sparked interest in nanoparticles in the medical field is in drug delivery, and more specifically for gene therapy. The active agent is expected to fit between the layers of the clay particle and be released by exchange or breakdown of the clay nanoparticles *in vivo*.

The nanoscale dimensions of these particles may be utilized in gene therapy to enable penetration of nucleic acids or drugs through the cell wall and into the cells' cytoplasm or nucleus to prevent and/or treat disease [3]. The transport and release of the drug into the cell is highly dependent on the interaction between the biomolecule and nanoparticle, as well as their interaction with the physiological environment [4]. It is therefore of key importance to understand the physical and

chemical properties of the nanoparticle carriers, and the effect of different ion dopings on their structure.

A range of inorganic nanoparticles have been used for DNA delivery [5]. Among these, LDHs have recently attracted much attention for use as drug/gene carriers. They may be represented by the formula  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2](A_x \cdot y\text{H}_2\text{O})$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent metal ions, and  $A^-$  can be any anion [6]. They possess favorable properties such as low cytotoxicity, excellent biocompatibility [7, 8], and a high surface area for drug loadings [9].

Other significant clay particles include silicates belonging to the smectite family, including fluoromica and hectorite. These nanoparticles have a 2:1 layer structure consisting of two tetrahedral sheets sandwiching an octahedral sheet through sharing of apical oxygens [10].

Interlayer spacings and morphology of the clay particles are usually determined using XRD and TEM, however small platelet size and lack of long-range order can interfere with full analysis [11]. As PALS is unlikely to be affected by these properties it is of interest to test the feasibility of PALS as an alternative tool for characterizing clays.

## 2. Experimental procedure

Two types of LDH nanoparticles were synthesized to assess the effect of different ions within their structure on particle interlayer spacing. The structural characteristics of these nanoparticles as well as other commonly studied clay nanoparticles were assessed using XRD and PALS.

MgAl-LDH and MgGd-LDH were synthesized using a co-precipitation method similar to that reported by Xu *et al.* [12]. Gadolinium was used in the synthesis of MgGd-LDH since Gd (2.54 Å) has a larger atomic radius than Al (1.82 Å), which was expected to affect the structural properties of the LDH. In brief, MgAl-LDH was prepared by mixing 7.5 mL of a mixed metal salt solution containing  $\text{MgCl}_2$  (0.4 M) and  $\text{AlCl}_3$  (0.2 M) and adding it to 30 mL base solution containing  $\text{Na}_2\text{CO}_3$  (0.03 M) and NaOH (0.3 M), under vigorous stirring. Following 10 mins of stirring at room temperature, an LDH slurry was obtained by washing and centrifuging at 4500 rpm for 5 mins at 25°C three times. The LDH slurry was re-dispersed in 26.5 mL Milli-Q water and hydrothermally treated. More specifically, the dispersion was transferred into a Teflon lined stainless steel autoclave and placed into a preheated oven at 100°C for 4 hours, resulting in a stable, homogenous suspension of LDH nanoparticles. MgGd-LDH was made in a similar manner to that described above, except the  $\text{AlCl}_3$  was replaced by  $\text{Gd}(\text{NO}_3)_3$ . Following hydrothermal treatment, the LDHs were allowed to cool for at least 3 hours and freeze-dried for characterization with XRD and PALS.

Natural hectorite ( $\text{Na}_{0.4}\text{Mg}_{2.7}\text{Li}_{0.3}\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) laponite ( $\text{Na}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{0.7}$ ) and fluoromica ( $\text{K}[\text{Mg}_{2.44}\text{Mn}_{0.24}][\text{Si}_{3.82}\text{Mn}_{0.18}]\text{O}_{10}\text{F}_2$ ) (ME-100, CBC Japan) were used as received.

*PALS measurements* were carried out using a fast-fast spectrometer with detectors comprising of a BC418 plastic scintillator coupled to a Burle 8850 photomultiplier tube. The positron source consisted of ~30  $\mu\text{Ci}$  of  $^{22}\text{NaCl}$  sealed in 7  $\mu\text{m}$  thick Kapton foil (grade HN from Goodfellow) and was sandwiched between two identical samples. The time resolution of the system is about 200 ps as determined from analysis of a spectrum of high purity, annealed nickel. The spectra comprise of at least 2 million counts and have been analysed using PASCual version 1.3.0 [13].

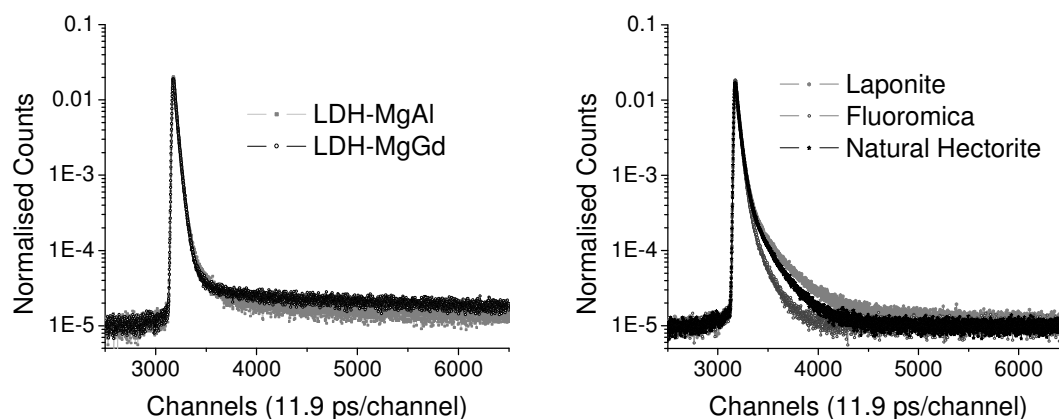
*XRD studies* were performed using a Philips PW1830 Bragg-Brentano X-ray diffraction system with Cu  $K\alpha$  radiation used at  $\lambda = 1.5418 \text{ \AA}$ , goniometer = 173 mm and tension at 40 kV and 40 mA. Measurements were taken between 4° and 40° at a rate of 0.008 °/s and a step size of 0.04°. Results were expressed as average nanometre distances between silicate layers, calculated from Bragg's law,  $\lambda = 2d \sin \theta$ , where  $\lambda$ =wavelength of the incident X-ray beam,  $2\theta$ =diffraction angle and  $d$ =interlayer distance.

## 3. Results and Discussion

Two types of LDH clay particles (MgAl-LDH and MgGd-LDH) were synthesized in a similar manner with  $\text{Al}^{3+}$  substituted by the large cation  $\text{Gd}^{3+}$  for the latter clay. Natural hectorite, laponite and fluoromica were purchased and used without further modification. Though similar in structure the

laponite has a higher ratio of  $\text{Si}^{4+}$  (1.46 Å) and  $\text{Mg}^{2+}$  (1.72 Å) atoms compared with hectorite, and fluoromica has similar structure but contains different types and size cations,  $\text{K}^+$  (2.77 Å) and  $\text{Mn}^{2+}$  (1.79 Å) ions in its structure providing different interlayer spacing.

Lifetime spectra for the LDH and clay particles are shown in Figure 1. Significant differences between the spectra suggest that PALS is sensitive to the structural differences in the samples. The spectra could be deconvoluted into either three or four discrete lifetime components. The longer components,  $\tau_3$  and  $\tau_4$ , which exceed 1 ns are more interesting for the present study as they arise from o-Ps pick-off annihilation in nano-pores.



**Figure 1.** Positron lifetime spectra for LDH (Left), and smectite clay particles (Right) studied.

The o-Ps lifetimes, intensities and their pore sizes for spherical and square channel geometries using the RTE model [14] are shown in Table 1, along with their XRD interlayer spacings. The pore sizes may provide an indication of the size of free volume holes present in the interlayer space. For the LDH materials XRD  $d$ -spacings of 7.7 and 3.8 Å were observed for MgAl-LDH, and these decreased by a factor of  $\sim 1.6$  in MgGd-LDH, when the larger Gd ion was substituted into the layered structure. PALS showed that both LDH particles could be deconvoluted into four components. The lifetimes and the corresponding intensities are smaller for LDH synthesised with Gd compared to Al. This could be due to the larger spatial extent of Gd compared to Al. This is in qualitative agreement with the XRD results.

$\tau_3$  equates to sub-nanometre pores, with diameters in the range of 6.1 and 5 Å, for MgAl-LDH and MgGd-LDH, respectively. The  $\tau_4$  values are significantly larger and are apparent in the long tail of the spectra, shown in Figure 1, which extends to the end of the channel range. Converting  $\tau_4$  to a pore size gives dimensions significantly larger than the interlayer spacing derived from XRD, for any geometry assumed. If a square channel geometry is assumed then this gives rise to 25 Å and 18 Å pores for MgAl-LDH and MgGd-LDH, respectively.

Significant nano-porosity was also observed in the smectite clay particles. Fluoromica and hectorite could be deconvoluted into three components. If a square channel geometry is assumed, then  $\tau_3$  equates to channel widths of 3.9 Å and 5.1 Å, for fluoromica and hectorite respectively. The intensity of this component ( $I_3$ ) is 8.8% for fluoromica and 12.2% for hectorite. This suggests that both the size and concentration of free volume holes in the interlayer spacing is larger for hectorite. This is consistent with LDH findings indicating substitution of larger metal ions into the clay structure decreased pore size. However, PALS results for fluoromica were not consistent with XRD findings, which showed a larger  $d$ -spacing in fluoromica than hectorite. Differences between XRD and PALS may be attributed the level of hydration of samples for both types of analyses.

Four components could be extracted for laponite, indicating the presence of large pores not observed in the other smectite clays. It was noted that the  $\tau_3$  pore sizes for laponite and hectorite are not significantly different. This can be attributed to their similar chemical composition. In contrast the

presence of large pores in laponite indicates an effect of the higher large metal ion concentrations compared with hectorite. These values also complement XRD findings, where laponite has the largest  $d$ -spacing among the clays studied. The o-Ps intensity for laponite is also larger than any of the other particles studied,  $I_3+I_4 = 15.4\%$ , suggesting the highest concentration of pores.

**Table 1-** o-Ps lifetimes and intensities for the clay particles studied, pore dimensions calculated using the RTE model for spheres and square channels and XRD basal spacing

Sample	PALS								XRD		
	$\tau_3^{\#}$ (ns)	$I_3^{\#}$ (%)	$\tau_4^{\#}$ (ns)	$I_4^{\#}$ (%)	Pore diam.		Channel width		2 $\theta$	$d$ -spacing (Å)*	
					$d_3$ (Å)	$d_4$ (Å)	$r_3$ (Å)	$r_4$ (Å)		001	002
LDH-MgAl	1.82 (0.05)	3.1 (0.2)	40 (1)	4 (1)	6.1	33	4.4	25	11.4 23.3	7.7	3.8
LDH-MgGd	1.35 (0.06)	2.3 (0.4)	24 (1)	3 (1)	5	21	3.5	18	18.7 29.7	4.8	3
Natural Hectorite $\text{Na}_{0.4}\text{Mg}_{2.7}\text{Li}_{0.3}\text{Si}_4\text{O}_{10}(\text{OH})_2$	2.24 (0.01)	12.2 (0.1)	-	-	6.9	-	5.1	-	7.7 19.5	11.4	4.5
Laponite $\text{Na}^{+}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-}_{0.7}$	2.50 (0.04)	13.5 (0.1)	18.4 (0.4)	1.9 (0.1)	7.3	16.6	5.5	13.6	7.0 19.6	12.7	4.5
Fluoromica $\text{K}[\text{Mg}_{2.44}\text{Mn}_{0.24}][\text{Si}_{3.82}\text{Mn}_{0.18}\text{O}_{10}\text{F}_2]$	1.55 (0.01)	8.8 (0.1)	-	-	5.5	-	3.9	-	7.2 9.3	12.3	9.5

\*Distance between layers.  $d_{001}$  and  $d_{002}$  refer to the first two basal reflections.  $\#$  Mean (SD)

The identification of such structural properties of nanoparticles is a key step to understanding their behavior as drug delivery vehicles. Large and numerous pores may facilitate high concentrations of drug loading and sustained release compared with particles with smaller voids. Further investigation into the effect of different ion and/or drug dopings on nanoparticle structure is warranted.

#### 4. Conclusions

The interlayer spacing of clay nanoparticles was assessed using PALS and conventional XRD methods, and their results were compared. PALS showed promise as a useful alternative tool for analysing the microstructure of clay nanoparticles, demonstrating sensitivity in detecting differences in pore sizes in response to changes in metal ion dopings within the clay structures.

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