Supporting information

Characterization of phosphate sequestration by a lanthanum modified bentonite clay: A solid-state NMR, EXAFS and PXRD study

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Appendix SI-1. Synthesis of lanthanum phosphate model compounds

Monazite ($LaPO_4$) was prepared by high temperature synthesis: 3.486 g of lanthanum oxide (Aldrich 99.99 %) and 2.461 g of ammonium dihydrogenphosphate (Aldrich 99.99+ %) were ground together thoroughly in their dry state using an agate pestle and mortar. The powder mixture was then placed in a recrystallized alumina crucible with its corresponding alumina lid attached. These were introduced into a chamber furnace (Lenton Furnaces UAF15/10) and heated in air at 60 °C/h to 300 °C. After 3 h at 300 °C, the temperature was raised 200 °C/h to 1200 °C. After 48 h at 1200 °C, the material was cooled at 200°C/h to room temperature. XRD showed monoclinic crystal structure, space group $P2_1/n$. (PDF 83-651).

Rhabdophane ($LaPO_4 \cdot 1.4H_2O$) was synthesized by a method described by Wang et al:[1] An opaque solution was immediately formed by mixing aqueous solutions of 0.1 M lanthanum(III) chloride and 0.1 M sodium dihydrogen phosphate. The solution was heated at 100°C, for 3 h and subsequently cooled to room temperature. A white precipitate was formed upon addition of acetone and this was isolated by centrifugation. The precipitate was re-dispensed in deionized water followed by a further addition of acetone and centrifugation to remove excess of starting materials repeated five times. The resulting white precipitate was dried at room temperature for 2 days. TGA showed 1.4 moles of total water, including 0.54 moles of zeolitic water. XRD showed hexagonal crystal structure, space group $P6_222$ (PDF 46-1439).

Appendix SI-2 Thermogravimetric analyses

Thermogravimetric analyses were performed on a Perkin Elmer TGA 4000. 10 mg of sample was heated in a nitrogen atmosphere at a rate of 10 °C min^{-1} from 30 °C to 995 °C. Determination of water content is available in Table SI-1.

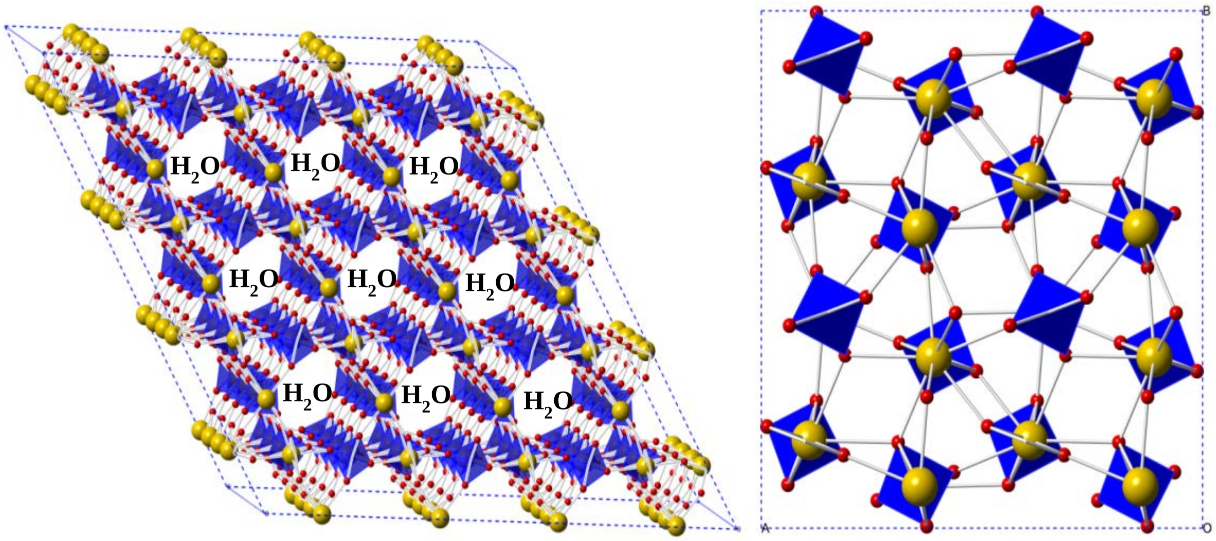
Table SI-1. Determination of water content with thermogravimetric analysis

Compound	**Temperature (°C)**	**Weight loss (%)**	***n*** **H_2O**
$LaPO_4 \cdot n\, H_2O$	30-200	5.5(2)	0.75(3)
	200-900	4.3(2)	0.54(3)
	30-900	9.7(1)	1.39(2)

$$n\,H2O = \frac{M_{initial} - M_{LaPO4}}{M_{H2O}};\ M_{initial}\left[\frac{g}{mol}\right] = \frac{M_{LaPO4}\left[\frac{g}{mol}\right]}{(1 - weightloss)}$$

$$M_{LaPO_4} = 233.88\frac{g}{mol};\ M_{H_2O} = 18.02\frac{g}{mol}$$

The literature is inconsistent in the way of reporting the water content; some report only the water contained inside the channels whereas others report the total water content.[2-6] In the present study we employ the total water content.



Rhabdophane
Hexagonal, $P6_222$

Monazite
Monoclinic, $P2_1/n$

Figure SI-1: Crystal structures of rhabdophane and monazite.[7] The one dimensional channels in rhabdophane contain up to three water molecules per formula unit, as indicated by H_2O.

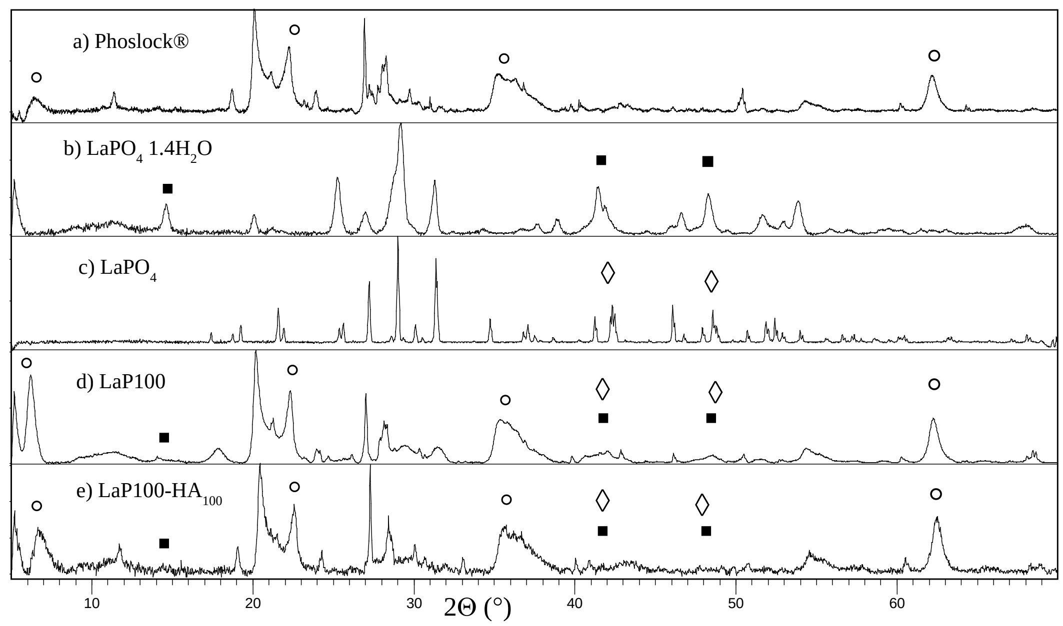


Figure SI-2: PXRD diffractograms of a) Phoslock, b) $LaPO_4 \cdot 1.4H_2O$ (rhabdophane), c) $LaPO_4$ (monazite), d) LaP100 and e) LaP100-HA_{100}. The reflections marked by ○, ■, and ◊ originate from Phoslock®, rhabdophane and monazite, respectively. The low intensity of the La phosphate phase for LaP100 and LaP100-HA_{100} reflects the only 4.4 w/w% La in Phoslock. The relative narrow reflections for monazite ($LaPO_4$) are indicative of a highly crystalline sample with a low surface area.

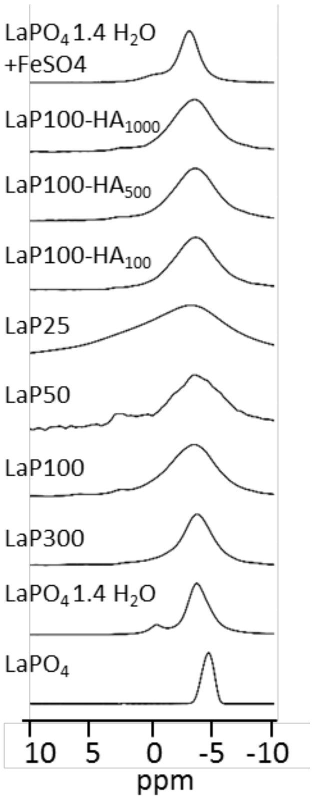


Figure SI-3: Expansion of the ^{31}P MAS NMR spectra in the region -10 to 10 ppm. Two sites are observed for all samples except $LaPO_4$, as rhabdophane contains two sites, the bulk phosphate at ($\delta_{iso}(^{31}P) \approx -3.5$ ppm and surface groups (δ_{iso} ($^{31}P) \approx 0$ ppm (see discussion in the text).

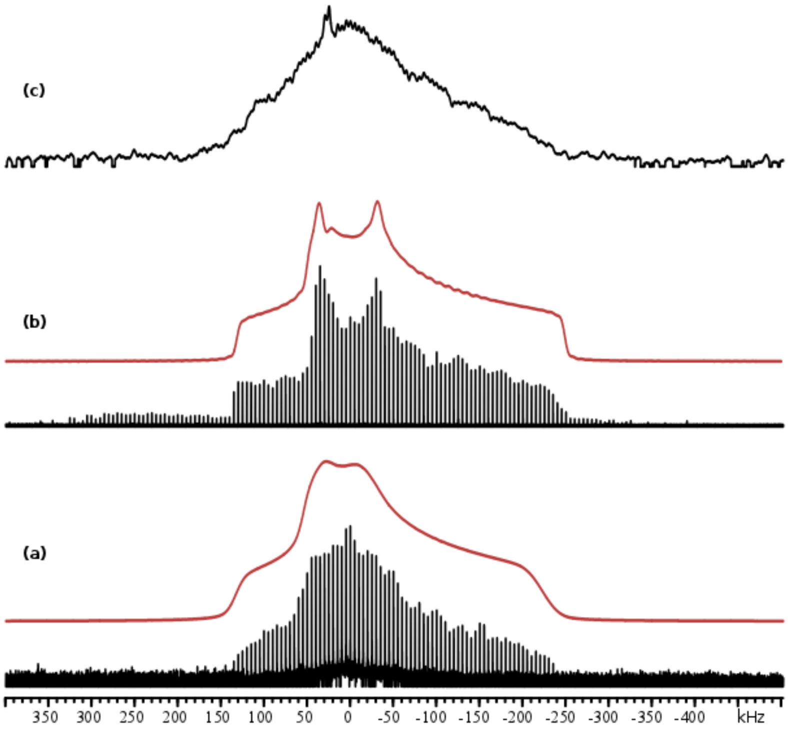


Figure SI-4: Static ^{139}La NMR spectra of a) Phoslock, b) $LaPO_4$ and c) $LaPO_4 \cdot 1.0\ H_2O$ recorded at 21.1 T with simulations (in red) using the optimized parameters in Table 2. Only a static spectrum of rhabdophane could be obtained at ambient temperature due to ionic motion (see discussion in article).

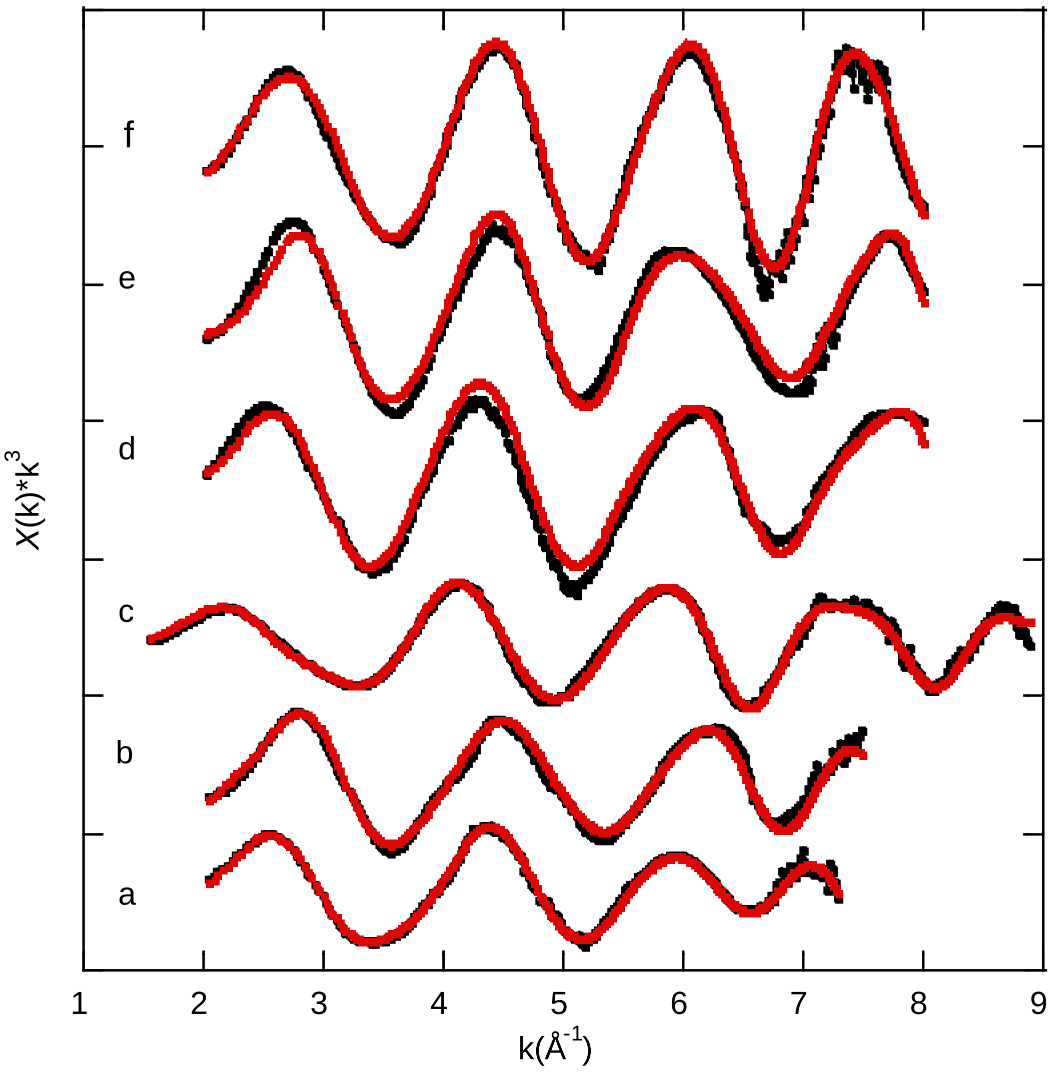


Figure SI-5 EXAFS experimental (black) and fitted (red) spectra for the three model compounds a) $LaPO_4 \cdot 1.4\ H_2O$ (rhabdophane), b) $LaPO_4$ (monazite) and c) $La_2(CO_3)_3 \cdot 8\ H_2O$ (lanthanite) as well as Phoslock® with a 100 % theoretical phosphate loading without (d) LaP100) and with (e) the presence of 500 µM humic acids (LaP0-HA$_{500}$). Moreover, LaP0-HA$_{500}$ is a reference samples of Phoslock® exposed to 500 µM humic acids and no phosphate (f). The spectra are shifted 5 units upwards for clarification. The mean La-O bond distances determined from the analysis of these EXAFS spectra are reported in Table 3. In Table SI-2 is the fitted data shown.

Table SI-2. EXAFS fitted data, including number of scattering pathways (fixed during refinement), *N*, bond distances, *d*, and Debye-Waller factor, σ^2.

		La-O		**La-O-P**		**La-O-C**	
	N	***d*/Å**	**σ^2/Å^2**	***d*/Å**	**σ^2/Å^2**	***d*/Å**	**σ^2/Å^2**
$LaPO_4\cdot 1.4H_2O$	8	2.457(1)	0.0233(1)				
	16			3.519(2)	0.0118(3)		
$LaPO_4$	9	2.522(1)	0.0196(7)				
	18			4.162(2)	0.0304(2)		
$La_2(CO_3)_3\cdot 8H_2O$	10	2.562(1)	0.0102(4)				
	20					4.00(1)	0.012(1)
LaP100	8	2.477(3)	0.0067(6)				
	16			3.575(1)	0.0043(1)		
LaP100-HA$_{500}$	9	2.523(3)	0.0074(1)				
	18			3.68(1)	0.0056(1)		
LaP0-HA$_{500}$	10	2.555(3)	0.0117(7)				
	20					3.23(1)	0.014(2)

Appendix SI-3

Adsorption study with different P compounds

A sample (50 mL, triplicate) with one of the following four P compounds (phytic acid dipotassium, adenosine 5’-triphosphate disodiumsalt, D-Glucose 6-phosphate monosodium and sodium pyrophosphate tetrabasic) and Phoslock dosed in a ratio of 1:100 from a stock solution sufficient to remove 100% of the concerned P species. Along with these samples were controls without Phoslock measured.

All samples were placed on shaking table for seven days, followed by centrifugation and measurement of total phosphorous (TP) in solution with Inductively Coupled Plasma Instrument with Optical Emission Spectroscopy (ICP), Optima 2100 DV, Perkin Elmer.

Table SI-3. Removal in percentage, from adsorption study with different P compounds and sufficient Phoslock® added to be able to remove 100%.

P compound	Removed P(%)
Phytic acid	67 (27)
ATP	9 (15)
Glucose	0 (3)
Pyrophosphate	19 (9)

References for supporting information

1. Wang, X.; Gao, M., A facile route for preparing rhabdophane rare earth phosphate nanorods. *J. Mater. Chem.* **2006,** *16*, (14), 1360.
2. Lucas, S.; Champion, E.; Bernache-Assollant, D.; Leroy, G., Rare earth phosphate powders $RePO_4$ nH_2O (Re = La, Ce or Y) II. Thermal behavior. *J. Solid State Chem.* **2004,** *177*, (4-5), 1312-1320.
3. Boakye, E. E.; Mogilevsky, P.; Hay, R. S., Synthesis of Nanosized Spherical Rhabdophane Particles. *J. Am. Ceram. Soc.* **2005,** *88*, (10), 2740-2746.
4. Glorieux, B.; Matecki, M.; Fayon, F.; Coutures, J. P.; Palau, S.; Douy, A.; Peraudeau, G., Study of lanthanum orthophosphates polymorphism, in view of actinide conditioning. *J. Nucl. Mater.* **2004,** *326*, (2-3), 156-162.
5. Ben Moussa, S.; Ventemillas, S.; Cabeza, A.; Gutierrez-Puebla, E.; Sanz, J., Structure of trihydrated rare-earth acid diphosphates $LnHP_2O_7{\cdot}3H_2O$ (Ln=La, Er). *J. Solid State Chem.* **2004,** *177*, (6), 2129-2137.
6. Anfimova, T.; Li, Q.; Jensen, J. O.; Bjerrum, N. J., Thermal Stability and Proton Conductivity of Rare Earth Orthophosphate Hydrates. *Int. J Electrochem. Sci.* **2014,** *9*, (5), 2285-2300.
7. Hellenbrandt, M., The Inorganic Crystal Structure Database (ICSD)—Present and Future. *Crystallogr. Rev.* **2004,** *10*, (1), 17-22.