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EXAFS STUDIES OF LANTHANIDE COORDINATION IN CRYSTALLINE PHOSPHATES AND AMORPHOUS PHYTATES

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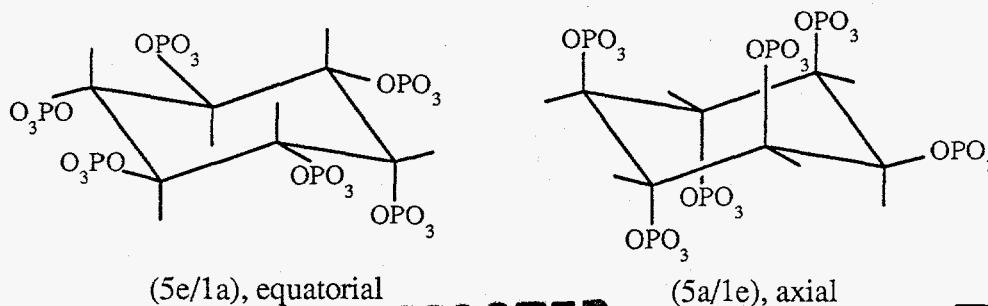
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INTRODUCTION

As part of the Efficient Separations and Processing Integrated Program of the U.S. Department of Energy, technologies are being developed that can stabilize radioactive and hazardous contaminants in order to reduce their potential to migrate from buried waste matrices. This report is part of a study to immobilize actinide ions in the near-surface environment by reacting them with organophosphorus complexants that decompose to inert, stable phosphates. In the initial phase of this study, the lanthanide ions Nd^{3+} and Gd^{3+} were used as models for the trivalent actinides Pu^{3+} , Am^{3+} , and Cm^{3+} . Phytic acid, *myo*-inositol hexakis(dihydrogenphosphate), was chosen as the organophosphorus complexant. The goal of this part of the project was to determine the bonding in precipitated lanthanide phytates.

Inositol phosphates are the major phosphorus-containing components of cereal grains, and they participate in transport of calcium in cell metabolism. Phytic acid complexes and precipitates divalent and trivalent metal ions, but the solubility of these salts varies with pH and concentration.¹ Phytic acid is most readily handled in its completely neutralized (basic) form as the dodecasodium salt hydrate. Two conformations of phytate have been described in the literature: one (5a/1e or axial) has five axial phosphates and one equatorial phosphate around the C_6H_6 ring, and the other (5e/1a or equatorial) has equatorial axial phosphates and one axial phosphate around the ring.



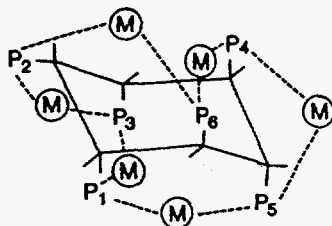
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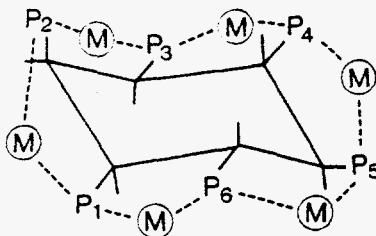
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The structure of the hydrate $C_6H_6(PO_4Na_2)_6 \cdot 38H_2O$ has been determined² to be (5a/1e). In aqueous solution, ^{13}C and ^{31}P NMR studies have shown³⁻⁵ that the (5e/1a) conformation predominates in acid and that the (5a/1e) predominates in base. Another ^{31}P NMR study⁶ showed more complex behavior. Since the sodium phytate is a highly basic species, its (5a/1e) conformation in the solid is consistent with the aqueous species at high pH characterized by most authors.

Studies of phytic acid-metal ion equilibria and structure models are limited to Mg^{2+} , Ca^{2+} , and some transition metal ions. Martin and Evans found up to 4.8 Ca^{2+} bound to one phytate, with the maximum ratio at 0.006 M $[Ca^{2+}]$ and 0.001 M phytate⁷ and they propose a 6:1 Ca^{2+} /phytate ratio with the (5a/1e) conformation:



For the 6:1 Cu^{2+} /phytate species these authors⁸ propose the (5e/1a) conformation:



The protonation constants of phytic acid and metal-ligand stability constants for several lanthanide ions with phytic acid in aqueous solution have been determined by potentiometry.⁹ The strongest phytic acid-lanthanide complexes are formed in acid solution, as is normally the case.

The infrared spectrum of phytic acid¹⁰ has strong absorption bands at 1060 cm^{-1} , which was assigned to $\nu(P-O-C)$ and 1400 cm^{-1} , which was assigned to $\nu(P=O)$. Phytin is the neutral mixed Mg^{2+}/Ca^{2+} salt of phytic acid. Its infrared spectrum was reported¹⁰ to show a metal-oxygen vibration at 460 cm^{-1} and a strong absorption band at 980 cm^{-1} that is characteristic of the P-O-P bond stretch in pyrophosphate ($P_2O_7^{4-}$).

We were not aware of any spectroscopic or crystallographic studies of solid metal phytates other than sodium phytate. Therefore we undertook to prepare solid lanthanide phytates and to characterize their lanthanide coordination by EXAFS. If the bonding in lanthanide phytates is similar to that in lanthanide phosphates, then the phytates should be insoluble and should decompose gradually to crystalline and inert phosphates.

SAMPLE PREPARATION AND CHARACTERIZATION

Crystalline orthophosphates $NdPO_4 \cdot xH_2O$ and $GdPO_4 \cdot xH_2O$ were used as standards. The orthophosphates $NdPO_4 \cdot xH_2O$ and $GdPO_4 \cdot xH_2O$ (Table 1) were precipitated by adding 0.05 M lanthanide nitrate solutions to dilute phosphoric acid solutions, buffered to pH 1 or pH 5 with $NH_3(aq)$. The pH of the mixtures were readjusted to pH 1 or pH 5 and the mixtures were held at $20\text{ }^\circ\text{C}$ or $50\text{ }^\circ\text{C}$ for three days. The precipitates were separated by

centrifugation and were dried in air at 100 °C. This temperature is below the temperature of first water loss (200-234 °C) and well below the reported transition temperature of 500-600 °C¹¹ to the anhydrous LnPO₄ (monoclinic, monazite). Our X-ray powder diffraction confirmed that the NdPO₄·xH₂O and GdPO₄·xH₂O had the hexagonal structure^{11,12}. Mooney did not locate the water molecules but she proposed that there was room for no more than alternate filling of three sites per unit cell with Z = 3, i.e. (moles H₂O)/(moles PO₄) = x = 0.5. Other researchers have reported 0 < x < 2. Thermogravimetric analyses of our preparations showed water content 0.5 < x < 1.

To prepare solid phytates, dilute (ca. 0.01 M) aqueous solutions of Nd³⁺ and Gd³⁺ nitrates were reacted with dilute sodium phytate solution at pH 3.1-3.2 in a ratio of 1:1 metal:phytate. Immediate precipitates formed, which were centrifuged, washed with water, recentrifuged, and dried at 95 °C in air (Table 1). Both Nd and Gd phytates were amorphous to X-ray powder diffraction.

Table 1. Samples for EXAFS studies

Description	Preparation	Structure (Literature)	Structure (Found)
NdPO ₄ ·xH ₂ O	Precipitate at pH 5, 20 °C	Hexagonal	Hexagonal
Nd phytate	Precipitate 1:1 ratio at pH 3.2, dried air 95°C		Amorphous by powder X-ray diffraction
Nd phytate (heated, brown)	Precipitate 1:1 ratio at pH 3.2, TGA air 500°C		Amorphous by powder X-ray diffraction
GdPO ₄ ·xH ₂ O	Precipitate at pH 5, 20 °C	Hexagonal	Hexagonal
GdPO ₄ ·xH ₂ O	Precipitate at pH 5, 50 °C	Hexagonal	Hexagonal
Gd phytate	Precipitate 1:1 ratio at pH 3.2, dried air 95°C		Amorphous by powder X-ray diffraction

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Infrared spectra were taken of all samples (two are shown in Figure 1). The IR spectrum of NdPO₄·xH₂O is consistent with that reported¹³: the PO₄³⁻ site symmetry is consistent with C₂ symmetry (which is lower than the D₂ symmetry required by the space group preferred by Mooney). The IR spectrum of Nd phytate is rather similar, showing a distinct peak at 990 cm⁻¹ which was seen in calcium-magnesium phytate¹⁰.

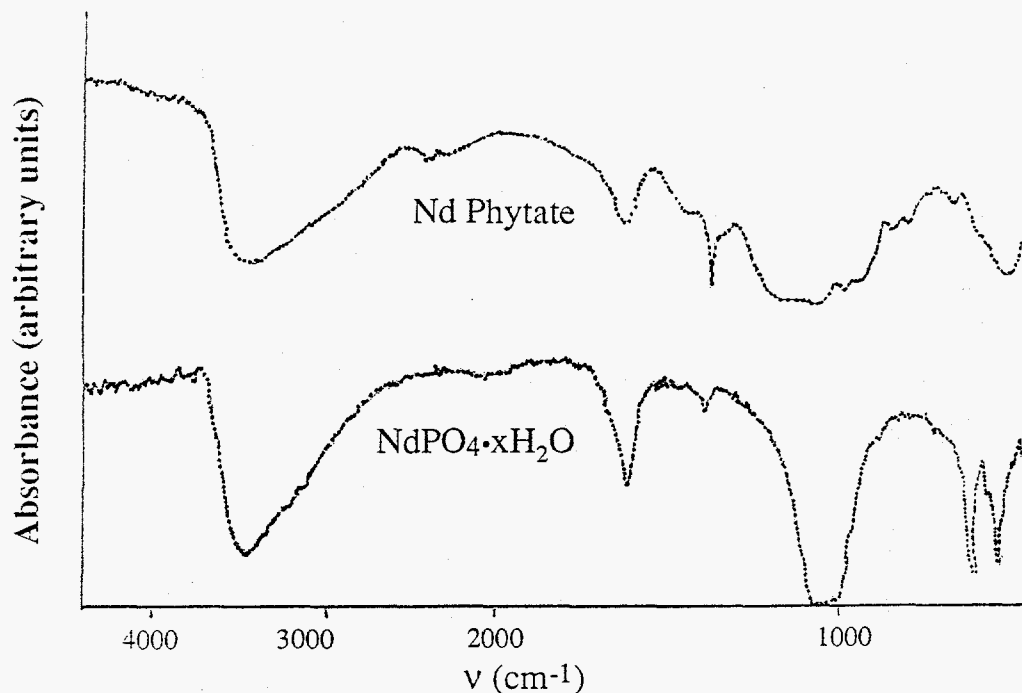


Fig. 1. The infrared spectra of Nd phytate and $\text{NdPO}_4 \cdot x\text{H}_2\text{O}$.

EXAFS DATA ACQUISITION AND ANALYSIS

Appropriate amounts of phosphates and phytates (Table I) were diluted with boron nitride powder in order to give an edge jump of ~ 1 across the Nd and Gd L_{III} absorption edges. The samples were mounted in 1/8" thick X-ray cells consisting of a polyethylene frame with Kapton windows on each side. All spectra were acquired at room temperature in transmission mode at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beamline 4-1 (unfocused) using a Si(220) double-crystal monochromator. Harmonic rejection was achieved by detuning the monochromator by 50% relative to the maximum incoming flux measured in I_0 . The data were calibrated by simultaneously measuring spectra for Nd and Gd metal foils, defining the first inflection point of their L_{III} edges at 6208 and 7243 eV, respectively.

EXAFS data reduction was performed by standard methods using the suite of programs EXAFSPAK developed by G. George of SSRL.¹⁴ Data reduction included pre-edge background subtraction followed by spline fitting and normalization (based on the Victoreen falloff) to extract the EXAFS data above the threshold energies, E_0 , defined at 6225 and 7260 eV respectively. Due to the closeness of the L_{II} and L_{III} absorption edges, the EXAFS data range was limited to $k = 11^{-1} \text{ \AA}$ for Nd and $k = 13 \text{ \AA}^{-1}$ for Gd. Curve-fitting analyses were performed using EXAFSPAK to fit then raw k^3 -weighted EXAFS data. The theoretical EXAFS modeling code, FEFF6, of Rehr et al.¹⁵ was used to calculate the backscattering phases and amplitudes of the different neighboring atoms which were included in the fits. For FEFF calculations, the atomic parameters for $\text{NdPO}_4 \cdot x\text{H}_2\text{O}$ and $\text{GdPO}_4 \cdot x\text{H}_2\text{O}$ were taken from Mooney.¹² EXAFS spectra and Fourier transforms are shown in Figures 2 and 3. Bond lengths and coordination numbers are given in Table 2.

DISCUSSION

For both phosphate samples, the bond distances and coordination numbers found by EXAFS are in very good agreement with crystallographic values. The neodymium-oxygen distances (2.41 and 2.62 Å) and coordination numbers (6 and 2) in the Nd phytate samples are similar to those in $\text{NdPO}_4 \cdot x\text{H}_2\text{O}$ (2.41 and 2.58 Å, CN 4 and 4). The same is true for the Gd samples except that only 7 Gd-O bonds are seen in Gd phytate. If each lanthanide is coordinated to oxygens of two adjacent phosphates on a phytate ring, it must be coordinated to an oxygen on another phosphate in the same ring, to a second phytate ring,

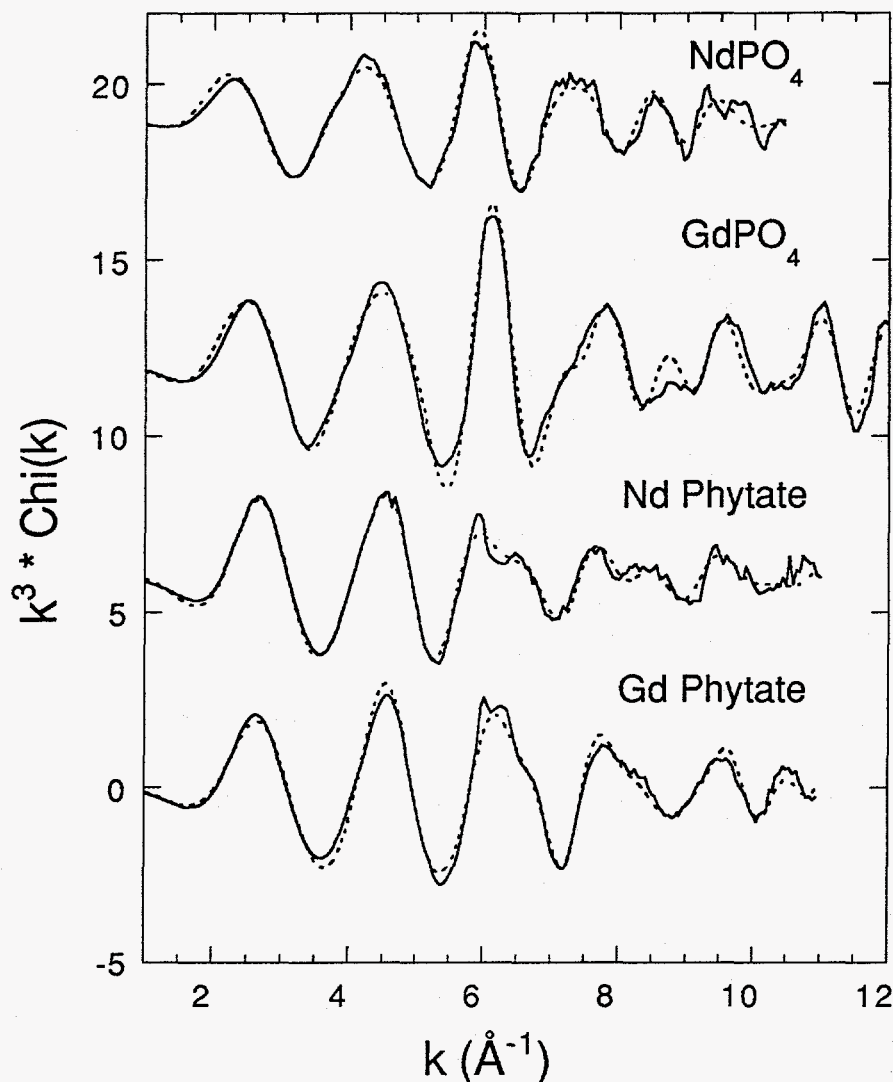


Fig. 2. k^3 weighted EXAFS spectra at Nd or Gd L_{III} edge. Top to bottom: $\text{NdPO}_4 \cdot x\text{H}_2\text{O}$, $\text{GdPO}_4 \cdot x\text{H}_2\text{O}$, Nd phytate, Gd phytate. Solid line, experiment; dashed line, fitted.

or to water molecules to complete its coordination sphere. It is worth noting that $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$ converts upon heating to monazite (monoclinic structure, for NdPO_4 nine Nd-O at distances¹⁶ 2.42-2.76 Å); the phytates do not have the monazite coordination geometry.

The shortest Nd-P distances (3.20 Å) in $\text{NdPO}_4 \cdot x\text{H}_2\text{O}$ were found in the $\text{NdPO}_4 \cdot x\text{H}_2\text{O}$ EXAFS but were not found in the Nd phytate; a parallel situation exists for the Gd

samples. This observation is consistent with the expectation that the metals are bridged between two phosphates, as proposed by Martin and Evans (*vide supra*), rather than having bidentate (intraligand) metal-phosphate coordination. Three Gd-Gd interactions at 4.59 Å were seen in the Gd phytate. These near neighbors imply that there are four Gd³⁺ ions bonded on at least some phytate rings in a manner inconsistent with the 1:1 Gd-phytate preparation ratio and inconsistent with the model of Martin and Evans^{7,8} that metal ions bridge adjacent phosphates on the ring. Perhaps some of the phytate has begun to decompose, although our continuing work has shown that lanthanide phytates require two weeks or more at 85 °C to decompose to crystalline phosphates.

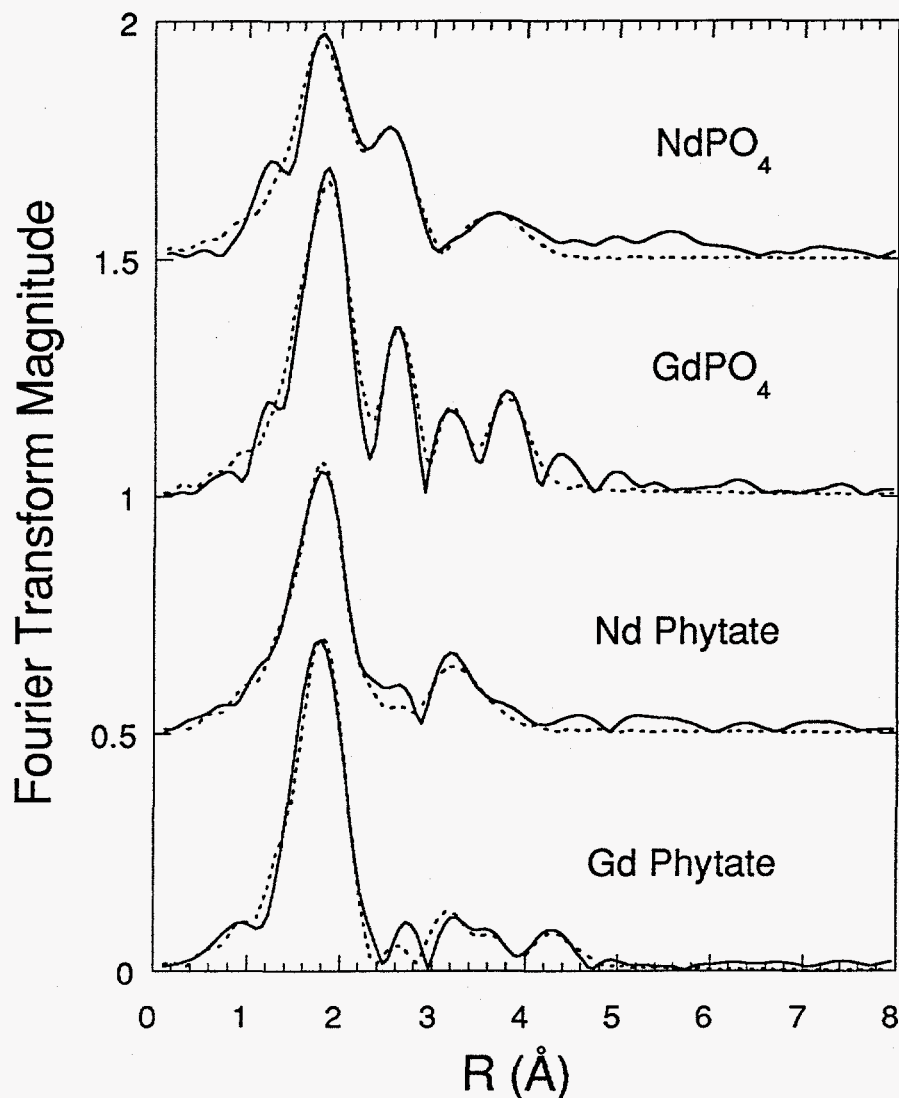


Fig. 3. Fourier transforms of Nd and Gd EXAFS from Fig. 2 (top to bottom, NdPO₄·xH₂O, GdPO₄·xH₂O, Nd phytate, Gd phytate). Solid line, experiment; dashed line, fitted.

There has been one X-ray absorption spectroscopy study¹⁷ of lanthanide orthophosphates. This was an energy-level study of the 3d levels 3d_{5/2} and 3d_{3/2} in single-crystal LnPO₄ (monazite or zircon structures) at the M_{4,5} edge and did not yield EXAFS parameters. Therefore our work appears to be the first EXAFS study of lanthanide

Table 2. EXAFS Results Compared with Crystallographic (Diffraction) Parameters

Bond	EXAFS			Diffraction	
	d(Å) ^a	CN ^b	$\sigma^2(\text{Å}^2)^c$	d(Å)	CN
NdPO ₄ ·xH ₂ O, 20 °C					
Nd-O	2.41	4	0.0091	2.32	4
Nd-O	2.58	4	0.0077	2.64	4
Nd-P	3.19	2	0.0080	3.17	2
Nd-P	3.81	4	0.0183	3.65	4
Nd-Nd	4.11	4	0.0175	4.11	6
GdPO ₄ ·xH ₂ O, 20 °C					
Gd-O	2.39	8	0.0110	2.29	4
Gd-O				2.60	4
Gd-P	3.12	2	0.0070	3.16	2
Gd-P	3.68	4	0.0125	3.60	4
Gd-Gd	4.03	4	0.0123	3.93	6
GdPO ₄ ·xH ₂ O, 50 °C					
Gd-O	2.39	8	0.0115	2.29	4
Gd-O				2.60	4
Gd-P	3.12	2	0.0059	3.16	2
Gd-P	3.68	4	0.0110	3.60	4
Gd-Gd	4.03	4	0.0102	3.93	6
Nd Phytate					
Nd-O	2.41	6	0.0126		
Nd-O	2.62	2	0.0069		
Nd-P	3.89	2	0.0078		
Gd Phytate					
Gd-O	2.37	7	0.0116		
Gd-P	3.83	1	0.0028		
Gd-Gd	4.59	3	0.0133		

^a Bond distances

^b Coordination numbers (for M-O) or nearest neighbors (for M-P and M-M)

^c σ = Debye-Waller factor

phosphates and indicates that lanthanide L_{III}-edge spectra are appropriate for obtaining lanthanide coordination environments in phosphates.

We hope to ascertain whether the lanthanide phytates adopt the (5e/1a) conformation found for phytic acid at low pH by molecular modeling and ³¹P NMR.

ACKNOWLEDGEMENTS

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