

Characterization of uranium minerals from Chihuahua using synchrotron radiation

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Abstract

Uranium mineral deposits in the vicinity of Chihuahua City (northern Mexico) have motivated a multidisciplinary investigation due to their techno-environmental importance. It provides a broad scope study of representative mineral samples extracted from the San Marcos deposit, located northwest of Chihuahua City. The zone of interest is in the source of the Sacramento River, which runs at Chihuahua City. The high uranium content of the San Marcos deposit, which was formed by hydrothermal mineralization, has resulted in elevated levels of uranium in surface and ground water, fish plants and sediments in this region. Mineral identification of the uranium-bearing phases was accomplished with a suite of techniques. Among these phases are those called metatyuyamunite ($\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3-4 \text{H}_2\text{O}$) and becquerelite [$\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8(\text{H}_2\text{O})$]. It was decided to study an almost pure metatyuyamunite sample extracted from Peña Blanca Chihuahuan uranium ore and to synthesize the becquerelite, using a modified procedure from a published one. In the current work the crystal structure of metatyuyamunite is presented, resolved by the Rietveld refinement. Both samples were studied by X-ray Absorption Fine Structure at Beamline 2-3, Stanford Synchrotron Radiation Lightsource. In the present work both the spectra and Extended X-ray Absorption Fine Structure parameters are presented.

Keywords: Uranium; becquerelite; metatyuyamunite; XRD-Rietveld refinement
synchrotron radiation; EXAFS.

Los yacimientos minerales en los alrededores de la Ciudad de Chihuahua, al norte de México, han motivado una investigación multidisciplinaria debido a su importancia técnica y ambiental. Dicha investigación proporciona un estudio amplio de muestras de los minerales representativos extraídos del yacimiento de San Marcos, Al Noroeste de la Ciudad de Chihuahua. La zona de interés es el nacimiento del río Sacramento, que corre a lo largo de la ciudad. El alto contenido de uranio del yacimiento de San Marcos, que se formó por una mineralización hidrotermal, ha dado como resultados elevados niveles de uranio en aguas superficiales y subterráneas, peces, plantas y yacimientos de la región. La identificación de las fases minerales se realizó mediante diversas técnicas. Entre esas fases está la metayuyamunite ($\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3-5 \text{H}_2\text{O}$) y la becquerelita [$\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8(\text{H}_2\text{O})$]. En esta investigación se decidió estudiar una muestra casi pura de metatyuyamunite extraída del yacimiento de uranio chihuahuense de Peña Blanca y también sintetizar la becquerelita siguiendo un procedimiento modificado de uno publicado. En este trabajo se presenta la estructura cristalina de la metatyuyamunite resuelta mediante un refinamiento de Rietveld. Ambas muestras se estudiaron usando la técnica de estructura fin de la absorción de rayos X en el haz 2-3 de la Fuente de Radiación Sincrotrónica de Stanford, California. También se presentan en el artículo los espectros y los parámetros obtenidos de la estructura fin de la absorción de rayos X en la zona extendida.

Descriptores: Uranio, becquerelita; metatyuyamunite; refinamiento de Rietveld;
radiación sincrotrónica; EXAFS.

Introduction

Great part of Chihuahua City is located on an alluvial valley called Chihuahua-Sacramento. It is part of the geological system "Basin and Range" in Northern Mexico. Around Chihuahua City are located several uranium deposits. The greatest one is the Peña Blanca ore, at the NE, which was exploited in the 1980's. At least two of the ores may contribute with radioactive contents to the water running into the Chihuahua-Sacramento Valley: The Pastorias zone at the SW and the Majalca-San Marcos zone to the NW. More extensive characterization of the San Marcos zone is provided in Ref. 1. In the mineralogical characterization of San Marcos deposit the following radioactive species were identified

Uranophane ($\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot 6(\text{H}_2\text{O})$),

Metatyuyamunite ($\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3-5(\text{H}_2\text{O})$),

Masuyite ($\text{Pb}(\text{UO}_2)_3\text{O}_3(\text{OH})_2 \cdot 3(\text{H}_2\text{O})$),

Becquerelite ($\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8(\text{H}_2\text{O})$)

And uraninite, (UO_{2+x}).

The study of the natural radioactivity is usually performed in order to obtain information about the levels of dangerous contaminants released to the environment where they can be in contact with living organisms [2,3]. Once the radioactive material is released, it can enter the human body by either ingestion (of contaminated food or water) or inhalation (of suspended radioactive particles). Normally, uranium is present in nature in the form of three isotopes: ^{234}U , ^{235}U y ^{238}U . There are several oxidation states of uranium that can be found, however, only the values of +4 and +6 are of real geological significance. When uranium is found in primary igneous minerals, it presents

the +4 value and it can be rapidly oxidized during weathering to the uranyl ion (UO_2^{+2}) that presents the +6 valence value of uranium. The uranyl ion is typically coordinated by four, five or six ligands, arranged at the equatorial vertices of square, pentagonal and hexagonal bipyramids, respectively. The bipyramids are capped by the O atoms of the uranyl ions. This characteristic variation of the uranium valences provides it certain facility to mobilize in the environment which can produce disequilibria between the parent and daughter isotopes in the disintegration chain. [4].

In a recent study [5] it was concluded that the high natural radioactive isotope concentrations at the northwest of the Chihuahua-Sacramento Valley, mainly in the mineralized deposits of San Marcos, is the zone which to a great extent contributes to the high contents of uranium observed in the alluvial deposit, as well as in superficial and ground waters. Furthermore, the great values of activity ratio $\text{U}234/\text{U}238$ in water, not only near the outcrops, but also in the city, indicate that the Chihuahua valley is almost totality an uraniumiferous zone. The specific activity in water samples is greater than the limit for alpha emitter, allowed by the Mexican official norm of water quality for human consumption. All these considerations provide a clear need to actually know the oxidation state of the uranium that is present in the geological environment of the Chihuahua city in order to be able to predict more precisely the contamination paths that are causing the situation that was previously discussed.

To achieve the latter, there are some analytical tools like the X-ray absorption fine structure (XAFS) that may be applied [6]. XAFS is a well established technique that analyzes the molecular structures at a local level providing information about the geometry and electronic organization around the absorbent atom [7]. Regarding the

importance that the uranyl ion has in the environment, there is a published catalog of the XAFS spectroscopy of 17 phases of this specie [8]. However, this publication doesn't include the oxyhydroxide Becquerelite ($\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_{6.8}(\text{H}_2\text{O})$) neither the uranyl-vanadates, particularly the Metatyuyamunite ($\text{Ca}[(\text{UO}_2)_2(\text{VO}_4)_2] \cdot 3.5(\text{H}_2\text{O})$) variations of the uranyl ion. Finch and Ewing [9] have concluded that oxyhydroxide based upon sheets of uranyl pentagonal bipyramids are the first minerals to form when the reduced uranium primary mineral uraninite, UO_2+x , is altered in moist oxidizing surroundings. Moreover, the Metatyuyamunite crystal structure was not reported in the most recently published crystallographic database [10]. Thereby, the purpose of this research is to refine a crystal structure for the Metatyuyamunite added to the XAFS spectroscopy analyses of the both the Metatyuyamunite and the Becquerelite species.

Materials and methods

Sample preparation:

Becquerelite:

In order to be able to study this specie, it is necessary to have a significantly pure sample. Our problem here is that Becquerelite, although present in the geological environment of the study zone, is present in complex materials with other minerals that make impossible its precise analysis. Hence, it was necessary to synthesize this uranyl phase with controlled conditions in the laboratory. The applied method was a modification of Gorman-Lewis et al. [11]. The reactants were 0.313 g enriched ^{238}U uranyl acetate ($\text{UO}_2(\text{CH}_3\text{-COO})_2(\text{H}_2\text{O})$), 0.5 JT Baker calcium carbonate (CaCO_3) and 4 cm^3 redistilled water. A 23 ml Parr Teflon pressurized bomb was used as the reactor and it was washed several times with redistilled water in an isothermal oil bath a

temperature of 147°C for one hour each time in order eliminate as much HF as possible. The reactants were mixed in the Teflo recipient and in to the Parr bomb. The system was introduced in to the isothermal oil bath at a temperature of 147°C ($\pm 2^\circ\text{C}$) for 50 hours. Once completely cold, the Teflo recipient containing the sample was put under a 500W incandescent lamp at a 20cm distance, in order to evaporate the remaining water and allow the crystallization process of the Becquerelite. Optic Microscopy and X-ray Diffraction analysis were performed to the crystallized sample.

Metatyuyamunite:

This phase was extracted from rocks with high mineral content of the Peña Blanca uranium ore [12]. Next, the fin powdered sample was dried in a laboratory furnace at 110° for 24 hours to ensure that the present phase is Metatyuyamunite and not Tyuyamunite. An X-ray Diffraction analysis was performed to the sample.

Crystal structures:

Becquerelite $\text{Ca}[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2 \cdot 8(\text{H}_2\text{O})$ belongs to the oxyhydroxides groups of uranyl compounds. Its structure, an orthorhombic cell with spatial group $\text{Pn}2_1\text{a}$, was analyzed by Burns and Li [13] using single-crystal XRD. Its hierarchy among uranyl compounds was described in Ref. 14, like a sheet of edge-sharing uranyl pentagonal bipyramids, with three hydroxyl anions in each equatorial plane. Distances between uranium U^{+6} and both axial and equatorial oxygens are represented in Fig. 1, based on XRD structure proposed by Burns and Li [13].

Metatyuyamunite $\text{Ca}[(\text{UO}_2)_2(\text{VO}_4)_2] \cdot 3\text{-}5(\text{H}_2\text{O})$ bealongs to the uranyl vanadates group, represented in the hierchical group [14] by the francevillite $\text{Ba}_{0.96}\text{Pb}_{0.04}[(\text{UO}_2)_2(\text{VO}_4)_2]_2(\text{H}_2\text{O})_5$. These compounds contain sheets based upon edge

sharing uranyl pentagonal bipyramids, edge sharing squares VO_5 pyramids as well as triangles. Metatyuyamunite is the dry form of the mineral, the other form being tyuyamunite $Ca[(UO_2)_2(VO_4)_2] \cdot 8(H_2O)$. In the case of Metatyuyamunite Ca, a low valence cation, is located in the interlayer of the structure and provides the linkage between sheets with 3 to 5 H_2O groups.

XAFS:

Both samples were prepared from pulverized mineral. The powders were weighted in an analytical scale. The weights to be placed in one square centimeter were calculated to yield 90-100% of the absorption of the incident beam, using HEP-HAESTUS code [15]. Both samples were sealed in kapton tape. The metatyuyamunite sample, once sealed, was placed in a container with silica gel to avoid moisture from the environment.

Uranium LIII-edge EXAFS spectra were collected at room temperature at the Stanford Synchrotron Radiation Lightsource (SSRL) on bending magnet beamline 2-3. The sample holder, in the case of the Metatyuyamunite, had a Nitrogen gas flu to avoid moisture from the environment. The incident X-ray beam was monochromatized using a doublecrystal $Si(220)$, $\Phi=0^\circ$ monochromator. Vertical slits in front of the monochromator were set to 1mm. Spectra were collected in transmission mode using Ar-fille ionization chambers. The monochromator was detuned 40-70% to reduce the harmonic content of the beam. Eight scans were collected and average for these samples.

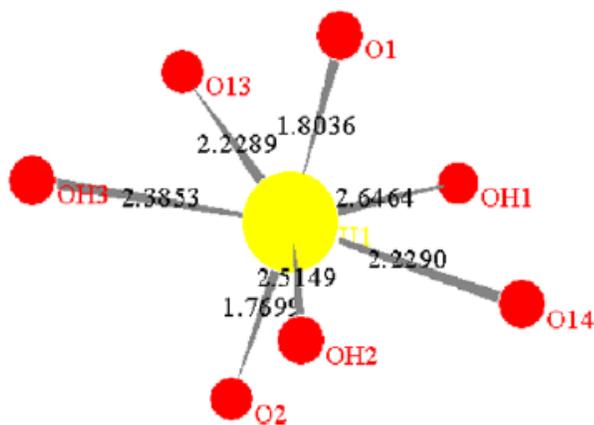


FIGURE 1. Becquerelite bipyramid with corresponding distances from U6+ cation and O2- anions.

EXAFS data were processed and analyzed using the Athena and Artemis graphical interfaces 0.8.058 version [15] to IFEFFIT [16]. Calibrated scans were average and background-subtracted. Spline fitting as performed using the Autobok parameters $R_{\text{bck}}=0.75$, $k\text{-weight}=3$ $dk=1$. The atomic coordinates from the published Becquerelite XRD-derived crystal structure [13] and the Metatyuyamunite proposed crystal structure (detailed below), were used to generate 4.5 Å radius clusters for the calculations. Coordination numbers (N) were fixed to crystallographic values; R (interatomic distance), σ^2 (Debye-Waller-type factor based on a Gaussian distribution of interatomic distances), and ΔE_0 (the difference between the threshold Fermi level of the theoretical phase shift and backscattering amplitude functions and the experimental data) were given initial seed values and they were allowed to move during the non-linear least squares fitting routine. R, X_V^2 and ΔE_0 values were linked for shells fixed with backscattering phase and amplitude functions calculated for the same scattering potentials (e.g., O_{eq} , O_{ax}). The amplitude factor S_0^2 , was fixed to values from 0.68 to 0.9

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for the becquerelite different oxygen links, and to 1 for the Metatyuya project. Only the first MS paths for both species were included in the fit. The reduced chi-squared value χ^2_{ν} and the R factor values were used in this study to evaluate the quality of the fit. The Ca cation distance to uranium core in both species is greater than the fitting radius.



FIGURE 2. Microphotograph of the synthetic becquerelite.

TABLE I. Crystal structure of Metatyuyamunite Space group: Pbcn; Crystal system: Orthorhombic a = 8.375(3), b = 10.584(3), c=16.856(5)

element	x	y	z	tag	occ.
Ca	0.0000	0.6609	0.2500	Ca	1
V	0.3473	0.0318	0.9570	V	1
O	0.3591	0.9970	0.8637	O1	1
O	0.3004	0.2560	0.7749	O2	1
O	0.1900	0.5210	0.6775	O3	1
O	0.0000	0.9677	0.2500	O4	1
O	0.4394	0.3305	0.6088	Oax1	1
O	0.5235	0.2977	0.3975	Oax2	1
O	0.4388	0.0979	0.5188	Oeq1	1
O	0.3496	0.5099	0.4870	Oeq2	1
O	0.2116	0.2973	0.4667	Oeq3	1
U	0.4791	0.3153	0.5036	U	1

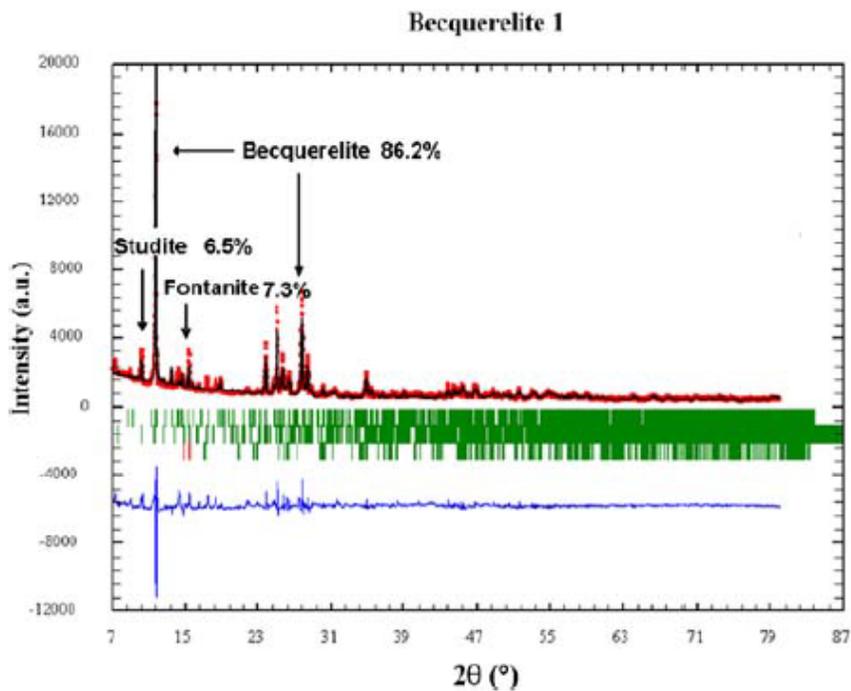


FIGURE 3. XRD pattern of the synthesis product.

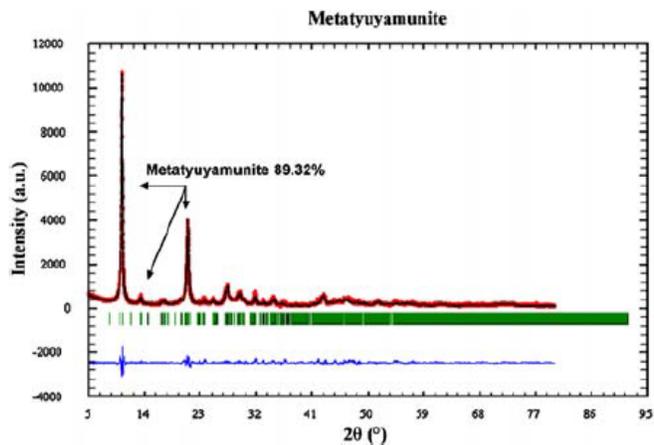


FIGURE 4. XRD pattern from the Metatyuyamunite dried sample.

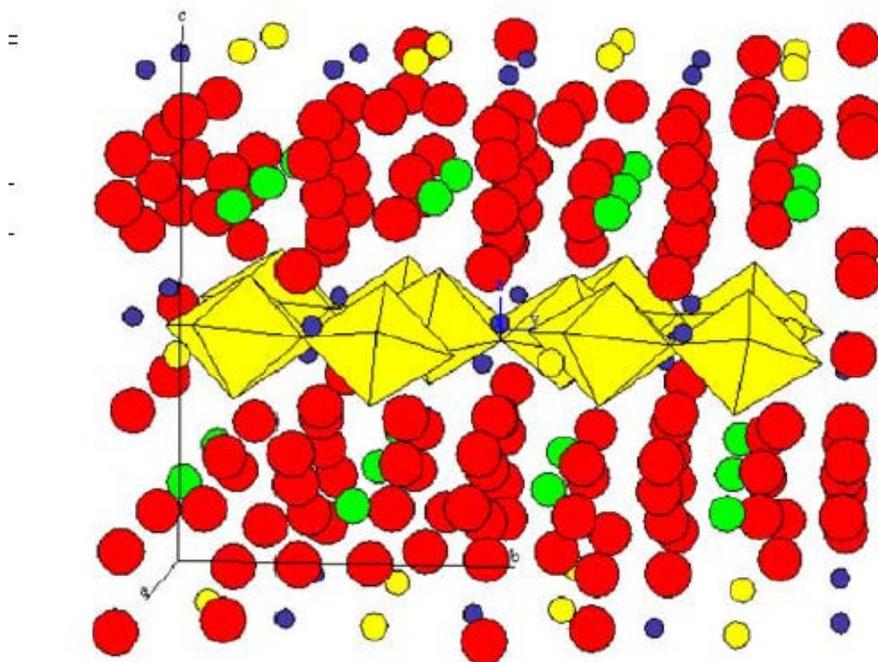


FIGURE 5. Metatyuyamunite crystal structure, view along the b axis.

Results and discussion

Sample preparation

Becquerelite:

The optic microscopy micrograph showed color and size uniformity in the synthesized sample. Furthermore, we were able to observe a characteristic yellowish crystal expected from the Becquerelite as shown in Fig.2. The XRD pattern showed the characteristic Becquerelite diffraction peaks in addition to some other known uranium minerals and uranium and calcium oxides (see Fig.3). However the Becquerelite specie represents 86.2% of the sample which is a sufficient percentage to perform the XAFS analysis. Besides we were able to identify all peaks in the pattern.

Metatyuyamunite

The XRD pattern of the dried sample showed that the Metatyuyamunite is the major species, and the minor peaks could also be identified (see Fig. 4). We can observe that the Tyuyamunite characteristic diffraction peak is not present which means that the drying process performed to the sample was successful. Rietveld data processing was performed with program Fullprof [17]. Raw diffraction data contained a superposition of Metatyuyamunite maxima plus peaks from calcite, quartz and cristobalite contaminants. A first stage toward structure analysis was the crucial cleaning-out of impurities' signals. This was done by means of Rietveld modeling of the impurities weighted diffraction fingerprint and subtraction from the observed pattern.

Crystal structure refinement

Starting model for Metatyuyamunite was the francevillite ($\text{Ba}_{0.96}\text{Pb}_{0.04}[\text{UO}_2]_2(\text{VO}_4)_2 \cdot 5(\text{H}_2\text{O})$) structure, with Ba and Pb cations being substituted by Ca cation. Space group Pbcn was preserved, lattice parameters were adjusted according to the observed peaks' positions and atomic positions were refined by employment of Fullprof's routine RBG for rigid body rotations. Convergence of

calculated XRD pattern to the experimental (virtually purified one was reasonable, with agreement factors $R_p=12\%$, $\chi^2_\nu=10$. Fig. 5 describes the metatyuyamunite crystal structure. Table I resumes the obtained crystallographic data and Fig. 6 shows representative interatomic distances in the pentagonal uranyl bipyramid.

TABLE II. EXAFS fitting results for the Becquerelite sample, and a comparison with XRD derived interatomic distances.

Mineral	Shell	N ⁺	EXAFS				R %	XRD R (Å)
			R (Å)	$\sigma^2(\text{Å}^2)$	ΔE_O	χ^2_ν		
Becquerelite	O _{ax}	2				15.1	1.9	
	O ₁	1	1.745(0.027)	0.004*	12.34(2.35)			1.7699
	O ₂	1	1.826(0.018)	0.004*	12.34(2.35)			1.8036
	O _{eq}	5						
	O ₁₄	2	2.100(0.062)	0.029*	9.986*			2.2289
	OH ₁	1	2.468(0.095)	0.004*	14.26*			2.6464
	OH ₂	1	2.336(0.095)	0.004*	12.57*			2.515
	OH ₃	1	2.207(0.095)	0.004*	12.57*			2.3853
	U ₅	2						
	U ₁	1	4.426(0.301)	0.019*	11.25*			3.8085
	U ₂	1	4.461(0.301)	0.019*	11.25*			3.8438
	U ₄	1	4.485(0.301)	0.019*	11.25*			3.868
	U ₂	1	4.510(0.301)	0.019*	11.25*			3.8934

() Estimated standard deviations.

+ Fixed to crystallographic values during fitting

* Parameter fixed during fitting after a previous approximation.

XAFS

Becquerelite

Becquerelite XAFS spectrum shows characteristic features of uranyl cation in the XANES zone. Its EXAFS spectrum is similar to that of other oxyhydroxides reported by Catalano and Brown [8]. EXAFS interpretation by fitting of ab initio functions using IFEFFIT is complicated by the range of first and second-shell interatomic distances. Furthermore, there are two equivalent sites in the equatorial plane of the bipyramid occupied by O²⁻ anion, while there are three sites corresponding to hydroxyls, with different distances. For fitting these hydroxyl-uranium bonds were grouped like similar

path, and their EXAFS parameters are all the same. Uranyl bond distances agree with the XRD-derived reference within the uncertainties. That is not the general case for the other distances. The relatively high values of ΔE_0 may be considered as not so large, if taking into account that the U LIII absorption edge is located at 17172.25 eV. Referring to discussion in the paper of Ref. 8, Becquerelite distinct shells with differences in interatomic distances close to the intrinsic distance resolution ΔR of EXAFS spectroscopy ($\Delta R = \pi / (2 \Delta k \text{ \AA}^{-1}) = \pi / (14.2 \text{ \AA}^{-1}) = 0.22 \text{ \AA}$, where Δk is the k-range of data being fit were not accurately fit causing significant errors in interatomic distances and Debye-Waller factors (see Table II). However the accuracy of the fit accessed by the χ^2_{ν} value, is good, as it can also be seen graphically in Fig.7.

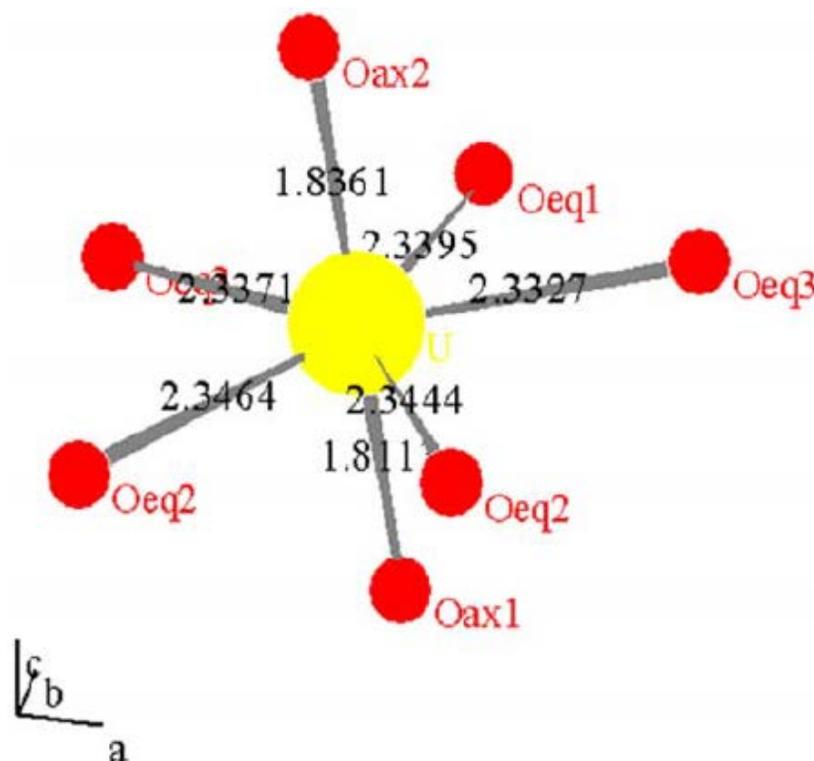


FIGURE 6. Metatyuyamunite bipyramid with corresponding distances from U^{+6} cation to O^{-2} anions.

TABLE III. EXAFS fitting results for the Metatyuyamunite sample, and a comparison with XRD derived interatomic distances.

Mineral	Shell	N ⁺	EXAFS				XRD		
			R (Å)	$\sigma^2(\text{Å}^2)$	ΔE_O	χ^2_r	R %	R (Å)	
Metatyuyamunite	O _{ax}	2							
		O ₁	1	1.820(0.005)	0.0027*	14.487(0.51)	84.2	5.09	1.8113
		O ₂	1	1.845(0.005)	0.0027*	14.487(0.51)			1.8361
	O _{eq}	5							
		O ₁₋₁	1	2.278(0.03)	0.0028*	13.227(0.51)			2.3395
		O ₂₋₁	1	2.327(0.005)	0.0008*	13.227(0.51)			2.3444
		O ₂₋₂	1	2.329(0.005)	0.0008*	13.227(0.51)			2.3464
		O ₃₋₁	1	2.448(0.013)	0.0027*	14.487(0.51)			2.3327
		O ₃₋₂	1	2.453(0.013)	0.0028*	13.227(0.51)			2.3371
	V	4							
		V ₁	1	3.234(0.013)	0.002*	4.92*			3.2722
		V ₂	1	3.361(0.013)	0.002*	4.92*			3.2722
		V ₃	1	4.256(0.013)	0.02*	8.9151*			3.8986
		V ₄	1	4.2735(0.013)	0.02*	8.9151*			3.9154
	U	1	3.835*	0.0054*	6.7124*			3.9271	

() Estimated standard deviations.

+ Fixed to crystallographic values during fitting

* Parameter fixed during fitting after a previous approximation

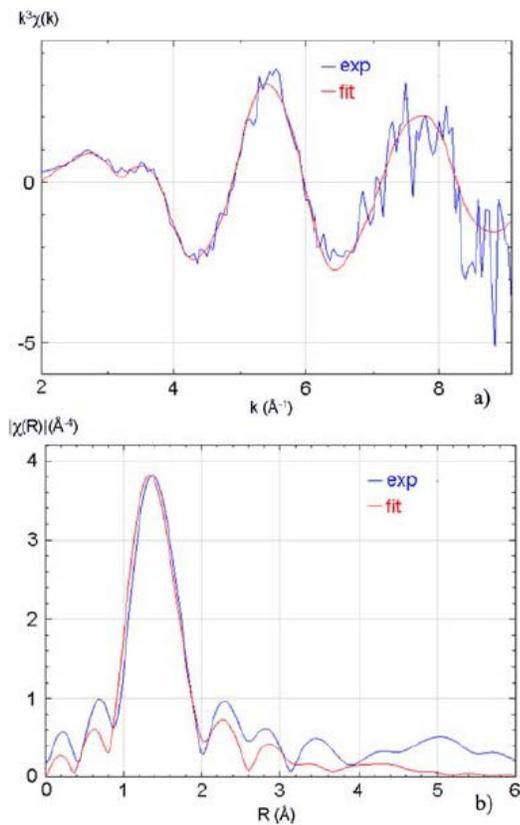


FIGURE 7. Spectra of the Becquerelite sample: EXAFS function χ (top) and fit in R (bottom).

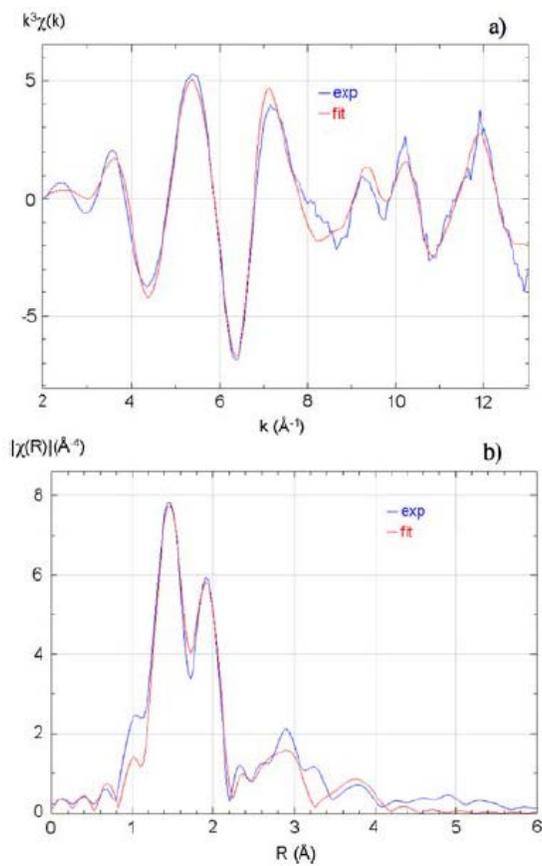


FIGURE 8. Spectra of the Metatyuyamunite sample: EXAFS function χ (top) and fit in R (bottom).

Metatyuyamunite

In the case of the Metatyuyamunite, there are no published EXAFS spectra of similar compounds to compare with the one we obtained. However, we found certain likeness with the meta-autunite spectra, which instead of five oxygens, has only four in the bipyramid. Metatyuyamunite distinct shells with differences in interatomic distances close to the intrinsic distance resolution ΔR of EXAFS spectroscopy ($\Delta R = \pi / (2 \Delta k \text{\AA}^{-1}) = \pi / (22.2 \text{\AA}^{-1}) = 0.14 \text{\AA}$) were not accurately fit causing significant error in interatomic distances and Debye-Waller factors (see Table III). Nevertheless the accuracy of the fit accessed by the χ^2_{ν} value, is fine as it can also be observed graphically in Fig. 8.

Conclusions

Structure of Metatyuyamunite has been refined using the Rietveld method on a powder XRD pattern. Structure parameters are given and they correspond well with the structure characteristic of uranyl vanadates [14,18].

Given the similarities of other oxyhydroxides species spectra reported in Ref. 8 and the one of Becquerelite, it is confirmed that, in the case when uranyl is present in a noncrystalline phase in environmental samples or adsorbed on surfaces, it is not possible to identify the exact oxyhydroxide species of the group by only performing an EXAFS analysis. The same may be asserted about Metatyuyamunite EXAFS spectrum. This confirms the statement previously discussed in Ref. 8 that the EXAFS spectra is not like a fingerprint for uranyl compounds. Then it is necessary to have more information about the elements contained in the sample to be able to interpret the EXAFS spectra and fully characterize the sample.

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