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SUPPLEMENTARY INFORMATION

Spectroscopic markers for uranium(VI) phosphates: a vibronic study

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1 Extraction of spectral information

The PL and Raman spectra were fitted in energy scales (cm^{-1}) using Voigt, Gaussian or Lorentzian functions with the free software fityk release 0.9.8 by Marcin Wojdyr under GNU General Public License as published by the Free Software Foundation.

The raw PL and reflectance spectra were acquired on two commercially available instrumentations yielding spectra on the wavelength scale with software acquisitions in nm units. The spectra are more familiar and thus easier to interpret visually on the wavelength scale. We have preferred to present the directly recorded spectra on the wavelength scale. Therefore we have kept wavelength units λ in Figure 3 and we have added a reciprocal top scale in wavenumber (cm^{-1}) units. For keeping a linear energy scale we present here the PL spectra in wavenumbers (Fig. S2) after transformation of intensities in $\lambda^2 I(\lambda)$ [1].

2 Calculations

2.1 Classical calculation of vibrational frequencies

Empirical ν_1 and ν_3 stretching frequencies have been obtained with the formulas of Bartlett and Cooney provided the U-O distances are known. In the case of uranyl phosphate hydrates, there is good agreement with experimental frequencies observed either in Raman or IR spectra (Table S1). Additionally we have reported estimates of the stretching force constant derived from Badger's rule.

Table S1 - Calculated empirical frequencies and stretching force constants of the U-O bonds in the investigated uranyl phosphate hydrates obtained from crystallographic data with the Bartlett and Cooney formulas and Badger 's rule (Equations 1).

d_{U-O}(Å)	ν_1 (cm^{-1})	ν_3 (cm^{-1})	k (mdyn.$Å^{-1}$)
1.770	841	936	5.832
1.816	795	873	4.673
1.775	836	929	5.689
1.780	831	921	5.550
1.811	800	879	4.783
1.795	816	901	5.160
1.771	840	934	5.803
1.797	814	898	5.110
1.778	833	924	5.605
1.744	870	975	6.661
1.768	843	939	5.891
1.807	804	884	4.874
1.841	772	841	4.170
1.808	803	883	4.851
1.746	867	972	6.592
1.748	865	969	6.524
1.801	810	892	5.014

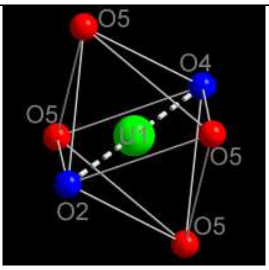
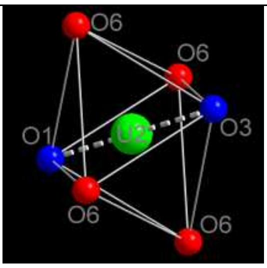
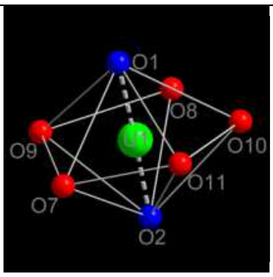
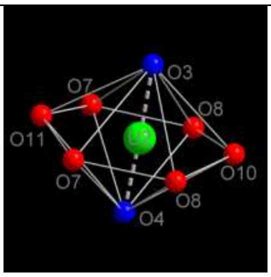
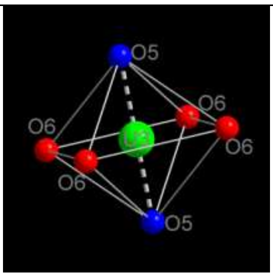
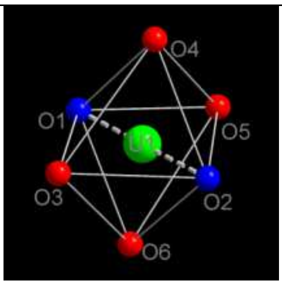
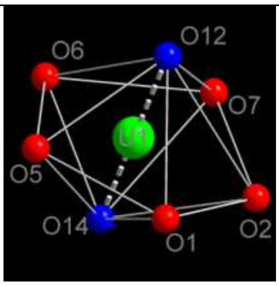
2.2 DFT calculation of vibrational frequencies

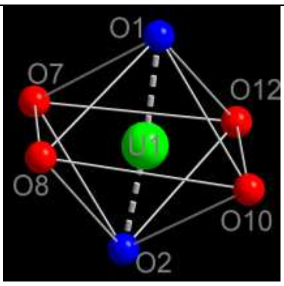
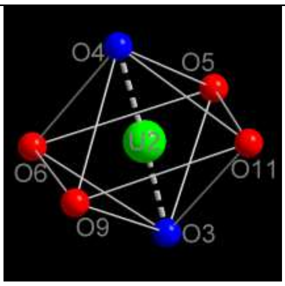
Conventional optimization of ions in free gas state performed for the present minerals led to unrealistic changes of their internal coordinates, as well as to overestimated frequencies. The uranyl and phosphate ions were therefore extracted from the crystals with their geometry directly observed by XRD techniques. The experimental structure of metauranocircite II containing $6H_2O$ was chosen for modeling the vibrations of the uranocircite mineral.

The vibrational calculation was carried out without any structural optimization using the DFT suite of programs Gaussian09 [2] and Q-Chem [3]. Vibrational calculations were performed on ions with experimentally observed bond lengths and angles. Direct DFT vibrational calculations on experimental, non-optimized structures resulted in zero frequencies for rotations and translations *with no imaginary frequencies insuring that a local minimum in the potential energy surface was present*.

Several basis sets were tried for DFT calculations of uranyl ions. Since uranium is a very heavy element with high atomic mass m = 238 g.mol^{-1} a relativistic basis set is required. We found that the choice of the Stuttgart RLC ECP (relativistic large core) basis set from Dolg et al. [4,5] was a good compromise for the program Gaussian we have at our disposal. We obtain best match with experimental frequencies when using the hybrid-generalized-gradient-approximation (GGA) B3LYP exchange-correlation (XC) functional. Each uranyl site present in the different crystallographic structures has been considered, e.g. three calculations were performed for phosphuranylite and two for metatorbernite and uranocircite. For the DFT calculations of the PO_4^{3-} ions we have chosen the simpler basis set LANL2DZ [6,7] for the P atom. We use the GGA Perdew-Burke-Ernzerhof (PBE) XC functional [8]. For oxygen atoms we have included basis sets with triple zeta valence functions plus one set of polarizations and one set of diffuse functions (6-311++G**). Trials at LANL2DZ/PBE level for uranium show that uranyl stretching frequencies are slightly modified while the bending modes appear at lower frequencies between 100 and 175 cm^{-1}: metatorbernite – 123 – 144 wn; phosphuranylite – 124 – 141 – 161 wn; saleeite – 101 wn; ulrichite – 175 wn; uranocircite – 127 – 131 wn.

2.3 Molecular depictions of uranyl sites with notation used in Table 2

Metatorbernite 2 sites U		
		
Phosphuranylite 3 sites U		
		
Saleeite	**Ulrichite**	
		
Metauranocircite II 2 sites U		

3 Photoluminescence and diffuse reflectance spectra

The spectra presented in the main text have been obtained under microscope objective x40 with a UV micro-Raman setup Jobin-Yvon LabRam. The spot size on sample is about 4 µm. The spectra bear resemblance to those obtained with a Jobin-Yvon fluorimeter Fluorolog (Fig. S1) with spot size of about 5 mm but they convey more information. However, the PL spectrum of phosphuranylite is more structured with the Fluorolog experiment. In Fig. S2, the PL same spectra as in Fig. 3a are presented on a linear wavenumber scale, after intensity transformation.

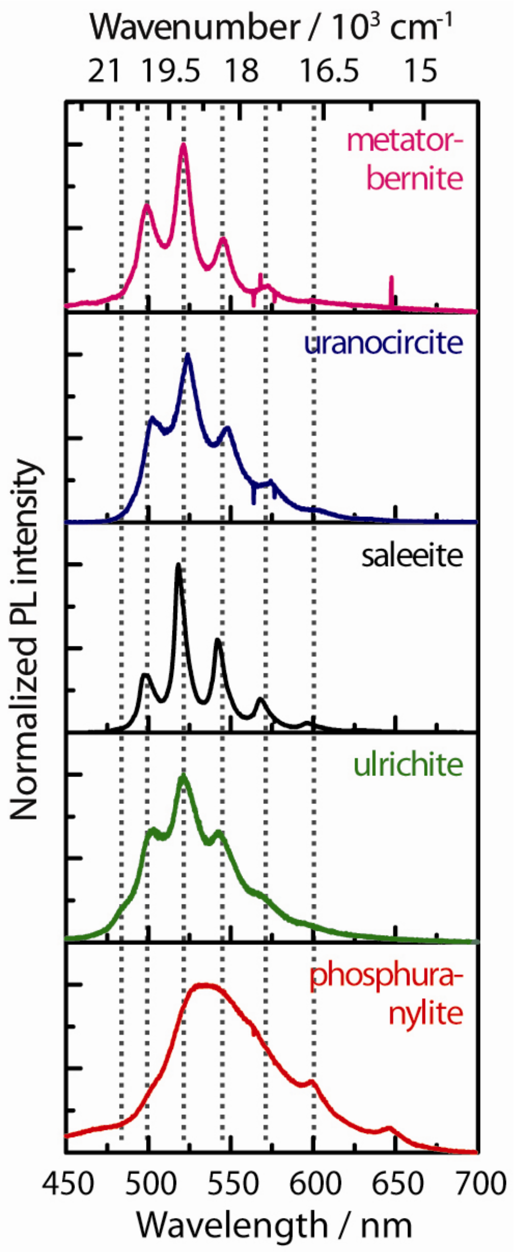


Figure S1 – Photoluminescence spectra of the five uranyl phosphate minerals for a monochromatic excitation λ_0 = 325 nm (3.81 eV) recorded on a Jobin Yvon Fluorolog-3 spectrometer using a Xenon lamp (500 W) and a charge-coupled-device detector.

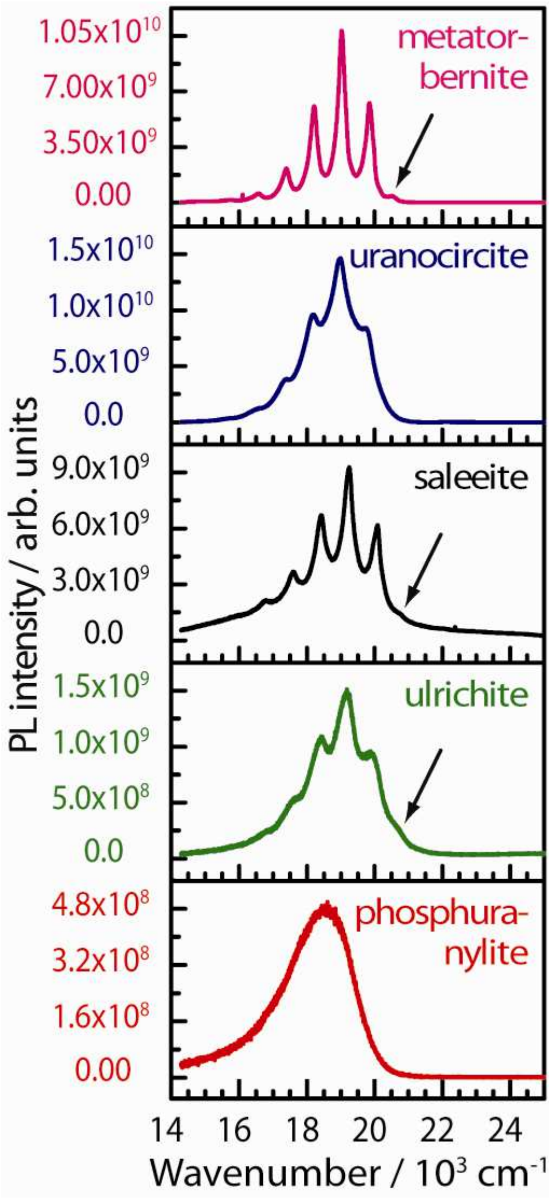


Figure S2–Photoluminescence spectra of the five uranyle phosphate minerals for a laser excitation λ_0 = 325 nm (3.81 eV) recorded on a Jobin-Yvon LabRam microprobe and presented on a linear wavenumber scale, after intensity scaling by λ^2 (λ: wavelength) [1]. The arrows indicate the hot bands characteristic of the excited vibrational state of the O-U-O stretching.

Fig. S3 displays the diffuse reflectance spectra obtained with an integrating sphere between 325 nm and 650 nm. Estimates of the electronic gap energy can be made with Kubelka-Munk transformation. Table S2 compiles the experimental electronic transitions found in PL and reflectance experiments in energy unit (cm^{-1}), with the observed vibronic gap values.

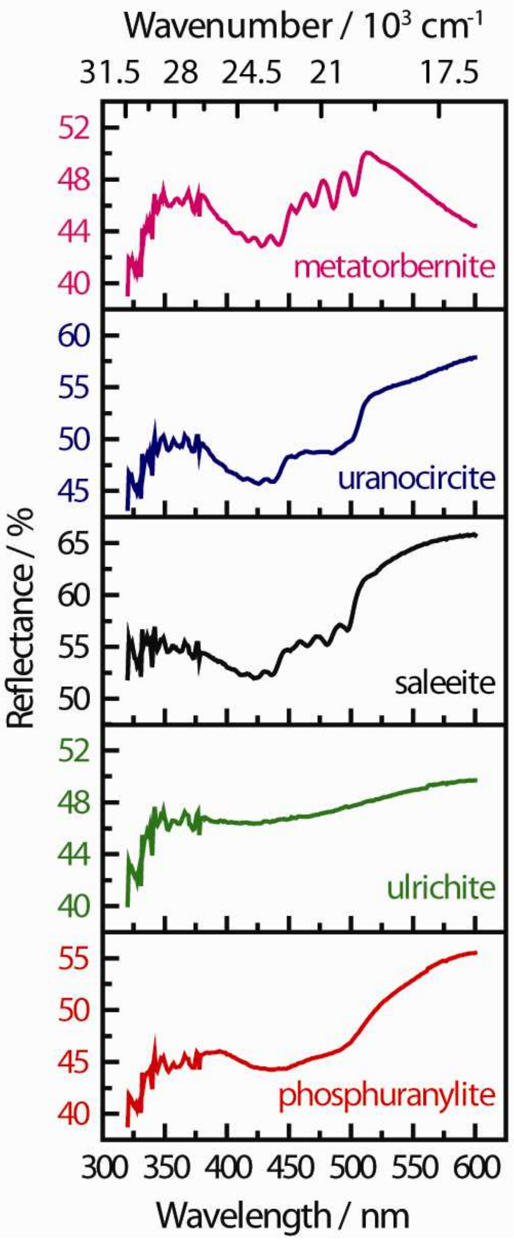


Figure S3 – UV-visible diffuse reflectance of the five uranyl phosphate minerals recorded between 325 nm and 650 nm.

Table S2. Main electronic transitions in cm^{-1} units observed for the uranyl phosphate minerals from photoluminescence (PL) and diffuse reflectance experiments[a]. H: hot band. From spectral fits to the data. Energy intervals in cm^{-1} between consecutive vibronic bands are given in rows labelled vibronic gaps.

Mineral	PL transitions (cm^{-1})	Absorption transitions[b] (cm^{-1})
Ulrichite	16822, 17616, 18407, 19163, 19901, 20587H	24938, 24331, 23697, 22988, 22321, 21598
Vibronic gaps	794, 791, 756, 738, 686H	607, 634, 709, 667, 723
Uranocircite	16555, 17369, 18170, 18977, 19771, 20446H	24938, 24230, 23530, 22883, 22000, 21300, 20618, 19920
Vibronic gaps	814, 801, 807, 794, 675H	708, 700, 647, 883, 700, 682, 698
Metatorbernite	16545, 17371, 18211, 19023, 19842, 20542H	24630, 23923, 23364, 22624, 21930, 21276, 20576, 19920
Vibronic gaps	826, 840, 812, 819, 700H	707, 559, 740, 694, 654, 700, 656
Saleeite	16811, 17553, 18393, 19228, 20060, 20760H	24938, 24331, 23641, 22883, 22173, 21505, 20790, 20121
Vibronic gaps	742, 840, 835, 832, 700H	607, 690, 758, 710, 668, 669, 653
Phosphuranylite	18524 (poorly resolved)	23696, 22936, 22321, 20325
Vibronic gaps		760, 615

[a] Transition energy can be obtained in nm or eV by dividing 10^7 by the wn in cm^{-1} or by dividing the wn by 8065.6, respectively. [b] Derived from diffuse reflectance spectra presented herein.

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