

Uranium speciation in weathered granitic waste rock piles: an XAFS investigation ESI

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Geological background

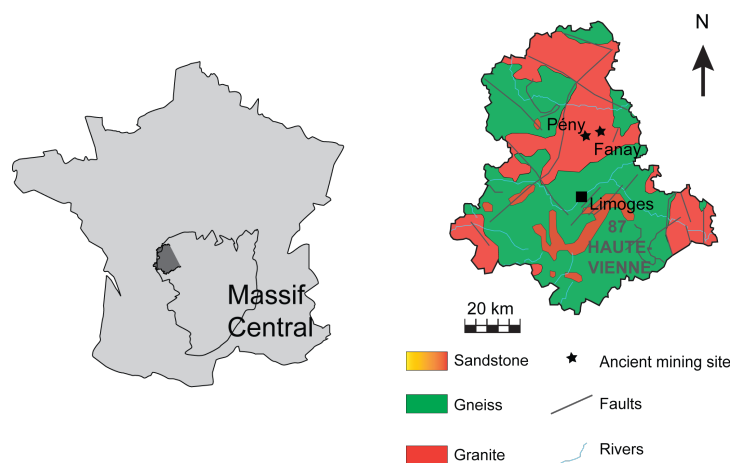


Figure S1 Geological background and location of the sites

EXAFS: Experimental and analytical procedures

Data were analyzed as described. Normalization was accomplished by shifting the dead time-adjusted fluorescence counts divided by the counts from the ion chamber monitoring the incident beam intensity to set the value of a second order polynomial fit through the pre-edge region to zero at 17185 eV and then multiplying this ratio so that the value of a third order polynomial fit through the post-edge was unity at this energy. The spectra from each detector for each scan was inspected prior to either including or excluding it in the signal/noise-weighted average over detector elements, and each scan was compared against the others prior to averaging with the same weighting scheme. The EXAFS was determined by approximating the smooth atomic background with a polynomial spline function calculated after fitting the edge region with the sum of an arctangent and a Gaussian function with an amplitude that fit $\sim 80\%$ of the white line in the spectrum and subtracting it from the data. Care was taken to ensure that the splines for all of the spectra had identical numbers of regions and polynomial orders and similar nodes. After this background was subtracted from the data it was renormalized to account for the falloff in the total absorption with energy, dividing the spectrum by this amount. Fourier transforms were performed after the application of a sine window function, except where square windows are noted to minimize the distortion of the amplitudes in back transformed or Fourier filtered spectra. Metrical parameters were obtained via non-linear least squares curve-fits over the range $k=2.7-13.5 \text{ \AA}^{-1}$, utilizing the single scattering formulation and amplitude and phase parameters. Two spectra that were exceptionally noisy were fit over a shorter range, as noted.

After substantial trial and error to overcome the ambiguity of EXAFS with respect to the numbers and types of neighbor shells, all spectra were fit with a combination of five waves from the oxo and two equatorial O neighbors, a P/Si/Al neighbor around 3.1 \AA , and the multiple scattering U-oxo contribution. Because of the proximity of their atomic numbers, P, Si, and Al cannot be distinguished in curve-fits, necessitating the use of other chemical information when available to determine the best choice of element. The overall number of floating parameters was maintained with the number allowed for this k and R range. Additional constraints on the ranges of ΔE_0 's, Debye-Waller factors, total numbers of equatorial atoms, a shift of the multiple scattering distance from twice the single scattering one were also utilized, so that, in those cases where

parameter correlation might have caused certain ones to become nonphysical can be prevented. Amplitudes and phases were derived from calculations with the Feff code, using the structure of schoepite as the input. The exception was the multiple scattering U-O wave from the oxo ions that is very difficult to calculate accurately because of its sensitivity to disorder within the unknown materials. In this case, empirical amplitudes and phases were obtained by Fourier filtering this contribution in the average of the eight best scans after subtraction of the other neighbor shells from the curve-fits. Errors are the deviation from the minimum that gives a 10% larger value of the least squares error for the contribution of each particular wave in the overall fit. Linear combination analysis was performed using the set of reference samples on the k^3 weighted EXAFS spectrum in the Athena software. The weight percentage of different reference samples is the only parameter that was varied to minimize the χ^2 value in the fits.

Table S1: EXAFS best fit parameters for the standards. R1) Soddyite, R2) Autinite, R3) Kaolinite, R4) Smectite, R5) Illite. N is the coordination number and R the distance. σ^2 is the Debye Waller factor of the considered scattering path. ΔE_0 is the energy of the threshold.

		O – oxo	O – eq 1	O – eq 2	O – eq 3	Al/Si/P[1]	Al/Si/P[2]	msoxo	Extra
		U							
R 1	R (Å)	1.81±0.01	2.32±0.02	2.48±0.02		3.15±0.02		3.62±0.04	3.87±0.02
	N	2.1±0.5	3.0±0.8	1.9±0.5		1.7±0.5		1.9±0.6	2.8±0.8
	σ^2 (mÅ)	39±21	63±18	62±20		71±16		59±40	65
	ΔE_0	0.0±3.7	-1.0±2.9	-1.0±3.0		1.5±2.8		-1.0±3.0	0.2
		U							
R 2	R (Å)	1.81±0.01	2.31±0.02	2.51±0.02	2.70±0.02	3.10±0.02	3.27±0.02	3.63±0.04	
	N	2.3±0.5	4.5±1.0	2.0±0.6	1.3±0.4 65	1.5±0.5	1.5±0.5	2.5±0.9	
	σ^2 (mÅ)	35	54±17	44±24	0.6	40±22	40±22	35	
	ΔE_0	0.8±4.1	0.6±2.8	0.6±3.1		2.3±3.4	2.3	-0.2±3.9	
		Si/Al							
R 3	R (Å)	1.78±0.02	2.28±0.02	2.43±0.02	2.57±0.02	3.10±0.02	3.36±0.05	3.57±0.05	3.62±0.02
	N	2.3±0.6	1.9±0.6	2.1±0.6	1.2±0.4 65	1.1±0.4	2.0±0.4	2.0±0.1	0.9±0.3 60
	σ^2 (mÅ)	35	35	25	-2.1	60	55±8	55	-4.0
	ΔE_0	-3.1±4.9	-2.1±3.9	-2.1±3.7		-4.6±3.3	-4.1±6	-4.1±6.0	
		U							
R 4	R (Å)	1.80±0.01	2.32±0.02	2.53±0.02		3.11±0.03		3.62±0.06	
	N	2.4±0.6	2.8±0.8	2.3±0.7		1.5±0.5		2.1±0.1	
	σ^2 (mÅ)	36±30	76±20	67±21		106±20		56±8	
	ΔE_0	0.8±4.0	0.3±3.0	0.3±3.0		2.3±2.4		-0.2±4.5	
		U							
R 5	R (Å)	1.80±0.01	2.30±0.02	2.48±0.02		3.08±0.02	3.26±0.2	3.61±0.03	
	N	2.3±0.5	3.3±0.9	3.2±0.9		1.8±0.5	1.1±0.3	1.2±1.0	
	σ^2 (mÅ)	39±21	79±20	90±22		77±16	50±18	59±15	
	ΔE_0	-1.0±3.8	-2.0±2.7	-2.0±2.7		0.5±3.0	0.5	-2.0±3.5	

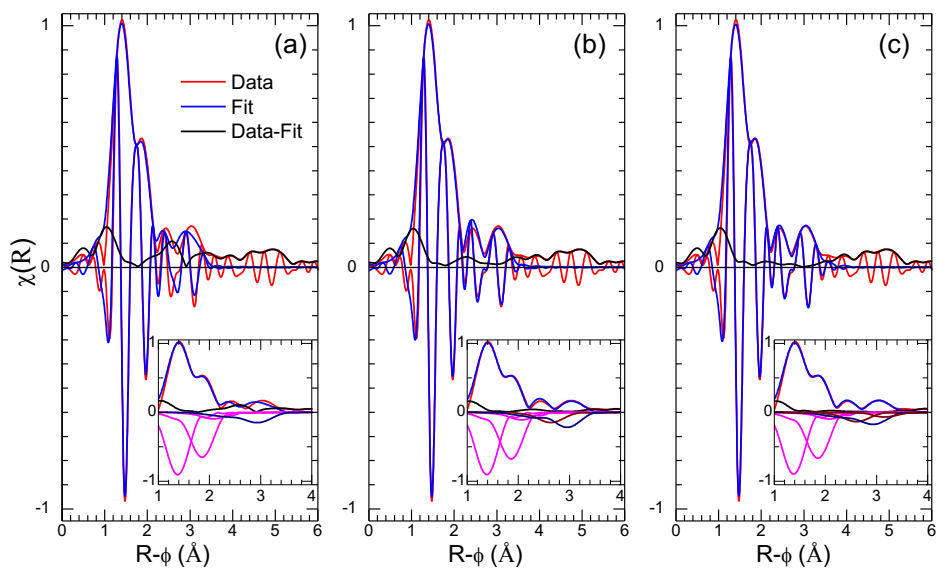


Figure S2. EXAFS $\chi(R)$ fits of autunite with - 2 equatorial, 1 axial U-O shell, and a multiple scattering U-O shell (a), - including P shell at 3.01 Å, - including another P shell at 3.6.

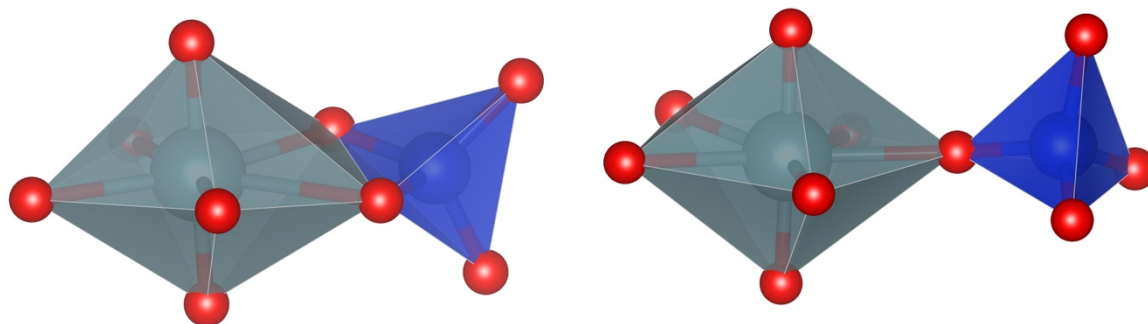


Fig. S3. Local geometry of U complex coordinated in the bidentate (left) and monodentate (right) configurations with equatorial oxygen. U-O forms highly oblate trans-dioxo geometry which can be linked to SiO_4^{2-} or PO_4^{3-} . The tetrahedral SiO_4^{2-} is replaced by AlO_6^{2-} octahedra for the U-Al sorption complex.

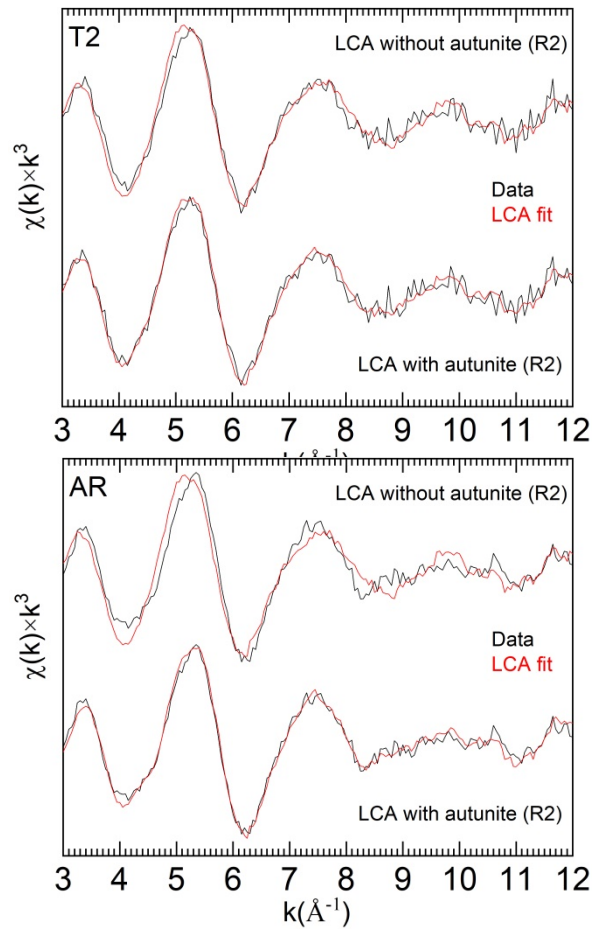


Figure S4. Linear combination analysis of T2 and AR samples with and without including $\chi(k)$ spectrum of autunite (R2) in the LCA fitting. As presented in the main text, the inclusion of R2 component improve the quality of fits for the T2 and AR samples.

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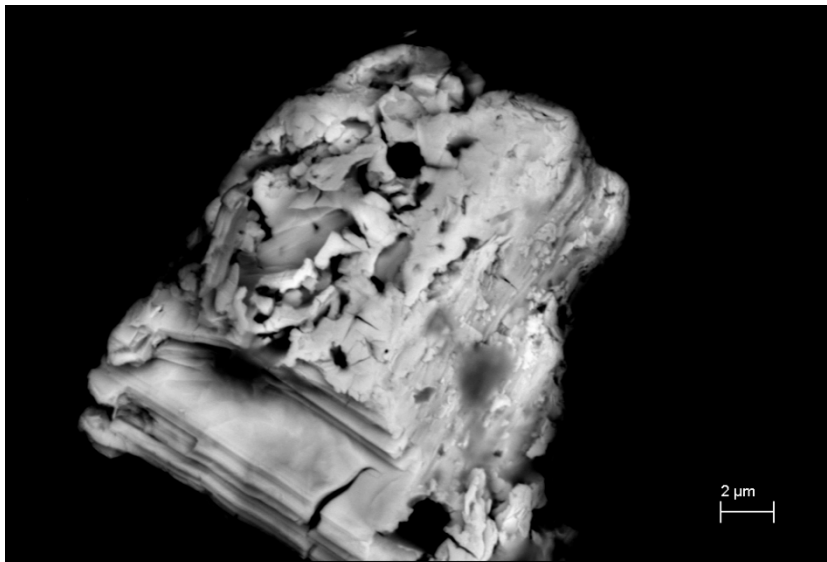
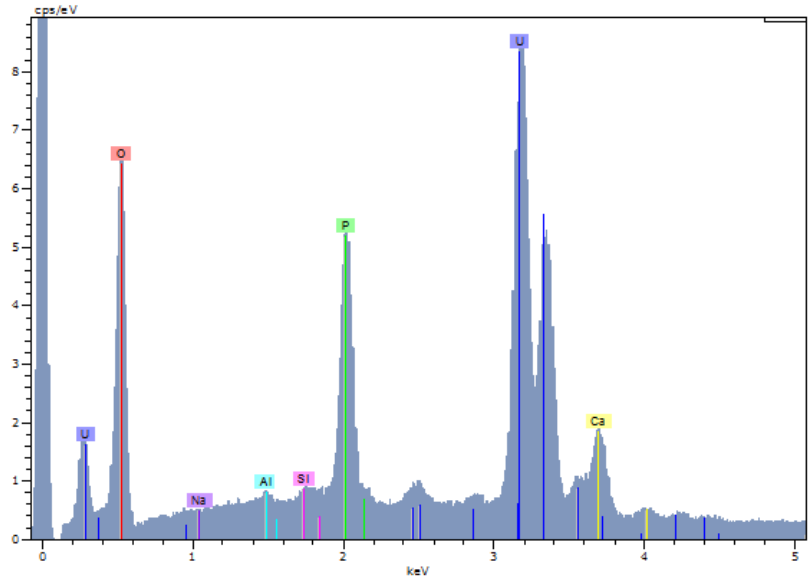


Fig. S5.EDS spectrum and SEM image of sample CFA (a filtered fine fraction of the arena A).