Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

A Multi-technique Study of Altered Granitic Rock from Krunkelbach Valley Uranium Deposit, Southern Germany

Ivan Pidchenko[a,b], Stephen Bauters[a,b], Irina Sinenko[c], Simone Hempel[d], Lucia Amidani[a,b], Dirk Detollenaere[e,g], Laszlo Vinze[e], Dipanjan Banerjee[f,g], Roelof van Silfhout[h], Stepan Kalmykov[c], Jörg Göttlicher[i], Robert J. Baker[j], Kristina Kvashnina[a,b,c*]*

[a] *The Rossendorf Beamline at ESRF – The European Synchrotron, CS40220, 38043 Grenoble Cedex 9, France*
[b] *Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, PO Box 510119, 01314 Dresden, Germany*
[c] Lomonosov Moscow State University, Department of Chemistry, 119991 Moscow, Russia
[d] Technical Universität Dresden, Institute of Construction Materials, DE-01062 Dresden, Germany
[e] Department of Chemistry, X-ray Imaging and Microspectroscopy Research Group, Ghent University, Ghent, Belgium
[f] Department of Chemistry, KU Leuven, Celestijnenlaan 200F, Box 2404, B-3001 Leuven, Belgium
[g] Dutch-Belgian Beamline (DUBBLE), European Synchrotron Radiation Facility, 71 avenue des Martyrs, CS 40220, 38043 Grenoble Cedex 9, France
[h] The University of Manchester, School of Electrical and Electronic Engineering, Sackville Street, Manchester M13 9PL, United Kingdom
[i] Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation (IPS), P.O. 3640, D-76021 Karlsruhe, Germany
[j] School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland

***Corresponding authors:**

Dr. Ivan Pidchenko, E-mail: ivan.pidchenko@gmail.com

Dr. Kristina Kvashnina, E-mail: kristina.kvshnina@esrf.fr

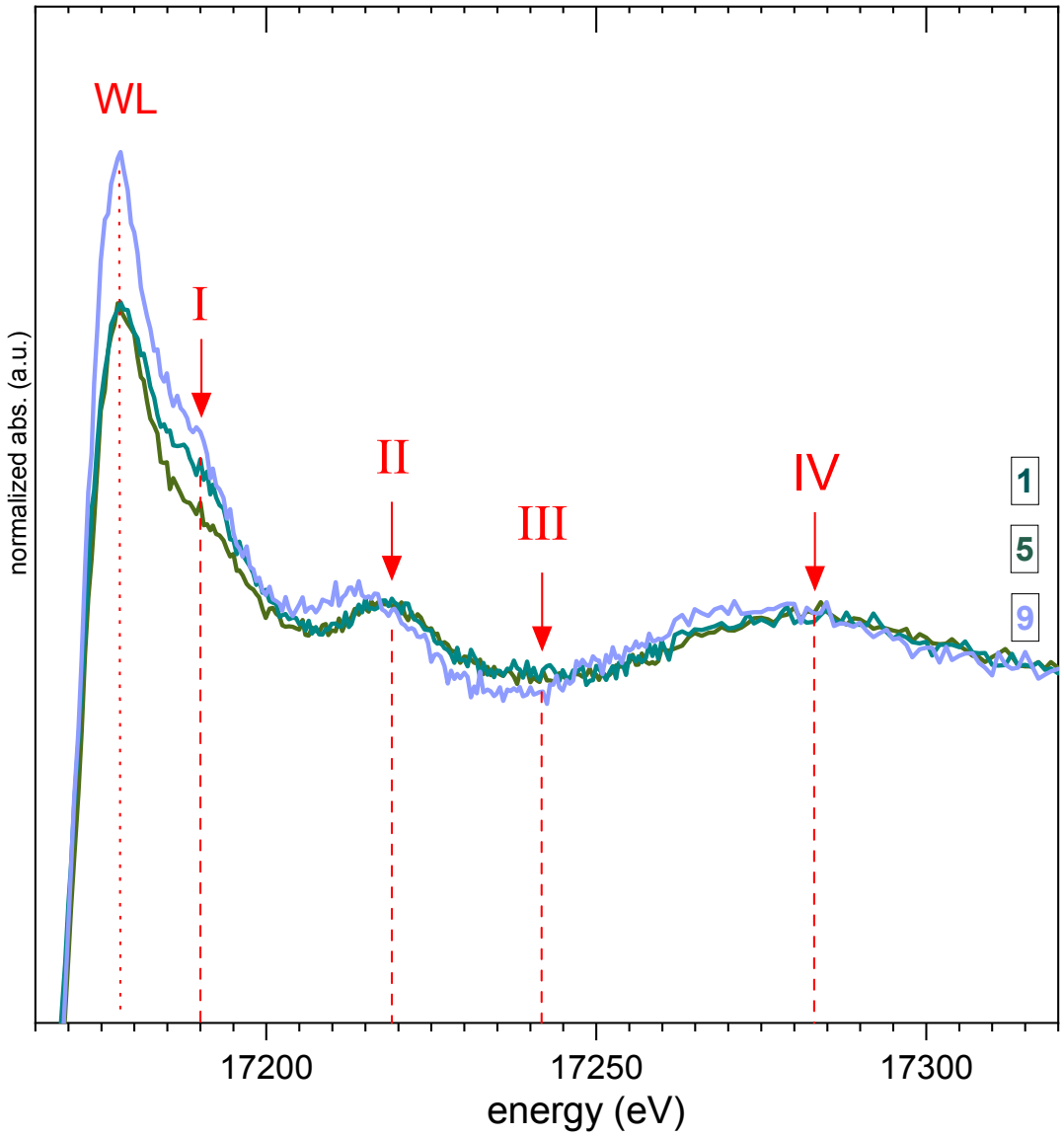

Fig. S1 U L_3 edge μ-XANES spectra of two spots from area with intense U signal (1 and 5) and one spot from low intensity U area (9). Spectra are plotted together for comparison of the relative intensity of the WL.

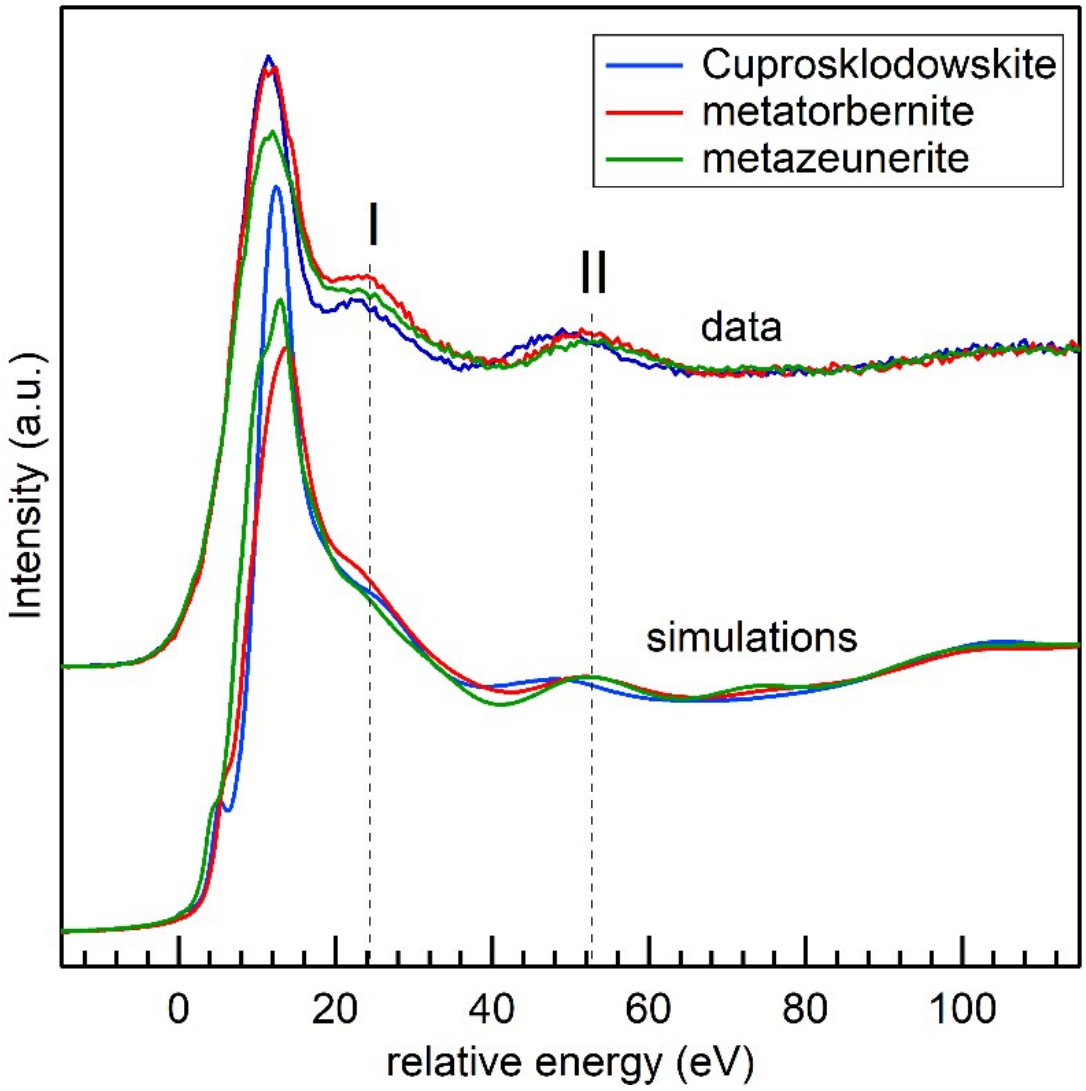

Fig. S2 Experimental (upper) and theoretical simulations (lower) of U L_3 edge HERFD-XANES spectra for Cuprosklodowskite, metatorbernite and metazeunerite using FDMNESS code. Feature I and II indicate spectral regions used for the fingerprint analysis.

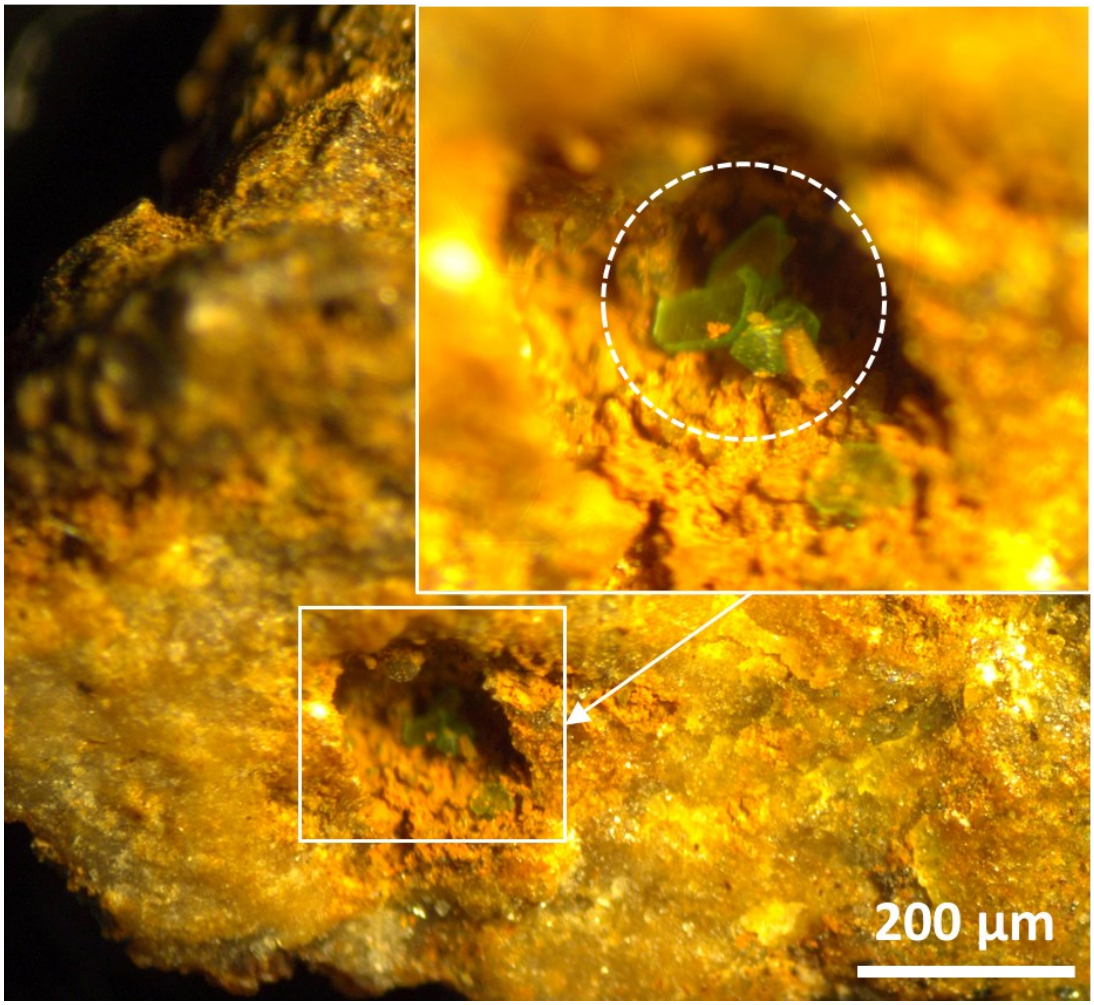

Fig. S3 Microphotograph of the cavity and flat-shaped vitreous green crystals selected for Raman analysis.

U L_3 edge high-energy resolution fluorescence detected (HERFD) X-ray absorption near edge structure (XANES) spectroscopy

U L_3 edge HERFD-XANES measurements were performed using Johann-type emission spectrometers installed at Rossendorf (BM20) beamline of the European Synchrotron (ESRF) in Grenoble, France.[1] The incident energy was selected using the <111> reflection from a double Si crystal monochromator. The sample, analyser crystal and photon detector (Si drift diode) were arranged in a vertical Rowland geometry. The U L_3 edge HERFD-XANES spectra were obtained by recording the maximum intensity of the U $L_{\alpha 1}$ emission (E = 13,616 eV) as a function of the incident energy. The emission energy was selected using the <880> reflection of three (BM20) spherically bent Si crystal analysers (with 0.5 m bending radius) aligned at 71.5° Bragg angle. The spectra were collected at different spots by recording from 1 up to 20 spectra per spot.

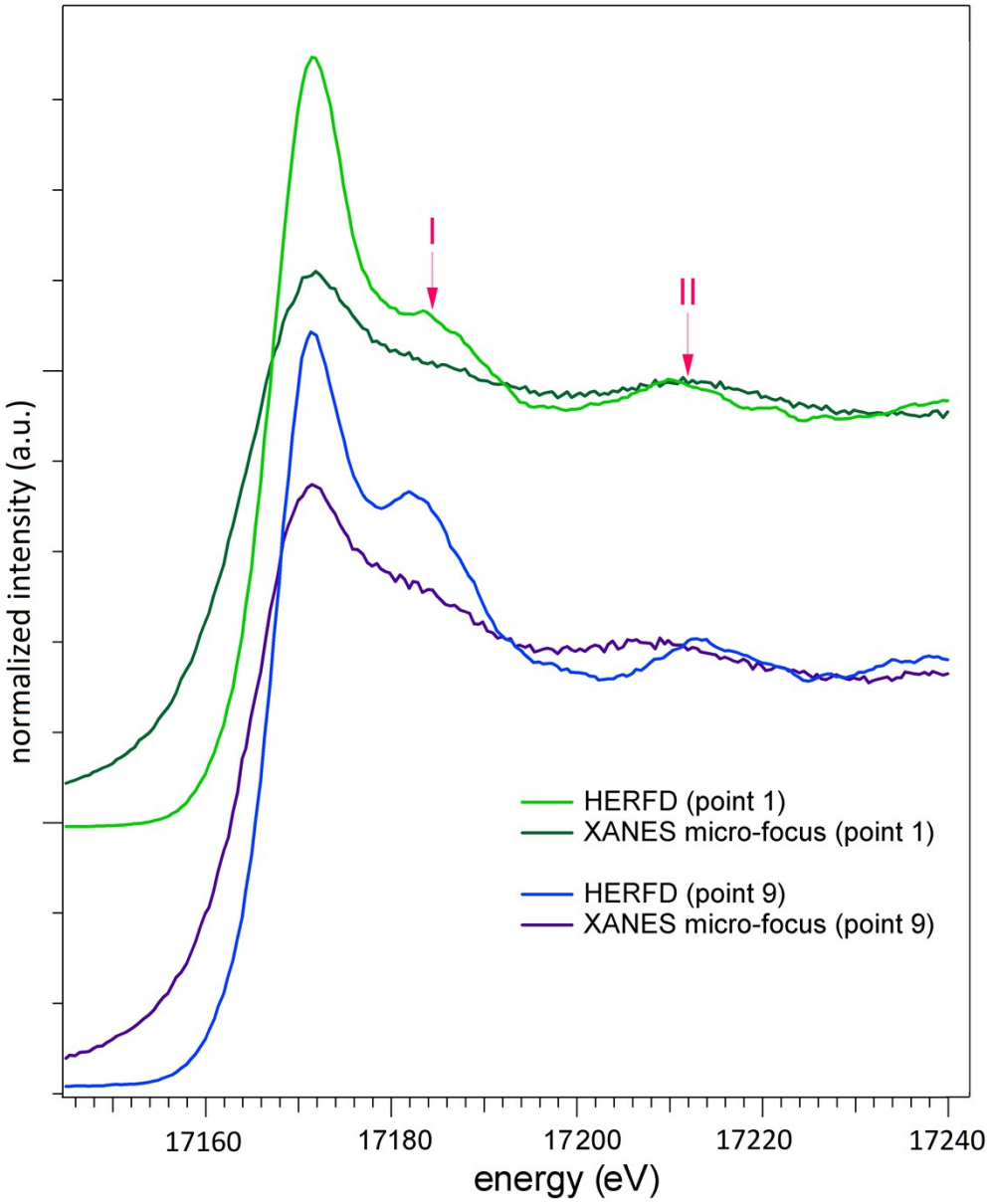

Fig. S4 Comparison of U L_3 edge micro-focus and HERFD-XANES spectra collected from 2 spots of the rock. All spectral features for HERFD spectra are much better resolved.

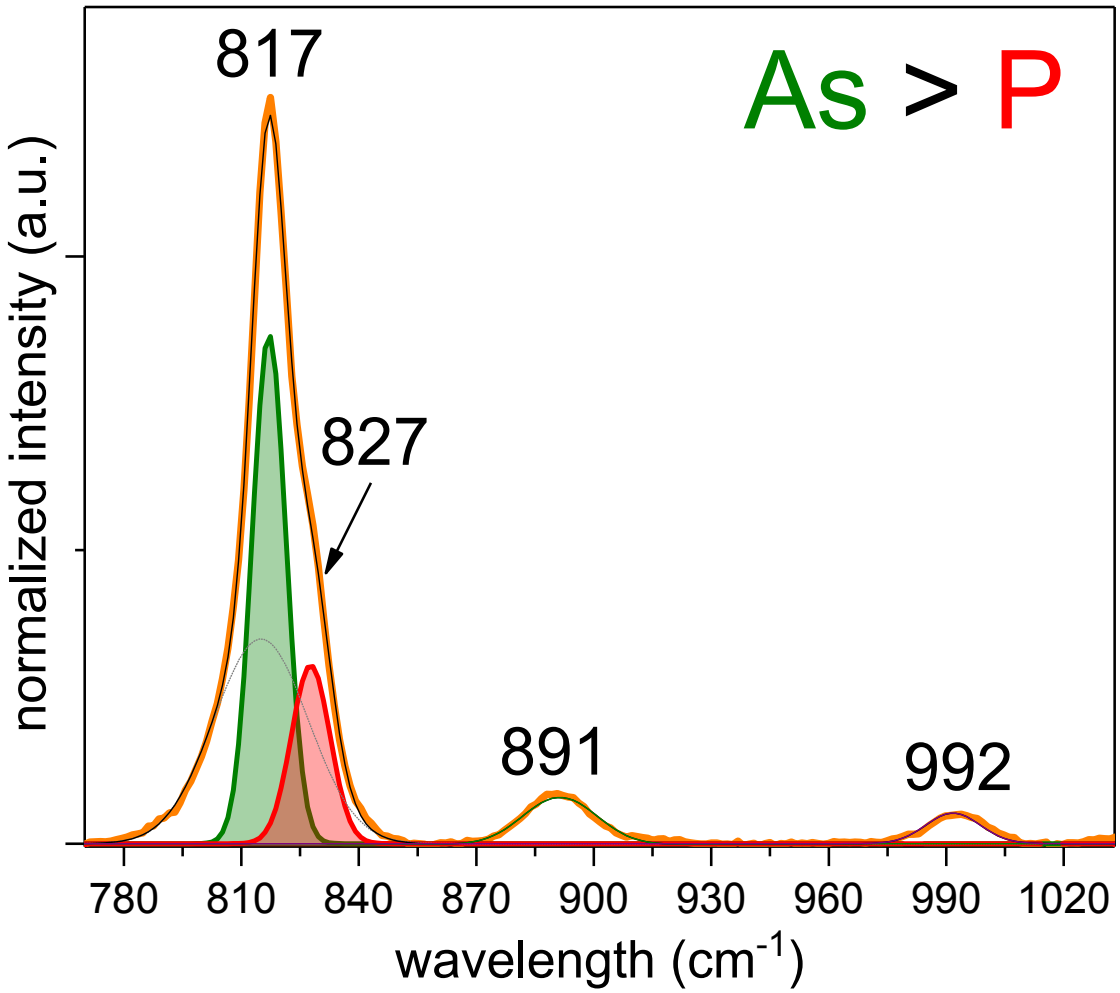

Fig. S5 Raman spectrum deconvolution using Fityk program.[2]

Table S1 Uranium mineral species identified in Krunkelbach mine.[3,4]

Mineral *group/species*	Chemical formula
Oxides/hydroxides	
Uraninite/Pitchblende	UO_{2+x}
Ianthinite	$U^{4+/5+}(UO_2)_5O_7{\cdot}10H_2O$
Billietite	$Ba(UO_2)_6O_4(OH)_6{\cdot}8H_2O$
Wölsendorfite	$(Pb,Ca)U_2O_7{\cdot}2H_2O$
Schoepite	$(UO_2)_8O_2(OH)_{12}{\cdot}12H_2O$
Metaschoepite	$(UO_2)_8O_2(OH)_{12}{\cdot}10H_2O$
Vandendriesscheite	$PbU_2O_7{\cdot}12H_2O$
Curite	$Pb_3(UO_2)_8O_8(OH)_6{\cdot}3H_2O$
Clarkeite	$(Na,Ca,Pb)(UO_2)O(OH){\cdot}H_2O$
Studtite	$[(UO_2)(O_2)(H_2O)_2]{\cdot}H_2O$
Carbonates	
Rutherfordite	UO_2CO_3
Joliotite	$(UO_2)CO_3{\cdot}nH_2O$
Sulfates	
Zippeite	$K_3(UO_2)_4(SO_4)_2O_3(OH){\cdot}3H_2O$
Uranopilite	$(UO_2)_6(SO_4)O_2(OH)_6{\cdot}14H_2O$
Johannite	$Cu(UO_2)_2(SO_4)_2(OH)_2{\cdot}8H_2O$
Tungstates	
Uranotungstite	$(Fe,Ba,Pb)(UO_2)_2(WO_4)(OH)_4{\cdot}12H_2O$
Phosphates	
Torbernite	$Cu(UO_2)_2(PO_4)_2{\cdot}8\text{-}12H_2O$
Metatorbernite	$Cu(UO_2)_2(PO_4)_2{\cdot}8H_2O$
Autunite	$Ca(UO_2)_2(PO_4)_2{\cdot}11H_2O$
Metaautunite	$Ca(UO_2)_2(PO_4)_2{\cdot}6\text{-}8H_2O$
Saleeite	$Mg(UO_2)_2(PO_4)_2{\cdot}8H_2O$
Uranocircite	$Ba(UO_2)_2(PO_4)_2{\cdot}8\text{-}12H_2O$
Metauranocircite II	$Ba(UO_2)_2(PO_4)_2{\cdot}6H_2O$
Bassetite	$Fe^{2+}(UO_2)_2(PO_4)_2{\cdot}8H_2O$
Bergenite	$Ca_2Ba_4(UO_2)_9(PO_4)_6O_6{\cdot}16H_2O$
Phosphuranylite	$(H_3O)_3KCa(UO_2)_7(PO_4)_4O_4{\cdot}8H_2O$
Arsenates	
Heinrichite	$Ba(UO_2)_2(AsO_4)_2{\cdot}10H_2O$
Metaheinrichite	$Ba(UO_2)_2(AsO_4)_2{\cdot}8H_2O$
Zeunerite	$Cu(UO_2)_2(AsO_4)_2{\cdot}12H_2O$
Metazeunerite	$Cu(UO_2)_2(AsO_4)_2{\cdot}8\text{-}12H_2O$
Novacekite	$Mg(UO_2)_2(AsO_4)_2{\cdot}8\text{-}12H_2O$
Abernathyite	$K(UO_2)(AsO_4){\cdot}3H_2O$
As-uranospathite	$(F,Cl)_{0.5}(UO_2)_2(AsO_4)_2{\cdot}20H_2O$
Kahlerite	$Fe(UO_2)_2(AsO_4)_2{\cdot}12H_2O$
Nielsbohrite	$K(UO_2)_3(AsO_4)(OH)_4{\cdot}H_2O$
Arsenuranylite	$Ca(UO_2)_4(AsO_4)_2(OH)_4{\cdot}6H_2O$
Silicates	
Coffinite	$USiO_4$
Uranosilite	$UO_3{\cdot}7SiO_2$
Soddyite	$(UO_2)_2SiO_4{\cdot}2H_2O$
Uranophane	$Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O$
β-uranophane	$Ca(UO_2)_2(SiO_3OH)_2{\cdot}nH_2O$
Ba-uranophane	$Ca(UO_2)_2(SiO_3OH)_2{\cdot}nH_2O$
Cuprosklodowskite	$Cu(UO_2)_2(SiO_3OH]_2{\cdot}6H_2O$
Kasolite	$Pb(UO_2)(SiO_4){\cdot}H_2O$

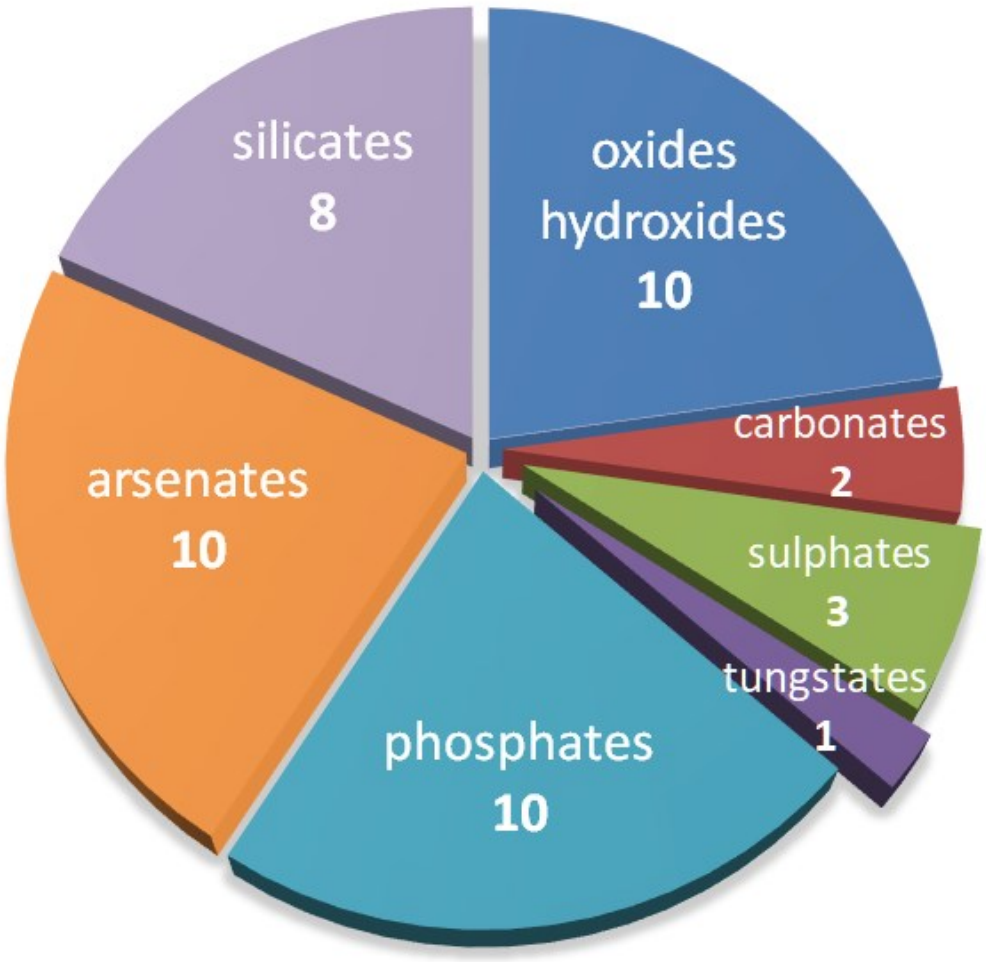

Fig. S6 Distribution of U minerals by group and number of species identified in Krunkelbach U mine.

Notes and References

1. Kvashnina, K.O. and Scheinost, A. A Johann-type X-ray emission spectrometer at the Rossendorf beamline. *Journal of Synchrotron Radiation* 2016, ***23***, 836-841.
2. Wojdyr, M., Fityk: a general-purpose peak fitting program. *Journal of Applied Crystallography* 2010, ***43***, (5), 1126-1128.
3. Bültemann, H. W.; Bültemann, W. D. *The Uranium Deposit Krunkelbach in the Southern Black Forest, Federal Republic of Germany*; IAEA-TECDC-361, 1986; pp 247-260.
4. Walenta, K.; Hatert, F.; Theye, T.; Lissner, F.; Röller, K., Nielsbohrite, a new potassium uranyl arsenate from the uranium deposit of Menzenschwand, southern Black Forest, Germany. *European Journal of Mineralogy* 2009, ***21***, (2), 515-520.