

Lloyd *et al.* 2009. The morphologies and compositions of depleted uranium particles from an environmental case-study.

Appendix 1

XAS spectra, fitting data, and XRD of standards

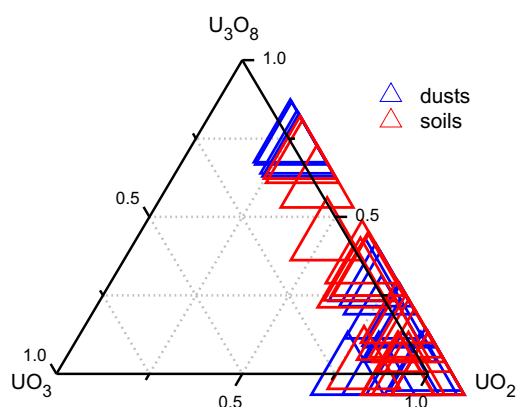
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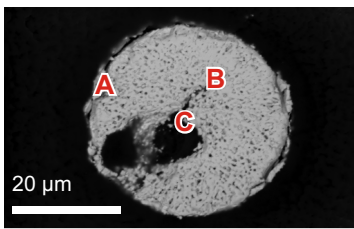
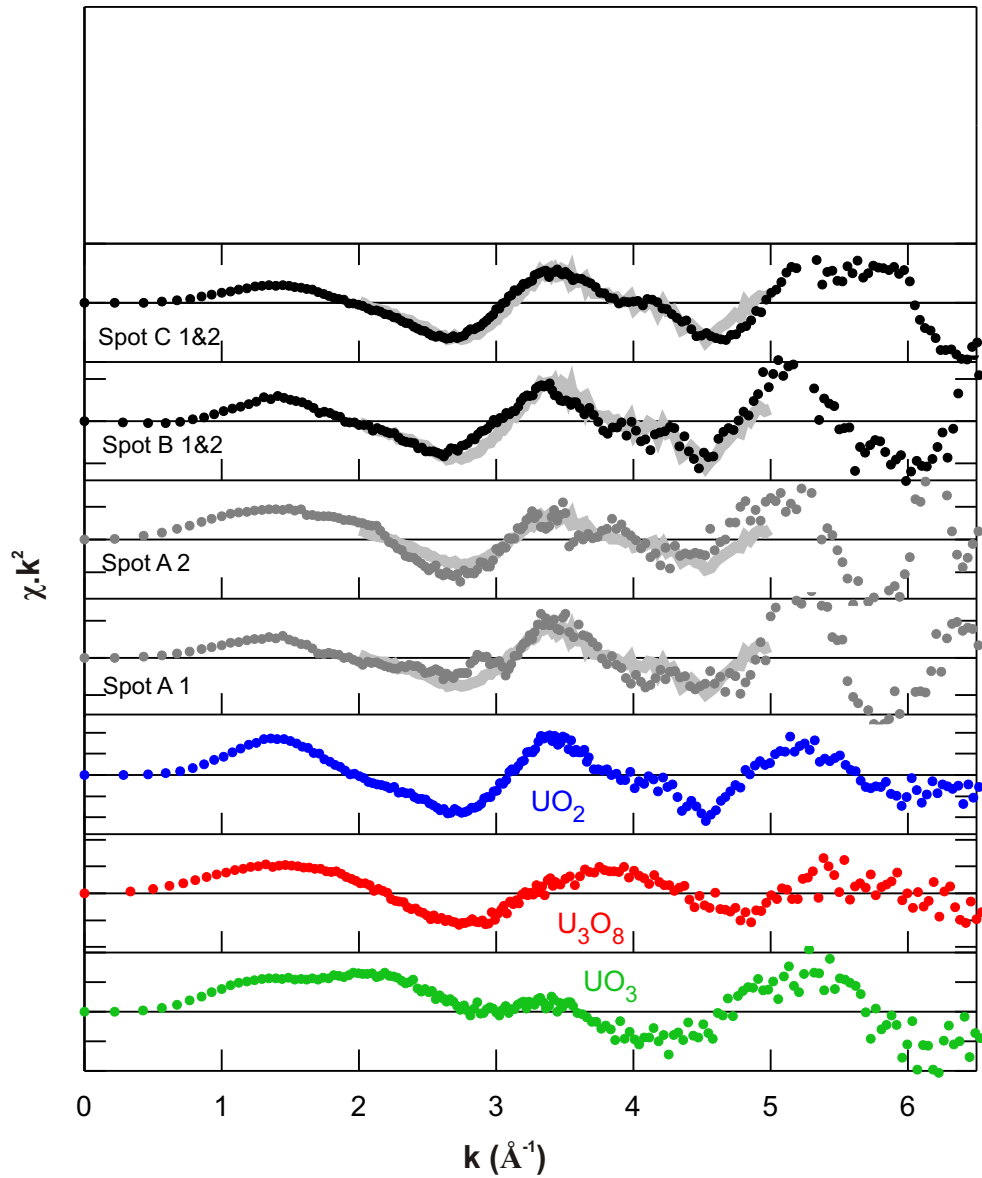
EXAFS introduction

EXAFS spectra, $\chi_k(k)$, are presented on the following pages, for all of the uranium oxide micro-spheres analysed for this study. The sample data are plotted (dots) with the least-squares fitting of the standards (lines).

The standards are characterised as follows: UO_2 has a characteristic slant on the second dominant oscillation, whereas U_3O_8 has a broad symmetric curve; UO_3 has a distinct ‘shoulder’ on the first oscillation. These features are the focus of the EXAFS fitting. In these spectra, the fourth and subsequent dominant oscillations ($k > 6.5 \text{ \AA}^{-1}$) are within the data noise, and are highly susceptible to spline fitting, so are excluded. The region $k = 2 - 5 \text{ \AA}^{-1}$ is removed from the white line, is least susceptible to spline fitting, and the features are prominent with respect to data noise. Least-squares fittings of the three standard spectra have been applied to the sample spectra across this region (after interpolation).

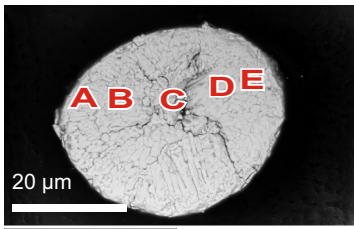
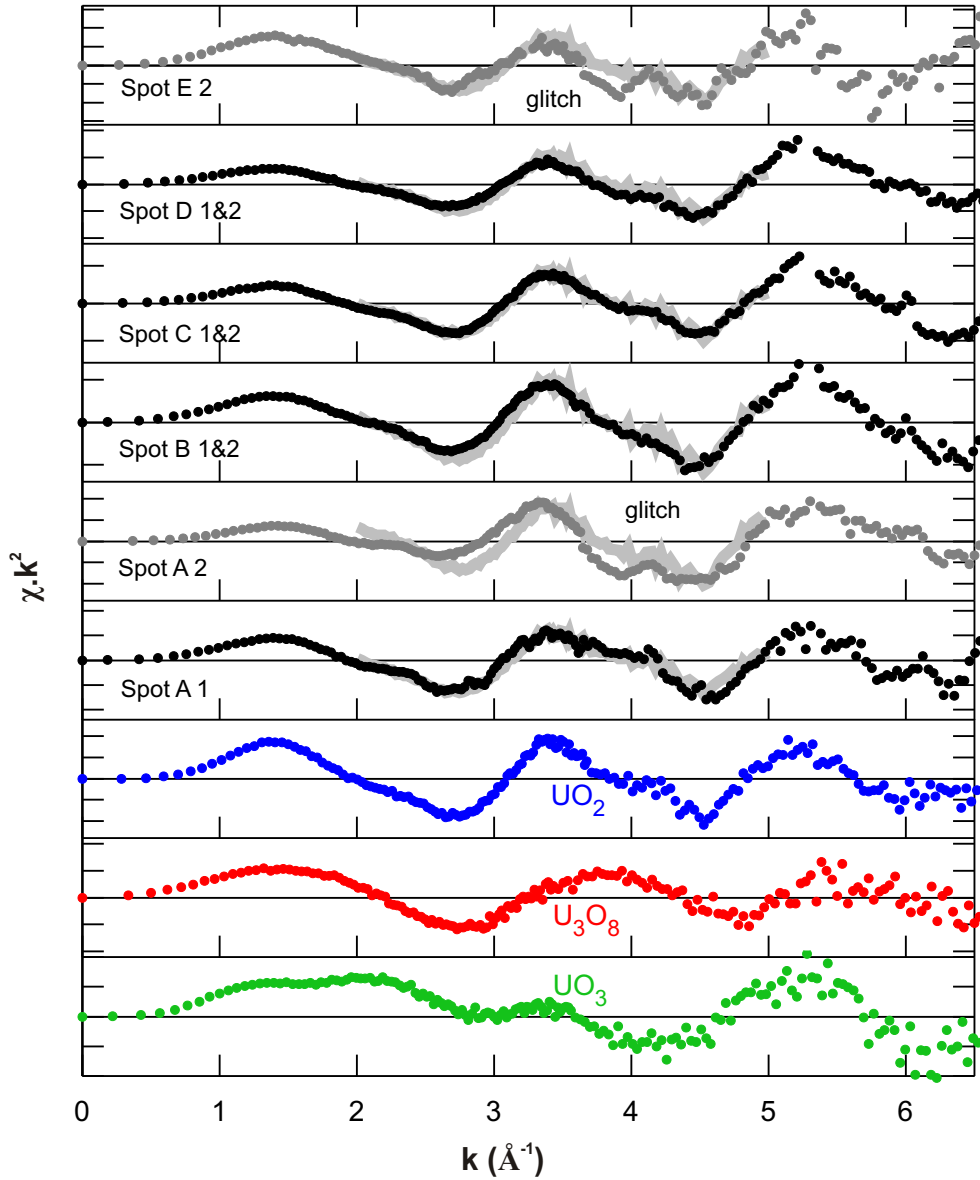
Some of the sample spectra (shaded grey) are noisy and cannot be determined ($R^2 < 0.7$), this is due to the beam interacting with smaller amounts of material, at the edges and near cavities in the particles. Spectra with obvious glitches have also been rejected. The remaining fitting data are tabulated in Appendix 1.3, and plotted below as a ternary diagram (reprinted from Figure 5 of the associated paper, with symbols scaled to typical uncertainty).





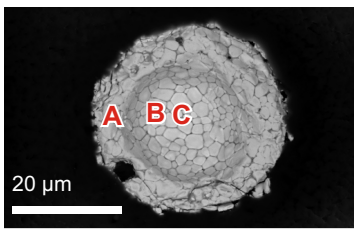
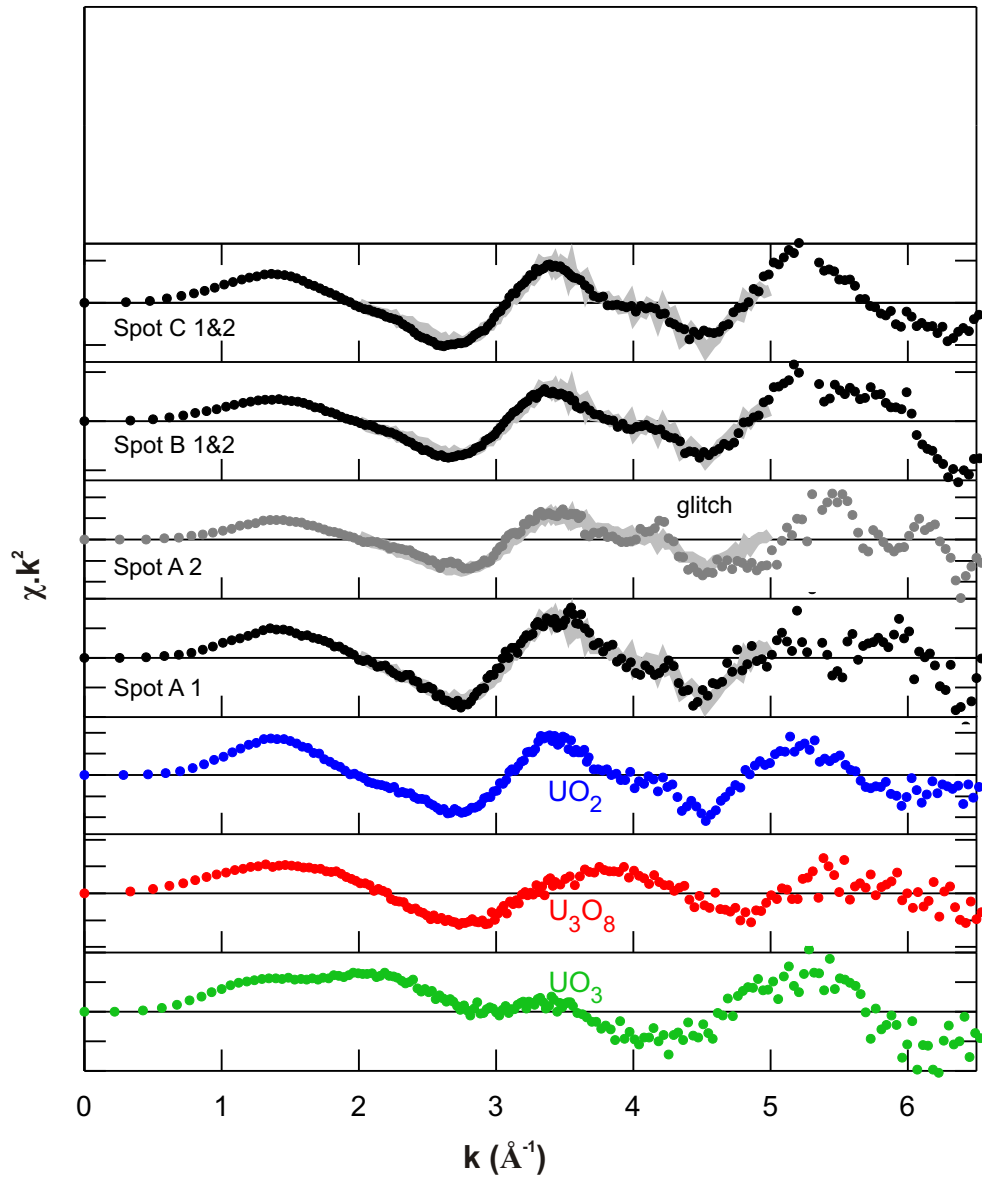
Sample NSL0090 (dust), Particle 1

approx. locations of spot analyses



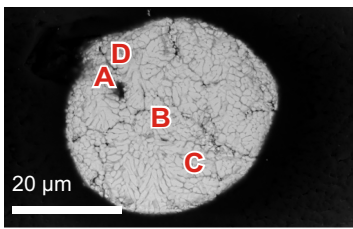
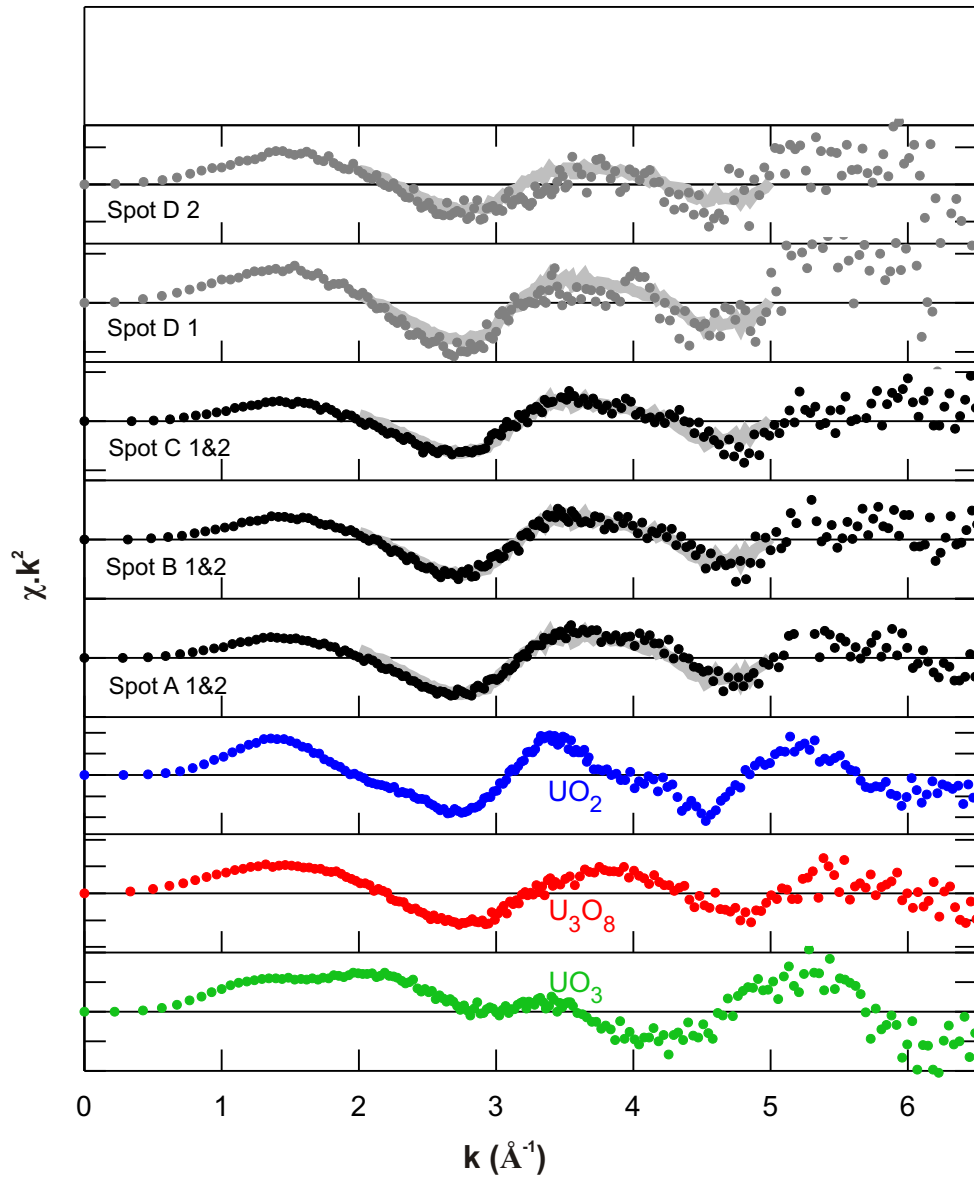
Sample NSL0090 (dust), Particle 17

approx. locations of spot analyses



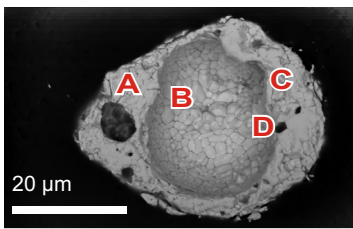
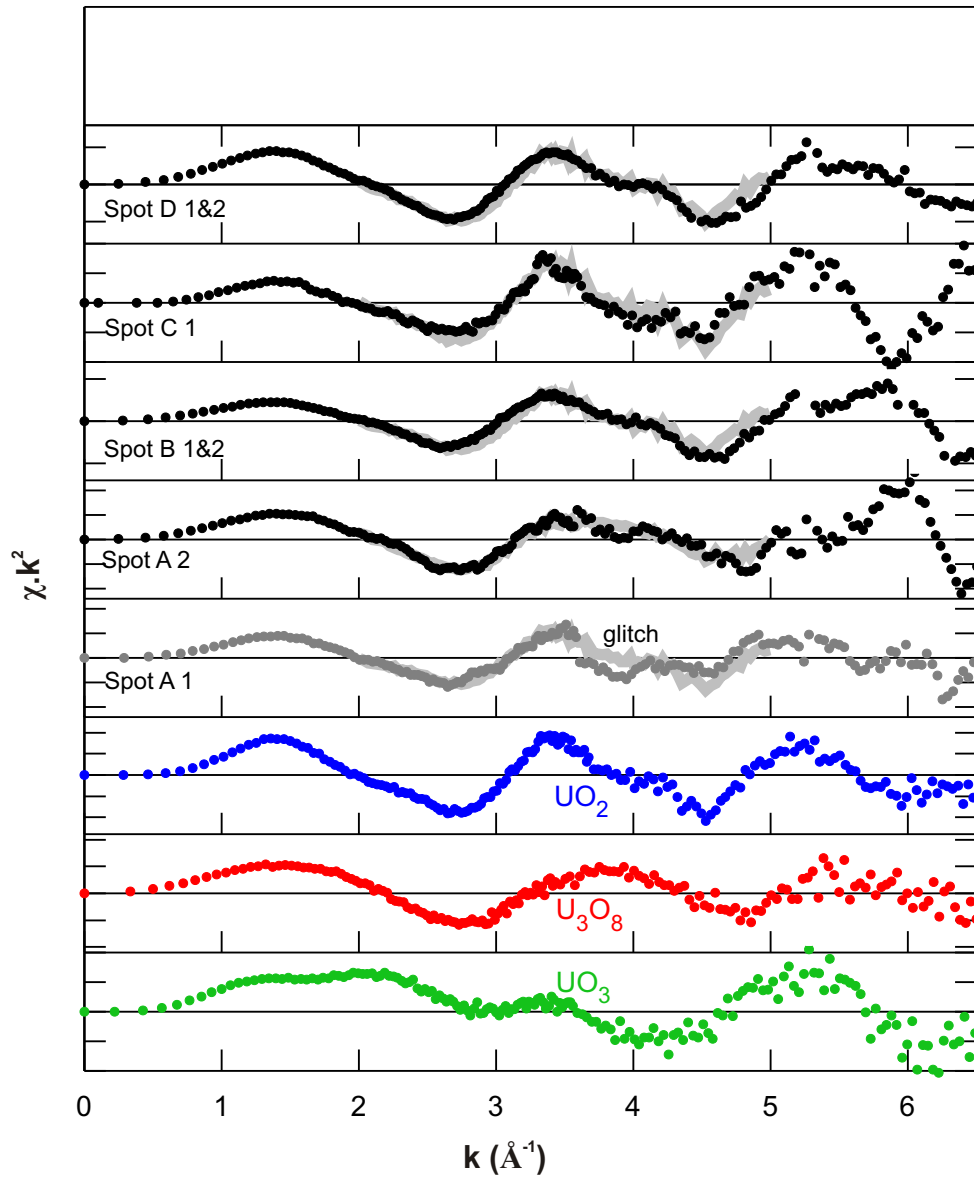
Sample NSL0090 (dust), Particle 2

approx. locations of spot analyses



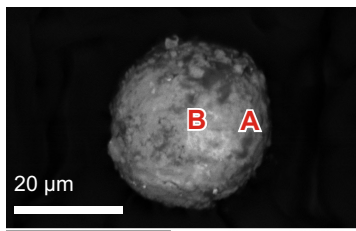
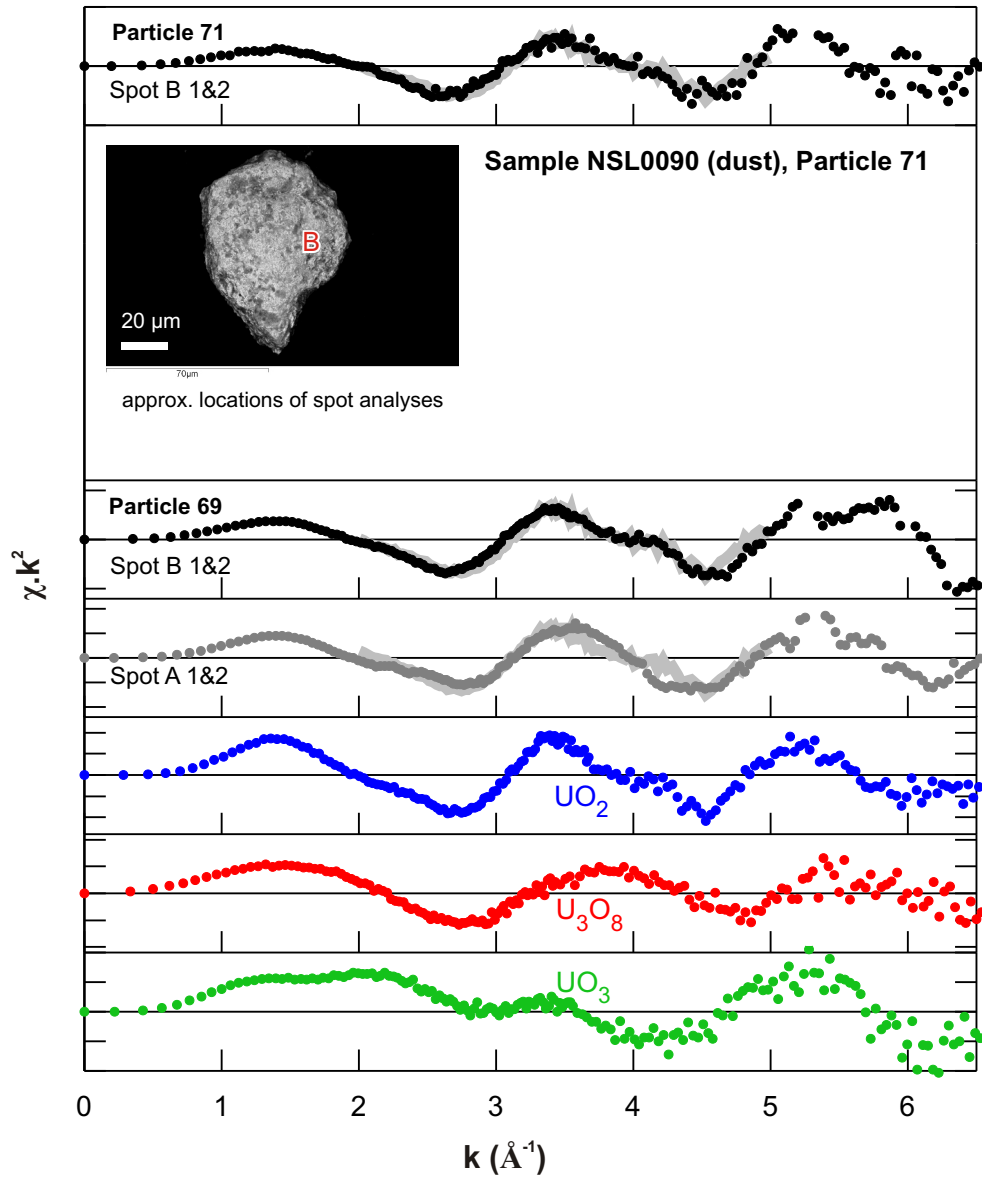
Sample NSL0090 (dust), Particle 23

approx. locations of spot analyses



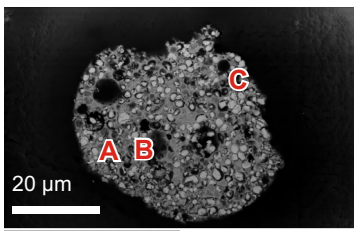
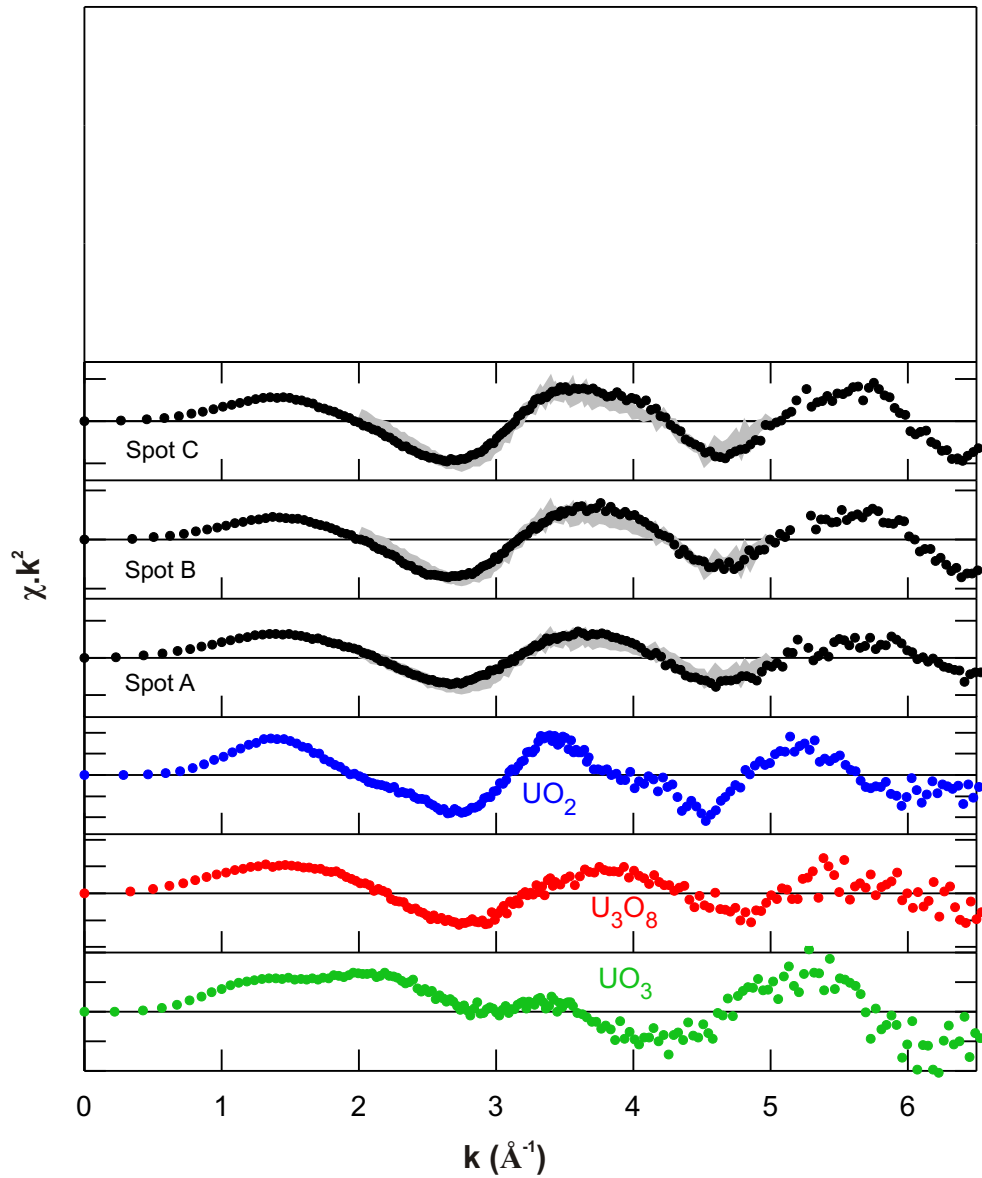
Sample NSL0090 (dust), Particle 3

approx. locations of spot analyses



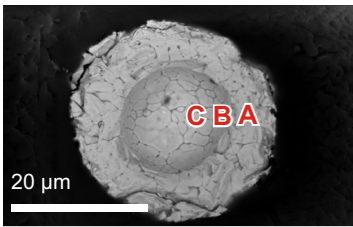
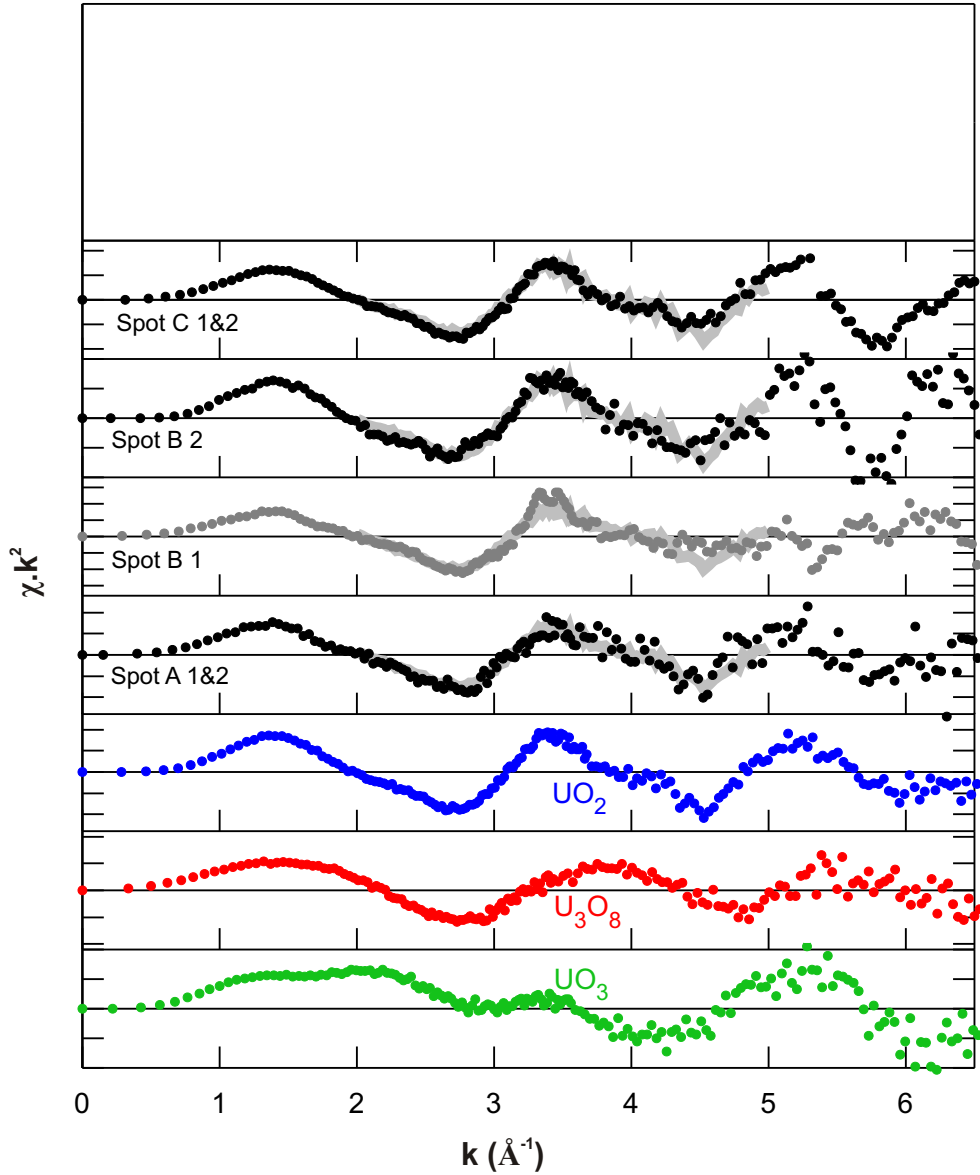
Sample NSL0090 (dust), Particle 69

approx. locations of spot analyses



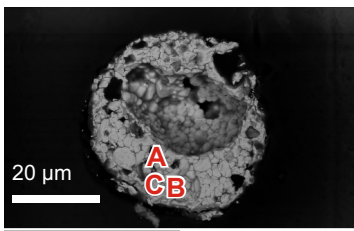
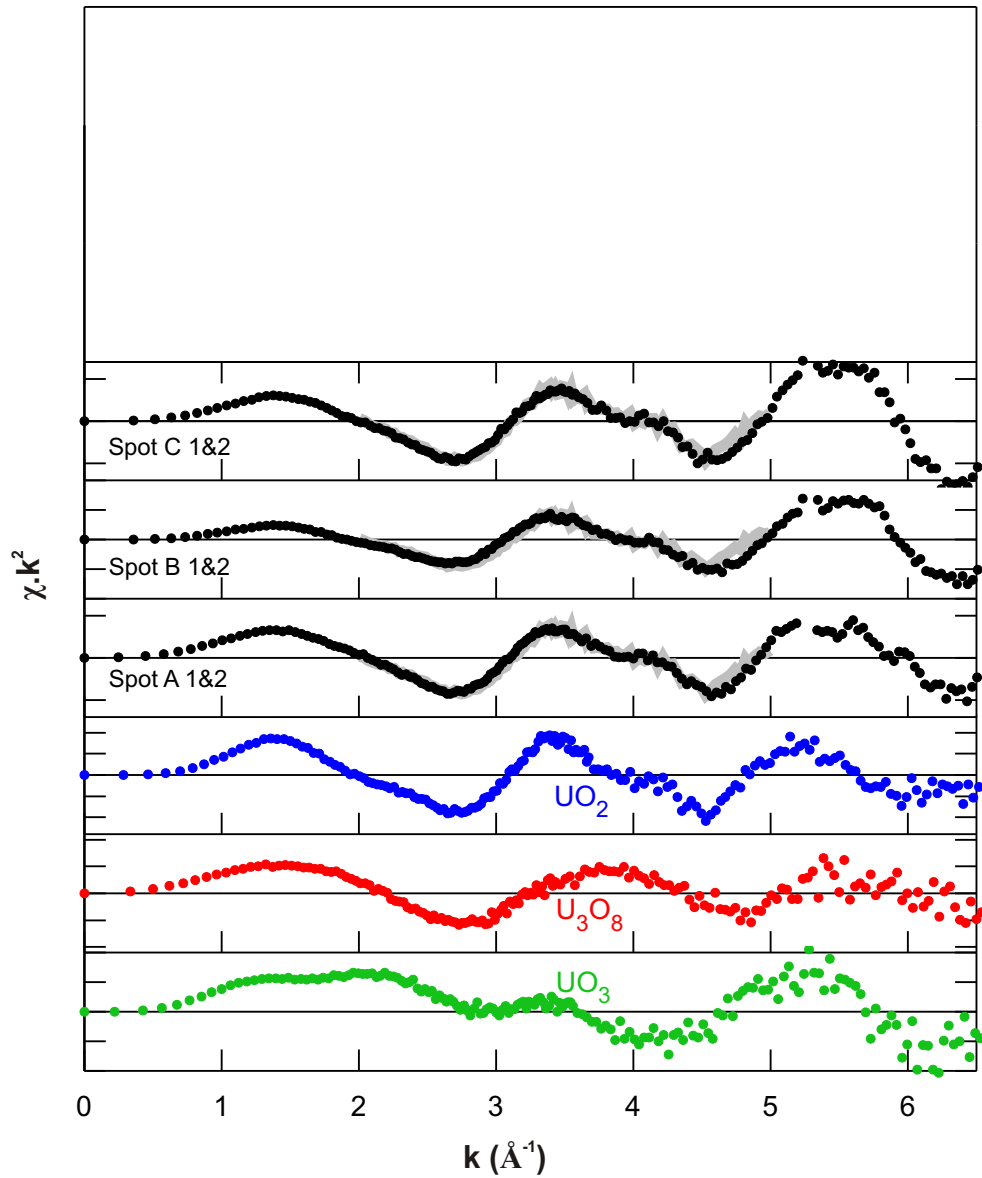
Sample NSL0161 (soil), Particle 1

approx. locations of spot analyses



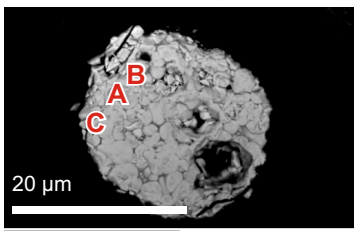
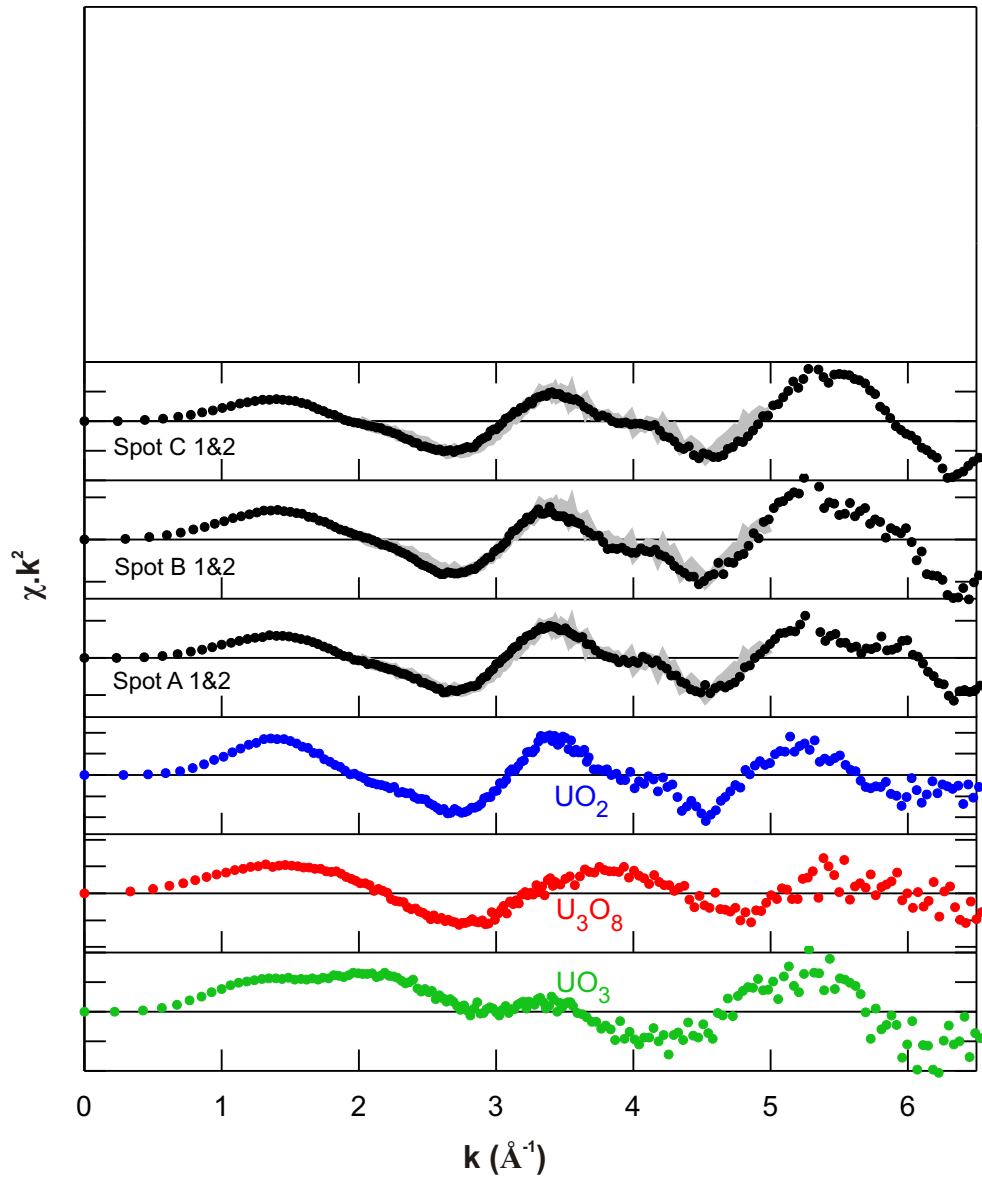
Sample NSL0100 (soil), Particle 12

approx. locations of spot analyses



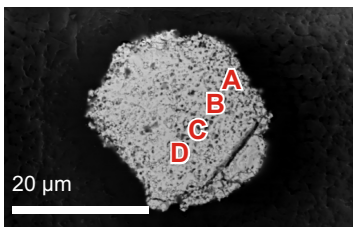
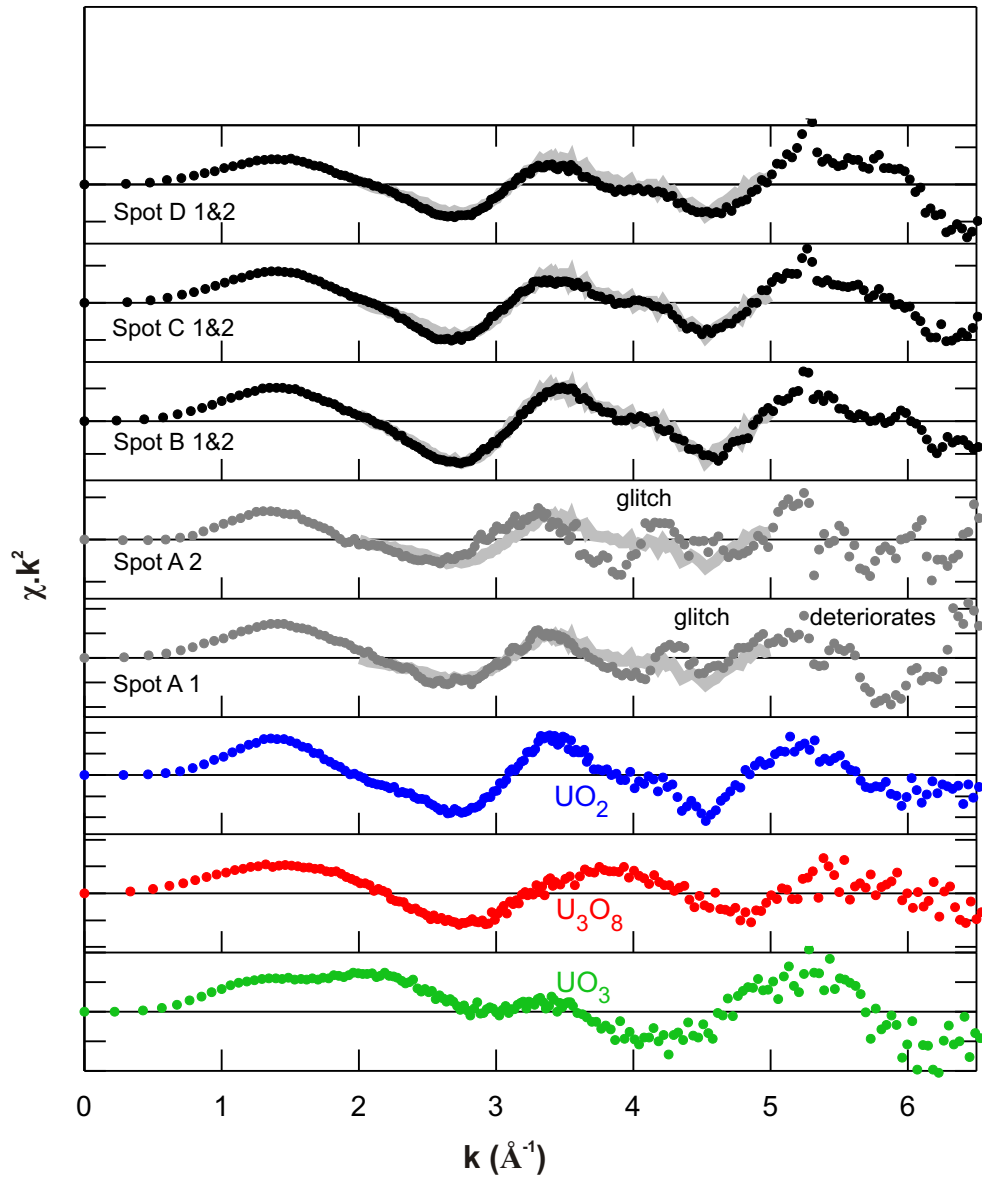
Sample NSL0100, Particle 15

approx. locations of spot analyses



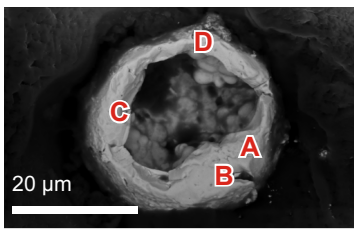
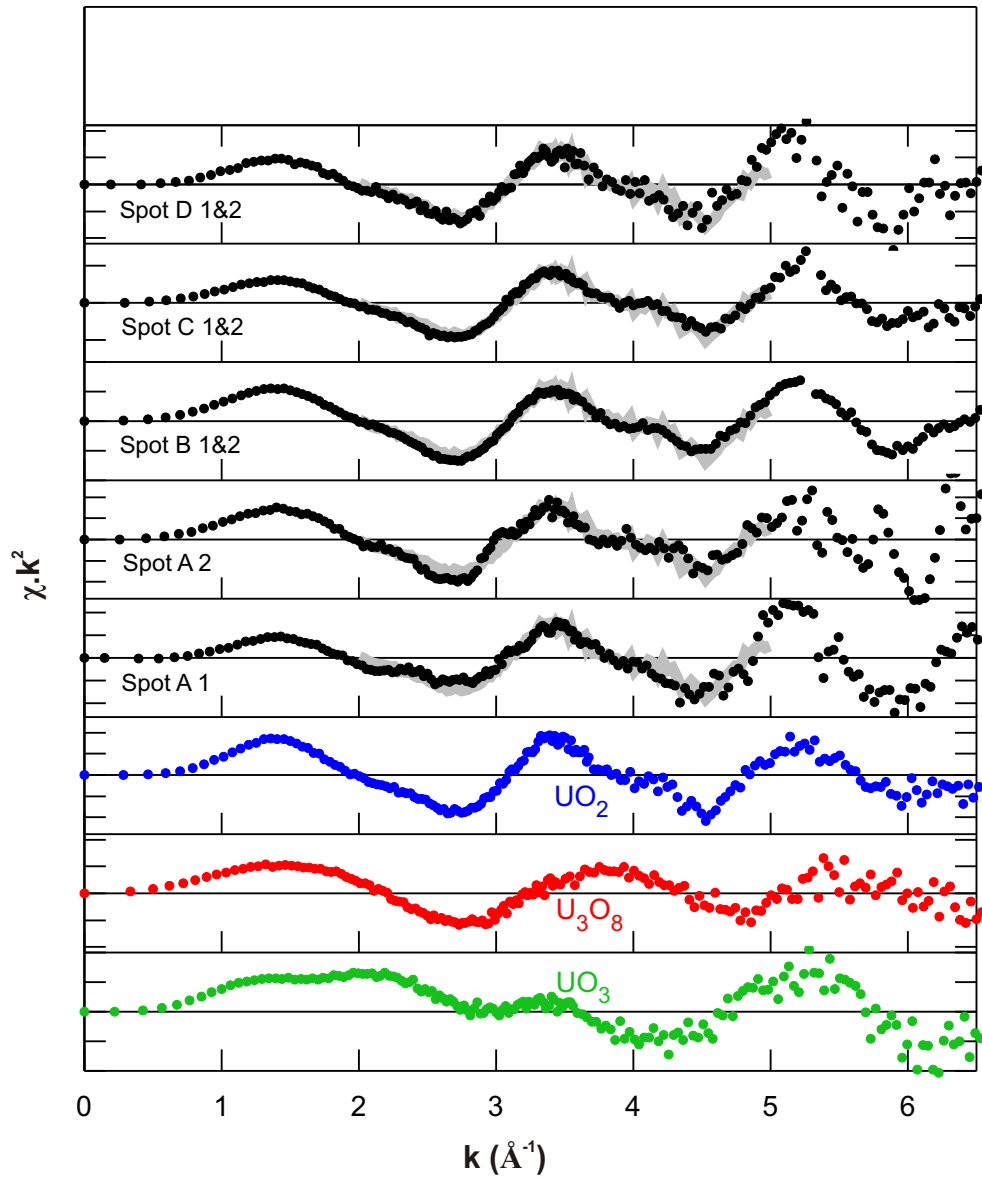
Sample NSL00100 (dust), Particle 17

approx. locations of spot analyses



Sample NSL0100 (soil), Particle 2

approx. locations of spot analyses



Sample NSL0100 (soil), Particle 7

approx. locations of spot analyses

Fitting Data Summary

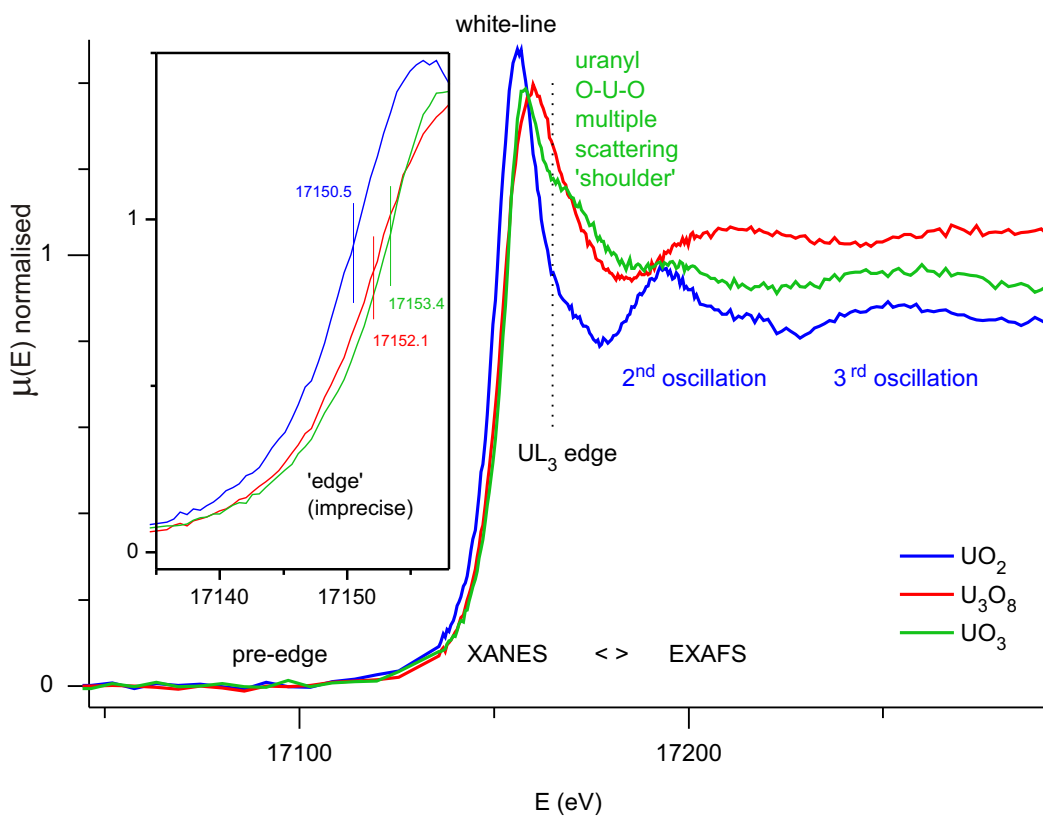
M1P17A1 refers to Mount 1 (sample NSL0090, dust), Particle 17, Spot A, Replicate 1.

	analysis	Adj. R-Square	UO₂ (%)	±	U₃O₈ (%)	±	UO₃ (%)	±	
dusts	M1P17A1	0.90	72	7	28	14	0	--	
	M1P17B	0.90	78	6	0	--	22	9	
	M1P17C	0.96	98	5	0	--	2	8	
	M1P17D	0.87	87	8	0	--	13	11	
	M1P1B	0.76	100	12	0	--	0	--	
	M1P1C	0.91	74	7	26	13	0	--	
	M1P23A	0.92	26	5	74	10	0	--	
	M1P23B	0.91	29	5	71	10	0	--	
	M1P23C	0.86	30	7	70	13	0	--	
	M1P2A1	0.92	78	7	18	12	4	10	
	M1P2B	0.95	99	6	1	11	0	--	
	M1P2C	0.95	100	6	0	--	0	--	
	M1P3A2	0.88	27	6	73	12	0	--	
	M1P3B	0.86	87	10	11	19	2	14	
	M1P3C1	0.86	93	9	0	--	7	12	
	M1P3D	0.90	68	7	30	13	2	10	
	M3P69B	0.92	84	7	16	13	0	--	
	M3P71B	0.89	85	9	15	16	0	--	
	soils	M4P12A	0.85	67	9	30	17	3	13
		M4P12B2	0.86	100	10	0	--	0	--
M4P12C		0.92	95	8	0	14	5	11	
M4P15A		0.95	68	5	32	9	0	7	
M4P15B		0.89	83	8	17	15	0	--	
M4P15C		0.95	64	5	36	9	0	--	
M4P17A		0.95	93	6	7	11	0	--	
M4P17B		0.91	82	7	2	12	16	10	
M4P17C		0.91	88	7	12	14	0	--	
M4P1A		0.90	31	6	69	11	0	--	
M4P1B		0.93	32	5	68	9	0	--	
M4P1C		0.92	40	5	60	10	0	--	
M4P2B		0.97	51	3	43	6	6	5	
M4P2C		0.94	68	5	32	10	0	--	
M4P2D		0.88	66	7	28	13	6	10	
M4P7A1		0.83	92	10	0	--	8	15	
M4P7A2		0.87	100	10	0	--	0	--	
M4P7B		0.94	85	6	11	11	4	8	
M4P7C		0.96	90	5	10	10	0	--	
M4P7D		0.87	92	9	0	--	8	13	

XANES

XANES spectra for the three uranium oxide standards, showing increasing energy of edge position with increasing oxidation state.

Estimates of edge positions from the samples range 17147-17151 eV.



X-RAY DIFFRACTION ANALYSIS

Powder X-ray diffraction (XRD) analysis was carried out using a *PANalytical X'Pert Pro* series diffractometer equipped with a cobalt target tube, *X'Celerator* detector and operated at 45kV and 40mA. The powdered samples were scanned from 4.5 - 85° 2 θ at 2.76° 2 θ / minute. Diffraction data were initially analysed using *PANalytical X'Pert Highscore Plus version 2.2a* software coupled to the latest version of the International Centre for Diffraction Data (ICDD) database.

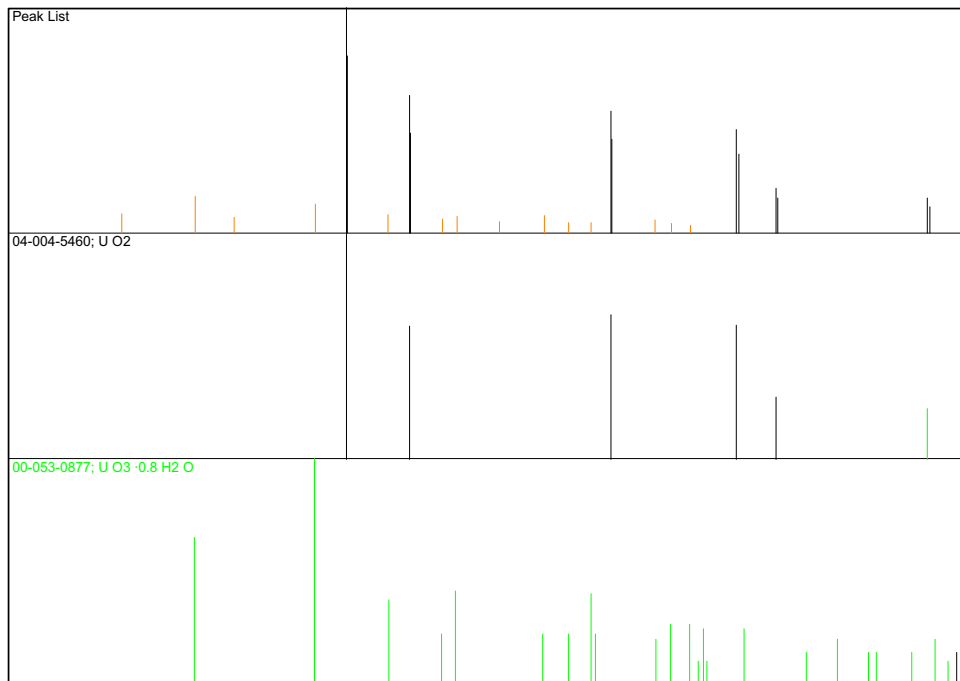
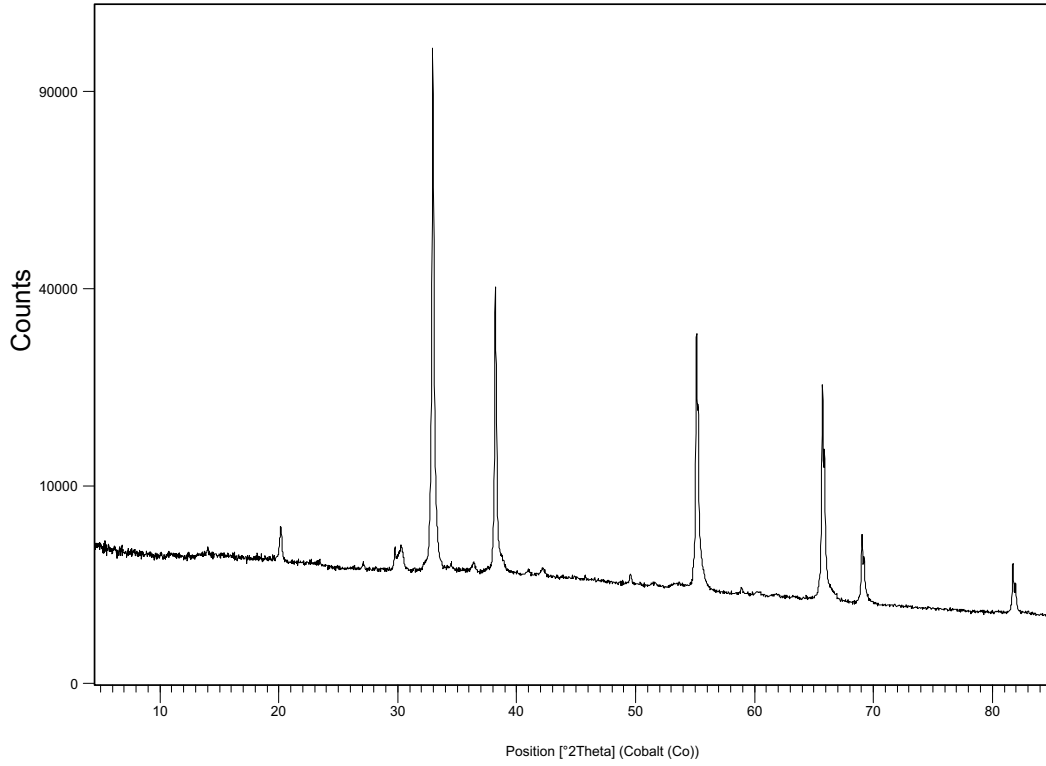
A lack of appropriate data files in the Inorganic Crystal Structure Database (ICSD) for the identified phases meant that quantification using the Rietveld refinement technique was impossible for these samples (e.g. Snyder and Bish 1989). Therefore, phase concentrations were semi-quantitatively estimated on the basis of relative X-ray peak intensity: major (>25%), minor (5-25%) and trace (<5%).

Sample	Major phase(s)	Trace phase(s)	Comments
'UO ₂ '	UO ₂	UO ₃ · 0.8H ₂ O	Other very minor peaks remain unattributed
'UO ₃ '	γ -UO ₃ , UO ₃ · 0.8H ₂ O	not detected	none
'U3O8'	U ₃ O ₈ (picked), UO ₃ · 2H ₂ O (metaschoepite), UO ₃ · 0.8H ₂ O	not detected	none

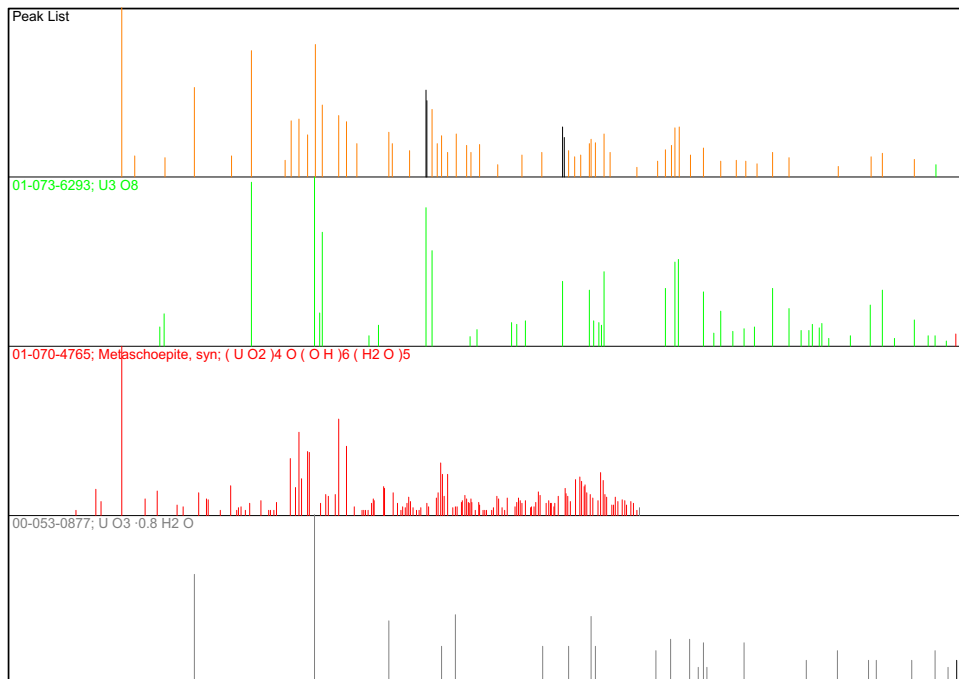
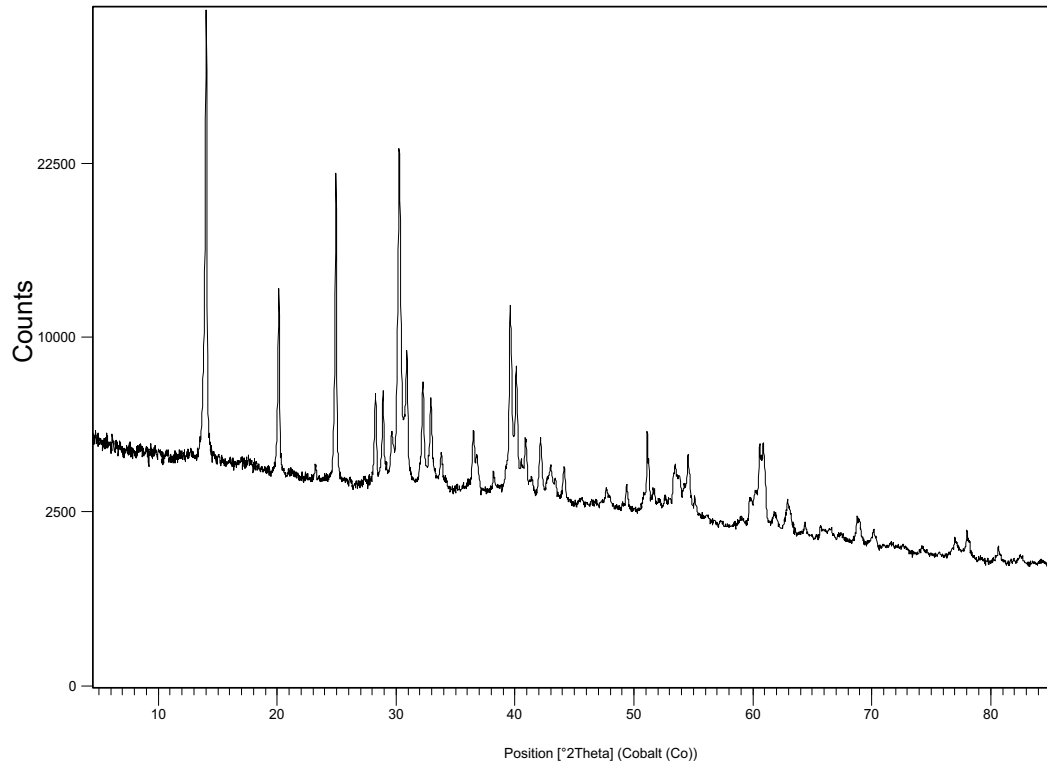
Table 1. Summary of powder X-ray diffraction analyses

Snyder, R.L., and Bish, D.L. (1989) Quantitative analysis. In D.L. Bish, and J.E. Post, Eds. *Modern powder diffraction*, p. 101-44 Mineralogical Society of America, Washington DC, USA.

'UO₂' compound with trace dehydrated schoepite



'U₃O₈' compound (black U₃O₈ grains were picked from this powder)



'UO₃' compound (γ-phase) with metaschoepite and dehydrated schoepite (U⁶⁺ species)

