Supplementary Information for

Extreme Condition High Temperature and High Pressure Studies of the K-U-Mo-O System

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1. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM/EDS) Analysis

(a) $K_2[UO_2(Mo_2O_7)_2]$

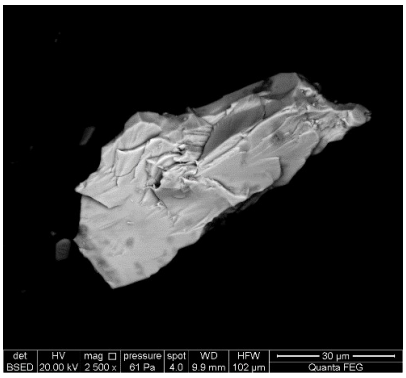

Figure S1a. SEM micrograph $K_2[UO_2(Mo_2O_7)_2]$.

Table S1a. Normalised (to U content) EDS result for $K_2[UO_2(Mo_2O_7)_2]$.

Element	U	K	Mo
Total	1.00	2.08	4.52

(b) $K_2[(UO_2)_2(Mo(VI)_4Mo(IV)(OH)_2)O_{16}]$

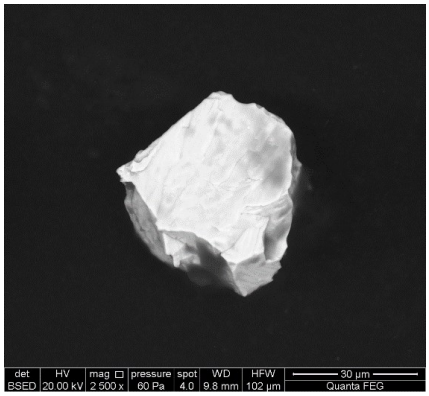

Figure S1b. SEM micrograph $K_2[(UO_2)_2(Mo(VI)_4Mo(IV)(OH)_2)O_{16}]$.

Table S1b. Normalised (to U content) EDS result for $K_2[(UO_2)_2(Mo(VI)_4Mo(IV)(OH)_2)O_{16}]$.

Element	U	K	Mo
Total	1.00	1.39	1.93

(c) $K_3[(UO_2)_6(OH)_2(MoO_4)_6(MoO_3OH)]$

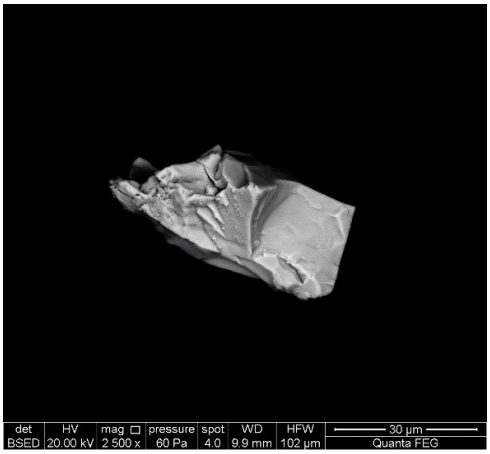

Figure S1c.

Table S1c. Normalised (to U content) EDS result for $K_3[(UO_2)_6(OH)_2(MoO_4)_6(MoO_3OH)]$.

Element	U	K	Mo
Total	1.00	0.47	1.30

(d) $K_5[(UO_2)_{10}MoO_5O_{11}OH]\cdot H_2O$

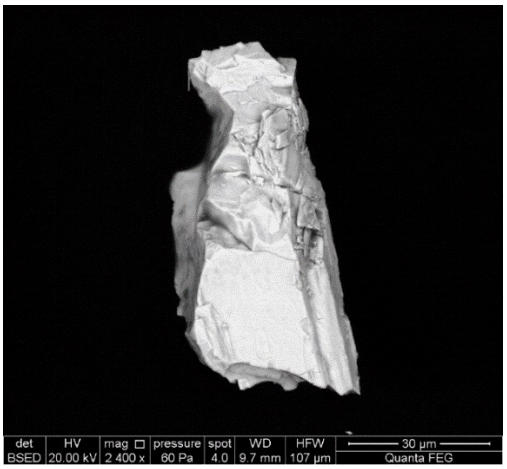

Figure S1d.

Table S1d. Normalised (to U content) EDS result for $K_5[(UO_2)_{10}MoO_5O_{11}OH]\cdot H_2O$.

Element	U	K	Mo
Total	1.00	0.54	0.13

2. Bond Valence Sums (BVS) Calculations

BVS calculations were undertaken for the cations in all compounds in this investigation using the parameters reported by Burns and co-workers[25]. The parameters provided by Brese and O'Keeffe[26] were used for all other atoms.

Table S2a. BVS calculations for $K_2[UO_2(Mo_2O_7)_2]$.

	U	Mo(1)	Mo(2)	K	**Σ**
O1	$1.7069^{x2\downarrow}$			0.26	**1.97**
O2	$0.63^{x2\downarrow}$	1.29		0.12	**1.97**
O3	$0.56^{x2\downarrow}$	0.70	0.81		**2.07**
O4		0.54	0.47 + 0.93		**1.94**
O5		1.45	0.36	0.15	**1.96**
O6		1.85		0.18	**2.03**
O7		0.22	1.56	0.1	**1.88**
O8			1.72	0.18	**1.90**
Σ	**5.80**	**6.03**	**5.87**	**1.00**	

Table S2b. BVS calculations for $K_2[(UO_2)_2(Mo(VI)_4Mo(IV)(OH)_2)O_{16}]$.

	U	Mo(1)	Mo(2)	K	**Σ**
O1		1.67	$0.49^{x2\downarrow}$	0.32	**2.48**
O2	$0.54^{x2\downarrow}$	1.27		0.11	**1.92**
O3	$0.51^{x2\downarrow}$	1.36		0.08	**1.95**
O4	$2.02^{x2\downarrow}$			0.26	**2.28**
O5		1.35	$0.26^{x2\downarrow}$	0.19	**1.81**
O6			$1.03^{x2\downarrow}$		**1.03**
Σ	**6.14**	**5.65**	**3.56**	**0.96**	

Table S2c. BVS calculations for $K_3[(UO_2)_6(OH)_2(MoO_4)_6(MoO_3OH)]$.

	U(1)	U(2)	U(3)	U(4)	Mo(1)	Mo(2)	Mo(3)	Mo(4)	K(1)	K(2)	K(3)	K(4)	**Σ**
O1	0.49					1.40			0.11 $^{x2\downarrow}$				**2.00**
O2		0.54				1.54							**2.08**
O3	0.49						1.50						**1.59**
O4	0.54					1.48			0.05 $^{x2\downarrow}$				**2.07**
O5	0.54							1.54					**2.08**
O6	1.77								0.20 $^{x2\downarrow}$				**1.97**
O7	1.68												**1.68**
O8			0.54$^{x2\downarrow}$			1.55							**1.99**
O9		1.74											**1.74**
O10		0.50			1.52 $^{x2\downarrow}$								**2.02**
O11		0.56						1.47					**2.03**
O12		0.51						1.50					**2.01**
O13	0.60				1.52 $^{x2\downarrow}$								**2.12**
O14		0.48					1.54						**2.04**
O15			1.91										**1.91**
O16			1.74								0.23	0.13	**2.1**
O17			0.53$^{x2\downarrow}$				1.45			0.19		0.11	**2.28**
O18		1.71									0.24		**1.95**
O19				1.72						0.06			**1.78**
O20				1.81						0.21	0.24	0.12	**2.28**
O21			0.36							0.08	0.13	0.11	**0.68**
O22				0.58 $^{x2\downarrow}$			1.51						**2.09**
O23				0.58 $^{x2\downarrow}$				1.55					**2.13**
O24				0.35						0.23	0.16	0.13	**0.87**
Σ	**6.11**	**6.04**	**6.17**	**6.21**	**6.08**	**5.96**	**6.00**	**6.06**	**0.70**	**0.78**	**0.99**	**0.60**	

Table S2d. BVS calculations for $K_5[(UO_2)_{10}MoO_5O_{11}OH]\cdot H_2O$

	U(1)	U(2)	U(3)	U(4)	U(5)	U(6)	U(7)	U(8)	U(9)	U(10)	Mo(1)	K(1)	K(2)	K(3)	K(4)	K(5)	K(6)	K(7)	**Σ**
O1		0.58		0.81		0.64													**2.03**
O2			0.57				0.80	0.63							0.11				**2.11**
O3						1.22			0.40	0.49									**2.11**
O4	0.67						0.72	0.58											**1.97**
O5								1.15		0.50				0.18	0.15				**1.98**
O6	0.60			0.66	0.64									0.11					**2.01**
O7	0.66			0.75				0.58											**1.99**
O8	0.71					0.76			0.64										**2.11**
O9	1.47								0.47					0.14	0.14				**2.22**
O10		1.10							0.54	0.40									**2.04**
O11		0.85						0.66		0.57									**2.08**
O12			0.64	0.76		0.66													**2.06**
O13		0.56				0.75	0.65												**1.98**
O14		0.70			0.66		0.69												**2.05**
O15	1.59												0.27	0.19		0.09	0.43		**2.49**
O16								1.46							0.20				**1.66**
O17				1.23						0.54					0.05				**1.82**
O18		0.48			0.52						0.97								**1.97**
O19							1.30		0.54					0.07	0.05				**1.96**
O20	0.41				0.51						1.08								**2.00**
O21		1.34																0.31	**1.64**
O22				1.59								0.15				0.19			**1.93**
O23			0.53					0.49			0.92								**1.94**
O24						1.74						0.17	0.22						**2.13**
O25			0.50			0.43					1.02								**1.95**
O26									1.62			0.12	0.25						**1.99**
O27										1.69								0.14	**1.83**
O28									1.69									0.16	**1.85**
O29					1.49											0.10		0.21	**1.80**
O30							1.46											0.22	**1.68**
O31										1.66		0.15				0.14	0.32		**2.27**
O32			1.73									0.19				0.09	0.17		**2.18**
O33			1.65									0.12			0.13				**1.90**
O34											1.85	0.20	0.16						**2.21**
O35					1.53								0.32	0.12		0.06		0.09	**2.12**
O36			0.45		0.56											0.06	0.23		**1.30**
OW1													0.18					0.12	**0.30**
Σ	**6.12**	**5.59**	**6.07**	**5.80**	**5.91**	**6.21**	**5.63**	**5.54**	**5.90**	**5.85**	**5.82**	**1.10**	**1.41**	**0.80**	**0.83**	**0.71**	**1.16**	**1.24**	

3. Selected Bond Lengths of Title Compounds

Table S3a. $K_2[UO_2(Mo_2O_7)_2]$.

U-O(1) x2	1.773(6) Å	Mo(1)-O(2)	1.812(4) Å
U-O(2) x2	2.277(5) Å	Mo(1)-O(3)	2.056(5) Å
U-O(3) x2	2.337(4) Å	Mo(1)-O(4)	2.135(4) Å
K-O(1)i	2.752(5) Å	Mo(1)-O(5)	1.770(4) Å
K-O(1)ii	3.074(5) Å	Mo(1)-O(6)	1.679(5) Å
K-O(2)	2.913(5) Å	Mo(2)-O(3)	1.984(4) Å
K-O(5)	2.823(5) Å	Mo(2)-O(4)i	2.184(5) Å
K-O(6)	2.773(5) Å	Mo(2)-O(4)ii	1.933(4) Å
K-O(7)	2.974(5) Å	Mo(2)-O(5)	2.283(5) Å
K-O(8)	2.763(5) Å	Mo(2)-O(7)	1.743(4) Å
		Mo(2)-O(8)	1.704(6) Å

Table S3b. $K_2[(UO_2)_2(Mo(VI)_4Mo(IV)(OH)_2)O_{16}]$.

U-O(2) x2	2.277(10) Å	K-O(4)ii	2.808(12) Å
U-O(3) x2	2.300(7) Å	K-O(5)	2.743(9) Å
U-O(4) x2	1.790(9) Å	Mo(1)-O(1)	1.717(7) Å
K-O(1)i	2.691(8) Å	Mo(1)-O(2)	1.819(9) Å
K-O(1)ii	3.089(10) Å	Mo(1)-O(3)i	2.032(8) Å
K-O(2)	2.949(8) Å	Mo(1)-O(3)ii	2.064(9) Å
K-O(3)	3.088 (8) Å	Mo(1)-O(5)	1.796(9) Å
K-O(4)i	3.090(10) Å	*Mo(2)-O(1) x 2	2.1565(10) Å
K-O(4)ii	2.997(9) Å	*Mo(2)-O(1) x 2	1.869(2) Å

Table S3c. $K_3[(UO_2)_6(OH)_2(MoO_4)_6(MoO_3OH)]$.

U(1)-O(1)	2.410(9) Å	Mo(1)-O(10) x 2	1.746(10) Å
U(1)-O(3)	2.410(10) Å	Mo(1)-O(13) x 2	1.751(12) Å
U(1)-O(4)	2.359(9) Å	Mo(2)-O(1)	1.781(10) Å
U(1)-O(5)	2.361(10) Å	Mo(2)-O(2)	1.750(10) Å
U(1)-O(6)	1.756(11) Å	Mo(2)-O(4)	1.764(9) Å
U(1)-O(7)	1.782(11) Å	Mo(2)-O(8)	1.745(11) Å
U(1)-O(13)	2.306(11) Å	Mo(3)-O(3)	1.756(10) Å
U(2)-O(2)	2.356(10) Å	Mo(3)-O(14)	1.747(12) Å
U(2)-O(9)	1.759(11) Å	Mo(3)-O(17)	1.765(11) Å
U(2)-O(10)	2.407(9) Å	Mo(3)-O(22)	1.753(12) Å
U(2)-O(11)	2.337(11) Å	Mo(4)-O(5)	1.746(10) Å
U(2)-O(12)	2.388(10) Å	Mo(4)-O(11)	1.765(11) Å
U(2)-O(14)	2.425(11) Å	Mo(4)-O(12)	1.753(10) Å
U(2)-O(18)	1.759(11) Å	Mo(4)-O(23)	1.746(11) Å
U(3)-O(8) x2	2.356(10) Å	K(1)-O(1) x 2	2.963(11) Å
U(3)-O(15)	1.708(16) Å	K(1)-O(4) x 2	3.243(10) Å
U(3)-O(16)	1.763(16) Å	K(1)-O(6) x 2	2.736(10) Å
U(3)-O(17) x2	2.369(10) Å	*K(2)-O(16)	2.74(3) Å
U(3)-O(21)	2.566(14) Å	*K(2)-O(19)	3.18(3) Å
U(4)-O(19)	1.774(16) Å	*K(2)-O(20)	2.70(3) Å
U(4)-O(20)	1.744(17) Å	*K(2)-O(21)	3.08(3) Å
U(4)-O(22) x 2	2.318(12) Å	*K(2)-O(24)	2.68(3) Å
U(4)-O(23) x 2	2.317(11) Å	*K(3)-O(16)	2.94(3) Å
U(4)-O(24)	2.582(15) Å	*K(3)-O(18)	2.91(3) Å
		*K(3)-O(20)	2.92(3) Å
		*K(3)-O(21)	3.06(3) Å
		*K(3)-O(24)	3.06(3) Å
		*K(4)-O(11)	3.20(3) Å
		*K(4)-O(12)	3.18(3) Å
		*K(4)-O(13)	3.20(3) Å
		*K(4)-O(18)	3.15(3) Å
		*K(4)-O(23)	3.13(3) Å

Table S3d. $K_5[(UO_2)_{10}MoO_5O_{11}OH]\cdot H_2O$

U(1)-O(4)	2.28(3) Å	U(6)-O(13)	2.261(17) Å	K(1)-O(32)	2.75(4) Å
U(1)-O(6)	2.31(4) Å	U(6)-O(24)	1.79(4) Å	K(1)-O(33)	2.80(3) Å
U(1)-O(7)	2.28(3) Å	U(6)-O(36)	2.46(4) Å	K(1)-O(34)	2.69(4) Å
U(1)-O(8)	2.22(4) Å	U(7)-O(2)	2.20(3) Å	*K(2)-OW1	2.72(3) Å
U(1)-O(9)	1.83(4) Å	U(7)-O(4)	2.19(4) Å	*K(2)-O(15)	2.64(6) Å
U(1)-O(15)	1.82(6) Å	U(7)-O(13)	2.225(19) Å	*K(2)-O(24)	2.65(4) Å
U(1)-O(20)	2.49(3) Å	U(7)-O(14)	2.25(4) Å	*K(2)-O(26)	2.65(5) Å
U(2)-O(1)	2.27(3) Å	U(7)-O(19)	1.93(5) Å	*K(2)-O(34)	2.79(4) Å
U(2)-O(10)	1.95(5) Å	U(7)-O(30)	1.88(4) Å	*K(2)-O(35)	2.54(4) Å
U(2)-O(11)	2.15(4) Å	U(8)-O(2)	2.26(4) Å	*K(3)-O(5)	2.85(4) Å
U(2)-O(13)	2.31(3) Å	U(8)-O(4)	2.30(3) Å	*K(3)-O(6)	3.01(4) Å
U(2)-O(14)	2.21(3) Å	U(8)-O(7)	2.30(3) Å	*K(3)-O(9)	2.84(4) Å
U(2)-O(18)	2.43(3) Å	U(8)-O(11)	2.26(4) Å	*K(3)-O(15)	2.69(5) Å
U(2)-O(21)	1.87(3) Å	U(8)-O(16)	1.84(4) Å	*K(3)-O(19)	3.05(6) Å
U(3)-O(2)	2.32(3) Å	U(8)-O(23)	2.42(3) Å	*K(3)-O(35)	2.91(4) Å
U(3)-O(12)	2.24(4) Å	U(9)-O(3)	2.50(3) Å	K(4)-O(2)	2.93(4) Å
U(3)-O(23)	2.35(4) Å	U(9)-O(8)	2.34(4) Å	K(4)-O(5)	2.84(4) Å
U(3)-O(25)	2.43(4) Å	U(9)-O(9)	2.44(4) Å	K(4)-O(9)	2.84(4) Å
U(3)-O(32)	1.71(4) Å	U(9)-O(10)	2.37(4) Å	K(4)-O(16)	2.75(4) Å
U(3)-O(33)	1.80(4) Å	U(9)-O(19)	2.34(5) Å	K(4)-O(19)	3.18(4) Å
U(3)-O(36)	2.48(4) Å	U(9)-O(26)	1.74(4) Å	K(4)-O(33)	2.89(4) Å
U(4)-O(1)	2.20(3) Å	U(9)-O(28)	1.79(3) Å	*K(5)-O(15)	3.04(6) Å
U(4)-O(6)	2.23(3) Å	U(10)-O(3)	2.39(3) Å	*K(5)-O(22)	2.79(5) Å
U(4)-O(7)	2.20(4) Å	U(10)-O(5)	2.40(4) Å	*K(5)-O(29)	2.99(3) Å
U(4)-O(12)	2.17(4) Å	U(10)-O(10)	2.52(4) Å	*K(5)-O(30)	3.19(4) Å
U(4)-O(17)	1.91(5) Å	U(10)-O(11)	2.28(4) Å	*K(5)-O(31)	2.87(3) Å
U(4)-O(22)	1.77(5) Å	U(10)-O(17)	2.38(5) Å	*K(5)-O(32)	2.99(4) Å
U(5)-O(6)	2.28(3) Å	U(10)-O(27)	1.81(4) Å	*K(5)-O(35)	3.14(4) Å
U(5)-O(14)	2.28(3) Å	U(10)-O(31)	1.75(3) Å	*K(6)-O(22)	2.72(5) Å
U(5)-O(18)	2.35(2) Å	Mo(1)-O(18)	1.94(3) Å	*K(6)-O(29)	2.44(5) Å
U(5)-O(20)	2.40(4) Å	Mo(1)-O(20)	1.86(3) Å	*K(6)-O(30)	2.51(5) Å
U(5)-O(29)	1.89(4) Å	Mo(1)-O(23)	1.95(3) Å	*K(6)-O(32)	2.78(5) Å
U(5)-O(35)	1.82(4) Å	Mo(1)-O(25)	1.89(4) Å	K(7)-OW1	2.95(5) Å
U(5)-O(36)	2.31(4) Å	Mo(1)-O(34)	1.67(4) Å	K(7)-O(21)	2.53(3) Å
U(6)-O(1)	2.28(4) Å	K(1)-O(22)	2.83(5) Å	K(7)-O(27)	2.67(4) Å
U(6)-O(3)	1.98(3) Å	K(1)-O(24)	2.86(4) Å	K(7)-O(28)	2.70(4) Å
U(6)-O(8)	2.15(4) Å	K(1)-O(26)	3.10(3) Å	K(67)-O(29)	2.71(4) Å
U(6)-O(12)	2.29(3) Å	K(1)-O(31)	2.97(4) Å	K(7)-O(30)	2.76(4) Å
				K(7)-O(35)	3.19(3) Å