UCRL-CR-139073-PT-2

Interim Report on Task 1.2: Near Equilibrium Processing Requirements – Attrition Milling Appendices Part 2 of 2 To Lawrence Livermore National Laboratory for Contract B345772

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U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

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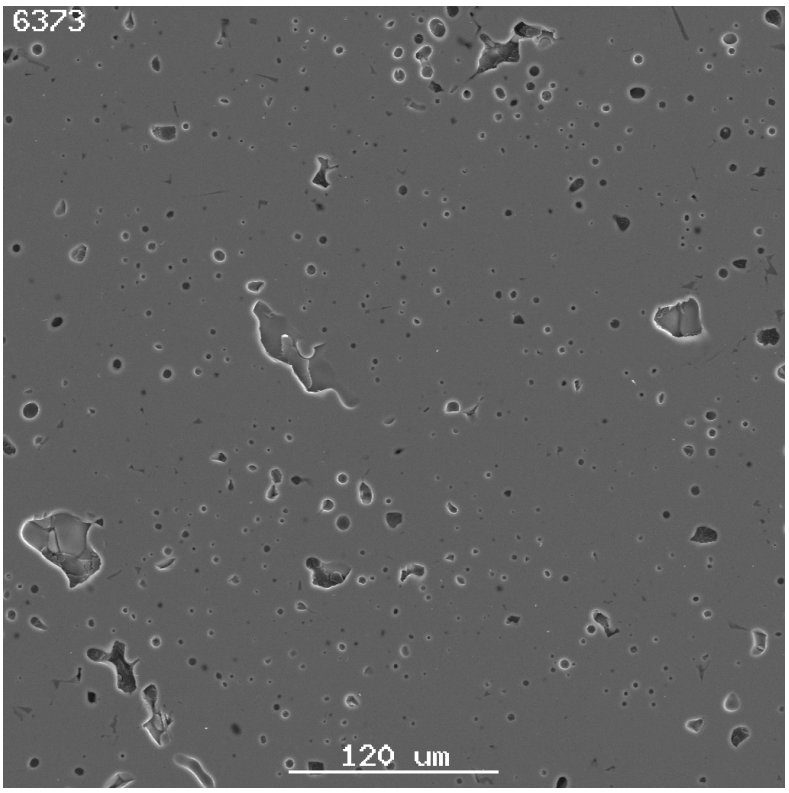
APPENDIX A

SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS OF THE CERIUM/CERIUM/ZIRCONIUM-BASELINE SAMPLES

(a)



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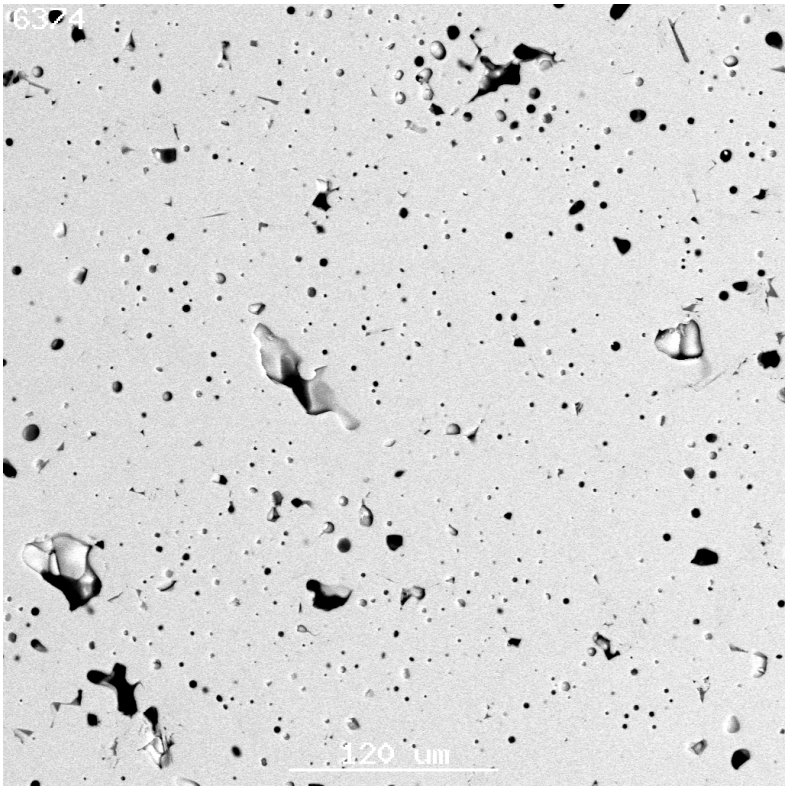
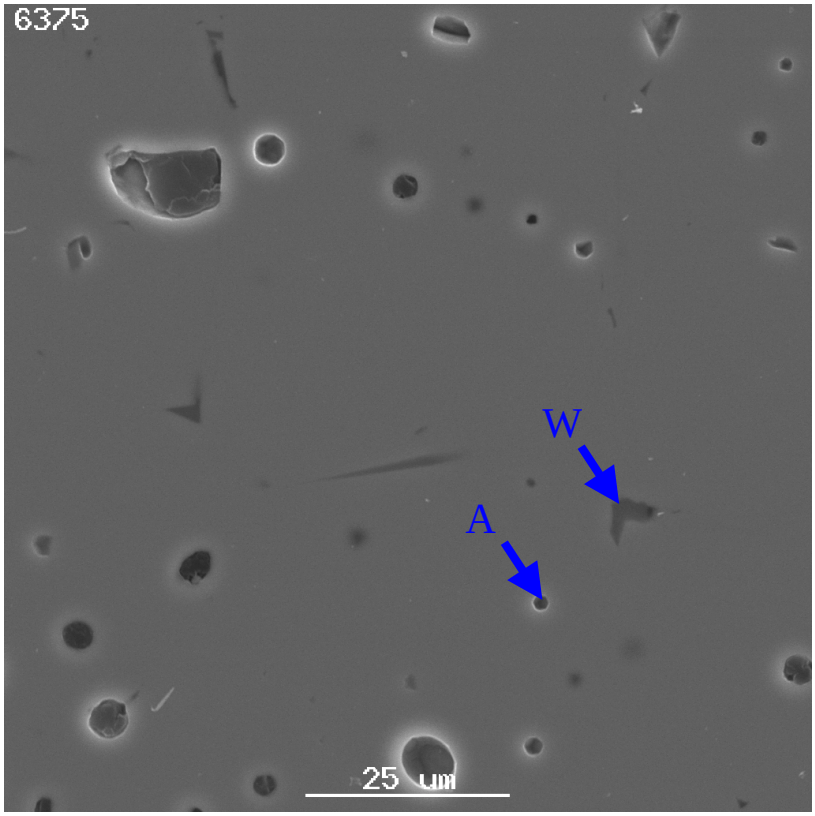
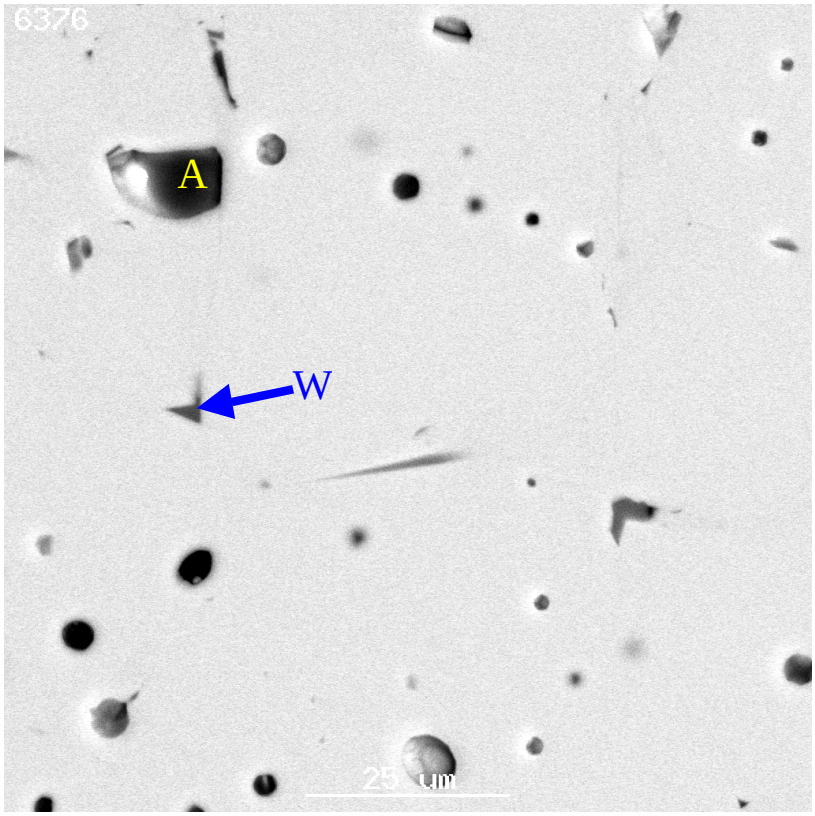


Figure A-1: (a) and (c) Secondary electron micrographs and, (b) and (d) backscattered electron micrographs of L000138 - a Ce/Ce/Zr-baseline composition sample made by sintering at 1350°C in air for 4 hours from oxide-route, 1 kg scale, dry-attrition milled powder. The sample is mostly pyrochlore with a trace (<1 vol. %) of what appears to be whitlockite (W). Porosity (A) is present.

(c)



(d)



(a)

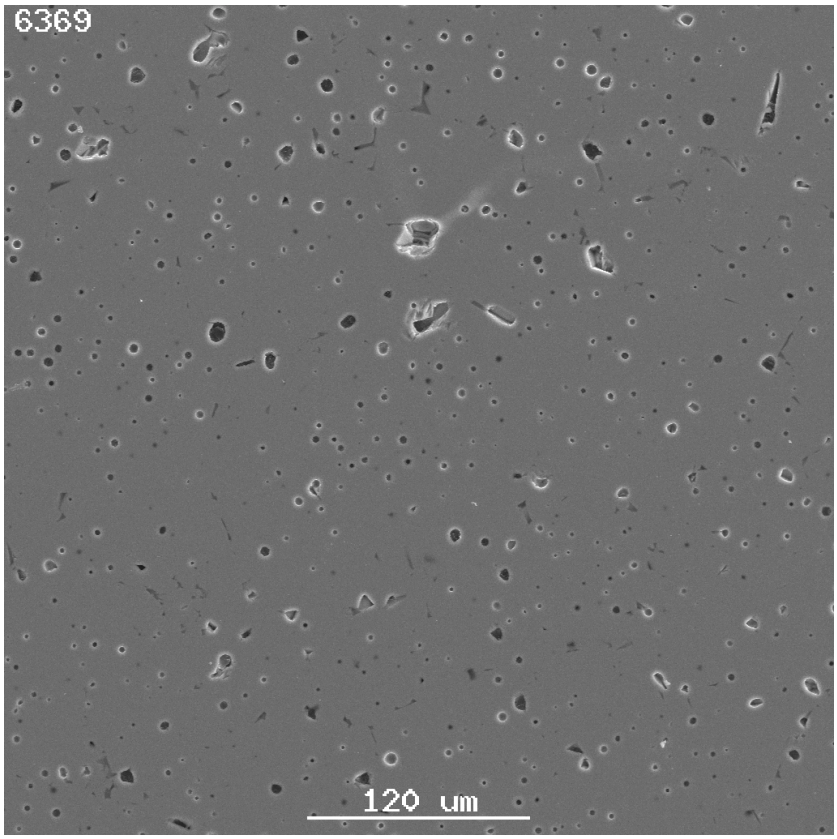
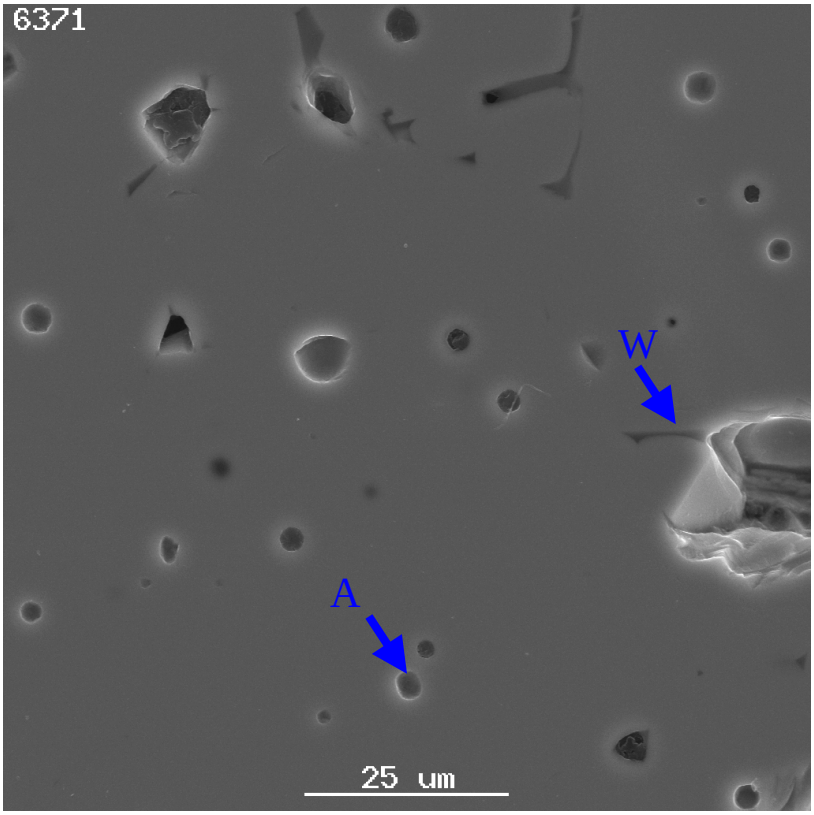
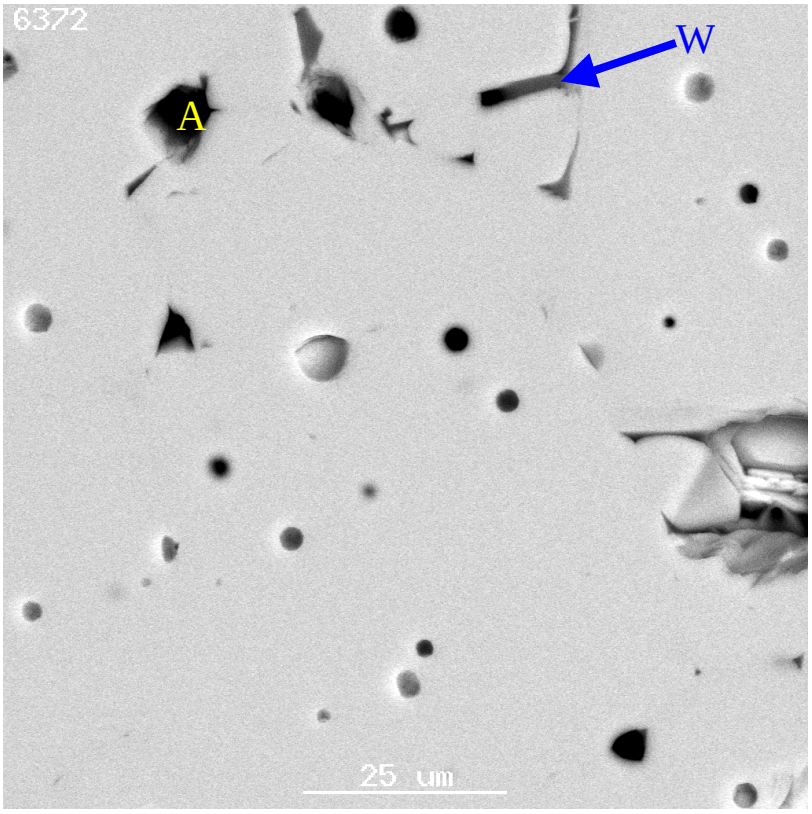


Figure A-2: (a) and (b) Secondary electron micrographs and (c) backscattered electron micrograph of L000139 - a Ce/Ce/Zr-baseline composition sample made by sintering at 1350°C in air for 4 hours from oxide-route, 1 kg scale, wet-attrition milled powder. The sample is mostly pyrochlore with a trace (<1 vol. %) of what appears to be whitlockite (W). Porosity (A) is present.

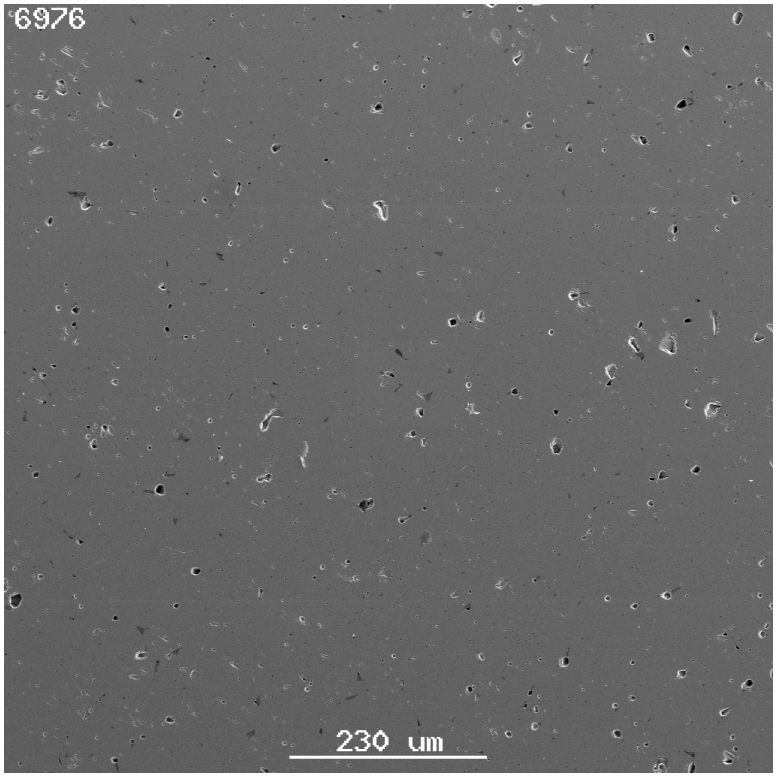
(b)



(c)



(a)



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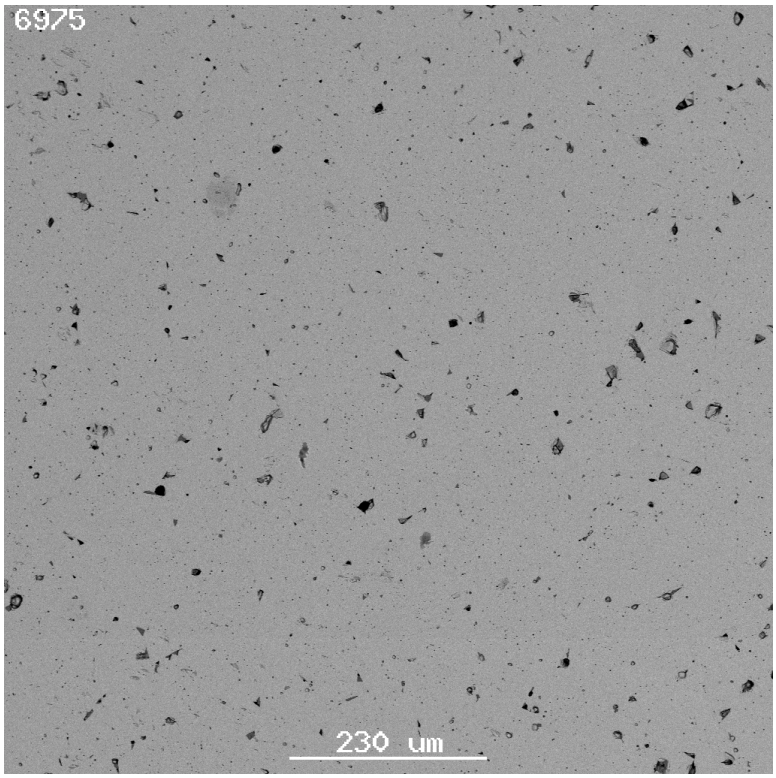
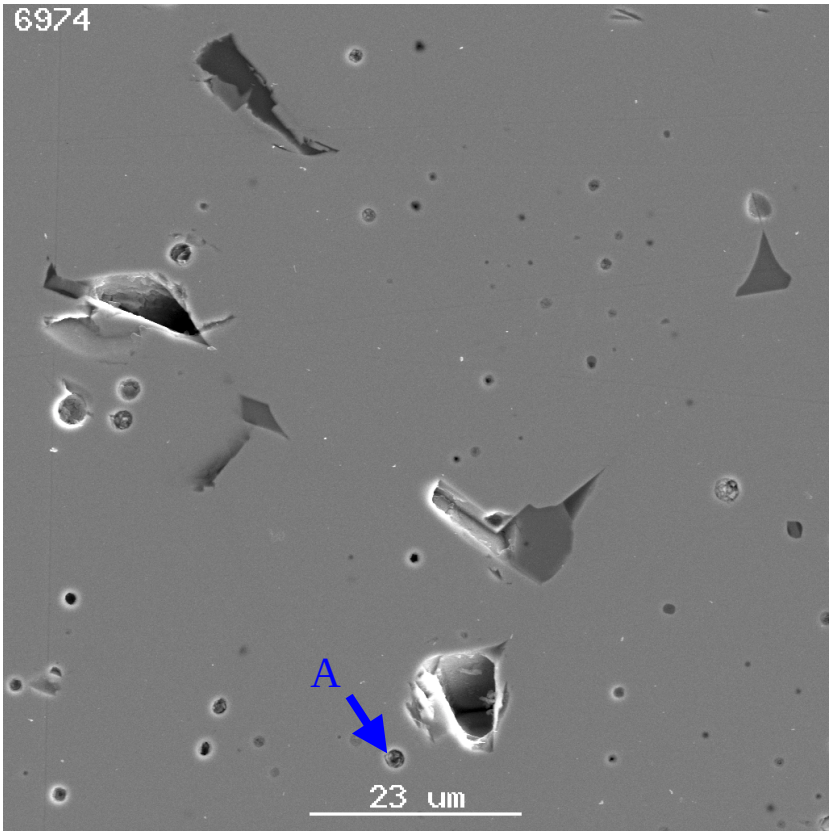


Figure A-3: (a) and (c) Secondary electron micrographs and, (b) and (d) backscattered electron micrographs of L991004 a Ce/Ce/Zr-baseline composition sintered at 1350°C in air for 4 hours and made from wet-attrition milled oxide-route powder (10 g powder batch size, made using quick-change attritor pot). The matrix is pyrochlore. Whitlockite (W) and a silicate glass phase (G) were also detected (at < 1 vol. %). Micrographs (c) and (d) are taken from a selected area to illustrate the whitlockite and glass phases present. Porosity (A) is also present.

(c)



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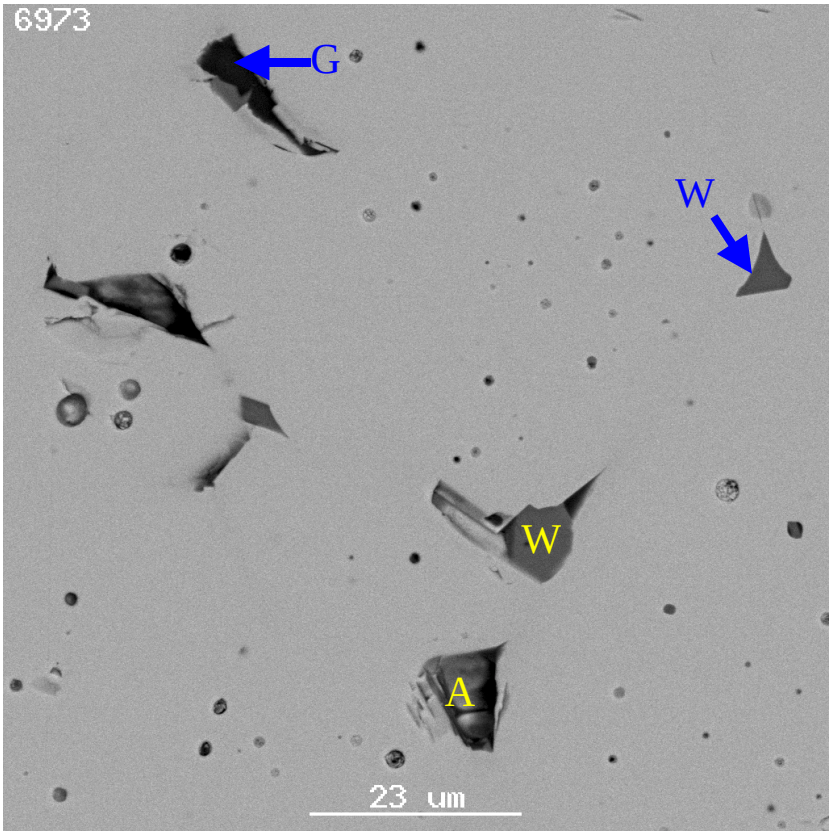
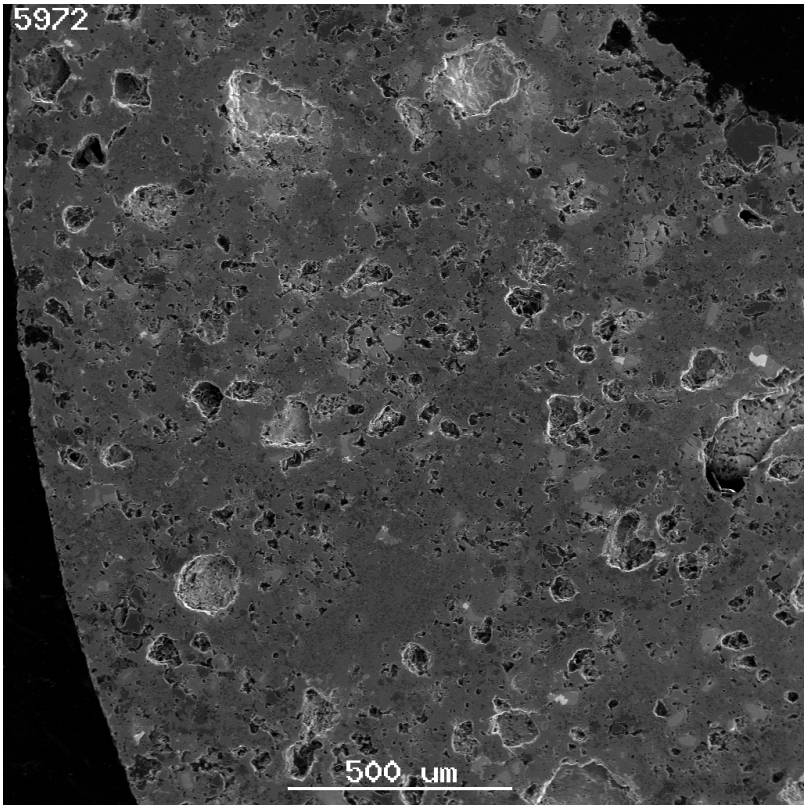


(a)



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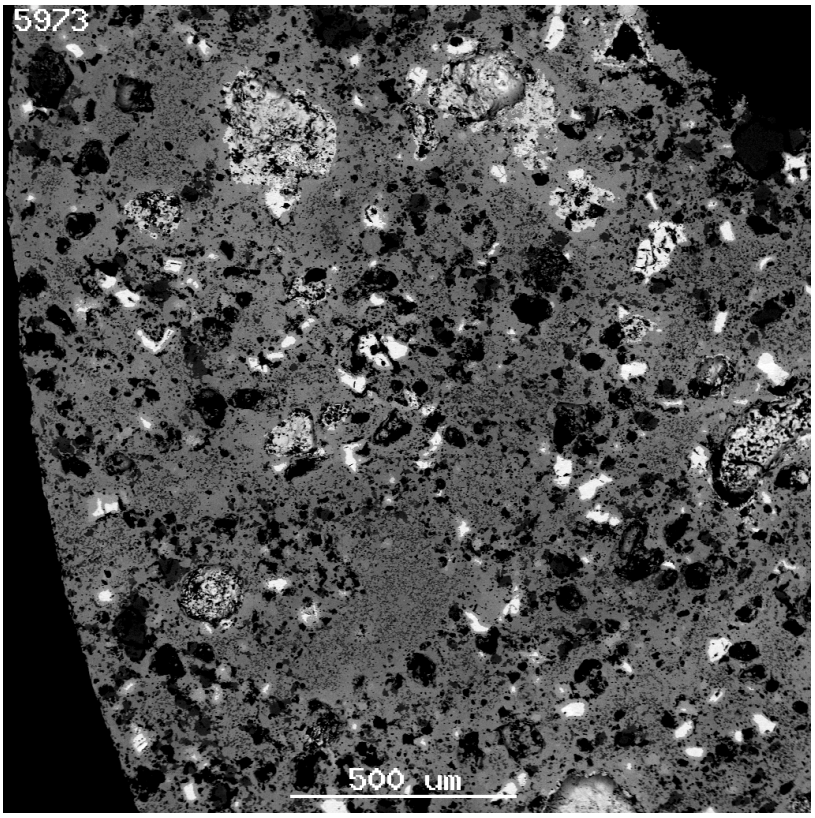
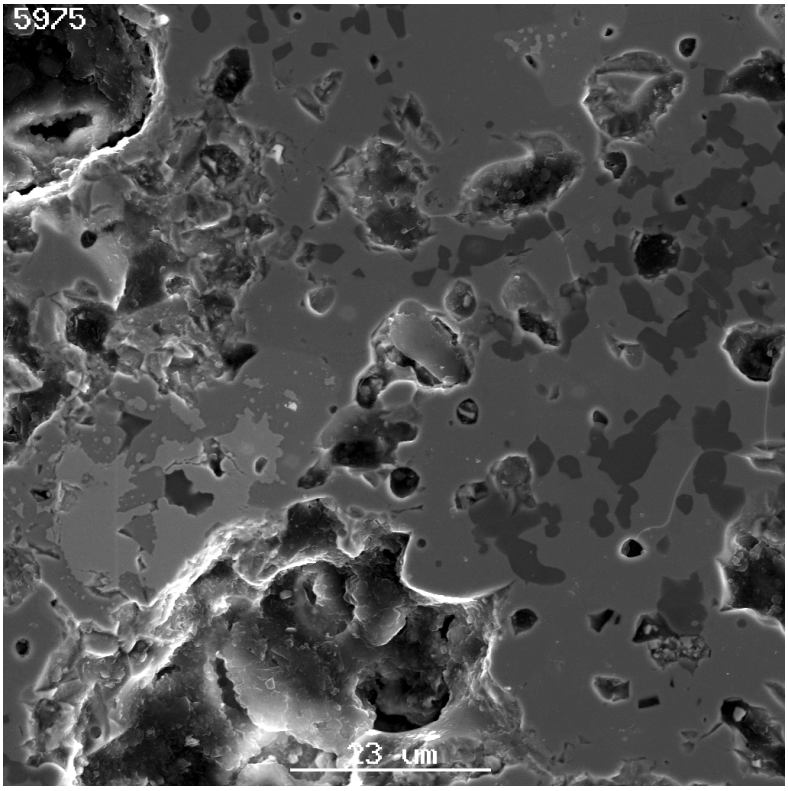


Figure B-1: (a) and (c) Secondary electron micrographs and, (b) and (d) backscattered electron micrographs of mws99-0586 (composition B1-2, oxide-route with high-fired ThO_2 and UO_2, dry-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore. Th/U-brannerite (light grey grains), Hf-doped rutile (dark-grey) grains and a small amount of zirconolite (Z), regions in the matrix that are a slightly darker grey than the pyrochlore – see (c). The zirconolite is probably the 4M polytype. Residual grains of the high-fired ThO_2 (white in (b) and (d)) are

(c)



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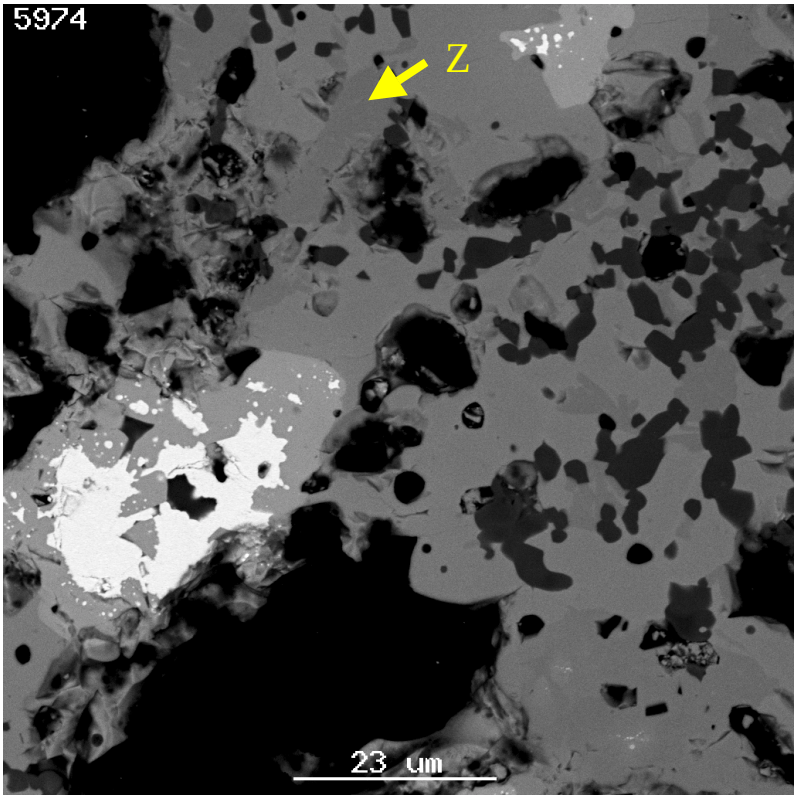
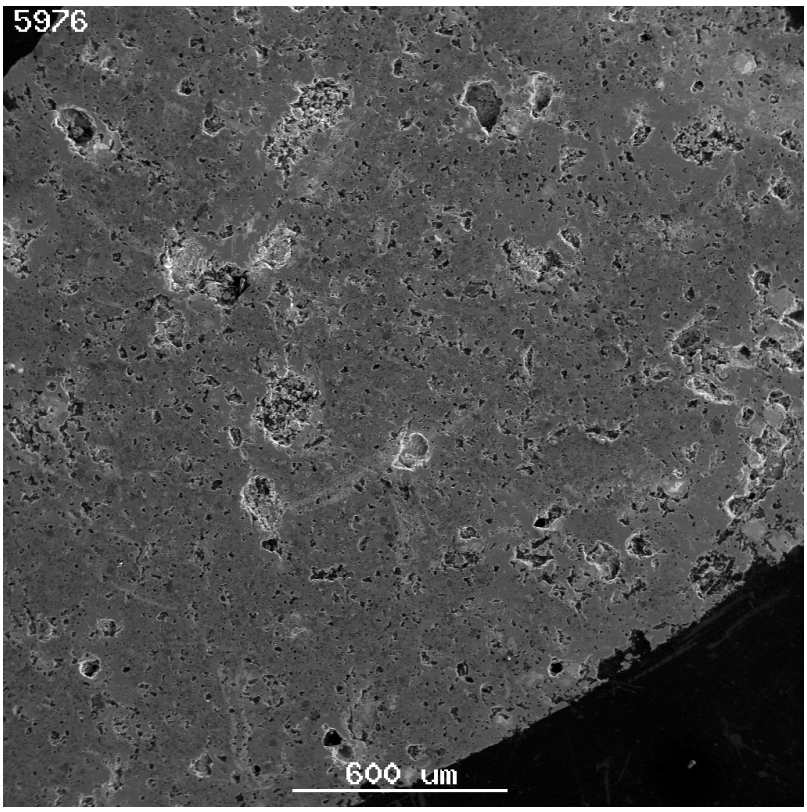


(a)



(b)

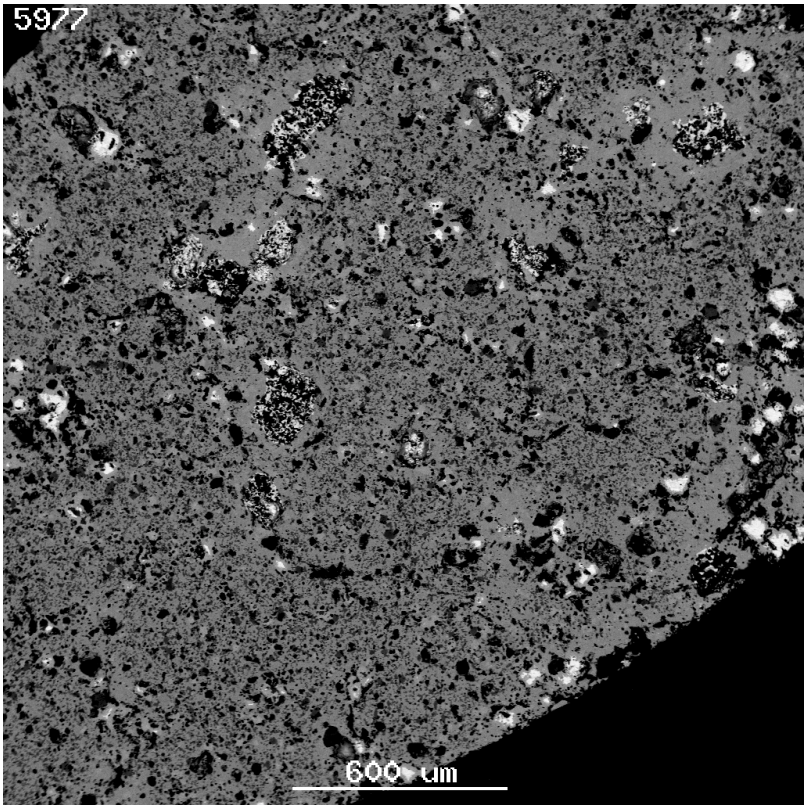
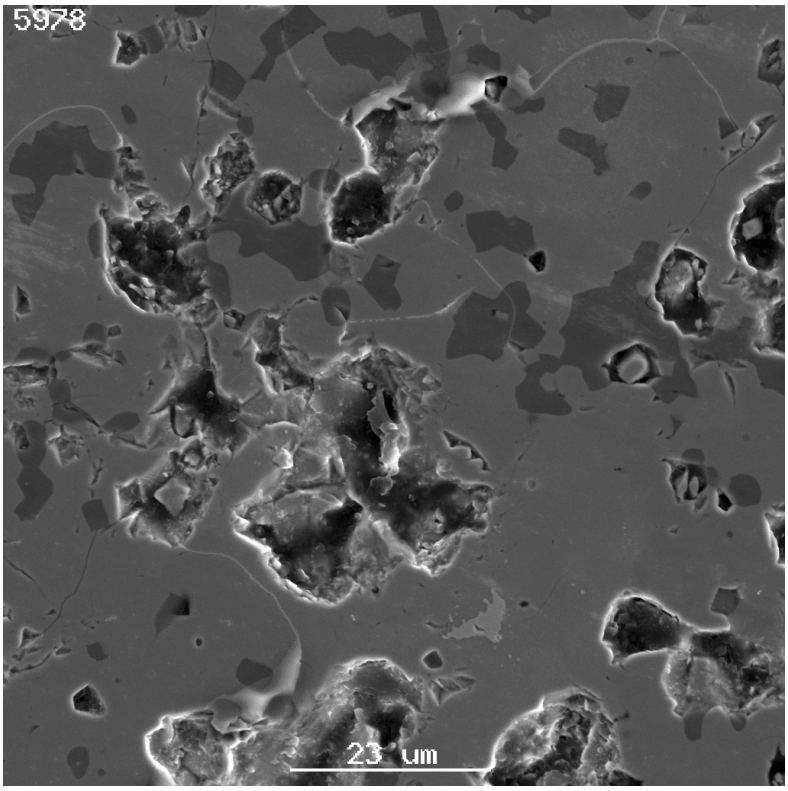
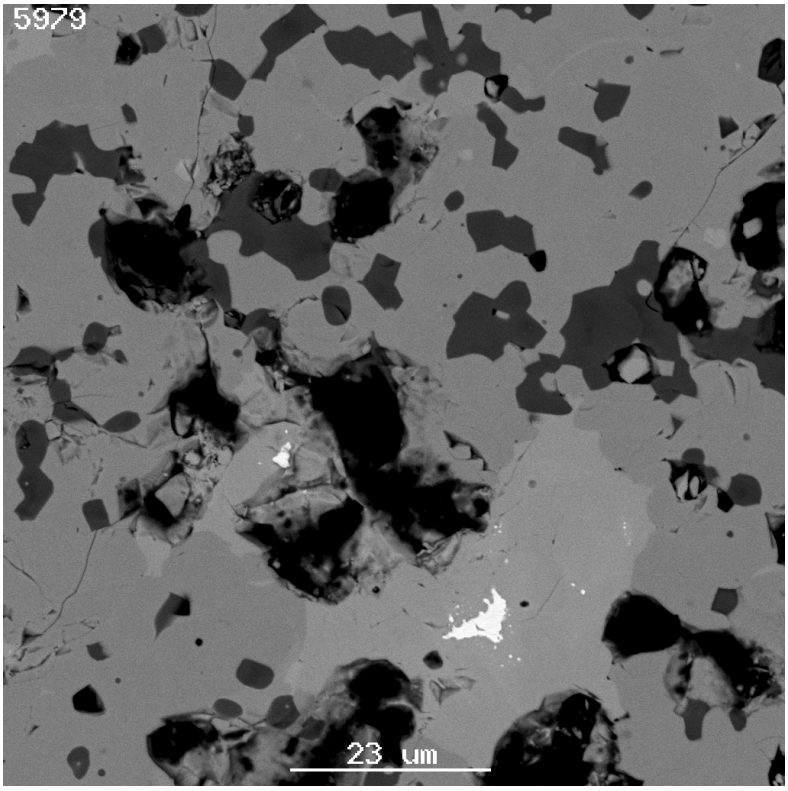


Figure B-2: (a) and (c) Secondary electron micrographs and, (b) and (d) backscattered electron micrographs of mws99-0587 (composition B1-2, oxide-route with high-fired ThO_2 and UO_2, wet-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore. Th/U-brannerite (light grey), Hf-doped rutile (dark-grey) grains and ThO_2 (white in (b) and (d)) are present. Zirconolite was not detected.

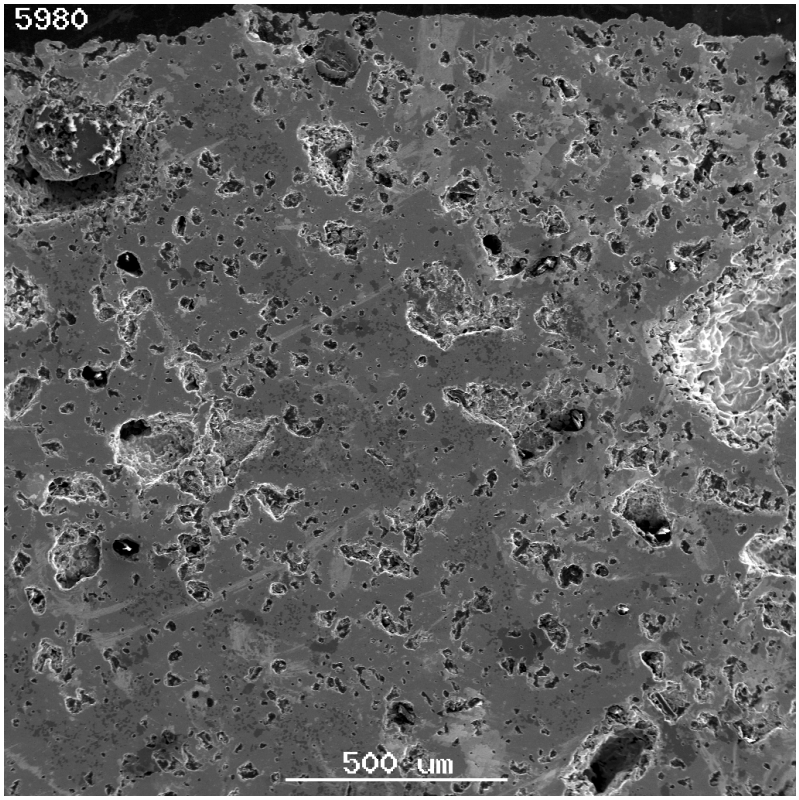
(c)



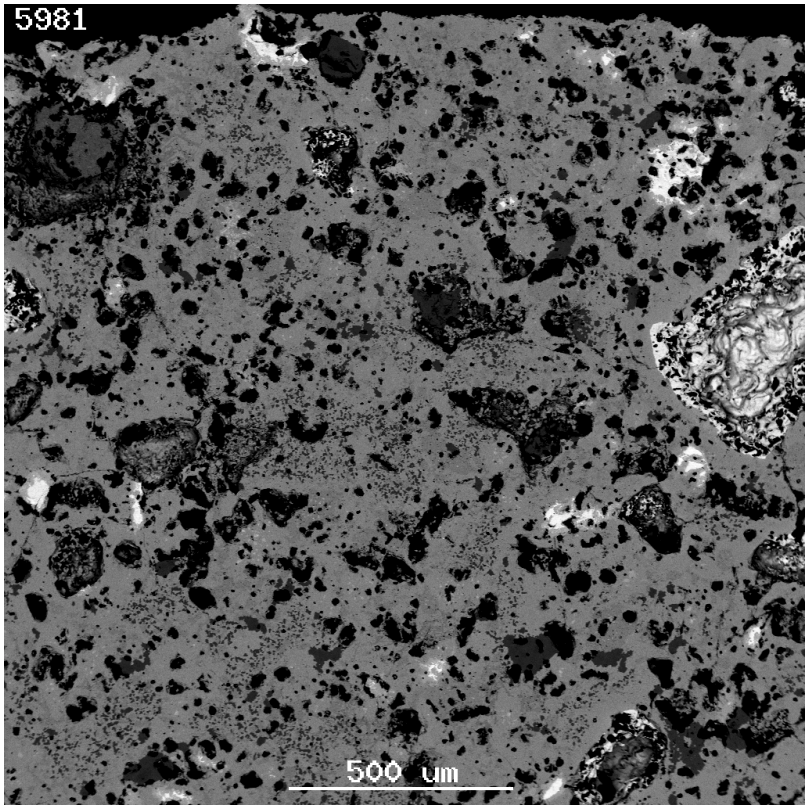
(d)



(a)

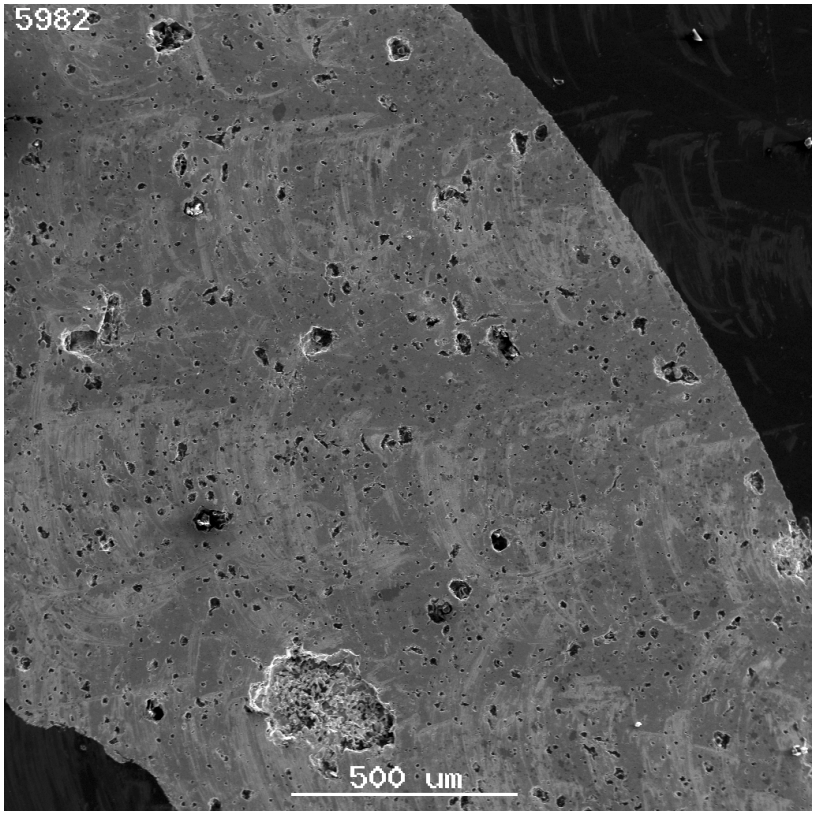


(b)



FigureB-3: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws99-0589 (composition B1-4, oxide-route with high-fired ThO_2 and UO_2, dry-attrition milled, sintered at 1350°C in air for 4 hours). The sample is very porous and inhomogeneous. It contains pyrochlore, zirconolite, Th/U-brannerite, intergranular and triple point glass, Hf-doped rutile (dark-grey) and

(a)



(b)

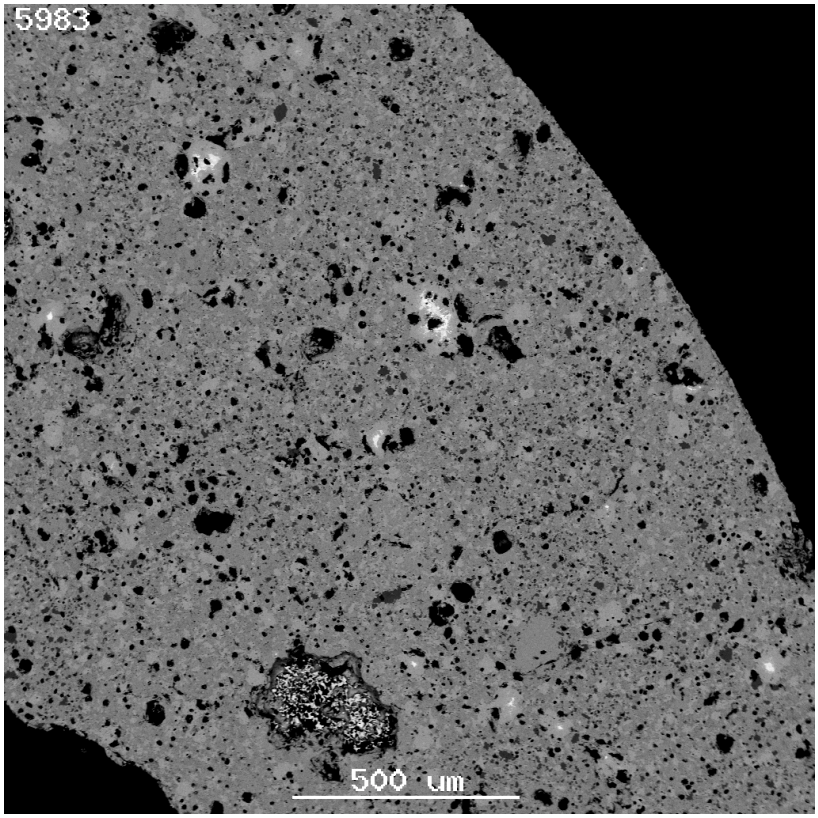
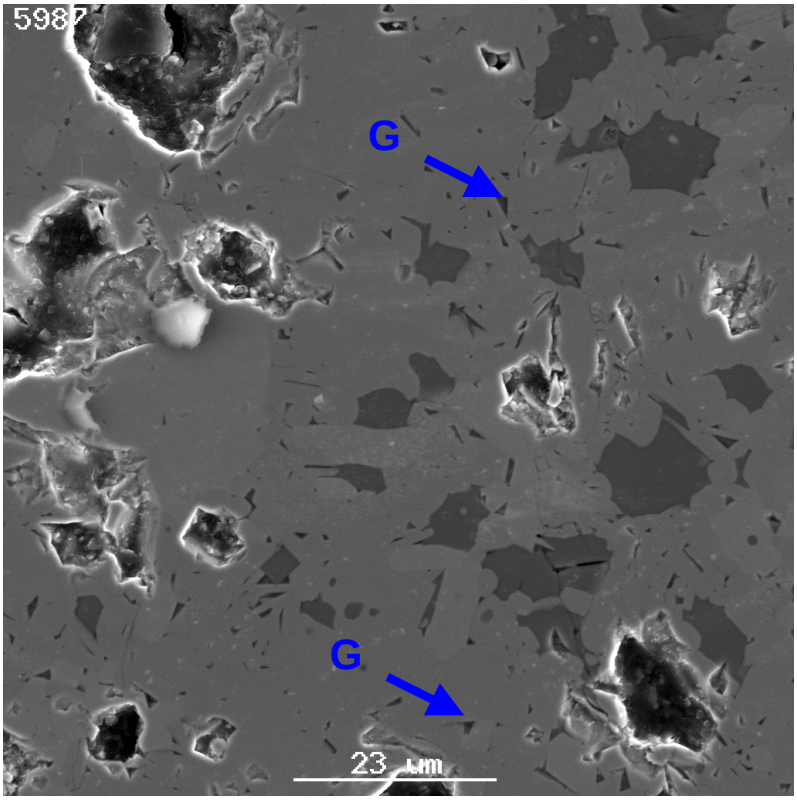


Figure B-4: (a) and (c) Secondary electron micrograph and, (b) and (d) backscattered electron micrographs of mws99-0591 (composition B1-4, oxide-route with high-fired ThO_2 and UO_2, wet-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore with some 2M zirconolite (2M, darker grey). Th/U-brannerite (light grey grains), Hf-doped rutile (dark-grey) and an intergranular triple point glass (G) are present. Some ThO_2 (white in (b) and (d)) is also present inside some of the brannerite grains. The sample is much more homogeneous than the dry attrition

(c)



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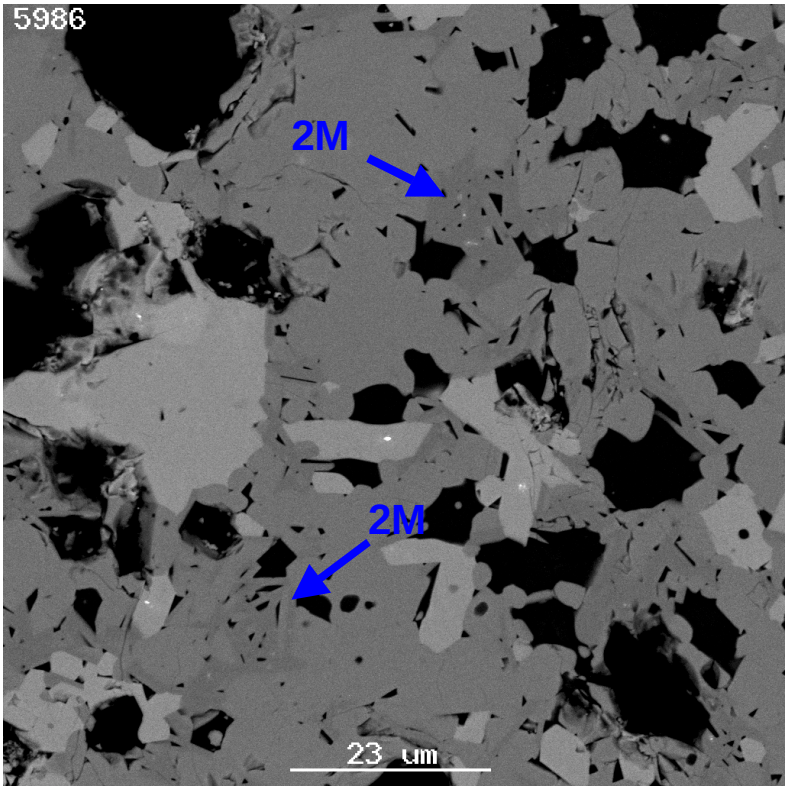
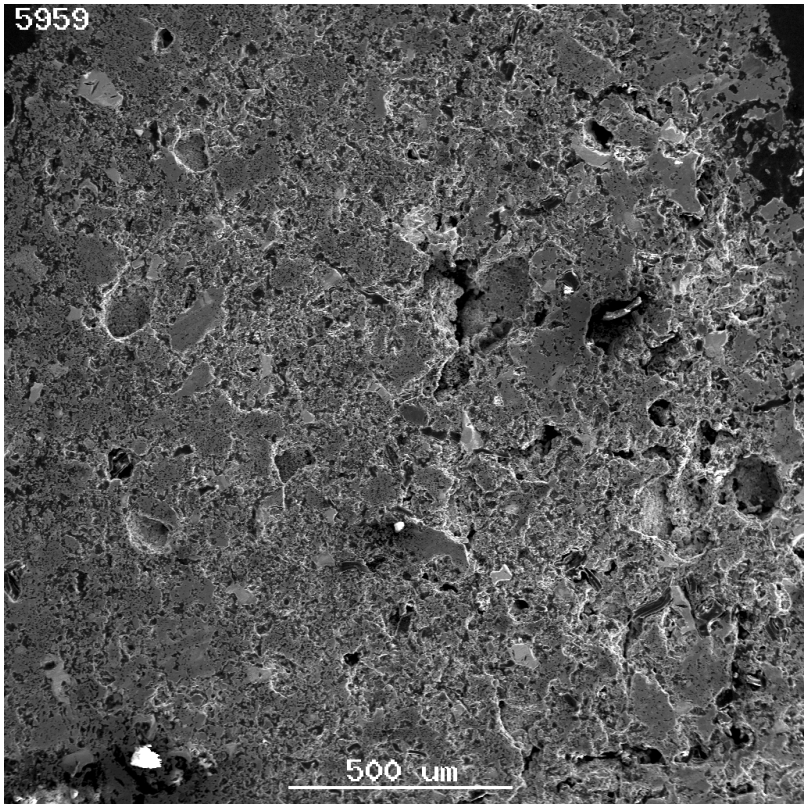


(a)



(b)

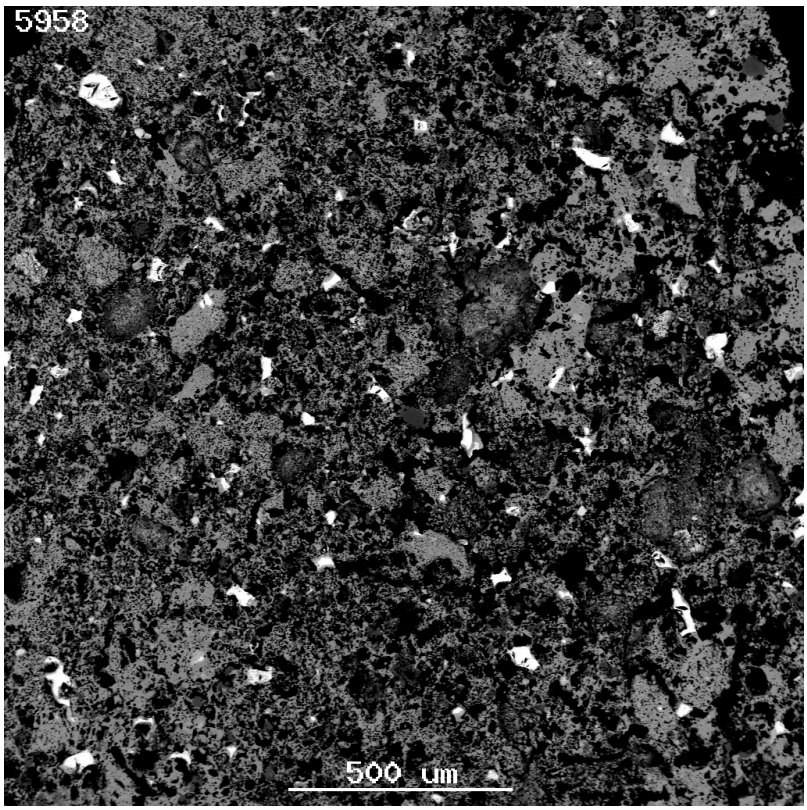
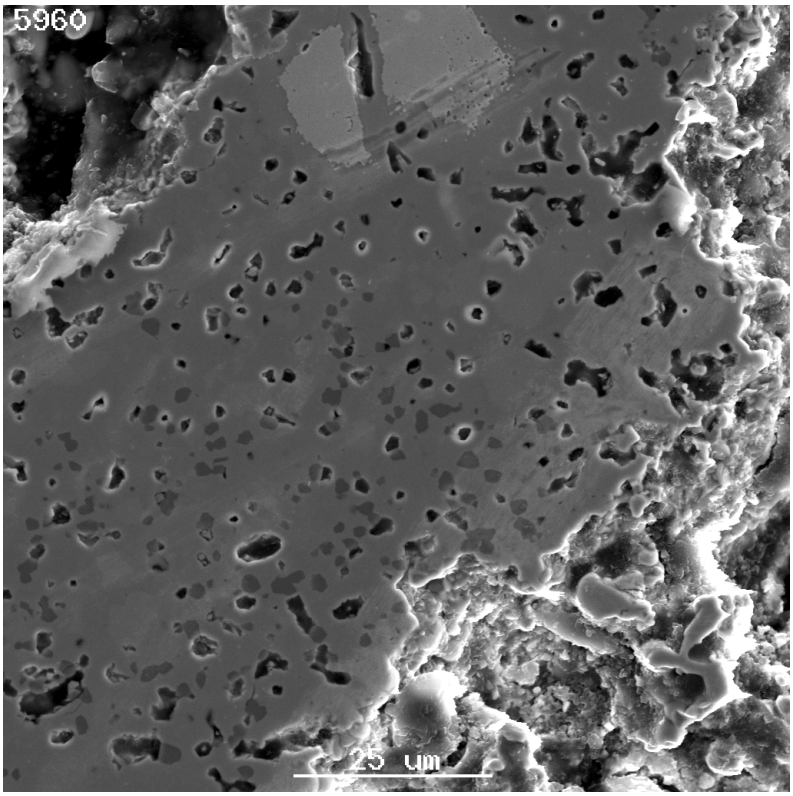


Figure B-5: (a) and (c) Secondary electron micrographs and, (b) and (d) backscattered electron micrographs of mws99-0578 (composition B1-10, oxide-route with high-fired ThO_2 and UO_2, dry-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is a mixture of pyrochlore and zirconolite (pyrochlore is the lighter of the two). Th/U-brannerite (light grey grains) and Hf-doped rutile (dark-grey) grains are present; as are laarge lumps of ThO_2 (white) from incomplete milling of the ThO_2 agglomerates in the green powder. The sample is very porous and inhomogeneous

(c)



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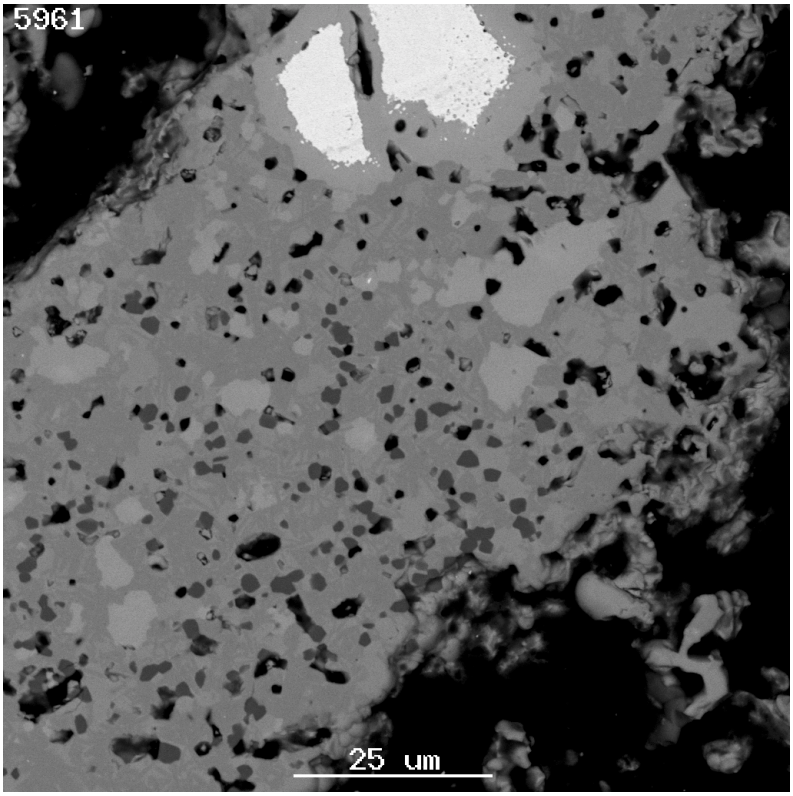
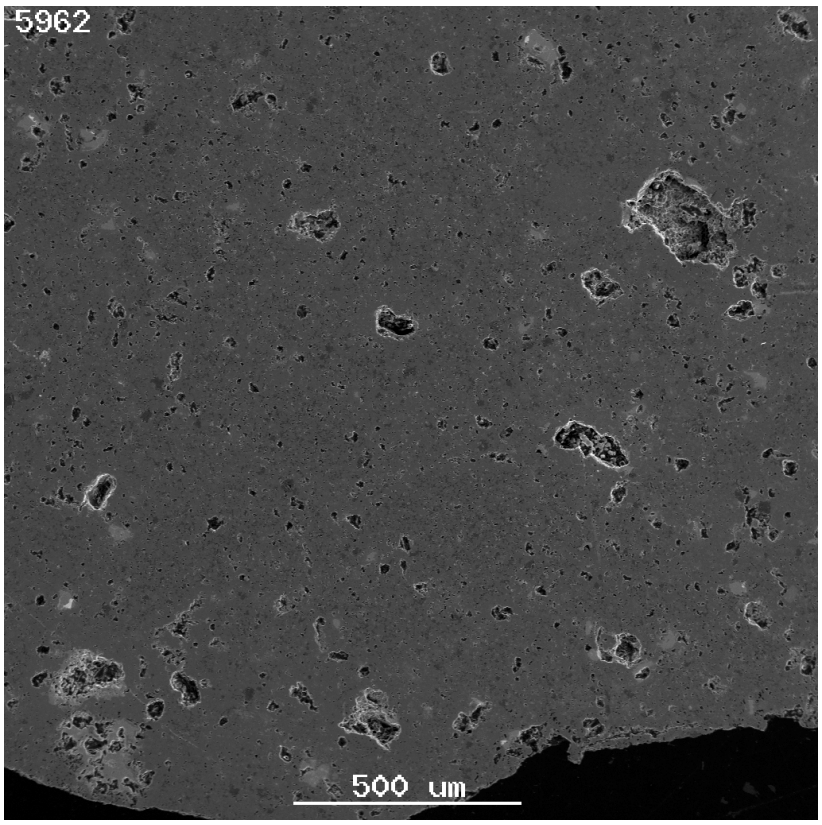


(a)



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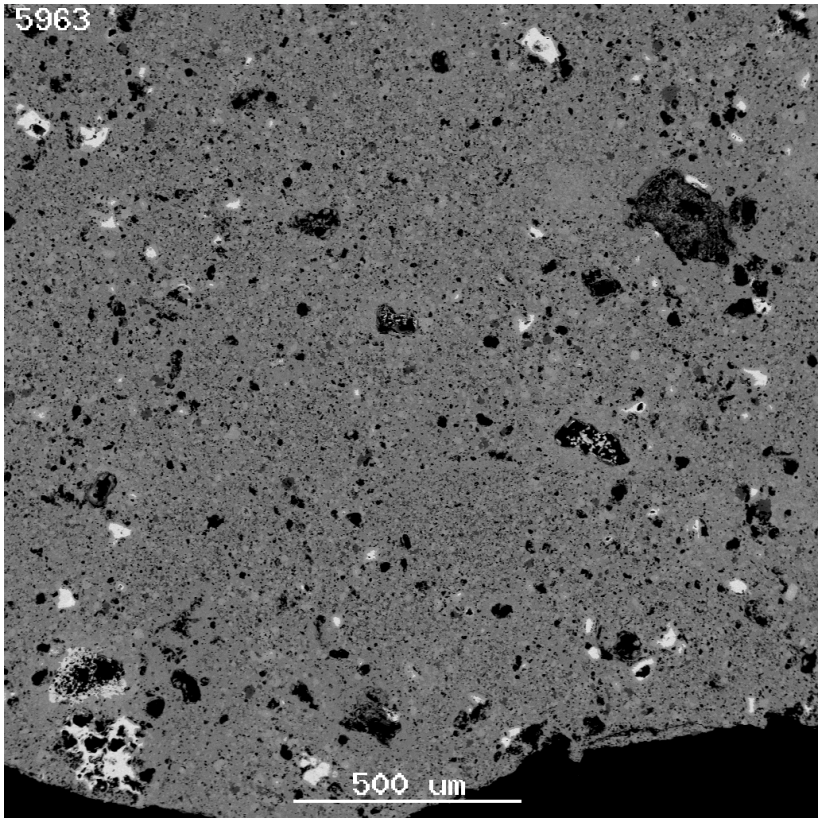
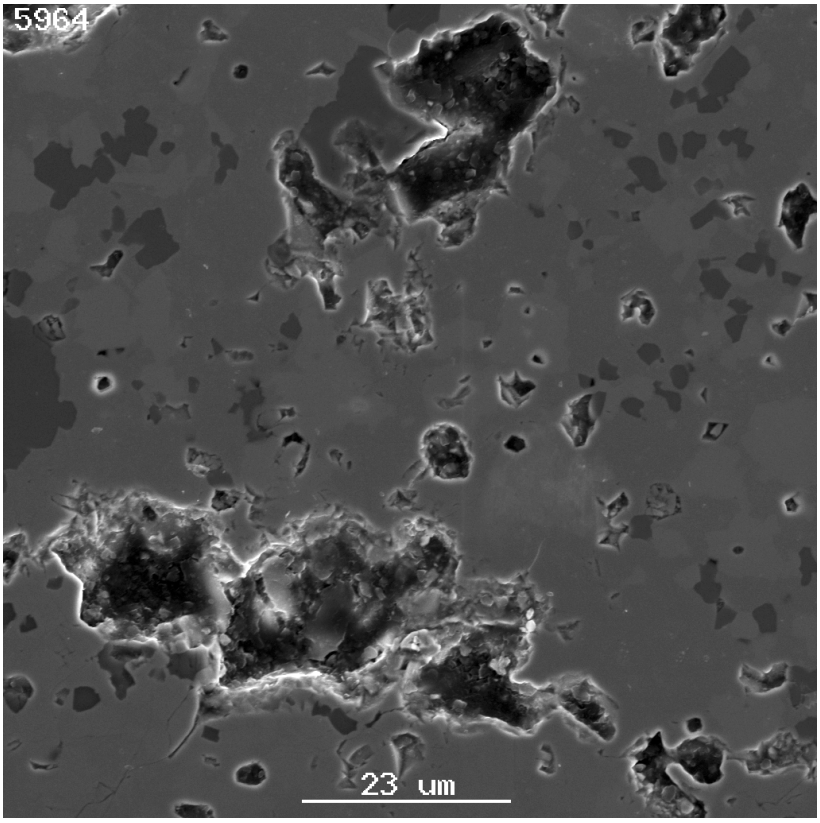


Figure B-6: (a) and (c) Secondary electron micrographs and, (b) and (d) backscattered electron micrographs of mws99-0580 (composition B1-10, oxide-route with high-fired ThO_2 and UO_2, wet-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is a mixture of pyrochlore and zirconolite (pyrochlore - the two lighter of the two). Th/U-brannerite (light grey grains) and Hf-doped rutile (dark-grey) grains are also present; as are residual grains of ThO_2 (white regions in (b)) and porosity (see (a) and (c)). The sample is more homogeneous than the dry attrition milled sample

(c)



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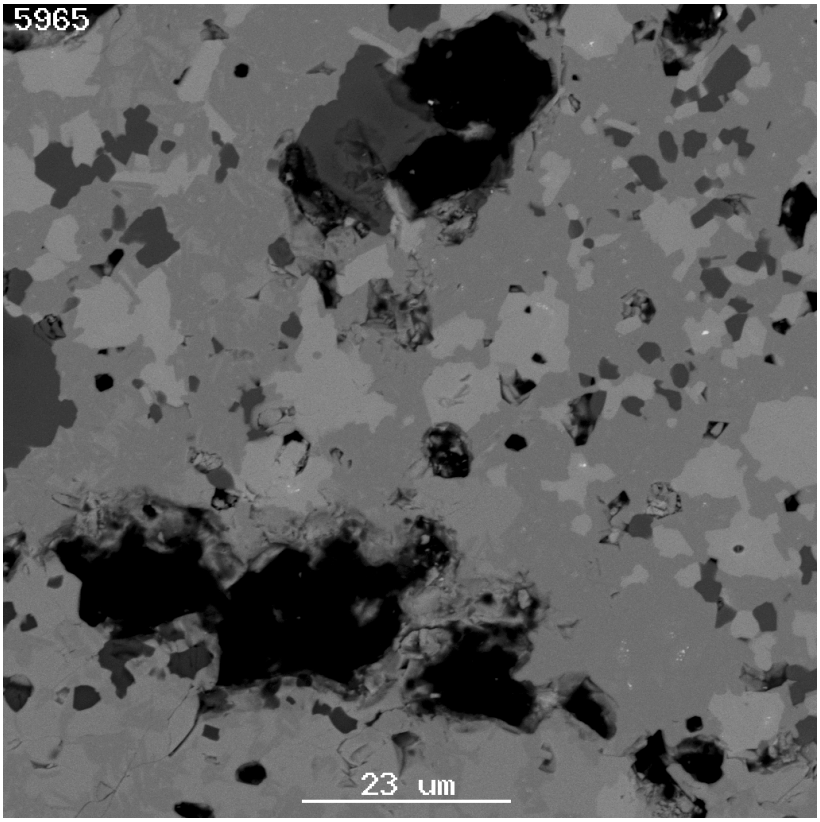
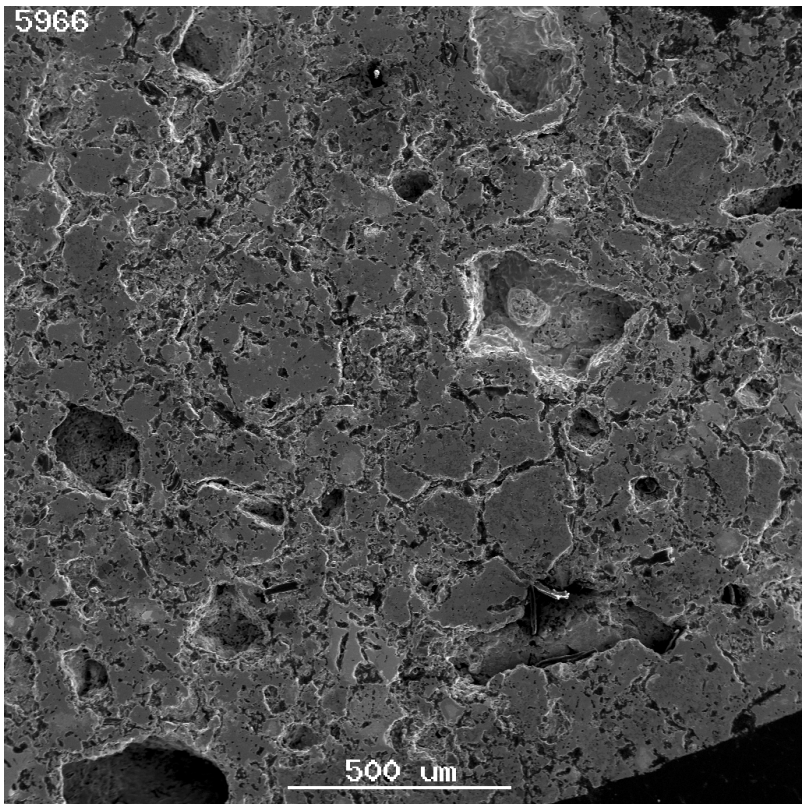


(a)



(b)

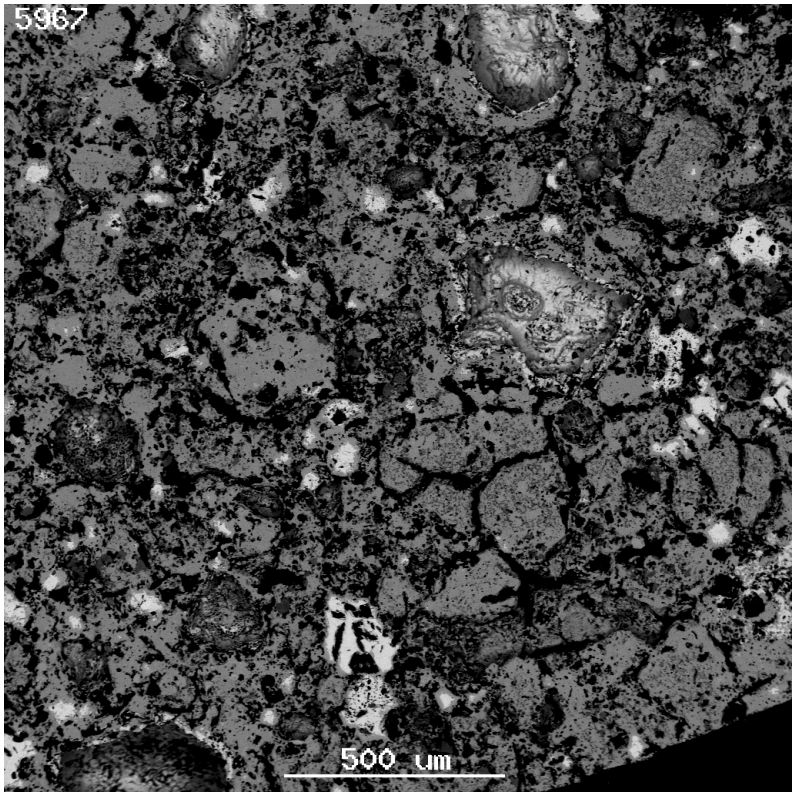
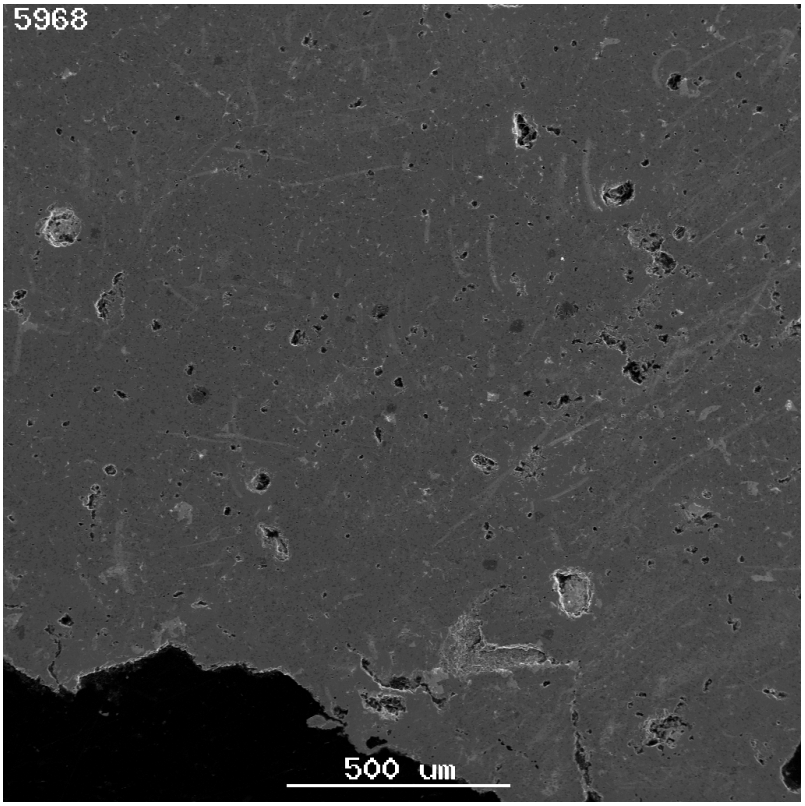


Figure B-7: (a) Secondary electron micrograph and, (b) backscattered electron micrograph of mws99-0582 (composition B1-12, oxide-route with high-fired ThO_2 and UO_2, dry-attrition milled, sintered at 1350°C in air for 4 hours). The sample is very porous and inhomogeneous indicating that little if any milling has occured. It contains pyrochlore, Th/U-brannerite (light grey grains), Hf-doped rutile (dark-grey) and large lumps of ThO_2 (white in (b)).

(a)



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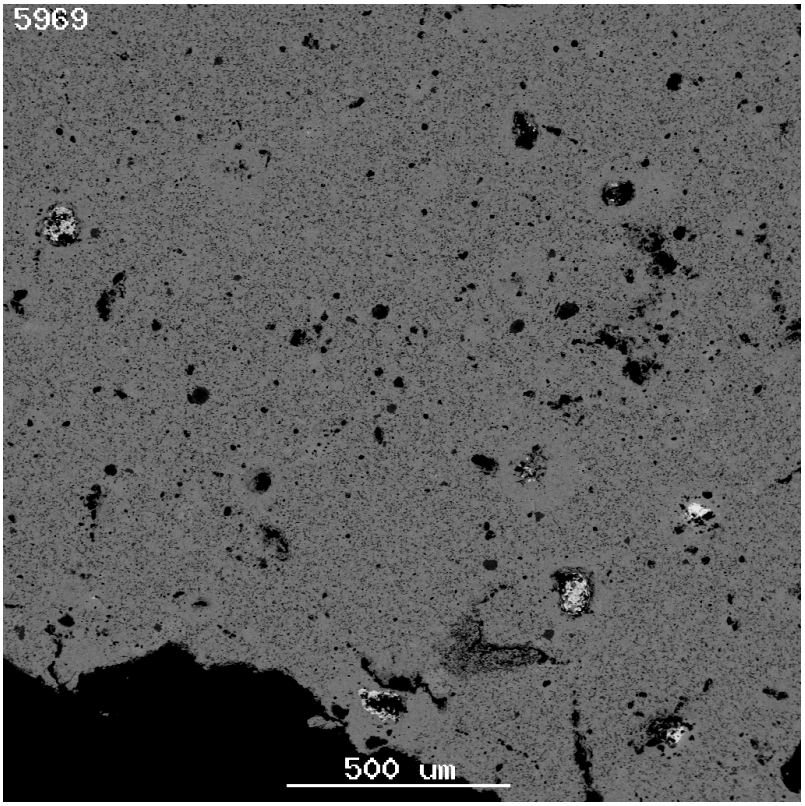
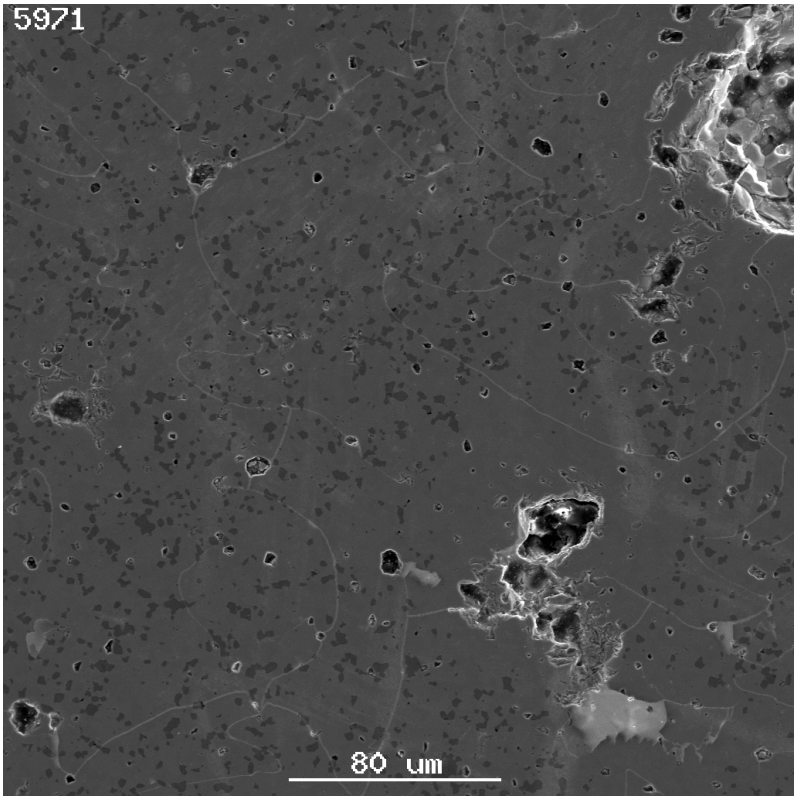
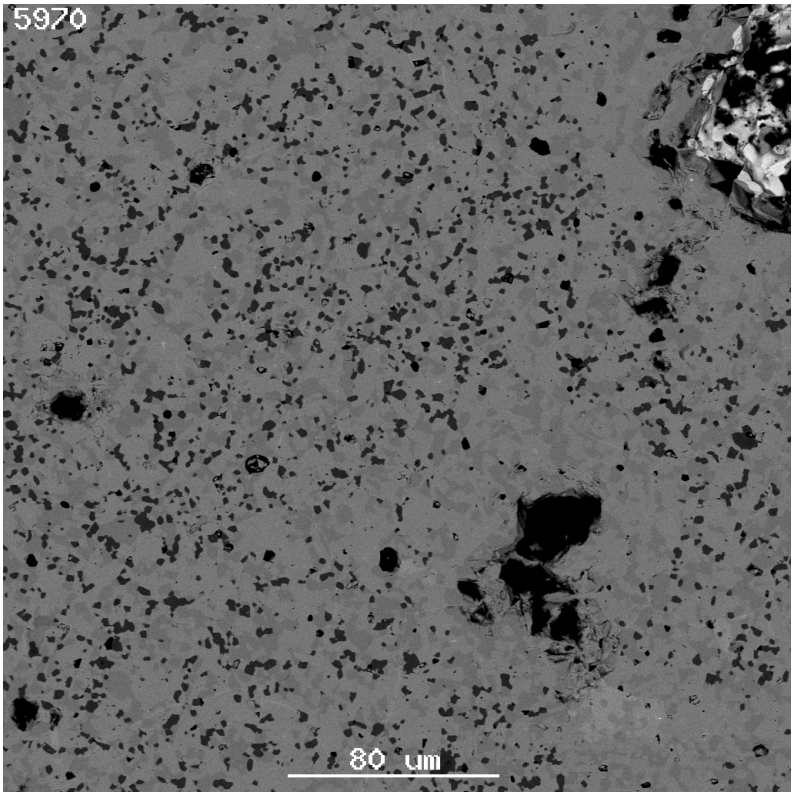


Figure B-8: (a) and (c) Secondary electron micrographs and, (b) and (d) backscattered electron micrographs of mws99-0584 (composition B1-12, oxide-route with high-fired ThO_2 and UO_2, wet-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is a mixture of pyrochlore and Th/U-brannerite (light grey grains). Hf-doped rutile (dark-grey grains) is present and this phase appears to be deficient around the pores and at the surface of the pellet. Some residual grains of the high-fired ThO_2 (white in (b)) are also present.

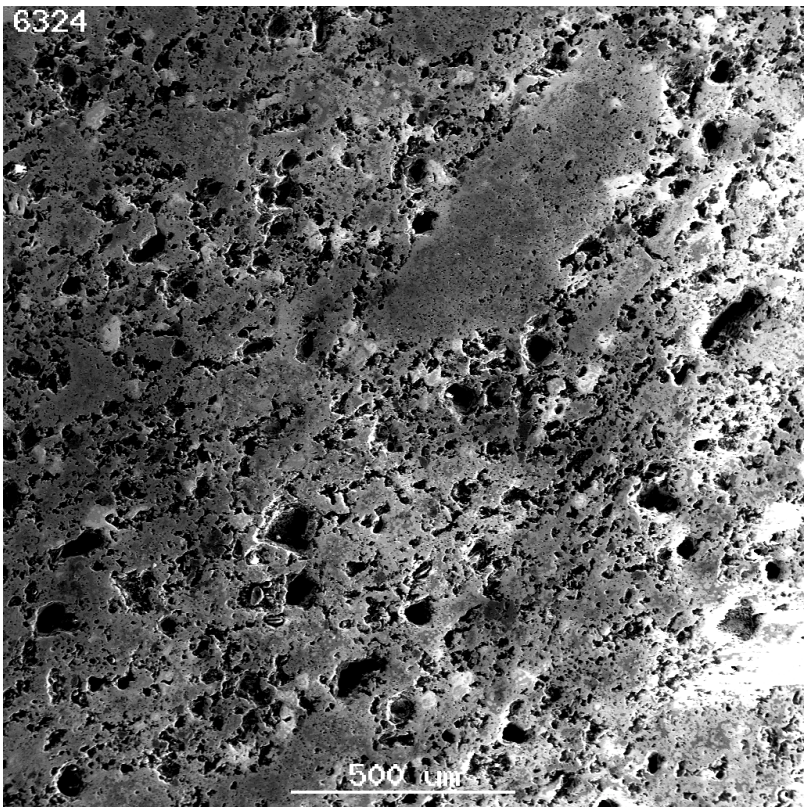
(c)



(d)



(a)



(b)

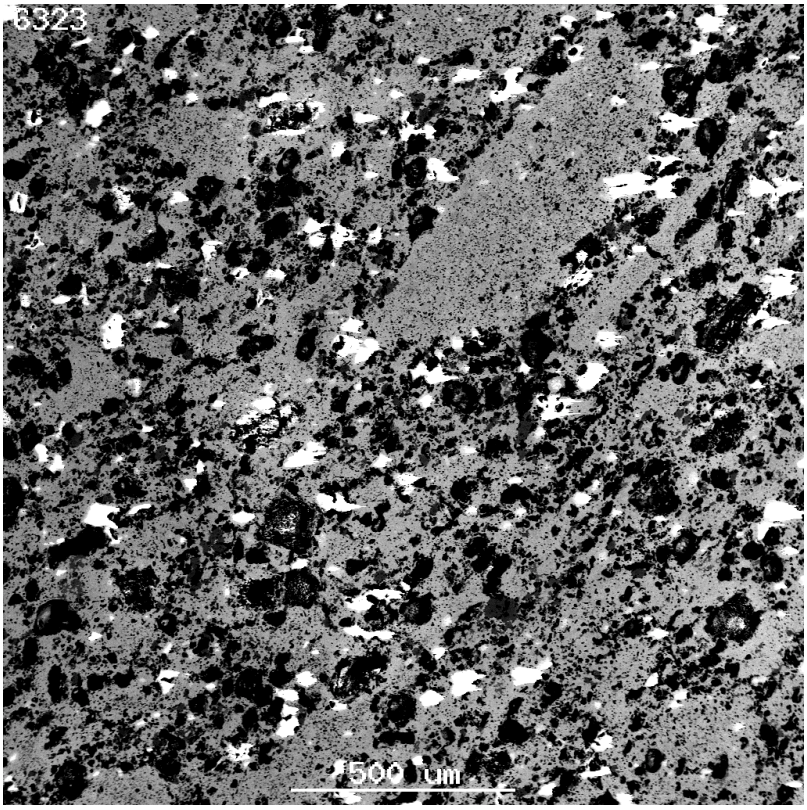
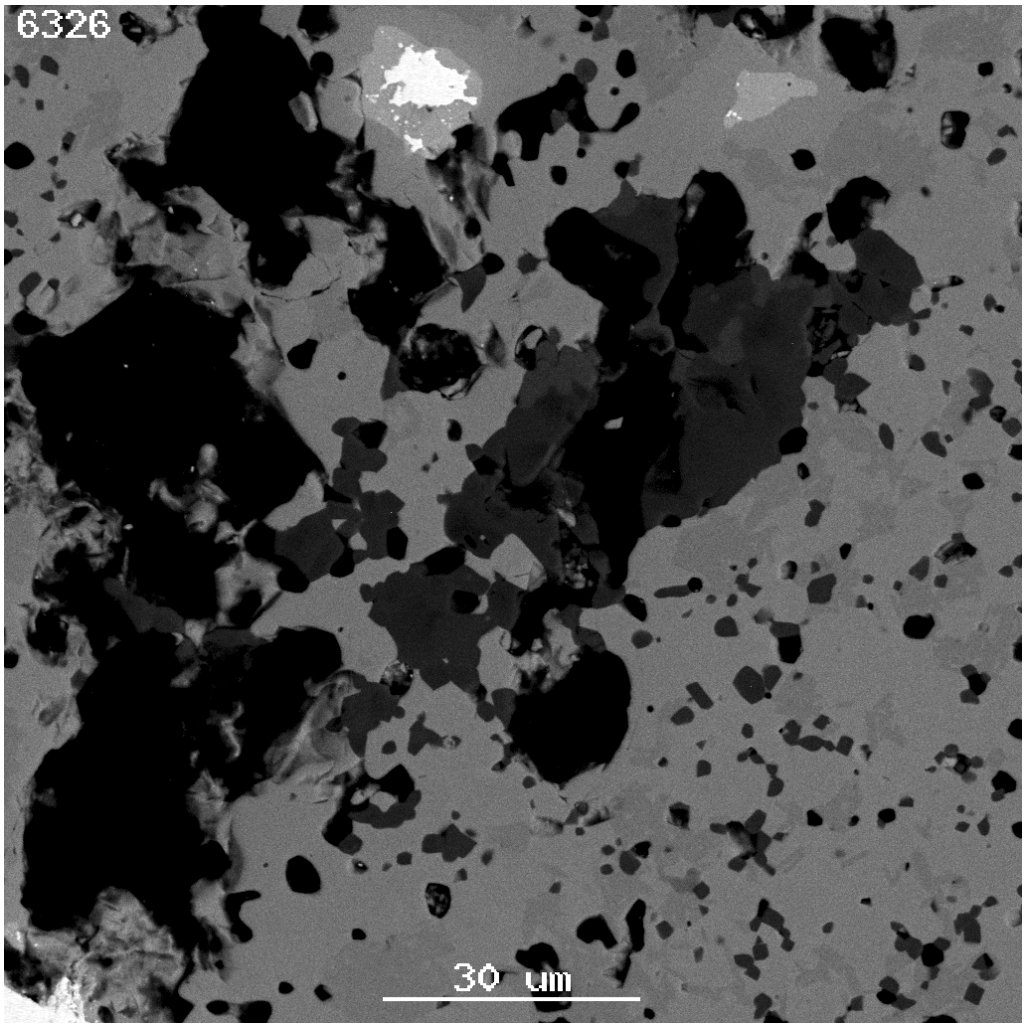
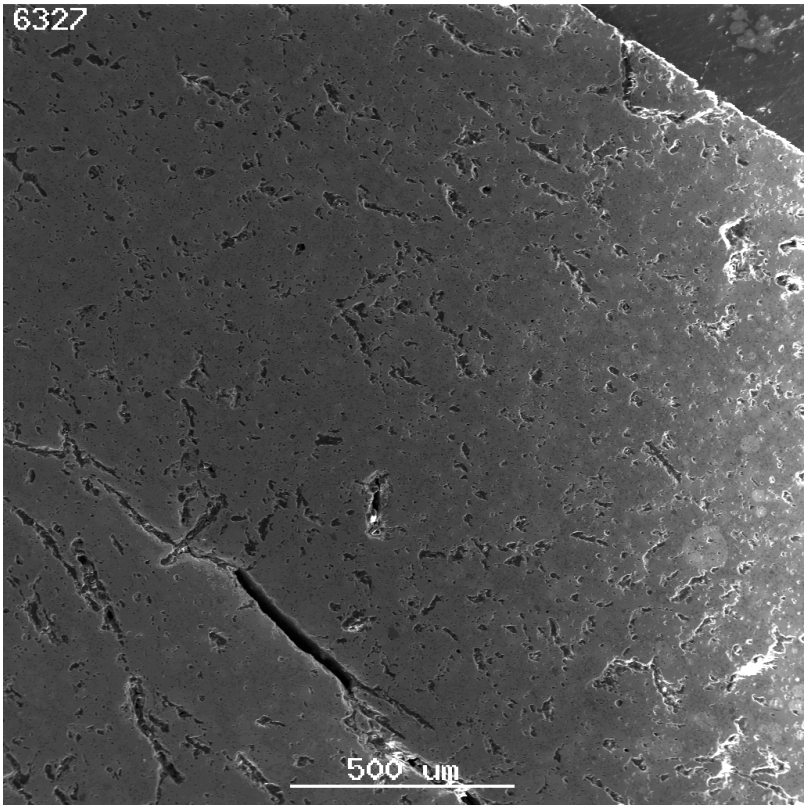


Figure B-9: (a) Secondary electron micrograph and, (b) and (c) backscattered electron micrographs of mws00-0609 (composition B1-14, oxide-route with hand ground, high-fired ThO_2 and UO_2, dry-attrition milled, sintered at 1350°C in air for 4 hours). The sample is heterogeneous, porous and highly agglomerated (see (a) and (b)). Phases detected include pyrochlore (grey matrix), which varies in composition across the sample (see (c)). The darker grey regions in the pyrochlore may be 4M zirconolite, Th/U-brannerite (lighter grey regions in matrix), and Hf-doped

(c)



(a)



(b)

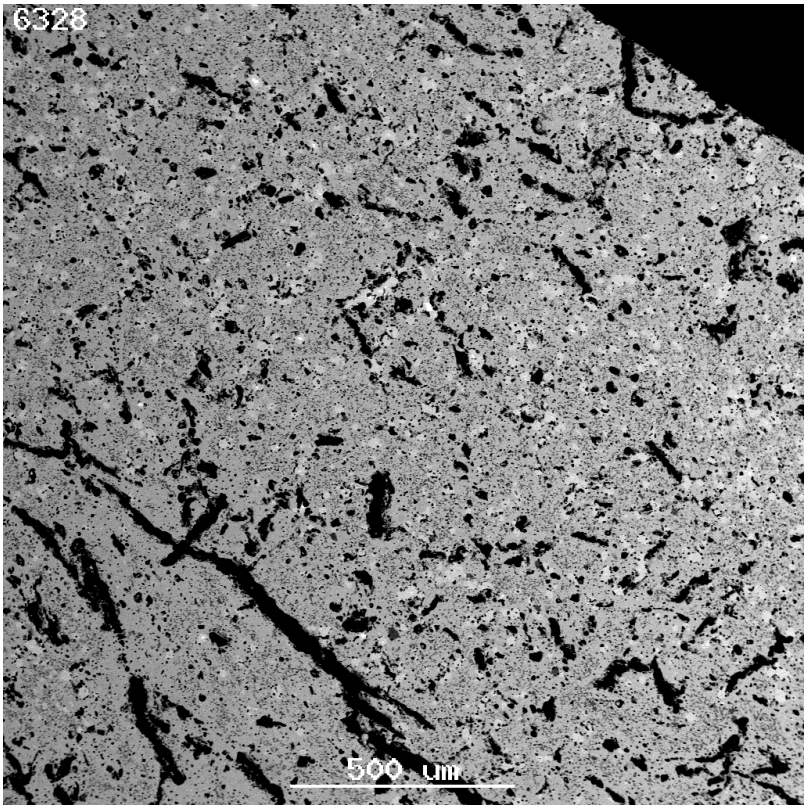
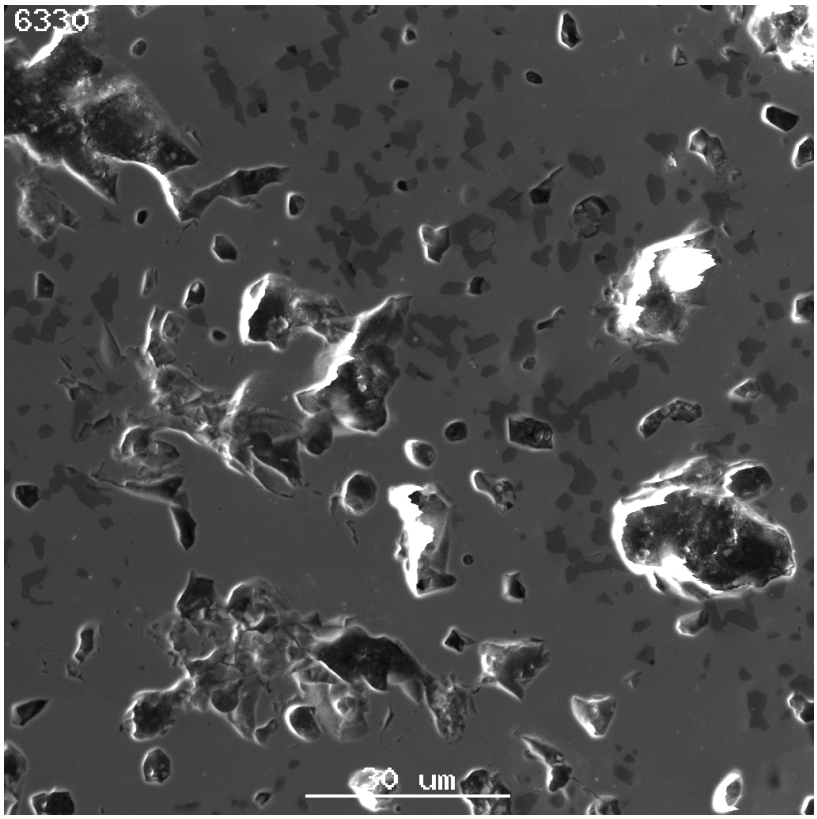
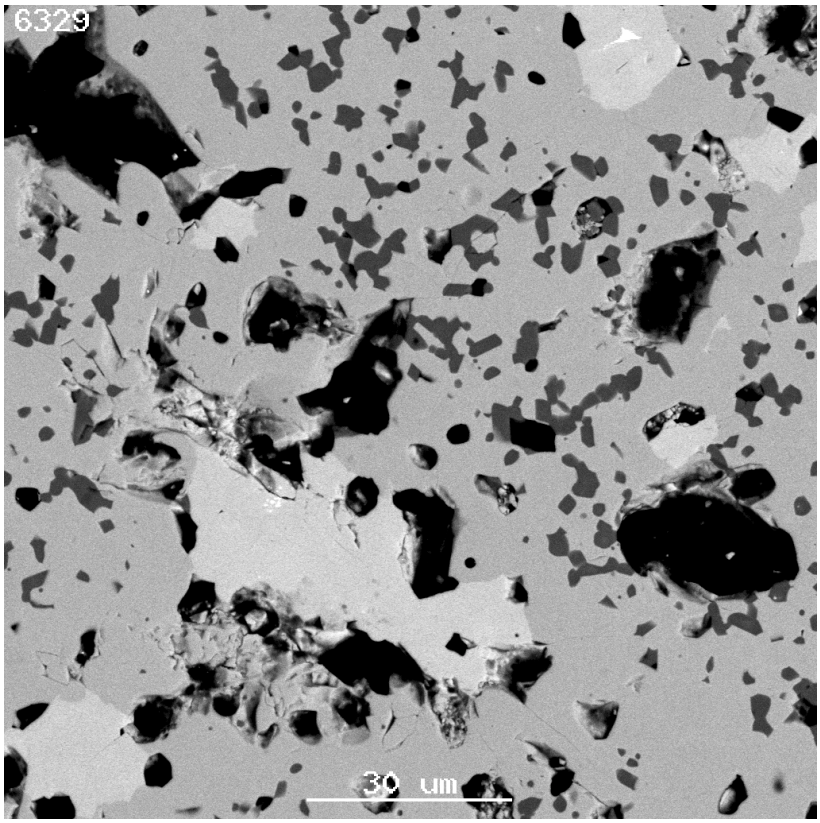


Figure B-10: (a) and (b) Secondary electron micrographs and, (c) and (d) backscattered electron micrographs of mws00-0610 (composition B1-14, oxide-route with hand ground, high-fired ThO_2 and UO_2, wet-attrition milled, sintered at 1350°C in air for 4 hours). The sample is more homogeneous than the dry milled sample. The matrix is pyrochlore, brannerite (light-grey) is also present as is Hf-doped rutile (dark-grey). There is less residual thoria (white regions inside brannerite grains) than in the dry milled sample. There is still some porosity and its arrangement

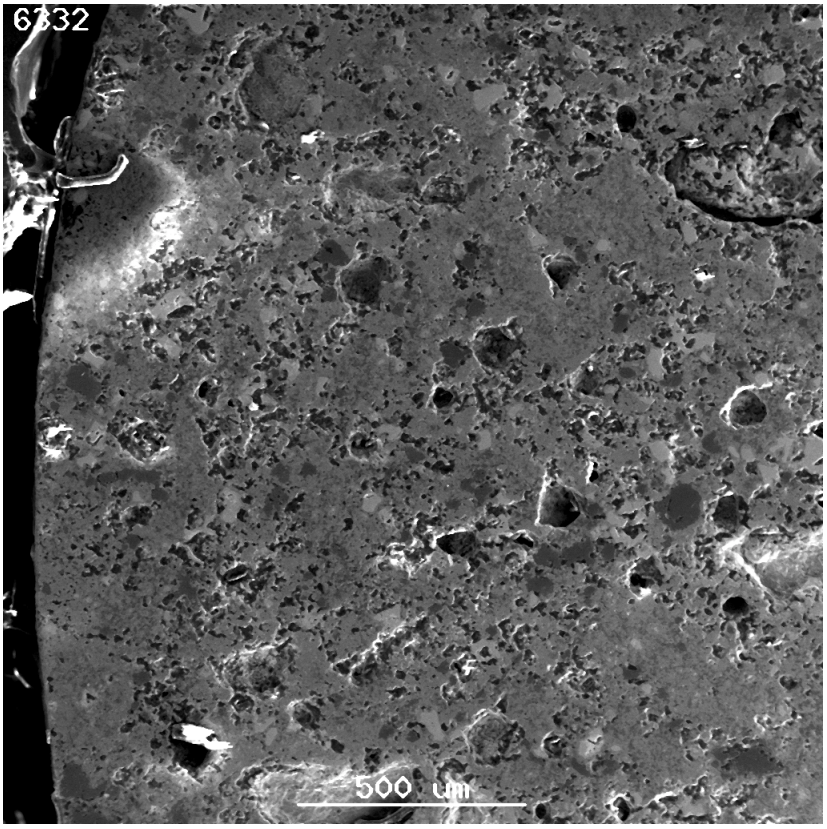
(c)



(d)



(a)



(b)

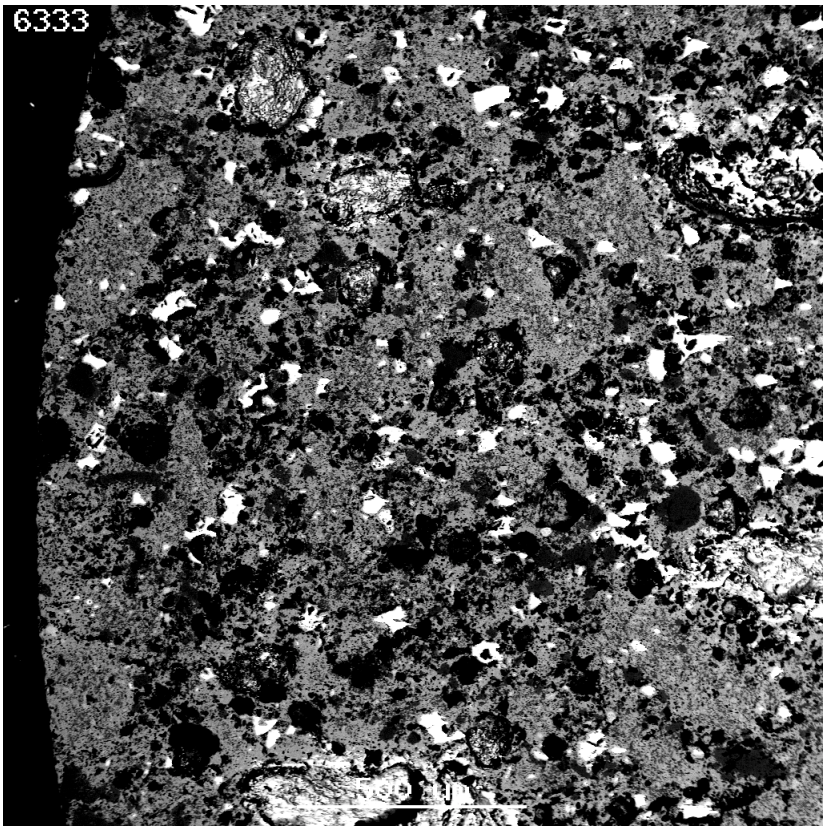
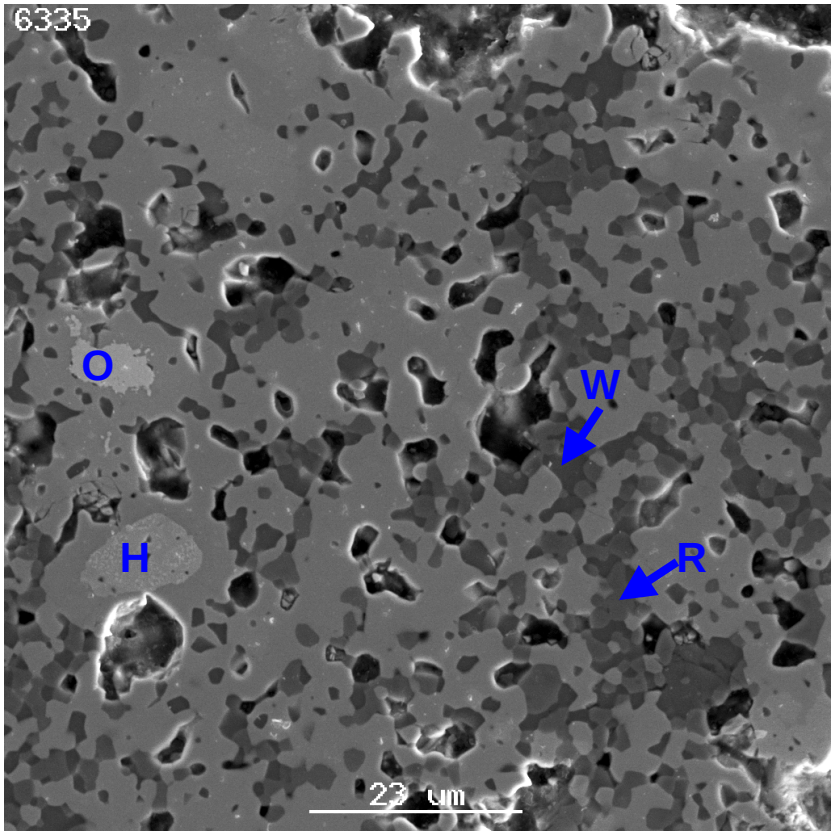
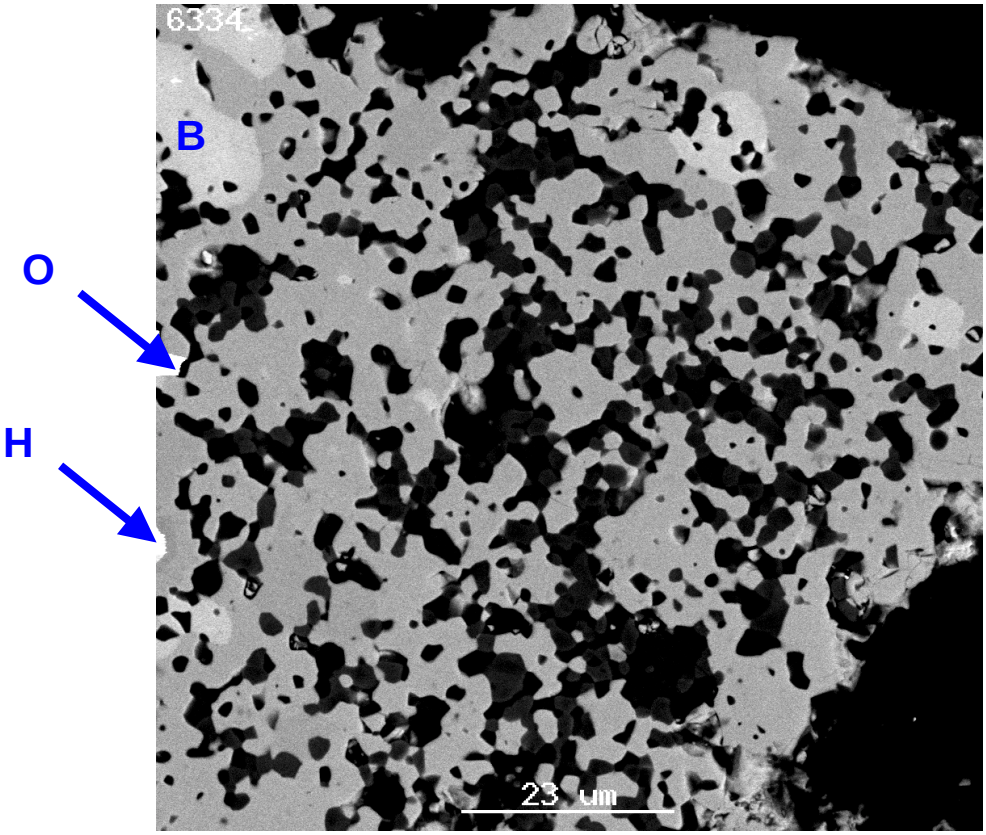


Figure B-11: (a) and (b) Secondary electron micrographs and, (c) and (d) backscattered electron micrographs of mws00-0611 (composition B1-16, oxide-route with hand ground, high-fired ThO_2 and UO_2, dry-attrition milled, sintered at 1350°C in air for 4 hours). The sample is inhomogeneous and contains regions of unreacted thoria (O, light-grey-white) and hafnia (H). The matrix is pyrochlore. Brannerite (B, light grey) is present as is whitlockite (W) and Hf-rutile (R). Both of the latter are dark-grey with whitlockite being darker than rutile (see (c)). The sample is porous

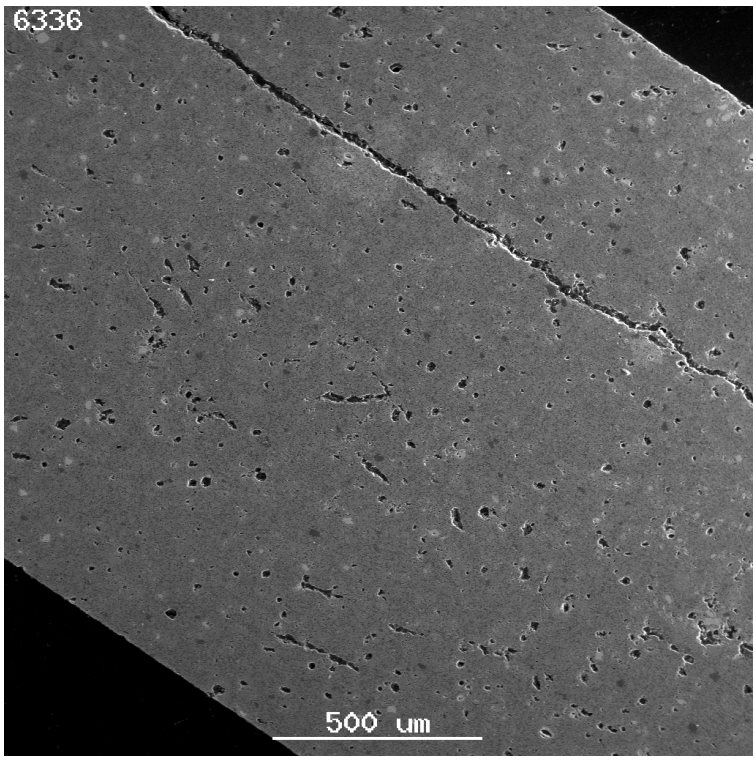
(c)



(d)



(a)



(b)

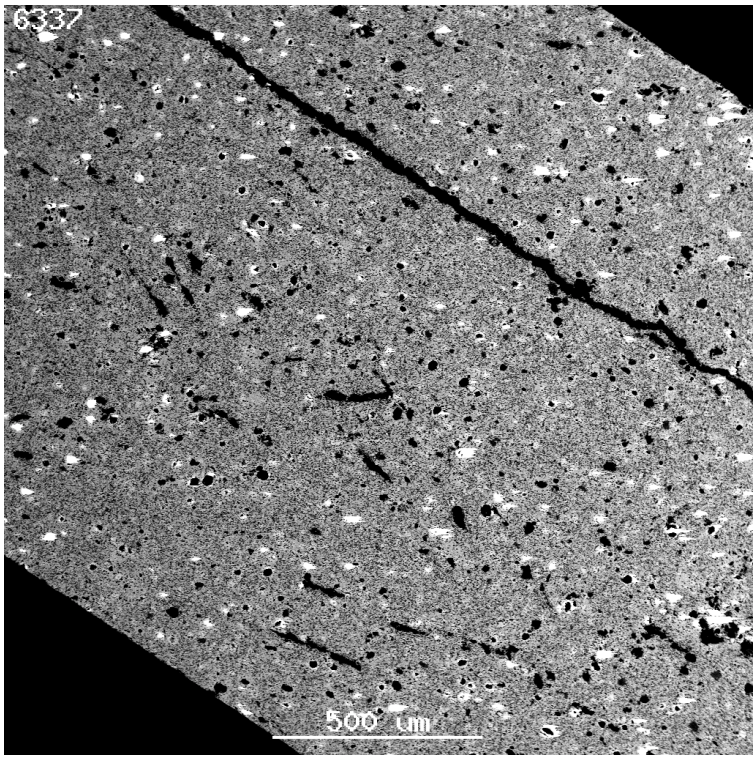
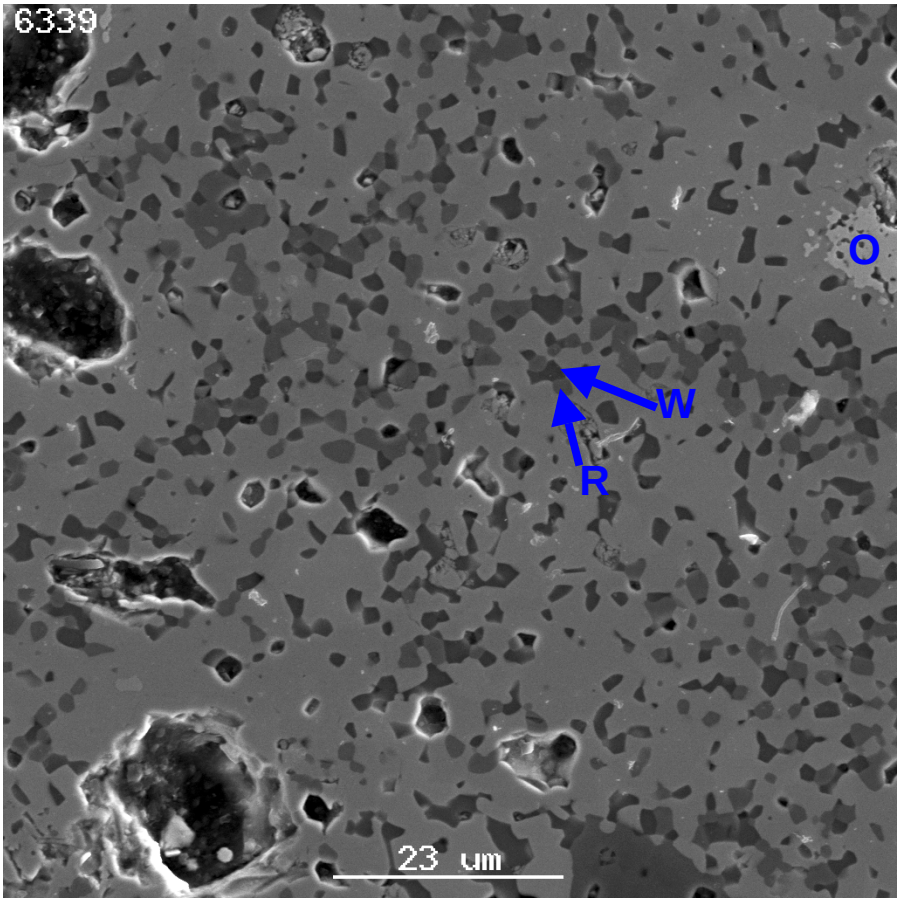
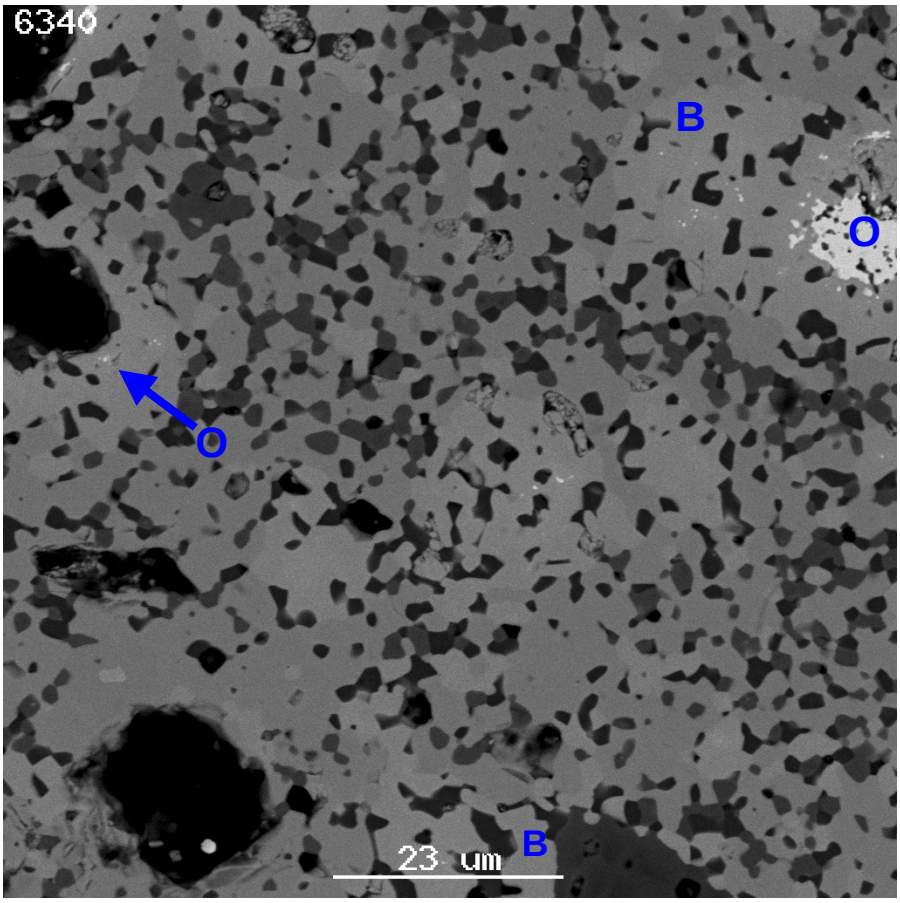


Figure B-12: (a) and (b) Secondary electron micrographs and, (c) and (d) backscattered electron micrographs of mws00-0612 (composition B1-16, oxide-route with hand ground, high-fired ThO_2 and UO_2, wet-attrition milled, sintered at 1350°C in air for 4 hours). The sample is more homogeneous than the dry attrition milled sample (Fig B1-11). Thoria (O, light-grey) was found inside brannerite grains. The matrix is pyrochlore. Brannerite (B, light grey) is present as is whitlockite (W) and Hf-rutile (R). Both of the latter are dark-grey with whitlockite being darker

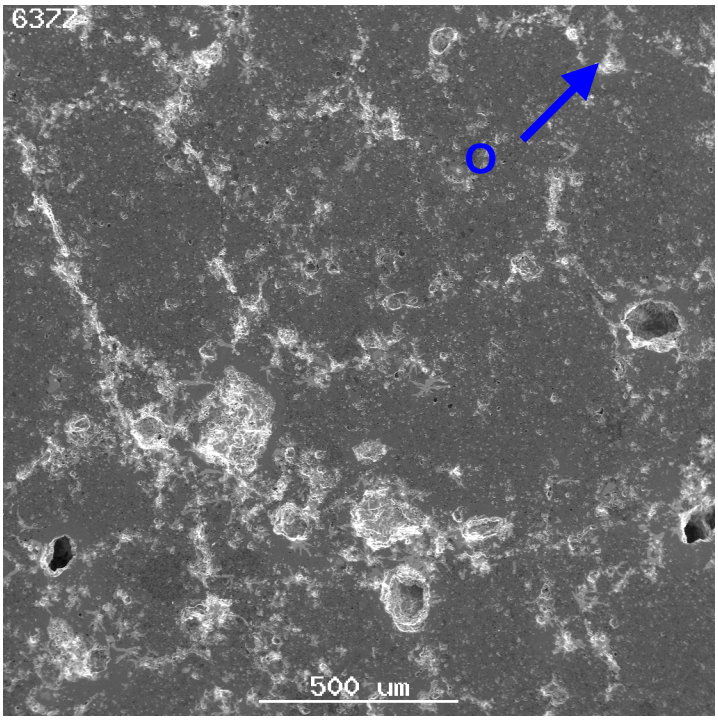
(c)



(d)



(a)



(b)

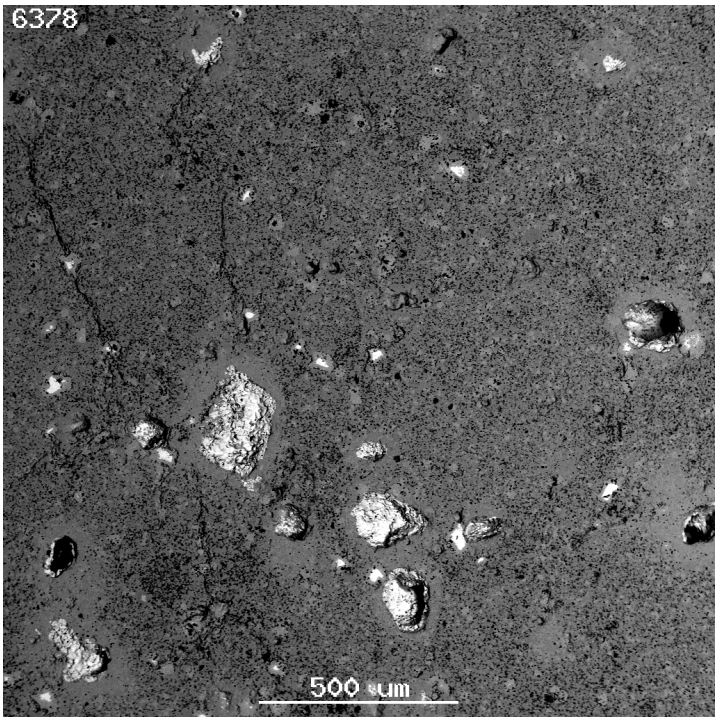
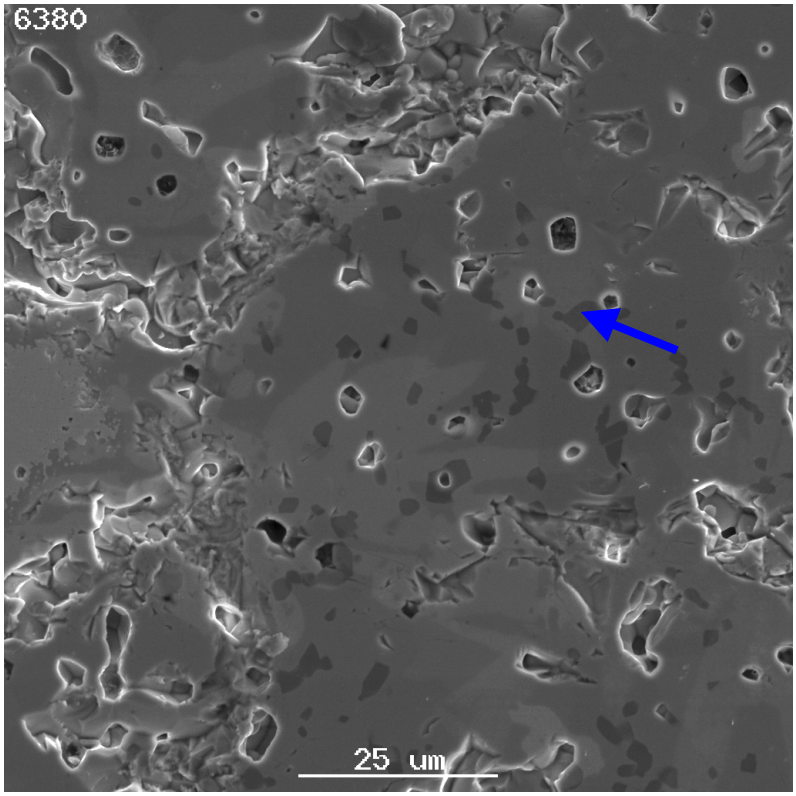
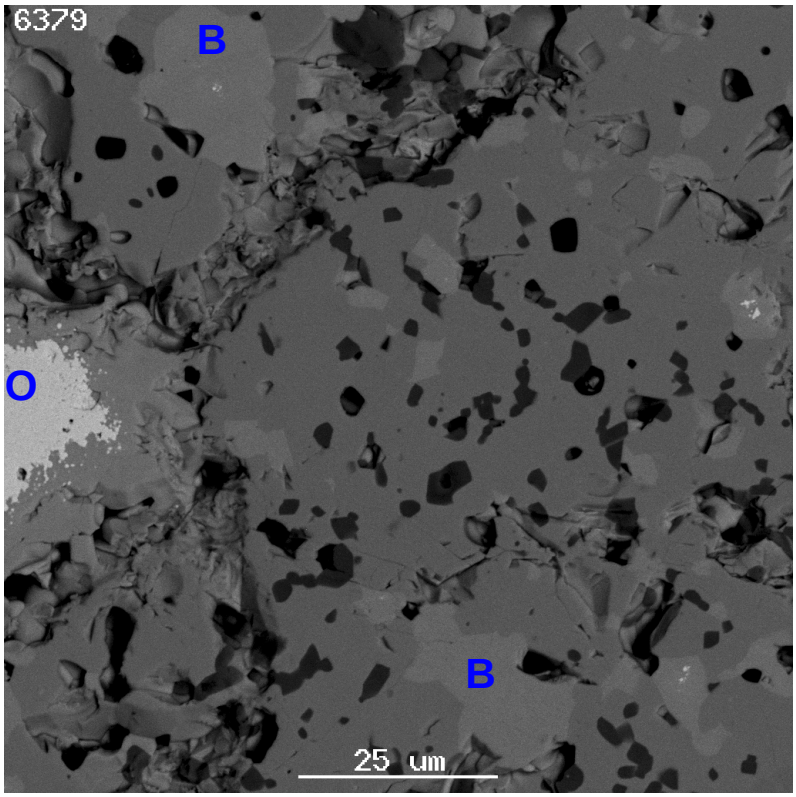


Figure B-13: (a) and (b) Secondary electron micrographs and, (c) and (d) backscattered electron micrographs of mws00-0652 (composition B1-2, oxide-route) that has been re-attrition milled, with stops every 10 mins to break up the cake. The sample was sintered at 1350°C in air for 4 hours. The sample is more homogeneous than the initial dry attrition milled sample (Fig B1-1). The matrix is pyrochlore. Thoria (O, light-grey) was found inside brannerite grains. Brannerite (B, light grey) is present as is Hf-rutile (R).

(c)



(d)



(a)

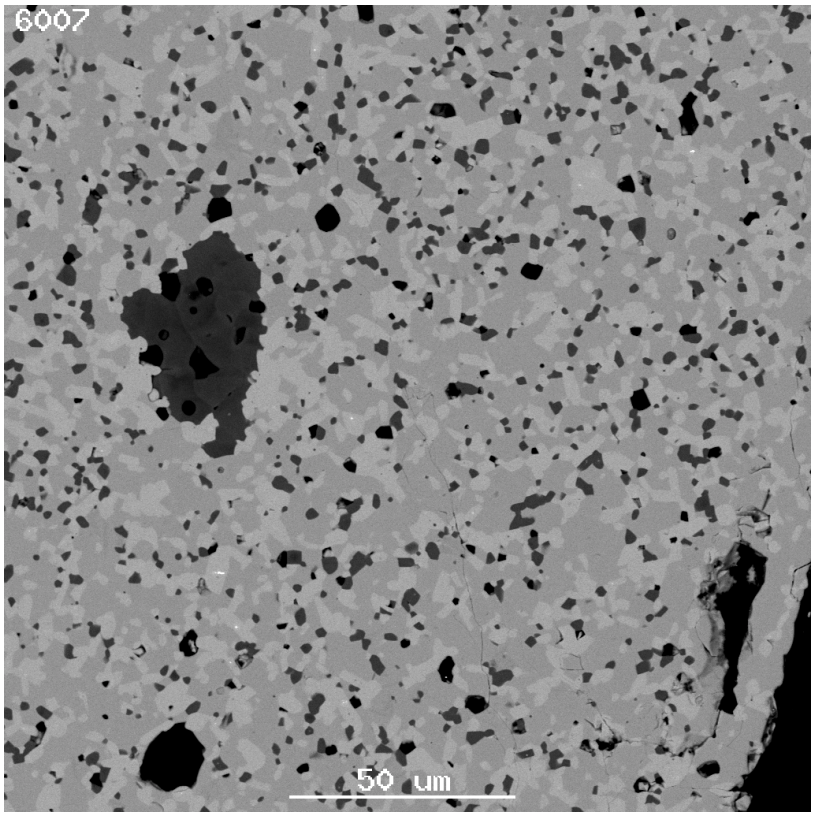
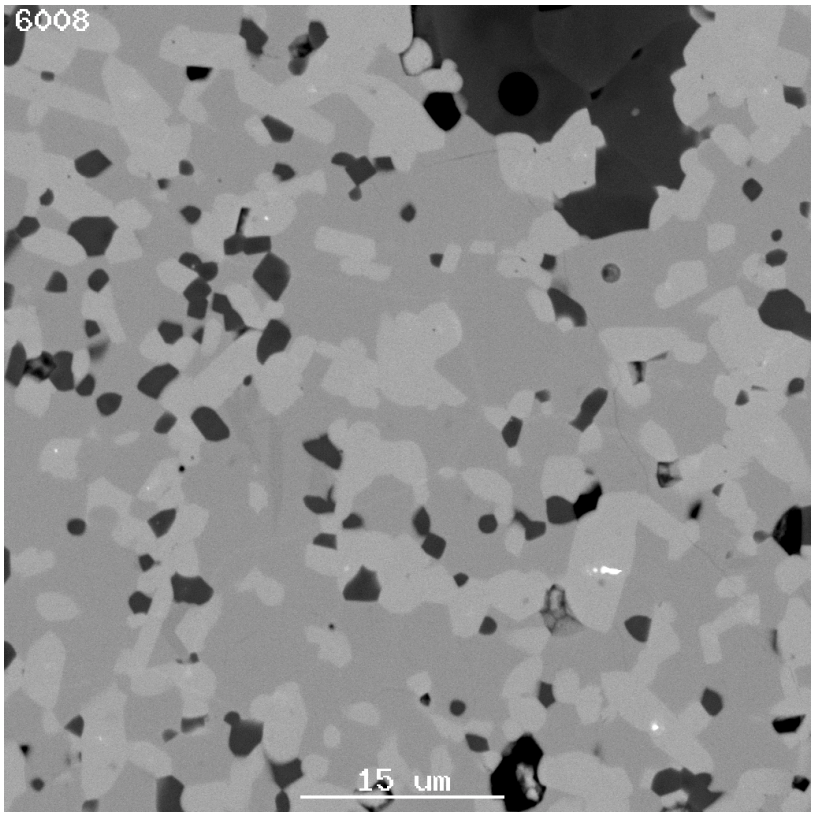
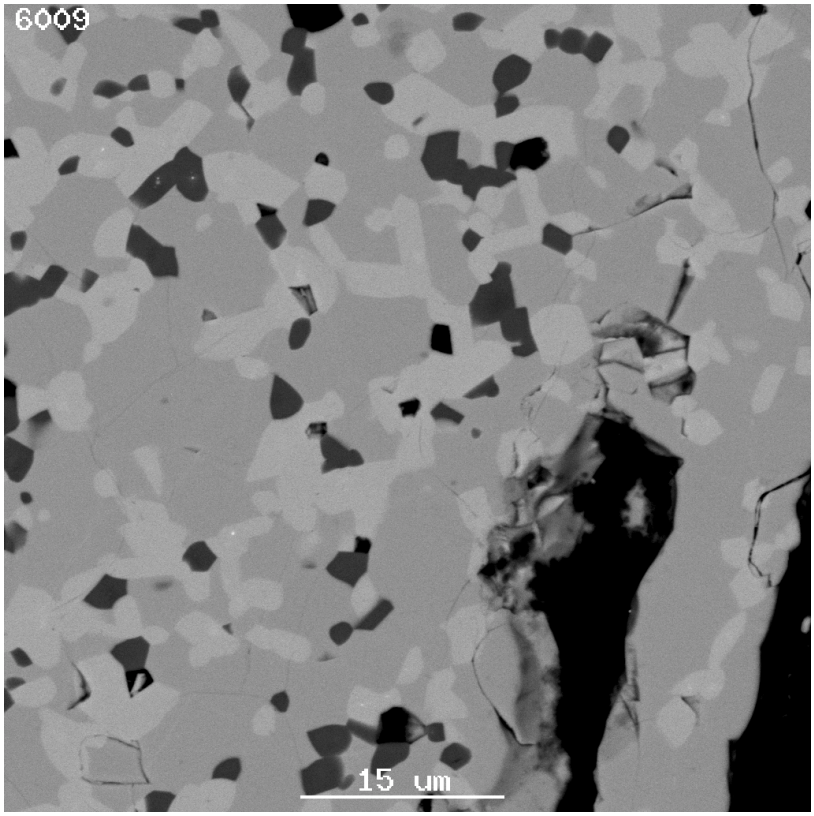


Figure C-1: (a), (b) and (c) backscattered electron micrographs of mws99-0606 (composition B1-2, oxide-route, wet-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is pyrochlore. Th/U-brannerite (light grey grains), Hf-doped rutile (dark-grey) grains, some $(Th,U)O_2$ (white spots inside some brannerite grains) and porosity (black in (b) and (c)) are present. It can be seen that the exterior (c) and interior (d) of the pellets are similar, except for a deficiency in rutile in the outer 15 – 20 μm of the pellet.

(b)



(c)



(a)

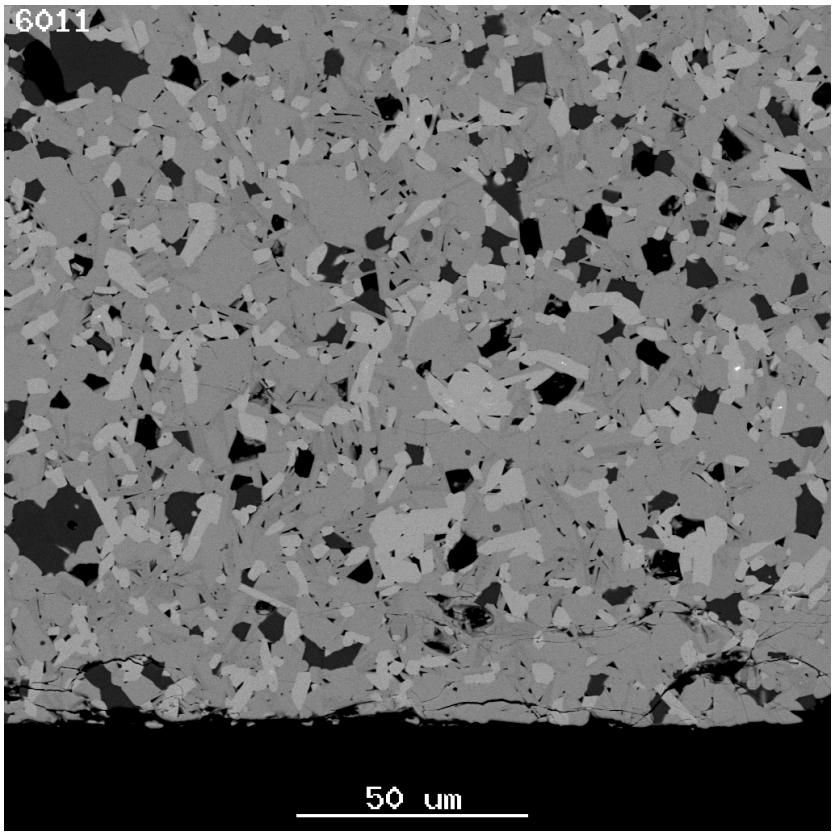
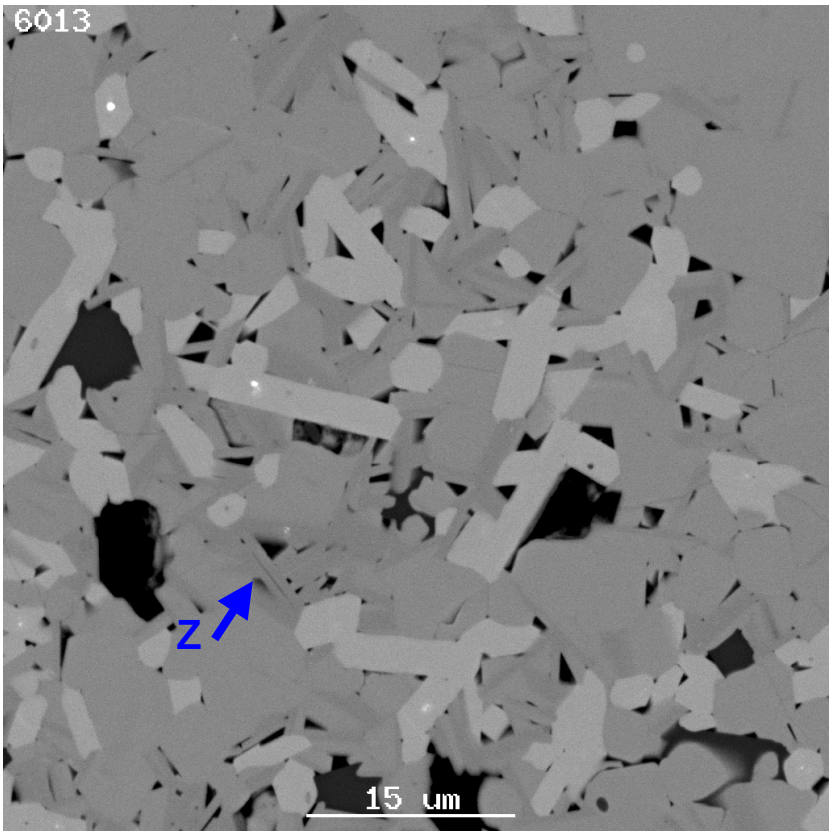
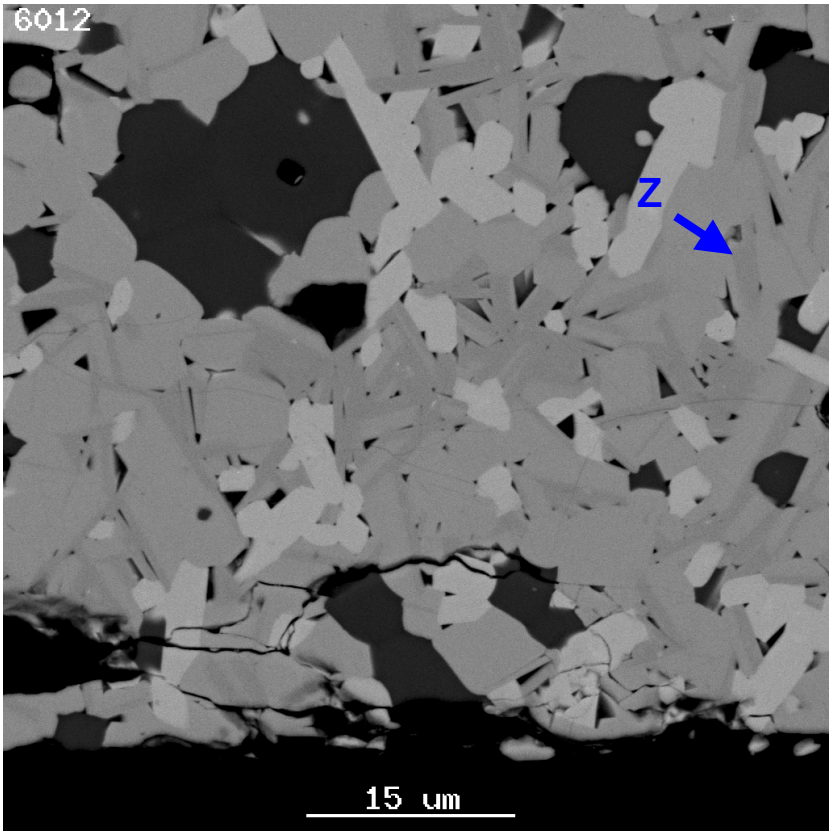


Figure C-2: (a), (b) and (c) backscattered electron micrographs of mws99-0608 (composition B1-4, oxide-route, wet-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is mainly pyrochlore. Th/U-brannerite (light grey grains), zirconolite, (Z, slightly darker more elongated grains than pyrochlore), Hf-doped rutile (dark-grey), $(Th,U)O_2$ (white spots inside some brannerite grains) and porosity (black) are present. It can be seen (see (a)) that the exterior and interior of the pellets are similar.

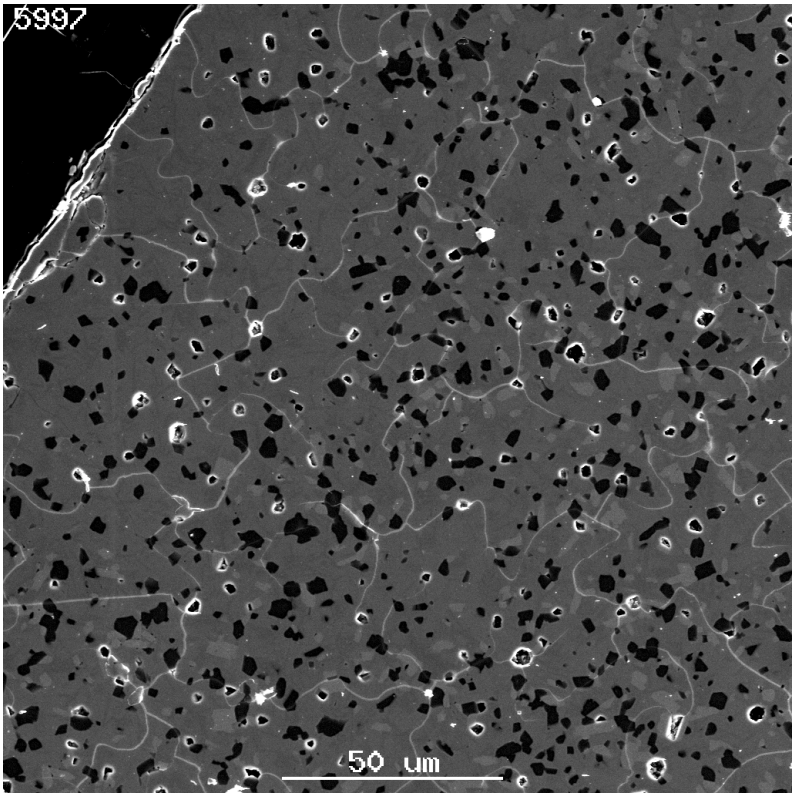
(b)



(c)



(a)



(b)

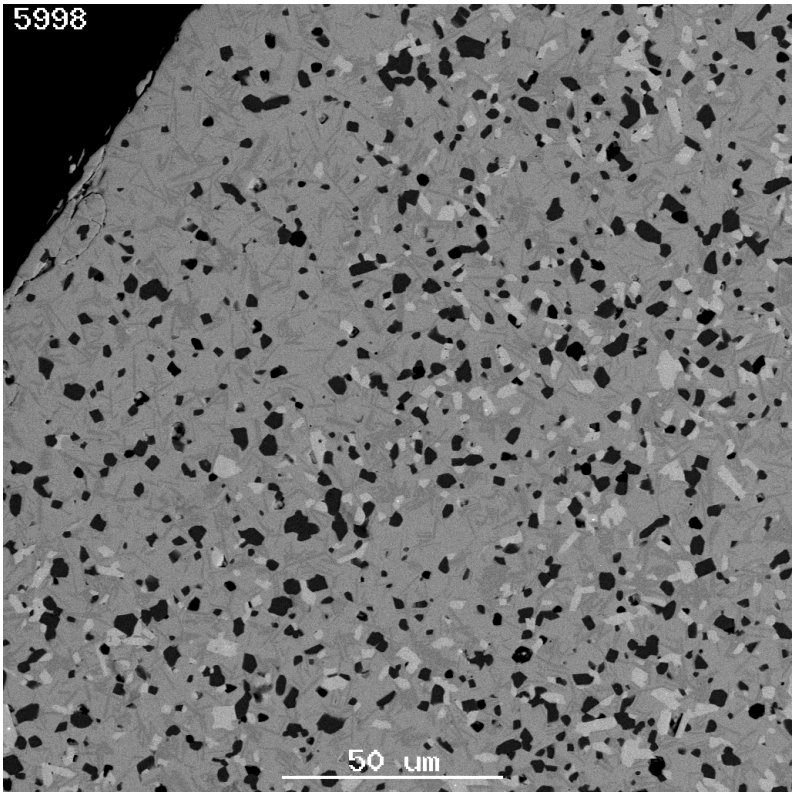
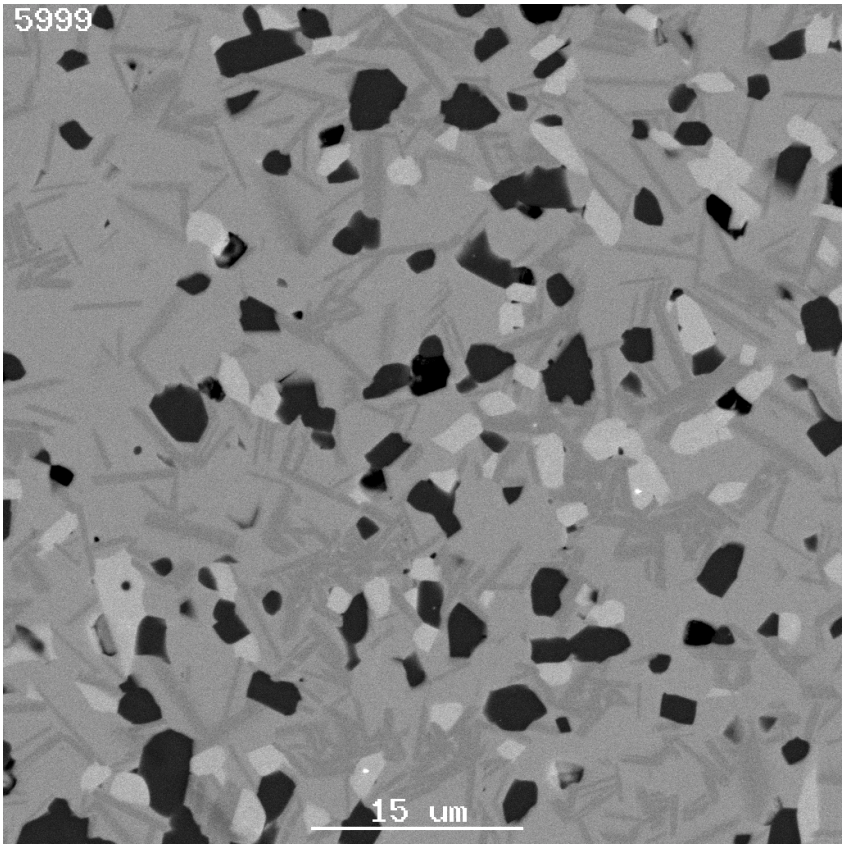
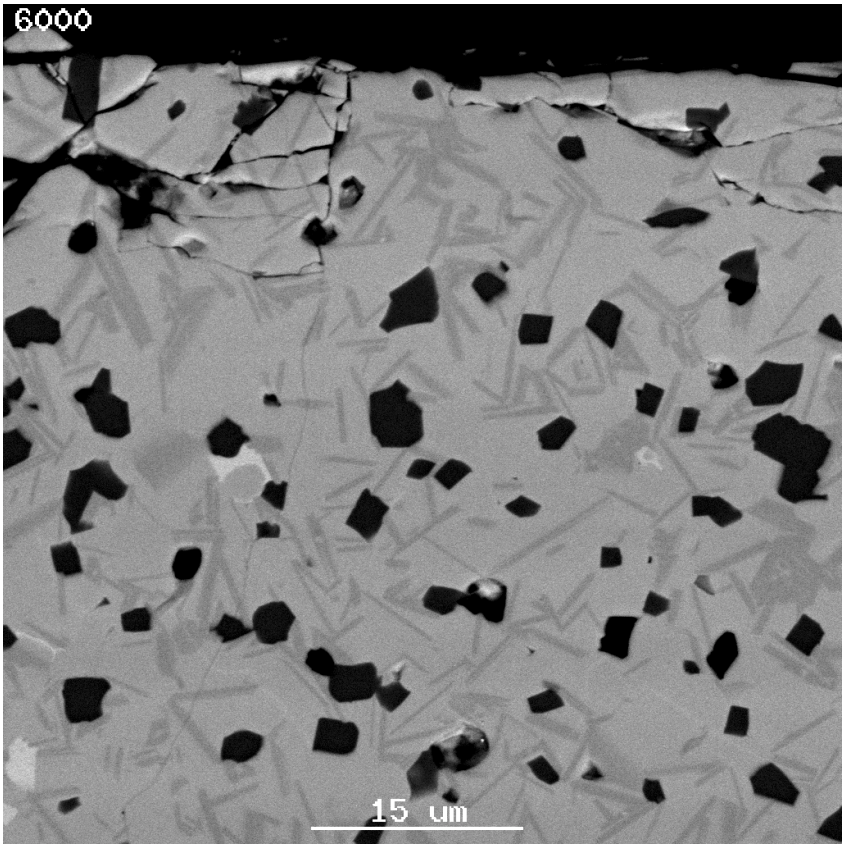


Figure C-3: (a) Secondary electron micrograph and, (b), (c) and (d) backscattered electron micrographs of mws99-0602 (composition B1-10, oxide-route, wet-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is a mixture of pyrochlore and 2M zirconolite – the zirconolite is the darker grey of the two. Th/U-brannerite (light grey grains), Hf-doped rutile (dark-grey), a trace of $(Th,U)O_2$ (white spots inside some brannerite grains) and porosity (black in (b), (c) and (d)) are also present. It can be seen that the exterior (d) and interior (c) of the pellets are similar, except that the

(c)



(d)



(a)

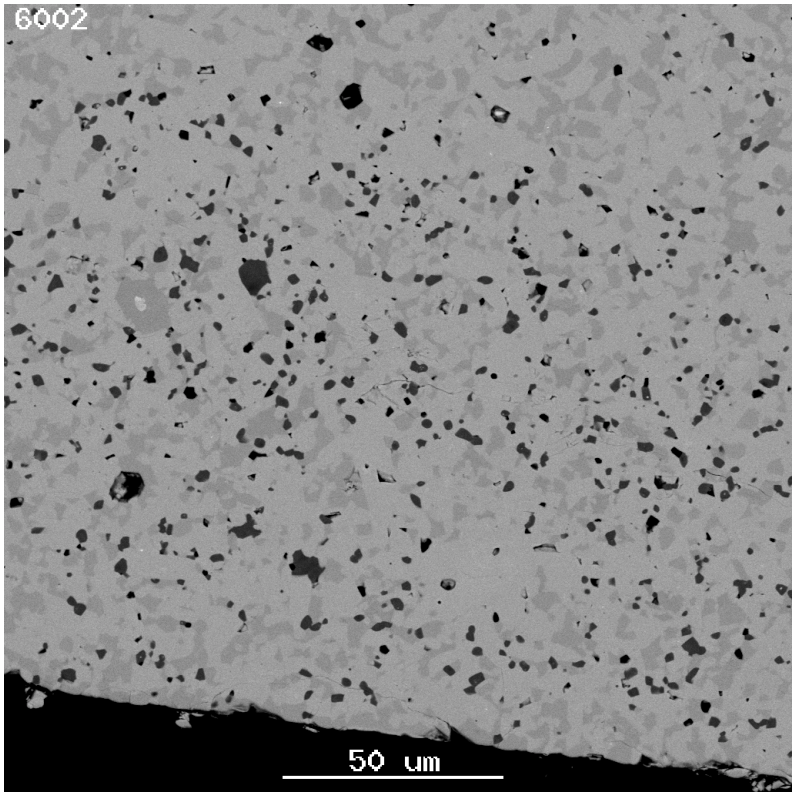
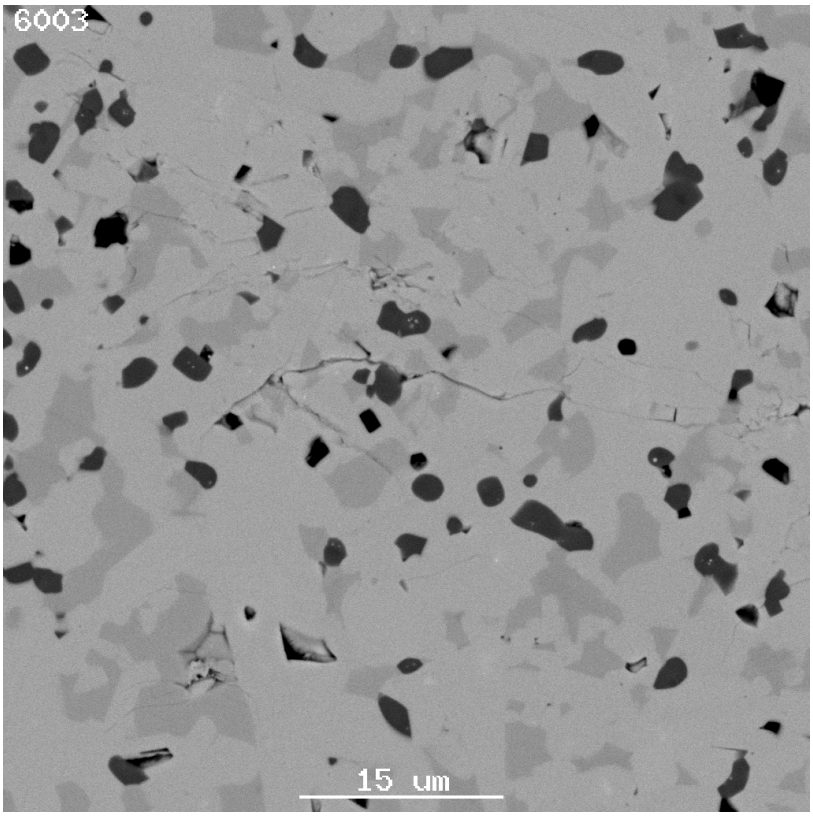
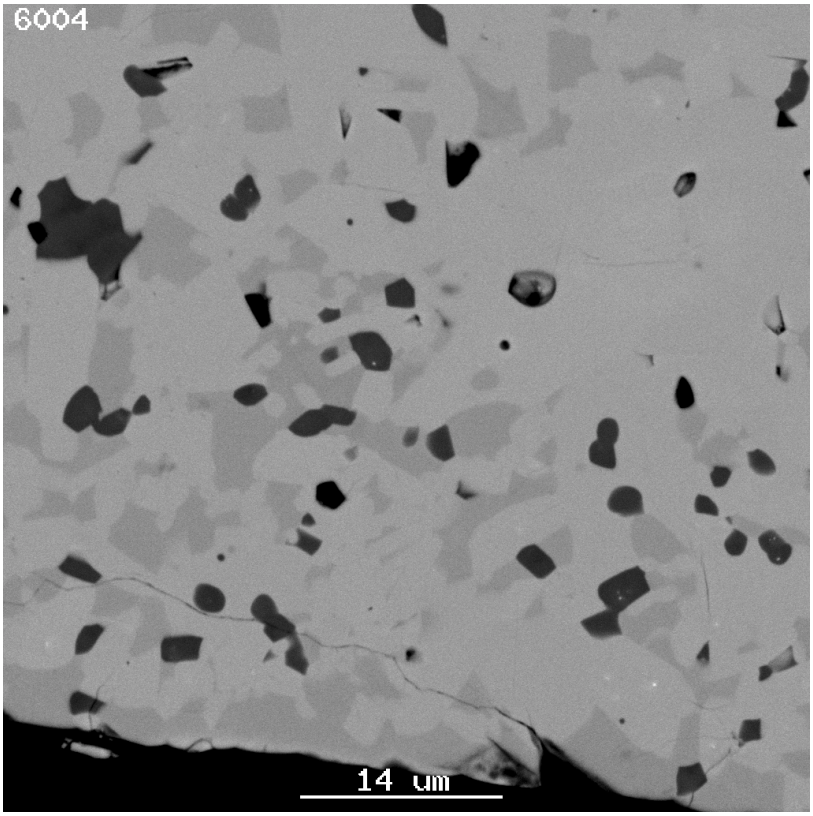


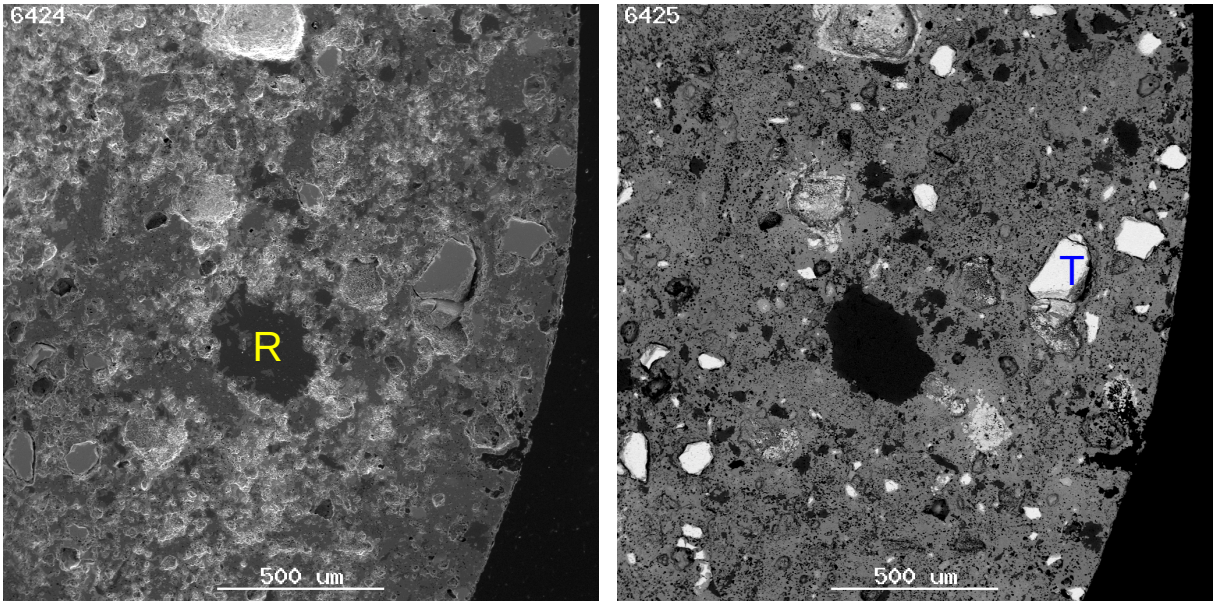
Figure C-4: (a), (b) and (c) backscattered electron micrographs of mws99-0604 (composition B1-12, oxide-route, wet-attrition milled, sintered at 1350°C in air for 4 hours). The matrix is a mixture of pyrochlore and Th/U-brannerite (light grey grains). Hf-doped rutile (dark-grey), the occasional spot of $(Th,U)O_2$, which can be found inside some brannerite grains (white spots), and porosity (black) are also present. It can be seen that the exterior (d) and interior (c) of the pellets are similar.

(b)



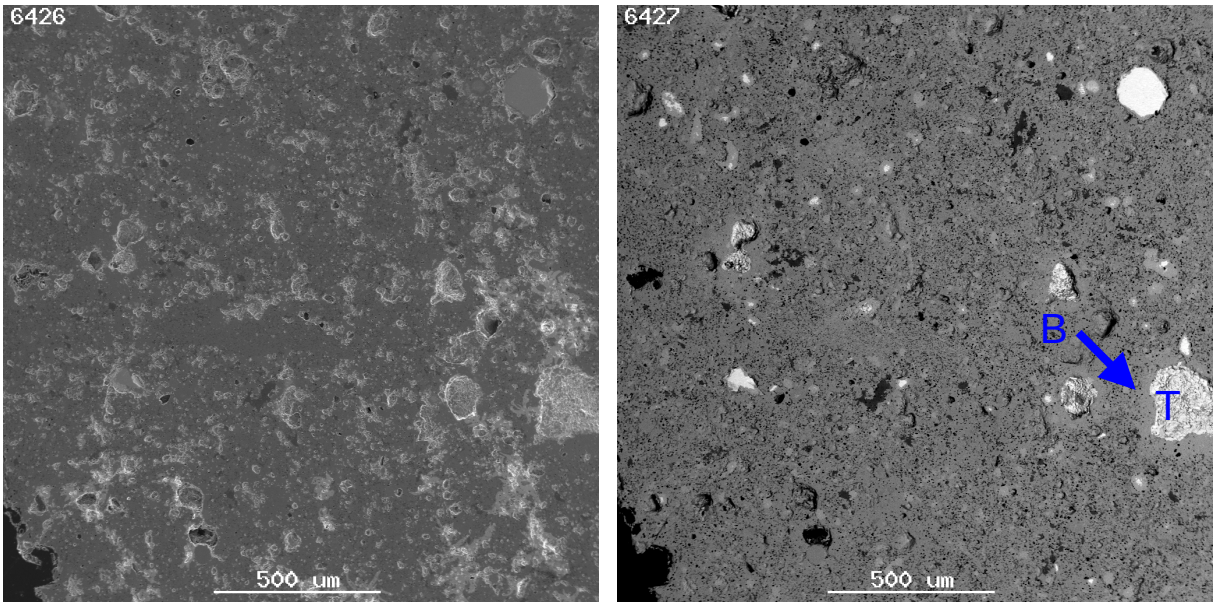
(c)





(a) (b)

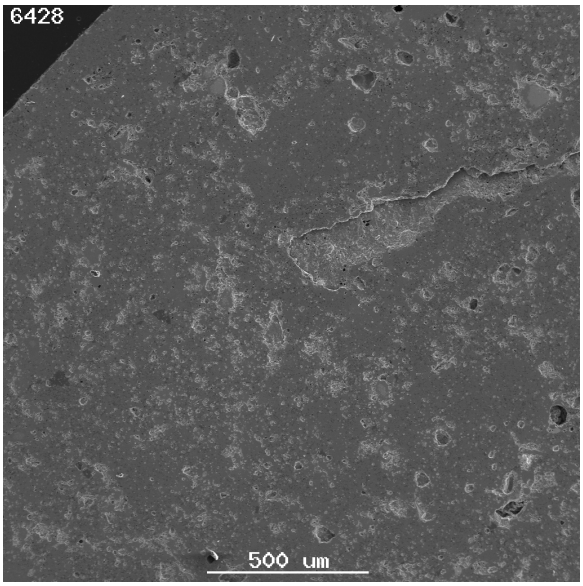
mws00-0666 dry attrition milled 10 min./1 pass

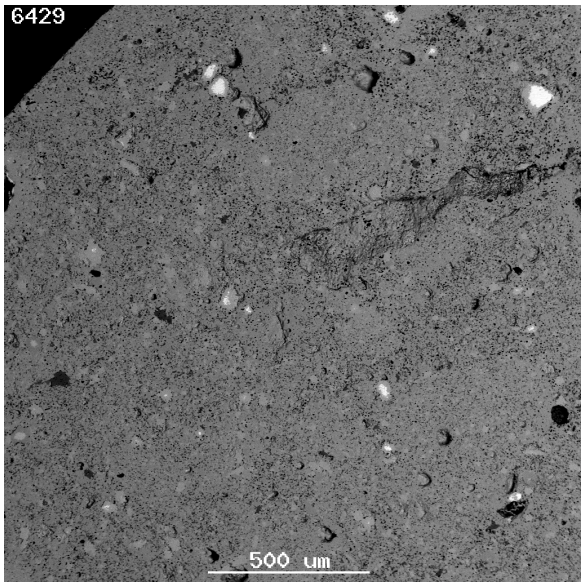


(c) (d)

mws00-0667 dry attrition milled 20 min./2 passes

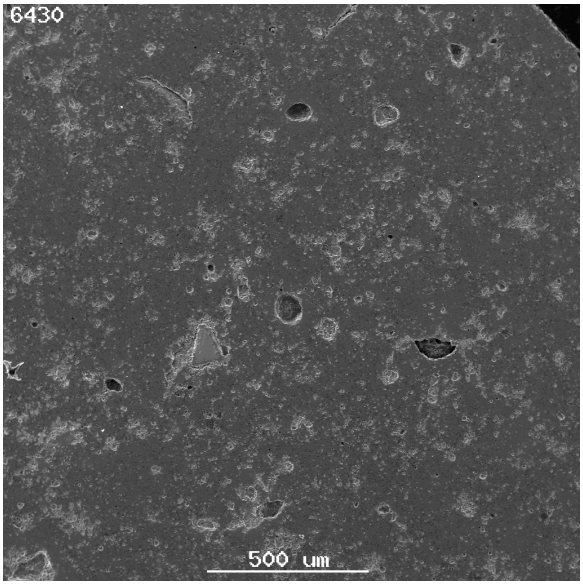
Figure D-1: (a), (c) (e) and (g) Secondary electron micrographs and, (b), (d), (f) and (h) backscattered electron micrographs. These show the effect of attrition milling time on the microstructure of the oxide-route Th/U/Hf-baseline composition. The samples were made by cold pressing a pellet from the milled powders and sintering the pellet at 1350°C in air for 4 hours. The samples are composed of a matrix of pyrochlore with rutile (dark-grey, R), brannerite (light-grey, B) and thoria (white to light-grey, T). Traces of hafnium oxide were also detected in the samples. The amount of porosity decreases with milling time.

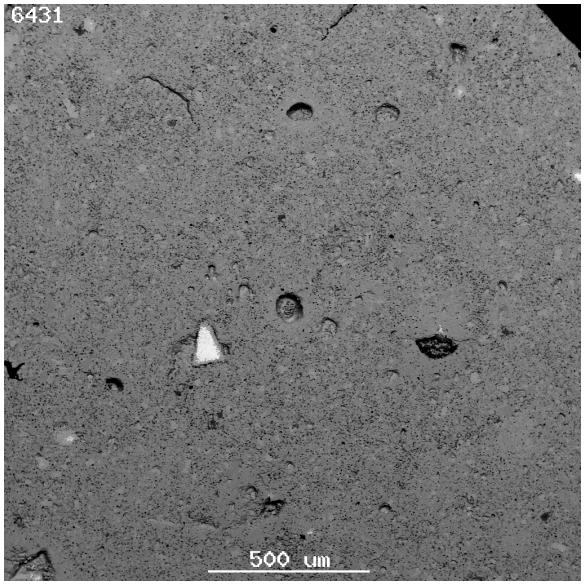




(e) (f)

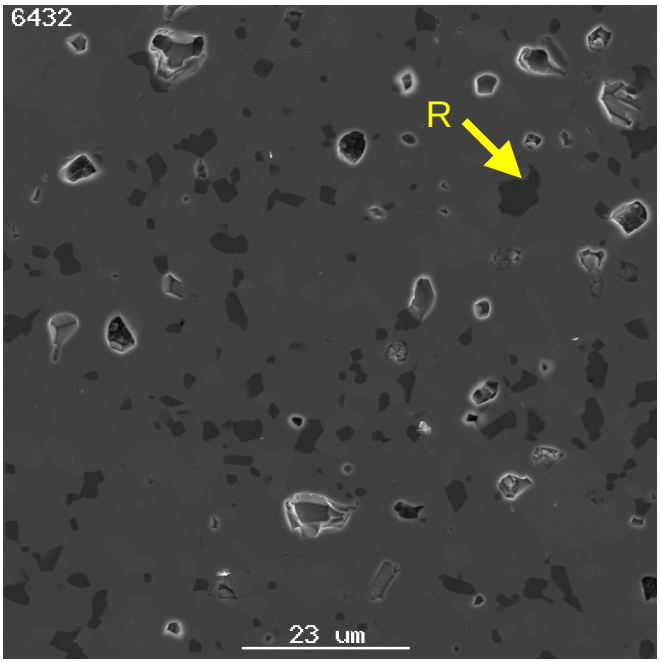
mws00-0668 dry attrition milled 30 min./3 passes



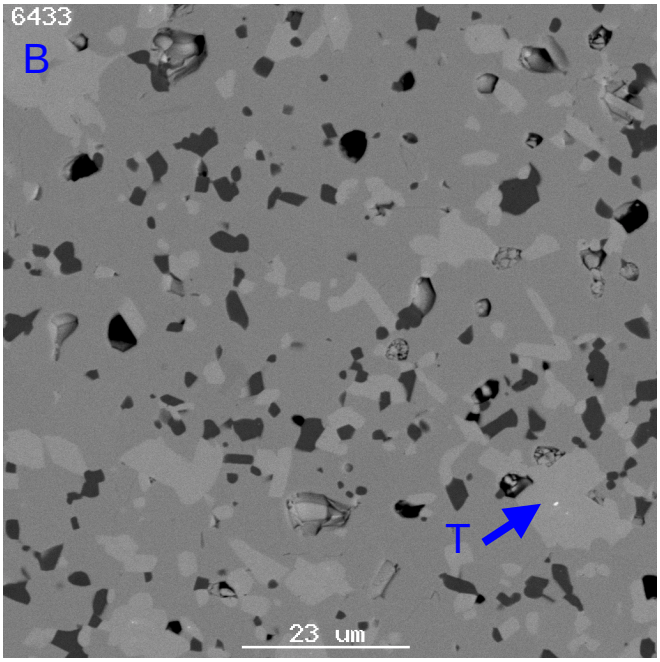


(g) (a)

mws00-0670 dry attrition milled 45 min./4 passes



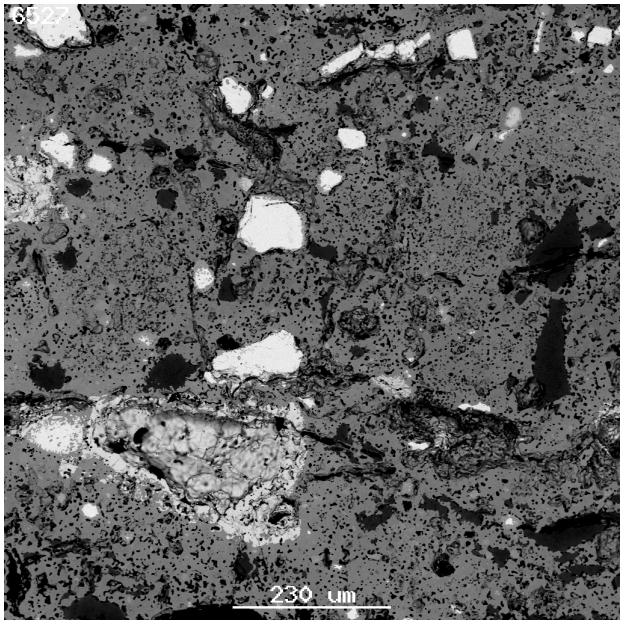
(a)



(b)

Figure D-2: (a) Secondary electron micrograph and (b) backscattered electron micrograph of mws00-0670, a sample made by cold pressing and sintering a pellet at 1350°C in air for 4 hours. The starting powder was a Th/U/Hf-baseline composition that had been attrition milled for 45 minutes. A higher magnification of the microstructure of this sample is given in fig. D-1 (g) and (h). The micrographs in this picture show a typical region of the sample away from the thoria aggregates. The sample is composed of a matrix of pyrochlore with rutile (dark-grey, R), brannerite (light-grey, B) and thoria (white to light-grey, T). Some porosity (see (a)) is also

(a) 10 min./1 pass
mws00-0671



(b) 20 min./2 passes
mws00-0672

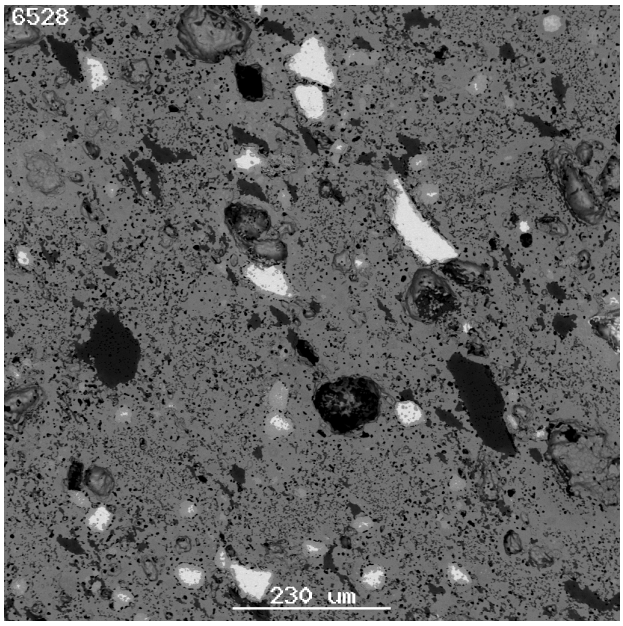
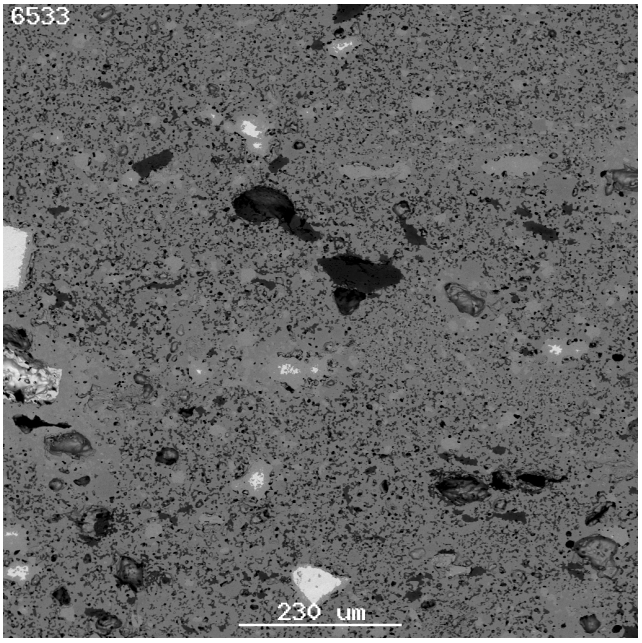
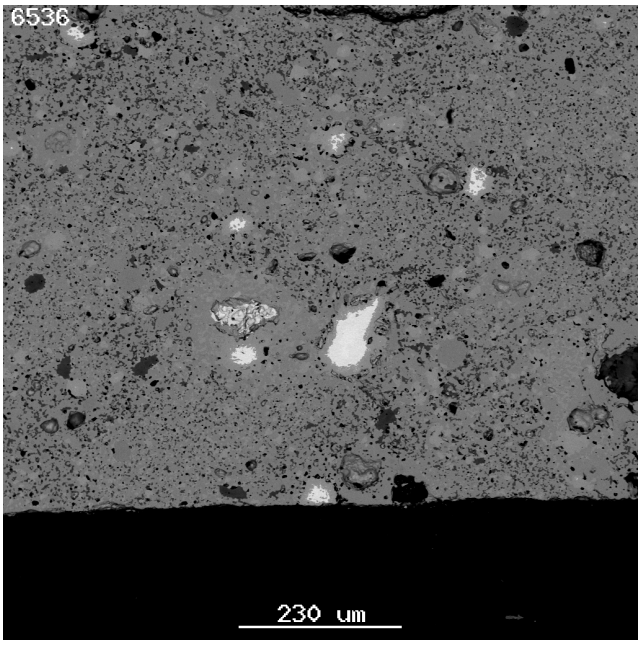


Figure D-3: (a)-(e) backscattered electron micrographs. These show the effect of attrition milling time on the microstructure of the oxide-route Th/U/Hf-baseline composition. The samples were attrition milled using the modified 110 cc quick-change pot. The samples were made by cold pressing a pellet from the milled powders and sintering the pellet at 1350°C in air for 4 hours. The samples are composed of a matrix of pyrochlore with rutile (dark-grey, R), brannerite (light-grey, B) and thoria (white to light-grey, T). The amount of porosity and thoria can be seen to decrease with milling time.

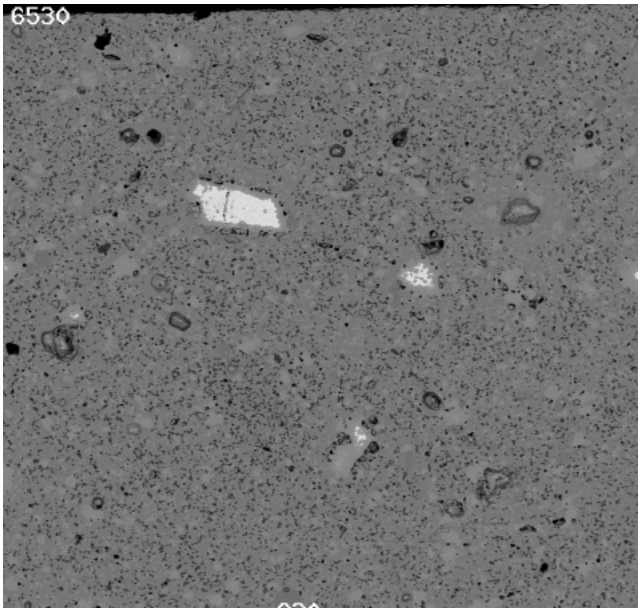
(c) 30- min./3 passes
mws00-0673

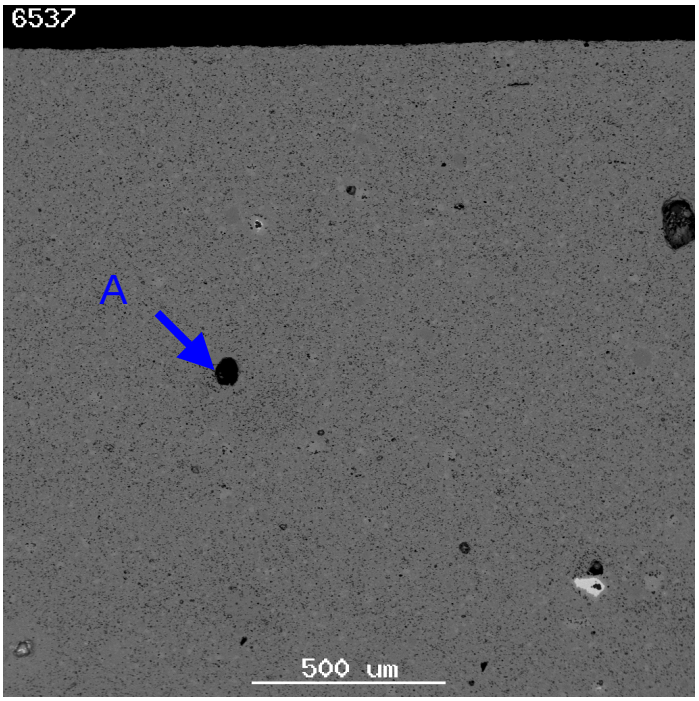


(d) 45 min./4 passes
mws00-0680



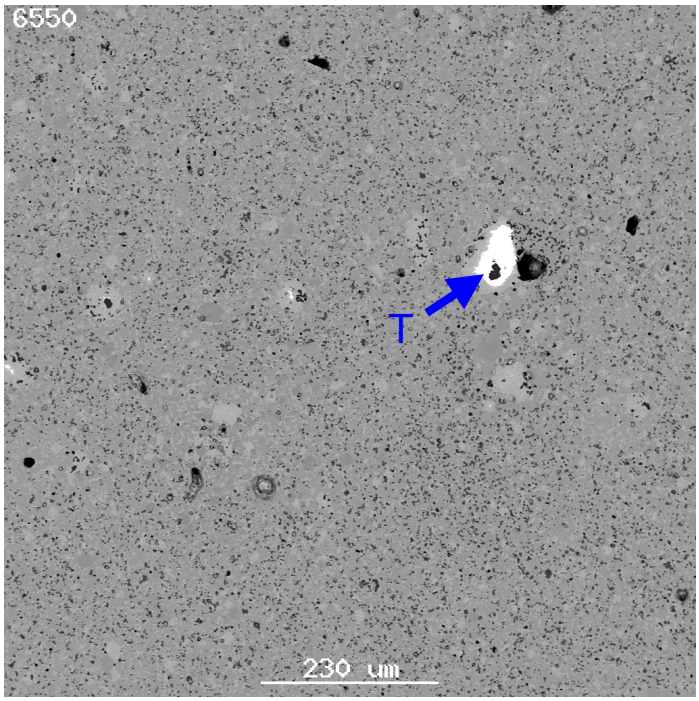
(e) 65 min./6 passes
mws00-0674



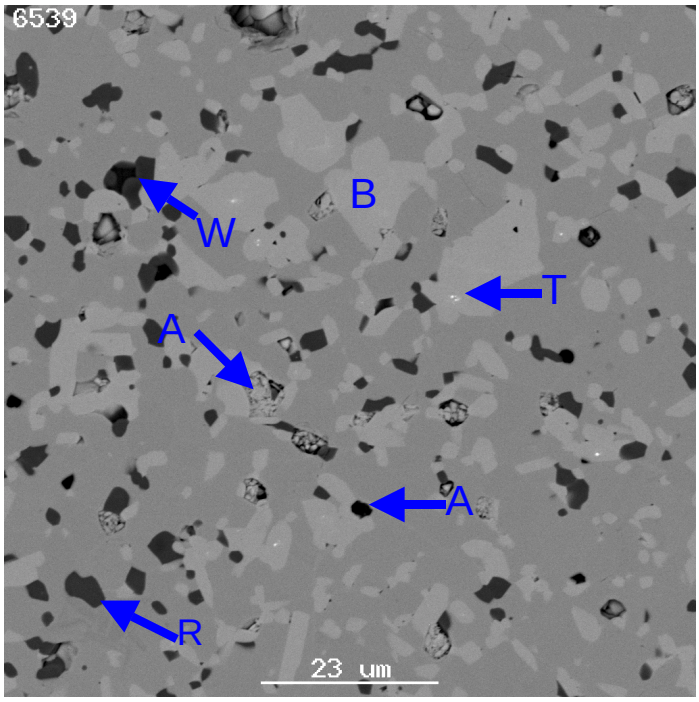


(a)

Figure D-4: (a) – (c) backscattered electron micrographs of mws00-0683, a sample made by cold pressing and sintering a pellet at 1350°C in air for 4 hours. The starting powder was a Th/U/Hf-baseline composition that had been attrition milled under near optimal conditions for 65 minutes/6 passes with breakup of the powder cake every 10 minutes. The sample is relatively homogeneous and is composed of a matrix of pyrochlore with rutile (dark-grey, R) and brannerite (light-grey, B). A few grains of whitlockite associated with rutile grains (W, black in (c)) were detected, but these are rare. The thoria (white to light-grey, T) is present as a large lump and as fine areas inside brannerite grains. Porosity (A, black) is also present.

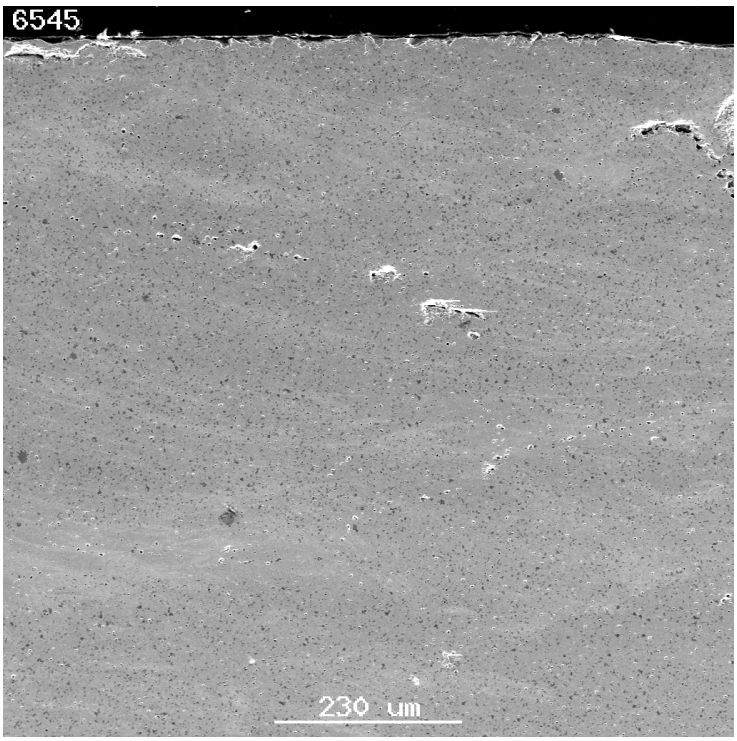


(b)



(c)

(a)



(b)

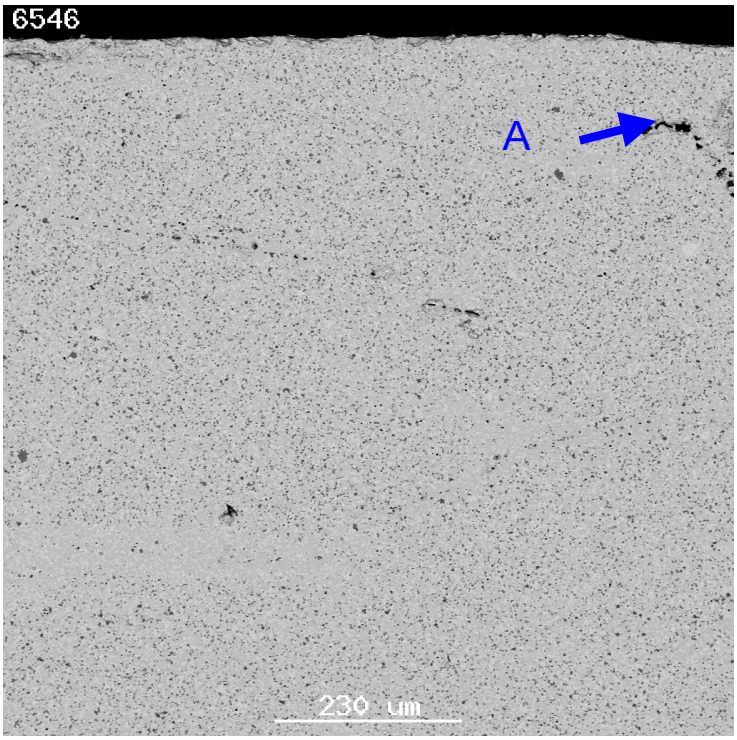
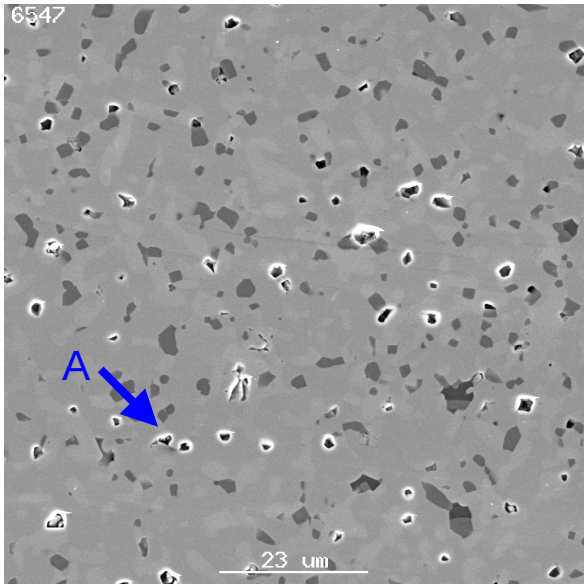
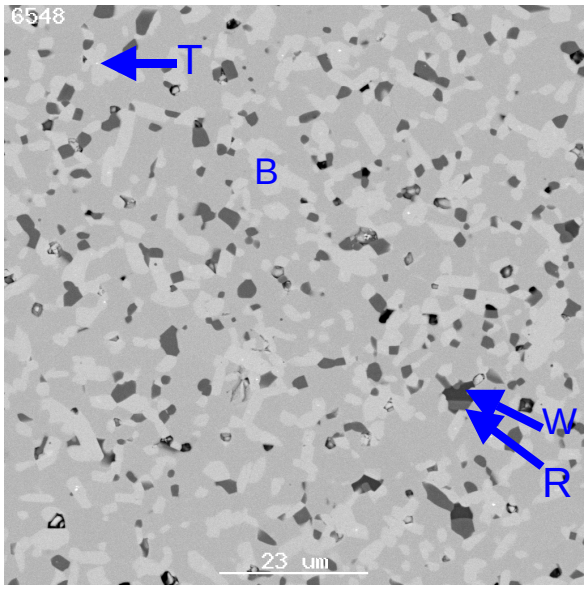


Figure D-5: (a) and (c) secondary electron micrographs and (b), (d) and (e) backscattered electron micrographs of mws00-0688, a sample made by cold pressing and sintering a pellet at 1350°C in air for 4 hours. The starting powder was a Th/U/Hf-baseline composition that had been wet attrition milled for 65 minutes. The sample is relatively homogeneous and is composed of a matrix of pyrochlore with rutile (dark-grey, R) and brannerite (light-grey, B). A few grains of whitlockite associated with rutile grains (W, black in (d)) were detected, but these are rare. Only a trace of thoria (T, white) was found; it is present as fine areas inside a few brannerite grains. Porosity (A, black) is also present.

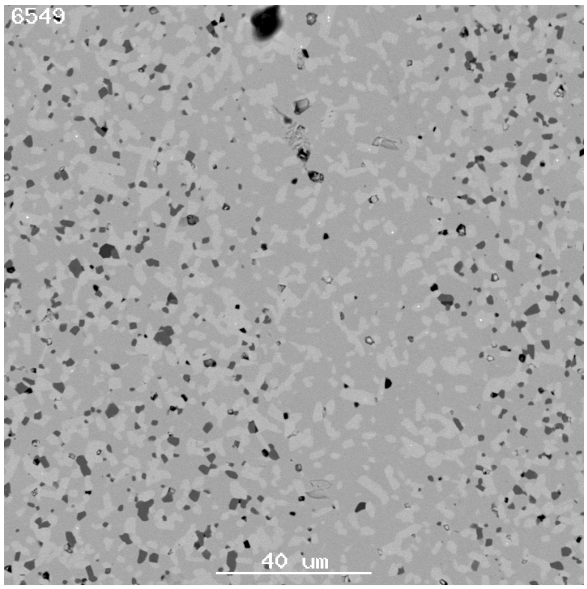
(c)

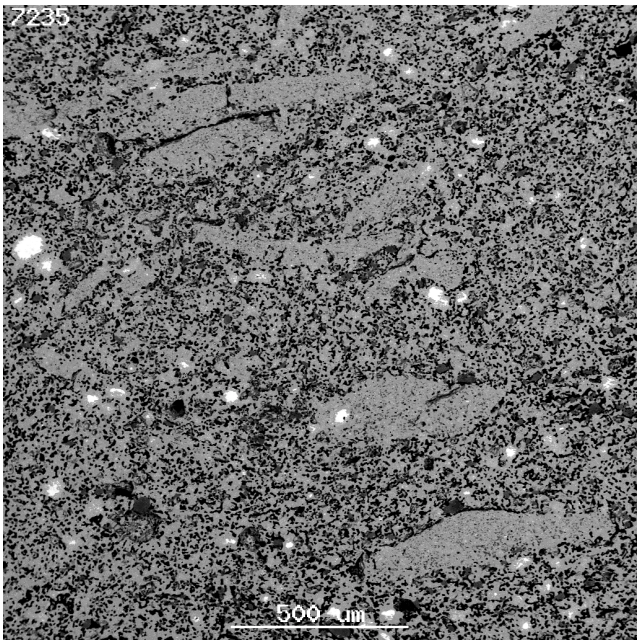


(d)

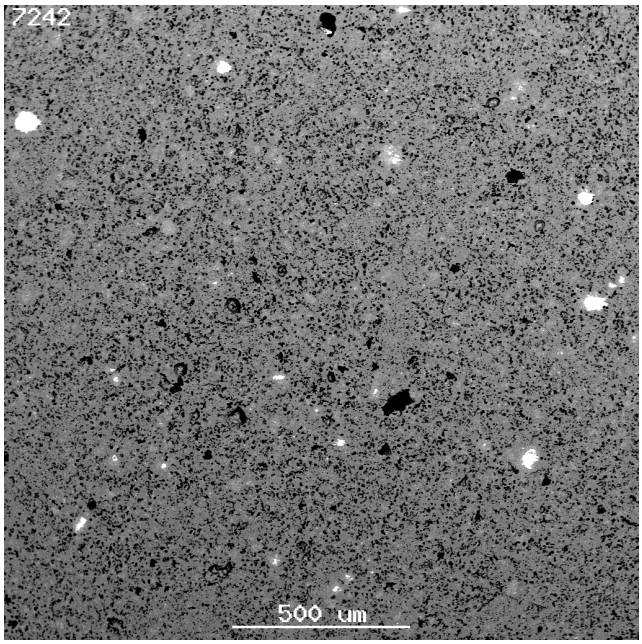


(e)

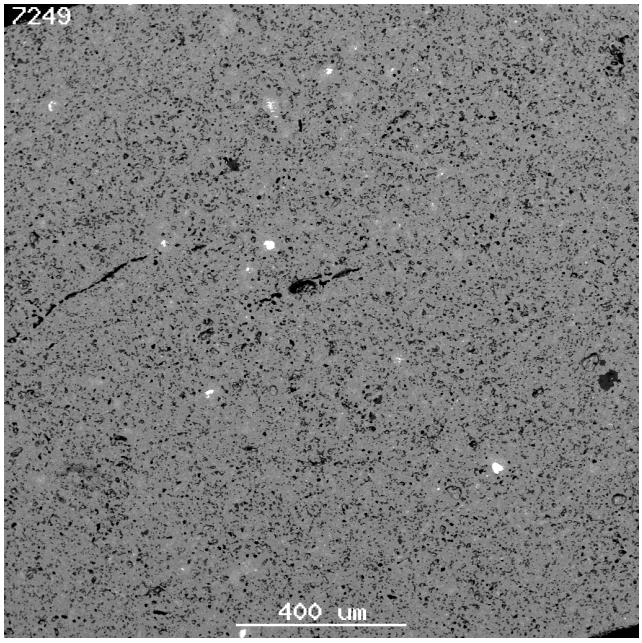




(a)



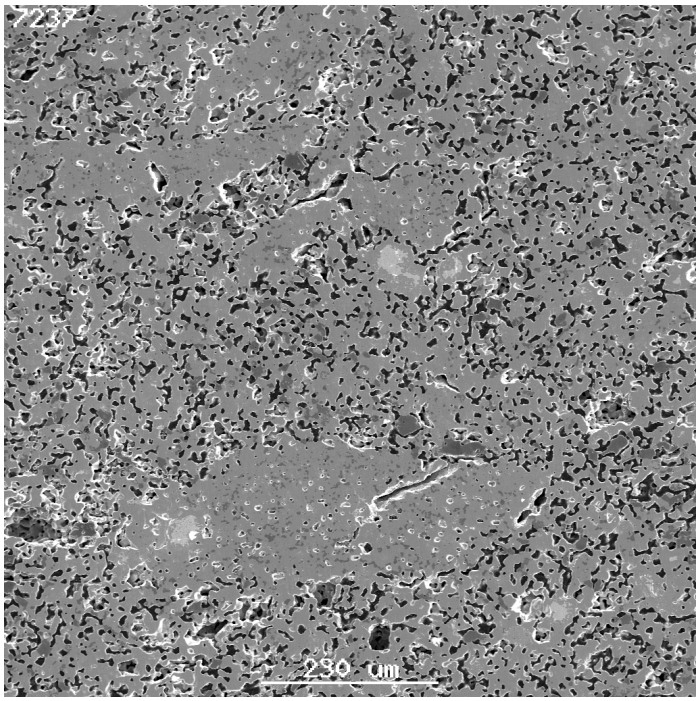
(b)



(c)

Figure E-1: Backscatter electron micrographs of the sintered (1350°C/4h/air) Pu/U/Hf-baseline samples attrition milled for (a) 10 min.-1 pass (Pu14201), (b) 60 min.-6 passes (Pu14202) and (c) 100 min.-10 passes (Pu14203). The figure is taken at low magnification to illustrate the progressive improvement in homogeneity with milling time. The size and number of actinide oxide aggregates (white grains) decreases with increased milling.

(a)



(b)

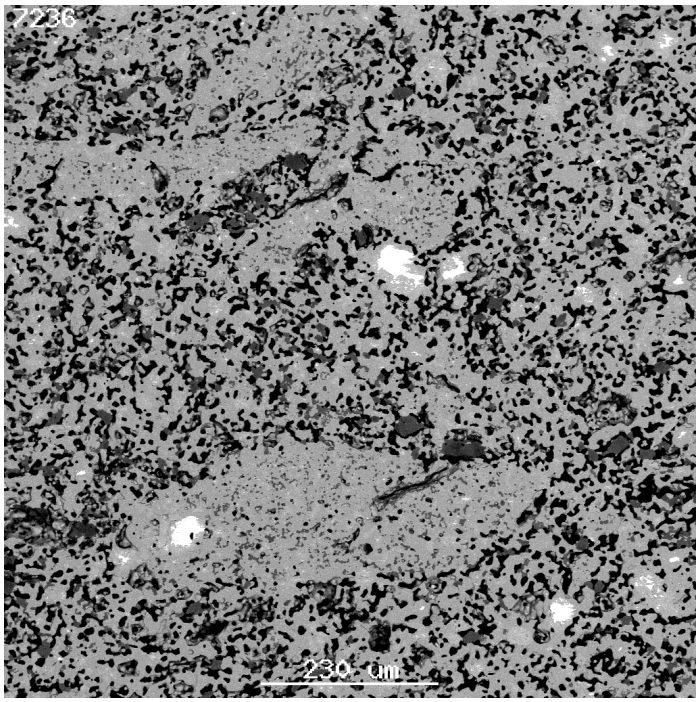
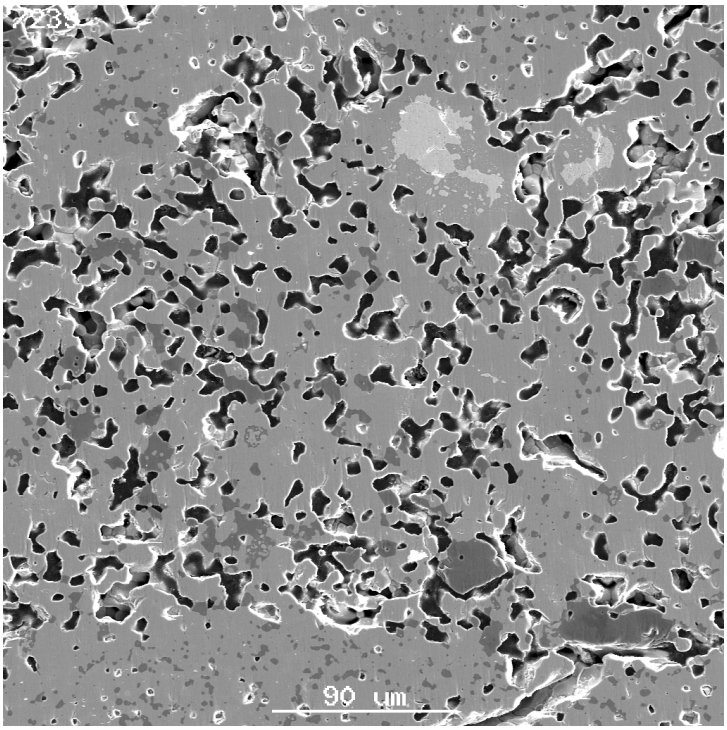
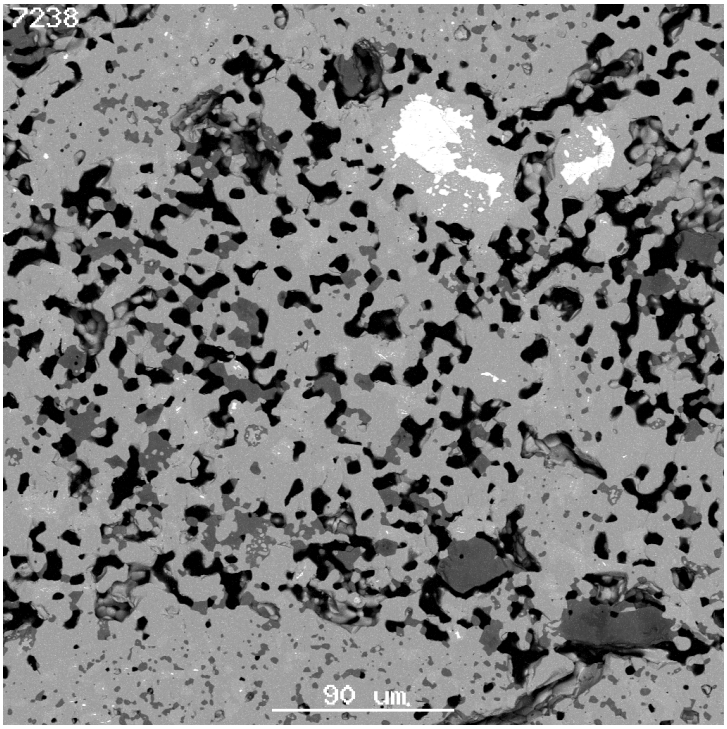


Figure E-2: (a), (c) and (e) Secondary electron micrographs (SEI) and (b), (d) and (f) backscatter electron micrographs (BSE) of the sintered (1350°C/4h/air) Pu/U/Hf-baseline sample Pu14201 that had been attrition milled for 10 min./1 pass. The sample consists of pyrochlore (grey matrix), brannerite (light grey in BSE micrographs, e.g., see (f)), rutile (dark-grey) and actinide oxide (white in BSE micrographs). The larger actinide oxide particles are "unreacted" PuO_2, whereas the small actinide oxide particles inside the brannerite grains (as can be seen in, e.g., (f)) contain U and a trace of Ca, Gd and Hf. The sample is porous (see SEI micrographs) and contains evidence of residual precursor agglomerates up to ~ 500μm long.

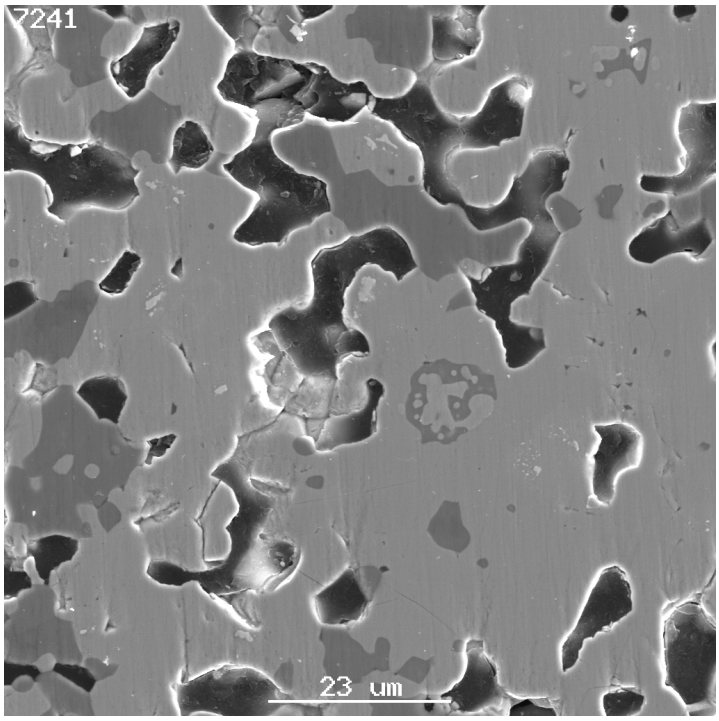
(c)



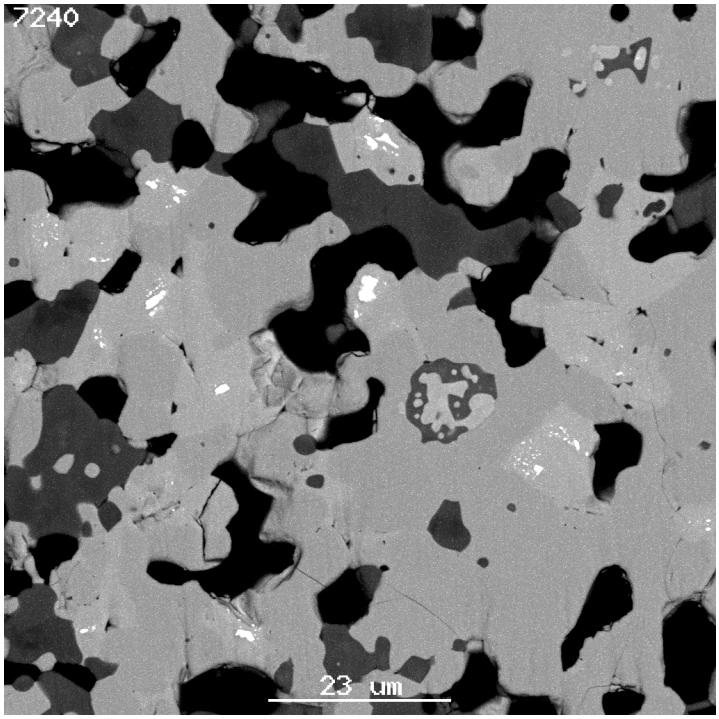
(d)



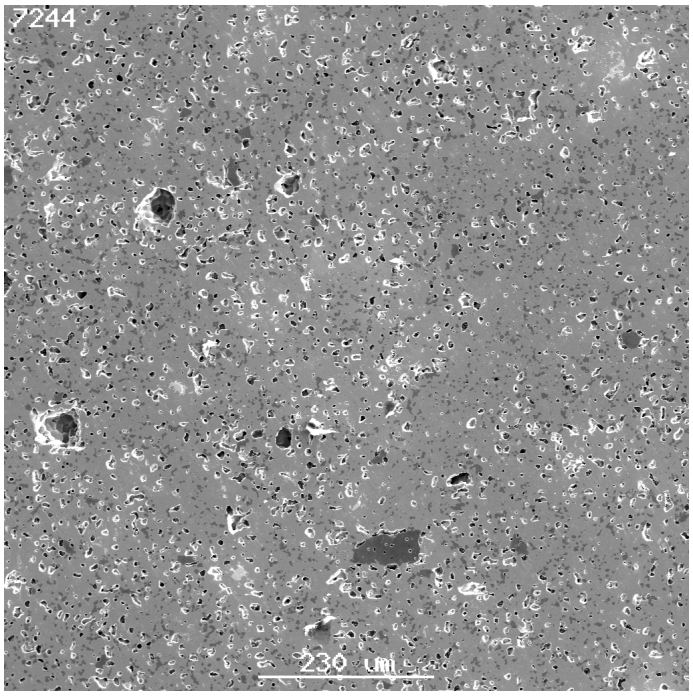
(e)



(f)



(a)



(b)

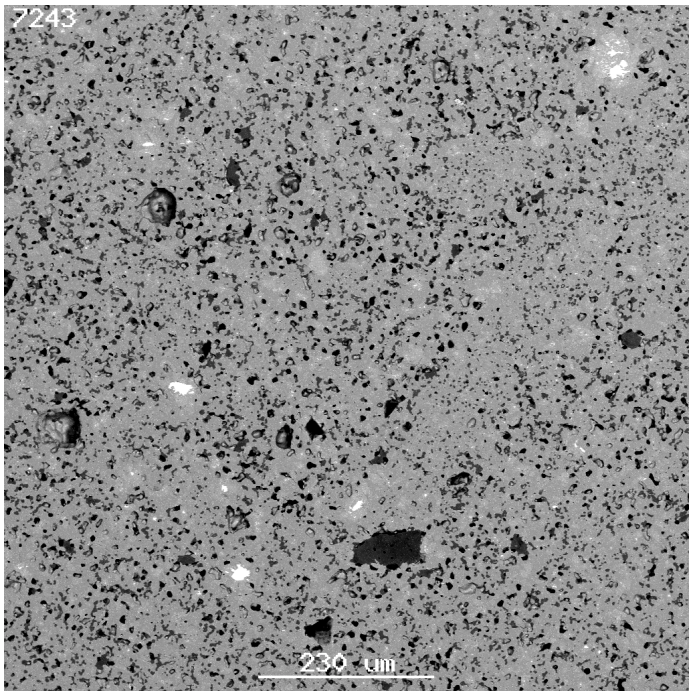
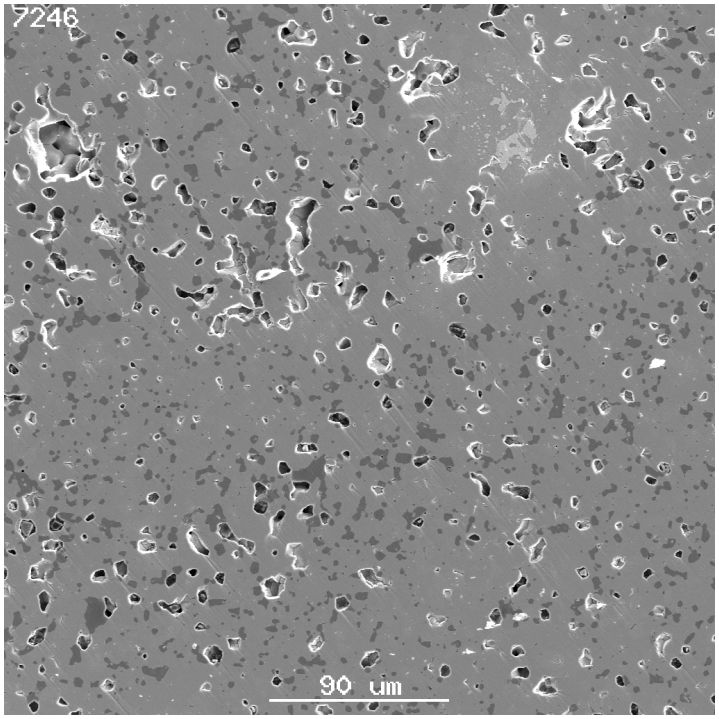
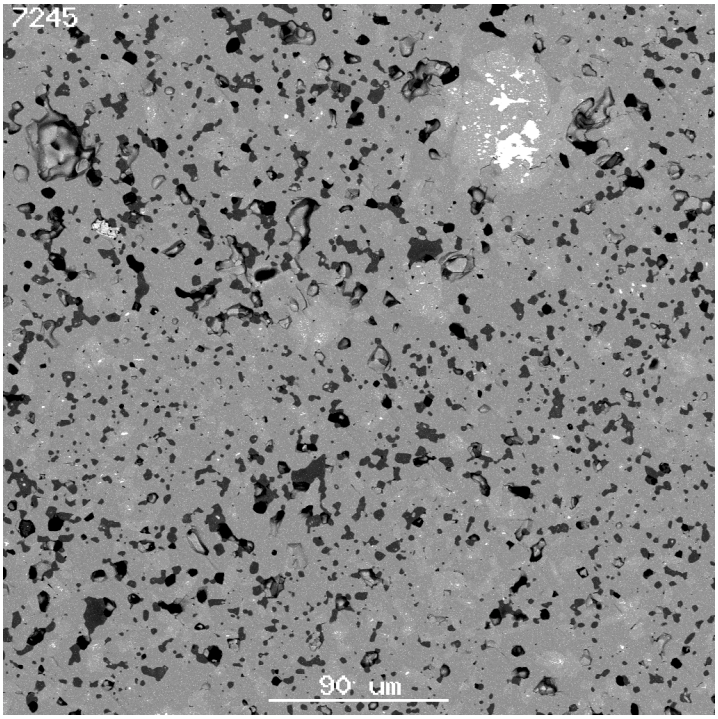


Figure E-3: (a), (c) and (e) Secondary electron micrographs (SEI) and (b), (d) and (f) backscatter electron micrographs (BSE) of the sintered (1350°C/4h/air) Pu/U/Hf-baseline sample Pu14202 that had been attrition milled for 60 min./6 passes. The sample consists of pyrochlore (grey matrix), brannerite (light grey in BSE micrographs, e.g., see (f)), rutile (dark-grey) and actinide oxide (white in BSE micrographs). The larger actinide oxide particles are "unreacted" PuO_2, whereas the small actinide oxide particles inside the brannerite grains (as can be seen in, e.g., (f)) contain U and a trace of Ca, Gd and Hf. The sample is much less porous (see SEI micrographs) and more homogeneous than the single pass milling (fig. F-2).

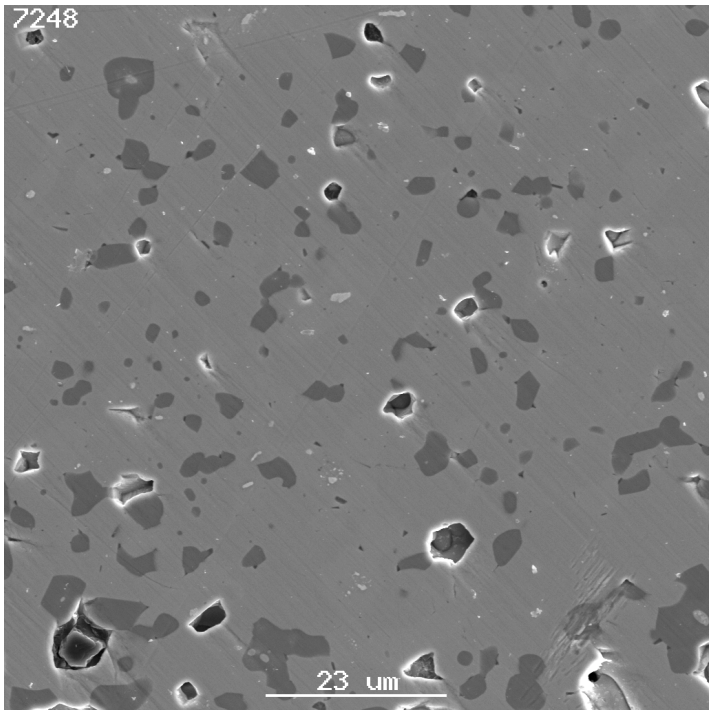
(c)



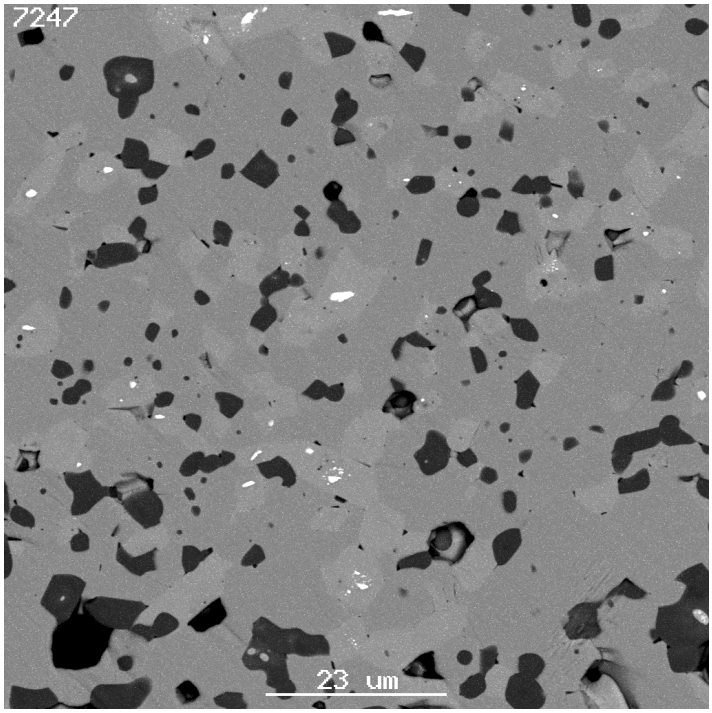
(d)



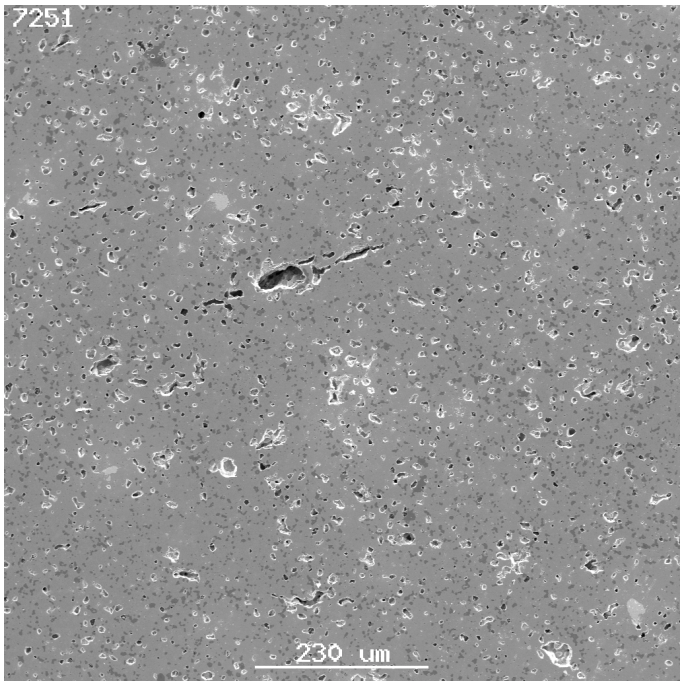
(e)



(f)



(a)



(b)

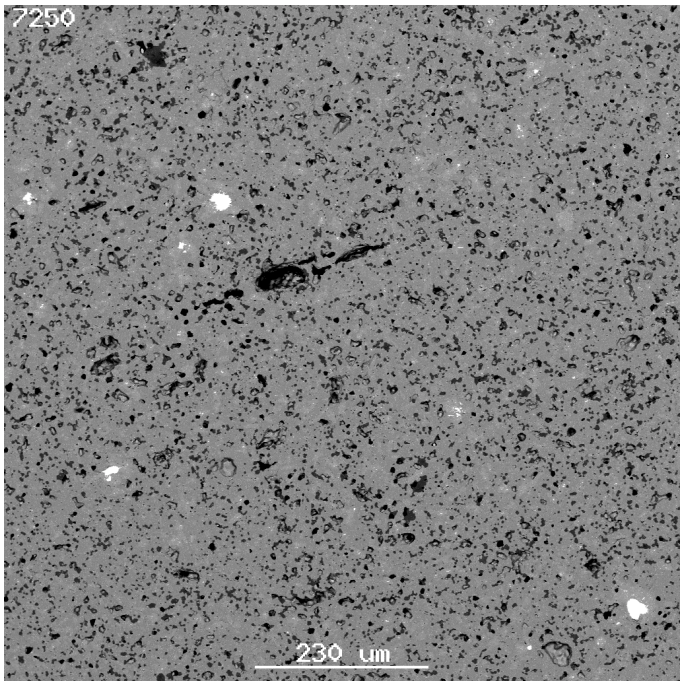
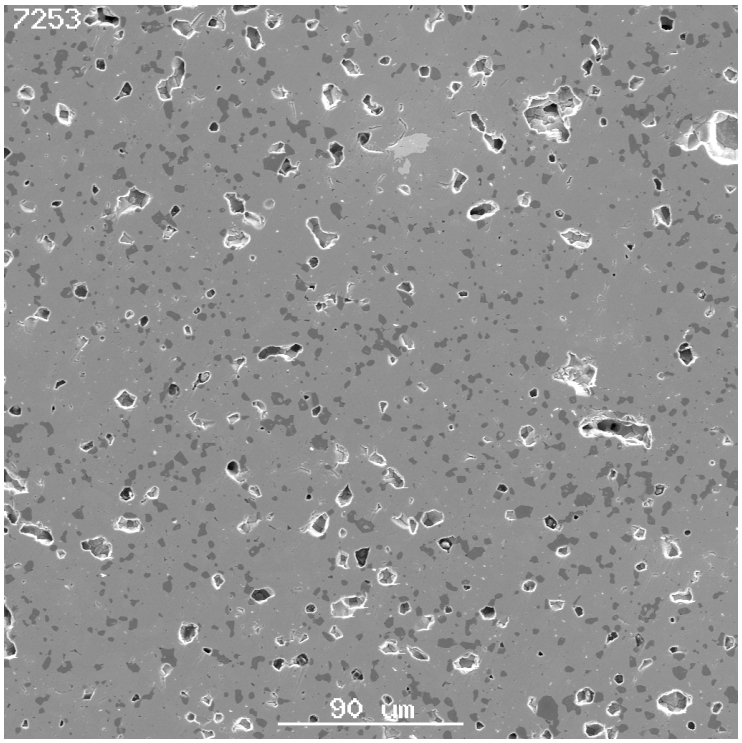
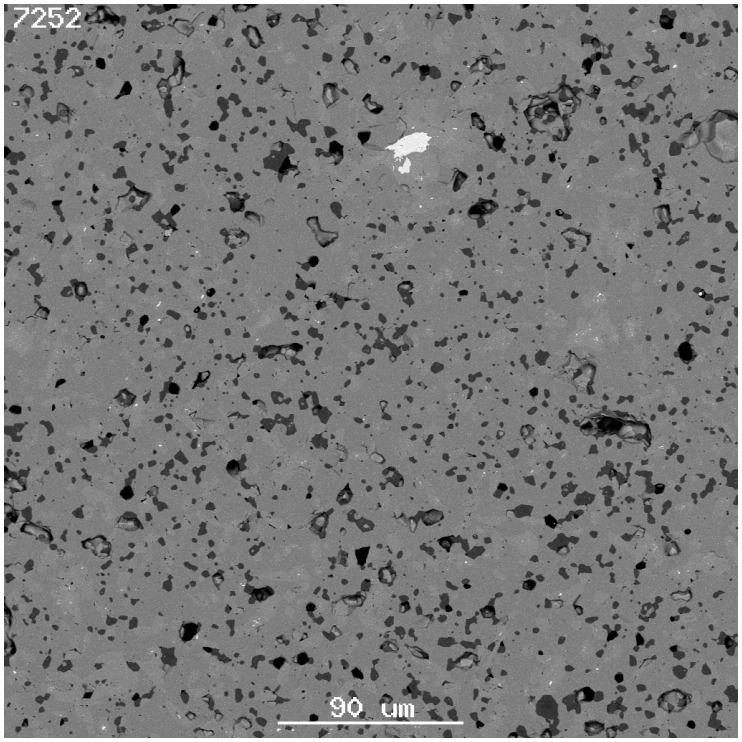


Figure E-4: (a), (c) and (e) Secondary electron micrographs (SEI) and, (b), (d) and (f) backscatter electron micrographs (BSE) of the sintered (1350°C/4h/air) Pu/U/Hf-baseline sample Pu14203 that had been attrition milled for 100 min./10 passes. The sample consists of pyrochlore (grey matrix), brannerite (light grey in BSE micrographs, e.g., see (f)), rutile (dark-grey) and actinide oxide (white in BSE micrographs). The larger actinide oxide particles are "unreacted" PuO_2, whereas the small actinide oxide particles inside the brannerite grains (as can be seen in, e.g., (f)) contain U and a trace of Ca, Gd and Hf. The increased milling time has substantially reduced the porosity (see SEI micrographs) compared to samples attrition milled for shorter periods (see figs. F-2 and F-3). The sample is comparable to the dry and wet ball milled baseline ceramics.

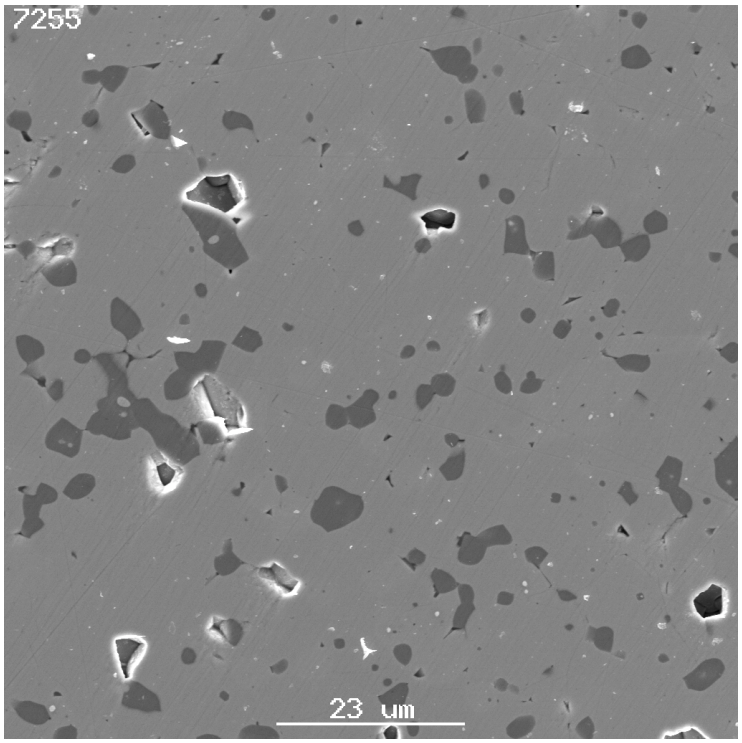
(c)



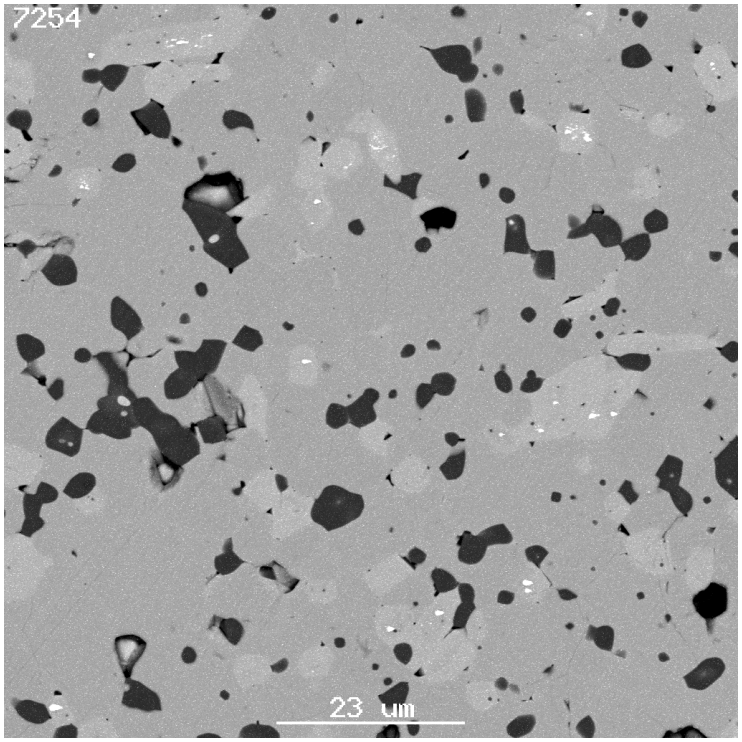
(d)



(e)



(f)



A. APPENDIX A: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS OF THE CERIUM/CERIUM/ZIRCONIUM-BASELINE SAMPLES

A.1 EDS ANALYSES

Table A-1: EDS analyses of phases (number of cations) found in the oxide-route Ce/Ce/Zr- baseline composition batches made via dry and wet attrition milling. Pellets were prepared from powders by sintering in air at 1350°C for 4 hours.

Method/sample No.	**Dry**	**L000138**	**Wet**	**L000139**
Phase	**Pyrochlore**	**Whitlockite #**	**Pyrochlore**	**Whitlockite #**
~ abundance (vol. %)	> 99	< 1	> 99	< 1
Element $				
oxygen	7	8	7	8
Ca	0.69 – 0.82	2.40	0.78	1.75
Gd	0.18 – 0.22	0.10	0.18	0.11
Zr	0.17 – 0.27	0.11	0.25	0.10
Ce +	0.62 – 0.69	0.30	0.60	0.42
Ti	2.04 – 2.13	0.17	2.12	0.98
P $		1.72		1.20
Total	3.90 – 3.96	4.79	3.95	4.58

$ Impurity in the TiO_2 raw material.
# Composition difficult to measure due to small grain size, figures here are given as a guide only.
+ Ce analysed as Ce^{4+}.

Table A-2: EDS analyses of phases (number of cations, except for glass which is given as element wt. %) found in the pellet L991004 (Ce/Ce/Zr-baseline composition, oxide-route wet attrition milled that had been sintered in air at 1350°C for 4 hours.

Phase	**Pyrochlore**	**whitlockite**	**glass from process contamination**
~ abundance (vol. %)	> 99	< 1	< 1
Element $			(wt. %)
oxygen	7	8	48
Ca	0.77	2.39	4.5
Gd	0.21	0.07	
Zr	0.22		1.3
Ce +	0.73	0.30	3
Ti	2.00		9.5
P $		1.93	
Mg		0.13	
Si		0.04	72
Al			7.5
K			2
Na			0.7
Total	3.94	4.87	100

$ Impurity in the TiO_2 raw material.
\+ Ce analysed as Ce^{4+}.

A.2 XRD ANALYSES

Table A-3: A summary of the XRD results for sintered samples made by sintering at 1350°C for 4 hours in air (Ce/Ce/Zr-baseline ceramic made by wet attrition milling.

Description			
Sample No. /description	**XRD Description**	**XRD File Name.**	**Phases detected**
L991004 / milled in small pot	powder	s16248	pyrochlore

The above Table contains a list of the raw XRD data files. Note that s*.raw files are Siemens D500 Diffractometer data files (Co K-alpha). The raw data files are on the computer disk enclosed with this report.

APPENDIX B

SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES MADE USING HIGH-FIRED THORIUM AND URANIUM OXIDES

B. APPENDIX B: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES MADE USING HIGH-FIRED THORIUM AND URANIUM OXIDES

B.1 EDS ANALYSIS RESULTS

Table B-1: EDS analyses of phases (number of cations) of the pellets of the pellet mws00-0610 (B1-14, nominally 10 % perovskite composition) and mws00-0612 (B1-14 10 % phosphate-doped composition). Both samples are made from oxide-route powders that hav been wet attrition milled. Pellets were prepared by sintering in air at 1350°C for 4 hours.

		mws00-0610	B1-14			mws00-0612	B1-16		
Phase	**pyrochlore**	**brannerite**	**Thoria**	**rutile**	**pyrochlore**	**brannerite**	**Whitlockite**	**Thoria**	**rutile**
~ abundance (vol. %)	73 - 79	15 - 20	1 - 2	5	52 - 69	20 - 30	5	1 -3	5 - 10
Element									
oxygen	7	6	2	2	7	6	8	2	2
Ca	1.06 - 1.09	0.06 – 0.10	not done	0.003 - 0.009	1.01	0.06	2.51 – 2.53	0.02	0.04
Gd	0.21 - 0.24	0.08 – 0.10		0 – 0.003	0.24 – 0.36	0.11 – 0.13	0.18 – 0.23	0.02	0 – 0.006
Hf	0.22 – 0.25	0.09 – 0.13		0.08	0.24 – 0.30	0.12	0.01	0.004	0.09
Th	0.19 – 0.21	0.45 – 0.62		0 – 0.002	0.09 - 0.11	0.52 – 0.65	0.01 - 0 02	0.91	0 – 0.002
U $	0.36 – 0.39	0.20 – 0.28		0.005	0.33 - 0.40	0.22 – 0.27	0.01 - 0.03	0.05	0.005 – 0.0
Ti	1.96 - 1.99	1.99 – 2.01		0.90 – 0.93	1.91 – 2.06	1.88 – 1.94	0.08 – 0.15	0.001	0.87
P						0 – 0.01	1.89 – 1.96		0.008
Mg #							0 – 0.04		
Total	4.09 - 4.10	3.05 – 3.08		1.00	4.04 – 4.10	3.06	4.84	1.02	1.02

Mg is a trace impurity

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

Table B-2: EDS analyses of phases (number of cations) of a sintered sample (1350°C/4 hours/air) made using the re-milled baseline composition (B1-2) powder containing high-fired ThO_2 and UO_2. This had firstly been dry attrition milled for 45 mins, then re-milled for 45 mins with the cake being broken up at 10, 20 and 30 minute intervals during the second milling stage.

	mws00-0652			
Phase	**pyrochlore**	**brannerite**	**thoria**	**rutile**
~ abundance (vol. %)	75	10	10	5
Element				
oxygen	7	6	2	2
Ca	1.03 – 1.06	0.05 – 0.07	0.01	0.01
Gd	0.23 – 0.25	0.12	0.01	0.000 - 0.004
Hf	0.23	0.13	0.001	0.04 - 0.08
Th	0.20	0.51 – 0.55	0.98	0.001
U $^{\$}$	0.37	0.22 – 0.26	0.003	0.005
Ti	1.98 – 2.01	1.96 – 1.99		0.91 – 0.94
Total	4.07 – 4.09	3.05 – 3.07	1.01	1.01

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

B.2 XRD RESULTS

Table B-3: A summary of the XRD results for samples made from "high-fired thorium and uranium oxides.

Description - Processing Route	XRD Description	XRD File Name.	Phases Detected
Attrition milled 45 mins			
mws99-0585 B1-2 dry-attrition milled	ground pellet	s16187	pyrochlore, ,thorianite, 4M zirconolite, trace brannerite, possibly rutile
mws99-0587 B1-2 wet-attrition milled	ground pellet	s16188	pyrochlore, brannerite, rutile, probably thorianite
mws99-0589 B1-4 dry-attrition milled	ground pellet	s16189	pyrochlore, 2M zirconolite, brannerite, rutile, thorianite
mws99-0589 B1-4 wet-attrition milled	ground pellet	s16190	pyrochlore, 2M zircon0lote, brannerite, possibly rutile
mws99-0577 B1-10 dry-attrition milled	ground pellet	s16183	pyrochlore, 2M zirconolite, brannerite, rutile, thorianite
mws99-0579 B1-10 wet-attrition milled	ground pellet	s16184	pyrochlore, 2M zirconolite, brannerite, rutile, thorianite
mws99-0581 B1-12 dry-attrition milled	ground pellet	s16191	pyrochlore, brannerite, rutile, thorianite
mws99-0583 B1-12 wet-attrition milled	ground pellet	s16192	pyrochlore, brannerite
mws00-0609 B1-14 dry-attrition milled	exterior surface	s16283	pyrochlore, brannerite, rutile, possibly thorianite and possibly some zirconolite
"	ground pellet	s16287	pyrochlore, brannerite, rutile, thorianite, small amount of zirconolite (probably 4M)
mws00-0610 B1-14 wet-attrition milled	exterior surface	s16284	pyrochlore, brannerite, rutile
"	ground pellet	s16288	pyrochlore, brannerite, rutile
mws00-0611 B1-16 dry-attrition milled	exterior surface	s16285	pyrochlore, brannerite, rutile, whitlockite
"	ground pellet	s16289	pyrochlore, brannerite, rutile, whitlockite, possibly thorianite
mws00-0612 B1-16 wet-attrition milled	exterior surface	s16286	pyrochlore, brannerite, rutile, trace whitlockite
"	ground pellet	s16290	pyrochlore, brannerite, rutile, whitlockite, possibly thorianite
Re-attrition milled Batch- total 90 mins			
mws00-0652/ B1-2 dry-attrition milled	ground pellet	s16432	pyrochlore, brannerite, rutile, possibly thorianite

s*.raw files are Siemens D500 Diffractometer data files (Co K-alpha). The raw data files are on the computer disk enclosed with this report.

B.2.1 B1-2

The dry attrition milled sample's XRD pattern has very weak brannerite peaks, relatively intense thorianite peaks and 4M zirconolite peaks. Pyrochlore, brannerite, rutile and probably thorianite were observed in the wet attrition milled sample's XRD pattern. The results are consistent with the SEM analysis (Figs. B-1 and B-2). The remilled batch had weak thorianite peaks and the XRD pattern appears to show it consists mainly of pyrochlore with brannerite and some rutile.

B.2.2 B1-4

The results show similar trends to the B1-2 results with very weak brannerite peaks and strong thorianite peaks in the XRD pattern of the dry attrition milled sample and barely detectable thorianite in the wet attrition milled sample. The impurities have resulted in 2M zirconolite formation. The results are consistent with the SEM results (Figs. B-3 and B-4).

B.2.3 B1-10

The XRD patterns are consistent with the SEM analysis. The dry attrition milled sample has more intense thorianite peaks present in its XRD pattern than the wet attrition milled sample. This is at the expense of brannerite. The results are consistent with the SEM analysis (Figs. B-5 and B-6).

B.2.4 B1-12

The XRD results show similar trends to the B1-10 composition results, with the dry attrition milled sample having more intense thorianite peaks present in its XRD pattern, at the expense of brannerite, than the wet attrition milled sample. The results are consistent with the SEM analysis (Figs. B-7 and B-8).

B.2.5 B1-14

The wet attrition milled sample has XRD patterns with more intense brannerite and less intense thorianite peaks than the dry milled sample. In both samples the exterior has more intense pyrochlore peaks and relatively less intense secondary phase peaks than the interior, leading one to suspect that rutile may be deficient or orientated near the surface of the pellet, as was observed in some samples reported on elsewhere [*]. Zirconolite (probably the 4M polytype) was observed in the dry attrition milled sample's XRD pattern.

The wet attrition milled sample has less intense thorianite and more intense brannerite peaks its XRD pattern than the dry attrition milled sample.

The results are consistent with the SEM analyses of these samples (Figs. B-9 and B-10) and are

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[*] M W A Stewart and E R Vance, *Interim Report on Task 3: Immobilisation Process/Equipment – Task 3.4: Non-destructive Evaluation,* ANSTO Materials Division Report No. R00m011, 30 April 2000, Materials Division, ANSTO, Lucas Heights, Australia

similar to previous wet and dry ball milled results [**].

B.2.6 B1-16

For the dry attrition milled sample the exterior and interior XRD patterns are similar except that the rutile, whitlockite and thorianite peaks are slightly less intense in the surface XRD pattern.

The wet milled attrition milled sample also has less intense rutile, whitlockite and thorianite peaks in the surface XRD pattern. The pattern is similar to the dry milled pattern except that the wet attrition milled sample has less intense rutile and thorianite peaks and slightly stronger brannerite peaks. The results are consistent with the SEM analyses (Figs B-11 and B-12).

[**] M W A Stewart, E R Vance, R A Day and A Brownscombe, *Interim Report on Task 1.2: Near Equilibrium Processing Requirements*, ANSTO Materials Division Report No. R99m012, 1 April 1999, Materials Division, ANSTO, Lucas Heights, Australia

APPENDIX C

SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES MADE USING PRE-GROUND, HIGH-FIRED THORIUM AND URANIUM OXIDES

C. APPENDIX C: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES MADE USING PRE-GROUND, HIGH-FIRED THORIUM AND URANIUM OXIDES

C.1 EDS ANALYSES

Table C-1: EDS analyses of phases (number of cations) found at the exterior and interior of the pellet mws99-0606 (B1-2, baseline composition, oxide-route wet attrition milled) that had been sintered in air at 1350°C for 4 hours.

Phase	interior pyrochlore	interior brannerite	interior rutile	exterior pyrochlore	exterior brannerite	exterior rutile
~ abundance (vol. %)	65-75	15-25	5-7	65-75	15-25	5
Element						
oxygen	7	6	2	7	6	2
Ca	1.04	0.06	0.002	1.05	0.07 – 0.13	0.004
Gd	0.29	0.15 – 0.18	0.001	0.25	0.13-0.17	0.001
Hf	0.27	0.07 – 0.14	0.08	0.27	0.15	0.09
Th	0.15	0.33 – 0.37	0.001	0.15	0.32-0.34	0.001
U $	0.41	0.35	0.003	0.41	0.36	0.005
Ti	1.94	2.02	0.91	1.96	1.99	0.90
Total	4.10	3.08	1.00	4.09	3.07	1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

Table C-2 - EDS analyses of phases (number of cations, except for the glass phase which is given in wt. % of element present) found at the exterior and interior of the pellet mws99-0608 (B1-4, baseline + impurities composition, wet attrition milled) that had been sintered in air at 1350°C for 4 hours.

	interior					exterior				
Phase	**pyrochlore**	**brannerite**	**zirconolite**	**rutile**	**glass** *	**pyrochlore**	**brannerite**	**zirconolite**	**rutile**	**glass** *
~ abundance (vol. %)	60-70	15-20	10-15	5	1-2	60-70	15-20	10-15	5	1-2
Element					**(Wt. %)**					**(Wt. %)**
oxygen	7	6	7	2	35	7	6	7	2	35
Ca	1.03	0.09	0.75	0.005	not analysed	1.01	0.07	0.77	0.001	13
Gd	0.24	0.13	0.19	0.001		0.24	0.13	0.20.		4
Hf	0.16	0.12	0.65	0.06		0.17	0.12	0.64	0.06	7
Th	0.17	0.36	0.06	0.001		0.17	0.36	0.06	0.001	2.5
U $	0.42	0.36	0.14	0.01		0.42	0.38	0.13	0.01	8
Ti	1.96	1.97	1.90	0.91		1.96	1.97	1.89	0.91	9
Al	0.03	0.04	0.11	0.01		0.05	0.05	0.11	0.015	4
Mg	0.02		0.09			0.02		0.10		1.5
Ga	0.02	0.01	0.15					0.16		2.5
Ta	0.02	0.01		0.01		0.02	0.01		0.005	
W	0.01					0.01				
Mo										
Na										1
K										0.1
Si										10
B										
Fe										0.1
Cr										
Ni										
P										3
Total	4.08	3.09	4.04	1.01	100	4.08	3.08	4.04	1.00	100

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

* The glass composition is variable across the sample and the analysis is prone to error, values here are given as a guide only.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

Table C-3 - EDS analyses of phases (number of cations) found at the exterior and interior of the pellet mws99-0602 (B1-10, zirconolite-rich composition, attrition milled) that had been sintered in air at 1350°C for 4 hours.

	interior					exterior				
Phase	**pyrochlore**	**zirconolite**	**brannerite**	**Th,U-oxide***	**rutile**	**pyrochlore**	**zirconolite**	**brannerite**	**Th,U-oxide***	**rutile &**
~ Abundance (Vol. %)	35-45	35-45	10-15	<1	5-7	38-48	38-48	1-3	<1	3-5
Element										
oxygen	7	7	6		2	7	6	7		2
Ca	1.03	0.78	0.06		0.001	0.99	0.81	0.07 – 0.10		0.003
Gd	0.24	0.18	0.10 – 0.13		0.001	0.23	0.17	0.10		0.001
Hf	0.14	0.60	0.08		0.04	0.14 - 0.18	0.50 – 0.56	0.10		0.04
Th	0.22	0.06	0.46		0.001	0.21 - 0.24	0.07 – 0.10	0.34 – 0.43		
U $	0.36	0.10	0.38		0.01	0.35 - 0.39	0.11 –0.16	0.26 – 0.33		0.01
Ti	2.03	1.96	1.97		0.94	2.01	1.96 - 1.99	1.95 – 2.13		0.94
Al	0.05	0.33	0.07		0.01	0.06	0.28 – 0.34	0.08		0.01
Total	4.09	4.01	3.08		1.00	4.08	4.03	3.09		1.01

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.

& Rutile is present but was not analysed, it contains Hf in a similar amount to previous samples (~0.1 formula units).

* Too small to analyse accurately.

Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

The standard error in the measurements is ~ 1 %.

Table C-4 - EDS analyses of phases (number of cations) found at the exterior and interior of the pellet mws99-0604 (B1-12, brannerite-rich composition, attrition milled) that had been sintered in air at 1350°C for 4 hours.

	Interior					Edge			
Phase	**pyrochlore**	**brannerite**	**Thoria** +	**Hafnia** +	**rutile**	**pyrochlore**	**brannerite**	**Thoria** +	**rutil**
~ abundance (vol. %)	45-55	45-55	< 1	< 1	5	45-55	45-55	< 1	5
Element									
oxygen	7	6			2	7	6		2
Ca	0.80 - 1.05	0.09 – 0.11			0.003	1.10	0.10		0.00
Gd	0.19	0.14			0.001	0.21	0.13 – 0.16		
Hf	0.25 - 0.34	0.15 – 0.16			0.11	0.26	0.15		0.11
Th	0.09 – 0.17	0.25 – 0.36			0.002	0.11	0.25 0.28		0.00
U $	0.46 – 0.50	0.34 – 0.41			0.006	0.50	0.40 – 0.43		0.00
Ti	1.94 - 2.04	2.00			0.88	1.92	2.01		0.89
Total	3.94 – 4.07	3.09			1.00	4.11	3.09		1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
\+ Present but not measured.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the measurements is ~ 1 %.

C.2 XRD RESULTS

Table C-5: A summary of the XRD results for sintered samples made by sintering at 1350°C for 4 hours in air (Th/U/Hf-doped ceramic made by wet attrition milling with premilled ThO_2 and UO_2).

Description - Processing Route			
Composition/sample No.	**XRD Description**	**XRD File Name.**	**Phases Detected**
B1-2/mws99-0606	As fired pellet surface top	s16207	pyrochlore, brannerite and possibly rutile
	ground surface of pellet	s16198	pyrochlore, brannerite and possibly rutile
	powder with W reference	t2560	pyrochlore, brannerite, tungsten
B1-4/mws99-0608	As fired pellet surface top	s16200	pyrochlore, brannerite, rutile and 2M zirconolite + additional "zirconolite" peak at 0.557 n
	ground surface of pellet	s16209	pyrochlore, brannerite, rutile and 2M zirconolite + additional "zirconolite" peak at 0.557 n
	powder with W reference	t2561	pyrochlore, brannerite, tungsten, 2M zirconolite + additional "zirconolite" peak at 0.557 nı
B1-10/mws99-0602	As fired pellet surface top	s16194	pyrochlore, brannerite, rutile and 2M zirconolite + additional "zirconolite" peak at 0.56 nr
	ground surface of pellet	s16203	pyrochlore, brannerite, rutile and 2M zirconolite + additional "zirconolite" peak at 0.56 nr
	powder with W reference	t2558	pyrochlore, brannerite, tungsten, rutile and 2M zirconolite + additional "zirconolite" peak 0.56 nm
B1-12/mws99-0604	As fired pellet surface top	s16205	pyrochlore, brannerite, rutile
	ground surface of pellet	s16196	pyrochlore, brannerite, rutile
	powder with W reference	t2559	pyrochlore, brannerite, tungsten, possibly rutile

The above Table contains a list of the raw XRD data files. The s*.raw files are Siemens D500 Diffractometer data files (Co K-alpha radiation) and the t*.* files are Scintag Diffractometer files (Cu K-alpha radiation). The raw data files are on the computer disk attached to this report.

C.2.1 B1-2

The brannerite peaks are more intense in the ground surface XRD pattern than in the exterior surface XRD pattern. The powdered sample is also similar to the ground surface.

C.2.2 B1-4

The additional peak at ~ 0.557 nm was also observed in the XRD pattern of the top of the pellets. The ground surface pattern has less intense zirconolite peaks and a prominent but smaller 0.557 nm peak. The XRD pattern of the powdered sample is similar to that of the ground pellet except that the 0.557 nm peak is much smaller, the zirconolite peaks are much less intense and the brannerite peaks are more intense.

The results are very similar to those of the wet ball milled sample sintered in air.

C.2.3 B1-10

The XRD pattern of the top of the pellet appears to exhibit be some orientation effects. An additional peak at ~ 0.557 nm was observed in the XRD pattern of the top of the pellet. The XRD pattern of the ground surface of the pellet has more intense brannerite and rutile peaks than the XRD pattern of the exterior surface.

The results are very similar to those of the wet ball milled sample sintered in air except that the brannerite peaks are less intense.

C.2.4 B1-12

The XRD pattern of the ground surface of the pellet has more intense brannerite than the XRD pattern of the exterior surface.

The results are very similar to those of the wet ball milled sample sintered in air.

APPENDIX D

SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES MADE USING PRE-GROUND LOW-FIRED THORIUM OXIDE AND PRE-GROUND HIGH-FIRED URANIUM OXIDE

D. APPENDIX D: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR SAMPLES MADE USING PRE-GROUND LOW-FIRED THORIUM OXIDE AND PRE-GROUND HIGH-FIRED URANIUM OXIDE

D.1 EDS ANALYSES

Table D-1: EDS analyses of phases (number of cations) found at in the pellet mws99-0670 that had been sintered in air at 1350°C for 4 hours. This sample was made from oxide-route powder of composition B1-2, baseline ceramic, that had been dry attrition milled for 45 minutes in the standard 110cc quick change pot with, the powder cake being broken up every 10 minutes (4 passes).

Phase	**pyrochlore**	**brannerite**	**Thoria**	**rutile**
~ abundance (vol. %)	60 - 73	20 - 30	2-5	5
Element				
oxygen	7	6	2	2
Ca	1.06	0.08	0.02	0.009
Gd	0.24	0.12	0.005	0.001
Hf	0.24	0.14		0.09
Th	0.17	0.40	0.95	0.002
U $	0.41	0.32	0.03	0.008
Ti	1.98	2.00	0.002	0.90
Total	4.09	3.07	1.01	1.01

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

Table D-2: EDS analyses of phases (number of cations) found at in the pellet mws99-0674 that had been sintered in air at 1350°C for 4 hours. Made from oxide-route powder of composition B1-2, baseline ceramic, that had been dry attrition milled for 65 minutes in the modified 110cc quick change pot, with the powder cake being broken up cake every 10 minutes (6 passes).

Phase	**pyrochlore**	**brannerite**	**Thoria**	**rutile**
~ abundance (vol. %)	65 - 77	15 - 25	3 -5	5
Element				
oxygen	7	6	2	2
Ca	1.06 – 1.09	0.08	0.03	0.01
Gd	0.21 - 0.24	0.12	0.004	0.001
Hf	0.23	0.13		0.08
Th	0.16	0.37 – 0.44	0.96	0.006
U $^{\$}$	0.43	0.30 – 0.36	0.02	0.001
Ti	1.99	1.98 – 2.01	0.003	0.91
Total	4.08 – 4.10	3.07 $^{+}$	1.02	1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
\+ Despite compositional variations the elements always added up to this total.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %

Table D-3: EDS analyses of phases (number of cations) found at in the pellet mws99-0683 that had been sintered in air at 1350°C for 4 hours. Made from oxide-route powder of composition B1-2, baseline ceramic, that had been dry attrition milled for 65 minutes under near optimal conditions, with the powder cake being broken up cake every 10 minutes (6 passes).

Phase	**pyrochlore**	**brannerite**	**thoria**	**rutile**
~ abundance (vol. %)	69 - 74	20 - 25	1	5
Element				
oxygen	7	6	2	2
Ca	1.08	0.09	0.02	0.007
Gd	0.24	0.13	0.01	0.003
Hf	0.23	0.13		0.08
Th	0.14	0.36	0.94	0.001
U $	0.44	0.35	0.03	0.007
Ti	1.97	2.02	0.01	0.90
Total	4.10	3.08	1.01	1.01

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

Table D-4: EDS analyses of phases (number of cations) found at in the pellet mws99-0688 that had been sintered in air at 1350°C for 4 hours. Made from powder of composition B1-2, baseline ceramic, oxide-route that had been wet attrition milled for 65 minutes in the modified 110cc quick-change pot.

Phase	**pyrochlore**		**brannerite**		**thoria** [&]	**rutile**
~ abundance (vol. %)	75		20		< 1	5
Element	Rutile containing region	Rutile deficient region	Rutile containing region	Rutile deficient region		
oxygen	7	7	6	6	2	2
Ca	1.09	1.10	0.08	0.15		0.01
Gd	0.23	0.21	0.16	0.10		0.001
Hf	0.25	0.26	0.15	0.14		0.09
Th	0.14	0.14	0.34	0.36		0.001
U [$]	0.46	0.48	0.37	0.36		0.004
Ti	1.94	1.92	2.00	1.99		0.90
Total	4.10	4.10	3.08	3.10		1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
& Found inside brannerite grains, not measured.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.
The standard error in the individual measurements is ~ 1 %.

D.2 XRD RESULTS

Table D-5: A summary of the XRD results for samples made by sintering at 1350°C for 4 hours in air (Th/U/Hf-doped baseline) made b dry attrition milling using low-fired pre-ground ThO_2.

Description - Processing Route			
Sample No. /Milling time/type	**XRD Description**	**XRD File Name.**	**Phases Detected**
Calcined after attrition milling			
mws00-0666/10 min./dry	ground face of pellet	s16435	Pyrochlore, brannerite, thorianite, rutile
mws00-0667/20 min./dry	ground face of pellet	s16436	Pyrochlore, brannerite, thorianite, rutile
mws00-0668/30 min./dry	ground face of pellet	s16437	Pyrochlore, brannerite, rutile, probably thorianite
mws00-0667/45 min./dry	ground face of pellet	s16438	Pyrochlore, brannerite, rutile, possibly thorianite
Calcined before attrition milling in modified pot			
mws00-0681/45 min./dry	ground face of pellet	s16482	Pyrochlore, brannerite, rutile, possibly a trace of thorianite
	top surface of pellet	s16488	Pyrochlore, brannerite, rutile
mws00-0677/65 min./dry	ground face of pellet	s16481	Pyrochlore, brannerite, rutile
Calcined before attrition milling - Milled under optimal conditions			
mws00-0684/65 min./dry	ground face of pellet	s16489	Pyrochlore, brannerite, rutile
	top surface of pellet	s16483	Pyrochlore, brannerite, rutile
mws00-0689/65 min./wet	ground face of pellet	s16491	Pyrochlore, brannerite, rutile
	top surface of pellet	s16485	Pyrochlore, brannerite, rutile

The above Table contains a list of the raw XRD data files. The s*.raw files are Siemens D500 Diffractometer data files (Co K-alpha radiation). The raw data files are on the computer disk enclosed with this report.

Generally, all the XRD patterns are similar. Pyrochlore brannerite, rutile and sometimes thorianite were detected. The amount of thorianite detected in the XRD patterns decreases with milling time and the amount of brannerite appears to increase.

APPENDIX E

SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR THE PU-DOPED BASELINE SAMPLES

E. APPENDIX E: SCANNING ELECTRON MICROGRAPHS, ENERGY DISPERSIVE X-RAY SPECTROMETRY, IMAGE ANALYSIS AND X-RAY DIFFRACTION RESULTS FOR THE PU-DOPED BASELINE SAMPLES

E.1 EDS ANALYSES

Table E-1: EDS analyses of phases (number of cations) found at in the Pu/U/Hf-baseline sample that had been sintered in air at 1350°C for 4 hours. This was made from oxide-route dry attrition milled powder. The milling conditions were near optimal for the setup used with the milling being stoped every 10 minutes to break up the powder cake. Previous results on wet ball milled, oxide-route Pu/U/Hf-baseline composition that was sintered in Ar is given for comparison.

Sample No.	**Pu14203 Attrition Milled**				**Pu68 Wet Ball Milled**			
milling time	**100 min./10 passes**				**16 hr.**			
Sintering conditions	**air/1350°C /4h**				**air/1350°C /4h**			
Phase	**pyrochlore**	**brannerite**	**actinide oxide +**	**rutile**	**pyrochlore**	**brannerite**	**actinide oxide +**	**rutile**
~ abundance (vol. %)	78 - 80	15	1	5 - 7	80	15	< 1	5
Element								
oxygen	7	6	2	2	7	6	2	2
Ca	1.07	0.11	0.04	0.002	0.99	0.08	0.11	0.001
Gd	0.26	0.18	0.05		0.24	0.14	0.08	0.002
Hf	0.23	0.12	0.02	0.09	0.22	0.11	0.03	0.08
Pu	0.23	0.25	0.77	0.001	0.21	0.21	0.40	0.001
U $	0.42	0.42	0.15	0.005	0.41	0.53	0.42	0.009
Ti	1.89	2.02		0.91	1.98	2.00	0.04	0.91
Total	4.10	3.10	1.03	1.00	4.05	3.08	1.07	1.00

$ The uranium is taken to be U^{4+} for analysis purposes, though the U could be in the 4+, 5+ or 6+ redox states in the air fired samples.
\+ The analysis was taken from regions inside brannerite grains.
Note: the absence of a value for an element means that the element is present in amounts below the detection limits of the EDS system.

E.2 XRD RESULTS

Table E-2: A summary of the XRD results Pu/U/Hf-baseline oxide route samples that had been sintered in air at 1350°C for 4 hours. Tl powders for these samples have been made via dry attrition milling

Description - Processing Route			
Sample No./ attrition mill time	**XRD Description**	**XRD File Name.**	**Phases Detected**
Pu14201 /1 0 min. – 1 pass	polished surface of pellet mounted in epoxy	s17016	Pyrochlore, brannerite, rutile
Pu14202 / 60 min. – 6 passes	polished surface of pellet mounted in epoxy	s17017	Pyrochlore, brannerite, rutile, trace PuO_2
Pu14203 / 100 min – 10 passes	polished surface of pellet mounted in epoxy	s17018	Pyrochlore, brannerite, rutile, possible trace of PuO_2

The above Table contains a list of the raw XRD data files. The s*.raw files are Siemens D500 Diffractometer data files (Co K-alpha radiation). The broad peaks at 15 – 25° 2-theta are due to the mounting resin. The raw data files are on the computer disk enclosed with this report.

The XRD patterns indicate the presence of pyrochlore brannerite and rutile. PuO_2 may be present in some of the patterns, but the peaks are wea