3.2 Ga detrital uraninite in the Witwatersrand Basin, South Africa: Evidence of a reducing Archean atmosphere

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DATA REPOSITORY

EMPA Analysis

The chemical composition of uraninite was measured with a CAMECA SX100 Universal EPMA equipped with five wavelength-dispersive spectrometers and a Princeton Gamma-Tech (PGT) energy-dispersive spectrometer at the University of Manitoba in August, 2016. An electron beam current of 20 nA, and an accelerating voltage of 15 kV was used. Beam size was 1 μm. Uraninite grains with especially high Pb contents were selected for SIMS isotopic analysis, as they were the most likely to be older than the host sediments.

SIMS Analysis

Uranium and lead isotope ratios in uraninite from the Witwatersrand Basin were measured using a CAMECA 7f SIMS instrument at the University of Manitoba in November 2016, using methods similar to those described in Sharpe and Fayek (2016). Prior to analysis, samples were cleaned by immersion in an ultrasonic cleaner in four ten minute stages: first a dilute soap solution, then water, distilled water and finally ethanol. Once cleaned, samples were sputter-coated with a ~200Å layer of gold to provide a conductive surface.

Analysis was performed using a ~9 nA, O^- primary beam accelerated at 12.5 kV. The beam was focused by a 750 μm aperture in the primary column to a spot size of 15x30 μm. In order to maximize sensitivity, an energy bandpass of ±25 eV and a 150 μm image field were used in concert with the largest contrast (400 μm) and field (1800 μm) apertures. The sample accelerating voltage used was + 7.95 kV, while the electrostatic analyzer in the secondary column set to accept +8.00 kV, thus creating a 50 V offset which served to maximize U isotope count rates while minimizing hydride isobaric interferences. Flat-topped peaks were produced using entrance slits set to 36.9 μm, and a mass resolving power (measured at 10% valley) of 1300. The magnetic field was switched in order to measure the following U and Pb isotopes: $^{204}Pb^+$, $^{206}Pb^+$, $^{207}Pb^+$, $^{235}U^+$, and $^{238}U^+$. Analyses comprised 40 cycles and lasted ~7 minutes. Common Pb was detected, with $^{206}Pb/^{204}Pb$ ratios ≥150 for all the samples used in the study.

Errors

The two main sources of error in SIMS measurements are spot-to-spot reproducibility between multiple points on the reference material (RM), and within-spot error associated with a single analysis. Counting statistics determine the within-spot error, while spot-to-spot reproducibility is a measure of the reproducibility of the repeated analyses of the RM during an analytical session. For a detailed discussion of how these are calculated, see Sharpe and Fayek, 2016.

The within-spot errors for the $^{206}Pb/^{238}U$ ratios were 0.1%, while $^{207}Pb/^{235}U$ within-spot errors ranged from 0.4-0.7%, averaging 0.5%. Spot-to-spot reproducibility for $^{206}Pb/^{238}U$ ratios ranged from 0.5-4.9%, averaging 2.1%, while Spot-to-spot reproducibility for $^{207}Pb/^{235}U$ ratios ranged from 0.6-5.7%, averaging 2.6%.

Calibration

During each analytical session, three RMs were each analyzed three times, and the SIMS values were plotted vs the true values to construct a calibration curve, which was then used to correct the SIMS values of the unknown samples. The equation describing the curve is:

$$R_{TRUE} = a*R_{SIMS}^2 + b*R_{SIMS}. \quad (1)$$

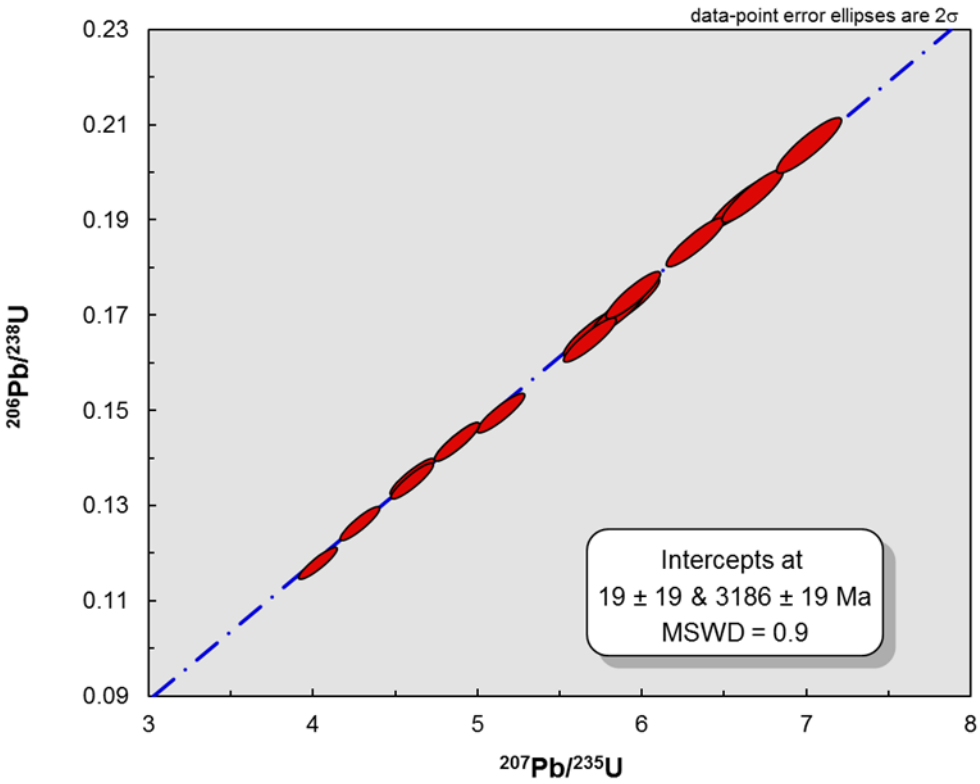
where R_{TRUE} is the true U-Pb ratio, a and b are the coefficients taken from the calibration curve, R_{SIMS} is the measured U-Pb ratio, and the y-intercept is 0. For a more detailed description of the method used, see Sharpe and Fayek (2016).

Figure DR1. U-Pb Concordia plot of isotopic data from Dominion Reef uraninite.

Figure DR2. Back-scattered-electron image of hydrothermal uraninite from the Dominion Reef, showing the margin of a quartz pebble containing euhedral and vein uraninite.

Figure DR3. U-Pb Concordia plot of isotopic data from a uraninite population from the Vaal Reef.

Figure DR4. U-Pb Concordia plot of isotopic data from a second uraninite population from the Vaal Reef.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0.23
0.21
0.19
0.17
0.15
0.13
0.11
0.09
206Pb/238U
3
4
5
6
7
8
207Pb/235U
Intercepts at
19 ± 19 & 3186 ± 19 Ma
MSWD = 0.9

Figure DR1

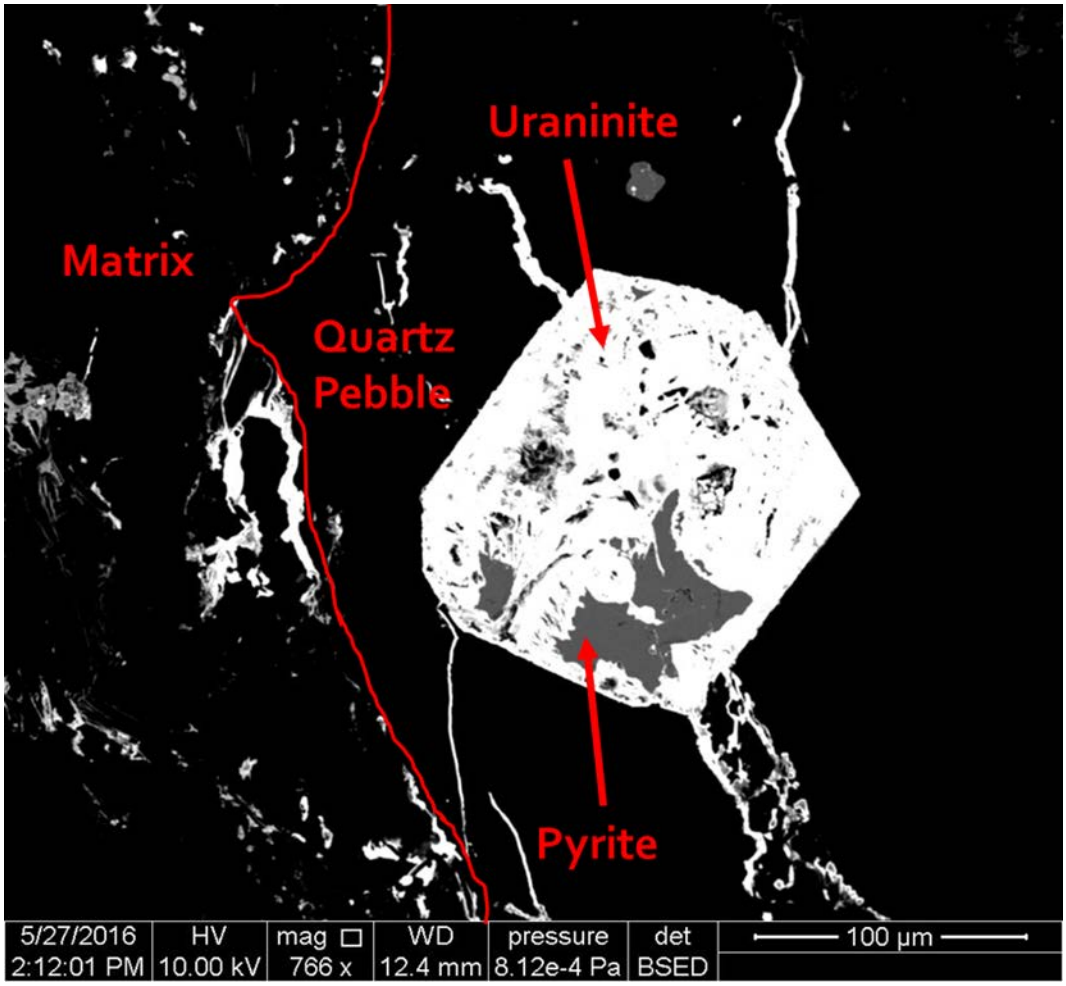
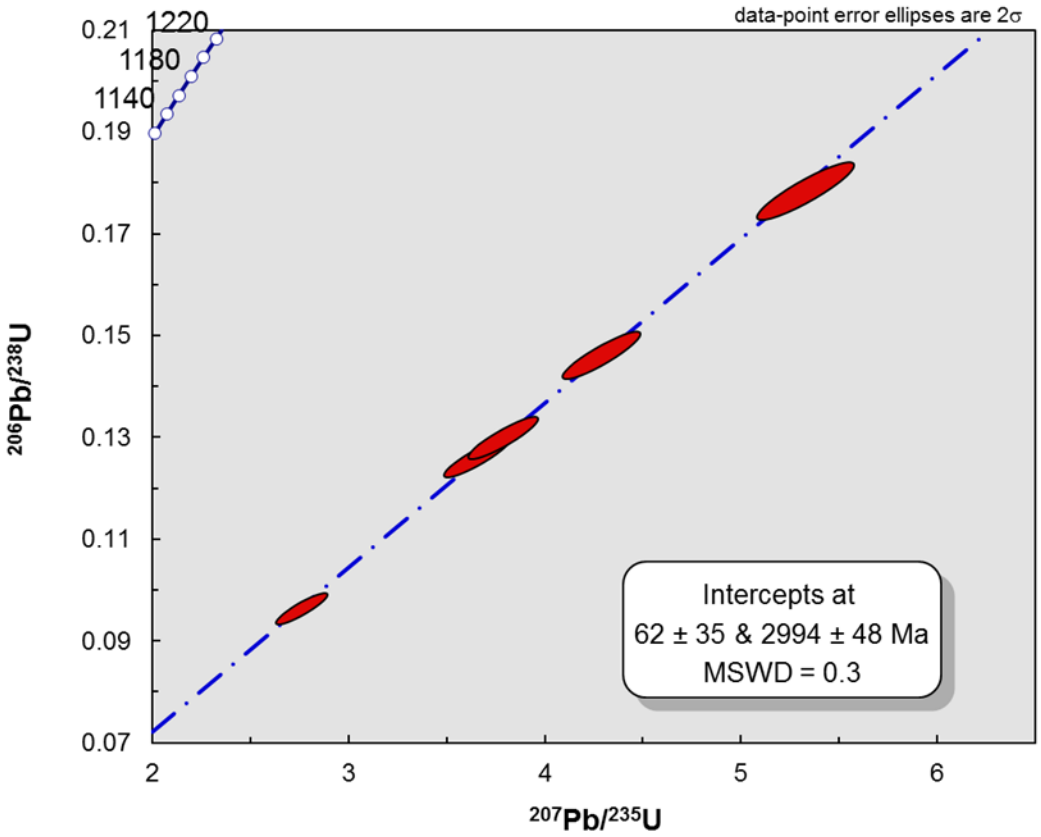

Uraninite
Matrix
Quartz
Pebble
Pyrite
5/27/2016
2:12:01 PM
HV
10.00 kV
mag
766 x
WD
12.4 mm
pressure
8.12e-4 Pa
det
BSED
100 µm

Figure DR2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1220
1180
1140
0.21
0.19
0.17
0.15
0.13
0.11
0.09
0.07
206Pb/238U
2
3
4
5
6
207Pb/235U
Intercepts at
62 ± 35 & 2994 ± 48 Ma
MSWD = 0.3

Figure DR3

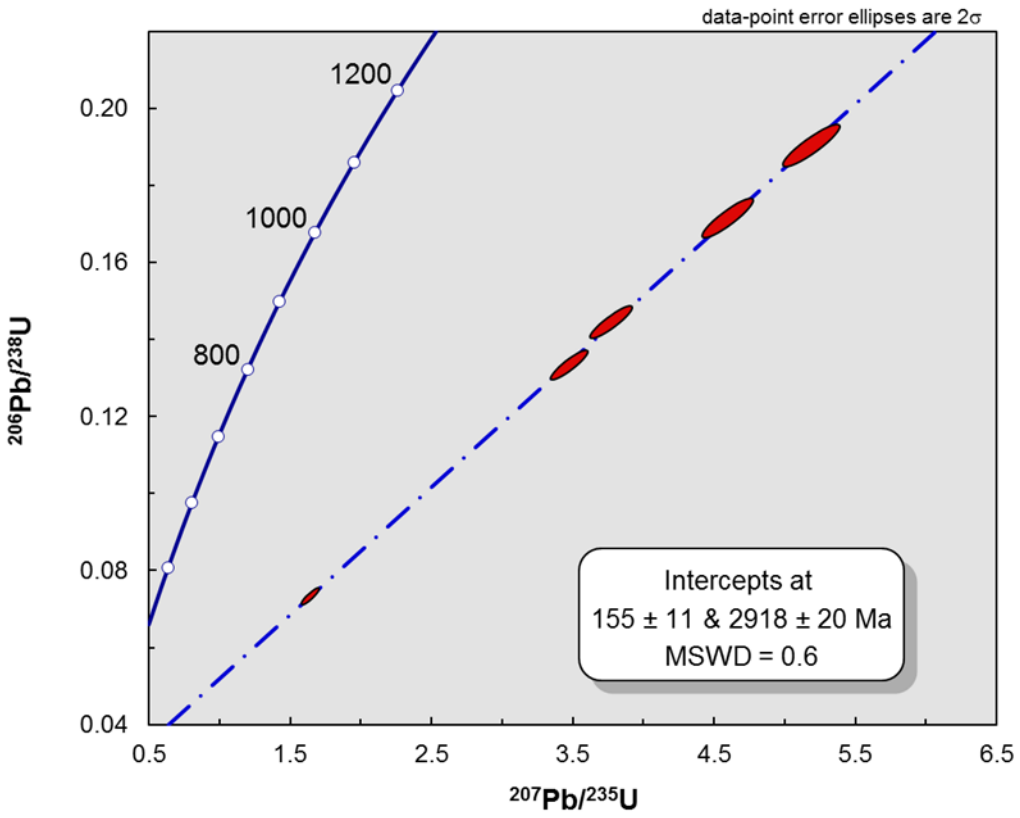
data-point error ellipses are 2σ
1200
1000
800
0.20
0.16
0.12
0.08
0.04
0.5
1.5
2.5
3.5
4.5
5.5
6.5
206Pb/238U
207Pb/235U
Intercepts at
155 ± 11 & 2918 ± 20 Ma
MSWD = 0.6

Figure DR4

101

102 TABLE DR1. MAJOR ELEMENT COMPOSITON DATA FROM ELECTRON MICROPROBE ANALYSIS OF URANINTE FROM THE
103 WITWATERSRAND BASIN, SOUTH AFRICA.

Reef	Mineral	U (Wt %)	Th (Wt %)	Pb (Wt %)	S (Wt %)	Si (Wt %)	Ti (Wt %)	Ca (Wt %)	Fe (Wt %)	Al (Wt %)	P (Wt %)	Y (Wt %)	O (Wt %)	Total (Wt %)
D	Urn	57.34	7.45	10.11	<DL	0.30	0.13	1.30	0.40	0.04	0.06	2.22	11.53	90.88
D	Urn	54.20	8.91	14.86	<DL	0.36	0.21	0.82	0.42	0.04	0.11	0.82	11.33	92.08
D	Urn	53.92	5.88	10.68	0.26	0.31	0.24	1.34	0.32	<DL	0.10	3.08	11.49	87.62
D	Urn	54.69	5.61	17.24	0.64	0.40	0.20	1.42	0.37	0.03	0.12	0.54	11.87	93.13
D	Urn	54.79	5.79	17.06	0.63	0.31	0.16	1.47	0.22	<DL	0.12	1.09	11.91	93.55
D	Urn	50.77	5.14	18.23	1.85	1.34	0.12	1.49	0.72	0.03	0.04	1.97	14.05	95.75
D	Urn	51.86	5.95	14.79	1.14	1.41	0.06	1.56	0.48	<DL	0.06	1.97	13.40	92.68
D	Urn	59.03	2.81	10.88	0.88	1.53	0.11	1.79	0.28	0.08	0.06	1.70	13.42	92.57
D	Urn	57.54	5.00	12.86	0.79	1.25	0.15	1.52	0.35	0.08	0.03	1.63	13.18	94.38
D	Urn	54.58	4.95	17.54	1.30	1.47	0.10	1.27	0.29	0.11	0.03	1.07	13.60	96.31
V	Urn	51.01	6.67	28.08	3.23	0.10	<DL	0.49	0.20	<DL	<DL	0.20	13.68	103.7
V	Urn	60.86	2.34	20.40	1.71	0.14	<DL	0.76	0.11	<DL	<DL	0.96	12.57	99.85
V	Urn	61.97	3.06	18.77	1.27	0.15	0.03	0.65	0.13	<DL	<DL	1.00	12.30	99.33
V	Urn	57.41	4.28	21.67	2.06	0.48	0.03	0.59	0.18	0.03	<DL	0.80	13.20	100.7
V	Urn	61.06	3.17	19.27	1.74	0.47	<DL	0.62	0.23	0.15	<DL	0.76	13.13	100.6
V	Urn	57.88	6.51	16.79	1.27	0.78	0.22	0.46	0.15	0.11	<DL	0.99	12.98	98.14
V	Urn	57.62	5.63	19.08	1.54	0.37	0.08	0.38	0.18	0.03	<DL	1.25	12.67	98.83
V	Urn	62.35	2.25	18.40	1.27	0.49	0.12	0.69	0.13	0.07	<DL	0.79	12.67	99.23
V	Urn	60.72	2.60	17.72	1.57	0.91	0.22	0.58	0.18	0.09	0.09	1.19	13.50	99.37
V	Urn	64.62	1.00	16.07	1.01	1.11	0.19	0.68	0.20	0.14	0.08	0.49	13.21	98.8
V	Urn	64.10	1.73	16.20	0.99	1.09	0.35	0.55	0.14	0.14	0.12	0.65	13.34	99.4
V	Urn	61.64	1.71	15.27	1.15	1.45	0.29	0.61	0.22	0.32	0.15	1.16	13.85	97.82
V	Urn	64.15	2.73	17.76	1.49	0.48	0.13	0.72	0.18	0.07	<DL	1.02	13.23	102
V	Urn	56.70	7.26	12.40	0.84	2.04	1.24	0.59	0.23	0.20	0.16	0.88	14.60	97.14
V	Urn	67.91	2.83	10.79	0.39	1.04	0.14	0.66	0.11	0.14	0.04	0.47	12.69	97.21

V	Urn	63.96	1.53	16.04	1.28	1.03	0.54	0.49	0.11	0.12	0.10	0.35	13.47	99.02
V	Urn	57.38	2.30	25.22	2.86	0.12	<DL	0.64	0.20	0.03	<DL	0.51	13.52	102.8
V	Urn	56.20	5.08	18.56	1.34	0.14	<DL	0.55	0.05	<DL	<DL	1.26	11.81	94.99
V	Urn	59.75	1.40	24.21	2.94	0.16	<DL	0.84	0.30	<DL	<DL	0.33	13.80	103.7
V	Urn	57.40	3.73	22.23	2.31	0.09	<DL	0.36	0.13	<DL	<DL	1.40	12.99	100.6
V	Urn	58.02	3.25	23.38	2.37	0.08	<DL	0.37	0.10	<DL	<DL	1.11	13.06	101.7
V	Urn	60.36	3.81	19.00	1.49	0.19	<DL	0.97	0.22	<DL	<DL	0.86	12.58	99.48
V	Urn	63.60	1.30	15.64	1.50	1.47	0.38	0.53	0.14	0.17	<DL	0.41	14.20	99.34
V	Urn	57.53	4.97	16.06	1.15	0.88	0.13	0.50	0.12	0.09	<DL	1.37	12.66	95.46
V	Urn	63.26	2.99	15.32	1.49	1.26	<DL	0.59	0.09	0.19	<DL	0.60	13.69	99.48
V	Urn	62.22	2.72	19.10	1.54	0.71	0.11	0.58	0.15	0.10	<DL	0.43	13.17	100.8
V	Urn	60.92	1.83	16.69	1.66	1.50	0.00	0.72	0.12	0.15	0.12	0.74	13.97	98.42
V	Urn	57.00	4.60	22.07	1.80	0.23	0.05	0.46	0.15	0.03	<DL	0.81	12.62	99.82
V	Urn	57.93	2.93	22.98	2.36	0.26	<DL	0.34	0.11	<DL	<DL	1.10	13.16	101.2
V	Urn	60.87	1.95	26.32	3.08	0.98	<DL	0.47	0.09	0.10	0.03	0.50	15.19	109.6
V	Urn	57.09	1.96	26.04	2.75	0.98	0.04	0.55	0.17	0.10	<DL	0.31	14.37	104.4
V	Urn	65.02	2.93	13.15	1.15	1.37	0.68	0.53	0.18	0.14	0.07	0.22	13.92	99.36
V	Urn	60.95	2.79	18.58	1.54	0.81	0.30	0.45	0.12	0.08	0.05	0.48	13.23	99.38
V	Urn	59.94	3.09	20.49	1.95	0.45	0.04	0.64	0.09	0.05	<DL	0.65	13.13	100.5
V	Urn	56.06	5.42	21.59	1.74	0.90	0.13	0.55	0.16	0.08	0.13	0.69	13.60	101.1
D	Hurn	61.33	<DL	16.99	<DL	0.33	0.07	0.46	0.29	0.09	0.40	0.52	11.25	91.73
D	Hurn	63.72	<DL	15.13	<DL	0.24	0.04	0.75	0.32	<DL	0.22	0.36	11.15	91.93
D	Hurn	62.04	<DL	16.32	<DL	0.17	<DL	0.68	0.29	0.03	0.52	0.51	11.40	91.96
D	Hurn	62.62	<DL	16.59	1.79	0.29	<DL	0.43	1.82	0.08	0.14	0.19	13.22	97.17
D	Hurn	68.73	<DL	8.14	<DL	0.39	<DL	1.50	0.48	0.03	0.08	0.38	11.69	91.42
D	Hurn	65.35	<DL	13.06	<DL	0.52	<DL	0.98	0.46	0.12	0.09	0.39	11.54	92.51

Abbreviations: D = Dominion, V = Vaal, Urn = uraninite, Hurn = hydrothermal uraninite, DL = detection limits.

TABLE DR2. U-Pb ISOTOPE RATIOS IN URANINITE FROM THE WITWATERSRAND BASIN, SOUTH AFRICA

Reef	Corrected $^{207}Pb/^{235}U$	1σ Error (%)	Corrected $^{206}Pb/^{238}U$	1σ Error (%)
Vaal	3.4800	3.2	0.1336	2.4
Vaal	1.6480	3.2	0.0735	2.4
Vaal	3.7785	3.2	0.1449	2.4
Vaal	4.6041	3.2	0.1719	2.4
Vaal	5.1970	3.2	0.1905	2.4
Vaal	3.6568	3.8	0.1263	2.6
Vaal	3.7852	3.8	0.1300	2.6
Vaal	4.2882	3.8	0.1464	2.6
Vaal	5.3270	3.8	0.1786	2.6
Vaal	2.7627	3.8	0.0965	2.6
Dominion	4.0269	2.4	0.1182	2.3
Dominion	4.5983	2.4	0.1363	2.3
Dominion	5.1414	2.3	0.1498	2.3
Dominion	6.6101	2.4	0.1940	2.3
Dominion	4.6016	2.3	0.1355	2.3
Dominion	4.8743	2.3	0.1438	2.3
Dominion	4.8743	2.3	0.1438	2.3
Dominion	4.2853	2.3	0.1266	2.3
Dominion	5.6776	2.3	0.1663	2.3
Dominion	5.9417	2.3	0.1732	2.3
Dominion	6.3212	2.3	0.1856	2.3
Dominion	5.8520	2.3	0.1708	2.3
Dominion	6.6734	2.3	0.1953	2.3
Dominion	7.0178	2.3	0.2059	2.3
Dominion	5.9447	2.3	0.1746	2.3
Dominion	5.6824	2.3	0.1651	2.3

Note: U/Pb ratios are true ratios corrected based on the methods described in Sharpe and Fayek (2012). Ages are determined from Concordia plots of corrected U/Pb ratios of uraninite analyzed in this study. Error correlations used are 0.9. Errors on Concordia plots are 2σ.

REFERENCES CITED

Sharpe, R. and Fayek, M., 2016, Mass bias corrections for U-Pb isotopic analysis by secondary ion mass spectrometry: Implications for U-Pb dating of uraninite: Rapid Communications in Mass Spectrometry, v. 30, p. 1601–1611.