

APPENDIX 1 – ANALYTICAL METHODS

Assay

Assay data was acquired using the services of Intertek Minerals, Adelaide. A total of 67 elements were measured using a variety of methods as outlined by Ehrig et al. (2012). A summary of data attained can be found in Table A1.

MLA

Automated mineralogy was completed using a Mineral Liberation Analyzer (MLA) at ALS Mineralogy, Brisbane, to attain bulk modal mineralogy (Table A3) and detailed uranium mineralogy (Table A4) for all samples. Details about the MLA system and measurement modes are documented in Gu (2003). Basically it consists of an automated SEM which is controlled by special software to allow for continuous measurement of data. Measurement modes used for the current study were x-ray modal (XMOD) and sparse phase liberation mapping (SPL_Lite). The XMOD method was utilized to attain bulk modal mineralogy of each sample (Table A3), whilst the SPL_Lite method was used to target U- and Pb-bearing grains to attain mineral association and more detailed compositional information pertaining to these phases. These results were then compared to SEM observations to ensure the main U-minerals had been identified. The detailed mineral list used can be found in Table A2, whilst a summary of minerals associated with uraninites can be found in Table A4. Mineral association data is acquired using the SPL_Lite measurement technique. The SPL_Lite method targets selected minerals (uraninite in this case), and a measurement of the perimeter of each uraninite grain is measured. Then the length of the boundary between any other mineral which is touching the uraninite is also measured. A relative proportion (in wt%) of each mineral found in contact with the uraninite can thus be estimated, and this is recorded as

the mineral association. For each sample, an average value is taken for all uraninite grains measured, as displayed in Table A4.

EPMA

Quantitative analysis of uraninites was obtained using a Cameca SX-Five Electron Probe Micro-Analyzer (EPMA) at Adelaide Microscopy, University of Adelaide. A total of 28 elements were measured. The standards used are listed below:

- Astimex Albite for Na $K\alpha$
- Astimex Almandine Garnet for Si $K\alpha$, Al $K\alpha$, Mg $K\alpha$, Fe $K\alpha$
- Astimex Apatite for P $K\alpha$, Astimex Barite for Ba $L\alpha$
- Astimex Celestite for Sr $L\alpha$
- Astimex Marcasite for S $K\alpha$
- Astimex Rhodonite for Mn $K\alpha$
- Astimex Rutile for Ti $K\alpha$
- Astimex Sanidine for K $K\alpha$
- Astimex Gallium Arsenide for As $L\alpha$
- Chalcopyrite (P and H Developments, UK) for Cu $K\alpha$
- Wollastonite (P & H Developments, UK) for Ca $K\alpha$
- Silver Telluride (P & H Developments, UK) for Te $L\alpha$
- Astimex Niobium for Nb $L\alpha$
- Synthetic Pb Glass – K227 (NIST) for Pb $M\beta$
- Rare Earth Glass Standard – REE1 (Drake and Weill 1972) for Y $L\alpha$
- Huttonite (David Steele) for Th $M\alpha$
- UO_2 (David Steele) for U $M\beta$

- single element synthetic REE glasses for Ce L α , La L α , Pr L β , Nd L β , Sm L β , Gd L β (Edinburgh Materials and Microanalysis Centre, University of Edinburgh)
- Zircon (C.M. Taylor Company) for Zr L α .

Key aspects for EPMA include: 1) identification of all elements present; 2) determination of possible spectral interferences; and 3) selection of background positions which accommodate all elements present. High resolution wavelength spectrometer scans were completed to identify all possible elements and to allow for accurate background point setting. The selection of background positions is even more arduous when REY are present due to many cross-interferences (Donovan et al. 1993; Goemann 2011); and these elements are present in varying quantities at OD. Details of crystal type, count times and off-peak interference corrections can be found in Table A5. The HREE-oxides were <mdl (minimum detection limit; identified from full wavelength spectrometer scans).

Acquisition order was adjusted to optimize all spectrometer usage (roughly equal measurement times for all spectrometers) and also measure any elements that may be affected by beam damage first, namely: P K α , Pb M β , Na K α , Mn K α , K K α . Furthermore for these elements, the intensity data was corrected for Time Dependent Intensity (TDI) loss (or gain) using a self-calibrated correction. Both unknown and standard intensities were corrected for dead-time, with standard intensities also being corrected for standard drift over time.

Reproducibility of EPMA results was monitored by measuring select standards (UO₂, K227, REE1 and almandine garnet) as unknowns throughout each EPMA run. This highlighted the stability of the probe over time and also allowed for the removal of any data in cases of significant drift. The standard deviations (SD) for repeated analysis of these standards over a 4 month period were: 0.35 for U (n=44), 0.41 for Pb (n=41), 0.11 for Y (n=52), 0.10 for Si (n=46), and 0.18 for Fe (n=46). This however is dependent on the availability and quality standards available.

Mean MDL values for each element were calculated and can be found in the footer of Tables A6-A10. Based on 1 σ , mean precision (wt%) was also estimated: U \approx 0.073, Pb \approx 0.037, Th \approx 0.017, Na \approx 0.010, Mg \approx 0.0045, Al \approx 0.0034, Si \approx 0.0048, P \approx 0.0043, S \approx 0.0059, K \approx 0.0034, Ca \approx 0.0075, Ti \approx 0.0039, Mn \approx 0.018, Fe \approx 0.013, Cu \approx 0.018, As \approx 0.013, Zr \approx 0.014, Nb \approx 0.017, Y \approx 0.024, Ce \approx 0.016, La \approx 0.012, Pr \approx 0.037, Nd \approx 0.042, Sm \approx 0.035, Gd \approx 0.037, Sr \approx 0.010, Ba \approx 0.012.

Elemental mapping was completed on a zoned uraninite with a total of 13 elements being mapped using PET and LPET crystals. Wavelength-Dispersive-Spectroscopy (WDS) was used to measure: Ce L α , P K α , Ca K α , Y L α , and Pb M α . In contrast, Energy-Dispersive-Spectroscopy (EDS) was used to measure: Si K α , Fe K α , U L α , S K α , Cu K α , La L α , Nd L α , and Ti K α . Dwell time per point was 180 ms.

FIB-SEM

The FEI Helios NanoLab 600 DualBeamTM FIB-SEM platform (Adelaide Microscopy, University of Adelaide) is equipped with Energy Dispersive X-ray Spectroscopy (EDXS) detector, Electron Back-Scattered Diffraction (EBSD) detector, and solid-state Scanning Transmission Electron Microscopy (STEM) detector. The platform allows secondary electron and back-scatter electron imaging and mapping; *in-situ* preparation and thinning of TEM foils, 3D ‘slice and view’ analysis; phase and grain orientation data from Electron Back Scatter Diffraction, and compositional point analysis and mapping via EDXS. Furthermore, the Scanning Transmission Electron facility can be used to image textures and aid in phase identification and mapping of elements of TEM foils with sub-micron resolution. The integrated use of all of these analytical instruments and examples of the methodologies and applications in ore mineralogy is given by Ciobanu et al. (2011).

HR-TEM

A Philips 200CM transmission electron microscope, equipped with a double-tilt holder and Gatan digital camera (Adelaide Microscopy, University of Adelaide), was used for electron diffraction and high-resolution imaging. Measurements on the diffractions were performed using DigitalMicrograph™ 3.11.1. Indexing of minerals was checked by diffraction simulations using WinHREM™ 3.0 software and data from the American Mineralogist Crystal Structure Database (<http://rruff.geo.arizona.edu/AMS/amcsd.php>). Winwulff© 1.4.0 (JCrystalSoft) was also used to interpret electron diffraction patterns. The instrument is also equipped with an Energy Dispersive X-ray (EDX) spectrometer allowing compositional information to be obtained on inclusions. Although qualitative rather than quantitative, the resolution of the EDS extends down to the scale of tens or hundreds of nanometers.

Additional References

Donovan, J.J., Snyder, D.A. and Rivers, M.L. (1993) An improved interference correction for trace element analysis, *Microbeam Analysis*, 2, 23-28.

Drake, M.J. and Weill, D.F. (1972) New rare earth element standards for electron microprobe analysis, *Chemical Geology*, 10, 179-181.

Goemann, K. (2011) Challenges in electron probe microanalysis 60 Years after Castaing: examples from complex uranium and rare earth element minerals from Northern Australian ore deposits, *Microscopy and Microanalysis*, 17, 578-579.

Gu, Y. (2003) Automated scanning electron microscope based mineral liberation analysis: an introduction to JKMRC/FEI Mineral Liberation Analyzer, *Journal of Minerals & Materials Characterization & Engineering*, 2, 33-41.

APPENDIX 2 – COMPOSITIONAL DATA

EPMA data presentation and filtering

Initial data collation involved calculation of means for each textural class within a given sample. However, compositional differences between grains in individual samples contribute to a dilution of the characteristic signatures of each class. For this reason, data are reported as means of analyses from the same grain; separate means are calculated for parts of the grain showing chemical and/or textural similarity.

Further data filtering was undertaken to remove spot analyses which do not correspond to compositionally homogenous uraninite. Points which had higher than expected Al_2O_3 (>0.5 wt%), SiO_2 (>7 wt%), Fe_2O_3 (>3 wt%), Cu_2O (>1.5 wt%), or SO_3 (>0.5 wt%) were excluded. ‘Anomalous’ concentrations of these components are attributable to mineral impurities and fine-grained intergrowths with sericite, chlorite, hematite and sulfides. In some cases, concentrations of one or more elements were $<\text{mdl}$ in individual spot analyses. A value of half the individual spot analysis mdl was utilized for calculation of the mean given in Tables 2-5, A6-A10, and for all subsequent statistical analysis and data plotting.

Attempts were made to combine elemental oxide concentrations which displayed similar relative trends (i.e. elevated vs. depleted). The most apparent of these was wt% ($\text{SiO}_2 + \text{CaO} + \text{Fe}_2\text{O}_3$), referred to as “Alteration Factor” (AF). Elemental ratios were also calculated to see if these aid data segregation and/or if trends could be recognized on the plots. The most important of these is Pb/U, which is commonly used to predict chemical age.

EPMA data

Additional EPMA data to complement data in Tables 2-5 can be found in Tables A6-A10.