Appendix – Analytical Methods

Scanning Electron Microscopy

Scanning electron microscopic (SEM) analysis was conducted using a Quanta 450 Field Emission Gun (FEG) SEM with silicon-drift detector (Adelaide Microscopy, The University of Adelaide). Operating conditions were: 20 keV accelerating voltage, 60 Pa chamber pressure, 0° tilt, 10-11 mm working distance, a spot size of 4-5.

Electron Probe Microanalysis

All quantitative analysis of uraninite composition was obtained using a Cameca SX-Five electron probe micro-analyzer (EPMA) equipped with 5 tunable wavelength-dispersive spectrometers at Adelaide Microscopy, The University of Adelaide. Operating conditions were 15 keV accelerating voltage, 100 nA beam current, 40° takeoff angle, with 0.5 to 1 μm-sized beam. Refer to Macmillan *et al.* (2016) for full details.

Sample Preparation

Standard petrographic thin sections were prepared by Adelaide Petrographics. The first step involved impregnation of drill-core rock sample with araldite GY191 and Hardener HY951. Once cured, the surface araldite was removed by sanding using 1200 grit fixed media (wet and dry sand paper). Sample was then polished on a ceramic lap with 6 µm diamond paste for 2 to 10 minutes as needed. The next steps involved polishing the sample using textmet (Buehler textmet 1500 8” PSA) cloth lap with 3 µm diamond paste for 30 – 60 minutes; with 1 µm diamond paste for 40 – 60 minutes; and with 1 or ¼ Kemet WP diamond solution for 30 – 60 minutes. Then, additional polishing and cleaning steps were included to ensure optimal sample preparation for EBSD analysis. This included a final polish of the sample using Struers MD Chem lap Kent polisher with Struers colloidal silica product (OP-S Non-Dry) for 2 hours. Ultrasonic cleaning was also used as required to avoid cross contamination (especially important for the removal of colloidal silica).

Samples were then coated with a 1.5 to 2 nm thick carbon film via thermal evaporation using a Quorum Q150TE vacuum evaporator to minimize charging during the analysis. The carbon-coat thickness needs to be adequate to prevent surface charging, but needs to be thinner than standard SEM carbon-coating (5-20 nm) as otherwise only a weak electron diffraction pattern will be observed.

Focused Ion Beam-SEM and FIB Electron Backscatter Diffraction

The FEI Helios NanoLab 600 DualBeamTM focused ion beam (FIB)-SEM platform (Adelaide Microscopy, The University of Adelaide) is equipped with an energy dispersive X-ray spectroscopy (EDXS) detector, an EBSD detector, and a solid-state scanning transmission electron microscopy (STEM) detector. Due to the choice of installed analytical detectors and dual electron and ion beams, the following can be attained: secondary electron and back-scatter electron imaging and mapping; the preparation of TEM foils and other 3D ‘slice and view’ microscopic analyses; phase and grain orientation from EBSD; compositional point analysis and mapping from EDXS. Furthermore, the STEM detector can be used to image textures and aid in phase identification and mapping of elements of TEM foils at even higher nanometer resolution. The integrated use of these analytical instruments and their application to micron- and nanoscale characterization of ore minerals is discussed by [Ciobanu *et al.* (2011)](#_ENREF_1).

The EBSD analysis (also referred to as Orientation Imaging Microscopy, OIM) was conducted on an EDAX-TSLTM EBSD system which is equipped with a Hikari camera. Samples were mounted onto an analysis stub using Ag-Dag rather than carbon tape (since carbon tape can melt during the long analysis times, causing the sample to move whilst mounted). For EBSD analysis, the total sample tilt needs to be 70º. This was achieved by fitting the mounted sample on a 45º tilted sample holder, and then further tilting the specimen by 30º. EBSD patterns were collected at 20 kV and 2.7 nA with a working distance ranging between 10 and 13 mm. The OIM Data Collection (Version 5.2) was used for data collection, and the OIM Analysis (Version 4.5) was used for data analysis and interpretation.

Successful EBSD analysis requires the availability of crystallographic structure files for all phases of interest. Structure files for both UO2 and Cu5FeS4 can be found within the TSL database, and were used for EBSD indexing. Measurement of UO2 was of most importance, so all settings and parameters (*i.e.,* gain, exposure) were optimized to attain the best possible electron back-scatter pattern (EBSP) for UO2 rather than other phases within the mapped areas (*i.e.,* bornite and fluorite). The presence of uranium oxides with different stoichiometry (*e.g.*, U3O7, U4O9, U3O8 *etc.*) was also tested, with structural files generated based on the work of Desgranges *et al.* (2009) and Andersson *et al.* (2013). Indexing based on the structural files of the higher oxide phases proved problematic, and in the majority of cases, the uranium phase indexed most closely to UO2 rather than any of the higher oxide phases. Furthermore, high-resolution transmission electron microscopy (HR-TEM) was also used (see below), to test if superstructures/higher oxides of uranium could be observed. In all tested cases there was no evidence for the presence of these oxides, and thus uraninite was assumed to be best represented by the UO2 phase.

For cobweb crystals, the uraninite, bornite and fluorite are all found closely intergrown with one another and unfortunately these all have similar structures. Hence, structural variation alone is insufficient to distinguish between the phases. For this reason energy-dispersive spectroscopy (EDS) data were simultaneously collected. Chemical Indexing (ChI-scan) could then be conducted where the measured element concentrations from EDS could be used as inputs for principal component analysis (PCA), and the components generated by this analysis assigned to individual mineral phases. This is a similar process to that outlined by [Nowell and Wright (2004)](#_ENREF_6).

The raw data collected was then imported into the OIM Analysis software. EBSD data often requires cleanup when there are isolated points that are not indexed or have been indexed incorrectly due to the presence of dust particles on the sample surface, surface roughness, or from overlapping patterns at grain boundaries. The OIM Analysis program offers several cleanup routines, aimed at minimizing incorrect indexing. Two data cleanup methods were used: ‘Grain CI Standardization’ and ‘Grain Dilation’, both with grain tolerance angle of 5º and minimum grain size of 2 µm. The first of these methods is required to recover a portion of the data with a low Confidence Index (CI) value but the correct orientation, thus maximizing the fraction of points that are indexed correctly. The second method modifies the orientations of points which do not belong to any grains but have neighboring points which do belong to grains. This is particularly important for mapping grain boundaries, where the diffracting volume may be a combination of different crystal lattices and may initially be indexed incorrectly. Although cleanup procedures can rectify such issues, caution must be taken to avoid unnecessary data smoothing that may result in the loss of micro-structural detail.

There are a number of ways in which EBSD data can be processed, including: Confidence Index (CI), Image Quality (IQ), and Inverse Pole Figure (IPF) mapping. Additional details for these methods, which are not covered within the manuscript, are given in the subsequent text.

There are two main methods used to assess the reliability of the indexing process, the CI and the ‘fit’ between the measured and theoretical bands. To attain EBSD data, automated indexing was used and involves matching the measured and theoretical EBSP bands. There are usually several possible orientations which may satisfy any given pattern. CI is a measurement of the probability of an orientation solution based on using a voting scheme such that $CI={\left(V\_{1}-V\_{2}\right)}/{V\_{IDEAL}}$, where V1 and V2 are the number of votes for the first and second solutions, and VIDEAL is the total possible number of votes from the detected EBSP bands ([TexSEM 2007](#_ENREF_8)). CI values range from 0 to 1, but can be misleading, and in many cases a low CI (~0.2) can be assigned to a pattern that is correctly indexed. The ‘fit’ parameter defines the average angular deviation between the theoretical EBSP bands and the measured EBSP bands based on the orientation obtained from the voting procedure.

Indexing was completed based on the ‘ideal’ UO2 and bornite structures (see Analytical Methodology). To assess the quality of the obtained EBSD data, comparison of the ‘fit’ value (often reported as the mean angular deviation, MAD) is generally used rather than CI. For the current study, ‘fit’ values ranged between 1.3º and 2.0º for UO2, and from 1.84º and 2.17º for bornite. Comparison of these ‘fit’ values with other published data for uraninite is not possible since uraninite has not traditionally been analyzed using EBSD. However, much of the published EBSD analysis conducted on zircons requires MAD values of < 1.7º for the data to be considered of adequate quality ([Timms *et al.* 2006](#_ENREF_9); [Reddy *et al.* 2007](#_ENREF_7); [Nemchin *et al.* 2009](#_ENREF_5); [Moser *et al.* 2011](#_ENREF_4)). The average ‘fit’ values recorded for uraninite as part of this study are similar to those recorded for the published zircon work, hence the results achieved here were deemed acceptable.

Since optimization of the EBSP was conducted on the uraninite phase, comparison of bornite ‘fit’ values to those in the literature was not conducted. Due to the extensive sample characterization already completed on these samples ([Macmillan *et al.* 2016](#_ENREF_3)) and the simultaneous collection of EDS composition data for the main phases, phase assignment of UO2 versus bornite was considered accurate. Other possible reasons for the poorer quality of bornite indexing compared to UO2 may be attributable to ([Nowell & Wright 2004](#_ENREF_6)): i) different polishing rates for UO2 compared to bornite, thus causing surface relief differences; ii) large changes in the average atomic number of the phases may also lead to variation in the measured EBSP intensity. If these variations are large enough, it may be difficult to correctly identify the band positions within the patterns for all phases. Since measurement of the UO2 was of greatest importance to this study, the settings and parameters were optimized to attain the best possible EBSP for UO2 rather than bornite. Also, since uraninite has a higher atomic weight than bornite it is likely that stronger EBSPs will be produced for uraninite.

High-resolution Transmission Electron Microscopy

A Philips CM200 high-resolution transmission electron microscope (HR-TEM), equipped with a double-tilt holder and Gatan digital camera (Adelaide Microscopy, The 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). Additionally, Winwulff© 1.4.0 (JCrystalSoft) was 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.

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