THE EVOLUTION OF URANINITE, COFFINITE AND BRANNERITE FROM THE OLYMPIC DAM IRON OXIDE-COPPER-GOLD-SILVER-URANIUM DEPOSIT: LINKING TEXTURAL OBSERVATIONS TO COMPOSITIONAL VARIABILITY

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TABLE OF CONTENTS

CHAPTER 3: URANINITE FROM THE OLYMPIC DAM IOCG-U-AG DEPOSIT: LINKING TEXTURAL AND COMPOSITIONAL VARIATION TO TEMPORAL EVOLUTION 67

ABSTRACT

Interpretations of mineral textures have long been used to better understand the processes involved in the formation of mineral deposits. At the Olympic Dam iron-oxide-copper-gold (IOCG)-Ag-U deposit, South Australia, the genesis and evolution of the U-mineralization is difficult to reconstruct unequivocally. Uraninite, coffinite and brannerite are the dominant U-minerals, however previous studies have focussed on the parts of the deposit which have elevated U-grade and are dominated by massive- or vein-type uraninite. Few prior studies documented the textural and chemical variability of these minerals from a broad range of samples throughout the deposit. Based on detailed mineralogical and microanalytical analysis, this study has addressed some of these shortcomings. The data and interpretation thereof allow for models and hypotheses to be made about the formation and alteration mechanisms involved in forming the mineral textures as observed today.

Two generations of uraninite have been identified, and these can be split into four main textural classes. The early generation consists of the primary, zoned and cob-web textural classes. These represent single uraninite crystals with high-Pb and ΣREE+Y (ΣREY), which have been progressively altered both chemically and texturally. The simplest cubic, euhedral morphology is displayed by the primary uraninites, which also often exhibit oscillatory and sectorial zonation of lattice-bound Pb and ΣREY, and commonly have elevated Th contents. Zoned uraninites are typically coarser, sub-euhedral to prismatic grains and contain unique zonation patterns defined by distinct zones of high- and low-Pb and ΣREY which differ to the zoning contained within the primary uraninites. The greatest heterogeneity is observed within the cob-web class, with variable hexagonal to octagonal morphologies, varying degrees of rounding, and rhythmic intergrowths of uraninite with Cu-(Fe)-sulfides ± fluorite from core to margin. There is also a late generation of uraninite which occurs in the highest-grade parts of

the deposit and exists as μm-sized grains to aphanitic varieties which form larger (up to mm-sized) aggregates and vein-fillings. Late uraninites typically have lower-Pb, but higher Ca±Si contents compared to the early generation. The early crystalline uraninites are only sparsely preserved, with the more massive-aphantitic uraninite representing the majority of the uraninite contained within the deposit.

Nanoscale characterization of selected uraninite crystals from the early generation has revealed these have a defect-free fluorite structure, and contain lattice-bound Pb+ΣREY within chemically distinct zones or domains. Micro- and nanoscale inclusions of galena, Cu-(Fe)-sulfides and REY-minerals are also present within the cob-web uraninites. The presence of both lattice-bound Pb within distinct zones and domains, as well as inclusions of galena within these uraninites, are attributed to healing of radiogenic damage via solid-state trace-element mobility, and subsequent fS_2-driven percolation of a Cu-bearing fluid allowing for inclusion nucleation and recrystallization. Crystal-structural formulae for uraninite have been calculated, and the key underlying assumption for these formulae is that lattice-bound radiogenic Pb is present, at least in part, in the tetravalent state. To distinguish the two uraninite generations, in addition to the textural and chemical differences, the oxidation state $[U^{6+}/(U^{4+}+U^{6+})]$ was calculated and it was revealed that these potentially experienced different formation conditions. The early uraninites are thought to have formed from higher temperature, granite-derived hydrothermal fluids, with later hydrothermal alteration of the zoned and cob-web types; whereas the late uraninites have formed hydrothermally at lower temperatures (<250 °C).

Additional characterization of the zoned and cob-web uraninite using electron backscatter diffraction (EBSD) has further developed our understanding of the processes involved in their evolution. Zoned uraninite has been interpreted to have formed as a result of multiple superimposed effects, including alteration of initial oscillatory zoning (as displayed by the primary uraninite) from interaction with hydrothermal fluids and/or from self-annealing of radiation damage. Zones of weakness were created within uraninite as a result of the accumulation of defects and dislocations into tilt boundaries that correlate to one of the active slip systems in uraninite. High diffusivity pathways were generated along these zones of weakness, and aided in element mobility and exchange between uraninite and the hydrothermal fluid/s. The rhythmic intergrowths of uraninite and Cu-(Fe)-sulfides, of which the cob-web uraninites comprise, are attributed to replacement of uraninite by bornite. Replacement is thought to be controlled by the inherent chemical zoning (of Th) within the uraninite crystal, and part of the replacement occurs via coupled dissolution-reprecipitation (CDR) reaction. Initially, the bornite inherits the crystallographic orientation of the parent uraninite, but different orientations of bornite are possible due to epitaxial nucleation. Based on the presence of Cu-(Fe)-sulfide ± fluorite inclusions and the chemistry of the proposed replacement, it is suggested that replacement was driven by a F-rich hydrothermal fluid that was also enriched in Cu, S, Fe and Ca. This is the first known study which integrates the use of EBSD and other micro- and nanoscale characterization techniques to study uraninites and associated minerals. The application of CDR-driven replacement to systems which have no common chemical constituents is also at present unique. The combined use of various micro- and nanoscale characterization techniques has therefore provided some fresh insights into the reactions and enhanced our knowledge about the evolution and progressive *in-situ* alteration of uraninite at Olympic Dam.

Much of the past work conducted on the U-minerals at Olympic Dam has indicated that there were numerous cycles of U dissolution and reprecipitation, but few studies have further explored this hypothesis. Both brannerite and coffinite have also been characterized in the present study. Brannerite has a diverse morphology which ranges from complex irregular-

shaped aggregates, irregularly-shaped blebs, replacement bands, and discrete elongate seams. The internal structure of brannerite consists of randomly orientated hair-like needles and blades to a mix of uniform-massive or bleb-like irregular masses. Compositions range between that of uraniferous rutile and stoichiometric brannerite. The more uniform-massive brannerite blebs, typically have higher ΣREY, Pb, Nb ± As contents compared to the more needle-like, irregular-shaped, aggregated brannerite which contains elevated Fe, Mg ± Mn ± Na ± K. Based on chemical and textural observations, brannerite has been grouped into four distinct groups. Coffinite is typically globular to collomorph in appearance, and is often found on the margin of quartz grains and nucleates from a range of minerals including Cu-(Fe)-sulfides, galena, brannerite, uraninite, and chlorite. Variations in Ca, ΣREY, P ± As ± Nb appear to be responsible for much of the chemical heterogeneity. Three different coffinite groups have been identified based on chemical variability and textural observations, however there are some textural differences and variable mineral associations within these groups. It is likely that the textural heterogeneity is due to local variation in fluid-rock interactions.

It is concluded that brannerite and coffinite are a result of a late-stage U-event(s), and this may have involved the dissolution and/or reprecipitation of earlier precipitated uraninite, or may have involved a fresh influx of U. Factors which support late-stage formation of both brannerite and coffinite include their low-Pb contents and the occurrence of coffinite on the edges of uraninite or brannerite, indicating that the coffinite may have formed after either of these minerals. Additional features like banding, scalloped edges, alteration rinds, variable compositions etc. are also indicative that these minerals may have formed as a result of alteration and by processes which occur after initial deposition of the mineral on which they occur.

The precipitation of uraninite, brannerite and coffinite all require different conditions and chemical components, thus it is unlikely a single fluid could precipitate all of these minerals at one time. It is clear that some of the uraninites precipitated early in the formation of the deposit, but deciphering the subsequent generations of U-minerals is somewhat subjective. The results of this study will clearly document the range of textures and compositions of uraninite, brannerite and coffinite found within the Olympic Dam deposit and will provide evidence for a number of mechanisms which have contributed to their textural appearance. But, the genetic implications of these findings and what they mean for the genesis of the deposit remains unconstrained and will undoubtedly form the basis for future research.

DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of The University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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PREFACE

This thesis comprises of a portfolio of publications which have either been published, or submitted for publication. The journals in which these papers have been published and/or submitted are American Mineralogist, The Canadian Mineralogist, and Mineralogical Magazine. All of the manuscripts are closely related, and summarize much of the micro-and nanoscale analytical data and observations that were made as part of this project. Many recommendations have been made at the end of this thesis as a direct result of the key findings of this research, and it is hoped that many of these are further explored at a later date.

The key aims of this project and significance of the work undertaken are addressed in the Abstract and Section 1.5. There are four papers which form the basis of this thesis:

1. Macmillan, E., Cook, N.J., Ehrig, K., Ciobanu, C.L. and Pring, A. (2016) Uraninite from the Olympic Dam IOCG-U-Ag deposit: linking textural and compositional variation to temporal evolution. American Mineralogist, 101, 1295-1320, <http://dx.doi.org/10.2138/am-2015-5411>.

2. Macmillan, E., Ciobanu, C.L., Ehrig, K., Cook, N.J., and Pring, A. (2016) Chemical zoning and lattice distortion in uraninite from Olympic Dam, South Australia. American Mineralogist <http://dx.doi.org/10.2138/am-2016-5753>.

3. Macmillan, E., Ciobanu, C.L., Ehrig, K., Cook, N.J., and Pring, A. (2016) Replacement of uraninite by bornite via coupled dissolution-reprecipitation: evidence from texture and microstructure. Submitted to The Canadian Mineralogist (in review at the time of thesis submission).

4. Macmillan, E., Cook, N.J., Ehrig, K., and Pring, A. (2016) Chemical and textural interpretation of late stage coffinite and brannerite from the Olympic Dam IOCG-Ag-

U deposit. Submitted to Mineralogical Magazine (in review at the time of thesis submission).

The final chapter of this thesis consists of a complete reference list of all publications cited within any of the manuscripts and chapters contained in this thesis. To avoid duplication, individual chapters do not contain their own reference lists, unless this list is part of a publication. All supplementary data submitted with each of the four main papers can be found in the appendices, as can additional conference abstracts, and other co-authored publications that have been produced. The appendices consist of the following:

A. Supplementary data for Paper 1.

B. Supplementary data for Paper 2.

C. Supplementary data for Paper 3.

D. Supplementary data for Paper 4.

E. Macmillan, E. and Pring, A. (2014) An integrated analytical approach in deciphering complex uranium mineral textures. Proceedings of the Joint International Conference on Nanoscience and Nanotechnology (ICONN) and Australian Conference on Microscopy and Microanalysis (ACMM), 2014, Adelaide, Australia.

F. Macmillan, E., Cook, N.J., Pring, A., Ehrig, K., and Foden, J. (2014) Evolution of uraninites at Olympic Dam: Deciphering complex textures, chemistry and temporal history. Poster presented at the 11th South Australian Exploration and Mining Conference, Adelaide, Australia.

G. Macmillan, E., Cook, N.J., Ciobanu, C.L., Ehrig, K., Kamenetsky, V.S., Thompson, J., and Pring, A. (2015) Evolution of uranium minerals at Olympic Dam, South Australia.

Proceedings from SEG2015 – Conference of the Society of Economic Geologists: World-Class Ore Deposits: Discovery to Recovery, 2015, Hobart, Australia.

H. Macmillan, E., Cook, N.J., Ehrig, K., Ciobanu, C.L. and Pring, A. (2016) The evolution of uraninite, coffinite and brannerite at the Olympic Dam IOCG-U-Ag deposit – linking textural observations to compositional variability. Abstract for Australian Earth Sciences Convention 2016, Adelaide, Australia.

I. Cook, N.J., Ciobanu, C.L., Ehrig, K., Macmillan, E. and Netting, A. (2015) Mineralogical and microanalytical characterization of uranium mineralization. Australian Institute of Mining and Metallurgy (AusIMM) Uranium Conference, Adelaide, June 2015.

J. Ehrig, K., Liebezeit, V., Macmillan, E., Lower, C., Kamenetsky, V.S., Cook, N.J. and Ciobanu, C.L. (2015) Uranium mineralogy versus the recovery of uranium at Olympic Dam. Australian Institute of Mining and Metallurgy (AusIMM) Uranium Conference, Adelaide, June 2015.

K. Li, K., Pring, A., Etschmann, B., Macmillan, E., Ngothai, Y., O'Neill, B., Hooker, A., Mosselmans, F. and Brugger, J. (2015) Uranium scavenging during mineral replacement reactions. American Mineralogist, 100, 1736-1743.

L. Li, K., Brugger, J., Pring, A., Ngothai, Y., Etschmann, B., Zhao, J., and Macmillan, E. (2013) Uranium transport and deposition in iron-oxide-copper-gold deposits (IOCG's): An experimental approach. Goldschmidt 2013 Conference Abstracts, Florence, Italy.