THE EVOLUTION OF APATITE IN IRON-OXIDE-COPPER-GOLD MINERALIZATION OF THE OLYMPIC CU-AU PROVINCE: UNRAVELING MAGMATIC AND HYDROTHERMAL HISTORIES THROUGH CHANGES IN MORPHOLOGY AND TRACE ELEMENT CHEMISTRY

SASHA KRNETA

This thesis is submitted for the degree of Doctor of Philosophy

in the

School of Physical Sciences, Department of Earth Sciences,

at

The University of Adelaide



November 2017

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ABSTRACT

Iron-oxide-copper-gold (IOCG) mineralization is expressed in various forms across some 700 km of the eastern Gawler Craton throughout the N-S striking Olympic Cu-Au Province. In all instances, IOCG mineralisation and the rocks that host it contain variable concentrations of apatite with varying morphological and chemical characteristics. A large body of work has demonstrated apatite's ability to chemically reflect the physiochemical conditions under which it formed and act as tracers of magmatic and hydrothermal processes. This is confirmed throughout the IOCG deposits and prospects studies as part of this work.

Magmatic apatite hosted within the Roxby Downs Granite, the dominant host to the Olympic Dam deposit displays characteristics indicative of a complex magmatic history. Namely, nano-scale, oriented inclusions of pyrrhotite and fluorite within the cores of apatite closely associated with mafic enclaves are indicative of the granites protracted interaction with mafic melts. Their chondrite-normalized rare earth element (REE) fractionation trends are light REE (LREE) enriched and vary when altered by hydrothermal fluids along with the concentrations of several other elements. Magmatic apatite hosted in other intrusives displays similar behaviour when altered, but contains higher concentrations of Cl, Sr, and lower Mn which vary systematically with regards to bulk rock basicity.

Many of the deposits and prospects within the Olympic Cu-Au Province exhibit a chemical and mineralogical zoning grading from early, reduced and later, oxidized hydrothermal assemblages as evidenced by changes in the dominant Fe-oxide, Cu-Fe-sulphide species and as we report herein, changes in apatite. Within the early, reduced, high-temperature expressions of IOCG mineralisation throughout the Province, apatite is abundant, making up, alongside magnetite, the bulk of the mineralisation. Such apatite is dominantly near end-

member fluorapatite characterized by LREE-enriched chondrite-normalized signatures and variable but measurable concentrations of S and Cl.

Overprinting of the magnetite-dominant reduced assemblages by later oxidised hematite-sericite altering fluids results in LREE-loss within the early, hydrothermal and magmatic apatite. Such hematite-sericite altered zones along with newly formed apatite display middle REE (MREE) enriched signatures and are devoid of many of the other trace elements present in magmatic and early hydrothermal apatite, such as S and Cl. This behaviour is observed within the Olympic Dam deposit, as well as the Wirrda Well and Acropolis prospects.

Late apatite hosted within the high-grade massive bornite mineralisation of Olympic Dam and within chalcopyrite-barite-rich zones of the Acropolis prospects displays extreme MREE-enriched REE-signatures with positive Eu-anomalies. The latter characteristic is unique amongst all other apatite examined as part of this study and highly anomalous globally. Numerical modeling shows that the evolution in apatite trace elements, and in particular REE signatures is the direct result of fluid evolution within IOCG systems. Given this association, the various assemblages within IOCG systems are classified according to REE-signature and the use of apatite in mineral exploration and as a petrogenetic tool is discussed in detail.

The modeling of REE behaviour in hydrothermal fluids typical of IOCG mineralised systems has offered important insights into the transport and deposition of REE within Olympic Dam and possibly other IOCG systems. Specifically, REE are transported primarily as REE-Cl species and deposited under conditions of suppressed REE-Cl activity. The propensity of the LREE to occur as Cl-complexes explains both their significantly greater enrichment in IOCG systems when compared to the HREE, as well as their preferential depletion in apatite during hematite-sericite alteration.

DECLARATION

I certify that this work contains no material which has been accepted for the award of any

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ACKNOWLEDGEMENTS

Firstly, I would like to express my deepest gratitude to the two hardest working and most passionate geologists at the University of Adelaide, my academic supervisors Prof. Nigel Cook and Dr. Cristiana Ciobanu. Thank you for your tireless support, encouragement and advice. I feel fortunate to have been your student. The knowledge that I have acquired thanks to your willingness to go above and beyond stands as the solid foundation on which my future success, professional and otherwise, will be built. For this I am forever grateful. Thank you Nigel for your patience and support, particularly with regards to the energy you invested in making me a better writer. Cristi, thank you for your unwavering support and for pushing me to accomplish even the most impossible tasks, for the late nights on the SEM and the Sunday afternoons.

I would also like to express my gratitude to my external supervisor, Dr Kathy Ehrig for her support, advice, encouragement and for her willingness to make time for, and entertain the ideas of a young geologist. Thank you for your genuine interest and support, thank you for all the discussions, not only with regards to the research, but the mining industry and life in general. I would also like to express my gratitude for the financial support that I received from BHP and the site visits to Olympic Dam that you made possible. The next coffee is on me.

Thank you to all of the staff at Adelaide Microscopy for their assistance on countless occasions. In particular Mr. Angus Netting, Mr. Ken Neubauer, Ms Aoife McFadden, Dr Animesh Basak and the especially "the man with the plan" Dr. Benjamin Wade.

I would also like to thank my fellow Ph.D students Luke George, Matthew Paul and

especially my dear friend Alkis Kontonikas-Charos for all of your support, advice and all the

good times that we have shared over the years.

A big thank you to all of the friends and family that I am so fortunate to have, especially my

parents Zlatko and Aldina Krneta and my younger siblings Sanja and Sara for their support

and encouragement, particularly during those times that were the hardest, and for making me

the man that I am today. Thank you, to my close friends Ben Crago and Petar Kolundzic and

my fiancées family for all of their encouragement and support.

Lastly, I would like to thank my fiancée Rhiannon for the support and encouragement that she

has given me over the course of my Ph.D and for her unwavering belief that I could do it.

Thank you.

"Our virtues and our failings are inseparable, like force and matter. When they separate, man

is no more."

-Nikola Tesla

"Life without dreams is meaningless, impoverished and grey."

-Dr. Nele Karajlic

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PREFACE

This thesis comprises of a portfolio of manuscripts which have been published or prepared for submission, in international peer-reviewed journals. The journals in which these papers have been published are 'Lithos' (Chapter 2, published), 'Minerals' (Chapter3, published), 'Journal of Geochemical Exploration' (Chapter 4, published). Chapters 5 and 6 will be submitted for publication in a revised and abridged form. All five chapters are closely related, and summarize key findings and interpretations of apatite morphology and geochemistry within iron-oxide copper-gold systems, that were made as part of this project. 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 these are explored at a later date.

The five chapters which form the basis of this thesis are:

- 2. Krneta, S., Ciobanu, C.L., Cook, N.J., Ehrig, K. and Kontonikas-Charos, A., 2016. Apatite at Olympic Dam, South Australia: a petrogenetic tool. Lithos, 262, 470-485.
- Krneta, S., Ciobanu, C.L., Cook, N.J., Ehrig, K. and Kontonikas-Charos, A. 2017.
 Rare earth element behaviour in apatite from the Olympic Dam Cu-U-Au-Ag deposit,
 South Australia. Minerals 7(8), 135.
- Krneta, S., Cook, N.J., Ciobanu, C.L., Ehrig, K. and Kontonikas-Charos, A., 2017.
 The Wirrda Well and Acropolis prospects Gawler Craton, South Australia: insights into evolving fluid conditions through apatite chemistry. Journal of Geochemical Exploration 181, 276-291.
- 5. Krneta, S., Ciobanu C.L., van der Kerke, K, Cook, N.J., Ehrig, K. and Basak, A. Crystal structural modification and mineral inclusions in apatite from Olympic Dam, South Australia. (to be submitted in a revised and abridged form)

6. Krneta, S., Ciobanu, C.L., Cook, N.J. and Ehrig, K. Numerical modeling of REE trends in fluorapatite: snapshots of fluid evolution in a giant hydrothermal system. (to be submitted in a revised and abridged form)

Key findings and implications of this work, as well as future avenues of research, are summarized in Chapter 7.

Chapter 8 contains all supplementary material for the main papers outlined above, as well as additional conference abstracts, and other co-authored publications that have been generated during the PhD candidature. The additional material is as follows:

- A. Supplementary material for Chapter 2 (Paper 1).
- B. Supplementary material for Chapter 3 (Paper 2).
- C. Supplementary material for Chapter 4 (Paper 3).
- D. Supplementary material for Chapter 6.
- E. Krneta, S., Ciobanu, C.L., Cook, N.J., Ehrig, K. and Kamenetsky, V.S., 2016. REY-signatures in apatite monitor the evolution of IOCG systems:examples from Olympic Dam and Acropolis, South Australia. Abstract, Australian Earth Science Convention, Adelaide, 26-30 June, 2016, unpaginated.
- F. Krneta, S., Ciobanu, C.L., Cook, N.J., Ehrig, K., Kamenetsky, V.S., 2015. Apatite in the Olympic Dam Cu–U–Au–Ag deposit. In: Mineral Resources in a Sustainable World, Proceedings, 13th Biennial SGA Meeting, Nancy, France, August 2015, Vol. 3, pp. 1103-1106.
- G. Krneta, S., Ciobanu, C.L., Cook, N.J., Ehrig, K. and Kamenetsky, V.S., 2016. REY-signatures in apatite monitor the evolution of IOCG systems: examples from

Olympic Dam and Wirrda Well, South Australia. Abstract, International Geological Conference, Cape Town, South Africa, August 27- September 4 2016, unpaginated.

- H. Krneta, S., Ciobanu, C.L., Cook, N.J., Ehrig, K. and Kamenetsky, V.S., 2015. Apatite in the Olympic Dam IOCG system and adjacent prospects insights into magmatic and hydrothermal evolution. Abstract, Society of Economic Geologists Conference, Hobart, TAS, September 27-30, unpaginated.
- I. Krneta, S., Ciobanu, C.L., Cook, N.J., Ehrig, K. and Kamenetsky, V.S., 2016. Apatite in the Olympic Dam IOCG system and adjacent prospects insights into magmatic and hydrothermal evolution. Conference poster, Society of Economic Geologists Conference, Hobart, TAS, September 27-30.
- J. Kontonikas-Charos, A., Ciobanu, C.L., Cook, N.J., Ehrig, K., Krneta, S.K., Kamenetsky, V.S., 2017. Feldspar evolution in the Roxby Downs Granite host to Feoxide Cu-Au-(U) mineralisation at Olympic Dam, South Australia. Ore Geology Reviews 80, 838-859.

The final chapter of this thesis consists of a complete reference list of all publications cited within any of the manuscripts, chapters, supplementary and additional material submitted as a component this thesis.