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

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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 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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"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

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.
3. 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.
4. 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 Fe-oxide 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.