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# Scavenging of Uranium in Experimental and Natural Samples

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# Table of Contents

<b>Abstract</b> .....	<b>v</b>
<b>Declaration</b> .....	<b>vii</b>
<b>Acknowledgements</b> .....	<b>ix</b>
<b>List of publications</b> .....	<b>xi</b>
<b>Chapter 1 Introduction</b> .....	<b>1</b>
1.1 Uranium Production in Australia .....	3
1.2 Uranium Ores Deposits .....	5
1.3 Uranium Minerals .....	6
1.4 Mineral Replacement and Coupled Dissolution Reprecipitation Mechanism .....	7
1.5 Scavenging of Trace and Minor Elements in CDR Reactions .....	11
1.6 Mineral Replacement Reactions in the Fe-Cu-S system .....	13
1.7 Research Objects .....	16
1.8 References .....	17
<b>Chapter 2 Research methodology</b> .....	<b>21</b>
2.1 Natural samples .....	23
2.2 Synthesis of uraninite .....	25
2.3 Preparation of buffer solution .....	25
2.4 Hydrothermal experiments .....	26
2.5 Powder X-ray diffraction (XRD) .....	28
2.6 Scanning electron microscopy (SEM) .....	29
2.7 Transmission electron microscopy (TEM) .....	31
2.8 Chemical analysis of solid products .....	33
2.9 X-ray absorption near edge structure (XANES) spectra analysis .....	34
2.10 Megapixel synchrotron X-ray fluorescence mapping and data analysis .....	35
2.11 References .....	36
<b>Chapter 3 Uranium scavenging during mineral replacement reactions</b> .....	<b>39</b>
3.1 Abstract .....	43

3.2	Introduction .....	44
3.3	Starting materials .....	45
3.4	Experiments and characterization .....	47
3.5	Results .....	48
3.5.1	U-free runs .....	48
3.5.2	UO <sub>2+x</sub> (s) as uranium source .....	49
3.5.3	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> as uranium source .....	52
3.5.4	XANES spectroscopy .....	53
3.6	Discussion .....	55
3.6.1	Effect of uranium on the reaction within the hematite core .....	55
3.6.2	Effect of uranium on the replacement reaction and uranium scavenging .....	56
3.6.3	Implications for element scavenging and IOCG deposits .....	58
3.7	Acknowledgements .....	61
3.8	References .....	61
<b>Chapter 4 The exsolution of chalcopyrite from bornite digentite solid solution under hydrothermal conditions: an example of a back replacement reaction.....</b>		<b>65</b>
4.1	Abstract .....	69
4.2	Introduction .....	70
4.3	Samples and methods .....	71
4.4	Results and Discussion .....	72
4.5	Final words .....	80
4.6	Acknowledgement .....	81
4.7	References .....	81
<b>Chapter 5 Ore petrography using megapixel X-ray imaging: Rapid insights into element distribution and mobilisation in complex Pt and U-Ge-Cu ores .....</b>		<b>83</b>
5.1	Abstract .....	89
5.2	Introduction .....	91
5.2.1	Chemical ore petrography and aims of this study .....	91
5.2.2	Mapping elemental distribution in ore samples .....	91
5.2.3	Hard X-ray fluorescence mapping: the revolution of fast detectors .....	93

5.3	Sample selection and geological background .....	96
5.4	Methods.....	99
5.4.1	Sample preparation.....	99
5.4.2	Sample characterisation.....	99
5.4.3	MSXRF mapping and data analysis .....	100
5.5	Results.....	101
5.5.1	Platinum distribution in a mineralized saprolith sample from Fifield, NSW.	101
5.5.2	Roll-front deposits in the Lake Frome Embayment: complex textures and elemental composition in low-temperature ore forming environments .....	104
5.5.3	Germanium mobility in a polymetallic hydrothermal system at Barrigão .....	107
5.5.4	Moonta IOCG: late uranium enrichment associated with mineral replacement reactions.....	110
5.6	Discussion .....	113
5.6.1	Imaging the distribution of grains of precious metals.....	113
5.6.2	Fast mapping of the distribution of dilute componenets in ores .....	114
5.6.3	Unravelling processes by linking chemistry with textural observation.....	115
5.7	Outlook.....	117
5.8	Acknowledgements.....	118
5.9	References.....	118
<b>Chapter 6 Conclusion.....</b>		<b>129</b>
6.1	Mechanisms of uranium scavenging in mineral replacement reaction .....	131
6.1.1	Uranyl nitrate as uranium source.....	131
6.1.2	UO <sub>2+x</sub> as uranium source .....	132
6.2	Dissolution-precipitation and exsolution reactions.....	132
6.3	Observation on the natural uranium-bearing minerals.....	133
6.4	Future work.....	135
6.4.1	Uranium scavenging during other mineral replacement reactions.....	135
6.4.2	Synthesise brannerite under hydrothermal conditions .....	136
6.5	References.....	138
<b>Appendix A .....</b>		<b>141</b>
<b>Appendix B.....</b>		<b>149</b>
<b>Appendix C .....</b>		<b>159</b>



# Abstract

The hypothesis that interface coupled dissolution-precipitation reactions (ICDR) can play a key role in scavenging minor elements has been investigated via exploring the fate of U during the experimental sulfidation of hematite to chalcopyrite and the exsolution of chalcopyrite from bornite digenite solid solution (*bdss*) under hydrothermal conditions. The results of experiments with two kinds of Uranium (U) sources; either as solid  $\text{UO}_{2+x}(\text{s})$  or as a soluble uranyl complex, differed from the U-free experiments. In the reactions from hematite to chalcopyrite under 220-300 °C hydrothermal conditions, pyrite precipitated initially, before the onset of chalcopyrite precipitation. In addition, when  $\text{UO}_{2+x}(\text{s})$  was included in the experiments, enhanced hematite dissolution led to increased porosity and precipitation of pyrite+magnetite within the hematite core. However, in uranyl nitrate bearing experiments, abundant pyrite formed initially, before being replaced by chalcopyrite. Uranium scavenging was mainly associated with the pyrite precipitation, as a result that a thin U-rich layer along the original hematite grain surface precipitated out. In the reactions of chalcopyrite exsolution from *bdss* during annealing under hydrothermal conditions in a solutions nominally containing Cu(I) and hydrosulfide in a  $\text{pH}_{25^\circ\text{C}} \sim 6$  acetate buffer, a similar U-rich rim was observed along the original grain when uranyl nitrate as U-source was included in the reactions. The precipitation of uranium was related to the presences of  $\text{HS}^-$  in buffer. Chemical mapping and X-ray absorption near edge structure (XANES) spectroscopy showed the  $\text{UO}_{2+x}(\text{s})$  was the mainly restricted to the U-rich layer. The two sets of experiments demonstrate that the presence of minor components can affect the pathway of ICDR reactions. Reactions between U- and Cu-bearing fluids and hematite or chalcopyrite can explain the Cu-U association prominent in some iron oxide-copper-gold (IOCG) deposits.

In this study, synchrotron-based X-ray fluorescence (SXRF) mapping was used to trace the distribution of uranium in natural samples from different geological contexts (sandstone-hosted U-deposit; IOCG) for investigating the deportment of uranium and its paragenesis in the context of thin-section scale textural complexity. It has been confirmed that the enrichment of U occurs via late dissolution-reprecipitation reactions in the bornite ores of the Moonta and Wallaroo IOCG deposits (South Australia), and that the U distribution in the ores of sandstone-hosted U-deposit is complex. Image analysis also revealed a number of new results for other minor elements, e.g. (i) the distribution of  $\mu\text{m}$ -sized Pt-rich grains and evidence for Ti-mobility during the formation of schistosity at the Fifield Pt prospect (New South Wales, Australia); (ii) the presence of Ge contained in organic matter and of Hg minerals associated within quartzite clasts in the Lake Frome U ores (South Australia); and (iii) confirmation of the two-stage Ge-enrichment in the Barrigão deposit, with demonstration of the presence of Ge in solid solution in the early chalcopyrite (Portuguese Iberian Pyrite Belt).

# 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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# List of publications

This PhD thesis is of publication format. Three papers constructed this PhD thesis, including

## ONE PUBLISHED PAPER

- 1 **Kan Li**; Allan Pring; Babara Etschmann; Edeltraud Macmillan; Yung Ngothai; Brian O'Neill; Anthony Hooker; Fred Mosselmans; Joel Brugger, Uranium scavenging during mineral replacement reactions, *American Mineralogist*, 2015, 100, 8-9: 1728-1735

## ONE ACCEPTED MANUSCRIPT:

- 2 **Kan Li**; Barbara Etschmann; Nicholas Rae; Frank Reith; Chris G. Ryan; Robin Kirkham; Daryl Howard; Diogo R.N. Rosa; Carla Zammit; Allan Pring; Yung Ngothai; Antony Hooker; Joël Brugger, Ore petrography using megapixel X-ray imaging: Rapid insights into element distribution and mobilisation in complex Pt and U-Ge-Cu ores, accepted pending revisions in *Economic Geology*

## ONE MANUSCRIPT IN DRAFT:

- 3 **Kan Li**; Joël Brugger; Yung Ngothai; Allan Pring, The exsolution of chalcopyrite from bornite digenite solid solution under hydrothermal conditions: an example of a back replacement reaction, to be submitted to a geochemistry journal.

## OTHER PUBLICATIONS RELATED TO THIS THESIS:

### REFEREED JOURNAL PAPERS

- A Carla Zammit; **Kan Li**; Barbara Etschmann; Joël Brugger; Frank Reith, Geobiology of *in situ* uranium leaching, *Advanced Materials Research*, 2013, 825, 372-375
- B Victor M. Okrugin; Elena Andreeva; Barbara Etschmann; Allan Pring; **Kan Li**; Jing Zhao; Grant Griffiths; Gregory R. Lumpkin; Gerry Triani; Joël Brugger, Microporous gold: Comparioson of textures from nature and experiments, *American Mineralogist*,

2014, 99, 1171-1174

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- C Jing Zhao; Allan Pring; Joël Brugger; Fang Xia; **Kan Li**; Yung Ngothai, Hydrothermal mineral replacement reactions and their applications in mining and processing, 5<sup>th</sup> *International Seminar on Process Hydrometallurgy, 2013, Santiago, Chile*