
Scavenging of Uranium in Experimental and Natural Samples

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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 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 μm -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

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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: Comparison of textures from nature and experiments, *American Mineralogist*,

2014, 99, 1171-1174

REFEREED CONFERENCE PAPER

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