MECHANISMS AND KINETICS OF PSEUDOMORPHIC MINERAL REPLACEMENT REACTIONS AND THEIR APPLICATIONS IN MATERIALS SYNTHESES

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This thesis is submitted for the degree of Doctor of Philosophy

in

School of Chemical Engineering

at

The University of Adelaide

February 2009

Adelaide, Australia

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Abstract

Although pseudomorphic mineral replacement reactions are common in all geological environments and many industrial processes, few studies have been devoted to understanding the mechanisms and kinetics of these reactions. The subjects of this thesis are to understand the mechanisms and kinetics of pseudomorphic replacement reactions by detailed experimental studies on model systems, and to apply the principle of these reactions in the syntheses of novel materials.

The mechanisms of pseudomorphic replacement reactions were revealed by a thorough kinetic and textural study of the replacement of pentlandite, $(Fe,Ni)_9S_8$, by violarite $(Ni,Fe)_3S_4$, under mild hydrothermal conditions (80˚C to 210˚C). Reaction kinetics shows a complex dependence on various physical and chemical parameters including temperature, sample texture of mineral assemblage, pH, and concentrations of various reaction species (e.g., oxidants, metal ions). Textural observations show a sharp phase boundary and a porous product. Both kinetic and textural results indicate a coupled dissolution–reprecipitation mechanism. The coupling between pentlandite dissolution and violarite precipitation is controlled by local solution chemistry as well as the epitaxial nucleation of violarite onto the pentlandite substrate. The latter was confirmed by electron backscatter diffraction (EBSD) analysis that pentlandite and violarite share a common crystallographic orientation. The rate limiting step depends on solution chemistry and controls the degree and length scale of pseudomorphism: pentlandite dissolution being rate limiting at mild acidic to neutral conditions ($1 < pH < 6$) results in high degree pseudomorphism (length

scale <20 nm), of which violarite precisely preserves not only the overall morphology but also textural details (e.g., lamellae) of pentlandite; while violarite precipitation being rate limiting in strong acidic conditions (pH 1) the reactions produces low degree pseudomorphism (length scale ~10 μm), of which the overall morphology is only roughly preserved without preservation of textural details.

The principle of pseudomorphic replacement reactions have been applied to the syntheses of two complex thiospinels, violarite, $(Ni,Fe)_3S_4$, and linnaeite, Co_3S_4. Violarite is very difficult to prepare by the traditional dry synthesis route, which requires several months' annealing and still only results in an impure product. By contrast, pure violarite was synthesized by hydrothermal pseudomorphic replacement within a few days, and the composition is tunable by simply changing temperature, the compositions of the solution and of the pentlandite precursor.

Pseudomorphic replacement reactions have also been applied to the syntheses of zeolite monoliths composed of three-dimensional ordered arrays of nanocrystals with uniform size and crystallographic orientation. Such materials have potential applications but have never been prepared. This work demonstrates that pseudomorphic replacement reactions are suitable routes for this purpose by synthesizing monoliths of analcime ($NaAlSi_2O_6 \cdot H_2O$) as an illustration using natural leucite ($KAlSi_2O_6$) crystals as precursors. The leucite crystals have inherent three-dimensional hierarchical structure of uniformly sized lamellar twins arising from the cubic to tetragonal phase transition. Such uniform lamellar texture was

precisely preserved during hydrothermal pseudomorphic replacement reactions in pH buffered NaCl solutions, resulting in three-dimensionally ordered arrays of cubic analcime nanocrystals. Moreover, these analcime nanocrystals have uniform size and crystallographic orientation, which is due to epitaxial nucleation and growth controlled by the leucite precursors. Pseudomorphic mineral replacement reactions make possible the syntheses of zeolites monoliths with very sophisticated shapes and could be used to synthesize other advanced functional materials.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma 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.

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Signed…….. Date ……..

Acknowledgements

Firstly I would like to thank my supervisors Prof. Allan Pring, Dr Yung Ngothai, A/Prof. Brian O'Neill, and Prof. Guorong Chen, for introducing me to this exciting project and for their endless enthusiasm, support, encouragement, and numerous invaluable advices and discussions in the last 3 years. Without their great input I would never have had such an incredible international experience or produced this thesis.

I am particularly grateful to Dr. Joël Brugger of South Australian Museum who went through all the details to clarify many points in the published papers. He constantly encouraged and motivated me and was always available to share problems and successes. I am also indebted to Mr. Jason Peak, Mr. Brian Mulcahy, and Mr. Jeffrey Hiorns of Chemical Engineering Workshop for building up and maintaining the hydrothermal reactors, to Dr. Peter Self, Mr. John Terlet, Mr. Angus Netting, and Mr. Len Green of Adelaide Microscopy for their technical assistance with FESEM, EPMA and EBSD instruments, to Mr. Ben McHenry of South Australian Museum for prompt responses to requests for chemicals and lab equipments, and to Ms. Mary Barrow of the School General Office for assistance with administrative matters relating to my PhD candidature. I appreciate Prof. Andrew Putnis and Dr. Christine Putnis of University of Münster, who shared their knowledge of replacement reactions as well as crystal twinning. I am grateful to Mr. Steve Laurie of the Sedgwick Museum, University of Cambridge, for supplying the leucite crystals. I also acknowledge Dr. Andrew Studer of Australian Nuclear Science and Technology Organization for helping me with my AINSE Award. I offer my special thanks to A/Prof. Haipeng Wang of Curtin University of Technology for the assistance in admission and scholarship applications, unreserved suggestions of doing a PhD, and constant encouragement over emails and phones.

I would also like to thank fellow PhD students Brake Tooth, Peter Elliott, Gujie Qian and Yoo Hyun Sung, Postdoctoral fellows Dr. Barbara Etschmann and Dr. Pascal Grundler, and Honorary Research Associate Dr. Mike Snow, for some insightful discussions and suggestions, or experimental assistance. Additional thanks go to Dr. Christophe Tenailleau for some preliminary experimental data, and a Singapore exchange student Miss. Winnie Wanni Lim, for conducting some flow-through experiments at the early stage of the project.

I wish to acknowledge Australian Department of Education, Science and Training, for the Endeavour International Postgraduate Research Scholarship, University of Adelaide, for the living allowance, Australian Institute of Nuclear Science and Engineering, for the AINSE Postgraduate Research Award, and South Australian Museum, for the SAM Supplementary Scholarship.

Finally, I thank my parents and sister for their continual support and understanding. I would like to share this gorgeous moment with my wife, Jinwen, who deserves special thanks for always being supportive and patient.

Preface

This thesis is submitted as a portfolio of publications according to the "*PhD Rules & Specifications for Thesis*" of the University of Adelaide. The journals in which the papers were published or submitted are closely related to the research field of this work. The citation information is listed and the journals are ranked in the order of impact factor in reference to their scientific significance (*Journal Citation Report 2007*, Thomson ISI).

Journal Title	Impact Factor†	2007 Total Cites*	Immediacy Index‡	Cited Half-life§
Chemistry of Materials	4.883	43179	0.632	5.5
Geochimica et Cosmochimica Acta	3.665	32873	0.719	>10
Reaction Kinetics and Catalysis Letters	0.584	1191	0.084	8.2

† The journal Impact Factor is the average number of times articles from the journal published in the past two years have been cited in the JCR year.

* The Total Cites is the total number of citations to the journal in the JCR year.

‡ Immediacy Index measures the average number of times that an article, published in a specific year within a specific journal, is cited over the course of the same year.

§ Cited Half-life measures the number of years, going back from the current year, that account for half the total citations received by the cited journal in the current year.

The main body of the thesis is based on the following four papers.

1. **Xia, F.**, Brugger, J., Chen, G., Ngothai, Y., O'Neill, B., Putnis, A., and Pring, A., (2009) Mechanism and kinetics of pseudomorphic mineral replacement reactions: A case study of the replacement of pentlandite by violarite. *Geochimica et Cosmochimica Acta*, **73**, 1945-1969. Copyright of this paper belongs to Elsevier Ltd.

2. **Xia, F.**, Zhou, J., Pring, A., Ngothai, Y., O'Neill, B., Brugger, J., Chen, G., and Colby, C., (2007) The role of pyrrhotite (Fe_7S_8) and the sample texture in the hydrothermal transformation of pentlandite ($(Fe,Ni)_9S_8$) to violarite ($(Ni,Fe)_3S_4$). *Reaction Kinetics and Catalysis Letters* **92**, 257-266. Copyright of this paper belongs to Akadémiai Kiadó and Springer Publishers.
3. **Xia, F.**, Zhou, J., Brugger, J., Ngothai, Y., O'Neill, B., Chen, G., and Pring, A., (2008) Novel route to synthesize complex metal sulfides: hydrothermal coupled dissolution-reprecipitation replacement reactions. *Chemistry of Materials* **20**, 2809-2817. Copyright of this paper belongs to American Chemical Society.
4. **Xia, F.**, Brugger, J., Ngothai, Y., O'Neill, B., Chen, G., and Pring, A., (2009) Three dimensional ordered arrays of nanozeolites with uniform size and orientation by a pseudomorphic coupled dissolution-reprecipitation replacement route. Submitted to a chemistry journal.

Some relevant components of the work have been published in other journal papers, peer-reviewed conference papers, and peer-reviewed conference abstracts. These have been included in the thesis as appendices.

A. **Xia, F.**, Chen, G., Pring, A., Brugger, J., Ngothai, Y., O'Neill, B., Colby, C., Tenailleau, C., Wang, H., and Yang, Y. (2007) Kinetics and mechanism of hydrothermal alteration from pentlandite to violarite. *Acta Geologica Sinica-Chinese Edition* **81**, 1378-1390. Copyright of this paper belongs to Geological Society of China.
B. **Xia, F.**, Pring, A., Ngothai, Y., O'Neill, B., Brugger, J., Chen, G., and Colby, C. (2007) The catalytic role of pyrrhotite in hydrothermal alteration of pentlandite to violarite. *Chemeca 2007 – the 35th Annual Australian Chemical Engineering Conference*, 2007, Melbourne, Australia.

C. **Xia, F.**, Ngothai, Y., Brugger, J., O'Neill, B., Chen, G., and Pring, A. (2009) Mechanism of pseudomorphic mineral replacement reactions revealed by a combined textural and kinetic study. *Geofluids Conference VI, 2009*, Adelaide, Australia. Published in *Journal of Geochemical Exploration,* 2009, **101**, 113. Copyright of this paper belongs to Elsevier Ltd.

D. **Xia, F.**, Zhao, J., Brugger, J., Ngothai, Y., O'Neill, B., Chen, G., and Pring, A. (2009) Preservation of multiscale lamellar twinning texture and crystallographic orientation in the replacement of leucite by analcime. *Geofluids Conference VI, 2009*, Adelaide, Australia. Published in *Journal of Geochemical Exploration,* 2009, **101**, 115. Copyright of this paper belongs to Elsevier Ltd.

E. **Xia, F.**, Pring, A., Ngothai, Y., O'Neill, B., Brugger, J., Chen, G., and Colby, C. (2007) Hydrothermal synthesis of $FeNi_2S_4$, a thiospinel. *Chemeca 2007 – the 35th Annual Australian Chemical Engineering Conference*, 2007, Melbourne, Australia.

F. Brugger, J., **Xia, F.**, and Pring, A. (2008) Mineral synthesis using the coupled dissolution-reprecipitation route. *Goldschmidt 2008 - the 18th V.M. Goldschmidt™ Conference*, 2008, Vancouver, Canada. Published in *Geochimica et Cosmochimica Acta*, 2008, **71**, A118. Copyright of this paper belongs to Elsevier Ltd.

G. **Xia, F.**, Ngothai, Y., Brugger, J., O'Neill, B., Chen, G., and Pring, A. (2009) Three dimensionally ordered arrays of nanozeolites with uniform orientation. *The 8th World Congress of Chemical Engineering*, 2009, Montréal, Canada.

H. **Xia, F.**, Zhao, J., Brugger, J., Ngothai, Y., O'Neill, B., Chen, G., and Pring, A. (2009) Experimental synthesis of auriferous arsenian pyrite/marcasite by pseudomorphic replacement of pyrrhotite. *Geofluids Conference VI, 2009*, Adelaide, Australia. Published in *Journal of Geochemical Exploration,* 2009, **101**, 114. Copyright of this paper belongs to Elsevier Ltd.

I. **Xia, F.**, Brugger, J., A, Pring. (2009) Arsenian pyrite formation: solid-state diffusion or dissolution-reprecipitation replacement? *SGA 2009 - The 10th Biennial Meeting of The Society for Geology Applied to Mineral Deposits*, 2009, Townsville, Australia.

J. **Xia, F.**, Pring, A., Ngothai, Y., O'Neill, B., Brugger, J., Chen, G., and Colby, C. (2007) The mechanism of pentlandite oxidation in the temperature range 530-600 ºC. *Chemeca 2007 – the 35th Annual Australian Chemical Engineering Conference*, 2007, Melbourne, Australia.

K. **Xia, F.**, Pring, A., Ngothai, Y., O'Neill, B., Brugger, J., Chen, G., and Colby, C. (2007) The kinetics of pentlandite oxidation in the temperature range 530-600 ºC. *Chemeca 2007 – the 35th Annual Australian Chemical Engineering Conference*, 2007, Melbourne, Australia.

L. Zhao, J., **Xia, F.**, Chen, G., Brugger, J., Grundler, P., and Pring, A. (2009) Hydrothermal calaverite decomposition using the orthogonal experimental design method. *Geofluids Conference VI, 2009*, Adelaide, Australia. Published in *Journal of Geochemical Exploration,* 2009, **101**, 130. Copyright of this paper belongs to Elsevier Ltd.