
HYDROTHERMAL STUDIES ON MINERAL REPLACEMENT REACTIONS IN THE GOLD-SILVER- TELLURIUM AND COPPER-IRON-SULFUR SYSTEMS

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TABLE OF CONTENTS

| | |
|--|-----|
| ABSTRACT | v |
| DECLARATION | vii |
| ACKNOWLEDGEMENTS | ix |
| CHAPTER 1 INTRODUCTION | 1 |
| 1.1 Mineral replacement reaction and coupled dissolution reprecipitation mechanism | 4 |
| 1.1.1 Pseudomorphism..... | 8 |
| 1.1.2 Porosity and fine cracks..... | 10 |
| 1.2 Mineral replacement reactions among gold-(silver)-tellurides | 13 |
| 1.3 Mineral replacement reactions among copper iron sulfides | 17 |
| 1.4 Research objects..... | 23 |
| 1.5 References | 24 |
| CHAPTER 2 RESEARCH METHODOLOGY | 33 |
| 2.1 Natural mineral samples..... | 35 |
| 2.2 Preparation of buffer solution | 36 |
| 2.3 Hydrothermal experiments..... | 38 |
| 2.4 Powder X-ray diffraction | 40 |
| 2.5 Scanning electron microscope (SEM)..... | 43 |
| 2.6 Electron backscatter diffraction (EBSD) | 44 |
| 2.7 Chemical analysis of solid products..... | 47 |
| 2.8 Solution inductively coupled plasma mass spectrometry (ICP-MS) | 48 |
| 2.9 References | 49 |
| CHAPTER 3 DISSOLUTION-REPRECIPITATION VERSUS SOLID-STATE DIFFUSION: MECHANISM OF MINERAL TRANSFORMATION IN SYLVANITE, (AuAg)₂Te₄, UNDER HYDROTHERMAL CONDITIONS | 51 |
| Abstract | 55 |

| | |
|--|----|
| 3.1 Introduction | 55 |
| 3.2 Samples and methods | 56 |
| 3.2.1 Preparation of natural samples..... | 56 |
| 3.2.2 Preparation of buffer solutions | 56 |
| 3.2.3 Hydrothermal experiments | 56 |
| 3.2.4 Solid-state diffusion (dry runs)..... | 57 |
| 3.2.5 X-ray diffraction (XRD)..... | 57 |
| 3.2.6 Scanning electron microscopy (SEM)..... | 57 |
| 3.2.7 Electron backscatter diffraction (EBSD)..... | 57 |
| 3.2.8 Chemical analysis of solid products | 57 |
| 3.2.9 Inductively coupled plasma mass spectrometry (ICP-MS)..... | 57 |
| 3.3 Results | 57 |
| 3.3.1 Hydrothermal reactions | 57 |
| 3.3.2 Controls on hydrothermal reaction mechanism and kinetics..... | 59 |
| 3.3.3 Solid-state reactions..... | 61 |
| 3.4 Discussion | 61 |
| 3.4.1 Dissolution-precipitation versus solid-state diffusion..... | 61 |
| 3.4.2 Chemical reactions in the replacement process | 64 |
| 3.4.3 Applications and implications for reactions under hydrothermal conditions..... | 67 |
| 3.5 Acknowledgements | 67 |
| 3.6 References cited | 67 |

CHAPTER 4 EXPERIMENTS STUDY OF THE FORMATION OF CHALCOPYRITE AND BORNITE VIA THE SULFIDATION OF HEMATITE: MINERAL REPLACEMENTS WITH A LARGE VOLUME INCREASE.....69

| | |
|--|----|
| Abstract | 73 |
| 4.1 Introduction | 73 |
| 4.2 Samples and methods | 74 |
| 4.2.1 Hematite and magnetite sources | 74 |
| 4.2.2 Preparation of solutions and chemicals | 74 |
| 4.2.3 Hydrothermal experiments | 74 |
| 4.2.4 Analysis methodology | 75 |

| | |
|---|----|
| 4.3 Results | 76 |
| 4.3.1 Conditions of chalcopyrite and bornite formation..... | 76 |
| 4.3.2 Products and textures..... | 76 |
| 4.3.3 Effect of the nature of iron source | 78 |
| 4.3.4 Effect of background solution | 78 |
| 4.3.5 Effect of reaction temperature | 78 |
| 4.4 Discussion | 79 |
| 4.4.1 Reaction mechanism for the replacement of hematite by chalcopyrite..... | 79 |
| 4.4.2 Reaction end-points: the roles of nucleation and growth | 81 |
| 4.4.3 Replacement reactions with large volume increases | 81 |
| 4.5 Implications..... | 83 |
| 4.6 Acknowledgement..... | 83 |
| 4.7 References cited | 83 |

CHAPTER 5 THE REPLACEMENT OF CHALCOPYRITE BY BORNITE UNDER HYDROTHERMAL CONDITIONS.....85

| | |
|--|-----|
| Abstract | 88 |
| 5.1 Introduction | 89 |
| 5.2 Samples and methods..... | 91 |
| 5.2.1 Preparation of starting samples | 91 |
| 5.2.2 Hydrothermal experiments | 92 |
| 5.2.3 Analysis methodology | 93 |
| 5.3 Results | 94 |
| 5.3.1 The replacement of chalcopyrite by bornite | 94 |
| 5.3.2 The controls on the rate of the transformation and composition of the products | 97 |
| 5.3.3 The exsolution of <i>bdss</i> to bornite and digenite..... | 98 |
| 5.4 Discussion | 99 |
| 5.4.1 Reaction mechanism..... | 99 |
| 5.4.2 The composition of bornite and the exsolution of digenite and bornite..... | 102 |
| 5.5 Acknowledgement..... | 103 |
| 5.6 References | 104 |

| | |
|--|------------|
| CHAPTER 6 CONCLUSIONS | 107 |
| 6.1 Dissolution-precipitation vs. solid-state diffusion | 109 |
| 6.2 Experimental study of the formation of chalcopyrite and bornite via the sulfidation of hematite | 111 |
| 6.3 The replacement of chalcopyrite by bornite under hydrothermal conditions | 112 |
| 6.4 Future Work | 113 |
| 6.4.1 The role of silver in the gold silver tellurides replacement reactions | 113 |
| 6.4.2 The replacement of bornite by chalcopyrite | 114 |
| 6.4.3 The effects of sulfur on the formation of minerals in Cu-Fe-S system | 115 |
| 6.4.4 The composition of digenite-bornite solid solution..... | 115 |
| 6.4.5 The replacement of hematite by magnetite..... | 116 |
| 6.5 References | 116 |
| APPENDIX | 119 |
| Appendix A Mechanism of mineral transformations in krennerite, Au_3AgTe_8 , under hydrothermal conditions | 119 |
| Appendix B A novel pre-treatment of calaverite by hydrothermal mineral replacement reactions..... | 133 |
| Appendix C Syntheses and crystallization of mineralogically relevant chalcogenide glasses..... | 141 |
| Appendix D Single-pass flow-through reaction cell for hightemperature and high-pressure in situ neutron diffraction studies of hydrothermal crystallization processes..... | 149 |
| Appendix E A novel route for the synthesis of mesoporous and low-thermal stability materials by coupled dissolution-precipitation reactions: mimicking hydrothermal mineral formation..... | 161 |
| Appendix F Hydrothermal mineral replacement reactions and their applications in mining and processing..... | 171 |

ABSTRACT

Over the past decades, a number of hydrothermal studies were undertaken on the mineral replacement reactions using hydrothermal method, which mostly proceeded via a coupled dissolution-reprecipitation (CDR) mechanism. However, most of experimental studies have been focused on mineral replacement reactions at relative low pressures and at low to medium temperatures. For hydrothermal mineral deposits set at higher temperature, such as porphyry copper systems or intrusion-related gold deposits, solid-state diffusion may be significant due to the high mobility of the metal ions, and solid-state reactions may compete kinetically with the CDR mechanism. Thus, to investigate the possible interaction between CDR reactions and solid state reactions, we designed a set of hydrothermal studies into the mineral replacement reactions in both Au-Ag-Te and Cu-Fe-S systems.

The mineral replacement of sylvanite was studied under hydrothermal conditions, exploring the effects of temperature (160-220 °C), pH (2-10), and redox conditions on the sample textures and reaction kinetics. Sylvanite transformed to Au-Ag alloy and a range of other gold-(silver)-telluride phases as intermediate products, including petzite (Ag_3AuTe_2), hessite (Ag_2Te), an Ag-rich-Te-depleted calaverite-I ($\text{Au}_{0.78}\text{Ag}_{0.22}\text{Te}_{1.74}$) and a normal calaverite-II ($\text{Au}_{0.93}\text{Ag}_{0.07}\text{Te}_2$). The textures of products are very complex due to the interplay between solution-driven interfaces coupled dissolution-reprecipitation (ICDR) reactions and solid-state diffusion driven processes. The complex interaction among solid-state diffusion and ICDR reactions under hydrothermal conditions is due to the high solid-state mobility of Ag ion in the Au-Ag-Te system.

The hydrothermal synthesis of chalcopyrite was performed via the sulfidation of hematite in solutions containing Cu(I) (as a chloride complex) and hydrosulfide, at pH near the pK_a of $H_2S(aq)$ under hydrothermal conditions. Due to the large positive volume increase, the sulfidation of hematite by chalcopyrite follows a dissolution reprecipitation mechanism progressing via both direct replacement and also overgrowth. Distinct from other solution mediated ICDR reactions (e.g. the transformation from pentlandite to violarite) (Xia et al. 2009), no distinct porosity structures were observed in the quenched product grains. This is probably due, at least in part to the large volume increase during the reactions. This work investigated the nature of CDR reaction with large volume increase at relative high temperatures and high pressures, and improved our understanding of the physical chemistry of chalcopyrite formation in nature.

To explain the transformation mechanism of chalcopyrite and bornite intergrowths, we reported the replacement of chalcopyrite by bornite in solutions containing Cu(I) (as a chloride complex) and hydrosulfide over the temperature range 200-300 °C. Results show that chalcopyrite was replaced by bornite under all studied conditions. The reaction proceeds via a CDR reaction mechanism and with some additional overgrowth of bornite. The bornite product formed at 300 °C for 24 hrs is Cu-rich corresponding to compositions in the bornite-digenite solid solution (*bdss*) $Bn_{90}Dg_{10}$, which can exsolve into digenite lamella in a bornite host during the further annealing in the original solution at 150 °C and 200 °C for 24 to 120 hrs. The exsolution of *bdss* is another example of solid-state diffusion under hydrothermal conditions.

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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