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

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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)$_9$S$_8$, by violarite (Ni,Fe)$_3$S$_4$, 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)\textsubscript{3}S\textsubscript{4}, and linnaeite, Co\textsubscript{3}S\textsubscript{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\textsubscript{2}O\textsubscript{6}·H\textsubscript{2}O) as an illustration using natural leucite (KAlSi\textsubscript{2}O\textsubscript{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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The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works.

Signed………………………………………………………….. Date ………………………..
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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.

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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).

<table>
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<th>Impact Factor†</th>
<th>2007 Total Cites*</th>
<th>Immediacy Index‡</th>
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</table>

† 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.


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.


Chapter 1

INTRODUCTION
Chapter 1. Introduction

1.1 Background

Pseudomorphic mineral replacement reactions are reactions in which secondary mineral or mineral assemblage chemically occupies the space previously occupied by the primary mineral in the presence of geochemical fluids (MERINO and DEWERS, 1998). The most distinct feature of these reactions is that the overall outward morphology and often the fine internal textural details of the primary minerals are preserved by the secondary mineral or mineral assemblage. In this thesis, terms such as mineral replacement, replacement, transformation, and alteration, all refer to pseudomorphous mineral replacement reactions. Mineral replacement reactions are striking and widespread natural phenomena, occurring during the courses of chemical weathering, hydrothermal alteration, deuteritic alteration, diagenesis, metasomatism, or even metamorphism (see review, PUTNIS, 2002). For example, saprolites often replace parent rocks in tropical weathering (e.g., NAHON and MERINO, 1997); aluminosilicate minerals commonly replace other less stable aluminosilicate minerals under hydrothermal environments (e.g., PUTNIS et al., 1994; LABOTKA et al., 2004); and dolomite usually replace limestones in metasomatic processes (e.g., TUCKER, 2001). Therefore, mineral replacement reactions are closely related to the formations of soils and rocks, and to the genesis of various ore bodies. Mineral replacements are also common in industrial processes, for example leaching in hydrometallurgy (e.g., BOATENG and PHILLIPS, 1984), or cation exchange processes in zeolites for waste water treatment (e.g., PANSINI et al., 1991). Thus, a clear understanding of mineral replacement reactions is extremely important and has many implications for petrology, geochemistry, mineralogy, hydrometallurgical minerals engineering, and materials syntheses.
Although the research on mineral replacement reactions has a long history, for example, comprehensive studies had already carried out in the 1850s (see e.g., Chapter 2 in Bischof, 1854), our knowledge regarding the mechanisms and kinetic behaviour of such reactions is still very limited. This situation had led to extensive modern studies using various techniques and methods (e.g., Rendón-Angeles et al., 2000a; Putnis, 2002; Labotka et al., 2004; Eda et al., 2006; Merino, 2006; Putnis and Putnis, 2007; Pollok et al., 2008). These modern studies, however, resulted in disagreements with respect to various aspects of the replacement mechanisms. We noticed that these studies rarely concern the reaction kinetics, and even where they did, the researchers only considered the kinetics of overall reactions (e.g., Suárez-Orduna et al., 2007). Nevertheless, a clear kinetic understanding is usually sufficient to reveal the correct mechanisms (Levenspiel, 1999), and may help us to resolve these disagreements.

This project has been established jointly by the Department of Chemical Engineering of The University of Adelaide, and Department of Mineralogy of South Australian Museum. The principle aim is to study the kinetics of the mineral replacement reactions under hydrothermal conditions and reveal the mechanisms. The second principle aim is to explore the applications of pseudomorphic mineral replacement reactions in the syntheses of novel materials.
1.2 Literature review

To avoid repetition of the introduction sections in the individual papers, this section does not seek to provide a comprehensive literature review, but rather to give a brief and critical summary of the literature, aiming to identify the knowledge gaps and the relationship of the literature to the experimental program.

1.2.1 The distinct characteristics

Pseudomorphic mineral replacement reactions may occur whenever minerals do not achieve equilibrium with the surrounding fluids (PUTNIS and MEZGER, 2004). Examples include the replacement of leucite by analcime (PUTNIS et al., 1994), quartz by gibbsite (NAHON and MERINO, 1997), and calcium fluorapatite by calcium hydroxyapatite (RENDÓN-ANGELES et al., 2000a). There are some common features of mineral replacement reactions summarized by PUTNIS (2002). (1) Shape inheritance: product minerals inherit the shape (volume, texture, or even crystallographic information) of their parent minerals. This phenomenon is also described as pseudomorphism. (2) Porous products: product minerals possess nano- or micro-pores, cracks and channels. (3) A sharp reaction front between the parent and product phase; this front moves towards the interior of the parent mineral during the process. (4) Mineral replacement reactions are sensitive to the behavior and properties of the fluid. These features are clearly illustrated in the replacement of chlorapatite by hydroxyapatite (Fig. 1.1).
Fig. 1.1 SEM images of the cross sections of a partially replaced chloraparite by hydroxyapatite under hydrothermal conditions at 500 °C in a 6.25 M KOH solution for 3 h. Morphology (left) shows porous texture of the hydroxyapatite phase and a sharp reaction front. Cl X-ray line scan (right) reveals a chemically distinct reaction front (YANAGISAWA et al., 1999).

1.2.2 The mechanisms

Pseudomorphic replacements occur in the presence of geochemical fluids, hence it is reasonable to consider the important role the fluid phase has in the process, i.e., the replacement involves dissolution and precipitation sub-processes. This view has been widely accepted and has been used to interpret various replacement patterns (MERINO et al., 1993; WANG et al., 1995; NAHON and MERINO, 1997; PUTNIS and MEZGER, 2004). However, some studies proposed that mineral replacement reactions are controlled by solid-state diffusion processes. These studies were usually based on systems in which the product phase shares some common chemical elements and a similar crystal structure with the parent phase (THORNBER, 1975; WARNER et al., 1992; EDA et al., 2006; HUNGER and BENNING, 2007). The authors often argued that the transfer of crystallographic structure from the parent to the product phase would be impossible under the context of dissolution and precipitation.
For dissolution and precipitation, a coupled dissolution-reprecipitation reaction mechanism has been proposed to explain how the pseudomorphism occurs during the replacement (Maliva and Siever, 1988a; Maliva and Siever, 1988b; Merino et al., 1993; Wang et al., 1995; Nahon and Merino, 1997). This mechanism requires that the rate of the dissolution of the parent mineral at the reaction front must equal to the rate of the precipitation of the product mineral. Following this mechanism, as the reaction advances, the volume of the product precipitated equals the volume of precursor dissolved for a specific period of time, and the precipitation occurs just adjacent to the dissolution sites. Indeed, Solberg and Hansen (2001) reported a mineral replacement reaction in the CaSO$_4$·1/2H$_2$O-CaSO$_2$·2H$_2$O system with equal rates between dissolution of CaSO$_4$·1/2H$_2$O and reprecipitation of CaSO$_2$·2H$_2$O using a synchrotron X-ray diffraction technique. However, dispute remains regarding the origin of the coupling. Merino and co-authors proposed that the coupling is caused by the local stress at the reaction front (Merino et al., 1993). This mechanism suggested that the growth of secondary mineral induces local stress which can adjust the rate of dissolution and precipitation and cause the coupling. Ferry (2000) reported that the coupling is related to the molar Gibbs free energy change at the reaction front. In the case of negative molar volume change, the Gibbs free energy of the product is lower than that of the precursor, thus pseudomorphic replacement occur. In contrast, in the case of positive molar volume change, the Gibbs free energy of the reaction would be positive, precipitation should occur elsewhere; hence no pseudomorphs can be developed. Putnis (2002) suggested that the coupling is controlled by the local fluid composition. The growth of the product phase changes the solution composition, which influence the rate of dissolution. In turn, the dissolution of the parent phase also changes the solution composition, which adjusts the growth rate of the product phase. In this way, the dissolution is coupled with the precipitation.
1.2.3 The length scale of pseudomorphism

The length scale of pseudomorphism means the length scale of textural features that can be preserved in the pseudomorphic replacement reactions. This length scale often differs greatly from one case to another. Many replacement reactions can preserve very fine textural features as small as nanometer scale, for example, the hydrothermal replacement of SrSO₄ by SrF₂ (RENDON-ANGELES et al., 2006), the replacement of bones by calcite in Australian opal fields (PEWKLIANG et al., 2008), the replacement of leucite by analcime (PUTNIS et al., 2007), and the replacement of chlorapatite by hydroxyapatite (YANAGISAWA et al., 1999). There are also many other replacement reactions that preserve large length scale features but lose fine textural details, for example, the replacement of SrSO₄ by Sr(OH)₂ (RENDÓN-ANGELES et al., 2006), and the replacement of calcite by opal (PEWKLIANG et al., 2008). The reasons for these observations had remained unexplained.

1.2.4 The preservation of crystallographic orientation

In some replacement reactions, the products not only preserve the volume and shape, but also inherit the crystallographic orientation of the precursors. Examples include the replacement of chlorapatite by hydroxyapatite (ELLIOTT and YOUNG, 1967; YANAGISAWA et al., 1999), fluorapatite by hydroxyapatite (RENDÓN-ANGELES et al., 2000a), and KBr by KCl (PUTNIS and MEZGER, 2004; PUTNIS et al., 2005). YANAGISAWA et al. (1999) suggested that the dissolved components are large clusters rather than ionic species, so that ion exchange takes place on the surface of such clusters and thereby generating a new crystal with an identical structure. However, other researchers argued that this hypothesis contradicts the previous albitization studies using ¹⁸O isotope as a tracer (O'NEILL and TAYLOR, 1967; O'NEILL, 1977). The distribution of ¹⁸O isotope in the product phase indicated that all the bonds were broken and reconstructed during the reactions. It was
assumed that at the interface between precursor and product feldspars there exists a thin fluid film, which is considered to be the possible media of crystallographic information transfer by Putnis (2002). Later work by Putnis et al. (2005) suggested that lattice mismatch between the parent and product mineral is an important influence on the transfer of crystallographic information. This is more likely to occur when incremental changes in equilibrium compositions accompany the continuous changes in lattice parameters (Putnis et al., 2005).

1.2.5 Porous textures of reaction products

The porous textures of products in mineral replacement reactions are direct consequences of mineral-fluids interactions. Some researchers postulated that the porous texture is simply the result of a decrease in molar volume between reactants and products (Brenan, 1993; Rendón-Angeles et al., 2000b). However, this is inconsistent with the finding in the replacement of leucite by analcime. In this reaction, the product has larger molar volume, but a porous texture is still observed (Putnis et al., 1994). Similar results were also reported by Walker et al. (1995) who studied the replacement of cryptoperthite by patch perthite. Since the bulk chemical composition is constant during this reaction, the subsequent very small volume change is unable to account for the larger amount of micropores observed. Walker et al. (1995) concluded that a material removal process must occur during the reaction. To simplify the discussion, Putnis (2002) studied the simple model system NaCl-KCl-H₂O. Based on the solubility diagram he pointed out that in a mineral replacement reaction, the absolute translated mole quantity should also be taken into account while considering the total volume change. A small quantity of product with a larger molar volume could also lead to porous texture.
The development of micropores and subsequent coarsening in the reaction products facilitate the dissolution-reprecipitation reaction by providing possible paths for fluid infiltration and chemical transport (NAKAMURA and WATSON, 2001; PUTNIS and MEZGER, 2004). Nevertheless, pore size does affect the reaction because the threshold supersaturation for nucleation in a finely porous medium significantly exceeds that for a free fluid (PUTNIS et al., 1995; PUTNIS and MAUTHE, 2001). Additionally, very fine pores would hinder mass transport if their sizes are similar to or smaller than the size of the fluid molecular or transported materials. In this case, a solid-state diffusion controlled reaction may occur (GEISLER et al., 2005).

### 1.2.6 Kinetics

The understanding of kinetics is a prerequisite to the understanding of many geochemical processes, thus considerable research efforts have been put into the kinetic studies of mineral dissolution and precipitation (LASAGA, 1998). In the last decades, many dissolution or precipitation kinetic studies on a wide range of minerals have been carried out, and the kinetic theories have been developed simultaneously. These studies have lead to a greater understanding of the mechanisms of mineral dissolution and precipitation. Examples of kinetic studies regarding mineral dissolution, precipitation, and the development of kinetic theories are summarized in Table 1.1.

In spite of the important role of the kinetics to reveal the mechanisms, kinetic studies on mineral replacement reactions are very rare. An early example is the replacement of calcite by fluorite (GLOVER and SIPPEL, 1962). Recent kinetic studies include the replacement of leucite by analcime (PUTNIS et al., 2007), and celestite by strontianite (SUAREZ-ORDUNA et al., 2007). A common limitation of these studies is that they only considered the overall...
Table 1.1 Summary of kinetic studies of mineral dissolution, precipitation, and the development of kinetic theories.

<table>
<thead>
<tr>
<th>Work</th>
<th>References</th>
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<tr>
<td><strong>Dissolution kinetic studies</strong></td>
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<tr>
<td>Goethite</td>
<td>LAKIND and STONE (1989)</td>
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<td>Kaolinite</td>
<td>HUERTAS et al. (1999)</td>
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<td>Basaltic glass</td>
<td>GISLASON and OELKERS (2003)</td>
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<td>Quartz</td>
<td>DOVE and CRERAR (1990)</td>
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<td>BERGER et al. (2002)</td>
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<td>KNAUSS and WOLERY (1986)</td>
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<td>Montmorillonite</td>
<td>ROZALÉN et al. (2008)</td>
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<td>Monazite</td>
<td>OELKERS and POITRASSON (2002)</td>
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<td><strong>Precipitation kinetic studies</strong></td>
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<td>NAGY and LASAGA (1992)</td>
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**Kinetic theories development**

The effect of temperature
- CASEY and SPOSITO (1992)

The application of mineralogical approaches to the crystal dissolution kinetics
- LASAGA and LÜTTGE (2004)

The applicability of the classic Aagaard-Helgeson rate law
- GIN et al. (2008)

The \textit{ab initio} quantum mechanical approach
- XIAO and LASAGA (1994)
- XIAO and LASAGA (1996)

The consideration of rate constants, effective surface area, and the hydrolysis
- HELGESON et al. (1984)

The principle of detailed balancing
- RIMSTIDT and BARNES (1980)
- GANOR et al. (2005)

1.2.7 The sensitivity to fluid properties

The fluid phases play a central role in mineral replacement reactions, because they act as media for mass transport to and from the reaction sites (JAMTVEIT et al., 1990). The interaction between a pore-free mineral and a bulk fluid could begin at the solid-fluid interface, then generate a sharp reaction front between the reactant and product and move this front towards the interior of the mineral, until it is completely replaced by the product (LABOTKA et al., 2002; PUTNIS et al., 2005).
The abilities to dissolve minerals and to transport reaction species are the two major fluid properties that control the replacement reactions (Putnis, 2002). The varying ability of a fluid to dissolve different mineral phases is the basis of the replacement reactions. Replacement always occurs in ways that more soluble phases are replaced by less soluble phases (e.g., Putnis et al., 2007). The solubility of minerals is influenced by the composition and P-T conditions of the fluids. The direction of replacement reaction may change upon the change of fluid composition, for example, leucite is replaced by analcime in a sodium rich solution (Putnis et al., 2007), but the replacement is reversed in a potassium rich solution (Savage et al., 2001). The fluid composition affects reaction rates by changing the saturation state of involved minerals (Nahon and Merino, 1997). For example, mineral replacement reactions in lateritic weathering can take place at pH 4, but not at pH 3 (Wang et al., 1995). The P-T condition changes the chemical and physical properties of the fluids and influences their mass transport ability. That’s why, apart from the temperature effect, hydrothermal reactions are distinct from those taking place under normal conditions, because hydrothermal fluids tend to have low interfacial energies (Han, 2005), and thus have better infiltration abilities making them better mass transport media (Beere, 1975).

In spite of the important role that the fluid plays in mineral replacement reactions, detailed studies on the effect of fluid properties on the reaction mechanisms and kinetics of mineral replacement reactions have not been carried out.

1.2.8 Summary

In light of the above summary of the literature, it is clear that although previous investigations have made considerable contributions to the understanding of mineral
replacement reactions, controversial views remain regarding the mechanism of these reactions. Some authors believe that the replacement reactions are driven by solid-state diffusion processes, while others argue that they actually involve dissolution and precipitation processes. Some suggested that the coupling between dissolution and precipitation is caused by the non-hydrostatic stress, but others proposed that it was controlled by solution chemistry. What’s more, the understanding of the origin of the length scale of pseudomorphism is severely lacking; the transfer of crystallographic orientation in some cases, and the formation of porosity are still poorly understood; the detailed kinetic studies considering all processes involved in replacement reactions, and their behavior to the effects of fluid compositions and P-T conditions has never been carried out, yet kinetics reflect the mechanisms and can lead us to a better understanding of mineral replacement reactions. Finally, the potential applications of pseudomorphic mineral replacement reactions, such as in mineral exploration, metallurgic engineering, and materials chemistry, have rarely been explored.

1.3 Research objectives

Based on the limitations of previous work, the principal objective of this project is set to understand the mechanism and kinetics of mineral replacement reactions based on a detailed experimental kinetic and textural study on a complex replacement reaction of pentlandite by violarite. The principle of replacement reactions will be applied in materials syntheses including two complex metal sulfides, violarite and linnaeite, and a novel three dimensional ordered arrays of nanozeolite.

The detailed objectives of this project are:

- To probe the role of the fluid phases, to determine whether replacement reactions are solid-state diffusion processes, or dissolution-precipitation processes.
To understand the cause of coupling between primary mineral dissolution and secondary mineral precipitation by studying the processes occurring at the dissolution and the precipitation fronts.

To discuss the origin of the length scale of pseudomorphism.

To correlate reaction kinetics, textures and porosity with systematic variations in composition and texture of the starting material, temperature, and fluid composition (pH, redox, concentration of metal ions).

To develop a generalized kinetic model which can be used to analyze other mineral replacement reactions.

To explore the possible applications of pseudomorphic replacement reactions in materials syntheses, including metal sulfides and novel zeolites.

1.4 Thesis organization

To achieve these objectives, the appropriate experimental methods were employed, which are described in Chapter 2. The main body of the thesis is divided into two parts: the study of mechanisms and kinetics of mineral replacement reactions (Chapter 3 and 4), and the application of these reactions in materials syntheses (Chapter 5 and 6). Therefore, Chapter 3 presents a detailed kinetic and textural study on the replacement of pentlandite by violarite, which revealed the detailed reaction mechanisms, including the role of the fluid phase, the cause of the coupling, the origin of the length scale of pseudomorphism, the correlation of reaction kinetics, textures and porosity with systematic variations in composition and texture of the starting material, temperature, and fluid composition, and proposes a kinetic model to understand the coupling and its consequences. Chapter 4 further discusses the effect of pyrrhotite and sample texture on the replacement of pentlandite by violarite. Chapter 5 applies the principle of replacement reactions to the
syntheses of pure metal sulfides, violarite and linnaeite. Violarite is very difficult to synthesize by the traditional silica tube techniques but can be easily synthesized using pseudomorphic mineral replacement reactions. Chapter 6 employs the principle to prepare novel three dimensional ordered arrays of nanozeolites with uniform size and orientation, and adjustable overall size and morphology. This is the first time such unique features have achieved in zeolite research. Chapter 7 provides the overall conclusions of the investigation and findings of the research, and discusses possible future research directions.

Relevant publications are included in the Appendices. These publications discuss the mechanisms and kinetics of pseudomorphic mineral replacement reactions (Appendices A to D), apply these reactions in the syntheses of novel materials (Appendices E to H), and in the understanding of mineral formation (Appendix I) and the processes of pyrometallurgy (Appendices J and K) and hydrometallurgy (Appendix L). These publications were presented in journals in other language (Chinese) or peer-reviewed international conferences. Particularly, Appendices J and K present pseudomorphic mineral replacement reactions under dry condition; Appendix H and I extends the application in the understanding of an important economic mineral, auriferous arsenian pyrite/marcasite.
1.5 References


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CHAPTER 1. INTRODUCTION


CHAPTER 1. INTRODUCTION


RIMSTIDT, J. D. and BARNES, H. L., 1980. The kinetics of silica-water reactions. 


Chapter 2

Methodology
Chapter 2. Methodology

This research involves sulfide minerals syntheses, hydrothermal reactions, powder X-ray diffraction analysis, scanning electron microscopic analysis, electron probe microanalysis, and electron backscatter diffraction analysis. These methods/techniques and the involved instruments are described below.

2.1 The syntheses of sulfide minerals

The standard silica-tube technique (VAUGHAN and CRAIG, 1978) was employed to synthesize the metal sulfides, including pentlandite \((\text{Fe,Ni})_9\text{S}_8\), cobaltpentlandite \(\text{Co}_9\text{S}_8\), violarite \((\text{Ni,Fe})_3\text{S}_4\), and monosulfide solid solution \((\text{Fe,Ni})\text{S}\). The silica tubes used in this research are typically ~150 mm in length, 10 mm in internal diameter, and 1 mm in thickness (Fig. 2.1 and Fig. 2.3a). In a typical synthesis, starting materials (see Table 2.1) were precisely weighed to give the desired composition. These were then mixed, and introduced into silica tubes, connected to a vacuum line (Fig. 2.1) and sealed under vacuum by high temperature gas/oxygen flame using a welding torch (Fig. 2.1 inset). The tubes were placed in muffle furnaces or ovens (Fig. 2.2) at an angle of ~ 45º, heated slowly to the synthesis temperature and annealed following different schemes depending on compositions. Detailed annealing schemes for these metal sulfides are described in Chapters 3-5. Following annealing, the silica tubes were removed from the furnaces/ovens using tongs and quenched immediately in a bucket of cold water; the tubes were held vertically during quench to get products in the cylinder form. The syntheses of pentlandite and cobaltpentlandite require the tubes to be cooled slowly in the furnace. These different cooling schemes were designed according to the phase diagrams of the involved sulfides. After cooling, the product should sit at the bottom of the tube (Fig. 2.3b). The metal
sulfides were recovered by cutting off the top part of the tubes using a diamond saw (Fig. 2.3c). For better homogeneity and purity, the product may be ground, reintroduced to another tube, sealed, and submitted to another annealing scheme.

**Table 2.1** A summary of starting elements for the synthesis of metal sulfides

<table>
<thead>
<tr>
<th>Elements</th>
<th>Supplier</th>
<th>Form</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>Aldrich</td>
<td>flakes</td>
<td>99.99+%</td>
</tr>
<tr>
<td>Fe</td>
<td>Aldrich</td>
<td>1 mm diameter wire*</td>
<td>99.9+%</td>
</tr>
<tr>
<td>Ni</td>
<td>Aldrich</td>
<td>0.5 mm diameter wire*</td>
<td>99.9+%</td>
</tr>
<tr>
<td>Co</td>
<td>Aldrich</td>
<td>100 mesh powder</td>
<td>99.9+%</td>
</tr>
</tbody>
</table>

*Wires were cut to short pieces ~ 5 mm in length before use.

**Fig. 2.1** The vacuum line and the welding torch (left inset) used to seal silica tubes. The vacuum is monitored by a vacuum gauge (right inset).
Fig. 2.2 Muffle furnaces (blue) and ovens (white) used in this work. These furnaces/ovens are programmable and the temperature can be controlled precisely within ±1 °C. The maximum working temperatures of the furnaces and ovens are 1150 °C and 500 °C, respectively.

Fig. 2.3 (a) A typical silica tube used in this study. (b) Pentlandite product in silica tubes. (c) Pentlandite removed from silica tubes.
2.2 Hydrothermal reactors

2.2.1 Flow-through closed-loop reactors

Hydrothermal flow-through closed-loop reactors (Fig. 2.4) were designed for kinetic and mechanism studies of pseudomorphic replacement reactions. These reactors were constructed using 316 stainless steel fittings. Most of these fittings were ordered from *Swagelok*. The fluid flow is generated by thermosyphon: heat the fluid in the reservoir by a heating jacket on one side and cool it on the other side of the loop. The maximum designed fluid temperature is 300 °C. The maximum pressure is 85 bar absolute, which is the saturation pressure of pure water at 300° C. The possibility of over-pressurization of loop is avoided by the use of a *Swagelok* pressure relief valve to a containment reservoir (sufficient volume to retain all liquid discharge). The volume of the reservoir, the expansion tank, and the reaction cell are 150 mL, 75 mL, and 25 mL, respectively. The total internal volume of the reactor, including tubing, is about 260 mL. Detailed operation procedure of flow-through reactors is described in Chapters 3-5.

2.2.2 Static batch reactors

Teflon lined stainless steel static batch reactors with varying internal volumes were constructed for probing the reaction mechanisms (Fig. 2.5). These reactors are as large as 260 mL, and as small as 18 mL. The reason to use these reactors is because Teflon is inert to the fluids and minerals and thus we can avoid effects of impurities dissolved from the reactor. The maximum working temperature for Teflon reactors is around 300 °C (e.g., page 91 in *BYRAPPA and YOSHIMURA, 2001*), but to avoid deformation in long experiments in this research, most of the runs were carried out below 210 °C in furnaces/ovens (Fig. 2.2). Detailed operation procedure for static batch reactors is described in Chapters 3-6.
Fig. 2.4 Schematic diagram (left) and picture (right) of one of the 316 stainless steel thermosyphon driven hydrothermal flow-through closed-loop reactors.
Fig. 2.5 Schematic diagram (left) and picture (right) of Teflon lined stainless steel static batch reactors. In the schematic diagram: 1, Teflon cap, 2, stainless steel cap, 3, Teflon body, 4, stainless steel body, 5, hydrothermal reaction fluid, 6, sample.

2.3 Powder X-ray diffraction (XRD)

Powder X-ray diffraction is a very powerful and simple technique for phase identification and quantification. The basic principle is that when X-ray penetrates through or reflects from the sample, it is diffracted by the crystal lattice planes \( \{hkl\} \) according to the classic Bragg’s law:

\[
\lambda = 2d \sin \theta
\]

where \( \lambda \) is the wavelength of the X-ray, \( d \) is the distance of the \( \{hkl\} \) planes, and \( \theta \) is the diffraction angle. By comparing the obtained diffraction pattern to the standard one from a database, the involved phases can be identified and subsequently quantified. Detailed principle of X-ray diffraction is available in, for examples, Pecharsky and Zavali (2003) and Putnis (1992).

Powder X-ray diffraction patterns in this research were collected on a HUBER Guinier Imaging Plate Camera G670 with CoK\(\alpha\)1 radiation (\(\lambda=1.78892 \text{ Å}\)) (Fig. 2.6) at Mineralogy Department, South Australian Museum. The X-ray is generated by an ATPS XRD 1000 X-
ray tube at 35 kV and 34 mA, and filtered by an asymmetrically ground and curved quartz (SiO₂) monochromator. The function of the HUBER Imaging Plate Camera is based on the image properties of a 330 x 15 mm X-Ray sensitive storage film, which is arranged in a focal circle 180 mm in diameter. The image information of a diffraction pattern on the film is read out with a laser scanner. A focused laser beam (30 x 50 μm) excites photoluminescence on the film which is detected by a photomultiplier. The obtained signal is amplified, digitized by an A/D-converter and transferred to the memory of the controlling computer. The image plate records diffraction patterns with 2θ range from 4° to 100°, and angle resolution of 0.005°.

In a typical experiment, around 5 mg of sample was ground in acetone, spread uniformly to give a thin film on a MYLAR X-ray film, which was then carefully mounted into the oscillation unit and exposed to X-ray for 60 minutes.

The phase characterizations and crystallite size estimation were performed with the aid of the Jade software. The quantitative phase analyses and unit cell refinements were performed by the Rietveld method using a computer program called Rietica for Windows (v.1.7.7) (Hunter, 1998) The refinement is a series of least-square processes, in which the background, the cell parameters (a, b, c, α, β, γ), the phase scale (S), and the peak shape parameters (U, V, W, Gam0, Gam1, Gam2 of a Pseudo-Voigt function) are refined one-by-one based on initial crystal structures from International Crystal Structure Database. The quality of the refinement is monitored in terms of agreement indices or R values (Kisi, 1994; McCusker et al., 1999). The weight-profile R value, \( R_{wp} \), is defined as

\[
R_{wp} = \left\{ \frac{\sum w_i \left[ y_i(\text{obs}) - y_i(\text{cal}) \right]^2}{\sum w_i [y_i(\text{obs})]^2} \right\}^{1/2}
\]  

(1.2)
where $y_i^{(obs)}$ is the observed intensity at step $i$, $y_i^{(cal)}$ the calculated intensity, and $w_i$ the weight. Ideally, the final $R_{wp}$ should approach the statistically expected $R$ value, $R_{exp}$,

$$R_{exp} = \left[ \frac{(N - P)}{N} \sum_i w_i y_i^{(obs)} \right]^{1/2}$$

(1.3)

where $N$ is the number of observations and $P$ the number of parameters. Thus for a good refinement the ratio between $R_{wp}$ and $R_{exp}$ (called ‘goodness-of-fit’),

$$\chi^2 = \frac{R_{wp}}{R_{exp}}$$

(1.4)

should approach 1. Once good refinement has been achieved, the percentages of the involved phases are automatically calculated by the equation,

$$w_p = \frac{(SZMV)_p}{\sum_i (SZMP)_i}$$

(1.5)

where $w_p$ is the weight percentage of phase $P$, $S$ the scale factor, $Z$ the number of formula units per unit cell, $M$ the molecular weight of the formula unit, and $V$ the volume of unit cell. $i$ represents each phase. More information about the Rietveld method is available in books, e.g., **Young (1993)**, and **Pecharsky and Zavalij (2003)**.

---

**Fig. 2.6** The HUBER Guinier Imaging Plate Camera G670 for powder X-ray diffraction.
2.4 Scanning electron microscopic (SEM) analysis

Scanning electron microscopic analyses were carried out on a Philips XL30 Field Emission Scanning Electron Microscope (FESEM) (Fig. 2.7) at the Adelaide Microscopy, University of Adelaide. The microscope is equipped with an EDAX® Energy Dispersive X-ray Spectrometer (EDS), a secondary electron (SE) detector, and a backscattered electron (BSE) detector. The EDS was used for semi-quantitative chemical determinations with 120 sec data acquisition time. The SE and BSE detector were used to obtain secondary and backscattered micrographs, respectively. The working distances for SE and BSE modes were set to 10 mm in most cases. For textural investigations, grains were embedded into epoxy resin blocks and polished. The polished blocks were preliminary examined by an oil-immersion reflected-light optical microscope at the South Australian Museum, and selected samples were then carbon film coated by a Denton DV-502 vacuum evaporator, and examined under the backscattered electron mode. The accelerating voltage was maintained at either 15 kV or 20 kV depending on samples to achieve the best contrast and resolution.
2.5 Electron probe microanalysis (EPMA)

A Cameca SX51 electron microprobe (Fig. 2.8) at Adelaide Microscopy, University of Adelaide, was used to quantify the chemical composition of the mineral samples. The instrument is equipped with four Wavelength Dispersive X-ray Spectrometers (WDS), one Energy Dispersive X-ray Spectrometer (EDS), and an optical microscope. The analyses were undertaken on carbon coated polished blocks using an accelerating potential of 20 kV and a specimen current of ~20 nA. The sample surface was focused with the help of the view provided by the optical microscope. The counting time for each element and the background was set to 30 seconds. Natural pentlandite (Astimex #36) and cobaltite (Astimex #19) were used as standards for Fe, Ni, and S, and Co, respectively.
2.6 Electron backscatter diffraction (EBSD) analysis

Electron backscatter diffraction (EBSD) is a growing technique in the analyses of crystallographic orientation distribution of crystallites in metals, minerals, ceramics, and other condensed materials (SCHWARTZ et al., 2000). The principle of EBSD to resolve the crystallographic orientation is that when an primary electron beam hit the sample, elastic backscattered electrons are scattered from the sample; some of these scattered electrons are diffracted by the crystal lattice planes \( \{hkl\} \) according to the Bragg’s law (Eq. 2.1). These diffracted electrons can be recorded in a fluorescent screen, forming the so called Kikuchi pattern. Similar to X-ray diffraction, the electron diffraction pattern represents the crystal structure, but it is very sensitive to the crystallographic orientation with an angle resolution of \( \sim 1^\circ \). By collecting Kikuchi patterns point by point (or mapping) in an area of interest, and resolving the orientation of crystallite from each Kikuchi pattern, crystallographic
orientation distributions of the involved phases are obtained (Fig. 2.9). The three commonly used forms of orientation distribution representations in terms of sample and/or lattice plane orientation are, pole figures and inverse pole figures, represented in terms of stereographic projections, and orientation distribution functions projected in Euler space. In this research, pole figures were used to represent orientation distribution of pentlandite, violarite, leucite, and analcime (see Chapter 3 and 6). Detailed principle and applications of EBSD is available in, for example, SCHWARTZ et al. (2000).

![Fig. 2.9](image)

(a) An electron backscatter diffraction pattern of a particular point of the leucite phase. (b) The pattern is indexed based on leucite crystal structure (ICSD code: 9826). (c) The resolved crystal orientation of that point relative to the sample surface.

Electron backscatter diffraction (EBSD) analyses were preformed using either an EDAX-TSL™ EBSD system or a HKL EBSD system at Adelaide Microscopy, University of Adelaide. EBSD of pentlandite and violarite were analysed by the EDAX-TSL™ EBSD system equipped on a FEI Helios NanoLab DualBeam™ FIB/SEM platform (Fig. 2.10). The freshly polished samples were left uncoated, but areas around those selected for analyses were painted with carbon dag in order to reduce charging. The sample surface was then milled with the focused gallium ion beam (30 kV and 2.8 nA) at an angle of 10° (Fig. 2.11a) to remove the surface layer distorted by the mechanical polishing process.
Following that, the sample was turned around to face the Hikari EBSD camera, and tilted to 70° with respect to the camera (Fig. 11b). EBSD patterns were collected at 30 kV and 6.5 nA, and a working distance of ~9 mm. Crystallographic data for pentlandite and violarite were taken from the MINCRYST database. The OIM Data Collection (V5.2) was used for data collection, and the OIM Analysis (V4.5) was used for data interpretation.

Fig. 2.10 The FEI Helios NanoLab DualBeamTM FIB/SEM platform.
Leucite and analcime were analysed on the HKL EBSD system equipped on a Philips XL30 FESEM (Fig. 2.7). The samples were embedded in epoxy resin, ground with 800 grit and 1200 grit sandpapers for 30 seconds, polished with 3 μm and 1 μm diamond pastes for 10 minutes, and finally polished with 0.04 μm colloidal silica suspension for 3 hours on a STRUERS Tegra polishing system (TegraPol-21 + TegraForce-5 + TegraDoser-5) at Ian Wark Research Institute, University of South Australia. Ultrasonic cleaning was performed before and after each polishing step to avoid cross contamination. This sample preparation procedure ensures the excellent surface quality for EBSD analyses. Because leucite and analcime are non-conducting minerals, the samples were coated with a thin carbon film to minimize the electron charging. The thickness of the carbon coating is critical because if the coating is too thin, the imaging and EBSD are seriously affected by electron charging; but if the coating is too thick, the electron diffraction signals are weakened. We coated the samples with ~1.5 nm thick carbon films and got good EBSD results. The sample was pre-
tilted to 70º before the chamber was sealed. The analyses were performed at 20 kV accelerating voltage, 0.6 nA specimen current, and a working distance of 20 mm. The EBSD patterns were recorded using a Nordlys camera. The HKL Channel 5 software package was used for data collection and processing. Crystal structural data for leucite and analcime were from the ICSD database (leucite code: 9826; analcime code: 15811).

2.7 References


Chapter 3

MECHANISM AND KINETICS OF PSEUDOMORPHIC MINERAL REPLACEMENT REACTIONS: A CASE STUDY OF THE REPLACEMENT OF PENTLANDITE BY VIOLARITE

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Mechanism and kinetics of pseudomorphic mineral replacement reactions: A case study of the replacement of pentlandite by violarite

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Erratum on Chapter 3

Page 48 (journal page 1946): Bottom left column, “debates” should be “debate”.

Page 52 (journal page 1950): At the end of Fig. 2 caption, add “The white curve in (l) is a backscatter electron line scan, revealing that the reaction zone is less than 150 nm in size”.

Page 58 (journal page 1956): Right column the second paragraph, “(PO_{2\text{g}} \sim 0 \text{ atm})” should be “(PO_{2\text{g}} \sim 0.21 \text{ atm})”.

Page 58 (journal page 1956): Bottom right column, delete “units”, as pH doesn’t have a unit.
Chapter 4

THE ROLE OF PYRRHOTITE (Fe$_7$S$_8$) AND THE SAMPLE TEXTURE IN THE HYDROTHERMAL TRANSFORMATION OF PENTLANDITE ((Fe,Ni)$_9$S$_8$) TO VIOLARITE ((Ni,Fe)$_3$S$_4$)

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The role of pyrrhotite (Fe$_7$S$_8$) and the sample texture in the hydrothermal transformation of pentlandite ((Fe,Ni)$_9$S$_8$) to violarite ((Ni,Fe)$_3$S$_4$). *Reaction Kinetics and Catalysis Letters, 2007, 92 (2), 257-266.*

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CHAPTER 4. THE ROLE OF PYRRHOTITE AND INITIAL SAMPLE TEXTURE


Reaction Kinetics and Catalysis Letters, v. 92(2), pp. 257-266
NOVEL ROUTE TO SYNTHESIZE COMPLEX METAL SULFIDES: HYDROTHERMAL COUPLED DISSOLUTION-REPRECIPITATION REPLACEMENT REACTIONS

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Novel Route To Synthesize Complex Metal Sulfides: Hydrothermal Coupled Dissolution–Reprecipitation Replacement Reactions

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Chapter 6

THREE DIMENSIONAL ORDERED ARRAYS OF NANOZEOLITES WITH UNIFORM SIZE AND ORIENTATION BY A PSEUDOMORPHIC COUPLED DISSOLUTION-REPRECIPIRATION REPLACEMENT ROUTE

Xia, F.\textsuperscript{a}, Brugger, J.\textsuperscript{b,c}, Ngothai, Y.\textsuperscript{a}, O'Neill, B.\textsuperscript{a}, Chen, G.\textsuperscript{d}, Pring, A.\textsuperscript{b,c}

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Three dimensional ordered arrays of nanozeolites with uniform size and orientation by a pseudomorphic coupled dissolution-reprecipitation replacement route. Submitted to a chemistry journal.

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Three Dimensional Ordered Arrays of Nanozeolites with Uniform Size and Orientation by a Pseudomorphic Coupled Dissolution-Reprecipitation Replacement Route

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Chapter 7

CONCLUSIONS
Chapter 7. Conclusions

The major contribution of this thesis is that it advances our knowledge of the pseudomorphic replacement reactions especially regarding aspects of the role of the fluid phases, the cause of coupling between dissolution and precipitating, the implication of the rate limiting steps, the origin of the length scale of pseudomorphism, and the effects of the physical texture of mineral assemblage to the replacement reactions. The second major contribution of this thesis is that the principle of pseudomorphic mineral replacement reactions has been applied to the materials syntheses.

7.1 Mechanisms and kinetics of replacement reactions

This work demonstrates that detailed mechanisms of pseudomorphic mineral replacement reactions can be revealed by combined kinetic and textural studies. The kinetic and textural study of the replacement of pentlandite by violarite tells us that the replacement is very sensitive to physico-chemical parameters including temperature, pH, concentrations of metal ions, type and concentrations of oxidants, solid-weight-to-fluid-volume-ratio, specific surface area, and physical texture of the primary mineral or mineral assemblage. All these features point to a coupled dissolution-reprecipitation mechanism, in which the fluid phase plays a central role. The porous texture of violarite and the contractionary nature of the replacement in terms of volume indicate that the replacement occurs under non-hydrostatic stress free conditions. This means that non-hydrostatic stress is not responsible for the coupling. Instead, the coupling between primary mineral dissolution and secondary mineral precipitation is mainly controlled by the solution composition at the reaction front. It works in such a manner that primary mineral dissolves into the local solution, making the solution supersaturated with respect to the secondary mineral. The secondary mineral precipitate from the solution immediately following primary mineral
dissolution with the same rate but the locality of the precipitation depends on the rate limiting step of the overall reaction. If primary mineral dissolution is the rate limiting step, the secondary mineral precipitation would occur adjacent to the primary mineral dissolution sites. In this case, high degree pseudomorphism dominates, resulting in the preservation of textural features on the nanometer scale. On the other hand, if secondary mineral precipitation is the rate limiting step, the secondary mineral tends to precipitate away from the primary mineral dissolution sites, and often overgrowth occurs. In this case, low degree pseudomorphism controls the overall replacement, leading to the loose preservation of textural features on larger length scales, and sometimes no pseudomorphism occurs. The coupling is also controlled by the surface of the primary mineral because the surface acts as a substrate for secondary mineral nucleation. This explains why the crystallographic information is transferred from the primary mineral to the secondary mineral, and why sometimes metastable secondary mineral rather than thermodynamically more stable phases replace the primary mineral.

7.2 The applications in materials syntheses

This work also demonstrates that the principle of pseudomorphic mineral replacement reactions can be applied to materials syntheses. The first demonstration is the syntheses of two thiospinels, violarite and linnaeite. Violarite is usually synthesized by the traditional silica-tube method, but this method has two major limitations: (1) time-consuming as the process usually needs a few months’ annealing time, and (2) difficult to avoid impurities, for example, the best purity achieved in this work is only about 72%. The main cause of these limitations is that violarite is a mineral with low thermostability, so that the annealing temperature must be sufficient low to avoid the formation of other phases. The pseudomorphic replacement route illustrated in this thesis solves these two problems. By
designing a pseudomorphic replacement reaction starting with pure pentlandite and keeping the reaction condition favouring pentlandite dissolution being rate limiting, pure violarite can be synthesized by replacing pentlandite in only a few days. What’s more, compared to the silica-tube method, the pseudomorphic replacement route can adjust the composition of violarite over a range of Fe/Ni ratios. This is achieved by simply changing reaction parameters such as pH, temperature, and the composition of starting pentlandite. Therefore, the pseudomorphic replacement is ideal for synthesising materials with low thermostability. An important feature of the synthesized violarite and linnaeite is that they contain numerous nano- and micro-pores, making them potential candidate in the applications as mesoporous materials.

The second demonstration is the synthesis of a zeolite, analcime, starting from leucite. This application makes best use of the most unique feature of replacement reactions, i.e., pseudomorphism. The starting leucite consists of inherent three-dimensional ordered network of nanometer scale twin planes, which can be regarded as three-dimensional ordered arrays of nano-lamellae. Such amazing texture can be precisely preserved into the analcime product by designing the reaction conditions under which leucite dissolution is rate limiting so that nano-scale textural features can be retained. What’s more, the substrate role of leucite to the precipitation of analcime has led to the inheritance of crystallographic orientation from leucite to analcime. Thus, the replacement reaction finally results in a zeolite monolith consisting of three-dimensionally ordered arrays of nanocrystals with uniform size and crystallographic orientation. Such unique features have promising applications but remained a challenge for materials scientists. Additionally, the pseudomorphic feature also makes it possible to prepare materials with very sophisticated
shapes possible, provided precursors with the same shape are available or can be prepared, and quite often, the shape design in precursors are much easier to realise.

7.3 Future work

This work reveals the mechanisms of pseudomorphous mineral replacement reactions, but there are some problems to be solved in the future. These are discussed in the following.

1. The reactions in this study were monitored \textit{ex situ}, so that the observed reaction texture may not be the same as that under the reaction conditions. For examples, the cooling and quenching process may induce some of the observed cracks, and may also induce some precipitation. \textit{In situ} study can reveal the real mechanism of mineral replacement reactions, thus it can provide a clearer picture of what’s happening during the reaction under hydrothermal conditions. \textit{In situ} monitoring the reactions by neutron diffraction is ideal for this purpose and is thus highly recommended for the following reasons. First, compared to X-ray, neutrons are highly penetrative through the reactors and hence it is easy to use reactors with thick walls that are critical for high pressure hydrothermal reactions. Second, it is easy to get high signal to noise ratio in modern neutron diffractometers. Third, it is possible to use small solid-weight-to-fluid-volume-ratio, so that the fluid composition doesn’t vary significantly during the course of the reaction. Actually, the flow-through reactors used in this study were designed for \textit{in situ} neutron diffraction at Lucas Heights, Sydney, on Australian’s new generation of neutron reactor, the OPAL reactor. The Wombat Neutron Diffraction Beam Line at Lucas Heights has the power to detect a million neutrons a second and to produce data on the structure of materials in milliseconds (\textit{Studer et al.}, 2006), thus the monitoring process is also real time, and may detect some “hidden intermediate reactions” which are impossible to observe by conventional \textit{ex situ} techniques. However, due to the delay of the beam time these experiments are to be carried out in the future.
2. All the reactions in this study were conducted in closed systems, in which fluid composition keep changing with time. As a consequence, the reaction may respond differently with time as well. However, keeping the solution in steady state is a critical prerequisite for quantitative kinetic studies (Lasaga, 1998; Oelkers et al., 2001). Therefore, reactions in open mixed flow-through reactors are to be studied in future work to accurately work out the rate equation. Furthermore, with open mixed flow-through reactors, the effect of the fluid flow to the mechanisms and kinetics on replacement reactions can be studied. The fluid flow continually changes the fluid composition and the laminar and turbulent flows may increase the nucleation energy barrier. With extremely fast flow in open systems, the fluid may never reach supersaturation to precipitate the secondary mineral, thus the process simply becomes the dissolution of starting mineral and replacement reaction won’t occur. These ideas are to be tested in future work.

3. This work confirms the mechanisms by kinetic and textural study, but using isotope distribution to reveal the mechanism is a more popular technique in the literature (see Introduction in Chapter 3). Thus, a further isotopic study of the replacement of pentlandite by violarite can be complementary to this work. The isotopic study could be carried out using S isotopes rather than Ni or Fe isotopes because S forms the framework of the structures, so the exchange of metal ions between the solid and the solution does not distinguish solid-state diffusion to dissolution-reprecipitation.

4. This work suggests that the geometry and distribution of porosity and cracks and their origin in the product phase is very important to the replacement reactions because they control the behavior of fluid flows. However, little is known about porosity/cracks evolution during the replacement process. Future work aiming at the understanding of
porosity/cracks of the replacement reaction is recommended. This can be done by ex
situ study using gas adsorption method, or the mercury intrusion method (SING et al.,
1985). However, a much better technique is to use small angle neutron scattering
(SANS) or small angle X-ray scattering (SAXS) to study the porosity evolution in situ.
This avoids the disadvantage of ex situ methods that the porosity may have been
changed during cooling or quenching processes, and the observed pore geometry may
have been deformed during grinding and polishing processes. Also SANS may provide
an alternative to determine mineral solubility in situ under extreme P-T conditions by
comparing the measured porosity and the theoretical porosity which can be calculated
from molar volume difference between primary and secondary minerals.

5. This work examines a complex replacement to show that simple model even works
well in complex systems. However, a complex system makes quantification a great
challenge, for example, concurrent determination of concentrations of S, Ni, and Fe is
almost impossible, and thus conclusions have to be made based on some indirect
observations. Replacement reactions on simple systems have been explored (RENDÓN-
ANGELES et al., 2000; PUTNIS and MEZGER, 2004; SUAREZ-ORDUNA et al., 2007), but
none of them are based on sulfide system. Primary work on the replacement of
cobaltpentlandite by linnaeite (Chapter 5) suggests that this simple system works well.
Thus, detailed study on this system is suggested in future work.

6. This work makes a hypothesis based on the induction period observed in the
replacement of pentlandite by violarite that the precipitation of secondary mineral on
the primary mineral only needs to occur at the beginning of the replacement; as soon as
a thin film of secondary mineral forms, later precipitation will occur onto the secondary
mineral. This hypothesis needs to be validated by future work. For example, conduct a
replacement reaction starting with a dense polycrystalline sample in which the
crystallites are not uniformly oriented, and see whether the product is uniformly
oriented or has the same orientation texture as its precursor. The primary mineral
should be sufficient dense to avoid fluid entering the phase. This can be a challenge
because, for example, the twin planes in the leucite phase are big enough for the fluid
to enter the structure (Chapter 6).

7. In the replacement of pentlandite by violarite using pentlandite/pyrrhotite assemblage
as starting materials, the pyrrhotite phase was replaced by a mixture of marcasite and
pyrite after the replacement of pentlandite by violarite. These interesting side
replacement reactions, possibly the replacement of pyrrhotite by marcasite/pyrite, and
the replacement of marcasite by pyrite, are worthy of further detailed investigations.

8. The synthesized nanoanalcime arrays have such amazing features but unfortunately
analcime itself is not an important zeolite in industrial applications. Therefore,
adjustment of the product phase to industrial important zeolites, such as Zeolite A, Y or
beta, is to be carried out. This could be done by adding some structure-directing-agents
(SDA) such as tetrapropylammonium (TPA) during the reaction (Davis, 2002; Cundy
and Cox, 2003).

9. This work only explores the application of pseudomorphic mineral replacement
reactions in the syntheses of materials. However, such reactions are very common in
other fields such as in hydrometallurgical engineering, in waste water treatment, and in
the fossilization. Applications into these fields and other possible fields are yet to be
explored.
7.4 References


Appendix A

KINETICS AND MECHANISM OF HYDROTHERMAL ALTERATION FROM PENTLANDITE TO VIOLARITE

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紫硫镍矿交代镍黄铁矿的水热反应机理及动力学

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THE CATALYTIC ROLE OF PYRRHOTITE IN HYDROTHERMAL ALTERATION OF PENTLANDITE TO VIOLARITE

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The catalytic role of pyrrhotite in hydrothermal alteration of pentlandite to violarite

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Abstract

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Appendix C

MECHANISM OF PSEUDOMORPHIC MINERAL REPLACEMENT REACTIONS REVEALED BY A COMBINED TEXTURAL AND KINETIC STUDY

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Mechanism of pseudomorphic mineral replacement reactions revealed by a combined textural and kinetic study

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Appendix D

**Preservation of Multiscale Lamellar Twinning Texture and Crystallographic Orientation in the Replacement of Leucite by Analcime**

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Preservation of multiscale lamellar twinning texture and crystallographic orientation in the replacement of leucite by analcime

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Appendix E

HYDROTHERMAL SYNTHESIS OF FeNi₂S₄, A THIOSPINEL

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Hydrothermal synthesis of FeNi$_2$S$_4$, a thiospinel

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Abstract


NOTE:
This publication is included on pages 167-173 in the print copy of the thesis held in the University of Adelaide Library.
Appendix F

MINERAL SYNTHESIS USING THE COUPLED DISSOLUTION-REPRECIPITATION ROUTE

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Mineral synthesis using the coupled
dissolution-reprecipitation route

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NOTE:
This abstract is included on page 177 in the print copy of the thesis held in the University of Adelaide Library.
Appendix G

THREE DIMENSIONALLY ORDERED ARRAYS OF NANOZEOLITES WITH UNIFORM ORIENTATION

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The 8\(^{th}\) World Congress of Chemical Engineering, 2009, Montréal, Canada.
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Three dimensionally ordered arrays of nanozeolites with uniform orientation. The 8th World Congress of Chemical Engineering, 2009, Montréal, Canada.

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THREE DIMENSIONALLY ORDERED ARRAYS OF NANOZEOLITES WITH UNIFORM ORIENTATION

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This publication is included on pages 181-186 in the print copy of the thesis held in the University of Adelaide Library.
Appendix H

Experimental Synthesis of Auriferous Arsenian Pyrite/Marcasite by Pseudomorphic Replacement of Pyrrhotite

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Experimental synthesis of auriferous arsenian pyrite/marcasite by pseudomorphic replacement of pyrrhotite

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Appendix I

ARSENIAN PYRITE FORMATION: SOLID-STATE DIFFUSION OR DISSOLUTION-REPRECIPITATION REPLACEMENT?

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Arsenian Pyrite Formation: Solid-State Diffusion or Dissolution-Reprecipitation Replacement?

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Appendix J

THE MECHANISM OF PENTLANDITE OXIDATION IN THE TEMPERATURE RANGE 530-600 ºC

Xia, F.\textsuperscript{a}, Pring, A.\textsuperscript{b}, Ngothai, Y.\textsuperscript{a}, O'Neill, B.\textsuperscript{a}, Brugger, J.\textsuperscript{b}, Chen, G.\textsuperscript{c}, Colby, C.\textsuperscript{a}

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The mechanism of pentlandite oxidation in the temperature range 530-600°C

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Appendix K

THE KINETICS OF PENTLANDITE OXIDATION IN THE TEMPERATURE RANGE 530-600 °C

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The kinetics of pentlandite oxidation in the temperature range 530-600ºC

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Appendix L

HYDROTHERMAL CALAVERITE DECOMPOSITION USING THE ORTHOGONAL EXPERIMENTAL DESIGN METHOD

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