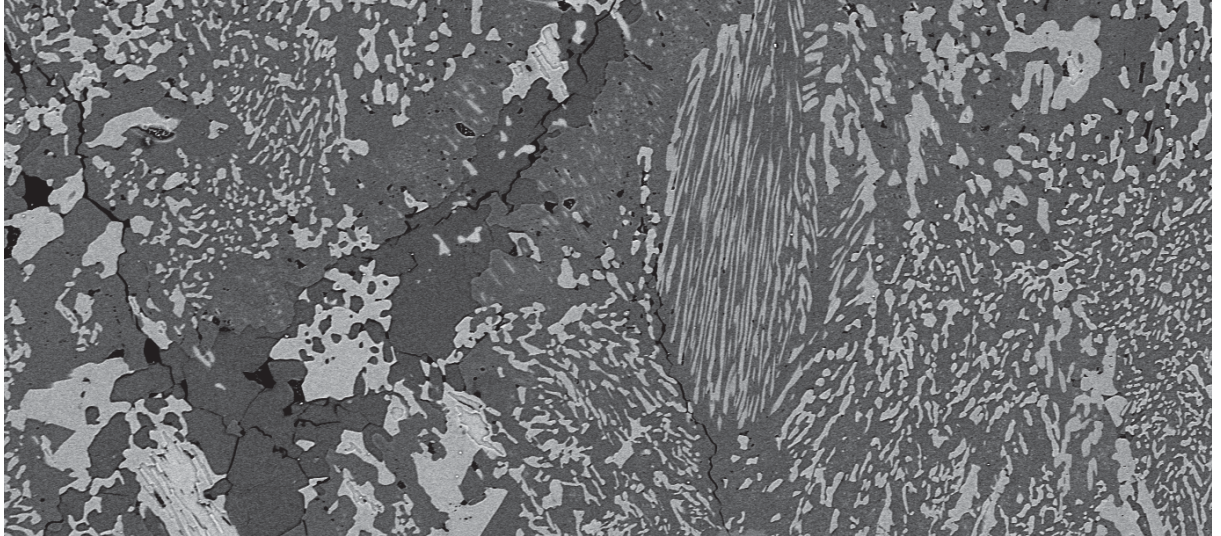


AUSTRALIAN RESEARCH COUNCIL CENTRE OF EXCELLENCE
FOR CORE TO CRUST FLUID SYSTEMS (CCFS) AND GEMOC,
DEPARTMENT OF EARTH AND PLANETARY SCIENCES



MACQUARIE
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FLUID-ROCK INTERACTION: FROM SIMPLE SINGLE CRYSTALS TO COMPLEX NATURAL SYSTEMS

by

Liene Spruzeniece

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Abstract

Fluid is present in many tectonic settings in the Earth's crust and plays a fundamental role in controlling chemical, physical and kinetic properties of rocks in both static and dynamic environments. This PhD project aims to provide a deeper understanding of the interaction between fluid, rock microstructure and chemical reactions by combining experimental and field approaches.

In the experimental studies, a variety of aspects of fluid-mediated mineral replacement are explored in controlled static conditions. This study demonstrates that in simple salt systems fluid-mediated replacement reactions can create deformation-resembling microstructures. Similar microstructures in natural samples may be misinterpreted as resulting from crystal-plastic deformation. The experiments on polycrystalline materials reveal that the microstructures of reaction products as well as the reaction pathways can vary dramatically depending on the rate-limiting step in the replacement process (either dissolution, component transport or precipitation) and can be modified by varying fluid composition. Even slight changes in the chemistry of the reactive fluid determine if the reaction is controlled by grain boundary geometry, crystallographic orientation or reaction-generated porosity. Furthermore, this study demonstrates that in systems, where fluid undergoes continuous compositional evolution during interaction with the parent material, rapid dissolution-precipitation processes can create mineralogically and structurally complex, symplectite microstructures. The thesis is concluded with a field study, comparing samples deformed in fluid-limited versus fluid-abundant conditions. The two cases display significant differences in the activated deformation mechanisms and chemical processes, indicating dramatically different rheologies and paths of microstructural evolution.

Results of this thesis show that the presence of a reactive fluid in geologic systems is more than just a kinetic factor. Fluid can control the mechanisms that govern deformation and mineral reactions on a fundamental level. In-depth

understanding of these controls can lead to more accurate models for predicting the consequences of fluid-rock interaction in a variety of physio-chemical systems.

STATEMENT OF ORIGINALITY

All the material presented in this thesis is, to the best of my knowledge, my own original research, except where acknowledged otherwise. No part of this thesis has been submitted to any other university or institution.

Liene Spruzeniece

Date

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1. Introduction

1.1. FLUID-ROCK INTERACTION: AN IMPORTANT PROCESS IN THE EARTH'S CRUST

Although the amount of the free fluid in the Earth's crust is relatively small, it plays a major role in many geological processes, such as weathering (e.g. Røyne et al., 2008; Maher, 2010), ore formation (Yardley and Cleverley, 2013), metasomatic alteration reactions (e.g. Etheridge et al., 1983; Putnis and Austrheim, 2010), earthquake generation (e.g. Sibson, 1996; Barnhoorn et al., 2010; Wintsch and Yeh, 2013), and shear zone development (Austrheim, 1987; Fusseis and Handy, 2008; Menegon et al., 2015).

In the last decades, a major effort has been made to advance our understanding of the diverse role of fluid in crustal systems, demonstrating that fluid is both a chemical and mechanical agent during mineral reactions and deformation in the crust (e.g. Wintsch, 1985; Wheeler, 1987). Experimental studies demonstrate that mineral replacement reactions in the presence of a chemically reactive fluid commonly proceed by a fluid-mediated coupled dissolution-precipitation mechanism. This is a markedly different process to mineral equilibration via volume diffusion, predominant in fluid-absent conditions (Putnis, 2009). In addition, syn-deformational fluids can introduce a number of fluid-mediated deformation mechanisms, for example, reaction-induced fracturing (Jamtveit et al., 2000), pressure-solution (Wintsch and Yi, 2002) and granular fluid pump (Fusseis et al., 2009). These are controlled by fluid-mediated dissolution-precipitation reactions that have low activation energy and can weaken the crust dramatically.

In the light of a large number of recent studies, the integration of physical and chemical feedbacks of fluid-rock interaction still prevails as one of the least understood and most challenging aspects of crustal dynamics.

1.2. MINERAL REPLACEMENT IN A PRESENCE OF A REACTIVE FLUID

This and further sections in the introduction focus on the mechanisms and microstructural expression of pseudomorphic mineral replacement reactions in order to provide a background for the performed experimental studies, that display such microstructures.

The rocks in the Earth are in a constant state of equilibration with the external conditions they are exposed to. Any changes in temperature, pressure or system chemistry triggers mineral reactions that tend to re-equilibrate the rock composition with the external conditions. These equilibration reactions proceed via either of the two main mechanisms (Fig. 1):

- (1) Volume diffusion; and/or
- (2) Coupled dissolution-precipitation.

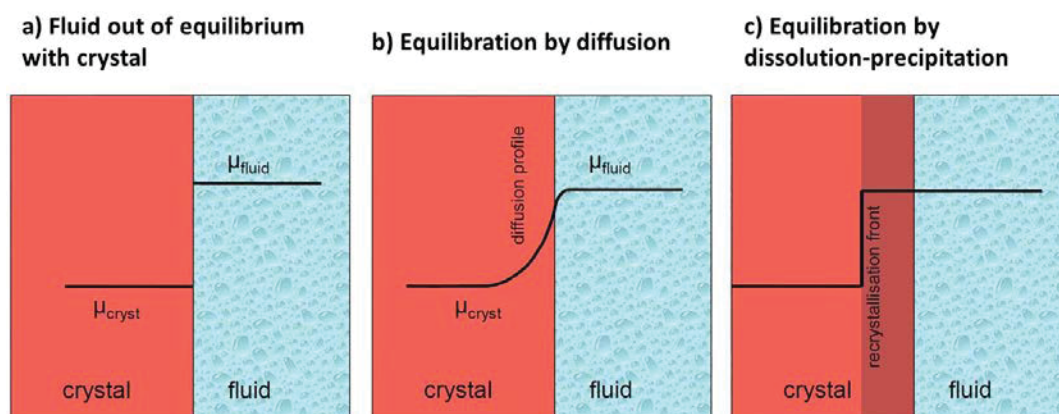


Figure 1. Schematic illustration of the equilibration between the fluid and parent crystals displaying three scenarios: (a) the non-equilibrium state; (b) equilibration by volume diffusion produces a smooth gradient in chemical potential; (c) equilibration by dissolution-precipitation produces a new phase which is in equilibrium with the fluid, but not with the crystal (Putnis, unpublished).

In the absence of a fluid and at high temperature conditions volume diffusion is the dominant reaction mechanism. It involves the movement of disequilibrium components via the crystal lattice without the destruction of the crystallographic framework. The rates of diffusional processes can be described by Fick's first law (Fick, 1855) that states that the flux of material in one direction is proportional to the concentration (now chemical potential) gradient in the system. Volume diffusion rates are very small for most silicate minerals at natural metamorphic temperatures (Brady and Yund, 1983; Watson and Cherniak, 1997). Hence, the completion of mineral reactions requires rock exposure to high metamorphic temperatures for long geological timescales in a range of millions of years (e.g. Dégi et al., 2010). The compositional

gradients between the parent and product minerals of diffusion reactions should be smooth, as determined by the gradients in the chemical potential (Fig. 1b).

In the presence of a fluid, dissolution-precipitation is the primary reaction mechanism in most crustal conditions due to the markedly higher rates and lower activation energies compared to the volume diffusion (Putnis and Austrheim, 2012; Wintsch and Yi, 2002). The reactions that are controlled by dissolution and precipitation involve three steps that can be either coupled or uncoupled in space and time: (1) dissolution of the parent mineral at the mineral-fluid interface; (2) component transport in the fluid film to and from the reaction sites; (3) precipitation of a product phase that is less soluble in respect to the fluid composition. Here the research focusses on coupled dissolution-precipitation reactions, where all three steps have similar kinetics. Mineral replacement by coupled dissolution-precipitation can produce pseudomorphic products, similar to those of diffusion reactions and therefore is possible to misinterpret. However, the mechanisms of coupled dissolution-precipitation reactions (Fig. 2) are fundamentally different from the mechanisms of diffusional reactions (O'Neil and Taylor, 1967; Putnis, 2009).

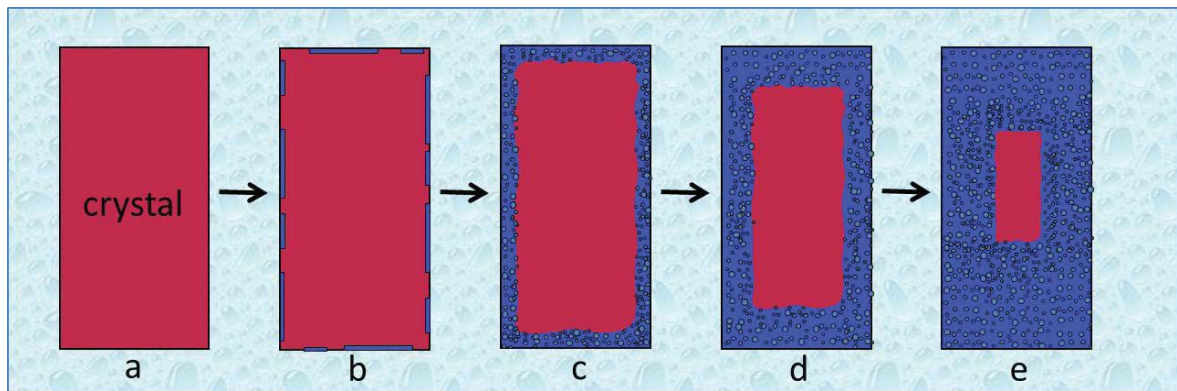


Figure 2. A schematic illustration of mineral replacement by a coupled dissolution-precipitation mechanism (Putnis and Austrheim, 2010). (a) parent crystal is in a contact with a reactive fluid, (b) the dissolution of the parent crystal at the interface with fluid produce supersaturation in the fluid, leading to the nucleation of a product phase on the surface of the parent crystal, (c) the new product phase is porous thus preserving the contact between parent/fluid, (d) – (e) the reaction interface is sharp and migrates inward in the parent crystal as long as the reaction-generated porosity preserves the contact between the reactive parent and fluid.

Several characteristics can be used to recognize products of coupled dissolution-precipitation reactions in the rock record. Those are (Putnis, 2002, 2009; Ruiz-Agudo et al., 2014):

- Sharp reaction interfaces between the parent and product minerals with no chemical gradient in the parent grain;
- Porosity in the reaction products, that provides fluid pathways during the reaction. However, the lack of porosity is not indicative for diffusional reaction processes, as it can be coarsened or healed during later processes (Putnis et al., 2005);
- Rapid reaction rates.

1.3. REPLACEMENT BY COUPLED DISSOLUTION-PRECIPITATION MECHANISMS IN EXPERIMENTS

Initially the replacement reactions in the presence of a reactive fluid were considered to occur via diffusional cation exchange processes through an otherwise intact crystal structure, commonly referred as “leaching” reactions (e.g. Casey et al., 1993). The early experimental evidence that mechanisms of fluid-mediated mineral are principally different from diffusional equilibration reactions was obtained from hydrothermal studies using ^{18}O -enriched fluids (O’Neil and Taylor, 1967, 1969). Here the exchange of ^{18}O and ^{16}O isotopes between the fluid and parent demonstrated that the replacement reaction in the presence of a fluid, involved, not only cation exchange, but a complete breakdown of the oxygen bonds and destruction of the parent crystal structure.

More recently major insights into coupled dissolution precipitation reactions have been obtained from hydrothermal experimental studies performed on a variety of materials ranging from analogue salts systems (Putnis and Mezger, 2004; Putnis et al., 2005) to carbonates and phosphates (Rendón-Angeles, 2000; Kasiopas et al., 2011; Perdikouri et al., 2013) and even low solubility silicate minerals, such as feldspar (Labotka et al., 2004; Niedermeier et al., 2009; Hövelmann et al., 2010), apatite (Harlov et al., 2005), and zircon (Geisler et al., 2007).

The early experimental studies on salt systems (Putnis and Mezger, 2004; Putnis et al., 2005) expanded the understanding of the principal processes involved in replacement by coupled dissolution-precipitation reactions (Fig. 1). In addition, the main microstructural features of such reactions were identified, such as pseudomorphic growth of the reaction products, the existence of sharp reaction interfaces, the

development and role of the reaction-generated porosity (Fig. 3a) and the loss of this porosity during the prolonged crystal exposure to the fluids. The porosity generation (Fig. 3a, b, d) (Hövelmann et al., 2010; O'Neil and Taylor, 1969; Putnis et al., 2005) and/or reaction-induced fracturing (Perdikouri et al., 2013) was found to be intrinsic features of such reactions, as they provide the pathways for the reactive fluid to the reaction interface. Interestingly it has been shown that porosity can be generated even during volume-increase reactions (Putnis et al., 2007; Xia et al., 2009b) as a result of relative solubility differences between the parent and product minerals in the reaction fluid. It has also been shown that the morphologic and crystallographic relationship between the parent minerals and reaction products depends on the coupling between the dissolution and precipitation rates that can be fine-tuned by varying the composition of the reaction fluid (Fig. 3g-h) (Xia et al., 2009a, 2009b). However, the bulk fluid composition used in experiments does not necessarily reflect the fluid composition at the reaction interface. The fluid at the reaction interface tends to become enriched in components from the dissolving parent, obtaining a different ultra-local chemical state (Putnis and Mezger, 2004). Due to this ultra-local state of the interface fluid, complex chemical zoning patterns (Borg et al., 2014) or mineralogically zoned rims (Jonas et al., 2015) can be developed from the fluid with unchanged bulk composition, resembling diffusional gradients. This has been demonstrated to be a transient feature (Borg et al., 2014), that becomes homogenized with prolonged exposure to the fluid (Fig. 3d-e).

Only a few experimental studies (Jonas et al., 2014; Etschmann et al., 2014; Pedrosa et al., 2016) have been done on polycrystalline samples, investigating the role of a rock microstructure on the progression of coupled dissolution-precipitation reactions. The results are inconclusive, but suggest that the grain boundary networks in some cases controls the replacement (Fig. 3j). The study by Pedrosa et al. (2016), however, shows that fluid composition may have a primary role on the replacement processes.

Further studies on structurally and chemically complex fluid-rock systems could help to solve more specific questions on the wide range of aspects related with fluid-rock interaction in nature.

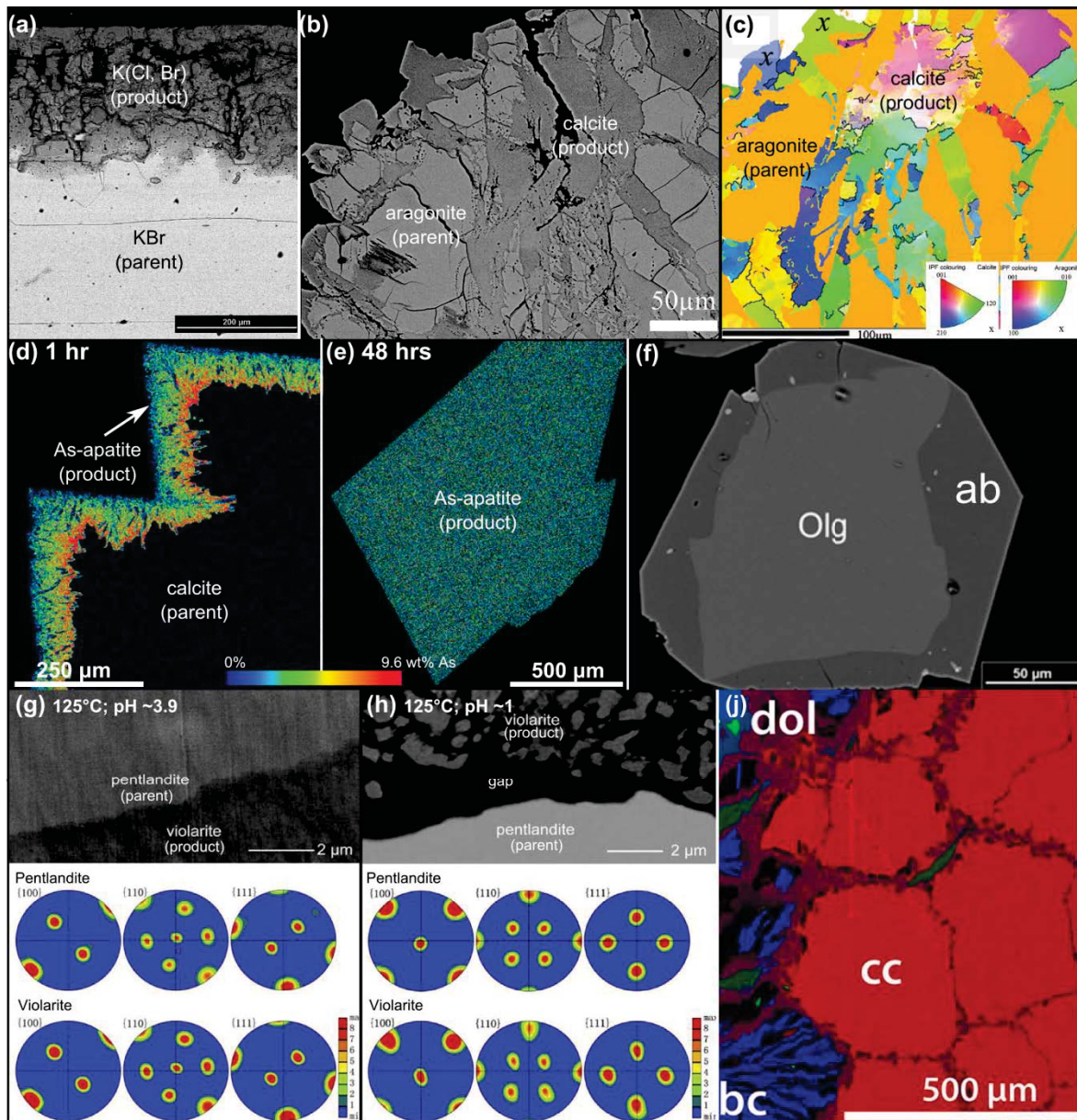


Figure 3. Coupled dissolution-precipitation microstructures in experiments. (a) BSE image of KBr crystal, pseudomorphically replaced by a porous reaction product, composed of KCl-KBr solid solution (Putnis & Mezger, 2004); (b)-(c) aragonite replacement by calcite. The replacement is associated with fracturing and porosity in the reaction product, EBSD image (c) shows that all aragonite parts have the same crystallographic orientation (Perdikouri et al., 2013); (d)-(e) Arsenic concentration in an As-rich apatite replacing a calcite crystal. Note the zoned, complex As distribution in the reaction rim after 1 hr of experiment and much lower, homogenous As content after 48 hrs of experiment where the calcite grain is fully replaced by As-rich apatite (Borg et al., 2014); (f) albite pseudomorphically replacing an oligoclase grain, separated by a sharp reaction front (Hovelmann, et al., 2010); (g)-(h) BSE images and pole figures of pseudomorphic pentlandite replacement by violarite. Note the gap on the reaction interface and higher distortion in violarite crystallographic orientations for the experiments performed using a fluid with lower pH (Xia et al., 2009). (i) chemical map of a partly replaced polycrystalline calcite (cc) sample. Note the dolomite (dol) associates with grain boundaries (Etschmann et al., 2014).

1.4. EVIDENCE OF COUPLED DISSOLUTION-PRECIPITATION REACTIONS IN NATURE

In this section examples from some field studies are given, where microstructural characteristics of coupled dissolution-precipitation reactions have been recognized in a variety of crustal settings. This is in no way an exhaustive review but rather a brief highlight of some characteristic cases.

In upper crustal settings, where the availability of a free fluid is high, coupled dissolution-precipitation is a common mechanism for mineral replacement and known to occur in many environments. Typical coupled dissolution-precipitation microstructures have been reported to form during weathering, as observed in gedrite gneisses, where amphibole breaks down into smectite (Banfield and Barker, 1994), peridotite serpentinisation during seafloor metasomatism, where olivine transforms into lizardite $\pm$ brucite along reaction-generated fracture networks (Fig. 4a) (Plümper et al., 2012) as well as in diagenetic processes, for example albitisation of detrital feldspar in sedimentary basins (Land and Milliken, 1981).

In middle and lower crustal settings, where fluid percolation is limited, the metasomatic alteration reactions are mostly related to faults, fractures and shear zones. A good example is granitic rocks in the Bamble area, SE Norway (Engvik et al., 2008), where large-scale albitisation fronts are closely associated with fractures. At the microscale, plagioclase grains in these rocks display sharp interfaces with pseudomorphic micro-porous albite – muscovite aggregates (Fig. 4b). Albite grains in these altered domains often display the same crystallographic orientation as the adjacent plagioclase parent grains. Another study by Pearce et al. (2013) reports coupled dissolution-precipitation controlled replacement in ore deposits, where calcite is replaced by dolomite and siderite. The replacement in this case is associated with twin planes in the parent calcite grains and seems to produce low-angle boundaries in the reaction products, even though all other evidence suggests that the alteration occurred in static conditions. Interestingly similar cases, showing higher lattice distortions in replacement products compared to parent grains, with seemingly no evidence of deformation, have been observed in other field studies (Brady et al., 2004; McNamara et al., 2012; Mukai et al., 2014), although the explanations of the mechanism that generates these distortions have been inconclusive.

In the lower crust, a well-recognized classic example of fluid-mediated mineral alteration processes is eclogite facies shear zones, exposed near Bergen, in Western Norway (Austrheim, 1987; Jamtveit et al., 2000). Here the garnet grains in the altered parts of the rocks have complex chemical zoning patterns (Erambert and Austrheim, 1993), where sharp interfaces in each grain separate areas of granulite- and eclogite facies chemical signatures (Fig. 4c). It has been interpreted to represent incomplete replacement by dissolution-precipitation controlled reactions. While no porosity in the replaced parts of these garnet grains were observed, in some cases high concentration of fluid inclusions indicate that the garnet rims grew in a fluid-rich environment.

Dissolution-precipitation reactions can also play a significant role in the deformation of the Earth's crust. In a presence of differential stresses, the fluid-pressure can vary highly on a grain scale, leading to stress-controlled chemical potential gradients. Pressure-solution is a deformation mechanism, where shape changes in the rock fabric are achieved by dissolution at the grain surfaces that are normal to σ_1 direction and subsequent precipitation of the dissolved material parallel to the σ_3 direction (e.g. Rutter, 1983). Figure 4d shows truncation of zoned amphibole grains, observed in lower crustal amphibolites that indicate deformation by pressure-solution mechanisms (Stokes et al., 2012). Increasing amount of evidence of dissolution-precipitation features in middle and lower crustal shear zones is reported in recent studies (Wintsch and Yi, 2002; Füsseis et al., 2009; Marsh et al., 2009; Stokes et al., 2012), suggesting the significance of fluid-mediated deformation mechanisms in all crustal settings.

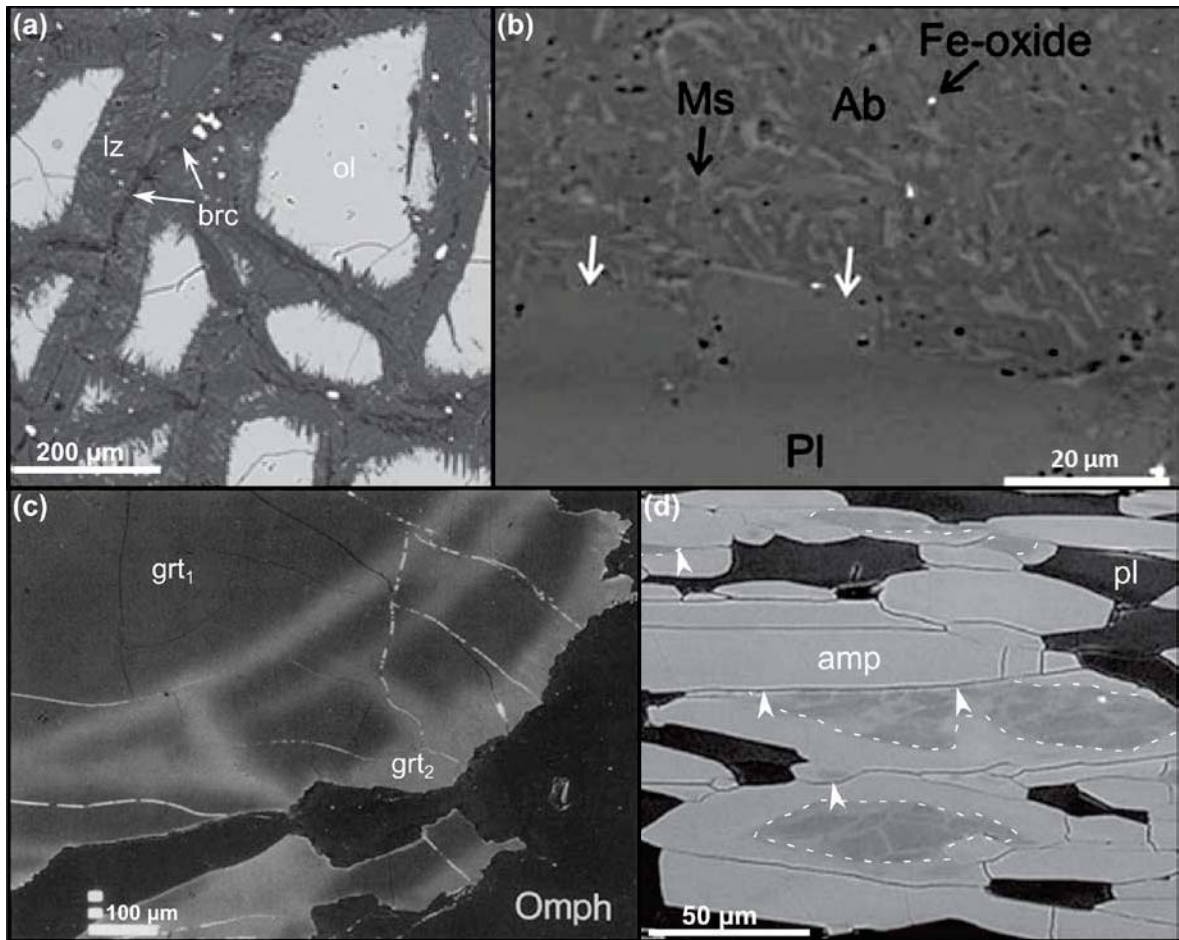


Figure 4. Coupled dissolution-precipitation microstructures in nature. (a) serpentized olivine (lizardite $\pm$ brucite) associated with reaction-induced fracture network (Plümper et al, 2012); (b) plagioclase replaced by albite. Note the porosity and muscovite grains in the albite. The white arrows mark the reaction front (Engvik et al., 2008); (c) complex zoning in a garnet grain from eclogitised granulites. Grt1 – garnet with granulite facies composition, grt2 – garnet with eclogite facies composition, enriched in almandine (Erambert & Austrheim, 1993). (d) mineral relationship in an amphibolite facies shear zone. Note the truncation surfaces (marked with white arrows) and amphibole grains, some with complex actinolite cores (Stokes et al., 2012).

1.5. AIMS OF THIS STUDY

As outlined above, there are several aspects in our knowledge and understanding of fluid-rock interaction that are still poorly understood. This project aims to fill some of these gaps by advancing our ability to link the physical state of the rock with the chemical state of the fluid-rock system in order to gain a deeper understanding of the fundamental mechanisms that control fluid-rock interaction and develop more detailed theories for interpreting rock microstructures in natural settings.

The main questions addressed in this work are:

- How does rock microstructure affect fluid and mass transfer pathways?

- In what way does fluid percolation and associated mineral reactions affect rock microstructure?
- What is the role of fluid composition on the mineral reactions and fluid pathways in a rock?
- How does deformation affect fluid-rock interaction?
- How does fluid-rock interaction affect deformation?

1.6. RESEARCH APPROACH

A combination of experimental and field studies is used in a step-by-step approach, where increasingly more complex systems are explored in each subsequent chapter of the thesis (Fig. 5).

The new research in the thesis starts (Chapter 2) with a simple experimental study on single salt crystals, where the main variable is the pre-experiment internal sample microstructure; it proceeds to experiments with polycrystalline and polyphase materials (Chapters 3 and 4), that add the effects of grain boundaries and reactive secondary minerals. For simplicity, all experiments are performed at static conditions. In the last chapter (Chapter 5), the knowledge, gained in the experimental studies, is applied to understand processes in a natural geological scenario, where fluid-rock interaction occurs during deformation. The chosen field study allows comparison of microstructures formed at high versus low fluid-rock ratios.

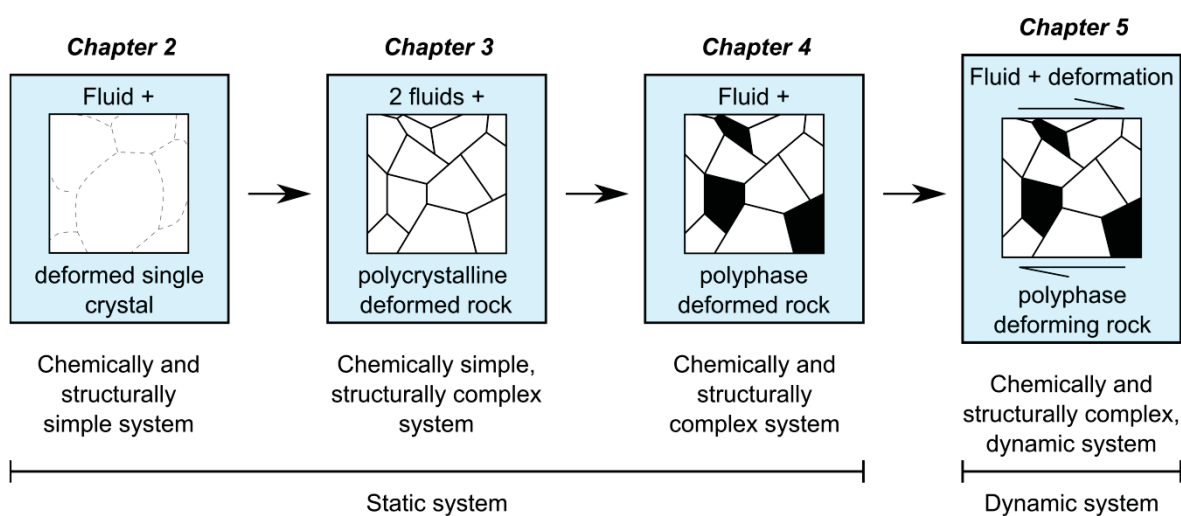


Figure 5. Schematic representation of the approach strategy and link between the individual studies presented in this thesis.

The integration of experiments and field studies is a powerful approach for investigating geological processes. The field studies are essential for defining the research questions, formulating the initial hypothesis and to characterize the actual systems. However, the natural record allows the examination of only final, frozen-in microstructures and reaction products, but offers little direct evidence of the process dynamics and controlling factors involved. The benefit of an experimental approach is the ability to test the hypotheses formulated during field studies, in controlled environments, allowing in-situ observations and straight-forward evaluation of any parameter of interest. Experimental systems, however, are always simplified and may not include all parameters that control the studied processes in nature. Therefore, verification of the experimental results needs to be sought in nature. The combination of experiments and field studies overcomes the limitations of each individual technique to obtain an in-depth understanding of complex processes.

1.7. SET-UP OF THESIS

The thesis consists of 3 experimental studies where fluid-rock interaction is explored via static hydrothermal replacement experiments (Chapters 2 – 4) and a field study of natural shear zones, where fluid infiltration and mineral reactions were simultaneous with deformation (Chapter 5).

Chapter 2 presents a study of a simple experimental model-system that investigates the structural alteration of salt crystals during their interaction with a reactive fluid. Hydrothermal replacement reactions were performed on two sets of samples: (1) single crystals with undeformed lattices and (2) single crystals with deformation microstructures. The results reveal that the replacement is epitaxially controlled and preserves the general microstructural features and grain orientations of the parent crystals. However, the imperfect epitaxy generates new subgrain- and grain boundaries as well as lattice distortions that are not easily distinguished from real deformation microstructures.

Chapter 3 is an experimental study that explores fluid-rock interaction in natural polycrystalline carbonate samples. This component of the study shows that slight variations in fluid composition determine if the mineral replacement proceeds

along grain boundaries or exploits reaction-created porosity as pathways for mass transfer.

In **Chapter 4**, high temperature hydrothermal experiments are performed on natural structurally and chemically complex polyphase samples. Additionally, ^{18}O -doped fluids are used to track the oxygen redistribution during fluid-rock interaction. The reaction products of these experiments resemble symplectite intergrowths that are traditionally considered to form via solid-state volume diffusion reactions. Microstructural, chemical and isotopic evidence is used to propose an alternative model for symplectite formation via dissolution-precipitation mechanisms. The proposed model provides an insight into the mass transfer scales and element mobility in complex, developing microstructures as well as the evolution of the fluid itself during its interaction with a rock.

Chapter 5 is a field study that investigates the rheology and mineral reactions in deformed granitoids. The geological setting allows comparison of the microstructures formed in fluid-limited versus fluid-abundant deformation conditions. The two scenarios display dramatically different strengths, chemical processes and paths of microstructural evolution, accentuating the significance of a fluid in crustal deformation.

1.8. PUBLISHED PARTS OF THE THESIS

Parts that are published or have been submitted for publication:

Chapter 2 has been submitted to the journal “Geology” in January 2016 (Deformation-resembling microstructure created by fluid-mediated replacement reactions).

Co-authors are Sandra Piazzolo and Helen E. Maynard-Casely.

Chapter 4 has been submitted to the Journal of Metamorphic Geology in March 2016 (Symplectites: Products of dissolution-precipitation reactions). Co-authors are Sandra Piazzolo, Nathan Daczko, Andrew Putnis and Matt Kilburn.

Chapter 5 has been published in Solid Earth, Vol. 6, pp. 881-901, 2015 (Strain localization in brittle-ductile shear zones: fluid abundant vs. fluid-limited conditions (and example from Wyangala area, Australia)). Co-author is Sandra Piazzolo.

The experimental designs (Chapter 2-4) and ideas for the field study (Chapter 5) were initially proposed by Sandra Piazzolo (SP) and further developed in discussions between SP and the author of the thesis. Most of the experimental work and sample characterization was carried out by the author. The data analysis and interpretations were conducted by the author with significant scientific support from SP. The manuscripts were predominantly written by the author, but highly benefited from the revisions by SP and other co-authors.

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Conference proceedings:

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Spruzeniece, L., Piazzolo, S. Fluid-controlled fabric development across a brittle-ductile shear zone: an example from a Wyangala Batholith, Australia. AGU Fall meeting, San Francisco, CA, USA, 15-19 December, 2014. Oral presentation (Appendix D)

Spruzeniece, L., Piazzolo, S., Schmatz, J. How deformation affects reaction rates: new insights from phase transformation experiments in the KBR-KCL-H₂O system. AESC Australian Earth Sciences Convention, Sustainable Australia, Newcastle, NSW, Australia, 7-10 July, 2014. Oral presentation (Appendix E)

Spruzeniece, L., Piazzolo, S., Daczko, N. Deformation in an Open System: Fluid Assisted Brittle-Viscous Deformation Coupled with Volume Change in a

Greenschist Facies Shear Zone (Wyangala, Australia). Biennial Meeting of the Specialist Group in Tectonics and Structural Geology (SGTSG), Thredbo, NSW, Australia, 2-8 February, 2013. Oral presentation (Appendix F)

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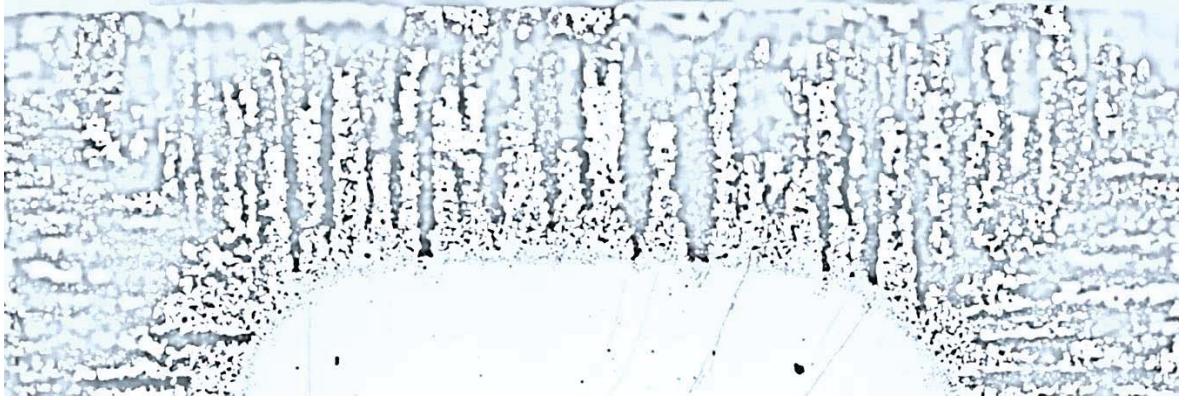
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“Crystals are like people, it is the defects in them which make them interesting.”

/Frederick Charles Frank/

CHAPTER 2

2. Deformation-resembling microstructure created by fluid-mediated replacement reactions

ABSTRACT

Deformation microstructures, characterized by in-depth quantitative tools, are now widely used for reconstructing tectono-metamorphic events recorded in rocks. Although deformation in crustal settings is often accompanied and/or succeeded by fluid-mediated mineral reactions, it remains unclear how such an alteration affects rock microstructure. We have conducted a series of experiments where undeformed and deformed parent KBr crystals are reacted with a saturated KCl-H₂O fluid at room temperatures (21-23°C) and atmospheric pressure for durations of 0.5 to 8 hours in the absence of differential stress. Reaction products inherit the general microstructural features from their parents, including subgrains, subgrain boundaries and internal deformation within the subgrains. However, the reaction also produces new deformation-resembling microstructures, such as misorientations in crystal lattices and new subgrain-resembling domains, separated by low-, and in some cases, high angle boundaries. Our results show that potentially misleading microstructures can form during fluid-mediated replacement reactions under static conditions. We propose a set of criteria, which may help in distinguishing microstructures produced by deformation from microstructures created during rock alteration by a fluid.

2.1. INTRODUCTION

Rocks affected by crystal-plastic deformation in the dislocation creep regime exhibit characteristic microstructures. At the grain scale these include, undulose lattice distortions, subgrains, subgrain boundaries and, at a whole specimen scale, crystallographic preferred orientations (CPO). During the last 20 years major efforts have been made to use these microstructures for obtaining quantitative information on deformation conditions and processes (e.g. Twiss, 1977; Trimby et al., 1998; Stipp et al., 2010; Svahnberg and Piazzolo, 2010). The underlying assumption for such interpretations is that the final microstructures as found in the rocks at the Earth surface have remained identical to the original microstructures produced during deformation occurring at higher pressure (P) and temperature (T) conditions. However, in many crustal settings, deformed rocks are used as pathways for

metasomatic fluids (Austrheim, 1987; Menegon et al., 2015) and undergo post-tectonic fluid-mediated mineral reactions as a result (Hippertt, 1998). How the rock microstructure is affected by interaction with fluid is rarely considered in these interpretations, either ignoring the effects of fluid alteration or assuming that such effects are easily distinguishable from the original deformation microstructures. This assumption has been recently challenged in several field studies. A study by Pearce et al. (2013) shows an example, where low-angle boundaries in metasomatic siderite is a feature of crystal nucleation and growth during fluid-mediated replacement, instead of being a result of deformation and recovery. Other authors (Brady et al., 2004; McNamara et al., 2012) have suggested that metasomatic assemblages can inherit CPO patterns from their parent minerals, leading to misinterpretations of the timing for deformation events. Inherited CPO are also proposed to be responsible for anisotropy in mantle serpentinites (Boudier et al., 2010), mantle wedge peridotites (Nagaya et al., 2014) and post-perovskite in the lower mantle (Dobson et al., 2013).

In this study we use the KBr-KCl mineral system to experimentally explore the effect of fluid-mediated replacement reactions on in-detail characteristics of mineral microstructure. The opportunity of direct comparison between pre- and post-experimental microstructures allows us to define criteria for distinguishing between deformation and reaction-produced features. Our results have implications for interpreting rock microstructural signatures in metasomatic settings, a scenario common in crustal and mantle rocks (Putnis and Austrheim, 2010; Gréau et al., 2011).

2.2. MATERIALS AND METHODS

Optically clear single crystals of high purity (>99% KBr; TedPella, Inc.) were reacted with a saturated KCl-H₂O solution at room T and atmosphere P (GSA Data Repository). Reactions were performed on two sets of samples; set I representing undeformed KBr crystals and set II representing KBr crystals that have been experimentally deformed in order to produce microstructures characteristic to crystal-plastic deformation (Appendix B).

After experiments samples were characterized by Backscatter Electron imaging (BSE), Energy Dispersive X-ray (EDX) spectroscopy Electron Backscatter Diffraction (EBSD) and Neutron Diffraction analysis (Appendix B).

2.3. RESULTS

Reactions are rapid; ~1 mm thick replacement rim can be produced in 4 h (Table B1). The sample dimensions before and after experiments remain identical, however a part of each crystal is replaced by a porous reaction product (Fig. 1A). The product is a solid-solution between KBr and KCl and exhibit ~30% porosity (Fig. 1B, C). The pores are often connected in channels that show elongation normal to the reaction interface. The reaction interface is irregular (Figure 1A).

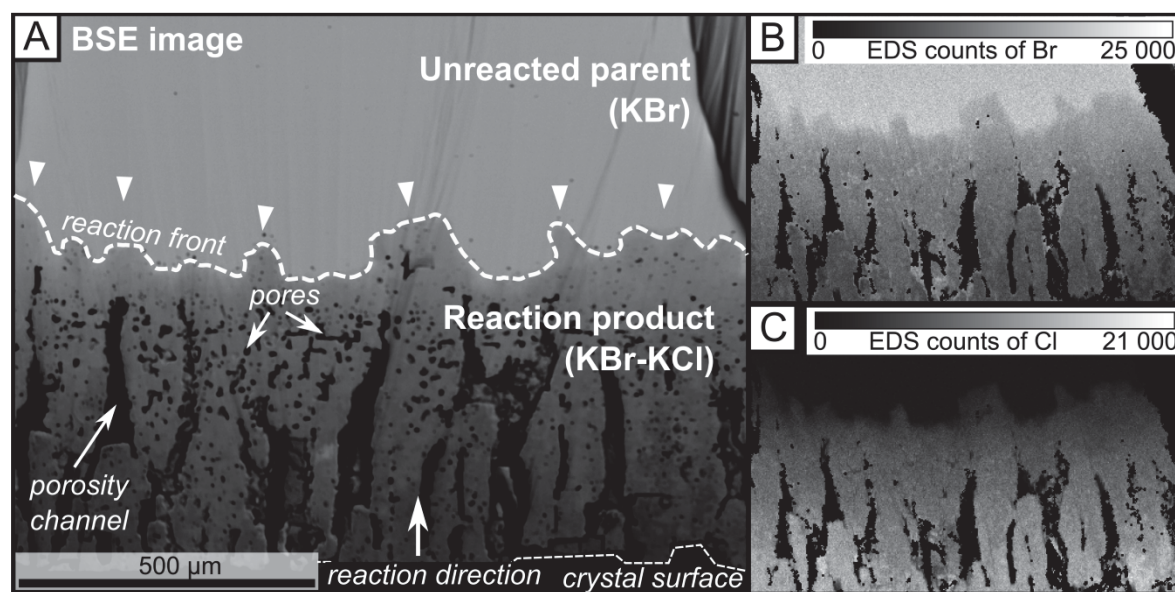


Figure.1. General characteristics of a sample after experiment. A – Backscatter electron (BSE) micrograph; note the irregularity of the reaction front (white triangles mark highly advanced parts). B, C – EDS counts of Br and Cl.

2.3.1. Crystal structure in bulk samples

With increasing experiment duration neutron diffraction data show that the Bragg reflection intensity of parent [200] peak (at $\sim 53.8^\circ$) decreases, while the intensity of product [200] peak increases and trends towards the ideal KCl [200] reflection at 55.9° . For set I samples, parent and product peaks are perfectly aligned on the ω – 2θ gradient, the angular spread low ($<1^\circ$) but for longer experiments increases to $\sim 2^\circ$ in the product phases (Fig. 2A-C). For set II samples, the peaks of the parent and product are again aligned along the ω – 2θ gradient. The parents show angular spread in a range between 6 and 10° , while the products have smaller spread in the short experiments, but with increasing reaction times obtain a similar spread to their parents (Fig. 2D-F).

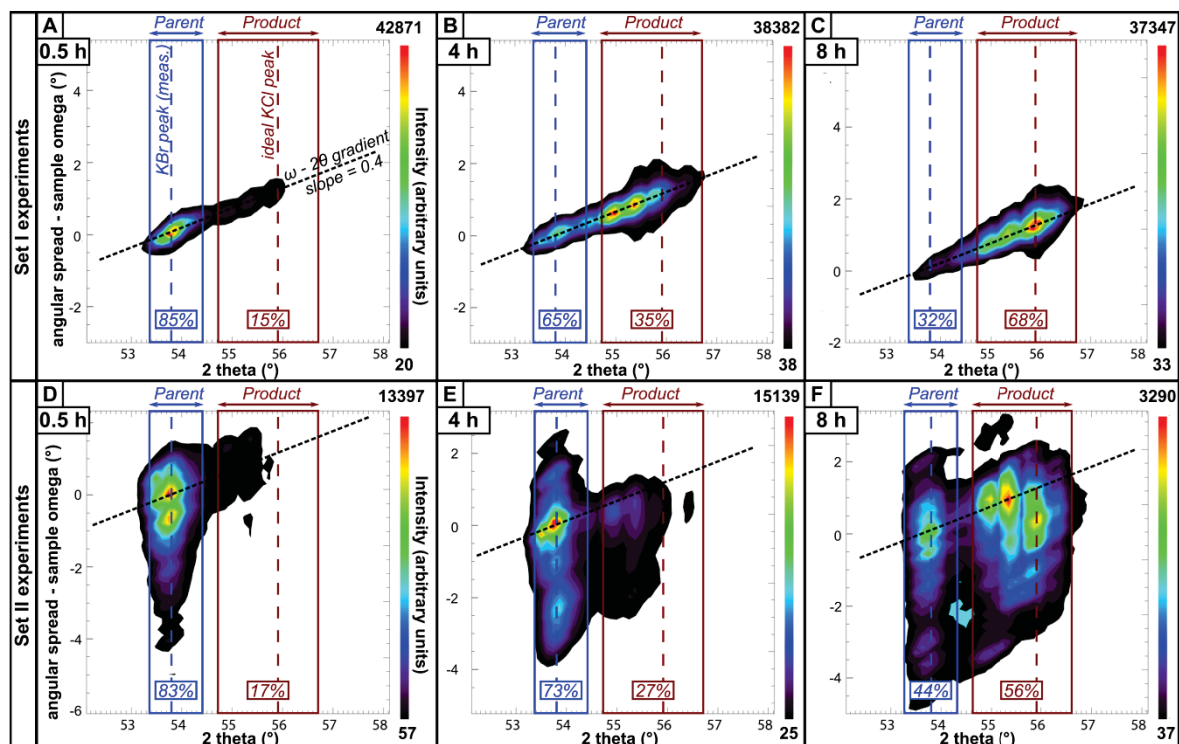


Figure 2. Neutron-diffraction data. A-C - set I samples; B-F - set II samples; x-axis (2θ) represents lattice parameters in the analysed samples, the ideal positions for KBr and KCl are marked with dashed lines and the observed range for parent (KBr) and product (KBr-KCl) reflections are marked with blue and red boxes; y-axis (sample ω) represents angular spread ($^\circ$) in the samples relative to the parent reflection peak; ω - 2θ gradient describes positions where parents and products are in an ideal crystallographic alignment.

2.3.2. Detailed microstructural analysis of sample cross-sections

All samples are monocrystalline. Set I parents have minimal internal distortion mostly within a range of the analytical error (0.2°) (Fig. 3A, G-profile 1). while set II parents have a polygonal substructure, where distinct, often straight and continuous, 1° and 2° boundaries separate subgrains (Fig. 3D; G-profile 2). The pole figures in set II parents show clusters with two branches in $\sim 120^\circ$ angle (Fig. 3E(i)), while 2 - 5° rotation axes cluster close to $[110]$ (Fig. 3E(ii)), reflecting the main slip system $\{110\}\langle 100\rangle$ (Fig. B3B), rotation axis clusters near $[111]$ and $[112]$ are also common.

The products in all experiments exhibit higher lattice distortion than their parents, but on a grain scale preserve the same single crystal orientation (Fig. 3A-F). Low angle boundaries (1 - 10°) in products are more abundant, more irregular and less continuous. In set II products low angle boundaries can be traced across the reaction front into the adjacent parent grains (Fig. 3D). In comparison to parents, products show a wider orientation spread (Fig. 3 B(i)-F(i)), 2 - 5° rotation axes are more scattered, often around different crystallographic directions (Fig. 3B(ii)-F(ii)). The MAD in

products mainly falls between 0.25° and 0.75° with low frequencies at higher angles, while set II parents show MAD maximum at 1.25° (Fig. 3H). Set II products can display same slip system as their parents (Fig. B3C), or imperfect apparent slip system $\{112\}\langle 112\rangle$. Set I products, although never deformed may show a rotation axis – boundary trace relationships consistent with an apparent activation of the $\{112\}\langle 110\rangle$ and $\{100\}\{100\}$ slip systems (Fig. B3A).

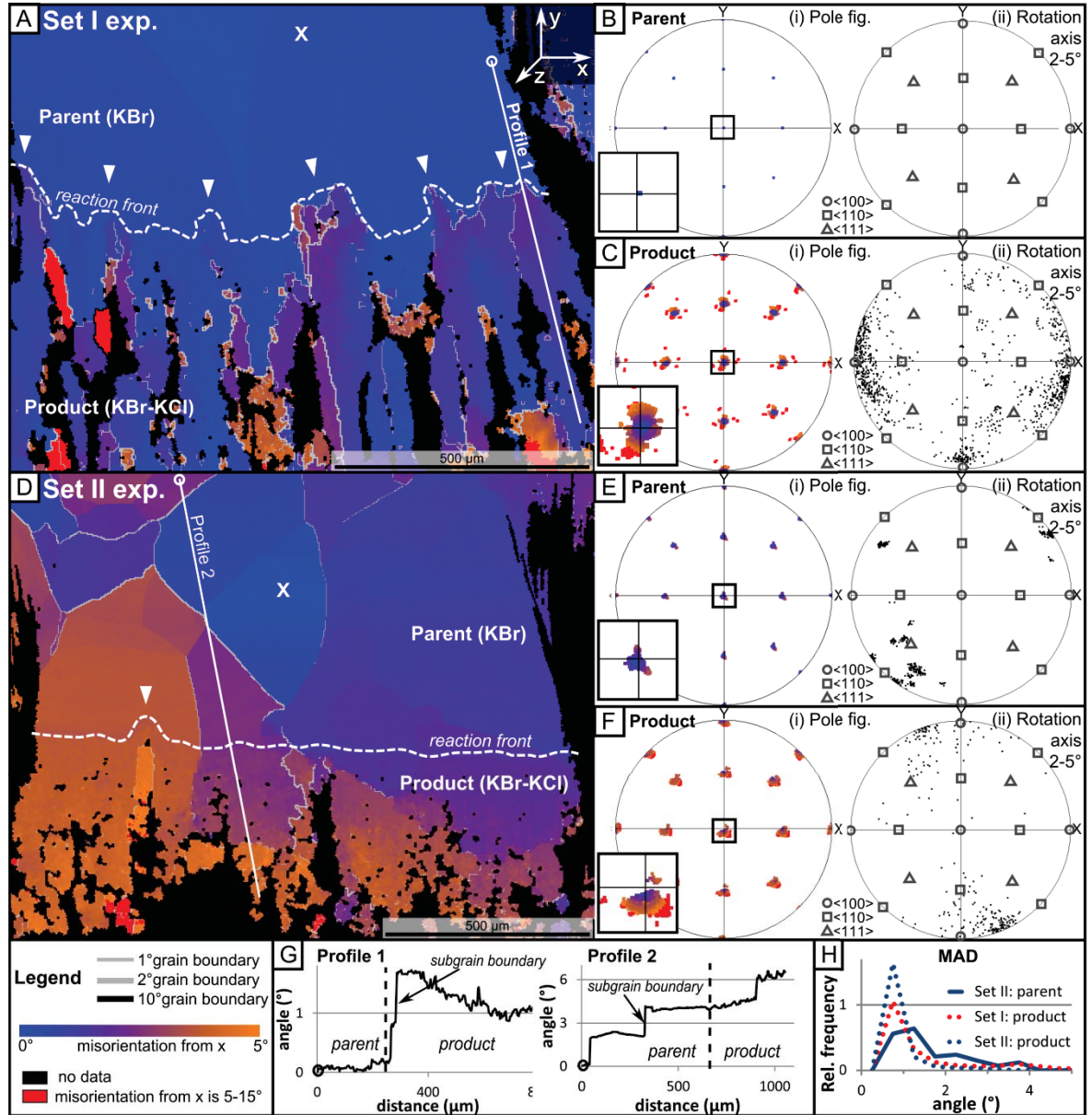


Figure 3. EBSD data. A) – C) set I experiment; D) – F) set II experiment. A) and D) show crystallographic orientations in a sample cross-section from a reference point (white cross); white triangles marks advanced parts in the reaction front that correlate with highly misoriented parts in the product phase; B(i), C(i), E(i) and D(i) show pole figures (equal area, lower hemisphere) for parent and product phases as marked in A and D. Same colour scheme and reference frame is used; B (ii)-(iii), C (ii)-(iii), E (ii)-(iii), F (ii)-(iii) show 2-5° rotation axis in sample coordinates (equal area, lower hemisphere projection); G - misorientation angle variations across the profiles marked in A and D; H - misorientation angle distribution (MAD).

2.4. DISCUSSION

2.4.1. Reaction mechanism

A number of studies have used the KBr-KCl-H₂O system as a simple experimental analogue for understanding fluid-mediated replacement reactions (Putnis and Mezger, 2004; Putnis et al., 2005; Pollok et al., 2011). As demonstrated by Putnis and Mezger (2004), in the presence of a fluid KBr-to-KCl replacement proceeds by a complete destruction of the original crystal structure and is best explained as a fluid-mediated reaction involving coupled dissolution and precipitation, instead of diffusional cation exchange mechanisms as in solid-state (Putnis, 2009). Our observations of rapid reaction rates, porosity in the reaction products and sharp compositional interfaces are consistent with the criteria for recognizing coupled dissolution and precipitation reactions, thus in the following discussion the obtained microstructures will be discussed in this context.

2.4.2. Formation of the reaction microstructure

The good alignment of parent and product reflection peaks in neutron diffraction data (Fig. 2) indicates that products precipitate in a close orientation to their parents. In shorter experiments the products display smaller angular spreads compared to the parents, because only a part of the crystal is replaced. In experiments, where replacement is close to completion, the angular spread in the related parent and product phases is very similar (Fig. 2C, F). This is confirmed by EBSD data showing that the orientations of the reaction products mostly fall within a 5° range from their parent orientations (Fig. 3A, D).

Although never described in detail, this overall orientation inheritance has been previously observed in other fluid-mediated replacement experiments (Rendón-Angeles, 2000; Putnis and Mezger, 2004; Xia et al., 2009) and attributed to epitaxial growth, when product precipitation is crystallographically controlled by the surface of the dissolving parent (Putnis, 2009).

Here we demonstrate that the near-perfect epitaxy can occur not only at the overall grain-scale, but also on an intragrain scale. Replacement of deformed parents (set II) create products that inherit parents' intracrystalline features (low-angle

boundaries, subgrains, subgrain-scale lattice distortions) (Fig. 3D). In addition to the inherited boundaries, new low-angle boundaries form within the products. This is especially obvious for set I samples, where parents do not display such features. In a classical view subgrain and low-angle grain boundaries are considered to be a result of solid-state deformation by dislocation creep. However, the absence of differential stresses during and after the experiments demonstrates that similar features can be produced in static conditions.

Here we propose two main causes for the observed microstructures in the reaction products. At the first order epitaxy controls the overall relationship between parent and product, and at the second order, local misorientations in the product, distinct from the parent, develop in response to locally variable reaction kinetics. As demonstrated by Xia et al. (2009), the degree of epitaxy during fluid-mediated replacement reactions is dependent on the fluid composition. Xia et al. (2009) deduced that higher epitaxy is achieved in experiments, where dissolution is slower than precipitation and limits the reaction rate. In our experiments, this can be seen on a single crystal scale, where fingering of the reaction interface (Fig. 1) indicates local variations in reaction kinetics. Importantly, the replaced domains with the highest misorientations from the parent crystal occur adjacent to the parts in the reaction front that are the most advanced into the sample interior (Fig. 3D). Here the higher rate of dissolution, in respect to precipitation, prevents a perfect replication of the parent microstructural features. Low-angle boundaries form near kinetic reaction instabilities, for example, on the sides of a reaction “finger” protruding into the crystal.

2.5. IMPLICATIONS

This study shows that microstructures produced by static crystal growth during fluid-mediated replacement reactions can bear striking similarities to the microstructures formed by crystal-plastic deformation in dislocation creep regime. Features such as new subgrains (Fig. 3A, D), internally distorted crystal lattices (Fig. 3G) and apparent slip systems (Fig. B3) forms in reaction products in the absence of differential stress, even replacing samples with no deformation history.

This observation highlights a challenging problem for interpreting metasomatic mineral assemblages, common in many crustal high-strain zones and some mantle

settings. Even when the fluid-alteration is recognized in the rock, the question remains: when and how the microstructures in the metasomatic products were produced? Did they form by deformation, succeeding the metasomatism? Were they inherited from previously deformed parent phases? Or were they created by fluid-mediated replacement reactions in the absence of deformation? The answer significantly affects the interpretation of the metasomatic/metamorphic and tectonic events in the rock history.

Based on our observations we suggest that microstructures created or inherited during fluid-mediated replacement reactions can be recognized from the ones produced in deformation by:

- (1) highly irregular subgrain- and grain boundaries with high variations in lattice misorientations, especially if the adjacent parent grains show annealing features;
- (2) subgrain boundary geometries that tend to be perpendicular to the reaction interface and/or are not consistent with possible stress directions;
- (3) differing rotation axis distribution and slip system solutions in corresponding parents and products, even when microstructures are visually similar.

Consequently, it is imperative that an in-depth microstructural and microchemical characterization is necessary to allow for reliable interpretation of complex rock histories.

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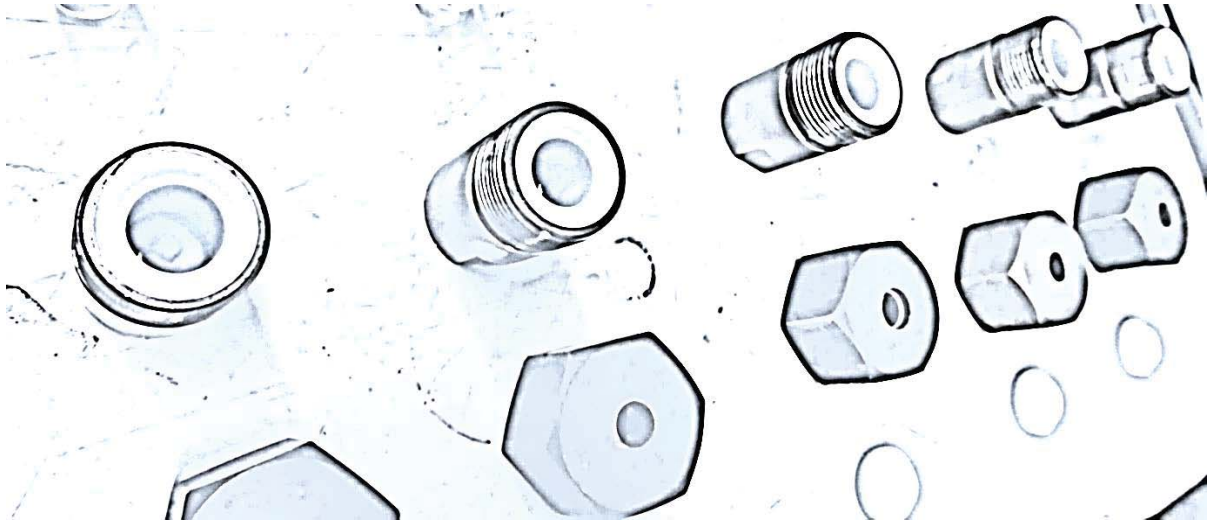
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“I don’t drink water, because if water can erode rock, think what it can do to flesh.”

/Jarod Kintz/

CHAPTER 3

3. The role of fluid chemistry, grain boundaries, phase boundaries and deformation in fluid-mediated mineral replacement reactions

PREAMBLE

This chapter forms the basis of a fourth publication to be submitted to the international Journal “Chemical Geology”. It is largely structured as a manuscript, however, additional ^{18}O mapping and EMP analysis are planned before its final completion and submission. The required future work for completing this study is discussed in the section “Additional analysis planned”.

ABSTRACT

The main objective of this study is to experimentally investigate fluid-rock interaction in rocks with complicated natural microstructures. In particular, the interests of this project focus on how do: (1) fluid composition; (2) grain boundary geometry; (3) phase boundaries and (4) pre-existing deformation microstructure affect the progress of fluid-mediated mineral replacement reactions. In this study naturally deformed calcite-rich samples were exposed to reactive hydrous phosphate solutions at temperatures of 180 °C and vapour pressures; for durations from 1 – 15 days. Two sets of experiments were performed. In Set 1 experiments, fluorine-containing phosphate solutions (1.0 M $(\text{NH}_4)_2\text{HPO}_4$ + 0.1 M NH_4F) were used, while Set 2 experiments were performed with sodium chloride-containing phosphate solutions (1.0 M $(\text{NH}_4)_2\text{HPO}_4$ + 0.5 M NaCl). Two starting materials used in both sets of experiments were: (1) Carrara marble (CarM) consisting almost exclusively of calcite with annealed microstructure and (2) naturally deformed impure limestone sample (BHD4-7).

The results show major differences in the reaction microstructures, rates of reactions and mode of replacement between the experimental sets. In Set 1 experiments reactions mainly proceed through reaction-generated porosity in a direction normal to the sample surface, reaction rates are fast and samples are fully replaced in ~15 days. In Set 2 experiments, only ~10% of samples are replaced after 15 day experiments and reaction primarily associates with grain boundaries and pre-existing fractures in the sample. We suggest that the observed differences in the reaction progress are controlled by the differences in the relative kinetics of transport versus dissolution-precipitation processes in each system, demonstrating that even

minor differences in the reaction fluid composition can highly modify the chemistry and reactivity of the whole system. The reaction rates and pathways in samples were also affected by the grain boundary density and orientation as well as individual grain crystallographic orientation. On the other hand the presence of phase boundaries and internal strain in the grains had minor or no effect on the reaction progression in all experiments.

3.1. INTRODUCTION

The amount of free fluid in the Earth's crust is relatively small, but it is of major importance for many geological processes, such as mineral reactions (Putnis and Austrheim, 2010), mass and energy transfer (Yardley, 2009), deformation mechanisms (Wintsch and Yi, 2002) and physical properties of the rock (Jamtveit et al., 2000). The understanding of fluid pathways in a rock and fluid-rock interaction along these pathways is therefore crucial for understanding crustal dynamics and also of great interest to the mineral resource industry as many mineral deposits are formed as a consequence of fluid-rock interaction (Yardley and Cleverley, 2013).

Field evidence indicates that fluid transport in a low permeability crustal rock primarily occurs by a channelized flow, where fractures, shear zones and grain boundaries are the most efficient pathways displaying the most extensive fluid alteration (Austrheim, 1987; Menegon et al., 2015). However, completion of any fluid-mediated mineral alteration process requires pervasive permeability on a subgrain scale. This is thought to be a reaction-induced feature where the dis-equilibrium between the fluid and solution first dissolves the metastable parent phase, and second, precipitates a more stable porous reaction product (Putnis, 2009). Only volume-deficient reactions can reach a completion as the porosity of the replacing phase is critical to maintain fluid access to the reactive surfaces. However, most experimental studies to date have focused on fluid-rock interaction in simple, idealized systems, where perfect single crystals are replaced by fluid (Harlov et al., 2005; Hövelmann et al., 2010; Qian et al., 2010). Only recently such experiments have been performed on polycrystalline samples (Etschmann et al., 2014; Jonas et al., 2014; Pedrosa et al., 2016) that are closer to natural systems.

In this study we take the next step in exploring fluid-rock interaction in more complex polycrystalline, polymineralic, naturally deformed rocks. The objectives of this study are to investigate how fluid-rock interaction and replacement reactions are affected by: (1) variations in fluid composition; (2) grain boundary network; (3) phase boundaries; (4) internal deformation microstructure in the parent minerals.

The presented study advances our understanding of the factors influencing the nature of fluid-flow in systems, where external fluid interacts with a polycrystalline rock. In particular, our results are highly applicable to the nature and evolution of hydrothermal systems in particular those related to ore genesis and retrogression of the crust.

3.2. MATERIALS AND METHODS

3.2.1. Experimental procedure

3.2.1.1. *Starting material and experimental fluids*

The samples used in this study were cut from two natural calcite-rich thick sections (CarM and BHD4-7) in sizes of $\sim 2.5 \times 2.5 \times 2.5$ mm. All samples were cleaned with deionized (Milli-Q) water and ethanol, oven dried at 40°C for 24 hrs and weighed. The sample initial weight varied between 0.05664 to 0.7202 g (Tab. 1).

Two sets of solutions were prepared for experiments, using a same stock solution, made from a diammonium phosphate powder ($(\text{NH}_4)_2\text{HPO}_4$; Acrōs Organics, >99%), diluted in a deionized (Milli-Q) water with an addition of ammonium fluoride (NH_4F ; Alfa Aesar GmbH, 98.0%) or sodium chloride (NaCl ; Merck, 99.5%) powders in concentrations of:

- Set 1: 1 ml of 2 M $(\text{NH}_4)_2\text{HPO}_4$ + 0.1 ml of 2 M NH_4F + 0.9 ml H_2O , further referred as fluorine-containing phosphate solution.
- Set 2: 1 ml of 2 M $(\text{NH}_4)_2\text{HPO}_4$ + 0.5 ml of 2 M NaCl + 0.5 ml H_2O , further referred as sodium chloride-containing phosphate solution.

Repeat experiments were performed on BHD4-7 starting material for 5 and 15 days durations, where instead of deionized water, ^{18}O -enriched water was used. Previous experimental studies (Putnis and Mezger, 2004; Kasiopas et al., 2011;

Perdikouri et al., 2013) have shown that oxygen isotope redistribution can be used as an indicator for determining reaction mechanisms and to provide evidence on the relative timing for the growth of reaction products.

3.2.1.2. Experiments

The experiments were performed at the University of Muenster, Institute of Mineralogy (Germany), using hydrothermal autoclaves. Each sample was placed into a Teflon-lined autoclave together with 2 ml of a respective phosphate solution at temperatures of 180°C and vapour pressures, for durations of 1 to 15 days (Table 1). On termination, the autoclaves were cooled down to room temperatures within 5 min. The samples were removed from the autoclaves, washed in deionized (Milli-Q) water, oven-dried at 40°C for 24 hr, weighed, embedded in epoxy and polished to half of their height to reveal reaction interfaces in cross-section.

Table 1. Experimental samples and conditions. In experiments AC42-45, fluid was doped with ^{18}O isotope. Abbreviations: exp. = experiment, dur. = duration, wt. = weight, bef. = before, aft. = after.

<i>T = 180 °C; P = vapor; fluid = 2 ml</i>											
	Exp. dur.	Sample	Sample	Sample	Fluid pH		Fluid pH			replaced	
Sample	(days)	wt. bef.	wt. aft.	wt. Δ	bef.	pH T	after	pH T	pH Δ	area%	Sample
<i>Experiments with fluid 1 (1 M (NH₄)₂HPO₄ + 0.1 M NH₄F)</i>											
AC7	1	0.06446	0.06573	0.00127	7.97	19.5	8.438	19.4	0.468	25.3	BHD4-7
AC12	2	0.06322	0.06482	0.00160	7.813	19.6	8.529	19.8	0.716	40.3	BHD4-7
AC11	5	0.06612	0.06824	0.00212	7.97	19.5	8.872	19.7	0.902	58.5	BHD4-7
AC19	10	0.07048	0.07294	0.00246	7.844	19.9	9.075	20.5	1.231	90.8	BHD4-7
AC20	15	0.06985	0.07237	0.00252	7.844	19.9	9.192	20.4	1.348	100.0	BHD4-7
AC42	5	0.05664	0.05971	0.00307	7.844	19.9	8.856	18.8	1.012	84.5	BHD4-7 + ¹⁸ O
AC43	15	0.06083	0.06442	0.00359	7.844	19.9	9.078	18.8	1.234	100.0	BHD4-7 + ¹⁸ O
AC13	1	0.06517	0.06617	0.00100	7.813	19.6	8.253	19.8	0.440	24.0	CarM
AC14	2	0.05990	0.06132	0.00142	7.813	19.6	8.434	19.8	0.621	35.8	CarM
AC17	5	0.06498	0.06720	0.00222	7.844	19.9	8.868	20.5	1.024	64.4	CarM
AC18	10	0.06889	0.07123	0.00234	7.844	19.9	9.046	20.5	1.202	81.7	CarM
AC21	15	0.06393	0.06628	0.00235	7.844	19.9	9.181	20.5	1.337	92.7	CarM
<i>Experiments with fluid 2 (1 M (NH₄)₂HPO₄ + 0.5 NaCl)</i>											
AC22	1	0.07202	0.07214	0.00012	7.772	20.0	7.696	20.0	-0.076	2.1	BHD4-7
AC23	2	0.06636	0.06645	0.00009	7.772	20.0	7.653	20.1	-0.119	3.5	BHD4-7
AC24	5	0.07108	0.07126	0.00018	7.772	20.0	7.026	20.2	-0.746	4.7	BHD4-7
AC25	10	0.06848	0.06874	0.00026	7.772	20.0	7.660	20.1	-0.112	5.9	BHD4-7
AC26	15	0.06878	0.06920	0.00042	7.772	20.0	7.585	20.1	-0.187	8.6	BHD4-7
AC44	5	0.05860	0.05898	0.00038	7.772	20.0	7.565	18.8	-0.207	7.7	BHD4-7 + ¹⁸ O
AC45	15	0.06013	0.06052	0.00039	7.772	20.0	7.684	18.8	-0.088	8.7	BHD4-7 + ¹⁸ O
AC27	1	0.06371	0.06394	0.00023	7.772	20	7.686	20.2	-0.086	1.6	CarM
AC28	2	0.06125	0.0614	0.00015	7.772	20	7.671	20.3	-0.101	2.3	CarM
AC29	5	0.06645	0.0669	0.00045	7.772	20	7.731	20.3	-0.041	8.2	CarM
AC30	10	0.07032	0.07077	0.00045	7.772	20	7.662	20.3	-0.11	8.8	CarM
AC31	15	0.06405	0.06477	0.00072	7.772	20	7.651	20.4	-0.121	11.2	CarM

3.2.2. Analytical Methods

The initial sample characterization before and after experiments was performed at the Geochemical Analysis Unit (GAU), Macquarie University. Backscatter Electron (BSE) images (Fig. 2) were obtained with Carl Zeiss IVO Scanning Electron Microscope (SEM) at high-vacuum conditions with an accelerating voltage of 15 kV, beam current of 3 nA and at working distances of 12 mm.

Detailed imaging of the fine grained reaction rims and mineral identification of the fine-grained phases were performed at the Australian Centre for Microscopy and Microanalysis, University of Sydney. A Carl Zeiss Sigma VP SEM with a field emission gun (FEG) was used as it gives 2-3 times better resolution compared to an SEM with a tungsten filament gun at the same beam currents (Humphreys et al., 1999). The images were collected under high vacuum conditions with an accelerating voltage of 3 kV and at working distances of 3.5–5 mm. The mineral identification in the reaction rims was performed with Oxford Instruments Aztec integrated EBSD/EDS system. The high resolution FEG EBSD maps were carried out on samples tilted to 70° with accelerating voltages of 15 kV, work distances of 11 mm and step sizes of 0.25 μm . Channel 5 analysis software from HKL Technology was used for the post-acquisition processing of the stored Kikuchi bands.

The area% mode estimations of the secondary minerals in the starting material and reaction products after experiments were carried out by image analysis with NIH Image Java-based software ImageJ (<https://imagej.nih.gov/ij/>). All mineral abbreviations used in the following text follow those suggested by (Kretz, 1983).

3.3. RESULTS

The experiments were performed on two starting materials, CarM and BHD4-7. These were chosen to test how different microstructures affect the progress of fluid-mediated mineral reactions. Sample CarM represents a polycrystalline, monomineralic, relatively undeformed material with few internal crystal plastic deformation features (Fig. 1a; Jonas et al., 2014) and BHD4-7 is a polymineralic, polycrystalline material with significant crystal plastic deformation microstructure (Fig. 1b-d). Here we mainly focus on results from experiments with BHD4-7 starting material. Similar experiments with

CarM-type materials have been reported by Jonas et al. (2014) and Pedrosa et al. (2016). Here, CarM experiments are used as a simpler analogue for comparison with BHD4-7.

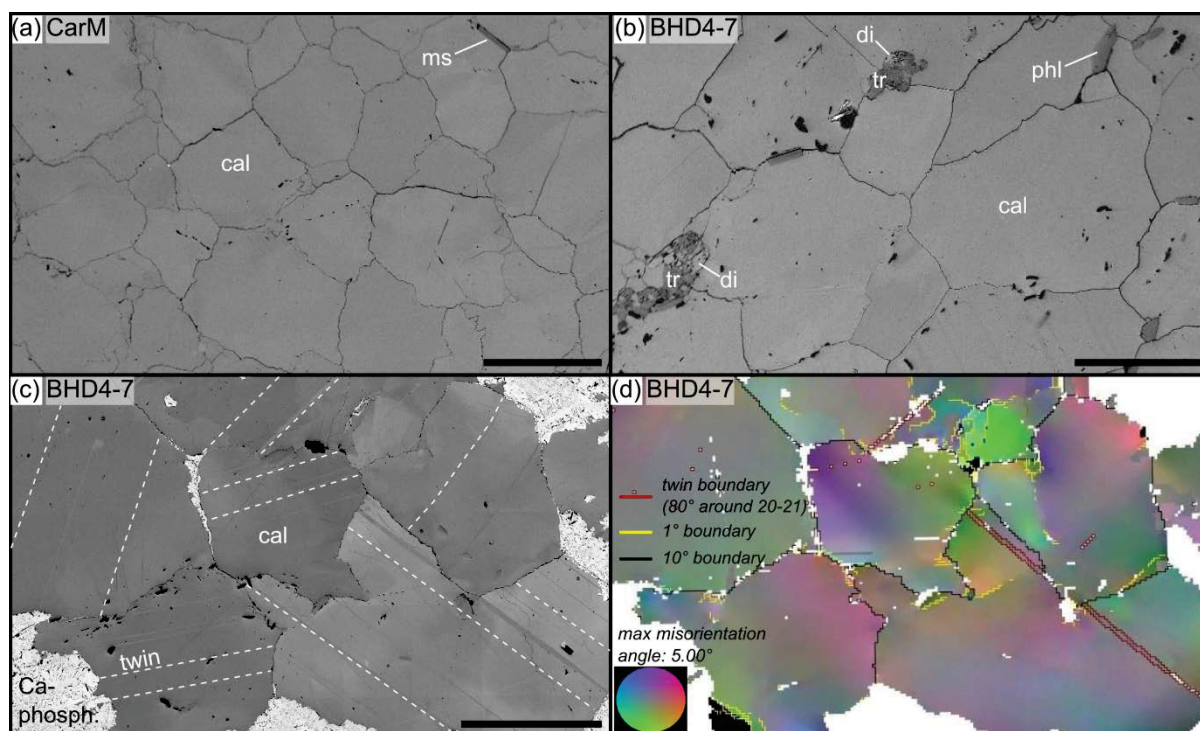


Figure 1. General characteristics of the starting materials. Scale is 200 μm in all images. (a) BSE image of CarM; (b) BSE image of BHD4-7; (c) high resolution BSE image of BHD4-7. The colour variations in calcite grains partly represent orientations in crystal lattice, dashed lines mark calcite twins; (d) EBSD map of (c), showing misorientations within individual calcite grains. Step size is 4 μm , no noise reduction was performed as it removes the real twin boundaries.

3.3.1. Starting material

3.3.1.1. CarM

CarM (Fig. 1a) is a polycrystalline, almost monomineralic calcite marble with an annealed microstructure. It comes from a metamorphosed carbonate platform, exposed near Carrara, NW Tuscany, Italy and has been used in many experimental studies due to its purity, relatively fine grain size and annealed microstructure (e.g. Oesterling et al., 2007).

The samples prepared for the experiments are almost entirely composed of calcite. Secondary minerals do not exceed 1 area% mode, mainly represented by 20 - 100 μm large muscovite grains. Calcite is chemically homogenous and contains minor amounts of Mg (0.01 X_{Mg} , where $X_{\text{Mg}} = \text{Mg}/(\text{Mg}+\text{Ca})$). The calcite grains are typically

50 – 200 μm across, equidimensional, commonly display 120° triple junctions, do not show any preferred crystallographic orientation and have relatively minor internal deformation microstructure. Twins are rare.

3.3.1.2. BHD4-7

BHD4-7 (Fig. 1b-d) is a polymineralic, naturally deformed and metamorphosed impure limestone. It comes from the southernmost part of the Oslo Palaeo rift, SE Norway and was collected from the Porsgrunn-Langesund contact aureole, ~ 83 m from the intrusive contact (courtesy of A. Harstad).

The samples prepared for the experiments are mainly composed of calcite and $\sim 10\%$ to 15% secondary minerals, including phlogopite, diopside and tremolite. Phlogopite associates with grain boundaries, while diopside and tremolite occur as porphyroblasts, overgrowing the calcite matrix. Diopside and tremolite are commonly observed in a pseudomorphic replacement relationship (Fig 1b, 3b).

Calcite is chemically homogenous with X_{Mg} ranging from 0.005 – 0.006. Calcite grains are equidimensional or elongated with aspect ratios of up to 2. Grains range in size from 50 – 500 μm , with an average grain size above 200 μm . As the starting material is obtained from natural samples that have undergone deformation, the lattices of the calcite grains are crystal-plastically deformed (Piazolo et al., 2007). Twins, subgrain boundaries and lattice misorientations are common in most grains (Fig. 1c-d). The lattices of individual grains typically show variations in misorientation angles from 2° – 5° , where the highest distortions and the highest subgrain boundary concentration is associated with grain triple junctions and second phase boundaries (Fig. 1d, cf. Fig. 5e).

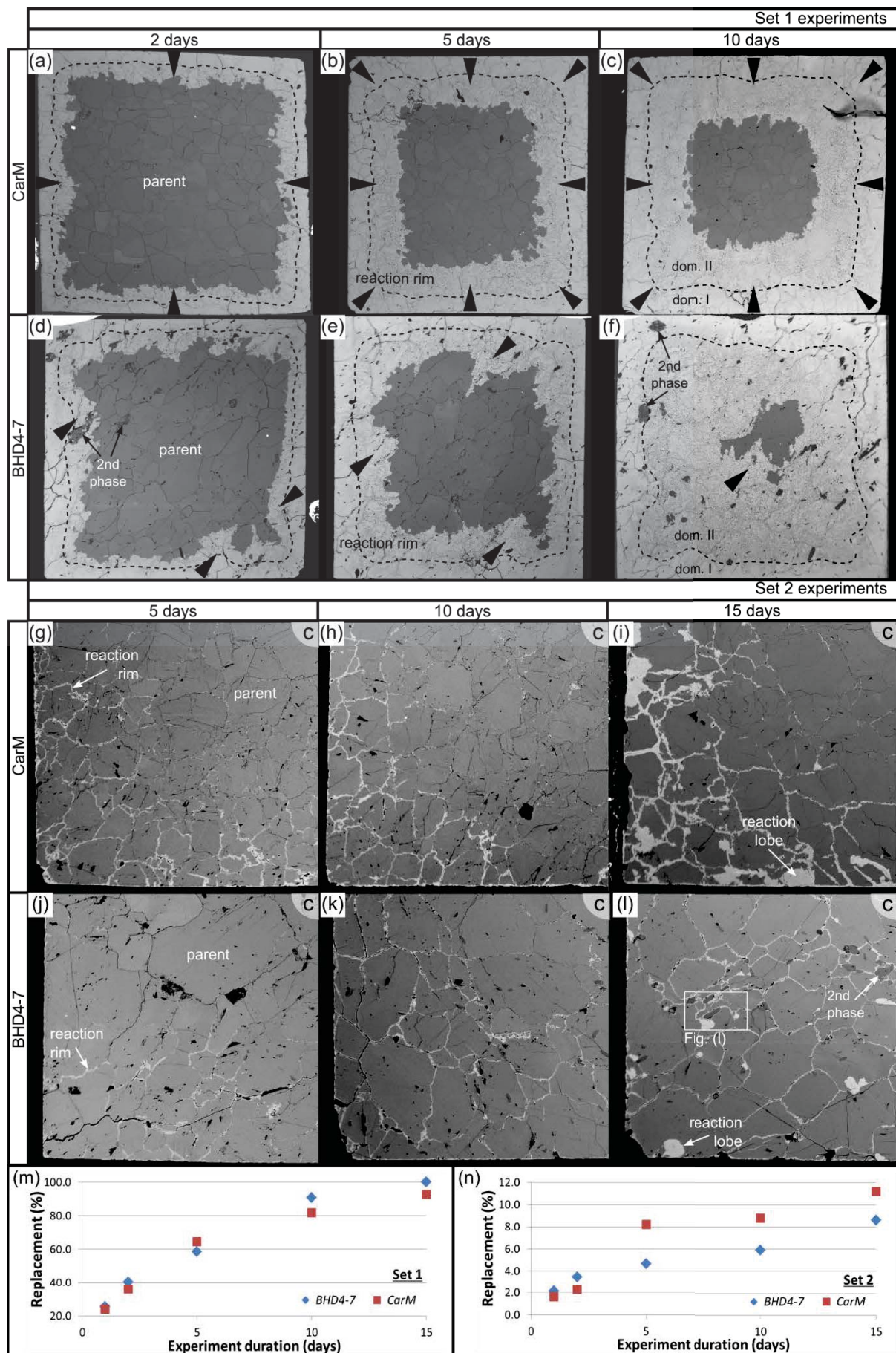


Figure 2. Typical characteristics of the reacted samples. Black arrows mark reaction direction. All samples are 2.5x2.5 mm in size. (a)-(f) BSE images of samples after Set 1 experiments, reacted for 2, 5 and 10 days, where (a)-(c) represents CarM starting material and (d)-(f) represents BHD4-7 starting material. The black dashed lines mark the boundary between domain I and II. Note the asymmetry of the reaction rim in (d)-(f). (g)-(l) BSE images of samples after Set 2 experiments reacted for 5, 10 and 15 days. Only a quarter of each sample is shown (c marks the sample's centre). (g)-(i) represents CarM starting material and (j)-(l) represents BHD4-7 starting material. Note that (g)-(i) display a higher replacement mode, but in (j)-(l) the rims are further advanced towards the centre of the samples. (m)-(n) area% mode of the reaction products after Set 1 and Set 2 experiments, respectively showing results from both starting materials (see Table 1).

3.3.2. General characteristics of samples after Set 1 experiments

Following experiments with the fluorine-containing phosphate solution, the samples are surrounded by fine-grained, highly porous reaction rims (Fig. 2a-f). The original external sample dimensions are preserved after all experiments, but the thickness of the reaction rims increases and the modal area of the unreacted parent material decreases with increasing experiment duration (Table 1). Only calcite grains are replaced, while the secondary minerals (e.g. diopside, tremolite, quartz) that are surrounded by reaction products do not show significant changes in chemistry, shape and distribution compared to the secondary minerals in unreacted samples (Fig. 1b, 3a-b). Even after full replacement, the original boundaries of the calcite grains can still be traced in the reaction rims (Fig 3a & e-h).

The reaction front, in experiments where the CarM starting material was used, is generally subparallel to the outer surfaces of the samples. The reaction front displays protrusions towards the sample interior along calcite grain boundaries. These protrusions are typically 50 – 100 μm long and rarely exceed the diameter of the adjacent calcite grains that borders them (Fig 2a-c). The reaction front, in experiments with the BHD4-7 starting material, is asymmetric (Fig. 2d-f) with 100 – 200 μm long protrusions towards the sample interior that associate either with calcite grain boundaries or twin directions (Fig. 3e-g, 5d-e).

The reaction products are heterogeneous. On a sample scale, two distinct domains can be recognized, based on grain and porosity sizes (Fig 1a-c):

- (1) Domain I is very fine-grained ($<5 \mu\text{m}$) with fine porosity and has relatively homogenous appearance in BSE images (Fig. 3a, c). It occurs near the outer parts of the replacement rim (Fig. 2a-f).

- (2) Domain II is coarser, with typical grain sizes ranging from 5-10 μm (Fig. 3a, d). It is commonly located adjacent to the reaction front in the inner parts of the replacement rim and along the boundaries of the replaced calcite grains (Fig. 2a-f).

Mineralogically, both domains are represented by Ca-phosphate with varying amounts of F and Mg component. While the distribution of Mg is inconsistent, as it can be either present or absent in both domains, F in most cases associates with domain I. The EBSD analysis indicates that most products in both domains have hexagonal crystal structure with lattice dimensions similar to apatite, hydroxyapatite or fluorapatite. In lesser amounts grains with trigonal structures, corresponding to whitlockite lattice parameters are also observed. However, the distribution of the detected minerals in the reaction rim is unclear from the collected data and further EMP analysis is required to fully understand the mineralogy of the reaction rims. It is also important to note that all reaction rims contain a small fraction of 1-10 μm large calcite grains (Fig. 3d, g, h). Even after the 15 day long experiments, such grains are still present. Their crystallographic orientations are close to those of the adjacent unreacted calcite parent grains or twins in the unreacted calcite grains (Fig. 5a). It is also interesting to note that the traces of calcite twins (“ghost” twins) can be recognized in the Ca-phosphate domains that replaces calcite grains (Fig. 3f-g).

No simple crystallographic relationship was observed between calcite and apatite grains (Fig. 5c). Apatite grains in the reaction rim often display constant crystallographic orientation over $\sim 50 - 200 \mu\text{m}$ large areas that contain dense networks of small angle boundaries (Fig. 5a), while the BSE images show that these areas are composed of multiple individual grains (Fig. 5b). Importantly, the pre-existing grain boundary network is still visible, often rims of coarser apatite grains decorates the outer boundaries of the replaced calcite grains (Fig. Xe).

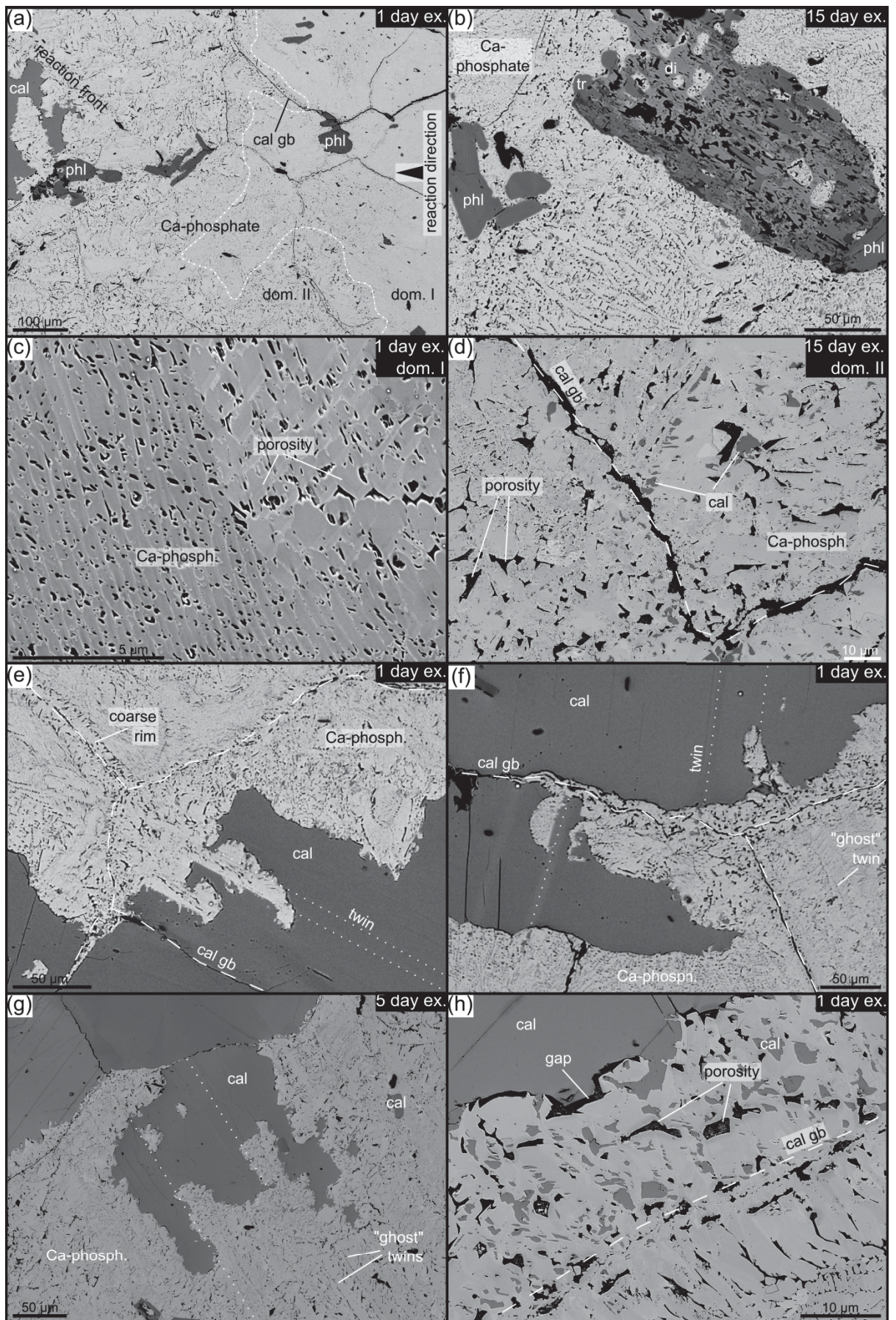


Figure 3. BSE images of typical reaction microstructures after Set 1 experiments. The reaction products are brighter than parent phases, twin boundaries are marked with dotted lines, the grain

boundaries (gb) of the replaced calcite are marked with dashed lines, duration of experiments are denoted on each image. Note the coincidence of the protrusions in the reaction front with twins and grain boundaries of calcite.

3.3.3. General characteristics of samples after Set 2 experiments

Following experiments with sodium chloride-containing phosphate solution, the samples preserve their external dimensions as before the experiment, but are surrounded by $\sim 5\text{-}10\text{ }\mu\text{m}$ thick reaction rims along their outer surfaces and calcite grain boundaries (Fig. 2g-l). The thickness of the reaction rims along pre-existing boundaries is very similar in all experiments below 10 days duration. In all samples from the long duration experiments (10 and 15 days), parts of the reaction rims show local widening (Fig. 4a, c) or irregular lobes protruding from the grain boundary towards the interiors of calcite grains (Fig. 4b, g-h). These lobes are often, but not always, located only on one side of the grain boundary and can reach widths of up to $\sim 100\text{ }\mu\text{m}$ at their central parts. The replacement mode is higher in experiments with CarM starting material that has smaller calcite grain size and denser grain boundary network, while in experiments with BHD4-7 starting material, the reaction rims extend deeper into the sample interior, compared to the CarM samples reacted for the same durations (Fig. 2).

The reaction rims consist of Ca-phosphates with a composition that is similar to apatite, but it also contains a minor Na and Mg component. In the reaction rims, EBSD analyses indicate the presence of apatite- and whitlockite-type crystal structures (Fig. 6a-b). Apatite is mostly associated with areas that lack a Mg-component and is located adjacent to calcite grain boundaries. In BSE images, apatite commonly displays well-defined crystal faces and grains in sizes from 1 to 5 μm . Apatite dominated areas exhibit relatively low porosity (Fig. 4c-d, f). Whitlockite occurs either as up to 5 μm large grains at the calcite grain boundaries (Fig. 4e) or as very fine grained ($<1\text{ }\mu\text{m}$) highly porous domains at the front of the reaction rims bordering calcite grains (Fig 4c-d). Crystallographically, whitlockite shows some degree of epitaxy with respect to the adjacent calcite grains (Fig. 6c-d). This relationship is weaker along $\{10\text{-}10\}$ axis. No simple relationship was observed between apatite and calcite or whitlockite grains. Whitlockite grains also display many low-angle boundaries that are not common in the apatite grains (Fig. 6a-b).

In the reaction lobes that occur in samples reacted for 10 and 15 days, the Ca-phosphates are relatively coarse grained (up to 10 μm) (Fig. 4g-h) and have a minor Mg-component.

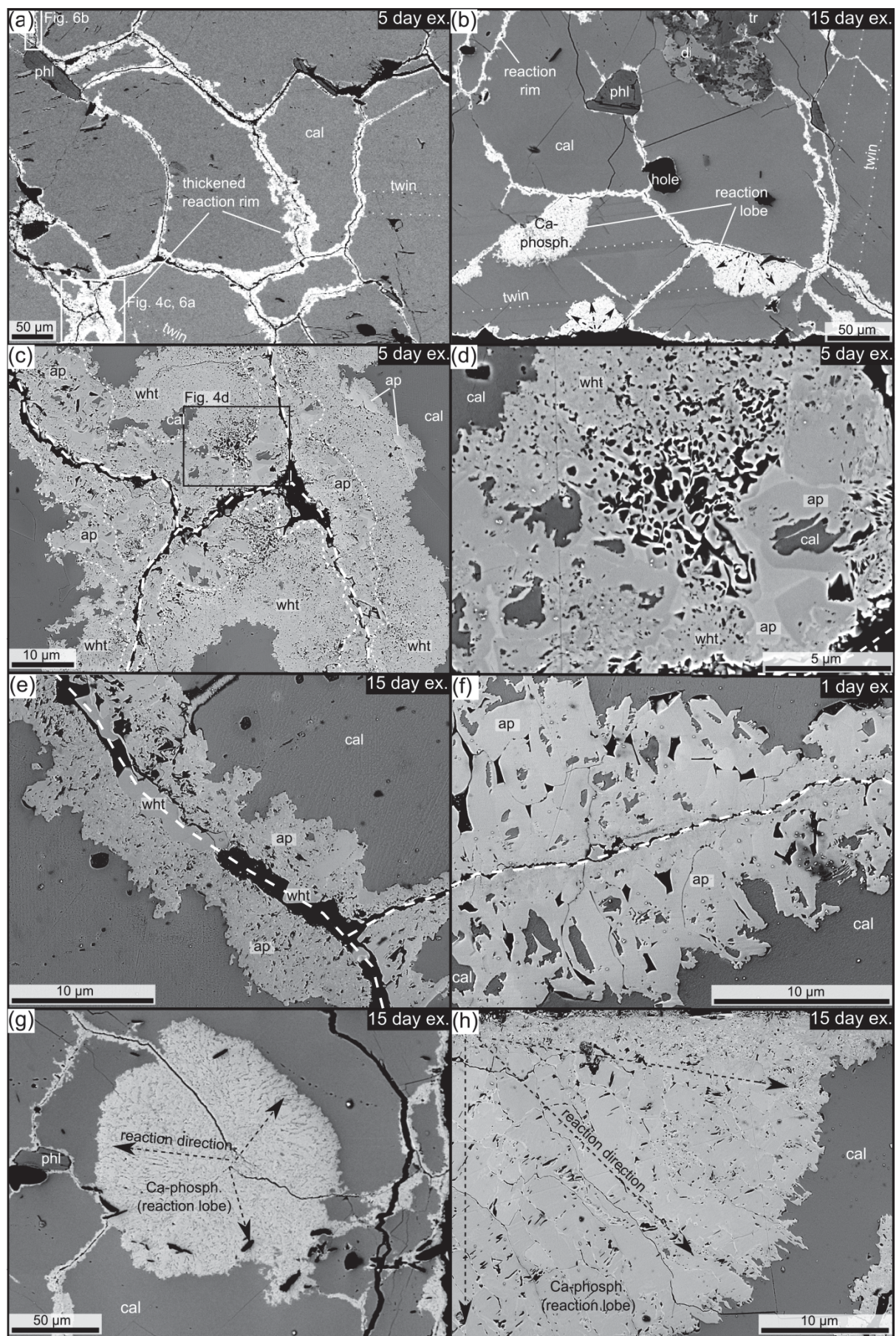


Figure 4. BSE images of typical reaction microstructures after Set 2 experiments. The reaction products are brighter than parent phases, twin boundaries are marked with dotted lines, the grain

boundaries (gb) of the replaced calcite are marked with dashed lines, duration of experiments are denoted on each image.

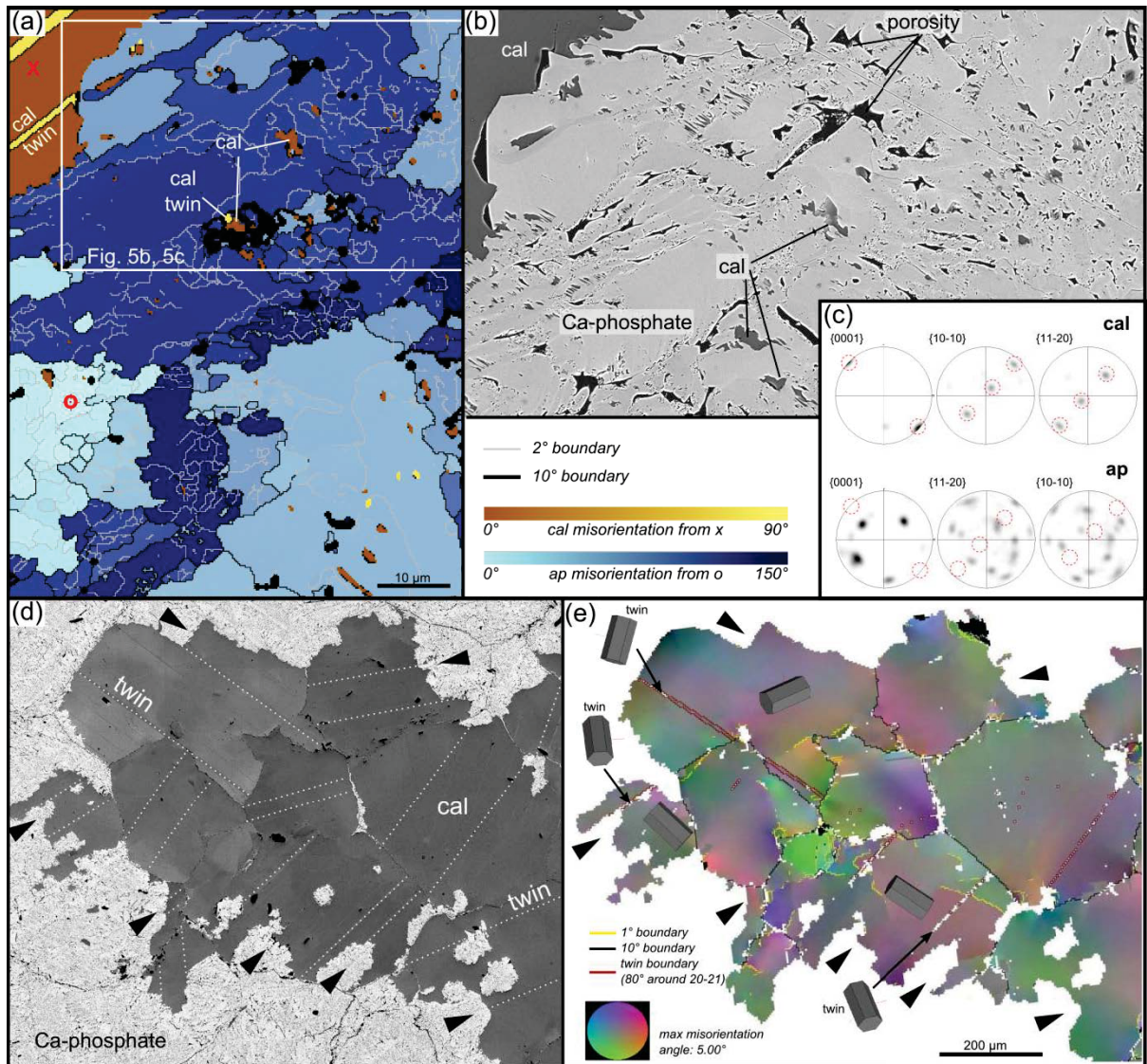


Figure 5. EBSD data showing crystallographic features of the reaction products for Set 1 experiments: (a) orientation map showing relative misorientations of calcite and apatite in respect to sites x and o. Note the orientations of the small calcite grains in the apatite domains, coinciding with the orientations of the adjacent unreacted grain and its twins on the upper left corner; (b) Higher resolution BSE images of the area marked in (a), showing complex microstructure of the apatite domain; (c) pole figures of the crystallographic orientation data for the calcite and apatite in (a). All data are plotted as one point per grain using equal-area projection on the lower hemisphere; (d) BSE image of calcite/apatite interface in sample, reacted for 5 days. The twins in calcite are marked with dotted lines, the black arrows marks the sites, where the protrusions of the reaction front coincide with twin orientations in the adjacent calcite grains; (e) EBSD map of (d) showing the crystallographic features of the unreacted calcite grains. The misorientations within the individual grains are displayed in 5° range.

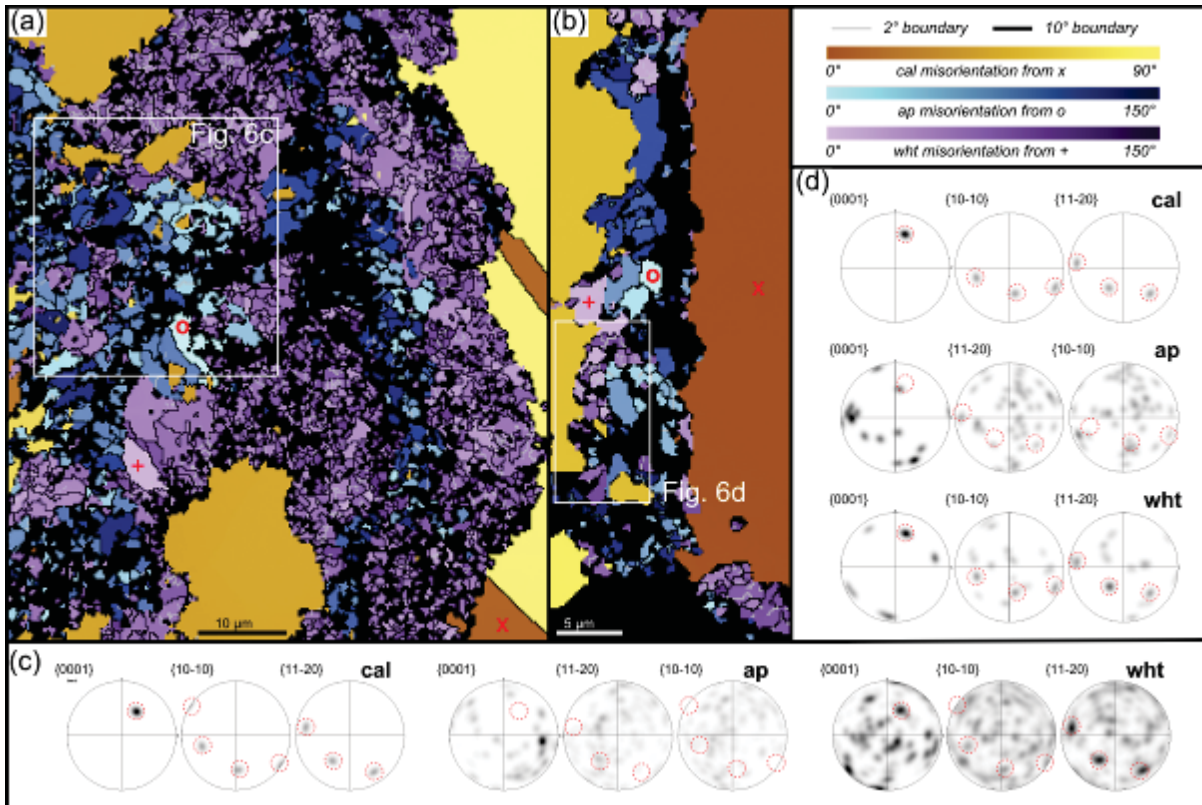


Figure 6. Crystallographic features of the reaction products for Set 2 experiments. (a)-(b) EBSD maps showing relative misorientations of calcite and apatite in respect to sites x and o. (a) is obtained from the same area as BSE image in Fig. 4c. (c) and (d) pole figures of the crystallographic orientation data for the calcite, apatite and whitlockite in the marked areas in (a) and (b), respectively. All data are plotted as one point per grain using equal-area projection on the lower hemisphere;

3.4. DISCUSSION

3.4.1. Reaction mechanism

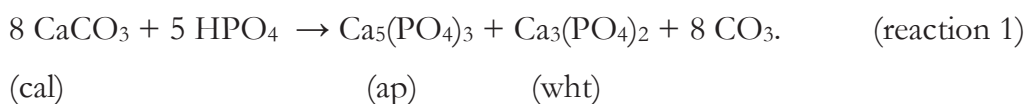
Previous hydrothermal experiments on calcite-to-apatite replacement (Kasioptas et al., 2011; Jonas et al., 2014, 2013; Pedrosa et al., 2016) have demonstrated that such reactions proceed by coupled dissolution-precipitation (CDP) mechanisms (Putnis, 2009). CDP reactions are mediated by a reactive fluid that dissolves the parent minerals and precipitates products that are less soluble in respect to the fluid they are in contact with. If the dissolution and precipitation processes are kinetically coupled at the reaction interface, the replacement proceeds in a pseudomorphic manner, preserving the outer dimensions, morphology, and in some cases crystallographic orientation of the parent mineral (Xia et al., 2009). CDP reactions can also produce compositionally (Borg et al., 2014) and/or mineralogically (Etschmann et al., 2014) zoned reaction rims that may resemble diffusional profiles. This occurs because the

fluid at the reaction interface becomes progressively enriched in components from the dissolving parent grains. Such changes in interface fluid composition then leads to changes in the composition of the precipitating product minerals that incorporate increasingly higher proportions of components from their parents (Putnis et al., 2005). The products of CDP reactions commonly display high porosity, resulting from a combination of volume and solubility differences between the parent and product minerals. This porosity is crucial for the continuation of the replacement as it maintains the contact between the fluid and metastable parent mineral, allowing the exchange of components between the two (Putnis, 2009).

The microstructural characteristics observed in this study, including pseudomorphism, porosity of the reaction rims and sharp compositional interfaces between the product and parent minerals are consistent with the observations in previous experimental studies in similar reaction systems (Jonas et al., 2014; Pedrosa et al., 2016) and criteria for recognizing coupled dissolution-precipitation reactions (Putnis, 2009).

3.4.2. Mineral reactions

Whitlockite and apatite (possibly including hydroxyapatite and fluorapatite) are the main reaction products in all experiments and calcite is the main reactive phase. As secondary parent minerals do not display any evidence of dissolution or change in chemistry (Figs 1b, 3a-b, 4a-b) we assume that they were not involved in the replacement reactions. In the experimental system presented here, fluid provides the only source of P for the reaction products and calcite is the only source of Ca, indicating that the overall reaction can be described as:

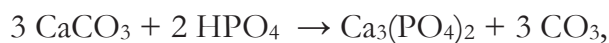


The trace amounts of F that were detected in the Set 1 product minerals comes from the addition of NH_4F to the reaction fluid, and the NaCl component in the fluid for Set 2 experiments explains the minor amounts of Na and Cl, detected in Set 2 reaction products. The trace amounts of Mg, detected in whitlockite and, possibly some apatite grains, can be attributed to the Mg component in the parent calcite grains that also substitutes for Ca in the product mineral lattices.

The data do not allow us to unequivocally resolve the specifics of the mineral reactions involved in each set of experiments. Three scenarios are possible:

Scenario 1: Whitlockite and apatite are both primary reaction products and form simultaneously as described by reaction 1. Such a scenario is not consistent with the observed reaction microstructures. The reaction 1 suggests the production of apatite and whitlockite in equal proportions (50:50). In case of Set 1 experiments, only minor amounts of whitlockite is detected in the reaction domains. In case of Set 2 experiments, whitlockite and apatite have different spatial distribution (Fig. 4c, 6a-b) suggesting that they form in different stages of reactions.

Scenario 2: Calcite replacement is a two-step process, where whitlockite forms as the primary product phase in a reaction:

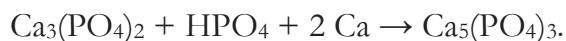


(reaction 2)

(cal)

(wht)

and is subsequently replaced by apatite:



(reaction 3)

(wht)

(ap)

This scenario has been reported to take place in other hydrothermal experiments on calcite to Ca-phosphate replacement (Eanes, 1970; Jarcho et al., 1979) that suggests a sequence: amorphous Ca-phosphate $\rightarrow$ β -tricalcium phosphate (whitlockite) $\rightarrow$ apatite. The main reason for such a process is a presence of Mg in the reaction fluid, that inhibits direct apatite precipitation (Eanes and Posner, 1968) but increases the stability of β -tricalcium phosphate (whitlockite), where Mg ions partially substitute for Ca (Trautz, 1955).

No amorphous material was observed in this study; however, several lines of evidence indicate that whitlockite may be a transitional phase before the formation of apatite. The reaction fluid in both sets of experiments must contain small amounts of Mg, released during calcite dissolution. In Set 1 experiments only small amounts of whitlockite are present, but these experiments show fast reaction kinetics and might represent a case, where whitlockite-to-apatite replacement is rapid and only rare whitlockite grains are preserved even at the reaction fronts. In Set 2 experiments, whitlockite typically occurs at the reaction fronts (Fig. 4a-b) and has a crystallographic

relationship with calcite that could indicate its primary origin (Fig. 4c-d), while apatite is located on the outer parts of the reaction rims that have formed earlier and have a prolonged interaction with reaction fluid, suggesting that such a subsequential alteration reaction can explain the features observed in experimental Set 2.

Scenario 3: Both, apatite and whitlockite precipitates from the fluid directly, but at different stages of reaction, in response to the evolution of the interface fluid composition. This scenario cannot be excluded for Set 2 experiments, where the apatite precipitation may be the first stage of calcite replacement, when the fluid near the grain surfaces is similar to the bulk fluid composition, which does not contain a sufficiently high Mg component to precipitate apatite. As the dissolution-precipitation reaction proceeds towards the sample interior, the fluid becomes relatively enriched in Mg-component from the dissolving calcite parent grain and starts to precipitate whitlockite, as the presence of Mg prevents apatite formation. While both product minerals are in direct contact with the calcite parent grain during their formation, only whitlockite is epitaxial as the hexagonal apatite crystal structure does not match to the trigonal calcite structure.

Further information that can help to pinpoint the operating scenario can be obtained by mapping the ^{18}O distribution in the reaction products. The minerals that form during the early stages of fluid-rock interaction from the ^{18}O -doped reaction fluid will contain higher $^{18}/^{16}\text{O}$ ratios than minerals that form during the later stages from fluid that has become enriched in ^{16}O component, released by the dissolution of minerals in the parent samples.

3.4.3. The effect of fluid composition on reaction kinetics, progression and microstructures

As shown in Figure 2a-l, the variation of the reaction fluid has a major effect on the reaction kinetics, progression and distribution of the reaction products.

In Set 1 experiments, where the fluorine-containing phosphate solution became more alkaline during the experiment, the reaction rate is much faster than in Set 2. In addition, the replacement front is generally parallel to the sample surface (Fig. 2a-f), suggesting that replacement was mainly controlled by the initial fluid-rock interface and progressed through the reaction-generated porosity in a direction, normal to the

sample surface. Structural heterogeneities in the starting material, such as grain- and twin boundaries and minor fractures, thus plays only a secondary role in controlling the reaction pathways.

In set 2 experiments, where a sodium chloride-containing phosphate solution was used and the pH of the fluid hardly changed, reaction rates are slow. The replacement on a sample scale is primarily controlled by the grain boundary network (Fig. 2g-l). It is notable that the porosity within the reaction products is significantly lower in Set 1 relative to Set 2 at least for the first 10 days of the experiments. However, after 10 days, most grain boundaries are surrounded by reaction rims and further reaction progresses only locally into grain interiors. This second stage is characterized by locally thickened reaction rims and development of irregular lobes protruding towards grain interiors from seemingly random points in a sample (Figs 2i, j & 4a-b, g-h).

The reasons for the two contrasting scenarios observed in Set 1 and Set 2 experiments could be explained in a framework of dissolution-precipitation replacement mechanisms. In general, fluid-mediated mineral replacement can be understood as a process consisting of three serial steps: (1) component transport towards and away from the reaction sites and (2) reaction which encompasses both the dissolution of parent minerals (reaction part I) and the precipitation of less soluble product minerals (reaction part II) similar to the serial steps during dissolution precipitation creep (Rutter, 1983). Each of the steps can have a different rate and the slowest one is considered to be the controlling factor of the overall reaction rate. Our experiments show that the relative rates of transport and reaction are governing not only the reaction rates but also the microstructural development due to differences in reaction progression in space and time. It is clear that the reaction rate of Set I is much higher than that of Set II (Fig. 2). This is attributed to the fact that the reactive fluid of Set I is more aggressive than the fluid in Set II, perhaps due to the presence of Na in the fluid of Set II.

At the same time, the fast dissolution-precipitation reaction of Set I results in the transport of reactive fluid to the reactive surface and controls the reaction rate and reaction progression. In Set I, porosity within the reaction products must be sufficient

to allow transport through the reacted rim resulting in the microstructures seen with no preference of grain boundaries as loci of replacement (Fig. 2a-f). The effect of faster transport along grain boundaries is only seen in BHD4-7. The situation is different for Set 2 experiments. Here, the rate of reaction is much slower, due to the difference in the reactivity of the fluid. At the same time, the slight difference in chemistry of the reactive fluid causes a decrease in the reaction porosity. This relationship results in very slow access of fluid to the reactive surface once the replacement rim has reached thickness in order of few 10s of a micron. Reaction can only progress at interfaces between reactive fluid and parent mineral, therefore fluid transport along grain boundaries controls the loci and rate of reaction. This then results in the reaction paths that follow the pre-existing grain boundaries closely, with little effect of time on the width of the reaction rim (Fig. 2g-l). However, porosity coarsens with time (Putnis et al., 2005), and therefore after 10 days of experiments the reaction-generated porosity has locally sufficiently coarsened to allow fluid access to grain interiors resulting in the blebs of reaction products (Fig. 4b, g, h).

The dissolution and precipitation rates seem to be coupled in both sets of experiments as the reaction products are pseudomorphic and, in case of whitlockite, which has matching crystal structure to calcite, displays epitaxy (Xia et al., 2009). Gaps on interfaces occur locally, but these are on the scale from $\sim 0.5 - 1 \mu\text{m}$ in Set 1 experiments and $< 0.5 \mu\text{m}$ in Set 2 experiments, comparable with the differences in the initial dimensions of reaction-generated porosity in both cases.

3.4.4. How do deformation microstructures affect replacement?

In static reaction systems only indirect effects of deformation can be considered. These include deformation-produced subgrain-scale features, such as twins, subgrain boundaries and an increased amount of lattice defects in the pre-deformed minerals, and on a sample-scale, preferred crystallographic orientation, reduced grain sizes and grain boundary geometries such as shape preferred orientations may also be influential.

Heterogeneity of structural features in the parent calcite grains seems to localise faster kinetics of replacement reactions in Set 1 experiments, and to a lesser extent, in Set 2 experiments. Twins and twin boundaries often associate with advanced reaction

fronts (Figs 3e-g & 5d-e). In Set 1 experiments, the observed protrusions in the reaction front along twin boundaries is $\sim 100\text{-}200\text{ }\mu\text{m}$, comparable to what is observed along grain boundaries. These faster reaction rates along calcite twins may be related with different dissolution rates along specific crystallographic orientations, a feature observed in hydrothermal experiments with fluorite single crystals (Godinho et al., 2012, 2014). Alternatively, twin planes may play a role similar to grain boundaries by providing easier pathways for the reactive fluid. However, the rates of fluid-mediated mass transfer directly depend on the width of the fluid pathways. The width of twin boundaries is sub-nanometer-scale; orders of magnitude narrower than the width of grain boundaries and even reaction-generated porosity and thus are unlikely to allow the same reaction rates. Subgrain boundaries in the calcite parent grains are less common than twin boundaries and do not display any relationship with the protrusions of the reaction front (Fig. 5e). Hence, orientation related faster reaction rates are likely to be the main reason for our observations.

Grain boundary geometry has a significant role on the reaction progress in both sets of experiments. In Set 1 experiments, the asymmetry of the reaction rim, displayed by sub-samples of BHD4-7, is closely associated with the orientation of grain boundaries and shape preferred orientation of the deformed calcite grains (Fig. 2d-f). This is in contrast to the concentric, regular geometry of the reaction rim in CarM samples, where the calcite has equidimensional grain shapes (Fig. 2a-c). In Set 2 experiments, where the reaction mostly proceeds along the grain boundaries, a positive feedback between smaller grain size and faster reaction progression is observed (fig. 2g-l). The replacement mode in CarM samples (apart from 1 and 2 day experiments) is always higher, compared to BHD4-7 samples that have larger grain sizes and a lower density of grain boundaries (Table 1, Fig. 2g-l).

3.4.5. How do secondary minerals affect replacement?

This study is only concerned with physical effects of secondary minerals during fluid-rock interaction, therefore experimental temperatures were kept relatively low ($180\text{ }^{\circ}\text{C}$) in order to prohibit dissolution of silicates that could complicate the studied system. The main secondary minerals (phlogopite, diopside and tremolite) in the reacted samples have not shown any evidence of dissolution or chemical alteration

(Fig. 3a-b), confirming that they were not involved in the replacement reactions. The main effect of secondary minerals in such systems thus might be related to the role of polyphase boundaries as fluid- and reaction pathways. In comparison to single-phase boundaries, polyphase boundaries have less ordered structure with weaker bonding and different interfacial energies that could facilitate fluid and mass transfer processes (Renard et al., 2001).

However, in the studied experimental system they seem to have negligible or no effect on the reaction progress. In both sets of experiments the reaction and its extent at polyphase boundaries does not differ from those along single-phase boundaries (Figs 3g & 4a-b). In the Set 2 experiments, the thickened reaction rims and reaction blebs observed in the longest duration experiments, are rarely associated with polyphase boundaries and are common along single phase boundaries. We conclude that even if polyphase boundaries may have some role on facilitating fluid flow and mineral reactions in other systems, the results of this study do not indicate different conditions or processes along polyphase boundaries.

3.5. CONCLUSIONS AND FUTURE WORK

The performed experiments support the recent findings (Pedrosa et al., 2016) of the significant impact that even small changes in fluid composition can impose on reaction microstructures and kinetics. The relationship between mass transfer, reaction progression and dissolution-precipitation kinetics seem to be the main reason controlling the microstructures developed in these experiments. Fast dissolution-precipitation compared to transport rates leads to a steady movement of the whole reaction front, where the mass transfer is controlled by reaction-generated porosity and not grain boundaries. On the other hand, slower reaction rates, coupled with less reaction-generated porosity favours the exploitation of grain boundaries as primary reaction pathways. Importantly, due to the differences in resultant microstructures, a lack of complete replacement may not indicate low fluid-rock ratios or low fluid-rock exposure times.

The grain boundary network and deformation microstructure in the reacted samples has a significant effect on reaction progression. Both grain and twin boundaries facilitate replacement reactions in all samples. However, while grain

boundaries enhance reactions by providing easy fluid pathways, the reactions along twins are most likely increased due to crystallographically enhanced dissolution rates.

The results of this work can help to create conceptual and numerical models for understanding fluid flow and reaction pathways in natural systems that have complicated mineralogy and can be exposed to a variety of fluids.

3.6. ADDITIONAL ANALYSIS PLANNED

The chemical data presented in this study are only preliminary, as access to EMP was limited during completion of this thesis. EDS data provides a distinction between the main minerals in the samples, however, the reaction products are characterized by subtle differences in Mg, F and Cl components that can not be resolved by EDS analysis. Detailed EMP point analysis and mapping will be performed while the thesis is examined. Further work will also involve mapping of ^{18}O distribution that was added in the reaction fluid as an additional tracer for the extent and chronology of fluid-rock interaction. The oxygen isotope mapping will be performed in collaboration with The University of Western Australia in Perth using a high resolution ion-microprobe (NanoSIMS), similar to that completed in Chapter 4.

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"Non-equilibrium produces its own order and correlation scales. It creates consistencies. It therefore leads us to rethink about order and disorder"

/Ilya Prigogine/

CHAPTER 4

4. Symplectite formation in the presence of a reactive fluid: Insights from hydrothermal experiments

ABSTRACT

This study describes the microstructural and chemical development of symplectites, obtained in hydrothermal mineral replacement experiments. During the experiments polymineralic feldspar-rich samples were exposed to sodium-silicate-H₂O solutions at 600 °C and 2 kbar confining pressures for durations of 12 hr to 20 days. Fluid-rock interaction resulted in highly complex reaction rims involving two varieties of kelyphitic symplectite-resembling microstructures consisting of a nanometre-scale intergrowth of gehlenite-zeolite and grossular-zeolite grains. The experimental use of ¹⁸O-doped fluids reveals not only that the reactions involved exchange of oxygen isotopes between the rock and fluid, suggesting fluid mediated dissolution-precipitation as the main reaction mechanism, but also the relative sequence of phase growth. Based on the progressive microstructural and chemical evolution of symplectite structures, observed in the performed experiments, a conceptual model for their formation is proposed. We suggest that the combination of fluid mediated open-system mass exchange, reaction generated porosity and ultra-local chemical variations of the interface fluid composition plays a significant role in controlling the formation of symplectite in the presence of a reactive fluid phase.

Our results may have important implications for understanding the fundamental processes involved in symplectite formation in nature and the interpretation of the geological history of mineral assemblages that exhibit symplectite microstructures.

Keywords: symplectite, fluid-rock interaction, hydrothermal experiments, oxygen isotope, microstructure

4.1. INTRODUCTION

Symplectites are reaction microstructures characterized by fine-grained vermicular intergrowths of two or more minerals. These microstructures are common in metamorphic rocks, especially those that have undergone retrogression and/or deformation (Vernon, 2004). Examples come from a wide range of geodynamic

environments including mantle peridotites (Godard and Martin, 2000; Takahashi and Arai, 1989), crustal amphibolites (Misch and Onyeagocha, 1976), granulites (Dégi *et al.*, 2010) and eclogites (Joanny *et al.*, 1991), deformed granitoids (Cesare *et al.*, 2002), kimberlites (Ringwood and Lovering, 1970) and even extra-terrestrial rocks from Mars (Rost *et al.*, 2009), Earth's moon (Bell *et al.*, 1975) and the asteroid belt (Patzner and McSween, 2012).

The origin of symplectite microstructures has been a subject of discussion since their first description. The most commonly proposed mechanisms responsible for symplectite formation involve: (1) melt crystallization (Hibbard, 1979), (2) exsolution during cooling (Schwantke, 1909) or (3) solid-state replacement reactions triggered by changes in temperature and pressure conditions (Becke, 1908). In addition to the fundamental interest in the generation of these microstructures, symplectites are also considered as valuable indicators of pressure-temperature-time paths during metamorphism, rates and efficiencies of diffusion processes and recorders chemical evolution of the reaction system.

In the recent literature, most authors support the view that symplectites develop by some form of replacement reaction as in many cases partly replaced parent grains can be seen in a contact relationship with the symplectite. The characteristic vermicular grain shapes in such models are attributed to slow nucleation rates of at least one of the intergrowth-forming minerals, as well as to slow diffusion rates of symplectite components that promote elongate rather than equidimensional grain shapes. The spacing of mineral grains in the symplectite lamellae has been proposed to reflect diffusion distances in the reaction system (Putnis 1992; Vernon 2004). Based on assumptions of isochemical diffusion-controlled reaction systems (Ashworth and Chambers, 2000), attempts have been made to use symplectite morphologies for quantitative estimation of diffusion rates (Dégi *et al.*, 2010) and temperatures (Joanny *et al.*, 1991).

However, it is also often reported (even in the same studies) that hydrous fluids or melts are involved in symplectite reaction (Daczko *et al.*, 2002; Dégi *et al.*, 2010; Obata, 2011; Shimizu *et al.*, 2008) enabling long-scale mass transfer and providing necessary components for the nucleation of symplectite minerals. As argued by Claesson (1998), the access of a late fluid was the most important factor for the

nucleation of kelyphytic symplectites in the Rymmen gabbro. The role of a fluid has also been discussed in relation to myrmekite formation; a special type of symplectite in granitic rocks, characterized by localized K-feldspar replacement with Na-rich plagioclase and quartz intergrowth. Due to the frequent occurrence of myrmekites in deformed rocks and the association with local high-stress sites at the edge of the host grains, the nucleation of myrmekite has been attributed to the enhanced stress and strain energies (Simpson and Wintsch, 1989; Passchier and Trouw, 2005). However, the study of Vernon (1991) argues that deformation-facilitated fluid access to the reaction sites might be a more important factor for myrmekite formation than strain energy. This has been further supported by the study of Menegon et al. (2006) who demonstrate the role of water-rich fluid in mediating long-distance mass transfer, required for the symplectite reactions, although in their study deformation is considered to be important in the early stages.

We present results from static hydrothermal experiments where symplectites were produced via a series of kinetically rapid fluid-mediated dissolution-precipitation reactions. The experiments of varied durations allow an insight into the temporal development of these microstructures and provide clues on factors that control the growth and morphology of symplectites in fluid-mediated reaction systems.

4.2. MATERIALS AND METHODS

4.2.1. Experimental procedure

Polycrystalline rectangular samples of $\sim 1.7 \times 1.7 \times 3$ mm size were cut from naturally deformed anorthosite collected at Qarliit Nunaat in SW Greenland ($63^{\circ}56'58.4845''$ N and $51^{\circ}11'08.3279''$ W) (Svahnberg and Piazzolo, 2010, 2013). After cutting, samples were cleaned with deionized water, oven dried at 40°C for 24 hr and weighed. For each experiment, each sample was welded into a gold capsule with a sodium silicate- H_2O solution ($\sim 7\%$ NaOH, $\sim 13\%$ SiO_2 , $\sim 30\%$ H_2O ; $\sim 50\%$ ^{18}O -enriched H_2O (grade 97%; *Campro Scientific*)) in weight proportions of rock to fluid equal to 1:1. Previous studies have shown that oxygen exchange kinetics is an important indicator for reaction mechanisms in such experiments (e.g. Putnis and Mezger, 2004; Kasiopas et al., 2011; Perdikouri et al., 2013). Therefore, the fluid was

oxygen isotope labelled, by adding ^{18}O -enriched water to the fluid solution that enabled tracing of oxygen redistribution during experimental fluid-rock interaction. After welding, all capsules were tested for leakage by a heat treatment at 90°C for 24 hr. Only those capsules that had the same weight before and after the heat treatment were considered sealed and used for experiments.

The hydrothermal experiments were performed at the University of Muenster, Institute of Mineralogy (Germany), using Cold-Seal Pressure Vessels (CSPV). Two capsules were loaded into each vessel, then T and P were gradually increased to 600°C and 2 kbar within a 2 hr time period. Experiment durations ranged from 0.5 to 20 days. To test the reproducibility of the results, repeat experiments for each duration (except 0.5 days) were performed (Table 1). On termination, the vessels were cooled down to room temperature within 20 min. The capsules were weighed again to ensure seal integrity during the experiments. Samples were removed from the capsules, washed in distilled water, oven-dried at 40°C for 24 hr, cut in half to reveal reaction interfaces in a cross-section and embedded in epoxy.

Table 1. Samples and experimental conditions; Avg. - average; Ex. dur. - experimental duration. To derive the min. (minimum) and max. (maximum) thicknesses of the reaction rims, BSE images of samples were quantitatively analysed using ImageJ (<http://imagej.nih.gov/ij/>) processing software, subsequently compared and averaged.

T= 600°C; P= 2 kbar; ratio of rock to fluid is 1:1											
		Initial composition (vol.% mode)				Reaction rim thickness (μm)					
						Replacement			Type I overgrowth		
Sample	Ex. dur. (days)	Pl	Hbl	Bt	Ep	Avg.	Min	Max	Avg.	Min	Max
W21	0.5	95	5	0	0.1	9.3	6.4	13.1	10.8	8.5	13.1
W18	1	76	2	19	1.9	11.4	6.4	18.5	15.1	9.4	24.5
W19	1	89	8	2	0.4	14.6	10.4	19.5	14.6	7.7	21.8
W12	5	73	16	10	1.3	23.3	17.1	31.7	23.3	14.1	43.2
W15	5	75	15	8	1.0	20.2	13.6	29.1	32.6	22.1	44.7
W13	10	62	26	11	1.0	31.8	25.6	40.2	39.5	21.1	69.3
W14	10	90	7	2	0.9	26.3	18.6	32.7	27.1	14.1	39.2
W16	20	80	13	7	0.5	44.7	31.7	66.8	24.6	16.1	38.7
W17	20	77	19	3	1.0	34.7	22.6	48.2	31.5	20.1	60.8

4.2.2. Analytical Methods

The initial sample characterization before and after experiments was performed at the Geochemical Analysis Unit (GAU), Macquarie University, Australia. Backscatter Electron (BSE) images (Fig. 1) were obtained with Carl Zeiss IVO Scanning Electron Microscope (SEM) at high-vacuum conditions with an accelerating voltage of 15 kV, beam current of 3 nA and at working distances of 12.5 mm. Major-element compositions were analysed using a CAMECA SX100 Electron Microprobe (EMP) with five wavelength dispersive spectrometers with an accelerating voltage of 15 kV and beam current of 20 nA. Most analyses were performed with a focused ion beam (2–3 μm), except the analyses of the replacement rim (Fig. 1; domains I, II and III), where the individual grain sizes were beyond the resolution limits of EMP and only bulk compositions were determined using a defocused beam with a diameter of 5–10 μm .

Detailed imaging of the fine grained reaction rims and mineral identification of the fine-grained phases were performed at the Australian Centre for Microscopy and Microanalysis, University of Sydney. A Carl Zeiss Sigma VP SEM with a field emission gun (FEG) was used as it gives 2–3 times better resolution compared to an SEM with a tungsten filament gun at the same beam currents (Humphreys and Brough, 1999). The images were collected under high vacuum conditions with an accelerating voltage of 3 kV and at working distances of 3.5–5 mm. The mineral identification in the reaction rims was performed with Oxford Instruments Aztec integrated EBSD/EDS system. The high resolution FEG EBSD maps were carried out on samples tilted to 70° with accelerating voltages of 15 kV, work distances of 11 mm and step sizes of 0.25 μm . Channel 5 analysis software from HKL Technology was used for the post-acquisition processing of the stored Kikuchi bands.

All mineral abbreviations used in the following text follow those suggested by Kretz (1983).

4.2.3. Isotope imaging and quantification

Isotopic imaging was performed using the CAMECA NanoSIMS 50 at the University of Western Australia. The sample was mounted in a one-inch resin disk, polished, and coated with Au to provide electrical conductivity at high voltage.

Secondary ion images were acquired using a focused Cs^+ primary ion beam, with a nominal beam diameter of approximately 100 nm. The electron multipliers were positioned to detect the secondary ions $^{16}\text{O}^-$, $^{18}\text{O}^-$, $^{28}\text{Si}^-$, $^{27}\text{Al}^{16}\text{O}$, and $^{40}\text{Ca}^{16}\text{O}$, simultaneously. As the sample is an insulator, a normal incidence electron gun provided charge compensation at the sample surface. Images were acquired from areas $30 \times 30 \mu\text{m}$ at a pixel resolution of 512×512 , with a primary beam current of approximately 2.8 pA. Each image consists of the sum of multiple frames of relatively short scan time (5ms/pix). This was done in an attempt to further minimise charge build up on the surface. Despite this, some images still exhibit intensity gradients.

Analyses were chained to produce large mosaics. All areas were pre-sputtered to 10^{17} Cs ions/ cm^2 prior to imaging. All images were corrected for 44 ns detector deadtime and processed using the NRIMS plugin for ImageJ (<http://nrims.harvard.edu/software>). Isotope images are displayed using a Hue-Saturation-Intensity scale, where the natural abundance is set to blue and enrichments are displayed on a colour scale towards magenta. This method allows enhanced visualisation of small isotopic variations (Lechene *et al.*, 2006).

4.3. RESULTS

4.3.1. Starting material

The experimental rock samples all come from a single hand specimen with some heterogeneity in mineral composition. Hence, the composition at the scale of the individual samples varies (Table 1). Plagioclase (pl_1) is the dominant mineral in all samples (62-95 area% mode). Plagioclase has a chemically homogenous bytownite composition (An_{88-90}) (Table 2), except for minor parts adjacent to amphibole and biotite, where it is locally andesine (An_{30-33}). Pl_1 grains are 0.1 – 1 mm large, equant or slightly elongated and often exhibit 120° triple junctions (Fig. 1a). As the natural samples have undergone deformation, pl_1 displays deformation twins and lattice misorientations ranging up to 7° across the individual grains. Hornblende (2-26 area% mode) and biotite (0-11 area% mode) grains are the dominant secondary minerals in the samples (Table 1). Hornblende composition varies between tschermatic hornblende and tschermakite (by the classification schemes of Leake *et al.* (1997) and

Leake et al. (2004). Biotite contains a significant phlogopite component in the range of $X_{\text{phl}} (\text{Mg}/(\text{Fe}+\text{Mn}+\text{Ca}+\text{Mg}))$ 0.76 – 0.77 and is partially altered to chlorite (Table 2) along some grain boundaries. Hornblende grains show little internal deformation ($<1^\circ$ misorientation), while biotite grains display pronounced kink bands and highly distorted lattices. Epidote (clinozoisite group, Table 2) constituting 0–2 area% mode is an accessory mineral in the experimental samples (Table 1).

Table 2. EMP mineral chemistry data and structural formulae. Abbreviations used for mineral names are pl – plagioclase, amp – amphibole, ep – epidote, mca – mica, amorph – amorphous, pct – pectolite, grt – garnet, bytw – bytownite, czo – clinozoesite, bt – biotite, phl – phlogopite, olg – oligoclase, ab – albite, zeo – zeolite, gh – gehlenite, grs – grossular

	Parent					Reaction product						
						Overgrowth rims				Replacement rim		
	Pl ₁	Amp	Ep	Mca	Amorp phase	Pl ₂	Pl ₃	Pct	dom I	dom II	dom III	Grt
SiO ₂	45.45	44.76	38.84	38.07	67.21	63.68	67.96	54.26	44.60	39.65	40.08	39.68
TiO ₂		0.06		0.16								
Al ₂ O ₃	34.52	16.33	28.46	22.34	7.46	23.36	20.10	0.32	34.71	31.91	31.63	23.16
Cr ₂ O ₃												
FeO		10.60	5.83	9.78	0.88	0.18	0.19	0.06	1.07			
MnO		0.20	0.10	0.07				0.07				
MgO		13.88		18.15	0.61	0.06		0.21	1.10			
CaO	18.30	12.09	24.63		0.41	4.47		32.40	0.74	15.08	15.82	36.48
Na ₂ O	1.40	1.76		0.19	5.77	10.16	12.77	10.29	15.78	14.39	12.59	0.43
K ₂ O		0.32		9.63	0.60	0.06	0.18		1.53	0.78	0.84	0.06
Cl		0.03		0.05								
F				0.08								
NiO				0.13								
Total	99.67	100.03	97.86	98.65	82.94	101.97	101.20	97.61	99.53	101.81	100.96	99.81
# oxygens	8.00	23.00	13.00	22.00	n/a	8.00	8.00	9.00	12.00	n/a	n/a	12.00
Si	2.10	6.31	3.17	5.31		2.78	2.95	3.17	3.15			2.98

Al	1.88	2.71	2.74	3.68	1.20	1.03	0.02	2.88	2.05			
Ti	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00			
Cr		0.00	0.00	0.00			0.00	0.00	0.00			
Fe+3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
Fe+2	0.00	1.25	0.40	1.14	0.01	0.01	0.00	0.06	0.00			
Mn	0.00	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00			
Mg	0.00	2.92	0.00	3.78	0.00	0.00	0.02	0.12	0.00			
Ca	0.91	1.83	2.15	0.00	0.21	0.00	2.03	0.06	2.93			
Na	0.13	0.48	0.00	0.05	0.86	1.08	1.16	2.16	0.06			
K	0.00	0.06	0.00	1.71	0.00	0.01	0.00	0.14	0.01			
Sum	5.02	15.59	8.46	15.70	5.06	5.08	6.40	8.56	8.03			
Mineral classification	bytw	Fe-tsch	czo	bt-phl	amorph Si-Na	olg	ab	pct	Na-zeo	gh + zeo	grs + zeo	grs
Mg/(Mg+Fe2)		0.87										1.00
Fe3/(Fe3+Alvi)		0.47										
Ca/(Ca+Mg+Mn+Fe)												
Mg/(Fe+Mn+Mg+Ca)				0.77								
Mn/(Fe+Mn+Mg+Ca)				0.00								
Fe/(Fe+Mn+Mg+Ca)				0.23								
Ca/(Fe+Mn+Mg+Ca)				0.00								
Ca/(Ca+K+Na)	0.88					0.19	0.00					
K/(Ca+K+Na)	0.00					0.00	0.01					
Na/(Ca+K+Na)	0.12					0.80	0.99					

4.3.2. General characteristics of the reaction rims

After the experiments, all samples are surrounded by reaction rims that also extend into the sample interiors along grain boundaries (Figs 1a-f, 2e, f & 3d). Amphibole and epidote grains are partially replaced by richterite, while biotite is partially replaced by muscovite near the surfaces that were exposed to the fluid. The focus of this study is the reaction rims developed adjacent to the original pl_1 grains, where symplectite microstructures are observed. These rims are mineralogically and structurally complex (Fig. 1a-f, h). With respect to the pre-experiment sample surface, we distinguish the following domains in each reaction rim: (1) an overgrowth domain outside the boundary; (2) a boundary zone and (3) a replacement domain within the sample (Fig. 1d-f).

The overgrowth domains are classified into two types. Type 1 overgrowth is a polycrystalline zone of 5-100 μm large Na-rich plagioclase grains ($pl_{2,3}$) that is in direct contact with the pre-experiment sample surface (Figs 1b-f; 2e-f). The $pl_{2,3}$ grains in the overgrowth rim display well-defined crystal faces and intergranular porosity. Crystallographically, $pl_{2,3}$ grains have similar orientations to the adjacent pl_1 grains (within 5° – 20°), even where separated by replacement rims (Fig. 4a-b). Type 2 overgrowth rims are amorphous, pervasively fractured and have a composition rich in Na and Si. A high density of 1–5 μm large pores commonly decorates the outer margins of Type 2 overgrowths (Fig. 1a-f).

In the replacement rim, three mineralogically and morphologically distinct domains are recognized (Fig. 1b-f): (1) domain I is the furthest from the interface with pl_1 and consists of nano-porous Na-rich zeolite, intergrown with small amounts of nanometer-sized grains of an unidentified second mineral (possibly gehlenite or pectolite as it displays similar brightness in BSE images to the gehlenite grains in domain II and the pectolite grains in the Type II overgrowth); (2) symplectite domain II is located in between the porous domain I and symplectite domain III or adjacent to the pl_1 in the areas where domain III is not present. It is characterized by a symplectite of sub-micrometre sized zeolite and gehlenite grains; (3) symplectite domain III is associated with fractures and grain boundaries and typically shares an interface with pl_1

grains. It is represented by a symplectite of a sub-micrometre- to micrometre sized zeolite and grossular grains.

The overgrowth and replacement rims are separated by a sub-micron wide boundary zone. This boundary zone marks the pre-experiment sample surface and is decorated by a discontinuous trail of pectolite grains and porosity (Figs 1b-f & 2e-f).

There is a consistent change in the reaction rim thickness (Fig. 1g) and composition (Fig. 1h) with respect to the experiment duration. The average width of replacement rim increases from 9 μm in a 0.5 day experiment to 40 μm in 20 day experiments, while the rate of the replacement decreases with time. The composition of the replacement rim changes such that with increasing experiment duration, the combined area% of the porous domain I and symplectite domain II decreases from 93% to 33%, while the area% of the symplectite domain III increases from 7% to 67%.

In the type 1 overgrowth rim, large variations can be seen between samples. About 10 μm difference is observed in samples from experiments with the same duration (Table 1). Samples from shorter experiments sometimes display thicker type 1 overgrowth than samples from longer experiments. Type 1 overgrowth rims from short experiments have lower porosity and larger grain sizes than the respective rims from longer experiments (Fig. 1b-c). The composition of plagioclase in the overgrowth rims from short experiments (pl₂) has higher Ca-component (An₁₈₋₂₀ in samples reacted for 0.5 days) compared to the plagioclase (pl₃) in longer experiments (An₁₋₀ after 20 day reaction) (Table 2).

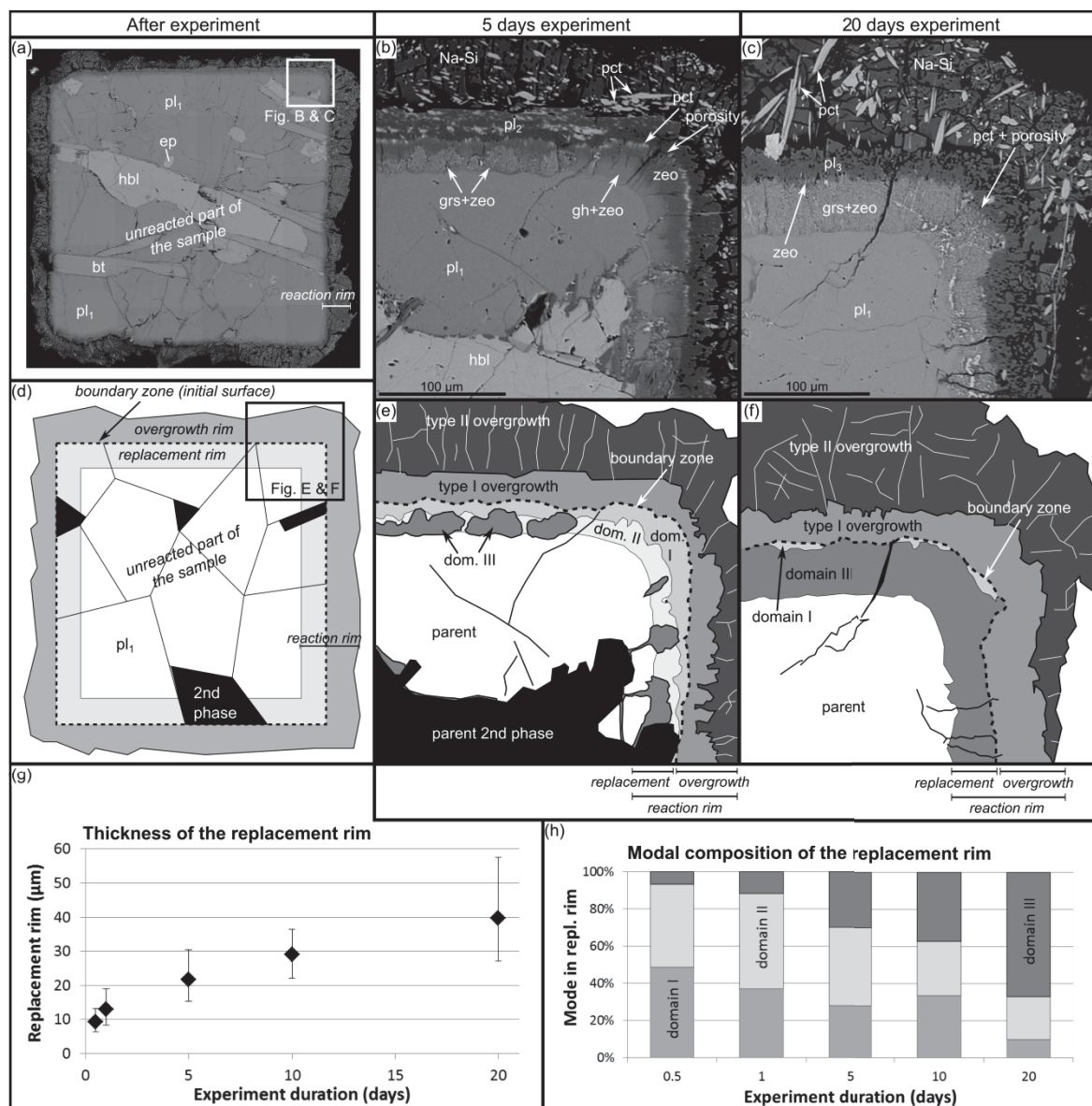


Figure 1. General microstructural features of the reacted samples. (a)-(c) are BSE images of the samples after experiment. (a) - cross-section of the whole sample, (b) – sample after 5 days of experiment, (c) – sample after 20 days of experiment; (d)-(f) are schematic drawings of the Figures (a)-(c). (g) – the average thickness and the variation range of the replacement rim (consisting of domain I, II and III) after 0.5, 1, 5, 10 and 20 days of experiments; (h) – the modal composition of the replacement rim for each experiment duration.

4.3.3. Symplectites in the reaction rim

4.3.3.1. General characteristics

The two types of symplectites, distinguished in the replacement rim in domains II and III, respectively, have different mineral assemblages. However, chemical mapping shows that they have overall very similar compositions (Table 1). The main difference is a slightly higher Na-content in gehlenite-zeolite symplectite (domain II) compared to the grossular-zeolite symplectite (domain III).

Morphologically both symplectites share many common features. They have a sharp boundary with the parent bytownite (pl_1) grains at the reaction front (Figs 2a, c, e, f & 3a, d). The reaction front is relatively straight laterally and generally subparallel to the outer boundary of the replacement rim. The other boundary of both symplectites in domain I and II is also sharp on a nanoscale, but lobe-shaped and highly irregular (Figs 2a, c, e, f & 3a-b). Both symplectites are composed of a zeolite matrix and skeletal grains of a second mineral (Figs 2a-f, 3a-d & 4a). In symplectite domain II this second mineral is gehlenite (Fig. 2b, d); while in symplectite domain III it is grossular (Fig. 3b-c). The typical length of gehlenite grains ranges from a few nm to 500 nm. Grossular grains in domain III are on average coarser and can reach sizes $>1\ \mu\text{m}$. Near the reaction front with pl_1 , gehlenite (domain II) or grossular (domain III) grains are closely spaced, and often kelyphitic, having highly elongated shapes sub-perpendicular to the reaction front (Figs 2c & 3a-b, d). Away from the reaction front gehlenite/grossular grains become coarser and show smaller aspect ratios. It is common to observe the association between gehlenite/grossular grains and porosity in zeolite, particularly near the interface with the porous zeolite in domain I (Figs 2b, d, d & 3b-c).

Figure 4 shows that the minerals in the reaction rim display crystallographic preferred orientations but, with an exception of pl_1 and pl_2 grains, do not have an obvious topotactic relationship to each other. Several spatially defined “orientation families” can be distinguished in the symplectite domain III, where groups of neighbouring individual grains are similarly oriented within a range of $10\text{--}20^\circ$. This is clearly observed in the coarser-grained grossular (Fig. 4b-c), but, as seen from pole figures (Fig. 4c), also occurs for zeolite and gehlenite.

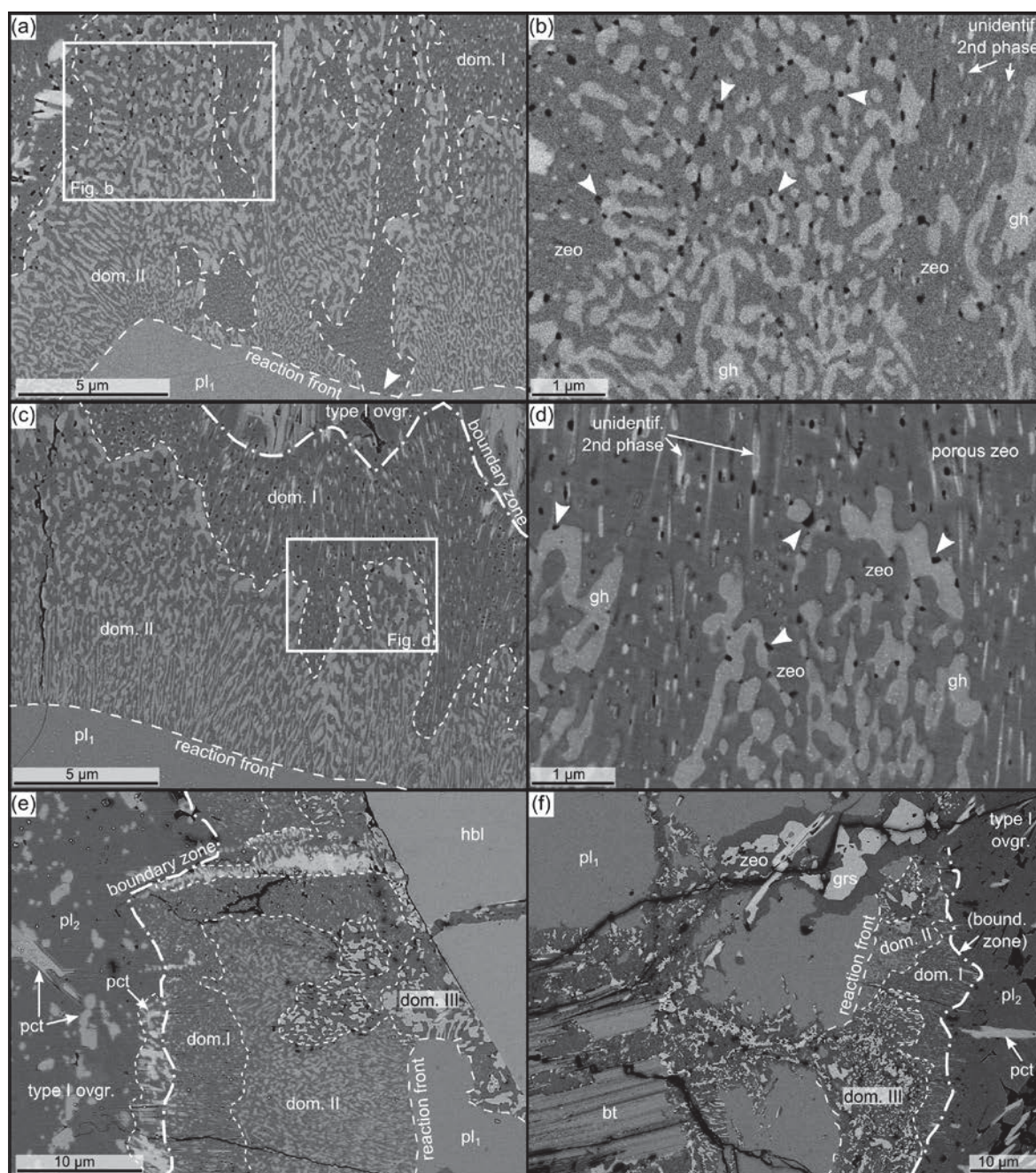


Figure 2. BSE micrographs of typical reaction microstructures in short experiments. (a) - 12 hr experiment showing interface of the reaction rim and parent pl₁ grain. Domain I is nano-porous zeolite with small amounts of sub-micrometre sized non-identified second mineral grains, domain II is gehlenite-zeolite symplectite. The white arrowhead marks a discontinuity in domain II where domain I has a direct interface with pl₁ grain. (b) - a higher magnification image of the marked area in (a). The white arrowheads mark the association of the gehlenite grains with porosity in zeolite. (c) - 1 day experiment showing the interface of the reaction rim and parent pl₁ grain. Note that the domain 2 is continuous along the interface, but has an irregular outer boundary. (d) - a higher magnification image of the marked area in (c). The white arrowheads mark the association of the gehlenite grains with porosity in zeolite. (e) - image of a reaction rim after a 5 day experiment showing the association of domain III and pl₁-hornblende boundary in the parent sample. Note the presence of domain I along the boundary zone with type I overgrowth. (f) - image of a reaction rim after a 5 day experiment showing the association of domain III and pl₁-biotite boundary in the parent sample. Note ~10 μm large grossular grain on the grain boundary.

4.3.3.2. *Short duration experiments*

For simplicity of description, the experiments of durations from 12 hr – 5 days are referred as “short experiments” whereas the experiments of durations from 10 – 20 days are referred as “long experiments”.

As shown in Figs 2 & 3, the symplectite microstructures are significantly different depending on the experiment duration. In the short experiments the symplectite domain II is typically found on the inner part of the replacement rim in direct contact with the pl₁ grain, while the porous domain I occurs on the outer part of the rim (Fig. 2a, c, e). Domain II can reach widths of $\sim 20\ \mu\text{m}$ but does not extend to the outer boundary of the replacement rim. The porous domain I, however, in the shortest performed experiments of 12 hr duration can be occasionally seen in direct contact with pl₁, where domain II is laterally discontinuous (Fig. 2a). The contact between domain I and pl₁ is not observed in experiments with longer durations. A nano-porosity can be observed in the outer parts of symplectite domain II near the contact with the domain I. Gehlenite grains in these sites seem to be connected across multiple pores, sometimes displaying zigzag shapes that are associated with the pore geometry (Fig. 2b, d). The second mineral in domain I is also associated with pore-spaces and is elongated in a direction sub-perpendicular to the reaction front (Fig. 2b, d). The symplectite domain III, represented by a grossular and zeolite intergrowth, in the short experiments occurs directly along grain boundaries and fractures (Figs 1e & 2e, f). It is fan- or lobe shaped, and extends perpendicular to the reaction front.

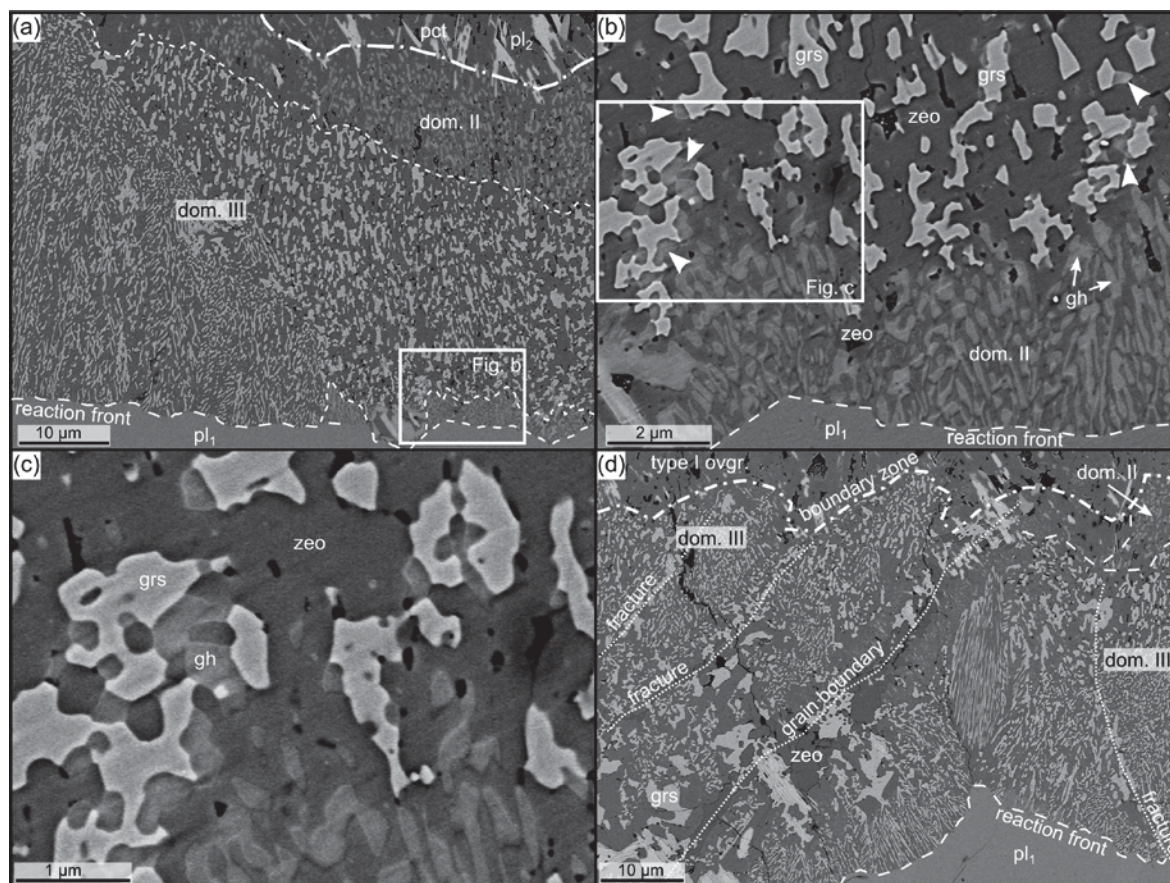


Figure 3. BSE micrographs of typical reaction microstructures in long experiments. (a) – image of a reaction rim after a 20 day experiment. The domain III is widespread even away from grain boundaries. Note that domain II borders the boundary zone with type I overgrowth and domain I is absent. (b) – a higher magnification image of the marked area in (a) showing the interface between domain II and III. The arrowheads show contact relationships between gehlenite and grossular grains. (c) – a higher magnification image of the marked area in (b) showing the contact between gehlenite and grossular grains in detail. (d) – image of a reaction rim near the grain boundary after 20 days experiment. Note the different morphologies of grossular-zeolite symplectite in domain III. Domain I is absent, the type I overgrowth borders either domain II or III.

4.3.3.3. Long duration experiments

The experiments of 10 and 20 day durations display a widespread distribution of the symplectite domain III, even away from the fractures and grain boundaries (Fig 3a). In many sites, especially near the grain boundaries it extends over the whole width of the replacement rim (Fig. 3d). The grossular in domain III displays a variety of geometries, ranging from parallel highly elongated grains to irregular or equidimensional ones (Fig. 3d). Near the fractures and grain boundaries, the grossular is coarser-grained reaching individual grain sizes of up to 15 μm .

The symplectite domain II is less continuous compared to the short experiments. Where the domain III is present, domain II occurs either on the inner or outer part of the replacement rim (Fig. 3a, d). The porous domain I is absent in many

sites of the replacement rim (Fig. 3a, d). Where it occurs, it is located on the outer parts of the rim, adjacent to the boundary with the overgrowth domain I.

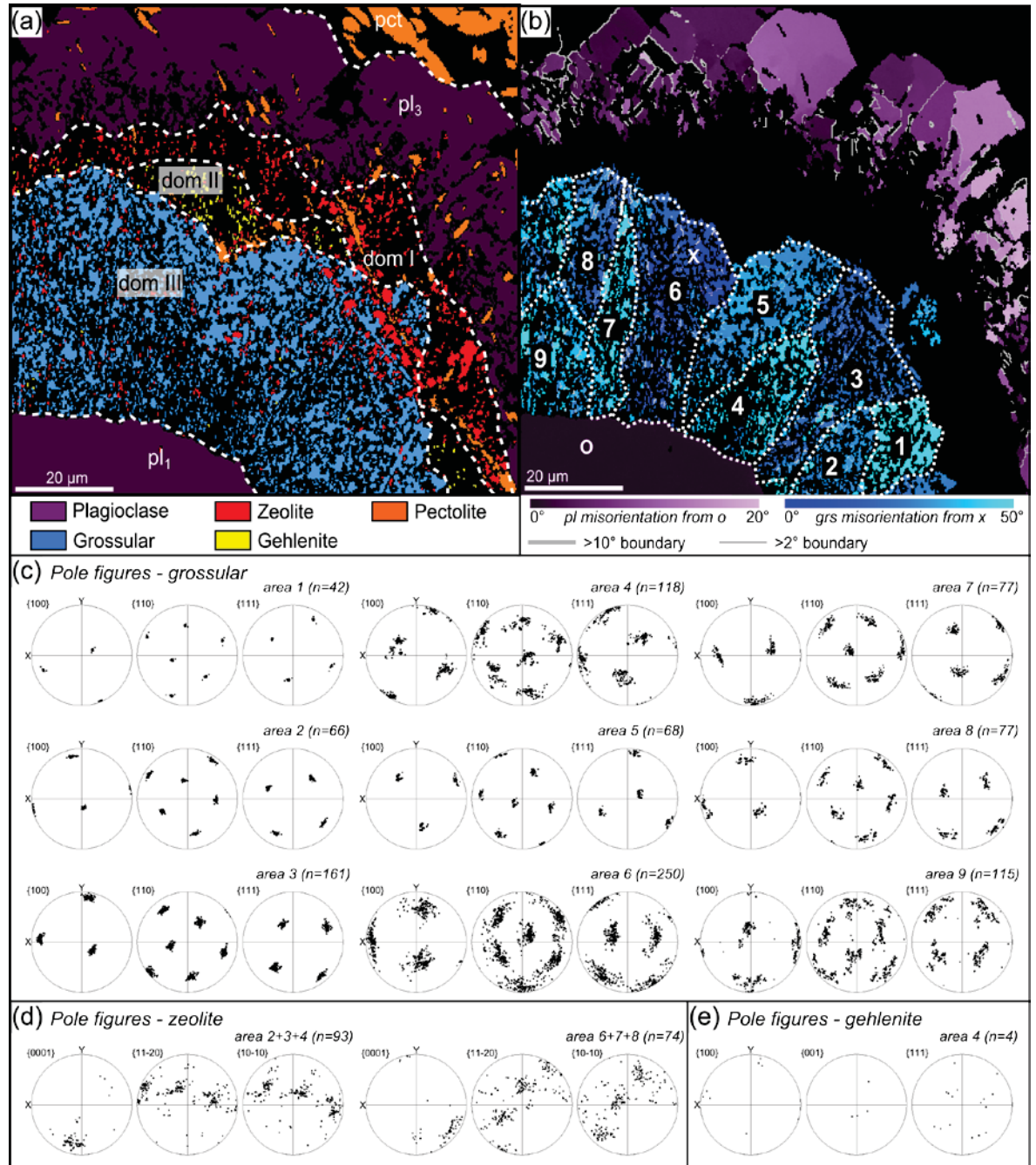


Figure 4. Crystallographic features of the reaction products. (a) – mineral distribution map of the reaction rim and adjacent *pl₁* grain; (b) - orientation map of (a) showing the relative misorientations of plagioclase and grossular grains in respect to sites *o* and *x*, respectively. The dotted lines and numbers label distinct “orientation families” in the grossular-zeolite domain (domain III) that consist of multiple individual grains with similar crystallographic orientations; (c)-(e) – pole figures of the crystallographic orientation data for the areas as marked with numbers in (b). All data are plotted as one point per grain using equal-area projection on lower hemisphere, *n* = number of points.

4.3.4. Isotope analysis

Figure 5 shows results of oxygen isotope analysis in samples from 10 and 20 day experiments (W14, W17; Table 1). The reaction products in both samples have considerably higher $^{18/16}\text{O}$ values compared to their adjacent unreacted parent grains. Pl_1 and hornblende have consistent natural abundance $^{18/16}\text{O}$ values of around 0.002, in other words ^{18}O constitutes 0.2 atom% of the measured oxygen isotopes (Fig. 5j). The only areas that show increased ^{18}O concentrations of up to 8 at% outside the reaction rim occur along fractures and grain boundaries. Fractures transecting pl_1 grains have $^{18/16}\text{O}$ profiles exhibiting a smooth change of the $^{18/16}\text{O}$ ratio with increasing proximity to the fracture, in contrast to the fractures in parent hornblende grains that exhibit a sharp enrichment in ^{18}O near the contact with the unaltered parent grain.

4.3.4.1. 10 day experiments

The highest ^{18}O values in this sample are observed in the type I overgrowth rim (Fig. 5b, j-prof. 1), where ^{18}O concentration gradually decreases from ~ 23 at% at the boundary zone with the replacement rim to ~ 17 at% towards the outer part of the sample. In the replacement rim, the ^{18}O concentration profiles show an opposite trend, with decreasing values, towards the sample interior. Domain I displays a decrease in ^{18}O values from ~ 12 at% to ~ 10 at% towards its inner boundary, while in domain II ^{18}O concentration decreases from ~ 10 at% to ~ 5 at% towards the interface with the unreacted pl_1 grain. At this interface no gradient is observed in the pl_1 , where the ^{18}O concentration rapidly drops to the natural abundance (0.2 at%) over a distance of less than a micrometre.. The spatial distribution of $^{18/16}\text{O}$ values in the domain II is slightly heterogeneous (Fig. 5a-b). In the ^{18}O concentration profiles few relatively rapid drops by $\sim 2 - 4$ at% can be observed (Fig. 5j; prof. 1), however it is difficult to correlate them with any physical features in BSE images, due to the very fine-grained nature of domain II.

4.3.4.2. 20 day experiments

In this experiment, the respective reaction domains show lower $^{18/16}\text{O}$ values compared to the same reaction domains in the sample reacted for 10 days (Fig. 5j; prof. 1-7). The highest ^{18}O concentration is again observed in the type I overgrowth rim that

is characterized by a decreasing gradient from ~ 11 at% to 8 at% ^{18}O towards the sample interior (Fig. 5j-prof. 2, 3, 4). Similarly, a decreasing gradient from ~ 8 at% to 0.2 at% ^{18}O towards the reaction interface with the unreacted pl_1 grain can be seen in domain III (Fig. 5j-prof. 2-7). There is no rapid drop in ^{18}O concentration near the reaction front with the unreacted pl_1 grains, however the ^{18}O -concentration in the parent grains never exceeds natural abundances of $\sim 0.2 - 0.3$ at%. The oxygen isotope distribution throughout domain III is very heterogeneous, characterized by a patchy pattern (Fig. 5b, d-g), where the sizes and shapes of the ^{18}O -poor areas resemble the distribution and morphology of grossular grains embedded within the zeolite matrix as seen in the BSE images (Fig. 3a). The high variance between ^{18}O -poor and -rich areas is especially obvious near the outer parts of domain III, characterized by high average ^{18}O concentrations. As seen from the line profiles, ^{18}O concentration in these parts can vary by $2 - 4$ at% on a scale of $1 - 2 \mu\text{m}$ (Fig. 5H; profile 4-6).

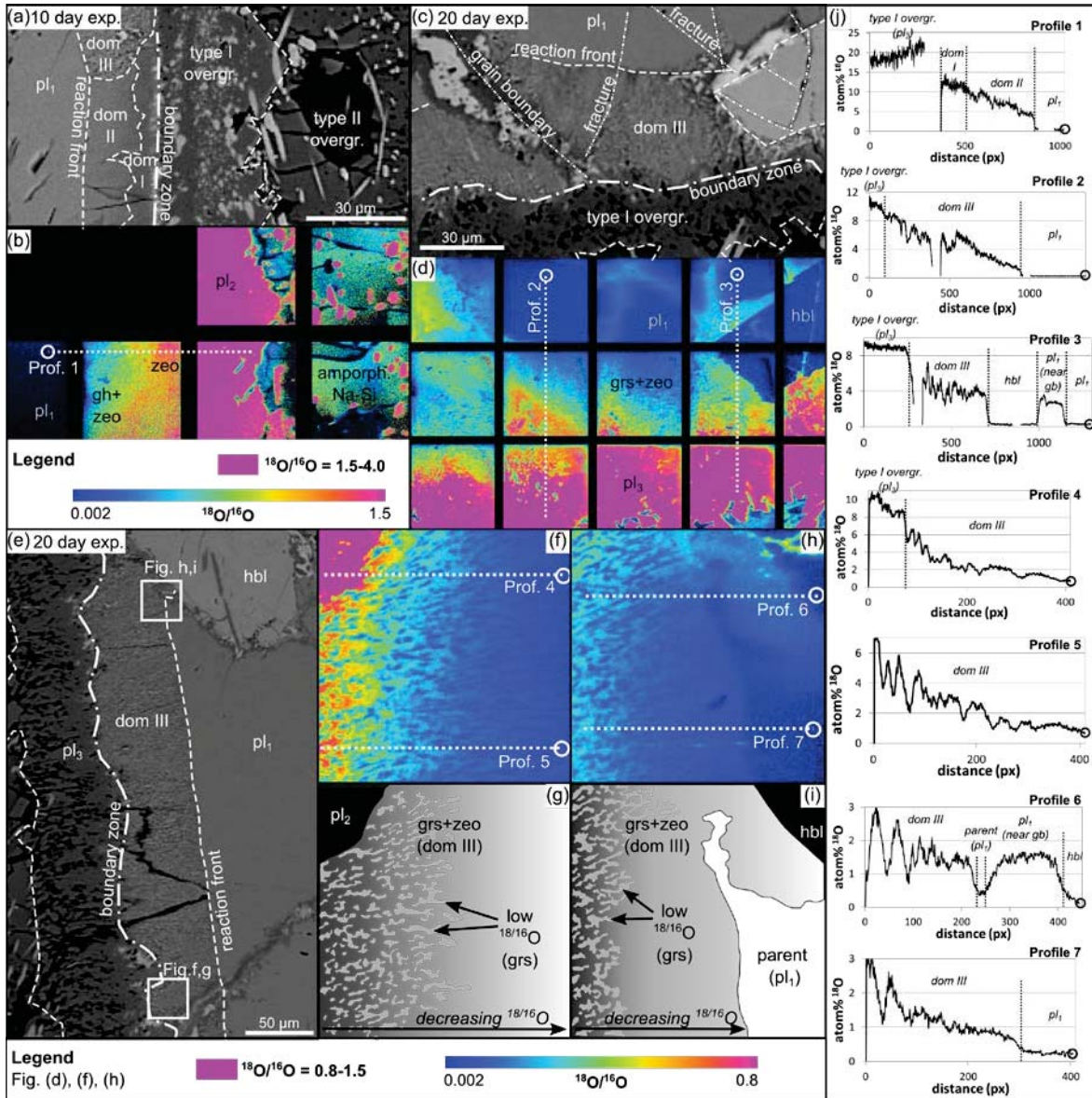


Figure 5. Isotope analysis. (a) - BSE image of a reaction rim after 10 day experiment; (c), (e) - BSE images of the reaction rim after 20 day experiments; (b), (d) - $^{18}\text{O}/^{16}\text{O}$ value distribution maps of (a) and (c); (f), (h) - $^{18}\text{O}/^{16}\text{O}$ value distribution maps over the areas labelled in Fig. (e) The $^{18}\text{O}/^{16}\text{O}$ ratio is displayed on a HSI scale where blue represents natural abundance (0.002), and enrichment of ^{18}O shifts along the colour scale towards magenta; (g), (i) - schematic drawings of (f) and (h) with the main features labelled; (j) line profiles as marked on figures (b), (d), (f) & (h), showing atom% ^{18}O calculated as $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O}) \times 100$.

4.4. DISCUSSION

4.4.1. Reaction mechanism: Diffusion versus dissolution and precipitation

Symplectite formation is traditionally considered to be a volume-diffusion driven replacement reaction (Vernon, 2004; Field, 2008), while more recent studies

presents evidence of grain boundary diffusion (Goergen and Whitney, 2012a, 2012b) and fluid-mediated long distance mass transfer (Menegon *et al.*, 2006) controlling symplectite reactions. Fluid, however, is not only a kinetic agent in metamorphic systems but has an ability to trigger dissolution-precipitation processes that are fundamentally different from diffusional reactions in dry rocks (Putnis, 2009; Wintsch and Yi, 2002).

In this study, several lines of evidence indicate that the observed symplectite microstructures formed by dissolution-precipitation mechanisms. Firstly, the increased $^{18}/^{16}\text{O}$ values in the reaction rims compared to the unreacted parts of the sample (Fig. 5a-j) suggest that oxygen atoms from the ^{18}O -enriched fluid were incorporated in the reaction products. This observation cannot be explained by volume-diffusion mechanisms as the experimental temperatures are too low to account for the $^{18}\text{O}/^{16}\text{O}$ exchange at the observed durations (Cole and Chakraborty, 2001; O'Neil and Taylor, 1967). On the other hand, isotope redistribution is expected in fluid-mediated dissolution-precipitation reactions (Labotka *et al.* 2004; Niedermeier *et al.* 2009; Perdikouri *et al.* 2013), where the original parent mineral is locally dissolved at the reaction interface and the replacing products grow from the components available in the ^{18}O -enriched interfacial fluid. Although the observed gradual decrease in ^{18}O concentrations from the overgrowth and replacement rims towards the reaction interface with pl₁ grain (Fig. 5j) may resemble diffusional profiles, such isotope (Perdikouri *et al.*, 2013) and compositional (Borg *et al.*, 2014) gradients are also common for dissolution-precipitation reactions, where the reaction products that precipitate first typically contain a high amount of fluid-derived components (^{18}O), while at later stages as the replacement progresses towards the parent interior, the interface fluid becomes “diluted” by components from the dissolving parent (^{16}O), resulting in products with lower $^{18}/^{16}\text{O}$ values. The rapid decrease in ^{18}O concentration at the interfaces with pl₁ and hornblende grains (Fig. 5j; prof. 1, 3), also supports the idea that ^{18}O redistribution was controlled by dissolution-precipitation, rather than volume diffusion reactions.

In addition to the data on oxygen isotope redistribution (Fig. 5), the rates of replacement rim growth ($\sim 20\ \mu\text{m}$ in 12 h experiments; Tab. 1) are orders of magnitude faster than any measurements of cation diffusion in feldspars (Brady and Yund, 1983;

Behrens et al., 1990; Giletti and Shanahan, 1997) and the microstructural evidence of sharp nanometre-scale compositional interfaces between parents and products, porosity in the replacement rim and the reactions that associate with grain boundaries and fractures are also typical criteria, used for recognizing fluid-mediated dissolution-precipitation reactions (Putnis 2002; Putnis 2009). Pseudomorphism and epitaxy in such reactions occurs if dissolution and precipitation processes are kinetically coupled at the reaction interfaces (Xia *et al.*, 2009).

4.4.2. Reactions, nature of fluid and associated microstructural development

Here, we discuss the chemical and morphological development of the observed symplectite microstructures within a framework of fluid-mediated dissolution-precipitation processes as the main reaction mechanism (Fig. 6). The particular reactions described in the following sections are specific to this study, however, the general processes that are involved in the reactions can be used to understand symplectite generation in a more conceptual way (Section 4.3. and Fig. 7). The chemical formulae of minerals used in the interpreted mineral reactions are given in Table 3.

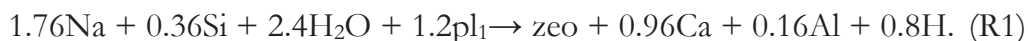
Table 3. Abbreviations and chemical formulae for the minerals as used in the reaction equations

Abbreviation	Mineral	Formula
pl1	bytownite	$\text{Na}_{0.2}\text{Ca}_{0.8}\text{Al}_{1.8}\text{Si}_{2.2}\text{O}_8$
pl2	albite	$\text{NaAlSi}_3\text{O}_8$
pl3	oligoclase	$\text{Na}_{0.8}\text{Ca}_{0.2}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8$
zeo	zeolite (natrolite)	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
pct	pectolite	$\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$
gh	gehlenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$
grs	grossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$

4.4.2.1. Stage I: Formation of domain I

The initial reaction starts at the surfaces of pl₁ grains that are exposed to the Na-Si solution, enriched in ¹⁸O (Fig. 6a). The high ¹⁸O values in domain I (Fig. 5j-prof.1), its widespread distribution in the short experiments, at places extending over the whole width of the replacement rim (Fig. 2a) and the association with the pre-

experiment sample-fluid interface in all experiments (Fig. 2a, c, e, f) suggest that it is the first reaction product that forms during the fluid interaction with the samples. The reaction proceeds by coupled dissolution-precipitation mechanisms, where Na-rich zeolite pseudomorphically replaces the metastable Ca-rich pl₁ via reaction:



The high ¹⁸O values in zeolite near the outer parts of domain I (Fig. 5j; prof. 1) suggest a high fluid-derived component, while the gradual decrease in ¹⁸O concentrations towards the sample interior reflects the increasing incorporation of parent-derived components, released in the interface fluid due to the dissolution of pl₁.

4.4.2.2. Stage II: Formation of the type I overgrowth rim

The excess Ca and Al, released in reaction 1 locally supersaturate the fluid near the sample surface, leading to a precipitation of pl₂ (oligoclase) and pectolite as overgrowth rims (Figs 1b-c, e-f & 6b):



It is important to note that pl₂ grains, produced in reaction 2, have a close crystallographic relationship with the unreacted pl₁ grains, while the replacement rim separating both minerals shows a variety of orientations (Fig. 4b). In a context of dissolution-precipitation processes the relationship between pl₁ and pl₂ can only be attained by epitaxially controlled nucleation (Niedermeier *et al.*, 2009), suggesting that the first pl₂ grains that nucleated in reaction 2, were in a direct contact with pl₁. Thus the timing of reaction 2 must have been almost simultaneous and coupled with reaction 1, before the surface of pl₂ grain is completely transformed into zeolite. Interestingly, in the short experiments the highest ¹⁸O values are observed in inner parts of the type I overgrowth rim and decreases outwards, opposite to the trend observed in the replacement rim (Fig. 5j; prof. 1). This the decrease in ¹⁸O concentration gradient is, again, consistent with the growth direction of the type I overgrowth rim. The first pl₂ grains that directly nucleated on the initial sample surface contains the highest amounts of ¹⁸O, while the pl₂ that formed at later stages have relatively higher ¹⁶O component suggesting continuous changes in the surface fluid composition after prolonged interaction with the parent sample.

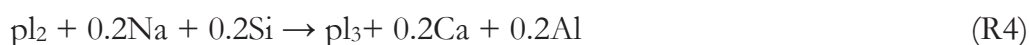
4.4.2.3. Stage III: Formation of domain II and re-equilibration of the type I overgrowth

Both, zeolite that forms in reaction 1 and pl₂ that forms in reaction 2, display a pervasive porosity (Figs 2b-c & 3b-d) that allows the continued access of the fluid to the reaction front and enables the continued progression of the reaction front towards the sample interior (Fig. 6c). However, the growing thickness of the replacement and overgrowth rims may lead to a partial closure of the system by hindering the mass exchange between the bulk fluid that surrounds the sample and the interface fluid at the reaction front. We suggest that the development of symplectite domain II is a result of such a process, when the accumulation of components released from the dissolving pl₂ (Ca, Al) in the interface fluid triggers the precipitation of gehlenite grains in the porosity of previously formed zeolite (domain I), creating the characteristic symplectite microstructure of domain II (Figs 2a-d & 6c):



The precipitation of secondary minerals in the porosity of primary reaction products, to a lesser extent, has been occasionally reported in other hydrothermal experimental studies (Harlov *et al.*, 2005; Hövelmann *et al.*, 2010). In the studied system this is supported by the observed temporal development of the reaction microstructures in respect to the increasing experiment durations. The domain II first appears adjacent to the reaction front and shows expansion towards the outer part of the replacement rim in longer experiments, while domain I “retreats” from the reaction front towards the outer part of the replacement rim (Figs 2a, c, e, f & 3a, d). The association of the pores and gehlenite grain on the interfaces between both domains (Fig. 2b, d) and the non-identified nano-sized minerals near the pores in domain I may represent the first stages in the evolution of domain I into domain II. As seen from the isotope data (Fig. 5j; prof. 1), domain II has lower ¹⁸O concentrations than domain I inferring a higher parent-component (¹⁶O). The fine-scale heterogeneity in ¹⁸/¹⁶O values (Fig. 5b) in domain II and the sharp 2-4 at% drops in ¹⁸O concentrations displayed by the line profiles (Fig. 5j; profile 1) may represent the later generation product (gehlenite) that precipitates at stages when fluid is highly enriched in the parent-sourced components.

Simultaneously the partial closure of the mass transfer between the bulk and interface fluid is also reflected by the evolution of the reaction products at the sample outer surface. As shown in Fig. 1b-c, plagioclase in the type I overgrowth rim becomes more porous in longer duration experiments indicating an onset of dissolution at the later stages of experiments. In addition, Table 2 demonstrates compositional change of oligoclase (pl₂) in 24 hr experiments into albite (pl₃) in 20 day experiments. This may be reflecting the shortage of Ca that was initially released in the bulk fluid from the dissolving pl₁ grains, but is now consumed in the gehlenite-forming reactions at the reaction front, leading to the dissolution-precipitation controlled replacement of the initially formed oligoclase (pl₂) grains into albite (pl₃) by the fluid that has a higher Na-content (Fig. 6c):



The generally lower ¹⁸O component in the pl₃, compared to pl₂ (Fig. 5j; prof. 1-4) may also indicate that reaction products are repeatedly reworked by dissolution-precipitation reactions after their formation. In such context, opposite ¹⁸O concentration gradient in longer experiments, showing decrease towards the sample interior may reflect the secondary re-equilibration direction where pl₂ grains formed in the reaction 2 interacts with the ¹⁸O-rich bulk fluid at the outer surface of the overgrowth rim.

4.4.2.4. Stage IV: Formation of domain III

Another process seems to take place in association with mineral boundaries and fractures. In these settings the fluid composition is affected by the interaction with minerals other than plagioclase (hornblende, biotite and epidote) producing symplectites that mainly consist of grossular and zeolite (domain III). The consistent increase in the area% of domain III and decrease in area% and continuity of domain II (Fig 1, 2 & 3) with longer durations of experiments, as well as the contacts between gehlenite and grossular grains, where grossular seemingly grows on pre-existing gehlenite grains (Fig. 3b-c), indicate that grossular in symplectite domain III may be a replacement after gehlenite (Fig. 6d) and domain III represents an evolved domain II:



The heterogeneous, patchy ^{18/16}O distribution in domain III (Fig. 5b, d-h) showing low ^{18/16}O values in grossular grains, compared to the zeolite matrix, further

support the non-contemporaneous origin of both minerals, suggesting grossular growth at the stages of reaction when fluid was highly enriched in parent-derived components. The coarser porosity in the grossular-zeolite symplectites compared to the gehlenite-zeolite symplectites (Figs 2b-d & 3b-c) suggests that the grossular-forming reactions may have involved a negative volume change or were accompanied with late dissolution along grain boundaries in the symplectite. The coarser grain sizes of grossular grains compared to the replaced gehlenite grains may indicate continuous dissolution-precipitation along the grain boundaries after the reaction 5. Sometimes small amounts of vesuvianite ($\text{Ca}_{10}\text{Mg}_2\text{Al}_4(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)_5(\text{OH})_4$) occur with grossular-zeolite symplectites near the mineral boundaries of pl₁ and biotite. The formation of vesuvianite requires magnesium that can only be sourced from biotite or hornblende in our experimental system and thus supports the argument that the boundary fluid carries components from minerals other than plagioclase.

4.4.2.5. Stage V: Formation of type II overgrowth rim

The type II overgrowths that consist of an amorphous Na-Si phase (Fig. 1a-f) is most likely a late feature, formed during quenching of the experiment.

In summary, the observed reactions in our experiments are not isochemical. The reactions involve mass transfer throughout the sample, progressive ultra-local scale evolution of the interfacial fluid composition during its interaction with the reacting parent minerals and continuous modification of initially formed reaction products by the interaction with the evolving fluid.

It is also interesting to note that although Al is often considered immobile for metasomatic mass balance reactions (Eilu et al. 2001; Rolland et al. 2003; Spruzeniece & Piazzolo 2015), the microstructural observations in this study and in similar experiments on hydrothermal replacement of feldspar minerals (Hövelmann *et al.*, 2010) suggest that it may not be true for all metasomatic systems.

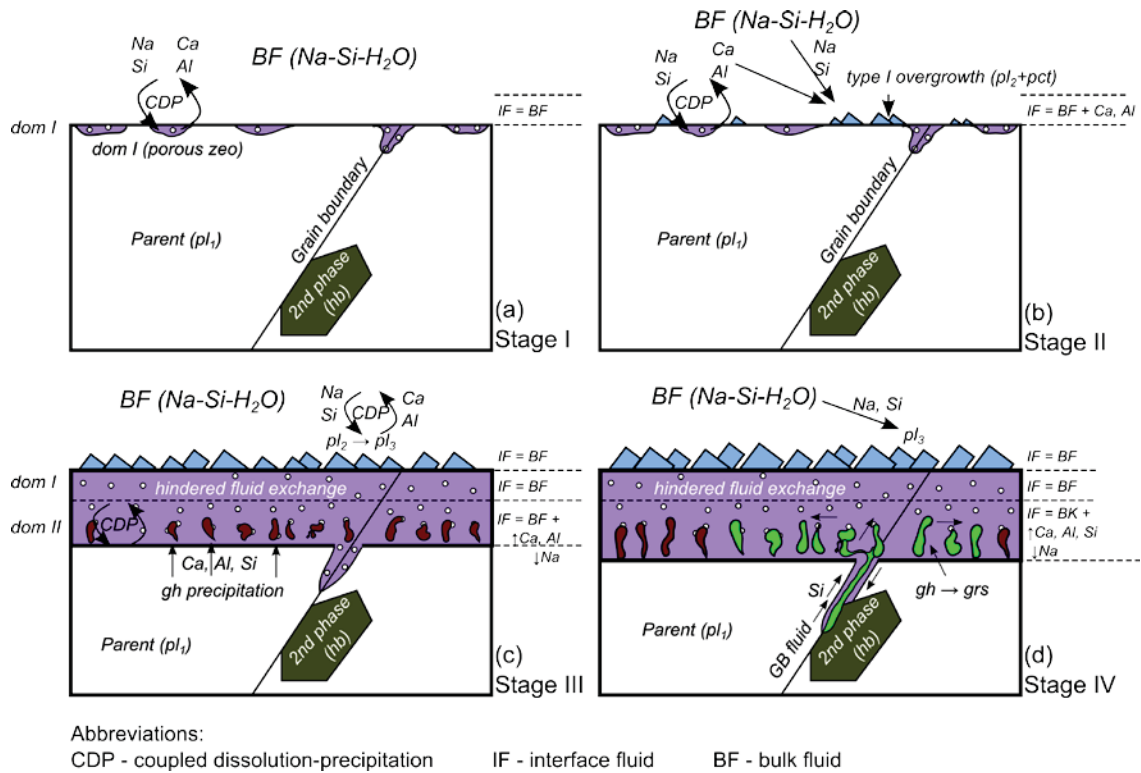


Figure 6. Interpretations of mineral reactions in the studied experimental system (see text for details). (a) formation of domain I; (b) formation of type I overgrowth; (c) formation of domain II and re-equilibration of type I overgrowth; (d) formation of domain III.

4.4.3. Conceptual model for symplectite formation by dissolution-precipitation mechanisms

We suggest that the symplectite features observed in this study and interpreted reactions in Sect. 4.2 can be further summarized into a general, conceptual model that does not depend on specific mineral assemblages or chemical properties of the reaction system. It involves two main steps:

- (1) The exposure of a parent mineral to a reactive fluid (Fig. 7a) that initiates a coupled dissolution-precipitation reaction and pseudomorphically replaces the parent grain with a porous reaction product (domain I) (Fig. 7b). The porosity in the product phase is an intrinsic feature for dissolution-precipitation controlled replacement reactions as it allows the continuation of the reaction by retaining the contact between the fluid and the reactive parent grain interface (Putnis, 2009).
- (2) The saturation of the interface fluid composition with a secondary product mineral that precipitate in the primary reaction-generated porosity of the earlier reaction product, creating a symplectite-resembling microstructure as

in domain II (Fig. 7c). One possible mechanism for such changes in fluid composition may be inhabitation of mass exchange between the bulk and interface fluids with the growth of the reaction rim, leading to the accumulation of components from the dissolving parent mineral in the interface fluid.

Further fluid movement through the rock and continued reaction may occur via a combination of reaction-generated porosity, and through the new grain boundaries in the symplectite domain. Ostwald ripening processes or continuous dissolution-precipitation near the new grain boundaries of symplectite minerals may lead to coarsening of the initial microstructure thus the final symplectite morphology do not reflect the distribution of the initial porosity and symplectite minerals. Presumably, the formation of the overgrowth rims that was observed in the experimental samples may not be essential for the development of a symplectitic microstructures. However, it may have contributed to symplectite formation in our experiments by inhibiting the component exchange between the bulk fluid and the interface fluid.

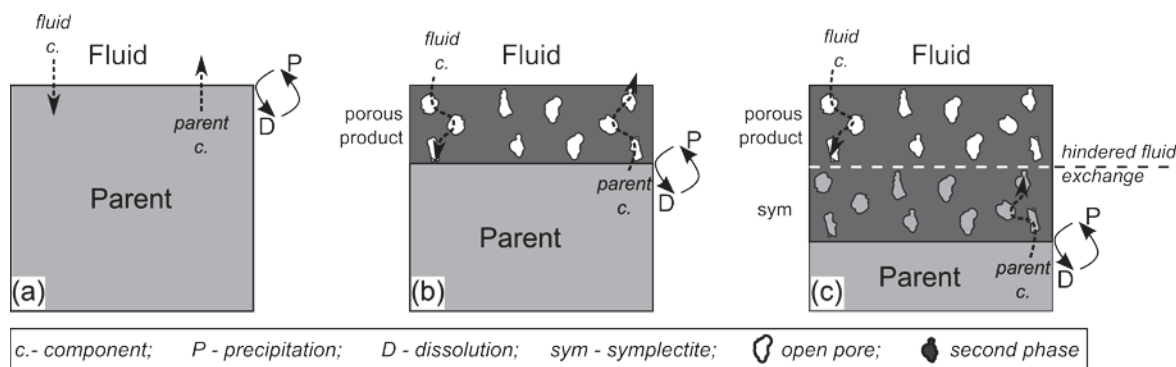


Figure 7. Conceptual model for the development of a symplectite microstructure via dissolution-precipitation mechanisms. See text for the details.

4.4.4. Experiment vs nature

When compared to natural symplectites, the symplectites obtained in this study bear a close microstructural resemblance to the kelyphitic rims found around garnet grains in lower crust and mantle settings (Dégi *et al.*, 2010; Obata, 2011). In both cases the symplectite microstructures are characterized by radial micro-to-nanometre scale intergrowth of two or more minerals that pseudomorphically replace parent grains. In both cases skeletal elongated mineral grains are enclosed in the matrix of a second mineral. The skeletal grains are often elongated perpendicular to the parent interface

but become more irregular towards the outer rim of the symplectite. Here we interpret these geometries to be a partial reflection of the mass transfer pathways, controlled by the primary porosity channels, altered by later coarsening and re-working processes. Interestingly, the elongated, subparallel shapes of the symplectite mineral grains are often observed in natural symplectite. In the context of volume diffusion mechanisms this feature is explained by faster diffusion parallel to the movement direction of the reaction front, compared to the direction perpendicular to that. Based on such assumption Obata (2011) uses the “law of normality” as a geometrical tool to reconstruct relative growth rates of a symplectite in a garnet peridotite. His results suggest significant variations in the reaction rates along different surfaces of the parent mineral and during different stages of the reaction that are difficult to explain by volume diffusion mechanisms, driven by changes in P-T conditions. In dissolution-precipitation reactions, where the reaction rates depend on fluid access to the reactive interfaces, such variations in symplectite thicknesses are expected.

Furthermore, recent studies using X-ray tomography (Morishita *et al.*, 2003) have revealed that the symplectite minerals that in two-dimensions (2D) appear as many individual grains, are interconnected in three-dimensions (3D) as complex, dendritic single grains. This explains the EBSD observation in our study (Fig. 4a-c) and also in natural symplectites (Obata and Ozawa, 2011), where groups of two-dimensionally unconnected neighbouring grains have similar crystallographic orientations indicating that they may be a part of a larger single grain in 3D. In most diffusion-dominated systems such grain shapes require large surface energy and are attributed to low nucleation rates combined with low diffusion vs growth rate. Here we propose that the formation of such large, dendritic grains could be controlled by the geometry of the interconnected reaction-generated porosity in dissolution-precipitation reactions.

Interestingly many natural kelyphites are not isochemical and occur along fractures and like-mineral boundaries, where no disequilibrium exists. Such observations strongly indicate the presence of a fluid and its involvement in the nucleation and growth of the reaction products. Furthermore, as shown by many recent studies (e.g. Wintsch & Yi 2002; Putnis & Austrheim 2010), in the presence of fluid at most crustal conditions, volume diffusion mechanisms will be outcompeted by

dissolution-precipitation mechanisms that are kinetically more efficient. The chemical gradients across symplectite domains that are occasionally used to support volume-diffusion models (Dégi *et al.*, 2010) cannot be used as conclusive evidence of reaction mechanisms as they may also be produced by dissolution-precipitation reactions (Putnis and Mezger, 2004). A diffusional chemical gradient in a parent mineral near the interface with symplectite, on the other hand, is a more convincing argument for diffusion controlled symplectite reactions.

4.5. IMPLICATIONS AND CONCLUSIONS

Our experimental data demonstrates that symplectite-resembling microstructures can be formed by fluid-mediated dissolution-precipitation reactions occurring when a rock is exposed to a reactive fluid. Although an increasing number of recent studies recognize the role of a fluid and grain boundary diffusion as factors that control the reaction kinetics and mass transfer during symplectite formation, the generation of a symplectite microstructure is still largely understood and subsequently utilised for rock history interpretations in a framework of volume diffusion mechanisms.

In this study, we suggest that the presence of a fluid may initiate different reaction mechanisms compared to fluid-absent systems and exert particular controls over the final microstructures. As a consequence, no reliable estimations of P-T conditions, diffusion distances and timescales can be drawn from such reaction products due to the heterogeneity in reaction progression and the non-isochemical nature of it. As observed in this study, symplectite microstructures can form within hours at temperatures of 600 °C in natural feldspathic samples, and the geometric properties and mineral relationships in such microstructures are strongly controlled by the relative solubilities of parent/product(s), ultra-local chemical variations in the fluid and reaction-generated porosity networks that regulate the grain size, shape and spacing in the symplectite lamellae.

It should be noted that the fluid composition used in the experiments and the resultant symplectite mineral assemblages are uncommon in nature and the performed experiments may not account for important factors in natural systems (such as differential stress, high confining pressures, variations in T and P, rock-fluid ratio, etc).

The presented experimental results also do not exclude a possibility that natural symplectites may develop by volume/grain boundary diffusion reactions alone, however, the proposed model represents one additional, possibly important scenario for developing symplectite microstructures in settings, where a reactive fluid is present.

The following characteristics observable in natural samples are indicative for the presence of a fluid during symplectite generation and therefore suggest that fluid mediated dissolution–precipitation processes with porosity generation and subsequent destruction may be responsible for the formation of symplectites. These characteristics are:

- (3) evidence of a chemically open system at a scale of the symplectite, where the symplectites are not isochemical with respect to the parent grain(s);
- (4) distinct symplectite bearing reaction rims along fractures and grain boundaries in areas where the inferred reactants cannot have been in contact with each other and elemental exchange must have involve a long-distance fluid-assisted transfer;
- (5) flat homogenous chemical profiles in parent grains lacking diffusional gradients near the interface with the symplectite;
- (6) presence of porosity in the symplectite domains;
- (7) presence of asymmetric and irregular symplectite reaction rims with varying thicknesses and discontinuities at the scale of a reaction rim surrounding one parent grain.

Interestingly, although the common occurrence of symplectites in retrogressive settings, and in cases of myrmekite, in deformed granitoids have been used to evoke models of decompression- and stress related growth mechanisms by diffusive reaction mechanisms, the same settings are also characterized by migration of metasomatic fluids. Consequently, in our view symplectite formation due to metasomatic fluid influx rather than decompression or differential stress variations may need to be considered as a viable alternative symplectite formation mechanism in these settings.

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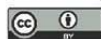
“Hell is sitting on a hot stone reading your own scientific publications”

/Erik Ursin/

CHAPTER 5

5. Strain localization in brittle-ductile shear zones: fluid abundant vs. fluid-limited conditions (and example from Wyangala area, Australia)

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Strain localization in brittle–ductile shear zones: fluid-abundant vs. fluid-limited conditions (an example from Wyangala area, Australia)

L. Spruzeniec and S. Piazzolo

Australian Research Council Centre of Excellence for Core to Crust Fluid Systems/GEMOC, Department of Earth and Planetary Sciences, Macquarie University, NSW, Sydney, Australia

Correspondence to: L. Spruzeniec (liene.spruzeniec@mq.edu.au)

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Abstract. This study focuses on physiochemical processes occurring in a brittle–ductile shear zone at both fluid-present and fluid-limited conditions. In the studied shear zone (Wyangala, SE Australia), a coarse-grained two-feldspar–quartz–biotite granite is transformed into a medium-grained orthogneiss at the shear zone margins and a fine-grained quartz–muscovite phyllonite in the central parts.

The orthogneiss displays cataclasis of feldspar and crystal-plastic deformation of quartz. Quartz accommodates most of the deformation and is extensively recrystallized, showing distinct crystallographic preferred orientation (CPO). Feldspar-to-muscovite, biotite-to-muscovite and albitization reactions occur locally at porphyroclasts' fracture surfaces and margins. However, the bulk rock composition shows very little change in respect to the wall rock composition. In contrast, in the shear zone centre quartz occurs as large, weakly deformed porphyroclasts in sizes similar to that in the wall rock, suggesting that it has undergone little deformation. Feldspars and biotite are almost completely reacted to muscovite, which is arranged in a fine-grained interconnected matrix. Muscovite-rich layers contain significant amounts of fine-grained intermixed quartz with random CPO. These domains are interpreted to have accommodated most of the strain. Bulk rock chemistry data show a significant increase in SiO₂ and depletion in NaO content compared to the wall rock composition.

We suggest that the high- and low-strain microstructures in the shear zone represent markedly different scenarios and cannot be interpreted as a simple sequential development with respect to strain. Instead, we propose that the microstructural and mineralogical changes in the shear zone centre arise from a local metasomatic alteration around a brittle precursor.

When the weaker fine-grained microstructure is established, the further flow is controlled by transient porosity created at (i) grain boundaries in fine-grained areas deforming by grain boundary sliding (GBS) and (ii) transient dilatancy sites at porphyroclast–matrix boundaries. Here a growth of secondary quartz occurs from incoming fluid, resulting in significant changes in bulk composition and eventually rheological hardening due to the precipitation-related increase in the mode and grain size of quartz. In contrast, within the shear zone margins the amount of fluid influx and associated reactions is limited; here deformation mainly proceeds by dynamic recrystallization of the igneous quartz grains.

The studied shear zone exemplifies the role of syn-deformational fluids and fluid-induced reactions on the dominance of deformation processes and subsequent contrasting rheological behaviour at micron to metre scale.

1 Introduction

The brittle–ductile transition zone (BDTZ) represents the strongest part of the Earth's crust (Kohlstedt et al., 1995), the main seismogenic layer (e.g. Sibson, 1982; Scholz, 2007), and is a major source and transport region for ore-forming fluids (e.g. Kolb et al., 2004). However, it is also the least-understood part of the continental crust, where the rheological strength estimates and assumptions of rock deformation mechanisms vary widely.

BDTZ is defined as a transitional layer between the pressure-dependent brittle rheology of the upper crust and thermally activated viscous creep in the lower crust (Handy et

al., 2007). Highly localized shear zones control deformation at this depth. The strength of BDTZ is often estimated using power-law rheology of quartz, which is the weakest and most abundant phase in granitic assemblages. Experimental data demonstrate that power-law creep in quartz can be activated at temperatures as low as 300 °C, while feldspar, being another abundant mineral in granitoids, has a high frictional strength up to temperatures of 500 °C (Passchier and Trouw, 2005).

However, in nature, brittle–ductile shear zones are often found to be altered by syn-tectonic fluids (e.g. McCaig et al., 1990; Goncalves et al., 2012; Wintsch and Yeh, 2013). The chemical and physical consequences of fluid–rock interaction have been subject of many studies demonstrating the major effects fluid has on rock rheology. Infiltration of pressurized fluid can cause brittle failure even at high confining pressures (Byerlee, 1990), allowing frictional deformation at high temperatures and low differential stresses. An increasing number of field studies recognize fluid-induced brittle precursors as the main cause for shear zone nucleation in the middle crust (Pennacchioni and Mancktelow, 2007; Fusseis and Handy, 2008; Menegon et al., 2008; Menegon and Pennacchioni, 2010; Kilian et al., 2011; Brander et al., 2012). The fluid presence in brittle–ductile shear zones is typically associated with a variety of weakening mechanisms: (1) chemical breakdown of feldspars into weak hydrous minerals (White and Knipe, 1978; Hippertt, 1998; Oliot et al., 2014); (2) reaction-controlled grain size reduction by growth of fine-grained metasomatic assemblages (White and Knipe, 1978; Kilian et al., 2011); (3) switch of the dominant deformation mechanisms from solid state power-law rheology to fluid-facilitated Newtonian flow (Menegon et al., 2008; Wintsch and Yi, 2002; Brander et al., 2012); and (4) hydrolytic weakening in minerals deforming by crystal-plastic mechanisms (Tullis and Yund, 1980; Karato et al., 1986). Based on these observations the strength of the BDTZ is suspected to be orders of magnitude lower compared to the estimates from the quartz-based rheology (Bos and Spiers, 2002; Mariani et al., 2006; Park et al., 2006; Marsh et al., 2009). However, the particular role and contribution of each weakening mechanism is still under debate.

Another incompletely understood problem is the mechanism of the generation of fluid pathways in middle crust. As pointed out by Mancktelow (2006), the fact that fluid flows into and along shear zones, rather than being expelled, requires a brittle component and local pressure drops during deformation. This conclusion has led to a concept of a dynamic porosity suspected to exist even at high lithostatic pressures. The recent work by Fusseis and collaborators (Fusseis et al., 2009; Menegon et al., 2015) highlights the importance of deformation in maintaining fluid pathways in the crust. At the same time, the study by Billia et al. (2013) provides potentially direct observations of a significant intergranular porosity within brittle–ductile shear zone fabrics, suggesting high dynamic permeability during deformation.

In many cases the difference between fluid-abundant and fluid-limited/absent conditions is difficult to assess in natural shear zones. Often only one of the two scenarios is preserved. This study takes advantage of the occurrence of fluid-facilitated and fluid-restricted deformation within the same brittle–ductile shear zone, providing the opportunity to discern the particular microstructural changes and rheological effects caused by syn-tectonic fluids. Our results demonstrate the microstructural and rheological difference in each case and reveal the interplay between the dynamics of fluid flux, deformation mechanism and strain localization within the middle crust.

2 Geological setting

2.1 Regional geology

The studied shear zone belongs to the Wyangala shear zone system, which is developed within the Wyangala batholith, situated in the Eastern Lachlan Fold belt (Fig. 1), one of the three structural regions in the Lachlan orogeny, SE Australia (Gray, 1997). The Eastern Lachlan Fold belt consists of voluminous granitic to granodioritic plutons and mafic volcanics, quartz-rich turbidites, carbonates and shales (Vandenberg and Stewart, 1992). The regional tectonic reconstructions suggest that the Lachlan orogeny formed during an accretion of a volcanic island arc along the eastern margin of Gondwana 450 to 340 Ma in a back-arc or fore-arc basin during a rifting phase in the Ordovician (Foster et al., 2009).

The Eastern Lachlan subprovince displays characteristic N–S-trending, eastward-dipping fault-thrust systems (Glen, 1992; Gray, 1997). The plutons are elongated parallel to these fault systems. Narrow contact aureoles in the host rock and undeformed margins of the plutons are considered to support a passive emplacement along pre-existing fault planes (Paterson and Tobisch, 1992; Paterson et al., 1990). The crystallization ages of the plutons in the Eastern Lachlan province are estimated from geochronological studies and show a range between 435 and 425 Ma (Lennox et al., 2005; Squire and Crawford, 2007). The recent zircon Sensitive High-Resolution Ion Microprobe (SHRIMP) U–Pb study by Lennox et al. (2014) dates the crystallization of the Wyangala granite as late Silurian (425.2 ± 3.5 Ma).

Smaller-scale shear zones overprinting the major fault system are seen along the eastern margins of the granitic plutons. These are westward-dipping, generally N–S-trending and indicate a west-over-east sense of shear (Paterson et al., 1990). The Wyangala shear zone system belongs to one such structure, located on the eastern margin of the Wyangala granite. The main shearing event for these shear zones is estimated by the Ar–Ar method using recrystallized K-feldspar (Lennox et al., 2014) to have occurred 375–365 Ma, corresponding to the late Devonian Tabberabberan deformation event.

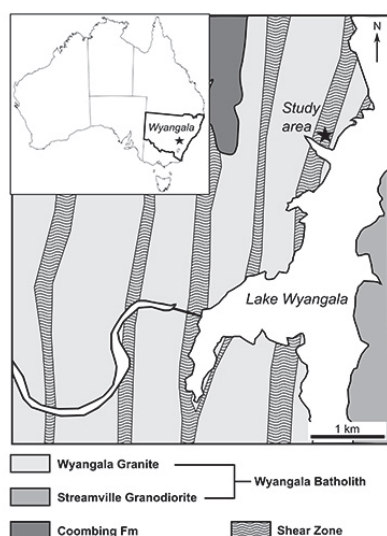


Figure 1. Locality map showing the position of Wyangala area in a regional context (inset) and the location of the studied outcrop on a simplified geological map (modified after Czarnota, 2002).

2.2 Outcrop and general sample description

The study area is located in the vicinity of Wyangala Dam about 25 km SE of Cowra, NSW (33°56.855' S and 148°57.982' E; Fig. 1). The outcrop exposes a weakly to strongly deformed granitic massif. The wall rock is a weakly foliated monzogranite with up to 8 cm large feldspar phenocrysts, quartz filling the interstices and biotite marking the incipient, discontinuous foliation planes (Fig. 2c).

Based on the structural and mineralogical properties we distinguish 2 domains within the studied shear zone: (1) orthogneiss in the shear zone margins and (2) phyllonite in the central part. The transition from the wall rock into orthogneiss occurs over a 0.5–1 m distance, characterized by a gradual decrease in grain sizes and a development of a thin-spaced, continuous foliation, defined by phyllosilicates. Feldspar grains become more fragmented towards the shear zone centre, and quartz is more and more arranged in elongated lenses or layers (Fig. 2a, c).

The boundary between the orthogneiss and phyllonite is sharp and marked by a sudden strengthening of foliation and disappearance of feldspar grains (Fig. 2a, c). The central domains display centimetre- to millimetre-scale alteration between two types of phyllonites (Fig. 2b). Phyllonite A is composed of fine, muscovite-dominated matrix surrounding large, elongated quartz grains. These large quartz grains in phyllonite A have similar sizes to quartz in the wall rock. Phyllonite B contains more quartz than phyllonite A but

has a larger matrix mode and exhibits higher phase mixing (Fig. 2c).

In total 9 samples were collected from all distinguished lithologies, representing wall rock, orthogneiss and both types of phyllonite.

3 Methods

3.1 Sample selection and preparation

Samples were cut perpendicular to the foliation (yz plane) and parallel to the stretching lineation (x axis) and polished down to $\sim 30 \mu\text{m}$ thickness for thin sections. In total 16 thin sections were prepared for detailed optical and chemical analysis. For electron backscatter diffraction (EBSD) analysis a colloidal silica–water solution (mixed in proportion 80:20) was used at the final stage of polishing for 3–5 min to reduce surface damage produced by mechanical polishing. All thin sections were carbon-coated for scanning electron microscopy (SEM) analysis.

In order to ensure comparability, all quantitative analysis, including X-ray fluorescence (XRF), EBSD, point counting and image analysis were carried out on the same 4 selected samples, representing each shear zone domain (W17 – wall rock; W13b – orthogneiss; W21b – phyllonite A; W21c – phyllonite B). Their locations are given in Fig. 2a, b.

The mineral abbreviations used in the following sections follow the recommendations of Kretz (1983).

3.2 Mineral chemistry and cathodoluminescence (CL) imaging

The chemical composition of the rock-forming minerals was determined using energy dispersive spectrometry (EDS) on a Carl Zeiss IVO SEM at the Geochemical Analysis Unit (GAU, Macquarie University), using the AzTec software from Oxford Instruments. The analytical accuracy of anhydrous phases, such as feldspars, is 0.1 to 0.2 wt%. The analyses were performed at high-vacuum conditions with an accelerating voltage of 15–20 kV, with a beam current of 5.0–10.0 nA at working distances from 12 to 12.5 mm. The same operating conditions, except for the accelerating voltage which was kept at 15 kV, were used for cathodoluminescence (CL) imaging of quartz microstructures.

3.3 Orientation analysis and data processing

Crystallographic orientation data were acquired using HKL NordlysNano high-sensitivity Electron Backscatter Diffraction (EBSD) detector and indexed with AzTec analysis software (Oxford Instruments) at the Geochemical Analysis Unit (GAU, Macquarie University). The analyses were carried out on a sample tilted to 70° angle, in high-vacuum conditions with 20 kV accelerating voltage and a beam current of 8.2 nA, at working distances from 9 to 13 mm. The typical

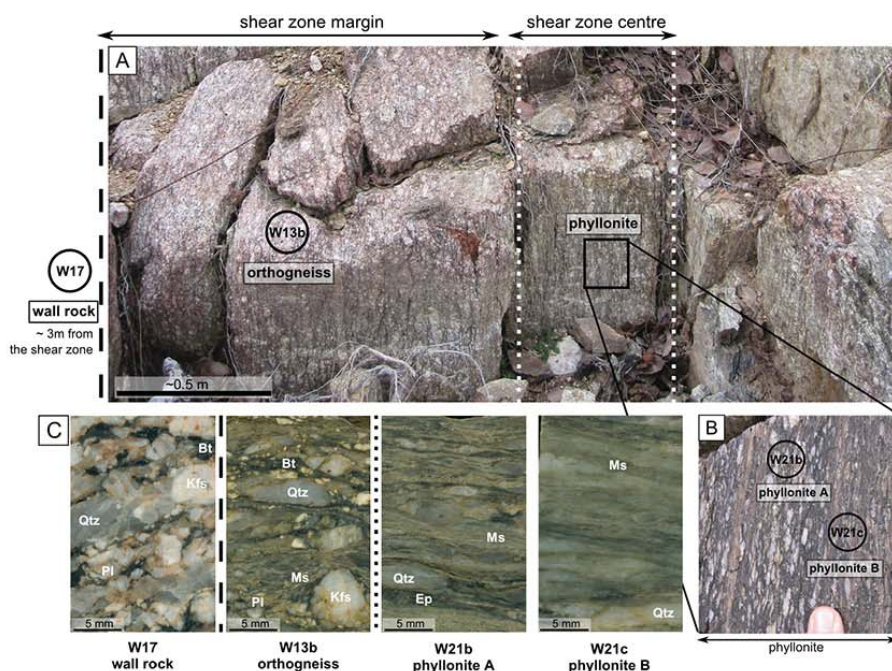


Figure 2. Outcrop and hand specimens. (a) Photo of the studied outcrop showing the different shear zone domains and collection sites of four studied representative samples (W17; W13b; W21b; W21c), which were further used for all the quantitative analysis; (b) fine-scale alternation between phyllonite A and phyllonite B in the central part of the shear zone; (c) sequence of representative samples collected in a transect across the shear zone.

step sizes ranged from 1 to 5 μm , depending on the required resolution and the average grain size in the region of interest. Simultaneously with EBSD data, EDS data were collected to assist with the phase determination during post-processing of the acquired data.

Channel 5 analysis software from HKL Technology was used for the post-acquisition processing of the stored EBSD patterns. The obtained EBSD maps contained from 5 to 26 % of non-indexed points (zero solutions), mostly resulting from the difficulty to index phyllosilicates. The map quality was first improved by a “standard” noise reduction following the procedure of Prior et al. (2002) and Bestmann and Prior (2003). The second step included the removal of “fake grains” (all grains with area smaller than a squared step size), where grains were determined by a minimum grain boundary angle of 10° and subgrains were defined by a boundary angle of $2\text{--}10^\circ$ in intra-grain regions. After the processing procedure, indexing in all maps except for one exceeded 80 % and was close to 100 % for quartz-dominated areas.

Pole figures were calculated using one point per grain, and plotted on the upper-hemisphere equal-area projections with stretching lineation parallel to the x axis and foliation normal to the z axis. All maps and data sets were rotated consistent with a dextral shear sense as determined by asymmetry of

quartz orientations. In the field it was not possible to determine shear sense unequivocally.

3.4 Modal composition

The modal amounts of mineral phases (Fig. 3a) were determined using the point-counting method for the four representative thin sections. A minimum of 1000 points for each thin section were counted. Modal amounts of quartz microstructures (Fig. 3b) were estimated on the same four thin sections using manually outlined optical micrographs and the imaging software Image J (<http://imagej.nih.gov/ij/index.html>). As one quartz microstructure (Qtz_3 ; details in the following) is very fine grained and occurs in mixtures with muscovite, it could not be quantified directly and thus was estimated by subtracting the sum of the other two quartz microstructure modes ($Qtz_1 + Qtz_2$; details in the following) from the total quartz mode determined by point counting.

3.5 Whole-rock analysis

Bulk whole-rock major-, minor- and trace-element concentrations were measured by XRF analysis for the four chosen representative samples from each shear zone domain

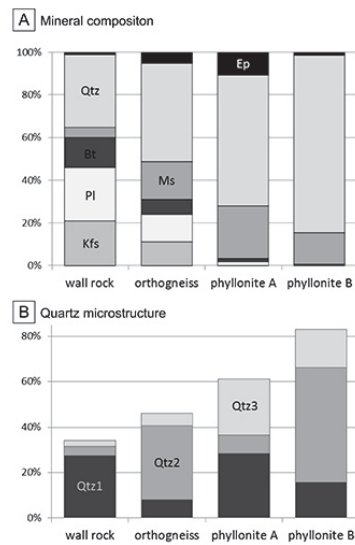


Figure 3. (a) Measured modal mineral compositions of each shear zone domain (Kfs – K-feldspar; Pl – plagioclase; Bt – biotite; Ms – muscovite; Qtz – quartz; Ep – epidote). (b) The estimated modal amounts of different quartz microstructures in each shear zone domain (see text for details).

(Fig. 2a). Samples were processed into fine powders and analysed with a PANalytical PW2400 Sequential WDXRF Spectrometer at the University of New South Wales. Obtained data sets are presented in Table A1.

3.6 Isocon method

To quantitatively evaluate the mass transfer between the shear zone domains, we used the isocon method by Grant (1986) based on the composition–volume equations proposed by Gresens (1967). It allows estimating the absolute change in the concentration for each individual oxide using the following equation:

$$\Delta M_j = \left(\left(\frac{C_i^p}{C_i^a} \right) \left(\frac{C_j^a}{C_j^p} \right) - 1 \right) \times 100, \quad (1)$$

where ΔM is the mass change in percent; (C) is concentration; superscripts (p) and (a) stand for protolith and altered sample; subscripts (i) and (j) stand for immobile and mobile elements.

The slope of the isocon ($S = (C_i^a/C_i^p)$) reflects the total mass difference between each two analysed samples. The absolute change in the total mass (in %) thus was estimated using the equation

$$\Delta M_{\text{total}} = \left(\left(\frac{1}{S} \right) - 1 \right) \times 100. \quad (2)$$

For the isocon construction and calculations we assumed the immobility of aluminium (Al_2O_3) as (i) it has been shown to be immobile during the deformation of granitoids in greenschist facies shear zones (Eilu et al., 2001; Rolland et al., 2003) and (ii) it is consistent with microstructural observations in the studied samples.

4 Results

4.1 Optical microstructures, phase abundance and mineral chemistry

4.1.1 Wall rock: weakly foliated monzogranite

The wall rock consists of 34 % quartz, 25 % plagioclase, 21 % K-feldspar, 14 % biotite, 5 % muscovite and <1 % accessory minerals (zoisite, apatite, chlorite, zircons and Fe–Ti oxides) (Fig. 3a).

The most typical quartz microstructure in the wall rock, further referred to as Qtz₁ (Fig. 3b, 4), is characterized by up to 5 mm long grains with anhedral, equidimensional or slightly elongated shapes having aspect ratios of ~1 to 1.5. Intracrystalline deformation features such as undulose extinction and deformation lamellae are common in these grains; subgrains occur occasionally. Quartz additionally occurs as fine-grained, largely monocrystalline aggregates associated with Qtz₁ grains (Fig. 4a). These microstructures are referred to in the following as Qtz₂. In the wall rock Qtz₂ constitutes only a minor amount (Fig. 3b).

Plagioclase and K-feldspar in the wall rock typically occur as 5–8 mm large, euhedral or subhedral grains, referred to as Pl₁ and Kfs₁, respectively (Fig. 4). Pl₁ displays normal compositional zoning characterized by Ca-enriched cores (ab_{59–81}) and Na-rich rims (ab_{92–94}). The cores are heavily altered to fine-grained muscovite, K-feldspar and epidote, while the rims rarely contain inclusions. Intergrown clusters of two or three Pl₁ grains are common. Euhedral Pl₁ grains occasionally occur in the interiors of larger Kfs₁ grains. All Kfs₁ (or_{96–100}) are perthitic, with albite (ab_{96–98}) lamellae covering about 20 % of the grain area (Fig. 4b, c). These grains often exhibit fragmentation and pull-apart fractures filled with fibrous or blocky quartz and biotite. The individual fragments of Kfs₁ however are not significantly displaced with respect to each other.

Biotite (Bt₁) is the dominant phyllosilicate in the wall rock assemblage (Fig. 3a) and occurs as up to 5 mm long grains (Fig. 4a). Rarely, up to 3 mm long muscovite (Ms₁) grains can also be seen in the wall rock (Fig. 4c). Typically phyllosilicates display well-developed cleavage and minor kinking and fracturing. Apatite and zircon occur as inclusions in Bt₁ grains.

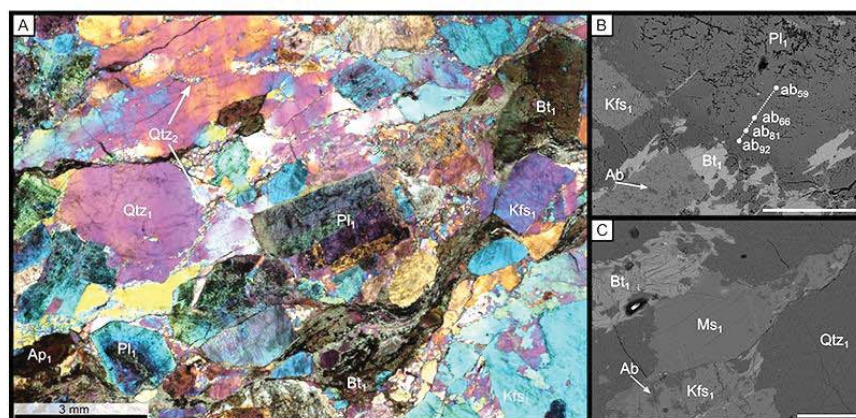


Figure 4. Typical microstructures and mineral assemblages in the wall rock; scale bar for (b)–(c) is 200 μm . (a) Optical micrograph (crossed polarizers with gypsum plate inserted) showing undulose extinction in quartz (Qtz_1), transecting Qtz_1 grains, euhedral feldspar grains (Pl_1 , Kfs_1) and Bt_1 . Arrows points to developing Qtz_2 domains, which often associate with Qtz_1 grains; (b) BSE image showing compositional zonation in plagioclase Pl_1 and albite exsolution lamellae in Kfs_1 ; (c) BSE image showing the microstructure of the igneous phyllosilicates (Bt_1 and Ms_1) characterized by large cleaved and kinked grains.

4.1.2 Shear zone margin: orthogneiss

The orthogneiss is composed of 46 % quartz, 18 % muscovite, 13 % plagioclase, 11 % K-feldspar, 7 % biotite and 5 % epidote (Fig. 3a).

Up to 70 % of quartz in this domain (Fig. 3b) is represented by the fine-grained Qtz_2 aggregates (Fig. 5a, c, f). The average sizes of Qtz_2 grains are between 15 and 25 μm ; the grains have aspect ratios of about 1.8 and display a shape-preferred orientation (SPO). Qtz_1 -type grains are rare ($\sim 8\%$ of all quartz) and commonly surrounded by mantles of Qtz_2 aggregates. Qtz_1 grains are typically up to 1 cm long, with aspect ratios between 3 and 4, and display undulose extinction, subgrains, slightly serrated boundaries and intragranular bands and patches of Qtz_2 aggregates (Fig. 5a, f). Another quartz microstructure referred to in the following as Qtz_3 can be distinguished in the orthogneiss (Fig. 3b). It is characterized by very fine grain sizes and often intermixed with fine-grained muscovite (Fig. 5a, d, e). Here, it is mainly seen in strain shadows of feldspar grains.

Both plagioclase and K-feldspar form up to about 3 mm long grains with aspect ratios of 1.5–1.8. Due to the microstructural and chemical similarity with feldspars in the wall rock, we refer to them as Pl_1 and Kfs_1 . Both, Pl_1 and Kfs_1 occur in association with fine-grained muscovite (Ms_2) mantles (Fig. 5a–c). While Pl_1 grains tend to have rounded and irregular shapes, Kfs_1 forms clusters of angular grains and display intragranular fractures, rotated fragments, bookshelf structures and pull-aparts. The fractures and strain shadows of feldspar grains are filled with a non-perthitic K-feldspar, further referred to as Kfs_2 ; fine-grained

albitic plagioclase (ab_{95-99}), referred to as Pl_2 ; fine-grained quartz (Qtz_3) and muscovite (Ms_2) mixtures (Fig. 5d, e).

Phyllosilicates in the orthogneiss are mostly represented by Ms_2 (Fig. 3a). Biotite and epidote are commonly present in the Ms_2 -rich bands but are not in direct contact with feldspar grains.

4.1.3 Shear zone centre: phyllonite A

The mineralogy of phyllonite A is dominated by quartz (62 %), muscovite (25 %) and epidote (11 %), with minor amounts of plagioclase ($\sim 1.7\%$) and biotite ($\sim 1.4\%$) (Fig. 3a).

Qtz_1 grains are larger than in the orthogneiss, approaching sizes comparable to Qtz_1 in the wall rock (Fig. 6a). They are typically elongated with aspect ratios close to 4 and length up to 8 mm. Intracrystalline deformation structures – including undulose extinction, subgrains and deformation lamellae – are common. Fine-grained aggregates of Ms_2 , Qtz_3 , Ep_2 and Pl_2 form thick layers around Qtz_1 grains. In some parts this matrix can consist of up to 70 % of very fine Qtz_3 -type grains with average grain sizes of about 5–8 μm and aspect ratios of 1.8–1.9. The tails of Qtz_1 grains commonly consist of mixtures of fibre-shaped Qtz_3 – Ms_2 (Fig. 6d).

The monomineralic, fine-grained aggregates of Qtz_2 in phyllonite A constitute only 13 % of the total quartz mode, in contrast to the high abundances in the orthogneiss (Fig. 3b). They show a similar relationship to Qtz_1 grains as in orthogneiss but do not form thick mantles.

Feldspars are represented by up to 1 mm large Na-rich (ab_{97-100}) plagioclase (Pl_2) grains (Fig. 6a, c). They are commonly surrounded by Ms_2 -rich matrix and epidote clus-

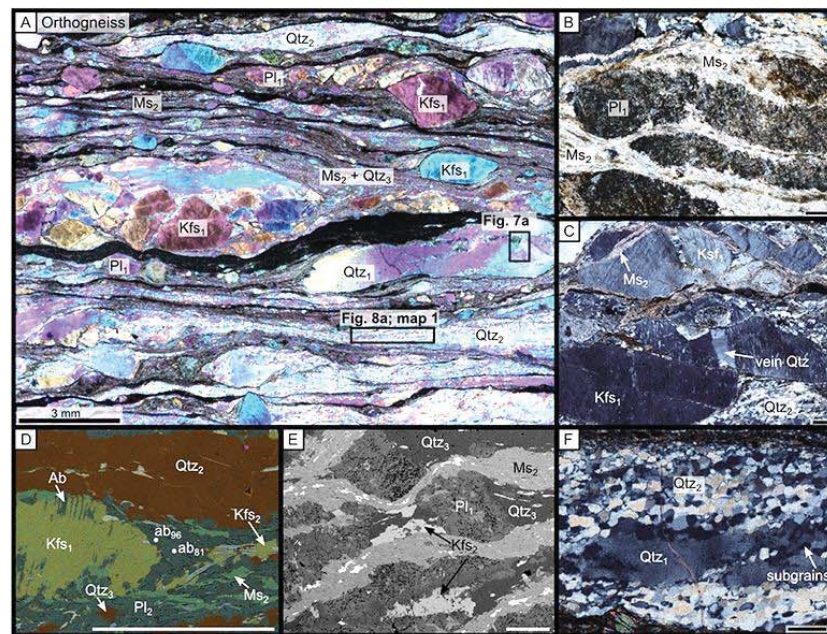


Figure 5. Typical microstructures and mineralogy in orthogneiss; scale bar for (b)–(f) is 200 μm . (a) Optical micrograph (crossed polarizers with gypsum plate inserted) showing large fractured feldspar grains (Kfs_1 and Pl_1); undulose extinction in quartz (Qtz_1); fine-grained, monomineralic domains of Qtz_2 ; and thin, muscovite-rich mantles surrounding Kfs_1 and Pl_1 . (b) Optical micrograph (crossed polarizers) showing fine-grained muscovite (Ms_2) corona around plagioclase (Pl_1). (c) Optical micrograph (crossed polarizers) showing book-shelf fractures in K-feldspar (Kfs_1) and muscovite (Ms_2) aggregates associated with fractures and grain boundaries. (d) EDX-derived compositional map showing Kfs_1 grain with albite exsolution lamellae and Pl_2 , Qtz_3 , Kfs_2 and Ms_2 in the strain shadow, where the small plagioclase grains have variable compositions typically having oligoclase cores and albite rims. (e) BSE image showing Pl_1 porphyroclasts with Qtz_3 and Kfs_2 in the strain shadows and Ms_2 forming strain caps. (f) Optical micrograph (crossed polarizers) showing Qtz_1 grain surrounded by Qtz_2 aggregates. Qtz_1 displays undulose extinction and subgrains exhibiting similar sizes to Qtz_2 grains.

ters and display well-pronounced, parallel fracture sets filled by Ms_2 . Some of the Pl_2 grains are twinned and have undulose extinction.

4.1.4 Shear zone centre: phyllonite B

Samples from phyllonite B are mainly composed of quartz (83%) and muscovite (15%), with small amounts of epidote (~1.5%), biotite (~0.3%) and minor plagioclase (~0.1%) (Fig. 3a).

The microstructure in phyllonite B consists of centimetre-to millimetre-scale alternating bands of mixed, fine-grained aggregates of Qtz_3 – Ms_2 . Variations in the modal amounts of the two phases characterize the layering (Fig. 6b, g). Ms_2 grains are typically 10–20 μm in length, aligned subparallel to the main foliation and homogeneously mixed with Qtz_3 . Muscovite-poor layers display typical Qtz_1 – Qtz_2 associations, similar to the ones in orthogneiss, with elongated up to 5 mm long Qtz_1 grains in the central parts, surrounded by mantles of the fine-grained Qtz_2 . In muscovite-rich do-

main, very fine grained Qtz_3 is homogeneously intermixed with fine-grained Ms_2 . The grain size of Qtz_3 depends on the Ms_2 amount present (Fig. 6g). It varies from 8 μm in domains with 30% muscovite to 20 μm in domains with 5% Ms_2 .

4.2 Crystallographic orientation analysis

Crystallographic preferred orientation (CPO) analysis focuses on quartz microstructure. No EBSD analysis is necessary for muscovite, where c axis is perpendicular to the elongation of the grain, and the majority of the grains display well-pronounced elongation parallel to the general foliation. Feldspars show dominantly brittle deformation; thus no specific crystallographic orientation data were sought for these. In the following, we characterize in detail the different quartz types as identified from optical analysis.

4.2.1 Qtz_1 porphyroclasts

Figure 7b shows a combined pole plot for six Qtz_1 -type grains from all deformed shear zone domains. The bulk ori-

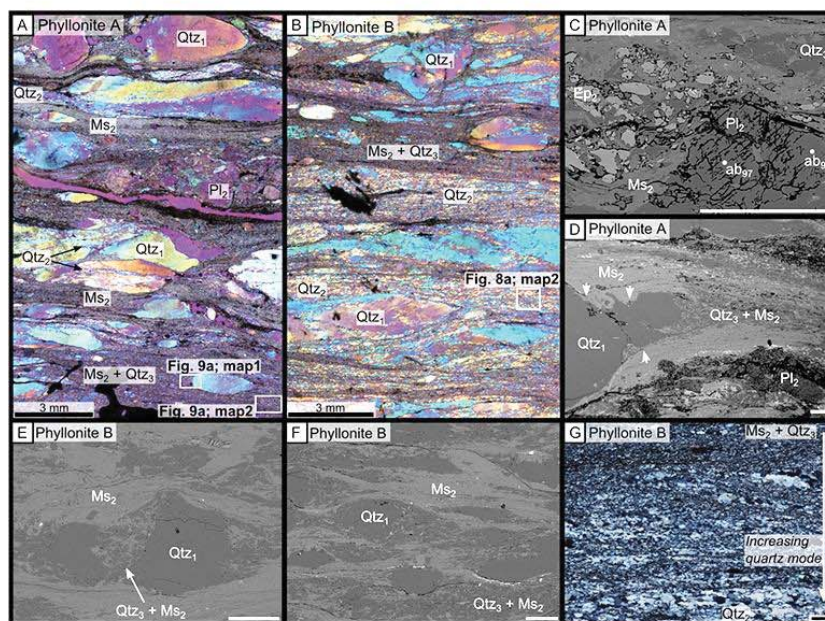


Figure 6. Typical microstructures and mineralogy in phyllonite A and B; scale bar for (b)–(g) is 200 μm . (a)–(b) Optical micrographs (crossed polarizers with gypsum plate inserted), (c)–(f) BSE images and (g) optical micrograph with crossed polarizers: (a) overview of microstructures in phyllonite A; (b) overview of microstructures in phyllonite B; (c) fractured plagioclase grain surrounded by mantle of muscovite, epidote and quartz; (d) quartz grain having irregular boundaries with muscovite (noted with arrows) and mixed quartz–muscovite layer in the strain shadow; (e) the extensional site between two Qtz₁ grains filled by mixed quartz–muscovite aggregates; (f) Qtz₁ grains in muscovite–quartz matrix, showing the tendency of monomineralic muscovite layers to occur parallel to the shear direction and quartz–muscovite mixtures to occur in the strain shadows; (g) fine-grained matrix in phyllonite B showing variations of the quartz to muscovite modal amounts on the millimetre scale.

entation of these grains is non-random, with the poles of *c* axis clustering 5–45° clockwise from *z* direction. This arrangement is consistent with the general shear sense in the analysed samples. In the second pole figure (Fig. 7b), a CPO pattern of a single strongly deformed Qtz₁ grain is presented, showing the range of internal deformation in the crystal lattice. Two *c* axis maxima appear next to the opposite poles of *z* direction, lying on the same great circle.

Internally Qtz₁ grains show a high degree of lattice distortions, with high abundance of subgrain boundaries, most of them oriented approximately at 45° angles to the foliation plane (Fig. 7a). The variations of internal misorientation across a single grain can reach more than 40° (Fig. 7c; profile 1). Dauphine twin boundaries, identified by the $60 \pm 2^\circ$ lattice rotation around the *c* axis, are common (Fig. 7a). They typically occur as irregular patches in highly deformed internal parts or along highly stressed edges of the grains.

4.2.2 Qtz₂ aggregates

Grain orientations in the fine-grained Qtz₂ domains always display a strong CPO. In the areas surrounding Qtz₁ porphy-

roclasts, the CPO of Qtz₂ grains tends to cluster close to the porphyroclast orientation, with a slight rotation towards the centre of the pole figure (Fig. 8b; map 1). In the homogeneous Qtz₂ domains, devoid of Qtz₁ grains, the CPO of Qtz₂ is arranged in an asymmetric Type Ia crossed-girdle pattern (Passchier and Trouw, 2005), subparallel to *z* direction and synthetic with the shear direction (Fig. 8b; map 2).

Subgrain and Dauphine twin boundaries are common (Fig. 8a). The variations in internal misorientation angles across single grains typically range from 2 to 4° but can reach up to 9° misorientation in the largest grains (Fig. 8c).

4.2.3 Qtz₃ in muscovite–quartz mixtures

Two associations of Qtz₃ grains were analysed in phyllonite A and phyllonite B: one from a tail of a Qtz₁-type grain, another from an interior of a fine-grained quartz–muscovite band (Figs. 6a, 9a). The crystallographic orientation of Qtz₃ grains at the tails of Qtz₁ typically cluster close to the orientation of the Qtz₁ grain (Fig. 9b; map 1). Often the Qtz₃ grains in these tails form string-like aggregates. Misorientation profiles across individual grains parallel to the elongation

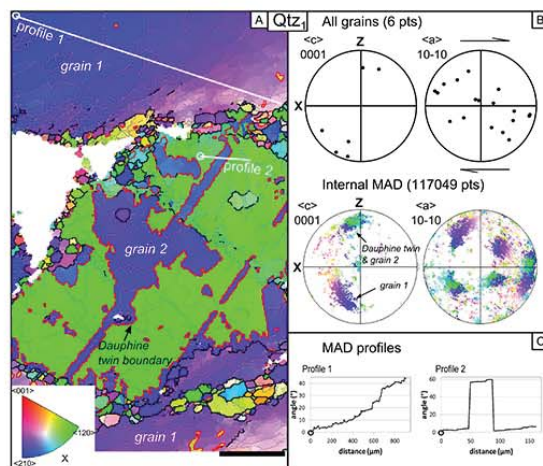


Figure 7. (a) GB (grain boundary) + IPF (inverse pole figure) map of a Qtz₁ grain from orthogneiss (acquisition location marked in Fig. 5a), scale bar 200 μm . Subgrain boundaries are marked as grey lines, grain boundaries are black and Dauphine twin boundaries are red. White pixels are non-indexed points or other phases. (b) Pole figure plots showing the crystallographic orientations of all analysed Qtz₁ grains (top) and internal misorientation angle distributions of each pixel in the map (a) (bottom). (c) Misorientation profiles across two selected regions in the map (a), where the profiles are marked with white lines and the white circle represents starting position.

gation of these “strings” do not exceed 15° between adjacent grains (Fig. 9c; profile 1).

In contrast, Qtz₃ grains in the matrix-forming Qtz–Ms bands display close-to-random CPO (Fig. 9b; map 2ii). Domains with smaller muscovite content may have similar, or slightly larger, grain sizes but show much stronger CPO than muscovite-rich domains (Fig. 9b, map 2i vs. map 2ii). Despite the small grain size (average 8 μm) the individual Qtz₃ grains display subgrains, Dauphine twinning and lattice bending, typically ranging from 1 to 3°, but angles up to 13° are not uncommon (Fig. 9c; profile 2).

4.3 Cathodoluminescence (CL) microstructures

CL pattern imaging of quartz is a commonly used, powerful technique for distinguishing multiple growth events and fluid/melt influx events in igneous (e.g. D’Lemos et al., 1997), metamorphic (e.g. Bergman and Piazzolo, 2012) and sedimentary rocks (e.g. Demars et al., 1996). Accordingly, we performed CL imaging to investigate the potential difference in patterns developed in Qtz₂ and Qtz₃ microstructure, present in the orthogneiss and phyllonite, respectively. As shown in Fig. 11, several differences can be recognized.

The quartz in the orthogneiss was analysed from the monocrystalline Qtz₂ domains, which are seen in the tails

of the recrystallizing porphyroclasts. The CL image displays a polygonal structure where the lighter central areas are enclosed by darker rims (Fig. 11a). Comparison of the CL image and EBSD map, acquired from the same area, shows that the dark rims in the CL pattern coincide mainly with grain, and in some cases subgrain, boundaries (Fig. 11b).

In phyllonite B, quartz was analysed from the fine-grained, mixed Qtz₃–Ms₂ domains. In general, the CL pattern for Qtz₃ is more intricate than that of Qtz₂. It consists of thin, lighter lines, cross-cutting darker quartz grains (Fig. 11c). These linear features do not represent any visible cracks or grain boundaries. Lighter and darker polygons are also seen adjacent to each other, and the variations in CL shading do not correspond to grain boundaries. In summary, the variations in the CL patterns of Qtz₃, in contrast to the patterns in Qtz₂, are clearly intragranular in nature (Fig. 11d, e).

4.4 Whole-rock geochemistry

Figure 10a shows that the chemical composition of the orthogneiss closely resembles the composition of the wall rock. The slope of the isocon approximates 1 and, all the major elements lie near to the isocon. Slight enrichment in CaO and depletion in Mn₃O₄, MgO, P₂O₅ and K₂O may be related to the heterogeneity of the analysed samples.

The element concentrations in phyllonite A deviate from the isocon more significantly (Fig. 10b; Table A1). SiO₂ and FeO are enriched, reflecting the increased quartz and epidote modes in phyllonite A (Fig. 3a). All the other major elements, especially Na₂O, are depleted. The major loss in Na₂O (–79%) coincides with the decrease in feldspar mode from 46% in the wall rock to 1.7% in phyllonite A (Fig. 3a). Furthermore, the isocon itself lies below the “constant mass” line (dashed line in Fig. 10), indicating a total mass increase of 12.2% compared to the wall rock domain.

Phyllonite B maintains the chemical trends displayed by phyllonite A but shows more extreme deviations from the wall rock composition (Fig. 10c; Table A1). The isocon slope of 0.29 equates to a total mass gain of 239%. Large gains in SiO₂ (+332%) concentration correspond to the increase in quartz mode from 34% in the wall rock to 83% in phyllonite B (Fig. 3a). Na₂O again shows depletion; the near-zero concentration reflects the loss of feldspars in the shear zone centre.

5 Discussion

5.1 Orthogneiss and phyllonite: same protolith, or not?

The studied shear zone displays two mineralogically and structurally different domains: (1) marginal domains containing orthogneiss, similar in composition to the wall rock, and (2) central domains with muscovite–quartz phyllonite exhibiting a significant change in bulk rock chemistry. An important question regarding the interpretation of the shear

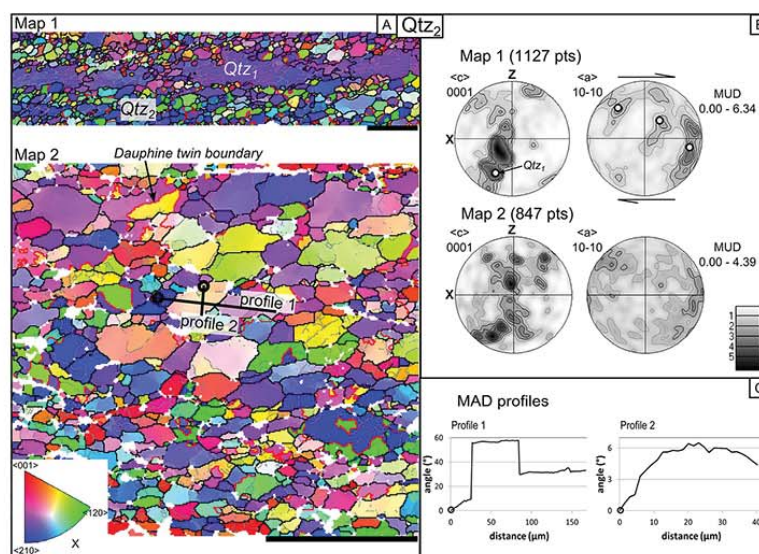


Figure 8. (a) GB (grain boundary) + IPF (inverse pole figure) map of Qtz₂ microstructures (acquisition locations marked in Figs. 5a, 6b), scale bars 200 μm. (b) Pole figures of the crystallographic orientation data for map 1 and map 2, plotted as one point per grain using equal-area projection and the upper hemisphere. The white dot in the pole figure for map 1 marks the orientation of the Qtz₁ grain, which occurs at the central part of the Qtz₂ domain. (c) Misorientation profiles across two selected regions in map 2, where the profiles are marked by black lines and the circle represents starting position.

zone microstructures is whether both of these domains originated from the same protolith, or whether they represent pre-existing heterogeneities in the wall rock, such as dykes, veins or compositional layering.

The mineralogical and chemical similarity between the orthogneiss and the wall rock, as well as the gradual microstructural and mineralogical change over a broad transition zone clearly implies a wall-rock-type protolith for the orthogneiss domains. In contrast, the origin of the central phyllonites with markedly different chemical and microstructural characteristics is more ambiguous to interpret. Two scenarios can be envisaged: (i) local alteration of the wall-rock-type protolith by a metasomatic fluid or (ii) initial heterogeneity in the wall-rock-type protolith, such as a quartz-rich vein overprinted by the mylonitic deformation. Although the quartz vein scenario cannot be completely ruled out, no direct evidence was found to support it. Phyllonite A, which is still relatively similar to the wall rock composition, does not display a sharp boundary with the quartz-enriched phyllonite B (Fig. 2b). Within the wall rock, there is no evidence of pre-mylonitic quartz veinlets. On the other hand, asymmetric reaction rims, metasomatic minerals in pressure shadows and dilational sites and syn-tectonic fracturing of porphyroclasts with associated localized but discontinuous quartz growth in extensional sites indicate the presence of a metasomatic fluid during the deformation. This, together with the consistent trends in chemical and mineralogical changes towards the

shear zone centre (Fig. 10), suggests a metasomatic, rather than a vein-derived, origin for phyllonites.

5.2 Mineral reactions and mass transfer

The metasomatic system in Wyangala shear zones bears many similarities to the alteration patterns in other fluid-affected greenschist facies shear zones, where the feldspar breakdown to phyllosilicates and albitization of feldspars is a consistent trend (Ramberg, 1949; Kerrich et al., 1980; Pryer and Robin, 1995; Hippertt, 1998; Wintsch and Yeh, 2013). The general reaction can be summarized as follows: plagioclase + K-feldspar + biotite + H₂O = muscovite + quartz + albite + epidote.

Further below, the particular reactions are interpreted from the specific mineral relationships observed in orthogneiss and phyllonites. The chemical formulas for the minerals as used in the reactions are given in Table 1.

5.2.1 Orthogneiss: reactions and local mass transfer in a closed, fluid-limited system

The mineral composition of orthogneiss differs from the wall rock by increased modes of muscovite, quartz and epidote, and decreased amounts of feldspar and biotite (Fig. 3a).

The new metasomatic muscovite (Ms₂) occurs as fine-grained aggregates, aligned subparallel to the foliation fab-

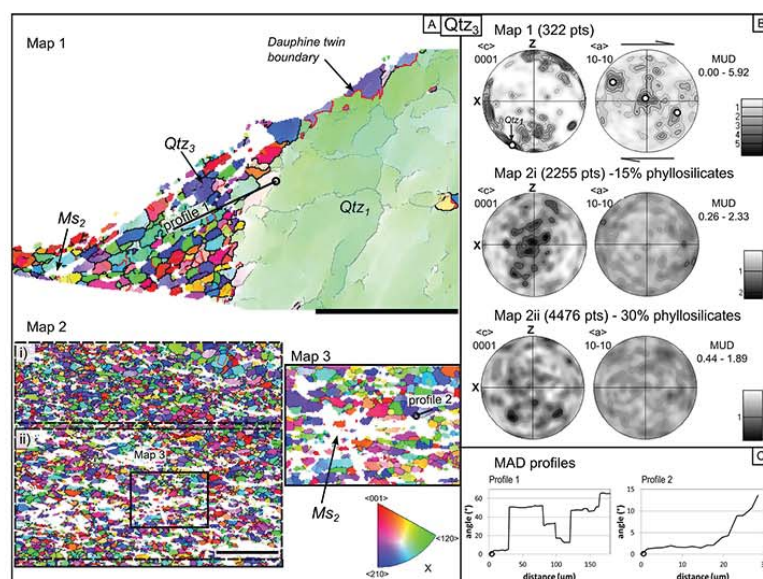
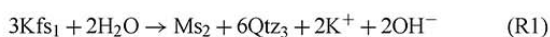
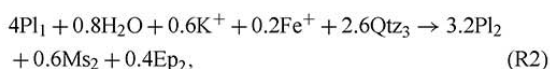


Figure 9. (a) GB (grain boundary) + IPF (inverse pole figure) map of Qtz_3 microstructures in phyllonites (acquisition locations marked in Figs. 5a, 6b). Map 2 is separated in two areas for pole figure plots. Area (i) represents quartz-rich part (15% muscovite), while area (ii) has large muscovite mode (30% muscovite). Map 3 is an enlarged image from map 2b, showing subgrain-scale microstructures; scale bars are 200 μm long. (b) Pole figures of the crystallographic orientation data for map 2(i) and map 2(ii), plotted as one point per grain using equal-area projection and the upper hemisphere. The white dot in the pole figure for map 1 marks the orientation of the Qtz_1 grain, which occurs at the central part of Qtz_2 domain. (c) Misorientation profiles across two selected regions in map 1 and map 3, where the profiles are marked by black lines and the circle represents starting position.

ric. Muscovite-rich bands often surround or cross-cut the igneous feldspars (Pl_1 and Kfs_1) and biotite (Bt_1) (Fig. 5b–e). Plagioclase, more often than K-feldspar, is surrounded by fine-grained muscovite–epidote mantles. Reactions responsible for these fabrics can be written as



and



where small amounts of pore fluid, probably provided by deformation-facilitated breakdown of igneous biotite (Bt_1) and muscovite (Ms_1) interact with the metastable igneous feldspars. As a result Kfs_1 (Reaction R1) breaks down to form muscovite (Ms_2), releasing silica and K^+ in the solution, both of which together with small amounts of Fe^+ , derived from the biotite breakdown, can be further incorporated in Reaction (R2), where igneous plagioclase of andesitic composition (Pl_1) breaks down to form albitic feldspar (Pl_2), muscovite (Ms_2) and epidote (Ep_2). Pryer and Robin (1995) described a similar multi-stage reaction sequence involved in the albitization of K-feldspar to form flame perthite.

Table 1. Abbreviations and chemical formulae for the minerals as used in the reaction equations.

Abbreviation	Mineral	Formula
Ep_2	epidote	$Ca_2Fe_{0.5}Al_{2.5}(SiO_4)_3(OH)$
Kfs_1 , Kfs_2	K-feldspar	$KAlSi_3O_8$
Ms_2	muscovite	$KAl_3Si_3O_{10}(OH)_2$
Pl_1	oligoclase	$Ca_{0.2}Na_{0.8}Al_{1.5}Si_{2.5}O_8$
Pl_2	albite	$NaAlSi_3O_8$
Qtz_3	quartz	SiO_2

The presence of intergranular fluids is necessary for the transport of the reaction components, as the parent minerals and reaction products often do not occur in a direct contact relationship. The growth of Kfs_2 in pressure shadows and extensional sites (Fig. 5d, e) especially suggests that material transport is controlled by a pressure gradient, where the nucleation of new phases preferably occurs in low-pressure dilational sites. The lack of perthite lamellae in the metasomatic Kfs_2 indicates the immiscibility of K^+ and Na^+ in the conditions of alteration. Ca content in Pl_1 promotes the formation of epidote (Ep_2). The excess Fe^+ necessary for Ep_2 production is possibly released from Bt_1 , which is also seen

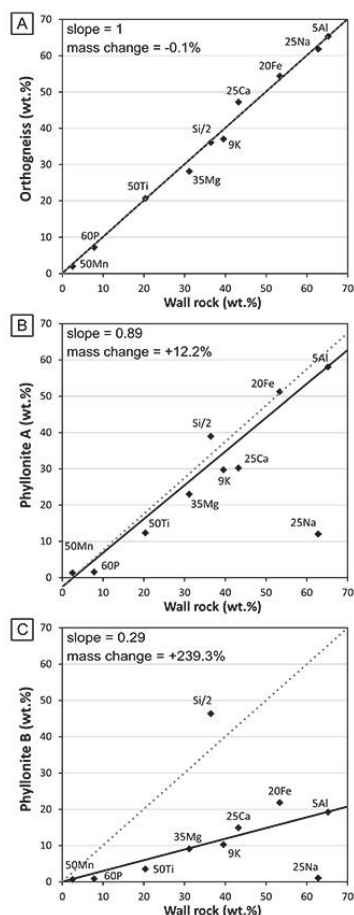


Figure 10. Isocon diagrams (Grant, 1986) showing major element concentrations for (a) orthogneiss, (b) phyllonite A and (c) phyllonite B plotted against the wall rock composition. The dashed line represents a situation of a zero mass change. The isocon (solid line) is constructed assuming immobile Al_2O_3 . Elements enriched in the altered domains lie above the isocon; the elements which are depleted lie below. Scaling factors (shown in front of each element) have been applied to avoid data clustering. The detection error is smaller than the diameter of the data points (cf. Table A2).

to break down to Ms_2 . Quartz released in Reaction (R1) is not seen to intermix with muscovite but rather precipitate in strain shadows and fractures (Fig. 5e), suggesting high mobility of silica in the circulating fluid.

Indications of Na^+ mobility in fluid come from the observations of albitic rims and veinlets associated with Kfs_1 and can be described by a simple exchange reaction:



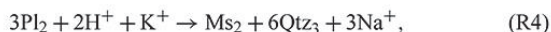
possibly governed by interface-coupled dissolution–precipitation processes (Putnis, 2009), as a fluid phase must participate in the reaction as a transport medium for Na^+ and K^+ , as they are not always available from the surrounding phases (Fig. 5d).

In summary, the microstructures in orthogneiss suggest metastability of the wall rock assemblage during the deformation. The major reactions are feldspar-to-muscovite and biotite-to-muscovite breakdown; albitization of feldspars; and growth of metasomatic K-feldspar (Kfs_2), albite (Pl_2), epidote (Ep_2) and quartz (Qtz_3), indicating a local mobility of K^+ , Na^+ , Ca^+ , Fe^+ and Si^+ . However, the bulk rock composition of orthogneiss is highly similar to the wall rock composition (Fig. 10a) excluding the possibility of a large-scale mass transfer during alteration. A minor amount of free fluid is required to enable Reactions (R1) and (R2) to occur and to facilitate the transport of the components in all described reactions. Thus, the reactions in orthogneiss are best explained by limited fluid influx and dominance of local element “recycling” in “closed-system” conditions, where mass transfer did not exceed distances of millimetres to centimetres.

5.2.2 Phyllonite A and B: reactions and mass transfer in an open, fluid-abundant system

Both phyllonites display dramatic changes in mineral and chemical composition with respect to the wall rock (Fig. 10b, c). Mineralogically, the differences include almost complete loss of K-feldspar, plagioclase and biotite, as well as increase in muscovite, quartz and epidote (Fig. 3a) content.

No igneous K-feldspar (Kfs_1) or plagioclase (Pl_1) remnants were observed in phyllonites, but the rare albite grains (Pl_2) typically associated with muscovite–quartz–epidote mantles, can either be products of the breakdown reactions of Pl_1 – with Pl_2 , Ms_2 , Ep_2 and Qtz_3 as reaction products (Reaction R2) – or a result of an arrested/incomplete breakdown of Pl_2 :



resulting in the production of muscovite (Ms_2) and quartz (Qtz_3) and the release of Na^+ in the pore fluid.

Although in some cases Reaction (R2) may be operating, Reaction (R4) is necessary to explain the eventual disappearance of albite and the general trend of Na^+ depletion indicated by the XRF data (Fig. 10b, c).

Both domains in the central part of the shear zone indicate net mass gains, mainly due to the increased Si^+ concentration. The modal analysis also shows the increase in the quartz content in both domains, suggesting external influx of Si^+ fluids. No loss of Si^+ is observed in the adjacent orthogneiss, excluding the possibility of a lateral transport.

In summary, the chemical reactions described in this section requires “open-system” conditions with an influx of external Si^+ -rich hydrous fluid, undersaturated in Na^+ .

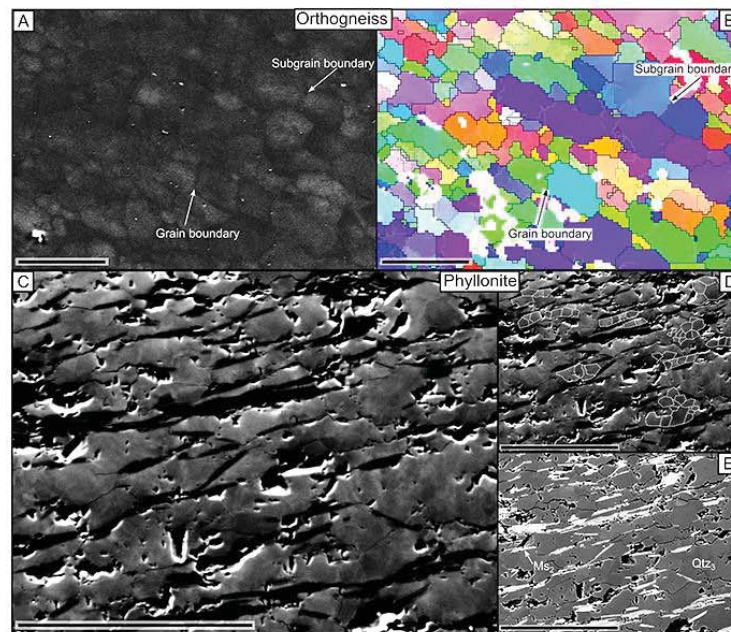


Figure 11. CL, EBSD and BSE images of quartz domains in orthogneiss and phyllonite B; scale bar is 100 μm . (a) CL patterns from a Qtz_2 domain showing a structure consisting of lighter polygons surrounded by darker rims; (b) EBSD image of (a) showing the grain and subgrain boundary network; (c) CL pattern from a Qtz_3 – Ms_2 domain showing a structure dominated by thin intragranular bright lines or polygons, bordering or surrounding darker polygons; (d) area (c) with some of the polygonal structure traced; (e) BSE image of area (c) showing mineralogy and grain boundaries.

5.3 Deformation mechanisms and strain localization

5.3.1 Shear zone margins: orthogneiss

Deformation in shear zone margins occurs mainly via crystal-plastic and cataclastic processes. Ductile deformation is concentrated in quartz, while feldspar deforms in a brittle manner.

The larger Qtz_1 grains, representing porphyroclastic remnants of the igneous quartz, show abundance of undulose extinction, deformation lamellae and subgrain boundaries, indicating the operation of dislocation creep processes (White, 1977; Poirier, 1980; Urai et al., 1986). The finer-grained Qtz_2 , often surrounding porphyroclasts (Qtz_1), has similar sizes and shapes to the subgrains, suggesting formation by subgrain rotation (SGR) recrystallization. The presence of serrated grain boundaries suggests a component of bulging (BLG) recrystallization involving low-temperature grain boundary migration (Hirth and Tullis, 1992), where bulging may have been partly facilitated by intergranular fluids (Mancktelow and Pennacchioni, 2004). CL patterns from orthogneiss domains also support the origin of Qtz_2 by dynamic recrystallization. The newly developed grain boundaries show a distinctly different CL signature (Fig. 11), con-

sistent with grain boundary generation within fluid and trace-element conditions different to that of the original igneous Qtz_1 . The fact that Qtz_2 , further interpreted as the recrystallized fraction in the orthogneiss, represents close to 70 % of the orthogneiss and forms interconnected, fine-grained layers suggests relatively low rheological strength of quartz in the particular assemblage, highlighting the significance of crystal-plastic processes in the strain accommodation.

Combined EBSD data for analysed Qtz_1 grains shows c axes oriented synthetically oblique to the shear direction. This pattern has been previously documented to occur in mid-crustal mylonites and interpreted as a selective preservation of only those grains, which are optimally oriented for a slip on basal planes (Menegon et al., 2011).

The CPO of the recrystallized Qtz_2 grains either clusters around the orientation of the adjacent porphyroclast (Fig. 8b; map 1), reflecting a “parent”-controlled misorientation relationship during a progressive subgrain rotation (Kruse et al., 2001; Stünitz et al., 2003), or, in cases when the recrystallized fraction is higher, displays a hybrid between an asymmetric single-girdle and crossed-girdle patterns (Fig. 8b; map 2), indicating slip on prism $\langle a \rangle$ and rhomb $\langle a \rangle$ crystal systems (Schmid and Casey, 1986; Law et al., 1990).

Porphyroclastic remnants of the igneous feldspar phenocrysts (Pl₁ and Kfs₁) display clusters of angular, internally fractured and slightly displaced grains (Fig. 5a, c), indicating deformation via cataclasis. The relatively small displacement between the individual fragments suggests that fracturing itself plays a minor role in the accommodation of the finite strain. The distribution of low-solubility minerals (Ms₂) at high-stress sites between porphyroclasts and perpendicular to the shortening direction in contrast to the distribution of more soluble phases (Pl₂, Qtz₃, Kfs₂) in strain shadows (Fig. 5e) suggests that mass transfer occurred dominantly by pressure solution, involving a fluid phase (Rutter, 1983; Wintsch and Yi, 2002). Accordingly, elements with higher mobility – such as Si⁴⁺, Ca²⁺, Na⁺ and K⁺ – were transported by fluid and precipitated in the locally occurring low-pressure sites, while the elements of lower mobility, in this case Al³⁺, were immediately incorporated in the Ms₂ structure, which was the new, more stable mineral phase after the dissolution of Kfs₁ and Pl₁. It is important to note that the largest displacement between feldspar fragments occurs where they are surrounded by the thickest mantles of the reaction products (Fig. 5a). This observation indicates strain partitioning from feldspars to the newly created reaction products as soon as a thick-enough mantle is formed.

5.3.2 Shear zone centre: phyllonite

Phyllonite A and phyllonite B in the shear zone core structurally display many similarities in terms of Qtz₁ and Qtz₂ microstructures. Qtz₁ grains in both domains are internally deformed and shows development of subgrain boundaries, while Qtz₂ grains have a strong CPO indicating rotation from porphyroclast orientation towards rhomb <a> and prism <a> slip systems (Fig. 8b; map 1; Schmid and Casey, 1986) with an increasing degree of recrystallization. The relatively minor fraction of the recrystallized quartz (Qtz₂) in phyllonite A suggests strong strain partitioning into the surrounding muscovite-rich matrix.

The two main differences between phyllonite A and phyllonite B domains are (1) quartz-to-muscovite ratio and (2) matrix-to-clast ratio, both of which are higher in phyllonite B (Figs. 3a, b; 6a, b).

All muscovite in both phyllonites is of metasomatic origin (Ms₂), formed either by a breakdown of igneous biotite or in feldspar reactions (Reactions R1, R2) and distributed by pressure solution processes, as Qtz₃ tends to be associated with extensional sites in strain shadows and fractures, while muscovite is concentrated in high-stress sites around porphyroclasts, subparallel to the foliation. The consistent SPO of the muscovite grains with elongation subparallel to the shear direction thus may be controlled by syn-tectonic growth in the direction of maximum elongation.

Local variations in muscovite abundance throughout the phyllonites affect the deformation behaviour of quartz. In the fine-grained muscovite-rich layers (Ms₂ = 90–30 %) quartz

occurs as Qtz₃-type grains and displays a lack of a clear CPO pattern (Fig. 9b; map 2). Qtz₃ CPO becomes increasingly weaker with increased amounts of muscovite (Fig. 9b; map 2i and map 2ii). The lack of CPO coupled with the small grain sizes and phase abundance is consistent with GBS as the main deformation mechanism (Kruse and Stünitz, 1999; Ree et al., 2005; Svahnberg and Piazzolo, 2010). The elongated grain shapes in these domains and the abundance of intracrystalline deformation features (Fig. 9a, c) suggest that grain boundary sliding was accommodated by dislocation glide (Rybacki et al., 2010; Svahnberg and Piazzolo, 2010).

A special case of Qtz₃ microstructures can be seen on the tails of larger porphyroclasts (Fig. 9a; map 1) where CPO clusters around the orientation of the adjacent porphyroclasts (Fig. 9b; map 1). This is consistent with quartz precipitation from pore fluids at low-pressure sites, where the nucleation of the new grains is host-controlled. Their elongated shape subparallel to the main foliation suggests anisotropic growth of minerals commonly reported to occur during pressure-solution processes (Passchier and Trouw, 2005).

Feldspars are rare in the phyllonite and thus play a minor role in the bulk rock rheology. The prominent fracture sets filled by fine-grained muscovite suggest mechanochemical breakdown processes. The albitic composition of Pl₂ is interpreted as a result of interface-coupled dissolution–precipitation reactions (Putnis, 2009) as indicated by arrested replacement structures in the less-altered orthogneiss, where asymmetric albite rims occur around Kfs₁ and Pl₁. Simultaneously, albite grains may also form by neo-nucleation processes from pore fluid where a chemically different composition is obtained in response to the disequilibrium state between the deformation conditions/fluid composition and igneous feldspars. This scenario has been previously suggested by Stünitz and Fitz Gerald (1993) for similar shear zones in the Wyangala area. Both of these options indicate fluid-accompanied mass transfer processes in the shear zone.

5.4 Deformation conditions

The deformation conditions within the studied shear zone are estimated from (1) syn-tectonic mineral assemblages, (2) recrystallization microstructures in quartz and (3) CPO patterns in the dynamically recrystallized quartz domains.

The observed reactions (Sect. 5.2) – such as the breakdown of feldspars and biotite to muscovite, albitization of K-feldspar and plagioclase, and formation of epidote – commonly occur in many middle crustal shear zones, deformed at greenschist facies conditions (Hippertt, 1998; e.g. Kerrich et al., 1980; Park et al., 2006). In combination with the brittle–ductile rheology expected at middle crustal depths, this gives the first indication of the deformation conditions.

More accurate temperature ranges can be obtained by analysing deformation microstructures in quartz. Microstructural features – such as undulose extinction, subgrain development, bulged grain boundaries and CPO patterns in

the quartz-rich domains – indicate the operation of crystal-plastic processes (Hirth and Tullis, 1992; Stipp et al., 2002). Crystal plasticity in quartz occurs by one of the three mechanisms: bulging (BLG), subgrain rotation (SGR) or high-temperature grain boundary migration. Which one of these is the most dominant largely depends on temperature. In our samples, SGR is the dominant recrystallization regime in quartz. The lobate grain boundaries observed for the recrystallized quartz grains indicate a minor component of grain boundary migration typical of the BLG recrystallization regime. In nature, the transition from BLG to SGR is found to occur at temperatures between 350 and 400 °C (Stipp et al., 2002). However, bulging-type microstructures in quartz have been reported to form as a result of post-deformational activity of grain boundary fluids (Mancktelow and Pennacchioni, 2004). This imposes some uncertainty on the lower temperature constraint.

Quartz CPO pattern therefore is a better indicator for deformation temperatures, as it does not strongly depend on the absence or presence of fluid (Mancktelow and Pennacchioni, 2004). Our samples show CPO patterns characterized by a combination of basal and prism slip (Fig. 8b; corresponding to temperatures between 300 and 400 °C; Schmid and Casey, 1986). Other authors interpret similar patterns as being indicative of deformation at temperatures close to 400 °C (Stipp et al., 2002; Lee et al., 2012). The latter temperature range is supported by the observations of frequent Dauphine twins, which in quartz form in temperatures between 300 and 400 °C (Wenk et al., 2007; Menegon et al., 2011).

There are no direct indicators for the confining pressure; however, an approximate estimate based on the obtained temperature range (300 to 400 °C), can be drawn using an assumption of a normal geothermal gradient (30 °C km⁻¹). Assuming the average density of continental crust (2.8 g cm⁻³), depths of 11 and 13 km and pressures between 3.02 and 3.57 kbar can be obtained.

5.5 Model for shear zone development

In this section we discuss a conceptual model for the development of the studied brittle–ductile shear zone. It is important to note that, although feldspar-to-muscovite reactions in the shear zone centre indicate softening and thus shear zone narrowing, the strain gradient in the studied shear zone does not represent a progressive fabric evolution with time as would be expected for an ideal Type II shear zone (Means, 1995). As we further discuss, the shear zone margins and shear zone centre experienced vastly different geological and fluid history due to a brittle precursor. A hypothetical example of such a case has been theoretically investigated by Means (1995), demonstrating how the deformation can proceed by different scenarios inside and outside the initial zone of cataclasis even when the late fabrics across the strain gradient show an apparently progressive evolution.

Here we propose a three-stage temporal development of the studied shear zone, distinguishing between two cases, representing different domains, namely case I – the shear zone margins – and case 2: the central domains (Fig. 11).

5.5.1 Stage 1: localized cataclasis

We suggest that the first stage of the deformation was marked by high effective stresses and fluid pressures leading to brittle failure and formation of a cataclastic fracture zone in the granitic protolith (Fig. 12a). This interpretation is based on the observation of the abundance of the large, only weakly deformed quartz porphyroclasts, in phyllonite A (Fig. 6a). If shear localization had initiated through crystal plasticity, then quartz would be highly recrystallized as seen in the orthogneiss (Fig. 5a). The preservation of the Qtz₁ grains can only be possible if the weak matrix of reaction products in the central parts of the shear zone is created early in the deformation history and partitions most of the strain before any significant recrystallization of quartz takes place.

5.5.2 Stage 2: ductile deformation

Stage 2 is marked by ductile deformation in response to the initial cataclastic stage. Brittle failure (stage 1) resulted in a localized zone of interconnected fault-fracture mesh as described by Sibson (1996). The opening in brittle fractures and dilatancy-related pressure fluctuations around the fractures facilitated and localized the infiltration of external fluids. Subsequent microstructural development and rheology in the shear zone was mainly controlled by its proximity to this initial fracture zone. The sharp boundary separating the orthogneiss and phyllonites is interpreted to represent the extent of the initial cataclastic damage zone affected by high fluid fluxes, and the largely intact crystalline wall rock with restricted pathways for fluid infiltration (Fig. 12a, b). This distinction is also reflected in differences in phase distribution (Fig. 3a), microstructures (Figs. 3b, 4, 5) and whole-rock chemistry (Fig. 10).

Case I in Fig. 12b represents deformation at fluid-limited conditions in the shear zone margins, outside the initial cataclastic zone (Fig. 12b). Syn-tectonic retrograde reactions of igneous biotite (Bt₁) and muscovite (Ms₁) provide pore fluid which migrates along fractures and grain boundaries, facilitating microcracking, pressure-solution processes and mineral reactions to weak fine-grained polycrystalline phases (Fig. 5).

The majority of igneous quartz grains behave as a weak phase, developing subgrain and new grain boundaries through a progressive distortion of the crystal lattice. Up to 70 % of the igneous quartz recrystallizes into fine-grained interconnected aggregates, accommodating most of the strain by dislocation creep processes, a typical deformation behaviour for monomineralic quartz domains (Obée and White, 1985; Fliervoet and White, 1995). Simultaneously, the ig-

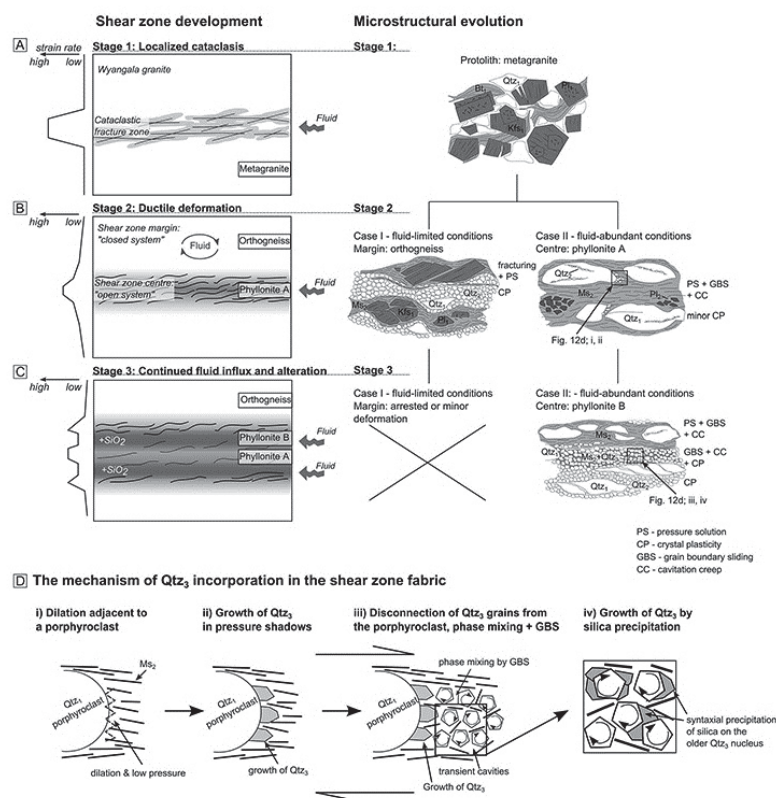


Figure 12. (a–c) Schematic illustration of the temporal (stages) and spatial (cases) fabric development of the studied shear zone; (d) the proposed mechanism for Qtz₃ incorporation in the shear zone fabrics. Refer to the text for details.

neous feldspar phenocrysts undergo fragmentation by brittle failure (Fig. 5). CL patterns seen in the dynamically recrystallized Qtz₂ in the orthogneiss (Fig. 11a, b) are consistent with the presented scenario. The dark grain and subgrain boundaries indicate that recrystallization occurred at fluid conditions different to the original igneous conditions. The fact that the grain boundaries are dark is consistent with a syn-tectonic fluid containing CL signal suppressing trace elements such as Ti or Al (Rusk et al., 2008; Bestmann and Pennacchioni, 2015). However the limited amount of fluid available from the local reservoirs, and possibly the slow rates of its release, do not permit rapid weakening to take place. Consequently, strain localization is limited and deformation occurs throughout the rock.

Case II (Fig. 12b) represents deformation at fluid-abundant conditions in the shear zone centre. Here we assume that fabrics in phyllonite A is an early stage in the evolution of the central shear zone domains. This assumption is based on the fact that mineralogically and chemically phyllonite A is closer to the wall rock composition than to phyllonite B

(Fig. 10b, c). In the shear zone centre, the cataclastic protolith provides easy fluid pathways, and the dilatational low-pressure sites facilitate the infiltration of external fluids, leading to widespread and rapid mineral reactions of the metastable igneous wall rock assemblage. As a result, the load-bearing feldspar framework is rapidly destroyed and the newly produced matrix of fine-grained reaction products localizes the strain. The deformation is mainly accommodated by pressure solution processes and reaction creep in the fine-grained matrix of the reaction products. As proposed by Wintsch and Yi (2002), pressure-solution-controlled reactions can be an efficient deformation mechanism in middle crust due to the low activation energy required, leading to significant shape and volume changes even at low differential stresses (Wintsch and Yi, 2002). Consequently, the fraction of dynamically recrystallized quartz in phyllonite A is small and the remnant quartz porphyroclasts preserve sizes similar to the igneous grains in the wall rock (Fig. 6a).

5.5.3 Stage 3: Continued fluid influx and alteration

Phyllonite B represents phyllonite A fabric, modified by a prolonged fluid percolation (Fig. 12c). The chemical and mineral evidence of SiO_2 gains in the phyllonites (Figs. 3a, 10c) indicates that a significant amount of quartz is incorporated during the deformation. We suggest that this “new” quartz has been added in the phyllonite B microstructure through local precipitation from a pore fluid in transient dilatational sites, similar to the creep cavitation process described by Fusses et al. (2009) and Menegon et al. (2015). The first stages of the silicification may be related to stress and strain heterogeneities in the vicinity of porphyroclasts. As seen in phyllonite A, the initial matrix, resulting from the feldspar and biotite breakdown reactions, contains little quartz. However, the mixed fine-grained Qtz_3 – Ms_2 aggregates typically occur in the strain shadows of Qtz_1 and feldspar porphyroclasts, where the rheologic contrast between the rigid clasts and the soft matrix is high, promoting dilation (Passchier and Trouw, 2005; Mamtani et al., 2011). Low pressures in the dilatational voids attract pore fluids and enable the precipitation of material from the super-saturated fluids (Fig. 12di). Initially the growth of the new material occurs on the surface of Qtz_1 porphyroclasts, as seen by the related CPO patterns of the adjacent Qtz_3 grains (Fig. 9a, b; map 1; Fig. 12dii). With increasing length of these “tails” and “necks”, Qtz_3 grains become disconnected from the porphyroclasts (Fig. 12diii) and, due to the fine grain sizes, transit toward the deformation by GBS, as is indicated by the random CPO patterns (Fliervoet et al., 1997) (Fig. 9a, b; map 2ii). The further fluid flow (Závada et al., 2007; Rybacki et al., 2008) and silicification is then localized in these fine-grained quartz–muscovite layers by cavitation creep mechanisms. When a cavity is created next to an existing quartz grain, the nucleation of new silica will occur syntactically due to kinetic advantages in inheriting the crystallographic orientation (Fig. 12div). Some of the subgrain boundaries observed in Qtz_3 grains (Fig. 9a; map 3) thus may reflect separate events of silica precipitation, rather than dynamic recrystallization in Qtz_3 . As a result the individual grains will increase in size and the interparticle spacing of the second phases (Ms_2) will also increase, leading to the development of quartz- instead of muscovite-dominated polyphase layers. CL signature of Qtz_3 grains in these polyphase layers is distinctively different from the dynamically recrystallized Qtz_2 in the orthogneiss (Fig. 11), often displaying intricate internal patterns consisting of lighter and darker domains and lines. As the CL signal in quartz is shown to correlate with Ti content and other trace elements (Rusk et al., 2008), we suggest that these patterns reflect continuous precipitation of silica from a slightly changing intergranular fluid.

The Qtz_3 grain coarsening may continue until the increasing grain sizes and quartz mode lead to the switch to dislocation creep mechanisms within the fine-grained material. The resulting drop in strain rates by switching from GBS deformation to dislocation creep will arrest or greatly decrease the porosity generation (i) within the fine-grained material itself and (ii) at porphyroclast–matrix boundaries, leading to the hardening of the phyllonite B domain. In this case, the resulting microstructure displays CPO and resembles Qtz_2 layers, attributed to the origin by dynamic recrystallization. This interpretation is supported by the fact that the “reaction” quartz (Qtz_3) cannot account for all the increase in quartz mode in phyllonite B compared to the wall rock (Fig. 3b), and thus at least part of the Qtz_2 microstructure must also have an external origin.

We suggest that the shear zone may be abandoned completely once it becomes rheologically hard, leading to the activation of a new fracture in the adjacent host rock. This could happen when the rock deforms dominantly by dislocation creep and not cavitation creep due to fluid flux and cavitation-creep-related increase in quartz grain size and abundance.

6 Conclusions

The studied shear zone represents an example of a brittle–ductile deformation in the middle crust accompanied by circulating syn-deformational fluids. The fluid flow was highly localized in narrow central parts of the shear zone due to a cataclastic precursor and rapid metasomatic reactions, which created necessary porosity for fluid infiltration. As a result two structurally and chemically different domains developed across the shear zone, depending on the availability of the fluid. The “fluid-limited” shear zone margins experienced little effect of chemical processes during the deformation, preserving the granitic assemblages similar to the wall rock and deforming mainly by crystal-plastic processes in quartz. In contrast, the “wet” shear zone centre experienced extreme chemical alteration, rapid reduction in grain sizes by chemical breakdown reactions and a development of interconnected foliation partitioning the strain. The fine grain sizes further enabled fluid infiltration and creep cavitation coupled with grain boundary sliding in the highly anisotropic reaction fabric. Consequently, circulating pore fluids led to further alteration of the shear zone fabric and rheology by mineral reactions, mass transfer and incorporation of significant amounts of “external” quartz.

In summary, the existence of an initial brittle fracture system facilitated enhanced fluid flow, rapid reaction and subsequent phase mixing. This then enabled strain localization and focussed fluid flow due to creep cavitation and associated fluid pumping.

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6. Discussion

In the following, the main findings of this thesis are synthesized and discussed in the larger context of natural geological systems.

6.1. FLUID COMPOSITION AND THE MINERALOGY OF REACTION PRODUCTS

While it is well known that crustal fluid can be represented by a variety of chemical compositions (Yardley and Bodnar, 2014), the evolution of the fluid composition during its interaction with a rock is not well understood. With some exceptions (e.g. Kusebauch et al., 2015), many studies in natural systems assume that fluid retains constant chemical properties during a single interaction with a rock. As a result, any indication of changes in fluid composition are often interpreted as a new metasomatic event, associated with new infiltration of external fluids.

However, the experiments presented in this thesis shows that single-fluid systems can simultaneously produce a range of compositionally heterogeneous reaction products, characterized by chemical gradients (Chapter 2) or co-existence of different mineral associations (Chapter 3 and 4). As temperature and pressure conditions in these experiments were kept constant in all studies, such microstructures suggest that the fluid underwent compositional evolution during the progression of the reaction. This is the case even at nominally high fluid-rock ratios, where the dissolution of the parent samples should not have a significant effect on the bulk fluid composition. This has been shown in previous studies of coupled dissolution-precipitation reactions (Borg et al., 2014; Putnis et al., 2005) to result from ultra-local chemical evolution of a thin fluid layer at the reaction interface, that interacts with the dissolving parent and can compositionally differ from the bulk fluid. Chapter 4 demonstrates that in more complex polymineralic materials, the fluid can simultaneously attain a different chemical state at several interfaces, such as the reaction front, sample surface and phase boundaries, producing highly complex reaction products. Similarly, the two mineralogically different reaction products (apatite and whitlockite) observed after the

replacement of calcite (Chapter 3) are both formed from the same bulk fluid, at the same P-T conditions, but also involve local heterogeneity in the fluid composition, either spatially or temporally.

6.2. FLUID COMPOSITION AND THE MICROSTRUCTURE OF THE REACTION PRODUCTS

In all experimental studies, it is possible to observe a strong connection between the chemical state of the reaction fluid and the microstructure of the reaction products. It has been discussed in earlier studies that the crystallographic relationship between parents and products of fluid-mediated replacement depends on the coupling between dissolution and precipitation processes at the reaction interface (Putnis, 2009, 2002; Xia et al., 2009a). Xia et al. (2009a) was the first study to experimentally demonstrate that the relative kinetics of dissolution versus precipitation and thus, the crystallographic relationship between the parent and product can be modified by varying pH of the fluid. In this thesis the microstructures of such reaction products are characterized to a subgrain-scale, revealing that overall pseudomorphic and epitaxial replacement can still create highly complex intracrystalline features. Reaction-generated low angle grain boundaries and crystal lattice distortions were observed in KCl replacing KBr (Chapter 2), whitlockite and apatite replacing calcite (Chapter 3) and albite replacing bytownite (Chapter 4). The observations from the KCl-KBr system (Chapter 2) suggest that such lattice distortions often correspond to local protrusions in the reaction front that represent slightly higher reaction rates. That is again an ultra-local feature, but represents variations in the reaction kinetics, and possibly, interface fluid composition that is further recorded in the reaction microstructure. The presence of such reaction-generated low-angle boundaries in all performed replacement experiments, suggest that they may be a common outcome of fluid-mediated mineral reactions, and therefore expected in natural metasomatic settings. Such a reaction-related origin for microstructural defects in minerals are rarely considered for the interpretations of natural samples. However it may closely resemble microstructures produced by crystal-plastic deformation (Chapter 2) and lead to misinterpretation of the rock record.

Furthermore, the study in Chapter 3 demonstrates that more significant variations in the reaction fluid chemistry can also lead to a very different progression of the mineral reactions, even when the product assemblages formed during these reactions are similar. The likely factor controlling the variation in the microstructure is, again, the relative difference between the kinetics of dissolution, transport and precipitation processes that is affected by the chemical state of the fluid-rock system. The reaction microstructure therefore can contain information of the fluid chemistry that is often an uncertain parameter in natural systems.

6.3. THE FLUID PATHWAYS IN A ROCK

Fluid pathways either depend on existing microstructural features in a rock or can be produced during fluid-rock interaction. It is important to note that the reaction pathways in a rock may not fully represent fluid pathways. If a fluid is in chemical equilibrium with the percolated mineral assemblage, it can pass through a rock without leaving much evidence. The flow of a non-reactive fluid will be most likely be controlled by grain boundary- and fracture networks; or in case of high pore-fluid pressures new pathways can be generated by local stress variations causing hydraulic fracturing or dilatational granular flow (Chapter 5). The reactive fluids, on the other hand can generate pathways by reaction-assisted fracturing (Jamtveit et al., 2000) or porosity (Putnis et al., 2005) due to the relative solubility- and volume differences between the parent and product phases. Reaction-generated porosity is the only type of pathway that allows pervasive fluid percolation through a rock and completion of any replacement reactions (Putnis, 2002). This porosity can be modified by a fluid composition, as it was observed in Chapter 3. Interestingly, it is also observed that at specific fluid compositions the crystallographic orientation of the parent grains may become important in the replacement process, possibly related with higher dissolution rates at specific crystal faces that can facilitate fluid movement through the rock (Chapter 3).

The above findings have several important implications for the recognition of past fluid pathways in a rock. Observations of limited reactions products within a rock, does not necessarily mean that there was limited fluid, limited time of exposure to a fluid and low fluid-rock ratio. The amount of reaction products formed is highly

dependent on the pathways allowing a reactive fluid to be transported and get in contact with the reactive rock interface. If the replacement reaction does not produce a high porosity itself, the new product phases effectively amour the interface and thus no further reaction can occur except different fluid pathways are exploited (e.g. grain boundaries) (Chapter 3).

6.4. FLUID ROCK INTERACTION AND ITS RELATIONSHIP TO DEFORMATION

The influence of deformation on the character, rate and microstructures produced by fluid mediated reactions has to be considered in the light of two endmember scenarios. Scenario I is when a deformed rock, subsequent to deformation is subjected to a reactive external fluid. Here, the microstructures such as the grain boundary network can, but do not have to have a significant effect on reaction progression. Scenario II is when deformation and fluid influx are directly related both in space and time.

The study, presented in Chapter 5 demonstrates that shear zone development at a presence of a reactive fluid cannot be modelled or predicted by classic kinetic, thermodynamic and rheological laws. The fluid-mediated mineral reactions and associated physical feedbacks do not only enhance the kinetics of deformation but completely transform the process of microstructural and chemical development in the shear zone, as suggested by the evidence of separate evolutionary paths between the parts of the shear zone that were exposed to low or high amounts of the fluid.

Future work involving experiments in dynamic systems may reveal more about the relative importance of specific parameters that are involved in fluid-rock interaction during deformation.

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7. Conclusions

- Fluid-rock interaction is a physio-chemical process that controls and is controlled by both, mineralogical and microstructural characteristics of a rock.
- The fluid undergoes continuous chemical evolution during its interaction with a rock, often on an ultra-local scale. As a result single fluid-rock interaction event can produce highly complex reaction products.
- The microstructures produced in fluid-mediated replacement reactions depends on the system kinetics, particularly the relative rates of dissolution, transport and precipitation.
- Even small differences in a fluid composition significantly affect the use of a rock microstructure for the progression of a reaction as well, as the microstructures generated during fluid-rock interaction. The ultra-local scale evolution in the fluid chemistry during its interaction with a rock may lead to a diversity of microstructures in the same metasomatic event, even if the bulk fluid composition remains the same.
- The fluid is more than just a kinetic agent in mineral reactions and deformation. The chemical and physical processes in a rock in the presence of fluid proceed by fundamentally different mechanisms, compared with the rock that do not interact with a fluid.

At the current stage, when good theories of the fundamental mechanisms, governing fluid-mediated mineral reactions and deformation mechanisms exist, it is beneficial to take the next step and transition to more complex experimental systems that incorporate the effects of grain boundaries, secondary minerals and deformation. The way how these microstructural/mineralogical factors affect rock interaction with a fluid may not be always directly projected to the field-scale from experiments with simple systems.

Appendix A

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Appendix A

Table A1. Whole-rock geochemical data. Major element concentrations and mass balance calculations of the selected samples from wall rock, orthogneiss, phyllonite A and phyllonite B. Detection error for the measurements is given in Table A1.

Sample location	Measured concentrations (wt%)				Scaling factor	As plotted in isocon diagrams (wt%)				Mass change rel. to Al ₂ O ₃ (Eq. 1) (%)		
	W17 wall	W13b orthogneiss	W21b phyllonite A	W21c phyllonite B		W17 wall	W13b orthogneiss	W21b phyllonite A	W21c phyllonite B	W13b orthogneiss	W21b phyllonite A	W21c phyllonite B
Na ₂ O	2.51	2.47	0.48	0.04	25	62.80	61.85	12.03	1.03	−1.62	−78.51	−94.46
MgO	0.89	0.80	0.66	0.26	35	31.15	28.11	23.00	9.10	−9.87	−17.14	−0.89
Al ₂ O ₃	13.04	13.05	11.62	3.84	5	65.19	65.26	58.08	19.22	0.00	0.00	0.00
SiO ₂	72.89	72.13	77.94	92.75	1	36.45	36.07	38.97	46.37	−1.15	20.01	331.66
P ₂ O ₅	0.13	0.12	0.03	0.01	60	7.80	7.20	1.56	0.84	−7.79	−77.55	−63.46
K ₂ O	4.39	4.11	3.30	1.14	9	39.55	37.03	29.74	10.27	−6.47	−15.60	−11.90
CaO	1.73	1.89	1.21	0.60	25	43.23	47.20	30.23	14.90	9.08	−21.52	16.95
TiO ₂	0.41	0.41	0.25	0.07	50	20.40	20.65	12.35	3.55	1.12	−32.05	−40.96
Mn ₃ O ₄ *	0.05	0.04	0.03	0.01	50	2.50	1.95	1.30	0.65	−22.08	−41.63	−11.79
Fe ₂ O ₃	2.67	2.72	2.56	1.09	20	53.38	54.40	51.24	21.86	1.80	7.74	38.94
Sum	98.71	97.75	98.07	99.82						−1.08	11.50	243.06
LOI (cal c)	1.29	2.25	1.94	0.18						74.40	68.76	−51.76
LOI (meas)	0.95	1.18	2.13	0.63						24.08	151.66	124.99
Total	99.66	98.93	100.20	100.45						−0.84	12.84	241.94
Total mass change (Eq. 2)										−0.11	12.24	239.27

* By the procedure at Mark Wainwright UNSW analytical centre manganese is measured as Mn₃O₄.**Table A2.** Absolute and relative error for the whole-rock chemical data.

Major element (wt %)	Absolute error (wt %)	Relative error (%)
90	±0.1 to 0.2	±0.1 to 0.2
50	±0.1	±0.2
10	±0.05 to 0.1	±0.5 to 1
1	±0.01 to 0.02	±1 to 2

Appendix B

EXPERIMENTAL PROCEDURE DETAILS

The starting material for all experiments were undeformed high purity single KBr crystals (>99% KBr; TedPella, Inc.) initially purchased in sizes of 1x1x1 cm. For set II experiments part of crystals were deformed at Macquarie University, using a high temperature oven heated to 700°C and a steel press applying 4 bar normal stress (σ_1) for duration of 17 h. No confining pressure was applied. After deformation, samples were cooled down to room temperature over duration of 12 h. As a result ~7-12% shortening was achieved and all set II samples exhibited partly annealed crystal-plastic deformation microstructures, such as subgrains and undulose lattice distortions (e.g. Urai et al., 1986; Trimby et al., 1998) (Fig. 3D).

For each reaction experiment crystals from both sets of samples, the undeformed set I- and the deformed set II, were cleaved with a razorblade to sizes of ~3x4x7 mm and coated with a water resistant glue, leaving only one side (4x7 mm) exposed for the reactive fluid.

Each crystal was immersed in 15 ml of a saturated KCl-H₂O solution and kept at room (23±1°C), and atmosphere pressures for durations of 30 min to 8 h (Table B1). After experiments, samples were removed from the solution and gently dried using a paper tissue.

Table B1. Samples and experimental conditions

Conditions: T= 22-23°C; P=atmosphere; fluid = sat. KCl-H ₂ O				
Sample no.	Exp. duration (h)	Strain in sample (% of shortening)	Reaction rim (μ m)	Replacement (%)
RKBr48	2	0	700	24
RKBr49	2	12	620	22
RKBr56	0.5	0	516	15
RKBr57	0.5	11	540	17
RKBr58	4	0	1020	35
RKBr59	4	7	900	27
RKBr60	8	0	1650	68
RKBr61	8	13	1630	56

Sample Preparation for EBSD Analysis

After the experiments ~2 mm thick slices were cleaved from the central parts of each sample, perpendicular to the reacted surface, so the interface between the parent crystal and reaction rim was exposed in the cross-sections. As KBr and KCl are highly

soluble in water, the polishing for EBSD analysis was performed with a focused argon (Ar) ion beam using IB-09010CP Cross section polisher at OptoFab node, Australian National Fabrication Facility. Each sample was polished for 2-3 h using a beam with a diameter of 500 μm , $\sim 190\text{--}210\ \mu\text{A}$ top current, $\sim 80\text{--}90\ \mu\text{A}$ bottom current (Fig. B1).

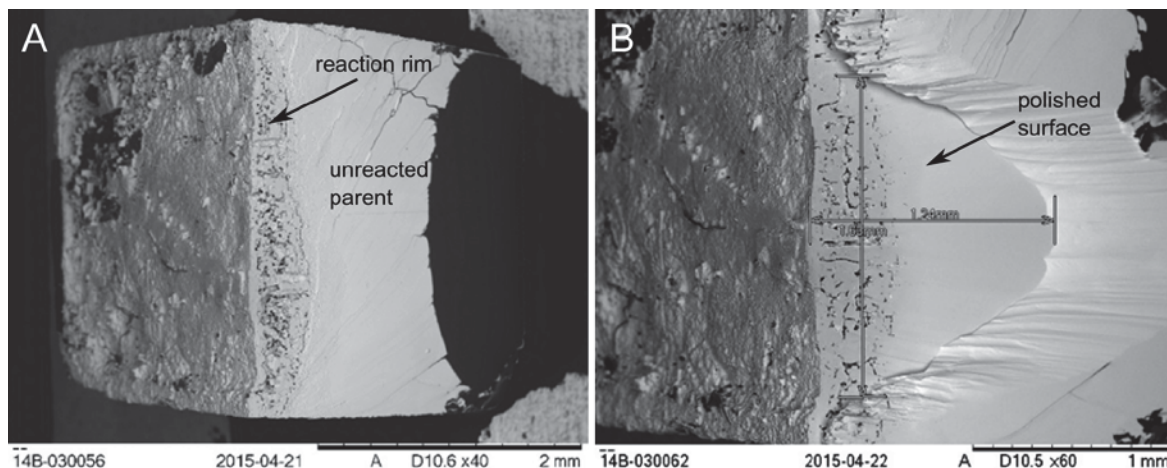


Figure B1. Cleaved cross-section of the reacted sample before (A) and after (B) ion beam polishing

EBSD data collection and analysis

Crystallographic orientation data were acquired using Carl Zeiss IVO Scanning Electron Microscope (SEM) with HKL NordlysNano high-sensitivity Electron Backscatter Diffraction (EBSD) detector at the Geochemical Analysis Unit (GAU) in Macquarie University. The analyses were performed with AzTec analysis software (Oxford Instruments) on samples tilted to 70° angle, at high-vacuum conditions with accelerating voltage of 20-30 kV, beam current of 8-8.2 nA at working distances from 17-22 mm. The high working distances were used to avoid shadowing effects from edges surrounding the ion-beam polished area. Step sizes of 3 μm were used for all maps.

Crystallographic orientation data were processed using Channel 5 analysis software from HKL Technology. Noise reduction included the removal of wild spikes, extrapolation of zero solutions by iteration to 6 neighbours and application of Kuwahara filter with the grid size of 3x3, smoothing angle of 2° and artefact angle of 1° .

For the presented EBSD maps, the KBr-KCl reaction rim was always indexed using KBr structural solution that showed a better fit than KCl unit cell. To test if the choice of the indexed phase does not affect the obtained orientation data, raw Kikuchi

patterns were re-analysed using KCl structural solution. As shown in Figure DR2 no significant effect was detectable, however the range of orientation and the amount of subgrain boundaries (especially in Fig. B2A) is higher than if indexed with KBr solution (Fig.3).

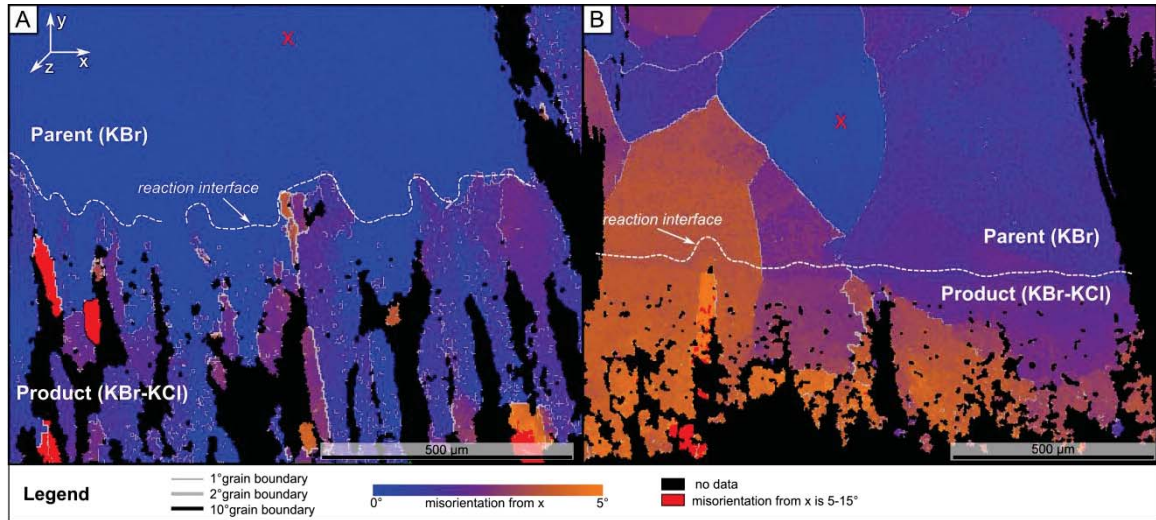


Figure B2. Samples depicted in Fig.3A, D reanalyzed using KCl structural solution. A – undeformed, partly replaced sample; B – deformed partly replaced sample. Note that although the graininess and the amount of low angle boundaries is higher, the general microstructure is very similar as in Fig. 3A, D.

Slip systems for individual subgrain boundaries were determined following the procedures of Prior et al. (2002), Reddy et al. (2007), Piazzolo and Jaconelli (2013). Figure B3 show the typical slip system solutions for subgrain boundaries in the product phase from set I experiments (Fig. B3A) and parent (Fig. B3B) and product (Fig. B3C) phases from set II experiments. The analysed subgrain boundaries are marked on Figure B3D, E.

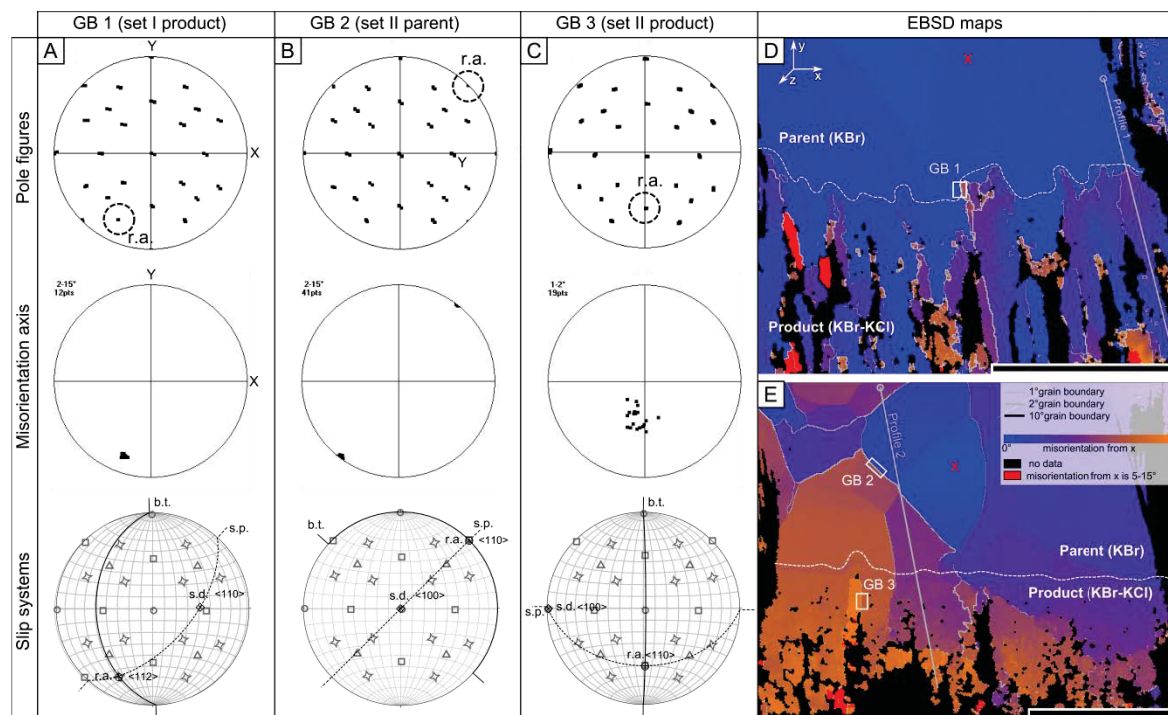


Figure B3. Subgrain boundary trace analysis. The analysed grain boundaries (GB) in A-C are marked in figures D and E. Slip system solutions typically show tilt boundary geometries, however for GB 2, twist boundary is also possible, although not showed in the figure.

Neutron Diffraction Analysis

Bulk crystallographic properties of the experimental samples were characterized using high-intensity neutron powder diffractometer (WOMBAT) at the Bragg Institute in the Australian Nuclear Science and Technology Organisation (ANSTO). Analysis was performed on ~ 4 mm thick slices cleaved from 6 partly replaced samples (RKBr56, 57, 58, 59, 60, 61; Table B1). The neutron diffraction data were collected in 0.2° steps for the [200] peaks using incident wavelength of $2.95 \text{ \AA}$ with no radial collimator movement. The diffraction intensities were plotted in 2-dimensional graphs (Fig. 2) for each analysed sample, where x-axis represents sample lattice parameters, measured as 2θ angles, and y-axis represents angular spread in the samples, measured as sample ω angles. The peak position for KBr [200] on 2θ (plotted as blue dashed line in Fig. 2) is consistent in all samples and was estimated from the maximum reflection intensity to be $\sim 53.8^\circ$ that equates to a lattice parameter of $a = 6.52 \text{ \AA}$. As product phase in all experiments is a solid solution between KBr and KCl, the peak position for KCl [200] could not be estimated from the measured data. Instead a measurement of Slagle and McKinstry (1966) at 55.9° was used as a standard (red dashed line in Fig. 2).

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Appendix C

Introduction

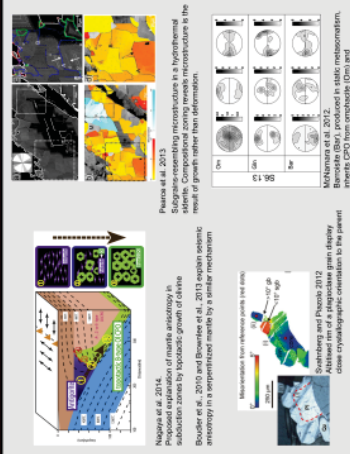
Rock deformation by crystal-plasticity produces a specific microstructure:
(1) angular foliations in crystal lattices; (2) subgrains; (3) grain boundaries with specific geometries; and (4) crystallographic preferred orientation (CPO).

These features are widely used to interpret tectonic and chronologic history, as well as to estimate deformation conditions, including temperature, differential stresses, strain rate, kinematic context and material rheologies. In many crustal environments, however, deformation is accompanied or succeeded by an infiltration of a metasomatic fluid.

THE QUESTIONS:

How do metasomatic fluid-mediated reactions affect rock microstructure?
How such a microstructure be recognized and distinguished from the original microstructure?

Ambiguous metasomatic microstructures in nature



Implications for interpreting structural observations and seismic anisotropy data in crust and mantle

Experiments

Low PT experiments - salts:



Material = single crystals of KBr
* undeformed
* deformed (~10% shortening)
Fluid = sat. KCl
T = 22-23 °C
P = atm.
Duration = 30 min - 18 h

High PT experiments - silicates:



Material = polycrystalline fsp-bt-bh gneiss
Fluid = Na-SH₂O solution
T = 600 °C
P = 2 kbar
Duration = 5 - 20 days



Deformation-resembling

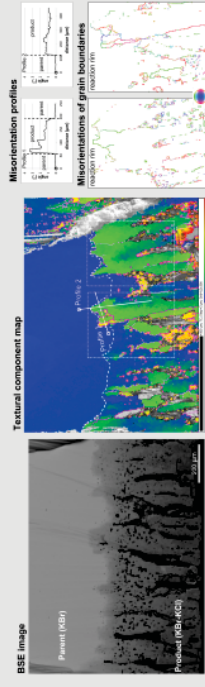
microstructure created by metasomatic reactions

Lena Sprunzice and Sandra Piazolo

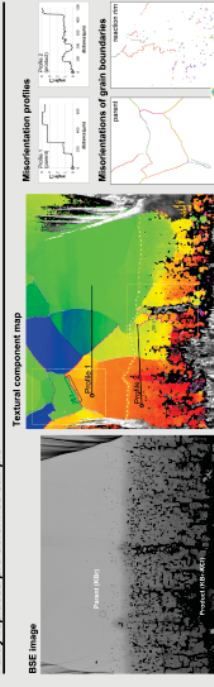
Australian Research Council Centre of Excellence for Core to Crust Fluid Systems (CCFS), Department of Earth and Planetary Sciences, Macquarie University, NSW, Sydney, Australia

Results: salts

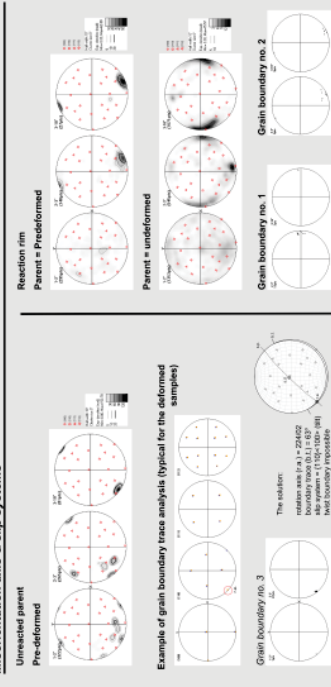
Partly replaced undeformed sample



Partly replaced pre-deformed sample

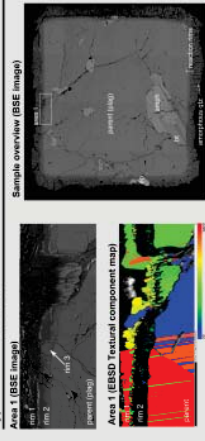


Misorientation axis & slip systems

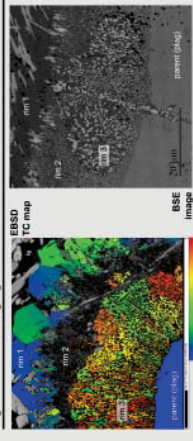


Results: silicates - preliminary data

Typical microstructures



High resolution imaging



Conclusions

In fluid-mediated phase transformation experiments on deformed samples the reaction products display the preservation of the pre-existing microstructure.

Experiments on undeformed samples lead to a formation of a deformation-resembling microstructure in the product phases, despite no differential stress was applied.

The metasomatic microstructure, compared to the deformation microstructure, is typically characterized by a higher irregularity in the subgrain and grain boundary traces, wider spread in misorientation axis directions and inconsistent or impossible solutions for slip systems.

Data from high PT silicate-experiments confirm the results of low PT salt-system experiments, suggesting the fundamental applicability of the observed results and associated processes for silicates at high PT conditions.

Microstructures of metasomatised rocks can be misleading and should be interpreted with a care

Acknowledgments

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Appendix D

Fluid-controlled fabric development across a brittle-ductile shear zone: an example from a Wyangala Batholith, Australia

Liene Spruzeniece¹ and Sandra Piazzolo¹

¹Australian Research Council Centre of Excellence for Core to Crust Fluid

Systems/GEMOC, *Department of Earth and Planetary Sciences, Macquarie University, 2109 NSW Australia*

This study focuses on the rheology and mineral reactions in a brittle-ductile shear zone within the Wyangala Batholith, SE Australia. In the shear zone, a coarse-grained two feldspar-quartz-biotite granite is transformed into a fine-grained quartz-muscovite mylonite.

The samples from shear zone margins display cataclasis of feldspar and crystal-plastic deformation of quartz. Quartz accommodates most of the deformation and is extensively recrystallized showing distinct crystallographic preferred orientations (CPO). Feldspar-to-muscovite, biotite-to-muscovite and albitization reactions occur locally at fracture and porphyroclast margins. However, the bulk rock composition shows very little change in respect to the wall rock composition.

In the shear zone centre, quartz occurs as large, weakly deformed porphyroclasts, in sizes similar to that in the wall rock, suggesting that it has undergone little deformation. Feldspars and biotite are almost completely reacted to muscovite, which is arranged in a fine grained interconnected network. Muscovite has accommodated most of the strain. Muscovite rich layers contain significant amounts of fine grained intermixed quartz with random CPO. XRF bulk rock analysis suggests a significant increase in SiO₂ and depletion in NaO content compared with the wall rock composition.

We suggest that the high and low strain fabrics represent markedly different scenarios and cannot be interpreted as a simple sequential development with respect to strain. The large quartz clasts in the central parts of the shear zone have never undergone the structural development displayed by the low strain domain. We interpret that the fabrics in the shear zone centre have formed due to fluid influx probably along an initially brittle fracture where hydration reactions dramatically changed the rheological property of the rock. Subsequent ductile deformation focussed in the newly produced muscovite-quartz layers, thus original quartz grains did not recrystallize. In contrast, in the shear zone margins the amount of fluid and reactions was limited therefore deformation was taken up mainly by the relatively weak original igneous quartz.

The studied shear zone exemplifies the role of fluids and fluid-induced reactions on contrasting rheological behaviour at local scales.

Appendix E

THE EFFECT OF DEFORMATION ON REACTION RATES: NEW INSIGHTS FROM PHASE TRANSFORMATION EXPERIMENTS IN THE KBr-KCl-H₂O SYSTEM

Spruzeniece, Liene¹, Piazzolo Sandra², Joyce Schmatz³

¹*Department of Earth and Planetary Sciences, Macquarie University, 2109 NSW Australia*

²*Department of Earth and Planetary Sciences, Macquarie University, 2109 NSW Australia*

³*Institute of Structural Geology, Tectonics and Geomechanics, RWTH Aachen University, Germany*

Many natural processes such as weathering, diagenesis, metasomatism and metamorphism involve phase transitions in mineral-fluid systems. Recent experimental studies on feldspars, apatite and zircon, show that mineral reactions in the presence of a reactive fluid occur by solvent mediated phase transformation over extremely short timescales ranging from hours to weeks. This has important implications for geological processes classically viewed as occurring over millions of years.

However, to date all phase transformation experiments have been carried out on undeformed perfect crystals, while in nature chemical alteration in minerals has been found to clearly associate with deformation microstructures such as subgrain boundaries, twins and crystal defects. Understanding the role deformation microstructures play on the rates of mineral phase transformations is essential for our fundamental understanding of large-scale geodynamic processes on Earth as in nature reaction and deformation go commonly hand in hand.

We present first results from a series of hydrothermal experiments designed to examine effects of deformation microstructures on the reaction rates in undeformed and deformed salt single crystals. The experimentally deformed crystals exhibit presence of subgrain boundaries, bend lattices and hair fractures. Two main sets of static experiments have been performed: (a) replacement experiments on large sample volumes and (b) see-through experiments on thin sample slices allowing real time observation of reaction progression under reflected light microscope. In the static experiment series undeformed and pre-deformed (13% strain) KBr single crystals were reacted with saturated KCl-H₂O solution at room temperatures (24°C ± 0.5°C) and atmospheric pressures for durations of 5, 10, 30, 60 and 120 min. The reaction resulted in a development of a highly porous KCl rim around the relic core of KBr crystal. The volume and external morphology of the original crystal was preserved in all cases and the reaction interface was sharp even on microscale. Small (<50 µm), new euhedral KCl crystals arranged in linear formations appeared in the cores of the deformed samples presumably reflecting fluid infiltration through subgrain boundaries or pre-existing microfractures, while the cores of undeformed samples stayed unaltered. In addition deformed samples developed 8-15% thicker reaction rims compared to the undeformed samples suggesting a considerable increase in reaction rates associating with deformation.

In see-through experiments the reaction front showed a distinctly different behaviour for deformed versus undeformed samples. The results of this study suggest that deformation microstructures can significantly enhance reaction rates and influence the microstructures developed during phase transformations.

Appendix F

Deformation in an Open System: Fluid Assisted Brittle-Viscous Deformation Coupled with Volume Change in a Greenschist Facies Shear Zone (Wyangala, Australia).

Liene Spruzeniece¹, Sandra Piazzolo¹ and Nathan Daczko¹

¹*Department of Earth and Planetary Sciences, Macquarie University, 2109 NSW Australia*

At mid crustal levels deformation is commonly accompanied by fluids which results in a complex interaction between mechanical and chemical processes.

This study presents microstructural and chemical analysis across a strain gradient in a brittle-viscous shear zone within the Wyangala batholith, Australia. In the shear zone, a coarse grained granitic orthogneiss is transformed into a fine-grained quartz-muscovite mylonite. The early stages of deformation are characterized by feldspar cataclasis and feldspar-to-muscovite breakdown reactions. After the disappearance of feldspars, the mylonite has acquired a layered structure and deforms by dislocation glide in muscovite domains and crystal-plasticity in quartz domains.

Microstructures and mineral relationship indicate the fluctuation between fracturing, crystal plasticity and dissolution-precipitation across different structural domains in the shear zone and different stages in its evolution. The central parts of the shear zones show volume increase by 223%, mostly due to enrichment of SiO₂ indicating that syn-deformational fluids had a silicic composition. Deformation temperatures are estimated to be close to 400° using CPO patterns of dynamically recrystallized quartz.