

ABSTRACT

Title of Dissertation: EVOLUTION OF STRENGTH AND
PHYSICAL PROPERTIES OF CARBONATE
AND ULTRAMAFIC ROCKS UNDER
HYDROTHERMAL CONDITIONS

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Interaction of rocks with fluids can significantly change mineral assemblage and structure. This so-called hydrothermal alteration is ubiquitous in the Earth's crust. Though the behavior of hydrothermally altered rocks can have planet-scale consequences, such as facilitating oceanic spreading along slow ridge segments and recycling volatiles into the mantle at subduction zones, the mechanisms involved in the hydrothermal alteration are often microscopic.

Fluid-rock interactions take place where the fluid and rock meet. Fluid distribution, flux rate and reactive surface area control the efficiency and extent of hydrothermal alteration. Fluid-rock interactions, such as dissolution, precipitation and fluid mediated fracture and frictional sliding lead to changes in porosity and pore structure that feed back into the hydraulic and mechanical behavior of the bulk rock. Examining the nature of this highly coupled system involves coordinating

observations of the mineralogy and structure of naturally altered rocks and laboratory investigation of the fine scale mechanisms of transformation under controlled conditions.

In this study, I focus on fluid-rock interactions involving two common lithologies, carbonates and ultramafics, in order to elucidate the coupling between mechanical, hydraulic and chemical processes in these rocks. I perform constant strain-rate triaxial deformation and constant-stress creep tests on several suites of samples while monitoring the evolution of sample strain, permeability and physical properties. Subsequent microstructures are analyzed using optical and scanning electron microscopy.

This work yields laboratory-based constraints on the extent and mechanisms of water weakening in carbonates and carbonation reactions in ultramafic rocks. I find that inundation with pore fluid thereby reducing permeability. This effect is sensitive to pore fluid saturation with respect to calcium carbonate. Fluid inundation weakens dunites as well. The addition of carbon dioxide to pore fluid enhances compaction and partial recovery of strength compared to pure water samples. Enhanced compaction in CO₂-rich fluid samples is not accompanied by enhanced permeability reduction. Analysis of sample microstructures indicates that precipitation of carbonates along fracture surfaces is responsible for the partial restrengthening and channelized dissolution of olivine is responsible for permeability maintenance.

The results of this study provide insight into how fluid mediated processes can change the character of deformation and permeability evolution in porous rocks, with applications to geofluid reservoirs, oceanic tectonics and carbon sequestration.

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AND ULTRAMAFIC ROCKS UNDER HYDROTHERMAL CONDITIONS

by

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Foreword

In this document, the role of chemical interaction between pore fluid and porous rocks in the evolution of mechanical, transport and petrophysical properties of rocks is quantified. I use a laboratory-based approach, using a combination of traditional and modified geomechanical testing techniques to look at chemo-hydro-mechanical coupling in carbonate and ultramafic rocks. Two and three dimensional microstructural analysis is performed after experiments and related back to experimental observations. My methodology, results and implications for natural and engineered systems are discussed over the next five chapters.

- Chapter 1: I present the geological context and outstanding questions related to fluid-rock interactions. The concepts and background necessary to understand my methods and results are introduced.
- Chapter 2: I quantify the role of water weakening in the deformation and transport property evolution of porous carbonates. Mechanisms, the role of pore fluid chemistry and geological implications are discussed.
- Chapter 3: I quantify the effect of water and carbon dioxide-rich fluids on the mechanical and transport properties of dunites. Mechanisms and geological implications are discussed.
- Chapter 4: The mineralogy and microstructures of carbonated dunites are investigated in detail. A conceptual model to explain experimental

observations of mechanical and transport property evolution in the presence of carbon dioxide-rich fluid is proposed and discussed.

- Chapter 5: I measure the mechanical and petrophysical properties of natural samples of variably carbonated ultramafic rocks from northern Norway. Implications with regard to geophysical monitoring of alteration of the oceanic crust and engineered carbon disposal wells are discussed.

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Chapter 1: Introduction

1. Background

1.1 Fluid-rock interactions in the Earth's crust

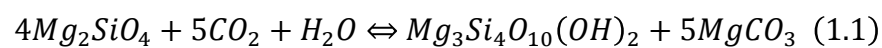
Fluids in the crust are ubiquitous; produced by processes such as metamorphic dehydration, degassing, compaction and meteoric infiltration; they exist at an enormous variety of compositions, temperatures and pressures. Fluid distribution and flux within the Earth's crust and mantle depend on the pore structure and transport properties of rocks. Physical properties of rocks can be substantially changed by pore fluids through diverse physical and chemical processes. Fluid-rock interaction is one of the most pervasive and important facets of the Earth system. On the Earth's surface, fluids play a vital role in chemical weathering of rocks by processes of hydration, hydrolysis, carbonation and dissolution. In seismogenic fault zones, there are well-established links between fluid pressure and seismicity [Raleigh et al., 1976]; fluids affect fault strength and slip behavior during the earthquake cycle [Sibson, 1976; Chester et al., 1993; Moore et al., 1996]. Hydration of the mafic oceanic crust is occurring around the entire planet, playing host to complex chemical reactions that may have produced the first building blocks of life [Sleep et al., 2004] and facilitating volatile recycling into the Earth's upper mantle [Bailey, 1980], and facilitating localized deformation along faults with long lived structural and tectonic implications [Boschi et al., 2006b; Moore and Rymer, 2007]. Driven by pressure gradients, gravity, thermal convection, capillary action, and intracrystalline diffusion, fluids are capable of transporting mass from the grain scale to the plate scale.

The implications of fluid rock interaction are planetary, but the mechanisms are often microscopic. Understanding a wide variety of diagenetic, metamorphic and tectonic processes requires quantitative knowledge of the rate of change of the transport properties of rocks under various conditions of pressure, temperature and pore fluid chemistry. In systems where fluid-rock interactions are involved, the feedbacks between the mechanical and chemical reactions and the evolution of pore geometry and concomitant change in permeability must be taken into account. Such systems are often complex; it is the role of experimental rock deformation to use controlled, small-scale experiments to isolate, compare and explore the mechanisms at play in the multi-scale processes.

1.2 Hydrothermal alteration and faulting

Alteration of the oceanic crust is often implicated in large-scale tectonic processes. The ocean crust is accreted as largely anhydrous mafic minerals, but is extensively altered by hydrothermal activity [Bach et al., 2004]. Hydration and carbonation of the ocean crust can result in dramatic modifications in mechanical properties.

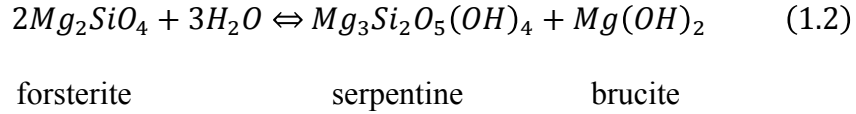
Some common alteration reactions in the oceanic crust are the reaction of forsterite, carbon dioxide and water to form talc and magnesite and the reaction of forsterite with water to form serpentine and brucite,



forsterite

serpentine

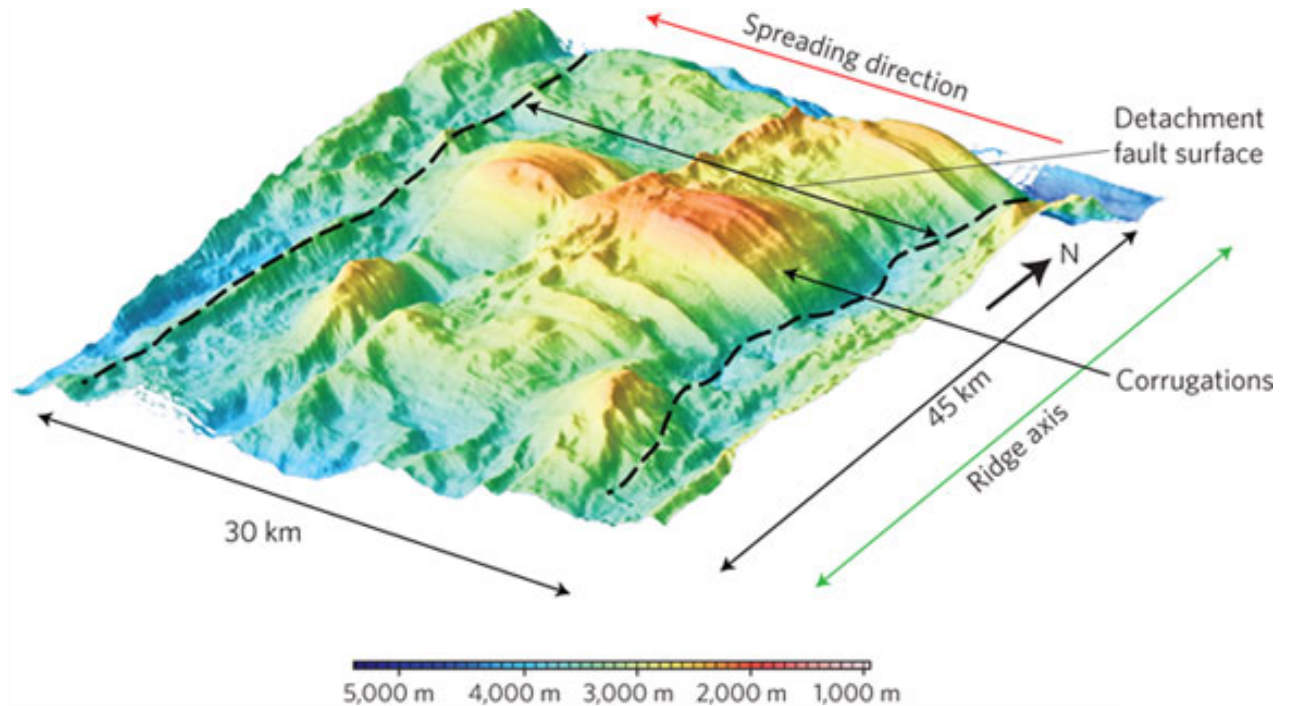
magnesite



The products of these reactions are phyllosilicates (talc and serpentine), carbonate (magnesite) and hydroxide (brucite). All of these products, and particularly the phyllosilicates, have lower strengths than olivine [Escartin et al., 2001; Escartin et al., 2008].

The presence of either of these phyllosilicates can dramatically alter the mechanical behavior of the oceanic lithosphere. Their modes of deformation, including kinking, delamination and dehydration, can contribute to elevated pore pressures [Escartin, 1997a,b; Escartin et al., 2008]. Even in small amounts, both serpentine and talc have been found to promote localization of deformation and slip on faults, and have been associated with the large displacements along oceanic detachment faults (i.e. Figure 1.4) [Escartin et al., 2003; Schroeder and John, 2004; Boschi et al., 2006; Cheadle and Grimes, 2010]. This effect can possibly play an important role throughout the entire thickness of the oceanic lithosphere [Hirth, 1998].

Figure 1.1. Bathymetry of Kane oceanic core complex from Cheadle and Grimes (2010). This detachment fault has more than 3 km vertical offset and accommodates at least 30 km of offset. Talc, amphibole and carbonates are all associated with this feature.



Talc has also been found in association with highly localized and high strain features in the continental crust. Talc occurrence in the continental crust can be associated with the contact between mafic and calc-silicate rocks, such as observed in the metamorphic core complexes of Sonora, northwestern Mexico [Nourse et al., 1994] or associated with similar lithologies as those found in oceanic core complexes, for instance the ophiolitic serpentinites within the metamorphic core complex on the D'Entrecasteaux Islands, Papua New Guinea [Little et al., 2007]. The presence of

talc in material from the San Andreas Fault has been used to explain the perplexing, near-perpendicular principal stresses along the strike slip plate boundary [Moore and Rymer, 2007].

Altered peridotite also plays an important role in subduction zones. Besides carrying molecular water into the upper mantle, serpentine and talc can contribute to the weakening of a subducting slab to a depth equivalent to a pressure of at least 8 GPa [Pawley and Wood, 1995]. Seismic observations suggest a low velocity layer at some slab-wedge interfaces [Kim and Clayton, 2015] that have been attributed to mantle metasomatism. In depth analysis of seismic data suggests that this feature is the result of slab-derived fluids migrating into the mantle wedge to form talc [Kim et al., 2013]. Alteration of this sort may also provide the weak interfaces necessary to explain so-called “silent earthquakes” [Frank et al., 2015].

Even with the dramatic effect that these reactions can have on oceanic tectonics, little attention is paid in the literature to the role of carbon-rich fluids in the evolution of physical properties with progressive reaction. The Linnajavri ophiolite has an ideal exposure of the transition from serpentinite to partially carbonated soapstone to fully carbonated listvenite [Beinlich et al., 2012].

1.3 CO₂ – ultramafic interaction

One proposed technology for carbon sequestration and storage is mineralization, the storage of carbon dioxide in stable carbonate minerals [Seifritz, 1990; Lackner et al., 1995; Kelemen et al., 2011]. Olivine is an attractive choice of reactant with carbon dioxide because it is so far out of equilibrium with atmospheric

levels of carbon dioxide. This process occurs naturally wherever minerals exist out of equilibrium with ambient carbon dioxide levels. Meaningful geologic sequestration would mean increasing the natural rate of carbonation by many orders of magnitude. This can possibly be accomplished by controlling the pressure, temperature and P_{CO_2} of carbonation [Kelemen, 2008]. Success in this endeavor entails a much greater understanding of the coupled chemical, mechanical and hydraulic evolution of this system than currently exists, though current research efforts are considerable.

The chemical interaction between olivine and carbon dioxide is well studied [Bearat et al., 2006; Gerdermann et al., 2007; Oelkers et al., 2008; Kelemen and Matter, 2008; King et al., 2010; Daval et al., 2011]. Ideal conditions for olivine carbonation are found to be 185 °C and elevated P_{CO_2} . General consensus is that olivine dissolution is the limiting step in the carbonation reaction in batch reactor and autoclave experiments, and that this rate can be enhanced by lowering the pH of the environment either through higher P_{CO_2} or additives such as citric acid. These experiments are run on finely ground powders with high surface areas and high fluid-solid ratios. Realistic in-situ carbonation projects would more likely be low surface area and low fluid-solid ratio cases. In such cases, mechanical and hydraulic evolution is likely to be limiting the factor.

The reaction of olivine with carbon dioxide to produce magnesite and quartz can have a solid volume increase of 88%. This increase in solid volume results in a decrease in pore volume and subsequent reduction in permeability. Observation of naturally carbonated systems suggests that some permeability maintaining mechanism

exists [Ludwig et al., 2006; Kelemen et al., 2011]. It has been suggested that rapid enough reaction can result in overpressurization and fracture [Fletcher and Merino, 2001; Scherer, 2004; Jamtviert et al., 2008; Rudge et al., 2010; Noriel et al., 2010]. Alternate mechanisms such as etch pit-nucleated fracture have also been suggested [Plummer et al., 2012]. Whether carbonation results in permeability reduction or enhancement is an active area of research.

Investigation into the permeability evolution of actively carbonating olivine aggregates has seen only limited success. Flow-through experiments on sintered olivine cylinders show a dissolution-dominated system with only minor carbonate precipitation [Andreani et al., 2009]. At 185 °C and 11 MPa P_{CO_2} , experiments showed that undersaturated fluid flow dissolved olivine near the point of inflow, but precipitated secondary minerals such as magnesite and siderite only in particular hydrodynamic environments such as dead ends in flow channels where there was reduced flow rate. As a result of the dissolution, initial permeability increased until it reach a steady-state value about 10% higher than the initial value.

Microstructural observation of experimentally carbonated natural peridotite has yielded promising results. Experiments at 100-200 °C and 15-20 MPa P_{CO_2} show olivine carbonation to be a self-limiting process [Hovelmann et al., 2012]. Reaction rims up to 50 μ m thick made of magnesite and silica formed around olivine grains. These rims appear to have remained permeable during their formation, allowing for continued olivine dissolution and secondary mineral precipitation. Initial porosities of 7-8% are reduced by 50% after 10% carbonation of olivine, suggesting that macroscopic permeability would be greatly reduced.

1.4 Calcite-water interaction

The main mechanisms of deformation in calcite are fracture, crystal plasticity and pressure solution. Pressure, temperature, chemical environment and strain rate determine which mechanism dominates the behavior of a given system. At low pressures and temperatures and high strain rates, brittle processes dominate. Macroscopically, brittle fracture can result in localized faulting or cataclasis, depending on the confining pressure, with higher pressures resulting in cataclasis [Friederic et al., 1989; Renner and Rummel, 1996; Baud et al., 2000; Vajdova et al., 2004]. At low temperatures and pressures and low strain rates, given the presence of pore fluid, solution transfer dominates. Pressure solution results from enhanced diffusive transfer through a thin fluid film at stressed grain boundaries [Rutter and Elliot, 1976]. At higher temperatures and pressure, crystal plasticity begins to dominate deformation. The most common types of crystal plasticity are dislocation creep, dislocation glide and mechanical twinning [Rutter and Elliot, 1976]. It has been shown that some modes of crystal plasticity play significant roles at temperatures and pressures only slightly above ambient conditions [Turner, 1953].

The presence of water can have a significant effect on each of these deformation processes. Water can lower the fracture energy of materials by surface adsorption. Adsorption of water to the surface of grains lowers their surface energy [Israelachvili, 1991], thus lowering the fracture energy. As microscopic fracturing plays a role in both localized brittle faulting and cataclastic flow, the presence of

water can influence both modes of plastic deformation as well as the transition conditions between the two modes.

Water is essential to pressure solution. Solution transfer can only be an efficient mechanism of mass transport if grains are fully wetted with a fluid. Solid diffusion is far too slow to cause significant mass transfer at upper crustal conditions on laboratory timescales. Diffusion rates are sensitive to temperature, so temperature and strain rate are the controlling factors over whether solution transfer is a dominant mechanism of deformation [Rutter and Elliot, 1976].

The interaction between water and crystal plasticity in calcite is less well understood. Hydrolytic weakening analogous to that active in quartz systems is not expected to operate in calcite, but it has been suggested that the interaction of a polar fluid with point defects can promote dislocation mobility [Westwood et al., 1967]. This effect is amplified by charged species dissolved in pore water.

1.5 Mechanisms of feedback: deformation and fluid transport

The behavior of the Earth system is essentially dynamic; thermal, physical and chemical gradients exist throughout the crust and mantle that drive complex and highly coupled behaviors. The work presented here deals primarily with the coupled evolution of porosity, permeability, deformation and chemical reaction in ultramafic and carbonate systems. Permeability affects the rate of fluid flow within a material. Enhancement or reduction of flow rate can cause changes in fluid pressure within a rock as well as stimulate or inhibit chemical reactions. Fluid pressure and chemical

reactions both contribute to deformation and pore space alteration, which is inherently coupled with permeability.

1.6 Permeability-porosity relationship

Permeability is an empirical quantity used to describe the ease of flow through a material. Permeability was first described in Darcy's Law: in one dimension,

$$Q = \frac{-\kappa A (P_1 - P_2)}{\eta L} \quad (1.3)$$

where Q is flow rate, κ is sample permeability, η is fluid viscosity, A is cross-sectional area of the sample, L is sample length and P_1 and P_2 are fluid pressures on either side of the sample. Permeability of different types of rocks varies more than 13 orders of magnitude, ranging from $<10^{-23} \text{ m}^2$ for unfractured igneous and metamorphic rocks to 10^{-10} m^2 for clean sand.

Measurement of permeability under hydrothermal conditions while pore structure evolves under thermal, chemical and mechanical loads is one of the most challenging tasks in experimental deformation. Permeability is inherently connected to porosity. A power law is often used to describe the dependence,

$$\kappa \propto \Phi^\alpha \quad (1.4)$$

where κ is permeability, Φ is porosity and α is typically a value between 1 and 3, but can possibly be as high as 10 or above [Zhu et al., 1999, 2007]. The value of α reflects the sensitivity of a material's permeability to changes in porosity, and can take on vastly different values depending on the specific micromechanisms of deformation.

In low porosity materials, localized failure is usually preceded by dilatancy, which may or may not produce a concomitant increase in permeability due to increased crack apertures and new microcracks increasing pore connectivity [Zoback and Byerlee, 1975]. In high porosity materials at high confining pressure, failure is cataclastic and leads to decreased porosity and permeability. Interestingly, high porosity materials at low confining pressure experience dilatancy and localized failure similar to low porosity materials, but it is generally accompanied by permeability reduction [Menendez et al., 1996]. This reduction is accounted for in the equivalent channel model by increased tortuosity [Zhu and Wong, 1996]. This highlights how essential an understanding of the evolution of not only porosity magnitude, but also pore geometry is in the coevolution of deformation and fluid flow.

Deformation of porous rocks affects pore geometry, and therefore permeability. Low permeability can lead to fluid overpressurization and hydrofracture, leading to increased porosity, which in turn may increase permeability. High permeability can lead to high flow rates and enhanced dissolution, which in turn can result in supersaturation of pore fluid and precipitation, which reduces porosity and concomitant permeability. The relationship between porosity and permeability is stress path dependent; it is not always simple, and requires analysis of the many feedbacks in play in a given system. Experimental constraints on porosity evolution due to specific processes and concomitant permeability changes are essential to a full understanding of many Earth processes.

1.7 Effective pressure law

Most porous rocks in the Earth's interior are filled with fluid; this fluid exerts a pressure on rocks that works opposite to overburden pressure. This adjusted pressure is the pressure to which materials actually respond. It is referred to as effective pressure, P_{eff} . Expressed mathematically, effective pressure is,

$$P_{eff} = P - P_f \quad (1.5)$$

where P_{eff} is effective pressure, P is the overburden and P_f is fluid pressure [Terzaghi, 1936]. Here, and in the rest of the dissertation, I use the current geophysical convention that positive stress is compaction and negative stress is extension.

Pressure is an isotropic, three-dimensional quantity that acts through the bulk of a material. An analogous quantity can be applied to forces acting on a plane, effective normal stress, σ . Expressed mathematically, effective normal stress is,

$$\sigma = \sigma_T - P_f \quad (1.6)$$

where σ_T is total normal stress. Effective normal stress is especially relevant to frictional processes.

1.8 Elasticity and plasticity

A material is said to deform elastically if the deformation is fully recoverable. In minerals, elastic strain is the result of distortion of a crystal lattice in response to stress, and is generally quite small (i.e. <1%). The elastic behavior of a given material is typically linear and can be quantified by moduli, coefficients linearly relating stress to strain.

Once a material has been deformed to its elastic limit, irrecoverable deformation occurs; this deformation is referred to as plastic. There are many mechanisms of plastic deformation including fracture, frictional sliding, dissolution, and crystal plasticity. Plasticity is complex and harder to parameterize simply than elasticity, rendering experimental data and microstructural analysis essential for a robust understanding.

2. Mechanisms of porosity change in rocks

Properties of rocks such as porosity, permeability and strength are often considered on the continuum scale; however, descriptions on this scale miss some of the detail required to confer the properties with intuitive physical meaning. The mechanisms of feedback between deformation, porosity and permeability often take place on the grain scale, and can involve increases and decreases in pore space as well as changes in pore geometry (Figure 1.2).

2.1 Porosity reduction

2.1.1 Compressibility

Compressibility, B , can be defined as the relative volume change of a material as a response to a change in pressure. Expressed mathematically, compressibility is,

$$B = \frac{1}{V} \frac{\partial V}{\partial P_{eff}} \quad (1.7)$$

where V is volume and P_{eff} is effective pressure. Compressibility is an elastic parameter, and it describes an instantaneous response to an infinitesimal change.

When an elastic porous solid is subjected to pressure, the pore space is compressed as well as the solid volume. Pore compressibility, B_ϕ , can be defined,

$$B_\phi = \frac{1}{V_\phi} \frac{\partial V_\phi}{\partial P_{eff}} \quad (1.8)$$

where V_ϕ is the pore volume. In general, pore compressibility is much greater than solid compressibility ($B_\phi \gg B$), so the majority of the deformation comes from pore space reduction. This is the primary mechanism of elastic porosity reduction in response to hydrostatic pressure change. In the following text, I will sometimes also refer to the bulk modulus, K , the reciprocal of compressibility.

2.1.2 Crack closure

Cracks are differentiated from pores by their relative dimensions. Pores are relatively the same size in each dimension (i.e. $x \approx y \approx z$), while cracks have one dimension significantly smaller than the other two (i.e. $x \approx y \gg z$). All natural materials have internal cracks. When a material is subjected to a pressure, these cracks tend to be pressed closed. This response leads to apparently high compressibility at low pressures [Walsh, 1965], only some of which is fully recoverable. The irrecoverable deformation is due to microplasticity of asperities along crack walls that are crushed when the cracks are pressed closed. Once the cracks have all been closed, a material's compressibility appears to go down, or the material stiffens.

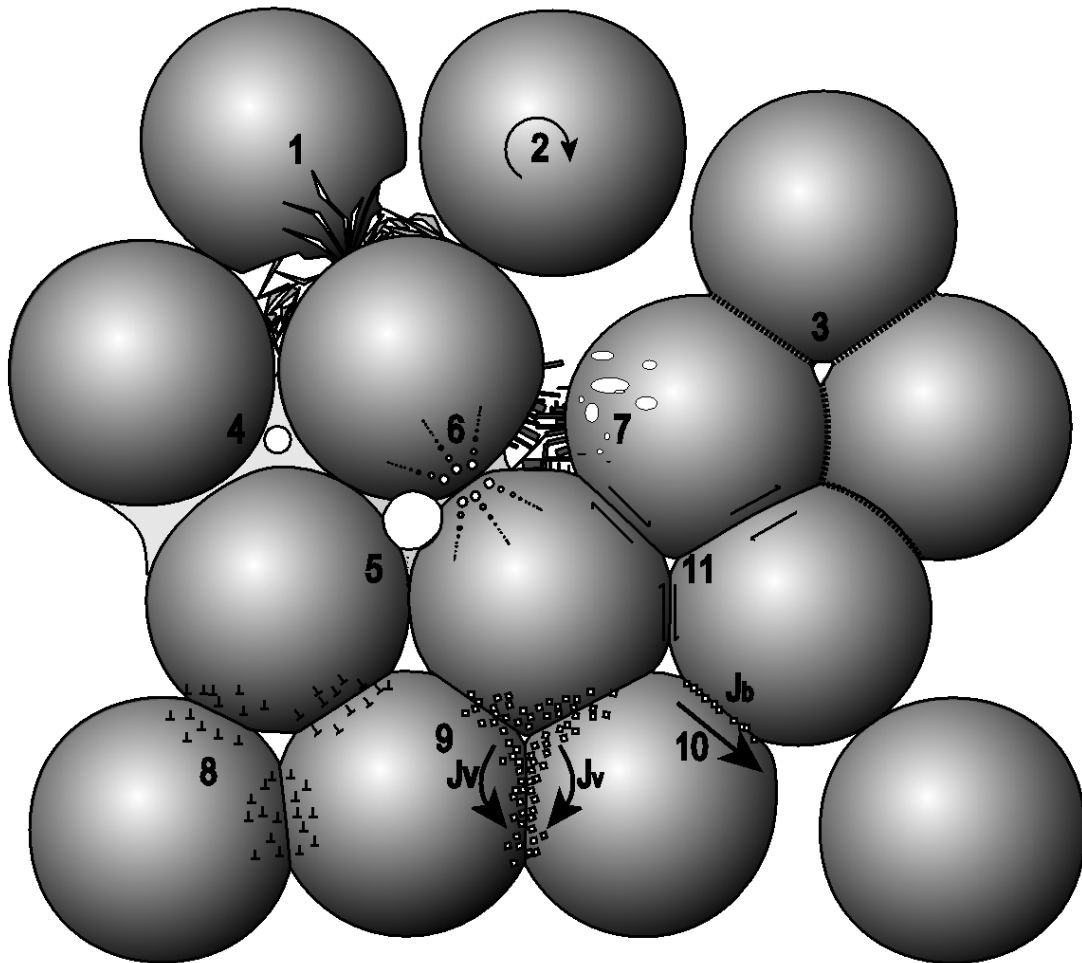
In many cases, these cracks often form a significant part of a pore space network's interconnections; once they are closed, a material's permeability can be significantly reduced. This is one of the most effective mechanisms of porosity reduction at low pressures.

2.1.3 Pore collapse

At very low pressures, elastic strain dominates. Compressibility is fully recoverable and crack closure is partially recoverable. As effective pressure is increased, porosity reduction by plastic deformation begins to dominate. Plastic pore collapse can result from grain comminution due to shear or tensile cracks or by crystal plasticity.

Although far field tensile stresses are uncommon in the Earth, stress on the grain scale can be tensile due to specific geometry. In porous rocks, high effective pressure can reduce pore space to the point that adjacent grains begin to impinge on one another. Impingement induces local tensile stress at grain contacts that can be large enough to cause grains to be fractured. This phenomenon is known as Hertzian fracture (Figure 1.1), and is the cause of porosity reduction due to grain crushing during hydrostatic loading in porous rocks [Zhang et al., 1990].

Figure 1.2. Schematic of deformation mechanisms adapted from [Evans et al., 1999]. 1-Fracturing at Hertzian contacts; 2-Frictional sliding; 3-Pressure solution; 4-Precipitation; 5-Healing via solution transfer with local cement source; 6-Crack healing; 7-Metamorphic reactions; 8-Crystal plasticity via dislocation motion; 9-Lattice diffusion; 10-Grain boundary diffusion; 11-Grain boundary sliding.



Cracking due to shear stress can cause grain comminution and pore collapse, a process referred to as shear enhanced compaction [Wong et al., 1997; Zhu et al., 1997; Baud et al., 2000; Vajdova et al., 2004].

At higher temperatures and pressures, deformation mechanisms such as dislocation creep, dislocation glide and twinning become operative. This crystal plastic deformation can also lead to pore collapse, as has been demonstrated in hot pressed calcite [Bernabe et al., 1982; Zhang et al., 1994; Zhu et al., 1995]. In some minerals, crystal plasticity is active at room temperature, such as twinning in calcite. When both crystal plastic and brittle behaviors operate simultaneously in a material, they can interact to enhance compaction and pore collapse [Vajdova et al., 2004; Lisabeth and Zhu, 2015].

2.1.4 Crack healing

At sufficiently high temperature and in the presence of fluid, crack healing can play a substantial role in reducing porosity. Crack healing consists of the diffusive transport of mass through fractures and the precipitation of solid material leaving only spherical and tubular fluid inclusions where the fracture once was. At temperatures in excess of 200 °C, this process occurs very rapidly on geologic timescales. In hydrothermal systems, crack healing can be one of the most dominant mechanisms of porosity change. At sufficiently high temperatures, crack healing timescales may set a lower limit for subcritical crack growth velocities [Smith and Evans, 1984].

2.1.5 Precipitation

Precipitation is a similar process to crack healing. Generally, when a pore space is filled with mass that has been transported only locally, it is referred to as crack healing. When the material filling a pore space has been transported from a remote location, it is referred to as precipitation. In addition, crack healing generally only involves precipitation of the same mineral that constitutes the solid matrix, whereas precipitation can be the result of more complex chemical reactions. In reality, the two behaviors exist in a spectrum. This process plays an important role in systems where pore fluid is strongly out of equilibrium with the solid matrix, such as in hydrothermal vents [Gribbin et al., 2012] and fluid-peridotite systems [Hovelmann et al., 2012].

2.2 Porosity production

2.2.1 Tensile cracks

Ideal tensile cracks are referred to as Mode I fractures, and create a positive change in volume. Mode I fractures propagate when the stress intensity factor at a crack tip reaches a critical value, K_{IC} . A material's stress intensity factor, K , for all fracture modes is given by,

$$K_x = Y\sigma(\pi c)^{1/2} \quad (1.9)$$

where σ is the effective normal stress, Y is a geometrical factor, x is the fracture mode and c is the half-length of a coin-shaped crack. Mode I is the dominant mode of microcracks in dilatant deforming materials. Tensile cracks nucleate at pre-

existing flaws in a material or at contacts between roughly spherical grains (i.e. Herzian fracture).

Tensile cracks can grow at stress intensities below the critical value. Such crack growth is referred to as subcritical. The velocity of subcritical crack growth is given by,

$$v = v_0 \exp(-H/RT) K^n \quad (1.10)$$

where H is the activation enthalpy, R is the gas constant, T is in K, and v_0 and n are constants [Atkinson, 1984]. The value of n , referred to as the subcritical crack growth index, depends on the mechanism of growth, which strongly depends on chemical environment.

One main mechanism of subcritical crack growth is stress corrosion by hydrolytic weakening, wherein a silicate bond is weakened by interaction with water. When water interacts with a Si-O-Si bond, two silanol groups are formed, Si-OH HO-Si, resulting in a much weaker bond. This process occurs at crack tips, allowing the crack to further propagate and clearing the way for water to interact with the next set of bonds [Brunner et al., 1961]. Other less well-characterized mechanisms of subcritical crack growth are dissolution, diffusion and microplasticity [Atkinson, 1984].

2.2.2 Shear cracks

In the presence of a deviatoric stress, shear cracking can be initiated. Shear cracking initiates when a critical shear stress is reached. The critical shear stress, τ_{crit} , is described by Mohr-Coulomb failure theory,

$$\tau_{crit} = c + \sigma \tan \phi \quad (1.11)$$

where τ_{crit} is the critical shear stress, c is the cohesion, σ is the effective normal stress and ϕ is the friction angle. Because critical shear stress is a function of effective stress, high pore pressure values can result in arbitrarily low critical shear stress. Shear failure along a preexisting crack occurs following the same criterion, without the cohesion.

$$\tau_{crit} = \sigma \tan \phi \quad (1.12)$$

Pre-existing cracks are present in all materials and when they are oriented at an angle to loading, shear stresses are induced sometimes causing rupture.

Chemical interaction plays a role in frictional processes involved in shear cracking and slip. It is often assumed that the frictional coefficient of crustal rocks is between 0.6 and 0.85 as characterized by Byerlee's canonical 1968 paper [Byerlee, 1968]. However, these values were derived from dry rocks. As soon as even a small amount of water is introduced to the system, frictional strength can be dramatically reduced. Water readily adsorbs to the surface of fractures, lowering surface energy and reducing critical stress for sliding [Dunning et al., 1984].

Adsorption of water and reduction of surface energy can play a role in cracking processes as well. It has long been known that the presence of water can lower fracture energy [Orowan, 1944]. This phenomenon has been used to explain water weakening in porous sandstone, the observation that yield stresses are reduced in water-saturated samples compared to dry samples [Baud et al., 2000]. Similar water weakening behavior has been observed in Solenhofn limestone, but the mechanism is less well understood [Rutter, 1974]. It is unclear whether this type of

weakening effect is temperature and/or pressure sensitive. Water weakening in calcite rocks continues to be an active area of research.

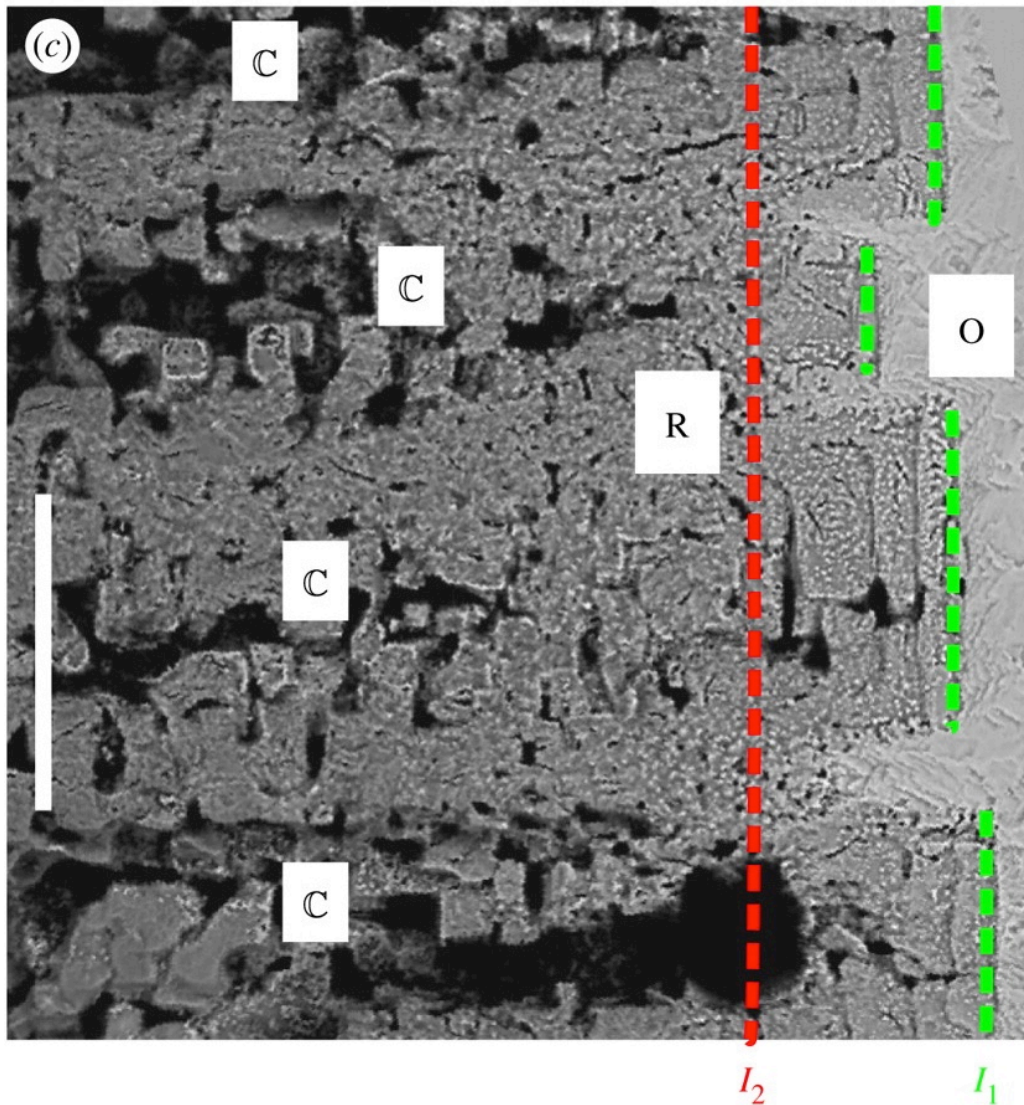
Purely shear cracks do not increase volume. In reality, shear cracks have terminations. Sliding on shear cracks induces tensile stresses at crack terminations that result in positive volume change. This phenomenon is known as wing cracking, and has been explored extensively in theory and experiment [Ashby, 1986; Baud et al., 1996]. Wing cracks are essential to the theory of deformation and failure in materials under compression.

Most Earth materials are under a far-field compressional stress; materials under compression tend to rupture along localized, planar failure surfaces [Rudnicki and Rice, 1975]. Most failures within the Earth are this type of localized, shear failures. The development of shear failure surfaces is progressive. Initial damage tends to be homogeneous, with microcracks formed by Herzian or wing cracking evenly distributed throughout a material. As crack density grows, microcracks begin to interact. Crack density becomes greatest within a damage zone that runs along a plane, the orientation of which is determined by the coefficient of internal friction of the material and the stress orientation. For a standard rock with a coefficient of internal friction of 0.6, this angle is 32° to σ_1 . When the crack density reaches a critical value, the material can no longer remain entire and a throughgoing, macroscopic shear fracture develops, and the material is said to have failed [Lockner et al., 1991; Tamarkin et al., 2012]. After a sample has failed, it can no longer support shear stress. The stress at which this failure occurs is known as the shear strength.

2.2.3 Dissolution

Dissolution is the removal of mass from a solid through chemical solution. It occurs anywhere that a pore fluid is under-saturated in a mineral with which it is in contact. Dissolution rates are sensitive to temperature, pressure and fluid composition. At low temperatures, fluid chemistry is the controlling factor in dissolution rates [Blum and Lasaga, 1988]; At higher temperatures, temperature effects become significant. Because dissolution also leads to evolution of pore fluid chemistry as well as pore geometry, dissolution rates and permeability can be strongly coupled [Andreani et al., 2009].

Figure 1.3. Image of $\text{KCl} \rightarrow \text{K}(\text{Cl},\text{Br})$ reaction front, adapted from Raufaste et al., 2010. Scale bar is 10 microns. Lighter grey material marked O is KCl, darker grey material marked R is $\text{K}(\text{Cl},\text{Br})$. The reaction interface is between the green and red perforated lines I_1 and I_2 . Primary porosity channels produced by the precipitation of $\text{K}(\text{Cl},\text{Br})$ are marked with C. This interface-coupled dissolution-precipitation reaction produces porosity that maintains fluid availability throughout the process.



Dissolution can produce a variety of changes in pore volume and geometry depending on whether it is homogenous or channelized and whether or not it is coupled with precipitation. Homogeneous dissolution occurs when dissolution is transport limited, when dissolved species remain in high concentrations within the solute at the interface with the substrate. The resulting surface morphology is smooth and sometimes undulating [Lasaga and Kirkpatrick, 1981]. Channelized dissolution occurs when dissolution is reaction limited and dissolved species are swiftly carried away from the substrate, leading to crystallographic and morphological control of morphology. The resulting surface morphology is pitted and rough [Lasaga and Kirkpatrick, 1981]. Localized dissolution features can lead to positive feedbacks, resulting in the lengthening of etch pits into quasi-cylindrical dissolution channels, sometimes called wormholes [Fred and Fogler, 1998]. When coupled with precipitation of a new phase or re-precipitation, so-called interface-coupled dissolution-precipitation can produce complex pore geometries, which may play a controlling role in many fluid-rock systems (i.e. Figure 1.3) [Putnis and Putnis, 2007; Raufaste et al., 2007].

3. Research outline

Chapter 1 has introduced the background and concepts necessary for the analyses in this dissertation. In Chapter 2, I will discuss the role of water weakening in porous carbonates, highlighting the role that pressure solution can play in the deformation and permeability evolution of monomineralic rock. Indiana limestone was chosen for this study because of its purity, limiting chemical reactions to the

dissolution and reprecipitation of calcium carbonate. In Chapter 3, I will discuss the effect of carbon dioxide and water on the deformation and permeability evolution of dunites. Again, a nominally monominerallic rock, Twin Sisters dunite, was chosen, but the instability of olivine in the presence of water and carbon dioxide leads to olivine dissolution being coupled with precipitation of secondary minerals, carbonates and hydroxides. In Chapter 4, I go into further detail of the microstructural analysis of experimentally carbonated dunite, with focus on the role of channelized dissolution and secondary mineral precipitation on the physical behavior of the samples. In Chapter 5, I discuss the physical characteristics of naturally carbonated ultramafites, and discuss the role that complex mineralogy can play in the reaction and deformation of ultramafic rocks.

Chapter 2: Effect of temperature and pore fluid on strength of porous limestone¹

2.1. Introduction

Carbonate rocks are an important rheological component of the upper crust. The mechanical behavior of porous carbonate rocks is of particular interest due to the large number of hydrocarbon reservoirs housed in carbonates (Roehl and Choquette, 1985) and seismogenic faults that exist in carbonate-dominated lithologies (Di Toro et al., 2011; Tisato et al., 2012; Tesei et al., 2013; Bullock et al., 2014). Understanding the evolution of the strength and transport properties of porous carbonate rocks under mechanical, thermal and chemical loads has broad implications in reservoir engineering and earthquake mechanics.

Deformation experiments provide quantitative characterization of mechanical behaviors of porous carbonate rocks under hydrothermal conditions (e.g., Heard, 1960; Rutter, 1972, 1974; Fredrich et al., 1989; Renner and Rummel, 1996; Yale and Crawford, 1998; Baud et al., 2000a; Vajdova et al., 2004, 2012; Rinses et al., 2005; Zhu et al., 2010; Cilona et al., 2012; Brantut et al., 2014). The failure modes of porous limestone samples transition from localized shear faulting to distributed cataclastic flow with increasing confining pressure, similar to the brittle-ductile transition observed in porous sandstones (e.g., Wong et al., 1997). At crustal

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temperatures, the inelastic pore volume change could be either dilatant (i.e., pore volume increase) or compactant (i.e., pore volume decrease). Shifts between dilatancy and compaction during deformation are common, which is a manifestation of a complex interplay between creation of new cracks and reduction of existing pore space (i.e., Baud et al., 2000a). In sandstones, the deformation mechanisms are primarily frictional sliding along grain boundaries and Hertzian fractures at grain contacts (e.g., Menendez et al., 1996). Previous studies show that the extensive grain-scale Hertzian fracturing in sandstones is accompanied by a drastic and anisotropic permeability reduction in the cataclastic flow regime (e.g., Zhu and Wong, 1997; Ngwenya et al., 2003; Zhu et al., 2007). In contrast, owing to activity of crystal plasticity and solubility of calcite, deformation of limestones may be strongly influenced by mechanical twinning and pressure solution even at low temperatures (e.g., Turner, 1953; Fredrich et al., 1989; Zhang and Spiers, 2005; Zhang et al., 2010). To date, systematic characterization of permeability change of porous limestones undergoing the brittle-ductile transition is scarce (e.g., Iscan et al., 2006).

The mechanical behaviors of rocks can be strongly modified by the presence of interstitial fluids. It is well established that the strength of rock is generally reduced by the presence of water (e.g., Heard, 1960). Water-weakening is the result of several mechanisms working in concert. Physically, the presence of water tends to embrittle rocks through pressurization and lubrication (e.g., Terzaghi, 1943; Hubbert and Rubey, 1959; Patterson, 1978). Chemically, additional weakening is caused by adsorption of water to grain surfaces and concomitant reduction of surface and fracture energies (e.g., Orowan, 1944; Rehbinder et al., 1948; Lawn, 1993), stress

corrosion (e.g., Atkinson, 1984; Atkinson and Meredith, 1987) and enhancement of diffusional processes such as pressure solution (e.g., Sorby, 1908; Weyl, 1959; Lehner, 1990; Zhang and Spiers, 2005).

The wide variety of water-weakening mechanisms, active over a large range of pressure, temperature and chemical environmental conditions, exerts important controls on brittle, semi-brittle and ductile rock deformation processes. In the brittle faulting regime, interstitial water has been shown to significantly reduce the strength of both low porosity granites and porous sandstones (e.g., Rutter and Mainprice, 1978; Chester and Logan, 1986; Lajtai et al., 1987; Hadizadeh and Law, 1991; Baud et al., 2000b), with some indication that the effect is reduced at higher confining pressures (e.g., Boozer et al., 1963). In the cataclastic flow regime, the presence of water leads to reduction of yield strength for shear-enhanced compaction (Read et al., 1995; Zhu and Wong, 1997; Baud et al., 2000b). At even higher pressures and temperatures, water can promote ductile deformation via crystal plasticity by altering defect chemistry and promoting the nucleation and diffusion of dislocations and other defects (e.g., Kronenberg, 1986; Fischer and Patterson, 1989; Farver and Yund, 1991). To date, the majority of studies on water-weakening focus on silica-dominated rocks; the effect of water on deformation of carbonate-dominated rocks is relatively less well-understood.

Several studies suggest that water can have a strong effect on the mechanical behavior of carbonate rocks. In highly porous chalks, yield strength appears to negatively correlate with activity of water in the pore space (Rinses and Flaageng, 1999; Rinses et al., 2005). A similar trend has been observed in moderate and low

porosity limestones (Rutter, 1972, 1974; Lebedev et al., 2014). Observations from the field, such as the Ekofisk oil field in the North Sea, suggest that water weakening may be pervasive in depleting reservoirs and can lead to field-scale fracturing (Teufel, 1991). It is clear more work is needed to understand the role of water in limestone deformation.

In an active tectonic setting or energy extraction field, the physical properties of porous carbonate rocks are dynamic quantities that evolve with the changing pressure and temperature conditions. To better understand the deformation and failure behaviors of porous carbonate rocks, the coupled mechanical, thermal and chemical processes must be investigated. Could a moderate temperature increase have a significant impact on the strength and inelastic behaviors of porous limestones? If so, what are the mechanisms responsible for such a thermal effect? Does the solubility of calcite play an important role in determining the overall mechanical strength of water-saturated carbonate rocks? To what extent does crystal plasticity such as mechanical twinning in calcite interact with microcracking? How does the permeability of porous limestones evolve during the brittle-ductile transition?

With these questions in mind, we perform triaxial deformation experiments on distilled water-saturated Indiana Limestone samples at a range of temperatures and pressures at reservoir conditions. Concomitant permeability evolution is measured during deformation. We present microstructural analysis of samples after deformation to elucidate the deformation mechanisms. Using a yield cap model (e.g., Rudnicki, 2004) based on bifurcation theory (e.g., Rudnicki and Rice, 1975), we quantify the

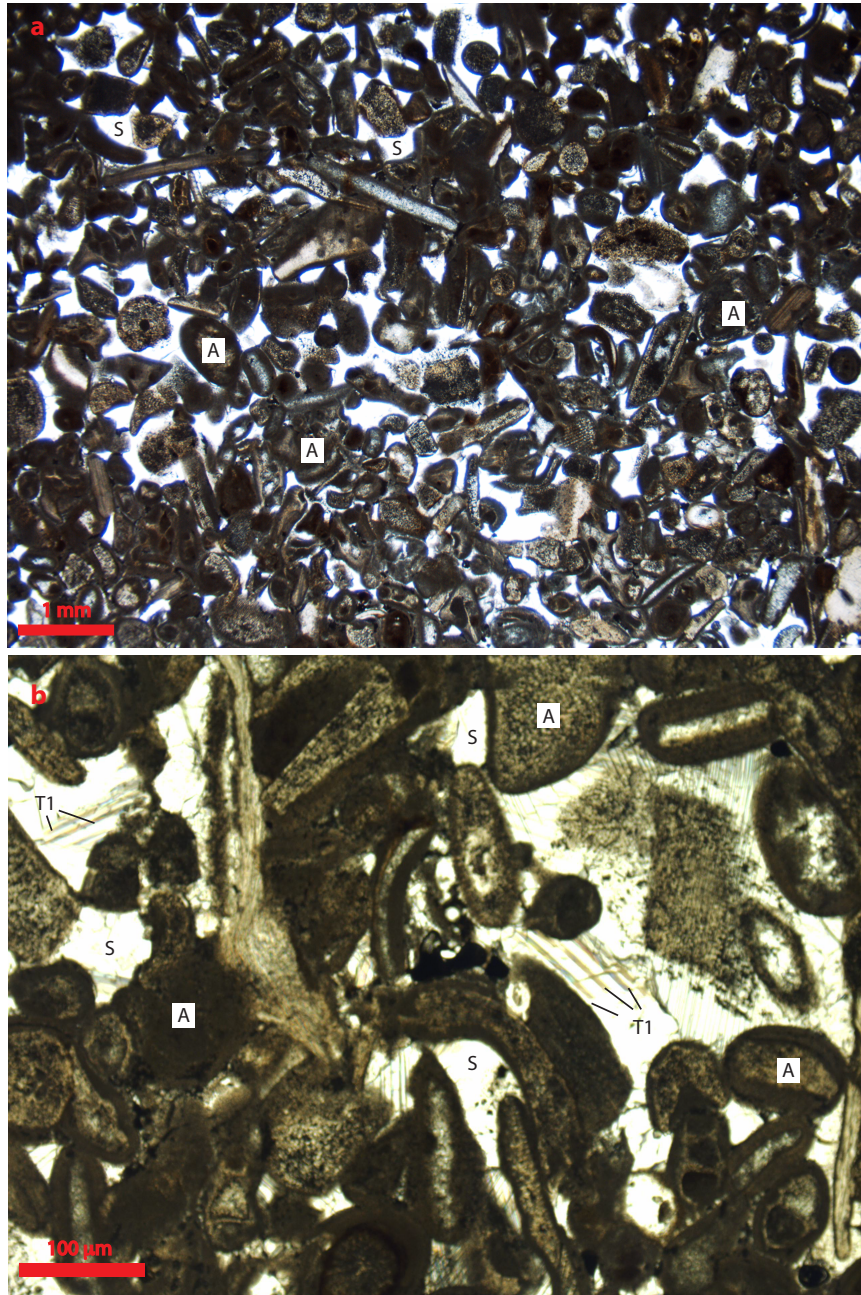
effects of pressure, temperature and pore fluid chemistry on the onset of yield in porous limestone samples.

2.2. *Experimental Procedure*

2.2.1 Sample Preparation

Indiana Limestone is a Mississippian calcarenite limestone from the Bedford-Bloomington locality of Indiana, USA. This limestone is nearly monomineralic, over 98% calcite by volume with ~1% magnesite and trace clay minerals and oxides (Indiana Limestone Handbook, 2007). Because its uniformity and availability, Indiana limestone is widely used in experimental studies. The rock is comprised of allochemical clasts cemented with sparry calcite. Allochemicals consist largely of bryozoan fossils but also include echinoderm and foraminifera fossils (Patton and Carr, 1982); they range in size from 200-2000 μm , and are coated with microcrystalline calcite micrites with much smaller grain size, typically $<5 \mu\text{m}$. Porosity is present both as macro-pores between allochemicals and micro-pores within allochemicals and between allochemicals and epitaxial micrites (Figure 2.1).

Figure 2.1. Optical photomicrographs of undeformed Indiana Limestone. a)
Overview of sample, showing dark fossil clasts and light sparry calcite cement. b)
Fossil clasts are largely undamaged with slight signs of diagenetic pressure solution,
while cement shows few, thick twins. Allochemical clasts are labeled, A. Sparry
calcite cement is labeled, S. High temperature twins are labeled T1.



For this study, blocks of Indiana Limestone were cored perpendicular to bedding and ground into right cylinders of diameter 25.4 mm and length 50.8 mm. Before experimentation, samples were dried in an oven for 48 hours and weighed. Initial porosity and permeability measurements were made using a helium porosimeter and a nitrogen permeameter, resulting in average values of 15.3% and

$1.2 \times 10^{-15} \text{ m}^2$, respectively. Prior to experiments, samples were placed in a vacuum chamber and saturated with distilled water for 24 hours. Porosity of each sample was also calculated using the difference in dry and saturated density; the results are in good agreement with values obtained using a porosimeter (Table 2.1).

All samples are jacketed with thin copper foil of 127 μm thickness. After seating the jacket to the sample at 5 MPa, two electrical resistance strain gages were placed orthogonally in the middle (on the opposite sides) of the sample to measure axial and radial strain. Strain gages have a precision of 10^{-5} .

Table 2.1. Initial permeability (k) and porosity (ϕ) for all samples.

Sample	k	ϕ
Name	mD	%
IndLs3-4b	1.0	16.3
IndLs3-5	0.9	15.9
IndLs 3-6	1.2	16.7

IndLs3-7	1.3	16.8
IndLs 3-8	1.6	16.8
IndLs3-9	1.6	16.7
IndLs3-10	1.5	15.5
IndLs3-12	1.1	15.8
IndLs3-14	0.9	15.8
IndLs3-15	1.5	16.7
IndLs3-16a	1.5	17.4
IndLs3-17	1.2	15.9
IndLs5-2	1.1	15.5
IndLs5-3	1.3	14.5
IndLs5-5	1.3	14.6
IndLs5-6	1.2	15.9
IndLs5-7	1.2	15.7
IndLs5-8	1.3	15.0

2.2.2 Experimental Conditions

Jacketed Indiana Limestone samples were deformed using a conventional triaxial deformation apparatus (NER AutoLab 1500). Data was captured using the integrated AutoLab acquisition system with a sampling rate of 0.5 s^{-1} (2 Hz). Samples were inserted into the pressure vessel and a small confining pressure (~ 2 MPa) was applied to brace the sample. A small pore pressure (~ 1 MPa) was then applied. At this stage, fresh distilled water is flushed through the sample from the pore pressure system, ensuring the initial pore fluid chemistry is pristine. After purging bubbles from the pore fluid system, the confining pressure and pore pressure were raised in sync until the pore pressure reached 10 MPa, at which point it was held

constant at $P_p=10\pm0.1$ MPa during deformation. For hydrostatic compaction, the next step is to raise temperature. For triaxial deformation tests, the confining pressure was raised to a preset value before raising temperature. In our experimental setup, the entire pressure vessel was heated with an external furnace to a chosen temperature. For the temperatures (23-75°C) used in this study, the heating process took ~6 hours, and temperature fluctuation is $\pm 1^\circ\text{C}$ throughout.

For hydrostatic tests, the confining pressure was increased at a rate of 2 MPa/min to a maximum value of 130 MPa. For non-hydrostatic tests, the confining pressure was first raised to a preset value, P_c (20 to 60 MPa), where it was kept constant with a stability of ± 0.1 MPa for the duration of experiments. After a desired temperature was reached, axial load was applied to the sample using a servo-controlled axial piston at a nominal strain rate of 10^{-5} s^{-1} . Differential load was measured using an internal load cell with a precision of 1 kN. The stiffness of the load frame is $\sim 4 \times 10^8 \text{ N/m}$. Permeability measurements were taken in-situ throughout deformations using complex pore pressure transient analysis (Boitnott 1997). This method requires only a very small volume of fluid to be passed through the sample, so there is not expected to be an effect on pore fluid chemistry.

Differential stress was calculated using the load measurements and the cross-sectional area of the sample cylinders. Radial strains were relatively small, so changes in cross-sectional area due to deformation were neglected. Effective mean stress, σ , was calculated using the relation, $\sigma = (\sigma_1 + \sigma_2 + \sigma_3)/3 - P_p$, where $\sigma_{1,2,3}$ are the principal stresses and P_p is the pore pressure. Volumetric strain was calculated using the relation for axisymmetric samples, $\varepsilon_v = 2\varepsilon_{33} + \varepsilon_{11}$, where ε_{33} and ε_{11} are radial

and axial strains, respectively. Volumetric strain was compared to changes in pore volume calculated using the displacement of the servo-controlled pore pressure intensifier piston, with good agreement during the initial stage of tests when solid matrix compressibility is small.

2.2.3 Distilled vs. Equilibrated Pore Fluids

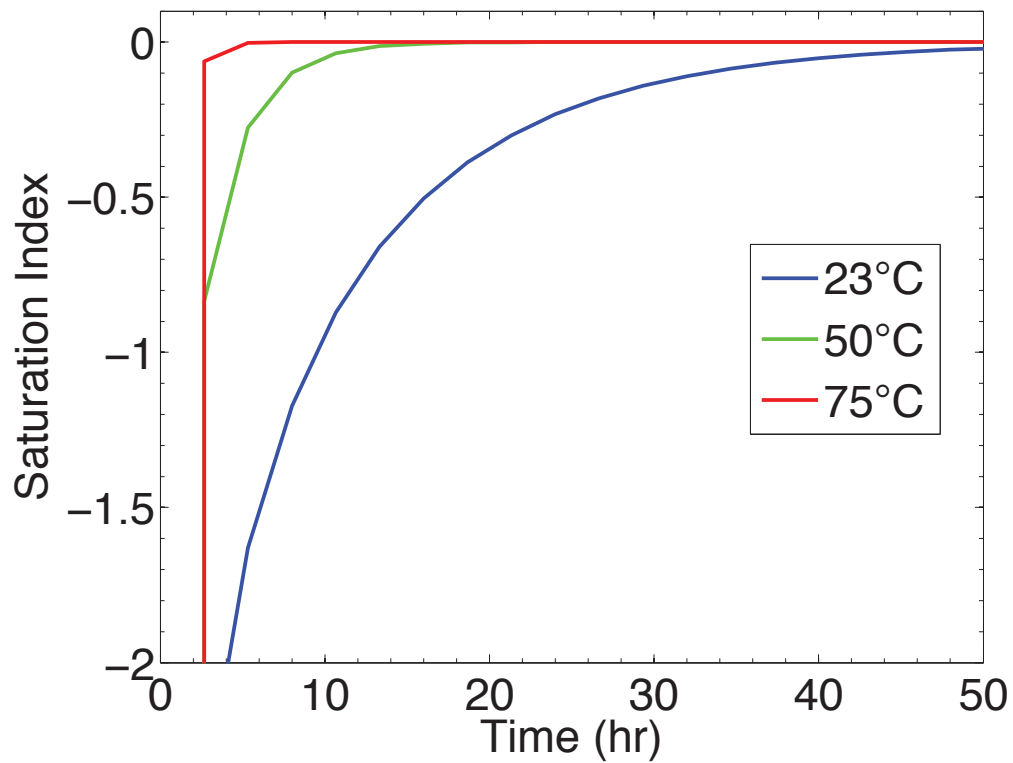
Because of the solubility of calcite in water, we expect an ion exchange between our limestone samples and the distilled water used as pore fluid. The rate of dissolution is expected to be the highest when a sample was first saturated with distilled water, and decreases with time as the ion concentrations in the fluid reaches an equilibrium with the solids in contact.

To investigate the effect of calcite dissolution on mechanical behaviors of porous limestones, we deformed samples at identical pressure and temperature conditions with both “distilled” (PF_0) and “equilibrated” ($\text{PF}_{\text{CaCO}_3}$) pore fluids. For PF_0 experiments, water saturated samples were deformed immediately after desired pressure and temperature conditions were reached. For $\text{PF}_{\text{CaCO}_3}$ experiments, after reaching desired pressure and temperature conditions, water-saturated sample was given an additional 24 hours to allow the pore fluid to equilibrate with the rock sample.

To understand the saturation state of our pore fluid we ran a simple PHREEQC model (Parkhurst, 1995) implementing Plummer et al.’s (1978) temperature dependent calcite dissolution kinetics. The model indicates that pore fluid saturation is reached in 6, 14 and 50 hours for runs at 75, 50 and 25°C

respectively (Figure 2.2). On average, a temperature ramp takes ~3-6 hours and a deformation test lasts ~2-3 hours. This means our PF_0 experiments are run while the pore fluid is still understaturated with respect to calcite and our $\text{PF}_{\text{CaCO}_3}$ experiments at 75°C are well-equilibrated. As such, compared to samples with PF_0 (without the 24 hours equilibrating period), dissolution in samples with $\text{PF}_{\text{CaCO}_3}$ is expected to be greatly reduced during deformation. Comparison of their mechanical behaviors sheds lights on the chemo-hydromechanical coupling in limestone deformation.

Figure 2.2. Calcite saturation index versus time from a PHREEQC model of pore water in a limestone sample at various temperatures. Pore water is saturated with respect to calcite when the saturation index reaches 0. Saturation is reached in 6 hours at 75°C, 14 hours at 50°C and 50 hours at 23°C.



2.2.4 Microstructural Analysis

At the conclusion of experiments, deformed samples were dried and epoxy-impregnated for thin section preparation and microstructural analysis. Impregnated samples were bisected axially and fashioned into double-polished thin sections. Microstructural observation was conducted using a Nikon LV-UEPI petrographic microscope.

2.3. Data

2.3.1 Mechanical Data

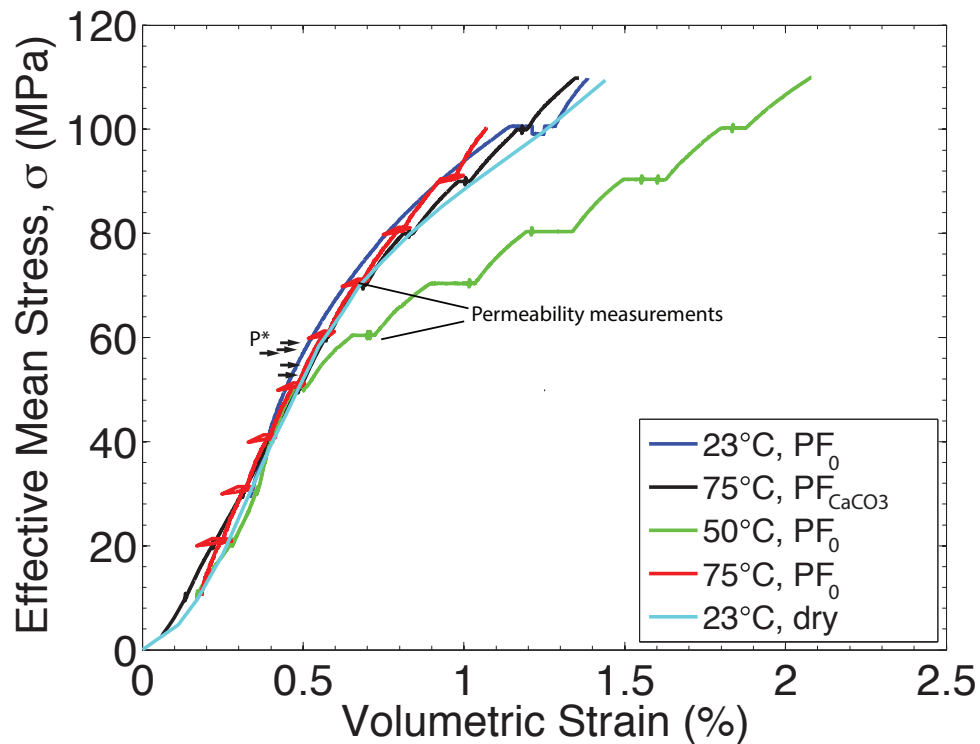
We adopt the convention that compressive stress and compactive strain (i.e. shortening and volume reduction) are positive. For conventional triaxial loading, the maximum and minimum stresses are along the axial and radial directions of the sample respectively, which are referred to as σ_1 and σ_3 (with $\sigma_2=\sigma_3$). Mechanical data is presented as differential stress ($\sigma_1 - \sigma_3$) as a function of axial strain or effective mean stress as a function of volumetric strain. For the purpose of the plastic yield cap analysis, differential stress is converted to equivalent shear stress, τ , using the relation, $\tau = (\sigma_1 - \sigma_3)/\sqrt{3}$, applicable for this loading configuration (e.g., Rudnicki, 2004).

2.3.1.1 Hydrostatic Experiments

Mechanical data from all hydrostatic compaction experiments are presented in Figure 2.3. The behavior of all samples can be generalized to three stages, (1) an initial non-linear compaction with decreasing apparent compressibility, (2) a quasi-linear compaction with constant compressibility and (3) a second non-linear compaction with increasing apparent compressibility. This behavior is typical of porous rocks with two populations of pore space, high aspect ratio micro-cracks that are easily closed at low confining pressure and quasi-spherical pores that are susceptible to collapse at higher confining pressures (e.g., Walsh, 1965). The beginning of the third stage of compaction indicates the initiation of plastic

deformation and pore collapse, and can be referred to as the grain crushing pressure or, P^* (e.g., Wong et al., 1997).

Figure 2.3. Effective mean stress versus volumetric strain during hydrostatic deformations at various temperatures. All samples show similar hydrostatic compaction behavior. The grain crushing pressure, P^* , is marked for each sample with an arrow, which represents the onset of plastic yield for hydrostatic deformation.



Our data (Figure 2.3) are consistent with Indiana Limestone compaction behavior from the literature (Rutter, 1974; Vajdova et al., 2004, 2012). The hydrostatic compaction curve for the sample saturated with distilled water at 23°C exhibits typical behavior with crack closure at 10 MPa, a bulk modulus of 21.0 GPa and a grain crushing pressure of 56.2 MPa. The sample hydrostatically compacted at

50°C exhibits a crack closure pressure of 10 MPa, a bulk modulus of 20.5 GPa, and grain crushing pressure of 52.1 MPa. The sample compacted at 75°C shows a bulk modulus of 21.2 GPa and a slight reduction of grain crushing pressure to 50.0 MPa. A modest increase in temperature does not affect the bulk modulus of the material, but appears to have a discernable if small effect on the onset of plastic compaction.

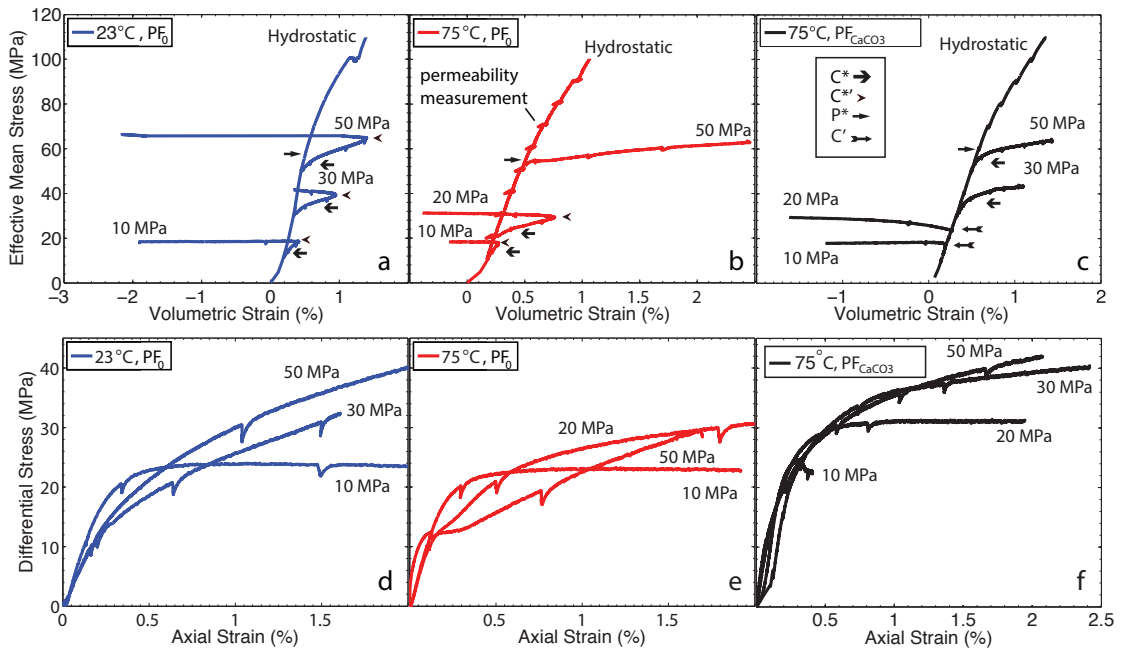
2.3.1.2 Deformation Experiments with PF_0

Triaxial deformation tests were performed at 23, 50 and 75°C and 10, 20 and 50 MPa effective pressures, $P_e = P_c - P_p$, where P_c and P_p are the confinement and pore pressure, respectively (Table 2.2). Deformation behavior of porous rocks can generally be separated into four stages (e.g., Wawersik and Brace, 1971; Lockner et al., 1992): (1) a stage of non-linear shortening with decreasing apparent compliance, (2) a stage of linear shortening, (3) a second non-linear stage with increasing apparent compliance during which the sample may or may not reach a peak stress followed by (4) strain softening or hardening (Figure 3). These stages correspond to (1) crack closure (Walsh, 1965), (2) quasi-elastic deformation, (3) initiation of plastic deformation which may include microcracking, crystal plasticity or both and (4) failure and post-failure.

At low confining pressures, samples often fail by localized brittle faulting, with dilatancy preceding the failure (e.g., Brace, 1978); the onset of dilatancy is referred to as C' (Figure 2.4c). At higher confining pressures, porous samples tend to fail by compactive cataclastic flow (e.g., Vajdova et al., 2004); the onset of this deformation stage can be seen clearly in the effective mean stress-volumetric strain

plot (Figures 2.4a-c) as the point at which the deformation curve deviates from the linear quasi-elastic behavior, and is referred to as C^* (e.g., Baud et al., 2000a). Because the volume reduction in triaxial deformation tests is greater than the hydrostatic compaction at a given effective mean stress, this phenomenon is called shear-enhanced compaction (Curran and Carroll, 1979; Wong et al., 1997). Because compaction is limited by existing void space, compactant cataclasis will eventually transition to dilatant cataclasis, represented by a change from a positive to a negative slope in effective mean stress-volumetric strain space; this transition is denoted as $C^{*'}$ (e.g., Baud et al., 2000a).

Figure 2.4. Mechanical data. Effective mean stress versus volumetric strain for samples deformed at a) 23°C with PF_0 , b) 75°C with PF_0 , and c) 75°C with $\text{PF}_{\text{CaCO}_3}$. Differential stress versus axial strain for samples deformed at d) 23°C with PF_0 , e) 75°C with PF_0 , f) 75°C with $\text{PF}_{\text{CaCO}_3}$. The onset of dilation is marked as C' . The onset of shear-enhanced compaction is marked as C^* and the onset of dilation thereafter is marked as $C^{*'}.$ The grain crushing pressure is marked as P^* . Samples show enhanced compaction as effective pressure increases. Elevated temperature appears to enhance hardening at elevated pressure.



Differential stress data as a function of axial strain for PF_0 experiments at 23°C are presented in Figure 2.4d. Effective mean stress data from these experiments are plotted as a function of volumetric strain accompanied by a hydrostat for reference in Figure 2.4a. All samples at this temperature failed by distributed deformation, with the onset of shear-enhanced compaction, C^* , following soon after

application of deviatoric stress. Strain hardening and the transition from shear-enhanced compaction to shear-enhanced dilation are observed in all samples. As effective pressure increases from 10 to 50 MPa, the overall volume reduction following C^* increases from $<0.5\%$ to $\sim 1.5\%$. While the inelastic and failure behaviors of water-saturated samples are qualitatively similar to those deformed at nominally dry conditions, at the same effective pressures, both C^* and $C^{*'} in water-saturated samples are significantly lower compared to those reported for dry samples (Vajdova et al., 2004). The apparent water-weakening has been reported in fine-grained Solnhofen Limestone at low to moderate temperatures (e.g., Baud et al., 2000a; Xiao et al., 2003), whereas water has little effect on the strength of Cararra Marble at temperature above 600°C (de Bresser et al., 2005).$

Systematic changes in mechanical behavior are observed in distilled water-saturated samples at elevated temperature. The stress-strain curves of PF_0 samples deformed at 75°C and effective pressures of 10, 30, and 50 MPa are presented in Figure 2.4e. Effective mean stress data from these experiments are plotted as a function of volumetric strain accompanied by a hydrostat for reference in Figure 3b. All samples failed by distributed deformation. The sample deformed at 10 MPa effective pressure shows very slight shear-enhanced compaction before beginning to dilate. The amount of strain softening is negligible as the sample is deformed to up to 2% of axial strain. The sample deformed at 20 MPa effective pressure exhibited shear-enhanced compaction, strain hardening and the transition to shear-enhanced dilation. The transition from compaction to dilation occurred at 0.8% volumetric strain. At 50 MPa, the highest effective pressure used in this study, the sample failed

by compactive cataclastic flow only, with no transition to shear-enhanced dilation observed. Moderate increases in temperature result in considerable reduction of yield strength.

2.3.2 Permeability Evolution in PF_0 Experiments

Permeability data was gathered in-situ throughout all experiments. Permeability data are presented in Figure 2.5. All samples show a monotonic permeability reduction during deformation. In all samples, the largest decrease in permeability occurs in the first $<0.2\%$ axial shortening, likely due the closure of pre-existing void space. As deformation progresses, permeability continues to decrease and up to 1 order of magnitude total permeability reduction is observed.

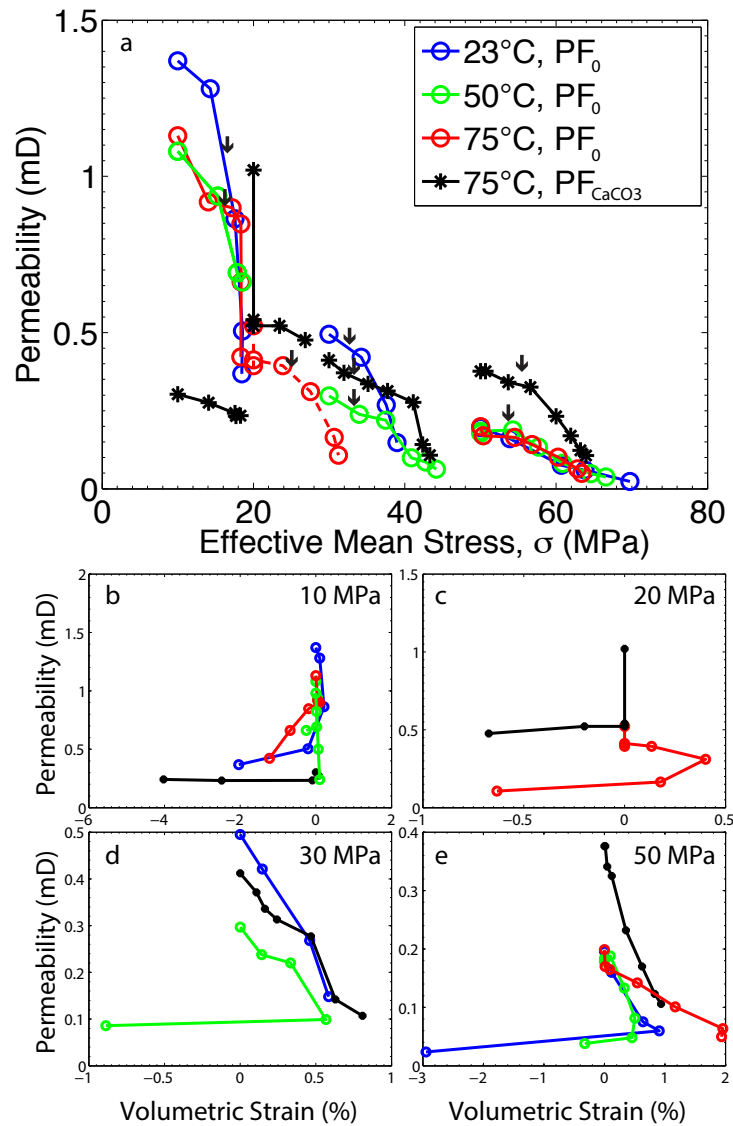
Table 2.2. Elastic moduli and plastic parameters for all experiments

Name	Temp °C	Pressure MPa	Fluid	C' σ MPa	C' DS MPa	C* σ MPa	C* DS MPa	K GPa	E GPa	ν	μ	β	h_{min}/E
IndLs3-4b	23	H	PF ₀	--	--	56.2	0	11.4	--	--	--	--	--
IndLs3-5	23	30	PF ₀	--	--	34.0	10.1	--	10.0	0.11	-0.20	0.08	-0.07
IndLs3-6	50	20	PF ₀	--	--	25.1	13.6	--	18.1	0.20	-0.18	0.02	-0.07
IndLs3-7	75	20	PF ₀	--	--	24.4	11.4	--	10.1	0.16	-0.33	0.08	-0.05
IndLs3-8	75	10	PF ₀	--	--	16.9	18.8	--	10.2	0.25	0	0.04	-0.09
IndLs3-9	23	50	PF ₀	--	--	52.3	5.2	--	12.4	0.15	-0.27	-0.03	-0.05
IndLs3-10	23	10	PF ₀	--	--	16.4	17.1	--	11.0	0.16	0	0.23	-0.10
IndLs3-12	50	30	PF ₀	--	--	34.6	12.0	--	8.2	0.17	-0.23	-0.04	-0.06
IndLs3-14	50	50	PF ₀	--	--	51.6	2.8	--	12.0	0.23	-0.40	0.02	-0.04
IndLs3-15	75	H	PF ₀	--	--	50.0	0	12.2	--	--	--	--	--
IndLs3-16a	50	H	PF ₀	--	--	52.1	0	11.8	--	--	--	--	--
IndLs3-17	75	50	PF ₀	--	--	--	--	--	--	--	--	--	--
IndLs5-2	50	10	PF ₀	--	--	15.9	17.9	--	17.4	0.21	0	0.49	-0.13
IndLs5-3	75	10	PF _{CaCO3}	21.6	17.3	--	--	--	16.0	0.23	-0.03	0.45	-0.12
IndLs5-5	75	H	PF _{CaCO3}	--	--	57.5	0	12.2	--	--	--	--	--
IndLs5-6	75	30	PF _{CaCO3}	--	--	34.8	14.6	--	15.5	0.15	-0.03	-0.13	-0.06
IndLs5-7	75	20	PF _{CaCO3}	25.4	15.7	--	--	--	13.9	0.20	-0.07	0.42	-0.11
IndLs5-8	75	50	PF _{CaCO3}	--	--	52.8	8.6	--	17.5	0.19	-0.34	-0.21	-0.04

Effective mean stress, σ , at C'; differential stress at C'; effective mean stress, σ , at C*; differential stress at C*; bulk modulus, K; Young's modulus, E; Poisson's ratio, ν ; coefficient of internal friction, μ ; dilatancy factor, β ; and hardening modulus, h_{min}/E . C* values listed for hydrostatic experiments are P*.

Figure 2.5. Permeability data. a) Permeability versus mean effective stress.

Permeability is reduced with increasing stress. The onset of shear enhanced compaction, C^* , is marked with an arrow. Permeability versus volumetric strain at b) 10 MPa, c) 20 MPa, d) 30 MPa, and e) 50 MPa effective pressure. Permeability is reduced even as samples dilate.



Samples deformed at low effective pressures start with higher initial permeabilities, but experience larger drops in permeability during deformation. Samples deformed at higher effective pressures start at lower permeabilities and show smaller drop in permeability. While the permeability values at the beginning of the deformation test vary from 0.2 to $1.4 \times 10^{-15} \text{ m}^2$, the variation in permeability of deformed samples at the end of deformation tests became much smaller, from 0.1 to $0.3 \times 10^{-15} \text{ m}^2$.

Samples undergone the shear-enhanced dilation do not exhibit an associated increase in permeability, indicating that stress induced microcracks do not form an effective flow network within the sample (Zhu and Wong, 1996).

2.3.3 Experiments with PF_{CaCO3}

The apparent thermal weakening observed in triaxial deformation experiments (Figure 2.4) is intriguing. Usually, thermal influences are linked to enhanced crystal plasticity at high temperatures. Because the temperature increase is moderate in this study, it is more likely that the coupling between thermal state and pore fluid chemistry plays an important role.

To address this issue, we ran an additional suite of experiments at 75°C with time (24 hours) to allow the pore fluid to equilibrate with the rock matrix. Data from the hydrostatic compaction experiment with equilibrium pore fluid is presented in Figure 2.3 with hydrostats from the PF₀ and dry experiments for comparison. With equilibrium pore fluid, the hydrostatic compaction at 75°C has a bulk modulus of 21.4 GPa and a grain crushing pressure of 57 MPa at 0.6% volumetric strain, much

stronger than the mechanical behavior of the sample deformed at the same temperature with PF_0 . This result suggests that the observed reduction in grain crushing pressure with increasing temperatures is likely facilitated by solution transfer rather than a direct thermal-mechanical effect.

Comparison of samples allowed to equilibrate with pore fluid for 24 hours (i.e., PF_{CaCO_3}) at 75°C to samples deformed immediately upon reaching pressure and temperature conditions (i.e., PF_0) bears several noteworthy observations (Figure 3). Effective mean stress data as a function of volumetric strain and the stress-strain curve for PF_{CaCO_3} experiments deformed at 4 different effective pressures at 75°C are presented in Figures 2.4c and 2.4f respectively. Samples deformed at both 10 and 20 MPa effective pressures show shear-induced dilation. After C', strain softening behavior is observed in the sample deformed at 10 MPa, with a peak stress of 24 MPa and a post-peak stress drop of 3 MPa. This result suggests that samples deformed with PF_{CaCO_3} exhibit an enhanced brittleness at the same pressure and temperature conditions, though no macroscopic localized shear bands are observed in any of the samples deformed at 75°C with PF_0 . The amount of strain softening is negligible in the sample deformed at 20 MPa effective pressure (Figure 2.4b), similar to the inelastic behavior of the sample deformed at 10 MPa with disequilibrium pore fluid (Figure 2.4d). Samples deformed at 30 and 50 MPa effective pressure with equilibrium pore fluid both exhibit shear-enhanced compaction with no transition to dilation.

The yield strength of samples deformed with PF_{CaCO_3} is markedly stronger. Samples deformed with equilibrium pore fluid also exhibit more dilatancy: For

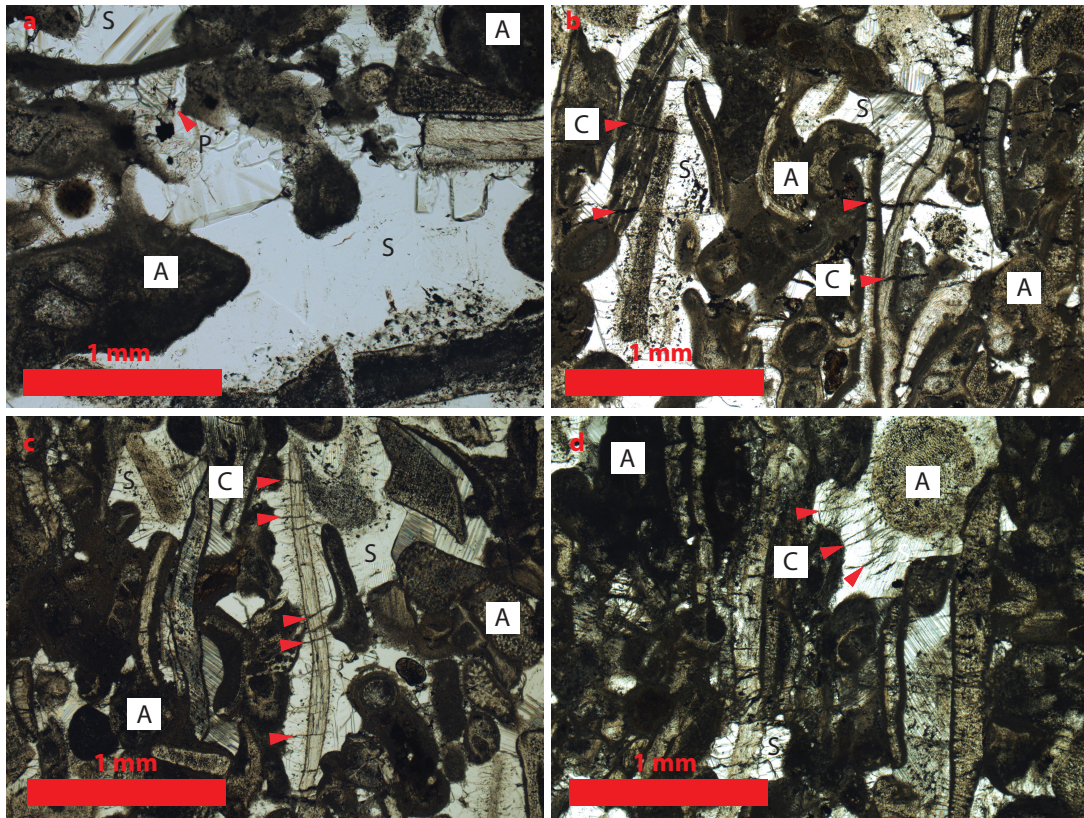
example, at 20 MPa effective pressure, the sample saturated with disequilibrium pore fluid shows a period of shear-enhanced compaction prior to dilatancy while the sample saturated with equilibrium pore fluid dilates immediately following C'. In all instances, the equilibrium pore fluid-saturated samples are stronger and more dilatant.

There is no significant difference in the permeability evolution of samples deformed with equilibrium pore fluid and disequilibrium pore fluid (Figure 2.5), consistent with previous observations that the stress-induced microcracks are not effective fluid paths in porous sedimentary rocks.

2.3.4 Microstructural Observations

The fabric of undeformed Indiana Limestone classifies it as a calcite-cemented grainstone (Dunham, 1962). There is no mud in the rock and the clasts were not bound together before induration. Figure 2.1 illustrates an undeformed sample. Allochems make up the bulk of the rock and are often surrounded by micrites. The space between allochemical clasts is partially filled with sparry calcite cement. Macropores exist within calcite cement while micropores are generally found within allochems and within micrite rims. There is some textural evidence of slight deformation during burial and diagenesis. Allochems can be seen indenting one another, indicating some degree of pressure solution. There is some initial density of twins in the sparry calcite cement. These twin tend to be relatively thick ($>>1\text{ }\mu\text{m}$), suggesting that they are twin type II following Burkhard's (1993) classification, and indicating nucleation at elevated temperatures ($>150^{\circ}\text{C}$).

Figure 2.6. Photomicrographs from experiments at 23°C, for samples deformed a) hydrostatically; b) at 10 MPa; c) at 30 MPa; and d) at 50 MPa effective pressures. In the hydrostatic sample, little damage is observed, few twins, some radial cracks around pore space as highlighted by the red arrow. In the deformed samples, microcracks are subparallel to the maximum principal stress σ_1 , which is horizontal. As the effective pressure increases, the aperture of microcracks (marked by red arrowheads) decreases, and the density of microcracks increases. Allochemical clasts are labeled, A. Sparry calcite cement is labeled, S. Mechanical twins become thinner and more numerous in samples deformed at higher effective pressures.



Microstructures from samples deformed with PF_0 show microcracking and mechanical twinning are both operative at all experimental conditions explored in this study (Figure 2.6). The hydrostatically deformed sample shows relatively little damage in forms of microcracking or mechanical twinning (Figure 2.6a). Sparry calcite remains generally untwinned and the twins that do exist are likely pre-existing due to their type II morphology. Twins at room temperature are more likely to be type I twins with thicknesses $<1\ \mu\text{m}$ (Burkhard, 1993), which can be seen clearly in deformed samples. The damage apparent in the hydrostatically deformed sample is the radial microcracks surrounding pre-existing pores. This damage was mostly likely incurred as the sample was stressed beyond its grain crushing pressure, leading to inelastic pore collapse (Walsh, 1965; Baud et al., 2000a). Microcracks that form due to this process do not show a preferred orientation, but rather follow local stress fields related to pore space and impinging grains.

Microcracking plays a much more important role in deformed samples. The sample deformed at 10 MPa effective pressure contains microcracks oriented subparallel to the maximum principal stress σ_1 direction (Figure 2.6b). Microcracks propagate both along grain boundaries and through allochemical clasts. Grain boundary cracks may lead to grain boundary sliding, grain rotation and the development of wing cracks (e.g., Brace et al., 1966).

Sparry calcite cement exhibits more type I twins in deformed samples (Figures 2.6b-d) than undeformed (Figure 2.1) or hydrostatically compacted samples (Figure 2.6a). Orientation of twins is controlled by the crystallographic structure. No preferred orientation in twinning is observed. However, twins appear to relate to the

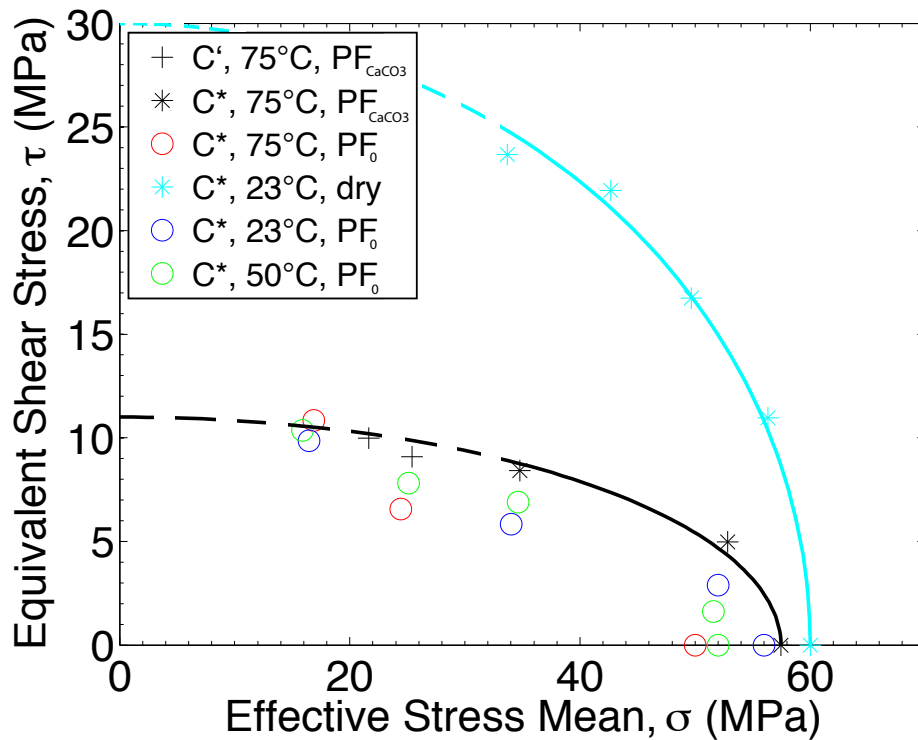
geometry of grains surrounding the cement (Figure 2.6), suggesting that they are induced by shear stresses imposed due to grain sliding and rotation. At 30 MPa effective pressure, twins and microcracks are also observed (Figure 2.6c). Microcracks appear to be narrower and more closely spaced and twin density has increased. At 50 MPa effective pressure twinning appears to be the dominant deformation mechanisms (Figure 2.6d). Most patches of calcite cement are extensively twinned and twin density is extremely high. Microcracks, where present, nucleate at areas of stress concentration such as grain-grain contacts and their orientation sometimes deviates from subparallel to the principal stress axis.

Inelastic compaction in all deformed samples is associated with pore collapse. Microporosity within allochems remains largely intact, in fact most allochems remain largely undamaged with the exception of microcracks that have nucleated in calcite cement and propagated through clasts and possibly some Hertzian contacts. Stress concentrations near the irregular macroporosity result in focused damage and comminution that lead to pore collapse. This is in good agreement with mechanical data that shows failure by shear-enhanced compaction. Microcracks do not appear to be interconnected, but rather contribute to pore collapse and reduction of pore interconnectivity, leading to the observed permeability reductions. The transition from microcrack dominated strain accommodation to mechanical twin dominated strain accommodation with increase in confining pressure is consistent with the increased energetic cost of opening new porosity against elevated pressure, as crystal plasticity along twin planes does not involve a change in volume.

2.4. Discussion

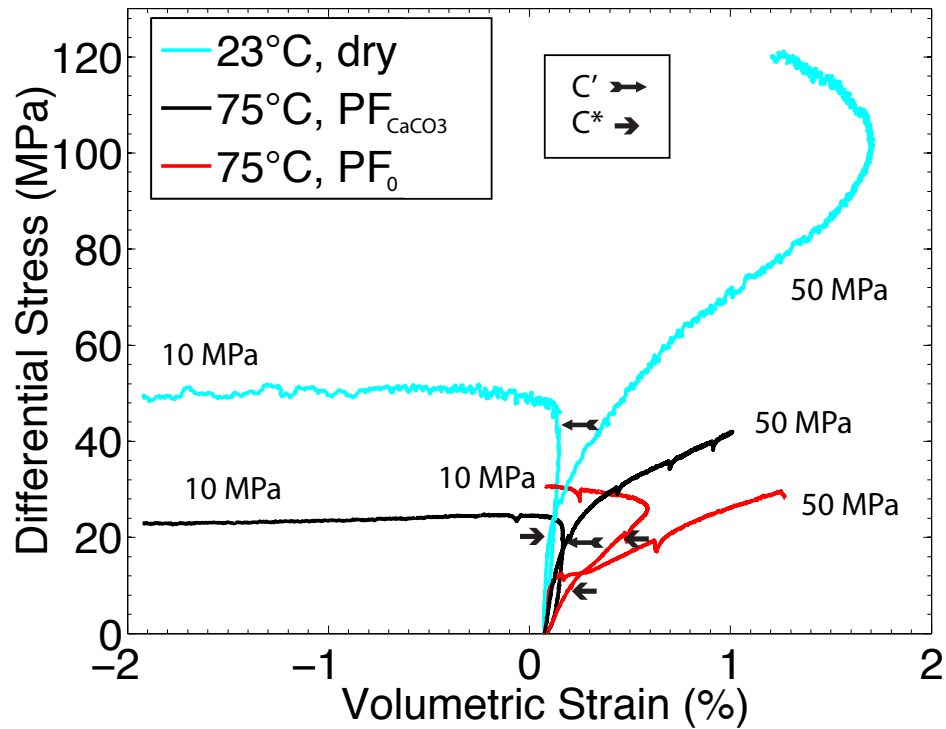
To quantify the effect of pore fluid saturation and temperature on the failure behavior of Indiana Limestone we adopt the elliptical yield cap model of Rudnicki (2004), wherein an initial yield surface is defined in shear stress-normal stress domain to represent the onset of shear enhanced compaction in critically stressed materials. We plot the onset of shear enhanced compaction, or C^* , from each experiment and draw best fit ellipses through the points. The effective mean stress at C^* is obtained from the experiments (Figure 2.4) and the equivalent shear stress is deduced from the differential stress as $\tau = (\sigma_1 - \sigma_3)/\sqrt{3}$, for axisymmetric samples (Rudnicki and Rice, 1975). Fitting elliptical caps through C^* s for dry samples (Vadjova et al., 2004) deformed at 23°C, as well as for the samples saturated with $\text{PF}_{\text{CaCO}_3}$ at 75°C is straightforward (Figure 2.7). In comparison, attempts to fit elliptical caps over stress states of C^* in samples saturated with PF_0 are inconclusive due to persisting large discrepancies. It is possible that such discrepancy is a manifestation of the solution transfer operated during deformation of these samples. More data are needed to elucidate the yield criteria for rocks under chemo-mechanical deformation.

Figure 2.7. Plastic yield caps. Open circles represent the onset of shear-enhanced compaction in PF_0 -saturated experiments from this study. Blue circles are 23°C, green circles are 50°C and red circles are 75°C. Black asterisks represent the onset of shear-enhanced compaction in $\text{PF}_{\text{CaCO}_3}$ -saturated experiments from this study. Black crosses are the onset of dilatancy in $\text{PF}_{\text{CaCO}_3}$ -saturated experiments. Cyan asterisks are dry data from Vajdova et al. (2004) for comparison. Lines are best-fit ellipses for the data based on an elliptical yield cap model (after Rudnicki, 2004). Yield strength for water-saturated limestone is drastically reduced compared to that of dry samples. Within the range explored in this study, effect of temperature on the yield strength is due to change in solubility.



Comparison of experiments performed with different pore fluids indicates that there are at least two effects contributing to enhanced deformation of porous limestone rocks at hydrothermal conditions: pressure solution and stress corrosion. Comparing volumetric strain versus differential stress data of dry samples to data from fluid-saturated samples (Figure 2.8), it is clear that pore fluid both reduces the strength of the limestone and promotes compaction. The samples saturated with PF_0 show the greatest amount of compaction owing to the additive effects of pressure solution and stress corrosion, with the stress corrosion acting to promote crack growth and pore collapse and the pressure solution removing material from high normal stress contacts and re-depositing it in void space. The samples saturated with PF_{CaCO_3} also show enhanced compaction compared to dry data, but not to the same degree as the PF_0 . This may be due to competing pore volume reduction due to pore collapse and pore volume increase due to stress corrosion-enhanced microcracking.

Figure 2.8. Differential stress versus volumetric strain. Data are from two sets of experiments, at 10 MPa and 50 MPa effective stress, respectively. The onset of dilation is marked as C'. The onset of shear-enhanced compaction is marked as C*. Elevated effective pressure promotes compaction. Pore fluid-saturation leads to dramatic enhanced compaction behavior compared to dry samples. Most samples fail by strain hardening. One sample at 10 MPa effective pressure and saturated with $\text{PF}_{\text{CaCO}_3}$ exhibits strain softening failure.



2.4.1 Effect of Temperature

To quantify the mechanical behavior of Indiana Limestone under hydrothermal conditions, we have compiled several elastic and plastic constitutive parameters for each experiment. These data are presented in Table 2.2. We calculate

Young's Modulus, E , as the slope of the differential stress-axial strain curve during the linear elastic portion of deformations, $E = d(\sigma_1 - \sigma_3)/d\varepsilon_a$. The bulk modulus is the slope of the volumetric strain versus effective mean stress for hydrostatic deformation, $K = d\sigma/d\varepsilon_v$. Poisson's Ratio, ν , is the negative ratio of radial strain to axial strain during the elastic portion of the deformation, $\nu = -\varepsilon_r/\varepsilon_a$. The coefficient of internal friction, μ , is the slope of the yield surface in stress space, $\mu = d\tau/d\sigma$. The dilatancy factor, β , is the slope of the tangent of the equivalent shear strain-volumetric strain curve, $\beta = d\phi/d\gamma$, where equivalent shear strain, γ , is equal to the second invariant of the deviatoric strain tensor (Rudnicki, 2004). The hardening modulus, h/E , is the amount of hardening the sample exhibits post-yield, $\frac{h}{E} = \frac{(\mu-\beta)^2}{18(1-\nu)} - \frac{1}{36}(\beta + \mu + 3N)^2$, where N is $1/\sqrt{3}$ for axisymmetric samples (Rudnicki and Rice, 1975).

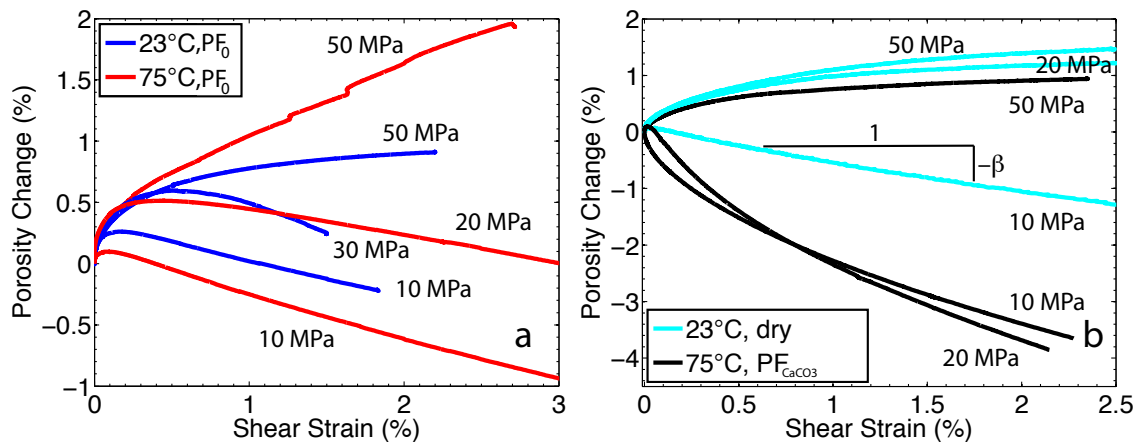
The dilatancy factor, β , is an excellent measure of the transition from dilatant to compactive cataclastic failure as it transitions from positive to negative values as confining pressure increases. Volumetric-shear strain curves for PF₀ samples deformed at room temperature and 75°C are presented in Figure 8a. At room temperature, as confining pressure increases from 10 MPa to 30 MPa, the initial β after yield is reduced from a value of 0.23 to 0.08. As deformation continues after yield, the value of β continues to evolve, first increasing as the sample softens, then decreasing as the sample hardens. When the confining pressure is further increased to 50 MPa, the value of β transitions to negative, indicating a transition from dilatant to compactive cataclasis. Initial β has a slightly negative trend with temperature, suggesting that compactive deformation mechanisms are enhanced at elevated

temperature. Volumetric-shear strain curves for $\text{PF}_{\text{CaCO}_3}$ samples deformed at 75°C and dry data are presented in Figure 2.9b. Fluid saturated samples exhibit greater dilatancy than dry samples, possibly due to stress corrosion induced microcracks.

It is noteworthy that quantifiable changes in the mechanical behavior of limestone can be induced by such a modest increase in temperature. Although variations in mechanical parameters are small, the behavior is systematic. Some variation in sample properties may be attributed to variability among natural samples, but consistent trends in mechanical behavior are not likely to be caused by this effect.

Figure 2.9. Porosity change as a function of shear strain for samples deformed at a) 23 (blue) and 75°C (red) with PF_0 , and b) dry (cyan) and 75°C (black) with $\text{PF}_{\text{CaCO}_3}$.

Effective pressures are marked next to curves. The slope of the tangent of these curves after the first inflection point is taken to be $-\beta$, the negative of the dilatancy factor. Samples generally transition from exhibiting more dilatancy at low effective pressure, to compaction at high effective pressure.



The main mechanisms accommodating deformation within the conditions we explored are microcracking, mechanical twinning and pressure solution.

Microcracking and mechanical twinning are known to be insensitive to temperature variations in this range (e.g. Rowe and Rutter, 1990), so it is likely that the observed behavior is due to pressure solution. There are significant changes in both ultimate solubility (e.g. Ellis, 1963) and dissolution rate (e.g. Sljoberg and Rickard, 1984) of calcite within the range of temperatures we explored. Changes in the saturation state of the pore fluid engender changes in the driving force for pressure solution (e.g. Lehner, 1990). Changes in the behavior of the samples at different temperature may be related to interplay between calcite solubility, dissolution rate and experimental duration.

2.4.2 Effect of Solubility

Samples allowed to equilibrate with pore fluid for 24 hours before deformation are stronger and exhibit more dilation than samples deformed upon thermal equilibration. Yield caps for samples at 75°C saturated with equilibrium and disequilibrium fluid are presented in Figure 2.7. One explanation for this observation is that the samples densify during the equilibration period; however, this is unlikely because the sample equilibrated at the highest temperature and pressure, where we would expect the most creep, compacted less than 0.1% during the hold period. The grain crushing pressure of the sample saturated with $\text{PF}_{\text{CaCO}_3}$ at 75°C is 57.5 MPa, or 96% of the grain crushing pressure of dry Indiana Limestone (Vajdova et al., 2004);

whereas the grain crushing pressure of the sample saturated with PF_0 at 75°C is 50.0 MPa, 83% that of dry Indiana Limestone.

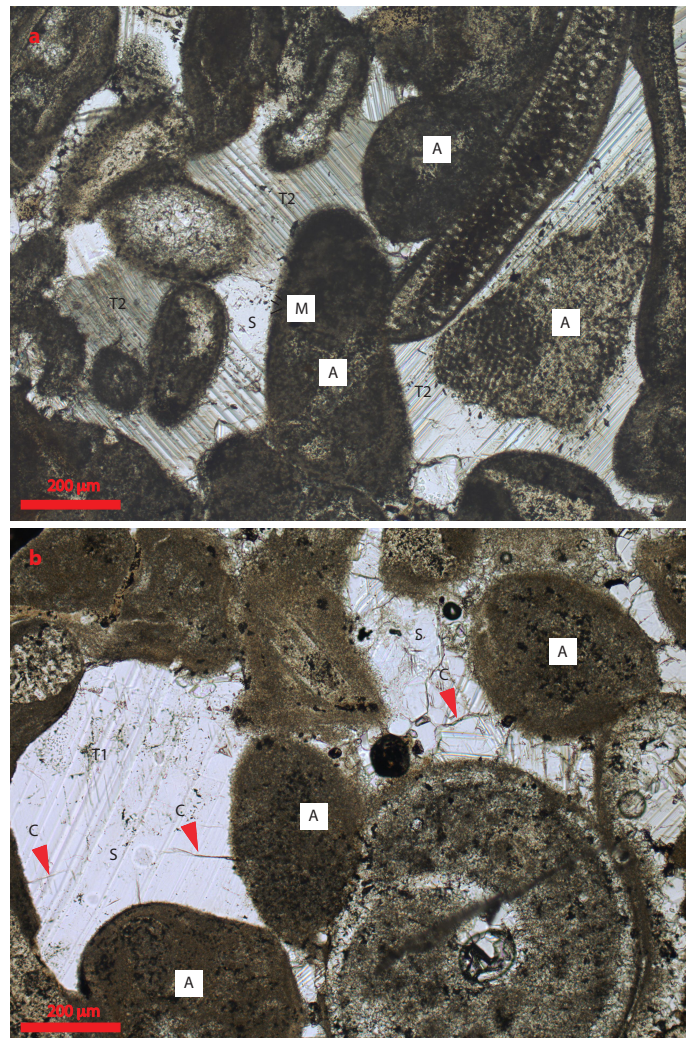
The deviation in strength of samples saturated with different fluids is greater at higher effective pressure. This implies that this chemical weakening mechanism plays a more dominant role at higher pressure. Microcracking and mechanical twinning are the two dominant deformation mechanisms in these samples, twinning being the more important of the two at elevated pressure. It is possible the chemical weakening mechanism is related to the interaction of pore fluid and crystal plasticity.

The interactions between microcracking and mechanical twinning are complex. Twins can result in geometrical mismatches, which concentrate stress and induce microcracks. Stresses at crack tips can cause mechanical twins. Twinning can relax stress and inhibit cracking. The most well-documented way water interacts with these processes is through stress-corrosion at crack tips (Atkinson, 1984; Atkinson and Meredith, 1987), but it is unclear the role water plays in mechanical twinning other than the ways it interacts with microcracking.

Microstructural comparison of samples saturated with equilibrium and disequilibrium pore fluids shows a substantially greater amount of twinning is present in disequilibrium samples (Figure 2.10). This is consistent with the more compactive behavior these samples exhibit compared to $\text{PF}_{\text{CaCO}_3}$ samples. The PF_0 may be more corrosive to the calcite than equilibrium fluid. This would lead to more damage to pore walls and would contribute to pore collapse and compaction. Additional twinning of calcite cement can accommodate the additional strain caused by pore collapse. Without this additional corrosive mechanism, the equilibrium samples

experience fewer but larger, through-going cracks, which in turn makes the sample stronger and more dilatant.

Figure 2.10. Photomicrographs of limestone samples deformed at 75°C and 50 MPa effective pressure with a) PF_0 , and b) PF_{CaCO_3} . Allochemical clasts are labeled, A. Sparry calcite cement is labeled, S. Microcrystalline micrites along grain boundaries are labeled, M. Low temperature mechanical twins are labeled T2. Sample deformed with PF_0 shows much more extensive twinning in calcite cement and fewer microcracks compared to sample deformed with PF_{CaCO_3} .



Insight can be gained by looking at the case study of the Ekofisk oilfield in the North Sea. Dramatic subsidence from reservoir depletion was only worsened by water injections meant to increase fluid pressure in the underlying chalk (Chin et al., 1993). Subsequent experimental work shows that chalk yield strength is reduced proportionately to the activity of water in its pore space (Rinsnes and Flaageng, 1999). In fully water or brine-saturated samples, seawater caused enhanced weakening compared to distilled water (Heggheim et al., 2005). This enhanced weakening appears to be temperature sensitive, and maybe caused by substitution of Mg for Ca in calcite at grain contacts and the higher solubility of high-Mg calcite (Korsnes et al., 2008). There is no Mg in the pore fluid in our experiments, but the solubility of calcite is greater in distilled water than in water with some amount of calcium carbonate in solution.

The enhanced solubility of calcite in disequilibrium experiments may result in enhanced pressure solution at points of contact. High surface-energy sites such as sharp edges that exist in the matrix structure may dissolve and re-precipitate in low energy areas. These sites would also be the most vulnerable to stress concentration, so their removal would discourage microcracking. Stress unable to dissipate through fracturing can be relieved by crystal plastic deformation, which is consistent with our observations of increased twin density in disequilibrium experiments. Observations at a very fine scale may be needed to fully constrain the nature of the interaction between microcracking, crystal plasticity and pore fluid.

2.4.3 Stress corrosion

Saturation with $\text{PF}_{\text{CaCO}_3}$ leads to a dramatic reduction in yield strength of the limestone (Figure 2.7), even with the reduced contribution from pressure solution. In micritic limestones compaction is typically driven by fractures that occur concentrically around quasi-spherical pores (Vajdova et al., 2010). In water-saturated rocks, pore space is filled with fluid, which interacts mechanically and chemically with the matrix rock, reducing strength and enhancing this compaction through several possible mechanisms.

The reduction in strength appears to be more pronounced near the brittle-ductile transition, where microcracking plays a dominant role in deformation. This suggests that the presence of pore fluid likely interacts with brittle mechanisms such as stress corrosion and subcritical crack growth. One possible explanation is reduction of fracture energy due to adsorption of water onto mineral surfaces and concomitant reduction in surface energy. A simple model of fracture mechanics states that fracture energy, G is equal to the energy necessary to produce the two surfaces of a new fracture, or twice the surface energy, γ (Griffith, 1920). The origin of this surface energy is the mismatch between atoms in the atomic lattice of a crystal and open space in case of a pore or the atoms of another crystal in the case of grain-grain contacts. The adsorption of a fluid to this surface reduces that energy, thus reducing the energy needed to initiate fracture (Israelachvili, 1991; Lawn, 1993). This mechanism has been invoked to explain similar water weakening in sandstones (Baud et al., 2000b).

The increased effect at low effective stress may also indicate alteration of frictional properties within the rock as well. A recent experimental study has shown that water reduces the frictional strength of calcite fault gouge (Violay et al., 2014). There is substantial pore space along fossil clast boundaries, allowing for significant interaction of grain boundaries with pore fluid. This may result in increased grain sliding and rotation. However, it is difficult to identify markers of grain sliding using microstructural analysis alone.

2.4.4 Geological Implications

Water weakening may play an important role in the rupture of carbonate bearing faults. Carbonate faults display several weakening mechanisms, including thermal decomposition (Han et al., 2007, 2010) and particle lubrication (Di Toro et al., 2011), but it is unclear the role water plays in fault rupture. Faults in carbonate bedrocks are common and display a range of morphologies, from localized shear planes to distributed shear zones with anastomosing faults (Tesei et al., 2013; Michie et al., 2014). The variety of fault zone architecture has been interpreted to represent different deformation mechanisms, with a transition from localized faulting and seismic rupture to distributed deformation and aseismic creep (Bullock, 2014). Changes in behavior are often attributed to variations in mineralogy and fabric. These factors are easy to observe in exhumed faults, but it is not as easy to discern the role of pore fluid once the faults have been uplifted. It is observed that distributed deformation and aseismic slip are common in clay-rich carbonate zones, but it is

possible that these zones also represent areas of high fluid flow and dynamic pore fluid chemistry, favoring pressure solution, crystal plasticity and distributed deformation.

There is some evidence that disturbing the chemical and mechanical equilibria in carbonate rocks can lead to rupture and seismicity. Recent advances in oil and gas recovery technologies involve the movement and disposal of large volumes of fluid in the subsurface. Development of new unconventional reservoirs in the United States and around the world is often in shales that are rich in carbonate and are often near carbonate lithologies. The central region of the United States is particularly rich in carbonates and also is the site of many newly developed reservoirs. The rate of seismicity in this area has recently increased substantially (Ellsworth, 2013). This is frequently attributed to reactivation of old faults due to over pressurization. However, the chemical state of the subsurface is as unknown as the mechanical stress-state. It is possible that weakening due to pore water dilution and mixing could contribute to rupture in these areas as well. The extent of chemical interaction between wastewater and disposal sites bears further investigation to ensure the safety and success of these endeavors.

2.5. Conclusions

We conducted deformation experiments on Indiana limestone samples and investigated effect of fluid and temperature on the mechanical behavior of Indiana Limestone. We observed clear water-weakening in carbonate rocks, which manifests as a reduction in yield strength of samples saturated with pore fluid compared to dry data from previous studies. This weakening effect appears to be sensitive to fluid composition as well as temperature. Samples saturated with distilled water exhibit

most weakening; whereas samples saturated with equilibrated fluids are stronger. Microstructural observation indicates mechanical twinning to be the dominant mechanism of deformation in distilled water saturated samples and microcracking to be the dominant mechanism when the pore fluid is equilibrated with the carbonates. The experimental data suggest that at reservoir conditions, solution transfer in carbonate rocks could promote crystal plasticity and suppress microcracking, thus exerts significant control in rock strength and failure mode. More work is needed to further constrain the precise mechanism of water-weakening in porous carbonates.

Chapter 3: The effect of CO₂-saturated brines on the mechanical and hydraulic behavior of dunite

3.1. Introduction

As levels of atmospheric carbon dioxide continue to rise, scientists and engineers search for strategies to mitigate climatic impacts. Carbon capture and storage (CCS) will play an important role in the near-term carbon budget [IPCC, 2014]. Due to its long-term stability, carbon mineralization, or the trapping of carbon dioxide in carbonate minerals, has garnered a lot of attention [Seifritz, 1990; Lackner et al., 1995].

Increased awareness of climate change and proposed geoengineering solutions have motivated a number of studies of the carbon dioxide – water – olivine system in the past decade, mostly focused on chemical and mineralogical evolution. Olivine is a common mineral, found in many basalts and in great abundance in ultramafites. The dissolution of olivine has one of the fastest rates among Mg-bearing minerals and the magnesium carbonate minerals produced are thermodynamically stable and relatively insoluble in groundwater [Guyot et al., 2011]. The olivine carbonation reaction is exothermic, so along with engineered injection tactics, an in-situ reservoir could be maintained at optimal reaction temperature without additional input of energy that could be cost effective [Kelemen and Matter, 2008]. The conversion of olivine to magnesite and quartz increases volume, which has been invoked as both a potential porosity reducing [Xu et al., 2004; Hovelmann et al., 2012] and porosity generating mechanism [Kelemen and Matter, 2008; Kelemen and Hirth, 2012].

There have been a number of studies of powdered olivine in batch reactors seeking to constrain carbonation rates [Chen et al., 2006; Kelemen and Matter, 2008; King et al., 2010; Daval et al., 2011; Olsson et al., 2012; Gadikota et al., 2013; Johnson et al., 2014], but experiments in aggregates suggest that reaction rates are controlled by grain-scale structure rather than kinetics [van Noort et al., 2008]. Flow-through experiments tend to yield dissolution-dominated behavior, with increases in pore space and permeability near injection sites and secondary mineral precipitation at sites of low hydraulic throughput [Andreani et al., 2009; Peuble et al., 2015a]. The olivine dissolution process is sensitive to flow rate, pore geometry and crystallographic orientation [Pueble et al., 2015b], suggesting that deformation may couple with this process. In stagnant-fluid reactors, precipitation is much more common, reducing porosity and permeability [Hovelmann et al., 2012].

One of the least well-understood aspects of geological carbon sequestration is the mechanical response of reservoir rocks to injection of carbon dioxide. Most of the research on geomechanical effects of carbon dioxide injection has focused on injection into saline aquifers [Hawks et al., 2005; Lucier et al., 2006; Rutqvist, 2012], and neglects chemo-mechanical feedbacks that may be relevant in more reactive reservoirs such as mafic or ultramafic hosted reservoirs. Tests monitoring the evolution of geometry and of fractures saturated with carbon dioxide saturated brines flowing through them indicate substantial changes that have hydraulic and mechanical consequences [Elkhoury et al., 2013]. The chemical alteration of wellbore cement by carbon dioxide has been investigated to better understand borehole stability [Kutchko et al., 2007; Mason et al., 2013], but there is a dearth of

data regarding the chemo-mechanical response of ultramafic reservoir rocks themselves to carbon dioxide injection.

Does the carbonation reaction affect the shear strength and deformation behaviors of the host rock? If so, how and what are the key micromechanisms responsible? Does the stress-induced cracking and dilatancy alter the permeability and thus affect carbonation rates? To answer these questions, we conducted a series of hydrostatic and triaxial deformation experiments on dunite samples undergoing carbonation reactions. These experiments were conducted at two different temperatures and 3 different pore fluids were used to elucidate the coupling between mechanical and chemical load. We measured stress, strain, permeability and fluid chemistry during carbonation reaction.

3.2. *Materials and methods*

Two suites of experiments were designed to test the mechanical response of ultramafic rocks to carbonation reactions, (1) long duration (up to 168 hours) hydrostatic pressing tests with continuous permeability, strain and fluid chemistry measurement, and (2) triaxial deformation tests, in which short hydrostatic pressing (up to 72 hour) is followed by triaxial loading. The first set of tests was conducted on samples saturated with either de-ionized water or CO₂-saturated 0.6 M NaHCO₃ brine. For the second set of tests, CO₂-saturated 1.5 M NaHCO₃ brine was also used as pore fluid in addition to the aforementioned two, to test the effect of bicarbonate concentration in the pore fluid.

SEM analyses of doubly polished thin sections were performed on a JEOL JXA 8900R Microprobe at 15 kV accelerating voltage and analyses of unpolished samples were performed on a Zeiss Auriga FIB-SEM between 3-5 kV accelerating voltage.

3.2.1 Sample Material

Experiments are run on thermally cracked Twin Sisters dunite, a uniform and nearly monomineralic pristine olivine rock from the Cascade Range near Bellingham, Washington, USA. Grains are equant and range from 0.2 to 2 mm in size. Mineralogy of the block from which samples were cored is approximately 99% olivine with trace chromite and enstatite and chromium diopside. The composition of the olivine is Fo₉₀ [Ragan, 1963].

Right cylinders 18.4 mm in diameter and 38.1 mm long were cored and ground out of dunite slabs. The initial permeability of the material was too low to be measured on a bench-top system ($<10^{-18} \text{ m}^2$), and was not suitable for flow-through experiments, so samples were thermally cracked to induce sufficient permeability. Thermal cracking was accomplished by heating samples to 1250°C in a gas-mixing furnace with a 3:1 CO-CO₂ atmosphere to prevent oxidation, then rapidly cooling. Cracks result from stresses induced by anisotropic thermal expansion and diffusion in olivine grains [Demartin et al., 2004]. After thermal treatment samples were measured in a nitrogen permeameter and had an average permeability of 10^{-15} m^2 . Thermal cracks were largely along grain boundaries and had high aspect ratios. The large increase in permeability attests to the interconnectivity of the new pore space.

3.2.2 Pore Fluid Preparation

Three compositions of pore fluid were used for experiments, de-ionized water, CO₂-saturated 0.6 M NaHCO₃ brine and CO₂-saturated 1.5 M NaHCO₃ brine. The CO₂-saturated brines were prepared by mixing the desired amount of NaHCO₃ with de-ionized water, then pressurizing an external fluid-mixing vessel with 3.6 MPa of CO₂. CO₂ pressure is limited by equipment constraints. The fluid is allowed to equilibrate for at least 48 hours before the sample is flushed. Using the online tool GEOPIG to calculate equilibrium constants for CO₂ dissolution reactions at experimental conditions, we obtain the pCO₂ during experiments to be 0.8 MPa. The fluid-mixing vessel is plumbed into the pore pressure system of the triaxial deformation apparatus, and the pressure controlled by upstream and downstream intensifiers in order to move the fluid through the system without depressurizing and degassing CO₂.

3.2.3 Experimental Procedure

Thermally cracked dunite cylinders were jacketed in copper foil and outfitted with foil strain gages, then vacuum saturated with de-ionized water. Instrumented samples were loaded into a triaxial deformation apparatus with a confining pressure of 15 MPa and a pore fluid pressure of 10 MPa, resulting in an effective confining pressure of 5 MPa. Once at pressure, the sample and vessel were heated using an external heater to 150°C with a thermal stability of 1°C throughout the duration of the

experiment. When the assembly reached thermal stability, the sample and all the plumbing was flushed with the chosen pore fluid for the experiment, de-ionized water or CO₂ brine.

For the long hydrostatic pressing experiments, samples were then allowed to react under hydrostatic pressure for 7 days. Strain data was collected every minute and permeability measurements were made every half-hour for the duration of the experiment. Pore fluid aliquots were collected periodically from the downstream side of the sample, acidified and analyzed for major cations using an inductively coupled plasma optical emission spectrometer.

For the triaxial deformation experiments, samples were allowed to react under hydrostatic pressure for 3 days. Strain data were collected every minute during the hydrostatic portion of the test. Permeability measurements were taken periodically. After 3 days, constant strain-rate triaxial deformations were performed on the samples. Stress and strain data were collected at a frequency of 0.5 Hz during the triaxial deformation and permeability tests were run periodically.

After experiments, samples were dried, a small portion cut off for unpolished SEM analysis, and the remaining sample epoxy impregnated and ground into doubly polished thin sections for optical and SEM inspection. Samples prepared for SEM analysis were sputter coated with approximately 5 nm of iridium and affixed to mounts with copper tape.

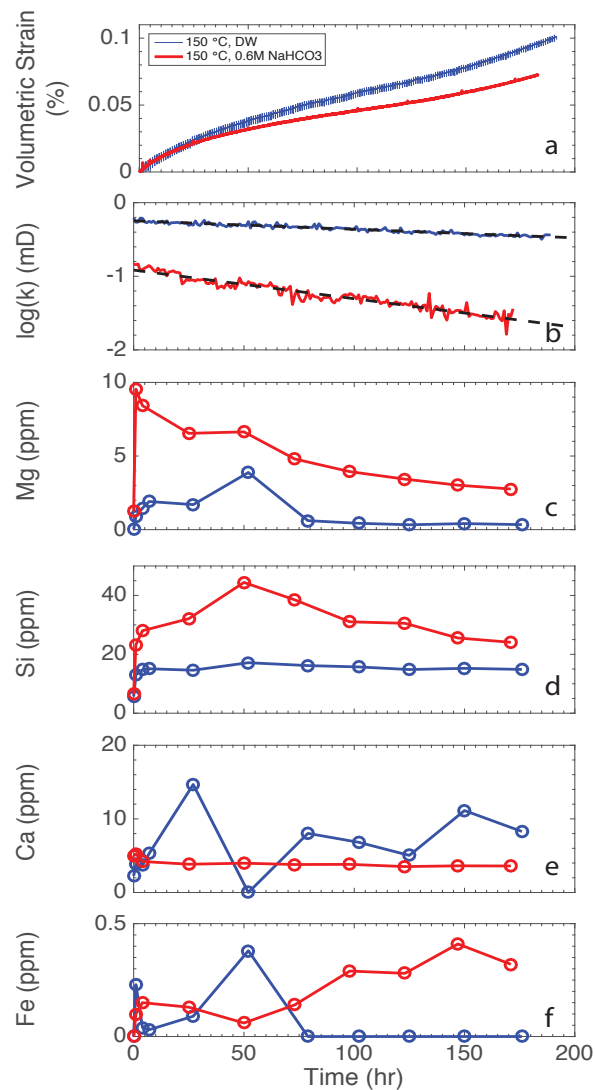
3.3. Results

3.3.1 Long hydrostatic experiments

During all long hydrostatic experiments, the sample saturated with carbon-rich brine shows reduced compaction, enhanced permeability reduction and different ion concentration evolution compared to the sample saturated with de-ionized water. All experiments were performed at 150°C with 10 MPa pore pressure and 15 MPa confining pressure. Mechanical data from the experiments are presented in Figure 3.1a. Both samples show three stages of compaction, an initial rapid phase, a second quasi-steady state and a third, accelerating stage. The sample saturated with carbon-rich brine shows similar initial compaction, reduced secondary compaction and an earlier apparent onset of tertiary compaction compared to the sample saturated with de-ionized water.

Although the sample saturated with carbon-rich brine exhibits reduced total compaction, the rate of permeability reduction is higher than that of the sample saturated with de-ionized water, as shown in Figure 3.1b. Both samples have a log linear reduction in permeability over the course of experiments, with no apparent direct correlation with compaction rate.

Figure 3.1. Data from long hydrostatic experiments. Data from experiments with de-ionized water are presented in blue while data from experiments with carbon-rich brine are presented in red. Experiments are performed at 150°C. a) Volumetric strain versus time, the de-ionized water sample shows more compaction than the carbon-rich brine sample. b) Permeability versus time, the sample saturated with carbon-rich brine has a steeper rate of permeability reduction. Dashed lines are log linear fits to the data. c-f) Ion concentrations in pore fluid versus time, trends indicate early olivine dissolution and later secondary mineral precipitation.



Ion concentrations (Mg^{2+} , Si^{2-} , Ca^{2+} , Fe^{2+}) in pore fluid evolves differently during hydrostatic pressing for samples with the two pore fluids. Chemical data from time-series fluid aliquots are presented in Figure 3.1c-f. The pore fluid from the sample saturated with carbon-rich brine shows an early spike and decay in Mg^{2+} , while the Si^{2-} in the pore fluid increases for ~50 hours before beginning to decrease. Ca^{2+} appears to remain flat for the duration of the experiment and Fe continuously increases. Pore fluid from the sample saturated with de-ionized water shows Mg^{2+} and Si^{2-} increase for ~50 hrs before beginning to decrease and no systematic trend in Ca^{2+} or Fe^{2+} .

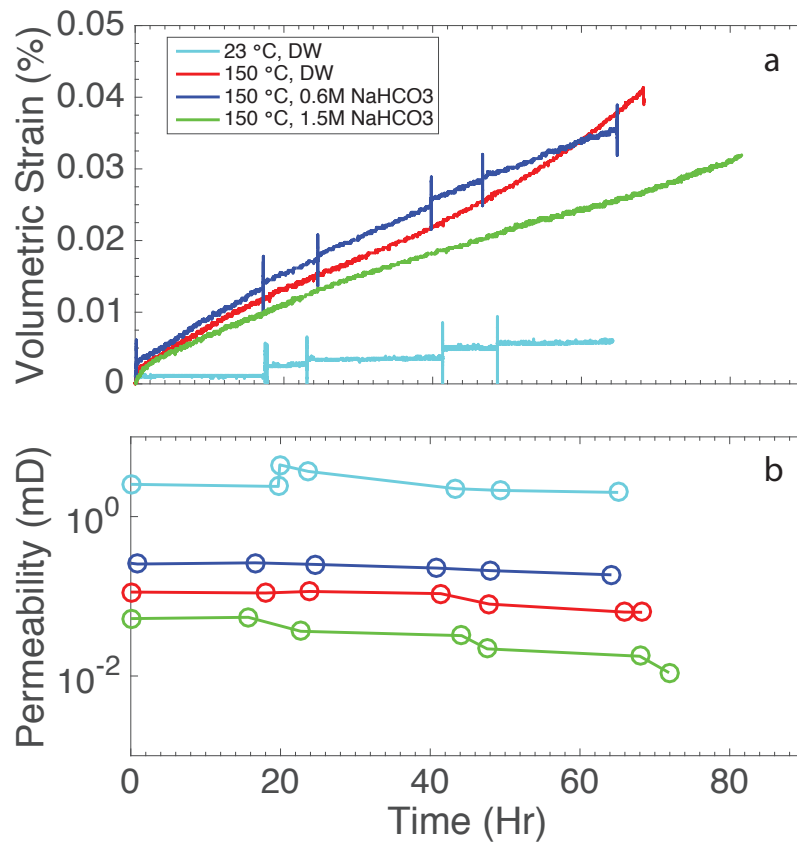
3.3.2 Short hydrostatic experiments

Bicarbonate concentration in pore fluid and temperature have an effect on the compaction of dunites. Mechanical data from all short hydrostatic experiments are presented in Figure 3.2a. All experiments were performed with 10 MPa pore pressure and 15 MPa confining pressure at room temperature or 150°C. The sample saturated with de-ionized water at room temperature shows the least compaction, under 0.01% total volumetric reduction. The sample saturated with de-ionized water at elevated temperature shows the most initial compaction, but is overtaken at ~55 hours by the sample saturated with the 0.6 M NaHCO_3 brine. The sample saturated with the 0.6 M NaHCO_3 brine shows slightly reduced compaction compared to the de-ionized water sample at elevated temperature at the beginning of the experiment, but the compaction rate increases toward the end of the experiment. The sample saturated

with the 1.5 M NaHCO_3 brine shows a further reduction in compaction compared to the low bicarbonate and de-ionized water samples.

Permeability is reduced over the duration of experiments for all pore fluid compositions. Permeability data from short hydrostatic experiments are presented in Figure 3.2b. Changes in permeability for the de-ionized water sample at room temperature are small. Among elevated temperature samples, there is the suggestion of an anti-correlation between permeability reduction and pore fluid bicarbonate concentration, but variability is small.

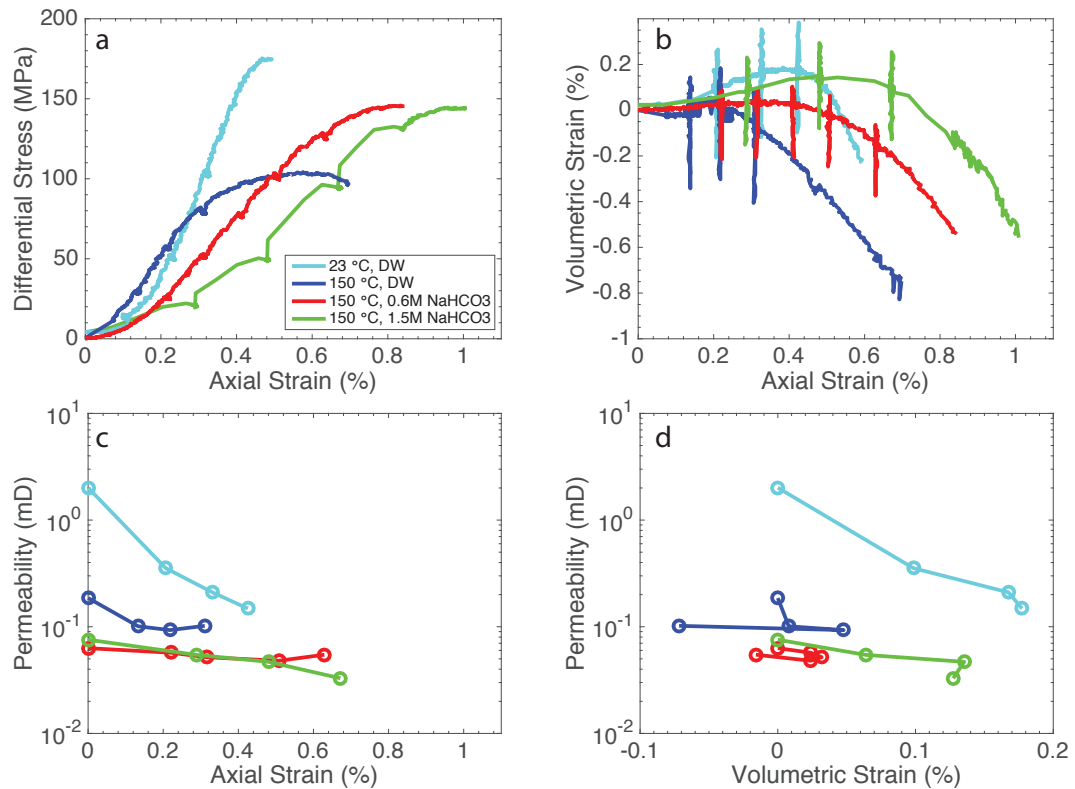
Figure 3.2. Data from short hydrostatic experiments. Data from experiments with de-ionized water at room temperature are presented in cyan, de-ionized water at elevated temperature are presented in blue, carbon-rich brine with 0.5 M NaHCO_3 are presented in red and carbon-rich brine with 1.5 M NaHCO_3 are presented in green. Experiments at elevated temperature are performed at 150°C. a) Volumetric strain versus time, the room temperature sample shows little compaction, while samples at elevated temperature compact for the entire duration of the experiment. Initial compaction appears to anti-correlate with bicarbonate concentration. Samples saturated with carbon-rich brine show a late increase in compaction rate. b) Permeability versus time, variation in permeability reduction is small, but appears to correlate with pore fluid bicarbonate concentration.



3.3.3 Triaxial deformations

Pore fluid composition and temperature have a strong effect on the deformation behavior and strength of dunite. Samples with 3 different pore fluids were deformed triaxially after the short hydrostatic pressing. Mechanical data are presented in Figure 3.3a-b. When differential stress is plotted against axial strain (Figure 3.3a), all samples show four stages of deformation, an initial compaction phase of the closure of oriented pre-existing cracks, a second phase of the quasi-elastic behavior, a third phase of dilation by microcracking and final phase of shear failure after the peak stress. Young's Modulus is calculated from the slope of the curve during the second stage. All samples fail by localized brittle faulting.

Figure 3.3. Data from triaxial deformation experiments. Coloring is the same as above for short hydrostatic experiments. a) Differential stress versus axial strain, the room temperature sample has the greatest shear strength, while the de-ionized water sample at elevated temperature has the lowest shear strength. Samples saturated with carbon-rich brine have lower apparent Young's moduli but intermediate shear strength. b) Volumetric strain versus axial strain, samples saturated with carbon-rich brine accommodate more axial strain before dilating. c,d) Permeability versus strain, all samples exhibit permeability reductions during triaxial deformation. The samples saturated with de-ionized water and 0.6 M NaHCO₃ brine at elevated temperature show slight permeability enhancements near failure.



The sample saturated with de-ionized water at room temperature has the highest Young's modulus, at 55.6 GPa, as well as the highest peak stress, 175 MPa. The sample saturated with de-ionized water at elevated temperature is less stiff, with a Young's modulus of 34.5 GPa, a 38% reduction, and has the lowest peak stress, 104 MPa, a 41% reduction. Samples saturated with carbon-rich brine show an even further reduction of Young's modulus, but attained higher peak stress than the de-ionized water sample at elevated temperature. The sample saturated with the 0.6 M NaHCO₃ brine has a Young's modulus of 28.7 GPa and a peak stress of 146 MPa. The sample saturated with the 1.5 M NaHCO₃ brine has a Young's modulus of 26.1 GPa and a peak stress of 150 MPa. A summary of this mechanical data is presented in Table 3.1.

Table 3.1. Summary of mechanical data for triaxial deformation experiments.

Name	Temp (°C)	Fluid Composition	Peak Stress (MPa)	E (GPa)
DUN-19	23	DW	175	55.6
DUN-18	150	DW	104	34.5
DUN-24	150	0.6 M NaHCO ₃ , CO ₂	146	28.7
DUN-23	150	1.5 M NaHCO ₃ , CO ₂	150	26.1

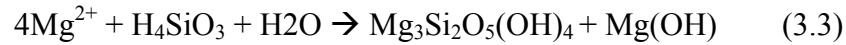
All samples show reductions in permeability during the triaxial deformations. Permeability data collected during deformations is presented in Figure 3.3c-d. The sample saturated with de-ionized water at room temperature has the highest initial permeability and shows the greatest reduction in permeability during triaxial deformation. The sample saturated with de-ionized water at elevated temperature and the sample saturated with the 0.6 M NaHCO₃ brine show reductions in permeability

until close to peak stress, when permeability increases slightly, likely indicating coalescence of microcracks. The sample saturated with the 1.5 M NaHCO₃ brine shows permeability reduction throughout the entire deformation.

3.4. Discussion

3.4.1 Evolution of pore fluid chemistry

Differences in the evolution of ion concentration in pore fluid during long hydrostatic experiments point to different dissolution-precipitation dynamics. The reactions occurring while olivine is hydrated and carbonated can be written,

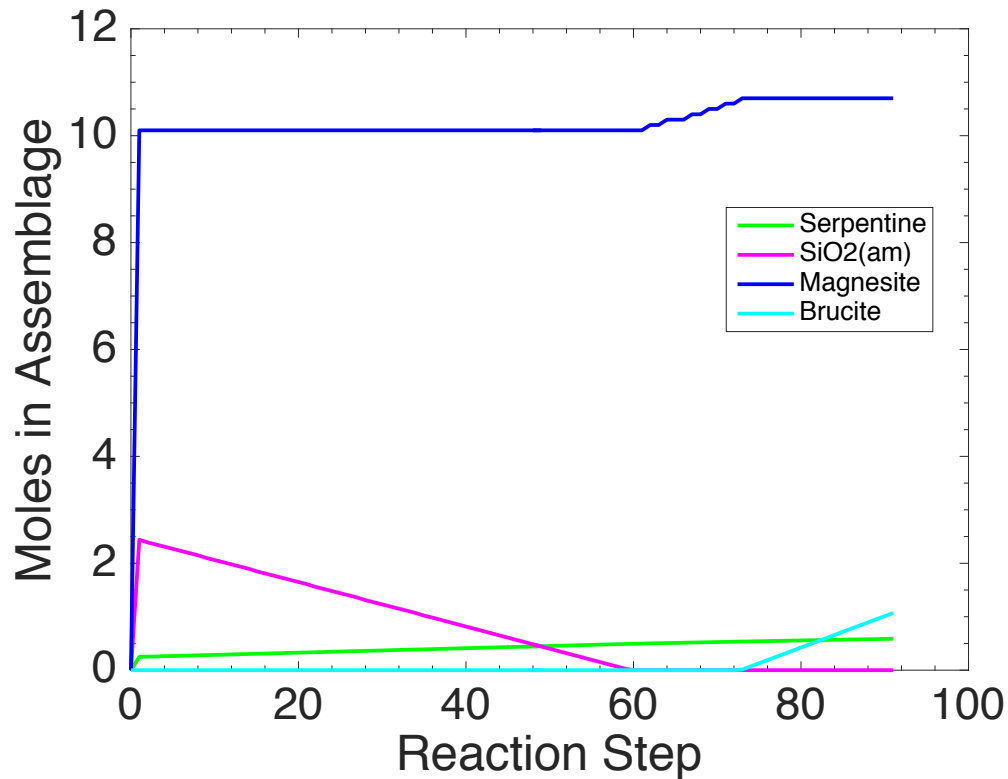


where the dissolution of forsterite releases Mg²⁺ and Si²⁻ into solution, the precipitation of magnesite, serpentine and brucite remove Mg²⁺ from solution and the precipitation of serpentine removes Si²⁻ from solution. The precipitation of amorphous silica (from the dissolved silicic acid) could also remove Si²⁻ from solution.

Samples saturated with both de-ionized water and carbon-rich brine show an early spike in both Mg²⁺ and Si²⁻ (Figure 3.1c,d), indicating that dissolution onsets rapidly at the beginning of experiments. From here the evolution of the ion

concentration in the two pore fluids diverge. We ran a reaction step model simulating our experimental conditions using the geochemistry modeling software PHREEQC to better understand the precipitation dynamics in our system (Parkhurst and Appelo, 1999). The results of this model for the carbon-rich brine are presented in Figure 3.4. The model shows that rapid magnesite precipitation begins immediately upon forsterite dissolution, due the reactivity of the dissolved Mg^{2+} and CO_2 . This is likely responsible for the drop in Mg^{2+} measured in the pore fluid of the carbon-rich brine sample. In the de-ionized water sample, Mg^{2+} continues to rise for ~50 hours, indicating that forsterite dissolution outpaces any secondary mineralization. Si^{2-} continues to rise in both pore fluids for ~50 hours, then is reduced continuously, likely the result of the sluggish precipitation of serpentine as shown in the reaction path model. It should be noted as well that in addition to the divergence in pore fluid chemistry evolution, the sample saturated with carbon-rich brine has a larger magnitude of dissolved cations for the entire duration of the experiment, indicating that dissolution is more vigorous in that sample.

Figure 3.4. Results of a reaction path simulation from PHREEQC. Early magnesite precipitation is the dominant reaction. Early amorphous silica is consumed by the slow precipitation of serpentine and later brucite. Simulation results agree with microstructural analysis of reaction textures and mineralogy in experimental samples.

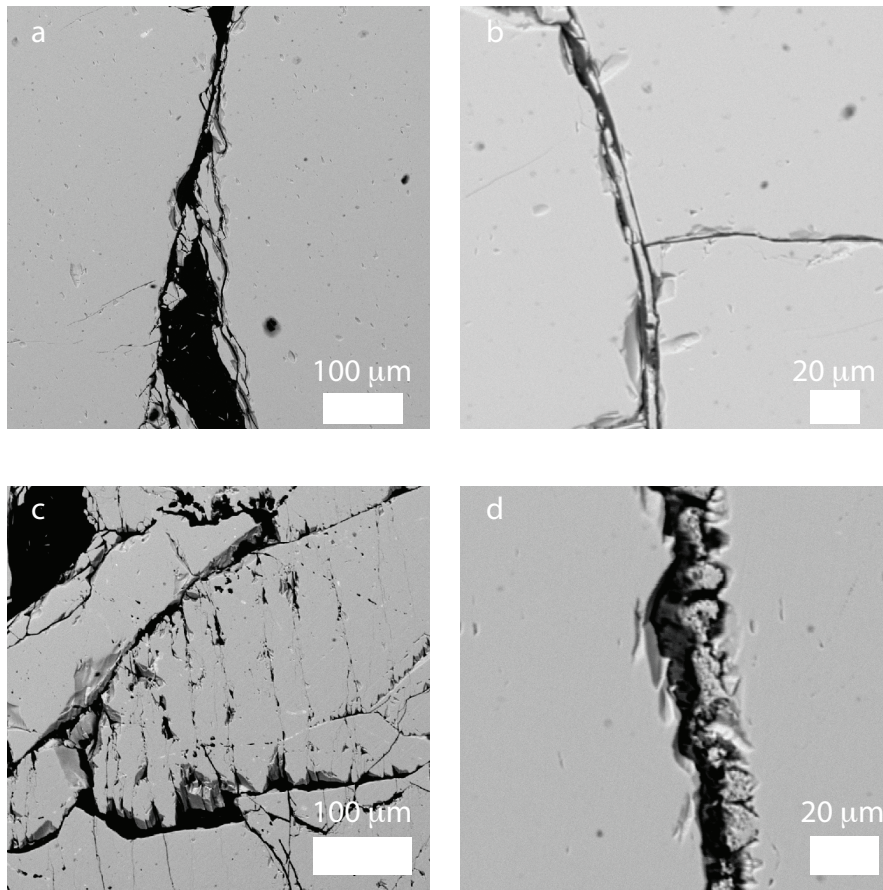


3.4.2 Effect of carbon-rich brine

The observed pore fluid chemistry change and predicted the reaction path model are consistent with the reaction microstructures produced during the experiments. Examination of traditional double-polished thin sections shows that carbon rich fluid enhances both the dissolution of olivine as well as precipitation of secondary minerals. Scanning electron microscope (SEM) backscattered electron

images of polished thin sections are presented in Figure 3.5. Samples saturated with de-ionized water show some alteration and nascent etch pits can be seen along crack surfaces (Figure 3.5a). Etch pits appear to have coalesced and broken pieces of coherent grain off into cracks (Figure 3.5b). Secondary mineralization is present, but in thin layers ($<1\ \mu\text{m}$) that are difficult to image.

Figure 3.5. SEM images of polished thin sections of samples from long hydrostatic experiments. a,b) Sample saturated with de-ionized water, alteration is focused around crack walls and mostly consists of dissolution features. Secondary minerals are not apparent at this scale. c,d) Sample saturated with carbon-rich brine, alteration is more substantial. Dissolution channelized into etch pits which coalesce at a distance beneath primary crack surfaces, perforating the crack walls. Secondary minerals are the dark material within cracks.

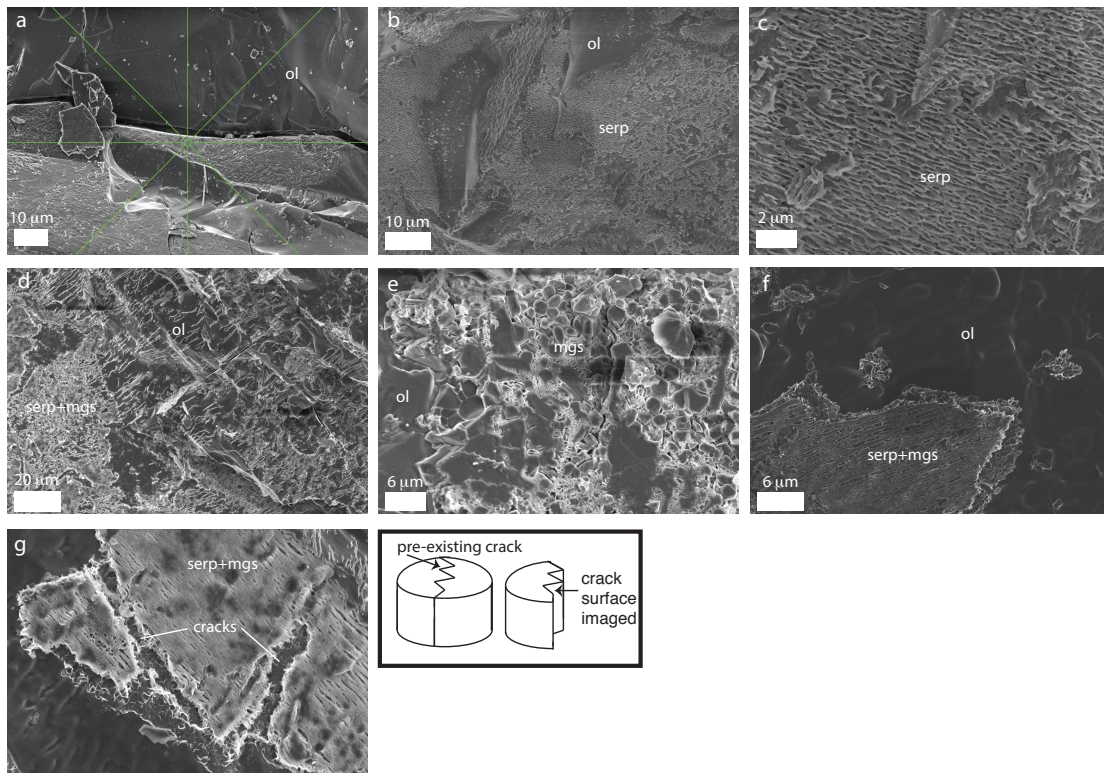


Samples saturated with carbon-rich brine show much more substantial alteration. Etch pits are apparent along all crack surfaces, and appear to grow in oriented, parallel bands (Figure 3.5c), suggesting some influence of stress or crystallographic orientation. Dissolution channels tend to perforate the crack surface and coalesce at some distance beneath the pre-existing cracks, which ultimately separate the altered surface from the rest of the intact grain (Figure 3.5d). Such alteration may be the onset of the hierarchical fractures and kernel patterns commonly observed in metasomatised rocks [Iyer et al., 2008; O'Hanley, 1991]. Secondary mineralization is ubiquitous on altered surfaces in layers 1 to ~10 μm thick, but was difficult to characterize due to equipment constraints. In order to take a look at the secondary minerals in greater detail, unpolished samples broken along pre existing cracks were imaged to inspect the crack walls.

SEM images of unpolished crack walls are presented in Figure 3.6. Pristine sample material is entirely olivine, with angular surfaces free of dissolution features and secondary minerals (Figure 3.6a). The sample saturated with de-ionized water (Figure 3.6b,c) shows rounding of edges and precipitation of serpentine along crack walls. Serpentine appears to grow in elongated flakes and remains porous, suggesting maintenance of fluid access to reactive surfaces. The sample saturated with carbon-rich brine shows more substantial secondary mineralization (Figure 3.6d-f). Serpentine and magnesite intergrow in porous layers along the crack walls. The mineralized layers appear discontinuous along the crack wall and have cracks that appear to have formed in-situ because of mineral growth within them (Figure 3.6f).

The layers do not appear to entirely block fluid access to reactive material and may be acting as proppants, keeping crack surfaces open.

Figure 3.6. SEM images of crack surfaces split along pre-existing cracks (insert) of samples from long hydrostatic experiments. A) Unreacted sample, olivine surfaces have angular features and no secondary mineralization. B) Overview of crack surface from sample saturated with de-ionized water, serpentine is precipitated along olivine surface. C) Close-up of de-ionized water sample, serpentine precipitates as elongate fin-like sheets and we infer to be porous and permeable. D) Overview of crack surface from sample saturated with carbon-rich brine, serpentine and magnesite intergrow across the surface. E) Close up of sample saturated with carbon-rich brine, serpentine and magnesite layers appear to be porous. F) Serpentine and magnesite layers are discontinuous, leaving some fresh olivine surfaces bare. G) Serpentine and magnesite layers appear to be cracked, another possible mechanism allowing continuous fluid access to the unreacted olivine.

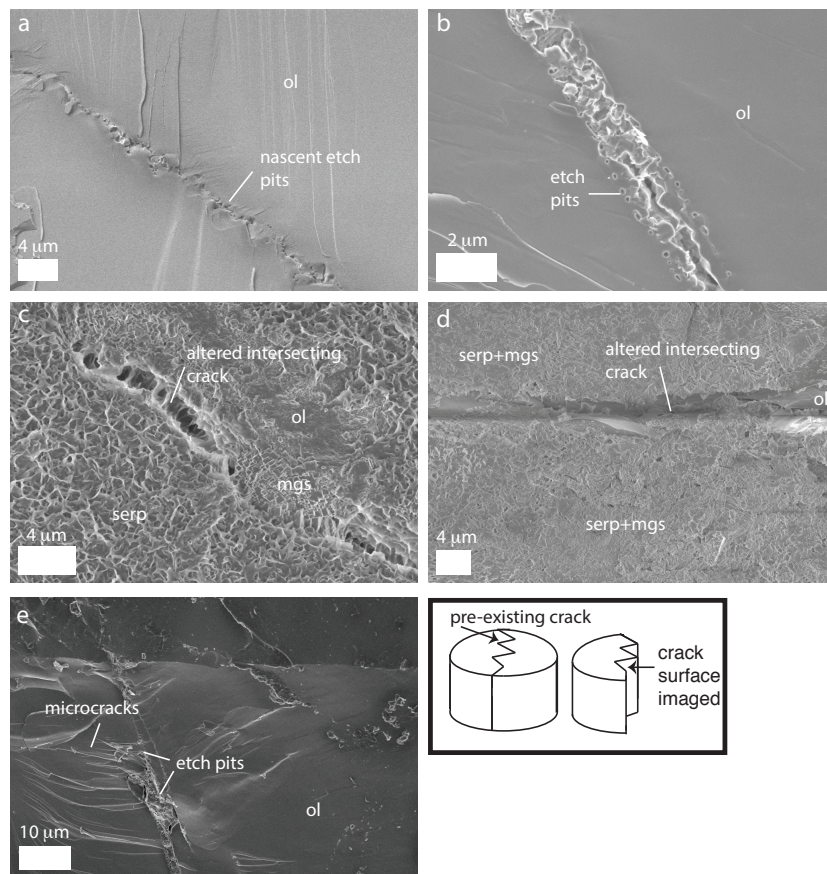


3.4.3 Effect of bicarbonate concentration

Microstructures from triaxial deformation tests after shorter period of hydrostatic pressing give us access to an earlier stage in the development of alteration along crack walls, and highlight the interaction of chemical reaction and mechanical deformation. SEM images of crack walls of unpolished samples from triaxial experiments are presented in Figure 3.7. Surface intersecting cracks are imaged to highlight the penetration of reactive fluids into the olivine. Differences in reaction microstructures among samples saturated with different fluids and under different conditions provide insight into variations in mechanical behavior. The sample saturated with de-ionized water at room temperature shows the least alteration (Figure 3.7a). Undulations in surface intersecting cracks indicate nascent etch pits, but that is the only apparent alteration feature. The sample saturated with de-ionized water at elevated temperature shows more developed dissolution features (Figure 3.7b). Etch pits form and begin to coalesce a small depth in from the surface of the crack. Some serpentine is observed precipitated along the crack wall. The sample saturated with low bicarbonate CO₂-brine shows much more substantial alteration (Figure 3.7c). Dissolution features tend to be prominent and channelized. Etch pits form an interconnecting network that coalesces at a distance down from pre-existing crack surfaces, perforating the olivine. Magnesite and serpentine are both observed precipitated on crack walls, but appear porous and have not grown to entirely cover the surface, leaving patches of olivine exposed for further reaction. The sample saturated with high bicarbonate CO₂-brine shows more precipitation than the low

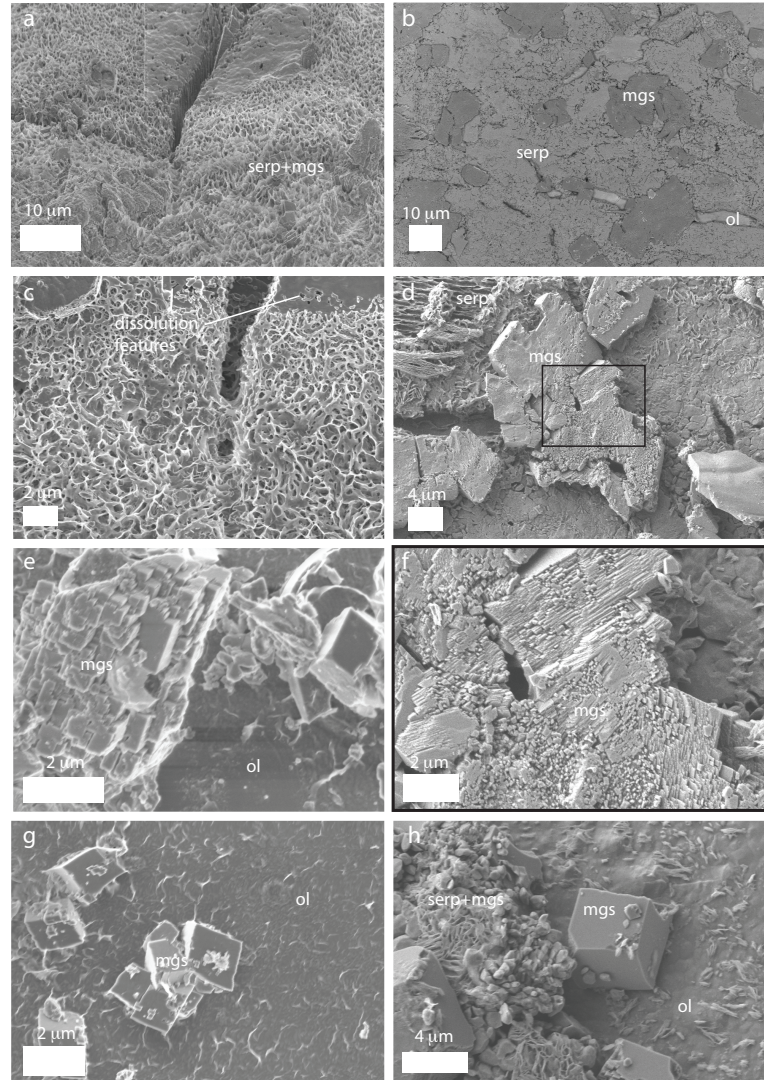
bicarbonate sample (Figure 3.7d). Surfaces appear armored with porous magnesite and serpentine intergrowths. Mechanical data from the hydrostatic portion of the experiment indicate that compaction had not ceased by the end of the experiment, suggesting that this porous layer is permeable, maintaining fluid communication with reactive surfaces.

Figure 3.7. SEM images of crack surfaces split along pre-existing cracks (insert) of samples from short hydrostatic experiments. Surface intersecting cracks are imaged to highlight fluid penetration. A) Sample saturated with de-ionized water at room temperature, crack shows little alteration. B) Sample saturated with de-ionized water at elevated temperature, crack shows incipient etch pits. C) Sample saturated with 0.6 M NaHCO_3 brine, crack shows extensive dissolution features and secondary mineralization. D) Sample saturated with 1.5 M NaHCO_3 brine, secondary mineralization is so dense that crack surface is no longer visible. E) Microcracks radiating out of etch pits in sample saturated with de-ionized water at elevated temperature. This enhancement of microcracking may explain the low shear strength of the sample.



The bicarbonate concentration of the CO₂-brine has an effect on the magnesite and serpentine precipitation textures. SEM images of precipitates from the carbon-rich brine samples are presented in Figure 3.8. The low bicarbonate sample shows a larger contribution of dissolution, with ubiquitous etch pits and cave-like surface-intersecting cracks. Magnesite and serpentine intergrow in sparse patches, leaving patches of olivine uncovered. The high bicarbonate sample has all of its olivine surfaces covered in secondary minerals, with olivine only apparent through splits in the mineralized layer. These splits sometimes have precipitants in them, suggesting that they form during experiments and are not decompression fractures during unloading. Magnesite tends to precipitate as compound crystals with many facets, although some well-formed single crystals are observed.

Figure 3.8. SEM images of samples saturated with carbon-rich brine from triaxial experiments. Higher bicarbonate concentration appears to lead to an enhancement in carbonate precipitation and a modification of precipitation morphology. A,C,E,G) Sample saturated with 0.6 M NaHCO_3 brine, dissolution features are dominant and magnesite tends to grow as well-terminated polyhedra or coarse aggregate crystals. B,D,F,H) Sample saturated with 1.5 M NaHCO_3 brine, precipitation is much more prominent, with most surfaces completely armored. Magnesite tends to grow as complex aggregate crystals.



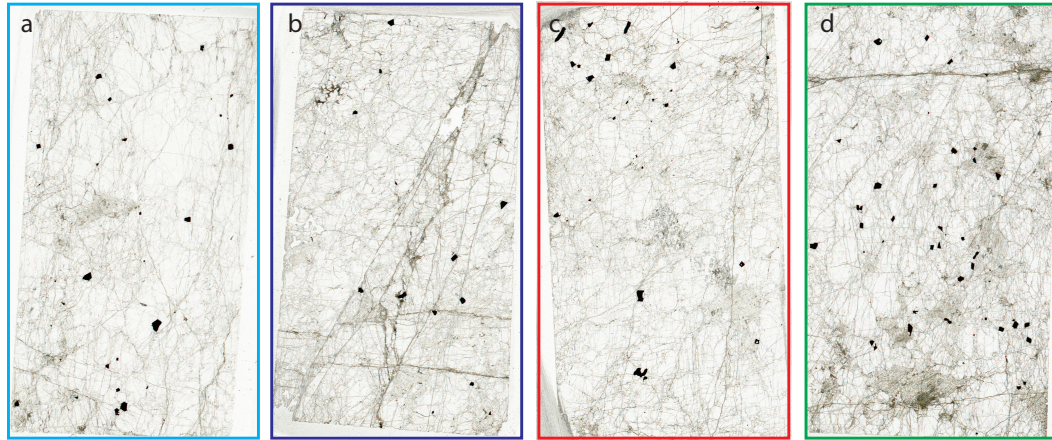
3.4.4 Effect of differential stress

Hydrothermal alteration of the dunite samples leads to modification of their mechanical behavior. A summary of peak stress and Young's modulus is presented in Table 3.1 and images of polished thin sections are presented in Figure 3.9. All samples failed by localized brittle fracture. Inspection of petrographic thin sections indicates that failure localized due to the interaction and coalescence of microcracks. The sample saturated with de-ionized water at room temperature has the highest shear strength and Young's modulus. SEM analysis shows that the sample shows very little alteration during the deformation test, so can be considered a control case for chemo-mechanical coupling. The sample saturated with de-ionized water at elevated temperature, in which dissolution features such as etch pits are observed (Figure 3.5), has the lowest shear strength, with a reduction of 41%, but intermediate Young's modulus. Macroscopic inspection of the post-failure sample shows a well-developed, through-going shear fracture. The pre-existing cracks are primarily along grain boundaries, leading to enhanced alteration of grain contacts, where most of the microcracking occurs. The reduction of shear strength can be explained by the presence of etch pits, which serve as stress concentrators and lower the stress required to fracture the rock. Microstructural observations corroborate this interpretation, as microcracks can be seen radiating out from the etch pits (Figure 3.7d). Precipitation of serpentine along crack surfaces may account for the reduction in apparent Young's modulus at low stress levels, before the onset of microcracking.

Samples saturated with CO₂-brine have intermediate strength between the room temperature and elevated temperature de-ionized water samples but the lowest

Young's moduli. Precipitation of serpentine and magnesite along crack surfaces again manifests as a reduction in apparent Young's modulus at low stress levels. The sample etch pit nucleation mechanism may be operating in these samples, but slightly tempered by the reduction in total porosity due to precipitation. More compliant secondary minerals may also dissipate stress along crack surfaces, causing rock to creep rather than fracturing. Armoring of surfaces by secondary minerals hampered observation of microcracking at very fine scale. Macroscopic observation of post-failure samples shows the development of several distributed shear fractures, suggesting that hydrothermal alteration encourages distributed over localized deformation.

Figure 3.9. Scanned images of polished thin sections of samples from triaxial deformations. A) Sample saturated with de-ionized water at room temperature shows significant microcracking. A localized fracture is observed on top half of the sample. B) Sample saturated with de-ionized water at elevated temperature show sharp throughgoing shear fractures. C) Sample saturated with 0.6 M NaHCO_3 brine appears to have more distributed shear fractures throughout. D) Sample saturated with 1.5 M NaHCO_3 brine shows evidence for well-formed distributed shear fractures throughout. Samples are 18mm across the short side.



3.4.5 CO_2 injection into reactive reservoirs

The mechanical response of reservoirs to injection and depletion has been studied mostly with regard to poroelastic effects [e.g. Grasso, 1992], some of which may be affected by the changes in mechanical characteristics observed in this study. Changes in the pore pressure of porous reservoirs have been observed to result in faulting and seismicity [Zoback and Zinke, 1992] as has been highlighted by recent

episodes of seismicity that result from wastewater storage [Ellsworth, 2013].

Injection into reservoirs can lead to pore pressure overpressurization and hydrofracture; depletion can lead to subsidence and evolution of reservoir stress state. Both these behaviors are the result of changes in pore pressure as a result of increasing or reducing the volume of water in the pore space. Changes in pore pressure may also result from a reduction in pore volume due to precipitation, or an increase in pore volume due to dissolution. Modeling studies of the injection of CO₂ into carbonate caprocks indicate that dissolution can lead to a net increase in pore space [Gauss et al., 2005], but the model did not take specific micromechanisms such as channelized dissolution into account, and may underpredict mechanical feedbacks.

If major projects to inject CO₂ into reservoirs of ultramafic and mafic rocks proceed, a greater understanding of the coupling between chemical alteration and mechanical deformation is necessary. Assuming elastic loading of a 1km reservoir alone, the reductions in Young's modulus observed in this study could result in 100's to 1000's of cm subsidence. The precipitation of compliant minerals along crack surfaces may result in not only reservoir compaction and subsidence, but may have substantial repercussions on the frictional behavior of pre-existing faults in the reservoir, a topic this study does not discuss and warrants more investigation. Dissolution of minerals may result in not only compaction and subsidence, but may encourage microcracking by concentrating stress. Cracking is a dilatant process, which increases total porosity, which may play a role in maintaining permeability and reactive surface area in reservoirs, but may also result in rupture and seismicity.

3.5. Conclusions

We performed hydrostatic compaction and triaxial deformation experiments on dunites under hydrothermal conditions. Permeability and sample porosity are reduced during hydrostatic pressing. The evolution of physical properties of ultramafic rocks reacted with water and CO₂ is complex and controlled by the chemo-mechanical coupling. Analysis of mechanical, chemical and microstructural data indicates that the compaction behavior of the dunite samples are controlled by channelized dissolution of olivine and the precipitation of secondary minerals such as serpentine and magnesite along pre-existing cracks. Layers of secondary minerals precipitated on crack walls are porous and allow continuous fluid-mineral contact. Alteration layers are no thicker than tens of microns, but occur along grain boundaries and so have substantial effects on the deformation behavior of the samples, causing considerable reduction in elastic modulus and shear strength. Reduction of Young's modulus appears to be the result of secondary mineralization along crack surfaces while reduction in strength is the result of the intensification of stress at channelized dissolution features. A greater understanding of this evolution is necessary for the safety and success of any future ultramafic or mafic carbon dioxide mineralization sites, and to better constrain the dynamics of deformation and hydrothermal alteration of the oceanic crust.

Chapter 4: Pattern formation during olivine carbonation: self-organization of dissolution processes²

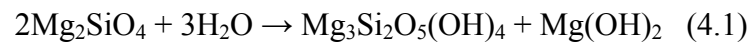
4.1 Introduction

Hydration and carbonation of ultramafic rocks are widespread on the surface of the Earth. Along mid-ocean ridges or at subduction zones, the olivine and pyroxene bearing rocks in the oceanic crust react with hydrothermal fluids to produce minerals such as serpentine, brucite, talc, magnesite and calcite [Deschamps et al., 2013]. These volatilization reactions cause vast physical and chemical changes in the geological systems that host them and their impacts on earth system, from oceanic tectonics [Escartin et al., 1997] to hydrothermal ecosystems [Kelley et al., 2005], are far-reaching. These reactions are exothermic, and can proceed vigorously and irreversibly. Where ultramafic rocks have been tectonically juxtaposed against metamorphosed carbonate bearing sediments, olivine and pyroxene can be entirely converted to carbonate and quartz [Beinlich et al., 2012; Falk et al., 2015]. As such, they have been suggested as a method of long-term geological carbon sequestration [Seifritz, 1990; Kelemen and Matter, 2008]. Yet the mechanism that allows these positive volume-changing reactions to proceed to completion is still elusive. We investigate the evolution of porosity and permeability of fractured dunites exposed to carbon dioxide saturated brine in laboratory experiments. We find that although

² In review, “Lisabeth, Harrison, Wenlu Zhu, Tiange Xing, Vincent De Andrade Pattern formation during olivine carbonation: self-organization of dissolution processes. (2016) Scientific Reports.”

precipitation of secondary minerals causes the total porosity of the sample to decrease, an interconnected network of porosity is maintained by perforation-channels produced through channelized dissolution and coupled carbonate precipitation. The self-organized pattern of these perforated-channels can explain textures observed in naturally hydrated and carbonated rocks and may provide a mechanism for the complete metamorphic reaction of low porosity rocks.

Volatilization reactions generally involve an increase in solid volume. Simple examples of the hydration and carbonation of forsterite such as,



for instance, result in solid volume changes of 46% and 88% respectively. These reactions require a sufficient supply of fluid reactants to be available within the pore space of the host rocks. In a simple system with 10% porosity, these reactions would only need to convert 8% and 6% of the forsterite respectively to reduce the porosity to 0. The conventional wisdom is that such volume increasing fluid-rock interactions are self-limiting, unless the reactants are precipitated outside of the host rock. However, in nature, it is common to observe entirely hydrated and/or carbonated peridotite, even in isochemical systems [Kelemen and Matter, 2008]. Reaction-driven cracking via force of crystallization is often invoked to explain the maintenance of porosity and permeability during fluid-rock reactions that increases

the solid volume [Jamtveit et al., 2008; Kelemen and Hirth, 2012]. While crystallization pressure induced fracturing is well known at unconfined conditions, such as salt crystallization producing fractures in cement, asphalt or structural stone, [e.g., Scherer, 2004], experimental evidence for reaction driven cracking under subsurface confinement is sparse and existing studies show limiting behaviors before observing fracturing [e.g., Andreani et al., 2009]. The lack of reaction driven cracking observed during olivine hydration and carbonation suggests an alternative mechanism for the maintenance of porosity and permeability in an actively volatilizing system that does not require conventional brittle fracturing.

Insight on the mechanism of fluid ingress into hydrating and carbonating rocks can be gained by looking at the resultant rock structures. Common hallmarks of these reactions are hierarchical fracture networks [Iyer et al., 2008; Royne et al., 2008], mesh-textures [Rumori et al., 2004], kernel patterns [O’Hanley, 1992] and layered veins [Andreani et al., 2007]. In Figure 1a-c, a unifying characteristic of the rock structures is the regular geometric features that occur on multiple scales: similar vein and fracture angles in the case of hierarchical fractures and mesh-textures, and evenly spaced layering in the case of kernel patterns and vein textures. This sort of pattern formation is typical of systems exhibiting local intensification (positive feedback) and lateral inhibition (negative feedback) [Jamtveit and Hammer, 2012]. “Which mechanisms are responsible for these feedbacks in volatilizing ultramafic rocks?” remains an open question.

4.2 Methods

4.2.1 Sample Material

The material used for these experiments is Twin Sisters dunite, a nearly monomineralic dunite with minor chromite and diopside. The average grain size is ~2 mm. The composition of the constituent olivine is Fo₉₀. Right cylinders 1.84 cm in diameter and 3.81 cm long were cored and ground out of dunite slabs. Initial porosity was <<1% and initial permeability was <10⁻¹⁸ m², so samples were thermally cracked to induce sufficient permeability for flow-through experiments.

Thermal cracking was accomplished by heating and rapidly cooling samples in a gas mixing tube furnace. Samples were put in a CO-CO₂ atmosphere to control oxygen fugacity and prevent oxidation during the heat treatment, brought to 1250°C, then rapidly cooled. The average sample porosity after thermal cracking was ~1% and the average permeability was 10⁻¹⁵ m². Samples were jacketed with thin (127 micron) copper foil and affixed with wire strain gages prior to experiments.

4.2.2 Experimental Procedure

CO₂ brine was prepared in an external mixing vessel prior to experiments. Brine was prepared by dissolving NaHCO₃ to a concentration of 0.6 M in distilled water. This brine was then put into a bolted closure reactor and the headspace purged. The CO₂ was then introduced to the vessel and pressurized to 3 MPa at room temperature. The vessel was then allowed to equilibrate for 48 hrs. This fluid was

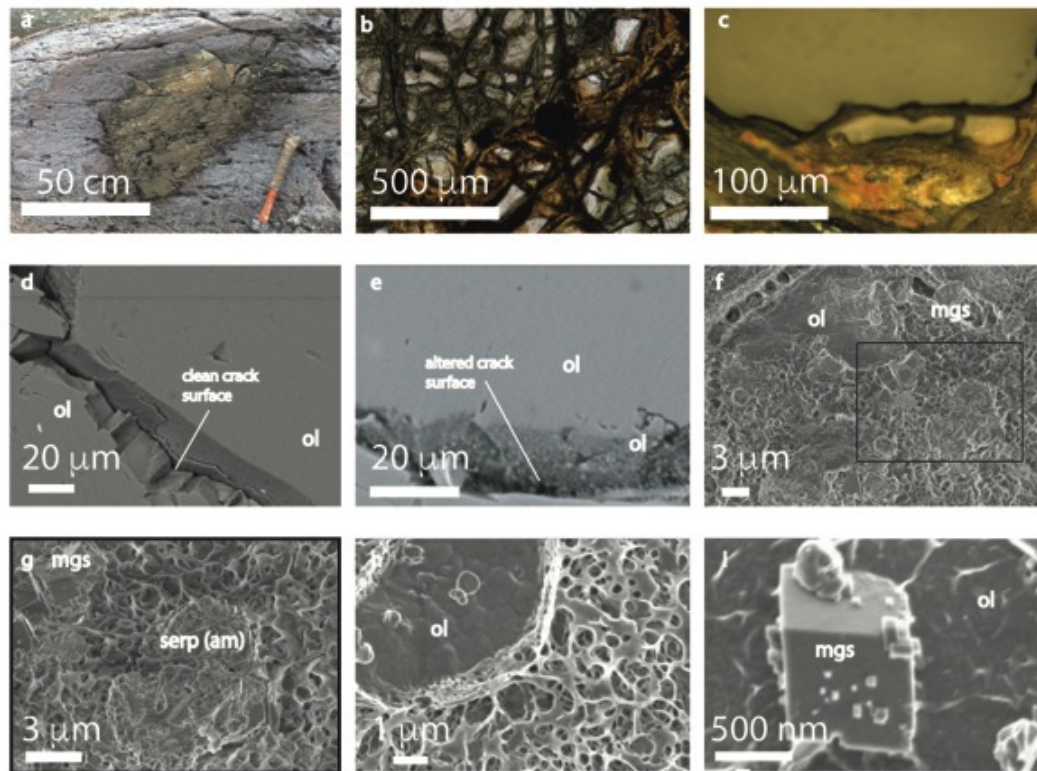
then flushed through the sample. The pH and $p\text{CO}_2$ at experimental conditions was calculated using GEOPIG [Johnson et al., 1992] to be 8 and 0.8 MPa, respectively.

Samples were loaded into the triaxial deformation apparatus saturated with distilled water and the pore fluid system purged of bubbles. The samples were then brought to 15 MPa confining pressure and 10 MPa pore pressure and the vessel heated to 150°C. The heating process takes ~8 hours to achieve thermal stability. The samples' pore fluid was then flushed with the designated fluid composition for a given experiment, either distilled water or CO_2 brine. Samples were then allowed to react and compact for three days while their strain is constantly monitored and permeability is spot-checked. Permeability was measured using pore pressure transient analysis [Botinott, 1997].

At the conclusion of three days of reaction, samples were deformed axially until failure to assess the change in their mechanical behavior. A nominal strain rate of 10^{-5} s^{-1} was used. Sample stress, strain and permeability were measured throughout deformation. At the conclusion of tests, samples were cooled, depressurized and prepared for microstructural analysis.

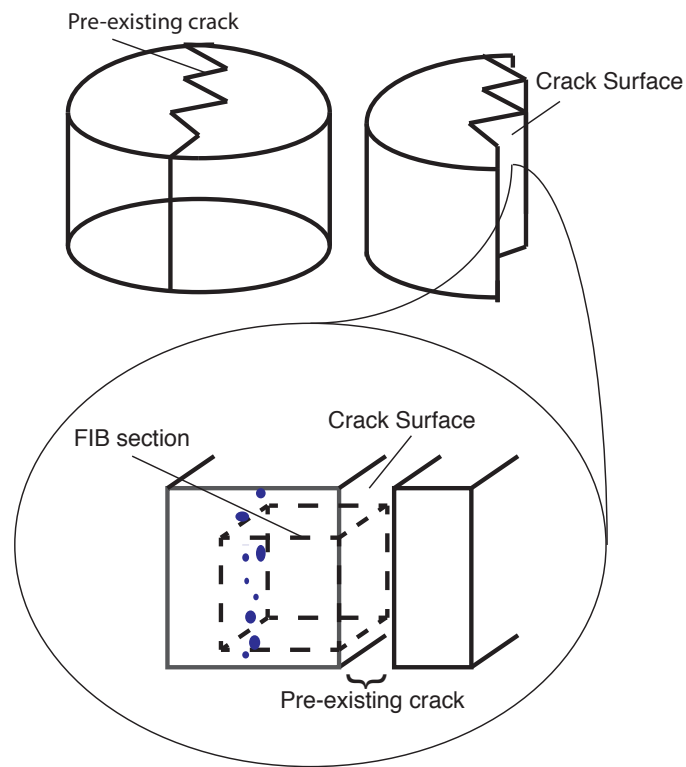
Samples were cut into several pieces and prepared for several methods of microanalysis. Part of each sample was epoxy impregnated, bisected axially and made into a traditional polished thin section. These thin sections were inspected using an optical microscope and regions of interest identified. The thin sections were then imaged using a SEM (Figure 4.1) and spot chemical analyses performed using EDS.

Figure 4.1. Volatilization microstructures in the field and the lab. a) Serpentinite core of a soapstone (magnesite-talc rock) illustrating radially inward carbonic alteration. b) Mesh texture in a partially serpentinized peridotite shows typical vein intersection angles and cores of unreacted olivine. c) Close-up view of layered vein in partially serpentinized peridotite. d) unreacted, thermally-cracked dunite. Crack surface is smooth with angular features. e) Thermally cracked dunite after several days reaction. Angular features have been smoothed and crack surface shows significant etch pits and secondary mineralization. f) Crack surface shows extensive dissolution pits and mineralization of platy serpentine, crystalline magnesite and amorphous material. g) Close-up view of amorphous material shows magnesite co-precipitating. h) Flattened olivine asperity surrounded by platy serpentine. i) Close-up view of well-terminated magnesite crystal covered with crystallites.



Unpolished portions of the samples were also analyzed to prevent damage to soft reaction products. Samples were broken along pre-existing crack surfaces to look at the area most exposed to fluid-rock interaction. FIB sections were cut into the crack face to examine the depth of penetration of fluids (Figure 4.2). Spot chemical analyses were performed using EDS to determine mineralogy of phases.

Figure 4.2. Schematic of FIB section. Samples were broken along pre-existing crack surfaces, the surfaces examined and FIB sections cut. FIB sections capture a cross-section ~10 microns down from the pre-existing crack surface.



4.2.3 Three dimensional microstructure analysis

FIB data were analyzed in 3D using several open source and commercial software packages. Image slices are first filtered to reduce noise using an edge-preserving, anisotropic diffusion filter then registered to reduced image translation due to FIB beam shifts using the open software package ImageJ (Shindelin et al., 2012). The stacked data were then converted and imported into the commercial software package Avizo where they were segmented using threshold segmentation into pore space and solid mineral. The pore space is then meshed and used as the flow geometry for a permeability tensor simulation. We obtained the tensor:

$$\mathbf{K} = \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 8 \times 10^{-18} \text{ m}^2 \end{vmatrix}$$

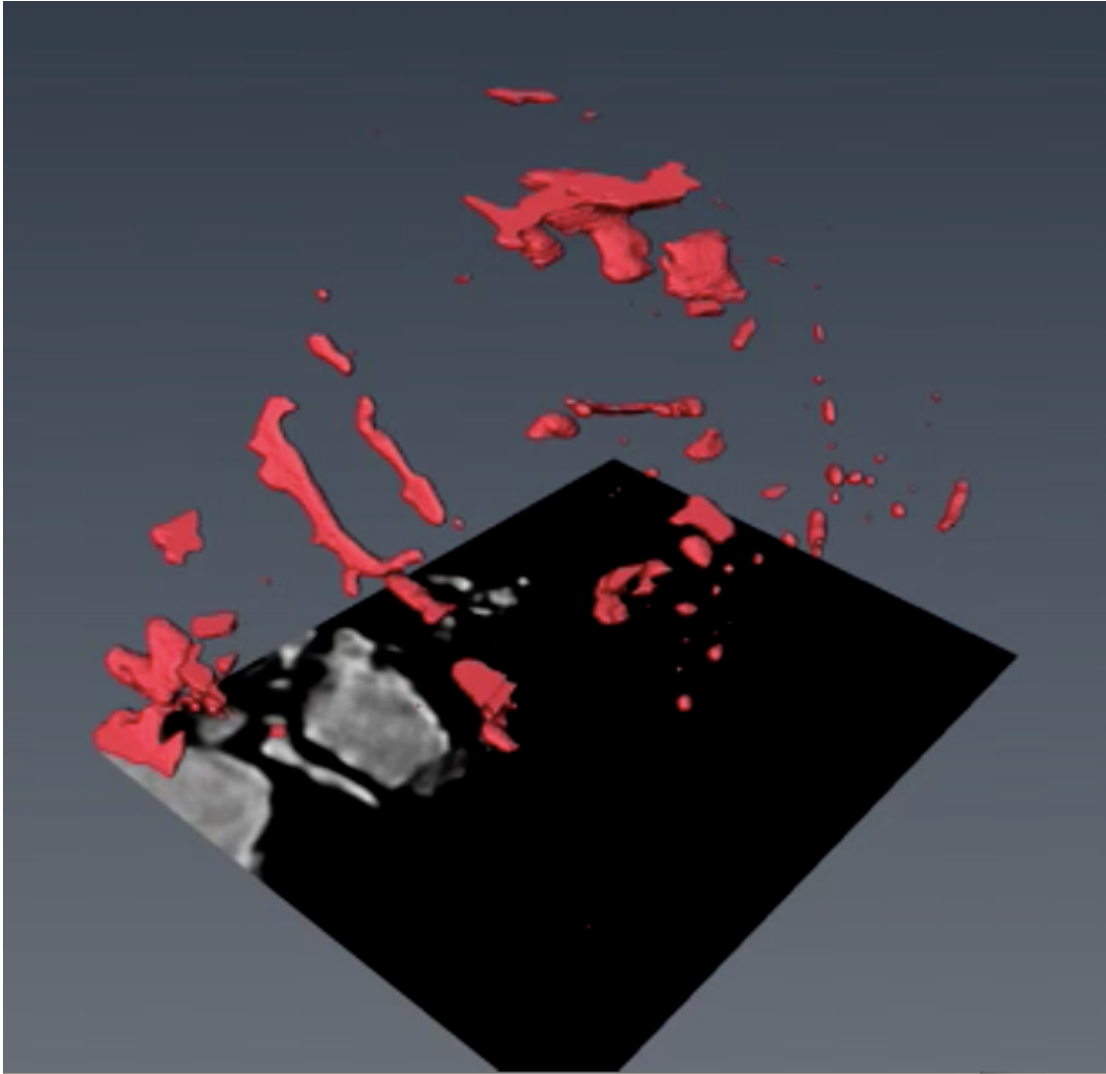
with the z-direction parallel to the original crack surface. The single non-zero component indicates that there is a particular direction of preferred flow, possibly related to the crystallographic orientation of the dissolving grain.

4.2.4 Nanotomography

We conducted X-ray nano-CT scan on olivine grains undergone 5 days of carbonation reaction at a confining pressure of 13MPa, pore pressure of 10MPa, and temperature of 200°C. The experiment was conducted using a transmission X-ray microscope (TXM) with an 8keV X-ray monochromatic beam at the beamline 32-ID

of the Advanced Photon Source of Argonne National Laboratory. A X-ray objective lens corresponding to a Fresnel zone plate with 60nm outermost zone width was used to magnify radiographs onto a detection system assembly comprising a scintillator (LuAG) , a Zeiss 5X optical microscope objective lens and an Andor Neo sCMOS camera. The Fresnel zone plate limits the spatial resolution to 60 nm, while the voxel size is 57 nm after binning. . Total 720 projection images were acquired in 180° rotation angle range (i.e, 0.25° per angular step) with 2s exposure time for each image. 3D reconstructions were performed with Tomopy, an open source collaborative framework for the analysis of synchrotron tomographic data [Gursoy et al., 2014]. Figure 4.3 is a 3D rendering visualization of the reconstructed slices, highlighting the segmentation of the wormhole shape porosity inside olivine grains.

Figure 4.3. 3D reconstruction of TXM data collected with the new full-field nanotomography instrument at the 32-ID beamline at the Advanced Photon Source at Argonne National Laboratory. Wormhole-like dissolution channels can be seen going all the way through olivine grains down to nanometer scales. Edge size is 15 μm .



Thresholding allows separation of different phases from the data sets for further analysis and quantification. Thresholding is a process where a grey value range representing a phase is identified and all voxels within that range are assigned a single value while all other voxels are disregarded as matrix [Heilbronner and Barrett, 2013]. In this experiment, global binarisation was conducted in Avizo 9 to isolate porosity. The threshold values are selected based on the grey value distribution histogram and image analysis. The grey values for the cropped sample distribute in the range between (2.97672×10^{-9} , 1.3161). It was found that the grey value histogram exhibits two peaks, which are likely to represent the pore and olivine respectively. Based on this and examination of the image, the grey value ranges between (2.97672×10^{-9} - 0.130552) was assigned to pore space. The olivine is represented by grey value between (0.30846 - 1.3161) while (2.97672×10^{-9} - 0.30846) is assigned to reaction precipitations (i.e. magnesite).

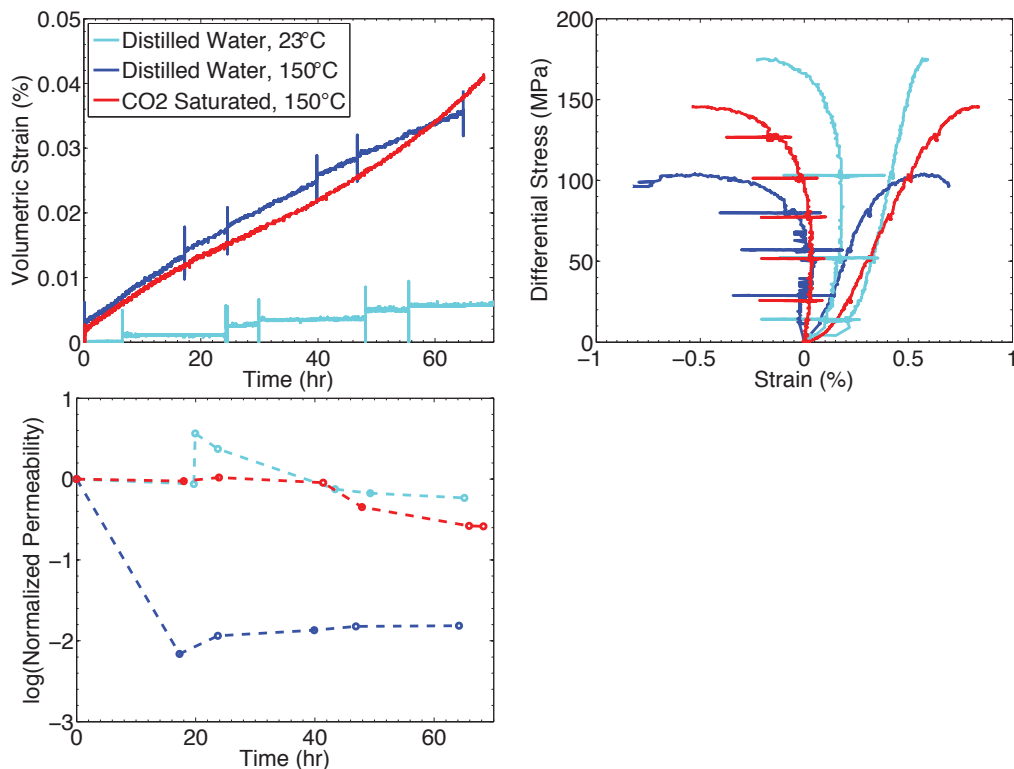
4.3 Results

4.3.1 Compaction, deformation and permeability reduction

To investigate the effect of chemically reactive fluids on the deformation and microstructural evolution of ultramafic rocks, we perform hydrostatic compaction experiments on thermally cracked dunites saturated with distilled water or CO₂-saturated brine (Figure 4.4). Sample volume change and permeability are monitored in-situ throughout three days of reaction at 15 MPa confining pressure, 10 MPa pore pressure and 150°C. One control experiment was conducted with distilled water at

room temperature. At the end of three days of reaction under hydrostatic loading, samples were deformed at a constant axial strain rate to assess the effect of the reaction on sample's elastic moduli and shear strength. Mechanical and permeability data from experiments are presented in Figure 4.4. After completion of experiments, samples were broken open along pre-existing cracks (Figure 4.2). Those crack surfaces are examined without polishing using scanning electron microscopy (SEM) coupled with focused ion beam (FIB) milling to examine three-dimensional (3D) structures and energy-dispersive x-ray spectroscopy (EDS) to discern mineralogy.

Figure 4.4. Mechanical and permeability data from experiments. A) volumetric strain versus time for hydrostatic creep experiments. The red curve is data from the sample saturated with CO₂ brine at 150°C, the dark blue curve is data from the sample saturated with distilled water at 150°C, and the light blue curve is data from the sample saturated with distilled water at 23°C. The room temperature sample shows little compaction, while the high temperature samples show more complex compaction behavior. B) Stress-strain curves for constant strain rate deformations after three days reaction. Coloring is the same as in (a). The sample saturated with CO₂ brine shows enhanced compaction compared to the sample saturated with distilled water. C) Normalized permeability versus time. Coloring is the same as above. Sample saturated with distilled water shows enhanced permeability reduction compared to the sample saturated with CO₂ brine.



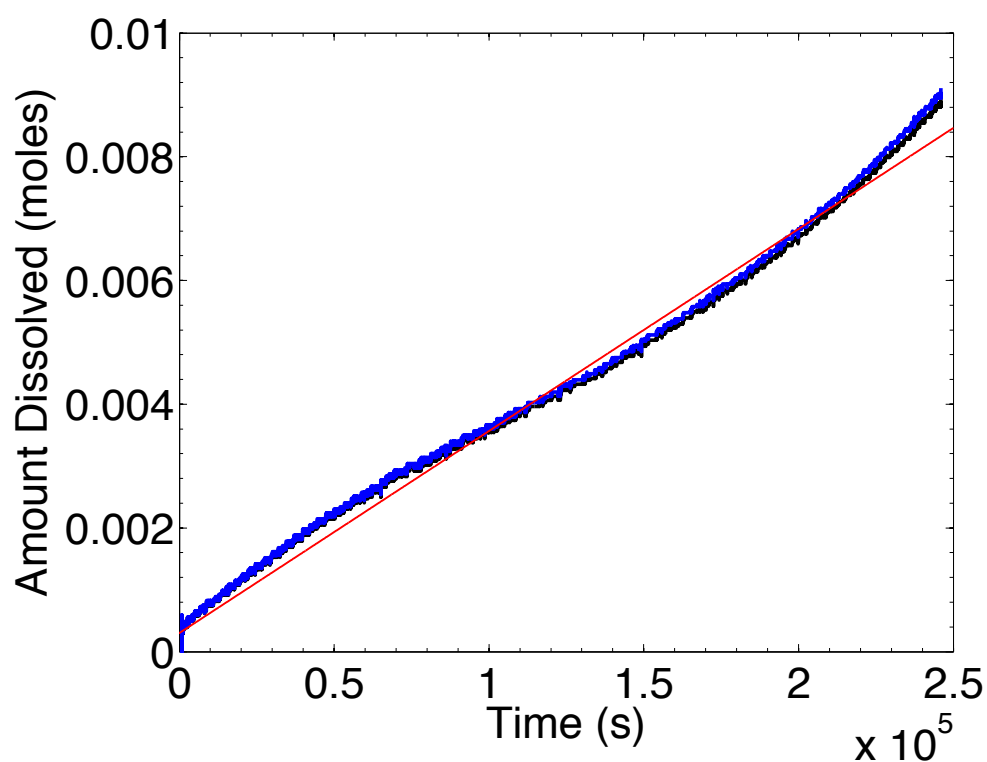
Mechanical behaviors of samples deformed with different pore fluids point to chemo-mechanical coupling. In the absence of any reaction, the sample with distilled water deformed at room temperature shows negligible compaction (Figure 4.4a). At 150°C, the sample with distilled water compacts with a monotonically decreasing rate during hydrostatic loading, which is consistent with dissolution-assisted closure of pre-existing cracks: Dissolution can be rigorous at contacting asperities with high concentrated stress, producing relatively high initial compaction rates. As the asperities are dissolved, they flatten, the local stress decreases and thus dissolution-assisted compaction slows down.

The sample with CO₂-saturated brine at 150°C shows similar behavior to the distilled water sample at the beginning of tests, with a decreasing compaction rate; however, after ~36 hours, the compaction rate begins to increase (Figure 4.4a). The compaction is initially less in the sample with CO₂-saturated brine compared to the distilled water sample, but the late-stage increase in compaction results in higher total compaction by the end of the hydrostatic portion of the experiment. The dissolution of asperities is also inferred to occur in the sample with CO₂-saturated brine, but the influence of the CO₂ results in a competitive process that is enhancing compaction and compaction rate. Triaxial compression tests indicate that the sample with distilled water has lower yield strength and more dilatancy after reaction than the sample with CO₂-saturated brine (Figure 4.4b).

The effective olivine dissolution rate can be calculated from our mechanical data. Assuming all of the sample compaction is the result of olivine dissolution, and using a typical specific surface area for thermally cracked crystalline rocks of 3 m⁻¹

[Darot et al., 1992], an effective dissolution rate of 10^{-12} mol/cm²s is obtained (Figure 4.5), a number that agrees well with rates obtained from batch reactor experiments at similar T, and pH conditions [Hanchen et al., 2006]. Previous studies have suggested that grain boundary structure may control effective olivine dissolution rate [van Noort et al., 2013]. Microstructural analysis of our samples after reaction indicates a feedback between dissolution and grain boundary structure that may provide a mechanism for maintaining porosity.

Figure 4.5. Moles of olivine dissolved versus time. The dissolution rate can be calculated from the slope of this curve.



4.3.2 Microstructural analysis

Microstructural observation of the samples after experiments shows that the chemo-mechanical coupling is caused by interplay of dissolution and precipitation processes at fluid-rock interfaces. SEM images of the experimental samples (Figure 4.1d-i) show that initial sample material is largely monomineralic olivine with trace chromite and pore space is almost entirely high aspect ratio thermal cracks. Due to the thermal cracking process (See Methods), samples are initially serpentine free. Crack surfaces are clean and edges angular (Figure 4.1d). The sample reacted with distilled water at room temperature shows slight rounding of angular edges, but surfaces remain clean. The distilled water sample at 150°C shows more pronounced rounding of angular edges. Crack surfaces show slight secondary mineralization of a platy mineral which EDS analysis indicates is serpentine (Figure 4.1e), as well as some amorphous material with a composition between serpentine and talc (slightly silica-enriched serpentine), although the topography of the unpolished surfaces rendered quantitative chemical analysis unreliable. On the whole, the microstructure of the sample with distilled water at 150°C suggests transport-controlled dissolution [Lasaga and Kirkpatrick, 1981]. In comparison, the sample with CO₂-saturated brine as pore fluid shows more prominent alteration. Surfaces exhibit substantial pitting (Figure 4.1f), indicating relatively rapid, reaction-controlled dissolution [Lasaga and Kirkpatrick, 1981]. Secondary mineralization is ubiquitous, with crack surfaces supporting inter-grown patches of amorphous material, serpentine, magnesite and hydrated magnesium carbonate (perhaps hydromagnesite or nesquehonite) (Figure 1g). The secondary mineralization appears to be highly porous (Figure 4.1i), some of

the most striking features of these samples are the deep, interconnected etch pits, some of which resemble wormholes [Ott and Oedai, 2015]. To investigate the 3D structure of these etch pits, several serial FIB sections were cut into the crack surface.

Analysis of the data from FIB sections shows the presence of a band of enhanced porosity parallel to and 8-10 μm beneath crack surfaces (Figure 4.6). Dissolution appears to be channelized and heterogeneous. Secondary porosity is quasi-spherical and/or quasi-cylindrical and is geometrically distinct from the high aspect ratio thermal cracks that make up the primary porosity. Unreacted samples and samples reacted with distilled water do not exhibit this feature (Figure 4.7). Induced porosity ranges from 20-60% within the highly porous band. Image analysis indicates that the secondary porosity is interconnected and exhibits anisotropic permeability.

Figure 4.6. Data from FIB serial section of altered dunite. a) FIB-section shows concentrated band of porosity ~ 8 microns down from the crack surface. b) Image analysis shows that porosity in the band varies from ~ 20 -60%. Colors correspond to porosity values. c) Top panel shows binarization of one slice of FIB data. Bottom panel shows average porosity along all slices in color and model results in bold black, with lines representing successive time-steps [25]. Spacing of porosity bands, R_c , agrees with model of induced porosity.

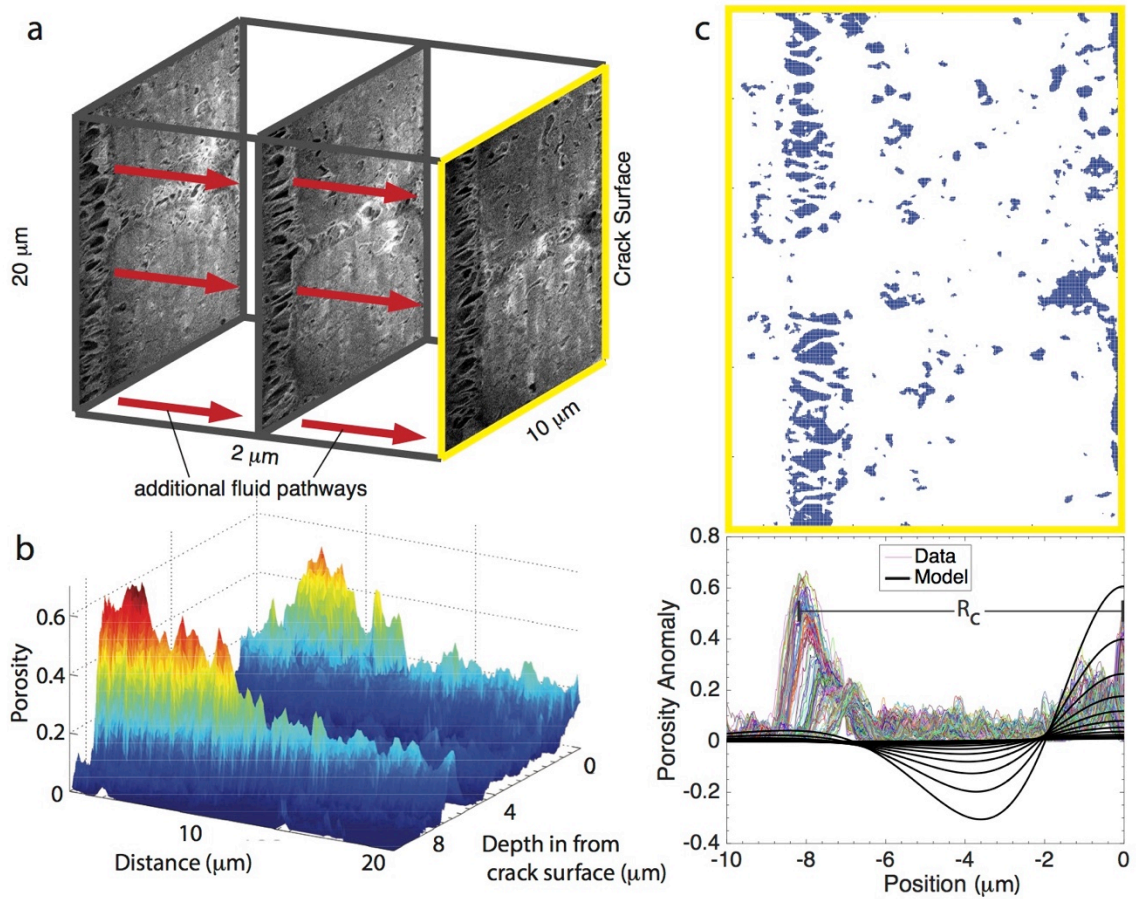
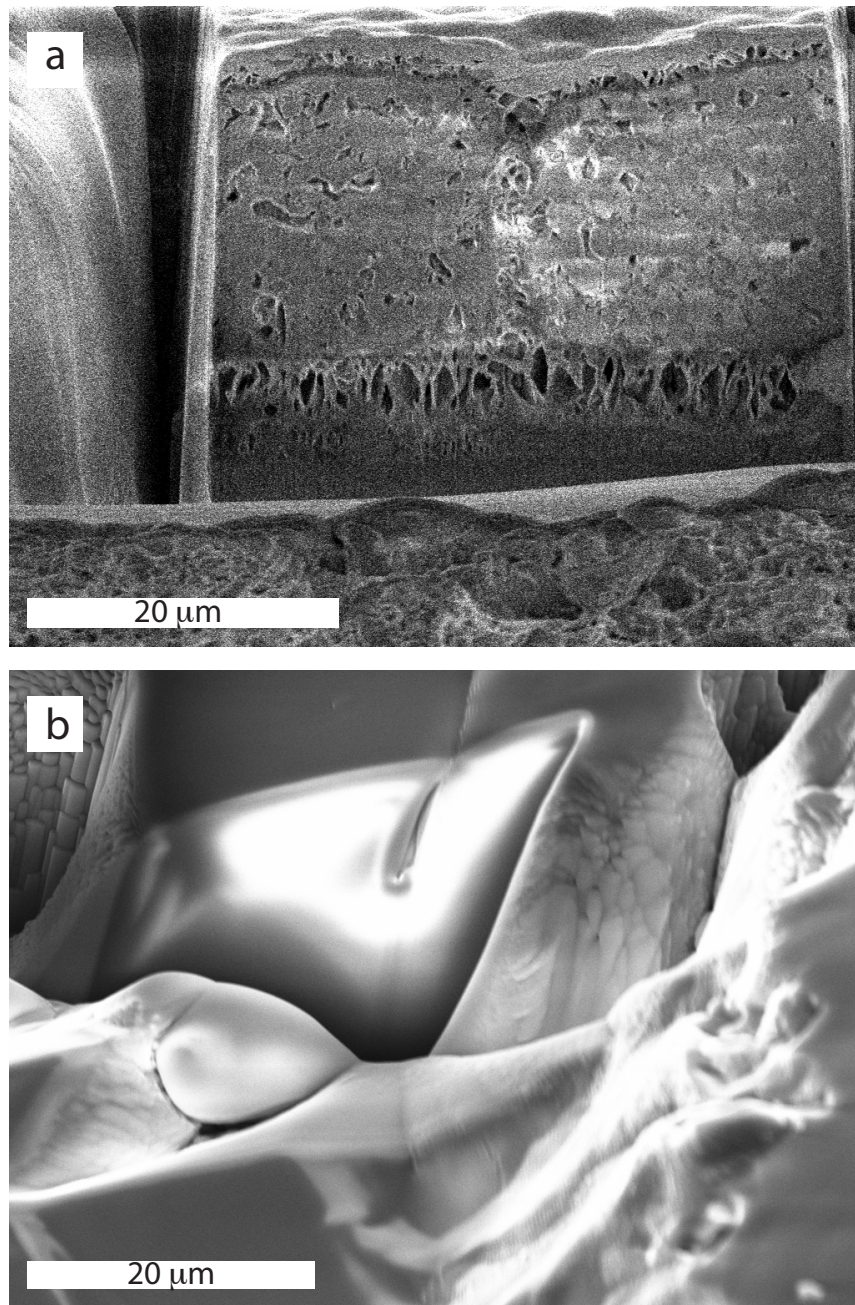


Figure 4.7. Overviews of FIB sections from a) sample saturated with CO₂ brine and b) unreacted sample. The altered sample shows significant dissolution channels into the crack surface, while the unaltered sample shows few features down from the crack surface.



4.3.3 Porosity band model

A model from Merino et al. [1983] was used to reproduce the experimentally observed dissolution patterns. This model couples stress-dependent dissolution with diffusion of dissolved species through stagnant fluid using the equations,

$$\frac{\partial \psi}{\partial \hat{t}} = -(1 - \bar{\phi}\psi)^{2/3}[\sigma - \sigma^{eq}(\psi)] \quad (4.1)$$

$$B\psi \frac{\partial \sigma}{\partial \hat{t}} = \frac{\partial}{\partial \hat{s}} \left(\psi^m \frac{\partial \sigma}{\partial \hat{s}} \right) - (1 - \bar{\phi}\psi)^{2/3}[\sigma - \sigma^{eq}(\psi)] \cdot [1 - \varepsilon e^{\lambda(1 + \omega\sigma)}] \quad (4.2)$$

where ψ is the porosity anomaly, $\hat{t}$ is dimensionless time, $\bar{\phi}$ is average porosity, σ is a measure of the chemical potential, $\sigma^{eq}(\psi)$ is a function describing the porosity dependence of chemical potential, B is a constant, $\hat{s}$ is dimensionless space, m is a power law constant, ε is the ratio of dissolved molar component to the solid molar volume, λ is a constant related to the stress dependence of chemical potential, and ω is related to the total chemical potential of the system. For details of the model, see Merino et al. (1983). These equations are solved using the MATLAB stiff solver ode15s, using the initial one-dimensional geometry of a small positive porosity anomaly representing a crack in an otherwise solid rock. The model shows that this porosity anomaly grows, and also induces a satellite band of porosity some distance in from the initial crack.

The model also predicts that such satellite porosity bands will form at a characteristic distance, R_c :

$$R_c = (D_c \bar{\phi}^m / kn^{1/3})^{1/2} \quad (4.3)$$

where D_c is the diffusion constant, k is reaction rate and n is the pore geometry parameter. Using the parameter values appropriate for our experimental conditions,

we get a value of 8.3 microns, in very good agreement with the observed 8-micron spacing of our secondary porosity, though this value should not be over-interpreted as the calculation is meant only to yield order of magnitude estimates. Parameters used in this calculation are presented in Table 4.1.

Table 4.1. Parameter values for characteristic distance calculation.

Parameter	Value
D_c	$10^{-8} \text{ cm}^2/\text{s}^{\text{a}}$
$\bar{\phi}$	$10^{-2}{}^{\text{b}}$
m	2^{c}
k	$4.4 \times 10^{-11} \text{ cm/s}^{\text{b}}$
$n^{-1/3}$	$3 \times 10^{-5} \text{ cm}^{\text{b}}$

a. Watson, 1991

b. this study

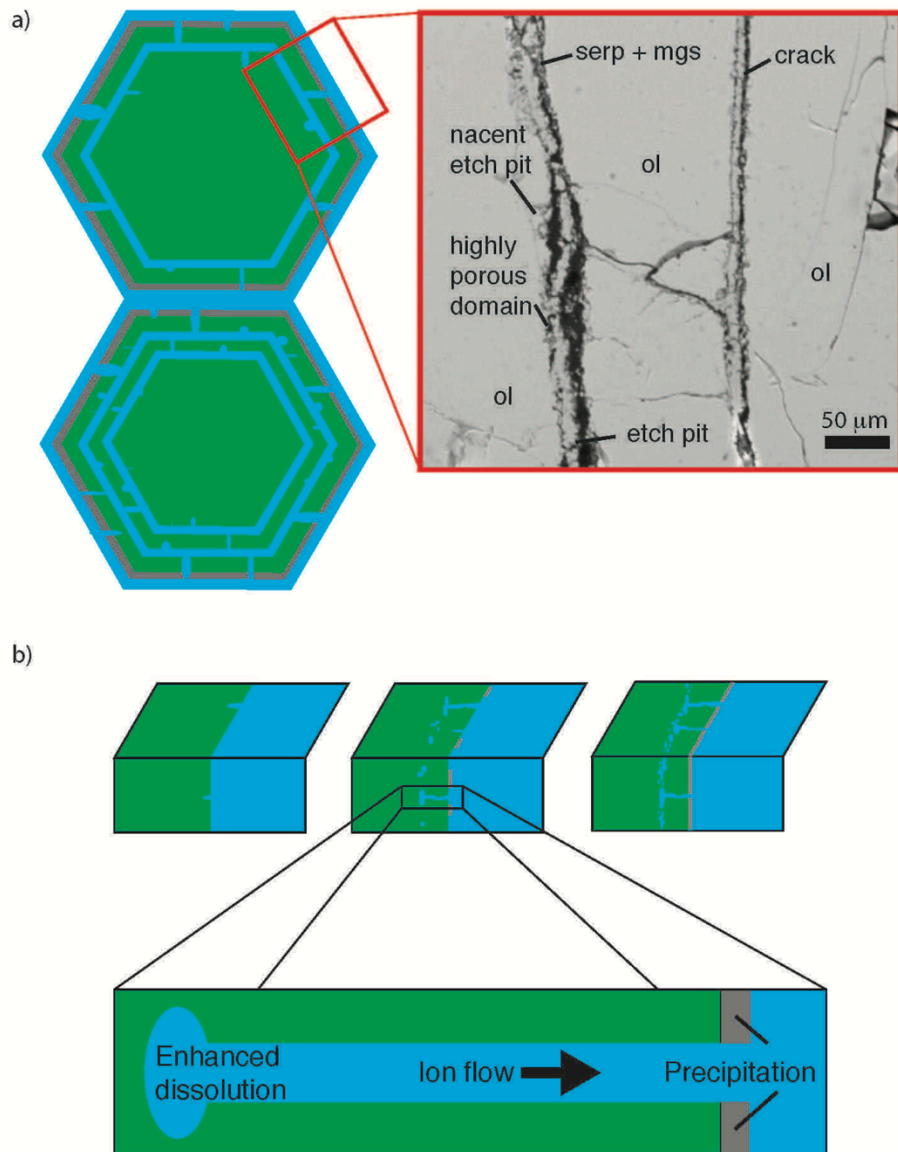
c. Merino et al., 1983

4.3.4 Conceptual Model

The mechanism for generating such secondary porosity is presented in Figure 4.8. Etch pit nucleation in olivine commonly begins at local chemical potential maxima caused by stress associated with near surface dislocations [Dove et al., 2005]. These etch pits are stress risers that enhance dissolution [Kamb, 1959], which results in a reactive instability and growth of quasi-cylindrical pores. Our experiments had static pore fluid, thus dissolved species transport is controlled mainly by diffusion. The coupling of this reactive instability and diffusion can induce satellite porosity bands with characteristic spacing [Merino et al., 1983]. Using the model from Merino et al. [1983] with parameters corresponding to our experimental conditions,

we can reproduce the 8 μm spacing; however, the magnitude of porosity change does not agree as well. The model assumes a monomineralic system with a single dissolved species and a simple one-dimensional geometry, deviations from which may explain these discrepancies. In our experiments, precipitation of secondary minerals constantly removes dissolved species from solution, causing their depletion and driving enhanced dissolution.

Figure 4.8. Conceptual model of locally enhanced compressive stress induced porosity bands. a) Inward growth of porosity bands causes radially inward alteration. Dissolution divides olivine grains into small domains with enhanced reactive surface area. b) Concentration gradient between zone of enhanced porosity and primary pore space leads to preferential flow of dissolved species, leading to positive feedback.



4.4 Discussion

Most secondary mineralization is observed along pre-existing crack surfaces, rather than within small secondary pores (Figure 4.1). The high curvature of the small pores suppresses precipitation [Putnis and Mauthe, 2001], leading to elevated concentrations of dissolved species in these pores compared to the bulk fluid, in which the concentrations of dissolved species are buffered by secondary mineralization. This results in a concentration gradient between the secondary pores and the primary pores, i.e., pre-existing cracks, which leads to a dynamic flow of dissolved species. This flow coupled with the stress-dependent growth of localized secondary porosity provides a mechanism for local intensification of deformation, while precipitation of secondary minerals along crack surfaces can laterally inhibit dissolution and deformation. The result is a self-organized pattern of locally intensified compressional stress-induced porosity bands (Figure 4.6).

This conceptual model is consistent with the interface-coupled dissolution-precipitation reactions understood to mediate phase transitions in many aqueous systems [Putnis and Punis, 2001]. In such reactions, reactive surface area is maintained by an asymmetry in dissolution and precipitation caused by the relative thermodynamic stability of the secondary phase. During olivine carbonation reaction, the rapid dissolution rate of olivine is coupled with the particularly sluggish precipitation of magnesium carbonate [Xu et al., 2013]. The asymmetry is so great, that channelized olivine dissolution can separate olivine grains into domains which are subsequently exposed on all sides to reactive fluid, eventually leading to a layered structure (Figure 4.8). In experiments on olivine aggregates with smaller grain sizes,

X-ray nano-Computed Tomography (nano-CT) shows these dissolution channels to entirely bifurcate grains in a process similar to dissolution facilitated sub-critical crack growth, which may provide a mechanism for the production of hierarchical crack networks absent critical fracture (Figure 4.3). In the presence of additional tectonic stress, these subcritical cracks may be further enhanced, leading to the commonly observed extensive fracturing in hydrating and carbonating peridotites [Plummer et al., 2012]. The enhanced deformation of samples exposed to the more reactive fluid in our experiments is consistent with this notion. This subcritical crack growth mechanism is commonly understood to control joint sets [Savalli and Engelder, 2005] with similar structural characteristics as observed in altered ultramafic rocks [Plummer et al., 2012].

4.5 Conclusions

In nature, metasomatized ultramafic rocks often exhibit structures suggesting self-organized fracture networks that appear to be controlled by interaction of chemical and physical stresses. Our experiments under controlled conditions demonstrate growth of secondary porosity during olivine carbonation amid dissolution and precipitation of secondary minerals. Hydrostatic compaction is accompanied by permeability reduction and reactive CO₂-brine enhances the reduction in permeability; however, samples saturated with reactive brine exhibit less permeability reduction during triaxial deformation due to the presence of interconnected dissolution channels. The microstructural evidence supports a mechanism that explains commonly observed structures through the formation of

locally intensified compressional stress-induced porosity bands and the propagation of dissolution assisted subcritical cracks. This type of deformation does not require a large force of crystallization to be exerted by the growth of secondary minerals in a confined pore space, allowing for the slow growth of fracture networks at subcritical stress intensities.

Chapter 5: Mechanical strength and physical properties of variably carbonated ultramafites from Linnajavrri, Norway

5.1 Introduction

5.1.1 Background

Carbon dioxide is one of the most common geological fluids. Its interaction with mafic and ultramafic rocks on the ocean floor at fracture zones and detachment faults and within ophiolite complexes leads to metasomatic transformations of economic and geodynamic importance. The interaction of carbon dioxide- and silica-rich fluid with ultramafic rocks is often called steatization, and involves the metasomatic alteration of olivine-pyroxene or serpentinite rocks into talc-carbonate rocks called soapstones [Hess, 1933]. If the fluids are extremely carbon-rich, the process can continue to completion, binding all the magnesium from olivine and pyroxene in magnesium carbonate, resulting in magnesite-quartz rocks known as listvenites. Serpentinite-soapstone-listvenite sequences are found in ophiolites adjacent to pelitic schists, and are sources not only of economic talc and magnesite deposits, but are also associated with gold mineralization [Qiu and Zhu, 2014].

The hydration and carbonation of the oceanic crust changes mechanical behavior, which facilitates oceanic spreading, particularly along slow and ultraslow segments of mid-ocean ridges. Large displacements at slower spreading centers are accommodated by localized deformation along highly altered surfaces. The alteration occurs at relatively low temperatures and results in talc and amphibole-rich fault

rocks [MacLeod et al., 2002; Escartin et al., 2003]. The resulting structure, several discontinuous shear zones underlain by one sub-horizontal decollement surface, called an oceanic core complex (OCC) is very similar the metamorphic core complexes observed in continental rifting environments [e.g. Crittenden, 1980; Wernicke, 1981]. Such features have been observed at the Mid-Atlantic Ridge (MAR) at 15° 45' N [Escartin et al., 2003], at the Kane core complex at 23° 30' N [Karson and Lawrence, 1997], at Dante's Dome at 26° 35' N [Tucholke et al. 2001] and at the Godzilla Mullion in the Phillippine Sea [Harigane et al., 2005]. In some cases these detachment faults are thought to accommodate up to several tens of kilometers of displacement along an extremely weak, localized shear zone [Karson et al., 2006]. This sort of coupled alteration-deformation is not limited to OCC's, but is also commonly observed in fracture zones as well, for instance at the MAR 15°20' N Fracture Zone [Bach et al., 2004], the Conrad Fracture Zone [D'Orazio et al., 2004] and at the Islas Orcadas Fracure Zone of the Southwest Indian Ridge [Kimball et al., 1985].

The structural, mechanical and mineralogical characteristics of these rocks can be long-lived and affect later tectonic deformation over the course of the supercontinent cycle [Wilson, 1966], influencing the obduction of ophiolites and possibly the initiation of subduction [Maffione et al., 2015]. Subaerially exposed ophiolites provide us an uncommon view of sub-ocean floor deformation. Talc and amphibole rich faults have been identified at the Troodos Ophiolite [Varga, 1991; Cann and McCaig, 2005], the Lizard Ophiolite [Gibbons and Thompson, 1991] and in several ophiolite terrains in the Alps and Apennines [Abbate et al., 1980; Treves and

Harper, 1994; Desmurs et al., 2001], all of which are interpreted to be oceanic faults. These tend to be very small features in the field, consistent with the extreme localization observed in modern oceanic faults. The rheology of metasomatized oceanic crust during dehydration is recognized to play an important role in subduction zone deformation [Escartin et al., 2005].

Another common feature of ophiolites are so-called ophicarbonates, often breccias, with abundant serpentine, magnesite, dolomite, chlorite and amphiboles. They are often interpreted as being associated with fracture zones [Lemoine, 1980; Fruh-Green et al., 1990; Treves et al., 1995; Pozzorini and Fruh-Green, 1996; Lagabrielle and Lemoine, 1997]. These rocks have been used as an endmember for proposed carbon sequestration projects and are used to constrain the natural uptake of carbon dioxide in ophiolites [Kelemen et al., 2011; Beinlich et al., 2010]. Economic talc deposits associated with this type of alteration are recognized to be the result of regional metamorphism and thrust faulting of ultramafites [Salem, 1992; O'Hanley, 1996; Karlsen et al., 2000] through contact metamorphism [Beaulieu, 1985] or possibly linked to processes at oceanic spreading centers [Alietti, 1959].

There is a relative paucity of data regarding the physical characteristics of ultramafic rocks as they undergo carbon-rich metasomatism; yet, evidence of CO₂-rock interaction in the form of talc and carbonate minerals are common in the oceanic crust. Magnetic susceptibility and seismic velocity have been used to constrain the hydration of ultramafic rocks in the field [Salisbury and Christensen, 1978; Toft et al., 1990], as well as in the laboratory [Malvoisin et al., 2012], but little attention has been paid to the transformations that occur in the presence of carbon dioxide, which

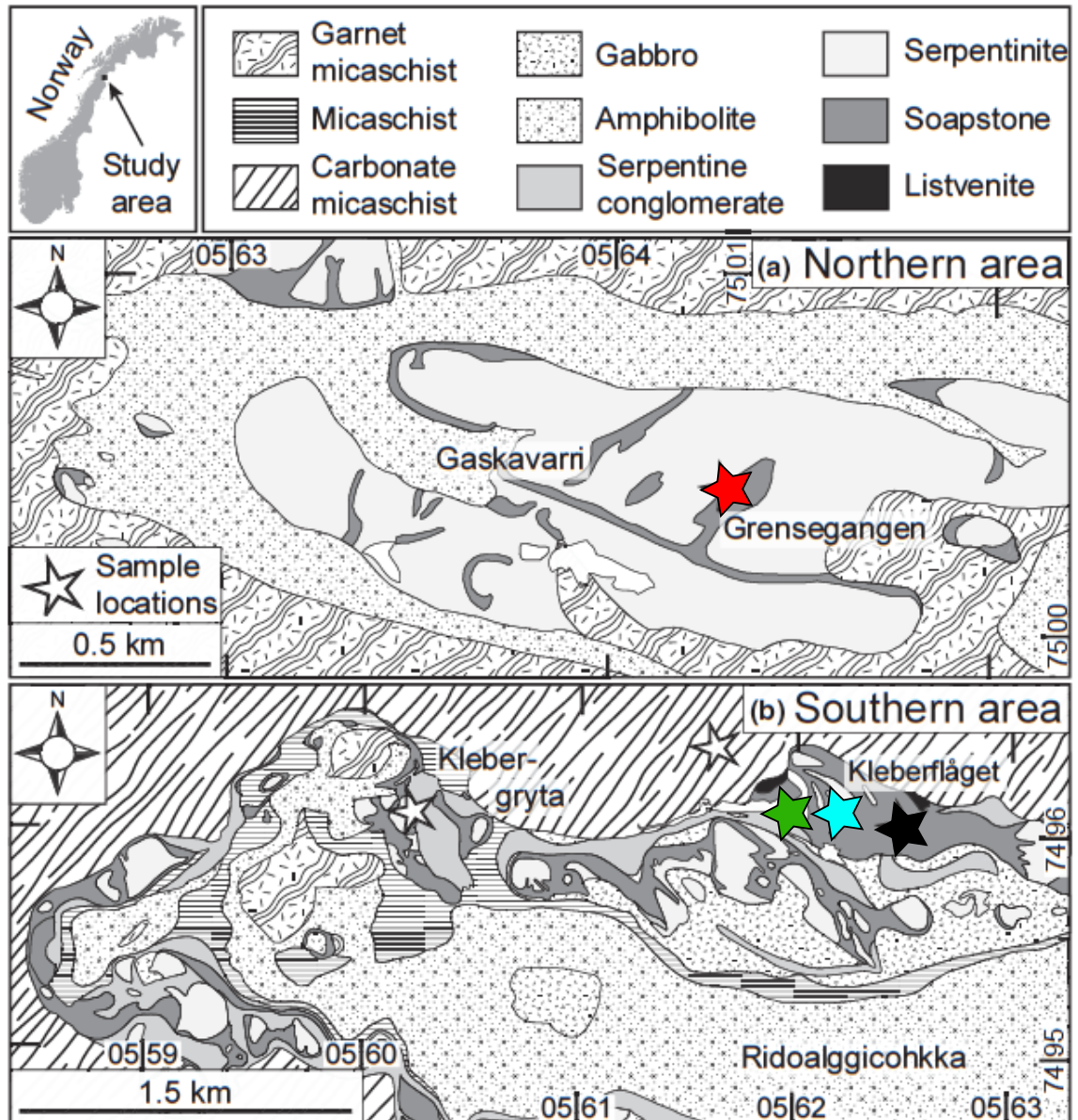
can complicate interpretation of geophysical data. How do the mineralogical and textural changes that occur during carbonation effect the petrophysical and mechanical characteristics of the rocks? A better understanding of the evolution of physical properties of ultramafic rocks as they undergo carbonic alteration can provide insight into processes in the oceanic crust at detachment faults and fracture zones, in subduction zones and also provide context for the monitoring of proposed engineered carbon sequestration efforts. I present in this paper the results of a series of petrophysical and geomechanical tests on variably carbonated ultramafic rocks from northern Norway in order to place some constraints on these characteristics.

5.1.2 Geologic Setting

The samples in this study were collected from Linnejavri, Norway, centered around 67°36'N and 16°24'E near the Swedish border. Samples were collected from a northern (Gaskavarri) and southern (Ridoalggicohkka) site (Figure 5.1).

The rocks in this area are part of a Caledonian nappe, thrust onto felsic Precambrian basement during the Caledonian orogeny [Rehnstrom and Corfu, 2004]. The ultramafites have been described as part of a tectonic mélange [Lindahl and Nilsson, 2008], obscuring their original provenance, but underlying amphibolite has been interpreted as altered oceanic crust, suggesting an inverted ophiolite sequence [Beinlich et al., 2010].

Figure 5.1. Geological maps of the two sample collection areas in Linnejavri, Norway, modified from Beinlich et al., 2012. Coordinates refer to UTM-zone 33W. Stars represent sample collection locations: red – soapstone-serpentinite interface, black – listvenite, blue – soapstone, green – serpentinite, white – samples analyzed in Beinlich et al., 2012.



Two suites of samples were collected, one from a diffuse reaction zone between a serpentinite and a soapstone from Gaskavarri and one from homogeneous bodies of serpentinite (hydrated peridotite), soapstone (partially carbonated) and listvenite (fully carbonated) from Ridoalggicohkka.

5.2 Methods

All samples were subjected to a series of three tests, ultrasonic velocity measurement, electrical impedance measurement and triaxial deformation. Prior to testing, dry and saturated densities were measured for each sample.

5.2.1 Ultrasonic velocity tests

Samples were vacuum saturated with de-ionized water for 24 hours, then affixed to sample holders, jacketed with heat-shrink polyolefin tubing and secured with steel tie-wires. Tests were performed undrained, so each side of the sample is sealed. Sample holders were equipped with piezoelectric transducers on either side of the sample, oriented to record one P-wave and two orthogonal S-waves. Samples were loaded into a pressure vessel and pressurized to 10 MPa confining pressure. Wave velocities were recorded by pulsing the piezoelectric transducers on one side of the sample and recording the response on the other side. Correcting for the sample length at a given pressure condition, the wave velocities can be calculated from the arrival time of the waveforms. Wave velocities were recorded every 10 MPa from 10-120 MPa, to test the pressure dependence of velocity.

5.2.2 Electrical resistivity tests

Samples are vacuum saturated with 3 g/L NaCl brine for 24 hours, then affixed to sample holders, jacketed with heat-shrink polyolefin tubing and secured with steel tie-wires. Sample holders are equipped with voltage and current electrodes on either end, with the current electrodes covered by a permeable insulator in order to record a true 4-electrode impedance measurement [Constable, 2015]. Sample ends are covered by a permeable silver electrode to ensure good electrical contact with the entire cross-section of the sample. Samples are loaded into a pressure vessel and pressurized to 20 MPa confining pressure and 10 MPa pore pressure and bubbles purged from the system. Impedances are measured by imposing an alternating current at a range of frequencies from 0.01 to 100000 Hz across the sample, to test the frequency dependence of impedance. Measurements were repeated every 10 MPa from 10-110 MPa effective confining pressure, to test for pressure dependence. Electrical impedance is the complex ratio of voltage to current in a circuit,

$$Z = \frac{V}{I} \quad (5.1)$$

by imposing a current and measuring the voltage across the sample, Z can be calculated. Because the V and I vary with time, there is both an amplitude and a phase response. The amplitude response is R , the resistivity and the phase response is X , the reactance. The resistivity can be understood as the resistance to current flow, and the reactance as an inherent capacitance.

5.2.3 Triaxial tests

Samples are dried in a vacuum oven at 50°C for 24 hours, jacketed in thin copper foil and affixed with axial and radial strain gages prior to experiments. Samples are then put in a triaxial deformation apparatus and pressurized to 50 MPa confining pressure. Axial deformations occur at a nominal strain rate of $3.5 \times 10^{-5} \text{ s}^{-1}$ and stress and strain data are collected at 0.5 Hz. Samples are deformed until failure then unloaded, epoxy impregnated and thin sections prepared for microstructural analysis.

5.3 Results and Discussion

5.3.1 Serpentine-soapstone interface

The northern Gaskavarri field site is a serpentinite mass with soapstone veins (Figure 5.2a). A diffuse contact between a soapstone vein and the serpentinite was sampled every few cm (Figure 5.2b) in order to test whether there is a systematic transition in petrophysical properties. All petrophysical measurements along the Lin-3 transect are presented in Figure 5.6.

Figure 5.2. Field images from the Gaskavarri site. A) outcrop of carbonated serpentinite, b) soapstone-serpentinite transect Lin3.

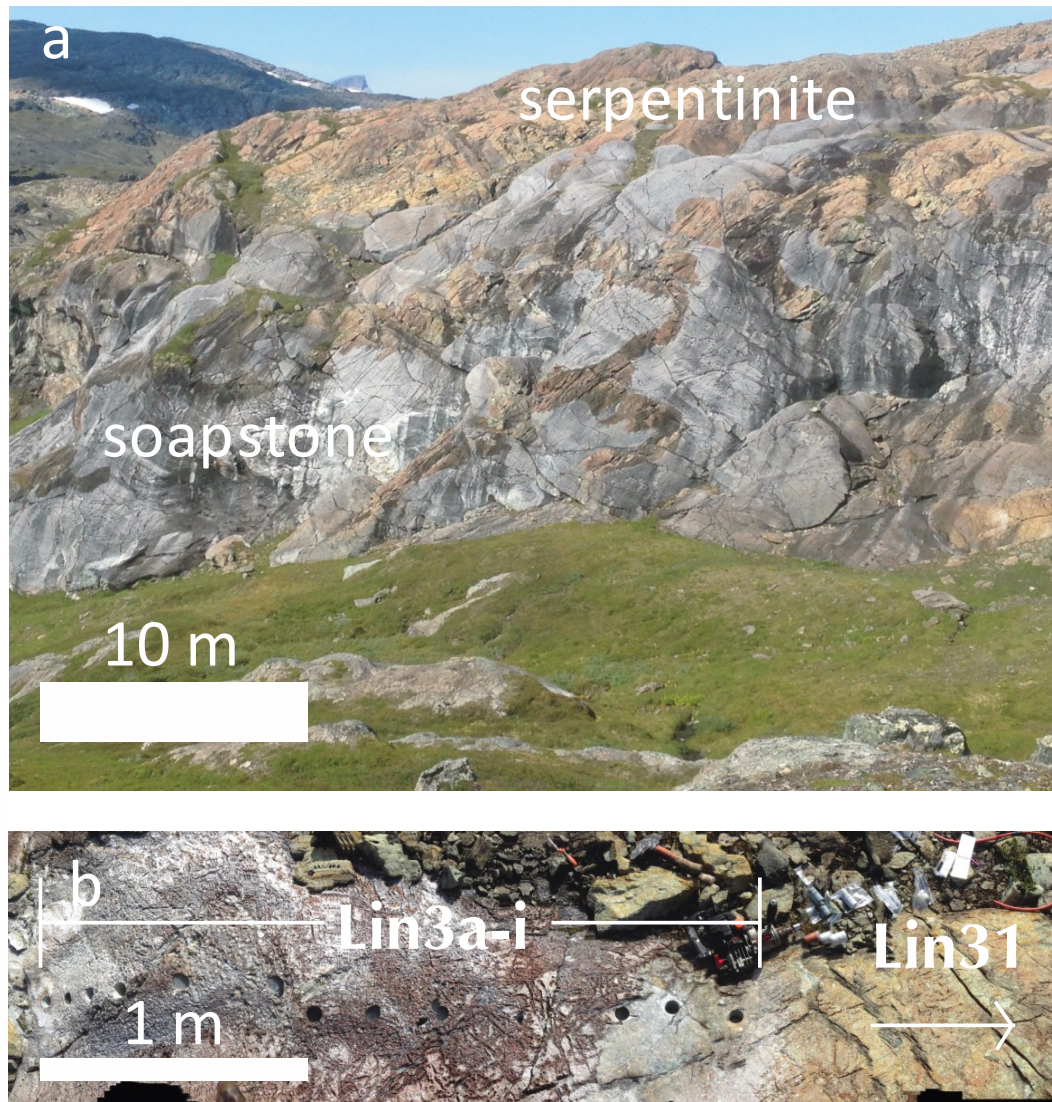
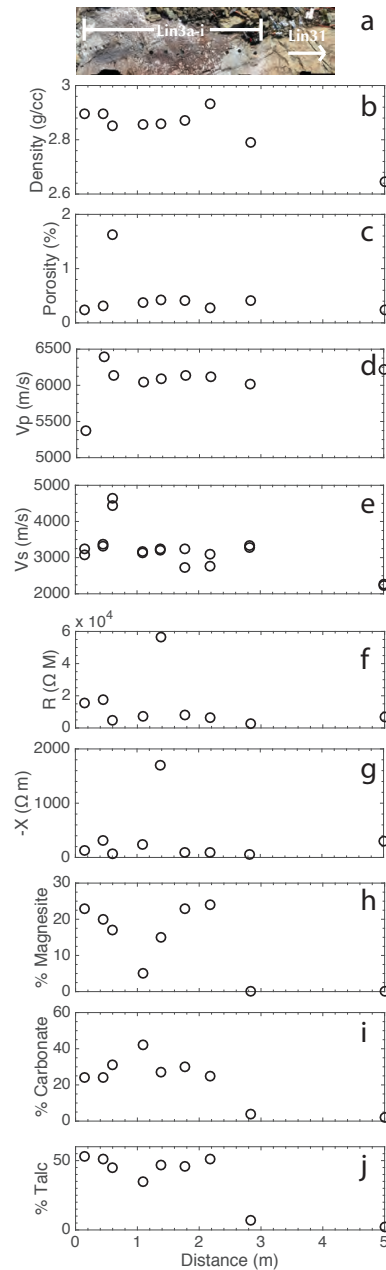


Figure 5.3. Petrophysical and mineralogical data from the Lin3 transect. All values are reported for 110 MPa effective pressure. A) image of Lin3 transect, b) density, c) porosity, d) P-wave velocity, e) S-wave velocity, f) resistivity at 0.01 Hz, g) reactance at 0.01 Hz, h) modal abundance of magnesite, i) total carbonate, and j) talc. Transition between serpentinite and soapstone happens sharply between 2 and 3 meters.



Mineralogical analysis of the samples (Figure 5.3g-i) indicated that although appearing diffuse at the outcrop scale, the contact between serpentinite and soapstone is actually fairly sharp. Modal abundance of talc and carbonate minerals jump from ~3 to ~50 and ~3 to ~20 within a meter between samples Lin3h and Lin3i. Some petrophysical measurements show some slight trends as the rock transitions from serpentinite to soapstone; density increases across the serpentinite-soapstone interface and porosity decreases. However, electrical impedance and elastic velocities do not show clear trends when mapped geographically.

5.3.2 Effect of carbonation extent

As only weak correlations were found in petrophysical properties along the Lin3 transect, and the serpentinite-soapstone contact was quite sharp, petrophysical properties are plotted against mineral content of the samples from the Lin3 transect, with talc or carbonate used as a proxy for carbonation extent. Modal abundances (volume percent) are estimated from thin sections and presented in Table 5.1.

Table 5.1. Mineral modes from Lin3 transect.

Sample	Distance (m)	Clinocllore	Dolomite	Serpentine	Magnesite	Magnetite	Talc
Lin_29	0	24	3	3	1	3	67
Lin_3a-13	0.15	17	1	3	23	3	53
Lin_30a	0.27	14	4	2	24	3	53
Lin_3b-13	0.45	18	4	2	20	4	51
Lin_3c-13	0.60	17	14	2	17	4	45
Lin_30b	0.80	16	4	2	27	2	50
Lin_3d-13	1.09	16	37	3	5	4	35
Lin_3e-13	1.38	18	14	3	15	4	47
Lin_3g-13	1.77	17	7	3	23	4	46
Lin_30c	1.80	19	9	3	19	2	49
Lin_3h-13	2.18	19	1	2	24	4	51
Lin_30d	2.60	17	7	3	23	4	46
Lin_3i-13	2.83	0	4	85	0	4	7
Lin_30e	3.10	0	3	83	0	7	7
Lin_31	5.00	0	2	95	0	1	2

Some correlations emerge when petrophysical properties are plotted against talc or carbonate in samples. Electrical resistivity shows a positive correlation with carbonation extent (Figure 5.4a,c,e). This is consistent with the consumption of magnetite during carbonic metasomatism, and possibly with changes in the grain and pore structure caused by deformation during emplacement. There does not, however, appear to be a correlation between electrical reactance and carbonation extent (Figure 5.4b,d,f). The source of electrical reactance in rocks is the capacitive nature of grain boundaries [Karato and Wang, 2013], so the lack of evolution with carbonation extent suggests that the metasomatism does not affect the inherent capacitance of the rocks, even as their resistance is changed.

Figure 5.4. Electrical impedance plotted against mineralogical content. Least squares linear regressions are added to each plot, along with the equations and R^2 for the fit. A) resistivity versus talc, b) reactance versus talc, c) resistivity versus magnesite, d) reactance versus magnesite, e) resistivity versus total carbonate, and f) reactance versus total carbonate. Resistivity has a positive correlation with talc and magnesite content.

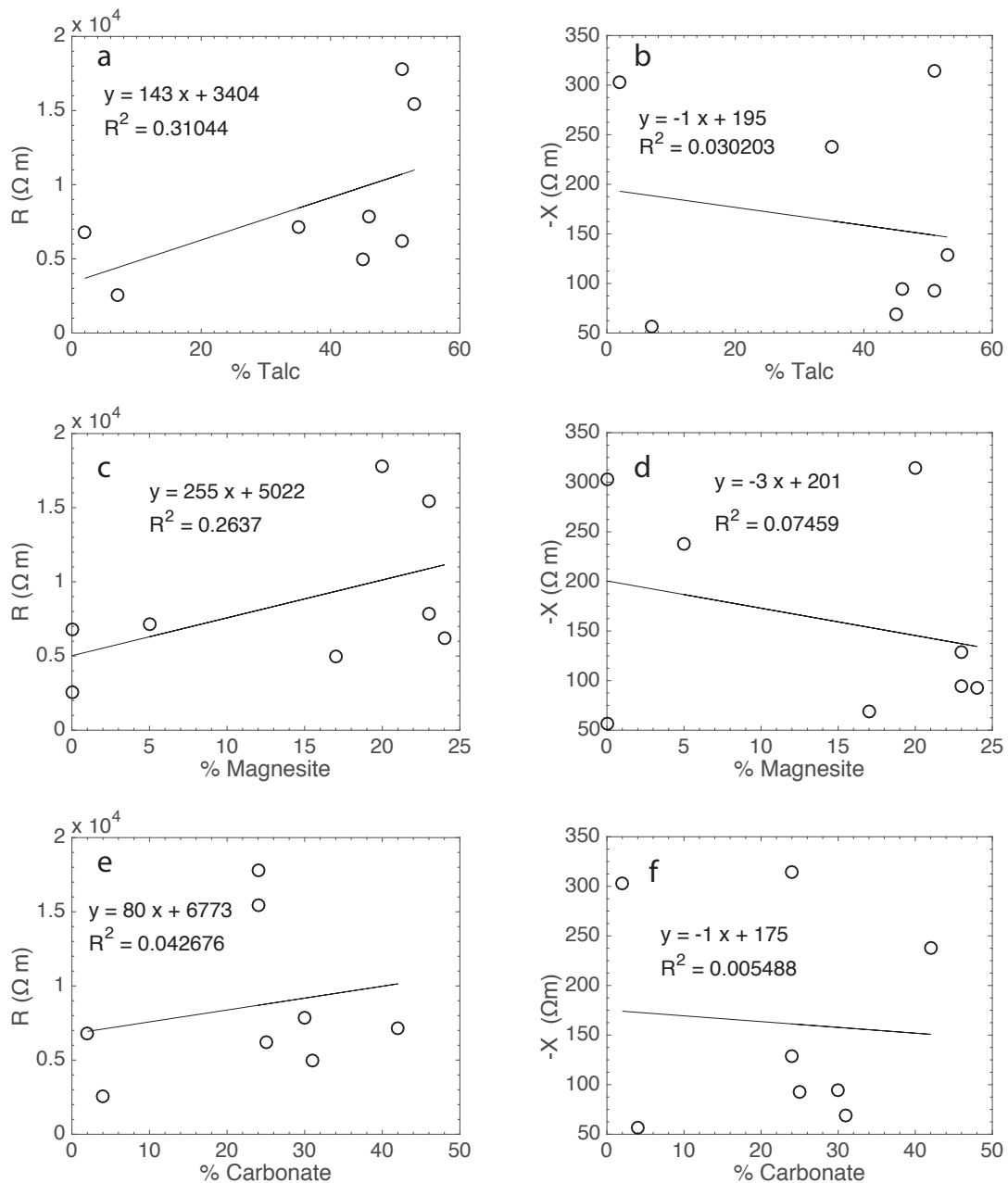


Figure 5.5. Elastic velocities plotted against mineralogical content. Two orthogonal S-wave polarizations are presented in black and blue. Least squares linear regressions are added to each plot, along with the equations and R^2 for the fit. A) P-wave velocity versus talc, b) S-wave velocity versus talc, c) P-wave velocity versus magnesite, d) S-wave velocity versus magnesite, e) P-wave velocity versus total carbonate, and f) S-wave velocity versus total carbonate. P-wave velocity is near constant as a function of different mineral contents, but S-wave velocity has a weak positive correlation with talc, magnesite and total carbonate.

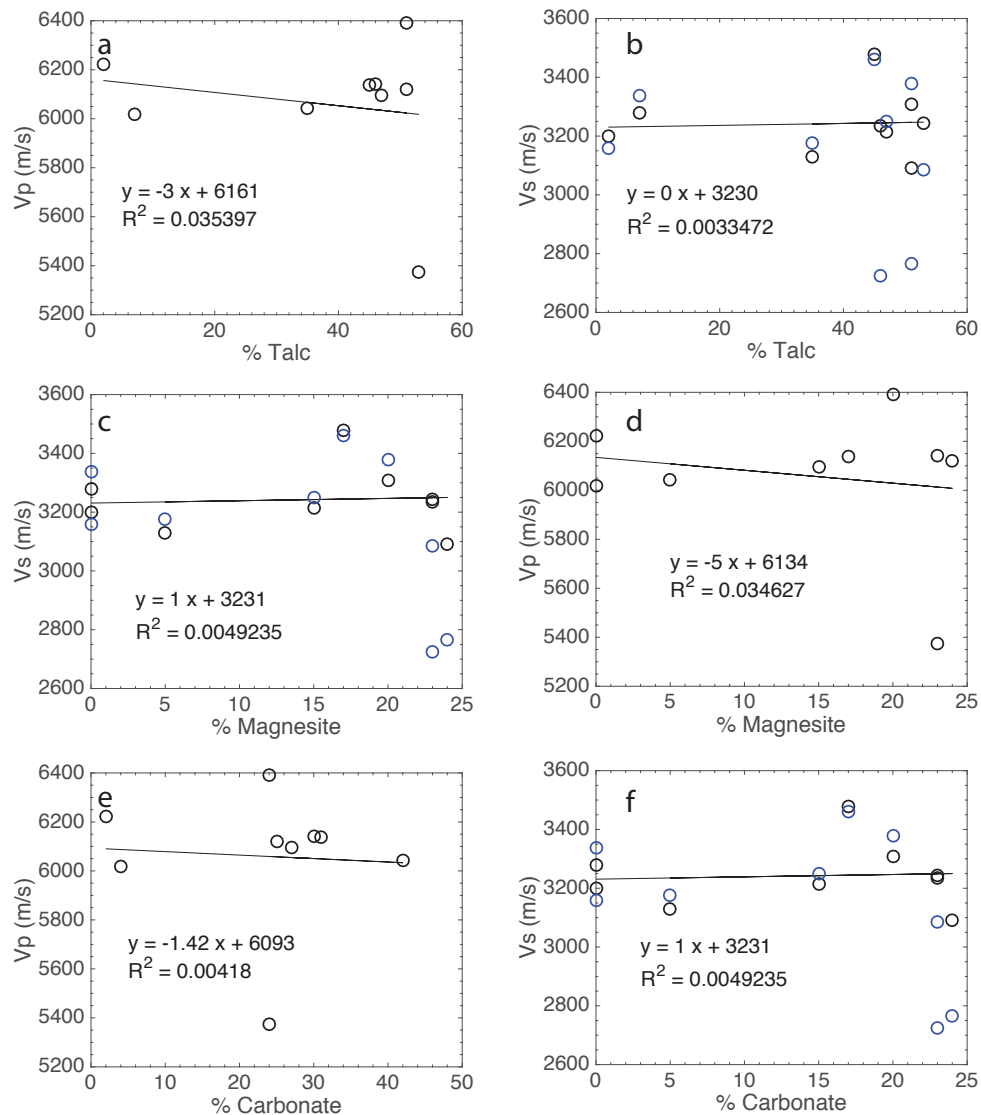
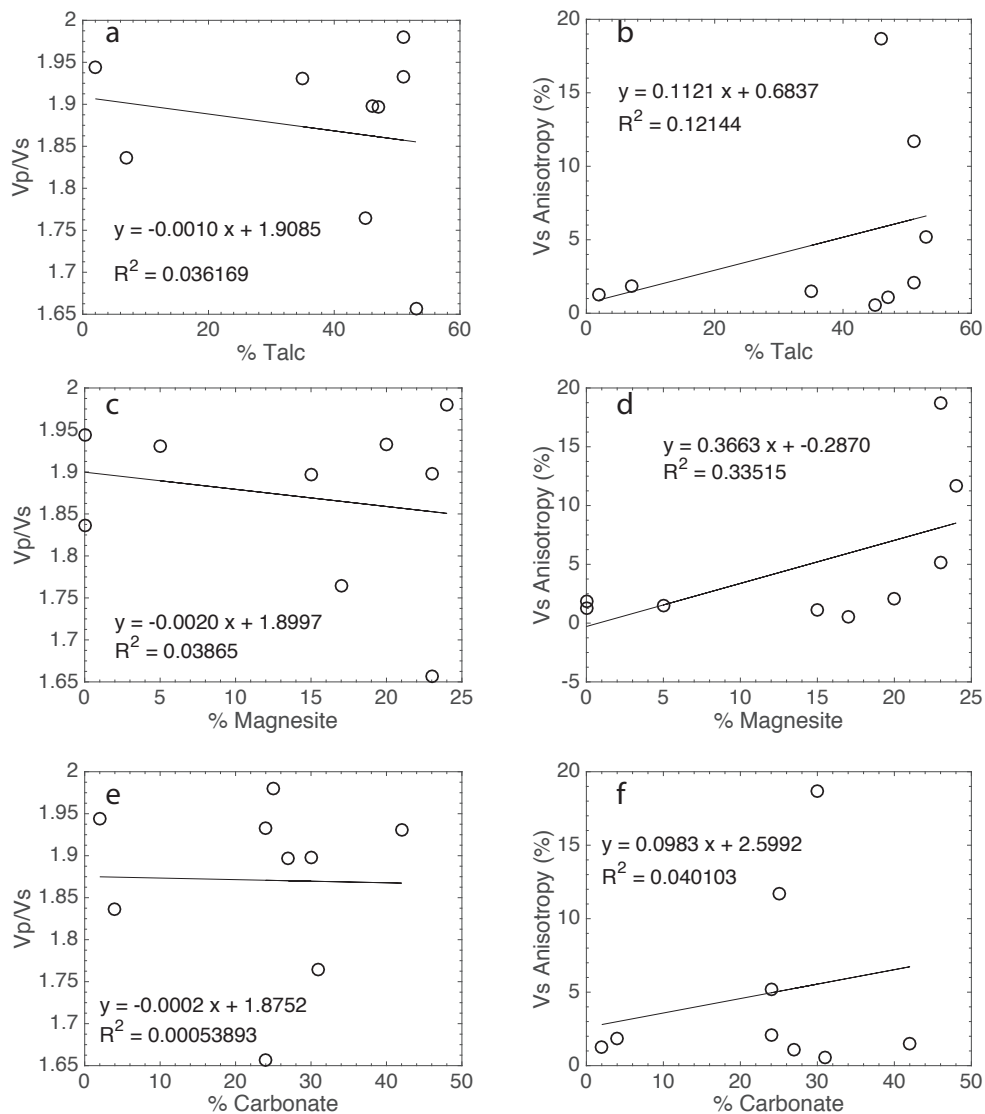


Figure 5.6. Vp/Vs and shear wave anisotropy plotted against mineralogical content.

Least squares linear regressions are added to each plot, along with the equations and R^2 for the fit. A) Vp/Vs versus talc, b) shear wave anisotropy versus talc, c) Vp/Vs versus magnesite, d) shear wave anisotropy versus magnesite, e) Vp/Vs versus total carbonate, and f) S-wave velocity versus total carbonate. Vp/Vs has a weak negative correlation with mineralogical content and shear wave anisotropy increases at high talc and magnesite contents.

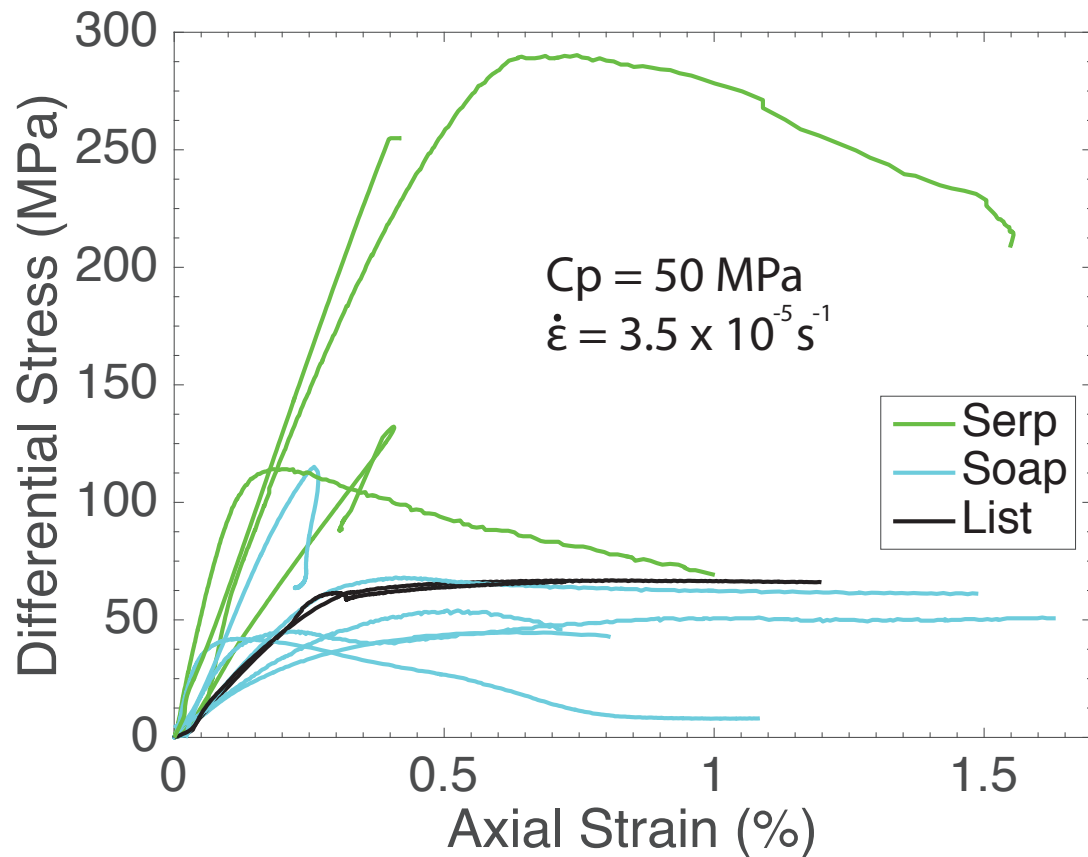


Elastic velocities also appear to evolve with carbonation extent. V_p values remain constant with respect to carbonation extent (Figure 5.5a,c,e), but V_s appears to have a weak positive correlation with carbonation extent (Figure 5.5b,d,f). As a result, V_p/V_s has a negative correlation with carbonation extent (Figure 5.6a,c,e). Looking at shear wave anisotropy (Figure 5.6b,d,f), there is a weak positive correlation with carbonation extent; however, there are several samples with high carbonation extent and low shear wave anisotropy. This is likely an effect of fabric development. The talc in soapstone displays elastic anisotropy [Mainprice et al., 2008] and tendency to flow plastically [Escartin et al., 2008], leading to the development of textures and sample-scale shear wave anisotropy.

5.3.3 Serpentinite, soapstone and listvenite geomechanics

Looking at the mechanical and petrophysical behavior of lithological endmembers can help frame data from the transitional outcrop. Homogeneous outcrops of serpentinite, soapstone and listvenite were sampled from the southern Ridoalggicohkka site (Figure 5.1b). Substantial changes in mineralogy and fabric during the transformation from serpentinite to soapstone to listvenite lead to differences in mechanical behavior. Data from constant strain-rate tests on all samples are presented in Figure 5.7. All samples failed by localized brittle fracture and displayed strain softening to weak hardening post-failure.

Figure 5.7. Differential stress versus axial strain for all samples. Green curves are serpentinite samples, blue soapstones and black listvenites. Serpentinites show higher average Young's moduli and strength than softer and weaker soapstones and listvenites.

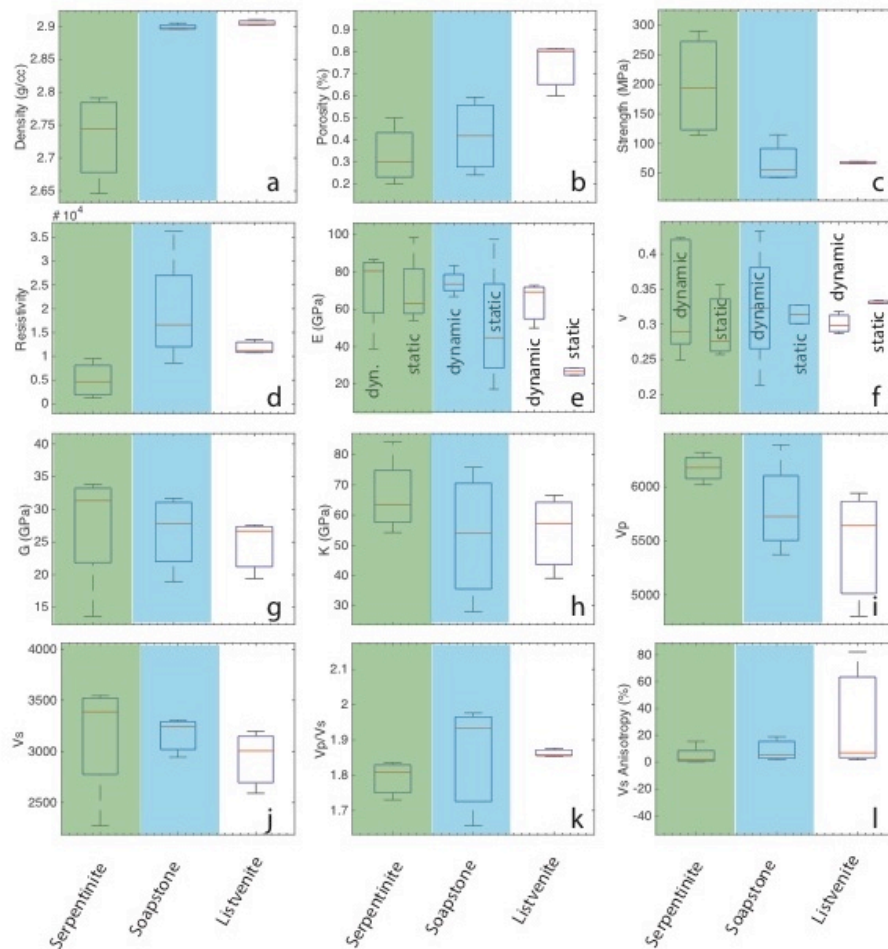


The serpentinites had the highest average shear strength, but also showed the largest range in strength, at $179 \pm 97 \text{ MPa}$ (Figure 5.8c). They also had the highest Young's modulus, $60 \pm 20 \text{ GPa}$ (Figure 5.8e, static values), and similar Poisson's ratio to the soapstones, 0.30 ± 0.05 (Figure 5.8f, static values). All samples displayed macroscopic shear fractures and exhibited strain-softening post-failure behavior.

The soapstones have nominally the same average shear strength as the listvenites, 67 ± 34 MPa (Figure 5.8c), but the strengths had a much greater range, and were generally lower than the listvenite values. They also had an intermediate Young's modulus, 51 ± 34 GPa (Figure 5.8e, static values), and nominally the same Poisson's ratio as serpentinites, 0.31 ± 0.02 (Figure 5.8f, static values). All samples displayed macroscopic shear fractures, but displayed sometimes-complex post-failure behavior. Some samples exhibited a period of strain softening followed by a period of hardening and, in some cases, a second peak stress accompanied by a second stage of strain softening. These samples typically exhibited multiple macroscopic shear fractures and curved fracture planes implying fault rotation and complex frictional behavior.

The listvenites had an average shear strength of 67 ± 0.54 MPa (Figure 5.8c). They also had the lowest Young's modulus, 27 ± 2.7 GPa (Figure 5.8e, static values), and the highest Poisson's ratio, 0.32 ± 0.00 (Figure 5.8f, static values). All samples displayed macroscopic shear fractures and exhibited very nearly flat post-failure behavior. The listvenite geomechanical response appears to be very uniform, probably owing to the homogeneity of our particular samples, and had much smaller standard deviations for all parameters than the other two lithologies.

Figure 5.8. Summary of geomechanical and petrophysical data from lithological endmember sample groups. Serpentine data is highlighted in green, soapstone blue and listvenite white. Means are plotted as horizontal red lines, the top and bottom of black boxes are the 75th and 25th percentiles, and whiskers extend to maximum and minimum values. A) density, b) porosity, c) strength, d) resistivity, e) Young's modulus, dynamic values are calculated from elastic velocities and static values are calculated from constant strain-rate tests, f) Poisson's ratio, dynamic and static values are calculated as for Young's modulus, g) Shear modulus, h) bulk modulus, i) P-wave velocity in m/s, j) S-wave velocity in m/s, k) ratio of P- to S-wave velocities, and l) shear wave anisotropy.



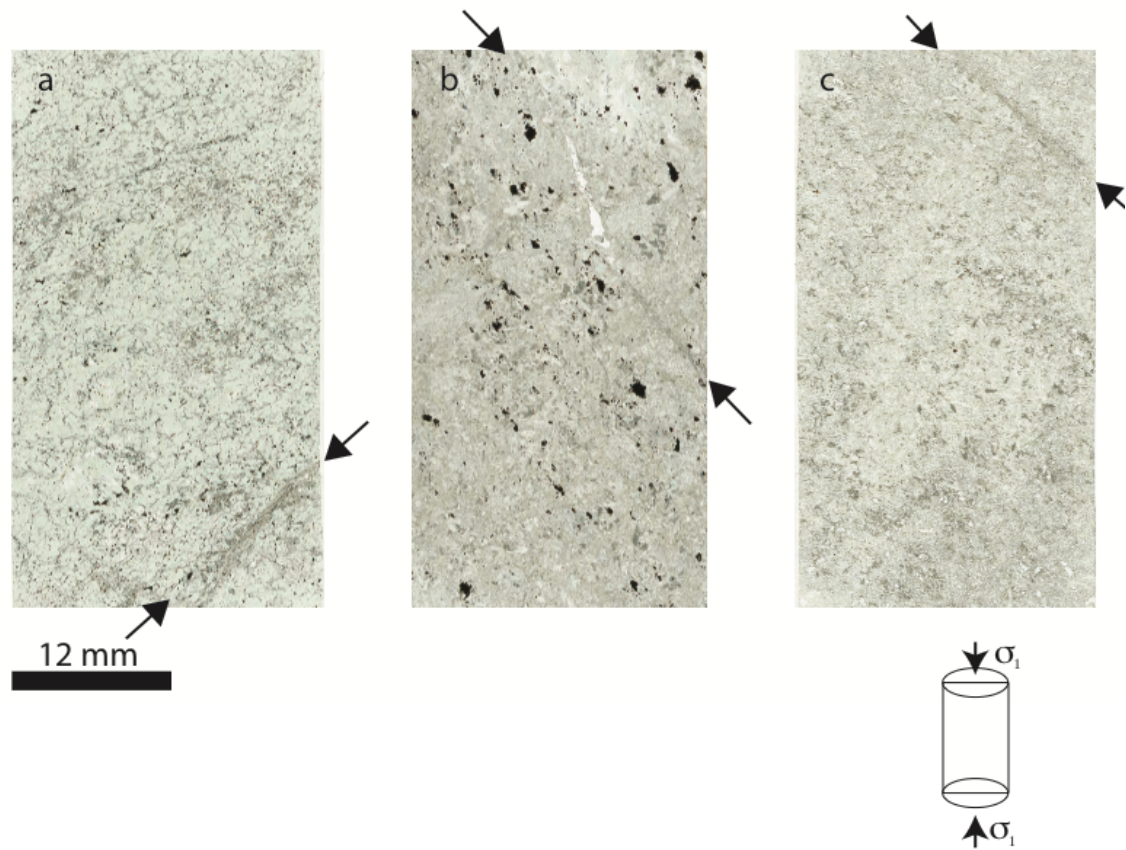
5.3.4 Microstructures

Analysis of microstructures helps elucidate deformation micromechanisms. Doubly polished, 30 μm thin sections were prepared and analyzed visually and with a petrographic microscope. Scanned images of axial sections of representative samples of each lithology cut perpendicular to fractures are presented in Figure 5.9. All samples failed by localized brittle faulting. Average fracture angles measured from the plane normal to the principal loading direction from the serpentinite, soapstone and listvenite samples are $42 \pm 2^\circ$, $30 \pm 2^\circ$ and $40 \pm 1^\circ$, respectively. Adopting a Mohr-Coulomb failure criterion, the internal frictional coefficient can be estimated with fracture angle using the equation,

$$\mu = \tan \varphi$$

where φ is the friction angle, compliment of twice the angle the fracture makes with respect to the loading direction ($\varphi = 90 - 2\theta$), we arrive at internal friction coefficients of 0.11 ± 0.03 , 0.58 ± 0.03 and 0.18 ± 0.02 , respectively. It should be noted that all these values are below the traditional Byerlee friction range of 0.6-0.85 [Byerlee, 1978]. However, Byerlee friction describes friction on pre-existing rock surfaces, and is most accurate for quartzofeldspathic rocks, and the lithologies explored in this study are rich in phyllosilicate minerals such as serpentine and talc, which are known to exhibit low frictional strength [Summers and Byerlee, 1977; Moore et al., 1996; Moore and Lockner, 1994].

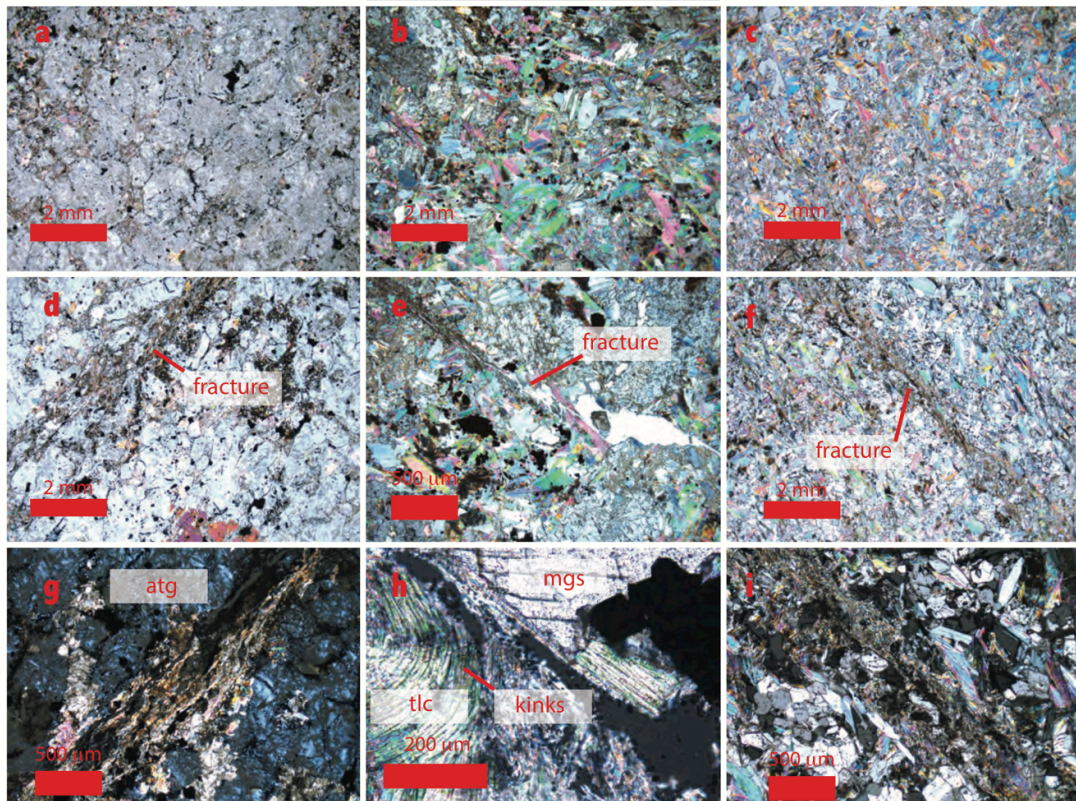
Figure 5.9. Scanned thin sections of deformed samples. Fractures are highlighted by arrows. Fracture angles are measured from the loading direction (inset). A) serpentinites sample with a fracture angle of 43° , b) soapstone sample with fracture angle of 30° . Fracture is not a straight plane, but exhibits some curvature, and c) listvenite sample with a fracture angle of 44° .



It is curious that the internal friction coefficient is highest in the soapstone, as the soapstone contains the largest volumetric fraction of talc, which has an extremely low coefficient of friction [Moore and Lockner, 2008]. Close inspection of the microstructure of deformed samples with a petrographic microscope provides some

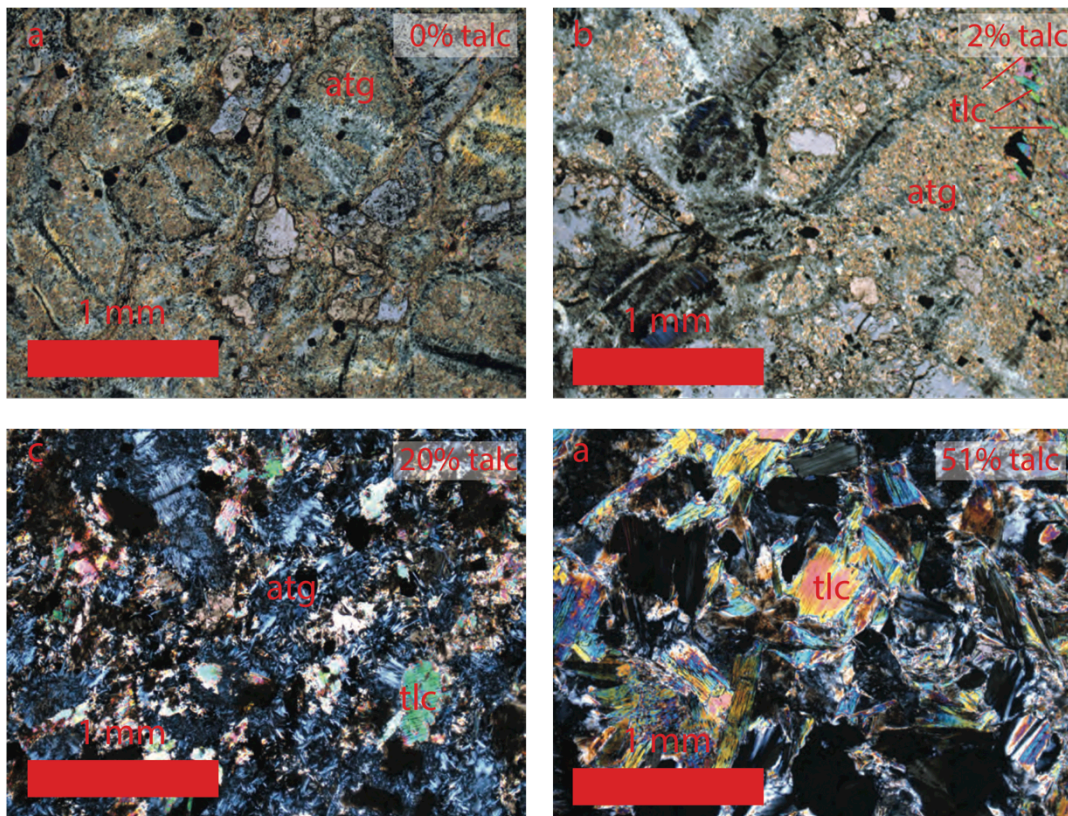
insight. Photomicrographs of representative samples of each lithology are presented in Figure 5.10.

Figure 10. Photomicrographs of deformed sample thin sections. All images are taken with cross polarizer in. A) serpentinite sample made mostly of antigorite serpentine with trace oxides and talc, b) soapstone composed of talc and magnesite with trace oxides, c) listvenite sample is slightly finer grained than other lithologies, with talc, magnesite, quartz and trace oxides, d) narrow fracture in serpentinite, e) fracture in soapstone also extremely narrow with slight undulation, f) similarly narrow fracture in listvenite, g) serpentinite fault appears armoured with talc, h) large talc grains adjacent to soapstone fault show extensive kinking, and i) listvenite fault surrounded by extremely fine-grained talc.



Serpentinite samples are composed of medium to large grained (50 μm to 2mm) antigorite with disseminated magnetite and trace talc along grain boundaries. Fractures are very sharp with damage apparently limited to ~ 200 μm adjacent to the fracture. The fracture surface is armored with fine-grained talc, but it is unclear whether this is the result of the mechanical concentration of pre-existing grain boundary talc, or if talc is produced by serpentine dehydration during fracture and sliding. There is a wide range in the strength of serpentinites in this study. This appears to be the result of talc along grain boundaries (Figure 5.11). Although talc is a relatively small volumetric fraction (~ 0 -20%) of the samples, its presence along weak planes such as grain boundaries and pre-existing fractures leads to a large bulk effect. Similar behavior has been reported for partially serpentinized peridotites [Escartin et al., 2001], where rocks with $\sim 5\%$ serpentine behave mechanically like 100% serpentinized rocks due to the presence of weak serpentine along grain boundaries. The further reaction to talc appears to have a similar affect and threshold.

Figure 5.11. Micrographs of samples illustrating variable talc abundances. All images presented here are captured with cross polarizers on. Antigorite serpentine can be distinguished by blue to khaki interference colors, and talc can be distinguished by bright, high interference colors. A) sample with no talc, b) sample with trace quantities of talc, c) sample with enough talc to armor grain boundaries, d) sample with large interconnected talc domains.



Soapstone samples are composed of fine to coarse grained (5 μm to 2 mm) talc with medium to large grained (20 μm to 1mm) magnesite and disseminated chromite. Fractures are highly localized, with damage limited to a region $\sim 100 \mu\text{m}$ from the fracture. Fractures occur within talc grains, but often pass by the boundaries

of large magnesite grains. Magnesite has a higher coefficient of friction than talc [Samuelson, 2012], and these large grains may be responsible for the relatively higher apparent internal friction coefficient of these samples. Talc along the fracture surface is extremely fine grained and extensively kinked. There is substantial evidence of crystal plasticity in large talc grains along the fracture.

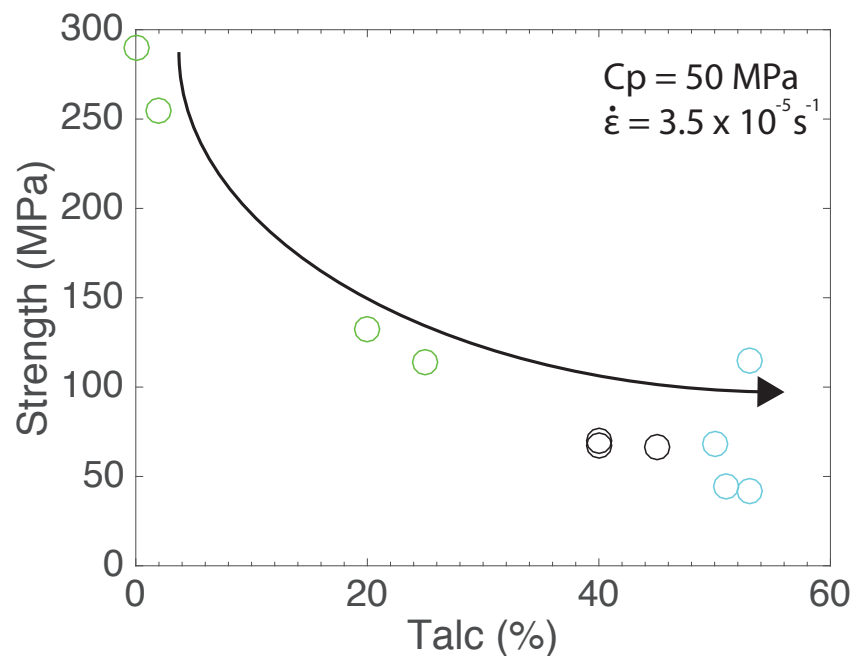
Listvenite samples are generally finer grained than the other two lithologies and composed of fine grained (10-50 μm) talc, magnesite and quartz with trace oxides. Fractures are also extremely narrow and occur mostly within talc, with damage zones limited to ~ 100 μm from the fracture. Talc along the fracture is extremely fine grained. The quartz grains do not appear to have the same strengthening effect that the magnesite has in soapstone, possibly because they are very fine and not interconnected, allowing them to move rigidly in the matrix of softer minerals.

The narrow nature of all observed fractures and the near absence of microcracks in the samples suggest that the deformation and failure of these samples is non-dilatant. Non-dilatant brittle deformation has been documented in serpentinites before [Escartin et al., 1997]. This could result in a low pressure dependence of the strength of these rocks and suppress dilatant hardening.

Talc abundance plays a controlling role in the strength of the samples. Serpentinites have a wide range of strengths, but when plotted against modal talc abundance it is clear that the observed weakening is a result of talc along grain boundaries. Sample strengths are plotted against modal talc abundance in Figure 5.12. However, above 20% talc, strength is relatively constant. Analysis of sample

microstructures shows that this threshold corresponds to the amount of talc needed to form connected talc layers along grain boundaries (Figure 5.11). This threshold is similar to reported values for the amount of serpentinization necessary for bulk peridotite properties to transition to serpentinite values [Escartin et al., 2001] and for talc-carbonate gouge layers to assume the frictional properties of talc [Giorgetti et al., 2015].

Figure 5.12. Sample strength versus modal abundance of talc. Serpentinities are represented in green, soapstones in blue and listvenites in black. All values reported are for experiments at 50 MPa confining pressure and $3.5 \times 10^{-5} \text{ s}^{-1}$ nominal constant strain rate. There is a sharp transition in strength from ~5% to ~20% talc, after which strength remains fairly constant. It is likely that this represents the threshold necessary to have continuous interconnected layers of talc along grain boundaries, allowing plastic deformation of talc to dominate the behavior of the bulk sample.

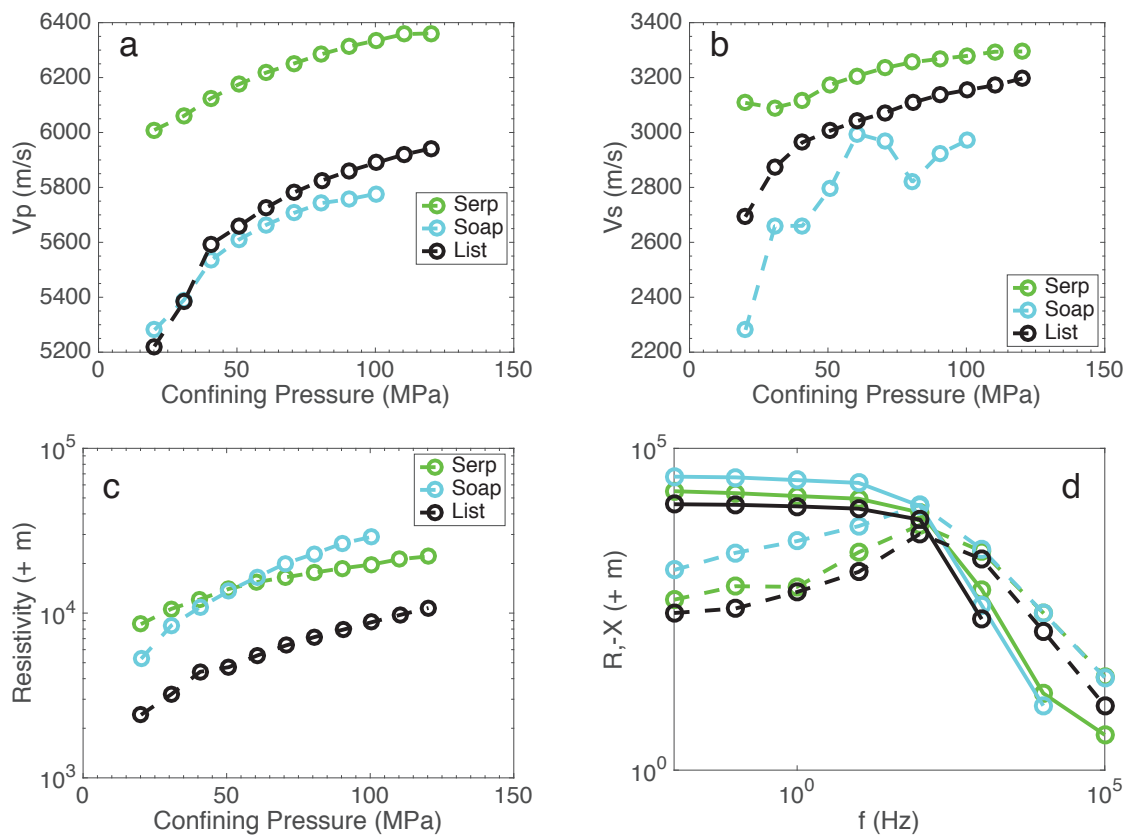


5.3.5 Serpentinite, soapstone and listvenite petrophysics

Serpentinites, soapstones and listvenites also show differences in petrophysical parameters, though some parameters were difficult to statistically resolve given the data collected. Petrophysical parameters measured and dynamic elastic moduli calculated from elastic wave velocities are presented in Figure 8. Both elastic velocity and electrical resistivity are pressure dependent (Figure 5.13a-c), and impedance is frequency dependent (Figure 5.13d). Pressure dependent changes in petrophysical parameters are largely due to reduction of porosity; this results in a higher density, directly increasing elastic velocities, and constricted fluid pathways leading to greater difficulty in flow of electric currents. The values reported here and in Figure 5.3 are those measured at the highest effective confining pressure, 110 MPa, in order to minimize the effect of porosity, which may be highly variable in any given rock at large scale, and thus maximize the effects of changes in mineralogy.

The frequency dependence of electrical resistivity is due to the scale dependence of the processes that transmit electrical currents in the rock. The resistivity of rocks is greatly reduced at higher frequencies, and magneto-telluric measurements are generally made at low frequencies (i.e. < 1 Hz). In addition, the electrical resistivity of rocks is generally constant with respect to frequency at all frequencies below a characteristic shoulder frequency (Figure 5.13d), 100 Hz in the case of all samples measured here; so impedances reported here and in Figure 8 are those measured at the lowest frequency, 0.01 Hz.

Figure 5.13. Pressure and frequency dependence of petrophysical properties for representative samples of each lithology. Color is the same as above. A) P-wave velocity versus confining pressure, samples initially have elevated elastic velocities at higher pressure due to the closure of pores and stiffening of the frame, b) S-wave velocity versus confining pressure, trend is the same as P-wave velocity, c) Resistivity versus confining pressure, trend is similar to that for elastic velocities, d) Electrical impedance versus frequency, resistivity is plotted with solid lines and reactance is plotted with dashed lines. All lithologies have a shoulder frequency in resistivity and a maximum reactance at 100 Hz. Resistivity is approximately constant below this shoulder frequency.



The resistivities of the three lithologies show considerable range, but resolvable difference. The serpentinite group has a mean resistivity of $4.99 \pm 3.79 \times 10^3 \Omega\text{m}$, the soapstone, $1.95 \pm 1.18 \times 10^4 \Omega\text{m}$ and the listvenite, $1.95 \pm 0.150 \times 10^4 \Omega\text{m}$. The increase in resistivity as serpentinites become soapstone is expected, as magnetite, a common constituent mineral in serpentinites, is consumed in the creation of siderite, Fe-bearing talc and chlorite [Beinlich et al., 2012]. P-wave velocity appears to have a negative correlation with carbonation extent, but differences between soapstones and listvenites are not statistically resolvable. The serpentinite group has a mean V_p of $6.17 \pm 0.128 \text{ km/s}$, the soapstone, $5.80 \pm 0.431 \text{ km/s}$ and the listvenite, $5.46 \pm 0.584 \text{ km/s}$. S-wave velocity appears to have a negative correlation with carbonation extent, but the trend is not as clear due to large variation among serpentinites. The serpentinite group has a mean V_s of $3.15 \pm 0.595 \text{ km/s}$, the soapstone, $3.17 \pm 0.194 \text{ km/s}$ and the listvenite, $2.93 \pm 0.310 \text{ km/s}$.

5.3.6 Geological implications

Typical seismic P-wave velocities in serpentinites are in the range of 5.5 to 6.5 km/s [Christensen, 1966]. The value reported here is on the higher end of that range, but seismic surveys sample much larger volumes of rock, which are likely to host fractures that lower elastic wave speeds. Soapstones and listvenites have somewhat lower P-wave velocities, but still within the average range. The lower range of listvenite V_p is below the lower threshold of serpentinite values, and may be resolvable in the field, but likely only in compliment of other observations such as local geology and structure. In a CO_2 injection scenario, time series monitoring may

also may these differences resolvable. Other seismic properties such as S-wave velocity, V_p/V_s and shear wave anisotropy do not exhibit as clear trends, so appear less attractive for identification and monitoring purposes.

Serpentinite resistivity tends to span orders of magnitude, and are often reported between 10^1 and $10^5 \Omega\text{m}$ [Blackman et al., 2014]. The values reported here are consistent with laboratory measurements of small specimens on the order of $10^4 \Omega\text{m}$ [Stesky and Brace, 1973; Parkhomenko, 1982]. Although an increase in resistivity from serpentinites to soapstones is resolvable, field scale measurements are much more sensitive to variations in porosity and permeability than intrinsic electrical properties [Archie, 1941]. Once again, in an injection scenario, benefit may be gained through time resolved measurement.

In order to use petrophysical properties to identify carbonated ultramafic rocks, variations must be identifiable within the resolution of monitoring techniques. Based on the data gathered in this study, the most robust change is in rock density, suggesting that gravity surveys coupled with standard geological observations may be the best option for identifying carbonated ultramafic rocks in the field, and monitoring active carbonation at future injection sites. Confoundingly, the carbonation of serpentinites leads to an increase in density, so carbonated bodies and unserpentinized peridotite bodies would produce similar gravity signals. This is an effect to consider when analyzing geophysical data from low temperature hydrothermal sites such as the Lost City on the Mid-Atlantic ridge [i.e. Fruh-Greene et al., 2003].

The large reduction in strength observed due to the presence of small amounts of talc is consistent with observations of talc along anomalously weak structures in the field. It has been noted that regional stress orientations in southern California are near normal to the San Andreas fault [Zoback et al., 1987], whereas assuming typical values of frictional strength, the orientations should be more acute. The observation of talc in samples of the fault core have been used to justify this anomalously weak behavior [Moore and Rymer, 2007]. Talc is also commonly identified along both oceanic and continental detachment faults [Macleod et al., 2002; Schroeder and John, 2004; Collettini et al., 2009]. It is a matter of debate whether trace amounts of weak minerals can lead to such large reductions in bulk frictional strength, but our results suggest it is the geometry of weak mineral layers rather than the volumetric abundance that controls rupture behavior.

5.4 Conclusions

We measured and compiled petrophysical and mechanical data from variably carbonated ultramafic rocks from Linnajavri, Norway. The rocks tend to become denser, more porous, weaker, and more electrically and acoustically impeditive as carbonation proceeds. The weakening observed in soapstones and listvenites compared to serpentinites is attributed to interconnected talc grains. Samples fail by highly localized brittle faulting with little associated dilatancy. Carbonic alteration of oceanic serpentinites may help facilitate longevity and large displacements along detachment faults, contributing to oceanic tectonics by accommodating spreading along mid-ocean ridges with limited melt supply. Variations of petrophysical

properties are small, but in regions with constrained geology, may be accessible to field geophysical measurement and monitoring. Prospects for monitoring engineered ultramafic carbonation are hopeful and would be greatly enhanced by time resolved observation.

Appendix A: Deformation apparatus

All experiments were run in an externally heated, servo-controlled Autolab 1500 triaxial deformation apparatus from New England Research (Figure A.1). The apparatus consists of a main pressure vessel with a hydraulic piston for the application of axial stress, an external furnace with a proportional-integral-derivative controller, and a pore pressure system with upstream and downstream servo-controlled intensifiers for independent pore pressure control. The furnace has a range of room temperature to 150°C with a stability of $\pm 1^\circ\text{C}$ once the system is at thermal equilibrium. Pressure transducers situated above and below the sample assembly in the pore pressure system allow for in-situ permeability measurements to be taken. Confining pressure and all pore pressure transducers have a range of 0-137.9 MPa, and the differential pressure transducer has a range of 0-206.84 MPa all with precision of 0.5%. All piston displacements are measured by linear variable displacement transformers (LVDT) with a range of 76.2 mm, a sensitivity of 0.0254 mm and an error of less than 0.15%. Axial stress is measured by an internal load cell with a range of 0-1 GPa with error less than 0.44%. The nominal machine stiffness is $4.0 \times 10^8 \text{ N/m}$. The loading assembly consists of a jacketed sample and two endcaps (Figure A.2). Temperature is measured by two thermocouples, one inside the external furnace and one adjacent to the sample in the pressure vessel, each routed through the temperature controller.

A saturated sample was jacketed in thin (0.127 mm) copper foil. The foil was then “seated” to the samples by applying 10 MPa of confining pressure to the sample.

Two axial and one radial foil strain gauges were then affixed to the side of the sample. The sample was joined to the endcaps by 6.35 mm-walled viton tubing, worm clamps and steel wire. Then entire assembly was then inserted inside the pressure vessel using mineral oil as confining medium to perform the given experiment.

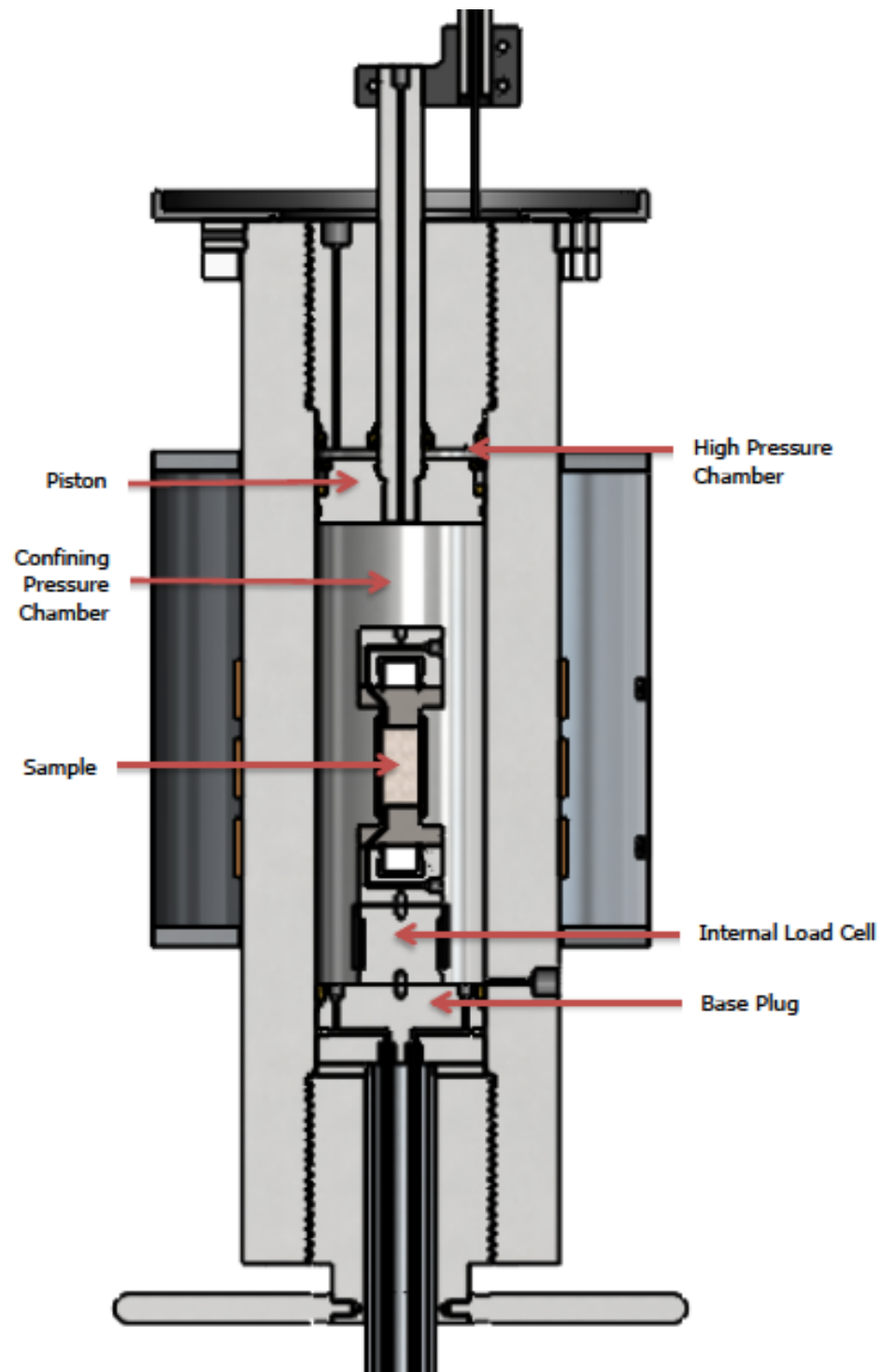


Figure A.1. Schematic of triaxial cell, modified from NER Autolab 1500 manual.

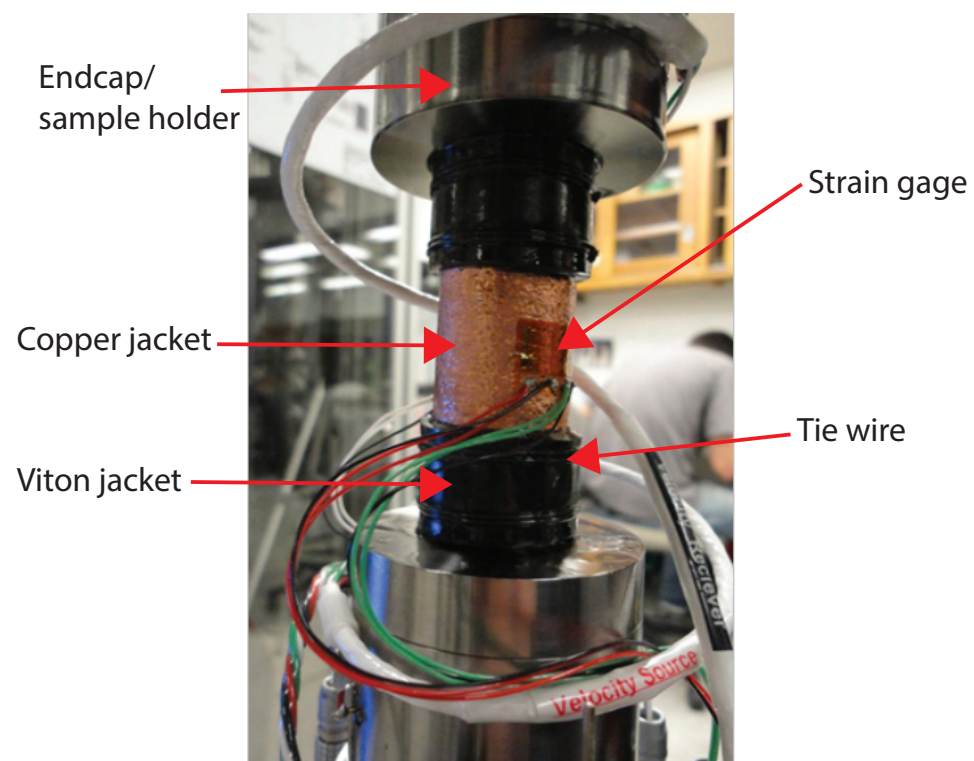


Figure A.2. Image of complete sample assembly.

Appendix B: Permeability measurement

Permeability data are collected during deformation using either the steady state flow method or complex pore pressure transient pulse analysis. Steady state measurements are made by imposing a constant flow rate through a sample of known length and diameter and measuring the pressure different across the sample, then using Darcy's Law to calculate the permeability. To perform complex pore pressure transient analysis, a transient (step-function) pressure pulse is introduced at the upstream of the pore pressure system and the downstream pore pressure response is recorded. Subsequently, sample permeability can be derived from the pressure response. Specifics of data reduction are presented in Boitnott [1997]. An example of the data from a permeability measurements is presented in Figure B.1.

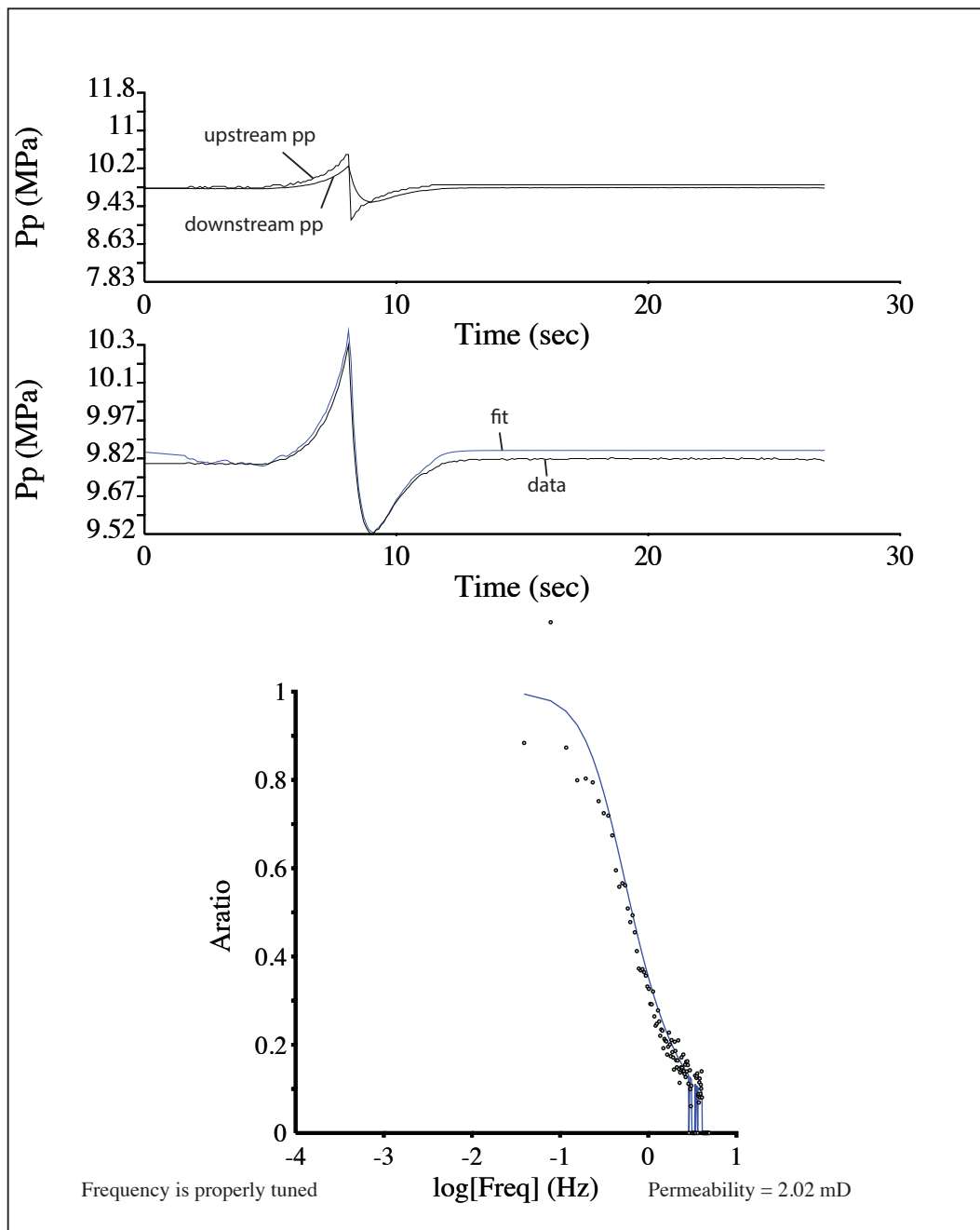


Figure B.1. Example permeability measurement.

Appendix C: Ultrasonic velocity system

Ultrasonic velocity measurements are made by affixing piezoelectric crystals to the sample holders on either side of a sample (Figure C.1). Three crystals are used one each side, one to record or transmit P-waves and two to record or transmit orthogonal S-waves. A broadband pulse centered at 500 kHz is sent through one set of crystals and the response is measured by the other. Arrival times are picked manually and picks are checked by correlating waveforms. An example of data from a velocity experiment is presented in Figure C.2.

Velocity data was additionally processed in MATLAB to reduce data. All waveforms were passed through a low-pass Butterworth filter to remove high frequency noise. First arrivals are hand-picked and used to calculate wave speed. An example of unfiltered and filtered data is presented in figure C.3.

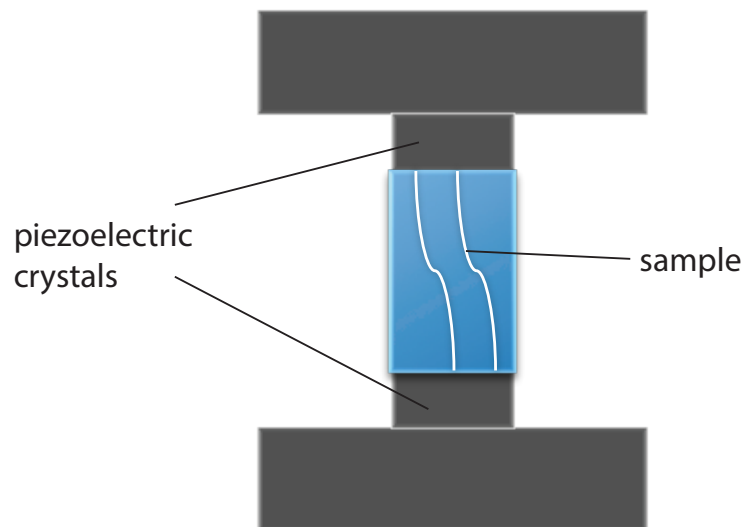


Figure C.1. Schematic of velocity measurement coreholders.

Ultrasonic Velocity Measurement Report

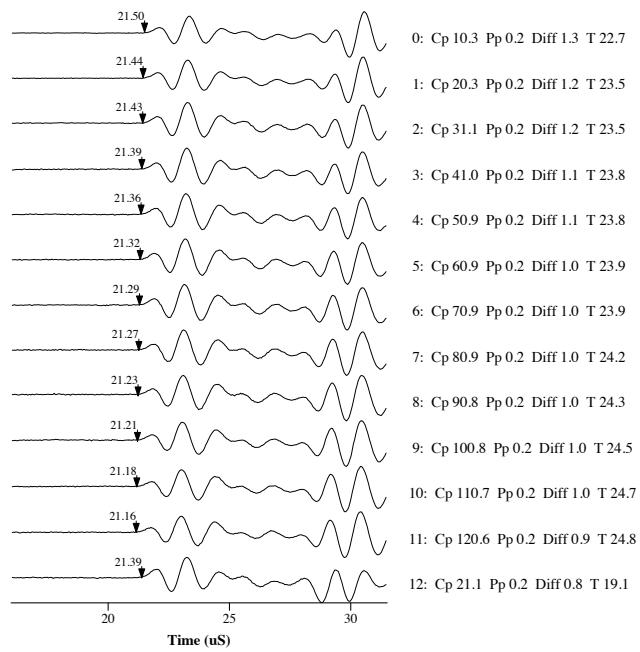
Sample and Experiment Information for File Lin12A_Velocity					
Well:		Organization:	NER		
Depth:	0.0 m	Transducer:	Vel_lin_Jul2014		
Formation:		Rock type:			
Dry bulk density:	2.500 gm/cm ³	Porosity:			
Sat. bulk density:	2.667 gm/cm ³	Pore fluids:			
Diameter:	25.40 mm	Entered Length:	76.20 mm		

Comments: User: lab on al1500-10f6 at Mon Mar 28 09:21:45 EDT 2016

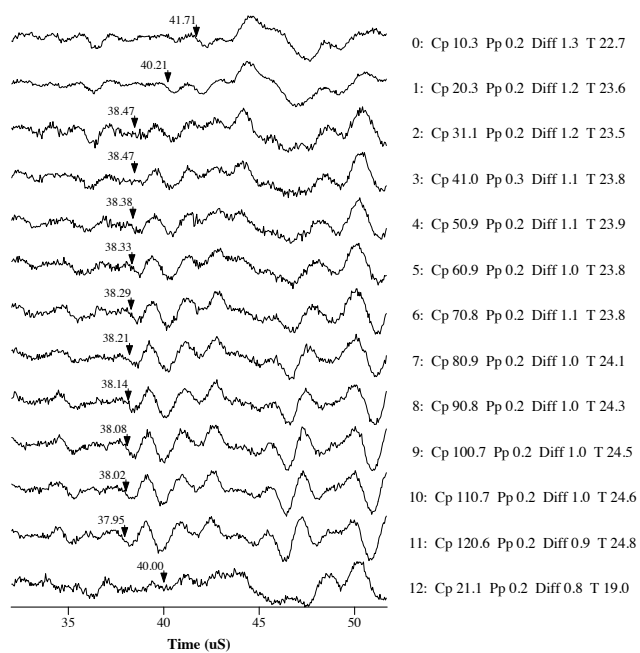
Expt name: 1459171305
 Expt date: Mon Mar 28 09:36:00 2016
 Print date: Mon Mar 28 13:29:36 2016
 A2D File: Lin12A_Velocity.a2d

Observed Velocities and Moduli for File Lin12A_Velocity									
Event	Conf	Pore	Diff	Temp	V_p	$V_s^{(1)}$	$V_s^{(2)}$	Young's Modulus	Poisson's Ratio
	MPa	MPa	MPa	°C	m/s	m/s	m/s	GPa	
0	10.3	0.2	1.3	22.7	5968	3018	2870	61.91	0.339
1	20.3	0.2	1.2	23.6	5997	3208	2963	67.03	0.320
2	31.1	0.2	1.2	23.5	6005	3461	3023	72.56	0.294
3	41.0	0.2	1.1	23.8	6022	3462	3036	72.90	0.295
4	51.0	0.2	1.1	23.9	6037	3475	3045	73.36	0.294
5	60.9	0.2	1.1	23.8	6054	3484	3049	73.68	0.295
6	70.9	0.2	1.1	23.9	6067	3491	3050	73.89	0.295
7	80.9	0.2	1.0	24.1	6081	3504	3071	74.57	0.294
8	90.8	0.2	1.0	24.3	6097	3515	3092	75.22	0.292
9	100.7	0.2	1.0	24.5	6109	3524	3071	75.08	0.294
10	110.7	0.2	1.0	24.6	6122	3534	3068	75.27	0.295
11	120.6	0.2	0.9	24.8	6134	3545	3071	75.58	0.295
12	21.1	0.2	0.8	19.1	6024	3236	3060	69.36	0.312

Waveform waterfall for p arrivals	
Experiment:	1459171305
Well:	
Depth:	0
File name:	Lin12A_Velocity



Waveform waterfall for s1 arrivals	
Experiment:	1459171305
Well:	
Depth:	0
File name:	Lin12A_Velocity



Waveform waterfall for s2 arrivals	
Experiment:	1459171305
Well:	
Depth:	0
File name:	Lin12A_Velocity

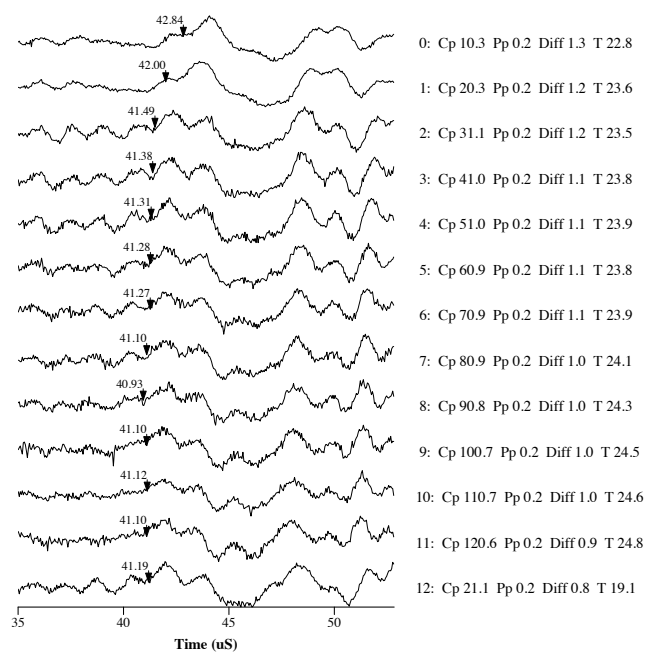


Figure C.2. Example of velocity data.

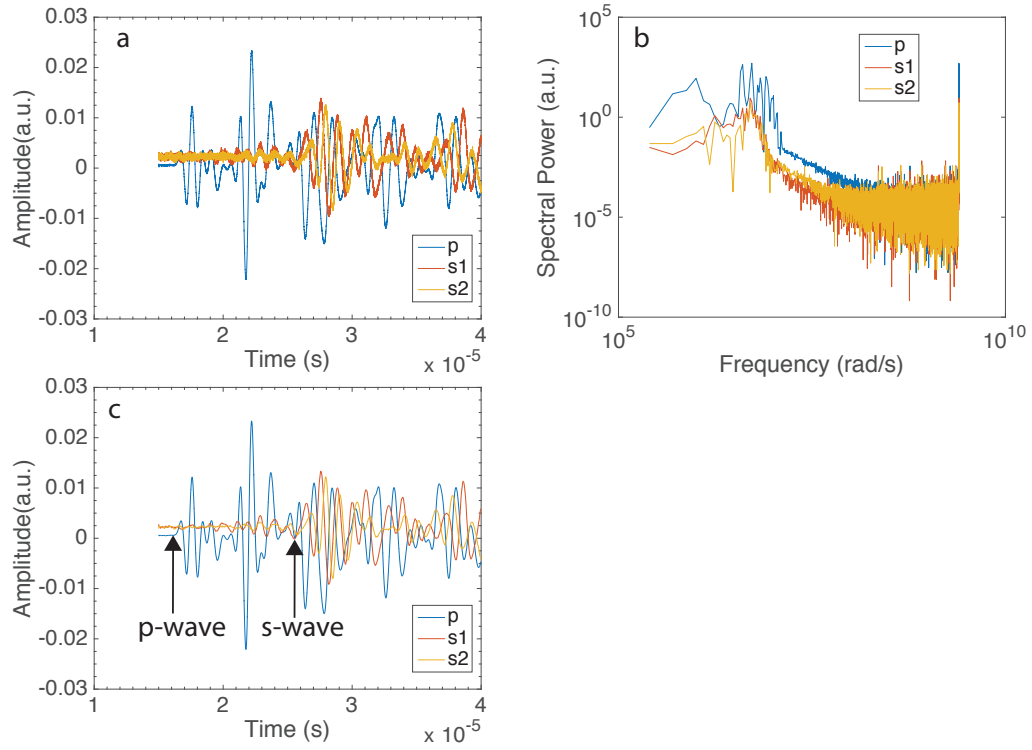


Figure C.3 Examples of processed velocity measurement data. a) Unfiltered waveforms, b) spectral power of the unfiltered waveform, c) filtered waveforms.

Appendix D: Resistivity measurement

Resistivity measurements are taken by affixing a voltage and a current electrode to each side of the sample, passing a current through the sample and measuring the voltage across the sample (Figure D.1). The voltage electrode is isolated from the sample surface by a porous insulating pad. Alternating current in the frequency range 10^{-2} to 10^5 Hz is passed through the sample using a signal generator (Figure D.2).

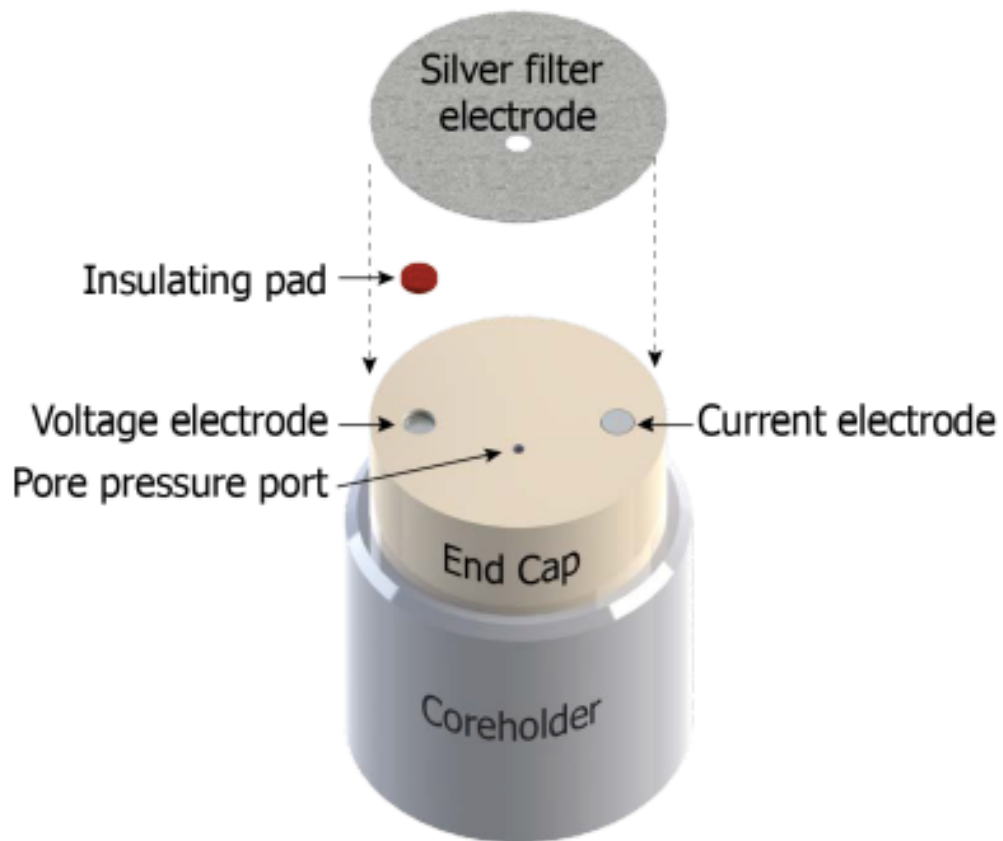


Figure D.1. Schematic of resistivity endcaps adapted from Autolab 1500 manual.

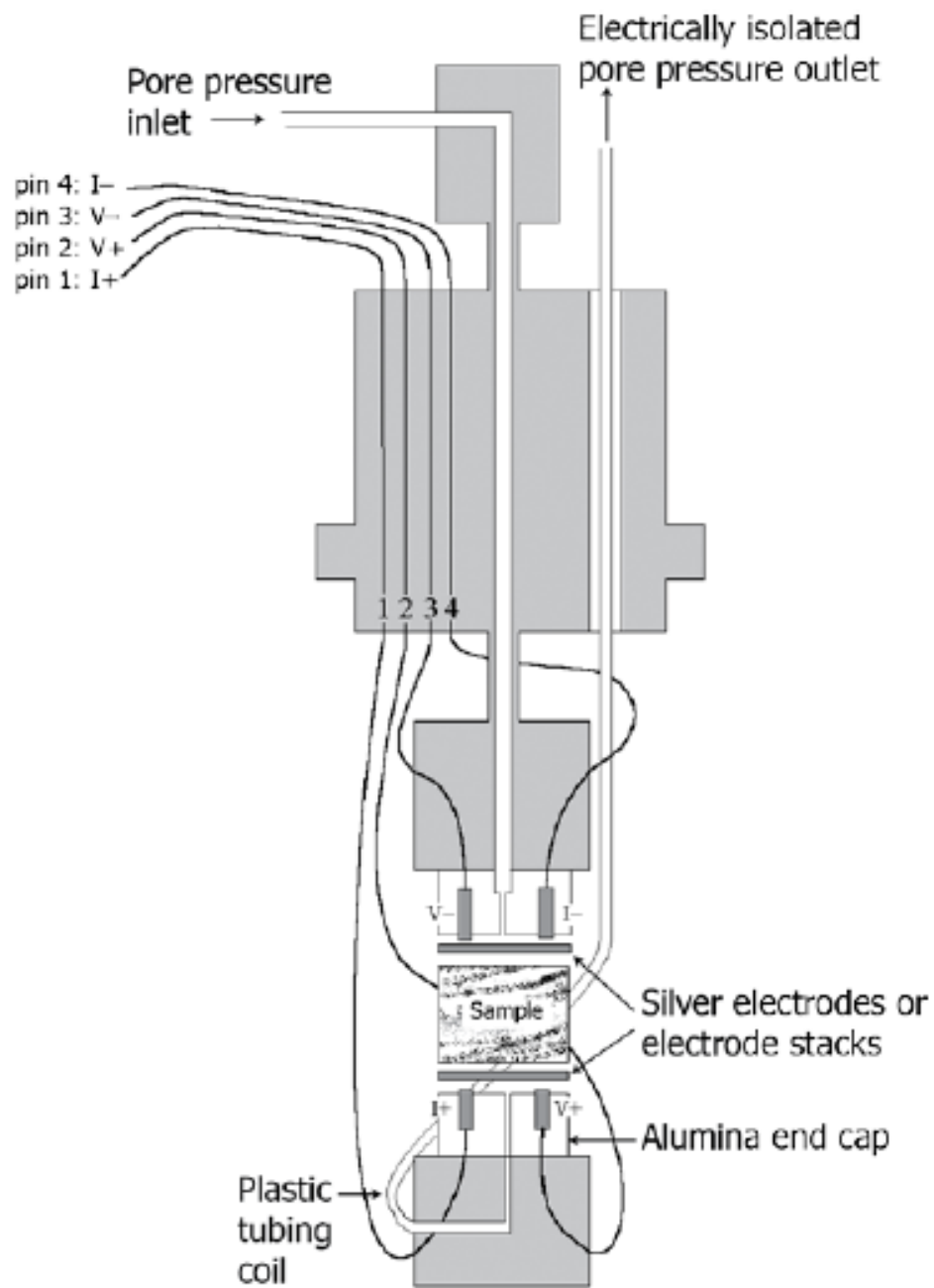


Figure D.2. Schematic of resistivity system adapted from Autolab 1500 manual.

Appendix E: Bifurcation analysis

A material is said to deform elastically if the deformation is fully recoverable. In minerals, elastic strain is the result of distortion of a crystal lattice in response to stress, and is generally quite small (i.e. <1%). The elastic behavior of a given material is quantified by moduli. One common modulus is Young's modulus, E , a measure of elastic strain along an axis in response to stress along that same axis. Young's Modulus is calculated,

$$E = d\sigma / d\varepsilon^e \quad (E.3)$$

where σ is effective stress and, and ε^e is elastic strain; it is the most common measure of a material's elastic response to shortening and is sometimes called simply the modulus of elasticity.

Another common elastic modulus is Poisson's ratio, ν , a measure of transverse to axial strain in a material. Poisson's Ratio is calculated,

$$\nu = -d\varepsilon_t^e / d\varepsilon_a^e \quad (E.4)$$

where ε_a^e is as above and ε_t^e is transverse elastic strain.

Once a material has been deformed to its elastic limit, irrecoverable deformation occurs; this deformation is referred to as plastic. There are many mechanisms of plastic deformation including fracture, frictional sliding, dissolution, and dislocation movement. Plasticity in general is harder to model than elasticity, but a number of quantities can be used to adequately represent the plastic behavior of materials.

One important quantity is the coefficient of internal friction, μ . The coefficient of internal friction is defined as,

$$\mu = \frac{d\tau}{d\sigma} \quad (E.5)$$

where τ is shear stress and σ is again effective normal stress; it is used to quantify the frictional processes that are involved in yielding such as slip along the surfaces of microcracks.

Another quantity used in plasticity analysis is the dilatancy factor. The dilatancy factor is defined as,

$$\beta = \frac{d\varepsilon_{\phi}^p}{d\gamma^p} \quad (E.6)$$

where ε_{ϕ}^p is plastic volumetric strain, and γ^p is plastic shear strain; it is used to quantify the volumetrically increasing processes that are involved in plastic deformation such as microcrack growth and microcrack formation. Total measured strain, ε_T , is the sum of both elastic and plastic strain.

A third relevant quantity is the hardening modulus, h/E . The hardening modulus is defined as,

$$\frac{h}{E} = \frac{(\mu - \beta)^2}{18(1 - \nu)} - \frac{1}{36}(\beta + \mu + 3N)^2 \quad (E.7)$$

where μ , β , and ν are as defined above and N is a geometric factor related to loading geometry, and in the case of axisymmetric loading is equal to $\frac{1}{\sqrt{3}}$; it is used to quantify the hardening response of a material after yield. All definitions are after Rudinicki and Rice [1975].

Appendix F: Three dimensional image processing

Three dimensional microstructural data are collected on a Zeiss Auriga FIB-SEM between 3-5 kV accelerating voltage. A trench is dug around the volume to be imaged, then SEM images are captured serially as the surface is milled away 2 nm at a time.

The image stack is then imported into ImageJ for image registration to correct for drift in the field of view. The registered images are then cropped so that only the region of interest is in frame.

The remaining image analysis is performed in commercial software package Aviso. To reduce noise, an anisotropic diffusion filter is employed. Anisotropic diffusion filters are an edge preserving smoothing filter [Weickert et al., 1998]. This technique uses a combination of Gaussian blurring and a priori knowledge of local gray-scale gradients to reduce noise while maintaining feature edges.

The registered, cropped and filtered data is then binarized by thresholding out porosity from solid material. A combination of tophat watershed and manual thresholding. The image volume is then binarized by assigning a value of 0 to the pore space and a value of 1 to the solid. This binarized pore image is then used for geometric and permeability measurements using the built-in Aviso quantification modules.

Appendix G: MATLAB script for simulation of porosity band

```

function dY=styloODE(y,x,nx,dx,phi0,seq,B,m,ep,el,w);

p=y(1:nx);
s=y(nx+1:2*nx);

dp=-((1-phi0*p).^(2/3)).*(s-seq(p));
dsdx=gradient(s,dx);dsdx(1)=0;dsdx(end)=0;
ds=(gradient((p.^m).*dsdx,dx)+dp.*(1-ep*el*(1+w*s)))./(B*p);

dY=[dp;ds];

% model parameters
phi0=0.01; % Initial porosity / porosity scale
V0=44; %cm^3/mole
P=5e7; %dynes/cm^2 50bar=5MPa
V0P=V0*P; %precompute
R=8.32e7; %gas constant ;erg/mole;
T=423; %temperature K
RT=R*T; % precompute
a=V0P/RT ; %elastic constant alpha
b=0; %elastic constant beta
w=(2*a+4*b)*phi0; % precompute
f=@(p)1-phi0*p; %solid fraction
seq=@(p)(exp(a./(f(p).^2)+b./(f(p).^4))-exp(a+b))./(w*exp(a+b));
%equilibrium sigma
% seq=@(p)exp(V0P./((1-phi0*p).^2))./(V0P*exp(V0P));
el=exp(a+b); %precompute exp(lamba); lamba=alpha+beta
ep=1e-6; %concentration of mobile components / solid molar density
B=ep*w*el; %precompute
m=2; %power law exponent

% setup problem

%% initial conditions
pb='uniform';
% pb='step';
% pb='random';
switch pb
    case 'step'
        disp('Starting conditions: step')
        xmin=-10;xmax=10; nx=100;
        x=linspace(xmin,xmax,nx)';
        dx=(xmax-xmin)/(nx-1);
        p0=x*0+2-0.5*atan(x)*2/pi;
        s0=seq(p0);
        tall=[0:0.5:3.5];
    case 'random'
        disp('Starting conditions: random')
        xmax=10; nx=500;
        x=linspace(0,xmax,nx)';

```

```

        dx=xmax/(nx-1);
        p0=x*0+1;
        %perturbation
        p0=p0+0.01*cumsum(rand(size(p0))-0.5);
        s0=seq(p0);
        tall=[0:0.5:4.5];
    otherwise
        disp('Starting conditions: uniform')
        xmax=10; nx=500;
        x=linspace(0,xmax,nx)';
        dx=xmax/(nx-1);
        p0=x*0+1;
        %perturbation
        p0=p0+0.01*exp((-1).*((1*x).^2));
        s0=seq(p0);
        tall=[0:0.5:5.5];
end

%% ODE solve
y0=[p0;s0];

Newton=0; %B=0.00001;
if Newton==1;
    disp('using forward Newton');
    dt=1e-6;
    yn=y0;tn=0;
    Y=yn;T=tn;
    for i=1:3;
        dy=styloODE(yn,x,nx,dx,phi0,seq,B,m,ep,el,w);
        yn=yn+dy;
        Y=[Y,yn];
        T=[T,tn];
    end
    Y=Y';
else
    disp('Using Runge Kutta')
    [T,Y]=ode15s(@(t,y)styloODE(y,x,nx,dx,phi0,seq,B,m,ep,el,w),...
        tall,y0);
end
% plot
p=Y(:,1:nx);
s=Y(:,nx+1:2*nx);
figure(1);clf;
subplot 211
plot(x,p);
xlabel('position'); ylabel('\Psi');
% legend(sprintf('%g',T))
legend(num2str(T))

subplot 212
plot(x,s);
xlabel('position'); ylabel('\sigma');
legend(num2str(T))

```

Appendix H: Additional SEM images of dunite samples

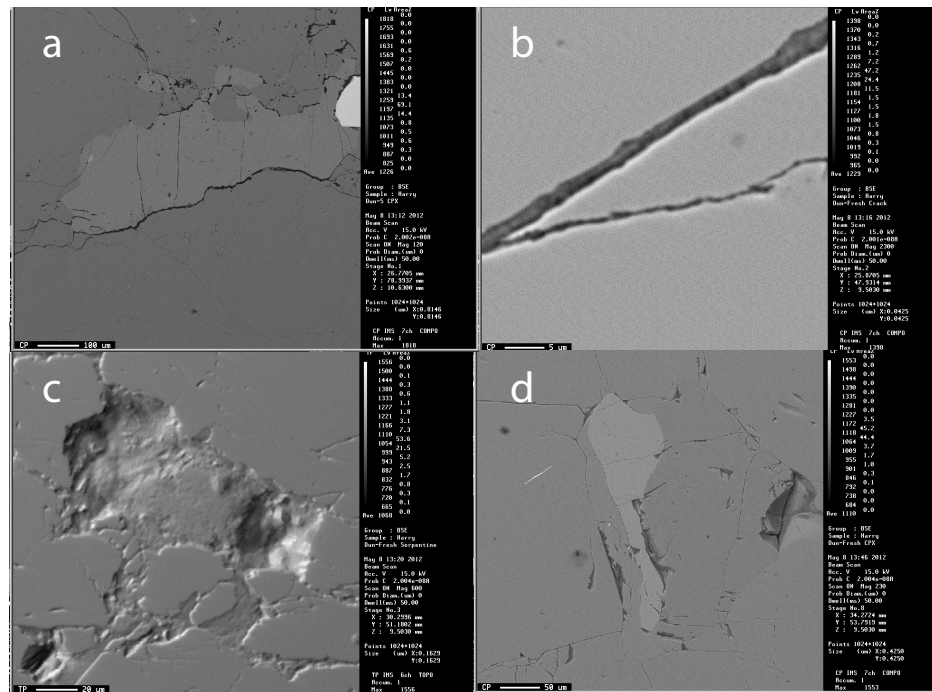


Figure H.1. SEM images of fresh dunite material. Light grey phase is clinopyroxene, dark grey olivine and pits are relic serpentine.

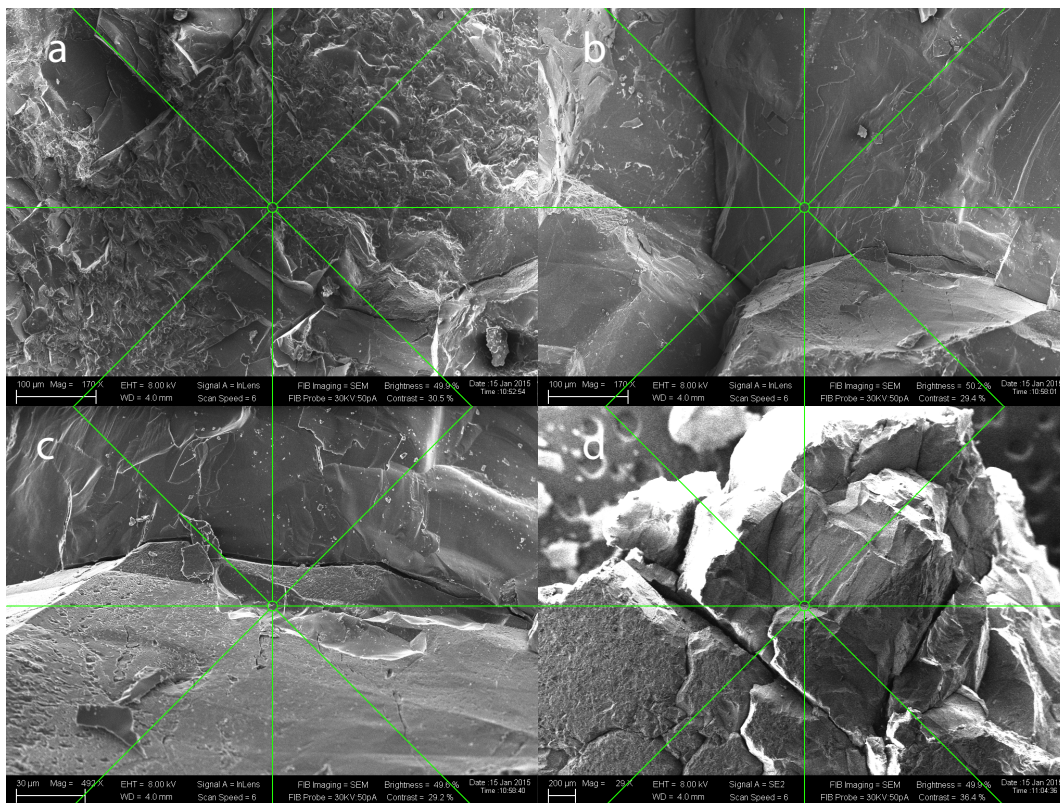


Figure H.2. SEM images of heat treated, unreacted dunite. Olivine is the only phase present.

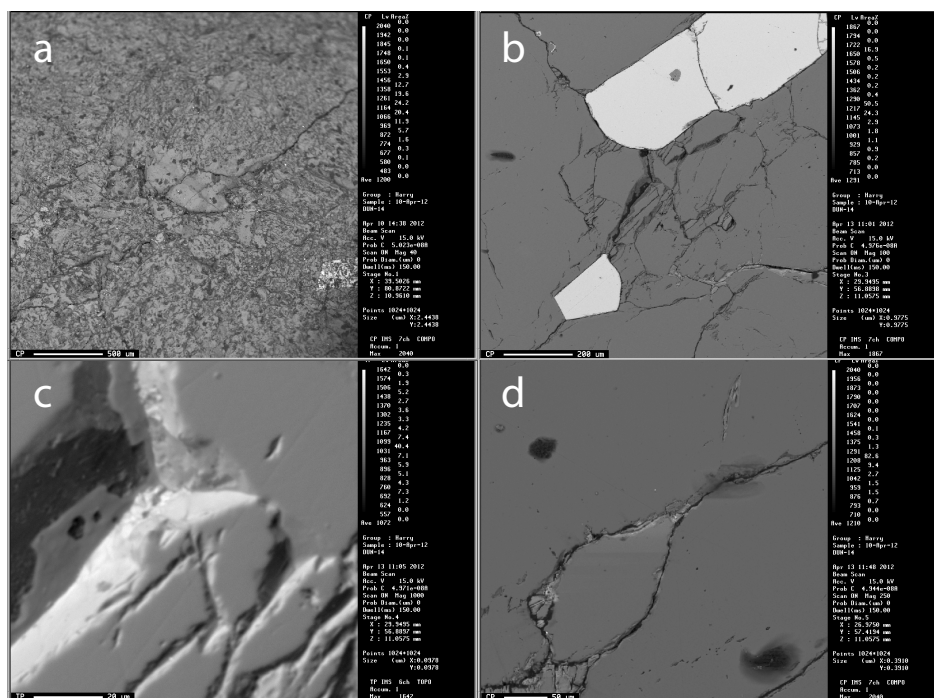


Figure H.3. SEM images of polished thin sections of dunite sample reacted with 0.6 M NaHCO₃ solution saturated with CO₂ at 150°C.

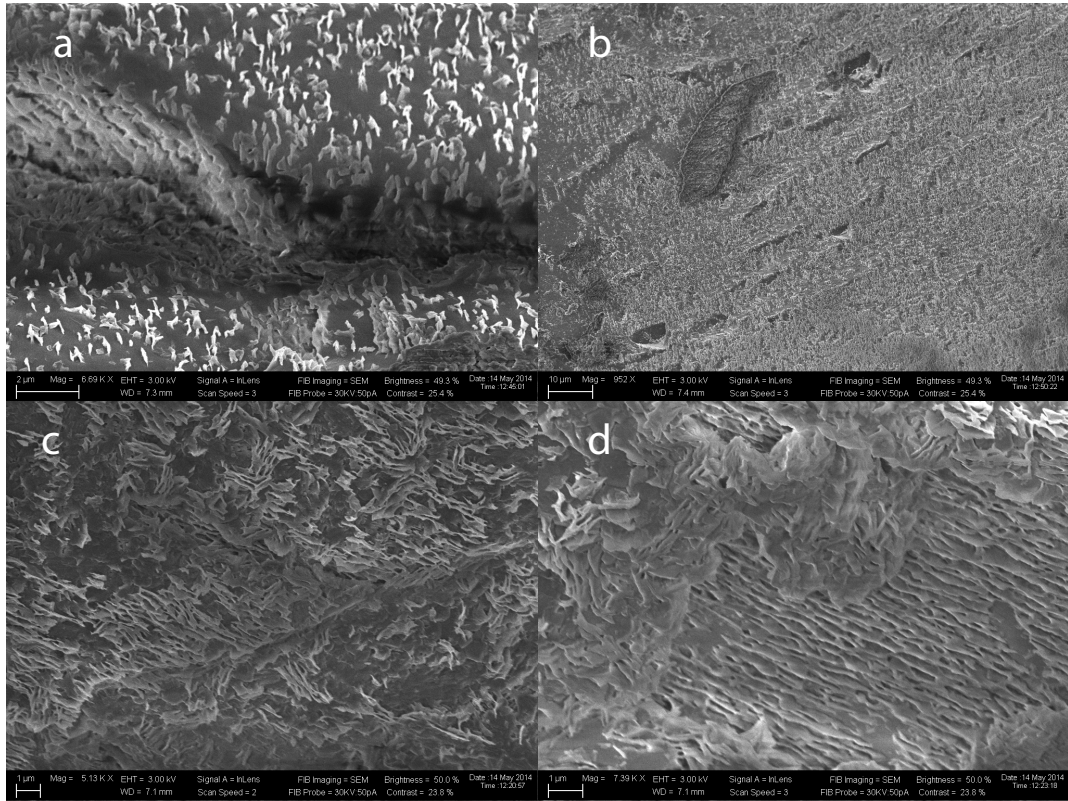


Figure H.4. SEM images of dunite sample reacted at 150°C with distilled water.

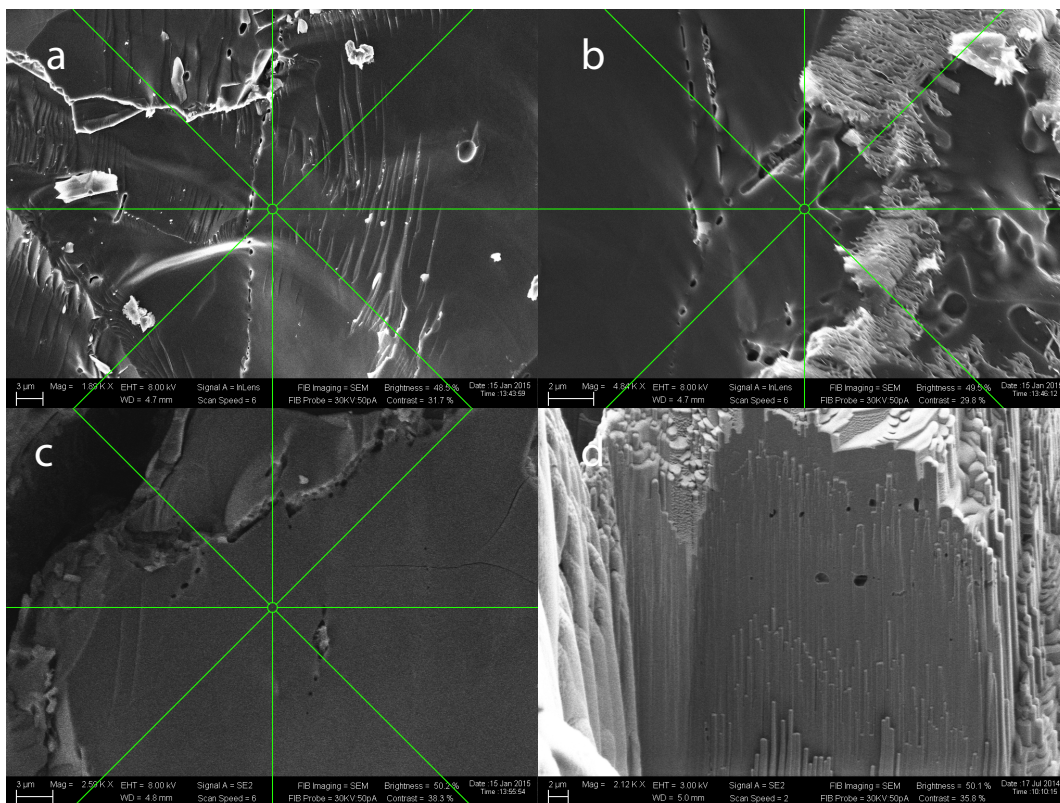


Figure H.5. SEM images of dunite samples reacted with 0.6 M NaHCO₃ solution saturated with CO₂ at 150°C.

Appendix I: Tabulated data from Linnejavri transect

Sample	Position	Density	Porosity	Talc	Magnesite	Total Carbonate	R	X	Vp	Vs1	Vs2	Anisotropy	Vp/Vs
	m	g/cc	%	%	%	%	Ωm	Ωm	m/s	m/s	m/s	%	
Lin3a-13	0.15	2.896	0.241	53	23	24	15460	128.3	5374	3244	3084	5.18	1.65
Lin3b-13	0.45	2.896	0.315	51	20	24	17780	314.7	6390	3307	3378	2.10	1.93
Lin3c-13	0.6	2.851	1.624	45	17	31	4956	68.89	6139	3479	3460	0.549	1.76
Lin3d-13	1.09	2.856	0.377	35	5	42	7140	237.9	6042	3130	3177	1.47	1.93
Lin3e-13	1.38	2.859	0.418	47	15	27	56680	1701	6095	3214	3250	1.10	1.89
Lin3g-13	1.77	2.872	0.413	46	23	30	7876	94.52	6141	3236	2726	18.7	1.89
Lin3h-13	2.18	2.932	0.276	51	24	25	6233	92.25	6120	3091	2767	11.7	1.97
Lin3i-13	2.83	2.791	0.412	7	0	4	2553	56.43	6019	3278	3339	1.82	1.83
Lin31	5	2.646	0.242	2	0	2	6769	302.8	6221	3200	3160	1.26	1.94

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