PROJECT SUMMARY

Overview:

We propose an interdisciplinary study of hydration, carbonation and oxidation of mantle peridotite interacting with aqueous fluids at temperatures below ~ 300?C. We will combine observations of outcrops and boreholes, geochemical analyses, structural measurements, geomechanical experiments and numerical modeling to investigate feedback between alteration and fluid transport, and quantify the resulting geochemical fluxes. Field observations and sampling will take place mainly in the Samail ophiolite of Oman, where peridotite has undergone spreading-ridge-related hydrothermal alteration, hydration and carbonation in the hanging-wall of the subduction zone that emplaced the ophiolite over metasediments, and subaerial weathering. Our research will provide matching funds and results that dovetail with the 2015-2018 International Continental Drilling Program (ICDP) Oman Drilling Project, and the many other related efforts just getting underway. We will continue our independently supported research on subduction zone alteration of mantle wedge peridotites at a range of pressures and temperatures, and work closely with other groups investigating seafloor and subduction-related peridotite alteration, in order to quantify the similarities and differences in alteration processes in these different tectonic environments, and generalize our results to global alteration processes and geochemical cycles.

Intellectual Merit :

Alteration of peridotite is an essential process in Earth dynamics. Hydration of oceanic crust and mantle, followed by subduction, supplies water to drive arc volcanism, and modulates the hydrogen content of the mantle over time. Carbonate formation during alteration of peridotite, near the surface and in the hanging wall in subduction zones, is an important but poorly characterized link in the carbon cycle. Oxidation of minerals and concomitant reduction of fluids produces H2 and hydrocarbons, and a niche for chemosynthetic microbes. Chemical weathering is as important as magmatism and plate tectonics in shaping the Earths surface. The interplay of chemical and physical mechanisms of peridotite alteration is not well understood, but will be transformed as a result of emerging understanding of equilibria and kinetics in peridotite alteration, and reaction-driven cracking that has left us poised on the brink of a breakthrough at this little-studied frontier. We will take advantage of low temperature, near surface, active peridotite alteration in Oman to study inputs, outputs, and the reaction zone in situ. Such a study is more difficult in smaller peridotite exposures with limited outcrop and more rainfall, nearly impossible in submarine hydrothermal systems, and completely impossible in studies of ancient systems. Such a comprehensive approach via 250 to 600 meter boreholes is very rare, if not unprecedented.

Broader Impacts :

As initially outlined in the ICDP Oman Drilling proposal, we seek funding for 20 graduate students, 10 from Oman and 10 US-based, to join in core description onboard the IODP drill ship, R/V Joides Resolution, while it is in port in 2016 and 2018. These students will work shoulder to shoulder in one of the world?s best core description labs with some of the world?s best core describers, in a unique, hands-on educational environment.

We will publish our data and results in peer-reviewed, international journals in a timely fashion, and make our data freely available on electronic databases as described in the data management plan (below). Continuing our current practice, we will make public presentations and publish general interest articles describing our research and its relevance to important societal issues. We will make annual reports available on a website.

We will contribute to the professional development of two postdocs (one of whom is a woman) and five Columbia, UCLA, ASU and WHOI grad students through their involvement with this project.

This study will produce a comprehensive understanding of a non-linear, far from equilibrium reactive transport system, which can be used as a template for investigations of many other, similar Earth processes. Furthermore, the knowledge resulting from our proposed study may be applied to design of engineered systems for geological CO2 capture and storage, generation of geothermal power, solution mining and extraction of oil and gas from unconventional, low-permeability reservoirs.

TABLE OF CONTENTS

For font size and page formatting specifications, see GPG section II.B.2.

	Total No. of Pages	Page No.* (Optional)*
Cover Sheet for Proposal to the National Science Foundation		
Project Summary (not to exceed 1 page)	1	
Table of Contents	1	
Project Description (Including Results from Prior NSF Support) (not to exceed 15 pages) **(Exceed only if allowed by a specific program announcement/solicitation or if approved in advance by the appropriate NSF Assistant Director or designee)**	27	
References Cited	8	
Biographical Sketches (Not to exceed 2 pages each)	12	
Budget (Plus up to 3 pages of budget justification)	10	
Current and Pending Support	9	
Facilities, Equipment and Other Resources	3	
Special Information/Supplementary Documents (Data Management Plan, Mentoring Plan and Other Supplementary Documents)	16	
Appendix (List below.) **(Include only if allowed by a specific program announcement/ solicitation or if approved in advance by the appropriate NSF Assistant Director or designee)**		

Appendix Items:

*Proposers may select any numbering mechanism for the proposal. The entire proposal however, must be paginated. Complete both columns only if the proposal is numbered consecutively.

Collaborative proposal: Alteration of mantle peridotite: Geochemical fluxes and dynamics of far from equilibrium transport

Principal Investigators: Peter Kelemen[1,2], Greg Hirth[3], Craig Manning[4], Jürg Matter[2,5], Heather Savage[2], Everett Shock[6], Rob Sohn[7], Marc Spiegelman[1,2,8], and Martin Stute[2,9] **Postdocs:** Sarah Lambart[2], Ole Ivar Ulven[10] **Collaborators (see support letters):** Gretchen Bernasconi-Green[11], Denton Ebel[12], Bethany Ehlmann[13], Uli Harms[14], Bjørn Jamtveit[10], Anders Malthe-Sorensen[10], Alissa Park[15], Jay Miller[16], Sobhi Nasir[17], Matt Schrenk[18], Damon Teagle[5], Alexis Templeton[19], Ed Young[4]

1: Earth & Environmental Sciences, Columbia Univ.; 2: Lamont Doherty Earth Observatory, Columbia Univ.; 3: Geological Sciences, Brown Univ.; 4: Earth & Space Sciences, UCLA; 5: National Oceanography Centre, Univ. Southampton 6: School of Earth & Space Exploration, ASU; 7: Geology & Geophysics, Woods Hole Oceanographic Inst.; 8: Applied Physics & Applied Math, Columbia Univ.; 9: Environmental Science, Barnard College; 10: University of Oslo; 11: Mineralogy & Petrology, ETH-Zurich; 12: Earth & Planetary Sciences, American Museum of Natural History; 13: Geological & Planetary Sciences, Caltech; 14: International Continental Drilling Program; 15: Earth & Environmental Engineering, Columbia Univ.; 16: IODP, Texas A&M Univ.; 17: Geology, Sultan Qaboos University, Oman; 18: College of Natural Science, Michigan State Univ.; 19: Geological Sciences, Univ. Colorado - Boulder

1 Introduction

1.1 Peridotite alteration is fundamentally important …

Alteration of peridotite is an essential process in Earth dynamics. Hydration of igneous, oceanic crust and mantle, followed by subduction, supplies huge volumes of water to drive arc volcanism, and maintains or even increases the hydrogen content of the Earth's mantle over time. Carbonate formation during alteration of peridotite, near the surface and in the hanging wall in subduction zones, is increasingly recognized as an important but poorly characterized link in the carbon cycle. Oxidation of minerals and concomitant reduction of fluids produces H_2 and hydrocarbons, and a niche for chemosynthetic microbes. Chemical weathering is as important as magmatism and plate tectonics in shaping the Earth's surface.

Almost everyone has seen altered peridotites – whether they know it or not – as a popular ornamental stone used for building facades and kitchen counters, in soapstone amulets and monumental statues. Mineral parageneses in altered peridotite comprise part of the canon of metamorphic petrology. However, unlike most iconic metamorphic processes, which occur in obscurity, deep in the Earth, peridotite alteration is ongoing and accessible, occurring at appreciable rates near the surface. For example, in their classic paper Barnes and O'Neil (Barnes & O'Neil 1969) estimated that dissolved Ca in a single, small alkaline spring was extracted via alteration of 10^3 to 10^4 tons of peridotite per year.

And no wonder … At near-surface temperatures, less than 200°C, the energy density (free energy per unit volume) for peridotite hydration and carbonation and oxidation is ~ 1.5 MJ/liter, about 5% of the energy density in liquid hydrocarbon fuels (Kelemen & Hirth 2012). In the upper crust, at ~ 200 MPa, mantle peridotite is unstable in the presence of water below ~ 700°C, unstable in the presence of CO_2-rich fluids below ~ 500°C, and it is unsafe at any speed at the high oxygen fugacity that prevails near the Earth's surface. Where plate tectonics and erosion expose fresh peridotite on the surface, this creates a chemical potential gradient unparalleled in both magnitude and extent, like a giant battery.

The energy spinning off from this chemical dynamo drives many of the fundamental processes that shape the Earth. Hydration of peridotite controls the rheology of oceanic transform faults and subduction zones, causes forearc uplift, fluxes arc magmatism, and lubricates the mantle. CO_2 fluxes via peridotite carbonation are comparable to those in hydrothermal alteration of oceanic crust and in arc volcanic gases. Peridotite alteration produces the most reduced natural fluids on the surface of the Earth, and generates steep compositional gradients that are exploited by chemosynthetic organisms. The combination of dissolved, reduced carbon species with FeNi alloy as a catalyst leads to abiotic synthesis of alkanes and alkenes (McCollom et al 2010). As a result of these factors, peridotite alteration sites have been invoked as likely sites for the origin of life on this and other planets. Finally, enhanced peridotite carbonation could play a significant role in CO_2 storage, and potentially offers a practical and inexpensive route to distributed, geologic CO_2 capture from surface waters and hence from the atmosphere.

1.2 … but we don't understand how it works

From a geodynamical point of view, we don't understand peridotite alteration at all. In particular, we don't understand the feedbacks between fluid flow and metamorphic reactions that – under some circumstances – allow the alteration process to proceed to completion. Alteration processes are thought to be uncommon because they are self-limited, via a variety of negative feedbacks described below. And yet, we commonly observe completely altered rocks at the surface, and – more remotely – we call upon such alteration to explain the properties of the seismically slow, buoyant "cold nose" in the mantle wedge above subduction zones, worldwide.

What's the problem? Consider this. In crystalline rocks, fluid porosity and permeability may be negligibly small, so alteration is supply-limited. Further, fluids enhance diffusion and are catalysts for recrystallization; prograde, "devolatilization" reactions produce fluids, in a positive feedback, while retrograde hydration and carbonation can consume fluid before recrystallization is complete. And, perhaps most importantly, alteration products may fill porosity, destroying permeable flow networks, and armoring reactive surfaces. The common presence of abundant, relict olivine and other mantle minerals in outcrop attests to the selective operation of peridotite alteration, despite the fact that olivine is thermodynamically unstable in the presence of water, and reacts readily, in near-surface conditions.

Given the tendency of alteration reactions to be self-limiting, it is remarkable that 100% hydrated peridotites, known as *serpentinites*, are also common. Less familiar, but of increasing scientific interest, are *listvenites*, 100% carbonated peridotites, and mixed assemblages such as *soapstone* (composed entirely of talc + dolomite or magnesite). How do these form, if alteration is self-limiting?

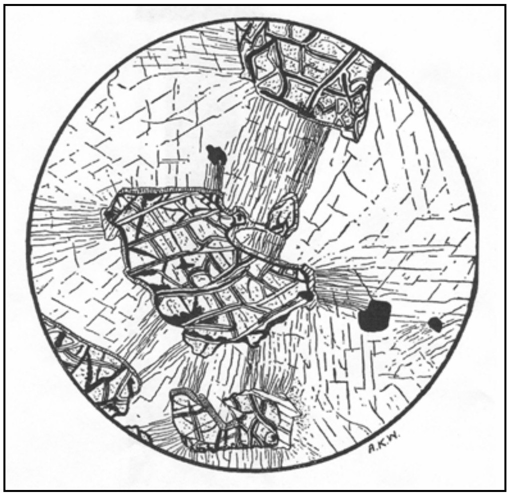


***Fig. 1**: Sketch from a photomicrograph, field of view 3 mm in diameter, of fractured olivine, enclosing veins of serpentine + magnetite, surrounded by unaltered plagioclase which has fractured as a result of volume change during olivine serpentinization* (Hatch et al 1949)

Two end-member explanations have been offered. Replacement reactions may occur at constant volume, in which expansion due to volatile addition and decreasing solid density is balanced by dissolution and export of formerly solid chemical components in a fluid (e.g., Carmichael 1986, Fletcher & Merino 2001). However, with notable exceptions, most studies of serpentinites, and our work on magnesite + quartz listvenites in Oman, indicate that alteration was nearly isochemical except for addition of H_2O and/or CO_2 (our unpublished results and, e.g., Coleman & Keith 1971, Shervais et al 2005). If so, such alteration must involve large increases in the solid volume. Initial porosity in fresh peridotite – mainly in fractures – is rarely greater than a few percent. In contrast, because hydration and carbonation add mass to the solids, combined with decreasing solid density, both involve more than 50% volume increase.

Thus, MacDonald and Fyfe (1985) proposed that stress due to volume expansion during serpentinization in an elastically confined system causes fractures, which provide continued access for fluids and expose new, reactive surfaces, in a positive feedback mechanism that allows 100% hydration. This explanation, extended to peridotite carbonation as well as hydration, is the topic of several recent studies of *reaction driven-cracking* (Jamtveit et al 2011, Kelemen & Hirth 2012, Kelemen et al 2011, Kelemen et al 2013c, Ulven et al 2014a, Ulven et al 2014b) and forms one of the primary hypotheses motivating our research.

1.3 Moving forward

So far, the theory describing reactive transport during peridotite alteration is only semi-quantitative, and thinly linked to observations (see Background section, below). Commonly employed thermodynamic expressions used to estimate the *pressure of crystallization*, and thus predict the likelihood of reaction-driven cracking, are clearly approximate and only offer upper bounds on stress. Data from natural systems, for example on crack density and the rate of deformation, are sparse. To date, experimental studies of the "force of crystallization", or "pressure of crystallization", (reviews in Kelemen & Hirth 2012, Noiriel et al 2010, Scherer 2004, Steiger 2005) have not yielded information on the effect of confining pressure on reaction-driven cracking. In addition to thermodynamic limits, reaction kinetics have an important influence on the presence or absence of reaction-driven cracking. Very slow reactions are likely to provide time for relaxation of crystallization pressure, for example via pressure solution. Rapid reactions close to equilibrium also reduce crystallization pressure. The kinetics of natural peridotite alteration reactions at low temperature remain poorly known. Rapid growth of crystals impinging on pore walls requires the presence of a nanofilm of fluid along the new mineral-host interface, held open by "disjoining pressure"; the magnitude of the disjoining pressure may varly significantly for different mineral-host pairs, fluid compositions, and PT conditions (e.g., Hövelmann et al 2012).

In our proposed study, we will map the conditions under which alteration is self-limiting, takes place at constant volume, or causes reaction-driven cracking, using laboratory experiments and field observations of the Samail ophiolite as benchmarks, and models to interpolate between and beyond these known points. We will determine the rates and mechanisms of peridotite alteration processes on length scales from microns to kilometers, and time intervals from seconds to tens of thousands or years. We will validate numerical models via comparison with laboratory and geological systems, and then apply our understanding on plate tectonic scales, over the time spans of global geochemical cycles. In so doing, we will quantify the consequences of peridotite alteration for the rheology of tectonic plate boundaries, and its role in global geochemical cycling of H_2O, CO_2, and other key components of the Earth system. Overall, we will create a "phase diagram", identifying the conditions where peridotite alteration is organized to produce rapid, extensive alteration and support abundant, diverse microbial ecosystems, the boundaries that delineate this geobiochemophysical Eden, and the quiet, empty deserts that surround it.

1.4 Related Projects in Oman and worldwide

In this section, we describe the ICDP Oman Drilling Project, other ongoing studies of peridotite alteration in Oman, and key future studies of peridotite alteration that will put Oman results in context. We wish to emphasize the synergies that arise from the combination of these different projects. A large number of investigators will focus on peridotite alteration in the coming years, with a particular emphasis on studies in Oman. Their results will complement data and interpretations arising from our proposed research, to form an exceptionally complete, multidisciplinary view of these essential processes within a broader global context. Now is the time to undertake our proposed study, in order to take advantage of other available funding, and develop ideas in an extensive, multidisciplinary, collegial discussion.

Field observations in our proposed research will be focused on alteration of peridotite in the Samail ophiolite in the Sultanate of Oman. The oceanic crust and upper mantle of the Samail ophiolite were thrust onto the Arabian continental platform in the Cretaceous, tilted, and exposed by erosion. The ophiolite is the largest, most intact, subaerial exposure of ocean crust and shallow mantle in the world.

In addition to these factors, we are focusing on Oman in the context of the International Continental Drilling Program (ICDP) Oman Drilling Project (Kelemen 2013b, Kelemen et al 2013b). This Project, with drilling in the winter from late 2015 through early 2018, involves 38 principal investigators based in eight different countries, led by the PI on this NSF proposal, Peter Kelemen. The Oman Drilling Project grew out of workshops in Palisades, NY and Oman with 77 and 87 participants, respectively, based in 15 countries. Reports on these workshops are in the ICDP proposal and other documents on the Project website, In addition to the 38 PI's, more than 24 other professors and research scientists have contacted the PIs over the past year asking to participate in the Oman Drilling Project. A comprehensive review of past research on the ophiolite, description of the scientific goals, and implementation plan for the Drilling Project is available online.

Scientific goals of the Oman Drilling Project include determining the rate, extent and processes of present day alteration and weathering, and the nature of the subsurface biosphere supported by and potentially accelerating alteration reactions, particularly in the exposed mantle peridotite section of the ophiolite. Also relevant to the topic of this proposal will be drilling the mantle hanging wall and metasedimentary foot wall of the basal thrust of the ophiolite, to study Cretaceous processes that formed fully carbonated peridotites (listvenite) in the hanging wall. Other goals of the multidisciplinary drilling project include understanding processes at oceanic spreading centers: melt transport in the shallow mantle; processes of igneous crustal accretion and cooling; and the temperature, depth and extent of hydrothermal alteration.

12 holes up to 600 meters deep are planned, with depth limited by cost and equipment available in Oman. Of these, 6 are intended primarily to study active, ongoing alteration of peridotite. A 7th hole will sample peridotite thrust over metasediments at the base of the ophiolite, and an 8th will recover altered peridotite from the crust/mantle transition zone. The 4 other holes will be drilled in lower crustal rocks. For this proposed study, we will have access to core and water samples from all of these.

The estimated ODP operational budget is approximately \$4M, and covers drilling, water sampling, geophysical logging, biological sampling, core description, core shipment, and project management. Core description will be on the Integrated Ocean Drilling Program (IODP) drill ship R/V Joides Resolution (JR) while it is in port for several months each year. The operational budget does not cover support of science personnel, including graduate students, nor for most of the geochemical analyses proposed here. We anticipate that participants in the Drilling Project will all raise funds for personnel and laboratory analyses of data and samples, providing related data that will greatly enrich understanding of our own results.

ICDP will provide $1.5M toward the $4M cost (support letter from Uli Harms, ICDP). As with all ICDP projects, the PI's and their colleagues are expected to raise matching funds for the balance of operational costs. The Sloan Foundation, in a grant to Kelemen for field studies related to the Deep Carbon Observatory, provided ~ $300k for operations, primarily for peridotite alteration. The Rock-Powered Life NASA Astrobiological Institute, led by PI Alexis Templeton (support letter), includes ~ $340k for operations, primarily biological sampling. IODP is considering provision of ~ $200k support for core description onboard the JR, including travel, room, board and salary for their technical staff (support letter from Jay Miller, IODP TAMU). Thus, about $2.2M are committed toward the $4M operational budget.

There are pending proposals in Germany, Norway and the UK that include $200k, $150k and $350k, respectively, for Oman Drilling operations. Additional proposals are planned in the UK and France. The budget in this proposal includes ~ $300k of operational support to drill two holes in altered peridotites, conduct tracer studies, and fund participation of Omani and US graduate students in core description onboard the Joides Resolution. Other experiments proposed here, in the boreholes and on core, as well as analytical work on water and core samples, are not included in the ICDP operational budget but will – of course – support the science objectives of the drilling project.

In the event that we fall short of the $4M operational budget, priority decisions will be made, based in part on the availability of matching funds for specific aspects of the ICDP approved project. In such a case, it is evident that boreholes and studies focused on peridotite alteration will be given highest priority. We will begin drilling in late 2015 or early 2016 with the funds in hand. For the moment, we continue to proceed with an open door for scientific participation, on the assumption that all proposed boreholes will be drilled.

In addition to the funding for the ICDP Oman Drilling Project, a variety of related studies are underway or proposed including: an NSF grant to PI Kelemen to study peridotite carbonation outcrops in Oman (see results of prior support), an NSF proposal by Kelemen, for studies of carbon mass transfer into the mantle wedge of subduction zones in a variety of different tectonic and PT regimes worldwide, a NASA project with PI Everett Shock that investigated fluid chemistry and microbial activity in alkaline springs and groundwater associated with peridotite alteration in Oman, and an ongoing NASA project to study aqueous alteration of ultramafic rocks in Oman as an analog for understanding Martian carbonates, with PI Bethany Ehlmann. Finally, IODP Expedition 357 , with Co-Chief Scientists Gretchen Bernasconi-Green and Beth Orcutt, will drill the Lost City, a peridotite-hosted hydrothermal system near the Mid-Atlantic Ridge. The results will be particularly important for the study proposed here, allowing us to quantitatively compare subaerial versus submarine alteration of peridotite (see support letter from Bernasconi-Green).

2 Background

2.1 Clarifying some terminology

Mineral hydration, carbonation and oxidation reactions are a vital part of many geologic processes. General terms used to describe these reactions include ***retrograde metamorphism***, which occurs when metamorphic and igneous rocks formed at high temperature, with low volatile contents, react with fluids at lower temperature; ***hydrothermal alteration***, when relatively volatile-poor rocks react with fluids, increasing the proportion of hydrous silicate, carbonate and oxide minerals in the crust and shallow mantle; and ***chemical weathering***, when surface waters and the atmosphere react with minerals to produce volume changes that cause cracking, spalling and grain size reduction. We refer to all three processes using the general term ***alteration*** in this proposal. Alteration is as important as magmatism and plate tectonics in shaping the Earth's surface.

Peridotite alteration provides the best-known, most common examples of hydration and carbonation. Mantle peridotite – and its primary constituent, the mineral olivine (Mg end-member Mg_2SiO_4) – is transported into the upper crust and to the Earth's surface by tectonic uplift and erosion. It is far from equilibrium with the atmosphere and surface waters, and reacts rapidly with aqueous fluids, even at low temperature (Malvoisin et al 2012, Martin & Fyfe 1970).

Peridotite alteration forms products of 100% hydration known as ***serpentinite***, e.g.

$$4Mg_2SiO_4+6H_2O = 2Mg_3Si_2O_5(OH)_4+2Mg(OH)_2 \text{ , olivine + water = serpentine + brucite} \quad (1)$$

less well known products of 100% carbonation known as ***listvenite***, e.g.

$$4Mg_2SiO_4+8CO_2 = 8MgCO_3+4SiO_2 \text{ , olivine + } CO_2 \text{ = magnesite + quartz} \quad (2)$$

and mixed products, such as ***ophicalcite*** (serpentine + carbonate minerals) and ***soapstone***, e.g.

$$4Mg_2SiO_4+5CO_2+H_2O = 5MgCO_3+Mg_3Si_4O_{10}(OH)_2 \text{ , olivine + } CO_2 + H_2O \text{ = magnesite + talc} \quad (3)$$

Peridotite oxidation reactions are also exemplary. Oxidation of divalent iron in olivine and other ferro-magnesian silicate minerals extracts oxygen from fluid to produce ferric-iron-rich oxides and hydroxi-oxides together with reduced fluid species, e.g.

$$3Fe^{2+}{}_2SiO_4+2H_2O = 2Fe^{2+}Fe^{3+}{}_2O_4+3SiO_2+2H_2 \text{, olivine + } H_2O \text{ = magnetite + silicate + hydrogen} \quad (4)$$

$$6Fe_2SiO_4+CO_2+2H_2O = 4Fe_3O_4+6SiO_2+CH_4 \text{, olivine + } CO_2 + H_2O \text{ = magnetite + silicate + methane} \quad (5)$$

$$8Fe_3O_4+CO_2+2H_2O = 12Fe_2O_3+CH_4 \qquad 4Fe_3O_4+CO_2+8H_2O = 12FeO(OH)+CH_4 \quad (6,7)$$

magnetite + CO_2 + water = hematite + methane   magnetite + CO_2 + water = goethite + methane

Extreme fluid products of peridotite oxidation reactions, rich in dissolved H_2 and saturated in native FeNi metal alloys, are among the most reduced natural waters on Earth. Direct evidence for the processes represented by reactions (4-7) is found in measurements of dissolved H_2 and CH_4 in serpentinizing fluids that emerge in hyperalkaline springs. Preliminary data from Shock's group shown in Fig. 2 indicate that concentrations both of these reduced gases increase with increasing pH, due to ongoing serpentinization.

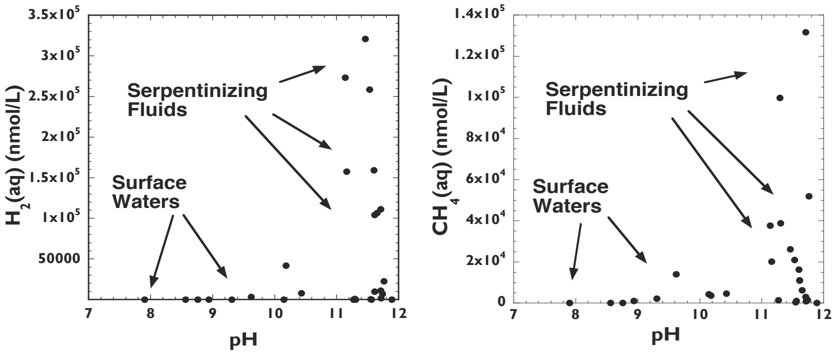


***Fig 2**. Concentrations of dissolved hydrogen and methane in hyperalkaline fluids produced by serpentinization and surface waters vs pH, from Canovas, P. and Shock, E.L., in prep, 2014.*

2.2 Geochemistry of low temperature peridotite hydration and carbonation

The classic paper of Barnes and O'Neil (1969), followed by geochemical modeling by Bruni et al (2002) and Paukert et al (2012b), established guidelines for understanding low temperature peridotite alteration. Interaction of rainfall with peridotite near the surface dissolves Mg from the rock and CO_2 from the air to produce pH 8 to 9, "***Type I***" Mg-HCO_3-rich fluids. When these fluids travel deeper and lose contact with the atmosphere, they precipitate hydrous Mg silicates (typically serpentine minerals), magnesite, dolomite, and hydrated Mg-carbonates, as well as dissolve Ca from pyroxenes in peridotite, to produce pH 11 to 12, "***Type II***", Ca-OH-rich, alkaline fluids. In turn, Type II fluids emerge at alkaline springs, where they take up CO_2 from the air to form travertine (calcite) terraces. These characteristics are common to ophiolite exposures worldwide, as well as submarine systems such as the Lost City Hydrothermal Field (e.g., Kelley et al 2001). However, as far as we know, Oman contains the world's most extensive outcrops of travertine terraces and carbonate-veined peridotite formed in this way.

Most peridotite-hosted, low temperature carbonate veins in Oman – as well as the travertine terraces – have ^{14}C ages < 50,000 years (Kelemen et al 2011, Kelemen & Matter 2008, Mervine et al 2013). These young ages, together with low oxygen isotope exchange temperatures, low clumped isotope temperatures, mineral phase equilibria recording Ultra Low Temperature metamorphism (ULT), and the presence of travertines growing from pH 12, Mg-free spring waters before our eyes, all indicate that the peridotite alteration system in Oman is active today, consuming 10^4 to 10^5 tons of CO_2 per year. Based on the drop in carbon concentration from Type I to Type II fluids (precipitated in subsurface Mg-carbonates), and the Ca content of Type II fluids (that will be precipitated in travertine at the surface), we pointed out that for every kg of travertine on the surface, ~ 5 to 15 kg of Mg-carbonate is precipitated along the subsurface reaction path (Kelemen et al 2011, Kelemen & Matter 2008).

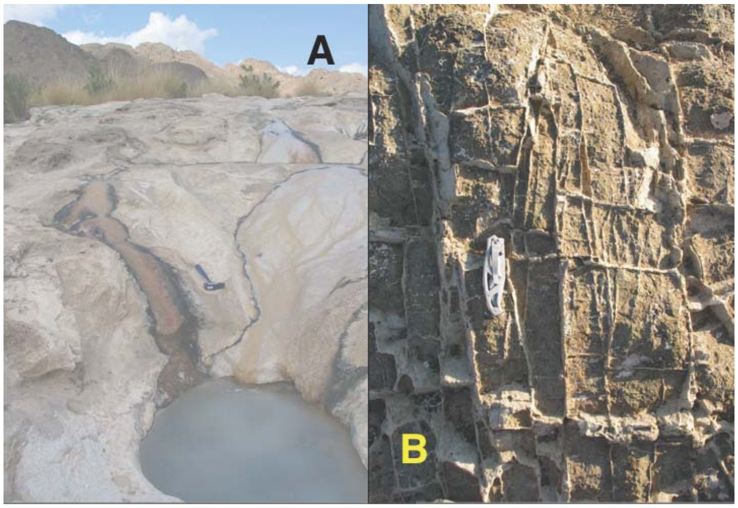


Fig 3: *A. Travertine (calcite) terraces and B. magnesite veins formed by low temperature peridotite alteration in Oman over the past 50,000 years.*

2.3 Petrology meets rock mechanics: Reactive flow in peridotite alteration

Precipitation, dissolution and volume change are fundamental aspects of peridotite alteration, as an easily studied, well known example of more general processes. Precipitation of new, solid phases from supersaturated aqueous fluids in pore space has been a focus of studies on salt weathering (reviews in Noiriel et al 2010, Scherer 2004, Steiger 2005). More recently, similar ideas formed the basis for models of chemical weathering, where precipitation of new minerals and resulting volume change are caused by fluid-rock reactions (e.g., Fletcher et al 2006). Here we summarize likely outcomes of these processes.

In an open system, precipitation of minerals from supersaturated fluids, and fluid-rock reactions leading to hydration, carbonation and/or oxidation, all add solid mass and reduce solid density, leading to an increase in volume. When fluid porosity is small (and/or constant) compared to solid volume changes, and transport of solute out of the system is minor, the total system volume increases. In contrast, mineral hydration and carbonation reactions in a closed system consume low-density fluid to produce denser hydrates and carbonates, leading to a decrease in porosity and system volume at constant mass.

These processes can produce (a) filling or compaction of porosity, decreasing permeability, and armoring of reactive surfaces (Aharonov et al 1998, Becker & Davis 2003, Emmanuel & Berkowitz 2006, Xu et al 2004), or (b) a large change in total volume causing fractures that provide continued access for fluids in a positive feedback (e.g., Jamtveit et al 2011, Kelemen & Hirth 2012, and references therein). Which outcome emerges in specific cases is determined in part by the “crystallization pressure”, which creates differential stress around growing crystals impinging on host phases. When stresses become high enough to induce “reaction-driven cracking”, this can maintain or increase permeability and reactive surface area, potentially leading to 100% hydration, carbonation and/or oxidation.

Reaction-driven cracking forms an important focus of our proposed research, but before we provide more background on that process, we describe another alternative outcome here. Over the past 40 years, most studies by metamorphic petrologists on mineral hydration and carbonation emphasized the possibility of equivalent dissolution and precipitation rates, maintaining constant volume. Fletcher & Merino (2001) provided a simple, quantitative description of the process. In a host mineral initially in equilibrium with fluid, acting as an elastic container for a growing new mineral, stress around the new mineral will rise. Because the free energy of the host mineral is linearly proportional to stress or pressure, evolution to higher stress destabilizes the host phase, which will begin to dissolve. Ultimately, dissolution of the host phase will occur at the same rate as crystallization of the new phase, at a constant stress:

$$P' = -RT\,ln(\Omega)/\Delta V_s = -\Delta G_r/\Delta V_s \tag{8}$$

where P' is the crystallization pressure (a deviatoric stress in excess of confining pressure), ΔG_r is the Gibbs Free Energy of a reaction, and ΔV_s is the change in solid volume resulting from this reaction. (notation as in Kelemen & Hirth, 2012). Thus, for a saturation state, $\Omega = 2$ (close to equilibrium), Fletcher & Merino calculated steady state stresses of 10’s of MPa for common replacement reactions. At moderate to high temperature, metamorphic reaction rates may be sufficiently fast to maintain small Ω and ΔG_r, so that a constant volume, steady state may commonly be attained. However, for systems far from equilibrium such as olivine + H_2O or olivine + CO_2 at ≤ 200°C, $|\Delta G_r| > 50$ kJ/mol, $\Omega > 10^6$, and equation (8) predicts stresses of 100's to 1000's of MPa. These stresses are sufficient to fracture crustal rocks. Thus, the near-constant volume process is not attainable in such far-from-equilibrium systems.

Recent work (Kelemen & Hirth 2012, Kelemen et al 2013c) compared thermodynamic and mineral physics estimates of the crystallization pressure resulting from volume changes during hydration and carbonation of the primary mineral constituent of peridotite, olivine. The crystallization pressure that drives reaction-driven cracking is limited by the available chemical potential energy. Approaches developed to describe the "force of crystallization" and salt weathering over the past 100 years (reviews in Kelemen & Hirth 2012, Noiriel et al 2010, Scherer 2004, Steiger 2005) also yield equation (8).

Kelemen & Hirth (2012) used equation (8), but questioned this approach, which describes the available at constant temperature and pressure. A better approximation to natural conditions (prior to deformation), might use the Helmholtz Free Energy, to describe available energy at constant temperature and volume:

$$P' = -\Delta F_r/\Delta V_s = -\Delta G_r/\Delta V_s + P\Delta V_r/\Delta V_s \tag{9}$$

where P is the confining pressure and ΔV_r is the volume change of the stoichiometric reaction including volatile components. There have been no experimental determinations of the effect of confining pressure on crystallization pressure. Our proposed laboratory experiments will determine this.

Kelemen & Hirth (2012) compared values from expressions (8) and (9) at several kilometers depth and ~ 250°C, to the surface energy of fractures generated by volume expansion due to olivine hydration. The surface energy yields stress > 260 ± 130 MPa for crystallization pressure, broadly consistent with the thermodynamic approach. However, this agreement is highly approximate. Equations (8) and (9) do not incorporate energy sinks such as exothermic heating, entropy changes, and/or thermal diffusion. Further, they do not account for reaction rate, coupled with "slow" stress relaxation processes such as viscous deformation (e.g., pressure solution). Thus, the expressions implicitly assume that all chemical potential energy is converted into stress. Other than a few studies on salt (Røyne & Dysthe 2012, and references therein), there has been no experimental work that would allow evaluation of this assumption. Another possible control on the maximum stress due to crystal growth may arise when the crystallization pressure equals the "disjoining pressure" (e.g., Espinosa-Marzal & Scherer 2010, and references therein). When the surface energy of interfaces between two disparate minerals is larger than the sum of the two fluid-mineral surface energies, the "disjoining pressure" gives rise to a nanofilm along grain boundaries that provides a diffusive path for continued mineral growth. It is thought that crystallization pressure cannot exceed the disjoining pressure, though the values of the relevant surface energies are unknown, and 3D grain boundary geometries may complicate this theory (Kelemen et al 2013c).

Our proposed experimental work will allow us to explicitly measure the ratios

$$P'/[-\Delta G_r/\Delta V_s] \quad \text{and} \quad P'/[-\Delta G_r/\Delta V_s + P\Delta V_r/\Delta V_s], \tag{10}$$

which describe the efficiency of conversion of chemical potential energy to differential stress. Finally, we will record crack density in rock samples and along borehole walls to place additional constraints on stress due to volume change during peridotite alteration.

In this context, the importance of our proposed observations and experiments cannot be overstated. In order to interpret observed textures, and to develop useful numerical models that incorporate essential physicochemical relationships but are not overly complex, it is crucial – and fairly easy – to resolve some of the fundamental uncertainties outlined here.

On the other hand, there have been several recent experiments on reactive flow of CO_2-rich aqueous fluids through porous peridotites. Reaction driven cracking has not been observed. Kelemen's collaborators observed very little alteration in confined, heat-treated Balsam Gap dunite in 20 hours (Lisabeth et al 2013). Others observed decreasing permeability, associated with crystallization in pore space in confined cylinders of sintered olivine+pyroxene crystals (pers. comm. Godard, 2013 and Andreani et al 2009), FIX THIS and unconfined cubes of partially serpentinized natural peridotite with 6-8% initial porosity (Hövelmann et al 2012). These results indicate that it may be challenging to identify the combination of variables that produce reaction-driven cracking in peridotite. For this reason, we have started with analogue experiments, to refine our understanding of the physico-chemical feedbacks, before progressing to experiments on peridotite. Further, investigation of a variety of chemical systems will allow us to generalize from peridotite alteration to other, similar processes involving different lithologies.

2.4 Hypotheses motivating our proposed research

1. ***Although pre-existing fractures play a role in peridotite alteration, reaction-driven cracking is caused by olivine hydration and carbonation.*** We will evaluate this experimentally, and via exploratory seismic observations in boreholes in zones of active peridotite alteration. Comparison of modeling results with observed spacing, size, orientation and – where possible – age distribution data on cracks and veins in outcrop and core will constitute a qualitative test of the applicability of these ideas to natural systems.

2. ***Cracking and vein formation during peridotite alteration in the Samail ophiolite has been a polygenetic process starting near the spreading ridge at ~ 96 Ma, and continuing to the present.*** Multiple generations of alteration assemblages will be identified using metamorphic petrology on mineral assemblages, conventional stable isotope thermometry (requiring knowledge or inference of fluid compositions), clumped isotope thermometry (on individual minerals, without inferences about fluid), and geochronology. Once the features of different vein generations have been delineated, the proportions of veins that formed in different tectonic settings at different times will be measured.

3. ***Reactive flow of fluid during alteration has three likely, end-member outcomes under different conditions: (a) self-limiting, negative feedbacks, e.g., clogging of pore space, (b) constant volume replacement, and (c) accelerating, positive feedbacks via reaction-driven cracking.*** We will seek to delineate the conditions favoring all three outcomes via experiments on analog materials, olivine aggregates, and natural drill core samples. We will develop the simplest possible physicochemical numerical models of these processes. Models will be tested against experiments, and in turn modeling results will inform experimental design. Applicability of model results to natural systems in Oman will be tested using predicted vs. observed spacing, size, orientation and age distribution of cracks and veins.

4. ***Mineralized fractures (veins) in altered peridotite retain significant porosity, including pores along olivine grain boundaries, providing a positive feedback between fracture formation, fluid access, and reaction progress.*** We will address this via detailed, multi-scale observations of crack and vein density, porosity, permeability, and capillary imbibition in core samples, together with experiments on reactive fluid flow through analog materials, olivine aggregates, and core samples.

5. ***Dissolution of silicates and solute transport out of rock volumes during low temperature peridotite alteration is minor compared with addition of H2O, CO2 and O2 to solid phases and decreasing density, so alteration increases the solid volume.*** Volatile-free compositions of protoliths and altered rocks are commonly identical, ruling out incongruent dissolution, suggesting that that fully serpentinized or carbonated rocks underwent >50% expansion. Alternatively, perhaps they underwent nearly congruent dissolution, so the bulk composition is unchanged despite substantial solute export. We will use water and rock compositions to assess changes in bulk composition, minimum water/rock ratios, and solute concentrations. Geochemical models that reproduce observed fluid compositions will constrain possible reaction paths. Ultimately, we will determine solid volume changes due to alteration.

6. ***Altered peridotites are significant reservoirs for hydrogen, carbon and other important components in the Earth's geochemical cycles.*** Drill core provides an exceptional opportunity for systematic studies of vein, host, and whole rock compositions, via careful core measurements of the volume of different lithologies coupled with systematic sampling, and by strip sampling (e.g., Hart et al 1999). We will construct geochemical sections for Oman peridotites altered near a spreading ridge, above a subduction zone and via ongoing subaerial weathering. We will compare our samples to ocean drilling cores, and ultimately to higher grade samples from the mantle wedge overlying subduction zones, to assess hydrogen, carbon, and other elemental fluxes and reservoirs related to peridotite alteration.

7. ***Peridotite alteration produces some of the steepest oxygen fugacity gradients on Earth.*** We will analyze fluid samples in specific borehole intervals for fO_2 and dissolved, reduced carbon and sulphur species, and combine these data with observations of mineral parageneses. Previous research indicates that we will find native, metallic FeNi in some partially hydrated peridotites, whereas other samples will have fully hydrated iron in hematite (Fe_2O_3) and/or iron oxy-hydroxides such as goethite ($Fe(OH)_3$), but the spatial proximity of oxidized and reduced zones, and its relationship to permeable fracture horizons, has never been characterized. Fe oxidation is thought to be the cause of volume expansion during chemical weathering, leading to fracture (e.g., Fletcher et al 2006). In the broader context of the ODP and the Rock-Driven Life NASA Astrobiology Institute, steep fO_2 gradients provide a source of energy for chemosynthetic organisms, and FeNi alloys are catalysts for abiotic hydrocarbon generation.

3 Overview of proposed research

We plan geological field work, fluid sampling and geophysical logs in boreholes, chemical and structural analyses of core samples, geochemical analyses of fluids, laboratory experiments, and numerical modeling, in an interconnected program. This will be a truly dialectical process, in which observations are not only used to design and validate models, but in which model results are used to guide observations and experimental design. Comparison of model results with observations will reveal instances in which data have been subtly misinterpreted, inadvertently filtered for "relevance", or overlooked. We seek and value such moments of recognition, which lead to new insights. Furthermore, field measurements of multi-scale fracture, vein and permeability structure in rock samples and boreholes will be used to design laboratory experiments. We will apply the results of observations and experiments to models at multiple scales. In turn, model results can be tested against observations of the spatial and temporal extent of peridotite alteration, of mineral parageneses, etc. Discrepancies between model results and observations will guide second and third phases of field work and experiments. Where is an alteration zone that is robustly predicted in models, but has not been observed? Why are observed parageneses in lab versus numerical experiments different?

3.1 Field Work

3.1.1 Crack observations in outcrop

Ongoing fieldwork in the Samail ophiolite will continue, with a special focus of cracks and veins. Because of the presence of an active ground water system replenished by 10 to 30 cm of rainfall per year, and the desert environment with very little vegetation, previous studies have documented the presence of exceptionally well-exposed examples of ongoing peridotite alteration (e.g., Clark & Fontes 1990, Kelemen et al 2011, Kelemen & Matter 2008, Neal & Stanger 1985), including dozens of alkaline springs produced by active mineral hydration and carbonation, and abundant carbonate veins in outcrop with ^{14}C "ages" generally < 50,000 years. As noted in the Background section, the general features of the active alteration process – such as spring water chemistry – are very similar in other exposed mantle peridotites worldwide.

Fig. 4: Outcrop of carbonate vein network in partially serpentinized mantle peridotite in Oman. Hammer for scale.

Our field observations will focus on quantifying size/frequency, spacing/frequency and petrologically constrained conditions of formation of crack/vein networks on a variety of scales. These data will quantify the controls on permeability and fluid flow. Because of the excellent exposure, we can document the major crack/vein networks over meter to kilometer scales. We will take measurements of crack density within a 1 m^2 grid at multiple locations. The fracture/vein length of every visible feature will be measured, to gain insight into cm scale cracking processes. Rock/vein samples will also be collected for thin section analyses of cracks on the microscale (Section 3.2). These field observations provide a 3D context to evaluate the scale of variability and the extent to which borehole observations can be extrapolated to a large rock volume.

3.1.2 Borehole observations

We will make observations in 250 to 600 m boreholes drilled during the Oman Drilling Project, as well as existing 200 to 400 meter wells maintained by the Omani Ministry of Water Resources. Only the upper 10 to 20 meters of each water-monitoring well are cased, and we plan a similar geometry for the new boreholes, permitting geophysical logs and other experiments requiring clear access to wall rocks. Wireline diamond drill holes with outside diameters of ~ 3 to 4 inches (76 to 97 mm) will be used to obtain core and for some logging and water sampling. Nearby rotary holes with outside diameters of 6 inches will permit use of logging tools with larger diameters, plus hole-to-hole permeability and tracer experiments. The new boreholes will be preferred sites for research, in most cases, because we will have core from the same or adjacent holes. In this proposal, we request funds to complete one diamond drill hole and one rotary hole. For the proposed research, we will have access to the 6 new holes for active peridotite alteration, the new hole from hanging wall peridotite into underlying metasediment, and the new hole in the crust-mantle transition zone of the ophiolite.

Preliminary logs (Fig. 5) and our recent sampling show that these holes intersect interfaces between ground water reactants (low pH) and characteristic Ca-OH-rich, carbon-poor alkaline waters (~ pH 12) formed via peridotite hydration and carbonation. Thus, we infer that the old and new boreholes reach into the active "reaction zone".

Geophysical wireline logging: Down-hole geophysical wireline logs will be recorded to obtain continuous records of a full suite of in situ physical and chemical properties of wall rocks and formation fluids. This program is described in detail in the 2014 ICDP Oman Drilling Project proposal, Section 5.1. We expect 80 to 100% core recovery, allowing detailed correlation of core and geophysical properties. For example, we will measure vertical, multi-scale variation of permeability, vein and crack density and aperture, differential stress, fluid composition and temperature. To complement permeability measurements on core, vertical heat-pulse flowmeter and impeller flowmeter logs will identify permeable zones, first at static conditions to discern ambient flow and then while pumping or injecting water into the borehole to locate zones of active inflow or outflow (Matter et al 2006, Molz et al 1994, Morin et al 1988).

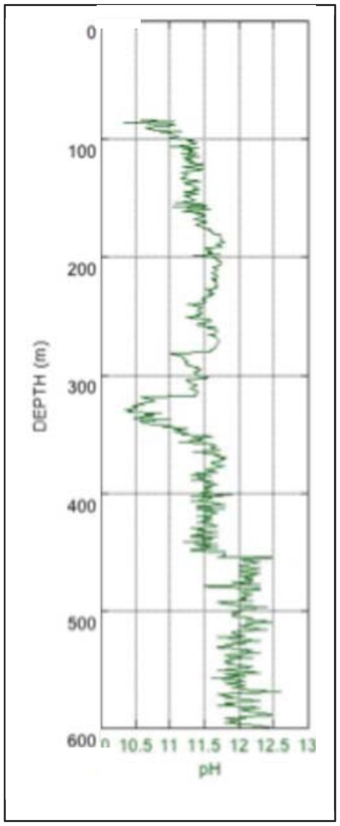


Fig. 5*: pH log from a monitoring well in actively altering peridotite (drilled by the Oman Ministry of Water Resources) showing stratified water compositions and abrupt excursions to lower pH where fractures carrying surface water intersect the borehole. Because so much hydrogen was produced from this well, it was cemented closed*

To determine fracture density and orientation we will obtain borehole televiewer logs using a slimhole instrument from Robertson Geologging to collect continuous, oriented, 360° views of the borehole walls. In combination with the flowmeter logs, televiewer logs will be used to identify fractures and cracks that contribute to fluid flow and connectivity between boreholes. Furthermore, we will use a continuous multi-sensor "water quality" probe from Robertson Geologging to measure pH, electrical conductivity, dissolved oxygen, pressure, and temperature. These logs will provide critical data regarding stratification of fluid properties as a function of depth, and help identify zones of mineral hydration and carbonation.

We are in the process of purchasing two water quality probes and a gas tight water sampler together with wireline gear with funding for the Oman Drilling Project from the Sloan Foundation, which we will use extensively in water monitoring wells during January 2015 to refine our choice of active alteration drill sites. Much of the more extensive logging will be conducted with slimline equipment from the Borehole Geophysics Group at the University of Montpellier, France, with funding from ICDP and other sources.

Borehole tests: To quantify fracture connectivity and formation permeability and storativity, conventional aquifer pumping tests using a straddle packer system will be performed. We will isolate conductive zones identified with flow meter and televiewer logs.

In addition, single hole push-pull tracer tests will be conducted in zones isolated by packers in rotary-drilled boreholes to quantify solute transport (advection, dispersion), and effective porosity (e.g., Istok et al 1997). A known volume of experimental water that contains low-level of tracers (e.g. bromide, sulfur hexafluoride) will be injected in the isolated target interval over a short period of time (a few hours, "push-phase"). The injected solution will be left in the isolated interval for some time (weeks to months) to disperse and mix with the aquifer water. After the incubation period, water will be pumped out in the same well ("pull-phase") and samples collected. Analyses of tracer concentrations in the retrieved fluid samples will be used to develop breakthrough curves and determine how fast groundwater moves away from the injection zone, as well as mixing rates, dispersivity, effective porosity and mixing rates between the injected solution and the ambient groundwater (e.g., Gelhar & Collins 1971, Hall et al 1991).

We will also perform reactive push-pull tests to study reactive transport processes, for example dissolution of carbonates and *in situ* CO_2 mineralization (e.g., Assayag et al 2009, Istok et al 1997, Yang et al 2014a). For studying mass transfer of carbon, we will inject aqueous fluids enriched in dissolved CO_2 in addition to conservative tracers. Water stored in a container at the surface will be dynamically equilibrated with CO_2 at the surface using a Liqui-cel membrane contactor from Liquicel. After the addition of tracers, a high-pressure membrane pump will be used to inject the mixture into a previously tested isolated low-permeability zone of the aquifer. During the injection the tracer/CO_2 ratios will be kept constant. We will use CO_2 that is isotopically (^{13}C, ^{14}C) distinct from the ambient carbon in the system. Changes in the tracer/CO_2 ratios and the isotopic composition of the CO_2 in the pull phase will allow us to quantify the *in-situ* dissolution and precipitation of minerals. As predicted by Paukert et al. (2012b), we expect to find that *in situ* mineral carbonation along the flow path from meteoric water to hyperalkaline groundwater is limited by the amount of CO_2 dissolved in the infiltrating meteoric water. By adding CO_2 we will determine *in situ* mineral carbonation rates by measuring the change in the dissolved carbon concentration between the “push” and “pull” phase.

3.1.3 Downhole seismology

We will conduct a novel downhole seismic experiment to detect and localize microearthquakes generated by reaction-driven cracking in two boreholes, which will allow us to constrain the rate and location of active alteration-related cracking in the vicinity of the boreholes. The utility of using small-aperture seismic networks to image reaction-driven cracking was recently demonstrated by Pontbriand and Sohn (2014), who observed high rates of microcracking events associated with anhydrite deposition beneath the active TAG hydrothermal mound on the Mid-Atlantic Ridge (26°N). The size, location, and rate of the events constrain the volume and location of the minerals being deposited in the subsurface, which are key parameters that are otherwise very difficult to constrain. Seismic monitoring provides the only in situ means to detect and study microcracking events generated by reaction-driven cracking, and thus provides an important complement to outcrop and laboratory studies of fluid and rock samples.

We will deploy a 12-element borehole seismic cable developed by the Engineering Seismology Group (ESG) for a period of one week in each of two boreholes located in zones of active peridotite alteration. The elements will consist of one force balance accelerometer (0.7-1000 Hz), one 4.5 Hz geophone (4.5 – 300 Hz), and ten 15 Hz geophones (15 – 1000 Hz) distributed across the vertical length of the borehole. Sensors deployed at depths that are cased will use magnetic couplings while those deployed at uncased depths will use bowsprings to ensure the sensors are properly coupled to the borehole walls. Continuous 32-bit data will be recorded at 4 kHz for each channel (each sensor has 3 orthogonal channels, for 36 total). ESG personnel will oversee installation and recovery of the cable from the boreholes, as well as data acquisition, as part of the equipment rental agreement.

The 36-channel data will be screened for microearthquakes by eye and by using Long-Term Average/Short-Term Average algorithms. The detectability of microcracking events depends primarily on their size and distance from the borehole. We expect to be able to detect M_L -1 events at distances of up to several hundred meters from the borehole. The relationship between event size (moment/magnitude) and the length-scale of crack/vein depends on the stress drop. The maximum amplitude of the stress drop is limited by the crystallization pressure, which in peridotite alteration reactions may be as high as 100 MPa (Kelemen and Hirth, 2012) – roughly the same stress drop as observed in laboratory salt weathering experiments (Steiger, 2005). Under these conditions ML -1 events can be generated by cracks/veins with length scales of ~ 1 m. Assuming that we can detect events of this size within a 400 x 400 x 400 m volume around the borehole, then by upscaling the fracture densities observed at the outcrop scale (Kelemen and Matter, 2008; Kelemen et al. 2011) we estimate there to be ~19 x 10^8 1 x 1 m veins within this volume. At steady-state conditions, assuming the average ^{14}C age of carbonate veins of 25,000 years is the average age of the corresponding fracture event, this corresponds to > 200 events/day, indicating that a borehole seismic network has the potential to constrain the spatial pattern and actual frequency of cracking events near the borehole. This is a novel pilot experiment; stress drops could be lower and/or cracking rates could be highly variable in time and space. Other than the seafloor observations of Pontbriand and Sohn (2014), we are not aware of similar work. We consider this aspect of the proposed research to be high risk, high reward.

3.1.4 Fluid and gas sampling and analysis

Our ongoing sampling of springs and surface water in Oman will continue as needed to supplement existing data and provide context for borehole observations. Fluid sampling in boreholes will be conducted using straddle packers to isolate a specific depth interval in the borehole and – after some time – to sample fluids present in the rocks surrounding that depth interval. Extensive, repeated collection of samples will capture changes due to active peridotite alteration. Alkalinity, electrical conductivity, pH, temperature, redox potential will be measured on site, together with spectro analysis for dissolved oxygen, ammonia, nitrate, sulfide, silica and phosphate.

Fluid and dissolved gas samples will be shipped to Columbia, Arizona State and Southampton for further analysis. The concentration of major ions (Na, K, Mg, Ca, Si, Cl, SO_4^{2-}, NO_3^-) will be analyzed by ion chromatography and ICP-AES at Columbia (supervised by Matter), and trace elements (Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, U, Sr, Rb, Zn etc.) by ICP-MS using the NIST standards (Columbia, Matter). Noble gases and tritium will be analyzed by mass spectrometry (Columbia, Matter, Stute). Dissolved gas concentrations (mainly H_2, CH_4) will be analyzed at Arizona State (supervised by Shock) by FID and RCP gas chromatography. These analyses will include light alkanes such as ethane, ethane and propane. Shock's lab will provide data for organic acid anions to account for all of the rock-driven reduction during serpentinization. Strontium isotope analyses of fluids will be measured at the University of Southampton (supervised by collaborator Damon Teagle, see support letter). Stable isotopes of carbon, oxygen and deuterium will be measured at the University of Southampton (supervised by Matter).

3.2 Analyses of core and other rock samples

For the Oman Drilling Project, including this proposed study, core description following IODP protocols, will be conducted onboard the IODP drill ship, R/V Joides Resolution (JR) in port (support letter from Jay Miller, IODP TAMU). Other than the R/V Chikyu, the JR hosts the best core description lab in the world. This will result in a complete, consistent description of ~ 6 km of core obtained during the Oman Drilling Project, of which more than half will be altered peridotite. Obviously, we cannot make detailed analyses of all this core in our proposed NSF study, but comprehensive shipboard observations will facilitate informed selection of representative and end-member samples, and provide context for our more detailed work.

A total of ~ 30 shipboard scientists, including a large cohort of Omani and US-based graduate students, will live and eat onboard the ship, and we will conduct 24-hour observations, assisted by IODP technicians, as for sea-going operations. We hope reviewers note that all of the core description results for peridotite holes will be relevant to the proposed project, but will be conducted by a science party of 30, mostly supported by other sources. This is one of many examples of the synergy between our proposed NSF research and the overall Oman Drilling Project. Separate teams will systematically record igneous mineralogy and textures, alteration parageneses, structural features, paleomagnetic data, and physical properties. Particularly valuable for our proposed research will be detailed logs of crack and vein spacing, thickness, orientation, cross-cutting relationships, and mineralogy. Geochemical analyses of selected samples during core description will involve ICP-OES whole rock analyses, plus analyses of H_2O, total carbon as CO_2, and other volatiles.

Additional analyses will be performed in the US and UK in this proposed study, on core and other rock samples collected in Oman including: 1) ICP-OES and XRD, 2) total carbon, total inorganic carbon, total organic carbon, and $\delta^{13}C$, 3) SEM and TEM, 4) ICP-MS, and 5) optical petrography, performed by the team described in this proposal. Use of thin sections for optical petrography, electron microprobe analyses, SEM and TEM analyses will take place mainly at Columbia and the joint Columbia – American Museum of Natural History labs (supervised by Kelemen) and Brown (supervised by Hirth). Strontium isotope analyses of rock samples and mineral separates will be measured at the University of Southampton (supervised by collaborator Damon Teagle, see support letter). Stable isotopes of carbon, oxygen and deuterium will be measured for some samples at the University of Southampton (supervised by Matter). Stable isotopes and non-random clumping of ^{13}C and ^{18}O will be measured on other samples at UCLA (supervised by Manning and collaborator Ed Young; see support letter).

Microstructural Analyses of Cracking and Alteration: Optical petrography, SEM and TEM, and micro X-ray computed tomography (CT) scanning, plus pore volume and specific surface area determined using the BET technique (supervised by Alissa Park, see support letter), will provide essential information on the spacing and width of veins and open porosity, the crucial microstructure surrounding crack tips, and the past and present pore structure of vein-filling materials. Imbibition experiments (Akin et al 2000, Schembre & Kovscek 2003, Sharma et al 2012) in the CT scanner at AMNH (supervised by collaborator Ebel; see support letter) will complement a variety of permeability measurement techniques to identify the spatial distribution of microporosity and nanoporosity accessible to hydrous fluids by capillary flow.

In addition to standard petrographic observations of mineral parageneses and textures, we will quantitatively measure cm- to 10μm-scale vein and crack distributions to complement larger scale measurements on outcrops and during core description. Qualitative experience, and preliminary, quantitative studies including micro CT on a few samples, indicate that altered peridotites, microscopic vein spacing is ~ 10 to 100 microns, substantially smaller than the original crystal size (commonly 1 to 10 mm) in the protolith. Vein widths are variable, some are less than 1 micron. Veins often contain micron scale porosity as well as mineral assemblages. Our density measurements, combined with SEM, TEM and X-ray tomography, have also demonstrated the presence of nano-scale porosity within the serpentine mineral structure. We will produce robust, nanometer to 100 meter size-width-frequency relationships that to evaluate proposed, engineered cracking methods, and as input for numerical modeling of alteration.

Reaction Extent, equilibrium: Whole rock compositions will be used to assess the extent and nature of fluid-rock mass transfer, via comparison of less altered protoliths and more altered products. As noted above and below, these data combined with fluid compositions and geochemical modeling will allow us to evaluate the full extent of mass and volume change during alteration, and – via interpretation of the relative mobility of different chemical species – to make inferences about the conditions (temperature, pH, etc) of the processes involved. Optical petrography and XRD data yield first order information on the solid mineral reactants and products involved in alteration, which can then be used as constraints on temperature and fluid composition (e.g., Falk & Kelemen 2014, Kelemen et al 2011, Streit et al 2012a).

Both laser microbeam and bulk rock ICP-MS trace element analyses will take place at Columbia, as will powder X-ray diffraction (XRD) and density measurements (supervised by Matter & Kelemen). Electron microprobe and laser ICP-MS measurements will used to evaluate the extent of chemical exchange equilibrium between different phases, for geothermometry where equilibrium was approached, and – using mineral and whole rock compositions – to constrain mineral proportions and reaction progress.

Stable carbon and oxygen isotope ratios, and $^{87}Sr/^{86}Sr$ in whole rocks, minerals and fluids will be measured at Southampton (supervised by Matter and collaborating scientist Teagle; see supporting letter). Clumped isotopologues will be analyzed at UCLA under the supervision of Manning. Stable carbon and oxygen isotope data for carbonate and silicate minerals will be used to evaluate the extent of isotope exchange equilibrium, together data on fluids for fluid-mineral oxygen isotope exchange thermometry, and together with $^{87}Sr/^{86}Sr$ measurements to constrain likely sources of carbon, oxygen and Sr in fluids participating in alteration (e.g., Falk & Kelemen 2014, Kelemen et al 2011, Streit et al 2012a).

Thermometry, relative age: We've found surprisingly good agreement between clumped isotope thermometry, conventional stable isotope thermometry (with assumptions about subsurface fluid compositions) and thermodynamic calculations on the pressure, temperature and fluid composition where observed mineral parageneses are stable (Falk & Kelemen 2014, Streit et al 2012a). For the thermodynamic calculations, we've been using Thermocalc (Holland & Powell 1998), with a simple interface and internally consistent data for a range of minerals. We will use all of these techniques, to check for mutual agreement and thus for the extent (or not) of equilibrium in the three systems.

The abundance of the rare isotopologue $^{13}C^{18}O^{16}O$ relative to other CO_2 isotopic species in calcite, dolomite and magnesite is temperature dependent, and is the basis for "clumped isotope" thermometers that only require analysis of a single mineral. This is ideal for our work on Cretaceous and Tertiary carbonation systems in Oman, for which metamorphic fluid compositions are not known, and for sorting out the temperatures – and thus ages – of superimposed alteration events in drill core. Streit et al. (2012a) used clumped isotope thermometry on products of low temperature mineral carbonation in Oman, where temperatures are independently known from conventional stable isotope partitioning and ULT mineral parageneses. All three techniques yielded mutually consistent temperature estimates from 20 to 60°C. Work on Cretaceous listvenites (fully carbonated peridotite composed of magnesite + quartz + Fe oxides and hydroxides) in the mantle section of the ophiolite, just above the basal thrust and underlying metasediments, show that CO_2 in carbonate minerals records formation temperatures of ~ 80-120°C, whereas soapstones elsewhere in the ophiolite record peridotite carbonation at ~ 250°C (Falk

2013, Falk & Kelemen 2014). In the proposed project, we will continue to perform such analyses in the stable isotope lab at UCLA, with supervision from PI Manning and collaborator Ed Young (support letter).

Geochronology: It is essential but difficult to delineate the ages of cross-cutting vein assemblages and superimposed alteration assemblages in rock samples and drill core. We will continue to send selected carbonate vein and water samples to the accelerator mass spectrometry facility at Woods Hole Oceanographic Institution for ^{14}C geochronology. So far, data suggest that a significant proportion of veins form near the surface, and are exposed and eroded on a ~ 25,000 year time scale, in a near-steady state. Where possible, we will also continue to use Rb/Sr isochrons for geochronology (supervised by Teagle). As mentioned above, we expect to resume use of short-lived Uranium decay series isotopes for geochronology with Prof. Ken Sims, under separate funding.

Note that geothermometry provides information on the equilibration temperatures in rocks, even for Ultra Low Temperature (ULT) metamorphism, but in Oman also provides information on the relative age of different alteration features. High temperature features formed near the paleo-spreading-ridge axis during formation of the ophiolite. Moderate temperature features near the basal thrust formed during 96-80 Ma emplacement of the ophiolite via subduction of metasediments. Laterites on some unconformities formed during late Cretaceous weathering. Additional features near these unconformities formed during Paleocene-Miocene burial beneath shallow carbonates. Low temperature assemblages, often associated with carbonates containing appreciable ^{14}C, continue to form via active, low temperature alteration today.

Geochemical modeling: Though useful for phase equilibrium calculations, Thermocalc provides inadequate information on dissolved fluid species. We have also been modeling fluid-rock reaction paths using EQ3/6 (Wolery & Jarek 2003) and the TOUGH2-TOUGHREACT software (Pruess 1991), which predict dissolved fluid species in detail and allow automated reaction path modeling (in 2D and 3D in the case of the TOUGH2 software). Manning and Shock will supervise EQ3/6 and TOUGH2 modeling, for which considerable care must be taken in choosing thermodynamic data that are accurate and suitable for the PT and composition range of interest. Shock's research group is assessing thermodynamic data for iron oxy-hydroxides, and incorporating these data in SUPCRT92 (Johnson et al 1992) and CHNOSZ (Dick 2008) codes, as well as the EQ3/6 package for reaction path modeling of serpentinization. In the present study they will evaluate data for Fe-bearing serpentinization products (Fe-brucite, Fe-chrysotile, etc.) and incorporate these data in the theoretical models.

More generally, geochemical modeling, aimed at reproducing observed mineral and fluid compositions, will be of great importance in assessing the extent of mass transfer – particularly export of solutes – during peridotite alteration. As noted at several points in this proposal, the extent of solid volume change depends on how much dissolution and export of components occurs during addition of H_2O and CO_2 via mineral hydration and carbonation. In turn, the extent of solid volume change is an important control on the negative ("clogging") and positive ("cracking") feedbacks that limit or accelerate alteration.

3.3 Rock Mechanics Experiments

3.3.1 Mechanical tests on natural rock

Mechanical tests on hydrated and carbonated peridotite will provide input on mechanical strength for numerical modeling, quantify the physical state of the rock at conditions where alteration reactions initiate, and constrain the role of pre-existing "high-temperature" alteration and crack topology on the tensile strength of the protolith prior to low temperature alteration. Deformation experiments on peridotite core samples will be conducted using the Paterson apparatus at Brown University (supervised by Hirth). Core samples from 10 to 15 mm in diameter will be deformed in deviatoric tension by servo-controlling the axial load ($\sigma3$) while increasing confining pressure ($\sigma1$) under controlled pore-fluid pressure. The axial load will be held constant, by retracting the axial piston, while confining pressure is increased. These tests are quite straightforward and, though they are not true tensile strength tests, they provide mechanical data that can be used to constrain tensile strength using standard approaches (e.g., Paterson & Wong 2005). Furthermore, they will provide mechanical data at the stress conditions in the near-surface environment in Oman, requiring little or no extrapolation. For comparison and calibration, tensile strengths will also be measured directly using standard techniques and apparatus that are available for our use free of charge in the Central Mechanical Testing Facility of the Division of Engineering at Brown University.

3.3.2 Experimental investigation of reactive cracking

As noted Section 1, the conditions controlling reaction-driven cracking are poorly understood, especially at geologically relevant confining pressures. To investigate feedbacks between reaction and cracking we propose a suite of experiments on peridotite. Experiments will include both fairly unaltered samples from the Josephine and Trinity peridotites, as well as more weathered samples from the Oman drill core. We expect that the weathered Oman samples may provide more microcracks to drive reaction rates.

Simple analog systems: Previous experiments on analog systems provide insight into the kind of crystallization pressures and fractures that are attainable. For example, “expanding mortar”, is a commercially available material composed mainly CaO (e.g., Huynh & Laefer 2009). Dry powder is mixed with water and poured into an open borehole (Figure 6). Despite a slight volume decrease when $Ca(OH)_2$ is produced, demolition mortar expands to form a solid network with about 50% air-filled porosity (Kelemen et al 2013c). The expansion creates stresses on the borehole wall and fractures the host rock, even though the slurry is not confined at the top. Remarkably, the mortar is strong enough to maintain ~ 50% porosity while fracturing rock.

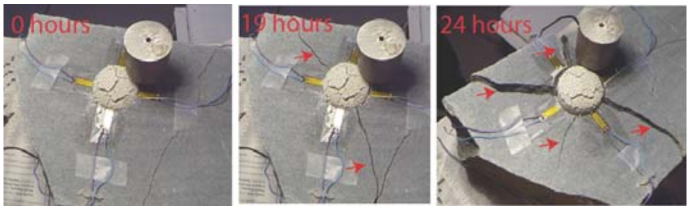


Fig. 6. *Expanding mortar experiment in a block of fresh diabase. After 19 hours, the first cracks are visible. New cracks continue to form in the following hours despite the presence of new free surface available created by the fracture of the rock.*

Preliminary crystallization pressure measurements: Building on the expanding mortar experiments, we began benchtop experiments on crystallization pressures during CaO hydration. We cold-pressed CaO powder to form cylinders with porosity ranging from 0.36 to 0.53. These were confined in steel, and compressed with an axial load of 0.1 to 4 MPa while water was introduced through a micro-porous frit. In all experiments the volume of cylinders increased, maintaining porosity > 20%. Experiments were stopped at reaction extents from 82-100%; all would probably reach 100% at longer durations. The pressure of crystallization for reaction (1) is then > 4 MPa. Experiments with higher loads are underway. These experiments will reveal the range of crystallization pressures resulting from CaO hydration CaO as well as the effect of pressure on reaction rate, and will facilitate design of triaxial experiments.

Fig. 7*: Design used to measure crystallization pressure during hydration of cold pressed CaO. A CaO cylinder is placed in a steel container. Constant pressure is applied on the top of the sample, and displacement of the piston with time is measured.*

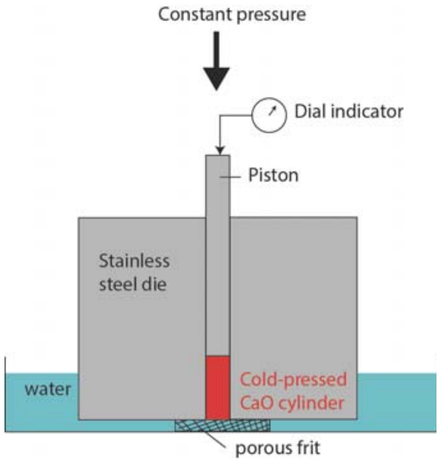
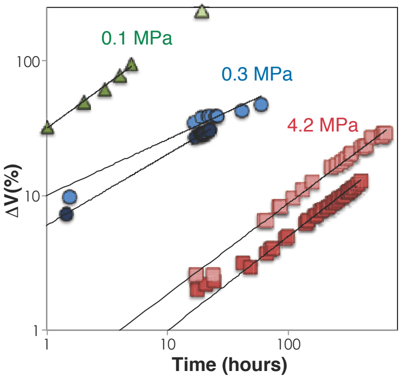


Fig. 8*: ΔV [=($V_{initial}$-V_{final})/V_{inital}*100] versus time. The evolution of ΔV is best fit by a power law. The reaction slows over time, either because of a reduction of permeability or consumption of the reactant. Because all experiments show the same slope despite increasing porosity during the reaction (from 37 to 62%), we prefer the latter explanation.*



Reaction driven cracking in a flow-through, open system*:* In the rock mechanics lab at Lamont, postdoc Sarah Lambart – supervised by Savage and Kelemen – will conduct experiments on unaltered peridotite, altered peridotite from Oman drill core, and crushed, cold-pressed aggregates of these samples. We will map geologically relevant combinations of confining pressure, temperature, volume change and fluid composition required for reaction-driven cracking in these systems.

Using a triaxial press with ports for fluid input and output, we will react H_2O or CO_2 with a peridotite cylinder embedded in inert, porous cylinders of Berea sandstone. In order to test the configuration of these experiments, we performed a benchtop experiment with a CaO cylinder embedded in a sandstone hollow cylinder, with water introduced via a porous frit at the bottom of the sample. Once we put the assemblage in water, the hollow cylinder broke in less than 5 minutes! This experiment demonstrates that reaction-driven cracking occurs in experiments with this geometry and we will be able to study fractures formed in the rheologically well-characterized sandstone around the peridotite cylinder.

We will investigate a range of conditions (20-400°C, 10-100 MPa confining pressure, 5-50 MPa pore pressure, 1-10 MPa axial load, variable P_{CO2} with pH buffered at ~ 6 using $NaHCO_3$) to map the limits of the reaction-driven cracking process. Cracking during experiments will be monitored using strain gauges and piezoelectric transducers (PZTs) attached to the sample, to record volumetric strain and acoustic emissions (AEs), respectively. AE number and location will be measured using up to 16 PZTs will be run through a 40 dB preamplifier and sampled at a rate of 10 MHz per channel.

As described above, some previous experiments with a similar geometry failed to produce fractures. Most used sintered olivine-rich aggregates (Andreani et al 2009, Godard et al 2013, Lisabeth et al 2013), and we hypothesize that nucleation sites for crystallization in the smallest pores (defects, brucite, …) were baked out during sample preparation. More troublingly, unconfined cubes of partially serpentinized natural peridotite with 6-8% initial porosity (Hövelmann et al 2012) underwent decreasing permeability and, despite ~ 10% conversion of olivine to carbonate, did not fracture.

Thus, in some of our experiments, crystallization may create an increasingly impermeable barrier. If clogging due to crystallization in pore space becomes a problem, we will use pairs of fluid reagents, for example with different pH, that are undersaturated in solid phases, but saturated when the two mix or interact chemically (e.g., Tartakovsky et al 2008), in which two fluid flow paths are separated by a tabular porous and polycrystalline matrix. Strain gauges epoxied along the length of the sample will provide information about the location of the reaction front. We can also run experiments with variable fluid pressure between the two flow paths in order to drive advective flow of one or the other fluid across the intervening porous material. Mixing may be maintained across the barrier, simultaneously with ongoing crystallization, via localized dissolution channels (e.g., Aharonov et al 1995, Hammer et al 2008, Kelemen et al 1995, Spiegelman et al 2001).

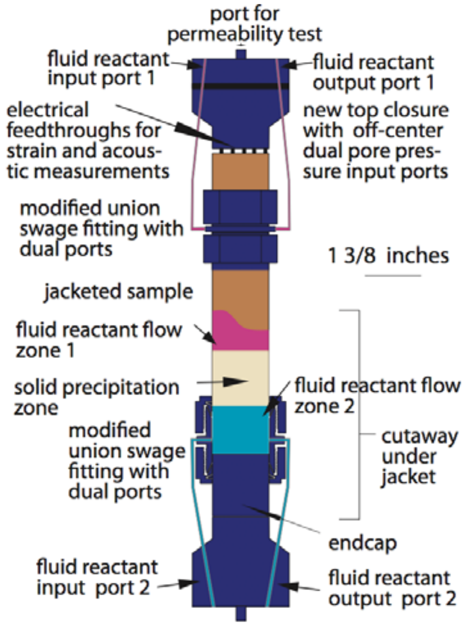


Fig. 9: Sample configuration for triaxial deformation apparatus at Lamont, modified to introduce two parallel flow paths across the cylindrical, porous polycrystalline sample.

We will run these experiments in a triaxial apparatus with independently servo-controlled axial, confining and fluid pressures. Axial load will be applied by a hydraulic ram at the end of the sample column, and measured by a load cell between the piston and the sample column. The apparatus is capable of confining pressures to 1 GPa, maintained by Argon gas. Pore fluid pressure is controlled by two servo-controlled, high-pressure piston cylinders connected to the top and bottom of the sample and attached to fluid reservoirs. This system has been used in many previous experiments (Karner & Schreiber 1993, Marone et al 1988, Scholz & Koczynski 1979, Scholz et al 1995). To run the parallel flow experiments, we will modify standard union swage fittings with additional ports for pore fluid input and output, to create two separate flow paths perpendicular to the long axis of the sample.

Sample cylinders will be 8.9 cm in length and 3.5 cm in diameter. Before adding water or CO_2, we will run permeability tests using argon with an imposed pressure oscillation. Permeability can be calculated from the phase lag and amplitude decay of pore pressure at the outlet (deMartin et al 2006, Fischer & Paterson 1992). Permeability during runs can be estimated once fluid begins to flow with a pressure transducer at the outlet and also, once top and bottom pressure equilibrate, with the oscillation technique.

We will periodically sample aliquots of the fluid effluent, and make chemical analyses of the input fluid and effluents using the Lamont ICP-MS facility, to constrain net gains and losses due to both crystallization and precipitation within the sample. At the end of the experiments, samples will be removed from the pressure vessel within their jackets. On some samples, we will perform micro X-ray computed tomography (micro CT) at the AMNH. This method will provide a 3D representation of resulting mineral precipitation patterns, porosity, and fracture networks (e.g., Derluyn et al 2013). Samples will be scanned at 18 microns/voxel edge. Some samples will also be infused with epoxy, cut into thin sections and examined by SEM and EDX to establish the reaction profile. Combined with microstructural analyses described below, these observations will reveal the length scale of the fracture network.

3.3.3 Physical properties and microstructural analysis of experimental and natural samples:

As noted above, we will measure permeability of natural and experimental samples in the course of rock mechanics experiments in the triaxial deformation apparatus at Lamont. These will be supplemented with measurements of density, porosity, surface area, permeability and capillary flow. In addition, imbibition experiments observed via micro-CT at AMNH, following the procedure outlined by Kovscek and co-workers (Akin et al 2000, Schembre & Kovscek 2003, Sharma et al 2012), will image the spatial distribution of capillary flow in natural and experimental samples.

Optical, TEM and SEM microscopy will be used to quantify microstructural and permeability evolution due to crystallization in pore space and reaction-driven cracking. We will characterize (a) evolution of reactive surface area with progressive alteration, (b) the size, spacing and aspect ratio of cracks and pores that which control permeability and capillary flow, (c) the shape and size of crystals growing in pore space, and (d) the porosity and spatial distribution of pore-size in vein filling material (which, for example, may control fluid availability at crack tips). Quantification of porosity/crack topology will constrain the stress states (though analysis of crack orientation) and fracture toughness (which depends on the magnitude of porosity and the aspect ratio of pores and cracks (Paterson & Wong 2005)) of the aggregates, to improve theoretical treatments of the cracking process and scaling of results in space and time.

Microstructural analyses can also be used to measure grain size and distribution in protoliths and reaction products in lab experiments, to investigate nucleation and growth kinetics, as well as provide a microstructural basis for extrapolating experimental results to natural systems. The microstructures of natural samples of partially and completely serpentinized and carbonated peridotite will be examined in the same way. We will compare crack density and reaction progress in natural samples with the temporal evolution of these characteristics in experimental samples.

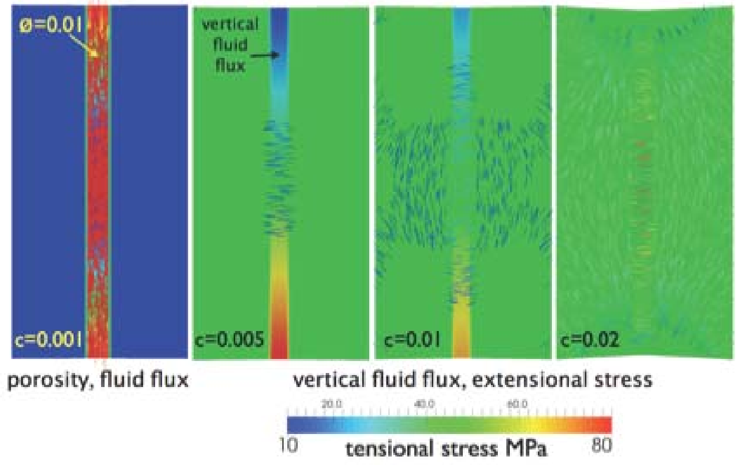
Recent advances in microscopy facilitate such analyses. In multi-phase materials, ion milling (the standard technique for preparing TEM samples) can lead to thinning at material interfaces, and alter the shapes of pores and cracks. Application of FIB (Focused Ion Beam) to prepare SEM and TEM samples will greatly mitigate these problems. A dual beam FIB is installed at the Brown University Microscopy Center. The "dual beam" in this case is a field emission SEM, making it possible to prepare surfaces for high resolution characterization (including chemical analysis). These types of characterization are gaining influence in unconventional oil and gas industry – such as microstructural analyses of oil shale (e.g., Ambrose et al 2010), as well as in the analysis of brittle micromechanics in fault rocks (e.g., Brantut et al 2008, den Hartog et al 2013, Picazo et al 2013). FIB analyses at Brown will be supervised by Hirth.

3.3.4 Numerical modeling

This project will provide a wealth of both experimental and field observational constraints on peridotite carbonation and hydration reactions and the mechanics of “reactive cracking.” To make the most of these observations requires a quantitative modeling framework for integrating observations to make improved inferences about the dynamics of these processes from grain to plate-boundary scales. Fundamental questions we would like to address include the rates and efficiency of peridotite alteration in lab and natural settings, the dynamics of reactive flow in brittle materials, whether these processes can be accelerated to provide viable means of carbon capture and/or storage, and how shallow processes of hydration and carbonation affect volatile transport in a variety of tectonic settings, e.g. subduction zones.

The challenge is to develop efficient, understandable models that are sufficiently “realistic” for the output to be usefully compared to experiments and multi-scale data on natural fluids and rocks. A minimal set of features includes relevant hydration and carbonation reactions that can produce large volume changes, fluid transport bringing reactants in and solutes out, consistent solid deformation, and a tractable computational approximation to cracking. Our team of researchers, each specializing in a suite of relevant computational tools, will work together to develop and explore such models. We have already made progress on a range of models including: **Finite Element (FEM)** continuum models that include both coupled reactive flow in poro-elastic media (Eichenbaum-Pikser et al 2013) (Figure 10a) as well as plate scale models for fluid flow in subduction zones (Wilson et al 2014), **Discrete Element (DEM)** models (Ulven et al 2014a, Ulven et al 2014b): (Figure 10b) with discrete cracks and simplified diffusive fluid transport, and **coupled DEM and GPU-enabled Lattice-Boltzmann Model (LBM)** for grain/pore scale modeling of coupled cracking and reaction (Sun et al 2013c).

The key technical issue is to combine the strength of each method into a more flexible modeling framework that can address the coupled interactions of fluids and brittle peridotite at a range of scales. Specific issues include adding more realistic reactions and discrete cracking to the FEM models, improved fluid-flow and reactions in DEM's for micro-scale modeling, and developing multi-scale techniques to integrate between the pore/lab/field and large scales. Fortunately, our team brings considerable expertise in all of the relevant areas. Wilson and Spiegelman have developed a general FEM modeling framework, TerraFERMA (Wilson & Spiegelman 2013). Together with WaiChing Sun (Civil Engineering Columbia) they are currently implementing techniques from Radovitsky et al. (2011) that use discontinuous Galerkin elements to include discrete failure on element edges to approximate cracks (Figure 11a), and adding capillary flow. Sun also has expertise in both Lattice-Boltzmann techniques that simulate pore-scale fluid flow, and multi-scale modeling methods for integrating micro-scale models in continuum models (Figure 11b,c). In addition to collaboration with Spiegelman and Wilson, Sun will work with Ole Ivar Ulven – a post-doc in Oslo working with Anders Malthe-Sorensen and Bjørn Jamtveit, who will visit LDEO frequently (see support letter) – to improve the fluid-flow calculations in Ulven's DEM-LBM reaction-driven cracking models (Figure 10b).



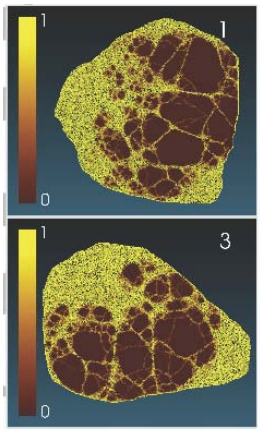


Figure 10: Examples of model results simulating fluid flow in reactive brittle materials. (a) FEM based poro-elastic model for fully coupled reactive Darcy flow and solid stress (Eichenbaum-Pikser et al 2013). (b) DEM model with diffusive fluid flow (Ulven et al 2014a, Ulven et al 2014b).

Given the complexity of these coupled problems, we feel it is useful to approach them with complementary methods. Comparison of results from different methods is extremely useful in determining which features are robust, as well as identifying any systematic numerical biases. Wherever possible, we will construct and publish benchmark problems for these systems. As our understanding improves we will consider developing hybrid multiscale codes. All TerraFERMA enhancements and new models will be released as open-source code.

Using this broad range of computational tools we will investigate a series of problems listed here. (1) Directly model the experiments to validate the computational models and interpret chemical and physical evolution of these reactive systems under controlled circumstances. In doing so, we will work closely with Manning and Shock to parameterize simple but sufficiently realistic thermodynamic models of serpentinization and carbonation with multi-component fluids. (2) Use the models to interpolate between and extrapolate beyond the experiments to map the P-T-X conditions for clogging vs cracking vs constant volume replacement, with a particular focus on understanding the role of confining pressure on rates and structures of crack generation (e.g. Figure 7). (3) Explore models in an attempt to reproduce and understand key observations such as the geometry of carbonate veins, potential crack-growth history and degree/efficiency of serpentinization observed in experiments, outcrops and core (e.g. Figures 3,4). (4)

Extrapolate these results to longer time scales than experiments, and longer length scales than boreholes and outcrops, to understand the implications of alteration processes on global geodynamics, particularly the transport and cycling of volatiles in subduction zones.

This modeling will provide the core of the PhD thesis of Owen Evans, whose primary advisor is Spiegelman in Applied Math. Evans will be also work with Sun, and with Wilson who is the primary developer, designer of the open-source modeling framework TerraFERMA. Wilson will also incorporate new features of these models into TerraFERMA for use by the general community.

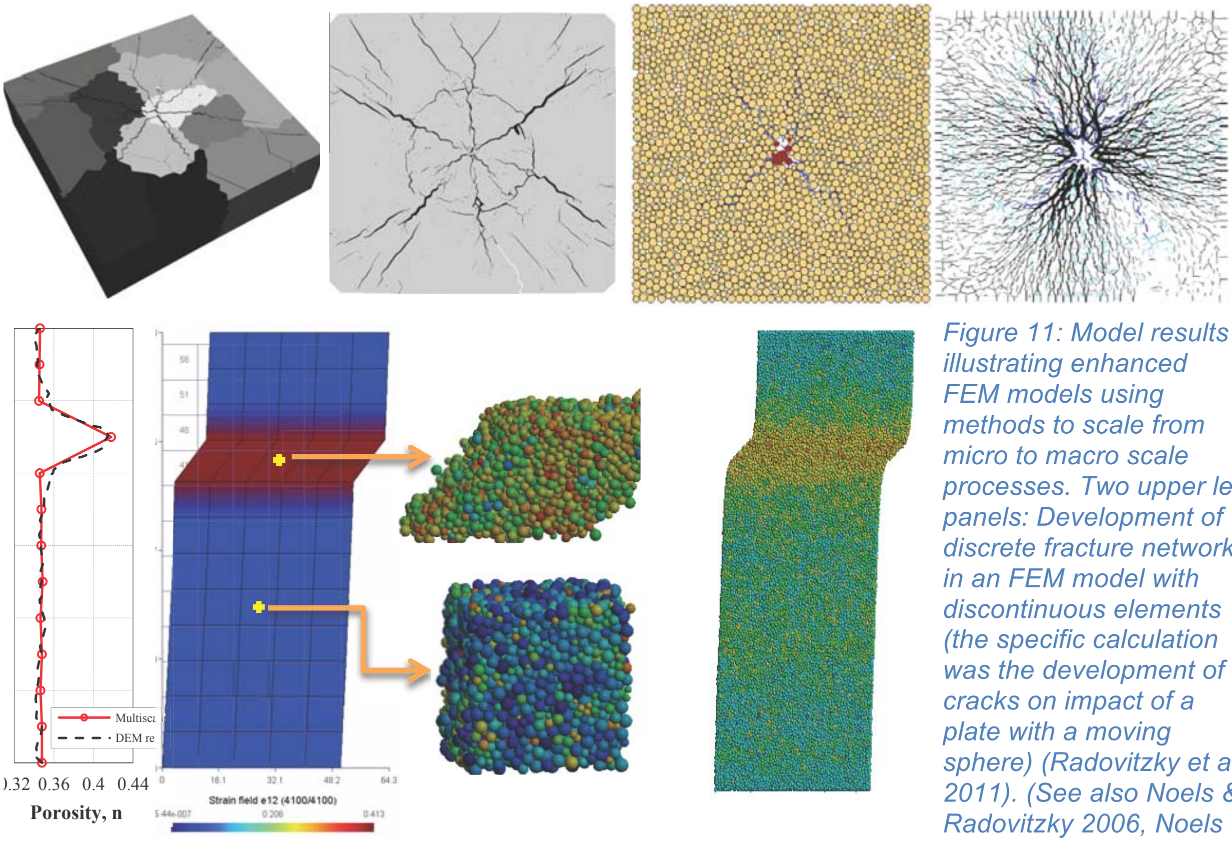


Figure 11: Model results illustrating enhanced FEM models using methods to scale from micro to macro scale processes. Two upper left panels: Development of discrete fracture network in an FEM model with discontinuous elements (the specific calculation was the development of cracks on impact of a plate with a moving sphere) (Radovitzky et al 2011). (See also Noels & Radovitzky 2006, Noels & Radovitzky 2008). Two upper right panels, DEM of simulated hydraulic-driven cracks and force chains from preliminary study by Sun. Lower panels: Comparison between DEM-FEM responses (left) and the pure DEM counterpart (right) from a pilot study (Sun et al 2013c) using micro-scale DEM modeling to upscale mechanical properties for use in macro-scale FEM models.

4 Relevance to Integrated Earth System Program Goals

Why such a big, interdisciplinary team?: Characterizing the interplay between fluid flow, reaction, and fracture during alteration is in its infancy, and requires expert input from specialists in rock mechanics (Hirth, Savage), geology and petrology (Kelemen, Manning), experimental petrology (Lambart, Manning), aqueous geochemistry (Manning, Shock), hydrology (Matter, Stute), and numerical modeling (Sun, Spiegelman, Wilson). As outlined in supporting letters, collaborators will provide additional expertise in isotope geochemistry (Teagle, Young), biogeoscience (Schrenk, Templeton), seafloor alteration (Bernasconi-Green), planetary science (Ehlmann), chemical engineering (Park) and micro CT imaging (Ebel). As it dovetails with the Oman Drilling Project, this project will involve participation from even more disciplines. Future work will include more biogeoscience, and electro-magnetic imaging to test methods for remote mapping of contrasting aquifer composition.

Coupling of dynamic processes across temporal and/or spatial scales: Our research will develop an integrated understanding of peridotite alteration coupled across space and time, addressing linkages among mantle, terrestrial, marine and atmospheric systems. We will address self-organization within and between these components of the whole Earth system, and the rates and mechanisms of the dynamic peridotite alteration system, involving essential feedbacks between interrelated chemical, mechanical and biological processes that interact on a variety of scales. Our project and the Oman Drilling Project will form the nucleus for a broad range of individual, investigator driven science funded through GEO's core research programs, capitalizing on ongoing, major NSF investment in ICDP.

Transcending the core programs of the Geosciences Directorate**:** We have assembled a scientific team that spans the boundaries of traditional disciplines supported by the Geoscience Directorate, to address fundamental questions about peridotite alteration, with profound implications for plate boundary rheology and geodynamics, global geochemical cycles, and the origin and evolution of life, using a diverse array of tools from traditional studies of applied math, mineral physics, metamorphic petrology, critical zone weathering, and chemical engineeering, among others.

5 Broader Impacts

Practical training of graduate students: In addition to our own graduate student participation in the laboratory research and borehole sampling described in this proposal, we have been planning much more extensive involvement of Omani graduate students in core description during the Oman Drilling Project (see the successful 2014 ICDP Oman Drilling proposal online). When we incorporated partial funding for this plan into a previous NSF FESD proposal, to our surprise, some reviewers objected to the focus on Omani students. Thus, in this proposal we are requesting funding for 10 Omani *and 10 US-based* graduate students (5+5 in year 1, 5+5 in year 3) to take part in core description as part of the science party onboard the Inregrated Ocean Drilling Program (IODP) R/V Joides Resolution while it is in port in years 1 and 3. These students will have an exceptional opportunity to learn core description techniques in the 2nd best lab in the world (the best is on IODP R/V Chikyu), working shoulder to shoulder with some of the best and most experienced core describers in the world. We will invite applications from graduate students. Successful applicants will be chosen by the PI's on this proposal, in consultation with the Project Steering Committee of the Oman Drilling Project, and particularly our collaborator Professor Sobhi Nasir at Sultan Qaboos University (support letter).

Dissemination of results: We will publish our data and results in peer-reviewed, international journals in a timely fashion, and make our data freely available on electronic databases as described in the data management plan (below). Continuing our current practice, we will make public presentations and publish general interest articles describing our research and its relevance to important societal issues. We will make annual reports available on a website, which we have already established.

Education of US-based graduate students and postdocs: We will contribute to the professional development of two postdocs (one of whom is a woman) at Columbia and four graduate students (Columbia, UCLA, ASU) through their involvement with this project.

Outreach to school-age children in the NY metropolitan area: Lamont Doherty Earth Observatory is currently involved in working with local K-12 schools to provide on-site tours and lab demonstrations for children at a variety of educational levels. Outreach personnel at Lamont are working with K-12 teachers to develop demonstrations that are in line with the Common Core Curriculum. The Rock Mechanics Lab at Lamont will be one of the labs involved in these tours. The work proposed here can easily be incorporated into the demonstrations, especially because of its relevance to carbon sequestration.

Emulating natural systems in geo-engineering: Recent research demonstrates that in engineered systems, peridotite mineral carbonation rates could be fast enough for significant CO_2 storage in solid carbonates, and for practical CO_2 capture from surface water (reviews: Kelemen et al. 2011 and in the Oman Mineral Carbonation Workshop Report online). The main obstacle to large scale testing and implementation is a lack of understanding of reaction-driven cracking, which we will address in the proposed research. Further, we have come to realize that engineered reaction driven cracking methods could be applied to enhanced geothermal systems, in situ mining, and extraction of unconventional hydrocarbon resources such as shale gas and coal bed methane. Study of natural peridotite alteration processes has been and continues to be an inspiration and guide to designing such engineered systems. Because it introduces all participants to unfamiliar, new ways of approaching shared problems, interaction between scientists engaged in these disparate but fundamentally similar endeavors creates fertile opportunities for breakthroughs in both basic and applied science.

Collaborative proposal: Alteration of mantle peridotite: Geochemical fluxes and dynamics of far from equilibrium transport

Results of prior support

Peter Kelemen: NSF EAR 1049905, $300,203, 3/11 to 2/14, now in no-cost extension, “Petrologic Study of Peridotite Carbonation in Oman: Temperature, Timing and Fluid Composition”, P.B. Kelemen sole PI.

Intellectual Merit: We are developing constraints on the temperature, pressure, fluid composition, timing, rates and physical mechanisms of natural peridotite carbonation, with a focus on field studies in Oman, and continuing our theoretical investigations of “reaction driven cracking” during mineral hydration, carbonation and oxidation. Three main settings for peridotite carbonation are represented in Oman: (1) Ongoing weathering, at 20 to 50°C and low pressure, producing Mg-rich carbonate veins in serpentinized peridotite, and alkaline springs that deposit travertine (Ca-carbonate) terraces. (2) Tertiary formation of extensive carbonate veins and clastic dikes in serpentinized peridotite beneath an unconformity, overlain by Eocene-Miocene limestone, at ~ 50 to 100°C. (3) Cretaceous formation of listvenites, in which peridotite was completely replaced by Mg-carbonate + quartz (± chromian mica ± relict chrome spinel) via reaction with C-rich fluids in the hanging wall of the subduction zone that emplaced the Samail ophiolite over carbonate-bearing metasediments at > 100°C. This third setting represents an unexpected, unexplored, potentially large reservoir in the global carbon cycle. Thermodynamic calculations and analysis of fracture patterns in rock samples indicates that the “pressure of crystallization” in peridotite carbonation and hydration reaches 100’s of MPa, sufficient to fracture rocks. **Broader Impacts:** ***Graduate education***: This project supported grad students Lisa Streit Falk and Amelia Paukert, Kelemen’s field work, and Kelemen’s role in advising Streit, Paukert, and grad student Jake Eichenbaum-Pikser. All data collected are available from peer-reviewed international journals (see below). ***Community contributions***: This grant supported report preparation on the 2011 Workshop on Carbonation of Mafic and Ultramafic Rocks, in Oman (Godard et al. 2011). $10k of supplementary funding for this grant, plus funds from ICDP and the Sloan Foundation’s Deep Carbon Observatory, supported attendees of the 2012 Oman Drilling Workshop in Palisades NY (reports from both workshops at this link; also see Kelemen, EOS 2013; Kelemen et al. Scientific Drilling 2013). ***Communication to peers**:* Kelemen gave more than 20 talks in 2011-14 on research supported by this grant at profession meetings and university colloquia. **Publications on research supported in part by this grant:** (Falk & Kelemen 2014, Gadikota et al 2014, Kelemen & Hirth 2012, Kelemen & Manning 2014, Kelemen et al 2011, Kelemen et al 2013b, Kelemen et al 2013c, Mervine et al 2013, Paukert et al 2012b, Peucker-Ehrenbrink et al 2012, Power et al 2013, Rioux et al 2012, Rioux et al 2013, Streit et al 2012a). **Reports on workshops supported in part by this grant:** (Godard et al 2011, Kelemen 2013b). **Abstracts of presentations on research supported in part by this grant:** (Ehlmann et al 2011, Ehlmann et al 2012a, Ehlmann et al 2012b, Eichenbaum-Pikser et al 2013, Falk & Kelemen 2013, Kelemen 2012, Kelemen 2013a, Kelemen & Hirth 2011a, Kelemen & Hirth 2011b, Kelemen et al 2013a, Lisabeth et al 2013, Matter et al 2011b, Matter et al 2012b, Mervine et al 2012, Paukert et al 2013a, Paukert et al 2011, Paukert et al 2012a, Paukert et al 2013b, Streit et al 2012b, Templeton et al 2013, VanTongeren & Kelemen 2013).

Greg Hirth: NSF, OCE-1049582, $363,600, 12/10-8/14, “Experimental Constraints on the Rheology and Seismicity of Subducting Lithosphere and the Slab-Wedge Interface”, with David Goldsby.

Intellectual Merit: We conducted experiments on serpentinites and fine-grained olivine aggregates at high pressure and temperature in a Griggs apparatus (Brown University) and using high-velocity friction rigs at Brown and INGV. We (1) determined the strength and mode of deformation of serpentinites (Chernak & Hirth 2010) (2) Studied feedbacks between reaction progress and rheology during dehydration of serpentinites to constrain conditions where reaction induced seismicity may occur (Chernak & Hirth 2010, Chernak & Hirth 2011, Proctor & Hirth 2014); (3) Explored high velocity frictional behavior of serpentinite and its evolution during reaction (Kohli et al 2011, Proctor et al 2014) and (4) Provided integrative analyses of these problems (Hirth & Guillot 2013). **Broader Impacts:** The results provide constraints for a wide range of scientists with interests in metamorphism, geodynamics, seismology, the physics of earthquakes, and fluid transport, crossing the boundaries between the new GEOPRISMS initiatives and Earth sciences in general. These projects formed the basis for parts of Ph.D. (Linda Chernak and Brooks Proctor) and undergraduate theses at Brown University (Arjun Kohli).

Craig Manning: NSF EAR-0711411, $309,100, 06/01/07–05/31/10, "Experimental investigation of non-traditional stable isotope fractionation in geological materials", PIs ED Young, CE Manning, EA Schauble

***Intellectual Merit*:** This project resulted in experimental calibrations of equilibrium Fe isotope fractionation between magnetite and fayalite, Mg isotope fractionation between spinel and forsterite, Ni isotope fractionation between nickel metal and nickel talc (silicate), and Si isotope fractionation between Si dissolved in iron metal and Si in silicate melt. The results are described in four papers: (Lazar et al 2012, Macris et al 2013, Shahar et al 2008, Shahar et al 2009). In addition, the experimental results have been corroborated by studies of Si isotope fractionation between metal and silicate in an enstatite meteorite, and of Fe and Mg inter-mineral fractionation in Earth's mantle (Macris et al 2014a, Macris et al 2014b, Young et al 2009, Ziegler et al 2010). ***Broader impacts*:** Three PhD theses were supported by the grant (former PhD students Shahar, Macris, and Lazar). The project resulted in fundamental data on the exchange of non-traditional stable isotopes. These data were provided via publication to the geochemical and cosmochemical communities for use in conducting thermobarometry on natural samples, and in understanding the crystal chemical controls on stable isotope partitioning.

Juerg M. Matter: Matter has had no prior support from NSF. Matter is the Columbia University lead PI on two major U.S. Department of Energy funded projects (ongoing): **Big Sky Carbon Sequestration Partnership, G131-12-W3521, $1,486,000**; and the **CarbFix project "Radiocarbon as a reactive tracer for tracking permanent CO_2 storage in basaltic rocks", U.S. DOE DE-FE00004847, $1,442,585**.

Intellectual Merit: We are developing ways to engineer in situ mineral carbonation of injected industrial CO_2 in basaltic rocks. We are also developing advanced geochemical monitoring, verification and accounting techniques for geologic CO_2 sequestration that are tested at CO_2 injection sites in deep aquifers in Montana (sedimentary basin) and in Iceland (basalt). The advanced monitoring techniques involve the active labeling of the injected industrial CO_2 with low levels of radiocarbon (^{14}C) as a reactive tracer in combination with the injection of non-reactive tracers. These tracers are used to directly monitor the dynamics and reactivity of the injected CO_2 and mobile formation fluids in deep geologic storage reservoirs. Measurements of their concentrations and changes in their ratios in retrieved fluid samples can be used to quantitatively characterize physical and geochemical processes at field scale. **Broader Impacts: Graduate education:** The CarbFix project has supported graduate students Diana Fernandez de la Reguera's and Jennifer Hall's MSci research. The Big Sky project supports part of Qiang Yang's postdoctoral research. The development of advanced monitoring techniques resulted in a new invention and an international patent application (M09-090/103237-102). **Communication to peers:** Matter gave more than 15 talks in 2012-2014 on research supported by these grants at profession meetings at university seminar and colloquia. Papers supported in part by these grants: (Aradóttir et al 2011, Gislason et al 2010, Matter et al 2011a, Matter et al 2014, Sigfusson et al 2014). **Abstracts of presentations on research support in part by this grant:** (Aradóttir et al 2011, Fernandez de la Reguera et al 2010, Gislason et al 2013, Matter et al 2012a, Matter et al 2011c, Matter et al 2013, Stute et al 2013).

Heather Savage: EAR-12-19488, 03/2012-04/2014 *"Investigating the Thermal Maturity of Organic Matter in Fault Zones with Laboratory Experiments"*, H. Savage & P. Polissar, PI's

Intellectual Merit: The objective of this grant was to determine the kinetic reactions of organic material in sedimentary rock under conditions of rapid heating. By fine-tuning our understanding of these reactions at rapid rates, we are able to use organic thermal maturity as an earthquake indicator on faults (Savage et al 2014). This project has established that biomarkers react at short time scales and high temperatures, making them an effective earthquake paleothermometer. ***Broader Impacts:*** This project supported an undergraduate researcher working on her senior thesis, as well as the two early-career PIs. As part of this grant, the undergraduate presented her results at the 2012, 2013 AGU meetings, the SCEC annual meeting 2013, and is first author on a paper accepted to *GCA* (Sheppard et al 2014).

Everett Shock: OCE-0826588 $1,528,590; 1 Sep 2008 – 31 Aug 2013**,** ETBC: Organic Geochemical Transformations and the Deep Biosphere -- Identifying the Food Sources for Microbes in Sedimentary Systems" (PI- Shock Co-I's Gould, Hartnett, Holloway, Williams)

Intellectual Merit**:* This project has revolutionized our ability to explore the transformations of organic compounds in water at the high temperatures and pressures of geochemical processes. Adapting methods from organic chemistry to establish the mechanisms of organic transformation reactions in geochemical processes that lead to petroleum generation and the production of organic food sources for heterotrophic microbes in the deep biosphere. Developing a systematic approach to mechanistic studies for families of organic compounds and individual functional groups. Providing the first comprehensive study of decarboxylation mechanisms in aqueous solution at high pressures and temperatures (Glein et al 2014). Expanding greatly on the scope of reversible redox and hydration reactions among alkanes, alkenes, alcohols and ketones in geochemical processes (Shipp et al 2013, Yang et al 2012, Yang et al 2014c). Differentiating between reversible and irreversible reactions involved in ketone (Yang et al 2014b, Yang et al 2012, Yang et al 2014c) and hydrocarbon (Shipp et al 2013, Shipp et al 2014b) transformations. ***Broader Impacts: Rebuilding the hydrothermal experimental capabilities and establishing analytical capabilities at ASU for small organic compounds using gas and ion chromatography that are also used by other researchers. Discovering new catalysts (sphalerite) for organic reactions with implications for green chemistry. Nurturing an interdisciplinary research group of geochemists and chemists who meet weekly to discuss progress with ongoing experiments and theoretical developments. Training and mentoring of seven PhD students (Chris Glein (2012), Jessie Shipp (2013), Ziming Yang (2014), Christa Bockisch, Kris Fecteau, Kristin Johnson, Kirtland Robinson) and one postdoctoral scholar. Undergraduates involved in this project are now in graduate school at UC San Diego and Cornell. **Other publications** research reports supported in part (Amend et al 2013, Manning et al 2013, Shipp et al 2014a, Shock & Canovas 2010, Shock et al 2013, Williams et al 2011).

Rob Sohn: OCE-01-37329, $480,804, "Seismicity, structure, and fluid flow of the TAG Hydrothermal System" (Sohn, PI; S.E. Humprhis and J.P. Canales co-PI's).

Intellectual Merit: Microearthquake, exit-fluid temperature, and bottom pressure data were contemporaneously acquired at the TAG active hydrothermal mound over a 1-year period to unravel the complex interactions between hydrothermal and tectono-magmatic processes, and these geophysical data were supplemented with hydrothermal fluid and biological sampling. The project was carried out over the course of four research legs from 6/03–11/04 on the *R/V*s *Atlantis, Maurice Ewing*, and *Knorr* (twice), including six dive days with both DSRV *Alvin* and ROV *Jason II.* The results of this multi-disciplinary field program and analyses have exerted a major influence on concepts of hydrothermal circulation at TAG and the nature of oceanic detachment faulting, and the most recent work has demonstrated that anhydrite deposition in the shallow crust generates small microearthquakes that can be used to constrain mineralization and flux rates. **Broader Impacts**: Over the course of the four research expeditions we provided at-sea training for more than 15 undergraduate and graduate students from international academic institutions. The project provided the basis for two Ph.D. one Master's thesis at WHOI. Eight journal articles have resulted from this grant to date: (Canales et al 2007, Copley et al 2007, deMartin et al 2007, Pontbriand & Sohn 2014, Sohn 2007a, Sohn 2007b, Sohn et al 2009, Zhao et al 2012).

Marc Spiegelman: NSF OCE-0841079/0841075, *``Collaborative Research: Advanced models of magma migration at convergent Margins"*, 2/1/2009-1/31/2011 + no-cost extension, $276k at LDEO, $56k at UM, M Spiegelman, PI, P van Keken, Co-PI

Intellectual Merit: This project provided support for Post-doc, Cian Wilson who developed a next-generation computational modeling framework for multi-physics problems (TerraFERMA: the Transparent Finite Element Rapid Model Assembler (Wilson & Spiegelman 2013, Wilson et al 2013a)) and used it to develop advanced models of coupled fluid-solid flow in subduction zones from the slab through the wedge (Wilson et al 2014). These new models explored and quantified the hypothesis that interaction of fluid flow with the solid rheology structure could significantly change the transport paths and efficiency of fluid-migration in subduction systems. In particular, we demonstrate three different modes of fluid transport that all enhance arc-wards migration of fluids and increase the local water content to increase the degree of hydrous melting (Wilson et al 2014, Wilson et al 2013b). The first mode is significant up-slab transport of fluid within narrow dehydrating layers in the slab, the second is lateral transport along the strong upper thermal boundary layer and the third is the development of non-linear porosity waves that can locally enhance the concentration of H2O available for fluxed melting. Comparing to previous models that do not include compaction pressure effects suggests that all of these mechanisms contribute to the relatively robust location of the primary arc with respect to earthquakes in the slab. In addition to two principal papers and a significant software release, this project provided partial support for 3 other publications (Davies et al 2011, Kramer et al 2012, van Keken et al 2011). **Broader Impacts:** This project provided training for an early career scientist and entrained an outstanding computational scientist into Earth Science. It developed a computational tool that is quite general with applications that extend well beyond geodynamics. TerraFERMA can be used for general finite element modeling with an emphasis on reusable and reproducible models for non-linear coupled systems such as coupled fluid-solid flow. TerraFERMA has been used to develop the poro-elastic reactive cracking models discussed in the present proposal. The code is open source and available in a pre-alpha developers release. Upon final acceptance of the manuscript, we will provide a full v0.1 release through CIG.

Martin Stute: NSF EAR-0746273 “Collaborative Research: Acquisition of New Instrumentation for Geochemical Studies in the Earth and Environmental Sciences” -10/1/2008-9/30/2013 $1,300,000, S.L. Goldstein, PI, R.F. Anderson, C. Class, P. Schlosser, M. Stute, co-PI’s

Intellectual Merit: This grant funded the acquisition of three major pieces of instrumentation, a multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS), a single collector icpms (SC-ICPMS) for isotope ratio and element concentration analyses, a noble gas mass spectrometer (NG-MS) and gas inlet system, plus peripherals. All three instruments are installed, and the MC-ICPMS and SC-ICPMS have been in operation since early 2012. Thermo Scientific performed the final acceptance tests during the first quarter 2014. All instruments supported by this grant are now in operation. **Broader Impact:** This grant made a major contribution to upgrading the infrastructure for geochemical research at LDEO. Most members of LDEO’s geochemistry community will use one of these instruments in their research, including research scientists, postdocs, graduate, undergraduate, and high school students, as well as researchers at the American Museum of Natural History and City University of New York.

WaiChing Sun: WaiChing (Steve) Sun has not yet been a PI on an NSF Award. He works on theoretical and computational geomechanics and multiscale modeling of fully coupled multi-physical systems, with special emphasis on understanding multiphysics coupling across spatial and temporal scales. His research focuses the understanding of multiphase materials under extreme conditions and enhancing predictive capabilities for engineering applications, including carbon sequestration, hydraulic fracture and soil liquefaction. His research includes the development of concurrent mutliscale model for strain localization problem (Sun & Mota 2014), derivation and computer implementation of small strain cap-plasticity model to capture pore collapses in limestone (Sun et al 2013a) and strain localization of sand (Sun 2013), formulations of stabilized mixed-field finite element model for large deformation multiphysics problems (Sun et al 2013d), modeling and homogenization of mechanical and hydraulic properties of porous media from CT images (Sun et al 2011a, Sun et al 2011b), applications of mathematical tools, such as graph theory (Sun et al 2013b) and Lie algebra (Mota et al 2013), and combined deterministic-stochastic method (Borja & Sun 2007, Borja & Sun 2008) for estimating co-seismic deformation, and modeling hydraulic fractures via a coupled discrete element and network flow model.

Collaborative proposal: Alteration of mantle peridotite: Geochemical fluxes and dynamics of far from equilibrium transport

Management and integration plan

Prof. Peter Kelemen at Columbia University will be the Project Director, and coordinate scientific research funded by this grant. Kelemen was lead PI on the NSF-funded Talkeetna Arc Continental Dynamics project and Co-Chief Scientist on ODP Leg 209, and so has experience in organizing such an operation. Kelemen will also supervise maintenance of a project website, and timely entry of observations into online databases. Lab Assistant Karen Benedetto will manage budgets, handle travel and group meetings, curate samples, and coordinate sample distribution.

To coordinate research and timely communication of results within the group, annual meetings will be held at Lamont. Additional group meetings will be at the fall AGU conference in San Francisco.

Dissemination of results to the scientific community and the public will be the responsibility of the investigators, collaborators and other participants in the ordinary course of their professional careers.

Senior investigators	**Institution**	**Primary responsibilities**	**Main tasks**
Greg Hirth	Brown	microstructure, rheology	2,3,5,6,10
Peter Kelemen	Columbia U	coordination, petrology, feedbacks	1 through 10
Craig Manning	UCLA	phase equilibria, aqueous geochemistry	1,4,8,9,10
Jürg Matter	Columbia U	geochem, hydrology, physical prop's	1,2,3,10
Heather Savage	Columbia U	rock mechanics	5,6,9,10
Everett Shock	Arizona State	aqueous geochemistry, dissolved gases	1,2,4,8,9,10
Rob Sohn	WHOI	downhole seismometers	7,10
Marc Spiegelman	Columbia U	modeling, feedbacks	2,3,8,9,10
Martin Stute	Barnard Coll	borehole experiments	1,2,10

Tasks: 1. Downhole logging and sampling; 2. Field work; 3. Analyzing geophysical logs; 4. Petrology and geochemistry; 5. Structure, physical properties & rheology; 6. Rock mechanics experiments; 7: Seismic observations in boreholes 8. Modeling; 9. Education; 10. Synthesis: From near-surface alteration to shallow mantle processes

Ongoing tasks prior to proposed grant period, 2014-15

Fieldwork: Jan 2015; liaison with Omani Ministries for permitting drill sites; pH, conductivity, salinity, temperature, depth logging of open water monitoring wells in peridotite, continued detailed mapping of carbonate vein networks in Oman, particularly Wadi Fins (Figure 4), mapping of ICDP drill sites

Fluids and gases: January 2015, sampling water (but without packers …) from boreholes and springs. Meanwhile, analysis of 2012-13 samples at Arizona State is ongoing. Preliminary results in Figure 2.

Analyses of rocks: Prepare samples from 2012-13 (not yet processed ...) for thin sections & whole rock analyses; locate thin sections, powders, and/or rock samples from mid-ocean ridge peridotites (some already at Lamont); send samples for thin sections and ICP-OES; complete training of de Obeso and undergrad Daniel Nothaft in XRD and carbon analysis. Measure carbon concentration in selected samples - from Oman, mid-ocean ridges, mantle wedge together with standards to ensure that these measurements are accurate and precise at the levels in partially serpentinized peridotites with little or no observed carbonate (~ 500 ppm C). No stable or Sr isotope analyses are anticipated in 2014-15.

C-O and C-H isotopologues: PhD student de Obeso, working with former PhD student, now WHOI postdoc Lisa Streit Falk, will do clumped isotope thermometry on carbonates from altered peridotites in Oman in the lab of Dr. Weifu Guo at WHOI.

Analog experiments on reaction driven cracking: Underway. Preliminary results in Figs. 7-9.

Triaxial press experiments: Press modification is complete, pilot experiments are beginning.

Structural analysis: Begin measurements of crack spacing in large rock specimens (decimeter to 100 micron scale) and thin sections. We do not plan SEM and TEM imaging in 2014-15. Begin micro CT imaging of experimental and natural samples. We will continue to measure densities and imbibition rates of samples, to quantify porosity, permeability, and capillary flow. These measurements will be combined with analyses of pore volume and specific surface area using the BET technique (Quantachrome NovaWin BET Analyzer).

Numerical modeling: Underway. Preliminary results of continuum modeling, completed by Spiegelman, Wilson, and former grad student Jake Eichenbaum-Pikser are in Figure 10. Spiegelman, Wilson and Sun will begin modifying their code to specifically model triaxial press experiments in 2015-16. Norwegian postdoc Ole Ivar Ulven will visit in spring semester 2015 to begin discrete element modeling.

Annual meeting: 1st meeting at Lamont in Sept. 2015, to share early results and coordinate future work.

Tasks in year 1, 2015-16

Fieldwork: Detailed mapping and rock sampling around boreholes to be logged and sampled. Supervise drilling.

Geophysical logging: Purchase and assembly of packers and related equipment, shipment to Oman, initial logging of four to six boreholes.

Core description: Two months onboard R/V Joides Resolution in Capetown in (northern) summer.

Fluids and gases: Initial sampling during logging, later sampling in packed intervals before departure from Oman. Analysis of Jan 2016 samples at ASU, Lamont & Southampton before Dec 2016.

Analyses of rocks: Continued sample processing & shipment as described above. Initial ICP-MS trace element analyses on selected samples, chosen based on XRF data to be representative of the spectrum of variation. Continued ICP-OES, XRD, carbon analyses of bulk rocks. Electron probe analyses of minerals in thin section. Stable and Sr isotope analyses in Southampton (by Matter & Teagle) commence, on samples based on XRF data.

C-O and C-H isotopologues: Analyses will commence. We have tentatively decided to do these at UCLA for efficiency of sample distribution. Initial analyses on carbonate minerals will include interlaboratory comparison for samples previously analyzed at Caltech and WHOI. If this proves problematic, we hope to resume this work at Caltech or WHOI. Begin exploratory analyses of C-O and C-H isotopologs in Oman fluids. Experiment with methods for analysis of low concentration samples.

Mechanical tests: These will commence with samples taken near boreholes used for logging and fluid sampling. Coordination with structural measurements to ensure that representative samples are tested, and with modeling effort to inform choice of failure criteria in models.

Analog experiments: Completed during 2015-16. Prepare and submit paper.

Piston cylinder experiments: Should be well underway and possibly completed.

Triaxial press experiments: Experiments on CaO hydration in sandstone jackets. Permeability measurements on peridotite core from Oman.

Structural analysis: Continued measurements of crack spacing in core, rock specimens (decimeter to 100 micron scale), experimental run products, and thin sections. Samples for permeability measurement chosen using structural data. Train students in SEM and TEM imaging, and start work on important samples identified from optical analysis. Continue to measure densities, pore volume and specific surface area in a large group of samples, including all samples analyzed by SEM and TEM. Micro CT imaging of core and experimental samples

Numerical modeling: Central year for modeling of triaxial experiments. Continued development of idealized continuum and discrete element models, to hone our intuition about the overall process of reaction-driven cracking,.

Annual meeting: September 2016, share results, modify plans based on results to date.

year 2, 2016-17

Fieldwork: Detailed mapping and rock sampling around boreholes to be logged and sampled. Supervise drilling.

Geophysical logging: Second logging of four to six boreholes. Shipment of equipment back to US.

Borehole tests: Shipment of equipment to Oman. Initial tests in four to six boreholes.

Fluids and gases: Second, third and/or fourth sampling in time series, using packers. Analysis of all samples taken in Jan, 2017, at ASU, Lamont and Southampton before end of 2017.

Analyses of rocks: Continued sample processing as described above. Initial ICP-MS trace element analyses on selected samples, chosen based on ICP-OES data to be representative of the spectrum of variation. Continued ICP-OES, XRD, carbon analyses of bulk rocks. Electron probe analyses of minerals in thin section. Stable and Sr isotope analyses in Southampton (by Matter & Teagle) continue on selected samples, based on OCP-OES data as for trace element analyses.

C-O and C-H isotopologues: Main year for clumped C-O measurements for thermometry, focused on samples that have also been analyzed for stable isotopes in Southampton, and for non-traditional stable isotopes at UCLA. Main year for C-O and C-H isotopologs in fluid samples from Oman.

Mechanical tests: Continuing, with a wider range of samples to determine natural variability in Oman; comparative studies of samples from other environments, particularly from mid-ocean ridges.

Analog experiments: Paper preparation and submission.

Triaxial press experiments: Complete experiments on CaO, with jackets of sandstone. Initiate reaction experiments on peridotite. Prepare and submit paper(s) on CaO. Continue permeability measurements.

Structural analysis: Continued quantitative measurements of crack spacing in large rock specimens (decimeter to 100 micron scale), experimental run products, and thin sections. Extensive SEM and TEM imaging of selected samples (based on optical and geochemical data). Continue to measure densities, pore volume and specific surface in a large group of samples, including all samples analyzed by SEM, TEM, micro-CT.

Numerical modeling: Complete modeling of triaxial experiments, prepare and submit paper. Continued development of idealized continuum and DEM models. Start development of large-scale models of mid-ocean ridges, oceanic fracture zones and/or "leading edge of the mantle wedge".

Annual meeting: September 2017, share results, modify plans based on results to date.

year 3, 2017-2018

Fieldwork: Return to areas of previous field study, particularly higher temperature Cretaceous and Miocene listvenites and carbonate vein networks, to evaluate similarities and differences compared to observations in and around boreholes. Prepare and submit paper on field observations, probably combined with macro- and micro-structural data.

Geophysical logging: Data analysis, preparation and submission of paper(s).

Borehole tests: Second tests in four to six boreholes. Ship equipment back to US. Data analysis, preparation and submission of paper(s).

Downhole seismometers: Deploy & recover instruments, analyze data, prepare and submit paper.

Fluids and gases: Data analysis, preparation and submission of paper(s).

Analyses of rocks: Selection of samples based on need to complete comprehensive data set. ICP-MS trace element analyses on selected samples, chosen based on OCP-OES data to be representative of the spectrum of variation. Continued ICP-OES, XRD, carbon analyses of bulk rocks. Electron probe analyses of minerals in thin section. Stable and Sr isotope analyses in Southampton (by Matter & Teagle) continue, samples selected based on XRF data. Preparation and submission of paper(s).

C-O and C-H isotopologues: Complete C-O measurements for thermometry and analysis of C-O and C-H isotopologs in fluids, preparing comprehensive data sets. Prepare and submit paper(s).

Mechanical tests: Final tests will focus on exploring anomalies in past two years. Coordination with structural measurements to ensure that representative samples are tested, and with modeling effort to inform choice of failure criteria in models.

Triaxial press experiments: Complete experiments on peridotite. Prepare and submit paper(s).

Structural analysis: Complete measurements. Using these data, prepare and submit paper(s).

Numerical modeling: Complete development of idealized continuum and DEM models. Complete development of large-scale models of mid-ocean ridges, oceanic fracture zones and/or "leading edge of the mantle wedge". Prepare and submit papers.

Annual meeting: September 2018, share results, make plans for comprehensive overview papers.

And beyond …

Well beyond the end of the proposed grant period, we will faithfully work to complete papers on our substantive research results, in keeping with our responsibility to report our results to our peer community and the public. While we are sure that there will be "spinoff" projects, we do not anticipate proposing a 2nd large grant for this multi-disciplinary group to continue focused work in Oman.

Collaborative proposal: Alteration of mantle peridotite: Geochemical fluxes and dynamics of far from equilibrium transport

References cited in this proposal

Aharonov E, Tenthory E, Scholz CH. 1998. Precipitation sealing and diagenesis - 2. Theoretical analysis. *J. Geophys. Res.* 103: 23,969

Aharonov E, Whitehead JA, Kelemen PB, Spiegelman M. 1995. Channeling instability of upwelling melt in the mantle. *J. Geophys. Res.* 100: 20433-50

Akin S, Schembre JM, Bhat SK, Kovscek AR. 2000. Spontaneous imbibation characteristics of diatomite. *J. Petroleum Sci. Eng.* 25: 149-65

Ambrose R, Hartman R, diaz campos m, Akkutlu IY, Sondergeld C. 2010. *New pore-scale considerations for shale gas in place calculations*. Presented at SPE Unconventional Gas Conference

Amend JP, LaRowe DE, McCollom TM, Shock EL. 2013. The energetics of organic synthesis inside and outside the cell. *Phil. Trans. Roy. Soc. London B* 368: 20120255

Andreani M, Luquot L, Gouze P, Godard M, Hoisé E, Gibert B. 2009. Experimental study of carbon sequestration reactions controlled by the percolation of CO2-rich brine through peridotites. *Environ. Sci. Technol.* 43: 1226-31

Aradóttir ES, Sigurdardóttir H, Sigfussion B, Gunnlaugsson E. 2011. CarbFix: a CCS pilot project imitating and accelerating natural CO2 sequestration. *Greenhouse Gases Science and Technology* 1: 106-18

Assayag N, Matter J, Ader M, Goldberg D, Agrinier P. 2009. Water-rock interactions during a CO2 injection field-test: Implications on host rock dissolution and alteration effects. *Chemical Geology* 265: 227-35

Barnes I, O'Neil, Jr. 1969. Relationship Between Fluids in Some Fresh Alpine-Type Ultramafics and Possible Modern Serpentinization, Western United States. *Geological Society of America Bulletin* 80: 1947-&

Becker K, Davis E. 2003. New evidence for age variation and scale effects of permeabilities of young oceanic crust from borehole thermal and pressure measurements. *Earth Planet. Sci. Lett.* 210: 499-508

Borja R, Sun W. 2007. Estimating inelastic sediment deformation from local site response simulations. *Acta Geotech.* 2: 183-95

Borja R, Sun W. 2008. Coseismic sediment deformation during the 1989 Loma Prieta earthquake. *J. Geophys. Res.* 113: 10.1029/2007JB005265

Brantut N, Schubnel A, Rouzaud JN, Brunet F, Shimamoto T. 2008. High-velocity frictional properties of a clay-bearing fault gouge and implications for earthquake mechanics. *Journal of Geophysical Research-Solid Earth* 113

Bruni J, Canepa M, Chiodini G, Cioni R, Cipolli F, Longinelli A, Marini L, Ottonello G, Zuccolini MV. 2002. Irreversible water-rock mass transfer accompanying the generation of the neutral, Mg-HCO3 and high-pH, Ca-OH spring waters of the Genova province, Italy. *Applied Geochem.* 17: 455-74

Canales JP, Sohn RA, deMartin BJ. 2007. Crustal structure of the TAG segment (Mid-Atlantic Ridge, 26°10'N): Implications for the nature of hydrothermal circulation and detachment faulting at slow-spreading ridges. *G-cubed* 8: doi:1029/2007GC001629

Carmichael DM. 1986. Induced stress and secondary mass transfer: Thermodynamic basis for the tendency toward constant-volume constraint in diffusion metasomatism. In *Chemical Transport in Metasomatic Processes*, ed. HC Helgeson, pp. 237-64

Chernak LJ, Hirth G. 2010. Deformation of antigorite serpentinite at high temperature and pressure. *Earth Planet. Sci. Lett.* 296: 23-33

Chernak LJ, Hirth G. 2011. Syn-deformational antigorite dehydration produces stable fault slip. *Geology* 39: 847-50

Clark ID, Fontes JC. 1990. Paleoclimatic reconstruction in northern Oman based on carbonates from hyperalkaline groundwaters. *Quaternary Res.* 33: 320-36

Coleman RG, Keith TE. 1971. A chemical study of serpentinization, Burro Mountain, California. *J. Petrol.* 12: 311-28

Copley JTP, Jorgensen PBK, Sohn RA. 2007. Assessment of decadal-scale ecological change at a deep Mid-Atlantic hydrothermal vent and reproductive time-series in the shrimp Rimicaris exoculata. *J. Mar. Biol. Ass. U.K.* 87: 859-67

Davies DR, Wilson CR, Kramer SC. 2011. Fluidity: A fully unstructured anisotropic adaptive mesh computational modeling framework for geodynamics. *Geochemistry, Geophysics, Geosystems* 12: n/a-n/a

deMartin B, Hirth G, Evans B. 2006. Experimental constraints on thermal cracking of peridotite at oceanic spreading centers. *AGU Monograph* 148: 167-85

deMartin BJ, Sohn RA, Canales JP, Humphris SE. 2007. Kinematics and geometry of active detachment faulting beneath the TAG hydrothermal field on the Mid-Atlantic Ridge. *Geology* 35: 711-4

den Hartog SaM, Niemeijer AR, Spiers CJ. 2013. Friction on subduction megathrust faults: Beyond the illite-muscovite transition. *EARTH AND PLANETARY SCIENCE LETTERS* 373: 8-19

Derluyn H, Griffa M, Mannes D, Jerjen I, Dewanckele J, Vontobel P, Sheppard A, Derome D, Cnudde V, Lehmann E, Carmeliet J. 2013. Characterizing saline uptake and salt distributions in porous limestone with neutron radiography and X-ray micro-tomography. *Journal of Building Physics* 36: 353-74

Dick JM. 2008. Calculation of the relative metastabilities of proteins using the CHNOSZ software package. *Geochemical Transactions* 9

Ehlmann BL, Cardace D, Hoehler T, Blake D, Kelemen P. 2011. Terrestrial serpentinizing systems as mineralogical, geochemical (and biological?) analogues for Mars. *Workshop on Analogue Sites for Mars Missions: MSL and Beyond, March 5-6, 2011* Abstracts at http://www.lpi.usra.edu/meetings/analogues2011/abstracts.pdf

Ehlmann BL, Kelemen PB, Pinet P, Mustard JF, Launeau P. 2012a. Aqueous alteration of ultramafic rocks in Oman: An analog for understanding carbonates on Mars. *International Conference on the Geology of the Arabian Plate and the Oman Mountains, 7-9th January, 2012, Sultan Qaboos University, Muscat, Sultanate of Oman*

Ehlmann BL, Kelemen PB, Pinet P, Mustard JF, Launeau P, Ceuleneer G. 2012b. Aqueous alteration of ultramafic rocks in Oman: An analog for understanding carbonate and serpentine on Mars. *Lunar and Planetary Science Conference Abstract* in press

Eichenbaum-Pikser JM, Spiegelman MW, Kelemen PB, Wilson CR. 2013. A new model of reaction-driven cracking: fluid volume consumption and tensile failure during serpentinization. *Fall Meeting AGU, San Francisco CA 9-13 Dec*: MR33B-2327

Emmanuel S, Berkowitz B. 2006. Suppression and stimulation of seafloor hydrothermal convection by exothermic mineral hydration. *Earth Planet. Sci. Lett.* 243: 657-68

Espinosa-Marzal RM, Scherer GW. 2010. Mechanisms of damage by salt. *Geological Soc. London Spec. Pub.* 331: 61-77

Falk ES. 2013. *Carbonation of peridotite in the Oman ophiolite*. Columbia University, New York. 183 pp.

Falk ES, Kelemen PB. 2013. Fully carbonated peridotite (listvenite) from the Samail ophiolite, Oman. *FAll Meeting AGU* San Francisco CA 9-13 Dec: MR22A-03

Falk ES, Kelemen PB. 2014. Geochemistry and petrology of listvenite in the Oman Ophiolite: Complete carbonation of peridotite during ophiolite emplacement. *Geochim. Cosmochim. Acta* in revision

Fernandez de la Reguera D, Stute M, Matter JM. 2010. Laboratory experiments on CO2 dissolution in water for carbon sequestration. *2010 Fall Meeting, AGU San Francisco, Calif., 13-17 Dec.*: Abstract GC31C-0899

Fischer GJ, Paterson MS. 1992. Measurement of permeability and storage capacity in rocks during deformation at high temperature and pressure. In *Fault Mech. transport properties rocks*, ed. B Evans, T-F Wong, pp. 213-52. New York: Academic Press

Fletcher RC, Buss HL, Brantley SL. 2006. A spheroidal weathering model coupling porewater chemistry to soil thickness during steady-state denudation. *Earth Planet. Sci. Lett.* 244: 444-57

Fletcher RC, Merino E. 2001. Mineral growth in rocks: Kinetic-rheological models of replacement, vein formation, and syntectonic crystallization. *Geochim. Cosmochim. Acta* 65: 3733-48

Gadikota G, Matter J, Kelemen PB, Park A-HA. 2014. Chemical and morphological changes during olivine carbonation for CO2 storage in the presence of NaCl and NaHCO3. *Physical Chemistry Chemical Physics* 16: 4679-93

Gelhar LW, Collins MA. 1971. General Analysis of Longitudinal Dispersion in Nonuniform Flow. *Water Resources Research* 7: 1511-21

Gislason SR, Oelkers EH, Sigfusson B, Matter JM, Stute M, Gunnlaugsson E, Gunnarsson I, Aradottir ES, Sigurdardottir H, Mesfin K, Alfredsson HA, Wolff-Boenisch D, Arnarsson MT, Broecker WS. 2013.

Solubility and mineral storage of CO2 in basalt. *Goldschmidt Conference Abstracts*: DOI: 10.1180/minmag.2013.077.5.7

Gislason SR, Wolff-Boenisch D, Stefansson A, Oelkers E, Gunnlaugsson E, Sigurdardottir H, Sigfusson B, Broecker W, Matter J, Stute M, Axelsson G, Fridriksson T. 2010. Mineral sequestration of carbon dioxide in basalt: The CarbFix project. *Int. J. Greenhouse Gas Control* 4: 537-45

Glein C, Gould I, Lorance E, Hartnett H, Shock E. 2014. Mechanisms of decarboxylation of phenylacetic acids and their sodium salts in water and high temperature and pressure. *Geochim. Cosmochim. Acta* in press

Godard M, Kelemen PB, Nasir S, Teagle D. 2011. WORKSHOP REPORT: Geological carbon capture & storage in mafic and ultramafic rocks; IODP/ICDP Workshop on the role of oceanic and continental scientific drilling, http://ccs-oman2011.org/.

Godard M, Luquot L, Andreani M, Gouze P. 2013. Incipient hydration of mantle lithosphere at ridges: A reactive-percolation experiment. *Earth Planet. Sci. Lett.* 371-372: 92-102

Hall SH, Luttrell SP, Cronin WE. 1991. A Method for Estimating Effective Porosity and Ground-Water Velocity. *Ground Water* 29: 171-4

Hammer Ø, Dysthe DK, Lelu B, Lund H, Meakin P, Jamtveit B. 2008. Calcite precipitation instability under laminar, open-channel flow. *Geochim. Cosmochim. Acta* 72: 5009-21

Hart SR, Blusztajn J, Dick HJB, Meyer PS, Muehlenbachs K. 1999. The fingerprint of seawater circulation in a 500-meter section of ocean crust. *Geochim. Cosmochim. Acta* 63: 4059–80

Hatch FH, Wells AK, Wells MK. 1949. *The Petrology of the Igneous Rocks*. London: Thomas Murby and Co. 469 pp.

Hirth G, Guillot S. 2013. Rheology and tectonic significance of serpentinite. *Elements* 9: 107-13

Holland TJB, Powell R. 1998. An internally consistent thermodynamic data set for phases of petrological interest. *J. Metamorphic Geol.* 16: 309-43

Hövelmann J, Austrheim H, Jamtveit B. 2012. Microstructure and porosity evolution during experimental carbonation of a natural peridotite. *Chem. Geol.* 334: 254–65

Huynh M-P, Laefer DF. 2009. Expansive cements and soundless chemical demolition agents: state of technology review *11th Conference on Science and Technology, Ho Chi Minh City Vietnam, October 21-23*

Istok JD, Humphrey MD, Schroth MH, Hyman MR, O'Reilly KT. 1997. Single-Well, “Push-Pull” Test for In Situ Determination of Microbial Activities. *Ground Water* 35: 619-31

Jamtveit B, Kobchenko M, Austrheim H, Malthe-Sorenssen A, Royne A, Svensen H. 2011. Porosity evolution and crystallization-driven fragmentation during weathering of andesite. *J. Geophys. Res.* 116: B12204, doi:10.1029/2011JB008649

Johnson J, Oelkers E, Helgeson H. 1992. Supcrt92 - a Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1-Bar to 5000-Bar and 0-Degrees-C to 1000-Degrees-C. *Computers & Geosciences* 18: 899-947

Karner SL, Schreiber BC. 1993. Experimental simulation of plagioclase diagenesis at P-T conditions of 3.5 km burial depth. *Pure Appl. Geophys.* 141: 221-47

Kelemen PB. 2012. In situ mineral carbonation in peridotite for CO2 capture & storage: Prospects for Oman. *International Conference on the Geology of the Arabian Plate and the Oman Mountains, 7-9th January, 2012, Sultan Qaboos University, Muscat, Sultanate of Oman* Abstract

Kelemen PB. 2013a. Keynote: Reaction-driven cracking. *Min. Mag., Goldschmidt Conf. Abstr.* 77(5): 1444

Kelemen PB. 2013b. Planning the drilling of the Samail Ophiolite in Oman. *EOS* 94: 32

Kelemen PB, Hirth G. 2011a. Reaction-driven cracking during hydration and carbonation of olivine: Implications for in situ CO2 capture and storage (Invited). *presented at 2011 Fall Meeting, AGU, San Francisco, Calif., 5-9 Dec.*: Abstract GC51B-0968

Kelemen PB, Hirth G. 2011b. Retrograde replacement, reaction-driven cracking and rheology. *AGU Fall Meeting Abstracts* 41

Kelemen PB, Hirth G. 2012. Reaction-driven cracking during retrograde metamorphism: Olivine hydration and carbonation. *Earth Planet. Sci. Lett.* 345-348: 81–9

Kelemen PB, Hirth G, Savage HM. 2013a. Investigating Reaction-Driven Cracking. *Fall Meeting AGU* San Francisco CA 9-13 Dec: MR33B-2326

Kelemen PB, Manning CE. 2014. Re-evaluating carbon fluxes in subduction zones: What goes down, mostly comes up. *Proc. Nat. Acad. Sci.* invited, in revision

Kelemen PB, Matter J, Streit EE, Rudge JF, Curry WB, Bluztajn J. 2011. Rates and mechanisms of mineral carbonation in peridotite: Natural processes and recipes for enhanced, in situ CO2 capture and storage. *Ann. Rev. Earth Planet. Sci.* 39: 545-76

Kelemen PB, Matter JM. 2008. In situ carbonation of peridotite for CO2 storage. *Proc. Nat. Acad. Sci. USA* 105: 17,295-17,300

Kelemen PB, Rajhi AA, Godard M, Ildefonse B, Koepke J, MacLeod C, Manning C, Michibayashi K, Nasir S, Shock E, Takazawa E, Teagle D. 2013b. Scientific drilling and related research in the Samail Ophiolite, Sultanate of Oman. *Scientific Drilling J.* 15: 64-71

Kelemen PB, Savage H, Hirth G. 2013c. Reaction-driven cracking during mineral hydration, carbonation and oxidation. In *Poromechanics V: Proceedings of the Fifth Biot Conference on Poromechanics*, ed. C Hellmich, B Pichler. Reston VA: American Society of Civil Engineers

Kelemen PB, Whitehead JA, Aharonov E, Jordahl KA. 1995. Experiments on Flow Focusing in Soluble Porous-Media, with Applications. *J. Geophys. Res.* 100: 475-96

Kelley DS, Karson JA, Blackman DK, Fruh-Green GL, Butterfield DA, Lilley MD, Olson EJ, Schrenk MO, Roe KK, Lebon GT, Rivizzigno P. 2001. An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30 degrees N. *Nature* 412: 145-9

Kohli AH, Goldsby DL, Hirth G, Tullis T. 2011. Flash weakening of serpentinite at near-seismic slip rates. *J. Geophys. Res.* 116

Kramer SC, Wilson CR, Davies DR. 2012. An implicit free surface algorithm for geodynamical simulations. *Physics of the Earth and Planetary Interiors* 194-195: 25-37

Lazar C, Young ED, Manning CE. 2012. Experimental determination of equilibrium nickel isotope fractionation between metal and silicate from 500 degrees C to 950 degrees C. *Geochim. Cosmochim. Acta* 86: 276-95

Lisabeth HP, Zhu W, Kelemen PB. 2013. The Effect of CO2-Saturated Brines on the Hydraulic and Mechanical Behavior of Dunite. *Fall Meeting AGU, San Francisco CA 9-13 Dec*: MR33B-2328

MacDonald AH, Fyfe WS. 1985. Rate of serpentinization in seafloor environments. *Tectonophys.* 116: 123-35

Macris CA, Young ED, Craig M. 2014a. Crystal chemical constraints on Inter-mineral Fe isotope fractionation and implications for Fe isotope disequilibrium in San Carlos mantle xenoliths: a crystal chemical perspective. *Geochim. Cosmochim. Acta* in press

Macris CA, Young ED, Manning CE. 2013. Experimental determination of equilibrium magnesium isotope fractionation between spinel, forsterite, and magnesite from 600 to 800 degrees C. *Geochim. Cosmochim. Acta* 118: 18-32

Macris CA, Young ED, Manning CE. 2014b. Experimental determination of equilibrium magnesium isotope fractionation between spinel, forsterite, and magnesite from 600 °C to 800 °C. *Geochim. Cosmochim. Acta* 118: 18-32

Malvoisin B, Brunet F, Carlut J, Rouméjon S, Cannat M. 2012. Serpentinization of oceanic peridotites: 2. Kinetics and processes of San Carlos olivine hydrothermal alteration. *J. Geophys. Res.* 117: doi:10.1029/2011JB008842

Manning CE, Shock EL, Sverjensky DA. 2013. The Chemistry of Carbon in Aqueous Fluids at Crustal and Upper-Mantle Conditions: Experimental and Theoretical Constraints. In *Carbon in Earth*, ed. RM Hazen, AP Jones, JA Baross, pp. 109-48. Chantilly: Mineralogical Soc Amer

Marone C, Rubenstone J, Engelder T. 1988. An Experimental Study of Permeability and Fluid Chemistry in an Artificially Jointed Marble. *J. Geophys. Res.* 93: 13763-75

Martin B, Fyfe WS. 1970. Some experimental and theoretical observations on kinetics of hydration reactions with particular reference to serpentinization. *Chem. Geol.* 6: 185-202

Matter JM, Broecker W, Gislason SR, Gunnlaugsson E, Oelkers E, Stute M, Sigurdardóttir H, Stefansson A, Wolff-Boenisch D, Axelsson G, Sigfússon B. 2011a. The CarbFix Pilot Project – storing carbon dioxide in basalt. *Energy Procedia* 4: 5579-85

Matter JM, Carson C, Stute M, Broecker WS. 2012a. Reactive tracer techniques to quantitatively monitor carbon dioxide storage in geologic formations. *2012 Fall Meeting, AGU, San Francisco, Calif., 3-7 Dec.*: Abstract H44B-05

Matter JM, Kelemen PB, Mervine EM, Paukert AN, Streit E. 2011b. Geologic Carbon Dioxide Capture and Storage via Low-Temperature Carbonation of Peridotite (Invited). *presented at 2011 Fall Meeting, AGU, San Francisco, Calif., 5-9 Dec.*: Abstract GC43E-01

Matter JM, Kelemen PB, Paukert A, Mervine EM, Shock E. 2012b. Geochemical constraints on in situ mineral carbonation of mantle peridotite in the Samail Ophiolite, Oman. *International Conference on the Geology of the Arabian Plate and the Oman Mountains, 7-9th January, 2012, Sultan Qaboos University, Muscat, Sultanate of Oman* Abstract

Matter JM, Stute M, Broecker WS. 2011c. Tracking permanent CO2 storage in basaltic rocks using conservative and reactive tracers at the CarbFix injection site, Iceland. *Min. Mag., Goldschmidt Conf. Abstr.* 75(3): 1374

Matter JM, Stute M, Hall J, Mesfin K, Gislason SR, Oelkers EH, Sigfusson B, Gunnarsson I, Aradottir ES, Alfredsson HA, Gunnlaugsson E, Broecker WS. 2013. Quantification of CO2-fluid-rock reactions using reactive and non-reactive tracers. *2013 Fall Meeting, AGU, San Francisco, Calif. 9-13 Dec.* : Abstract V41A-2753

Matter JM, Stute M, Hall J, Mesfin K, Snaebjornsdottir SO, Gislason SR, Oelkers EH, Sigfusson B, Gunnarsson I, Aradottir ES, Alfredsson HA, Gunnlaugsson E, Broecker WS. 2014. Monitoring permanent CO2 storage by in situ mineral carbonation using a reactive tracer technique. *Energy Procedia* in press

Matter JM, Waber HN, Loew S, Matter A. 2006. Recharge areas and geochemical evolution of groundwater in an alluvial aquifer system in the Sultanate of Oman. *Hydrogeology Journal* 14: 203-24

McCollom TM, Sherwood Lollar B, Lacrampe-Couloume G, Seewald JS. 2010. The influence of carbon source on abiotic organic synthesis and carbon isotope fractionation under hydrothermal conditions. *Geochim. Cosmochim. Acta* 74: 2717-40

Mervine EM, Humphris SE, Sims KWW, Kelemen PB, Jenkins WJ. 2013. Carbonation rates of peridotite in the Samail Ophiolite, Sultanate of Oman constrained through 14C dating and stable isotopes. *Geochim. Cosmochim. Acta* 126: 371-97

Mervine EM, Sims KWW, Kelemen PB, Humphris SE. 2012. 14C and 230Th-238U dating of carbonates in the Samail Ophiolite, Oman: Determining timescales of natural carbon sequestration through alteration of mantle peridotite. *International Conference on the Geology of the Arabian Plate and the Oman Mountains, 7-9th January, 2012, Sultan Qaboos University, Muscat, Sultanate of Oman* Abstract

Molz F, Boman G, Young S, Waldrop W. 1994. Borehole Flowmeters - Field Application and Data-Analysis. *Journal of Hydrology* 163: 347-71

Morin R, Hess A, Paillet F. 1988. Determining the Distribution of Hydraulic Conductivity in a Fractured Limestone Aquifer by Simultaneous Injection and Geophysical Logging. *Ground Water* 26: 587-95

Mota A, Sun W, Ostien JT, Foulk JW, III, Long KN. 2013. Lie-group interpolation and variational recovery for internal variables. *Comput. Mech.* 52: 1281-99

Neal C, Stanger G. 1985. Past and present serpentinization of ultramafic rocks: An example from the Semail ophiolite nappe of northern Oman. In *The Chemistry of Weathering*, ed. JI Drewer, pp. 249-75. Holland: D. Reidel Publishing Company

Noels L, Radovitzky R. 2006. A general discontinuous Galerkin method for finite hyperelasticity. Formulation and numerical applications. *International Journal for Numerical Methods in Engineering* 68: 64-97

Noels L, Radovitzky R. 2008. An explicit discontinuous Galerkin method for non-linear solid dynamics: Formulation, parallel implementation and scalability properties. *International Journal for Numerical Methods in Engineering* 74: 1393-420

Noiriel C, Renard F, Doan M-L, Gratier J-P. 2010. Intense fracturing and fracture sealing induced by mineral growth in porous rocks. *Chem. Geol.*: 197-209

Paterson MS, Wong T-f. 2005. *Experimental rock deformation-the brittle field*: Springer

Paukert AN, Matter J, Kelemen P, Sonnenthal E. 2013a. Reactive Transport Modeling to Assess Geological CO2 Storage via Mineral Carbonation in Peridotite. *Min. Mag., Goldschmidt Conf. Abstr.* 77(5): 1935

Paukert AN, Matter JM, Kelemen PB, Shock E, Havig JR. 2011. Prospects for Enhancing In Situ CO2 Mineralization in the Peridotite Aquifer of the Samail Ophiolite. *presented at 2011 Fall Meeting, AGU, San Francisco, Calif., 5-9 Dec.*: Abstract GC51B-0959

Paukert AN, Matter JM, Kelemen PB, Shock EL, Havig JR. 2012a. CO2 capture and storage in peridotite aquifers of the Samail Ophiolite, Sultanate of Oman. *International Conference on the Geology of the Arabian Plate and the Oman Mountains, 7-9th January, 2012, Sultan Qaboos University, Muscat, Sultanate of Oman* Abstract

Paukert AN, Matter JM, Kelemen PB, Shock EL, Havig JR. 2012b. Reaction path modeling of enhanced in situ CO2 mineralization for carbon sequestration in the peridotite of the Samail Ophiolite, Sultanate of Oman. *Chem. Geol.* 330: 86-100

Paukert AN, Sonnenthal EL, Matter J, Kelemen PB. 2013b. Modeling reaction-driven cracking during mineral carbonation in peridotite for CO2 sequestration. *Fall Meeting AGU* San Francisco CA 9-13 Dec: MR22A-08

Peucker-Ehrenbrink B, Hanghoj K, Atwood T, Kelemen PB. 2012. Rhenium-osmium isotope systematics and platinum group element concentrations in oceanic crust. *Geology* 40: 199-202

Picazo S, Manatschal G, Cannat M, Andreani M. 2013. Deformation associated to exhumation of serpentinized mantle rocks in a fossil Ocean Continent Transition: The Totalp unit in SE Switzerland. *Lithos* 175: 255-71

Pontbriand CW, Sohn RA. 2014. Microearthquake evidence for reaction-driven cracking within the Trans-Atlantic Geotraverse (TAG) active hydrothermal deposit. *J. Geophys. Res.* 119: 822-39

Power IM, Harrison AL, Dipple GM, Wilson S, Kelemen PB, Hitch M, Southam G. 2013. Carbon mineralization: From natural analogues to geoengineered systems. *Rev. Min. & Geochem.* 77: 305-60

Proctor B, Hirth G. 2014. Role of pore fluid pressure on transient strength changes and fabric development during serpentine dehydration at mantle wedge conditions. *Earth Planet. Sci. Lett.* in revision

Proctor B, Mitchell TM, Hirth G, Goldsby D, Zorzi F, DiToro G. 2014. Dynamic weakening of serpentinite gouges and bare-surfaces at seismic slip rates. *J. Geophys. Res.* in press: doi:10.1002/2014JB011057

Pruess K. 1991. *TOUGH2: A general-purpose numerical simulator for multiphase fluid and heat flow. Rep. LBL-29400; Other: ON: DE92000755 United States10.2172/5212064Other: ON: DE92000755Mon May 14 08:16:59 EDT 2007OSTI; NTIS; GPO Dep.LBNL; EDB-91-145527English*

Radovitzky R, Seagraves A, Tupek M, Noels L. 2011. A scalable 3D fracture and fragmentation algorithm based on a hybrid, discontinuous Galerkin, cohesive element method. *Computer Methods in Applied Mechanics and Engineering* 200: 326-44

Rioux M, Bowring S, Kelemen P, Gordon S, Dudas F, Miller R. 2012. Rapid crustal accretion and magma assimilation in the Oman-UAE ophiolite: High precision U-Pb zircon geochronology of the gabbroic crust. *J. Geophys. Res.* 117: doi:10.1029/2012JB009273

Rioux M, Bowring S, Kelemen P, Gordon S, Miller RB, Dudas F. 2013. Tectonic development of the Samail ophiolite: High precision U-Pb zircon geochronology and Sm-Nd isotopic constraints on crustal growth and emplacement. *J. Geophys. Res.* 118: 2085-101

Røyne A, Dysthe DK. 2012. Rim formationoncrystalfacesgrowinginconfinement. *J. Crystal Growth* 346: 89-100

Savage HM, Polissar PJ, Sheppard RE, Rowe CD, Brodsky EE. 2014. Biomarkers heat up during earthquakes: New evidence of seismic slip from the rock record. *Geology* 42: 99-102

Schembre JM, Kovscek AR. 2003. A technique for measuring two-phase relative permeability in porous media via X-ray CT measurements. *J. Petroleum Sci. Eng.* 39: 159-74

Scherer GW. 2004. Stress from crystallization of salt. *Cement and Concrete Research* 34: 1613-24

Scholz CH, Koczynski TA. 1979. Dilatancy Anisotropy and the Response of Rock to Large Cyclic Loads. *J. Geophys. Res.* 84: 5525-34

Scholz CH, Lèger A, Karner SL. 1995. Experimental diagenesis: Exploratory results. *Geophys. Res. Lett.* 22: 719-22

Shahar A, Young ED, Manning CE. 2008. Equilibrium high-temperature Fe isotope fractionation between fayalite and magnetite: An experimental calibration. *Earth Planet. Sci. Lett.* 268: 330-8

Shahar A, Ziegler K, Young ED, Ricolleau A, Schauble EA, Fei YW. 2009. Experimentally determined Si isotope fractionation between silicate and Fe metal and implications for Earth's core formation. *Earth Planet. Sci. Lett.* 288: 228-34

Sharma J, Inwood SB, Kovscek AR. 2012. Experiments and analysis of multiscale viscous fingering during forced imbibition. *SPE Journal*: 1142-59

Sheppard RE, Polissar PJ, Savage HM. 2014. Organic thermal maturity as a proxy for frictional fault heating: experimental constraints on methylphenanthrene kinetics at earthquake timescales. *Geochim. Cosmochim. Acta* in press

Shervais JW, Kolesar P, Andreasen K. 2005. A field and chemical study of serpentinization, Stonyford, California: Chemical flux and mass balance. *Int. Geol. Rev.* 47: 1-23

Shipp J, Gould I, Herckes P, Shock E, Williams L, Hartnett H. 2013. Organic functional group transformations in water at elevated temperature and pressure: Reversibility, reactivity, and mechanisms. *Geochim. Cosmochim. Acta* 104: 194-209

Shipp J, Gould IR, Shock EL, Williams LB, Hartnett HE. 2014a. The effects of minerals on organic functional group transformations in experimental hydrothermal systems. *Geochim. Cosmochim. Acta* in prep.

Shipp J, Gould IR, Shock EL, Williams LB, Hartnett HE. 2014b. Sphalerite is a geochemical catalyst for carbon-hydrogen bond activation. *Proc. Nat. Acad. Sci.* 111: 11,642-11,5.

Shock E, Canovas P. 2010. The potential for abiotic organic synthesis and biosynthesis at seafloor hydrothermal systems. *Geofluids* 10: 161-92

Shock EL, Canovas P, Yang Z, Boyer G, Johnson K, Robinson K, Fecteau K, Windman T, Cox A. 2013. Thermodynamics of organic transformations in hydrothermal fluids. *Rev. Mineral. Geochem.* 76: 311-50

Sigfusson B, Gislason SR, Matter JM, Stute M, Gunnlaugsson E, Gunnarsson I, Aradottir ES, Sigurdardottir H, Mesfin K, Alfredsson HA, Wolff-Boensich D, Arnarson MT, Oelkers EH. 2014. Solving the carbon dioxide buoyancy challenge: The design and field testing of a dissolved CO2 injection system. *Int. J. Greenhouse Gas Control*

Sohn RA. 2007a. Stochastic analysis of exit-fluid temperature records from the active TAG hydrothermal mound (Mid-Atlantic Ridge, 26°N), 1. Modes of variability and implications for sub-surface flow. *J. Geophys. Res.* 112: doi:10.1029/2006JB004435

Sohn RA. 2007b. Stochastic analysis of exit-fluid temperature records from the active TAG hydrothermal mound (Mid-Atlantic Ridge, 26°N), 2. Hidden Markov Models of flow episodes, . *J. Geophys. Res.* 112: doi:10.1029/2007JB004961

Sohn RA, Thomson RE, Rabinovich AB, Mihaly SF. 2009. Bottom pressure signals at the TAG deep-sea hydrothermal field: Evidence for short-period, flow induced ground deformation. *Geophys. Res. Lett.* 36: doi:1029/2009GL040006

Spiegelman M, Kelemen PB, Aharonov E. 2001. Causes and consequences of flow organization during melt transport: The reaction infiltration instability in compactible media. *Journal of Geophysical Research-Solid Earth* 106: 2061-77

Steiger M. 2005. Crystal growth in porous materials – I: The crystallization pressure of large crystals. *J. Crystal Growth* 282: 455-69

Streit E, Kelemen P, Eiler J. 2012a. Coexisting serpentine and quartz from carbonate-bearing serpentinized peridotite in the Samail Ophiolite, Oman. *Contrib. Mineral. Petrol.* 164: 821-37

Streit E, Kelemen PB, Eiler JM, Goldstein SL. 2012b. Listvenite from the Oman Ophiolite: Complete carbonation of peridotite during hydrothermal alteration by CO2-rich fluids. *Fall Meeting AGU* San Francisco CA 3-7 Dec: V43C-2842

Stute M, J. H, Matter JM, Mesfin K, Gislason SR, Oelkers EH, Sigfusson B, Gunnlaugsson E, Gunnarsson I, Aradottir ES, Sigurdardottir H, Axelson G, Broecker WS. 2013. Tracer applications to verify carbon mineralization in Icelandic basalts. *Goldschmidt Conference Abstracts*: DOI: 10.1180/minmag.2013.077.5.19

Sun W. 2013. A unified method to predict diffuse and localized instabilities in sands. *Geomech. Geoeng.* 8: 65-75

Sun W, Andrade JE, Rudnicki JW. 2011a. Multiscale method for characterization of porous microstructures and their impact on macroscopic effective permeability. *Int. J. Numerical Meth. Eng.* 88: 1260-79

Sun W, Andrade JE, Rudnicki JW, Eichhubl P. 2011b. Connecting microstructural attributes and permeability from 3D tomographic images of in situ shear enhanced compaction bands using multiscale computations. *Geophys. Res. Lett.* 38

Sun W, Chen Q, Ostien JT. 2013a. Modeling the hydro-mechanical responses of strip and circular punch loadings on water-saturated collapsible geomaterials. *Acta Geotech.*: 1-32

Sun W, Kuhn MR, Rudnicki JW. 2013b. A multiscale DEM-LBM analysis on permeability evolutions inside a dilatant shear band. *Acta Geotech.* 8: 465-80

Sun W, Kuhn MR, Rudnicki JW. 2013c. A multiscale DEM-LBM analysis on permeability evolutions inside a dilatant shear band. *Acta Geotechnica* 8: 465-80

Sun W, Mota A. 2014. A multiscale overlapped coupling formulation for large-deformation strain localization. *Comput. Mech.* 54: 803-20

Sun W, Ostien JT, Salinger AG. 2013d. A stabilized assumed deformation gradient finite element formulation for strongly coupled poromechanical simulations at finite strain. *Int. J. Numerical Analytical Meth.* 37: 2755-88

Tartakovsky AM, Redden G, Lichtner PC, Scheibe TD, Meakin P. 2008. Mixing induced precipitation: Experimental study and multiscale numerical analysis. *Water Resources Research* 44: doi:10.1029/2006WR005725

Templeton A, Mayhew L, Miller H, Streit L, Kelemen P. 2013. Habitability and Hydrogen Generation in Perditotite Aquifers. *Min. Mag., Goldschmidt Conf. Abstr.* 77(5): 2321

Ulven OI, Jamtveit B, Malthe-Sorenssen A. 2014a. Reaction driven fracturing of porous rocks. *J. Geophys. Res.* 119: doi:10.1002/2014JB011102

Ulven OI, Storheim H, Austrheim H, Malthe-Sorenssen A. 2014b. Fracture initiation during volume increasing reactions in rocks and applications for CO2 sequestration. *Earth Planet Sci. Lett.* 389: 132-42

van Keken PE, Hacker BR, Syracuse EM, Abers GA. 2011. Subduction factory: 4. Depth-dependent flux of H2O from subducting slabs worldwide. *Journal of Geophysical Research* 116: 15-PP.

VanTongeren JA, Kelemen PB. 2013. The Composition of the Lower Crust of the Oman Ophiolite. *Min. Mag., Goldschmidt Conf. Abstr.* 77(5): 2399

Williams LB, Holloway JR, Canfield B, Glein CR, Dick JM, Hartnett HE, Shock EL. 2011. *Birth of Biomolecules from the Warm Wet Sheets of Clays Near Spreading Centers*. New York: Springer

Wilson CR, Spiegelman M. 2013. Software: TerraFERMA v0.1a --- The Transparent Finite Element Rapid Model Assembler, open-source repository: bitbucket.org:/tferma/tferma.

Wilson CR, Spiegelman M, van Keken P. 2013a. TerraFERMA: the Transparent Finite Element Rapid Model Assembler for multiphysics problems in the Earth sciences. *G-cubed* submitted

Wilson CR, Spiegelman M, van Keken PE, Hacker BR. 2014. Fluid flow in subduction zones: The role of solid rheology and compaction pressure. *Earth and Planetary Science Letters* 401: 261-74

Wilson CR, Spiegelman M, van Keken Peter E, Hacker Bradley R. 2013b. Fluid flow in subduction zones: the role of solid rheology and compaction pressure. *EARTH AND PLANETARY SCIENCE LETTERS* submitted

Wolery TW, Jarek RL. 2003. Software User’s Manual EQ3⁄6, Version 8.0. US Department of Energy, Office of Civilian Radioactive Waste Management, Office of Repository Development, Software Document Number 10813-UM-8.0-00,376.

Xu WY, Apps JA, Pruess K. 2004. Numerical simulation of CO2 disposal by mineral trapping in deep aquifers. *Applied Geochem.* 19: 917-36

Yang Q, Matter J, Stute M, Takahashi T, O'Mullan G, Umemoto K, Clauson K, Dueker ME, Zakharova N, Goddard J, Goldberg D. 2014a. Groundwater hydrogeochemistry in injection experiments simulating CO2 leakage from geological storage reservoir. *International Journal of Greenhouse Gas Control* 26: 193-203

Yang Z, Gould I, Williams LB, Shock EL. 2014b. The influence of minerals on hydrothermal reactions of ketones. *Geochim. Cosmochim. Acta* in prep.

Yang Z, Gould IR, Williams LB, Hartnett HE, Shock EL. 2012. The central role of ketones in reversible and irreversible hydrothermal organic functional group transformations. *Geochimica Et Cosmochimica Acta* 98: 48-65

Yang Z, Lorance ED, Bockisch C, Williams LB, Hartnett HE, Shock EL, Gould IR. 2014c. Hydrothermal photochemistry as a mechanistic tool in organic geochemistry: The chemistry of dibenzyl ketone. *J. Organic Chem.* 79: 7861-71

Young ED, Tonui E, Manning CE, Schauble E, Macris CA. 2009. Spinel-olivine magnesium isotope thermometry in the mantle and implications for the Mg isotopic composition of Earth. *Earth Planet. Sci. Lett.* 288: 524-33

Zhao M, Canales JP, Sohn RA. 2012. Three-dimensional seismic structure of a Mid-Atlantic Ridge segment characterized by active detachment faulting (Trans-Atlantic Geotraverse, 25°55'N-26°20'N). *G-cubed* 13: 10.1029/2012GC004454

Ziegler K, Young ED, Schauble EA, Wasson JT. 2010. Metal-silicate silicon isotope fractionation in enstatite meteorites and constraints on Earth's core formation. *Earth Planet. Sci. Lett.* 295: 487-96