

**Field observations and theoretical studies  
relevant to enhanced in situ carbonation  
of peridotite**

**Peter B. Kelemen, Jürg Matter  
& Lisa Streit**

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# Field observations and theoretical studies relevant to enhanced *in situ* carbonation of peridotite

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**ABSTRACT** – Veins formed by carbonation of peridotite in the large thrust sheet of mantle peridotite in the Sultanate of Oman are ~ 1000 times younger than previously believed, occurring mainly in a relatively shallow weathering horizon (Kelemen & Matter, 2008). Accelerating this process via drilling and rock fracture, plus heating, could provide a globally significant sink for atmospheric CO<sub>2</sub>. Exothermic carbonation of olivine can reach a self-heating condition, in which heating due to reaction balances cooling due to advection and diffusion, maintaining temperature at an optimum value for rapid carbonation, ~ 10<sup>6</sup> faster than at 25°C (Kelemen & Matter, 2008). Volume changes due to carbonation can cause fracture that in turn exposes unreacted olivine and enhances permeability. We review work on natural peridotite carbonation, including recent observations of carbonate vein mineralogy and crack geometry in peridotites, relevant to evaluating and extending these hypotheses.

## BACKGROUND

### Peridotite mineral carbonation for solid CO<sub>2</sub> storage

Tectonically exposed peridotite from the Earth's upper mantle, composed mainly of the mineral olivine, has been considered promising reactants for conversion of atmospheric CO<sub>2</sub> to solid carbonate (Lackner et al., 1995). However, engineered techniques for *ex situ* mineral carbonation are problematic. Kinetics are slow unless olivine is ground to powder, heat-treated, and held at elevated pressure and temperature (e.g., Lackner et al., 1997; Gerdemann et al., 2003). Currently, this is impractical (Mazzotti et al., 2005). It may be more practical to carbonate peridotite *in situ*, eliminating quarrying and transportation, and capitalizing on thick peridotite massifs to reduce diffusive heat loss and maintain fluid pressure. The potential sink for atmospheric CO<sub>2</sub> is enormous. In Oman, a thrust sheet of oceanic crust and upper mantle known as the "Oman ophiolite" is ~ 70,000 km<sup>3</sup> (Nicolas et al., 2000). ~ 30% of this volume is peridotite. Adding 1 wt% CO<sub>2</sub> to the peridotite would consume ¼ of all atmospheric CO<sub>2</sub>. Full carbonation of peridotite forming magnesite, dolomite and/or calcite + quartz, incorporates 30 to 40 wt% CO<sub>2</sub>. Ophiolites similar in size are in Papua New Guinea (~ 10,000 km<sup>2</sup> in outcrop), New Caledonia (~ 6000 km<sup>2</sup>) and along the east coast of the Adriatic Sea (several ~ 4000 km<sup>2</sup> massifs).

### Proposed exothermic self-heating of peridotite during hydration

Mantle peridotite is ordinarily beneath the Earth's crust, more than 6 km below the seafloor and 40 km below the land surface. It is far from equilibrium with air and water at the Earth's surface. Its exposure via thrust faults along tectonic plate boundaries creates an accessible reservoir of chemical potential energy. Fyfe (1974) proposed that exothermic hydration of olivine to form the hydrous mineral serpentine may heat peridotite. This may contribute to the heat source driving convection at the serpentine- and carbonate-rich Lost City hydrothermal vent system near the Mid-Atlantic Ridge (Kelley et al., 2001; Lowell & Rona, 2002), but this is controversial. Data suggest that Lost City fluids cooled from > 200°C, and apparent water/rock ratios are too high for substantial exothermic heating (Allen & Seyfried, 2004; Seyfried et al., 2007; Boschi et al., 2008). The high initial temperature may require a magmatic heat source at depth. Models of fluid flow suggest that exothermic heating

is important when rock temperatures are  $> 170^{\circ}\text{C}$  (Emmanuel & Berkowitz, 2006). We infer that an initial magmatic heat source could trigger the exothermic self-heating mechanism. Water/rock ratios may vary in a multi-porosity system.

#### **Proposed reaction driven cracking during peridotite hydration**

MacDonald & Fyfe (1985) proposed that increasing solid volume associated with hydration of peridotite (serpentinization) produces stresses that fracture surrounding rock, as further investigated for serpentinization (e.g., O'Hanley, 1992; Evans, 2004; Shervais et al., 2005; Iyer et al., 2008; Jamtveit et al., 2008) and granite weathering (Fletcher et al., 2006). Like the self-heating hypothesis, the reaction-driven cracking hypothesis is debatable. Mineral deposition or expansion in pore space may reduce permeability and limit hydrothermal alteration (e.g., Lowell et al., 1993; Fontaine et al., 2001), as proposed for serpentinization (Lowell & Rona, 2002; Cipolli et al., 2004). In addition, Martin & Fyfe (1970) observed decreasing reaction rates with time for olivine serpentinization at constant temperature, attributed to armouring of reactive olivine surfaces with serpentine, and Emmanuel & Berkowicz (2006) modelled this process. However, extensive outcrops of completely serpentinized and carbonated peridotite indicate that alteration is not always self-limiting.

### **GEOCHEMICAL STUDIES: REVIEW AND NEW DATA FROM OMAN**

#### **Formation of alkaline waters via peridotite hydration at low temperature**

Near-surface, relatively low temperature serpentinization is ongoing within peridotite massifs in California, Oregon, Oman, New Caledonia, Liguria and Cyprus (e.g., Barnes et al., 1967; Barnes & O'Neil, 1969; Bruni et al., 2002; Neal & Shand, 2002) and at the Lost City hydrothermal deposit on the Mid-Atlantic Ridge (e.g., Kelley et al., 2001; Früh-Green et al., 2003). Two main types of waters are found in springs arising from serpentinizing peridotite: (1)  $\text{Mg}^{2+}\text{-HCO}_3^-$  type, hereafter Type 1, with  $\text{pH} \sim 8\text{-}9$ , 40-300 ppm Mg,  $< 10$  ppm Ca and 200-1400 ppm  $\text{HCO}_3^-$  ( $\sim 150$  to 1000 ppm  $\text{CO}_2$ ), and relatively high oxygen fugacity, and (2)  $\text{Ca}^{2+}\text{-OH}^-$  type, Type 2, with  $\text{pH} > 11$ , low oxygen fugacity, 30-70 ppm Ca,  $< 10$  ppm Mg, and negligible  $\text{CO}_2$  contents. Types 1 & 2 have stable isotope ratios indicating derivation via reaction of meteoric water with hydrating peridotite at low temperature, consistent with oxygen and hydrogen isotope data on serpentinites (Wenner & Taylor, 1974) and with fluid compositions. Fluid from serpentinization at higher temperatures would have lower pH, for example (Allen & Seyfried, 2003; Palandri & Reed, 2004). Modelling (e.g., Bruni et al., 2002; Cipolli et al., 2004) reveals the role of carbonate precipitation during formation of Type 1, and transformation of Type 2 from Type 1. Bruni et al. showed that Type 1 forms via reaction with peridotite in systems open to the atmosphere, whereas Type 2 evolves to Type 1 in a closed system.

#### **Precipitation of travertine at alkaline springs**

Type 2 springs in California are associated with deposition of travertine and carbonate cemented conglomerates, because Type 2 waters combine with atmospheric  $\text{CO}_2$  to form calcite. Larger travertines are observed around alkaline springs in peridotite in Oman (e.g., Neal & Stanger, 1985; Clark & Fontes, 1990). Travertine on the surface continues beneath alluvium in the subsurface. Our reconnaissance indicates at least  $10^{11}$  kg of  $\text{CO}_2$  in travertine and carbonate cemented conglomerate in the Oman ophiolite (Kelemen & Matter, 2008).

#### **Formation of carbonate veins and carbonated peridotite, "listwanite"**

Carbonate veins in peridotite are common in ophiolites, and in altered peridotite on the seafloor. Massive carbonate veins, and completely carbonated peridotite bodies

known as listwanite or listwaenite (e.g., Naldrett, 1966; Hansen et al., 2005; Robinson et al., 2005) and metamorphosed, carbonated peridotites known as ophicalcites have been studied in detail (e.g., Trommsdorff & Evans, 1977; Jedrysek & Sachanbinski, 1994; Pozzorini & Früh-Green, 1996).

In Oman, carbonate veins in peridotite (~ 100 microns to 1 m wide) and listwanites (100's of meters wide) were thought to be 30-90 million years old, related to formation of oceanic crust, ophiolite emplacement, and/or Eocene extension (e.g., Neal & Stanger, 1985; Wilde et al., 2002; Nasir et al., 2007; Python et al., 2007). However, Clark & Fontes (1990) obtained  $^{14}\text{C}$  ages of 840-36,000 years for carbonate veins in peridotite adjacent to an actively forming travertine. Kelemen & Matter (2008) obtained an average  $^{14}\text{C}$  age of ~ 26,000 years for carbonate veins far from springs, consistent with coeval formation of sub-surface carbonate veins and surficial travertine during ongoing alteration of peridotite in Oman. Note that listwanite ages remain uncertain.

We can estimate carbonation rates assuming (a) all carbon in Type 1 waters is consumed to form magnesite ( $\text{MgCO}_3$ ), and/or dolomite ( $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$ ) during formation of Type 2, and (b) Ca in Type 2 - Type 1 is precipitated as calcite ( $\text{CaCO}_3$ ) as Type 2 waters reach the surface. In California, Type 1 has ~ 0.2 mmol Ca/liter, and up to 24 mmol carbon/liter (Barnes & O'Neil, 1969). Type 2 has essentially no carbon, and ~ 1.5 mmol Ca/liter (compilation in Kelemen & Matter, 2008). For every mole of calcite near the surface, ~  $24/(1.5-0.2)$  or 18 moles of magnesite could form in the sub-surface. Barnes & O'Neil (1969) measured flow of 3 liters/second at one spring, corresponding to consumption of ~ 2.5 gm of atmospheric  $\text{CO}_2$  per second, or ~ 57.5 tons of  $\text{CO}_2$  per year.

There is a maximum of ~ 8 mmol/l, carbon in Oman Type 1, lower than in California, while Ca concentration is ~ 0.8 mmol/liter, higher than in California. There is essentially no carbon, and ~ 1.6 mmol Ca in Type 2. If, for every mole of near surface calcite,  $8/(1.6-0.8)$  or 10 moles of magnesite are precipitated as veins, this yields ~  $10^{12}$  kg of  $\text{CO}_2$  in veins, consistent with an independent estimate from vein abundance in Oman peridotites far from alkaline springs (Kelemen & Matter, 2008). Together with the average vein age, this yields  $\text{CO}_2$  uptake in Oman via peridotite carbonation of  $4 \cdot 10^7$  kg/year. To consume  $10^9$  tons of  $\text{CO}_2/\text{yr}$ , this rate must be enhanced by a factor of ~ 25,000.

#### **Mineral assemblages in carbonate veins in Oman peridotite**

The hypotheses and observations outlined above suggest that formation of Type 1, and/or transition from Type 1 to Type 2 waters, is accompanied by precipitation of Mg-rich carbonate (magnesite, dolomite, hydro-magnesite, ...), with little or no precipitation of Ca-rich carbonate (calcite, ...). This explains the dramatic drop in Mg and carbon concentrations from Type 1 to Type 2 waters, together with the slight increase in Ca concentration. Consistent with this, X-ray diffraction and electron microprobe analyses (Streit et al., in prep.) indicate that veins far (> 1 km) from alkaline springs and travertine are dominated by magnesite and dolomite, with almost no calcite. Travertines are mainly calcite. Veins near Type 2 springs contain both Mg- and Ca-rich carbonates; these may form during mixing of Type 1 shallow ground water with ascending Type 2 water. Despite the reduced nature of Type 2 waters, sulfate minerals such as barite – rather than sulfides – in veins attest to locally high oxygen fugacity, perhaps during mixing of Type 1 and Type 2. Potassium feldspar in some samples, rather than hydrous, K-bearing minerals, suggests high  $\text{CO}_2$  fugacity for some veins.

Silicate minerals in our vein samples are mainly serpentine and relict pyroxene, with

no brucite or talc. This suggests that carbonation during vein formation was limited to reactions like olivine + fluid = serpentine + magnesite,  $4\text{Mg}_2\text{SiO}_4 + 4\text{H}_2\text{O} + 2\text{CO}_2 = 2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{MgCO}_3$ . Large listwanites in Oman (Neal & Stanger, 1985; Stanger, 1985; Wilde et al., 2002; Nasir et al., 2007) contain talc and quartz, indicating more extensive carbonation via  $4\text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} + 5\text{CO}_2 = \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  [talc] +  $5\text{MgCO}_3$ , and  $4\text{Mg}_2\text{SiO}_4 + 8\text{CO}_2 = 4\text{SiO}_2$  [quartz] +  $8\text{MgCO}_3$ . Although listwanites clearly record higher  $\text{CO}_2$  fugacity than the carbonate veins in serpentinized peridotite, the cause of this is not yet clear to us. This has obvious importance for enhancing natural peridotite carbonation *in situ*.

### **ENHANCING RATES: THERMAL MODEL RESULTS**

Kelemen & Matter (2008) used a simple 1D model of combined advection, diffusion and reaction to model thermal evolution of carbonating and serpentinizing peridotite. As in a more complex serpentinization model (Emmanuel & Berkowitz, 2006), we found that an “threshold temperature” is required for reaction rates to be fast enough to overcome cooling via advection and diffusion. However, peridotite carbonation has a lower threshold temperature than serpentinization because (1) over the temperature interval from 25 to > 200°C, olivine carbonation (Gerdemann et al., 2003) is much more rapid than serpentinization (Martin & Fyfe, 1970) at a given temperature and grain size; (2) the enthalpy change due to carbonation is about twice as large, per kg of olivine, as the enthalpy change due to serpentinization; and (3) the maximum rate for olivine carbonation is attained at, e.g., 185°C and 150 bars  $\text{CO}_2$  pressure, whereas the maximum rate for serpentinization of olivine is not attained until 260°C.

Olivine carbonation at 185°C and a few hundred bars  $\text{CO}_2$  pressure may be  $\sim 10^6$  times faster than carbonation at 25°C involving surface water in equilibrium with the atmosphere. Thus, using optimistic but not unrealistic assumptions, we predict that if a volume of peridotite is pre-heated to 185°C, it can sustain constant temperature via exothermic carbonation while pure  $\text{CO}_2$  is injected at 300 bars and 25°C at a flow rate of  $\sim 0.040$  m/s. At these conditions, our one dimensional model delivers  $\sim 0.166$  kg  $\text{CO}_2$ /s to a  $1 \times 1 \times 1000$  m<sup>3</sup> rock volume, and consumes  $\sim 0.127$  kg  $\text{CO}_2$ /s to form solid magnesite. All olivine is consumed after about 190 days, consuming  $\sim 2000$  tons  $\text{CO}_2$ /1000 m<sup>3</sup>, or – scaling up –  $2 \cdot 10^9$  tons  $\text{CO}_2$ /km<sup>3</sup> at  $\sim 4 \cdot 10^9$  tons/yr.

### **ENHANCING RATES: REACTION DRIVEN CRACKING**

The experiments used to calibrate reaction rates for our model were done on  $\sim 70$  micron olivine powder, whereas natural peridotites have a lower reactive surface area and – over some time – a lower available reactive volume. Our thermal modelling was done with a constant “reactive volume” of 0.01%, meaning that the reactive volume in natural peridotite over a given time interval is estimated to be 10,000 times smaller than in 70 micron powder. Using a constant reactive volume term is “optimistic”, since solid carbonate reaction products could armor unreacted olivine over time, drastically reducing the reactive volume with reaction progress. Alternatively, reaction-driven cracking could increase the reactive volume with time. This is a focus of ongoing research. Meanwhile, we offer the following qualitative, geological reasoning. Cracks filled with serpentine commonly form an isotropic network, often with three mutually orthogonal orientations. The smallest veins commonly have spacings of 10 to 100 microns, well below the grain size of the peridotite protolith. Cracks filled with carbonate also form a network of mutually orthogonal veins, with spacing down to 1 mm in some cases. Such a pervasive

fracture network is not observed in un-altered peridotite, and is inconsistent with tectonically driven deformation. Instead, it probably forms as a result of alteration. Completely serpentinized peridotites lacking any unaltered olivine are common, and completely carbonated peridotites (listwanites) are observed. If alteration had a negative feedback on permeability, then 100% serpentinization or carbonation would be rare, restricted to thin diffusive boundary layers near open fluid conduits.

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**From:** "Terres, Richard UCS" <Richard.R.Terres@pdo.co.om>  
**Subject:** RE: Mineralization in ophiolite  
**Date:** September 17, 2008 7:12:50 AM GMT+02:00  
**To:** "Peter Kelemen" <peterk@ldeo.columbia.edu>  
 1 Attachment, 26.0 KB

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Peter,

Please find attached our letter of support – if you need an actual signed “hardcopy” to submit, let me know.

Regards,

Rick

## *Richard Terres*

UCS  
Corporate Strategy & Portfolio Manager  
GN 263, MAF  
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Phone: 24675448

-----Original Message-----

**From:** Peter Kelemen [mailto:peterk@ldeo.columbia.edu]

**Sent:** Sunday, September 14, 2008 17:14

**To:** Terres, Richard UCS

**Subject:** Re: Mineralization in ophiolite

hi Rick,

In the next few days, would be best.

The absolute deadline is October 1, but I will be traveling between Wednesday and Oct 9, so it will be difficult - but not impossible - for me to get the letter to the right people after Tuesday night

In summary, by Tuesday night would be great, but after that would still work.

Best wishes,

Peter Kelemen

On Sep 13, 2008, at 11:10 PM, Terres, Richard UCS wrote:

Peter – by when do you need the letter?

Rick



# Shell Exploration & Production

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12<sup>th</sup> of September 2008

To whom it may concern

Dear Sirs,

Shell is conducting exploratory research on CO<sub>2</sub> geosequestration in mafic rocks as an alternative option for GHG mitigation. To support its research Shell is developing with Dept. of Earth & Environmental Sciences, Columbia University a collaborative research effort to investigate subsurface CO<sub>2</sub> storage in peridotites in Oman.

Yours sincerely

A handwritten signature in black ink, appearing to read 'Nadja Muller', with a horizontal line above the first few letters.

Nadja Muller  
Senior CO<sub>2</sub> sequestration scientist, Exploratory Research  
Shell International Exploration and Production B.V.

## *Richard Terres*

UCS  
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-----Original Message-----

**From:** Peter Kelemen [<mailto:peterk@ldeo.columbia.edu>]  
**Sent:** Thursday, September 11, 2008 18:13  
**To:** Terres, Richard UCS  
**Cc:** Juerg Matter  
**Subject:** Re: Mineralization in ophiolite

Dear Richard,

Jürg Matter and I are contributing to a Columbia University proposal to the US Dept. of Energy for an "Energy Frontiers Research Center" to be based here. We will highlight the potential for our research on in situ capture and storage of CO<sub>2</sub> in peridotite, and in this context we have written about our plans to work with PDO in Oman, eventually drilling injection wells and testing our ideas about accelerated CO<sub>2</sub> uptake in hot peridotite at depth.

Would you please write a short supporting letter that we could include with the proposal, confirming your plans to work with us on this research? I am sure that funding of a DOE Energy Frontiers Research Center at Columbia would be to our mutual benefit.

Thanks in advance.

Best wishes,

Peter Kelemen

Arthur D Storke Professor

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SUBJECT: PETROLEUM DEVELOPMENT OMAN SUPPORT FOR COLUMBIA UNIVERSITY RESEARCH INTO CO2 SEQUESTRATION THROUGH MINERAL TRANSFORMATION

Petroleum Development Oman (PDO) is committed to operating responsibly and to minimizing Greenhouse Gas (GHG) emissions while honouring its primary business objective of oil and gas production for the Sultanate of Oman.

PDO has been producing oil and gas for over 40 years and has developments in over 100 fields. The company operates a total of 18 production stations and has an active stock of over 3800 wells. Currently, half of PDO's oil production utilizes primary recovery mechanisms and half is from waterflood developments; but, within the next decade over a third of its production will come from major miscible gas injection, chemical and thermal Enhanced Oil Recovery (EOR) developments. To drive the implementation of this maturing portfolio, PDO has an increasing energy requirement and if unchecked, its GHG emissions will increase proportionally.

PDO is aggressively pursuing a number of activities and technologies in an effort to minimize its GHG footprint, including: reduction of flaring, Production Station energy efficiency improvements, reduction of deep water disposal, better power planning, widespread deployment of power station waste heat cogeneration and solar steam and power generation. Simultaneously, in an effort to capture and store CO2 emissions from its power stations, PDO is also evaluating saline aquifer sequestration, CO2 miscible gas injection and permanent CO2 storage through the mineral transformation of ultra-mafic rocks – such as that proposed by Columbia University.

PDO is uniquely positioned to support Columbia University in a project focused on the mineral transformation and sequestration of CO2. PDO's 100,000 km<sup>2</sup> operating licence is bordered by Oman's vast outcrops of peridotite-bearing rocks. In addition, large alluvial fans of peridotite debris underlie much of PDO's area of operations and may provide an alternative sequestration target. PDO has an extensive drilling and logistics operation (with both light and heavy drilling rigs) and understands the requirements to fracture and inject fluids in various rock types. PDO has a Sustainable Development group that can help facilitate appropriate Oman Ministry approvals for a drilling and testing programme as envisioned by Columbia University. Finally, PDO's management already has budgeted funds to assist with the local logistics of this project, starting in 2009. PDO takes its environmental obligations seriously and looks forward to a fruitful relationship with Columbia University.

Regards,

Richard Terres  
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Petroleum Development Oman

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September 16, 2008

Peter Kelemen, Arthur D. Storke Memorial Professor,  
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Lamont-Doherty Earth Observatory of Columbia University  
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Dear Peter,

I am enthusiastic to participate in your research project investigating *in situ* carbonation of peridotite and basalt. The proposed center promises to be a source of exciting and productive research for a number of reasons, among the most prominent of which are the quality and productivity of the collaborators and the opportunity to create a synthesis of geochemical experiments, microstructural observations, field geophysics tests, laboratory investigations, and theoretical calculations. Such an integrated approach is certainly mandated by the complexity of engineering in the subsurface environment. Among the basic scientific questions that remain to be understood is the nature of the coupling of mechanical deformation and chemical reactions.

I sincerely believe that careful, well-designed, and innovative experiments of that coupling can be conducted using our triaxial deformation apparatus. Because we can independently control the pressure, flow rate, and chemistry of the pore fluid, permeability and storativity can be measured under hydrothermal conditions of elevated lithostatic pressure and temperature, while loaded in triaxial conditions. The ability to independently vary each of these parameters provides a sensitive tool to understand the complex interplay of reactions and deformation in the rock samples.

Owing to the integration of data from field tests, laboratory experiments, and numerical computation, it should be possible to begin to understand the complex issues scaling in space and time that would be inaccessible to any one set of techniques taken alone. I look forward to participating in this exciting collaboration.

With kind regards,

Brian Evans  
Professor of Geophysics