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

Peter B. Kelemen, Jürg Matter & Lisa Streit

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

Peter B. Kelemen, Jürg Matter and Lisa Streit[1]

[1] *Lamont Doherty Earth Observatory, Columbia University, Palisades NY, USA 10964*

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 CO2. 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, ~ 10^6 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_2 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_2 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_2 is enormous. In Oman, a thrust sheet of oceanic crust and upper mantle known as the "Oman ophiolite" is ~ 70,000 km^3 (Nicolas et al., 2000). ~ 30% of this volume is peridotite. Adding 1 wt% CO_2 to the peridotite would consume ¼ of all atmospheric CO_2. Full carbonation of peridotite forming magnesite, dolomite and/or calcite + quartz, incorporates 30 to 40 wt% CO_2. Ophiolites similar in size are in Papua New Guinea (~ 10,000 km^2 in outcrop), New Caledonia (~ 6000 km^2) and along the east coast of the Adriatic Sea (several ~ 4000 km^2 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°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) Mg^{2+}–HCO_3- type, hereafter Type 1, with pH ~ 8-9, 40-300 ppm Mg, < 10 ppm Ca and 200-1400 ppm HCO3- (~ 150 to 1000 ppm CO_2), and relatively high oxygen fugacity, and (2) Ca^{+2}–OH- type, Type 2, with pH > 11, low oxygen fugacity, 30-70 ppm Ca, < 10 ppm Mg, and negligible 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 1 evolves to Type 2 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 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 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}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}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 ($MgCO_3$), and/or dolomite ($Ca_{0.5}Mg_{0.5}CO_3$) during formation of Type 2, and (b) Ca in Type 2 - Type 1 is precipitated as calcite ($CaCO_3$) 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 CO_2 per second, or ~ 57.5 tons of 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 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 CO_2 uptake in Oman via peridotite carbonation of 4 10^7 kg/year. To consume 10^9 tons of CO_2/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 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, $4Mg_2SiO_4 + 4H_2O + 2CO_2 = 2Mg_3Si_2O_5(OH)_4 + 2MgCO_3$. 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 $4Mg_2SiO_4 + H_2O + 5CO_2 = Mg_3Si_4O_{10}(OH)_2$ [talc] $+ 5MgCO_3$, and $4Mg_2SiO_4 + 8CO_2 = 4SiO_2$ [quartz] $+ 8MgCO_3$. Although listwanites clearly record higher 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 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 CO_2 pressure may be ~ 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 CO_2 is injected at 300 bars and 25°C at a flow rate of ~ 0.040 m/s. At these conditions, our one dimensional model delivers ~ 0.166 kg CO_2/s to a 1 x 1 x 1000 m^3 rock volume, and consumes ~ 0.127 kg CO_2/s to form solid magnesite. All olivine is consumed after about 190 days, consuming ~ 2000 tons CO_2/1000 m^3, or – scaling up – $2 \cdot 10^9$ tons CO_2/km^3 at ~ $4 \cdot 10^9$ tons/yr.

ENHANCING RATES: REACTION DRIVEN CRACKING

The experiments used to calibrate reaction rates for our model were done on ~ 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.

REFERENCES

Allen, D.E. & Seyfried, W.E., 2003, Compositional controls on vent fluids from ultramatic-hosted hydrothermal systems at mid-ocean ridges: An experimental study at 400 degrees C, 500 bars: Geochim. Cosmochim. Acta,67,1531-1542.

—, 2004, Serpentinization and heat generation: Constraints from Lost City and Rainbow hydrothermal systems: Geochim. Cosmochim. Acta,68,1347-1354.

Barnes, I., LaMarche, V.C. & Himmelberg, G., 1967, Geochemical evidence of present-day serpentinization: Science,156,830-832.

Barnes, I. & O'Neil, J.R., 1969, Relationship between fluids in some fresh alpine-type ultramafics and possible modern serpentinization, western United States: GSA Bull.,80,1947-1960.

Boschi, C., et al., 2008, Isotopic and element exchange during serpentinization and metasomatism at the Atlantis Massif (MAR 30 N): Insights from B and Sr isotope data: Geochim. Cosmochim. Acta,72,1801-1823.

Bruni, J., et al., 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.,17,455-474.

Cipolli, F., et al., 2004, Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modeling of CO2 sequestration in serpentinite aquifers: Applied Geochem.,19,787-802.

Clark, I.D. & Fontes, J.C., 1990, Paleoclimatic reconstruction in northern Oman based on carbonates from hyperalkaline groundwaters: Quaternary Res.,33,320-336.

Emmanuel, S. & Berkowitz, B., 2006, Suppression and stimulation of seafloor hydrothermal convection by exothermic mineral hydration: Earth Planet. Sci. Lett.,243,657-668.

Evans, B.W., 2004, The serpentinite multisystem revisited: Chrysotile is metastable: Int. Geol. Rev.,46,479-506.

Fletcher, R.C., Buss, H.L. & Brantley, S.L., 2006, A spheroidal weathering model coupling porewater chemistry to soil thickness during steady-state denudation: Earth Planet. Sci. Lett.,244,444-457.

Fontaine, F.J., Rabinowicz, M. & Boulegue, J., 2001, Permeability changes due to mineral diagenesis in fractured crust: Implications for hydrothermal circulation at mid-ocean ridges: Earth Planet. Sci. Lett.,184,407-425.

Früh-Green, G.L., et al., 2003, 30,000 years of hydrothermal activity at the Lost City vent field: Science,301,495-498.

Fyfe, W.S., 1974, Heats of chemical reactions and submarine heat production: Geophys. J. Roy. Astr. Soc.,37,213-215.

Gerdemann, S.J., et al., 2003, Carbon dioxide sequestration by aqueous mineral carbonation of magnesium silicate minerals: Report number DOE/ARC-2003-018, OSTI ID: 898299,8 pp.

Hansen, L.D., et al., 2005, Carbonated serpentinite (listwanite) at Atlin, British Columbia: A geological analogue to carbon dioxide sequestration: Can. Mineral.,43,225-239.

Iyer, K., et al., 2008, Reaction-assisted hierarchical fracturing during serpentinization: Earth Planet. Sci. Lett.,267,503-516.

Jamtveit, B., Malthe-Sorenssen, A. & Kostenko, O., 2008, Reaction enhanced permeability during retrogressive metamorphism: Earth Planet. Sci. Lett.,267,620-627.

Jedrysek, M.O. & Sachanbinski, M., 1994, Stable-isotope and trace-element studies of vein ophicarbonates at Gogolow-Jordanow serpentinite massif (Poland): A contribution to the origin of ophiaragonite and ophimagnesite: Geochem. J.,28,341-350.

Kelemen, P.B. & Matter, J.M., 2008, In situ carbonation of peridotite for CO2 storage: Proc. Nat. Acad. Sci. USA,submitted.

Kelley, D.S., et al., 2001, An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30 degrees N: Nature,412,145-149.

Lackner, K.S., Butt, D.P. & Wendt, C.H., 1997, Progress on binding CO2 in mineral substrates: Energy Conversion & Management,38,S259-S264.

Lackner, K.S., et al., 1995, Carbon dioxide disposal in carbonate minerals: Energy,20,1153-1170.

Lowell, R.P. & Rona, P.A., 2002, Seafloor hydrothermal systems driven by the serpentinization of peridotite: Geophys. Res. Lett.,29,1531, doi 10.1029/2001GL014411.

Lowell, R.P., Vancappellen, P. & Germanovich, L.N., 1993, Silica precipitation in fractures and evolution of permeability in hydrothermal upflow zones: Science,260,192-194.

MacDonald, A.H. & Fyfe, W.S., 1985, Rate of serpentinization in seafloor environments: Tectonophys.,116,123-135.

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

Mazzotti, M., et al., 2005, Mineral carbonation and industrial uses of CO2, in Metz, B., et al., eds., IPCC Special Report on Carbon Dioxide Capture and Storage: Cambridge, UK, Cambridge University Press,319-338.

Naldrett, A.J., 1966, Talc-carbonate alteration of some serpentinized ultramafic rocks south of Timmins, Ontario: J. Petrol.,7,489-499.

Nasir, S., et al., 2007, Mineralogical and geochemical characterization of listwaenite from the Semail ophiolite, Oman: Chemie Der Erde,67,213-228.

Neal, C. & Shand, P., 2002, Spring and surface water quality of the Cyprus ophiolites: Hydrol. Earth Sys. Sci.,6,797-817.

Neal, C. & Stanger, G., 1985, Past and present serpentinization of ultramafic rocks: An example from the Semail ophiolite nappe of northern Oman, in Drewer, J.I., ed., The Chemistry of Weathering: Holland, D. Reidel Publishing Company,249-275.

Nicolas, A., et al., 2000, Accretion of Oman and United Arab Emirates ophiolite: Discussion of a new structural map: Marine Geophys. Res.,21,147-179.

O'Hanley, D.S., 1992, Solution to the volume problem in serpentinization: Geology,20,705-708.

Palandri, J.L. & Reed, M.H., 2004, Geochemical models of metasomatism in ultramafic systems: Serpentinization, rodingitization, and sea floor carbonate chimney precipitation: Geochim. Cosmochim. Acta,68,1115-1133.

Pozzorini, D. & Früh-Green, G.L., 1996, Stable isotope systematics of the Ventina Ophicarbonate Zone, Bergell contact aureole: Schweiz. Min. Pet. Mitt.,76,549-564.

Python, M., et al., 2007, Oman diopsidites: A new lithology diagnostic of very high temperature circulation in mantle peridotite below oceanic spreading centers: Earth Planet. Sci. Lett.,255,289-305.

Robinson, P.T., et al., 2005, Geochemistry and origin of listwanites in the Sartohay and Luobnsa ophiolites, China: Int. Geol. Rev.,47,177-202.

Seyfried, W.E., Foustoukos, D.I. & Fu, Q., 2007, Redox evolution and mass transfer during serpentinization: An experimental and theoretical study at 200 C, 500 bar with implications for ultramafic-hosted hydrothermal systems at Mid-Ocean Ridges: Geochim. Cosmochim. Acta,71,3872-3886.

Shervais, J.W., 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.

Stanger, G., 1985, Silicified serpentinite in the Semail nappe of Oman: Lithos,18,13-22.

Trommsdorff, V. & Evans, B.W., 1977, Antigorite-ophicarbonates: Contact metamorphism in Valmalenco, Italy: Contrib. Mineral. Petrol.,62,301-312.

Wenner, D.B. & Taylor, H.P., 1974, D/H and 18O/16O studies of serpentinization of ultramafic rocks: Geochim. Cosmochim. Acta,38,1255-1286.

Wilde, A., Simpson, L. & Hanna, S., 2002, Preliminary study of Cenozoic alteration and platinum deposition in the Oman ophiolite: J. Virtual Explorer,6,7-13.