WORKSHOP REPORT

Geological carbon capture & storage in mafic and ultramafic rocks

IODP/ICDP Workshop on

the role of oceanic and continental scientific drilling

Co-sponsors: European Science Foundation, Inter-Ridge, Sultan Qaboos University,
UK-IODP, US Consortium for Ocean Leadership, US National Science Foundation

Carbonate veins in altered peridotite, Sultanate of Oman, Kelemen & Matter Proc. (US) Nat. Acad. Sci, 2008; Kelemen et al. Ann Rev. Earth Planet. Sci. 2011.

Image from http://www.panoramio.com/photo/18535750

Al Fahm Theatre, Sultan Qaboos Cultural Centre
Sultan Qaboos University, Muscat, Sultanate of Oman

8-10th January, 2011

with field excursions 11-12 January, 2011

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Summary

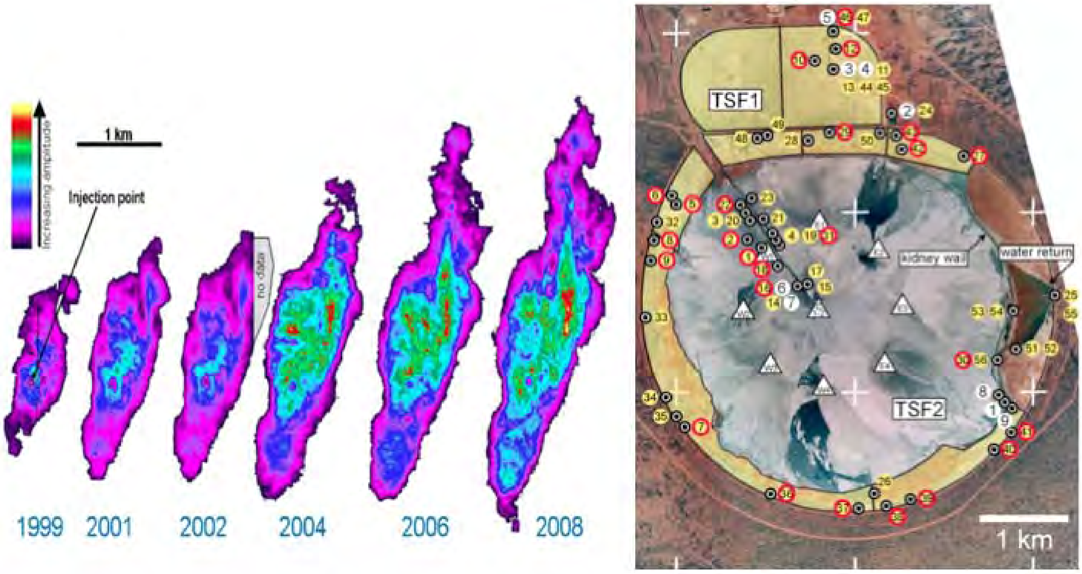
Reduction of greenhouse gas emissions and mitigation of the effects of increasing atmospheric concentrations of these gases are among the most pressing technological challenges to society in this century. Given international needs for continued economic growth and development, fossil fuels will supply energy essential for growth, so that CO_2 capture and geological carbon storage will be key components of mitigation strategies. *In situ* mineral carbonation may be the safest and most effective means to achieve this. In addition to storage, geological carbon capture – via fluid/rock reactions that remove carbon from air or surface waters – may provide an alternative to industrial CO_2 capture and transport, a method for mitigating distributed emissions from vehicles and agriculture, and a route to achieve "negative emissions" should atmospheric CO_2 concentrations become unacceptably high in the future.

A workshop hosted by the Sultan Qaboos University in Muscat (Sultanate of Oman) in January 2011, brought together scientists from communities associated with the Integrated Ocean Drilling Program (IODP) and the International Continental Scientific Drilling Program (ICDP), joined by colleagues from the geothermal, chemical, and mining industries. The aim of this workshop was to advance research on carbon capture and storage in ultramafic and mafic rocks. The interest in these rocks stems from their high potential for mineral carbonation – reaction with CO_2-bearing fluids to form inert, non-toxic, stable carbonate minerals.

Workshop participants formulated integrative scientific questions and the identification of potential implementation approaches. Five key conclusions were reached.

1. The potential for several different, engineered mineral carbonation methods should be explored *in parallel*, by integrated, international research networks, including (a) carbonation of ultramafic mine tailings and sediments, (b) *in situ* carbonation of ultramafic rocks (peridotite), and (c) *in situ* carbonation of mafic rocks (basalt). No one can foresee the size or urgency of the societal demand for CO_2 storage in the coming century, nor is it possible to predict the outcome of ongoing research on alternative or complementary methods.

Use of mine tailings, and potential use of sediments rich in mafic or ultramafic clasts (a), avoids drilling, hydraulic fracture, and other reservoir conditioning costs of *in situ* mineral carbonation, and the quarrying, transportation and grinding costs of engineered ex situ methods. Some potential sites for carbonation of mine tailings offer rates and storage capacities similar to those achievable via injection of CO_2 in to subsurface pore space. Over the long term, *in situ* mineral carbonation via circulation of CO_2-bearing fluids through mafic and ultramafic rocks (b&c) offers much larger uptake capacity, and provides elevated temperature and pressure, enhancing mineral carbonation rates. Current lab and field data indicate that mineral carbonation in ultramafic rocks (b) is orders of magnitude faster than in mafic rocks (c), but mafic rocks are orders of magnitude more abundant near the Earth's surface, and kinetic experiments comparing rates for both ultramafic and mafic rocks at the same conditions have not yet been completed.



Statoil Sleipner plume: www.geoexpro.com

Mt Keith mine tailings, Australia

G. Dipple, UBC

Figure 1: Comparison of plume of CO_2 injected into subsurface pore space, about 1 km below the seafloor at Sleipner (Statoil, North Sea), compared to the ultramafic tailings at the Mt Keith Nickel mine (Australia) at approximately the same scale. Engineered mineral carbonation at Mt. Keith might achieve uptake at ~10^5 tons per year, about 10x less than the injection rate at Sleipner. Total storage at Sleipner will be about 2 10^7 tons. Total capacity in the Mt. Keith tailings could be around 5 10^7 tons. One can predict with confidence that less than 1% of the CO_2 stored in mine tailings at Mt. Keith would be returned to the atmosphere over 100 to 1000 years. Image from keynote talk by Prof. Greg Dipple of the University of British Columbia, Canada.

Figure 2: Sites of medium-scale experiments on injection of CO_2-rich fluids into mafic volcanic rocks (basalts) in Iceland (CarbFix) and Washington State (US, Big Sky). Image from keynote talk by Prof. Damon Teagle of the University of Southampton, UK.

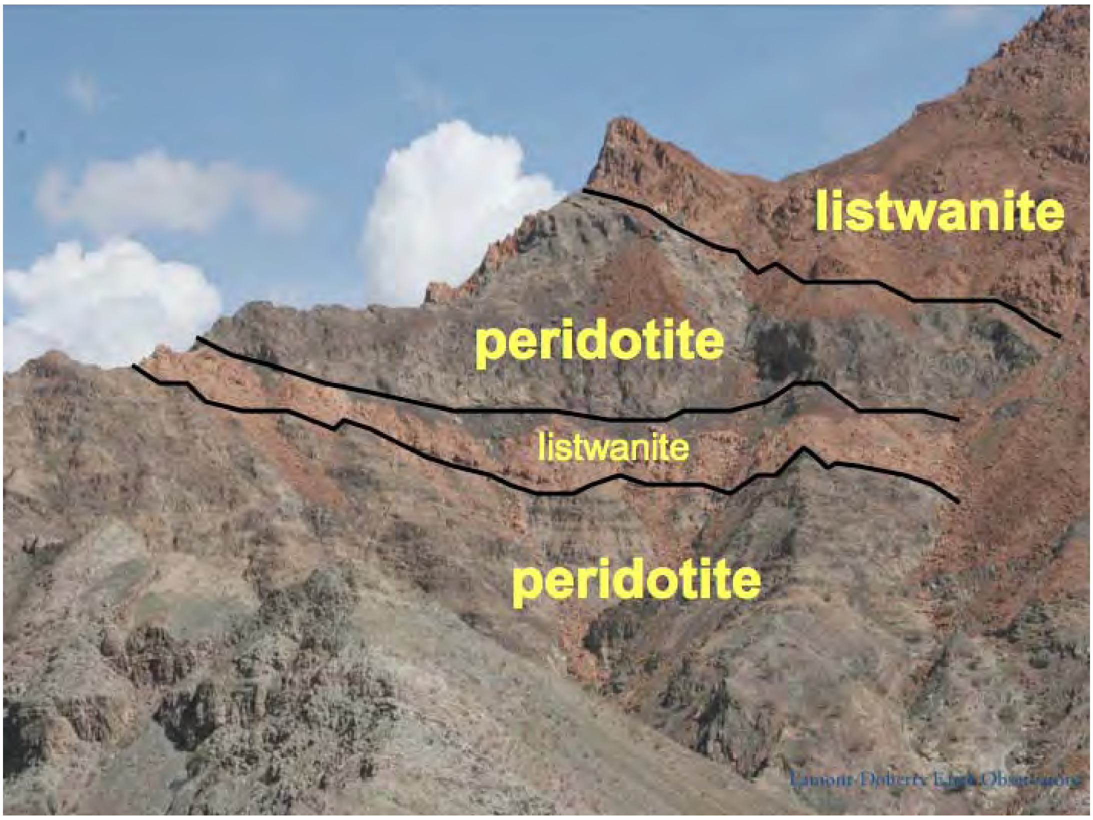


Figure 3: Red bands of fully carbonated peridotite (listwanite, composed of magnesite ($MgCO_3$), quartz, and chromian spinel) in light green, partially serpentinized peridotite on MoD Mountain near Fanjah, Oman, visited on post-conference field trip. The lower band is about 15 meters thick, the upper band is ~ 200 meters thick, extending for about 5 km EW by 2 km NS, so the total mass of CO_2 stored on MoD Mtn is ~ 1 billion tons. Kelemen et al. Ann. Rev. Earth Planet. Sci. 2011.

2. It is necessary to understand the physical properties of potential mineral carbonation sites. Specifically, it is essential to quantify permeability, porosity, mineralogy (igneous minerals, plus extent and nature of existing alteration), fracture toughness and other material properties as a function of lithology and depth.

Ongoing, medium-scale experiments on geologic storage of CO_2 in mafic volcanics (basalt) in Washington State (US) and Iceland have begun to provide detailed data on these lithologies. Similar data on physical properties of ultramafic rocks are almost entirely lacking, and should be a key focus of future research via scientific drilling.

3. It is necessary to understand coupled chemical reaction and fluid transport in natural mineral carbonation systems better, especially in two key areas:

First, scientists need to understand how some natural systems achieve full carbonation (100% of Mg, Ca and even Fe in carbonate minerals) and operate over 10's to 100's of thousands of years without filling of pore space or armoring of reactive minerals. Reaction-driven cracking and formation of dissolution pits apparently maintain or enhance permeability and reactive surface area under some conditions. What are the conditions necessary for this?

Second, given laboratory data on methods to accelerate reaction rates by factors of 10^6 to 10^7, compared to rates in the natural weathering environment, quantifying the natural rate is an essential benchmark for estimating what can be achieved in engineered systems.

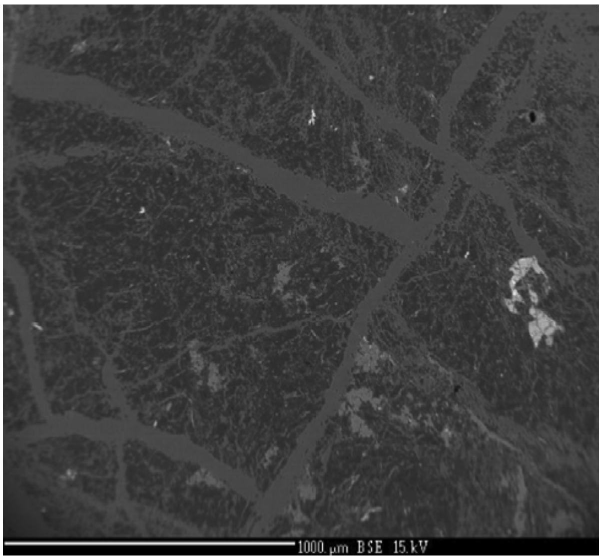
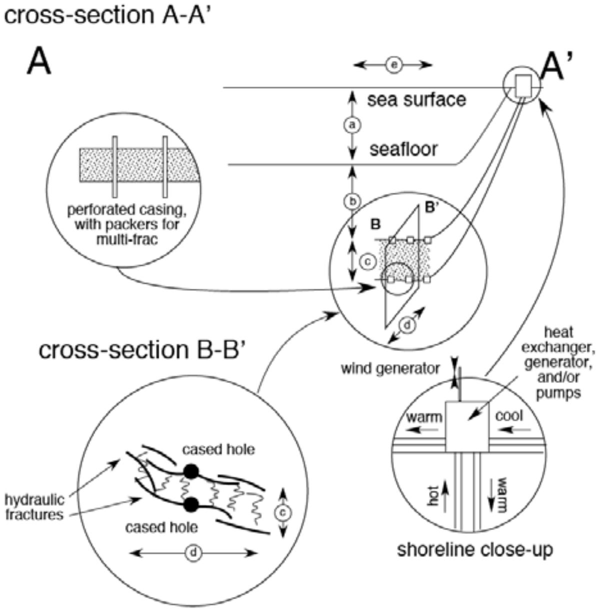


Figure 4: Back-scatted electron image of fully carbonated peridotite (listwanite), composed of magnesite (magnesium carbonate, $MgCO_3$, dark grey matrix), quartz (light grey veins showing hierarchical, cross-cutting relationships, filling cracks with spacing < 100 microns) and relict chromian spinel (bright grain at right). Image from keynote talk by Prof. Peter Kelemen, Columbia University, & Streit et al., paper in prep.

Figure 5: Notional design of shoreline installation for capture and storage of CO_2 from thermal convection of seawater through sub-seafloor peridotite via thermal convection, with low-grade geothermal power as a by-product.



4. Scientific drilling has two key roles to play, (a) study of natural processes throughout the world, and (b) characterization of potential sites for CO_2 storage experiments.

(a) Areas of active mineral carbonation forming extensive deposits include ophiolites (especially the Samail ophiolite in Oman and the United Arab Emirates, plus some known sites in, e.g., New Caledonia (on- and offshore), northern California and Italy), and submarine hydrothermal systems near the mid-ocean ridges (especially, the Lost City hydrothermal system near the Mid-Atlantic Ridge). Volumetrically important, diffuse mineral carbonation is documented in seafloor volcanic rocks.

(b) Studies of mineral carbonation in mine tailings are ongoing, especially in Australia and Canada. For the foreseeable future, drilling and injection (or thermal convection) of fluids into mafic and ultramafic rocks will be far less expensive on-land rather than at sea, whereas potential surface deformation and leakage hazards will have less human impact offshore. The best sites for pilot experiments and full scale carbon storage may involve shoreline drilling into submarine reservoirs.

5. The scientific community will probably need to take the lead in mineral carbonation research in the near future, developing and quantifying practical methods for use by government and industry when a consensus arises on the need for these techniques.

Energy industry interest in mineral carbonation, while strong during in the previous decade, waned in 2009-2011. This stemmed largely from concern over slow or stalled implementation of policies for carbon management, internationally and in some countries with large CO_2 emissions, and from the perception that *injection* of CO_2 into sub-surface pore space is a well known, widely used technique (for example, in Enhanced Oil Recovery) that can be used for potentially easy, inexpensive and safe carbon *storage*. A danger is that, even if some mineral carbonation techniques are less energy intensive and more effective than industrial CO_2 capture and storage in pore space, momentum and economies of scale will lead to large-scale implementation of less efficient methods. Medium-scale experiments on the feasibility of injection for carbon storage, ongoing in several areas, will provide cost, reliability and safety information that will allow comparison of storage in pore space to more speculative estimates for mineral carbonation.

Research funding for mineral carbonation research is available from several national and international (EU) agencies. Researchers can also focus on a wide range of related topics of fundamental scientific importance, such as (a) the role of ultramafic rock alteration in generation of abiotic hydrocarbons and its potential relevance to the origin of life, and (b) the role of alteration processes including reaction-driven cracking, in creating primary permeability in some rock formations, with potential application to engineered methods for, e.g., shale gas extraction and enhanced geothermal systems.

Discussions outlined specific, new science plans for international ocean and continental drilling programs. Immediately after the Workshop, a group of participants submitted a proposal for an ICDP sponsored workshop on scientific drilling in the Samail ophiolite in Oman. In addition to more traditional questions about the formation and evolution of oceanic crust, scientific drilling in Oman will investigate present-day alteration processes, their relationship to the deep biosphere, and their potential for acceleration to achieve carbon capture and storage via *in situ* mineral carbonation. The proposal was approved by the ICDP, and the workshop will be held in Oman in late 2012 or early January, 2013.

This report presents a compilation of key ideas and potential experiments that were discussed and highlighted during the workshop. The first section of this report briefly summaries the structure of the workshop and the information from the Keynote lectures. We then summarize the discussions of the Breakout Groups. Points of consensus from each Breakout Group are detailed in the section, “Scientific challenges and new paths for research”.

Figure 6: Field trip participants at the "Center of the Universe", in the mantle section of the Samail ophiolite.

1. Introduction

Motivation for this workshop

Reduction of greenhouse gas emissions and mitigation of the effects of increasing atmospheric concentrations of these gases are among the most pressing technological challenges to society in this century. Climate change due to anthropogenically elevated levels of atmospheric greenhouse gas concentrations is a slow moving emergency with uncertain outcomes, but serious detrimental societal consequences are probable. When an international consensus is reached on the need for action, the available time for successful implementation of mitigation strategies may be short. Given the unpredictable outcome, in terms of climate, societal response, and successful mitigation, it is important for research to proceed – in parallel – on a large variety of options for reducing emissions and reducing high levels of atmospheric greenhouse gases, knowing that only some options will be successful and widely adopted.

Despite recognition of the likelihood that fossil fuel emissions are contributing to increasing atmospheric greenhouse gas concentrations, fossil fuel use and atmospheric CO_2 and CH_4 concentrations have continued to increase in the 21st century. The reasons for this are clear: Continued well-being in industrialized countries is predicated on economic growth, while developing countries see every reason to continue on their path toward prosperity. While energy conservation can reduce fuel use by a significant factor, such efforts will have little impact if demand for automobile transportation, home appliances, and electronic devices continues to grow exponentially, as it has over the past 150 years. The recent global recession served as a reminder of the need for growth, and the impacts of slow growth are far more universal and widely acknowledged than the subtle, gradual effects of climate change.

As a result, capture of greenhouse gases, and geological carbon storage, are key components of most mitigation strategies. *In situ* mineral carbonation may be the safest and most effective means to achieve this. In addition to storage, geological carbon capture via fluid/rock reactions that remove carbon from air or surface waters may provide an alternative to industrial CO_2 capture and transport, and a route to achieve “negative emissions” should atmospheric greenhouse gas concentrations become unacceptably high in the future.

This workshop engaged the scientific communities associated with the Integrated Ocean Drilling Program (IODP) and the International Continental Scientific Drilling Program (ICDP) to review how these programs can most effectively contribute to research on geological capture and storage of CO_2, with particular focus on the potential for storage in ultramafic and mafic rocks. They were joined by colleagues from the hydrocarbon, mining and related industries, and with policy makers. In addition to formulating specific research strategies, this group hopes to raise the profile of research on geological carbon capture and storage. The purpose of the workshop was not to *promote* mineral carbonation, but instead to encourage and organise research so that we will be in a position to take an objective scientific and engineering assessment of whether mineral carbonation can work at a useful scale and to evaluate potential negative impacts such as costs, pollutants, or better investments.

Mineral carbonation in mafic and ultramafic rocks

Ultramafic and mafic rocks are abundant at the Earth's surface. They are rich in divalent cations such as Mg, Ca and Fe, and hence have a high capacity for formation of solid carbonate minerals, e.g., magnesite ($MgCO_3$), calcite ($CaCO_3$) and siderite ($FeCO_3$) during weathering and hydrothermal alteration. Provided they are protected from rain water, carbonate minerals are stable at Earth surface conditions, and so can store CO_2 permanently. Mafic rocks (basalts, gabbros) are the most abundant igneous rocks at the Earth's surface, while ultramafic rocks (mainly peridotites, rich in the mineral olivine also known as "peridot") have the largest mineral carbonation capacity and fastest known carbonation kinetics amongst the major lithologies at Earth's surface.

Observations of active and ancient hydrothermal systems demonstrate rapid and abundant formation of carbonate minerals via reaction of fluids with these rocks. Yet, the potential for storage in mafic and ultramafic rocks is much less well understood compared to storage in pore space in sedimentary rocks, largely because sedimentary rocks form source and reservoir formations for large hydrocarbon resources, whereas mafic and ultramafic rocks do not. Therefore, in contrast to the many ongoing large pilot studies of CO_2 injection into pore space in sedimentary basins, the high carbonation potential of ultramafic and mafic rocks has received relatively little attention.

From a geological perspective, natural mineral carbonation is inextricably linked with mineral hydration, occurring mainly in near-surface hydrothermal and weathering environments. Understanding of natural processes provides essential insight into design of enhanced, *in situ* mineral carbonation systems. At the workshop, we explored opportunities to couple basic research on enhanced mineral carbonation techniques with ongoing, complementary studies of hydrothermal alteration and weathering, and of chemosynthetic biological communities in these environments.

Support

Major financial support for the meeting was raised from Integrated Ocean Drilling Program Management International, Inc. (IODP-MI), Sultan Qaboos University (SQU), the US National Science Foundation (NSF), the European Science Foundation (ESF), UK-IODP, InterRidge and the (US) Consortium for Ocean Leadership. The meeting was also officially sponsored by the International Continental Scientific Drilling Program (ICDP).

Participation

The workshop was attended by 87 registered participants from 15 countries: Australia, Canada, China (PRC), France, Germany, The Netherlands, Hungary, Iceland, Italy, Japan, Norway, Oman, Switzerland, the UK and the US (Appendix A). The opening ceremony was attended by Her Royal Highness, Mona Al Saaid and His Excellency Dr. Ali Bin Saud Al Bimani, Vice Chancellor of Sultan Qaboos University. Addresses were given by Dr. Saif Al-Bahri, Dean of the College of Science, and Prof. Peter Kelemen, Chairman of the Workshop.

Goals

By bringing together specialists researching the biogeochemical, mineralogical, mechanical and hydrodynamic processes associated with the reaction and storage of CO_2-rich fluids in ultramafic and mafic rocks, with representatives from industry, the workshop had 5 principal aims:

1. To integrate knowledge of natural hydrothermal systems, laboratory experiments and numerical modeling to define the required characteristics for geological carbon storage in ultramafic and mafic rocks, and potentially for geological carbon capture as well.
2. To review the first injection tests in mafic reservoirs, and identify potential sites for developmental deployment of this nascent technology in on-shore and submarine environments in both mafic and ultramafic rocks
3. To develop partnerships between scientists and engineers from industry and the oceanic and continental scientific drilling communities working in related but not overlapping fields, to harness knowledge from existing experience, and to evaluate the potential for CO_2 storage in igneous rocks, and its environmental, economical and societal benefits.
4. To outline plans for continental and marine drilling experiments to acquire key data from natural systems for mineral carbonation in mafic and ultramafic rocks and make pilot experiments testing proposed techniques for enhancing natural rates.

5. To evaluate the environmental, economical and societal costs and benefits of CO_2 storage in mafic and ultramafic rocks

The workshop was organized as a series of presentations alternating with breakout sessions for discussion (see schedule in Appendix B). After a plenary lecture summarizing the general state of knowledge on CO_2 capture and storage from the point of view of chemical engineering, keynote lectures were on natural and enhanced geological storage of CO_2 in mafic and ultramafic rocks, experimentally determined rates of CO_2 reaction with rocks, processes in which volume expansion due to formation of hydrous minerals and/or carbonates leads to fracture, experience with monitoring permeability and CO_2 storage at sea and on land, use of ultramafic mine tailings for mineral carbonation, ongoing projects involving CO_2 injection into mafic rocks, and methods for engineered hydraulic fracture in the geothermal power and mining industries. Small working groups met to discuss mineral carbonation on land and at sea, monitoring of CO_2 storage sites, geophysical rock properties necessary for CO_2 storage, ideal storage site characteristics on land and beneath the seafloor, and the role that could be played by ICDP and IODP in this new field of research.

An important goal or the workshop was to create synergies between scientists working in CCS research and on natural analogues. Therefore, after the workshop, two optional, one day field trips were organized to build a common basis of knowledge and to favor discussion between these different scientific communities, part of which have little to no knowledge of the geology of the ultramafic and mafic reservoirs targeted for CCS studies. On Day 1, we explored the unique outcrops, exposed in the Oman Mountains, illustrating the processes of forming solid minerals containing CO_2, including spectacular white travertine deposits and associated "blue pools". Day 2 aimed at offering a broad overview of the geology of the Oman ophiolite, from ultramafic outcrops to the mafic igneous crust (See Appendix E – Field excursion guide).

2. Keynote Lectures

A perspective from chemical engineering (Darton)

The first plenary lecture was by Prof. Richard Darton of Oxford University, on chemical separation of CO_2. This talk laid out a framework for the challenges facing society and the daunting scale of the industrial processes required for effective carbon capture and storage. Increasing levels of atmospheric CO_2 due to human activity is causing global warming and ocean acidification. Human CO_2 emissions from the burning of hydrocarbon fuels and from cement manufacture (not including deforestation) are ~32 gigatons CO_2 per year or ~80 megatons per day. Although there are efforts to promote renewable energy and its use is increasing, this increase is from a very low level, and the supply of primary energy remains largely based on fossilised carbon. In 2009 the primary energy supply was ~11.2 Gtoe (gigatons of oil equivalent) and with increased energy use, particularly in the developing world, this is likely to double by 2050. Assuming consensus is reached that it is desirable to decrease CO_2 emissions, society faces a major choice, either to avoid CO_2 emissions through the use of renewable or alternative energy sources, or to avoid releasing CO_2 to the atmosphere through capture and storage.

Because almost 50% of emissions are from stationary sources (e.g., electricity generation plants emitting ~15 gigatons of CO_2 per year) it would be helpful to capture significant CO_2 at the source and store it close to the point of capture. Removal of CO_2 from flue gases is technically feasible but would require a very large new industry and significant (but not prohibitive) capital investment to retrofit existing plants or build new ones. Direct capture of CO_2 from air using solvents is not cost effective [as recently reiterated in a technical assessment by the American Physical Society, http://www.aps.org/about/pressreleases/dac11.cfm].

Major issues remain with the storage of CO_2 once it is captured, and mineral carbonation should be an important component of storage plans.

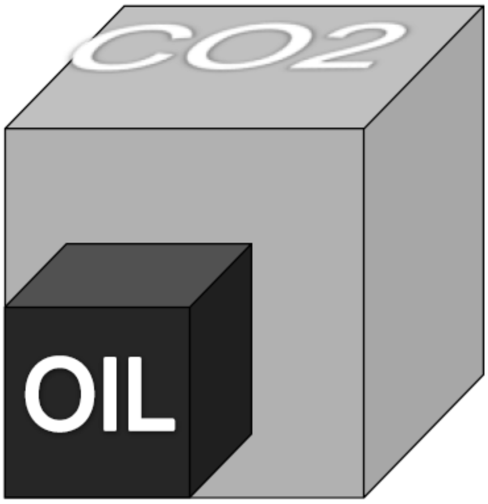


Figure 7: Carbon capture and storage will require the development on a short timescale of a large new industry. If the present day CO_2 production from stationary sources (~15 gigatons CO_2 per year) were stored as supercritical fluid, it would fill a volume of 32.1 billion cubic meters per year, which is a cube with dimensions of 3.2 km. In comparison, global oil production is ~3.9 billion tons or ~4.5 billion cubic meters per year, a cube with dimensions of 1.65 km. Hence, in order to store all current emissions from hydrocarbon fuel used at stationary power sources, carbon capture and storage would have to become an industry several times larger than the oil industry, with consequent impacts on water, chemical and industrial supplies, and storage reservoirs. It will probably be preferable to pursue a parallel approach, reducing hydrocarbon fuel use in parallel with a CO_2 capture and storage strategy.

Can mineral carbonation play a role in carbon capture and storage? (Teagle, Kelemen, Oelkers, Gouze, Dipple, Jamtveit)

The chemical weathering of silicate rocks is the principal mechanism by which the Earth regulates atmospheric CO_2 concentrations over geological timescales to maintain Earth's climate within a relatively narrow temperature window of habitability (e.g., Berner et al., 1983). The challenge for mineral carbonation approaches to carbon capture and storage is to adapt relatively slow geological processes to work on human time scales. Simply stated, the weathering of silicate rocks can be considered as:

$$2CO_2 + H_2O + (Ca,Mg,Fe)SiO_3 = (Ca,Mg,Fe)^{2+} + 2HCO_3^- + SiO_2$$

and the formation of calcium carbonate in the oceans as:

$$2HCO_3^- + (Ca,Mg,Fe)^{2+} = (Ca,Mg,Fe)CO_3 + CO_2 + H_2O$$

giving a net reaction of:

$$\mathbf{CO_2 +} (Ca,Mg,Fe)\mathbf{SiO_3 =} (Ca,Mg,Fe)\mathbf{CO_3 + SiO_2}$$

These simple end-member reactions are of course complicated by the presence of other elements and although many reactions for mineral carbonation are thermodynamically favorable they compete with numerous other reactions (e.g., clay mineral formation). What is also clear from the above reaction is that tons of mineral reactant are required per ton of CO_2 captured (Table 1) and these reactions produce multiple tons of mineral product.

Table 1. Mineral reactants and products (following Oelkers et al., Elements, 2008)

Reactants tons$_{min}$/tons$_C$				**Products carbonates only tons$_{CO3}$/tons$_C$**
~6	$Mg_2SiO_4 + 2CO_2$ **Mg-olivine**	=	$2MgCO_3 + SiO_2$ **Magnesite** + Quartz	**~7**
~10	$CaMgSi_2O_6 + 2CO_2$ **Mg-clinopyroxene**	=	$CaMg(CO_3)_2 + 2SiO_2$ **Dolomite** + Quartz	**~9**
~23	$CaAl_2Si_2O_8 + CO_2 + 2H_2O$ **Ca-Plagioclase**	=	$CaCO_3 + Al_2Si_2O_5(OH)_4$ **Calcite** + Kaolinite	**~8**
~9	$\{Na_{0.08}K_{0.01}Ca_{0.26}Mg_{0.28}Fe^{II}_{0.17}Fe^{III}_{0.02}Ti_{0.02}Al_{0.36}SiO_{3.45}\}$ **Basaltic glass** + $2CO_2$		$(CaMgFe)_2(CO_3)_2$ + clays + accessory phases	**~9**

However, although mineral carbonation requires tons of reactant per ton of CO_2 captured, there are vast resources of mostly unaltered sub-aerial and submarine mafic and ultramafic rocks (e.g., ocean islands, flood basalts, ophiolites, ocean ridge flanks). Many of these resources are located close to major industrial sources of CO_2.

Basalt flows (e.g., Big Sky project or ocean ridge flanks) can be used as porous reservoirs for storage or as reagents to react with CO_2 or HCO_3^-–bearing fluids to form carbonate minerals. Additional sources of finely ground basaltic materials may come from mine tailings, beach sands, volcanic tuffs, and glacial tills where industrial or erosional processes have created large amounts of reactive surface area. Geological weathering and hydrothermal alteration processes are natural analogs for potential industrial processes. Understanding how these processes operate now and in the past may provide guidance on how to optimize industrial mineral carbonation.

Figure 8: Flood basalts in East Greenland, part of 6 km thick section erupted in ~ 1 million years. Similarly thick sub-aerial and near-shore sections of basaltic lava flows are common worldwide, for example the Columbia River basalt in Washington State (US), extensive sections in Iceland, and mid-ocean ridge basalts near shore, as at the Juan de Fuca Ridge off the NW Coast of the US and Canada. (Photo S. Bernstein).

In contrast to mafic rocks, which are made up of the minerals plagioclase and clinopyroxene (see Table 1) the key constituent of ultramafic rocks is the mineral olivine (Mg_2SiO_4), the most reactive of the silicate minerals. Although ultramafic rocks are less abundant than mafic rocks there are still significant ultramafic resources and these rock types are host to important metal deposits (e.g., Cu-Ni sulfides, Cr-PGE deposits). Natural mineral carbonation occurs at rapid geological rates in both submarine and subaerial peridotite exposures (see Figure 3)

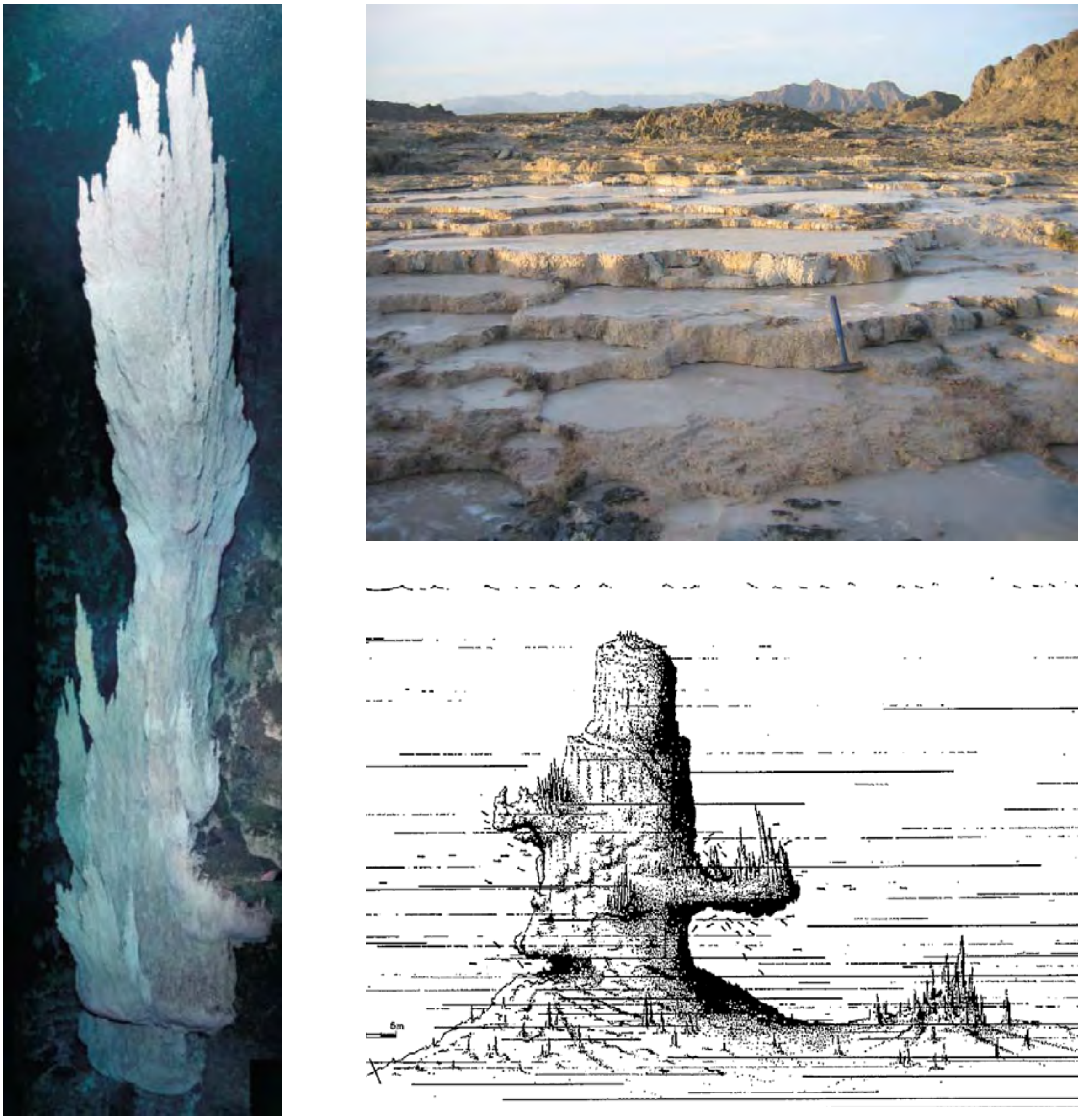


Figure 9: Left: 10 m tall calcium carbonate chimney at the peridotite-hosted Lost City hydrothermal deposit, ~ 1 km below sealevel near the Mid-Atlantic Ridge (Kelley et al. Science 2005). Top right: Calcium carbonate travertine deposit deposited by peridotite-hosted, alkaline springs in Oman (Kelemen & Matter Proc (US) Nat Acad Sci 2008). Lower right: 35 m tall calcium carbonate chimney deposited by peridotite-hosted, alkaline spring 40 m below sea level, Baie de Prony, New Caledonia (Launey & Fontes, Géologie de la France, 1985).

Reactivity of mafic and ultramafic rocks from different environments in presence of CO_2–bearing fluids (CO_2-gas, supercritical CO_2, CO_2-saturated water or brine, seawater)

CO_2-rich fluids are in chemical disequilibrium with ultramafic and mafic rocks. Injection of CO_2-rich fluids will induce reactive processes at the fluid-rock interface, such as dissolution of mantle silicates (olivine) and precipitation of carbonates (carbonation). The parameters controlling these reactions (e.g., temperature, fluid pressure, kinetics) can be studied in laboratory experiments and natural environments but many key parameters are poorly quantified.

Laboratory experiments to date show that the olivine reacts to form carbonates hundreds or thousands of times faster than other common, rock-forming minerals including plagioclase, the most abundant mineral in mafic rocks (although, as pointed out by Erik Oelkers, there has been no systematic study of olivine and plagioclase carbonation rates at identical conditions). Laboratory and geological observations also suggest that mafic rocks react more rapidly, and form more carbonate, than "felsic" rocks with less Mg, Ca and Fe, and more Na, K, Al and Si. Laboratory carbonation of ground olivine, with an average particle diameter ~ 70 microns, reach rates of magnetite formation of up to 50% per hour at 185°C and > 70 bars P_{CO2}. Extrapolation to "grain sizes" or fracture spacing ~ 1 m yields rates up to 50% per year, providing that permeability and reactive surface area can be maintained on this scale.

Silicate hydration and carbonation reactions involve condensation of fluid or gas components to form solid minerals, and thus are intrinsically exothermic – they release thermal energy. This energy can in principle be harnessed, for example to maintain a reacting rock volume at the temperature where reaction rates are optimized.

Laboratory experiments suggest that under special circumstances, mineral precipitation can be rate limiting compared to reactant dissolution. This may arise during carbonation of olivine to form magnesite, which is notoriously slow to nucleate and grow. Engineered approaches would need to overcome sluggish precipitation.

Commonly there is disagreement between results from experimentation (at all scales) and geochemical modeling, which this requires further calibration.

Volume changes during hydration and carbonation processes and feedback effects on the mechanical and hydraulic properties of the media.

It is intuitive that reactions increasing the solid volume may be self-limiting because they fill pore space and armor reactive surfaces. However, based in part on geological evidence for 100% carbonation of some rocks, it is inferred that mineral carbonation may enter a "reaction-driven cracking regime" in which permeability and reactive surface area are maintained or even enhanced in a positive feedback process. Increasing solid volume can lead to large, anisotropic stresses within the rock, causing fracture, as in the better-known process of "salt weathering". Conversely, some metamorphic hydration and carbonation reactions take place at constant volume, with export of excess mass away from the reacting rock volume via pressure solution and fluid transport. In order to evaluate and design potential, engineered *in situ* mineral carbonation systems, it is absolutely essential to understand the mechanisms controlling these processes.

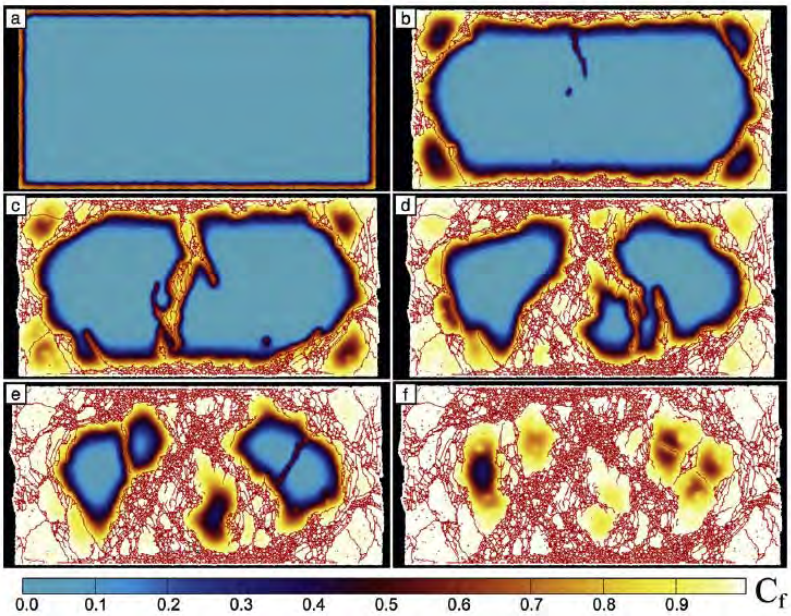


Figure 10: Model of positive feedback during mineral hydration or carbonation, involving fluid flow in fractures, fluid-solid reaction, and fracture caused by increasing solid volume (Royne et al. EPSL 2008).

Characterization of hydrodynamic properties before, during and after injection (Becker)

The simplest physical and hydrodynamic properties, such as permeability, porosity, fracture size and spacing, temperature, fluid composition, and their variation with formation age and depth below the surface, are not well known for our target lithologies. On land, measurement of these properties is routine for aquifers and petroleum reservoirs, but has rarely been done in mafic and ultramafic rocks. IODP scientists have developed highly innovative methods for measuring these properties in submarine drill holes. Because the drilling process itself disrupts many of the properties of interest, it is necessary to establish long term monitoring of holes as they return to a steady state condition using “CORK” instruments. There are preliminary data from the ocean ridge flanks but the lateral extents of permeable horizons and their horizontal and vertical connectivity from the m to km scale are very poorly quantified.

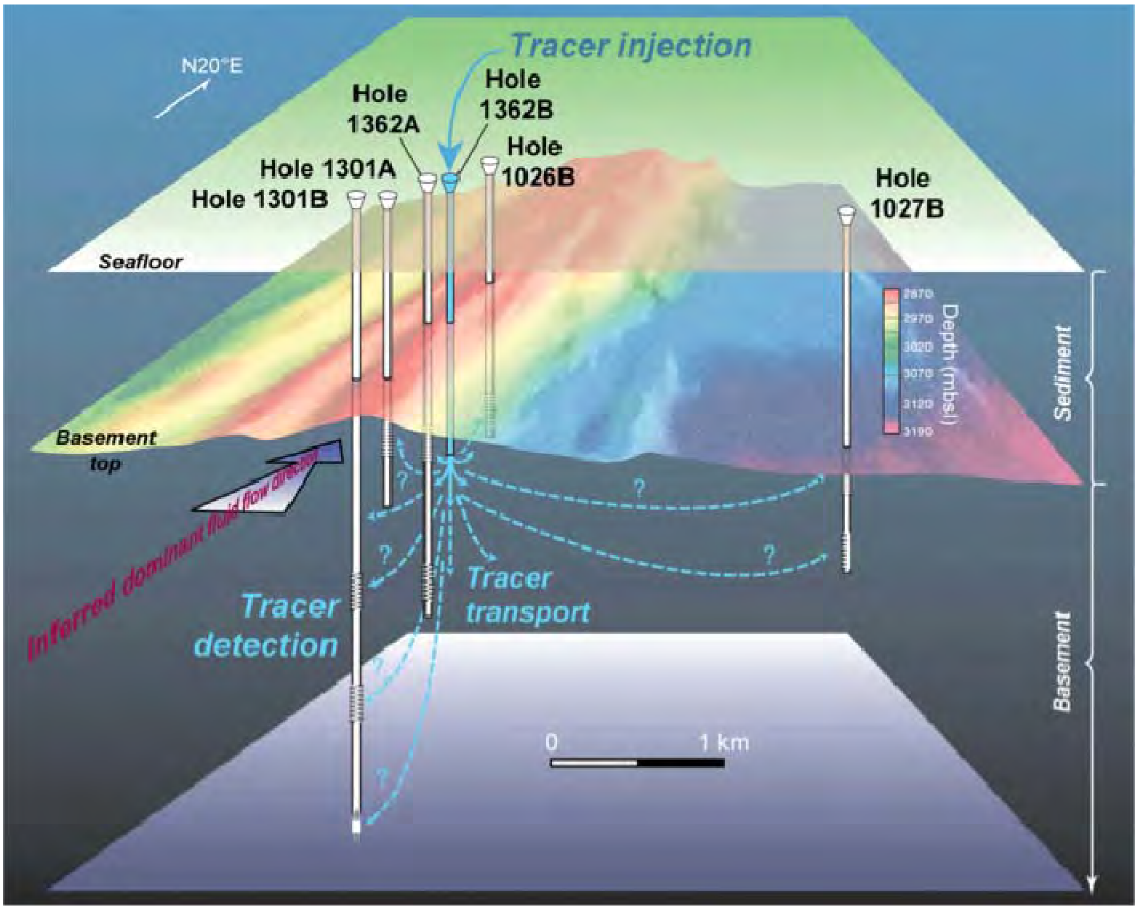


Figure 11: Prototype tracer experiment begun by IODP scientists in 2010, involving "CORK" observatories in multiple drill holes in mid-ocean ridge basalt lavas along the Juan de Fuca Ridge under the leadership of Prof. Andy Fisher of UCSC. This methodology could be used for pilot studies of CO_2 injection into submarine lithologies. Image, courtesy of J. Cowan, from keynote talk by Prof. Keir Becker of the University of Miami.

Ongoing CO_2 injection into mafic rocks (Matter, Gislason, McGrail)

Injection of CO_2 into pore space in basalts is one technique currently under development. This is underway in the Columbia River flood basalts as part of the DOE-affiliated Wallula Basalt Sequestration Pilot Project (Big Sky Partnership, DOE, USA). Another pilot project in Iceland, CarbFix, is scheduled to begin injection of CO_2 into basalts in Iceland in 2011. The Workshop benefited from a good engagement from Big Sky and CarbFix participants, as some of the principal scientists involved were members of the Steering Committee and gave keynote talks. These studies are of great interest because of the potentially enormous volumes of high porosity basalt overlain by sedimentary cap rocks in both offshore and onshore environments. Also, these techniques “split the difference” between (a) more or less conventional CO_2 injection into pore space, which has been applied to enhanced oil recovery for decades, and (b) new ideas about *in situ* mineral carbonation for CO_2 storage. There has been a growing recognition, for many applications of CO_2 injection into pore space, that injection wells for CO_2-rich fluid must be coupled with production wells for ambient aqueous fluid in pore space in order to achieve efficient storage.

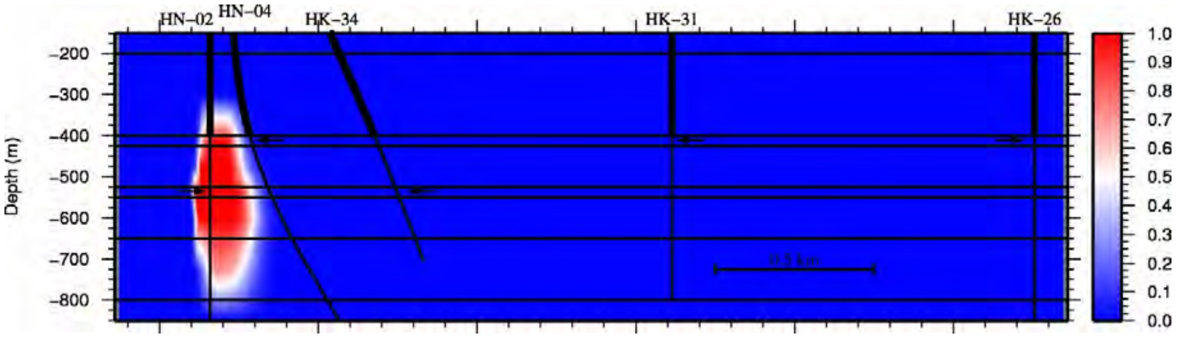


Figure 12: Model of CO_2 concentration (color scale) in pore fluid for the CarbFix experimental geometry, in a cross-section with injection at well HN-02 and production of ambient pore fluid from well HN-04 (injection and production 2 kg/s) after three years with 2.5 % porosity. Image from Edda et al. Contam. Hydrol. 2011.

Hydraulic fracture stimulation in geothermal, gas hydrate and mining applications (Baria, Bunger)

Effective, enhanced mineral carbonation in low porosity/permeability ultramafic systems will almost certainly require “hydraulic stimulation” of rock formations at depth. Hydraulic fracture has long been employed to enhance the flow of oil from reservoir rocks, and is being intensively developed – more systematically – for enhanced geothermal systems, *in situ* leaching of mineral deposits, stoping in underground mining, and extraction of gas from “tight” shale reservoirs with very low permeability. All of these applications, including in situ mineral carbonation, share similar requirements for creation or reactivation of a dense network of inter-connected fractures, with approximately uniform distribution of fluid flux throughout the network. The large, European Union geothermal pilot project at Soultz has demonstrated that relatively wide separation between injection and production wells minimizes the creation of “short circuits” guiding most of the fluid flow along a few favorable pathways. Experiments with hydraulic fracture of crystalline rocks in Australia use paired “straddle packers” and perforated casing to create ~ 1 m fracture spacing at a reasonable cost.

3. Summary of Working Group Discussions

Working groups had a variety of overlapping topics and goals. In order to avoid redundancy, we have summarized the main points of working group discussions using overarching categories that incorporate input from several different groups.

Characterizing potential mafic and ultramafic storage reservoirs

It is crucial to understand such factors as permeability, porosity, fracture size and frequency, mineralogy, and rock composition in any potential site for engineered mineral carbonation. However, the physical, mineralogical and chemical properties of potential reservoirs for solid storage of carbon in carbonate minerals are very poorly characterized, and their systematic (?) global variation with depth, and with geographical or tectonic setting is almost unknown.

Oddly, pioneering studies of carbonation in seafloor basalts as a function of depth in drill core recovered from the seafloor (e.g., research and review in Alt & Teagle GCA 1999) have been more extensive than potentially easier studies of on-land volcanic rocks. Even in peridotites, less commonly targeted for ocean drilling than basalts, our best information on "average" CO_2 contents as a function of depth comes from seafloor drilling (e.g., Kelemen et al. Ann Rev. Earth Planet. Sci. 2011, Früh-Green et al. AGU Monograph 2004) rather than from on-land investigations. Similarly, there has been more work on porosity and permeability in the volcanic, upper sections of typical oceanic crust, via dredging, drilling and field work in analogous ophiolite settings, than on sub-aerial basalt exposures with the notable exception of the potential nuclear waste site at Hanford in Washington State (US), and the ICDP drilling program in Hawaiian basalts.

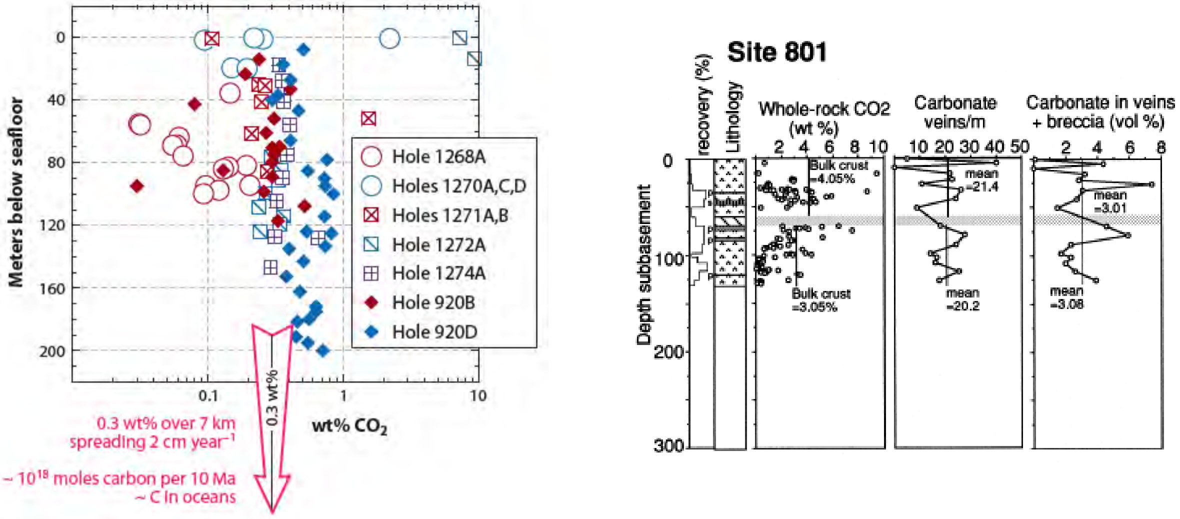


Figure 13: Variation of CO_2 contents and carbonate vein distribution as a function of depth in oceanic scientific drill holes. Right: CO_2 concentration in altered peridotite core samples from the Mid-Atlantic Ridge. Figure from Kelemen et al. Ann. Rev. Earth Planet Sci. 2011. Left: CO_2 concentration and carbonate vein abundance in drill core from mafic lavas in Atlantic Ocean crust. Figure from Alt & Teagle GCA 1999.

This situation has been changing as a result of the pilot studies of CO_2 injection into pore space in sub-aerial basalts, in Iceland and in the Columbia River basalts of Washington State

(US), which involves detailed characterization of rock properties with depth in an array of spatially associated boreholes.

Despite an overall intuition, supported by field observations at the surface, that peridotite reservoirs are substantially less permeable than basalts, there is almost no information on rock properties of ultramafic rocks as a function of depth below the surface. Again, this may soon change as a result of ongoing ICDP drilling in South African komatiites (ultramafic lava flows), and the proposed scientific drilling in the Samail ophiolite of Oman, for which ICDP has approved a planning workshop in late 2012 or early 2013. Still, these developments leave plenty of room for additional investigations of these important properties, both globally for a comprehensive understanding, and in specific, potential sites of carbon storage.

The evolution of mineralogy, composition and physical properties as a function of formation age is also very poorly known. An early hypothesis that the extent of mineral carbonation in seafloor basalts increases with plate age is now in question, and there is essentially no information on this topic for ultramafic lithologies. More generally, the distribution of seafloor ultramafic rocks remains poorly understood, and their extent at depth is almost unknown. Studies of these basic geological relationships, and the mineralogic and bio-geochemical evolution of these rocks during hydrothermal alteration in both sedimented and unsedimented ridge systems, should be a motivation for exploratory mapping via dredging and submersible studies, and included in the oceanic drilling research plans.

Characterizing natural mineral carbonation systems

It is hard to overemphasize the importance of understanding natural mineral carbonation systems, to facilitate design of engineered systems. There are three main reasons for this.

First, using laboratory kinetic data to predict rates of *in situ* mineral carbonation requires calibration using (at least) grain sizes applicable to target rock formations, or (better) rates of natural mineral carbonation at surface conditions.

Second, natural mineral carbonation systems hosted in ultramafic rocks (and mafic rocks?) remain active for tens to hundreds of thousands of years, avoiding negative feedbacks such as clogging of pore networks, armoring of reactive surfaces, and exhaustion of rock reactants along preferred fluid pathways. In order to design engineered systems that also bypass these barriers, it is essential to understand coupled reaction and fluid transport in these natural systems. In particular, fully carbonated peridotites (listwanites), and analogous, fully hydrated peridotites (serpentinites) have dense fracture networks (< 100 micron spacing) which are commonly symmetrical in three dimensions, suggesting that they form as a result of differential stress due to increasing solid mass during uptake of fluid components and decrease of solid density.

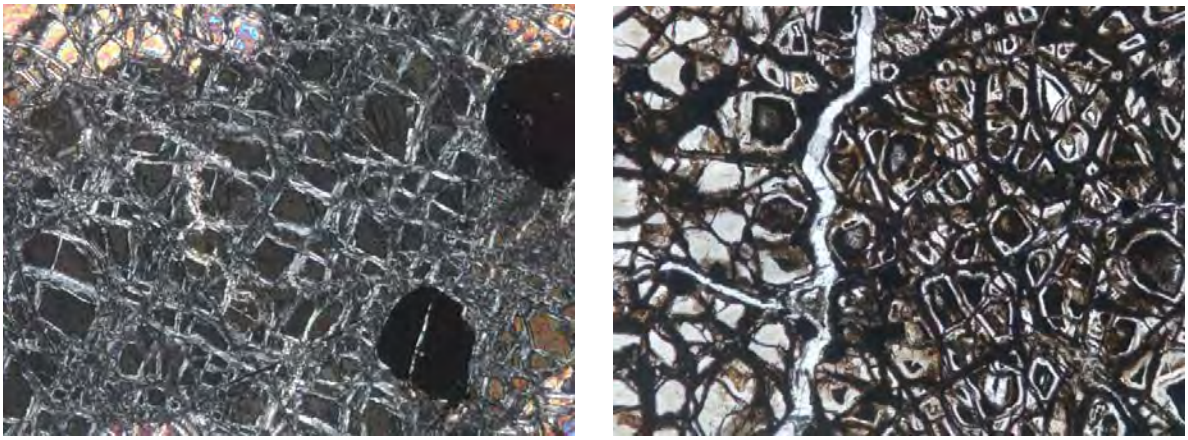


Figure 14: Photomicrographs of dense fracture networks hosting alteration veins in altered peridotite from the Samail ophiolite. Field of view ~ 1 mm for both photos. Right: Serpentine veins on fractures in unaltered olivine. Left: Composite serpentine and carbonate veins along fractures, surrounding fully hydrated pseudomorphs of olivine fragments. Photos: P. Kelemen.

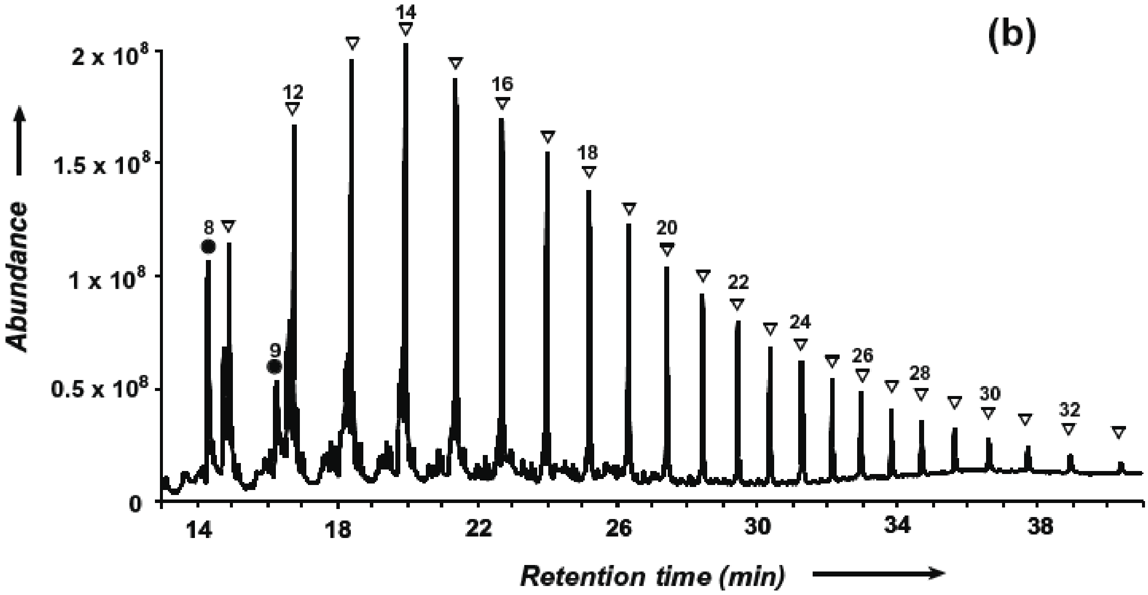
Third, when considering geologic capture as well as storage of CO_2, natural systems demonstrate that reaction of surface waters with ultramafic rocks (and mafic rocks?) removes almost all carbon from fluid products observed in peridotite-hosted, alkaline springs. This process is not *analogous* to proposed engineered methods, it *is the same as the proposed process*. Understanding how to initiate fluid convection through such systems is all that is required to produce the engineered replicas of the natural system.

Synergy with related research

There is currently great research interest and activity in a variety of processes involving carbonation and/or hydration of ultramafic and mafic rocks. Among the topics of greatest interest are the following:

First, oxidation of iron during peridotite hydration and carbonation leads to reduced fluid compositions with dissolved hydrogen (H_2) and reduced, dissolved carbon species such as methane (CH_4) and carbon monoxide. Fluids eventually become so reduced that they can precipitate native metal alloys such as awaruite (FeNi metal). While this has been understood for decades, renewed interest in these processes stems largely from new observations of natural systems (particularly, peridotite-hosted, submarine hydrothermal systems), quantitative experiments, and geochemical models indicating that (a) these ingredients facilitate chemosynthetic metabolism at the base of the food chain in the sub-surface biosphere, (b) reduced carbon species in aqueous fluid, and catalytic surfaces such as FeNi metal combine to form alkanes and alkenes on laboratory time scales (e.g., McCollom et al. GCA 2010). Abiotic production of organic polymers is of interest as a possible pathway for the origin of life, as an analogy for chemosynthetic metabolism, and as a possible source of hydrocarbon fuel.

Figure 15: Left: Burning methane emitted from hydrating peridotite along the coast of Turkey near Mt. Chimaera. According to legend, lightening ignited the methane to form a beacon used by Mediterranean mariners for millennia. Bottom: Total ion chromatograms from GC–MS analysis of run products of experiments on reduced, carbon-monoxide-bearing aqueous fluids with FeNi metal catalysts. Inverted triangles identify n-alkanes, while closed circles are n-alkan-1-ols. Smaller peaks surrounding each n-alkane are primarily n-alkenes. Numbers indicate the carbon chain length of the compounds. Figure from McCollom et al. GCA 2010.



Second, the near surface rocks on early planets, in our solar system and elsewhere, may commonly be composed of undifferentiated, mafic to ultramafic rocks that are exposed to CO_2-rich atmospheres. For example, based on spectroscopic studies, ancient, carbonated peridotites were recently discovered on the surface of Mars. Thus, study of mafic and ultramafic rock alteration provides insight into planetary evolution.

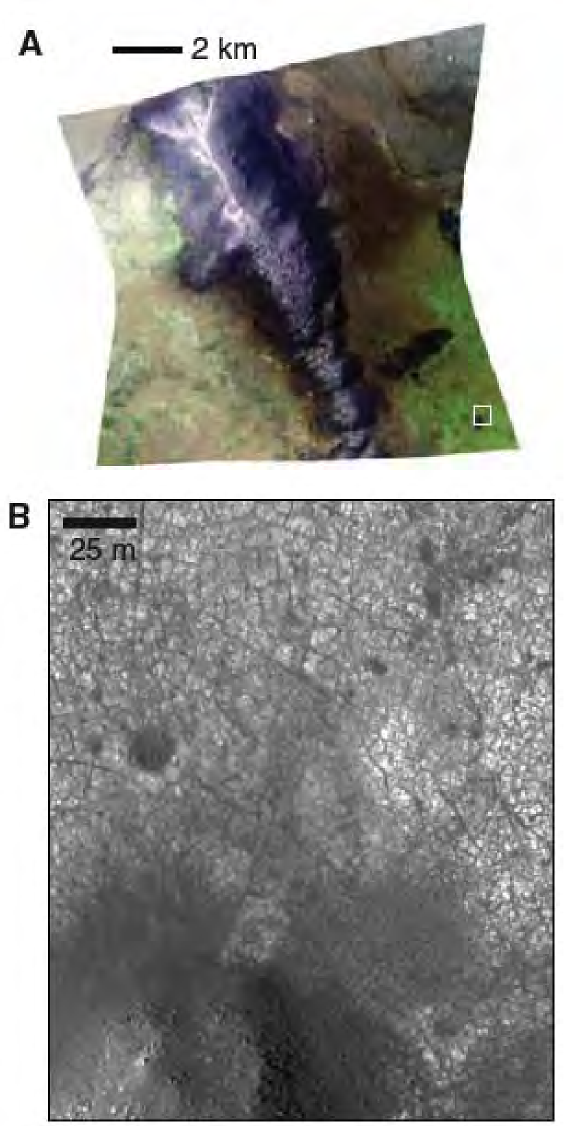


Figure 16: Images of carbonated ultramafic rocks on the surface of Mars, from Ehlmann et al. Science 2008. In A, carbonate is green, olivine is yellow to brown, phyllosilicate is blue, and an overlying mafic unit is purple. The small rectangle outlines the area of (B). The closeup in B shows carbonated peridotite, which is overlain by a mafic knob at the bottom of the image.

Third, the presence of hydrated peridotites is often invoked as an important factor in large scale geodynamic processes. The hydrous magnesium silicate mineral serpentine may control the rheology of subduction zone thrusts, the strength of rifting oceanic plates, the nature of earthquakes and localized deformation along transform plate boundaries, the buoyancy and longevity of the “cold nose” in the mantle wedge above subduction zones, and so on. Carbonation of peridotite often leads to the formation of a hydrous magnesium silicate called talc, more silica-rich than serpentine. Talc has the lowest known coefficient of friction among rock forming minerals, and may play a key role in fault zone lubrication in a number of settings. Understanding the process that controls peridotite alteration, particularly the presence of localized versus regionally diffuse hydration and carbonation, is crucial to provide a sound theoretical basis for these geodynamic hypotheses.

Finally, characterizing the degree of natural mineral carbonation, and other hydrothermal alteration, will have the added value of leading to a better understanding of the global carbon cycle. It has been proposed that carbonation of seafloor basalts consumes a mass of carbon equivalent to the carbon content of the ocean every 1 million years (e.g., Alt & Teagle GCA 1999) and that carbonation of peridotite exposed on the seafloor consumes an equivalent mass every 10 million years (Kelemen et al. Ann. Rev. Earth Planet. Sci. 2011), but these estimates are – at best – only accurate to within an order of magnitude.

All of these lines of inquiry are closely linked, and well-suited to collaborative, interdisciplinary research focused on studies of drill core, observations in drill holes, and exploration of the surrounding rocks. From a practical point of view, they also offer the potential for highly diversified sources of research funding from a broad range of national and international agencies and private foundations.

Site selection criteria for drilling related to *in situ* storage of CO_2

Elevated temperature, up to ~ 120 to 250°C of olivine, enhances mineral carbonation kinetics, as does elevated partial pressure of CO_2. Thus, potential advantages of in situ mineral carbonation methods include (a) insulation of the reacting volume from low temperature surface conditions by overlying rocks with low thermal conductivity, (b) preservation of high fluid pressures due to lithostatic or hydrostatic load from overlying rocks and fluid networks, and (c) presence of elevated temperature at depth, especially in areas with an elevated geothermal gradient. The geothermal gradient below ~ 100 m depth but in the upper few km of the Earth, away from plate boundaries, generally ranges from about 15 to 30°C per km depth. Thus, for an area with an average surface temperature of 20°C, 120°C might be reached at ~ 3 to 10 km depth. Near plate boundaries with active volcanism, especially along oceanic spreading ridges, the gradient can be much higher. On the other hand, drilling costs per meter of depth rise almost exponentially with increasing depth. Such conditions dictate selection of a site with a high geothermal gradient, when possible.

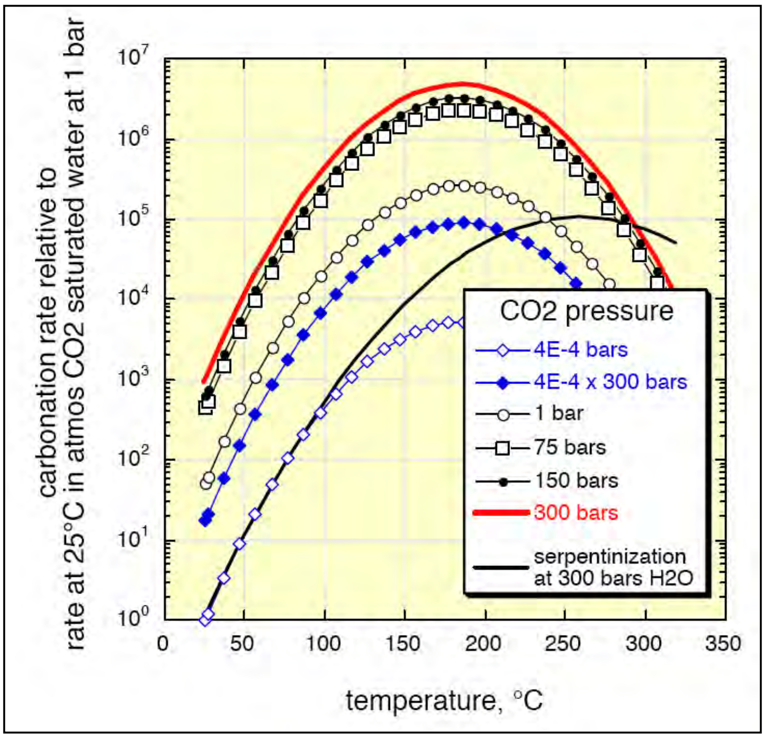


Figure 17: Carbonation rate enhancement, relative to the rate at 25°C and atmospheric P_{CO2}, as a function of elevated temperature and partial pressure of CO_2. Figure from Kelemen & Matter, Proc. (US) Nat. Acad. Sci. 2008, who fit experimental data on the rate of olivine carbonation from O'Connor et al., DOE Final Report 2004, and the rate of olivine hydration from Martin & Fyfe CMP 1970.

For CO_2 capture from stationary industrial sources, it is obviously desirable to choose carbon storage reservoirs as near as possible to the source. However, this criterion can be overemphasized. Though the initial capital cost is high, transportation of fluids through pipelines is surprisingly inexpensive, on the order of $1 to $8 per ton of CO_2 per 250 km at rates of 40 to 5 megatons per year, respectively, for the mature CO_2 transportation network in the US (IPCC Special Report on Carbon Dioxide Capture and Storage, 2005). However, note that these low costs at high flow rates require a downstream storage site sufficient to consume the delivered flux. Tanker shipment of supercritical CO_2 is substantially more costly, though use of otherwise empty LPG tankers on their return from producer to consumer is sometimes discussed.

Drilling and injection costs are substantially higher for seafloor compared to onland sites, by approximately a factor of ten for comparable depths and applications. On the other hand, environmental and societal impacts of leakage and ground deformation may be substantially reduced at submarine sites. It may be optimal to access shallow, submarine storage reservoirs via drilling from the shoreline, as schematically illustrated in Figure 5. Pipelines may also be used for CO_2 transport to near-shore, submarine sites.

The presence of an impermeable caprock is commonly invoked as an essential ingredient for carbon storage sites. This is indeed desirable. However, note that this criterion is far more important for sites where long term storage will be in the form of buoyant, CO_2-rich (or methane-rich!) fluids. Where storage sites are deep and cold, as in ancient, near-seafloor lavas, CO_2-rich fluids will be denser than aqueous fluids, so that the presence of an impermeable cap is less important. Similarly, where rapid mineral carbonation takes place, and long term storage will be in the form of inert, stable carbonate minerals, the presence of a low permeability caprock remains advantageous, but an *impermeable* cap may not be required.

Consensus was reached on the need to support the development of experimental CO_2 storage projects in mafic and ultramafic rock formations. Only field-scale tests will allow evaluation of the different methods envisaged for delivering and storing CO_2. While injection of CO_2-rich fluids into mafic lava formations is underway, there are no pilot sites for carbon storage in ultramafic rock formations yet. Studies at such a site would be an invaluable complement to the two on-going pilot projects in mafic lavas.

As a first step toward future off-shore and on-land pilot studies, the participants defined ideal characteristics for ***experimental sites***, where an engineered pilot study can be carried out, and for ***study areas***, where information can be gathered to address scientific and technical requirements for the pilot site:

(i) Study areas and experimental sites should be well-surveyed areas (geophysics, hydrogeology, availability of baseline monitoring over years, e.g. to control seasonal variability) where subsurface biosphere can be (is) characterized; multiple holes are necessary to allow cross-hole studies (to allow tracer tests for example);

(ii) Study areas should allow observations relevant to other scientific objectives, e.g. paleo-oceanographic and tectonic objectives for oceanic drilling, sub-surface biosphere, present-day weathering, melt extraction and crustal formation studies for onland drilling.

(iii) Experimental sites should be close to CO_2 production sites, have a sufficient permeability to allow large of CO_2 fluxes, have a seal (e.g., sedimentary cap-rock) and also, be scalable to larger studies. If the North Sea injection project by Statoil at Sleipner is taken as a benchmark, an “pilot site” should involve injection of ~ 1 kT CO_2 per year, whereas a “full-scale site” would involve injection of ~ 1MT per year.

(iv) The sub-surface at experimental sites should preferably be dominantly composed of fresh igneous minerals (olivine, pyroxenes, plagioclase) to favor reactivity (heavily-altered hydrothermal systems should be avoided);

(v) Concerns over permitting and societal acceptance may be addressed via creation of offshore CO_2 storage reservoirs. To limit costs, sites should preferentially be close to land with drilling from the shoreline if possible;

(vi) Where storage of CO_2-rich fluids in pore space will be as important as storage in solid carbonate minerals, and where achieving rapid mineral carbonation at high temperature is not a priority, sub-seafloor storage sites should be in deep water (at water depths>2700m, CO_2 is denser than seawater at < 10°C, reducing the need for caprock).

Possible target areas were proposed for experimental and pilot sites. Potential sites abound on-land in basalts and flood basalts. The most favorable basaltic sites would allow a combination of CO_2 storage and hydrocarbon research (e.g., China, Norway, Kudu Gas fields, Deccan …). Ultramafic lavas (komatiites), although they represent only small volumes, could be attractive local storage reservoirs (e.g., southern India, South Africa, Australia). Proposed off-shore study areas in basalts are Juan de Fuca and the 504B/896 area (drilled and open thus allowing cross hole studies), and for experimental sites, the deep pyroclastic zones adjacent to ocean islands (e.g., Iceland) and flood basalts (close to shore such as the north Atlantic), where sparse submarine observations can be supplemented by more extensive studies of more easily accessed subaerial exposures.

Possible on-land and near-shore, submarine ultramafic massifs – both study sites and experimental sites – are in the Samail ophiolite of Oman and the United Arab Emirates, the US Pacific Northwest (particularly in northern California, where the Trinity peridotite extends in the subsurface beneath the Cascades volcanic chain, and where some peridotite massifs of the Franciscan subduction mélange are in the Geysers region, both with well-known, elevated geothermal gradients), Baja California, Nicoya Peninsula in Costa Rica, New Caledonia, southeastern Spain (Ronda) and northern Morocco (Beni Boussera), Adriatic, Cyprus, Tuscany (geothermal), and North Queensland, Australia (Marlborough which is near many coal-fired electric power plants). Papua New Guinea hosts large peridotite massifs, some of which extend beneath volcanic chains, but was generally considered to be too remote.

Figure 18: Dark colored peridotite in the mantle section of the Cretaceous Samail ophiolite, unconformably overlain by Eocene limestone, dipping offshore along the northern coast of Oman near the capital city of Muscat. Photo from http://www.beauxsonges.fr/IMG/jpg/H0H7YH1W1111111.jpg.

Potential, offshore, deeper-water study areas in ultramafic basement were suggested: *Natural hydrothermal systems*: peridotite-hosted mineral carbonation processes are ongoing at the Lost City, Rainbow, Galicia Margin, and the ultraslow spreading Lena Trough hydrothermal systems. *Proposed experimental sites* in the oceans were mostly near shore ultramafic formations associated with the afore-mentioned, large orogenic peridotite massifs.

General site selection criteria for geological *capture* and storage of CO_2

Geologic capture of CO_2 by reaction of surface waters with ultramafic rocks may be an effective alternative to industrial capture of CO_2 followed by geologic storage. Site selection for this approach differs significantly from selection of a site for injection of fluids with high CO_2 concentrations. For example, a low permeability caprock may be unnecessary. Furthermore, because of the low concentration of CO_2 in surface waters, it will be necessary to circulate a huge volume of water through the rock reactant to capture a significant mass of carbon. Thus, though CO_2 uptake will be supply limited even at low temperature and correspondingly slow reaction rates, a high geothermal gradient will be desirable to drive thermal convection and escape the cost of pumping.

Obviously, the ocean represents a huge reservoir of surface water equilibrated with atmospheric CO_2, whereas in most places fresh water is relatively scarce and in high demand. However, extraction of CO_2 from, e.g., oceanic bottom water will have no impact on atmospheric greenhouse gas concentrations, so it is necessary to return CO_2-depleted fluid to the sea-surface, where it will draw down CO_2 from the air. Furthermore, because fluid will be heated during reaction with sub-surface rocks, it is desirable to extract heat from the produced, CO_2-depleted fluid – with generation of geothermal power as a possible by-product – before returning the fluid to the surface ocean.

All of these considerations suggest that near-shore sites are desirable.

Enhanced weathering of mafic and ultramafic mine tailings, sediments, etc

Although the workshop was focused on the potential contribution of scientific drilling to CO_2 storage, a keynote address by Prof. Greg Dipple of the University of British Columbia focused on “enhanced weathering” of ultramafic mine tailings, without drilling. Several other conference participants made poster presentations that also focused on enhanced weathering of ultramafic mine tailings or sediments rich in ultramafic clasts, either at focused sites (e.g., tailings piles) or via broadcast of ultramafic mineral powder over extensive areas of the Earth’s surface.

Figure 19: Abundant sources of medium- to fine-grained ultramafic reactants could be used in enhanced weathering for mineral carbonation. Right: Green sand beach in Hawaii, where olivine weathers out of a cinder cone. Left: Serpentinite mine tailings from an abandoned asbestos mine in northern Vermont. From http://farm4.static.flickr.com/3446/3894521827_d54dfc96b1.jpg and http://www.chemexplore.net/asbestos-tailings-Vermont.jpg.

Unlike sub-surface, *in situ* mineral carbonation techniques which require a lot of additional site characterization, lab experiments, and theoretical calculations, proposed methods of enhanced weathering of mafic and ultramafic mine tailings are ready for full-scale tests. Workshop participants were pleasantly surprised by documentation of rates of natural carbonation of serpentine-rich mine tailings that appear to be much faster than laboratory rates, perhaps because natural serpentine fibers have high ratios of reactive surface area to volume. These studies would not only document the potential for this specific technique, and provide an early example of successful geological storage of carbon in solid minerals, but would also provide valuable data for development of techniques for enhanced weathering via broadcast of ultramafic powder, and for *in situ*, sub-surface mineral carbonation. In Oman, powdered ultramafic material is a widespread waste product of chromite mining, which could be used in pilot experiments at a very low cost.

Kinetics / fluid flow / reaction / efficiencies

Reactivity of mafic and ultramafic systems, and resulting changes of their properties over time, will strongly depend on the nature of the infiltrated fluid, that is a fluid far from equilibrium with the rock in the case of CO_2 injection (e.g., supercritical CO_2, CO_2 enriched / saturated water or brine) or a fluid close to equilibrium with atmospheric CO_2 – and closer to equilibrium with rocks – in natural hydrothermal systems. Natural mineral carbonation is inextricably linked with mineral hydration, occurring mainly in near-surface hydrothermal and weathering environments. Inasmuch as mineral hydration reduces the available free energy for mineral carbonation, natural processes should be studied – and engineered techniques developed – with an eye to minimizing hydration of rock reactants.

Studies of reaction rates in natural systems should characterize the processes limiting/enhancing transport and carbonation efficiency over a range of temperatures and pressures, for conditions in on-land weathering to deep-seated sub-seafloor hydrothermal sites, including reaction kinetics and rate-limiting processes (reaction rims, exhaustion of reactants), role of climate, substrate materials, catalysis, reactive surface area, and the biological role in mineral dissolution and precipitation.

Monitoring, verification and accounting

Monitoring, Verification and Accounting (MVA) procedures will be key ingredients for the development of any carbon storage process or test site. Industrial users and society will need confidence in the permanence of CO_2 storage, protections against well / reservoir leakage, and methods to verify the amounts of CO_2 stored (for safety and economic standpoints). There will be a need for MVA for health, safety and environmental concerns (e.g., to protect groundwaters and ecosystems) but also for assignment of “carbon credits” and payment. There will need to be strong public perception that mineral carbonation projects are safe and for investors that they are effective and profitable. One of the key challenges in monitoring of CO_2 emissions at the surface near storage sites will be to distinguish between CO_2 derived from industrial versus natural sources. Though it is obvious, it is necessary to point out that monitoring, verification and accounting are greatly eased where medium- to long-term storage is in the form of inert, stable, dense carbonate minerals rather than mobile, buoyant CO_2-rich fluids.

Specific designs for borehole tools and techniques being developed to study ultramafic and mafic lithologies over long periods of time in locally extreme conditions (e.g., sub-seafloor) during scientific drilling programs (e.g., CORK pressure monitoring and CORK OsmoSamplers for chemical monitoring) will be a major asset to developing MVA methods in ultramafic and mafic rocks. The expertise in long term management of projects and boreholes, developed over the years by the scientific drilling community, will also be useful for developing the integrated engineering and scientific network necessary to develop any future CO_2 storage projects.

Environmental and safety issues

Environmental concerns about CO_2 storage include: (a) displacement of saline water from subsurface pore space, with potential for migration of saline fluids into potable water supplies. Similar issues arise for migration of fluids (b) used in hydraulic stimulation (mainly water but with a few percent additives whose exact nature is often proprietary) or (c) with dissolved metals derived from peridotites and basalt host rocks (e.g., Ni, Cr, As, Pb, U, Rn, F). Additional concerns include (d) the potential for increased earthquake activity due to “lubrication” of fractures by injected fluids, and (e) the potential for significant surface deformation associated with increasing fluid or solid carbonate mineral volume at depth.

Active and transparent public outreach and engagement will be essential, even for relatively small test projects. The primary often-repeated advice from workshop participants currently involved in the CarbFix and Big Sky test projects is to develop a formal public engagement plan with project partners and execute it from the very outset of planning. Scientists need to commit to regular, open and transparent communications with stakeholder groups and local media.

Again, where reaction kinetics permit medium- to long-term storage of CO_2 in solid form, it should be relatively easy to persuade stakeholders that hazards from leakage are minimal.

Scientific organization

Despite its potential, particularly for permanent CO_2 storage in solid carbonate minerals, development of CO_2 storage in mafic and ultramafic formations is still in its infancy. Only two pilot experiments have begun in basaltic reservoirs, compared to more than 20 pilots projects in sedimentary reservoirs, including at least 6 in Europe (Source : International Energy Agency Agency Greenhouse Gas R&D Programme). This is due mainly to oil industry familiarity with injection of fluids into pore space in sedimentary formations, and a corresponding lack of interest in other potential storage reservoirs. While CO_2 injection is a routine part of Enhanced Oil Recovery, the fate of CO_2 injected into mafic and ultramafic rocks, and the associated costs (economic and environmental) and efficiencies, are comparatively poorly known. Research and development on *in situ* mineral carbonation in these formations may often "fall between two chairs": it can seem too applied for support from basic science funding agencies, and too poorly understood for full-scale pilot projects.

Nevertheless, the strong potential for CO_2 storage in these rock formations is clearly recognized by the scientific community. The development of new techniques adapted for long-term geological CO_2 storage demands both fundamental research on the physical, petrological and bio-chemical processes in natural and enhanced hydrothermal systems, and a strong interaction with industry and society, to meet economic, environmental and societal demands. This program for research and development will need the development of planning structures and networks in which scientists and engineers to work together regularly.

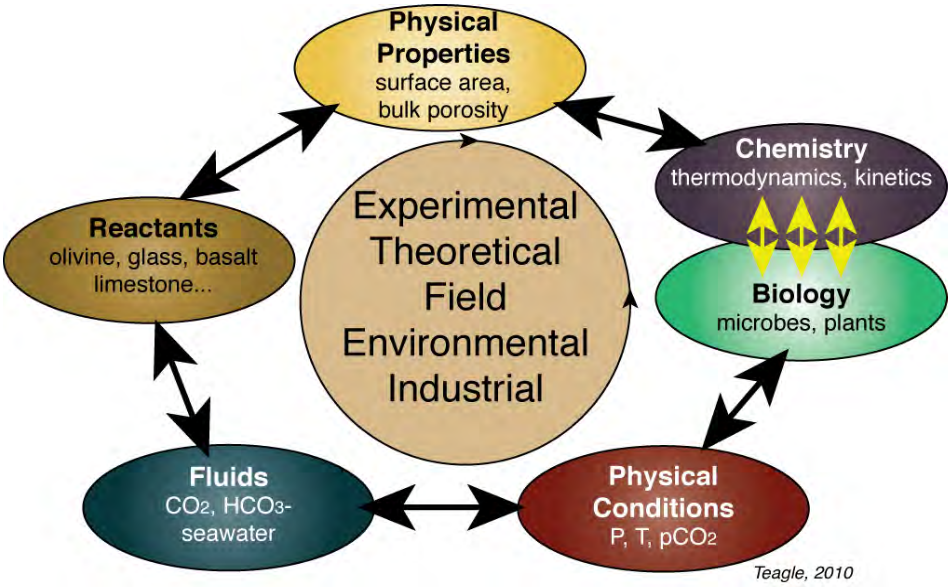


Figure 20: Flow chart summarizing the research and technological requirements for the development of geological storage in mafic and ultramafic rock formations. Image from keynote talk by Prof. Damon Teagle.

During the workshop, we discussed development of networks to couple fundamental research on enhanced mineral carbonation techniques (such as in mine tailings) with ongoing, complementary studies of hydrothermal alteration and weathering, and of chemosynthetic biological communities in these environments, and applied technologies of CO_2 storage. Several national (e.g., NSF, DOE) and international research agencies (e.g., EU funding agencies) could help to develop such integrated research networks.

The collaborative efforts of ICDP and IODP will be needed to assess and then overcome the technological challenges involved in the development of carbon storage in ultramafic and mafic reservoirs. Scientific drilling will be an invaluable asset to tackle one of the major challenges for the development of carbon storage, understanding how to apply lab and modeling studies to full-scale, engineered, *in situ* systems.

Geological carbon capture & storage and, more extensively, global carbon fluxes are also topics of interest for other scientific initiatives, such as the Deep Carbon Observatory (DCO). The DCO is a recent multidisciplinary and international initiative dedicated to the study of Earth's deep carbon cycles. One of its research themes is the study of deep carbon reservoirs to provide information for design of engineered CO_2 storage (Energy, Environment and Climate Working Group). A workshop on "Reaching the Mantle Frontier: Moho and Beyond" at the Carnegie Institution of Washington recently explored the possible synergies between the scientific targets of DCO and IODP.

Finally, immediately after our Workshop, an international group of scientists submitted a proposal for an ICDP sponsored workshop to develop a full proposal for scientific drilling in the Samail ophiolite in Oman. Our proposal was successful, and the ensuing planning workshop will be held in Oman in late 2012 or early 2013. The Samail ophiolite is composed of mafic and ultramafic rocks formed at a submarine spreading center, via processes very similar to those at mid-ocean ridges today. This multi-disciplinary effort will address several objectives, including a focus on characterizing past hydrothermal modification, present day alteration processes, physical properties such as permeability and fracture size-frequency distribution, the deep biosphere, and the potential for acceleration to achieve carbon capture and storage via *in situ* mineral carbonation. This proposal, with lead PI Peter Kelemen, has 22 formal proponents, including Dr. Ali Al Rajhi, Director of the Geological Survey of Oman and Associate Director General of Minerals in the Ministry of Commerce and Industry, and Prof. Sobhi Nasir, Head, Geology Department, Sultan Qaboos University. The proponents and a larger group of co-proponents include scientists from Australia, Canada, France, Germany, Italy, Japan, Oman, Switzerland, the UK and the US. It is anticipated that participation by representatives of the Omani Ministry of the Environment and Ministry of Water Resources will be essential to design an effective strategy for scientific drilling in Oman.

Conclusions

A key outcome of this workshop was the formulation of integrative scientific questions and the identification of potential implementation approaches. Five key conclusions were reached.

1. The potential for several different, engineered mineral carbonation methods should be explored *in parallel*, by integrated, international research networks, including (a) carbonation of ultramafic mine tailings and sediments, (b) *in situ* carbonation of ultramafic rocks (peridotite), and (c) *in situ* carbonation of mafic rocks (basalt). No one can foresee the size or urgency of the societal demand for CO_2 storage in the coming century, nor is it possible to predict the outcome of ongoing research on alternative or complementary methods.

2. It is necessary to understand the physical properties of potential mineral carbonation sites. Specifically, it is essential to quantify permeability, porosity, mineralogy (igneous minerals, plus extent and nature of existing alteration), fracture toughness and other material properties as a function of lithology and depth.
3. It is necessary to understand coupled chemical reaction and fluid transport in natural mineral carbonation systems better, especially in two key areas.
4. Scientific drilling has two key roles to play, (a) study of natural processes throughout the world, and (b) characterization of potential sites for CO_2 storage experiments.
5. The scientific community will probably need to take the lead in mineral carbonation research in the near future, developing and quantifying practical methods for use by government and industry when a consensus arises on the need for these techniques.