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

Conveners:

Marguerite Godard, Peter Kelemen, Sobhi Nasir, and Damon Teagle

Steering committee:

M. Godard[1], P. Kelemen[2], S. Nasir[3], D. Teagle[4], A. Al Rajhi[5], Wolfgang Bach[6], Keir Becker[7], A. Bonneville[8], Greg Dipple[9], Gretchen Früh-Green[10], Sigurdur Gíslason[11], Dave Goldberg[2], Philippe Gouze[1], Marc Hesse[12], Benoit Ildefonse[1], Juerg Matter[2], Philippe Pézard[1], Kiyoshi Suyehiro[13].

[1]CNRS/UM2, France; [2]LDEO, USA; [3]SQU, Oman; [4]NOCS, UK; [5]OGS, Oman; [6]MARUM, Germany; [7]RSMAS, USA; [8]PNL, USA; [9]UBC, Canada; [10]ETHZ, CH; [11]UI, Iceland; [12]UTexas, USA; [13]IODP-MI, Japan

Sponsors:

Integrated Ocean Drilling Program Management International, Inc. (IODP-MI), the International Continental Scientific Drilling Program (ICDP), the European Science Foundation (Magellan Fund), InterRidge, Sultan Qaboos University (SQU), UK-IODP, US National Science Foundation, US Consortium for Ocean Leadership.

Contents

Summary

1. Introduction

- Motivation for this workshop
- Mineral carbonation in mafic and ultramafic rocks
- Support
- Participation
- Goals

2. Keynote Lectures

- A perspective from chemical engineering (Darton)
- Can mineral carbonation play a role in carbon capture and storage? (Teagle, Kelemen, Oelkers, Gouze, Dipple, Jamtveit)
  - o *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)*
  - o *Volume changes during hydration and carbonation processes and feedback effects on the mechanical and hydraulic properties of the media.*
- Characterization of hydrodynamic properties before, during and after injection (Becker)
- Ongoing CO_2 injection into mafic rocks (Matter, Gislason, McGrail)
- Hydraulic fracture stimulation in geothermal, gas hydrate and mining applications (Baria, Bunger)

3. Summary of Working Group Discussions

- Characterizing potential mafic and ultramafic storage reservoirs
- Characterizing natural mineral carbonation systems
- Synergy with related research
- Site selection criteria for drilling related to *in situ* storage of CO_2
- General site selection criteria for geological *capture* and storage of CO_2
- Enhanced weathering of mafic and ultramafic mine tailings, sediments, etc
- Kinetics / fluid flow / reaction / efficiencies
- Monitoring, verification and accounting
- Environmental and safety issues
- Scientific organization

Conclusions

Appendices

Appendix A – Workshop Agenda
Appendix B – Workshop Participants
Appendix C – Abstracts of posters (and white papers)
Appendix D – Lecture presentation files
Appendix E – Field guide

Photograph of the conference participants:

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.

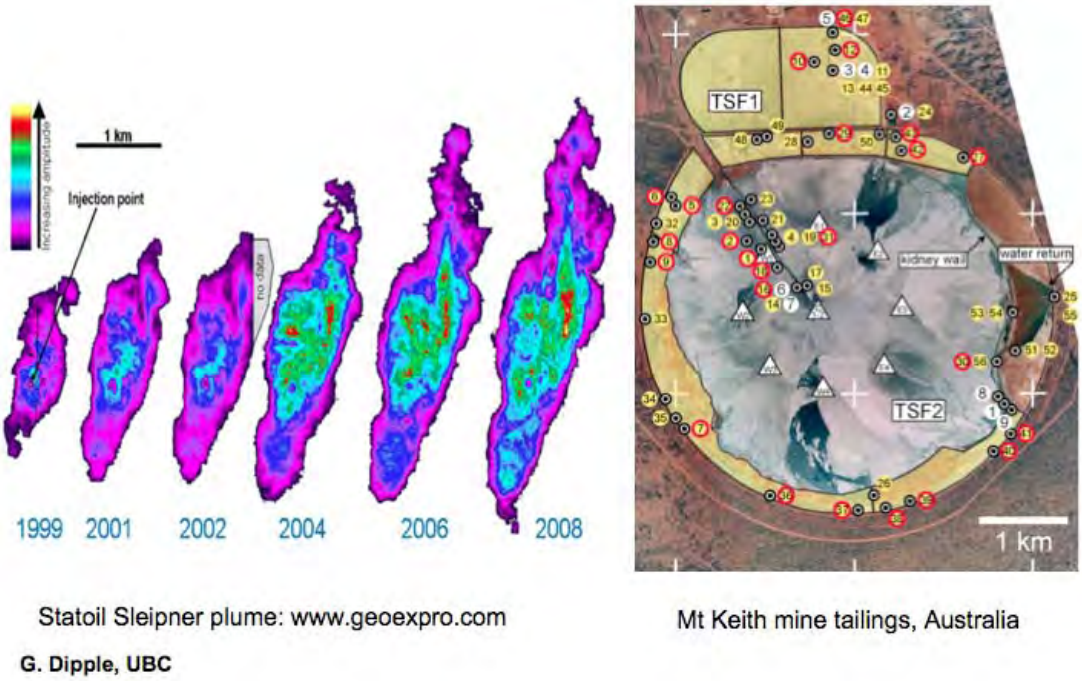


Figure 1: Comparison of plume of CO_2 injected into subsurface pore space, about 1 km below the seafloor at Sleipner (Statoil, North Sea), compared to the ultramafic tailings at the Mt Keith Nickel mine (Australia) at approximately the same scale. Engineered mineral carbonation at Mt. Keith might achieve 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.

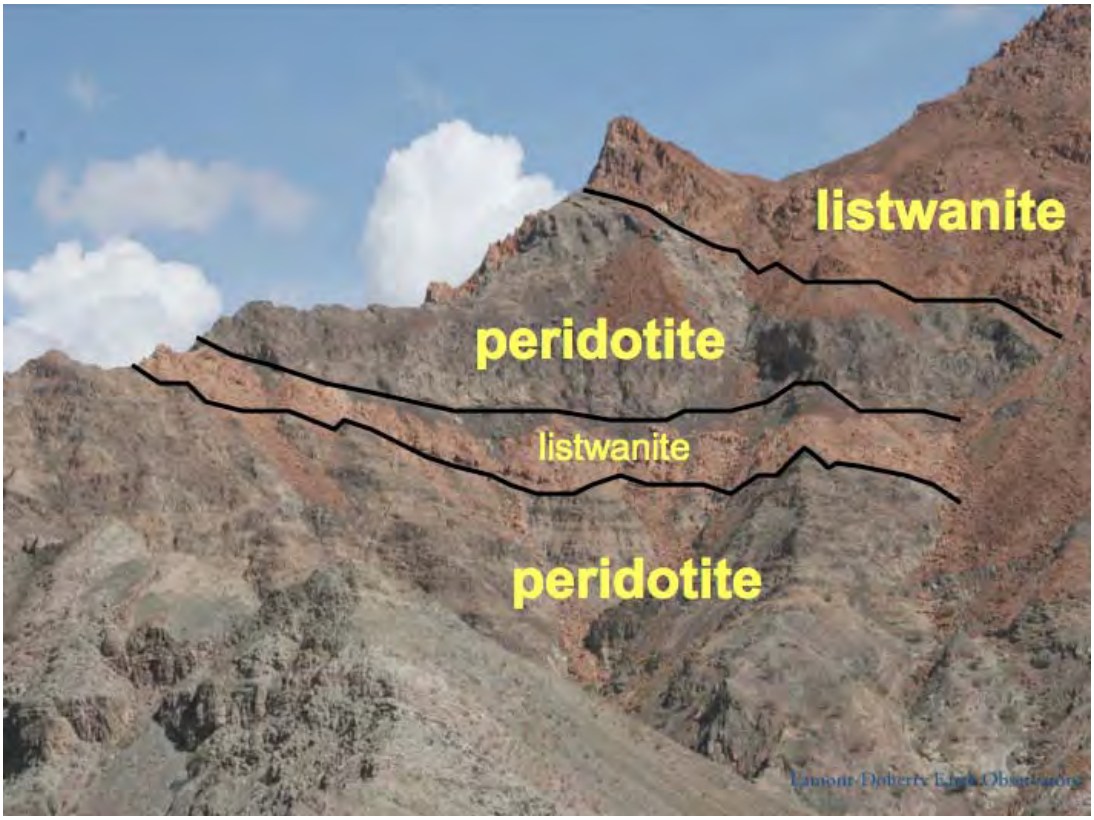


Figure 3: Red bands of fully carbonated peridotite (listwanite, composed of magnesite ($MgCO_3$), quartz, and chromian spinel) in light green, partially serpentinized peridotite on MoD Mountain near Fanjah, Oman, visited on post-conference field trip. The lower band is about 15 meters thick, the upper 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.

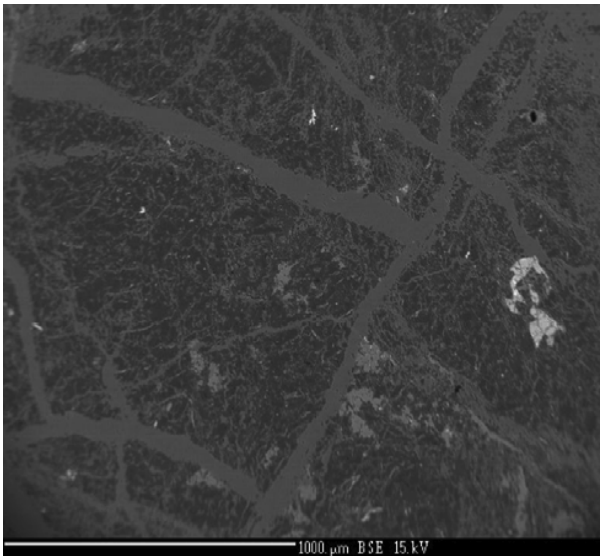
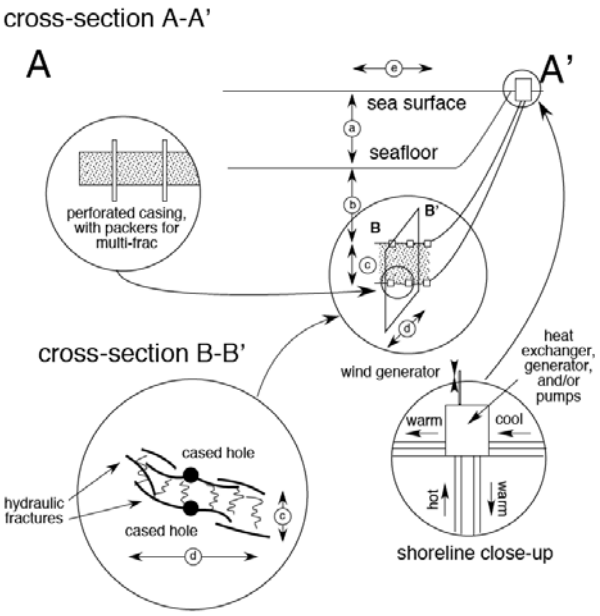


Figure 4: Back-scatted electron image of fully carbonated peridotite (listwanite), composed of magnesite (magnesium carbonate, $MgCO_3$, dark grey matrix), quartz (light grey veins showing hierarchical, cross-cutting relationships, filling cracks with spacing < 100 microns) and relict chromian spinel (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	$Mg_2SiO_4 + 2CO_2$	=	$2MgCO_3 + SiO_2$	**~7**
	Mg-olivine		**Magnesite** + Quartz	
~10	$CaMgSi_2O_6 + 2CO_2$	=	$CaMg(CO_3)_2 + 2SiO_2$	**~9**
	Mg-clinopyroxene		**Dolomite** + Quartz	
~23	$CaAl_2Si_2O_8 + CO_2 + 2H_2O$	=	$CaCO_3$ +	**~8**
	Ca-Plagioclase		$Al_2Si_2O_5(OH)_4$	
			Calcite + Kaolinite	
~9	$\{Na_{0.08}K_{0.01}Ca_{0.26}Mg_{0.28}Fe^{II}_{0.17}$		$(CaMgFe)_2(CO_3)_2$ +	**~9**
	$Fe^{III}_{0.02}Ti_{0.02}Al_{0.36}SiO_{3.45}\}$		clays + accessory	
	Basaltic glass + $2CO_2$		phases	

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)

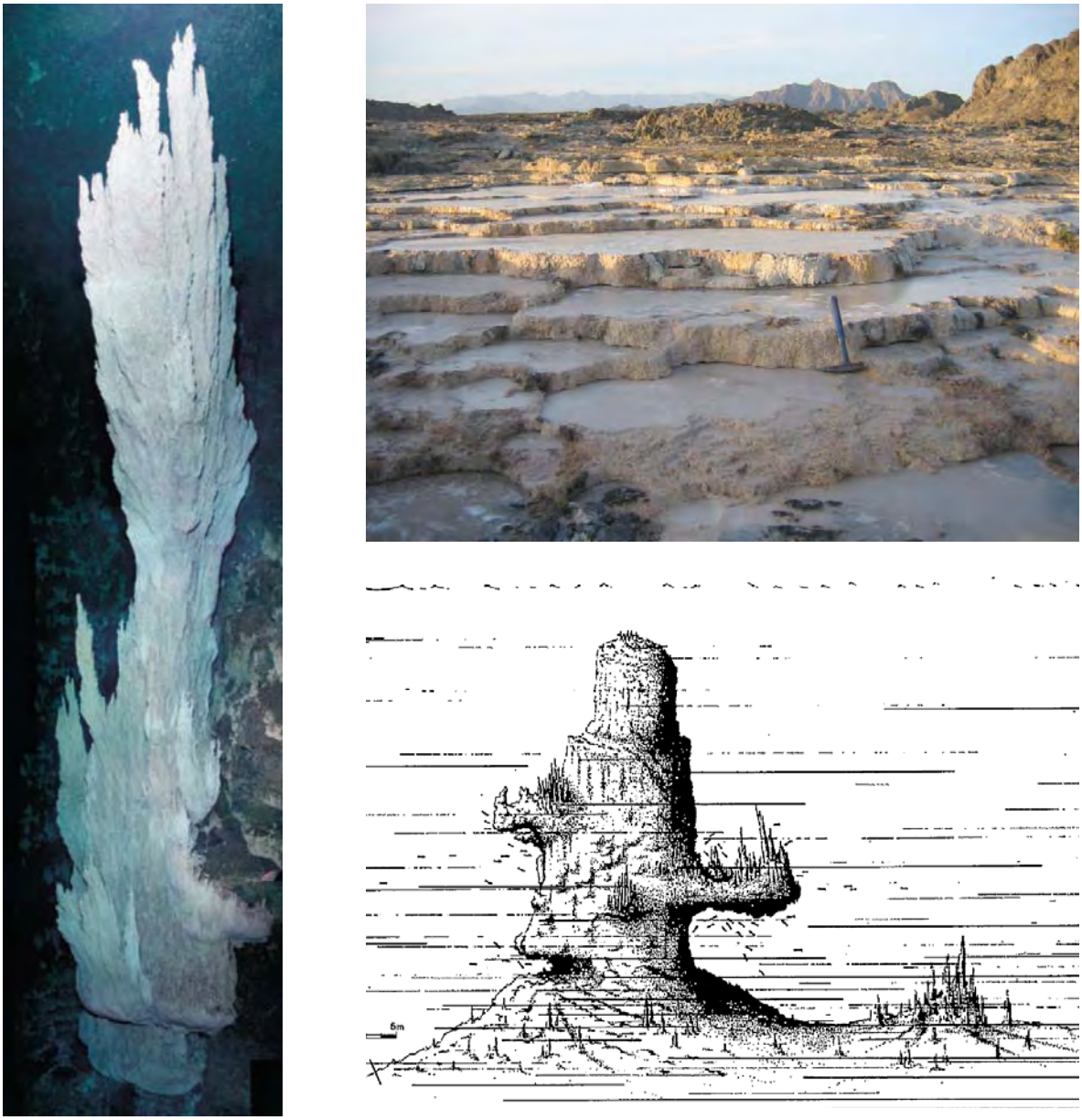


Figure 9: Left: 10 m tall calcium carbonate chimney at the peridotite-hosted Lost City hydrothermal deposit, ~ 1 km below sealevel near the Mid-Atlantic Ridge (Kelley et al. Science 2005). Top right: Calcium carbonate travertine deposit deposited by peridotite-hosted, alkaline springs in Oman (Kelemen & 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.

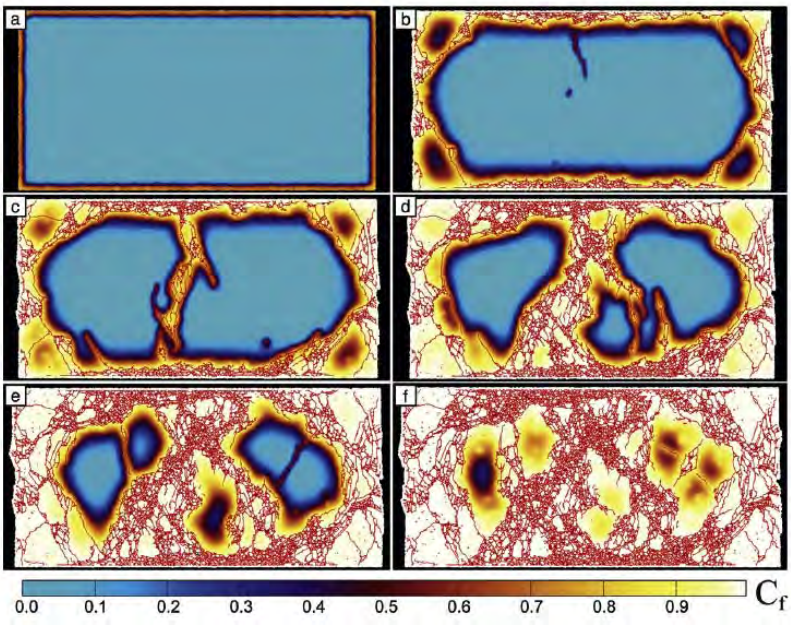


Figure 10: Model of positive feedback during mineral hydration or carbonation, involving fluid flow in fractures, fluid-solid reaction, and fracture caused by increasing solid volume (Royne et al. EPSL 2008).

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.

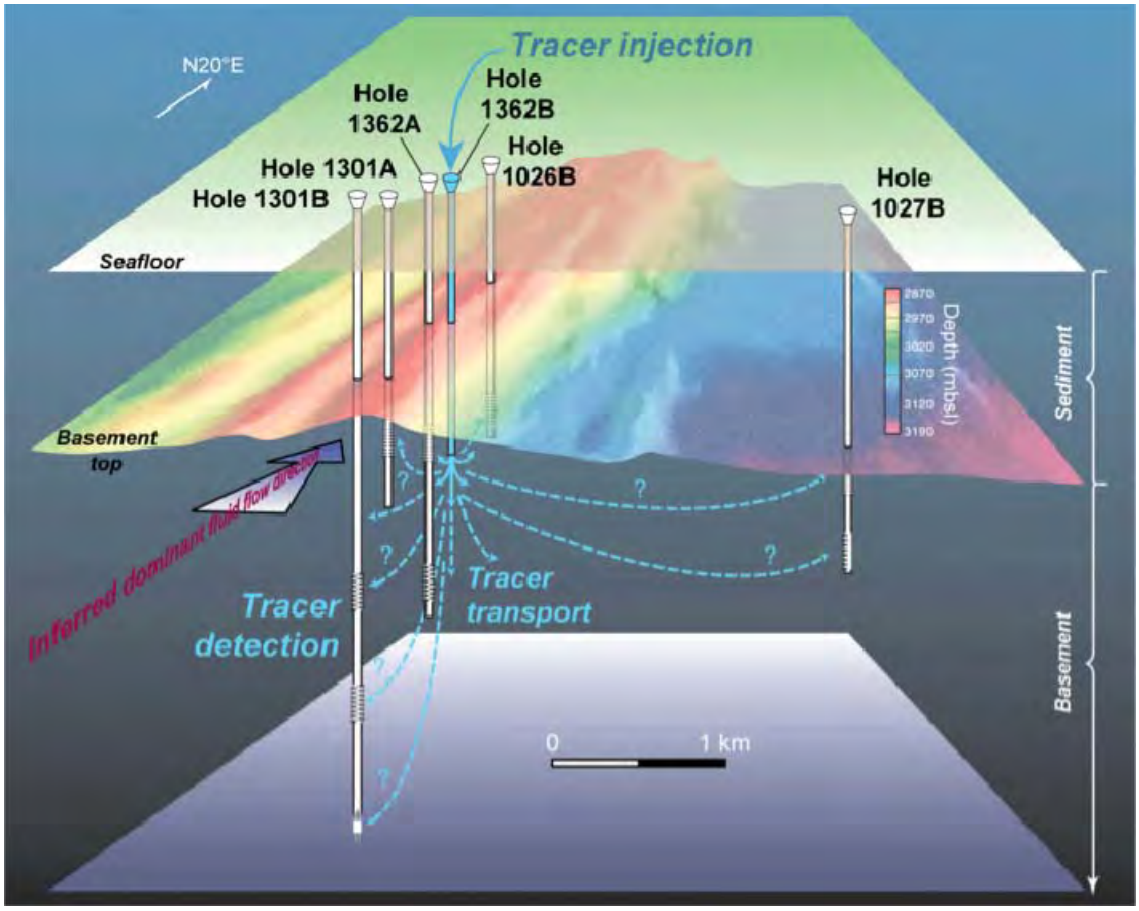


Figure 11: Prototype tracer experiment begun by IODP scientists in 2010, involving "CORK" observatories in multiple drill holes in mid-ocean ridge basalt lavas along the Juan de Fuca Ridge under the leadership of Prof. Andy Fisher of UCSC. This methodology could be used for pilot studies of CO_2 injection 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.

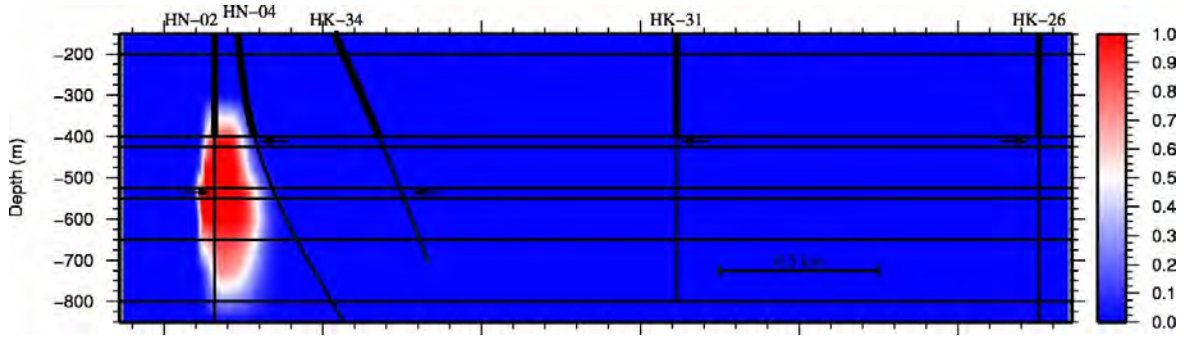


Figure 12: Model of CO_2 concentration (color scale) in pore fluid for the CarbFix experimental geometry, in a cross-section with injection at well HN-02 and production of ambient pore fluid from well HN-04 (injection and production 2 kg/s) after three years with 2.5 % porosity. Image from Edda et al.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

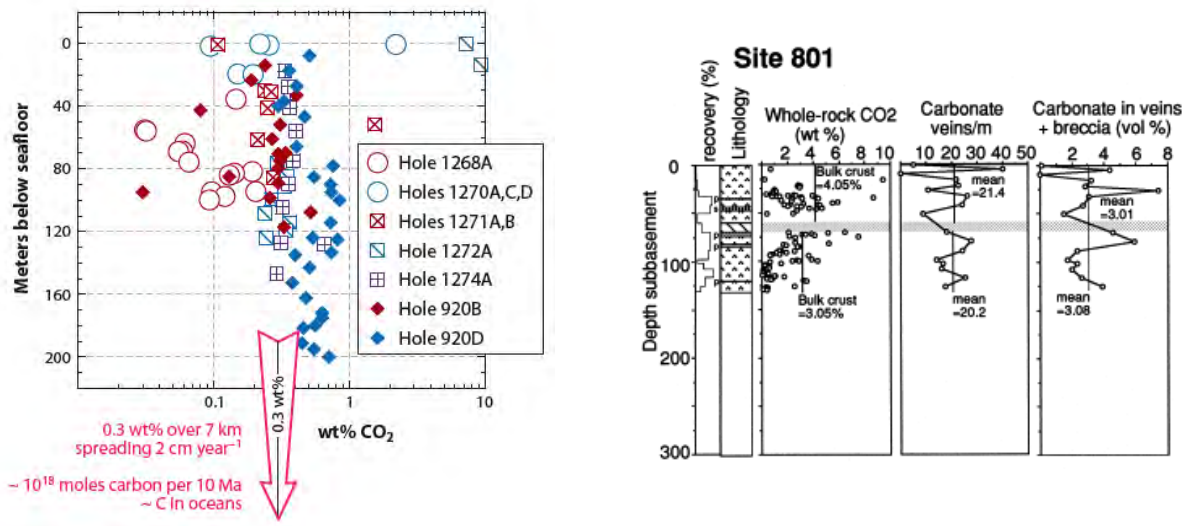


Figure 13: Variation of CO_2 contents and carbonate vein distribution as a function of depth in oceanic scientific drill holes. Right: CO_2 concentration in altered peridotite core samples from the Mid-Atlantic Ridge. Figure from Kelemen et al. Ann. Rev. Earth Planet Sci. 2011. Left: CO_2 concentration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

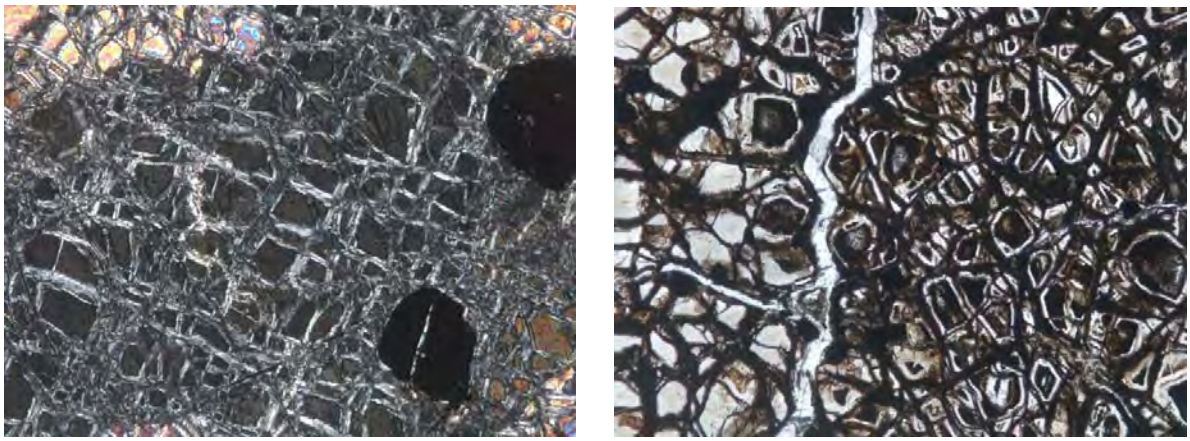


Figure 14: Photomicrographs of dense fracture networks hosting alteration veins in altered peridotite from the Samail ophiolite. Field of view ~ 1 mm for both photos. Right: Serpentine veins on fractures in unaltered olivine. Left: Composite serpentine and carbonate veins along fractures, surrounding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

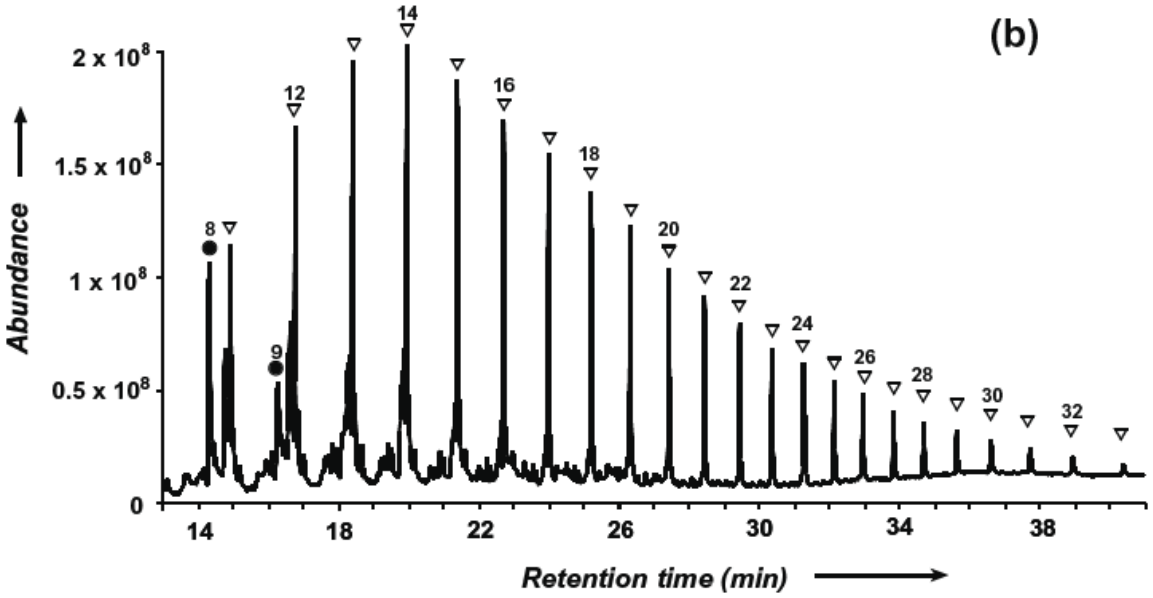


Figure 15: Left: Burning methane emitted from hydrating peridotite along the coast of Turkey near Mt. Chimaera. According to legend, lightening ignited the methane to form a beacon used by Mediterranean mariners for millennia. Bottom: Total ion chromatograms from GC–MS analysis of run products of experiments 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.

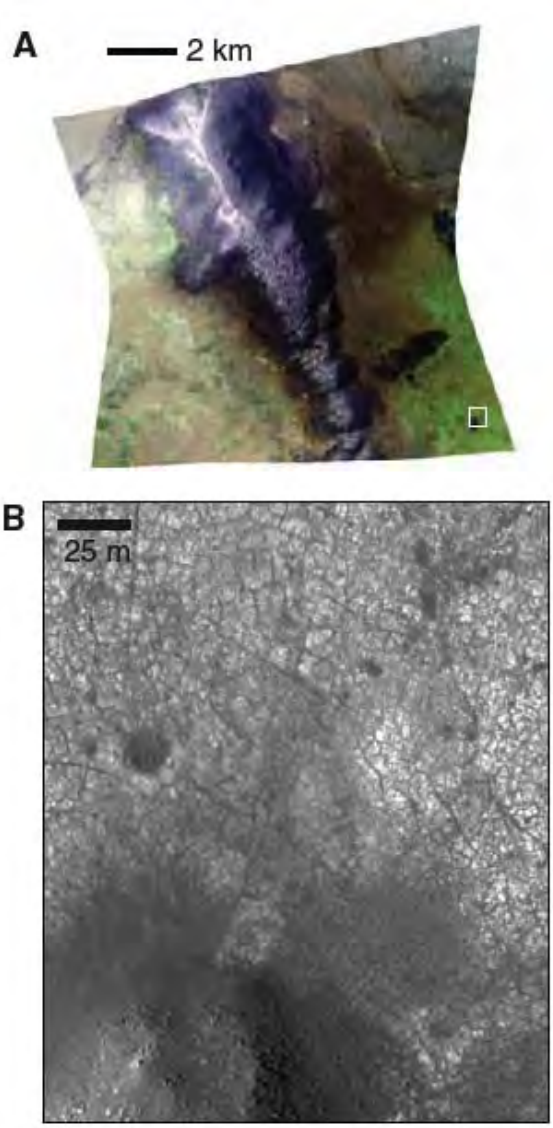


Figure 16: Images of carbonated ultramafic rocks on the surface of Mars, from Ehlmann et al. Science 2008. In A, carbonate is green, olivine is yellow to brown, phyllosilicate is blue, and an overlying mafic unit is purple. The small rectangle outlines the area of (B). The closeup in B shows carbonated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

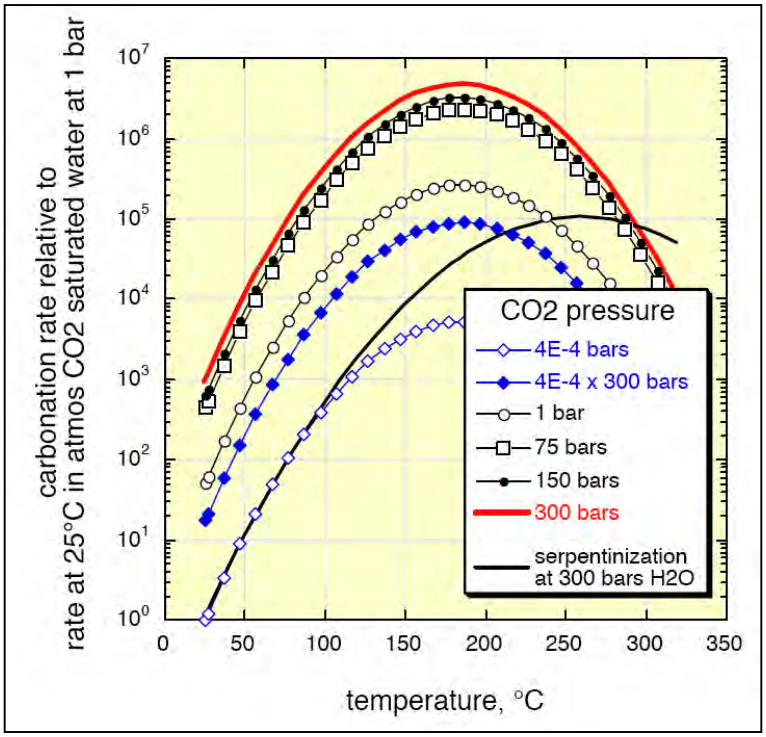


Figure 17: Carbonation rate enhancement, relative to the rate at 25°C and atmospheric P_{CO2}, as a function of elevated temperature and partial pressure of CO_2. Figure from Kelemen & Matter, Proc. (US) Nat. Acad. Sci. 2008, who fit experimental data on the rate of olivine carbonation from O'Connor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

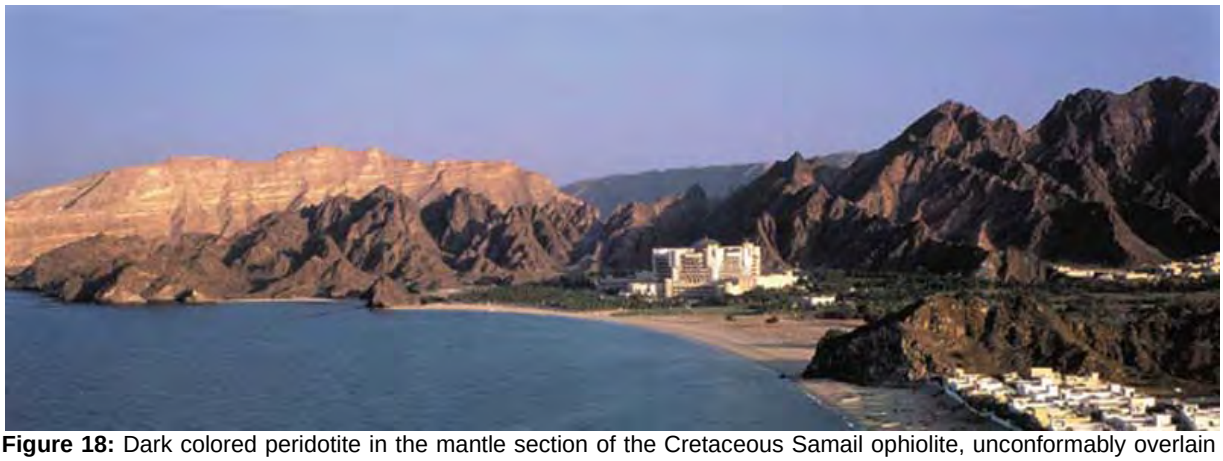


Figure 18: Dark colored peridotite in the mantle section of the Cretaceous Samail ophiolite, unconformably overlain by Eocene limestone, dipping offshore along the northern coast of Oman near the capital city of Muscat. Photo from http://www.beauxsonges.fr/IMG/jpg/H0H7YH1W1111111.jpg.

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.

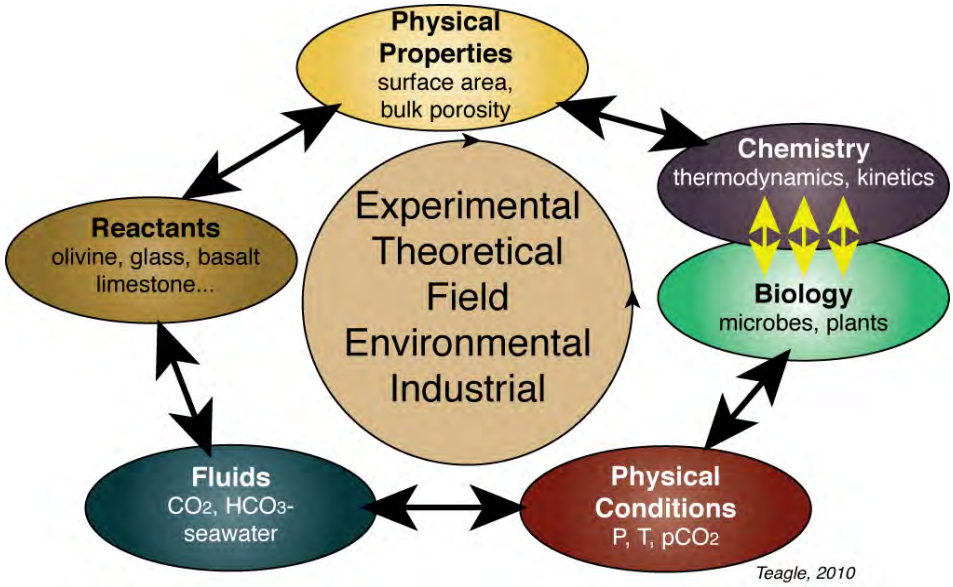


Figure 20: Flow chart summarizing the research and technological requirements for the development of geological storage in mafic and ultramafic rock formations. Image from keynote talk by Prof. Damon Teagle.

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.

Appendices

Appendix A: List of Participants

Appendix B: Workshop Agenda

Appendix C: pdfs of Keynote lectures

Appendix D: Poster Abstracts

Appendix E: Post-meeting field trip guide

Appendix A: List of Participants

87 participants *(including 10 PhD students and 11 post-docs and young scientists).* 32 participants were European (Iceland not included) and 13 from the Sultanate of Oman.

Muriel Andreani	**	ENS-Université de Lyon, France	muriel.andreani@univ-lyon1.fr
Caitlin Augustin	*	School of Marine and Atmospheric Science University of Miami, USA	c.augustin@umiami.edu
Hafidh Khlafan Al Ghanami		Ministry of Commerce, Sultanate of Oman	-
Abdulrahman Al Harthi		Department of Earth Science, Sultan Qaboos University, Sultanate of Oman	-
Mohamed Issa Al Harthi		Ministry of Commerce, Sultanate of Oman	-
Talal Al Hosni		Sultan Qaboos University, Sultanate of Oman	hosni@squ.edu.om
Zhair Al Suleimani		Public Authority for Electricity and Water, Sultanate of Oman	-
Saleh Al-Anboori		Ministry of Oil & Gas, Sultanate of Oman	-
Abdelmajeed Abdullah Al-Ansari		Ministry of Commerce , Sultanate of Oman	-
Yahya Al-Wahaibi		Sultan Qaboos University, Sultanate of Oman	ymn@squ.edu.om
Ibrahim Ashour		Department of Petroleum and Chemical Engineering, Sultan Qaboos University, Sultanate of Oman	ashour@squ.edu.om
Roy Baria		MIL-TECH UK Ltd	roybaria@onetel.com
Keir Becker		University of Miami - RSMAS, USA	kbecker@rsmas.miami.edu
Claire Bendersky	*	Lamont Doherty Earth Observatory, USA	claireb@ldeo.columbia.edu
Pascale Benezeth		Laboratoire des Mécanismes et Transferts en Géologie (LMTG-CNRS)-Toulouse, France	benezeth@lmtg.obs-mip.fr
Dominique Bernard		ICMCB-CNRS, France	bernard@icmcb-bordeaux.cnrs.fr
Eleanor Berryman	*	McGill University, Canada	eleanor.berryman@mail.mcgill.ca
Márton Berta	*	ELTE University, Budapest, Hungary	marci87@chello.hu
Chiara Boschi		Institute of Geosciences and Earth Resources-CNR, Italy	c.boschi@igg.cnr.it
Françoise Boudier		Université Montpellier 2, France	Francoise.Boudier@gm.univ-montp2.fr
Andrew Bunger		CSIRO Earth Science and Resource Engineering, Australia	andrew.bunger@csiro.au
Richard Darton		University of Oxford, UK	richard.darton@eng.ox.ac.uk
Henri Dick		Woods Hole Oceanographic Institution, USA	hdick@whoi.edu
Andrea Dini		Institute of Geosciences and Earth Resources-CNR, Italy	a.dini@igg.cnr.it

Gregory M. Dipple		University of British Columbia, Canada	gdipple@eos.ubc.ca
Steve Ehreinberg		Shell Chair, Sultan Qaboos University, Sultanate of Oman	sne@squ.edu.om
Issa El-Hussain		Sultan Qaboos University, Sultanate of Oman	elhussain@squ.edu.om
Katy Evans		Curtin University, Australia	k.evans@curtin.edu.au
Gretchen Früh-Green		ETH Zurich, Switzerland	frueh-green@erdw.ethz.ch
Eric Gaidos		Department of Geology and Geophysics, University of Hawaii, USA	gaidos@hawaii.edu
Pablo Garcia Del Real	*	Stanford University, USA	gdelreal@stanford.edu
Sigurdur Gislason		Institute of Earth Sciences, University of Iceland	sigrg@raunvis.hi.is
Marguerite Godard		CNRS-Géosciences Montpellier, France	Marguerite.Godard@um2.fr
David S. Goldberg		Lamont-Doherty Earth Observatory, USA	goldberg@ldeo.columbia.edu
Philippe Gouze		CNRS-Géosciences Montpellier, France	Philippe.Gouze@um2.fr
Marc Hesse	**	University of Texas at Austin, USA	mhesse@jsg.utexas.edu
Astrid Holzheid		Universität Kiel, Germany	holzheid@min.uni-kiel.de
Richard Hunwick		Integrated Carbon Sequestration Pty Ltd (ICS), Australia	richard@hunwickconsultants.com.au
Benoît Ildefonse		CNRS - Géosciences Montpellier, France	benoit.ildefonse@um2.fr
Karthik Iyer	**	The Future Ocean, IfM-GEOMAR, Germany	kiyer@ifm-geomar.de
Bjorn Jamveit		PGP, University of Oslo, Norway	bjorn.jamtveit@geo.uio.no
Junfeng Ji		School of Earth Sciences and Engineering, Nanjing University, P. R. China	jijunfeng@nju.edu.cn
Kevin Johnson		University of Hawaii, USA	kjohnso2@hawaii.edu
Natalie Johnson	*	Stanford University, USA	nataliej@stanford.edu
Jens Kallmeyer		University of Potsdam, Institute of Earth and Environmental Sciences, Germany	kallm@geo.uni-potsdam.de
Peter Kelemen		Columbia University, USA	peterk@LDEO.columbia.edu
Juergen Koepke		Leibniz University Hannover, Germany	koepke@mineralogie.uni-hannover.de
Marvin Lilley		School of Oceanography, University of Washington, USA	lilley@u.washington.edu
Harrison Lisabeth	**	Columbia University, USA	hlisabeth@gmail.com
Kristin Ludwig		Consortium for Ocean Leadership, USA	kludwig@oceanleadership.org
Sarah Mackintosh	**	The University of Nottingham, UK	Sarah.Mackintosh@nottingham.ac.uk
Jagan Mahadevan	**	The University of Tulsa, USA	jmahadevan@utulsa.edu
David Manning		University of Newcastle, UK	David.Manning@newcastle.ac.uk

Juerg Matter		Lamont-Doherty Earth Observatory of Columbia University, USA	jmatter@ldeo.columbia.edu
B. Peter McGrail		Pacific Northwest National Laboratory, USA	pete.mcgrail@pnl.gov
Travis L. McLing		Idaho National Laboratory, Center for Advanced Energy Studies, USA	travis.mcling@inl.gov
Bénédicte Menez		CNRS - Institut de Physique du Globe de Paris, France	menez@ipgp.fr
Peter Michael		The University of Tulsa, USA	pjm@utulsa.edu
Katsuyoshi Michibayashi		Shizuoka University, Japan	sekmich@ipc.shizuoka.ac.jp
Jay Miller		Integrated Ocean Drilling Program	miller@iodp.tamu.edu
Christophe Monnin		CNRS- Université Paul Sabatier, France	monnin@lmtg.obs-mip.fr
Sobhi Nasir		Sultan Qaboos University, Sultanate of Oman	sobhi@squ.edu.om
Eric Oelkers		CNRS- Université Paul Sabatier, France	oelkers@lmtg.obs-mip.fr
Jonas Olsson	*	Nordic Volcanological Institute, Institute of Earth Sciences, University of Iceland	jolsson@hi.is
Mike Oristaglio		Yale University, USA	michael.oristaglio@yale.edu
Jason Ornstein	*	New York University, USA	jmo326@nyu.edu
Amelia Paukert	*	Columbia University, USA	anp2119@columbia.edu
D. Graham Pearson		University of Alberta, Canada	gdpearso@ualberta.ca
Robert Podgorney		Idaho National Laboratory and Center for Advanced Energy Studies, USA	robert.podgorney@inl.gov
Herbert Poellmann		University of Halle, Germany	herbert.poellmann@geo.uni-halle.de
Bernhard Pracejus		Sultan Qaboos University, Sultanate of Oman	pracejus@squ.edu.om
Valentina Prigiobbe	**	University of Texas at Austin, USA	valentina.prigiobbe@mail.utexas.edu
Barbara Ransom		National Science Foundation, USA	bransom@nsf.gov
Lars Ruepke		The Future Ocean - IFM-GEOMAR; Germany	lruepke@ifm-geomar.de
Olaf Schuiling		Institute of Geosciences, Utrecht University, The Netherlands	schuiling@geo.uu.nl
Nina S.C. Simon	**	Environmental technology, Norway	nina.simon@ife.no
Sven Sindern		RWTH Aachen University, Germany	sindern@rwth-aachen.de
Michael Styles		British Geological Survey, UK	mts@bgs.ac.uk
Narasimman Sundararajan		Sultan Qaboos University, Sultanate of Oman	visvid12@squ.edu.om
Yutaro Takaya	*	Department of Systems Innovation, Graduate School of Engineering, University of	tt097074@mail.ecc.u-tokyo.ac.jp

		Tokyo, Japan	
Damon Teagle		University of Southampton, UK	dat@noc.soton.ac.uk
H. Henry Teng		Nanjing University/George Washington University, USA	hteng@gwu.edu
Masako Tominaga	**	Dept. of Geology and Geophysics - WHOI, USA	mtominaga@whoi.edu
Reinier Van Noort	**	HPT-Laboratory, Utrecht University, The Netherlands	vannoort@geo.uu.nl
A. Joshua West	**	University of Southern California Earth Sciences, USA	joshwest@usc.edu
Anthony Williams-Jones		McGill University, Canada	anthony.williams-jones@mcgill.ca
Liang Zhao		School of Earth Sciences and Engineering, Nanjing University, P. R. China	zhaoliang@nju.edu.cn

Note: **PhD student, **Post-doc and young scientist*

Appendix B: Workshop Agenda

The 3-day workshop was organized as a series of invited talks and discussions in working groups as well as during poster sessions. Session coordinators provided short reviews of each day discussions. Invited talks were organized as:

- Keynote presentations: 30 min talk and followed by 10 min questions & discussion
- Coordinated presentations of fundamentals scientific and technical issues: 20 min talks followed by 10 min questions & discussion

• Friday January 7, 2011

19:00-22:00 Registration & Icebreaker at Sultan Qaboos University
(Faculty Club Restaurant near Administration building)

• Saturday January 8, 2011

08:00-09:00 Further Registration "On Site" - Sultan Qaboos University

09:00-10:20 Opening ceremony

09:05 Recitation from the Holy Quran
09:10 Address by Dr. Saif Al-Bahri – Dean, College of Science
09:20 Address by Prof. Peter Kelemen - Chairman of the Conference
09:30-10:10 CO2 emissions: Capture them or avoid them, it's a big challenge - *R. Darton - Univ of Oxford, UK*

Summary: The world economy runs on the consumption of a large and increasing flow of fossil carbon fuel, which is currently generating some 30 billion tpy of carbon dioxide. Whether we plan to sequester this flow (CCS), or avoid it (low-Carbon economy) the challenge is a huge one. We have to consider both the scale of the engineering, and the scale of societal change. We also have to consider the role that could be played a number of different technologies, since it seems unlikely that there will be a single preferred path of change.

10:10-10:20 Closing Ceremony

10:20-10:50 Coffee break

10:50-11:30 Potential for in situ geological storage in mafic rocks: Fundamental mechanisms and lessons from field observation – *D. Teagle – NOCS, UK.*
11:30-12:10 Potential for in situ geological storage in ultramafic rocks: Fundamental mechanisms and lessons from field observation – *P. Kelemen – LDEO, USA.*

12:15-13:45 Lunch

13:45-14:15 Fundamental mechanisms of CO2 mineral storage: lessons from laboratory experiments- *E. Oelkers – Univ. Toulouse, France.*
14:15 - 14:45 Feedbacks between reactions and hydrodynamic properties of reacting media: lessons from experiments - *Ph Gouze – Univ. Montpellier, France.*
14:45 - 15:15 Physical feedbacks during mineral carbonation: field observations, experiments and models - *B. Jamtveit – Univ. Oslo, Norway.*

15:15-15:45 Coffee break

15:45-16:15 Hydrogeology: Field observation & lessons from IODP - *K. Becker - RSMAS, USA.*
16:15-16:45 Monitoring and verification of CO_2 storage - *J. Matter – LDEO, USA.*
16:45-17:15 Summary of day

17:15-19:30 Discussions around Posters (Refreshments available)

19:30-20:30 Dinner

• Sunday January 9, 2011

08:30-09:00 Coffee on Site
09:00-09:40 Enhanced weathering and carbon mineralization in mine waste: acceleration potential and implications for carbon sequestration – *G. Dipple- UBC, Canada.*
09:40-10:00 Organize people into breakout sessions.
10:00-10:40 Working Groups I: Theme and coordinators
WG1 - Natural systems & in situ storage in the seafloor (processes and IODP targets): K. Becker/G. Früh-Green
WG2 - Natural systems & in situ storage on land (ICDP targets): T. McLing/S. Mackintosh
WG3 - Enhanced weathering options - mine tailings/industrial waste: D. Teagle/J. West
WG4 – Kinetics, fluid flow, reaction, efficiencies: V. Prigiobbe / K. Evans
10:40-11:10 Coffee available
11:10-12:30 Working Groups I (continues)

12:30-14:00 Lunch

14:00-15:00 Ongoing projects:
- CarbFix - *S. Gislason -U. of Iceland.*
- Big Sky- *P. McGrail – PNNL, USA.*
15:00-16:00 Summaries of Working Group Discussions

16:00-16:30 Coffee break

16:30-17:10 Technical challenges, lessons from engineered geothermal system for CCS - *Roy Baria – EGS Energy Ltd, UK.*
17:10-18:00 Summaries of Working Group Discussions (Part 2) & Actions for Day 3 (reminder of WGII program)
18:00-19:30 Discussions around Posters (Refreshments available)

19:30-20:30 Dinner

• Monday January 10, 2011

08:30-09:00 Coffee on Site
09:00-09:40 Creating surface area and conductivity in ultramafic rocks by using extremely closely spaced hydraulic fractures- *A. Bunger – CSIRO, Australia.*
09:40-10:00 Organize people into breakout sessions (Working Groups II)...
10:00-10:40 Working Groups II: Theme and coordinators
WG1 - submarine site characteristics: M. Godard & P. Michael
WG2 - onland site characteristics: G. Pearson & M. Oristaglio
WG3 - permeability, hydraulic fracture, reactive surface area: G. Dipple & A. Bunger
10:40-11:10 Coffee available
11:10-12:30 Working Groups II (continues)

12:30-14:00 Lunch

14:00-14:30 A last look at the Posters
14:30-16:00 Summary of Working Group II Discussions

16:00-16:30 Coffee break

16:30-18:00 Summary of Working Group Discussions
18:00-19:00 Close Formal Meeting

19:30-20:30 Dinner

Appendix C: pdfs of Keynote lectures

List of scientific presentations

• Saturday January 8, 2011

1 . CO_2 emissions: Capture them or avoid them, it's a big challenge - *R. Darton - Univ of Oxford, UK*

Summary: The world economy runs on the consumption of a large and increasing flow of fossil carbon fuel, which is currently generating some 30 billion tpy of carbon dioxide. Whether we plan to sequester this flow (CCS), or avoid it (low-Carbon economy) the challenge is a huge one. We have to consider both the scale of the engineering, and the scale of societal change. We also have to consider the role that could be played a number of different technologies, since it seems unlikely that there will be a single preferred path of change.

2. Potential for in situ geological storage in mafic rocks: Fundamental mechanisms and lessons from field observation – *D. Teagle – NOCS, UK.*

3. Potential for in situ geological storage in ultramafic rocks: Fundamental mechanisms and lessons from field observation – *P. Kelemen – LDEO, USA.*

4. Fundamental mechanisms of CO_2 mineral storage: lessons from laboratory experiments- *E. Oelkers – Univ. Toulouse, France.*

5. Feedbacks between reactions and hydrodynamic properties of reacting media: lessons from experiments - *Ph Gouze – Univ. Montpellier, France.*

6. Physical feedbacks during mineral carbonation: field observations, experiments and models - *B. Jamtveit – Univ. Oslo, Norway.*

7. Hydrogeology: Field observation & lessons from IODP - *K. Becker - RSMAS, USA.*

8. Monitoring and verification of CO_2 storage - *J. Matter – LDEO, USA.*

• Sunday January 9, 2011

9. Enhanced weathering and carbon mineralization in mine waste: acceleration potential and implications for carbon sequestration – *G. Dipple- UBC, Canada.*

10. CarbFix Project - *S. Gislason -U. of Iceland.*

11. Wallula Project - *P. McGrail – PNNL, USA.*

12. Technical challenges, lessons from EGS for CCS - *Roy Baria*, *EGS Energy Ltd, UK*

• Monday January 10, 2011

13. Creating surface area and conductivity in ultramafic rocks by using extremely closely spaced hydraulic fractures- *A. Bunger – CSIRO, Australia.*

1 . R. Darton - Univ of Oxford, UK.

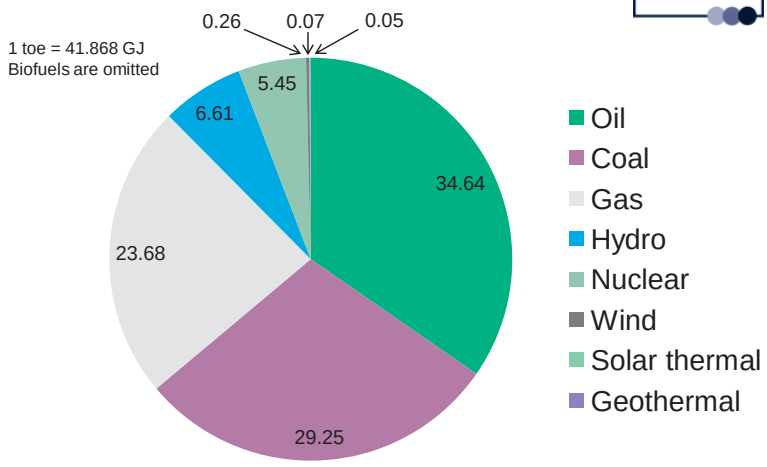
CO_2 emissions: capture them or avoid them, it's a big challenge.

IODP/ICDP Workshop on Geological Carbon Capture & Storage in Mafic and Ultramafic Rocks

Muscat, Oman, 8-10th January 2011

Richard Darton
Co-Director, Oxford Geoengineering Programme
President, European Federation of Chemical Engineering

Department of Engineering Science
University of Oxford

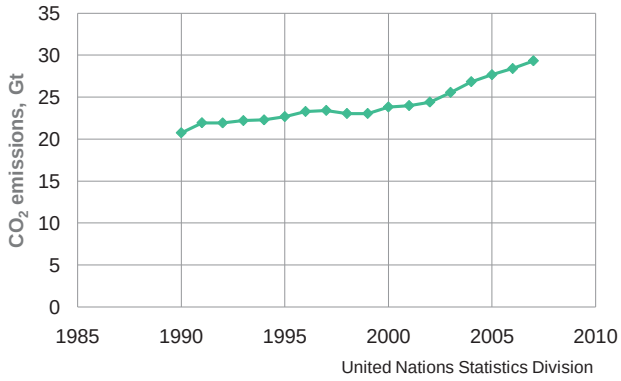


2009 Primary energy supply, by type, %
Total is 11.2 Gtoe

2

Data include cement-related emissions and omit effects of deforestation.

China and USA each produce about 20% of total.



Human activity related CO_2 emissions - currently running at around 80 million tpd

3

Consequences

- Carbon dioxide production due to human activity is causing global warming and ocean acidification.
- Renewable energy is being promoted, and its use is increasing, but from a very low level, and
- The supply of primary energy remains largely based on fossilised carbon.
- So it would be helpful to be able to capture a significant quantity of CO_2 – and hide it away close to the point of capture...

4

IEA, IPCC

The location of stationary CO_2 emission sources

~8000 sources produce ~15 bn tpy

5

CO_2 Capture

- Capturing CO_2 is a widely applied separation process:
  - At the front end of cryogenic air separation plants where CO_2 and water are removed
  - In natural gas production
  - In ammonia manufacture, and other chemical processes
- Absorption (with solvent), adsorbent (with porous solid) or membrane processes are the common methods
- The process must supply the *work of separation*. The efficiency is low (<10%), so the major operating expense is energy input to the separation engine. Waste heat must be dumped (2nd law)
- Some consumption of chemical is unavoidable as well
- Capture (from flue gas) takes ~70% of the costs of CCS*

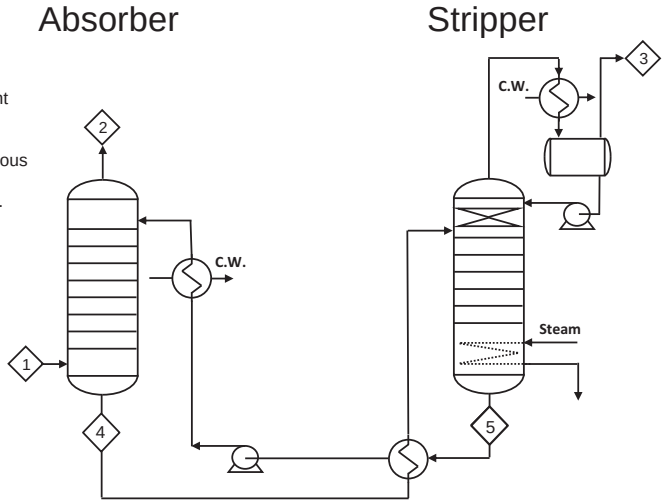
6

*CCS=Carbon Capture and Storage

Amine treating
Design and Costs - scheme

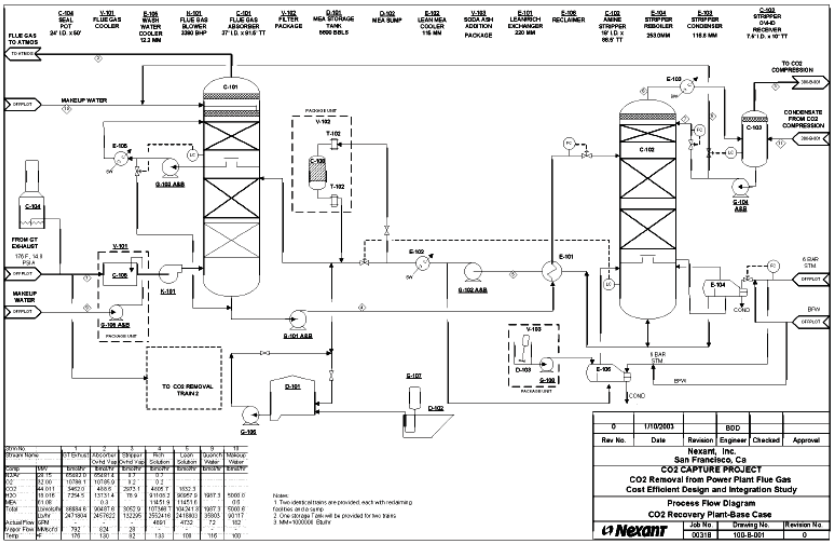
Streams
1. Feed gas
2. Treated gas
3. CO_2 product
4. Rich (fat) solvent
5. Lean solvent

The amine, in aqueous solution, reacts reversibly with CO_2.



7

Amine treating
Design and Costs - PFD



8

Amine treating
Design and Costs - Capital

A retrofit post-combustion plant removing 1 million tpy CO_2 from flue gas (86% capture) costs around US$ 96 million (2009 prices installed):

absorbers	26.0
l/r ht exchrs	18.3
reboilers	14.5
regenerators	9.6
feed cooler	8.7
flue gas blowers	8.7
pumps	7.7
other	2.9
Total $US mill	96.4

Two absorbers, each 11 m dia and 20 m tall.

Design is largely determined by the volume of gas treated, and the percent capture.

Warning: These costs have been carefully calculated, but must be regarded nevertheless only as indicative, because of the very many uncertainties in project and process specifications.

9

Amine treating
Design and Costs - Capital

To capture 1 bn tpy CO_2 would require 1000 such plants treating flue gas, at an approximate total cost of US$ 100 billion.

OR

We might capture 15 bn tpy in 8000 plants at a capital cost around $US 1 trillion – this treats all large stationary sources of CO_2.

CO_2 from flue gas: 70 000 tpy plant, Malaysia

10

Amine treating
Design and Costs - Operating

Energy:
Removal of CO_2 from flue gas by amine treating takes around 150-200 MJ/kmol (1-1.3 kWh/kg). Integrated with a power plant it can use cheap low grade steam.

Cooling water:
~85 t/tCO_2

Other:
Electricity, chemicals, pure water

Total costs for CCS including CO_2 drying, compression, transport and storage ~20-200 US$/t$CO_2$. Deployment could begin when price reaches a stable 25-30 US$/t$CO_2$. For a power plant, around 25% of the output might be taken by CCS.

11

CO_2 Capture
Summary

CO_2 removal from flue gas is technically feasible now. The capital investment is large but … (Shell's capex ~US$ 25 bn/y)

Calculations here are based on MEA treating, but other options exist. Integration of CCS in new-build reduces costs. The opex is also feasible. Storage capacity?

But, for this very large new industry:

Worldwide stable market/regulation for CO_2 is needed.

Manufacturing enough solvent (adsorbent, membrane) will be a big challenge. Eg MEA is made from ammonia and ethylene oxide.

Environmental impact will be considerable – plant, chemicals, water. Public reaction?

12

What about “Air capture”?

Why not just take the CO_2 out of the air?

There are some difficulties:

In the scheme, one 11m dia column at atmospheric pressure retrieves ~ 515 000 tpy CO_2. This treats a **flue gas** flow of 39 10^3 kmol/h.

The same flow of **air**, 39 10^3 kmol/h, at 86% capture, yields 5862 tpy of CO_2, only 0.0114 as much.

To capture 1 billion tpy CO_2 from air using MEA would thus take about 100 000 such plants, processing 1 trillion tpy air, at an installed cost of many trillions of $US.

The basic problem is the low concentration of CO_2 in air (from the point of view of a separation process). Flue gas capture is optimised when discharging treated gas with a CO_2 concentration around 10 times **higher** than that of air.

Could research yield better air capture processes?

13

What about “Air capture”?

Columbia University

The claim

The CO_2 scrubber: wind blows through the adsorber and is purified.

The inescapable energy-cost RT.ln(100/x), is **0.18-0.37 kWh/kg CO_2** of low grade heat*. CO_2 in air is x %.

The minimum, reversible work of separation is, from 1st and 2nd law, RT.ln(100/x) + RT.((100-x)/x).ln(100/(100-x)), at constant T, P, which with x=0.039% is **0.136 kWh/kg CO_2** .

If “low grade heat” is at 150C, Carnot efficiency is 0.307: we need **≥ 0.443 kWh_{th}/kg CO_2**. The claim seems impossible.

14 * According to D Mackay, Sustainable Energy - without the hot air, Chapter 31, UIT Cambridge 2009

What about "Air capture"?

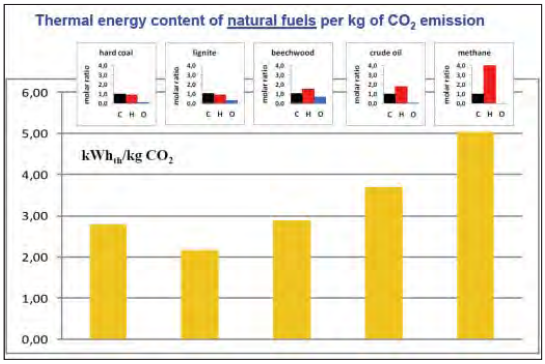
But it is worse than this. Real separation processes are far from reversible, needing at least 4x as much heat, i.e. > 2 $kWh_{th}/kg\ CO_2$ compared with the claimed 0.18-0.37 kWh/kg.

The real cost in thermal energy may well be much larger than this.

Could research lead to better air capture processes?

MEA treating of flue gas takes ~ 1 $kWh_{th}/kg\ CO_2$, close to the theoretical minimum for air capture. Investment in flue gas treating will be preferred to investment in air capture.

If heat required > 2$kWh_{th}/kg\ CO_2$ it is cheaper to replace lignite-fired electricity generation.



DECHEMA

15

What about "Air capture"?

So "NO!" to air capture which aims to produce pure CO_2 for storage, at least until all flue gas is treated.

But we could capture CO_2 from air if we…

- grow plants or other biomass to take up CO_2 : a separation process fuelled by solar energy (but costly in land area).

- utilise minerals/rock which take-up CO_2, to form eg calcite and accelerate this natural process. Is this feasible at large scale? It avoids thermodynamic limits in separating CO_2.

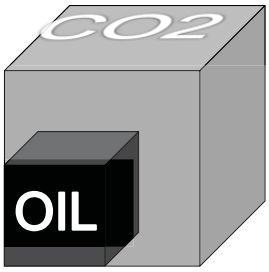
16

CCS – size of the industry

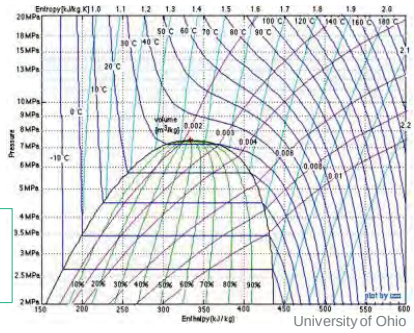
If we capture all 15 bn tpy CO_2 from stationary sources, and compress to critical point (73.82 bar) we obtain 32.1 bn m^3, which is a cube of side 3.2 km.

World oil production is 3.88 bn tpy, = 4.52 bn m^3, a cube of side 1.65 km.

In terms of volume, CCS is potentially a larger industry than the oil business.



CO_2
Vc = 0.00214 m^3/kg
Tc = 31.1 ºC
Pc = 7.382 MPa



University of Ohio

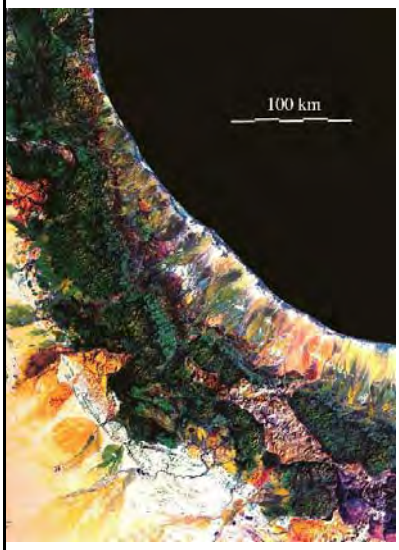
17

Conclusions

CO_2 emissions: capture them or avoid them, it's a **big** challenge.

- Plant to remove most CO_2 from stationary sources using known technology would cost ~US$ 10^{12} and use about 25% of the heating value of the fuel burnt.
- We would need to store ~30 km^3 of super-critical CO_2 annually.
- The environmental impact of such a huge new industry needs to be explored – water, chemicals, storage.
- Mineralisation of CO_2 could be important in both capture, and storage.
- A stable international market in C/CO_2 is needed.
- **We really need to move to a low carbon economy!**

2. D. Teagle – NOCS, UK.



Geological Carbon Capture & Storage using Mafic and Ultramafic rocks

IODP/ICDP Workshop on the role of oceanic and continental scientific drilling

Sultan Qaboos University
Muscat, Sultanate of Oman
8-10 January, 2011

Geological storage of CO_2 using mafic rocks:
Mechanisms and observations

Damon A.H. Teagle

National Oceanography Centre, Southampton
University of Southampton, UK

In Situ Geological CO_2 Storage using Mafic Rocks

Why?

- Environmental and Societal **Risks** of high atmospheric CO_2
- Carbon a major **energy** source for 21st Century
- Global energy **demand** likely to double by 2050
- Turgid progress in **international agreements** to reduce CO_2 emissions
- No effective international **market** for Carbon
- Improving CO_2 capture at source **technology**. But…. what to do with it?
- What will a **500-600…. ppmv CO_2** world be like?

We may need to try and **reduce atmospheric CO_2**

Why CO_2 Storage using Mafic Rocks?

Because this is the principal mechanism for natural CO_2 regulation on geological time scales

Can natural processes be applied on Human Timescales?

Black Rocks vs White Rocks

What is a Mafic rock? Basalt, Gabbro

An igneous rock with an abundance of dark-coloured **Mafic** Mg & Fe-bearing silicate minerals

e.g.,

Olivine: $(Mg, Fe)_2SiO_4$

Orthopyroxene: $(Mg,Fe)_2Si_2O_6$

Clinopyroxene: $Ca(Mg,Fe)Si_2O_6$

Also could include:

Amphibole: (Hornblende): $Na,Ca_2(Fe,Mg,Al)_5(Si,Al)_8O_{22}(OH)_2$

Biotite: $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$

Commonly with:

Plagioclase Feldspar: $Na_{(1-x)}Ca_xAl_{(1+x)}Si_{(3-x)}O_8$

Fe-Ti oxide: $(Fe,Ti)_3O_4$

Contrast with **Felsic** or **Silicic** Rocks "White Rocks" – e.g., Granite

Quartz: SiO_2

Alkali Feldspar: $KAlSi_3O_8$, $NaAlSi_3O_8$

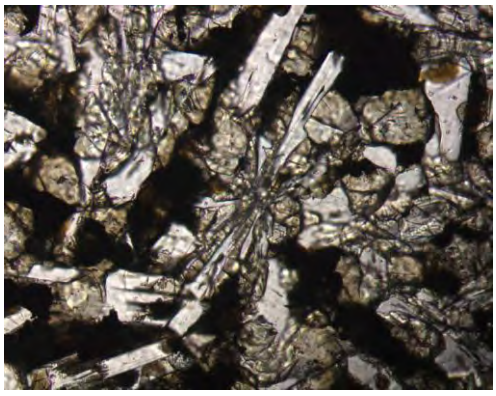
White mica/muscovite: $KAl_2(AlSi_3O_{10})(OH)_2$

Rocks with >90% Mafic Minerals = Ultramafic

Typical major element chemical analysis of a Basalt

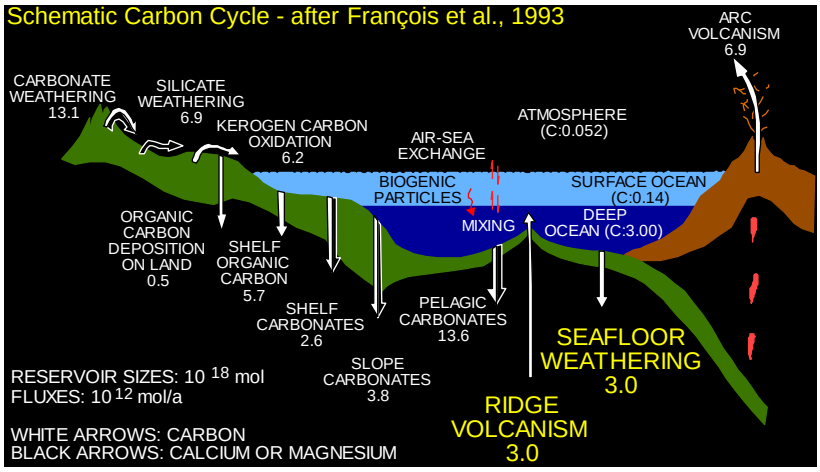
e.g., Sample of mid-ocean ridge basalt (MORB) from the East Pacific Rise
ODP Leg 206-1256D-4R-4, 76-80 cm

Oxides in weight %	
SiO_2	50.07
TiO_2	3.00
Al_2O_3	11.60
Fe_2O_3	18.47
MnO	0.21
MgO	4.76
CaO	8.39
Na_2O	2.77
K_2O	0.17
P_2O_5	0.24
Loss on Ignition	0.20
Total	99.88



Thin section in plane polarized light

The Global Carbon Cycle



Silicate rock weathering:

$$2CO_2 + H_2O + CaSiO_3 = Ca^{2+} + 2HCO_3^- + SiO_2$$

Carbonate formation in the oceans

$$2HCO_3^- + Ca^{2+} = CaCO_3 + CO_2 + H_2O$$

$$\mathbf{CO_2 + CaSiO_3 = CaCO_3 + SiO_2}$$

Mineral Reactions: Ingredients, Products, and Scale

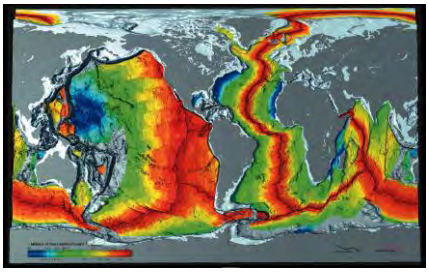
Reactions with real minerals: ***(following Oelkers et al., 2008 Elements 4:333)***

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

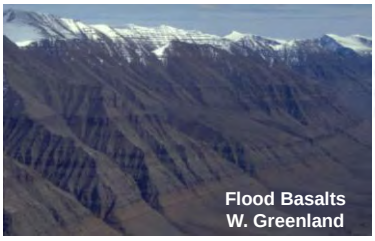
- Reactions are thermodynamically **favorable**; Do occur in nature
- **Compete** with other more favorable reactions, H_2O, O_2 – clays, $Fe(O,OH)_x$, serpentine
- **Calcite** most common alteration phase in the geological record

Mg -> clays, oceans

HUGE mafic rock resources are available

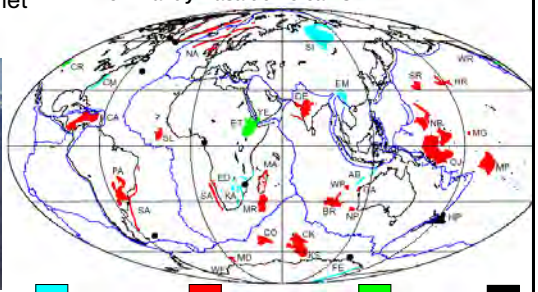


Ocean Crust ~60% of Earth's planet
Mostly *relatively* unaltered



Ocean Islands

Large Igneous Provinces
Huge sub-aerial and submarine eruptions:
up to 30 km thick, >10,000 km^2, 10^6 years
Dominantly Basaltic Volcanism

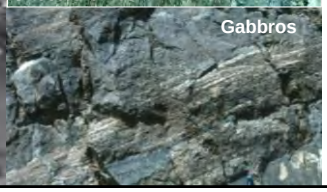


>150 Ma **150 - 50 Ma** **50 - 0 Ma** **Undated**

Eldholm & Coffin, 2000

HUGE mafic rock resources are available….

Ophiolites – **ancient ocean crust preserved on-land**
e.g., Troodos, Cyprus; Semail, Oman *(also Archean Greenstone Belts)*



And the **siliciclastic sedimentary products** of the erosion of mafic terranes

HUGE mafic rock resources are available….

Mine tailings and waste from major Ore Deposits
Cu, Zn, Cr, Ni, PGEs, Au, + Aggregate

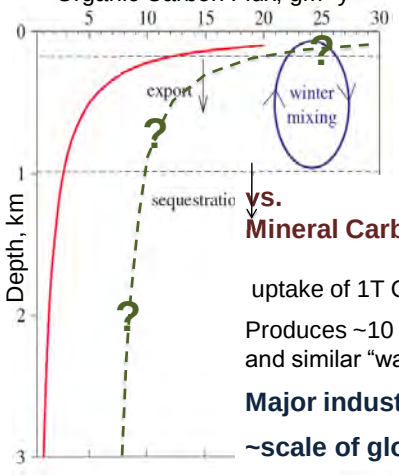
Wide range of on-land and off shore approaches

- Sub-aerial/submarine basalt flows as CO_2 **Reservoirs**
- **React**ing sub-aerial/submarine flows
  with CO_2 or HCO_3^- solutions to form $CaCO_3$
- Passive or Active **Enhanced Weathering** to form carbonates:
  - Mine tailings
  - Mafic siliciclastic sediments
  - Volcaniclastic sediments – tuffs, scoria, ash
  - Greenstone belt-derived tills
  - Mafic beach sands
  - Mg-, Ca-rich industrial waste
- React rock to form **High Alkalinity Solutions** to add to oceans
  accelerate terrestrial silicate weathering cycle?

Saffron vs. Potato Approaches

e.g., Ocean Iron Fertilization

A pinch of Fe



vs.

Mineral Carbonation

uptake of 1T C = >10T mineral

Produces ~10 T carbonate
and similar "waste" minerals

Major industrial undertaking

~scale of global mining industry

Large Mass transfers = $$$ and energy

Active Experiments - CO_2 reaction with with Basalt

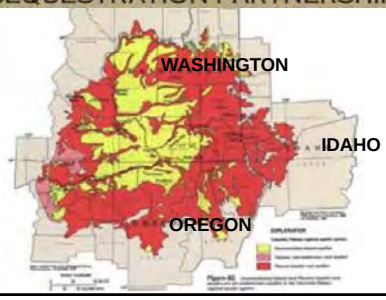
Gislason Sunday
McGrail 2 to 3 pm

CO_2 Fixation into Basalts
Hellisheiói Geothermal
Iceland

carbfix

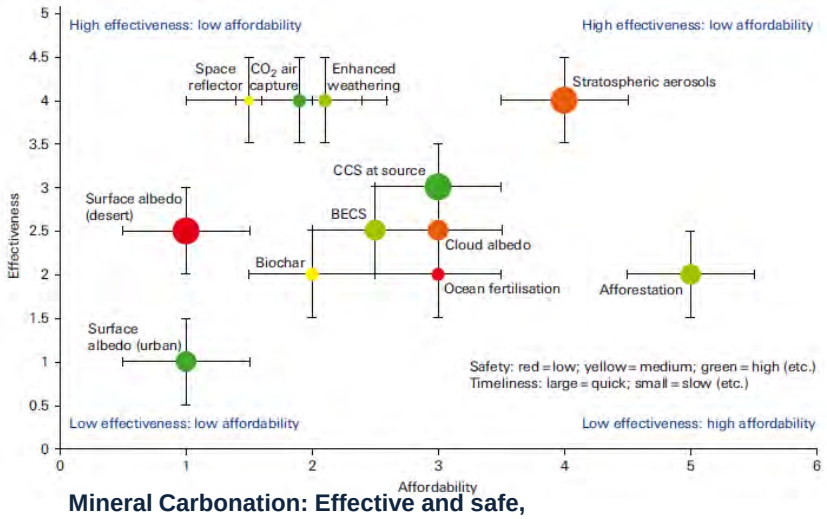
BIGSKYCARBON
SEQUESTRATION PARTNERSHIP

Columbia River Basalts
>174,000 km³



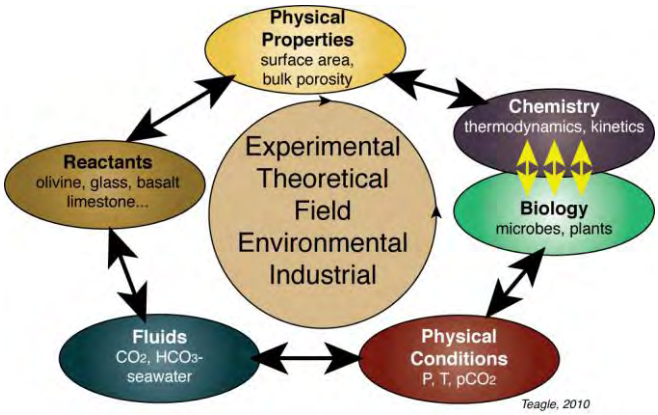
An Assessment of Geoengineering Options:

"Geoengineering the climate. Science, governance and uncertainty" (Roy. Soc., 2009)



Mineral Carbonation: Effective and safe,
But expensive and slow…….

For Mineral Carbonation to be energy and cost efficient and effective on a societal time scale

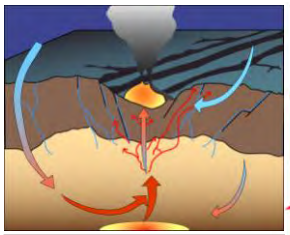


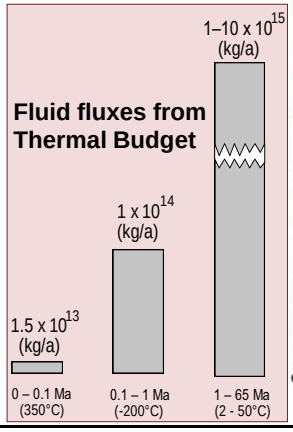
We need to make mineral-fluid reactions very efficient

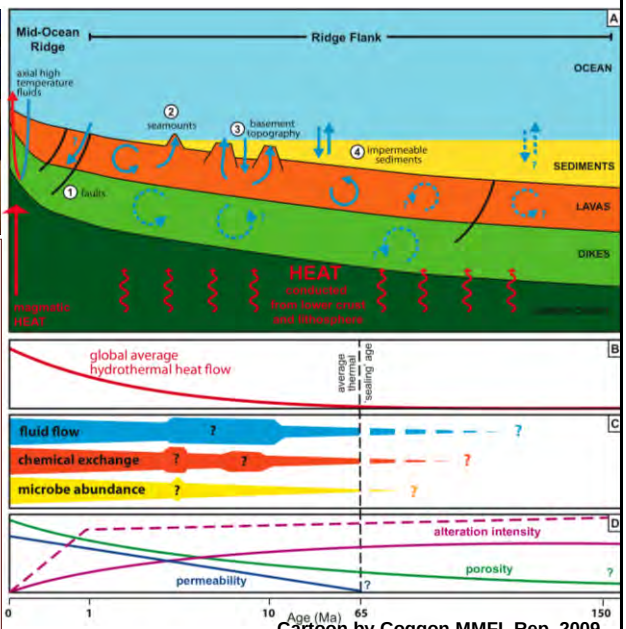
e.g.,
- enhance mineral dissolution rates
- avoid "waste" mineral formation
- maintain interconnected flow paths

Can we learn from Natural Analogs?

Ridge flank hydrothermal circulation





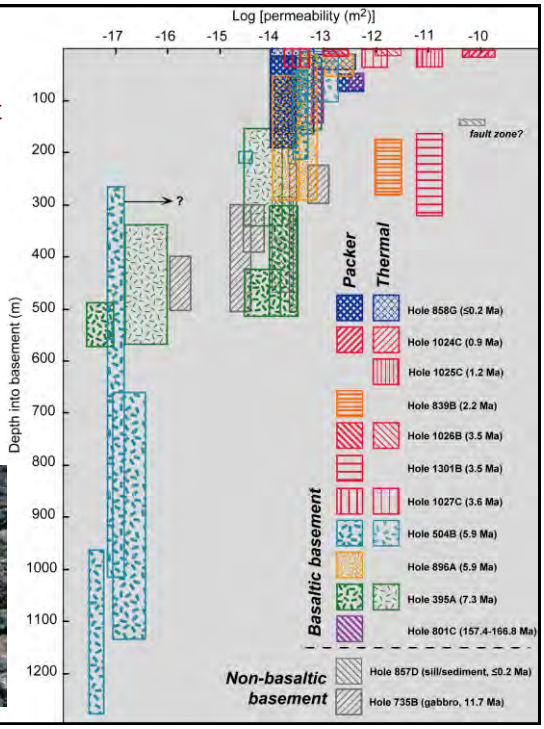


Cartoon by Coggon MMFL Rep. 2009

Summary of permeability measurements in oceanic crust

(Becker, Fisher, 1997)

- Variability = seven orders of magnitude; some consistency of depth trends
- Higher values in upper 300 m of basement, but few data from deeper
- Higher values within narrower zones (when tested), evidence for heterogeneity



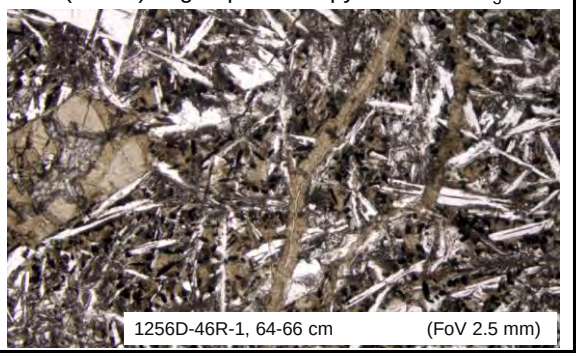
But what actually happens in nature?

$2Mg_2SiO_4$ + $Mg_2Si_2O_6 + 4H_2O$ = $2Mg_3Si_2O_5(OH)_4$
Olivine **Mg-OPX** **Serpentine**

(conundrum: carbonates when present ~CaCO3)

Seafloor basalts: commonly very fresh, **interstitial glass** only reactant (x Myrs, active seawater flow, 30-60° C)
Carbonate is a **minor**, late stage alteration phase

Background Gray Altered Basalt (15 Ma): Mg-saponite ± pyrite ± $CaCO_3$



But what actually happens in nature?

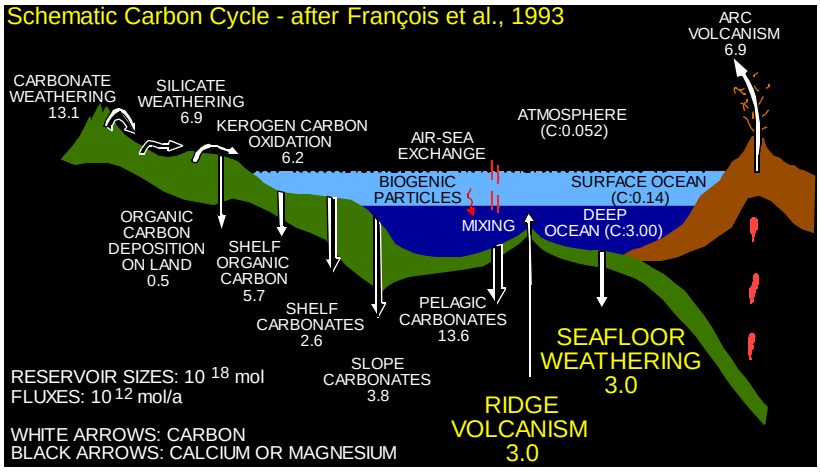
Seafloor basalts continued:

"Black", "Brown" and "Green" Halos around veins:

Partial reaction to Celadonite, Fe(O,OH)x ± Mg-saponite
$K[(Mg,Fe^{2+}),(Fe^{3+},Al)]Si_4O_{10}(OH)_2$ **$(Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2.nH_2O$**

Hole 1256D

The Global Carbon Cycle



Silicate rock weathering:

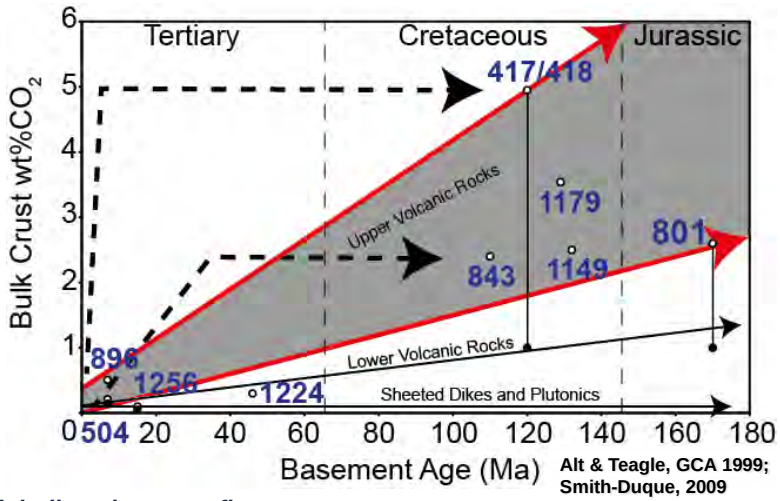
$$2CO_2 + H_2O + CaSiO_3 = Ca^{2+} + 2HCO_3^- + SiO_2$$

Carbonate formation in the oceans

$$2HCO_3^- + Ca^{2+} = CaCO_3 + CO_2 + H_2O$$

$$\mathbf{CO_2 + CaSiO_3 = CaCO_3 + SiO_2}$$

Carbonate uptake by the ocean crust



Alt & Teagle, GCA 1999; Smith-Duque, 2009

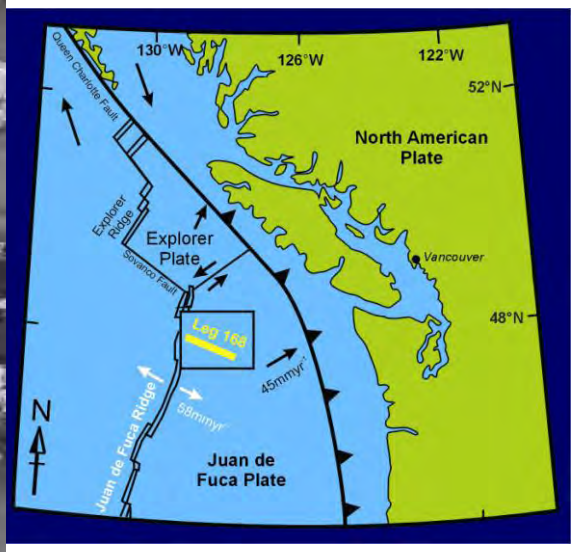
High bulk carbonate reflects:

Age? or

Oceanic conditions during hydrothermal circulation?

Experiments on the eastern flank of the Juan de Fuca Ridge

(see also Becker 15:45; Goldberg)



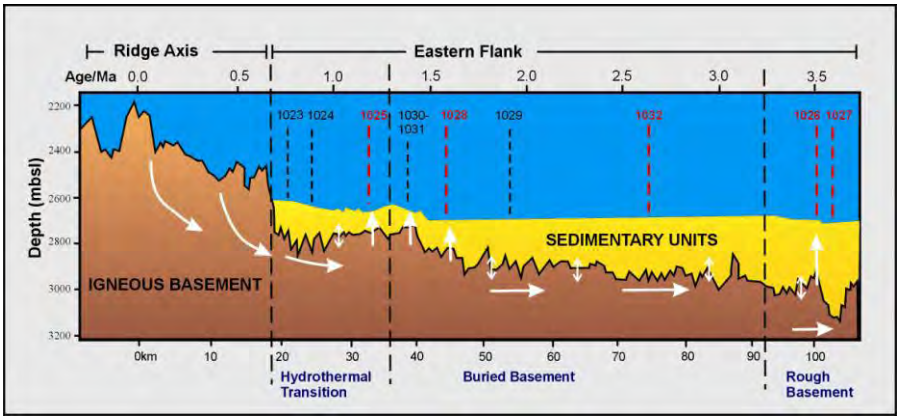
ODP Leg 168:

- Drilled 10 sites along an 80 km transect across the eastern ridge flank
- Recovered cores consisted of:

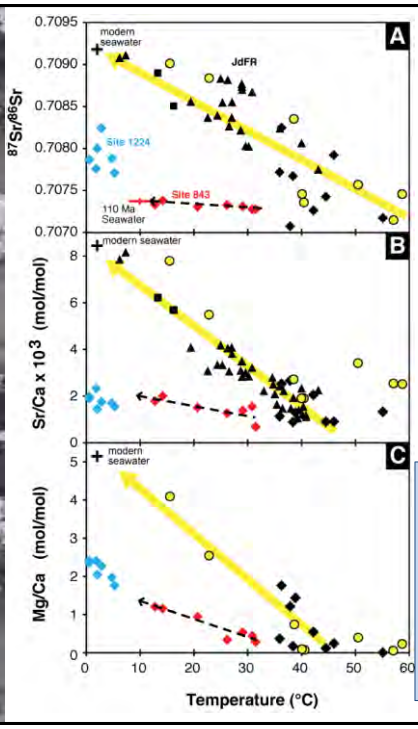
  (i) 100-500 m of sediment

  (ii) <60 m of igneous basement (0.8 – 3.6 Ma)
- Pore fluids were sampled
- $CaCO_3$ veins were recovered from 5 of the sites

The Leg 168 Drilling Transect



Compositions of the lowermost sediment pore fluids record the evolution of the seawater-derived ridge flank fluid as it is heated and reacts with the basement.



For Juan de Fuca Ridge:

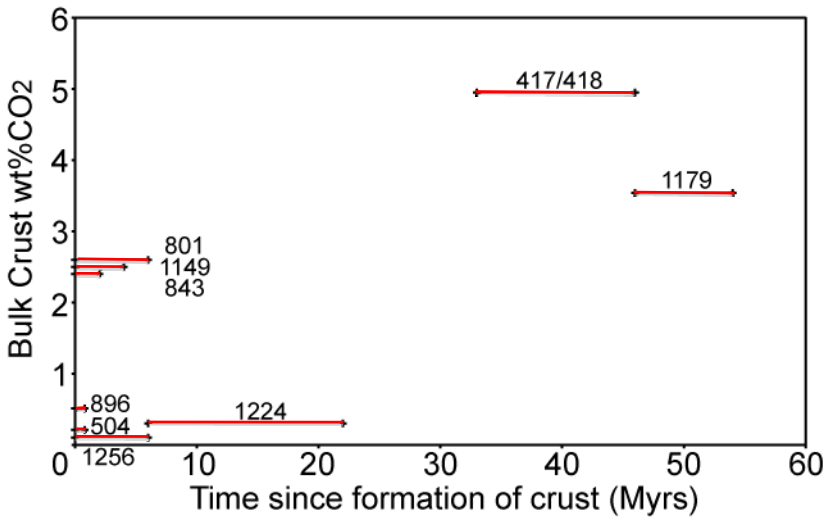
- Using appropriate partition coefficients for aragonite and calcite, the Mg/Ca and Sr/Ca ratios of the fluids they precipitated from were calculated.
- $CaCO_3$ record the same temperature-dependent fluid evolution as the near-basement pore fluids

(**Coggon et al., 2004**)

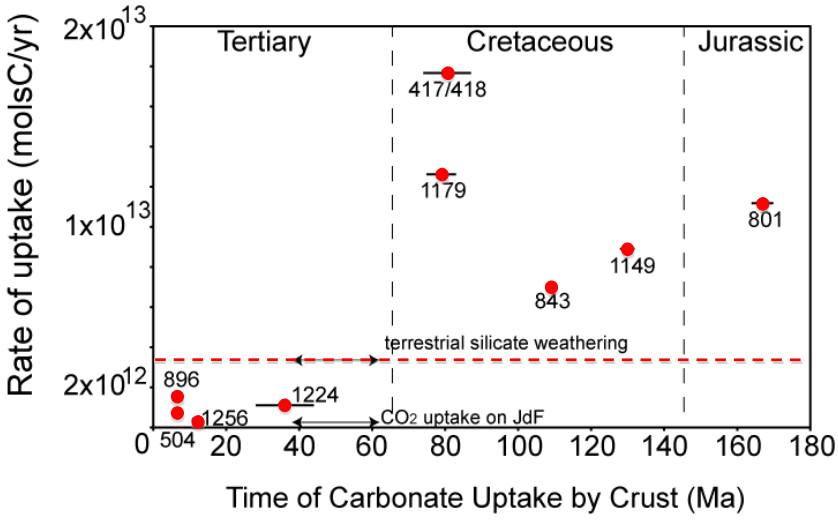
- Apply approach to vein suites from ancient oceanic crust to estimate past seawater Mg/Ca and Sr/Ca (**Coggon et al., 2010**)

- **Also yields information on:**
- past **minimum** ocean bottom water temperatures
- the **timing** of formation of the carbonate veins
- the **duration** of "effective" hydrothermal circulation at a particular site

Timing and Duration of Carbonate Formation after Crustal Formation



Carbonate uptake by hydrothermal alteration of oceanic crust



Seafloor carbonate implications:

- CO_3 of Mesozoic crust >> Tertiary crust
- Carbonate formation generally within 10-20 Myrs
- High CO_3 contents of Mesozoic crust
  reflect Mesozoic oceanic conditions
  (High T, low Mg/Ca, high pCO_2….)
- There may be carbonate "events"
  where ppt of ocean floor CO3 >>
  terrestrial silicate weathering

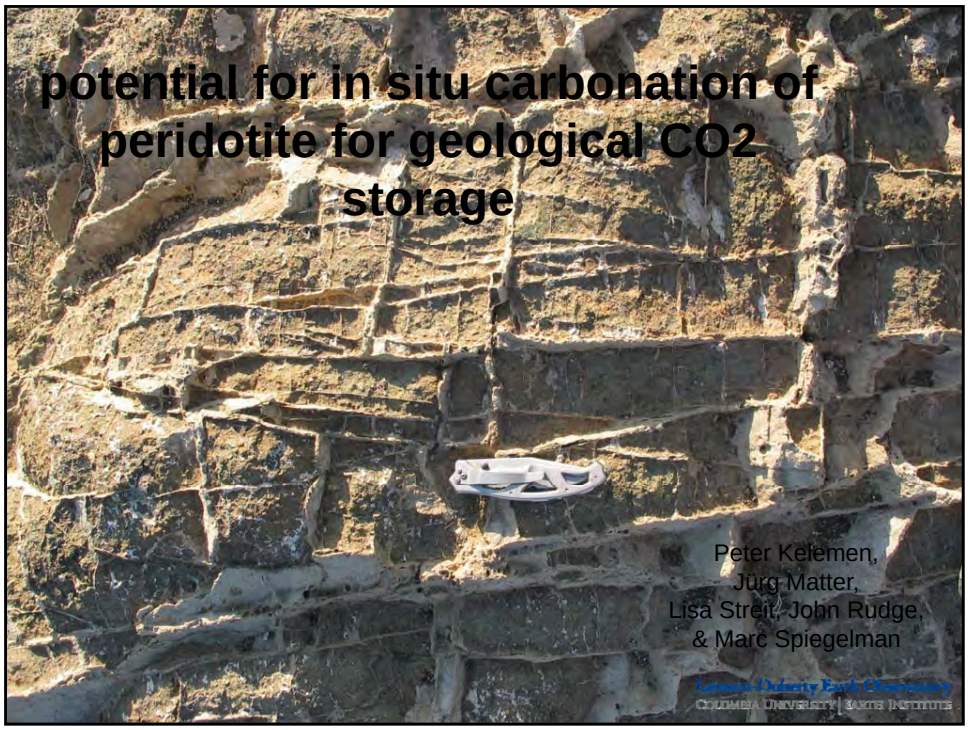
i.e., fluid-rock reaction conditions bring the huge mass of seafloor mafic rocks into the silicate weathering cycle

Understanding active and past mineral carbonation systems may provide important clues about:

How the Earth deals with elevated pCO_2

How to make industrial-scale mineral carbonate most efficient

3. P. Kelemen – LDEO, USA.



ex situ & in situ mineral carbonation

natural example of in situ carbonation in Oman

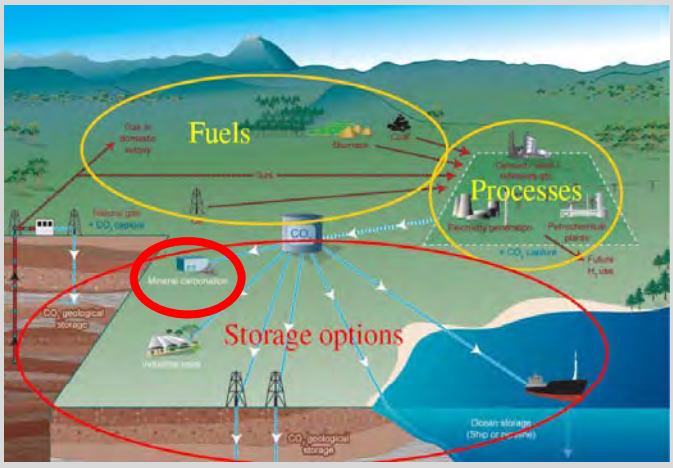
possible methods for accelerating and sustaining rates

at high rates (185˚ C, high PCO2),
energy from reaction can help to
sustain high temperatures

large volume changes … due to reaction can
maintain permeability & reactive surface area

capture from seawater rather than smokestack

geological CO2 storage

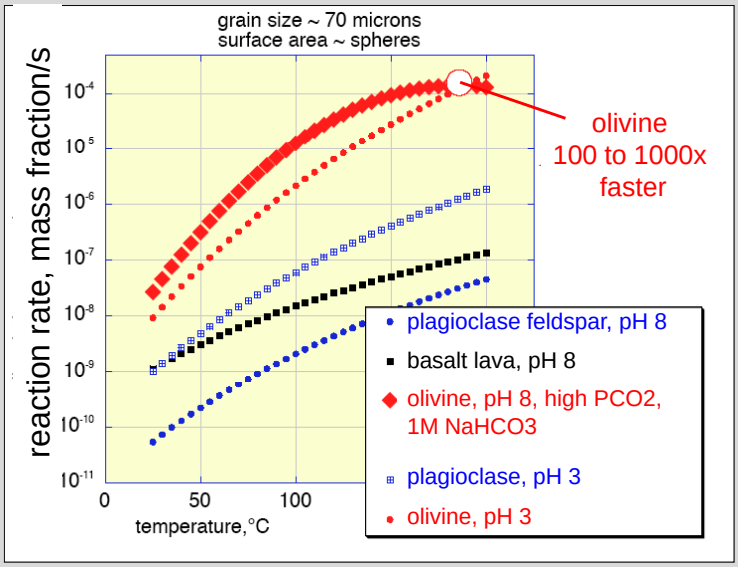


natural rock-forming minerals + CO2 = solid carbonate minerals

Source: IPCC Special Report on Carbon Dioxide Capture and Storage

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

mineral carbonation: olivine (Mg2SiO4) is fastest



Matter & Kelemen, Nature Geoscience, 2009

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

ex situ mineral carbonation: expensive

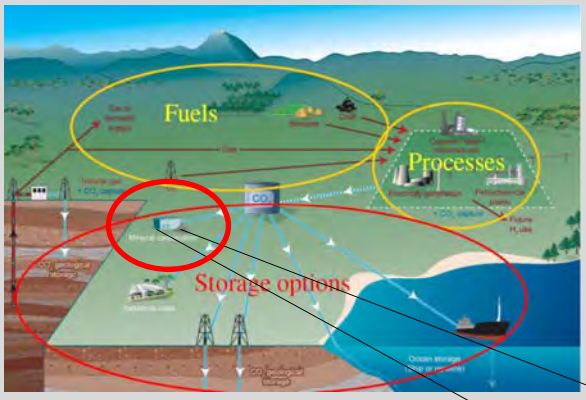
IPCC Report on Carbon Capture & Storage, 2005
Chapter 7: Mineral carbonation and industrial uses of carbon dioxide
Marco Mazzotti et al.

The technology is … not yet ready for implementation.

The best case studied so far is [carbonation of] olivine

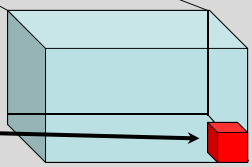
⇒ 60-180% more energy

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute



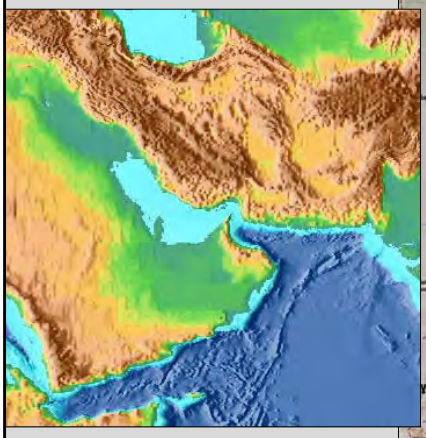
small blue building:
proportion of scientists
working on
mineral carbonation
mostly, *ex situ*,
"at the smokestack",
proposed 1990

little red room
in small blue building:
proportion of scientists studying
in situ mineral carbonation,
in the Earth

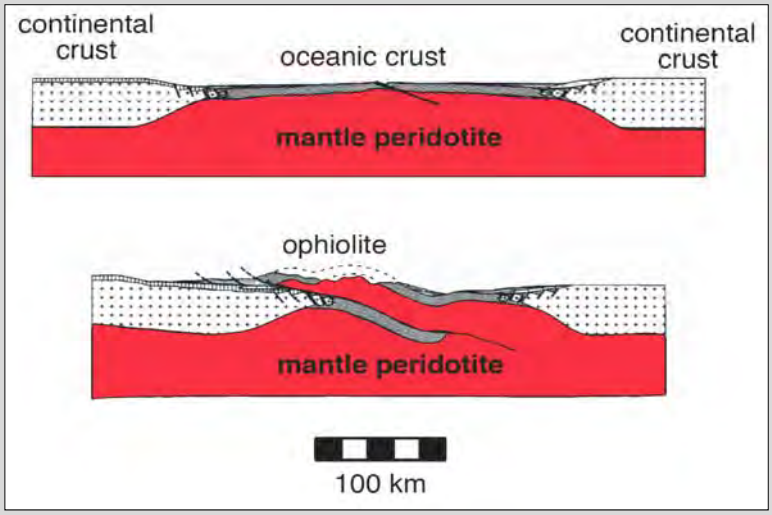


Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

mountains of
northern Oman
composed of oceanic
crust & upper mantle



emplacement of olivine-rich rock (peridotite) near the surface



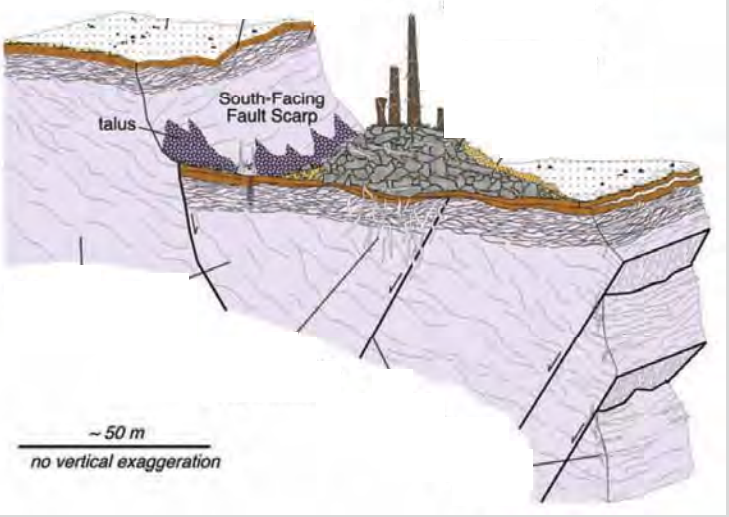
modified from Coleman, Ophiolites, Kluwer, 1977

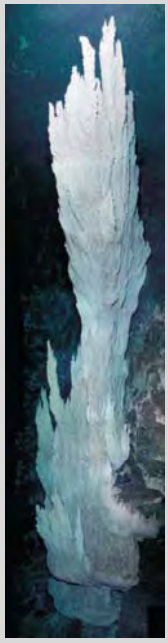
Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

in situ mineral carbonation in peridotite

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

geologic CO2 **capture** & storage





Lost City hydrothermal vents, Mid-Atlantic Ridge
Kelley et al., Nature 2001, Science 2005; Früh-Green et al., Science 2003

Lamont-Doherty Earth Observatory
Columbia University | Farth Institute

serpentinization (hydration) of olivine ± pyroxene (not balanced)

$Mg_2SiO_4 \pm Mg_2Si_2O_6 + H_2O = Mg_3Si_2O_5(OH)_4 \pm Mg(OH)_2$
Mg-olivine Mg-pyroxene serpentine brucite

mixed hydration and carbonation

$4Mg_2SiO_4 + 4H_2O + 2CO_2 = 2Mg_3Si_2O_5(OH)_4 + 2MgCO_3$
Mg-olivine serpentine magnesite

$4Mg_2SiO_4 + H_2O + 5CO_2 = Mg_3Si_4O_{10}(OH)_2 + 5MgCO_3$
Mg-olivine talc magnesite

full carbonation of olivine

$4Mg_2SiO_4 + 8CO_2 = 8MgCO_3 + 4SiO_2$
Mg-olivine magnesite quartz

adding Calcium

$4Mg_2SiO_4 + CaMgSi_2O_6 + 6H_2O + CO_2 = 3Mg_3Si_2O_5(OH)_4 + CaCO_3$
Mg-olivine CaMg-pyroxene serpentine calcite

$4Mg_2SiO_4 + CaMgSi_2O_6 + 7H_2O = 3Mg_3Si_2O_5(OH)_4 + \mathbf{Ca(OH)_2}$
Mg olivine CaMg-pyroxene serpentine dissolved calcium hydroxide

$\mathbf{Ca(OH)_2} + CO_2 = H_2O + CaCO_3$
dissolved calcium hydroxide s calcite

Lamont-Doherty Earth Observatory
Columbia University | Farth Institute

serpentinization (hydration) of olivine ± pyroxene (not balanced)

$Mg_2SiO_4 \pm Mg_2Si_2O_6 + H_2O = Mg_3Si_2O_5(OH)_4 \pm Mg(OH)_2$
Mg-olivine; Mg-pyroxene; serpentine; brucite

mixed hydration and carbonation

$4Mg_2SiO_4 + 4H_2O + 2CO_2 = 2Mg_3Si_2O_5(OH)_4 + 2MgCO_3$
Mg-olivine; serpentine; magnesite

$4Mg_2SiO_4 + H_2O + 5CO_2 = Mg_3Si_4O_{10}(OH)_2 + 5MgCO_3$
Mg-olivine; talc; magnesite

full carbonation of olivine

$4Mg_2SiO_4 + 8CO_2 = 8MgCO_3 + 4SiO_2$
Mg-olivine; magnesite; quartz

adding Calcium

$4Mg_2SiO_4 + CaMgSi_2O_6 + 6H_2O + CO_2 = 3Mg_3Si_2O_5(OH)_4 + CaCO_3$
Mg-olivine; CaMg-pyroxene; serpentine; calcite

$4Mg_2SiO_4 + CaMgSi_2O_6 + 7H_2O = 3Mg_3Si_2O_5(OH)_4 + \mathbf{Ca(OH)_2}$
Mg olivine; CaMg-pyroxene; serpentine; dissolved calcium hydroxide

$\mathbf{Ca(OH)_2} + CO_2 = H_2O + CaCO_3$
dissolved calcium hydroxide s; calcite

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

serpentinization (hydration) of olivine ± pyroxene (not balanced)

$Mg_2SiO_4 \pm Mg_2Si_2O_6 + H_2O = Mg_3Si_2O_5(OH)_4 \pm Mg(OH)_2$
Mg-olivine; Mg-pyroxene; serpentine; brucite

mixed hydration and carbonation

$4Mg_2SiO_4 + 4H_2O + 2CO_2 = 2Mg_3Si_2O_5(OH)_4 + 2MgCO_3$
Mg-olivine; serpentine; magnesite

$4Mg_2SiO_4 + H_2O + 5CO_2 = Mg_3Si_4O_{10}(OH)_2 + 5MgCO_3$
Mg-olivine; talc; magnesite

full carbonation of olivine

$4Mg_2SiO_4 + 8CO_2 = 8MgCO_3 + 4SiO_2$
Mg-olivine; magnesite; quartz

adding Calcium

$4Mg_2SiO_4 + CaMgSi_2O_6 + 6H_2O + CO_2 = 3Mg_3Si_2O_5(OH)_4 + CaCO_3$
Mg-olivine; CaMg-pyroxene; serpentine; calcite

$4Mg_2SiO_4 + CaMgSi_2O_6 + 7H_2O = 3Mg_3Si_2O_5(OH)_4 + \mathbf{Ca(OH)_2}$
Mg olivine; CaMg-pyroxene; serpentine; dissolved calcium hydroxide

$\mathbf{Ca(OH)_2} + CO_2 = H_2O + CaCO_3$
dissolved calcium hydroxide s; calcite

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

storage capacity in peridotite

peridotite in Oman > 350 km long, 15 km wide, 3 km thick
density 3300 kg/m^3

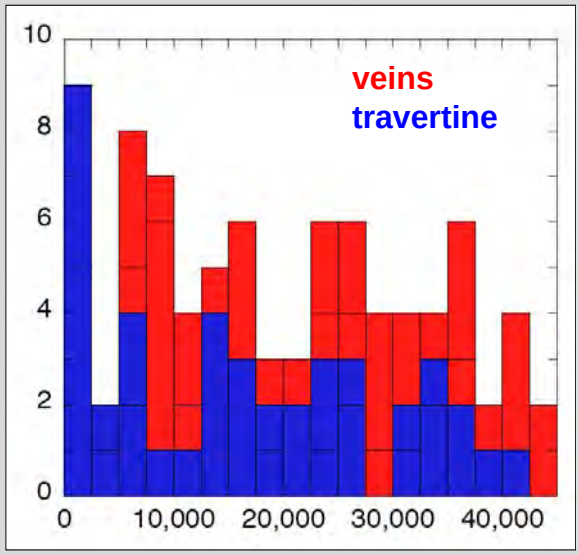
CO2/fresh peridotite ~ 0.6
~ 33 trillion tons CO2 in Oman
350 wedges, could store all current CO2 output for 1000 years

could store > 100 trillion tons worldwide
> 10x more than "upper bound" for pore space

OK, but what about rates?

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

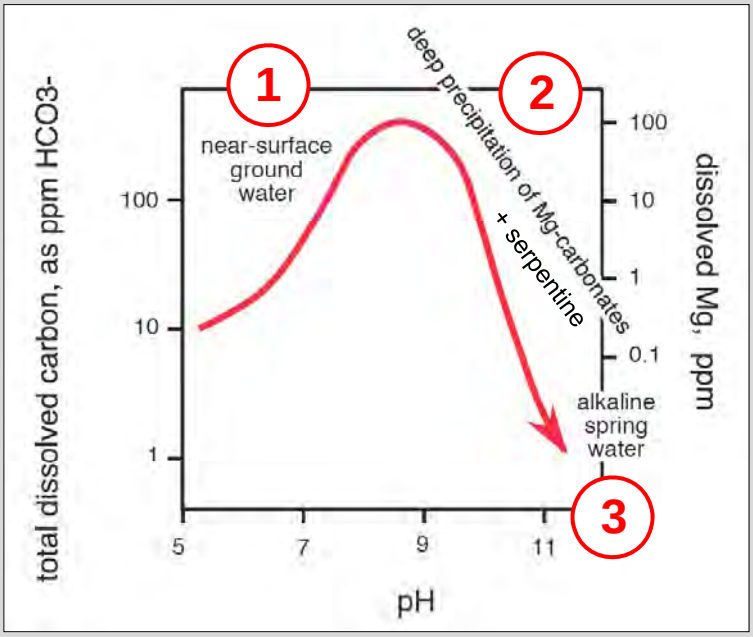
Clark & Fontes, plus our 2007 & 2008 samples



plus 2 that are too old to date

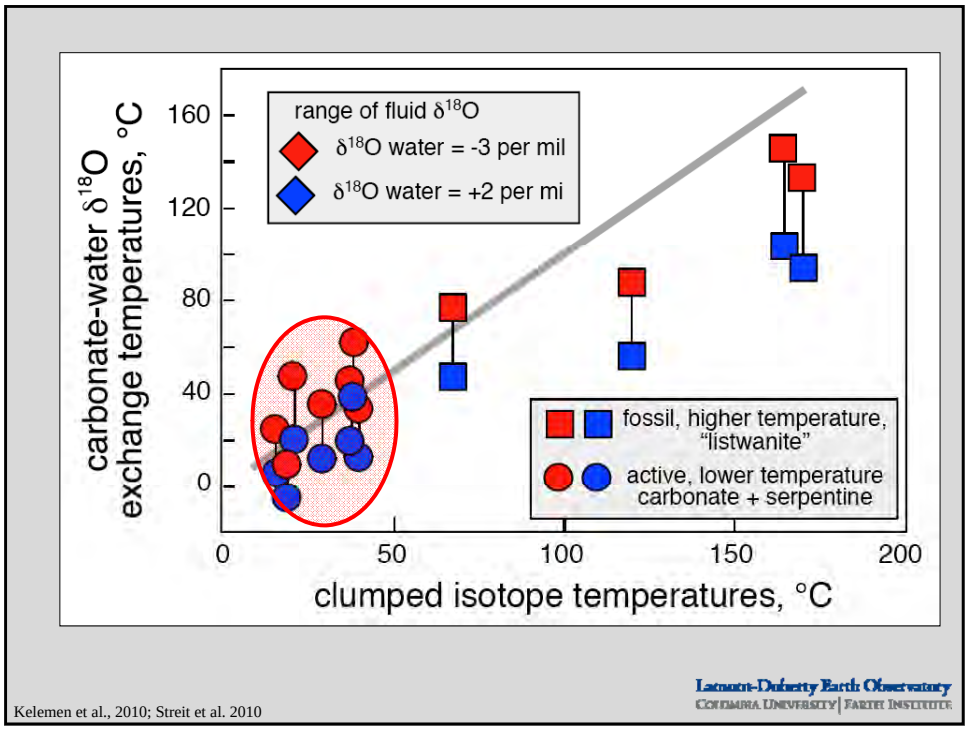
Kelemen & Matter, 2008; Kelemen et al., 2010

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

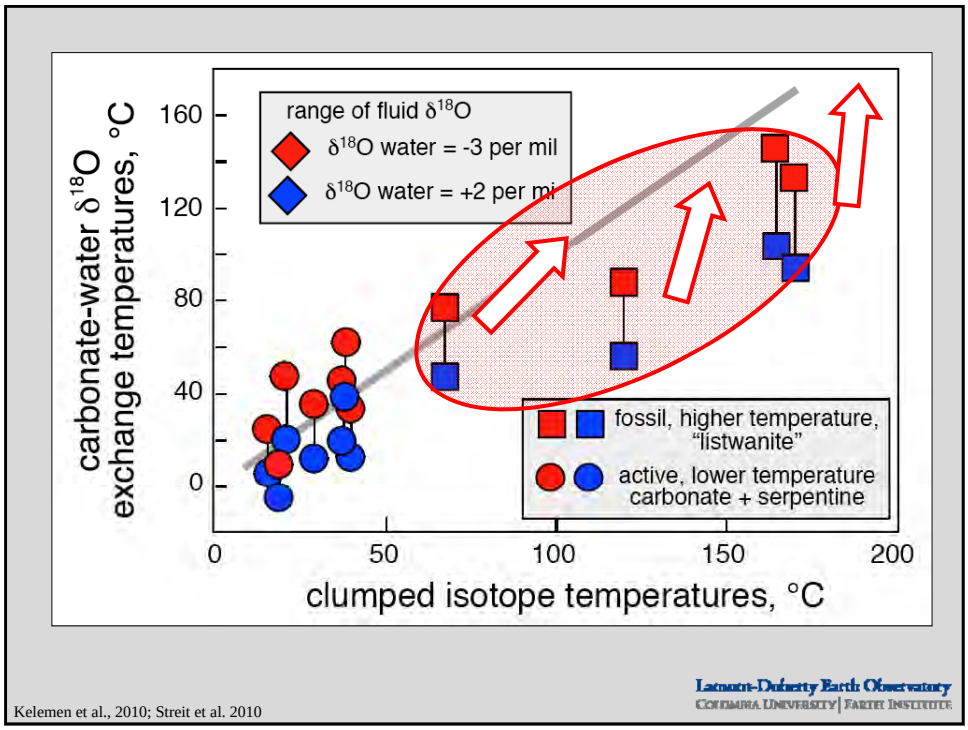


Bruni et al App Geochem 2002

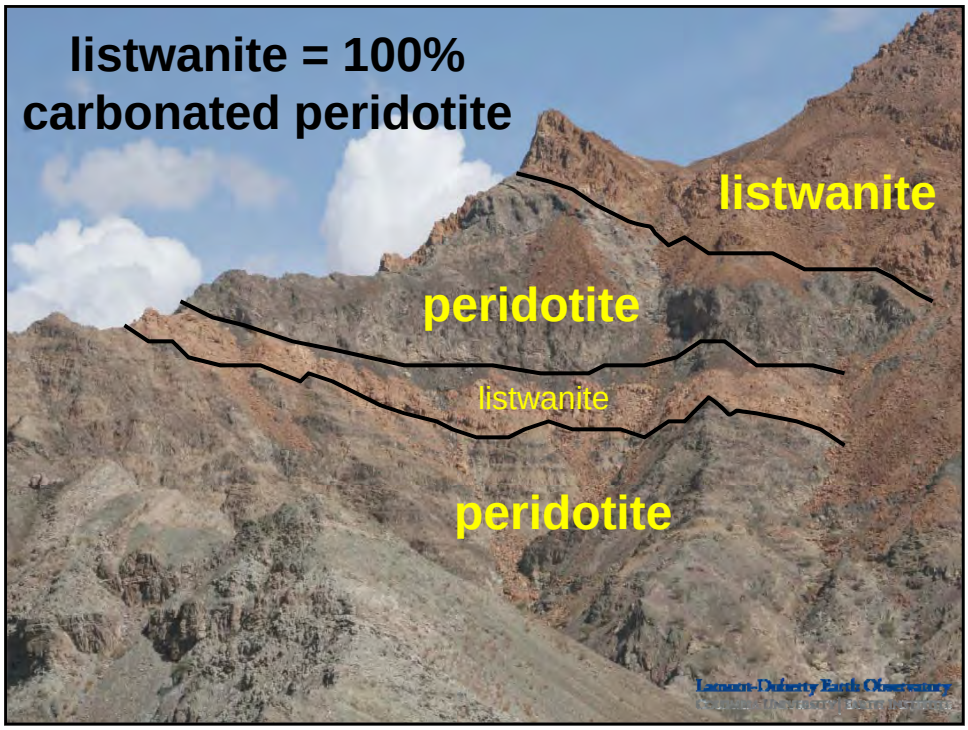
Lamont-Doherty Earth Observatory
Columbia University | Earth Institute



Kelemen et al., 2010; Streit et al. 2010



Kelemen et al., 2010; Streit et al. 2010



natural peridotite carbonation rate

rate of solid carbonate formation in Oman now
overall ~ 10^4 to 10^5 tons CO2/yr

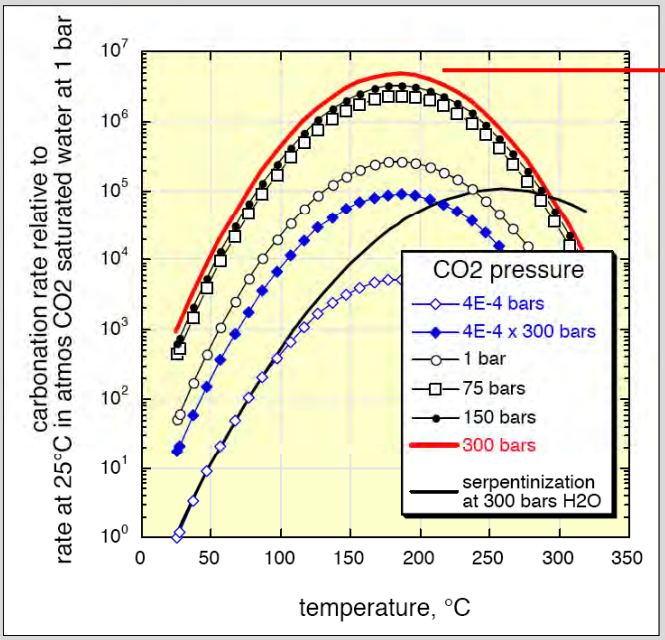
in actively carbonating upper 15 m
~ 1000 tons CO2/km^3/yr, 1 gm CO2/m^3/yr

FAST BUT NOT FAST ENOUGH

for comparison,
human emissions ~ 35 10^9 tons/yr

Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

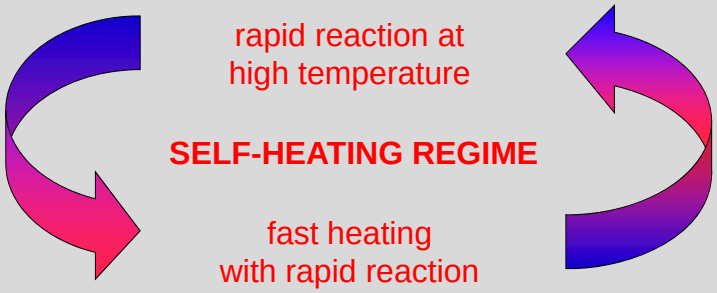
Lamont-Doherty Earth Observatory
Columbia University | Earth Institute



x 1000 tons/km^3/yr
=
~ 1 Gt/km^3/yr

Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

reactions that condense fluid or gas to form solid usually evolve heat, and increase solid volume



Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

zero-dimensional thermal model

$dT/dt =$

$(T_{in}-T)\ \rho_f\ C_p^f\ \phi\ w/(\rho_s\ C_p^s\ d)$ — advective fluid flow

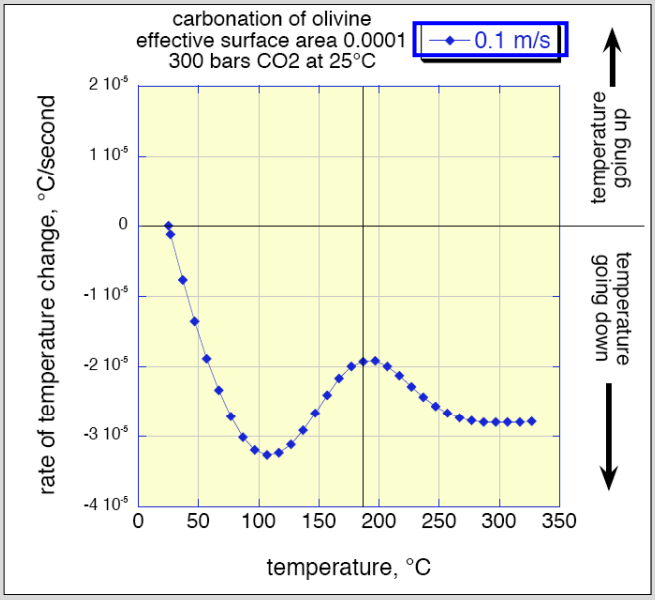
$-\ (T-T_o)\ \kappa/\ d^2$ — thermal diffusion

$+\ \Gamma(T,P_{CO2})A\Delta H/[C_p^s(1-\phi)+C_p^f(\phi)]$ — heating from reaction

10^{-4} = 1 m "grain size", not 70 microns

Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

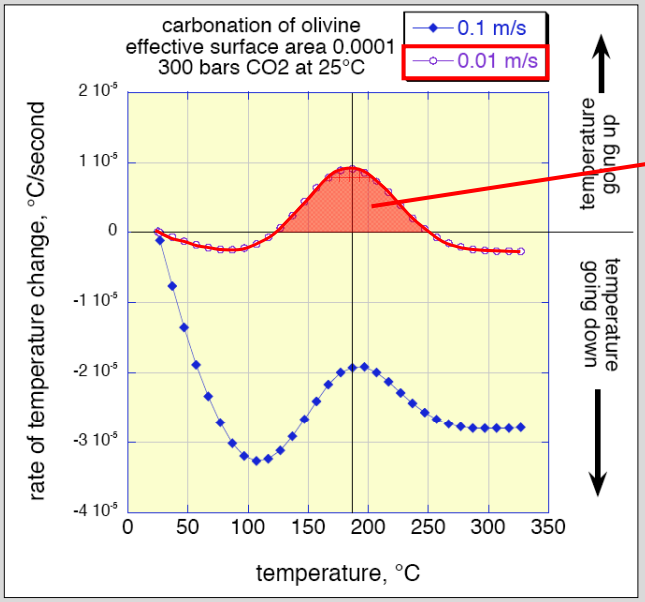


temperature change
=
cooling from cold fluid
+
cooling to surroundings
+
heating from reaction

here:
rapid flow
⇒ cooling

Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

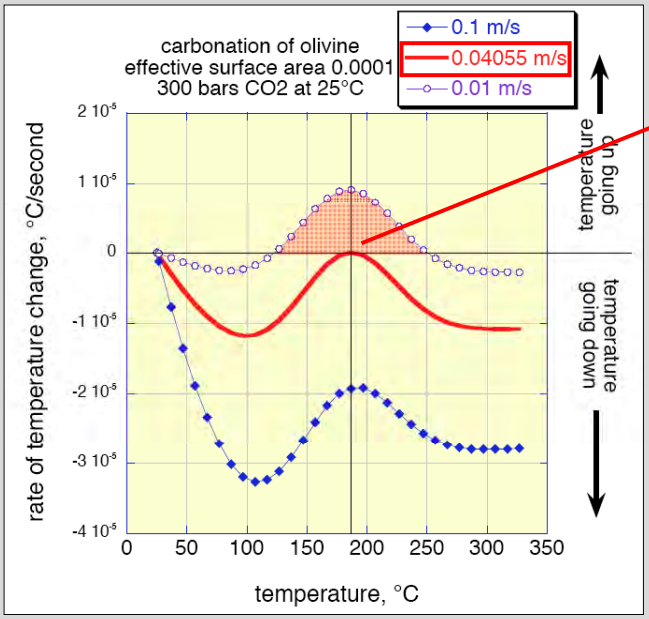


self heating regime

here: slower flow ⇒ heating becomes important

Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute



no change

here: flow rate tuned to maintain constant temperature at optimal reaction rate

Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

zero-dimensional thermal model

$dT/dt =$

$(T_{in}-T)\ \rho_f\ C_p^f\ \phi\ w/(\rho_s\ C_p^s\ d)$ — advective fluid flow

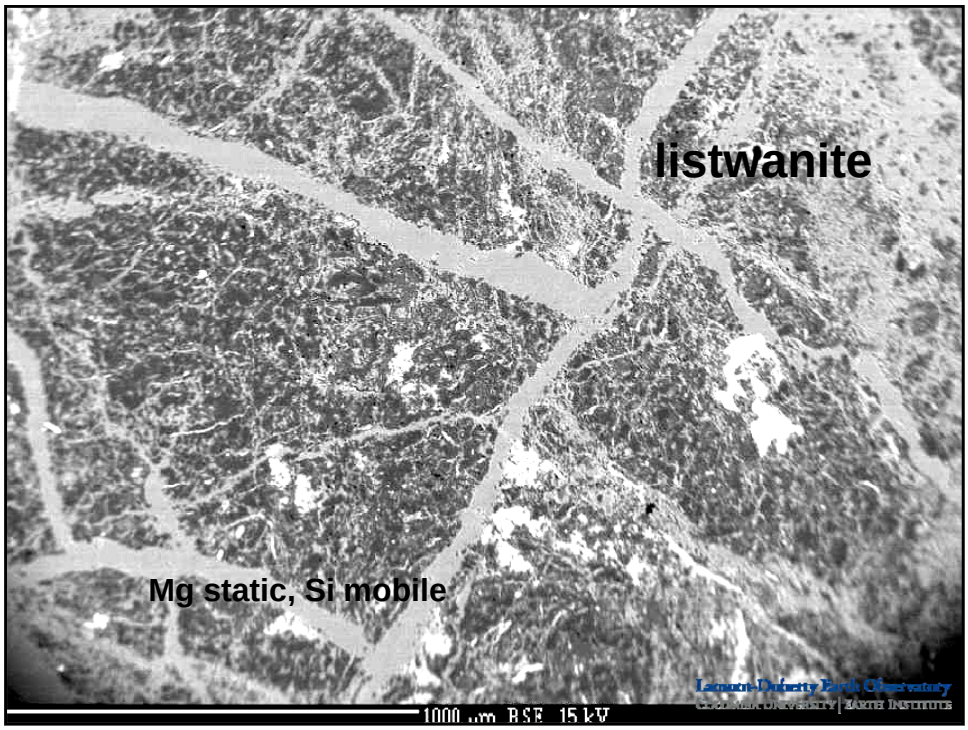
$-\ (T-T_o)\ \kappa/d^2$ — thermal diffusion

$+\ \Gamma(T)\ A\ \Delta H/[C_p^s(1-\phi)+C_p^f(\phi)]$ — heating from reaction

Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

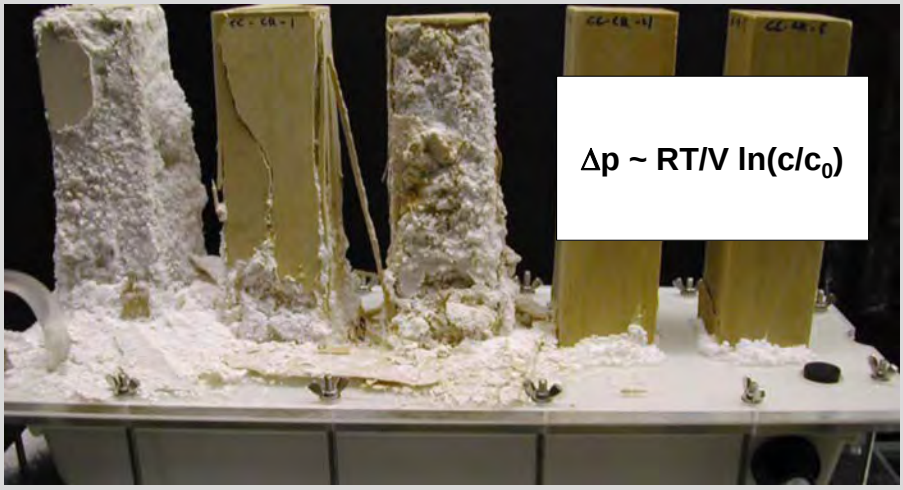
listwanite
Mg static, Si mobile


listwanite
Mg static, Si mobile
1000 um BSE 15 kV

reactions that condense fluid or gas to form solid usually evolve heat and increase solid volume

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

reaction-driven cracking: salt in limestone



Prof. George Scherer, Princeton University http://web.mac.com/gwscherer1/SchererGroup/Salt_Crystallization.html

Scherer, G., J Crystal Growth 2004; Steiger, J. Crystal Growth, 2005; Saldi et al., GCA 2009

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

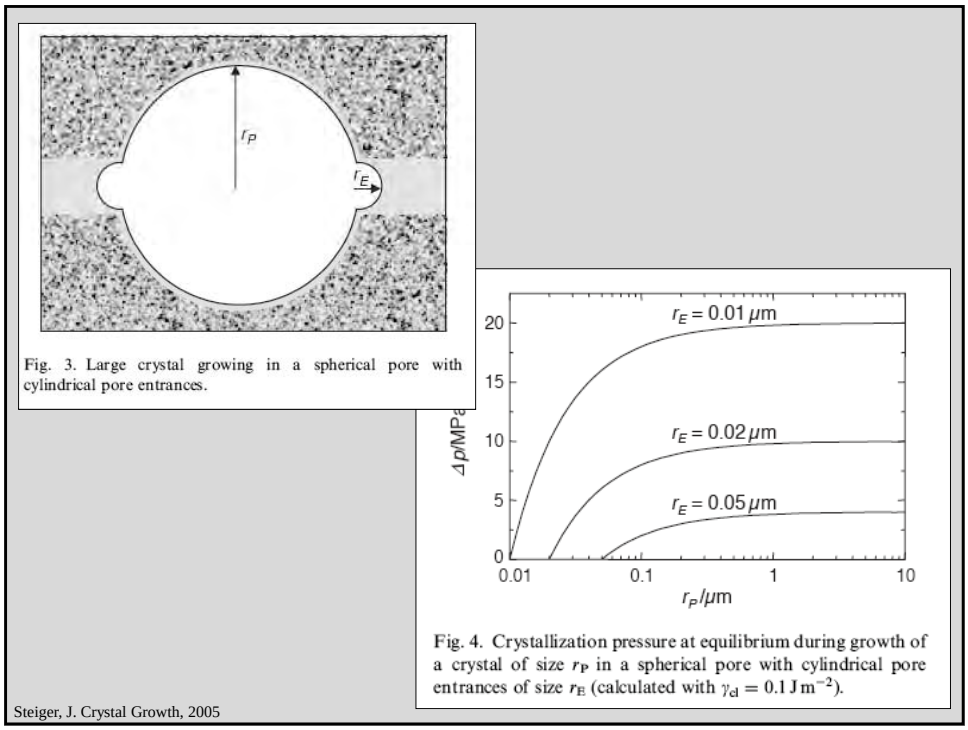
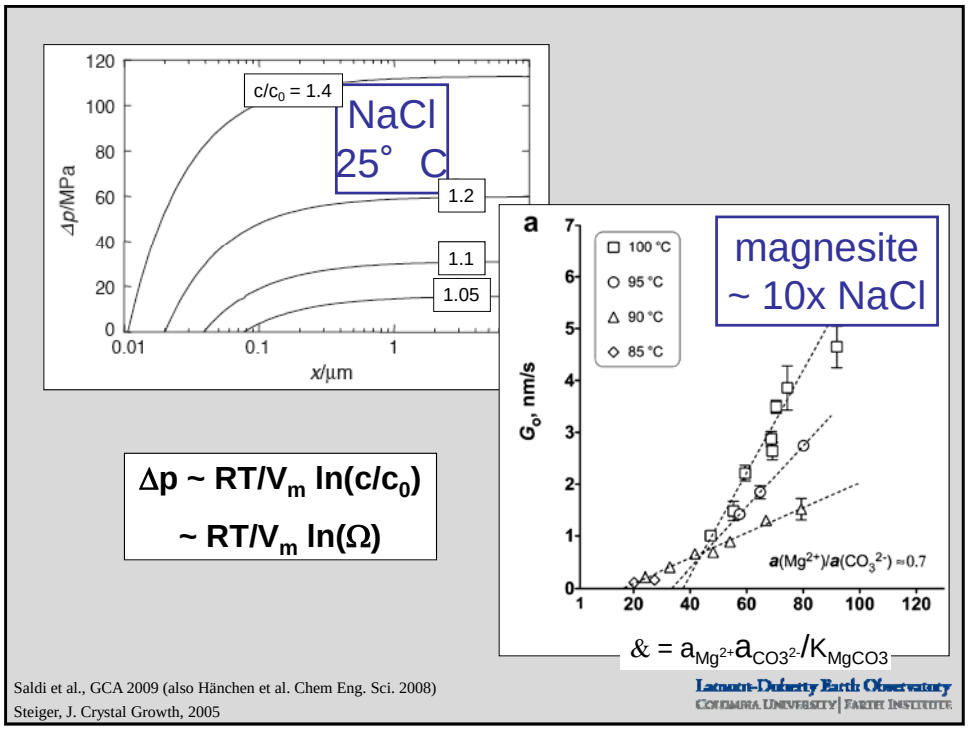


Fig. 3. Large crystal growing in a spherical pore with cylindrical pore entrances.

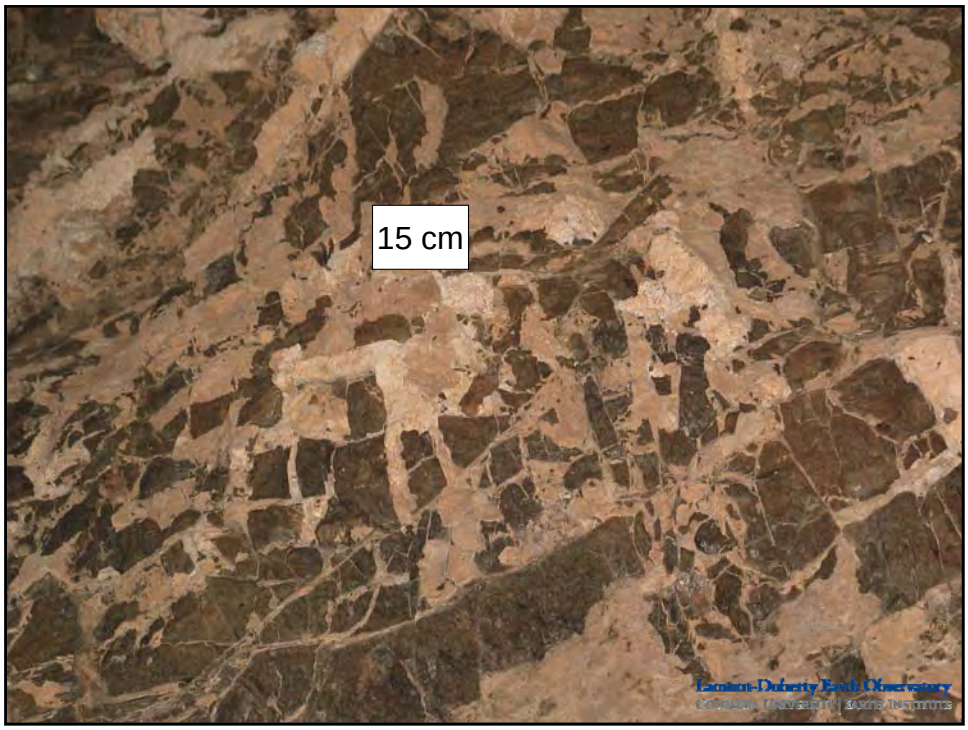
Fig. 4. Crystallization pressure at equilibrium during growth of a crystal of size r_P in a spherical pore with cylindrical pore entrances of size r_E (calculated with $\gamma_{cl} = 0.1\,J\,m^{-2}$).

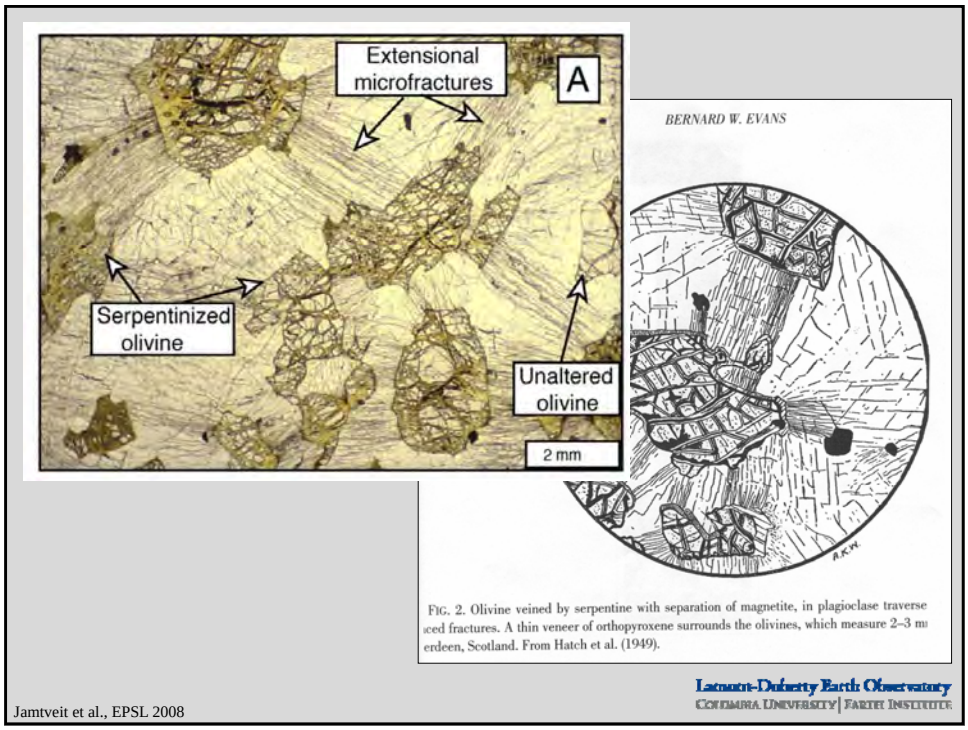
Steiger, J. Crystal Growth, 2005

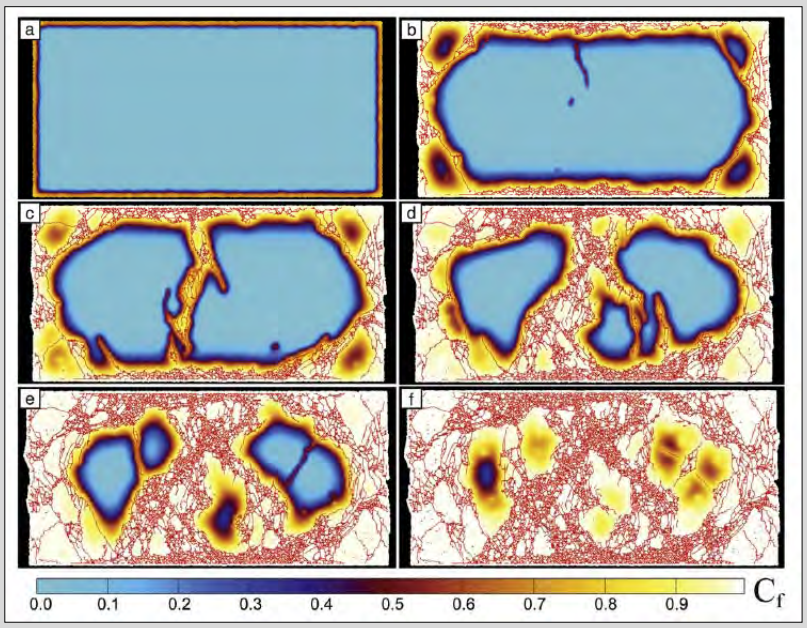


Saldi et al., GCA 2009 (also Hänchen et al. Chem Eng. Sci. 2008)
Steiger, J. Crystal Growth, 2005

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute


15 cm
Lamont-Doherty Earth Observatory

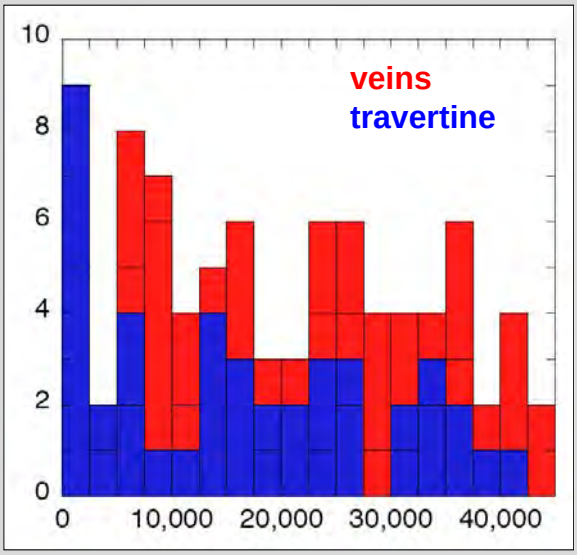

Extensional microfractures
A
Serpentinized olivine
Unaltered olivine
2 mm
BERNARD W. EVANS
FIG. 2. Olivine veined by serpentine with separation of magnetite, in plagioclase traverse
ced fractures. A thin veneer of orthopyroxene surrounds the olivines, which measure 2–3 m
erdeen, Scotland. From Hatch et al. (1949).
Lamont-Doherty Earth Observatory
Columbia University | Earth Institute
Jamtveit et al., EPSL 2008



Royne et al. EPSL 2008 (Fletcher & Brantley, EPSL 2006; O'Hanley Geology 1992; MacDonald & Fyfe Tectonophys. 1985)

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

Clark & Fontes, plus our 2007 & 2008 samples

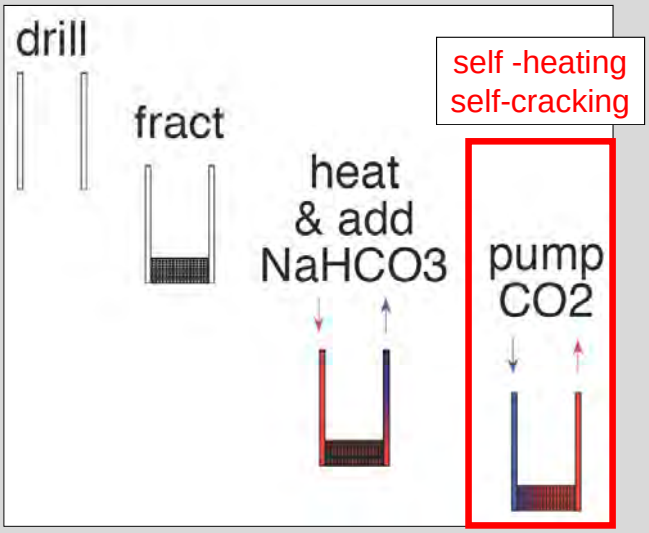


plus 2 that are too old to date

Kelemen & Matter, 2008; Kelemen et al., 2010

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

in situ mineral carbonation with pre-heating



Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

what if little is done
and 600 (or 500, or 400) ppm CO2 is too much?
⇒ "negative emissions"

(at best, carbon capture from fossil fuel power plants achieves zero emissions)

OPTIONS

dispersal of aerosols in the stratosphere

large increase in "standing stock" of biomass

carbon capture at biofuel power plants (+ storage)

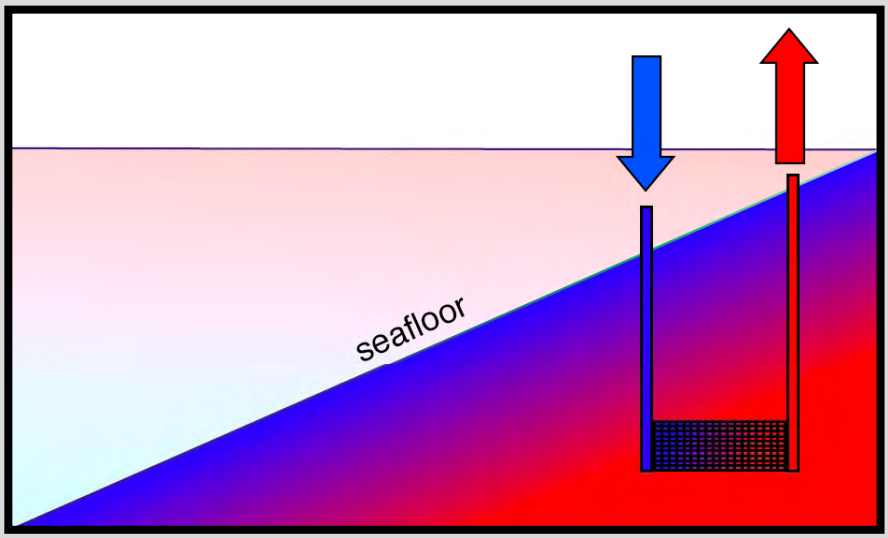
direct air capture of CO2 (+ storage)

geologic CO2 capture & storage, using shallow seawater

energetically challenging, capture & store
400-600 ppm CO2 from air, 100-200 ppm from seawater
100 to 1000x more dilute than 120,000 ppm from flue gas

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

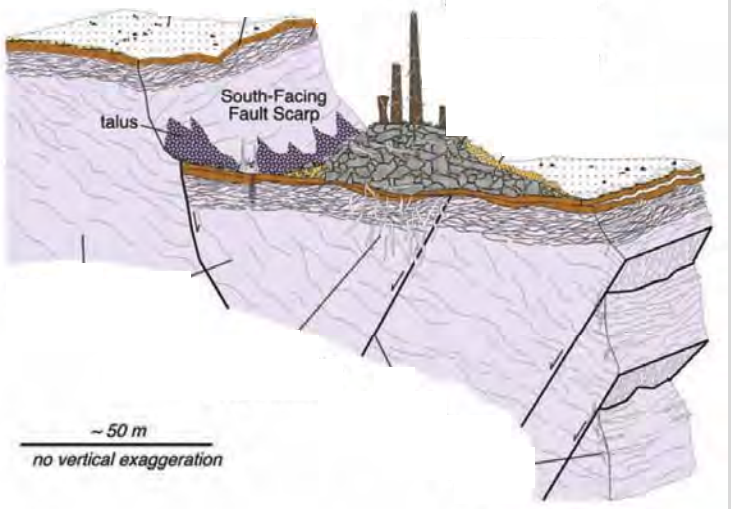
seawater as a CO2 transport fluid?

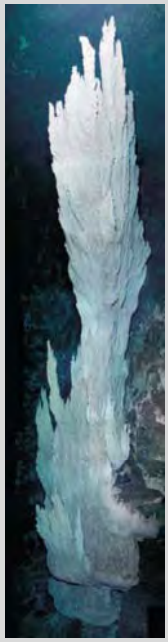


Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

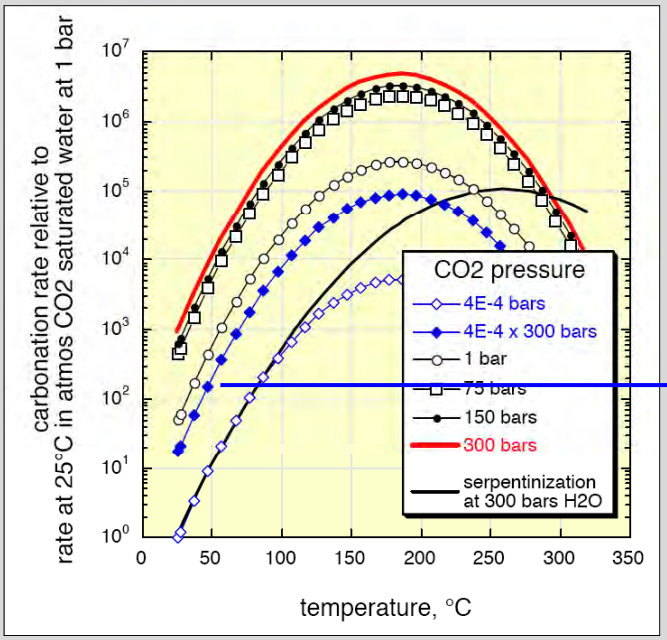
geologic CO2 **capture** & storage





Lost City hydrothermal vents, Mid-Atlantic Ridge
Kelley et al., Nature 2001, Science 2005; Früh-Green et al., Science 2003

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

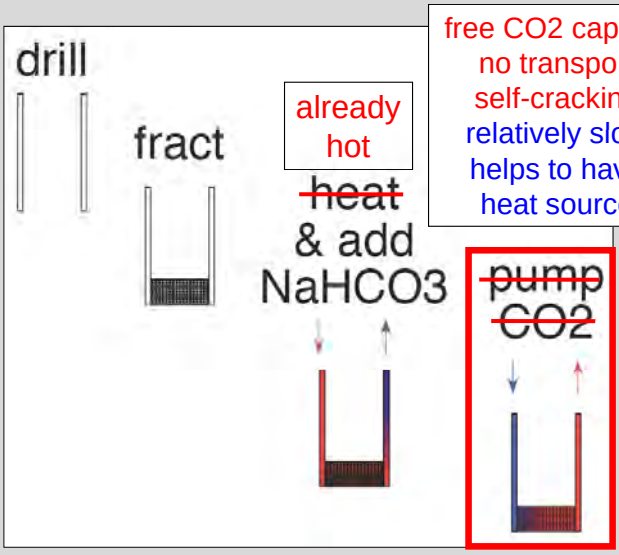


practical bound for supply-limited transport of CO2 in seawater

Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute

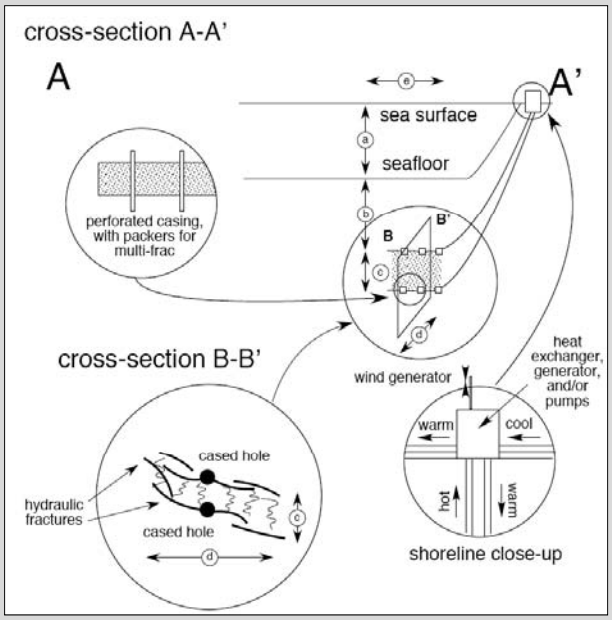
in situ CO2 *capture* and storage



free CO2 capture
no transport
self-cracking
relatively slow
helps to have
heat source

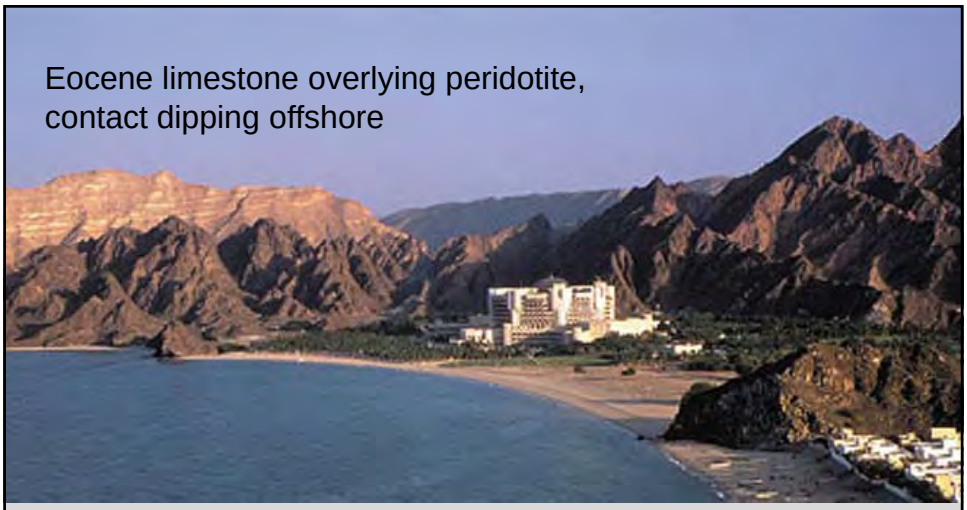
Kelemen & Matter, Proceedings of the National Academy of Sciences, 2008

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute



Total Fantasy, 2010

Lamont-Doherty Earth Observatory
Columbia University | Earth Institute



drill from coast, react offshore

minimizes drilling costs &
societal impacts
(ground deformation, possible induced seismicity,
possible ground water contamination

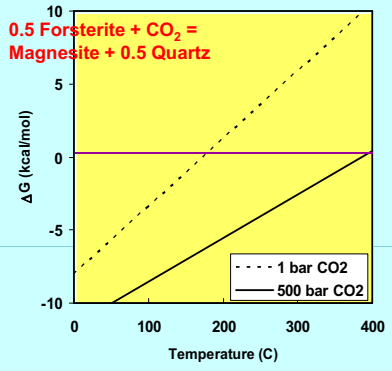
thank you for your attention

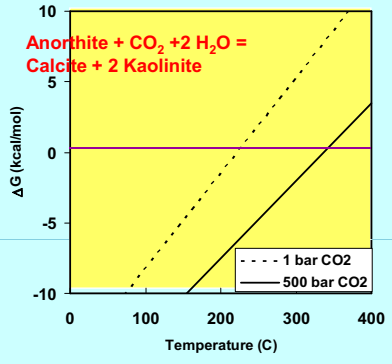
4. E. Oelkers – Univ. Toulouse, France.

The kinetics of Mineral Carbonation

Eric H. Oelkers
Experimental Geochemistry and Biogeochemistry
GET/Université Paul Sabatier, Toulouse, FRANCE

Carbon sequestration from the point of view of thermodynamics





Some challenges of Mineral Carbonation

→ Carbonation reactions tend to be volume positive
→ Secondary minerals other than carbonates can precipitation
→ Rocks that tend to be good sources of divalent cations tems to not have good cap-rocks
→ Risks of CO_2 leaks to the surface
→ Linking point sources to potential carbonation sites
→ Difficulties in carbon capture
→ Optmizing CO_2 dissolution into formation waters
→ Seconday minerals may slow reaction rates
→ Reactions can be slow

The overall process:

basalt
$SiAl_{0.36}Ca_{0.30}Mg_{0.25}Fe_{0.17}O_{3.35}$

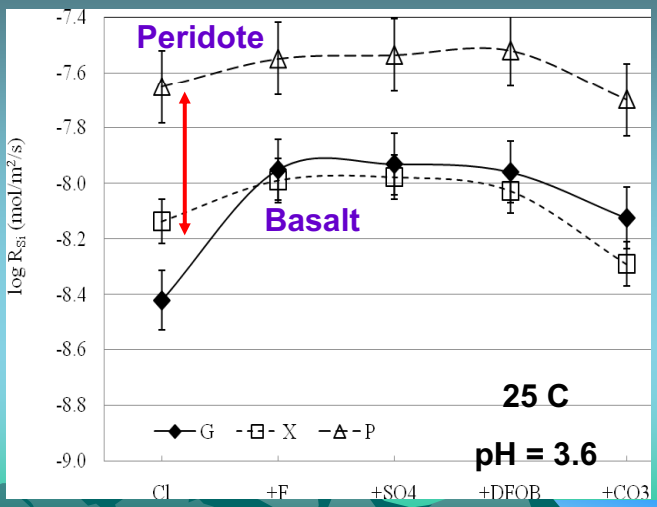
+ CO_2 =

peridotite
$SiAl_{0.08}Mg_{1.32}Fe_{0.14}O_{3.42}$

+ CO_2 =

Calcite
Magnesite
siderite

Relative dissolution rate of basalt and olivine CO_2 charged seawater (Wolff-Boenisch et al. 201x)



Fluid/solid evolution along flow path in basalt

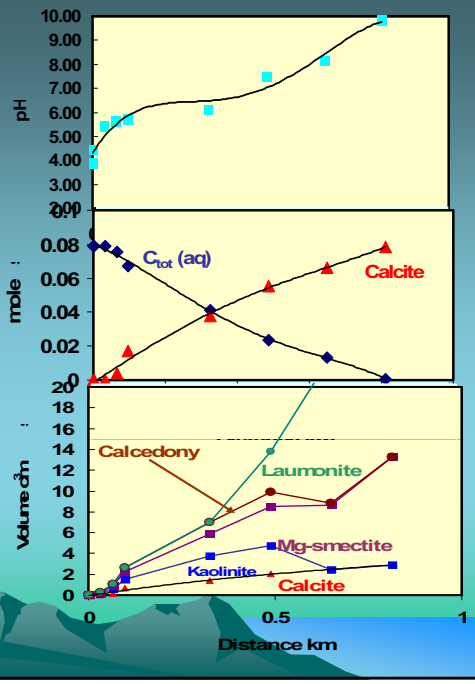
Original rock = 100% basaltic glass

Fracture width = 1 cm

Flow rate = 1 km/yr

T = 150 C

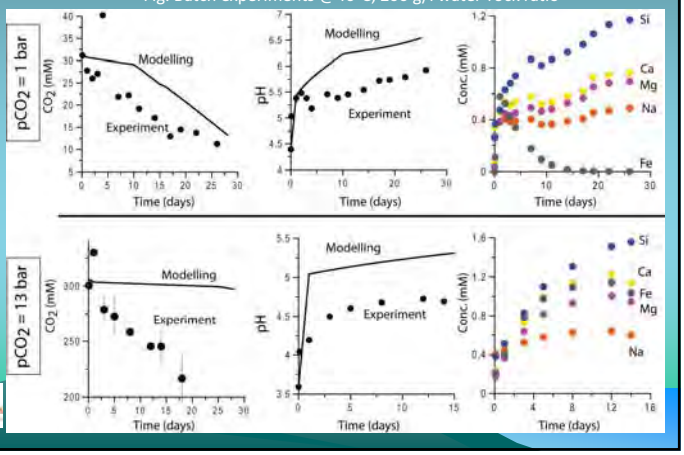
Inlet solution = 0.1 m NaCl equilibrated with 10 bar CO_2



Experiments of basalt carbonation (Gysi, 2011)

-CO_2 in solution mineralizes rapidly forming Mg, Fe, Ca and Mn carbonates
-The model and experimental results need to be tuned together (still loose ends)
-The rate of CO_2 mineralization between experiments and model compares well only at low pCO_2

Fig. Batch experiments @40°C, 200 g/l water-rock ratio



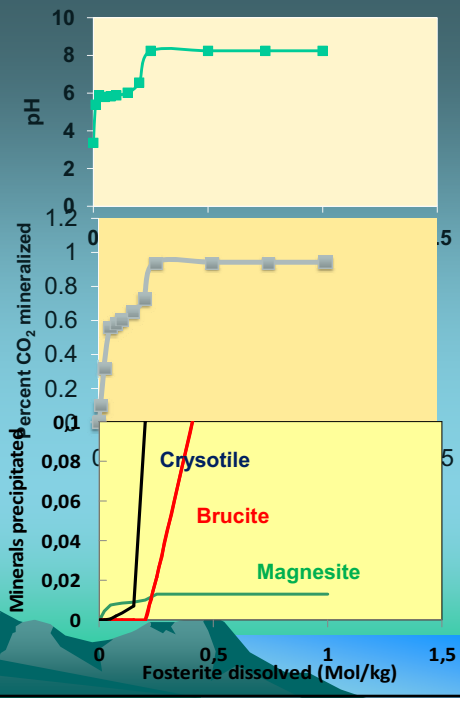
UNIVERSITY OF ICELAND

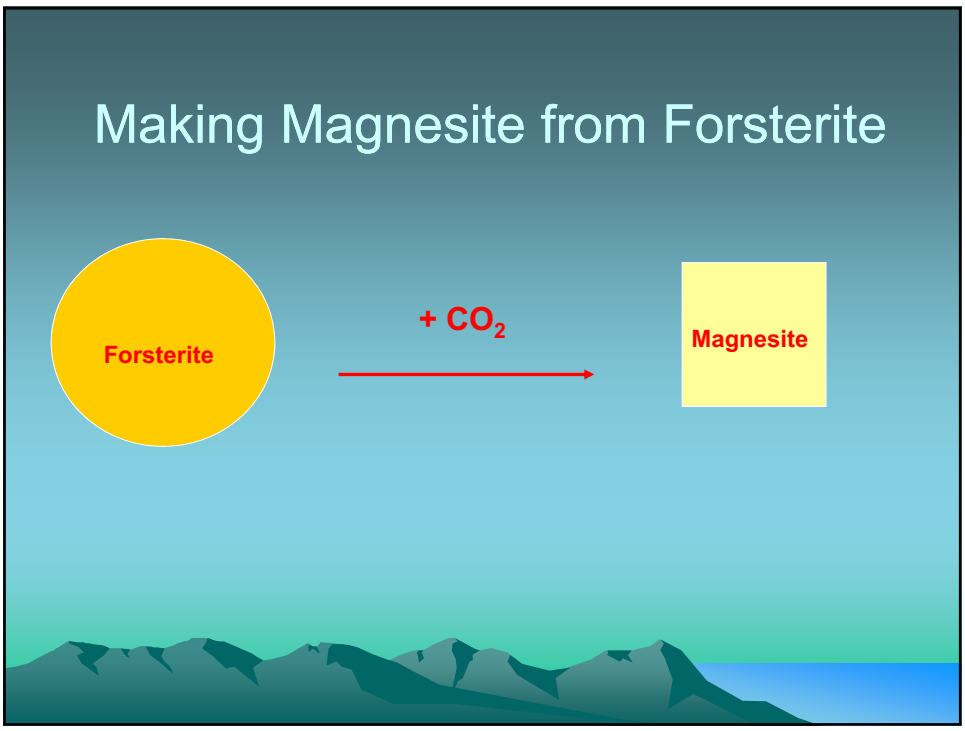
Fluid/solid evolution in Peridotite

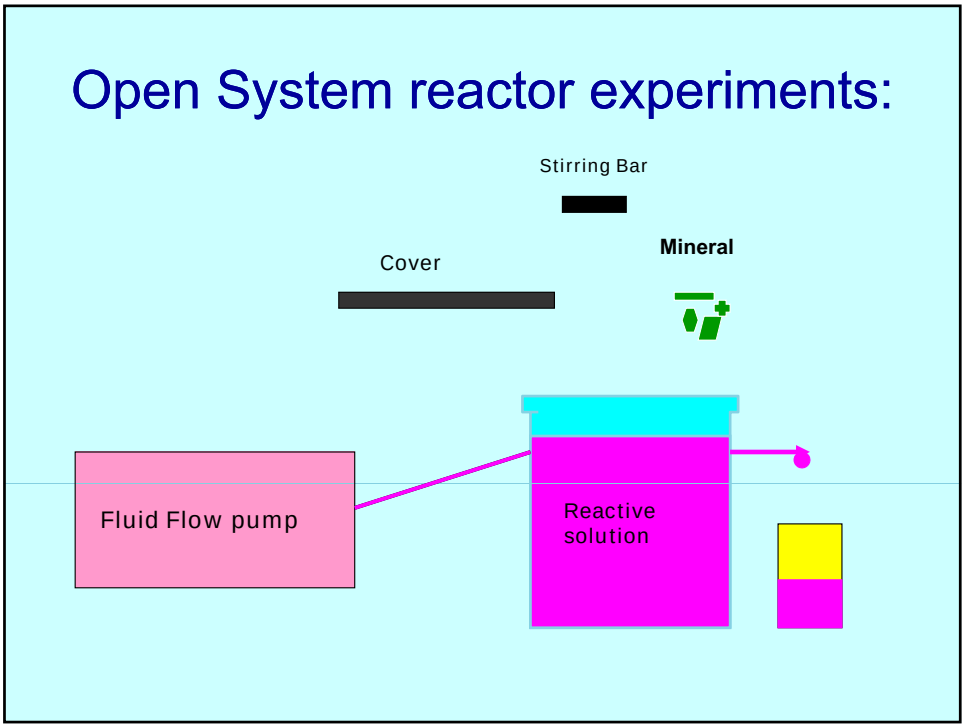
Original rock = 100% forsterite

T = 100 C

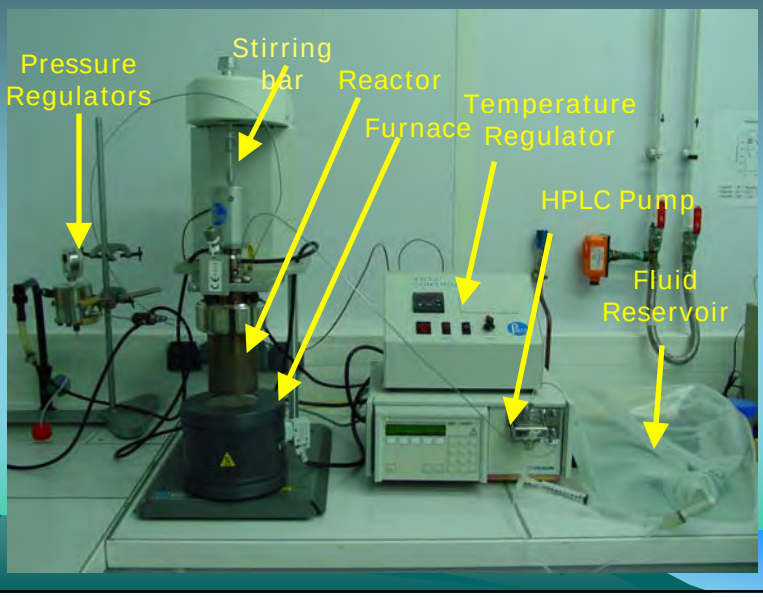
Inlet solution = 0.1 m NaCl equilibrated with 10 bar CO_2

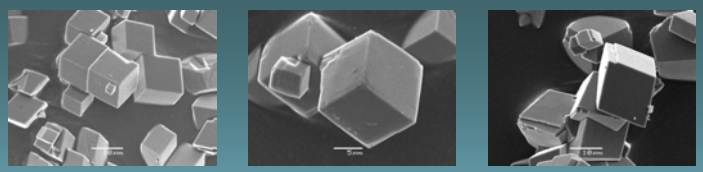



Making Magnesite from Forsterite
Forsterite
+ CO_2
Magnesite

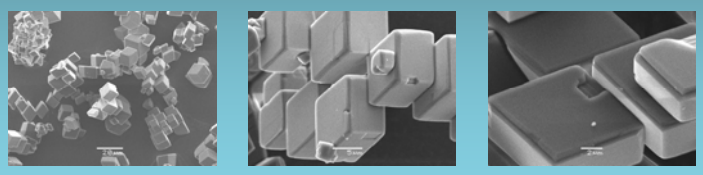

Open System reactor experiments:
Stirring Bar
Cover
Mineral
Fluid Flow pump
Reactive solution

High Temperature Open system reactors

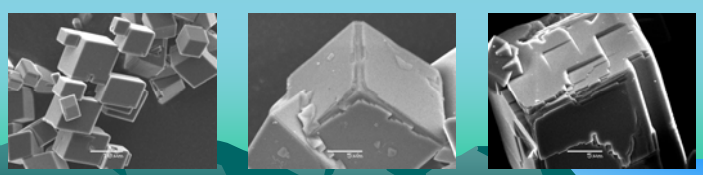




SEM photomicrographs of $MgCO_3$ synthetic powders



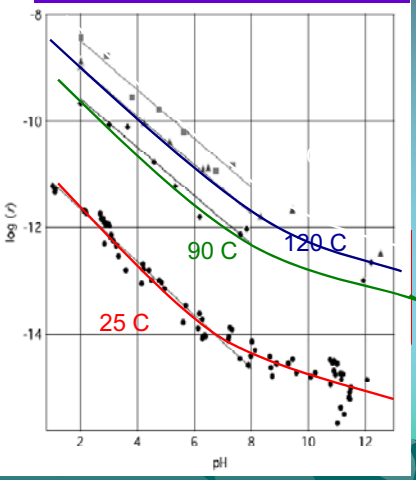
SEM photomicrographs of $MgCO_3$ synthetic powders



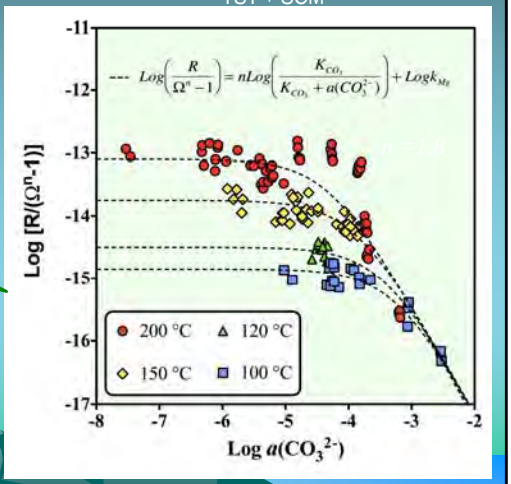
$MgCO_3$ Precipitation rates as a function of $a(CO_3^{2-})$ from 100 to 200 °C

(Saldi et al., 2011)

Forsterite Dissolution rates (Hanchen et al., 2006)



TST + SCM



Making Magnesite from Forsterite

Forsterite

+ CO_2

Magnesite

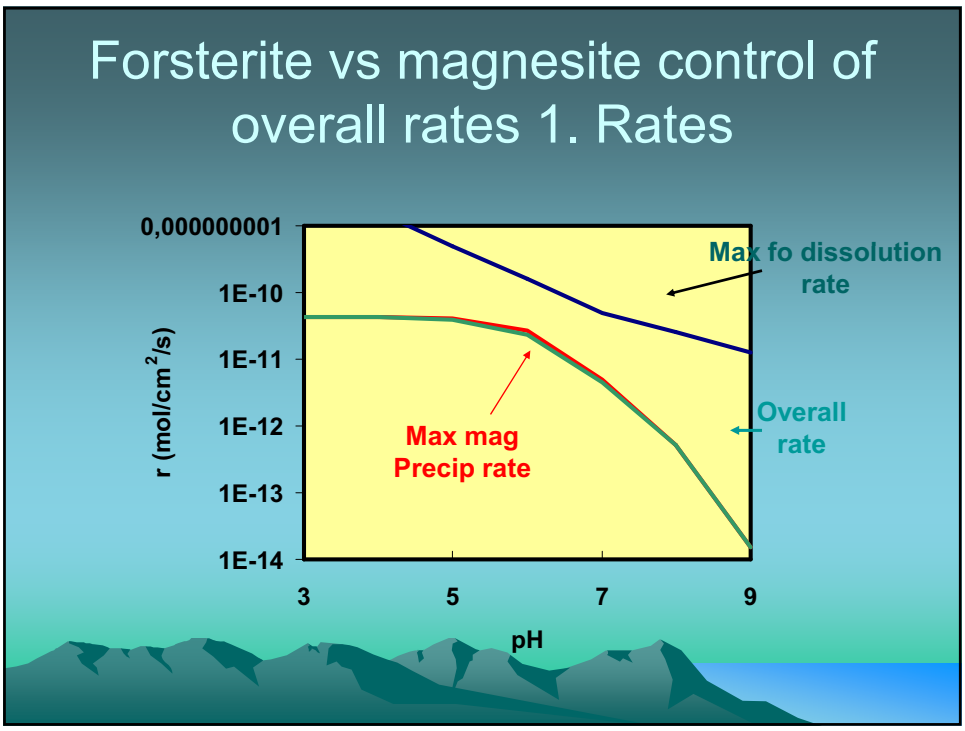
$r = ks(1-\Omega)$

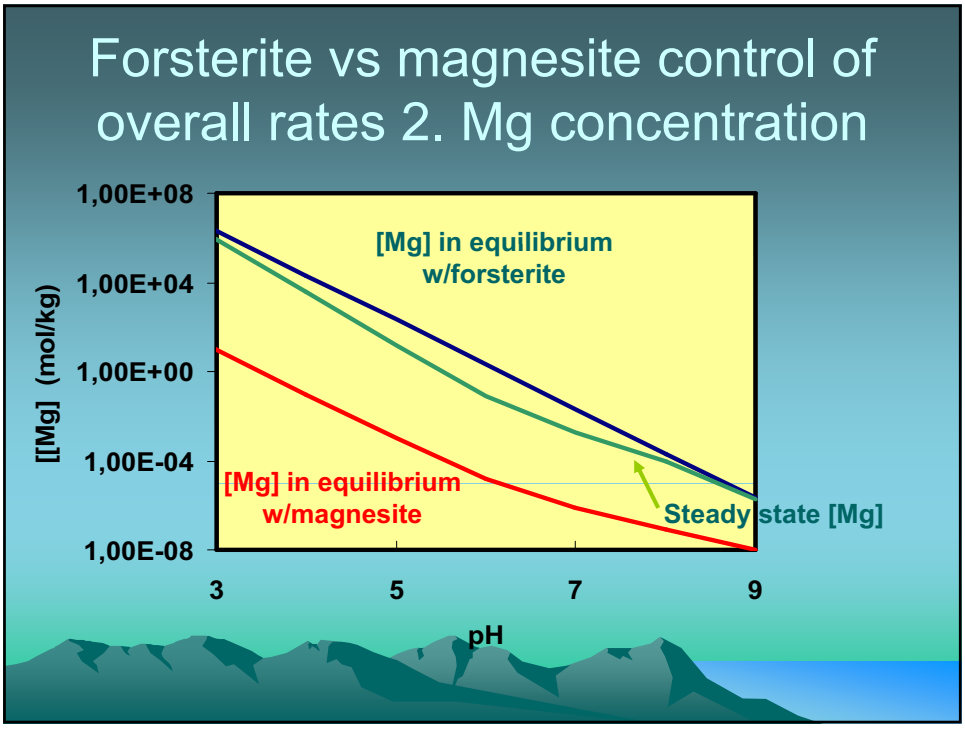
$r=ks(1-a^2_{Mg2+}a_{SiO2}/Ka^4_{H+})$

$r = ks(\Omega-1)^2$

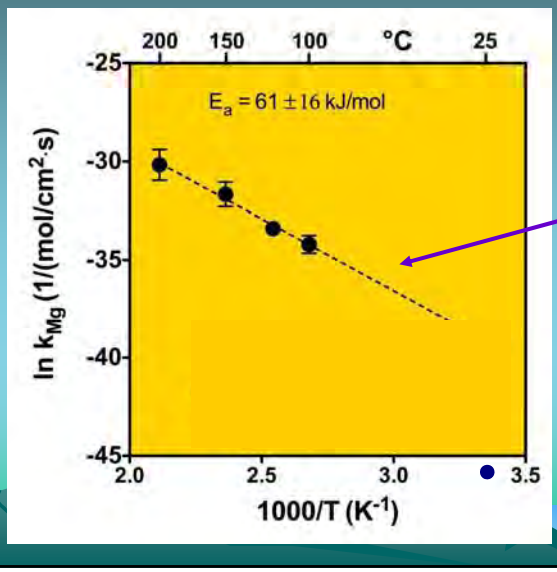
$r=ks(1-a^2_{Mg2+}a_{CO2}{}^{-2}/K)$

T = 120 C, 10 bar CO2, [Si] fixed by amorphous Si


Forsterite vs magnesite control of overall rates 1. Rates
0,000000001
1E-10
1E-11
1E-12
1E-13
1E-14
r (mol/cm2/s)
3
5
7
9
pH
Max fo dissolution rate
Overall rate
Max mag Precip rate

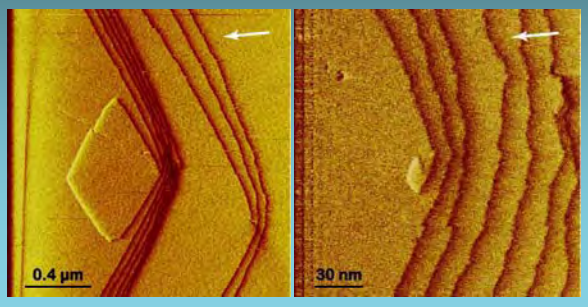

Forsterite vs magnesite control of overall rates 2. Mg concentration
1,00E+08
1,00E+04
1,00E+00
1,00E-04
1,00E-08
[[Mg] (mol/kg)
3
5
7
9
pH
[Mg] in equilibrium w/forsterite
[Mg] in equilibrium w/magnesite
Steady state [Mg]

Magnesite precipitation rates as a function of temperature



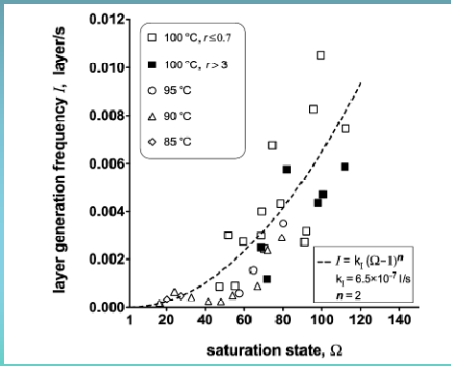
No measured rate below ~90 C

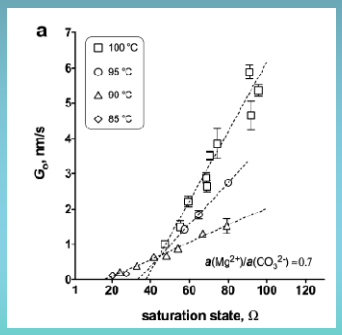
Magnesite growth observed by AFM



Spiral growth is found to be the main mechanism driving MgCO3 growth under all experimental conditions:
80 °C < T < 120 °C and 25 < Ω < 200

Magnesite Growth rates from AFM Saldi et al. (2009)



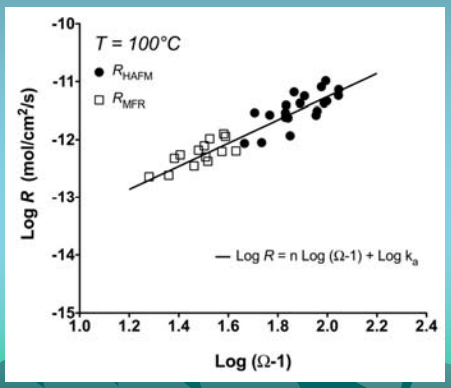


new layer generation rates

Step advancement rate

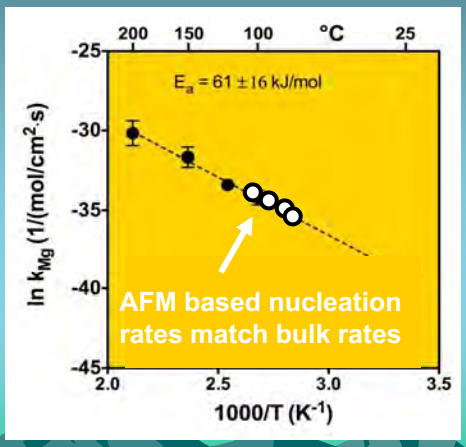
Rates from AFM experiments

AFM precipitation rates (proportional to nucleation rates) are consistent with bulk rates and nucleation by spiral growth being rate controlling

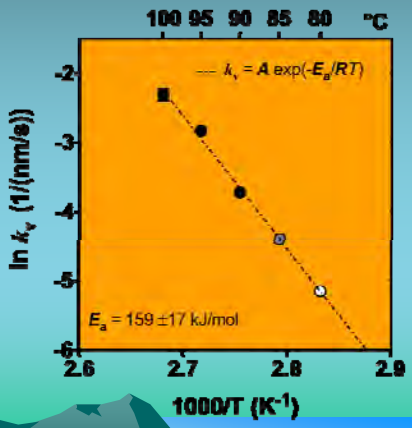


Temperature variation of rates from AFM experiments

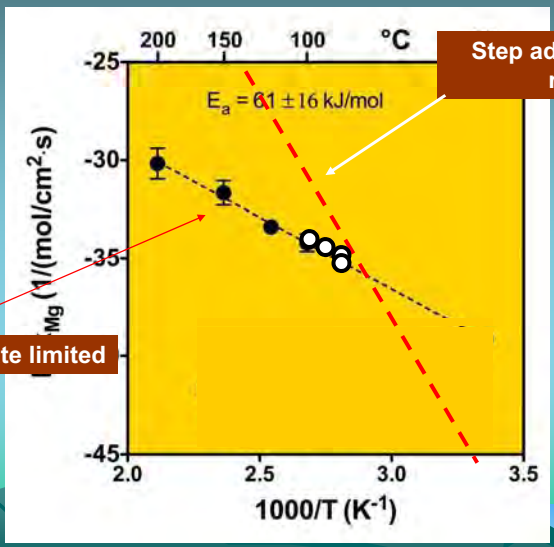
Overall r

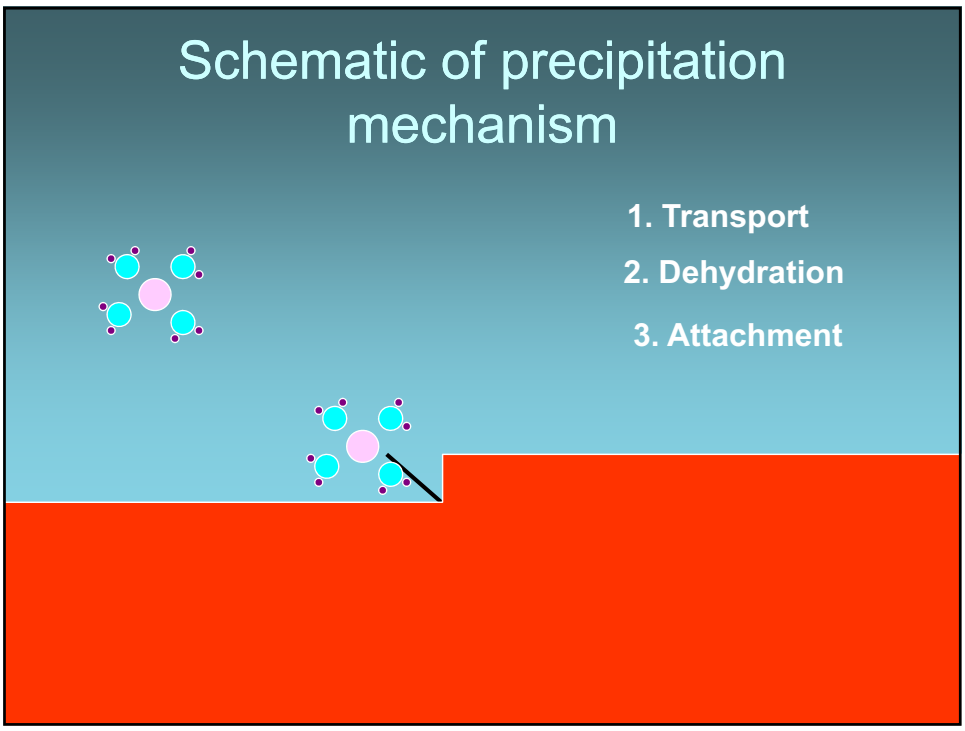


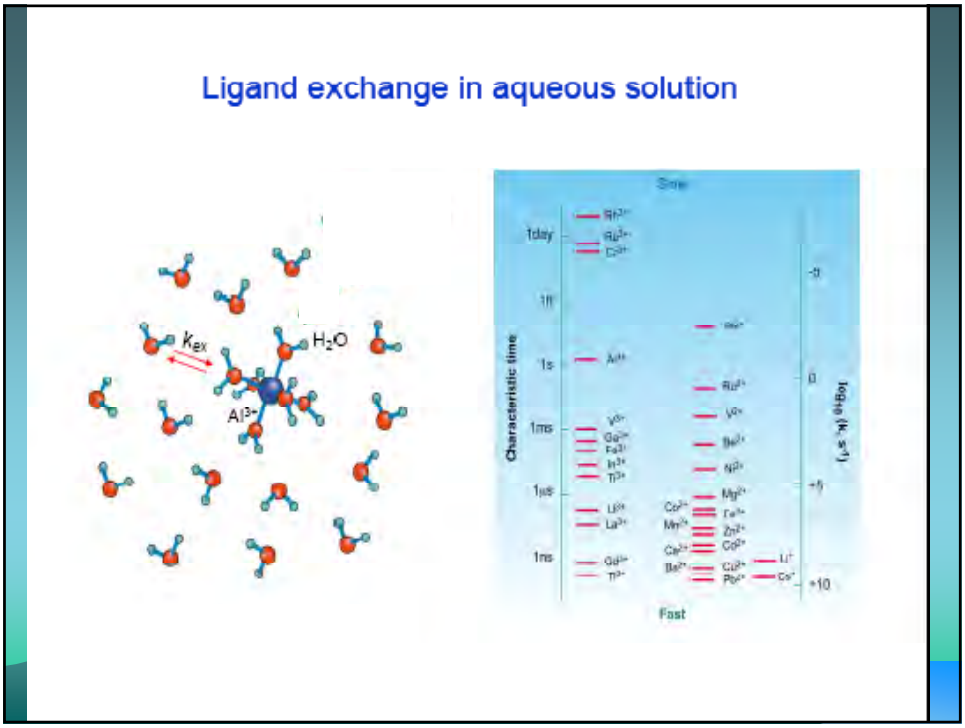
But step advancement rates decrease dramatically with temperature!!!



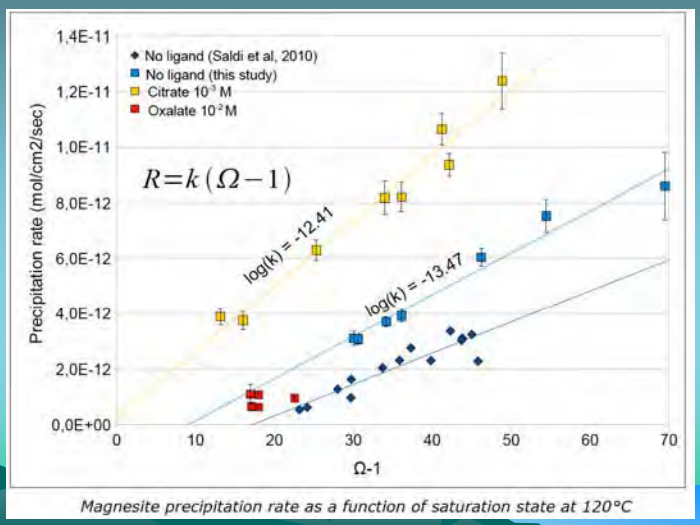
Magnesite precipitation rates at ambient temperatures




Schematic of precipitation mechanism
1. Transport
2. Dehydration
3. Attachment

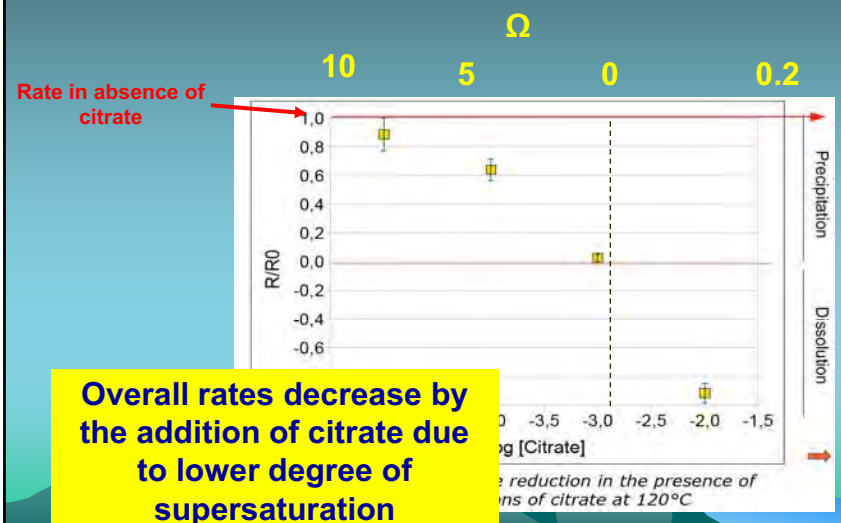

Ligand exchange in aqueous solution
k_{ex}
H_2O
Al^{3+}
Characteristic time
1day
1h
1s
1ms
1μs
1ns
Fast
log (k_{ex} / s^{-1})

Is there any way to accelerate magnesite precipitation rates? Citric Acid (Gautier thesis)



Magnesite precipitation rate as a function of saturation state at 120°C

Citrate acid 2 (Gautier thesis): Overall rate at constant [Mg], [$CO_3$2-] and pH



Overall rates decrease by the addition of citrate due to lower degree of supersaturation

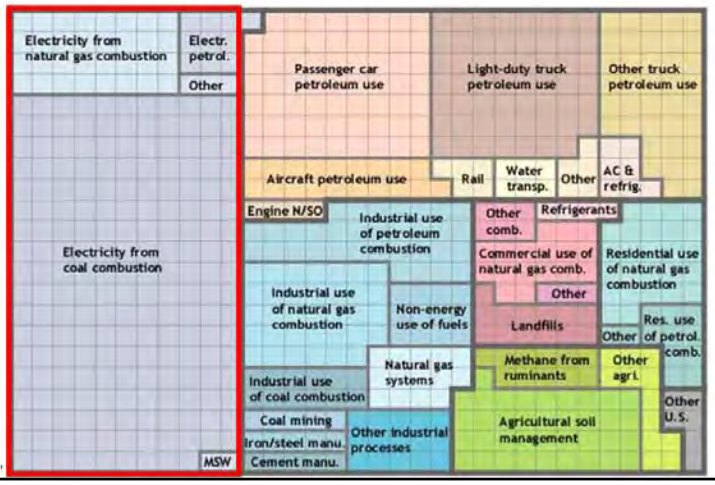
But if we can precipitate magnesite where would if be best to do our carbonation?

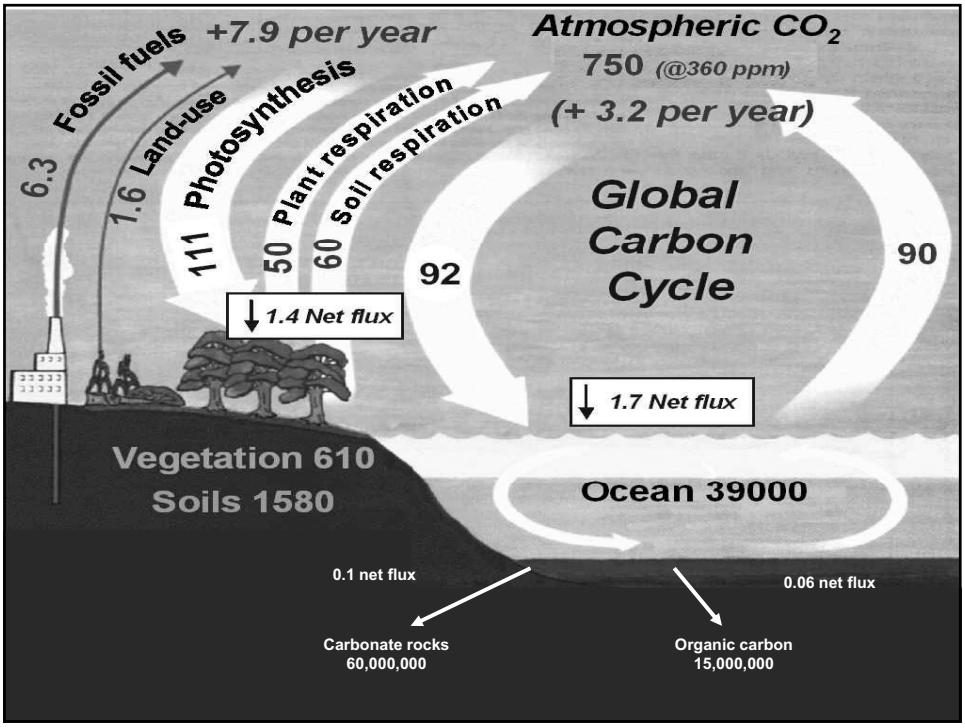
Oman Ophiolite

The Oceans

Less than half CO_2 emissions come from point sources

Power plan emissions





Some global Mg math

Concentration of Mg in oceans = 1400 ppb

Mass of worlds oceans = 1.37×10^{21} kg

Mass of Mg in worlds oceans = 1.9×10^{7} gT

Mass of C this could fix in magnesite = 1.9×10^{7} gT

Fraction of this C required to fix annual global anthoprogenic CO_2 emissions:

1/100,000

Would it be best to do our carbonation in the oceans?

Oman Ophiolite

Need to dissolve rock
Need to find volume
Need to capture and inject

The Oceans

Mg already present in fluid
Virtually unlimited volume
CO_2 dissolves in naturally

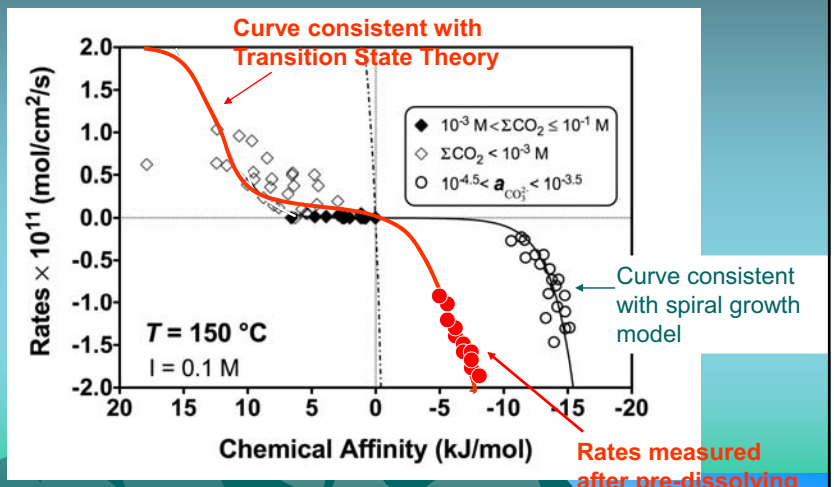
The kinetics of Mineral Carbonation

Eric H. Oelkers
Experimental Geochemistry and Biogeochemistry
GET/Université Paul Sabatier, Toulouse, FRANCE

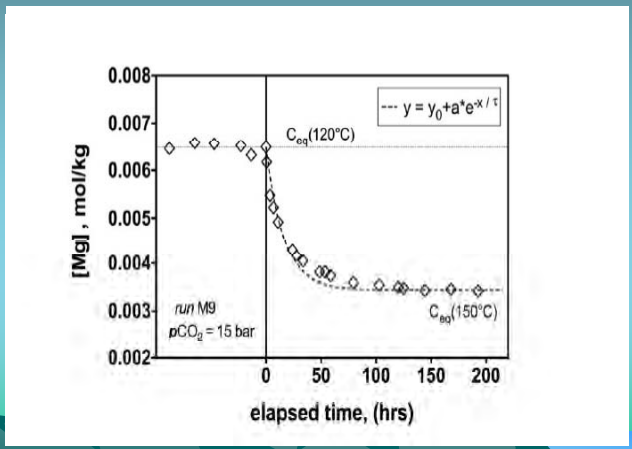
Some insights

1) Steady-state dissolution is not the opposite of precipitation. Precipitation requires creation of new active sites through nucleation whereas dissolution itself creates it active sites.
2) Transient precipitation is the opposite of dissolution and validates transition state theory.

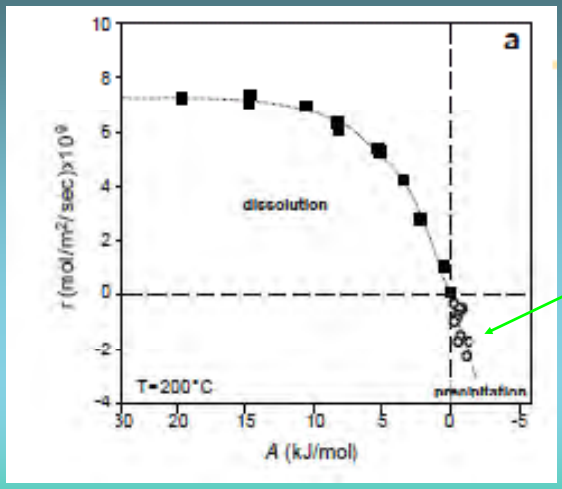
Rates on this magnesite in mixed-flow reactors (Saldi, 2009)



Dissolving magnesite before precipitation in closed-system reactors (Saldi, 2009)

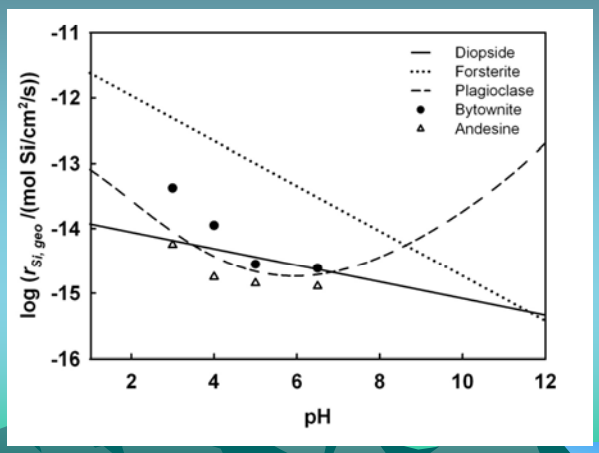


Returning to quartz for a clearer view… Gautier (1997)



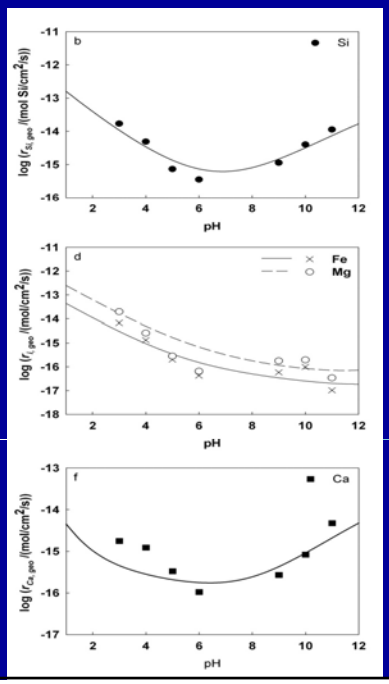
Precipitation rates measured after quartz was first dissolved

Dissolution of crystalline basalts



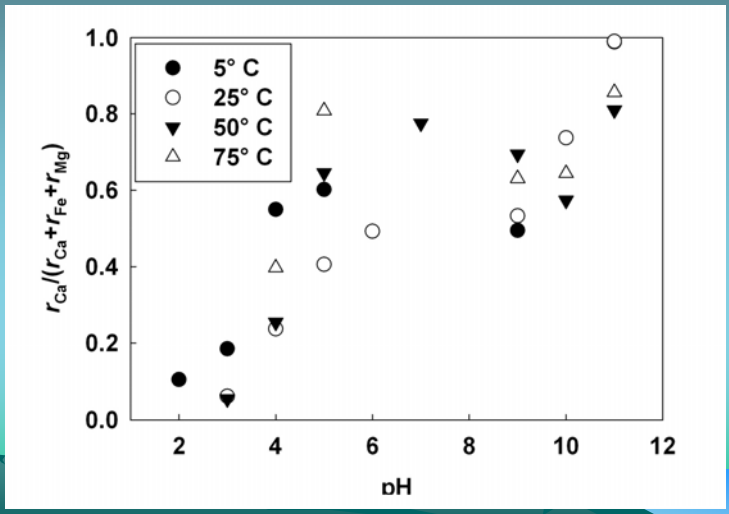
Element release rate from crystalline basalts

(Guðbrandsson et al. 2011)

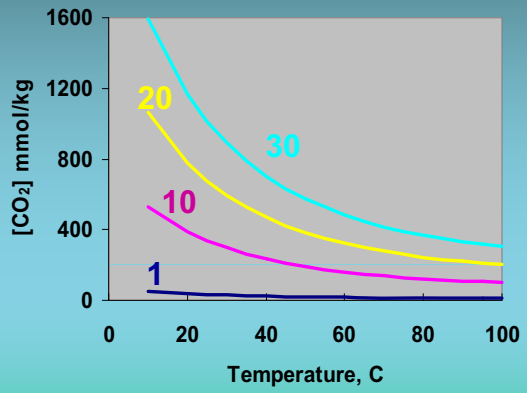


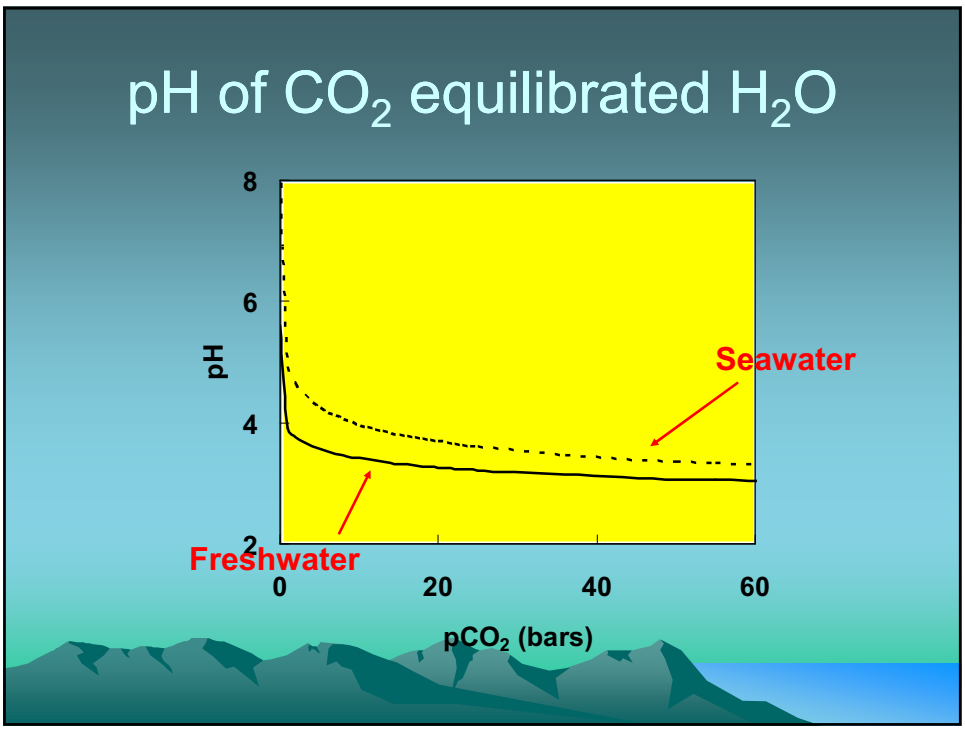
Acid Basalt dissolution is domonated by Mg and Fe release

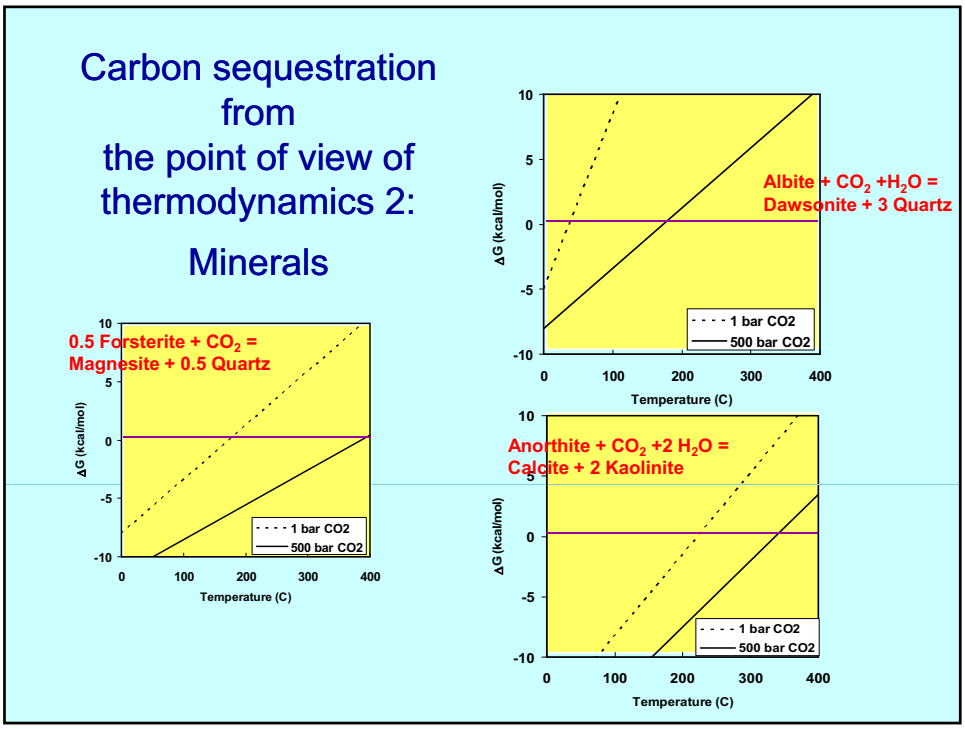
(Guðbrandsson et al. 2011)

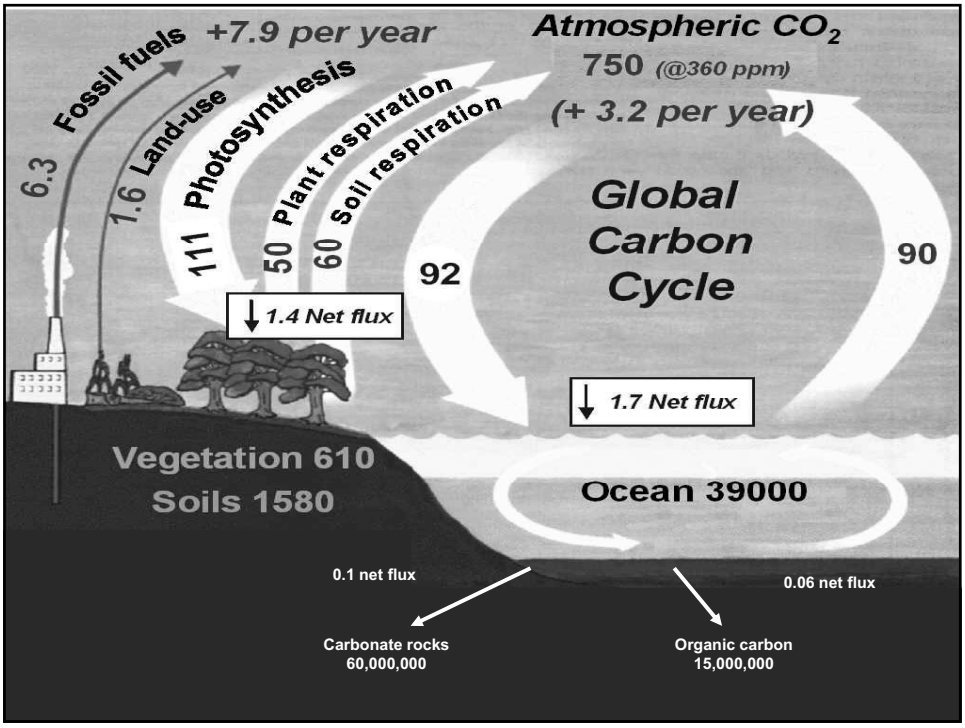


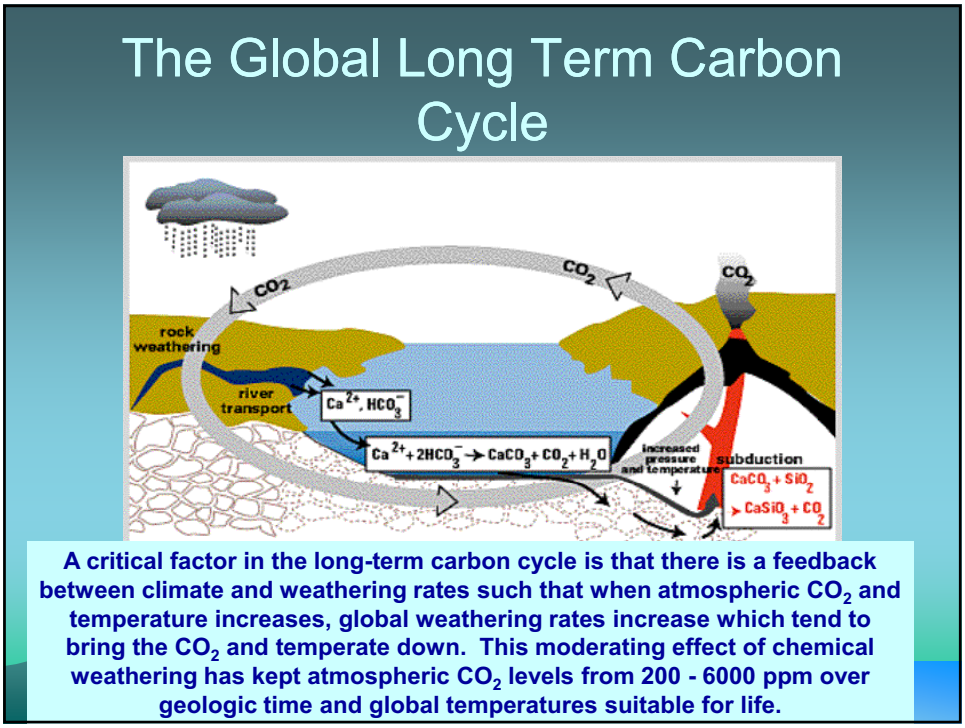
Carbon sequestration from the point of view of thermodynamics 1: CO_2 Solubility



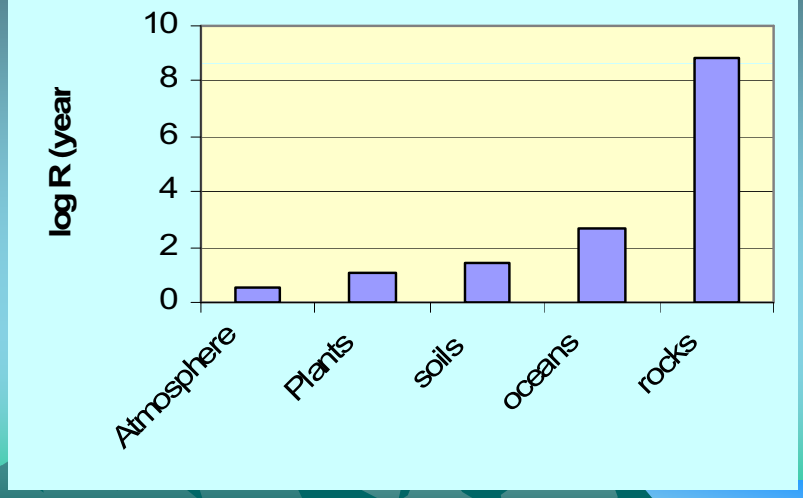

pH of CO_2 equilibrated H_2O
8
6
4
2
pH
Seawater
Freshwater
0
20
40
60
pCO_2 (bars)


Carbon sequestration from the point of view of thermodynamics 2:
Minerals
0.5 Forsterite + CO_2 = Magnesite + 0.5 Quartz
Albite + CO_2 +H_2O = Dawsonite + 3 Quartz
Anorthite + CO_2 +2 H_2O = Calcite + 2 Kaolinite
ΔG (kcal/mol)
Temperature (C)
1 bar CO2
500 bar CO2


Fossil fuels +7.9 per year
Atmospheric CO_2
750 (@360 ppm)
(+ 3.2 per year)
6.3
1.6 Land-use
111 Photosynthesis
50 Plant respiration
60 Soil respiration
92
90
Global Carbon Cycle
1.4 Net flux
1.7 Net flux
Vegetation 610
Soils 1580
Ocean 39000
0.1 net flux
0.06 net flux
Carbonate rocks 60,000,000
Organic carbon 15,000,000

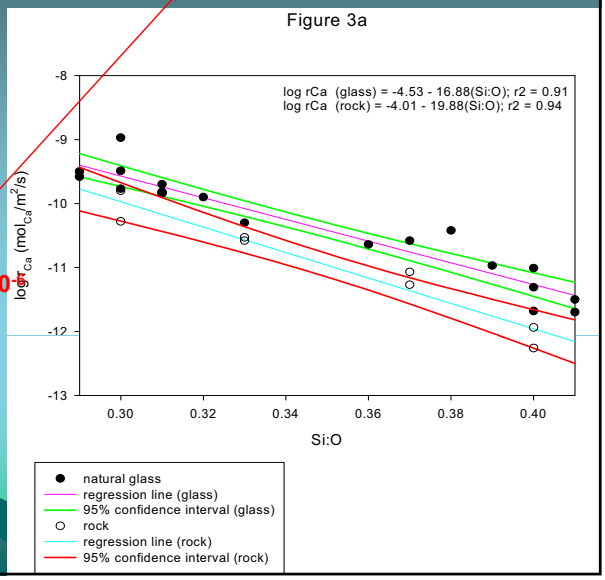

The Global Long Term Carbon Cycle
CO_2
CO_2
CO_2
rock weathering
river transport
Ca^{2+}, HCO_3^-
$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$
increased pressure and temperature
subduction
$CaCO_3 + SiO_2$
$\rightarrow CaSiO_3 + CO_2$
A critical factor in the long-term carbon cycle is that there is a feedback between climate and weathering rates such that when atmospheric CO_2 and temperature increases, global weathering rates increase which tend to bring the CO_2 and temperate down. This moderating effect of chemical weathering has kept atmospheric CO_2 levels from 200 - 6000 ppm over geologic time and global temperatures suitable for life.

Residence times of global carbon reservoirs



Comparison of Silicate dissolution rates with calcite precipitation rates 25 C ~ neutral pH

Calcite Precipitation Rate ~ 10^{-4} mol/mol²/s



The carbonation of sandstone

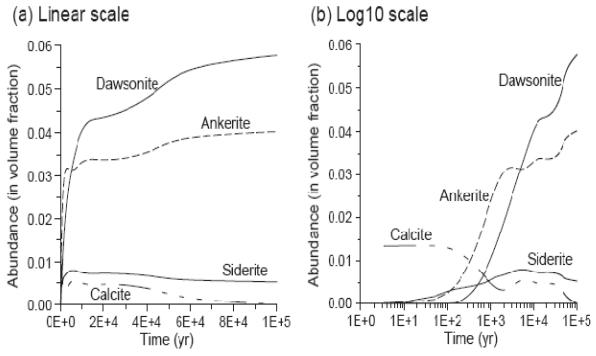
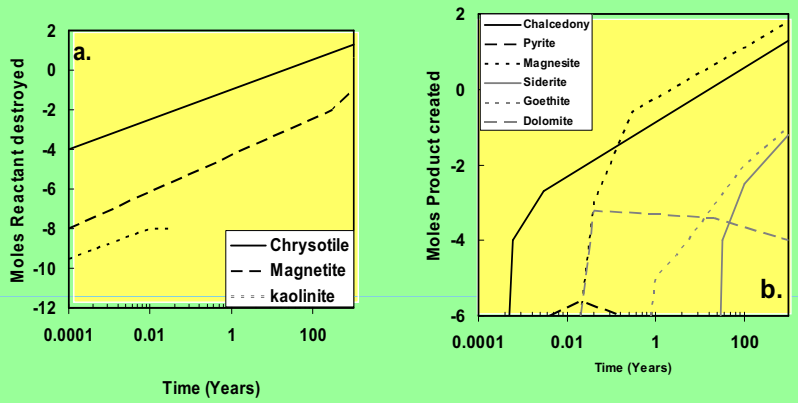


Fig. 4. Abundances of carbonate minerals over time in the sandstone. Some CO_2 is immobilized by precipitation of siderite, but more significant by precipitation of ankerite and dawsonite. Precipitation of carbonate minerals occurs primarily before 10,000 years (a). To emphasize the evolution at initial times, we use a log10 scale for time (b).

Carbonation of serpentanite (after Marini, 2007)



Do carbonate minerals really precipitate at ambient conditions?

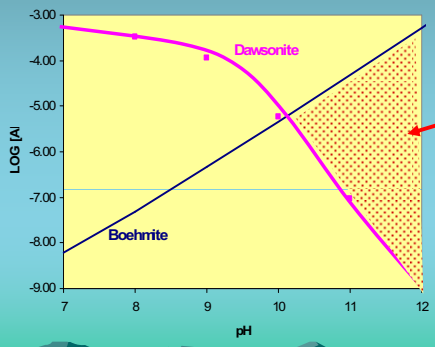
- Examples:

Dawsonite
$NaAl(CO)_3(OH)_2$

Magnesite
$Mg(CO)_3$

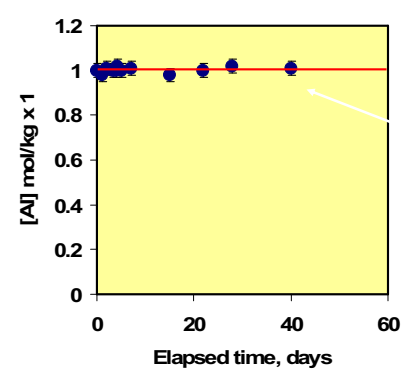
Can we directly precipitate dawsonite ($NaAlCO_3(OH_2)$) from the atmosphere?

Solubility of boehmite and dawsonite in NaOH solutions in equilibrium with atmospheric CO_2



In this region boehmite will dissolve and dawsonite will precipitate

Dawsonite self-sequestration system results (Decereq et al., 2009+)



No evidence of dawsonite precipitation

$Na^+ + Al(OH)_4^- + CO_2 = NaAlCO_3(OH)_2 + H_2O$

Magnesite dissolution /precipitation rates at 25 C

Pokrovsky and Schott, 1999

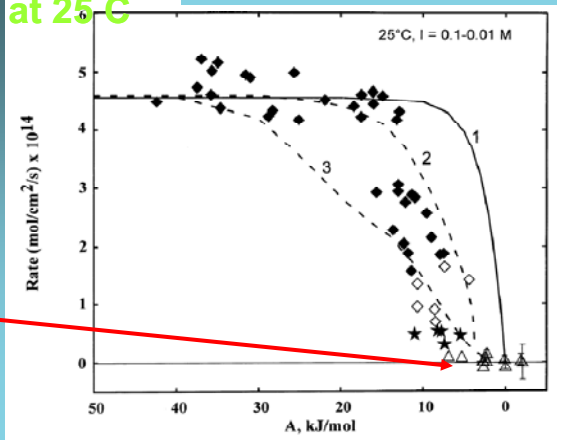
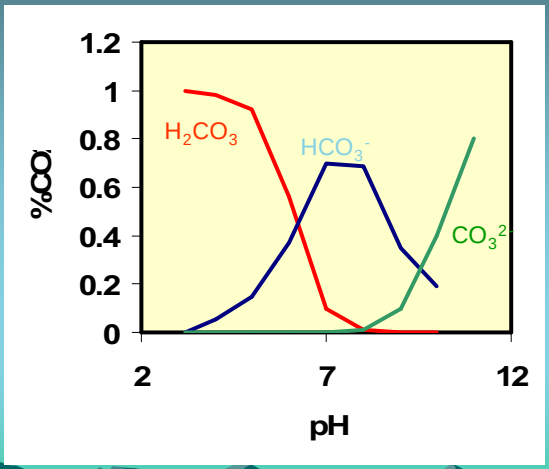


Fig. 5. Magnesite overall dissolution rate at 25°C and pH > 5 as a function of chemical affinity for I = 0.1–0.01 M. Total carbonate concentration: ◆, $\Sigma CO_2 \leq 10^{-3}$ M; ◇, $\Sigma CO_2 = 0.01$ M; ★, $\Sigma CO_2 = 0.02$ to 0.03 M; △, $\Sigma CO_2 = 0.05$ to 0.10 M.

1: Calculated using Eqn. 5 with the assumption $R_2 = 4.57 \times 10^{-14}$ = const;
2: Calculated using Eqn. 20 with I = 0.01 M, $[Mg^{2+}]_{tot} = 10^{-5}$ M, and $\Sigma CO_2 = 10^{-3}$ M;
3: Calculated using Eqn. 20 with I = 0.1 M, $[Mg^{2+}]_{tot} = 10^{-1}$ M, and $\Sigma CO_2 = 10^{-2}$ M.

No Magnesite precipitation observed at 25° C!

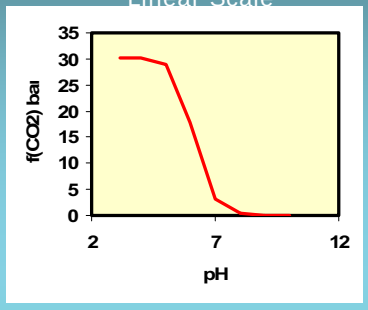
Solute speciation/complexing stabilize CO_2



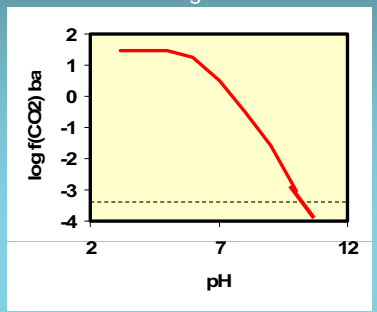
Any mineral reaction that increases pH or complexes aqueous carbonate stabilizes injected/dissolved CO2

But what if no mineralization occurs: CO2 fugacity of a 1 molal solution as a function of pH

Linear Scale

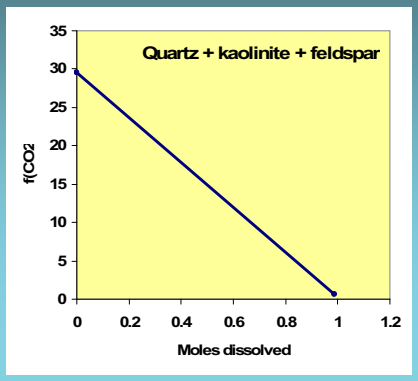


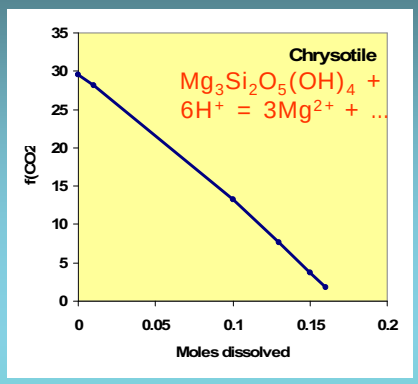
Log Scale



Just neutralizing the solution stabilizes the CO_2!!

Several Examples Of Alkalinity Scavenging/Stabilizing Dissolved CO_2





Why do minerals fail to precipitate?

Mineral dissolution from the Kossel Crystal viewpoint

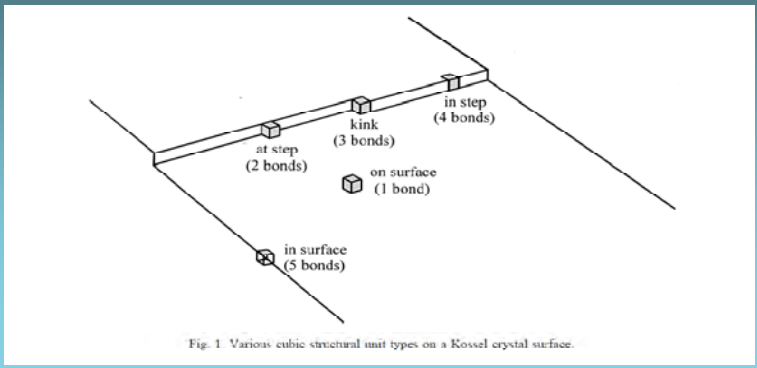


Fig. 1. Various cubic structural unit types on a Kossel crystal surface.

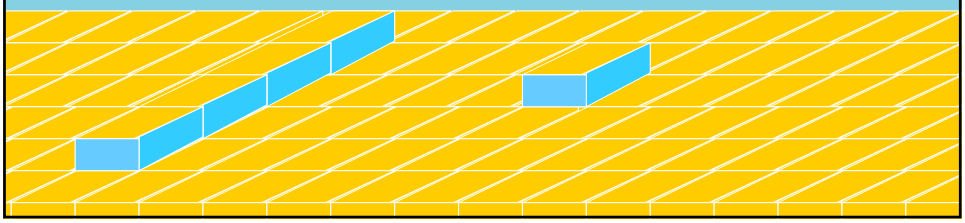
1. The less bonded, the faster rates….

$$r_1 << r_2 << r_3 << r_4 << r_5$$

2. Overall rates sum of all contributions…

$$r_{total} = r_1 + r_2 + r_3 + r_4 + r_5$$

Surface Evolution during dissolution



Edges dominate the active sites

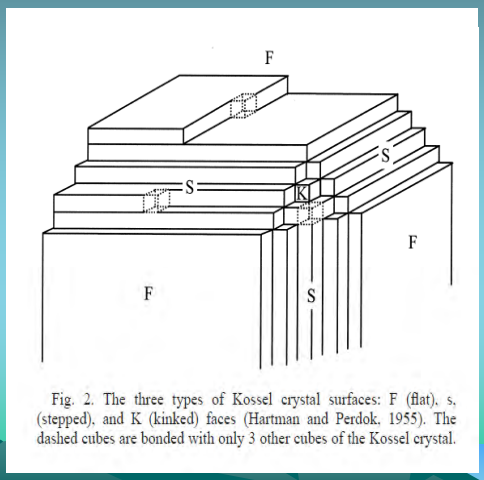
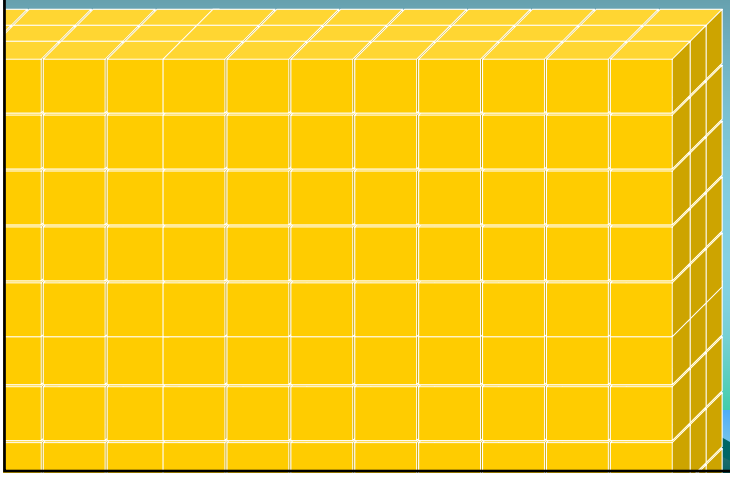


Fig. 2. The three types of Kossel crystal surfaces: F (flat), s, (stepped), and K (kinked) faces (Hartman and Perdok, 1955). The dashed cubes are bonded with only 3 other cubes of the Kossel crystal.

Dissolution creates new active sites…..



Transition State Theory

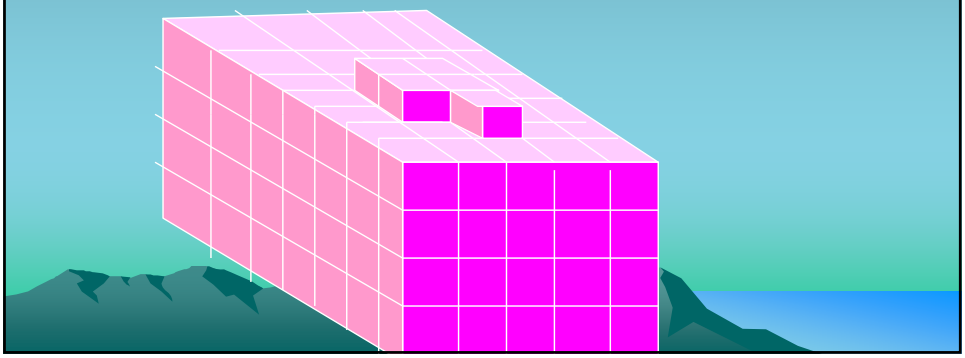
Mineral <-> A <-> B <-> Activated complex1 -> Products

$r_+ = k_+$[Activated Complexes]

$r_- = k_-$[Activated Complexes]

Overall rate:

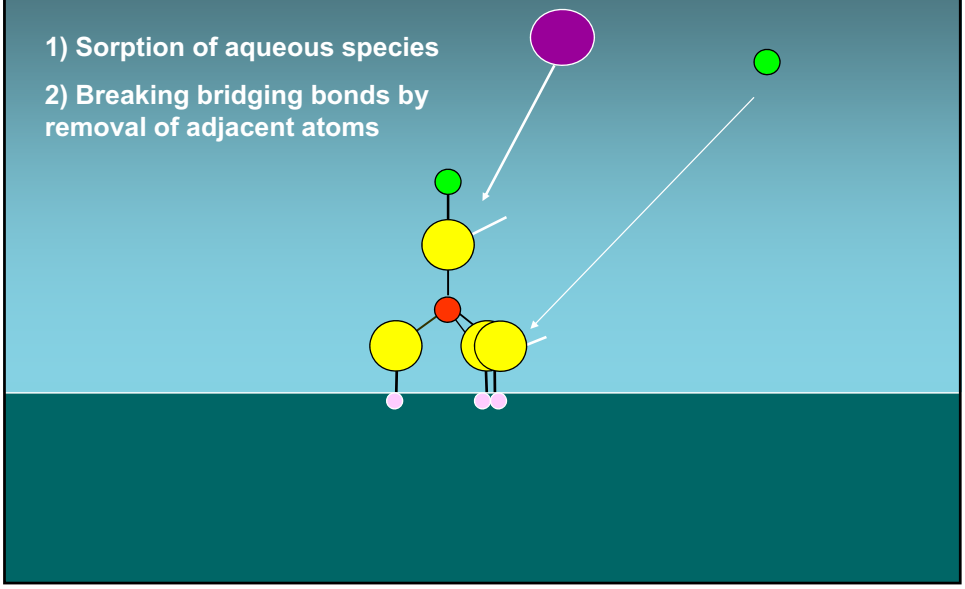
$r = r_+ - r_- = r_+ (1-\exp(-A/\sigma RT))$



Activated Complex Formation

1) Sorption of aqueous species

2) Breaking bridging bonds by removal of adjacent atoms



Reaction mechanism reveals how rates vary with concentration 'far from equilibrium': quartz

Quartz (SiO_2) + nH_2O = Activated complex

[Activated complexes] = K $[H_2O]^n$

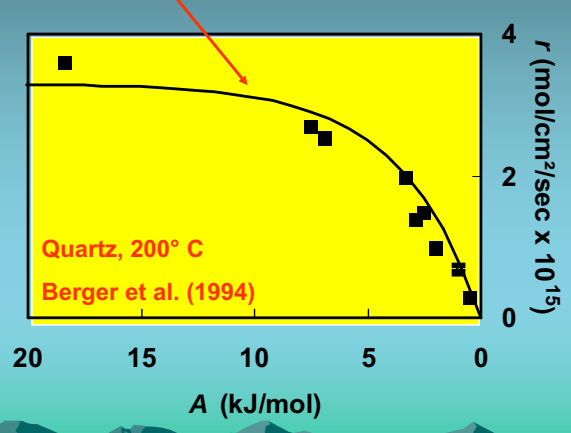
$r_+ = k$ [Activated complexes] = k K $[H_2O]^n$

$r = r_+ - r_- = r_+ (1-\exp(-A/\sigma RT))$

$r = r_+ - r_- =$ k K $[H_2O]^n (1-\exp(-A/\sigma RT))$

Example: Quartz Dissolution

r= k (1-exp(-A/RT))



Reaction mechanism: kaolinite

Kaolinite – Al^{3+} = Activated complex + $3H^+$

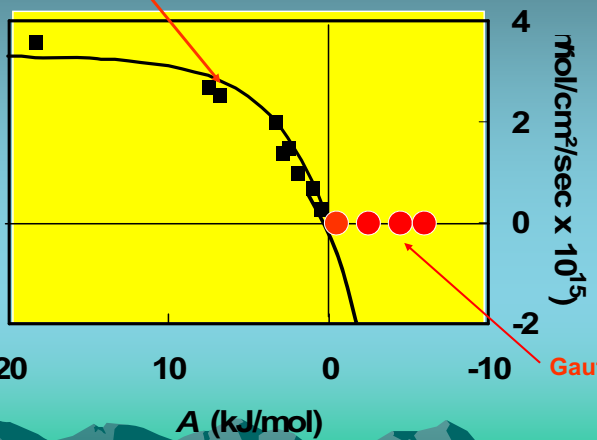
[Activated complexes] = K $[H^+]^3$ /$[Al^{+3}]$

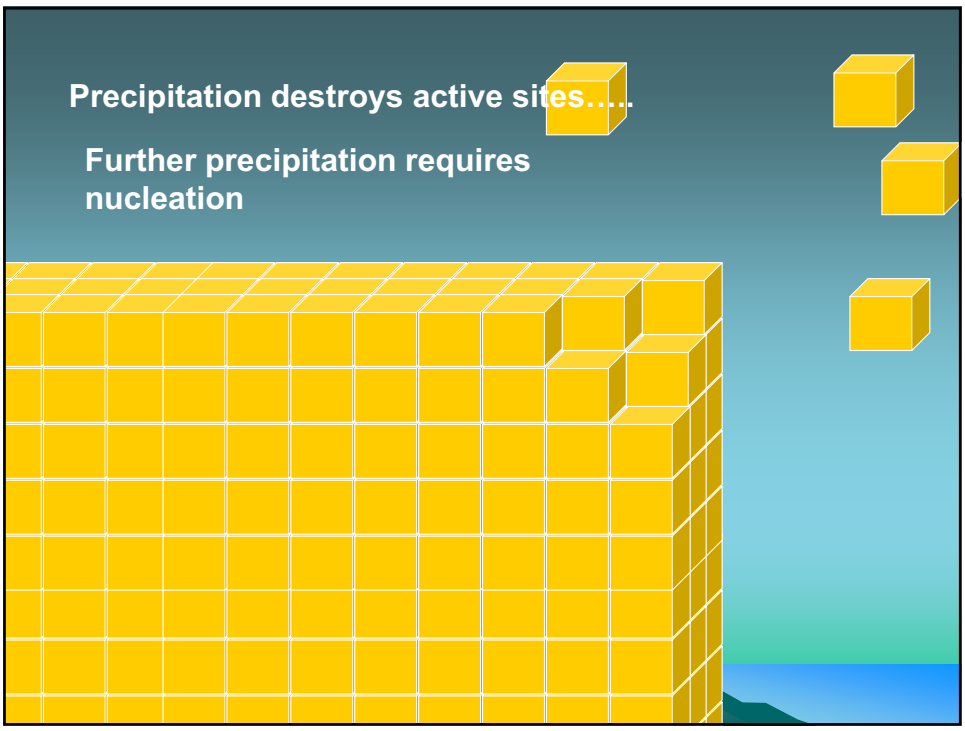
r_+ = k [Activated complexes] = k K $[H^+]^3$ /$[Al^{+3}]$

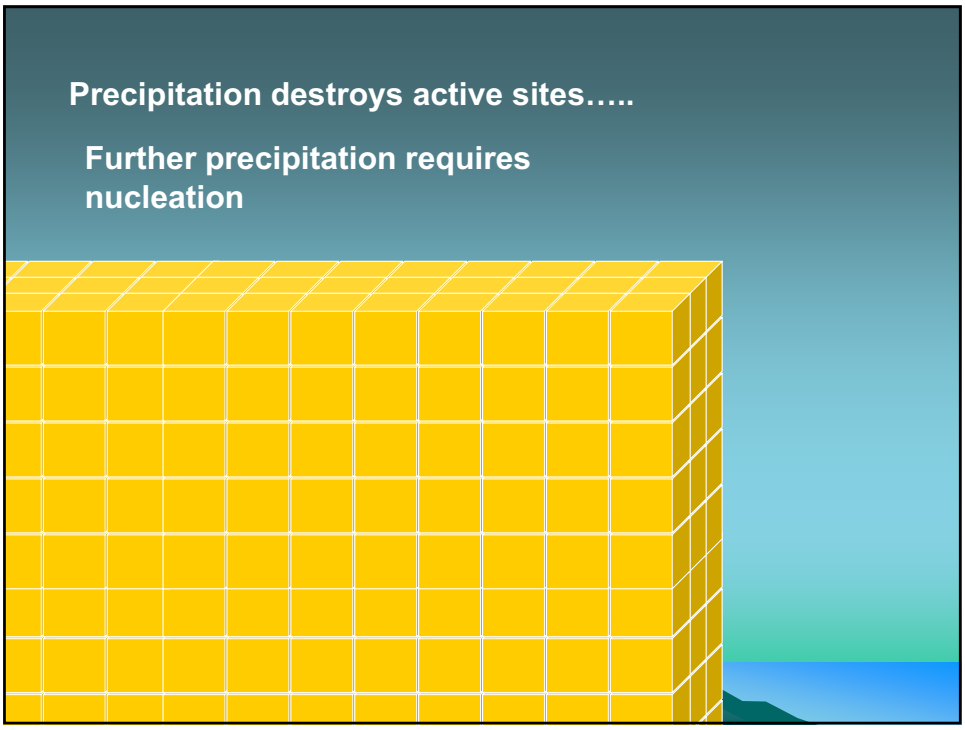
$r = r_+ - r_- =$ k K $[H^+]^3$ /$[Al^{+3}]$ (1-exp(-A/σRT))

But what of precipitation?? Example quartz

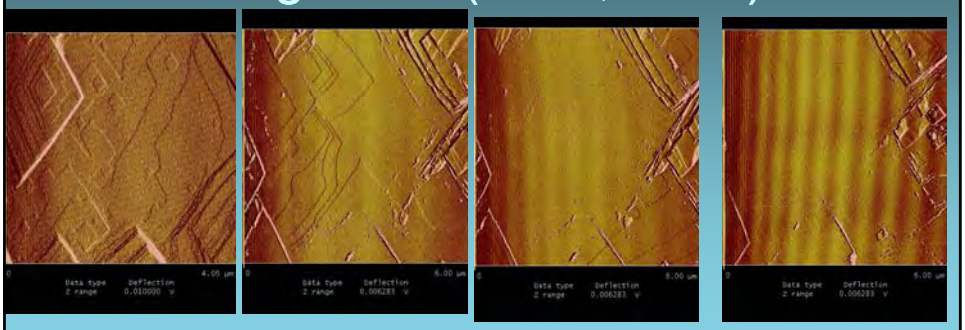
r= k (1-exp(-A/RT))




Precipitation destroys active sites…..
Further precipitation requires nucleation


Precipitation destroys active sites…..
Further precipitation requires nucleation

This is nicely illustrated with Magnesite (Saldi, 2009)

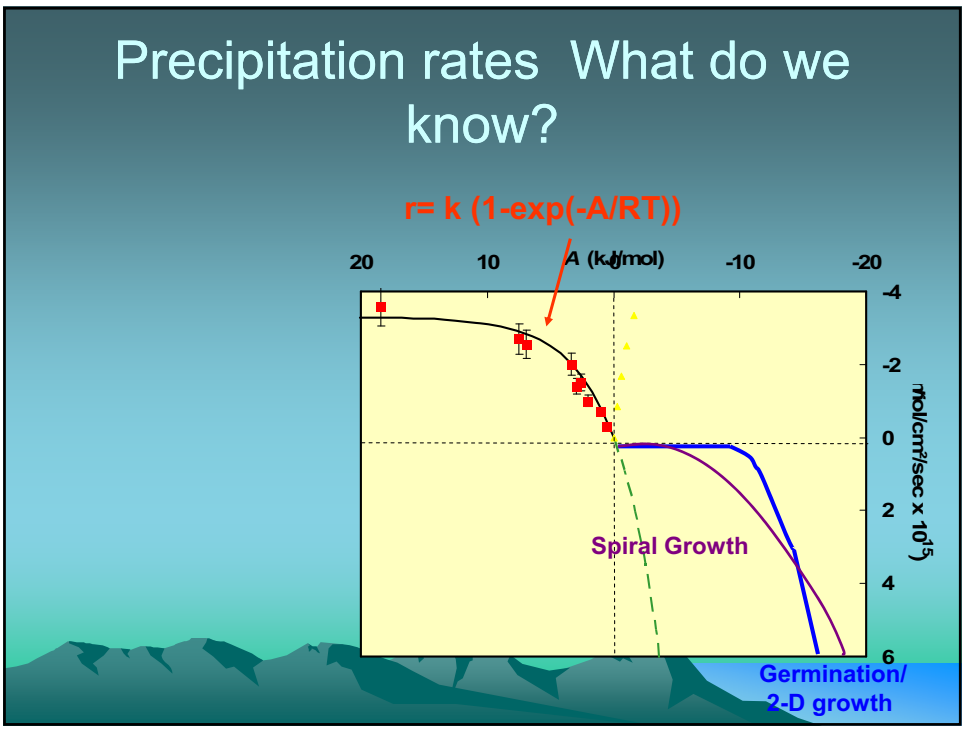


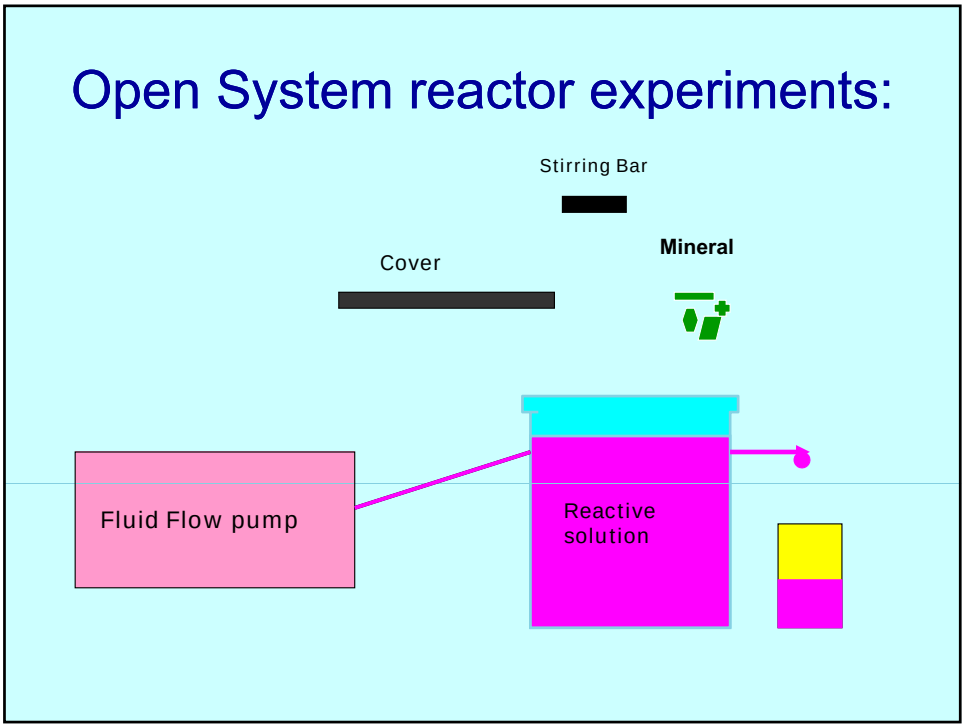
Time during precipitation →

Etch pits like grain edges fill then become unreactive……

What does this mean for precipitation??

1) To get precipitation to go long-term nucleation must occur.
2) Short term precipitation may be the inverse of dissolution.
3) Long-term precipitation is NOT the inverse of dissolution

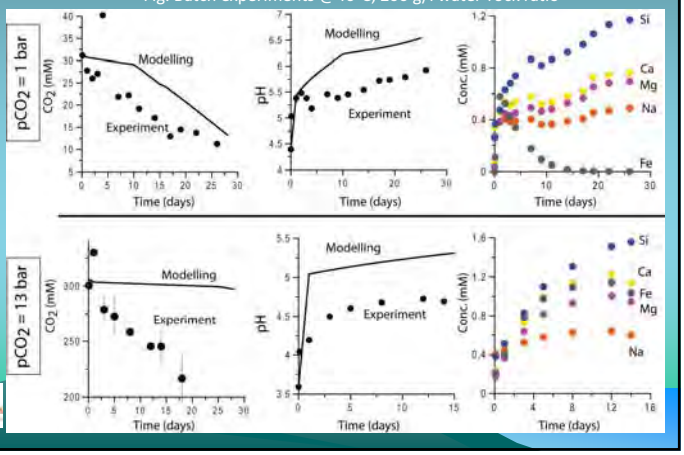

Precipitation rates What do we know?
r= k (1-exp(-A/RT))
20
10
A (kJ/mol)
-10
-20
-4
-2
0
2
4
6
mol/cm²/sec x 10⁻¹⁵
Spiral Growth
Germination/
2-D growth


Open System reactor experiments:
Stirring Bar
Mineral
Cover
Fluid Flow pump
Reactive
solution

Yet Experiments suggest foration of a low T Mg bearing carbonate (Gysi, 2011)

-CO_2 in solution mineralizes rapidly forming Mg, Fe, Ca and Mn carbonates
-The model and experimental results need to be tuned together (still loose ends)
-The rate of CO_2 mineralization between experiments and model compares well only at low pCO_2

Fig. Batch experiments @40°C, 200 g/l water-rock ratio



Some Evident conclusions

- In terms of 'safety' dissolution of CO_2 during injection is obvious
- In the absence of mineral sequestration fluid/mineral reactions stabilize dissolved CO_2 by alkalinity mining
- Each of these benefits/lessons of CARB-FIX is fully portable to any subsurface storage site

Magnesite dissolution /precipitation rates at 25 C

Pokrovsky and Schott, 1999

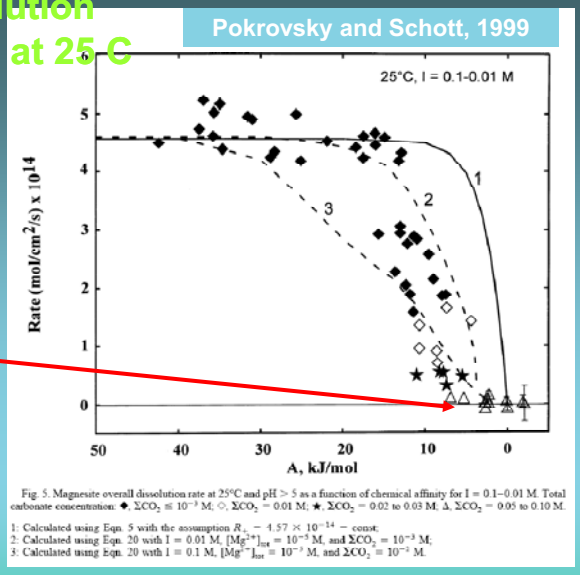


Fig. 5. Magnesite overall dissolution rate at 25°C and pH > 5 as a function of chemical affinity for I = 0.1–0.01 M. Total carbonate concentration: ◆, $\Sigma CO_2 \leq 10^{-3}$ M; ◇, $\Sigma CO_2 = 0.01$ M; ★, $\Sigma CO_2 = 0.02$ to 0.03 M; △, $\Sigma CO_2 = 0.05$ to 0.10 M.

1: Calculated using Eqn. 5 with the assumption $R_+ = 4.57 \times 10^{-14} = \text{const}$;
2: Calculated using Eqn. 20 with I = 0.01 M, $[Mg^{2+}]_{tot} = 10^{-5}$ M, and $\Sigma CO_2 = 10^{-3}$ M;
3: Calculated using Eqn. 20 with I = 0.1 M, $[Mg^{2+}]_{tot} = 10^{-3}$ M, and $\Sigma CO_2 = 10^{-2}$ M.

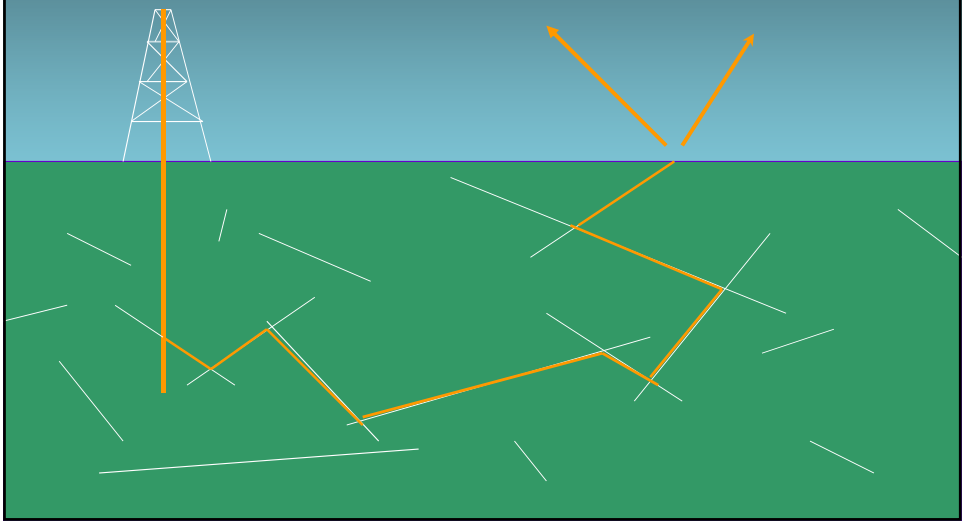
No Magnesite precipitation observed at 25° C!

Table: Some potential source minerals for carbon mineralization

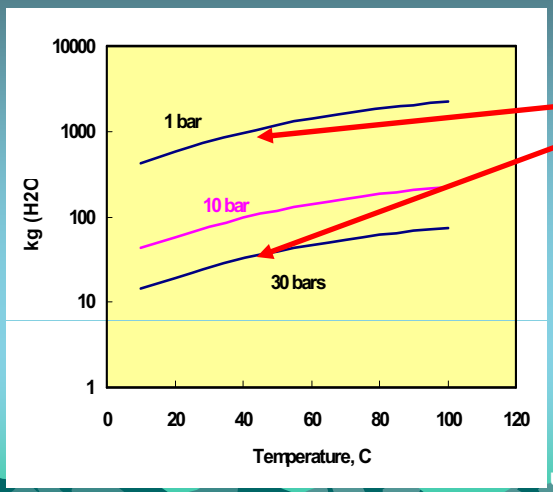
Solid	Chemical Formula	Tons required to sequester 1 ton of carbon
Wollastonite	$CaSiO_3$	9.68[a]
Forsterite	Mg_2SiO_4	5.86[b]
Serpentine/Chrysotile	$Mg_3Si_2O_5(OH)_4$	7.69[b]
Anorthite	$CaAl_2Si_2O_8$	23.11[a]
Basaltic Glass	$Na_{0.08}K_{0.008}Fe(II)_{0.17}Mg_{0.28}Ca_{0.26}Al_{0.36}Fe(III)_{0.02}SiTi_{0.02}O_{3.45}$	8.76[c]

a)as calcite
b)as magnesite
c)assuming all Ca, Mg, and Fe are converted into calcite, magnesite, and siderite, respectively.

The CO_2 mineral fixation process in the sub-surface



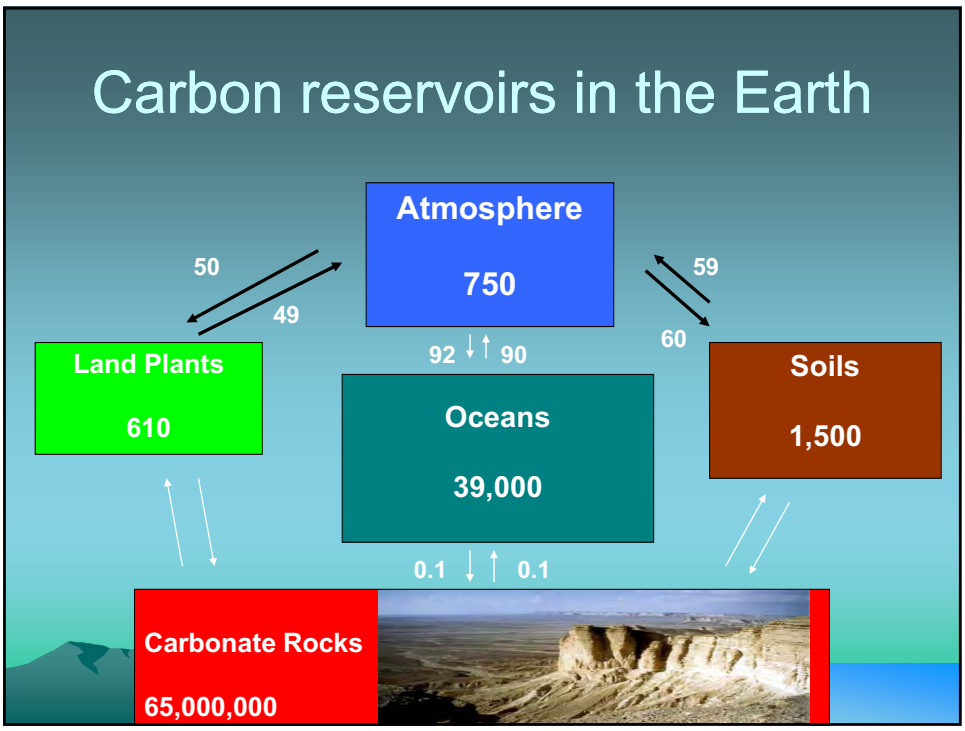
Kg of H_2O needed to dissolve 1 Kg of CO_2

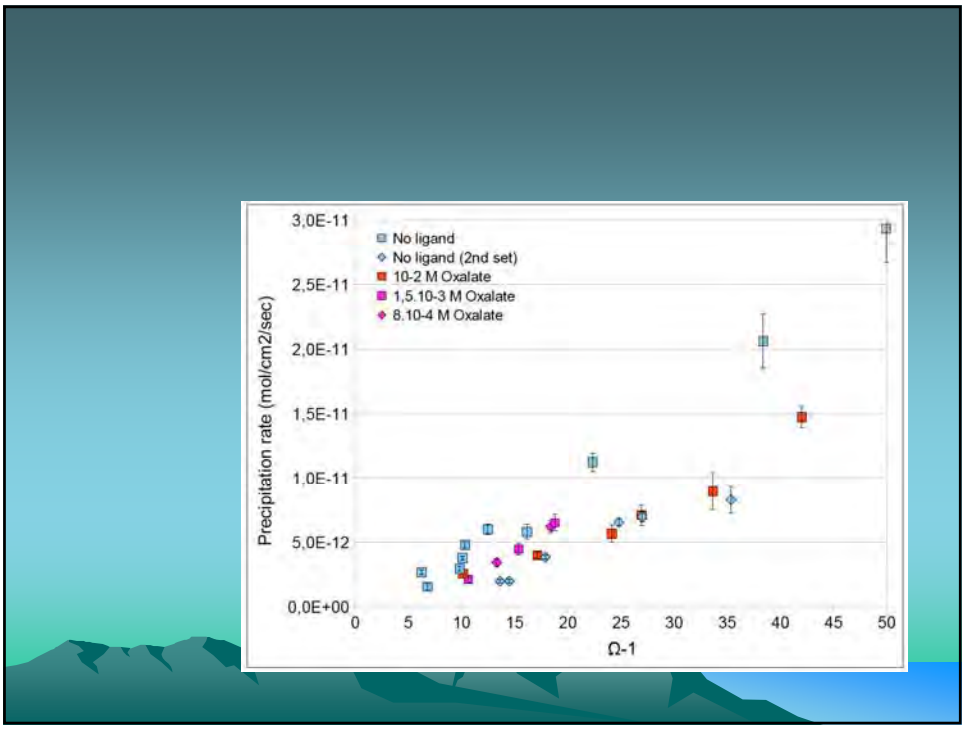


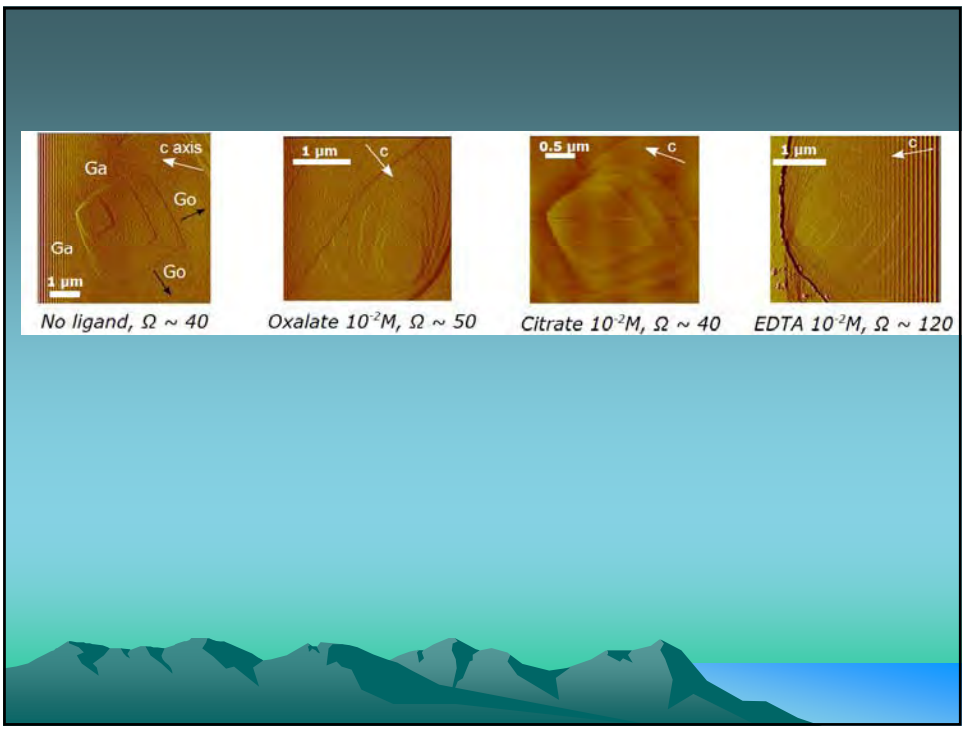
~ 1000 kg of H_2O is needed to dissolve 1 kg of CO_2 at 1 bar at 40 C

But only ~ 35 kg is needed at 30 bar

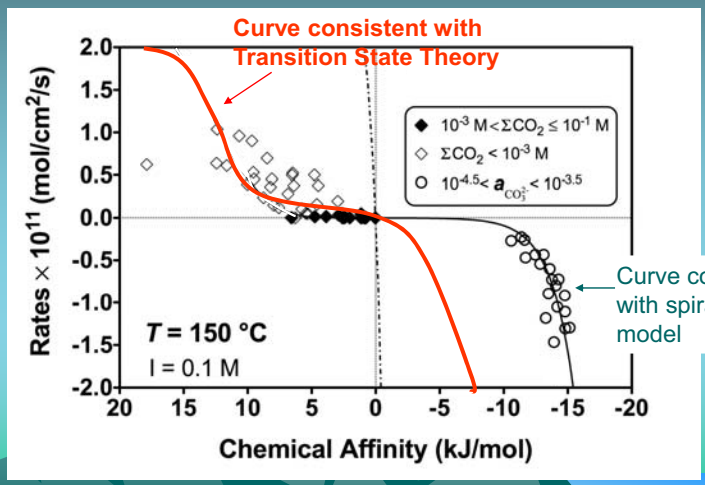
using PHREEQC


Carbon reservoirs in the Earth
Atmosphere
750
50
49
59
60
Land Plants
610
92
90
Oceans
39,000
Soils
1,500
0.1
0.1
Carbonate Rocks
65,000,000


Precipitation rate (mol/cm2/sec)
3,0E-11
2,5E-11
2,0E-11
1,5E-11
1,0E-11
5,0E-12
0,0E+00
No ligand
No ligand (2nd set)
10-2 M Oxalate
1,5.10-3 M Oxalate
8.10-4 M Oxalate
0
5
10
15
20
25
30
35
40
45
50
Ω-1



Rates on this magnesite in mixed-flow reactors



5. Ph Gouze – Univ. Montpellier, France.

Feedbacks between reactions and hydrodynamic properties of reacting media: New insights from lab-scale flow-through experiments

Philippe Gouze [1*] , Marguerite Godard[1+], Muriel Andréani[2], Linda Luquot[1*], Steve Peuble[1+]

Géosciences, U. de Montpellier - CNRS, France
LST, U. de Lyon – ENS, France

* Transport in Porous Media group Montpellier
[+] Geochemistry group Montpellier

philippe.gouze@um2.fr

Outlines

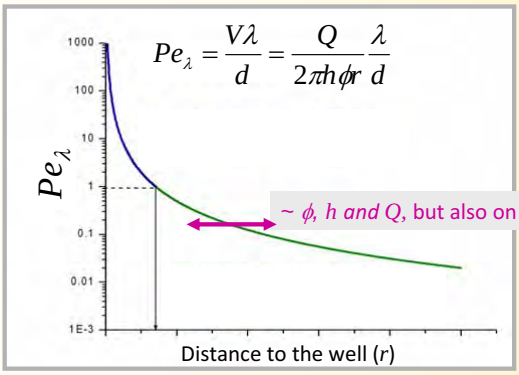
- **Some important features for quantifying mass transfers (incl. carbonation) induced by the injection of CO_2-enriched water in olivine reservoir from a well …..**
- **2 sets of percolation experiments performed on low porosity sintered materials:**

A) proxy of olivine-rich layers in basaltic rocks : ~96 % olivine Fo88, ~4% MORB, <1% Chromite
B) proxy of dunites : ~97 % olivine Fo90, ~2% Clinopyroxene, <1% Cr-spinel

These experiments reproduce the expected *in situ* conditions in the vicinity of the well during the injection.

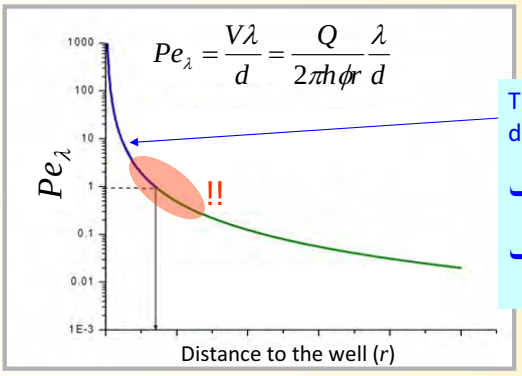
Why are flow-through experiments needed for quantifying mass transfers?

When injecting a CO_2-rich water in the reservoir from a well …..



When injecting a CO_2-rich water in the reservoir from a well …..

1) Average fluid velocity V decreases with increasing distance from the well (r).

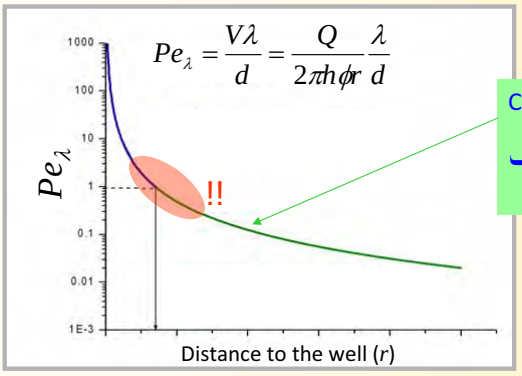


The homogenization of the fluid (composition) does not exist … even at pore scale (λ) !

➥ chem. micro-environments develop

➥ chemical REV cannot be defined
➥ "local scale" models are needed

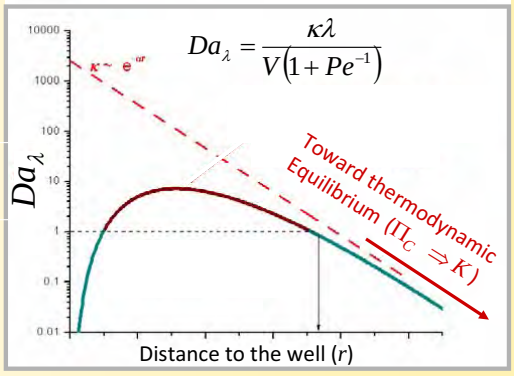
1) Average fluid velocity V decreases with increasing distance from the well (r).



Concentration homogenization @ scale $\leq \lambda$

➥ chemical REV exists
➥ standard ADE-R model can be used

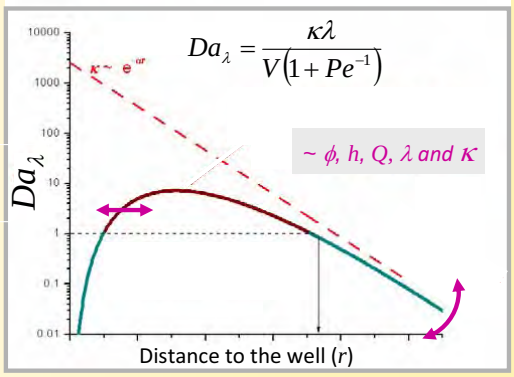
1) Average fluid velocity V decreases with increasing distance from the well (r).



When injecting a CO_2-rich water in the reservoir from a well …..

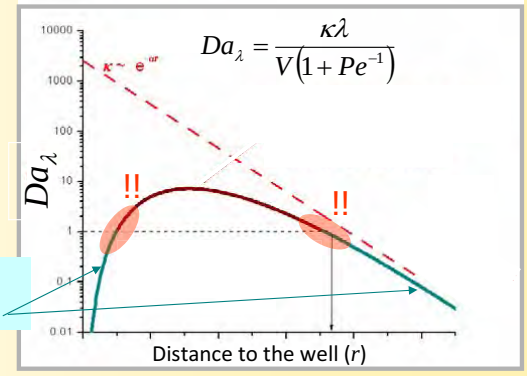
1) Average fluid velocity V decreases with increasing distance from the well (r).
2) Effective reaction rate κ decreases with increasing distance from the well (r).

$$\kappa \propto k\sigma\left(1-\frac{\Pi_{C_i}}{K}\right)$$



1) Average fluid velocity V decreases with increasing distance from the well (r).
2) Effective reaction rate κ decreases with increasing distance from the well (r).

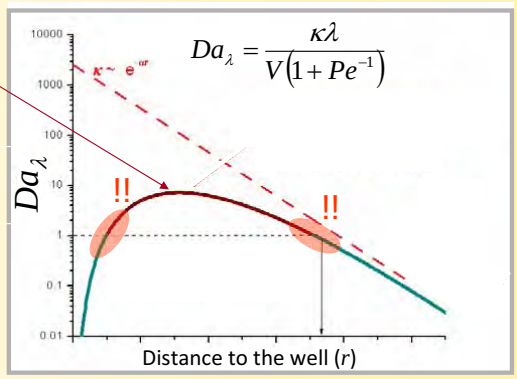
Mass transfers are controlled by the reaction kinetics (dissolution / precipitation)



1) Average fluid velocity V decreases with increasing distance from the well (r).

2) Effective reaction rate κ decreases with increasing distance from the well (r).

Mass transfers are controlled by the rate of renewing of the reactants (and the transport of the products) at (from) the reaction zones.

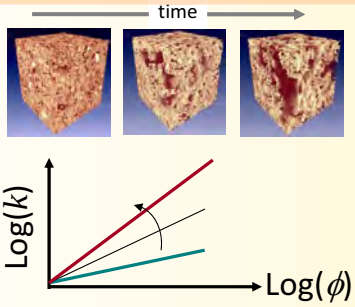


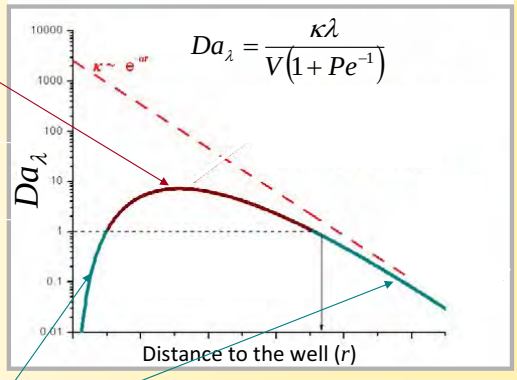
1) Average fluid velocity V decreases with increasing distance from the well (r).

2) Effective reaction rate κ decreases with increasing distance from the well (r).

Localized dissolution

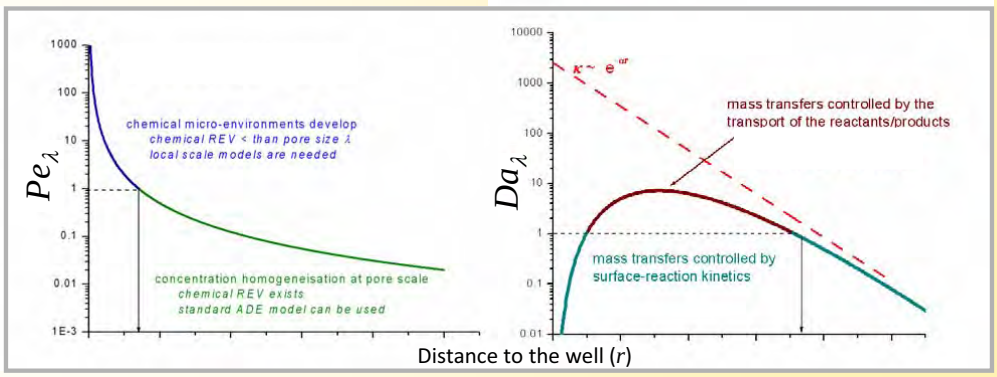
➥ heterogeneity increases





Homogeneous dissolution

Why are flow-through experiments needed for quantifying mass transfers?

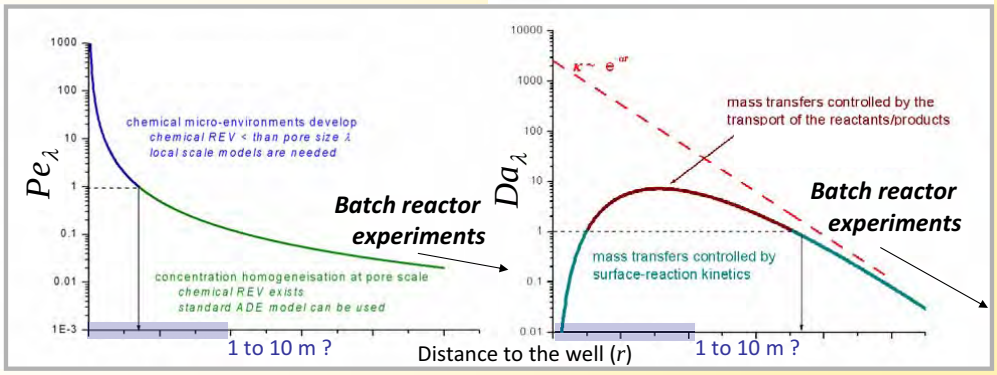


When injecting a CO_2-rich water in the reservoir from a well …..

Distinctly different reaction regimes are expected as a function of *r*

➥ **Flow-through experiments are required for investigating coupled flow, transport & reactions mechanisms and model mass transfers versus *r* and *t*.**

Why are flow-through experiments needed for quantifying mass transfers?



When injecting a CO_2-rich water in the reservoir from a well …..

Distinctly different reaction regimes are expected as a function of *r*

➥ **The rate and the sustainability of the mass transfer, as well as the storage capacity will depend strongly on the changes occurring in the vicinity of the well …. i.e. where the flow rate controls mass transfers.**

Géosciences Montpellier

- **Percolation experiments performed on low porosity sintered materials:**

A) proxy of olivine-rich layers in basaltic rocks :
~96 % olivine Fo88, ~4% MORB, <1% Chromite

B) proxy of dunites :
~97 % olivine Fo90, ~2% Clinopyroxene, <1% Cr-spinel

- **The experiments reproduce the expected *in situ* conditions in the vicinity of the well for the injection of water "almost saturated" in CO_2 @ temperature 180°C and pressure 12MPa.**

Sintered olivine-rich "basalt" : ~96 % olivine Fo88, ~4% MORB, <1% Chr

Three experiments @ low flow rate

Q = 0.0016 mL.min^{-1} ϕ = 6.02% Pe ≈ 0.1
Q = 0.016 mL.min^{-1} ϕ = 6.15% Pe ≈ 1
Q = 0.016 mL.min^{-1} ϕ = 4.35% Pe ≈ 1

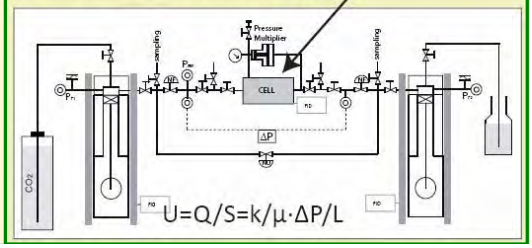
Pressure P = 12 MPa

Confining pressure 13.2 MPa

Temperature T = 180°C

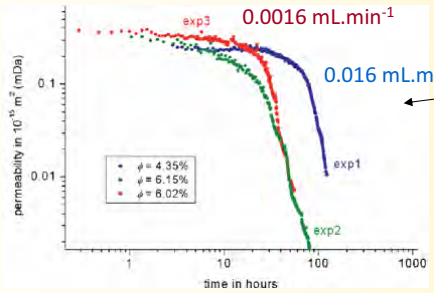
Composition of injected fluid:
MilliQ water
+ 0.5 mol/L $NaHCO_3$
+ 0.03 mmol/L Mg
then mixed with CO_2 (pCO_2 = 10 MPa)

pH @ 180° (calculated) = 6.5.



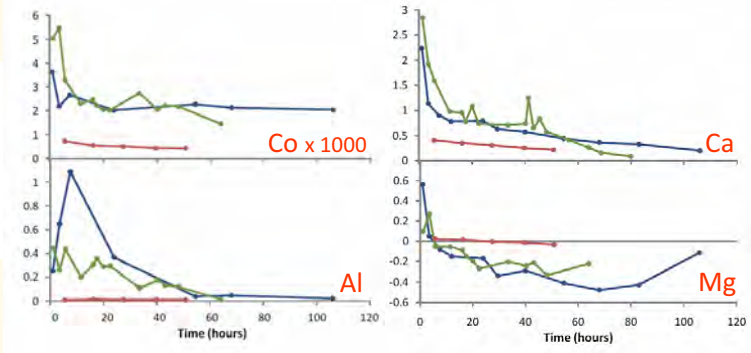
Sintered olivine-rich "basalt" : ~96 % olivine Fo88, ~4% MORB, <1% Chr

Permeability drops rapidly

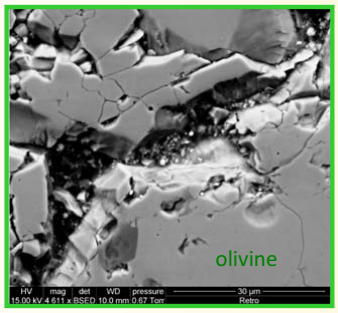


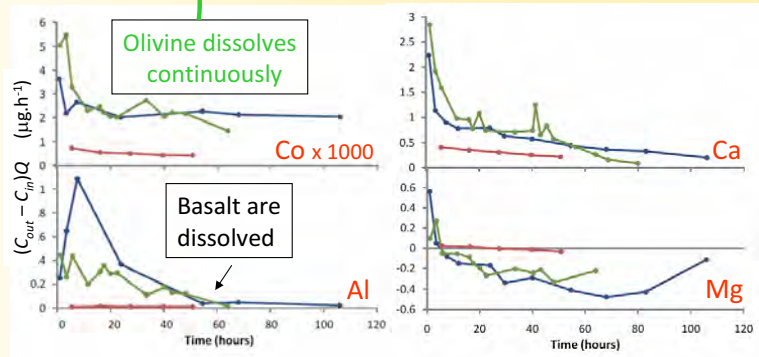
Effective rate $(C_{out} - C_{in})Q$ (µg.h^{-1})

If > 0 : the element is leached out
If < 0 : the element is trapped in the sample

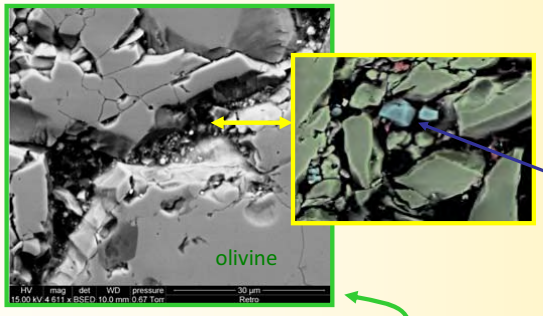


Sintered olivine-rich "basalt" : ~96 % olivine Fo88, ~4% MORB, <1% Chr

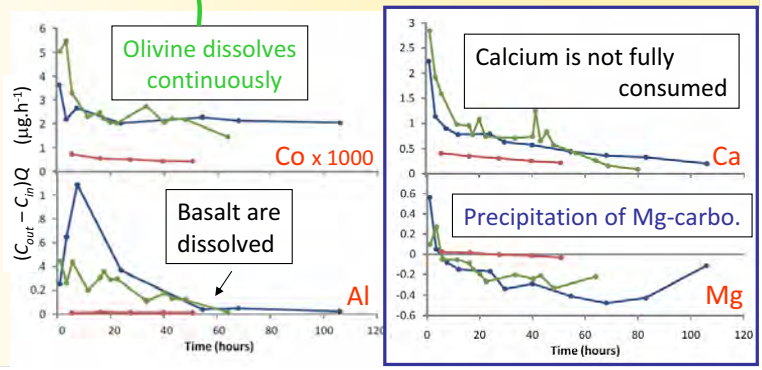




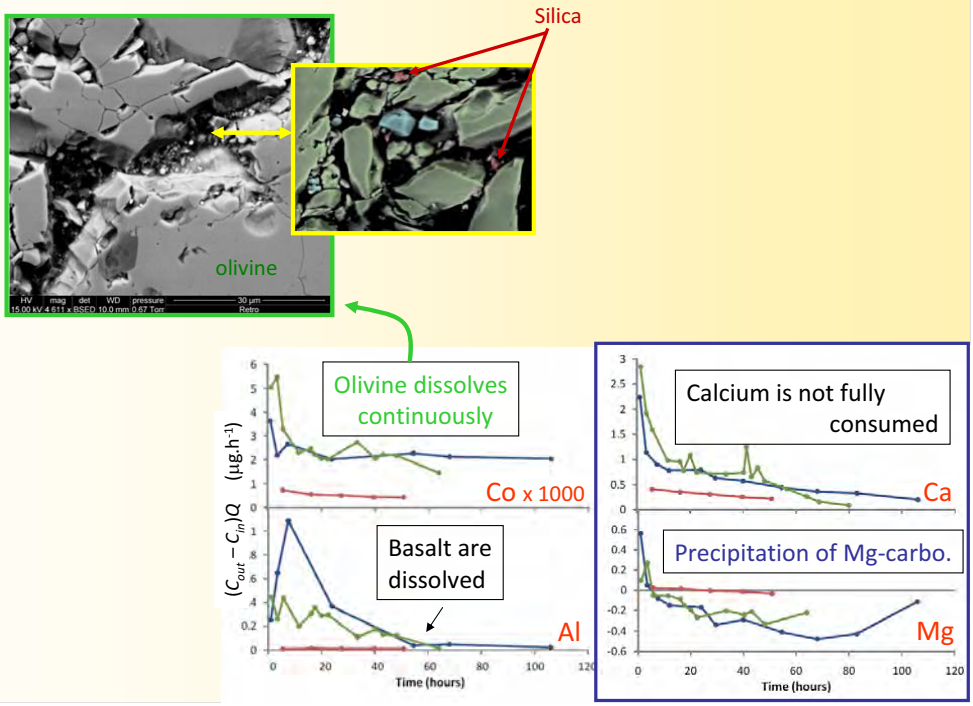
Sintered olivine-rich "basalt" : ~96 % olivine Fo88, ~4% MORB, <1% Chr



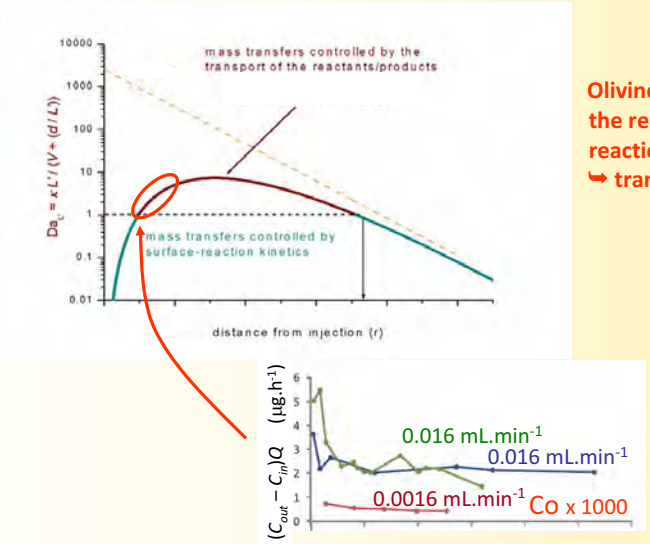
Ca-Mg(-Fe) carbonates



Sintered olivine-rich "basalt" : ~96 % olivine Fo88, ~4% MORB, <1% Chr

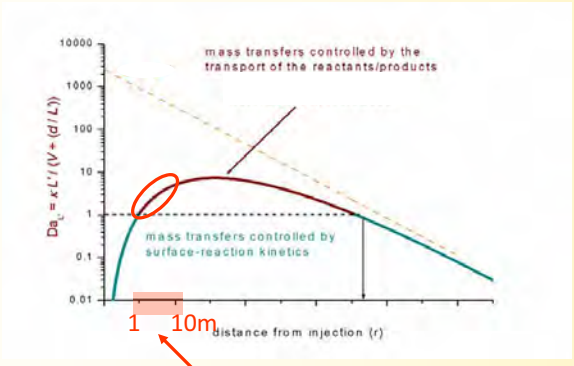


Sintered olivine-rich "basalt" : ~96 % olivine Fo88, ~4% MORB, <1% Chr



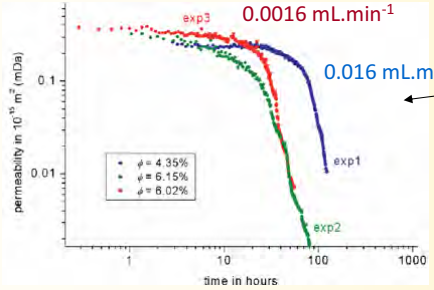
Olivine dissolution is controlled by the renewing of the reactants at the reaction surfaces :
➥ transport-controlled dissolution

Sintered olivine-rich "basalt" : ~96 % olivine Fo88, ~4% MORB, <1% Chr

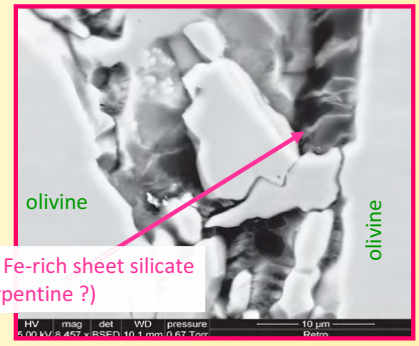


Assuming :
200 m thick layer
11 $m^3.h^{-1}$ injection (~ 0.1 MT/y)

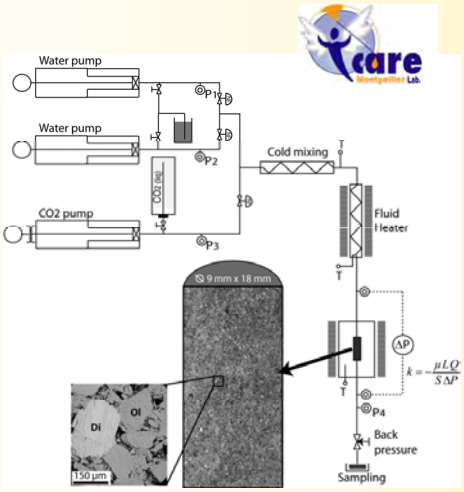
Sintered olivine-rich "basalt" : ~96 % olivine Fo88, ~4% MORB, <1% Chr



Permeability drops rapidly



Low porosity sintered dunite : ~97 % olivine Fo90, ~2% Cpx, <1% Cr-sp



Experiment 1 : Sint_dun1
$\phi = 0.07$
$\langle Pe \rangle \approx 10$
Q = 0.2 and 0.1 mL /min

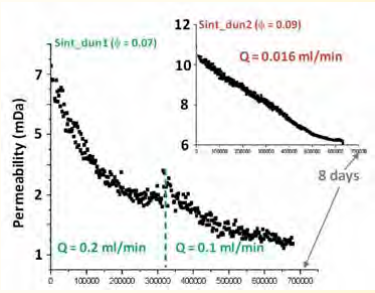
Inlet fluid composition:
$[NaHCO_3]$ = 0.4 moles/L
[NaCl] = 1 moles/L
[Ca] = 8.58 10^{-5} moles/L
[Mg] =2.2310^{-4} moles/L

Experiment 2 : Sint_dun2
$\phi = 0.09$
$\langle Pe \rangle \approx 1$
Q = 0.016 mL /min

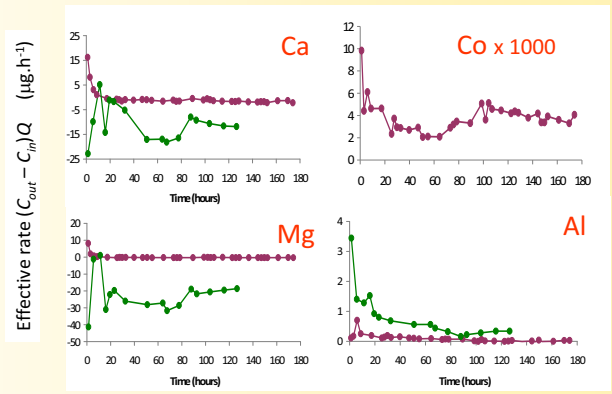
Inlet fluid composition:
$[NaHCO_3]$ = 0.4 moles/L
[NaCl] = 1 moles/L
[Ca] = 8.50 10^{-5} moles/L
[Mg]= 3. 10^{-5} moles/L

Pressure P = 12 MPa (confining pressure = 110% x P)
Temperature T = 180°C
PCO_2 = 10 MPa

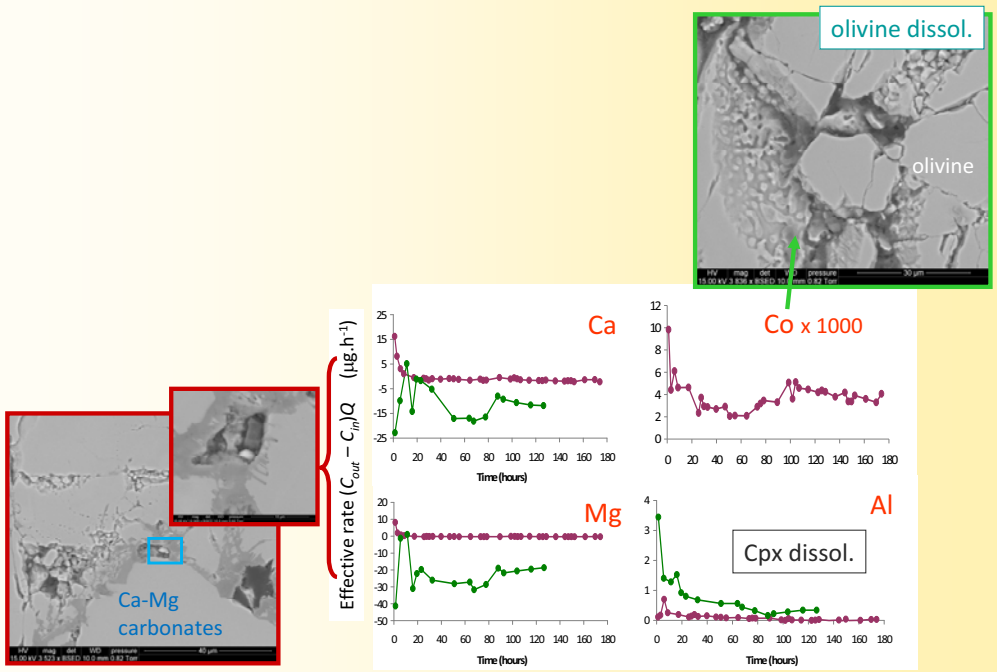
Low porosity sintered dunite : ~97 % olivine Fo90, ~2% Cpx, <1% Cr-sp

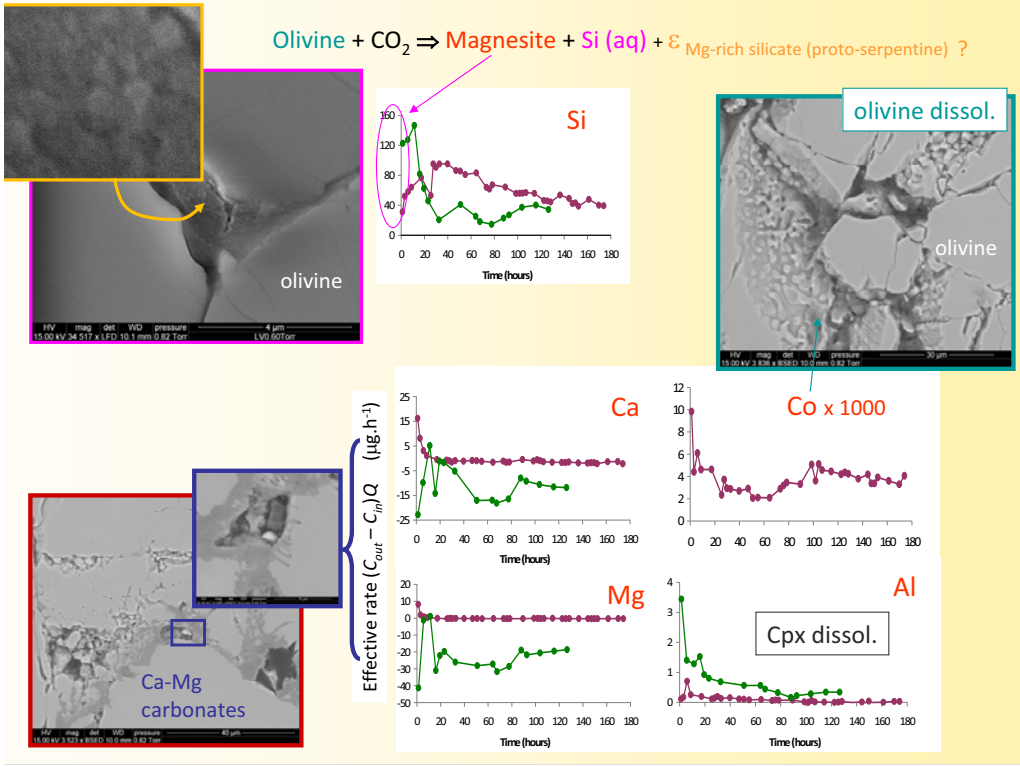


Permeability drops

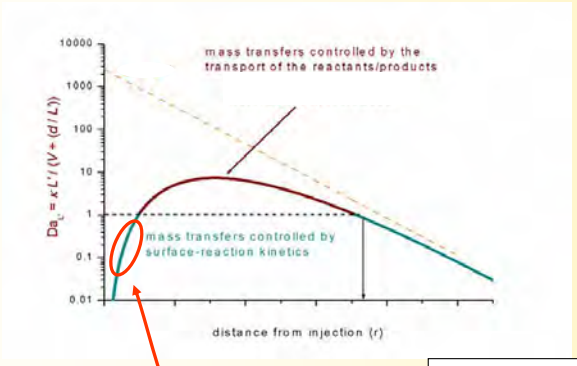


Low porosity sintered dunite : ~97 % olivine Fo90, ~2% Cpx, <1% Cr-sp



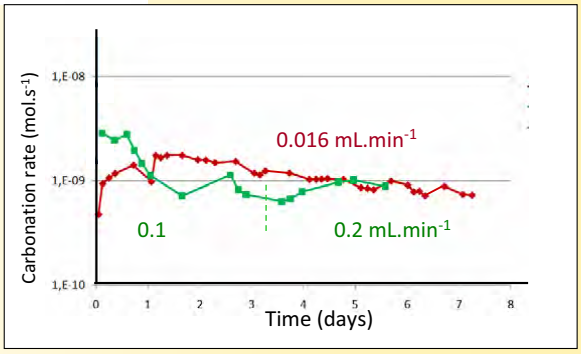


Low porosity sintered dunite : ~97 % olivine Fo90, ~2% Cpx, <1% Cr-sp

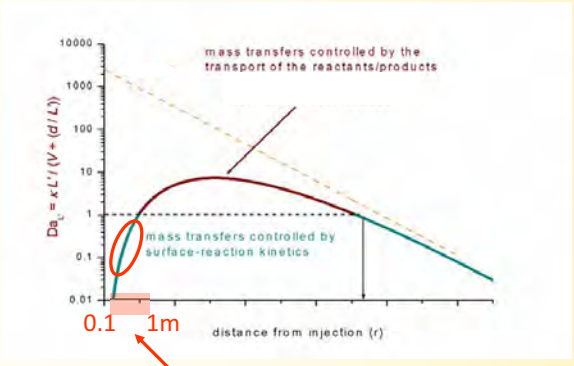


Carbonate formation is independent of the flow rate:

➥ **kinetic-controlled precipitation**



Low porosity sintered dunite : ~97 % olivine Fo90, ~2% Cpx, <1% Cr-sp



Assuming :
200 m thick layer
11 $m^3.h^{-1}$ injection (~ 0.1 MT/y)

Conclusions

➥ **The dissolution of the olivine, the basalt glasses and the Cpx and the precipitation of carbonates and phyllosilicates are fast and occur simultaneously at pore scale.**

- the asymptotic total mass transfer is about 0.15 % of the initial rock mass per day !
  ➥ 0.50 % of the initial rock volume is carbonated at the end of experiment sint_dun1 (6 days)

- carbonate grains (+ silica and/or serpentine-like coating) are observed in the vicinity of the olivine dissolution patterns and act to decrease the permeability.

Actually, as we are dealing with low porosity systems (i.e. close to the percolation threshold porosity) small changes in porosity (here < 0.4 %) may have huge impact on permeability close to the well ➥decreasing injectivity.

Increasing the flow rate (while inducing fissures by hydrofrac methods) will act not only at increasing the spreading of the CO_2-rich fluid, but also at displacing the highly reactive zone far away from the well, while promoting hydrodynamic-controlled mass transfers ➥promoting heterogeneous mass transfers.

Merci de votre attention ….

6. B. Jamtveit – Univ. Oslo, Norway.

PHYSICAL FEEDBACKS DURING MINERAL CARBONATION: FIELD OBSERVATIONS, EXPERIMENTS AND MODELS

WILL VOLATILIZATION-REACTIONS CAUSE CLOGGING OF PORE SPACE AND PREVENT LARGE SCALE FLUID-ROCK INTERACTION

Bjørn Jamtveit

w/contrib. from
Anders Malthe-Sørenssen, Haakon Austrheim, Anja Røyne, and Christophe Raufaste

PHYSICS OF GEOLOGICAL PROCESSES

nature Vol 456 | 4 December 2008 doi:10.1038/nature07464

LETTERS

Large tundra methane burst during onset of freezing

Mikhail Mastepanov[1], Charlotte Sigsgaard[2], Edward J. Dlugokencky[3], Sander Houweling[4,5], Lena Ström[1], Mikkel P. Tamstorf[6] & Torben R. Christensen[1]

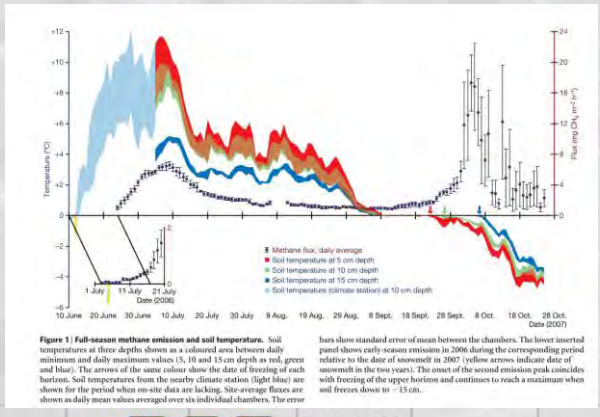
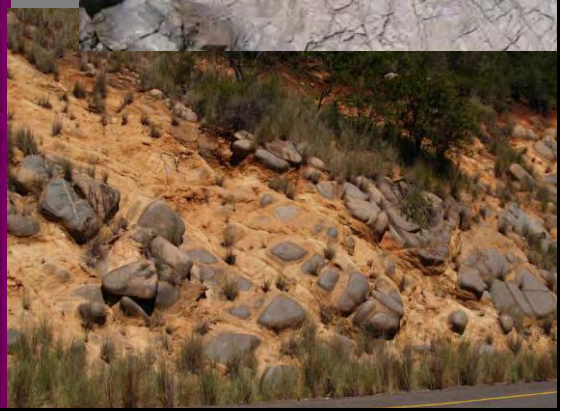


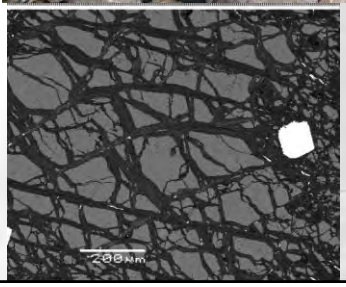
Figure 1 | Full-season methane emission and soil temperature. Soil temperatures at three depths shown as a coloured area between daily minimum and daily maximum values (5, 10 and 15 cm depth as red, green and blue). The arrows of the same colour show the date of freezing of each horizon. Soil temperatures from the nearby climate station (light blue) are shown for the period when on-site data are lacking. Site-average fluxes are shown as daily mean values averaged over six individual chambers. The error bars show standard error of mean between the chambers. The lower inserted panel shows early-season emission in 2006 during the corresponding period relative to the date of snowmelt in 2007 (yellow arrows indicate date of snowmelt in the two years). The onset of the second emission peak coincides with freezing of the upper horizon and continues to reach a maximum when soil freezes down to ~15 cm.

PHYSICS OF GEOLOGICAL PROCESSES

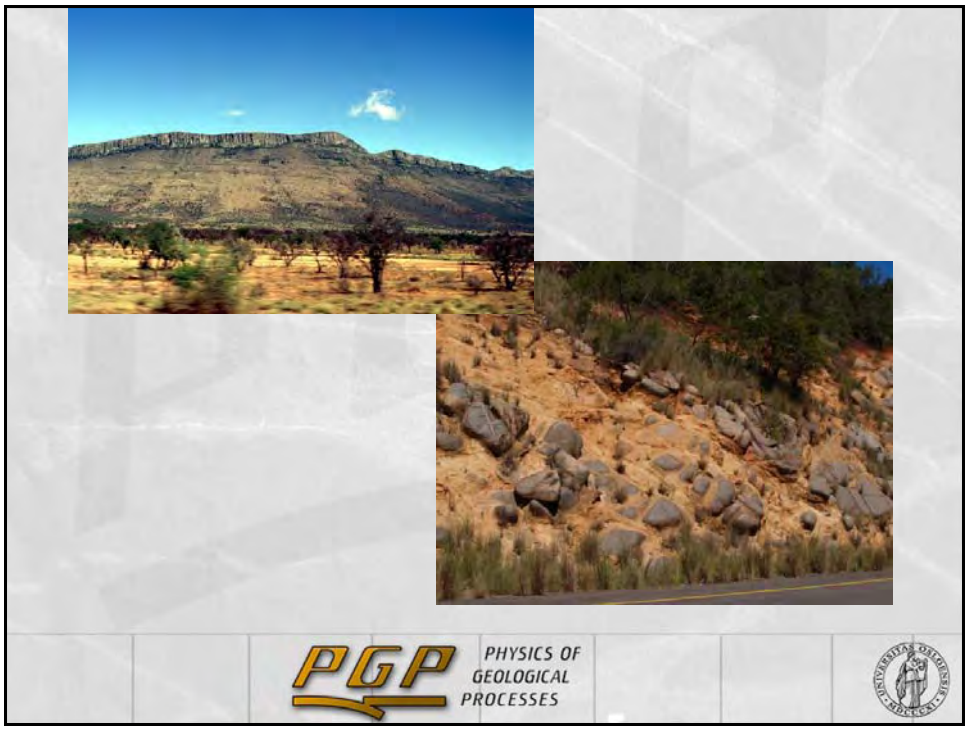
Hydration

- Serpentinization
- Weathering
- Amphibolitization





Serpentinization:
Fracturing across scales


PGP
PHYSICS OF
GEOLOGICAL
PROCESSES

Carbonation front
PGP
PHYSICS OF
GEOLOGICAL
PROCESSES

PGP
PHYSICS OF
GEOLOGICAL
PROCESSES

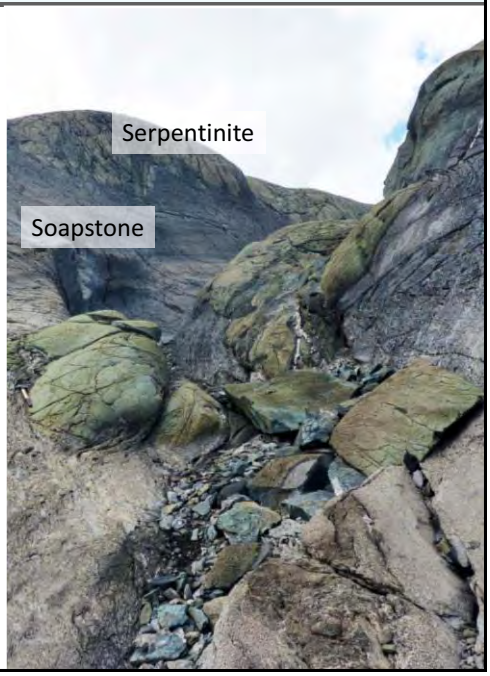
PGP
PHYSICS OF
GEOLOGICAL
PROCESSES

Massive carbonatization of serpentinite: The Linnajavri soapstone

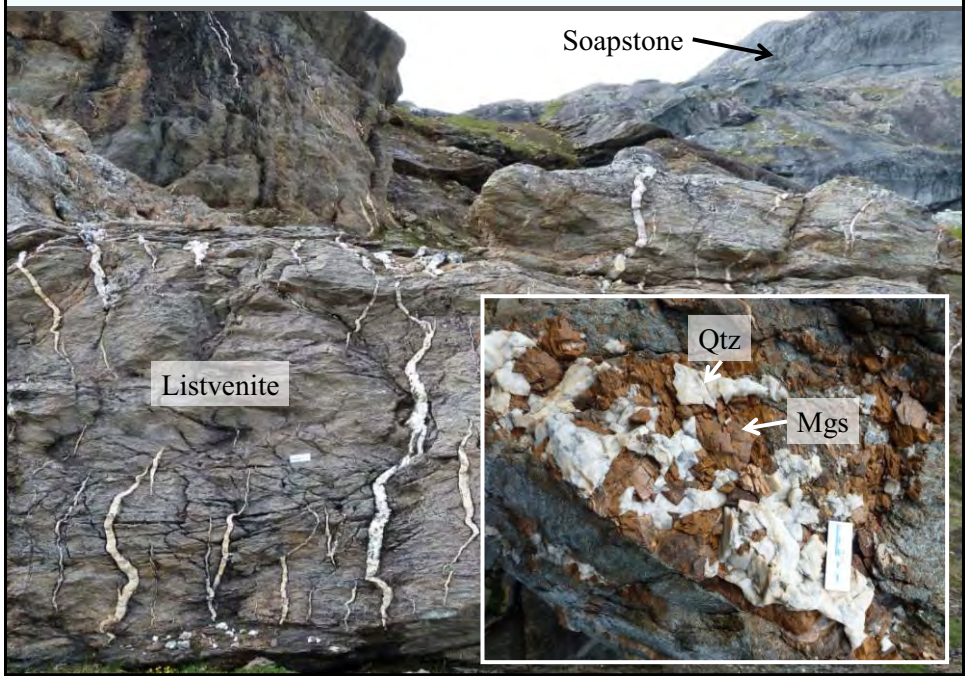
- ~20 soapstone bodies
- >100 Mt soapstone in total (Lindahl & Nilsson, 2008)
- ~40 vol. % carbonate in the soapstone

→~20 Mt CO_2 stored in the soapstone only

- Norway's CO_2 emission in 2009: 42.4 Mt



Listvenitization

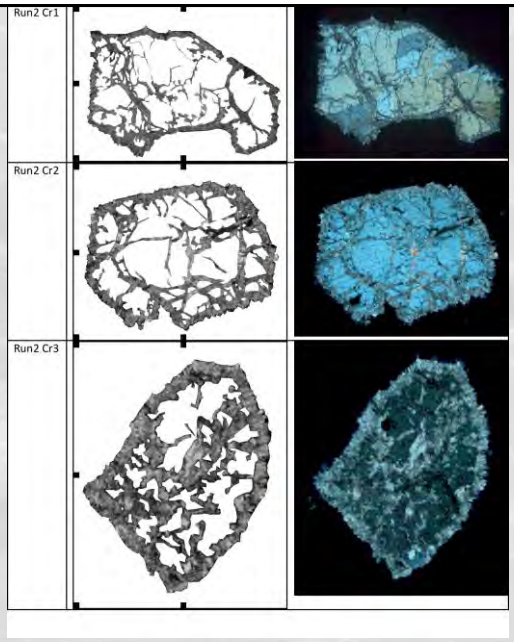


PGP PHYSICS OF GEOLOGICAL PROCESSES

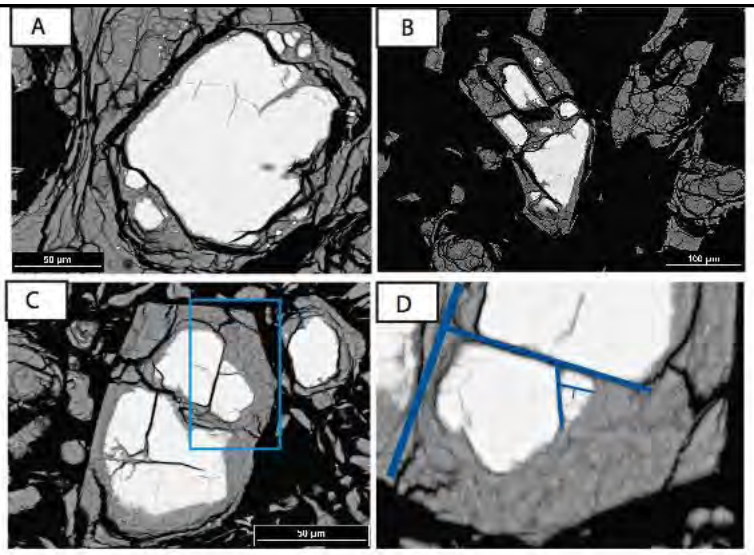
Reaction driven fragmentation (ex: plexiglass in aceton)

PGP PHYSICS OF GEOLOGICAL PROCESSES

Aragonite -> Calcite



PGP PHYSICS OF GEOLOGICAL PROCESSES



Leucite + NaCl + H_20 = Analcime + KCl

Jamtveit, Putnis, Malthe-Sorenssen, Contrib. Min. Petrol, 2009

SWELLING PRESSURE

PHYSICS OF GEOLOGICAL PROCESSES

From Ostapenko, Geokhimiya, 1976

Hydration of periclase (MgO) to brucite ($Mg(OH)_2$)

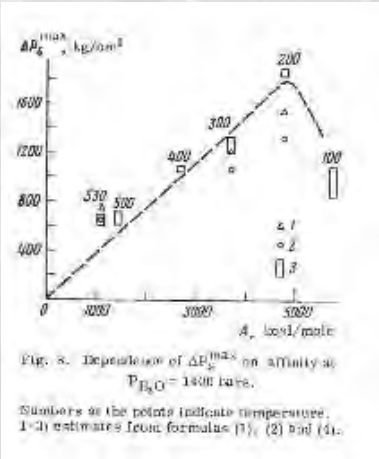


Fig. 8. Dependence of ΔP_s^{max} on affinity at P_{H_2O} = 1400 bars.

Numbers at the points indicate temperatures. 1–3) estimates from formulas (1), (2) and (4).

PHYSICS OF GEOLOGICAL PROCESSES

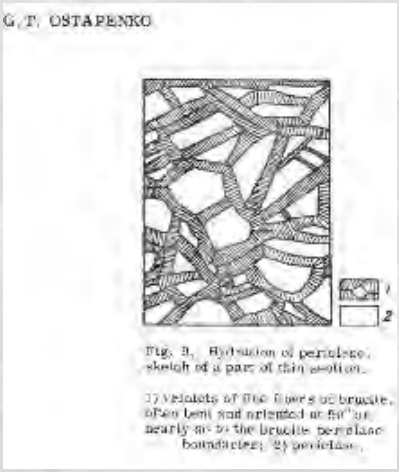
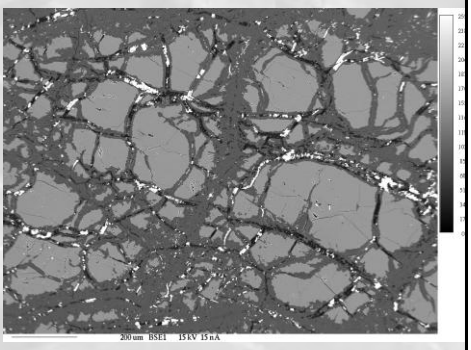

G. T. OSTAPENKO

Fig. 3. Hydration of peridotite, sketch of a part of thin section.

1) Veinlets of fine fibers of brucite, often twinned and oriented at 60° or nearly at 0° to the brucite-peridotite boundaries; 2) peridotite.



Olivine mesh-texture

PGP PHYSICS OF GEOLOGICAL PROCESSES

From:

AH McDonald and WS Fyfe, 1985, Rate of serpentinization in seafloor environments, *Tectonophysics*, 116: 123-135

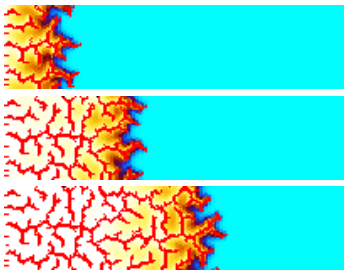
TABLE 3
Swelling pressures produced by the reaction 2 Forsterite + $3H_20$ → 1 Serpentine + Brucite when $P_{hydrostatic}$ = *1200 bar, and* $P_{solid} = PH_2O$, *eq +2600*

T (° C)	Swelling pressure (bar)	Effective swelling pressure (bar)
180	4323.0	1723.0
200	4980.0	2380.0
240	3984.0	1294.0
260	3206.0	606.0
280	2057.0	

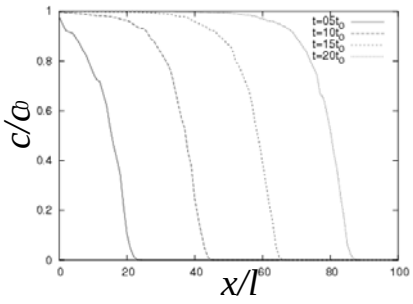
PGP PHYSICS OF GEOLOGICAL PROCESSES

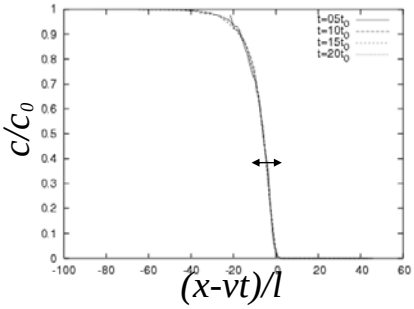
Malthe-Sørenssen, A., Jamtveit, B., and Meakin, P., 2006, Fracture patterns generated by diffusion-controlled volume changing reactions. *Phys. Rev.Letters*, 96, art no. 245501

Front dynamics (1D)



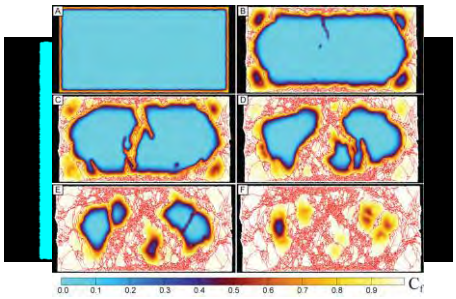
- Front propagates with constant *v* and *w*
- Contrast to diffusion or advection-diffusion





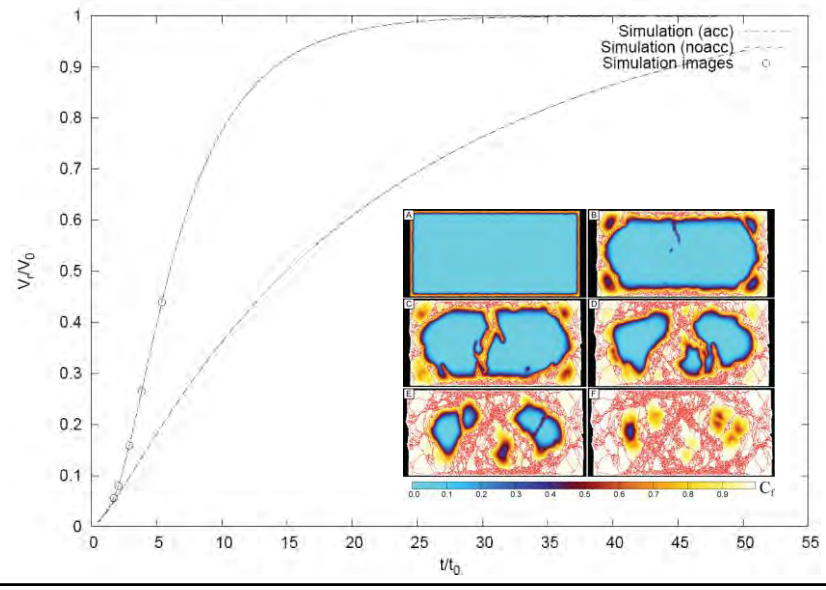
Røyne, A., Jamtveit, B., et al., 2008, Controls on weathering rates by reaction induced hierarchical fracturing. *Earth and Planetary Science Letters*, 275, 364-369

(2D) Reaction rate

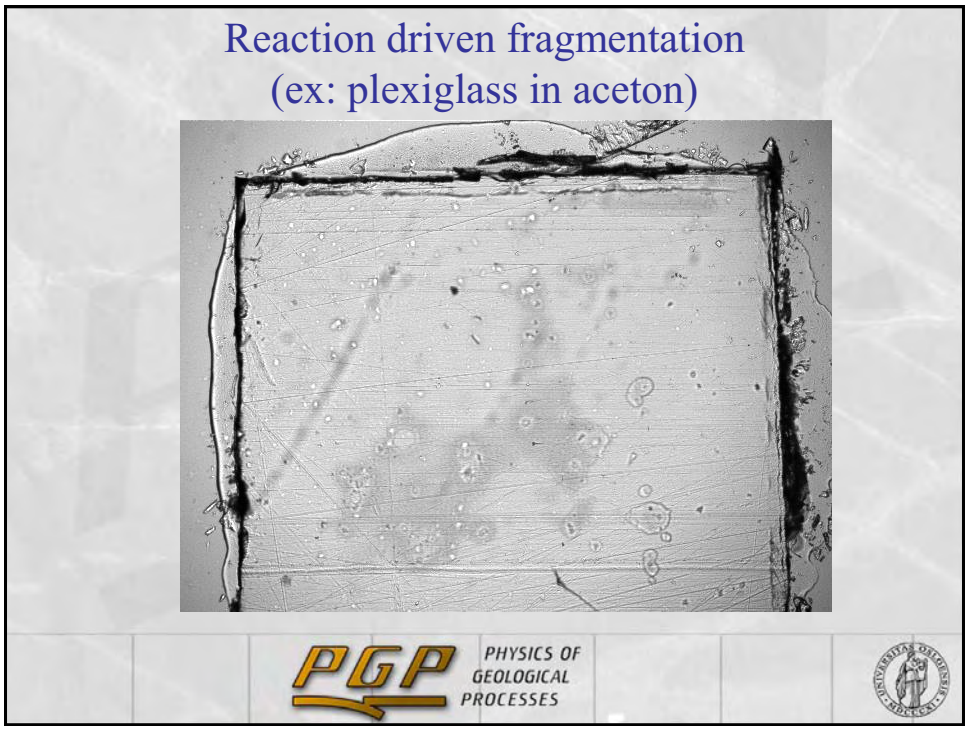


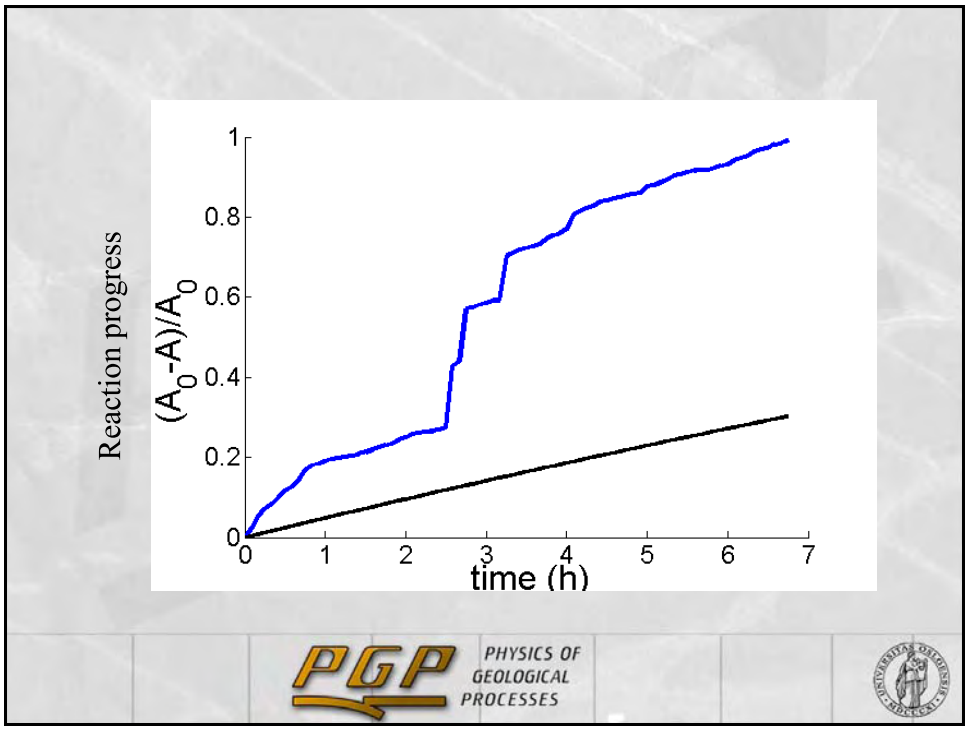
Røyne, A., Jamtveit, B., et al., 2008, Controls on weathering rates by reaction induced hierarchical fracturing. *Earth and Planetary Science Letters,* 275, 364-369

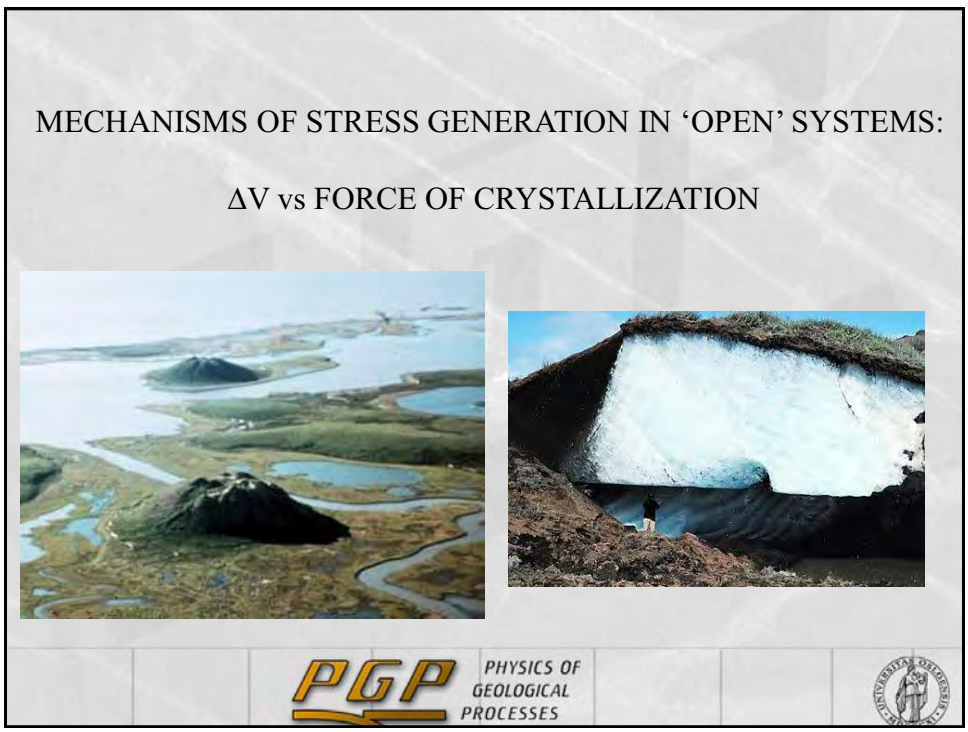
(2D) Reaction rate



PGP
PHYSICS OF
GEOLOGICAL
PROCESSES

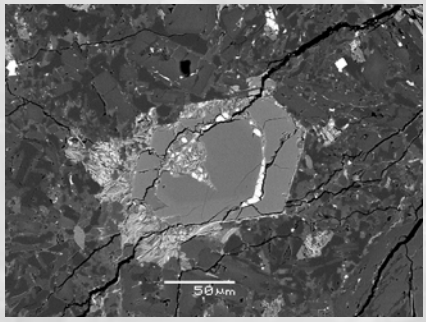

Reaction driven fragmentation
(ex: plexiglass in aceton)
PGP
PHYSICS OF
GEOLOGICAL
PROCESSES

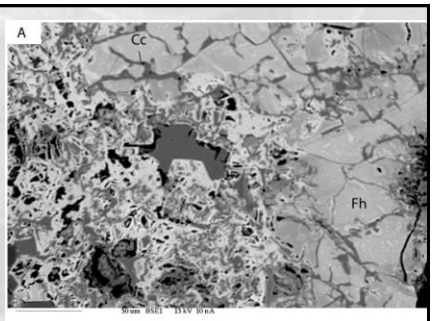

Reaction progress
$(A_0-A)/A_0$
time (h)
0
0.2
0.4
0.6
0.8
1
0
1
2
3
4
5
6
7
PGP
PHYSICS OF GEOLOGICAL PROCESSES

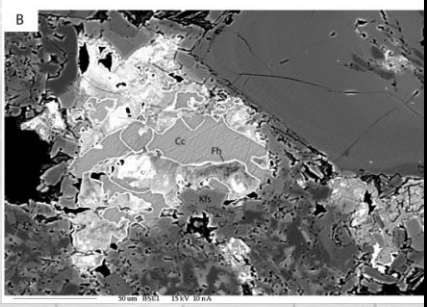

MECHANISMS OF STRESS GENERATION IN 'OPEN' SYSTEMS:
ΔV vs FORCE OF CRYSTALLIZATION
PGP
PHYSICS OF GEOLOGICAL PROCESSES

PGP
PHYSICS OF
GEOLOGICAL
PROCESSES

PGP PHYSICS OF GEOLOGICAL PROCESSES







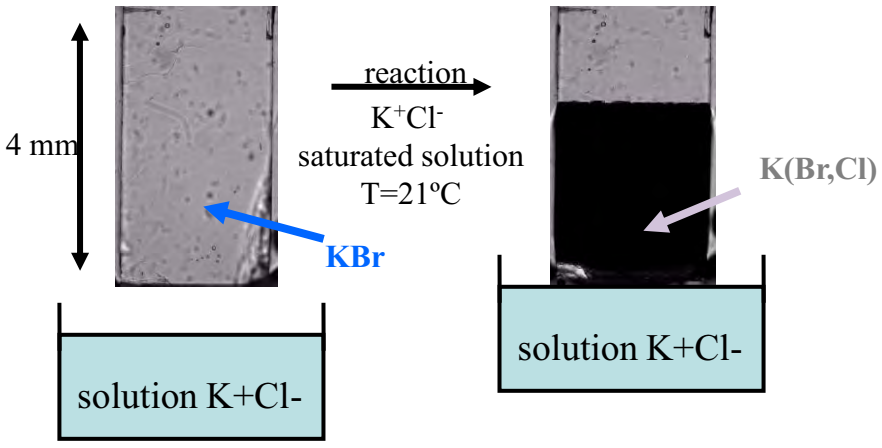
PGP PHYSICS OF GEOLOGICAL PROCESSES

Porosity production during replacement reactions

PGP PHYSICS OF GEOLOGICAL PROCESSES

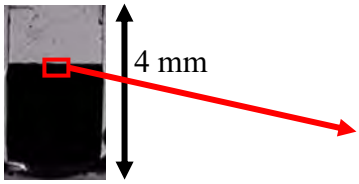
Raufaste, Jamtveit, John, Meakin, Dysthe, 2011,The mechanism of porosity formation during solvent-mediated phase transformations. *Proceedings of the Royal Society A* (in press)

☐ model system KBr-KCl-H_2O

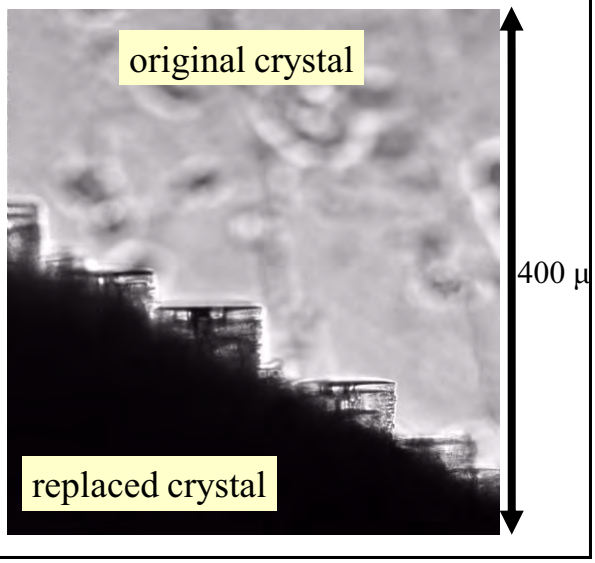


I – qualitative observations

☐ interface of reaction

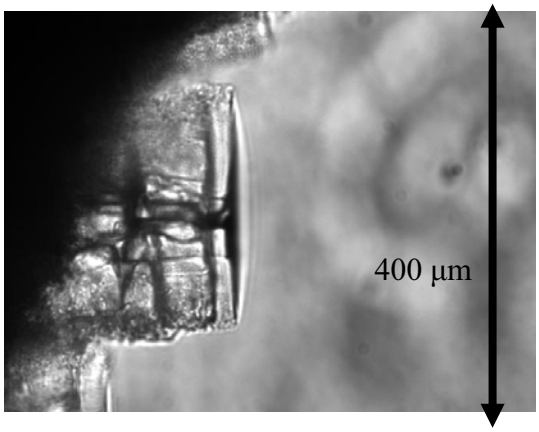


- presence of a layered structure at the interface
- they are aligned along the original crystal directions
- they are non-porous (excepted in the middle)



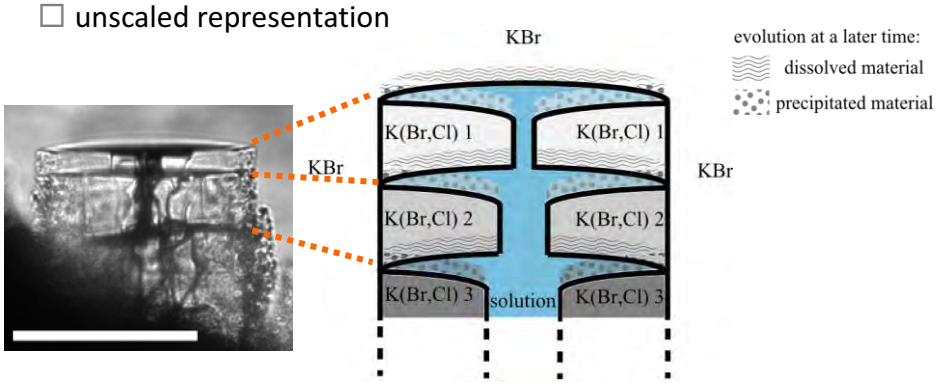
I – qualitative observations

- movie accelerated 100x
- the structures seem to translate as a whole



IV – mechanism

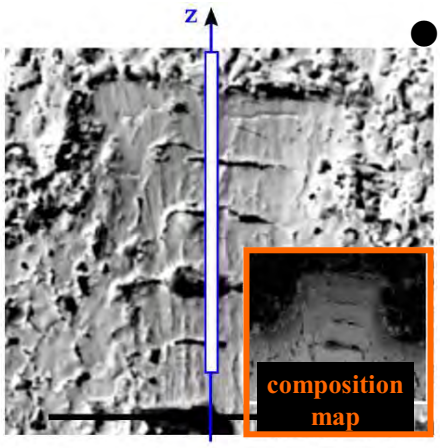
☐ unscaled representation



● Dissolution on one side of the liquid-filled space, precipitation on the other side.

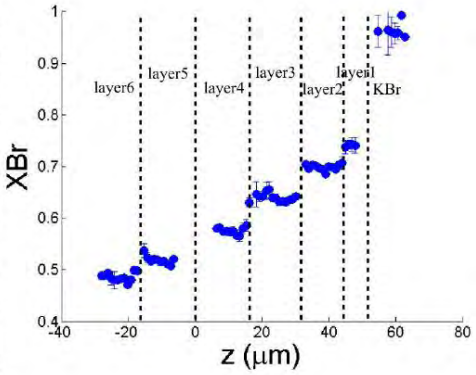
III – quantitative measurements

☐ microprobe analysis



BSE image

● each layer has a homogeneous composition



composition profile

Conclusions

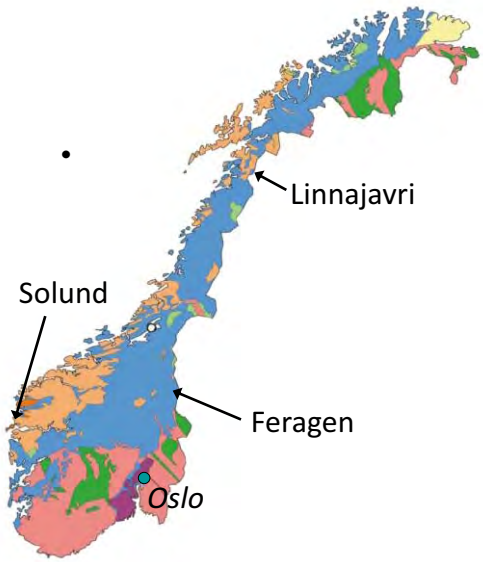
- The rate of carbonation will be controlled by the supply of fluid to the reacting interface
- Without reaction driven porosity/permeability production, any pre-existing permeability will be clogged by volatilization reactions
- Volatilization reactions in 'closed' systems often produce sufficient stresses (from the volume change of the reactions) to drive fragmentation of the reactive rock volume
- In 'open' systems, connected porosity towards the reactive interface may be generated by a) fragmentation by the force of crystallization or b) porosity generation by growth/dissolution processes

PGP PHYSICS OF GEOLOGICAL PROCESSES

- The fragmentation process provides first-order controls on fluid migration rates in low permeable reactive systems
- Hierarchical domain division may accelerate the reaction rate with time (due to increasing rate of surfaces area production)

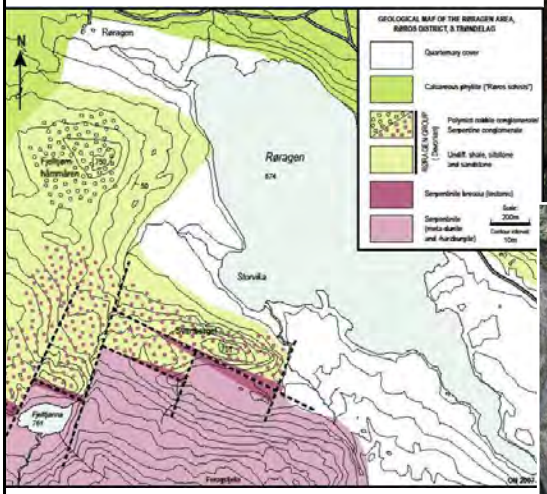
PGP PHYSICS OF GEOLOGICAL PROCESSES

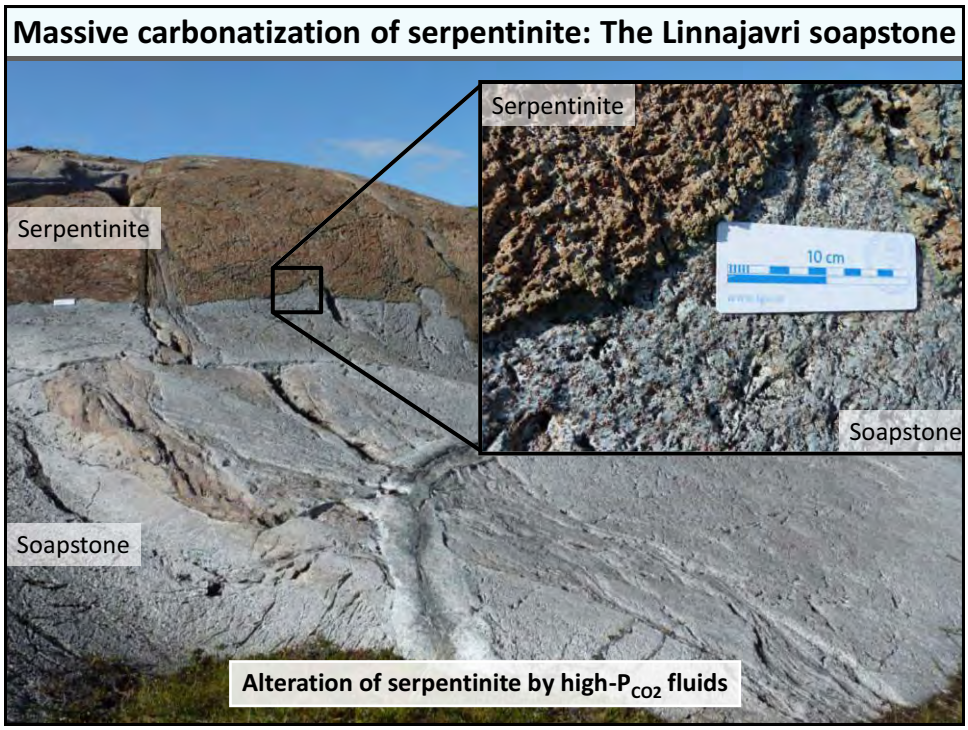
Carbonatized ultramafites in three environments

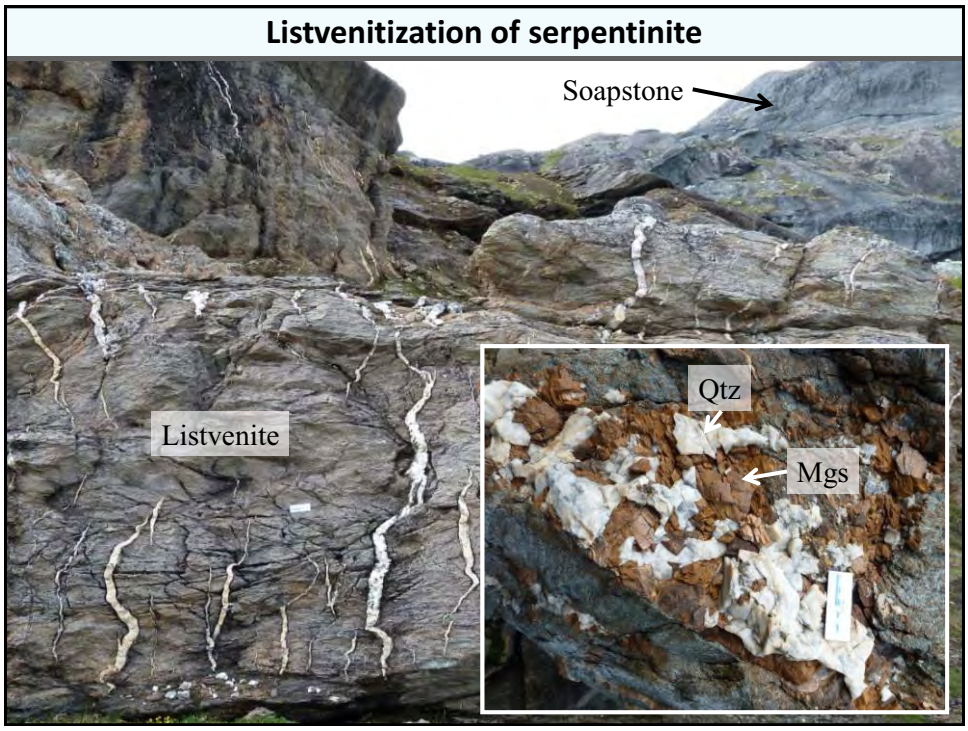


Fracturing & carbonatization: The Feragen Ultramafic Body

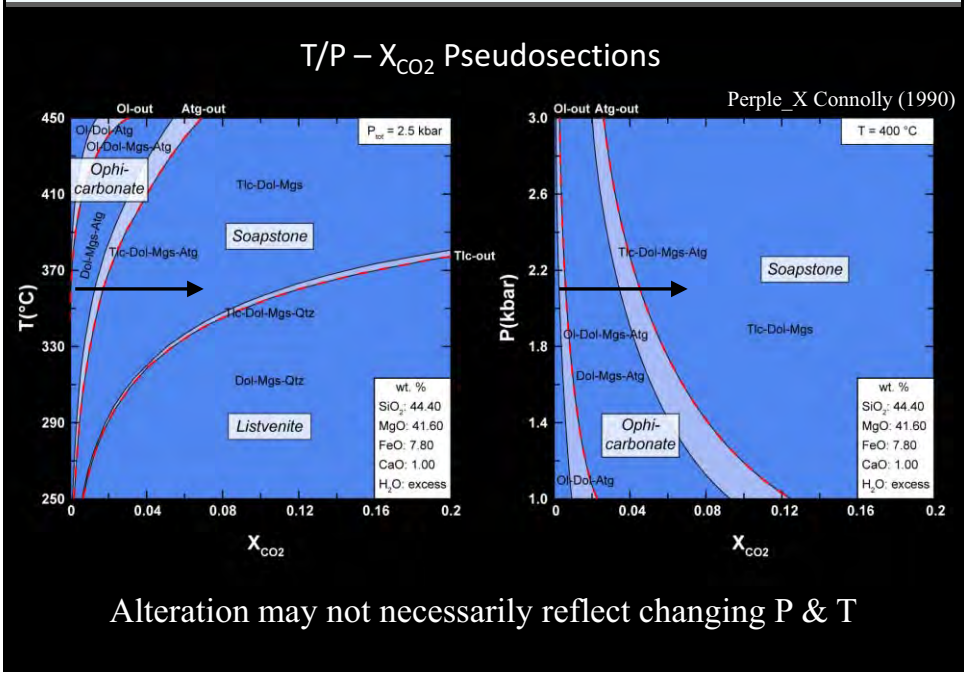
Reaction-induced fracturing:
Increase of the reactive surface area
& fluid pathways



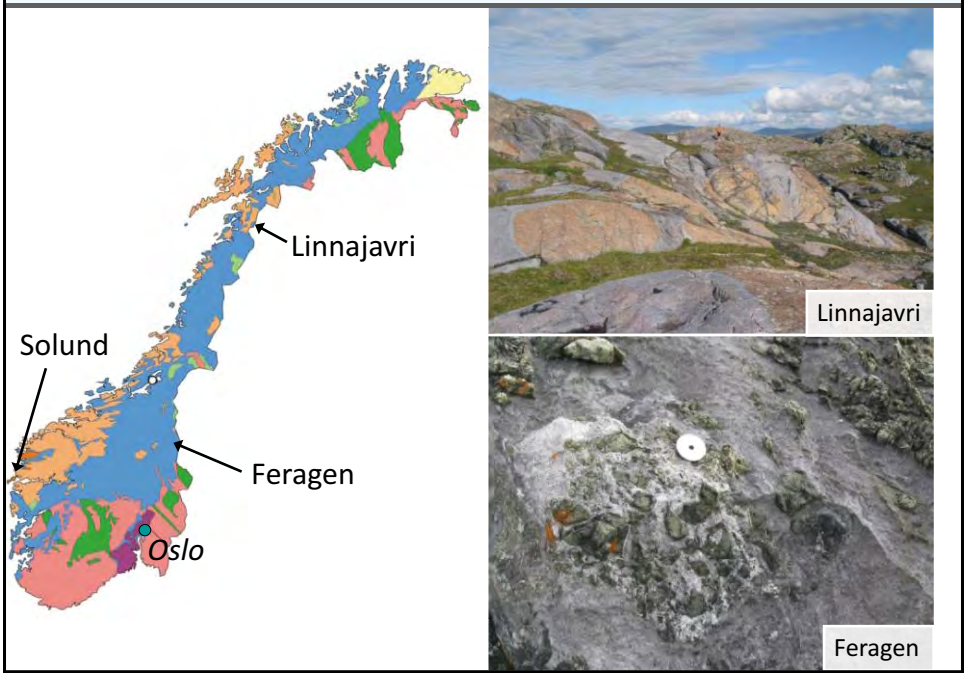

Massive carbonatization of serpentinite: The Linnajavri soapstone
Serpentinite
Serpentinite
10 cm
Soapstone
Soapstone
Alteration of serpentinite by high-P_{CO2} fluids


Listvenitization of serpentinite
Soapstone
Qtz
Mgs
Listvenite

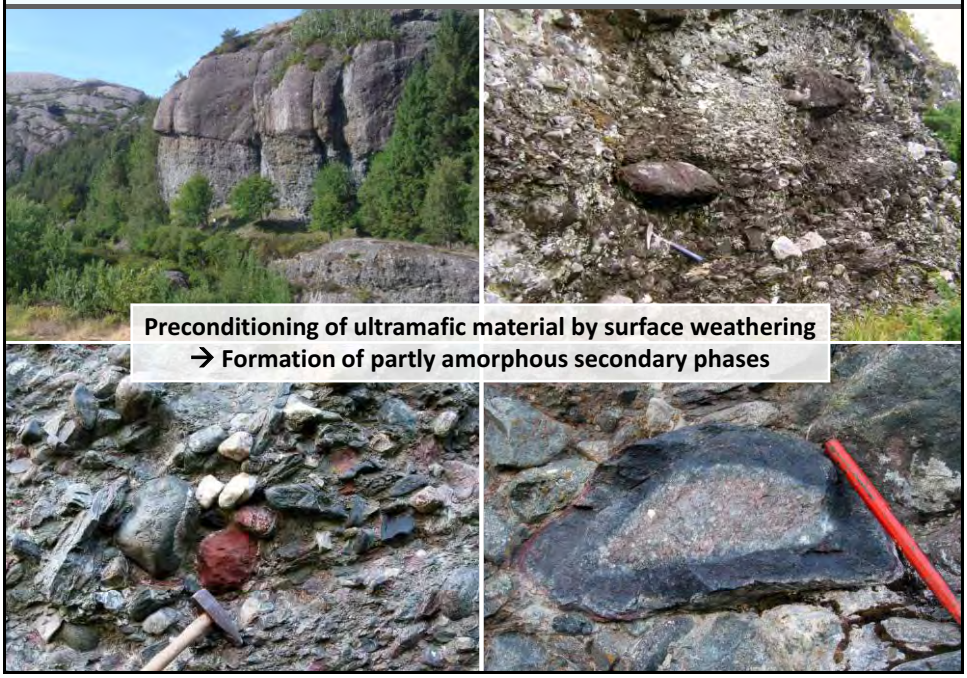
Peridotite alteration as a function of pCO_2



Carbonatized ultramafites in three environments



The Solund basin: Reaction of weathered peridotite with Ca-fluids



The Solund micro-laboratory: Alteration by diagenetic Ca-fluids

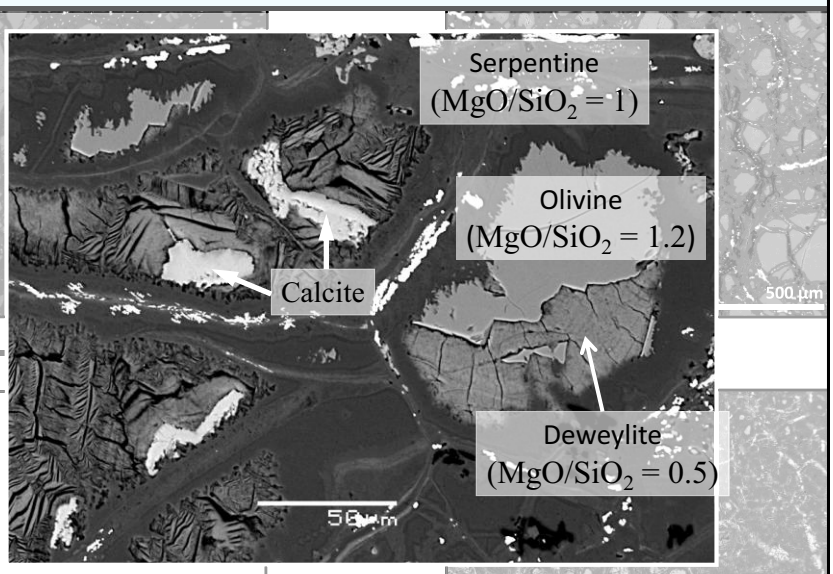
Carbonatization of allochtonous peridotite

Formation of calcite instead of magnesite

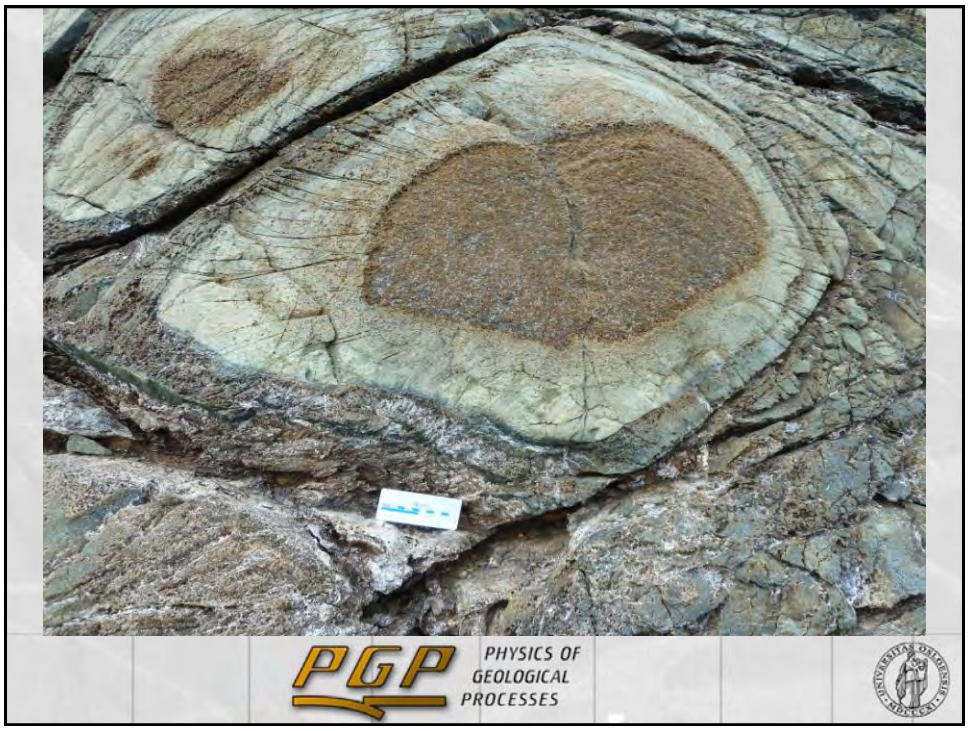
Beinlich et al. (2010

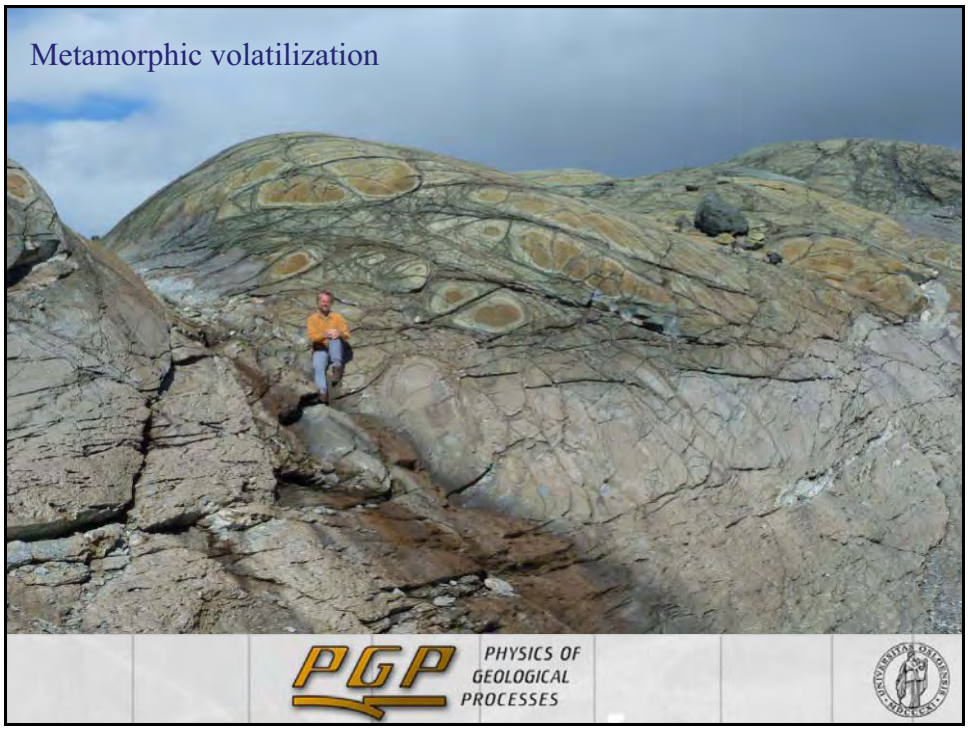
Poster on natural & experimental replacement reactions of the Solund Peridotites
(1) Austrheim et al. → Wednesday 15.12. Poster # GC31B-0866
(2) Hövelmann et al. → Wednesday 15.12. Poster # GC31B-0862

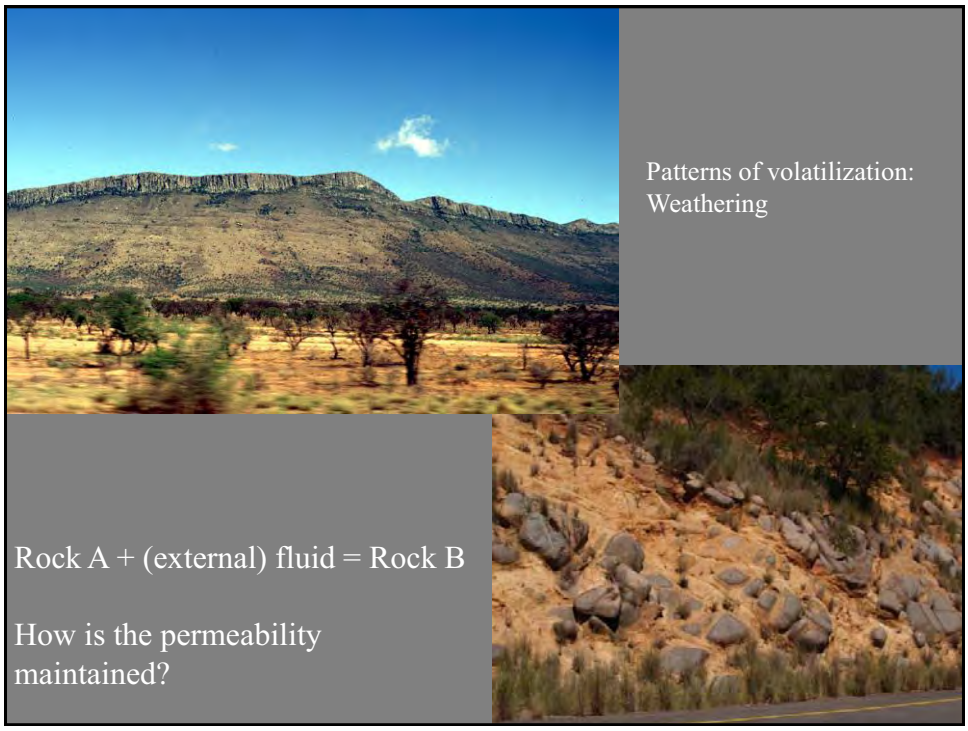
The Solund micro-laboratory: The impact of weathering



Calcite seems to replace the breakdown product after olivine




Metamorphic volatilization
PGP
PHYSICS OF
GEOLOGICAL
PROCESSES


Patterns of volatilization:
Weathering
Rock A + (external) fluid = Rock B
How is the permeability
maintained?

7. K. Becker - RSMAS, USA.

Hydrogeology: Field Observations and Lessons from DSDP/ODP/IODP Crustal Holes

CCS Workshop, Sultan Qaboos U., Oman, Jan. 8 2011

Keir Becker
University of Miami - RSMAS

With special thanks to:
Andy Fisher
U. of California Santa Cruz
Earl Davis
Geological Survey of Canada
Geoff Wheat
U. of Alaska
Tom Pettigrew
formerly ODP, Mohr Engineering
and many other collaborators…

Financial Support: ODP+IODP, NSF, GSC

CCS Workshop, KB #1

Hydrogeology: Field Observations and Lessons from DSDP/ODP/IODP Crustal Holes

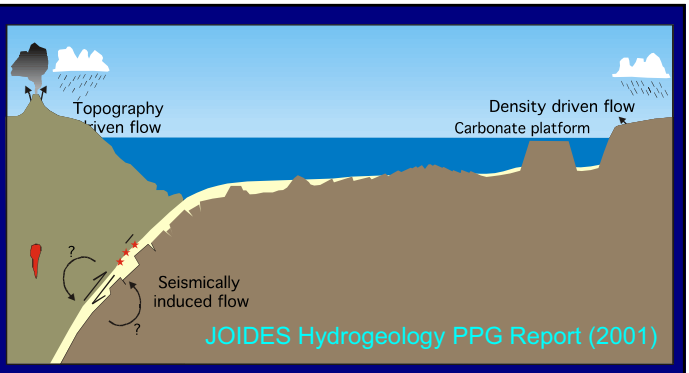
I. Summary of scientific results - and implications for CCS
Note that nearly all results to date are in sedimented upper oceanic crustal holes - very little yet in oceanic mantle holes.

II. ODP/IODP technological capabilities - and applicability to CCS experiments
ODP/IODP CORK monitoring concept can be adapted for CCS prototype experiments.

III. Programmatic lessons with respect to post-2013 IODP

CCS Workshop, KB #2

Subseafloor Hydrogeology: Primary ODP/IODP Theme Since COSOD II (1987)

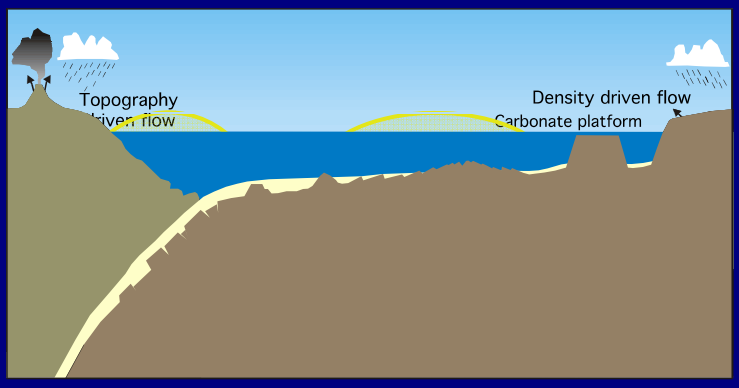


- Volume ≈ oceans circulates through crust @<1 Myr
- Accounts for ~25% of Earth's heat loss
- Major effect on ocean and formation chemistry
- Formation of ore bodies
- Key role in gas hydrate systems (C cycle)
- Association with earthquakes at convergent margins
- Nutrient source for many seafloor ecosystems
- Subsurface biosphere

CCS Workshop, KB #3

Two Primary DSDP/ODP/IODP Focus Regimes to Date:

1. Ocean crust with thermally-driven fluid flow
2. Subduction systems with compaction-driven flow

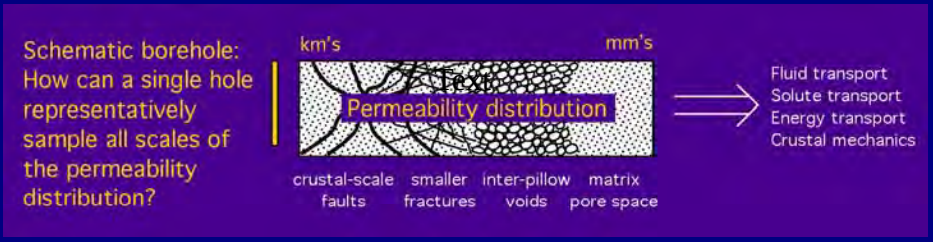


- What do the results in ocean crust suggest about the potential for CCS in mafic/ultramafic oceanic crust/mantle?
- How well are the ODP/IODP techniques applicable in prototype borehole CCS experiments?

CCS Workshop, KB #4

Controlling Role of Formation Permeability

Permeability E ability of a medium to allow through-flow of fluids
• Controls flow of fluids and effects on formation state and evolution
• Relatively easy to conceptualize, even to measure on lab sample
• But in nature, it has a multiscalar distribution and is very difficult to quantify, even with ODP/IODP cores and holes.



Recent results in ODP/IODP have provided or will provide:
• More ways to to sense ocean crustal permeability (e.g., CORKs)
• Indications of scale dependence of upper crustal permeability
• Constraints on actual flow pathways in upper oceanic crust

CCS Workshop, KB #5

Methods to Determine Permeability of Igneous Oceanic Crust

• Packer experiments - since 1979

• Borehole flow measurements - since 1970's

• Sealed-hole CORK experiments - since 1991
- Yield in-situ pressure for interpretation of permeability from flow
- Transmission of tidal loading signals and tectonic transients constrain hydraulic diffusivity and permeability

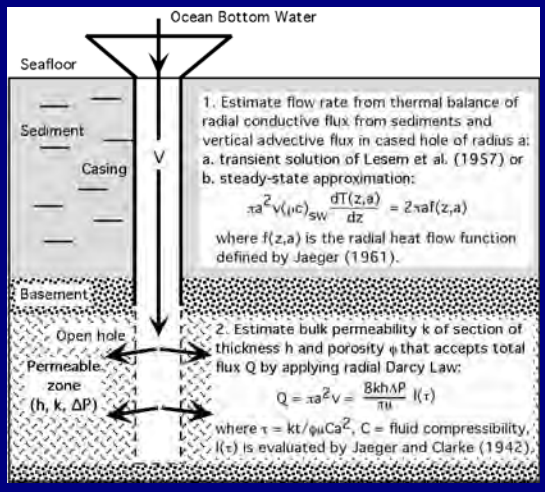
• Modeling, e.g., to simulate heat flow variations associated with basement topography

Increasing Measurement Scale
+
(to some degree)
Apparent Permeabilities In Young Crust

CCS Workshop, KB #6

Common Observation in Crustal Reentry Holes Since 1970's: Downhole Flow of Ocean Bottom Water into Upper Basement

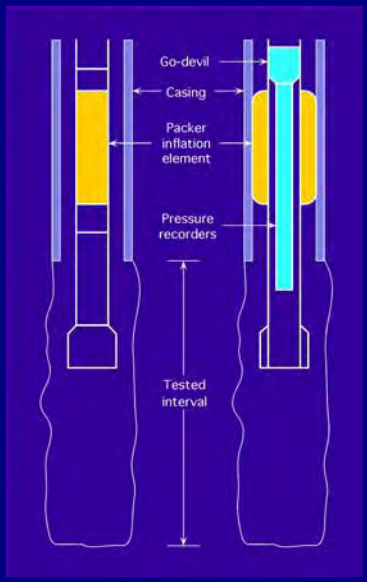
- Downhole flow verified by temperature logs and borehole fluid samples; confounded efforts to sample basement formation fluids.
- Showed oceanic basement is much more permeable than overlying sediments.
- Temperature profiles were interpreted to estimate downhole flow rate and permeability of upper basement zone accepting downhole flow.
- Rarer examples produced basement fluids uphole.



CCS Workshop, KB #7

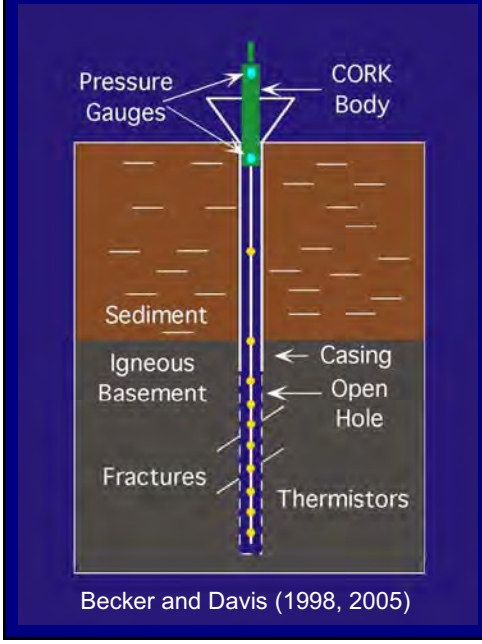
Determining Average Permeability of Upper Oceanic Basement with Drillstring Packer

- Inflatable packer seals the hole, then allows average permeability of isolated formation to be assessed by monitoring pressures during controlled pumping of seawater from rig floor into the formation.
- Early results indicated upper few hundred m of upper oceanic basement is several orders of magnitude more permeable than overlying sediments or deeper basement.
- Provided reference crustal permeability profile used in numerical models of hydrothermal circulation.
- Permeable, porous uppermost basement ≈ seismic Layer 2A.
- Became routine capability in ODP/IODP upper crustal holes - but not yet applied in subseafloor ultramafics.



CCS Workshop, KB #8

Post-1990: ODP CORK Hydrogeological Observatory



Becker and Davis (1998, 2005)

Motivation: Seal reentry holes to prevent hydrological perturbation and allow reestablishment of in-situ conditions, with capabilities for:

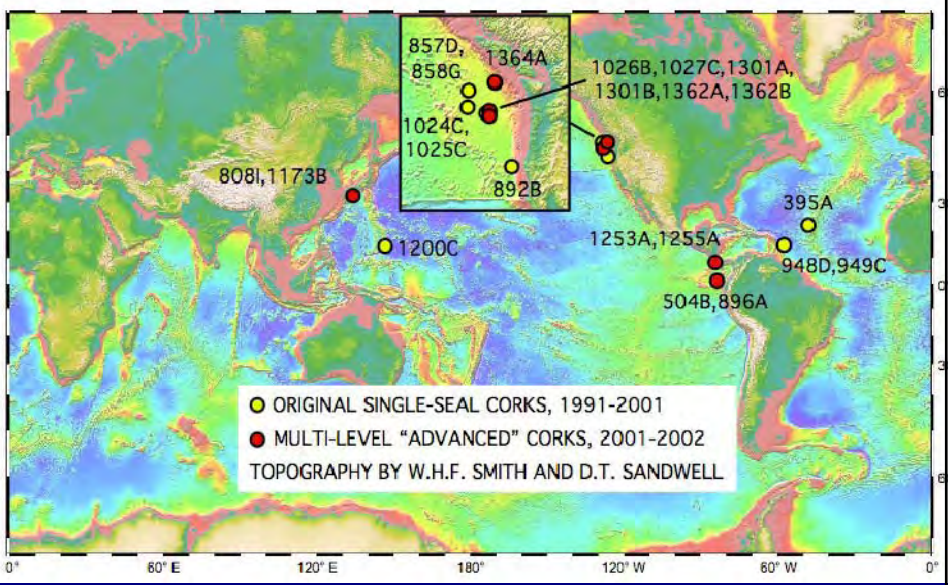
- Long-term monitoring of T & P for
- Background in-situ values
- Hydrologic transients
- Subsurface tidal loading effects
- Transients of tectonic origin
- Sampling of formation fluids
- Active hydrologic formation testing
- In situ microbiological experiments
- Future: carbonation experiments?

Successful CORK monitoring requires a natural cap rock - as for CS monitoring?

>25 installed since 1991 in sedimented ocean crust and subduction settings.

CCS Workshop, KB #9

ODP/IODP CORK Installations, 1991-2010



CCS Workshop, KB #10

Hole 395A and CORK in 2001

Hole 1026B and CORK-II in 2008

Photos from DSV ALVIN

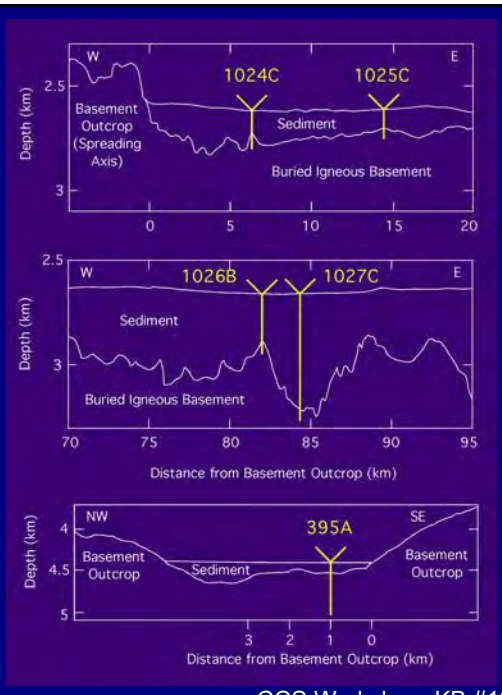
Female Graneledone Pacifica guarding pressure data logger

CCS Workshop, KB #11

Ridge-flank CORKs

near JFR, CRR, and MAR record nearly hydrostatic formation pressures and locally isothermal upper basement temperatures even at paired sites where there are large variations in sediment thickness.

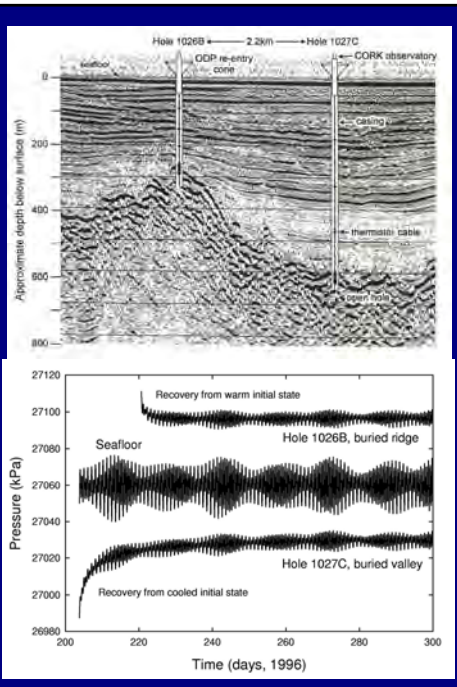
- This requires high rates of lateral fluid flow in basement and very high formation permeabilities.
- Prior to CORKing, ridge-flank holes in sedimented basement highs produced warm fluids while holes in sedimented basins drew cold bottom water into oceanic basement.



CCS Workshop, KB #12

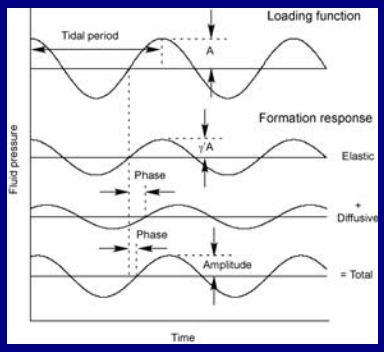
Paired CORKs in 3.4 Ma crust on east flank of Juan de Fuca Ridge with active off-axis hydrothermal circulation

CORK data resolved the small pressure differentials associated with the circulation system. Young oceanic crust is very transmissive (permeable), so even these small differentials drive very large fluid fluxes.

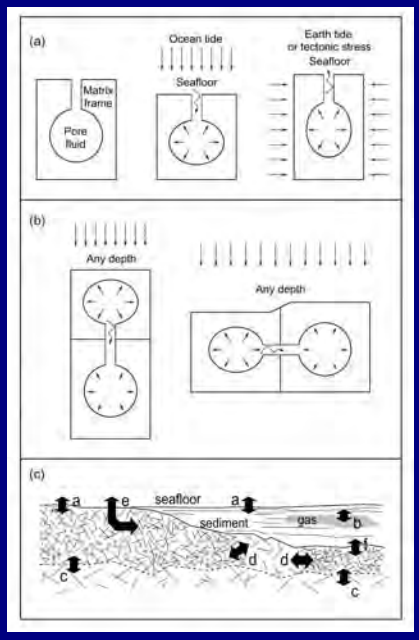


CCS Workshop, KB #13

CORKs Record Formation Pressure Response to Seafloor Tidal Loading



Response in formation pore pressures is a combination of elastic and diffusive components.
- Instantaneous elastic response depends on loading efficiency γ, a function of the elastic parameters of the fluid, solid, and matrix.
- Diffusive response depends on hydraulic diffusivity, a function of permeability, viscosity, storage coefficient.

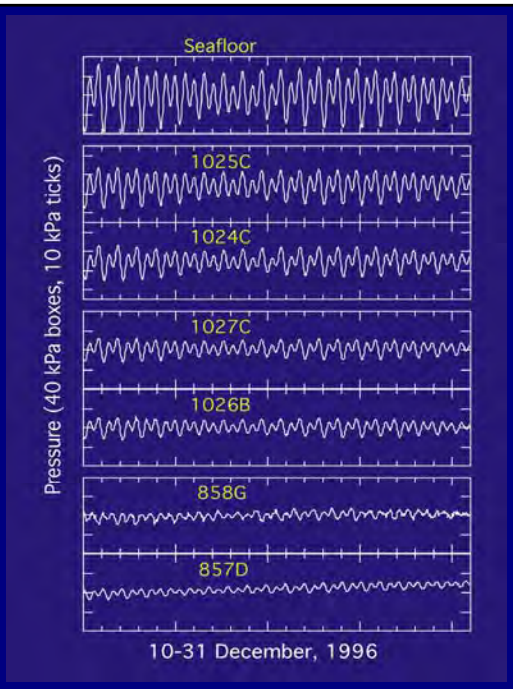


CCS Workshop, KB #14

Attenuation of Seafloor Tidal Loading Signals Recorded in 6 NE Pacific CORKs

These records also show differences in phase, allowing the elastic parameters and hydraulic diffusivity along the propagation pathway to be estimated.

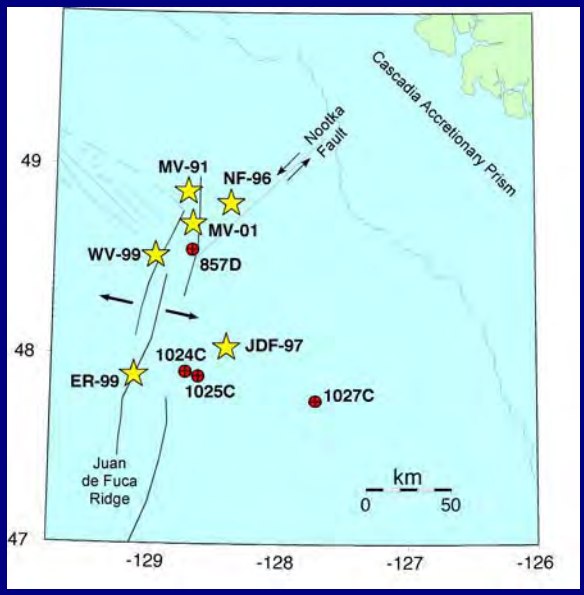
If the formation properties change with time (e.g., under influence of carbonation), then the phase/attenuation will change and the change can be monitored.



CCS Workshop, KB #15

Subseafloor Pressure Transients from Tectonic Strain Loads

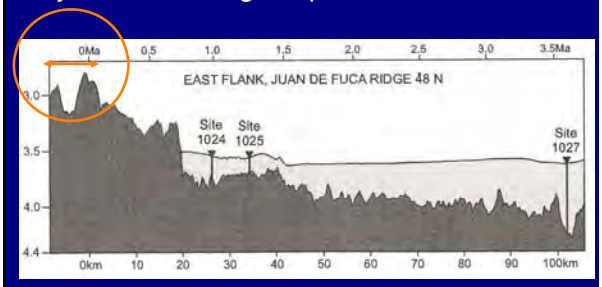
After the tidal loading signals are filtered from the CORK formation pressure records, other signals are evident. These include responses to strain-induced loads at the times of regional earthquakes. See Davis et al, JGR, 2001.



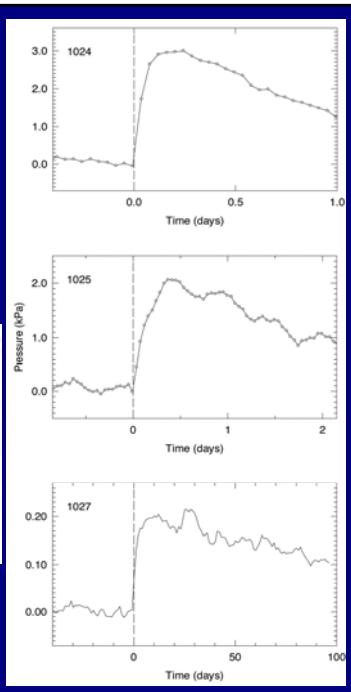
CCS Workshop, KB #16

Examples of strain signals:

Co-seismic strain recorded at Juan de Fuca ridge flank CORKs associated with June 1999 extensional event at the spreading axis - successfully simulated with an elastic dislocation model followed by lateral drainage of pressurized fluids.



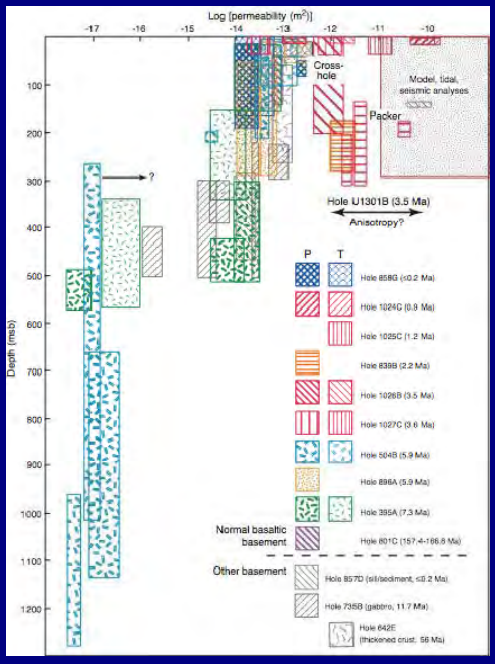
The long-period hydrologic recovery allows estimate of formation permeability at scales of many km's.



CCS Workshop, KB #17

Summary of Permeability Results from Upper Oceanic Crust

- Scales are 10^{-18} to 10^{-10} m^2 and 0-1300 m into basement
- 10^{-12} m^2 = 1 Darcy (a desirable value for aquifers/reservoirs)
- Upper few hundred m of upper oceanic basement is several orders of magnitude more permeable than overlying sediments or deeper basement.
- Highest values are in very young crust and/or likely fault zones.
- No values yet from ultramafics - but it might be predicted that matrix is relatively impermeable so that fault-controlled permeability will be dominant



CCS Workshop, KB #18

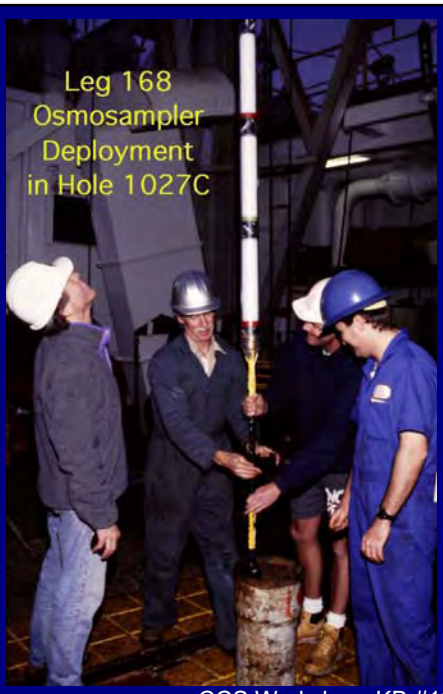
Fluid Sampling via CORKs

- Original CORKs used 1/2" teflon tubing from formation to wellhead valves, but this did not work well.

- A major improvement was development of self-contained OsmoSamplers installed on the sensor string and recovered years later.

- The latest multi-zone "CORK-II" and "L-CORK" designs incorporate capability to deploy OsmoSamplers for fluid geochemical and microbiological objectives both (1) deep in sealed holes and (2) at wellhead valves with access to in-situ fluids via small-diameter tubing.

- These features should be adaptable for CCS monitoring.

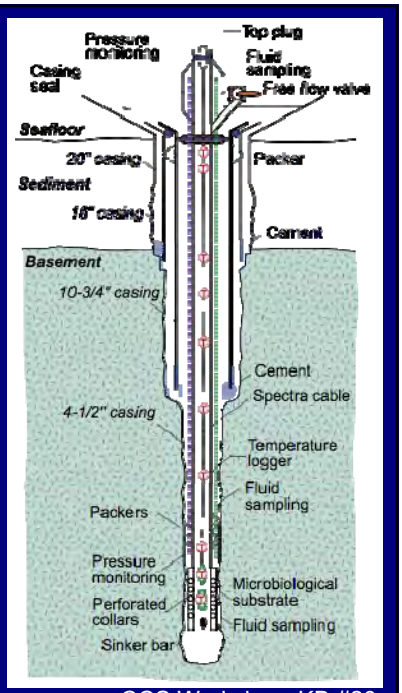


CCS Workshop, KB #19

Latest "L-CORK" system as on IODP Exp. 327 (2010)

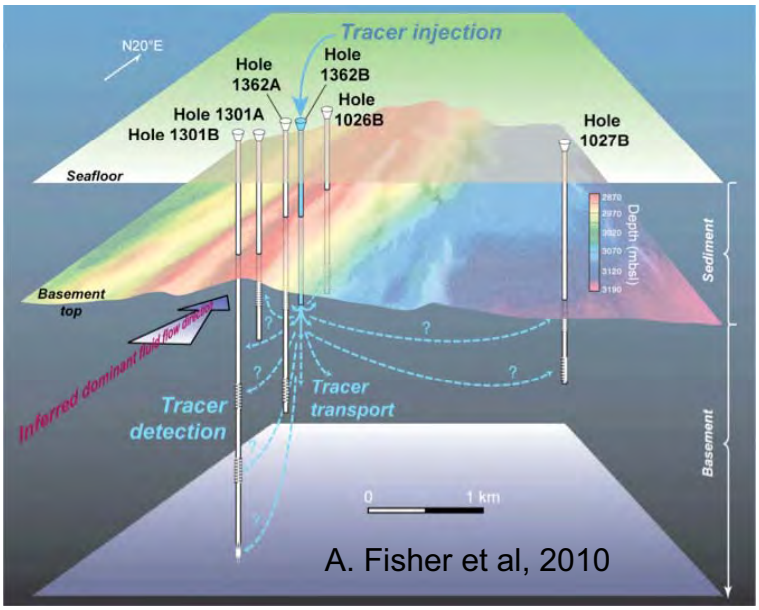
Fisher et al (in press)

- Four nested casing strings
- Multiple sealing systems
- Multiple monitoring levels with packers
- Tubing umbilical extends from seafloor to depth, to bring fluids and pressure signals to surface gauges
- Sensors/samplers suspended in hole:
- Memory temperature loggers
- Fluid/gas "OsmoSamplers"
- Microbiological experiments
- CO_2-related monitors in future?
- "L" refers to 4"-dia. "lateral" free-flow valve - intended for producing formation fluids but could also be adapted for pumping large quantities of liquid CO_2



CCS Workshop, KB #20

CORK-to-CORK Tracer Injection Experiments Started in 2010 - a site opportunity for prototype CCS experiments?



A. Fisher et al, 2010

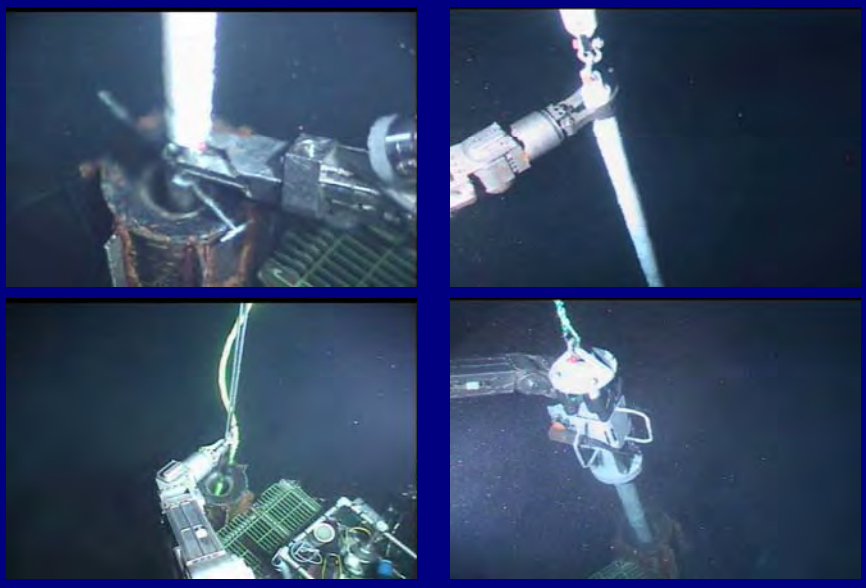
CORKs: Submersible Support from National Funding Agencies (e.g., NSF, JAMSTEC,…)

CORKs require submersible servicing on ~2-3 yr intervals (data download, battery or instrument exchanges).

- Alvin: 1991, 1993, 1994, 1995, 1997-2002, 2004-2009
- ROPOS: 1992, 2004
- Nautile: 1995, 1998
- Jason/Jason II: 1998, 2003, 2010, 2011
- MPL Control Vehicle: 1999, 2001
- Kaiko-10k: 2002, 2003
- Kaiko-7k: 2006-2009, 2011
- HyperDophin, 2009
- Shinkai 6500: 2004

CCS Workshop, KB #21

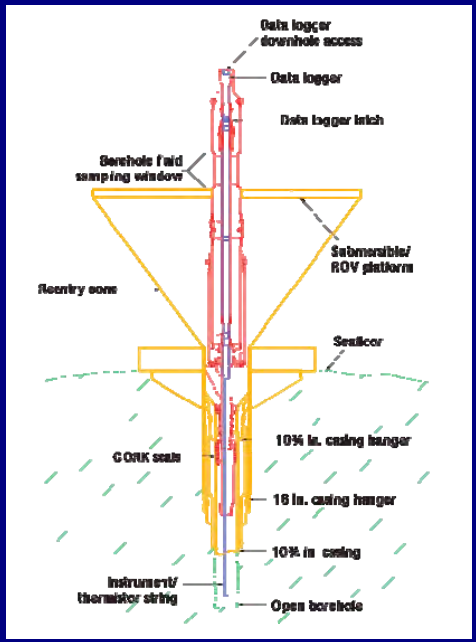
Inserting ~200-m osmosampler/thermistor string in Hole 1026B using DSV ALVIN, 2008



CCS Workshop, KB #22

CORK Funding Model

- Red/orange = CORK 'infrastructure' funded by ODP/IODP
- Blue = CORK scientific instrumentation funded by national agencies (e.g., NSF) based on regular research proposals
- Submersible servicing operations (expensive!) also require funding from national agencies based on research proposals.
- Extra funding requires extra work by proponents - but outside funding represents an opportunity to leverage actual scheduling of IODP operations.



CCS Workshop, KB #23

Selective Update on post-2013 IODP

- IODP SAS Executive Committee (SASEC) and Int'l Working Group (IWG+) will meet Jan 18-21 to finalize many aspects.
- Acronym IODP is expected to be retained - but redefined as International Ocean Discovery Program.
- A streamlined proposal evaluation process and simpler Science Advisory Structure will be implemented starting mid-2011.
- First proposals for post-2013 IODP to be submitted for Oct 1 2011.
- Strong proposals are expected to be forwarded relatively quickly for implementation.
- Societal and agency priorities for IODP may be emphasized more for post-2013 program (e.g., CCS?).
- Community workshops are expected to play a more significant role in defining and producing priority IODP proposals - a clear opportunity for this CCS Workshop.

CCS Workshop, KB #24

8. J. Matter – LDEO, USA.

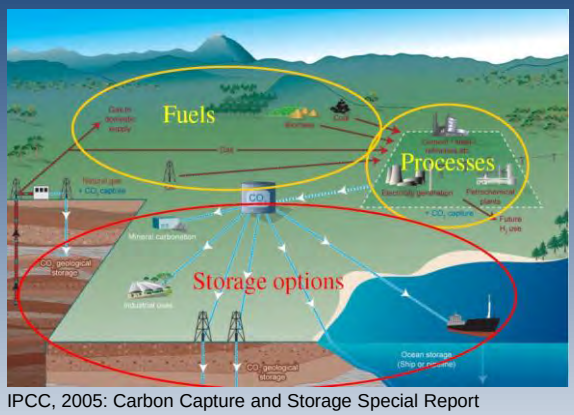
Monitoring, Verification & Accounting (MVA)

Jürg M. Matter
Lamont-Doherty Earth Observatory, Columbia University
New York

Muscat, Sultanate of Oman
January 8, 2011

Lamont-Doherty Earth Observatory
COLUMBIA UNIVERSITY | EARTH INSTITUTE

Carbon Capture and Storage



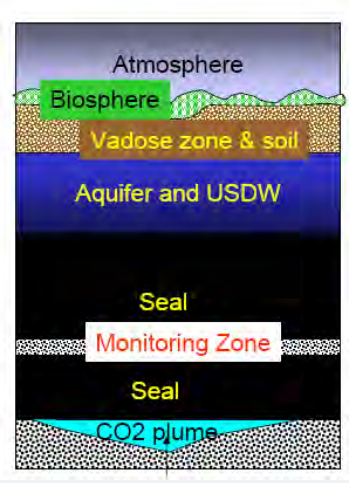
IPCC, 2005: Carbon Capture and Storage Special Report

Capture → **Transport** → **Injection Storage** → **MVA**

Challenges

- ❑ Permanence of CO_2 storage
- ❑ Integrated CCS Projects
- ❑ Monitoring, verification and accounting of CO_2 storage

Monitoring Zones



Source: S. Hovorka (BEG)

- Atmosphere
- Biosphere
- Soil and vadose zone
- Aquifer and USDW
- Formation above injection zone
- Injection zone – CO_2 plume

Purpose of MVA

- tracking the CO_2 plume in the subsurface
- **evaluate CO_2-fluid-rock interactions**
- ensuring that injection, observation and abandon wells are not leaking
- evaluate and monitor mitigation efforts in case of leakage
- verify quantity of injected CO_2
- ensure that ground water resources and ecosystems are protected
- ensure human health and safety
- provide data to calibrate and validate numerical models of CO_2 storage

Why is MVA Needed?

- Health, safety, and environmental concerns
- Reservoir economics (ECBM, EOR, EGR)
- Required by regulators
- Credits/emissions trading/liability reduction
- Research objectives
- Public acceptance

– How does the public know that a project is safe?

– How do investors know that a project is effective?

MVA Approach

- There is no single approach and technique

-> all is site specific

- Develop a tailored MVA program, which is specific to each site
- Use multiple techniques to monitor CO_2 storage
- Extent of MVA program will depend on injection volumes, duration of project phases, potential risks for migration and leakage.

Monitoring Phases

1. **Pre-Operation Phase:** Baseline conditions, geological characterization, risk assessment
2. **Operation Phase:** CO_2 injection
3. **Closure Phase:** Abandoning and plugging of wells, site restoration
4. **Post-closure Phase:** Ongoing monitoring to demonstrate successful performance and safety

Atmospheric Monitoring

Objectives	Primary Technologies	Secondary Technologies	Additional Technologies
Ambient CO_2 concentration CO_2 surface flux		CO_2 detectors Laser systems, LIDAR*	Eddy Covariance (surface flux) Advanced Leak Detection System Isotopes

*LIDAR(Light Detection and Ranging): Optical remote sensing technology. Aircraft based LIDAR and GPS can be used to measure uplift and produce extremely accurate elevation models.

Source: U.S. Department of Energy / NETL, Monitoring, Verification and Accounting of CO2 stored in deep geologic formations. Best Practice Manual (2009)

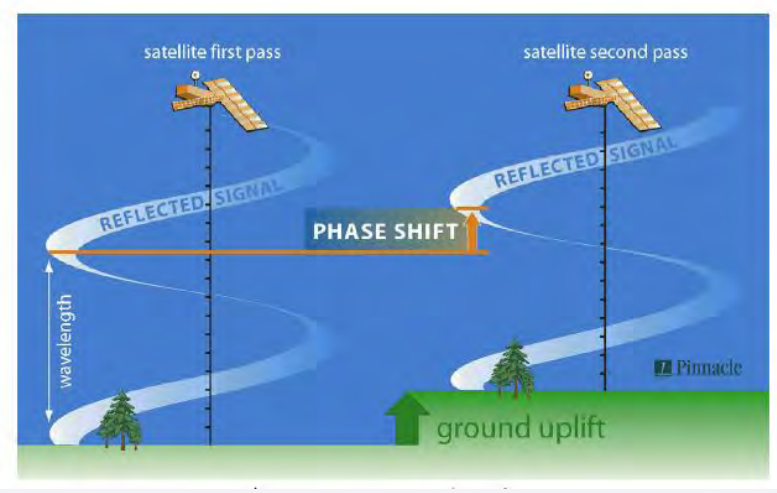
Near-Surface Monitoring

Objectives	Primary Technologies	Secondary Technologies	Additional Technologies
Groundwater monitoring Soil gas monitoring Crustal deformation Leak detection Vegetative Stress	Geochemical analysis	Isotope analysis Aerial photography Shallow 2-D seismic Soil gas sampling Flux chambers	Noble gases Perfluorocarbons Geophysics: Conductivity Tiltmeters Remote Sensing – InSar*

*InSar (Interferometry for Synthetic Aperture Radar): detect ground motion with millimetric exactness using radar satellite images

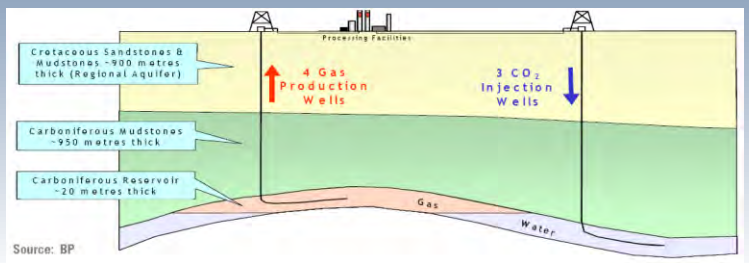
Source: U.S. Department of Energy / NETL, Monitoring, Verification and Accounting of CO2 stored in deep geologic formations. Best Practice Manual (2009)

InSar (Interferometry for Synthetic Aperture Radar)

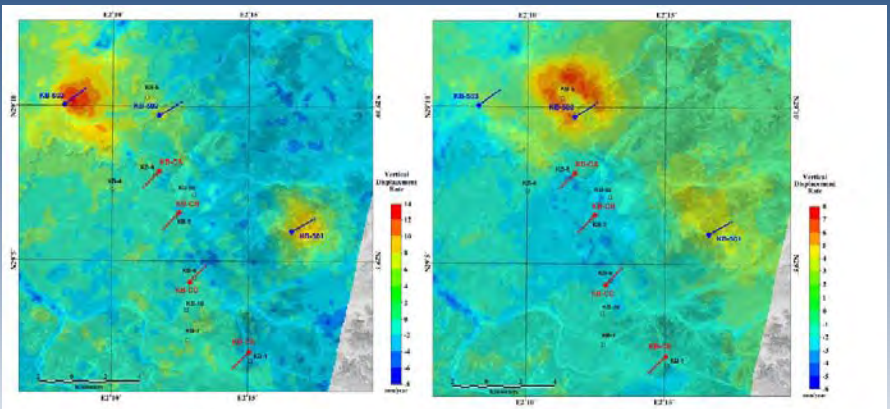


Source: McColpin, 2009

In Salah (Algeria)



Vertical Heave Rate 7mm/yr



(a) (b)

Figure 3. Vertical displacement rates detected by DInSAR stacking of terms (a) from 2004/7/31 to 2005/9/24, and (b) from 2005/9/24 to 2008/5/31. Note the upheaval rate changes around KB-502 and KB-503 before and after 2005/9/24.

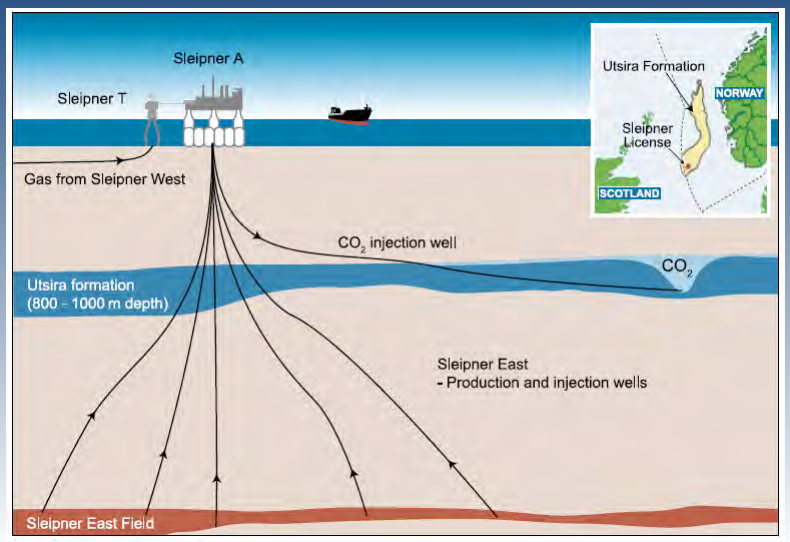
Source: Onuma & Ohkawa, 2009

Subsurface Monitoring

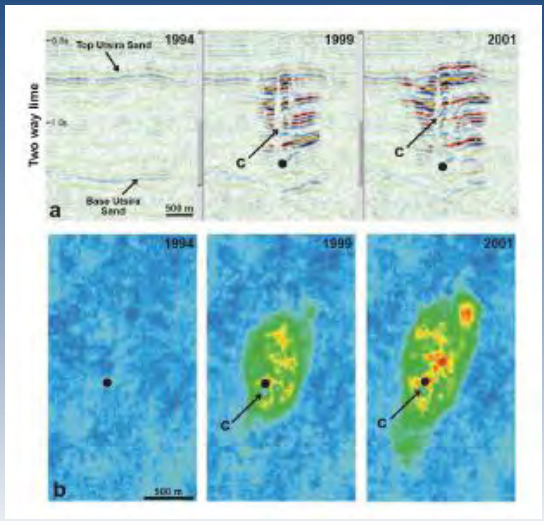
Objectives	Primary Technologies	Secondary Technologies	Additional Technologies
Groundwater monitoring Soil gas monitoring Leak detection Subsurface reservoir characterization Plume tracking Well integrity test	Injection Fluid Monitoring Formation Fluid Monitoring Core collection Wireline Logging: T, noise, cement bond, density, gamma ray, sonic Physical Testing: Annulus pressure Injection volume/rate Wellhead P Reservoir P/T	Seismic Surveying: Acoustic (2D,3D) VSP Geochemistry: Brine/Fluid Chemistry Tracer Injection Wireline logging: Temperature log Reservoir saturation logs Optical logs	Geophysical: Crosswell seismic Microseismic Resistivity Time-lapse Gravity

Source: U.S. Department of Energy / NETL, Monitoring, Verification and Accounting of CO2 stored in deep geologic formations. Best Practice Manual (2009)

Sleipner CO_2 Storage Project



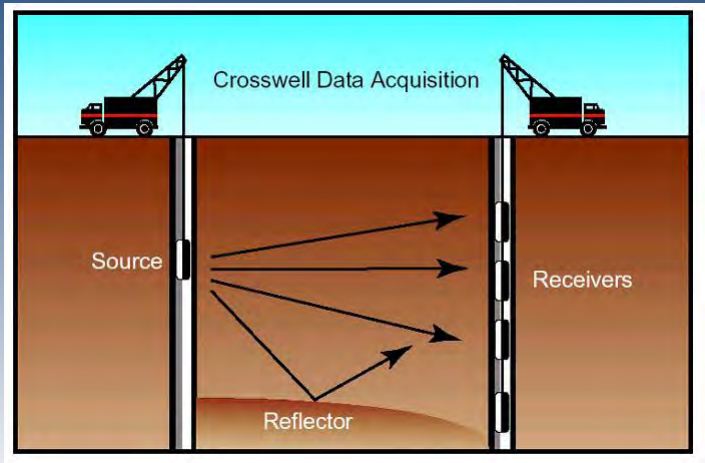
Surface Seismic Survey - Sleipner



- Semi-quantitative, no CO_2 mass balance
- Dissolution/mineral trapping monitoring not possible

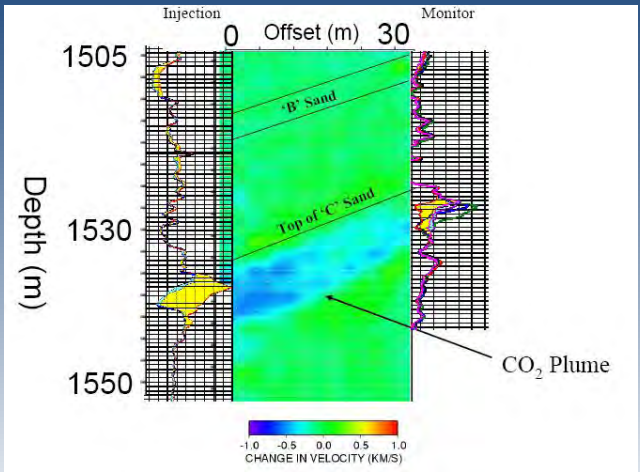
Source: Arts et al. 2004

Crosswell Seismic Survey



Source: Harris & Langan, Geophysical Corner

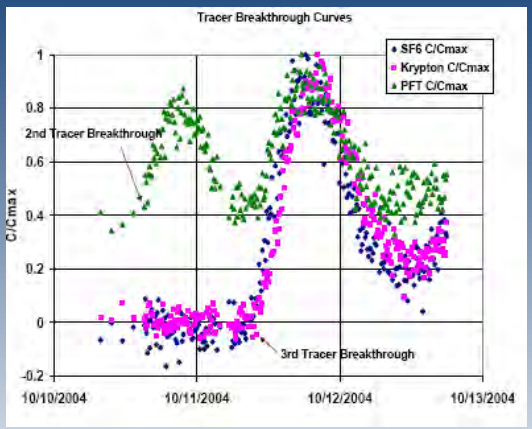
Crosswell Seismic Survey



- High resolution but smaller sample volume
- No mass balance and dissolution/mineral trapping monitoring not possible

Source: Daley et al. 2005

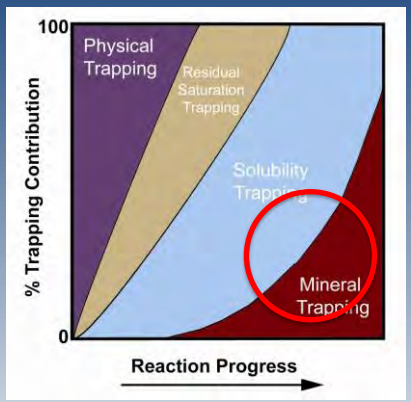
Tracers



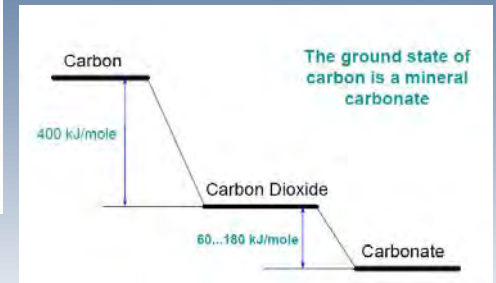
- requires well penetration and perforation, sampling apparatus
- labor intensive
- only technique to monitor solubility/mineral trapping
- plume tracking possible
- leakage detection possible

Source: Freifeld et al. (LBNL)

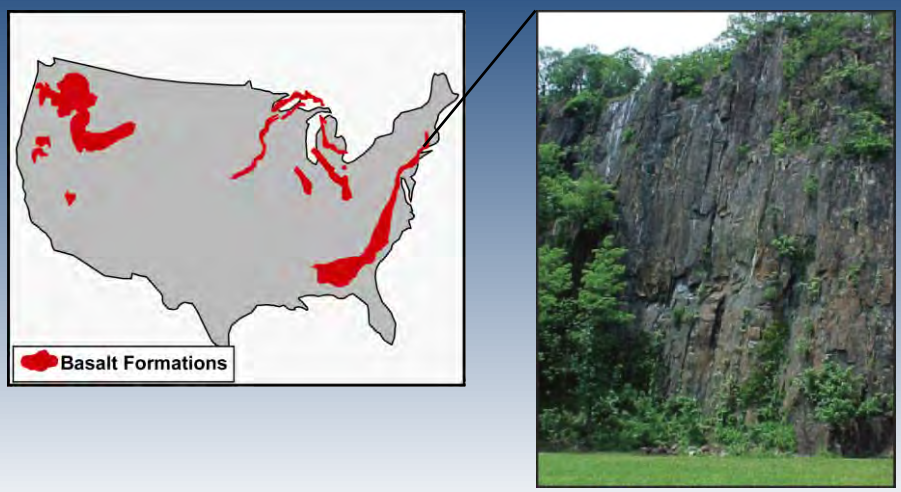
Permanent Storage – Mineral Carbonation



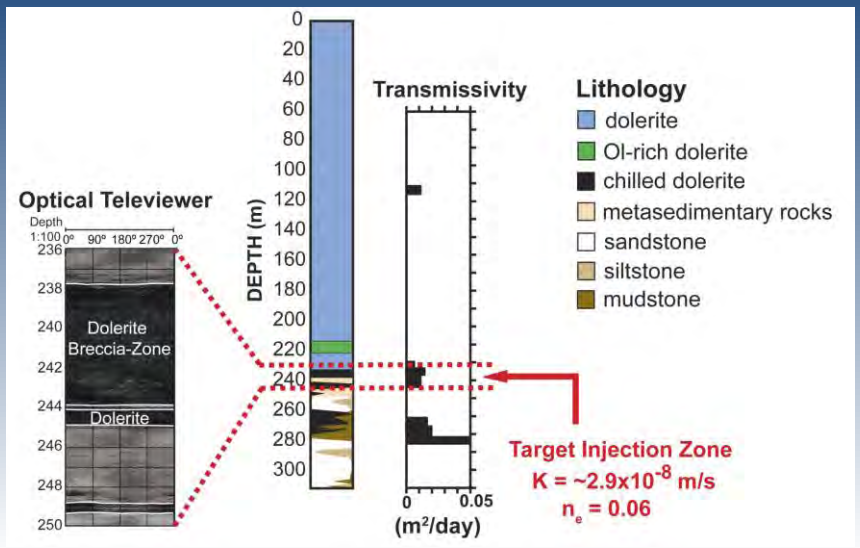
Modified from : IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage.



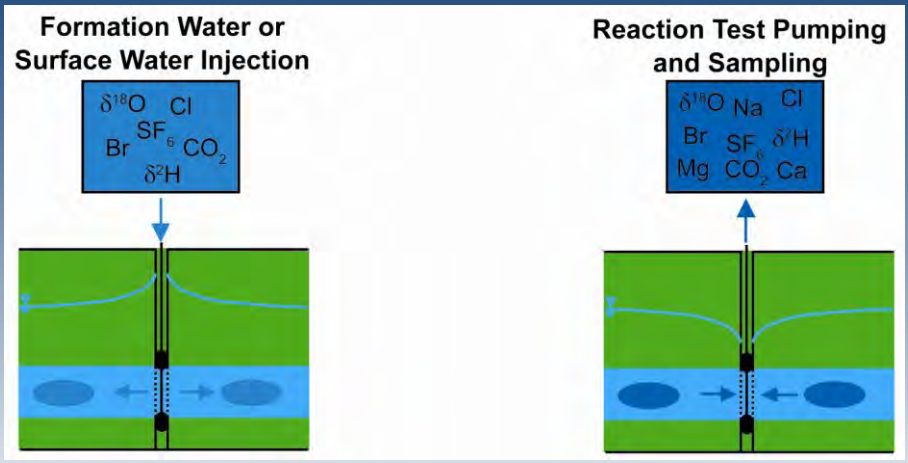
Palisades Sill – Newark Basins



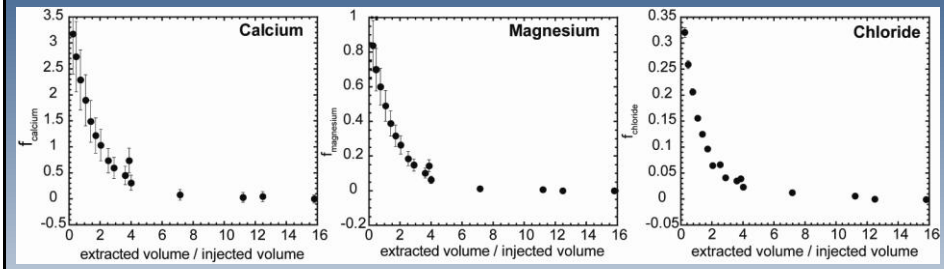
CO_2 Injection Zone



Single Well Push-Pull Test



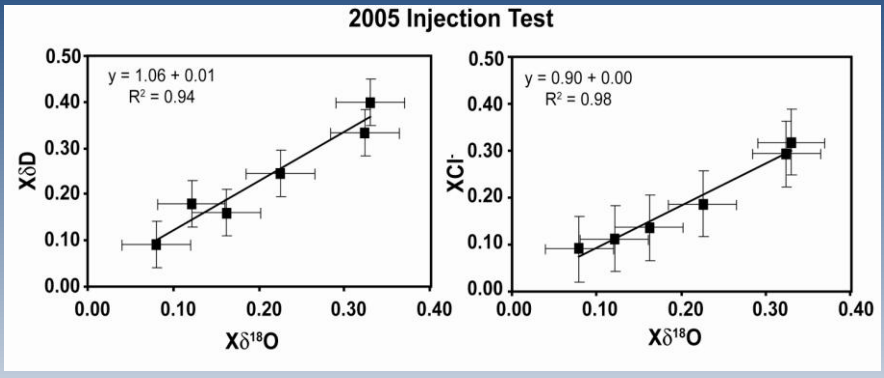
Breakthrough Curves



$$f_i = (C_{measured} - C_{background}) / (C_{injected})$$

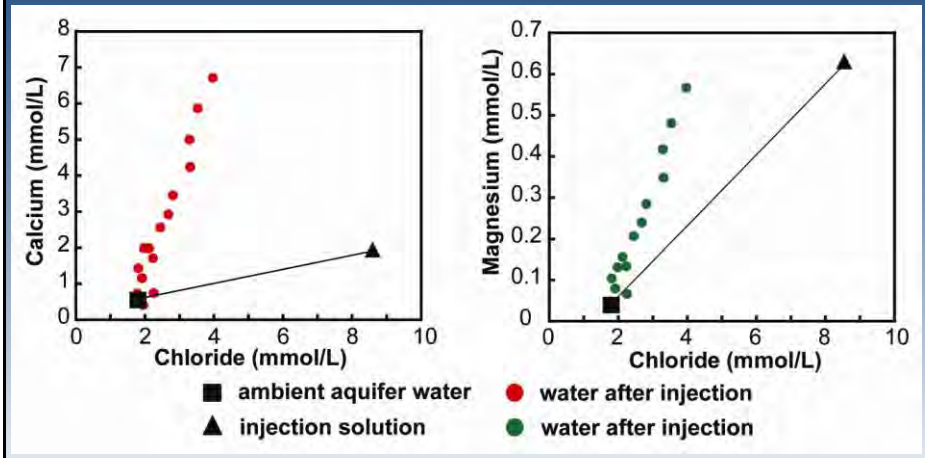
Matter et al. 2007, G[3]

Mixing



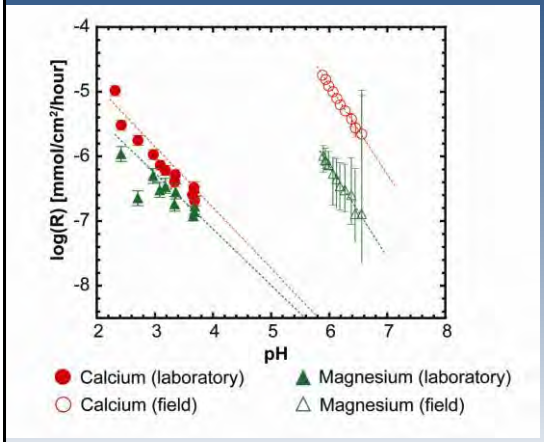
$$[\text{Tracer}]_{\text{ext water}} = X\,[\text{Tracer}]_{\text{IW}} + (1\text{-}X)\,[\text{Tracer}]_{\text{BW}}$$

Water-Rock Reaction



Matter et al. 2007, G³

Dissolution Rates



Matter et al. 2007, G³

$$R = C_{react}(t) \cdot V_{pumped}(t) / t_r \cdot A$$

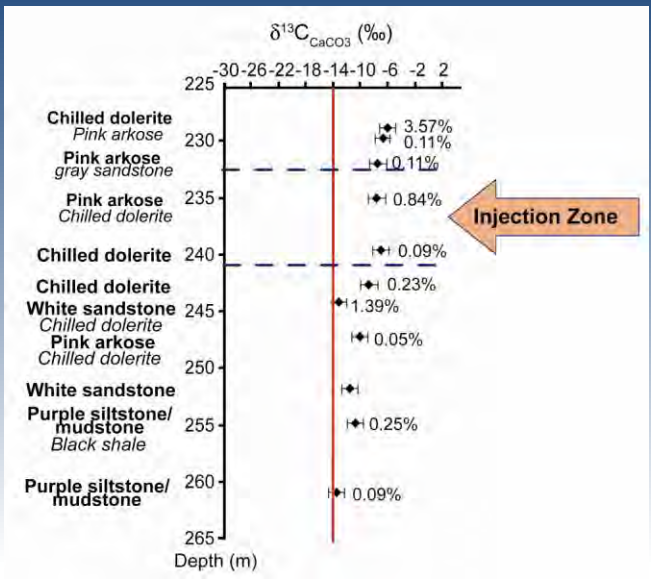
- Ca-release rate 9x10^{-6} mmol/cm^2/h

-> 0.08 g/m^2/day

- Mg-release rate 5x10^{-7} mmol/cm^2/h

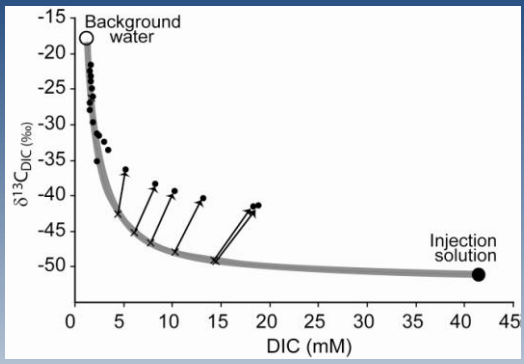
-> 0.003 g/m^2/day

Calcium Source



Assayag et al., Chemical Geology, 265 (2009)Ari

Carbon Isotope Tracer



$$\delta^{13}C_{mix} = \left[\frac{DIC_{IW}\cdot\delta^{13}C_{IW} - DIC_{BW}\cdot\delta^{13}C_{BW}}{DIC_{IW} - DIC_{BW}}\right] + \left[\frac{DIC_{BW}\cdot DIC_{IW}\left(\delta^{13}C_{BW} - \delta^{13}C_{IW}\right)}{DIC_{mix}\left(DIC_{IW} - DIC_{BW}\right)}\right]$$

$$\delta^{13}C_{DIC-add} = (DIC_{ES}\delta^{13}C_{DIC-ES} - DIC_{mix}\delta^{13}C_{DIC-mix}) / \Delta DIC$$

$\delta^{13}C_{DIC\text{-}add}$ is between -21‰ and -13‰ (±10‰)

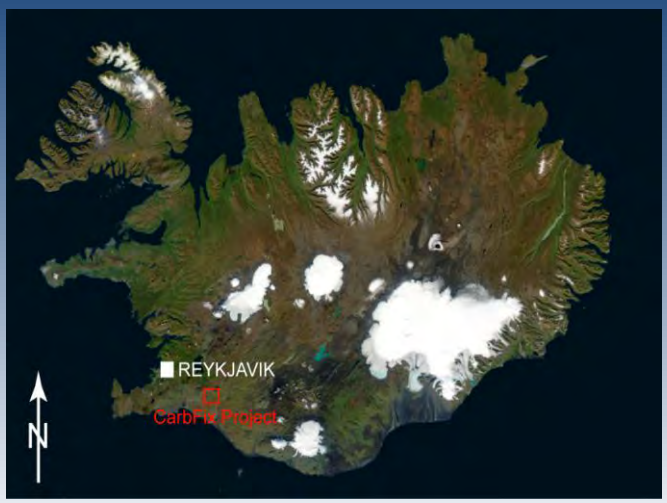
Assayag et al., Chemical Geology, 265 (2009)

Mass Balance of CO_2 Consumption (moles)

	Injected H_2CO_3	Pumped H_2CO_3	Reacted H_2CO_3	H_2CO_3 reacted by mixing	H_2CO_3 reacted by dissolution of carbonates	H_2CO_3 reacted by cation ex-change	H_2CO_3 reacted by silicate dissolution
Mean	53	25	28	**0.7**	**14.8**	**5.9**	**5**
Sigma		5	5	0.25	2	3	4.5

Carbonate Dissolution > Cation Exchange > Ca, Mg Silicate Dissolution > Mixing

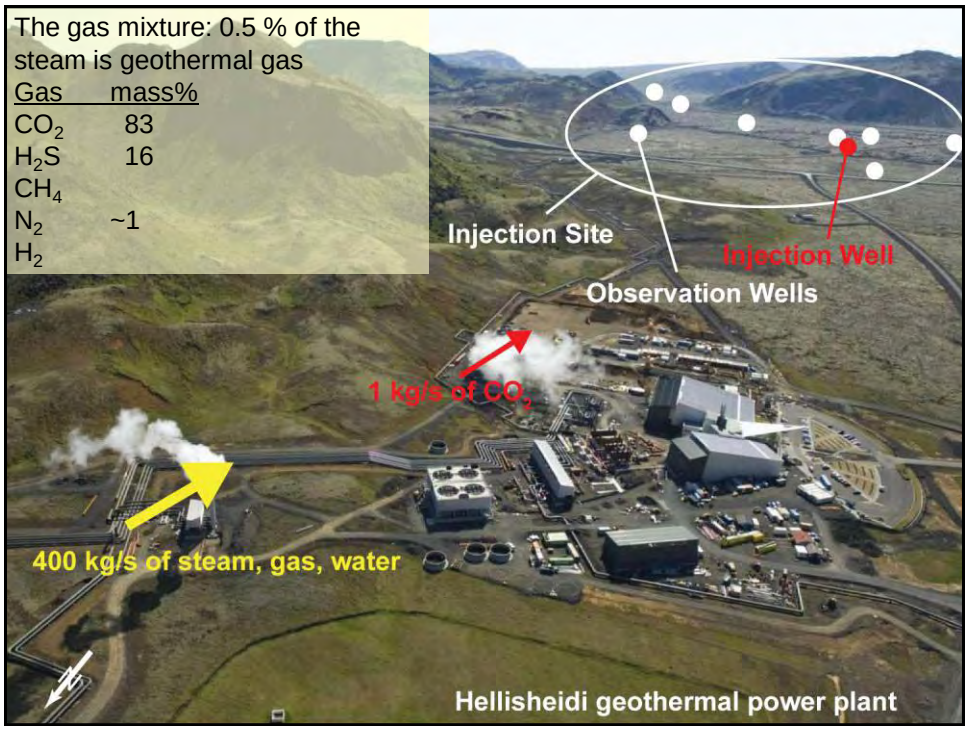
CarbFix Project Iceland



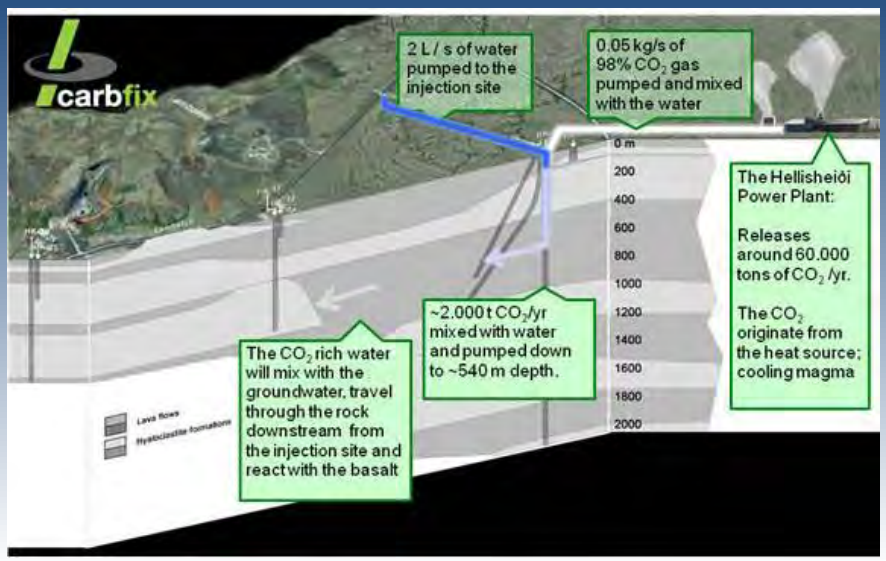
- in situ mineralization in basaltic rocks
- monitoring, verification and accounting of stored CO_2

The gas mixture: 0.5 % of the steam is geothermal gas

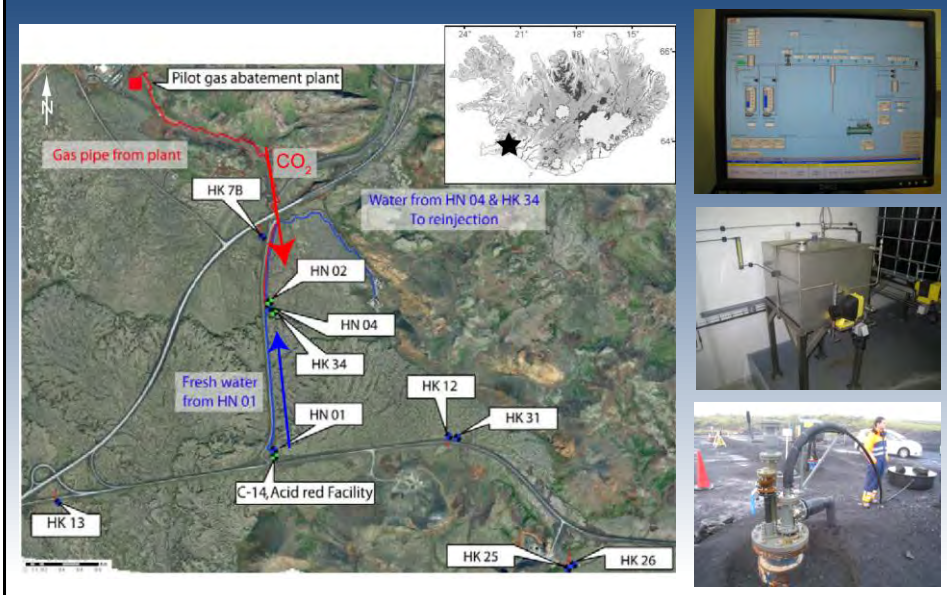
Gas	mass%
CO_2	83
H_2S	16
CH_4	
N_2	~1
H_2	



CarbFix CO_2 Storage Project



CarbFix Test Site - MVA



MVA Needs Quantification

- Distinguish stored CO_2 from natural CO_2 sources

Radiocarbon Tagging Method

➢Labeling the injected CO_2 with an isotopic tracer

$^{12}CO_2$ -> $^{14}CO_2$

Carbon-14 (^{14}C) as a MVA tool

Carbon Isotopes

Stable: ^{12}C - 98.93%

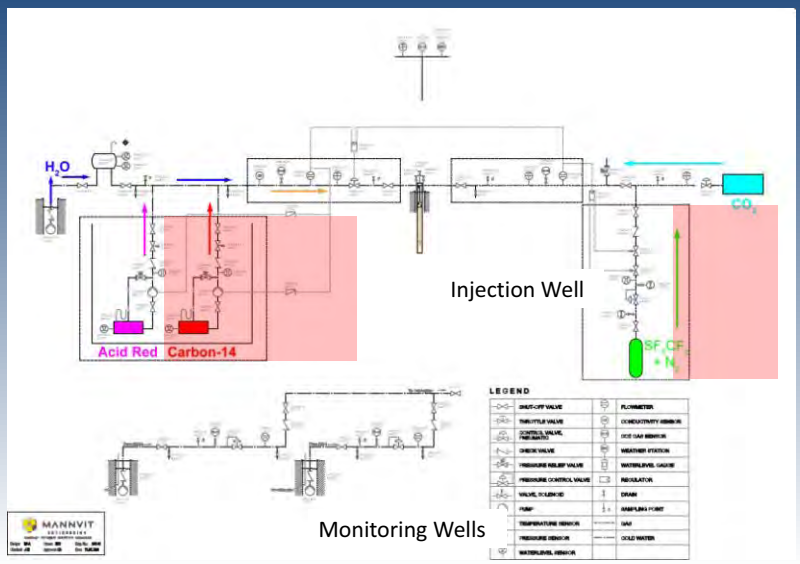
^{13}C - 1.07% $^{13}C/^{12}C = 0.01$

Radioactive: ^{14}C 1ppt $^{14}C/^{12}C = 1.3x10^{-12}$

half-life of about 5730 years

- deep reservoirs have no or very small amounts of ^{14}C
- ^{14}C is a smart tracer for:
  - reaction processes (dissolution – precipitation)
  - biogeochemical processes
  - mixing processes in combination with conservative tracers
  - inventory of stored CO_2
- Tagging of 1Gt CO_2 requires 320 grams of pure ^{14}C

CarbFix MVA Approach



CarbFix CO_2 Injection Test Parameters

- 0.07 kg/s CO_2 over 12 months -> 4.95×10^7 moles of CO_2
- total amount of co-injected water is 6.2×10^7 L
- 20 mCi (7.4×10^8 Bq) injected over 12 months
- [^{14}C]bicarbonate ($NaHCO_3$) in 100 L storage solution (-> for 6 months)
- ^{14}C activity in injected water is 320 PicoCi/L (12 Bq/L)

THANK YOU

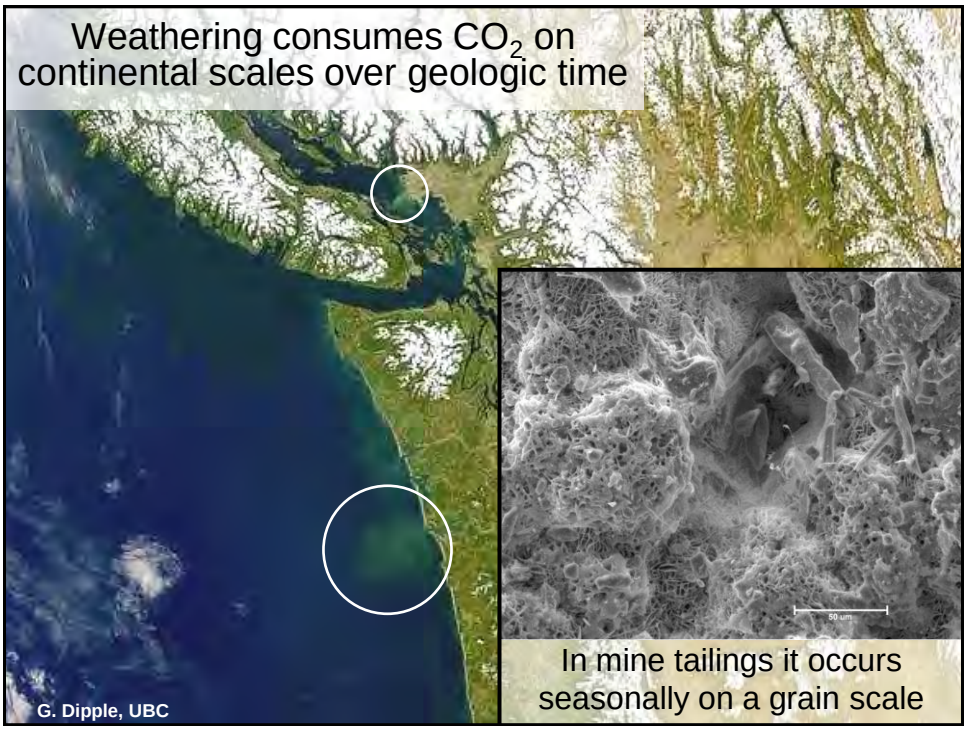
9. G. Dipple- UBC, Canada.

Enhanced weathering and carbon mineralization in mine waste: acceleration potential and implications for carbon sequestration

Greg Dipple, Sasha Wilson, Ian Power, Shaun Barker, Sergio Bea, Uli Mayer, Stewart Fallon, Gordon Southam

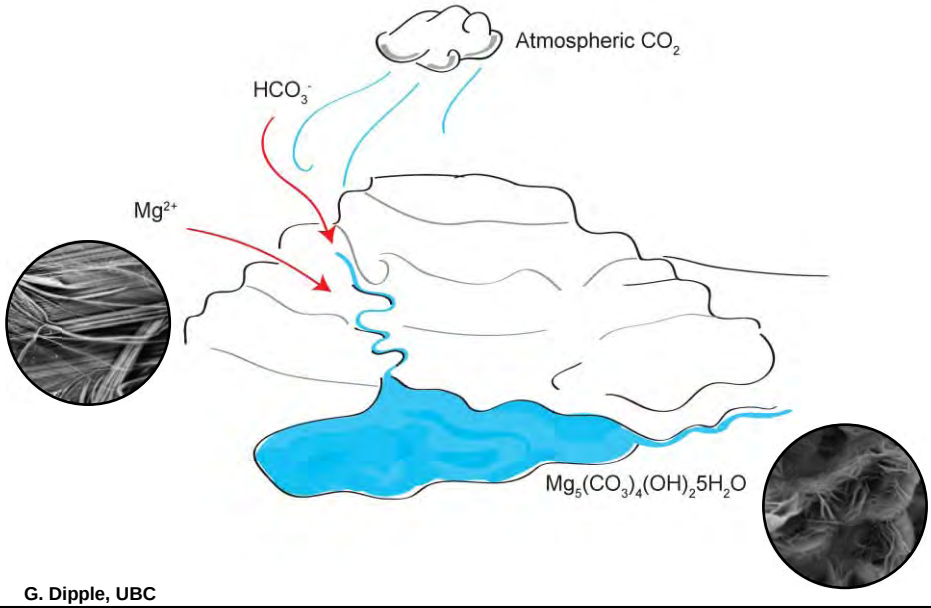
- Atmospheric carbon dioxide is mineralized in some mine tailings
- Fixation rates significant and amenable to acceleration (not dissolution limited, but in some cases CO_2-limited)
- Acceleration could turn some mining operations GHG-neutral, global impact in 100's MTonnes per year.
- Rates are consistent with laboratory mineral dissolution experiments
- CO_2-limited systems may have a distinctive ^{13}C signature.
- Mine tailings are testing grounds for sub-surface carbon storage
  - (scale, complexity, accessibility)

Weathering consumes CO_2 on continental scales over geologic time



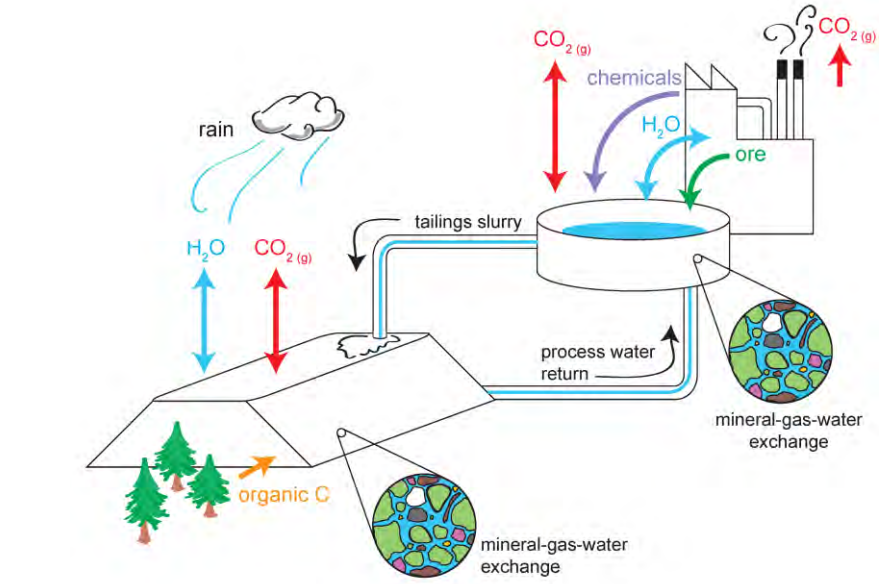
In mine tailings it occurs seasonally on a grain scale

Weathering in Mine Tailings

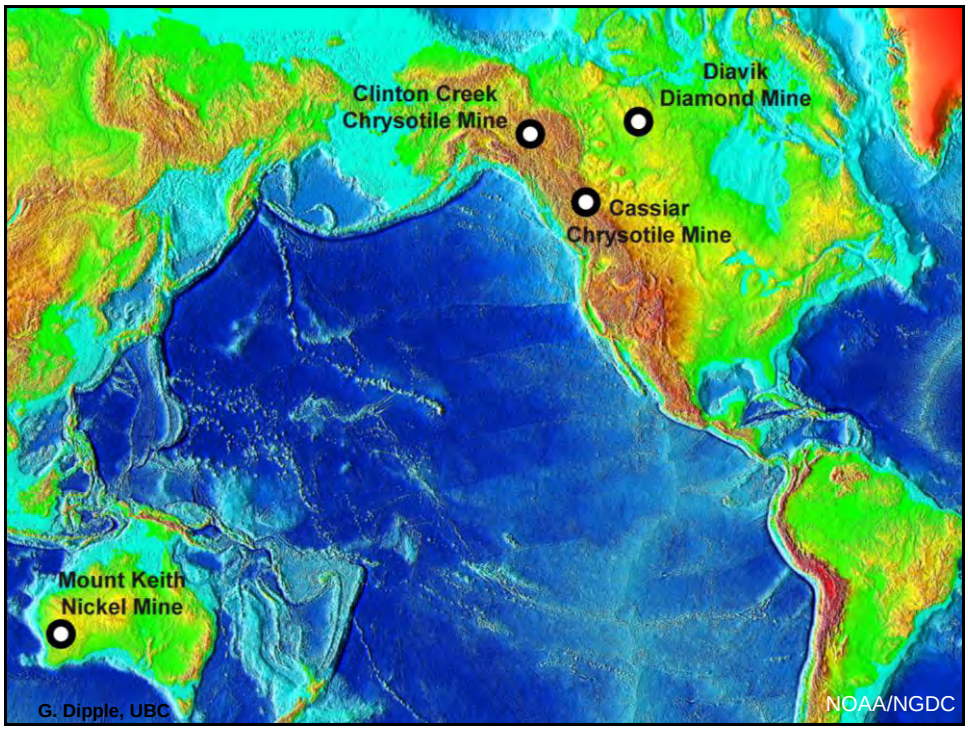


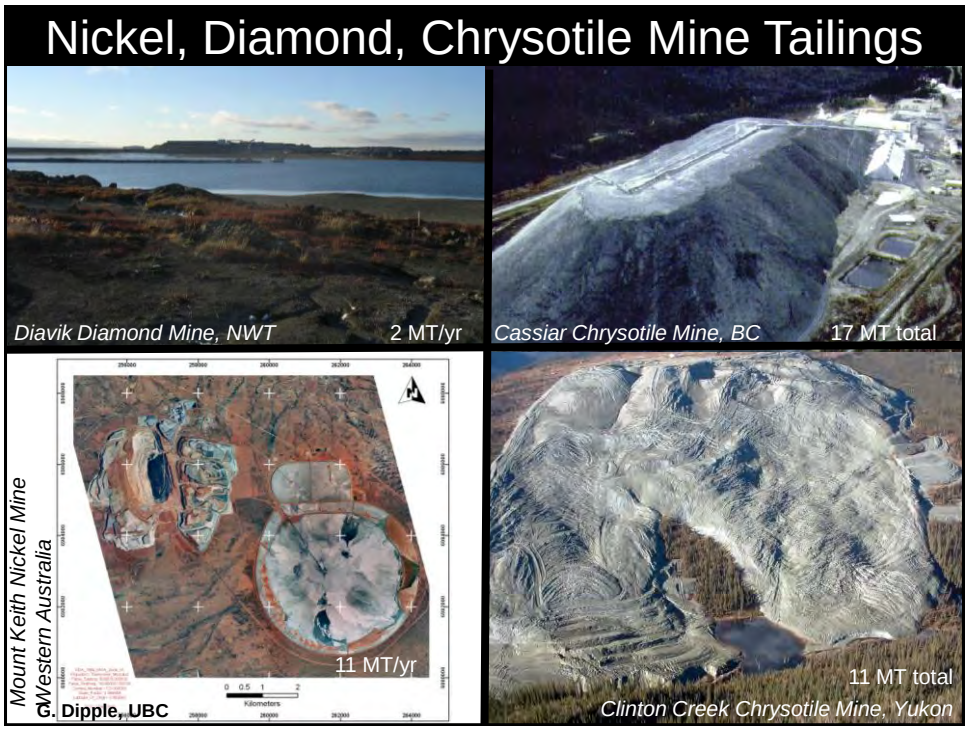
G. Dipple, UBC

Mine Operations Carbon Cycle

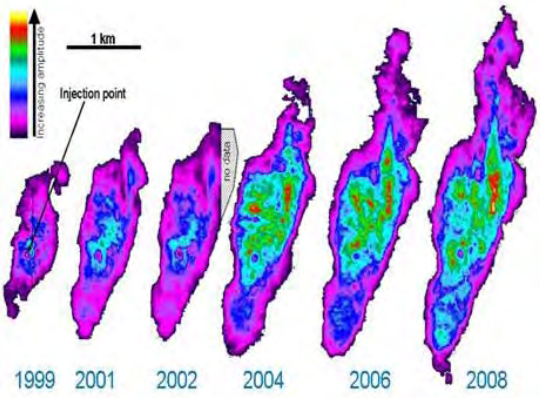


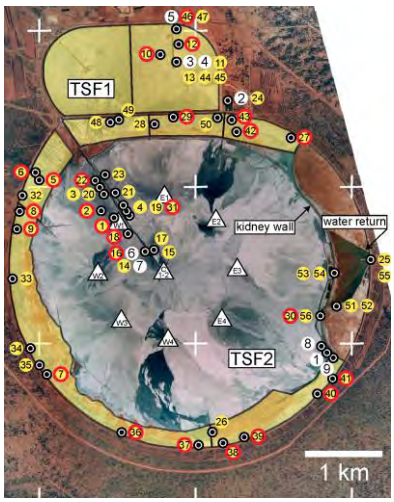
G. Dipple, UBC


Clinton Creek
Chrysotile Mine
Diavik
Diamond Mine
Cassiar
Chrysotile Mine
Mount Keith
Nickel Mine
G. Dipple, UBC
NOAA/NGDC


Nickel, Diamond, Chrysotile Mine Tailings
Diavik Diamond Mine, NWT
2 MT/yr
Cassiar Chrysotile Mine, BC
17 MT total
Mount Keith Nickel Mine
Western Australia
11 MT/yr
G. Dipple, UBC
11 MT total
Clinton Creek Chrysotile Mine, Yukon

Large, Accessible and Naturally Complex

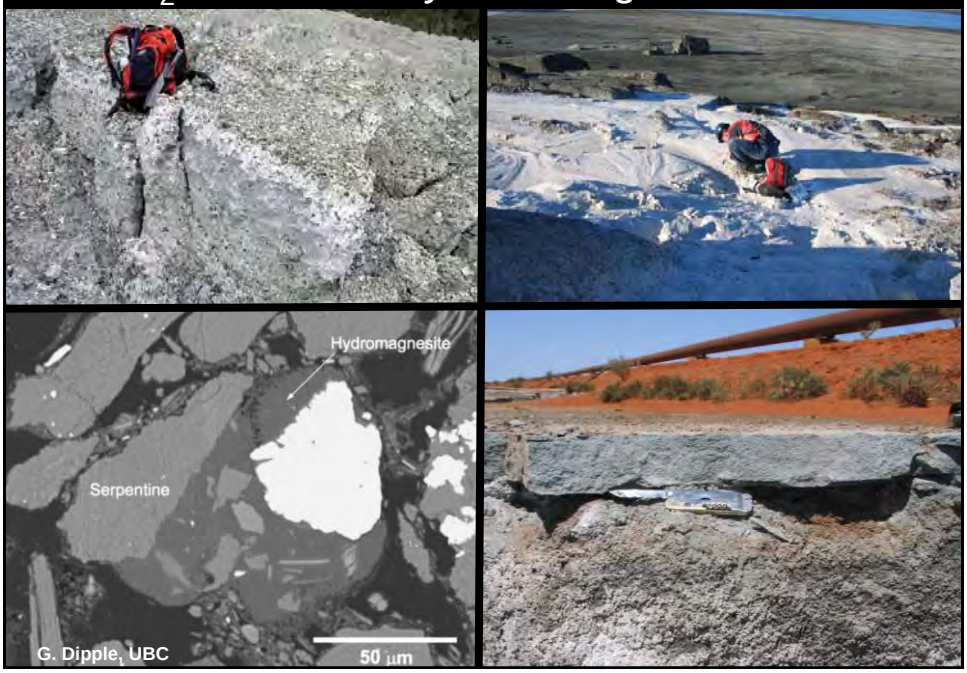


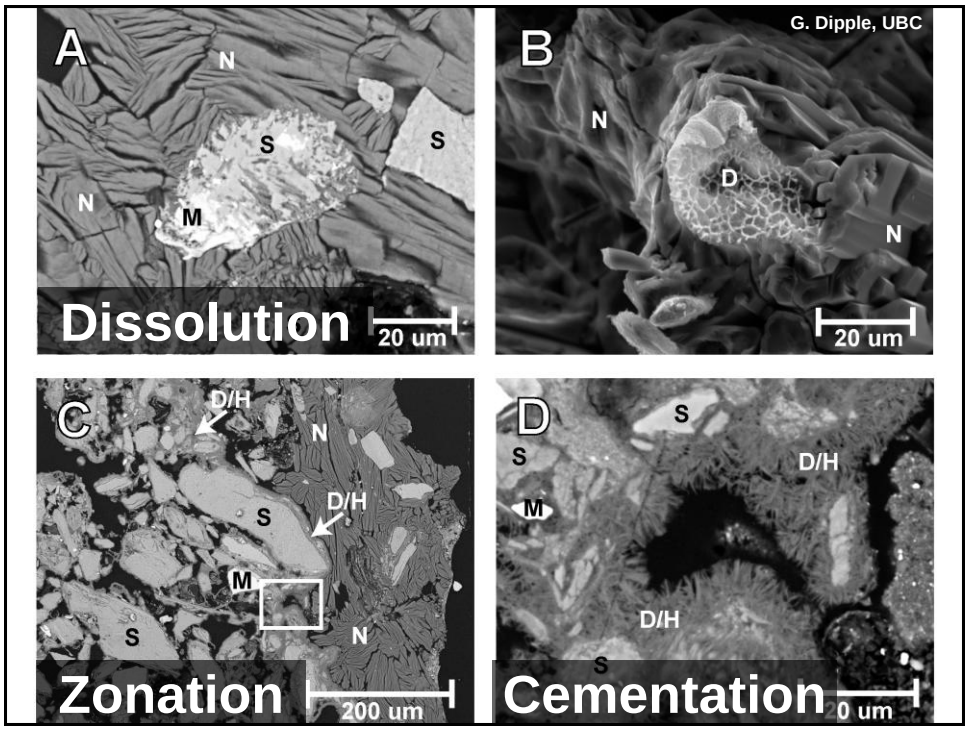


Statoil Sleipner plume: www.geoexpro.com

G. Dipple, UBC

CO_2 Fixation in Hydrated Mg-Carbonates



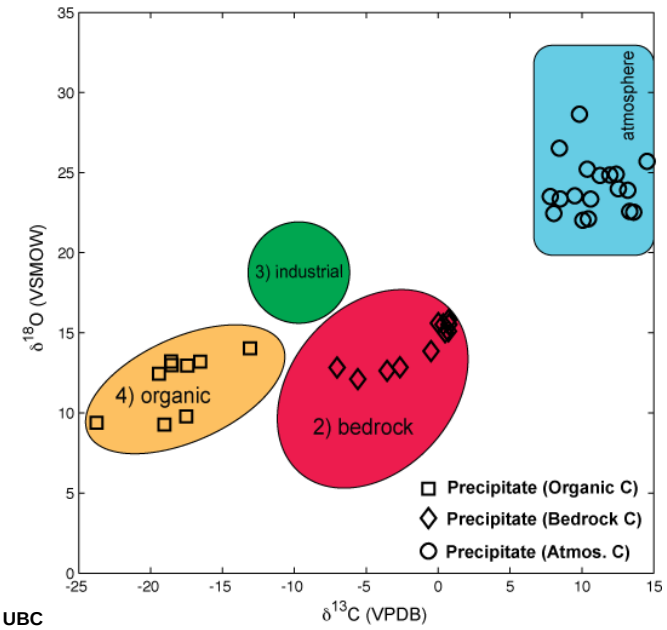


Mineral Hosts to Carbon

Mineral Name	Cation(s)	Formula
Hydromagnesite	Mg	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
Dypingite	Mg	$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$
Nesquehonite	Mg	$MgCO_3 \cdot 3H_2O$
Lansfordite	Mg	$MgCO_3 \cdot 5H_2O$
Chlorartinite	Mg	$Mg_2(CO_3)(OH)Cl \cdot 2H_2O$
Aragonite	Ca	$CaCO_3$
Vaterite	Ca	$CaCO_3$
Natrite	Na	Na_2CO_3
Thermonatrite	Na	$Na_2CO_3 \cdot H_2O$
Natron	Na	$Na_2CO_3 \cdot 10H_2O$
Trona	Na	$Na_3(CO_3)(HCO_3) \cdot 2H_2O$
Gaylussite	Na, Ca	$CaNa_2(CO_3)_2 \cdot 5H_2O$
Northupite	Na, Mg	$Na_3Mg(CO_3)_2Cl$

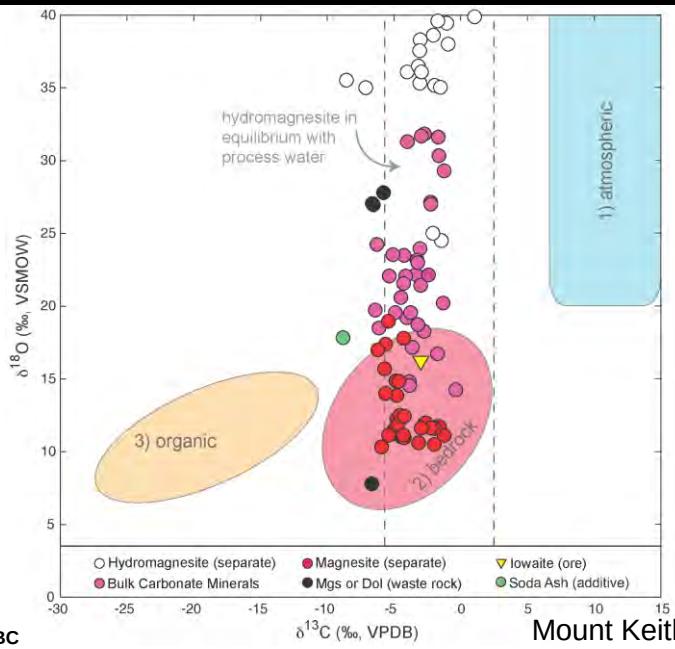
G. Dipple, UBC

Carbon Fingerprinting: Reservoirs



G. Dipple, UBC

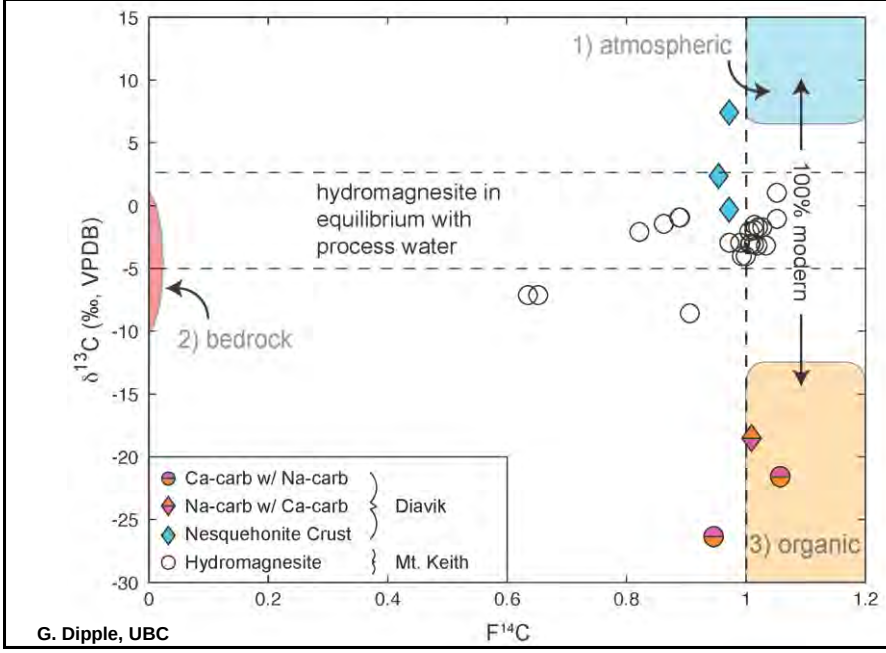
Carbon Fingerprinting



G. Dipple, UBC

Mount Keith Ni Mine

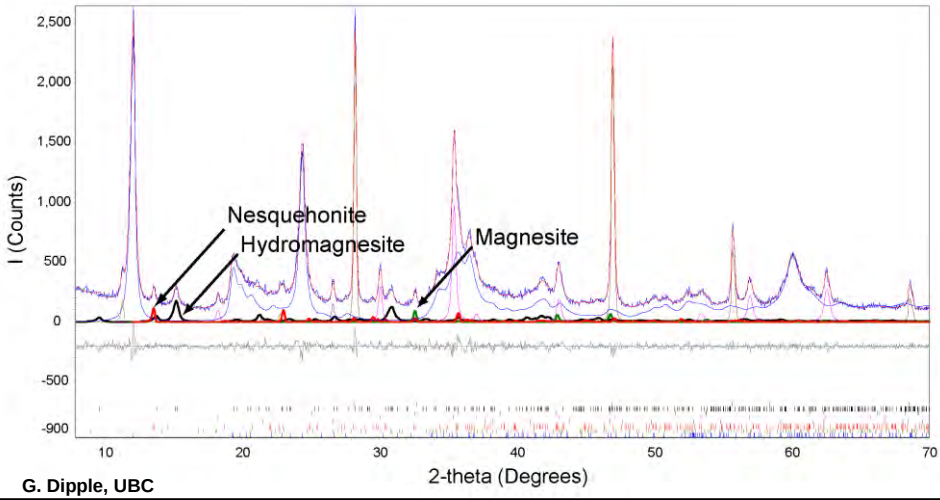
Carbon Fingerprinting



G. Dipple, UBC

Quantifying Carbon Up-Take with XRD

- 1.8 wt% nesquehonite + 7.7 wt% hydromagnesite
- 1.4 wt% magnesite



G. Dipple, UBC

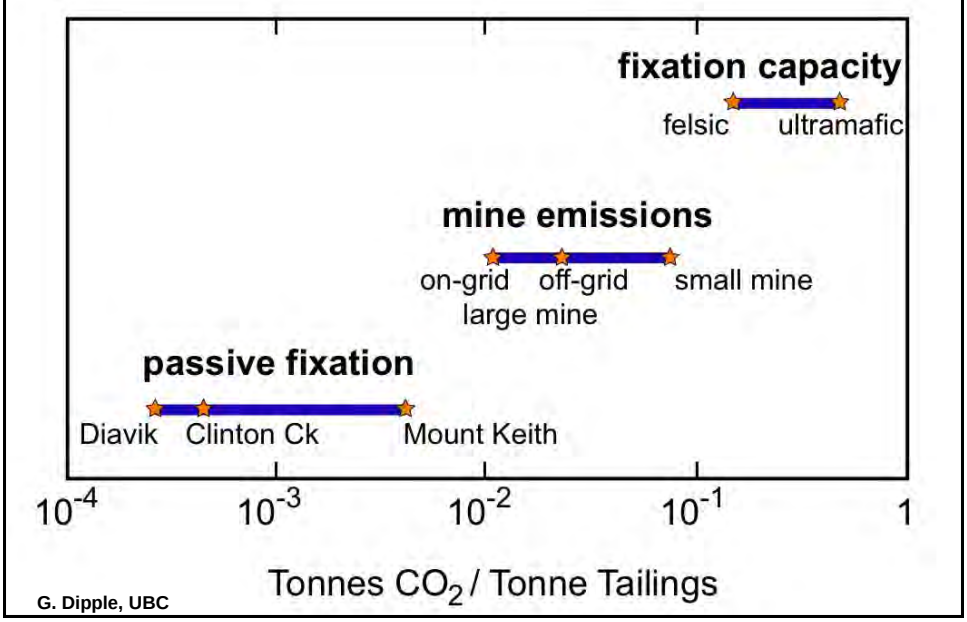
Amount of sequestered carbon can be significant

Clinton Creek mine tailings contain approx. 160,000 tonnes CO2

Amount of sequestered carbon can be significant

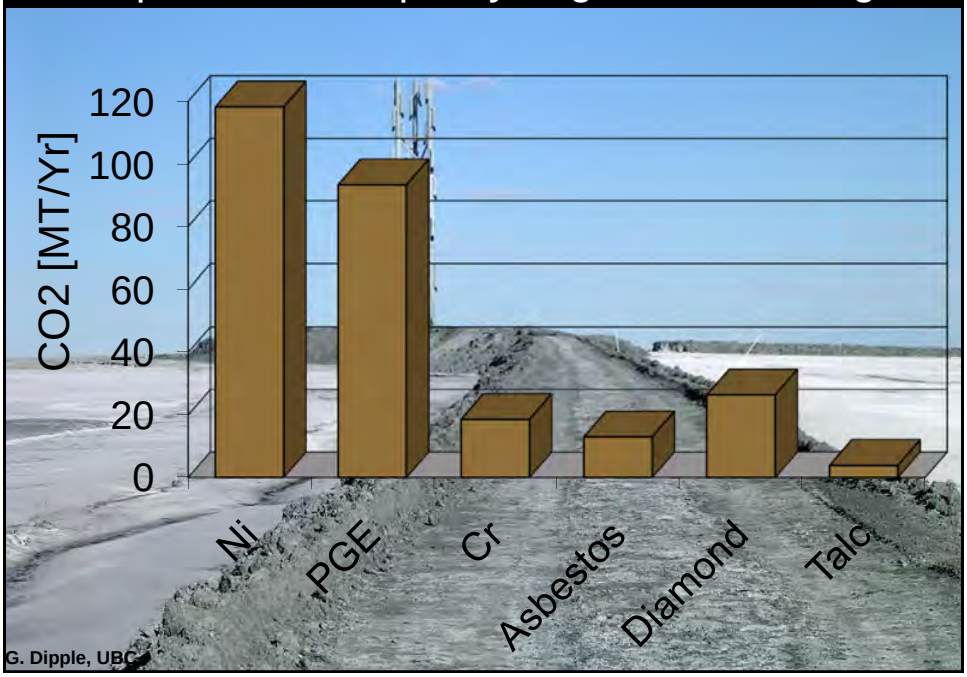
Large mining operations can fix 50-100 kilotonnes CO_2/yr

Annual Rates and Capacity



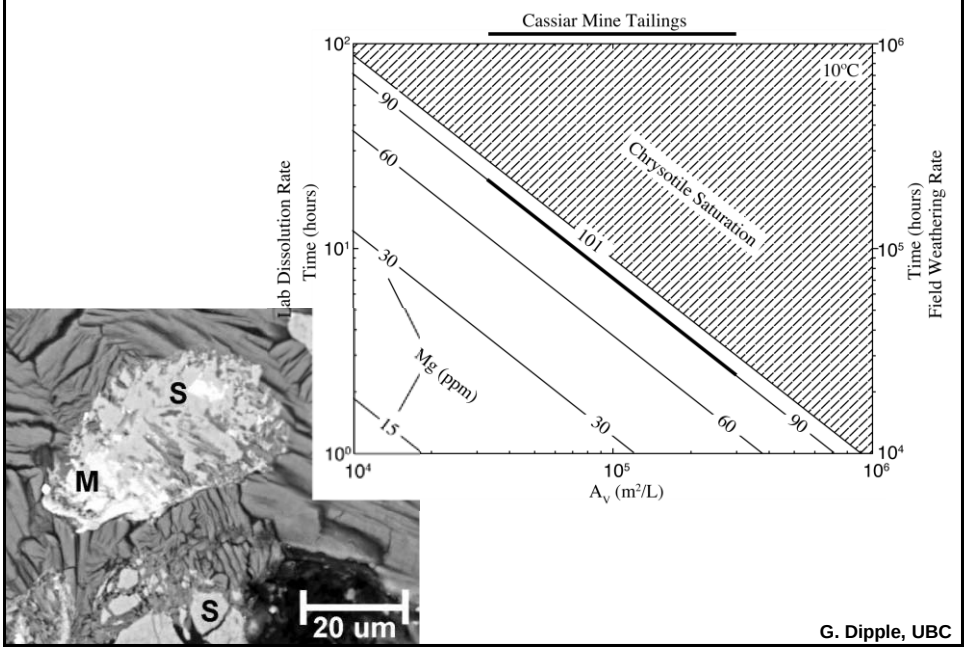
G. Dipple, UBC

Sequestration Capacity: Mg-Silicate Tailings



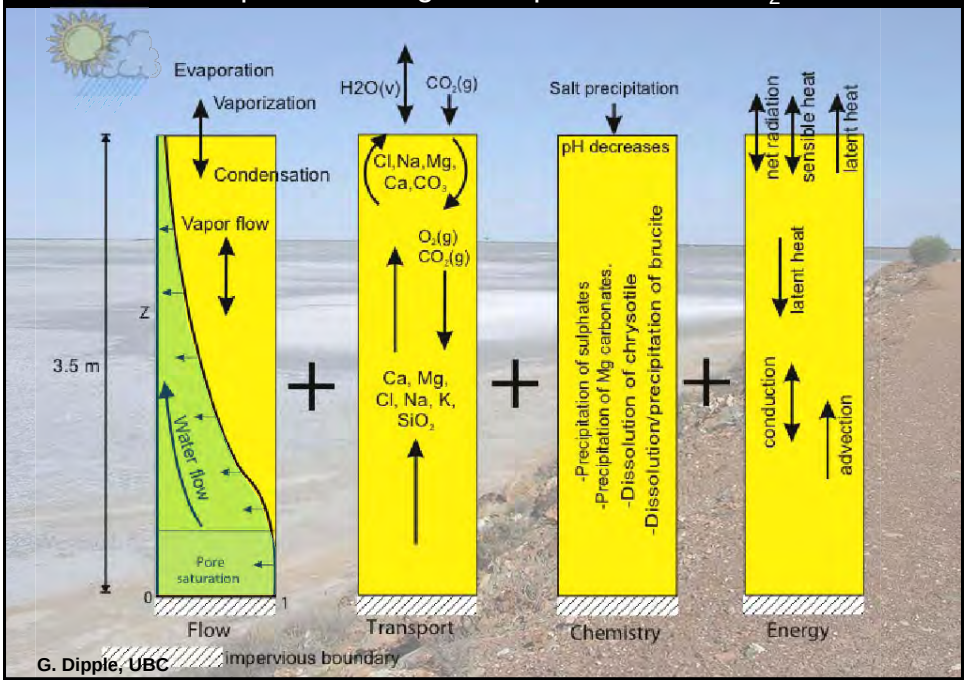
G. Dipple, UBC

Mineral Dissolution Rates in Tailings

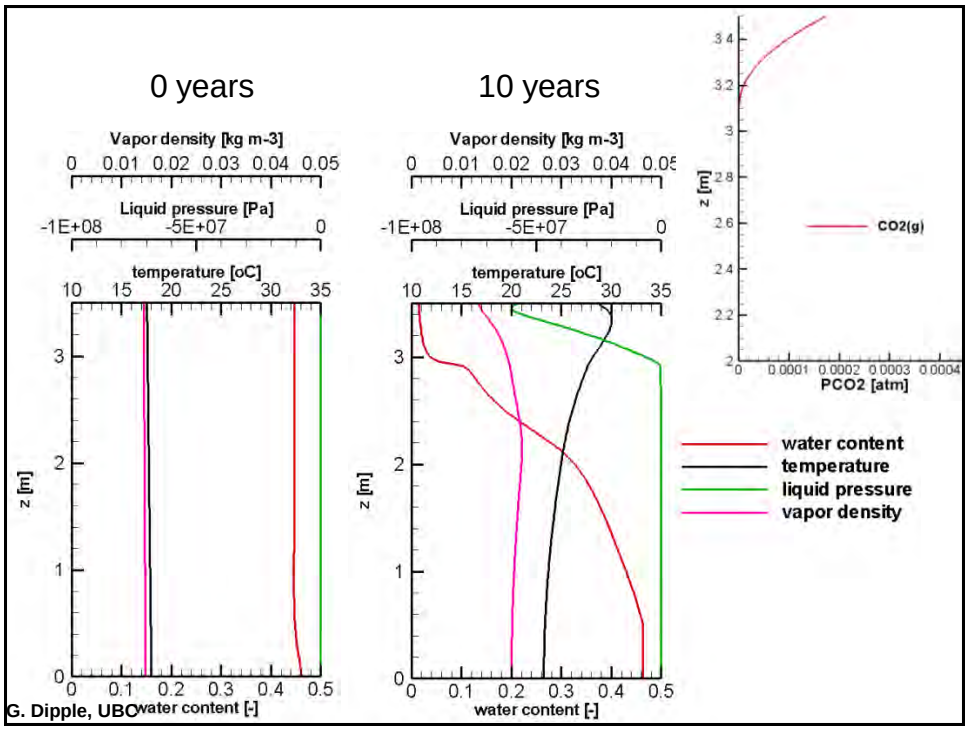


G. Dipple, UBC

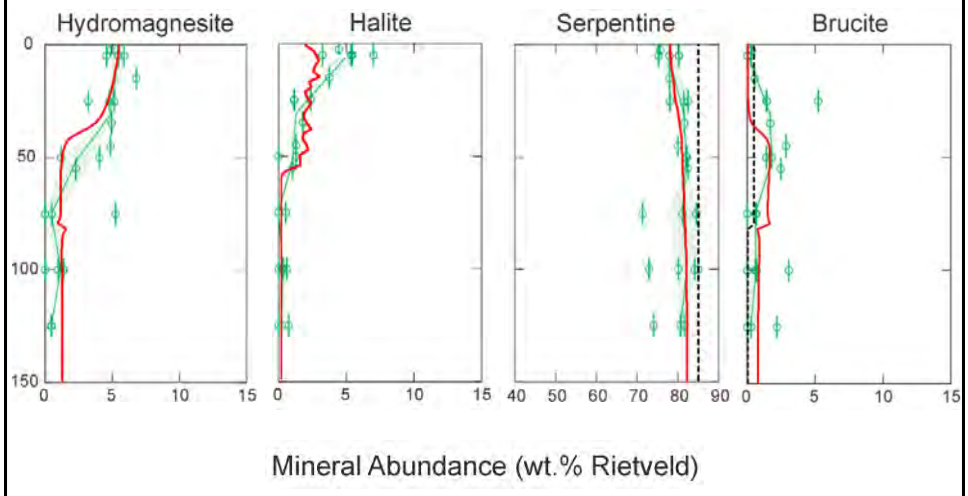
Reactive Transport Modeling of Evaporation and CO_2 Drawdown

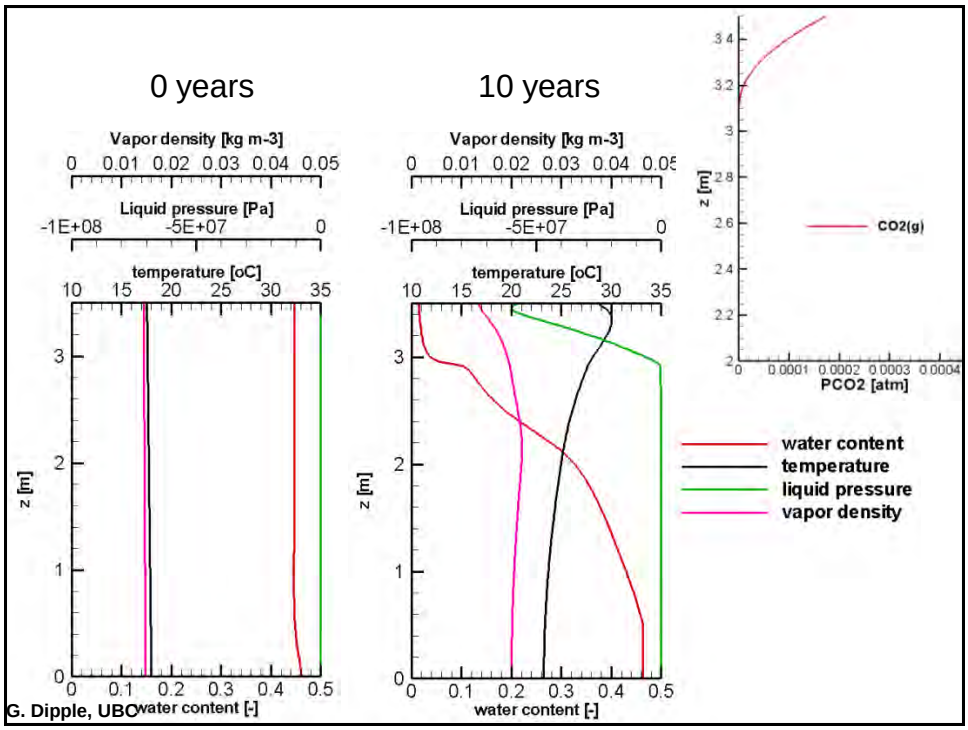


G. Dipple, UBC

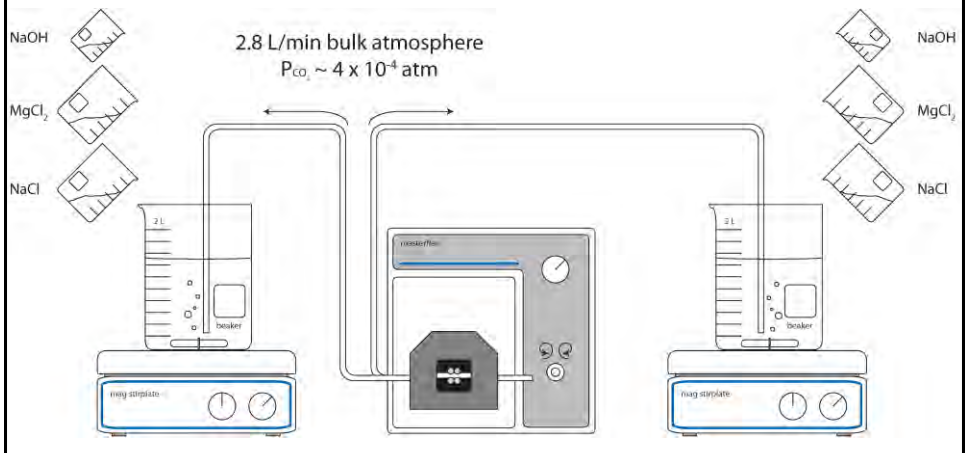


Mineral Abundance after Ten Years

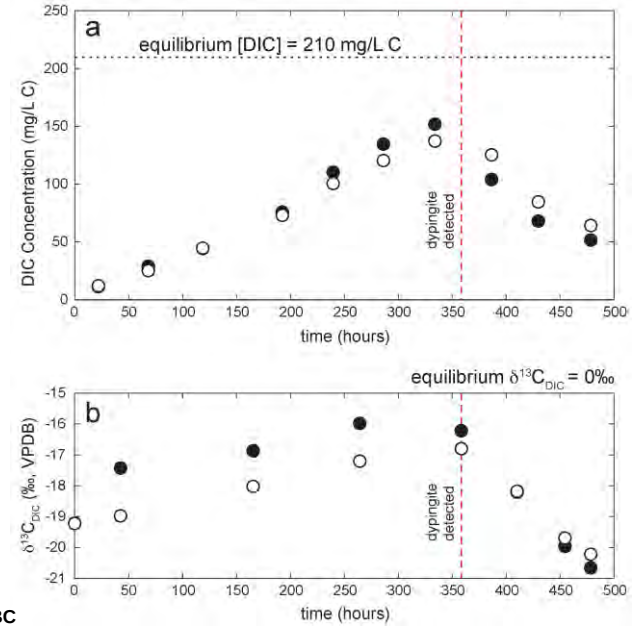




Brucite Carbonation Experiments

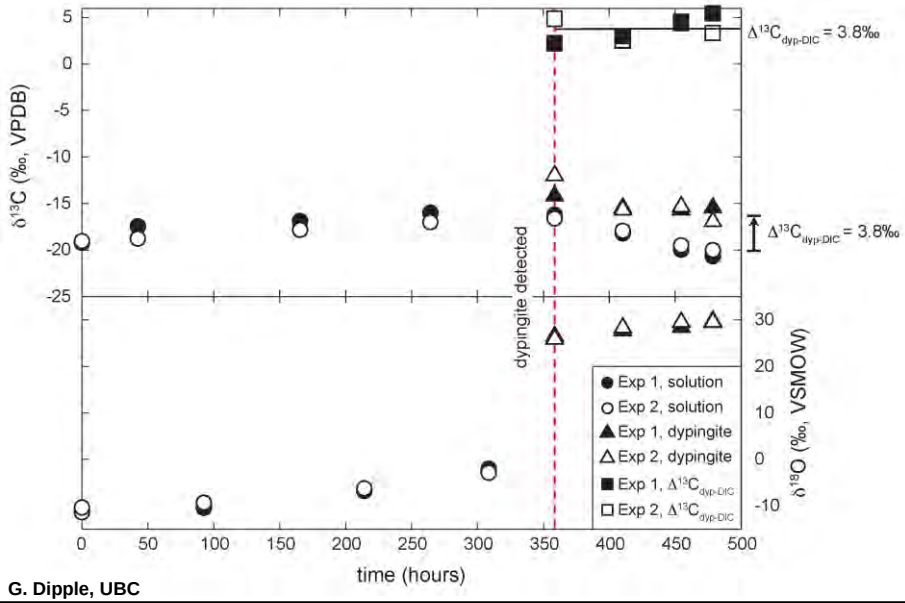


Gas-Fluid ^{13}C Disequilibrium: CO_2 Limited System



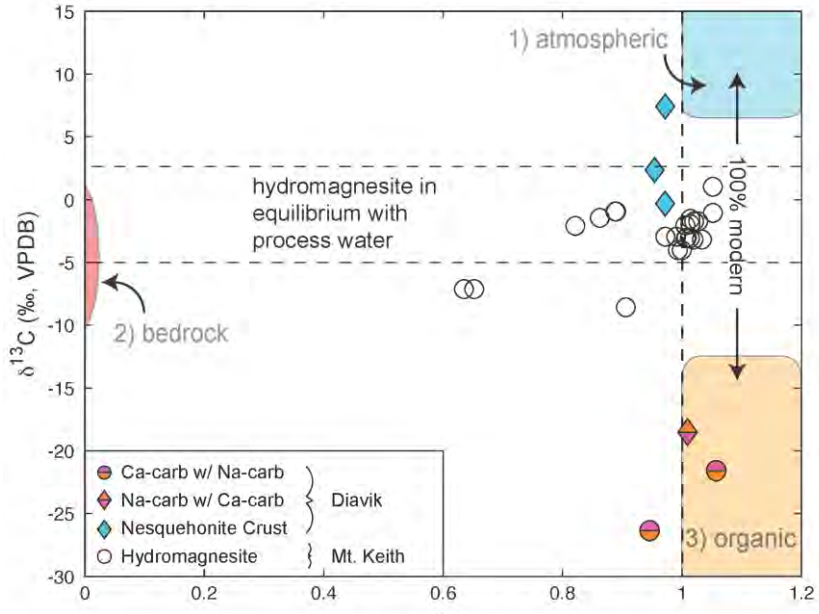
G. Dipple, UBC

Gas-Fluid ^{13}C Disequilibrium: CO_2 Limited System



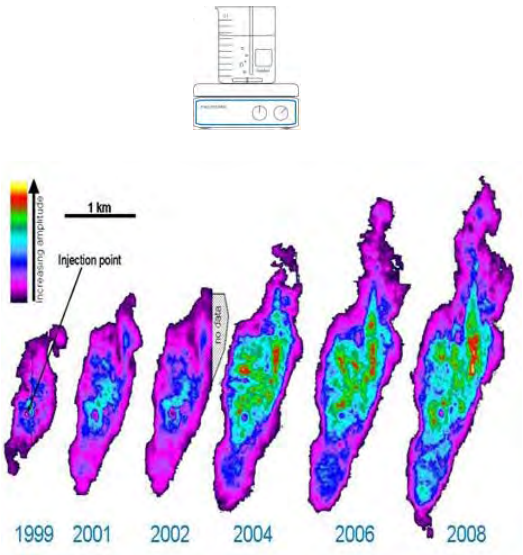
G. Dipple, UBC

Carbon Fingerprinting

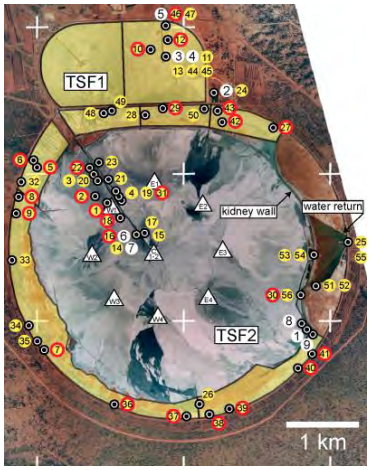


G. Dipple, UBC

Tailings are Useful Proxies for the Subsurface



Statoil Sleipner plume: www.geoexpro.com



- Size
- Accessibility
- Natural Complexity

G. Dipple, UBC

10. S. Gislason -U. of Iceland.

The Carbfix Project: Mineral CO_2 Sequestration into Basalt

Sigurdur R. Gislason[(1)], Wallace S. Broecker[(2)], Eric H. Oelkers[(3)], Einar Gunnlaugsson[(4)], Holmfridur Sigurdardottir[(4)] Bergur Sigfusson[(4)], Helgi Alfredsson[(1)], Edda Sif Aradóttir[(4)],Juerg M. Matter[(2)], Martin Stute[(2)], Domenik Wolff-Boenisch[(1)], Andri Stefansson[(1)], and Gudni Axelsson[(5)]

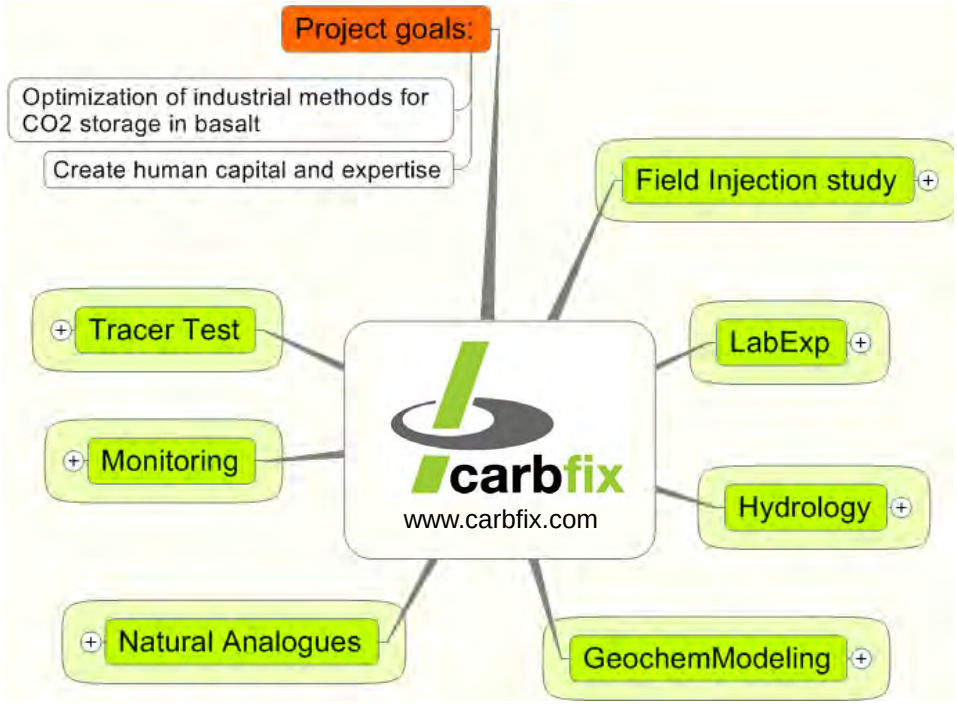
(1) Institute of Earth Sciences, University of Iceland, Iceland

(2) Earth Institute, Columbia University, USA

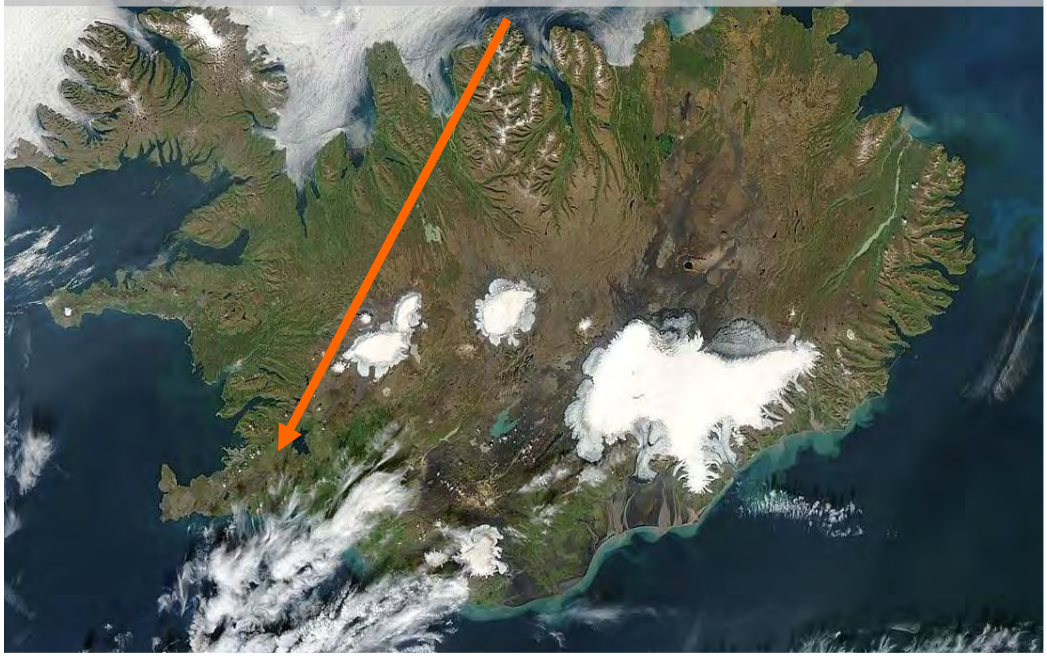
(3) CNRS, Université Paul Sabatier, France

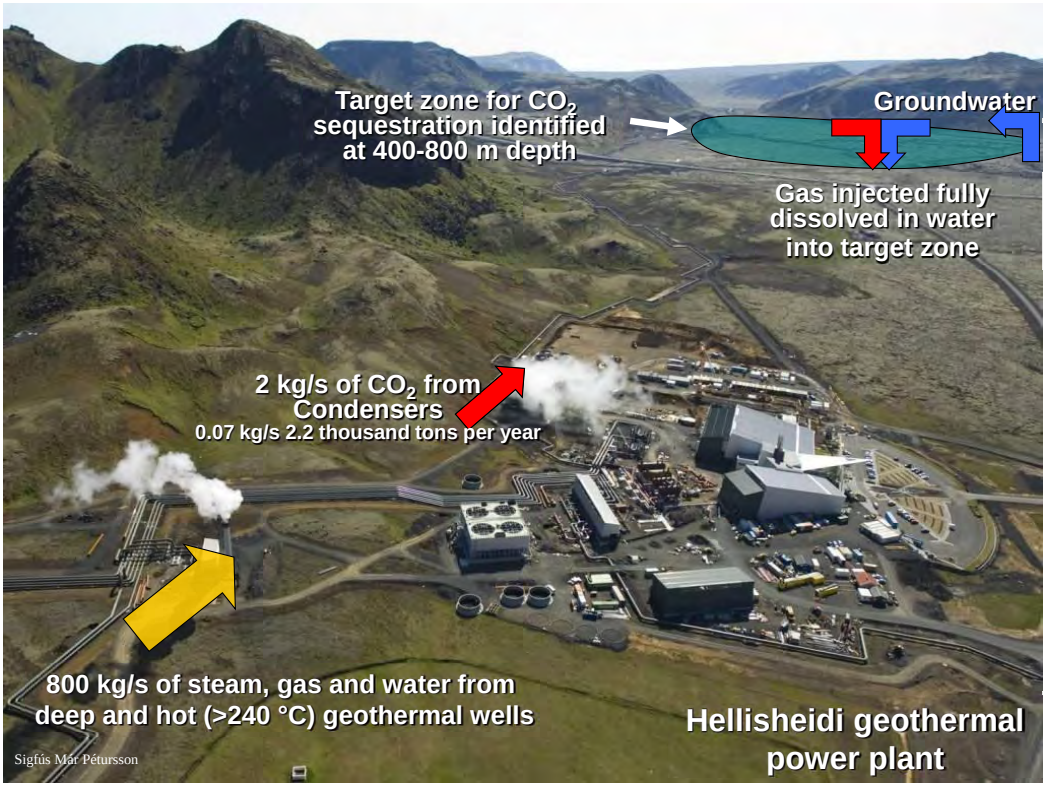
(4) Reykjavik Energy, Iceland

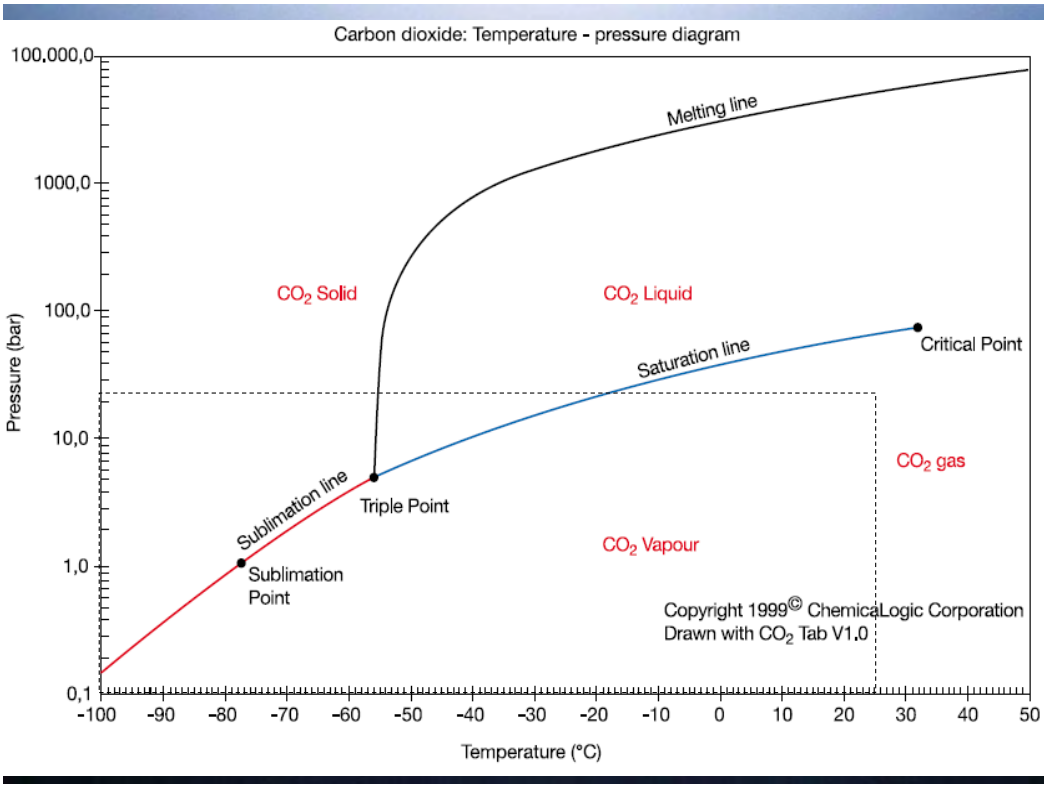
(5) Icelandic Geosurvey, Iceland

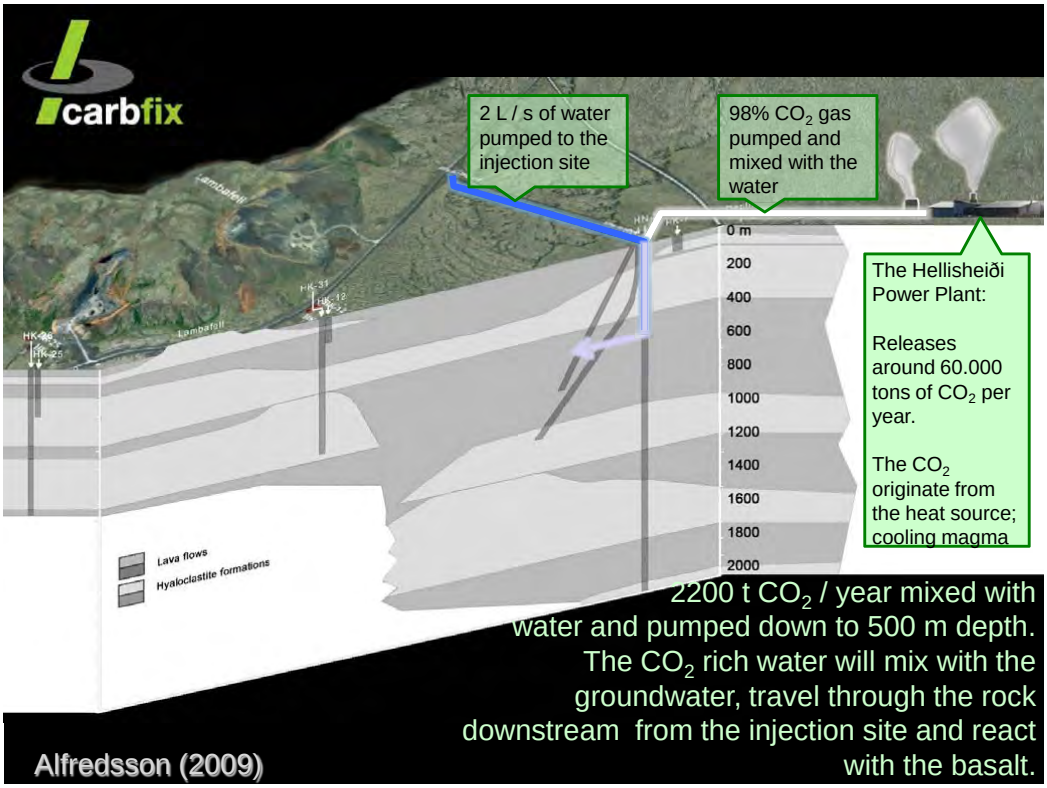


MINERAL CO_2 SEQUESTRATION INTO BASALT: THE CARBFIX PROJECT

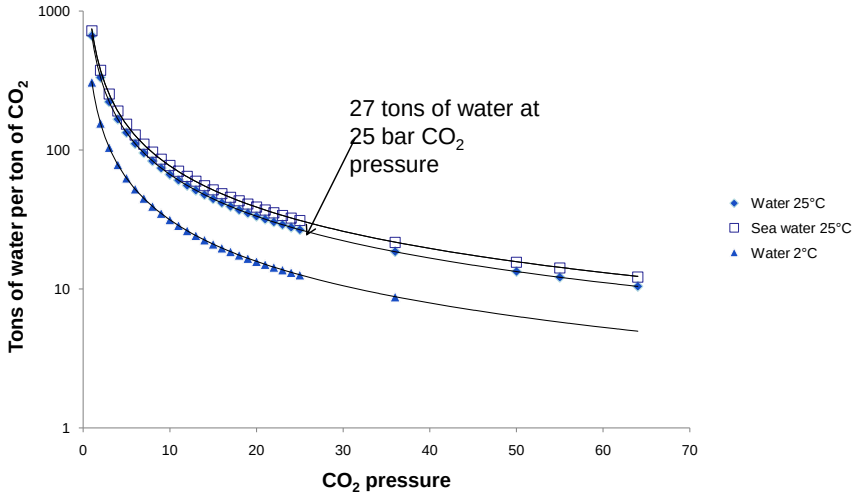





Carbon dioxide: Temperature - pressure diagram
Pressure (bar)
100.000,0
1000,0
100,0
10,0
1,0
0,1
Melting line
CO2 Solid
CO2 Liquid
Saturation line
Critical Point
CO2 gas
Sublimation line
Triple Point
CO2 Vapour
Sublimation Point
Copyright 1999© ChemicaLogic Corporation
Drawn with CO2 Tab V1.0
-100 -90 -80 -70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50
Temperature (°C)

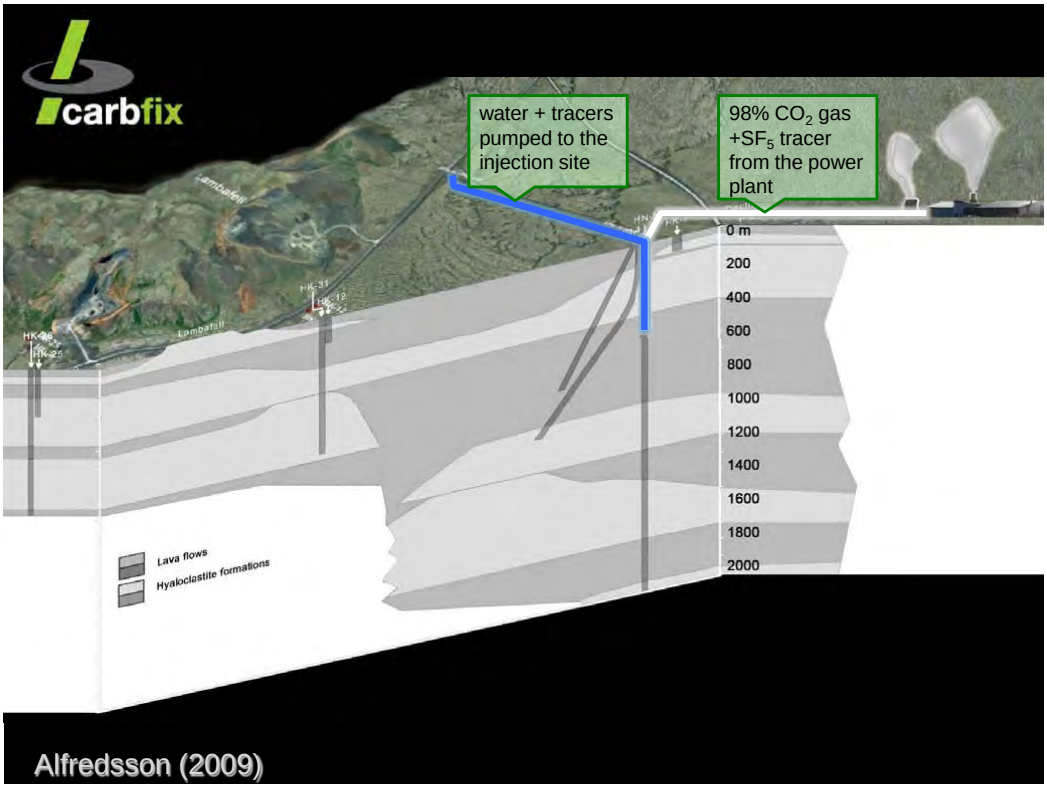

carbfix
2 L / s of water pumped to the injection site
98% CO2 gas pumped and mixed with the water
The Hellisheiði Power Plant:
Releases around 60.000 tons of CO2 per year.
The CO2 originate from the heat source; cooling magma
0 m
200
400
600
800
1000
1200
1400
1600
1800
2000
Lava flows
Hyaloclastite formations
2200 t CO2 / year mixed with water and pumped down to 500 m depth. The CO2 rich water will mix with the groundwater, travel through the rock downstream from the injection site and react with the basalt.
Alfredsson (2009)

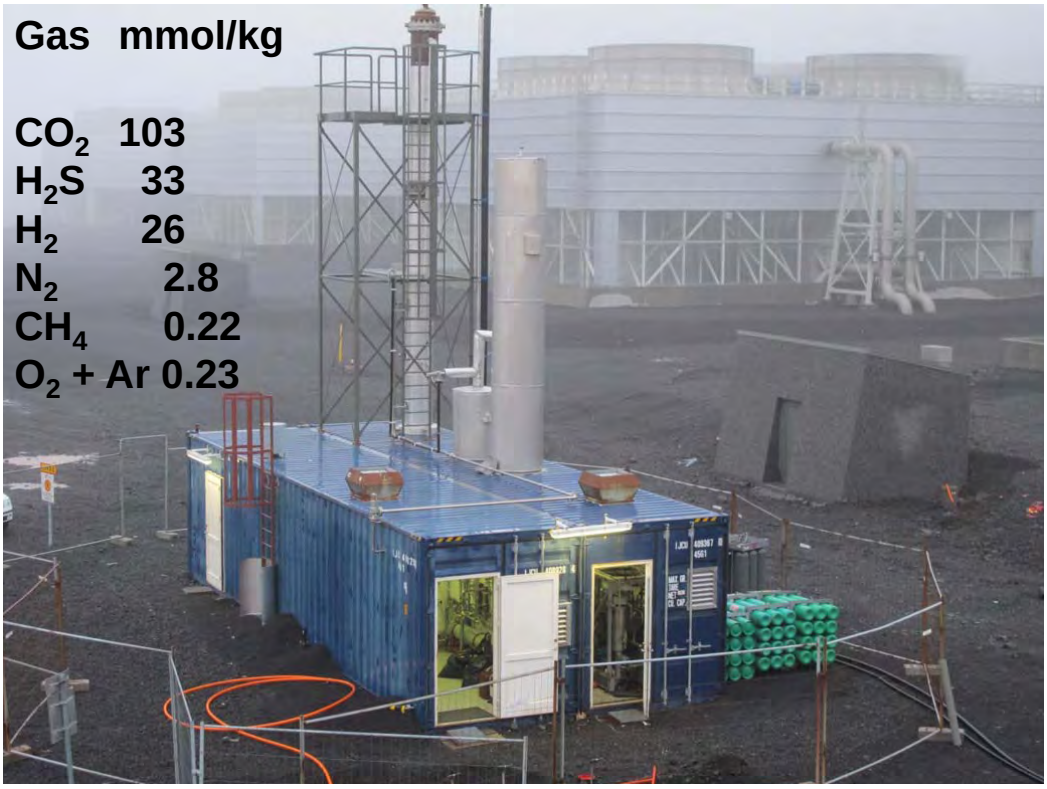
Water demand as a function of CO_2 pressure



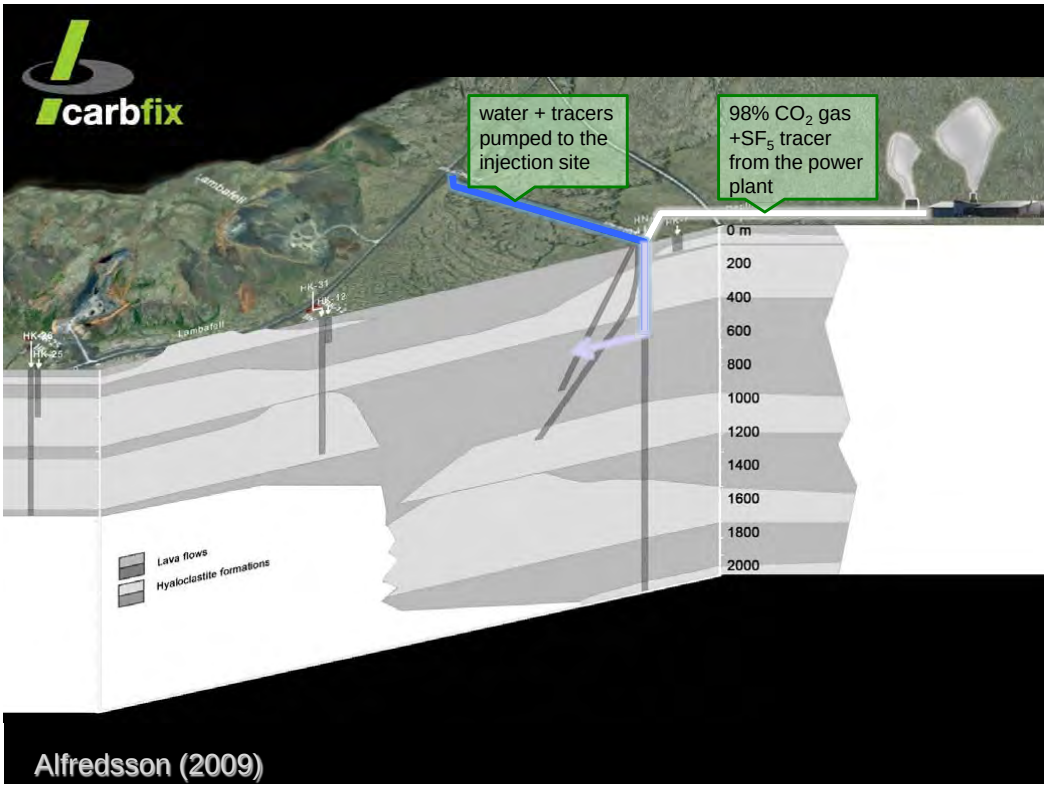
Gislason et al. 2010 IJGGC

fluorescent dye tracer
^{14}C tracer


carbfix
water + tracers pumped to the injection site
98% CO_2 gas +SF_5 tracer from the power plant
0 m
200
400
600
800
1000
1200
1400
1600
1800
2000
Lava flows
Hyaloclastite formations
Alfredsson (2009)


Gas mmol/kg
CO_2 103
H_2S 33
H_2 26
N_2 2.8
CH_4 0.22
O_2 + Ar 0.23

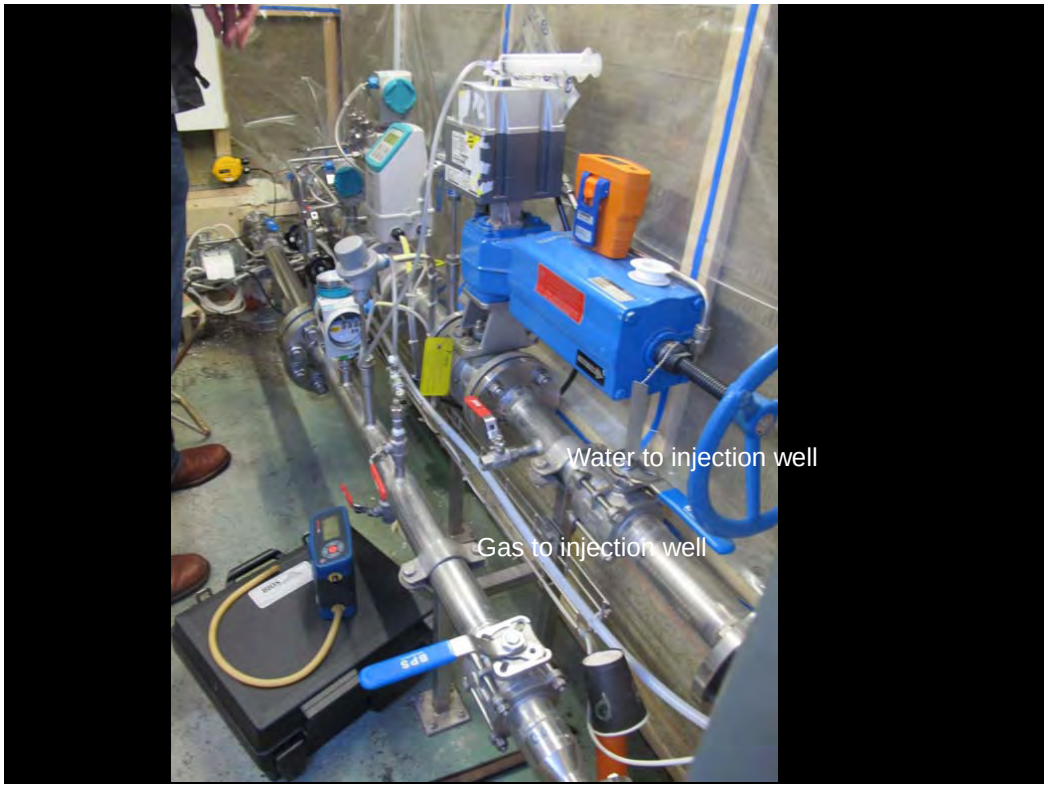
SF_5 volatile tracer

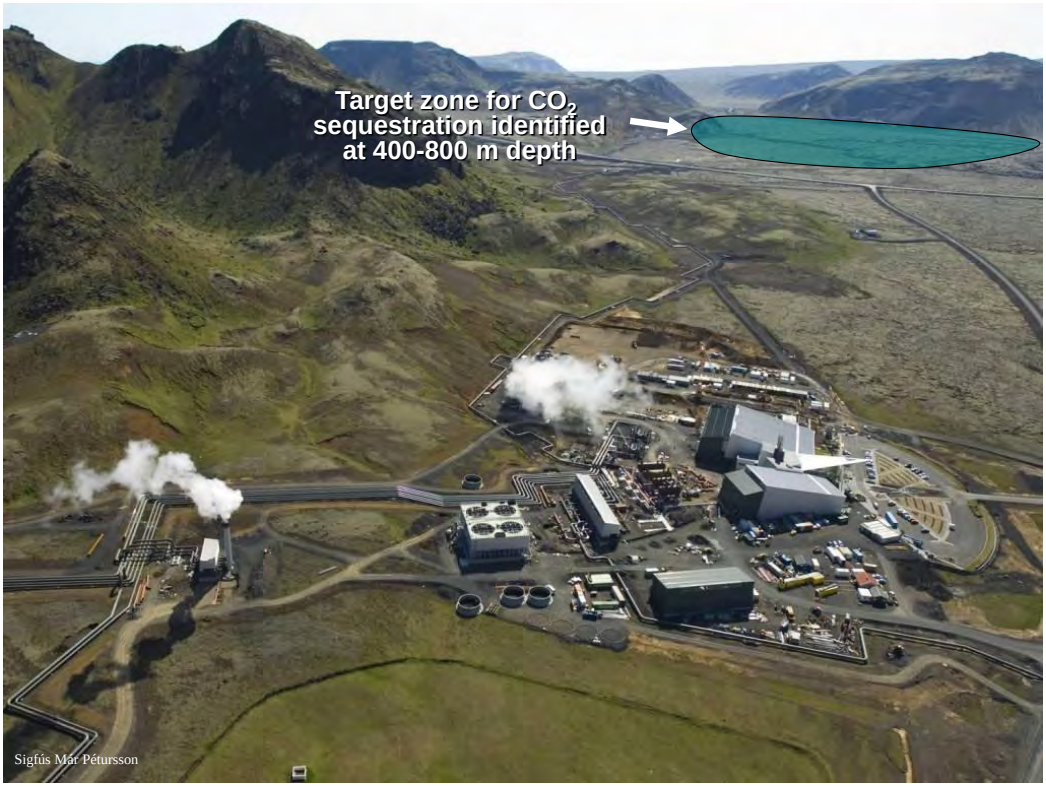

carbfix
water + tracers pumped to the injection site
98% CO_2 gas +SF_5 tracer from the power plant
0 m
200
400
600
800
1000
1200
1400
1600
1800
2000
Lava flows
Hyaloclastite formations
Alfredsson (2009)

Injection well HN-2
Opening into the head space
Gas + tracer
Water + tracers
Sampling pipe

Monitoring hut
Monitoring well, HK-34

Monitoring well, HK-34
Monitoring well, HN-4


Water to injection well
Gas to injection well


Target zone for CO_2 sequestration identified at 400-800 m depth
Sigfús Már Pétursson

Dissolution and precipitation

Dissolution reactions:

$CO_2 + H_2O \rightarrow HCO_3^- + H^+$

Basaltic Glass $+ xH^+ \rightarrow Mg^{2+} + Ca^{2+} + Fe^{2+} + \ldots\ldots$

$\mathbf{Mg_2SiO_4} + 4H^+ \rightarrow 2Mg^{2+} + 2H_2O + SiO_2(aq)$

Forsterite

$\mathbf{CaAl_2Si_2O_8} + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 2SiO_2(aq) + 4H_2O$

Ca-plagioclase

Precipitation reactions:

$(Fe,Ca,Mg)^{2+} + CO_2 + H_2O \rightarrow \mathbf{(Fe,Ca,Mg)CO_3} + 2H^+$

Siderite, Calcite, Magnesite

19

CO_2 fixation by dissolution of Ca-plagioclase and precipitation of kaolinite and calcite

$\mathbf{CaAl_2Si_2O_8} + CO_2 + 3H_2O \longrightarrow \mathbf{Al_2Si_2O_5(OH)_4} + \mathbf{CaCO_3} + H_2O$

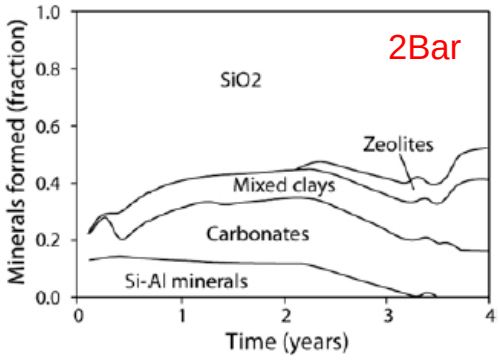
Copyright NHM Picture Library

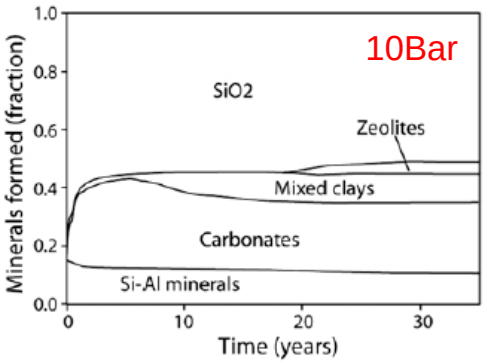
Dissolution of basaltic glass

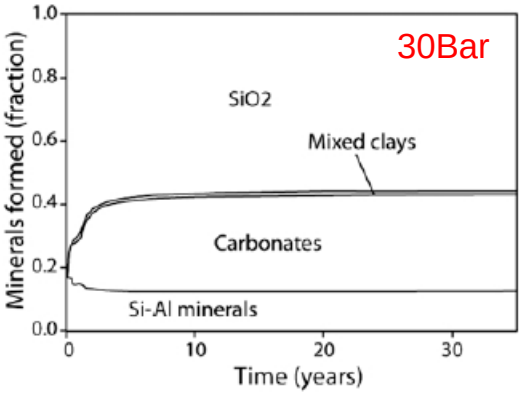
$\mathbf{SiAl_{0.36}Ti_{0.02}Fe(III)_{0.02}Ca_{0.26}Mg_{0.28}Fe(II)_{0.17}Na_{0.08}K_{0.008}O_{3.36}} + 6.72\ CO_2 + 3.36H_2O$

$\longrightarrow Si^{+4} + 0.36Al^{3+} + 0.02Ti^{+4} + 0.02Fe^{3+} + 0.17Fe^{2+} + 0.26Ca^{2+} + 0.28Mg^{2+} +$

$0.08Na^+ + 0.008K^+ + 6.72HCO_3^-$



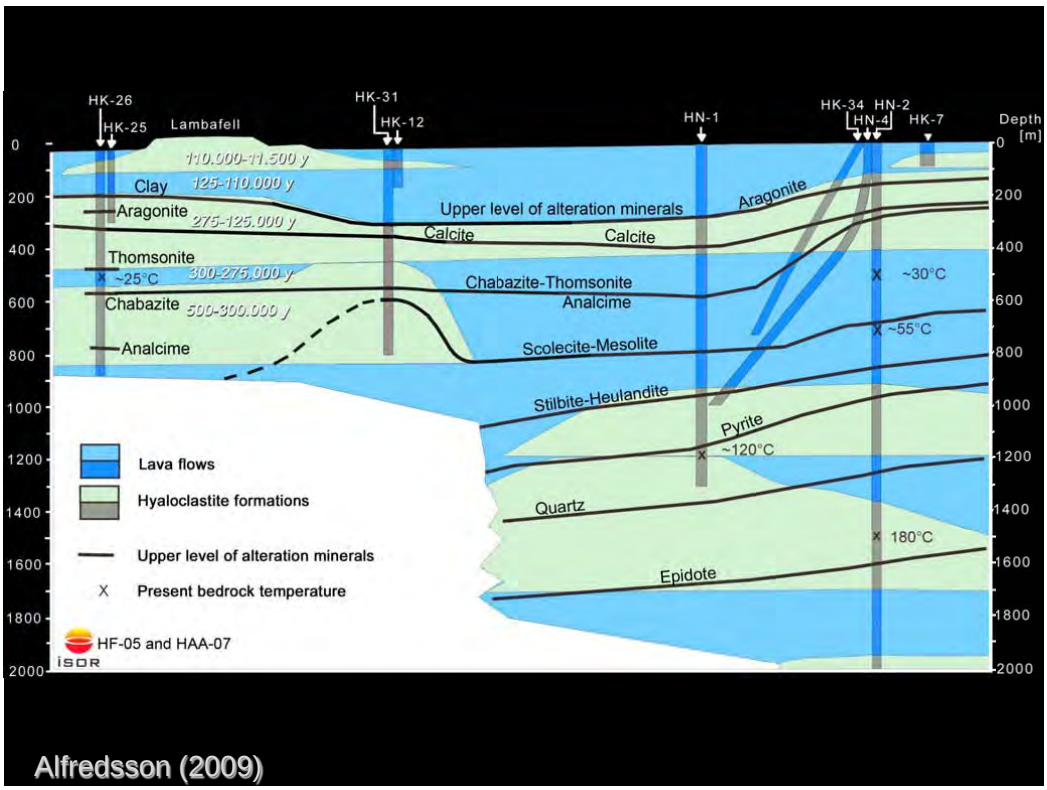




Batch reactor simulations at 25°C (Gysi&Stefansson, Min.Mag.2008)

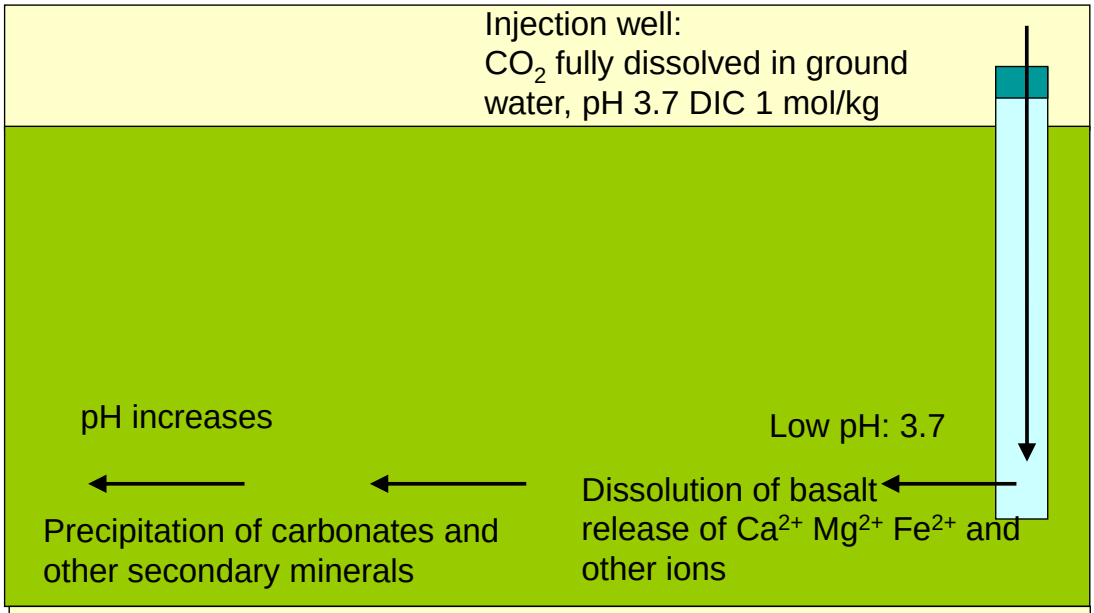
Carbonate fraction increases with increasing pCO_2

Mixed clays: celadonite, Ca-Fe-Mg smectites, Fe-Mg smectites and chlorite
Carbonates: calcite, dolomite, siderite, magnesite and Mg-Fe carbonate
Si-Alminerals: allophane, imogolite and kaolinite



Alfredsson (2009)

A Conceptual Model



Reservoir will gradually clog up by precipitation of secondary minerals

11. P. McGrail – PNNL, USA.

Battelle
The Business of Innovation

The Wallula Basalt Sequestration Pilot Project

B. P. McGrail, F. A. Spane, E. C. Sullivan, D. H. Bacon, and G. Hund

Energy & Environment Directorate
Battelle Pacific Northwest Division

International Ocean Drilling Program Workshop
Geological Carbon Capture & Storage in Mafic and Ultramafic rocks

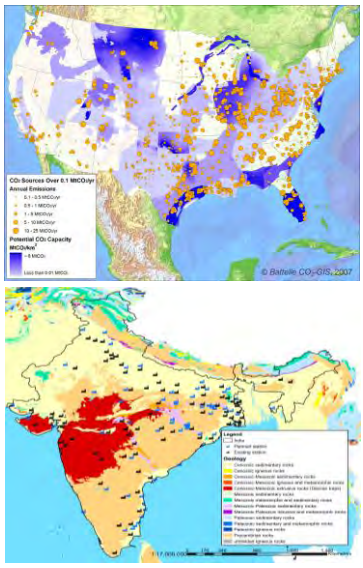
Muscat, Oman
January 9, 2011

1

Battelle
The Business of Innovation

Why CO_2 Storage in Basalts?

- Flood basalts represent some of largest geologic structures on the planet but have received comparatively little attention
- Located in key regions (NW and SE U.S., India) where conventional storage options are limited
- Over 30 years and >$400M of prior DOE investment in understanding basalt/aquifer systems in the Pacific Northwest U.S. that can be leveraged
- Aquifer and gas storage experience
- Unique geochemistry results in conversion of CO_2 to carbonate minerals through both aqueous *and* supercritical phase reactions
- Since GHGT-6 in 2003, much additional work is now underway
  - Laboratory-based projects (4+ in the U.S., UK, India)
  - Field projects (CarbFix and Wallula Pilot)



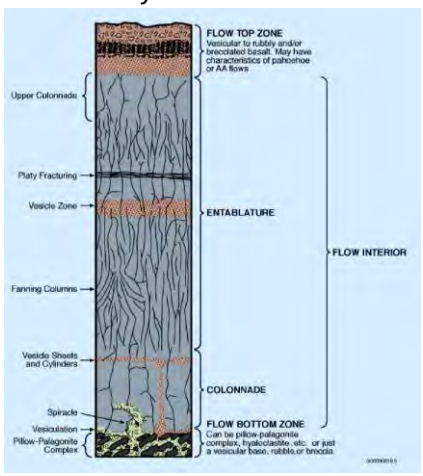
2

Flood Basalt Features Relevant to CO_2 Sequestration

- Formation process
  - Giant volcanic eruptions
    - Low viscosity lava
    - Large plateaus
  - Multiple layers
- Primary structures
  - Thick impermeable seals
    - Caprock (flow interior)
    - Regional extensive interbeds
  - Permeable vesicular and brecciated interflow zones
    - Injection targets
    - 15-20% of average flow

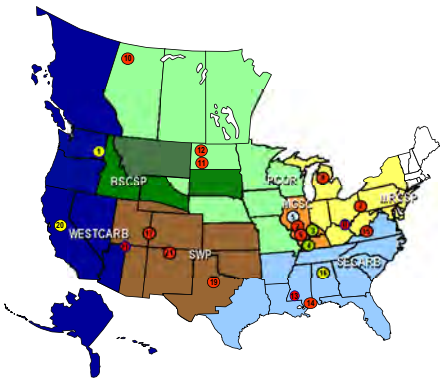
Flowtop Breccia

Layered Basalt Flow



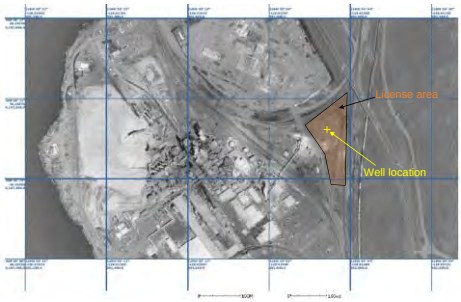
Overview

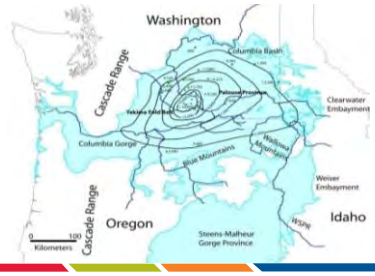
- Big Sky Carbon Sequestration Partnership Phase II Demonstration
- Seismic survey conducted December 2007
- Final site selected in June 2008
- Land Use Agreement signed August 2008
- Drilling commenced January 2009
- Drilling/characterization ended May 2009 (TD 1222 m bgs)
- Site characterization topical report issued December 2009
- 1000 MT CO_2 injection permit application submitted February 2010
- WADoE issued DNS August 2010
- Permit approved October 2010
- Injection start Spring 2011



Regional Carbon Sequestration Partnerships

Wallula Field Site Overview



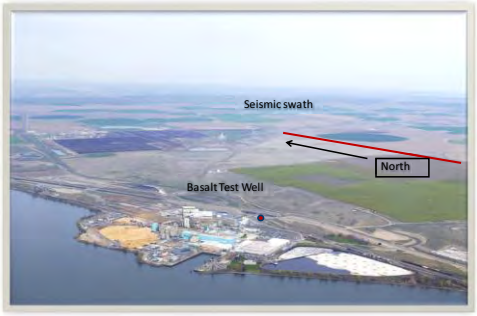


- Located where some of the deepest and thickest basalt exists in the region
- Paper mill site provides secure location on an active industrial site with utilities and paved road access adjacent to site
- Shallow reservoir hydrologic property data will assist plant owner with aquifer storage project design
- Boise, Inc. management proactive in supporting early stage R&D for emissions reductions

5

Seismic Survey

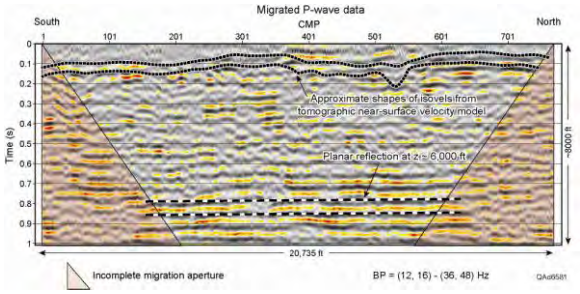
- Seismic survey completed 12/07/2007
- Field tests immediately prior to initiation of the seismic acquisition showed that ground roll could be suppressed by eliminating frequencies below 12 Hz, and by using (for each seismic source station) four vibroseis sweeps
- Optimized sweep resulted in longer production of high frequency source energy and a desirable flattened frequency spectrum
- The swath design of five receiver lines flanked by two source lines, together with the use of the optimized sweep design, results in a dominant frequency of 80 HZ at the target interval of 3,000-4,000 feet, and a fold of 200
- Raw field records of the 2D data acquired confirm acquisition of P-wave and converted wave data
- No faulting or fracture zones are indicated at the site



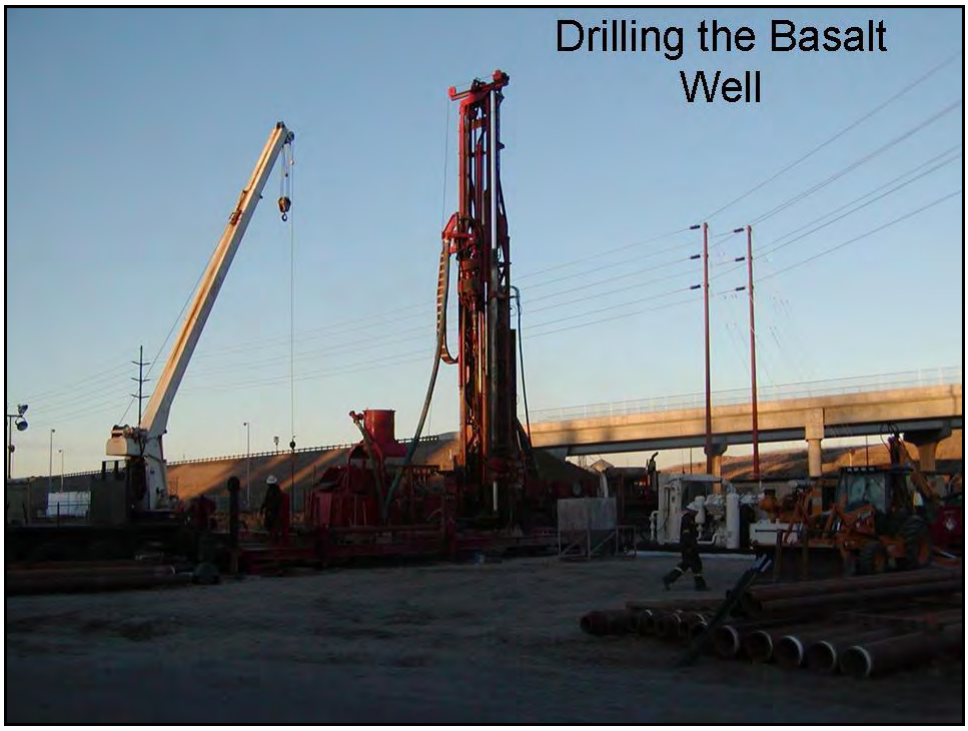
6

Post-Acquisition Spectral Balancing and Removal of Shear Wave Noise Provided Good Quality Seismic Images in Deep Basalts

Battelle
The Business of Innovation

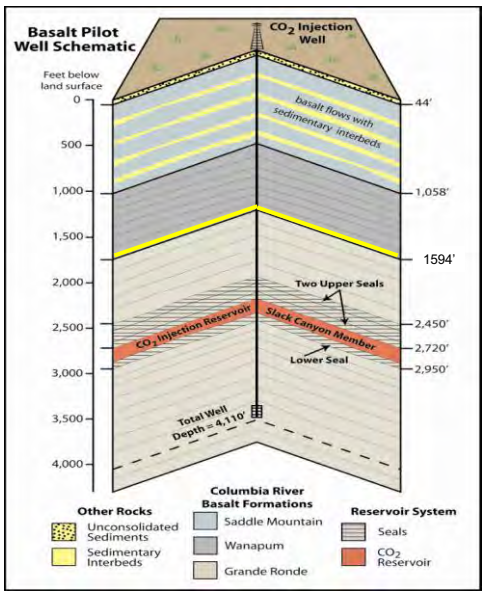


7



Battelle
The Business of Innovation

Stratigraphy at Wallula Pilot

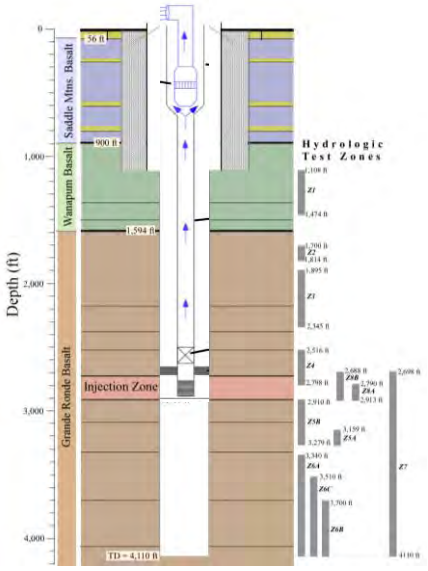


9

Battelle
The Business of Innovation

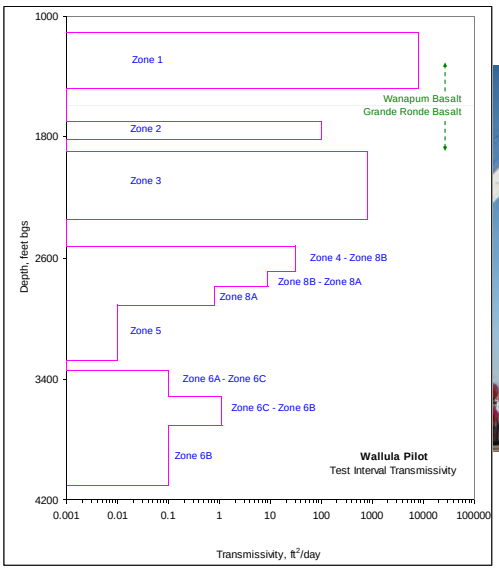
Hydrogeologic Characterization

- Used a progressive drill-and-test characterization strategy
- Downhole packer test system isolated the underlying test zone from the overlying open borehole section
- Groundwater samples from injection zone (and deeper) had multiple analytes exceeding primary and secondary drinking water standards
- Caprock characterization performed using multi-step, constant-head injection pressure tests
  - Maximum surface injection pressure of 1.1 MPa (150 psig) and injection flow-rate measurement down to 0.1 mL/min
  - Permeabilities were extremely low in the microdarcy and sub-microdarcy range
- Interflow zone characterization used a combination of methods (Slug, Drill Stem Test, Step-Drawdown/Recovery, Constant-Rate Pumping , Drawdown & Recovery, Pulse)

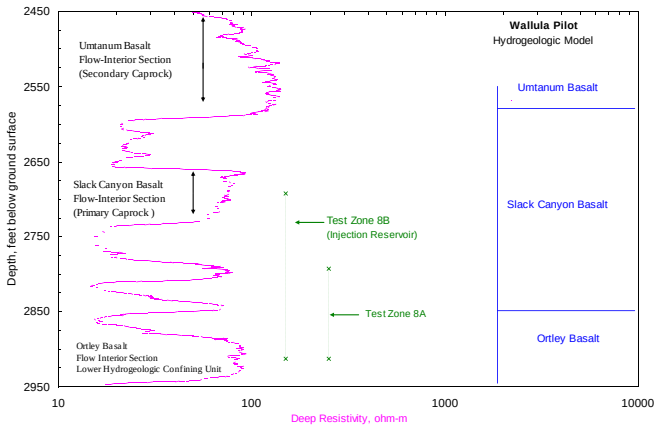


10

Packer Tool Assembly Deployment



Resistivity Log Detail Near Injection Zone



Selected injection zone transects three interconnected basalt flows that offer unique potential for scientific study of CO_2 migration, reaction, and mineralization processes

Testing the Rotary Sidewall Drill Tool on a Sample of Basalt

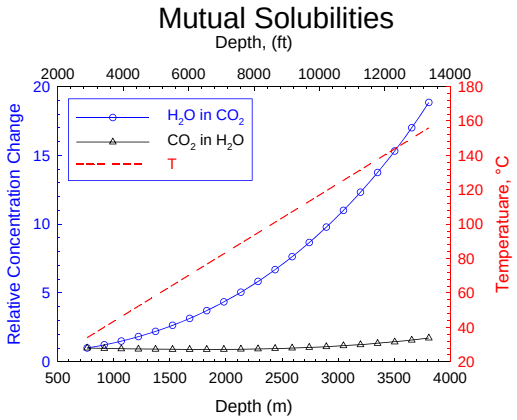
Cores and Image Log From Test Zone

Battelle
The Business of Innovation

14

Impacts of Reservoir Depth on Phase Behavior of CO_2-H_2O Mixtures

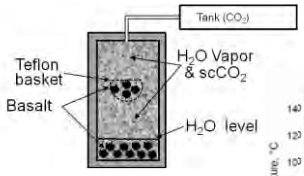
- CO_2 resides as a water saturated buoyant supercritical fluid dissolving into formation waters
- Mutual solubilities
  - CO_2 solubility in water varies little with pressure and temperature
  - H_2O solubility in $scCO_2$ is strongly dependent on temperature at pressures >100 bar
- Impacts of depth on mineral transformation kinetics is potentially greatest in wet $scCO_2$



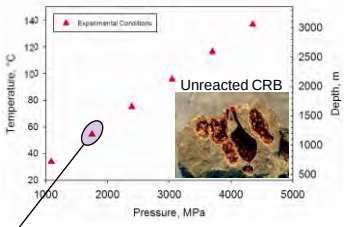
15

Mineralization Studies

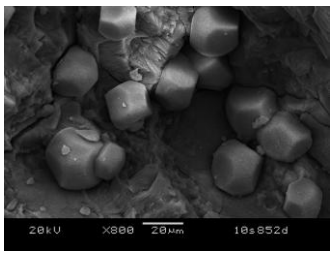
- Basalt (Grouse Creek)
  - Drill cuttings
  - Vesicular
  - Secondary minerals
    - chlorite, heulandite, and cristobalite
- Sample Position
  - Wet scCO2
  - Aqueous phase
- Samples exposed to P-T conditions representative of range of depths (800-3000 m bgs)

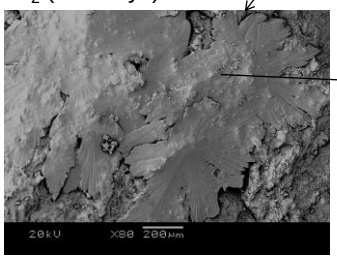


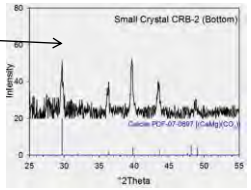
Reservoir Conditions



H_2O saturated $scCO_2$ (180 days)



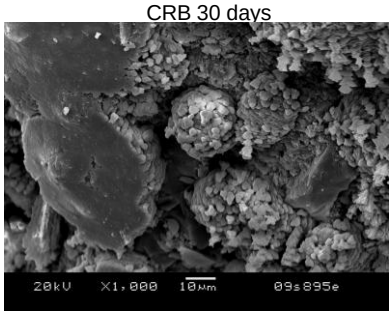




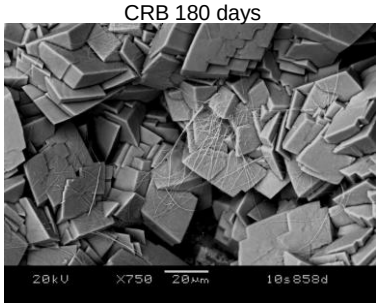
16

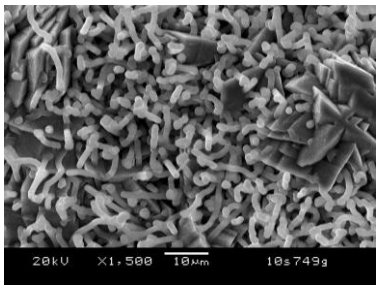
Results from Tests with Wet $scCO_2$ at Depths >2500 m

CRB 30 days



CRB 180 days





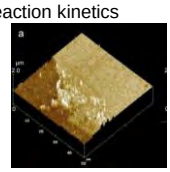
- Test Conditions
  - 137°C
  - 31.0 MPa (4496 psi)
- 30 Day Testing
  - Layers of discrete platelets covering nodules (ankerite)
  - Extensive in short period of time
- 180 Day Testing
  - Carbonate layer converts to rhodochrosite like structure
  - Chemistry indicates increase Fe content
  - Long cylindrical rods of amorphous silica

17

IS³ – In Situ Supercritical Suite

High-Pressure/ Temperature MAS-NMR
- Dissolution, ligand-exchange
- nucleation
- Mineral carbonation rxns & kinetics

Hyperbaric AFM
- Transformation mechanisms and reaction kinetics



Micromodel System

Real-Time Optical Spectroscopy Cell
- Role of water activity in mineral transformations
- Structure of species at solid-fluid interfaces

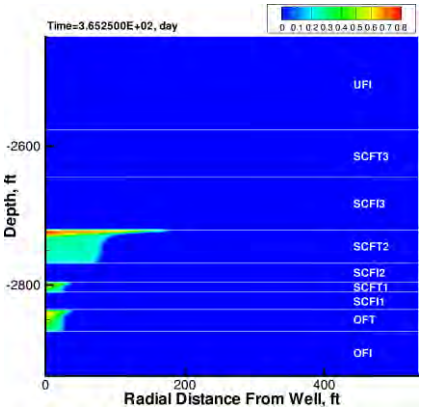
In Situ High Pressure XRD

18

Injection Permit Process

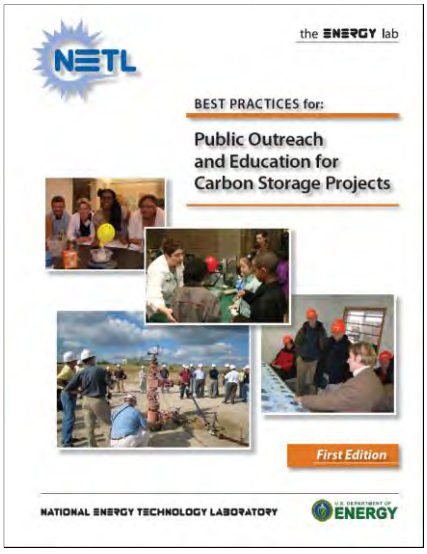
- In July 2008, Washington State adopted formal rules for geologic sequestration projects in the State UIC program (WAC 173-218-115)
  - Simplified subset of requirements for pilot studies (≤1000 MT CO_2)
  - Injection allowed only in reservoirs containing non-potable water
  - AKART required for CO_2 source
  - Borehole interconnection of "distinct" aquifers not allowed
  - 5-yr limit on permit
- SEPA process conducted in parallel with permit application process
- Seven month permit review & resolution process
- State issued DNS on 8/30/2010
- Public notice of intent to issue a discharge permit occurred 9/7/2010
- **Permit issued on 10/15/2010**
- Pre-injection activities in progress

STOMP-CO2 Simulation of 1000 MT Injection



19

Public Outreach



- Develop a formal public engagement plan with project partners and execute it
- Commit to regular, open, and transparent communication with stakeholder groups and local media

20

Battelle
The Business of Innovation

Conclusion

- Successful drilling and site characterization program has resulted in State Agency issuance of first CO_2 injection permit for a flood basalt CO_2 sequestration test
- **Additional collaborators welcome**
- Acknowledgements:
  - Big Sky Regional Carbon Partnership Program led by Montana State University
  - Partner Institutions:UI, Columbia University, INL, Oregon State University, WA Department of Natural Resources, Institut de Physique du Globe (France), National Geophysical Research Institute (India), Vernadsky Institute of Geochemistry and Analytical Chemistry (Russia)
  - Industrial Partners: Boise, Inc., Shell Exploration & Production Company, Portland General Electric, Schlumberger

Battelle
The Business of Innovation
BOISE

21

12. Roy Baria, EGS Energy Ltd, UK.

TECHNICAL CHALLENGES, LESSONS FROM ENGINNERED GEOTHERMAL SYSTEM FOR C C S

BY
ROY BARIA
egs | ENERGY Ltd ©

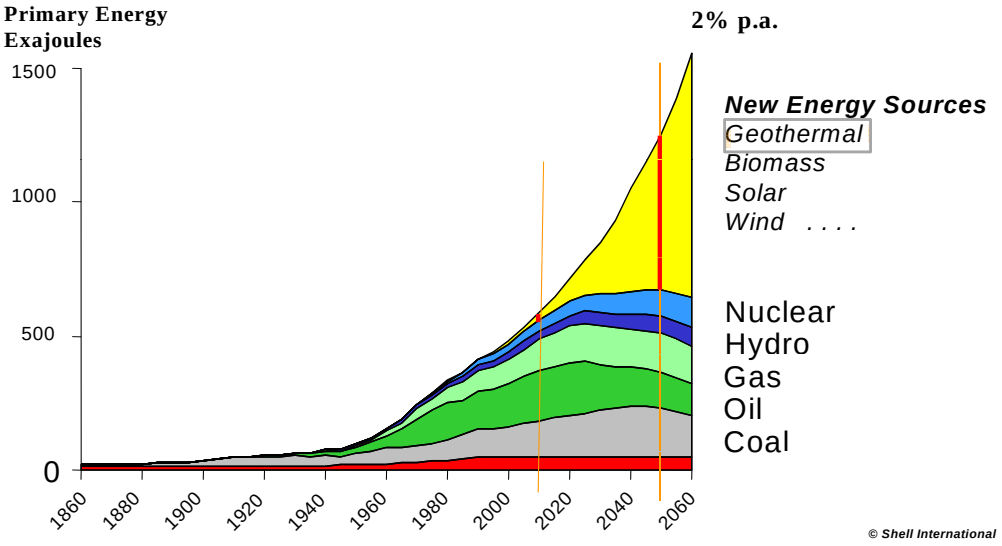
© EGS Energy Limited 2010

TALK OVERVIEW

1. Energy demand, supply trends & new sources
2. Definition of concepts and historical developments
3. Experience & knowledge acquired to date
4. Possible application to C C S

1. Future world energy demand and supply trends

Sustained Growth Scenario



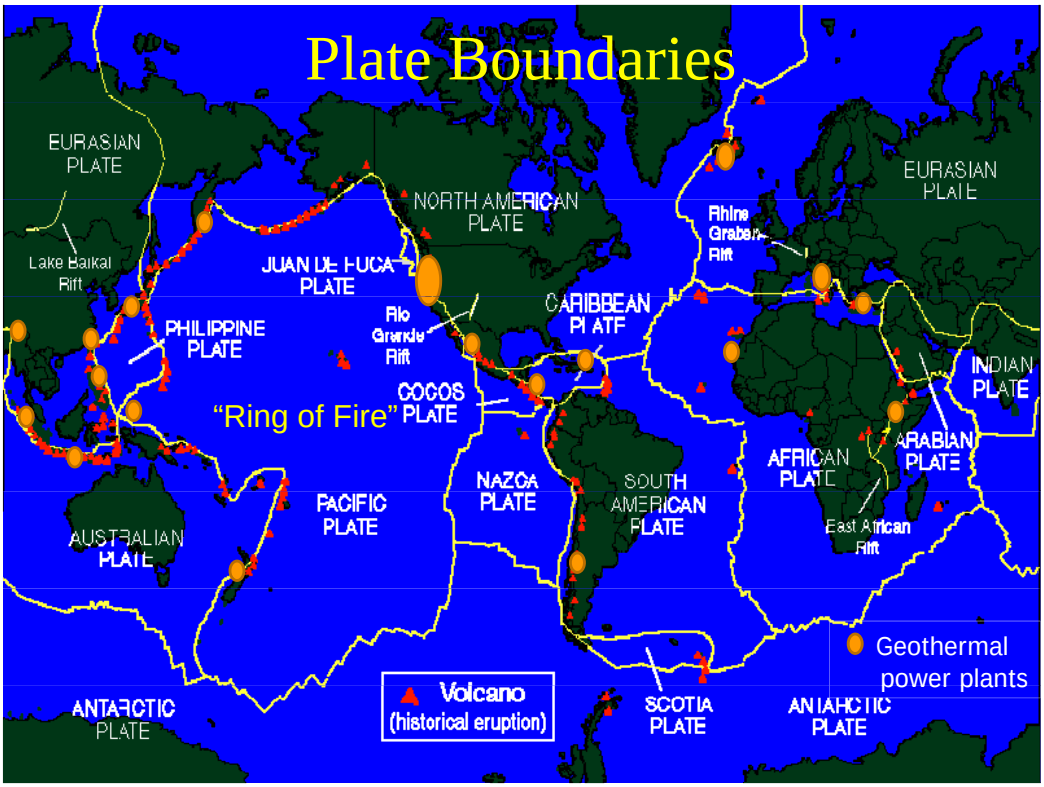
GEOTHERMAL ENERGY

1. HYDROTHERMAL ENERGY

2. ENGINEERED GEOTHERMAL SYSTEMS
- **a. Hot Dry Rock**
- **b. Hot Wet Rock**
- **c. Hot Fractured Rock**
- **d. Enhanced Geothermal System**

3. GROUND HEAT PUMP

© EGS Energy Limited 2010



OBSERVATION & CONCLUSION:

- Hydrothermal has an important role to play but is limited to margins of continental plates & thus has limited resource

- **E**ngineered **G**eothermal **S**ystem can enhance the resource ***significantly*** but complex technology is needed to exploit it.

© EGS Energy Limited 2010

GLOBAL ESTIMATE OF THE GEOTHERMAL POTENTIAL

1. HYDROTHERMAL = 1TWe

2. Non-electrical heating inc. (Ground heat pump) = 4.2TW(th),

3. EGS (under discussion) = 4.5TWe

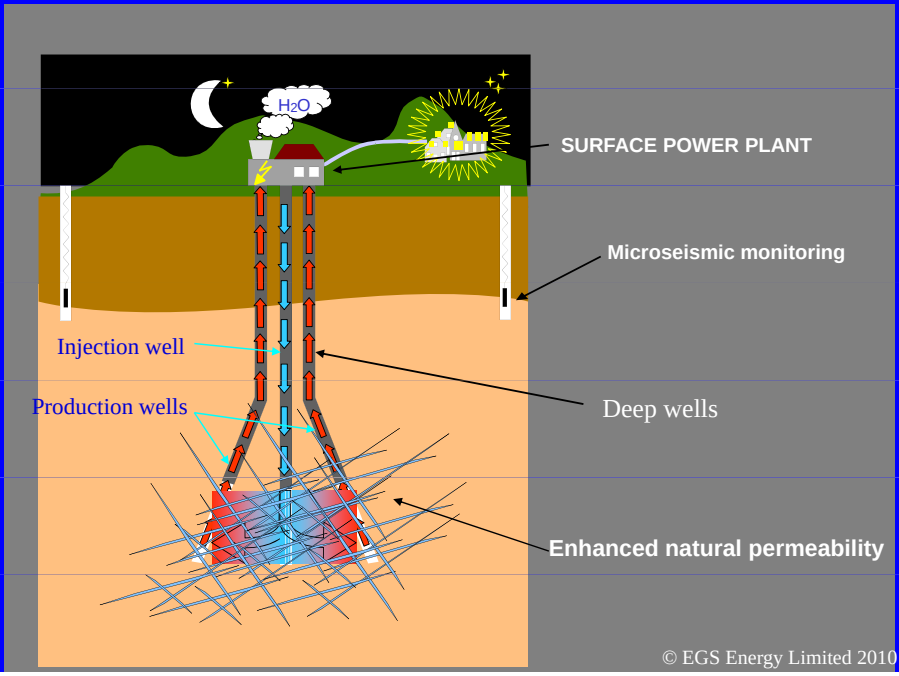
4. Others (super critical, magma) = 0.7TWe

2006 World wide electrical generation was ~ 2.1 TWe

Data from IEA/GIA web page

© EGS Energy Limited 2010

BASIC EGS CONCEPT



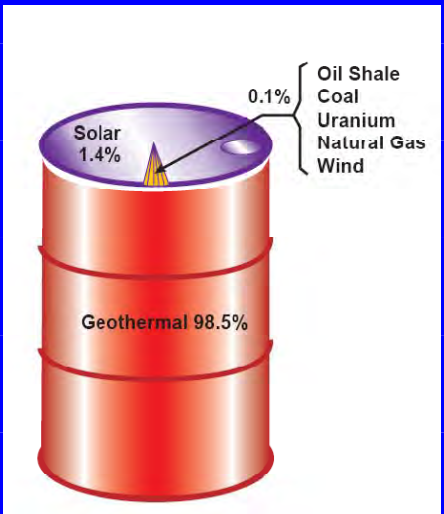
© EGS Energy Limited 2010

PERCEPTION OF STORED ENERGY IN THE ROCK-MASS

- If one cools 1 km^3 of granite from 200 °C by 20 °C, this is equivalent to:
- 15 000 GWh thermal or
- 10 MWe for 20 years or
- 1 275 000 tons of oil

© EGS Energy Limited 2010

US Energy Resource Base



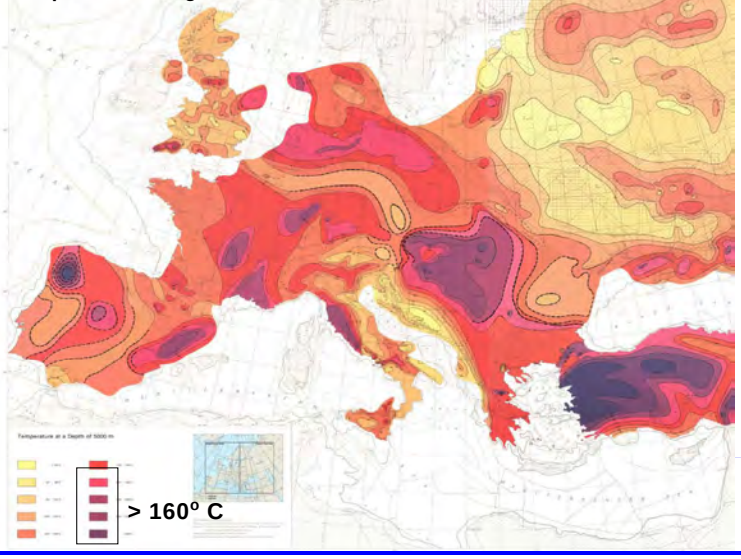
Sources:

Geothermal: MIT Report
Solar: "Characterization of U.S. Energy Resources and Reserves", Meridian Corporation 1989
Wind: "An Assessment of the Available Windy Land Area and Wind Energy Potential in the Contiguous United States", PNL 1991
Uranium: "Forward-Cost Uranium Reserves by State", EIA 2003
Coal: "International Energy Annual", EIA 2003
Natural Gas: "International Gas Reserves and Resources", EIA 2006

POTENTIAL RESOURCE IN W. EUROPE

Geothermal Energy - A Commitment to Sustainable Development

Utilize 5% of the rock volume located at a depth of 5000 m and with temperatures of greater than 160° C:



EU resources could :

*** support 130 GWe of power generation capacity**

*** generate ~900 TWh (E 45 bln/yr - market)**

*** similar to 1995 electricity generation of Europe's nuclear capacity.**

*** 35% of current EU consumption.**

2. Definition of EGS concepts and historical developments

RECAP WHAT WE HAVE LEARNT !
CONCEPTS ON HOW RESERVOIRS ARE CREATED

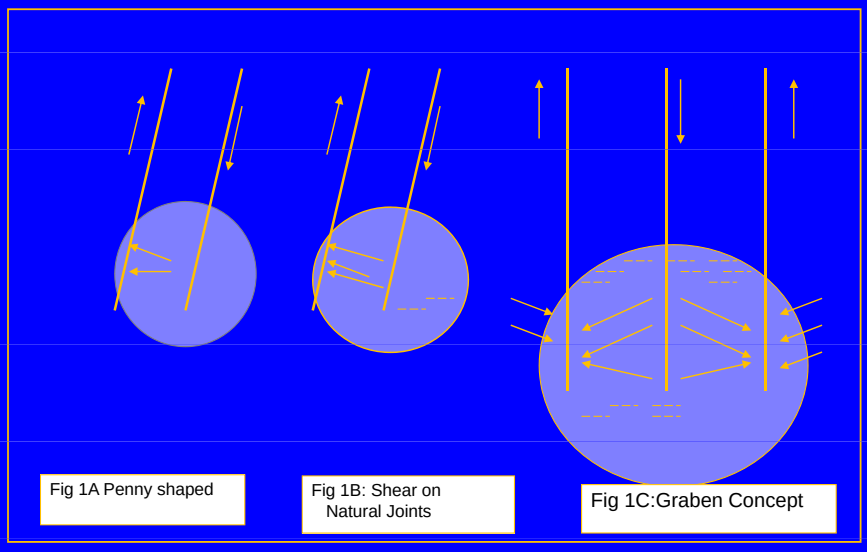


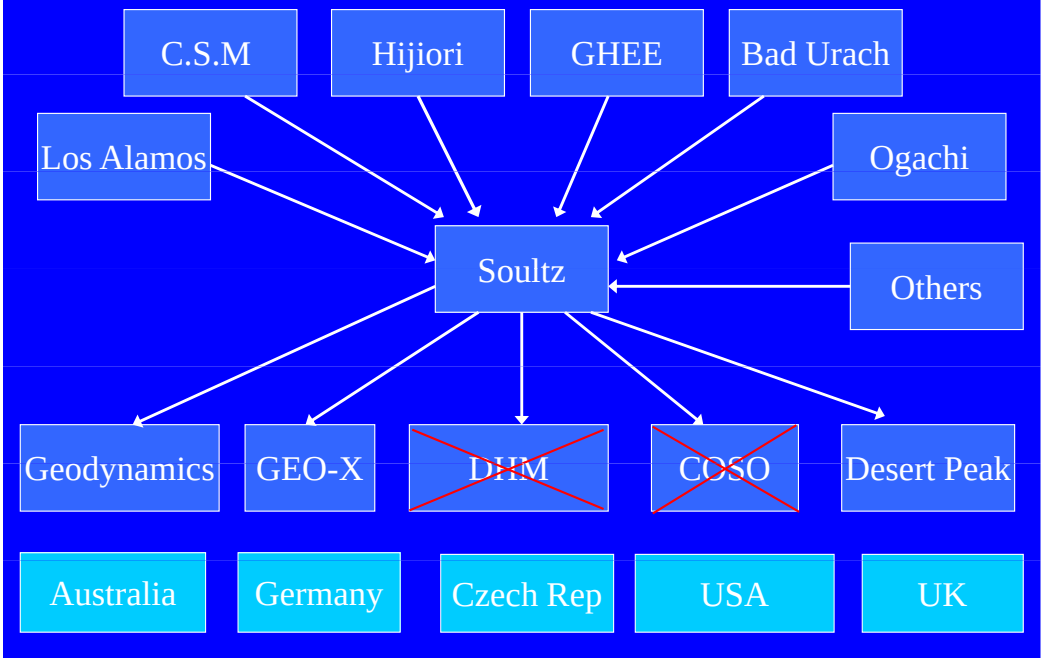
Fig 1A Penny shaped

Fig 1B: Shear on Natural Joints

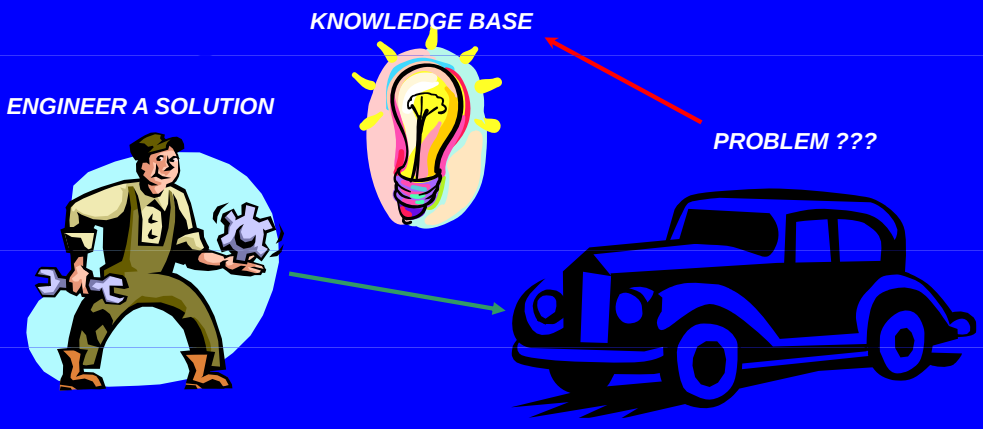
Fig 1C:Graben Concept

© EGS Energy Limited 2010

1987-2007 Soultz European Project ?



ACQUIRED ENOUGH KNOWLEDGE TO BE ABLE TO SOLVE MOST DIFFICULTIES



© EGS Energy Limited 2010

3. Experience & knowledge acquired to date

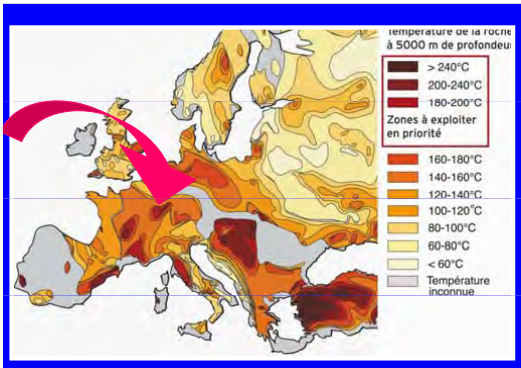
ECONOMIC REQUIREMENTS

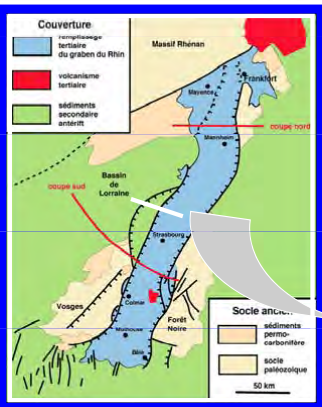
1. DRIVEN BY ECONOMICS: **Target 5-6 MWe /module**

- LIFE OF THE SYSTEM: ~20 Years
- TEMP/DEPTH OF THE WELLS: ~ 200° C
- SEPARATION BETWEEN WELLS: ~600 m
- PRODUCTION FLOW RATE: ~75 Kg/s
- FLOW IMPEDANCE: 0.1MPa/l/s
- WATER LOSS: 10% MAX
- THERMAL DRAWDOWN 10%
- CONTACT SURFACE AREA: 10 million m^2
- RESERVOIR ROCK VOLUME 300 million m^3
- INTEREST RATE FOR THE CAPITAL: 5%
- SUPPORT : No CO_2 levy support etc

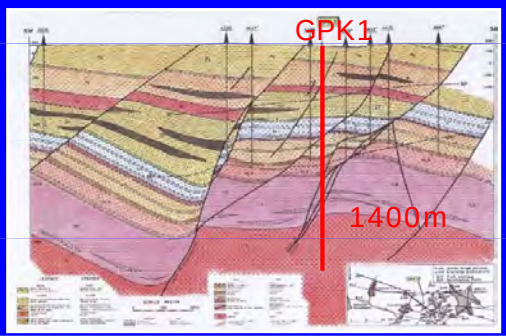
Economic study by Shock ~1975 for UK DoE

© EGS Energy Limited 2010





Location of Soultz Project



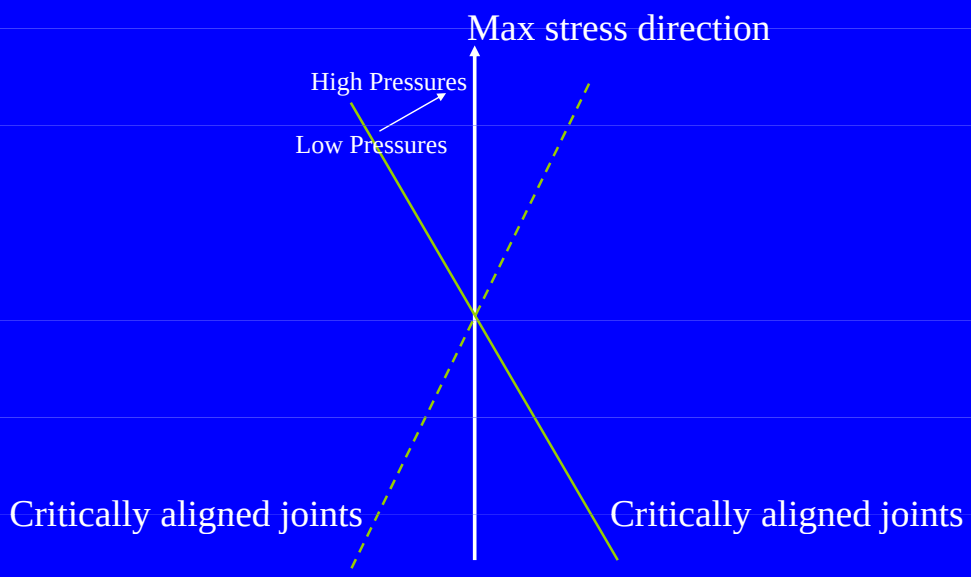
Pechelbronn oil field shallow basement

Rhine Graben Tectonics

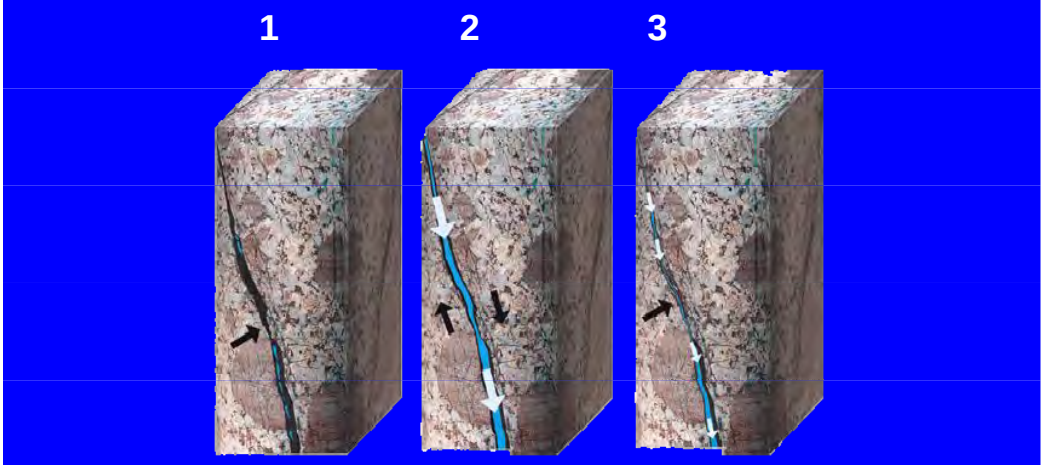
© EGS Energy Limited 2010

RESERVOIR CREATION MECHANISMS

PREDOMINANT MODE DURING STIMULATION IS *SHEAR*



© EGS Energy Limited 2010



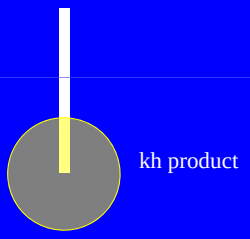
© EGS Energy Limited 2010

LET'S LOOK AT THE PURPOSE OF STIMULATION

TWO REASONS:

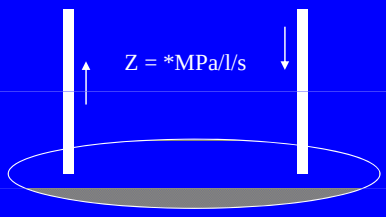
1. IMPROVE NEAR WELLBORE IMPEDANCE

High flow rate, explosives, high viscosity jell, jell with proppant, acids etc



2. IMPROVE PERMEABILITY BETWEEN THE WELLS

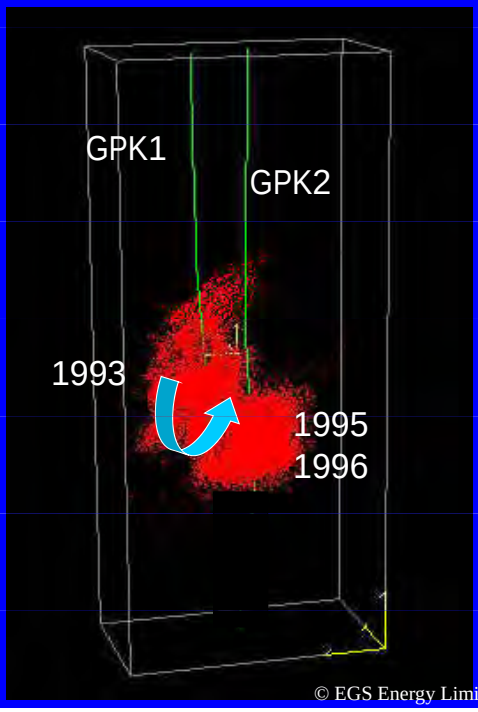
High flow rate water, jells 30-1000cp, jell with proppant, brine, acids, new concept?



© EGS Energy Limited 2010

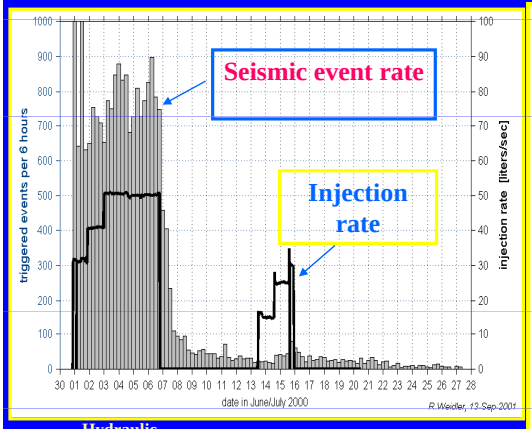
4 months Circulation Test in 1997

- Duration : 4 months
- Separation of wells: 450 m
- Injection in GPK1 : 25 l/s
- Injection Pressure 4 MPa-> 2MPA
- Production in GPK2 : 25 l/s
- 142°C output temperature
- 244 000 m³ fluid circulated
- 250 – 220 kW used
- Production 10-11MWth
- Impedance 0.23 MP/l/s
- Control corrosion & precipitation
- Zero water loss



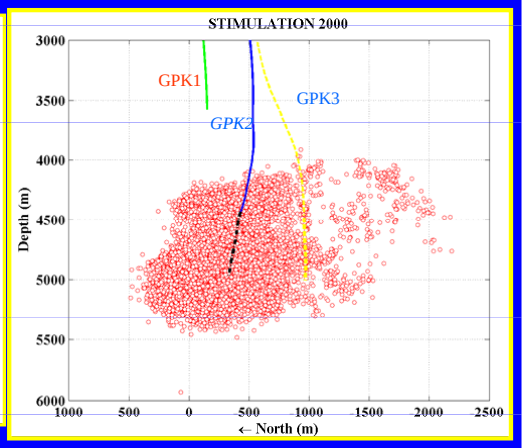
© EGS Energy Limited 2010

Hydraulic Stimulation of GPK2 in 2000



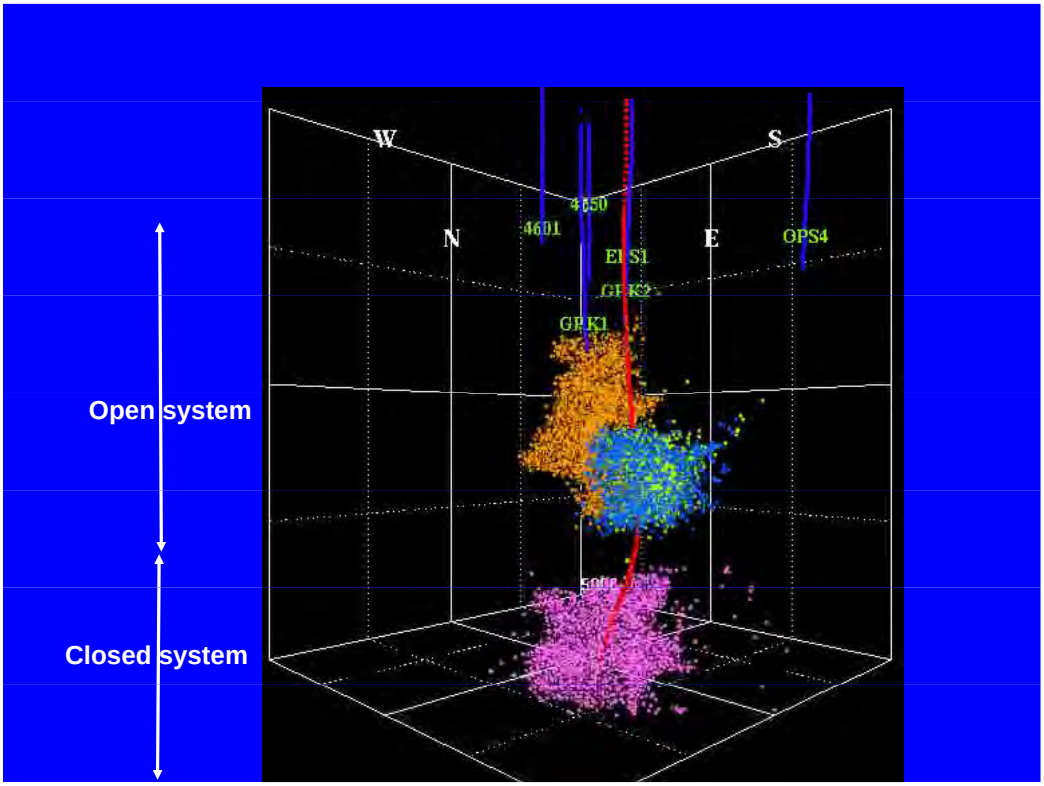
Hydraulic stimulation

Injectivity test

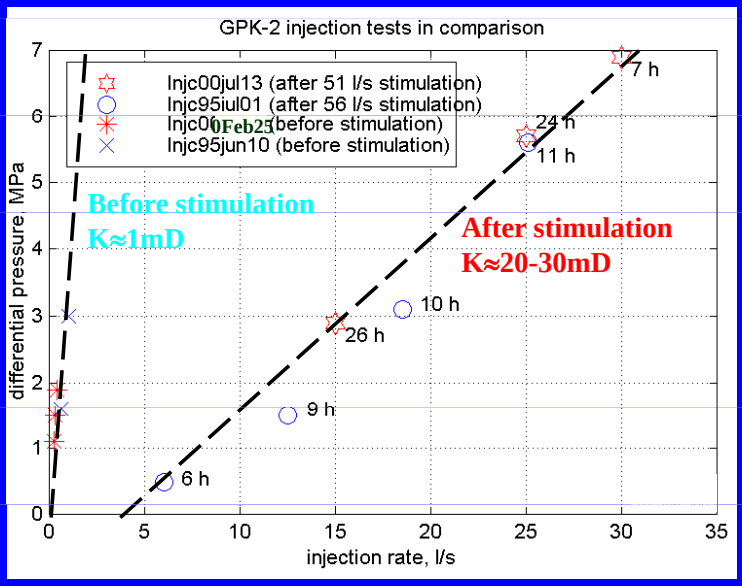


30,000 triggered events ➡ **14,000 located events**

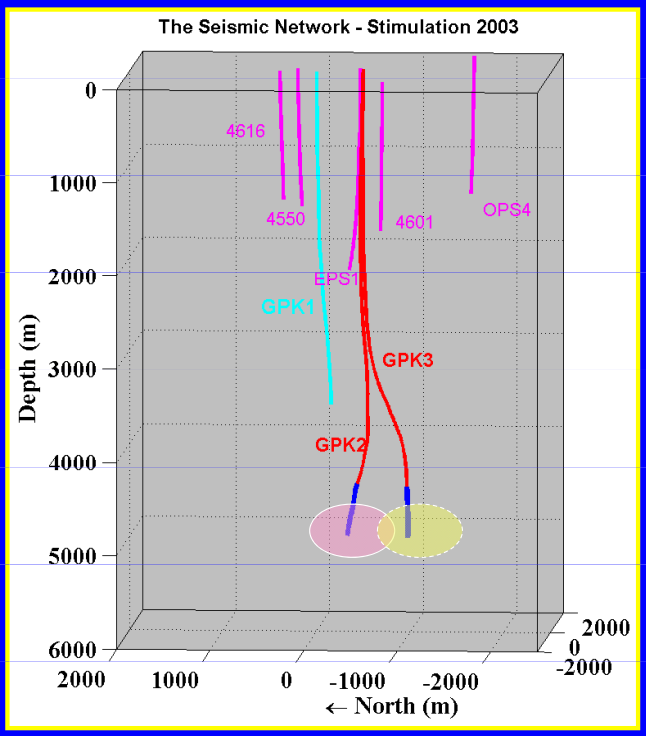
© EGS Energy Limited 2010



Injection test overpressures: 1995 & 2000

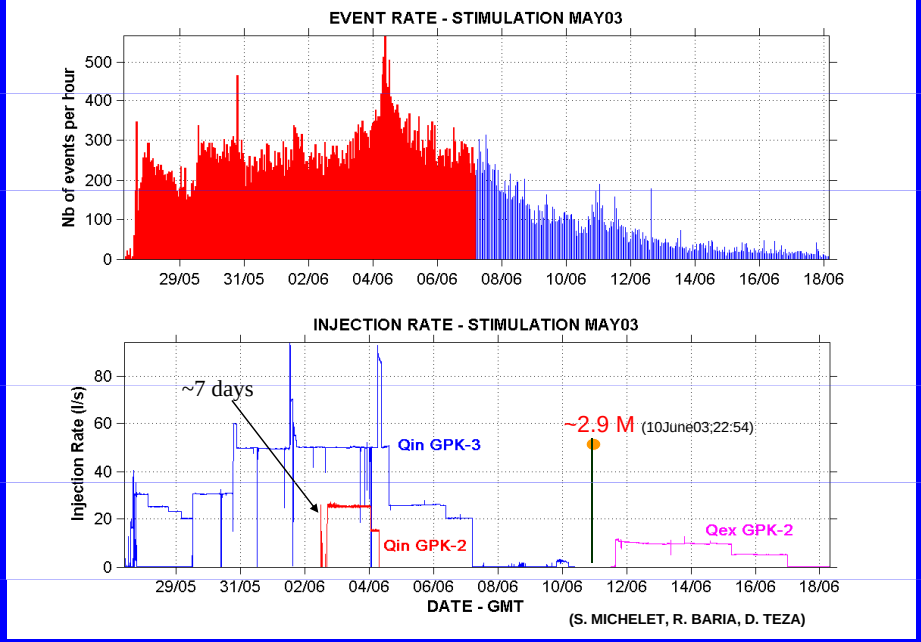


>> internal reservoir permeability was strongly enhanced (x20-30)

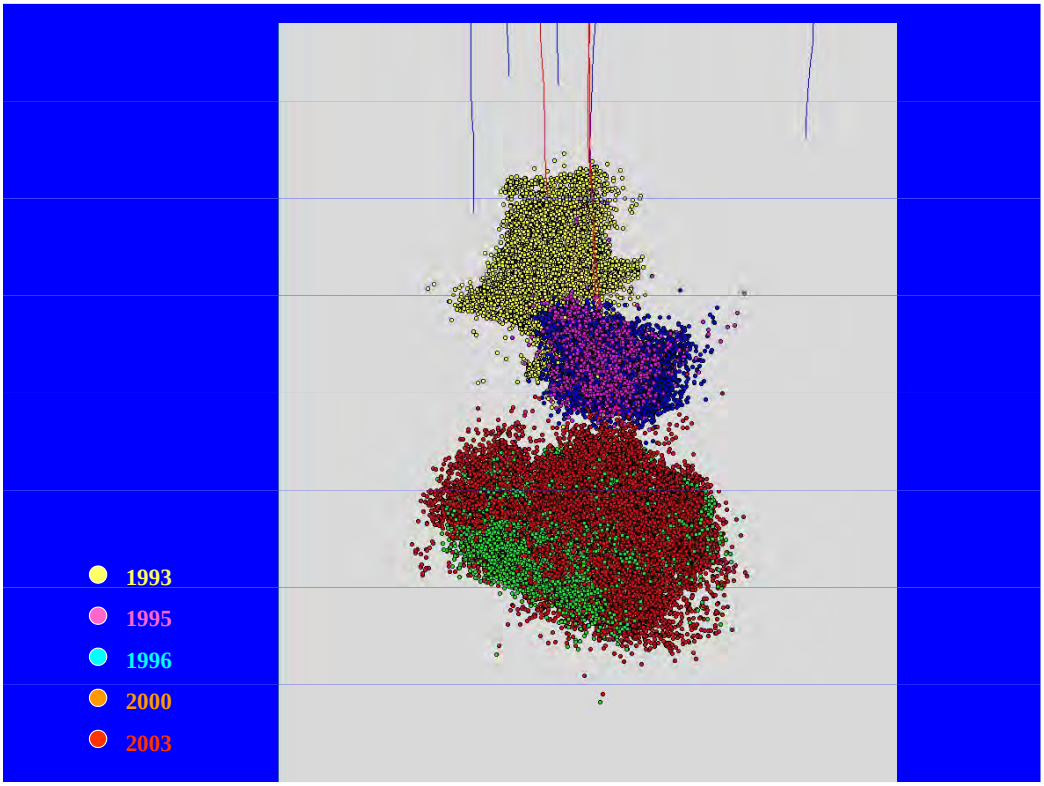


© EGS Energy Limited 2010

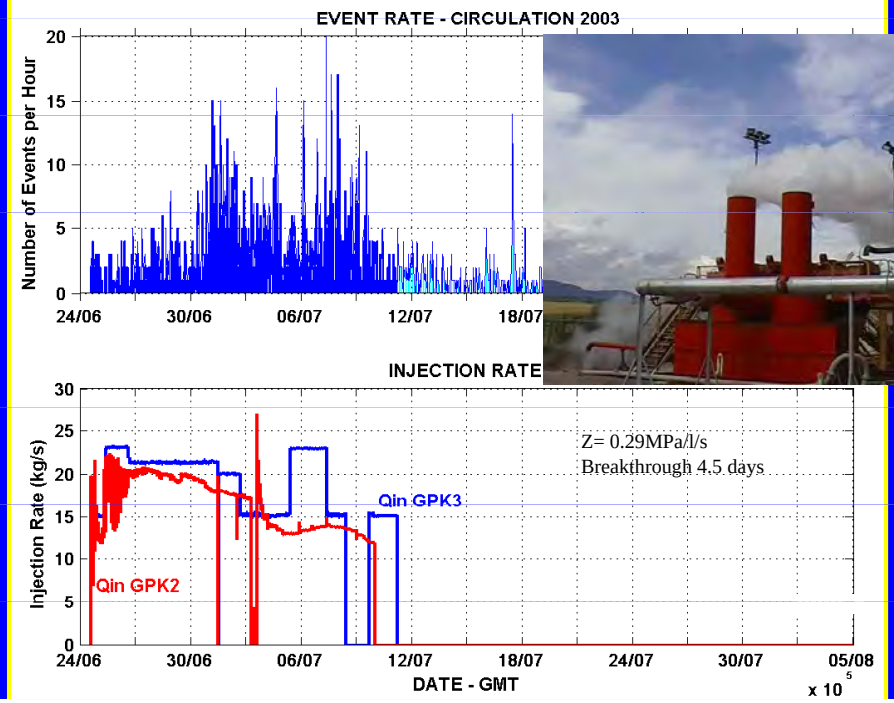
GPK3 STIMULATION IN 2003



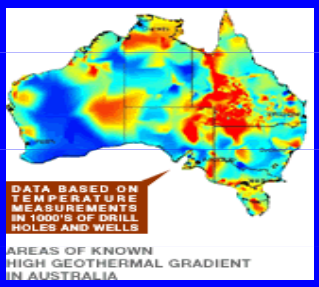
© EGS Energy Limited 2010



3 weeks of circulation between GPK2 & GPK3



Commercial exploitation of EGS



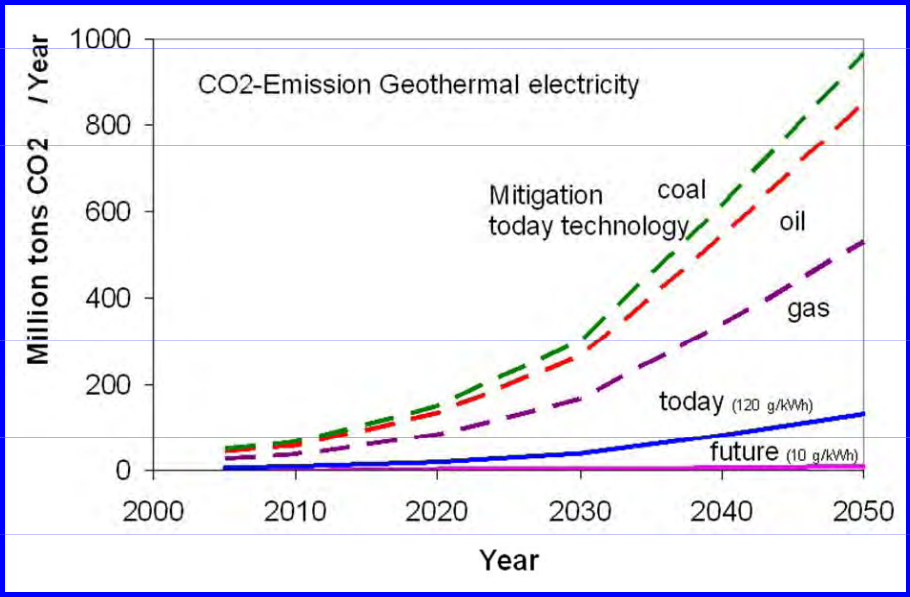
Geodynamics in Australia
http://www.geodynamics.com
.+ **eight other companies**

GEO-X in Germany
http://geox.quintx.de
+ Four others programmes

ORMAT
Desert Peak
Reno
NEVADA
USA

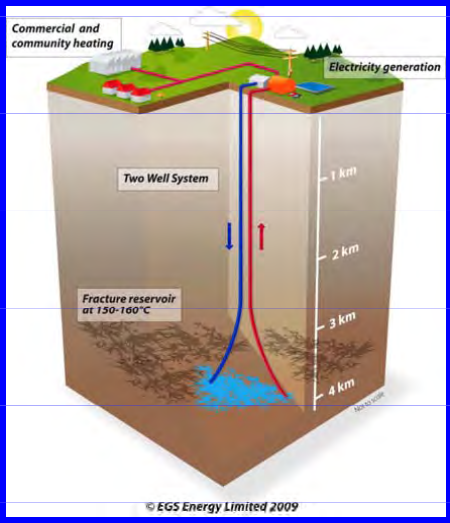
egs ENERGY Ltd in UK
http://www.egs-energy.com
+ three others programmes

Mitigation potential of geothermal power plants in the world based on data of Table 6 and assumptions for emission of 120 g CO2/ kWh for today and 10 g CO2/kWh for future technology.



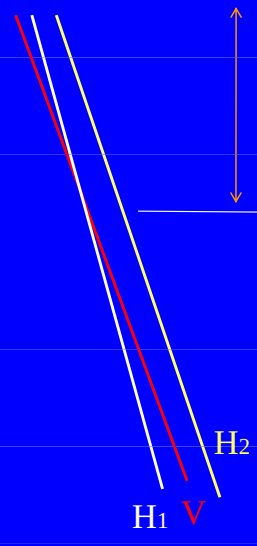
© EGS Energy Limited 2010

Schematic of the proposed commercial EGS plant in the UK.



© EGS Energy Limited 2010 32

POSSIBLE APPLICATION FOR CCS



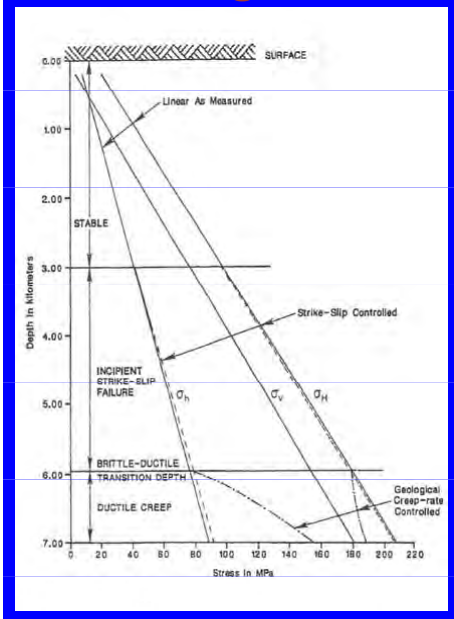
NORMAL FAULTING

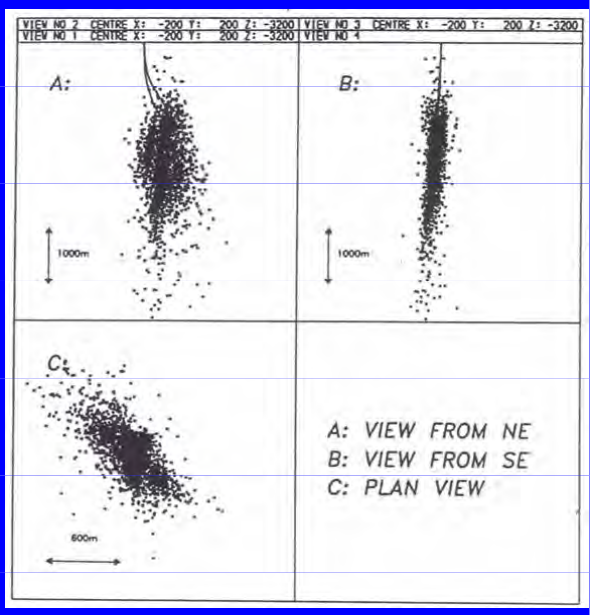
Fracture growth : Horizontal to upward

STRIKE-SLIP FAULTING

Fracture growth : Horizontal to downwards

Reservoir growth

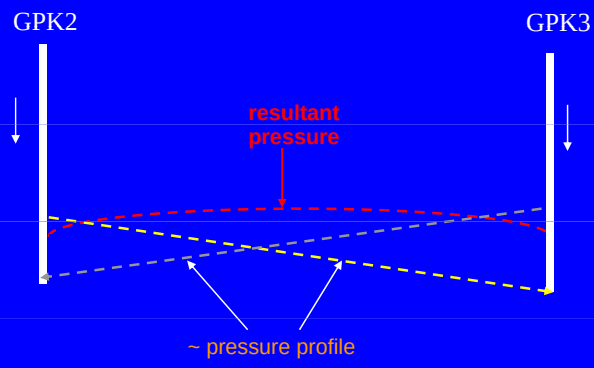


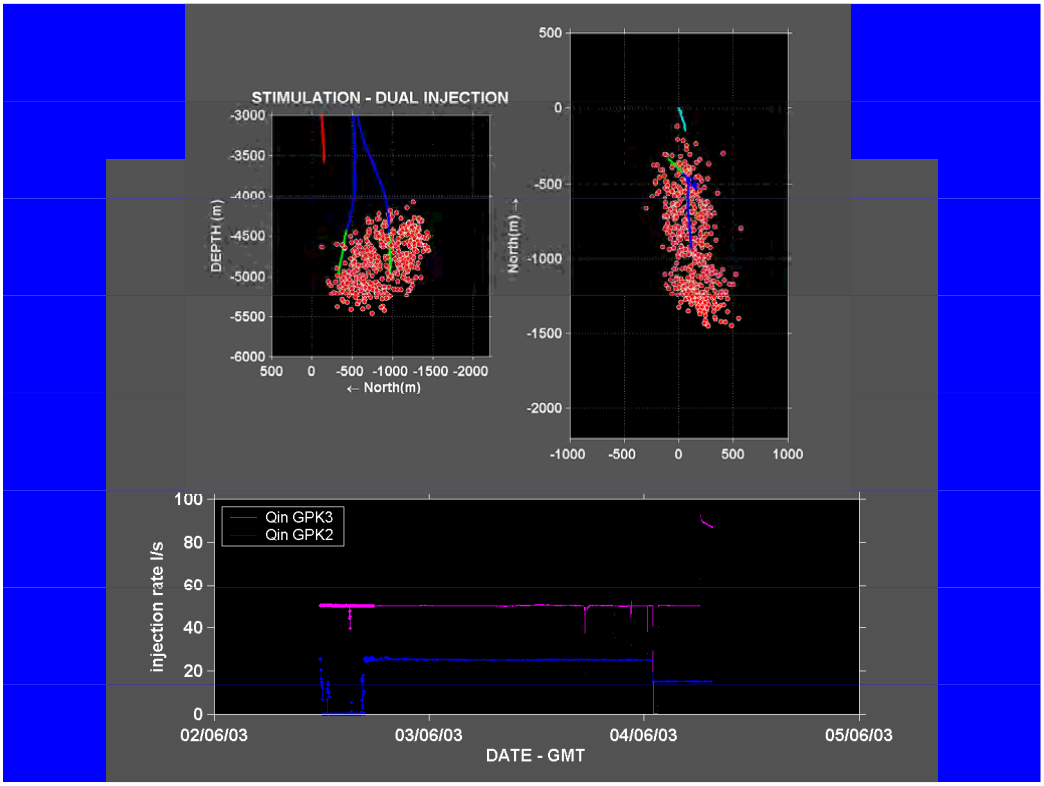


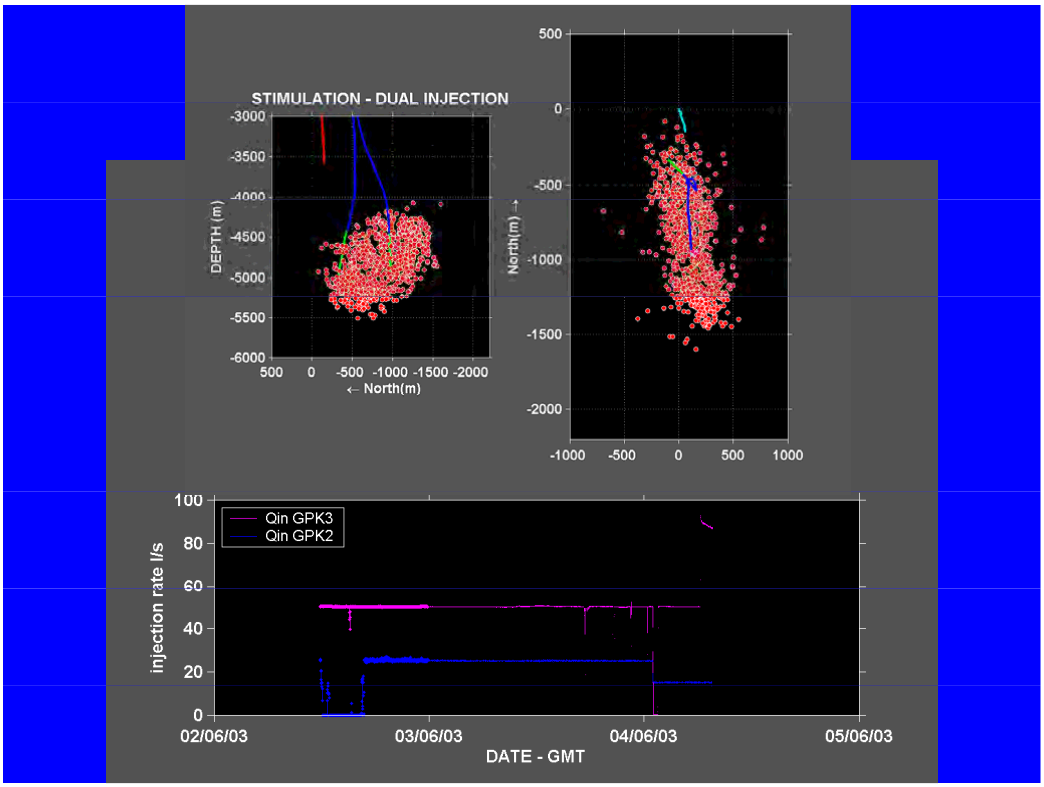
© EGS Energy Limited 2010

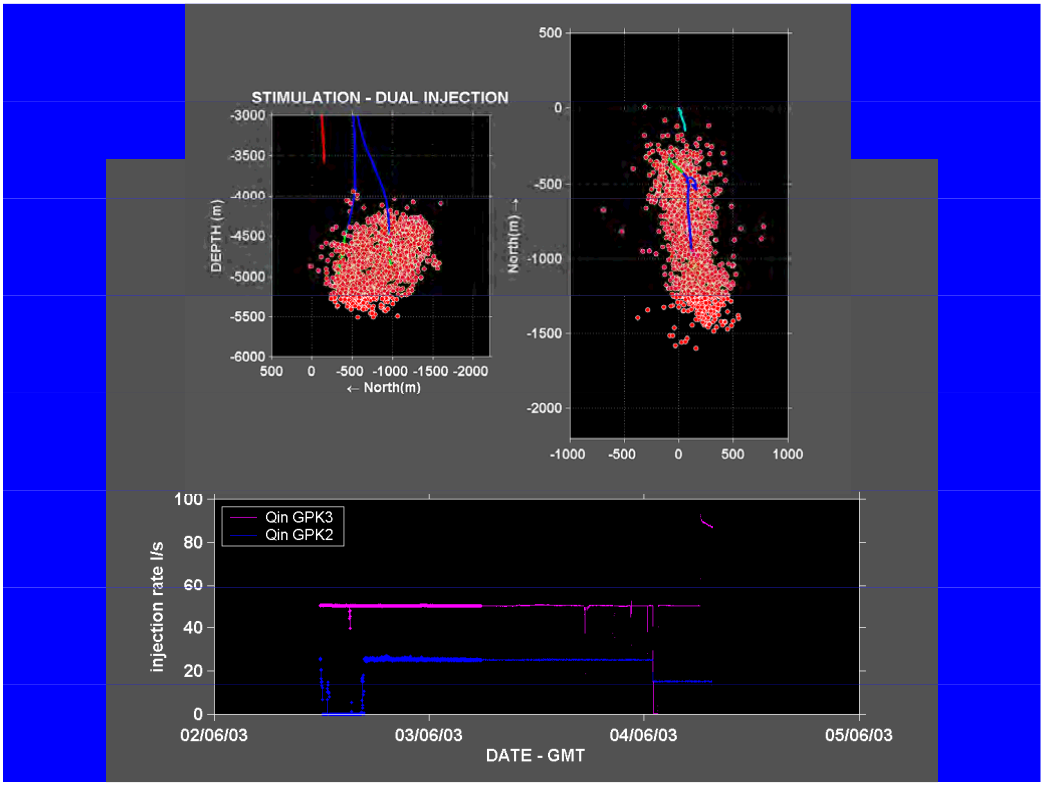
RECENTLY DEVELOPED TECHNIQUE (FOCUSSED STIMULATION)

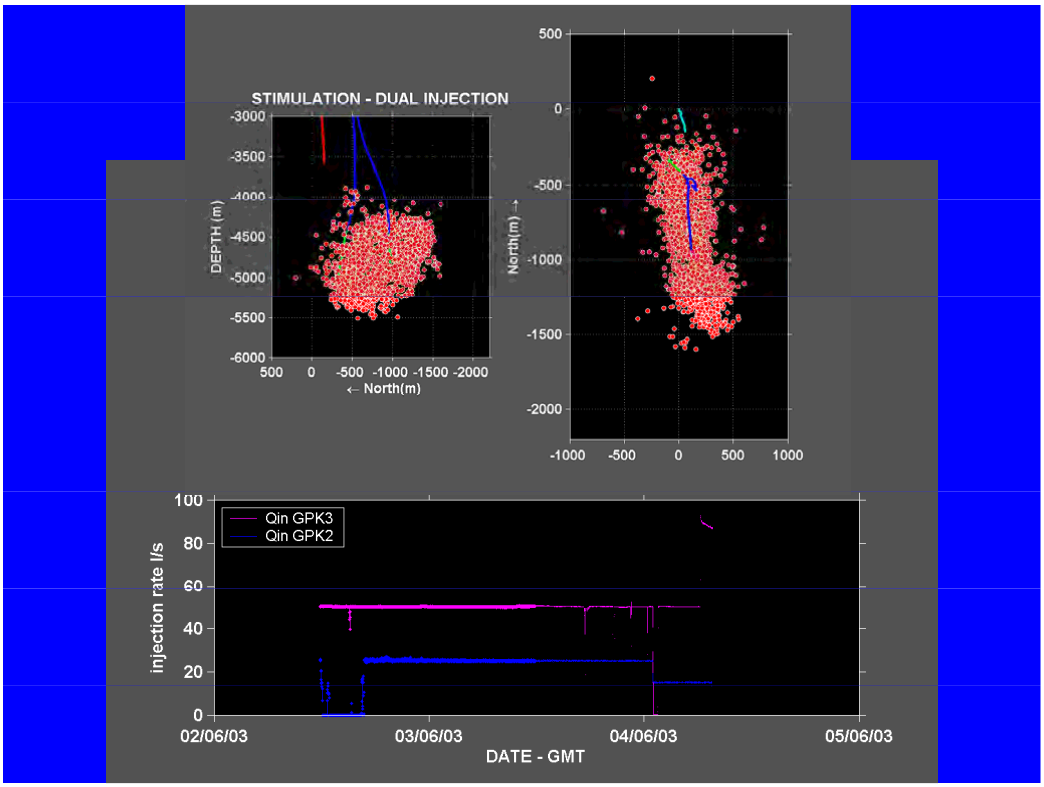
INJECTING IN TWO WELLS SIMULTANEOUSLY

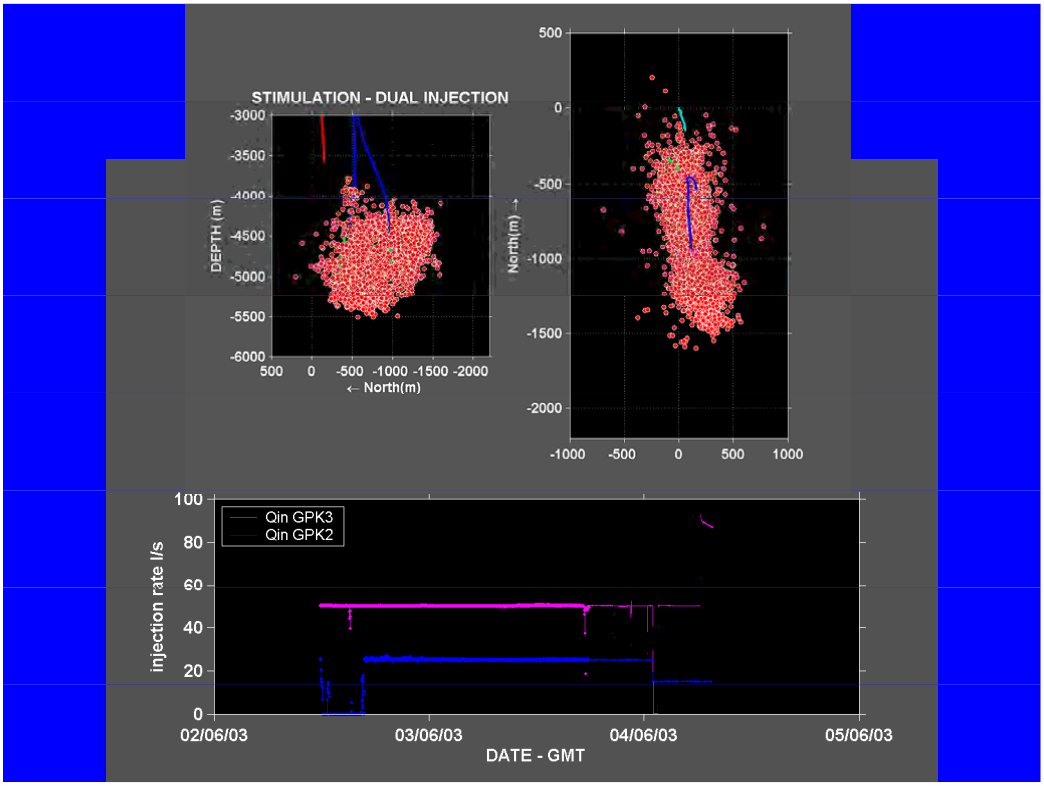


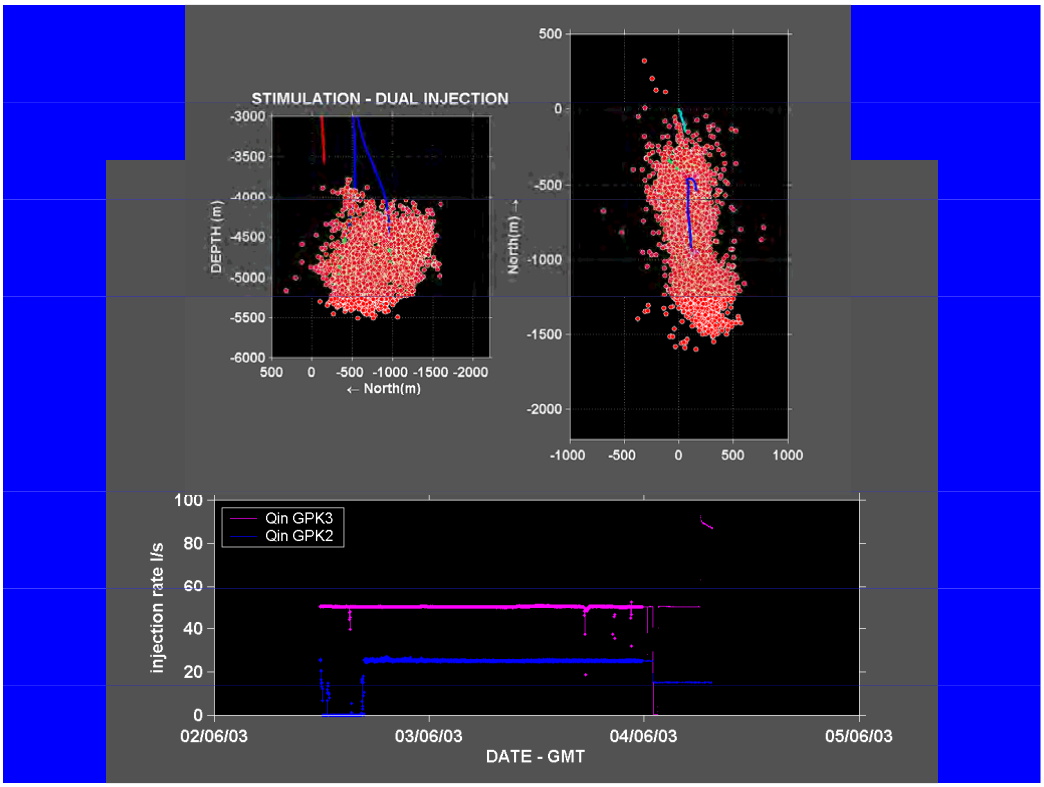



STIMULATION - DUAL INJECTION
DEPTH (m)
-3000
-3500
-4000
-4500
-5000
-5500
-6000
500 0 -500 -1000 -1500 -2000
← North(m)
North(m) →
500
0
-500
-1000
-1500
-2000
-1000 -500 0 500 1000
Qin GPK3
Qin GPK2
injection rate l/s
100
80
60
40
20
0
02/06/03
03/06/03
04/06/03
05/06/03
DATE - GMT

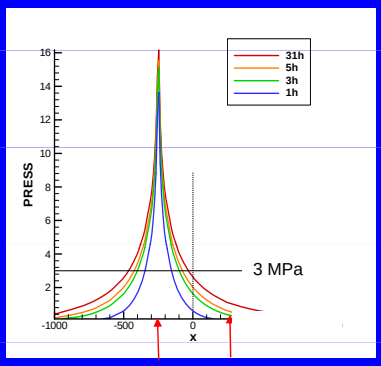

STIMULATION - DUAL INJECTION
DEPTH (m)
-3000
-3500
-4000
-4500
-5000
-5500
-6000
500 0 -500 -1000 -1500 -2000
← North(m)
North(m) →
500
0
-500
-1000
-1500
-2000
-1000 -500 0 500 1000
Qin GPK3
Qin GPK2
injection rate l/s
100
80
60
40
20
0
02/06/03
03/06/03
04/06/03
05/06/03
DATE - GMT


STIMULATION - DUAL INJECTION
DEPTH (m)
-3000
-3500
-4000
-4500
-5000
-5500
-6000
500 0 -500 -1000 -1500 -2000
← North(m)
North(m) →
500
0
-500
-1000
-1500
-2000
-1000 -500 0 500 1000
Qin GPK3
Qin GPK2
injection rate l/s
100
80
60
40
20
0
02/06/03
03/06/03
04/06/03
05/06/03
DATE - GMT

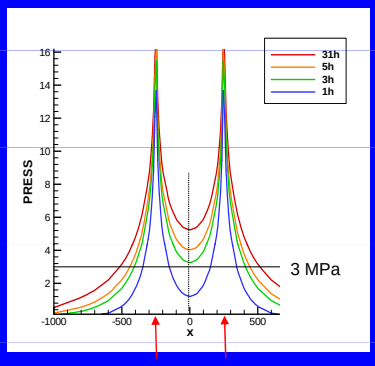

STIMULATION - DUAL INJECTION
DEPTH (m)
-3000
-3500
-4000
-4500
-5000
-5500
-6000
500 0 -500 -1000 -1500 -2000
← North(m)
North(m) →
500
0
-500
-1000
-1500
-2000
-1000 -500 0 500 1000
Qin GPK3
Qin GPK2
injection rate l/s
100
80
60
40
20
0
02/06/03
03/06/03
04/06/03
05/06/03
DATE - GMT



Case 1: Single well injection



Case 2: Two well injection "focused"



Initial far-field permeability = 10 mD
Initial near well permeability = 1 D
Injection flow = 100 l/s

3 MPa ISOBARS AFTER 30 h of injection (nearly steady state)

Courtesy of Geowatt

FIN

13. A. Bunger – CSIRO, Australia.

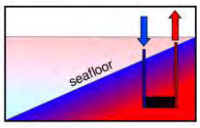
www.csiro.au

Creating surface area and conductivity in ultramafic rocks by using extremely closely spaced hydraulic fractures

Andrew Bunger, Rob Jeffrey, Xi Zhang
CSIRO Earth Science and Resource Engineering
Melbourne, Australia

CCS Oman, 8-10 January 2011, Muscat, Oman

CSIRO



From: Kelemen and Matter, PNAS, 2008

Motivation

An in situ transformation
from rock mass to reactor

by hydraulic fracture stimulation that supports rock mass pre-heating

and creation of and access to reactive surface area

This Presentation

What is hydraulic fracturing?

How do hydraulic fractures tend to behave?

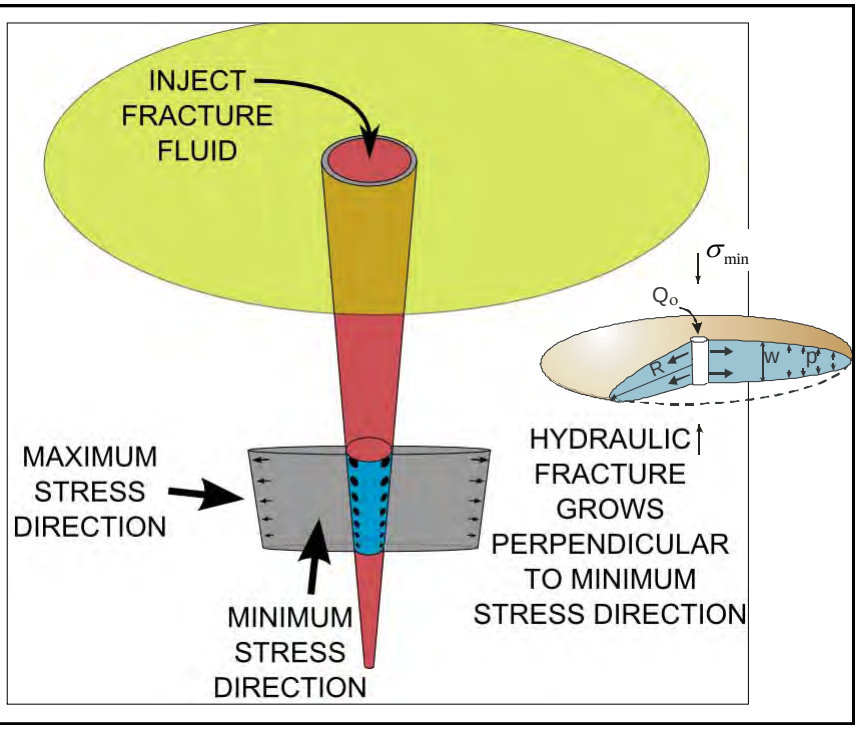
What lessons can be learned from…

Waste disposal?

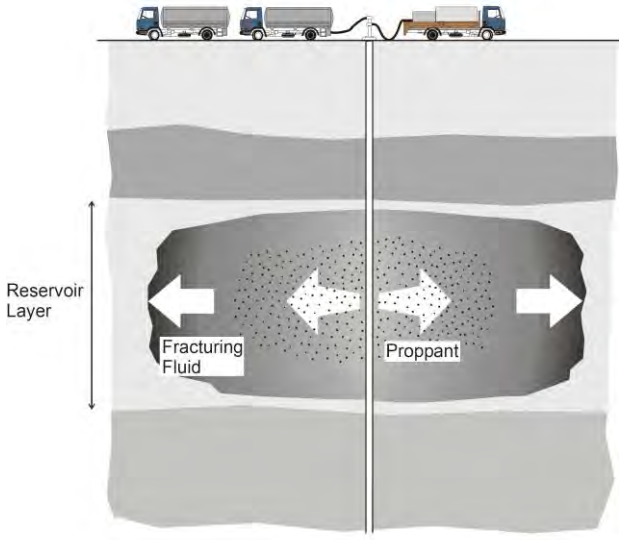
Geothermal?

Shale gas?

What is the most promising approach for in situ mineralisation?



Traditional Hydraulic Fracturing



From: Adachi, PhD Thesis, 2001

From: http://www.demotix.com/news/390106/hydraulic-fracturing-working-under-pressure

Personality of Hydraulic Fractures

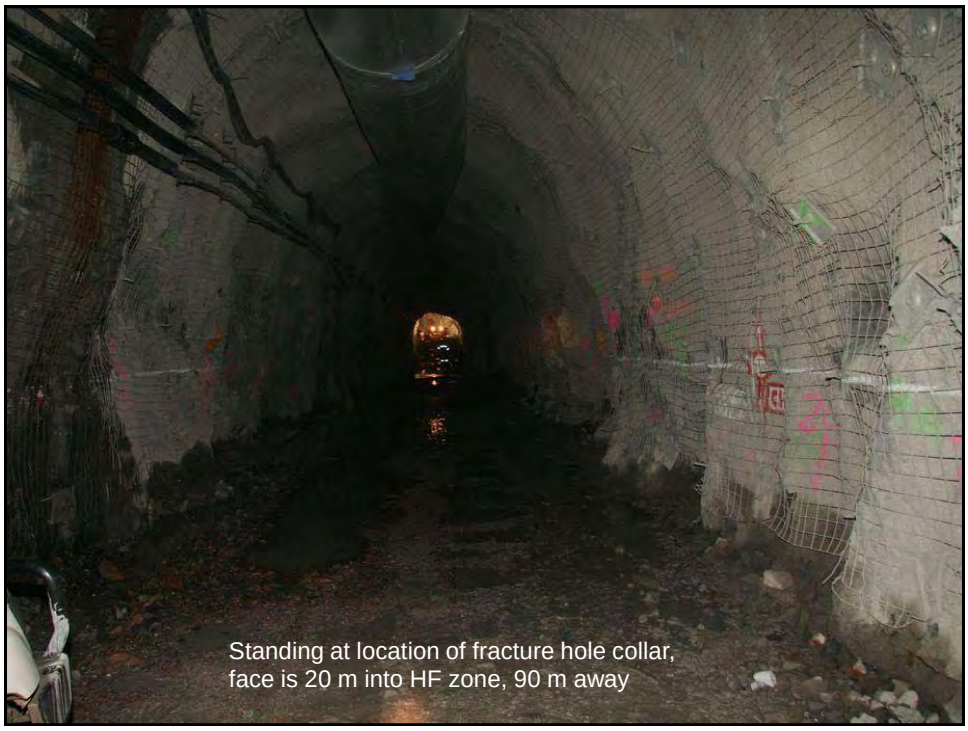
- They are lazy (energy minimising)
- Result: They take the easiest path in light of
  - Stress
  - Structure
  - Flow
- Resistance to flow less for larger channels – winners win
- Our observations in mine through experiments consistent with this paradigm (Jeffrey et al., SPE Journal, 2009)
  - Single dominant channels – 2-3 strands at most
  - Stair-stepping morphology as stress and structure control

$$q = -\frac{w^3}{12\mu}\frac{\partial p}{\partial x}$$

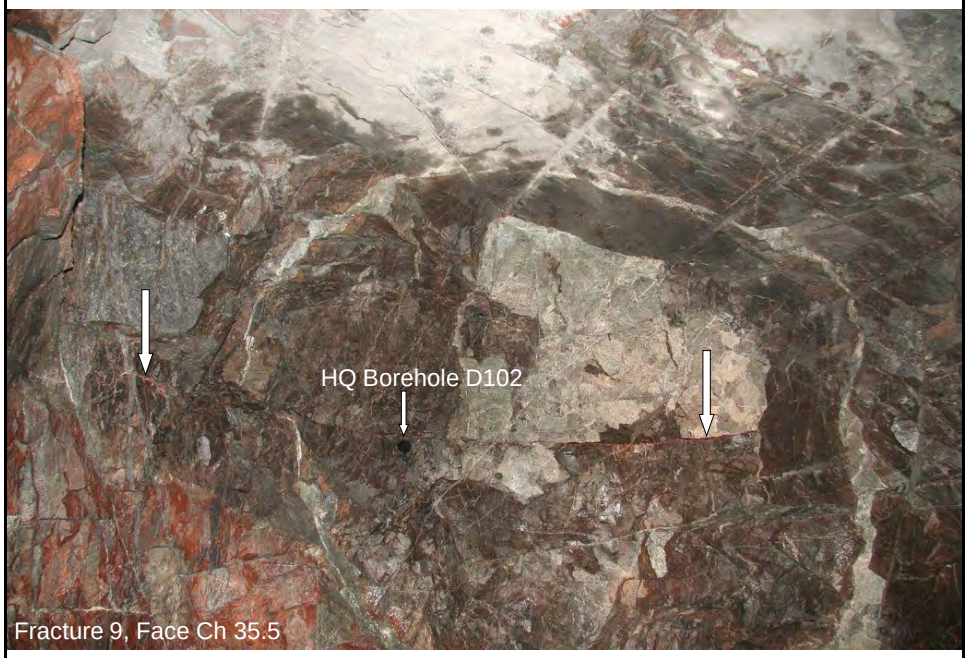
$$\text{fluid flux} = \frac{1}{\text{resistance to flow}} \times \text{fluid pressure gradient}$$

$$\text{resistance to flow} = \frac{12 \times \text{fluid viscosity}}{(\text{fracture opening})^3}$$

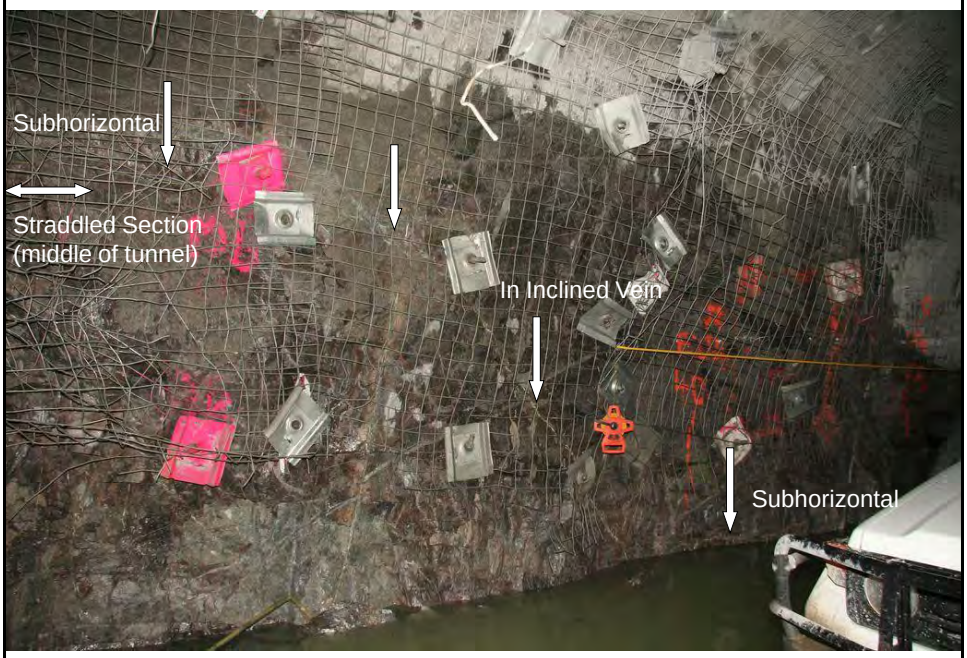
↑ Flow preference to larger fractures

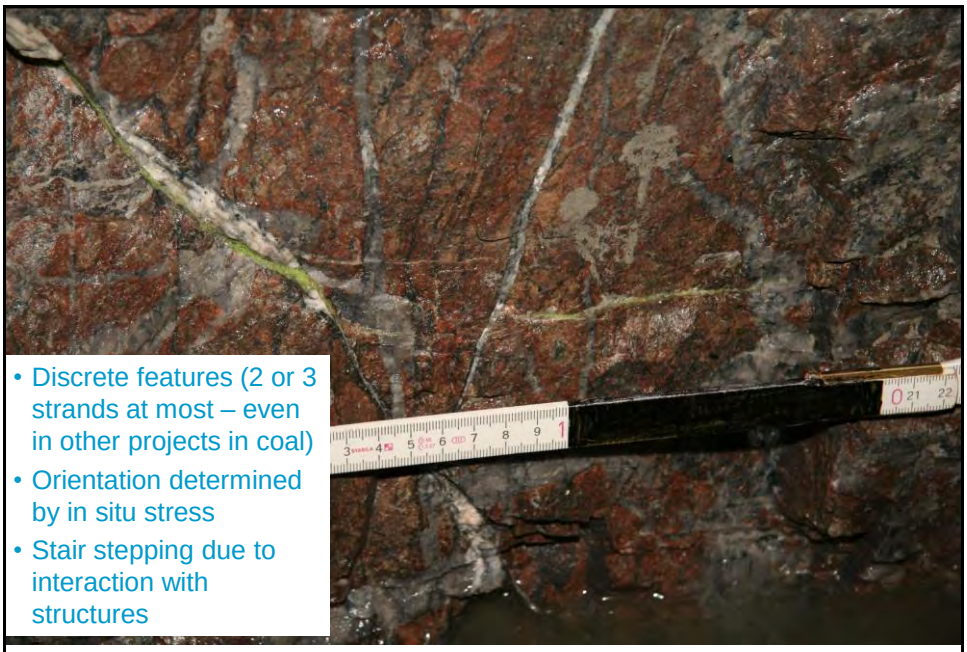


Drill Jumbo working at the face, Ch 54



Fracture 9, Face Ch 35.5





Green plastic proppant in hydraulic fracture placed during E48 consortium project (Jeffrey et al., SPE Journal, 2009)

Single planar fracture probably not sufficient for in situ mineralisation

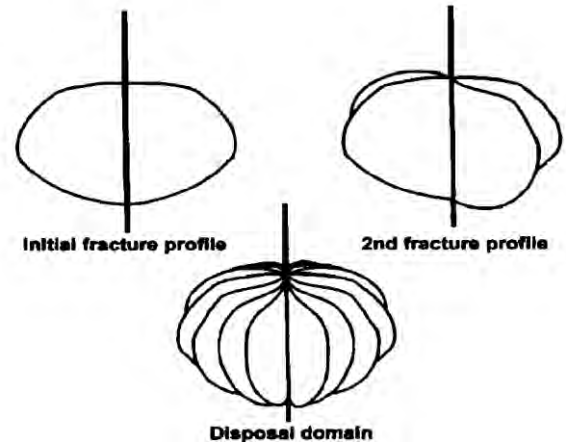
What are industrial analogues for multiple fracturing?

1

Waste Injection

“Disposal Domain”

Waste Injection: “Disposal Domain”



From: Willson et al., 37th USRM, 1999

Disposal Domain for CCS: Problems

From Abou Sayed et al. 2003:

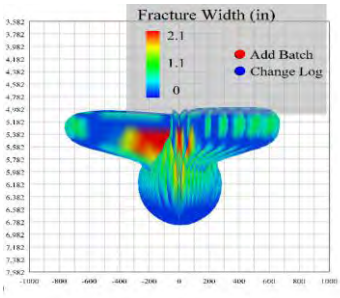
Will work for

- Weak, soft rocks
- Highly permeable rocks
- Minimum Stress ~ Intermediate Stress

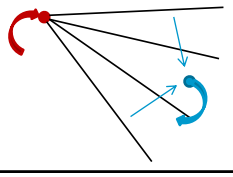
Not likely to be conditions in mafic/ultramafic rock masses

Most importantly

Spoke geometry fine for disposal, not ideal for circulation



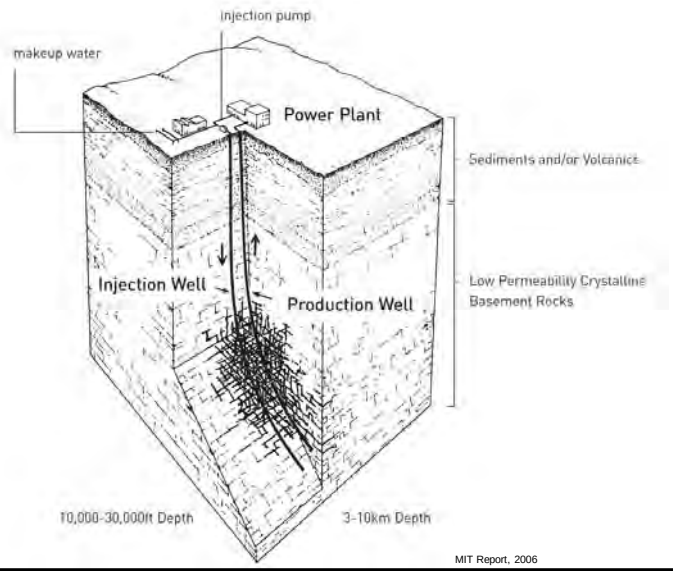
SPE/IADC 79804



2

Engineered Geothermal Systems

Engineered Geothermal Systems (EGS)



MIT Report, 2006

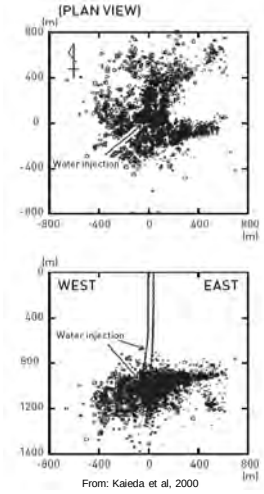
Geothermal: "Stimulated Volume" Part 1

Approach:

- Long duration, high volume, **low flow rate** and pressure injection into **long open hole section**
- **Monitor** microseismic events
- **Drill** next well into microseismic cloud

Is it the right approach?

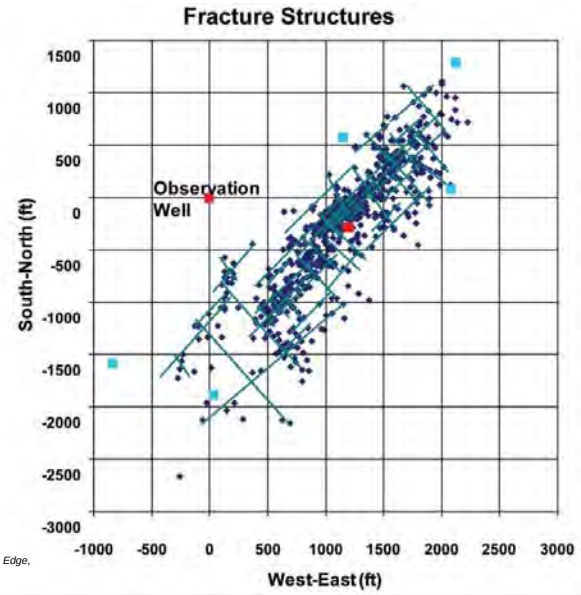
- Consider the **biggest problem**
  Flow localises to most conductive feature
- Consider the **limitations** from wellbore conditions
  Hot, broken open hole
- Consider **purpose**
  Is it compatible with CCS need to **rapidly heat** the rock?



From: Kaieda et al, 2000

3
Shale Gas

Shale Gas: "Stimulated Volume" Part 2



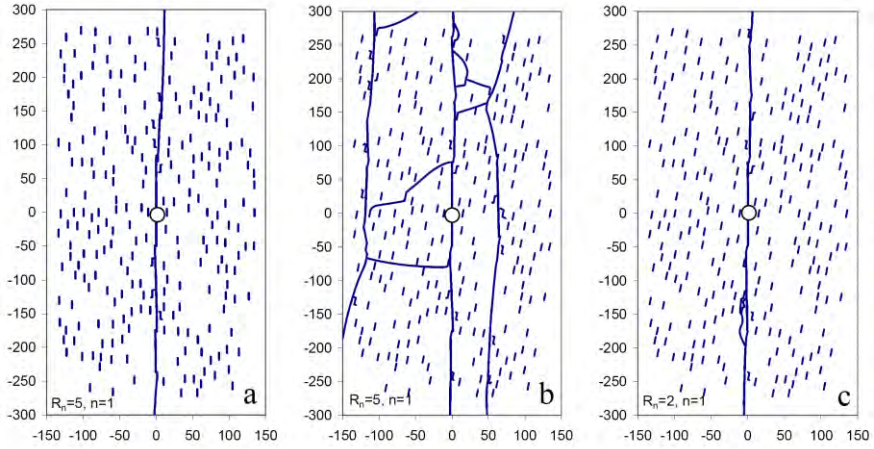
From: J Miskimins, *The Cutting Edge*, 2009, courtesy Pinnacle Technologies

Shale Gas Stimulated Volume: Maybe in shale but in hard rock?

R_n = 5, Aligned flaws $(\sigma_{hmax} - \sigma_{hmin} \approx 0.2 - 2\,\text{MPa})$

R_n = 5, Inclined flaws $(\sigma_{hmax} - \sigma_{hmin} \approx 0.2 - 2\,\text{MPa})$

R_n = 2, Inclined flaws $(\sigma_{hmax} - \sigma_{hmin} \approx 0.5 - 5\,\text{MPa})$



$$R_n = \frac{p_{frac} - \sigma_{hmin}}{\sigma_{hmax} - \sigma_{hmin}} = \frac{\text{net fracturing pressure}}{\text{differential in situ stress}}$$ ← 1-10 MPa typical

From: J Olson and A Dahi-Taleghani, SPE 119739, 2009

4

Explosive Proppant

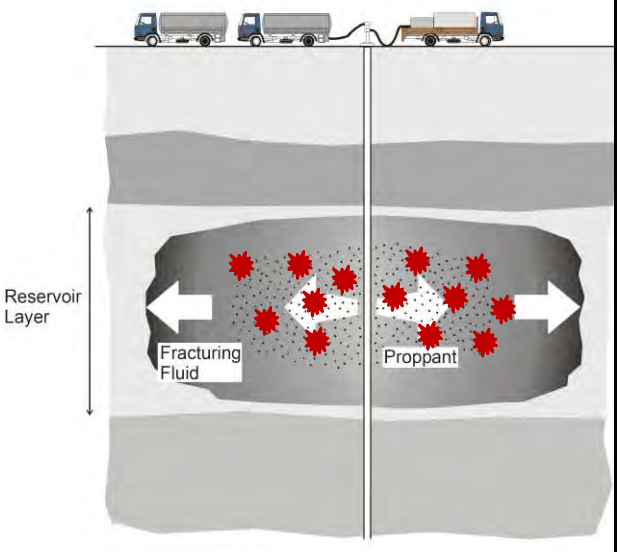
Explosive proppant?

Pan American Oil trials ca 1970

Problems

- Hard to detonate (need >3 mm thickness almost everywhere)
- Effect extremely localised (might be better in ultramafics)
- 11 November 1970

Source: Ralph Veatch (former Amoco, Pers. Comm.)



THE BRYAN TIMES

Requiem rite, simple burial for DeGaulle

Nixon other leaders exchange courtesies

Propane gas blast kills four, injures two others

Ratification of UAW pact next stop to end strike

Board seeks state ok of water plant plans

Premature oil well explosion kills 9

Heny Ford named bank director

Ends 34 year postal career

ATTENTION MOOSE MEMBERS LOBSTER TAIL or T-BONE STEAK

Premature oil well explosion kills 9

TULSA, Okla. (UPI) — A potent mercury explosive, being readied to blast a dead oil well back to life, detonated near nine huddled oilfield workers Wednesday night, killing them all, gouging a 50-foot crater and knocking out power for miles around.

A ninth victim was found at daybreak today. Small white flags swirled in the wind, marking spots where searchers picked up bodies or parts of them.

Police first reported that a portable oilfield crane struck high voltage overhead power lines, buckled and fell onto a van loaded with explosives.

But a Pan American Oil Co. official today blamed the death and destruction on a premature blast of the mercury explosive, which set off dynamite and nitroglycerine in a nearby truck.

"There were bits and pieces of bodies scattered everywhere," one deputy sheriff said.

Pan American, a subsidiary of Standard Oil of Indiana, holds a lease on the field northeast of Tulsa, which contains one inactive oil well. The nine workers, members of a seismic crew, had been conducting tests to determine if the well could be reactivated.

The mercury explosion shattered a nearby van loaded with dynamite, nitroglycerine and mercury. The blast blew a crater 50 feet wide and 10 feet deep in the ground and knocked down power lines, leaving three area communities without electricity through the night.

Explosive experts were called to the scene today to remove a 55-gallon drum of the mercury explosive. Pan American ordered police to keep unauthorized persons one mile from the blast site.

The crane truck was blown on its side, twisted and bent near the crater. The van was blown against a tree, its passenger compartment ripped from top to bottom.

r casualty ord listed

Americans had been killed in action after noon today so the period would not extend beyond the 48 hours.

U.S. combat deaths for the week ending last Saturday rose to 31 from the five-year low of 24 the week before, the U.S. command announced. They said the combined total of 31 dead and 104 wounded was the lowest overall casualty figure for a week since the seven-day period ending Oct. 23, 1965.

Despite the slowdown in action, two more U.S. helicopters were shot down Wednesday, both in the Mekong Delta. They brought to 4,116 the total of helicopters lost from all

(Continued on page 3)

Waste injection — Not for circulating

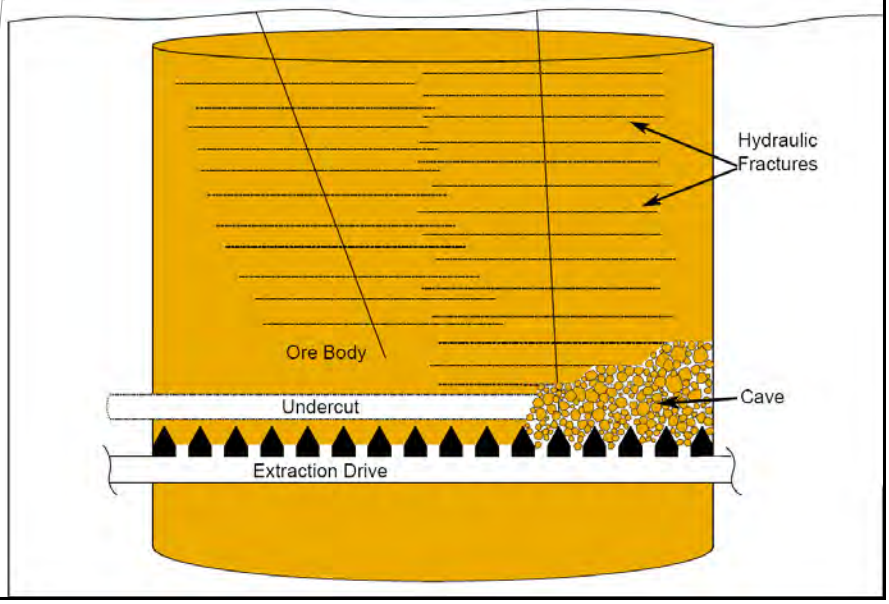
Geothermal — Not for rapid heating; Too limited

Shale gas — In situ conditions too dissimilar

Explosive proppant — Ineffective and dangerous

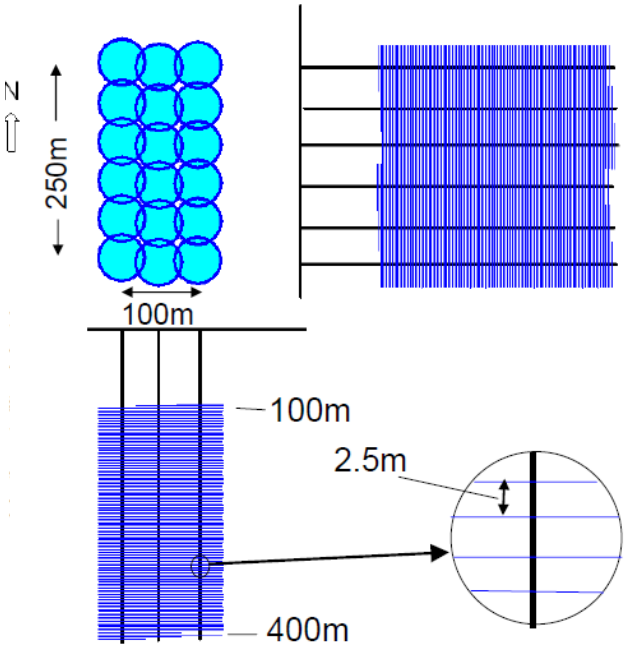
Appropriate Industrial Analogue?

Preconditioning for Block Caving

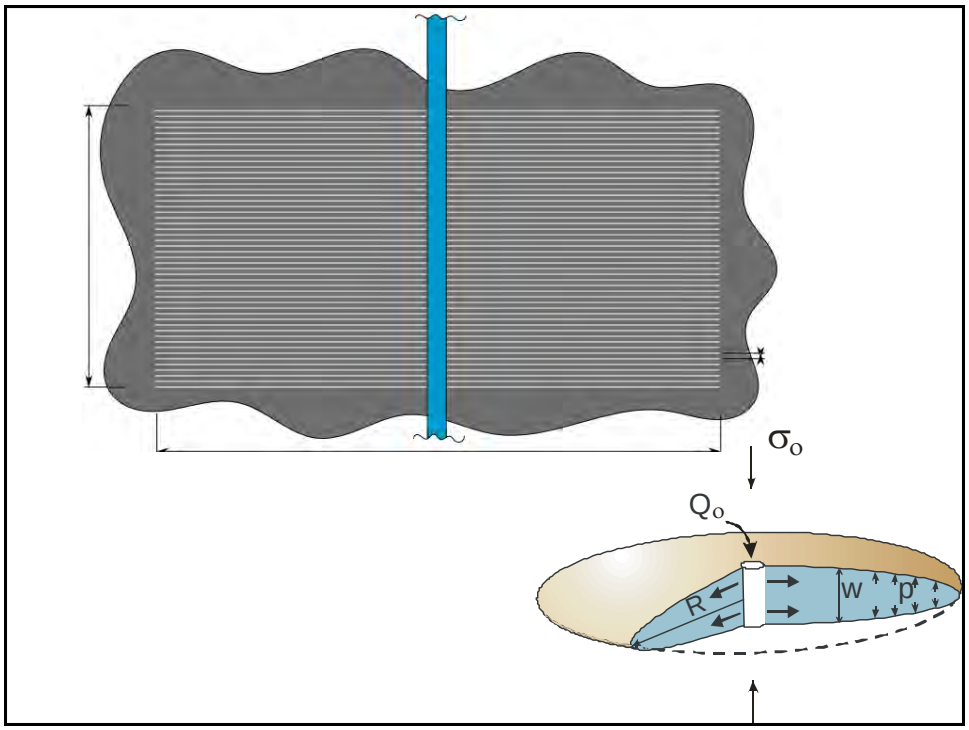


Northparkes E48 Mine
Australia

- 2000 hydraulic fractures
- 18 vertical boreholes
- 2.5 m spacing
- 20 Mega litres of water
- AU$5M (includes tiltmeter monitoring but not drilling)



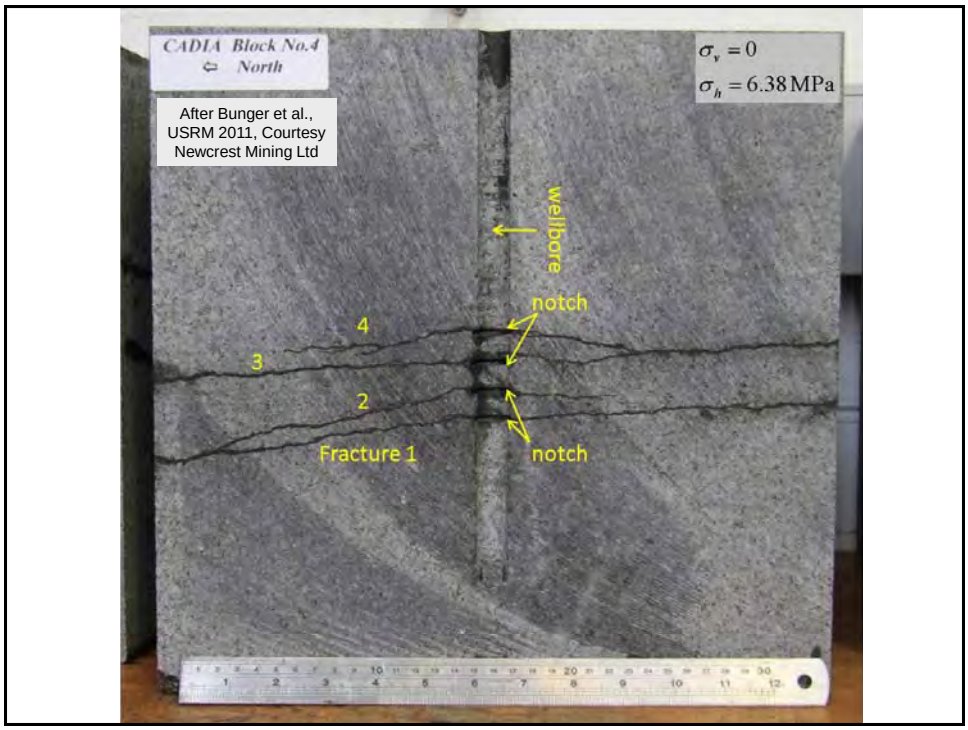
To scale for 30 m radius fractures

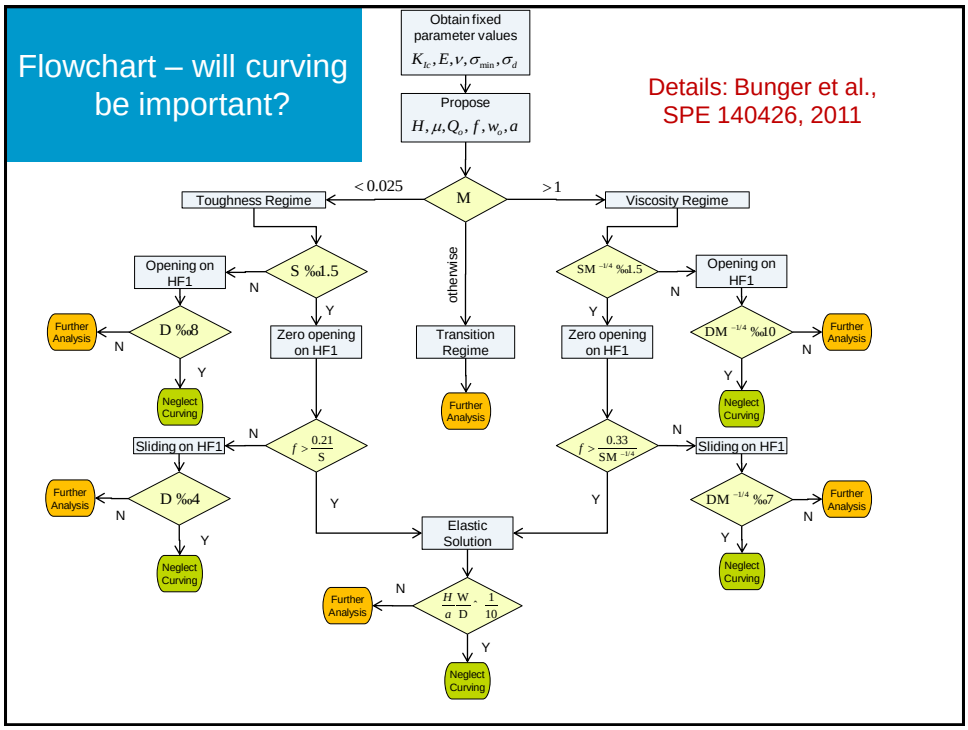


Why Closely-Spaced HF?

- Best for rock mass heating
  - Circulation
  - Uniformity
  - Shortest time
- Greatest exposure of reactive surface area
- Possible stress reorientation during carbonation – future fractures in new orientation
- Scalable for economic models
  e.g. frx/length of well, $/frx, area/frx, kg CO2/area etc.

How close can the spacing be?


CADIA Block No.4
North
After Bunger et al., USRM 2011, Courtesy Newcrest Mining Ltd
$\sigma_v = 0$
$\sigma_h = 6.38\,\text{MPa}$
wellbore
notch
4
3
2
Fracture 1
notch


Flowchart – will curving be important?
Details: Bunger et al., SPE 140426, 2011
Obtain fixed parameter values $K_{Ic}, E, \nu, \sigma_{min}, \sigma_d$
Propose H, μ, Q_o, f, w_o, a
M
< 0.025
> 1
otherwise
Toughness Regime
Viscosity Regime
S ‰1.5
Opening on HF1
D ‰8
Further Analysis
Neglect Curving
Zero opening on HF1
Transition Regime
Further Analysis
$f > \frac{0.21}{S}$
Sliding on HF1
D ‰4
Further Analysis
Neglect Curving
SM $^{-1/4}$ ‰1.5
Opening on HF1
DM $^{-1/4}$ ‰10
Further Analysis
Neglect Curving
Zero opening on HF1
$f > \frac{0.33}{SM^{-1/4}}$
Sliding on HF1
DM $^{-1/4}$ ‰7
Further Analysis
Neglect Curving
Elastic Solution
$\frac{H}{a}\frac{W}{D} > \frac{1}{10}$
Further Analysis
Neglect Curving
Y
N

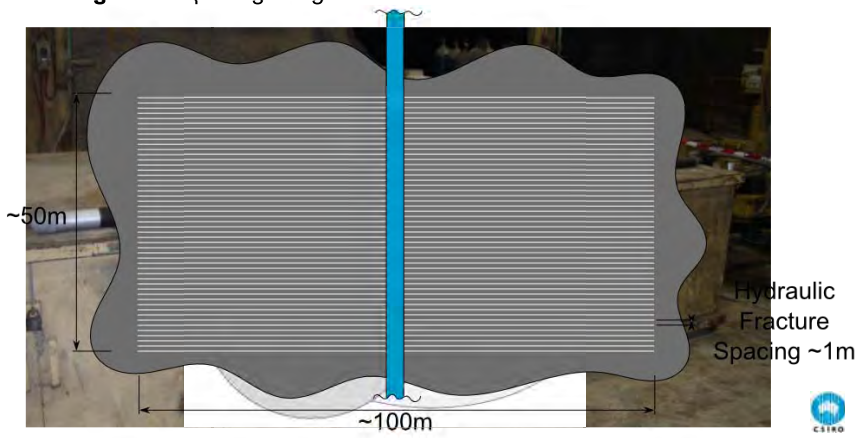
Result: Minimum spacing in range of hundreds of millimeters to a few meters

Spacing of 1 m or less possible if appropriately designed

A few other possible limitations to explore

Other Possible Limitations on Spacing

- Non-symmetric "stacking"
- Isolation method – e.g. length of isolation packers
- Rock heterogeneity
- **Target** 1 m spacing – e.g. 50 m section with 50 HFs at 50 m radius



Conclusions

- Much can be learned from industry experience, but…
- Drawing appropriate lessons requires considering each method's
  - Setting
  - Limitations
  - Objectives
- Promising way forward for in situ mineralisation is through closely spaced HFs

Appendix D: Poster Abstracts

Theme 1: Field observations

Ophiolite studies

1	*C. Boschi, L. Dallai, A. Dini, G. Gianelli, G. Ruggieri*	CO2 mineralogical sequestration in serpentinized peridotite at Malentrata (Tuscany, Italy)
2	*G. L. Früh-Green, M. D. Lilley, E. Schwarzenbach, S. Q. Lang, S. Méhay, S. M. Bernasconi, M. Molinari and L.Marini*	Alkaline Fluids and Carbonate Deposition in Modern Serpentinizing Environments
3	*Monnin C., Chavagnac V., Ceuleneer G., Boulart C and Hoareau G.*	The chemistry of hyperalkaline springs, gases and precipitates in Oman and in the Ligurian Alps (Northern Italy). Some recent observations.
4	*F. Boudier, A. Baronnet and B. Dewandel*	Lizardite in the sub-oceanic mantle of the Oman ophiolite
5	*A.M. Lacinska, M.T. Styles*	Barzaman Formation in the United Arab of Emirates: a natural analogue for permanent CO2 fixation using ultramafic rocks.
6	*Evans, K.A. & Frost, B.R.*	Field Observations of Carbonate Formation in Weathered Ultramafic Rocks, New Caledonia
7	*P. Garcia Del Real*	CO2 Sequestration Ultramafic Rocks: Insights from the Red Mountain Magnesite District, California
8	*Meyer, F.M., Sindern, S., Schardt, C., Urai, J., Gutberlet, M., den Brok, B., Clauser, C., Blaschek, R., Kukla, P., Rüde, T.R., Stanjek, H., Littke, R.*	Assessment of direct aqueous in situ carbonation procedures in ophiolitic detritus
9	*J. Koepke, P.E. Wolff, H. Strauss, D. Garbe–Schönberg*	Towards a reference profile for fast–spreading oceanic crust: Petrology and geochemistry of the "Wadi Gideah" cross section in the Southern Oman ophiolite.

Studies of oceanic lithosphere and basaltic crust

10	*H.J.B. Dick & J. Snow*	The Distribution and Emplacement of Serpentinized Peridotite in the Ocean Basins
11	*P. J. Michael*	Some Opportunities and Challenges for Sequestering CO2 in Arctic Seafloor Peridotites
12	*B. Ildefonse, M. Andréani, E. Hoisé, A. Delacour, J. Escartin, M.*	Geology of the Rainbow Massif, with evidence of carbonation in a serpentinite seafloor

	Godard, J. Dyment, Y. Fouquet	
13	*F. Lartaud, C.T.S. Little, M. de Rafelis, G. Bayon, B. Ildefonse, J. Dyment, N. Le Bris*	Fossil Bivalves in the Rainbow Area: New Insight into the Diversity and Evolution of Chemosynthetic Communities
14	*M. Tominaga and F. Klein*	Downhole magnetic and physical property logging of serpentinized peridotite and carbonate-altered serpentinite.
15	*K. Becker, A. T. Fisher, D. Winslow, T. Tsuji, S.Mrozewski & IODP Exp 327 Scientists*	IODP Packer Experiments in Young Juan de Fuca Crust Suggest Lateral Continuity of Hydrological Structure on Ridge-parallel Scale of ~1 km
16	*K. A. Ludwig, C.-C. Shen, D. S. Kelley, H. Cheng and R. L. Edwards*	U-Th systematics and ages of carbonate chimneys at the Lost City Hydrothermal Field
17	*Chavagnac V., Boulart C., Monnin C., Castillo A.*	Spatial and temporal variability of fluid and gas chemical compositions at the Lucky Strike hydrothermal vent site, Mid-Atlantic Ridge.
18	*D. Goldberg, A. Slagle*	Carbon storage below the sea floor: potential sites for crustal studies
19	*D.A.H. Teagle, R.M. Coggon, H. Pälike, J. C. Alt and C.E. Smith-Duque*	Did seafloor carbonation regulate high pCO2 on the ancient Earth?
20	*R.D. Schuiling*	Let the Earth help us to save the Earth

On-shore basaltic aquifers & reservoirs

21	*J. Olsson, S. L. S. Stipp and S. R. Gislason*	Toxic metal mobility following the injection of CO2 into basaltic aquifers
22	*T. L. McLing, R. W. Smith, R. K. Podgorney*	Field Characterization of the Soda Springs Mafic Rock CO2 Sequestration Analogue Site, Idaho, USA
23	*C. Wu, J. Ji, Z. Wang, Y. Chen, L. Liu and L. Gu*	Depleted basaltic oil and gas reservoirs: Potential economic and efficient reservoirs for CO2 sequestration

Sedimentary basins

24	*KIRÁLY, C., BERTA, M.,FALUS, G., SZÉKELY, E. and SZABÓ, C.*	Geochemical and petrophysical estimation studies on sedimentary rock samples from the Pannonian Basin, Hungary

Industrial waste & urban soils

25	*E. J. Berryman, A. E. Williams-Jones, A. A. Migdisov, S. van der Laan*	CO2 Sequestration by carbonation of steel slag
26	*David A. C. Manning, Phil Renforth and Carla-Leanne Washbourne*	Carbonation of artificial silicate minerals in urban soils: rates and mechanisms in passive surface systems

Theme 2: Laboratory studies

27	*Andreani M.*	Natural versus experimental peridotite carbonation: a microstructural study
28	*M. Godard, S. Peuble, L. Luquot & Ph. Gouze*	Experimental study of CO2 sequestration in a basalt- olivine matrix: Coupling and feedback effects of transport, hydration and carbonation processes
29	*K. Beier, W.-A. Kahl, A. Holzheid*	Dissolution experiments of potential reservoir materials in CO2-bearing saline fluids
30	*T. A. Haug & N. S. C. Simon*	Dissolution and carbonation of mechanically activated olivine – implications for in-situ CO2 sequestration in mafic and ultramafic rocks?
31	*K. T. M. Johnson, B. P. McGrail, and H. T. Schaef*	Geologic CO2 Sequestration Experiments with Hawaiian Picritic Basalts
32	*N. C. Johnson, B.Thomas, K. Maher, D. K. Bird, R. J. Rosenbauer, G. E. Brown, Jr*	Kinetics of olivine carbonation for the geologic storage of carbon dioxide
33	*K. Pöhler, Ch. Lempp & H. Pöllmann*	Mineralization of serpentinite rocks with CO2 at different states of structural disintegration
34	*J. Koepke, S. Feig, J. Berndt*	Experiments in hydrous tholeiitic and peridotitic systems at shallow pressures: Constraints on magmatic processes in the Oman paleoridge
35	*L. Luquot, M. Andreani, M. Godard, P. Gouze, B. Gibert, G. Lods*	Serpentinization of sintered olivine during seawater percolation experiments
36	*D. Le & J. Mahadevan*	Impact of Capillarity on Salt Crystallization in Porous Media
37	*R. R. Adhikari, J. Kallmeyer*	Hydrogenase enzyme assay: a promising technique for the quantification of microbial activity in subsurface environments

38	*B. Ménez, E. Gérard, S. Dupraz, H. A. Alfreðsson, S. R. Gíslason, H. Sigurðardóttir, François Guyot*	Impact on the deep biosphere of CO2 geological sequestration in (ultra)mafic rocks and retroactive consequences on its fate
39	*K.G. Mesfin, D. Wolff-Boenisch and S.R. Gislason*	Dissolution of basaltic glass in seawater at 1000C and 70 bars CO2 pressure. Implications for CO2 mineral sequestration
40	*H. Pöllmann*	The formation of carbonate containing LDH´s in basic rocks
41	*V. Prigiobbe*	Enhanced olivine dissolution using oxalate and citrate
42	*V. Prigiobbe*	Magnesite precipitation at high temperation and high CO2 pressure
43	*Kevin M. Rosso, Alain HR Bonneville, Jian Z Hu, David W Hoyt, Zheming Wang, Alan S Lea, H. Todd Schaef, B. Peter McGrail, and Mark D. White*	Fundamental Science for Geologic Carbon Sequestration: Laboratory Probes for Understanding Trapping Mechanisms at the Microscopic Scale
44	*P. Sauer, J. Kallmeyer*	A new incubator for biological high pressure experiments with elevated gas saturation
45	*M. Schmidt, H. Pöllmann, H. Marbler, K. Erickson, C. Lempp*	A new autoclave system for the “in situ” investigation of carbonation reactions of basic rocks with waste CO2
46	*L.S. Shirokova, G. Stockman, P. Bénézeth, O.S. Pokrovsky, E. Gerard, B. Menez, H. Alfredsson*	Effect of heterotrophic bacteria on olivine and basaltic glass dissolution in the context of CO2 storage in basalts
47	*A. S. Templeton, L. E. Mayhew, G.E. Lau, and T. M. McCollom*	Exploring links between the speciation of Fe and the activity of thermophilic methanogens during the hydration and carbonation of ultramafic rocks
48	*Y. Takaya, K. Nakamura, Y. Kato*	Experimental study on the CO2-water-basalt interaction: Implications for a carbonate formation sequence during CO2 basaltic aquifer storage
49	*Van Noort R., Spiers C. J. , Kandianis M. T., Drury, M. R., and ten Grotenhuis, S.M.*	Peridotite fracture surface reaction rates for in-situ CO2-mineralization in ophiolites
50	*Van Noort R., Spiers C. J. , Kandianis M. T., Drury, M. R., and ten Grotenhuis, S.M.*	Fracture propagation during in-situ mineral carbonation in peridotite
51	*Z. Wang, E. Bolton, S. Karato, Jay Ague, D. Bercovici, M. Oristaglio,W. Zhu, and K. Johnson*	Integrated Experimental and Modeling Studies of Mineral Carbonation

52	*Zhu, W. and Lisabeth, H.*	Carbonation Reaction Driven Permeability and Porosity Evolution in Thermally Cracked Dunites.
53	*A. J. West*	The potential for carbon sequestration by accelerated weathering of mafic rocks at ambient pCO2
54	*S. Wilson, S. Barker, A. Harrison, I. Power, G. Dipple, K. U. Mayer, V. Atudorei*	Dissolution of CO2 gas is rate limiting to C sequestration in high-salinity alkaline brines
55	*L. Zhao, L. Sang, J. Chen, J. Ji, and H. H. Teng*	Aqueous Carbonation of Natural Brucite for CO2 Sequestration
56	*G. Caramanna, Y.Wei, M. Maroto-Valer, M. Steven*	Study of potential chemical effects of CO2 leakage into sediments and groundwater
57	*S. Mackintosh, K. Bateman, M. Maroto-Valer, M. Hall*	The Effect on Porosity and Permeability of North Sea Sandstones Post Mineral Carbonation

Theme 3: Hydrodynamic and thermodynamic modelling

58	*C. M. Augustin, P. K. Swart & T. H. Dixon*	Computational modeling for carbon dioxide sequestration
59	*D. Bernard, M Decain*	A generic approach for pore scale modelling of coupled transport and geochemical reactions during CO2-saturated-water flow.
60	*M. Hesse, J. Neufeld, A. Riaz*	Convective Dissolution of CO2
61	*M. Hesse, V. Prigiobbe*	Convection in porous and fractured systems with an exothermic reaction
62	*R. K. Podgorney, A. L Slagle, T. L. McLing and D. S. Goldberg*	Numerical Simulation of Carbon Dioxide Sequestration in Deep-Sea Basalts
63	*F. Klein*	Heterogeneous phase equilibria during carbon sequestration into serpentinized peridotite: Using the fluid chemistry as a monitor of carbonation progress
64	*S. Krevor*	*WITHDRAWN* Bringing mineral carbon dioxide sequestration down to earth: Thermodynamic considerations using realistic reactant and product phases.
65	*Iyer, K., Rüpke, L.H. and Morgan, J.P.*	Feedbacks between mantle hydration and hydrothermal convection at ocean spreading centers.
66	*L. Ruepke, K. Iyer, and J. Phipps Morgan*	Simulations of oceanic lithosphere serpentinization

67	*J. Phipps Morgan, L. Rüpke & K. Iyer*	*WITHDRAWN* Bend-Faults and Hydrothermal Circulation at Oceanic Trenches

Theme 4 : Development of new techniques with application to field scale characterization

68	*R. Pollyea, J. P. Fairley, R. K. Podgorney and Travis L. McLing*	Developing fracture density models using terrestrial laser scan data
69	*D.G. Pearson, T. Stachel, R. Stern & R. Ekart.*	Geochemical microsampling techniques as an aid to understanding the sources and timing of carbonate formation in ultra-mafic rocks - application to CCS studies

Theme 5 : Societal impact

70	*J. M. Ornstein*	Identifying tools used to inform public attitudes and influence behavior in favor of Carbon Mineralization

Theme 6 : Industrial applications

71	*G. Caramanna, S. Mackintosh, M. Maroto-Valer*	Mineral Carbonation in Oman
72	*Richard Hunwick* *Integrated Carbon Sequestration Pty Ltd*	Ex-situ mineralisation using the ICS Process

I - Keynote presentation

1 - Creating surface area and conductivity in ultramafic rocks by using extremely closely spaced hydraulic fractures.

A. Bunger, R. Jeffrey, X. Zhang

CSIRO Earth Science and Resource Engineering, Melbourne, Australia

Producing the necessary permeability and reactive surface area in a target ultramafic formation promises to be one of the key technical challenges that must be successfully addressed if in situ carbon storage is to become viable. The goal of such an operation is to create a highly permeable, uniform and pervasive network of fractures. In this sense, the design criteria bear similarities to Engineered Geothermal Systems. However for carbon storage in ultramafic rocks, one will not typically face the extreme conditions of temperature and stress that are intrinsic to géothermal targets. As such, one can make use of a wider range of downhole tools, such as isolation packers and abrasive jetting tools for wellbore slotting, which are more difficult to apply in géothermal applications. Furthermore, in carbon storage applications there is a greater value placed on création of new reactive surface area by creating new fractures rather than relying almost exclusively on permeability enhancement by shear mobilisation of pre-existing fractures as is typical for geothermal applications. For this reason carbon storage stimulation should make use of openingmode hydraulic fracturing instead of the lower-injection-pressure techniques used to stimulate shear fracturing in the geothermal industry.

Past field trials and ongoing development of hydraulic fracturing for preconditioning ore bodies for block cave mining have demonstrated that thousands of hydraulic fractures can be successfully grown to a radius greater than 30 m in a rock mass with less than 3 meters spacing between them. In order to predict how these closely spaced hydraulic fractures will interact and how thèse interactions could lead to diminished effectiveness of the stimulation, we present numerical results obtained from a coupled hydraulic fracturing simulator that accounts for interaction of multiple hydraulic fractures including crack path deflection. Most importantly, these simulations show that parallel systems of hydraulic fractures can be expected for arbitrarily close spacing provided that certain conditions, embodied by the values of several dimensionless groups of parameters, are met. Whether these conditions for parallel growth are satisfied has partly to do with in situ conditions that are not in the control of the engineer. However, there are engineering choices, such as the wellbore orientation along with the fluid and proppant characteristics, which can impact on whether a series of hydraulic fractures will tend to form a closely-spaced, parallel array.

Of course there will be limits on the closeness of the hydraulic fracture placement that will arise from factors that lie outside of our model, such as rock heterogeneity. There will also be practical limitations arising from, for example, the length of the isolation packers. Finally, there will be economic limitations arising from the time and energy required for each hydraulic

fracture that is placed. Nonetheless, the numerical results we present open the door for engineering the desired characteristics of the ultramafic rock mass for carbon storage applications through creation of an array of hydraulic fractures at close spacing that was not previously considered to be possible.

II – Posters

37 - Hydrogenase enzyme assay: a promising technique for the quantification of microbial activity in subsurface environments

Rishi Ram Adhikari, Jens Kallmeyer (kallm@geo.uni-potsdam.de)

Institute of Earth and Evironmental Sciences,
University of Potsdam,
Karl-Liebknecht-Straße 24,
14476 Potsdam, Germany

The subsurface biosphere is the largest microbial ecosystem and the largest energy reservoir on Earth. Despite recent technical advances, very little is known about biogeochemical processes in the deep subsurface. In recent years much has been achieved in the development of new technologies for a clean future energy supply. One major component of these new technologies is the exploitation of the deep subsurface either as an energy resource or a storage facility, for example CO2 storage, geothermal energy or biogenic hydrocarbon generation.

Without profound knowledge of biologically mediated processes and their reaction to anthropogenic changes it is difficult to assess the long-term stability and feasibility of any type of geotechnical utilization. To maintain optimal performance, appropriate techniques have to be developed in order to control/monitor microbial activity. Processes like biocorrrosion, biofouling and biofilm formation can significantly affect geotechnical installations.

For the quantification of microbial turnover processes, most of the currently available techniques focus on specific processes like sulfate reduction, denitrification or methanogenesis. These techniques are specific to certain microbial process. However, microbial ecosystems in the subsurface are very complex, and many processes proceed simultaneously. Therefore such specific techniques do not provide a complete overview of the total microbial activity. Enzyme or molecular assays provide a more general approach of microbial activities as they target key metabolic compounds rather than specific processes.

The Hydrogenase enzyme assay is the most promising technique because the enzyme is ubiquitous in microbes. It catalyzes the interconversion of molecular hydrogen and/or water into protons and electrons. The protons are used for the synthesis of ATP, thereby coupling energy-generating metabolic processes to electron acceptors such as carbon dioxide, sulfate or elemental sulfur. Since it is a radioisotope assay, it is very sensitive and thereby overcomes the limitations usually set by insufficiently high minimum detection limits of other approaches that quantify, for example fluorescence.

The hydrogenase-tritium assay has the potential to become a key tool for the detection and quantification of total microbial activity in subsurface environments, either natural or anthropogenically influenced.

27 - Natural versus experimental peridotite carbonation

Andreani M.[1], Pollet-Villard M.,[1] Luquot L.[2], Menez B.[3], Peuble S.[2], Auzende A-L.[3], Godard M.[2], Gouze P.[2]

1 : LST, ENS-Université Lyon1, UMR5570 France ; 2 : GM, UMR5243 Montpellier, France ; 3 : IPGP, Paris, France.

The carbonation of ultramafic rocks is, theoretically, the most efficient reaction to trap CO_2 irreversibly in the form of solid carbonates, as predicted by equilibrium thermodynamic calculations. However, the success of *in situ* carbonation in large ultramafic aquifers or oceanic ultramafic exposures does not only rely on the thermodynamic conditions of chemical reactions, but also on their feedback effects on the reactive surface area that controls mass transfers locally, and on the reservoir porosity and permeability. In addition, side reactions like serpentinisation, catalytic effects and/or redox reactions that can be expected in such complex natural system. Their occurrence and implications on the carbonation process have not been explored yet and requires detailed study of natural carbonation zones.

Firstly, we investigate the relations between rock heterogeneity, fluid flow and chemical reactions by performing flow-through percolation experiments of a CO2-enriched, alkaline water within sintered dunite samples at 160°C, 120 bars. Two different cation compositions of the aqueous fluid (cation-depleted and aquifer-type) have been tested for the same Peclet number (transfer regime), pH and PCO2. Both experiments result in carbonate formation +/- phyllosilicate and oxides, but in a contrasting permeability evolution and outlet fluid composition. Indeed, injection of a cation-rich water leads to a rapid decrease of the permeability and a strong retention of elements in the rock sample in the form of abundant carbonate and poorly crystallized phyllosilicates of serpentine type. In opposition, injection of the cation-depleted water mainly results in carbonate formation with rare talc-like phyllosilicate and a strong silica release in the oulet fluid, while permeability is maintained at a near-constant value. In this latter case, the nature of products varies between main flow zones and diffusion dominated zones which testify for differential mass transfers at a micrometric scale under these far-from-equilibrium conditions. This phenomenon tends to locate carbonates outside main flow paths which ensure the sustainability of permeability at the experiment time-scale.

Secondly, we compared those results with the reactions textures of natural carbonated zones observed in peridotites collected during the IODP 304 expedition that drilled the Atlantis Massif (30°N MAR). Those carbonated zones are associated with abundant talc veins and are bounded by talc-tremolite shear zones. Similar associations of carbonate, porous phyllosilicate and oxides are observed in the close vicinity of relict olivine grains that have undergone a previous stage of serpentinisation. Among the submicrometric dark clusters widely-distributed in the late phyllosilicate, Raman microspectroscopy reveals, both in the first and second order spectra, the presence of various type of organic matter, from poorly-ordered carbonaceous compounds to more carbonified material. The formation conditions of this material remain to be investigated in details but its association with the late carbonation texture suggests that CO2 conversion may not be limited to solid carbonate formation in natural systems.

Those results underline the importance of fluid composition, transport properties and potential complex side reactions on the efficiency and durability of in-situ carbonation of ultramafic bodies.

58 - Computational modeling for carbon dioxide sequestration

Caitlin M. Augustin[1], Peter K. Swart[1], Timothy H. Dixon[1]

1 RSMAS/MGG University of Miami 4600, Rickenbacker Causeway, Miami, FL 33149
caugustin@rsmas.miami.edu - pswart@rsmas.miami.edu - tdixon@rsmas.miami.edu

There are three major outcomes of carbon sequestration in reservoirs. Stable sequestration, characterized by carbonate precipitation, limited subsurface fluid migration and reservoir pressures remain consistent is the most desired outcome. The other two results of injection are either deformation on the Earth's surface, a potential indicator of fracture and leakage within a compromised reservoir or viscous fingering and migration of the carbons dioxide plume out of an open reservoir. Both of these scenarios have potentially devastating implications.

To understand the relationship between the injected carbon dioxide and key reservoir formation characteristics it is vital to accurately model the sequestration environment. Accurate modeling of the reservoir system is essential to realizing the potential of geologic carbon dioxide sequestration and mitigating the heath and safety hazards associated with this technology.

In hydrocarbon fields, it is known that the total stresses can change during fluid-pressure depletion. However, it is not yet understood whether fluid injection will have significant effects on total stresses in a reservoir scale sequestration. We have hypothesized that the ground deformation signal is a key component in accurately modeling both the geochemical and geophysical reactions within a reservoir and thus will take an integrated modeling approach using the combined finite-discrete element method. By using data specific to the Farnham Dome, Utah, injection site we will originate code dedicated to modeling the impact of micro-level reactions on the entire reservoir system.

Through a combination of our original code and geochemical computational software such as the Geochemist's Workbench, we aim to understand the effects of CO2 injection on the geomechanical reservoir structures. Although our simulations are based on data available for the Farnham Dome, Utah sequestration site, the techniques used for their analysis are equally relevant to the general sequestration environment.

15 - IODP Packer Experiments in Young Juan de Fuca Crust Suggest Lateral Continuity of Hydrological Structure on Ridge-parallel Scale of ~1 km

Keir Becker[1], Andrew T. Fisher and Dustin Winslow[2], Takeshi Tsuji[3], Stefan Mrozewski[4],

1 University of Miami – RSMAS
2 University of California, Santa Cruz
3 Graduate School of Engineering, Kyoto University
4 Borehole Research Group, Lamont-Doherty Geological Observatory Exp 327 Scientists

During IODP Expedition 327 to the eastern flank of the Juan de Fuca Ridge, a drillstring packer was used to assess the average permeability of ~100 m of 3.3 Ma basaltic crust in Hole U1362A beginning about 190 m below the sediment-basement interface. This zone is approximately the same as was tested during Expedition 301 using the same techniques in Hole U1301B, about 800 m to the SSE of Hole U1362A. In both holes, the packer inflation seats were chosen primarily on the basis of logging data that is surprisingly consistent between the two holes despite the 800 m separation in a ridge-parallel sense. In fact, the caliper and drilling penetration records show nearly identical sequences of in-gauge and out-of-gauge sections and rates of penetration, suggesting considerable structural continuity between the two sites. The packer tests indicate virtually identical average permeabilities of ~2 x 10**-12 m**2 in the tested sections in both holes. In Hole U1301B, a shallower section was also tested and shown to be more permeable, but the corresponding section could not be tested in Hole U1362A due to failure of the packer inflation element. In combination with the indications of laterally consistent structure, the similarity of values in the tested sections of both holes suggests a lateral continuity of the layered permeability structure between the two holes. This is not proof, but may be the first direct indication of such hydrogeological continuity, which in the past has been assumed from isolated single-hole packer tests with little justification.

29 - Dissolution experiments of potential reservoir materials in CO2-bearing saline fluids

K. Beier, W.-A. Kahl, A. Holzheid

University Kiel, Institute for Geosciences, Experimental & Theoretical Petrology, Kiel, Germany

Chemical interaction processes between injected CO2, saline fluids and potential reservoir materials are experimentally investigated in this study as part of the joint project CO2-MoPa. The aim of the experimental study is to derive kinetic data of different polymineral and monomineral natural materials that can be used as input-parameter for dimension and risk analyses.

Caused by complex reservoir conditions experiments with simplified parameters have been accomplished. For example monomineral grain phases (calcite, dolomite, orthoclase, anorthite) were used as components of reservoir rocks. Furthermore a synthetic model brine (TDS: ~156 g/L) based on a natural formation water of a Lower Cretaceous sandstone was chosen. All experiments were performed in closed teflon autoclaves and a titanium reactor (Parr Instruments) at temperatures of 100°C / 150°C and a total pressure of ~85 bar. Run durations varied from 1 to 30 days. Chemical changes between the initial and the post-run fluids during the experiments were monitored by ICP-OES analyses (inorganic chemistry lab, D. Garbe-Schönberg, IfG, CAU Kiel).

Dissolution rates (R) of the mineral phases were derived based on the determined changes of cation concentrations in the fluid phases. The following observations could be made based on the Ca-concentration changes of the experiments with calcite: (1) During the first 10 days no equilibrium was achieved. Between 10 and 20 days the dissolution rate values of all calcite experiments converge. The equilibrium state was achieved after 20 days. (2) Larger grain size fractions compared to the smaller grain size fraction exhibits higher dissolution rates by a factor of 23. At first glance this is an unexpected observation because smaller grain size fractions result, by definition, in larger reactive surfaces and consequently in higher dissolution rates. One possible reason for this observation was proved by the help of microcomputer-tomography (μ-CT) analyses. These analyses show that two different grain size fractions exhibit nearly the same grain phase volume. The analyses also show, that the pore thickness distribution varied between these two grain size fractions: while the smaller grain size fraction is dominated by smaller pore radii, pores with larger radii dominate the larger grain size fraction. These observations indicate different permeabilities in the samples, which in turn affects the solution behavior. (3) A comparison between experimental and literature data of dissolution rates of calcite show a wide range of R-values. These variations could be caused by, e.g., different reactor types: experiments in mixed-flow reactors result in permanent disequilibrium states due to continuous feeding of fresh material, while experiments in batch reactors induce equilibrium after defined run durations, resulting in lower dissolution rates as observed in our study. Furthermore the choice of complex, high mineralized model brines causes large numbers of chemical interactions which might also result in lower dissolution rates. Detailed analyses of the feldspar experiments are currently in progress and will be – in addition to the calcite experiments – presented at the meeting.

59 - A generic approach for pore scale modelling of coupled transport and geochemical reactions during CO2-saturated-water flow.

D. Bernard, M Decain. CNRS, University of Bordeaux, ICMCB, France,
bernard@icmcb-bordeaux.cnrs.fr

To explore the viability of CO2 geological storage, it is prime importance to better understand the kinetics of geochemical processes occurring after injection. For that purpose, different types of experiments are carried out in laboratory; first, reaction rates of relevant minerals are measured in storage conditions. Second, reactive percolation experiments are performed at the core scale to develop the phenomenological knowledge and to validate the macroscopic numerical models. Even with completely characterised porous samples, with fluid chemical analysis, and pressure drop and fluid flow measurements at regular time intervals, it is difficult to validate (or invalidate) the principles of a macroscopic numerical model. Most of the times some of the measured parameters (generally the rate of reaction or the reactive surface) must be considered as fitting parameter in order to numerically reproduce the experimental results. One approach to solve this problem is pore scale modelling of flow and reactive transport in order to understand the phenomena and develop an adapted change of scale strategy.

The objective of our project is to develop a generic approach for pore scale numerical modelling of coupled fluid flow, transport and geochemical reactions, within 3D domains built from micro tomography data. Fluid flow is described by Stokes' equations solved on steady state using an artificial compressibility approach. Species transports are described by classical transport equations in terms of concentrations where diffusion is modelled by Fick's law. The geochemical model consists in the number of species to be considered, the number of speciation equilibrium verified in each point of the fluid phase, and the expressions of the reaction rates at the fluid/mineral interface. Those reaction rates define the boundary conditions required to solve the transport equations.

In the resulting model, the number of unknowns (N, the number of species to be considered) must be equal to the number of equations. We have Ns speciation equilibrium and a relation expressing the electro neutrality of the solution at each point. To close the system, (N-Ns-1) transport equations are required. Those transport equations are written for elements (excluding H and O) by summing the transport equations of all the different species containing the specified element. The numerical model is solved on the regular grid defined by the voxels of 3D image coming from the micro tomography. Time integration is performed by an explicit formulation, and finite volume is used for spatial discretization. Presently, micro geometry is not modified by dissolution or precipitation. The first case we treated with this approach is the case of calcite dissolution during CO2-saturated-water flow. The considered species are H+, OH-, HCO3-, Ca2+, CO32-, and CO2* (Na+ and Cl- are added for ionic force stabilization). Three speciation equilibrium and electro neutrality provide four relations, and the system is closed by transport equations for C and Ca. First, the steady state fluid flow is calculated for an initial solution in equilibrium with calcite. At time t=0, a modified solution (higher CO2 concentration) is injected and the evolution with time of the six species concentrations are computed until

steady state. Typical results like the effective dissolution rate as a function of the mean pore velocity are presented for different geometries and two CO2 partial pressures.

To conclude, the application to mafic rocks, and solutions to take into account micro geometry modifications are delineated.

25 - CO_2 Sequestration by carbonation of steel slag

E. J. Berryman(1), A. E. Wittiams-Jones(1), A. A. Migdisov(1), S. van der Laan(2

(1)Department of Earth & Planetary Sciences, McGill University, Montreal, Canada
(2)Corus RD&T, Ceramics Research Centre, lJmuiden, The Netherlands

The stable and non-toxic nature of the products has made mineral carbonation the preferred approach to C02 sequestration. Whereas most research has focused on olivine, larnite, a major constituent of steel slag has a similar structure and thus similar sequestration potential. This presents a great opportunity for the steel industry to reduce its carbon footprint. This study investigates reactions during the dissolution and carbonation of steel slag. Experiments were conducted on 2 - 3 mm diameter steel slag grains consisting of larnite (Ca2SiO4), with significant P, calcium ferrite (Ca2Fe2O5), containing Mn and Al, and Mg-wuestite ((Mg,Fe)O), with appreciable Mn. The experiments involved pumping HzO-COz fluid (XCO2 = 0.05) through a flow{hrough reactor containing these grains. Temperature ranged from 120"C to 200"C, the pressure was 'l 50 bar and the flow rate was 3.00 ml/min. Effluent samples were taken every three hours for the duration of an experiment (3 to 7 days) and analyzed for Ca, Si, Mg, Fe, P and Mn. The reacted slag was analyzed by SEM from which mineral maps were constructed using PARC software. The fluid composition was characterized by initially high concentrations of Ca (1 .59 to 2.25 mmol/L), and lower concentrations of Si (0.34 to 3.03 mmolll) and then a decline in these concentrations to steady state values. As the system reached steady state, concentrations of Si approached or exceeded concentrations of Ca, with values ranging between 0.13 - 0.28 mmol/L and 0.01 - 0"05 mmol/L, respectively. With increasing temperature of an experiment, Ca concentration decreased while 5i increased. Concentrationsof Mg and Fe never exceeded 0.09 mmol/L. Those of P and Mn mimicked Ca. The contrasting behavior of Ca and Si in a single experiment is interpreted to reflect incongruent dissolution of Ca-bearing minerals and preferential release of Ca, whereas in experiments at different temperatures, it is considered to indicate retrograde and prograde solubility of calcite and silica, respectively. The PARC imaging reveals that the reacted slag grains can be divided into three reaction zones: the un-reacted core, the reaction layer, and the dissolved framework. The un-reacted core is composed of the slag-forming minerals. Surrounding the core is the reaction layer, consisting of Ca-carbonate and -phosphate phases that replaced larnite during interaction with the CO2-bearing fluid. Beyond this zone, the carbonate phase was undersaturated in the solution and dissolved, leaving a porous Al and Fe oxide framework around the edge of the grain. Mg-wuestite is present throughout, indicating that it was inert during fluid-slag interaction. These results indicate the important role of steel slag as a potential CO2 sequestration material. Previous studies emphasized the necessity for small grain-size to ensure that carbonation of the silicate goes to completion. This is because coating of larger grains by silica (incongruent dissolution of olivine) or carbonate isolâtes the olivine from the fluid and prematurely terminates the carbonation reaction. However, this study shows that comminution of the slag to fine grain-size is unnecessary owing to the fact that the calcium ferrite which surrounds larnite crystals dissolves easily, thereby providing pathways for the fluid to react with the larnite. This finding highlights an important economic advantage of using steel slag as a carbonation material. Infuture studies, we will focus on the kinetics of larnite dissolution and

carbonation in order to constrain the optimum conditions for efficient larnite and slag carbonation.

1 - CO2 mineralogical sequestration in serpentinized peridotite at Malentrata (Tuscany, Italy).

C. Boschi, L. Dallai, A. Dini, G. Gianelli, G. Ruggieri*

1 Institute of Geosciences and Earth Resources, CNR, Italy
** corresponding author: c.boschi@igg.cnr.it*

Serpentinite-hosted magnesite deposits are common throughout the world and occur as veins or stock work bodies of cryptocrystalline magnesite, with minor amount of talc, quartz and dolomite (Boschi et al., 2009). Metric to kilometric magnesite veins are resulting from prolonged interaction between CO2-bearing meteoric/hydrothermal fluids and serpentinized ultramafic rocks and represent natural analogues of induced CO2 mineralogical sequestration. Their study can complement laboratory and demonstration studies and provide opportunity to constrain the boundary conditions for CO2-bearing phases to form. Since several years our research focus on the serpentinite-hosted magnesite deposits that are placed at the northern periphery of the active Larderello–Travale geothermal field (Tuscany, Italy) where granite intrusions were cored at depth of about 3300–4800 m. The presence of the geothermal field entails that the buried rocks are naturally warmed at anomalous temperature; in this area, at a depth less than 1000 m below ground level, the temperature is about 150°C (Boschi et al., 2008). This peculiar geological situation enhances, in presence of CO2-rich fluids, a spontaneous carbonation of buried serpentinites and could be an ideal place to test in situ CO2 mineralogical sequestration of unaltered buried serpentinites. Boschi et al., (2008) evaluated that outcropping Tuscan serpentinites can store up to 100 gigatons of CO2, equivalent to 40-220 years of total Italian emissions (approximately 580 Mt/yr for the year 2010). Even assuming that only the 10% of the ophiolite bodies can be transformed into magnesite, the amount of sequestered CO2 is in any case important. Mineral carbonation is believed to be the safest option for sequestration but needs substantial further research before its efficiency can be estimated. Injection of CO2 modifies ambient formation waters, inducing fluid-rock reactions that may lead to the immobilization of injected CO2. Our ongoing project has the chance to define the temporal and spatial chemical evolution of the CO2-rich fluids responsible for the carbonate precipitation. At Malentrata, serpentinite host rocks were completely transformed to a brownish friable mineral assemblage of opal, chromian montmorillonite, Fe-rich magnesite and minor iron sulfides and oxides. The pervasive alteration of serpentinite was accompanied by the formation of a network of magnesite and dolomite veinlets, and large magnesite–dolomite veins along major tectonic structures. The major veins are characterized by the following crystallization sequence: i) early Fe-poor magnesite, ii) Fe-rich magnesite and dolomite cementing the early brecciated magnesite vein infill, and iii) late quartz, chalcedony and opal. The mineral assemblage observed both in veins and in host rock is indicative of low-temperature hydrothermal alteration driven by Si- and CO2-rich fluids under relatively low pH conditions. Here, we summarize our previous results and we report new trace elements and stable isotope data (C,O) on host rocks and vein samples. Transects of the major carbonate veins, together with unaltered, partially altered and totally altered host rocks have been selected in order to investigate the evolution of the chemical species in the fluids. The knowledge of the chemical-physical features of the fluids, the saturation/precipitation of the mineral species and the pH value of the solution in function of the time is fundamental to

reproduce this process in laboratory or for in situ and ex situ induced mineral carbonation.

5 - Lizardite in the sub-oceanic mantle of the Oman ophiolite.

Françoise Boudier, Alain Baronnet and Benoit Dewandel

(contact: Francoise.Boudier@gm.univ-montp2.fr)

Our contribution refers to a sample of harzburgite 60% serpentinized that has been the object of our interest for more than 10 years, not because it is a key specimen, but on the reverse because it is totally representative of the very homogeneous lizardite development in the 500km long 10km thick exposed mantle in the Oman ophiolite, and also of the least serpentinized peridotites collected from the ocean floor.

The sample originates from Wadi Khafifah in the Wadi Tayin massif. The fracture pattern has been measured in the area and related with the peridotite large-scale anisotropy. The sample is oriented, allowing scale transfer from kilometre to nanometer.

We illustrate the following results:
-The lizardite veining forms a regular network of 50µm thick veins, spaced 100-300µm, isolating olivine kernels, ignoring grain boundaries. The lizardite veining system is related with olivine-preferred orientation of the harzburgite protolith.
-High resolution transmission microscopy shows that the veins are filled with columnar lizardite having the basal plane (001)liz in contact with olivine, but not in topotactic crystallographic relationships with the host crystal. The lizardite columns are the pseudofibers observed at optical microscope, and that have grown inwards olivine grains, initiated along the microcrack network imaged by the lizardite mesh.
-The voids figured at nanoscale between columns insure chemical transfer from the olivine-lizardite interface to the interconnected network imaged in the median part of the lizardite veins, maintaining an open system during the process of serpentinization.
-The fluid driven open system explains the very limited volume increase at microscale during the developent of lizardite, volume expansion that is evaluated.

71 - Mineral Carbonation in Oman

Dr Giorgio Caramanna, Dr Sarah Mackintosh, Prof Mercedes Maroto-Valer

Centre for Innovation in Carbon Capture and Storage (CICCS) - Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

Carbon Capture and Storage (CCS) is a vital technology in which atmospheric anthropogenic CO_2 is injected and stored in subsurface reservoirs and therefore mitigates global warming due to the increased levels of this greenhouse gas.

A different approach to CO_2 storage in reservoirs is the fixation of CO_2 by means of specifically enhanced chemical reactions. CO_2 may react with some minerals, such as Mg silicates (Maroto-Valer et al., 2005).

The geology of Oman provides many suitable locations for the carbonation of minerals. There is a widespread presence of mafic and ultramafic rocks as components of the Semail Ophiolite. These rocks represent the main source for Mg-silicates to be used in the CO_2 mineralisation process (Kelemen and Matter, 2008). The setting of the ophiolite and the environmental conditions allow a very good outcrop of the rocks (Lippard and al., 1986).

Several sources of high volume CO_2 emissions produced by power plants (mainly fired by gas turbines), are suitable for CCS in Oman. The power-plants are close to the main outcrop of the ophiolite thus reducing the associated cost for transport of the carbon dioxide to the mineralisation plant. The average concentration of CO_2 in the exhaust fumes is around 4 – 5 %. Currently, available mineralisation methods request capture techniques suited to concentrate the CO_2 from this level to much higher values before the carbonation process could be performed.

The resulting products of the CO_2 carbonation are large volumes of rocks. Depending on the process and on the typology of available minerals the requested weight of rock for the sequestration of 1 metric tonne of carbon dioxide ranges from 3 to 6 metric tons (Zevenoven and Kohlmann, 2001). Due to the local conditions in Oman (large availability of free surfaces) the storage of these by-products should not present a problem. There is also the possibility, to be fully explored yet, that these products could be used as building materials, i.e. for road constructions, reducing the costs of the whole process.

The aim of this work is to consider the various methods that could be applied in CO_2 mineralisation in Oman.

56 - Study of potential chemical effects of CO_2 leakage into sediments and groundwater

G. Caramanna[*], Y. Wei[*], M. Maroto-Valer[*], M. Steven[**]

** Centre for Innovation in Carbon Capture and Storage (CICCS), Energy and Sustainability Research Division, Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom*
*** School of Geography, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom*

Geological storage of CO_2 has been proposed as a viable strategy to reduce CO_2 emission. In this case CO_2 is injected underground in geological formations that are expected to host the CO_2 for very long periods (IPCC, 2005). It may be possible to have leakage from the storage site and the injection points. This may result in CO_2 affecting the chemistry of the sediments.
The main potential effect of an increased level of CO_2 in the sediments is the lowering of the pH; and the resultant acidified environment may be prone to modify the chemistry of the soil with mobilization of potential pollutants such as heavy metals and alterations in the availability of nutrients (Ardelan et al., 2009). In this work, a lab rig is developed to analyze these effects in a controlled and simplified environment.

The core of the rig is a vertical Plexiglas column hosting the sediments. At the base of the column CO_2, both as gas and dissolved in water, are injected. Sensors will be able to monitor pH variations and the soil-moisture. Interstitial water and sediments samples will be collected to verify the potential chemical modifications due to the presence of CO_2.

The outcomes of this study are:

- data collection on soil pH variations as a function of the CO_2 added
- verification of the possible effects of soil acidification on nutrient concentrations and on the mobilization of heavy metals as potential pollutants
- verification of the rate of CO_2 dissolution into the interstitial water
- verification of the influence of the soil moisture on the CO_2 diffusion

The lab model results will be compared with the data from the field-lab facility “ASGARD” (Artificial Soil Gassing and Response Detection) where a controlled release of CO_2 is performed at shallow depth and soil geochemistry changes and plant responses are studied (West and al., 2009).
Preliminary lab tests on ASGARD soil samples highlighted that when exposed with 100% CO_2 the soil pH does not change significantly as well the nutrients and toxic elements concentration. When a 99% CO_2 and 1% SO_2 mixture was used the pH lowered significantly and high concentration of Al (a toxic element) was found.

References

- *Ardelan M., Steines E., Lierhagen S., Linde S. (2009) Effects of experimental CO_2 leakage on solubility and transport of seven trace metals in seawater and sediment. Science of The Total Environment, 407, 6255-6266.*
- *IPCC, (2005) Bert Metz, Ogunlade Davidson, Heleen de Coninck, Manuela Loos and Leo Meyer (Eds.) Cambridge University Press, UK. pp 431.*

- *West J., Pearce J., Coombs P., Ford J., Scheib C., Colls J., Smith K., Steven M. (2009) The Impact of Controlled Injection of CO_2 on the Soil Ecosystem and Chemistry of an English Lowland Pasture. Energy Procedia, 1, 1863-1870.*

17 - Spatial and temporal variability of fluid and gas chemical compositions at the Lucky Strike hydrothermal vent site, Mid-Atlantic Ridge.

Chavagnac V., Boulart C., Monnin C., Castillo A.

Laboratoire Mécanismes et Transfert en Géologie, 14 Avenue Edouard Belin, 31400 Toulouse FRANCE

Numerous acidic submarine hydrothermal sites have been discovered, sampled and studied along the Mid-Atlantic ridge between 14ºN and 38ºN near the Azores hot spot. Most hydrothermal systems lie on basaltic substratum and only a few of them on ultramafic rock substratum. The Lucky Strike hydrothermal field was discovered in 1992 during the joint US-French FAZAR expedition on a volcanic segment at 37º50'N at 1700m water depth (Langmuir et al., 1997). The high-temperature hydrothermal fluids (up to 328ºC) have been collected in 1993 and 1994 by the French and American teams. The results of their chemical composition are reported in Von Damm et al. (1998), Charlou et al., (2000) and Cooper et al. (2000). The features of the Lucky Strike fluids are variable chlorinities lower than seawater, low hydrogen sulfide, low metal concentrations and high gas contents. The distinct chemical end-members indicate a significant geographic control of the venting system and fluid chemistry is strongly affected by phase separation at depth. The Lucky Strike hydrothermal field has not been sampled until the recent cruises that we conducted.

In the present poster we present the chemical composition of high-temperature hydrothermal fluids and associated gases collected at this site during the sea cruises "BATHYLUCK" in 2009 and "MoMARSAT" in 2010 in order to assess the spatial and temporal variabilities of the chemical composition of hydrothermal fluid discharges. Numerous fluid discharges on the western side of the lava lake were sampled and compared to previous data. Initial results confirm that fluid chemistry is strongly affected by phase separation at depth as well as the geographic control of fluid plumbing system. In samples collected in 2010, several hydrothermal fluids are strongly enriched in gases by a factor of 10 compared to values measured on samples collected in 1993 and 1994. Charlou J.L., Donval J.P., et al. (2000). "Compared geochemical signatures and the evolution of Menez Gwen (37º50'N) and Lucky Strike (37º17'N) hydrothermal fluids south of the Azores Triple Junction on the Mid Atlantic Ridge." Chemical Geology 171: 49-75. Cooper M.J., Elderfield H., et al. (2000). "Diffuse hydrothermal fluids from Lucky Strike hydrothermal vent field: evidence for a shallow conductively heated system." Journal of Geophysical Research 105(B8): 19369-19375. Langmuir C.H., Humphris S., et al. (1997). "Hydrothermal vents near a mantle hot spot: the Lucky Strike vent field at 37ºN on the Mid-Atlantic Ridge." Earth and Planetary Science Letters 148: 69-91. von Damm K.L., Bray A.M., et al. (1998). "The geochemical controls on vent fluids from the Lucky Strike vent field, Mid-Atlantic Ridge." Earth and Planetary Science Letters 160: 521-536.

10 - The Distribution and Emplacement of Serpentinized Peridotite in the Ocean Basins

Henry JB Dick[1], Jonathan Snow[2]

1 Woods Hole Oceanographic Institution
2 University of Houston

The abundance of mantle peridotites along the global ridge system is much larger than previously thought, indicating that significant proportions of the seafloor accreted at slower spreading ridges is actually paved by partially serpentinized mantle peridotite. Long sections of ocean crust formed at ultraslow spreading rates below 12 mm/yr consist of amagmatic accretionary segments, where the mantle is pulled directly to the seafloor, covered locally by only scattered basalt flows. The absence of gabbroic rock in the dredge suites from these amagmatic segments demonstrates a very low magmatic budget, in contrast to transform walls and anomalous regions of the Mid-Atlantic Ridge such as the area around the 15°20' Fracture Zone, where both abundant peridotite and gabbro are sampled. Similarly, initial formation of oceanic spreading centers during slow continental breakup, as at Lena Trough, appear to be largely amagmatic. Large areas of ultramafic rock, however, are exposed by detachment faulting and asymmetric spreading at spreading >12 mm/yr. Another unanticipated anomaly is that mantle rocks are abundantly exposed along ridges rifting ridge centered hot spot plateaus at the Azores and Marion-Edward hot spots, indicating much thinner crust than previously supposed. An accurate estimate of how much serpentinized peridotite is exposed on the seafloor (including sedimented basement) instead of basaltic crus is difficult to make, but probably lies somewhere between 15 and 25% of the slow spread ocean crust.

There are several mechanisms by which serpentinized peridotiteare emplaced to the seafloor. On the margins of rift valley serpentinites appear to be intruded up major boundary faults, as in the southern MARK region of the Mid-Atlantic Ridge. More typically, asymmetric seafloor spreading produced by detachment faulting, as at Kane Megamullion, expose oceanic core complexes comprised of serpentinized peridotite, and/or lower crustal gabbros. These detachment faults may expose the plutonic foundation of nearly entire magmatic ridge segments, or only a portion of them, as commonly occurs at transform faults where the crust thins dramatically. At ultraslow spreading rates, and at faster rates with relatively cold lithosphere along the MAR, exposure of serpentinized peridotite occurs by normal faulting with alternating dips during relatively symmetric spreading, producing blocks with fault heaves of ~ 6 km and throws of ~ 1 km.

The degree of alteration of mantle peridotites emplaced to the seafloor and at depths shallower than MOHO is unresolved. Many authors believe that the MOHO can be a serpentinization front based on the existence of seismic MOHO below the crust-mantle boundary exposed on transform walls, as at Atlantis Bank in the Indian Ocean. Others, based on seismic P and S wave ratios, find this unlikely. In addition, however, seismic and gravity studies of large mantle outcrops at oceanic core complexes and at amagmatic spreading segments, suggest that there may be a 0.5-Km or more of serpentinized peridotite. On the other hand, fresh mantle peridotite is dredged from recently emplaced fault blocks at the ultra slow spreading the Gakkel Ridge. This suggests that our impression of the extent of

serpentinization of shallow mantle rocks may be due to the fact that the faults that expose them also localize the circulation of sea water and serpentinization.

6 - Observations of Carbonate Formation in Weathered Ultramafic Rocks, New Caledonia

Evans, K.A. (1), Frost, B.R. (2)

(1) Applied Geology, Curtin University, Perth, Australia: K.evans@curtin.edu.au
(2) Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming, USA.

Formation of magnesite ($MgCO_3$) by reaction of olivine (Mg_2SiO_4) with CO_2-bearing fluids has been proposed to have practical potential in the mitigation of anthropogenically-driven rises in atmospheric CO_2. However, laboratory experiments for simple chemical systems often result in armouring; the formation of a crust of reacted material on olivine that prevents further CO_2 access to the reacting grain.

In contrast, olivine rocks in natural environments often display up to 100% reaction with infiltrating fluids. Magnesite is produced at a wide range of pressure, temperature and fluid compositions. The formation of magnesite in weathering environments is of particular interest because these conditions can be attained easily without any requirement for significant energy input. Here, observations of the distribution of magnesite in the weathering profile of ultramafic rocks exposed in ophiolites of New Caledonia are presented, and preliminary conclusions are drawn for engineered CO_2 sequestration in ultramafic rocks.

New Caledonia is a tropical island (21 degrees S) so weathering is lateritic in nature. Typical soil profiles consist of a few metres to 10s of metres of red-weathering lateritic soil that is often overlain by ferricrete crusts or nodules. Two observations are pertinent to the use of ultramafic rocks in engineered CO_2 sequestration projects.

1. Where soil profiles can be observed, monomineralic magnesite veins are present in greatest quantities at intermediate depths of a few metres. Above this depth, veins are present, but appear to be dissolving or otherwise reacting away. Effective sequestration requires the soil-water interactions in this zone to be understood.

2. Magnesite often occurs in laminated veins with serpentine, where 100% removal of olivine has occurred. Observations are consistent with the possibility that the combination of hydration reactions, which have a high positive volume change of reaction, with carbonation reactions, produces conditions in which armouring of olivine grains does not occur and hydration/carbonation reactions may proceed to completion. Such a combination of hydration and carbonation may prove effective in engineered geosequestration applications.

These field observations require further research and analysis to prove useful in a quantitative way. Nevertheless, the field observations provide insights into the carbonation process that may prove useful in engineered carbon sequestration applications.

2 - Alkaline Fluids and Carbonate Deposition in Modern Serpentinizing Environments

Gretchen L. Früh-Green (1), Marvin D. Lilley (2), Esther Schwarzenbach (1), Susan Q. Lang (1), Sabine Méhay (1,4), Stefano M. Bernasconi (1), Marco Molinari (3) and Luigi Marini (3)

1 ETH Zurich, Department of Earth Sciences, 8092 Zurich, Switzerland
2 School of Oceanography, University of Washington, Seattle, WA 98195, USA
3 Laboratorio di Geochimica, DipTeRis - Università di Genova, Italy
4 Earth, Atmospheric and Planetary Sciences Department, MIT, Cambridge, MA 02139, USA

The alteration of mantle rocks during serpentinization is a fundamental process that has significant geochemical and biological importance in marine systems, subduction zone processes, and present-day weathering of mantle rocks on land. Here we present a geochemical and isotopic study of alkaline fluids and carbonate precipitates from high alkaline, Ca-OH springs associated with present-day serpentinization in variably serpentinized peridotites of Liguria (Northern Italy) and compare these with the marine Lost City hydrothermal system (Atlantis Massif, Mid-Atlantic Ridge).The low temperature hydrothermal system at Lost City is characterized by carbonate-brucite structures that are deposited from high pH fluids (9-11) with elevated hydrogen and methane contents resulting from serpentinization processes at depth (Kelley et al., 2005). In Liguria, fluids originating from deep aquifers circulate through serpentinites or less commonly lherzolites of the Gruppo di Voltri and produce Mg-rich to Ca- or Na-rich, alkaline waters (Bruni et al., 2002; Cipolli et al., 2004). The Ca-OH springs in Liguria are characterized by pH of 11-12, high Ca concentrations, varying sulfur-contents and negligible bicarbonate or carbonate concentrations. The concentrations of methane have remained constant for the past 10 years, which suggests relatively stable rates of water-rock interaction and carbon fluxes. The Ca-OH springs are less abundant than Mg-bicarbonate-springs, but are significant in terms of methane fluxes and the implied potential for CO2 uptake from the atmosphere. Similar to the Lost City system, methane in the Ligurian springs is enriched in 13C and points to an origin derived from mantle carbon. The spring waters have elevated concentrations of DOC and variable total N, but show no correlation with other elements. C- and O-isotopes of the carbonate deposits show strong depletions within a large range, reflecting kinetic disequilibrium during diffusive uptake of atmospheric CO2. Here we discuss the links between the inorganic reactions during serpentinization and cycling of carbon in these high pH systems.

References:
Cipolli et al., 2004, Appl. Geochem., 19: 787–802;
Bruni et al., 2002, Appl. Geochem., 17:455–474;
Kelley et al., 2005, Science, 307(5714): 1428-1434

7 - CO2 Sequestration Ultramafic Rocks: Insights from the Red Mountain Magnesite District California

Garcia Del Real, P., Maher, K., Bird, D.K., Brown, G.E., Jr.

In situ carbonation of ultramafic rocks, while providing a means to store anthropogenic CO_2 in a stable mineral form, is thought to present significant technical challenges due to the low effective permeability of the host rock, the positive volume change associated with carbonation, and the slow reaction kinetics of mineral dissolution and precipitation. However, many ultramafic rocks show substantial mineral carbonation, demonstrating the potential to sequester CO_2 via this process. An excellent example of a natural analogue for in situ CO_2 sequestration in ultramafic rocks is found at the Red Mountain Magnesite District, Santa Clara Co., CA, ~100 km SE of San Francisco. Here, large underground cryptocrystalline magnesite deposits (~10^6 tons) occur in a variably serpentinized peridotitic segment of the Del Puerto Ophiolite. Volumetrically, the ophiolite has the potential to sequester about 13 Gt of carbon, equivalent to the CO_2 emissions generated by ~12,000 1 GW coal-fired power plants in a year. To understand the origin of the magnesite deposits and the implications for CO_2 sequestration in ultramafic rocks, physical, geochemical, and isotopic data are combined to develop a model consistent with field observations. At Red Mountain, we find three generations of magnesite formation: (1) nodular bodies (~1 cm to ~50 cm diameter) that replace ultramafic lithologies; (2) fracture-filling stockwork (~1 to 5 cm thick) and massive (up to ~500 m long, several m thick) magnesite veins extending to depths of ~150 m and cross-cutting serpentinized peridotite; and (3) magnesite and serpentinite breccia cemented by later magnesite. Dolomite, huntite, and minor rhodochrosite complete the carbonate assemblage; opal, opal-quartz, and quartz veins are constrained to shear planes and appear to post-date magnesite formation. Thus, silica does not inhibit magnesite precipitation at this site. Pervasive shearing of ultramafic rocks aids in the development of initial fractures through which fluids can easily infiltrate. Based on minimal alteration of the ultramafic rocks, the fluid-rock reactions that generated the Mg-bearing fluids likely did not occur at the site of magnesite mineralization, but somewhere within a different zone in the ultramafic body. Contacts between fracture-filling magnesite and the ultramafic minerals are sharp and lack evidence of extensive metasomatic reactions, suggesting rapid precipitation at moderate to cool temperatures and shallow depths, consistent with relatively low $\delta^{18}O_{SMOW\text{-}Magnesite}$ (26.0 ± 2.1‰) and $\delta^{13}C_{PDB\text{-}Magnesite}$ (-11.6 ± 2.4‰). Localized in situ angular magnesite and serpentinite breccia cemented by later magnesite illustrate the ability of the carbonate-forming fluids to perform work on their lithologic environment during upwelling and decompression. This may represent a thermodynamically favored system, where the interplay of compression and expansion of fluids results in a self-sustaining process that opens physical pathways for carbonate precipitation. The tectonic shearing, fracturing, and brecciation of the host rocks provide the necessary permeability for CO_2 storage in ultramafic rocks, consistent with previous studies of ultramafic natural analogues for CO_2 sequestration.

28 - Experimental study of CO2 sequestration in a basalt- olivine matrix: Coupling and feedback effects of transport, hydration and carbonation processes

M. Godard, S. Peuble, L. Luquot & Ph. Gouze

Géosciences Montpellier, CNRS, Université Montpellier 2, 34095 Montpellier, France

Injection of CO2-rich fluids into (ultra-)mafic aquifers is one of the methods envisaged for mitigation of increasing atmospheric CO2 due to burning of hydrocarbons. Ultramafic and mafic rocks are rich in divalent cations (Mg, Ca and Fe); interaction with CO2-rich fluids will enhance the carbonation reactions commonly observed in these rocks during alteration and aging, and thus could provide one of the safest means of long-term CO2 storage. However, the role of reaction-transport processes has yet to be investigated in order to predict the efficiency and sustainability of carbonation in these highly reactive systems.

We present the results of experiments of CO2-rich fluid percolation through sintered analogues of olivine-accumulation zones in basaltic flows (~95% olivine Fo87, MORB glass, minor chromite). Experiments were carried out on the ICARE-2 experimental bench at a total pressure P=12MPa (confining pressure = 110% x P), temperature T = 180°C for 90 to 130 hours. The injection rate of CO2-rich fluids (MilliQ water enriched with 0.5 mol/L NaHCO3, PCO2 = 10 MPa, pH = 6.7) is 1 cm3/h. The initial porosity and permeability of samples ranges from 3 to 7% and 250.10-18 to 2500.10-18 m2 respectively.

Injection of CO2-fluids results in a strong drop in permeability, down to ~5. 10-18m2 at the end of the experiments, although dissolution occurs during experiments: (i) analyses of outlet fluids show a continuous increase in Si and Fe concentrations and high (yet decreasing with time) concentrations in Ca and Mg; (ii) a strong increase in porosity is observed upstream (up to 18% from 2-D image analyses of reacted samples) while porosity stays constant downstream. Petrological analyses indicates the development of two reaction zones along percolated samples characterized by : (i) upstream, basalt (+/- olivine) dissolution and precipitation of abundant ankerite type (Ca,Mg & Fe rich) carbonates, probably after basalt; (ii) downstream, incomplete dissolution of basalt and the growth of relatively large (up to 5 microns) Mg-Fe rich phyllosilicates perpendicular to (at the expense of ?) olivine surface. Although limited in space, carbonation appears to be an efficient process: ~ 0.015g of CO2 per gram of sample is stored as carbonates during experiments, that is, if these results were directly upscaled to the size of an injection site, an average yield of ~45 kg/m3/day (or 45 Mt of CO2/km3/day compared to the production of the Helleishidi test site which is ~160 tons CO2 per day (Gislason et al., IJGGC, 4(3), 537-545, 2010)). However, the decrease in permeability also observed during experiments may ultimately reduce carbonation efficiency. It probably results from the precipitation of phyllosilicates, a reaction typically associated to hydration of (ultra-)mafic rocks. We posit that the observed localization of dissolution-precipitation processes is due to feedback effects between reactive transport and reaction kinetics, and that these mechanisms are controlled by the CO2-injection rate. Further experiments are needed to test this hypothesis.

18 - Carbon storage below the sea floor: potential sites for crustal studies

D. Goldberg, A. Slagle.

LDEO, Palisades, NY

Deep-sea basalt formations offer a unique opportunity for carbon dioxide sequestration that combines both vast volumes of accessible pore space and base-cation-rich silicate rocks, without several of the drawbacks associated with continental saline formations. Deep-sea basalt erupts from volcanic ridges across all the world's oceans, forming pillow lavas and lava flows on the seafloor, and concurrently, large void spaces in between them. These formations are buried over time, producing highly permeable aquifers within the oceanic crust. The advantages of these deep-sea basalt aquifers as a target formation for geological CO2 sequestration arise from providing multiple physical/chemical trapping mechanisms for injecting CO2 into the subsurface. In particular, the chemical reactivity of these formations with injected fluids ultimately produce stable and non-toxic carbonates, acting as a natural, in situ weathering reactor, and thus significantly reducing the risk of post-injection leakage over long time periods.

Field data from scientific ocean drilling and other geophysical surveys suggests that shallow layers in the basaltic ocean crust offers high porosity and permeability, sufficiently closed water-rock circulation pathways, and long fluid retention times. Elevated fluid temperatures in the crust also facilitate CO2-basalt chemical reactions. We propose that pilot injection studies are conducted to establish the viability of these reservoirs for CO2 sequestration. Initial studies could re-occupy pre-existing crustal drill holes, inject supercritical CO2, and monitor the fate of the basement fluids – similar to the recent fluid tracer experiments that IODP conducted near the Juan de Fuca ridge – utilizing nearby semi-permanent, sealed-in instruments and fluid samplers.

We also assess the scientific potential of deep-sea basalt locations among various oceans for long-term carbon sequestration. We consider locations along the flanks of both spreading and aseismic oceanic ridges (i.e., arising from seafloor spreading or mid-plate volcanism, respectively) and use site-specific criteria such as drill sites with basement penetration, permeability and/or porosity data to evaluate each potential target region. Using broad constraints for CO2 trapping in deep-sea basalt, we compute potential injection volume and prioritize several promising regions, some of which occur within pipeline distances to populated areas and stationary CO2 sources.

Our results indicate that deep-sea basalt reservoirs with vast storage potential occur in many oceans and several source regions around the globe. Detailed site-specific research, pilot experiments, and risk sensitivity analyses should be conducted in each geographic setting. To establish their full benefit, the enormous worldwide volumes and low-risk stability of CO2 sequestered in deep-sea basalt aquifers must be valued in a broad economic context, that is, considering a true assessment of geological sequestration reservoir size, capture and transportation methods, the risk of leakage and potential future damages, as well the practicality and public acceptance of a particular site location.

30 - Dissolution and carbonation of mechanically activated olivine – implications for in-situ CO2 sequestration in mafic and ultramafic rocks?

*T. Anette Haug1 & Nina S. C. Simon1**

*1 Dep. of Environmental Technology, Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway. *presenting author: nina.simon@ife.no*

Ultra-mafic rocks as in-situ host rock for CO2 storage via mineral carbonation are an alternative to geological storage of CO2 in aquifers/depleted oil reservoirs, or industrial carbonation processes. One advantage of this process compared to sub-surface storage in aquifers is that ultra-mafic rocks are reactive. Therefore, permanent mineral trapping of CO2 may occur instead of solely physical trapping of pure CO2 or CO2 dissolved in brine in the pores of the rock. In-situ carbonation of ultra-mafic rocks, however, critically depends on the reaction rates of the constituent minerals under the given conditions.

Olivine is a major constituent of ultra-mafic rocks, and it has been studied extensively as a feedstock mineral for industrial carbonation purposes. Haug et al. (1) carried out olivine dissolution experiments based on mechanical activation of olivine to study the effect of varying material characteristics. The original purpose of the experiment was to study pretreatment of olivine for industrial purposes, but the results may have implications for in-situ carbonation, and for reactions of other minerals as well. An increase in olivine dissolution rate by three orders of magnitude was obtained by mechanical activation. The most likely explanation for the increase in dissolution rate is a reduction in crystallinity, as observed by XRD analyses. The decrease of particle size and the increase of specific surface area as measured by BET do not seem to significantly influence reaction rates.

Low crystallinity may also explain the preferred carbonation of deweylite over olivine and serpentine described from peridotite clasts in the Devonian Solund basin, Western Norway (2). Deweylite is an extremely fine grained clay-like aggregate of amorphous to poorly crystalline, hydrous, low temperature alteration products after olivine. The high carbonation rates of deweylite compared to olivine or serpentine have been confirmed experimentally (3). Crystallinity may be more important for reaction rates than reactive surface area. We therefore propose to further study the role of crystallinity for carbonation reactions in industrial and natural processes.

References:

1. T. A. Haug, R. A. Kleiv, I. A. Munz, Applied Geochemistry 25, 1547 (2010).

2. A. Beinlich, H. Austrheim, J. Glodny, M. Erambert, T. B. Andersen, Geochim Cosmochim Ac In Press, Corrected Proof, (2010).

3. A. Beinlich, J. Hövelmann, O. Plümper, H. Austrheim, Geophysical Research Abstracts 12, EGU2010 (2010).

60 - Convective Dissolution of CO2

Marc Hesse (1), J. Neufeld, A. Riaz

(1) Department of Geological Sciences, University of Texas at Austin, mhesse@jsg.utexas.edu

Geological carbon dioxide (CO2) storage is a means of reducing anthropogenic emissions. Dissolution of CO2 into the brine, resulting in stable stratification, increases storage security. The dissolution rate is determined by convection in the brine driven by the increase of brine density with CO2 saturation. We present a new analogue fluid system that reproduces the convective behaviour of CO2-enriched brine.

Laboratory experiments and high-resolution numerical simulations show that the convective flux scales with the Rayleigh number to the 4/5 power, in contrast with a classical linear relationship. A scaling argument for the convective flux incorporating lateral diffusion from downwelling plumes explains this nonlinear relationship for the convective flux and provides a physical picture of high Rayleigh number convection in a porous medium and predicts the CO2 dissolution rates in CO2 accumulations. These estimates of the dissolution rate show that convective dissolution can play an important role in enhancing storage security.

61 - Convection in porous and fractured systems with an exothermic reaction

M. Hesse (1), V. Prigiobbe

(1) Department of Geological Sciences, University of Texas at Austin, mhesse@jsg.utexas.edu

In the absence of active injection the rate of the carbonation reaction is limited by the convective flux that can be sustained by the thermal background gradient. In the absence of a reactions, the strength of the flux is characterized by the scaling between the Nusselt number (dimensionless heat flux) and the Rayleigh number (advective/diffusion transport). The carbonation reaction is driven by the advection of CO2 charged brine across a solubility gradient and hence its efficiency is directly proportional to the convective flux. Because the reaction is exothermic, it provides a local heat source directly proportional to the strength of the convective flux. This heat source can provide both a positive and a negative feedback depending on its location relative to the flow pattern and hence increase or decrease the convective flux and with it the rate of carbonation. Since both silicate dissolution and carbonate precipitation are favored as the temperature increases the reaction occurs in the downwellings. Heat released by the reaction is likely to have an effect on the structure of the downwellings and is likely to reduce their intensity - hinting at a potentially self-limiting process.

71 - Ex-situ mineralisation using the ICS Process

Richard Hunwick

Managing Director
Integrated Carbon Sequestration Pty Ltd
Suite 6, 12-18 Tryon Road
Lindfield NSW 2070 Australia
Phone: +61 2 9416 4513 or +61 418 964 384
richard@hunwickconsultants.com.au
www.integratedccs.com.au

The Integrated Carbon Sequestration (ICS) Process, which is patented in Australia, South Africa, and with patents pending in most other countries, promises to be an alternative to in-situ geological carbon storage in many parts of the world.

Compared with in-situ processes, ex-situ processes inherently incur higher costs because of the rock mining, grinding and other materials-handling operations involved. Offsetting these costs are the much higher degree of mineral conversion, shorter detention times and tighter control of the carbonation processes, plus avoidance of any risks of leakage of highly compressed carbon dioxide, from fraccing-induced tremors, and of adverse effects impacts on water tables and groundwater more generally.

The ICS Process further offsets these materials-handling costs (as components of total life-cycle CCS costs) by avoiding the need to handle carbon dioxide as a pure gas: the Process seamlessly converts carbon dioxide in flue gases or other streams e.g. raw natural gas, and hydrogen production from fossil fuels, to mineral carbonates. It thereby avoids the cost and energy penalties involved in stripping carbon dioxide from a capture solution and compressing it to supercritical pressures for subsequent storage.

The Sultanate of Oman is ideally situated as a source of ultramafic rocks capable of being shipped or otherwise transported to coastal power stations and other point sources of carbon dioxide throughout the Persian Gulf, and further afield to South and Southeast Asia, where most of the growth in global carbon dioxide emissions is occurring.

The poster paper will outline the basic chemistry, and provide information on mass and energy balances, and the life-cycle economics of the Process when applied to massive, accessible structures such as the Oman Ophiolite, and distant power stations.

12 - Geology of the Rainbow Massif, with evidence of carbonation in a serpentinite seafloor

B. Ildefonse(1), M. Andréani(2), E. Hoisé(3), A. Delacour(4), J. Escartin(5), M. Godard(1), J. Dyment(5), Y. Fouquet(6)

(1) Géosciences Montpellier, CNRS-Université Montpellier 2, Montpellier, France; (2) LST, ENS-Université Lyon 1, Lyon, France; (3) Laboratoire de Géologie, ENS, Paris, France; (4) DTP, OMP-Université Paul Sabatier, Toulouse, France; (5) IPGP, CNRS, Paris, France; (6) Ifremer, DRO-GM, Plouzané, France

The ultramafic-hosted Rainbow hydrothermal field is located on a massif at a non-transform offset between the AMAR and South AMAR ridge segments, at 36°14'N along the Mid-Atlantic Ridge (MAR). This massif shares some characteristics with other oceanic core complexes (OCCs), like the common dome morphology. During the two MoMARDREAM cruises (in July 2007 on R/V Pourquoi Pas ? and in Aug-Sept 2008 on R/V Atalante), we studied the structural context of the hydrothermal system and the lithology of the massif. Hydrothermal and basement rock samples were recovered by dredging and diving (using the manned submersible Nautile and the ROV Victor), complementing prior sampling realized during the FLORES (1997) and IRIS (2001) cruises.

The tectonic of the Rainbow Massif is dominated by a N-S trending fault pattern on its western flank and a series of SW-NE fault-related ridges crosscutting the massif. Available focal mechanisms indicate that tectonic extension is perpendicular to N30-50° trending-direction. The active high-temperature hydrothermal system is located in the area were these two systems crosscut.

Mantle peridotites (spinel harzburgites and dunites) were the dominant recovered rock type; they show petrographic characteristics of both melt-rock and fluid-rock interaction. Melt-rock interaction is evidenced by typical interstitial texture and high REE concentrations (1xCI). Variable degrees and styles of serpentinization and deformation (commonly undeformed or displaying talc-serpentine foliated schist into faults) were identified. Serpentinites are frequently oxidized and can be highly enriched in iron oxide veinlets, also indicated by the high FeO contents of some samples. In addition to ultramafic rocks, gabbros, cm- to dm-thick gabbroic veins, and basalts (including fresh glass) were recovered from talus and sediments on the SW and NE massif flanks. Massive chromitite was also recovered in one dredge haul. The inferred lithological variability of the Rainbow massif footwall is consistent with that of OCCs studied along the MAR and Southwest Indian Ridge. The stockwork of the hydrothermal system has been sampled on two locations on the western side of the present-day hydrothermal field, along N-S trending normal fault scarps and within the talus underneath. It is mainly made of massive sulfides, strongly altered serpentinites, and breccias containing clasts of iron sulfide and/or iron oxide impregnated serpentinites.

The abundant sediment cover of the massif precludes continuous geological mapping and completely successful dredging. Sediments were commonly found lithified in most sampled locations, as a likely result of the diffuse venting of high Ph, low T, methane-rich, serpentinite-derived fluids. Sedimentary breccias (with serpentinite and/or basalt elements in a carbonate matrix) were very commonly sampled, indicating efficient carbonation of in the footwall

serpentinites of the Rainbow OCC, and/or in the talus rocks on the flanks of the dome.

65 - Feedbacks between mantle hydration and hydrothermal convection at ocean spreading centers

Karthik Iyer, Lars H. Rüpke, and Jason Phipps Morgan*

**Corresponding author: The Future Ocean, IFM-GEOMAR, Wischhofstr. 1-3, 24148 Kiel, Germany. Email: kiyer@ifm-geomar.de. Tel: +49 431 600 2866. Fax: +49 431 600 2941.*

Hydration of the oceanic lithosphere is an important and ubiquitous process which alters both the chemical and physical properties of the affected lithologies. One of the most important reactions that affect the mantle is serpentinization. The process of serpentinization results in a drastic decrease in the density (up to 40%), seismic velocity and brittle strength as well as water uptake of up to 13wt% of the ultramafic rock. In this paper, we use numerical models to study the amount and extent of serpentinization that may occur at mid-ocean ridges and its effects on fluid flow within the lithosphere. The two dimensional, FEM model solves three coupled, time-dependent equations: (i) mass-conserving Darcy flow equation, (ii) energy conserving heat transport equation and (iii) serpentinization rate of olivine with feedbacks to temperature (exothermic reaction), fluid consumption and variations in porosity and permeability (volume changes). The thermal structure of the ridge is strongly influenced by rock permeability in addition to the spreading velocity of the ridge. Increased rock permeability enhances hydrothermal convection and results in efficient heat mining from the lithosphere whereas higher spreading velocities result in a higher thermal gradient. Serpentinization of the oceanic mantle, in turn, depends on the aforementioned, competing processes. However, serpentinization of mantle rocks is itself likely to result in strong variations of rock porosity and permeability. Here we explore the coupled feedbacks. Increasing rates of serpentinization lead to large volume changes and therefore, rock fracturing thereby increasing rock porosity/permeability while as serpentinization reaches completion, the open pore space in the rock is reduced due to the relative dominance of mineral precipitation. Although, variations in the relation between porosity and permeability and serpentinization before the reaction reaches completion do not significantly affect the degree of serpentinization, unreasonably large portions of the mantle would be serpentinized if rock closure does not occur at the final reaction stage. The amount of water trapped as hydrous phases within the mantle shows a strong dependency on the spreading velocity of the ridge with water content ranging from 0.18x105 kg/m2 to 2.52x105 kg/m2. Additionally, two distinct trends are observed where the water content in the mantle at slow-spreading ridges drops dramatically with an increase in spreading velocity. The amount of water trapped in the mantle at fast-spreading ridges, on the other hand, is lower and does not significantly depend on spreading velocity.

References:

Iyer, K., Rüpke, L.H. and Morgan, J.P., 2010. Feedbacks between mantle hydration and hydrothermal convection at ocean spreading centers. Earth and Planetary Science Letters, 296(1-2): 34-44.

31 - Geologic CO2 Sequestration Experiments with Hawaiian Picritic Basalts

K. T. M. Johnson, University of Hawaii

B. P. McGrail, and H. T. Schaef, Pacific Northwest National Laboratory

Capturing and storing anthropogenic carbon dioxide in deep geologic formations is a potential CO2 mitigation solution being studied to reduce adverse effects of increasing greenhouse gas concentrations on the global climate. Basalt formations, widespread globally, are currently being considered as a long term storage option. Because combustion gas streams often contain impurities, it is also important to consider contaminants (e.g., SO2, N2, and O2) that could be co-injected with CO2. Injecting to depths greater than 800 m, these CO2 gas mixtures will reside as water-wet supercritical fluids in contact with the basalt reservoir rocks. Here we examine reaction products resulting from exposing Hawaiian picrite basalts to water equilibrated with scCO2, water bearing scCO2, and mixtures containing gaseous sulfur compounds.

Hawaiian basalts in this study were fresh, vesicular, and olivine-rich (20+vol%). Basalts, crushed or in large pieces, were exposed to wet supercritical fluid and aqueous dissolved gases for 80 to 550 days at 100 bar and 50°-100°C. Post-reacted basalt in the pure scCO2 system showed the least amount of reactivity. Carbonate precipitates formed discrete circular coatings on the olivine grain surfaces after 550 days of exposure to the aqueous dissolved CO2. However, the olivine surface was significantly altered in just 80 days after exposure to wet scCO2 containing 1% SO2. The most reactive basalt components were olivine grains, with surfaces dominated by cracks and precipitates of Mg-S compounds (Fig.1). Chemistry determined by SEM-EDS indicated the cracked surface was depleted in Mg and rich in Si. Minor amounts of sulfur were detected in this leached layer as well. Exposed olivine interiors were found to have the original olivine chemistry. Surface precipitates associated with the olivine crystals include hexahydrite (MgSO4●6H2O), magnesium thiosulfate hydrate (MgS2O3●6H2O), along with three different hydrated sulfite phases. These types of experiments illustrate the potential basalt formations hold for long term storage of CO2 and the importance of understanding supercritical phase chemical reactions involved in geologic carbon sequestration.

32 - Kinetics of olivine carbonation for the geologic storage of carbon dioxide

Natalie C. Johnson [1,2], Burt Thomas[3], Kate Maher[2], Dennis K. Bird[2], Robert J. Rosenbauer[3], Gordon E. Brown, Jr [1,2]

1 Dept of Chemical Engineering, Stanford University, Stanford, CA, USA
2 Dept of Geological and Environmental Science, Stanford University, Stanford, CA, USA
3 United States Geologic Survey, Menlo Park, CA, USA

One potential method to sequester carbon dioxide (CO2) over geologic time periods is mineral carbonation, specifically the thermodynamically favored reaction of CO2with Mg-silicate minerals to produce Mg-carbonate minerals.The present study seeks to examine the kinetic behavior of the dissolution of olivine and subsequent precipitation of magnesiteand silica in a unique batch reactor that allows for liquid and gas samples to be withdrawn over time in order to monitor reaction progress without altering the conditions in the reactor.The reactions were performed at 60oC and 100 bar CO2pressure. Quantitative x-ray diffraction analysis revealed that 9% of the initial silicate was converted to carbonate. The addition of 1 g/L salicylic acid improved the conversion to 33%.Large amounts of an amorphous, silicon-rich phase were also observed. Solution analysis using inductively coupled plasma (ICP) showed that dissolution rates change with time, pH, and possibly saturation state of secondary phases.In future studies, hydrated Mg-silicate minerals will be used as the feedstock material in order to investigate the carbonation kinetics of the more abundant rock.

24 - Geochemical and petrophysical estimation studies on sedimentary rock samples from the Pannonian Basin, Hungary

KIRÁLY, Csilla1; BERTA, Márton[1]; FALUS, György[2]; SZÉKELY, Edit[3], SZABÓ, Csaba[1]

1 Lithosphere Fluid Research Lab (LRG), Eötvös University Budapest (ELTE)
2 Eötvös Loránd Geophyiscal Institute of Hungary (ELGI)
3 Budapest University of Technology and Economics (BME)

Saline aquifers are considered to have the largest capacity for Carbon Capute and Sequestration (CCS) because their pore water cannot be used for drinking and for agricultural activities. In the Pannonian Basin (Hungary) there are a few sedimentary subbasins filled up by sedimentary rock sequences containing such aquifers, which have significant potential for CCS in Hungary. The chosen study area in the Pannonian Basin is the Jászság Subbasin, well known by numerous seismic profils and hydrocarbon exploration wells. As Hungary is situated in the middle of the Pannonian Basin, its emissions could be significantly reduced by CCS. That is the major reason to find a suitable place for CCS.

During the evolution of the Pannonian Basin, large paleorivers brought huge amounts of sediments from NE and NW to this sedimentary system including from deep water to deltaic sequences. The process filling up the area resulted in reservoir quality sandstones and clayey units acting as seals above the sandstones.

The chosen sedimentary formations (Szolnok Formation for storage, and Algyő Formation for cap rock) now form a hidrogeologically coherent regional system suggesting a large potential for storage capacity without significant pressure increase on long-term industrial usage for CCS. However, the system is not homogenous: there are siltstone interbeddings both in the Szolnok and the Algyő Formations as it is seen on well-logs of hydrocarbon exploration wells. The siltstone in these formations does not have porosity high enough to serve as storage rock, whereas the permeability is not small enough to be a good sealing rock. That is why we try to avoid sampling siltstone-rich layers in the whole Jászság Basin. On the other places, and depth intervals we have used drilling cores to get a realistic quality and representative quantity of the tested formations.

Our detailed studies deal with the sandy Szolnok Formation. This sedimentary rock is basically sandstone. Its bottom is nearly 1000 to 3500 m deep under the surface, thus it would be used as a storage rock. Its cap rock could be the Algyő Formation with more than 1000 m thickness, and a clayey composition.

These potential rock associations are examined in detail in our ongoing research. We are doing ex situ tests to observe the behavior of the rocks when injecting supercritical CO2 in the saline pore water. All the tests were performed on pressure, composition and temperature conditions representing the planned injection conditions. These results are presented in our poster, as the used methods could be useful also for experiments with ultramafic rocks. Tests are made on both of the storage and cap rocks. Moreover, we are also making some tests with samples from the boundary of cap and reservoir formations to determine the geochemical

reactions and petrophysical changes taking place on the highly critical part of the storage complex in order to ensure long term safe storage.

63 - Heterogeneous phase equilibria during carbon sequestration into serpentinized peridotite: Using the fluid chemistry as a monitor of carbonation progress

Frieder Klein, Woods Hole

Oceanographic Institution & Laboratory for Atmospheric and Space Physics

A major challenge for in situ carbonation of serpentinized peridotite will be to monitor the reaction progress during and subsequent to CO2 injection. Here I propose to use the chemistry of interacting fluids to approximate changes in mineralogy, that inevitably take place when serpentinized peridotite undergoes infiltration of a CO2-rich (or enriched) fluid. Away from the injection site several metasomatic zones will develop as a function of time and mass of the infiltrating fluid. These metasomatic zones can be represented by the following major mineral assemblages: 1) magnesite+quartz, 2) talc+magnesite+quartz, 3) talc+magnesite, 4) serpentine+magnesite+talc, 5) serpentine+magnesite, 6) serpentine+brucite+magnesite, and 7) serpentine+brucite±olivine±orthopyroxene (the protolith).

It can be anticipated that with constant rate of fluid infiltration each boundary between two adjacent zones will move laterally away from the injection site. Once the whole sequence of metasomatic zones is established no major qualitative change in the composition of the zones should take place.

Steep geochemical potential gradients of both CO2,aq and SiO2,aq between the injection site, where the system is entirely controlled by the composition of the infiltrating fluid, and zone 7 (i.e. distal to the injection site, where the fluid composition is controlled by serpentinized peridotite) promote metasomatic mass transfer of CO2,aq, that ultimately drive the formation of carbonate. Thermodynamic reaction path models predict that a stair-step pattern in aCO2,aq, aSiO2,aq, fO2,g, fS2,g and pH will develop between zones 2, 4, and 6 (buffered to virtually constant, quasi invariant values), while zones 3 and 5 have a transitional (univariant) geochemical character. At a given temperature and pressure the concentrations of CO2,aq and SiO2,aq, together with fO2,g, fS2,g and pH (e.g., measured in wells distal to the injection site) will be indicative of the dominant phase equilibria. Since relatively small amounts of fluid suffice to accomplish a complete carbonation of serpentinite at temperatures below 300 °C, the models predicts that prolonged fluid infiltration (i.e. high water-to-rock mass ratios) can result in the decarbonation and silicification of carbonate. Real-time monitoring and speciation of CO2,aq, SiO2,aq, fO2,g, fS2,g and pH would help to identify the saturation states of solid phases and prevent unintended liberation of already sequestered CO2.

34 – Experiments in hydrous tholeiitic and peridotitic systems at shallow pressures: Constraints on magmatic processes in the Oman paleoridge

J. Koepke, S. Feig, J. Berndt

contact: koepke@mineralogie.uni-hannover.de, Leibniz University Hannover, Germany

The Oman ophiolite is regarded to present the best proxy of fast-spreading oceanic crust on land. However, the Oman ophiolite is regarded as subduction zone-related, and the nature of this subduction zone is still under controversial discussion ("classical" subduction zone versus "intraoceanic thrusting" or "shallow subduction"; see discussion in Boudier and Nicolas, 2007). In this paper we show that those lithologies present in the Oman ophiolite classical related to supra-subduction zone magmatism can be produced in "normal" MORB-type systems at shallow pressures just by adding water. Three series of experiments were performed, as outlined in the following.

(1) Water-saturated partial melting of oceanic gabbros between 900 and 1000°C at 200 MPa produces a characteristic interstitial paragenesis consisting of An-enriched plagioclase, orthopyroxene and pargasite plus a plagiogranitic melt. Petrographic and microanalytical investigation of gabbros from the Oman ophiolite revealed the presence of the characteristic residual mineral paragenesis, implying a model that water-rich fluid phases percolated through the fresh, still very hot gabbro triggering partial melting and producing the typical plagiogranites which often can be observed as late intrusions in the Oman ophiolite.

(2) Crystallization experiments in a hydrous gabbroic system demonstrate that at pressures higher than 100 MPa with bulk water content of 2-3 wt%, wehrlites can be produced by the accumulation of early crystallized olivine and clinopyroxene at temperatures between 1040 and 1080°C. The experimental data imply that many of the enigmatic crustal wehrlites in the Oman ophiolite can be explained by the addition of a small amount of water to the gabbroic crystal mushes.

(3) Water-saturated partial melting experiments using a typical Oman harzburgite as starting material were performed at shallow pressures. The experimental results show that the formation of distinct, lithologies known from the Oman ophiolite like high-Ca boninitic rocks, depleted gabbronorites, and residual dunites including chromitites, could be interpreted as a result of a process of fluid-induced partial melting of sub-Moho harzburgite below the Oman paleoridge at temperatures between 1100 and 1200°C.

The combined experimental data imply that special lithologies related to a "late-stage magmatism" in the Oman ophiolite, like plagiogranites, boninites, depleted gabbronorites, and some types of dunites, can be explained by interaction of hydrous fluids with deep crustal gabbros and the sub-Moho mantle at shallow pressure, respectively. The best model for explaining the magmatic scenario is "intraoceanic thrusting" or "shallow subduction" according to Boudier and Nicolas (2007). A classical (deep) subduction zone is not necessary as prerequisite for this type of plutonic suite.

Literature

Boudier, F. and Nicolas, A. (2007) Comment on "dating the geologic history of Oman's Semail ophiolite: insights from U–Pb geochronology". Contrib Mineral Petrol, doi 10.1007/s00410-007-0189-5

9 - Towards a reference profile for fast–spreading oceanic crust: Petrology and geochemistry of the "Wadi Gideah" cross section in the Southern Oman ophiolite.

J. Koepke, P.E. Wolff, H. Strauss, D. Garbe–Schönberg

contact: koepke@mineralogie.uni-hannover.de, Leibniz University Hannover, Germany

Ocean crust formed at fast–spreading rates exhibits a relatively uniform seismic stratigraphy and is regarded as layered and relatively homogeneous, in contrast to oceanic crust generated at slow–spreading ridges. Importantly, theoretical models on magmatic accretion of the oceanic crust, thermal models, mass balance calculations for the whole ocean crust, or general alteration models only exist for fast–spreading systems. However, due to the lack of exposures and drilled sections of the deep basement of fast–spread crust, most models for fast–spread crust are not tested up to date by using natural samples. Therefore, it is necessary to perform complementary studies of ophiolites, in particular the Oman ophiolite, which is regarded to present the best example of fast–spreading oceanic crust on land, and which played a vital role in developing crucial paradigms for understanding sea floor spreading.

During February 2010 we undertook a detailed field campaign on the Wadi Gideah which is located in the Wadi–Tayin Massif in the southern part of the Oman ophiolite in order to sample a complete section through the whole ophiolite. The southern massifs of the Oman ophiolite are regarded as the best area for studying primary "normal" fast-spreading ridge processes, where the so-called "late-stage magmatism" is widely absent. Up to now, our profile contains ~100 samples from mantle peridotites, gabbros to dikes and lavas. This profile is representative for fast–spread oceanic crust both in terms of completeness of the crust–forming structural components and in coherence of geochemical and petrological data to be obtained, thus well–suited for shedding light on crustal accretion processes and the evolution of primary and secondary geochemical cycles of fast–spreading oceanic crust. In order to obtain data sets as coherent as possible (major and trace elements, isotopes, and microanalytical results), we will follow a modern concept to perform all analytical investigations on the same samples. Our study follows an approach of an US working group in the late 1970s to obtain a complete profile through the Oman ophiolite (Pallister & Hopson, 1981, J. Geophys. Res. 86). Today, 30 years later after tremendous increase of knowledge on the geodynamics of ocean ridges especially due to ship–based science and due to continuous research on the Oman ophiolite, many of the paradigms valid at that time changed making it necessary to resample/reinterpret the Wadi-Gideah profile.

In this study we present our first data obtained, in order to present geochemical and petrological logs of the Wadi-Gideah section. Main interest at this stage of the project is to focus on the mineral chemical evolution as well as the bulk major/trace element compositional evolution. Far-reaching goals are to elaborate the complete evolution of the hydrothermal alteration cycles (by using Sr, O, S, and other suitable isotopes) and a "modern" mass balance considering the state of the art knowledge. Finally, the Oman reference profile provide scientific support for the drilling of the Integrated Ocean Drilling Program (IODP) at Site 1256 (equatorial Pacific) where the deepening of the present hole down into the gabbro crust is scheduled for 2011.

64 - Bringing mineral carbon dioxide sequestration down to earth: Thermodynamic considerations using realistic reactant and product phases.

Sam Krevor, Ph.D

Department of Energy Resources Engineering
Stanford University

skrevor@stanford.edu

In making the case for the sequestration of CO2 in mineral form, whether through the injection of CO2 into a subsurface rock formation or engineering the transformation in a chemical reactor, researchers often cite the thermodynamic favorability of the processes as a motivating factor. Most studies provide as an example chemical conversion the reaction of forsteritic olivine with CO2 to form magnesite and amorphous silica. This chemical conversion, however, is not generally representative of what would likely take place in an industrial process. On the mineral reactant side, serpentinized rocks are far more widespread globally than deposits of pure forsterite. In addition, ultramafic rocks are often intermixed with mafic rocks and have substantial percentages of pyroxene minerals. On the product side, kinetic limitations at the temperature and pressure conditions at which conversion processes are being considered do not always favor the production of magnesite. The formation of a less thermodynamically stable phase such as nesquehonite, hydromagnesite, or even brucite is at times a likely necessary precursor to the ultimate conversion into magnesite. Consideration of reactant phases other than olivine, and product phases other than amorphous silica and magnesite, will dramatically change the thermodynamic calculus of conversion processes, and under certain temperature and pressure conditions negate the driving force altogether. These considerations are essential in bringing a realistic outlook to the potential for any variation on a mineral CO2 sequestration process.

5 - Barzaman Formation in the United Arab of Emirates: a natural analogue for permanent CO2 fixation using ultramafic rocks.

Alicja M. Lacinska[1], Michael T. Styles[1]*

Anthropogenic release of CO2 into the atmosphere from burning fossil fuel and deforestation adds substantially to the natural greenhouse effect, causing warming of the Earth. As a consequence the atmospheric CO2 concentration has risen from 280 ppm during the pre-industrial times to 380 ppm today (Matter, Kelemen, 2009).

One of the proposed solutions for removing CO2 from the atmosphere is its permanent fixation into minerals stable on the Earth surface, such as carbonates. The principal concept of this solution is to turn silicate into carbonate. Mg-rich silicates, such as serpentine and/or olivine are the suggested minerals for use in carbonation process. The technology of carbonation requires significant pre-treatment to speed up reactions to a time scale suitable for an industrial process. The pre-treated substrate, magnesium ions or oxide is reacted with dissolved CO2. The dissolved CO2 dissociates to bicarbonate and carbonate ions and in the presence of divalent cations (Mg2+) from the pre-treated minerals, the two components react to form a thermodynamically stable mineral, magnesite.

In our study we present a natural analogue for CO2 sequestration by mineral carbonation. The study area is a magnificently exposed desert area in the United Arab Emirates (UAE), where a large volume of ophiolite-derived silicate conglomerate (Barzaman Formation) has reacted with CO2 and been transformed in to the stable (MgCa) carbonate mineral - dolomite. Peridotite is strongly out of equilibrium with air and water at the Earth`s surface (Kelemen, Matter, 2008), and its alteration provides a high proportion of Mg that is available for further reactions. Both the dissolution of Mg-rich minerals (olivine, pyroxene and serpentine) and their further alteration to dolomite have taken place in the near surface environment in an arid to semi-arid climate. The carbonation of peridotite conglomerate was sequential. Smaller sandy components of the conglomerate matrix were affected first, being completely replaced. The second stage was replacement of the larger clasts resulting in the formation of concentric chemical zonation, with the outer zone of the pebbles now composed of dolomite and the inner core composed of the remnant unaltered silicate minerals.

From simple calculations of the volume of the Barzaman Formation in the UAE, and based on the assumption that at least 50% of the Formation is now composed of dolomite, we can deduce that about 5x109 tonnes of CO2 has been permanently fixed into a thermodynamically stable carbonate mineral at the Earth's surface and that it has been there for millions of years (since the Miocene ? 10 mA). This is a natural example of the large-scale transformation of silicate in to carbonate rock that demonstrates a permanent storage solution for captured CO2. We do not know the time scale of this transformation but it gives support for the potential and feasibility of the technological process of carbonation of ultramafic rocks that is now being intensively studied by many research units around the world.

13 - Fossil Bivalves in the Rainbow Area: New Insight into the Diversity and Evolution of Chemosynthetic Communities

F. Lartaud(1), C.T.S. Little(2), M. de Rafelis(3), G. Bayon(4), B. Ildefonse(5), J. Dyment (6), N. Le Bris (1)

(1) LECOB, Observatoire Océanologique Banyuls sur Mer, UPMC Paris 06, Banyuls-sur-Mer, France; (2) C.T.S., University of Leeds, Leeds, UK; (3) ISTeP, UPMC Paris 06, Paris, France; (4) Géosciences Marines, IFREMER, Plouzané, France; (5) Géosciences Montpellier, CNRS-Université Montpellier 2, Montpellier, France; (6) IPGP, CNRS, Paris, France.

Hydrothermal circulation at ultramafic-hosted sites supports a large variety of high- and low-temperature hydrothermal vents and associated ecosystems. Along the Mid-Atlantic Ridge (MAR), different types of habitats for chemosynthetic-based organisms have been identified in a serpentinization context, e.g. the high temperature vents at Rainbow and Logatchev, and the low temperature, off-axis Lost City vents. Each displays a certain degree of isolation and endemic taxa. Much remains to be understood about the temporal dynamics and biogeography of these communities over geological time scales. During the MOMARDREAM_08 cruise (August 2008), numerous dead bivalve shells and associated carbonates were dredged from close to the active Rainbow vent field (36°N). These fossils point to past hydrothermal activity on top of a heavily sedimented ultramafic structure, 2.6 km east of the Rainbow field (site DR 9) at 24 ± 0.2 kyr, and on the slope of the same structure, 1.2 km north-east to Rainbow field (site DR 11) at 192 ± 12 kyr. At the younger site abundant shells of the vesicomyid bivalve genus Phreagena, previously unknown from the MAR, are distributed over a large area and associated with rarer specimens of the thyasirid bivalve Thyasira. At the older site, specimens of the mussel Bathymodiolus azoricus are abundant and co-occur with a few specimens of Phreagena and Thyasira. This diversity of bivalves is not seen in the living vent community at Rainbow.

The isotopic signatures of bivalve shells from both DR 9 and DR 11 suggest influence of oxidized methane on the sediment pore water DIC, which is consistent on Oceanic Core Complexes environments. There is a contrast between Phreagena shells, which are enriched in 13C, and Thyasira shells, which are highly depleted in 13C suggesting different mechanisms of carbon fixation for these bivalves. At off-axis sites like DR 9 and DR 11, both sediment cover and the availability of methane and sulphide, and possibly even hydrogen, as electron donors for autotrophic symbionts offer a wide variety of suitable habitats for chemosynthetic species. The spatial distribution and geochemical diversity of serpentine-hosted habitats might have favoured a more diverse fauna to colonize these habitats, and could have played a major role in the ability of chemosynthetic vent and seeps species to disperse over ocean basin scales.

36 - Impact of Capillarity on Salt Crystallization in Porous Media

Duc Le, Jagan Mahadevan

email: jmahadevan@utulsa.edu

When a gas is injected into a porous medium that is partially saturated with ionic liquids supersaturation may occur due to drying and hence lead to crystallization of salts. In this poster we present results from a recent study on crystallization of salts due to evaporation. A reactive transport model for the evolution of solid and liquid concentrations of salt, in porous media, due to evaporation by gas flow is presented. The model takes into account the impact of capillary-driven liquid film flow on the evaporation rates as well as the rate of transport of salt through those films. It is shown that at high capillary wicking numbers and high dimensionless pressure drops, supersaturation of brine takes place in the higher drying rate regions in the porous medium. This leads to solid salt crystallization and accumulation in the higher drying rate regions in the porous medium. In the absence of wicking, there is no transport and accumulation of solid salt. Results from experiments of flow-through drying in rock samples are compared with model prediction of salt crystallization and accumulation. The model may be applied easily to include precipitation reactions in addition to drying related effects which are expected to occur during the injection of carbon di-oxide during sequestration.

35 - Serpentinization of sintered olivine during seawater percolation experiments

Linda Luquot (1), Muriel Andreani (2), Marguerite Godard (1), Philippe Gouze (1), Benoit Gibert (1), Gérard Lods (1)

(1) Géosciences Montpellier, CNRS, Université Montpellier 2, F-34095 Montpellier,
(2) Laboratoire des Sciences de la Terre, Université Lyon 1, F- 69622 Villeurbanne

Hydration of the mantle lithosphere exposed at slow spreading ridges leads to significant changes of the rock rheological, geophysical, mineralogical and geochemical properties, and to the production of large amounts of H2 and CH4, and of complex carbon molecules that support primitive ecosystems. The onset and efficiency of these hydrothermal processes requires penetration and renewal of fluids at the mineral-fluid interface. However, the mechanisms and the depth of fluid penetration are still poorly understood. Moreover, serpentinization is exovolumic, if a mass-conservative system is assumed, or chemical elements are leached out to conserve rock volume. Thus, the durability and extent of serpentinisation depends of the system capacity to create space and/or to drive mass transfers. In order to investigate these hydrodynamic and chemical mechanisms, we did a series of laboratory experiments during which seawater was injected in sintered San Carlos olivine samples at conditions representative of low temperature ultramafic hydrothermal systems.

The percolation-reaction experiments were carried out using the ICARE 2 experimental bench at a confined pressure of 19 MPa and a temperature of 190°C; water flow was set at a constant specific discharge of 0.06 mL/h. During experiments (up to 23 days), permeability decreases continuously although the high Si concentrations in outlet fluids indicate steady olivine dissolution. Fluids are also depleted in Fe and Mg, suggesting precipitation of Fe- and Mg-rich mineral phases; SEM and AEM/TEM analyses of the reacted samples allowed to characterize hematite and poorly crystallized serpentine, both formed at the expense of olivine. Mass balance calculations indicate that, on average, 15 wt. % olivine was dissolved while the same mass of serpentine (+/- brucite) was formed; concurrently, porosity decreased from ~ 12% to 5 %. We infer that the structure of the newly formed serpentine resulted in the clogging of fluid paths and explain the decrease of permeability during experiments. Hematite (<1 wt.%) is also observed, indicating redox reactions. The estimated total hydrogen content of outlet fluids is 4.5 mmol/kg. Although these values are in the same range as those measured at the Lost City hydrothermal vent (e.g., (Kelley et al, 2001)), they are significantly lower than theoretical estimates of hydrogen composition of serpentinisation fluids (e.g., 21-170 mmol/kg, Wetzel & Shock, 2000). We infer that these differences result, in part, from poor fluid renewal at the mineral interface during experiments, and maybe also in natural systems. These experimental results are used to constrain numerical reactive transport models and better understand the scale and efficiency of serpentinization reactions (effective reaction rates in porous/fractured media) at the scale of spreading ridges.

References :
Kelley et al., Nature, 412, 145-149, 2001 ;
Wetzel & Shock, JGR, 105, 8319-8340, 2000.

16 - U-Th systematics and ages of carbonate chimneys at the Lost City Hydrothermal Field

Kristin A. Ludwig (1, 3); Chuan-Chou Shen (2); Deborah S. Kelley (3); Hai Cheng (4); R. Lawrence Edwards (4)

Contact Information:
1) Now at Consortium for Ocean Leadership, kludwig@oceanleadership.org, 206-293-5384
2) Department of Geosciences, National Taiwan University, Taiwan, ROC
3) School of Oceanography, University of Washington, Seattle, WA
4) Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN

The Lost City Hydrothermal Field (LCHF) is a serpentinite-hosted vent field located 15 km west of the spreading axis of the Mid-Atlantic Ridge. In this study, uranium-thorium (U-Th) geochronological techniques have been used to examine the U-Th systematics of hydrothermal fluids and the 230Th ages of hydrothermally-precipitated carbonate chimneys at the LCHF. Fluid sample analyses indicate that endmember fluids likely contain only 0.0073 ng/g U or less compared to 3.28 ± 0.03 ng/g of U in ambient seawater. For fluid samples containing only 2-21% ambient seawater (1.1-11 mmol/kg

Mg), Th concentration is 0.11 to 0.13 pg/g and surrounding seawater concentrations average 0.133 ± 0.016 pg/g. The 230Th/232Th atomic ratios of the vent fluids range from 1 ± 10 to 11 ± 5 ×10-6, are less than those of seawater, and indicate that the vent fluids do not contribute a significant amount of non-radiogenic 230Th to the LCHF carbonate chimney deposits. Chimney 238U concentrations range from 1-1-10 ug/g and the average chimney corrected initial d234U is 147.2 ± 0.8, which is not significantly different from the ambient seawater value of 146.5 ± 0.6. Carbonate Th concentrations range broadly from 0.0038 ± 0.0003 to 125 ± 16 ng/g and 230Th/232Th atomic ratios vary from near seawater values of 43 ± 8 × 10-6 up to 530 ± 25 × 10-3. Chimney ages range from 17 ± 6 yrs to 120 ± 13 kyrs. The youngest chimneys are at the intersection of two active, steeply dipping normal faults that cut the Atlantis Massif; the oldest chimneys are located in the southwest portion of the field. Vent deposits on a steep, fault-bounded wall on the east side of the field are all <4 kyrs old, indicating that mass wasting in this region is relatively recent. Comparison of results to prior age-dating investigations of submarine hydrothermal systems shows that the LCHF is the most long-lived hydrothermal system known to date. It is likely that seismic activity and active faulting within the Atlantis Massif and the Atlantis Fracture Zone, coupled with volumetric expansion of the underlying serpentinized host rocks play major roles in sustaining hydrothermal activity at this site. The longevity of venting at the LCHF may have implications for ecological succession of microorganisms within serpentinite-hosted vent environments.

57 - The Effect on Porosity and Permeability of North Sea Sandstones Post Mineral Carbonation

Dr Sarah Mackintosh, Mr Keith Bateman, Prof Mercedes Maroto-Valer, Dr Matthew Hall

Carbon Capture and Storage (CCS) is considered to be a reliable method to reduce the atmospheric injection of CO2 of anthropogenic origin and therefore to mitigate global warming due to the increased levels of this greenhouse gas. Currently, research is mainly focused on geological storage. Large volumes of CO2 could be safely stored in specific geological structures able to retain it for geological periods. The trapping mechanisms involved in geological storage are similar to the ones that occur naturally for the hydrocarbon reservoirs. Long-term monitoring is requested both during and after the injection phase to assure that there are no leakages from the storage site.

A very different approach to the problem is the fixation of carbon dioxide in very specific rocks where an “in situ” reaction of CO2 with the hosting rocks forms solid carbonate minerals. This system could be used to capture and store billions of tons of CO2 per km3 of rock per year, while eliminating the need for monitoring CO2 leakage. (Huijgen, W. Comans, R. 2004).

The extent of mineral trapping in the reservoir will largely depend on the in-situ mineralogy, the pressure, temperature, pH and rate of injection (Matter, J. and Keleman, P. 2009). Sandstone aquifers appear to be the most attractive for geological storage due to their porosity, permeability and buffering ability (Rochelle et al., 2004). Fluid–rock reactions that increase the solid volume, such as the carbonation of anhydrous silicates, are often self-limiting because they fill porosity, reduce permeability, and create 'reaction rims' that act as diffusive boundary layers between unreacted minerals and fluid injection (Matter, J. and Keleman, P. 2009). However, there may be positive feedback regimes in which high reaction rates at high temperature are sustained by exothermic heating, and permeability and reactive surface area maybe maintained or enhanced by cracking in response to large increases in the solid volume. If these regimes can be accessed, in- situ carbonation offers a rapid, relatively inexpensive, and essentially permanent method for CO_2 capture and storage.

The controls on permeability evolution during carbonation represent the most crucial avenue for future research on this topic (Kelemen, P Matter, J, 2008). Therefore, in order to study how porosity and permeability changes during in-situ carbonation, experiments have been designed to flow CO_2 through rock cores. Data will be presented on porosity and permeability from a North Sea sandstone rock core. The core will be analysed using a CT scanner. This data will be used to analyse what effect permeability evolution will have on mineral carbonation over time.

References

Energy Research Centre of the Netherlands (2004) Carbon Dioxide Sequestration by Mineral Carbonation
Huijgen, W Comans, R Kelemen, P. B. & Matter, J. (2008) In situ carbonation of peridotite for CO_2 storage. Proc. Natl Acad. Sci. 105, 17295–17300.
Matter, J. and Keleman, P. (2009) Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation Nature Geoscience 2, 837 – 841

Rochelle C. A., Czernichowski-Lauriol I., Milodowski A. E. (2004) The impact of chemical reactions on CO2 storage in geological formations: a brief review In Geological storage of carbon dioxide vol. 233 Baines S. J., Worden R. H. 87–106 London, UK Geological Society Special Publications

26 - Carbonation of artificial silicate minerals in urban soils: rates and mechanisms in passive surface systems

David A. C. Manning, Phil Renforth and Carla-Leanne Washbourne

School of Civil Engineering and Geosciences, Newcastle University, UK
david.manning@ncl.ac.uk

Calcium silicate minerals occur widely in soils in cities and at industrial sites. Derived ultimately from Portland cement, they accumulate as a consequence of demolition of pre-existing structures. Alternatively they may contribute to soils within the cover over accumulations of steel slag in the vicinity of steel works.

In survey work at a number of sites in the north of England (Renforth et al., 2009), we have investigated the precipitation of calcium carbonate in soils of different ages. Within 10 years after demolition, urban soils can accumulate up to 30 kg/m^2 (300 T/ha) of carbon as calcite. This is twice as much as typically occurs as organic C in agricultural soils (approx. 17.5 kg/m^2 or 175 T/ha).

Carbon and oxygen isotope data consistently show plots that trend towards highly negative values for $\delta^{13}C$ and $\delta^{18}O$. These plots are very similar to those widely observed for natural pedogenic carbonate minerals from a range of environments, but extend to more negative values typical of carbonates produced in high pH environments in which kinetic fractionation takes place. Thus the formation of urban soil carbonates involves mixing of plant-derived carbon and carbonation associated with hydroxylation. Typically, over 95% of the carbon in urban pedogenic carbonates is derived from the atmosphere through soil carbonation reactions, some biologically driven.

The rate of formation of soil carbonates in urban systems can be estimated from a combination of field observations and modeling and is of the order of 0.5 mg C m^{-3} sec^{-1}, or about 15 kg C m^{-3} per year. The limiting factor is the availability of calcium silicate minerals. If restricted to those derived from artificial materials such as cement and slags, their carbonation merely compensates for the CO_2 lost on calcining mined limestone raw materials involved in their production. However, the global potential of carbonation of artificial silicates is substantial, estimated to be equivalent to 190 – 332 million tonnes C.

Given the limited availability of artificial silicates, it is necessary to consider carbonation of natural calcium silicate rocks, and the role of plant growth and related processes on carbonation.

Renforth, P., Manning, D. A. C. and Lopez-Capel, E. (2009) Carbonate precipitation in artificial soils as a sink for atmospheric carbon dioxide. Applied Geochemistry, 24, 1757-1764.

22 - Field Characterization of the Soda Springs Mafic Rock CO2 Sequestration Analogue Site, Idaho, USA

Travis L. McLing, Robert W. Smith, Robert K. Podgorney, William Smith***

*The Center for Advanced Energy Studies,
**Idaho State University

Analogue sites are particularly relevant and useful to the study geologic carbon dioxide sequestration for a number of reasons, particularly because they offer the opportunity to examine a system that has operated on a time scale (centuries to eons) that laboratory and field experimentation (days to decades) cannot compare. One such example of a mafic rock CO2 analogue is the Soda Springs site located in Caribou County of Southeastern Idaho, USA. At this site, CO2 and formation fluids generated by the dissolution of Paleozoic carbonates at depth are migrating and reacting with a series of shallower thoelitic basalt flows that host a fresh water aquifer. We believe that the layered basalt flows are acting as a reactive barrier to the vertical migration of the deep CO2 charged fluids. However, in several cases the CO2 charged reservoir fluids make it to the surface and are expressed as either carbonated springs, or as a cold-water geyser that was caused by wells that encounter the system at depth. Analysis of these sources of water shows a steady evolution of groundwater from unaffected by the basalt (deep wells) to more fully reacted (springs). Data from this system makes a compelling argument for the ability of basalt flow to maintain containment for CCS applications. Our study has shown that CO2 charged fluids migrating upwards are being neutralized by mineral dissolution and precipitation within the basalt flows. These neutralization reactions have resulted in a specific chemical signature being imparted to the formation fluid that can be used to determine which minerals are dissolving and precipitating. Through and integrated study of this natural analogue site including field and laboratory experiments, the relative roles of mineral dissolution and precipitation and phase assemblage are being characterized for this basalt-hosted system. The benefit of studying this natural analogue is that it has been active for many 1000's of years and depending on sample location and depth, the resulting fluid chemistry carries the chemical signature (tracer) indicative of the degree of reaction within the basalt formation. Additionally, the study of this system is helping define the appropriate laboratory scale experiments that will be needed to accomplish the larger objective of the project, understanding changes in aqueous geochemistry associated with progressing CO2-water-interactions.

38 - Impact on the deep biosphere of CO2 geological sequestration in (ultra)mafic rocks and retroactive consequences on its fate

Bénédicte Ménez [1, 2], Emmanuelle Gérard [1, 2], Sébastien Dupraz [1, 2, 3], Helgi Arnar Alfreðsson[4], Sigurður Reynir Gíslason[4], Hólmfríður Sigurðardóttir[5], François Guyot [1, 2]

1 Equipe Géobiosphère actuelle et Primitive, IPGP/IMPMC, CNRS UMR7154, Paris, France
2 Centre de Recherches sur le Stockage Géologique du CO2 (IPGP/TOTAL/SCHLUMBERGER/ADEME)
3 Bureau de Recherches Géologiques et Minières (BRGM), Orléans, France
4 Institute of Earth Sciences, University of Iceland, Reykjavik, Iceland
5 Reykjavik Energy, Reykjavik, Iceland

Due to their reactivity and high potential of carbonation, mafic and ultramafic rocks constitute targets of great interest to safely and permanently sequestrate anthropogenic CO2 and thus, limit the potential major environmental consequences of its increasing atmospheric level. In addition, subsurface (ultra)mafic environments are recognized to harbor diverse and active microbial populations that may be stimulated or decimated following CO2 injection (± impurities) and subsequent acidification. However, the nature and amplitude of the involved biogeochemical pathways are still unknown. To avoid unforeseen consequences at all time scales (e.g. reservoir souring and clogging, bioproduction of H2S and CH4), the impact of CO2 injection on deep biota with unknown ecology, and their retroactive effects on the capacity and long-term stability of CO2 storage sites, have to be determined. We present here combined field and experimental investigations focused on the Icelandic pilot site, implemented in the Hengill area (SW Iceland) at the Hellisheidi geothermal power plant (thanks to the CarbFix program - University of Iceland/Reykjavik Energy/French CNRS /Columbia University consortium). This field scale injection of CO2 charged water is here designed to study the feasibility of storing permanently CO2 in basaltic rocks and to optimize industrial methods. Prior to the injection, the microbiological initial state was characterized through regular sampling at various seasons. DNA was extracted and amplified from the deep and shallow observatory wells, after filtration of 20 to 30 liters of groundwater collected in the depth interval 400-980 m using a specifically developed sampling protocol aiming at reducing contamination risks. An inventory of living indigenous bacteria and archaea was then done using molecular methods based on the amplification of small subunit ribosomal RNA genes (SSU rDNAs). The stratigraphic levels targeted to store the injected CO2 as aqueous phase harbor numerous new species close to cultivable species belonging to the genus Thermus or Proteobacteria species known to be linked in particular with the hydrogen and iron cycles. After injection, the evolution of these microbial communities will be monitored using the Denaturing Gradient Gel Electrophoresis technique. Beyond the ecological impact of storing high levels of CO2 in deep environments, particularly important is the ability of intraterrestrial microbes to potentially interact with the injected fluids. For example, carbonation has been shown to be strongly influenced by microbiological activities that can locally modify pH and induce nucleation of solid carbonates. To improve the understanding of these processes and to better constrain the influence of deep biota on the evolving chemical and petrophysical properties of the reservoir, an experimental and numerical modeling is carried out in parallel, using model strains representative of the subsurface (including acetogens, sulphate and iron reducing bacteria), as single-species or as consortia. A set of batch experiments in presence of crushed olivine or basalts was especially

designed to evaluate how microbial activity could overcome the slow kinetics of mineral-fluid reactions and reduce the energy needed to hasten the carbonation process.

39 - Dissolution of basaltic glass in seawater at 1000C and 70 bars CO2 pressure. Implications for CO2 mineral sequestration

K.G. Mesfin, D. Wolff-Boenisch and S.R. Gislason

Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland

Mineral sequestration of CO_2 in mafic rocks offers long-term storage of CO_2. It requires the combination of divalent metals with dissolved CO_2 to form carbonate minerals. This method of *in-situ* CO_2 sequestration is a long lasting method as the resulting carbonates can be stable for millions of years. The most copious sources for these divalent cations are dominantly peridotitic and basaltic rocks rich in Mg, Fe, and Ca. The rapid dissolution rates of silicate minerals in these rocks results in consumptions of protons and release of divalent metals which enhances the formation of carbonate minerals. Various methods have been proposed for the CO_2 injection, such as separate supercritical CO_2 phase or CO_2 fully dissolved in water. Both end-members have drawbacks. Supercritical CO_2 is less dense than its surrounding fluids and rocks, which will pose problems in fractured basaltic rocks. On the other hand, 27 tons of water is needed to fully dissolve 1 ton of CO_2 at 25°C. Thus, this water demand limits the applicability of the latter method of injection in the terrestrial environment. However, in coastal areas and on the ocean floor there is endless supply of seawater.

We have carried out an experiment at 100°C and 70 bars CO_2 pressure to address the effect of sea water on the dissolution rate of MORB (Mid Ocean Ridge Basalt) glass. The experiment imitates conditions that exist within the oceanic crust at about 450 m depth of CO_2 injection with an average geothermal gradient of 220^0C/km. We use a 6.4L pressure vessel from Parr Instruments® constructed from T4 grade titanium. The vessel is equipped with gas inlet valve, liquid sampling valve, rupture disk, gas release valve and a pressure gauge. Temperature is controlled by placing the pressure vessel inside a heater which is also responsible for attaining the desired pressure in the system. Seawater collected far off the SW shore of Iceland was placed inside the reactor together with powdered and washed basaltic glass (45-125mm size fraction) and pressurized with CO_2 using a CO_2 cylinder source up to ~45bars. The vessel was then heated to a final temperature of 100^0C causing the internal pressure to increase to 70 bars, driving the CO_2 into supercritical conditions. Periodic pressurized samples have been taken to monitor the solute concentration and thus reaction progress. A sampling cylinder connected to the liquid sample valve is used to sample from the pressure vessel which contains 12ml when completely filled. The sampling procedure is based on creating a pressure gradient between the sampling cylinder and the reactor, the pressure on the vessel being higher than that of the sampling cylinder. To create this gradient (which increases with increasing pressure) the sampling cylinder is pressurized with nitrogen. The CO_2 from the samples is then collected into a 0.5M KOH base and the dissolved inorganic carbon (DIC) subsequently analysed using IC. Results of this experiment with respect to the evolution of solute chemistry and the precipitation of secondary phases will be presented.

8 - Assessment of direct aqueous in situ carbonation procedures in ophiolitic détritus

Meyer1, F.M., Sindern1, S., Schardt1, C., Urai2,3, J., Gutberlet3, M., den Brok3, B., Clauser4, C., Blaschek4, R., Kukla5, P., Rüde6, T.R., Stanjek7, H., Littke8, R.

1 Institute of Mineralogy and Economic Geology, RWTH Aachen University Germany
2 Structural Geology, Tectonics and Geomechanics, RWTH Aachen University
3 German University of Technology in Oman, Muscat Oman
4 Applied Geophysics and Geothermal Energy, RWTH Aachen University
5 Geological Institute, RWTH Aachen University Germany
6 Hydrogeology, RWTH Aachen University
7 Clay and Interface Mineralogy, RWTH Aachen University
8 Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University

Contact: sindern@rwth-aachen.de

Igneous ultramafic rocks containing Mg-rich minerals such as olivine, pyroxene or serpentine are particularly suitable for CO2-sequestration. This is certainly also true for mining wastes derived from such rocks or detrital components in the vast alluvial fan deposits of Oman. So far no comprehensive mapping of the storage potential has been reported from ophiolite-derived sediments. This poster presents a concept for the assessment of the sequestration potential and CCS suitability of detrital depositories in Oman.

Data on reaction rates of ophiolitic detritus is scarce and individual rock materials would require a more detailed study. However, preliminary model calculations for CO2-sequestration from flue gases indicate the feasibility of gas injection into an alluvial fan aquifer. For a hypothetical injection reservoir with an areal extent of 10 km2 and a mean thickness of 100 m mass balance calculations yield 9.07x108 to 5.44x109 t of sequestered CO2 depending on the abundance of Mg-silicate minerals. On the basis of a modern 800 MW coal fired-power station the CO2 storage capacity of such a reservoir would be equivalent to more than 200 years of CO2 sequestration. To turn such theoretical consideration into an applicable technical concept further constraints have to be considered. In-situ CO2 sequestration will increase the volume of the réaction products leading to a permeability change in the reservoir. In addition, other minerals associated with mafic minerals may have either deleterious or catalytic effects. Furthermore, reaction rims around mafic minerals may shield them and attenuate the reaction. Carbonates, which can be present in detritus derived from ophiolitic sequences, would also have a negative effect. The presence of SO2 in the flue gas, however, could be of advantage in terms of reaction progress. Considering all variables discussed above it is évident that detailed petrographic studies are one prerequisite for an evaluation of any sequestration mass balance.

Furthermore, the availability and quality of water – not produced for other purposes - in deeper aquifer of the alluvial fans has to be included into the overall environmental balance of the CCS technology.

Preliminary calculations suggest that the sequestration process runs more effectively in high-salinity aquifers. Sealing aquicludes and hydraulic windows are of concern to establish an

environmentally sound technology. Much will depend on the internal structure of the fans which is widely unknown today.

11 - Some Opportunities and Challenges for Sequestering CO2 in Arctic Seafloor Peridotites

Peter J. Michael Dept. of Geosciences, Univ. of Tulsa, 800 S. Tucker Dr., Tulsa, OK, 74104 USA 01-918-631-3017; pjm@utulsa.edu

The ubiquitous and often complete serpentinization of peridotites encourages scientists and engineers to consider these rocks for mineralogic trapping of CO2 because it shows that peridotites will react completely with fluids. Mesh-textured olivines suggest that olivine is consumed by hydration reactions along fractures, producing a mineral that has one mole of H2O for every 1.5 moles of Mg. Perhaps carbonation reactions would proceed similarly.

The AMORE 2001 expedition discovered extensive outcrops of partly-serpentinized peridotite along Gakkel ridge on the seafloor of the Arctic Ocean at >5000m water depth. The expedition recovered some of the freshest seafloor peridotites ever found, demonstrating that fresh, unserpentinized rock may exist at shallow levels in the ocean crust. Finding fresh peridotite at shallow levels within the crust may be important, because drilling would be minimized.

The Gakkel peridotites may offer special opportunities for storing CO2. Firstly, it may be possible to exploit the phase stabilities of CO2 along with the frigid Arctic climate to aid in concentrating and liquefying CO2 at the surface. Much less compression or cooling would be needed for conversion to a liquid compared to other locations. Secondly, the great ocean depth may provide some assistance in adiabatically heating CO2 during pumping, which may be necessary to make it more reactive. Thirdly, because of the different compressibilities of CO2 and H2O, the great ocean depth may also be important because liquid CO2 would be denser than liquid water at those pressures.

The Arctic also presents obvious logistical challenges for working in an extreme environment of an ocean that is covered by moving ice (at least at the present time). Although it may be unrealistic to exploit the Gakkel ridge peridotites for CO2 storage, this brief contribution serves to raise some points for discussion.

3 - The chemistry of hyperalkaline springs, gases and precipitates in Oman and in the Ligurian Alps (Northern Italy). Some recent observations.

Monnin C., Chavagnac V., Ceuleneer G., Boulart C and Hoareau G.

Laboratoire Mécanismes et Transfert en Géologie and Laboratoire Dynamique Terrestre et Planétaire, 16 Avenue Edouard Belin, 31400 Toulouse France

Discharge of aqueous fluids produced by serpentinization is observed on the seafloor but also in ultramafic formations exposed on continents. Hyperalkaline springs and associated gas production have been studied in Oman in the 80s (NEAL and STANGER, 1984) and more recently in the Ligurian Alps (CIPOLLI et al., 2004; FRUEH-GREEN et al., 2009). We have conducted field studies in 2009 and 2010 to sample aqueous fluids, gases and precipitates in the alkaline springs in the ophiolites of Oman and of Liguria (Northern Italy). We here present some of our recent observations.

The aqueous fluids in Oman and Liguria bear common characteristics wit those at sites like Lost City, such as high pH, low silica and carbonate alkalinity content but also differences such as different températures and Ca concentrations. Whereas brucite formation is commonly observed in Oman, it is never found in Liguria. Calcium carbonate formation occurs as calcite in Liguria and calcite/aragonite in Oman. Traces of magnesite and dolomite have been rarely found. We have sampled gas bubbles in the springs that show that H2 is more abundant in Oman and CH4 dominates in Liguria.

Preliminary considerations on the solubility of the various minerals and on the thermodynamics of the water-rock interactions in aqueous systems at elevated pHs provide first insights into the carbonatation mechanisms of the alkaline fluids and the associated atmospheric CO2 capture.

References :

Cipolli F., Gambardella B., Marini L., Ottonello G., and Vetuschi Zuccolini M. (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 Geochemistry 19(5), 787-802.

Frueh-Green G. L., Schwarzenbach E. M., Méhay S., Lilley M. D., Bernasconi S. M., Molinari M., and MariniL. (2009) Alkaline Fluids and Reduced Volatiles in Modern Serpentinizing Environments. Eos Trans. AGU, Fall Meet. Suppl., 90(52).

Neal C. and Stanger G. (1984) Past and present serpentinization of ultramafic rocks; an example from the Semail ophiolite nappe of Northern Oman. In Proceedings of the NATO Advanced Research Workshop on the The chemistry of weathering (ed. T. Drever), pp. 249-275. Reidel Publishing Company.

21 - Toxic metal mobility following the injection of CO2 into basaltic aquifers

J. Olsson [1,2], S. L. S. Stipp[2] and S. R. Gislason[1].*

1 Nordic Volcanological Institute, Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland.
2 Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 København Ø, Denmark.

** Corresponding author: jolsson@nano.ku.dk (J. Olsson)*

Injection of CO2 into rocks creates corrosive CO2 charged waters with the pH of 4 to 3 [1]. The low pH can lead to mobility of toxic metals at the early stage of water/rock interaction [2]. Dilution and rock dissolution, especially of mafic rock, will increase the pH and lead to precipitation of carbonates and other secondary minerals. The question remains, how fast are the toxic metals sequestrated by precipitation and/or adsorption to the secondary minerals. The 2010 eruption of the Eyjafjallajökull volcano, Iceland, provides a unique opportunity to study the mobility of toxic metals, related to the injection of CO2 into shallow basaltic aquifer and the ensuing precipitation of carbonates.

Following the first phase of the eruption from 20 March to 12 April 2010, the change in conductivity of the rivers in the vicinity of the volcano was mostly associated with direct contact of surface waters with new lava or ash. However, in July 2010, a new strong outlet of riverine CO2 was observed on the north side of the volcano via the river Hvanná, which indicates deep degassing into the water. A white mineral layer; at some places more than 1 cm thick, for hundreds of meters downstream was observed. The precipitation was identified solely as calcite with X-ray diffraction. A gradual decrease of; the conductivity from 1.8 to 1.1 mS/cm, alkalinity from 20.8 to 8.8 meq/kg, the concentration of Ca, K, Mg, Sr, SO4, Ba and CO2, and an increase in the pH from 6.5 to 8.5, were strongly correlated to the amount of precipitated travertine. The water temperature was below 5 °C and an elevated atmospheric CO2 partial pressure was detected near the river. The river water degassed downstream, pH increased, resulting in calcite supersaturation and precipitation as commonly observed in travertine deposits [3].

We are currently measuring the bulk aquatic and travertine trace metal concentrations, and the surface composition of the calcite will be studied. This study can reveal whether the calcite scavenges toxic metals such as As, Cr and Cd, that are released during the early stage of water-rock-CO2 interaction at low pH [2,4].

References:

[1] S. R. Gislason, et al., International Journal of Greenhouse Gas Control 4, pp. 537 (2010)
[2] T. H. Flaathen, et al., Applied Geochemistry 24, pp. 463 (2009)
[3] Ø. Hammer, et al., Geofluids 5, pp. 140 (2005)
[4] B. Sigfusson, et al., Environmental Science and Technology 42, pp. 8816 (2008)

70 - Identifying tools used to inform public attitudes and influence behavior in favor of Carbon Mineralization

Jason Mathew Ornstein

New York University

There are tools used to engage the public about environmental improvements through technology. Such tools are used by both the public and private sector to inform public attitudes towards environmental improvements through the allocation of public budgets or consumption (purchases). In support of these tools, an expanding body of research on what informs public opinions and impacts behavior concerning environmental issues is annually published. Several journal articles and other periodicals were reviewed to identify where successes and failures in environmental public awareness lie. The successes and failures were synthesized through 15 research and white papers on Carbon Capture and Storage (CCS) public awareness presented at the September 2010 Green House Gas Control Technologies Conference in Amsterdam, Netherlands, and the October 2010 Carbon Capture and Sequestration Summit in Washington DC. It was established that CCS communication often targets propitious segments as opposed to those who minimize cognitive effort when consuming environmental information. A common theme was the ability to engender trust through 'green' brand equity as the backbone of any successful environmental public awareness campaign. Another common theme was the ability to establish stakeholder segments in the public through cultural theory as the destination for differentiated communication. The findings were used to identify tools and set standards for a future public awareness campaigns in the Carbon Mineralization sector which exploits the sector's environmental competitive advantage.

69 - Geochemical microsampling techniques as an aid to understanding the sources and timing of carbonate formation in ultra-mafic rocks - application to CCS studies

D.G. Pearson, T. Stachel, R. Stern & R. Ekart.

University of Alberta, Department of Earth and Atmopspheric Sciences
gdpearso@ualberta.ca

Modern microsampling instrumentation is capable of obtaining highly precise C, O and Sr isotopic measurements plus full trace element compositions on single crystals or parts of single crystals of primary and secondary minerals in ultra-mafic rocks. A combined analytical approach that fully characterises carbonate and other secondary minerals in peridotite is the key to understanding fluid-rock ratios, fluid sources and the timing of carbonate formation in such rocks. Sr isotopes have the potential to be both tracers of source and to date crystallisation of carbonate, either through comparison to the seawater Sr curve or through isochron-type approaches. Sr isotopes can also be used as a stable isotope tracer and can be added to the list of non-conventional stable isotopes that include Mg, Ca, Fe and Cr that may all add valuable information about fluid sources, pathways and redox processes during the carbonation of peridotite. We discuss the suitability of both insitu analytical techniques such as SIMS and LA-ICPMS together with micro-sampling TIMS to tackling analytical problems and highlight some of the information that these systems can offer in understanding peridotite CCS issues.

67 - Bend-Faults and Hydrothermal Circulation at Oceanic Trenches

Jason Phipps Morgan - Cornell University, Ithaca, NY, USA
Lars Rüpke - IfM-GEOMAR, Kiel, DE
Karthik Iyer - IfM-GEOMAR, Kiel, DE

It is well known that mid-ocean ridges are a key site for chemical interactions between oceanic crust and the hydrosphere, and that these interactions modulate the chemistry of the oceans. While this field is relatively mature, it is becoming increasingly evident that the oceanic lithosphere may strongly interact with the hydrosphere as it bends when it enters a trench in the initial phase of plate subduction. This geological process, bend-faulting, (cf. Ranero et al., 2003) is likely to be a tectonic environment where seawater can interact with relatively cool mantle lithosphere that is unstable with respect to serpentinization processes. Inspired by the well-known occurrence of ophiocarbonates in Alpine ophiolites, we have been studying this process with models of coupled marine hydrothermal flow and metamorphism within idealized lithosphere undergoing bend-faulting. The potential applications for Earth's long-term carbon cycle may be significant. For example, a simple mass balance shows that a 1% carbonate fraction within a 20% serpentinized region from 0-5km beneath the oceanic moho will subduct more chemically bound carbon than overlying crust and sediments — an atmosphere's worth of CO2 every 40ky. More than this amount of sub-moho serpentinization occurs in many of our simulations, and is also consistent with observed sub-Moho seismic velocity reductions in regions undergoing bend-faulting today. Likewise, observed ophiocarbonates typically have a carbonate fraction much larger than 1%. To us, this poorly understood process clearly merits further exploration!

62 - Numerical Simulation of Carbon Dioxide Sequestration in Deep-Sea Basalts

Robert K. Podgorney[1], Angela L Slagle[2], Travis L. McLing[1] and David S. Goldberg[2]

1 Idaho National Laboratory and Center for Advanced Energy Studies, Idaho Falls, ID
2 Columbia University, Lamont Doherty Earth Observatory, Palisades NY

Deep-sea basalt formations offer a unique opportunity for sequestration of anthropogenic carbon dioxide. These formations offer a number of positive storage attributes, including vast volumes of accessible pore space, multiple physical trapping mechanisms, and calcium-magnesium rich silicate host rock which may allow for [relatively] rapid mineral trapping. In addition to their numerous storage attributes, deep-sea basalt formations are also widely distributed over the globe, further increasing their appeal. Previous studies have suggested that these formations have the capacity to accommodate a significant amount of fossil fuel generated carbon dioxide at locations within pipeline distances of population centers and stationary sources. This study focuses on developing a numerical framework to examine both the physical and mineralogical trapping of carbon dioxide in these deep-sea basalts, using sediment-covered basalt formations on the Juan de Fuca plate off the west coast of North America as a working example.

While the goal of this study is to evaluate the physical and mineral trapping of the carbon dioxide in deep-sea basalts, numerical modeling the fluid flow and geochemical behavior of water-salt-CO2 mixtures at pressure and temperature conditions typical of these environments requires a stepwise approach. Numerically representing the conceptual understanding of the undisturbed system is an essential first step in this process, followed by an examination of the behavior associated with the injection of carbon dioxide into the system, and lastly with the incorporation of reactive geochemistry between the fluid phases and the host reservoir rock. The current results detail the methodology employed in the analysis and present simulation results examining the physical trapping mechanisms, injection capacity and rates, carbon dioxide distribution within the basalt formation, and impacts of supercritical and dissolved phases of carbon dioxide. Details on planned reactive geochemistry simulations will also be presented.

33 - Mineralization of serpentinite rocks with CO2 at different states of structural disintegration.

K. Pöhler, Ch. Lempp & H. Pöllmann, Martin-Luther-University, Halle-Wittenberg (Germany)

Mineral-trapping is a safe and sustainable mode of greenhause gas reduction. However, in most cases it appears as a long term mode, not useful for quick results. In contrary, the carbonisation reaction of CO2 with ultramafic rocks offers a short term mode of mineral trapping in distinct regions, where ultramafic rocks are dominant. Nevertheless, the time span and the effect of this mineralization reaction of ultramafic rocks with fluidal CO2 also depends on the available reactive surface within the rock mass. This dependence between reactive surface within the rock and the mineralization process has been studied in a geomechanical and mineralogical study. At the scale of dm3-volumes rock samples have been disintegrated by controlled loading under triaxial conditions in order to generate defined networks of (micro) fissures and cracks. Accordingly, different states of structural disintegration and strength of rocks are prepared to react with supercritical CO2. This aims be able to quantify the dependence of the size of reactive surface and carbonisation reaction in the rock. The results of these lab experiments should be later transferred to the field-scale of faults and joints to define the conditions for a most effective mineralization.

One of the evaluated ultramafic samples is a serpentine from Zoeblitz(Saxony)/Germany.

Mechanical studies and geochemical studies were done to describe changes during the treatment with supercritical CO2. The strength tests represent the transition from continuum to discontiuum (rock character to rock mass character) by receiving more cracks, pores and (macro) fissures, that may create new pathways for gases and liquids with increased reactivity. The rock mechanic properties and the knowledge about the mineralogical interaction between rock and CO2 are very important to understand the behaviour of this rock under the influence of CO2.

The geological development of the investigated serpentine begins in the Precambrian, where magma was intruded into the earths crust. During Variscan collision the body was folded and metamorphosed into serpentinite. X-ray diffraction analyses indicate the minerals talc, lizardite, magnetite, actinolithe and clinochlore. Thin sections revealed, that olivine is serpentinized and garnet is chloritized. Fibrillar silk shiny minerals of the serpentinite group are passing through the rock. The petrophysical analyses showed a porosity in average of n = 0,89 % and an average density of ρd = 2,4 g/cm³.

The strength-tests were carried out with several multistage triaxial compression tests and one uniaxial compression test. The unconfined compressive strength is 103 MPa.

In the triaxial test the strength increased up to 320 MPa due to the confining pressure of 50 MPa. In general the samples cracked at the maximum stress level difference, that was reached at the first loading step. The following loading steps were conducted at different conditions of effective stress differences in order to evaluate the disintegration of the rock structure. Visualization of generated fractures can be reached by thin sections and staining the cut surface with coloured epoxy resin. The stressed samples were transformed for the experiments within

small laboratory autoclaves (~36cm³). Conditions of 100°C and 100bar were chosen to ensure the supercritical phase field of CO2. Expected results are: growth of new carbonatite containing minerals on mineral surfaces, alteration appearances, solutions in pore space and mineralization reactions.

40 - The formation of carbonate containing LDH´s in basic rocks

Herbert Pöllmann

University of Halle/Saale

Von Seckendorffplatz 3

06120 Halle

herbert.poellmann@geo.uni-halle.de

The LDH group of minerals are built of alternating layers, consisting of metals charged M2+ and M3+ forming hydroxide layers of brucite type with full occupation of the cation positions, charged positively and also negatively charged interlayers with varying contents of-water, also called interlayers. The M2+ : M3+ ratio can be variable within wide ranges depending on the metal cations. The positive layer charge is compensated by the interlayer anions. The general formula of hydrotalcite group LDH is

[M2+1-XM3+X(OH)2][(AY-)X/Y (H2O)n] with

M2+ = Mg2+, Mn2+, Fe2+, Ni2+, Cu2+, Zn2+, Co2+

M3+ = Al3+, Cr3+, Mn3+, Fe3+, Co3+, Ni3+, Ga3+, In3+, Y3+

Natural layered double hydroxides are generally formed under ambient or slightly elevated temperatures, under ambient pressures and under slightly acidic to alkaline conditions. Several members of the LDH group can be formed during metasomatic alteration of mafic und ultramafic rocks at temperatures up to 200°C.

Staß (probably 1990) reported in a study on the medicament Talcid® (Bayer AG), composed mainly of hydrotalcite and used as an antacid, that the LDH buffer in an acidic environment (0.1 M HCl) to pH 4, even at an surplus of acid and with different ratios of Talcid® (respectively hydrotalcite) to acid.

The formation of LDH´s has been reported in many different basic rocks. Their formation can be enhanced when high surfaces are obtainable, as they often exist in mine tailings. Preliminary laboratory results show that LDH´s can be formed easily from mixtures of metal(2+) and metal(3+) solutions. In presence of CO2, LDH´s can be used as a mineralizer phase for carbon dioxide.

Literature

Pöllmann,H.: Mineralization of wastes and industrial residues, Shaker, (2010)

68 - Developing fracture density models using terrestrial laser scan data

Ryan Pollyea[1], Jerry P. Fairley[1], Robert K. Podgorney[2] and Travis L. McLing[2]

1 Center for Advanced Energy Studies and University of Idaho
2 Center for Advanced Energy Studies and Idaho national Laboratory

Characterizing fracture heterogeneity for subsurface flow and transport modeling has been of interest to the hydrogeologic community for many years. Currently, stochastic continuum and discrete fracture representations have come to be accepted as two of the most commonly used tools for incorporating fracture heterogeneity into subsurface flow and transport models. In this research, ground-based lidar data are used to model the surface roughness of vertical basalt exposures in the East Snake River Plain, Idaho (ESRP) as a surrogate for fracture density. The surface roughness is modeled by discretizing the dataset over a regular grid and fitting a regression plane to each gridblock. The standard deviation of distance from the block data to the regression plane is then assumed to represent a measure of roughness for each gridblock. Two-dimensional plots of surface roughness from ESRP exposures indicate discrete fractures can be quantitatively differentiated from unfractured rock at 0.25- meter resolution. This methodology may have broad applications for characterizing fracture heterogeneity. One application, demonstrated here, is to capture high resolution (low noise) covariance statistics for building stochastic property sets to be used in large scale flow simulations. Additional applications may include using surface roughness datasets as training images for multiple-point geostatistics analysis and for constraining discrete fracture models.

41 - Enhanced olivine dissolution using oxalate and citrate

Valentina Prigiobbe

We studied olivine dissolution kinetics under operating conditions suitable for ex situ aqueous minéral carbonation for CO2 storage. Mineral carbonation is a Carbon Capture and Storage (CCS) technology based on a chemical reaction that mimics weathering at high temperature and at high CO2 fugacity (fCO2).

Metal-oxide bearing materials, such as natural silicates and industrial alkaline residues undergo pre-treatment and dissolution prior reaction with CO2 to produce stable carbonates, in which CO2 is bound, and quartz.

Mineral carbonation is more energy intensive then other CCS technologies such as storage into saline aquifer, therefore research is needed to optimize the process, e.g., throughout the acceleration of the silicate dissolution that is the kinetics limiting step. Dissolution is favored by temperature, proton concentration, and specific organic and inorganic chemicals.

In this work, we studied the effect of organic salts containing oxalate and citrate ions on the dissolution of gem-quality San Carlos olivine (Mg1.82Fe0.18SiO4). Flow-through experiments were performed at 90 and 120°C, at fCO2 between 4 and 81 bar, and in a solution containing either sodium oxalate or sodium citrate in the concentration range between 0.001 m and 0.1 m. pH was varied between 2 and 7 by adding HCl, LiOH, and adjusting fCO2. Sodium oxalate and sodium citrate enhanced dissolution, the highest effect of one order of magnitude was observed in presence of 0.1 m of oxalate, at 120°C, and above pH 5. In this pH region, the dominant species are the diprotonated ions, i.e., oxalate to which the enhancement effect was ascribed. The overall dissolution process was described by population balance equation coupled with a mass balance equation for olivine equivalent.

Far from the equilibrium conditions for dissolution were applied in all the experiments in order to achieve always the same type of dissolution mechanism limited by the reaction at the solid/liquid interface. We described such a reaction as the adsorption of two ions (proton and oxalate) on one surface olivine site and we derived through surface complexation modeling a specific dissolution rate equation which resemble a Langmuir isotherm.

42 - Magnesite precipitation at high temperation and high CO2 pressure

Valentina Prigiobbe

Precipitation of magnesite (MgCO3) is hindered by the high dehydration energy to incorporate magnésium ions into the crystal structure, therefore the formation of unstable and hydrated Mg-carbonates such as nesquehonite and hydromagnesite is kinetically favored. Precipitation kinetics of MgCO3 depends on temperature, PCO2, supersaturation ratio and other procès variables such as CO32- and Mg2+ activity ratio, Mg2+ concentration, pH, ionic strength, and water activity. To investigate systematically the effect of these process variables, kinetics experiments were performed using a MgCl2-CO2-Na2CO3 aqueous system at 90, 120, and 150°C, at 100 bar of PCO2, varying MgCl2 between 0.012 and 0.36 m and Na2CO3 between 0.08 and 0.52 m.

The system was monitored with online Raman spectroscopy to follow the time evolution of the solution and suspension composition and modeled using a geochemical package EQ3/6.

We observed two mechanisms of precipitation: direct formation of magnesite and simultaneous precipitation of hydromagnesite and magnesite followed by the transformation of hydromagnesite into magnesite. The fastest magnesite precipitation of 20 min was observed at 150°C. At 120°C in the same range of supersaturation ratios applied at 150°C, the process was slower and in the high supersaturation ratio range, the growth of magnesite was slowed down by the co-precipitation with hydromagnesite.

On the overall, temperature and supersaturation controlled the precipitation process, and in particular in the condition suitable for crystal formation the initial total concentration of Mg2+ defined the type of précipitation mechanism. High concentrations of Mg2+ inhibited the direct magnesite formation due to the High dehydration energy needed to incorporate this ion in the crystalline structure. Therefore, co-precipitation was favored and lengthened the overall process.

43 - Fundamental Science for Geologic Carbon Sequestration: Laboratory Probes for Understanding Trapping Mechanisms at the Microscopic Scale

Kevin M. Rosso, Alain HR Bonneville, Jian Z Hu, David W Hoyt, Zheming Wang, Alan S Lea, H. Todd Schaef, B. Peter McGrail, and Mark D. White

Pacific Northwest National Laboratory, Richland, Washington USA

Storage of carbon dioxide and other greenhouse gases in deep geologic formations represents one of the most promising technology options for reducing the impacts of continued fossil fuel use on climate change. However, there is an ever-present need to be able to demonstrate in a scientifically defensible manner that CO2 will remain stored over the long-term in the geological formation where it is injected. Mineralization to carbonates is an important process not only in the near-term for injectivity, but also over the long-term with respect to caprock integrity and overall reservoir permanence. For example, an important issue is to be able to predict the long-term migration of supercritical CO2 (scCO2) upward along faults or fractures in caprock, a process that can be either progressively enhanced or impeded depending on specific mineral transformations that occur and their effects on local permeability. Mineralization of scCO2 to carbonates couples in complex ways to the availability and reaction rates of minerals bearing cations needed for stable carbonate formation. The vast majority of previous research has focused on mineral reactivity in aqueous solutions containing CO2 from a co-existing scCO2 phase. However, at the caprock-fluid interface over the long-term, direct interaction with the scCO2 fluid itself is more important as the buoyant plume displaces or dessicates residual aqueous solution. Mechanisms of mineral interfacial reactions with wet or water-saturated scCO2 are unknown, and measurement of kinetic and thermodynamic data for mineral transformation reactions in these fluids present unique challenges. Such data are virtually non-existent at present. This paper will present development of a unique set of high-pressure and temperature and capable instruments, called the in situ supercritical suite, that is being developed to advance the fundamental understanding of reaction mechanisms in these fluids and provide data critical for reactive transport simulations meant to predict the ultimate fate of subsurface CO2.

66 - Simulations of oceanic lithosphere serpentinization

L. Ruepke (1), K. Iyer (1), and J. Phipps Morgan (2)

(1) The Future Ocean, Kiel, IFM-GEOMAR, Germany (lruepke@ifm-geomar.de),
(2) Dept. of Earth & Atmospheric Sciences, Cornell University, USA

Seawater circulation through oceanic lithosphere and the associated hydration reactions play a key role in many geological processes and settings. At mid-ocean ridges, hydrothermalism mines heat from the young ocean floor, causes hydration of mafic and ultramafic rocks, and is associated with the formation of ore deposits. At active margins, bending and faulting at the trench outer rise may again trigger deep seawater circulation and hydration. One key hydration reaction is the serpentinization of mantle rocks. The transformation of a dry peridotite to a wet serpentinite results in an uptake of ~13wt.% of water, a volume increase and density decrease of ~40%, and a strong decrease in mechanical strength. These drastic changes in rock properties illustrate the importance of quantifying the degree of serpentinization caused by deep seawater circulation. For this purpose, we have developed a new hydrothermal convection model that also accounts for serpentinization. The key feedbacks of the reaction on fluid flow, i.e. variations in permeability due to volume changes and reaction induced fluid consumption, are all accounted for. We have applied this model to two test cases: hydrothermal convection at mid-ocean ridges and bend-faulting related hydration of subducting plates. For the mid-ocean ridge test case, we have coupled a kinematic thermal ridge model to the hydrothermal convection model. The coupled model allows us to study the feedbacks between serpentinization and hydrothermal flow. We find that, on the one hand, hydrothermal convection is not confined to the crust but may extend well below the Moho. On the other hand, pervasive serpentinization has the ability to close pore space and reduce permeability thereby hindering flow. Similar processes occur at subduction zones. Bend-faulting of subducting lithosphere, may provide the pathways for seawater to reach and react with the cold lithospheric mantle to make serpentine. To test this hypothesis, we explore under which conditions seawater may reach the mantle and what the likely hydration pattern around fault zones are.

44 - A new incubator for biological high pressure experiments with elevated gas saturation

Patrick Sauer, Jens Kallmeyer

Institute of Earth and Evironmental Sciences,
University of Potsdam,
Karl-Liebknecht-Straße 24,
14476 Potsdam, Germany

(kallm@geo.uni-potsdam.de)

High pressure is a key feature of the deep subsurface, microorganisms living at these depths are adapted to this pressure. The vast majority of biological high-pressure experiments was carried out on marine samples. Bianchi & Garcin (1993) found that in incubations under atmospheric pressure the metabolic rate of pressure-adapted deep-sea microorganisms decreases. However, Jannasch & Wirsen (1982) found that at high pressure, the incorporation of carbon was similar or lower than at atmospheric pressure, depending on the substrate used. Up to now the results from high-pressure incubations do not provide a concise picture about the effects of pressure on microbial activity. There is an important physical difference between high and low pressure: the solubility of gases. So far, most if not all high-pressure incubations were performed with systems that just simulated hydrostatic pressure, not the true in-situ gas saturations. This may well be the reason for the inconclusive results. At elevated pressure, concentrations of gases e.g. carbon dioxide or methane, are significantly higher than under atmospheric conditions (Weiss, 1974). This is an important issue in order to simulate true in-situ conditions, because metabolic rates, incorporations of nutrients and pH values are affected by higher partial pressure of gases (Bernhardt et al., 1988).

The need to gain results under true in-situ conditions and to control the partial pressure of dissolved gases requires a high-pressure incubation system that allows not just controlling hydrostatic pressure but also the concentration of dissolved gases. We are developing an inexpensive, high-pressure incubation system that can be used for both static and flow through experiments in order to manipulate the composition and concentration of the flow through gas and medium.The System is composed of the high-pressure vessel with a length of 45 cm and a volume of 250 cm3. Inside this vessel hangs the actual incubator, made from a sleeve of PVDF (Polyvinylidene fluoride), a flexible, inert and gas impermeable plastic. The sleeve is closed with two metal stoppers, coated with gold to protect them against corrosive processes. Pressure is transmitted to the sample through the flexible walls of the tubing, the pressure medium (demineralized water) is completely separated from the sample.

To control partial pressure of gases and to equilibrate the gases with liquid, a temperature-controlled pre-incubator is used. Pressure of up to 600 bar is applied through a modified HPLC pump. For flow-through experiments a second pump circulates the sample liquid trough the incubator.

(1) Bianchi A., Garcin J.: Deep-Sea research I, 1993: 40, 1703 – 1710
(2) Jannasch H. W., Wirsen C. O.: AEM, 1982: 43, 1116 – 1124
(3) Weiss R. F.: Marine Chemistry, 1974: 2, 203 – 215
(4) Bernhardt G., et al.: Appl. Microbial Biotechnol, 1988: 28, 176 – 181

45 - A new autoclave system for the “in situ” investigation of carbonation reactions of basic rocks with waste CO2

Michael Schmidt[1], Herbert Pöllmann[1], Herwig Marbler[1], Kirsten Erickson[1], Christof Lempp[1]

1 Martin-Luther-Universität Halle Wittenberg, Geowissenschaften, Halle/Saale, Germany

herbert.poellmann@geo.uni-halle.de

For safe long term storage of CO2 in situ carbonation or mineralisation of basic rocks or other suitable materials such as basic industrial residues or building materials is one of the encouraged options. In order to gain knowledge about possible carbonation reactions an autoclave setup was designed in which in situ carbonation reactions can be simulated under various temperature and pressure regimes. The designed system consists of two separate BERGHOF BR-2000 autoclaves with a volume of 2 litres each /1/. Both autoclaves are equipped with PTFE inserts as well as heating jackets. Besides multiple valves each autoclave is equipped with a thermocouple and a pressure gauge. Also stirring is possible in one of the reactors. The large size of the autoclaves allows cylindrical samples of up to 70 x 240 mm. In addition to a batch mode both autoclaves can be coupled through an annular Swagelok® pipe system. In this mode liquids can be circulated through rocks samples. For liquid circulation a magnetic pump is embedded in the system. It is made from a stainless steel pipe with PTFE lining. On both ends magnets are mounted. A non-return valve is build into the suction side. A PTFE lined magnet is used as piston. With this pump a continuous flow of 50ml/min at 1Hz is possible. Venting of the whole system with CO2 or N2 is done through valves in the pipe system which can also be used for sample extraction. CO2 as gaseous phase or liquid phase is delivered through a Teledyne ISCO D500 high pressure syringe pump. This pump allows a defined flow of CO2 through the autoclave and thus the sample. Liquids can be extracted for sampling on each autoclave individually. The extraction valve can also be attached to a in situ measuring stage for pH, conductivity and redox potential. The measuring stage is made of three sequentially connected PTFE vessels in which the measuring cells are placed. The system can also be used for laboratory investigations on carbon capture and storage.

Literature:

/1/ SCHMIDT M., PÖLLMANN H., Marbler H.,Erickson K., Lempp C., (2010): „Construction of an autoclave system for the study of geochemical/mineralogical rock behaviour under reservoir conditions during the sequestration of CO2“; Poster, 88. Tagung der Deutschen Mineralogischen Gesellschaft, Münster (Germany), p.218

20 - Let the Earth help us to save the Earth

R.D. Schuiling, Institute of Geosciences,

Utrecht University
phone: 0031 30 2535006 e-mail: schuiling@geo.uu.nl

Massive sequestration of CO2 can be achieved by the enhancement of the natural process of chemical weathering. This process has kept the CO2 concentration of the atmosphere within bounds throughout geological history. It is a cheap, sustainable and energy-efficient approach, and can be carried out with standard mining and milling technology. It makes use of the mineral olivine olivine, the most widespread silicate mineral in the world. Olivine weathers easily in contact with CO2 and water, according to the reaction:

$Mg_2SiO_4 + 4\ CO_2 + 4H_2O \rightarrow 2\ Mg^{2+} + 4\ HCO_3^- + H_4SiO_4$

The resulting Mg-bicarbonate waters are carried by rivers to the oceans, where they will ultimately be stored as carbonate sediments (limestones and dolomites). Theses slightly alkaline waters help to counteract the ongoing acidification of the oceans.

46 - Effect of heterotrophic bacteria on olivine and basaltic glass dissolution in the context of CO_2 storage in basalts

L.S. Shirokova[1], G. Stockman[2], P. Bénézeth[1], O.S. Pokrovsky[1], E. Gerard[3], B. Menez[3], H. Alfredsson[2]

[1]*Géochimie et Biogéochimie Expérimentale, LMTG, CNRS, Université de Toulouse, 14 Avenue Edouard Belin 31400, Toulouse, France*
[2]*Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavík, Iceland*
[3]*Institut de Physique du Globe de Paris, 1 rue Jussieu, 75238 Paris, France*

This work is aimed at quantification of olivine (Fo_{92}) and amorphous basaltic glass (β-glass) dissolution kinetics in batch and mixed-flow reactors in the presence of aerobic gram-negative bacteria (*Pseudomonas reactants*, HK 31.3) extracted from deep underground oxygen-bearing water of basaltic aquifer. The release rate of mineral constituents was measured as a function of time in the presence of live, actively growing, dead cells and bacterial exometabolites in constant-pH (6 to 9), bicarbonate-buffered (0.001 to 0.05 M), nutrient-rich and nutrient-free media in batch reactors at 0-30 bars of CO_2. Dissolution rates were also measured in mixed-flow reactors at pH 6 and 8-9 in the presence of live and dead bacteria in nurtrient-rich and nutrient-free solutions. Intracellular uptake and reversible surface adsorption of Mg, Si and β-glass constituents by live and inactivated cells were assessed in growth and adsorption experiments. In most studied conditions, the dissolution is stoichiometric with respect to Mg and Si release and no formation of secondary phases was evidenced by microscopic examination of post-reacted grains. For olivine dissolution in batch reactors at 30 bar pCO_2 and 0.05 M $NaHCO_3$ in the presence of live bacteria, we observed a plateau of constant Mg and Si concentration after 500-700 hrs of reaction time in solutions undersaturated with respect to all possible secondary phases. SEM observation of reacted grains revealed the presence of biofilm-like surface coverage that may prevent mineral dissolution during long-term exposures. Mineral-free experiments demonstrated that concentrations of Mg, Si and β-glass constituents in solution were not affected by the presence of live and dead bacteria via possible intracellular uptake or reversible adsorption at the surface.

Olivine and β-glass dissolution rates measured in flow-through reactors were not affected by the presence of dead and live bacteria at pH > 8 in 0.01 M $NaHCO_3$ solustions, and only in circumneutral, CO2-free solutions, the bacteria increase the dissolution rate, probably due to surface complexation of exudates and lysis products. Overall, this work demonstrates inhibiting rather than accelerating effect of bacterial activity on olivine and β-glass reactivity under conditions of CO_2 storage and negligible effect of bacteria and their lysis products and exometabolites on mineral dissolution in alkaline, carbonate-bearing solutions.

48 - Experimental study on the CO_2-water-basalt interaction: Implications for a carbonate formation sequence during CO_2 basaltic aquifer storage

Yutaro Takaya[1], Kentaro Nakamura[2], Yasuhiro Kato[1]*

[1] *Department of Systems Innovation, Graduate School of Engineering, University of Tokyo, Tokyo 113-8656 Japan*
[2] *Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Kanagawa 237-0061 Japan*
Email address : tt097074@ mail.ecc.u-tokyo.ac.jp

The CO_2 aquifer storage is one of the most promising methods to stabilize atmospheric CO_2 concentration[1]. However, there is a major concern with the large scale implementation of CO_2 aquifer storage whether injected CO_2 will be stored safely over a long period of time. The geochemical trapping is an important mechanism for providing long-term security of CO_2 aquifer storage and a series of transformation where injected CO_2 (liquid or supercritical phase) changes to more stable phases (ions, minerals) through the reactions between aquifer water and host rocks. Quite recently, a basaltic aquifer receives particular attention as a suitable candidate for CO_2 aquifer storage because basaltic rocks contain high concentrations of Ca, Mg, Fe and Na that can enhance CO_2 geochemical trapping via acid neutralization and carbonate mineral formation[2]. So we conducted CO_2-water-basalt interaction experiments on three types of fresh to altered basaltic rocks and theoretical calculations using geochemical modeling software (PHREEQC) to examine the carbonate mineral formation sequence in basaltic aquifers.

The fresh basalt (non-altered basalt) is composed of olivine, plagioclase, and basaltic glass. On the other hand, the basic schist (high-T altered basalt) consists completely of secondary greenschist minerals (albite, epidote, chlorite, actinolite, quartz), and the seamount basalt (low-T altered basalt) is mainly composed of secondary clay minerals (celadonite, smectite, Fe-oxyhydroxide). In our experiments, the cations eluted from fresh basalt and basic schist are mostly Mg and Na, while the fluids reacting with seamount basalt contain large amount of Na and K with noticeably higher pH. This suggests that Na and K eluted from clay minerals play an important role in acid neutralization. Our experiments further demonstrate that, regardless of alteration types, a Na-dominant condition emerges at an early stage of the CO_2 storage in a basaltic aquifer, leading to dawsonite ($NaAlCO_3(OH)_2$) precipitation. The saturation indexes of dawsonite in the reacted solutions with basaltic rocks calculated by PHREEQC also represent higher values than the other carbonate minerals. The present findings lead us to propose a new perspective on carbonate formation sequence of dawsonite → siderite → calcite/dolomite in basaltic aquifers.

References:
[1] IPCC: IPCC Special Reports, Carbon Dioxide Capture and Storage (2005) 431pp
[2]Goldberg et al., Proc. Natl. Acad. Sci. U. S. A. 105 (2008) 9920-9925

19 - Did seafloor carbonation regulate high pCO2 on the ancient Earth?

Damon A.H. Teagle1, Rosalind M. Coggon2, Heiko Pälike1, Jeffrey C. Alt3 and Christopher E. Smith-Duque1

1. School of Ocean and Earth Science, University of Southampton, National Oceanography Centre–Southampton, European Way, Southampton, SO14-3ZH, UK; dat@noc.soton.ac.uk
2. Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, Exhibition Road, London SW7 2AZ, UK.
3. Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1005, USA.

Whether the formation of new crust at oceanic spreading centres and its hydrothermal alteration at the ridges and across the vast ridge flanks is a source or sink of carbon to the oceans is an important parameter in understanding the Earth system. Changes in spreading rates (e.g., [1]) and the age-area distribution of the ocean crust (e.g., [2]) may impact the global carbon cycle if the uptake of carbon during ridge flank circulation is a persistent processes. The amount of carbon taken up by the ocean crust remains poorly quantified due to under sampling [3] but carbonate veins are much more abundant in Mesozoic ocean crust compared to Tertiary crust.

A new approach to estimate past seawater chemistry [4] from suites of carbonate veins formed within the ocean crust during ridge flank circulation, provides additional information on the timing and duration of carbonate vein forming events. As calcium carbonate is one of the latest phases to form during ridge flank hydrothermal circulation, the timing of carbonate vein formation also gives a measure of the duration of effective chemical exchange between the oceans and ocean crust at a particular site. This new approach shows that carbonate veins form in discrete events (<10 Myr.s) in relatively young crust although the time elapsed between crustal accretion and vein precipitation is variable. This suggests that carbonate vein formation is not a persistent process and that greater carbonate uptake by the oceanic crust during the Mesozoic reflects past oceanic conditions (e.g., pCO2, T). The rate of carbonate mineral formation during these episodes is large compared to other major Earth system processes such as modern terrestrial weathering. There may be chemical or physical thresholds in the Earth system that when crossed, engages the huge basaltic reservoir of the oceanic basement into the weathering system, providing a mechanism to rapidly draw down through calcium carbonate precipitation CO2 dissolved in ocean bottom waters.

Oceanic conditions and fluid-rock reactions of the Mesozoic provide guides to the nature of industrial approaches that might be attempted to sequester significant quantities of atmospheric CO2 through accelerating and up-scaling modern rates of seafloor fluid-rock interaction and carbonate formation.

[1] Muller, et al., Science 319, 1357 (2008); [2] Seton et al., Geology 37, 687 (2009); [3] Alt, and Teagle, Geochim. Cosmochim. Acta 63, 1527 (1999). [4] Coggon et al., Science, 327:1114-1117 (2010).

47 - Exploring links between the speciation of Fe and the activity of thermophilic methanogens during the hydration and carbonation of ultramafic rocks

Alexis S. Templeton, Lisa E. Mayhew, Graham E. Lau, and Thomas M. McCollom

Department of Geological Sciences and Laboratory for Space Physics
University of Colorado at Boulder

It is now well established that ultramafic rocks such as peridotite are excellent targets for the natural and accelerated carbonation of olivine, pyroxenes and serpentine group minerals. However, the temperature-dependence and kinetics of several reactions of interest are not yet well constrained. Similarly, there also exists intense interest in determining the thermodynamics and kinetics of the low-temperature hydration of ultramafic rocks during serpentinization processes, which controls the rates of H2 (and CH4) generation that could sustain subsurface biological systems. Our specific interest is the intersection between competing hydration and carbonation reactions at temperatures <150C, where the reaction kinetics are relatively sluggish and yet (i) in-situ CO2-injection projects will reside at these temperatures for at least part of their lifetimes and (ii) there is potential for subsurface rock-hosted microbial communities to thrive during the water-rock reaction and directly affect the secondary mineralization pathways. In particular, we are interested in elucidating the potential role of microbial organisms in catalyzing mineral dissolution and subsequent H2 consumption coupled to methanogenesis vs. mineral carbonation under in-situ conditions.

At this IODP/ICDP workshop, we are keen to discuss our hypotheses and how they could be tested in active and fossil ultramafic systems that have experienced partial serpentinization and/or carbonation. In our poster we will present recent results from laboratory experiments where we have been growing a thermophilic methanogen during the low-temperature reaction of basalt, olivine, Fe0, and peridotite with CO2-rich seawater under highly reducing conditions. In these experiments, we measure the extent of H2 generation during the rock-water reaction in the presence and absence of microorganisms, and determine the rates of conversion of H2 and CO2 to CH4 as the reactions proceed. In addition, because a key control on H2 generation is the oxidation of Fe(II) to Fe(III) associated with the reduction of water to H2, we have been developing several synchrotron-based x-ray scattering and spectroscopic approaches to spatially-and temporally-resolve variations in the distribution and speciation of Fe within complex geological samples. These measurements enable us to quantitatively determine the abundance, structural identity and average oxidation state of Fe-bearing secondary mineral products that form in the biological vs. abiotic systems. In the long-term, we anticipate that our analytical protocols, experimental results and analysis of natural samples will help to define some of the key microbe-mineral interactions that should be considered in the design, validation and monitoring of in-situ CO2 reaction with ultramafic rocks.

14 - Downhole magnetic and physical property logging of serpentinized peridotite and carbonate-altered serpentinite.

Masako Tominaga1 and Frieder Klein1,2 (1. WHOI, 2. LASP)

Magnetic data can be used to detect the locations and extent of serpentinization and mineral carbonation reactions on land and within the seafloor from millimeter to kilometer scales. This possibility has been manifested from a series of terrestrial and marine geological/geophysical observations. Serpentinization of peridotite usually results in the formation of magnetite, awaruite, tetrataenite, and other magnetic minerals while steatitization, carbonation and seafloor weathering processes overprint the magnetic signal recorded in serpentinite. Magnetic susceptibility and density relationships indicate that serpentinization reaction pathways are amazingly variable. Recent experimental petrographic, theoretical and experimental studies suggest that serpentinization can – depending chiefly temperature and fluid flux – proceed with or without the formation of significant amounts of magnetite; in the latter case, most of the iron is captured by brucite and serpentine. Subsequent carbonation of serpentinite will result in a profound rise in oxygen and sulfur fugacity, expressed in the replacement of magnetite by hematite (or goethite) and Ni-Fe alloys by sulfur-rich sulfides. The physical properties of magnetite and hematite are distinctively different from one to the other: magnetization (Fe_3O_4: Fe_2O_3 = 480K: 2.5K A/m), magnetic susceptibility (abundance of magnetic minerals)(Fe_3O_4: Fe_2O_3=0.1-20 : 0.001-0.0001 SI), and resistivity (Fe_3O_4: Fe_2O_3 =5x10-5 -x103: 3.5x10-3-x107); and thus, these values can serve as proxies to determine the degree of carbonation. Moreover, neutron spectroscopy can also be used for the direct measurement of elemental concentration of Ca, C, and Fe. For continental and marine carbonate sequestration via drilled holes, we propose that using a combination of downhole logging tools, including magnetometer (e.g., the Göttingen Borehole Magnetometer, a new MMM under development at LDEO), magnetic susceptibility probe (e.g., a new MMS under development at LDEO), neutron spectroscopy (e.g., Elemental Capture Spectroscopy Sonde by Schlumberger), as well as a FormationMicroscanner and a 1D-resistivity tool, prior and after CO_2-injection will be a promising approach to detect and quantify these changes in mineralogy and hence provide valuable information about the extent of carbonation reactions. Continuous logging will particularly help us evaluate intervals of poor/no rock recovery rates. Because carbonation of serpentinized peridotite provides a promise of safe, long-term storage of large amounts of CO_2 with little risk of accidental release, further basic research is imperative (1) to advance our knowledge on the correlation between serpentinization and carbonation processes and changes in physical properties; and (2) to better constrain the magnetic signal stored in mostly opaque phases of carbonate-altered serpentinites.

49 - Peridotite fracture surface reaction rates for in-situ CO2-mineralization in ophiolites

Van Noort R.[1], Spiers C. J. [1], Kandianis M. T.[2], Drury, M. R.[3], and ten Grotenhuis, S.M.[1]

1 HPT-Laboratory and 3 Mantle Petrology Group, Utrecht University , Faculty of Geosciences, P.O. box 80021, 3508 TA Utrecht, The Netherlands, vannoort@geo.uu.nl
2 Shell Innovation, Research and Development, P.O. Box 481, Houston, TX 77001-0481, USA

Mineralization of carbon dioxide by subsurface reaction with olivine-rich peridotite has recently been proposed as a potential CO2-sequestration method. The abundance of olivine rocks at and near Earth's surface, and the stability of the product mineral phases, notably magnesite and silica, make this an interesting option, especially as the in-situ temperatures and CO2-injection pressures will strongly enhance olivine dissolution and hence carbonation rates. The key issues controlling the effectiveness of peridotite carbonation as a CO2-storage solution are the creation of fresh surface area by hydrofracturing or reaction-driven fracture, as well as the rates of dissolution and precipitation reactions at fracture surfaces. Dissolution at the latter may proceed far more slowly than for crushed olivine or peridotite. Ongoing dissolution at natural peridotite fracture surfaces may be inhibited by a decrease in fracture surface reactivity as less reactive minerals such as serpentine and pyroxene begin to dominate the surface composition. Additionally, the precipitation of product phases on the fracture surfaces may prevent further dissolution.

We report experimental research that characterizes the evolution of dissolving peridotite (fracture) surfaces and the rates of dissolution and carbonation at these surfaces under conditions relevant for in-situ CO2-sequestration in peridotite bodies. Our experiments showed olivine dissolution from peridotite fracture surfaces proceeding at rates that were similar to, or higher than, the rates of dissolution of pure olivine under open system conditions. Microstructural observations showed that mesh-serpentinization, rather than inhibiting surface dissolution, allowed fluids to penetrate into the rock and promoted dissolution of olivine beyond the fracture surface despite the reduced olivine content. Under closed system conditions, where serial olivine dissolution and magnesite precipitation take place, product phases precipitated on the dissolving surfaces, but did not appear to inhibit progressive dissolution. However, under these conditions, changes in fluid composition and fluctuations in pH, occurring as a result of ongoing dissolution, resulted in dissolution rates that were approximately an order of magnitude slower.

Our results thus suggest that relatively rapid dissolution of olivine from fracture surfaces under in situ conditions can continue over long durations, but only if open system conditions are maintained. Under closed-system conditions, changes in fluid composition will hinder olivine dissolution substantially. Considering the geomechanical challenges of in-situ CO2-mineralization, CO2-mineralization using peridotites may only be feasible if CO2-rich fluids are injected into the peridotite, exposed to a subsurface fracture network, and subsequently pumped back to the surface where evaporation will result in the formation of hydrous magnesium-carbonate and silica phases.

50 - Fracture propagation during in-situ mineral carbonation in peridotite

Van Noort R.[1], Spiers C. J. [1], Kandianis M. T.[2], Drury, M. R.[3], and ten Grotenhuis, S.M.[1]

1 HPT-Laboratory and 3 Mantle Petrology Group, Utrecht University , Faculty of Geosciences, P.O. box 80021, 3508 TA Utrecht, The Netherlands, vannoort@geo.uu.nl
2 Shell Innovation, Research and Development, P.O. Box 481, Houston, TX 77001-0481, USA

Subsurface mineralization of carbon dioxide in peridotite bodies is currently being investigated to evaluate its potential as a method of CO2-sequestration. The abundance of peridotites at or near Earth's surface as well as the potential formation rates and stability of mineral phases produced from the reaction of CO2 with these rocks support the application of this approach; however, geological sequestration of CO2 in dense, crystalline peridotites involves considerable geomechanical challenges. First, peridotite rock is non-porous and exhibits low permeability, therefore the sequestration of CO2 by injection and in-situ mineralization requires fracturing the host rock to create porosity and permeability. In addition, the reaction between CO2-rich hydrous fluids and olivine, to form magnesite and silica, produces a significant increase in solid volume (~84%) that may result in the filling and sealing of created fractures and eventually limit the volume of CO2 that can be injected. To attain the extent of carbonation required for substantial CO2-storage in the subsurface, new fracture surface area must be generated continuously and rapidly enough to ensure the rate of fracture surface area creation exceeds that at which surface area is consumed by the precipitation of product phases. A key question to consider before employing CO2-mineralization in peridotites as a storage solution is whether reaction-driven fracturing will occur, on timescales that allow for sequestration, via a pathway that involves solid volume expansion associated with product mineral precipitation and the development of a force of crystallization.

Thermodynamic modeling has shown that the carbonation of olivine under conditions relevant for in-situ CO2-storage can, via a force of crystallization effect, result in very large effective stresses that are well in excess of the in-situ stress and tensile strength of the rock. To evaluate the occurrence of stress generation and the timescale of stress development in a carbonating peridotite fracture, we conducted experiments under confined conditions to directly measure the magnitude of force development that results from olivine carbonation.

With the exception of one experiment, a force of crystallization did not develop. Post-mortem microstructural observations showed that magnesite precipitation led to pore occlusion, grain boundary cementation and the inhibition of CO2-transport within the simulated peridotite fracture. Slow diffusive transport of dissolved CO2 through the sample and into grain boundaries, thus inhibited the development of a force of crystallization within the duration of our experiments. For in-situ CO2-mineralization in peridotite bodies, this implies that diffusion of CO2 through the fracture network to crack tips will limit subsurface mineralization. Estimates from our work also suggest a reaction-driven fracture-propagation rate of 1m per 300-6000 year, which indicates that reaction-driven fracture rates will have to be enhanced significantly to attain meaningful rates of CO2-storage.

51 - Integrated Experimental and Modeling Studies of Mineral Carbonation

*Z. Wang, E. Bolton, S. Karato, Jay Ague, D. Bercovici, M. Oristaglio**
Yale University, Geology & Geophysics, New Haven, CT 06520-8109;

W. Zhu, Department of Geology, University of Maryland, College Park, MD 20742

K. Johnson, Department of Geology and Geophysics, University of Hawai'i at Manoa, Honolulu, HI 96822

**Correspondence: michael.oristaglio@yale.edu*

We report on a new project integrating geochemical and geomechanical lab experiments and 3D multi-phase reactive transport models, with the goal of developing rigorous estimates of the carbon sequestration potential of in-situ mineral carbonation (Bickle, 2009; Oelkers et al., 2008; Kelemen and Matter, 2008). The planned three-year project started in October 2010 with support from the National Energy Technology Laboratory of U.S. Department of Energy and the Yale Climate & Energy Institute. The geochemical experiments include both closed-system and flow-through conditions, with the starting silicate minerals or rocks ground and sieved to different grain sizes, then measured for grain-size distribution and surface area. The experiments are intended to map reaction kinetics in a simple system where sample powders are heat-treated at given P-T conditions with known carbon dioxide and water fugacity. Flow-through experiments will use dense hot-pressed (or sintered) starting material – such as dunite, harzburgite, lherzolite, basalt or gabbro – with some controlled porosity. The experiments will attempt to characterize dissolution rates of environmentally sensitive or economic metals during the reaction.

The geomechanical experiments include two major components: (1) mechanical tests monitoring the permeability and strength of the fluid-rock system during carbonation, and (2) x-ray micro-tomography of pore geometry. Electron microscopy will be used to place constraints on microscopic processes affecting mechanical properties. Most experiments will use samples of controlled grain-size and porosity. Evolution of pore-space geometry during reaction and deformation will be monitored by x-ray tomography at a synchrotron facility; evolution of permeability during chemical reactions will also be monitored, sometimes in the presence of external stress. Isotopic labeling experiments will help understand the role of mineral dissolution and precipitation. Geochemical and geomechanical experiments will also be carried out on natural rock samples in the later phases of the project.

The lab experiments will be compared and calibrated with results from a 3D numerical code combining models of multiphase fluid flow through porous, fractured media with models of reactive transport and deformation (an extension of the framework described in Bolton et al., 2004). A series of "scaling-up" simulations will study the effects of heterogeneity at different scales, with the goal of providing design parameters for future field tests. In particular, the project will supply data on the carbonation capacity of several important basaltic rock types in Hawai‘i.

53 - The potential for carbon sequestration by accelerated weathering of mafic rocks at ambient pCO2

A. Joshua West

Department of Earth Science, Univ of Southern California, Los Angeles, CA USA

The imperative for exploring a wide range of technologies for carbon capture and storage (CCS) is now well recognized. One of the shortcomings of many approaches to CCS is the pre-requisite for capture of CO2, to provide a concentrated source for injection into geologic formations, such as mafic and ultramafic rocks. While there is existing technology for capture from power plants, the cost of capture and transport constitutes a major proportion of total costs associated with CCS (Rubin 2008). Moreover, capture of active emissions from power plants does not provide capability for removing CO2 already in the atmosphere, and the technology for direct capture from ambient air remains untested and may struggle to be cost-effective.

Increasing the rate of alkalinity production from in-situ natural weathering reactions at the Earth's surface ("accelerated natural weathering") would avoid this problem of carbon capture, because CO2 would be passively removed from the atmosphere through aqueous equilibration with natural waters. However, such weathering processes are generally viewed as operating far too slowly to make a meaningful contribution to carbon sequestration on timescales relevant to human society. Natural silicate weathering at the Earth's surface is estimated to remove CO2 from the atmosphere equivalent to approximately 150 Mt C per year (Gaillardet et al. 1999), over an order of magnitude smaller than the 5.5 Gt C emitted by fossil fuel combustion (IPCC 2007).

Nonetheless, there is a wide range in natural weathering rates observed at the modern Earth's surface. Observed natural atmospheric CO2 removal by basalt weathering (Dessert et al. 2003) ranges from ~3 t C km-2 yr-1 to ~75 t C km-2 yr-1. For an illustrative calculation, if all basalt (6.8 x 10^6 km2 of the modern Earth's surface) weathered at the highest observed rates today, then basalt weathering would sequester ~0.5 Gt C yr-1, making a significant contribution to total carbon sequestration. This is a simplistic, first-order calculation but illustrates that, if weathering rates can be increased over large areas even within the range observed today, this process could play a meaningful role in an integrated strategy for atmospheric CO2 removal. What remains unclear is whether there are methods that could be employed to significantly increase weathering rates over large areas of land surface. This poster will summarize some of the theoretical potential scope for accelerating in-situ natural weathering rates of mafic and ultra-mafic rocks, at ambient CO2 concentrations, and will describe the experimental work that we are currently initiating to explore these possibilities quantitatively.

References

(1) Dessert, C. et al. 2003. Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. Chemical Geology 202: 257-273.

(2) Gaillardet, J. et al. 1999. Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. Chemical Geology 159: 3–30.

(3) IPCC. 2007. Climate Change: The physical science basis. Cambridge University Press, Cambridge UK.

(4) Rubin, E.S. 2008. CO2 Capture and Transport. Elements 4: 311-317.

54 - Dissolution of CO2 gas is rate limiting to C sequestration in high-salinity alkaline brines

Siobhan Wilson[1], Shaun Barker[2], Anna Harrison[2], Ian Power[2], Greg Dipple[2], K. Ulrich Mayer[1], Viorel Atudorei[3].

[1]Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1405, U.S.A.
[2]Mineral Deposit Research Unit, The University of British Columbia, Vancouver, BC V6T 1Z4, Canada
[3]Department of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM 87131-0001, U.S.A.

Secondary hydrated Mg-carbonate minerals that form within ultramafic tailings from some mines are safe and durable traps for carbon. Mineralization of carbon dioxide (CO_2) in ultramafic mine tailings can occur on a scale that is significant relative to the greenhouse gas emissions of mine operations, and it has been suggested that carbonation of Mg-silicate mine tailings may be used by some mining operations to offset their greenhouse gas emissions.

Dypingite [$Mg_5(CO_3)_4(OH)_2{\cdot}{\sim}5H_2O$], a hydrated Mg-carbonate mineral, was precipitated from high-pH, high salinity solutions to investigate controls on carbon fixation and to identify the isotopic characteristics of mineral sequestration in mine tailings. In our free-drift synthesis experiments, dypingite formed within three weeks by carbonation of brucite [$Mg(OH)_2$].

$\delta^{13}C$ values of dissolved inorganic carbon content and synthetic dypingite are significantly more negative than those predicted for equilibrium exchange of CO_2 gas between the atmosphere and solution. The measured $\delta^{13}C$ of aqueous carbonate species is consistent with a kinetic fractionation that results from a slow diffusion of atmospheric CO_2 into solution. Modeling using PHREEQC indicates the concentration of dissolved inorganic carbon expected at equilibrium with atmospheric CO_2 pressure is not reached in the experimental solutions. Upon precipitation of hydrated magnesium carbonates, models predict stabilization of dissolved inorganic carbon concentrations. During dypingite precipitation however, dissolved inorganic carbon concentrations decrease and $\delta^{13}C$ values become more negative, indicating that the rate of CO_2 uptake into solution was outpaced by the rate of carbon fixation within the precipitate. This implies that CO_2 gas uptake is rate limiting to CO_2 fixation. $\delta^{13}C$ of carbonate mineral precipitates in mine tailings and of DIC in mine process waters display similar ^{13}C-depletions that are inconsistent with equilibrium fractionation. Thus, the rate of carbon fixation in mine tailings and geochemically similar environments may also be limited by supply of CO_2. Carbon sequestration could be accelerated by increasing the partial pressure of CO_2 in tailings ponds and natural ultramafic formations, or by using chemicals that enhance the uptake of gaseous CO_2 into aqueous solution.

23 - Depleted basaltic oil and gas reservoirs: Potential economic and efficient reservoirs for CO_2 sequestration

Changzhi Wu, Junfeng Ji, Zhengyu Wang, Yan Chen, Lianwen Liu and Lianxing Gu*

School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, China
**Present author; Email address: jijunfeng@nju.edu.cn*

Continued use of fossil fuels has led to the realization that carbon capture and storage should be a component of any realistic plans to cap or reduce atmospheric CO_2 concentrations. In this regard, it has been suggested that unminable coal beds, deep ocean disposal, saline aquifers, and depleted oil and gas reservoirs be used for CO_2 sequestration and storage. The main advantage of these repositories is their large potential storage volume. Underground basaltic formations have recently emerged as an important host medium for in-situ mineral CO_2 sequestration due to the rocks' relative rapid chemical reaction with CO_2 - satureated pore water. Here, we present preliminary survey results on the basalt in the Bohaiwan basin of China and the estimate of the carbon storage potential.

The Bohaiwan basin is one of numerous petroleum-producing Mesozoic-Cenozoic basins in the coastal areas of eastern China. These basins are generally considered to have been formed by back arc extension as the Pacific plate subducted beneath the eastern margin of the Asia continent to form a large amount of calc-alkaline volcanic rocks. The basin has a size of 1200 by 2600 km or a total area of about 200 thousand km^2. We found more than 10 layer of basalts that are interbeded with hydrocarbon source rocks, covering an area of more than 20,000 km^2. The total thickness of the basalt varies from 0 to 1500 meters with average around 150 meters. Preliminary calculation shows a total volume of 3,000 billion m^3 underground basalts. Geochemically, these rocks are rich in Ca, Mg and Fe. Chemical analysis of 41 of basalt samples from Xiaoliaohe, one of depression of the Bohaiwan basin, yields a mean value of 8.10 wt%, 6.11 wt% and 4.45 wt% for CaO, MgO and FeO, respectively.

Vesicles are abundant in the upper and lower portions of lava flows. Cooling fractures are also commonly seen in these basalts. It appears that these basalts have high enough porosity and permeability for carbon storage. In addition, there are low-permeability interbedded sediments and some impermeable basalts and tuffs overlying individual basalt flow that can act as caps or barriers to prevent CO_2 migration or at least slow the migration sufficiently to allow time for the mineralization reactions to occur.

We estimate a total 3, 000 km^3 of basalts with an average bulk porosity of 3%. This translates to 90 km^3 of potential pore volume for CO_2 storage in this basin alone. Assuming one-third of the total volume can be used for storage, the total injection amounts to about 27 Gt of CO_2 by carbonate.

55 - Aqueous Carbonation of Natural Brucite for CO2 Sequestration

Liang Zhao1, Liqin Sang1, Jun Chen1, Junfeng Ji1, and H. Henry Teng1,2

1Department of Earth Sciences, Nanjing University, Nanjing, Jiangsu, 210093, PRC
2Department of Chemistry, the George Washington University, Washington, DC, 20052, USA

Experimental study is carried out at conditions of room temperature and moderate CO2 pressure to examine the carbonation reaction of natural brucite in aqueous environment. Two sets of initial conditions are examined, one is brucite in pure water, and the other is in 1% HCl. Time-dependent XRD analysis shows that carbon fixation process begins within 30 min of the experiments irrespective of the original makeup of the slurry. Ensuing measurements by XRD and FT-IR reveal that nesquehonite (> 78%) is by far the dominant C-bearing species in the carbonate mineral product assembly. Minor product components observed in water are basic magnesium carbonate hydromagnesite and dypingite; when HCl is added in the starting slurry, chloride-bearing artinite replaces hydromagnesite. However, thermodynamic calculation suggests that the assembly of such composition is most likely a kinetically favored product at the experimental conditions which are more strongly saturated with respect to hydromagnesite and magnesite than to nesquehonite. A pseudo first-order rate law is found to best describe the time-dependent measurements for both water and HCl experiments. Moreover, fitting the rate expression to the experimental data yields a higher rate constant for the experiments performed in HCl solutions. The faster kinetics relative to that in water implies that the carbonation reaction may be a multi-stepped process, involving first the dissolution of brucite and CO2 to generate Mg2+ and CO32-, followed by precipitation of magnesium carbonate phases from aqueous solutions. This leads to our proposition that direct heterogeneous reaction between hydrated CO2 and solid phase of Mg(OH)2 is probably not the pathway for the overall carbonation process. Assuming the upper limit of carbon content Cmax = 8.7% (based upon that of nesquehonite), measured total carbon in the product Ctot show a carbonation rate of 83.9% and 94.3% for brucite in HCl and DDW at the end of 2.5 hr experiments. However, significant amount of brucite (~ 30 to 40%) remains unreacted in HCl, sharply contrasting to < 5% in DDW. This may be caused by the carbonation product forming a protective coating on brucite particles due to the initial fast kinetics of precipitation reaction in the HCl experiments.

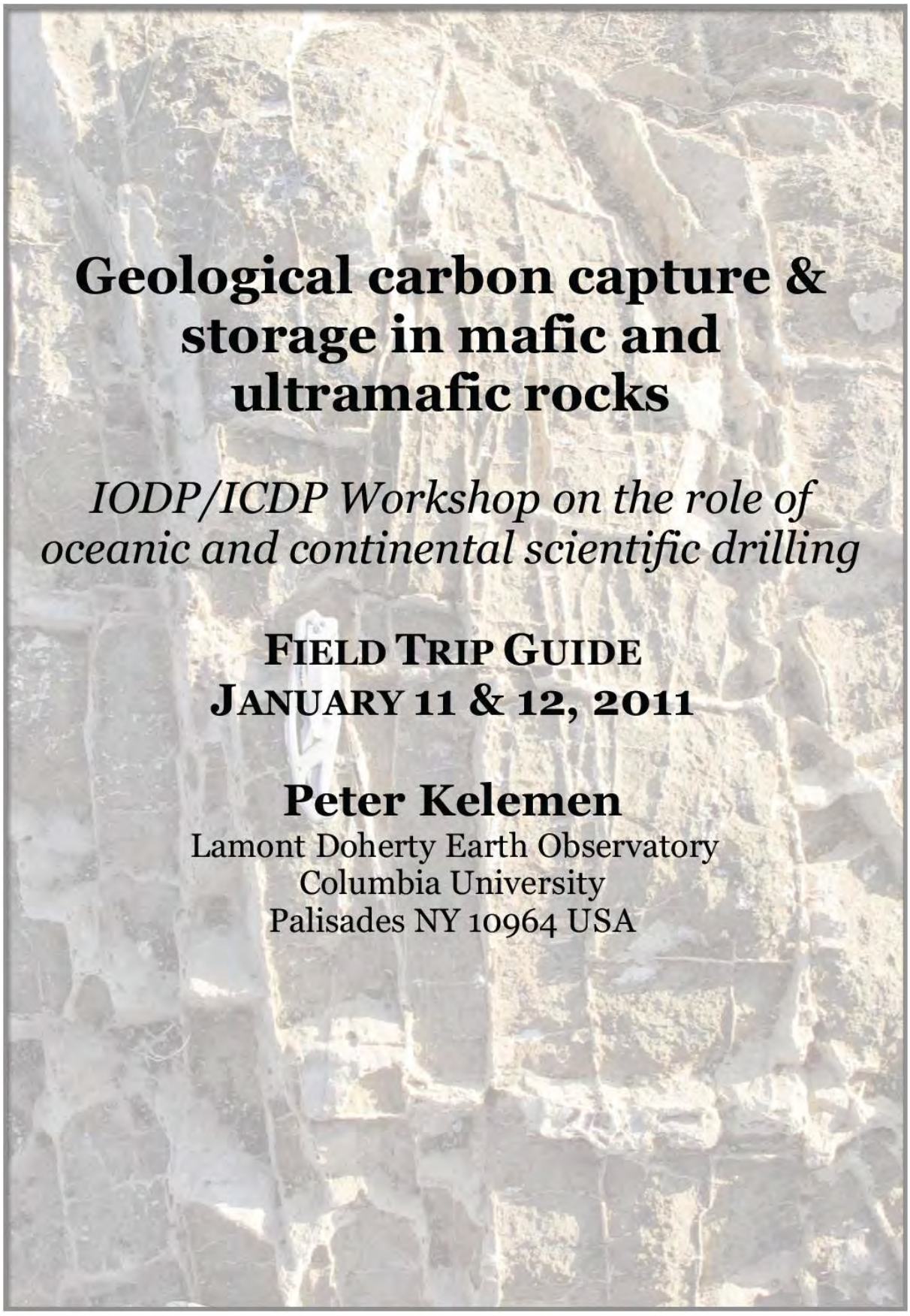
52 - Carbonation Reaction Driven Permeability and Porosity Evolution in Thermally Cracked Dunites.

Zhu, Wenlu. *University of Maryland.* *wzhu@umd.edu*

Lisabeth, Harrison. *Columbia University.* *hpl2105@columbia.edu*

Capture and storage of atmospheric CO2 by the reaction Olivine + CO2 ‡ Magnesite appears to be one of the safest long-term options for CO2 sequestration. The carbon is held in a stable, solid phase unlike gaseous storage in coal or salt formations. The reaction is exothermic and has a positive change in solid volume. By circulating CO2-rich brines through thermally-cracked, natural dunite samples, we seek to understand the effect this change in volume plays on the evolution of permeability and porosity in natural systems.

Appendix E: Post-meeting field trip guide



Geological carbon capture & storage in mafic and ultramafic rocks

IODP/ICDP Workshop on the role of oceanic and continental scientific drilling

FIELD TRIP GUIDE
JANUARY 11 & 12, 2011

Peter Kelemen
Lamont Doherty Earth Observatory
Columbia University
Palisades NY 10964 USA

Geological carbon capture & storage in mafic and ultramafic rocks
IODP/ICDP Workshop on the role of oceanic and continental scientific drilling

FIELD TRIP GUIDE, JANUARY 11 & 12, 2011

Peter Kelemen, Columbia University

Overview : On Day 1 we will visit two large travertine deposits with active alkaline springs emerging from peridotite, and then a large escarpment exposing late Cretaceous listwanite (fully carbonated peridotite, magnesite + quartz + relict chromian spinel). On Day 2, we will visit three carbonate vein localities, as well as seeing a general overview of lithologies in the Oman ophiolite. If time permits, we may also visit a third alkaline spring.

Section 1 : Simplified description of peridotite alteration at low temperature

Peridotite is a rock type composed of > 40% of the mineral olivine (with gemstone name “peridot”). Typical residual mantle peridotite exposed on the seafloor and in ophiolites is composed of 70 to 85% olivine, together with dunite with more than 95% olivine. Carbonation of the mineral olivine occurs together with hydration via the simplified reactions

(1a) $4Mg_2SiO_4$ (Mg-olivine) + $4H_2O$ + $2CO_2$ = $2Mg_3Si_2O_5(OH)_4$ (Mg-serpentine) + $2MgCO_3$ (magnesite)

(1b) $4Mg_2SiO_4 + H_2O + 5CO_2 = Mg_3Si_4O_{10}(OH)_2$ (talc) + $5MgCO_3$

(1c) $4Mg_2SiO_4 + 8CO_2 = 4SiO_2$ (quartz) + $8MgCO_3$

and after hydration by progressive carbonation via the simplified reactions

(1d) $4Mg_2SiO_4 + 6H_2O = 2Mg_3Si_2O_5(OH)_4 + 2Mg(OH)_2$ (Mg-brucite)

(1e) products of 1d + $2CO_2 = 2Mg_3Si_2O_5(OH)_4 + 2MgCO_3 + 2H_2O$

(1f) products of 1e + $3CO_2 = Mg_3Si_4O_{10}(OH)_2 + 5MgCO_3 + 5H_2O$

(1g) products of 1f + $3CO_2 = 4SiO_2 + 8MgCO_3 + 6H_2O$

These reactions are written with no components other than H_2O and CO_2 in fluids, but of course they can take on infinite variety when other key components – such as Ca^{2+}, aqueous SiO_2, H_2, sulfur species, and O_2 – are considered to be transported in fluids.

The second and third most abundant minerals in peridotite are Ca-poor pyroxene (often called orthopyroxene or opx, with Mg-endmember enstatite, $Mg_2Si_2O_6$) and Ca-rich pyroxene (often called clinopyroxene or cpx, with Mg-endmember diopside, CaMg Si_2O_6). To understand natural peridotite carbonation, one simplified reaction is particularly important:

(1h) $4Mg_2SiO_4 + CaMgSi_2O_6 + 6H_2O + CO_2 = 3Mg_3Si_2O_5(OH)_4 + CaCO_3$ (calcite)

This reaction often takes place in stages, e.g.,

(1i) $4Mg_2SiO_4 + CaMgSi_2O_6 + 7H_2O = 3Mg_3Si_2O_5(OH)_4 + Ca^{2+}(aq) + 2OH^-(aq)$

in the subsurface, and then

(1j) $Ca^{2+}(aq) + 2OH^-(aq) + CO_2(aq \text{ or } gas) = CaCO_3 + H_2O$

when fluids modified by reaction with peridotite form travertine at or near the surface.

Mantle peridotite generally has molar Mg/(Mg+Fe), or Mg#, of ~ 0.9. Iron is dissolved in silicates (e.g., $Mg_{1.8}Fe_{0.2}SiO_4$ olivine) and oxides. During hydration and carbonation, reaction products such as serpentine, talc, magnesite and dolomite and calcite have higher Mg# than the olivine and pyroxene reactants Excess iron is commonly taken up by hydroxides such as goethite (FeO(OH)) and brucite ($(Mg,Fe)(OH)_2$), in oxides such as hematite (Fe_2O_3) and magnetite, (Fe_3O_4), and in metal alloys rich in Fe and Ni such as awaruite. Initial stages of reaction in rock-dominated systems often involve oxidation of iron from Fe^{2+} in silicates such as olivine to Fe^{3+} in oxides. These and other reactions lead to reduced oxygen fugacity and increased hydrogen fugacity in product fluids, e.g.,

(1k) $6Fe^{2+}{}_2SiO_4 + 7H_2O = 3Fe^{2+}{}_3Si_2O_5(OH)_4(\text{Fe-serpentine}) + Fe^{3+}{}_2Fe^{2+}O_4(\text{magnetite}) + H_2(aq)$

In this way, fluids become increasingly reduced as the fluid/rock ratio decreases, and eventually saturate in Fe-Ni alloys. Fluids from serpentinizing peridotites have low Eh, and enhanced levels of dissolved hydrogen and methane, as observed in Oman. From the perspective of mineral carbonation, the main impacts of these redox reactions are to impart a geochemical signal (low Eh, high fH_2) to fluids produced by hydration of peridotite at low water/rock ratios, and the potential for reduction of carbon species, including breakdown of carbonate minerals to form graphite and methane, e.g.,

(1l) $MgCO_3 + 2H_2 = Mg(OH)_2$ (or aqueous $Mg^{2+} + 2OH^-$) $+ H_2O + C$ (graphite)

and

(1m) $MgCO_3 + 4H_2 = Mg(OH)_2 + H_2O + CH_4$ (methane).

The reactions listed here and their associated mineral parageneses were explored decades ago (e.g., Evans, 1977; Greenwood, 1967; Johannes, 1969; Kerrick, 1974; Skippen, 1974; Trommsdorff and Evans, 1977a, b). As noted by these previous workers, peridotite carbonation reactions progressively form increasingly SiO_2-rich silicates as Mg (and Ca) are incorporated into carbonate minerals with increasing CO_2-contents in fluid at a given pressure and temperature (Figure 1). In the absence of H_2O-rich fluids, the maximum thermal stability of carbonate minerals in peridotite bulk compositions at 2 kb are around 520°C for breakdown of magnesite + quartz to form opx + CO_2, and 560°C for breakdown of magnesite + opx to form olivine + CO_2 (Johannes, 1969). At lower P_{CO2}, in the presence of aqueous fluids and/or at lower total pressure, the thermal stability of carbonate minerals is reduced.

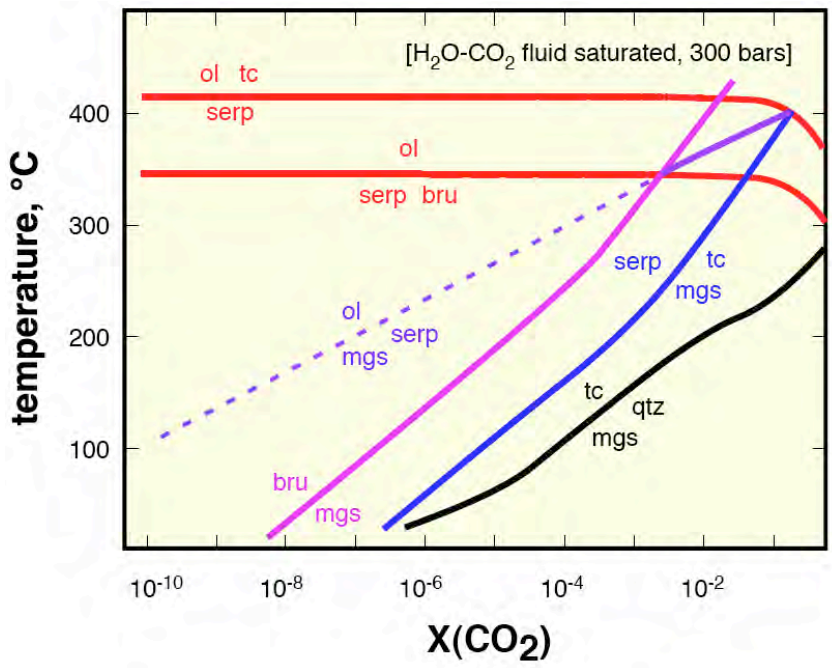


Figure 1 : Schematic phase diagram for reactions involving brucite (bru), olivine (ol), serpentine (serp, chrysotile), talc (tc), quartz (qtz) and magnesite (mgs) in the system MgO--SiO2--H2O--CO2, saturated in H2O--CO2 fluid at 300 bars, calculated using Thermocalc (Holland & Powell CMP 1998). This is Figure 1 in Kelemen et al., Annual Reviews in Earth & Planetary Sciences (AREPS), 2011 in press.

As originally explained by Barnes, O'Neil and co-workers (Barnes et al., 1967; Barnes and O'Neil, 1969; Barnes et al., 1978), and quantified by Bruni, Cipolli, Marini and co-workers (Bruni et al., 2002; Cipolli et al., 2004), low temperature reaction between surface waters and peridotite generally takes place in three steps. First, meteoric water reacts with peridotite in equilibrium with the atmosphere, increasing dissolved Mg^{++} and HCO_3^- concentrations to form "*Mg-HCO_3 waters*", also called "*Type I waters*". Type I waters are found in shallow ground water in peridotite massifs worldwide.

In the second step, sub-surface reaction, out of equilibrium with the atmosphere, leads to precipitation of Mg-carbonates such as magnesite and dolomite, together with serpentine and clay minerals. Though Ca is a minor constituent of the peridotite, contained mainly in pyroxene minerals, it is almost completely excluded from serpentine and clay, and the concentration of Ca^{++} in resulting fluids rises even when dolomite $CaMg(CO_3)_2$ is precipitating. Dissolution of Ca-bearing pyroxenes also leads to very high pH, as in reaction (1i), above, while reactions such as (1k) reduce the oxygen fugacity to very low values (e.g., Barnes and O'Neil, 1969; Bruni et al., 2002; Cipolli et al., 2004; Evans, 2008; Frost, 1985; Janecky and Seyfried, 1986). Carbonate precipitation, via reactions (1a-1g), together with reactions such as

(2) $Mg^{++} + HCO_3^- + OH^- = MgCO_3 + H_2O$,

lowers the total carbon concentration in resulting fluids to nearly zero (Barnes and O'Neil, 1969; Bruni et al., 2002; Cipolli et al., 2004). The result is production of high pH, low fO_2, low carbon "*Ca-OH waters*", sometimes called "*Type II waters*". These form alkaline springs that emerge from peridotite catchments worldwide.

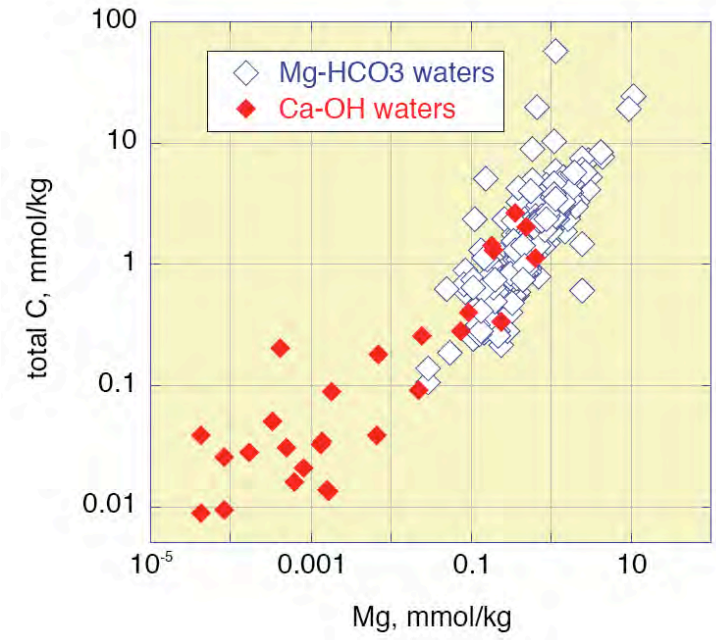


Figure 2 : Mg and C concentrations in Mg-HCO3 fluids (surface water, groundwater) and Ca-OH fluids (alkaline spring waters) from peridotite hosted aquifers in California, New Caledonia, Italy and Oman. Reaction progress is from upper right to lower left, as reaction between Mg-HCO3 fluids and peridotite forms Mg-carbonate minerals and serpentine plus Mg- and C-depleted Ca-OH waters. This is Figure 11 in Kelemen et al. AREPS 2011.

In a third step, alkaline spring waters react with the atmosphere (or mix with shallow ground water), precipitating calcite and lowering the pH to neutral values via reactions such as (1j).

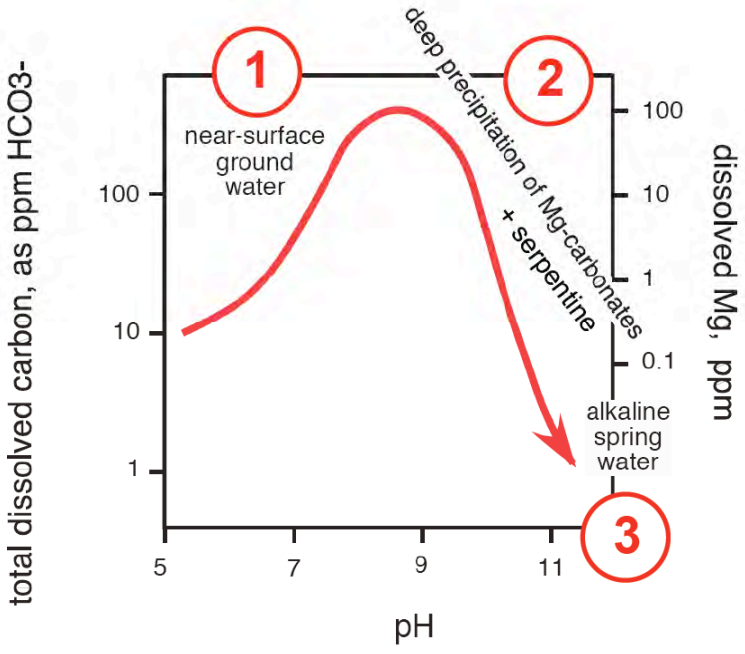


Figure 3: Schematic illustration of evolution of ground water reacting with peridotite at low temperature. In Step 1, rain water dissolves peridotite and takes up atmospheric CO2 to form Mg-HCO3 rich waters. Some of these continue reaction with peridotite away from equilibrium with the atmosphere, and precipitate Mg-carbonates (magnesite, dolomite) plus hydrous Mg-silicates (serpentine, …) to form Ca-OH rich waters with almost no dissolved C or Mg.

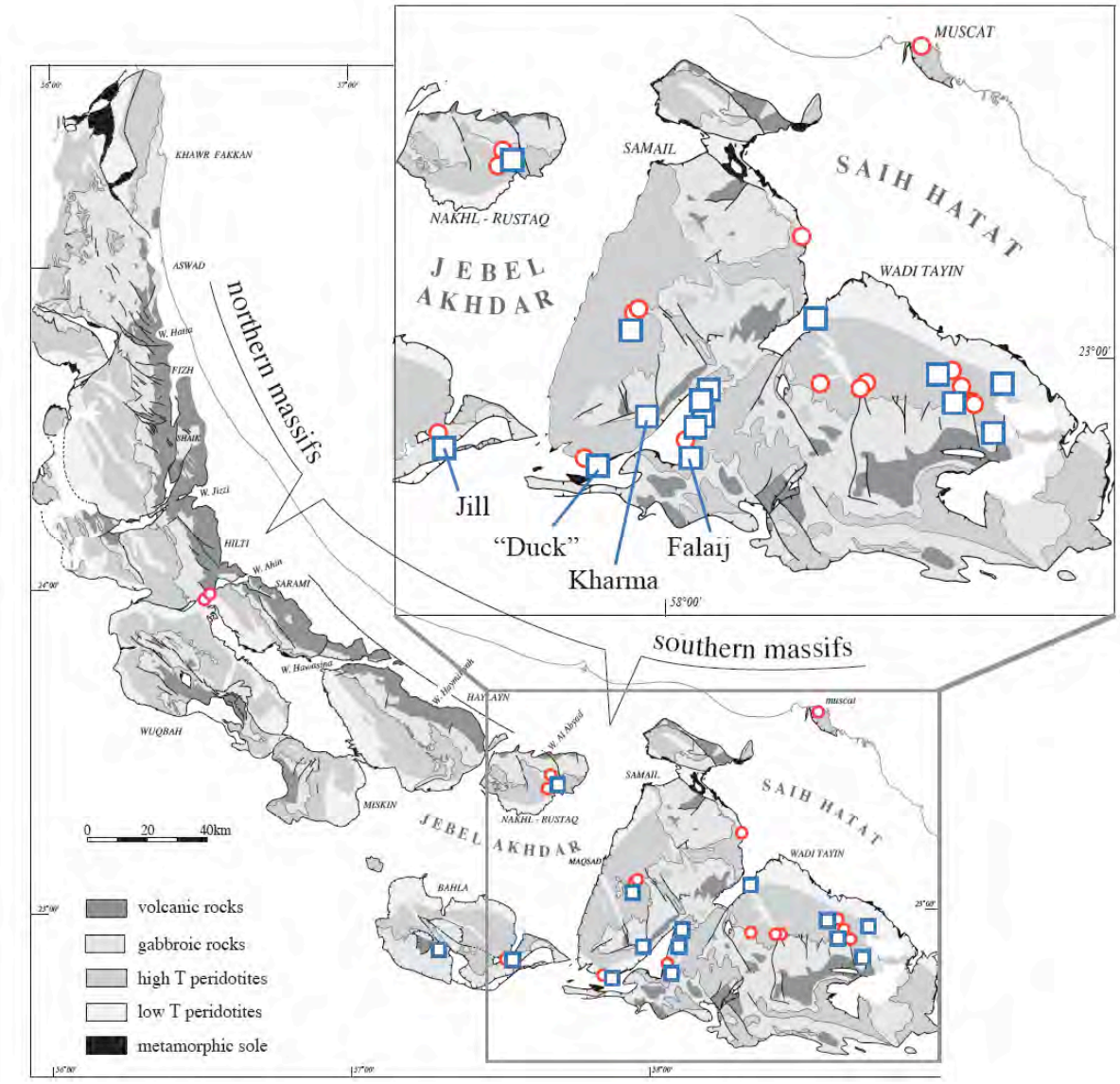


Figure 4a: Geologic map of the Oman ophiolite from Nicolas et al. MGR 2000, with locations of carbonate samples dated using ^{14}C (red circles) and locations of known travertine deposits in the Bahla, Samail and Wadi Tayin ophiolite massifs (blue squares; for perimeter maps of the "Duck", Kharma and Falaij travertines, see Kelemen & Matter PNAS 2008 Figure S3). We only show locations of travertines that we have personally observed, and there are probably many more even in the southern massifs. In addition to travertine deposits on the surface, there are thick trravertine deposits forming within alluvial and gravel terraces. We have not been able to estimate the extent of these. This is Figure S1 from Kelemen & Matter PNAS 2008. We have visited numerous alkaline springs and travertines in more northerly massifs, but we have not updated this figure.

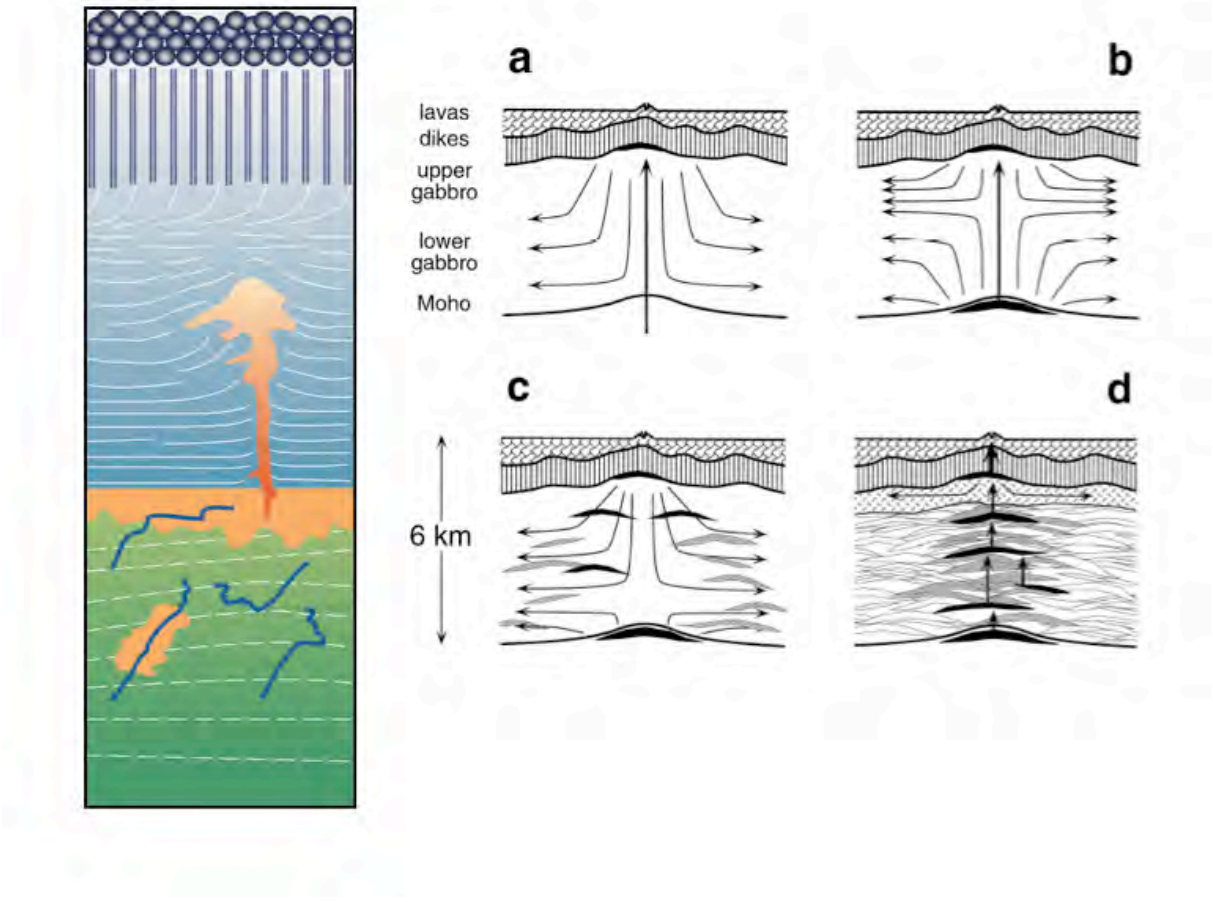


Figure 4b: Left, schematic crustal section of the Oman ophiolite, from the Universite de Montpellier II, http://www.gm.univ-montp2.fr/spip/spip.php?article207&var_recherche=oman, probably very similar to the structure of oceanic crust formed at intermediate to fast spreading ridges. Upper oceanic crust: top layer, lavas erupted on the seafloor with characteristic tube and "pillow" morphology. Below, dikes within dikes within dikes, known as sheeted dikes, were among the first indicators that ophiolites formed at submarine spreading ridges. Lower oceanic crust: Intrusive gabbros, composed mainly of plagioclase, pyroxene and olivine, with steep foliation near top, and nearly horizontal modal layering at bottom, intruded away from the ridge axis by pyroxene-rich "wehlrites". Lower gabbros are mostly "cumulate", meaning that they formed by partial crystallization of a magma, followed by efficient extraction of most of the remaining liquid to form igneous rocks higher in the section (dikes and lavas). Right, from Kelemen et al., EPSL 1997, possible mechanisms for accretion of oceanic lower crust, ranging from (a) a gabbro glacier in which gabbros crystallize in a single, shallow magma chamber and then flow downward and outward by melt lubricated ductile deformation, to (d) sheeted sills, in which all gabbros crystallize in many small melt lenses at about the depth where we find them now.

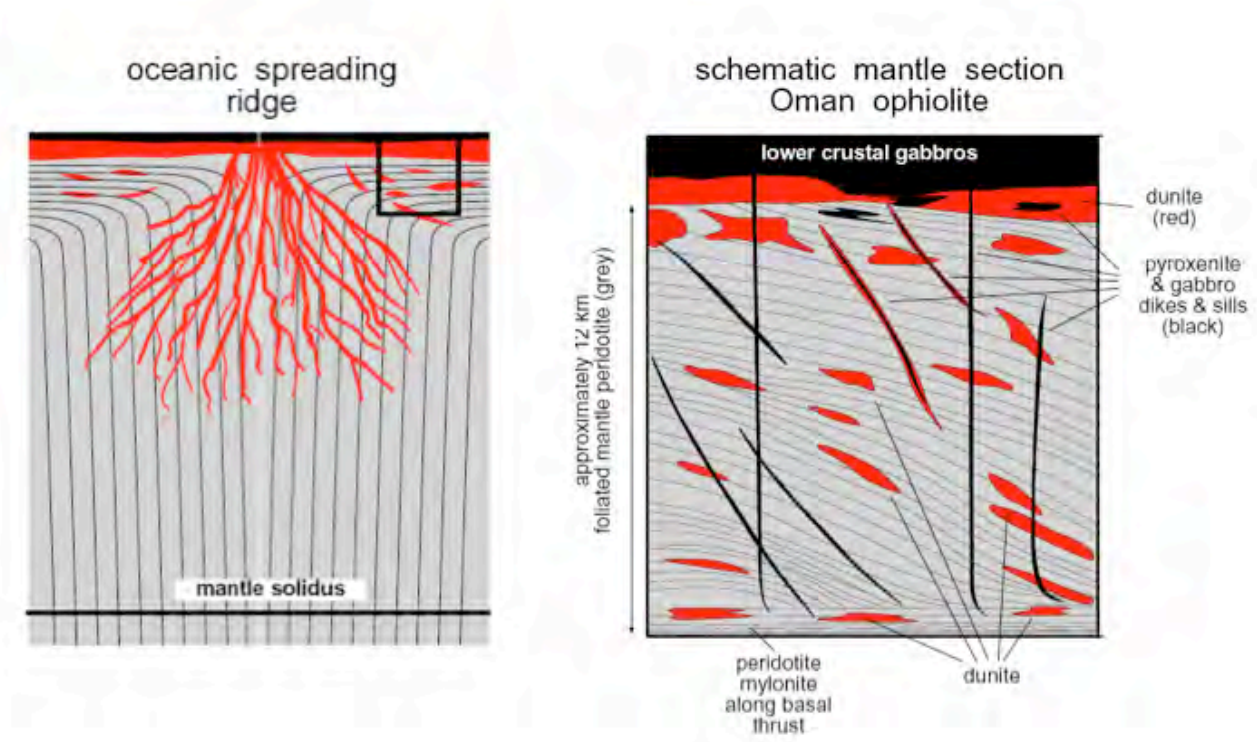


Figure 4c: Schematic mantle section of the Oman ophiolite, right, together with interpretation from Kelemen et al. Nature 1995, G-cubed 2000, and Braun & Kelemen, G-cubed 2002. Schematic Oman section modified from Lippard et al., The Ophiolite of Northern Oman, Blackwell, Oxford, 178 pp., 1986. Black rocks are gabbroic dikes: tabular intrusions of gabbroic rocks (gabbronorite, gabbro, ...) and pyroxenite (websterite, clinopyroxenite, orthopyroxenite) cutting mantle foliation at a high angle, and therefore formed after ductile deformation of the peridotite. These dikes are mainly NOT in chemical equilibrium with the melts that formed the igneous crust. However, most mantle dikes are parallel to the sheeted dikes in the overlying oceanic crust, indicating that they must have formed in the ridge-related stress field. Red rocks are dunites (>90% olivine, with accessory chromian spinel) which are deformed along with the peridotite, but locally cut pyroxene rich banding. Mineral compositions in dunites ARE in equilibrium with the melts that formed the igneous crust. Black dikes with red rims illustrate "high temperature dikes" in which gabbro has a dunite reaction zone; these tend to be somewhat deformed, like the dunites and unlike tabular dikes. Grey banded rocks are mantle peridotites, mainly harzburgites (~ 75% olivine, 20% orthopyroxene, 5% chromian spinel) that are residues of melting and melt extraction. Banding illustrates planar foliation marked by olivine crystallographic fabrics, pyroxene-rich banding, and spinel and pyroxene lineation. The mantle foliation in Oman is mainly parallel to the paleo-seafloor and the base of the crust. The nearly horizontal orientation of the foliation is thought to be due to corner flow in the mantle beneath an oceanic spreading ridge. Dunites in the mantle section of the Oman ophiolite show a power law width/frequency distribution, with many small ones and just a few large ones, interpreted as forming a coalescing network as shown at left. Focused porous flow of melt through dunite conduits would have been sufficient to form the overlying oceanic crust, and flow in the widest dunites would have preserved melt compositions in equilibrium with the mantle at a depth of ~ 45 km below the seafloor. Many dunites in ophiolite mantle sections, including Oman, show evidence for formation by replacement of their host rocks, via reaction between pyroxene-bearing peridotite and olivine-saturated melt, for example (at constant temperature or enthalpy) 1 orthopyroxene + 1 melt1 = 0.7 olivine + 1.3 melt2. There is commonly a thick layer of dunite in the crust-mantle transition zone (MTZ), perhaps formed in situ by a combination of reaction with ascending, olivine-saturated melt and precipitation of olivine during the initial stages of cooling and crystallization. In some locations with thick dunites at the MTZ, underlying foliation in the mantle is steep, perhaps indicating a frozen "diapir" of upwelling mantle that was never transposed by plate spreading.

Section 2: Day 1

We will drive from the area near Sultan Qaboos University through the towns of Rusayl, Fanjah, Samail and almost to the regional center for the northern interior, Nizwa. This is the Wadi Samail route, the main route from the coast to the interior since pre-historic times. During the drive, we will pass just east of the huge eastern escarpment of the Jebel Akdar, an anticlinorium composed largely of autochthonous Mesozoic and Paleozoic shelf carbonates. We will be driving through the edge of the

Samail massif of the Cretaceous Samail ophiolite (zircon ages in gabbros and 40Ar39Ar ages from amphibolites in the sole thrust ~ 96 Ma). From Fanjah past Samail we will be mainly in low lying extensively altered peridotites. The contact between the peridotites and the limestones is dotted with small outcrops of the parautochthonous Hawasina group sediments: calc-arenites, limestones, cherts, sandstones, and some bright red outcrops of fully carbonated peridotite (listwanite). The contacts between the different rock types are, in essence, reactivated thrust faults, which carried the Oman ophiolite, and the rumpled rug of the underlying Hawasina sediments, from east to west onto the Arabian continental margin from about 90 to 70 Ma. now with a normal sense of shear associated with uplift of the Jebel Akdar.

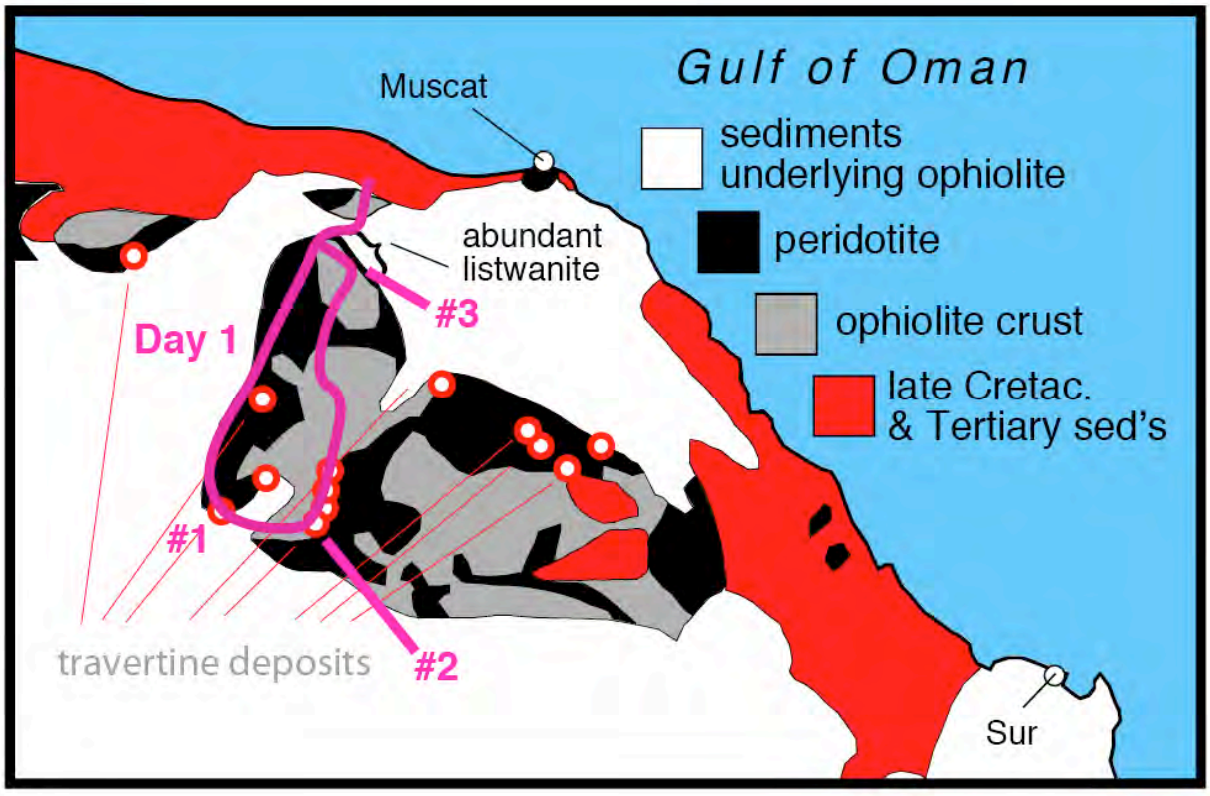


Figure 5: Schematic geologic map showing route and main field trip stops on Day 1.

Cooling ages in the Jebel Akdar are early Eocene (Poupeau et al., Geology 1998). To me, the topographic relief on the escarpment looks much younger. However, there are few if any earthquakes in this part of Oman. The new highway is not a good place to stop, but we will make a photo stop at some point.

As we come out onto the alluvial plain flanking the Oman mountains, we will turn southeast and drive along the low relief, low angle exposure of the basal thrust of the ophiolite, over the Hawasina group. We will turn north and drive into the mantle peridotite exposures for stop 1.

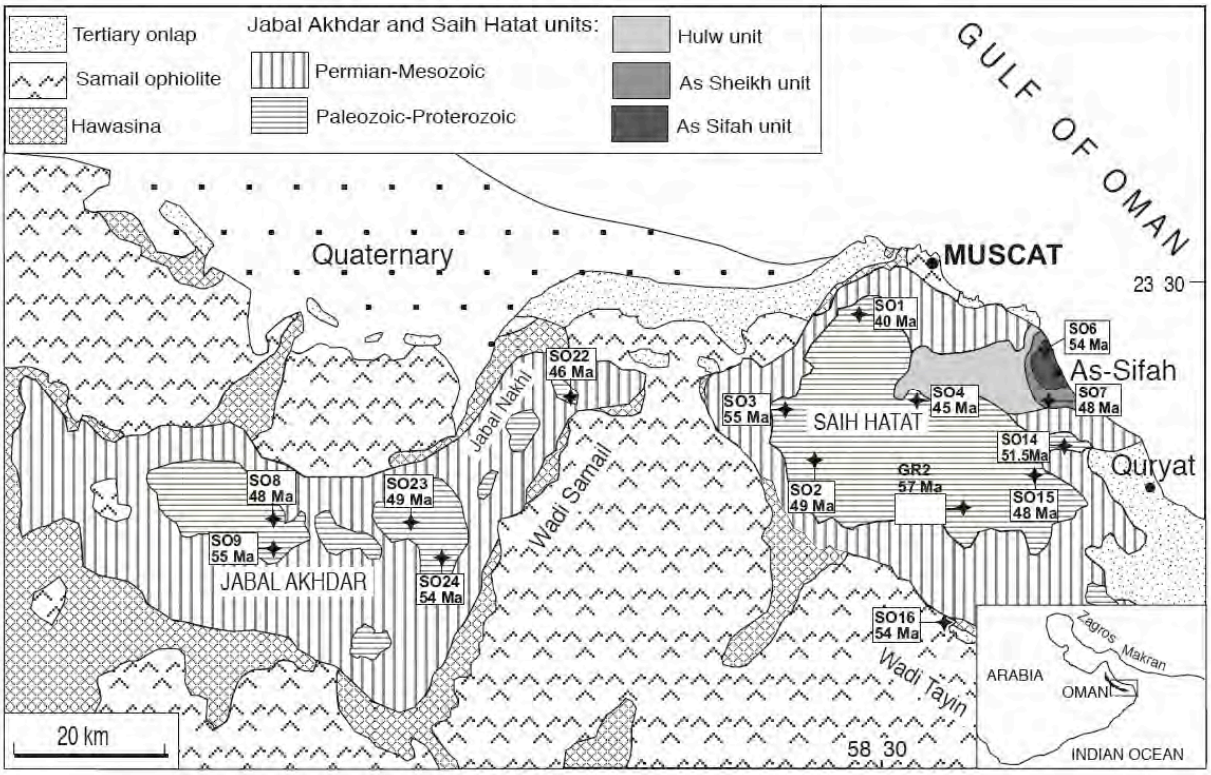


Figure 6: Geologic map of this area with apatite fission track ages, from Poupeau et al. Geology 1998.

*****

Stop 1: "Duck" travertine and associated veins.

We will drive close to (onto?) travertine terraces partially covered by alluvium. It is interesting to speculate on the subsurface extent of the alluvium. There are several active, alkaline springs here, where the following field measurements were made during sampling in 2009.

location	E	N	pH	T, °C	Eh, mV
Lungs	585584	2522988	11.76	26.3	-247
Jimi	585589	2523004	11.77	27.1	-220
Africa	585582	2523248	11.51	24.5	-187
downstream from Jimi	585880	2523239	11.90	20.7	50

Salinities in the alkaline waters are high, compared to similar alkaline springs in California, and some white crusts in the soil around the Duck travertine are salt rather than carbonate. ^{14}C "ages" of eight samples from these travertines range from ~ 1600 to 37,000 years; one of the underlying veins has a ^{14}C "age" of ~ 5700 years.

In the area just "upstream" of the travertine, we made extensive measurements of the orientiation of carbonate veins in peridotite, to quantify the observation that many or most veins for three, mutually orthogonal sets. The data and photos in Figure 7 come from this area. The data in Figure 7 are for three dimensional intersection angles.

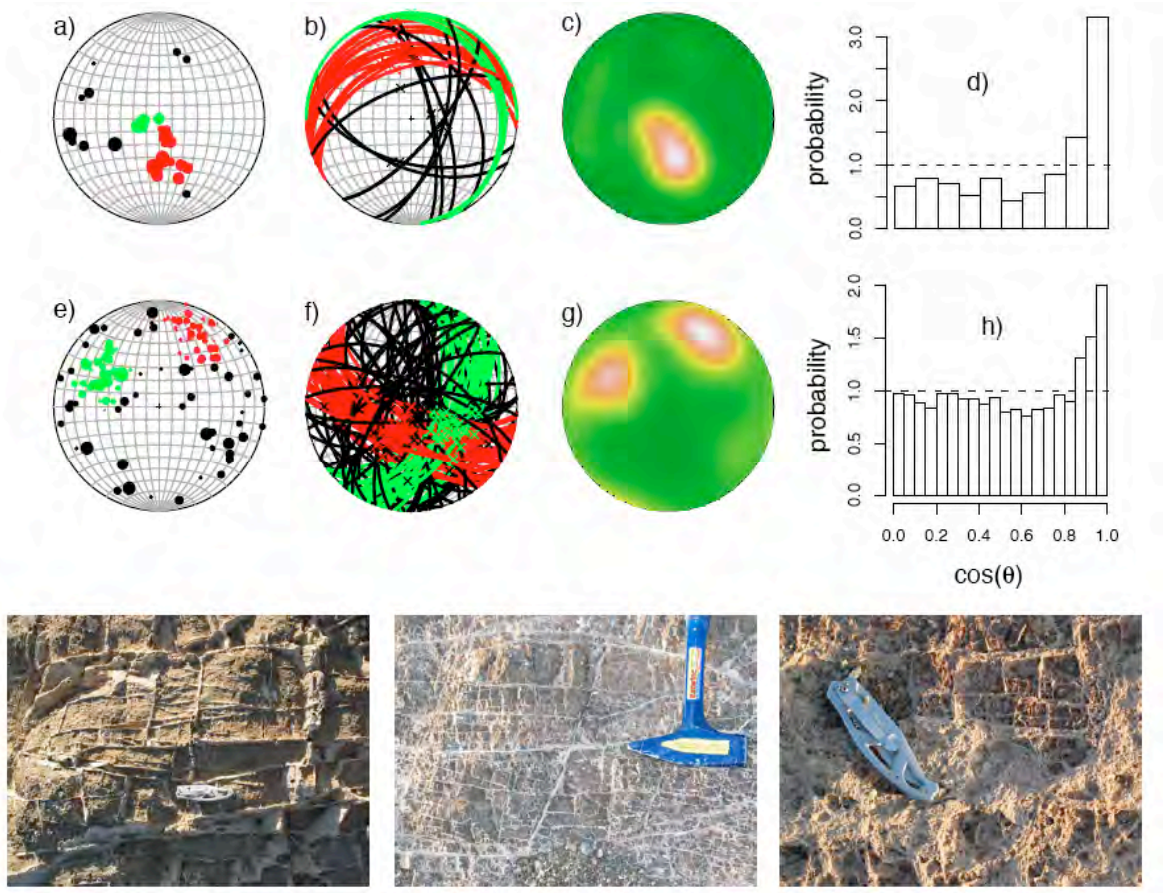


Figure 7: This is Figure 9 in Kelemen et al., Annual Reviews in Earth & Planetary Sciences (AREPS) 2011, in press. Stereo-plots and histograms: Orientations of tabular carbonate veins in peridotite at this locality, approximately 21.86°N, 57.51°E. Panels (a--d) are for measurements of vein orientations measured on nearly vertical outcrop surfaces, while panels (e--h) are for vein orientations measured on a nearly horizontal outcrop surface nearby. Red symbols and lines are for all planes having poles within 25° of the density maximum. Green symbols are for all planes with poles within 25° of the density maximum for all data excluding the measurements with red symbols. Panels a & e, poles to planes, projected on a lower hemisphere stereonet. Panels b & f, planes projected on a lower hemisphere stereonet. Panels c & g, contoured density of poles using a von Mises kernel with kappa = 10, projected on a lower hemisphere stereonet. Panels d & h, histograms of intersection angles; 90° intersections are the best represented group in both data sets. There are few intersections of steeply dipping veins with the steep outcrop surfaces of (a-d), and few intersections of nearly horizontal veins with the subhorizontal surface of (e-h). If the two data sets were equal in size, one could combine them to produce a statistical representation of the three mutually orthogonal vein sets that constitute a majority of the carbonate veins in this area. Photos: Outcrop scale, hierarchical networks of carbonate veins in peridotite at this locality. Left to right, progressively smaller and more closely spaced carbonate veins (fov 0.5 m, 0.4 m, 0.2 m). In bottom half of lower image, peridotite is 100% replaced by carbonate. Thin sections from the upper two outcrops show sharp sided carbonate veins in a partially serpentinized peridotite host containing little or no carbonate, and 20 to 40% olivine.

In case you are wondering, the two dimensional intersection angles of veins visible on a typical outcrop surface are “apparent angles” for the intersection in three dimensions. However, where 90° intersections are observed in 2D, this is also the true 3D intersection angle, and in addition this observation indicates that the outcrop surface is perpendicular to both orthogonal vein sets. To verify this for yourself, imagine an oblique, planar section through a 3D, 90° vein intersection. Apparent vein intersection angles will be less than or greater than 90°, and will be complementary (e.g, 60° and 120°). As the planar section is rotated to be perpendicular to the veins, the apparent angles will approach 90°.

Initially, we interpreted these data to be supportive of the hypothesis that the veins formed in a nearly isotropic stress field (perhaps correct) and therefore that they might have formed in response to

volume expansion due to serpentinization and carbonation. Unfortunately for us, it is common to observe three mutually joint intersections, for example in quarry stone, and so our observations are not uniquely diagnostic of cracking driven by volume expansion.

Note that in these photos as oriented in Figure 7, subhorizontal veins are larger than subvertical veins. It is apparent that most subhorizontal fractures hosting veins formed before subvertical fractures hosting veins, since the steep fractures commonly terminate where they intersect the nearly horizontal fractures. This is qualitatively consistent with the hypothesis of Fletcher et al. (EPSL 2006), followed by Royne et al. (EPSL 2008) and Rudge et al. (EPSL 2010), in which a diffusive reaction zone around an initial fracture undergoes hydration (or carbonation) with increasing solid volume, creating large stresses at the edge of the reaction zone where the chemical potential driving the reaction goes through zero. This stress causes a fracture between the expanded boundary layer and the unaltered rock. The detached, expanded layer buckles, causing cross-fractures which intersect the larger, initial fracture at ~ 90°. The process then repeats.

*****

Driving from Stop 1 to Stop 2, we will continue close to the low angle, basal thrust of the ophiolite over the Hawasina sediments. A relatively small anticline of the Hawasina will be visible in the center of the broad Wadi Mahram, flanked to the west and east by peridotite.

*****

Stop 2: Falaij travertine

The Falaij outcrop is quite similar to that at Duck, but the travertine is much better developed, and veins in the underlying peridotite are less well exposed. We will visit relatively spectacular parts of the Falaij travertine. While there, we will discuss stable isotope and ^{14}C “age” observations from this and other travertine and vein outcrops.

Here are some 2009 field data for active alkaline springs at Falaij:

location	E	N	pH	T, °C	Eh, mV
Falawj	608145	2525713	11.52	29.1	-810
Angry Worm	608140	2525730		24.1	
Cistern of Joy			11.68	25.1	
Cistern of Joy			11.8	20.7	
Cistern of Joy			11.82	18	

^{14}C “ages” of eight samples from the Falaij travertines range from ~ 0 to 27,000 years. More generally, our ^{14}C “ages” for all but two of 44 peridotite hosted travertine and carbonate vein samples from the low T system are < 50,000 years (Figure 8), suggesting that low T peridotite alteration is close to a steady state in which carbonates form in a shallow weathering horizon at about the same rate that this horizon is removed by erosion.

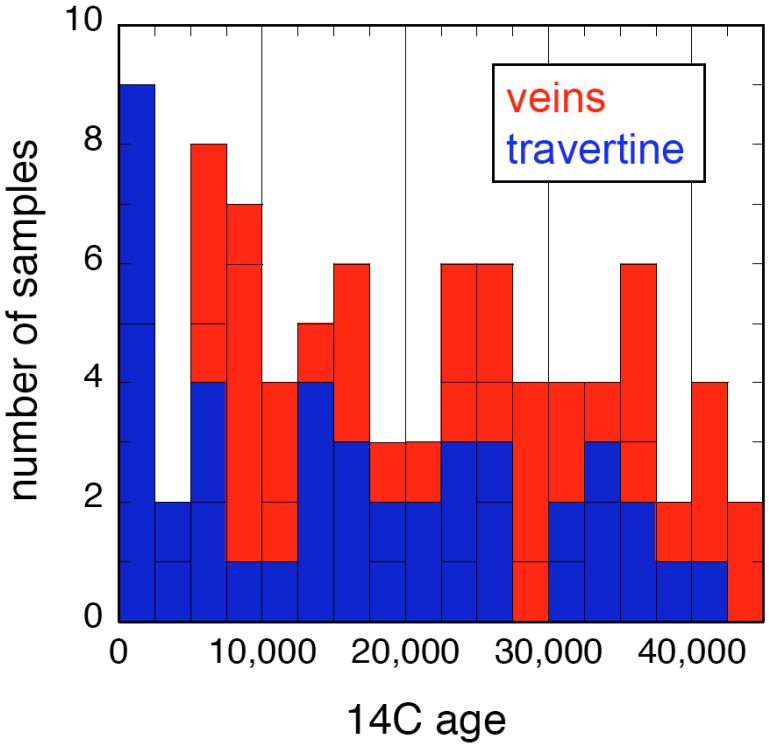


Figure 8: Updated ^{14}C age histogram including the data reported by Kelemen and Matter PNAS 2008, and additional data for analogous, additional samples with sample preparation and ^{14}C analyses performed in the same manner.

Based on the ^{14}C data, and on geochemical considerations outlined in Section 1, we infer that travertines and subsurface carbonate veins form simultaneously. Mass balance ([decrease in C from Mg-HCO3 to Ca-OH waters]/[decrease in Ca during travertine precipitation]) suggests that 5 to 15 times more carbonate precipitates as veins in the subsurface, compared to the mass of travertine forming on the surface.

Mineral-fluid and clumped stable isotope thermometry yield low temperatures for vein precipitation, consistent with this hypothesis. We collected preliminary, whole rock data on oxygen and carbon isotopes in peridotite-hosted travertine and vein samples from Oman (Figure 9). These show two important features, (1) apparent equilibrium of older travertines with ground water and spring water, recording near-surface temperatures, and (2) kinetic fractionation of both carbon and oxygen isotopes in travertine samples less than 1000 years old. Some of our samples are sufficiently pure calcite (travertine) or magnesite (veins) that the oxygen isotope ratio for the whole rock is a close approximation for the ratio in the minerals. For calcite-rich travertine with ^{14}C ages > 1000 years and carbonate veins composed mainly of calcite, typical $\delta^{18}O$ is 23 to 26 ‰ relative to SMOW. If calcite formed in equilibrium with typical Oman ground waters and alkaline spring waters having $\delta^{18}O$ from -2 to 1 ‰, they record ^{16}O – ^{18}O exchange at ~ 23 to 60°C (Chacko and Deines GCA 2008; O'Neil et al. J Chem Phys1969), approximately equivalent to the seasonal range of air temperature in Oman.

With the exception of two veins (from near the oasis of Tuf) and all listwanite samples, our samples of carbonate veins in peridotite show systematically heavier $\delta^{18}O$ and $\delta^{13}C$ compared to travertine. We tentatively attribute this to variable proportions of carbonate and silicate minerals, all close to equilibrium with relatively similar fluid compositions. Two nearly pure magnesite veins have $\delta^{18}O$ of 35 to 36 ‰, yielding magnesite – water oxygen exchange temperatures of ~ 33 to 49°C (Chacko and Deines, 2008). Less precise data for a third magnesite-rich vein yield $\delta^{18}O$ of 30 ‰, corresponding to 58 to 74°C.

The temperatures calculated here, for stable isotope exchange between peridotite-hosted carbonates and ground water in Oman, are consistent with observed temperatures of alkaline spring waters, and

temperatures of hydrogen isotope fractionation between gas and alkaline spring waters in Oman (Neal and Stanger EPSL1983). Similarly, in the California Coast Ranges calcite and dolomite-bearing travertines with $\delta^{18}O$ of 20 to 25 ‰ and magnesite veins with $\delta^{18}O$ of 27.6 to 28.2 ‰ (Barnes et al. Econ Geol 1973; Blank et al. Planet Space Sci 2009) record equilibrium with local waters at 15 to 40°C. All of these data suggest that magnesite veins in partially carbonated peridotites and alkaline spring waters are genetically related, and form via fluid-rock reaction at near-surface temperature in a shallow weathering horizon, as hypothesized by Kelemen & Matter PNAS 2008. Peridotite-hosted carbonates from seafloor samples and the Alps have very restricted δ13C from ~ -4 to 3, and show a range of $\delta^{18}O$ corresponding to expected depositional and metamorphic temperatures, from near 0°C for samples formed near the seafloor to more than 100°C in Alpine metamorphic rocks.

The kinetic stable isotope fractionation observed in Oman travertine samples is also of interest. Figure 9 shows that peridotite-hosted travertines in Oman and from other continental settings (northern California, northern Canada) show a strong correlation between $\delta^{18}O$ and $\delta^{13}C$. This correlation is absent in peridotite-hosted carbonate veins in Oman, and in peridotite-related carbonates from the Alps and from the seafloor. The correlation in travertines has been explained as the result of stable isotope fractionation during diffusive CO_2 uptake from the atmosphere, and/or to biologically mediated precipitation of carbonate minerals. Clark et al. (GCA 1992) presented a persuasive combination of experimental data and theoretical reasoning to support the hypothesis that carbon and oxygen isotope fractionation occur via abiotic, kinetic processes in a thin film of aqueous fluid overlying travertine depositing from alkaline fluids (pH 11-12) characteristic of alkaline springs forming peridotite-hosted travertines. As for kinetic stable isotope fractionation during biological precipitaton of carbonate (McConnaughey GCA 1989a,b), Clark et al. proposed that carbon isotope fractionation occurs during preferential uptake of light, ^{12}C in hydroxylation of $CO_2 + OH^-$ to form HCO_3^-, an essential step in forming solid carbonate. Equilibrium partitioning of oxygen isotopes causes OH^- to be ~ 40 ‰ lighter than H_2O in aqueous fluid (Green and Taube J Phys Chem 1963). McConnaughy showed that such effects are maximized in high pH solutions.

An additional point to make about peridotite-hosted carbonates in Oman is that their $^{87}Sr/^{86}Sr$ ratios apparently record a mixture of Sr from mantle and present-day seawater Sr (Figure 10). If C isotopes and Sr isotopes are derived from the same source, one can rule out input of C and Sr from underlying metasediments. Limestones with $^{87}Sr/^{86}Sr$ similar to peridotite-hosted carbonates have higher $\delta^{13}C$, while clastic metasediments with $\delta^{13}C$ similar to peridotite-hosted carbonates have higher $^{87}Sr/^{86}Sr$. Also, the Sr isotope ratios in the travertines and veins, and in peridotite leachates, are higher than in Cretaceous seawater, indicating that Sr addition, and perhaps some serpentinization and carbonation, are post-Cretaceous.

*****

Stop 2A: Tunnel to base of alluvium overlying serpentinized peridotite near Falaij.

Debris from tunneling shows abundant carbonate cement in alluvial gravels composed mainly of angular peridotite fragments. A sample of the carbonate from the tunnel debris was too old to date by ^{14}C geochronology (>45,000 years).

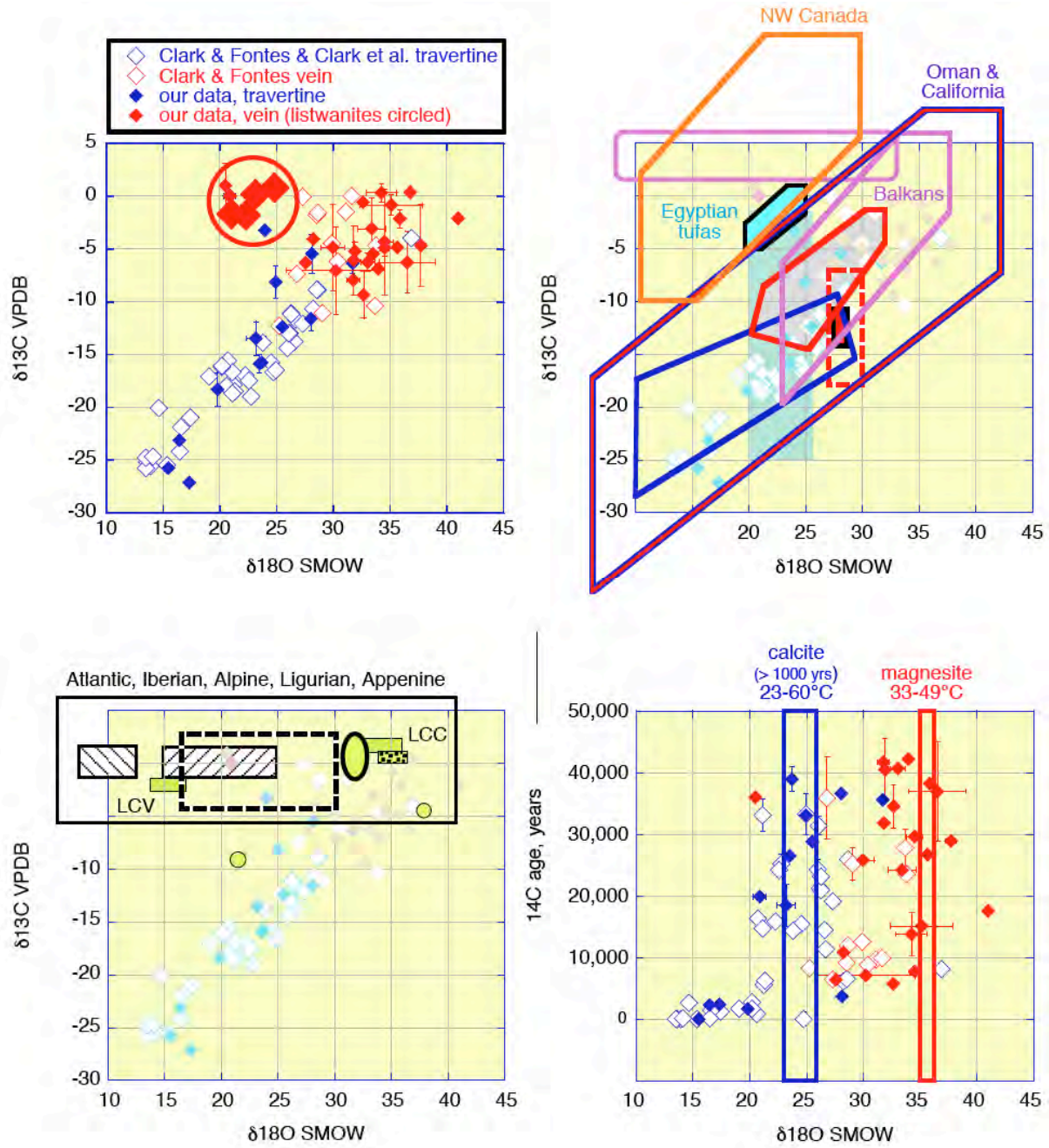


Figure 9: Whole rock stable isotope data on peridotite-hosted carbonate veins, and surficial travertine deposits associated with alkaline springs in peridotite catchments, in the ophiolite massifs of northern Oman. ^{14}C ages are in radiocarbon years before 1950. For our data, error bars for ^{14}C ages are shown for those samples with replicate analyses. For data of Clark and Fontes, Quat Res1990, analytical precision and data on replicate analyses are not given for stable isotope data, but precision is listed (and shown) for ^{14}C ages. In addition to data from Oman, outlined fields are for data from peridotite-hosted carbonate deposits in northern California (red and blue), Egypt (light blue), Balkans (purple), NW Canada (orange), Mid-Atlantic Ridge (light green), and Europe (black). This is Figure 4 in Kelemen et al. AREPS 2011.

Blue outline: "scums," "sludges" and travertines associated with Ca-OH type alkaline springs (O'Neil and Barnes, 1971); red with gray background: Ca-Mg carbonate veins (O'Neil and Barnes, 1971); dashed red: hydromagnesite veins (O'Neil and Barnes, 1971); filled red rectangle: magnesite veins (Barnes et al. 1973); light blue band, $\delta^{18}O$ only, Del Puerto ophiolite travertine (Blank et al. 2009b). Light blue polygon with black outline (Smith et al. 2004). Purple polygons (Fallick et al. 1991). Orange polygon (Wilson et al. 2009). Light green rectangles show range of data for carbonate chimneys (LCC) and calcite veins in surrounding host rocks (LCV) from the Lost City hydrothermal area along the Mid-Atlantic Ridge (Früh-Green et al. 2003). Light green circles and oval: calcite in veins and "ophicarbonates" drilled from the Iberian Margin continent-ocean transition; compositions of 36 out of 38 samples lie in oval with bold outline (Agrinier et al. 1996; Agrinier et al. 1988; Evans and Baltuck, 1988; Milliken and Morgan, 1996). Light green dotted rectangle: aragonite in serpentinized peridotites dredged from the Mid-Atlantic Ridge (Bonatti et al. 1980). Black dashed rectangle: Calcite in Ligurian and Appenine ophicalcite deposits, ranging from lower (heavy $\delta^{18}O$) to higher metamorphic grade (light $\delta^{18}O$, Barbieri et al. 1979). Diagonally ruled, black rectangles: right, calcite in oceanic ophicarbonates affected by later Alpine regional metamorphism (Früh-Green et al. 1990); left, calcite in contact metamorphosed ophicarbonates in the Bergell aureole, Val Malenco (Abart and Pozzorini, 2000; Pozzorini and Früh-Green, 1996).

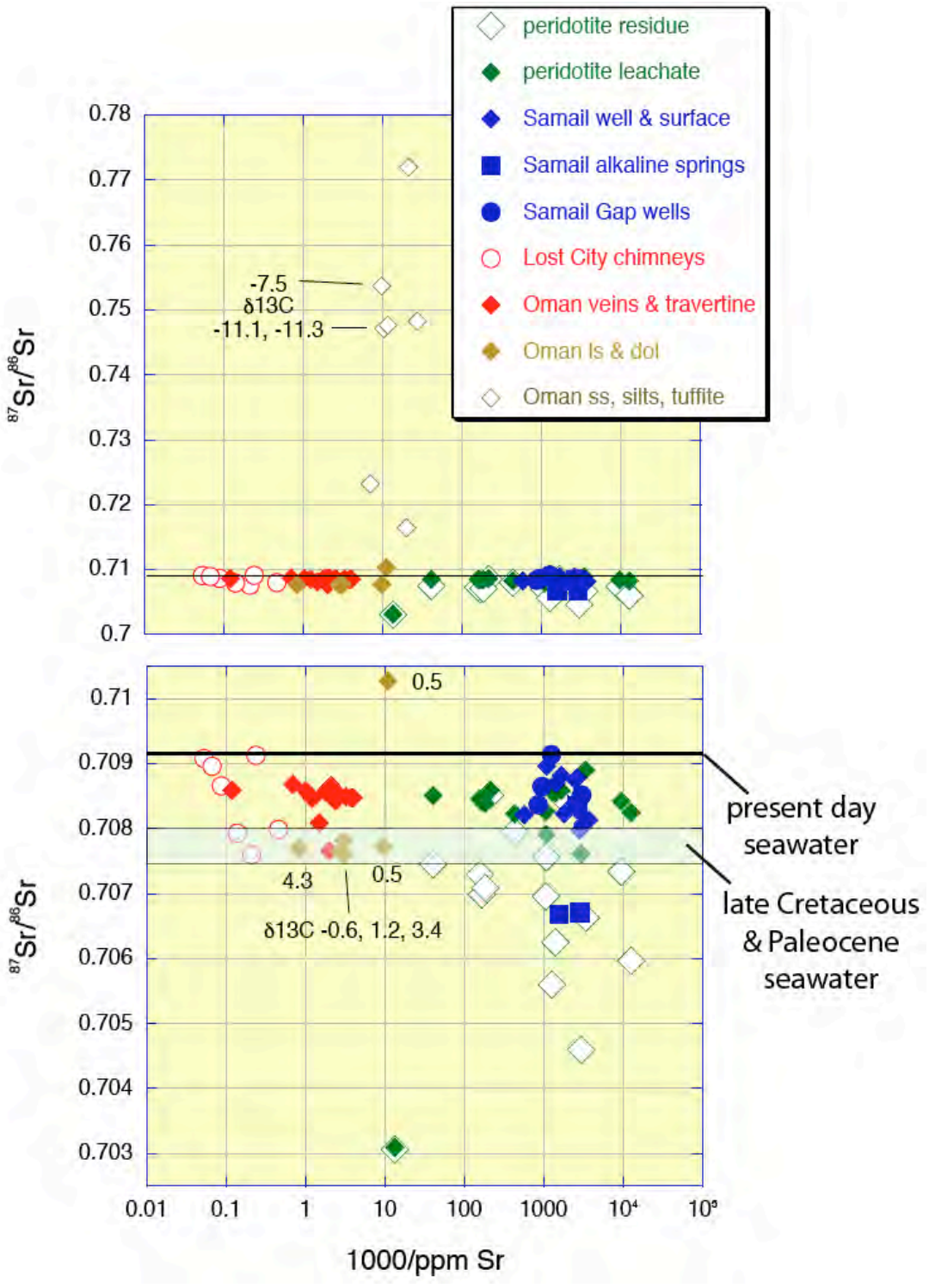


Figure 10: Sr isotope compositions for our samples, compared to samples of partially hydrated peridotites from the same massifs as our samples (Gerbert-Gaillard, Montpellier PhD thesis 2002, supervised by Dr. Marguerite Godard), sediments beneath the Oman peridotite (Weyhenmeyer, Bern PhD thesis 2000, supervised by Prof. Albert Matter), groundwater and alkaline spring waters from the Oman peridotite (Weyhenmeyer, 2000), and carbonate deposits from the Lost City hydrothermal deposit on the Mid-Atlantic Ridge (Früh-Green et al. Science 2003). This is Figure S3 in Kelemen et al. AREPS 2011.

*****

From Stop 2 to Stop 3 will drive north up Wadi Mahram to the Ibra-Samail highway, mainly in upper mantle and lower crustal outcrops of the ophiolite. On the highway, we will head north, back toward Muscat. The east facing escarpment of Jebel Akdar will come back into view. Just before the intersection with the main road linking Nizwa and Muscat, we will turn NE toward the large ridge of listwanite flanking the huge Wadi Mansah on the north.

*****

Stop 3: MOD listwanites

The ophiolite contains both listwanite, and "normal," partially serpentinized peridotite hosting carbonate veins. Listwanites are fully carbonated peridotites, in which all Mg-silicates have been converted to Mg-carbonates + quartz (Figure 12) via reactions such as 1a to 1g in Section 1. Most of our listwanite samples also contain relict chromian spinel. Some workers require that the term listwanite be restricted to rocks with magnesite + quartz + chromian white mica (fuchsite, aka mariposite), but we do not follow this convention. There have been several studies of listwanites in Oman (Nasir et al. Geol Rundsch 2007; Stanger Lithos 1985; Wilde et al. J Virtual Expl 2002). All known listwanite outcrops in the Oman ophiolite are within 500 meters of the basal thrust where peridotite was carried over Hawasina group metasediments. We have done most of our work on listwanites enclosed entirely within altered peridotite, and with relict chromian spinel indicating that they replaced peridotite, in order to avoid confusion about the chemical composition of the protolith prior to carbonation.

As described above, most of the peridotite-hosted carbonate veins in partially altered peridotite form in currently active "low T" systems at 30 to perhaps 60°C involving meteoric water. In contrast, listwanites formed in fossil "high T" systems that probably reached ~ 200°C, similar to four different localities in Canada where listwanites record temperatures between 200 and 250°C (Hansen et al. Can Min 2005; Madu et al. Econ Geol 1990; Schandl and Naldrett Can Min 1992; Schandl and Wicks Econ Geol 1991). Figure 9 shows that our listwanite samples analyzed so far have lower $\delta^{18}O$ than carbonate veins in partially serpentinized peridotites, supporting the hypothesis that they formed at higher temperature than the active, low T system. Without knowledge of fluid compositions during listwanite formation, this is difficult to quantify. However, preliminary clumped isotope thermometry (Figure 13, from Streit et al. in prep.), for which fluid compositions are not needed, also suggests that the listwanites formed at a peak temperature ~ 200°C, similar to listwanites elsewhere.

We infer that the extensive listwanites in the Oman peridotites -- billions of tons of fully carbonated peridotite -- are late Cretaceous or Paleocene, based on one locality in which they replace mantle peridotite, which was thrust onto the Arabian continent beginning at ~96 Ma (e.g., Hacker Science 1994), and are unconformably overlain by late Paleocene to Eocene conglomerate and limestone (23.44°N, 56.19°E).. If so, they probably formed from fluids rich in CO_2, because magnesite + quartz are not stable, and break down to form talc + CO_2, in the presence of H_2O-rich fluids at 200°C (Figure 14). All known listwanites in Oman are found within 500 m of the basal thrust where peridotites overlie CO_2-bearing metasediments. It is likely that CO_2-rich fluids, formed by metamorphic dehydration of the underlying sediments as they were overthrust by hot peridotite, rose into the peridotite to form the listwanites metamorphic dehydration of the underlying sediments as they were overthrust by hot peridotite, rose into the peridotite to form the listwanites.

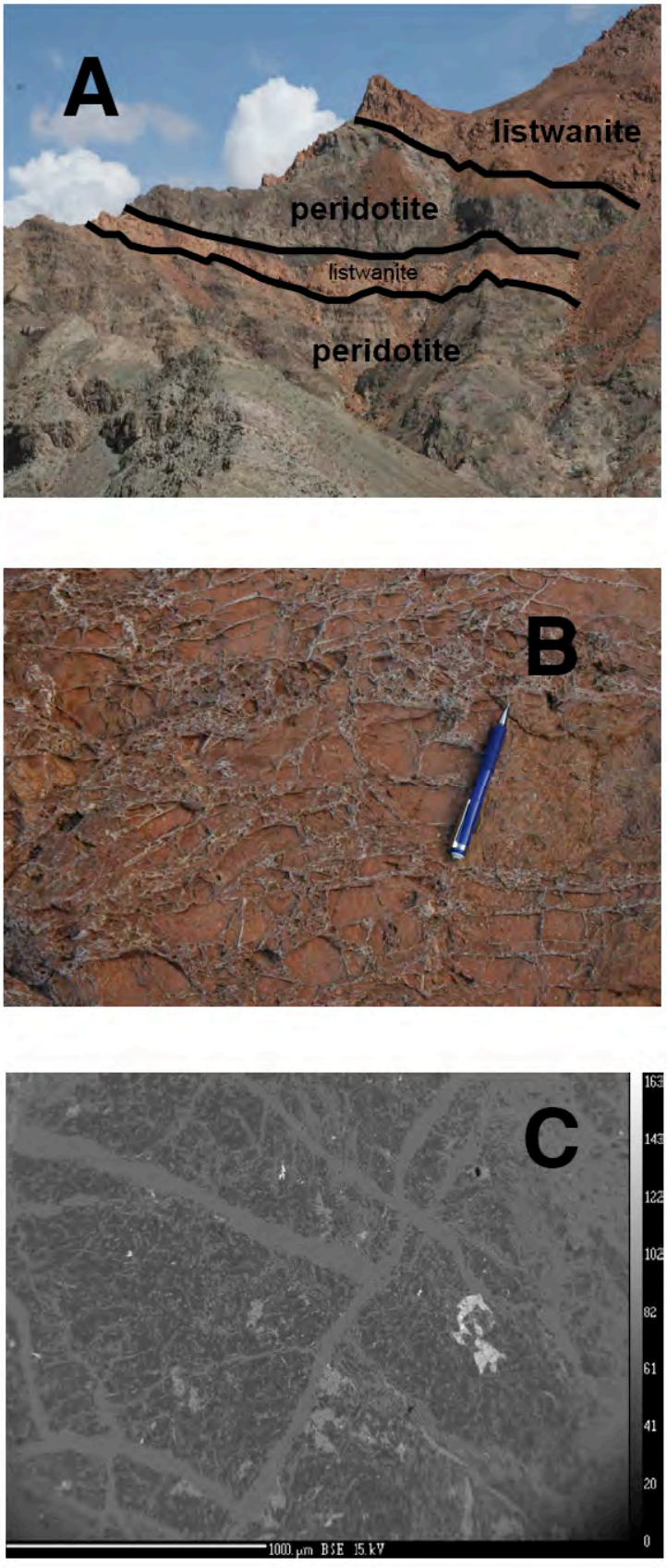


Figure 12: Outcrop and thin section scale photographs of listwanites replacing peridotite in the ophiolite massifs of northern Oman. A. Gently east dipping listwanite band about 10 m true thickness, approximately parallel to banding in partially serpentinized peridotite, and overlying, thicker band of listwanite along ridge in Oman at Stop 3, approximately 23.37°N, 58.19°E. This area is structurally just a few hundred meters from the basal thrust, juxtaposing peridotite with ophiolitic mélange and underlying sedimentary conglomerates in this region. (Kelemen photo, field of view (fov) 500 m). B. Typical quartz vein texture in listwanite talus block, same location. (Kelemen photo, fov 0.5 m). C. Backscattered electron image of listwanite from same location, with dark gray = magnesite, light gray = quartz, white = relict chromian spinel. (Streit photo, fov 0.0025 m). This is Figure 8 in Kelemen et al. AREPS 2011,.

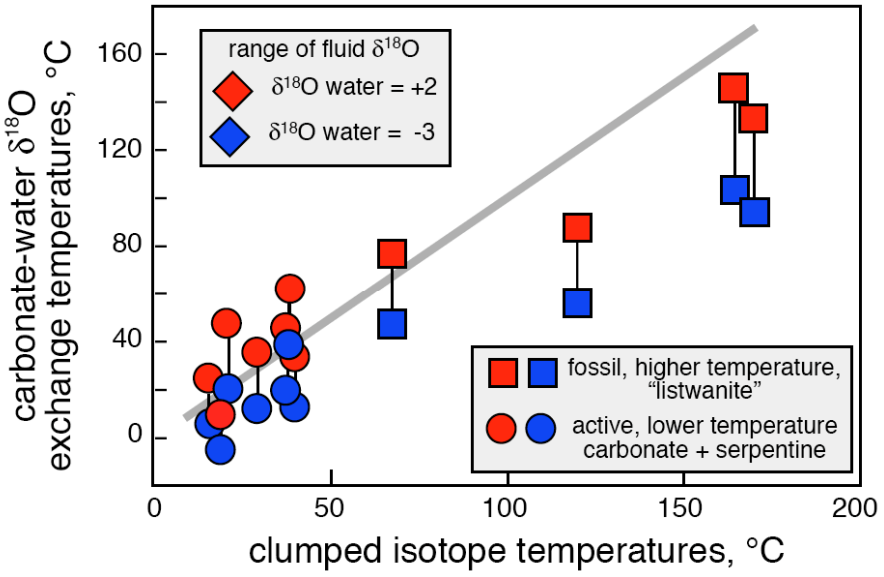


Figure 13: Preliminary clumped isotope thermometry from Streit et al., in prep., based on data collected in John Eiler's lab at Caltech, compared to conventional stable isotope mineral-fluid thermometry. Carbonate veins in altered peridotite (circles), from the currently active low T system, record mineral-fluid and clumped isotope temperatrures less than 75°C. Listwanite samples (squares) record clumped isotope temperatures as high as 170°C, and we infer that peak temperatures were even higher. Note that we do not know the fluid composition during formation of the late Cretaceous listwanites, so that the vertical axis not very meaningful for the listwanite data.

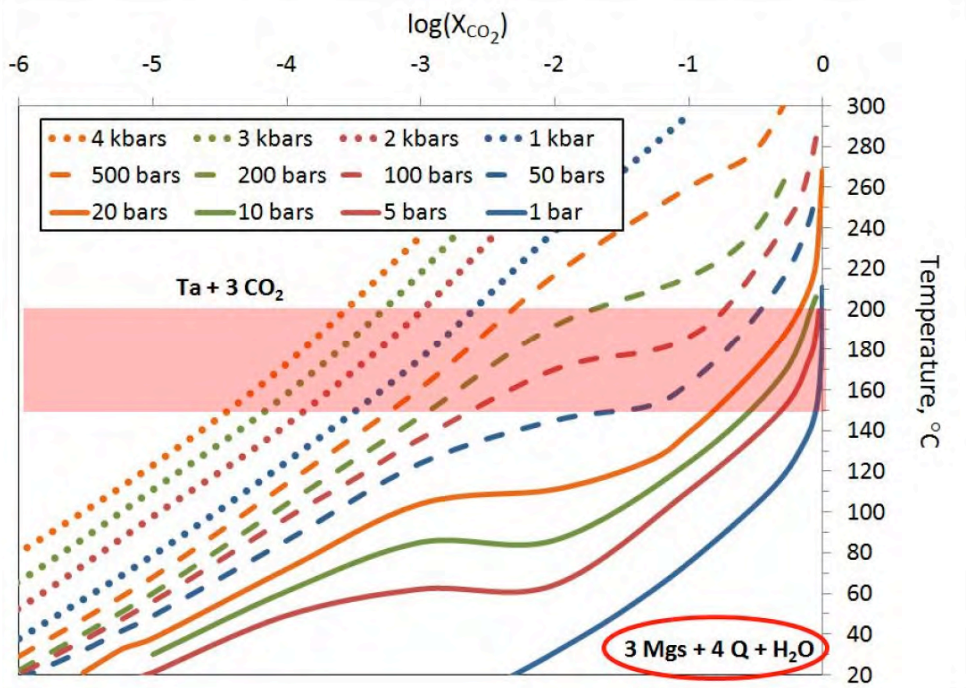


Figure 14. Mole fraction CO2 in H2O-CO2 fluid ($X(CO_2)$) versus temperature, for the reaction talc + CO_2 = magnesite + quartz + H2O, calculated for Mg-endmembers using Thermocalc (Holland and Powell, 1998). At a given pressure, the assemblage magnesite + quartz at high temperature is only stable in the presence of CO_2-rich fluids. The shaded band shows the likely temperature of formation of Oman listwanites. The pressure of listwanite formation is not well constrained, but was probably less than 4 kb. This is Figure 2 in Kelemen et al. AREPS 2011.

Section 3: Day 2

We will, again, drive through Fanjah, and then take the highway to Ibra. From Ibra, we will travel north through the village of Batin, passing through buttes of peridotite and Hawasina group metasediments rising from the alluvial gravel plain. As we enter the mountains, we will be in gabbroic lower crustal rocks in the Wadi Tayin massif of the Samail ophiolite, and then in underlying mantle peridotite near a pass. If time permits, we will stop to look at the view from a small hill flanking the pass. We will then descend into a huge dunite body that forms an important part of the Wadi Tayin mantle section.

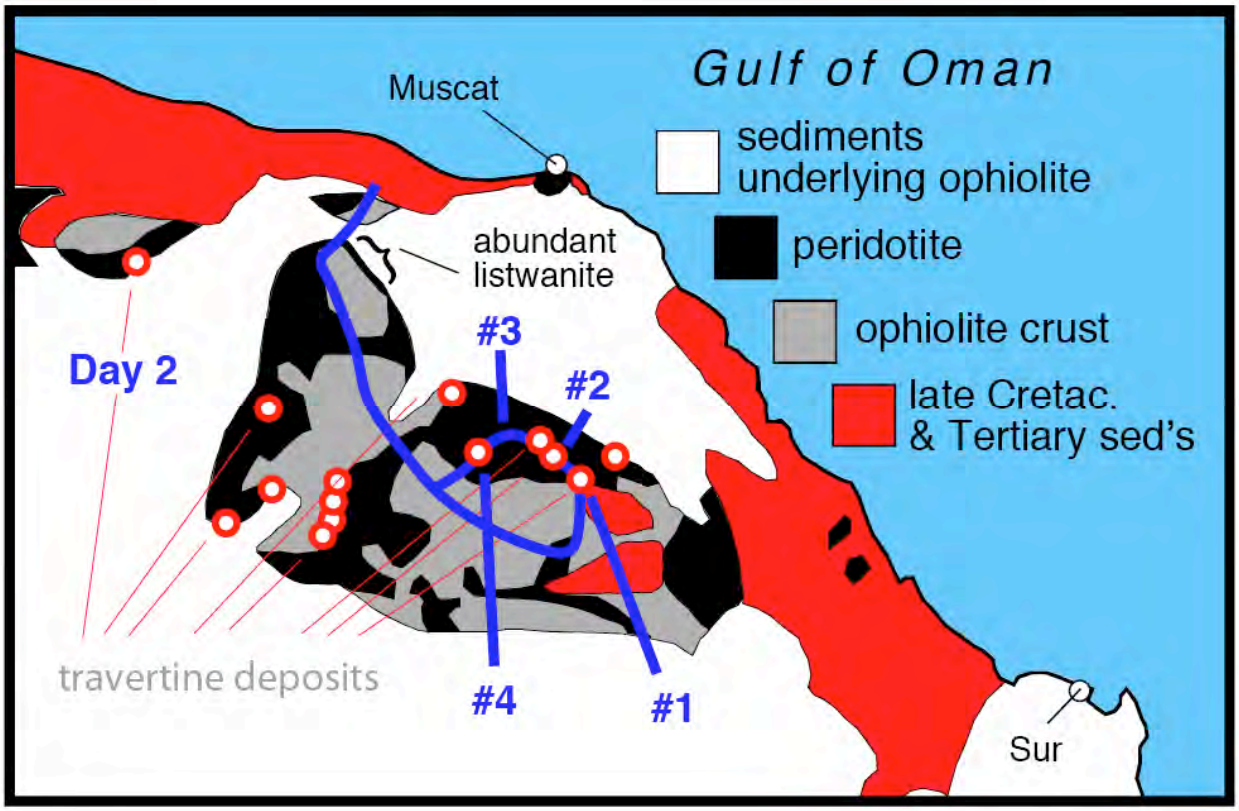


Figure 15: Schematic geologic map showing route and main field trip stops on Day 1.

*****

Stop 1: Massive magnesite veins in the Batin dunite

We will walk to massive magnesite veins in brecciated, altered peridotite. ^{14}C ages from this locality range from ~ 15,000 to 29,000 years. Some parts of these veins are nearly pure magnesite, and yield mineral-fluid $\delta^{18}O$ partitioning temperatures of 33 to 49°C (depending on the assumed fluid). The massive vein system is subhorizontal. The hanging wall peridotites are brecciated, and fragments of peridotite are isolated within carbonate in3D (Figure 16).

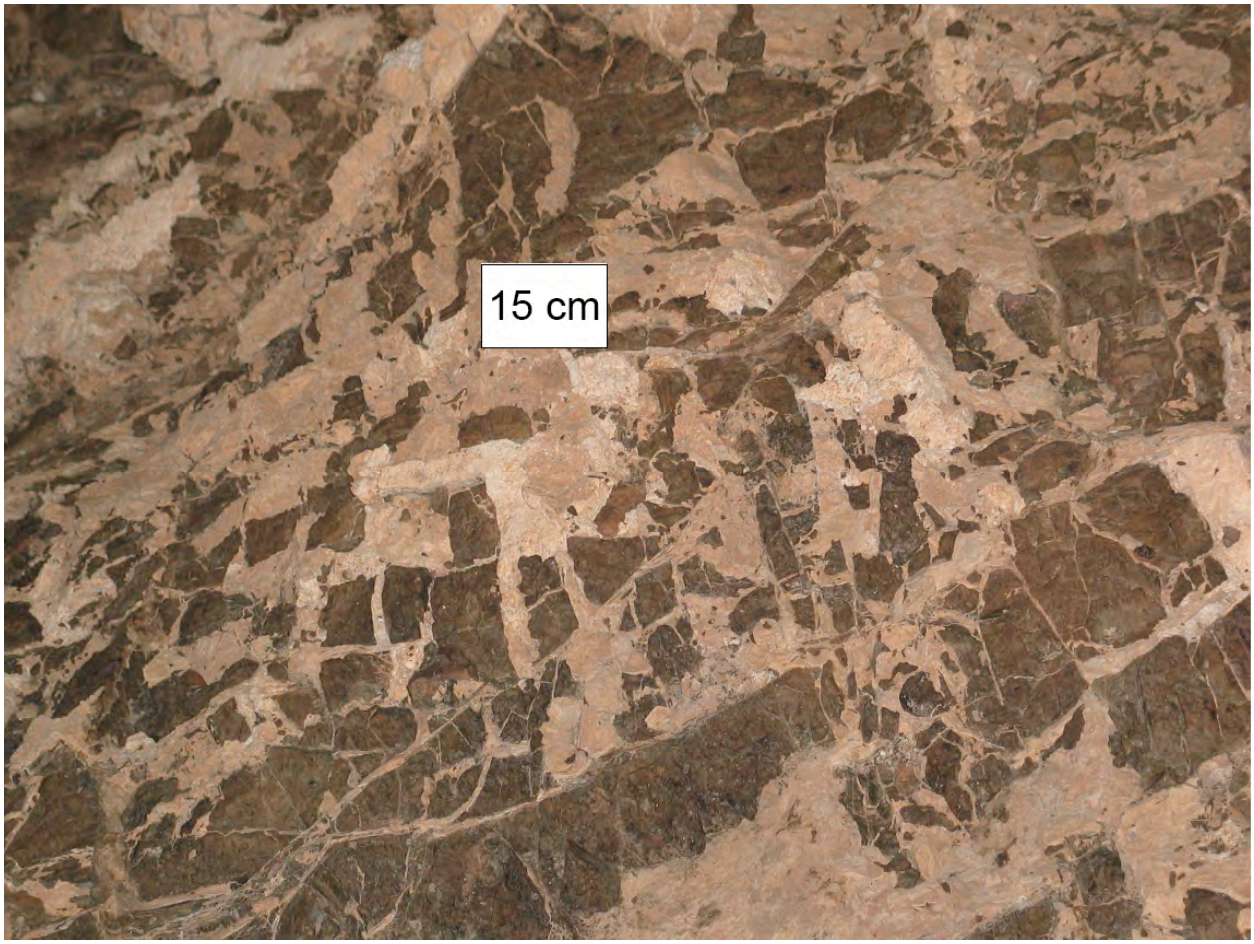


Figure 16: Carbonate veined peridotite within the Batin dunite.

This indicates that the volumetric expansion that separated the peridotite fragments was coeval with carbonate vein precipitation. In turn, this supports, though it does not prove, the hypothesis (MacDonald & Fyfe CMP 1985; Jamtveit et al., 2008; Royne et al. 2008; Rudge et al. EPSL 2010) that solid volume expansion associated with peridotite hydration (serpentinization) and carbonation causes compressive stresses that, in turn, fracture the host rock, maintaining or enhancing permeability and reactive surface area. Because this hypothesis is often questioned, here we include some illustrations (Figure 17, Figure 18) from Jamtveit et al. EPSL 2008, Royne et al. EPSL 2008 and Evans Int Geol Review 2004 in which volume expansion due to serpentinization clearly caused fracture of surrounding plagioclase crystals.

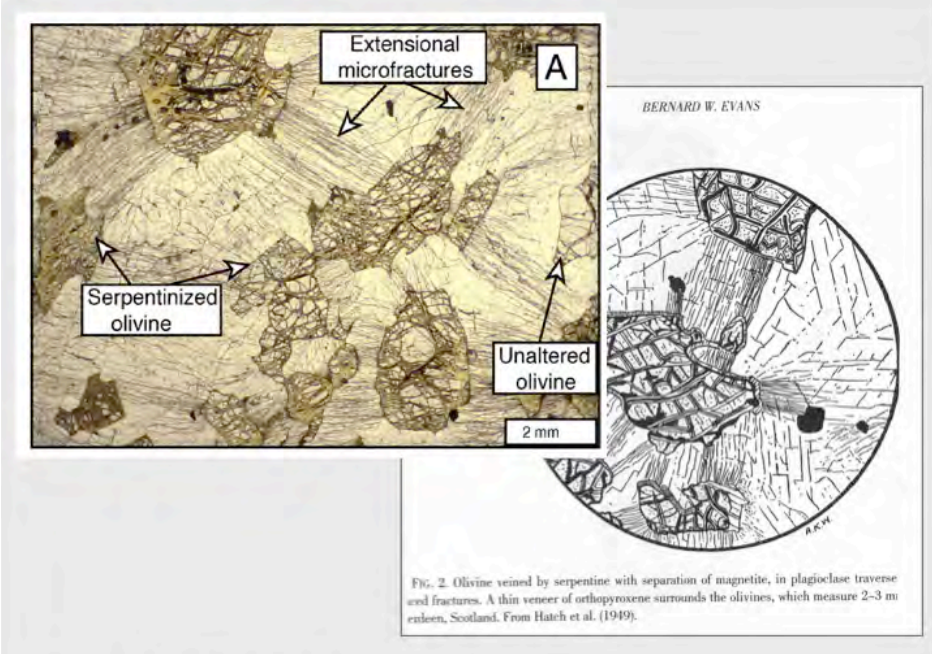


Figure 17: Illustrations of gabbroic rocks composed of igneous olivine + plagioclase showing fractures in plagioclase resulting from volume expansion due to partial serpentinization of olivine. (Jamtveit et al. EPSL 2008 and Evans Int Geol Review 2004)

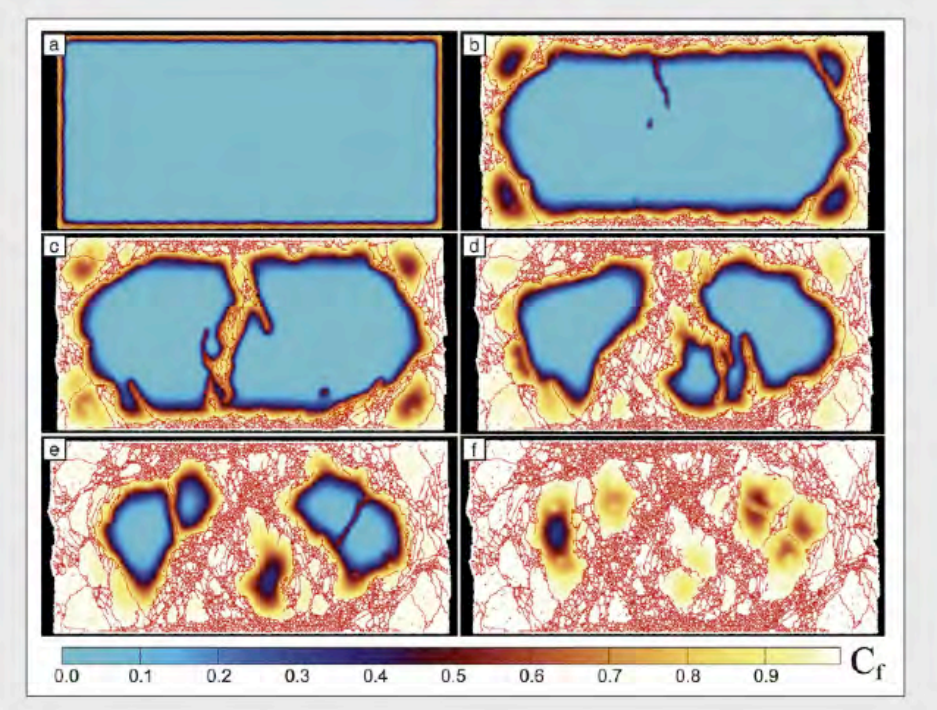


Figure 18: Results of modeling reaction driven cracking resulting from solid volume expansion due to metamorphic hydration or carbonation reactions, from Royne et al. EPSL 2008. Blue protolith is confined on top and bottom, and can expand to left and right. White material results from volume expanding reaction between fluid and protolith. Red fractures resulting from stress due to reaction provide a fast transport path for fluid.

In turn, these hypotheses are related to similar ideas about weathering (e.g., Fletcher et al. EPSL 2006) and frost cracking, as well as a relatively well developed, quantitative literature on fractures caused by crystallization of salt from evaporating water in pore space (e.g., Scherer Cement & Concrete 2004; Steiger, J Crystal Growth 2005a,b).

*****

Stop 1A: Short hike to regional viewpoint

If time and parking space permit, we will make another stop near Stop 1, and hike about 1 km to a regional viewpoint. From here, one can see one of the largest expanse of mantle peridotite in the Samail ophiolite, in which abundant, nearly horizontal dunites with thicknesses of 70 meters or more are hosted by darker colored residual mantle harzburgites. Dunites are thought to be high porosity conduits for focused melt transport through the upper mantle, preserving disequilibrium between mid-ocean ridge basalts and pyroxene minerals over the upper 40 km of their ascent path.

To the east, one can see Eocene carbonates overlying the peridotites. The contact is marked by discontinuous laterites overlying a heavily weathered horizon of black colored serpentinites.

Our sample of the massive carbonate at the parking spot (travertine? vein?) has a ^{14}C age of 32,000 years.

*****

Stop 2: Small magnesite veins, and carbonate cemented conglomerates, in Wadi Dhuli

Here we will hike a few hundred meters to see a typical outcrop of weathered peridotite hosting millions of millimeter-scale magnesite veins (Figure 19). Two small veins in the same hand sample have ^{14}C ages of ~ 12,000 and 15,000 years. Along the Wadi, we will also see outcrops of carbonate-cemented conglomerate/alluvium with peridotite clasts (Figure 20). Two samples of cement from this locality yield ^{14}C ages of ~ 14,000 and 20,000 years, while veins cutting the cement have ages of ~ 4000 and 7000 years. Some outcrops have a gradational relationship in which the base of the alluvial terraces contains isolated clases supported by the carbonate matrix, whereas the tops are clast supported with much less cement. We hypothesize that these terraces are gradually "inflated" by continuous carbonate precipitation.

Figure 19: Small magnesite "potato chips" in weathered, serpentinized peridotite, Wadi Dhuli.

Figure 20: Multiple generations of carbonate cement in alluvial terraces in this locality, inflating peridotite alluvium. This is Figure 4 in Kelemen & Matter PNAS 2008.

*****

Stop 3: Small carbonate veins in road cut

This brief stop reveals small carbonate veins on virtually all joint surfaces in a new road cut near the pass between Wadi Dima and Wadi Khafifah. ^{14}C ages for for small veins from this outcrop are ~ 11,000, 27,000, 38,000 and 42,000 years. Weathered outcrops around this road cut reveal few if any of these small carbonate veins. We interpret this to indicate that small carbonate veins have dissolved in rain water, perhaps with reprecipitation at depth, whereas road cuts reveal the actual distribution of small veins. That said, the 14C ages could be for mixtures derived from multiple dissolution and reprecipitation events.

*****

Stop 4: Khafifah travertine

If time permits, we will visit a travertine deposit within a fairly rapidly running (in the winter) fresh water drainage. Beautiful white travertine of variable thickness forms from alkaline springs emerging beneath the fresh water flow.

location	E	N	pH	T, °C	Eh, mV
Fish Pond	645796	2533418	10.56	18.8	-172
Bubbles	645784	2533430	11.68	18.5	-186
Eden	645780	2533441	11.89	23.8	-338
Glazed Kidney				22.6	
Dubya	645857	2533372	11.63	16.6	
Aqueduct	645906	2533393	8.99	21.6	
Waditorium	645927	2533408	8.59	24.8	

*****

Stop 5: Lower crustal, layered gabbro

If time permits, in either Wadi Khafifah or in Wadi Nassif, we will visit spectacular outcrops of lower crustal, layered gabbros. For those not acquainted with ophiolites – or the theoretical structure of oceanic lower crust formed at intermediate- to fast-spreading mid-ocean ridges – the igneous crust has three distinct layers. The lower crust is composed of gabbros – plutonic rocks with about 60% plagioclase feldspar, and variable proportions of calcium-rich pyroxene and olivine. In the Wadi Tayin massif in Oman, some of the more evolved gabbros higher in the crustal section also contain hornblende. In other parts of Oman and in some oceanic samples, some of the more evolved gabbros contain calcium-poor pyroxene. The lower crustal gabbros in the Wadi Tayin massif are relatively pure cumulates, igneous rocks formed by partial crystallization of a primitive, mantle derived melt, after which the remaining liquid ascended to crystallize higher in the crustal section.

Additionally, *if there is interest and time permits*, we can walk 2 km upstream in Wadi Nassif to view clast supported alluvial fan underlain by inflated, carbonate matrix supported alluvial blocks, in turn underlain by carbonate veined bedrock with fragments spalling off to add to alluvium from beneath.

*****

Stop 6: Sheeted dikes

If time permits, we will visit a typical outcrop of sheeted dikes. Sheeted dike outcrops are composed entirely of fine-grained dikes, cracks filled with melt that – in some cases – fed volcanic eruptions on the seafloor, after which melt stagnated and crystallized to form these solid, tabular, nearly vertical intrusions. While dikes in, e.g., continental crust intrude older rocks of all compositions, in sheeted dike outcrops, the wall rocks for each dike are composed entirely of just slightly older dikes. Fine-grained chilled margins record dike margins, while coarser crystals formed in the more slowly cooled dike centers. In some cases, younger dikes intruded the center of slightly older dikes, splitting the older ones. Sheeted dike outcrops are rarely spectacular to look at, but they have been very important in the discovery that ophiolites represent a continuous “ingot” of igneous crust formed at submarine spreading ridges.

*****

Stop 7: Submarine lavas, aka pillow lavas

If time permits, we will visit an outcrop of submarine lavas, with characteristic morphology known as "pillow lavas" formed by seafloor eruptions. There are much more spectacular outcrops of pillow lavas in the massifs of the Samail ophiolite that are further north in the Oman mountains, but we thought that the field trip participants would like to round out the field trip by seeing this characteristic feature in outcrop.

Pillow lavas form when erupting lavas chill rapidly on the seafloor. The exterior of the emerging lava forms a hard shell around still hot, flowing lava, forming tubes ending in rounded "pillows".

The composition of lavas in the Samail ophiolite has been the subject of much study and interest, because it is subtly but systematically different from the composition of lavas recovered from mid-ocean ridges. Trace element ratios in the Samail lavas, and in other ophiolites, have affinities with lavas formed in chains of volcanoes, known as volcanic arcs, above subduction zones, for example in the "Ring of Fire" around the Pacific Ocean. This has led to the hypothesis that ophiolites all formed at submarine spreading ridges associated with volcanic arcs, in fore arcs or back arc settings, rather than at typical mid-ocean ridges. However, few if any ophiolites contain typical volcanic arc lithologies, such as ash, pumice and volcanoclastic rocks formed on and around subaerial volcanoes. Thus, many workers believe that ophiolites represent nascent or immature arcs. However, no currently forming examples are known.

A related observation is that the oldest metamorphic rocks along the basal thrust have ages that are almost identical to the igneous ages in the ophiolite crust. This is true of the Samail ophiolite but also in other examples including the Troodos ophiolite in Cyprus and the Josephine ophiolite in SW Oregon. It has been proposed that some or all of these might have formed at typical mid-ocean ridges, but that the initiation of the thrust faults that transported ophiolites onto continental margins created "subduction zones" extending into the region of mantle melt production, imparting arc-like geochemistry to the last spreading ridge lavas, just before cessation of magmatism.