

---

# **GEOLOGICAL CARBON CAPTURE & STORAGE IN MAFIC AND ULTRAMAFIC ROCKS**

---

*Muscat, Sultanate of Oman  
8-10 January, 2011*

**Abstracts**

*Updated Dec. 10, 2010*

## Keynote

- 1 *A. Bunger, R. Jeffrey, X. Zhang* Creating surface area and conductivity in ultramafic rocks by using extremely closely spaced hydraulic fractures

## Posters

- 2 *R. R. Adhikari, J. Kallmeyer* Hydrogenase enzyme assay: a promising technique for the quantification of microbial activity in subsurface environments
- 3 *Andreani M.* Natural versus experimental peridotite carbonation: a microstructural study
- 4 *C. M. Augustin, P. K. Swart & T. H. Dixon* Computational modeling for carbon dioxide sequestration
- 5 *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
- 6 *K. Beier, W.-A. Kahl, A. Holzheid* Dissolution experiments of potential reservoir materials in CO<sub>2</sub>-bearing saline fluids
- 7 *D. Bernard, M Decain* A generic approach for pore scale modelling of coupled transport and geochemical reactions during CO<sub>2</sub>-saturated-water flow.
- 8 *E. J. Berryman, A. E. Williams-Jones, A. A. Migdisov, S. van der Laan* CO<sub>2</sub> Sequestration by carbonation of steel slag
- 9 *C. Boschi, L. Dallai, A. Dini, G. Gianelli, G. Ruggieri* CO<sub>2</sub> mineralogical sequestration in serpentinized peridotite at Malentrata (Tuscany, Italy)
- 10 *F. Boudier, A. Baronnet and B. Dewandel* Lizardite in the sub-oceanic mantle of the Oman ophiolite
- 11 *G. Caramanna, S. Mackintosh, M. Maroto-Valer* Mineral Carbonation in Oman
- 12 *G. Caramanna, Y. Wei, M. Maroto-Valer, M. Steven* Study of potential chemical effects of CO<sub>2</sub> leakage into sediments and groundwater
- 13 *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.
- 14 *H.J.B. Dick & J. Snow* The Distribution and Emplacement of Serpentinized Peridotite in the Ocean Basins
- 15 *Evans, K.A. & Frost, B.R.* Field Observations of Carbonate Formation in Weathered Ultramafic Rocks, New Caledonia
- 16 *G. L. Früh-Green, M. D. Lilley, E. Schwarzenbach, S. Q. Lang, S. Méhay, S. M. Bernasconi, M.* Alkaline Fluids and Carbonate Deposition in Modern Serpentinizing Environments

- 17** *P. Garcia Del Real* CO2 Sequestration Ultramafic Rocks: Insights from the Red Mountain Magnesite District, California
- 18** *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
- 19** *D. Goldberg, A. Slagle* Carbon storage below the sea floor: potential sites for crustal studies
- 20** *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?
- 21** *M. Hesse, J. Neufeld, A. Riaz* Convective Dissolution of CO2
- 22** *M. Hesse, V. Prigiobbe* Convection in porous and fractured systems with an exothermic reaction
- 23** *B. Ildefonse, M. Andréani, E. Hoisé, A. Delacour, J. Escartin, M. Godard, J. Dymont, Y. Fouquet* Geology of the Rainbow Massif, with evidence of carbonation in a serpentinite seafloor
- 24** *Iyer, K., Rüpke, L.H. and Morgan, J.P.* Feedbacks between mantle hydration and hydrothermal convection at ocean spreading centers.
- 25** *K. T. M. Johnson, B. P. McGrail, and H. T. Schaefer* Geologic CO2 Sequestration Experiments with Hawaiian Picritic Basalts
- 26** *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
- 27** *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
- 28** *F. Klein* Heterogeneous phase equilibria during carbon sequestration into serpentinitized peridotite: Using the fluid chemistry as a monitor of carbonation progress
- 29** *J. Koepke, S. Feig, J. Berndt* Experiments in hydrous tholeiitic and peridotitic systems at shallow pressures: Constraints on magmatic processes in the Oman paleoridge
- 30** *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.
- 31** *S. Krevor* Bringing mineral carbon dioxide sequestration down to earth: Thermodynamic considerations using realistic reactant and product phases.

- 32 *A.M. Lacinska, M.T. Styles* Barzaman Formation in the United Arab of Emirates: a natural analogue for permanent CO<sub>2</sub> fixation using ultramafic rocks.
- 33 *L. Luquot, M. Andreani, M. Godard, P. Gouze, B. Gibert, G. Lods* Serpentinization of sintered olivine during seawater percolation experiments
- 34 *F. Lartaud, C.T.S. Little, M. de Rafelis, G. Bayon, B. Ildefonse, J. Dymont, N. Le Bris* Fossil Bivalves in the Rainbow Area: New Insight into the Diversity and Evolution of Chemosynthetic Communities
- 35 *D. Le & J. Mahadevan* Impact of Capillarity on Salt Crystallization in Porous Media
- 36 *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
- 37 *S. Mackintosh, K. Bateman, M. Maroto-Valer, M. Hall* The Effect on Porosity and Permeability of North Sea Sandstones Post Mineral Carbonation
- 38 *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
- 39 *B. Ménez, E. Gérard, S. Dupraz, H. A. Alfreðsson, S. R. Gíslason, H. Sigurðardóttir, François Guyot* Impact on the deep biosphere of CO<sub>2</sub> geological sequestration in (ultra)mafic rocks and retroactive consequences on its fate
- 40 *K.G. Mesfin, D. Wolff-Boenisch and S.R. Gíslason* Dissolution of basaltic glass in seawater at 1000C and 70 bars CO<sub>2</sub> pressure. Implications for CO<sub>2</sub> mineral sequestration
- 41 *P. J. Michael* Some Opportunities and Challenges for Sequestering CO<sub>2</sub> in Arctic Seafloor Peridotites
- 42 *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.
- 43 *J. Olsson, S. L. S. Stipp and S. R. Gíslason* Toxic metal mobility following the injection of CO<sub>2</sub> into basaltic aquifers
- 44 *J. Phipps Morgan, L. Rüpke & K. Iyer* Bend-Faults and Hydrothermal Circulation at Oceanic Trenches
- 45 *R. K. Podgorney, A. L Slagle, T. L. McLing and D. S. Goldberg* Numerical Simulation of Carbon Dioxide Sequestration in Deep-Sea Basalts
- 46 *K. Pöhler, Ch. Lempp & H. Pöllmann* Mineralization of serpentinite rocks with CO<sub>2</sub> at different states of structural disintegration
- 47 *H. Pöllmann* The formation of carbonate containing LDH's in basic rocks
- 48 *R. Pollyea, J. P. Fairley, R. K. Podgorney and Travis L. McLing* Developing fracture density models using terrestrial laser scan data
- 49 *V. Prigiobbe* Enhanced olivine dissolution using oxalate and citrate
- 50 *V. Prigiobbe* Magnesite precipitation at high temperature and high CO<sub>2</sub> pressure

- 51 *T. L. McLing, R. W. Smith, R. K. Podgorney* Field Characterization of the Soda Springs Mafic Rock CO<sub>2</sub> Sequestration Analogue Site, Idaho, USA
- 52 *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
- 53 *J. M. Ornstein* Identifying tools used to inform public attitudes and influence behavior in favor of Carbon Mineralization
- 54 *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
- 55 *Kevin M. Rosso, Alain HR Bonneville, Jian Z Hu, David W Hoyt, Zheming Wang, Alan S Lea, H. Todd Schaefer, B. Peter McGrail, and Mark D. White* Fundamental Science for Geologic Carbon Sequestration: Laboratory Probes for Understanding Trapping Mechanisms at the Microscopic Scale
- 56 *L. Riepke, K. Iyer, and J. Phipps Morgan* Simulations of oceanic lithosphere serpentinization
- 57 *P. Sauer, J. Kallmeyer* A new incubator for biological high pressure experiments with elevated gas saturation
- 58 *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 CO<sub>2</sub>
- 59 *R.D. Schuiling* Let the Earth help us to save the Earth
- 60 *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 CO<sub>2</sub> storage in basalts
- 61 *D.A.H. Teagle, R.M. Coggon, H. Pälke, J. C. Alt and C.E. Smith-Duque* Did seafloor carbonation regulate high pCO<sub>2</sub> on the ancient Earth?
- 62 *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
- 63 *Y. Takaya, K. Nakamura, Y. Kato* Experimental study on the CO<sub>2</sub>-water-basalt interaction: Implications for a carbonate formation sequence during CO<sub>2</sub> basaltic aquifer storage
- 64 *M. Tominaga and F. Klein* Downhole magnetic and physical property logging of serpentinized peridotite and carbonate-altered serpentinite.
- 65 *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 CO<sub>2</sub>-mineralization in ophiolites

- 66 *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
- 67 *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
- 68 *A. J. West* The potential for carbon sequestration by accelerated weathering  
of mafic rocks at ambient pCO<sub>2</sub>
- 69 *S. Wilson, S. Barker, A. Harrison, I.  
Power, G. Dipple, K. U. Mayer, V.  
Atudorei* Dissolution of CO<sub>2</sub> gas is rate limiting to C sequestration in high-  
salinity alkaline brines
- 70 *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 CO<sub>2</sub> sequestration
- 71 *L. Zhao, L. Sang, J. Chen, J. Ji, and  
H. H. Teng* Aqueous Carbonation of Natural Brucite for CO<sub>2</sub> Sequestration
- 72 *Zhu, W. and Lisabeth, H.* Carbonation Reaction Driven Permeability and Porosity Evolution  
in Thermally Cracked Dunites.
- 73 *Richard Hunwick* Ex-situ mineralisation using the ICS Process  
*Integrated Carbon Sequestration Pty Ltd*

## **I - Keynote presentation**

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

*A. Bungler, 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 these 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

## 2 - A new incubator for biological high pressure experiments with elevated gas saturation

*Patrick Sauer, Jens Kallmeyer*

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

[\*\(kallm@geo.uni-potsdam.de\)\*](mailto: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 cm<sup>3</sup>. 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 through 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*

### 3 - Natural versus experimental peridotite carbonation

Andreani M.<sup>1</sup>, Pollet-Villard M.<sup>1</sup>, Luquot L.<sup>2</sup>, Menez B.<sup>3</sup>, Peuble S.<sup>2</sup>, Auzende A-L.<sup>3</sup>, Godard M.<sup>2</sup>, Gouze P.<sup>2</sup>

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<sub>2</sub> 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 CO<sub>2</sub>-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 PCO<sub>2</sub>. 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 outlet 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 CO<sub>2</sub> 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.

#### 4 - Computational modeling for carbon dioxide sequestration

*Caitlin M. Augustin<sup>1</sup>, Peter K. Swart<sup>1</sup>, Timothy H. Dixon<sup>1</sup>*

*1 RSMAS/MGG University of Miami 4600, Rickenbacker Causeway, Miami, FL 33149  
[caugustin@rsmas.miami.edu](mailto:caugustin@rsmas.miami.edu) - [pswart@rsmas.miami.edu](mailto:pswart@rsmas.miami.edu) - [tdixon@rsmas.miami.edu](mailto: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 carbon 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 health 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 CO<sub>2</sub> 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.

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

*Keir Becker<sup>1</sup>, Andrew T. Fisher and Dustin Winslow<sup>2</sup>, Takeshi Tsuji<sup>3</sup>, Stefan Mrozewski<sup>4</sup>,*

*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  $\sim 2 \times 10^{-12} \text{ m}^2$  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.

## 6 - Dissolution experiments of potential reservoir materials in CO<sub>2</sub>-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 CO<sub>2</sub>, saline fluids and potential reservoir materials are experimentally investigated in this study as part of the joint project CO<sub>2</sub>-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.

## **7 - A generic approach for pore scale modelling of coupled transport and geochemical reactions during CO<sub>2</sub>-saturated-water flow.**

*D. Bernard, M Decain. CNRS, University of Bordeaux, ICMCB, France,  
[bernard@icmcb-bordeaux.cnrs.fr](mailto:bernard@icmcb-bordeaux.cnrs.fr)*

To explore the viability of CO<sub>2</sub> geological storage, it is of 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  $N_s$  speciation equilibrium and a relation expressing the electro neutrality of the solution at each point. To close the system,  $(N - N_s - 1)$  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 CO<sub>2</sub>-saturated-water flow. The considered species are H<sup>+</sup>, OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, and CO<sub>2</sub>\* (Na<sup>+</sup> and Cl<sup>-</sup> 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 CO<sub>2</sub> 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 CO<sub>2</sub> partial pressures.

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

## 8 - CO<sub>2</sub> 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, IJmuiden, The Netherlands*

The stable and non-toxic nature of the products has made mineral carbonation the preferred approach to CO<sub>2</sub> 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 (Ca<sub>2</sub>SiO<sub>4</sub>), with significant P, calcium ferrite (Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>), containing Mn and Al, and Mg-wuestite ((Mg,Fe)O), with appreciable Mn. The experiments involved pumping H<sub>2</sub>O-CO<sub>2</sub> fluid (X<sub>CO<sub>2</sub></sub> = 0.05) through a flow-through reactor containing these grains. Temperature ranged from 120°C to 200°C, the pressure was 150 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 mmol/L) 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 Si increased. Concentrations of 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 CO<sub>2</sub>-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 CO<sub>2</sub> 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 isolates 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. In future 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.



## 9 - CO<sub>2</sub> 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](mailto: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 CO<sub>2</sub>-bearing meteoric/hydrothermal fluids and serpentinized ultramafic rocks and represent natural analogues of induced CO<sub>2</sub> mineralogical sequestration. Their study can complement laboratory and demonstration studies and provide opportunity to constrain the boundary conditions for CO<sub>2</sub>-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 CO<sub>2</sub>-rich fluids, a spontaneous carbonation of buried serpentinites and could be an ideal place to test in situ CO<sub>2</sub> mineralogical sequestration of unaltered buried serpentinites. Boschi et al., (2008) evaluated that outcropping Tuscan serpentinites can store up to 100 gigatons of CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> modifies ambient formation waters, inducing fluid-rock reactions that may lead to the immobilization of injected CO<sub>2</sub>. Our ongoing project has the chance to define the temporal and spatial chemical evolution of the CO<sub>2</sub>-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 CO<sub>2</sub>-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.

## **10 - 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 50 $\mu$ m thick veins, spaced 100-300 $\mu$ m, 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)<sub>liz</sub> 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 development of lizardite, volume expansion that is evaluated.

## 11 - 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<sub>2</sub> 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<sub>2</sub> storage in reservoirs is the fixation of CO<sub>2</sub> by means of specifically enhanced chemical reactions. CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> in the exhaust fumes is around 4 – 5 %. Currently, available mineralisation methods request capture techniques suited to concentrate the CO<sub>2</sub> from this level to much higher values before the carbonation process could be performed.

The resulting products of the CO<sub>2</sub> 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<sub>2</sub> mineralisation in Oman.

## 12 - Study of potential chemical effects of CO<sub>2</sub> 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<sub>2</sub> has been proposed as a viable strategy to reduce CO<sub>2</sub> emission. In this case CO<sub>2</sub> is injected underground in geological formations that are expected to host the CO<sub>2</sub> 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<sub>2</sub> affecting the chemistry of the sediments. The main potential effect of an increased level of CO<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub>.

The outcomes of this study are:

- data collection on soil pH variations as a function of the CO<sub>2</sub> 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<sub>2</sub> dissolution into the interstitial water
- verification of the influence of the soil moisture on the CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> the soil pH does not change significantly as well the nutrients and toxic elements concentration. When a 99% CO<sub>2</sub> and 1% SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> on the Soil Ecosystem and Chemistry of an English Lowland Pasture. Energy Procedia*, 1, 1863-1870.

### **13 - 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 14°N and 38°N 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 37°50'N at 1700m water depth (Langmuir et al., 1997). The high-temperature hydrothermal fluids (up to 328°C) 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 (37°50'N) and Lucky Strike (37°17'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 37°N 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.

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

*Henry JB Dick<sup>1</sup>, Jonathan Snow<sup>2</sup>*

*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 crust 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 peridotite are 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.

## 15 - 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](mailto:K.evans@curtin.edu.au)

(2) Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming, USA.

Formation of magnesite ( $\text{MgCO}_3$ ) by reaction of olivine ( $\text{Mg}_2\text{SiO}_4$ ) with  $\text{CO}_2$ -bearing fluids has been proposed to have practical potential in the mitigation of anthropogenically-driven rises in atmospheric  $\text{CO}_2$ . However, laboratory experiments for simple chemical systems often result in armouring; the formation of a crust of reacted material on olivine that prevents further  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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.

## 16 - 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 CO<sub>2</sub> uptake from the atmosphere. Similar to the Lost City system, methane in the Ligurian springs is enriched in <sup>13</sup>C 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 CO<sub>2</sub>. 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*



## 17 - CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> via this process. An excellent example of a natural analogue for in situ CO<sub>2</sub> 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<sup>6</sup> 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<sub>2</sub> 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<sub>2</sub> 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  $\delta^{18}\text{O}_{\text{SMOW-Magnesite}}$  ( $26.0 \pm 2.1\text{‰}$ ) and  $\delta^{13}\text{C}_{\text{PDB-Magnesite}}$  ( $-11.6 \pm 2.4\text{‰}$ ). 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<sub>2</sub> storage in ultramafic rocks, consistent with previous studies of ultramafic natural analogues for CO<sub>2</sub> sequestration.

## 18 - Experimental study of CO<sub>2</sub> sequestration in a basalt- olivine matrix: Coupling and feedback effects of transport, hydration and carbonation processes

*M. Godard, S. Peuble, L. Luquot & Ph. Guuze*

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

Injection of CO<sub>2</sub>-rich fluids into (ultra-)mafic aquifers is one of the methods envisaged for mitigation of increasing atmospheric CO<sub>2</sub> due to burning of hydrocarbons. Ultramafic and mafic rocks are rich in divalent cations (Mg, Ca and Fe); interaction with CO<sub>2</sub>-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 CO<sub>2</sub> 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 CO<sub>2</sub>-rich fluid percolation through sintered analogues of olivine-accumulation zones in basaltic flows (~95% olivine Fo<sub>87</sub>, MORB glass, minor chromite). Experiments were carried out on the ICARE-2 experimental bench at a total pressure  $P=12\text{MPa}$  (confining pressure = 110% x P), temperature  $T = 180^\circ\text{C}$  for 90 to 130 hours. The injection rate of CO<sub>2</sub>-rich fluids (MilliQ water enriched with 0.5 mol/L NaHCO<sub>3</sub>,  $P_{\text{CO}_2} = 10\text{MPa}$ , pH = 6.7) is 1 cm<sup>3</sup>/h. The initial porosity and permeability of samples ranges from 3 to 7% and 250.10<sup>-18</sup> to 2500.10<sup>-18</sup> m<sup>2</sup> respectively.

Injection of CO<sub>2</sub>-fluids results in a strong drop in permeability, down to ~5. 10<sup>-18</sup>m<sup>2</sup> 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 CO<sub>2</sub> 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/m<sup>3</sup>/day (or 45 Mt of CO<sub>2</sub>/km<sup>3</sup>/day compared to the production of the Helleishidi test site which is ~160 tons CO<sub>2</sub> 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 CO<sub>2</sub>-injection rate. Further experiments are needed to test this hypothesis.

## 19 - 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 CO<sub>2</sub> sequestration arise from providing multiple physical/chemical trapping mechanisms for injecting CO<sub>2</sub> 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 CO<sub>2</sub>-basalt chemical reactions. We propose that pilot injection studies are conducted to establish the viability of these reservoirs for CO<sub>2</sub> sequestration. Initial studies could re-occupy pre-existing crustal drill holes, inject supercritical CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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.

## 20 - Dissolution and carbonation of mechanically activated olivine – implications for in-situ CO<sub>2</sub> sequestration in mafic and ultramafic rocks?

T. Anette Haug<sup>1</sup> & Nina S. C. Simon<sup>1\*</sup>

<sup>1</sup> Dep. of Environmental Technology, Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway. \*presenting author: [nina.simon@ife.no](mailto:nina.simon@ife.no)

Ultra-mafic rocks as in-situ host rock for CO<sub>2</sub> storage via mineral carbonation are an alternative to geological storage of CO<sub>2</sub> 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 CO<sub>2</sub> may occur instead of solely physical trapping of pure CO<sub>2</sub> or CO<sub>2</sub> 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 Acta* In Press, Corrected Proof, (2010).
3. A. Beinlich, J. Hövelmann, O. Plümper, H. Austrheim, *Geophysical Research Abstracts* 12, EGU2010 (2010).

## 21 - Convective Dissolution of CO<sub>2</sub>

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

*(1) Department of Geological Sciences, University of Texas at Austin, [mhesse@jsq.utexas.edu](mailto:mhesse@jsq.utexas.edu)*

Geological carbon dioxide (CO<sub>2</sub>) storage is a means of reducing anthropogenic emissions. Dissolution of CO<sub>2</sub> 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 CO<sub>2</sub> saturation. We present a new analogue fluid system that reproduces the convective behaviour of CO<sub>2</sub>-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 CO<sub>2</sub> dissolution rates in CO<sub>2</sub> accumulations. These estimates of the dissolution rate show that convective dissolution can play an important role in enhancing storage security.

## 22 - 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@jsq.utexas.edu](mailto:mhesse@jsq.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 CO<sub>2</sub> 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.

### **23 - 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. Dymont(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 Nautilie 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 where 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.

## 24 - 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](mailto: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  $0.18 \times 10^5$  kg/m<sup>2</sup> to  $2.52 \times 10^5$  kg/m<sup>2</sup>. 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.*



## 25 - Geologic CO<sub>2</sub> Sequestration Experiments with Hawaiian Picritic Basalts

*K. T. M. Johnson, University of Hawaii*

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

Capturing and storing anthropogenic carbon dioxide in deep geologic formations is a potential CO<sub>2</sub> 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., SO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>) that could be co-injected with CO<sub>2</sub>. Injecting to depths greater than 800 m, these CO<sub>2</sub> 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 scCO<sub>2</sub>, water bearing scCO<sub>2</sub>, 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 scCO<sub>2</sub> 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 CO<sub>2</sub>. However, the olivine surface was significantly altered in just 80 days after exposure to wet scCO<sub>2</sub> containing 1% SO<sub>2</sub>. 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 hexahydrate (MgSO<sub>4</sub>•6H<sub>2</sub>O), magnesium thiosulfate hydrate (MgS<sub>2</sub>O<sub>3</sub>•6H<sub>2</sub>O), along with three different hydrated sulfite phases. These types of experiments illustrate the potential basalt formations hold for long term storage of CO<sub>2</sub> and the importance of understanding supercritical phase chemical reactions involved in geologic carbon sequestration.

## 26 - Kinetics of olivine carbonation for the geologic storage of carbon dioxide

Natalie C. Johnson<sup>1,2</sup>, Burt Thomas<sup>3</sup>, Kate Maher<sup>2</sup>, Dennis K. Bird<sup>2</sup>, Robert J. Rosenbauer<sup>3</sup>, Gordon E. Brown, Jr<sup>1,2</sup>

*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 (CO<sub>2</sub>) over geologic time periods is mineral carbonation, specifically the thermodynamically favored reaction of CO<sub>2</sub> with 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 magnesite and 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 60°C and 100 bar CO<sub>2</sub> pressure. 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.

## **27 - Geochemical and petrophysical estimation studies on sedimentary rock samples from the Pannonian Basin, Hungary**

*KIRÁLY, Csilla<sup>1</sup>; BERTA, Márton<sup>1</sup>; FALUS, György<sup>2</sup>; SZÉKELY, Edit<sup>3</sup>, SZABÓ, Csaba<sup>1</sup>*

*1 Lithosphere Fluid Research Lab (LRG), Eötvös University Budapest (ELTE)*

*2 Eötvös Loránd Geophysical Institute of Hungary (ELGI)*

*3 Budapest University of Technology and Economics (BME)*

Saline aquifers are considered to have the largest capacity for Carbon Capture 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 profiles 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 Algyó Formation for cap rock) now form a hydrogeologically 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 Algyó 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 Algyó 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 CO<sub>2</sub> 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.

## **28 - 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 CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2,aq</sub> and SiO<sub>2,aq</sub> 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 CO<sub>2,aq</sub>, that ultimately drive the formation of carbonate. Thermodynamic reaction path models predict that a stair-step pattern in aCO<sub>2,aq</sub>, aSiO<sub>2,aq</sub>, fO<sub>2,g</sub>, fS<sub>2,g</sub> 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 CO<sub>2,aq</sub> and SiO<sub>2,aq</sub>, together with fO<sub>2,g</sub>, fS<sub>2,g</sub> 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 CO<sub>2,aq</sub>, SiO<sub>2,aq</sub>, fO<sub>2,g</sub>, fS<sub>2,g</sub> and pH would help to identify the saturation states of solid phases and prevent unintended liberation of already sequestered CO<sub>2</sub>.

## **29 – 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 gabbro-norites, 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 gabbro-norites, 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*

### **30 - 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.

### **31 - 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](mailto:skrevor@stanford.edu)

In making the case for the sequestration of CO<sub>2</sub> in mineral form, whether through the injection of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> sequestration process.

### **32 - Barzaman Formation in the United Arab of Emirates: a natural analogue for permanent CO<sub>2</sub> fixation using ultramafic rocks.**

*Alicja M. Lacinska<sup>1\*</sup>, Michael T. Styles<sup>1</sup>*

Anthropogenic release of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. The dissolved CO<sub>2</sub> dissociates to bicarbonate and carbonate ions and in the presence of divalent cations (Mg<sup>2+</sup>) 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 CO<sub>2</sub> 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 CO<sub>2</sub> and been transformed into 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 5x10<sup>9</sup> tonnes of CO<sub>2</sub> 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 into carbonate rock that demonstrates a permanent storage solution for captured CO<sub>2</sub>. 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.



### 33 - 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 H<sub>2</sub> and CH<sub>4</sub>, 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, Wetzell & 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 ;*

*Wetzell & Shock, JGR, 105, 8319-8340, 2000.*

### **34 - 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. Idefonse(5), J. Dymont (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) ITeP, 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  $24 \pm 0.2$  kyr, and on the slope of the same structure, 1.2 km north-east to Rainbow field (site DR 11) at  $192 \pm 12$  kyr. At the younger site abundant shells of the vesicomid 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  $^{13}\text{C}$ , and *Thyasira* shells, which are highly depleted in  $^{13}\text{C}$  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.

### **35 - 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.

### 36 - 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  $^{230}\text{Th}$  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  $3.28 \pm 0.03$  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  $0.133 \pm 0.016$  pg/g. The  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratios of the vent fluids range from  $1 \pm 10$  to  $11 \pm 5 \times 10^{-6}$ , are less than those of seawater, and indicate that the vent fluids do not contribute a significant amount of non-radiogenic  $^{230}\text{Th}$  to the LCHF carbonate chimney deposits. Chimney  $^{238}\text{U}$  concentrations range from 1-10 ug/g and the average chimney corrected initial  $d^{234}\text{U}$  is  $147.2 \pm 0.8$ , which is not significantly different from the ambient seawater value of  $146.5 \pm 0.6$ . Carbonate Th concentrations range broadly from  $0.0038 \pm 0.0003$  to  $125 \pm 16$  ng/g and  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratios vary from near seawater values of  $43 \pm 8 \times 10^{-6}$  up to  $530 \pm 25 \times 10^{-3}$ . Chimney ages range from  $17 \pm 6$  yrs to  $120 \pm 13$  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 serpentinitized 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.

### **37 - 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> with the hosting rocks forms solid carbonate minerals. This system could be used to capture and store billions of tons of CO<sub>2</sub> per km<sup>3</sup> of rock per year, while eliminating the need for monitoring CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 CO<sub>2</sub> 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*

### **38 - 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](mailto: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<sup>2</sup> (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<sup>2</sup> or 175 T/ha).

Carbon and oxygen isotope data consistently show plots that trend towards highly negative values for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . 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<sup>-3</sup> sec<sup>-1</sup>, or about 15 kg C m<sup>-3</sup> 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<sub>2</sub> 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.*

### **39 - Impact on the deep biosphere of CO<sub>2</sub> geological sequestration in (ultra)mafic rocks and retroactive consequences on its fate**

*Bénédicte Ménez<sup>1,2</sup>, Emmanuelle Gérard<sup>1,2</sup>, Sébastien Dupraz<sup>1,2,3</sup>, Helgi Arnar Alfreðsson<sup>4</sup>, Sigurður Reynir Gíslason<sup>4</sup>, Hólmfríður Sigurðardóttir<sup>5</sup>, François Guyot<sup>1,2</sup>*

*1 Equipe Géobiosphère actuelle et Primitive, IPGP/IMPMP, CNRS UMR7154, Paris, France*

*2 Centre de Recherches sur le Stockage Géologique du CO<sub>2</sub> (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 sequester anthropogenic CO<sub>2</sub> 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 CO<sub>2</sub> injection ( $\pm$  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 H<sub>2</sub>S and CH<sub>4</sub>), the impact of CO<sub>2</sub> injection on deep biota with unknown ecology, and their retroactive effects on the capacity and long-term stability of CO<sub>2</sub> 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 CO<sub>2</sub> charged water is here designed to study the feasibility of storing permanently CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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.

## **40 - Dissolution of basaltic glass in seawater at 100°C and 70 bars CO<sub>2</sub> pressure. Implications for CO<sub>2</sub> 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<sub>2</sub> in mafic rocks offers long-term storage of CO<sub>2</sub>. It requires the combination of divalent metals with dissolved CO<sub>2</sub> to form carbonate minerals. This method of *in-situ* CO<sub>2</sub> 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<sub>2</sub> injection, such as separate supercritical CO<sub>2</sub> phase or CO<sub>2</sub> fully dissolved in water. Both end-members have drawbacks. Supercritical CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> injection with an average geothermal gradient of 220°C/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<sub>2</sub> using a CO<sub>2</sub> cylinder source up to ~45bars. The vessel was then heated to a final temperature of 100°C causing the internal pressure to increase to 70 bars, driving the CO<sub>2</sub> 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<sub>2</sub> 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.



## **41 - Some Opportunities and Challenges for Sequestering CO<sub>2</sub> 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](mailto:pjm@utulsa.edu)*

The ubiquitous and often complete serpentinization of peridotites encourages scientists and engineers to consider these rocks for mineralogic trapping of CO<sub>2</sub> 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 H<sub>2</sub>O 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, un-serpentinized 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 CO<sub>2</sub>. Firstly, it may be possible to exploit the phase stabilities of CO<sub>2</sub> along with the frigid Arctic climate to aid in concentrating and liquefying CO<sub>2</sub> 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 CO<sub>2</sub> during pumping, which may be necessary to make it more reactive. Thirdly, because of the different compressibilities of CO<sub>2</sub> and H<sub>2</sub>O, the great ocean depth may also be important because liquid CO<sub>2</sub> 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 CO<sub>2</sub> storage, this brief contribution serves to raise some points for discussion.

## **42 - 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 with those at sites like Lost City, such as high pH, low silica and carbonate alkalinity content but also differences such as different temperatures 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 H<sub>2</sub> is more abundant in Oman and CH<sub>4</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 Marini L. (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.*

### 43 - Toxic metal mobility following the injection of CO<sub>2</sub> into basaltic aquifers

J. Olsson<sup>1,2\*</sup>, S. L. S. Stipp<sup>2</sup> and S. R. Gislason<sup>1</sup>.

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](mailto:jolsson@nano.ku.dk) (J. Olsson)

Injection of CO<sub>2</sub> into rocks creates corrosive CO<sub>2</sub> 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 sequestered 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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, SO<sub>4</sub>, Ba and CO<sub>2</sub>, 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 CO<sub>2</sub> 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-CO<sub>2</sub> 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)

#### **44 - 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 CO<sub>2</sub> 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!

## 45 - Numerical Simulation of Carbon Dioxide Sequestration in Deep-Sea Basalts

*Robert K. Podgorney<sup>1</sup>, Angela L. Slagle<sup>2</sup>, Travis L. McLing<sup>1</sup> and David S. Goldberg<sup>2</sup>*

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-CO<sub>2</sub> 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.

## **46 - Mineralization of serpentinite rocks with CO<sub>2</sub> 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 greenhouse gas reduction. However, in most cases it appears as a long term mode, not useful for quick results. In contrary, the carbonisation reaction of CO<sub>2</sub> 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 CO<sub>2</sub> 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 dm<sup>3</sup>-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 CO<sub>2</sub>. 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 Zoebnitz(Saxony)/Germany.

Mechanical studies and geochemical studies were done to describe changes during the treatment with supercritical CO<sub>2</sub>. The strength tests represent the transition from continuum to discontinuum (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 CO<sub>2</sub> are very important to understand the behaviour of this rock under the influence of CO<sub>2</sub>.

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  $\rho_d = 2,4\text{ g/cm}^3$ .

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 ( $\sim 36\text{cm}^3$ ). Conditions of 100°C and 100bar were chosen to ensure the supercritical phase field of CO<sub>2</sub>. Expected results are: growth of new carbonatite containing minerals on mineral surfaces, alteration appearances, solutions in pore space and mineralization reactions.

## 47 - 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](mailto:herbert.poellmann@geo.uni-halle.de)

The LDH group of minerals are built of alternating layers, consisting of metals charged  $M^{2+}$  and  $M^{3+}$  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  $M^{2+} : M^{3+}$  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

$[M^{2+}_x M^{3+}_y (OH)_z] [(AY)_x / Y (H_2O)_n]$  with

$M^{2+} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}$

$M^{3+} = Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Ga^{3+}, In^{3+}, Y^{3+}$

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 CO<sub>2</sub>, LDH's can be used as a mineralizer phase for carbon dioxide.

### **Literature**

*Pöllmann, H.: Mineralization of wastes and industrial residues, Shaker, (2010)*

## 48 - Developing fracture density models using terrestrial laser scan data

*Ryan Pollyea<sup>1</sup>, Jerry P. Fairley<sup>1</sup>, Robert K. Podgorney<sup>2</sup> and Travis L. McLing<sup>2</sup>*

*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.



## 49 - Enhanced olivine dissolution using oxalate and citrate

*Valentina Prigiobbe*

We studied olivine dissolution kinetics under operating conditions suitable for ex situ aqueous mineral carbonation for CO<sub>2</sub> 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 CO<sub>2</sub> fugacity (fCO<sub>2</sub>).

Metal-oxide bearing materials, such as natural silicates and industrial alkaline residues undergo pre-treatment and dissolution prior reaction with CO<sub>2</sub> to produce stable carbonates, in which CO<sub>2</sub> is bound, and quartz.

Mineral carbonation is more energy intensive than 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 (Mg<sub>1.82</sub>Fe<sub>0.18</sub>SiO<sub>4</sub>). Flow-through experiments were performed at 90 and 120°C, at fCO<sub>2</sub> 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 fCO<sub>2</sub>. 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.

## 50 - Magnesite precipitation at high temperature and high CO<sub>2</sub> pressure

*Valentina Prigiobbe*

Precipitation of magnesite (MgCO<sub>3</sub>) is hindered by the high dehydration energy to incorporate magnesium 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 MgCO<sub>3</sub> depends on temperature, P<sub>CO<sub>2</sub></sub>, supersaturation ratio and other process variables such as CO<sub>3</sub><sup>2-</sup> and Mg<sup>2+</sup> activity ratio, Mg<sup>2+</sup> concentration, pH, ionic strength, and water activity. To investigate systematically the effect of these process variables, kinetics experiments were performed using a MgCl<sub>2</sub>-CO<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub> aqueous system at 90, 120, and 150°C, at 100 bar of P<sub>CO<sub>2</sub></sub>, varying MgCl<sub>2</sub> between 0.012 and 0.36 m and Na<sub>2</sub>CO<sub>3</sub> 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 Mg<sup>2+</sup> defined the type of precipitation mechanism. High concentrations of Mg<sup>2+</sup> 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.

## **51 - Field Characterization of the Soda Springs Mafic Rock CO<sub>2</sub> 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 CO<sub>2</sub> analogue is the Soda Springs site located in Caribou County of Southeastern Idaho, USA. At this site, CO<sub>2</sub> and formation fluids generated by the dissolution of Paleozoic carbonates at depth are migrating and reacting with a series of shallower tholeiitic 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 CO<sub>2</sub> charged fluids. However, in several cases the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>-water-interactions.

## 52 - Assessment of direct aqueous in situ carbonation procedures in ophiolitic détritius

Meyer<sup>1</sup>, F.M., Sindern<sup>1</sup>, S., Schardt<sup>1</sup>, C., Urai<sup>2,3</sup>, J., Gutberlet<sup>3</sup>, M., den Brok<sup>3</sup>, B., Clauser<sup>4</sup>, C., Blaschek<sup>4</sup>, R., Kukla<sup>5</sup>, P., Rude<sup>6</sup>, T.R., Stanjek<sup>7</sup>, H., Littke<sup>8</sup>, 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](mailto:sindern@rwth-aachen.de)

Igneous ultramafic rocks containing Mg-rich minerals such as olivine, pyroxene or serpentine are particularly suitable for CO<sub>2</sub>-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 CO<sub>2</sub>-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 km<sup>2</sup> and a mean thickness of 100 m mass balance calculations yield 9.07x10<sup>8</sup> to 5.44x10<sup>9</sup> t of sequestered CO<sub>2</sub> depending on the abundance of Mg-silicate minerals. On the basis of a modern 800 MW coal fired-power station the CO<sub>2</sub> storage capacity of such a reservoir would be equivalent to more than 200 years of CO<sub>2</sub> sequestration. To turn such theoretical consideration into an applicable technical concept further constraints have to be considered. In-situ CO<sub>2</sub> sequestration will increase the volume of the reaction 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 SO<sub>2</sub> in the flue gas, however, could be of advantage in terms of reaction progress. Considering all variables discussed above it is evident 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.

## **53 - 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.

## **54 - 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 Atmospheric Sciences*  
[gdpearso@ualberta.ca](mailto: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.

## **55 - 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 CO<sub>2</sub> 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 CO<sub>2</sub> (scCO<sub>2</sub>) 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 scCO<sub>2</sub> 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 CO<sub>2</sub> from a co-existing scCO<sub>2</sub> phase. However, at the caprock-fluid interface over the long-term, direct interaction with the scCO<sub>2</sub> 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 scCO<sub>2</sub> 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 CO<sub>2</sub>.

## 56 - 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.



## **57 - 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](mailto:kallm@geo.uni-potsdam.de))*

*Institute of Earth and Environmental 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 CO<sub>2</sub> 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 biocorrosion, 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.

## 58 - A new autoclave system for the “in situ” investigation of carbonation reactions of basic rocks with waste CO<sub>2</sub>

Michael Schmidt<sup>1</sup>, Herbert Pöllmann<sup>1</sup>, Herwig Marbler<sup>1</sup>, Kirsten Erickson<sup>1</sup>, Christof Lempp<sup>1</sup>

<sup>1</sup> Martin-Luther-Universität Halle Wittenberg, Geowissenschaften, Halle/Saale, Germany

[herbert.poellmann@geo.uni-halle.de](mailto:herbert.poellmann@geo.uni-halle.de)

For safe long term storage of CO<sub>2</sub> 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 CO<sub>2</sub> or N<sub>2</sub> is done through valves in the pipe system which can also be used for sample extraction. CO<sub>2</sub> as gaseous phase or liquid phase is delivered through a Teledyne ISCO D500 high pressure syringe pump. This pump allows a defined flow of CO<sub>2</sub> 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 CO<sub>2</sub>“; Poster, 88. Tagung der Deutschen Mineralogischen Gesellschaft, Münster (Germany), p.218

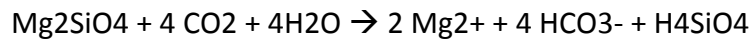
## 59 - Let the Earth help us to save the Earth

*R.D. Schuiling, Institute of Geosciences,*

*Utrecht University*

*phone: 0031 30 2535006 e-mail: [schuiling@geo.uu.nl](mailto:schuiling@geo.uu.nl)*

Massive sequestration of CO<sub>2</sub> can be achieved by the enhancement of the natural process of chemical weathering. This process has kept the CO<sub>2</sub> 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, the most widespread silicate mineral in the world. Olivine weathers easily in contact with CO<sub>2</sub> and water, according to the reaction:



The resulting Mg-bicarbonate waters are carried by rivers to the oceans, where they will ultimately be stored as carbonate sediments (limestones and dolomites). These slightly alkaline waters help to counteract the ongoing acidification of the oceans.

## 60 - Effect of heterotrophic bacteria on olivine and basaltic glass dissolution

### in the context of CO<sub>2</sub> storage in basalts

*L.S. Shirokova<sup>1</sup>, G. Stockman<sup>2</sup>, P. Bénézech<sup>1</sup>, O.S. Pokrovsky<sup>1</sup>,  
E. Gerard<sup>3</sup>, B. Menez<sup>3</sup>, H. Alfredsson<sup>2</sup>*

<sup>1</sup>*Géochimie et Biogéochimie Expérimentale, LMTG, CNRS, Université de Toulouse, 14 Avenue Edouard Belin 31400, Toulouse, France*

<sup>2</sup>*Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavík, Iceland*

<sup>3</sup>*Institut de Physique du Globe de Paris, 1 rue Jussieu, 75238 Paris, France*

This work is aimed at quantification of olivine (Fo<sub>92</sub>) and amorphous basaltic glass ( $\beta$ -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<sub>2</sub>. Dissolution rates were also measured in mixed-flow reactors at pH 6 and 8-9 in the presence of live and dead bacteria in nutrient-rich and nutrient-free solutions. Intracellular uptake and reversible surface adsorption of Mg, Si and  $\beta$ -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<sub>2</sub> and 0.05 M NaHCO<sub>3</sub> 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  $\beta$ -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  $\beta$ -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<sub>3</sub> solutions, and only in circumneutral, CO<sub>2</sub>-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  $\beta$ -glass reactivity under conditions of CO<sub>2</sub> storage and negligible effect of bacteria and their lysis products and exometabolites on mineral dissolution in alkaline, carbonate-bearing solutions.

## 61 - Did seafloor carbonation regulate high pCO<sub>2</sub> on the ancient Earth?

*Damon A.H. Teagle<sup>1</sup>, Rosalind M. Coggon<sup>2</sup>, Heiko Pälke<sup>1</sup>, Jeffrey C. Alt<sup>3</sup> and Christopher E. Smith-Duque<sup>1</sup>*

*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., pCO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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).*

## **62 - 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 H<sub>2</sub> (and CH<sub>4</sub>) 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 CO<sub>2</sub>-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 H<sub>2</sub> 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, Fe<sub>0</sub>, and peridotite with CO<sub>2</sub>-rich seawater under highly reducing conditions. In these experiments, we measure the extent of H<sub>2</sub> generation during the rock-water reaction in the presence and absence of microorganisms, and determine the rates of conversion of H<sub>2</sub> and CO<sub>2</sub> to CH<sub>4</sub> as the reactions proceed. In addition, because a key control on H<sub>2</sub> generation is the oxidation of Fe(II) to Fe(III) associated with the reduction of water to H<sub>2</sub>, 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 CO<sub>2</sub> reaction with ultramafic rocks.

### **63 - Experimental study on the CO<sub>2</sub>-water-basalt interaction: Implications for a carbonate formation sequence during CO<sub>2</sub> basaltic aquifer storage**

*Yutaro Takaya*<sup>\*1</sup>, *Kentaro Nakamura*<sup>2</sup>, *Yasuhiro Kato*<sup>1</sup>

<sup>1</sup> *Department of Systems Innovation, Graduate School of Engineering, University of Tokyo, Tokyo 113-8656 Japan*

<sup>2</sup> *Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Kanagawa 237-0061 Japan*

*Email address: tt097074@mail.ecc.u-tokyo.ac.jp*

The CO<sub>2</sub> aquifer storage is one of the most promising methods to stabilize atmospheric CO<sub>2</sub> concentration[1]. However, there is a major concern with the large scale implementation of CO<sub>2</sub> aquifer storage whether injected CO<sub>2</sub> will be stored safely over a long period of time. The geochemical trapping is an important mechanism for providing long-term security of CO<sub>2</sub> aquifer storage and a series of transformation where injected CO<sub>2</sub> (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<sub>2</sub> aquifer storage because basaltic rocks contain high concentrations of Ca, Mg, Fe and Na that can enhance CO<sub>2</sub> geochemical trapping via acid neutralization and carbonate mineral formation[2]. So we conducted CO<sub>2</sub>-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<sub>2</sub> storage in a basaltic aquifer, leading to dawsonite (NaAlCO<sub>3</sub>(OH)<sub>2</sub>) 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*

## 64 - Downhole magnetic and physical property logging of serpentinized peridotite and carbonate-altered serpentinite.

*Masako Tominaga<sup>1</sup> and Frieder Klein<sup>1,2</sup> (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<sub>3</sub>O<sub>4</sub>: Fe<sub>2</sub>O<sub>3</sub> = 480K: 2.5K A/m), magnetic susceptibility (abundance of magnetic minerals)(Fe<sub>3</sub>O<sub>4</sub>: Fe<sub>2</sub>O<sub>3</sub>=0.1-20 : 0.001-0.0001 SI), and resistivity (Fe<sub>3</sub>O<sub>4</sub>: Fe<sub>2</sub>O<sub>3</sub> =5x10<sup>-5</sup> -x10<sup>3</sup>: 3.5x10<sup>-3</sup>-x10<sup>7</sup>); 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<sub>2</sub>-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<sub>2</sub> 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.



## 65 - Peridotite fracture surface reaction rates for in-situ CO<sub>2</sub>-mineralization in ophiolites

*Van Noort R.<sup>1</sup>, Spiers C. J.<sup>1</sup>, Kandianis M. T.<sup>2</sup>, Drury, M. R.<sup>3</sup>, and ten Grotenhuis, S.M.<sup>1</sup>*

*1 HPT-Laboratory and 3 Mantle Petrology Group, Utrecht University, Faculty of Geosciences, P.O. box 80021, 3508 TA Utrecht, The Netherlands, vannoot@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 CO<sub>2</sub>-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 CO<sub>2</sub>-injection pressures will strongly enhance olivine dissolution and hence carbonation rates. The key issues controlling the effectiveness of peridotite carbonation as a CO<sub>2</sub>-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 CO<sub>2</sub>-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 CO<sub>2</sub>-mineralization, CO<sub>2</sub>-mineralization using peridotites may only be feasible if CO<sub>2</sub>-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.

## 66 - Fracture propagation during in-situ mineral carbonation in peridotite

*Van Noort R.<sup>1</sup>, Spiers C. J.<sup>1</sup>, Kandianis M. T.<sup>2</sup>, Drury, M. R.<sup>3</sup>, and ten Grotenhuis, S.M.<sup>1</sup>*

*1 HPT-Laboratory and 3 Mantle Petrology Group, Utrecht University, Faculty of Geosciences, P.O. box 80021, 3508 TA Utrecht, The Netherlands, vannoot@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 CO<sub>2</sub>-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 CO<sub>2</sub> with these rocks support the application of this approach; however, geological sequestration of CO<sub>2</sub> in dense, crystalline peridotites involves considerable geomechanical challenges. First, peridotite rock is non-porous and exhibits low permeability, therefore the sequestration of CO<sub>2</sub> by injection and in-situ mineralization requires fracturing the host rock to create porosity and permeability. In addition, the reaction between CO<sub>2</sub>-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 CO<sub>2</sub> that can be injected. To attain the extent of carbonation required for substantial CO<sub>2</sub>-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 CO<sub>2</sub>-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 CO<sub>2</sub>-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 CO<sub>2</sub>-transport within the simulated peridotite fracture. Slow diffusive transport of dissolved CO<sub>2</sub> 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 CO<sub>2</sub>-mineralization in peridotite bodies, this implies that diffusion of CO<sub>2</sub> 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 CO<sub>2</sub>-storage.

## 67 - 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](mailto: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.

## 68 - The potential for carbon sequestration by accelerated weathering of mafic rocks at ambient pCO<sub>2</sub>

*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 prerequisite for capture of CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> removal by basalt weathering (Dessert et al. 2003) ranges from ~3 t C km<sup>-2</sup> yr<sup>-1</sup> to ~75 t C km<sup>-2</sup> yr<sup>-1</sup>. For an illustrative calculation, if all basalt (6.8 × 10<sup>6</sup> km<sup>2</sup> of the modern Earth's surface) weathered at the highest observed rates today, then basalt weathering would sequester ~0.5 Gt C yr<sup>-1</sup>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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. CO<sub>2</sub> Capture and Transport. *Elements* 4: 311-317.

## 69 - Dissolution of CO<sub>2</sub> gas is rate limiting to C sequestration in high-salinity alkaline brines

*Siobhan Wilson<sup>1</sup>, Shaun Barker<sup>2</sup>, Anna Harrison<sup>2</sup>, Ian Power<sup>2</sup>, Greg Dipple<sup>2</sup>, K. Ulrich Mayer<sup>1</sup>, Viorel Atudorei<sup>3</sup>.*

<sup>1</sup>*Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1405, U.S.A.*

<sup>2</sup>*Mineral Deposit Research Unit, The University of British Columbia, Vancouver, BC V6T 1Z4, Canada*

<sup>3</sup>*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<sub>2</sub>) 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<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·~5H<sub>2</sub>O], 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)<sub>2</sub>].

δ<sup>13</sup>C values of dissolved inorganic carbon content and synthetic dypingite are significantly more negative than those predicted for equilibrium exchange of CO<sub>2</sub> gas between the atmosphere and solution. The measured δ<sup>13</sup>C of aqueous carbonate species is consistent with a kinetic fractionation that results from a slow diffusion of atmospheric CO<sub>2</sub> into solution. Modeling using PHREEQC indicates the concentration of dissolved inorganic carbon expected at equilibrium with atmospheric CO<sub>2</sub> 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 δ<sup>13</sup>C values become more negative, indicating that the rate of CO<sub>2</sub> uptake into solution was outpaced by the rate of carbon fixation within the precipitate. This implies that CO<sub>2</sub> gas uptake is rate limiting to CO<sub>2</sub> fixation. δ<sup>13</sup>C of carbonate mineral precipitates in mine tailings and of DIC in mine process waters display similar <sup>13</sup>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<sub>2</sub>. Carbon sequestration could be accelerated by increasing the partial pressure of CO<sub>2</sub> in tailings ponds and natural ultramafic formations, or by using chemicals that enhance the uptake of gaseous CO<sub>2</sub> into aqueous solution.

## 70 - Depleted basaltic oil and gas reservoirs: Potential economic and efficient reservoirs for CO<sub>2</sub> 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: [jjunfeng@nju.edu.cn](mailto:jjunfeng@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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> sequestration due to the rocks' relative rapid chemical reaction with CO<sub>2</sub>-saturated 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<sup>2</sup>. We found more than 10 layer of basalts that are interbedded with hydrocarbon source rocks, covering an area of more than 20,000 km<sup>2</sup>. 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<sup>3</sup> 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<sub>2</sub> migration or at least slow the migration sufficiently to allow time for the mineralization reactions to occur.

We estimate a total 3,000 km<sup>3</sup> of basalts with an average bulk porosity of 3%. This translates to 90 km<sup>3</sup> of potential pore volume for CO<sub>2</sub> 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<sub>2</sub> by carbonate.

## 71 - Aqueous Carbonation of Natural Brucite for CO<sub>2</sub> Sequestration

*Liang Zhao<sup>1</sup>, Liqin Sang<sup>1</sup>, Jun Chen<sup>1</sup>, Junfeng Ji<sup>1</sup>, and H. Henry Teng<sup>1,2</sup>*

*<sup>1</sup>Department of Earth Sciences, Nanjing University, Nanjing, Jiangsu, 210093, PRC*

*<sup>2</sup>Department of Chemistry, the George Washington University, Washington, DC, 20052, USA*

Experimental study is carried out at conditions of room temperature and moderate CO<sub>2</sub> 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 CO<sub>2</sub> to generate Mg<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>, followed by precipitation of magnesium carbonate phases from aqueous solutions. This leads to our proposition that direct heterogeneous reaction between hydrated CO<sub>2</sub> and solid phase of Mg(OH)<sub>2</sub> is probably not the pathway for the overall carbonation process. Assuming the upper limit of carbon content C<sub>max</sub> = 8.7% (based upon that of nesquehonite), measured total carbon in the product C<sub>tot</sub> 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.

## **72 - Carbonation Reaction Driven Permeability and Porosity Evolution in Thermally Cracked Dunites.**

*Zhu, Wenlu. University of Maryland. [wzhu@umd.edu](mailto:wzhu@umd.edu)*

*Lisabeth, Harrison. Columbia University. [hpl2105@columbia.edu](mailto:hpl2105@columbia.edu)*

Capture and storage of atmospheric CO<sub>2</sub> by the reaction Olivine + CO<sub>2</sub> ⇌ Magnesite appears to be one of the safest long-term options for CO<sub>2</sub> 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 CO<sub>2</sub>-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.



### **73 - 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](mailto:richard@hunwickconsultants.com.au)*

*[www.integratedccs.com.au](http://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 fracturing-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.