

**Calorimetric Investigation of Olivine Carbonation
as a mechanism of Carbon Sequestration**

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By

Chuen Wing Lam

Thesis Advisor

Gregory E. Ravizza

**I certify that I have read this thesis and that, in my opinion, it is
satisfactory in scope and quality as a thesis for the degree of
Bachelor of Science in Global Environmental Science.**

THESIS ADVISOR

**Gregory E. Ravizza
Department of Geology and Geophysics**

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Abstract

According to numerous global-scale climate models, continuously increasing anthropogenic CO₂ emissions will cause drastic consequences for climate. In an attempt to solve the on-going climate challenge, scientists have proposed various large-scale geological sequestration of CO₂ from our atmosphere. Olivine carbonation is considered as a promising carbon sequestration method due to the long-term stability of product minerals, magnesite and quartz. Examining reaction rate and thermodynamics of olivine-CO₂-H₂O reaction to form magnesite and quartz can provide data needed to determine if this approach is too costly to be practical. The goal of this project is to use calorimeter to quantify the enthalpy and reaction rate of olivine carbonation reaction under conditions considered to be close to optimal for mineral carbonation. These data are needed to predict the heat generation under optimal temperature of 185°C and our limited pressure of 700psi. If this reaction is very exothermic and rapid, then this will help to lessen the energetic cost associated with achieving the high temperatures and pressures required to drive olivine carbonation. If this project is successful, the results will represent an important contribution to evaluating the utility of olivine carbonation as a carbon sequestration method. Significant exothermic reaction has been documented by heat flux changes and 16.7% of the initial CO₂ is captured during the course of experiment under sealed calorimetric system. The heat production of olivine carbonation is still not yet measurable due to experimental artifacts that have prevented accurate heat flux measurements.

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Introduction and Background

The Climate Challenge

Stabilizing atmospheric greenhouse gases has become one of the greatest challenges of mankind in the 21st century. The increasing rate of greenhouse gas emissions, in particular carbon dioxide emissions, is having a significant impact on the global greenhouse effect, and potentially causing dramatic climate changes according to numerous global-scale climate models. Quaternary geologic, isotopic, and glaciological records indicate that the earth's climate system can be extremely sensitive and even fragile (Kump et al. 2000). The imbalance between anthropogenic CO₂ emission and the natural carbon sinks will eventually extend the effects on global warming, not only to the atmosphere but included, among others, the ocean acidification and the fertilization of oceanic and terrestrial ecosystem (Lackner 2003). Positive feedbacks are commonly observed during the transition period between glacial and interglacial era within multi-millennial time scale. These feedbacks may result in threshold responses that potentially alter earth's climate in a relatively longer time period (Kump et al. 2000). Both past climatic records from Greenland and mountain glaciers ice cores and simulations of Earth's future climate models from IPCC 2006 indicate that subtle changes within the earth's system may result in amplified feedbacks. As a result, scientists, as well as politicians have urged immediate actions in attempt to address the concerns on climate change. Reduction of carbon dioxide emissions becomes inevitable, in order to stabilize the phenomenon of the greenhouse effect. The strategies to solve this ever-changing problem require a delicate balance between economics, politics, and a complete understanding of environmental technology (Oelkers et al. 2008). Every important decision in the future that society makes to solve the current climate

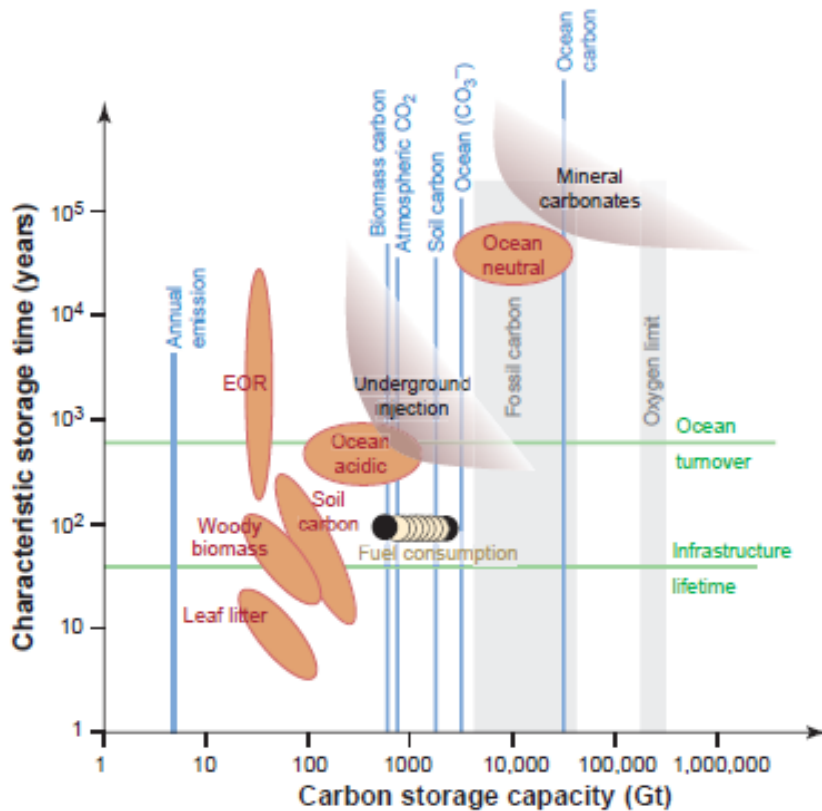
challenge should be supported by the best available scientific knowledge. One side of the solution is the conservation and development of non-fossil fuel energy sources. Meanwhile, alternative solution, such as carbon sequestration (see next section), also plays an important role in reducing global atmospheric greenhouse gases concentrations.

Demands for Fossil Fuel

The demand of fossil fuel will only increase in the foreseeable future if no alternative sources of energy are developed and be ready to use. The Energy Information Administration estimates an increase in world energy consumption of 60% between 1999 and 2020 (Lackner 2000). This estimation has excluded the exponential growth of future population and its corresponding demand in energy for the next century. Although the world's leading countries are developing strategies and examining new sources of energy to halt the rise of CO₂, the developing countries are facing economic difficulties and shortages of applicable technologies to keep pace with the ongoing movement. However, the worldwide political situation also changes rapidly. Development of alternative energy sources and accelerating consumption of fossil fuels happen simultaneously within major developing countries, such as, China and India. Over 5000 gigatons of carbon (GtC) are currently stored as fossil fuels worldwide. While the consumption rate is only 6GtC per year, fossil fuels are presented in sufficient quantities to fuel the entire planet for at least 50 years (Lackner et al. 2008). Fossil fuel, therefore, will still remain as a dominant source of energy among most of the world's nations. Unless there are revolutionary scientific breakthroughs to greatly reduce the price of other clean, easy-installed and effective alternative sources of energy, an additional strategy to halt CO₂ rise is highly needed.

Carbon Sequestration, Strategy for reducing CO₂ emission

The current climate challenge and growing demands in fossil fuel have focused the attention onto carbon capture and storage technologies, carbon sequestration. According to the IPCC special report on Carbon Dioxide Capture and Storage (IPCC, 2005), carbon sequestration is considered the single most promising solution to solve the ongoing increases of greenhouse gases emissions. Large-scale carbon sequestration strategies include the capture of carbon dioxide generated by electrical power plants, and of that already present in the atmosphere. Carbon sequestration also includes strategies to dispose CO₂. To choose the best carbon sequestration approach, two factors should be priorities in consideration: estimated storage capacity and average storage time (Fig 1.)(Lackner 2003). If society decides to reduce current carbon emissions primarily based on carbon sequestration, the total required carbon storage in the 21st century is estimated to exceed 600 Gigatons of Carbon (GtC), and would possibly reach up to 2,400 GtC (Lackner 2003). Figure 1. shows various carbon sequestration methods based on the estimated storage capacities and times. The lower left corner includes most of the bio-sequestration methods. Generally, bio-sequestration methods have short storage times and low storage capacities compared to geological sequestration methods, which occupy the upper right corner.



Estimated storage capacities and times for various sequestration methods. The "fossil carbon" range includes at its upper end methane hydrates from the ocean floor. The "oxygen limit" is the amount of fossil carbon that would use up all oxygen available in air for its combustion. Carbon consumption for the 21st century ranges from 600 Gt (current consumption held constant) to 2400 Gt. "Ocean acidic" and "ocean neutral" are the ocean's uptake capacities for carbonic acid and neutralized carbonic acid, respectively. The upper limits of capacity or lifetime for underground injection and mineral carbonates are not well constrained. EOR stands for enhanced oil recovery.

Figure 1. Estimated Storage capacities and times for various sequestration methods (Lackner 2003)

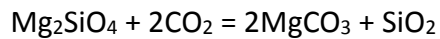
Olivine carbonation is classified as one of the major mechanisms of geologic sequestration and would be included in the mineral carbonation field in figure 1. On geologic time scales and at ambient surface temperature silicate weathering and subsequent mineral precipitation, naturally consumes atmospheric carbon dioxide, sequestering it as solid carbonate minerals.

Enhancing the natural weathering process becomes conceptually appealing due to its stability of the resulting carbonate minerals and massive storage capacity. The mass of carbon currently in the atmosphere is approximately 800GtC where ~39,000,000 GtC are stored in carbonate rocks in the Earth's crust (Oelkers et al. 2008). About 0.1 GtC are captured per year by mineral weathering and require up to 8,000 years consuming the global atmospheric CO₂ inventory (Kelemen and Matter 2008). Research shows, it is possible to enhance the rate of carbonate formation under certain circumstances including high temperature. The reaction rate can reach up to 1 million times more rapid compared to the natural reaction rate and could potentially consume billions of tons of atmospheric CO₂ every year (Kelemen and Matter 2008). As a result, mineral carbonation has comparative advantages over other carbon sequestration methods in term of effectiveness. In specific, olivine carbonation certainly stores atmospheric carbon relatively permanently in comparison with photosynthetic carbon fixation. The technology, however, is still immature. Kinetics of olivine and serpentine carbonation are slow in laboratory experiments unless reactants are finely grounded to increase surface area. Other challenges including the maintenance of optimal pressure and temperature are still underdeveloped. Before scientists are able to thoroughly understand the kinetics and effectively address these issues, the costs associated with mineral carbonation, in specific, olivine carbonation are still poorly known (Kelemen and Matter 2008).

Olivine Carbonation

Earth's mantle is largely composed of olivine minerals [(Mg, Fe)₂SiO₄] and pyroxene [(Ca,Mg,Fe)₂Si₂O₆] (Kelemen and Matter 2008). These minerals react constantly with water and CO₂ in the atmosphere to form serpentine, magnetite and carbonates (calcite, magnesite, and

dolomite) (Kelemen and Matter 2008). Numerous onsite studies have been launched in attempt to investigate the geology and to approximate the volume of carbonate deposits formed through the weathering of peridotite. In Samail ophiolite, Oman, natural mineral carbonation consumes up to 4×10^7 kg of atmospheric CO_2 per year (Kelemen and Matter. 2008). In particular, the studies of olivine—magnesite reaction, which can be represented as the following chemical equation, draw most of the interest due to its relatively high reactivity among other minerals.



Mg-olivine + Carbon Dioxide = Magnesite + Quartz

Based on these findings, Kelemen and Matter estimate that up to 10% of the annual anthropogenic CO_2 flux could be consumed if this natural weathering reaction within the Oman ophiolite could be accelerated 100,000 times through weathering horizon extension and thermal expansion. Mineral carbonation, in addition, is suggested to evolve 760KJ of energy per kilogram of Olivine (Kelemen and Matter 2008). If this model is true and is feasible in the real world setting, olivine carbonation would be economically favorable. The reaction can also be sustained by its self-generated heat and achieve “minimal energy cost”. Laboratory experiments also show a conversion of over 80% of magnesite in less than an hour under proper set of condition is possible (Gerdemann et al 2003). These geologic and laboratory studies provide valid evidences on the potential effectiveness of mineral carbonation

Theoretically, injecting CO_2 rich fluid under optimal temperature could enhance the rate of olivine carbonation. The reaction rate maximizes at 185°C and 150 bars CO_2 pressure (Fig 2), as the temperature approaches the equilibrium phase boundary between serpentine and

magnesite. Kelemen and Matter propose an equation to estimate the carbonation rate using $\leq 75\mu\text{m}$ of olivine grain and is illustrated as (Fig 2),

$$\Gamma = 1.15 \cdot 10^{-5} (P(\text{CO}_2), \text{bar})^{1/2} \exp[-0.000334(T-185^\circ\text{C})^2]$$

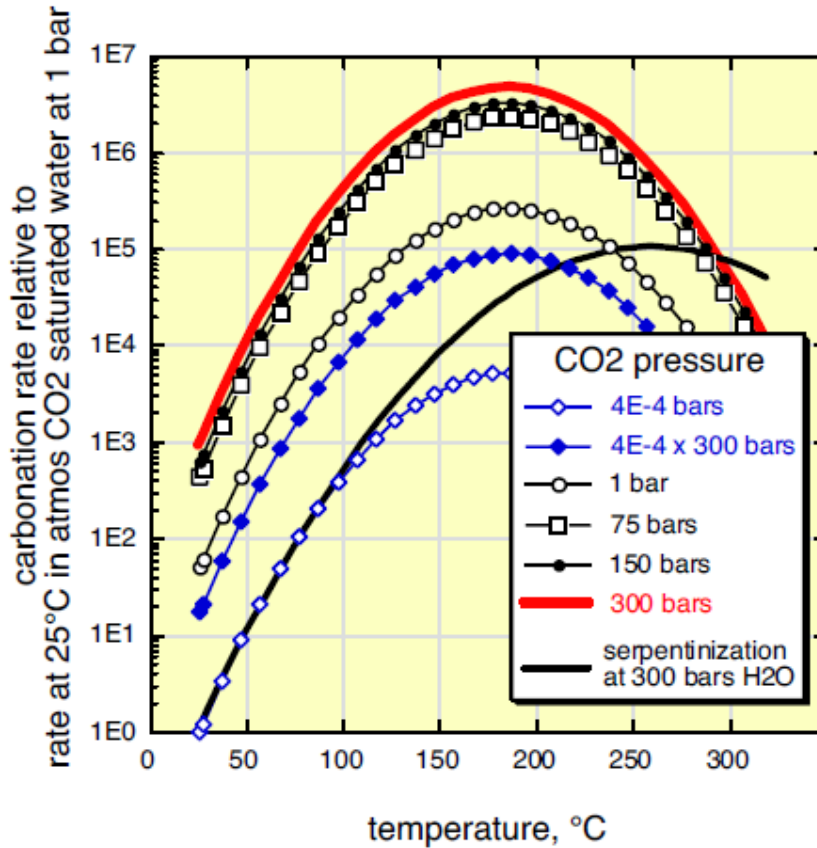


Figure 2. Rate of olivine carbonation as a function of temperature and pressure, compared with the rates at 25°C for surface water equilibrated with the atmosphere at 1 bar (Kelemen and Matter 2008).

The optimal temperature is limited at 185°C primarily due to two factors: (1) Carbon dioxide solubility decreases and two immiscible CO₂-rich and H₂O-rich fluid form (Gerdemann et al 2003, Shyu 1996). (2) Magnesite formation becomes thermodynamically less favorable than serpentine formation because of the formation of immiscible CO₂-H₂O fluids. Both fluids are thermodynamically unstable and constantly interact. Heat flux measurements become complex

when the thermodynamic instability needs to be taking into account. Partial pressure of CO₂, in addition, is directly proportional to the rate of reaction. Higher the partial pressure enhances the CO₂ activity, and thus, enhances the reactivity of the overall olivine carbonation (Fig. 3) (Gerdermann et al 2003).

Beside the rate of reaction, the exothermic property of olivine carbonation also maximizes at the optimal temperature of 185°C and optimal pressure of 150bar (Kelemen and Matter 2008). When designing strategy for large-scale industrial olivine carbonation, in either in situ or ex situ settings, the exothermic property of olivine carbonation is crucial. To maintain the internal temperature in reaction site, however, factors including, availability of water, thermal diffusivity, mineral's dimensions, porosity of fluid and chemical/physical properties of involved materials are equally important.

To summarize the significance of olivine carbonation, it is extremely important to understand the limitation of the carbonation reaction. The current understandings of olivine carbonation primarily base on the experimental report of Gerdermann et al 2003 and the model simulation of Kelemen and Matter 2008. Both of their works are simple representation of this complicated weathering process. In this senior project, two major concerns that have not been raised in Gerdermann's and Kelemen's paper will be further investigated.

First of all, how exothermic can olivine carbonation be? Kelemen and Matter proposed that 760kJ of energy would be generated for every kilogram of carbonated olivine. However, theoretical calculation on enthalpy change from Gerdermann et al. suggests a production of 10.3Kcal or 43.12kJ for every mole of olivine reacted at room temperature. This theoretical calculation further suggests that only 7.20kJ of energy would be generated for every kilogram of Olivine reacted. These mismatching information, possibly due to pressure and composition differences, lead to a question on the fundamental effectiveness of self-sustained olivine

carbonation. Calorimetric investigation is performed in this senior project to accurately measure the exothermic property of olivine carbonation when pressure and temperature are both maintained. If the exothermic property of olivine carbonation is overestimated, olivine carbonation would become economically less appealing because additional amount of energy would be needed to support the reaction.

Second of all, experimental data constraining the rate and enthalpy of olivine carbonation are very limited. In addition the calculation by Kelemen and Matter do not account for the effects of fluid immiscibility. In CO₂-H₂O system, the interaction of supercritical CO₂ fluid and H₂O at temperature of 185°C and pressure of 150atm suggested by Gerdermann et al and Kelemen and Matter was not mentioned in either of their publications. Such an interaction was well described in studies of Enhanced Oil Recovery (Shyu et al 1996). Shyu et al examined property of CO₂-H₂O binary system under similar condition. To maintain the phase equilibrium at 185°C and 150atm, two immiscible fluids, a CO₂-rich layer and a H₂O-rich layer, as well as a pressurized gas phase would be created. Submerging olivine in either CO₂ or H₂O-rich layers would significantly alter the rate of reaction, as well as the enthalpy of the carbonation process. The actual impacts, nevertheless, are still poorly known. In attempt to better understand the overall effects of binary interaction, EDS analyzes are carried to compare the different in composition when pressurized CO₂-rich fluid and pressurized H₂O-rich fluid are used separately. Results will be compared and conclusion on the overall effectiveness of olivine carbonation will be drawn based on the measureable rate that olivine carbonation processes, the total energy generated throughout the course of experiment. Ultimately, data of the sort production in this study are required to determine if olivine carbonation is an appealing approach of carbon sequestration.

Obtaining the perfect recipe, specifically in determining the appropriate proportion of CO₂ and H₂O in order to maximize the carbonation process, requires full understanding of the kinetics of olivine carbonation and the thermodynamics of CO₂-H₂O interaction. Due to limited experiment data and poor understanding on binary CO₂ and H₂O interacting system during olivine carbonation, there is an obvious need in addressing these major concerns before olivine carbonation is accepted as a practical and economically favorable approach of carbon sequestration. The recipe is not only the first step to implement any large-scale industrial olivine carbonation, but also the ultimate and ideal goal of this senior research project. However, at the scope of this project, this goal is yet still too far.

Methods

Strategy

To study the reaction of olivine carbonation qualitatively and quantitatively, using facilities available, two distinct approaches are chosen. The first approach, closed system oven experiment, is designed to qualitatively observe visual changes on the olivine crystals surfaces under optimal temperature at 185°C and the maximum CO₂ pressure resistance of our glass tubes at approximately 50bar, but with various mixture compositions. This approach provides a broad vision on how changing CO₂ mole fraction would affect olivine surface deposits. Analyzing surface deposits allows us to estimate regions in the CO₂-H₂O phase equilibrium graph where olivine carbonation is most favorable. Once we know how olivine carbonation proceeds in various mixtures, calorimetric quantitative measurements are performed to further investigate thermal properties, such as enthalpy olivine carbonation under the most favorable condition that we are able to achieve. Products and residues after both oven experiments and calorimeter experiments are subjects to analyze using energy dispersive system, also known as, energy dispersive X-ray spectroscopy (EDS) to evaluate the extent of reaction. However, due to limitation on time, only sample from oven experiment has been examined. In the calorimeter experiment, besides directly examining surface alternation under EDS, the reaction can also be monitored or quantified by measured pressure drops and heat generation.

Close System Oven Experiment

Closed system oven experiments are designed to observe the visual change on the olivine crystals surface after carbonation. To achieve the desired pressure of CO₂, dry ice is used, not only to generate our desired pressure inside the experimental glass tubes, but also serve as carbon source. After recording the mass of materials, including olivine crystals, dry ice and water, glass tubes are sealed completely by propane-oxygen torch. As safety precaution, the sealed glass test tubes are placed inside steel pipes closed at each end with threaded caps. The encased tubes are then placed into an oven that has been programmed to maintain at temperature of 185°C for over 50 hours to provide sufficient time for any possible reaction. After cooling down the oven, the sealed test tubes are opened and the crystals are removed and examined using EDS.

Under the optimal condition for olivine carbonation at 185°C and, in our condition of limited 50 bar pressure, two immiscible fluids, one as CO₂-rich and one as H₂O-rich, form (fig. 4). As temperature increases, solubility of carbon dioxide in water decreases (Gerdermann et al. 2003). Immiscible fluids exist at equilibrium (Shyu et al 1995). The corresponding pressure generated by the interaction of the two immiscible fluids is strictly related to the CO₂ mole fraction and temperature and is calculated using Duan et al. 2008 Equation of States (EOS) model.

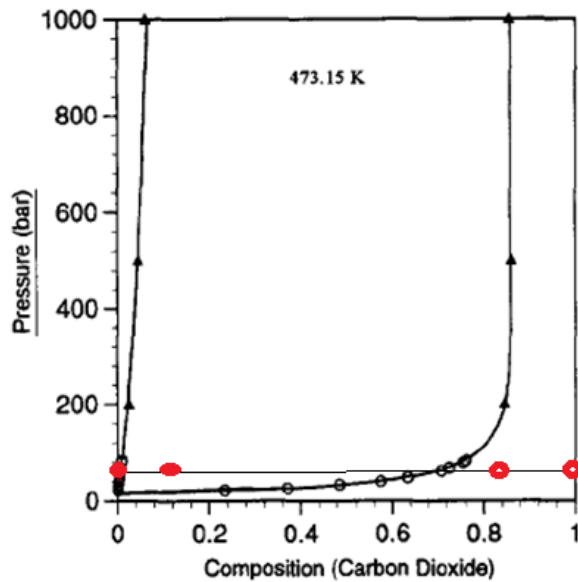


Figure 3. Phase diagram for CO₂ + H₂O at 473.15K. Red Circles indicate the conditions we try to achieve in our experiments (Shyu et al 1997)

To address the variations of immiscible fluids, 4 different fractions of CO₂ were proposed, 1) A pure H₂O fluid, 2) A H₂O-rich fluid with 0.2 xCO₂ concentration, 3) A CO₂-rich fluid with 0.8 xCO₂ concentration, 4) A pure CO₂ phase. These four experiments use similar size of olivine crystals. Each tube has approximately 1.5-2g of dry ice initially. This amount is decided based on the pressure tolerance of our glass tubes. Ideally, each glass tube can sustain maximum of 60atm pressure. However if stress accumulates in the tips of the tubes as they are sealed with the torch they will fail at lower pressures. In fact, several tube experiments exploded in the oven. At room temperature, 2g of dry ice corresponds to 40bar of pressure. When the test tubes are heated up to 185°C, the corresponding pressure could possibly reaches up to 92bar based on Duan et al Equation of State (EOS). The actual pressure, under Duan's CO₂-H₂O equation of state model is 10% lower than the pressure that the ideal gas law suggested because the compressibility factor (Z) decreases away from 1 as the mole fraction of CO₂

decreases (Duan et. al. 2008). The limiting factor in this experiment is water and approximately 2g of water is used in all of our tubes (Table 1).

	Pure H ₂ O	H ₂ O-rich	CO ₂ - rich	Pure CO ₂
Amount of Dry Ice (mole)	0.00	0.0309	0.0528	0.0729
Amount of Water (mole)	0.0605	0.168	0.0112	0.00
xCO ₂	0.00	0.155	0.825	1.00
Pressure (bar) at 25C	0	13.00	37.66	79.27
Pressure (bar) at 185C	47.78	42.75	92.08	119.638

Table 1. Composition of 4 sample tubes in closed system oven experiment (3sig.fig.)and their corresponding pressure at room temperature

The major technical challenge of this closed system oven experiment is sealing off the glass tubes. To perfectly seal the test tubes, gas exchange between the tubes and outside environment should be minimized. If gases are trapped between melting glass during sealing, weak point would produce. Glass tubes would then break easily at the weak point when all dry ice has melted completely or later when it heats up. The major gas exchange encountered is the melting of dry ice when it co-exists with water and the relatively hot olivine surface. To solve this problem, liquid nitrogen is used to freeze all materials at the bottom of the glass tubes while the mouth of the glass tube is being sealed on the top.

Calorimetric Investigation of Olivine Carbonation

The calorimetric approach is designed to quantify the thermal properties of olivine carbonation. Heat flux into or out of the sample cell can be measured continuously. Under proper conditions, these heat flux measurements can be used to determine the enthalpy of reaction. Shown in Figure 5 is a schematic diagram of the calorimetric system. At the heart of the calorimetric system is a Calvet-Tian calorimeter (Setaram Model BT2.15).

Calorimeter

A calorimeter is a device invented specifically to perform highly accurate heat flow measurements which occur during chemical reactions and/or physical transformations. Calorimeters are commonly used to determine thermodynamic properties of materials such as heat capacity, heat of vaporization, and heat of fusion. In this study, a Setaram Model BT2.15 II differential scanning calorimeter was employed. Figure 5 shows a schematic diagram of this calorimeter.

A differential scanning calorimeter measures the amount of heat absorbed or released by a sample to the calorimetric block and compares it to the amount of heat absorbed or released by a reference to the calorimetric block. When the sample undergoes a physical and/or chemical change, more or less energy will be absorbed by the sample cell compared to the reference cell.

As shown in Figure 5, the BT2.15 calorimeter employed in this study has two experimental chambers which are connected to the calorimetric block by an array of thermocouples. One experimental chamber contains the reference cell, which is empty,

vacuumed, and sealed. The other experimental chamber contains the sample cell. The BT2.5 calorimeter can perform experiments on relatively large samples over a wide range of temperatures and pressures. The temperature range of the calorimeter goes from -196C to 200C, is measured by a thermosensor located between the sample and reference chamber, and is adjusted using resistance wiring and liquid nitrogen. The sample cell has a maximum pressure rating of 1500psi, or 103.4bars and is connected to a 6.35 mm (0.25 inch) o.d., 5.0 mm (0.194 inch) i.d. stainless steel tube. Gas can be transported into and out of the sample cell via this stainless steel tube. The volume of the sample cell is 8.5 milliliters.

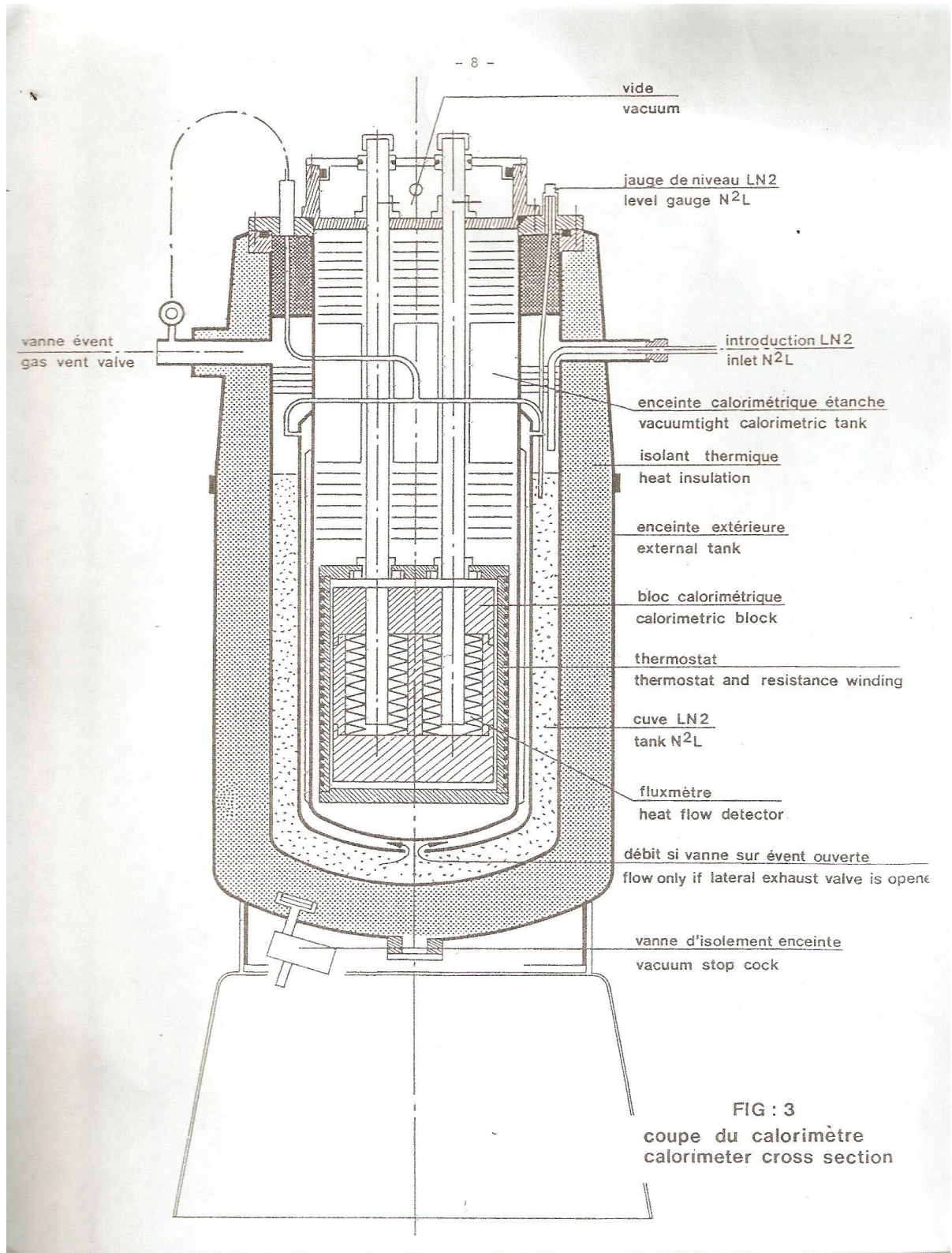


Figure 4. Calorimeter cross section (Calorimeter Manual)

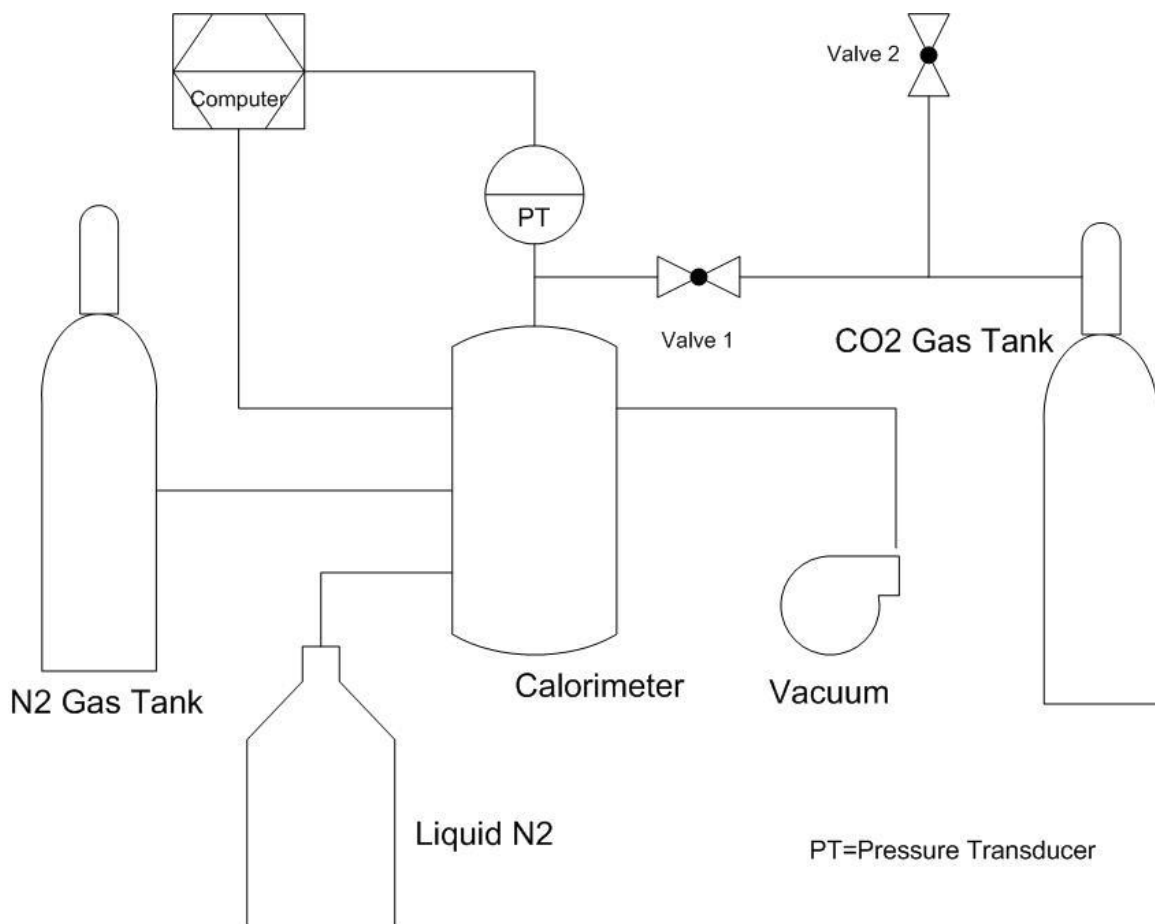


Figure 5. Calorimeter system and Gas supply lines schematic diagram.

Gas supply lines

The sample cell in the calorimeter is connected to a 6.35 mm (0.25 inch) o.d., 5.0 mm (0.194 inch) i.d. stainless steel tube, which allows for gases to be transported into and out of the cell. This gas tubing is connected to a pressure transducer (PT) located at the entrance to the calorimeter. The pressure transducer records the pressure within the cell. The sample cell and the pressure transducer are connected to both a vacuum pump and Grade 4.0 (i.e. 99.99% purity) carbon dioxide bottle. The vacuum pump is used to evacuate the circulating nitrogen gas

inside the calorimeter and gas lines between experiments and is connected to valve 2.

Nevertheless, there is a possibility that the fine grain samples would leave the cell during vacuum. In this case, valve 2 is closed and the gas lines would not be evacuated.

Grade 4.0 (i.e. 99.99% purity) nitrogen gas is also employed both as a purge gas for the gas lines, as well as, a purge gas for the calorimeter. The nitrogen line for the calorimeter is split into two legs. One line feeds directly into the calorimeter as a circulation gas. The other line is used to purge the gas lines between experiments.

Validating the methodology, heat capacity measurement

A calorimeter is a powerful tool for heat flow measurements because of its accuracy and sensitivity. Calorimeters are capable of measuring fractions of a microwatt of heat flow. To verify the accuracy of the calorimeter, specific heat capacity measurements of alumina and olivine were conducted. Specific heat capacity (c) is defined as the amount of energy (Q) required to increase the temperature of a known mass (m) of substance. Since initial mass is weighted and programmed rate of heat change are known, the heat capacity (c) is calculated based on the heat transferred (Q) to the sample. Measuring the specific heat capacity of alumina or olivine required two different experiments; one experiment without the sample and one experiment with the sample.

The protocol used to determine the specific heat capacity of alumina or olivine was as follows: the temperature of the calorimeter was set at 25°C and both the sample and reference cells were inserted into their respective chambers. The calorimeter was evacuated twice with a vacuum pump and filled with dry Grade 4.0 nitrogen gas. This was done to prevent moisture in

the air from entering the calorimeter chambers and affecting the heat flow readings. Both the sample and reference cells were then vacuumed, filled with dry Grade 4.0 nitrogen gas, and vacuumed again. Once the calorimeter has reached steady-state, the experimental program was started. The temperature of the calorimeter was held at 25C for one hour. The temperature was then ramped from 25C to 195C at a rate of 0.15K/min, and then held at 185C for one hour. The calorimeter was then cooled back to 25C. This experiment gives the heat flow to the cell. A known mass of alumina or dunite was then added to the sample cell, and the above procedure was repeated. The results of the verification experiments are given in Section 4.2.1.

Measuring Heat Generation of Olivine Carbonation

The results of the alumina and dunite heat capacity experiments demonstrate the accuracy of the calorimeter. After confirming the performance and capability of the calorimeter, a protocol similar to section 2.3.3 was used to measure the heat generation of olivine carbonation in a water/CO₂ environment. Similar to section 2.3.3, two experiments were required to measure the heat generation of olivine carbonation; one experiment with only water and carbon dioxide and one experiment with water, carbon dioxide, and olivine.

The protocol used to determine the heat generation of olivine carbonation was as follows: the calorimeter was set to 25C. A milliliter of distilled and deionized water was pipette into the sample cell to obtain a H₂O-rich fluid with CO₂ mole fraction of 0.23 under 600psi of CO₂ pressure because Gerderman et al. experiments and the oven experiments both suggest that H₂O rich fluid is more favorable for olivine alternation. The sample cell was sealed and both the

sample cell and reference cell were inserted into the calorimeter. The calorimeter was evacuated twice with a vacuum pump and filled with dry Grade 4.0 nitrogen gas to prevent moisture in the air from entering the calorimeter chambers and affecting the heat flow readings. The sample cell was vacuumed evacuated, filled with nitrogen gas to 20 psi, vacuum evacuated, and then filled with carbon dioxide to 600 psi for safety reason because the CO₂ regulator has maximum pressure output of only 800psi. Once the calorimeter has reached steady-state, the experimental program was started. The temperature of the calorimeter was held at 25C for one hour. The temperature was then ramped from 25C to 195C at a rate of 0.15K/min. The calorimeter was then held at 185C for three hours. The calorimeter was cooled back to 25C. This experiment gives the heat flow to the cell, a milliliter of DI water, and the carbon dioxide gas in the sample cell.

A second nearly identical experiment is then performed. The only difference between the two experiments is that in this experiment, a known mass of dunite was added to the sample cell. The amount of DI water in the sample was then increased to 2.5 milliliters. Given the density of olivine is 3.3g per cubic centimeter, maximum of 8.25g dunite powder would need to have all the water covering the dunite powder. Another set of experiments, one without dunite and one with dunite, were then performed.

Designing the most stable set-up under the uncertainty of CO₂-H₂O interaction has been the major challenge since the calorimetric approach is adapted. There are several factors, including pressure, temperature, and CO₂ mole fraction that could alter the rate of reaction. Allowing only one variable but other factors constant is the most ideal. Pressure, in specific, is one of the most challenging factors to monitor. Since the pressure transducer is located outside the calorimeter at room temperature connected with gas pipes, convection may occur allowing

heat transfer from the reaction cell to the pressure transducer and associated steel tubing. In our initial calorimeter runs a large CO₂ chamber (500ml) was attached to the calorimeter cell in order to maintain a nearly constant pressure during the course of an experiment. However, over the course of time we began to suspect that convection within the system was responsible for high frequency variations in heat flux measurements and large negative heat flux measurements. In order to minimize these effects we moved to successively smaller heat reservoirs; first to 150ml and finally to only the pressure transducer connected to the reaction cell via a short length of steel tubing. As discussed below, this gave rise to substantial pressure variation during the course of the experiment, but produced smoother time resolved heat flux measurements.

Developing appropriate methodology for accurate and precise calorimetric investigation on olivine carbonation consumed majority of our time. Although calorimetry has great potential to address our hypotheses, the thermodynamic is complicated enough to raise numerous technical concerns that need to be solved. The best adjustment has been applied and the current setting is considered as the most appropriate and generates minimum errors. Significant reactions are documented from the heat flux curve.

Results

Close System Oven Experiments – EDS Analysis

Results of oven experiments suggested most extensive olivine alteration is found in fluid of low mole fraction of CO_2 (Fig. 6.). Olivine crystal submerged in pure water after high temperature treatment also shows interesting precipitation (Fig. 7). The orange-red deposit indicates the formation of iddingsite, the common hydrothermal alteration product of olivine in weathering process (deer et. al 1966). The actual composition of the precipitation, due to the time constrain of our project, has never been examined. High CO_2 mole fraction fluid, on the other hand, shows the least surface alteration visually.

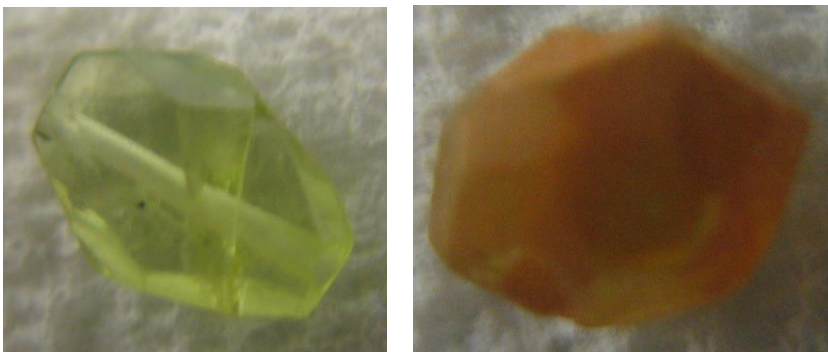


Figure 6. Visual comparison of untreated Olivine Crystal , sample 1 (Left) and Olivine crystal treated under fluid of low CO_2 mole fraction, sample 3 (right). Extensive surface alteration is observed in H_2O -rich fluid.

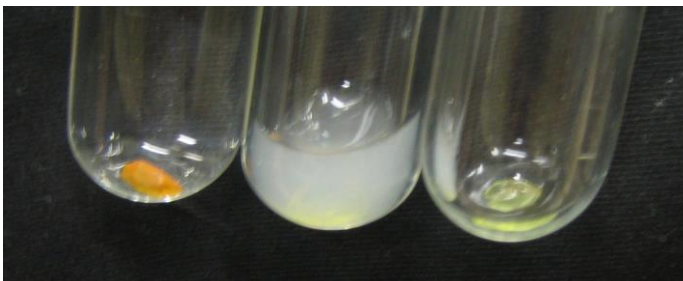


Figure 7. Visual comparison of H_2O -rich fluid with $x\text{CO}_2 = 0.155$, Sample 3 (left), pure H_2O (middle) and CO_2 -rich fluid with $x\text{CO}_2 = 0.825$, sample 2 (right). Surface alteration is not observed in pure H_2O fluid, instead we see formation of white precipitation.

The treated olivine crystals were further analyzed using energy-dispersive X-ray spectroscopy (EDS) on a micrometer scale of resolution to closely examine their surface alternated features. Olivine crystal that treated under high CO₂ mole fraction fluid (Sample 2) has similar surface features with the untreated olivine crystal (Sample 1). This result suggests the minimal surface alternation happens under CO₂-rich fluid (Fig. 8). Unlike sample 1 and sample 2, the olivine crystal that has treated under low CO₂ mole fraction fluid (Sample 3) shows extensive olivine alternation (Fig. 8).

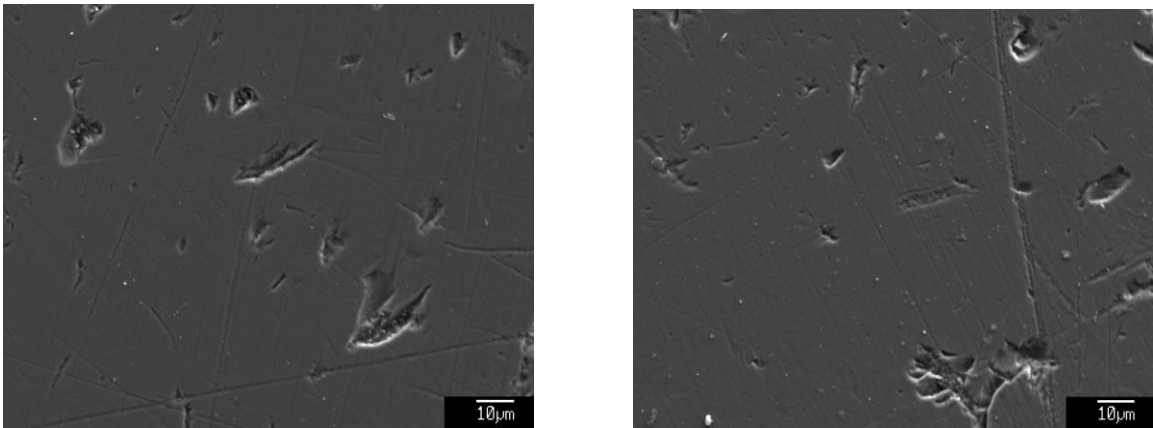
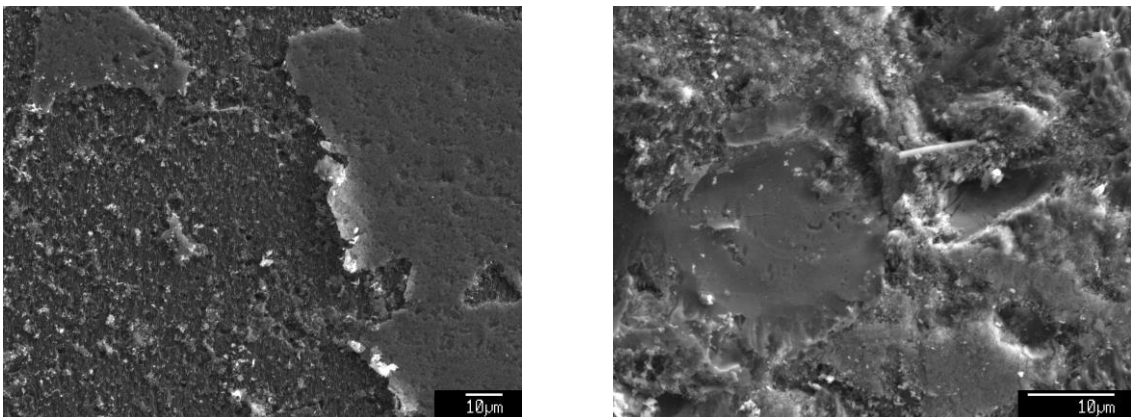


Figure. 8. EDS Microscopic visual comparison on olivine crystal surface that treated under solutions with various CO₂ mole fraction with resolution of 10 micrometer. Sample 1-- Untreated olivine crystal (above left), Sample 2 – Olivine crystal treated with high CO₂ mole fraction fluid (above right), and Sample 3-- olivine crystal treated with low CO₂ mole fraction fluid (lower left and right) shows various degree of extensive surface alternation.



Microscopic surface analyses show, however, there is no evidence of significant magnesite formation on the surface of any of the samples studied. Small amount of carbon deposits are detected from EDS analysis. However, it does not directly relate to magnesite formation because fine graphite coating has been applied prior to the EDS analysis to enhance the conductivity of the sample. This is required to allow electrons from the Scanning electron microscope (SEM) beam to flow away from the sample surface. Most of the deposits on the surface of sample 3 are still composed of Magnesium (Mg), Silicon (Si), and Oxygen (O) with unreacted olivine (Fig. 9).

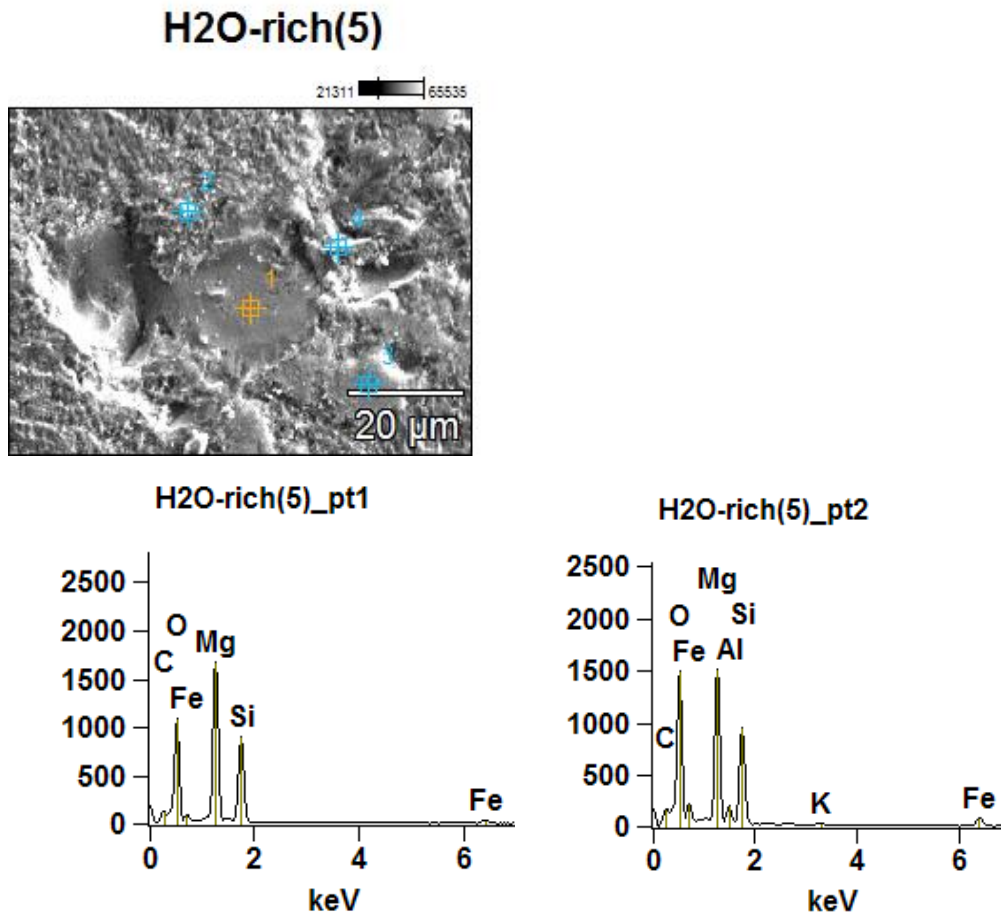


Figure. 9. EDS analysis of surface deposits composition on sample 3, olivine crystal that treated under H₂O-rich fluid. Spikes on particular energy range indicates detection on particular elements.

At point 1 and point 2, besides ordinary elements of Mg, Si, O, and iron(Fe) impurity from the olivine crystal, as well as C from the graphite coating, Aluminium (Al) deposits are found, surprisingly, at multiple points on sample 3 surface (Fig. 9). The finding of Al deposit is somewhat unexpected since, theoretically, no reaction should observe in associate with Al during olivine carbonation. Formation of Al deposits is commonly observed in the nature, presented in the form of clay. However, no Al detected on the olivine surface prior to the experiment. The only possible explanation is the interaction between the low CO₂ mole fraction fluid and the experimental glass tubes causing the formation of Al deposits. This observation suggests glass may not be an ideal container for olivine carbonation reaction because Al-deposits are even more likely to form than magnesite.

In short, fluid of low mole fraction of CO₂ shows greater alteration on olivine crystal surface. This suggests H₂O-rich fluid is more favorable for olivine alteration compared to CO₂-rich fluid. However, no significant formation of magnesite are observed on the crystal's surface to prove olivine carbonation actually proceeded or the reaction is too minor that the chance of finding magnesite is simply too low. Aluminium-deposits, surprisingly, are found frequently on the olivine crystal. This finding suggests an interaction between the experimental glass tubes and the H₂O-rich, CO₂-poor fluid. Such an interaction may potentially reduce the rate of olivine carbonation. The closed system oven experiments, as a result, do not show that olivine carbonation proceeded extensively in any of our glass tubes and allow formation and deposition of neither magnesite nor quartz. The experiment, nevertheless, do proved that low CO₂ mole fraction, or H₂O-rich fluid is more favorable for alteration of olivine.

Calorimetric analysis

The calorimeter heat flux records indicate the consumption of CO₂ and heat also generates during the experiments conducted. The results support the occurrence of exothermic reaction of olivine alteration, as well as its ability to consume CO₂. However, the results do not match with literatures, such as, Kelemen and Matter, and Gerdemann et al., proposed. Some reasons, for example, experimental artifacts and the lack of catalysts turn out to be crucial in achieving the optimal rate of reaction. Therefore, we are carefully not to interpret our results as direct measurement of heat produced by olivine carbonation.

Validation of calorimetric methodology, Heat capacity calculation

As we discussed above in the methodology section, to obtain the of total heat generation throughout the experimental time frame of olivine carbonation, performing the heat capacity measurement of dunite powder is necessary to validate the function of calorimeter. Heat flux (Q) is represented as a function of temperature (T). To enhance the accuracy of the heat capacity calculation, the heating rate (ΔT) must be constant over time. At temperature range of 40°C and 186°C, heating rate is the most stable compared to the first few hours of experiment. This range of temperature is used for all experimental calculation. Subtracting the blank baseline to the dunite baseline gives the net heat absorbed (ΔQ) by the dunite powder. Applying equation, $\Delta Q = m \cdot C_p \cdot \Delta T$, when the mass and heating rate are known and no pressure reservoir are used, the heat capacity of dunite powder (C_p) calculated is accurate and precise and has error within 0.02% (Fig. 10). Note that, when we examine carefully on the two base lines, the vacuumed blank baseline and the dunite baseline; minor fluctuations are observed. To

avoid over or under estimation of the actual flux, it is necessary to smoothen the curve with 3rd order polynomial before we calculate (Fig. 10).

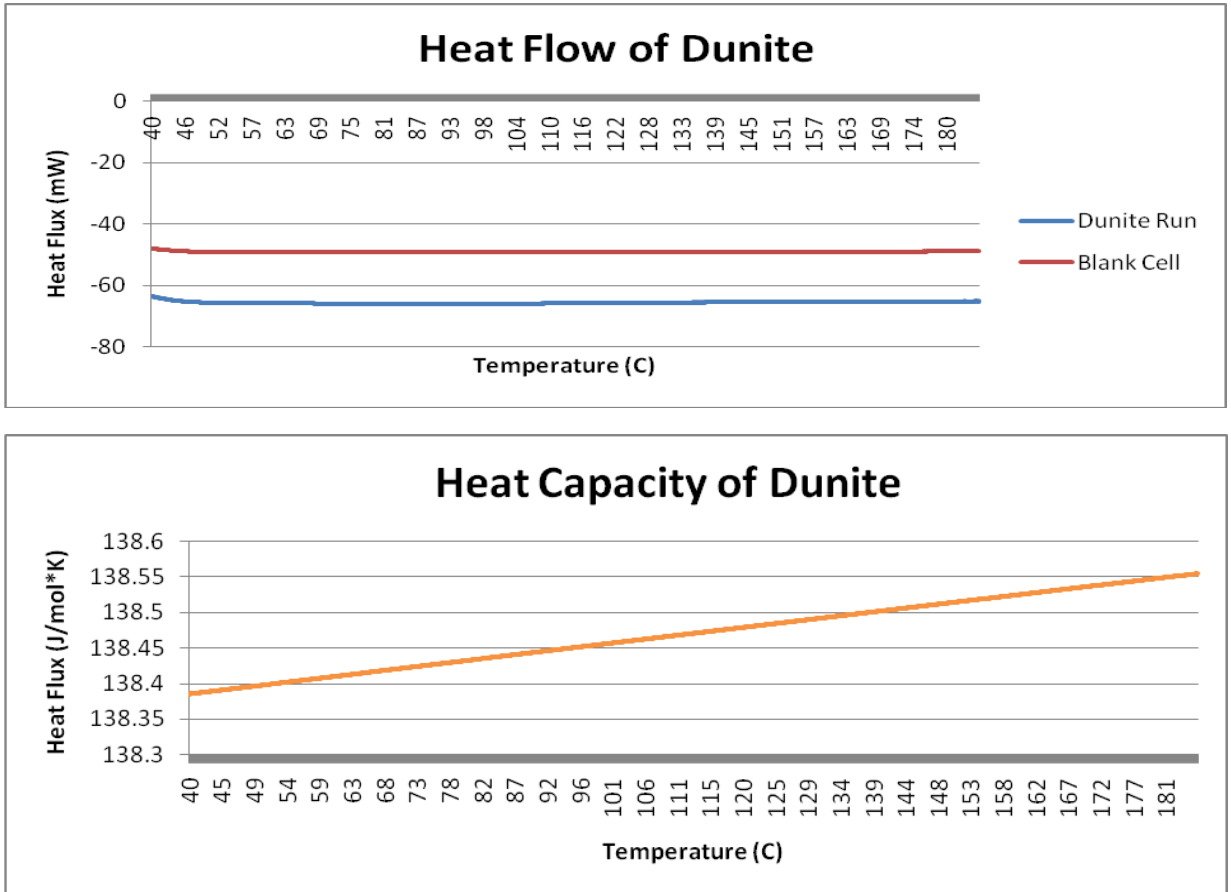


Figure. 10. Calculated heat capacity of dunite in unit of $J \cdot mol^{-1} \cdot K^{-1}$. It is calculated as $Q(\text{dunite}) - Q(\text{blank})$ (Above). Theoretical heat capacity of olivine at 100C is $136.53 J \cdot mol^{-1} \cdot K^{-1}$. The calculated value is accurate and precise with less than 0.02% of error.

Calculating the heat generation – Verifying the exothermic property

Successfully obtained the accurate heat capacity of dunite powder shows that the current setup with no pressure reservoirs yield accurate heat flux data. Using this setup, the exothermic property of olivine carbonation can be calculated from equation,

$$Q(\text{Olivine Carbonation}) = Q(\text{CO}_2\text{-H}_2\text{O-Dunite}) - Q(\text{CO}_2\text{-H}_2\text{O}) - Q(\text{Dunite}) \quad \text{--- (2)}$$

Repeating the same method that we used to obtain the baseline of dunite, we obtain the baseline of CO₂ and H₂O. Exact same mass of dunite, CO₂ and H₂O are then reacted under the exact same heating profile. To determine the heat produced by reactions inside the cell we assume that energy required to heat the reactants separately is exactly equal to the heat required to heat the reactants simultaneously. Note that we have also made the implicit assumption that the heat of reaction of other unintended reaction is negligible. After applying equation (2), negative value of heat flux indicates endothermic reaction and positive heat flux indicates exothermic reaction. The expected net positive heat flux (ΔQ) after the subtractions from equation (2) is, in theory, the heat generated from olivine carbonation.

In Figure 11, set up with Dunite-CO₂-H₂O (blue curve) requires more energy to heat up because the cell contains more mass in comparison with setup of CO₂-H₂O (Red curve). The thermosensor records a more endothermic reaction as the cell heats up at the beginning of the experiment when the temperature is at 40°C to 155°C (Fig. 11). As the temperature of the calorimeter approaches the optimal temperature of 185°C, the red curve intersects with the blue curve. In other words, the heat absorbed by dunite-CO₂-H₂O setup is less than CO₂-H₂O setup even though the dunite-CO₂-H₂O setup contains more mass (Fig. 11). The exothermic property of olivine carbonation is even more obvious when the three heat flux curves are applied to equation (2) to calculate the actual “net” heat flux of olivine carbonation (Fig. 12). At about 100°C, exothermic reactions are recorded (Fig. 12). The reaction is even more exothermic as it proceeds and approaches the optimal temperature of 185°C (Fig. 12). After integrating the heat generation curve, the total heat generated between 40°C and 185°C is 560J. Due to the increasing interaction between liquid water and gaseous CO₂ causing more rapid internal convection, the heat flux signal shows greater magnitude of instability compared to the dunite

experiments (Fig. 10 & Fig. 11). To eliminate errors during subtraction, the heat generation is approximated after the actual heat flux curves are smoothed by 3rd order polynomial. The same best fit approach produces a lower R² value than dunite experiment. The confidence in its accuracy, therefore, has reduced, but the results are, still, considered as a reliable indicator of the exothermic property of olivine carbonation.

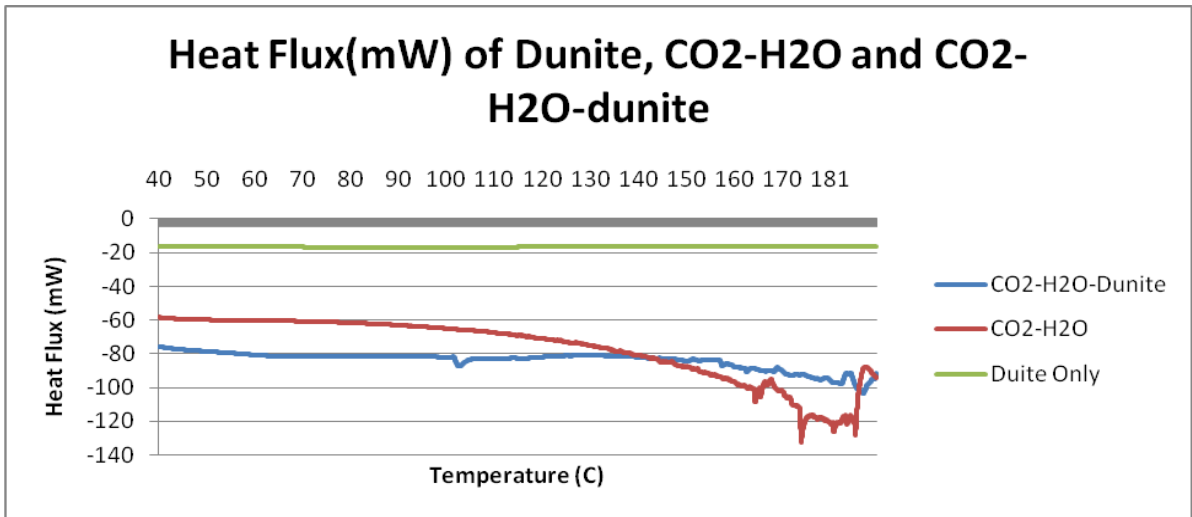


Figure. 11. Heat flux of Dunite, CO2-H2O, and CO2-H2O-dunite in three separated experiments under similar condition.

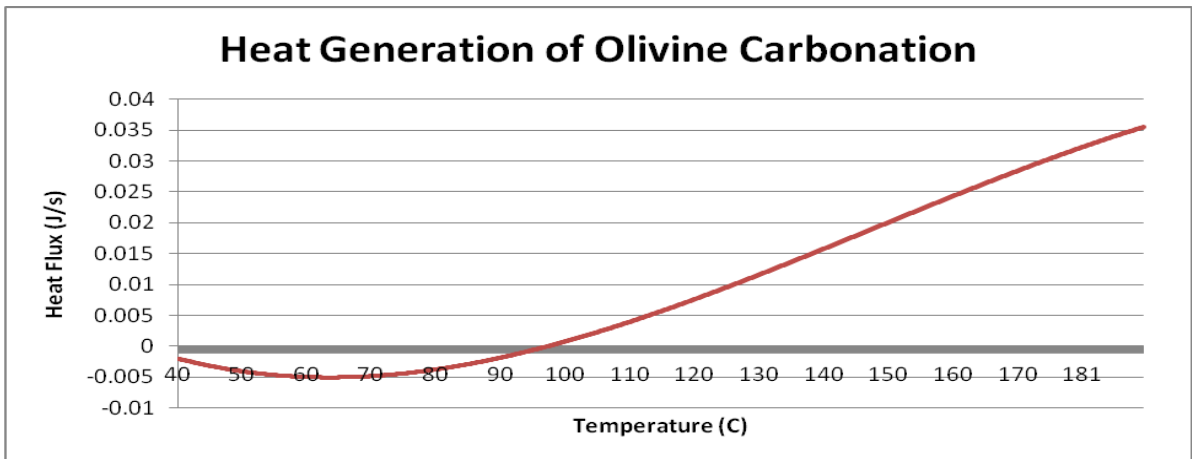


Figure. 12. Heat Generation of Olivine Carbonation throughout the experimental time frame using best fit curve. As temperature increases, more exothermic the reaction is. Calculation error $\pm 0.005\text{J/s}$.

Amount of Carbon sequestered

The amount of carbon sequestered is indicated by the drop of CO₂ pressure in a close environment within the experimental time frame. For our most current experiment at April 5th 2010 (Fig. 13), initial pressure at room temperature is 593psi and the final pressure at room temperature is 503psi. A 90psi of pressure decrease or 16.7% of initial pressure drop is documented. 90psi of pressure at room temperature, according to ideal gas law, represents 0.0025mole of CO₂. A consumption of 0.025 mole of CO₂ suggests 0.176g of olivine is reacted and carbonated. Based on this result, the amount of olivine carbonated are insignificant. Therefore, the chance of discovering magnesite deposits on the surface of 8g of experimental products under EDS microscopic analysis is extremely small. This result has been duplicated in our most recent experiment on April 26th, 2010. The exact same setting was applied and the amount of carbon captured is identical. A 90psi, or 6.2bar of pressure drop has been documented. This experimental result has further confirmed the carbon capture ability of olivine, and the performance of our experimental setup. An earlier experiment performed on December 11th, 2009 also indicates pressure drops throughout the course of experiment (Fig. 14). The data, however, has not been further investigated because the amount of dunite used was 0.5g. The corresponding pressure drop throughout the course of experiment is minor. Moreover, baseline approach was not yet deployed, thus, heat generation calculation were still not available.

Both Figure 13 and Figure 14 indicate pressure drop when temperature is held constant at 185°C. Although the pressure drops in both experiments are insignificant, it still clearly signifies the consumption of CO₂. In specific, experiment 040510 shows increasing heat flux while pressure drops at the same time. This non-ideal gas law phenomenon supports an

exothermic reaction happening inside the reaction chamber, very possibly due to olivine carbonation (Fig. 14). In experiment 121109, although the heat flux recorded fluctuated notably, the pressure drop is clear (Fig. 15). Experiment 121109 does not necessary prove the exothermic property of olivine carbonation. Both experiment 121109 and experiment 040510 agree on CO₂ consumption during olivine carbonation.

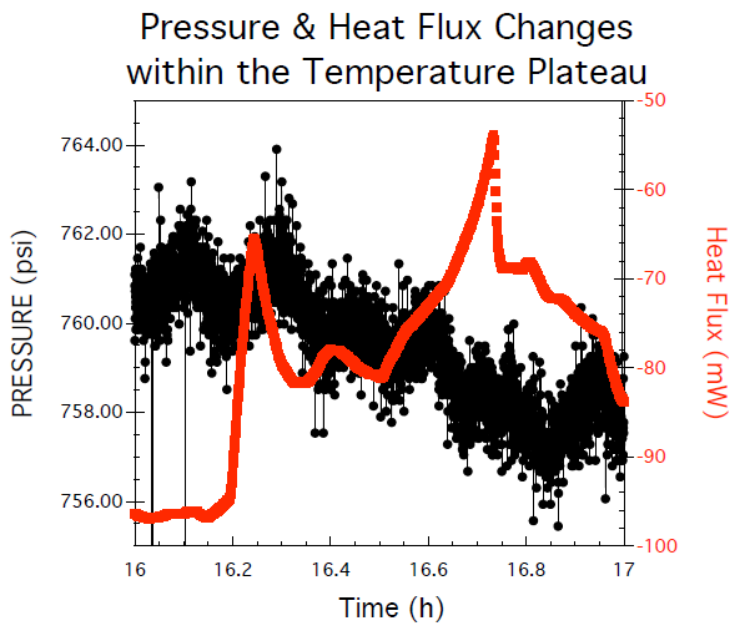


Figure 13. Pressure & Heat Flux Changes within the 185C temperature plateau at experiment 04/05/10. Pressure drops from 761psi to 757psi throughout an hour of time course and heat flux increase by approximately 20mW.

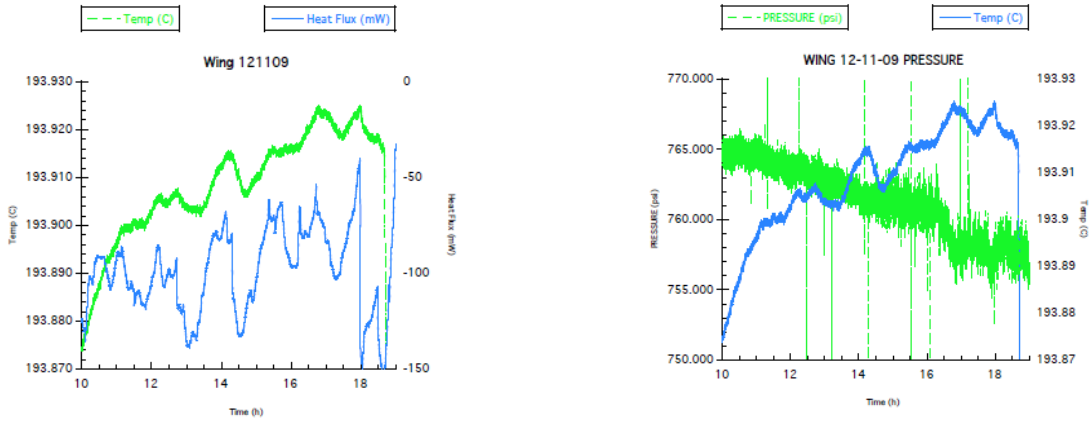


Figure 14. (Left) Temperature and heat flux profile at 194C temperature plateau in 2 hours time frame at experiment 121109. And, (Right) Temperature and pressure profile at 194C temperature plateau in the same 2 hours experimental time course at 121109. Pressure drops from 765psi to 755psi within 2 hours.

Discussion

Experimental Artifacts

Calculation and data from calorimetric investigations support our initial hypothesis that olivine carbonation consumes CO₂ and generates heat during reaction. However, we suspect our results are inaccurate because of our experimental artifacts. The heat flux data we collected are unsatisfying due to thermal instability. The heat flux curves from the calorimetric experiments should be stable with minimal degree of fluctuation and on short time scales. In our heat capacity measurement experiments, the outcome was satisfying because the heat flux curves maintained at a nearly constant value and matched the expected know values. However, when water is present in the reaction cell, substantial fluctuation has been documented. Below I discuss three possible reasons for these fluctuations.

First of all, the nature of olivine is very susceptible to hydrothermal alteration, such as weathering process (Deer et. al 1966). Byproducts of olivine carbonation including serpentine, iddingsite, bowlingite, talc, and others may form, if unintended side reaction do occur, the measured heat flux cannot reflect heat production of olivine carbonation alone. Instead it would reflect the net heat produced or consumed by all reaction. These non-carbonate alteration products maybe mixed intimately and sometimes are very difficult to precisely indentify using optical methods (Deer et. al 1966). The heat fluctuation may be caused by other olivine alteration mechanisms. For example, if different reactions become important at different times during the experiment this could produce unstable changes in measured heat flux we have measured. Nevertheless, all the olivine alterations do not consume CO₂ but only the formation of magnesite consumes CO₂. Knowing the amount of CO₂ consumed can directly estimate the corresponding heat generated based on enthalpy calculation. Moreover, magnesite formation

generates the most significant amount of heat compared to other olivine alteration mechanisms (Kelemen and Matter 2008). It is reasonable to ignore all the other alteration mechanisms when calculating the total amount of heat generated.

Second of all, as mentioned in the method section, two immiscible fluids of CO₂-rich with high CO₂ mole fraction and H₂O-rich with low CO₂ mole fraction, as well as a gas phase exist in equilibrium at temperature of 200°C and 50bar (Shyu et al 1996). Although at temperature of 200°C and pressure of 50bar, CO₂ gas alone, still, exists mostly at gas phase; the formation of the immiscible fluids in the CO₂-H₂O binary system could greatly affect the rate of reaction. The result of close system oven experiment suggests fluid at low CO₂ mole fraction is most favorable for olivine alteration. Water enables ions to dissolve and precipitate because it is a polar solvent. On the other hand, CO₂-rich fluid does not alter the crystal's surface in our oven experiments. We suspect this is because the CO₂-rich fluid solutions are less effective solvents for the ions that dissolve and re-precipitate in order for the olivine carbonation reaction to proceed. This is perhaps because of its non-polar character. The two extreme outcomes highlight the importance in understanding CO₂-H₂O phase relations and the corresponding effects on olivine carbonation inside the calorimeter. Therefore, it is one of goal to achieve the real water-rich phase suggested by Shyu et. al, with xCO₂ of 0.05. However, we cannot be certain of the detailed phase relations within the reaction cell because of the temperature gradients introduced in the calorimeter system by the pressure transducer (See the following paragraph). In short, in our calorimeter experiment, there are no appropriate adjustments available to address this concern.

Finally, the calorimetric approach does not allow us to perform a truly closed system thermal investigation due to technical difficulties. Since heating up the calorimeter is time consuming, especially it takes up to 20 hours to achieve our optimal temperature of 185°C. Any

leaks, which have a very high chance to occur, would totally waste the time and effort that have been invested in each close system experiment. Moreover, technically, doing the close system experiment is relatively difficult and may have too much safety concerns. As a result, an open system calorimeter setting is the only available and feasible setup we have at this stage of our project (Fig. 5). The major challenge of the open system experiment is the installation of the pressure transducer. The pressure transducer is essential in a technical point of view because it indicates the instant pressure inside the reaction tube. It is extremely useful in detecting leaks and monitoring pressure input, as well as calculating amount of carbon captured by the end of the experiment. The pressure transducer, however, needs to be installed outside of the calorimeter block and the heating element. It is located outside of the calorimeter at room temperature connected with gas pipes (Fig. 5). This setup creates large temperature gradients between the pressure transducers at room temperature and the reaction chamber at 185°C. This temperature gradient drives the internal convection within the gas pipes, where water vapor condenses and evaporates simultaneously and energy is constantly escaped to the environment. This phenomenon provides another possible explanation for the fluctuation in the heat flux data because as temperature increases, the CO₂ and H₂O mixture becomes exponentially increasingly endothermic. This endothermic behavior suggests more heat is absorbed by the sample chamber. Since no reaction is supposed to happen inside the sample cell, the extra heat absorbed must leave to the surrounding environment at the gas pipe. The total heat generated in olivine carbonation in our open system calorimeter experiment, furthermore, is 560J, which is equivalent to 3.2KJ for every gram of olivine “reacted”. Comparing our calculation with that calculated from thermodynamic data by Kelemen and Matter 2008, our value is almost two times larger than the theoretical value that they suggested. If convective heat loss from the calorimeter is systematically larger in the CO₂-H₂O mixture than in the CO₂-

H₂O-dunite mixture, this could easily account for the unexpectedly large heat of reaction we have measured.

Comparison to previous works, Is olivine carbonation promising as expected?

Although the experimental artifacts do not allow us to accurately quantify the heat flux associated with olivine carbonation, the CO₂ consumed indicated by pressure drop after the calorimeter returned to room temperature, is a solid evidence supporting olivine carbonation. The same result of 90psi, or 6.205bar of pressure drop, moreover, has been reproduced again in our latest experiment of 04/23/2010 under the same condition at experiment 04/05/2010. Without any use of catalysts, such as NaCl and NaHCO₃, around 16.7% of the initial CO₂ has been consumed. This extent of reaction is small compared to those reported by Gerdemen et al. and suggesting that olivine carbonation is slower than we expected.

Although the calorimeter is a powerful tool for investigating thermodynamics of most of the physical and chemical reaction, it may not be suitable to measure the complicated reaction of olivine alteration which multiple reactions are possible. In addition, the heat flux data will always be suspected unless we can eliminate the effects of convection or locate the pressure transducer within the calorimeter block. Before we can operate the calorimeter without heat loss artifacts, no conclusion can be drawn as to whether or not the highly exothermic character of olivine carbonation predicted by thermodynamic data can be achieved in actual experiments.

Based on the EDS analysis of olivine surface samples reacted in the seal tube experiments, forming magnesite is not as easy as we expected at the beginning stage of our research project. Until now, we, still, cannot be optimistic towards Gerdermann et. al 2003's research on their extensive rate of olivine carbonation. In addition, water-rich fluid with low CO₂

mole fraction is essential for olivine alteration or even olivine carbonation. This has important implications for the amount of heat and water required to make olivine alteration proceed. Without catalysts, the rate of reaction is slow and is not cost-effective for large-scale sequestration. Use of catalysts, for example increasing the ionic strength of the reaction solution, represents one approach that we have not investigated. Therefore, although we have had limited success sequestering carbon in our experiments, olivine carbonation may still have potential as a means of carbon sequestration.

Conclusion

Carbon sequestration is one the most promising solutions in reducing the stress on our climate system caused by anthropogenic carbon emission. Olivine carbonation still remains of its interest to investors, including the U.S. Department of Energy due to its permanent stability. Prior to this senior research, numerous articles, such as Lackner et al. 2003 and Oelkman et al. 2008, have already described the implication of olivine carbonation and its potential effects on stabilizing the climate. However, Gerdeman et al. 2003 is the only experimental studies that have been conducted on olivine carbonation, while Kelemen and Matter focus on radiocarbon dating on existing geologic formation and provide 1-dimensional and thermodynamic calculation on the possibility of in situ mineral carbonation. Limited research has been done in answering the concerns raised in this senior research which are vitally important in determining the effectiveness of olivine carbonation.

Due to experimental artifacts, the initial questions raised are not yet fully answer. The results, do confirm that, magnesite formation is not as easy as the previous studies have proposed. Comparison of the results of this work to those of Gerdemann et al suggest that a H₂O-rich fluid, and high ionic strength catalysts are essential for effective carbonation reaction, but still, these factors may not be able to maximize the reaction rate. In other words, sequestering carbon into geologic formation most likely requires significant amount of initial inputs of water. Moreover, the setup of our calorimeter (Fig. 5), in certain degree, simulates the real-world geologic olivine carbonation. Scientists currently proposed of pumping CO₂ into deep geologic formation may experience the same challenge that our experiments have encountered (Oelker et al. 2008). A calorimeter block, similar to the deep geologic formation, serves as a source of heating element. The pressure transducer at room temperature is similar to the

surface of the geologic formation. The temperature gradients that generated in our calorimeter setup will appear as well in the real-world geologic formation. Internal convection, formation of olivine alteration byproducts, as well as supercritical CO₂-H₂O fluid interaction within the geologic reservoir will happen very similarly in the real-world setting. Solving these major challenges in our calorimeter system is the key to implementing olivine carbonation in industrial scale.

In short, the exothermic property of olivine carbonation rate that aimed to investigate in this project is not fully confirmed. Olivine carbonation, more precisely, the magnesite formation was not achieved in the seal tube experiment. However, CO₂ consumption documented in the calorimeter experiments suggests olivine carbonation was achieved. Additionally, the overall heat generation throughout the experiment exceeds the theoretical calculation. This suggests that real world olivine carbonation, similar to our calorimeter setting, can be very exothermic. It has a relatively high possibility that olivine carbonation can be self-sustained by its own heat in geologic formation. To more effectively continue our investigation, achieving the optimal condition with minimal experimental artifacts is definitely essential. After a yearlong research, although our results, most of the time, are discouraging, it also suggests that olivine carbonation at geologic formation may be not be cost effective when is implemented, I still remain optimistic towards the future development of olivine carbonation as a mechanism of carbon sequestration.

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