

CO₂ Sequestration in Basalt: Carbonate Mineralization and Fluid Substitution

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SUMMARY

Basalt rocks contain some of the most reactive minerals when in contact with CO₂-water mixtures. The chemical reaction between minerals rich in calcium, magnesium and iron and carbonic acid precipitates carbonates in the pore space. This process would increase the elastic moduli and velocity of the rock. At the same time, the higher compressibility of CO₂ over water changes the elastic properties of the rock, decreasing the saturated rock bulk modulus and the P-wave velocity. Reservoirs where the rock properties change as a result of fluid or pressure changes are commonly monitored with seismic methods. Here we describe experiments to study the feasibility of monitoring CO₂ migration in a reservoir and CO₂-rock reactions for a sequestration scenario in basalts. Our goal is to measure the rock's elastic response to mineralization with non-contacting ultrasonic lasers, and the effect of fluid substitution at reservoir conditions at seismic and ultrasonic frequencies.

INTRODUCTION

Storage of carbon dioxide in the subsurface may be a large-scale option to reduce emissions into the atmosphere. The effectiveness of sequestering CO₂ into deep reservoirs depends on the reservoir storage capacity, stability and risk of leakage (Holloway, 2001; Davis et al., 2003; Torp and Gale, 2004; Rochelle et al., 2004; Benson and Cole, 2008). Carbonate mineral precipitation is a promising rock-fluid chemical reaction for sequestering CO₂, in particular in basalt rocks (McGrail et al., 2006; Rogers et al., 2006; Matter et al., 2007; Oelkers et al., 2008; Gislason et al., 2010; Schaef et al., 2010). If this reaction occurs, changes in the elastic properties of basalts will be the combination of fluid substitution of CO₂ with water and carbonate precipitation. Quantifying these elastic changes will determine the feasibility of remotely monitoring the reservoir with seismic waves.

Seismic methods are widely used to monitor changes in the reservoir rock properties. However, layered basalts pose a considerable imaging challenge, mostly due to strong scattering from the sharp impedance contrasts between basalt flows and their sedimentary inter-beds (Pujol et al., 1989). Borehole seismic acquisition may be less affected by scattering due to its shorter propagation length. We have designed laboratory experiments to simulate reservoir in-situ conditions to estimate changes in elastic and rock properties for a CO₂ injection scenario in basalts to be monitored by seismic methods. Our ultimate goal is to quantify the effect of both fluid substitution and chemical alteration on the elastic properties, and their relation to changes in rock properties such as porosity and permeability. During this process, we will also model Gassmann's equa-

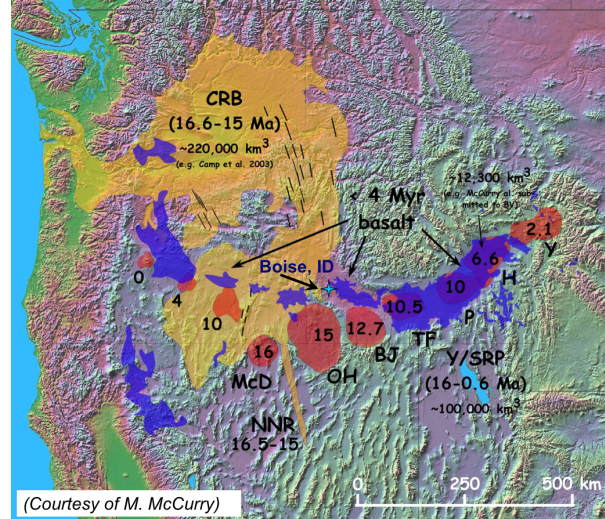
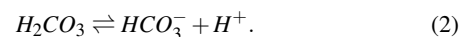
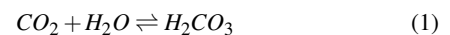


Figure 1: Location and extend of the Snake River Plain (SRP) Basalts, Columbia River Basalts (CRB) and Northern Nevada Rift (NNR) Basalts. Numbers are the age of the basalts in millions of years. The sub-groups within the SRP Basalts are defined by time of eruption of the Yellowstone *hotspot*, from older to younger: McDermitt (McD), Owyhee-Humboldt (OH), BruneauJarbidge (BJ), Twin Falls (TF), Picabo (P), Heise (H) and Yellowstone Plateau (Y). The volume of the CRB and the SRP basalts are referenced.

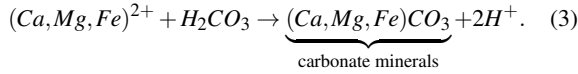
tion and analyze the applicability of this theory to the basalt rocks under study and if so, under which circumstances it can be applied.

Mineralization of CO₂ into carbonate minerals would occur from the combination of water-carbon dioxide mixtures and divalent metal cations (Ca²⁺, Mg²⁺, Fe²⁺). These cations can be present in low saturation in formation waters. However, host rocks rich in such metals and with high dissolution rates are the target for long term sequestration and mineralization. Basalt rocks are rich in Ca, Mg and Fe cations and poor in silica, which translates into high dissolution rates of these metals compared to high-silica rocks. The first step for this rock-fluid interaction is that carbonic acid (H₂CO₃) can dissociate into bicarbonate (HCO₃⁻) and H⁺ ions, lowering the pH of the water:

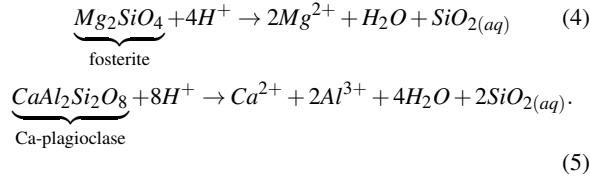


Divalent metal cations in the water can precipitate as carbonates as follows:

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The reaction in equation 3 will only occur if the hydrogen ions are consumed by a different reaction. The following equations show two of several reactive basalt minerals consuming the free hydrogen and releasing new divalent metal cations into the water (Gislason and Hans, 1987; Matter et al., 2007). These free cations will then react with the CO₂-water mixture (equation 3) to precipitate as carbonates.



McGrail et al. (2006) and Schaef et al. (2010) show significant carbonate mineralization on crushed samples from the CRB and other basalts around the world. Super-critical CO₂ is mixed with water at 100°C and 10.3 MPa pressure and they precipitate carbonates in as early as 87 days. The time required to precipitate carbonates depends on the available divalent metal cations – which is proportional to the dissolution rate of the mineral – fluid temperature and pressure, solution composition, CO₂ saturation and pore surface area. In addition to the apparent favorable chemical conditions for CO₂ sequestration, flood basalts are widespread around the world and can possibly host large amounts of CO₂ (McGrail et al., 2006).

In collaboration with the Idaho National Laboratory and the University of Idaho, a program is underway to study the feasibility of reaction, storage and monitoring of CO₂ in the Snake River Plain (SRP) basalt flows. Figure 1 shows the extend of the SRPB and the nearby Columbia River Basalts (CRB). Several samples of top flow basalts were collected in the field and are being measured in the laboratory to understand both fluid substitution and carbonate mineralization effects on rock elastic properties as a result of CO₂ injection.

BASALT ROCK PROPERTIES

The basalt rocks in this study were collected from outcrops near Hagerman, Idaho. Two sets of three cylindrical samples were cored. The first set will be used for the mineralization experiment and cores are 1 inch in diameter and 1.5 inches in length. For the fluid-substitution experiment we will use larger samples at 1.5 inches in diameter and 2 inches in length. We have performed a detailed petrographical analysis to compare the basalt rock samples before and after mineralization and study its control on the elastic rock properties. Figure 2 shows thin sections for two of the three samples. Sample B1 and B3 are similar, with large pores and minerals and gray-black in color. Sample B2 has smaller pores and minerals and is of gray-greenish color. Table 1 shows measured porosity

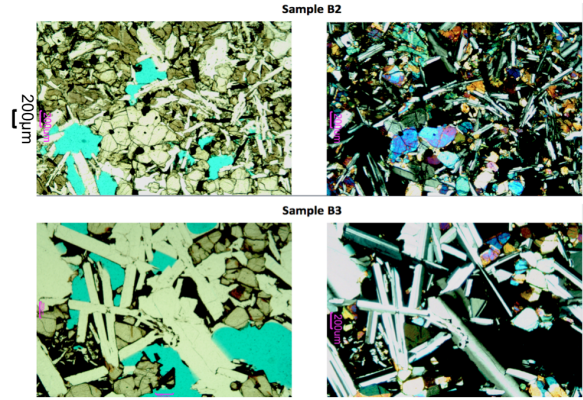


Figure 2: Thin section of samples B2 and B3. On the left, blue is epoxy filling the pore space. On the right the same thin sections are shown with polarized light to recognize the different minerals. White is plagioclase, blue and yellow is pyroxene. Observe the difference is pore and mineral size.

SAMPLE	ϕ_{He} (%)	ϕ_{Hg} (%)	k (mD)
B1	19.0	9.9	1.49
B2	13.9	10.3	0.19
B3	16.1	11.2	1.86

Table 1: Helium (He) and Mercury injection (Hg) porosity for the basalt samples. Permeability is measured at 1000 psi confining pressure and has Klinkenberg correction applied.

and permeability of the three basalts. From mercury injection we estimate that the pore throat size is between 15 and 100 microns for sample B2, but sample B1 and B3 show two pore size distributions at 0.7-8 and 15-100 microns. The difference in pore throats suggests that there is significant variation in this pore surface area, an important parameter controlling mineralization. 3D micro CT-scans (Figure 3), quantify the distribution of material density in the rock and we expect to use this technology to quantify 3D carbonate mineralization. X-ray diffraction and X-ray fluorescence were also acquired for all samples, and despite the visual differences among samples, the mineralogical composition of the three basalts is similar (Table 2).

The petrographical data described here will be collected again after the basalt mineralization experiment is completed. These

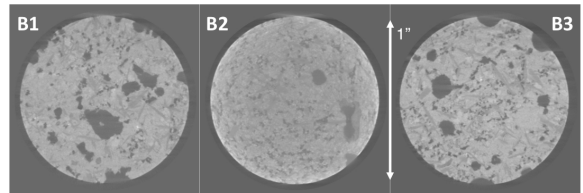


Figure 3: CT-scans where black is pore space and lighter gray represents higher material densities.

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MINERAL	B1	B2	B3
Plagioclase (%)	62.7	67.3	66.3
Pyroxene(%)	19.3	15.1	13.0
Olivine (Fosterite) (%)	13.8	12.2	15.5
Gypsum (%)	1.7	0.7	0.6
Ilmenite (%)	2.5	4.7	4.6

Table 2: X-ray diffraction in percent volume. B1, B2 and B3 are similar in chemistry, but other petrographical data is different especially for B2 with respect to B1 and B3.

data will also be used to constrain and model the elastic response of basalt rock for a CO₂ sequestration scenario.

ELASTIC PROPERTY MEASUREMENTS: PRE-MINERALIZATION

We have measured the ultrasonic response of three 1 inch basalt samples and define the record as the baseline for the mineralization experiment. With this experiment we want to quantify the change in elastic response before and after carbonate mineralization. The experiment is designed to measure dry rocks to only observe the effect of carbonate mineral formation in the pore space. Rock changes due to carbonate mineralization will be quantified from direct arrivals and coda waves. Samples are measured at room conditions and ultrasonic frequencies for this experiment. Waves are created and measured by lasers, a non-contacting technique, that would eliminate the potential coupling error between the rock sample and the use of transducers. The physical acoustic laboratory at Boise State University uses a Spectra Physics pulsed Nd:YAG source laser to create ultrasonic waves by thermoelastic expansion of the sample at the point of illumination. The receiver laser is a Bossa Nova TEMPO interferometer that measures the displacement of the sample at the spot size of the receiver beam in the direction of the beam. Figure 4 is a shot record acquired on the side of sample B2. The P-wave direct arrival is clearly seen, followed by reflections, wave conversions and surface waves. We have acquired 0.1 s of data to have long enough recordings to not only study changes in direct waves, but also in the coda.

Bench-top ultrasonic measurements were also acquired with Panametrics transducers ($f_d \sim 0.25$ MHz) to get basic velocity properties. The dry P-wave velocity is 3.35 km/s, 4.32 km/s and 3.36 km/s for samples B1, B2 and B3, respectively. When samples are saturated with water, the P-wave velocity increases to 4.74 km/s, 5.14 km/s and 4.82 km/s for the same three samples. The dry V_p/V_s ratio varies between 1.5 and 1.8 and the dry S-wave velocity is 2.19 km/s, 2.52 km/s and 1.88 km/s, for samples B1, B2 and B3, respectively. This data shows the control of porosity on the velocities. B1 and B3 have similar P-wave velocities, and these are lower than the velocity for B2. This is in agreement with lower porosities in B1 and B3 with respect to B2. Shear wave velocities have the same relation to porosity as for P-waves. However, there is a greater difference in S-wave velocities between B1 and B3 than for P-waves.

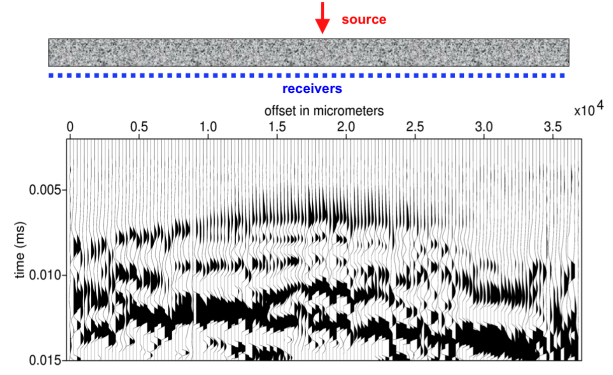


Figure 4: Shot record for dry sample B2 at atmospheric conditions acquired with ultrasonic lasers. The direct P-wave arrives between 0.0059 and 0.008 ms, this yields a P-wave velocity of 4.23 km/s. The record was acquired scanning the side of the cylindrical sample as shown on the sketch above.

MINERALIZATION EXPERIMENT

To simulate the in-situ conditions for the rock-fluid reactions described in equations 3 to 5 we use a pressure vessel where water and CO₂ are mixed and pressurized to between 1200 psi and 1500 psi to work with supercritical CO₂. By increasing the fluid pressure we can dissolve more carbon dioxide in water. We use tap water because it contains Ca, Mg and Fe cations. The three 1 inch basalt cores are inserted in the vessel, vacuum is applied and the vessel is filled with a water-CO₂ mixture. The vessel is heated to 100°C to simulate reservoir temperatures and speed chemical reactions. These conditions will remain for the length of the experiment. The pressure vessel is built with a high pressure pH sensor to monitor the alkalinity of the water. The pH for CO₂-water mixtures at the described pressure and temperature varies between 3 and 3.5. The pH of water-CO₂ mixtures increases with increasing temperature and decreases with increasing pressure. We will remove the samples from the vessel at 15, 30 and 45 weeks. At each stage we will acquire ultrasonic laser scans as shown in Figure 4, and at the final stage we will re-acquire all the petrophysical data described above.

LOW AND HIGH FREQUENCY ELASTIC PROPERTIES FOR WATER-CO₂ SATURATED BASALTS

The effect of water-CO₂ mixtures in the pore space alone for the 1.5 inch core samples is being prepared to be measured on these basalt rocks in a pressure vessel at Colorado School of Mines. This equipment is capable of measuring elastic properties from seismic to ultrasonic frequencies with independent confining and pore pressure. Batzle et al. (2006) and Adam et al. (2009) explain the setup of the low frequency experiment and apparatus.

Gassmann's equation is commonly used to determine changes in the seismic properties of reservoir materials when fluid sub-

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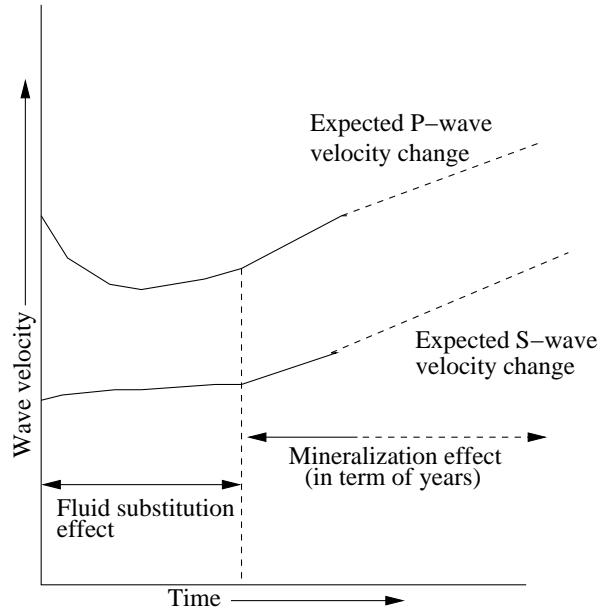


Figure 5: Sketch of the fluid substitution and carbonate mineralization effect on basalt samples. At early times the P-wave velocity will decrease (and S-wave increase) as CO₂ mixes and replaces formation water. This will be followed by period where mineralization and fluid substitution occur at the same time, to be later dominated by carbonate mineralization and a decrease the CO₂ fluid as it is consumed by the chemical reactions.

stitution takes place. Fluid substitution is the initial effect that will take place due to CO₂ injection in a layered basalt reservoir. As a first step for characterizing the CO₂ scenario in basalts we use the measured room-conditions ultrasonic velocity and density of our basalt samples (see previous section). We use this data and Gassmann's equation to model the changes in velocity from 100% water to 100% CO₂ on sample B2 (less porous sample), assuming at this stage that Gassmann's theory applies to these rocks. We will check this assumption as the experiments progress and more data is collected.

The dry P- and S-wave velocity of basalt sample B2 is 4.32 km/s and 2.52 km/s, measured from bench-top ultrasonic transducer measurements. The measured dry rock bulk density for this sample is 2.65 g/cm³, which together with the velocity yields a dry rock bulk modulus of 27.02 GPa and a shear modulus of 16.8 GPa. The average mineral bulk modulus is 80.9 GPa estimated using a Voigt-Reuss-Hill average based on data from the XRD analysis (Table 2). The fluid bulk modulus was estimated from the NIST fluid property calculator at 1300 psi and 100°C. Fresh water and supercritical CO₂ at these conditions have a bulk modulus of 2.3 and 0.01 GPa, respectively. We model that the saturated bulk modulus will decrease from 33.9 GPa to 27.1 GPa from water to CO₂ full saturations. This represent a change of 25% on the bulk modulus. Because CO₂ is highly compressible, the overall rock bulk modulus does not significantly change from a dry to fully CO₂ saturated rock.

For this fluid replacement the P-wave velocity will decrease by 4.5% and the S-wave velocity will increase by 2.5%. Because samples B1 and B3, are more porous than B2 we will expect greater changes in modulus and velocity. In this calculation, change in the shear modulus after CO₂ injection due to varying pore pressure is ignored, as well as the mineralization process and its effects in the bulk and shear moduli. The mineralization effect on velocity cannot be determined at the moment due to lack of knowledge and field experiments.

DISCUSSION

We expect the effect of mineralization and CO₂ fluid substitution in basalts to produce competing changes on the bulk modulus and wave velocity. On one hand, precipitating carbonate minerals in the pore space of basalt would decrease the porosity and stiffen the rock frame, increasing the elastic modulus of the rock. On the other hand, CO₂ fluid substitution for water would decrease the elastic modulus of the saturated basalt because the fluid bulk modulus is lower than that for water. Figure 5 shows the anticipated qualitative change in the P- and S-wave velocities of basalts. Initially, fluid substitution would dominate over mineralization. After several months or years, the mineralization effect on seismic velocities could be dominant over fluid substitution.

At the time of the SEG Annual Meeting we expect to have at least one post-mineralization elastic shot gather of the basalts samples, and quantify the change in velocity. The low frequency measurements would be completed, and the data analyzed. We will follow this analysis by studying the applicability of Gassmann's equation and how the combination of mineralization together with CO₂-water mixture affects the velocity of waves in basalt rocks.

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REFERENCES

- Adam, L., M. Batzle, K. T. Lewallen, and K. van Wijk, 2009, Seismic wave attenuation in carbonates: *Journal of Geophysical Research*, **114**.
- Batzle, M. L., D.-H. Han, and R. Hofmann, 2006, Fluid mobility and frequency-dependent seismic velocity — direct measurements: *Geophysics*, **71**, N1–N9.
- Benson, S. M., and D. R. Cole, 2008, CO₂ sequestration in deep sedimentary formations: *Elements*, **4**, 325–331.
- Davis, T. L., M. J. Terrell, R. D. Benson, R. Cardona, R. R. Kendall, and R. Winarsky, 2003, Multicomponent seismic characterization and monitoring of the CO₂ flood at Weyburn field, Saskatchewan: *The Leading Edge*, **22**, 696–697.
- Gislason, S. R., and P. Hans, 1987, Meteoric water-basalt interactions. I: A laboratory study: *Geochimica et Cosmochimica Acta*, **51**, 2827 – 2840.
- Gislason, S. R., D. Wolff-Boenisch, A. Stefansson, E. H. Oelkers, E. Gunnlaugsson, H. Sigurdardottir, B. Sigfusson, W. S. Broecker, J. M. Matter, M. Stute, G. Axelsson, and T. Fridriksson, 2010, Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project: *International Journal of Greenhouse Gas Control*, **4**, 537 – 545.
- Holloway, S., 2001, Storage of fossil fuel-derived carbon dioxide beneath the surface of the earth: *Annual Review of Energy and the Environment*, **26**, 145–166.
- Matter, J. M., T. Takahashi, and D. Goldberg, 2007, Experimental evaluation of in situ CO₂-water-rock reactions during CO₂ injection in basaltic rocks: Implications for geological CO₂ sequestration: *Geochemistry Geophysics Geosystems*, **8**.
- McGrail, B. P., H. T. Schaef, A. M. Ho, Y.-J. Chien, J. J. Dooley, and C. L. Davidson, 2006, Potential for carbon dioxide sequestration in flood basalt: *Journal of Geophysical Research*, **111**.
- Oelkers, E. H., S. R. Gislason, and J. Matter, 2008, Mineral carbonation of CO₂: *Elements*, **4**, 333–337.
- Pujol, J., B. N. Fuller, and S. B. Smithson, 1989, Interpretation of a vertical seismic profile conducted in the Columbia plateau basalts: *Geophysics*, **54**, 1258–1266.
- Rochelle, C. A., I. Czernichowski-Lauriol, and A. E. Milodowski, 2004, The impact of chemical reactions on CO₂ storage in geological formations: a brief review: *Geological Society of London, Special Publications*, **233**, 87–106.
- Rogers, K. L., P. S. Neuhoff, A. K. Pedersen, and D. K. Bird, 2006, CO₂ metasomatism in a basalt-hosted petroleum reservoir, Nuussuaq, West Greenland: *Lithos*, **92**, 55 – 82. (Magmatism and Tectonism of Greenland Rifts - A Tribute to C. Kent Brooks, Four decades of geological research in the Tertiary igneous province of east Greenland, held in honour of C. Kent Brooks).
- Schaef, H. T., B. P. McGrail, and A. T. Owen, 2010, Carbonate mineralization of volcanic province basalts: *International Journal of Greenhouse Gas Control*, **4**, 249–261.
- Torp, T. A., and J. Gale, 2004, Demonstrating storage of CO₂ in geological reservoirs: The Sleipner and Sacs projects: *Energy*, **29**, 1361 – 1369. (6th International Conference on Greenhouse Gas Control Technologies).