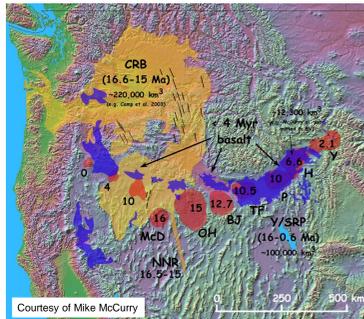


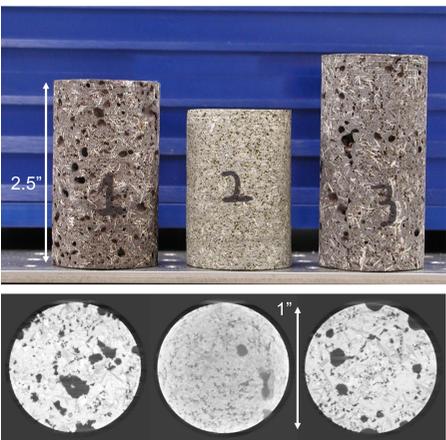
Abstract: Geologic sequestration of CO₂ is proposed as the only promising large-scale method to help reduce CO₂ gas emission by its capture at large point sources and subsequent long-term storage in deep geologic formations. Reliable and cost-effective monitoring will be an important aspect of ensuring geological sequestration is a safe, effective, and acceptable method for CO₂ emissions mitigation. Once CO₂ injection starts, seismic methods can be used to monitor the migration of the carbon dioxide plume. To calibrate changes in rock properties from field observations, we propose to first analyze changes in elastic properties on basalt cores. Carbon dioxide sequestration in basalt rocks results in fluid substitution and mixing of CO₂ with water and rock mineralizations. Carbon dioxide sequestration in mafic rocks creates reactions such as $Mg_2SiO_4 + CaMgSi_2O_6 + 4CO_2 = Mg_3Ca(CO_3)_4 + 3SiO_2$ whereby primary silicate minerals within the basalt react with carbonic acid laden water creating secondary carbonate minerals and silicates. Using time-lapse laboratory scale experiments, such as laser generated ultrasonic wave propagation; it is possible to observe small changes in the physical properties of a rock. The ultimate goal of the project is to track seismic changes due to fluid substitution and mineralization. Here we show velocity measurements at room conditions on three basalt core samples. We record elastic waveforms and estimate velocities in the basalts by using contacting and non-contacting ultrasonic techniques. The P-wave velocity increases by 20% to 40% from dry to water saturated conditions, and the average Vp/Vs ratio is 1.68 for dry samples. The porosity of our basalts ranges from 9% to 17% with pore throats from 10 to 100 microns in diameter. Petrographic analysis on the samples, such as CT-scans, thin sections, XRD, XRF and porosimetry, will aid in the characterization of the mineral composition and pore structure in these basalts and its correlation to changes in seismic properties resulting from fluid substitution and mineralization.

Basalt site



The samples for this project are from the Western Snake River Plain Basalts, shown in purple on the basalt distribution map in of the Northwestern United States. The samples were taken from outcrops near Hagerman, ID. To study elastic changes in the rocks due to fluid substitution from brine to carbon dioxide and rock mineralization, we first need to fully characterize the mineral composition and pore structure of our basalt samples. Next, we perform baseline ultrasonic laboratory measurements before mineralization.

Samples

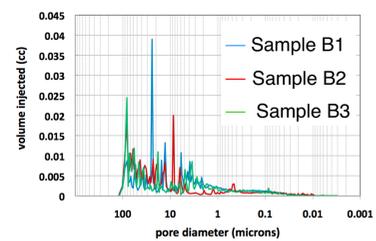


XRF								
Sample	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% CaO	% MgO	% Na ₂ O	% TiO ₂	% (K ₂ O), (Cr ₂ O ₃), (MnO), (P ₂ O ₅), (SrO), (BaO)
B1	44.72	13.67	19.65	8.64	5.96	2.4	3.41	< 1
B2	44.75	13.02	17.92	8.87	6.94	2.35	3.51	< 1
B3	45.44	14.3	16.58	8.91	6.57	2.45	3.36	< 1

XRD			
Sample/minerals	B1	B2	B3
Plagioclase - Labradorite (%)	62.7	67.3	66.3
Pyroxene - Hedenbergite(%)	19.3	15.1	13
Olivine - Forsterite (%)	13.8	12.2	15.5
Gypsum (%)	1.7	0.7	0.6
Ilmenite (%)	2.5	4.7	4.6
TOTAL (%)	100	100	100

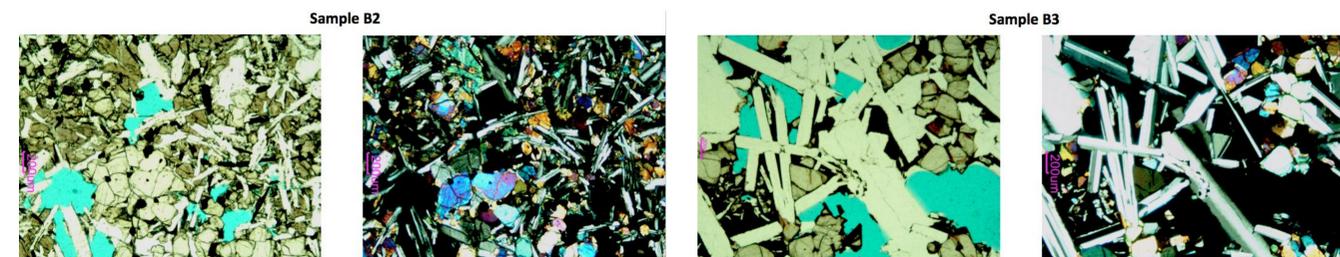
We will analyze two sets of three cores with diameters of 1" and 1.5". The first set will be used to study the precipitation of carbonate minerals due to the carbonic acid and its effect on ultrasonic velocities. The second set will be analyzed to understand the fluid substitution control on elastic velocities at seismic and ultrasonic frequencies and at reservoir conditions. On the left are pictures of the 1.5" diameter samples (top) and CT scans on 1" samples (bottom), dark colors represent low density (pore space) and light colors are high density.

POROSITY



Sample	Hg Porosity (%)	He Porosity (%)	Bench-top Porosity (%)	Grain Density (g/cc)
B1	9.88	16.64	11.84	3.04
B2	10.27	13.76	7.93	3.08
B3	11.22	14.86	8.43	3.04

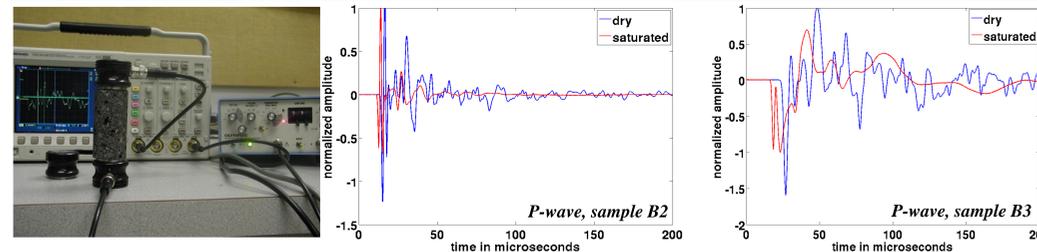
Sample porosity was measured by mercury injection (Hg) and helium porosimetry (He), as well as on the bench by saturating the samples with water. Differences between Hg and He porosities indicate that there is significant pore space that is not well connected.



Background

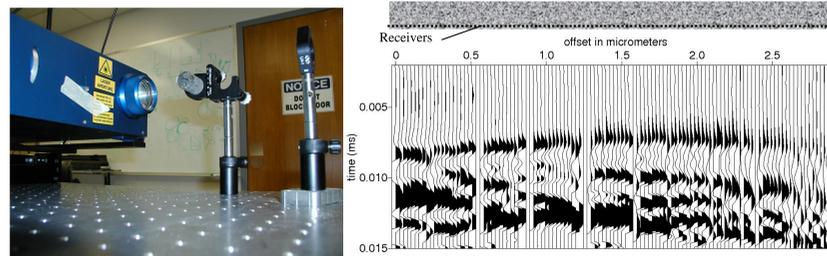
- Crushed basalt from the CRB flow in Washington was exposed to de-ionized water and carbon dioxide at a pressure of 10.3 MPa and a constant temperature of 90°C, calcite formed within 32 weeks (McGrail et al., 2006)
- Schaefer et al. (2010) analyze mineral precipitation on five basalt samples from different basalt flows in the world. The rock-fluid reactions occur when the forming minerals (interstitial glass, plagioclase and pyroxene) react with H₂O-scCO₂ and H₂O-H₂S-scCO₂ solutions. The samples come from borehole core (~600 m depth) and outcrops and they are crushed for the experiments (grains < 2mm). The fluids used are de-ionized water, pure CO₂ and H₂S, and the experiments are performed at 10.34 MPa and held at 100°C. Carbonate precipitation (mostly calcite) is observed as early as 86 days for a CRB, but most basalts show carbonate precipitation at 181 days (for H₂O-H₂S-scCO₂ mixture). The addition of H₂S to the H₂O-scCO₂ solution enhanced carbonate formation for some basalts, but for others the precipitation was slowed down as pyrite precipitated.

Baseline



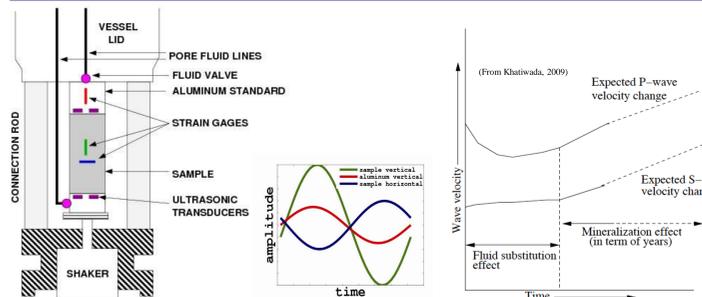
	B1	B2	B3
Dry P-wave velocity (Km/s)	3.35	4.32	3.35
Dry S-wave velocity (Km/s)	2.19	2.52	1.88
Saturated P-wave velocity (Km/s)	4.74	5.14	4.82
Vp/Vs dry	1.53	1.72	1.78

P- and S-wave velocities estimated from direct arrivals of the ultrasonic waves.



The non-contacting elastic wave source, which is a pulsed Nd:YAG laser, creates a thermoelastic expansion on the surface of the sample. A laser interferometer measures the displacement of the ultrasonic waves produced by the source. Here we show a split-spread shot gather with the direct P-wave arriving between 6.2 and 10 μs. Trace separation is 254 μm, and the scan spans 2.8 cm. This elastic wave measurement serves as the dry baseline for our basalt samples before mineralization.

Future work



Fluid substitution: Elastic velocity, modulus and attenuation will be measured on basalt samples at exploration seismic (f=5-500 Hz) and ultrasonic frequencies (f~10⁶ Hz). These properties will be measured at reservoir pressure conditions and different saturations, from full-saturation of either water or CO₂, and for different water-CO₂ mixtures. The pressure-velocity system can be controlled so that the pore pressure and the hydrostatic confining pressure acting on the samples can be varied independently.



Mineral precipitation: When basalt is exposed to carbon dioxide and water mixture, minerals in the basalt containing Ca, Mg and Fe cations react with the carbonic acid solution and precipitate into carbonate minerals. To test this mineralization for whole basalt samples and study their elastic properties, a pressure vessel system was built. Samples will be submerged in distilled water - CO₂ solution at reservoir pressure conditions (P= 8.3 - 9 MPa) but higher temperature conditions to accelerate chemical reactions (T=70-90°C) until the samples show carbonate precipitation.

References

- McGrail, B. P., H. T. Schaefer, A. M. Ho, Y.-J. Chien, J. J. Dooley, and C. L. Davidson (2006), "Potential for carbon dioxide sequestration in flood basalts", *J. Geophys. Res.*, 111, B12201, doi:10.1029/2005JB004169.
- H. T. Schaefer, B.P. McGrail, A.T. Owen (2010), Carbonate mineralization of volcanic province basalts, *International Journal of Greenhouse Gas Control*, 4, 249-261.

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