



Carbon Dioxide Storage in Stable Carbonate Minerals

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INTRODUCTION

Efficient CCS technologies would allow for the continued use of cheap, abundant fossil fuels for power generation in the United States and abroad for decades of reduced or negligible CO₂ emissions as carbon-free power generation methods are developed.

Recently, geochemical trapping has been examined as a possible method of CCS. This involves the injection of CO₂ into water within cavities of mafic rocks. Primary reaction products include magnesite and calcite from the release of divalent cations to the water. There are several advantages to this method, the greatest being stable sequestration over geologic time scales.

Garcia et al. (2010) performed laboratory trials with powdered olivine under a variety of grain sizes (20-200um), salinity conditions, durations (2-8 weeks), and solid/solution ratios (0-10). All trials were performed at 150° C and 150 bar. They found that up to 57% +/-2% of the initial CO₂ could be captured within relatively short time frames (2-4 weeks) and that olivine and other mafic and ultramafic rocks need further examination for CO₂ sequestration but show great promise.

In this study, the effect of grain size on CO₂ sequestration rate was observed at 150° C and 150 bar. Three different grain size ranges were studied: 425-250um, 250-180um, and <180um.

HYPOTHESES

Three hypotheses were tested over the course of this research.

H₁: When ground basalt is reacted with aqueous CO₂ under the specified P-T conditions, stable carbonate minerals will form.

- H_{1a}: Carbonates will not form under the tested conditions.

H₂: When different grain sizes (but identical masses) of basalt are reacted with aqueous CO₂, the largest amount of carbonate will form on the sample with the smallest grains (<180um), less on the middle grain size (250-180um), and the least on the largest grain size (425-250um).

- H_{2a}: There will not be a significant relationship between grain size and amount of carbonate formed.

H₃: The difference in the amount of carbonate formed will be smaller than the ratio of average surface areas. That is, the ratio of surface area to carbonate formed will not follow a 1:1 trend.

- H_{3a}: The relationship between carbonate formed and average surface area will not follow a statistically significant trend.

METHODS OF ANALYSIS

Basalt sample composition was determined by XRF at Franklin and Marshall College. XRF reveals typical alkali basalt composition, with over 15% mass due to oxides of magnesium and calcium, which are the predominant carbonate forming cations.

Specimen	AF-1
SiO ₂	51.7
TiO ₂	1.19
Al ₂ O ₃	17.04
Fe ₂ O ₃	5.56
FeO	2.56
MnO	0.13
MgO	7.18
CaO	8.28
Na ₂ O	3.82
K ₂ O	1.43
P ₂ O ₅	0.43
Total	99.32

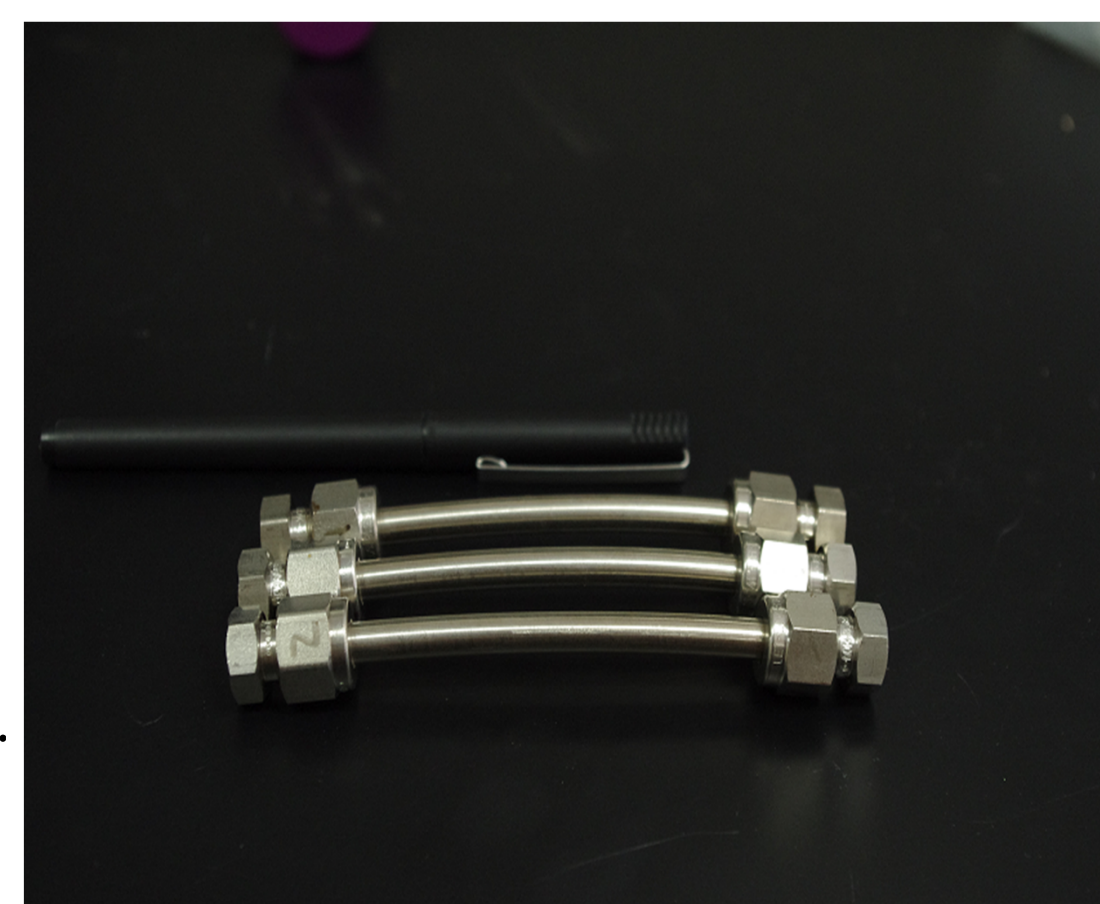
Decreasing grain size presented a larger surface area presented for reaction; this caused reaction rates of heterogeneous chemical reactions to increase. The difference in the liquid/solid interface area produced a change in the rate of precipitation with the smaller grains sequestering more CO₂ in a given time span. This was due to increased dissolution because of the larger surface exposed to the solution. Each halving of average grain size doubled the surface area for the same mass of sample.

This is the sample of vesicular basalt provided by B. Tattitch from the Boring Lava Fields of Washington State. Literature on the Boring Lava field reveals that the mineralogy is predominantly light-gray phyrlic olivine basalt, with scoria, cinders, tuff, and ash all present. This basalt sample contained between 5-10% glass.



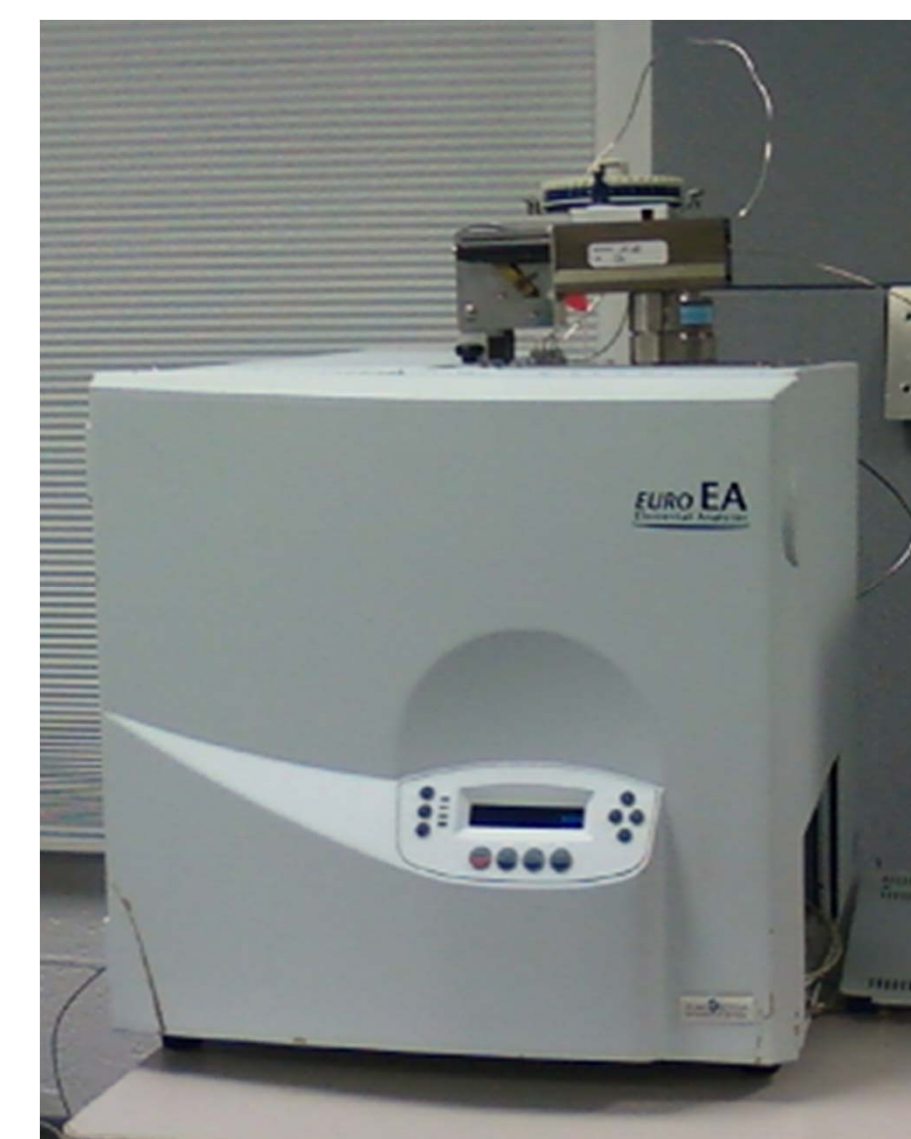
METHODS OF ANALYSIS

The basalt sample was crushed using a ceramic mortar and pestle and sieved into the three groups mentioned earlier: 425-250um, 250-180um, and <180um. The materials for reaction are dry ice and distilled water of laboratory standards. The samples were reacted in stainless steel Swagelok tubing of inner diameter 0.3 cm and length of 9.678 cm, resulting in volume of 0.648 cm³. Both ends were sealed by Swagelok stainless steel pressure fittings, resulting in a vessel capable of containing 260 bar.



Combining 0.100 gram of ground basalt, 0.100 gram of distilled water, and 0.0647g CO₂ gives the appropriate internal pressure of 150 bars at an externally applied 150° C. Equal ratios of basalt and water were chosen after analysis of Garcia et al., who found that a 1:1 ratio yielded the highest carbon capture compared to both higher and lower ratios for samples of this size. The total pressure of 150 bar comprises the partial pressures of both CO₂ and water. For the masses used and volume of the cylinder, P_{CO₂} is 145.3 bar and P_{H₂O} is 4.7 bar. This is corrected for the initial dissolution of the gaseous CO₂ and also for the volume occupied by the basalt sample. Calculation of the correct pressures and volumes involved the Law of Partial Pressures, the Antoine Equation for Vapor Pressure, and the Ideal Gas Law. Three samples of each grain size range were run at a time, for a total of nine individual trials and three 2 week periods.

At the end of the two week period, the tubes were removed from the oven and allowed to cool to ambient temperature. The tubes were then opened, and the contents poured into beakers. Distilled water was run through each tube to ensure the collection of all grains. The grains were then vacuum filtered on pre-massed filters and heated overnight at 140° C to remove any water content; sufficient for samples this minute. The dried grains and filters were then massed to determine the total mass increase from before and after reaction.



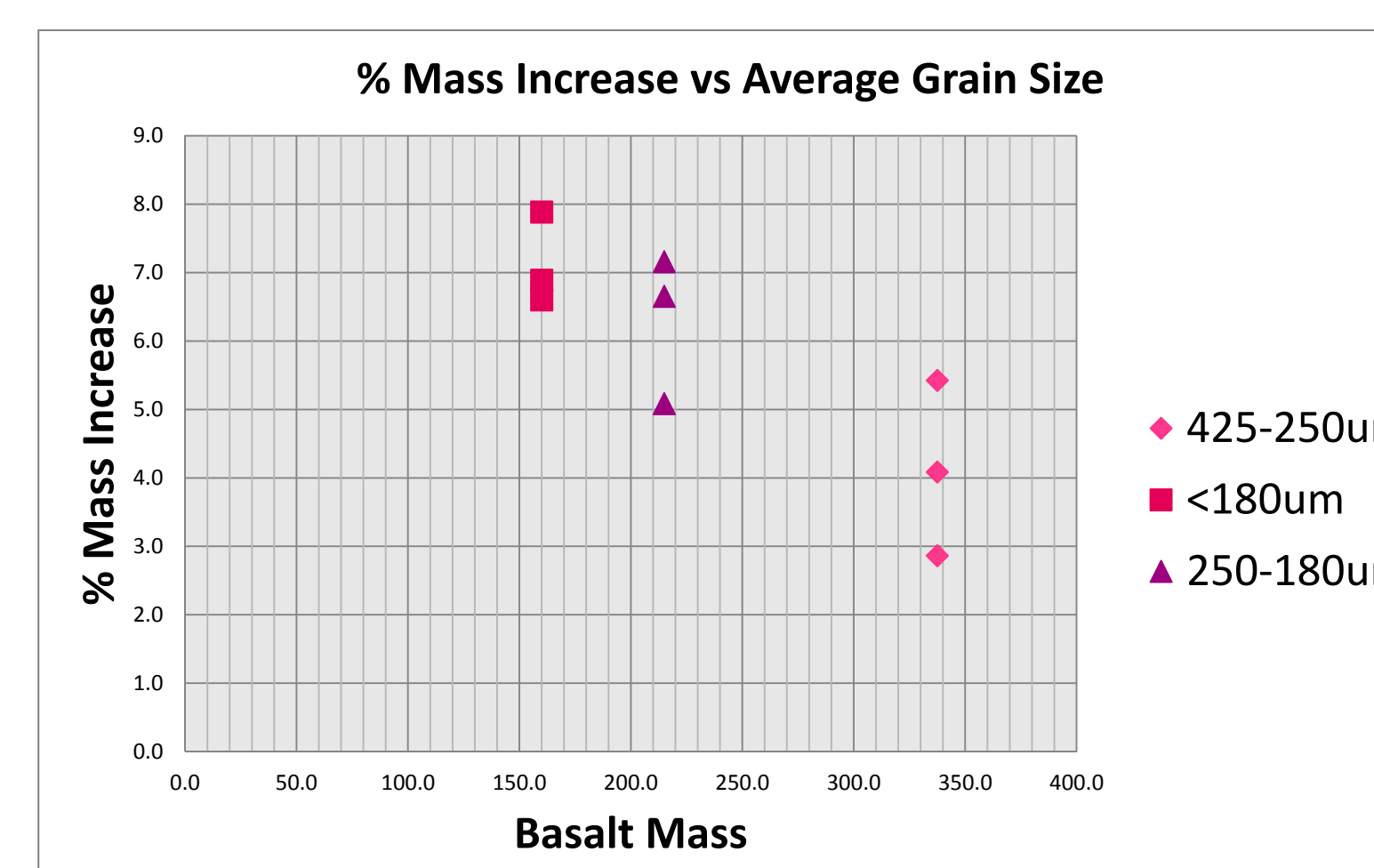
After mass difference analysis was complete, the Elemental Analyzer was used to determine the abundance of C within each sample. Each sample was run in triplets, and one sample of three trials of non-reacted powdered basalt was included, for a total of 30 samples. 8 urea standards were used for accuracy.

UNCERTAINTY

Uncertainties	Instrument	Specification	Observed
All masses	Sartorius C2P Microbalance	(+/-) 5 ug	(+/-) 20 ug for n=10
H ₂ O Volume	VWR 50-200uL Micropipette Model 821	(+/-) .5 uL	(+/-) .3 uL (by mass for n=10)
Thermometer	High Range Liquid Safety	(+/-) .5° C	Not tested
Oven Temperature	Checked with thermometer	N/A	148-153 C
XRF Data	PANalytical X'pert Pro x-ray diffractometer	1% on major elements	Not tested
C Abundance Data	Eurovector EA Elemental Analyzer	Dependent on sample size	Not tested

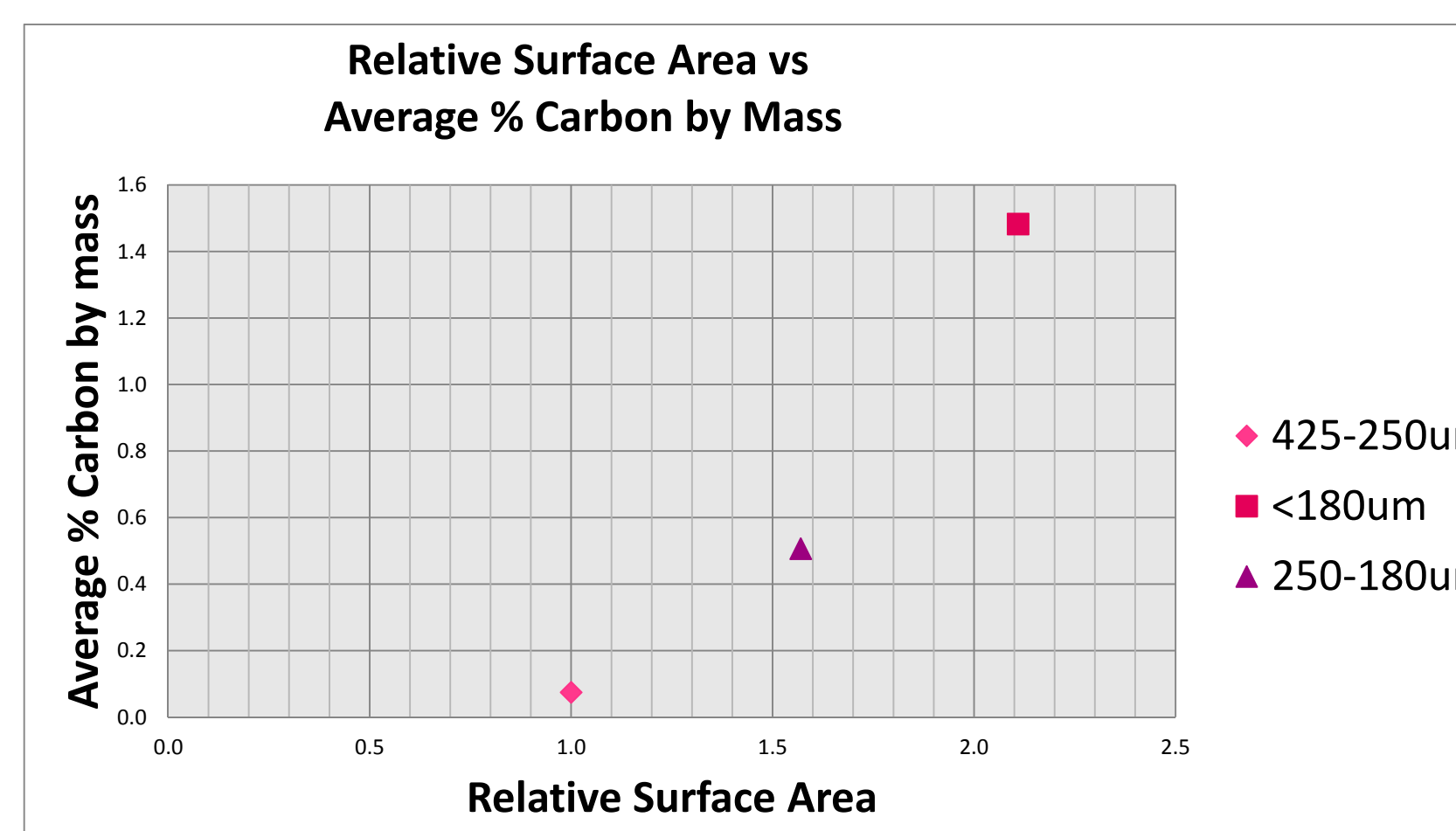
RESULTS

Mass Analysis Data						
Group	Trial	% Mass Increase	avg	STDEV	avg grain size	avg surface area
425-250um	1	4.085	4.125	1.281	337.5	177.75
425-250um	2	2.864			337.5	177.75
425-250um	3	5.425			337.5	177.75
250-180um	1	5.085	6.299	1.081	215	279.03
250-180um	2	6.653			215	279.03
250-180um	3	7.158			215	279.03
<180um	1	6.602	7.125	0.673	160	374.94
<180um	2	7.884			160	374.94
<180um	3	6.889			160	374.94



Elemental Analysis Data

Grain size	Name	RT (Sec)	Height (nA)	Type	Weight (mg)	Elem. Comp.	AVG. C %	STD DEV	AVG C% of Grain size/All Stan.	STD DEV of Grain Size/ All Stan.
N/A	STD-2.raw	234.6	10.52	Elem	0.06	38.77	6.85	8.457	30.20	8.90602
N/A	STD-3.raw	234.5	7.90	Elem	0.07	22.85				
N/A	STD-4.raw	234.1	8.72	Elem	0.07	25.88				
425-250um	ACF-1a.raw	234.7	1.98	Sample	6.65	0.06	0.08	0.026	0.07	0.02202
425-250um	ACF-1b.raw	234.6	1.98	Sample	7.00	0.06				
425-250um	ACF-1c.raw	234.6	3.11	Sample	6.27	0.11				
425-250um	ACF-2a.raw	235.7	2.83	Sample	7.12	0.09	0.07	0.015		
425-250um	ACF-2b.raw	234.9	1.94	Sample	6.85	0.06				
425-250um	ACF-2c.raw	234.7	2.07	Sample	7.62	0.06				
425-250um	ACF-3a.raw	234.8	1.83	Sample	7.00	0.06	0.08	0.031		
425-250um	ACF-3b.raw	234.6	3.43	Sample	6.48	0.11				
425-250um	ACF-3c.raw	235.7	2.14	Sample	7.29	0.06				
<180um	ACF-4a.raw	234.5	9.18	Sample	1.38	1.42	1.48	0.06	1.48	0.09685
<180um	ACF-4b.raw	234.5	6.63	Sample	0.97	1.46				
<180um	ACF-4c.raw	234.3	8.31	Sample	1.15	1.54				
<180um	ACF-5a.raw	234.5	6.66	Sample	0.87	1.64	1.53	0.127		
<180um	ACF-5b.raw	235.3	9.10	Sample	1.25	1.56				
<180um	ACF-5c.raw	234.6	8.41	Sample	1.29	1.39				
N/A	STD-6.raw	234.2	11.79	Elem	0.06	45.84	6.85	19.97		
N/A	STD-7.raw	235.4	7.23	Elem	0.09	17.60				
<180um	ACF-6a.raw	234.7	5.80	Sample	0.83	1.49	1.44	0.108		
<180um	ACF-6b.raw	234.6	6.13	Sample	0.99	1.32				
<180um	ACF-6c.raw	234.3	8.23	Sample	1.16	1.51				
250-180um	ACF-7a.raw	234.7	4.87	Sample	1.39	0.75	0.69	0.072	0.51	0.1528
250-180um	ACF-7b.raw	235.5	4.72	Sample	1.45	0.70				
250-180um	ACF-7c.raw	234.9	4.67	Sample	1.64	0.61				
250-180um	ACF-8a.raw	234.9	2.94	Sample	1.59	0.39	0.39	0.092		
250-180um	ACF-8b.raw	234.7	2.32	Sample	1.64	0.30				
250-180um	ACF-8c.raw	235.3	3.48	Sample	1.54	0.49				
250-180um	ACF-9a.raw	235.5	4.03	Sample	1.88	0.46	0.44	0.076		
250-180um	ACF-9b.raw	234.8	4.38	Sample	1.85	0.50				
250-180um	ACF-9c.raw	234.8	2.68	Sample	1.61	0.36				
250-180um	ACF-10a.raw	234.9	1.35	Unreact	6.21	0.05	0.05	0.007	0.05	0.00655
250-180um	ACF-10b.raw	235.9	1.41	Unreact	7.01	0.04				
250-180um	ACF-10c.raw	235.2	1.66	Unreact	6.36	0.06				
N/A	STD-9.raw	234.6	10.68	Elem	0.72	31.68	302	1.647		
N/A	STD-10.raw	234.6	9.16	Elem	0.64	30.52				
N/A	STD-11.raw	235.1	10.35	Elem	0.78	28.43				



CONCLUSIONS

A direct relationship is discovered between grain size and carbon captured. Looking at the mass difference data, the largest mass increase was found in the <180um group, less on the 250-180um group, and the least on the 425-250um group. Mass increases are in the 4-7% range, which is consistent with other reactions of this duration and conditions.

The Elemental Analysis reveals a similar trend, but of a different magnitude. The 425-250um group again produced the lowest yield of carbon, but this time it was an order of magnitude less than the <180um group instead of approximately 58% as much.

Both groups contain mass increases that are expected and appropriate for this type of reaction, rock, and conditions. The Garcia study saw higher yields for several reasons. The chief reason was due to the different mineral used: pure olivine. The magnesium and iron silicate contains a much higher percentage of divalent cations ready to be released and form new minerals. Another reason is due to the way the experiment was designed. In these experiments, the pressure was internally generated and as the CO₂ reacted, the pressure slowly decreased down to approximately 135 bar. The Garcia study generated the pressure externally via an autoclave.

Both the elemental and mass analyses revealed significant increases in the mass and carbon content of the basalt samples. H₁₀ is proven incorrect, and H₁ is tentatively deemed to be consistent with the results of these experiments.

Though differing by an order of magnitude, both the elemental and mass analyses revealed the largest mass increase and carbon abundance on the <180um grain size group, less on the 250-180um grain size group, and the least on the 425-250um group. As these differences show reproducibility and significant standard deviations, H₂₀ is proven incorrect, and H₂ is tentatively deemed to be consistent with the results of these experiments.

As the elemental and mass analyses data show similar trends but strongly different slopes, including one slope above 1:1 and one below 1:1, there is not enough data to refute H₃₀ and H₃ is deemed to be inconsistent with the data recorded.

SIGNIFICANT REFERENCES

Garcia, B. "Experiments and geochemical modelling of CO₂ sequestration by olivine: potential, quantification." Applied Geochemistry 25.9 (2010): 1383-1396. GeoRef. EBSCO. Web. 11 Nov. 2010.

Goldberg, D. Carbon dioxide sequestration in deep-sea basalt. Proceedings of the National Academy of Sciences. July 22, 2008; 105(29):9920-9925. Available from: GeoRef, Ipswich, MA. Accessed September 30, 2010.

McGrail, B. Peter. "Potential for carbon dioxide sequestration in flood basalts." Journal of Geophysical Research 111.B12 (2006): @B12201. GeoRef. EBSCO. Web. 28 Apr. 2011.

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