Carbon Dioxide Sealing Capacity: Textural or Compositional Controls?*

Constantin Cranganu[1], Hamidreza Soleymani[1], Sadiqua Azad[1], and Kieva Watson[1]

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[1]Department of Earth and Environmental Sciences, Brooklyn College, New York, NY, USA (cranganu@brooklyn.cuny.edu)

Abstract

The primary goal of this research was to investigate the factors controlling sealing capacity of caprocks and their respective contributions to seal capacity. Better understanding of the elements controlling sealing quality will advance our knowledge regarding the sealing capacity of shales and carbonates.

To assess the effect of textural and compositional properties on $scCO_2$ maximum retention column height we collected 30 representative core samples from caprock formations in three counties (Cimarron, Texas, Beaver) in Oklahoma Panhandle. We used mercury injection porosimetry (MIP), scanning electron microscopy (SEM), and Sedigraph measurements to assess the pore-throat-size distribution, sorting, texture, and grain size of the samples. Also, displacement pressure at 10% mercury saturation (Pd) and graphically derived threshold pressure (Pc) were determined by MIP technique. Moreover, EDS (Energy Dispersive X-Ray Spectrometer), specific surface area, and total organic carbon (TOC) measurements were performed to study various parameters and their possible effects on sealing capacity of the samples. Based on statistical analysis of our sample measurements from Oklahoma Panhandle, we assessed the effects of each group of properties (textural and compositional) on maximum $scCO_2$ height that can be hold by the caprock.

The range of $scCO_2$ column height for the samples used in this research is between 0.2–1,358 m. The average $scCO_2$ column height is 351 m. The depth interval around 1,400 m exhibits the largest values of $scCO_2$ column height. The above-mentioned interval is comprised of mainly Cherokee and Morrowan formations (shale seals).

We found a moderate positive relationship (+.16 for shale samples, and +.54, limestone samples) between $scCO_2$ column height and hard/soft mineral content index in shales and limestone samples. Average median pore radius and porosity display a strong negative correlation with $scCO_2$ column height.

One of the most important factors affecting sealing capacity and consequently the height of $scCO_2$ column is sorting of the pore throats. We observed a very strong positive correlation (+0.70) between pore throat sorting and height of CO_2 retention column in shales. This correlation could not be observed in limestone samples. This suggests that the pore throat sorting is more controlling the sealing capacity in shales, and shales with well-sorted pore throats are the most reliable lithology as seal. We observed that Brunauer–Emmett–Teller (BET) surface area shows a very strong correlation with CO_2 retention height in limestone samples (+0.93), while BET surface area did not show any correlation in shales (+0.09).

We also noticed that the median grain size has relatively moderate correlation with $scCO_2$ retention height (+0.20 for shales, -0.39 for limestones) Pore structure (intercrystalline, intergranular, and vuggy), based on SEM micrographs exhibits strong negative correlations with $scCO_2$ column height in both shales and limestones. One exception was noticed for IG structures in limestone (+0.81).

TOC display a very weak positive correlation with $scCO_2$ retention column heights (0.04 for shales, 0.10 for limestone samples). Bulk density displays relatively moderate positive correlation with $scCO_2$ column height (0.30 for shales, 0.58 for limestone samples). However, the skeleton density correlation differs for shales (0.29), and is negative for limestone samples (-0.66).

Reference Cited

Puckette, J., 2006, Naturally Underpressured Compartments And the Geologic Sequestration of Carbon Dioxide: Search and Discovery Article # 40210. Web Accessed October 24, 2014. http://www.searchanddiscovery.com/documents/2006/06088houston_abs/abstracts/puckette.htm?q=+textStrip:puckette.

Carbon Dioxide Sealing Capacity: Textural or Compositional Controls?

Constantin Cranganu, Hamidreza Soleymani, Sadiqua Azad, and Kieva Watson
Brooklyn College of the City University of New York
Dept. of Earth and Environmental Sciences

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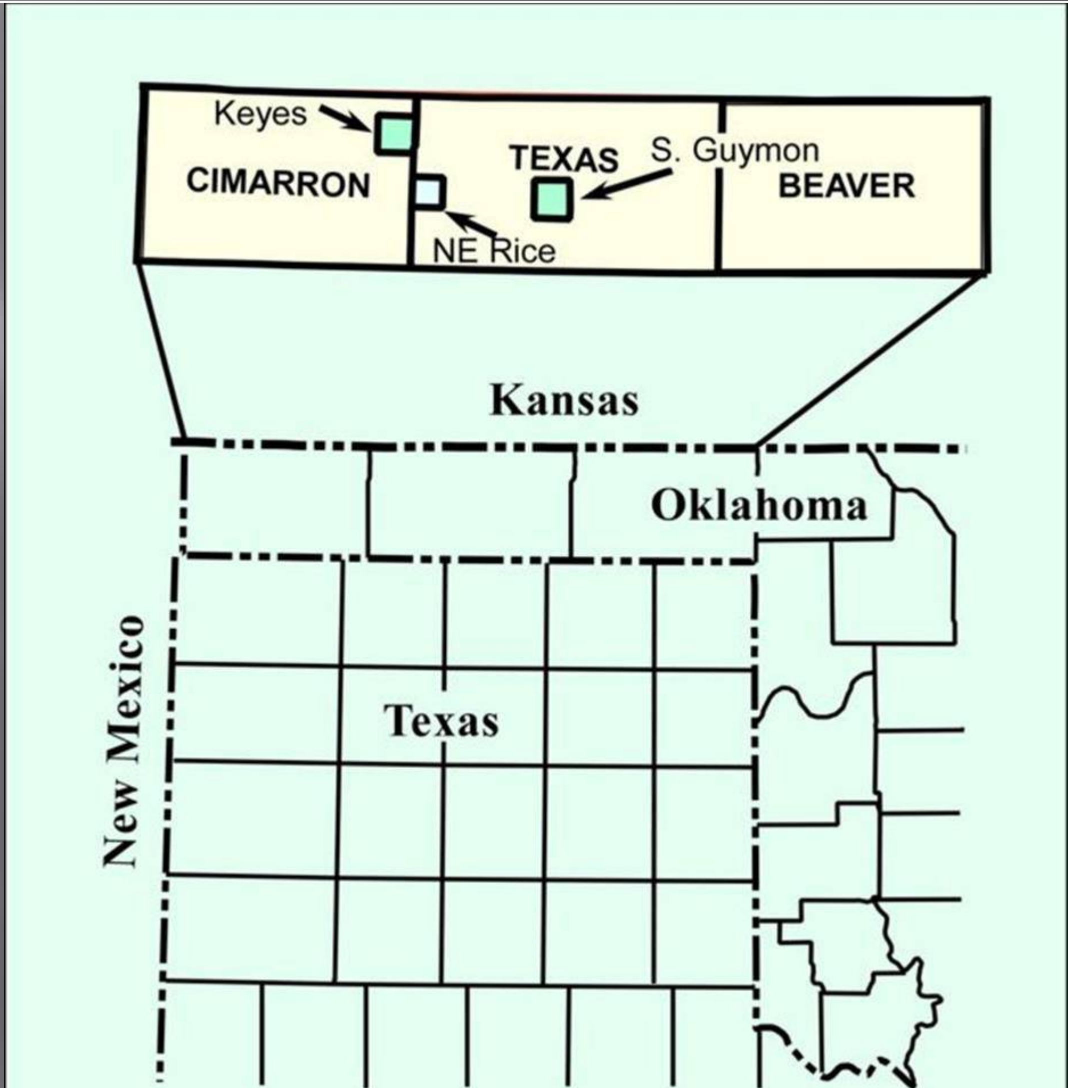
Research objective

The major objective of this research was to test whether textural parameters (e.g., the pore-throat size, distribution, geometry, and sorting, grain size, etc.) or compositional parameters (e.g., mineralogical content, compaction, cementation, organic matter content, carbonate content, etc.) of cap rocks control their CO_2 sealing capacity.

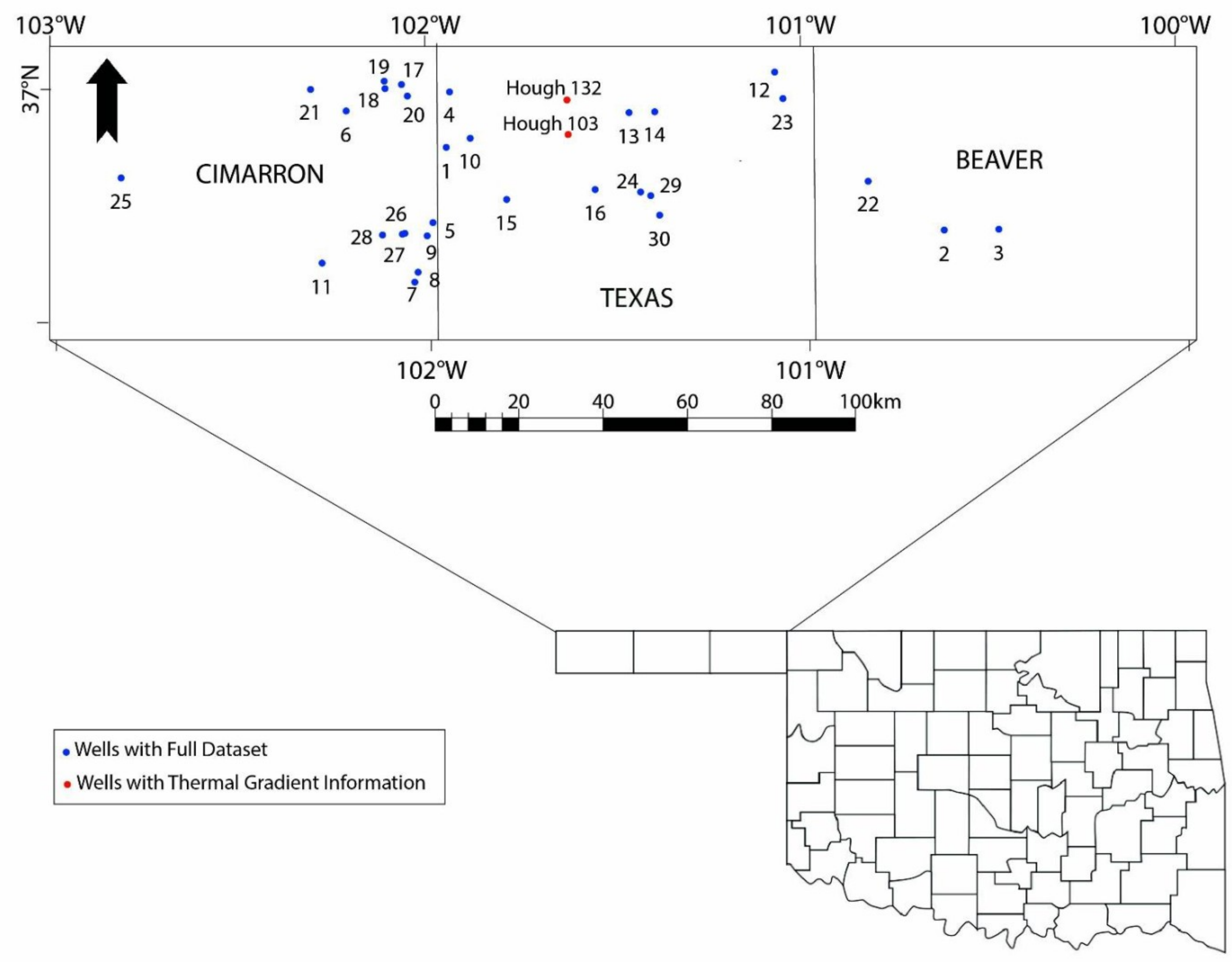
Technical Status

The three gas fields (Keys, NE Rice, and S. Guymon) investigated in this project



From Puckette, 2006

Technical Status



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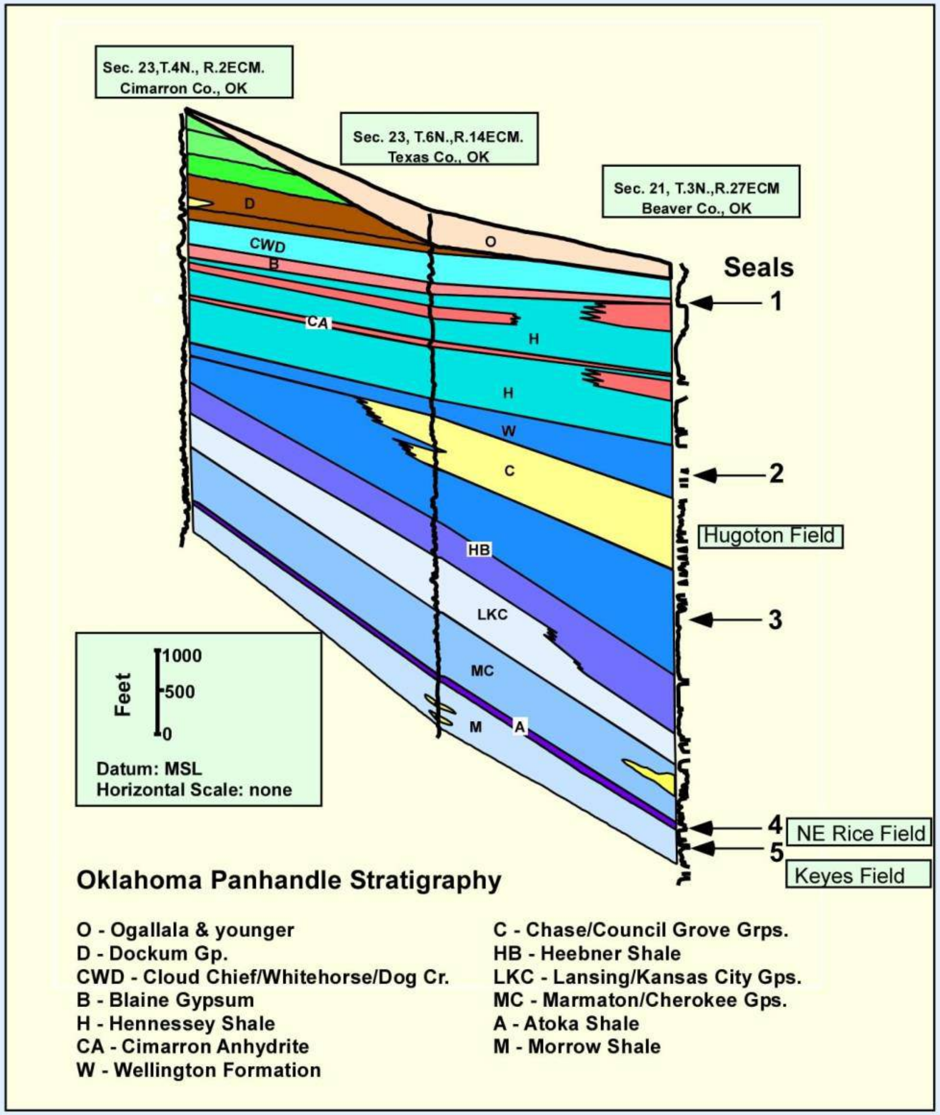

From Puckette, 2006

Regional Stratigraphy

Major Seal Intervals

1 - Hennessey Shale
2 - Wellington Formation
3 - U. Morrow/Atoka Shales
4 - L. Morrow Shales

Methods of investigation

- Thirty caprock samples from three depleted gas fields (Keyes, NE Rice, S. Guymon) and surrounding areas in Oklahoma Panhandle have been collected.
- For each sample the following measurements have been performed:
  - Mercury Intrusion Porosimetry (MIP)
  - SEM microphotography
  - EDS analysis
  - Surface area (BET)
  - Grain size
  - Source Rock Analysis and Total Organic Carbon (TOC)
  - XRD
  - Lithological descriptions

Results

ID #	FILE #	COUNTY	Formation	Top (ft)	Bottom (ft)	Lat	Long	Sample Image	Sample Description
1	120	TEXAS	Morrowan	4419	4466	36.84006	-101.94854	Pic	Gray medium grained quartz sandstone
2	163	TEXAS	Morrowan	4410	4459	36.84413	-101.93947	pic	Light brown medium to coarse grained sandstone
3	239	BEAVER	Marmaton	6720	6839	36.61827	-100.4896	Pic	Black fine grained lime mudstone
4	269	BEAVER	Des Moinesian	6430	6533	36.62177	-100.63258	Pic	Black fine grained lime mudstone
5	328	BEAVER	Permian	866	1030	36.50206	-100.94257	pic	reddish waxy anhydrite
6	334	BEAVER	Marmaton	6646	6676	36.61827	-100.4896	Pic	Black fine grained lime mudstone
7	868	TEXAS	Purdy	4524	4547	36.95927	-101.93526	Pic	Black fine grained Fissile shale
8	874	TEXAS	Morrowan	4559	4569	36.95239	-101.91719	pic	dark gray fine graineded limestone
9	878	TEXAS	Cherokee	4524	4600	36.6806	-101.98941	Pic	Black fine grained lime mudstone
10	900	CIMARRON	Morrowan	4496	4557	36.92432	-102.21267	Pic	Light brown fine grained quartz sandstone
11	946	BEAVER	Marmaton	6627	6741	36.61796	-100.48026	pic	Black fine graineded mudstone
12	953	BEAVER	Marmaton	6403	6462	36.62537	-100.50748	pic	Black fine graineded mudstone
13	3152	CIMARRON	Morrowan	4817	4916	36.53576	-102.20474	Pic	Black fine grained layered calcareous shale

Partial Master Table

Results

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File No.	County	Formation	Top (ft)	Bottom (ft)	Latitude (◦N)	Longitude (◦W)
120-8	TEXAS	Morrowan	4419	4466	36.8	-101.9

MIP Data Summary		
Median Pore Radius (Volume)	0.0278	µm
Median Pore Radius (Area)	0.0099	µm
Average Pore Radius	0.0188	µm
Bulk Density	2.5	g/cm^3
Apparent (skeletal) Density	2.7	g/cm^3
Porosity	6.1	%

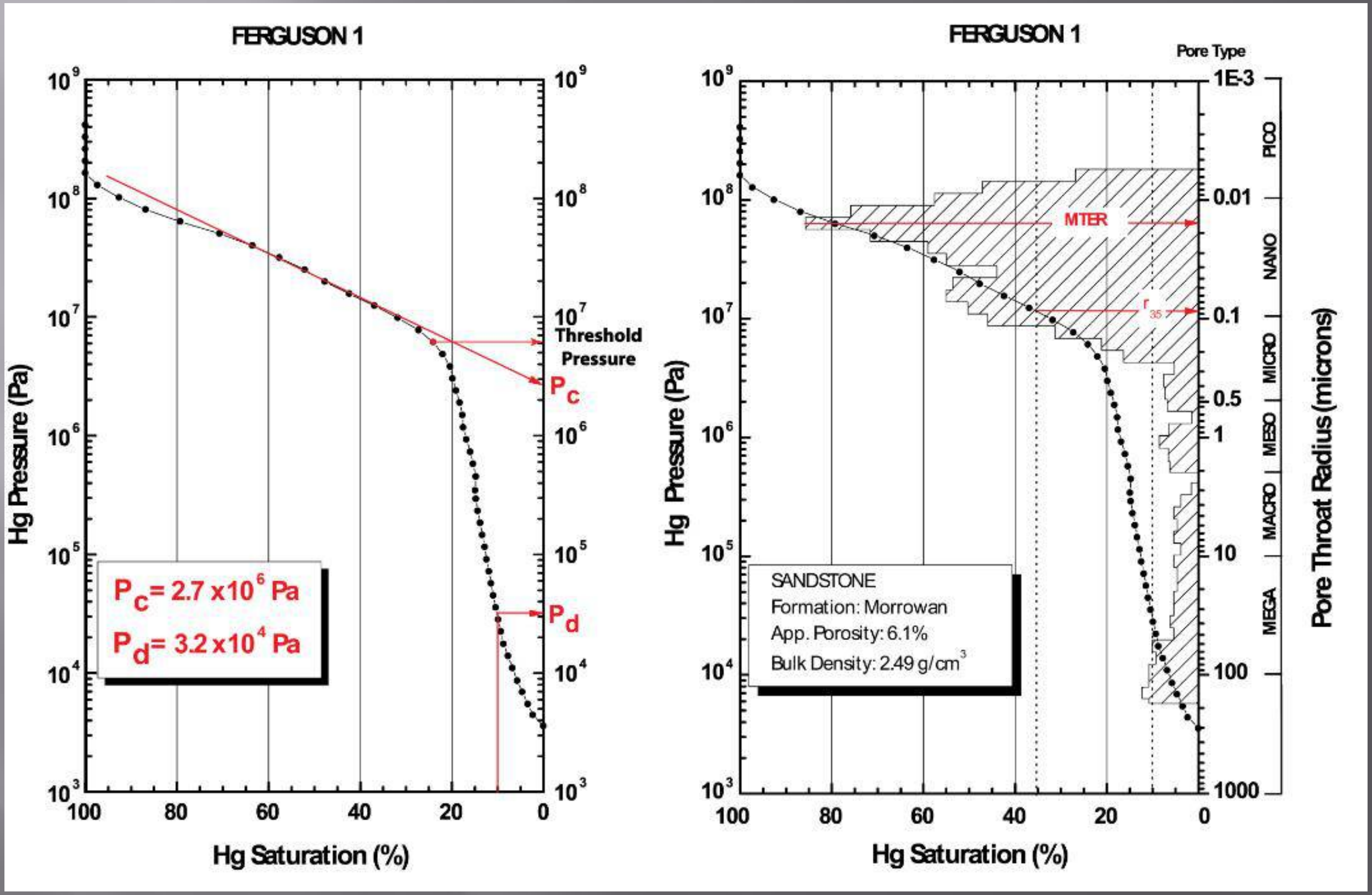
Organic Content		
TOC	1.29	wt% HC

Pore Structure Summary		
Pc	2.80	MPa
Pd (@ 10% Hg saturation)	0.03	MPa
BET Surface Area	8.1997	m^2/g
Median Grain Size	71.446	µm
R35	0.09	µm
Pore Throat Type	Nano	
Pore Throat Distribution	Unimodal	
Pore Throat Sorting	MS	
MTER	0.016	µm

XRD Analysis (wt%)										
Illite & Mica	Kaolinite	Chlorite	Quartz	K-Feldspar	Plagioclase	Calcite	Dolomite	Ankerite	Hematite	Pyrite
7.5	43.6	33.7	9.3	0.4	3.1	0	0	0	0	0

Sample # 1 – FERGUSON-1

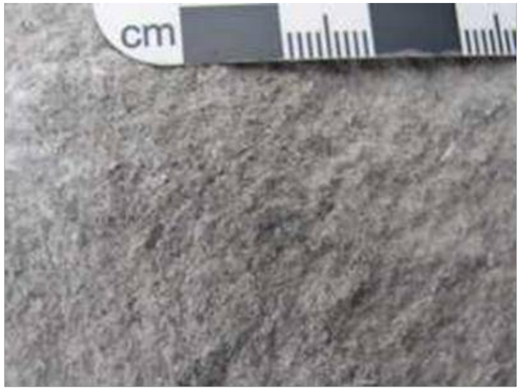
Results

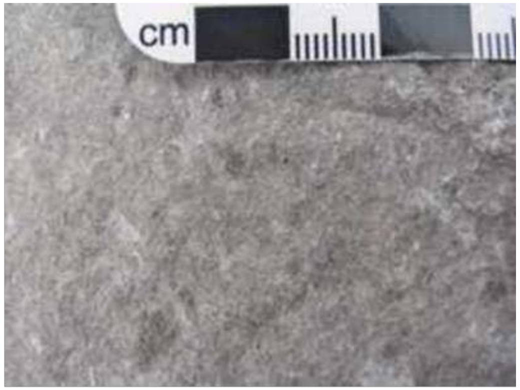


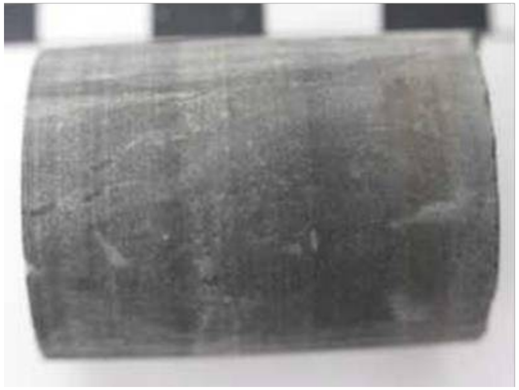
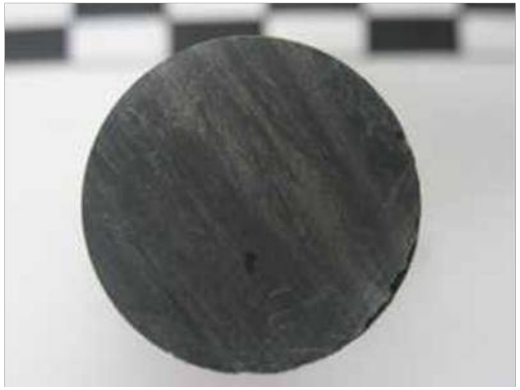
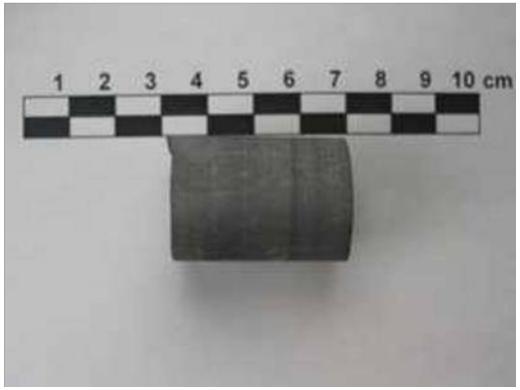
MIP analysis of sample #1.

Results

Sample #2 Shrauner-2 (depth 1,173 m)
Gray Limestone (Fine – Medium Grained)





Results

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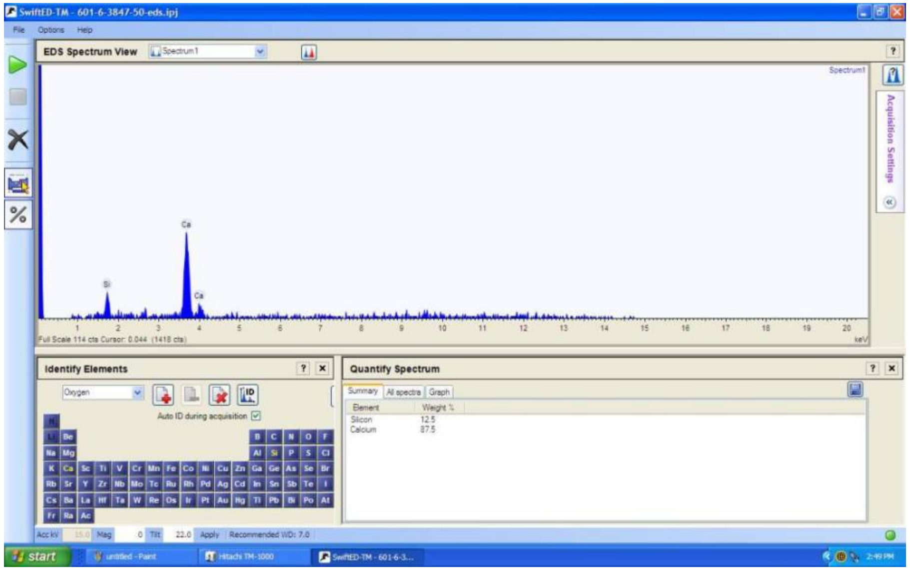
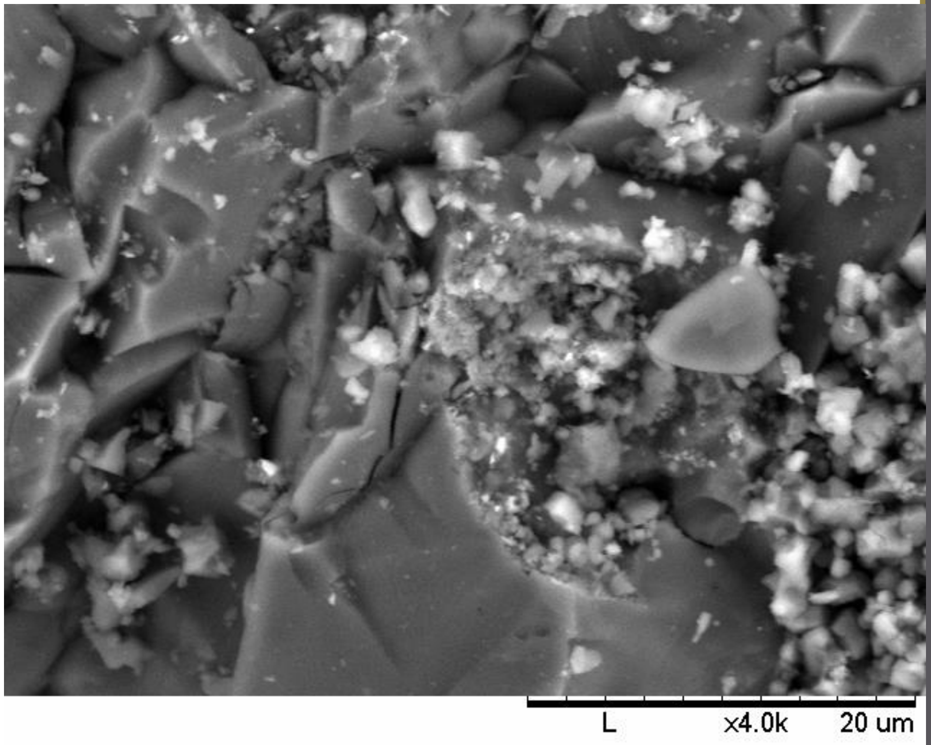
Sample #2 Shrauner-2 (depth 1,173 m)
Gray Limestone (Fine – Medium Grained)





EDS analysis indicating the predominance of Ca. An **XRD analysis** indicates 96.7% calcite

SEM microphotograph. Calcite crystals are abundant. Intercrystalline (IC) porosity

Results

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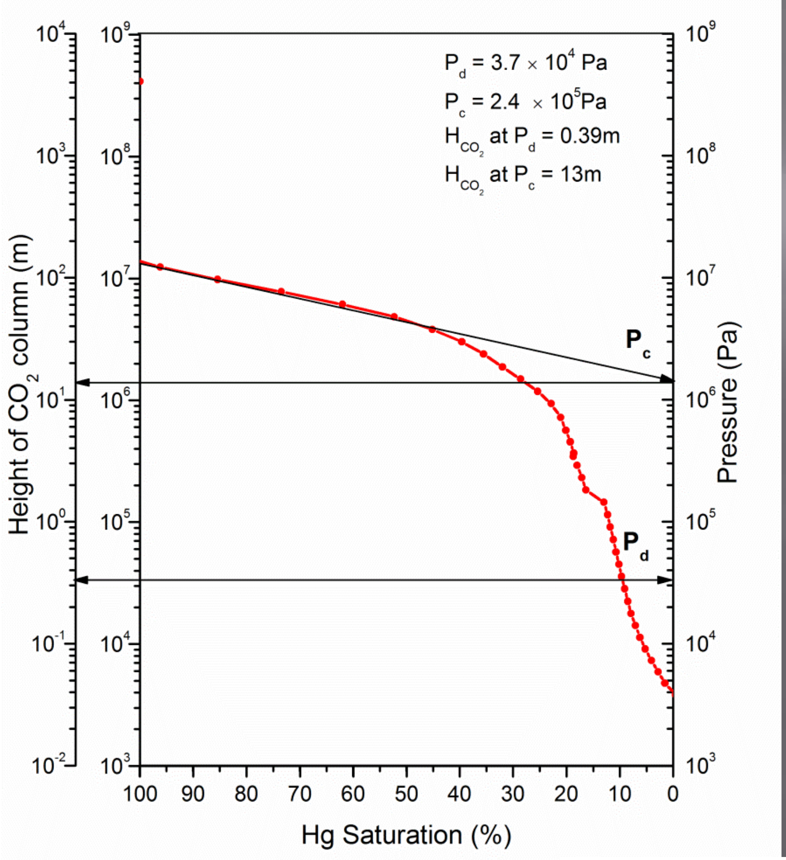
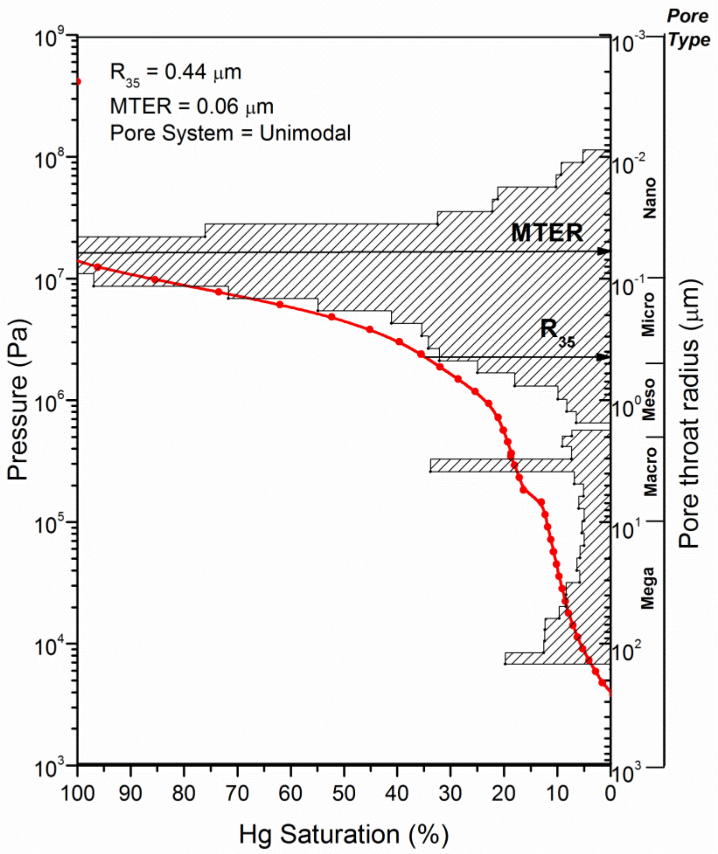
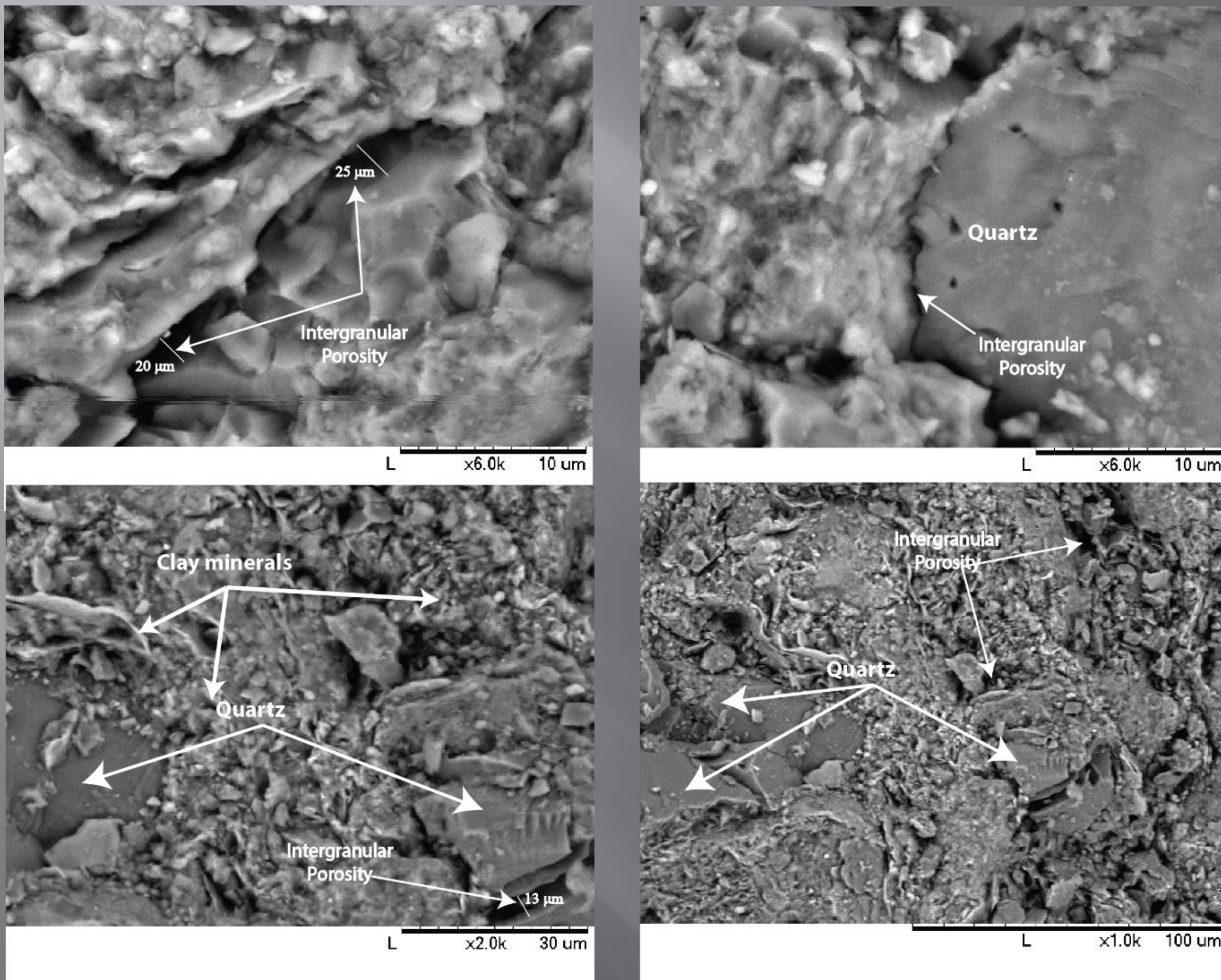
Mercury Intrusion Porosimetry Measurements





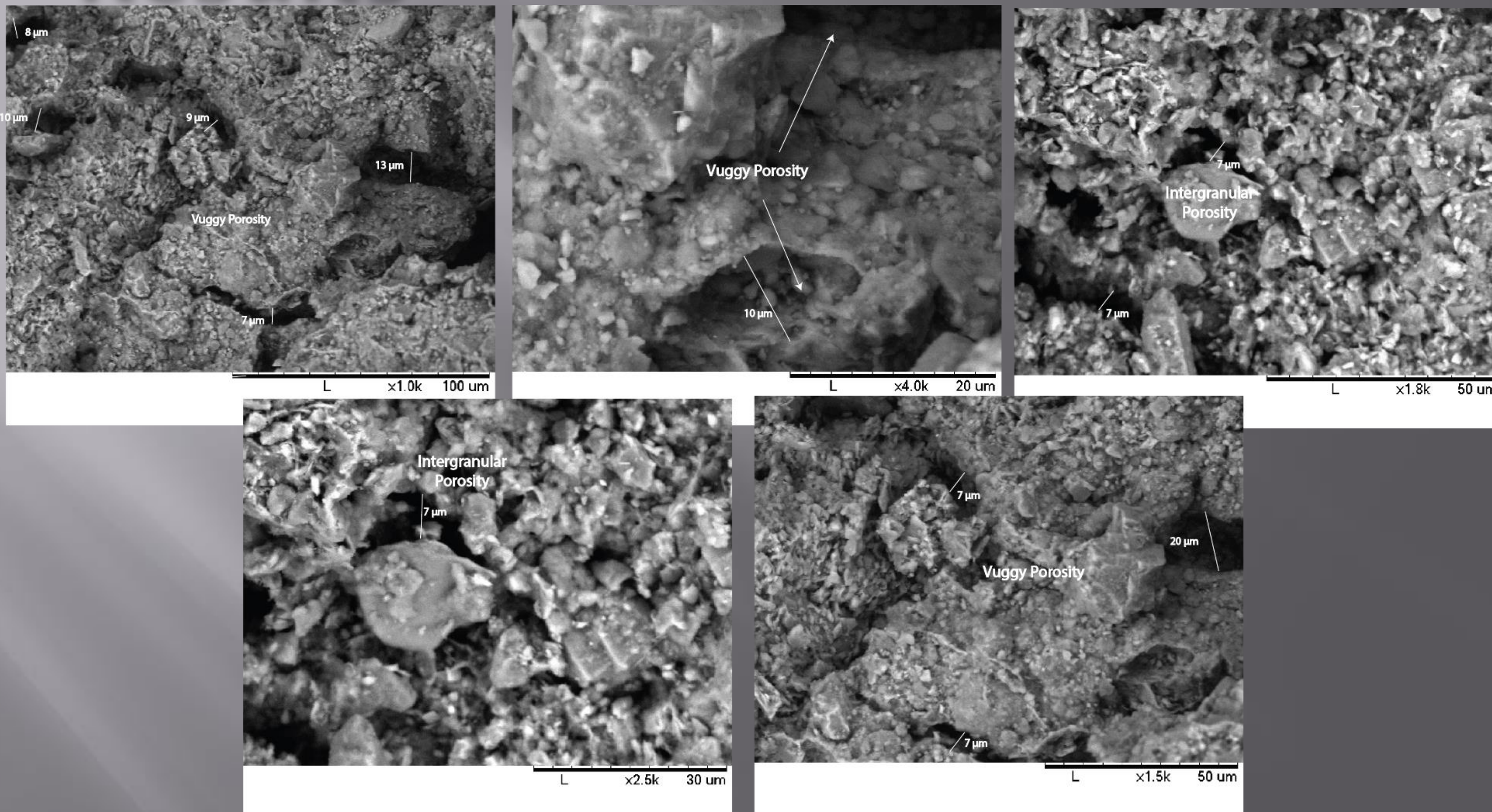
Sample #2 Shrauner-2

Results



SEM microphotographs of sample #1: Shale with mainly intergranular porosity. Descriptive score: 2, 4, 1 (out of 5) for Intercrystalline (IC), Intergranular (IG), and Vuggy (V) porosity, respectively.

Results



SEM microphotographs of sample #22: fine grained limestone, intergranular porosity with clear vuggy space. Descriptive score: 1, 3, 5 (out of 5) for IC, IG, and V porosity respectively.

Results

Surface Area Measurements

MICROMERITICS ANALYTICAL SERVICES *The Particle Testing Authority*

TriStar II 3020 V1.03 (V1.03) Unit 2 Port 3 Serial #: 571 Page 1

Sample: 601 F3
Operator: IAR/AT
Submitter: Brooklyn College
File: C:\...\06JUN\1103991.SMP

Started: 6/23/2011 10:09:32AM
Completed: 6/23/2011 12:45:41PM
Report Time: 6/23/2011 1:15:17PM
Warm Free Space: 6.6564 cm³ Measured
Equilibration Interval: 10 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.360 K
Sample Mass: 4.0348 g
Cold Free Space: 16.1008 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Comments: Degas at 110 C for 16h

Summary Report

Surface Area

Single point surface area at P/Po = 0.300959242: 0.5840 m²/g

BET Surface Area: 0.6087 m²/g

Sample #2 Shrauner-2

Results

Brooklyn College The City University of New York

Grain Size Measurements

MICROMERITICS ANALYTICAL SERVICES *The Particle Testing Authority*

Micromeritics Instrument Corporation

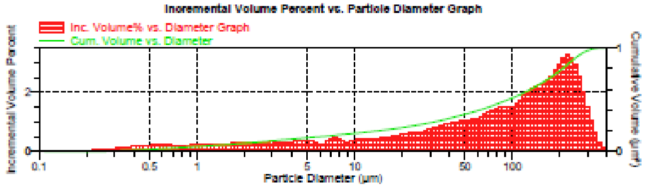
Saturn DigiSizer II 5205 V1.01 Saturn DigiSizer II 5205 V1.01 5200 LSHU V3.00 S/N 127 Page 1

Sample: 601
Operator: TN
Submitter: Brooklyn College of CUNY
File: C:\...\06JUN\1103991.SMP

Test Number:	2	Model:	(1.570, 0.1000000), 1.331
Analyzed:	6/22/2011 2:42:38PM	Material:	Sediment / Water
Reported:	6/22/2011 3:32:49PM	Background:	Water RI 1.331
Background:	6/22/2011 2:23:08PM	Smoothing:	Medium

Combined Report

Incremental Volume Percent vs. Particle Diameter Graph



Summary Report

Analysis Conditions

FlowRate:	12.0 l/m	Ultrasonic intensity:	100 %
Circulation time:	Not Used	Ultrasonic time:	60 sec

Sample

Sample Concentration: 0.02676 %
Obscuration: 37.2 %

Weighted Statistics (Volume Distribution)

		Std Dev of 2			Std Dev of 2
Mean	112.136	1.907	Mode	223.600	0.000
Median	93.794	2.285			

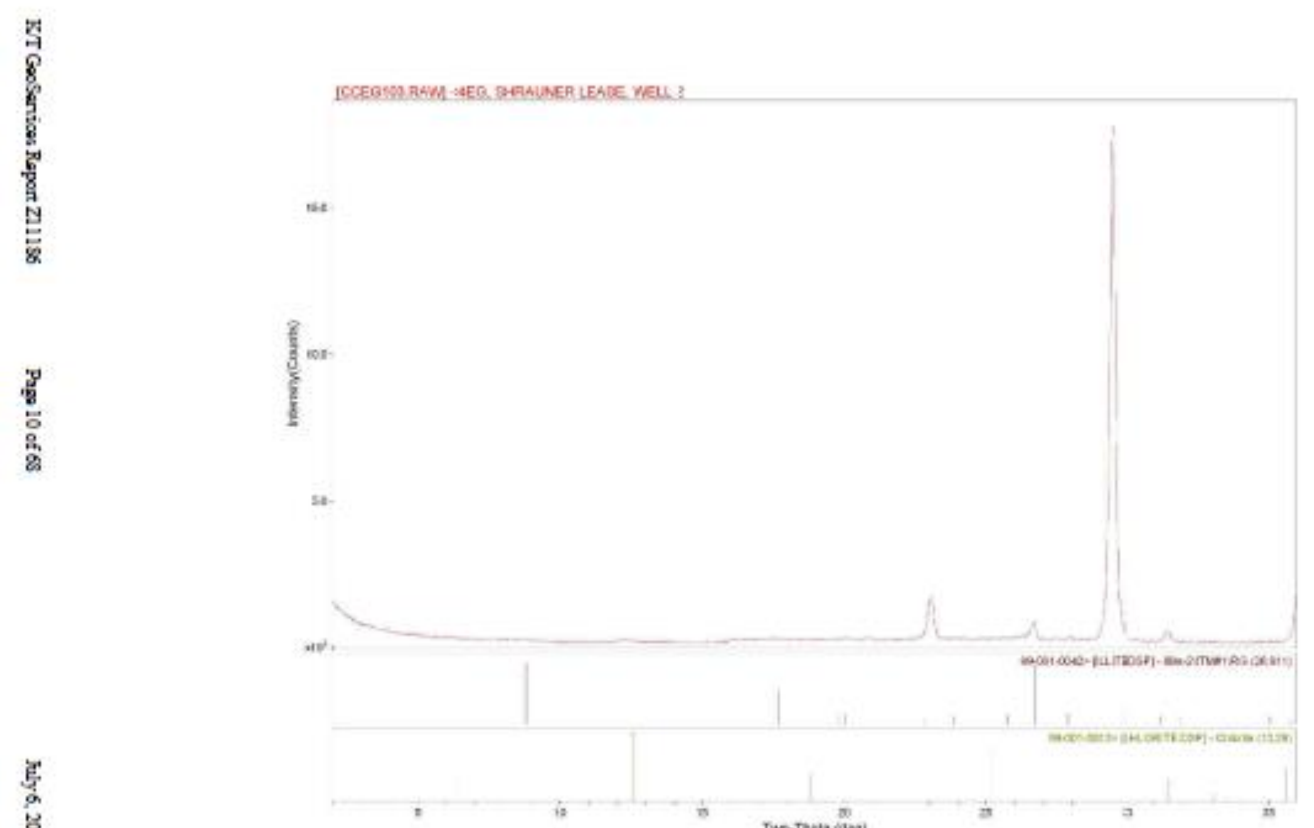
Selected Percentiles by Volume

Percent Finer	Diameter (µm)
90.0	249.193
50.0	93.794
10.0	2.888

Sample #2 Shrauner-2

Results

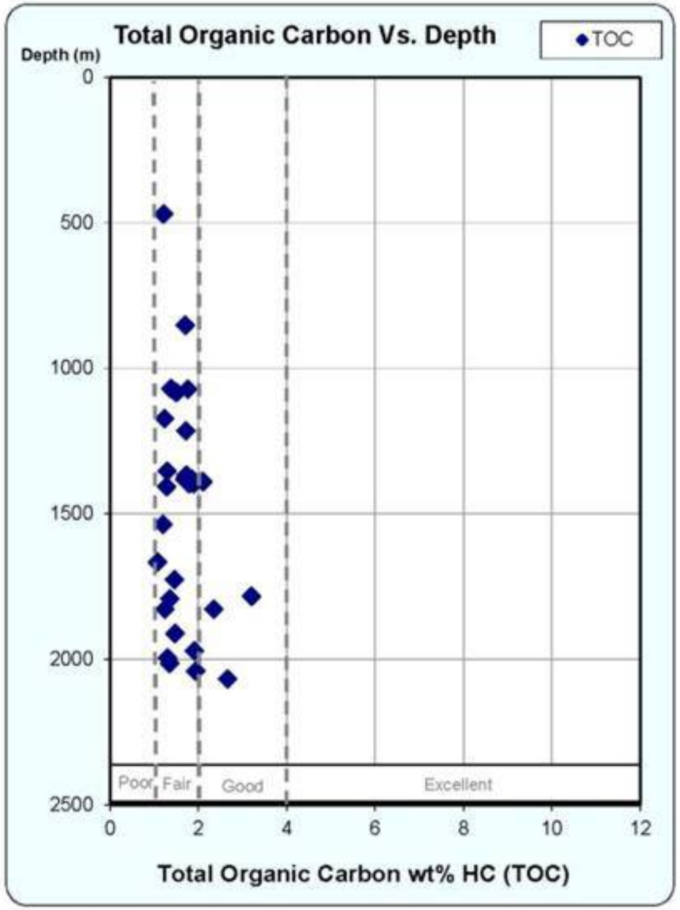
XRD Measurements

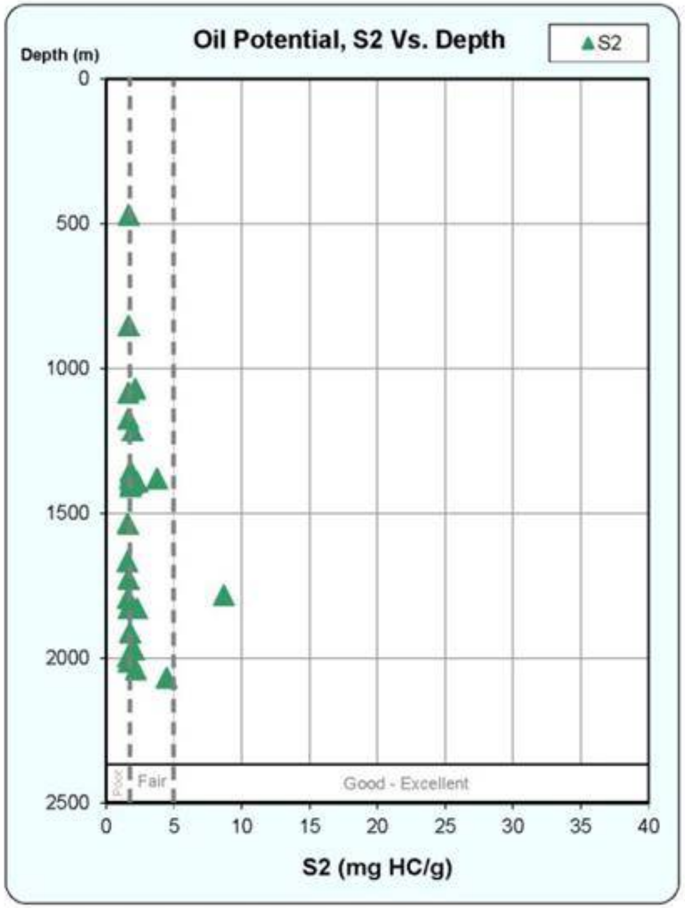


Sample #2 Shrauner-2

Results

Source-Rock Analysis and Total Organic Carbon (TOC)



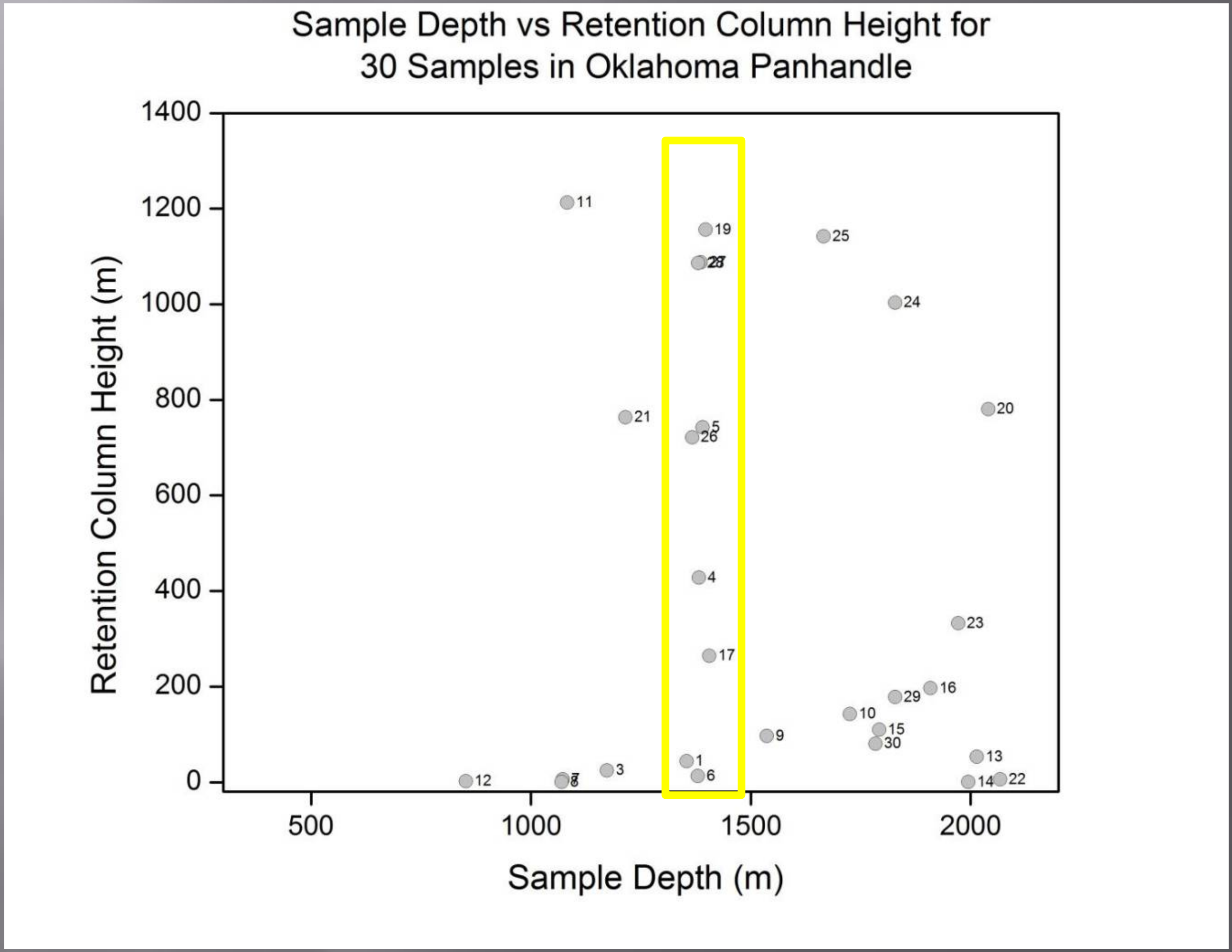


Results

ID#	Formation	Depth (m)	Temperature at sample depth (°C)	sc CO_2 density (kg/m³)	Water density (kg/m³)	Seal threshold pressure (Pc) (air-Hg) (MPa) contact angle (°0)	Seal threshold pressure (Pc) (brine-CO_2) (MPa) contact angle (°0)	ScCO_2 Retention column height (m) contact angle (°0)	ID#	Formation	Depth (m)	Temperature at sample depth (°C)	sc CO_2 density (kg/m³)	Water density (kg/m³)	Seal threshold pressure (Pc) (air-Hg) (MPa) contact angle (°0)	Seal threshold pressure (Pc) (brine-CO_2) (MPa) contact angle (°0)	ScCO_2 Retention column height (m) contact angle (°0)
1	Morrowan	1354	48.21	705.3	1073	2.7	0.03	**44.11**	16	Cherokee	1909	62.63	706.56	1073	12	0.01	**196.73**
2	Cimarron	470	25.21	NA	1073	1.3	1.3	**NA**	17	Keyes	1406	49.55	709.8	1073	16	0.01	**264.64**
3	Marmaton	1173	43.5	682.49	1073	1.6	0.04	**24.61**	18	Morrowan	1396	49.29	709.13	1073	NA	NA	**NA**
4	Purdy	1382	48.94	708.07	1073	26	0.01	**428.01**	19	Unknown	1397	49.33	709.18	1073	70	0.03	**1155.86**
5	Cherokee	1390	49.15	708.73	1073	45	12	**742.13**	20	Keyes	2040	66.04	711.31	1073	47	0.35	**780.63**
6	Morrowan	1380	48.87	707.82	1073	0.76	0.76	**12.5**	21	Cherokee	1215	44.6	687.38	1073	49	0.01	**763.35**
7	Topeka	1072	40.88	676.56	1073	0.37	0.24	**5.61**	22	Chester	2067	66.75	711.19	1073	0.34	0.01	**5.65**
8	Topeka	1070	40.82	676.55	1073	0.02	0.03	**0.36**	23	Atoka	1971	64.26	711.66	1073	20	0.02	**332.51**
9	Morrowan	1536	52.95	711.57	1073	5.8	0.91	**96.4**	24	Morrowan	1828	60.54	701.85	1073	62	0.01	**1003.52**
10	Morrowan	1726	57.87	701.99	1073	8.8	0	**142.49**	25	Mississippian	1666	56.31	704.76	1073	70	0.01	**1141.97**
11	Topeka	1083	41.15	676.81	1073	80	0.01	**1213.05**	26	Morrowan	1367	48.53	706.61	1073	44	0.07	**721.43**
12	Chase	852	35.15	625.88	1073	0.17	0.17	**2.28**	27	Morrowan	1386	49.04	708.38	1073	66	0.01	**1087.41**
13	Chester	2014	65.37	711.4	1073	3.2	0.01	**53.16**	28	Morrowan	1381	48.9	707.89	1073	66	0.01	**1085.95**
14	Keyes	1995	64.86	711.55	1073	0.03	0.03	**0.45**	29	Morrowan	1828	60.54	701.85	1073	11	0.01	**178.04**
15	Marmaton	1792	59.59	701.08	1073	6.8	6.8	**109.84**	30	Cherokee	1783	59.37	701.05	1073	5	6.1	**80.76**

scCO_2 retention column heights for 30 samples

Results



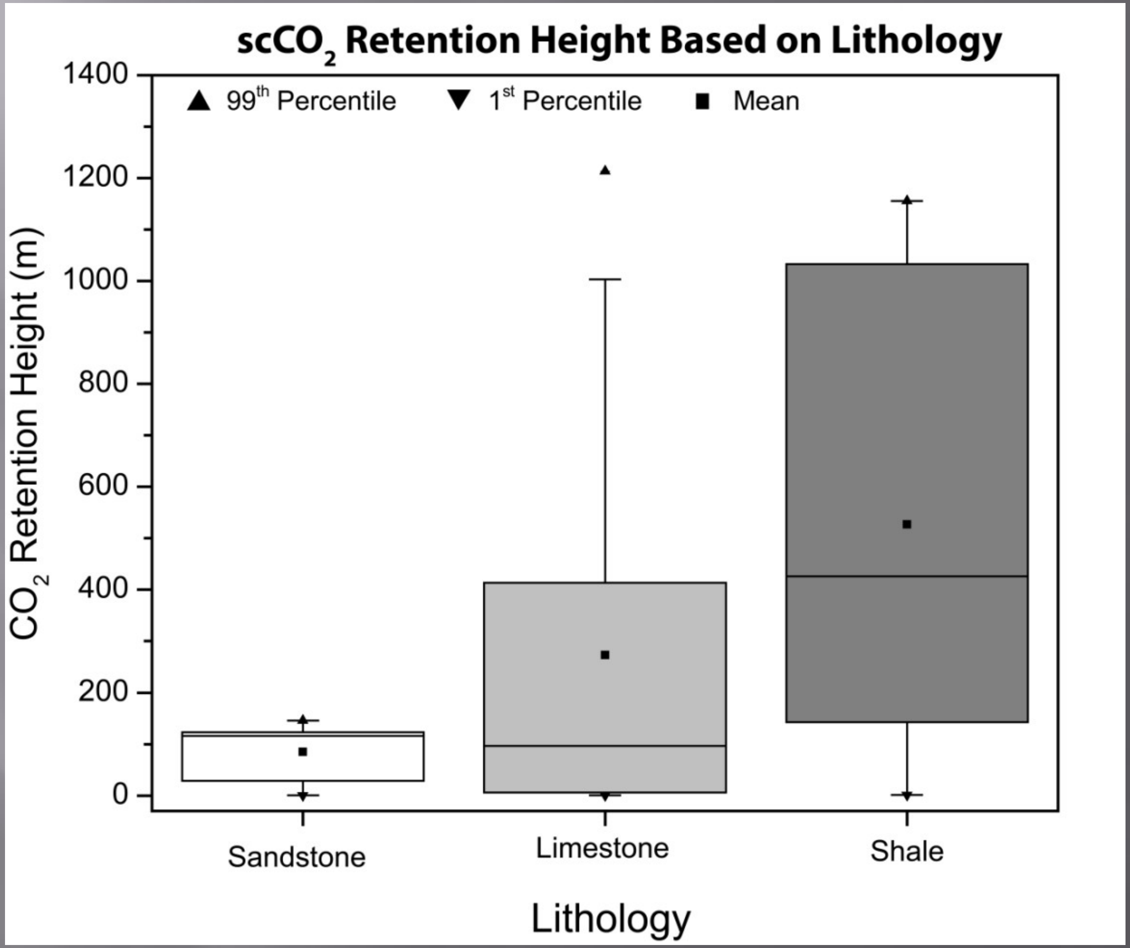
Around 1,400 m depth, samples display relatively higher $scCO_2$ retention column heights.

Results

Formation	Height of CO_2 (m)	Average Sample Depth in Formation (m)
Chase	65	834
Cherokee	412	1575
Chester	33	1866
Keys	214	1762
Marmaton	63	1482
Morrowan	428	1515
Purdy	263	1390
Topeka	286	1075

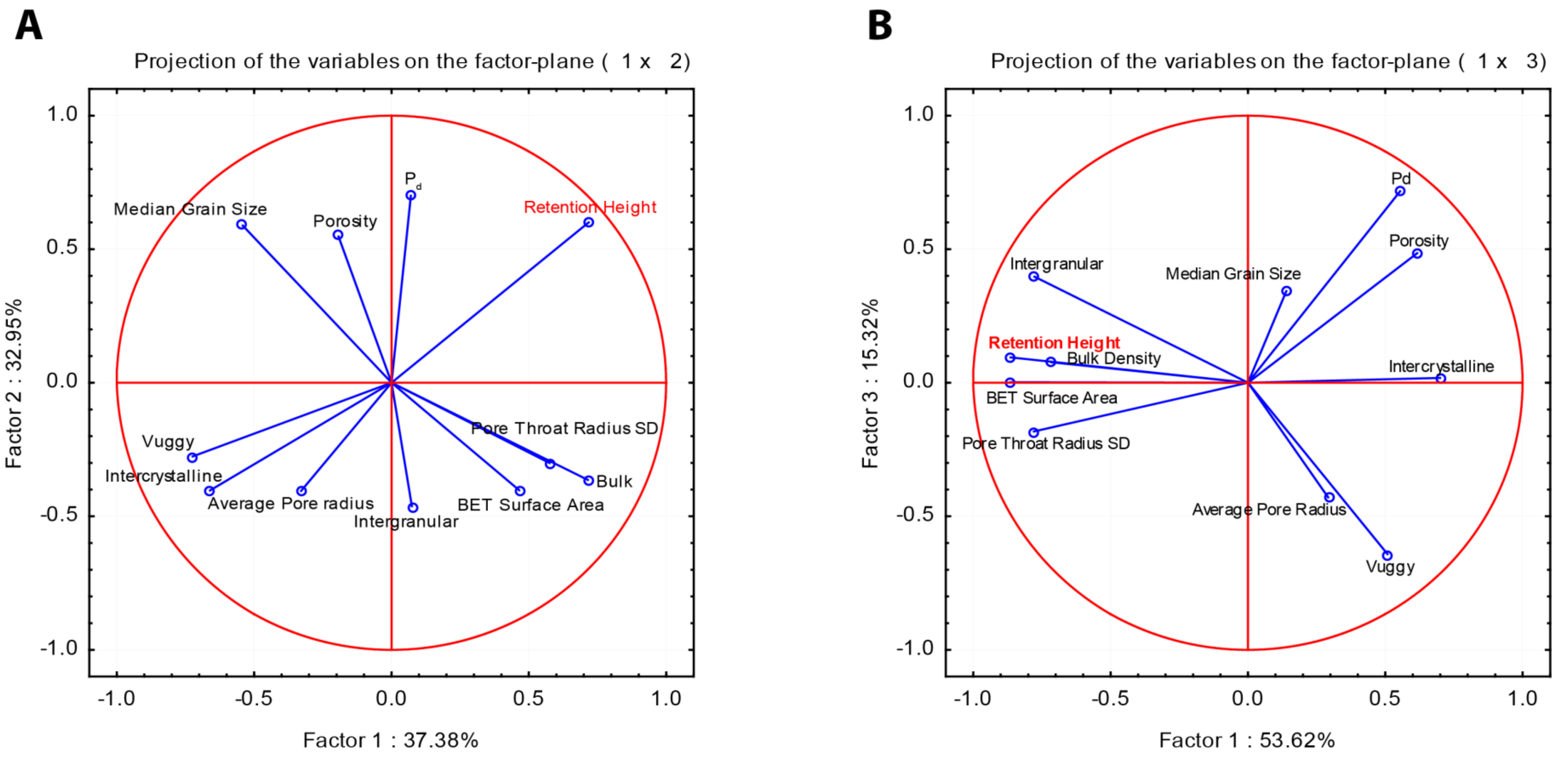
Summary of the major seal formations and their respective average $scCO_2$ retention column heights in Oklahoma Panhandle.

Results



Shales exhibit relatively higher $scCO_2$ retention column heights in comparison with limestone and sandstone samples

Results

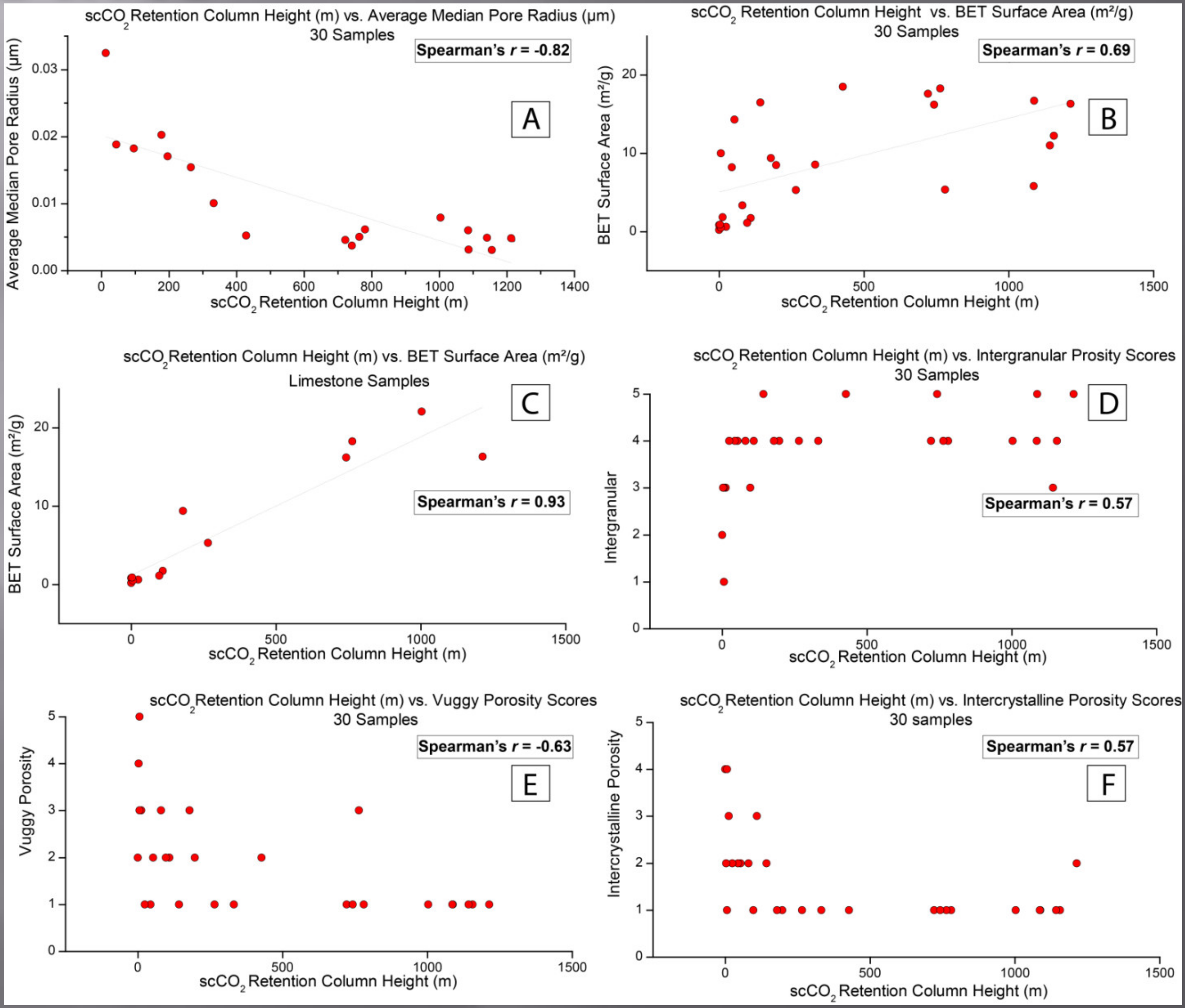


PCA Analysis

(A) shale samples

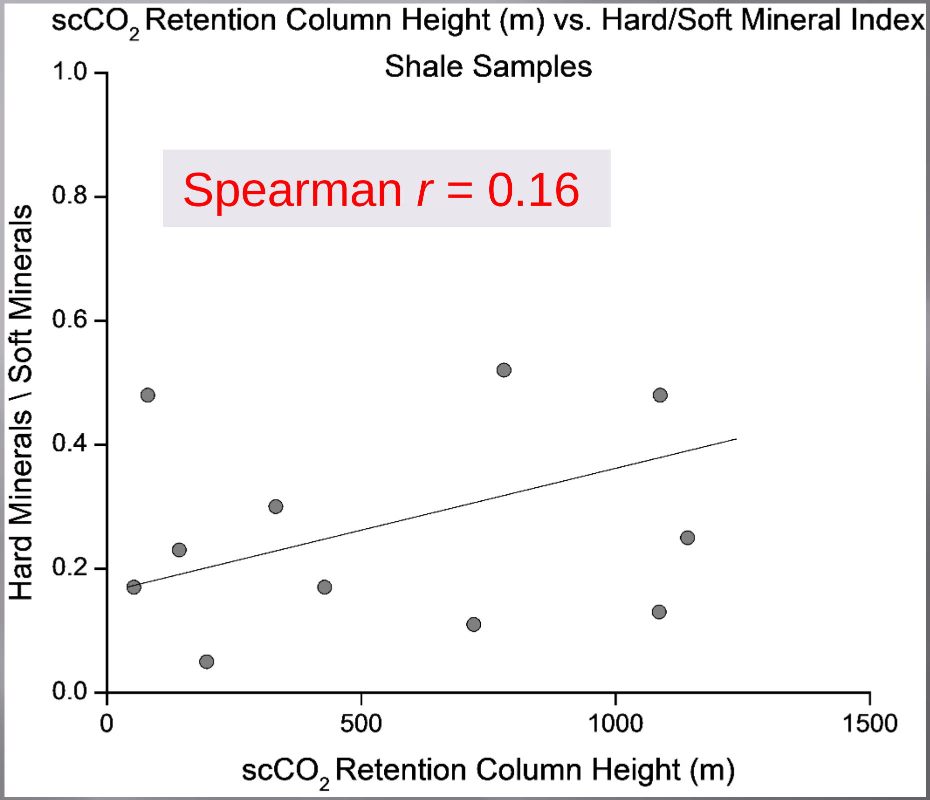
(B) limestone samples

Results

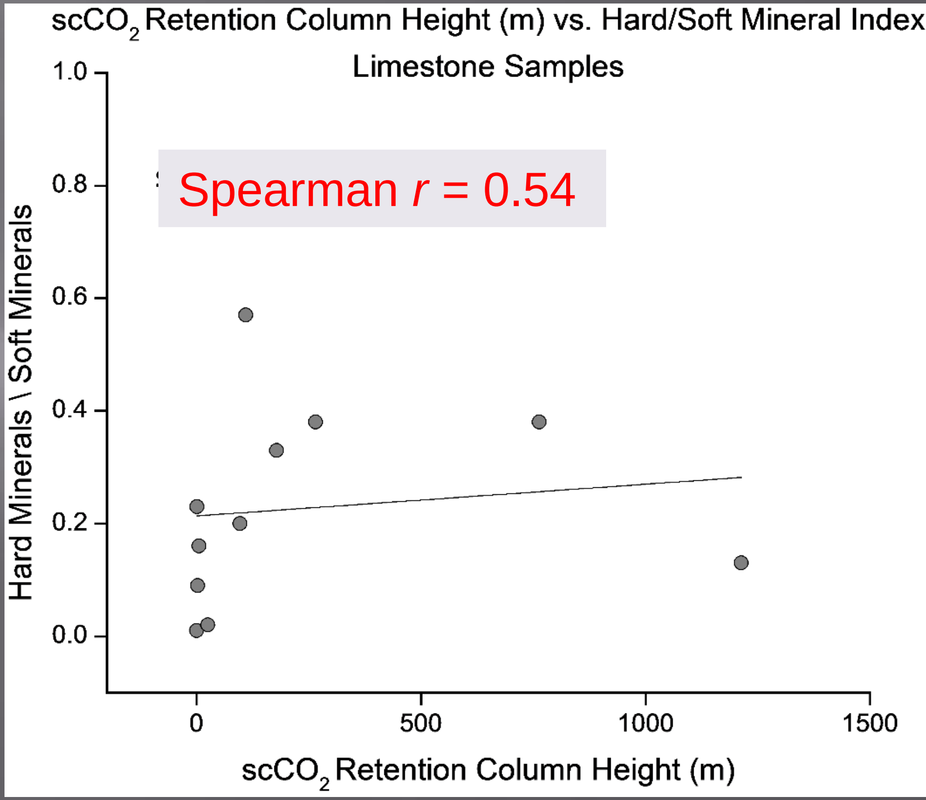


scCO2 Retention Column Height (m) vs. Average Median Pore Radius (µm)
30 Samples
Spearman's r = -0.82
A
Average Median Pore Radius (µm)
scCO2 Retention Column Height (m)
scCO2 Retention Column Height vs. BET Surface Area (m²/g)
30 Samples
Spearman's r = 0.69
B
BET Surface Area (m²/g)
scCO2 Retention Column Height (m)
scCO2 Retention Column Height (m) vs. BET Surface Area (m²/g)
Limestone Samples
C
Spearman's r = 0.93
BET Surface Area (m²/g)
scCO2 Retention Column Height (m)
scCO2 Retention Column Height (m) vs. Intergranular Prosity Scores
30 Samples
D
Spearman's r = 0.57
Intergranular
scCO2 Retention Column Height (m)
scCO2 Retention Column Height (m) vs. Vuggy Porosity Scores
30 Samples
Spearman's r = -0.63
E
Vuggy Porosity
scCO2 Retention Column Height (m)
scCO2 Retention Column Height (m) vs. Intercrystalline Porosity Scores
30 samples
Spearman's r = 0.57
F
Intercrystalline Porosity
scCO2 Retention Column Height (m)

Results

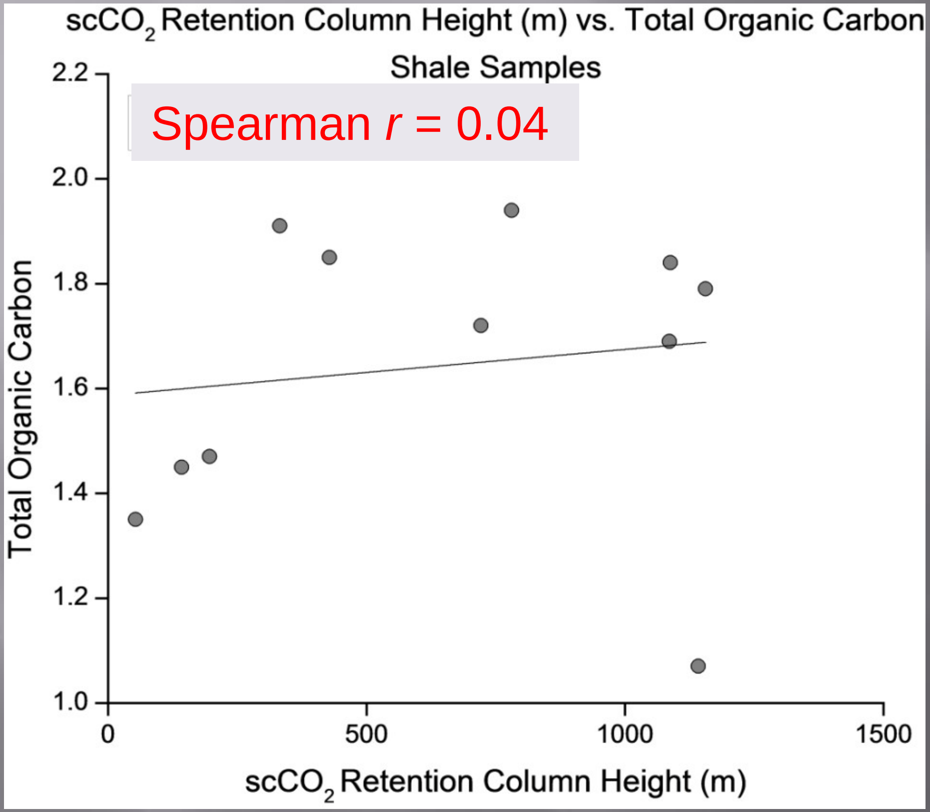


scCO$_2$ Retention Column Height (m) vs. Hard/Soft Mineral Index
Shale Samples
Spearman *r* = 0.16
Hard Minerals \ Soft Minerals
scCO$_2$ Retention Column Height (m)
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500

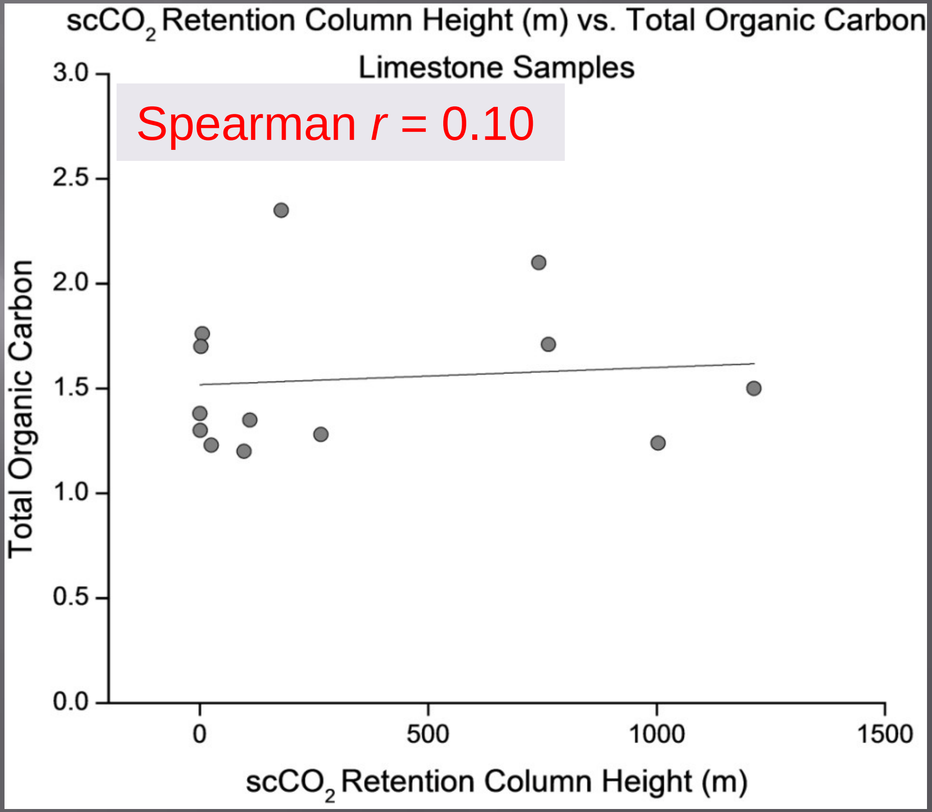


scCO$_2$ Retention Column Height (m) vs. Hard/Soft Mineral Index
Limestone Samples
Spearman *r* = 0.54
Hard Minerals \ Soft Minerals
scCO$_2$ Retention Column Height (m)
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500

Results



$scCO_2$ Retention Column Height (m) vs. Total Organic Carbon
Shale Samples
Spearman r = 0.04
Total Organic Carbon
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0
500
1000
1500
$scCO_2$ Retention Column Height (m)



$scCO_2$ Retention Column Height (m) vs. Total Organic Carbon
Limestone Samples
Spearman r = 0.10
Total Organic Carbon
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
$scCO_2$ Retention Column Height (m)

Results

$scCO_2$ Retention Column Height vs.	Shale Samples	Limestone Samples
Pore Throat Radius SD	0.20	0.65*
Average Mean Pore Radius	-0.78*	-0.76*
Total Porosity	0.03	-0.70*
Bulk Density	0.30	0.58*
Skeleton Density	0.29	-0.66*
BET Surface Area	0.09	0.93*
Intercrystalline Porosity	-0.75*	-0.61*
Vuggy Porosity	-0.67*	-0.40*
Intergranular Porosity	-0.19	0.81*
Hard/Soft Minerals	0.16	0.54
TOC	0.04	0.10
Median Grain Size	0.10	-0.18
Pore Sorting	0.70*	0.15

Spearman's rank correlation coefficients between various parameters and maximum retention column height. Asterisks indicate correlation coefficients with statistical significance of 95%.

Conclusions

- We estimated the sealing capacity of caprocks in the Oklahoma Panhandle in terms of $scCO_2$ column height that can be held back by a given seal.
- The range of $scCO_2$ column height for the samples used in this research is between 0.2 – 1,358 m.
- The average $scCO_2$ column height is 351 m.
- The depth interval around 1,400 m exhibits the largest values of $scCO_2$ column height.
- The above mentioned interval is comprised of mainly Cherokee and Morrowan formations (shale seals).

Conclusions

- We found a moderate positive relationship (+.16, shale samples, +.54, limestone samples) between $scCO_2$ column height and ***hard/soft*** mineral content index in shales and limestone samples.
- ***Average median pore radius*** and ***porosity*** display a strong negative correlation with $scCO_2$ column height.
- One of the most important factors affecting sealing capacity and consequently the height of $scCO_2$ column is ***sorting of the pore throats***. We observed a very strong positive correlation (+0.70) between pore throat sorting and height of CO_2 retention column in shales. This correlation could not be observed in limestone samples. This suggests that the pore throat sorting is more controlling the sealing capacity in shales, and shales with well sorted pore throats are the most reliable lithology as seal.

Conclusions

- We observed that ***Brunauer–Emmett–Teller (BET) surface area*** shows a very strong correlation with CO_2 retention height in limestone samples (+0.93), while BET surface area did not show any correlation in shales (+0.09).
- We also noticed that the ***median grain size*** has relatively moderate correlation with $scCO_2$ retention height (+0.20 for shales, -0.39 for limestones)
- ***Pore structure (IC, IG, V),*** based on SEM micrographs exhibits strong negative correlations with $scCO_2$ column height in both shales and limestones. One exception was noticed for IG structures in limestone (+0.81).

Conclusions

TOC display a very weak positive correlation with $scCO_2$ retention column heights (0.04 for shales, 0.10 for limestone samples).

Bulk density displays relatively moderate positive correlation with scCo2 column height (0.30 for shales, 0.58 for limestone samples).

However, the ***skeleton density*** correlation differs for shales (0.29), and is negative for limestone samples (-0.66)

Future Plans

- We are planning to incorporate permeability measurements (both absolute and relative) as a new structural/compositional variable in our model of caprock sealing capacity.
- We will run sensitivity test to estimate the importance of other parameters on $scCO_2$ column height:
  - various contact angles CO_2/brine (0°, 10°, 20°, or 60°)
  - various brine densities
  - various interfacial tensions

Bibliography

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