MONTANA STATE UNIVERSITY
College of ENGINEERING

Monday, January 19, 2015

Report to USGS Core Research Center

To Whom It May Concern:

On July 11, 2013, we obtained a total of 21 (twenty one) 1 inch diameter core samples from various shale cores stored at the USGS Core Research Laboratory in Denver, CO.

It was our intention to utilize a large number of these cores for testing a biologically-mediated mineral precipitation (referred to as 'biomineralization') technology for controlling the permeability of fractured shales.

In specific, it was our intention to perform X-ray CT imaging as well as permeability measurements of fractured shale cores to be utilized in the biomineralization experiments.

In the following report, we summarize the results obtained from the cores utilized in our studies. – We will be happy to return unused cores or continue utilizing them for our continued research and development activities.

We apologize for the delay in submitting this report however, this work is ongoing and follow-on research support was recently granted by the DOE (National Energy Technology Laboratory) and thus work with these cores is continuing.

Please do not hesitate to contact me with any questions regarding the report or the current location of these cores.

Sincerely,

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enclosures: (1) Report, (2) Signed USGS Core Research Center Policy and List of Samples

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Mountains & Minds

Report:

The following 21 (twenty one) 1 inch diameter core samples were obtained from the USGS Core Research Laboratory in Denver (CO) on July 11, 2013 (Table 1). It was our intention to utilize a large number of these cores for testing the biomineralization technology for controlling the permeability of fractured shales.

Table 1: List of shale cores obtained from the USGS Core Research Center (Denver, CO) and summary of information available from the USGS Core Research Center database.

For-mation	Library No.	Sample Depth	Operator/Well Name	State	Drill Date	TOC	Background Data Available
Bakken	S811	6,781	EOG Resources Flatwillow 1-31H	MT	7/11/2008	N/A	None
		6,782					
		6,784					
		6,784					
	E701	9,925	Oryx Energy Corp 1 Big Sky HD	MT	11/5/1990	8.42	LECO TOC, XRD, resistivity, TPH, mineralogy
	E722	7,755	Wascana Oil & Gas 5H Joyes State	MT	12/3/1997	0.8-0.9	LECO TOC, permeability, porosity, TPH
		7,756					
	E349	11,050	Texaco Inc. 5-1 Thompson Unit	ND	8/10/2005	N/A	LECO TOC, XRD porosity, mineralogy,
		11,051					
		11,067					
		11,069					
Green River	D172	4,783	Mapco Inc. 4-11D River Bend Unit	UT	5/28/1997	2.6	LECO TOC,
		4,788					
	E216	1,586	U S ERDA 1 Blacks Fork	WY	1/1/1991	N/A	LECO TOC, mineralogy,
		1,596					
		1,602					
		1,603					
	C689	444	Marine Minerals 1 Eden Valley	WY	Unknown	N/A	LECO TOC, mineralogy
		444					
		451					
		451					

TOC = total organic carbon

LECO TOC = total organic carbon as measured by a LECO instrument

XRD = X-ray diffraction

TPH = total petroleum hydrocarbon content

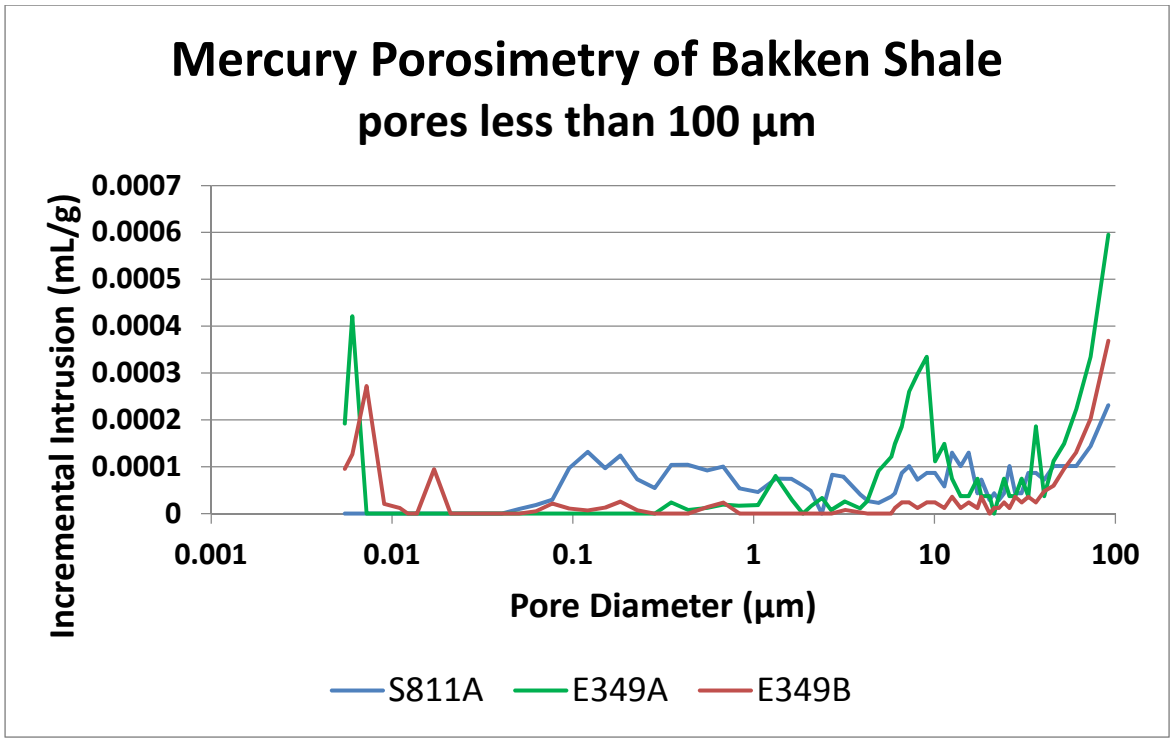
Various data were available at the USGS website for these cores and we performed additional analyses useful in characterizing the cores. Table 2 displays results of additional results obtained from Mercury Porosimetry and LECO-based Carbon and Sulfur analyses.

Table 2 Shale Porosity, Carbon, and Sulfur Analyses of USGS Core Research Center cores

Formation	USGS Core	Depth (ft)	Porosity by Hg Porosimetry			LECO Analyses	
			Total	Between 1 and 10 µm	< 100 µm	Carbon	Sulfur
Bakken	S811	6,781	- - -	- - -	- - -	- - -	- - -
		6,782	- - -	- - -	- - -	- - -	- - -
		6,784	4.33%	0.27%	1.00%	8.22%	1.90%
		6,784	- - -	- - -	- - -	- - -	- - -
	E701	9,925	- - -	- - -	- - -	18.5%	- - -
	E722	7,755	10.1%	- - -	- - -	0.85%	- - -
		7,756		- - -	- - -		- - -
	E349	11,069	- - -	- - -	- - -	- - -	- - -
		11,067	- - -	- - -	- - -	- - -	- - -
		11,050	4.04%	0.03%	0.50%	10.39%	- - -
		11,051	4.50%	0.39%	1.05%	6.89%	- - -
Green River	D172	4,783	14.55%	0.20%	0.60%	- - -	- - -
		4,788	- - -	- - -	- - -	2.60%	- - -
	E216	1,586	- - -	- - -	- - -		- - -
		1,596	8.25%	0.03%	4.72%	- - -	- - -
		1,602	- - -	- - -	- - -	- - -	- - -
		1,603	13.93%	0.14%	3.02%	- - -	- - -
	C689	444	6.66%	0.11%	1.85%	17.30%	2.24%
		444	- - -	- - -	- - -	- - -	- - -
		451	- - -	- - -	- - -	- - -	- - -
		451	5.39%	0.15%	2.70%	21.96%	1.28%

Shading indicates data already available on the USGS web site for these cores

Additional data from the Mercury Intrusion Porosimetry Analyses are shown in Figure 1



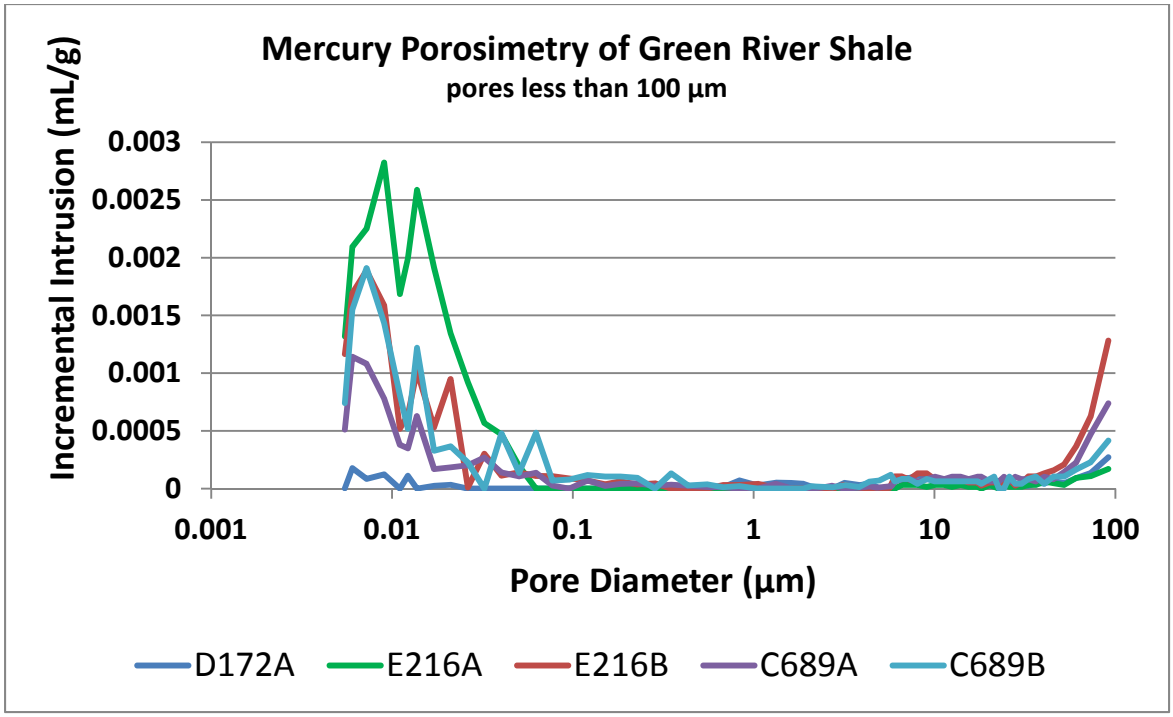


Figure 1: Mercury Porosimetry Data obtained for various shale cores from (A) the Bakken formation and (B) the Green River area. Only pore sizes estimated to be smaller than 100 µm are shown. S811A - S811/6784 ft; E349A - E349/11051 ft; E349B - E349/11050 ft; D172A – D172/4783 ft; E216A - E216/1596 ft; E216B - E216/1603 ft; C689A - C689/444 ft; C689B - C689/451 ft.

In addition, we performed X-ray computed tomography (CT) imaging on a number of these cores prior to and after biomineralization. X-ray CT can create 3-dimensional models at resolutions as high as 7 µm for the one inch diameter cores. Imaging was performed prior to and after biomineralization to evaluate where and how much mineralization occurred. CT scans were performed on the following cores and for several biomineralization experiments (Table 3). The instrument scanned the core (see an example in Figure 2), then rotated it slightly (by 0.7°), and scanned it again. This process was repeated until the core was rotated by a total of 270° to create redundancy. All the scans were combined to create a stack of cross sectional images across the length of the cores (see example in Figure 3).

Table 3 USGS Core Research Center cores that where imaged using X-ray computed tomography

Formation	USGS Core	Depth (ft)
Bakken	S811	6,784
	E349	11,050
	E349	11,051
Green River	D172	4,783
	E216	1,596
	E216	1,603
	C689	444
	C689	451

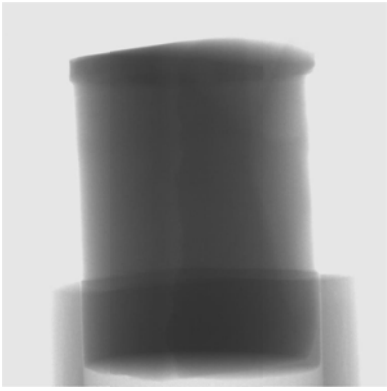


Figure 2: A single CT scan of a fractured core prior to biomineralization (core E349 11050).

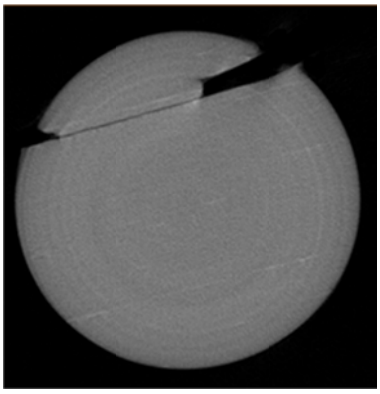


Figure 3: A 7 µm thick cross sectional image of the core displayed in Figure 2. Black indicates less dense material in this image.

The "stack" of cross sectional images, as shown in Figure 3, can be used to create a three dimensional model of the entire core. Subtractive image analysis as shown in Figure 4 was used sometimes to more clearly visualize changes that occurred. Subtractive imaging allows for a clearer visualization of the changes that occurred in cores during biomineralization. Subtractive imaging was performed by aligning the cross sectional images from before and after biomineralization (Figure 5). These images were then subtracted from one another so that any bright pixel from before biomineralization was removed from the

after biomineralization image. This left only the 'new' pixels. These 'new' pixels are the result of the core being exposed to the biomineralization process.

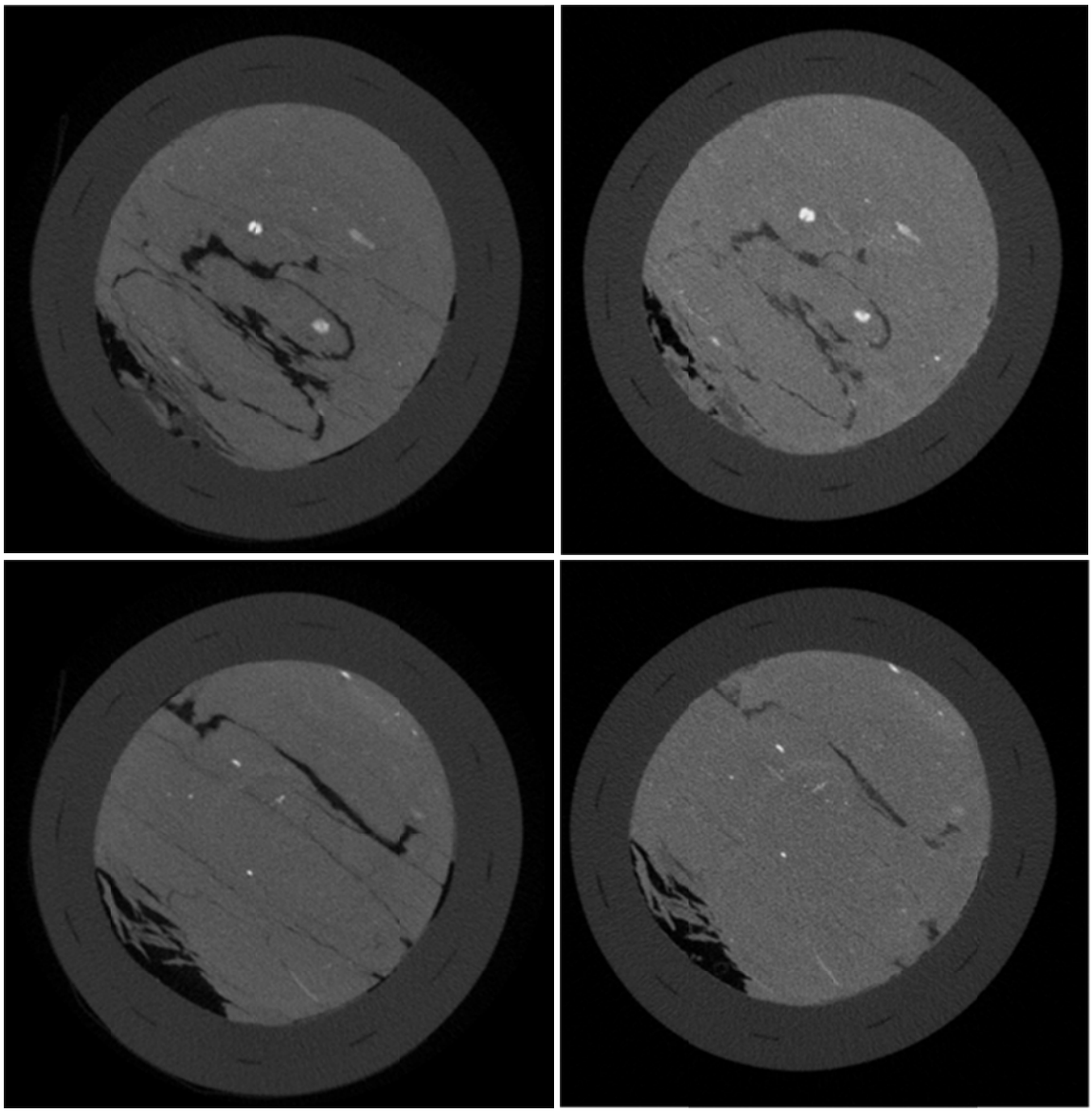


Figure 4: Comparison of a shale core before and after biomineralization. (A) core prior to biomineralization, (B) same location after biomineralization, there is still a significant space between the outer sleeve and the main part of the core in the bottom left of the images. However the fractures in the center portion of the core are clearly reduced in size. (C) the same core at another location (depth into the core) before and (D) after biomineralization. Bright spots in these images are caused by a shale component that is attenuating a large amount of the X-Ray signal, possibly a metal.

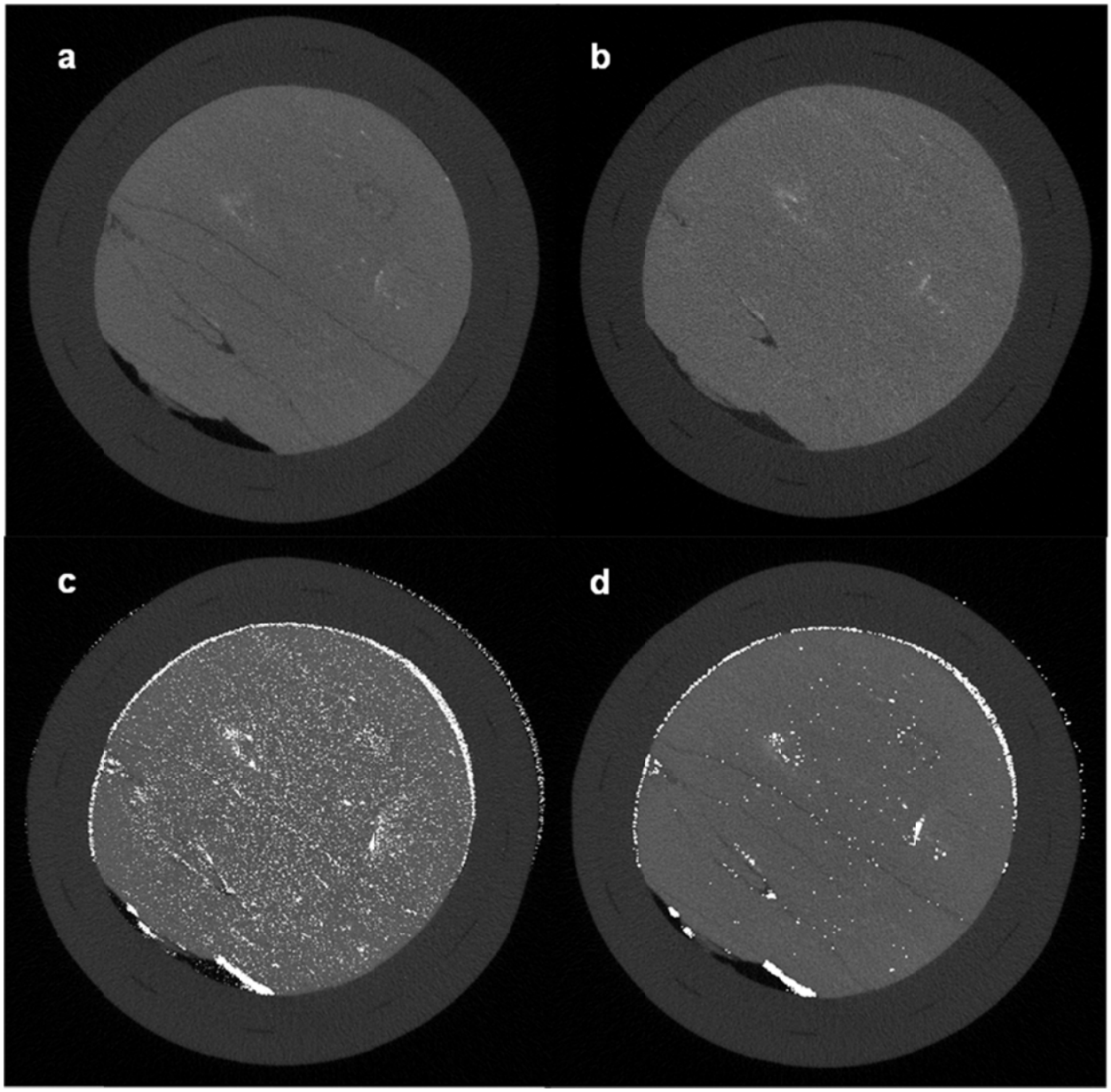


Figure 5: (A) X-ray CT cross section of shale core prior to biomineralization. The outer dark ring is the PVC sleeve. (B) X-ray CT scan after biomineralization. (C) is a composite image based on subtracting image A from image B and adding the difference (in bright white) to image A. (D) was created by reducing the noise in image C. Noise was reduced by eroding and dilating the binary image used to create image C[1].

[1] Sijbers, J. and Postnov, A. "Reduction of ring artefacts in high resolution micro-CT reconstructions." *Physics in Medicine and Biology* 49.14 (2004): N247.

Permeability measurements were conducted on artificially fractured cores. These cores were biomineralized and analyzed again. The following results regarding permeability prior to and after biomineralization were obtained (Table 4).

Table 4: Apparent (Darcy) Permeability and permeability reduction in shale cores through biomineralization

Core	Depth	Formation	Proppant added	Low Pressure Permeability (mD)	
				Initial	Final
C689	451'	Green River	Yes	6,130	0.51
E349	11,051'	Bakken	Yes	4,770	0.014
E349	11,067'	Bakken	Yes	6,730	0.080
E349	11,069'	Bakken	Yes	11,500	0.047

The Green River shale core (D172-4783) was biomineralized under elevated pressure in a system consisting of a Hassler type biaxial coreholder and high pressure syringe pumps (ISCO). The observed core permeability over the duration of the experiment is shown on a logarithmic scale in Figure 6.

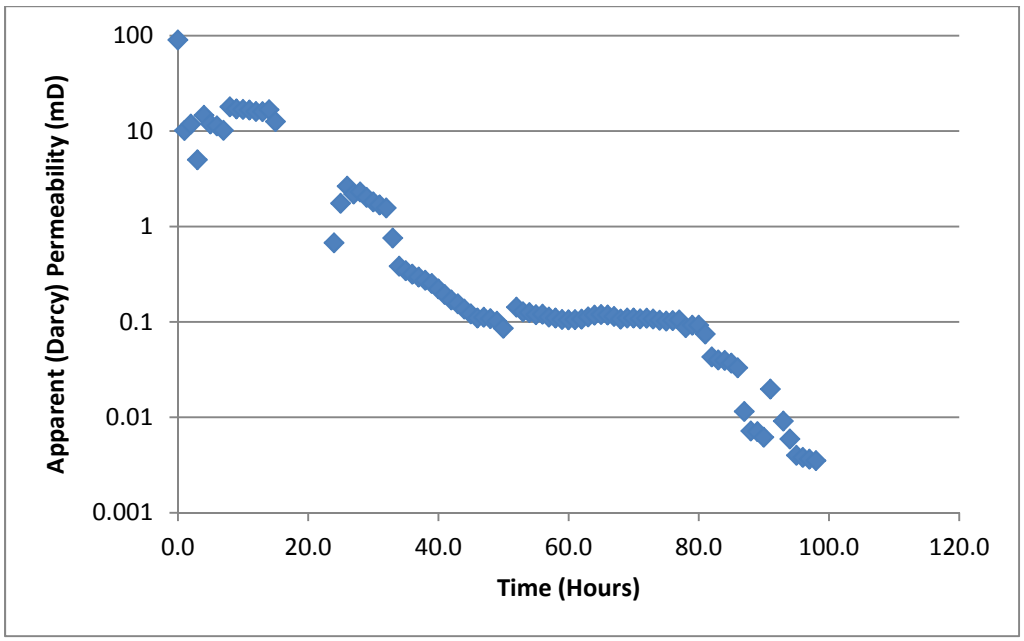


Figure 6: Relative Darcy permeability over time for the fractured Green River Core (D172-4783) during biomineralization under high pressure.

The proppant-filled Green River core started at an initial apparent permeability of 90 mD. The permeability was reduced to 3.7 µD through the biomineralization process within approximately 100 hours. The Green River Shale core experiment resulted in over four orders of magnitude reduction in apparent permeability. Mineral precipitation was evident after the experiment.

Lastly, material from the following cores was used for microbial enrichments using the following strategy:

A small piece of each core was wiped down with ethanol then each side was abraded using a flame sterilized Dremmel tool. After removing the outer layer each core was crushed into a powder. 100 mg of each powdered core was added to four different media. Two media were used for aerobic enrichments and two for anaerobic enrichments. Full media composition is available upon request.

Table 5 Cores used for enrichments

Core Number	Formation	Inoculation Date
S811 – 6781	Bakken	8/22/13
E349 – 11067	Bakken	8/22/13
E216 – 1586	Green River	8/22/13
C689 – 451	Green River	8/22/13
E701 – 9925	Bakken	8/26/13
E722 – 755	Bakken	8/26/13
D172 - 4788	Green River	8/26/13

Summary:

The data above were collected using cores obtained from the USGS Core Research Laboratory in Denver, CO. We will be happy to clarify any of the data provided in this report. We will also be happy to return unused cores or continue utilizing them for our continued research and development activities.