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CHEMICAL ANALYSIS OF PRESHOT ROCK
FROM THE RULISON EXPERIMENT

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December 14, 1971

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CHEMICAL ANALYSIS OF PRESHOT ROCK FROM THE RULISON EXPERIMENT

ABSTRACT

This report contains chemical assays of preshot rock samples from the Rulison emplacement hole.

INTRODUCTION

When nuclear explosives are used to stimulate gas production, a complex set of chemical reactions occur in the nuclear chimney formed by the nuclear detonation. These reactions determine the production of carbon dioxide and the distribution of radioactive elements. Because the course of these reactions depends on the chemical composition of the rock, the correct interpretation of the postshot reaction history depends on adequate sampling of the preshot environment.

In Gasbuggy, the first nuclear gas stimulation experiment, preshot rock samples were taken from an exploratory hole approximately 188-ft from the emplacement hole. Because it was not known how well these samples represented the actual medium at shot point, postshot data could not be interpreted with great confidence.

Rulison core samples, on the other hand, were taken from the actual emplacement hole and should be reasonably representative of the medium at shot point. Because Rulison is only the second experiment in nuclear gas stimulation, these samples provide a unique opportunity to extend our knowledge concerning the chemical reactions associated with this technique. The chemical composition of these samples together with Rulison postshot gas analyses are being used to establish a reaction history for Rulison. This reaction history can be used to predict the gas quality and radioactive contamination of future gas stimulation projects.

SAMPLING

Core samples were taken from the Rulison emplacement hole (R-E), Austral #25-95 Hayward "A", located in Section 25, T-7-S, R-29-W, Garfield County, Colorado. Mud was used as a coolant for drilling. Core Laboratories, Inc., Casper, Wyoming, processed the core and furnished us with samples. Samples numbered 361 and 371 were taken from approximately 4-in. lengths of full diameter (4-3/8-in.) core. Samples numbered 56-1 through 56-9 were taken from slabs cut lengthwise down the core as shown in Figs. 1a-1e. Slices approximately 1-in. square were cut from the interior

of each core section to minimize contamination from the drilling mud. Each slice was taken from the full length of each core section. The slices were crushed in a chipmunk crusher with alumina jaws. Composite samples were prepared from the crushed rock as shown with the lithologic log in Appendix A. The composite samples were pulverized in a tungsten carbide mill.

The lithological description of the core shown in Appendix A was used as a basis for preparing the composite samples. This lithological description is a copy of the description furnished to us by Core Laboratories. The core sections were also examined by Donald O. Emerson, Lawrence Livermore Laboratory, and his examination concurs with Core Laboratory's description. Estimates from thin sections by Iris Y. Borg shows the sandstone grain size to average about 145 μ , and the siltstone grain size to range from 13 to 51 μ .

ANALYSIS

Samples numbered 361 and 371 were analyzed on an as received basis. Their H₂O assay includes both free and bound water. Samples numbered 56-1 through 56-19 were dried at 110°C prior to analysis. Their H₂O assay includes bound water only. The H₂O was evolved from the samples by heating them to 1000°C in a vacuum. The H₂O was collected and weighed. The probable accuracy of this method is about $\pm 5\%$ of the H₂O content for rocks which do not contain hydrocarbons. However, hydrocarbons in all of these samples could react to bias the H₂O assay either high or low. Also, these samples were not properly preserved for H₂O assay. Therefore, the results shown in Table 1 probably have no relation to the actual H₂O content of the in situ rocks.

Results from the assay of C, H, and CO₂ are also given in Table 1. The probable accuracy of the results for C, H, and CO₂ is $\pm 5\%$ of the concentration or better. The values shown for C as CH_x and H as CH_x were calculated as follows:

$$C \text{ as } CH_x = \text{Total C} - C \text{ in } CO_2$$

$$H \text{ as } CH_x = \text{Total H} - H \text{ in } H_2O$$

The accuracy of the values calculated for C as CH_x and H as CH_x are limited by the accuracy of the parent analyses. In particular, the value for H in CH_x is only qualitative because of the indeterminate errors in the H₂O analysis.

Results for chemical analyses are given in Table 2. The probable accuracy of these results is $\pm 5\%$ of the concentration or better for concentrations $>1\%$. For concentrations $<1\%$, the probable accuracy of the results is $\pm 10\%$ of the concentrations or better.

Emission spectrographic results are given in Table 3. The probable accuracy of these results is $\pm 50\%$ of the concentration.

Rulison
R-E



Fig. 1a. Rulison core samples taken at depths designated. (See Appendix A for sample numbers at designated depths.)



Fig. 1b. Rulison core samples taken at depths designated. (See Appendix A for sample numbers at designated depths.)

Rulison
R-E

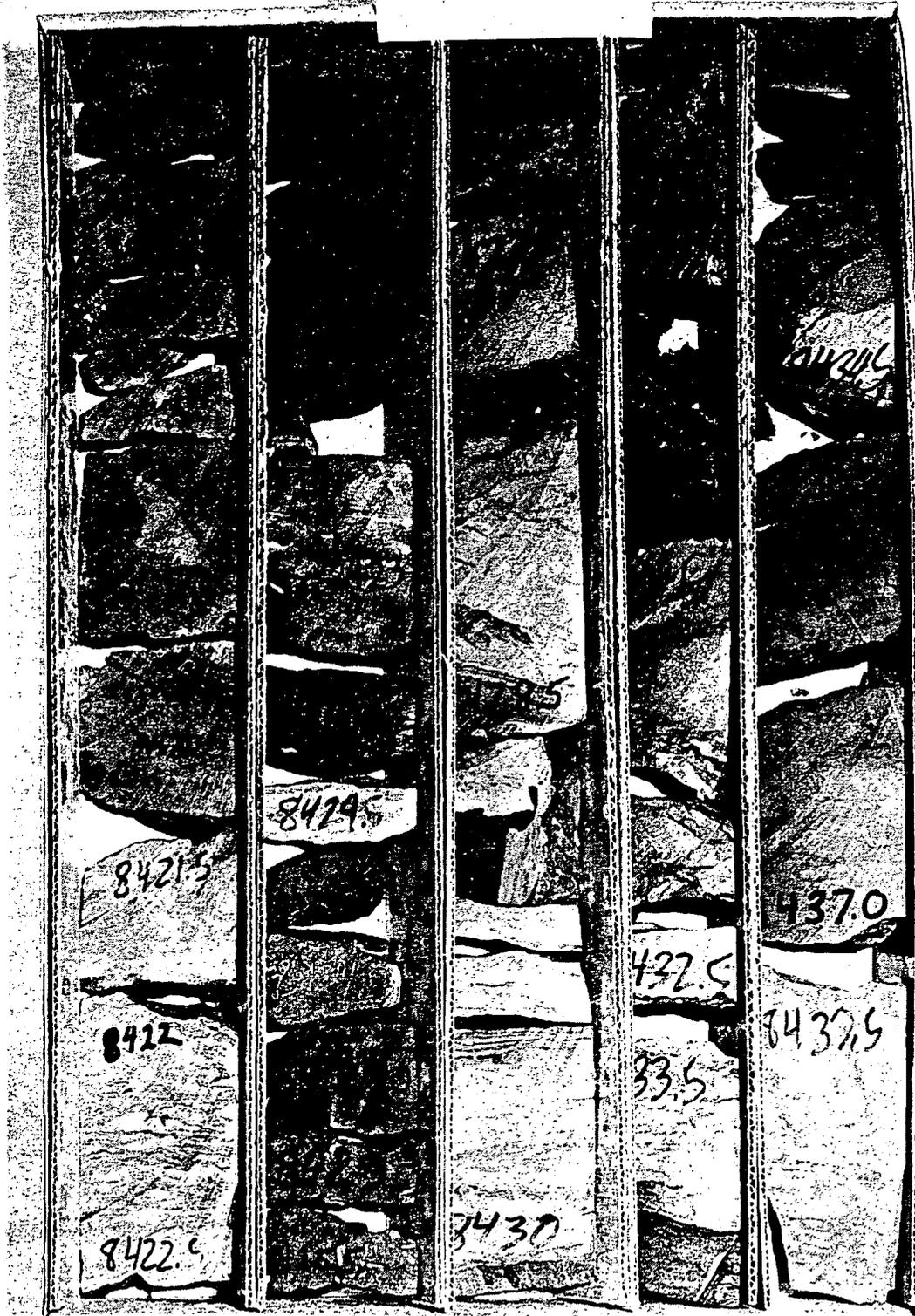


Fig. 1c. Rulison core samples taken at depths designated. (See Appendix A for sample numbers at designated depths.)

Rulison
R-E



Fig. 1d. Rulison core samples taken at depths designated. (See Appendix A for sample numbers at designated depths.)

Rulison

R-E

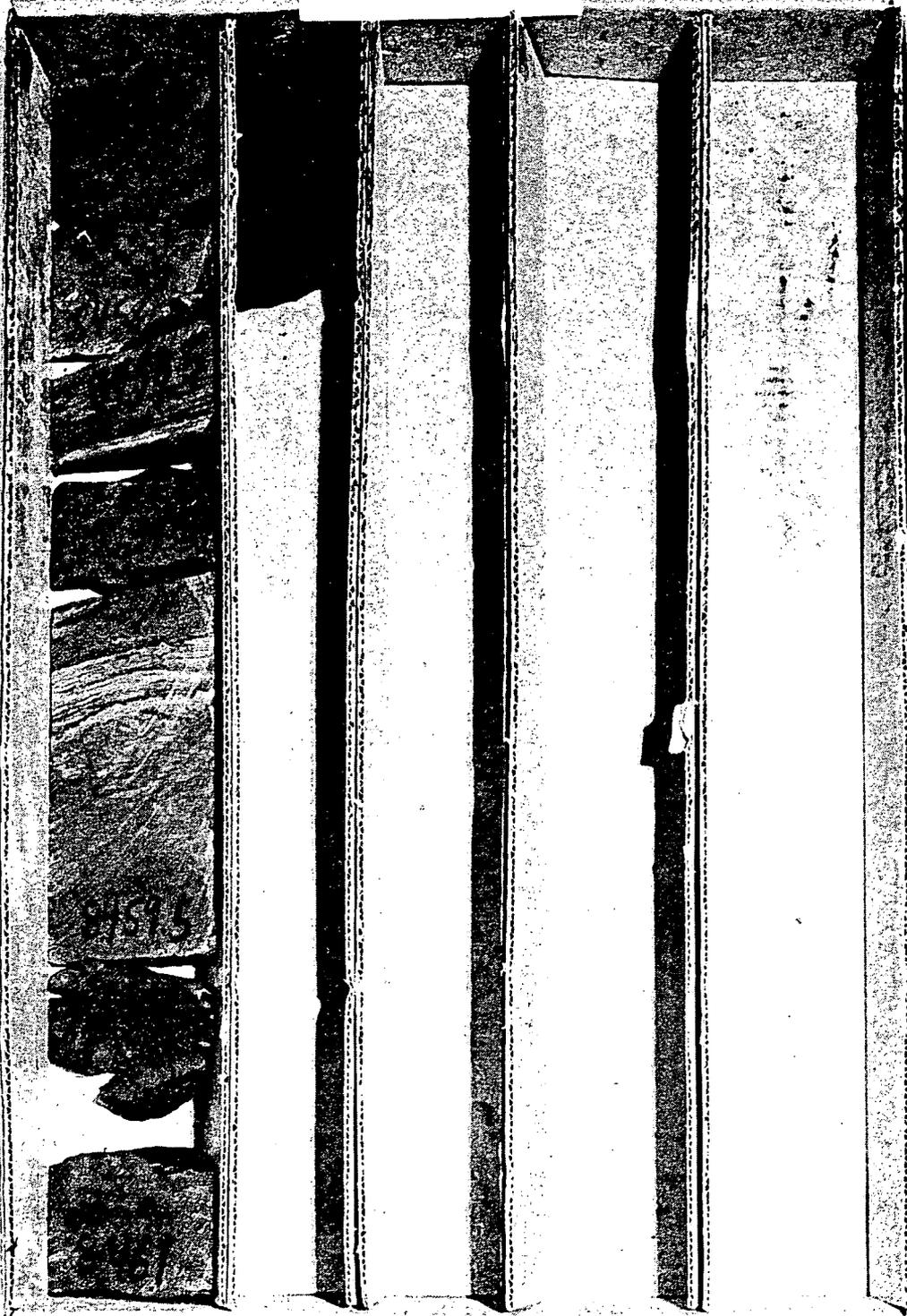


Fig. 1e. Rulison core samples taken at depths designated. (See Appendix A for sample numbers at designated depths.)

Table 1. Carbon-Hydrogen Balance.

Sample No.	Depth (ft)	Total H ₂	Total C	H ₂ O	CO ₂ ^a	C as CH _x	H as CH _x
56-1	8400-8406.5	0.15	1.32	1.0	4.31	0.14	0.04
56-2	8406.5-8407	0.28	2.54	1.9	6.65	0.73	0.07
56-3	8407-8410	0.35	2.92	2.0	6.50	1.15	0.13
56-4	8410-8411	0.45	1.84	3.0	4.07	0.73	0.12
56-5	8411-8413	0.14	2.46	0.8	8.47	0.15	0.05
56-6	8413-8415.5	0.36	2.45	1.1	5.85	0.85	0.24
56-7	8415.5-8418	0.47	2.52	2.9	4.92	1.18	0.15
56-8	8418-8419.5	0.74	5.73	3.4	0.17	5.68	0.36
56-9	8419.5-8421	0.39	2.79	2.5	7.77	0.87	0.11
56-10	8421-8422.5	0.28	2.47	1.3	7.28	0.49	0.14
56-11	8422.5-8425.5	0.53	2.61	3.3	1.76	2.13	0.16
56-12	8425.5-8430	0.36	2.66	1.0	6.43	0.91	0.25
56-13	8430-8435.5	0.38	3.39	2.2	8.74	1.01	0.14
56-14	8435.5-8439.5	0.38	1.49	2.6	3.74	0.47	0.09
56-15	8439.5-8445	0.40	2.73	2.4	5.82	1.14	0.13
56-16	8445-8447	0.37	1.82	2.5	5.14	0.42	0.09
56-17	8447-8449.5	0.46	0.84	3.3	1.30	0.49	0.09
56-18	8449.5-8454.5	0.43	1.64	2.0	4.40	0.44	0.21
56-19	8454.5-8462	0.46	2.99	2.7	5.58	1.47	0.16
361 ^b	8451	0.50	0.69	4.2	0.26	0.62	0.03
371 ^b	8405.7-8406	0.16	1.36	1.3	4.63	0.11	0.01

All results are wt%

^aCO₂ from carbonates only.

^bThese two samples were analyzed as received. Their water assay includes both free and bound water. Samples numbered 56-1 through 56-19 were dried at 110°C before analysis. Their water assay includes bound water only.

Samples for the mercury assay consisted of small chunks taken from the center of core slabs. Each core slab sampled contained 3-4 cubic inches of rock. Results are given in Table 4. The results given for the individual determinations show the heterogeneity of the mercury content of the rock.

These results indicate that the mercury content of the cores varies by a factor of 14 in the depth interval from 8404.5 to 8452-ft. Replicate determinations are given for three core slabs (8404.5-ft, 8443-ft, and 8451-52-ft) to indicate the heterogeneity within each slab. The largest variation is a factor of 6 in the concentration found on the three samples from the 8404.5-ft slab. The probable accuracy of the analytical procedure is ±20% of the concentration or better for concentrations of mercury in the range covered by these samples.

Table 2. Chemical analysis.

Sample No.	Depth (ft)	Ca	Al	Fe	Wt%			Si	Ti	Mn Wt ppm	Li ppm
					Mg	Na	K				
56-1	8400-8406.5	2.59	3.59	1.21	0.75	0.91	0.98				
56-2	8406.5-8407	3.41	5.25	2.20	1.33	0.73	1.55				
56-3	8407-8410	3.15	6.31	2.32	1.45	0.75	1.69				
56-4	8410-8411	2.47	8.52	1.20	1.19	0.66	2.58				
56-5	8411-8413	5.64	3.00	1.41	1.04	0.62	0.85				
56-6	8413-8415.5	3.31	6.71	1.56	1.38	0.73	2.09				
56-7	8415.5-8418	2.56	8.42	2.07	1.23	0.63	2.61				
56-8	8418-8419.5	0.27	8.16	0.77	0.34	0.67	2.23				
56-9	8419.5-8421	4.42	7.62	2.50	1.64	0.58	2.39				
56-10	8421-8422.5	3.87	4.48	2.47	1.19	0.59	1.27				
56-11	8422.5-8425.5	1.02	8.64	1.25	0.60	0.65	2.39				
56-12	8425.5-8430	3.40	6.32	2.17	1.31	0.66	1.84				
56-13	8430-8435.5	2.86	7.33	5.66	1.51	0.75	2.16				
56-14	8435.5-8439.5	2.31	7.65	1.46	0.97	0.83	2.26				
56-15	8439.5-8445	3.17	6.74	2.63	1.11	0.70	2.06	29.8	0.50	410	24
56-16	8445-8447	3.59	6.96	1.41	0.91	0.73	2.04	30.9	0.47	320	33
56-17	8447-8449.5	0.82	9.62	1.18	0.57	0.69	3.01	31.5	0.61	180	46
56-18	8449.5-8454.5	2.46	8.37	2.45	0.92	0.64	2.73				
56-19	8454.5-8462	3.05	8.11	2.36	1.07	0.49	2.47				
361	8451	0.31			0.45						43
371	8405.7-8406	2.95			0.70						14

DISCUSSION

Elemental analyses for samples numbered 361 and 371 were originally reported in a memorandum dated December 10, 1969. At that time, these samples were taken to represent a "typical" shale (316) and a "typical" sandstone (317) from Rulison.

A comparison of the CO₂ assay for these two samples with the CO₂ assay for samples 56-1 through 56-19 indicates the errors inherent in attempts to characterize rock formations with too few samples.

Based on the CO₂ assay for samples 361 and 371, and the lithological log which shows approximately 25% shale and 75% sandstone in the interval from 8400-ft to 8462-ft, the average amount of CO₂ present in the carbonates is 3.54 wt%. The average CO₂ present as carbonate in this same interval as calculated from the assay for samples 56-1 through 56-19 is 5.29 wt%.

Table 3. Spectrographic analysis.

Sample No.	56-15	56-16	56-17	361	371
Depth (ft)	8439.5- 8445	8445- 8447	8449.5 8454.5	8451	8405.7- 8406
<u>Wt%</u>	Al				2
	Fe				0.5
	Na				0.3
	K				<0.5
	Ti				0.2
	Ba				0.07
	Zr				0.02
	Sr				0.01
<u>Wt ppm</u>	Ni				10
	Mn				50
	Y	25	25	25	15
	Sc	15	15	15	5
	Yb	3	3	3	1
	Nd ⁰	20	20	20	<50
	Ce	50	50	50	<100
	Cr				<10
	Cu				<5
	Pb				<10
	Dy	<2	<2	<2	
	Eu	<1	<1	<1	
	La	35	35	40	40
B	75	75	100	50	20

ACKNOWLEDGMENTS

Robert W. Taylor, Donald O. Emerson, and Robert LaPoint prepared the composite samples. Robert Lim, Lewis Gregory, Miles Waggoner, and William Sunderland did chemical analyses. William Morris and Edgar Pack did the spectrographic analyses.

Table 4. Mercury assay.

Sample depth (ft)		ppb Hg (wt)
8404.5	Sandstone	19
8404.5	Sandstone	97
8404.5	Sandstone	16
8433.5	Sandstone and Siltstone Interbedded	46
8439.5	Shale	86
8441.5	Sandstone	9.2
8441.5	Sandstone	14
8443	Shale	100
8443	Shale	32
8443	Shale	130
8446	Shale	77
8451-52	Siltstone	30
8451-52	Siltstone	30
8451-52	Siltstone	20

APPENDIX A

Lithological Log of Core^a
Core Record

Company Austral Oil Co., Inc. Date 1-13 to 1-15-69
 Well #25-95 "A" Hayward Type core bbl. HYCALOG 4-3/8 in. core
 Field Rulison Formation Mesa Verde
 County Garfield State Colorado Elevation _____
 Remarks Field Lithology Log of Emplacement Hole, Cores #1, #2, #3

Sample No.	Core No.	From (depth)	To (depth)	Feet recvrd.	Lithological description
56-1	1	8400	06.5	6.5	Ss, gray, fine to med. grain, calcareous, sorting, well cemented.
56-2	1	8406.5	07	0.5	Ss, as above, with gray to black silty carbonaceous shale laminae.
56-3	1	8407	10	3	Ss, gray, very fine grain, calcareous, silty, black carbonaceous shale laminae, well cemented.
56-4	1	8410	11	1	Siltstone, gray, with gray to black carbonaceous shale.
56-5	1	8411	13	2	Ss, gray, very fine-fine grain, calcareous, black carbonaceous shale laminae, well cemented.
56-6	1	8413	15.5	2.5	Ss, gray, very fine grain, silty, very shaly, vertical fractures.
56-7	1	8415.5	18	2.5	Siltstone and shale, gray, sandy
56-8	1	8418	19.5	1.5	Siltstone and shale, gray, sandy with black carbonaceous shale and thin coal stringers.
56-9	1	8419.5	20.5	1	Ss, gray very fine grain, silty well cemented.
56-9		8420.5	21	0.5	
56-10	2	8421	22	1	Sh, as above, with stringers of black carbonaceous shale.
	2	8422	22.5	0.5	Ss, gray, very fine grain, calcareous, well cemented.
56-11	2	8422.5	25.5	3	Sh, black, carbonaceous, well indurated, with coal stringer at 8425.5.
56-12	2	8425.5	28	2.5	Sh, gray to black carbonaceous, well indurated.
	2	8428	29	1	Ss, gray, very fine grain, silty, calcareous, well cemented, vertical fracture.
	2	8429	30	1	Ss, as above, becoming very calcareous, vertical fracture.

APPENDIX A (continued)

Sample No.	Core No.	From (depth)	To (depth)	Feet recvrd.	Lithological description	
56-13	}	2	8430	32	2	Sh, gray to black, carbonaceous, well indurated, coal stringer at 8430.5.
		2	8432	35.5	3.5	Ss and Sh interbedded; Ss, gray, very fine grain, slightly calcareous, well cemented; Sh, gray to black, silty carbonaceous, vertical and diagonal fractures.
		2	8435.5	37	1.5	Sh, gray to black, carbonaceous, silty, well indurated.
56-14		2	8437	38.5	1.5	Ss and Sh interbedded, as interval 8432-35.5.
		2	8438.5	39.5	1	Ss, gray, very fine grain, slightly calcareous, well cemented, vertical fracture.
		2	8439.5	42	2.5	Sh, gray to black, carbonaceous, silty, sandy in 1/2 ft, well indurated, vertical and diagonal fracture.
56-15		3	8442	43	1	Sh, gray to black, carbonaceous, well indurated, vertical fracture.
		3	8443	44.5	1.5	Sh, gray to black, carbonaceous, well indurated.
		3	8444.5	45	0.5	Ss, gray, very fine grain, silty, carbonaceous, well cemented.
56-16		3	8445	46	1	Ss, gray, very fine grain, silty, shaly, well cemented, diagonal fracture.
		3	8446	47	1	Sh, gray, very silty, well indurated, vertical fracture.
56-17		3	8447	48.5	1.5	Siltstone, gray, shaly, well indurated, diagonal fracture.
		3	8448.5	49.5	1	Ss, gray, very fine grain, silty shaly, well cemented grading to siltstone.
56-18		3	8449.5	51	1.5	Sh, gray to black, silty, carbonaceous, well indurated.
		3	8451	52	1	Siltstone, gray, shaly, carbonaceous.
		3	8452	53	1	Ss, gray, very fine grain, silty, well cemented.
56-19		3	8453	54.5	1.5	Siltstone, gray, shaly, fossiliferous.
		3	8454.5	62	7.5	Shale, gray to black, silty, carbonaceous, well indurated.

^aFrom data furnished by Core Laboratories, Inc.

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