PREPRINTS

Symposia

Characterization and Chemistry of Oil Shales

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CHEMICAL CHARACTERIZATION OF AN OIL SHALE BED LYING WITHIN THE HEATH FORMATION, FERGUS COUNTY, MONTANA

By

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INTRODUCTION

Over 1,200 ft of core from the Heath Formation were obtained during an exploratory drilling project by the Montana Bureau of Mines and Geology in 1982. The results of that project are detailed in Derkey (1). Data derived from that study indicate that a thin, metalliferous oil-shale zone occurs in six of seven core holes over a 130-sq mi area (Figure 1). The average thickness of this oil shale zone is 6.2 ft. It has a weighted average* oil yield of 10.4 gal per short ton and is enriched in molybdenum, nickel, vanadium and zinc. Chromium is only locally anomalous.

Vine and Tourtelot (2, 3) were the first workers to describe the Heath Formation as containing above-average amounts of chromium and nickel. A decade later, Desborough and others (4) and Desborough and Poole (5) reported anomalous values of molybdenum, nickel, vanadium and zinc in the Heath Formation. Cox and Cole (6) summarized previous work concerning the oil potential of the Heath Formation. Published oil yields from within the study area range from 0 to 26.4 gal per short ton (4, 6-8).

EXPERIMENTAL

Sampling

Samples consisted of 0.5- to 2.6-ft core intervals, each generally representing a single lithology. The cores were cut along the longitudinal axis to provide a repository sample (1/4), lithological sample (1/2) and chemical analysis sample (1/4). The chemical analysis sample was crushed to 1/4-3/8 size and split at the Laramie Energy Technology Center (Wyoming), U. S. Department of Energy. The A split was taken for Fischer-Assay analysis while the B split was returned to the Montana Bureau of Mines and Geology. The B splits were dried at 110°C for 1 hr and pulverized using a Bico-Braun rotary pulverizer with alumina plates. The individual sample pulps were blended and placed in Kraft paper envelopes.

Fischer Assay

The Fischer Assay (ASTM D3904-80) was carried out in Laramie under the direction of Laurence G. Trudell for the entire 1,224-ft thickness of recovered drill core.

Sample Dissolution

Digestion A – 2-Gram samples were treated by a combined wet acid digestion of 6 ml HNO_3/2 ml $HClO_4$/2 ml H_2SO_4 taking the samples to dense fumes of $HClO_4$/H_2SO_4. After evaporating to near dryness, the cool pastes were treated with 4.7 ml HCl and 1.3 ml HNO_3. After mild heating and cooling, the samples were diluted to 100 ml.

Digestion B – 2-Gram samples were roasted for 4 hr at 450°C. Mixed acid consisting of 2 ml HF/2 ml HNO_3/6 ml HCl was added and heated slowly until evaporated to near dryness. The acid treatment was repeated. After evaporating to near dryness 1 ml HNO_3 and 3 ml HCl was added and evaporated to near dryness twice. 1.6 ml HNO_3 and 4.6 ml HCl was added, heated, cooled and diluted to 100 ml.

Extraction

2-Gram portions of selected shales were extracted with xylene using a Soxhlet extractor

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* Average value for stratigraphic unit, weighted for sample interval thickness. Weighted average = $\sum$ (sample concentration X sample interval thickness)/(total interval thickness).

(Corning 3480) for 48 hours. The extractor and upper section of the boiling flask were insulated in order to increase the extraction temperature. After cooling, the xylene-oil extract solution was filtered through .45μ membrane filters to remove shale fines. The xylene was removed from the extracted oil using a rotary evaporator (water aspirator; 50°C bath). The extracted oil was then weighed.

Dilution of Oils

The oil distillates from Fischer Assay, the oils recovered by xylene extraction, and oil standards were diluted 1 to 20 (w/v) in xylene. Conostan 21^{TM} blended oil (21 elements at 900 ppm), 5000 ppm Conostan cobalt single element oil and Conostan 75 base oil were similarly diluted in xylene. The diluted standards were mixed and diluted with 1:20 Conostan 75 base oil-xylene providing serial dilutions at decade levels from 500 to 0.05 ppm element.

Carbon Analyses

Total carbon content of selected shales was determined by ASTM D-3178-73. Carbonate content of the shales was determined by addition of 10% (v/v) H_2SO_4 to the shale contained in a flask connected to an Orsat gas buret. The solution was heated to boiling and flooded with water to transfer all the evolved gases into the buret. The evolved sulfur oxides and hydrocarbons were removed by absorption in permanganate and silver sulfate/sulfuric acid solutions, respectively. The carbon dioxide was then determined volumetrically by difference after absorption with saturated potassium hydroxide solution.

Atomic Absorption Analysis - Cobalt

The cobalt analysis of shale acid digests was accomplished using a Perkin-Elmer 603 following the manufacturer's instructions (direct nebulization, 240.7 nm, air-acetylene and background correction).

Multi-Element Analysis

Multi-element analysis of the oil shale digests and oil-xylene mixtures was accomplished using an Applied Research Laboratories Model 34000 induction coupled argon plasma emission spectrometer. Forward powers of 1600 and 2000 watts (2-turn load coil) were used for aqueous acid digests and xylene solutions, respectively. The manufacturer's operating instructions were followed with the exception that sample uptake was controlled by a Gilson Minipuls II^{TM} peristaltic pump. A computer iteration (9) which computes a correction factor (similar to an internal standard) was used to correct for the matrix effect caused by the varying concentration of the major elements in the shale.

Reflectance Measurements

A Leitz, incident-light microscope with oil immersion objectives was used to identify coal macerals and to assess sediment thermal maturity. Reflectance of the maceral vitrinite was measured with a MPV compact system photometer using methods outlined by Stach (10) and International Committee for Coal Petrology (11). Fifty measurements per polished plug for 2 plugs per sample were taken for a total of 13 core samples of coal collected from both above and below the oil shale zone. For each sample, 50 measurements were taken with polarized light and 50 with non-polarized light, always using a 546-nm interference filter. Mean vitrinite reflectance (R_o) was measured, rather than mean maximum reflectance.

RESULTS AND DISCUSSION

A single oil shale zone within the Heath Formation is correlated over a 130-sq mi area based on stratigraphic position, relatively high Fischer-Assay oil yields, and enriched metal content (1). The oil shale unit generally thickens eastward, ranging from 4.0 ft thick at the western edge of the study area to 3.4 and 5.7 ft thick in the central part of the area to 10.5 ft thick at the area's eastern edge.

Oil Yield and Organic Carbon

The average thickness of the oil shale is 6.2 ft. It has a weighted average oil yield of 10.4 gal per short ton and a weighted average organic carbon content of 11.4%. Oil yields of individual samples range from 3.1 to 20.0 gal per short ton. An almost 1:1 relationship exists between oil yield and organic carbon content (Figure 2). A similarly close relationship also has been reported for the Sunbury Shale and the Cleveland high-grade zone of the Ohio Shale in northeastern Kentucky (12).

Weighted average oil yield generally decreases as the unit thickens. Weighted average values range from 12.0 to 15.7 gal per short ton for 3.4- to 5.7-ft-thick oil shale in the western

and central parts of the study area to 8.1 and 8.6 gal per short ton for 10.5-ft-thick oil shale at the eastern edge of the area based on data from 24 samples from 6 core holes.

Metal Content

    Evaluation of Digestion Procedures - Replicate samples of 25 selected shales were analyzed by the two digestion procedures. The replication scheme included triplicate digestions by each procedure for 6 samples and duplicate digestions by each procedure for 2 samples; single digestions by each procedure were carried out for the remaining 17 samples. The plasma emission analyses for digestions A and B of sample nos. 32779, 32780 and 32781 are presented in Table I for selected elements. The HF-aqua regia digestion (digestion B) yielded better precision and dissolved more of the sample as demonstrated by significantly higher values obtained for Al, Fe, Mn, Nb, Ti, V and Zr and somewhat higher values for Mg, Na, Li and Sr. The elements Ca, Mn and Ag were definitely more soluble in the nitric/perchloric/sulfuric acid digestion (digestion A); and Cd, Cr, Cu, P and Zr were somewhat more soluble in digestion A. The elements Mo, Ni and Pb were dissolved equally by the two digestions. Digestion B was selected for the digestion of the remaining samples because of its overall efficiency and ease of implementation compared to digestion A.

TABLE I

COMPARISON OF ACID DIGESTION PROCEDURES

Sample Number	Digestion Procedure[a]	Ca %	K %	Al %	Mn ppm	Cr ppm	Cu ppm	Mo ppm
33085	A	7.9	.29	.97	190	49	31	130
		8.9	.22	.72	190	41	31	130
	B	17.1	.71	2.00	230	83	43	140
		16.8	.70	2.01	220	77	40	130
33086	A	6.3	.63	2.2	190	140	46	200
		3.4	.59	2.0	160	130	36	170
		10.0	.31	1.0	190	90	53	200
	B	12.8	1.05	3.6	200	190	58	200
		12.0	.98	3.4	200	180	54	200
		12.5	.99	3.5	200	180	54	200
33087	A	11.4	.11	.30	270	23	21	46
		9.1	.14	.41	260	27	19	49
	B	12.5	.30	.41	290	46	25	43
		12.4	.29	.49	290	47	28	46

Sample Number	Digestion Procedure[a]	Nb ppm	Ni ppm	Pb ppm	Sr ppm	V ppm	Zn ppm
33085	A	4.4	112	23	180	231	570
		4.9	112	30	210	190	560
	B	4.8	110	16	390	370	610
		4.4	102	7	400	360	580
33086	A	4.5	150	21	180	610	1160
		3.9	130	18	140	550	970
		6.1	160	54	240	370	1190
	B	3.9	150	27	360	830	1230
		2.7	140	22	360	810	1170
		3.5	150	27	350	800	1170
33087	A	4.7	41	33	160	90	21
		4.4	41	28	120	110	24
	B	8.2	33	11	240	180	25
		11.4	35	18	240	180	21

a. See text.

    Several pulverized samples were split in triplicate to provide control samples. The second and third splits were sent to the U. S. Geological Survey in Denver for Chemical analysis. The comparison of these data is given in Table II. The agreement between the data from the three laboratories using two different instrumental procedures is very good.

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TABLE II

COMPARISON OF MBMG AND USGS ANALYTICAL RESULTS OF SELECTED ELEMENTS FOR
SIX BLACK SHALE CORE SAMPLES OF THE HEATH FORMATION FROM THE
COX RANCH BOREHOLE

Sample No. and Oil Yield	Element	MBMG Metal Values (ppm) ICP Emission Spectroscopy			USGS Metal Values (ppm) X-Ray Fluorescence (Poole written commun. 1983)	ICP Emission Spectroscopy, (Lichte, written commun., 1983)	
32780	Cr	196	192	196	--	170	170
(7.5 gal/ton)	Mo	206	205	208	200	200	200
	Ni	154	152	155	100	140	150
	V	860	865	868	800	840	850
	Zn	1190	1130	1133	800	1000	1100
32804	Cr	116	121	117	--	110	110
(no oil)	Mo	18	20	17	<20	16	14
	Ni	61	70	62	<100	60	58
	V	154	159	156	<100	160	150
	Zn	72	100	81	<100	90	90
32809	Cr	55	57	58	--	55	56
(no oil)	Mo	2	5	3	<20	4	3
	Ni	58	57	58	<100	56	55
	V	61	62	63	<100	63	63
	Zn	45	36	33	<100	40	30
32829	Cr	330	336	346	--	300	300
(18.3 gal/ton)	Mo	690	703	717	700	670	680
	Ni	562	576	594	750	550	560
	V	2149	2209	2234	2500	2200	2200
	Zn	4948	5091	5127	3500	4700	4700
32844	Cr	112	118	125	--	110	110
(trace oil)	Mo	5	9	7	<20	8	6
	Ni	70	76	82	<100	74	77
	V	138	148	152	<100	150	140
	Zn	19	72	32	<100	30	30
32951	Cr	593	600	602	--	--	--
(14.7 gal/ton)	Mo	289	291	288	300	--	--
	Ni	313	319	320	300	--	--
	V	1312	1324	1324	1500	--	--
	Zn	2746	2761	2763	2000	--	--

-- Not determined.

Roasted Shale - Analysis of 95 roasted samples (digestion B) of the Heath Formation interbedded shale and limestone unit indicates that the enclosed oil shale zone is enriched in molybdenum, nickel, vanadium and zinc in six of seven core holes and in chromium in two of the six core holes. Weighted average values of these metals for the interbedded unit (excluding the oil shale zone) exceed average values for black shales but do not exceed thresholds that delineate metal-rich black shales as defined by Vine and Tourtelot (3).

Weighted average values for the oil shale in six core holes are 385 ppm Cr, 352 ppm Mo, 269 ppm Ni, 948 ppm V and 1,737 ppm Zn. These weighted average values reach a maximum of 525 ppm Cr, 515 ppm Mo, 326 ppm Ni, 1,088 ppm V and 2,420 ppm Zn in individual core holes. In comparison, weighted average values for the sampled portion of the interbedded unit (excluding the oil shale zone) in six core holes are 106 ppm Cr, 144 ppm Mo, 104 ppm Ni, 234 ppm V and 329 ppm Zn. These weighted average values reach a maximum of 221 ppm Cr, 178 ppm Mo, 154 ppm Ni, 374 ppm V and 816 ppm Zn in individual core holes.

The distribution of weighted average chromium, molybdenum, nickel, vanadium, zinc and oil values for the oil shale zone shows that chromium is a fairly good indicator of oil content, a fact which holds true for individual samples. Chromium and vanadium are enriched only within the oil zone. Chromium is enriched in all samples which yielded 14 or more gal oil per short ton, whereas vanadium is enriched in some, but not all, samples which yielded 6.6 or more gal oil per short ton. Molybdenum, nickel and zinc are less closely associated with oil yield. Molybdenum is

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enriched sporadically throughout the interbedded shale and limestone unit of the Heath Formation; high molybdenum values do not always correspond to high oil yields for individual samples. Nickel and zinc, for the most part, are enriched within the oil shale zone; a few high values occur in the enclosing interbedded shale and limstone unit. As with molybdenum, high nickel and zinc values do not necessarily correspond to high oil yields for individual samples.

Comparison of metal abundance of the Heath oil shale zone with other Paleozoic-age black shales of the United States indicates that the zone is most similar to the Sunbury Shale in northeastern Kentucky.

Fischer-Assay Oil Distillate – Metal values for oil distillates produced from 20 samples of the oil shale by the Fischer-Assay procedure are extremely low compared to values for corresponding roasted shale samples. Average values of selected metals in oil distilled from the oil shale zone are <1 ppm Cr, <1 ppm Mo, 7 ppm Ni, 23 ppm V and 2 ppm Zn based on weighted average values from six core holes. The major portion of these metals remained behind in the spent shale, as is shown by analysis of the spent shale.

Fischer-Assay Spent Shale – Metal values for 5 samples of the oil shale zone from which an oil product was removed by Fischer-Assay distillation are slightly higher than values for corresponding roasted shale samples (Table III). In comparison, the Fischer-Assay oil distillates have a very low metal content. Removal of the oil distillate has beneficiated the spent shale slightly.

TABLE III

COMPARISON OF MBMG EMISSION SPECTROSCOPY RESULTS OF SELECTED ELEMENTS FOR VARIOUS FRACTIONS OF FIVE METAL- AND OIL-RICH OIL SHALE SAMPLES

Sample Interval No. Oil Yield and Drill Hole	Element	Metal Content (ppm)				
		Shale Fractions			Oil Fractions	
		Oil Shale[a]	Fischer-Assay Spent Shale[b]	Inorganic Fraction[c]	Fischer-Assay Oil[d]	Organic Fraction[e]
32951/33520	Cr	598[f]	630	607	<1	<1
(14.7 gal/ton)	Mo	290[f]	318	289	1	1
Cox Ranch	Ni	317[f]	347	319	4	1
	V	1320[f]	1399	1215	20	45
	Zn	2758[f]	2982	2807	3	<1
33026/33521	Cr	621	692	664	<1	<1
(18.0 gal/ton)	Mo	337	354	359	<1	<1
Beaver	Ni	356	398	364	10	4
	V	1413	1510	1412	10	15
	Zn	4203	4471	4371	3	<1
33107/33523	Cr	572	634	594	<1	<1
(19.9 gal/ton)	Mo	483	558	500	<1	1
Middle Bench	Ni	407	478	416	11	<1
	V	1657	1848	1481	50	13
	Zn	3176	3723	3353	2	<1
33216/33522	Cr	569	630	541	<1	<1
(14.0 gal/ton)	Mo	298	333	291	<1	7
Red Hill	Ni	307	344	296	6	3
	V	1410	1510	1178	25	99
	Zn	2221	2502	2243	2	<1
33358/33524	Cr	700	811	700	<1	<1
(20.0 gal/ton)	Mo	397	429	367	<1	<1
Heath	Ni	398	443	365	9	7
	V	1586	1723	1374	21	53
	Zn	3490	3953	3494	2	<1

a. 500°C ash of core sample.
b. Core sample from which Fischer-Assay oil was distilled at 500°C.
c. Inorganic fraction of core sample derived by low temperature xylene extraction technique.
d. Oil derived from core sample by the modified Fischer-Assay procedure.
e. Organic fraction of core sample derived by low temperature xylene extraction technique.
f. Average value

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Inorganic Fraction - Metal values for the inorganic fraction of 5 samples of the oil shale zone in which xylene was used to disassociate the inorganic and organic fractions at a low temperature (120°C) are slightly less than values for corresponding roasted shale samples (Table III).

Organic Fraction - Metal values for the organic fraction of 5 samples of the oil shale zone in which xylene was used to disassociate the inorganic and organic fractions at a low temperature (120°C) are extremely low and very similar to values for corresponding Fischer-Assay oil distillates (Table III).

The xylene extracted fractions also exhibit color and odor properties which are different from those of the Fischer distillates. The color of the xylene extracted oil fractions ranged from dark yellow to red-brown. The xylene-extracted oil fractions did not have any odor. The Fischer distillates were often composed of 3 phases (water, dark brown oil and light gray grease). The Fischer distillates all possessed a strong, sharp, biting odor that is often associated with crude oil.

Reflectance

Average vitrinite reflectance values range from 0.49 to 0.64% reflectance for samples from a coal bed that occurs just below the oil shale zone (Table IV). This range indicates an immature to incipiently oil-mature coal bed and, thus, less oil-mature overlying rocks, if thermal maturity in this area is directly related to sediment burial depth.

TABLE IV

REFLECTANCE (% R_o) DATA

Core Hole	Depth (ft)	Sample Number	Number of Measurements	R_o(%)
Beaver	159[a]	33508	100	0.53
Cottonwood	101[a]	33507	100	0.53
Middle Bench	65[a]	33506	100	0.55
Red Hill	248[a]	33505	100	0.49
Heath	284[a]	33504	100	0.49
Cox Ranch	117	33509	100	0.55
	185	33510	100	0.61
	436	33500	100	0.70
Potter Creek	254[a]	33513	100	0.57
	258[a]	33512	100	0.64
	289	33503	----	contaminated
	312	33514	100	0.73
	324	33515	100	0.83

a. Coal bed which occurs just below the oil shale zone.

Reflectance values increase rapidly in the Potter Creek drill hole from 0.57% R_o (incipiently mature) at 254 ft depth to 0.83% R_o (oil-mature) at 324 ft depth. This rapid increase is probably due to the intrusion of a 6-ft-thick lamprophyre sill or dike at 340 ft depth, 16 ft below the lowermost coal. The high, 0.70% R_o value for the lowermost coal in the Cox Ranch core hole may also be the result of igneous activity; however, igneous rocks were not intersected in this core hole.

Conclusion

Shale samples from the Heath Formation have been analyzed to characterize their oil and metal content. The objective of this program was to determine whether or not these shales possessed any economic resource value. Early discussions about the Heath oil shale reasoned that a "low" oil yield shale might have economic value if metals in the shale were contained in the shale oil distillate as metal porphyrins. The emission spectrometric analysis of Fischer-Assay oil distillates proved that no significant amount of metals was found in the distillate. While the Fischer Assay does not provide an exact measure of the oil shale retorting process, we believe the data imply that commercial scale retorting of the Heath oil shale will not recover significant levels of metals.

We also subjected the Heath oil shale to solvent extraction to determine whether or not the retorting temperatures might be pyrolyzing any metal organic complexes in the shale. Emission spectrometric analysis of the xylene extracted oil found no significant metal content in the extracted oil. This final test suggests that the metal content is not carried by the labile organic fraction of the oil shale. The metal values of the Heath shale probably can not be economically recovered from
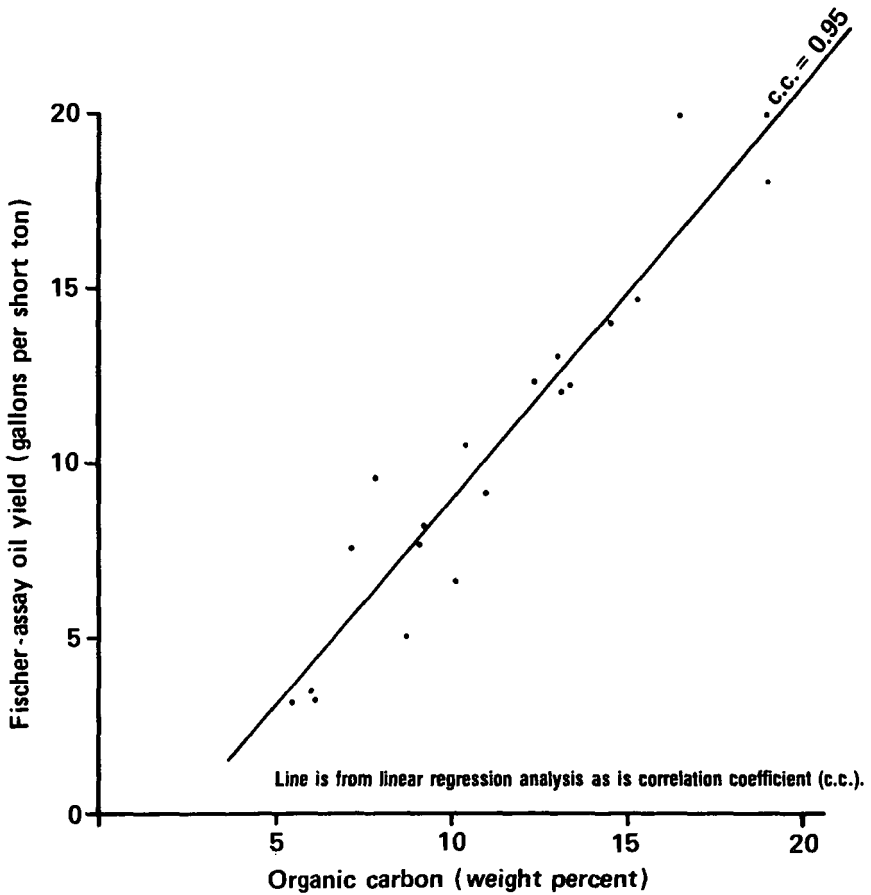
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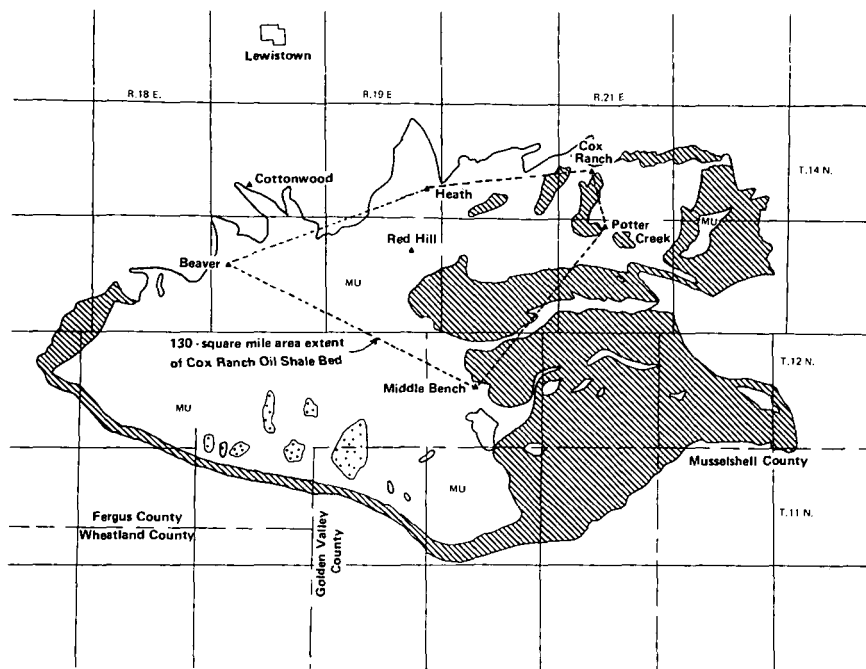
FIGURE 1

EXPLANATION

☐	Post - Pennsylvanian strata
▨	Pennsylvanian strata
MU	Mississippian strata
⋰	Pre - Mississippian strata
▲	MBMG core hole

LOCATION MAP

0   5   10
miles

0   10
kilometers
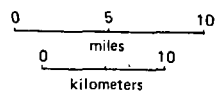
Generalized geologic map of central Montana
showing location of MBMG core holes

FIGURE 2

Plot of Fischer-assay oil yield vs. organic carbon for the oil shale bed based on 20 samples from 6 core holes.

the shale concurrent with a shale oil recovery process. This property does not enhance the economic potential of the Heath oil shale as an oil and metal resource.

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