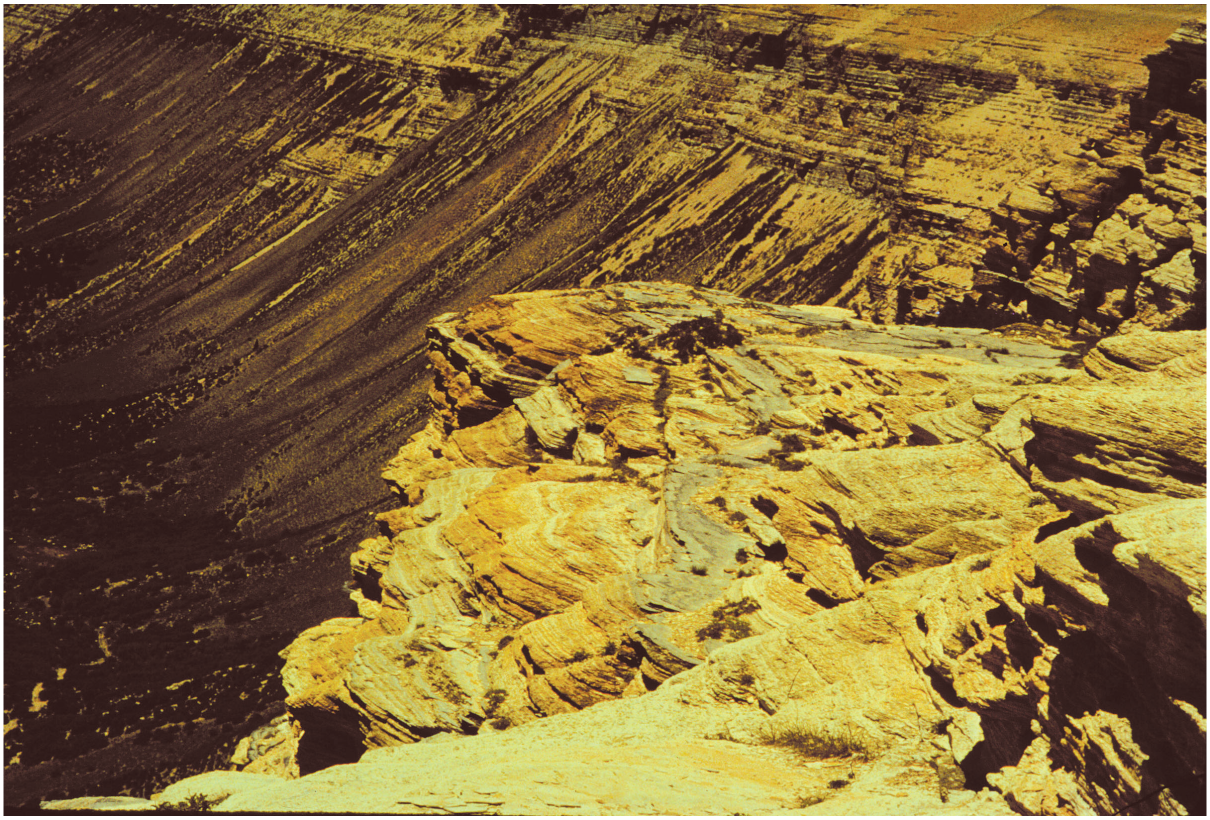
A Collection of Chemical, Mineralogical, and Stable Isotopic Compositional Data for Green River Oil Shale from Depositional Center Cores in Colorado, Utah, and Wyoming

By Michele L.W. Tuttle



Open-File Report 2009–1274

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
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Suggested citation:
Tuttle, M.L. 2009, A collection of chemical, mineralogical, and stable isotopic compositional data for Green River oil shale from depositional center cores in Colorado, Utah, and Wyoming: U.S. Geological Survey Open-File Report 2009–1274, 18 p.

Cover photograph: Mahogany zone, Green River Formation, Piceance Basin, Colorado

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
meter (m)	1.094	yard (yd)
	Volume	
cubic meter (m^3)	6.290	barrel (petrol., 1 barrel = 42 gal)
liter (L)	0.2642	gallon (gal)
cubic meter (m^3)	264.2	gallon (gal)
cubic meter (m^3)	0.0002642	million gallons (Mgal)
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter (m^3)	1.308	cubic yard (yd^3)
	Mass	
kilogram (kg)	2.205	pound avoirdupois (lb)
megagram (Mg)	1.102	ton, short (2,000 lb)
megagram (Mg)	0.9842	ton, long (2,240 lb)

Abbreviated Chemical Symbols

Abbreviation	Chemical Species	Abbreviation	Chemical Species
Ag	Silver	Na	Sodium
Al	Aluminum	Nb	Niobium
As	Arsenic	Nd	Neodymium
B	Boron	Ni	Nickel
Ba	Barium	P	Phosphorous
Be	Beryllium	Pb	Lead
Bi	Bismuth	Pr	Prasceodmium
$C_{carbonate}$	carbonate Carbon	Rb	Rubidium
$C_{organic}$	organic Carbon	S_{total}	total Sulfur
Ca	Calcium	S_{SO4}	sulfate Sulfur
Cd	Cadmium	$S_{disulfide}$	disulfide Sulfur
Ce	Cerium	$S_{organic}$	organic Sulfur
Cl	Chlorine	$S_{acid\text{-}volatile}$	acid-volatile Sulfur
Co	Cobalt	Sb	Antimony
Cr	Chromium	Sc	Scandium
Cs	Cesium	Se	Selenium
Cu	Copper	Sm	Samarium
Dy	Dysprosium	Sn	Tin
Er	Erbium	SO_4	Sulfate
Eu	Europium	Sr	Strontium
Fe	Iron	Ta	Tantalum
Ga	Gallium	Tb	Terbium
Gd	Gadolinium	Te	Tellurium
Ge	Germanium	Th	Thorium
Hg	Mercury	Ti	Titanium
Ho	Holmium	Tl	Thallium
In	Indium	Tm	Thulium
K	Potassium	U	Uranium
La	Lanthanum	V	Vanadium
Li	Lithium	W	Tungsten
Lu	Lutetium	Y	Yttrium
Mg	Magnesium	Yb	Ytterbium
Mn	Manganese	Zn	Zinc
Mo	Molybdenum	Zr	Zirconium
N	Nitrogen (as N)		

A Collection of Chemical, Mineralogical, and Stable Isotopic Compositional Data for Green River Oil Shale from Depositional Center Cores in Colorado, Utah, and Wyoming

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Abstract

For over half a century, the U.S. Geological Survey and collaborators have conducted stratigraphic and geochemical studies on the Eocene Green River Formation, which is known to contain large oil shale resources. Many of the studies were undertaken in the 1970s during the last oil shale boom. One such study analyzed the chemistry, mineralogy, and stable isotopy of the Green River Formation in the three major depositional basins: Piceance basin, Colo.; Uinta basin, Utah; and the Green River basin, Wyo. One depositional-center core from each basin was sampled and analyzed for major, minor, and trace chemistry; mineral composition and sulfide-mineral morphology; sulfur, nitrogen, and carbon forms; and stable isotopic composition ($\delta^{34}S$, $\delta^{15}N$, $\delta^{13}C$, and $\delta^{18}O$). Many of these data were published and used to support interpretative papers (see references herein). Some bulk-chemical and carbonate-isotopic data were never published and may be useful to studies that are currently exploring topics such as future oil shale development and the climate, geography, and

weathering in the Eocene Epoch. These unpublished data, together with most of the U.S. Geological Survey data already published on these samples, are tabulated in this report.

Introduction

Oil shale in the Eocene Green River Formation of Colorado, Utah, and Wyoming is estimated to be the equivalent of 1.8 trillion barrels of oil in place (Office of Technology Assessment, 1980). The history, incentives, and policy of Green River oil shale development is summarized in a Congressional Research Service report by Andrews (2006). The Naval Petroleum and Oil Shale Reserves were established in the 1920s when the Bureau of Mines began to develop methods to exploit oil shale. In the 1960s, commercial interest began and was later stimulated by the Federal synthetic fuels program, which was created in response to the oil embargo of the 1970s. During these decades, large amounts of funds were available for industrial, academic, and government research to study the formation and exploitation of this immense resource. The commercial oil shale projects and most of the Green River Formation research ended in the 1980s due to the decline in the price of oil that rendered oil shale development economically unfavorable. Today, the current high oil price and The Energy Policy Act of 2005 (EPACT) have revived interest in unconventional resources including oil shale, which now is considered a means of reducing dependence on foreign oil and improving national security (Andrews, 2006). In addition to the renewed interest in oil shale development, current research into Green River carbonate minerals provides insight into a variety of environmental factors during the Eocene Epoch such as atmospheric pCO_2, climate, geography, chemical weathering, and physical erosion (Norris and others, 1996; Smith and others, 2006, 2008; Lowenstein and Demicco, 2006).

Between 1983 and 1996, a series of published papers (Tuttle and others, 1983; Tuttle, 1988; Collister and Hayes, 1991; Dean and Anders, 1991; Tuttle, 1991a, b; Tuttle and Goldhaber, 1991, 1993; Pitman, 1996) presented geochemical data for a set of oil shale samples collected from depositional-center cores within the three major Green River basins in Wyoming, Utah, and Colorado (fig. 1). The major, minor, and trace chemistry, and some of the carbonate isotopic data collected on these samples, were not included in these publications. The purpose of this report is to make available the U.S. Geological Survey's chemical, isotopic, and mineralogical data collected on this well-described set of samples that are archived in the U.S. Geological Survey (USGS) Core Library, Denver, Colo. Previously unpublished carbon chemical and carbonate isotopic data for the Mahogany zone in three additional Green River cores (two in Colorado and one in Utah) also are included. The objective for publishing these data now in one report, and in a web accessible format, is to make them readily available to researchers conducting geochemical studies during this recent boom in the cycle of Green River Formation research.

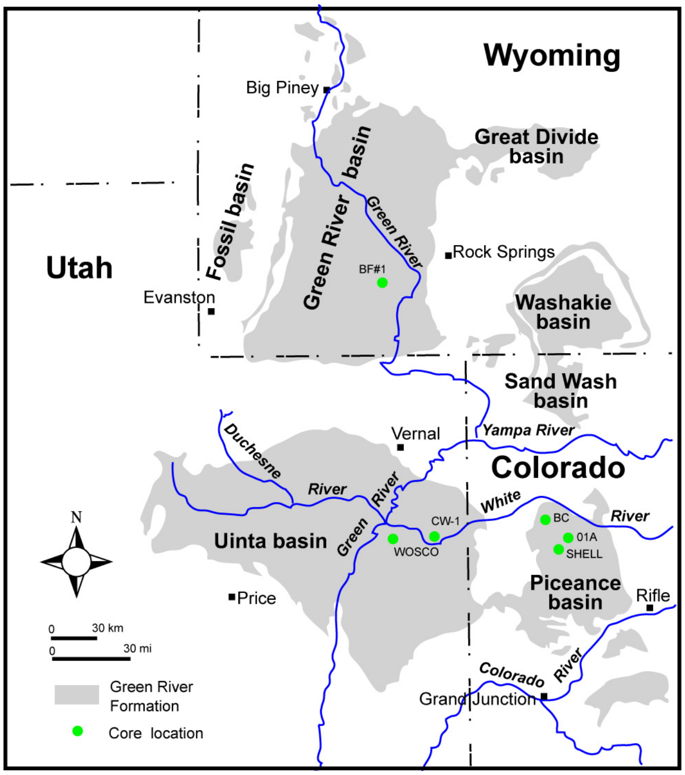

Figure 1. Map showing the extent of the Green River Formation and the approximate location of the Green River Formation cores (modified from Trudell and others, 1982).

Sample Collection

Table 1 lists the names and locations of drill holes discussed in this report, the depth interval and members sampled, and the number of samples collected from each core. Geologic sections of the U.S. Bureau of Mines (USBM) 01A core (01A), the USGS Coyote Wash-1 core (CW), and the Energy Research and Development Administration/Laramie Energy Research Center (ERDA/LERC) Black Forks no. 1 core (BF) are in Tuttle (1991a) and reproduced in figure 2. No attempt has been made to correct the depositional time lines that are reported from 1991 among the three basins (see new $^{40}Ar/^{39}Ar$ ages in Smith and others, 2008). Except for depth intervals, Mahogany zone samples from the Shell Oil Co. TR-1 23X-2 Federal core (SHELL) and the USBM Barcus Creek no. 1 core (BC) are similar to those from the Mahogany zone in the 01A core, and the samples from the WOSCO EX-1 core (WOSCO) are similar to those from the Mahogany zone in the CW core.

Hierarchical, unbalanced, analysis-of-variance sampling designs (Miesch, 1976) were used in sampling the cores to assure objectivity and optimal coverage given the limited resources for sample analysis. Designs for the 01A, CW, and BF cores are detailed in Tuttle (1991a). Samples from the SHELL, BC, and WOSCO cores were collected every three feet through the Mahogany zone. Additional samples from atypical intervals were also collected from these three cores and include zones of massive sulfides and unusual textures or bedding. In Colorado and Utah, a total of 231 samples were collected from the Mahogany Zone of the Green River Formation, 161 from the Parachute Creek Member below the Mahogany Zone, 26 samples from the Garden Gulch Member (Colo.), and 26 from the Douglas Creek Member (Utah). In Wyoming, 7 samples were collected from the Laney Member, 23 from the Wilkins Peak Member, and 5 from the Tipton Shale Member.

Samples were removed from the core with a water-cooled saw and promptly dried to minimize oxidation of sulfides and dissolution of salts. They were described with respect to lithology and megascopic appearance, and, in most cases, photographed. Thin sections were made of most samples (cut and ground in oil) and polished if sulfide minerals were observed. Splits of samples for analyses were ground with ceramic-plates to pass a 130-µm mean diameter mesh screen.

Table 1. Names and locations of drill holes, person(s) that described core and reference, depth interval and members sampled, and the number of samples from each core.

[USBM, U.S. Bureau of Mines; USGS, U.S. Geological Survey; ERDA/LERC, Energy Research and Development Administration/Laramie Energy Research Center; WOSCO, Western Oil Shale Corp.; SLM, Salt Lake Meridian; unpublished, no reference information on core description; MZ, Mahogany Zone; PC, Parachute Creek Member; GC, Garden Gulch Member; DC, Douglas Creek Member; L, Laney Member; WP, Wilkins Peak Member; TS, Tipton Shale Member]

Core name/ description	Basin	Location	Interval (m) & members sampled	Number of samples
USBM 01-A (01-A) Snyder and Terry (1977)	Piceance	NW1/4 NW1/4 SW1/4 of sec. 29, T 1 S, R 97 W, Rio Blanco County, CO	254 to 773 MZ, PC, GC	172 subset = 41
USGS Coyote Wash-1 (CW) Scott and Pantea (1982)	Uinta	SE1/4 SE1/4 NE1/4 of sec 22, T 9 S, R 23 E SLM, Uintah County, UT	571-1043 MZ, PC, DC	53
ERDA/LERC Blacks Fork #1 (BF) Trudell (unpublished)	Green River	SE 1/4 NE 1/4 of sec 24, T 16 N, R 108 W, Sweetwater County, WY	L, WP, TS	35
Shell Oil Co. TR-1 23X-2 Federal (SHELL) Culbertson (unpublished)	Piceance	NE1/4 SW 1/4 of sec. 2, T 2 S, R 98 W, Rio Blanco County, CO	311 to 376 MZ	82
WOSCO EX-1 (WOSCO) Smith and others (1976)	Uinta	SW 1/4 Se 1/4 of sec 36, T 9 S, R 20 E SLM, Uintah County, UT	689 to 719 MZ	48
USBM Barcus Creek #1 (BC) Unknown (unpublished)	Piceance	488’ south of north line, 2588’ east of west line, sec 21, T 1 N, R 99 W., Rio Blanco County, CO	46 to101 MZ	53

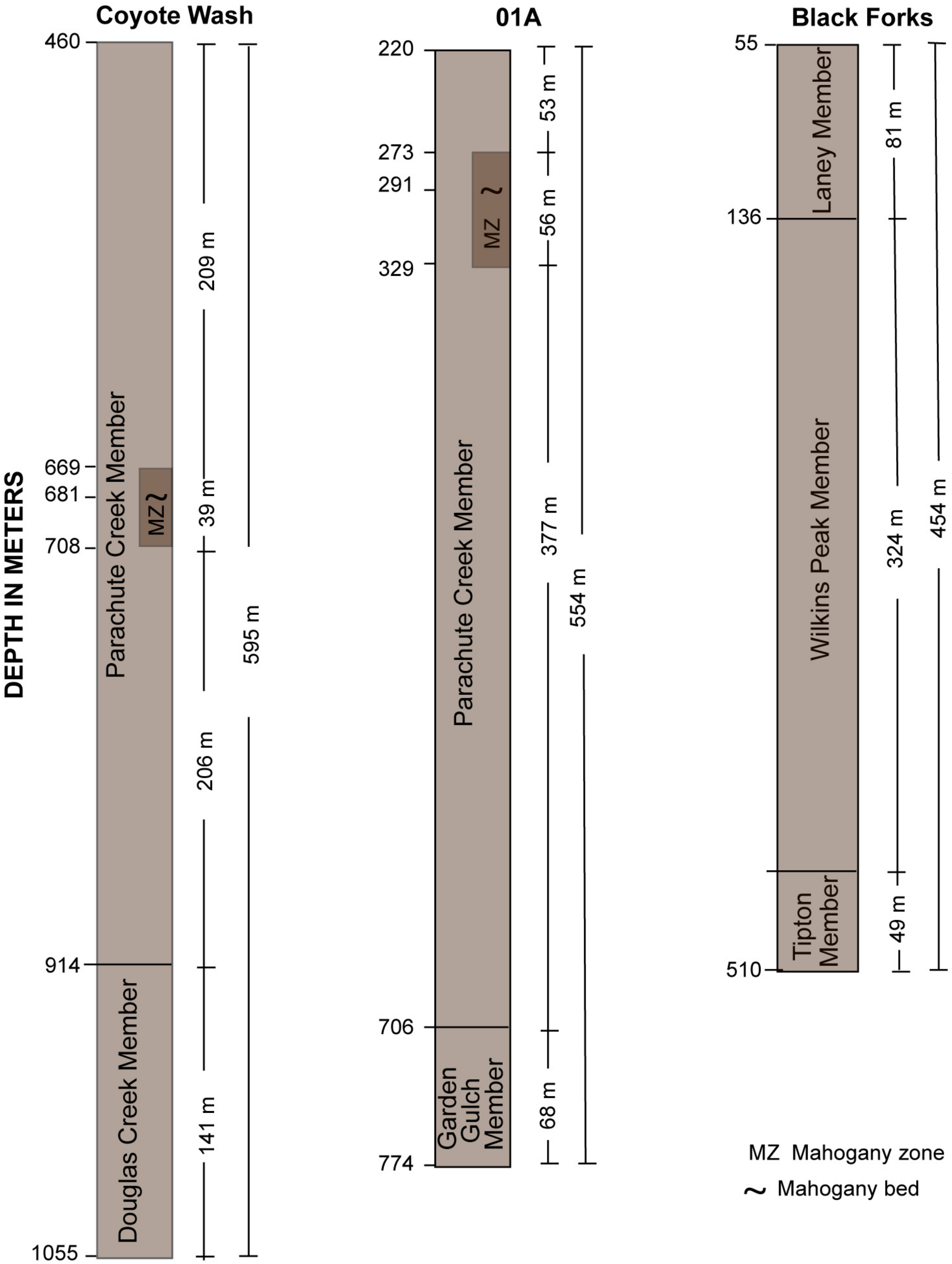

Figure 2. Geologic section of the 01A, CW, and BF cores (modified from Tuttle, 1991a).

Methods

Oil Yield, Chemical, and Isotopic Analyses

Oil yield (gal/ton) was determined by Fischer assay and most values reported herein were extrapolated from depth plots that were available with the core descriptions. The C_{total} and $C_{organic}$ concentrations were determined on untreated and HCl acid-treated samples using a Leco induction furnace with a thermal conductivity cell (Leco model WR-32). The $C_{carbonate}$ concentrations were determined by difference. The S_{total} concentrations were determined using a Leco induction furnace connected to an infrared detection system (Leco model IR-32). Major-oxide concentrations were analyzed by wavelength dispersive X-ray fluorescence spectroscopy (WDXRF) (Taggert and others, 1990). Major-, minor-, and trace-element concentrations were analyzed by inductively coupled plasma–atomic emission spectrometry (ICP-AES) (Briggs, 1990). Elements with concentrations below the ICP-AES lower limit of determination in all samples are listed in table 2. Rock-Eval pyrolysis data (H-index and O-index) were generated using the method of Espitalié and others (1977) described in Dean and Anders (1991). Sulfur species (sulfate, monosulfide, disulfide, and organosulfur) were separated by a scheme described in Tuttle and others (1986), and the concentrations of the different species were gravimetrically quantified. Sulfur isotopes were determined by conversion of products from the speciation scheme to SO_2 that was analyzed by mass spectrometry (MS) (the procedure and calibration standards used are discussed in Wasserman and others, 1992). Carbon and oxygen isotopes in carbonate minerals (calcite, dolomite, and water-soluble carbonates) were commercially obtained from Global Geochemistry Corporation, Canoga Park, Calif. Isotope data ($\delta^{34}S$, $\delta^{13}C$, and $\delta^{18}O$) were calculated by equation 1:

$$\delta \text{‰} = [(R_{sample} - R_{standard})/R_{standard}]\ (1000) \quad (1)$$

where R is the isotope ratio ($^{34}S/^{32}S$, $^{13}C/^{12}C$, or $^{18}O/^{16}O$). Sulfur isotopic data are reported relative to Cañon Diablo Troilite standard (CDT), carbon and oxygen isotopic data relative to Peedee Belemnite standard (PDB). Oxygen isotopic data is converted to values relative to Standard Mean Ocean Water (SMOW) by equation 2 (Hoefs, 1980):

$$\delta^{18}O_{SMOW}\ \text{‰} = 1.03086\ (\delta^{18}O_{PDB}) + 30.86. \quad (2)$$

Most chemical analytical methods report precision and accuracy to within 10 percent and isotope analyses to within 0.1 per mil. The average relative difference in percent (ARD) for data on 19 duplicate XRF analyses, 22 duplicate ICP-AES analyses, and 27 duplicate carbon and oxygen isotope analyses are reported in table 3. The relative difference in percent (RD) for each analytical duplicate pair is calculated by equation 3:

$$RD\ \% = (|x_1-x_2|/(|x_1+x_2|/2))(100), \quad (3)$$

where x's are duplicate analytical concentrations. The ARD in percent is calculated by equation 4:

$$ARD\ \% = (\Sigma(RD\%))/n, \quad (4)$$

where n is the number of analytical pairs. Except for TiO_2 (ARD 6.8 percent), values for XRF analyses are less than 5 percent. The ARD values for most of the ICP-AES elements are less than 10 percent (exceptions are Ba, 13 percent; Ni, 13 percent; Cr, 14 percent, Mo, 21 percent; and Cr, 26 percent). The ARD values for isotopes of carbonates ($\delta^{13}C$ and $\delta^{18}O$) are less than 3 percent.

Table 2. Elements with inductively coupled plasma–atomic emission spectrometry (ICP–AES) concentrations less than the lower limit of determination (LLD) in all samples analyzed

Element	LLD (mg/kg)	Element	LLD (mg/kg)
Ag	2	Ho	4
Au	8	Nb	4
Be	1	Pr	10
Bi	10	Sn	20
Cd	2	Ta	40
Dy	4	Tb	20
Er	4	U	100
Eu	2	Yb	1
Gd	10		

Table 3. Average relative difference in percent (ARD) for duplicate sample splits.

[major-, minor-, and trace-element analyses by wave-length dispersive X-Ray fluorescence spectroscopy (WDXRF) and inductively coupled plasma–atomic emission spectrometry (ICP-AES), and $\delta^{13}C_{carbonate}$ and $\delta^{18}O_{carbonate}$ analyses by mass spectrometry (MS)]

Element (method)	ARD %	Element (method)	ARD %
Al_2O_3 (WDXRF)	2.5	La (ICP-AES)	2.9
CaO (WDXRF)	2.3	Li (ICP-AES)	5.9
Fe_TO_3 (WDXRF)	2.6	Mg (ICP-AES)	2.3
K_2O (WDXRF)	2.1	Mn (ICP-AES)	5.3
MgO (WDXRF)	2.1	Mo (ICP-AES)	21
Na_2O (WDXRF)	3.5	Na (ICP-AES)	2.5
P_2O_5 (WDXRF)	1.3	Nd (ICP-AES)	10
SiO_2(WDXRF)	1.5	Ni (ICP-AES)	13
TiO_2(WDXRF)	6.7	Pb (ICP-AES)	9.8
Al (ICP-AES)	3.7	P (ICP-AES)	3.5
As (ICP-AES)	2.6	Sc (ICP-AES)	3.0
Ba (ICP-AES)	13	Sr (ICP-AES)	2.7
Ca (ICP-AES)	3.7	Th (ICP-AES)	6.4
Ce (ICP-AES)	4.9	Ti (ICP-AES)	3.2
Co (ICP-AES)	13	V (ICP-AES)	3.3
Cr (ICP-AES)	26	Y (ICP-AES)	2.7
Cu (ICP-AES)	14	Zn (ICP-AES)	2.8
Fe (ICP-AES)	5.5	$\delta^{13}C_{carbonate}$ (MS)	1.4
Ga (ICP-AES)	7.0	$\delta^{18}O_{carbonate}$ (MS)	2.9
K (ICP-AES)	1.7		

Results

Chemical, isotopic, mineralogical and sulfide petrographic data collected from core samples (table 1) are tabulated in the Appendix tables (tables 1-1 – 1-9). Mineralogical and petrological data are from Tuttle (1991a, b), sulfur speciation and isotope data are from Tuttle and Goldhaber (1991), Rock-

Eval pyrolysis data are from Dean and Anders (1991), and the carbonate isotopic data for samples from 01A and CW cores are from Pitman (1996).

Previous studies have shown that geochemical data can be traced within an oil shale basin, supporting the hypothesis that similar depositional conditions prevailed across large aerial extents. An excellent example of widespread depositional conditions is the correlation of sulfur cycles and chemistry throughout the Green River section in cores across the Piceance basin (Dyni, 1983; Tuttle and others, 1983). These types of data support the hypotheses that the data reported herein is representative of a large amount of the Green River oil shale within respective basins.

Archive of Oil Shale Samples and Core Literature

Ground and un-ground splits for most samples discussed in this report are archived at the USGS Core Library in Denver, Colo. Thin sections are currently housed with the author, but, in the near future, they will become part of the archive along with core descriptions, Fischer assay logs and data, sample/core photographs, sampling notebooks that include a detailed description for each sample, and relative XRD peak-height data. It is the hope of the author that these resources and the data published herein and in the cited references provide a useful starting place for future geochemical research on the Green River oil shale.

Acknowledgments

This compilation was funded by the U.S. Geological Survey Energy Resources Program. The author thanks the various researchers cited in this paper for their contribution to this Green River Formation geochemical database. Special thanks to the analysts who provided the major, minor, and trace chemical analyses, specifically Joseph Taggart and Paul Briggs of the U.S. Geological Survey, and to Monique Adams and Cyrus Berry for their thoughtful reviews of the manuscript and data files.

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Appendix 1

Table 1-1. Chemical and isotopic data for samples from the 01A core, Piceance basin, Colorado.

[insuff, insufficient amount recovered for isotopic analyses; blanks indicate no data]

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Table 1-2. Mineral and sulfide-mineral morphology data for samples from the 01A core, Piceance basin, Colorado. Data from Tuttle (1991a, b).

[Morphology (morph) key: A, anhedral; B, blades; E, euhedral; F, framboids; L, lens: S, iron-sulfide replacing oxide mineral grains; percent salt in Description is visually estimated]

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Table 1-3. Chemical and isotopic data for samples from the BF core, Green River basin, Wyoming.

[insuff, insufficient amount recovered for isotopic analyses; blanks indicate no data]

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Table 1-4. Mineral and sulfide-mineral morphology data for samples from the BF core, Green River basin, Wyoming.

[Morphology (morph) key: A, anhedral; B, blades; E, euhedral; F, framboids; L, lens: S, iron-sulfide replacing oxide mineral grains; percent salt in Description is visually estimated]

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Table 1-5. Chemical and isotopic data for samples from the CW core, Uinta basin, Utah.

[insuff, insufficient amount recovered for isotopic analyses; blanks indicate no data]

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Table 1-6. Mineral and sulfide-mineral morphology data for samples from the CW core, Uinta basin, Utah.

[Morphology (morph) key: A, anhedral; B, blades; E, euhedral; F, framboids; L, lens: S, iron-sulfide replacing oxide mineral grains; percent salt in Description is visually estimated]

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Table 1-7. Carbon chemical and carbonate isotopic data for samples from the BC core, Piceance basin, Colorado.

[blanks indicate no data]

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Table 1-8. Carbon chemical and carbonate isotopic data for samples from the SHELL core, Piceance basin, Colorado.

[blanks indicate no data]

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Table 1-9. Carbon chemical and carbonate isotopic data for samples from the WOSCO core, Piceance basin, Colorado.

[blanks indicate no data]

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