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A Review of the Organic Geochemistry of Shales

Patience C. Ho
Robert E. Meyer

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CHEMISTRY DIVISION

A REVIEW OF THE ORGANIC GEOCHEMISTRY OF SHALES

Patience C. Ho
Robert E. Meyer

NUCLEAR AND CHEMICAL WASTE PROGRAM
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TABLE OF CONTENTS

		Page
	ABSTRACT	v
	LIST OF TABLES	vii
1.	INTRODUCTION	1
2.	CHARACTERISTICS OF ORGANIC MATTER IN SHALES OF THE UNITED STATES	
	2.1 Precambrian Shales	2
	2.2 Paleozoic Shales	3
	2.3 Mesozoic Shales	12
	1.4 Cenozoic Shales	13
3.	SUMMARY	27
4.	CONCLUSIONS	28
5.	REFERENCES	29

A REVIEW OF THE ORGANIC GEOCHEMISTRY OF SHALES

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ABSTRACT

Shale formations have been suggested as a potential site for a high level nuclear waste repository. As a first step in the study of the possible interaction of nuclides with the organic components of the shales, literature on the identification of organic compounds from various shales of the continent of the United States has been reviewed. The Green River shale of the Cenozoic era is the most studied shale followed by the Pierre shale of the Mesozoic era and the Devonian black shale of the Paleozoic era. Organic compounds that have been identified from these shales are hydrocarbons, fatty acids, fatty alcohols, steranes, terpanes, carotenes, carbohydrates, amino acids, and porphyins. However, these organic compounds constitute only a small fraction of the organics in shales, and the majority of the organic compounds in shales are still unidentified.

LIST OF TABLES

Table		Page
I.	Organic Carbon Content of Paleozoic Shales	4
II.	Identified Organic Compounds in Paleozoic Shales	9
III.	Organic Carbon Content and the Identified Organic Compounds in Mesozoic Shales	14
IV.	Identified Organic Compounds in Bitumens of Cenozoic Shales	19
V.	Identified Organic Compounds in Kerogens of Cenozoic Shales	24

1. INTRODUCTION

The Sedimentary Rock Program (SERP) at the Oak Ridge National Laboratory (ORNL) is investigating shales in the United States for their potential suitability as host rocks for the disposal of high-level radioactive wastes (HLW). Geochemical conditions (e.g., temperature, pressure, groundwater chemistry, pH, redox conditions, host-rock mineralogy and chemistry) and the interaction of radionuclides, groundwaters, and host rocks provide the dominant controls for limiting the mobility of radionuclides that will be released when the waste packages ultimately fail. The geochemical conditions associated with the various shales being evaluated by the SERP may be quite different, and the shales may have varying capabilities for the retention of radionuclides. One of the important factors that has not received much attention is the interaction of the nuclides with the organic content of the shales. As a first step in this study, a literature review was conducted to search for information concerning the organic compounds that have been isolated and identified in various shales throughout the continental United States.

Sediments of all ages, including those as old as 3000 million years from the Precambrian era, contain organic matter. The organic matter that is deposited and preserved in sediments was synthesized by living organisms. The most important contributors of organic matter in sediments are phytoplankton, zooplankton, higher plants, and bacteria. The fate of organic matter that enters a sediment is governed mainly by tectonic events. It may undergo increasing burial and is subjected to diagenesis, catagenesis, and metamorphism (1).

Shales are one of the most common and widespread rock types in the United States (2). Thick deposits of shale can be found in almost every state of the United States, and these deposits cover a wide variety of geological times from the Precambrian through the Tertiary period. Because organic matter in shales has been considered as one of the principal sources of petroleum, considerable effort has been spent in recent years by the petroleum industry to determine the thermal maturity and the origin of the organic compounds in shales. If shale formations are to be used as a host for a high level radioactive waste repository, the possibility of interaction between nuclides and the organic matter must be considered. This study of interaction would be especially important if shales that have a high percentage of organic material are chosen as the host rock type for the repository.

2. CHARACTERISTICS OF ORGANIC MATTER IN SHALES OF THE UNITED STATES

During the history of the earth,the conditions for synthesis, deposition, and preservation of organic matter have changed considerably. From the Precambrian era to the Devonian era, the primary producer of organic matter was marine phytoplankton. Since the Devonian era, an increasing amount of primary production has been contributed by higher terrestrial plants. Presently, marine phytoplankton and terrestrial higher plants are estimated to produce about equal amounts of organic carbon (1). The organic material was subjected to extensive physical, biological, and chemical alteration. After this process much of the material became insoluble in common organic solvents or aqueous alkaline solvents; this insoluble portion of the organic material is referred to as kerogen. The relatively small fraction of the organic material soluble in the solvents is known as bitumen. In ancient sedimentary rocks (such as shale) kerogen represents more than 80% of the organic matter (1,3). Some of the low molecular-weight compounds present in bitumen have been identified. Only general structural information is known about the insoluble kerogen, although kerogen is the most abundant form of organic carbon on earth (1).

As mentioned above, the major portion of the organic material in shales is the insoluble kerogen. Chattanooga shale of marine origin has as much as 25% of organic matter (4) which is mostly kerogen. Procedures for identifying kerogen include physico-chemical analyses and petrographic analysis (3). Physical methods of separation are based on difference of specific gravity or differential wetting of the kerogen and minerals by two immiscible liquids (1, 5). Chemical procedures should be restricted to avoid an alteration of the chemical structure of kerogen (1). Oxidation, hydrogenolysis and pyrolysis are three methods of degrading kerogen to form lower molecular compounds, which are easier to analyze (1). The general physical methods of studying kerogen are electron diffraction, x-ray diffraction, infrared spectroscopy (IR), nuclear magnetic resonance (NMR), and thermal analysis.

Shales deposited during the Precambrian, Paleozoic, Mesozoic, and Cenozoic time periods will be discussed separately here. These shales cover almost the entire continent of the United States; the geological regions where shale deposits occur in the above geological eras are divided into the following regions: East Margin, East Interior, Gulf Coast, Great Plains, Rocky Mountains, Great Basin, Colorado Plateau, Great Valley, and Pacific Northwest (2).

2.1. Precambrian shales

Argillites and associated rocks of the Precambrian age are present in widely scattered locations of several geological regions of the United States. Some shales in the northern part of the Rocky

Mountains and in central Arizona were formed during this age (2). There is not much available data of organic content in shales occurring in this era. Eglinton et al. (6) reported the identification of isoprenoid hydrocarbons (including phytane and pristane) in oil seeping from the Precambrian Nonesuch Formation at the White Pine Mine, Michigan. n-Paraffins of C_4 to C_8, cyclopentanes, and cyclohexanes were also found in this Nonesuch shale, and the total organic content in this shale is 0.95% (7). Johns et al. (8) identified C_{18} to C_{21} isoprenoid alkanes, and Belsky et al. (9) as well as Burlingame et al. (10) identified C_{13} to C_{22} n-paraffins and isoprenoids (C_{16}-C_{21}) in the Soudan shale (2.7×10^9 years) from Minnesota.

2.2. Paleozoic shales

Shales in the Eastern Interior of the United States (including the Late Ordovician shales of Ohio, Pennsylvania, and New York, and the Devonian-Mississippian shales of the Appalachian, Illinois, and Michigan Basins, the Great Plains (including the Midcontinent and the Devonian-Mississippian black shales), the Rocky Mountain region (including several thick units of Devonian-Mississippian-Pennsylvanian age in Idaho), and the Great Basin of Nevada and Utah were formed during this era.

Some shales of the Paleozoic era (especially the Devonian and Devonian black shales) which contain high concentrations of organic matter, have for years attracted considerable attention as a possible source of energy. Hosterman et al. (11) reported that in the Appalachian Basin, the Devonian shale contains black and gray shale facies, and the black facies contain more organic carbon than does the gray. The black shale contains more than 2% by volume of organic matter (11,12). These widespread and continuous black shale units are known locally with different names such as the Marcellus, Middlesex, Rhinestreet, Genesee, Ohio, Antrim, New Albany, and Chattanooga, etc. The percentages of organic carbon content present in shales which formed during the Paleozoic era are summarized in Table I. Although some of the shales of this era (especially the Devonian black shale) have been extensively studied, the organic compounds have been identified for only a few of them. Johns et al. (8) reported the finding of C_{16} to C_{21} (except C_{17}) isoprenoids, C_{16} iso-alkane, and C_{18}-C_{19} cyclohexyl n-alkanes in Antrim shale from Michigan (north part of Chattanooga shale, late Devonian). Later McCarthy et al. (27) identified the C_{17} saturated isoprenoid hydrocarbon in the same Antrim shale. A study by Bray and Evans (28) showed the presence of heavy n-paraffins of C_{24} to C_{34} in shales of the Big Snowy Mountains of central Montana (Pennsylvanian and Mississippian ages), in Woodford and Chattanooga shales of Oklahoma and Tennessee (Mississippian age), and in shales of north central Texas (Pennsylvanian age). Normal paraffins and normal fatty acids were also found in the Chattanooga shale (Devonian) of Cherokee County, Oklahoma, in the New Albany shale (Devonian) of Cincinnati Arch, Kentucky, and in the

Table I. Organic Carbon Content of Paleozoic Shales

Geological Age	Shale, Location and Formation	Average Org Content	Reference
Mississippian	Woodford shale, Oklahoma	8.9 wt%	5
	Caney shale, Oklahoma	7.2 wt%	
Permian	Wolfcamp, Texas	4.08 wt%	
Devonian	Devonian shale of SW New York		11
	CHAUTAUQUA CO. (CORE SAMPLES)		
	Angola	0.31-1.31 wt%	
	Dunkirk	0.73-2.8	
	Hamilton	0.61-1.73	
	Hanover	∿0.4	
	Marcellus	3.02	
	Pipe Creek	0.45-5.09	
	Rhinestreet	0.52-3.01	
	CATTARAUGUS CO. (CORE SAMPLES)		
	Angola	0.18-0.36 wt%	
	Cashaqua	1.38	
	Dunkirk	0.14-0.69	
	Geneseo	0.71-1.58	
	Hamilton	0.41-2.34	
	Hanover	0.17-0.93	
	Marcellus	1.31-5.09	
	Middlesex	1.71	
	Penn Yan	2.21	
	Pipe Creek	0.23	
	Rhinestreet	0.44-2.48	
	West River	1.58-1.80	
	ERIE CO. (CORE SAMPLES)		
	Angola	0.29-0.61 wt%	
	Cashaqua	0.52	
	Dunkirk	1.35-1.84	
	Hamilton	0.49-2.91	
	Java	0.69-2.90	
	Marcellus	2.62	
	Middlesex	3.46	
	Rhinestreet	1.76-2.85	

Table I (Cont'd)

Geological Age	Shale, Location and Formation	Average Org Content	Reference
Devonian (Cont'd)	WYOMING CO. (CORE SAMPLES)		
	Cashaqua	0.63-0.77 wt%	
	Geneseo	1.84	
	Hamilton	0.44-1.41	
	Marcellus	6.23	
	Rhinstreet	1.78	
	West Falls	1.71-2.15	
	ALLEGANY CO. (CORE SAMPLES)		
	Cashaqua	0.35 wt%	
	Dunkirk	0.19-0.87	
	Geneseo	3.41	
	Hamilton	0.70-1.04	
	Marcellus	4.45	
	Middlesex	1.13	
	Penn Yan	1.69	
	Pipe Creek	0.20-0.98	
	Rhinestreet	0.30-0.72	
	West River	1.10	
	LIVINGSTON CO. (CORE SAMPLES)		
	Geneseo	0.14-1.81 wt%	
	Hamilton	0.35-2.45	
	Marcellus	6.67-14.23	
	Renwick	0.21-0.38	
	STEUBEN CO. (CORE SAMPLES)		
	Cashaqua	0.28-0.55 wt%	
	Dunkirk	0.70	
	Geneseo	0.67-2.23	
	Hamilton	0.30-3.09	
	Marcellus	1.92	
	Middlesex	0.44-1.52	
	Penn Yan	0.85	
	Rhinestreet	0.21-0.85	
	YATES CO. (CORE SAMPLES)		
	Geneseo	1.39 wt%	
	Hamilton	0.11-1.11	
	Marcellus	2.32	
	CHEMUNG CO. (CORE SAMPLES)		
	Geneseo	1.18-1.93 wt%	
	Hamilton	0.25-1.93	
	Marcellus	3.98	
	Middlesex	0.77	

Table I (Cont'd)

Geological Age	Shale, Location and Formation	Average Org Content	Reference
Devonian (Cont'd)	TOMPKINS CO. (CORE SAMPLES)		
	Ashbed	0.26 wt%	
	Geneseo	0.54-1.21	
	Hamilton	0.25-1.00	
	Marcellus	0.51-8.80	
	Renwick	0.23-0.86	
	CORTLAND CO. (CORE SAMPLES)		
	Geneseo	0.80-1.31 wt%	
	Hamilton	0.20-2.08	
	Marcellus	1.89-5.18	
	BROOME CO. (CORE SAMPLES)		
	Geneseo	0.43 wt%	
	Hamilton	0.14-0.47	
	Marcellus	1.30-6.86	
	CHENANGO CO. (CORE SAMPLES)		
	Hamilton	0.23-0.61 wt%	
	Marcellus	0.65-2.24	
	BRANAGAN CO. (CORE SAMPLES)		
	Hamilton	0.27-0.36 wt%	
	Marcellus	0.65-3.68	
	DELAWARE CO. (CORE SAMPLES)		
	Hamilton	0.41 wt%	
	Marcellus	1.63-2.81	
Devonian	Devonian black shale, Overton Co., Tennessee (Core Samples)	4.8-13.5 %	13
Devonian to Mississippian	Black shale, Rowan Co., Kentucky (outcrop samples)	0.4-15.5 %	13
	Perry Co., Kentucky	4.3	12
Devonian to Mississippian	Black shale, Appalachian Basin, New York (Core Samples)	0.5-20wt%(black) 4 wt% (gray)	14
	Ohio shale, Ohio and Kentucky Chattanooga shale (Dowelltown Member, Gassaway Member, TN) Chattanooga shale (Virginia) (Core Samples)	as high as 25%	14,15

Table I (Cont'd)

Geological Age	Shale, Location and Formation	Average Org Content	Reference
Devonian	New Albany shale, IL (CORE SAMPLES)		17,18
	Blocher shale		
	Selmier shale	1-15.6 wt%	
	Gassy Creek shale		
Devonian	New Albany shale, KY (CORE SAMPLES)		19
	Rockcastle Co.	10.3 wt%	
	Pulaski Co.	13.2	
	Adair Co.	12.9	
Devonian to Mississippian	Devonian shale, Appalachian Basin, Michigan Basin (Cover Ohio, Kentucky, Tennessee, Indiana, Michigan, Alabama)	∿13.7 wt%	20
Pennsylvanian	Excello Shale, Midcontinent and Illinois Basin	10-15 %	21
Pennsylvanian	Cherokee Group, Southeastern Kansas and Northeastern Oklahoma		22
	Greenish-gray shale	0.08-0.99 wt%	
	Olive-gray shale	0.55-4.75	
	Black (Phosphatic) shale	1.67-18.60	
Pennsylvanian to Permian	Meade Park Member shale and Retort Member shale of Wyoming, Utah, Idaho, Montana	8-10 wt%	23,24
Devonian	Mt. Union, Central Pennsylvania (CORE SAMPLES)		25
	Burket (black) shale	0.95 %	
	Mahantango (gray) shale	0.36	
	Marcellus (black) shale	4.36	
	Newton Hamilton(Onondaga) shale	5.93	
Devonian	Devonian black shale (CORE SAMPLE)		12
	Lincoln Co., West VA	2.9 %	
	Jackson Co., West VA	1.9	
Mississippian to Permian	Ellesmerian shale North Slope of	0-0.5 %	26
Devonian to Mississippian	Ellesmerian shale Alaska	1-4 %	

Heath shale (Mississippian) of the Big Snowy Uplift of Montana (29-31).

The Upper Pennsylvanian and Lower Permian Kansas shales include the Council Grove Group, the Shawnee Group, and the Lansing Group. Murphy et al. (32) reported that hydrocarbons were present in all examined members of the Council Grove Group (i.e., Speiser shale, Florena shale member, Nova limestone member, Johnson shale, and Hughes Creek shale member). The extracted normal alkanes exhibit a single smooth distribution from C_{12} to C_{26} with a maximum around C_{17}. Phytane ($C_{20}H_{42}$) and pristane ($C_{19}H_{40}$) are the two most abundant isoprenoid hydrocarbons; farnasane ($C_{15}H_{32}$) and steranes are also present. In the Shawnee Group (i.e., Jackson Park shale member, Heumader shale member, and Heebner shale member), there contains large amounts of extractable organic material. Among them, normal alkanes, lipid materials, isoprenoid, cholestane ($C_{27}H_{48}$), ergostane ($C_{28}H_{50}$) and sitostane ($C_{29}H_{52}$) have been identified. The Lansing Group, i.e., the Eudora shale member, is relatively rich in lipids. Besides normal alkanes, isoprenoids and steranes, aromatic hydrocarbons are also found in shale of the Lansing Group.

Carbohydrates are also found in shale deposited during this era. Rogers (33) reported the discovery of carbohydrates in Ordovician to Devonian shales of Indiana, Kentucky, Virginia, West Virginia, Pennsylvanian, Tennessee, New York, and Michigan.

Tang et al. (34) discovered that the major portion of the oxidized Devonian shale kerogen of cored Devonian shale originating near Cottageville, West Virginia, is composed of straight-chain mono- and di-carboxylic acids with large amounts in two series ranging from C_9 to C_{18} and C_6 to C_{16} respectively. Some benzene-substituted carboxylic acids were also detected in the oxidized Devonian shale kerogen. Branched alkanes are more abundant than normal alkanes in this Devonian shale kerogen. By gas chromatography-mass spectrometry (GC-MS) analysis of volatile products formed by stepwise pyrolysis of Appalachian Devonian black shale (Chattanooga shale) of Overton County, Tennessee, and Rowan County, Kentucky, two types of organic matter were found (35). One type shows a predominance of n-alkane and n-alkene products, and the other shows a predominance of aromatic compounds, such as would be expected from the degradation of lignin-type materials. These types of organic matter may suggest that the components were derived from humic material. Leventhal (36) found that stepwise-pyrolysis-gas chromatography of Antrim kerogen produced a wide range of products such as n-alkanes, and n-alkenes, isoprenoids, etc. Pyrolysis products from the shales of the Woodruff Formation and related black shales of the central Great Basin are mainly n-alkanes and alkenes with maxima at n-C_{12} and n-C_{17} (with only small amounts of products with more than 21 carbon atoms) (37). A summary of the identified organic compounds in Paleozoic shales is given in Table II.

Table II. Identified Organic Compounds in Paleozoic Shales

Geological Age	Shale, Location & Formation	Identified Organic Cpds in Shale Bitumen & Kerogen	Reference
Mississippian Mississippian Permian	Woodford shale, Oklahoma Caney shale, Oklahoma Wolfcamp, Texas	All contain paraffins (C_4-C_8, Cyclopentanes, Cyclohexanes	5
Devonian	Antrim shale (N. part of Chattanooga shale), Michigan	Isoprenoids (C_{16}-C_{21}, except C_{17}), Iso-alkane (C_{16}) Cyclohexyl n-alkane (C_{18},C_{19})	6
Devonian	" " "	C_{17} Isoprenoid	27
Devonian	Mt. Union Area, Central Penn: Burket shale Mahantango shale Marcellus shale Newton Hamilton (Onondaga shale)	All contain carbohydrates, amino acids, saturated hydrocarbons, aromatic hydrocarbons, polar compounds, asphaltenes	25
Pennsylvanian	Scurry Co. & Palo Co., Texas Fergus Co., Montana		28
Mississippian	Fergus Co., Montana Chattanooga black shale of Cherokee Co., OK and De Kalb Co., TN, & Kingman Co., KS	All contain n-paraffins of C_{24}-C_{34}	
Mississippian	Woodford shale, Carter Co., Oklahoma		
Devonian	Chattanooga shale, Cherokee Co., Oklahoma	fatty acids (C_{10}-C_{32}), n-paraffins (C_{12}-C_{31})	29-31
Devonian	New Albany shale, Cincinnati Arch, Kentucky	fatty acids (C_9-C_{31}), paraffins (C_{11}-C_{31})	31
Mississippian	Heath shale, Big Snowy Uplift, Montana	fatty acids (C_{10}-C_{32}), paraffins (C_{13}-C_{32})	31
Permian	Kansas Council Grove Group (Speiser shale, Florena shale, Johnson shale, Hughes Creek shale)	hydrocarbons (C_{12}-C_{26}), phytane, pristane, farnasane, steranes	32
Pennsylvanian	Kansas Shawnee Group (Heebner shale, Jackson Park shale, Heumader shale	n-alkane, phytane, pristane, cholestane ($C_{27}H_{48}$), ergostane ($C_{28}H_{50}$), sitostane ($C_{29}H_{52}$)	32

Table II (Cont'd)

Geological Age	Shale, Location & Formation	Identified Organic Cpds in Shale Bitumen & Kerogen	Reference
Pennsylvanian	Kansas Lansing Group - Eudora shale	n-alkane (C_{15}-C_{27}) isoprenoids, steranes, aromatic hydrocarbons	32
Pennsylvanian	Excello shale, Birch Creek Field, Oklahoma	n-fatty acids (C_{12}-C_{22}), isoprenoid acids, 3-4 or 4-5 unsaturated and C_{18} diunsaturated acids	33
Devonian	New Albany shale, Kentucky and Indiana	carbohydrates - 8 sugars, glucuronic acid, glycerol	34
Devonian	Romney Formation, W. VA	carbohydrates - 8 sugars, galacturonic acid, glucuronic acid, glycerol	34
Devonian	Millboro black shale, VA	carbohydrates - 5 sugars	34
Devonian	Antrim black shale, MI	carbohydrates - 7 sugars, galacturonic acid, glucuronic acid, glycerol	34
Devonian	Marcellus black shale, NY	carbohydrates - 5 sugars	34
Devonian Mississippian	Chattanooga shale, Central Tennessee: Upper, Middle & Lower Gassaway, Upper & Lower Dowelltown Maury Formation (TN)	carbohydrates - 7 sugars, glaturonic acid	34
Devonian	Marcellus Formation, PA Mohonoy black shale, Shamokin black shale	carbohydrates - 6 sugars, glycerol	34
Devonian	Mahantango Formation, Huntingdon Co., PA	carbohydrates - 6 sugars	34
Devonian	Marcellus black shale, Newton Hamilton and Mt. Union, Mifflin Co., PA	carbohydrates - 7 sugars	34
Ordovician to Tertiary	Simpson Formation: Marcellus black shale of Pennsylvania	carbohydrates - 5 sugars amino acids (alanine, glycine, valine, glutamic acid, aspartic acid, proline, laucine, cystine, tyrosine)	36

Table II (Cont'd)

Geological Age	Shale, Location & Formation	Identified Organic Cpds in Shale Bitumen & Kerogen	Reference
Mississippian to Cretaceous	Powder River Basin, Wyoming	hydrocarbons	37
Devonian	Devonian shale, Cottageville, W. Virginia	straight-chain mono-carboxylic acids (C_9-C_{18}), dicarboxylic acids (C_6-C_{16}) (all from oxidized kerogen)	38
Devonian	Chattanooga shale, Overton Tennessee & Rowan Co., KY	Pyrolysis products: n-alkane, n-alkene, aromatics	39
Devonian	Woodruff Formation, Central Great Basin	Pyrolysis products: n-alkanes, alkenes (with max C_{12} & C_{17})	41
Devonian	Chattanooga shale, Appalachian Basin	Pvrolysis products: substituted aromatics	41

2.3. Mesozoic shales

The principal Mesozoic shales of the United States are located in the northern parts of the Great Plains. Pierre shale, which is the most widespread shale in this area, was deposited in the Late Cretaceous age. It is found in subsurface in almost all parts of the northern Great Plains (2). Other major Mesozoic shales are scattered in substantial parts of the Rocky Mountains, Colorado Plateau Provinces, and the Easter Margin.

Breger et al. (42) reported that the Pierre shale of the Sharon Spring Member (in parts of Kansas, South Dakota, Nebraska, Wyoming, and Montana) are more organic rich than adjacent members. It contains as much as 8% organic carbon. The average organic content of the Mowry Formation shales, which comprises about 35,000 square miles including the Big Horn and the Wind River Basins, the Natroona Arch area, parts of the Shirley and Hanna Basins, and the west side of the Powder River Basin of Wyoming, is reported to be about 1 to 3% (43). The average content of extractable organic matter in the Cretaceous Mowry shale is about 400 ppm (0.04%). This is found in the northwestern part of Wyoming, and the extractable organic content increases southeastwardly reaching a value of 2,100 ppm (0.21%) in the Douglas area (44). Merewether et al. (45, 46) revealed that the average organic carbon content of lower upper Cretaceous shale from the Frontier Formation, Cody shale, Carlile shale, Greenhorn Formation, and Belle Fourche shale from Powder River Basin ranges is from 0.2 to 4.3 wt%. The organic carbon content of Cretaceous, Jurassic, and Triassic shales in the Ellesmerian sequence and Brookian sequence was reported to range from 1 to 4 wt% (26).

Normal fatty acids as well as normal paraffins containing between 12 to 34 carbons were found in two major shale units of the Powder River Basin (Mowry and Thermoplis shales) (29, 49). Normal fatty acids of C_{12} to C_{32} and normal paraffins of C_{13} to C_{35} were also present in shales from Weston County of Wyoming (29). Fan (48) revealed the presence of n-hydrocarbons (C_{13} to C_{32}), fatty acids (C_{13} to C_{33}), n-fatty alcohols (C_{10} to C_{30}), phytane and pristane in Pierre shale of Salt Creek and Red Bird of Wyoming. It is interesting to note that the organic content of shale in these particular areas contain significantly large amounts of C_{22} hydrocarbon (straight- and branched-chain) and C_{22} fatty alcohol. Amino acids, such as arginine, lysine, glutamic acid, etc., (total 18) were also found present in Pierre shale from the Salt Creek and Red Bird of Wyoming (48). Mackenzie et al. (50) identified pristane, steranes (and isomers), hopanes (and isomers), and acylic isoprenoid acids in Cretaceous shales of Wyoming Overthrust Belt, which includes Hilliard shale, Frontier shale, Aspen shale, Bear River shale and Mowry shale. Heavy n-paraffins of C_{23} to C_{34}, fatty acids of C_{14} to C_{34}, and fatty alcohols (normal and isoprenoid) of C_{12} to C_{26} were also reported in Cretaceous shale from the Eagle Ford section in Dallas and Wood

Counties of Texas (30, 51, 52), and the total organic carbon content of this shale is 15% (51).

Published literature related to the organic carbon content and the identified organic compounds in shales formed during the Mesozoic era is summarized in Table III.

2.4. Cenozoic shales

Most Cenozoic shales in the continent of the United States are located in the Gulf Coast, basins and platforms within the Rocky Mountains, the Colorado Plateau, the Great Valley of California, the Great Basin, and parts of the Pacific Northwest. The most studied shale in this geological era is the Green River Formation shale which was deposited during the Eocene period 40 to 60 million years ago. Due to its large organic content and enormous potential as an energy resource, considerable research has been done on this shale during the past few decades, and there is a large amount of literature concerning this shale. It is impossible to reference all of them in this report. Therefore, whenever possible, reference about this particular shale is made only to major contributions and to review papers.

The Green River Formation is restricted in the Colorado Plateau to the Uinta Basin of northeastern Utah and the Piceance Basin of northwestern Colorado; the unit is also present in the Green River and Washakie Basins of southwestern Wyoming (Rocky Mountains Province) (2).

The organic-rich Green River shale contains varying amounts of bitumen (soluble in benzene, n-hexane, and other common organic solvents) and varying amounts of kerogen (insoluble in organic solvents) (53, 54). Average values for components of the soluble extract in benzene from Piceance Creek Basin in Colorado, Green River Basin in Wyoming, and Uinta Basin in Utah are as follows: n-alkanes 3.4 - 3.9 wt%; branched and cyclic alkanes, 23.6 - 30.6 wt%; aromatic, 2.7 - 3.3 wt%; resins, 54.4 - 57.4 wt%; pentane insoluble 9.0 - 12.5 wt% (52). The polar portion of the soluble (in benzene) fraction is contained within the resins and pentane insolubles (55).

The Green River shale, especially that in the Piceance Basin of Colorado, has been studied extensively. Several research groups reported the isolation and identification of hydrocarbons from the Piceance Basin shale bitumen such as n-paraffins of C_{12} to C_{34} (28, 29, 56-59), isoprenoid hydrocarbons of C_{13} to C_{29} (8, 54, 59, 60) C_{30} alkene (57), cycloalkanes of C_nH_{2n} (C_{25}-C_{40}), C_nH_{2n-2} (C_{14}-C_{40}), C_nH_{2n-4} (C_{20}-C_{25}), C_nH_{2n-6} (C_{23}-C_{30}), and C_nH_{2n-8} (C_{24}-C_{32}) (61), and aromatic hydrocarbons, which include alkylbenzenes, alkyltetralins and monoaromatic alkenes (62). Other organic compounds separated from the Piceance Basin shale bitumen are aresteranes (8, 57, 61, 63, 64), triterpanes (8, 57, 61, 64, 65), steroids (65), hopanes (66),

Table III. Organic Carbon Content and the Identified Organic Compounds in Mesozoic Shales

Geological Age	Shale, Location & Formation	Average Org Content	Identified Org Cpds	Reference
Cretaceous	Frontier shale, Wyoming	1.99 wt%	Paraffins(C_4-C_8), Cyclopentanes, Cyclohexanes	5
Triassic	Chinle red shale, Utah	0.02 wt%	Paraffins(C_4-C_8), Cyclopentanes, Cyclohexanes	5
Cretaceous	Pierre shale, Sharon Spring Member	8 %		42
Cretaceous	Mowry Formation shale, Wyoming	1-3 %	n-paraffins (C_{12}-C_{34})	29,43,47
	" " "		Aliphatic acids (C_{14}-C_{30})	31
Cretaceous	Frontier Formation shale (Cody shale, Carlile shale Greenhorn Formation shale, Bell Fourche shale), Powder River Basin, Wyoming	0.2-4.3 wt%		45,46
Cretaceous	Colville Group shale, Alaska	1-2 wt%		
	Pebbe shale, Alaska	2-4		26
	Torok Formation shale, Alaska	1-2		
Jurassic	Kingak shale, Alaska			
Cretaceous	Cretaceous shale, Weston Co., Wyoming		n-fatty acids (C_{12}-C_{32}), n-paraffins(C_{13}-C_{35})	29,31
Cretaceous	Pierre shale, Salt Creek and Red Bird, Wyoming		n-paraffins (C_{13}-C_{32}), n-fatty acids (C_{13}-C_{33}), n-fatty alcohols (C_{10}-C_{30}), phytane, pristane, branched C_{22} hydrocarbon	48
Cretaceous	Pierre shale, Salt Creek and Red Bird, Wyoming		18 amino acids	49

Table III (Cont'd)

Geological Age	Shale, Location & Formation	Average Org Content	Identified Org Cpds	Reference
Cretaceous	Cretaceous shales, Wyoming Overthrust Belt		Pristane, steranes (C_{29} isomers), hopanes (C_{22} isomers), acylic isoprenoid acids, n-paraffins(C_{23}-C_{34}), fatty acids(C_{14}-C_{30})	50
Cretaceous	Eagle Ford shale, Dallas, Wood, Rusk, Denten Counties, Texas	15%	n-paraffins (C_{23}-C_{34}), fatty acids (C_{14}-C_{30}), fatty alcohols, isoprenoid alcohols	28,31 51,52
Cretaceous	Woodbine and Taylor shales, Rusk Co., Denton Co, Dallas Co., Texas		n-paraffins (C_{24}-C_{34})	28
Cretaceous	Colorado shale, Fergus Co., Montana		n-paraffins (C_{24}-C_{34})	28
Jurassic	Morrison shale, Fergus Co., Montana		n-paraffins (C_{24}-C_{34})	28

perhydro-carotenes (61, 67), and chloestane (65). Porphyrin, a class of compounds in which four pyrrole rings are united by bridge carbons to form a conjugated, macrocyclic structure is also found in the Piceance Basin shale (68, 69). The average molecular weight of porphyrin in shale of this area is ca. 508.

Fatty acids are another organic compound series that have been studied extensively in the shale bitumen and kerogen of this area (Piceance Basin of Colorado) to elucidate the relationships of these acids with hydrocarbons isolated from this formation. A homologous series of straight-chain carboxylic acids from C_{10} to C_{34} was reported by several research groups (29, 70-73). Besides the n-fatty, several series of isoprenoid acids (59, 60, 72-74, 77), cyclic acids (73), keto acids (73), aromatic acids (73, 75), and dicarboxylic acids (71, 73, 75) also have been reported. In addition, several series of alcohols, such as normal fatty alcohols of C_{12} to C_{26}, isoprenoid alcohols of C_{13} to C_{30} (51, 76-79), saturated triterpenoid alcohols of C_{27} to C_{30} (77), tetracyclic alcohols of C_{27} to C_{29} (79), and C_{30} pentacyclic alcohols of C_{27} to C_{29} (79), and C_{30} pentacyclic alcohols (79) are also present in the Piceance Basin shale bitumen.

The Uinta Basin of Utah contains some of the world's richest oil shales. The vast sediment thicknesses of the Wasatch, Green River, and Uinta Formations represent an enormous accumulation of sedimentary organic matter (80). Tissot et al. (81), Douglas et al. (82), Robinson (79), and Dorsselaer et al. (83) reported the isolation and identification of n-alkanes, cycloalkanes, aromatic hydrocarbons, isoprenoid hydrocarbons, steranes, hopanes, triterpanes, terpanes, and perhydro- -carotene from the shale bitumen of Uinta Basin. n-Alkanes, branched and cyclic alkanes, aromatics, steranes, pentacyclic triterpanes, perhydro- -carotene, polar compounds (including acids, alcohols, etc.) were also found in the Green River shale bitumen of Green River Basin, Wyoming (79, 73). Humic acids, an interesting marker of evolution during the immature stage (84), and carbohydrates (36) were also found in the Green River Formation shale.

Other shales from this geological time period that have been studied are Antelope (Miocene age) and Kreyenhagen (Eocene age) of California (85). Hopanes, mortanes, terpanes and steranes were separated from these shale bitumens.

The kerogen fraction of the Green River Formation is a polymer matrix, highly cross-linked by saturated hydrocarbons containing some aromatic nuclei, heteroatoms and many long isoprenoid and normal side chains (54). This type of kerogen is classified as Type I kerogen (1), which has a high initial H/C and low initial O/C ratios, and comprises much lipid material, particularly aliphatic chains. Robinson (79) reveals that in general, Green River kerogen appears to be composed of about 5-10% long-chain alkanes, 20-25% cyclic alkanes,

10-15% aromatic structures, and 45-60% saturated heterocyclic structures. Young and Yen (86, 87) suggested that the kerogen in the Mahogany zone contains 20-40% straight-chain aliphatic structures and that the kerogen matrix forms a three-dimensional network of nonchain clusters interconnected by long polymethylene crosslinks. Based on elemental analysis by Smith (88), the empirical formula for the Green River Formation kerogen at the Mahogany zone of Piceance Creek Basin may be $C_{215}H_{330}O_{12}N_5S$ with a minimum formula weight of ca. 3200. According to Robinson (53), the atomic H/C ratio of this kerogen is 1.53, which is comparable with the kerogen of the Green River Formation at the Uinta Basin of Utah (79, 81) and at the Green River Basin of Wyoming (79). However, studies by Robinson and Cook (89, 90) of cores taken from the Piceance Creek Basin of Colorado, the Green River Basin of Wyoming, and the Uinta Basin of Utah showed that there were significant differences in the properties of kerogen taken from different stratigraphic and geographic locations with the Green River Formation.

As mentioned above, shale kerogen can be degraded by chemical methods to lower-molecular-weight material to study the structures of this complex material. General methods which have been used to investigate the Green River shale kerogen are:)1) complete oxidation (53), (2) controlled step oxidation (53, 73, 91-97), (3) reduction (53, 98-102), hydrolysis (53, 98), and (5) pyrolysis (55, 57, 81, 102, 103). Among these methods, controlled oxidation and slow pyrolysis of kerogen have been widely used to yield small molecules which can be separated and identified by analytical methods. Organic compounds found in the oxidation and hydrolysis products of Green River Formation kerogen are mostly carboxylic acids, which occupy about 83% of the oxidation products. These carboxylic acids are classified as follows:

1) normal acids (C_5 - C_{36}) (70, 73, 96, 105),
2) isoprenoid acids (C_5 - C_{26}) (73, 95, 96, 106),
3) dicarboxylic acids (C_4 - C_{25}) (73, 96, 105),
4) cyclic acids (C_5 - C_{28}) (73, 105),
5) tetracyclic acids (C_{18} - C_{32}) (73),
6) pentacyclic acids (C_{26} - C_{34}) (73, 105),
7) aromatic acids (C_7 - C_{19}) (73, 105),
8) dicarboxylic aromatic acids (C_8 - C_{13}) (73),
9) tricarboxylic aromatic acids (C_9 - C_{12}) (73),
10) tricarboxylic acids (C_7 - C_{16}) (96),
11) tetracarboxylic acids (C_9 - C_{14}) (96),
12) keto acids (C_4 - C_{17}) (73, 105)

Other organic compound series found in the oxidation and hydrolysis products of kerogen are ketones (C_{13} - C_{18}) (97) and amino acids (107).

Kerogen can be also converted to soluble products at temperatures between 150 to 350°C. The soluble products obtained by thermal

degradation contain many of the structures present in the original kerogen. Cummins et al. (55) on heating the Green River shale kerogen (sample from a place near Rifle, Colorado) at 150 to 350°C for 0.5 to 360 days found a significant increase of oil from degradation of kerogen occurred between the temperature range of 250 to 350°C. The thermal product contains the largest amount of polar compounds at 150 to 200°C, the largest amount of branched and cyclic alkanes at 250°C, and the largest amount of n-alkanes at 350°C. The soluble thermal products become more aromatic as the temperature increases from 150 to 350°C. All of the branched and cyclic alkanes contained structures similar to the chain isoprenoid, sterane, and pentcyclic triterpane compounds found in the natural bitumen. The aromatic hydrocarbons may contain alkyltetralin structures similar to the alkyltetralin compounds isolated and identified in the benzene-soluble bitumen from the Green River shale. This may be an indication that both the insoluble kerogen and the soluble bitumen were formed from some of the same source materials. Some other research groups have indeed found that on pyrolysis of the Green River Formation kerogen, besides gas products (including methane, ethane, propanes, butanes, pentanes, CO, CO_2, N_2, H_2, and hydrogen sulfide), significant quantities of identifiable hydrocarbons, cyclohydrocarbons, steranes, triterpanes, cholestane, ergostane and stigmastane were also found (57, 81, 85, 103).

Steranes, terpanes, hopanes, and moretanes, those which can survive in the pyrolyzates, were also present in the kerogen pyrolyzate of Kreyenhagen (Eocene) and Antelope (Miocene) shales of California. Evidence indicates that biological markers such as steranes and terpanes are chemically bonded in some manner to form the complex kerogen.

Organic compounds which have been identified from either shale bitumens (Table IV) or shale kerogens (Table V) of the Cenozoic era are summarized in Tables IV and V.

Table IV. Identified Organic Compounds in Bitumens of Cenozoic Shales

Geological Age	Shale, Location & Formation	Identified Org Cpds	Reference
Eocene	Green River shale	n-paraffins(C_{13}-C_{33})	56
	Mahogany-Zone Bed	n-paraffins(C_{24}-C_{34})	27
	Rifle, Colorado	Isoprenoids(C_{13}-C_{21})	8,56
		Cycloalkanes:	61
		C_nH_{2n}(C_{25}-C_{40})	
		C_nH_{2n-2}(C_{14}-C_{40})	
		C_nH_{2n-4}(C_{20}-C_{25})	
		C_nH_{2n-6}(C_{23}-C_{30})	
		C_nH_{2n-8}(C_{24}-C_{32})	
		Aromatic Hydrocarbons (alklybenzenes, alkyltetralines,	62
		monoaromatic alkenes:	
		C_nH_{2n-6}(C_{12}-C_{25})	
		C_nH_{2n-8}(C_{12}-C_{27})	
		C_nH_{2n-10}(C_{15}-C_{32})	
		C_nH_{2n-12}(C_{17}-C_{31})	
		C_nH_{2n-14}(C_{18}-C_{29})	
		Acyclic isoprenoid alcohols (C_{13}-C_{20}), normal & isoprenoid	108
		Alcohols (C_{12}-C_{26})	51
		Stanols (C_{27}-C_{30})	76
		Saturated triterpenoid alcohols (C_{27}-C_{30})	77
		C_{27},C_{28},C_{29} steranes, C_{30}-pentacyclic triterpane	8
		tetracyclic steranes (C_{27}-C_{28})	63

Table IV (Cont'd)

Geological Age	Shale, Location & Formation	Identified Org Cpds	Reference
Eocene (Cont'd)	Green River shale Mahogany-Zone Bed Rifle, Colorado	porphyrins, triterpanes, steranes	57,69
		porphrin (complex with iron)	68
		perhydro-β-carotene (C_{40}-C_{78})	67
		fatty acids (saturated C_{14},C_{16},C_{18})	70
		isoprenoid acids (C_{14}-C_{18}), n-fatty acids (C_{14}-C_{18})	109
Eocene	Green River shale	n-paraffins(C_{12}-C_{33})	58
	Sulfur Creek, Colorado	n-paraffins(C_{11}-C_{17})	60
	(∿30 mi from Rifle, Colorado)	isoprenoids(C_{15}-C_{20})	58-60
		isoprenoid acids (C_{17}-C_{22})	74
		isoprenoid acids (C_{14}-C_{21})	72
		isoprenoid acids (C_{16}-C_{19})	59
		acyclic C_{19},C_{29} isoprenoid acids	60
		n-fatty acids(C_{10}-C_{30})	72
Eocene	Green River shale Grand Valley, Colorado	branched paraffins (C_{20}-C_{29})	61

Table IV (Cont'd)

Geological Age	Shale, Location & Formation	Identified Org Cpds	Reference
Eocene (Cont'd)	Green River shale Grand Valley Colorado	C_{27}-C_{29} steranes, triterpanes	64
		hopane(17α(H)-hopane)	66
		cholestane, pentacyclic triterpenes	65
		perhydro-β-carotenes pentacyclic triterpanes tetracyclic tris-homoditerpanes, tricyclic terpanes, tetracyclic steranes. 5-α-and 5-β-cholestane, 5-α- and 5-β-ergostane, 5-α- and 5-β-stigmastane, 5-α-pregnane	61,110, 111
Eocane	Green River shale, Mahogany Zone, Garfied Co., Colorado	n-paraffins(C_{12}-C_{33}), n-fatty acids(C_{10}-C_{33})	29
Eocene	Green River shale, Parachute Creek, Colorado (8 mi from Grand Valley, Colorado)	normal acids(C_5-C_{20}) branched acids(C_9-C_{10}) cyclic acids(C_5-C_{16}) keto acids(C_5-C_{15}) dicarboxylic acids(C_8-C_{18}) Aromatic Acids: phenyl- (C_7-C_{17}) naphthyl- (C_{11}-C_{17}) $C_nH_{2n-10}O_2$(C_{10}-C_{17})	73

Table IV (Cont'd)

Geological Age	Shale, Location & Formation	Identified Org Cpds	Reference
Eocene (Cont'd)	Green River shale, Parachute Creek, Colorado (8 mi from Grand Valley, Colorado)	Aromatic Acids: mono-, di-, trimethyl-benzoic acids mono-,di-,trimethyl-substituted phenyl propanoic acid, mono-, dimethyl substutited phenyl butanoic acid, indanoic acid, tetra-hydronaphthoic aicd, naphthoic acid	75
		isoprenoid acids (C_9-C_{10}), dicar-boxylic acids(C_{12}-C_{19}) n-fatty acids(C_7-C_{12})	71
Eocene	Green River shale, Colorado	C_{30} alkene, alkanes, aromatics	57
		n-fatty alcohols (C_{16}-C_{26}), isoprenoid alcohols	112
Eocene	Green River shale,	carbohydrates	36
	Piceance Basin, Colorado	Amino acids	113,114
Eocene	Green River shale	n-alkane(C_{20}-C_{40})	82
	Uinta Basin, Utah	isoprenoids, hopanes (C_{30}-C_{35}	79

Table IV (Cont'd)

Geological Age	Shale, Location & Formation	Identified Org Cpds	Reference
Eocene (Cont'd)	Green River shale Uinta Basin, Utah	except C_{31}) Steranes, pentacyclic triterpanes, perhydro-β-carotene, cycloalkanes, aromatics, alkanes, steranes, triterpanes	81
Eocene	Green River shale, Laney, Wikins Peak, Tipton Zones, Wyoming	n-alkane, isoprenoids, steranes, pentacyclic triterpanes, perhydro-β-carotene, hopane (C_{27}-C_{35})	79 83
Eocene	Kreyenhagen shale, Kreyenhagen, California	hopane, moretanes, terpanes, steranes	85
Miocene	Antelope shale, Antelope, California	hopane, moretanes, terpanes, steranes	85

Table V. Identified Organic Compounds in Kerogens of Cenozoic Shales

Geological Age	Shale, Location & Formation	Identified Org Cpds	Reference
Eocene	Green River shale, Mahogany Ledge (near Rifle, Colorado)	oxidation products:	96
		isoprenoid acids (C_{14}-C_{17})	
		monocarboxylic acids (C_9-C_{32})	
		dicarboxylic acids (C_6-C_{17}, C_{29})	
		tricarboxylic acids (C_7-C_{16})	
		tetracarboxylic acids (C_9-C_{14})	
		oxidation products:	70,115
		fatty acids (C_{14},C_{16},C_{18})	
Eocene	Green River shale, Sulfur Creek, Colorado	hydrolysis products:	106
		isoprenoid acids (phytanic, pristanic, farnesanic acids, trimethyltridecanoic acids)	
Eocene	Green River shale, Parachute Creek, Colorado	oxidation products:	73,105
		normal acids (C_5-C_{36})	
		branched-chain acids (C_5-C_{26})	
		cyclic acids (C_5-C_{28})	
		tetracyclic acids (C_{18}-C_{32})	

Table V (Cont'd)

Geological Age	Shale, Location & Formation	Identified Org Cpds	Reference
Eocene (Cont'd)	Green River shale Parachute Creek, Colorado	pentacyclic acids (C_{18}-C_{32})	
		aromatic acids (C_7-C_{19})	
		dicarboxylic acids (C_4-C_{25})	
		tricarboxylic aromatic acids (C_9-C_{12})	
		mono-unsaturated/cyclic acids (C_5-C_{18})	
		oxidation products: isopranoid acids (C_{14}-C_{22})	95
Eocene	Green River shale Uinta Basin, Utah	thermal products: alkanes, isoprenoid hydrocarbons, cyclic-alkanes	81
Eocene	Green River shale	thermal products: volatile organics, alkanes, alkenes, branched-cyclic alkanes, isoprenoids	57
		gammacerane, 5-α- and 5-β-steranes (C_{27}-C_{29}) cholestane, ergostane, stigmastane, terpanes	85,103

Table V (Cont'd)

Geological Age	Shale, Location & Formation	Identified Org Cpds		Reference
Eocene	Green River shale	oxidation products: ketones (major), isoprenoidal ketones, (C_{13}-C_{18})		97
		hydrolysis products: 12 neutral and acidic amino acids		107
Eocene	Kreyenhagen shale Kreyenhagen, California	steranes terpanes hopanes moretanes	comparable with those in bitumen	85
Miocene	Antelope shale, Antelope, California	hopanes moretanes	comparable with with those in bitumen	85

3. SUMMARY

1. The organic compounds found in shales are very difficult to isolate and identify. Up to date, only a small fraction of the organic compounds present in shales have been identified; most of them are still unknown.

2. The most studied shale is the Green River shale of the Cenozoic era, followed by the Pierre shale of Mesozoic era and the Devonian black shale of Paleozoic era. Very few reports discuss Precambrian era shales.

3. Organic compounds which have been identified from shales are as follows:

   (a) From bitumens

   Hydrocarbons - n-alkanes, isoprenoids, alkenes, cycloalkanes, aromatic hydrocarbons.
   Acids - n-fatty acids, isoprenoid acids, cyclic acids, aromatic acids, amino acids.
   Alcohols - n-fatty alcohols, isoprenoid alcohols, triterpenoid alcohols, tetracyclic alcohols, pentacyclic alcohols.
   Steroids
   Terpenoids
   Carbohydrates
   Porphyrins

   (b) From kerogens

   (I) From non-degradate kerogens
   Steroids
   Terpenoids

   (II) From degradate kerogens
   Hydrocarbons - n-alkanes, isoprenoids, alkenes, cyclicalkanes.
   Acids - n-fatty acids, isoprenoid acids, cyclic acids, aromatic acids, amino acids.
   Ketones
   Steranes
   Triterpanes

4. CONCLUSIONS

The motivation for the investigations concerning the organic content of shales has been, for the most part, related to the extraction of the energy content of the shales and not related to their potential use as a host for a high level nuclear waste repository. Therefore, there is little specific information concerning the possible interaction of radionuclides with the organic compounds. Because many elements such as technetium, uranium, and neptunium have fairly insoluble oxides in their lower valence states, the reducing potential of the organic compounds would be of especial interest. Also, information on specific interactions with nuclides to form insoluble compounds other than oxides in any valence state would be useful. It is evident that considerable study is needed on the nature of the organic compounds and groups in the shales that could possibly interact with the radionuclides present in nuclear waste. This review of the literature is intended to summarize what is known of the identity of the organic compounds present in shales, but it is also intended to be the necessary first step in the study of the interactions of the nuclides with the organic content of the shales.

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