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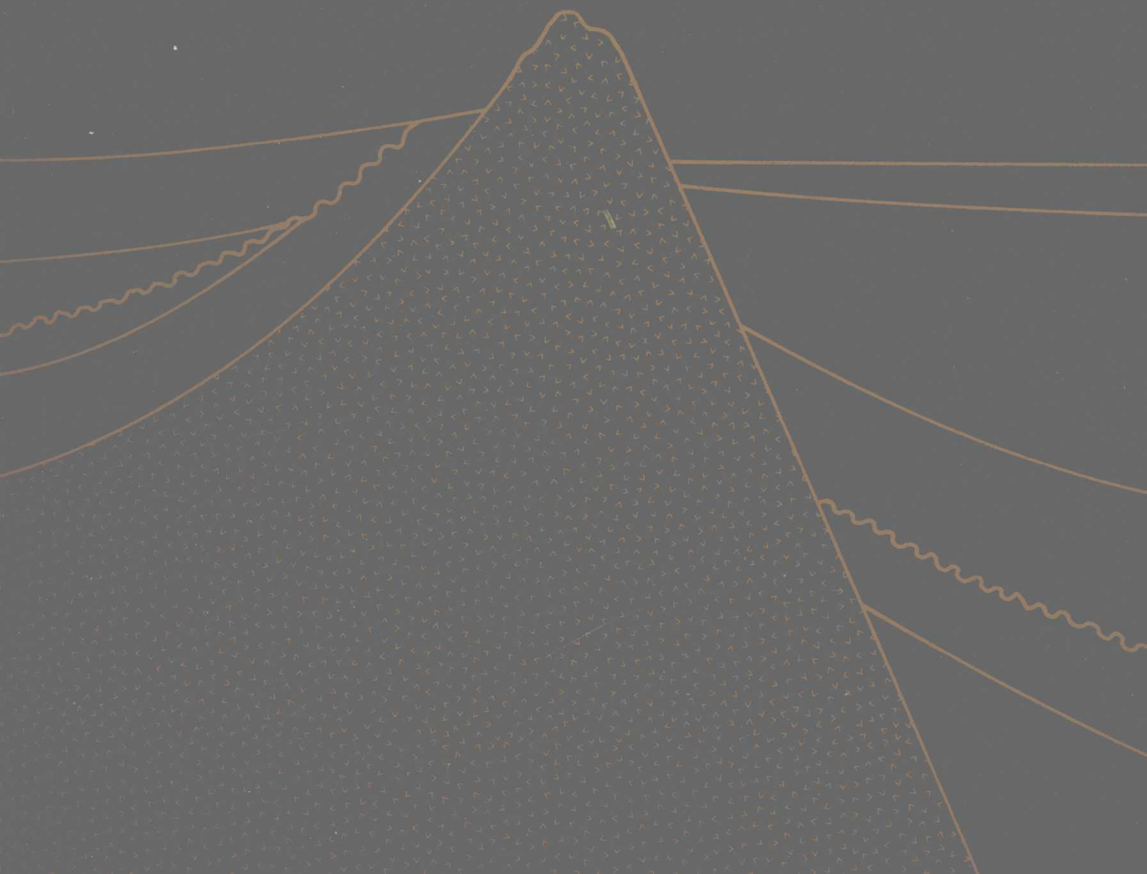

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To those pioneering scientists who were in the Geological Research Section of the former Carter Research Laboratory of Tulsa, Oklahoma, in the late 1940s and early 1950s.

Foreword

The continually rising standards of petroleum geoscience and oil search require an ever greater knowledge of the fundamental nature of petroleum, its origin, and its behavior in the rocks of the earth's crust. In the early stages of the petroleum era, most oil men were not much concerned about the *how, why,* and *when* of oil and gas; all they cared to know was *where.* Those years are gone, and it is now more and more recognized that the how, why, and when of petroleum are critical keys to where it should be sought.

Someone has said that we will never know the answers to the problems of the origin, migration, accumulation, and preservation of petroleum until the last drop is found. Perhaps this is so; but equally certain is it that we will not come close to finding this last drop until we know more of these answers.

With all the current talk of oil shortages and "running out of oil and gas," we still probably have not used up half of the earth's petroleum accumulations, and it is even questionable whether we have yet discovered half of them. It is a fact, however, that we have found the easiest, most accessible, and least expensive portion, and that the remainder will only be found and recovered through more sophisticated methods than those of the past. And these methods will in a large part be based on better knowledge of the chemical and physical properties of petroleum and the principles of chemistry and physics that control its origin, its movements, its concentration into commercial deposits, its preservation, and its ultimate recovery from the rocks. Moreover, this knowledge will benefit us not only as regards conventional oil and gas deposits but also with respect to alternative hydrocarbon sources such as asphalt sands, oil shales, coal gas, gas-charged waters, and the like.

It is therefore a great boon to petroleum geologists, geochemists, geophysicists, engineers, teachers, and all others who are concerned with the finding and recovery of petroleum that one of our most widely experienced and greatest contributors to petroleum geochemistry has taken time from his busy career to put together this monumental volume, *Petroleum Geochemistry and Geology.*

John M. Hunt received his Ph.D. in chemistry from Pennsylvania State University in 1946 and, after a year on the faculty there, spent the next sixteen years at the Standard Oil Company of New Jersey (now Exxon) exploration research laboratory in Tulsa, Oklahoma, where from 1956 to 1963 he was Head of Geochemical Research. In this position, he was brought into close contact with the manifold petroleum research and exploration activities of a major petroleum company. In 1964, he left industry to become Chairman of the Department of Chemistry and Geology at Woods Hole Oceanographic Institution, 1964–1967, and Chairman of the Department of Chemistry, 1967–1974. He is presently a Senior Scientist at Woods Hole.

Throughout his life career, Dr. Hunt has been vitally concerned with research and the application of research on the origin, migration, and emplacement of petroleum. He has published numerous articles, alone and in collaboration with others, many of which have marked outstanding advances in our knowledge of this topic. Among these are his studies of the composition of crude oil in relation to stratigraphy in Wyoming (1953), Hunt and Jamieson on source rocks of petroleum (1956), Kidwell and Hunt on the migration of oil in recent sediments in Venezuela (1958), Forsman and Hunt on the kerogen in sedimentary rocks (1958), Dunton and Hunt on the distribution of low-molecular-weight hydrocarbons in Recent and ancient sediments (1962), the composition and origin of Uinta Basin bitumens (1963), the origin of petroleum in carbonate rocks (1967), Dickey and Hunt on prospecting for stratigraphic traps (1972), and his studies of light hydrocarbons in deep sea drilling samples (1974–1978).

Dr. Hunt's professional career with Exxon and at Woods Hole is moreover ornamented by numerous excursions into fringe activities to both. He was a Distinguished Lecturer of the American Association of Petroleum Geologists (AAPG) in 1964 and has been a Lecturer on their Continuing Education Program since it started. He has been an Associate Editor of the Bulletin of the AAPG since 1966. He was Chairman of the JOIDES Advisory Panel on Organic Geochemistry for many years and is currently a member of it and of the JOIDES Panel on Passive Margins. He was Chief Scientist of a Red Sea expedition in 1966 and a Black Sea expedition in 1969, the results of the latter being published in AAPG Memoir No. 20. He has lectured on geochemistry in various countries all over the world, and his works in this field are among those from this country frequently quoted in foreign publications.

The scope of the book is immense, and it is truly a happy blend of chemistry and geology as related to petroleum. Following an introductory section (Part I) on carbon and the composition of petroleum, Part II of the book consists of three extensive chapters on how oil forms, how gas forms, and how they both migrate and accumulate. Part III is a two-chapter discussion of source and reservoir rocks. Part IV, titled "Applications," deals with seeps and surface prospecting, subsurface prospecting, crude oil correlation, and prospect evaluation. Abundant tables and figures, chapter summaries, and copious literature references at the end of the book add greatly to the clarity and usefulness of the work.

The history of scientific progress in exploration for petroleum is replete with examples of new approaches and new techniques that were slow to catch on at first but that, once accepted, were carried even too far in the enthusiasm that attended their early successes. The anticlinal theory, once established, long dominated exploration to the exclusion of many nonanticlinal trap prospects that we now know exist. Micropaleontology, heavy minerals, the electrical log, the reflection seismograph, the air-borne magnetometer, clay–mineral transformations, the stratigraphic trap, the new global tectonics, the bright spot, the thermal window—all are examples of worthy and once new concepts that have played a very helpful role in petroleum exploration, and continue to do so, but in the flush of victory have often been carried too far. Organic geochemistry is relatively young as regards widespread application to petroleum exploration, but its contribution has already been phenomenal. However, it too must be used with discretion and understanding, or we may run the risk of prejudicing its most effective utilization.

In the careful reading of Dr. Hunt's book, I think one cannot help but realize the variety and complexity of the problems involved in the geochemical approach, the uncertainties and unknowns that still remain, and the differences of opinion that exist. If we are to get the most in exploration results out of the great potential contributions of organic geochemistry, we need the benefit of the experience, learning, and stimulating views of several leaders in this field, each of whom may have somewhat different backgrounds of geochemical experience. Moreover, geochemistry must also be melded and integrated into proper balance, as Dr. Hunt has done, with the contributions of geology, geophysics, and other branches of geoscience, each of which plays its own important role in exploration for petroleum.

I trust that all who are interested in petroleum—the second most abundant fluid in the earth's crust after water—whether for the sake of pure science or for commercial exploration, whether in academia or as professional, practicing explorationists, will take occasion to read, study, and ponder this outstanding volume.

January 1979

Hollis D. Hedberg
Professor of Geology (Emeritus)
Princeton University

Preface

This book was written for students who have had the basic courses in geology and chemistry and also for oil company operating personnel who are interested in the application of geochemistry to petroleum exploration. It is intended to be used both as a text and as a reference book. It discusses both the geochemistry and the geology of petroleum, but the emphasis is on the former.

Thirty years ago, petroleum geochemistry was limited to a few studies by major oil companies on such subjects as surface prospecting, crude oil correlation, and source rock identification. Today, it is a highly diversified applied science with a variety of geochemical concepts and techniques playing an important role in exploration decisions. The objective of this book is to explain the basic principles of petroleum geochemistry and to show how this information can be effectively integrated with geology and geophysics in the search for oil and gas.

The outline of this book and the scope of subjects is written to be easily understood by the geologist as well as by the chemist. Each geochemical concept, such as carbon isotopes, is explained in detail prior to discussions on its application. The composition and uses of petroleum are presented at the beginning of the book, so that readers will fully understand the subject with which they are dealing.

There is a worldwide trend toward the simplification of measurement. The International System of Units (SI), sometimes referred to as the *metric system*, has been adopted by over 30 countries and is destined to become universal in science and commerce. Both SI and English units of measurement are given in this book (with round numbers given first), so that the reader may become accustomed to the SI system. Some conversion factors for SI and English units are given in the Appendix.

This book evolved from notes used in continuing education courses given to exploration operating personnel at industrial and university seminars. I have participated in such courses since the early 1960s, when the Jersey Production Research Company (formerly Carter Research Laboratory) of Tulsa, Oklahoma, held a school for the worldwide affiliates of Exxon. The late A. I. Levorsen, who was one of the outstanding speakers on our early faculty, first suggested that I write this book. I also was encouraged by the comments of students at courses given in major cities of the United States, Canada, South America, Europe, Africa, and the Middle East. In most of the courses, I kept notes on the frequently asked questions, and these have been answered here in detail, insofar as possible. I also was able to include some anecdotes from my visits to field operations in the United States, Canada, Venezuela, and the Soviet Union.

Today, petroleum geochemistry is a rapidly changing field. This book will provide a background for understanding the basic concepts and principles, but readers are encouraged to watch for new developments through the literature and continuing education courses. The literature on petroleum geochemistry is increasing so fast that I was not able to quote all the important papers in this field. I do want to thank my many friends in geochemistry who sent me preprints of their papers prior to publication and thereby enabled me to quote some recent references.

I am particularly grateful to the many reviewers who generously provided their time and expertise. Hollis Hedberg and James Gilluly were the geologists who made detailed comments on the entire manuscript. Jean Whelan reviewed all of the chemistry, and Brian Hitchon commented on the geochemistry. Chapter 6, on migration, was reviewed by Philip Low, Parke Dickey, Peter Gretener, and Gerard Lijmbach, who also reviewed Chapter 5.

Others who provided valuable comments on parts of the manuscript were A. O. Woodford, Thane McCulloh, T. P. Goldstein, Oliver Zafiriou, and K. O. Emery.

I am also grateful to my wife, Phyllis Laking, who handled references, permission letters, indexing, and many other time-consuming jobs. Her experience in previously publishing her own book, *The Black Sea—A Bibliography* (Woods Hole Oceanographic Institution, 1974) was valuable in handling this text.

Special thanks go to Sharon Callahan and Julie Kertyzak, who listened to endless numbers of tapes while typing the manuscript, and to Christine Johnson, who typed some of the early drafts.

January 1979 John M. Hunt

Abbreviations Used in Text

Å	angstrom (1×10^{-10}m)
°API	degrees API gravity
Ar	aromatic
ASTM	American Society for Testing and Materials
bbl	barrel
C_1	methane
C_2	ethane
C_{2+}	ethane, propane, butanes, and pentanes
C_3	propane
C_4	butanes
C_7	heptanes
C_4–C_7	butanes, pentanes, hexanes, and heptanes
C_{11+}	all hydrocarbons containing 11 or more carbon atoms
C_{15+}	all hydrocarbons containing 15 or more carbon atoms
^{12}C	stable isotope of carbon with an atomic mass of 12
^{13}C	stable isotope of carbon with an atomic mass of 13
C_{org} (or C_o, or C_T)	total organic carbon
C_{eff}	effective carbon
C_R	carbon residue (nonvolatile organic carbon)
CI	correlation index
cm	centimeter
COST	Coastal Offshore Stratigraphic Test
CPI	carbon preference index
d.a.f.	dry, ash free

DSDP	Deep Sea Drilling Project
DST	drill-stem test
E_a	activation energy
Eh	redox potential—a measure of the oxidizing or reducing intensity of the environment
EPR (ESR)	electron paramagnetic spin resonance
FID	flame ionization detector
G	specific gravity
GC	gas chromatography
GCMS	gas chromatography–mass spectrometry
GOR	gas–oil ratio
GPC	gel permeation chromatography
HC	hydrocarbon
IPOD	International Program of Ocean Drilling
IR	infrared
JOIDES	Joint Oceanographic Institutions for Deep Earth Sampling
kcal	1,000 calories
kHz	kilohertz (1,000 cycles/sec frequency)
kPa	kilopascal
LNG	liquefied natural gas (methane, ethane)
LPG	liquefied petroleum gas (propane, butanes, pentanes)
ls	limestone
MCF	thousand cubic feet
md	millidarcy
mg	milligram
μg	microgram
mi	mile
ml	milliliter
mm	millimeter
MP	melting point
MPa	megapascal
MT	metric ton (Mg, megagram in SI units)
MW	molecular weight
N	naphthene
NBS	National Bureau of Standards
n–d–M	refractive index–density–molecular weight
ng	nanogram
nm	nanometer
NMR	nuclear magnetic resonance
NSO	nitrogen, sulfur, oxygen

OCS	Outer Continental Shelf
OEP	odd–even predominance
OM	organic matter
P	paraffin
Pa	pascal
PAH	polycyclic aromatic hydrocarbon
PDB	Peedee belemnite (carbon isotope standard)
PF	pyrolysis–fluorescence
pH	the negative logarithm of the hydrogen ion concentration; a measure of the acidity or alkalinity of a solution (acids, less than 7; bases, more than 7)
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch
psia	pounds per square inch absolute
PVT	pressure–volume–temperature
R_a	reflectance in air
R_o	reflectance in oil immersion
sh	shale
SI	international system of units
ss	sandstone
STP	standard temperature and pressure, 0°C and 760 torr (133.3 Pa)
S.U.	Saybolt Universal (a viscosity measurement in seconds with a Saybolt viscosimeter)
T	temperature
TAI	thermal alteration index
TCD	thermal conductivity detector
TD	total depth
TG	thermal gravimetry
TLC	thin-layer chromatography
UV	ultraviolet
VI	viscosity index
‰	parts per thousand

The Geologic Time Scale

Era	North America			Europe			Approx. Age
	Period	Epoch	Age	Period	Epoch	Age	10^6 Years
Cenozoic	Quaternary	Recent		Neogene	Holocene		
		Pleistocene			Pleistocene		1.6
	Tertiary	Pliocene			Pliocene		5
		Miocene			Miocene		23
		Oligocene	Jacksonian	Paleogene	Oligocene	Chattian	37
		Eocene	Claibornian		Eocene	Bartonian	53
			Wilcoxian				
		Paleocene	Midwayan		Paleocene	Danian	65
Mesozoic	Cretaceous	Upper	Maastrichtian	Cretaceous	Upper	Maastrichtian	
			Senonian			Senonian	
			Turonian			Turonian	
			Cenomanian			Cenomanian	100
		Lower	Albian		Lower	Albian	
			Aptian			Aptian	
			Neocomian			Neocomian	136
	Jurassic	Upper	Kimmeridgian	Jurassic	Upper	Malm	
		Middle	Bathonian		Middle	Dogger	
		Lower	Toarcian		Lower	Lias	190
	Triassic	Upper	Keuper	Triassic	Upper	Keuper	
		Middle	Anisian		Middle	Anisian	
		Lower	Scythian		Lower	Scythian	

							230
Paleozoic	Permian	Upper Lower	Ochoan Guadalupian Leonardian Wolfcampian	Permian	Upper Lower	Zechstein Rotliegendes	
							280
	Pennsylvanian	Upper Middle Lower	Virgillian Missourian Desmoinesian Atokan Morrowan	Carboniferous	Upper	Stephanian Westphalian Namurian	
							325
	Mississippian	Upper Middle Lower	Chesterian Meramecian Osagean Kinderhookian		Lower	Viséan Tournaisian	
							360
	Devonian	Upper Middle Lower	Chautauquan Senecan Erian Onesquethawan Oriskanian Helderbergian	Devonian	Upper Middle Lower	Famennian Frasnian Givetian Couvinian Siegenian Gedinnian	
							400
	Silurian	Upper Middle Lower	Cayugan Niagaran Medinan	Silurian	Upper Lower	Ludlovian Wenlockian Llandoverian Valentian	
							435
	Ordovician	Upper Middle Lower	Cincinnatian Champlainian Canadian	Ordovician	Upper Middle Lower	Ashgillian Caradocian Arenigian	
							500
	Cambrian	Upper Middle Lower	Croixan Albertan Waucoban	Cambrian	Upper Middle Lower	Tuorian Amgan Aldanian	
							570
Precambrian	Proterozoic Archeozoic						

Contents