

Coal Structure

Martin L. Gorbaty, EDITOR

*Exxon Research and Engineering
Company*

K. Ouchi, EDITOR

Hokkaido University

Based on a symposium sponsored by
the Division of Fuel Chemistry
at the ACS/CSJ Chemical Congress,
Honolulu, Hawaii,
April 3-4, 1979.

ADVANCES IN CHEMISTRY SERIES

192

AMERICAN CHEMICAL SOCIETY

WASHINGTON, D. C.

1981



Library of Congress CIP Data

Coal structure.

(Advances in chemistry series; 192 ISSN 0065-2393)

Includes bibliographies and index.

1. Coal—Congresses.

I. Gorbaty, Martin L., 1942— . II. Ouchi, Kjöi, 1926— . III. American Chemical Society. Division of Fuel Chemistry. IV. ACS/CSJ Chemical Congress, Honolulu, 1979. V. Series.

QD1.A355 no. 192 [TP325] 540s [662.6'22]
ISBN 0-8412-0524-8 ADCSAJ 192 1-376 80-24104
1981

Copyright © 1981

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each article in this volume indicates the copyright owner's consent that reprographic copies of the article may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc. for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating new collective work, for resale, or for information storage and retrieval systems.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission, to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto.

PRINTED IN THE UNITED STATES OF AMERICA

Advances in Chemistry Series

M. Joan Comstock, *Series Editor*

Advisory Board

David L. Allara

Kenneth B. Bischoff

Donald D. Dollberg

Robert E. Feeney

Jack Halpern

Brian M. Harney

W. Jeffrey Howe

James D. Idol, Jr.

James P. Lodge

Marvin Margoshes

Leon Petrakis

Theodore Provder

F. Sherwood Rowland

Dennis Schuetzle

Davis L. Temple, Jr.

Gunter Zweig

FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Volumes in the ADVANCES IN CHEMISTRY SERIES maintain the integrity of the symposia on which they are based; however, verbatim reproductions of previously published papers are not accepted. Papers may include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

The need to produce additional liquid and gaseous fuels from coal is apparent. Today sophisticated and elegant engineering work is aimed at developing better coal conversion processes. However, these processes are based on chemistry that is at least 50 years old. Key limitations of this chemistry include poor selectivity and thermal efficiency, and high hydrogen consumption. New and more efficient processes will arise from breakthroughs in the chemistry of coal utilization, and these breakthroughs will have to come from a better understanding of coal structures.

Coal may be viewed as an organic rock. As such, it has an organic, an inorganic, and a physical structure. It is by nature a heterogeneous substance that varies from millimeter to millimeter in the same seam; coals of different rank formed from different species of plant matter during different geological periods in swamps hundreds or thousands of miles apart vary just as much. While it may not be possible to determine a coal structure absolutely, it is possible to determine key structural features of coals that affect their reactivity and ultimately their utility.

The coal science of today can be compared with the biochemistry of 50 or 75 years ago in the sense that the new tools required to answer key questions in that field were just then becoming available. Today major advances in magnetic resonance and other spectroscopic techniques make the hope of determining how carbon is arranged in coal a near reality.

This volume describes the current state-of-the-art understanding of the organic, inorganic, and physical structure of the substance called coal. After an introductory overview, which sets the field in perspective, the advances in applying new spectroscopic techniques to gain a better understanding of coal structure are described. Following this, current work on the organic, physical, and inorganic structures of coal is presented.

Many of the chapters in this volume originally were presented at a symposium sponsored by the Division of Fuel Chemistry of the American Chemical Society during the ADS/CSJ Chemical Congress in April 1979. Several have been revised and others added. We wish to thank the contributing authors for their efforts.

It is our belief that this volume can serve as a source of information and a base from which further science and technology advances will be made.

MARTIN L. GORBATY
Exxon Research and Engineering Company
P.O. Box 45
Linden, New Jersey 07036

K. OUCHI
Faculty of Engineering
Hokkaido University
Sapporo Japan 060

August 22, 1979

CONTENTS

Preface	vii
1. Coal Structure and Coal Science: Overview and Recommendations R. C. Neavel	1
2. An Estimation of Average Aromatic Ring Size on an Iowa Vitrain and a Virginia Vitrain B. C. Gerstein, L. M. Ryan, and P. D. Murphy	15
3. Magnetic Resonance Study of Labeled Guest Molecules in Coal .. B. G. Silbernagel, L. B. Ebert, R. H. Schlosberg, and R. B. Long	23
4. Nature of the Free Radicals in Coals, Pyrolyzed Coals, Solvent- Refined Coal, and Coal Liquefaction Products	37
H. L. Retcofsky, M. R. Hough, M. M. Maguire, and R. B. Clarkson	
5. Temperature Dependence of ^1H NMR Absorption in Coal and Pitch K. Miyazawa, T. Yokono, T. Chiba, and Y. Sanada	59
6. Application of ^{13}C , ^2H , ^1H NMR and GPC to the Study of Structural Evolution of Subbituminous Coal in Tetralin at 427°C	75
J. A. Franz, D. M. Camaioni, and W. E. Skiens	
7. Relation Between Coal Structure and Thermal Decomposition Products	95
P. R. Solomon	
8. Carboxylic Acids and Coal Structure	113
A. L. Chaffee, G. J. Perry, R. B. Johns, and A. M. George	
9. Structural Characterization of Coal: Lignin-Like Polymers in Coals R. Hayatsu, R. E. Winans, R. L. McBeth, R. G. Scott, L. P. Moore, and M. H. Studier	133
10. Short-Time Reaction Products of Coal Liquefaction and Their Relevance to the Structure of Coal	151
M. Farcasiu	
11. Characterization of Hydrolytically Solubilized Coal	161
R. E. Winans, R. Hayatsu, R. L. McBeth, R. G. Scott, L. P. Moore, and M. H. Studier	
12. The Chemistry of Acid-Catalyzed Coal Depolymerization	179
L. A. Heredy	
13. Deduction of the Structure of Brown Coal by Reaction with Phenol D. G. Evans and R. J. Hooper	191
14. The Alkylation of Coal	207
L. B. Alemany, C. I. Handy, and L. M. Stock	

15. Complications in the Reductive Alkylation of Coal	225
L. B. Ebert, D. R. Mills, L. Matty, R. J. Pancirov, and T. R. Ashe	
16. Data on the Distribution of Organic Sulfur Functional Groups in Coals	239
A. Attar and F. Dupuis	
17. Chemical Structure of Heavy Oils Derived from Coal Hydrogenation Determined by Mass Spectroscopy	257
S. Yokoyama, N. Tsuzuki, T. Katoh, Y. Sanada, D. M. Bodily, and W. H. Wiser	
18. The Effect of Reagent Access on the Reactivity of Coals	277
J. W. Larsen, T. K. Green, P. Choudhury, and E. W. Kuemmerle	
19. Physical and Chemical Structure of Coals: Sorption Studies	293
E. L. Fuller, Jr.	
20. The Nature and Possible Significance of Particulate Structure in Alkali-Treated Brown Coal	311
R. J. Camier, S. R. Siemon, H. A. J. Battaerd, and B. R. Stanmore	
21. The Ultrafine Structure of Coal Determined by Electron Microscopy	321
L. A. Harris and C. S. Yust	
22. Characterization of Iron-Bearing Minerals in Coal	337
P. A. Montano	
Index	363

Coal Structure and Coal Science: Overview and Recommendations

RICHARD C. NEAVEL

Exxon Research and Engineering Company, P.O. Box 4255, Baytown, TX

A new procedure for classifying coals is needed. This procedure must recognize both coal type (proportions of various macerals and minerals) and rank (stage of metamorphic development). An integrated program must be instigated to study a large number of vitrinite-rich samples covering a broad range of ranks. Fundamental properties, including molecular structures, must be related to responses of the samples in conversion processes. Properties and responses of liptinite and inertinite, and interactions of inorganics, subsequently must be integrated with the data from vitrinites. Multivariate statistical treatment of the data will be required. Until such a unified classification system is devised, we shall continue to be limited to applying empirical tests to predict process responses, a procedure hardly deserving to be called a science.

Coal is a sedimentary rock accumulated as peat, composed principally of macerals and subordinately of minerals, and containing water and gases in submicroscopic pores. Macerals (mas' er-als) are organic substances derived from plant tissues, cell contents, and exudates that were variably subjected to decay, incorporated into sedimentary strata, and then altered physically and chemically by natural (geological) processes.

Coal is not a uniform mixture of carbon, hydrogen, oxygen, sulfur, and minor proportions of other elements; nor is it, as is often implied, simply a uniform, polyaromatic, polymeric substance. Rather, it is an aggregate of microscopically distinguishable, physically distinctive, and chemically different macerals and minerals.

Coal is analogous to a fruitcake, formed initially as a mixture of diverse ingredients, then baked to a product that is visibly heterogeneous. The heterogeneous nature of coal is evident in Figure 1, a

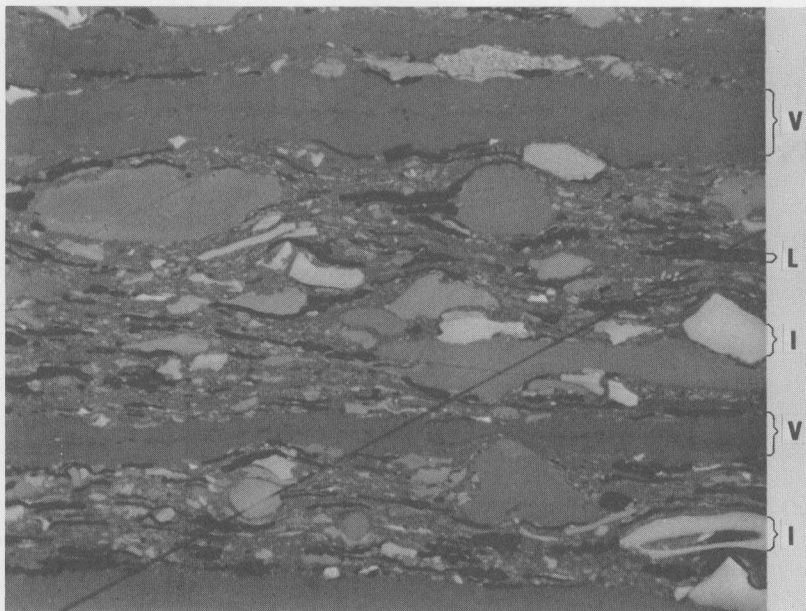


Figure 1. Photomicrograph of a polished surface of a bituminous coal. Representatives of the three major classes of maceral materials are identified: (V), vitrinite; (L), liptinite; (I), inertinite.

photomicrograph of a polished surface of a piece of typical coal. The different macerals reflect different proportions of incident light and are therefore distinguished as discrete areas exhibiting different shades of gray. It should be evident that any attempt to characterize the chemical structure of this coal without recognizing the organization of the elements and molecules into discrete substances would be like trying to describe the essence of a fruitcake by grinding it up and analyzing its elemental composition.

The heterogeneity of coal, exemplified by Figure 1, is inherited from the diversity of source materials that accumulated in a peat swamp. Coals may be compared, contrasted, and classified on the basis of variations in the proportions of these microscopically identifiable components. Such a classification is referred to as a classification according to type. Coals may also be classified according to how severely geological alteration processes, referred to collectively as metamorphism, have affected their properties; this is classification according to rank. These two classification methods are independent and orthogonal; therefore, within certain limits, any type of coal can be found at any rank.

Classification according to type involves the relative proportions of both the inorganic substances and the different organic substances. Because only the organic material is altered by metamorphic processes, rank

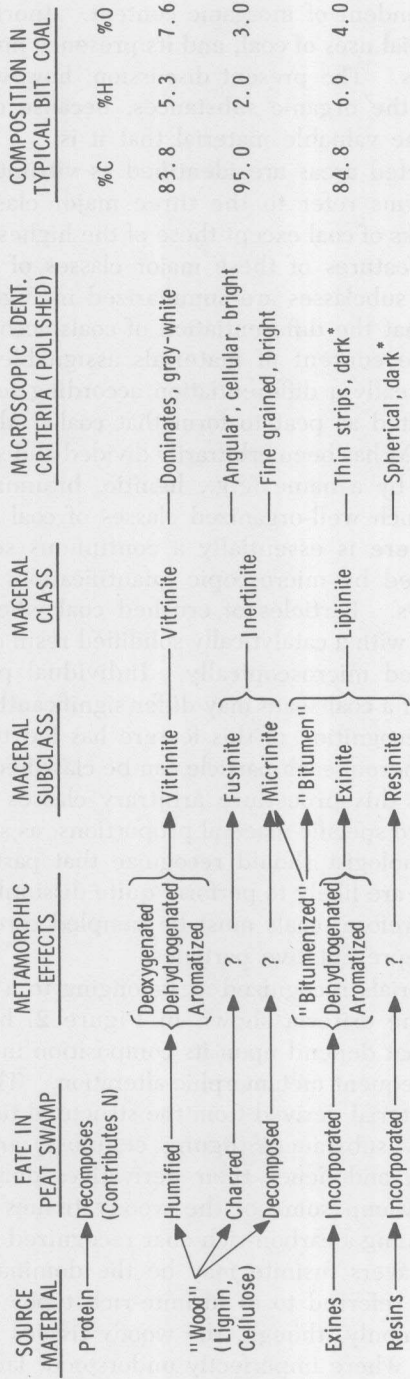
classification is independent of inorganic content. Inorganic material is significant in commercial uses of coal, and its presence must be accounted for in scientific studies. The present discussion, however, concentrates on the properties of the organic substances, because only the organic macerals make coal the valuable material that it is.

In Figure 1 selected areas are identified as vitrinite, liptinite, and inertinite. These terms refer to the three major classes of macerals recognizable in all ranks of coal except those of the highest ranks. A few of the more significant features of these major classes of macerals and of their more important subclasses are summarized in Figure 2. It can be seen from Figure 2 that the differentiation of coals according to type — viz., according to the content of materials assignable to each of the maceral classes — is really a differentiation according to the ingredients that initially accumulated as peat to form that coal. Although the rank scale according to ASTM has been arbitrarily divided and specific segments have been identified by a name (e.g., lignitic, bituminous, anthracitic coals), there are no such well-organized classes of coal types.

In this sense, there is essentially a continuous series of coals of different types, defined by microscopic quantification of their maceral (and mineral) contents. Particles of crushed coal when cemented together as a solid block with a catalytically solidified resin or plastic, can be polished and examined microscopically. Individual particles derived from different layers of a coal seam may differ significantly in maceral and mineral contents. Recognition of this feature has led to the concept of the microlithotype, wherein each particle can be classified according to its maceral content. In this procedure arbitrary classes of particles are recognized according to specific maceral proportions, as shown in Table I. The scientist or technologist should recognize that particles of the different microlithotypes are likely to perform quite dissimilarly when analyzed or processed; therefore, coals must be sampled carefully to prevent the selection of nonrepresentative particles.

Each of the materials recognized as belonging to a specific maceral class (according to the criteria shown in Figure 2) has physical and chemical properties that depend upon its composition in the peat swamp and the effects of subsequent metamorphic alteration. Thus, for instance, in all coals there is material derived from the structural tissues ("wood") of plants. These woody substances (lignin, cellulose) are the dominant components of plants, and hence their derivatives dominate in typical coals. In the peat swamp some of the woody tissues may have been pyrolyzed by fire, forming a carbon-rich char recognized as fusinite in the coal. In some coal layers fusinite may be the dominant maceral, and such layers would be referred to as fusinite-rich types of coal.

Much more commonly, though, the woody tissues accumulated below a water covering, where imperfectly understood, largely microbiological processes converted them to humic substances of somewhat variable



* In Low-Vol Bituminous and Anthracites, Liptinite Indistinguishable from Vitrinite

Figure 2. Principal features of the major classes of macerals

Table I. Classification of Microlithotypes (1)

	<i>Microlithotype</i>	<i>Maceral</i>	<i>Volume Percent</i>
<i>Monomaceralic</i>	Vitrite	Vitrinite (V)	>95%
	Liptite	Liptinite (L)	>95%
	Inertite	Inertinite (I)	>95%
<i>Bimaceralic</i>	Clarite	V + L	>95%
	Vitrinertite	V + I	95%
	Durite	I + L	95%
<i>Trimaceralic</i>	Duroclarite	V + I + L	$V > (I + L)$
	Clarodurite	V + I + L	$I > (L + V)$
	Vitrinertoliptite	V + I + L	$L > (I + V)$
	Carbominerite	V, L, I, and mineral matter (MM)	$20\% < MM < 60\%$

composition. These highly functionalized, aromatic, humic substances subsequently were altered by metamorphic processes (heat, pressure) into substances classifiable as one of the vitrinitic macerals. Therefore, the physical and chemical properties of the vitrinitic materials in a specific coal were conditioned largely by the magnitude of temperature and pressure to which they were subjected after burial. One could say that the properties of the macerals in a given coal reflect the rank of the coal; or, more correctly, one should say that the rank of the coal reflects the properties of macerals as conditioned by the severity of the metamorphic processes to which the coal was subjected.

One of the properties of macerals that changes progressively with metamorphic severity is the microscopically measurable reflectance of polished surfaces. When a sensitive photomultiplier cell mounted on a microscope is used, it is possible to measure objectively the absolute percentage of incident light reflected from very small areas (about 5 μm diameter) of polished coal surfaces. In Figure 3 is shown a series of reflectance distributions, each representing a sampling of the material in a coal of the rank indicated. These distributions are arbitrarily constructed to show what would happen to a given peat if it were to be subjected to increasingly more severe metamorphism. Recognize, of course, that these are slices through a continuum and that no jump from rank to rank is implied. Properties such as carbon content, oxygen content, degree of aromaticity, and many others could be substituted for the reflectance scale and a similar sort of picture would emerge. In Table II some typical values are shown for selected properties of vitrinite macerals in different rank coals. In Table III a number of the properties of nonvitrinite macerals are compared to those of vitrinite from coal of the same rank.

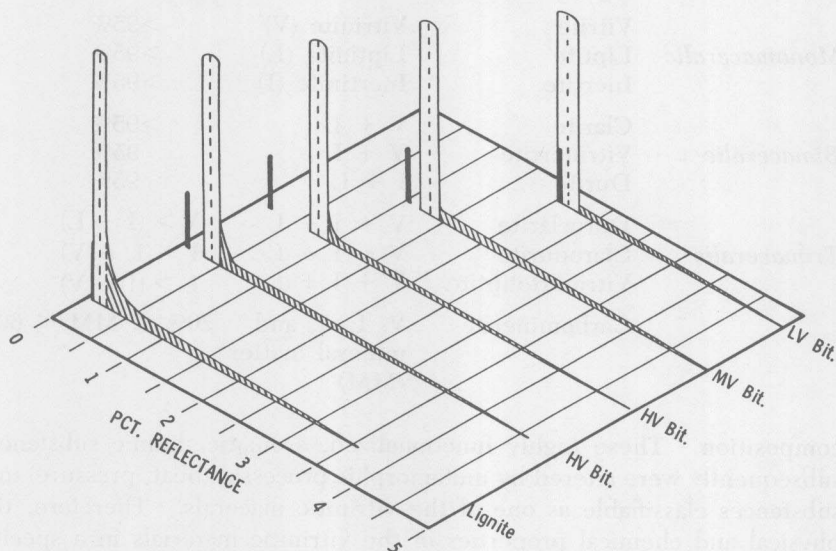


Figure 3. Reflectance distribution of macerals in typical coals with the same maceral contents but of different ranks ((■) liptinite; (□) vitrinite; (▨) inertinite)

Table II. Selected Properties of Vitrinites in Coals of Different Ranks

	Lignite	Subbitu- minous	Bitu- minous	Anthracite
Moisture capacity, wt % ^a	40	25	10	< 5
Carbon, wt % DMMF ^b	69	74.6	83	94
Hydrogen, wt % DMMF	5.0	5.1	5.5	3.0
Oxygen, wt % DMMF	24	18.5	10	2.5
Volatile matter, wt % DMMF	53	48	38	6
Aromatic C/total C	0.7	0.78	0.84	1.0
Density (He, g/cm ³)	1.43	1.39	1.30	1.5
Grindability (hardgrove)	48	51	61	40
Btu/lb, DMMF	11,600	12,700	14,700	15,200

^aThe values shown are typical for the ranks indicated and are not limiting.

^bDMMF = dry, mineral-matter-free basis.

Table III. Properties of Macerals Compared to Vitrinite in Same Coal (Subbituminous and High-Volatile Bituminous Only); Magnitude of Property Greater Than (>), Less Than (<), or Equal to (=) That of Associated Vitrinite

	<i>Fusinite</i>	<i>Micrinite</i>	<i>Exinite</i>
<i>Optical Properties</i>			
Reflectance	> >	>	<
Fluorescence			>
<i>Chemical Structure</i>			
Molecular weight			>
H/C ratio	< <	<	>
H aliphatic/H total; —CH ₂ ; hydroaromaticity			>
Fraction Aromatic C	>	>	<
Oxygen _{OH} /oxygen total	<		<
Unpaired spins by ESR	>		<
<i>Reactivity</i>			
Methane sorption	>		
Decomposition temperature			<
Oxidizability	<	<	<
Reduction with Li in Ethyl- enediamine	<	=	<

Typical U.S. coals are relatively vitrinite-rich. Therefore analyses of whole coals, when appropriately corrected for inorganic content, reflect, to a first approximation, the composition and properties of the included vitrinite. For this reason the parameters employed to classify coals according to rank reflect the rank (stage of metaphoric development) of the vitrinite. Calorific values or fixed carbon yields are calculated to a so-called mineral-matter-free basis for use in the ASTM classification of coals according to rank (2). It is essentially impossible to obtain inorganic-free samples; therefore, if organic matter is to be represented accurately in comparative studies of any of the organic properties of coal, analytical data must be converted to an inorganic-free basis. Commonly, a dry, ash-free (DAF, not MAF, which, unfortunately, is often used as an abbreviation for moisture-and-ash-free) basis is employed. It is preferable, however, to convert to a dry, mineral-matter-free (DMMF) basis, as discussed by Given and co-workers (3, 4, 5). In fact, the most meaningful assessment of coal rank or of the properties of coals of different ranks should be done with samples of concentrated vitrinite or on samples where the vitrinite comprises more than about 80% of the organic fraction. Because reflectance is closely correlative with many rank-sensitive properties and its determination can be made on vitrinite alone, it has become a widely accepted parameter to designate the rank of a coal (*see*

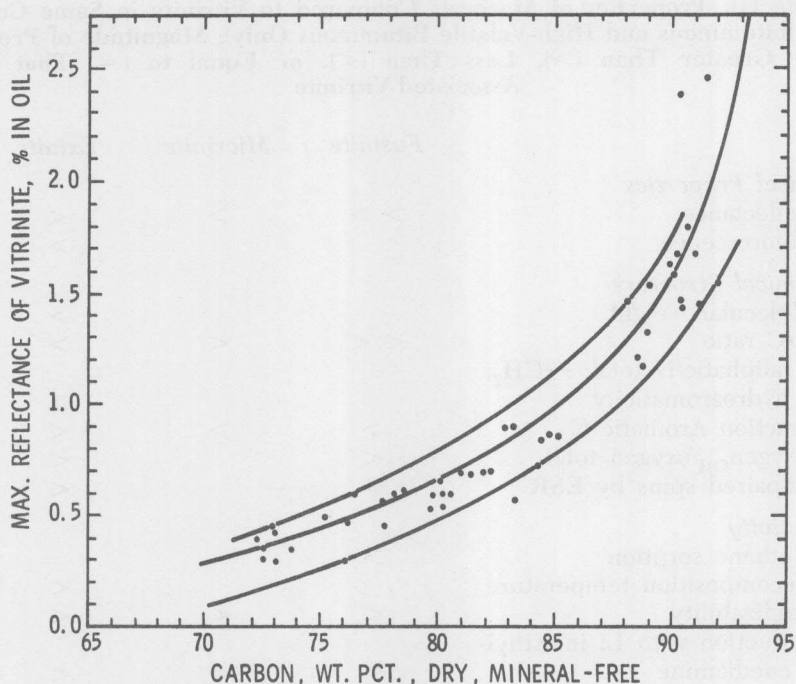


Figure 4. Correlation of reflectance of vitrinite and carbon content of coals (6)

Figure 4). Unfortunately, even when a reflectance value is available, it may not be reported in scientific publications. I strongly recommend that petrographic analyses and vitrinite reflectance be reported for samples on which structural studies are conducted.

Although many properties of vitrinites appear to change in a more or less parallel fashion as a result of metamorphism, there is considerable scatter in their correlation. Figure 5 is offered as evidence of this contention. The data plotted in Figure 5 are from coals containing more than 80% vitrinite on a DMMF basis (6). It is obvious that the progression from high to low H/C and O/C values reflects the influence of more severe metamorphic alteration; in other words, coals toward the lower-H/C-and-O/C end of the band are higher in rank. However, the fact that the data do form a band, rather than a linear progression, implies that there is not a simple scale that defines the rank progression. As Given and his co-workers have so eloquently shown, the geological-geographical disposition of U.S. coals appears to exert some, as yet undefined, influence on the intercorrelations of coal properties (7).

Clearly, neither geology nor geography is a property of coal and hence neither one can be measured. Different source materials, de-