Geochemistry of Marine Humic Compounds

M.A. Rashid

# Geochemistry of Marine Humic Compounds

With 133 Illustrations



Springer-Verlag New York Berlin Heidelberg Tokyo M.A. Rashid Atlantic Geoscience Centre Geological Survey of Canada Bedford Institute of Oceanography Dartmouth, Nova Scotia B2Y 4A2 Canada

Library of Congress Cataloging in Publication Data Rashid, M. A. (Mohammed A.) Geochemistry of marine humic compounds. Bibliography: p. 1. Humic acid. 2. Organic geochemistry. 3. Chemical oceanography. I. Title. GC116.R37 1985 551.46'01 85-14692

© 1985 by Springer-Verlag New York Inc. Softcover reprint of the hardcover 1st edition 1985 All rights reserved. No part of this book may be translated or reproduced in any form without written permission from Springer-Verlag, 175 Fifth Avenue, New York, New York 10010, U.S.A.

Media conversion by David E. Seham Associates Inc., Metuchen, New Jersey.

987654321

ISBN-13: 978-1-4615-7100-1 e-ISBN-13: 978-1-4615-7098-1 DOI: 10.1007/ 978-1-4615-7098-1

# Foreword

Some 90 years ago, the first information on the occurrence of dissolved organic matter in sea water was published. For 50 years after that revelation, little progress was made in identifying these dissolved "yellow substances." In the 1950s and 1960s, a few chemical oceanographers identified some specific dissolved organic compounds, but few of these pioneers fully appreciated their significance in terms of biological interactions, metal chelation, or interactions with sedimentary material.

When Mohammed Rashid began his work on marine humic compounds in the mid-1960s, he was one of only five scientists who had specifically designed their studies toward understanding the nature of these complex materials. Over the next decade, Dr. Rashid directed his research toward characterization of humic and fulvic compounds in the marine environment, the influence of humic substances on the growth of marine phytoplankton, the role of organic matter in complexing metals in sea water and marine sediments, the interaction between humic substances and clay minerals in marine environments, and the influence of organic matter on the geotechnical properties of marine sediments. As if the many papers produced from these scientific investigations were not sufficient, Dr. Rashid turned his attention to the geochemistry of hydrocarbons found in ancient and modern marine sediments. He viewed the maturation of hydrocarbons from the perspective of a continuum of diagenetic processes acting on the original organic matter in the sediments. Dr. Rashid also turned his attention to contemporary environmental concerns with special regard to the importance of organic matter in transporting pollutants or the degradation of natural organic matter and processed hydrocarbons in the marine environment.

A few years ago when Dr. Rashid considered the need for a comprehensive text to review the geochemistry of marine organic matter, I could not think of a more qualified scientist to write such a book. In this final product, one can see that Dr. Rashid's work is well represented. That is as it would be, even had the book been written by another. Certainly few could have attempted to cover the broad scope of this subject, from soil humic compounds to dissolved organic matter in sea water to hydrocarbons in marine sediments. Furthermore, Dr. Rashid has reviewed the field with an appreciation that can come only from one who has struggled with the difficulties of analyzing and characterizing the enormous range of organic substances found in the ocean. Dr. Rashid has included examples of analytical data that students as well as experienced researchers will find useful as a reference compendium. He has also included many illustrations derived from original research in a variety of specialized fields that help the reader to understand both the theoretical and empirical reactions of organic matter in a variety of environmental conditions.

Completion of the tasks of compiling the published information, synthesizing coherent chapters, and indexing this book has been especially difficult for Dr. Rashid, who became seriously ill during the past two years. He completed final revisions to the manuscript only days before he submitted to open heart surgery.

It is my great pleasure to join Dr. Rashid in the sincere hope that this book will be of service to the growing number of individuals studying the geochemistry of marine organic matter, and that it will in some measure spur our progress in understanding and quantifying this complex field.

> DALE E. BUCKLEY Atlantic Geoscience Centre Geological Survey of Canada Bedford Institute of Oceanography

# Preface

The high rate of primary production and the massive amount of organic matter that enters marine sedimentary deposits makes the oceans one of the largest reservoirs of organic carbon. Humic compounds constitute the predominant form of organic matter present in sea water and recent sediments. The products of their diagenesis are also common in ancient sediments. Humic compounds are strikingly ubiquitous in the biosphere, extremely complex in composition, and capable of many interactions in nature. There are hardly any geochemical reactions in the marine environments that are not influenced by these compounds. Some forms survive the ravages of geological time, while others yield a variety of economically important products through diversified diagenetic transformations. These compounds thus play a significant role in the geochemical history of soils and sediments. Despite their wide occurrence and significant contributions to geological and geochemical reactions, many marine and earth scientists are either unfamiliar with these compounds or have failed to recognize their full impact. After years of neglect, this situation is being remedied, as is evident from an increasing number of publications during the last 10 to 15 years outlining the chemical nature and geochemical significance of humic compounds. However, large gaps still persist in our knowledge and understanding of these naturally occurring organic compounds. This book is an attempt to provide an insight into the origin, distribution, and reactions of marine humic compounds and to point out the scope of research for future investigations.

In view of the rapid advances in the field of marine geochemistry, a critical review, resynthesis, and reevaluation of the existing information was considered pertinent. It is essential to make organic geochemistry an effective tool in solving many paleooceanographic and marine geological problems that are not easily solved by conventional methods. The origin and distribution of organic compounds, the process of humification, physico-chemical properties of humic compounds, and their reactions with metals and minerals are reviewed particularly with respect to the geological and geochemical implications of these reactions. Besides these topics, there are some discussions on the diagenetic transformations of humic compounds. Some attention has also been focused on the contemporary environmental and ecological problems. It is my earnest hope that the book will serve as a reference to both the new and experienced scientists in the field of marine geochemistry. It is further hoped that geologists,

soil scientists, water chemists, limnologists, ecologists, marine biologists, and scientists in related disciplines will be equally benefited by this book. At present, no suitable textbook on marine organic geochemistry is available for advanced students. The contents of this book will be of interest to them as well.

I am extremely grateful to the Management Committee of the Atlantic Geoscience Centre, Geological Survey of Canada, for providing me with an opportunity to write this book and all the necessary facilities to complete the task. My sincere thanks are also due to a number of my colleagues for valuable comments and criticisms on various parts of the manuscript. I am particularly grateful to D.E. Buckley, S.R.V. Durvasula, H. Kodama, M.K. Mahendrappa, A. Nissenbaum, A. Prakash, M. Schnitzer, and G. Vilks for their reviews of different chapters. My thanks are due to Cecilia Middleton for typing the initial manuscript, Art Cosgrove for drafting the illustrations, Joyce Wiley for editing, Kevin Robertson for his general assistance, and the staff of the BIO Library for their help in literature search. I am deeply indebted and grateful to Bill LeBlanc for his sustained and valuable help, without which my progress with this book would have been slow. Last but not the least, my deepest thanks go to my wife, Rashida, who provided immense encouragement and showed a great deal of patience throughout.

M.A. RASHID

# Contents

### CHAPTER 1 Origin and Distribution of Organic Compounds in the Marine Environment Introduction ..... 1 Inventory of Organic Carbon ..... 1 Geochemical Significance of Carbon-Containing Compounds ..... 2 Evolution of Life and Development of Organic Matter 3 Beginning of Life on Earth ..... 4 Primitive Organisms and their Evolution ..... 4 5 Higher Land Plants and Animals ..... Genesis and Survival of Organic Compounds During Geological Time ..... 6 Distribution of Organic Matter in Oceans and on Land ..... 7 Marine Primary Productivity and Factors Governing Productivity ..... 7 Global Marine Primary Productivity 16 Terrestrial Productivity and Its Impact on Oceans ..... 17 Nature and Fate of Organic Matter ..... 20 Transformations of Organic Matter in the Water Column 21 Origin, Concentrations and Nature of DOM and POM ..... 22 Aggregation, Sedimentation, and Distribution of Organic Matter ..... 26 Factors Affecting the Distribution of Organic Matter in Sediments ..... 28 Concentration of Organic Carbon in Surficial Sediments ..... 33 34 Summary ..... **CHAPTER 2** Humification-A Major Biogeochemical Phenomenon Introduction ..... 35 Nature of Microbial Population ..... 36 Bacteria ..... 36 37 Fungi ..... 37 Actinomycetes ..... Chemical Composition of Organisms 38 Some Major Cellular Constituents and Products of their Microbial 38 Degradation ..... 39 Proteins and Related Compounds and their Microbial Disintegration ... Carbohydrates, their Related Compounds and their Microbial Decomposition ..... 43 Lipids and Related Compounds ..... 46 Lignins and Products of their Degradation ..... 46 Formation and Transformations of Phenolic Compounds ..... 50 Formation of Humus ..... 52 Reactions of Phenolic Compounds with Nitrogenous Substances ...... 53 55 Reactions of Amino Acids with Sugars .....

Products of Humification	57
Factors Influencing Humification	60
Distribution of Humic Compounds in the Marine Environment	62
Concentrations of Humic Compounds in the Water Column	63
Concentrations of Humic Compounds in the Sedimentary Column	63
Summary	64

### CHAPTER 3

## Physico-chemical Characteristics of Marine Humic Compounds

Introduction	66
Major Components of Humic Substances	67
Major Phenolic and Aromatic Compounds	67
Major Aliphatic Constituents	72
Structural Configuration	74
Stability of Humic Compounds in Geological Times	77
Chemical Composition and Characterization	77
Elemental Analysis	77
Ratios of Different Elements and their Significance	83
Isotopic Composition and the Source of Organic Matter	85
Functional Groups	90
Factors Affecting the Distribution of Functional Groups	95
Electro-chemistry of Humic Molecules	96
Aliphaticity versus Aromaticity	97
Physical Properties	98
Some Striking Differences and Similarities in the Physico-chemical	
Characteristics of Marine and Terrestrial Humic Compounds	104
Summary	106

CHAPTER 4	
Organo-metal Reactions and their Geochemical Significance	
Introduction	108
Humus as a Natural Absorbent	108
Geochemical Scale of Metal Absorption	109
Enrichment of Trace, Transition, and Rare Metals in Humic-Rich	
Media	110
Physico-chemical Properties of Humic Compounds in Relation to Organo-	
metal Reactions	111
Functional Groups and their Role in Organo-metal Interactions	111
Molecular Weight Distribution and Organo-metal Reactions	112
Surface Area	113
Degree of Humification, Nature, and Source of Humic Compounds	113
Environmental Factors Affecting Organic Reactions	114
Mechanisms of Organo-metal Interactions	115
Surface or Physical Adsorption	115
Cation Exchange Reactions	115
Chelation and Complexing Reactions	118
Bonding Strength	123
Factors Affecting Bonding Strength	123
Measurement of Bonding Strength	124
Implications of Organo-metal Reactions	126
Geochemical Significance and Sedimentary Base Metal	
Accumulations	127
Economic Implications and Formation of Ores	137
Environmental Significance of Organo-metal Reactions	142
Ecological Implications	145
Research Proposals	145
Summary	147

### CHAPTER 5

Reactions of Humic Compounds with Sedimentary Minerals

Introduction	148
Clay Minerals and their Types	149
Structure and Classification of Clay Minerals	149
Electrical Charges	150
Clay Minerals of Marine Sediments	151
Other Minerals	153
Physico-chemical Properties of Humic Compounds and Organo-clay	155
	154
Complexes	154
Functional Groups	
Molecular Weight of Humic Compounds	156
Mechanisms of Organo-clay Interactions	157
Chemical Bondings	157
Physical Bondings	159
Effect of Environmental Parameters	160
Electro-chemical Model of Humic Compounds and Clay Minerals	
Depicting the Reaction Mechanisms	162
Ramifications of Organo-clay Complexes	165
Degradation and Decomposition of Rock-Forming Minerals	165
Flocculation of Colloidal Particles and Process of Sedimentation	167
Genesis of Minerals in Marine Sediments	170
Genesis of Clay Minerals and their Transformations	176
Catalytic Effect of Clay Minerals on the Formation and Transformation	170
of Humic Compounds	177
Organo-clay Complexes and Geotechnical Properties of Marine	1//
	170
Sediments	179
Effect of Humic Compounds on Concrete Structures and Underwater	10.1
Installations	184
A Few Research Proposals	185
Summary and Conclusions	187

### CHAPTER 6

Diagenetic Transformations of Humic Compounds

Introduction	188
Diagenesis	189
Early Diagenesis	189
Long-Term Diagenesis	
Catagenesis	204
A Few Major Chemical Changes During Catagenesis	205
Geochemical Factors Affecting Catagenesis	207
Metagenesis	211
Summary and Conclusions	211

# CHAPTER 7

Paleo- and Contemporary	Environmental	Impl	ications	of
Humic Compounds				

Introduction	213
Paleohumus as a Geological Marker and Environmental Indicator	213
Fossil Humus in Tracing Out the Early History of Life	213
Glacial and Interglacial Periods and Major Climatic Changes	
Geochronology and Geological Age Measurements	
History of Holocene Sedimentation	
Assessment of Paleoenvironments	223
Paleotemperatures of Sedimentary Basins	224
Identification of the Source of Organic Matter	

Potential Application of Humic Acid Geochemistry in Solving	
Geological Problems	227
Sea-Floor Spreading and Continental Drift	227
Stratigraphic Correlation	228
Sedimentary Processes	228
Contemporary Environmental Concerns	229
Interaction of Humic Compounds with Pollutants	229
A Few Major Reaction Mechanisms	231
Ultimate Fate and Behavior of Pesticides	235
Interactions of Humic Compounds with Hydrocarbons and Oils	235
Interactions of Humic Compounds with Inorganic Pollutants	238
Humic Substances as Pollution Indicators	243
Radioactive Waste Disposal	244
Ocean Dumping	245
Industrial Waste-Water Treatment	246
Summary	247

### CHAPTER 8

### Role of Humic Compounds in Aquatic Productivity

Introduction	248
Biological Conditioning of Sea Water and Primary Productivity	249
Key Organic Compounds of Biological Conditioning of Sea Water	249
Humic Compounds as Biological Conditioners	250
Humic Compounds and Growth Response of Phytoplankton	251
Physiological Responses of Phytoplankton on Humic Acid Enrichment	251
Molecular Weight Ranges of Humic Compounds and Growth	231
Response	253
Role of Humic Compounds on the Physiology and Metabolism of Higher	233
	255
Plants	
Stimulatory Effect of Humic Compounds on the Growth of Plants	256
Role in Nutrient Uptake	256
Possible Mechanisms of the Biological Effect of Humic Compounds	257
Metal Chelation Phenomena and Availability of Essential Trace	
Metals	257
Scavenging of Toxic and Heavy Metals	259
Interaction of Humic Compounds with Major Nutrients	261
Physiological Stimulation	264
Ecological Implications	265
Red Tide	266
Eutrophication	267
Succession of Species	269
Research Prospects	270
Summary	271
Bibliography	273
Index	293