

DEVELOPMENTS IN SEDIMENTOLOGY 48

Geochemistry of Sedimentary Carbonates

John W. Morse

*Department of Oceanography, Texas A&M University, College Station,
TX 77843, U.S.A.*

Fred T. Mackenzie

*Department of Oceanography, University of Hawaii, Honolulu, HI 96822,
U.S.A.*



ELSEVIER

Amsterdam — Oxford — New York — Tokyo 1990

TABLE OF CONTENTS

Preface	vii
Chapter 1. The CO₂-Carbonic Acid System and Solution Chemistry	1
Basic Concepts	1
Activity Coefficients in Solutions	10
Influences of Temperature and Pressure	20
The Carbonic Acid System in Seawater	26
Calculation of the Saturation State of Seawater with Respect to Carbonate Minerals	34
Concluding Remarks	38
Chapter 2. Interactions Between Carbonate Minerals and Solutions	39
Sedimentary Carbonate Minerals	39
Basic Concepts	39
Characteristics of Sedimentary Carbonate Minerals	40
Solubility Behavior of Carbonate Minerals	47
General Considerations	47
Calcite and Aragonite Solubility	51
Methods for the Calculation of Equilibrium Solution Composition Under Different Conditions	54
Surface Chemistry of Carbonate Minerals	64
Basic Principles	64
Adsorption of Ions on Carbonate Surfaces	68
Carbonate Dissolution and Precipitation Kinetics	72
Basic Principles	72
Reaction Kinetics in Simple Solutions	72
Reaction Kinetics in Complex Solutions	74
Concluding Remarks	85
Chapter 3. Coprecipitation Reactions and Solid Solutions of Carbonate Minerals	87
General Concepts	87
Background Information	87
Basic Chemical Considerations	88

Coprecipitation of "Foreign" Ions in Carbonate Minerals	93
Examples of Coprecipitation Reactions	93
General Models for Partition Coefficients in Carbonates.....	104
Magnesian Calcite	106
General Considerations.....	106
The Fundamental Problems.....	107
Experimental Observations	110
Hypothesis of a Hydrated Magnesian Calcite	122
Stable Isotope Chemistry.....	124
General Considerations.....	124
Oxygen Isotopes	125
Carbon Stable Isotopes.....	128
Concluding Remarks	131
 Chapter 4. The Oceanic Carbonate System and Calcium	
Carbonate Accumulation in Deep Sea Sediments.....	133
An Overview of Major Processes	133
The CO ₂ System in Oceanic Waters	135
The Upper Ocean.....	135
The Deep Sea.....	140
Saturation State of Deep Seawater with Respect to CaCO ₃ ..	144
Sources and Sedimentation of Deep Sea Carbonates	147
Sources.....	147
Sedimentation.....	149
The Distribution of CaCO ₃ in Deep Sea Sediments and	
Carbonate Lithofacies.....	152
General Considerations.....	152
The Distribution of CaCO ₃ in Surface Sediments.....	156
Factors Controlling the Accumulation of Calcium Carbonate	
in Deep Sea Sediments	162
General Relations.....	162
Factors Leading to Variability	165
Near Interfacial Processes.....	167
Variability of Calcium Carbonate Deposition in Deep Sea	
Sediments with Time	173
Influence of Glacial Times	173
The Impact of Fossil Fuel CO ₂ on the Ocean-Carbonate	
System.....	174
Concluding Remarks	176

Chapter 5. Composition and Source of Shoal-Water

Carbonate Sediments	179
Introduction.....	179
Shoal-Water Carbonates in Space and Time	179
Carbonate Grains and Skeletal Parts	181
Overview and Examples	181
Sediment Classification.....	189
Depositional Environments	193
Concluding Statement.....	193
Biom mineralization	195
General Aspects.....	195
Environmental Controls on Mineralogy.....	196
Stable Isotopes.....	197
Coprecipitation.....	200
Precipitation of Carbonates from Seawater.....	217
Carbonate Chemistry of Shallow Seawater	217
Abiotic Precipitation of CaCO_3 from Seawater	222
Sources of Aragonite Needle Muds.....	227
Formation of Ooids.....	230
Concluding Remarks	238

Chapter 6. Early Marine Diagenesis of Shoal-Water

Carbonate Sediments	241
Introduction.....	241
Some Preliminary Thermodynamic and Kinetic Considerations ..	241
Very Early Diagenesis.....	249
Major Diagenetic Processes.....	249
Pore Water Chemistry.....	251
Precipitation of Early Carbonate Cements.....	256
Dissolution of Carbonates	268
Concluding Remarks	275

Chapter 7. Early Non-Marine Diagenesis of

Sedimentary Carbonates	277
Introduction.....	277
Plate-Tectonic Controls on Diagenesis	280
General Considerations for Early Non-Marine Diagenesis.....	288
Major Types of Non-Marine Environments.....	288
Water Chemistry	289
Reactivity of Sedimentary Carbonates.....	291

Major Phase Transformations.....	293
The Transformation of Aragonite to Calcite	293
Dolomite Formation.....	295
Summary Remarks.....	308
Mass Transfer During Diagenesis.....	309
General Considerations.....	309
Geochemical Constraints on Mass Transfer	311
Beachrock Formation.....	313
Lithification in the Meteoric Environment	315
Introduction.....	315
The Meteoric Environment and Cement Precipitates.....	318
Bermuda: A Case Study of a Meteoric Diagenetic Environment...330	
Introduction.....	330
Geological Framework.....	331
Limestone Chemistry and Isotopic Composition.....	341
Water Chemistry	346
Carbonate Mass Transfer	350
A Brief Synthesis of Meteoric Diagenesis	353
Diagenetic Stages	353
Effect of Original Mineralogy	357
Climatic Effects.....	360
Rock-Water Relationships.....	364
Mixed Meteoric-Marine Regime	370
Concluding Remarks.....	370

Chapter 8. Carbonates as Sedimentary Rocks in

Subsurface Processes	373
Introduction.....	373
P,T, and X and Carbonate Mineral Stability.....	374
Subsurface Water Chemistry in Sedimentary Basins	380
Continuous Processes	384
Pressure Solution.....	384
Dolomitization	387
Mud to Spar Neomorphism	391
Secondary Porosity	393
Cementation in the Subsurface	396
Examples of "Models" of Long-Term Diagenesis	400
The Present Ocean Setting.....	400
The Present Continental Setting	423
Concluding Remarks.....	446

Chapter 9. The Current Carbon Cycle and Human Impact.....	447
Introduction.....	447
Modern Biogeochemical Cycle of Carbon.....	448
A Model for the Cycle of Carbon	448
Methane and Carbon Monoxide Fluxes.....	451
CO ₂ Fluxes	455
Human Impact on Carbon Fluxes.....	459
The Fossil Fuel and Land Use Fluxes	459
Observed Atmospheric CO ₂ Concentration Increase.....	464
Future Atmospheric CO ₂ Concentration Trends.....	468
Consequences of Increased Atmospheric CO ₂ Levels	471
The Oceanic System	479
Sources of Calcium, Magnesium, and Carbon	
for Modern Oceans	479
Mass Balance of Ca, Mg, and C in Present Oceans.....	497
Oceanic Mass Balance of Elements Interactive	
with Ca, Mg, and C.....	504
Concluding Remarks.....	509
 Chapter 10. Sedimentary Carbonates in the Evolution of	
Earth's Surface Environment.....	511
Introduction.....	511
Sedimentary Rock Mass-Age Distributions.....	512
Secular Trends in Sedimentary Rock Properties.....	517
Lithologic Types.....	517
Chemistry and Mineralogy.....	521
Carbon Cycling Modeling	553
Introduction and Development of a Global Model.....	553
Glacial-Interglacial Changes of Carbon Dioxide.....	565
Long-Term Changes of Atmospheric CO ₂	571
Phanerozoic Cycling of Sedimentary Carbonates.....	577
Synopsis of the Origin and Evolution of the Hydrosphere-	
Atmosphere-Sedimentary Lithosphere.....	582
Origin of the Hydrosphere	582
The Early Stages.....	584
The Transitional Stage.....	589
Modern Conditions	592
Concluding Remarks	596

Epilogue599

 Introduction.....599

 The Road Traveled.....599

 The State of the Art.....602

 Ever Onward604

References.....609

Index681