

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 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 |
| Biomineralization | 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

Index.....681