

# Carbon in Earth

75 *Reviews in Mineralogy and Geochemistry* 75

## TABLE OF CONTENTS

### 1

#### Why Deep Carbon?

*Robert M. Hazen, Craig M. Schiffrins*

FRONTIERS OF DEEP CARBON RESEARCH .....	4
ACKNOWLEDGMENTS.....	5
REFERENCES .....	5

### 2

#### Carbon Mineralogy and Crystal Chemistry

*Robert M. Hazen, Robert T. Downs  
Adrian P. Jones, Linda Kah*

INTRODUCTION .....	7
SYSTEMATIC CARBON MINERALOGY .....	8
Carbon allotropes.....	8
Carbides .....	13
Rhombohedral carbonates .....	19
The aragonite group.....	27
Other anhydrous carbonates .....	28
Hydrous carbonates .....	31
Minerals incorporating organic molecules .....	32
Mineral-molecule interactions.....	34
CONCLUSIONS: UNRESOLVED QUESTIONS IN CARBON MINERALOGY .....	35
ACKNOWLEDGMENTS.....	35
REFERENCES .....	36

### 3

#### Structure, Bonding, and Mineralogy of Carbon at Extreme Conditions

*Artem R. Oganov, Russell J. Hemley,  
Robert M. Hazen, Adrian P. Jones*

INTRODUCTION .....	47
THEORETICAL CONSIDERATIONS.....	48
ELEMENTAL CARBON .....	49
Stable phases .....	49
Metastable phases .....	52

Fullerenes at pressure .....	54
Ultrahigh-pressure phases .....	55
CARBIDES .....	55
MOLECULAR FRAMEWORK STRUCTURES .....	57
Carbon dioxide .....	57
Other compounds.....	61
CARBONATES .....	63
Behavior of $sp^2$ carbonates .....	63
High-pressure $sp^3$ carbonates.....	64
Silicate carbonates.....	66
CONCLUSIONS.....	68
ACKNOWLEDGMENTS.....	70
REFERENCES .....	70

## 4 Carbon Mineral Evolution

*Robert M. Hazen, Robert T. Downs,  
Linda Kah, Dimitri Sverjensky*

INTRODUCTION .....	79
STAGES OF CARBON MINERAL EVOLUTION .....	80
The era of Earth's accretion .....	81
The era of crust and mantle processing .....	83
The era of the evolving biosphere .....	86
CONCLUSIONS: UNRESOLVED QUESTIONS IN CARBON MINERAL EVOLUTION .....	96
ACKNOWLEDGMENTS.....	97
REFERENCES .....	97

## 5 The Chemistry of Carbon in Aqueous Fluids at Crustal and Upper-Mantle Conditions: Experimental and Theoretical Constraints

*Craig E. Manning, Everett L. Shock,  
Dimitri A. Sverjensky*

INTRODUCTION .....	109
Carbon in aqueous fluids of crust and mantle .....	110
Sources of carbon in aqueous fluids of the crust and mantle .....	110
OXIDIZED CARBON IN AQUEOUS FLUIDS AT HIGH $P$ AND $T$ .....	112
Aqueous fluids at high $P$ and $T$ .....	113
$CO_2$ - $H_2O$ mixing and miscibility.....	123
REDUCED CARBON IN AQUEOUS FLUIDS AT HIGH $P$ AND $T$ .....	128
$CH_4$ and $CO$ solubility in $H_2O$ .....	128
Kinetic inhibition of $CH_4$ formation.....	129
Reduced carbon and aqueous fluids at high $P$ and $T$ .....	131

CONCLUDING REMARKS.....	138
ACKNOWLEDGMENTS.....	138
REFERENCES .....	138

## 6

### Primordial Origins of Earth's Carbon

*Bernard Marty, Conel M. O'D. Alexander,  
Sean N. Raymond*

INTRODUCTION .....	149
CARBON IN THE UNIVERSE .....	150
Nucleosynthesis of carbon and stellar evolution .....	150
Galactic chemical evolution .....	152
Carbon in the interstellar medium and the presolar molecular cloud.....	152
Carbon content and isotopic composition of the solar nebula.....	152
Volatile abundances and isotope compositions in comets with special reference to carbon .....	154
Interplanetary dust particles .....	155
Meteorites .....	156
The organic matter in chondrites—relationship to IDPs, comets, and ISM.....	158
THE SOLAR SYSTEM: DYNAMICS.....	159
CLUES TO THE ORIGIN OF CARBON ON EARTH .....	165
Terrestrial carbon inventory .....	165
Volatile (C-H-N-noble gas) elemental and isotopic constraints .....	168
Inferences on the nature of Earth's building blocks .....	169
Is cosmic dust a major source of terrestrial volatiles?.....	170
CARBON TRAPPING IN EARTH .....	172
ACKNOWLEDGEMENTS .....	173
REFERENCES .....	173

## 7

### Ingassing, Storage, and Outgassing of Terrestrial Carbon through Geologic Time

*Rajdeep Dasgupta*

INTRODUCTION .....	183
CARBON INHERITANCE — MAGMA OCEAN CARBON CYCLE .....	184
Magma ocean carbon cycle during core formation .....	184
Magma ocean carbon cycle after core formation .....	191
CARBON RETENTION: MODULATING MANTLE CARBON BUDGET THROUGH THE WILSON CYCLE.....	200
Carbon cycle in an ancient Earth with greater thermal vigor: an era of more efficient outgassing?.....	201
Inefficient subduction of carbon in the Archean and Proterozoic?.....	203
Carbon ingassing in modern Earth .....	209
Stable forms of carbon in the modern mantle and carbon outgassing.....	214

CONCLUDING REMARKS .....	219
ACKNOWLEDGMENTS .....	220
REFERENCES .....	220

## **8**                      **Carbon in the Core: Its Influence on the Properties of Core and Mantle**

*Bernard J. Wood, Jie Li,  
Anat Shahar*

INTRODUCTION .....	231
CARBON ISOTOPES AND CARBON CONTENT OF THE CORE .....	233
DENSITY AND PHASE DIAGRAM CONSTRAINTS	
ON THE CARBON CONTENT OF THE CORE .....	238
The Fe-C phase diagram.....	238
Densities of iron carbides .....	239
Sound velocities of Fe, Fe <sub>3</sub> C and those of the inner core.....	241
CARBON IN THE CORE AND SIDEROPHILE ELEMENTS IN THE MANTLE.....	243
CONCLUSIONS.....	245
ACKNOWLEDGMENTS.....	247
REFERENCES .....	247

## **9**                      **Carbon in Silicate Melts**

*Huaiwei Ni, Hans Keppler*

INTRODUCTION .....	251
CARBON SOLUBILITY IN SILICATE MELTS .....	251
CO <sub>2</sub> solubility in nominally anhydrous melts.....	252
CO <sub>2</sub> solubility in hydrous melts.....	259
Solubility of C-O-H fluids under reduced conditions.....	263
CARBON SPECIATION IN SILICATE MELTS .....	266
Spectroscopic information on speciation.....	266
Carbon speciation in silicate glasses .....	270
Equilibrium carbon speciation in silicate melts.....	274
PHYSICAL PROPERTIES OF CARBON-BEARING SILICATE MELTS .....	277
Viscosity and electrical conductivity .....	277
Density and molar volume.....	280
Diffusivity of carbon .....	280
FUTURE DIRECTIONS .....	282
ACKNOWLEDGMENTS.....	282
REFERENCES .....	283

# 10

## Carbonate Melts and Carbonatites

*Adrian P. Jones, Matthew Genge  
Laura Carmody*

INTRODUCTION .....	289
CARBONATE MELTS .....	291
Physical properties.....	291
Atomic structure of carbonate melts.....	292
Carbonate melts as ionic liquids.....	292
Cation electronegativity ( $\chi$ ) .....	292
Speciation .....	294
Carbonate glasses .....	295
Atomic simulation of carbonates.....	296
CARBONATITES.....	296
Occurrence of carbonatites .....	298
Geochemistry of carbonatites .....	301
Carbonatite mineral deposits.....	304
Isotopic signatures of carbonatites .....	305
GENESIS OF CARBONATITE MAGMAS.....	308
Carbonate melt metasomatism .....	309
Carbonate melt crystallization of diamond.....	310
Magmas related to carbonate melts.....	310
FUTURE RESEARCH .....	311
Carbonatites at high-pressure .....	311
Melt structure of tetracarbonates? .....	312
ACKNOWLEDGMENTS.....	312
REFERENCES .....	312

# 11

## Deep Carbon Emissions from Volcanoes

*Michael R. Burton,  
Georgina M. Sawyer,  
Domenico Granieri*

INTRODUCTION: VOLCANIC CO <sub>2</sub> EMISSIONS	
IN THE GEOLOGICAL CARBON CYCLE .....	323
Carbon species in Earth degassing .....	325
METHODS FOR MEASURING GEOLOGICAL CO <sub>2</sub> EFFLUX.....	325
Ground-based measurements of volcanic plumes .....	325
Volcanic SO <sub>2</sub> flux measurements.....	327
Airborne measurements of volcanic plumes .....	328
Space-based measurements of volcanic plumes.....	329
Ground-based measurements of diffuse deep CO <sub>2</sub> .....	329
Diffusive degassing of deep CO <sub>2</sub> in tectonically active areas.....	330
Submarine measurements.....	331
REPORTED MEASUREMENTS OF DEEP CARBON FLUXES.....	332

Subaerial volcanism.....	332
Submarine volcanism .....	340
INVENTORIES OF GLOBAL VOLCANIC DEEP CARBON FLUX:	
IMPLICATIONS FOR THE GEOLOGICAL CARBON CYCLE.....	340
Estimates of global deep carbon emission rates.....	340
Comparison with previous estimates of subaerial volcanic CO <sub>2</sub> flux.....	342
Balancing CO <sub>2</sub> emission rates with weathering and subduction rates.....	342
THE ROLE OF DEEP CARBON IN VOLCANIC ACTIVITY.....	343
Original CO <sub>2</sub> contents of magma .....	343
Importance of a deep exsolved volatile phase on magma dynamics and eruptive style.....	344
MAGNITUDE OF ERUPTIVE DEEP CARBON EMISSIONS .....	344
SUMMARY .....	345
ACKNOWLEDGMENTS.....	346
REFERENCES .....	346

## 12

### Diamonds and the Geology of Mantle Carbon

*Steven B. Shirey, Pierre Cartigny,  
Daniel J. Frost, Shantanu Keshav,  
Fabrizio Nestola, Paolo Nimis,  
D. Graham Pearson, Nikolai V. Sobolev,  
Michael J. Walter*

INTRODUCTION TO DIAMOND CHARACTERISTICS.....	355
Introduction .....	355
Microscale components in diamonds .....	361
Internal textures in diamonds .....	368
DIAMOND FORMATION.....	369
Experimental and thermodynamic constraints of growth in the lithospheric mantle .....	369
Experimental and thermodynamic constraints of growth in the sub-lithospheric mantle .....	375
Stable isotopic compositions and the formation of diamonds.....	376
INCLUSIONS HOSTED IN DIAMONDS .....	382
Thermobarometry .....	382
Geochemistry and age .....	386
GEOLOGY OF MANTLE CARBON FROM DIAMONDS .....	396
Geodynamics, carbon mobility and reservoirs .....	396
OUTSTANDING QUESTIONS AND FUTURE WORK.....	406
ACKNOWLEDGMENTS.....	406
REFERENCES .....	406

# 13

## Nanoprobes for Deep Carbon

*Wendy L. Mao, Eglantine Boulard*

INTRODUCTION .....	423
SYNTHESIZING SAMPLES AT HIGH PRESSURES AND TEMPERATURES.....	423
High pressure.....	424
High temperature.....	424
Spatial resolution.....	425
<i>EX SITU</i> TECHNIQUES .....	426
Sample preparation: FIB-SEM.....	426
Characterization tools.....	428
<i>IN SITU</i> TECHNIQUES .....	435
Nanoscale X-ray diffraction .....	436
X-ray Raman spectroscopy.....	438
X-ray imaging.....	440
CONCLUSIONS AND OUTLOOK.....	444
REFERENCES .....	445

# 14

## On the Origins of Deep Hydrocarbons

*Mark A. Sephton, Robert M. Hazen*

INTRODUCTION .....	449
BIOGENIC ORIGINS OF DEEP HYDROCARBONS .....	449
Types of hydrocarbons.....	449
Diagenesis and kerogen formation .....	450
ABIOTIC ORIGINS OF DEEP HYDROCARBONS .....	451
Deep gas theories .....	451
Thomas Gold and the “Deep Hot Biosphere” .....	451
Evidence for abiotic hydrocarbon synthesis.....	452
DETERMINING SOURCE—CHEMICAL EVIDENCE .....	454
Pyrolysis experiments.....	454
Molecular biomarkers .....	455
DETERMINING SOURCE—GEOLOGIC EVIDENCE.....	457
Association with temperature and source rocks .....	457
SELECTED CASE STUDIES .....	458
Mountsorrel, United Kingdom .....	458
The Songliao Basin, China .....	459
CONCLUSIONS: UNRESOLVED QUESTIONS IN THE ORIGINS OF DEEP HYDROCARBONS.....	459
ACKNOWLEDGMENTS.....	460
REFERENCES .....	460

## 15

### Laboratory Simulations of Abiotic Hydrocarbon Formation in Earth's Deep Subsurface

*Thomas M. McCollom*

INTRODUCTION .....	467
ABIOTIC HYDROCARBONS IN EARTH'S UPPER MANTLE.....	468
The chemical and physical environment of Earth's upper mantle.....	468
Experimental studies of hydrocarbons at mantle conditions.....	468
Implications for mantle sources of hydrocarbons .....	473
ABIOTIC HYDROCARBON FORMATION IN CRUSTAL ENVIRONMENTS .....	474
Chemical and physical environments for hydrocarbon formation in the crust.....	474
Fischer-Tropsch-type synthesis .....	476
Alternative pathways for hydrocarbon formation in the crust.....	487
SOME DIRECTIONS FOR FUTURE STUDIES .....	490
ACKNOWLEDGMENTS.....	490
REFERENCES .....	490

## 16

### Hydrocarbon Behavior at Nanoscale Interfaces

*David R. Cole, Salim Ok,  
Alberto Striolo, Anh Phan*

INTRODUCTION .....	495
Probing C-O-H behavior with neutron scattering and NMR.....	498
NON-AQUEOUS FLUID ADSORPTION BEHAVIOR: EXPERIMENTAL .....	499
Background on adsorption concepts and approaches.....	499
C-O-H pore fluid densities.....	501
Hydrocarbon-interfacial microstructure .....	503
NON-AQUEOUS FLUID DYNAMICS AT INTERFACES: EXPERIMENTAL .....	506
QENS probe of hydrocarbons in nanopores .....	506
NMR probes of hydrocarbons in nanopores.....	509
Representative NMR studies .....	511
ATOMIC AND MOLECULAR-LEVEL SIMULATIONS .....	515
Properties of confined fluids: do they differ compared to the bulk?.....	515
Selected simulations of alkanes within alumina and silica-based pores .....	525
Simulation details .....	531
SUMMARY AND RECOMMENDATIONS.....	534
ACKNOWLEDGMENTS.....	535
REFERENCES .....	536

## 17

### Nature and Extent of the Deep Biosphere

*Frederick S. Colwell, Steven D'Hondt*

INTRODUCTION .....	547
EARLY STUDIES AND COMPREHENSIVE REVIEWS .....	547
WHERE WE ARE NOW – THE TERROIR OF SUBSURFACE LIFE.....	548
THE TOOLS THAT WE NEED .....	550
THERE'S NO PLACE LIKE HOME.....	553
IS DIVERSITY THE SPICE OF SUBSURFACE LIFE?.....	555
BIOMASS OF SUBSURFACE LIFE.....	557
PHYSIOLOGICAL PROCESSES OF SUBSURFACE LIFE.....	558
WHERE AND WHEN DOES LIFE IN THE SUBSURFACE REALLY MATTER TO US?.....	560
PROJECTIONS AND PRIORITIES FOR FUTURE STUDIES.....	562
Imagining how we might sample and visualize deep life.....	563
Unexplored adaptations of subsurface microbes.....	563
Unstudied physiologies and genotypes for the subsurface.....	564
Subsurface coupling of the living and the non-living.....	565
SUMMARY .....	566
ACKNOWLEDGMENTS.....	566
REFERENCES .....	566

## 18

### Serpentinization, Carbon, and Deep Life

*Matthew O. Schrenk, William J. Brazelton,  
Susan Q. Lang*

INTRODUCTION .....	575
THE PROCESS OF SERPENTINIZATION .....	575
Physical and chemical consequences of serpentinization .....	575
Types of serpentinizing habitats .....	577
BIOLOGICAL CONSEQUENCES OF SERPENTINIZATION .....	583
Metabolic strategies in serpentinite-hosted ecosystems.....	583
Challenges of high pH.....	591
Limitations to carbon fixation .....	591
Sources of nutrients .....	593
Microbe-mineral interactions .....	594
Serpentinization and the origins of life .....	594
WHERE DOES THE ABIOTIC CARBON CYCLE END AND BIOGEOCHEMISTRY BEGIN?.....	597
Abiogenesis in thermodynamic and experimental studies .....	597
Distinguishing biotic from abiotic processes .....	598
Linking abiotic and biological processes .....	599
COMMON THEMES AND UNCHARTED TERRITORY .....	600
ACKNOWLEDGMENTS.....	601
REFERENCES .....	601

## 19

### High-Pressure Biochemistry and Biophysics

*Filip Meersman, Isabelle Daniel,  
Douglas H. Bartlett, Roland Winter  
Rachael Hazael, Paul F. McMillan*

INTRODUCTION .....	607
PROTEINS AND POLYPEPTIDES .....	608
Structures of proteins and polypeptides .....	608
Thermodynamic considerations: volume <i>versus</i> compressibility arguments .....	609
The protein volume paradox.....	610
Mechanistic aspects of pressure-induced protein unfolding .....	611
Pressure effects on multimeric proteins and aggregates.....	612
Pressure effects on protein energy landscapes .....	613
From free energy landscapes to <i>P-T</i> phase diagrams .....	616
Kinetic aspects of the phase diagram .....	619
Relevance of biophysical studies on proteins to deep carbon .....	620
NUCLEIC ACIDS.....	620
LIPIDS AND CELL MEMBRANES .....	622
Lamellar lipid bilayer phases.....	622
Lipid mixtures, cholesterol, and peptides.....	626
Nonlamellar lipid phases .....	628
Biological and reconstituted membranes.....	630
Relevance of lipid biophysics for deep carbon.....	631
HIGH-PRESSURE MICROBIOLOGY AND BIOCHEMICAL CYCLES .....	632
Who’s down there? .....	632
Genomic attributes at depth.....	634
Metabolism: organic matter, energy and nutrients .....	636
ACQUISITION OF RESISTANCE TO GIGAPASCAL PRESSURES .....	637
Exploring extreme pressure limits for life.....	637
Acquisition of gigapascal pressure resistance by higher organisms.....	638
Resistance to extreme shock pressures.....	639
CONCLUSIONS.....	640
ACKNOWLEDGMENTS.....	640
REFERENCES .....	640

## 20

### The Deep Viriosphere: Assessing the Viral Impact on Microbial Community Dynamics in the Deep Subsurface

*Rika E. Anderson, William J. Brazelton,  
John A. Baross*

INTRODUCTION .....	649
DIVERSITY IN THE VIRAL WORLD .....	650
Viral life cycles.....	650
Viral sizes and morphologies.....	652

Genetic diversity .....	654
VIRAL IMPACTS ON HOST ECOLOGY AND EVOLUTION.....	654
Bottom-up effects: the biogeochemical impact.....	655
Top-down effects: altering population structure.....	655
Viral manipulation of genetic content and expression .....	657
VIRAL MANIPULATION OF THE DEEP SUBSURFACE BIOSPHERE .....	658
Hydrologically active regions of the subsurface .....	658
Deeply buried sediments .....	660
Viral impacts on surface-attached communities.....	661
Tools for analysis: viral metagenomics in the deep subsurface.....	662
VENTS, VIRUSES AND THE ORIGIN OF LIFE.....	666
Hydrothermal vents and the deep subsurface: key settings in the origin of life.....	666
The viral role in the origin of life .....	667
CONCLUSION.....	669
REFERENCES .....	670