

THE ORIGIN AND NATURE OF LIFE ON EARTH

The Emergence of the Fourth Geosphere

Uniting the conceptual foundations of the physical sciences and biology, this groundbreaking multi-disciplinary book explores the origin of life as a planetary process.

Combining geology, geochemistry, biochemistry, microbiology, evolution, and statistical physics to create an inclusive picture of the living state, the authors develop the argument that the emergence of life was a necessary cascade of non-equilibrium phase transitions that opened new channels for chemical energy flow on Earth. This full-color and logically structured book introduces the main areas of significance and provides a well-ordered and accessible introduction to multiple literatures outside the confines of disciplinary specializations, as well as including an extensive bibliography to provide context and further reading.

For researchers, professionals entering the field, or specialists looking for a coherent overview, this text brings together diverse perspectives to form a unified picture of the origin of life and the ongoing organization of the biosphere.

ERIC SMITH is External Professor at the Santa Fe Institute, Research Professor at George Mason University, and Principal Investigator at the Earth-Life Science Institute, Tokyo Institute of Technology. He is a physicist specializing in the origin of life, non-equilibrium systems, economics, and the evolution of human languages.

HAROLD J. MOROWITZ is Clarence J. Robinson Professor of Biology and Natural Philosophy at George Mason University. He was the founding director of the Krasnow Institute for Advanced Study at George Mason University, and is Chairman Emeritus of the Science Board at the Santa Fe Institute.

THE ORIGIN AND NATURE OF LIFE ON EARTH

The Emergence of the Fourth Geosphere

ERIC SMITH

*Santa Fe Institute
George Mason University
Tokyo Institute of Technology*

HAROLD J. MOROWITZ

George Mason University



CAMBRIDGE
UNIVERSITY PRESS

Cambridge University Press & Assessment
 978-1-009-63377-2 — The Origin and Nature of Life on Earth
 Eric Smith, Harold J. Morowitz
 Frontmatter
[More Information](#)



CAMBRIDGE
UNIVERSITY PRESS

Shaftesbury Road, Cambridge CB2 8EA, United Kingdom
 One Liberty Plaza, 20th Floor, New York, NY 10006, USA
 477 Williamstown Road, Port Melbourne, VIC 3207, Australia
 314–321, 3rd Floor, Plot 3, Splendor Forum, Jasola District Centre, New Delhi – 110025, India
 103 Penang Road, #05–06/07, Visioncrest Commercial, Singapore 238467

Cambridge University Press is part of Cambridge University Press & Assessment,
 a department of the University of Cambridge.

We share the University's mission to contribute to society through the pursuit of
 education, learning and research at the highest international levels of excellence.

www.cambridge.org

Information on this title: www.cambridge.org/9781009633772

© Cambridge University Press & Assessment 2016

This publication is in copyright. Subject to statutory exception and to the provisions
 of relevant collective licensing agreements, no reproduction of any part may take
 place without the written permission of Cambridge University Press & Assessment.

First published 2016

Reprinted 2018

First paperback edition 2025

A catalogue record for this publication is available from the British Library

Library of Congress Cataloging-in-Publication data

Names: Smith, Eric, 1965– author. | Morowitz, Harold J., author.

Title: The origin and nature of life on Earth : the emergence of the fourth
 geosphere / Eric Smith (Santa Fe Institute, George Mason University, Tokyo
 Institute of Technology), Harold J. Morowitz (George Mason
 University, Virginia).

Description: New York, NY : Cambridge University Press, [2016] | ?2016

Identifiers: LCCN 2015041999 | ISBN 9781107121881 | ISBN 1107121884

Subjects: LCSH: Life–Origin. | Earth (Planet)–Origin. | Biosphere. | Earth
 sciences.

Classification: LCC QH325 .S56 2016 | DDC 570–dc23

LC record available at <http://lcn.loc.gov/2015041999>

ISBN 978-1-107-12188-1 Hardback

ISBN 978-1-009-63377-2 Paperback

Cambridge University Press & Assessment has no responsibility for the persistence
 or accuracy of URLs for external or third-party internet websites referred to in this
 publication and does not guarantee that any content on such websites is, or will
 remain, accurate or appropriate.

Contents

<i>Preface</i>	<i>page</i> xiii
<i>Acknowledgments</i>	xxiii
1 The planetary scope of biogenesis: the biosphere is the fourth geosphere	1
1.1 A new way of being organized	1
1.1.1 Life is a planetary process	2
1.1.2 Drawing from many streams of science	5
1.2 The organizing concept of geospheres	6
1.2.1 The three traditional geospheres	7
1.2.2 The interfaces between geospheres	8
1.2.3 The biosphere is the fourth geosphere	10
1.3 Summary of main arguments of the book	12
1.3.1 An approach to theory that starts in the phenomenology of the biosphere	13
1.3.2 Placing evolution in context	16
1.3.3 Chance and necessity understood within the larger framework of phase transitions	22
1.3.4 The emergence of the fourth geosphere and the opening of organic chemistry on Earth	28
1.4 The origin of life and the organization of the biosphere	31
2 The organization of life on Earth today	35
2.1 Many forms of order are fundamental in the biosphere	35
2.1.1 Three conceptions of essentiality	37
2.1.2 The major patterns that order the biosphere	37
2.2 Ecosystems must become first-class citizens in biology	40
2.2.1 No adequate concept of ecosystem identity in current biology	40
2.2.2 Ecosystems are not super-organisms	41
2.2.3 Ecological patterns can transcend the distinction between individual and community dynamics	42
	v

2.3	Bioenergetic and trophic classification of organism-level and ecosystem-level metabolisms	42
2.3.1	Divergence and convergence: phylogenetic and typological classification schemes	43
2.3.2	The leading typological distinctions among organisms	45
2.3.3	Anabolism and catabolism: the fundamental dichotomy corresponding to the biochemical and ecological partitions	50
2.3.4	Ecosystems, in aggregate function, are simpler and more universal than organisms	51
2.3.5	Universality of the chart of intermediary metabolism	56
2.4	Biochemical pathways are among the oldest fossils on Earth	58
2.4.1	Evidence that currently bounds the oldest cellular life	58
2.4.2	Disappearance of the rock record across the Hadean horizon	58
2.4.3	Metabolism: fossil or Platonic form?	59
2.5	The scales of living processes	60
2.5.1	Scales of biochemistry	60
2.5.2	Scales of physical organization	64
2.5.3	Scales of information and control	64
2.6	Diversity within the order that defines life: the spectrum from necessity to chance	66
2.6.1	How contingency has been extrapolated from modern evolution to origins	67
2.6.2	Natural selection for change and for conservation	68
2.6.3	Different degrees of necessity for different layers	68
2.7	Common patterns recapitulated at many levels	70
3	The geochemical context and embedding of the biosphere	73
3.1	Order in the abiotic context for life	73
3.1.1	Many points of contact between living and non-living energetics and order	74
3.1.2	Barriers, timescales, and structure	75
3.2	Activation energy and relaxation temperature regimes in abiotic chemistry and metabolism	75
3.3	Stellar and planetary systems operate in a cascade of disequilibria	77
3.3.1	The once young and now middle-aged Sun	77
3.3.2	Disequilibria in the Earth are gated by a hierarchy of phases and associated diffusion timescales	82
3.4	The restless chemical Earth	106
3.4.1	Mafic and felsic: ocean basins and continental rafts	107
3.4.2	Three origins of magmas	108

Contents

vii

3.5	The dynamics of crust formation at submarine spreading centers	115
3.5.1	Melt formation and delivery at mid-ocean ridges	116
3.5.2	Tension, pressure, brittleness, and continual fracturing	117
3.5.3	Fractures, water invasion, buoyancy, and the structure of hydrothermal circulation systems	119
3.5.4	Chemical changes of rock and water in basalt-hosted systems	126
3.5.5	Serpentinization in peridotite-hosted hydrothermal systems	131
3.5.6	Principles and parameters of hydrothermal alteration: a summary	138
3.6	The parallel biosphere of chemotrophy on Earth	140
3.6.1	The discovery of ecosystems on Earth that do not depend on photosynthetically fixed carbon	140
3.6.2	The evidence for a deep (or at least subsurface), hot (or at least warm) biosphere	142
3.6.3	The complex associations of temperature, chemistry, and microbial metabolisms	148
3.6.4	Major classes of redox couples that power chemotrophic ecosystems today	150
3.6.5	Why the chemotrophic biosphere has been proposed as a model for early life	155
3.6.6	Differences between hydrothermal systems today and those in the Archean	157
3.6.7	Feedback from the biosphere to surface mineralogy	167
3.7	Expectations about the nature of life	168
4	The architecture and evolution of the metabolic substrate	170
4.1	Metabolism between geochemistry and history	170
4.2	Modularity in metabolism, and implications for the origin of life	173
4.2.1	Modules and layers in metabolic architecture and function	173
4.2.2	Reading through the evolutionary palimpsest	174
4.2.3	Support for a progressive emergence of metabolism	175
4.2.4	Feedbacks, and bringing geochemistry under organic control	175
4.2.5	The direction of propagation of constraints: upward from metabolism to higher-level aggregate structures	176
4.3	The core network of small metabolites	178
4.3.1	The core in relation to anabolism and catabolism	180
4.3.2	The core of the core	182
4.3.3	Precursors in the citric acid cycle and the primary biosynthetic pathways	183
4.3.4	One-carbon metabolism in relation to TCA and anabolism	192
4.3.5	The universal covering network of autotrophic carbon fixation	196
4.3.6	Description of the six fixation pathways	200

4.3.7	Pathway alignments and redundant chemistry	214
4.3.8	Distinctive initial reactions and conserved metal-center enzymes	216
4.3.9	The striking lack of innovation in carbon fixation	217
4.4	A reconstructed history of carbon fixation, and the role of innovation constraints in history	219
4.4.1	Three reasons evolutionary reconstruction enters the problem of finding good models for early metabolism	219
4.4.2	Phylogenetic reconstruction of functional networks	221
4.4.3	Functional and comparative assignment of biosynthetic pathways in modern clades	224
4.4.4	A maximum-parsimony tree of autotrophic carbon-fixation networks	230
4.4.5	A reconstruction of <i>Aquifex aeolicus</i> and evidence for broad patterns of evolutionary directionality	241
4.4.6	The rise of oxygen and the attending change in metabolism and evolutionary dynamics	244
4.4.7	Chance and necessity for oxidative versus reductive TCA	248
4.5	Cofactors and the first layer of molecular-organic control	249
4.5.1	The intermediate position of cofactors, feedback, and the emergence of metabolic control	249
4.5.2	Key cofactor classes for the earliest elaboration of metabolism	253
4.5.3	The complex amino acids as cofactors	261
4.5.4	Situating cofactors within the elaboration of the small-molecule metabolic substrate network	262
4.5.5	Roles of the elements and evolutionary convergences	264
4.6	Long-loop versus short-loop autocatalysis	268
4.7	Summary: continuities and gaps	269
4.8	Graphical appendix: definition of notations for chemical reaction networks	270
4.8.1	Definition of graphic elements	271
5	Higher-level structures and the recapitulation of metabolic order	273
5.1	Coupled subsystems and shared patterns	273
5.1.1	Shared boundaries: correlation is not causation	274
5.1.2	Different kinds of modularity have changed in different directions under evolution	275
5.2	Metabolic order recapitulated in higher-level aggregate structures	277
5.3	Order in the genetic code: fossils of the emergence of translation?	278
5.3.1	Context for the code: the watershed of the emergence of translation	283
5.3.2	The modern translation system could be a firewall	285

5.3.3	What kinds of information does a pattern contain, and how much?	287
5.3.4	Part of the order in the code is order in the amino acid inventory	290
5.3.5	Four major forms of metabolic order in the code	291
5.3.6	Rule combinations	302
5.3.7	Accounting for order	306
5.3.8	A proposal for three phases in the emergence of translation	319
5.4	The essential role of bioenergetics in both emergence and control	322
5.4.1	Energy conservation, energy carriers, and entropy	323
5.4.2	Three energy buses: reductants, phosphates, and protons	325
5.4.3	The cellular energy triangle	328
5.4.4	Geochemical context for emergence of redox and phosphate energy systems	330
5.5	The three problems solved by cellularization	331
5.5.1	Distinct functions performed by distinct subsystems	332
5.5.2	An exercise in transversality	333
5.6	The partial integration of molecular replication with cellular metabolism	337
5.7	Cellular life is a confederacy	338
6	The emergence of a biosphere from geochemistry	340
6.1	From universals to a path of biogenesis	340
6.1.1	On empiricism and theory: evaluating highly incomplete scenarios	341
6.1.2	The functions versus the systems chemistry of RNA	344
6.1.3	An emergent identity for metabolism or the emergence of a control paradigm?	349
6.2	Planetary disequilibria and the departure toward biochemistry	355
6.2.1	The partitioning role of the abiotic geospheres	356
6.2.2	Species that bridge geosphere boundaries to form the great arcs of planetary chemical disequilibrium	359
6.2.3	Mineral-hosted hydrothermal systems are pivotal in the sense that they are key <i>focusing centers</i> for chemical disequilibria	366
6.2.4	The alkaline hydrothermal vents model	368
6.3	Stages in the emergence of the small-molecule network	370
6.3.1	Carbon reduction and the first C—C bonds	371
6.3.2	rTCA: the potential for self-amplification realized and the first strong selection of the metabolic precursors	384
6.3.3	Reductive amination of α -ketones and the path to amino acids	387
6.3.4	A network of sugar phosphates and aldol reactions	388
6.4	The early organic feedbacks	389
6.4.1	C—N heterocycles	391
6.4.2	Cyclohydrolase reactions: purine nucleotides and folates	396

6.4.3	Thiamin-like chemistry: lifting rTCA off the rocks	398
6.4.4	Biotin: uses in rTCA and in fatty acid synthesis	399
6.4.5	Alkyl thiols	399
6.5	Selection of monomers for chirality	400
6.5.1	Degree of enantiomeric selection at different scales	400
6.5.2	Mechanisms and contexts for stereoselectivity	401
6.5.3	The redundancy of biochemical processes simplifies the problem of chiral selection	402
6.6	The oligomer world and molecular replication	403
6.6.1	Increased need for dehydrating ligation reactions	404
6.6.2	Coupling of surfaces and polymerization	405
6.6.3	Distinguishing the source of selection from the emergence of memory in a ribozyme-catalyzed era	407
6.7	Transitions to cellular encapsulation in lipids	409
6.7.1	Contexts that separate the aggregate transformation into independent steps	412
6.8	The advent of the ribosome	413
6.8.1	The core and evolution of catalysis	414
6.8.2	Catalytic RNA and iron	416
6.8.3	The origin of translation and the three-base reading frame	417
6.8.4	Reliable translation and the birth of phylogeny	419
6.9	The major biogeochemical transitions in the evolutionary era	420
6.10	Tentative conclusions: the limits of narrative and the way forward	421
7	The phase transition paradigm for emergence	424
7.1	Theory in the origin of life	424
7.1.1	What does a phase transition framing add to the search for relevant environments and relevant chemistry?	426
7.2	Arriving at the need for a phase transition paradigm	427
7.2.1	Why there is something instead of nothing	428
7.2.2	Selecting pattern from chaos in organosynthesis	430
7.2.3	The phase transition paradigm	431
7.2.4	Developing the stability perspective	432
7.2.5	A chapter of primers	435
7.3	Large deviations and the nature of thermodynamic limits	436
7.3.1	The combinatorics of large numbers and simplified fluctuation-probability distributions	437
7.3.2	Interacting systems and classical thermodynamics	439
7.3.3	Statistical roles of state variables	446
7.3.4	Phase transitions and order parameters	451
7.4	Phase transitions in equilibrium systems	452
7.4.1	Worked example: the Curie–Weiss phase transition	452

	<i>Contents</i>	xi
	7.4.2 Reduction, emergence, and prediction	466
	7.4.3 Unpredictability and long-range order	468
	7.4.4 The hierarchy of matter	471
	7.4.5 Parallels in matter and life: the product space of chemical reactions	479
	7.4.6 Oil and water	481
7.5	The (large-deviations!) theory of asymptotically reliable error correction	486
	7.5.1 Information theory as a mirror on thermodynamics	487
	7.5.2 The large-deviations theory of optimal error correction	488
	7.5.3 Transmission channel models	489
	7.5.4 Capacity and error probability	491
	7.5.5 Error correction and molecular recognition in an energetic system	496
	7.5.6 The theory of optimal error correction is thermodynamic	499
	7.5.7 One signal or many?	500
7.6	Phase transitions in non-equilibrium systems	501
	7.6.1 On the equilibrium entropy and living systems	502
	7.6.2 Ensembles of processes and of histories	509
	7.6.3 Phase transfer catalysis	510
	7.6.4 A first-order, non-equilibrium, phase transition in the context of autocatalysis	511
	7.6.5 The lightning strike analogy	520
	7.6.6 Conclusion: the frontier in the study of collective and cooperative effects	524
7.7	Technical appendix: non-equilibrium large-deviations formulae	525
	7.7.1 Master equation for the one-variable model of autocatalysis	526
	7.7.2 Ordinary power-series generating function and Liouville equation	527
	7.7.3 Escape trajectories and effective potential for non-equilibrium phases	531
	7.7.4 Gaussian fluctuations about stationary-path backgrounds	534
8	Reconceptualizing the nature of the living state	539
8.1	Bringing the phase transition paradigm to life	539
	8.1.1 Necessary order in the face of pervasive disturbance	542
	8.1.2 The role of phase transitions in hierarchical complex systems	544
	8.1.3 How uniqueness becomes a foundation for diversity	549
	8.1.4 Beyond origins to the nature of the living state	552
8.2	Metabolic layering as a form of modular architecture	554
	8.2.1 Herbert Simon's arguments that modularity is prerequisite to hierarchical complexity	554

xii	<i>Contents</i>	
	8.2.2 The modularity argument in a dynamical setting	558
	8.2.3 Error correction from regression to ordered thermal states	558
	8.2.4 The universal metabolic chart as an order parameter	559
	8.2.5 The use of order parameters in induction	561
	8.2.6 Control systems and requisite variety	566
	8.2.7 Biology designs using order parameters	568
8.3	The emergence of individuality	569
	8.3.1 Darwinian evolution is predicated on individuality	570
	8.3.2 How unique solutions give rise to conditions that support diversity	572
	8.3.3 The nature of individual identity	575
	8.3.4 Individuality within the structure of evolutionary theory	580
	8.3.5 The ecosystem as community and as entity	584
	8.3.6 Why material simplicity precedes complexity in the phase transition paradigm	586
8.4	The nature of the living state	587
	8.4.1 Replicators: a distinction but not a definition	589
	8.4.2 Life is defined by participation in the biosphere	591
	8.4.3 Covalent chemistry flux and other order parameters	591
	8.4.4 The importance of being chemical	593
8.5	The error-correcting hierarchy of the biosphere	597
	8.5.1 The main relation: a general trade-off among stability, complexity, and correlation length	597
	8.5.2 Simple and complex phase transitions	598
	8.5.3 Living matter as active data	601
	8.5.4 Patterns and entities in the biosphere	606
	Epilogue	608
	<i>References</i>	611
	<i>Index</i>	660

Preface

It has been almost a century since the inquiry into life's origin has been reinvigorated following several decades of quiescence influenced by Louis Pasteur's elegant experimental demonstration that microbes were not spontaneously generated in flasks of nutrient broth appropriately aerated to prevent the entry of airborne particles. It has been a century in which biochemistry and biophysics have completely altered our core understanding of the living world and consequently opened up a series of powerful experimental, theoretical, and computational approaches. In this new light, two of us independently thinking of first life were some fifteen years ago introduced by colleagues at the Santa Fe Institute who had detected some common points of interest in what we were investigating, one from the top down and the other from the bottom up – from the phenomenology of the living world with an emphasis on biochemistry and biophysics and from the underlying physics and chemistry and statistical theory that impose a necessary order.

A common theme was that life on Earth was not the outcome of an isolated event as suggested by the *Chance and Necessity* school but a planetary property that appeared early in the history of the planet and spread in a spontaneous way. What we designate life or proto-life has existed over most of the lifetime of planet Earth. The universality of the phenomenon and the massive flux of matter and energy due to the huge interaction of organisms and their products with the rest of planetary matter led us to return to the perceptive book *Geochemistry* by Kalervo Rankama and Th. G. Sahama [664], a work highly praised to one of us by the polymath G. Evelyn Hutchinson, dean of American ecologists. The two Finnish geochemists, acting as geological generalists, divided the planet into four *geospheres*: the lithosphere, the hydrosphere, the atmosphere, and the biosphere. The term “biosphere” had been introduced in 1875 by Eduard Suess and used in its modern sense some years later by the perceptive geochemist Vladimir Vernadsky.

What we wish to understand from a scientific point of view is how the newly formed planet, condensing approximately 4.6 billion years ago, was transformed over time into the present verdant world, home to millions of species and the abode of *Homo sapiens*, a taxon including individuals like ourselves, who are somehow impelled to ask the foundational questions that this work tries to answer. What was clear from the outset was that such a study must be embedded in the domains of physicists, chemists, geologists, and biologists

aided by the analytical tools of mathematics and reified by database mining and computation. Using the baseball phraseology of the double play (Tinker to Evers to Chance), we are in the world of Pauli to Pauling to Woese. Wolfgang Pauli provided a formalism to generate the periodic table of elements within the domain of quantum mechanics and particle physics. Linus Pauling has provided the context to see in a systematic way how these atomic elements give rise to a huge number of structures, large and small, that, comprehensibly, are able to perform exquisitely complex chemical functions. Carl Woese showed why in the whole world of biota, phylogeny in its most general sense must be understood from its biochemical foundations as well as seen from its more classical perspectives. He worked at incorporating biochemistry and molecular biology into a more global biological perspective. The whole and its parts must be studied jointly. Several names of scientists have been and will be mentioned in this preface and throughout the book. We tend to think of the discipline in terms of those predecessors upon whose shoulders we stand. Science at its best is a community of scholars, and we have been privileged to have some of these as colleagues and friends.

The universe of entities we deal with has something on the order of twenty million species, yet the metabolic charts of all of these species map in major parts onto a single chart of intermediary metabolism, whose representation was developed and refined by the lifetime labors of scientist Donald Eliot Nicholson and his colleagues. This continuity of metabolism over four billion years and countless present and extinct species argues against the view of life as the outcome of an improbable event. We reject the idea developed in *Chance and Necessity* by Jacques Monod [561] that life is a result of chance whose origin is unfathomable. This view is inconsistent with the world that we know and with the way the living geosphere functions as part of it. We have thus rejected all reliance on “frozen accidents” as a dead end to our investigation of the earliest biosphere. We have also minimized appeals to panspermia, because there is often too much of a “biogenesis-of-the-gaps” character to arguments: we reason at the level of components where we have been unable to form a systems understanding of chemistry on Earth. When some components seem difficult to account for on this planet, we appeal to planets whose chemistry is less well understood than our own as a source for them, generating a host of new system-assembly and causation problems seemingly more intransigent than those with which we began.

We have tried to be guided by an “Earth Scientists Oath” or paraphrasing the prophet Micah we have tried “To achieve a scientist’s love of honesty, to seek our limits of understanding, and to walk humbly in our universe.” Where we have tried to say things that are genuinely new, we have kept our approach embedded in well-understood science.

The wide range of opinions expressed in the scientific community makes it clear that we do not yet have a paradigm, even in its broadest outlines, to explain in any detail the origin of life. The number of fundamental transitions it entailed has been large and some have probably been overwritten by subsequent innovations. The problem will be with us for a long time to come. Within these limitations we hope that this book will aid the community in framing the best and most productive questions within reach of

current understanding. With this goal we include a more eclectic body of material than that usually found in writings on this subject. For example in Chapter 4 and Chapter 6 we review both experimental results on mineral organosynthesis and extensive analysis of variations within the post-LUCA diversification of metabolism, despite the fact the former are too simple and the latter too complex to serve as close models for the transition from geochemistry to the first biochemistry that is our main interest. We have attempted to make our choices so as not to bury the reader in details¹ but to illustrate the extent of repetition or convergence of key motifs, with citations to the primary literature that the interested reader might pursue. From each body of evidence we call out the patterns or mechanisms that we believe impose significant constraints on theories of origins at the difficult and obscure era when the metabolic substrate and its control systems were emerging.

From a somewhat different perspective, in Chapter 7 we provide a basic but wide-ranging review of the theory of stability from statistical mechanics and related disciplines. In part this is necessary because the key mathematical ideas underlying the theory of robust order, which have been one of the main achievements of mathematical physics within the last century, are poorly communicated outside the specific fields where they were derived. The application of formal principles of stability from non-equilibrium statistical mechanics to systems chemistry is a field currently in its infancy, bringing together complex suites of concepts from two already sophisticated fields. Yet it is an inevitable merger, because the emergence of the biosphere was not a compounding of misadventures but a restructuring of systems.

We believe that one of the greater services we can offer may be to lower the costs of entry for readers into each other's literature and main ideas. For human minds in society, professional disciplines have been the portals to expertise, but the emergence of the biosphere was not a respecter of human silos. Few readers who have spent a lifetime becoming experts in geochemistry, biochemistry, or microbiology will have happened across the fact that the theory of robustness in non-equilibrium systems continues seamlessly to the mathematics of asymptotically optimal error correction. Yet this continuity must have been fundamental to the emergence of hierarchical architecture capable of memory and control over metabolism on the route from minerals to cells. Conversely, for readers to whom the "thermodynamics" of error correction is every day's bread and butter (its carbohydrate and triglyceride), there are no easy paths into the enormous literatures of geochemistry and biochemistry that review, at affordable cost, the basic principles of organization in those disciplines. Yet it can only be in context of these principles that any theory of error correction might contribute to an understanding of biogenesis. Our choice of materials and approach is aimed at providing such bridges, so that as a community we might be less outsiders to each other's sensibilities to order in the world.

¹ Christian de Duve, in the fine book *Blueprint for a Cell* [183] deliberately avoided such byways in order to maintain focus on a central narrative and increase reader accessibility. His book, which rewards re-reading even after many years, deserves if anything more than the considerable influence it has already had.

Starting with the belief that conceptual frameworks as well as acquired empirical knowledge, technical methods, and examples from physics, chemistry, biology, and geology are necessary components of the study of biogenesis, we have tried to present material at levels satisfying to domain specialists as well as penetrable from a more general perspective. This sometimes involves saying things more than once at varying levels of detail. A series of boxes set off sub-topics or derivations that will be of interest to readers who want more detail, or glossaries of domain-specific terms to which the text refers repeatedly. Terms of art that might be mistaken for common-language expressions (a frequent problem in the shorthand of technical fields) are typeset in *italic* where they are first used in a chapter. A small subset of terms are highlighted with **boldface** where they are first discussed: these are topics that play a special role in the structure of arguments or signal key ideas. We have tried to strike a balance between inclusiveness and economy to engage the broad range of colleagues whose insights are essential to this story. Of course, our own limitations must be acknowledged.

In a more philosophical mode, we envision the goal of this branch of science as showing how the core of intermediary metabolism is a necessary consequence of galactic processes giving rise to some distribution of the elements of the periodic table, which under the right geochemical boundary conditions generate an autocatalytic network of chemicals capable of emerging subsequently through a series of transitions into more complex molecules and structures: the biosphere. This series of transitions follows matter and its internal states of organization from simplicity to complexity. At the lowest level, non-equilibrium thermal physics appears to be the analytical method of choice. At each transition, new paradigms become necessary as complexification leads to a broader range of possibilities and structures, and opportunities for path dependence. This we have envisioned as biology standing between physics and history, deterministic at the simplicity roots and rife with possibilities at its complexity shoots.

With the above in mind we turn to the organization of this monograph. The first five chapters deal with the phenomenological and its generalizations. What is life on the planet Earth like and how did it get that way? In choosing which aspects to review, we draw on what the core scientific disciplines have made it possible to understand, and within this we select the patterns that we believe best assemble into a system that is coherent within the more inclusive body of scientific laws. Chapter 6 sketches the synthesis that we believe the foregoing facts support.

Facts, however, are not self-interpreting, and proposed scenarios are not theories. Everything we review in the first five chapters is known within the scientific community, but the system we propose in Chapter 6 has not seemed an inevitable or even compelling interpretation to all readers, for reasons we understand. Chapters 7 and 8 introduce other parts of the reasoning that we believe are needed for inference from facts to theories. Chapter 7, like the first five chapters, does not speculate and sticks to what we know, but in this case we consider what is known about stability and its relation to information. To gently contradict Wittgenstein, the world is a totality of facts, *and* of things, and we believe the introductions to both work best when made in each other's company. Chapter 8 brings these two streams

together in what we hope will provide a foundation for a proper theory. It explains some of the priorities we have expressed in the first five chapters, from the perspective in Chapter 7 that a formal theory of stability and robustness exists and that it has implications. We note there, too, that one measure of the plausibility of a theory of biogenesis that begins in geochemistry is how naturally it connects to the concepts and not only the metaphor of evolution as biology understands them today.

The opening chapter attempts to explain and justify treating the planet's biota as a geosphere. This perspective, which makes life a planetary property or perhaps a galactic property, opens the way to a more general treatment of biology at its core as a system science rather than a strictly historical discipline as the *Chance and Necessity* adherents or some evolutionary theorists would urge us to believe. It makes the case that the biological generalist must take geochemistry and geophysics seriously. From the other side, recent studies in geochemistry show why mineralogy must recognize major influences from the biosphere.

Chapter 2 is an overview of life as we know it, and our first attempt to come to grips with its extraordinary unity-in-diversity. The biosphere is a hierarchical complex system that has created novel order at scales ranging from electrons to ecosystems. Patterns at many levels can inform us about earlier ages, and more informative than any one pattern is the way they fit together as a system. Life on the planet Earth probably began 3.8 to 4.0 billion years ago. At first it seems extraordinary that present-day organisms and ecosystems could tell us much about the earliest ancestors, but when we consider that all are linked by laws as well as by descent, the diversity of modern life offers windows on the laws that created pasts older than the deepest we can reach with historical reconstruction. This prospect first came into focus in 1955 when it was noted that there was a single metabolic chart onto which all species mapped fully or in part. Thus metabolism is a living fossil possibly older than any extant rock. This amazing persistence becomes more compelling and more comprehensible as a feature of metabolism in physiological and ecological context, where metabolic order is recapitulated and given its functional semantics. We might note parenthetically that a 1999 paper of ours on the reductive citric acid cycle brought a letter of interest from the then 90 year old still hard working map maker of metabolism, Dr. Nicholson.

Our ability to comprehend life as a meaningful system, not only recording the past in extant diversity but also expressing elements of timeless order, has been aided by Carl Woese's revolutionary phylogeny and the growth of vast databases such as KEGG, Meta-Cyc, and Reaxys to mention just a few. At many points in Chapter 2 we are compelled to recognize ecosystems as forms of organization in their own right, not merely as communities of taxa but as the carriers of patterns that remain necessary even if all the taxa are changed. From the chemical propensities of metabolism to the invariants of ecology we are encouraged to look for empirical generalizations and theoretical principles applicable to non-equilibrium systems.

Chapter 3 considers energy sources for the kinetic processes of the maturing planet and energy exchanges among the geospheres. Sources include fusion energy coming as radiation from the Sun, fission energy from radioactive elements, and above all the

disequilibrium between our planet's formative condition, still trapped in its interior, and an outer shell driven relentlessly away from that condition. The hero in this story is the active mantle, whether through volcanism, melt-separation of elemental states, or long-range subduction and upwelling in tectonics. These are the processes by which heat – alone too diffuse an energy source to drive chemistry far from equilibrium – is nonetheless the cause for a gateway through which the Earth's chemical disequilibrium is focused at narrow points in covalent bond dynamics. One of our most central messages will be that the biosphere, first and foremost, is a chemical conduit for the flow of electrons from higher to lower potentials. The thermodynamic “problem” of a lifeless Earth, which on our planet was “solved” by the emergence of a biosphere, was to facilitate the descent of electrons. In Earth's first life, and in some life today, part of this electron flux is not only coupled to, but occurs by means of, carbon fixation, the reduction of CO₂ by the formation of multi-carbon molecules. That conduit with accompanying chemistry self organized, we argue, a chemical phenomenon for which we find precedent in physical processes such as weather or lightning, the far from equilibrium yet inevitable ordered states of the atmosphere. This chapter focuses on the planetary restlessness that may have made it impossible to remain lifeless, and the ways the same processes sustain parts of the biosphere directly today.

Chapter 4 offers a detailed view of metabolism where the top down and bottom up approaches must make contact. There is now an enormous amount of data on genome sequence, chemical mechanism, macromolecular structure, and enzymology. By combining these, we may understand what functions molecules perform, what variations have been open to them, and how their present diversity came into existence historically. To understand metabolism we must recognize at least four levels of organization: the small-molecule synthetic networks, crucial intermediate cofactors (vitamins) that transfer components and complete networks, macromolecule synthesis and catalysis, and in some cases the organizational functions of cellular compartments. We argue that the historical sequence followed the molecular sequence from simple to complex, from small molecules to large, and that the layers of order we find in metabolism today likely reflect historical accretions that were watersheds, but not history-erasing floods. The elaboration of metabolism was not only hierarchical but also modular, indicating parallel streams of innovation, which could have occurred in somewhat independent places and times. The multilevel patterns of life suggest that constraints on what would ever be possible originated in metabolism and then propagated to higher levels.

On any account it is impressive that a small, network-autocatalytic cycle (the rTCA cycle) should be found running through the termini of the synthesis pathways of all essential monomers. Also remarkable is the almost mineral-like simplicity of direct reduction of one-carbon units used ubiquitously in extant life, sometimes furnishing alternative starting points to synthesize a few amino acids. The significance of these patterns compounds as we find that the same networks have anchored the very little innovation that ever occurred in carbon fixation, and that their catalysts are among the most distinctive and conserved in the biosphere. The bottom up focus on reaction mechanisms and considerations of control and stability privileges the same pathways that historically have been unchanging points of

reference to which all innovations were anchored. Metabolism is not only a list of components but a logic of relations, and it is in that logic that we find non-arbitrary constraints strong enough to have entrained later accretions of complexity.

Metabolism by itself does not a geosphere make, so Chapter 5 turns to the hierarchy of biology, the series of transitions that moves to macromolecules, coding and memory molecules, control, containment, and the integration of bioenergetics. These higher-level systems define the context for the chemistry of life as we know it, and the question central to biogenesis is whether they inherited or dictated that chemistry's logic. Whether we can infer the path from geochemistry to the first cells by extrapolating modern biochemistry backward in time turns on the answer to this question.

The chapter considers three distinct higher forms of organization: the emergence of ribosomal translation of peptides and with it a genetic code, the integration of redox and phosphate energy systems, and the diverse forms and functions of compartmentalization realized in modern cells. We find, in all three cases, either common modes of constraint expressed in biochemistry and in its higher-level supports, or more remarkably, the imprint of metabolic logic in systems that have evolved to distance and insulate their internal functions from the substructure of metabolism. The modular unfolding of metabolism seen in Chapter 4 must have been interwoven with innovations at higher levels that increased the interdependence of prebiotic systems on each other and led to their progressive separation from lithosphere/hydrosphere chemistry to become a distinct geosphere. The layers in this interweaving have led to the dense interdependence of forms of order at many levels in modern life, which appears as a chicken-egg problem if viewed as a whole. The remarkable observation is that enough independent identity or partial autonomy has been preserved in different subsystems to suggest at coarse scale the alternation of moves through which the unification of cellular life and its distinct planetary role were attained. Cellular life is both unified and diverse because it is a confederacy, a gathering together of diverse opportunities for order from the abiotic geospheres to create a new identity that remembers its roots but is distinct from them all.

The first five chapters describe the world as it functions today, or as we can reconstruct its past from directly available evidence. We interpret some strong and invariant patterns as necessary features or as remnants of stages through which life must have passed, when the historical reconstruction and mechanism jointly support such interpretations. In Chapter 6 we weave these interpretations into a proposed web of stages in biogenesis. Our proposed sequence is not a detailed scenario – many important transitions occurred about which we can offer little or no detail. Our sequence is meant as a kind of skeleton provided by the strong constraints – those stages that seem to us sufficiently necessary that they should both constrain scenarios and guide the questions we ask about how to bridge the gaps between them.

Chapter 7 introduces the idea that gives precision to an intuition of many investigators that the emergence of life may have been stochastic, but it was not accidental. We introduce the ideas of both equilibrium and non-equilibrium thermodynamic states, and the robust transitions between them known as phase transitions. Our most important problem

issuing from the first six chapters is how to describe and account for strong regularities in dynamical systems that also exhibit constant variation. Thermal phases provide the needed concept and a developed mathematics to study its ramifications. These phases are the carriers of physical laws even as the entities and events that make them up undergo constant change. This chapter provides a means to state, in language that is not metaphor or analogy, what we believe must be the foundation for a theory of the origin of life: via whatever chemical mechanisms are experimentally plausible, the emergence of the biosphere, particularly in its early stages, can only make sense as a cascade of non-equilibrium phase transitions.

Non-equilibrium states and their transitions have in recent years been extensively studied in certain areas of physics and chemistry. A gulf exists, however, between the relatively simple phenomena for which their potential is routinely explored, and the structurally rich phenomena that are the normal interests of most geochemists, organic chemists, biochemists, microbiologists, and specialists in other domains where they are almost unknown. We believe that any effort to separate what is chance in life from what is necessity, and to distinguish the patterns that reflect each, must eventually face questions of robustness and the relation between material and information, which will bring non-equilibrium statistical mechanics and structurally rich systems together to create a new frontier.

We provide systematic introductions to the most central concepts, which may be followed using elementary methods with some time and work. The reader who is unfamiliar with, or does not wish to push through, the various formalisms need not be put off. Our concern is with concepts, and although we will not traffic in metaphor, we describe these so that their applications to emergence can often be understood without heavy formalism.

One of the most important insights from the theory of phase transitions (equilibrium or otherwise) is that reductionist science is an enterprise of floors and ceilings. Each phase transition creates the robust forms of order that will participate in dynamics at or below its immediate scale. These ordered states, in chemistry, have been the building blocks from which life and evolution design. They remain in effect until the next phase transition constrains some of them, creating new levels of organization and typically greater complexity. Reductionist science, in its best sense, works because we can make falsifiable predictions at a given level without knowing what is above the ceiling or below the floor. In other words, the strength of reductionism is due to the simplifying effects of emergence. For the same mathematical reason, the emergence of a biosphere could only have been possible through a cascade of phases that buffered innovations at different levels from each other. If we can identify the transitions, we recognize the stages as lawful rather than accidental.

The earliest ordered phases in geochemistry were organizationally simple, though the search for them in the wide parameter range of the lithosphere/hydrosphere interface may be very difficult. As metabolic order developed, forms of individuality emerged, and evolutionary dynamics entered, they became increasingly complex.

An important consequence of the phase transition paradigm is that the origin of life and the organization of the biosphere cannot be understood as two separate topics. The

emergence of the biosphere was the Earth's departure from a metastable lifeless state and its subsequent collapse into the more stable condition that includes life. Chapter 8 develops the ramifications of these conclusions, and argues that from them we must reconceptualize the nature of the living state.

This chapter introduces three new topics, which have been present in the context of all the earlier chapters, and which must now be addressed in their own right. The first is the modular and hierarchical architecture of life. Fully understanding hierarchy invokes all dimensions of the phase transition paradigm: material stability and layers, information requirements and buffering, the needs for control in hierarchical systems, and the way life meets these by following paths of least resistance. The second is the emergence of individuality and with it the Darwinian world. We invert the conventional view of life as a property inherent in individuals, and recognize individuality as one mode of organization – albeit an important one – among many that enable life. From this perspective for the first time, we find it most natural to expect what we observed empirically in Chapter 2: that metabolism and the ecosystem define two of life's most fundamental universals, to which individuals may form many different relations.

Finally we offer systematic arguments for a view of what is essential to the living state that could not have stood on its own from intuition and scenarios, but from the full development of the phase transition paradigm seems to us inevitable. The biosphere is, most fundamentally, the geosphere on Earth that opens otherwise unreachable domains of organic chemical states and processes. It is maintained for the same reason as it emerged: the chemistry of life and all the hierarchy of structures that maintain it constitute a channel for relaxation of redox and other energetic stresses. This view reaches much further than is at first evident. Chemistry unifies the extraordinary diversity of living order – its complexity, its stability, the particularity of its conserved features, and its tight integration with the other geospheres – to a degree that no other starting point can.

With these eight chapters, then, we will hope to have left the reader with the following main contributions.

1. The major transitions that constituted the emergence of the biosphere were not defined by single and rare microscopic events, but by regime shifts in the behavior that was typical in dynamical, stochastic ensembles. Some of these are the familiar phase transitions of equilibrium condensed matter, but the distinctively biotic ones are inherently dynamical.
2. One of us wrote in 1968 that “The energy that flows through a system acts to organize that system.” Forty five years later two of us reiterate that point, but today a much more detailed picture can be drawn for the descent of electrons. A few channels for flow, used repeatedly, have given rise to the particular structures of biochemistry and life. Both from history and from mechanism, they are remarkably well positioned for the task. With a more advanced empirical and computational chemistry, it may not be beyond the ability of near generations to prove they are unique, at least in this planetary context.

3. A vision of the lawful nature of life might be expressed as “deriving intermediary metabolism from the periodic table of elements.” The larger question of whether biogenesis was a chance event or a necessary event is closely related. If it was necessary, to what extent are major features predictable from first principles? We argue for a large role for predictability in the earliest stages, with contingency and complexity entering through later transitions. The periodic table is not all the law needed to derive metabolism, but significant structure in biochemistry does derive all the way from properties of the elements. In some other cases we argue that it follows from higher-level but still essentially physical and energetic regularities such as orbital structure, network topology, and kinetics.
4. The phase transition paradigm, which accepts heavy dependence on complex and diverse boundary conditions (such as the Earth has likely always provided), but rejects a large early role for miracles even in catalysis, supports a view that the progression in molecular size and complexity defined the progression of emergence as well. Early geo-organic chemistry cast the die for metabolism, and metabolism then cast it for the rest of biochemistry. The earliest important regime change in catalysis was not through macromolecules but through cofactors; the progression to macromolecules was a complicated transition, made possible by a biosynthetic foundation that was stable and already partly selective.
5. Historical reconstruction can sometimes help us see beyond the history we can directly reconstruct. With appropriate functional context, it can identify the relative ages and directions of change even of very ancient features. In some cases we can argue not only that universal features are primordial, but that they reflect causes that were at work before genetic history originated and perhaps before cells. These are windows on some of the earliest steps from prebiotic to nascent biotic chemistry.
6. Our understanding of the biosphere must be chemical. Organic chemistry is not an accidental stage on which abstract principles of life perform a play that could be performed elsewhere. Chemistry matters in detail because it matters in principle. Some of the most important sources of stability and complexity in life would not be expressible in any other system. The ecosystem is the bridge from geochemistry to life, and carries much of what is deterministic and necessary in metabolic order. Species emerge further into the domain of chance and are secondary. Thus we never need to call the ecosystem a “super-organism” to acknowledge its integrity, because we recognize this as in some ways prior to organisms.
7. Higher levels of living organization seem to require not single transitions, but many transitions for each form. Among these the most enigmatic is the emergence of an oligomer world in which mRNA, tRNA, rRNA, and proteins are unified by ribosomal translation. Yet, as complex as this sequence of transitions must have been, and with large gaps remaining in our understanding of its intermediate stages, it emerged carrying striking signatures of metabolic order that are not parts of its modern function. The long exploration that led to cells, at the end of its wandering, arrived still at the order of metabolism, and enables us to know some things about it for the first time.

Acknowledgments

In the ten years prior to the authors of this book's beginning to interact, scientists and database builders were laying the foundations that we build on and informing us of their results. Jack Corliss told us of the theory of life's forming at undersea spreading centers and Larry Hochstein told us of the discovery of the reductive tricarboxylic acid cycle. The KEGG and Ecocyc databases were being assembled. Ribosomal sequencing was changing the world of taxonomy. Steen Rasmussen was developing artificial life and biogenesis studies at Los Alamos National Laboratories. Robert Hazen, George Cody, and Hatten Yoder were developing high-temperature, high-pressure organic chemistry at Carnegie Geophysics. Consultation with Walter Fontana and Leo Buss led to a study of the rTCA compounds in the Beilstein compendium with Jennifer Kostelnik and Jeremy Yang.

When we began to regularly interact it was during summers at the Santa Fe Institute, frequently joined by Shelley Copley. A phone call from an old colleague, Carl Woese, informed us of the opportunity of the FIBR grants: multi-year multi-institutional grants from the National Science Foundation. By this time we had been joined by Vijayasarathy Srinivasan. We were awarded a five-year, five-institution FIBR grant "From Geochemistry to the Genetic Code" centered at the Santa Fe Institute and Krasnow Institute of George Mason, with nodes also at University of Colorado, University of Illinois, and Carnegie Institution Geophysical Laboratory. This added to the senior staff Nigel Goldenfeld and Zaida Luthey-Schulten. Toward the end of the FIBR collaboration we were joined by Rogier Braakman. The insights, ideas, and interpretations of Shelley, George, Carl, Nigel, Rogier, and Vijay figure prominently in the following chapters as they do in our understanding of the subject.

The FIBR collaboration was made into an innovative and substantial educational effort through the gifted and committed work of Ginger Richardson, Mimi Roberts, Jim Trefil, Paige Prescott, Lokesh Joshi, Paul Cammer, and Carlos Castillo-Chavez.

Several colleagues have stood out as towering authorities or unique sources of vision and perspective as we have sought to find the correct frame through which to understand the living state. We must especially thank John Baross, Christian de Duve, Albert Eschenmoser, Georg Fuchs, Everett Shock, and Carl Woese.

The ways one depends on colleagues throughout the scientific network in coming to grips with a complex topic – for guidance and serendipity, for knowledge, for conceptual

growth, and for shared work – are too numerous to list. For these and much more we are grateful to Ariel Anbar, Jakob Andersen, Gil Benkö, Aviv Bergman, Carl Bergstrom, Tanmoy Bhattacharya, Elbert Branscomb, James Brown, Leo Buss, Jim Cleaves, Ken De Jong, David Deamer, Jennifer Dunne, Brian Enquist, Doug Erwin, Jim Ferris, Jessica Flack, Christoph Flamm, Walter Fontana, Steve Frank, Murray Gell-Mann, Chris Glein, John Hernlund, Kei Hirose, Ivo Hofacker, Peter Hrabar, Harald Huber, Nicholas Hud, Piet Hut, Sanjay Jain, Bill Jones Jr., Lokesh Joshi, Masafumi Kameya, Stu Kauffman, David Krakauer, Supriya Krishnamurthy, Irwin Kurland, Michael Lachmann, Manfred Laubichler, Pier-Luigi Luisi, Pablo Marquet, William Martin, Cormac McCarthy, Daniel Merkle, Stuart Newman, Harry Noller, Martin Nowak, Yoshi Oono, Stephen Ragsdale, Michael Russell, Van Savage, Peter Schuster, Cosma Shalizi, Peter Stadler, Yuichiro Ueno, Geoffrey West, George Whitesides, Loren Williams, Jon Wilkins, David Wolpert, William Woodruff, and Michael Yarus.

The manuscript has benefited greatly from review and recommendations by Elbert Branscomb, Nigel Goldenfeld, and Piet Hut, and from a gifted and expert statistics reviewer who has elected to remain anonymous. Our enduring thanks go to our publisher, Simon Capelin, for creating a beautiful volume and making it available to a wide readership, and to the excellent editors and designers at Cambridge University Press.

Our research over the years has been supported through the generosity of both institutions and individuals. Supporting institutions have been the Santa Fe Institute and the Krasnow Institute, the National Science Foundation, and the John Templeton Foundation. Individuals who have been staunch supporters as well as long-term friends are Jerry Murdock, William Melton, Jim and Celia Rutt (through the Proteus Foundation), and Bill Miller. Their belief in our work has not only been essential to its completion, but has been a source of deep personal gratification to us both.

The Santa Fe Institute has, uniquely, been home, and for its ongoing vision and able operation we are particularly grateful for Ellen Goldberg's tenure as president during the years that brought us together, and the skill and wisdom of Elisabeth Johnson as our grants manager. Wayne Coté and Bruce Bertram create a meeting environment that is second to none. Everything we have depended on in the Krasnow Institute has been possible only through the professionalism, energy, and goodness of Jane Wendelin and Jennifer Sturgis. We owe special thanks to Sara Bradley for obtaining permissions for graphics used in this volume.

Krastan Blagoev at NSF has been a long-term supporter and collaborator in a series of special workshops dedicated to recognizing the next paradigm. Jim Olds has been colleague and supporter for us both as director of the Krasnow Institute. DES has recently joined the Earth-Life Science Institute at Tokyo Tech where the manuscript was completed, and is a research scholar at the Ronin Institute in Montclair, New Jersey.

This book is dedicated to the memory of George Cowan, a brilliant scientist and institution builder and an exceptionally fine human being.