Chapter 1

The Emergence of Chemical Complexity: An Introduction

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The ancient origins of stars, planets and life may be viewed as a sequence of emergent events, each of which added to the chemical complexity of the cosmos. Stars, which formed from the primordial hydrogen of the Big Bang, underwent nucleosynthesis to produce all the elements of the Periodic Table. Those elements were dispersed during supernova events and provided the raw materials for planets and all their mineralogical diversity. Chemical evolution on Earth (and perhaps countless other planets and moons) led to life through a sequence of steps: the formation of biomolecules, the assembly of those molecules into organized molecular systems, and ultimately the appearance of self-replicating collections of molecules. Today, chemical complexification occurs at an ever accelerating rate through the efforts of chemists and chemical engineers.

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Introduction

The history of the universe has been one of inexorable, inevitable chemical complexification – a sequence of emergent evolutionary episodes from nucleosynthesis, to planet formation, to life. The collected essays of this volume review that epic 14 billion years of history and, in the process, touch on all of the natural sciences: physics, astronomy, geology, biology and, of course, chemistry. In short, this book retells the story of the emergence of everything (*1*).

Every step in this immense journey is an example of ordering by the process of emergence (Kauffman, this volume; *1,2*). Emergent systems occur when energy flows through an assemblage of interacting particles, such as molecules, sand grains, cells or stars. Each individual object, or "agent" in the jargon of emergence, responds only to its environment, yet the behavior of the collective whole is distinct from that of any individual agent. A single sand grain cannot form a rippled surface, nor can a single neuron be conscious.

Emergent behavior appears in countless systems all around us, all the time, including the interactions of atoms, automobiles, or ants. As energy flows through a collection of agents, they tend spontaneously to become more ordered and to display new, often surprising behaviors. At first blush, such patterning might seem to violate the second law of thermodynamics, which dictates a universal tendency for increasing entropy. Yet, as local patterns arise, energy is dissipated more efficiently in accord with the second law of thermodynamics (*3*). It is easy to focus on this increase in local order, while missing the key fact that the global entropy of the system increases.

In this volume the emergence of chemical complexity has been divided into three evolutionary episodes: stellar evolution and the emergence of elemental diversity, planetary evolution and the emergence of mineralogical diversity, and prebiotic chemical evolution. All of these episodes depend on evolutionary processes that produce change over time under selective pressure (Zaikowski, this volume), and all of them continue to this day.

Stellar Evolution and the Origin of Elements

The periodic table boasts almost 100 naturally occurring chemical elements, but that diversity was not present during the earliest stages of the universe. The Big Bang gave rise to just three elements – predominantly hydrogen, with lesser amounts of helium and lithium. Big Bang nucleosynthesis occurred within the first few minutes of the moment of creation, and for the next million years or so those three elements represented all the chemical complexity of the cosmos (Olive, this volume).

As the universe expanded and cooled, atoms clumped into the first hydrogen-rich stars. The largest of these luminous masses underwent dramatic sequences of nuclear fusion events, producing a cascade of heavier elements: beryllium, boron, carbon, nitrogen, oxygen, fluorine and more (Meyer, this volume). The fusion reactions of neon burning, oxygen burning and silicon burning produced more new elements, through atomic number 26 (iron). But iron, with the lowest energy per nucleon, is the end point of nuclear burning reactions. The largest stars, having exhausted their supply of nuclear fuel, underwent the rapid collapse and explosive rebound known as a supernova. Not only did this process generate all the other elements of the periodic table (primarily through neutron capture), but it also dispersed those elements into space (Parker & Meyer, this volume). In interstellar space, vast clouds of dust and gas concentrated as new generations of metal-rich stars and planets formed.

Mineralogical Evolution and the Origin of Planets

Life is perhaps the most dramatic example of chemical complexification, but the evolution of the mineral world represents an important precursor to life's origins. Earth today boasts almost 4300 known types of minerals, with as many as 50 new species recognized each year. Yet the mineralogical diversity now found at or near Earth's surface (< 3 km) was not present for much of the planet's history. Indeed, both the variety and relative abundances of near-surface minerals have evolved dramatically over 4.5 billion years of Earth history through a variety of physical, chemical and biological processes.

The early history of the solar system was marked by many processes of differentiation and fractionation. As the nascent Sun irradiated the protoplanetary environment, gradients in temperature and radiation led to significant chemical (Lewis, this volume) and isotopic (Clayton, this volume) fractionation.

Planetesimals of a protoplanetary environment form initially from a surprisingly small number of refractory condensed phases, such as corundum, spinel, graphite and SiC (Lodders, this volume). The most primitive materials to form Earth are represented by a class of meteorites called chondrites, which include a variety of stony meteorites that formed early in the history of the solar nebula. The most striking features of chondritic meteorites are chondrules, which are small spherical objects (typically << 1 cm diameter) that represent molten droplets formed in space by rapid heating and cooling in the nebula prior to accretion. Chondritic meteorites are simply accumulations of chondrules plus mineral grains and dust that have not been significantly altered by melting or differentiation, and thus represent the most primitive raw materials of the Solar System (Lipschutz, this volume).

Unaltered chondrites are characterized by extreme mineralogical parsimony, with no more than about twenty different mineral species (*4*). As planetesimal accretion progressed and chondrite parent bodies became larger, aqueous and thermal alteration led to new suites of minerals (*5,6*). Yet the total mineralogical repertoire of chondritic meteorites is limited to approximately 100 different mineral species.

Mineralogical diversity increased with the advent of asteroid melting and differentiation – processes that resulted in the large-scale separation of stony and metallic components. Differentiated meteorites include several classes of stony achondrites, as well as stony-iron and iron meteorites. Nevertheless, no more than ~150 mineral species are known to occur in all types of meteorites. These minerals, dominated by magnesium silicates, provided raw materials for the accreting Earth.

The accretion and rapid differentiation of Earth at approximately 4.55 Ga (Kleine, this volume), as well as the Moon-forming impact at about 4.5 Ga, led to new near-surface mineralogical diversity. Much of that diversification resulted from volcanic outgassing and fluid-rock interactions associated with formation of the atmosphere and oceans (Fegley, this volume). Indeed, dynamic interactions among the early atmosphere, lithosphere and hydrosphere were the principal mechanisms for Hadean mineral diversification (Rumble, this volume). An immediate mineralogical consequence of these interactions would have been copious formation of hydrous silicates and oxides, including serpentinization and the first significant production of clay minerals and perhaps zeolites.

From their inception at least 4.3 Ga ago (*7*), oceans would have increased steadily in salinity [predominantly Na, Ca, Mg and Cl, though ratios may have varied significantly over time (*8,9*)]. Ocean concentrations of sulfate and nitrate would also have increased owing to photolytic and lightning-induced reactions in the atmosphere and subsequent ocean-atmosphere exchange. These compositional changes would also have led to the first significant evaporate deposits on Earth, and associated sulfate, nitrate, and halide minerals, although no traces of evaporate minerals have been found prior to about 3.4 Ga (*10*).

The earliest shallow crustal igneous rocks on Earth would have been basalts. However, fractional melting in the presence of aqueous fluids and crystal separation led to the familiar variety of igneous rocks, including andesite, diorite, gabbro and granite. Recent discoveries of sedimentary zircon grains dated to 4.4 Ga have been interpreted to indicate that granite production (and by extension the first assembly of continental crust) was active within 150 million years of accretion (*11*). An important mineralogical consequence of granite formation was the enrichment of more than a dozen rare "pegmatophile" elements in residual fluids and the production of hundreds of distinctive pegmatite minerals.

While the timing of the beginnings of plate tectonics, in particular the commencement of large-scale subduction processes and associated crustal reworking and arc volcanism, remains a matter of intense debate (*12,13*), most researchers conclude that at least some form of subduction was active prior to 3 Ga (*14*). Significant mineralogical consequences of subduction include base metal deposition and associated precious metal concentrations that result from magmatic and volcanogenic processes (*15,16*). Yet another mineralogical consequence of plate tectonics was the uplift and subsequent exposure of regional metamorphic terrains – events which, for the first time, brought high-pressure mineral phases to near-surface environments.

Throughout Earth history, mineralogical evolution has been driven by cyclical selective processes: heating and cooling, melting and crystallization, burial and uplift, weathering and sedimentation, dissolution and precipitation. Each cycle modified preexisting mineral species and generated new physico-chemical niches. All new minerals thus arose from natural selective processing of older minerals.

The last billion years have witnessed a particularly dramatic increase in mineralogical diversity, primarily as a consequence of atmospheric oxygenation. To understand this Neoproterozoic and Phanerozoic acceleration in mineral evolution we must thus address another emergent chemical event – the origin of life.

Chemical Evolution and the Origin of Life

The origin of life may be modeled as a sequence of so-called "emergent" events, each of which added new structure and chemical complexity to the prebiotic Earth (*1,2*). The recognition and description of these varied emergent systems provides an important foundation for origins of life research, for life is the quintessential emergent phenomenon. From vast collections of interacting lifeless molecules emerged the first living cell.

The overarching problem with studying life's origins is that even the simplest known lifeform is vastly more complex than any non-living components that might have contributed to it. What now appears as a great divide between non-life and life reflects the fact that the chemical evolution of life must have occurred as a stepwise sequence of successively more complex stages of emergence. The challenge, therefore, is to establish a progressive hierarchy of emergent steps that leads from a pre-biotic ocean enriched in organic molecules, to functional clusters of molecules perhaps self-assembled or arrayed on a mineral surface, to self-replicating molecular systems that copied themselves from resources in their immediate environment, to encapsulation and eventually cellular life (*2*).

The Emergence of Biomolecules

The first vital step in life's emergence on Earth must have been the synthesis and accumulation of abundant carbon-based biomolecules. In the beginning, life's raw materials consisted of water, rock, and simple volcanic gases – predominantly carbon dioxide and nitrogen, but with local concentrations of hydrogen, methane, ammonia and other species. Decades of experiments have revealed that diverse suites of organic molecules can emerge from a variety of geochemical and cosmochemical environments.

The experimental pursuit of geochemical organic synthesis, arguably the best understood aspect of life's origin, began a half-century ago with the pioneering studies of University of Chicago graduate student Stanley Miller and his distinguished mentor Harold Urey (*17,18*). Together they established the potential role of organic synthesis that occurred in Earth's primitive atmosphere and ocean as they were subjected to bolts of lightning and the Sun's intense radiation (Bada et al., this volume).

Molecules formed in interstellar space represent another important source of life's building blocks (Ehrenfreund & Botta, this volume). A variety of organic species, including aromatic hydrocarbons, alcohols and sugars, represent a significant fraction of the more than 130 molecular species identified by radio astronomy (Ziurys, this volume; Halfen et al., this volume). These deep-space processes have been simulated in cryogenic laboratory experiments using UV radiation (Allamandola, this volume). The rich inventory of organic species brought to Earth in carbonaceous chondrite meteorites underscores the importance of extraterrestrial sources of biomolecules (Botta, this volume).

The discovery of deep-ocean ecosystems led to speculation that a hydrothermal vent, rather than earth's surface, might have been the site of life's origin (*19-21*). Recent experiments bolster this hypothesis. The most fundamental biological reaction is the incorporation of carbon atoms (starting with the gas carbon dioxide) into organic molecules. Many common minerals, including most minerals of iron, nickel, or copper, promote carbon addition under hydrothermal conditions (*22-24*). While deep-sea vents remain a highly speculative location for life's origins, mineral-rich hydrothermal systems did contribute to early Earth's varied inventory of bio-building blocks.

It now appears that anywhere energy and simple carbon-rich molecules are found together, a suite of interesting organic molecules is sure to emerge (*25*). In spite of the polarizing advocacy of one favored environment or another, experiments point to the likelihood that there was no single dominant source. By four billion years ago Earth's oceans must have become a complex, albeit dilute, soup of life's building blocks. Though not alive, this chemical system was poised to undergo a sequence of increasingly complex stages of molecular organization and evolution.

The Emergence of Organized Molecular Systems

Synthesizing biomolecules is relatively easy – some might argue too easy. Life's simplest molecular building blocks, including amino acids, sugars, lipids and bases, emerged inexorably through facile, inevitable chemical reactions in numerous prebiotic environments. Prebiotic processes also produced a bewildering diversity of seemingly useless molecules; most of the molecular jumble played no obvious role. The emergence of concentrated suites of just the right mix thus remains a central puzzle in origin-of-life research.

Life requires the assembly of just the right combination of small molecules into much larger collections – “macromolecules” with specific functions. Making macromolecules is complicated by the fact that for every potentially useful small molecule in the prebiotic soup, dozens of other molecular species had no obvious role in biology. Life is remarkably selective in its building blocks, whereas the vast majority of carbon-based molecules synthesized in prebiotic processes have no obvious biological use. Consequently, a significant challenge in understanding life’s chemical emergence lies in finding mechanisms by which the right combination of small molecules was selected, concentrated and organized into the larger macromolecular structures vital to life.

The oceans formed a weak solution in which it would have been difficult for advantageous combinations of molecules to react in the chemical path to life. Two processes, self-selection and surface organization, are likely to have led to molecular selection.

Phospholipid molecules, the building blocks of cell membranes, are “amphiphiles” that possess contrasting regions that are attracted to, and repelled by, water. Consequently, these molecules spontaneously self-organize into tiny cell-like spheres when placed in water (*26,27*). Nevertheless, most water soluble molecules don’t self organize and must be selected by another means. Recent experiments demonstrate that chemical complexity can arise at mineral surfaces where different molecules congregate and interact (*28*). Once confined and concentrated, small molecules tend to undergo reactions to form larger molecular species that aren’t otherwise likely to emerge from the soup (Ferris et al., this volume). Evaporating tidal pools, where rock and water meet and cycles of evaporation concentrate stranded chemicals, provide another scenario for origin-of-life chemistry (*29*). Deep within the crust and in hydrothermal volcanic zones mineral surfaces may have played a similar role, selecting, concentrating and organizing molecules on their periodic crystalline surfaces (*20,30*).

The Emergence of Self-Replicating Molecular Systems

Four billion years ago the molecular building blocks of life had been synthesized, and these molecules must have become locally concentrated on surfaces and through self-selection as they assembled into vesicles and polymers of biological interest. Yet accumulations of organic molecules, no matter how highly selected and intricately organized, are not alive unless they also possess the ability to reproduce.

The simplest self-replicating system consists of one type of molecule that makes copies of itself (*31*). Under just the right chemical environment, such an isolated molecule will become 2 copies, then 4, then 8 molecules and so on in a geometrical expansion. Such an “autocatalytic” molecule must act as a template that attracts and assembles smaller building blocks from an appropriate chemical broth. Although fascinating, single self-replicating molecules do not meet minimum requirements for life because they can't evolve.

More relevant to biological metabolism are systems of two or more molecules that form a self-replicating cycle or network (*32-34*). Living systems are distinguished from simple self-replicating collections of molecules because living systems must also incorporate a degree of sloppiness. Only through such mutability can the system experiment with new, more efficient reaction pathways and thus evolve.

Origin-of-life researchers focus primarily on two contrasting models of the first self-replicating system, metabolism and genetics. Metabolism is a cyclical chemical process in which chemicals react, thus releasing energy and manufacturing new useful molecules that reinforce the cycle. Metabolism requires a sequence of chemical reactions that work in concert. While a number of prominent researchers advocate a metabolism-first scenario (*1,2,20,21,24*), most origin experts favor a genetics-first scenario, with a self-replicating molecule that also passes information from one generation to the next – a genetic molecule like DNA or RNA (*35-38*). This so-called "RNA world" model rests on the dual ability of genetic material to catalyze reactions and transfer information. According to most versions of this hypothesis, metabolism emerged later as a means to make the RNA replication process more efficient.

The RNA world model is not without its difficulties. Foremost among these problems is the exceptional challenge in the prebiotic synthesis of RNA (*39-40*). Many of the presumed proto-metabolic molecules are easily synthesized in experiments that mimic prebiotic environments. RNA nucleotides, by contrast, have never been synthesized from scratch. Furthermore, even if a prebiotic synthetic pathway to nucleotides could be found, a plausible mechanism to link those nucleotides into an RNA strand has not been demonstrated. It is not obvious how useful catalytic RNA sequences would have formed spontaneously in any prebiotic environment. Perhaps, some scientists speculate, a simpler nucleic acid preceded RNA (*41-42*).

Whatever the scenario, metabolism first or genetics first, the origin of life required more than the replication of chemicals. For a chemical system to be alive, it must display evolution by the process of natural selection.

The Emergence of Natural Selection

Once a collection of molecules began to make copies of itself, natural selection was inevitable. Molecular selection, the process by which a few key molecules earned essential roles in life's origin, proceeded on many fronts. Some molecules were inherently unstable or highly reactive and so they quickly disappeared from the scene. Other molecules easily dissolved in the oceans and so were effectively removed from contention. Still other molecular species may have sequestered themselves by bonding strongly to surfaces of chemically unhelpful minerals or clumped together into gooey masses of little use to emerging biology.

In every geochemical environment, each kind of organic molecule had its reliable sources and its inevitable sinks. For a time, perhaps for hundreds of millions of years, a kind of molecular equilibrium was maintained as the new supply of each species was balanced by its loss. Such an equilibrium features nonstop competition among molecules, to be sure, but the system does not evolve.

The first self-replicating molecules changed that equilibrium. Even a relatively unstable collection of molecules can be present in significant concentration if it learns how to make copies of itself. The first successful metabolic cycle of molecules, for example, would have proven vastly superior to its individual chemical neighbors at accumulating atoms and harnessing energy. But success breeds competition. Inevitable slight variations in the self-replicating cycle, triggered by the introduction of new molecular species or by differences in environment, initiated an era of increased competition. More efficient cycles flourished at the expense of the less efficient. Evolution by natural selection had begun on Earth.

Two common processes – variation and selection – provide a powerful mechanism for self-replicating systems to evolve. For a system to evolve it must first display a range of variations. Natural systems display random variations through mutations, which are undirected changes in the chemical makeup of key biomolecules. Most variations are neutral or they harm the organism and are doomed to failure. Once in a while, however, a random mutation leads to an improved trait – a more efficient metabolism, better camouflage, swifter locomotion, or greater tolerance for extreme environmental conditions. Such beneficial variations are more likely to survive in the competitive natural world – such variations fuel the process of natural selection.

Competition drives the emergence of natural selection. Such behavior appears to be inevitable in any self-replicating chemical system in which resources are limited and some molecules have the ability to mutate. Over time, more efficient networks of autocatalytic molecules will increase in concentration at the expense of less efficient networks. In such a competitive milieu the emergence of increasing molecular complexity is inevitable; new chemical pathways overlay the old. So it is that life has continued to evolve over the past four billion years of Earth history.

Chemical Education and the Future of Chemical Complexification

This volume examines three major evolutionary episodes of chemical complexification: stellar evolution and the emergence of elemental diversity, planetary evolution and the emergence of mineralogical diversity, and prebiotic chemical evolution. The second volume in this series will consider the emergence and evolution of life. Have we come to the end of chemical complexity? Are we it?

The next volume will address this question by pointing to a fourth dramatic, ongoing episode of rapid chemical evolution – human engineering in the modern era. Physicists' deep understanding of nucleosynthesis and technological ingenuity has added more than a score of heavy elements to the periodic table. Naturalists' discoveries of the diversity of minerals and their distinctive physical and chemical properties have inspired the synthesis of countless thousands of new mineral-like compounds – many times the number of known natural species. Molecular biologists' deciphering of the genetic code and their development of genetic technologies has led to a growing number of genetically engineered lifeforms. And now, chemical complexification is accelerating as we learn more, and as we pass that knowledge on to our students.

These examples of highly accelerated, human-mediated evolution are more general examples of what Charles Darwin referred to as artificial selection [as opposed to the more gradual, undirected process of natural selection (*43*)]. Human knowledge and ingenuity can be used to design promising new configurations of elements and molecules, and then select the most successful products for further study and refinement.

The central driver of this continuing engineered complexification is effective chemical education, fostered by innovative ways of teaching chemistry (Halfen et al., this volume; Parker & Meyer, this volume; Venkataraman, this volume; Zaikowski et al., this volume). Armed with such powerful teaching aids, educators will continue to inspire a new generation of chemists to create new dimensions of chemical complexity.

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