The evolution of biogeochemistry: revisited

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Abstract The evolution of biogeochemistry, retraces the important historical steps in part, covered by Gorham (Biogeochemistry 13:199–239, 1991) in the 18–19th centuries—with new emergent linkages and trends in 20–21st centuries. In the post-phlogiston period, key synthetic connections are made between weathering, atmospheric chemistry, carbon cycling, and climate change. Early work in the 19th century, focused on weathering and the importance of organisms in the exchange of carbon dioxide between the rocks and the atmosphere, provided foundations for new analytical approaches. The role microbes in connecting abiotic and biotic processes begins to emerge, based largely on the existing knowledge of stoichiometry in agricultural soils and plants. This in part, leads to the founding of ecology and its linkages with evolution and biogeography. Verandsky boldly emerges in the 20th century, with his concepts of a biosphere and a noosphere, as concerns begin to arise about human impacts on nature. The development of organic geochemistry as a discipline, allowed for new roots to develop in the evolution of biogeochemistry through linkages between short and long-term carbon cycles. In the 20th century, a new interesting stoichiometry emerges in biogeochemistry—as related to the Green Revolution, human population growth, and eutrophification problems. The advent of long-term and large-scale experiments help to constrain the complexity of non-linearity and regional differences in fluxes and rates in biogeochemical work. A new age begins in the 21st century whereby molecular approaches (e.g. omics) combined with large-scale satellite, monitoring, survey, observatory approaches are combined in the development of Earth System models. These new connections with ecological/evolutionary genetics are one of the more dramatic and important aspects of biogeochemistry in modern times.

Keywords Biogeochemistry · Earth science · Ecology · Evolution geochemistry · Global change

This paper is dedicated to Eville Gorham, who passed away on January 14, 2020 at the age of 94. Well recognized for his work on acid rain, the National Academy of Sciences considered him a renaissance scholar—he was also the first person to write a comprehensive review on the history of biogeochemistry in 1991.
Introduction

Eville Gorham published a paper entitled Biogeochemistry: its Origins and Development, which provided the first historical account of how the discipline of Biogeochemistry came into existence (Gorham 1991)—and it has remained the gold standard on this topic. This eloquently written paper is the platform from which I further expound on in revisiting the historical development of Biogeochemistry. William H. Schlesinger wrote an article entitled Better Living Through Biogeochemistry (Schlesinger 2004) in which he wrote: “the chemistry of the arena of life—that is Earth’s biogeochemistry—will be at the center of how well we do, and all biogeochemists should strive to articulate that message clearly and forcefully to the public and to leaders of society, who must know our message to do their job well.” Schlesinger, a key figure in the formative years of Biogeochemistry, also describes this nascent field as “… the premier scientific discipline to examine human impacts on the global environment.” So, how have we as biogeochemists met that challenge for the past 16 + years, and how is that linked with the evolution of biogeochemistry? This in part, is one of the key reasons for writing this paper, to examine how the origins of this field came into existence, and how they link with the evolution and development of the discipline since the geochemist/mineralogist, Vladimir Ivanovich Vernadsky (1863–1945), the founder of Biogeochemistry, published his provocative book entitled Essays on Geochemistry and the Biosphere (Vernadsky 1926).

Born from multidisciplinary interactions between biological, geological, and chemical sciences early in the 19–20th centuries, biogeochemistry has continued to expand its scope in the 21st century on scales that range from microbiological/ ‘omics approaches (genomics, transcriptomics, proteomics, and metabolomics) to global elemental flux transfers in Earth System models (see Steffen et al. 2020). There continue to be a plethora of new biogeochemistry books and journals published each year with different foci on materials in sub-systems such as the soils, microbes, atmosphere, terrestrial plants, aquatic systems, and even the cosmos, to name a few. As argued in Gorham’s (1991) paper 30 years ago, biogeochemistry was a key unifying force during the late 19th and early 21st centuries. Interestingly, this was also when organismal and molecular biology began to separate, based largely on reductionist thinking, as early as the 1950s (Mayr 1961; Simpson 1967); which later resulted in the fracturing of many Biology departments in the 1980s and 1990s. Similarly, I believe biogeochemistry served to unite geobiology and geochemistry during these same tumultuous decades, when Geologists’ had to redefine and expand their boundaries—as they transitioned from Geology to Earth Science departments. Here, I explore the seemingly circuitous evolution of biogeochemistry, from its early origins to the present, and how it became an important interdisciplinary scientific discipline, that remains a vital beacon for the future of climate change science. Some may argue that a considerable amount of the historical information presented here could also be used in describing the history of Ecosystem Science (e.g. Carpenter et al. 1998), Earth System Science (e.g. Steffen et al. 2020), and beyond—and I would not object to that assertion. However, I would argue that the roots of biogeochemistry are different than Ecosystem Science and Earth System Science, in not being as centrally linked with ecology and geology, respectively. Perhaps the best way to view my perspective on this is to think about how biogeochemistry is distinctly separated within the Earth Sciences in the distinct categories commonly used for biogeochemistry sessions at a typical American Geophysical Sciences Meeting. Finally, as I am not a historian, this article is not meant to comprehensively cover the history of all the topics, individuals, organizations, etc. within the broad suite of scientific sub-disciplines that have intersected with biogeochemistry in its maturation. I have tried to use what I consider to be important historical pathways involving a select assemblage of discoveries and experimental approaches, not always in chronological order, with emphasis on particular bio-geo-chem-ical processes and elemental cycles that, in my humble opinion, cover the salient historical events of the discipline.

Disparate beginnings in the age of enlightenment: 17–19th centuries

Perhaps the earliest example of linking organic and inorganic substances with large earthly cycles, the rudiments of biogeochemistry, can in part, be traced to Empedocles (483–424 B.C.), who divided the physical universe into air, water, fire, and earth, as well as a
disciple of Confucius (551–479 B.C.), who developed the five universal element system (Browne 1944; Russell 1945; Degens 1989). However, as Gorham (1991) explains, it was not until the period between the 17th and 19th centuries, that we begin to see studies of photosynthesis (e.g. Plattes 1639; Hooke 1687; Priestley 1772), organic matter decomposition (e.g. MacBride 1674; Jameson 1800; Schwann 1837; Cohn 1872); metabolism (e.g. Davy 1813; Leibig 1840; Forschhammer 1865), plant nutrition (e.g. Digby 1669; Leibig 1855; Salm-Horstmar, 1856) and weathering (e.g. Home 1757; Hutton 1795; Thaer 1810; Bischof 1854), that really begins to set the stage for the emergence of biogeochemical concepts. For example, some of the first chemical budgets and descriptions of elemental cycles linked soil fertility (e.g. Plattes 1639; Lawes and Gilbert 1882; Dumas 1841) and plant transpiration to the hydrologic cycle (e.g., Halley 1687; Woodward 1699). In fact, Gorham (1991) posits such studies were key in the establishment of the: (1) pathways and key linkages of inorganic and organic substance processing with the hydrologic cycle; (2) importance of carbonic acid, generated via metabolic pathways, in weathering; (3) foundations in plant nutrition; (4) importance of microbes in organic matter decay and elemental cycles; and (5) recognition of elemental cycles on a global basis. From this early work, we see the conceptual emergence of the term biosphere, first used by Lamarck (1802) and more formally developed by Suess (1875). This concept was later adopted by Arrhenius (1896), who began to make important linkages between geochemistry and the biosphere. However, the true concept of biosphere, as we think of it today, was not realized until Vernadsky (1926) (Fig. 1)—as further promulgated by George Evelyn Hutchinson (1903–1991). Hutchinson (1970) writes that: “The concept played little part in scientific thought, however, until the publication, first in Russian in 1926 (actually 1924) and later in French in 1929 (under the title La Biosphere), of two lectures by the Russian mineralogist Vladimir Ivanovitch Vernadsky. It is essentially Vernadsky’s concept of the biosphere, developed about 50 years after Suess wrote, that we accept today. Vernadsky considered that the idea ultimately was derived from the French naturalist Jean Baptiste Lamarck, whose geochemistry, although archaically expressed, was often quite penetrating.” The boundaries between these different physical states of rock, gas, water, and organic matter (Fig. 1) change when phase transitions are thermodynamically in favor of a molecule that is catalyzed into transition to another state; understanding the controls of these transitions in the biosphere is central to biogeochemistry (see Degens 1989).

Early linkages in biogeochemistry: weathering, carbon cycle, and climate

Georges Cuvier (1769–1832), considered the founder of paleontology and by some, the greatest natural historian of all time (see Rudwick 1997), was not supportive of new theories of evolution in his time. Nevertheless, Cuvier was pivotal in establishing a linkage between organismal extinction and multiple catastrophic events (not just a single flood as preached in religion) (Fig. 2) in his book Discourse on the Revolutions of the Surface of the Earth published in 1827 (see Bard 2004). Other important linkages between geology and climate derive from the classic works of Charles Lyell (1797–1875) and Horace-Bénédict de Saussure (1740–1799) on the importance of weathering and erosion by glaciers. Luis Agassiz (1807–1883), further suggested linkages with glacier history and cold climatic events with extinctions, which was further adopted and supported by British
geologists’ Charles Lyell and William Buckland (1784–1856). Coupled with the work of physicists, like Joseph Fourier (1786–1830), Clause de Pouillet (1790–1863), and Josef Stefan (1835–1893), scientists also began to utilize new knowledge about solar constants and heat, to better understand the observed circulation of envelopes of air in Earth’s atmosphere (Bard 2004). As noted by Bard (2004), this set the stage for Irish engineer John Tyndall (1820–1893), to begin his examination on the effects of gas absorption and emission infrared rays on atmospheric warming (e.g. Tyndall 1863). According to Berger (1988), this unique coupling of natural history, geology, and physics, allowed for the foundational work by Thomas Chrowder Chamberlin (1843–1928), on glacial stages in Earth’s history, to be linked chemically by Svante Arrhenius (1859–1927)—thereby providing a connection between past changes in atmospheric CO2 and the ice ages (Arrhenius 1896; Chamberlin 1899). These brief historical vignettes on early climate change research not only provides critical linkages between carbon cycling, weathering, and climate change, but are provocative in their revelation of how large Earth cycles work in concert to control the biosphere. From here, I further explore the historical details on this important connection between weathering and climate—which is foundational in the early evolution of biogeochemistry.

It was the early drawings and writings by van Helmont and Marcello Malpighi (1628–1694) (Malpighi 1675), that allowed Nehemiah Grew (1641–1712) to ponder the existence of exchanges between air, rocks, and organisms (Grew 1682) (see Galvez and Gaillardet 2012). This was further explored by Stephen Hales (1677–1761), who introduced a new and ingenious experimental approach (vegetable sticks as pneumatic devices) to measure this “fixed air” that exchanged between rocks and organisms (Hales 1727). The “organisms” here, which are actually microbes, are based on the previously reported existence of single-celled organisms by Robert Hooke (1635–1702) and Antonie van Leeuwenhoek (1632–1723), which (Fig. 3)—which van Leeuwenhoek called “little animals” (Gest 2004). It was actually van Leeuwenhoek who in 1674 discovered bacteria (Gest 2004). With this in mind, Joseph Black (1728–1799) and Henry Cavendish (1731–1810), performed some experiments with “fixed air” (carbon dioxide), which fit largely into this story, and suggested that fixed air was a component of the atmosphere and an important chemical linkage between minerals and organisms (see Galvez and Gaillardet 2012). Remember, the use of the term fixed air was during Phlogiston period, first introduced by Johann Joachim Becher (1635–1682) and more formally by George Ernst Stahl (1659–1734) in the seventeenth century, whereby phlogiston, was considered a fire-like element released by certain combustible materials during combustion (see Chang 2010). It was Antoine Laurent Lavoisier (1743–1794) who led the charge against the phlogiston theory, by first introducing the term carbonic acid (Lavoisier 1781), and then carbonic gas (Lavoisier 1786), thereby replacing the term fixed air (see Galvez and Gaillardet 2012). Lavoisier adroitly recognized that it had a carbonaceous character, and was found in coal and carbonate rock. Eventually, with development of the atomic theory, Jonathan Dalton (1766–1844) and Jöns Jacob Berzelius (1779–1848) worked out the chemical formula for CO2 (Dalton 1808; Berzelius 1819), which allowed Gustav Bischof (1792–1870) and others, to make connections between carbonic acid and components of rock weathering (e.g. via dissolution) (e.g. Bischof 1826; Fournet 1833). This also allowed for early development of some of the biological and geological mechanisms controlling atmospheric CO2—via the burial of carbonaceous material in sedimentary rocks and emissions from volcanoes (e.g. Brongniard and Malagutti 1841; Ebelmen 1845, 1847) (Fig. 4) (see Galvez and Gaillardet 2012).

It was James Hutton (1726–1797), who first suggested that Earth could be described as a “superorganism” in his foundational work, The Theory of the Earth (Hutton 1795). It is worth noting as some have argued, that Hutton was influenced from previously published work by George Hoggart Toulmin (1754–1817), in particular his book The Antiquity and Duration of the World (Toulmin 1780) (see McIntyre 1963). However, is it unquestionable that Hutton and Toulmin, were very different in their overall philosophical and religious beliefs, which made their contributions uniquely distinguishable (see Hooykaas 1963). In particular, it was Hutton, who emphasized the uniformity of Earth, the incredible long-term cycles involved with continental destruction and creation, and the immeasurable age of the Earth (Hooykaas 1963). Nevertheless, it took almost
100 years for his work to be fully appreciated and expanded upon in a cross-disciplinary way. For example, Lyell (1833), in his second volume of the *Principles of Geology*, reported that biospheric carbon
from fresh plant material represented a very small fraction of the carbon in sediments from the Bay of Bengal, compared to soil-derived and even petrogenic material, which he called “waste of rocks and their organic content” (see Blattmann et al. 2018). The complexity of such carbon sources was later recognized by Matti Rufus Sauramo (1889–1958), allowing for petrogenic material to be included as a component of the larger carbon cycle (e.g. Sauramo 1938; Bolin 1970). This was important, as petrogenic material survives chemical weathering in rocks and remains in eroded sediments that are transported to distant regions (see Blattmann et al. 2019). In fact, this distinction between ancient and modern carbon remains vital in our understanding of carbon cycling today, as it relates to the fate of continentally-derived organic matter in the ocean derived from pedogenic versus petrogenic sources (see Blattmann et al. 2019).

It was French chemist, Jacques-Joseph Ébelmen 1814–1852), who first linked the importance of organic matter decay in rocks with the regulation of carbon dioxide and oxygen levels in the atmosphere (Ébelmen 1845) (see Berner and Maasch 1996). Others (e.g. Arrhenius 1896; Chamberlin 1899) followed suit, and developed a more elaborate understanding of the pathways of chemical weathering that linked atmospheric concentrations of carbon dioxide to Earth surface temperature. In fact, Chamberlin (1899) in his paper entitled *An Attempt to Frame a Working Hypothesis of the Cause of Glacial Periods on an Atmospheric Basis*, writes “It now becomes necessary to assign agencies capable of removing carbon dioxide from the atmosphere…” It is not surprising that such a prescient statement for this time, is now widely cited in the climate change literature.

Biogeography, evolution, and ecology—linkages with biogeochemistry

Scientists’ have long thought about what controls the distribution of animals and plants on the planet. As evolution and biogeography began to develop as scientific disciplines, more formal approaches emerged to explore the controls on the global distribution of organisms. Alexander von Humboldt (1769–1859), Alfred Forbes (1815–1854), and Thomas Henry Huxley (1825–1895) were some of the first scientists to promulgate the terms “evolution” and “biogeography,” in their writings, respectively. The early establishment of biogeography via geology, was not only critical in the discovery of the theory of evolution through natural selection by Darwin (1859) and Alfred Russel Wallace (1823–1913) (e.g. Wallace 1876), but also to biogeochemistry. The merging of evolution and biogeography allowed for the formal examination of present and past distribution patterns of biological diversity and linkages with environmental/historical causes (see Sanmartin 2012). Interestingly, I believe some of the first linkages between these early disciplines and biogeochemistry in part, began with naturalists’ interests in what were actually the bio-geo-chemical factors that control the distribution of plant and animal taxa (e.g. von Humboldt 1805; Forbes 1846; Darwin 1859; Wallace 1876). In particular, linkages with what eventually became known as ecological biogeography (discussed later), set the stage for a greater understanding of how organisms adapt temporally and spatially to different environmental conditions.

It was Ernst Haeckel (1834–1919) who first used the term ecology in the literature (Haeckel 1866) (see Coleman 1986; Kormondy 2012), as stated here: That the interactions between all neighboring organisms are extraordinarily important and that they exert far more influence on the change and adaptation of species than do the inorganic conditions of existence was first emphasized with due clarity by Darwin. Unfortunately, these very complicated relationships between organisms remain for the most part unknown, and this because we have so far failed to attend to the question. Here, in fact, there exists a huge and interesting as well as important area of future inquiry. Ecology or the theory of the economy of nature, this being a division of physiology and one which our textbooks have totally ignored, when seen from this perspective promises to reward us with splendid and surprising discoveries. After this seemingly vague introduction of ecology, we begin to see interests in the role of multicellular organisms in soil fertility, which allowed for further development of ecology—as an important link to biogeochemistry. For example, the Danish botanist, Eugenius Warming (1841–1924), redefined what Darwin called “rotation,” which we know today as plant succession, with his work in the Danish Jutland. Warming observed the unique role of earth worms in controlling the stages of growth by different plants and that the plants and their respective associations, represented a plant “community.”
(Warming 1895) (see Coleman 1986). In fact, the first book on ecology, published by Warming (1895), is still considered by many as the defining text that founded ecology as discipline (Goodland 1975; Coleman 1986; Kormondy 2012). As ecology begins to develop as a nascent field, we see significant benefits to agriculture—through new linkages between multicellular organisms and biogeochemistry in soils.

Agriculture and soil chemistry: early stoichiometric thinking

French chemists pioneered the way in developing an understanding of soil fertility from a chemical perspective. For example, Lemey’s (1717) paper on *The Origin of Nitre* was key in suggesting the importance of reciprocity between the interaction of animals and plants in soil chemistry. This allowed others like Claude Louis Berthollet (1748–1822) to explore linkages between plants and animals, which both contained nitrogen (Berthollet 1785), as well as “nitrates in potash” (Lavoisier 1790). This was picked up later by English agriculturalist, Jethro Tull (1674–1741), who emphasized the need for rotating crops (Tull 1731). However, it was the Scottish scientist, Francis Home (1719–1813), that continued to stress the need for understanding the importance of chemistry to improve agriculture practices (Home 1757). The humus theory, introduced by the Swedish chemist (Johan Gottschalk Wallerius 1709–1785), was also central at this time, and contended that plants obtained their nutrients from water soluble elements (e.g. C, H, N, O) found in humus (see Sparks 2006). Quite remarkably, much was learned during this time period about the linkages between atmospheric cycles and life, as described here by Aulie (1970): “In scarcely more than the last two decades of the eighteenth century, Joseph Priestley (1733–1804), Jan Ingen-Housz (1730–1799), Jean Senebier (1742–1809), and Saussure worked out the main paths of the oxygen and carbon dioxide cycles as they are known today.”

Sir Humphry Davy (1778–1829), with his discoveries of metals such as sodium, potassium, calcium, magnesium, strontium and barium, was highly influential in the application of chemical techniques to improve agricultural practices. For example, Davy (1813) argues that: “It is scarcely possible to enter upon any investigation of agriculture without finding it connected, more or less, with doctrines or elucidations derived from chemistry.” Davy (1813) uniquely combines the bio-geo-chem-istry of agriculture, using his own experiments and many other studies, by linking the mineralogy and formation of soils with biochemical of composition of plant material (e.g. organic acids, volatile oils, waxes), and how this relates to the effectiveness of different fertilizers and their respective chemistry. The French chemist, Jean-Baptiste Dumas (1800–1884), further developed the idea that the chemical composition of plants and animals was vital in understanding organic matter and elemental cycling in soils. For example, as stated by Dumas (1841) in the case of animals: “If the animal kingdom constitutes an immense apparatus for combustion, the vegetable kingdom, in its turn, constitutes an immense apparatus for reduction, in which reduced carbonic acid yields its carbon, reduced water its hydrogen, and in which also reduced oxide of ammonium and nitric acid yield their ammonium or their azote.” Similarly, the specific case for plants was made by Dumas and Jean-Baptiste Joseph Dieudonné Boussingault (1801–1887), as described here in Dumas and Boussingault (1844): “It is in plants, consequently that the true laboratory of organic chemistry resides; carbon, hydrogen, ammonium, and water, are the elements they work upon; and woody fibre, starch, gums, and sugars, on the one hand, fibrine, albumen, caseum and gluten, on the other, are the products that present themselves as fundamental in either organic kingdom of nature—products, however, which are formed in plants, and in plants only, and merely transferred by digestion to the bodies of animals.” These early studies linking chemistry and soil fertility, foundational as early examples of soil biogeochemistry, continue with important work by Boussingault, who was perhaps most critical in establishing connections between the exchange of nitrogen and soil organisms. In particular, he used novel chemical instrumentation in lab experiments to determine that atmospheric nitrogen, not just soil N, was an important part of the nitrogen cycling story (Boussingault 1838) (Fig. 5) (see Aulie 1970). As described in detail by Aulie (1970), this work inspired a debate in the literature, vital in the evolution of biogeochemistry, involving the “ammonia hypothesis” by Leibig (1840), largely inspired by Ferdinand de Saussure (e.g. Saussure 1804)—which led to further key work by Georges Ville (1824–1897) (e.g.)
Ville 1850). The Boussingault (1887) paper, represents a culmination of his work, which established the biochemical process of nitrification as a possible link for the role of microorganisms in element cycling in the biosphere. The next step was taken by Jean-Jacques-Theophile Schlöesing (1824–1919) and Charles-Achille Miintz (1846–1917), when they suggested the importance of microbes in the nitrification process (Schlosing and Miintz 1877), as more broadly suggested by Pasteur (1861) in his use of the term “ferments” (e.g. microbes) as important agents of change in nature (Aulie 1970). Finally, it should also be noted here, that the importance of the sulfur cycle in decay processes was also recognized at this time, as Daniell (1841) writes: …It has also been generally known that sulphuretted hydrogen is produced by processes of decay or fermentation, in which large quantities of animal matters are concerned.”

As the relationship between microorganisms and macronutrients in soils developed, a more stoichiometric-based approach in agricultural practices developed. In particular, the agriculturist, Sir John Bennet Lawes (1814–1900), was pivotal in developing the onset of the chemical fertilizer business. Building on a nascent understanding of stoichiometric linkages and metabolic processes in plants, Lawes et al. (1861) writes: “Numerous direct experiments showed, that when nitrogenous organic matter was submitted to decomposition in water, over mercury, in the absence of free oxygen, no free nitrogen was evolved. In fact, the evolution in question appeared to be the result of an oxidating process…Direct experiments also showed, that seeds may be submitted to germination and growth, and that nearly the whole of the nitrogen may be found in the vegetable matter produced…Although there can be no doubt of the evolution of hydrogen during the decomposition of

Fig. 5 Apparatus used by Boussingault to generate a “renewable” atmosphere (from Aulie 1970)
organic matter, and although it has long been admitted that nascent hydrogen may, under certain circumstances, combine with gaseous nitrogen and form ammonia.” Perhaps most notably, it was the German chemist, Justus von Liebig (1803–1873), who proposed that crop yield in agriculture was a function of the minimum quantity of nutrients, commonly known as “Liebig’s Law of the Minimum” (Liebig and Playfair 1840) (see Paris 1992). According to Liebig (1862): "Every field contains a maximum of one or more and a minimum of one or more different nutrients. With this minimum, be it lime or any other nutrient, the yield of crops stands in direct relation. It is the factor that governs and controls the amount or duration of the yields. Should this minimum for example be lime or magnesia, the yield of grain and straw, of beets, potatoes and clover will remain the same and be no greater even though the amount of potash, silica, phosphoric acid, etc., already present in the soil be increased a hundredfold. The crops on such a field, however, will be increased by a simple fertilization with lime” (see Browne 1942). Another point of clarification is that Phillip Carl Sprengel (1787–1859), who was largely responsible for disproving the “humus theory,” developed theory of the Law of the Minimum by suggesting the importance of mineral nutrients for plant growth (Sprengel 1838), not Liebig—as commonly professed (Browne 1944; Wendt 1950; Bohm 1987; Sparks 2006). Nevertheless, we now have a chemical basis for linking certain elemental cycles with plant growth, thereby connecting soil chemistry and biology—central to biogeochemistry. In fact, this allowed for the first long-term soil amendment experiments to enhance soil productively for agricultural crops (see van der Ploeg et al. 1999). More specifically, experiments examining NO₃ leaching from soils, as it related to N amendments (Goulding et al. 2000), actually occurred on Boussingault’s farm in Alsace, France (see Richter et al. 2007). Interestingly, some of the long-term plot sites still exist, like the hayfield site which began in 1856, that some refer to as”…the most long-term ecological study” (Tilman et al. 1994). However, the oldest know extant site, the Broadbalk wheat study (established in 1843), is located in southern England (see Jenkinson 1991; Richter et al. 2007).

Another interesting development around this time, that was eventually incorporated into application of soil quality in agriculture, was the importance of the mechanical action of animals on soil quality, oddly enough from Charles Robert Darwin (1809–1882)—albeit very late in his life (Darwin, 1881). The book by Darwin, entitled “The Formation of Vegetable Mould Through the Action of Worms with Observations on Their Habits,” introduced the idea that organisms play a critical role physical agents in the bioturbation of soils—which impacted soil quality. This is Darwin’s last scientific book publication (just 6 months before his death), and it explored a diversity of topics such as pedogenesis, weathering, formation of vegetable mould (e.g. topsoil, soil surface horizon, and worm castings), worm burrowing effects, soil fertility, plant nutrition, and even estimates of worm bioturbation on large regional-scale erosion budgets—as related to hydrologic cycles (Fig. 6) (see Feller et al. 2003). Interestingly, Darwin (1881) argues that the turnover of topsoil by worms in the UK was significant—particularly as it related to the frequency of soil passage through worm guts, as writes here: “had passed many times through, and would pass again many times through, the intestinal canal of worms” (see Feller et al. 2003). Darwin, who had already achieved international fame with his theory of evolution through natural selection, wrote this amazing book, largely unrecognized at the time, that essentially contained the central tenets of biogeochemistry. He recognized important linkages, from small-scale microbial/soil processes to regional budgets of soil turnover, that remain central to our current understanding of soil biogeochemistry and erosion. Unfortunately, Vasily Vasilyevich Dokuchaev (1846–1903), considered the founder of pedology, largely ignored the importance of Darwin’s contributions to concepts of soil formation at the time (Dokuchaev 1883) (see Edmunds and Bogush 2012), which resulted in this work being ignored for many years to come. While the importance of this book was eventually realized for its biopedologic importance (Feller et al. 2003), some have suggested that the reason it took almost 120 years to be recognized was that it was published when agriculture was focused on the importance of chemistry, during Leibig’s heyday (e.g. Leibig 1840) (see Feller et al. 2003). This work introduced the notion of organisms as engineers in nature, a concept still explored in our understanding of biogeochemical cycles in terrestrial and aquatic ecosystems (e.g. Jones et al. 1997).
While the chemistry of agriculture continued to develop there remained a lack of understanding of how microbes specifically interfaced with key elemental cycles. We now see Winogradsky’s work, which begins under the tutelage of Andrei Famintsyn (1835–1918), further expand the importance of using both lab and natural history approaches understanding natural systems—another critical step in biogeochemical history. In exploring the distribution of microbes in nature (Fig. 7), Winogradsky begins to make critical linkages between microbial and elemental cycles in soils—as he develops the conceptual view of the “cycle of life” (see Ackert 2007). Winogradsky, who at the time continued to be influenced by Famintsyn, was interested in combining physiological knowledge of nutrition and respiration of both animals and plants (Famintsyn 1883), essentially following the steps of Claude Bernard (1813–1878) (see Ackert 2007). All of this work was largely based on the earlier foundational works on organic matter cycling involving chemical transformations (Dumas 1841), fermentation—Louis Pasteur (1822–1895) (Pasteur 1861), and putrefaction—Ferdinand Cohn (1828–1898) (Cohn 1870). The essence of Winogradsky’s work, most notably results in the development of the theory of chemolithotrophy, while studying the sulfur-oxidizing bacterium *Beggiatoa* (Winogradsky 1887), and a mechanistic understanding of bacterial nitrification (Winogradsky 1891) (see Dworkin 2012). In his nitrogen work, Winogradsky was able to actually isolate nitrifying bacteria in pure cultures and then, examine the individual stages of ammonia being converted to nitrite—and then to nitrate, truly innovative at that time. These prolific discoveries by Winogradsky in part, provided a unique perspective on autotrophic bacteria and how their presence in nature would impact the cycling elements like sulfur, nitrogen, and iron in soils (Waksman 1953); he is commonly referred to as the founder of modern microbiology and by many, the first microbial
ecologist (see Dworkin 2012). Winogradsky’s work opened the door for exploring the role of microbes modifying the soil landscape and its ramifications in larger-scale nutrient cycles. Thus, the transition to a more formal approach to examining the interactive effects between environment and organisms was ripe, with a number of key scientists further contributing to the development of ecology as a discipline (e.g. F. A. Forel, Carl Semper, S. A. Forbes, Karl Mobius, and Julien Vesque).

Early thoughts of an anthropocene: good and bad

As agricultural science continued its development, naturalists began to think about the consequences of expanding agriculture, technology, and cities. If we briefly jump ahead for context, scientists have now agreed, that an Anthropocene epoch does exist and that it began around the mid-20th century (see Zalasiewicz et al. 2019, and references therein). The basis for this timeline is nicely illustrated when examining the human footprint on Earth—based on metrics like the percentage of net primary production sequestered, fossil net primary production (NPP) liberated as fossil fuels, and new forms of energy production of energy from other sources (Fig. 8) (Williams et al. 2016). Thus, while the concept of the Anthropocene continues to be improved in the 21st century, the notion of humans as driving agents of change in the biosphere is certainly not novel. Interestingly, while many scientists in the early 19th century were writing about the great potential of man’s achievements for the future, Lamarck (1817) was more cynical about the presence of man, as he writes here: “…In destroying everywhere the large plants that protect the soil in order to secure things to satisfy his greediness of the moment, man rapidly brings about the sterility of the ground on which he lives, dries up the springs, and chases away the animals that once found their subsistence there. He causes large parts of the globe that were once very fertile and well populated in all respects to become dead, sterile, uninhabitable, and deserted…” (see Burkhardt 1970, 2013). Similarly, George Perkins Marsh (1801–1882) published a book entitled The Earth as Modified by Human Action: Man and Nature (Marsh 1874a, b), which essentially marks the first discussion of modern ecological problems, as we know them today. In Marsh (1874a, b), he writes: “But man is everywhere a disturbing agent. Wherever he plants his
The proportions and accommodations are arrangements which insured the stability of existing arrangements are overthrown. Indigenous vegetable and animal species are extirpated, and supplanted by others of foreign origin, spontaneous production is forbidden or restricted, and the face of the earth is either laid bare or covered with a new and reluctant growth of vegetable forms, and with alien tribes of animal life.” Similarly, Vernadsky (1945) writes: “Proceeding from the notion of the geological role of man, the geologist A. P. Pavlov (1854–1929) in the last years of his life used to speak of the anthropogenic era in which we now live.” These early admonishments about human behavior and their threat to the environment serves as an appropriate segue to the history of biogeochemistry over the next two centuries—where the focus on human impacts becomes a dominant theme.

20th and 21st centuries: the formative years and new beginnings

Biogeochemistry—a new discipline born

I begin this section with some biographic details about the Father of Biogeochemistry, V.I. Vernadsky (Fig. 9). His prophetic book, The Biopshere, was published in 1926, translated into French in 1929, and finally translated into English 1997 (Langmuir 1997)—with a cover resembling that of a science fiction novel (Fig. 10). Vasily Dokuchaev, who founded the Russian school of soil science and soil geography, had perhaps the most influential impact on Vernadsky in his early career (see Edmunds and Bogush 2012). An important stage in his career was being invited to teach geochemistry at the Sorbonne, University of Paris in 1922. It was here that his incredible linguistic skills, fluent in 20 languages, allowed him to amass and read the expansive European literature now available to him. This is when Vernadsky really refined his ideas on the importance of organisms in the cycling of elements in the lithosphere, hydrosphere, and atmosphere (see Melua...
1990; Edmunds and Bogush 2012). These years in Paris were extremely productive for him; he published many scientific papers, perhaps most notably the *The Biopshere*. His last published work, *A Few Words About the Noosphere* (Vernadsky 1944), was published only a year before his death in Moscow in 1945. In this final work, his views on the impact of human industrialization on the biosphere, or transiting into a noosphere, which he posits the existence of entirely different “states” in the biopshere (see Edmunds and Bogush 2012). Vernadsky further expounds the Earth’s response as a superorganism to its new “state” in the noosphere, which would become an “intellectual prehistory” of the Gaia Hypothesis (see Grinevald 1998), promulgated by Lovelock (1972) and Lovelock and Margulis (1974) decades later. As noted by Melua (1990), this concept of a superorganism was not only visionary, but anachronistic when considering the widely accepted reductionist approach espoused by many of his contemporaries at that time (see Edmunds and Bogush 2012). Hutchinson proved to be an important proponent for Vernadsky’s concept of the Biosphere (Hutchinson 1970); this was logical progression as Vernadsky’s son George Vernadsky, at the time a faculty member of history at Yale University, was able to translate documents from his father’s work for Hutchinson (Edmunds and Bogush 2012). While Hutchinson served as an important advocate for the recognition of Vernadsky’s work, which had largely been ignored in the west at this time (Grinevald 1998), there was clearly beneficial cross-fertilization for both
scientists at the time (Lapo 2001). Finally, one could argue that Hutton (1795) first introduced the idea of studying Earth’s processes in the context of a super-organism, but it was Lovelock (1972) who further added the more biological emphasis on homeostatic regulation combined with geology, that further developed the Greek personification of Gaia as Mother Earth (Serafin 1988). While these ideas about Gaia were largely conceived as it related NASA’s exploration of life on other planets (Lovelock 1965), it was Lovelock’s friend and Nobel laureate in literature, William Golding, who upon learning about Lovelock’s hypothesis, suggested that it be named after The Greek Goddess of Earth, Gaia (Lovelock 1972).

Born in the age of the noosphere, biogeochemistry immediately takes on an important role in a world undergoing global change—asLikens (2004a)nicely summarizes here: “Biogeochemistry is a vibrant, robust and growing field. From the early writings of Vernadsky (1944, 1945) and Hutchinson (1944, 1950) to in-depth analyses of lake (Schindler, 1980) and forest ecosystems (Likens et al. 1977) the field now has matured and become more focused on problems at regional to global scales and those directly relevant to humans (e.g., Schlesinger 1997; Burke et al. 1998).” The emergence of modern biogeochemistry, between the 1970s and 1990s in part, arises from the demand to examine fluxes and reservoirs of chemical substances on a global scale (Jacobson et al. 1992), and the need better integrate environmental science (Jacobson et al. 2000). A few examples of how modern biogeochemistry has been defined are as follows: “…a study of the geochemistry of the surface of the Earth.” (Schlesinger 1991); “the study of biological controls on the chemistry of the environment and geochemical regulation of ecological structure and function” (Bashkin 2002); and “…the study of transport and transformation of matter and energy in ecosystems” (Kaye et al. 2006). In the general context of these definitions we now continue our journey on the evolution of biogeochemistry in the 20th and up through the 21st centuries.

An important part of the evolution of any science, as it is for biogeochemistry, is technological advancements along the way, which cannot be fully explored here. Briefly, Moran et al. (2016) have described such advancements, largely in the fields of microbial ecology, geochemistry, and informatics, as key understanding biogeochemical cycling in the global ocean. In general, this can certainly be argued for the other aforementioned sub-disciplines of biogeochemistry. Some of these technological advances over the past ca. 60 years are: basic local alignment search tool (BLAST) (e.g. Mount 2007); Fourier transform ion cyclotron resonance mass spectrometry (FT-IRMS) (e.g. Sleigher and Hatcher 2007; Kujawinski 2011; Moran et al. 2016); gas chromatography isotope ratio mass spectrometry (GC-IRMS)/compound-specific IRMS, gas chromatography mass spectrometry (GC–MS); liquid chromatography mass spectrometry (LC–MS); nuclear magnetic resonance spectroscopy (NMR) (see Mopper et al. 2007; Moran et al. 2016; Wakeham and Lee 2019; Sparks 2019, and references therein)—just to name a few. Similarly, the advent of Next-Generation sequencing (NGS) technologies in brief, has allowed for large-scale sequencing using molecular approaches on bacterial characterization (16S rRNA, DGGE, T-RFLP), which further developed into targeted amplification, metagenomics, RNA-seq, proteomics, Tn-seq (see Boughner and Singh 2016, and references therein). Moreover, development of recombinant DNA techniques, based on 16S rRNA, as originally proposed by Woese (1987), (see Hill et al. 2002; Theron and Cloete 2000) and 16S rRNA gene sequencing, allowed for the ability of explore microbial communities in natural systems (e.g. Kimura et al. 2007, and references therein). Finally, metagenomics, transcriptomics, proteomics, and lipidomics have forged a new relationship between evolutionary and molecular biology that has proven critical in biogeochemistry (see Wang et al. 2009; Simon and Daniel 2011; Moran 2015; Boughner and Singh 2016). With these molecular techniques, and others not discussed here, I will now continue to explore some of important trends and discoveries in biogeochemistry in the 20th and 21st centuries.

Geology to organic geochemistry—important links with biogeochemistry

As discussed earlier, the global importance of chemical processes involving how atmospheric CO₂ interacts with rocks during weathering to form dissolved salts and bicarbonate, was first proposed by Ebelmen (1845). The role of geology in the evolution of biogeochemistry continues in the 20th and 21st centuries. For example, as noted by Gaillardet and Galy (2008) early global sedimentary modeling work...
was inherently linked with plate tectonics theory. This work provided a foundation from which to base carbon cycling in shallow and deep reservoirs, and its linkages with climate change (see Gaillardet and Galy 2008, and references therein). This led to a more comprehensive views on the timescales of controls on sources and sinks of carbon such as, weathering processes and CO₂ consumption (e.g. Raymo et al. 1988), the burial and decay of sedimentary organic matter (e.g. Galy et al. 2007), and CO₂ degassing and fluxes (Gaillardet and Galy 2008).

While the term geochemistry was first used in 1868 by Christian Friedrich Schönbein (1799–1868), it was the publication led by Frank Wigglesworth Clarke (1847–1931), on chemical composition of Earth’s crust (Clarke and Washington 1924), that really led to the establishment of geochemistry as a separate discipline. Nevertheless, many still consider Victor Moritz Goldschmidt (1888–1947) the founder of modern geochemistry. The German mineralogist, Karl Hugo Strunz (1910–2006), who established mineral identification based on chemical composition and crystalline structure (e.g. Strunz 1941), was also key in the early stages of geochemistry. Finally, the importance of ionic radii in chemical bonding established in part, by Linus Pauling (1901–1994) (e.g. Pauling 1929) and Goldschmidt (e.g. Goldschmidt 1954), were critical in geochemistry and crystallography (see Degens 1989). These important chemical developments now allow in part, for perspectives on how biological compounds interact minerals in nature and how organic matter is chemically altered after being buried for millennia—we now see the emergence of yet another new discipline inherently linked with biogeochemistry, organic geochemistry (see Kvenvolden 2006, and references therein).

The origin of organic chemistry was an important step in the evolution of biogeochemistry because it allowed for the transition from geochemical-centric thinking—largely involving inorganic chemistry at the time, to the importance of organic compounds. The inception of organic geochemistry formally begins when Alfred E. Treibs (1899–1983) who first described linkages between porphyrin pigment molecules, found in shales, coals, and crude oils, and their biological sources in modern plants—such as chlorophylls (Treibs 1936) (see Kvenvolden 2006; Gaines et al. 2009). While Treibs is considered by many to be the father of organic geochemistry, Parker D. Trask (1899–1961) was also highly influential (Kvenvolden 2006) in its development. In essence, Trask introduced the broader geological linkages between bulk organic material in source sedimentary rock and source beds of petroleum (Trask and Patnode 1942). An important link between organic geochemistry and biogeochemistry, is the notion that like many of the fossils known to us (e.g. bones, shells etc.), fossil organic molecules can also be used as chemical biomarkers to provide a key to the past in ecosystems. Many of these biomarkers are preserved in sediments where fossil hard parts have not survived decay (Whiteside and Grice 2016). In fact, the amazing discovery of hemoglobin-derived porphyrins in a mosquito dated to be 50 million years old (Greenwalt et al. 2013), reveals the potential for other fossil molecules (e.g. Briggs and Summons 2014). These chemical biomarkers have been successfully used to link past changes in climate change with primary productivity, sediment redox, and beyond (see Peters et al. 2005; Gaines et al. 2009; Killops and Killops, 2013)—as well as tracing chemical/microbe processes in modern biogeochemical cycles (see Peters et al. 2005; Bianchi and Canuel 2011).

The application of novel chemical biomarkers/proxies, both organic and inorganic, in paleo-reconstruction has been particularly useful in understanding major biogeochemical shifts in Earth’s 4-billion-year history (see Lenton and Daines 2017), which are central in making predictions about future changes in global biogeochemical cycles. For example, over the past 30 years, a number of paradigms have suggested—albeit with considerable debate, that oxygenation of the atmosphere and ocean began with oxygenic photosynthesis in a reducing atmosphere in the Archean Eon > 2.7 billion years ago (see Lyons et al. 2014, and references therein). It was during the Great Oxidation ca. 2.4 billion years ago (see Kump and Barley 2007, and references therein), that the atmosphere reached a true oxidizing state allowing for oxygenation of the surface and deep ocean. While much of the banded iron formations (BIFs) are linked with this oxidation event (e.g. Poulton and Canfield 2011), some BIFs predate this back to 3.7 billion years ago and in part, likely reflect bacterial dissimilatory Fe(III) reduction (e.g. Czaja et al. 2013). This was followed by the Neoproterozoic-Paleozoic oxygenation ~ 0.6–0.4 Ga (see Lenton et al. 2014, and references therein) which resulted in persistent
oxygenation of the deep ocean—allowing for the rise of eukaryotic life (Lenton and Daines 2017). This now sets the stage for potential animal-sediment controls on biogeochemical redox reactions, with animal bioturbation estimated to have started ca. 540 Ma in shelf environments (see Lenton and Daines 2017, and references therein). This is important in the context of an early biosphere > 3.5 Ga being productive enough, with the earliest evidence of sedimentary organic carbon dating back to 3.7 Ga, thereby allowing for significant organic carbon burial in shelf sediments (Rosing 1999). When reflecting back to Darwin’s worms, current interests in the effects of poleward range shifts of organisms, due to global warming, on soil and sediment redox clearly point to the importance of the changing distribution/diversity of organisms on Earth, and how this impacts controls on biogeochemical cycles in the 21st century.

Biogeography in a changing world

In the 20th century, biogeography (as described earlier) branched into different sub-categories (see Sanmartin 2012) and understanding their respective differences, is critical in how they became linked with biogeochemistry. Briefly, these two general categories are: (1) ecological biogeography, which generally examines linkages with environmental factors with organismal distribution and adaptation (Morrone and Crisci 1995); and (2) historical biogeography, largely based on plate tectonic theory and the development of cladistics (Hennig 1966) and the notion that geological barriers (e.g. vicariance) cause organisms to evolve and adapt on Earth (see Cox and Moore 2010, and references therein)—with cladistics providing information about lineages (see Sanmartin 2012, and references therein). There is no doubt that biogeography, both old and new, has been central in our understanding the adaptation and movement of organisms across environmental gradients for many years (Forbes 1856; Wallace 1876; Lourie and Vincent 2004).

So, why is biogeography important to biogeochemistry in the 21st century? As Linder (2005) points out, understanding how the distribution of organisms across the planet came to be, can only be achieved by understanding how lineages diversify. Moreover, using newly emerging molecular systematics in recent decades will be key in understanding current and future organismal range expansions driven by global change (e.g. Scheffers et al. 2016). The American ecologist, Margaret Davis, has been a leader in using pollen data to examine how temperate- and boreal-forest species migrate. Davis and Shaw (2001) argue the importance of organismal adaptation and migration—as they write here: “...The unprecedented rates of climate changes anticipated to occur in the future, coupled with land use changes that impede gene flow, can be expected to disrupt the interplay of adaptation and migration, likely affecting productivity and threatening the persistence of many species.” Similarly, the cycling of organic matter and macronutrients can be altered in part, via bioturbation, as different communities of organisms and their respective feeding guilds and/or root structures, change from global change-driven range expansion, in both by terrestrial and aquatic systems. Thus, as global change “rearranges” the distribution of organisms across the planet in the 21st century, we can reflect back to earlier thoughts on biogeography, as Wallace (1876) writes: “nothing like a perfect zoological division of the earth is possible. The causes that have led to the present distribution of animal life are so varied, their action and reaction have been so complex, that anomalies and irregularities are sure to exist which will mar the symmetry of any rigid system” (see Spalding et al. 2007).

Eugene Warming’s early contributions in linking evolution and the role of plant-animal interactions in the development of plant communities (particularly in the tropics), proved to be foundational for the first tier of plant ecologists’ (e.g. Henry Chandler Cowles, Frederic E. Clements, and Alfred G. Tansley). Similar to the early work by Darwin on the role of metazoan animals (worms), this early work by Warming on plant ecology (described earlier) established the importance of top-down metazoans, in this case plants contributing to soil fertility. The general concept of top-down and bottom-up controls in ecosystems developed in the 90s and involves broader ecosystem interactions and predator–prey relationships (e.g. Hunter and Price 1992). Much of the earlier work on elemental cycling discussed thus far, had been bottom-up in nature, emphasizing broader ecosystem processes (e.g. weathering, atmospheric deposition, microbes, mineral interactions, hydrology). Later work on top-down and bottom-up controls has now more broadly expanded the role of trophic dynamics and
biodiversity on biogeochemical processes. For example, while contentiously debated at times, it is now generally agreed that organismal diversity can impact biogeochemical cycles (e.g. Chapin et al. 1997; Tilman et al. 2012).

Alfred James Lotka (1880–1949) was a pioneer in establishing early linkages between organisms and energy resources in natural populations, which was critical in the integration of population dynamics into the emerging field of ecology. Interesting, Lotka began his career with interests in developing a new field called physical biology. The general idea behind this was to combine physical biology and chemistry into one discipline that examined the changes in matter and the associated energy transfers. While he never accomplished this goal, his interests resulted in development of a book published in 1925 entitled Physical Biology, which in part expounded on host-parasite predator–prey relationships; this book was later published posthumously and reprinted as Elements of Mathematical Biology (Lotka 1956). His work would later develop into the famous Lotka-Volterra equations which focused more broadly on competition. The key principle of this work as stated by Lotka (1922a, b) was that: “...natural selection will operate to preserve and increase them, provided always that there is presented a residue of untapped available energy. The result will be to increase the total mass of the system, and, with this total mass, also the total energy flux through the system, since, other things equal, this energy flux is proportional to the mass of the system.” Similarly, he concludes “For the battle array of organic evolution is presented to our view as an assembly of armies of (plants), energy transformers-accumulators and engines (animals); armies composed of multitudes of similar units, the individual organisms.” One can argue that Lotka’s early work on organismal energetics and its linkage with population dynamics established a basis to move elaborate theories (beyond the food chain), with further works on population cycles and trophic webs by Charles Elton (1900–1991) (Elton 1958), and energetic approaches in systems ecology by Howard T. Odum (Odum and Pinkerton 1955)—which appeared shortly after Eugene P. Odum (1913–2000) published his groundbreaking Ecology book (Odum 1953). However, it is important to note that while Lotka-Volterra equations are limited to predator–prey interactions, it was the work of Vito Volterra (1860–1940) that allowed for the incorporation of competition—which became adopted more broadly for ecological interactions (Volterra 1926). Volterra’s work would eventually be tested experientially by the Russian ecologist, Gregory Gause (1910–1986) (Gause 1934, 1935). Hutchinson felt so strongly about the importance difference between Lotka-Volterra equations (predator–prey based model) and competition-based modeling/experimental work by Volterra and Gause, that he referred to the competition-based model as the Volterra-Gause equations (Hutchinson 1978)—which has remained in the literature today. Interestingly, it was Raymond Lindeman (1915–1942), a postdoc with Hutchinson, who published The Trophic Dynamic Aspect of Ecology (Lindeman 1942) that further expanded the application of this early population work by Lotka and others, and provided a foundation for development of systems ecology, not surprisingly by H.T. Odum, a student of Hutchinson (see Taylor 1988). Lotka’s contribution to ecology, while somewhat afield from his original goals in developing Physical Biology, served as an important step in the development of interdisciplinary thinking in ecosystem ecology and biogeochemistry.

As ecology continues to mature as a discipline, it is Hutchinson, strongly influenced by Vernadsky, and familiar with the works of August Thienemann (1882–1960) (e.g. Thienemann 1925) and Elton (1927), who now takes a pivotal role in the evolution of biogeochemistry. In 1957, Hutchinson, published the first volume of his groundbreaking four volume series, A Treatise on Limnology, which spanned a broad spectrum of topics covering the physics, chemistry, geography, and biology of freshwater systems (Hutchinson 1957a)—uniquely biogeochemical for the its time. Amazingly, in the same year, Hutchinson published his concept of an ecological niche (Hutchinson 1957b). This remains a transformational paper in ecology today, despite the fact that some have argued that Dutch botanist/microbiologist, Lourens Baas Becking (1895–1963) (through his influence by Martinus Beijerinck [1851–1931]), proposed the realized niche concept (Bass Becking 1934) well before Hutchinson (de Wit and Bouvier 2006). More importantly, in 1937 Theodosius Grygorovych Dobzhansky (1900–1975) published a book, entitled Genetics and the Origin of Species Dobzhansky (1932), that would now provide vital role in linking the gene as the mechanism of change for selective evolutionary
processes—that proved vital in understanding population and community dynamics (see Ayala and Fitch 1997). This important book, has been argued to be as important in unifying modern biology as a discipline, as that of Newton’s works in physics (Smocovitis 1996). In the context of work by Lotka and Ronald Aylmer Fisher (1890–1962), this publication was revolutionary in providing a new linkages between evolution and ecology—thereby forging the development of the discipline, evolutionary ecology, with such luminaries as David Lambert Lack (1910–1973), Robert MacArthur (1930–1972), and Richard Levins (1930–2016). As I will discuss later, this discovery may be even more important to 21st century biogeochemistry, which has become more reliant on new molecular genetic techniques in understanding adaptions to climate change and beyond. This has resulted in stronger linkages between evolution and biogeochemistry than ever before, and to quote Dobzhansky (1973): “Nothing in biology makes sense except in the light of evolution.”

A reemergence of stoichiometry

In the early 1930s Alfred C. Redfield (1890–1983) begins to explore molecular-organismal relationships that will set the stage for a new revolution in stoichiometry in the 20th century—as reflected here in the Redfield equation (e.g. Redfield 1958; Redfield et al. 1963) (Eq. 1):

$$106\text{CO}_2 + 16\text{NO}_3 + \text{H}_3\text{PO}_4 + 122\text{H}_2\text{O} \leftrightarrow [(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4] + 138\text{O}_2$$

(1)

While the early 1970s-1990s provided a basis for linking biogeochemical cycles in terrestrial and aquatic systems with climate (e.g., Garrels and Mackenzie 1971; Garrels et al. 1975; Holland 1978; Charlson et al. 1987; Degens 1989; Wollast and Mackenzie 1989; Schlesinger 1991), it was not until the year 1993 that we see publication of the first book entitled Earth System Science, that further launched the importance of biogeochemical cycles in understanding global fluxes (Jacobsen et al. 1993). This emphasis on fluxes across Earth’s different reservoirs was further synthesized in a book by Elizabeth Kay Berner and the late Robert A. Berner (1935–2015) entitled Global Environment: Water, Air, and Geochemical Cycles (Berner and Berner 1996). In 2000, a second edition of Earth System Science, published 7 years after the 1st edition, placed more emphasis on linking biogeochemical cycles with global change (e.g. Jacobson et al. 2000). One of the most important books on stoichiometry, in my opinion, was Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere, by Sterner and Elser (2002). This book paved the path for a new sub-discipline in ecology and created new linkages with biogeochemistry that continue today.

Before describing some historical examples of stoichiometric work in biogeochemistry, I will discuss a major change in the 20th century regarding global nitrogen cycling. Many early studies noted the relatively high abundance of nitrogen in our atmosphere (78%) as an aberration in the context of Earth’s present oxidation state—with the more stable form of nitrogen found as the nitrate ion in the global ocean (see Sillen 1966). The Haber–Bosch process (e.g. Haber 1913), represents an attempt to solve this problem of limited atmospheric N availability to organisms, particularly as it related to agricultural crops (see Hogberg et al. 2017, and references therein). Haber and Bosch ultimately succeeded, allowing this vast nitrogen reservoir in the atmosphere to be captured (fixed) with hydrogen derived from natural gas to produce ammonia (see Kandemir et al. 2013, and references therein). This development in the early 1900s changed the world by taking atmospheric nitrogen, largely unreactive for most life on the planet, and converting it to biologically-reactive nitrogen (fertilizer)—this was a major game-changer for the biosphere. In both terrestrial and aquatic systems, excessive inputs of macronutrients (e.g. P and N) as inorganic fertilizers, atmospheric emission of NOx) and detergents, continued to place a biogeochemical emphasis on growing stoichiometric imbalances in the biosphere (e.g. Vitousek et al. 1997; Howarth et al. 2002). The application of fertilizers to soils and natural waters dramatically increased worldwide changing the nitrogen cycle—as we knew it (e.g. Galloway et al 2004). This development, allowed for the Green Revolution which began in Mexico in the 1940s, and is largely responsible for the human population explosion (Smil 1999)—which by default, can be linked with all anthropogenically-driven changes in Earth’s biogeochemical cycles. Thus, much of the biogeochemical research in the late 20th and all of the 21st centuries, has been impacted by this discovery. I will revisit how
this neo-Malthusian Green Revolution experiment developed and how long-term soil experiments enhanced our understanding of potential soil productivity (via nutrient amendments)—which at the time was poorly understood (Richter et al. 2007). Amazingly, enhanced crop yields during the Green Revolution allowed the global human population to double in just 50 years; this resulted in the 1970 Nobel Peace Prize being awarded to Norman Borlaug (1914–2009)—a central figure in agricultural production research at this time (see Richter et al. 2007, and references therein).

The stoichiometric approach by Redfield and his predecessors (e.g. Lotka and Liebig), would provide the conceptual basis for a major discovery involving ocean biogeochemistry in the 1980s. This work, which focused on one of the greatest mysteries for oceanographers in the 20th century, addressed the importance of iron limitation as a possible explanation for lower phytoplankton production in open-ocean regions having high nutrients and low chlorophyll (HNLC) (e.g. Martin and Fitzwater 1988; Martin et al. 1991). Interestingly, this work later expanded into mesoscale iron-addition field experiments in the ocean (e.g. Coale et al. 1998), which allowed for testing the effects of nutrient limitation beyond the first trophic level—as limited by the Redfield ratio (e.g. Cochlan 2001). The “Iron Hypothesis” from Martin (1990) stated that greater inputs of atmospheric iron during dry glacial periods to HNLC regions in the ocean stimulated primary productivity and CO₂ drawdown, with the opposite occurring during interglacial periods. This work is reminiscent of the early historical linkages made between glaciers, climate change, and atmospheric chemistry by Cuvier, Lyell, Agassiz, de Saussure, Arrhenius, and Chamberlin, to name a few. However, this time our prowess is biogeochemistry was waiting to develop a more complete story.

As noted by Cutter (2005), the study on limitation not only provided a chemical proxy that linked global productivity with climate change, but also integrated physical drivers (e.g. Fe transport via global wind circulation patterns and upwelling). This work along with other early studies examining patterns of trace elements and primary production and the role organic compounds (i.e. ligands) in limiting the availability of certain metals to phytoplankton (e.g. Moffett 1995, and references therein). Finally, the Redfield equation which in part, illustrates the equilibrium between autotrophic productions and heterotrophic respiration, provided a stoichiometric grounding for linking past changes (coupled paleoredox proxies like pyrite) in atmospheric oxygen over geologic time (e.g. Berner and Canfield 1989). Cutter (2005) further explains that: “This demonstrates that the study of biogeochemistry is of global significance (or should be). And finally, the idea of balancing autotrophy and heterotrophy embodied in the Redfield equation has a lesson for today: net heterotrophy (e.g., including additional heterotrophy in the form of internal combustion engines) that is due to the respiration of “out of phase” (i.e., ancient) net autotrophy (fossil fuels) leads to excess CO₂ in the present-day atmosphere.

Over the past ca. 40 years, terrestrial biogeochemists continued to refine our understanding of how primary succession in plant communities relies on rock-derived nutrients like P and Ca, K via weathering and dust deposition—in contrast to the open-ocean, where nutrients like N are derived primarily from the atmosphere (see Powers and Marin-Spiotta 2017, and references therein). It is also important to note a book published by Hans Jenny (1899–1992) entitled Factors of Soil Formation: A System of Quantitative Pedology, which not only provided a unique perspective on the role of physical chemistry in soil formation, but more importantly that soils were a key component of the larger ecosystem system (Jenny 1941). On this notion, top-down effects of higher plants can impact the distribution and cycling of elements in soils. For example, while the bulk of plant tissue is comprised of lighter atmospherically-derived elements (e.g., C, H, O, N, and S), with only smaller amounts from composed of heavier elements commonly found in soils (e.g. Ca, Mg, K, and P) (e.g. Lambers et al. 1998), they can have significant impact on the uplift of these heavier elements, particularly K, to the soil surface (Jobbagy and Jackson 2004). This can have important implications particularly since there are constraints in stoichiometric ratios of N, P, and K on plants across different regions depending on the (e.g. Gordon and Jackson 2000; McGroddy et al. 2004).

Another example of one of the early pioneering projects in oceanography that began in the 1970s, largely in the “name” of marine chemistry, was the Geochemical Ocean Sections Study (GEOSECS) (Craig and Turekian 1980). This study proved to be an important link related to further developmental
nuances in stoichiometric-based work in biogeochemistry. This incredible systematic survey of ocean chemistry involved measurements of nutrients, trace metals, isotopes, and even linked them with carbon cycling, proved to be the most comprehensive understanding biogeochemical cycling in the ocean at that time (e.g. Broecker and Peng 1982) (see Anderson 2020, and references therein). This work inspired formation of the now widely known ocean project called GEOTRACES in 2003, which as according to Bob Anderson (2020) “was designed accelerate progress in this field of research, marine geochemists developed a coordinated international effort to systematically study the marine biogeochemical cycles of trace elements and their isotopes.” What is particularly interesting about the merging of marine chemistry and biogeochemistry in these programs is that measurements of trace metals before the mid-1970s were fraught with contamination issues (see Anderson 2020, and references therein). While the analytical advancements were eventually made to correct these problems (e.g. Bruland 1983), there remained geographical gaps in such trace metals measurements in addressing linkages with broader biogeochemical cycles, a major problem for GEOTRACES to address. As discussed eloquently in Anderson’s (2020) review, the accomplishments of this unique global-scale study are prolific. More specifically, they provide a broad geographic range of measurements of macronutrients (N, P, and Si), trace elements, and isotopes that explore important questions about fluxes and processes at ocean interfaces, internal cycling of trace elements and isotopes, and the development of proxies for paleo-applications. GEOTRACES in part, has shown us that distributions of major nutrients (N, P, and Si) in the ocean reflect biological consumption in surface waters, regeneration at depth, and redistribution by ocean circulation (Fig. 11) (see Anderson 2020). This study has provided unique elemental information that can now be used stoichiometric-based work that interfaces with new molecular genetics technique to explore biogeochemistry in the 21st century—Sprengel and Liebig would surely be impressed.

A focus on carbon sources/sinks, hot spots/hot moments, and critical zones

The rise in global air and sea-surface temperatures over the last century or so, has been driven by greenhouse gas production from fossil-fuel burning, deforestation, changes in agricultural practices, and overall land-use change (IPCC 2018). Consequently, much of the research in global biogeochemistry in the 21st century has been driven the pressing questions of how climate will continue to change the associated ramifications it may have on other biogeochemical processes in the biosphere. The global ocean absorbs an estimated 25% of the excess CO₂ in the atmosphere as well as much of the anomalous heat generated from global warming (Levitus et al. 2012). Consequently, there have been significant changes in the physical dynamics of the oceans (e.g., stratification, thermohaline circulation, sea-ice retreat, major ice sheet thinning, precipitation/evaporation), which serve as major drivers of ocean biogeochemistry (e.g. Doney et al. 2014, and references therein). For example, multi-stressor effects of ocean acidification (Feely et al. 2008), deoxygenation (Keeling et al. 2010) and warming has resulted in many deleterious effects on marine biota (Gruber 2011; Duarte et al. 2020, and references therein). Similarly, the CLAW hypothesis, named in sequence for the first letters of the surnames of co-authors in a paper by Charlson et al. (1987), proposed that dimethyl sulfide was produced by marine phytoplankton, in response to climate forcing, and resulted stabilization of temperature in Earth’s atmosphere. Now, while recent work has proposed that the CLAW hypothesis should be retired, due to a lack of unequivocal evidence that biologically-derived dimethyl sulphide creates cloud condensation nuclei (Quinn and Bates 2011), this hypothesis was important in stimulating new work in the marine boundary layer.

As in the ocean, understanding the role soils in mitigating climate change has been a central task for biogeochemistry over the last few decades. As illustrated by Schuur et al. (2015), Arctic soils (northern circumpolar permafrost region) represent about 15% of Earth’s soil biome, yet it contributes an amazing 50% to the total amount of organic carbon stored in the top-3 m of Earth’s soil biome (ca. 2050 Pg [Jobbagy and Jackson 2000])—excluding the Arctic soils. Soils also represent one of the largest land fluxes of carbon dioxide to atmosphere (98 ± 12 Pg C year⁻¹) (e.g.
Hashimoto et al. (2015). Linking biogeochemical work with climate mitigation is a key focus for biogeochemists in the 21st century. For example, when identifying key sources and sinks of terrestrial carbon, in terms of soil mitigation potential, wetlands, agriculture/grasslands and forests represented 72%, 47%, 9%, respectively (Bossio et al. 2020). Moreover, soils have been shown to be an important driver of climate

Fig. 11 Three dimensional view of concentrations of dissolved iron (Fe) in (a) the Atlantic and (b) the Pacific from the GEOTRACES project (from Anderson 2020)
change, as it holds three times more carbon than the atmosphere (see Bossio et al. 2020, and references therein).

One of the grand challenges in global biogeochemistry has been establishing the global inventories and fluxes in a heterogeneous world that is experiencing non-linear changes in climate change; this complexity leads to rates and inventories that are uneven spatially and temporally. To work through some of this complexity, some studies have adopted the convention of using biogeochemical hot spots (“patches that show disproportionately high reaction rates relative to the surrounding matrix”) and hot moments (“short periods of time that exhibit disproportionately high reaction rates relative to longer intervening time periods”) (McClain et al. 2003), which are purported to be useful signals of how Earth System may respond to anthropogenic change.

The land–ocean boundary has been shown to be globally important location for the oxidation and burial of carbon in biosphere (Canuel et al. 2012; Bianchi et al. 2018, and references therein). Much of the organic carbon in the global ocean is buried in the coastal margin, with river delta and non-deltaic shelf regions bury an estimated 114 Tg C year\(^{-1}\) and 70 Tg C year\(^{-1}\), respectively, with only ca. 6 Tg C year\(^{-1}\) buried in the open ocean (Burdige 2005). These large delta regions have also been shown to have some of the highest rates of organic matter, due to high rates of sediment deposition that create mobile muds that have redox conditions highly favorable decomposition (Aller 1998). Biogeochemists remain focused on these highly dynamic region, particularly since global-change drivers (e.g. dams, high nutrient loading, land-use change) have in part, changed fluxes of CO\(_2\) along the river continuum (e.g. Cole et al. 2007; Raymond et al. 2008) and at the coast (e.g. Cai 2011; Bauer et al. 2013; Laruelle et al. 2014). The northern permafrost region stores an estimated 1460–1600 Pg of organic carbon (e.g. Hugelius et al. 2014; Schuur et al. 2015). Consequently, thawing permafrost in the Arctic has been a key focus of in biogeochemical studies (e.g. Zimov et al. 2006; Schuur et al. 2008), particularly as it relates to mobilization from the watershed to the coast through rivers (see Bauer et al. 2013; Regnier et al. 2013, and references therein).

The land-sea boundary is also important with regard to transport of nutrients supporting coastal primary production via unconventional “out of sight out of mind” routes. One example is the fertilization of coastal systems through anthropogenically-generated nitrogen emissions (Paerl 1985). Subsequent work showed that in waters downwind from these emissions, from 20 to ~ 40% of “new nitrogen” supporting coastal primary production can be supported via this air sea transfer of a key limiting nutrient (Paerl et al., 2002). Finally, while the coastal ocean has been a key focus in recent years, it is important to remember that dissolved organic carbon represents the largest pool of reduced carbon in the ocean (ca. 662 Pg) (see Hansell and Carlson 2014). Understanding the age (e.g. Druffel and Williams 1990; Bauer et al. 1992) composition (e.g. Hedges 1992; Hertkorn et al. 2006; Shen and Benner 2018, and references therein) and cycling (e.g. Hansell et al. 2009) of this carbon pool has been central question in biogeochemistry for the past ca. 50 years (see Hansell and Carlson 2014).

Early interests in the importance of N versus P (e.g. Schindler 1974; Ryther and Dunstan 1971) has led to competing theories about these macronutrients in controlling eutrophication in aquatic systems (e.g. Schindler et al. 2008; Sylvan et al. 2006; Conley et al. 2009). We are now in a stage where the general agreement is more towards co-limitation of N and P in aquatic systems (e.g. Wurtsbaugh et al. 2019; Scott et al. 2019; Paerl et al. 2019). These studies have provided important foundations to for continued work as the complexity of biogeochemical cycling in aquatic systems continue to change under global change. This work has also been important in understanding linkages between algal bloom and the widespread hypoxia around the world (see Breitburg et al. 2018, and references therein).

In light of the importance of key boundaries as a place to focus on biogeochemical fluxes and rates, as harbinger to future climate change, biogeochemists began for formalize this approach with the concept of critical zones (Chorover et al. 2007). A critical zone, as defined by National Research Council (NRC 2001) is “a heterogeneous, near surface environment in which complex interactions involving rock, soil, water, air and living organisms regulate the natural habitat and determine availability of life sustaining resources.” As further explained by Chorover et al. (2007) “Especially near the sunlit surface of the Critical Zone, these interfaces associate with plant roots and soil organisms to form porous, aggregated structures.” While ecotones have always been on the
minds of ecologists,' Livingston (1903) defines them as ‘‘A stress line connecting points of accumulated or abrupt change,’’ much of the work in ecology has largely focused on ecotones in the context of locations where two communities change to begin to blend. The importance of critical zones, particularly as it relates to how these ‘‘natural’’ boundaries are changing in the Anthropocene have now expanded to aquatic systems (e.g. Bianchi and Morrison 2018).

The concept zones in biogeochemical work has been useful in understanding changes associated with the post-agricultural recovery of secondary tropical forests, which in many cases are now more abundant than primary forests (see Powers and Marin-Spiotta 2017, and references therein). Interestingly, differences in controls on the succession of tropical compared to temperate and boreal secondary forests is in part, due to steep weathering gradients of soils (e.g., extreme changes in precipitation over short altitudinal distances) that impact phosphorus availability in the tropics (Cleveland et al. 2011). Other earlier studies, have shown that atmospheric inputs, decomposition, biomass accumulation, and plant nutrient use efficiency are key in controlling nitrogen and phosphorus availability during different stages of primary and secondary succession (e.g. Gorham et al. 1979; Vitousek et al. 1989). From its early inception, the basic concepts of plant succession (e.g. Clements 1916) were modeled on the idea that nutrients will be conserved (Odum 1969) but that perturbation events will impact nutrient availability, and that these disturbance events will vary at different stages of succession (e.g. Robertson 1989; Vitousek and Rinters 1975). While these early models in some cases apply nicely to certain temperate forests (e.g. Hedin et al. 1995); the greater complexity of historical changes in the waxing and waning of agricultural/natural at tropical locations, from centuries to millennia (Chazdon 2014), make it difficult to establish stages of disturbance (Powers and Marin-Spiotta 2017). New and exciting work exploring N dynamics across climate gradients, have shown the complexity of soils differentially influenced by rock-derived nutrients and biological N fixers (Vitousek et al. 2019).

Biogeochemistry and the development of long-term, large-scale, whole-ecosystem, and survey experiments

It was 60 years ago when F. Herbert Bormann shared his idea that small watershed ecosystems could be used to study in part, the function of ecosystems and their linkages with hydrology, weathering, and atmospheric inputs (Likens 2004b). This ultimately led to the beginning of such a watershed study in the White Mountains of the New Hampshire, USA, known as Hubbard Brook Experimental Forest (HBEF) (Bormann and Likens 1967). A key finding from this foundational HBEF work at the watershed/landscape scale, was the inherent linkages between aquatic and terrestrial systems (e.g. Bormann and Likens 1979; Likens 2004b); this emphasized the need for ecosystem connectivity, paving the way for biogeochemistry in the 19 and 20th centuries (Hughes et al. 2017).

There have been important cross-fertilization episodes between oceanography and the foundation of ecosystems (Odum and Odum 1955), models of plankton studies (Riley 1946), and linkages between ecology an evolution (e.g. Hutchinson 1961); these studies were foundational in the evolution of future interdisciplinary research in biogeochemistry (Farrington 1987). Long-term ecological studies (LTEES), along with large geographic-scale satellite-based, modeling, and survey studies, have been pivotal in our understanding of global biogeochemical cycles and regulation and functioning of ecological communities. Some examples include: the Scientific Committee on Problems of the Environment (SCOPE); Long-Term Ecological Studies (LTER); Ocean Fertilizer Experiments (e.g. SOFeX); GEOTRACES; Ocean Time Series (e.g. Hawaii Ocean Time-series [HOT]; Ameriflux; BCG ARGO; Tara; Bermuda Atlantic Time-series [BATS]); Free-Air CO2 Enrichment (FACE) experiments; National Ecological Observatory Network (NEON); Ocean Gene Atlas; Large-scale Biosphere–Atmosphere Experiment (LBA); Geographic Information Systems (GIS); Deep Carbon Observatory; Gravity Recovery and Climate Experiment [GRACE]; Whole-Lake Experiments; Soil Moisture Active Passive [SMAP] missions, Regional Ocean Modeling System (ROMS); International Geosphere-Biosphere Programme (IGBP), and Earth System Models (ESMs) (see Carpenter et al. 2001; Hughes et al. 2017; Fennel et al. 2019; Chai
et al. 2020, and references therein). Programs with global reach tend to be limited in their observables and their ability to achieve detailed process resolution. All of these efforts have required large budgets, long-term funding of personnel, and a different level of communication for research teams (Likens 2004a). Finally, it would be remiss of me not to point out the vital role of Swedish meteorologist, Bert Rickard Johannes Bolin (1925–2007), in implementing the development of international programs that in part, interfaced biogeochemistry with climate change. For example, he first began coordinating international climate research efforts in the 1960, in 1979 Bolin and others formed the World Climate Research Programme (WCRP), in 1987 he, along with fellow Swedish soil ecologist Thomas Rosswall, and others led the formation of the International Geosphere-Biosphere Programme (IGBP), and was a key player in establishing the Intergovernmental Panel on Climate Change (IPCC) in 1988, where he served as its first chairman.

Large-scale studies in FACE, conducted in a series of networks in the U.S (Hendrey et al. 1999, and references therein), involved experimental manipulations that allowed for the investigation of the effects of nitrogen, soil moisture and temperature, in sub-hectare- to hectare-sized plots (e.g., Rustad et al. 2001), on biogeochemical cycles. While the early experiments were focused on trees and forest ecosystems, because of relatively large C flux associated trees in terrestrial ecosystems (Melillo et al. 1993; Bonan 2008), these experiments were conducted over a broad spectrum of ecosystems such as bogs, desert; grasslands; and deciduous, evergreen, and alpine forests (Norby and Zak 2011). Early observations on enhanced storage of C in terrestrial systems (via CO$_2$ fertilization effects in horticultural experiments) (e.g. Wittwer and Robb 1964); sparked questions about the importance of such negative feedbacks on the rise of atmosphere CO$_2$ (Cramer et al. 2001; Bonan 2008) and if this pattern would persist in the future (Matthews 2007; Norby and Zak 2011).

Another long-term terrestrial study that has been key in understanding the impact of climate change on soil carbon was conducted in Harvard Forest (Melillo et al. 2017). This 26-year-old study which began in 1991, showed that warming effects on soil in this mid-latitude hardwood forest occurred in different phases—as related to organic matter and CO$_2$ effluxes form soils. This work supported what much of the biogeochemical work in the 20-21st century which indicates long-term positive feedbacks from mid-latitude forest in a warming climate. This also agrees with the notion that soil organic matter is vulnerable to warming (e.g. Trumbore 2000). Melillo et al. (2017) further notes that complex interactions between nitrogen and soil organic matter losses (Melillo et al. 2011) will make future predictions about the response of soils to warming more uncertain.

Long-term observing system in oceans have also largely been focused on carbon cycling, which has continued in part, because 25 to 30% of the anthropogenic CO$_2$ emitted since the preindustrial era is absorbed by the ocean (Gruber et al. 2019). Consequently, many of these efforts systems have long been active in seeking long-term biogeochemical controls on air-sea carbon fluxes, food web dynamics, and rates of carbon transformations within the ocean interior (Benway et al. 2019, and references therein). Some of the first monitoring systems began as early as 1903 in Western Channel Observatory in the English Channel, 1948 in the Norwegian Sea (1948), and 1949 in the California Cooperative Oceanic Fisheries Investigations in the California Current System; see Benway et al (2019) for an extensive review on such systems. Today, many of the times-series use floating platforms, ship- and shore-based programs, stationary moorings, free-floating floats, guided gliders, satellites, single- and multi-platform observing networks (such as the Argo and Biogeochemical-Argo Programs, the Ocean Observatories Initiative, Ocean-SITES, the Marine Biodiversity Observation Network, and the Long-Term Ecological Research Program (Fig. 12) (Benway et al. 2019).

As eloquently summarized by Hughes et al. (2017, and references therein), LTEES have also been critical in environmental protection legislation in the Anthropocene (e.g. Willis et al. 2007; Lindenmayer and Likens 2009; Schindler and Hilborn 2015) in particular as it relates to, shifting baselines (e.g. Lovett et al. 2007), rare ecological events (e.g. Magnuson 1990; Doak et al. 2008), “acid rain” deposition (e.g. Likens and Bormann 1974; Gorham et al. 1984), species diversity (e.g. Sinclair et al. 2003), complex environmental drivers (e.g. Carpenter et al. 2001), “tipping points” (e.g. Scheffer et al. 2001; Carpenter et al. 2011), structure of ecological communities (e.g. Spiller and Schoener 1995; Losos et al. 2001), energy and nutrient dynamics (e.g. Odum and Smalley 1959;
Teal 1962), community structure and diversity (e.g. Paine 1966), “top-down” control of community structure (Estes and Palmisano 1974), and intermediate disturbances (e.g. Connell et al. 2004). Finally, the importance of LTEES, once again returned biogeochemically stoichiometric-based studies that advanced our understanding of: nitrogen-use efficiency (e.g. Raun and Johnson 1999); the importance of Fe and Al oxides in soils on P cycling (e.g. Chadwick et al. 1999); and the role of sulfur oxide pollution via deposition and acidification on soils on ecosystems (e.g. Driscoll and Likens 1982; Likens et al. 1996) (see Richter et al. 2007, and references therein).

Another important phase in aquatic biochemistry involved the use of whole-lake time-series experiments to examine trophic cascades and nutrient controls on primary productivity uniquely biogeochemical in character (e.g. Pace and Cole 1996; Carpenter et al. 2001). In one of a series of studies, the effects of different nutrient enrichments, across four lakes for a period of seven years, on zooplankton, primary production, planktonic bacteria, and CO2 exchange with the atmosphere, was examined (see Carpenter et al. 2001, and references therein). This work complemented previous studies that examined annual responses of different community-level and trophic change in these lakes (e.g. Carpenter et al. 1998; Cottingham and Carpenter 1998). This work importantly showed that trophic cascades impacted the effects of nutrient additions in lakes, reflective of the importance complex interactions between top-down and bottom-up effects in part, on primary productivity, CO2 fluxes, and bacterial cycling. More recent work on these lakes, now having been studied for 33 years, showed interesting relationships between water quality and long-term hydrologic changes, that could not have been detected without the whole-lake experimental approach. Another interesting facet in long-term biogeochemical research learned in the last 40 + years, is that when examining continuous data over these long timeframes, regime shifts across different trophic levels may occur and need to be accounted for as part of the evolution of the system (e.g. Pace et al. 2013). Clearly, whole-lake time-series experiments have proven to be vital in the history and future of biogeochemical work addressing complex global change questions.

Returning to stoichiometric work yet again, early interests in the importance of N versus P (e.g. Schindler 1974; Ryther and Dunstan 1971) has led to competing theories about the of these macronutrients in controlling eutrophication in aquatic systems (e.g. Schindler et al. 2008; Sylvan et al. 2006; Conley et al. 2009). We are now in a stage where the general agreement is more towards co-limitation of N and P in aquatic systems (e.g. Wurtsbaugh et al. 2019; Scott et al. 2019; Paerl et al. 2019). These studies, and the previously discussed whole-lake experiments, have provided important foundations to for continued work as the complexity of biogeochemical cycling in aquatic systems continue to change under global change. This work has also been important in understanding linkages between algal bloom and the widespread hypoxia around the world (see Breitburg et al. 2018, and references therein).
In a microbial world

In the 19th century, the importance of bacteria proved to be an important step understanding nitrification in soils (e.g. Winogradsky 1891)—this combination of lab and field techniques proved to be pivotal in the history of microbial ecology and biogeochemistry. Beijerinck (1913), the first to use the term microbiologie, or as we think of it today, microbial ecology, is responsible for the old microbiological tenet “...everything is everywhere, but, the environment selects...” And, as scientists’ continue to explore new links between elemental and microbial cycles, we can reflect back to Claude E Zobell (1904–1989) who writes: “The role of microorganisms in the carbon, nitrogen, sulfur, and phosphorus cycles in the sea as well as in the general circulation of organic compounds by processes analogous to those in the soil is usually taken for granted” (Zobell 1946). As microbial ecologists’ move into the 20th century, it becomes readily apparent that using cultural bacteria to examine biogeochemical cycles (e.g. Winogradsky 1891) is a problem, since only ca. < 1% of microbes from nature are thought to be culturable (Boughner and Singh 2016). This created a unique problem where using a small unrepresentative pool of culturable microbes to understand biogeochemical cycles in nature, led to the “great plate count anomaly” (Staley and Konopka 1985). This in part, led to the advent of Next-Generation sequencing (NGS) technologies mentioned earlier which in part, has solved that problem.

As noted in the Falkowski et al. (2008) paper entitled “The Microbial Engines That Drive Earth’s Biogeochemical Cycles”: “Earth is ~ 4.5 billion years old, and during the first half of its evolutionary history, a set of metabolic processes that evolved exclusive in microbes would come to alter the chemical speciation of virtually all elements on the planetary surface.” Consequently, our current environment reflects the historically integrated outcomes of microbial experimentation on a tectonically active planet endowed with a thin film of liquid water.”

The biological fluxes of a select group of light elements, which make up 95% of the biosphere (e.g., H, C, N, O, S, and P) and comprise the major components for building biological macromolecules (e.g. Deevey 1970a; Schlesinger 1997), are largely controlled by the microbially-mediated catalysis of redox reactions—also constrained by thermodynamics (Fig. 13) (Falkowski et al. 2008). In fact, Deevey (1970b) made a case of the defense of mud in harboring many of the microbes largely responsible for these redox reactions. A recent assessment of Deevey’s work further supports in part, the importance of mud as it relates to global change (Hale 2020). Coupled with a suite of abiotically-controlled acid–base reactions, these microbially-mediated redox reactions control external energy needed to maintain the larger biogeochemical cycles that evolved on the planet (Falkowski et al. 2008, and references therein). Another amazing discovery regarding redox reactions, was between electric currents found in marine sediments and the transfer of electron through sediments that were linked with redox reactions (Nielsen et al. 2010). More specifically, the oxidation of sulfide, linked with the reduction of oxygen just centimeters away, could not be explained based on conventional biogeochemistry, until the discovery long multicellular cable bacteria (Schauer et al. 2014). This work has redefined our understanding of redox reactions, so vitally important in suboxic marine sediments (see Middelburg 2018, and references therein) and to the cascade of redox reactions that consume oxygen on the planet (Nielsen et al. 2010). The development of micro-electrodes in sampling pore waters (Brendel and Luther 1995) was another major achievement in understanding redox/microbial spatial dynamics.

While soil bacteria and fungi constitute a large fraction of this heterotrophic respiration (35–69 Pg C year$^{-1}$) (Tian et al. 2015), there clearly remain many uncertainties on the feedback between such fluxes and climate change (Allison et al. 2010, and references therein). Consequently, new trends in next generation soil biogeochemical models are now beginning to incorporate carbon use efficiency to make better predictions of physio-logical changes across different bacterial taxa (e.g. Saifuddin et al. 2019, and references therein). Finally, it is noteworthy that many of the global-scale microbial models used today, derive from the classical original Michaelis–Menten (Johnson and Goody 2011) and reverse Michaelis–Menten (Schimel and Weintraub 2003) kinetics (see Moorhead and Weintraub 2018).

The importance of microbes as transformers of energy in the ocean really began to take shape in the 1970s and 1980s, which set the stage of future microbiome work (e.g. Moran 2015 and references
therein). After some of the technical problems of accurately counting microbes were beginning to be resolved (e.g. Francisco et al. 1973; Hobbie et al. 1977) other transformational papers from people like Lawrence Pomeroy (Pomeroy 1974), who recently passed away in 2020, were key in developing the microbial loop concept, which was further developed by Azam et al. (1983) (see Fenchel 2008, and references therein). The importance of microbial interactions was not only lacking clarity in terms of their role in food webs, but also the larger picture of the biological pump, which linked the uptake of CO₂ by primary producers with the transport organic carbon to the deep ocean as sinking particulate particle that transform to dissolved via microbially-mediated decay (see Moran et al. 2016, and references therein).
These concepts of particulate and dissolved organic matter cycling have been further developed by many researchers in more recent years (e.g. Jiao et al. 2011; Repeta 2015; Wakeham and Lee 2019, and references therein). The ocean microbiome, an ecological community of microorganisms that share an environment (see Jiao and Zheng 2011; Karl and Church 2014; Moran 2015; Thakur and Geisen 2019 and references therein), accounts for ca. 50% of all the primary production on Earth (e.g. Hansell 2013), and justifiably remains a key focus for biogeochemical research in the 21st century (see Moran et al. 2016, and references therein).

Using many of the new techniques developed over the last few decades we now know that bacteria and fungi, which from a diversity dominate soils, represent one of the most diverse microbiomes on Earth (see Bahram et al. 2018, and references therein). This is important as this new relationship between evolutionary/ecological genetics and biogeochemistry in the 21st century has allowed for examination of how these dominant microbes interface with soil biogeochemical processes in part, through gene function and taxonomic composition (e.g. Reed et al. 2014, and references therein). These techniques have allowed for further examination of how microbe interactions across taxonomic groups change across different global regions (see Bahram et al. 2018). This is particularly import in microbial biogeography, since single taxonomic groups have historically been the focus (see Lauber et al. 2009, and references therein)—with interactions across taxonomic groups largely ignored to date. Latitudinal gradients in response to climate warming show some interesting trends across latitudinal gradients—where these molecular techniques can lead to new advances in soil biogeochemistry. For example, the greatest carbon stocks remain in the higher latitudes, where the most discernable levels of climate change are occurring; this has resulted in a key directive for biogeochemical funding the 21st century (Crowther et al. 2019). Interestingly, this work supports earlier work in soils (Bass Becking 1934) and complements current work in the ocean (Sunagawa et al 2015) on latitudinal patterns of microbes—once again biogeochemistry is revising and exploring new linkages between biogeography and microbial ecology. Finally, understanding microbial interactions has developed as key focus in global biogeochemistry since new studies have revealed that that while some microbial work in concert together (e.g. Gougoulias et al. 2014), others show antagonist behavior with each other (e.g. Bahram et al. 2018)—both potentially leading to significant differences in global biogeochemical fluxes (e.g. C, N, S) in soils.

In the 21st century, the emphasis role of soil microbial communities in ecosystem services (e.g. mineralization) and its impact on diversity and productivity of plants (see Richter et al. 2018, and references therein). To fully explore such services often engages ecological concepts such as metacommunity theory (see Rillig et al. 2015, and references therein) and community coalescence (e.g. Rillig et al. 2016). Interestingly, the notion of over exchange of microbial communities in soils is derived from aquatic systems, where dynamic mixing (e.g. river confluences) (e.g. Souffreau et al. 2014) more easily allows for such transitions. Once again, if we harken back to Darwin’s worms (Darwin 1881), soil mixing activities by worms in has been shown to allow for such coalescence as microbes can be sorted by physical processes (e.g., breaking up soil aggregates), as well as physiological drivers (e.g. exchange between earthworm gut microbes and soil microbes), which are expected to occur with microarthropods and nematodes as well (Rillig et al. 2016).

Green chemistry and global change biogeochemistry

The origins of “green chemistry” movement can be traced back to Rachel Car森 (1907–1964) with her provocative book *Silent Spring* (Carson 1962), which led to an explosion of new fields of study chemistry and biogeochemistry (e.g. environmental chemistry, green chemistry, and sustainable chemistry) in 1980s and 1990s (e.g. Linthorst 2010). Perhaps the greatest recognition of such studies, within the framework of environmental chemistry—and actually biogeochemistry, was when F. Sherward Rowland, Mario Molina, and Paul Crutzen received the Nobel prize in 1985 for the discovery of the ozone hole over the Antarctic, which resulted in landmark legislation that banned the use of industrial chemicals (e.g. chlorofluorocarbons), responsible for the destruction of the ozone layer (see Graedel and Keene 1995). The chemical formula for ozone was first determined by Jacques-Louis Soret...
(1827–1890) (Soret 1865) and then and confirmed Schönbein (1867) (Rubin 2001).

The role of aerosols in global biogeochemical cycling, particularly as it relates to nutrient deposition (e.g. N, P, and Fe), has continued to be an important component of biogeochemistry (see Kanakidou et al. 2018, and references therein). It is worth noting here, the importance of Gorham’s early work on the atmospheric inputs of major ions to inland waters (Gorham, 1961).

As mentioned earlier, large-scale iron fertilization experiments further illustrate how such experiments, coupled with physical and chemical dynamics, and molecular techniques via biogeochemical approaches, have successfully enhanced our understanding of iron inputs, from upwelling and atmospheric inputs to controls productivity in certain regions of the ocean (e.g. Tripathy and Jena 2019, and references therein). Similarly, a large-scale biogeochemical approach that exploring controls on Hg deposition in the Florida Everglades revealed that Hg sources (e.g. function and spatial-scale) and deposition dynamics control the relative importance of global versus regional sources of Hg (Pollman et al. 2019, and references therein).

To no surprise, much the focus in biogeochemical research in the 21st century is related to global change. Duarte (2014) defines global change as “The global-scale changes resulting from the impact of human activity on the major processes that regulate the functioning of the Biosphere.” Schlesinger (2004) argues that biogeochemistry has emerged as the premier scientific discipline to examine human effects on the biosphere. Schlesinger, eloquently reflects on the role of how biogeochemistry has interfaced with environmental sciences by noting the importance of how biogeochemistry has served an integrator of information from many disciplines, to better understand the major drivers of elemental cycling on Earth, such as the” … mobilization of metallic elements from the Earth’s crust (Bertine and Goldberg 1971), their movement through the atmosphere (Lantzy and MacKenzie 1979), and their content in river flow (Martin and Meybeck 1979). For example, when we were able to articulate clear and complete budgets for the natural and perturbed global cycles of lead (Pb), the need to remove lead from gasoline appeared starkly before policy makers who knew the effects of excessive lead on human health…” (Schlesinger 2004).

As sub-disciplines of biogeochemistry continue to expand (e.g. Schulze 2015), it is interesting to note the emergence of urban biogeochemistry (e.g. Grimm et al. 2008). This sub-discipline which in part, merges urban ecology and environmental sciences (e.g. Pickett et al. 2011), involves the study of urban ecosystems, which are defined as locations where people live at high densities (< 186 people km⁻²) and in high numbers (usually a total population < 50,000), or where the built infrastructure covers a large portion of the land surface (see Kaye et al. 2006, and references therein). Nancy Grimm, a pioneer in the study of urban biogeochemistry, has noted the unique importance of cities as places where urban ecosystem processes are driven by novel controlling mechanisms (Grimm et al. 2008): “…Urban areas are hot spots that drive environmental change at multiple scales.” Interestingly, urban biogeochemistry fits within the early constructs of ecology from H.T. Odum, where he posited that cities are more wasteful in terms of energy consumption energy is consumed compared with natural systems—with urban metabolism more reliant on external matter and energy (Odum 1971). These highly populated areas, with a comparatively high human impact in relation to other ecosystems, have been linked with key drivers of human activity (engineering, urban demographic trends and household-scale actions) for future biogeochemical research (see Kaye et al. 2006, and references therein). In closing, I would like to quote Wallace S. Broecker (1931–2019) on his final thoughts about reducing CO₂ in the atmosphere in Broecker (2018)…people are uneasy about allowing humans to intervene in climate. Most ecologic interventions have created as many problems as they solved. However, as doing nothing will lead to irreparable loss of ice and species, careful thought must be given to the geoengineering option.

Conclusions

In my review of the evolution of biogeochemistry, I have retraced the important historical steps in part, covered by Gorham (1991) in the 18–19th centuries—with new emergent linkages and trends in 20–21st centuries. One notable omission, is that I did not cover the origin of life, as Gorham did in his review.
19th century

In the post-phlogiston period, we see key connections between weathering, atmospheric chemistry, carbon cycling and climate change (e.g. Bischof 1826; Tyndall, 1863; Arrhenius 1896; Chamberlin 1899). In particular, Ebelmen (1845) proposes that dissolved salts and bicarbonate can be formed from the weathering of rocks as related atmospheric carbon dioxide—launching us into the modern carbon cycle. The early work by Davy (1813) on weathering and the importance of organisms in the exchange of carbon dioxide between the rocks and the atmosphere, provided the foundation for new analytical approaches by Boussingault (1838), that allowed Dumas and Boussingault (1844) to make connections between carbon and nitrogen. All of this was strongly influenced by Lemey (1717) and Berthollet (1785). The emphasis on chemistry in understanding soil fertility for agricultural purposes continued with the examination of phosphorus and nitrogen for crops in a period emphasizing stoichiometry—in large part by Boussingault (1838), Sprengel (1828), Lawes et al (1861), Liebig (1862). Remarkably, this leads to the first examples of nitrogen amendments dating as back far as 1856. Another important development comes from the work by Darwin (1881) on vegetable mould and worms—which for the first time explored the role of multicellular organisms in soil fertility. The next important stage is establishing how microbes “fit” with what was known about the stoichiometry of soils and plants. Winogradsky “steals the show” with his discoveries of chemolithotrophy and mechanisms of nitrification (Winogradsky 1891). This also initiates the founding of ecology (Warming 1895). The early linkages between evolution and biogeography, prove to be fertile ground for further development of ecology, and a better understanding what controls the global distribution of organisms (e.g. von Humbolt, 1805; Forbes 1846; Darwin 1859). We also see the beginning of concerns about the impact of humans on Earth—as agriculture and industry expands (e.g. Marsh 1874a, b).

20–21st centuries

Vernadsky (1926) begins the century with his idea the biosphere and continues with the noosphere, as concerns about an Anthropocene continues. The field of biogeochemistry now formally emerges with Vernadsky and Hutchinson leading the way (e.g. Vernadsky 1945; Hutchinson 1950). The development of organic geochemistry by Treibs (1936) allowed for biogeochemical linkages to be made between the short and long-term carbon cycle. This also allowed for new bridges to be formed whereby chemical proxies could be used to understand biogeochemical shifts in Earth’s 4-billion-year history. Ecology continues to develop and grows with greater linkages to abiotic processes in ecosystems. We see Dobzhansky usher us into the world evolutionary genetics (Dobzhansky 1932), which will prove vital in the next century of biochemistry. A new surge in stoichiometry also emerges in biogeochemistry after the Green Revolution, human population growth, and eutrophication problems. New molecular with genetic markers allow for advances in biogeography and evolution that require ecological principles (e.g. population dynamics plant succession) to understand organismal distribution, particularly as range expansion begins to occur in a warming climate. Biogeochemists realize the difficulty of studying complex elements cycles and begin to expand their work on global reservoirs and fluxes (e.g. Degens 1989; Schlesinger 1991; Jacobson et al. 2000). The advent of long-term and large-scale experiments begin to help contain complexity of non-linearity and regional differences in fluxes and rates in biogeochemical work. This leads to more synergy that require multidisciplinary approaches, beginning more formally ca. 1960-1970s, which allows biogeochemistry to blossom in the 20th century. This begins a new age of combining molecular approaches (e.g. omics) with large-scale satellites, monitoring, surveys, and observatory approaches that ultimately are combined in Earth System models. These new connections with ecological/evolutional genetics are one of the more dramatic and important aspects of biogeochemistry in the 21st century.

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