



Heinrich D. Holland

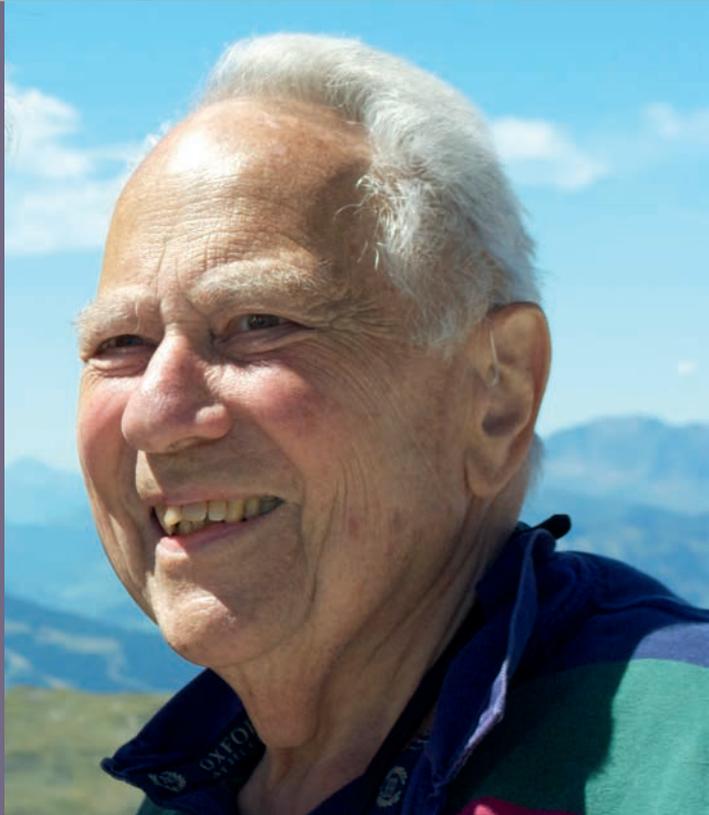
1927–2012

BIOGRAPHICAL

Memoirs

*A Biographical Memoir by
James F. Kasting*

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HEINRICH DIETER HOLLAND

May 27, 1927–May 21, 2012

Elected to the NAS, 1979

Heinrich D. Holland was a leading light in geochemistry for almost six decades. His early work was in seawater geochemistry and economic geology, particularly the formation of hydrothermal ore deposits. But his studies of ore deposits also led him to consider the history of the atmosphere and the rise of atmospheric oxygen. It is in this latter area that he made his greatest mark. He wrote two books and dozens of papers and book chapters on this topic. Holland did more than anyone to solidify the notion that atmospheric O₂ increased dramatically about halfway through Earth's history—an event now termed the "Great Oxidation Event," or GOE.

Holland earned a bachelor's in chemistry from Princeton University in 1946 and a Ph.D. in geochemistry from Columbia University in 1954. While working toward his doctorate, he became an instructor in geology at Princeton in 1950, eventually teaching there for 22 years. He moved to the Harvard University faculty in 1972 and remained there until he retired from teaching, though not from research and publishing, in 2005.



Heinrich D. Holland

By James F. Kasting

Heinrich Dieter “Dick” Holland was born in Mannheim, Germany, on May 27, 1927. His parents were Jewish, and although the family was not particularly observant, they found themselves in jeopardy when Adolf Hitler and his Nazi Party came to power in 1933. At the age of twelve, Dick and his younger brother Hans Joachim escaped from Nazi Germany to England just before the outbreak of World War II, as part of the Kindertransport program. These children from Nazi-occupied countries, unaccompanied by their parents, were temporarily taken into British homes. Dick and his brother went to a home in the countryside outside of London, before being sent by train to Scotland and then by ship to New York City, where they were met by their mother, who had also escaped. Lacking visas, they then traveled to the Dominican Republic, where they were



A young and dashing Dick Holland during his early years teaching in Princeton.

reunited with their refugee father and younger sister Anne. The family was then able to immigrate to the United States in 1940, settling in Kew Gardens, New York.

The young Dick Holland was an academic prodigy. He received a scholarship from the Stony Brook School in Stony Brook, New York, and graduated as valedictorian at the age of 16. Stony Brook was an evangelical Christian school, and Dick and his brother both became devout evangelical Christians themselves, although as Dick learned more and more about Earth's geological record, he gradually evolved towards a worldview that is often referred to as secular humanism. After Stony Brook, Dick won a full scholarship to Princeton University. He graduated from Princeton Phi Beta Kappa, with a B.A. in Chemistry, in 1946, having just turned 19. He served in the U.S. Army from 1946 to 1947, during which time he worked with Wernher von Braun's Peenemünde rocket group, which had been reassembled at Fort Bliss, Texas. Dick later described his main accomplishment there as serving as a translator between the wives of the German rocket scientists

and the men who delivered milk to their homes, all of whom spoke with thick Southern accents. But Dick also learned physics from a scientist named Ernst Stuhlinger, an expert in rocket control theory.

After his year in the Army was up, Dick intended to study rocketry in graduate school. Before he could enroll, though, he received a phone call from a professor at Columbia University named J. Laurence Kulp. Kulp was himself an academic prodigy, having received his Ph.D. in chemistry from Princeton at the age of 24, making him only

six years older than Dick. The two had been friends at Princeton, both through the department and through their church. Kulp was trying to establish a group in geochemistry and asked Dick if he wanted to become his graduate student. Dick accepted the offer and enrolled at Columbia, along with fellow students Paul Gast, Karl Turekian, and Wallace Broecker, all of whom later became famous in their own right. This may have been one of the most talented clusters of graduate students ever to work together in the same research group.

Kulp was a pioneer in radiometric dating and a leader in studies of radioactive fallout. He was the first to suggest, in 1953, that the strontium isotope ^{90}Sr could be used to trace radioactive fallout and its threat to humans, and his laboratory at Columbia was the first to measure it in soils, bones, and human food (cheese). He would later become a leader in studies of acid rain.

Dick's doctoral thesis was published in two parts (with Kulp in 1954) and dealt with riverine fluxes, ocean sedimentation, and, hence, the geochemical cycles of uranium, ^{230}Th and radium. The titles of these two papers sound very modern, as this type of study has since become a staple in geochemistry.

A lifetime in academia

Dick began teaching as an instructor in the Department of Geology at Princeton in 1950, while still working on his doctorate at Columbia. Looking back at those early years at Princeton, Dick later said that he had been uncomfortable, as he was actually younger than most of the graduate students in the department! He taught at Princeton for nearly 22 years before moving to Harvard in 1972. He would remain at Harvard for another 33 years, eventually assuming the title of H. C. Dudley Professor of Economic Geology.

In 1953 Dick married Alice Tilghman Pusey, a marriage that lasted until she passed away in 2010. The couple had four children between 1954 and 1959: Henry, Anne, John, and Matthew. Dick and Alice were generous and outgoing, hosting weddings for students in their home and becoming godparents to some of their students' progeny. Dick even served as "father of the bride" for several students. The close personal relationships that Dick formed with his students contributed in an important way to his scientific legacy.

Early career: seawater chemical evolution and ore deposits

Following his initial work on seawater radiochemistry with Kulp, Dick became interested in chemical processes occurring at mid-ocean ridges. A significant part of this work consisted of experiments that were performed in Dick's own hydrothermal lab, which he

maintained throughout his career. Studies with his Ph.D. student Mike Mottl in 1978-79 showed that magnesium (Mg) was taken up readily by high-temperature basalts, providing at least a partial solution to the question of how Mg is removed from the oceans. This, in turn, helped explain why dolomite, or calcium magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$), has not been forming during the last several tens of millions of years. Dick was also active in exploratory studies of the mid-ocean ridges, participating first in an unsuccessful attempt to find hydrothermal vents on the Mid-Atlantic Ridge, and then in more successful efforts along the East Pacific Rise, an 8000-mile-long tectonic elevation of the ocean floor stretching southward from southwestern Mexico.

Dick cemented his scientific reputation by applying thermodynamic principles to the study of hydrothermal ore deposits.

These are economically important sources of copper, zinc, lead, silver, and other metals that formed in a wide range of tectonic-thermal environments, from

those similar to the modern mid-ocean ridges, to island-arc terranes, to basins in great foreland settings. Two papers that were particularly influential were his 1959 and 1965 *Economic Geology* papers: "Some applications of thermodynamic data to problems of ore deposits. I. and II." These papers were the first to explain elegantly how to apply thermodynamics to understand the processes and environments for the formation of hydrothermal deposits of all types, not only those in the oceans but also those on land, and even those not associated with igneous activity.



A still young Dick lecturing at a venue thought to be a mine, (but not positively identified as such.)

Dick's 1972 paper entitled "Granites, solutions, and base metal deposits," which critically examined the classic hypothesis for the origin of magmatic-hydrothermal deposits and found that modern geochemical data strongly supported it, was also influential, and inspired follow-up experimental studies with his student Phil Candela. A memoir written by Dick's long-time collaborator Karl Turekian at Yale describes Dick as being the initiator of rigorous thermodynamic treatments of ore deposits, leading some to call him the "father of modern economic geology." Turekian and Dick co-edited the 9-volume *Treatise on Geochemistry*, published in 2004. They were working on the second edition of the *Treatise* at the time of Dick's death.



Dick at (right) with Antje Danielson on their Labrador trip in summer, 1991.
(Reproduced by permission of Andrew Macfarlane, Florida International University.)

Early work on atmospheric evolution

Although Dick's background was in geochemistry, it did not take long for him to apply his knowledge to understanding Earth's early atmosphere. When the distinguished petrologist Arthur Francis Buddington retired in 1959 after a long career at Princeton, Dick was one of a number of geochemists who contributed papers to a volume in Buddington's honor published in 1962. While most of the papers in the volume focused on petrology, Dick's contribution was entitled "Model for the Evolution of the Earth's

Atmosphere.” Dick was 35 years old when this book came out. While looking up material for this article, I pulled out a wrinkled old photocopy of this chapter that had been in my files since I was a graduate student at Michigan. Sections of it were underlined in red ink, helping me to recall that this was one of the papers—along with the 1964-67 series by Lloyd V. Berkner and L. C. Marshall—that sparked my own interest in atmospheric evolution.

In his chapter, Dick began by recounting work by Harold Urey and William Rubey. Urey was famous for a number of reasons, including his discovery of deuterium and his work on the Manhattan Project, which produced the atomic bomb that ended the war with Japan in 1945. But he was also well known for his arguments in favor of a strongly reducing early atmosphere containing substantial concentrations of hydrogen (H_2), methane (CH_4), and ammonia (NH_3). These compounds had been recently discovered in the atmospheres of Jupiter and Saturn, and Urey reasoned that Earth’s atmosphere should have been similar before hydrogen had had sufficient time to escape. Subsequent experiments in the early 1950s by Urey’s graduate student Stanley Miller showed that some of the building blocks of life—that is, amino acids—might have been produced by lightning strikes in such an atmosphere. The Soviet biochemist Alexander Oparin had proposed similar arguments well before this, but the laboratory demonstrations by Miller and Urey seemed to put this model on a solid footing.

Working at almost the same time, Rubey, a distinguished geologist whose many research interests included mountain building and the origins of the Earth’s atmosphere, took a completely different tack. He assumed that the Earth started off airless and that the atmosphere was built up from volcanic emissions. Volcanoes today emit mostly carbon dioxide (CO_2), and the most ancient preserved basalts appear roughly as oxidized as present day basalts, so Rubey concluded that the early atmosphere should have been rich in CO_2 and nitrogen (N_2)—not the H_2 - CH_4 - NH_3 mixture that Urey was proposing.

In his 1962 book chapter, Dick melded these two competing hypotheses together in a way that seemed entirely convincing—at least to me, as a young graduate student. He proposed a three-stage model for atmospheric evolution. Stage 1 occurred before the Earth’s core had formed. Metallic iron was still present in the upper mantle, and so volcanic gases released at that time were highly reduced, satisfying Urey’s requirement for a reduced early atmosphere. Around half a billion years into Earth’s history, the interior heated up from the decay of radioactive elements, melting it and allowing core formation to take place. Other workers would later demonstrate that the Earth formed hot as

a result of giant impacts during accretion, and that Earth's core formed during these impacts, but this new paradigm did not come along until the 1980s.

Stage 2 in Dick's model began after the core had formed. The mantle and crust were now free of metallic iron, and so water (H_2O), CO_2 and N_2 became the dominant outgassed species, just as Rubey had proposed. Dick was aware of evidence for detrital uraninite (UO_2) in ancient rocks, and so he suggested—correctly, we now think—that atmospheric oxygen (O_2) remained low during this time. UO_2 is a reduced mineral that is generally oxidized during weathering under today's O_2 -rich atmosphere. (Detrital minerals are grains eroded out of rocks and transported down streams and rivers without ever dissolving.)

Finally, Stage 3 in Dick's model began when sinks for O_2 were overwhelmed by the rate of production of O_2 from oxygenic photosynthesis and from photo-dissociation—a chemical breakdown of water vapor triggered by light, followed by the escape of its hydrogen to space. This allowed oxygen to accumulate in the atmosphere, leading to the O_2 -rich modern world that supports large animals like ourselves. The rate of production of O_2 from photo-dissociation and hydrogen escape was poorly understood at that time; nevertheless, Dick's analysis of the cause of the transition to an O_2 -rich Earth remains basically correct.

From this time on until his death, Dick was always at the center of scientific discussions concerning the rise of atmospheric O_2 . What follows is an abbreviated, and largely personal, view of how that debate proceeded and the important role that Dick played in it.

The great debate over the rise of atmospheric oxygen

Questions about the rise of atmospheric O_2 were hardly put to rest in 1962. For many years the biggest issue was: When did atmospheric O_2 first rise to appreciable concentrations? In his 1962 book chapter, Dick suggested that the transition occurred around 1.8 billion years ago, or 1.8 Ga (giga-aons) to a geologist. This is the time at which banded iron-formations (BIFs) essentially disappeared. BIFs are the source of most of the iron that we mine for the steel industry today; hence, they have long been objects of interest to economic geologists. Dick wrote a paper in 1973 arguing that their formation required long-distance transport of iron, and hence that the deep oceans must have been reduced during the time that BIFs were being deposited. This remains one of Dick's most important ideas. It doesn't necessarily tell us when the *atmosphere* became oxidized,

because the deep ocean and the atmosphere can remain significantly out of equilibrium with each other, but it shows that the deep oceans were indeed anoxic prior to 1.8 Ga.

Other geologists, notably Preston Cloud of the University of California, Santa Barbara, worked hard at identifying other geologic O_2 indicators that might help establish the time of the “Great Oxidation Event,” or GOE, as it is now called. Back in the early 1970s Cloud placed it at ~ 2.0 Ga, based on last occurrence of detrital uraninite and pyrite (FeS_2), along with the first occurrence of redbeds. Redbeds are sandstones containing oxidized, or *ferric*, iron that form in O_2 -rich environments. Radiometric dating techniques have improved since then, and other O_2 indicators have appeared, so we now place the GOE at about 2.45 Ga. Much of this evidence is summarized in Fig. 1, which first appeared (in black-and-white) in a 2006 paper by Dick that was part of the proceedings from a meeting of the Royal Geological Society of London held earlier that year.

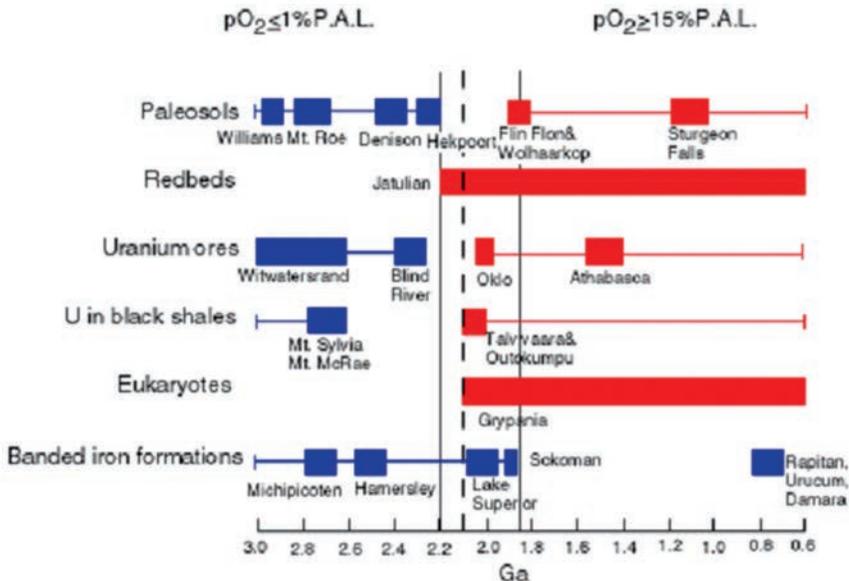


Figure 1. Diagram showing the ‘conventional’ geologic evidence for the rise of atmospheric O_2 . Blue boxes indicate low O_2 ; red boxes indicate high O_2 . Paleosols are ancient soils. Eukaryotes are organisms with cell nuclei. Banded iron-formations tell us about dissolved O_2 in the deep oceans. Additional non-conventional evidence comes from multiple sulfur isotopes. (Adapted from Holland, *Phil. Trans. Roy. Soc. London B* 361:903 (2006). Colorized by Yumiko Watanabe.)

Looking at this figure causes me to remember a talk that Dick gave at Penn State shortly after this paper came out. We were in a small conference room, and Dick was speaking to an audience of geoscience faculty and graduate students. Dick put up a B&W version of this figure on the viewgraph machine—we still had them at that time—and then spent the entire hour discussing it. I think he had brought other view graphs with him, but he never got beyond this one because we peppered him with questions about it. This remains the only 1-hour, 1-figure lecture that I have ever seen.

It would be impossible to discuss the history of this debate, and of Dick's role in it, without mentioning Dick's former graduate student Hiroshi Ohmoto. Hiroshi is a long-time colleague of mine at Penn State, now retired, so I know him quite well. Hiroshi was one of Dick's early grad students at Princeton, and he and his wife, Koya, were very close with Dick and Alice. Dick and Hiroshi worked together on hydrothermal ore deposits and published several papers together. Hiroshi wrote reviews of this subject in 1972 and 1986 that have garnered 500-600 citations each on Web of Science, so this work was well received and influential.

By the early 1990s, though, Hiroshi had developed his own interest in the rise of atmospheric O_2 , and his perspective was quite different from Dick's. For many years after that, Hiroshi argued that O_2 was present in the atmosphere at near-modern levels all the way back to 3.8 Ga. This, of course, is quite the opposite of what Dick and others had been advocating for many years. Hiroshi based his analysis on several different types of evidence, including the presence of ferric iron in Archean rocks, such as banded iron formations, cherts—mainly silicon dioxide (SiO_2)—and paleosols (ancient soils). Others would argue that some of the iron was oxidized later in Earth's history and that various anaerobic mechanisms exist for forming oxide BIFs (such as, phototrophic, iron-oxidizing bacteria), but Hiroshi insisted that free O_2 was involved in forming many of these deposits and that this implied that O_2 was present in appreciable concentrations in the Archean atmosphere.

Mass-independent fractionation of sulfur isotopes and the GOE

The debates between Dick and Hiroshi were sometimes painful to watch, especially knowing that the two had once been close friends. That is sometimes how science progresses, though, and in this case the argument eventually led to a major scientific discovery. The noted isotope geochemist Mark Thiemens, from UC San Diego, became aware of this debate, partly through conversations with Stanley Miller, who was now a colleague of his at San Diego. Thiemens is well known for his work on so-called

“mass-independent fractionation”—MIF, for short—of oxygen isotopes and what it tells us about the protosolar nebula. Isotopes with different mass numbers react chemically at different rates. Generally, a lighter isotope reacts faster than a heavier one.

In the case of oxygen, there are three stable isotopes: ^{16}O , ^{17}O , and ^{18}O . ^{16}O is the major isotope, and the other two are minor. ^{17}O differs from ^{16}O by one atomic mass unit (AMU), while ^{18}O differs by two AMU, so generally ^{17}O fractionates (separates) from ^{16}O by about half as much as does ^{18}O . But there are processes—for example, ultraviolet (UV) photolysis of CO—that fractionate O isotopes differently, and Thiemens, along with his mentor, Robert Clayton, of the University of Chicago, had done some of the earliest work on measuring triple-O isotopes in meteorites and trying to understand what they imply about Solar System formation.

Oxygen isotopes are of little help in understanding the GOE, but sulfur isotopes turn out to be extremely useful. Sulfur has four stable isotopes: ^{32}S , ^{33}S , ^{34}S , and ^{36}S . ^{32}S is the major isotope (~96 percent), ^{34}S is next (~4 percent), and the other two are both minor. Over the past several decades ^{32}S and ^{34}S have been used to study geo-biological issues, especially the origin and proliferation of sulfate-reducing bacteria. With his background in O isotopes and cosmochemistry, Thiemens realized that the other minor isotopes, ^{33}S and ^{36}S , might contain valuable information. Furthermore, he and his postdoc James Farquhar had already been studying them in Martian SNC meteorites (so named for locales in Shergotty, India; Nakhla, Egypt; and Chassigny, France, where samples were discovered), and they knew from experiments in their lab that sulfur MIF signals could be generated by UV photolysis of sulfur dioxide (SO_2). So they decided to find out what these minor S isotopes might tell them about terrestrial atmospheric evolution.

What they discovered was a revelation! Sulfur in rocks younger than ~2.4 Ga was always fractionated in the normal, mass-dependent way. But sulfur in older Archean rocks had strong MIF signatures, implying that short wavelength UV radiation must have penetrated deeply into the atmosphere at that time. And this, in turn, implied that atmospheric O_2 and its attendant ozone screen must both have been virtually absent. Thus, the story fit together perfectly, and it strongly supported the Cloud/Holland hypothesis that O_2 was scarce during the first half of Earth’s history.

“Whiffs” of O₂ and the causes of the GOE

The paper by Farquhar and colleagues did not end the debate between Dick and Hiroshi, although for many of us it resolved the question of when the GOE took place. It also ended a long, mostly private debate between Dick and me about the abundance of O₂ prior to the GOE. Dick had argued in his 1962 book chapter that H₂ should have been essentially absent from the Archean atmosphere because it would have been consumed by reaction with SO₂, the dominant sulfur gas released by surface volcanoes. But the atmospheric scientist James C. G. Walker had argued in papers and in his 1977 book, *Evolution of the Atmosphere*, that hydrogen should have been present in appreciable (0.01-0.1 percent) concentrations. Its concentration would have been determined by the balance between outgassing from volcanoes and escape to space. This, in turn, would have relegated O₂ to extremely low concentrations. I investigated, and confirmed, Walker’s hypothesis as part of my own Ph.D. thesis at the University of Michigan, in which I used a one-dimensional photochemical model to calculate vertical profiles for atmospheric O₂ during the Archean. Dick never quite bought this idea until the Farquhar, et al., paper came out, and my student Alex Pavlov and I were able to explain the data with our photochemical model.

After that, one would think that Dick and I would have ceased arguing, but that turned out not to be the case. Instead, this was just the beginning of a new discussion as to *why* the GOE took place when it did. This same debate is still in full swing today. Over the past decade, various authors have presented evidence for “whiffs” of oxygen back during the Archean, prior to the GOE. The term “whiffs” was coined by Ariel Anbar in a 2007 paper in *Science*. The evidence comes in the form of isotopic ratios of molybdenum (Mo) and chromium (Cr), along with carbon isotope ratios suggesting that free oxygen must have been present, so that aerobic methanotrophs (microorganisms that react CH₄ with O₂) could have created doubly fractionated organic carbon. (Additional evidence for early O₂ from organic biomarkers has now been discredited.)

The isotopic data suggest that O₂ was being produced as much as several hundred million years before the GOE, even if it did not accumulate permanently in the atmosphere. One point on which virtually all geologists and biologists agree is that the first organisms to produce O₂ were *cyanobacteria*, formerly called “blue green algae.” Cyanobacteria are true bacteria that can produce O₂ photosynthetically, and there is nearly incontrovertible genetic evidence that they invented this process and that all other organisms—for example, true algae and higher plants—copied it from them. One explanation for these

“whiffs” is that atmospheric O_2 may have increased transiently, then gone back down again before leaving a clearly identifiable signal in traditional O_2 indicators. So, Hiroshi may have been partly right: the Archean atmosphere may have been oxidizing at least part of the time. But the transition to a permanently oxidized atmosphere did not take place until about 2.4 Ga.



Dick with Bernard Poty at Chamonis, France, summer, 2011, a year before his death.

If cyanobacteria were producing oxygen well before 2.4 Ga, why did O_2 not rise much earlier? Dick and I talked about this every time we got together during the last 10 or 12 years of his life. Was the mantle more reduced back in the Archean so that volcanic gases were also more reduced? What was the role of serpentinization (a process by which Mg-rich rocks on the seafloor and continents can be oxidized by reaction with warm water)? And how strongly is this problem constrained by the carbon isotope record? Photosynthetic organisms fractionate ^{13}C relative to ^{12}C when they fix carbon, causing organic carbon to be isotopically depleted in ^{13}C relative to carbonate in sediments.

To first order, the carbon isotope composition of carbonates has not changed greatly since the Archean. Taken at face value, this suggests that organic carbon was being buried in sediments just as rapidly back in the Archean as it is today. And this, in turn, would imply that the O_2 sinks must have been much larger at that time, despite the fact that today's largest O_2 sink—oxidative weathering of the continents—was not operative. Alternatively, the carbon isotope record may be misleading us, because the continents were much smaller during the Archean and the rate of recycling of carbon through the surficial system was correspondingly slower. This was the thesis of one of Dick's last contributions on the topic, a 2009 paper entitled “Why the atmosphere became oxygenated: A proposal.”

Honors and retirement

During his long academic career, Dick also took numerous sabbaticals, four at the University of Hawaii, one each at Hebrew University in Jerusalem, Durham University in Northeast England, Imperial College in London, Heidelberg University in Germany, and two at Penn State University. He served as vice president (1969-70) and president (1970-71) of the Geochemical Society. He received numerous awards, including the Alexander von Humboldt Senior Scientist Award (1981-82), the V. M. Goldschmidt Medal of the Geochemical Society (1994), the Penrose Gold Medal of the Society of Economic Geologists (SEG) (1995), and the Leopold von Buch Medal of the Deutsche Geologische Gesellschaft (1998). Dick was Distinguished Lecturer for SEG in 1969 and Thayer Lindsley Lecturer in 1981-82. He was a Fellow of the American Academy of Arts and Sciences, the American Geophysical Union, and the Society of Economic Geologists, and a member of the U. S. National Academy of Sciences.

After his retirement from Harvard, Dick moved to Philadelphia in 2006, where he took up the position of Visiting Scholar in the Department of Earth and Environmental Science at the University of Pennsylvania. In this role he continued to interact with students and to pursue his geochemical interests until his death in 2012, publishing a paper with Andre Bekker that came out that year. He knew for some time that his health was failing and that he had only a short time to live. He had started another book recounting the history of the oxygen problem, but he realized that he did not have time to finish it. The last time I saw him, a few months before his death, he told me that it was more important to complete the paper with Andre than to finish the book. Dick still had ideas that he wanted to express, and although his body was becoming weak, his mind was still as strong as ever.

I will never forget Dick Holland. He was a friend and scientific mentor to me and to many others, and he made lasting contributions both to geochemistry and to our understanding of Earth's atmospheric evolution.

ACKNOWLEDGEMENTS

Mike Mottl, Tim Drever, Lee Kump, Mark Logsdon, Steve Phipps, Phil Candela, and Hiroshi Ohmoto all contributed ideas to this memoir. Thanks to Hiroshi for providing the photos. Much of the first three sections of this memoir is abstracted from a longer memoir written by Mottl, one of Dick's graduate students, for a special issue of the journal *Chemical Geology*, published in 2013. The reader is encouraged to look there for additional details about Dick's childhood and early career.

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