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FROM BLACK MUD TO EARTH SYSTEM SCIENCE: A SCIENTIFIC AUTOBIOGRAPHY

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DEDICATION

To my wife, Elizabeth Kay Berner, for her unstinting encouragement and understanding throughout the many years of my devoting myself to my research, and for her collaboration in the writing of three books.

PROLOGUE

This autobiography covers the past 55 years of my research in geochemistry. I try to show how chemical principles can be applied to a wide variety of geological problems, ranging from iron sulfide mineralogy, to carbonate chemistry in the oceans, to silicate mineral surface chemistry during weathering, to biogeochemical changes during early diagenesis, to plants and weathering, to models for the evolution of atmospheric oxygen and carbon dioxide. This may seem excessively broad but my approach to science has been and will be eclectic for which I do not apologize. My guiding principle is "How can chemical measurement or chemical theory solve a given problem?"

PART I. THE EARLY YEARS, 1953–1979
THE MAKING OF A GEOCHEMIST

The Beginning

I was strong in math and science in high school, so I entered Purdue University in 1953 with the intention of majoring in chemistry. I became completely dissatisfied with Purdue after about two months and decided to transfer to the University of Michigan after only one semester. At Purdue they kept pushing me towards engineering and, more importantly, there was a large lack of female students there. At Michigan I continued my interest in chemistry but found chemistry lab boring because there were no reasons given for having to spend endless hours analyzing unknown solutions for a whole list of elements. This led me to majoring in math and then in Physics. I found that these fields were too demanding and that they took too much time from partying and girls, which were my major interests. When it came to having to declare a major I was stuck with no ideas and considered even majoring in philosophy, which I found fascinating. My brother, Paul C. Berner a petroleum geologist at the time, suggested that I take a course in geology before declaring my major. I followed his advice and have never regretted it. I found geology sufficiently interesting but not nearly as intellectually demanding as physics or mathematics. Wow! I could continue to have fun and get good grades in science. Sophomoric reasoning at its worst.

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I learned a lot of geology in my junior and senior years and began to like it and take studying more seriously, getting lots of A grades. In my senior year at Michigan, I met my future wife, Betty, a stunning beauty, in of all things a structural geology class. There were very few female geology majors in those days and almost never any as good looking as Betty. (Betty was the daughter of the famous geologist, Marshall Kay, and this might help explain why she ended up in a structural geology class.) We went together to geology field camp in the summer of 1957 and by then we were steady dates so that I could protect her from the large number of potential male competitors. After field camp I did field work for my Masters thesis. This was a study mapping the Eocene sediments of Huerfano Park, Colorado with an eye to deducing the source of sandstones via cross bedding analysis.

During my Masters year at the U of M, I wrote up my thesis and decided to go into the oil business, like my brother and most of my fellow soft rock students. I actually interviewed and accepted a job with Shell Exploration. However, I never actually took the job. In the meantime, my brother convinced me that I had the where with all to go on for a Ph.D. At first I thought that I was not up to such a foreboding task and had to be argued into accepting the idea. Nobody in my family or any other relatives had ever gone that far in college. But I finally gave in when Shell told me that I could have a summer job with them before going on to graduate school. The question then became where to go for a Ph. D. My advisor at Michigan, Lou Briggs, insisted that I go to Harvard to work with a young sedimentary petrologist named Raymond Siever. However, I wanted to work with Bill Krumbein at Northwestern because I was beginning to appreciate the use of mathematics in studying sediments. I applied to both Harvard and Northwestern and was awarded fellowships in both places. Lou Briggs also kept emphasizing geochemistry and that Siever did some geochemistry and that the great geochemist, Robert Garrels was also at Harvard. (Fortuitously, both Garrels and Krumbein had already published an important paper about Eh and pH in classifying sediments.) Well, I had tried majoring in chemistry and didn't like it, but Lou persisted and Siever's sedimentological work was appealing. Finally I followed Lou's advice and accepted the fellowship to Harvard. Me going to Harvard? Good Lord, that was just about the best school in the country. Would I ever make it through there? I didn't think so. But I made it through and I am forever grateful to Lou Briggs for his advice and I even ended up being a geochemist.

Harvard: Ph. D. Thesis on Iron Sulfides and the Sulfide Electrode

I arrived at Harvard intending to do research in sedimentary petrology working with Ray Siever, with an emphasis on modern sediments. I was fortunate that my girl friend Betty accompanied me to Harvard as a fellow geology student. She obtained a master's degree from Radcliffe and then went to work as a computer programmer (and an important source of additional financial support after we were married in August of 1959). I took all the appropriate courses during my first two years and passed my qualifying oral exams. (I was told that I had passed the exams but not impressively.) I learned that geochemistry would be useful in my study of sediments and I also learned a lot from courses with Bob Garrels, especially on chemical thermodynamics. In fact, I later took a course in the Chemistry Department on this same subject. Ray Siever had invented a way to squeeze interstitial water from marine muds and I helped him do interstitial water "squeezing" in a short cruise near Cape Cod. He had deduced that the chemical analysis of interstitial waters is a sensitive indicator of incipient sediment diagenesis. Later I participated in a cruise to the equatorial Atlantic where I collected interstitial pore waters of deep-sea sediments for Ray. Eventually Ray published a paper (Siever and others, 1965) by Ray, myself and Kevin Beck who did chemical analyses of

my collected pore waters. We found that the major elements did not show large changes from the overlying seawater. However, this work whetted my desire to continue studying pore waters as will be seen below.

For a thesis Ray Siever suggested that I study the sediments of Barnstable Harbor, working during the summer, with the grand old man of the Woods Hole Oceanographic Institution, Alfred C. Redfield. Redfield, a biologist, I thought was an unusual mentor for me. Boy was I wrong. This man was a true natural scientist and had worked in many fields ranging from animal physiology to physical oceanography. I quickly found out that he also was well versed in geology. He was collecting sediment cores from marsh sediments in Barnstable on Cape Cod to use certain tidal grasses as indicators of past sea level change (after obtaining ^{14}C dates on them). I was his helper collecting the cores. On my own time I started mapping the different sediment types but this endeavor never came to fruition. Instead I became fascinated and perplexed by the black color of the subsurface of grass-free tidal flat muddy sediments that were in front of the marshes. The surface of the mud was reddish brown and this turned to black downward within a few centimeters of the surface. With further depth in the sediments the black color faded to a light gray color. What was the black material and why did it fade with depth? This was the beginning of my Ph.D. research. Chemistry would help me to solve the problem and Redfield's example of working in a variety of different fields would serve as an inspiration for my life's work. I went on my own and did not follow my advisor's original recommendations.

How could I figure out the nature of the black stuff? The literature mentioned an iron sulfide called "hydrotroilite" as the black coloring of modern muds but it was poorly defined with no verified chemical composition or crystal structure. I tried to isolate the black stuff from sediments at Barnstable, Woods Hole, and near Harvard but I could not obtain it in pure form to be able to subject it to x-ray diffraction or chemical analysis. It serves as a kind of "paint" on mineral grains and is readily oxidized to iron oxide by exposure to air. It was known that it formed by the reaction of H_2S from bacterial sulfate reduction with ferric oxyhydroxide "paint" on mineral grains carried into depositional sites. This explains the color change I noted at Barnstable. But what was the black stuff?

The solution to the black stuff problem had to start with the synthesis of pure iron sulfide. I tried this and found through many experiments that when iron metal reacts with H_2S, a product is found that, when quickly dried out of contact with air, gives a good x-ray diffraction powder pattern similar to an H_2S corrosion product called Kansite in the literature. All other syntheses, using Fe^{++} reacting with H_2S gave useless amorphous patterns. The powder pattern of the iron metal-H_2S reaction could be indexed and with great luck it proved to be tetragonal. I then took a leap out of my field, following Redfield's example, and tried to deduce the crystal structure of this iron sulfide. After much reading and many laborious calculations I was able to match the intensities of all diffraction lines by using the structure of red PbO (the mineral litharge) as a model. The position of atoms, according to my structure of tetragonal FeS is:

$$2 \text{ Fe in (a): } (000), (1/2, ½, 0)$$

$$2 \text{ S in (c): } (0, 1/2, 1/4), (1/2, 0, -¼)$$

A good match between measured and predicted data is shown in figure 1. Chemical analysis proved to be FeS with a little extra Fe. After extensively looking through the literature I discovered that I had a new mineral, but it was formed only in the lab. So I went to a "natural" location where the new tetragonal iron sulfide might be found. I selected the polluted tidal sediments of the Mystic River near Boston. As the tide came

Table 1. X-ray powder diffraction data for tetragonal FeS (unfiltered FeK radiation) and "kansite."

"Kansite"*	Tetragonal FeS				
d_{meas}. Å	d_{meas}. Å	d_{calc}. Å	hkl	I_{obs}.†	I_{calc}.
			100	‡	0
5.05	5.03	5.04	001	10	190
2.99	2.97	2.97	101	8	69
	2.60	2.60	110	2	15
2.32	2.305	2.31	111	8	94
			102	‡	0
	1.835	1.839	200	6	56
1.80	1.805	1.811	112	8	103
1.73	1.723	1.728	201	6	42
	1.677	1.681	003	2	8
	1.564	1.564	211	4	17
1.54	1.527	1.530	103	2	8
1.42	1.410	1.412	113	3	16
1.31	1.298	1.300	220	5	20.5
1.26	1.258	1.261	004	5	10
		1.257	221		15
	1.239	1.241	203	3	16
	1.190	1.192	301	1	5.5
	1.174	1.176	213	2	11.5
1.14	1.133	1.134	311	5	29
			310	‡	0
	1.055	1.056	312	8	100

* Data from Meyer *et al.* (*1*). † Relative intensities by visual estimation from powder photographs. ‡ Absent.

Fig. 1. Comparison of calculated and measured intensities of major forms for tetragonal FeS. Calculations based on the same structure as litharge (red PbO). Kansite refers to an iron corrosion product of unidentified structure (after Berner, 1962).

in, it brought seawater rich in sulfate that reacted with organic refuse to form hydrogen sulfide. The H_2S then reacted with iron trash that had been thrown into the river. I took a sample from near an old supermarket pushcart and while I was doing this some children on a nearby bridge looked down at me, knee deep in black muddy refuse, and

began to laugh at me. I thought that I could trick them and I called out that I was looking for gold. (Actually the FeS eventually converts to pyrite or fool's gold.) Their reply in classic Bostonese was "it ain't woith it mistah." But I thought it was "woith it" because the material carried back to the lab at Harvard, after treatment to remove elemental sulfur, showed an x-ray pattern the same as my synthetic tetragonal iron sulfide. I had discovered a genuine new mineral and had worked out its structure!

It turns out that I could not name my mineral. Soon after working out its structure, a crystallographer from the USGS came to Harvard who had a mineral with the same x-ray pattern as my tetragonal iron sulfide. I told him of my structure and the next thing I knew was that he and another person had prepared a paper naming a new mineral using my structure determination. I did not like this taking advantage of an unknown graduate student, so I quickly prepared a paper to beat them to publication. This resulted in my first sole author paper (Berner, 1962). The paper was accepted by Science but they would not let me give it a mineral name because they considered the trashy sediments of the Mystic River as not being natural. A few years later the USGS published a paper by the crystallographer and associate naming the same tetragonal iron sulfide as mackinawite and they added me as a coauthor because of my deduction of its crystal structure. I appreciated their ultimate consideration. However, they used the wrong first name for me. To this day I know of no other paper on iron sulfides or anything else by Richard Berner.

My thesis research at Harvard also included the synthesis and identification of another new black iron sulfide, Fe_3S_4 with the same structure and magnetism as magnetite. This phase was later named greigite by Brian Skinner who had found it in some lake sediments. In much later work at Yale, I was able to show that both greigite and mackinawite transform thermodynamically to pyrite, FeS_2. Pyrite is not a paint-like coloring phase and its formation from the black iron sulfides explains my observation made at Barnstable of the loss of black color at depth in the sediments.

In true Redfieldian manner, and due to the great interest of Bob Garrels in electrodes, I also did a detailed study of the behavior of a silver-silver sulfide electrode immersed in solutions of H_2S and in natural sulfidic marine sediments. I found that it gave an electrical potential mirroring that of the platinum electrode. From this I was able to deduce that the Eh or oxidation potential of a platinum electrode in sulfidic solutions is controlled by the half cell between dissolved sulfide and elemental sulfur. I used the electrode during another summer at Woods Hole working with John Kanwisher, a physiologist who had invented an electrode for measuring dissolved oxygen. Kanwisher was a mechanical genius; he designed and built almost all of his own equipment. My favorite story about him is that he once fastened radio transponders to the collars of sea gulls from around Woods Hole so that he could track their movement. He found a mysterious periodic signal that was a sort of back and forth motion. For a while he couldn't explain it, but then realized that the back and forth motion corresponded to ferry runs from Woods Hole to Nantucket Island. People on the ferries would throw food off the stern to flying sea gulls following the boat, and the sea gulls would catch the food in the air. So his mysterious sea gull migration was not an undiscovered natural pattern but something much more mundane. He also designed a way to have porpoises breathe into a funnel after leaping out of the water so that he could analyze the chemical composition of their breath. Kanwisher was a truly imaginative scientist.

During two summers at Woods Hole, I had not worked with a geologist or geochemist, but I had enjoyed very much my exposure to new fields. Finally, after four productive years at Harvard and Woods Hole, I graduated with a Ph.D. from Harvard in 1962. A picture of me as a Harvard grad student in 1961, is shown in figure 2.

Fig. 2. Photograph, taken in 1961, of Robert Berner while a graduate student at Harvard University.

Scripps: Sedimentary Sulfur and Dolomite

While at Harvard during the fall of 1961 I was given the opportunity to participate in a cruise to the Gulf of California by the Scripps Institution of Oceanography. Having worked on iron sulfides, I became interested in the diagenesis of sulfur and the sulfur cycle in general. I went and collected a number of sediment cores to be analyzed later for solid forms of sulfur in the anoxic sediments. It was necessary that I do some analyses for sulfide aboard the ship. For this purpose I was given a special lab. However, the "special lab" was a bait tank with no ventilation because the ship we used was an old fishing boat. My method involved some small amount of leakage of hydrogen sulfide into the air, but it didn't bother me because the smell seemed so slight. I should have realized that H_2S is heavier than air and could accumulate in the unventilated tank. A fellow scientist noted the smell of H_2S at the opening of the tank and went down the ladder, grabbed me and told me to get out right away. After climbing up into the atmosphere and breathing fresh air, I went back down into the tank. The H_2S was at a dangerous level and had a strong smell, but I had adjusted to the smell while I was in

the tank. I am fortunate that I was grabbed and removed from the tank. Hydrogen sulfide is a lethal gas and the guy actually saved my life.

I hadn't sufficient time to do the remaining analyses of the Gulf of California sediments, and after graduating from Harvard in June of 1962, I went back to Scripps to study my samples. It was quite an experience moving from the oldest part of the U.S., with its hide-bound traditions (Boston), to sunny southern California with its laid back, everything new and everything goes, atmosphere. At Scripps I worked under the tutelage of Tjeerd (Jerry) van Andel, a marine geologist. He provided me with all the lab space and equipment I needed to complete my analysis of sulfur in the Gulf of California sediments. During lunch hour, I participated, along with my wife Betty, in the traditional Scripps activity of body surfing. (This was useful training for later visits to Hawaii where the waves are much bigger.) One day a former professor that I had had at Michigan showed up visiting at lunch time and saw me coming from the beach in my swim suit. I said to him "Welcome to the Scripps Institution of Oceanography." He replied "Hurrumpf. The Scripps Country Club." Apparently, he didn't have the proper southern California attitude.

While at Scripps I did a study with Mel Peterson (who had also worked with Ray Siever at Harvard) on the formation of dolomite in a lake in eastern California. The formation of dolomite, a common mineral in ancient rocks, was a big mystery at that time, but recent discoveries in a few places had provoked the interest of sedimentary petrologists. Mel cleverly figured out how to separate dolomite crystals by size, using a continuous flow apparatus, and then date the size fractions with ^{14}C. By doing this we were able to calculate the rate of crystal growth of dolomite, something unknown at that time. Attempts to synthesize dolomite at room temperature had been notoriously difficult and our crystal growth rates showed why. We obtained rates of only hundreds of angstroms per thousand years.

Before going to Scripps I was offered an Assistant Professorship at the new Department of the Geophysical Sciences at the University of Chicago. Although a high honor, I turned down the offer because I wanted to finish my work on the Gulf of California sediments at Scripps. I owed it to Jerry Van Andel who was able to get me a Sverdrup Post-Doctoral Fellowship at Scripps and who had financed my trip to the Gulf of California. Also, I was hoping to get a job offer from Yale while at Scripps. I preferred Yale to Chicago. However, an offer from Yale never came and I was asked again to join the Chicago faculty. This time I accepted.

Chicago: Carbonate Pore Waters and My First Diagenetic Model

I spent two years (1963-1965) at the University of Chicago where I found stimulating colleagues. I enjoyed my contacts with Julian Goldsmith and with Joseph V. (Joe) Smith. Joe introduced me to an early version of the electron microprobe, which I used to study dolomite formation in samples from mid-Pacific atolls (Berner, 1965). I also did experiments on the electrolyte thermodynamics of seawater, which was a stretch at a place in the middle of the country. I had to buy large jugs of seawater shipped to me from the Woods Hole Oceanographic Institution. The department did help with laboratory equipment by having constructed, at my direction, a squeezer. This was a metal piston and cylinder device, invented by Ray Siever, for forcing the interstital waters out of mud samples. It was operated by the pressure from compressed air tanks.

Unfortunately, the living situation near the University of Chicago was unpleasant. We had brought from California our most precious belongings and stayed for about a week in the home of a professor who was on leave. A few days later the door of his apartment was broken down and the place robbed. Fortunately, we had already found a permanent home before the break-in and had moved out with all our belongings. After talking with a frightened neighbor we found out that the break-in burglar

entered even while the owners were present. The owner of the apartment that we borrowed upon our arrival was later attacked and beaten even in his own front yard. Crime was that common! We moved to a low crime area, but for financial reasons, it turned out to be over 20 miles from campus in Park Forest, Illinois. I traveled to work by train that sometimes took over an hour. This made it difficult to continue lab studies and train travel itself wasn't even safe. One time while heading home someone threw a rock through the train window just missing me and striking a woman who fell to the floor bleeding. I had to change trains just after this and never knew what happened to her. Crime was so high in Chicago that I could not find out in the Chicago newspapers whether the woman had died or not.

With my experience with Ray Siever in squeezing water out of sediments for chemical analysis, I realized that carbonate sediment pore waters had not yet been studied. During the summer of 1964, I tried to rectify this situation by conducting fieldwork on shallow water sediments of Bermuda and in Florida Bay (the body of water between the Florida mainland and the Florida Keys). In Florida, my Chicago field assistant and I, using my new squeezer, collected interstitial waters and then analyzed their chemistry on site. The results were eventually published (Berner, 1966). While stationed on Key Largo we tracked a hurricane on our charts that appeared to be heading right towards us. The keys were evacuated and everyone went up to Miami for safety. A local bartender at the Caribbean Club, a rather shabby building that had replaced the hotel where the famous movie "Key Largo" with Humphrey Bogart was made, tried to scare us about the large losses of life from previous hurricanes in the Keys. However, we stayed on Key Largo because we did not want to have to interrupt our makeshift lab with the squeezing device and air tanks that we had lugged down from Miami. We had the last laugh. At the last moment the hurricane changed course and headed right into Miami. The clear weather afterwards was ideal and we had virtually all the Keys to ourselves.

Overall, my scientific impression of the Department of the Geophysical Sciences, as compared to my living situation in Chicago, was quite positive. I especially appreciated the advice of geophysicist John Jamieson who encouraged me to publish a paper I had written on a model of dissolved sulfate in the interstitial waters of sediments. I felt that the interstitial water studies I had done needed some theoretical explanation but I was hesitant, as a field geologist, to plunge into the subject of deriving differential equations. However, remembering the example of Alfred Redfield, I went blindly ahead and published a paper (Berner, 1964). (Years later I wrote a whole book on this subject.)

Arrival at Yale

Before the rock throwing train incident in Chicago I had been offered an (non-tenured) associate professor position by the Department of Geology and Geophysics at Yale University. This is the place I preferred in the first place. Chicago tried to keep me by doubling my salary and promoting me to tenure after being there only 1.5 years. Yale couldn't match that but I had had enough of crime and gladly accepted the Yale offer. Upon arriving at Yale during the summer of 1965, now with wife and one year old son John, I found out that the delay in Yale offering me a position was enmeshed in academic politics. If I had been offered the position while I was at Scripps I would have happily accepted and skipped my two years at Chicago. However, there was disagreement at Yale as to whether I should be offered a job. Some faculty members wanted a stratigrapher or sedimentologist, whereas others wanted a geochemist. The latter group led by Karl Turekian and Syd Clark held out and eventually won the argument, thereby allowing Yale to make the offer. I didn't feel that I was qualified as a geochemist, because of my classical geology background, but if Yale wanted to call

me that and offer me a position, that was OK with me. This was my last academic move and I have been happily at Yale as a geochemist ever since.

I was assigned a room at Yale to be used as a laboratory, but it was filled with storage cabinets containing rocks. I was given funds by Yale to remove the rock cabinets, install electrical outlets, a large floor centrifuge, and buy a spectrophotometer, pH meter, electrodes and miscellaneous chemical supplies. I brought with me the mud squeezer made at Chicago that had proven to be so workable during my trips to Bermuda and the Florida Keys. The cost of all this was a few thousand dollars. Compare this with the hundreds of thousands to millions of dollars spent nowadays on setting up geochemical labs for mass spectrometer isotopic analysis. I was cheap! During my first few days in my new lab I had a strange experience. I found a young man operating my centrifuge and I asked him what he was doing. He could not answer and I found out that he was not a Yale student or even associated with Yale. His reply to me was simply "I like machines." Apparently some interloper had wandered into the Kline Geology Building and decided to play with laboratory equipment. I escorted him to the front door but had pangs of regret when I saw him heading for the nuclear physics accelerator building. More machines?

Iron Oxides and Electrodes

For the first four years at Yale I had no geology graduate students working under my supervision, but I did get a very bright student from the Biology Department. This was Roger Doyle, who was a physiology student interested in working with me on electrode chemistry. He showed, by a long series of current-potential measurements, that the platinum electrode in solutions of ferrous iron gave a potential expected for the couple Fe^{+2}/Fe^{+3}. This could help explain the meaning of Eh in iron-rich natural waters.

I later tried to make electrodes out of hematite and goethite to measure the Fe^{+2}/Fe^{+3} couple with the idea that the potential difference between the two minerals would be a direct measure of their relative thermodynamic stability. Since the reaction of hematite plus water going to goethite involves only the activity of water,

$$Fe_2O_3 \text{ (hematite)} + H_2O \rightarrow 2HFeO_2 \text{ (goethite)}$$

I could immerse both electrodes in solutions with varying salt content and find the equilibrium water activity where the potential difference was zero. However, I could not get goethite to conduct electricity (hematite worked fine) and had to give up what would have been a very rewarding experiment. I salvaged the experiment by measuring the differential solubility of the two minerals in hydrochloric acid solution. This led to the conclusion that finely crystalline yellow goethite (eg limonite) has no stability field relative to finely crystalline red hematite plus water under earth surface conditions. This result applies to both Earth and Mars (Berner, 1969a). This conclusion makes sense. Although goethite can persist metastably, it is a common observation that yellowish sediments convert to reddish sediments over time. Ancient red beds are common. How many ancient primary yellow beds (beds not oxidized by present day weathering) exist?

Pore Water Chemistry, Sedimentary Pyrite Formation, Adipocere, and Principles of Chemical Sedimentology

During the first four years at Yale, I did have a post-doc for one summer, Martha Scott from Texas A and M. She and I and a lab technician squeezed water out of sediments from nearby Long Island Sound and analyzed the pore waters for carbonate alkalinity and all ions that would affect alkalinity. This enabled me to look at interstitial waters of sediments where active bacterial sulfate reduction was occurring. As a result

of organic matter decomposition via sulfate reduction, negative charge was lost and replaced by bicarbonate:

$$2CH_2O + SO_4^{-2} \rightarrow H_2S + 2\ HCO_3^-$$
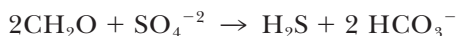
Additional bicarbonate alkalinity was added by ammonia derived from the deamination of proteinaceous organic debris:

$$NH_3 + H_2O \rightarrow NH_4^+ + HCO_3^-$$
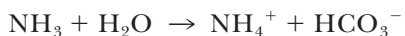
Altogether we were able to show charge balance with increasing depth in the sediments as sulfate was reduced, ammonia was produced, and carbonate alkalinity was produced. Our results were finally published considerably later (Berner and others, 1970).

The chemical origin of pyrite concretions and pyritized fossils had been a subject of considerable interest to me in my Harvard Ph.D. research and to sedimentary petrologists and paleontologists in general. This stimulated me in 1969 to construct an experiment to demonstrate the formation of pyrite concretions (Berner, 1969b). It was done in a one dimensional manner by putting a layer of sonified dead fish at the top of a large battery jar that had been filled with an artificial sediment consisting of quartz sand and kaolinite. The whole thing was then filled with seawater. Two tanks were prepared with one with iron oxide mixed into the kaolinitic sediment. The jars were set aside and color changes were followed with time. As days went on one could see a darkening downward of the sediment with no added iron. What was happening was that bacterial sulfate reduction was occurring in the fish layer with the produced H_2S diffusing downward and causing a slight darkening of the trace amounts of iron in the kaolinite. (The rate or downward darkening followed the square root of time, as expected from diffusion theory.) By contrast, in the tank with added iron, the fish layer got darker and darker and eventually became jet black. What was happening here was that organic molecules were diffusing downward from the fish layer as a result of bacterial decomposition. The organic molecules brought about reduction of the added iron and formation of dissolved Fe^{+2}. The ferrous ion then diffused upward towards the fish layer where it reacted with the H_2S produced there. The H_2S could not escape the fish layer because it became trapped by the upward defusing ferrous iron. I was producing the beginning of an iron sulfide-rich layer that could later become pyrite. The meaning of this experiment is that pyrite concretions should form where there is a local concentration of organic matter in otherwise low organic matter sediment. Hydrogen sulfide is produced within the organic mass and iron diffuses to it. This idea of the origin of pyrite concretions and pyritized fossils has subsequently been generally accepted by the scientific community (see for example, Raiswell, 1997). But the jar experiments showed the way.

Another experiment I did during this four year productive period, and without graduate students but with a lab technician, was to follow the decomposition of fish in seawater. Calcified replacements of the flesh of fossil fish were a mystery until I read about adipocere in an article by a former Yale chemistry professor, Werner Bergmann. Adipocere is the calcified fat of dead organisms and had been found in humans buried in wet ground as well as in fish. The chemical reaction is that the triglyceride fat in organic matter is naturally saponified by ammonia arising from the anoxic decomposition of proteins. The resulting long chain fatty acids then precipitate as calcium and magnesium salts that make up most of the adipocere. The form of the organism is well preserved by the calcified fat, as can be seen by an adipocere man at the Smithsonian Institution museum in Washington, D.C. Fish adipoceres had been found in anoxic sediments of a lake in New York state. Calcium carbonate replacements of ancient fossil fish bodies might be explained by the ultimate breakdown during diagenesis of calcium fatty acid salts to the more thermodynamically stable calcium carbonate.

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SEDIMENTARY PYRITE FORMATION

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ABSTRACT. Experimental study indicates that pyrite can be synthesized at neutral pH in concentrated sulfide solution and in natural sediments by the reaction of precipitated FeS with elemental sulfur at 65°C. Similar reaction at sedimentary temperatures is probable but should require several years for completion. Synthetic pyrite formed by this reaction is framboidal.

The major steps in the process of sedimentary pyrite formation are: bacterial sulfate reduction, reaction of H_2S with iron minerals to form iron monosulfides, and the reaction of iron monosulfides with elemental sulfur to form pyrite. Accordingly the important factors limiting pyrite formation in marine sediments are: the availability of organic matter that can be metabolized by sulfate-reducing bacteria, the diffusion of sulfate into sediments, the total concentration and reactivity of iron minerals, and the production of elemental sulfur.

In sediments from the coastal region of central Connecticut, the main factor limiting pyrite formation is the availability of metabolizable organic matter. Reactive iron and dissolved sulfate are present to excess, and essentially all FeS is transformed by elemental sulfur to pyrite. These sediments are probably typical of many terrigenous marine sediments overlain by aerobic waters. In lower iron sediments, especially carbonates, the principal limiting factor is more likely to be the concentration of reactive iron. In most sediments total iron content and diffusion of sulfate are not limiting.

Fig. 3. First page and abstract of a paper concerning the diagenetic formation of sedimentary pyrite (Berner, 1970). This paper has been cited over 800 times as of 2012.

In my rotting experiments, I followed the chemical changes as the fish decomposed. The first thing was a rise in pH due to the liberation of ammonia from proteins. Then various foul odors resulted from the formation of such things as putrescine, cadaverine, et cetera. My lab technician would take pipette samples of the seawater often for pH measurement and I found out with horror that she was pipetting *by mouth.* I stopped her when I discovered this and found out that she had no sense of smell. Considering the dangerous chemicals that were forming I required her forthwith to use a squeeze bulb with the pipette. After about two months of decomposition I treated the smelly remaining material with hydrogen peroxide to oxidize all remaining labile organic matter. I then took the remaining white solid and subjected it to x-ray diffraction. At very low incident angles I was able to identify calcium dipalmitate and calcium distearate. I had made adiopocere! (About 40 years later I was diagnosed with lymphoma and a diseased spleen—I believe it may have resulted from the use of an x-ray diffraction apparatus that shot x-ray beams laterally at spleen level at low angles necessary for identifying such long molecules. So much for science!)

Some major papers were written during the first four years at Yale that so far have not been discussed. Based on my previous studies of iron sulfides and of pyrite formation in sediments from Long Island Sound, I published a paper entitled Sedimentary Pyrite Formation (Berner, 1970). An example of the first page is shown in figure 3. To date (2012) this has been my second most cited paper, having been

referenced over 800 times. (The most cited paper is a 1984 update on the same subject.) It would be impossible to discuss the many subsequent papers that were affected by these two pyrite formation papers but I cite one recent review (Raiswell and Canfield, 2012). Having been encouraged by my use of differential equations in my diagenetic model for bacterial sulfate reduction, I published a theoretical mathematical paper on the rate of growth of spherical concretions (Berner, 1968). This was based on studies by crystal growth theorists, such as Arne Nielsen and F. C. Frank (the Frank of BCF theory). Many years later I was fortunate to meet Dr. Frank at a meeting of the National Academy of Sciences.

During a sabbatical semester break in 1969, I wrote my first book, "Principles of Chemical Sedimentology" (Berner, 1971), which is now out of print. In this book, I try to show how the basic principles of chemical thermodynamics and kinetics can be applied to the study of sediments and sedimentary rocks. It was not a big seller because most sedimentary petrologists and sedimentologists had little interest in chemistry. One prominent sedimentary petrologist even told me that there was no use for all this complicated chemistry in studying sedimentary rocks. Outcrops and thin sections were enough. This kind of attitude was the main reason why I defiantly decided to stop calling myself a sedimentary petrologist and took on the title of geochemist.

In 1971, after publishing my book and being offered teaching positions at other universities, Yale decided that they should promote me to full Professor. Providing me with tenure occurred earlier in 1968. This means that I had to be at Yale three years before I was found acceptable for tenure, even though I had held tenure at the University of Chicago before coming to Yale. Yale was following a traditional format; Chicago was hell bent for leather. The passage of three years from tenure to full professor was a bit faster than I had anticipated, but outside offers, a common method of prompting academic officials to act, helped my case. After 1971, I found that the outside offer approach was useful in getting appreciable salary raises, but never did Yale match what I was offered elsewhere.

John Morse and the Kinetics of Carbonate Dissolution

In 1969, while I was on my first sabbatical leave (mainly at home writing my first book) a graduate student was admitted to our Geology and Geophysics Department with marginal grades from the University of Minnesota. However, the marginal grades were in difficult subjects such as Quantum Chemistry. Upon my return to Yale, at the beginning of the fall, 1969 semester, a young man, with shoulder length hair and a vacant expression, came into my office and said. "Hey, man I'm your new student." Good Lord, where did he come from; I didn't admit him. My first response was "Do you love geology?" His response was quite positive, so I figured I would be stuck with him. Boy was I ever wrong! He turned out to be an outstanding student and later as a well known and respected scientist. (Most unfortunately he died prematurely in 2009.) His name was John W. Morse and he was my truly first student. (Roger Doyle got his degree in Biology and I never saw him again.)

John and I worked on the kinetics of the dissolution of calcium carbonate in the deep sea financed by the Chemical Oceanography section of the National Science Foundation. How carbonate dissolves in the deep sea is a subject of great interest as it relates to the CCD or carbonate compensation depth. The CCD is the depth where carbonate sediments disappear, due to dissolution, and are succeeded at greater depth by non-carbonate pelagic muds. We published several papers during the 1970's on the dissolution kinetics of calcium carbonate in seawater (Berner and Wilde, 1972; Morse and Berner, 1972; Morse, 1974; Berner and Morse, 1974). Most of the credit for this work goes to John. He invented an ingenious device (Morse, 1974) that allowed us to record in the lab the rate of dissolution of different forms of calcium carbonate in seawater held at a constant degree of undersaturation with the carbonate. Our work

was directly applicable to the observations of carbonate dissolution in the deep sea, both at the carbonate lysocline (the depth where the dissolution rate of foram shells is found to accelerate; Berger, 1970) and the carbonate compensation depth or CCD. Our results showed that there is a critical degree of undersaturation necessary for calcite dissolution, and that simple undersatuation is not sufficient to bring about total calcite removal. In this way, we showed that dissolution should occur well above the carbonate compensation depth and that the CCD represents only the depth where dissolution rate is faster then the supply rate of sedimenting calcium carbonate. The CCD is not simply the equilibrium boundary where seawater goes from supersaturation to undersaturation, as was commonly believed at that time. This conclusion was in agreement with the findings of field studies where minerals and foram tests were suspended at great depths in seawater, by Wolf Berger and Mel Peterson both of Scripps (Peterson,1966; Berger, 1967), and left for several months to undergo dissolution and weight loss. Berger's idea of the chemical lysocline agreed with our laboratory measurements of the critical degree of undersaturation when combined with chemical measurements of seawater chemistry at that depth (Berner and Wilde, 1972). Results from Morse and Berner (1972) are shown in figure 4.

John and I also found that trace levels of dissolved phosphate in seawater strongly affected the critical degree of undersaturation with greater phosphate extending the amount of undersaturation necessary to reach the critical point. We explained this in terms of the adsorption of phosphate ions on kink sites, or points of carbonate ion detachment, on the calcite surface. Using a model of Cabrera (the Cabrera of Burton, Cabrera and Frank or BCF theory) we could calculate that phosphate adsorption would lead to the formation of curved monomolecular steps (Berner and Morse, 1974).

After completing his research in a remarkably short time, 3.5 years, John Morse received the Ph.D. degree in early 1973 and promptly took up an assistant professor position at Florida State University. I was sorry to lose him. He went on through his career, publishing many important papers on the physical chemistry of carbonates and sulfides, to become ultimately a chaired professor at Texas A and M University. Unfortunately his untimely death came in 2009 at the age of only 63.

Nitrogen Diagenesis, Carbonate Dissolution, and Biogeochemical Cycling in Forests

My second, third and fourth students, Jeff Rosenfeld, Robin Keir, and Bill Graustein were my only other students through the 1970's. Rosenfeld completed a very nice study of the diagenesis of nitrogen in Long Island Sound sediments that included testing my theoretical diagenetic models for the nitrogen cycle. Robin Keir carried John Morse's experiments forward by inventing his own device for studying carbonate dissolution and applying it to pelagic forams. (John Morse had worked mainly on reagent grade calcite.) Robin also found a sort of critical undersaturation for calcite dissolution but he showed that a better description was in terms of a high order polynomial rather than a discontinuity in describing dissolution rate versus the degree of undersaturation. Bill Graustein was an unusual student. He chose his own thesis topic, biogeochemical cycling of major elements in trees of the Sierra Madre Mountains of New Mexico, and paid all his research costs plus travel and living expenses himself. His research took a long time but it was thorough and he made some major observations as to how elements are cycled by trees via weathering, biorecycling, and dust trapping. He found some fungal hyphae in soils that contained crystals of calcium oxalate as proof of the uptake of calcium ultimately from weathering. A paper on this topic (Graustein and others, 1977) was published by Science magazine where one of Bill's electron photomicrographs was used for a cover picture for their Christmas issue because the tiny crystals resembled shining stars.

SPHERES (mg cm⁻²yr⁻¹)
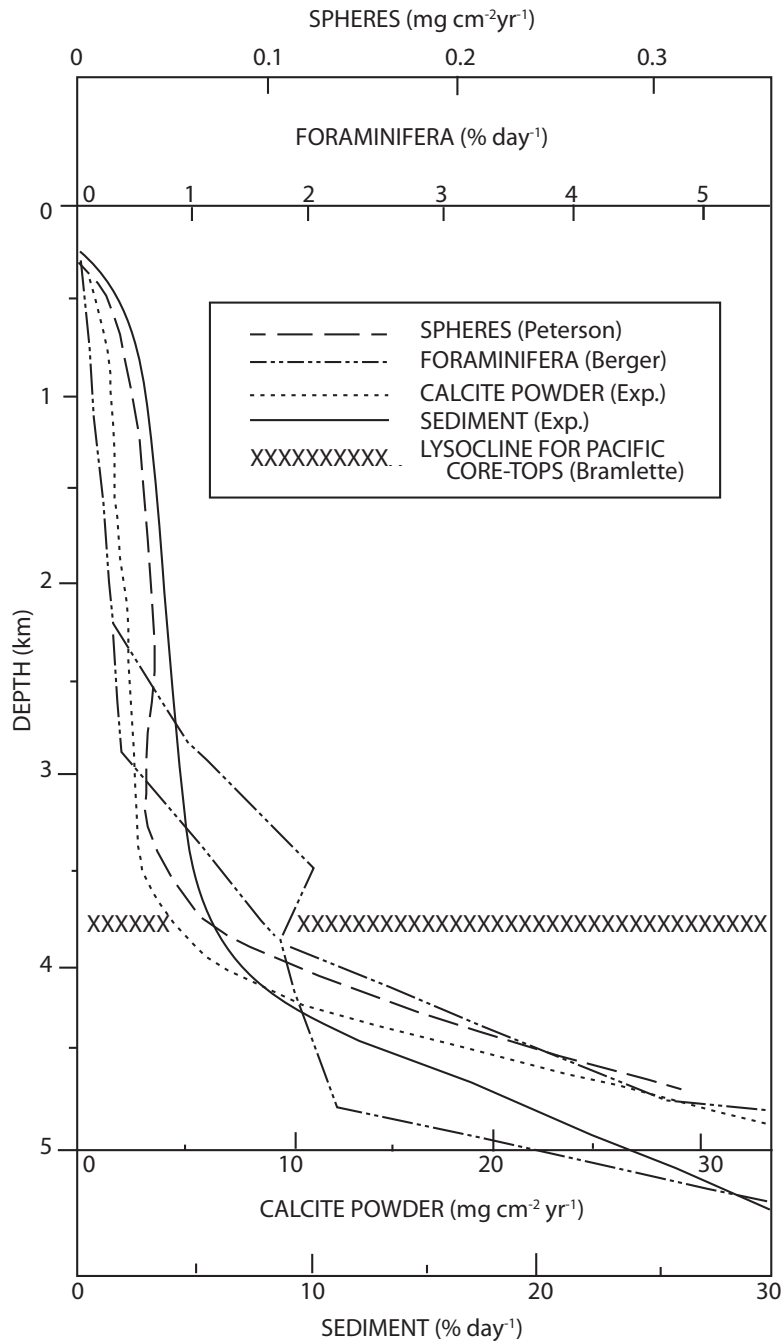
FORAMINIFERA (% day⁻¹)

Fig. 4. Plots of rates of calcite dissolution versus depth for a Pacific Ocean location near Midway Island. Field data are based on suspension of samples of foraminifera (Berger, 1967) and calcite spheres (Peterson, 1966) at fixed depth for a matter of months and measuring weight loss upon retrieval. Data for calcite powder and calcareous sediment are based on dissolution experiments conducted in the laboratory combined with water chemical data for the Midway site (Berner and Wilde, 1972). The depth of the lysocline in this area is based on calculations using the calcite abundance data of Bramlette (1961) (after Morse and Berner, 1972).

Florida Bay and the Fish Scare

With just four students over a decade and too many ideas of things that could be done, I was able to hire several post-Docs during the 1970's. The first one was Amitai Katz from Israel. Amitai did laboratory experiments on the transformation of aragonite to calcite and accompanied me in February of 1973 on a second trip to the Florida Keys to collect sediments for the analysis of phosphate in the interstitial waters of Florida Bay sediments. This second Keys visit didn't involve a hurricane but there was still plenty of excitement. Amitai and I occasionally went for swims in deep water areas where sharks had been seen. One guy would stand watch on the boat while the other one swam. The whole thing sort of unnerved Amitai. One evening I was reading a cheap paperback book I had found on shark attacks and mentioned some that had occurred near where we had been working. Amitai didn't want to hear about my shark book and, to calm himself, reached for the Gideon bible found in virtually all motels at that time. He opened the bible to a random chapter and up came Jonah in the belly of a whale. That was too much for him. He couldn't relax even reading the bible! The next day proved actually dangerous. We went swimming in an enclosed portion of the ocean intended to have shallow enough water for kids to swim in safely and be protected from sharks. This was not a place intended for tourists and there were no people there except us. The problem was that there was an intake pipe to let water into the enclosure and it could be used by reasonably small fish swimming into the enclosure which were then not able to find their way back out. As I swam toward deeper water within the enclosure with a pair of underwater goggles on (thank goodness), I saw about 50 long, narrow, silvery fish suddenly turn and all look at me. Help! They were barracudas. They apparently had become entrapped within the enclosure, couldn't find their way out, and were undoubtedly very hungry. I swam and ran shoreward so fast that I almost knocked over Amitai. After warning him not to go into the water I explained why. He then said, "No, please no killer fish again!"

Amitai and I were able to do scientifically what seems impossible. We took out a boat and collected a core early in the morning. After returning the boat to the boat rental agency we jumped in our rental car and drove to the Miami airport and soon boarded a plane carrying our core with us (these were the good old days of no security checks). We then flew to New York and returned to New Haven still carrying the core. Once in New Haven we went immediately to the lab and began extracting depth samples of interstitial water with my sediment squeezer. The expressed waters were then immediately filtered and analyzed for dissolved phosphate. The whole procedure, from taking the core from Florida Bay sediments to completing the analysis of dissolved phosphate, took about 18 hours. Speed was necessary to minimize changes in the chemistry of the sediment between collection and analysis. I wouldn't suggest this procedure to anyone else. A much better approach was used in my earlier 1964 visit to Florida Bay; we did all our squeezing and water chemical analyses on site in a Key Largo motel room converted into a lab. At any rate Amitai and I found that interstitial dissolved phosphate is lower in organic-rich carbonate sediments than it is in non-carbonate sediments with equivalent organic matter contents. The reason for this is the adsorption of phosphate onto the surfaces of the fine carbonate grains.

The Surface Chemistry of Feldspar Weathering

Around 1972 I learned that a new method, x-ray photoelectron spectroscopy or XPS, had been recently developed by the Swedish scientist Kai Siegbahn (for which he eventually was awarded the Nobel Prize.) This method can be used to determine the chemical composition of the outermost surface of a solid. I realized that it could be applied to examining the surface chemistry of feldspars that had undergone chemical weathering. There was a theory at that time (Wollast, 1967) that aluminum and/or

silicon-rich surface layers formed on feldspars during weathering and in laboratory experiments and these layers protected the feldspars from further dissolution by forming a protective barrier to molecular diffusion. XPS could be used to test this theory. I was fortunate that XPS equipment was housed in Yale's Chemistry Department, and I had my post-Doc Radomir Petrovic make XPS measurements of the surfaces of (1) samples of dry fresh potassium feldspar and (2) additional samples of the same feldspar after immersion in water at pH 4. This was done to repeat a set of experiments by Roland Wollast that predicted that these surface layers, after immersion in water at pH 4 for many days, formed and grew to become tens of nanometers in thickness. So Radomir repeated the Belgian experiment and analyzed the feldspar surfaces via XPS. However, he found no change in surface chemical composition after immersion the same number of days in pH 4 water. The fundamental question remained as to how thick a surface layer the XPS method sampled. Using sophisticated solid state physics arguments, such as phonon theory, Radomir calculated that the XPS method would see only the outermost few nanometers. It turned out later that he was correct when measurements by other scientists at different angles of known surface compositions were done to calibrate this new method. The overall result, therefore, was that no new aluminum and/or silicon rich layer was formed on the feldspar surface during reaction with water; therefore, the idea of an aluminous and/or siliceous protective surface layer on weathered feldspars was likely incorrect. These results (Petrovic and others, 1976) were not published until 1976, long after the research was done, because of the slowness of writing up results by Radomir who had left Yale to take up an assistant professorship at Northwestern University. After Radomir left, I had Marty Goldhaber (see below) repeat some of Radomir's XPS measurements and he got identical results; so we made Marty a co-author. It is probable that in 1972 we were some of the very few first persons to apply XPS to the study of geological materials.

A few years later post-Doc Rich Holdren continued our initial studies of the weathering of feldspar. He repeated the XPS work of Petrovic and Goldhaber finding the same results as we had found earlier, but now for both K and Na feldspars. We also looked at feldpars from soils isolated via ultrasonic cleaning to remove obstructing clay on the feldspar grains. More notably, we added a lot of observational data using the electron microscope. With the electron microscope we were able to discern that the etching of feldspars in soils undergoing weathering, and attack by hydrofluoric acid in the laboratory, takes place by the formation of etch pits, at dislocation outcrops on the feldspar surface (see fig. 5). The same etching pattern was found from a variety of soils, including a soil from a coal mining area where etching of the feldspar must have been done partly by sulfuric acid from pyrite weathering. Regardless of acid type, organic acids in most soils, sulfuric acid in coal mining soils, or hydrofluoric acid in the lab, the same etching pattern resulted, with etch pits aligned with the feldspar crystal structure. From these observations we concluded that feldspar weathering takes place by selective attack directly on the feldspar surface at points of excess energy such as dislocations (Holdren and Berner, 1979; Berner and Holdren, 1979). This shows that uniform weathering of the feldspar surface by diffusion through a protective surface layer enriched in aluminum and/or silicon is not a proper model for weathering. This reinforced the conclusions of our previous XPS work on feldspars.

Anoxic Diagenesis in Long Island Sound

Having studied pyrite formation in Long Island Sound sediments and with a continuing interest in interstital water chemistry I wanted to do more work on the early diagenesis of anoxic and sulfide-rich sediments (by early I mean the top meter or so of the sediments). Because of this, in the mid 1970's I hired two post-Docs who produced excellent research. They were Chris Martens from Florida State and Marty Goldhaber from UCLA. Chris devised a simple gas chromatographic method to measure dissolved
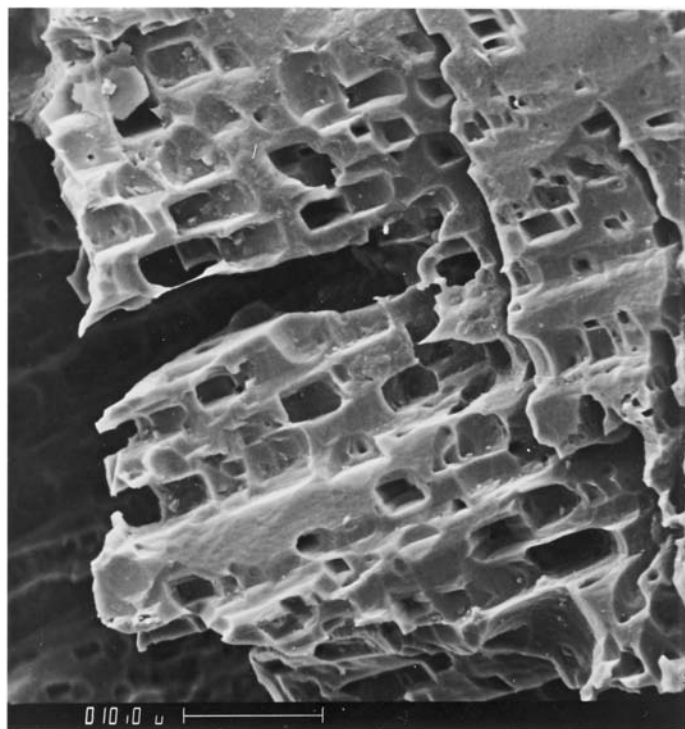
Fig. 5. Electron microscope photo of prismatic etch pits (shown in square cross section) developed on dislocations in feldspar from a soil in Piedmont, North Carolina. Scale is in micrometers (from Berner and Holdren, 1979).

methane in interstitial waters. He found (Martens and Berner, 1977) that methane didn't build up in sediments until virtually all sulfate is removed via bacterial sulfate reduction. The explanation offered by Chris was two-old. First, the bacteria that produce methane cannot compete with sulfate reducers for available hydrogen. This explains why methane production is more common in fresh water sediments than in marine sediments. Fresh water is much lower in sulfate (micromolar levels), than seawater (20-30 millimolar). The second reason is that our diagenetic modeling showed that methane must have reacted with sulfate. This idea, first rejected by experimental microbiologists who did not observe CH_4 consumption during bacterial sulfate reduction, showed that there is insufficient time in the lab to observe this reaction. Our measurements and modeling showed that it takes many years (Martens and Berner, 1974). Since that time there have been a number of studies that have verified this reaction and examined in detail how it occurs.

Chris Martens also made measurements of dissolved N_2 in interstitial waters of Long Island Sound sediments and showed in some locations that depleted dissolved N_2 was matched by depleted dissolved argon. Since argon is chemically inert the finding of depleted N_2 and Ar showed that stripping of these dissolved gases must have occurred by bubbles of methane rising upward through the sediments. The pore water methane analysis showed that saturation with respect to gaseous methane was achieved at depth in some sediments.

Marty Goldhaber came from the UCLA lab of Ian Kaplan. Marty was an expert on bacterial sulfate reduction and the effect of this process on sulfur isotope fractionation.

Marty became interested, with some prodding from me, in looking at the interstitial waters of Long Island Sound sediments in terms of sulfate reduction. I had already worked with Martha Scott on sulfate reduction in Long Island Sound sediments, with emphasis on alkalinity formation, but there was a lot more that needed to be done. I suggested to Marty a simple method for measuring the rate of sulfate reduction by taking a large sample (many kilograms) of black organic rich mud from a tidal flat and mixing it thoroughly in a new garbage can. (I have a picture of Marty hand mixing the foul smelling mud while holding his breath but he doesn't like me showing it.) Samples of the homogenized mud were then packed into a series of jars for future analysis for dissolved sulfate. The filled and sealed jars were allowed to sit for days and occasionally one was opened, the date recorded and the sample analyzed for dissolved sulfate. This is referred to as the simple jar method and we found a linear decrease of sulfate with time due to its bacterial reduction to hydrogen sulfide.

Marty and Chris joined with other students, Jeff Rosenfeld mentioned earlier, and two students of Karl Turekian, Kirk Cochran and Bob Aller, to do a massive study of sulfur chemistry, with additional measurements of dissolved ammonium, phosphate and bicarbonate and solid Cu and Zn, in the sediments at a single core site in Long Island Sound. Sulfate reduction was measured by jar experiments of samples of sediment taken from different depths and sulfate diffusion coefficients were measured by placing high sulfate and low sulfate mud cores in juxtaposition. The interstitial water and sediment sulfur data (for example pyrite) were interpreted in terms of diagenetic models. Our combined results led to a data-filled paper (Goldhaber and others, 1977) for which we adopted the group name of FOAM, or Friends of Anoxic Mud. This was intended as a sort of spoof of other acronym projects at that time that were being financed at a much higher financial scale; our FOAM effort required no additional special funding for the project. A copy of the FOAM abstract is shown in figure 6.

In the studies of diagenesis by previous students and the FOAM group, little attention was paid to phosphorus. This needed a remedy and the appropriate researcher was post-Doc Mike Krom. He measured (Krom and Berner, 1980a) the adsorption of P at various depths in the deeper anoxic portions of the sediment and found that adsorption there was far weaker than in the upper few oxic centimeters where strong adsorption occurs on detrital ferric oxides. (The latter agreed with my findings from the East Pacific Rise discussed below.) When the ferric oxide-rich surface sediments are buried during sedimentation, the adsorbed phosphorus is released as the iron is reduced. Because of bioturbation (stirring of the uppermost sediment by burrowing organisms) the released P is lost to the overlying seawater. This is a process for returning an essential nutrient, here phosphorus, for marine photosynthesis and is of global significance. Mike also measured the interstitial water diffusion coefficients of phosphate, ammonium ion, and sulfate (Krom and Berner, 1980b) by juxtaposing a deep core rich in the three elements with a shallow core low in the same ones and measuring concentrations of the three elements at various depths as diffusion occurred. The diffusion coefficients were then calculated from the data fitted to the appropriate equations for one dimensional diffusion between two flat surfaces.

Adsorption of P on Ferric Oxides

From laboratory experiments with John Morse I thought that phosphorus would be found adsorbed on calcium carbonate in deep sea sediments. To prove this I analyzed a series of samples, obtained from the Lamont Doherty Geological Observatory (LDGO), of highly varying carbonate content taken across the East Pacific Rise passing from the carbonate-rich crest downward across the carbonate compensation depth. I then analyzed each sample for phosphorus and carbonate content. Much to my amazement I found that calcium carbonate and phosphorus *anti*-correlated. How

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SULFATE REDUCTION, DIFFUSION, AND BIOTURBATION IN LONG ISLAND SOUND SEDIMENTS: REPORT OF THE FOAM GROUP

FOAM (Friends of Anoxic Mud)

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ABSTRACT. Sediment gravity and box cores were taken over the course of a 10-month period at a single station in Long Island Sound. A range of pore water and solid phase constituents were measured. Summer pore water profiles exhibit an upper zone from 1 to 8 cm in which concentrations of constituents, such as sulfate and alkalinity, do not change markedly with depth. The actual concentration levels, however, are significantly altered from bottom water values with the transition between bottom water and pore water occurring within the top 1 to 2 cm. The upper 8 cm zone is underlain by a much thicker one in which pore water profiles show trends indicative of progressive diagenesis involving bacterial sulfate reduction (for example, sulfate decrease). Winter pore water profiles do not show an upper zone of constant pore water concentration.

As an aid to interpreting the pore water data, direct measurements were made of sulfate reduction rates by incubating sediment aliquots under anaerobic conditions and following sulfate depletion with time. These rates fall in the range 2 to 77 mM sulfate/l pore water/yr and show a striking decrease with depth in the sediment column.

It is argued that the depth independent pore water profiles in the upper 8 cm of summer sediment arise from irrigation or particle mixing of sediment by macroinfaunal organisms (that is, bioturbation) rather than by lack of sulfate reduction. This conclusion is based on high measured rates of sulfate reduction in the upper 8 cm. Frequent recovery during coring of the deposit-feeding polychaete worm *Nephtys incisa* and presence of abundant iron-sulfide minerals in the upper 8 cm also support this conclusion. The vertical transport of pore water constituents arising from bioturbation during the summer is at least five times more rapid than by ionic diffusion. Such transport does not swamp out all effects of bacterial metabolism, as the latter process is so rapid in the upper 1 cm as to modify the chemistry of solutions passing through this interval. During winter the bioturbating activity of infauna decreases; hence pore water profiles are diffusion controlled.

Below the zone of bioturbation (0-8 cm), mass transport of sulfate is dominated by ionic diffusion and burial. Rates of sulfate reduction over the depth interval 10 to 80 cm were estimated from the sulfate profiles by mathematical modeling using a diffusion coefficient (4.0×10^{-6} cm^2/sec) measured on cores in the study area and a sedimentation rate (0.3 cm/yr) estimated by three independent techniques. Rates so calculated fall in the range 0 to 2 mM/l/yr and are in good agreement with values measured in the laboratory.

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Fig. 6. First page and abstract of the FOAM paper concerning anoxic diagenesis in Long Island Sound (Goldhaber and others, 1977).

could this be? Then it dawned on me that the non-carbonate portion of the sediment at this locality was rich in iron oxides formed via precipitation from seafloor hydrothermal springs. The correlation was between phosphorus and iron oxides. As mentioned above, Mike Krom and I had already studied the adsorption of phosphate on Fe oxides in Long Island Sound and this adsorption was a well known phenomenon; so the correlation made good sense. In fact, after this discovery, I did adsorption experiments using iron-rich deep sea sediment and spent 5 months in 1972 on a Guggenheim Fellowship at the EAWAG (Swiss Federal Institute for Water Resources and Water Pollution Research) lab in Switzerland studying phosphate adsorption, especially on iron oxides. My paper on the adsorption of volcanogenic Fe oxides was published (Berner, 1973) and the work has been verified by several later studies.

Further Work on Carbonates in Seawater

Having already studied calcite dissolution I decided to study its precipitation. In 1975, I published a paper on the role of magnesium in the crystal growth of aragonite and calcite in seawater (Berner, 1975). I did crystal growth experiments using the John Morse–designed constant saturation instrument (Morse, 1974) converted for studying precipitation, rather than dissolution. I used two synthetic sea waters, one with all major constituents for 35 parts per thousand salinity, and one with no magnesium but with the same 35 parts per thousand salinity made up with extra Na and Cl to balance the loss of Mg. Samples of pure aragonite or calcite were used to seed each experiment. I found, in the absence of Mg, that calcite crystal growth followed a similar plot of growth rate versus the degree of supersaturation as did aragonite crystal growth. By comparison, in sea water with normal Mg content, calcite crystal growth was inhibited until a fairly high degree of supersaturation was attained whereas inhibition by Mg was not found for aragonite. My interpretation was that Mg in seawater causes the metastable precipitation of calcite enriched in Mg, which is more soluble than pure calcite. Because of greater solubility, apparent supersaturation with respect to pure calcite is needed to start crystal growth of the Mg-enriched precipitating phase. Addition of very small amounts of Mg to otherwise Mg-free seawater did not affect results for calcite or aragonite; therefore, inhibition of growth by traces of a dissolved substance, called kinetic poisoning, could be eliminated for Mg. Further work (Davis and others, 2000), using ultrahigh resolution microscopy of calcite surfaces, has verified this Mg-enriched super solubility idea.

Kinetic poisoning of aragonite crystal growth by other substances was found in a later study (Berner and others, 1978). We found that, using the Morse constant saturation apparatus, certain organic compounds, specifically dissolved organic substances with carboxylated benzene groups, and phosphate, when added to solution in micromolar quantities, quickly stopped precipitation of aragonite while it was underway. We also found that the interstitial waters of Long Island Sound organic-rich sediments were supersaturated with respect to aragonite and calcite and resisted precipitation even when carbonates were mixed with the sediment. These sediments contained high concentrations of dissolved organic matter and phosphate that helped to explain their resistance to carbonate precipitation.

Furthering my interests in carbonate-seawater interaction, my wife Betty, myself and Robin Keir traveled to Bermuda in 1975 to study the sediments of the slopes of the Bermuda Pedestal. We found, via bottom grab sampling from a ship of the Bermuda Biological Station, that these sediments contain large concentrations of aragonitic pteropod debris, and we wanted to see if an aragonite compensation depth could be discerned. Aragonite is more soluble than calcite and any aragonite compensation depth would be expected to be appreciably shallower than that for calcite. We did find a loss of pteropod aragonite with depth with the aragonite compensation depth being

about 2000 meters (Berner and others, 1976). This is much shallower than 5000 meters found for the calcite compensation depth in this part of the Atlantic ocean.

<p align="center">PART II. THE AMAZING DECADE
1980–1990</p>

Early Diagenesis Book

In 1980, my second book was published entitled "Early Diagenesis; A Theoretical Approach." In it I present differential equations describing the changes in modern sediments with depth below the sediment-water interface. Due to the influence of Ray Siever, emphasis is on interstitial waters. Terms in the equations describe diffusion, both molecular and due to bioturbation; advection due to sediment burial and the movement of water via compaction; and "chemical" reaction including radioactive decay. A steady state, non-time dependent approach, is used in most of the book. Fundamental diffusion-advection-reaction equations are derived in the first part of the book and applications to actual sediment data, collected by us and by other workers, comprises the remainder. The book was a culmination of previous papers I had written on the subject of diagenetic modeling and of work done at Yale on Long Island Sound sediments. It was amazingly popular. I didn't think that people studying sediments were interested in all this mathematics, but I was wrong. The Institute for Scientific Information (ISI) cited the book as a Citation Classic, with more than a thousand citations within a decade of publication. Some examples of the influence of this book on further research on early diagenesis are the books by Boudreau (1997) and Burdige (2006).

The G Model

Since my 1964 paper on the subject I had had all sorts of ideas about how fast bacterial sulfate reduction occurred in sediments and what factors controlled its rate. The FOAM group measured rates of sulfate reduction but a proper theory was needed. A new graduate student named Joe Westrich arrived around 1980 well prepared in organic chemistry to help solve the problem. He devised ingenious laboratory experiments to check my ideas. He did this by using the radioactive isotope ^{35}S to measure sulfate reduction rate. This method allowed determination of rates that were far too slow to be detected by the "jar experiments" used in the FOAM study. He would inject ^{35}S labeled sulfate into samples of Long Island Sound sediment and then measure the production of ^{35}S labeled sulfide.

I had suggested that the nature of the organic matter used by sulfate reducing bacteria exerted a strong influence on the rate of sulfate reduction. This led to the so-called G Model. Organic matter buried in sediments was divided into different groups with reactivity of each group towards sulfate reduction represented by the rate constant k_i and the amount of each group represented by G_i. The rate of decomposition was assumed to follow first order kinetics. In this manner, the decay of total organic carbon G_T, via the sulfate reduction reaction:

$$2CH_2O + SO_4^{-2} \rightarrow H_2S + 2\ HCO_3^{-}$$
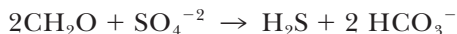
is represented by the expressions:

$$G_T = \sum G_i$$
$$dG_T/dt = -\sum k_i G_i$$

Joe tested these equations by taking bulk plankton collected from Long Island Sound seawater and subjecting it to aerobic decomposition for various periods of time. He then took dried samples of the fresh plankton, and that resulting from 72 days of oxic

rotting, and mixed each plankton sample with deep anoxic-sulfide-rich sediment where previous in situ measurements had shown low sulfate reduction rates. The added planktonic material accelerated the rate of organic matter decomposition, as determined via the above chemical reaction using ^{35}S for the rate of sulfate reduction. The rates for each sample were found to be directly proportional to the amount of added plankton (linear response), thereby verifying a fundamental assumption of the G model. The 72 day aged material produced a lesser acceleration of sulfate reduction than the fresh plankton. This agrees with the idea that organic matter that has undergone appreciable decomposition in the overlying oxic seawater will be less reactive (lower k_i value) for sulfate reduction than fresh material. Joe's experiments proved that the type of organic matter used by the sulfate reducing bacteria has a major effect on the rate of sulfate reduction. By doing additional experiments with Long Island Sound sediments, he showed that the organic matter used by the bacteria could be divided into at least three reactivity groups each with a different value for k_i. Further work by Joe, but published long after he had left Yale, shows that the effect of changing temperature on the rate of bacterial sulfate reduction in sediments is also a function of the nature of the organic matter used by the bacteria.

The G model has withstood testing with time as evidenced by our paper (Westrich and Berner, 1984) on this subject being cited over 500 times (as of 2012). However, my hopes that organic geochemists could deduce the nature of the reactivity groups have gone unanswered to my satisfaction. There is still a need to look at the types of organic compounds that are most reactive and those that are the least reactive during their oxidation by bacteria during sulfate reduction. I mean compounds existing in sediments, not compounds added to experiments in the laboratory that may not represent the real sedimentary ecological situation.

Joe Westrich besides being brilliant, was a very hard worker. His working hours often were all night long. I remember times when I would arrive in the morning to go to work and meet Joe going home to bed. Before leaving Yale, Joe was selected appropriately as the first winner of the Orville Prize for the most outstanding graduate student. After receiving the Ph.D. degree, his achievements were also recognized outside Yale by his being sought for faculty positions by three of the most prestigious U.S Universities. However, he turned them all down to go to work for the Shell Development Corporation. Joe came from a poor background and the idea of making money in industry was too tempting for him.

Editor of the American Journal of Science

Professor Phil Orville, an outstanding experimental petrologist, died prematurely in 1980, a big blow to our department. In his honor, a prize for the most outstanding graduate student was established and the first one was awarded to Joe Westrich, as stated above. Phil was also editor of the American Journal of Science. His death left a big hole in this highly regarded and very long lived (founded in 1818) journal. After much pleading I consented to take his place. Although editing is not my forte (I would much rather write a paper than read a paper) I felt that following Phil was my duty. I lasted for awhile, but could no longer spend so much time away from research; so I resigned in 1990 and took up the lesser position as associate editor. In the meantime, I was successful in persuading Professor Danny Rye to join the editorial staff and when I resigned, he basically replaced me. He still (2012) is an AJS editor and an excellent one.

Pyritized Shells

Having already done experiments on the diagenetic formation of pyrite shells, I wondered if an example of pyritization in modern sediments could be found. I read that rare pyritized clam shells had been discovered off the coast of Georgia, USA and

decided to visit this locality, along with my new student, Chris Reaves. Most pyritized shells are found only as fossils and the clam shells with pyrite provide modern analogues of how pyritization may occur. The best samples were found in the tidal flats of St. Catherine's Island off the coast of Georgia. The island is private and unoccupied but we were allowed to go there to do research. Facilities were crude and we stayed in ancient abandoned slave cabins. The most interesting thing, besides the pyritized shells, was the large collection of wild animals on the island. The island served as an overlow for the Bronx Zoo. We could see all sorts of wild animals, like monkeys, giraffes, gazelles, rhinos, et cetera, fenced in away from us fortunately. I experienced the weirdest sensation upon waking the first night. I heard what could best be described as jungle noises and with all this living in a crude and hot cabin. For a minute I wondered whether I had traveled far away to Africa.

Silicate Weathering in the Field

My interest in weathering from examining mineral surfaces and the mechanisms of weathering did not satisfy my desire to know how fast weathering occurs in the field. A new student, Mike Velbel, was the appropriate candidate for doing this. I took him with me on an expedition to collect pyroxenes and amphiboles undergoing weathering. My idea was to continue the study of surface chemistry, that we had applied to feldpars, and extend it to other minerals. I obtained maps of all major basic and ultrabasic rock bodies that were south of portions of the eastern U.S. that had been affected by Pleistocene glaciation. We did this to allow us to sample soils developed on pre-Pleistocene bedrock. This took us to the Coffman Hill diabase in Pennsylvania and areas around Franklin, in the westernmost portion of North Carolina. We obtained a large number of soils containing basic minerals, such as pyroxenes, that I wanted to study in terms of electron microscopy and XPS. In North Carolina, we visited the Coweeta Long Term Environmental Research area where considerable ecological work was being done. It looked like a good place to combine a study of weathering with the chemical analyses of stream waters that already had been done. This became Mike's thesis topic, and he later returned there for an extended stay.

Mike Velbel's thesis research consisted of an optical microscope, electron microprobe and x-ray diffraction study of soils from a watershed at the Coweeta location. From mass balance expressions for the major elements, Ca, Mg, K, and Na and a combination of stream and rainfall chemistry (done by others) with determinations of the composition of both primary minerals and weathering products, and the composition of biomass, Mike was able to determine the weathering rates of the principal minerals in the rocks of this area. He found that in parts of Coweeta, where there had been a loss of vegetation, there was an excess of the biological elements, Ca, Mg, and K released in the streams. This illustrates the importance of trees and other plants in storing major elements in their biomass. After leaving Yale, Mike joined the faculty of Michigan State University where he eventually became chairman of the Department of Geological Sciences.

The Mathematics of Bioturbation

Another student that arrived at the same time as Mike Velbel was Bernie Bourdeau. Bernie was a very different kind of scientist. He wanted to do an entirely theoretical thesis. Normally I expected my graduate students to do field work and/or laboratory experiments, but in the case of Bernie, and only this one time, I relented. Bernie did a theoretical study of sediment bioturbation through the use of complex mathematics. Bioturbation is the mixing of sediment and its contained pore water by macro-organisms living in and on the sediment. He was certainly bright, but when he turned in his thesis, I had trouble understanding it. I could follow the physical reasoning but not the complicated math. Bernie had been in contact with a German

mathematician about the use of integral equations and other things that I did not understand. I called in Professor George Veronis of our department to look at Bernie's math. (George was also a professor of applied mathematics.) Much to my surprise, George liked the thesis very much and found little wrong with it. In fact, George nominated Bernie for the Orville Prize that Bernie actually won. After obtaining the Ph.D. Bernie took a teaching position at Dalhousie University in his native Canada. Since that time Bernie has excelled in theoretical research and has been honored by his election as a Fellow of the Royal Society of Canada. He has even upstaged me by writing a book on the theory of early diagenesis that has largely supplanted mine (Boudreau, 1997).

The Diagenesis of Iron

Don Canfield came to work with me from the Chemistry Department of Miami University (Ohio). He turned out to be both a very hard working, brilliant and creative graduate student. His thesis was determining the kind of iron minerals that react with H_2S to form pyrite and how fast they react. He developed chemical extraction methods to identify and separate different iron minerals including ferrihydrite (semi-amorphous hydrous ferric oxide soluble in oxalate buffer), goethite, hematite, magnetite and biotite. Ferrihydrite reacts to form iron sulfides (and eventually pyrite) in minutes to hours. Fine grained goethite and hematite take longer but can be seen in sediments to become black in time scales of a year or less. We separated magnetite from Long Island Sound sediments and found pyrite beginning to form on the surface of the magnetite. Based on the rate of burial of the sediments we estimated that the time for the conversion of magnetite to pyrite ranges from 50 to about 1000 years (Canfield and Berner, 1987). For biotite we could find only a very few tiny adhering pyrite crystals on the surfaces of biotite grains at the bottom of cores with ages greater than 1000 years. If biotite is representative of ferruginous silicates in general, this means that the total conversion of Fe silicates to pyrite might never occur because of the eventual loss of hydrogen sulfide with depth.

Since leaving Yale with a Ph.D. in the late 1980's, Don Canfield has had an outstanding research record. He has become a leading expert on the biogeochemistry and paleo-oceanography of the sulfur cycle, especially during the Precambrian era. He has received many awards including the Urey and Vernadsky medals of the European Geochemical Society and was elected to the U.S. National Academy of Sciences in 2007.

The Geochemistry of Phosphorus

In thinking about the carbon cycle, I realized that a key element in it was phosphorus. It has been emphasized to be the limiting nutrient for photosynthesis in the ocean over geologic time (Holland, 1978). I had already touched on the subject by studying phosphate diagenesis in Long Island Sound with Mike Krom. In the late 1980's I had four graduate students undertake further research on sedimentary and marine phosphorus.

I was bothered by my overemphasis on dissolved phosphate in the interstitial water of sediments without proper consideration of the sediment solids. That is where my new student Kathleen Ruttenberg came in. Kathleen did an Herculean task of developing chemical extraction methods for discerning the different forms of phosphorus in sediments. Her extraction method, which she named SEDEX, has been adopted by many subsequent workers. She tested various extractant solutions on standards for the different forms of phosphorus: detrital apatite, authigenic carbonate fluorapatite (calcium phosphate that forms during early diagenesis), weakly adsorbed phosphate and phosphate strongly adsorbed on ferric oxides. After laborious trial and error she was able to discover the proper extraction solutions that could separate these different

forms of phosphorus. By applying her technique to sediments of Long Island Sound, the Mississippi Delta region, the deep sea and elsewhere, she showed that authigenic apatite occurs at low concentrations in most modern sediments. This means that previous estimates of the global rates of burial of phosphate in sediments were too low because most supposedly non-phosphatic sediments were neglected. It also means that the residence time of P in seawater has to be lower than was commonly accepted. Since leaving Yale in the late 1980's, Kathleen has continued her highly original research on phosphorus geochemistry at the Woods Hole Oceanographic Institution and later at the Oceanography Department of the University of Hawaii.

Philippe van Cappellen came from the oceanography department of the University of Brussels with excellent training in chemistry. After the work of Kathleen Ruttenberg I became interested in the crystal growth of apatite in seawater. I persuaded Philippe to construct laboratory equipment to study the crystal growth of fluorapatite from artificial seawater. He redesigned the apparatus originally designed by John Morse to be able to hold saturation state constant for fluorapatite. This was more complex than the Morse version that required only that Ca^{++}, pH and CO_2 be held constant. Philippe had to hold Ca^{++}, pH, CO_2, PO_4^{-3} and F^- constant. This he did and he studied how crystal growth rates varied with the degree of supersaturation and how they also varied with different concentrations of dissolved Mg. At the level of Mg found in normal seawater, he found that the rate of apatite precipitation, at a constant degree of supersaturation, was 15 to 20 times slower than in the absence of Mg. By creating conditions appropriate for the interstitial waters of marine sediments, he found that apatite growth rates would be so slow that only microscopic crystals would form. This is what was observed by Kathleen Ruttenberg in actual sediments.

Philippe also constructed a diagenetic model for the formation of phosphorite in marine sediments. Phosphorite is a type of marine sediment that is highly enriched in fluorapatite. In ancient sediments uplifted onto the continents, phosphorite is a major source of phosphorus for use in fertilizers. Philippe was able to improve my diagenetic modeling to allow for the attainment of a critical degree of supersaturation, in order to precipitate large amounts of fluorapatite. This could occur only in sediments that were sufficiently high in organic matter to provide phosphorus via bacterial decomposition of organic phosphorus and that also were deposited sufficiently slowly so that the phosphorite did not become diluted by ordinary detrital sediment particles. The model was applied to a phosphorite locality off the Pacific coast of Mexico (van Cappellen and Berner, 1988) and it correctly predicted the amount of phosphorite formed there.

After leaving Yale Philippe joined with another former graduate student, Ellery Ingall to construct a mathematical model of how the burial and diagenesis of phosphorus in euxinic (Black Sea-like, H_2S rich) sediments could serve as feedback mechanisms for changes in atmospheric oxygen over geologic time. Ellery and Philippe found that during diagenesis in euxinic sediments there is greater liberation of phosphorus back into seawater than occurs in normal marine sediments. Provision of extra P to the oceans from this process should result in greater organic productivity by plankton, and greater organic matter sedimentation, possibly leading to more euxinic basins (positive feedback) and greater O_2 liberated to the atmosphere and oceans during plankton photosynthesis (negative feedback). The negative feedback is based on the idea that more O_2 in the oceans inhibits the formation of euxinic bottom water. This work (van Cappellen and Ingall, 1996) has been cited by a large number of studies. After leaving Yale as another Orville Prize winner, Philippe worked at a number of institutions in Europe and the U.S. starting as a professor at Georgia Tech. Philippe now holds the prestigious Excellence Research Chair in Ecohydrology at the University of Waterloo in Canada.

At this point I feel that it is appropriate to introduce a little romance into this rather dry scientific discussion. I taught an undergraduate course at Yale on modern environmental problems and one of my students came to me quite upset. She was afraid that she might flunk my course, but I told here that I could help her. Her name was Victoria Knowles. I suggested that she discuss her problems with my teaching assistant who at the time was Philippe van Cappellen. He apparently was most helpful for her as she ended up with an A in the course. She liked the chemical aspect of the course so much that she decided to switch from the Geology and Geophysics Department to major in the Chemistry Department, but with me as her advisor. She liked the help of Philippe so much that they fell in love and ultimately they became married. It was quite amusing that they graduated at the same time, she with a B.S. in chemistry and he with a Ph.D. in geology and geophysics. After that they were married and went together to Georgia Tech.

Ellery Ingall, among other things having to do with phosphorus, studied organic phosphorus in marine sediments. He was able to discriminate the forms of organic phosphorus in terms of phosphate esters, polyphosphates, phosphonates and other phosphorus compounds. Determinations of organic phosphorus linkages were made via solid state NMR analysis under the direction of Kurt Zilm in the Chemistry Department. I was especially interested in the possibility that Ellery might find phosphonates. Phosphonates are distinctly different from phosphates because there is a direct bond between carbon and phosphorus in phosphonates. In phosphates, phosphorus is bonded to oxygen that is then bonded to carbon. I thought that a direct C—P bond would be resistant to microbiological decomposition because it doesn't lead directly to important biochemical molecules such as ATP. In this way, one might find phosphonates in ancient organic matter, having survived biological decomposition. I was excited that Ellery had actually found phosphonates and I believed that he was perhaps the first person to find these compounds in the marine environment. We submitted a paper to Nature on this subject but it was rejected out of hand; so we were stuck publishing in a geochemical journal (Ingall and others, 1990). After obtaining the Ph.D., Ellery eventually took up a teaching position at Georgia Tech, having been preceded there by his friend Philippe van Cappellen. Together they wrote a very important paper on the effects of phosphorus chemistry on the level of atmospheric oxygen, as described above. This occurred while Ellery was at the University of Texas at Port Aransas and Philippe at Georgia Tech. Ellery is now back at Georgia Tech.

Clay Mineral Diagnesis and Black Sea Chemistry

Graduate student Paul Schroeder came from an oil company and had definite ideas about what he wanted to do as a graduate student. He had funding from an oil company that helped me financially. He studied the slow diagenetic transition of smectite (a potassium-free clay mineral) to illite (a potassium containing clay mineral) in samples of sediments from the Gulf of Mexico that he brought with him. The sediments ranged over thousands of meters in depth. He was a mechanical genius and took charge of fixing and updating complex analytical equipment of the Geology and Geophysics Department. He did most of his work with Kurt Zilm of the Yale Chemistry Department using Nuclear Magnetic Resonance (NMR) equipment. This enabled him to deduce the structural state of aluminum in smectite and illite and how it changed during long term diagenesis. Upon graduation he took up a professorial position at the University of Georgia where he has taught clay mineralogy for many years. His distinction in this field has been recognized by his being elected recently to the position of President of the Clay Minerals Society.

Because of my continuing interest in the biogeochemistry of sulfur, I persuaded another graduate student, Tim Lyons, to do a field thesis on the sediments of the Black Sea. He was part of a joint expedition of the Woods Hole Oceanographic Institution

together with scientists from Turkey. He collected and chemically analyzed sediments from shallow water shelf sediments, from the steep slopes around the Black Sea basin and from the deepest portions of the central part of the Basin. The deep sea sediments are high in pyrite, FeS_2, and are directly overlain by bottom waters that are enriched in dissolved H_2S. They are finely laminated because of a total lack of stirring (bioturbation) by higher organisms due to the omnipresent lethal H_2S. As a result of a lack of bioturbation, individual fine cm sized laminations can be traced over hundreds of kilometers.

Tim showed that the shallow water shelf sediments are overlain by oxygenated waters and contain little pyrite. However, from cores taken on the shelves, he discovered in two locations pyrite-rich layers at shallow depths in the sediment. This was interpreted by Tim as indicating that the chemocline, the boundary between O_2-containing waters and underlying H_2S-containing waters, which is presently at a depth of about 100 meters, was much shallower (40-50 meters) at these places during the past 300 years (Lyons and others, 1993). The chemocline rose high enough for sulfide-rich waters to lap onto the Black Sea shelves and as a result there must have been massive killing of bottom fauna that had been previously accustomed to O_2-containing waters. Later studies by others have found deeply buried layers, in the deep sea sediments, which contain the organic remains of photosynthetic bacteria that once lived in H_2S containing water. This means that there were past times when H_2S-containing waters were shallow enough to provide light for photosynthesis while at other times the sulfidic waters were too deep. Thus, over a longer time scale, vertical movement of the chemocline has also occurred and is a natural phenomenon in the Black Sea. This means that the historical pyrite-rich layers that Tim found could have been due to natural causes and not to pollution by the countries surrounding the Black Sea. Tim is currently a professor at the University of California at Riverside and has become an expert on the sulfur geochemistry of Precambrian sediments.

Mafic Mineral Weathering Mechanisms

I needed someone to help me study the soils collected with Mike Velbel from basic rock bodies and for this I hired Lennart Sjoberg from Stockholm University and later Jacques Schott from the University of Toulouse France. I had attended Lennart's thesis defense in Stockholm and had visited Jacques in Toulouse during a sabbatical in 1978. They both examined the surfaces of partially dissolved pyroxenes and amphiboles, isolated from clay-free sonically cleaned soils, via x-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM). (The soils had been obtained by Mike Velbel and myslf earlier as described above.) Duplicating the work that Rich Holdren had done earlier, they also reacted fresh minerals with hydrofluoric acid to produce surface dissolution features. As with feldspars the XPS patterns of the weathered surfaces showed no change from the original composition of the mineral. Also, we found with SEM that the surfaces of hypersthene, augite and hornblende all showed etch pits. The etch pits were narrow, lens shaped and aligned with the c-axis of each crystal. Examples are shown in figures 7 and 8. Where the pits intersected one another in a side-by-side fashion, small "microcaves" developed. End-to-end intersection led to elongated grooves in the minerals. We could reproduce the same results by treating fresh minerals with hydrofluoroic acid. Our electron photomicrographs were so spectacular that when we published our results in Science magazine (Berner and others, 1980), the magazine chose one of our pictures, that looked like the inside of a cave (actually a micro cave about 20 micrometers across), for their cover. This was the second Science cover from our lab: the first from Bill Graustein of Christmas "stars" of calcium oxalate and now augite micro "caves."

Jacques Schott continued our work on XPS analysis (Schott and others, 1981). He found that in laboratory dissolution experiments at pH values characteristic of soils
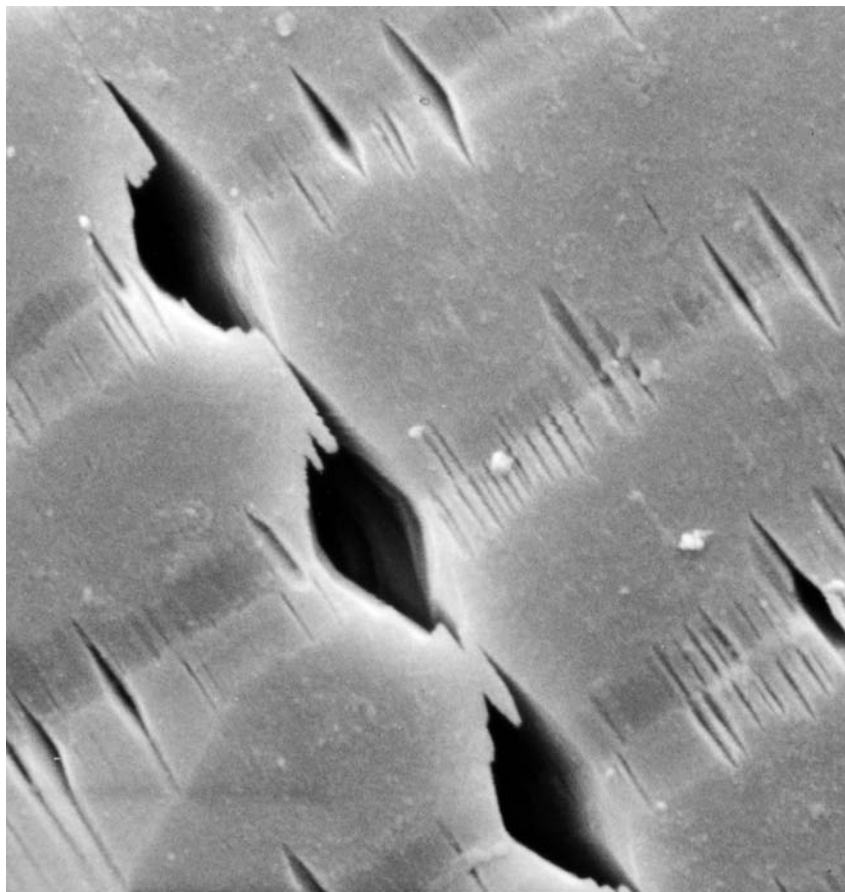
Fig. 7. Electron microscope photo of lens shaped etch pits in augite pyroxene. Note side-by-side intersections to form 10 micrometer "caves." The long axes of the pits are aligned with the c axis of the crystal (after Berner and Schott, 1982).

there was no development of a protective surface layer of altered composition but only change in cation content in the outermost few atomic layers. He found that treatment of pyroxene grains with strong HCl (pH = 1), too strong to represent most soils, did result in the formation of a pure silica surface layer, but the layer did not show crystallographic continuity with the underlying mineral structure and, thus, was not protective in the manner prescribed by the proponents of the protective surface layer theory. Jacques later refined the XPS method so that he could see changes in iron oxidation state from Fe^{+2} to Fe^{+3} on the surface of a weathered pyroxene (Schott and Berner, 1983).

Pyrite Formation over Phanerozoic Time and C/S Ratios

My work on pyrite had been noted by Professor Rob Raiswell at Leeds University in England and he contacted me about the possibility of working with me. He was a specialist on pyrite and pyrite concretions. I accepted and he came to Yale for a long visit. While he was here he and I collected over 600 samples of fossiliferous shales with ages ranging from the Cambrian to the Holocene (past 540 million years) and Rob analyzed them for their contents of organic carbon (C) and sulfide sulfur (S).

Fig. 8. Electron microscope photo of lens shaped etch pits in hypersthene (top) and augite (bottom). The greater abundance of etch pits in augite is due to dislocations occurring at the intersections of basal lamellae of slightly different chemical composition. Scale in micrometers (after Berner and Schott, 1982).

Fossiliferous shales were collected to avoid sediments deposited in anoxic basins where no life could survive on the bottom. For each age we found a good positive correlation between C and S. The C/S ratio for most sediments was similar to modern muds containing bottom fauna but Cambrian and Ordovician shales were found to have more sulfur relative to carbon, than later rocks (Raiswell and Berner, 1986). We ascribed this to the greater metabolizability of strictly marine organic matter that was the only source of organic matter for bacterial sulfate reduction before the rise of vascular land plants in the later Devonian. Land plant organic debris washed into the ocean would be less easily used by the sulfate reducing bacteria than marine organic matter. (It's the G model again.)

Rob and I also found that the C/S ratio of marine shales could be shown to correlate with the degree of heating during burial, as indicated by thermal indicators such as vitrinite reflectance (Raiswell and Berner, 1987). With heating up to temperatures characteristic of deep diagenesis and low-grade metamorphism, organic carbon is broken down to methane, carbon dioxide and other compounds, whereas pyrite is resistant to decomposition until high temperatures are obtained. Thus, by the use of the C/S ratio of rocks of a given age, one could discern the degree of deep burial and heating undergone by each rock.

We also used the C/S ratio of modern sediments to show how one could differentiate shales deposited under fresh-water versus marine conditions (Berner and Raiswell, 1984). Terrestrial fresh waters contain very little sulfate compared to seawater

so that the amount of H_2S formed by sulfate reduction is much less in fresh-water sediments. This leads to less pyrite in fresh water sediments and higher C/S ratios than found in marine sediments. This method was tested by analyzing Upper Carboniferous cyclothem shales that contained fossils indicating fresh water versus marine deposition and the method turned out to be successful over 90 percent of the time.

Rob and I published a paper (Berner and Raiswell, 1983) in which I did calculations of the original rates of burial of organic carbon and pyrite sulfur over Phanerozoic time using carbon and sulfur isotopic data and a computer model developed by Bob Garrels and Abe Lerman. Our results showed that there were large global variations in C/S over time with very low values during the early Paleozoic (600-400 million years ago), very high values during the late Paleozoic (350-250 million years ago), and intermediate values for the Mesozoic and Cenozoic (past 250 million years). This could be explained by data from the study of modern sediments. The C/S ratio of sediments of euxinic basins, such as the Black Sea, where there is H_2S in deep waters and no bottom fauna, have very low C/S ratios because of the abundance of pyrite in them. This leads to the suggestion that low C/S during the early Paleozoic was due to an abundance of euxinic basins. High C/S ratios for the late Paleozoic we explained in terms of a dominance of terrestrial plant organic debris, deposited on land and transported to the oceans by rivers. At both places a high C/S ratio would be expected. The later intermediate C/S values were similar to those for present "normal marine" sediments with bottom fauna (in other words, no H_2S in bottom waters). This study was rewritten and presented later as an address, by me as President of the Geochemical Society, to the Geological Society of America (Berner, 1984).

Rob Raiswell was a very hard worker and after his first extended visit he came to Yale several times for shorter periods during summers. This is how we got so much work done together. He was an amiable friend and I especially liked to go to a local pub with him and have a beer or two. I say a beer or two because he could consume large quantities of beer and still return to the lab and carefully perform such delicate actions as weighing tiny quantities of sediment or a chemical precipitate on a microbalance. I never could figure out how he did it.

The BLAG Model for Ancient Atmospheric CO_2

My former professor at Harvard, Bob Garrels, while being located at the University of South Florida, became interested in working with me and would come to Yale each summer for an extended visit. I learned much from our collaboration, which ended up with the publication of the now famous BLAG model (Berner and others, 1983). The term BLAG represents the combined initials of myself, Tony Lasaga, another professor at Yale, and Garrels. Garrels convinced me to become interested in the cycling of the elements. I already had done some calculations of carbon and sulfur cycling based on a model by Garrels and Abe Lerman of Northwestern University, but Bob urged me to consider the factors in the carbon cycle that affect the concentration of CO_2 in the atmosphere. I had previously read a paper, translated from a paper published originally in Russian in 1976 by the Russian geochemist Alexander B. Ronov, that assumed that CO_2 is controlled by volcanic degassing and uptake of the CO_2 by the weathering of calcium silicate minerals. The CO_2 is converted to dissolved bicarbonate during weathering and the bicarbonate is precipitated as calcium carbonate in the oceans after transport there by rivers. Combining weathering and carbonate precipitation, the overall reaction is:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$
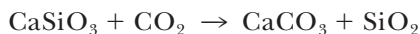
This reaction had been suggested by Harold Urey (Urey, 1952) as a possible control on atmospheric CO_2. Written backwards it represents the thermal breakdown at depth of

the carbonate to release CO_2 to the atmosphere via volcanoes and metamorphism. The reverse reaction was not considered by Ronov and without it there would be continuously increasing $CaCO_3$ over geologic time which is not observed. (The formula on the left is intended to represent all calcium silicates, not just $CaSiO_3$, which is the formula for wollastonite.)

Early on (about 1979 or 1980) I told Bob Garrels that I did not like Ronov's idea that silicate weathering responded directly to the concentration of CO_2 in the atmosphere, in other words, a linear response. Weathering in soils occurs by CO_2 (and organic acids) secreted by plant roots and associated symbiotic microflora, and not directly by atmospheric CO_2. I reasoned that one way weathering could respond to changes in atmospheric CO_2 was indirectly by means of the atmospheric greenhouse effect. With any rise in atmospheric CO_2, there would be global warming and greater rainfall that would increase the rate of uptake of CO_2 by chemical weathering. In this way, weathering could provide a negative feedback to atmospheric CO_2 variations.

Garrels and I were at a loss in constructing an adequate model for CO_2 through time and subsequently were greatly helped by collaborating with Tony Lasaga. Tony added a clever way to express the rate of calcium carbonate precipitation in the ocean to our idea of a greenhouse feedback and the assumption that global degassing, from volcanoes and metamorphic reactions, might be proportional to the rate of seafloor spreading. Tony came up with a time-dependent computer program that allowed us to put these and other assumptions into a model for CO_2 over a million year time scale. We chose the past 100 million years based on our belief that the Cretaceous (140 to 65 million years ago) was much warmer than at present due to a much higher level of atmospheric CO_2 and extra greenhouse warming. In fact, our calculations did show very high CO_2 concentrations for the Cretaceous. We were suggesting that global warming by CO_2, a hot topic at that time with regards to human effects on climate due to the burning of fossil fuels, might apply also to climates of the geologic past. We finally published the results of our modeling (Berner and others, 1983), after a two year unfortunately long delay by Lasaga who was busy with other research. (In the meantime the idea of a weathering-greenhouse feedback was published by Walker and others, 1981.) The model was labeled, soon thereafter, by others as the BLAG model. This model has been cited over 700 times (as of 2012) and has exerted a large influence on subsequent carbon cycle modeling, including my own. It led to my series of models for CO_2 labeled as the GEOCARB models.

Ancient Air in Amber

Wally Broecker of Columbia University, who was skeptical of the BLAG model, stated to me that he would believe in the chemical composition of ancient air if we could obtain a sample of it. This sounded impossible at the time. However, I found out that there was a conceivable way to get a sample. Bob Garrels suggested that I look at the gas bubbles enclosed in amber. Ed Roedder, in his book on fluid inclusions, had suggested that the bubbles commonly found enclosed in amber ought to be analyzed as they might represent a sample of ancient air. Amber is fossilized resin emitted by trees and during successive flows of resin and subsequent solidification, the resin could trap and preserve bubbles of air.

To analyze bubbles in amber, I needed samples of amber of known age and a way to do chemical analyses of the bubbles. Chemical analysis of a small sample of air in a tiny bubble sounded almost impossible to me. But there was a way to do it. Upon the advice of Danny Rye, I contacted Gary Landis of the U.S. Geological Survey in Denver who is an expert in analyzing gas and liquid inclusions in minerals using quadrupole mass spectrometry. He stated that his method was so sensitive that he could analyze a single bubble. Accordingly, I contacted a number of people who were known to study amber and obtained samples with ages ranging from Cretaceous to modern resin.

Modern resin could be used to check the method as it should contain bubbles of modern air of known composition. From the start I realized that analyzing the gas bubbles for CO_2 would be impractical because there are only very small concentrations of CO_2 in air and some CO_2 could form via the reaction of O_2 in trapped air with carbon of the resin. It would be better to look at the major gas O_2 because I had calculated that O_2 could well vary over geologic time.

During the spring of 1987, I sent amber samples to Gary Landis and his analyses showed that the gases in amber contained O_2 which seemed to vary with time, in the ratio O_2/N_2. Values of O_2/N_2 in the Cretaceous at 80 million years ago were considerably higher than at present. This was interesting because I was afraid that O_2 might be lost over time by reaction with the resin/amber. During the fall of 1987, I had a sabbatical leave, and I spent some time visiting Gary in Denver. I was present when he analyzed gas bubbles in modern resin and got what we thought was the composition of modern air. The air was not simply O_2 and N_2, which make up most of the composition of air; we also found minor CO_2. If the CO_2 had formed via the reaction of O_2 with the resin, or from respiration of possibly trapped bacteria, we reasoned that the molar sum of $CO_2 + O_2$ would represent the original trapped O_2. The sum, when divided by the amount of N_2, gave exactly the same ratio as O_2/N_2 in modern air. We thought that our method was vindicated!

We presented our results at the annual meeting of the Geological Society of America in Phoenix, Arizona about a week after my visit to Gary's lab. Earlier I had received a request for a press release based on an abstract by Gary and me on ancient air in amber that I had submitted to the meeting. I knew nothing about writing press releases and sought the counsel of Steve Schneider in Boulder, Colorado, who was very familiar with the media. (While I was visiting Gary, I also gave some talks at the National Center for Atmospheric Research, which brought me into contact with Schneider.) Steve rewrote my attempt at a press release to make it much more attractive to getting attention. I turned in the Schneider version of "Ancient Air in Amber" to the Geological Society publicity desk when I arrived in Phoenix.

I wasn't prepared for the reception I was going to get, thanks to Steve Schneider. When I gave my talk, based on the submitted abstract, there were a number of reporters present. Before the talk I was asked to attend a press conference where I explained what Gary and I had found. After that we were interviewed by none other than CNN News, the New York Times and Time Magazine. The evening of the talk I was told by my colleagues at Yale that our interview with CNN was included as part of their daily news. In the meantime, an article on our findings was published on the front page of the New York Times (and above the fold which means major news). Time magazine the next week published a picture of my hand holding a piece of amber. (One could see that my fingernails were embarrassingly dirty.) I was flabbergasted and didn't know how to handle all this publicity. Before this my biggest media exposure was in the local North Haven, CT newspaper as the father of my daughter, Susan, who was a local track star.

The publicity generated, mainly by the New York Times, led to constant telephone calls upon my return to Yale. I got so tired of the calls that I referred all further calls to Gary Landis. After all, it was his method that allowed for us to be able to analyze ancient air. Some publications had greatly modified the original story; for example, the Denver Post had a statement on the front page that dinosaur breath had been captured. We never talked about dinosaurs! The French magazine l'Express published an article saying that we had a new theory for the extinction of the dinosaurs. Even the Yale Alumni magazine, that never interviewed me, wrote an article describing Gary Landis incorrectly as my graduate student. I learned from newspaper articles sent to me by friends, that a lot of plagiarism occurs in the news media. I could often see the same

phrases that appeared originally in the New York Times. The article in the New York Times was written by James Gleick, who had interviewed me in Phoenix. (He became famous later when he wrote books about chaos theory and the life of Richard Feynman.) His description of our results was accurate, much more so than what was written subsequently in other places.

Gary and I wrote up our results, which were published as a short paper in the journal Science (Berner and Landis, 1988). Before publication our results were attacked on December 7, 1987 by Harmon Craig in a talk given at the American Geophysical Union meeting in San Francisco. (December 7! Were we being bombed also?) Craig claimed that he had analyzed amber bubbles and could find no O_2. I was telephoned by the Associated Press and United Press International, right after his talk, for my comments. I told them that the method used by Gary Landis was more sensitive than the gas chromatographic method used by Craig. This was true but I was getting dangerously into deep water since Craig was an expert on gas analysis and I wasn't. I told the media to also call Gary.

In the summer of 1988, Craig and his colleague Horibe, published a comment in Science (Horibe and Craig, 1988) where they claimed that our gas bubbles were contaminated by modern air that had diffused into the amber samples. This was based on diffusion experiments showing the uptake of gaseous argon by amber samples. Their argument was if Ar so readily diffuses into amber, so could O_2 and N_2 from modern air. We countered in a reply to Science that the argon could have been adsorbed in microfractures on the surface of the amber and may not have diffused *into* the amber. Amber was misrepresented by other critics as being porous to diffusion, using polyethylene as an example. Amber consists of cross-linked long chain terpenoid molecules and some ambers are so well structured that they give clear x-ray diffraction patterns. This should make amber far less amenable to molecular diffusion than linear polyethylene. An accompanying critical comment by two other authors also stated that air molecules could diffuse into amber as evidenced by "diffusion experiments" using propane gas. We calculated that the propane could easily have adsorbed onto the amber surface and not penetrated into the amber. We also found that the samples we had obtained bore no relation between O_2 content and time of exposure to modern air. Some high O_2 samples came from deep anoxic subsurface drill cores whereas some lower O_2 samples had been found washed up onto Baltic Sea beaches and exposed to air for a long time. Also, we found simple mixing patterns between other gases, such as CH_4 and CO_2 that suggests derivation from the amber and not loss via diffusion to the outside air.

Since we had published only a short paper in Science, I felt it necessary to publish a lot of additional results, that we had subsequently obtained on additional amber samples. This could bolster our argument against our critics. However, this paper was never published. After a year of pleading with Gary to add his section on how he did the analyses of the bubbles, he never wrote up anything. His method consisted of crushing the amber in vacuo to release gases from bubbles into the mass spectrometer, but a more definitive discussion of the method was needed. He had no doubt about the correctness of our conclusions.

An additional study was done by Gary, and his USGS colleague Larry Snee (Landis and Snee, 1991). They subjected tightly sealed amber samples to radiation in a nuclear reactor in order to convert potassium in the amber to ^{39}Ar. If diffusion were easy, the ^{39}Ar should migrate out of the amber into the surrounding space of the sealed quartz tubes. After three months of sitting after radiation, no ^{39}Ar was found outside of the amber in the tubes. This means that if diffusion of argon occurred, it was much slower than that stated by Horibe and Craig. This sounds like an ironclad argument, but it occurred to me that the potassium that was converted to ^{39}Ar might have resided

within tiny clay minerals and not in the amber matrix. Clay minerals could retain ^{39}Ar within their structures. However, the potassium could well have been within the amber because it is well known that potassium-rich solutions drain down tree trunks and successive flows of resin could include some of this potassium. My idea was corroborated by Landis and Snee who found, via energy dispersive x-ray maps, that most of the postassium in the amber was uniformly distributed.
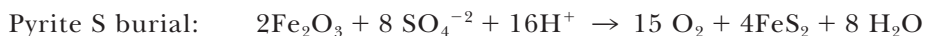
Gary Landis and Larry Snee also found that the isotopic ratio ^{40}Ar/^{36}Ar of argon adsorbed on the surface of amber gave values appropriate for the modern atmosphere whereas that released from the amber by decomposition at high temperature gave ^{40}Ar/^{36}Ar ratios appropriate for the age of the amber. Radiogenic ^{40}Ar forms over long times from the decay of ^{40}K and the ratio of it to nonradiogenic ^{36}Ar is often used to date rocks. Landis and Snee got the same ^{40}Ar/^{36}Ar ages for the ambers in rocks that had been dated by fossils and their stratigraphic position in the geologic record. This is further evidence for the idea that amber preserves ancient gases.

Even with the work of Landis and Snee, the opinion that we did not measure ancient air bubbles continues to the present. The critique of Harmon Craig, an expert on gas analysis in minerals, has predominated. In addition, I have been a weak self-critic in that I have had a hard time believing that O_2 molecules could remain in intimate contact with amber for 80 million years without reacting with it. I have not continued to fight this battle and neither has Gary Landis. Instead of trying to find another gas analyst to do more work on amber, I decided to quit this approach and try to deduce levels of ancient atmospheric O_2 by means of mathematical modeling.

Modeling of Atmospheric Oxygen

In 1989, Don Canfield and I published a paper (Berner and Canfield, 1989) where we did calculations of the level of atmospheric O_2 over Phanerozoic time (the past 540 million years). We based our calculations on the abundance of organic carbon and pyrite sulfur in sedimentary rocks. Burial of organic matter and pyrite, FeS_2, are the principal processes that release O_2 into the atmosphere. The production of organic matter by photosynthesis releases O_2 to the atmosphere. Any portion of this organic matter, that is not lost by the consumption of O_2 during respiration, becomes buried in sediments. Thus, for every atom of carbon buried, a molecule of photosynthetic O_2 remains in the atmosphere. In this way, carbon burial is a direct measure of O_2 production. A similar argument for O_2 production can be made for pyrite burial. One can represent these arguments succinctly by chemical reactions:

For O_2 production

Organic C burial: $CO_2 + H_2O \rightarrow CH_2O + O_2$

Pyrite S burial: $2Fe_2O_3 + 8\,SO_4^{-2} + 16H^+ \rightarrow 15\,O_2 + 4FeS_2 + 8\,H_2O$
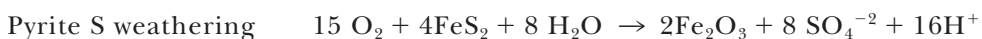
The reaction involving pyrite burial is complex and represents the summation of a number of reactions. These are (1) photosynthesis and burial of non-respired organic carbon; (2) bacterial sulfate reduction to H_2S using the buried organic matter; (3) reaction of hydrogen sulfide with iron minerals to form pyrite; (4) reaction of H^+ ions with bicarbonate to form CO_2.

To calculate the burial rates of organic carbon C, and pyrite sulfur S, during the geological past, we obtained analyses for these two from sediments of known age and time span. The rates of C and S burial were calculated from the duration, or elapsed time, of deposition of rocks of different ages multiplied by their C and S contents. We divided carbon-containing rocks into carbon-rich sediments of coal basins, remaining low-carbon terrestrial rocks, and marine sedimentary rocks. Data for carbon in coal basin sediments were calculated from analyses of rocks from drill cores (most carbon is

not in coal itself but disseminated in thin layers that are not economically mineable). It was assumed that there is no appreciable carbon in the remainder of terrestrial sediments that are mainly red beds. Data on carbon in marine sediments was taken from a compilation by Alexander Ronov of the USSR. For pyrite sulfur, the data for marine rocks over time, obtained earlier by Rob Raiswell and myself (Raiswell and Berner, 1986), were used, along with some estimates of the abundance of past Black Sea–like euxinic basins. There was assumed to be no pyrite in red beds and very little in coal basin sediments because of the very high C/S ratio of coals.

Rates of deposition of C and S only gives rates of O_2 production. We also needed rates of O_2 consumption. We assumed that oxidation during weathering of organic matter and pyrite exposed on the continents would provide a measure of consumption. Appropriate reactions, which are the reverse of the reactions to form O_2, are:

For O_2 consumption

Organic C weathering $CH_2O + O_2 \rightarrow CO_2 + H_2O$

Pyrite S weathering $15\,O_2 + 4FeS_2 + 8\,H_2O \rightarrow 2Fe_2O_3 + 8\,SO_4^{-2} + 16H^+$

To calculate values of O_2 over time we combined weathering and burial mass fluxes via the reactions shown above:

$$dO_2/dt = Fbg - Fwg + 15/8\,(Fbp + Fwp)$$

where: F refers to fluxes, t to time, b to burial, w to weathering, g to organic carbon and p to pyrite sulfur. Masses of O_2 over time were calculated so as to produce the present mass.

To get weathering fluxes we assumed that the rate of weathering would be directly proportional to the total mass of C or S at any given time multiplied by total global erosion rate. The variation of C and S masses over time was calculated from the initial masses at 540 million years ago, which were assumed to be similar to present day masses, and by adjusting each mass every million years to account for gain by burial and loss by weathering. Erosion rate was assumed to be equivalent to global deposition rate at the same time. Deposition rate was determined from total masses of the appropriate rocks for each time period corrected for loss via erosion since deposition.

Our results (see fig. 9) showed that there was a large maximum of about 35 percent O_2 during the Carboniferous and Permian (350 to 250 million years ago), a low value of about 15 percent during the Triassic (250 to 200 million years ago) and a secondary maximum at about 27 percent during the Cretaceous (140 to 65 million years ago). The present O_2 content of the atmosphere is 21 percent. The higher concentrations were due mainly to excessive organic carbon deposition in coal basins at the two times. Our results, therefore, suggest that atmospheric O_2 has varied appreciably over the past 600 million years. Later studies, based independently on the use of carbon and sulfur isotopes, were to verify these conclusions. It is also notable that higher than present values for the Cretaceous agree with the findings of our amber study although the theoretical O_2 concentrations are distinctly lower.

The Global Water Cycle and Global Environment

After our children had gone to college, my wife, Elizabeth Kay Berner, had more time to pursue research. This led to her writing a book, along with me, entitled "The Global Water Cycle" which was published in 1987. The book covered: the physical chemistry of water, the energy cycle as it affects the water cycle, processes that affect evaporation and cloud formation, and detailed discussions of rain, soil water, biological transpiration, lakes, rivers and estuaries. For each water reservoir, a huge amount of data on chemical composition was amassed with emphasis on how human activity had
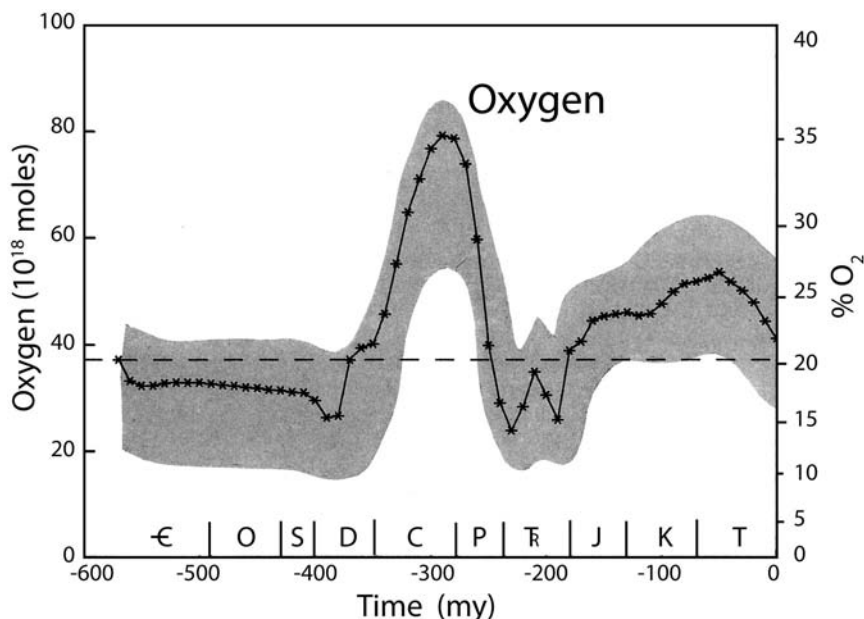
Fig. 9. Concentration and mass of atmospheric O_2 over Phanerozoic time as calculated from rock abundance data. The gray area represents estimates of errors in the calculations (after Berner and Canfield, 1989).

affected water composition. I helped her by contributing chapters on chemical weathering and ocean composition, but the remainder was all her doing. This book eventually led to an expansion to include air chemistry with detailed discussions of the greenhouse effect and the ozone hole. For air chemistry it relied a lot on new data aggregated from the literature by the Intergovernmental Panel on Climate Change (IPCC). The new book was retitled "Global Environment: Water, Air and Geochemical Cycles" and was published in 1996.

PART III. GEOCARB, AN ISOTOPIC O_2 MODEL, PLANTS AND WEATHERING,
EARTH SYSTEM SCIENCE 1990 TO 2001

GEOCARB

In 1990, I published a new model (Berner, 1991) for atmospheric CO_2 over Phanerozoic time (past 540 million years). The model was a combination of the carbon and sulfur isotope model of Garrels and Lerman (1984) and the BLAG model. The new model, which was later named GEOCARB I, was not time dependent, like the BLAG model, but allowed for a steady state for each million year time period. By steady state I mean that the input of total carbon (carbonate carbon plus organic carbon) to the ocean was equal to its output. Because the time necessary to reach steady state is considerably less than a million years and because the mean residence time of carbon in the ocean is only about 100,000 years, this approach is justified. Certainly steady state modeling is much simpler on a computer than was the BLAG model. Because of this, I neither needed Tony Lasaga's help for modeling nor could I call for help from Bob Garrels, as he had died in 1988. I was now on my own. I was becoming an Earth System Scientist, in other words, someone who uses a variety of approaches to study interactions of different portions of the Earth, in this case the atmosphere, the oceans, the

land and life. Student input to GEOCARB CO_2 modeling was minimal. They did their thing while I did mine.

The new model used the model of Garrels and Lerman but added several additional processes affecting atmospheric CO_2 that were not considered in the BLAG model. This includes the effect of mountain uplift on increased erosion and increased exposure of weatherable minerals to the atmosphere; the effect of the evolution of land plants on rates of CO_2 uptake by weathering; the effect of changes in paleogeography, due to continental drift, as they affect changes in rainfall and river runoff from the continents (major factors in weathering); and consideration of the amount of carbonate in sea floor undergoing subduction and degassing of CO_2 by thermal decomposition. Modeling results showed extremely high CO_2 levels during the early Paleozoic (540-350 million years ago), low values during the Permian and Carboniferous (350-250 million years ago, high values during the Mesozoic (250-65 million years ago) and values falling towards the present during the Cenozoic (past 65 million years). Since the modeling considers only very slow processes, occurring over millions of years, no changes due to the burning of fossil fuels by humans can be discerned.

Since the new model was for steady state, I had no simple method for calculating the concentration of CO_2 in the atmosphere from differences in inputs and outputs, as was done in the BLAG model. With much soul searching I figured out how to obtain the needed values of CO_2. The feedback expression for the effect of CO_2 on weathering rate in the BLAG model includes the effect of CO_2 on global mean temperature. Temperature changes were used to guide rates of weathering, with faster rates leading to faster CO_2 uptake by weathering. I reasoned that one could calculate independently the rate of calcium and magnesium silicate weathering as the difference between the burial of Ca and Mg carbonates and their weathering rates. The difference represents the weathering of Ca and Mg silicates and the burial of the derived Ca and Mg as carbonates in the ocean. (The carbonate weathering and burial rates were obtained by carbon isotope modeling.) Knowing the rate of silicate weathering, along with an expression for the effect of CO_2 on temperature as it affects silicate weathering, one could then calculate the concentration of CO_2 for each million years. Eureka! I had a new and much more mathematically simplified model for CO_2.

The new model was revised in 1994 (Berner, 1994) and given the name GEO-CARB II. I thank Tom Crowley, from Texas A and M University who at that time suggested that I have a name for my program. He also noted that I hadn't considered the evolution of the sun that would affect temperature in addition to the greenhouse effect. Solar radiation has increased about 5 percent over the past 540 million years, and the effect of this on global mean temperature cannot be ignored. I added the influence of solar radiation to greenhouse warming, as factors affecting temperature which in turn affects silicate and carbonate weathering. Other additions were: (1) distinction between the feedback expressions for silicate weathering and carbonate weathering; (2) the use of Sr isotopic composition of the ocean as a guide to the effect of uplift of mountains on rates of silicate weathering; (3) consideration of total area underlain by carbonate rocks for calculating carbonate weathering; (4) the use of new data on the rate of seafloor spreading and presumed global degassing over the past 150 million years; (5) formulation of an improved value for weathering rate before the rise of vascular land plants; (6) use of new data on the temperature coefficient and river runoff as they affect silicate weathering; and (7) the consideration of CO_2 fertilization on the rate of plant growth as it affects weathering rate.

The values of CO_2 versus time derived from the GEOCARB II model turned out to be not very different than those calculated by the original model. The principal differences occurred during the Cambrian and Ordovician Periods (540-440 million years ago) and during the Cretaceous Period (140-65 million years ago) where higher

values of CO_2 were found for the new model. In both models, and all succeeding modifications, the overall trend of CO_2 with time is in general agreement with the control of climate by the CO_2 atmospheric greenhouse effect. High CO_2 and high temperatures are found for the early Paleozoic and the Mesozoic and low CO_2 and low temperatures for the Carboniferous and Permian Periods and for the past 30 million years. High CO_2 helps to explain the observation of tropical plants and animals at high latitudes during the Cretaceous and low CO_2 helps to explain the vast and long lived continental glaciation that occurred during the Carboniferous and Permian periods. The presence of glaciers on Antarctica during the past 30 million years can also be explained by low values of atmospheric CO_2.

In 2001, I published a further revision of the GEOCARB model named GEOCARB III, co-authored with Zav Kothavala (Berner and Kothavala, 2001). Zav is a theoretical climatologist and he did some GCM (General Circulation Model) calculations in order for the model to be able to use the most up-to-date dependence of global mean surface temperature and river runoff on the level of atmospheric CO_2. Other major changes were (1) calculation of the effect of mountain uplift on weathering rates were calculated directly from the abundance of terrigenous sedimentary rocks over time and not from Sr isotopes. The age, mass and duration of deposition of terrigenous rocks, those formed by erosion on the continents and deposited either on the continents or in the ocean, are a direct measure of the rate of erosion. Erosion, which exposes fresh minerals to exposure for weathering, is assumed to be increased by mountain uplift as assumed in the earlier models for both O_2 and CO_2. Further changes from the GEOCARB II model were (2) inclusion of new GCM data on the mean temperature and river runoff for the continents over time, as they affect the rate of weathering; (3) separation of the effects of the weathering rate enhancement of early land plants (gymnosperms) from later land plants (angiosperms); and (4) revision of each land area as it affects river runoff. A plot of the results for GEOCARB III, with comparison to the results for GEOCARB II, is shown in figure 10.

Results again showed maintenance of the general trends found in GEOCARB I and GEOCARB II. That is high CO_2 values for the early Paleozoic, low values for the Permian and Carboniferous Periods, high values for the Mesozoic and overall diminishing CO_2 from 65 million years ago to the present. I began to believe that there was some validity to the modeling. This was given much greater support by the results of independent estimates of paleo-CO_2 using various indirect methods called proxies. The three principal proxies (see Royer and others, 2001b) are: the carbon isotopic composition of the carbonate in ancient soils (paleosols); the carbon isotopic composition of organic remains of specific plankton (small organisms that live near the surface of the oceans); and the stomatal density of fossil leaves. (Stomata are small holes in leaves that allow gases to enter and leave the leaf.) These methods, especially the paleosol method, found a similar CO_2 pattern to the GEOCARB modeling over the past 400 million years. After publishing three GEOCARB versions and a whole host of proxies, there is increasing evidence that global mean temperature correlates well with the level of atmospheric CO_2 on a long-term (million year) geological time scale.

The Structure of Carbonate Fluorapatite

During the period of 1990 to 2001, I had five new graduate students: Pierre Regnier, JiLong Rao, M. Ford Cochran, Katherine Moulton, and Steve Petsch. Pierre Regnier enrolled to work for a Ph. D. degree but for personal reasons had to leave Yale and obtained only a Master's degree. Pierre continued the experimental studies of Philippe van Cappllellen but for fluorapatite that included carbonate in its crystal structure. The fluorapatite that forms in the oceans invariably contains carbonate. Pierre, like Philippe, studied the kinetics of carbonate fluorapatite precipitation from both seawater and similar artificial seawater. The important contribution by Pierre was
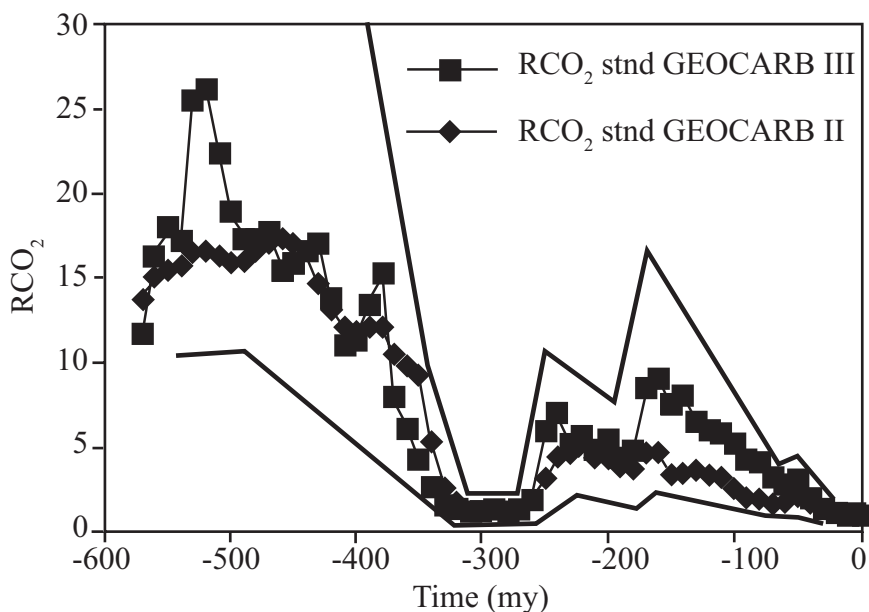
Fig. 10. Atmospheric carbon dioxide over the past 550 million years (Phanerozoic time) calculated by the GEOCARB II and III models. RCO_2 represents the mass of CO_2 at some past time to the rounded average for the past million years (250 ppm). The black lines represent estimates of error (after Berner, 1994; Berner and Kothavala, 2001).

to shed some light on the structural role of carbonate in apatite, which had been poorly defined. He did a Nuclear Magnetic Resonasnce (NMR) study of ^{13}C in apatite, that he had prepared using a ^{13}C-enriched solution. For the third time, Kurt Zilm, of Yale's Chemistry Department helped one of my students with NMR (the others were Paul Schroeder and Ellery Ingall). There was a theory that carbonate ion was present in carbonate fluorapatite in the form of a tetrahedral ion with the composition CO_3F^{-3} that substituted for PO_4^{-3}. Pierre found from his NMR work, and also from quantum mechanical calculations, that such an ion as CO_3F^{-3} did not exist in apatite. We published our work in the American Mineralogist (Regnier and others, 1994). This meant that a proper explanation of the position of carbonate in apatite still remained a mystery.

Jilong Rao and Chinese Rivers

Jilong Rao was my most interesting student. I first met him in China in 1988 when he was the director of the environmental program at Qingdao University. After our visits (my wife Betty accompanied me) to Qingdao and Beijing, he asked if he could come to Yale as a visiting researcher. I said yes and he came to Yale in 1989. As it turned out, he had to come to Yale as a matter of emergency. Several of Jilong's students had been present at the large demonstration in 1989 at Tiananmen Square in Beijing, which was put down by tanks. The authorities found out that he had sympathized with their participation in the demonstration, and as a result, he was demoted from full Professor and the director of the environmental laboratory to a very minor position. This was not the first time that he had suffered under the Chinese Communist regime. When he was a student in the late 1950's, the Maoist authorities discovered that he had written a private diary concerning birth control, a subject which at that time was

banned. He was thrown out of college and sent to work in coal mines where he developed a respiratory disease. During his banishment to the coal mines and elsewhere, he wrote a book on geochemical thermodynamics, a subject that was banned by Mao because it contained western thought. He said that he wrote it at night by candlelight so that he would not be caught. When the despotism was lessened, his book was ultimately published in China in 1979.

After arrival at Yale, Jilong asked if he could become my graduate student. I could support him as a visiting researcher only for one year, but as a student he could obtain a student fellowship from Yale and stay longer. Besides he had no intention of returning to China. He was bitter towards China and at the age of 50 he was willing to be a student again so that he could live in a free country. He was successful in bringing his wife and daughter with him, but he could not bring his son because the son was approaching military age. After much political activity, including the involvement of myself and Senator Lieberman of Connecticut, he was able to have his son leave China and come to the U.S. He used research that he had already done in China, on the chemistry of sediments in the Huang He (Yellow) River), for his thesis and he got the Ph.D. in just three years. During that time, he and I published a paper on the chemistry of phosphorus in sediments carried by the Amazon River and deposited in the ocean (Berner and Rao, 1994). We found that a large portion of phosphorus delivered to the sea came from desorption from iron oxides and the decomposition of organic phosphorus upon being deposited in the ocean. The samples that we analyzed were provided to me from others that had visited the Amazon River and its estuary.

After obtaining the Ph.D. degree, Jilong tried to get a teaching position at an American university. After many attempts he failed. The problem was that the universities were not willing to hire a 50+ year old man, with rather broken English, for an assistant professor position. He finally gave up and took a position at a bank in Boston as a systems programmer. He was an expert with computers and was of much help to me on programming problems when he was at Yale. The last that I heard from Jilong was that he had moved from Massachusetts to Southern California for the sake of his wife's health.

Plants and Weathering

One time in the early 90's while sitting on the banks of the Potomac River, upriver from Washington, D.C., I noticed plants apparently growing out of rocks. I had seen this before and at that time I became interested in how plants affect rock weathering. Upon reading the literature, I found out that plants accelerate weathering by: (1) rootlets plus associated symbiotic micro-flora secrete acids that attack minerals to obtain nutrients for the host plant; (2) organic soil litter decomposes to organic acids and carbonic acid that also attack and dissolve minerals; (3) on a regional scale plants re-circulate water via transpiration followed by resulting rainfall, and this helps to increase mineral-water contact time; (4) plant roots anchor clay-rich soil retarding erosion and allowing the retention of water and continued weathering of primary minerals.

Besides being an interesting phenomenon in its own right, the study of plants and how they affect the rate of silicate weathering is important in long-term carbon cycle modeling. Inputs to the GEOCARB model include the effect of plants on CO_2 uptake by chemical weathering and how the evolution of plants over the Phanerozoic has affected this rate of CO_2 uptake. Larger plants, such as trees, have much more extensive root systems than more primitive plants, such as mosses and liverworts, and as a result trees weather and fix CO_2 much faster. Such primitive plants were believed to populate the continents before the rise of trees. Therefore, the rise of trees and their increased CO_2 uptake by weathering, as compared to the more primitive plants, is a
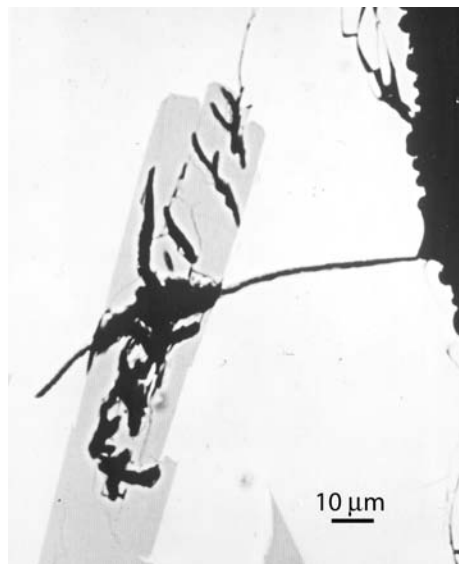
Fig. 11. Electron microscope photo of mineral dissolution by a mycorrhizal hypha leaching a plagio-clase feldspar phenocryst in young basalt from the island of Hawaii. The hypha extends from a former root (now detached and pictured as a dark space in the upper right corner of the photo). Note the preference to attack the calcium-rich plagioclase as opposed to the less Ca-rich glassy matrix of the basalt. Calcium is an important plant nutrient (after Cochran and Berner, 1996).

reasonable explanation for the large drop in CO_2 found during the Devonian period, 450 to 350 million years ago (see fig. 10).

My need to demonstrate and quantify the effect of plants on weathering led to the research of two graduate students. I created a thesis project for a brilliant new graduate student, Ford Cochran, working on the role of plants in weathering, with field trips to Hubbard Brook, New Hampshire, Mount St. Helens in the state of Washington, and the Big Island of Hawaii. He collected samples at all three places and in addition did some experimental work growing plants at a laboratory at Oak Ridge, Tennessee. Unfortunately, none of these projects were completed when he decided to leave Yale to work for the National Geographic. We did publish together some of his initial work on plants and weathering in Hawaii. Our finding of the role of mycorrhizae in weathering is illustrated in figure 11. Fortunately, some of the rocks that he had collected from Hawaii were sent to and studied much later by Mike Velbel.

Kathy Moulton came to work with me because she was interested in studying weathering in a cold climate. I assigned her to a project studying the role of trees as they affect the rate of weathering in Iceland. I had visited Iceland and had an excellent field tour through the island with Dr. Sigurdur (Siggi) Gislason. We picked out an ideal site for studying the weathering of basalt along the shores of a lake by the name of Skorradalur in western Iceland. Here Kathy collected water samples from small streams draining stands of evergreens, stunted birch trees, and sporadic mosses. After correcting for the chemical composition of precipitation for this area, she deduced the rates of the delivery of dissolved calcium and magnesium from each of the three areas from chemical analyses of water samples and measurements of stream flow over a seasonal cycle. This is a true test of the effect of vegetation on weathering because it was done in a small area with constant lithology and constant microclimate. There is no acid rain in this part of Iceland and the basalt that she studied is several million years old and is

located far from active hydrothermal activity as found elsewhere in Iceland. Chemical signatures indicative of hydrothermal activity were found to be absent. Kathy found that the rates of weathering under the birch trees and evergreens were 3 to 4 times as rapid as found under the mosses. These conclusions (Moulton and others, 2000) were later substantiated by Josh West, an undergraduate working with me on the chemical composition of the soils from the three areas. This is confirmation of the importance of vegetation in enhancing weathering rate. Her results were so important that they were incorporated into my GEOCARB modeling.

Kathy left Yale with a Ph.D. and a few years later took up the position of assistant professor at Kent State University. There she taught geohydrology, but her tenure was, unfortunately, very short. Tragically, she was killed by a motor vehicle while she was riding her bicycle. Her loss was felt deeply by Kent State and they started a fund for graduate student assistance under her name. Posthumously she co-authored a review paper in the Treatise of Geochemistry with my wife and I on the role of plants in chemical weathering (E. K. Berner and others, 2003). Her death was a great loss to geochemistry and to geohydrology.

A New Model for Atmospheric Oxygen

Steve Petsch came to Yale from Pennsylvania State University where he had received considerable training in organic chemistry. I convinced him to do Ph.D. research on the weathering of organic matter in black shales. This is a key process in the long term geological carbon cycle because the principal process of O_2 removal from the atmosphere is the oxidative weathering of organic matter. He collected weathered and unweathered samples of black shales from a variety of locations in the United States and subjected them to organic chemical analysis. He found that new, more oxidized compounds formed resulting in an increase in the O/C ratio of the shale organic matter. In a paper published with Tim Eglinton of the Woods Hole Oceanographic Institution and myself (Petsch and others, 2000), he states that pyrite loss precedes or accompanies organic carbon loss and that there is no preferential loss of N or S containing organic matter during weathering. Eventually the organic carbon in heavily weathered samples was totally lost and converted to carbon dioxide.

Steve Petsch also wrote with me a few papers on processes that affect the level of atmospheric oxygen. Several years before I had constructed a model based on the carbon and sulfur isotopic composition of seawater over the Phanerozoic using mass balances for the input and output fluxes to/from the oceans of different forms of carbon (carbonates, organic C) and of sulfur ($CaSO_4$ and pyrite). From changes in organic C and pyrite S weathering and burial rates, obtained from the model, values of changes in O_2 could be calculated (as explained earlier in the discussion of the Berner and Canfield modeling.) The problem was that the resulting mass of atmospheric O_2 obtained from the isotopic data fluctuated over time far too widely, from unrealistically high values to negative values. I tried every conceivable feedback mechanism and none were found sufficient to stabilize O_2 to reasonable values. One method, used earlier by Canfield and myself, involved division of carbon and sulfur reservoirs into "young" and "old" portions. The idea was that the young, more recently deposited organic matter and pyrite portions would be subjected to weathering more quickly, by uplift or sea level change, than older portions that were too deeply buried to undergo appreciable weathering. This provided negative feedback but not enough to give reasonable O_2 values via isotopic modeling.

The idea then hit both Steve and myself; why not let the isotopic fractionation of carbon and sulfur be a function of the level of O_2 with higher O_2 favoring greater fractionation? This led immediately to sufficient feedback to stabilize O_2 variations that appeared physically reasonable. The resulting O_2 values also greatly resembled those obtained by Berner and Canfield using a totally independent method. This was a

Eureka moment! However, is it reasonable that carbon and sulfur isotopic fractionation is actually a function of the level of atmospheric O_2? We needed independent confirmation of this new idea of O_2-dependent isotopic fractionation.

We got the confirmation! In the meantime I had met a plant physiologist named David Beerling at a meeting in London and asked him if he could perform experiments for plant growth under varying O_2 concentrations and measure the carbon isotopic fractionation between the plants and the CO_2 from which they grew. He did this in his lab at the University of Sheffield and found that higher O_2 levels do in fact increase carbon isotopic fractionation during growth. He could even explain it theoretically. The ratio O_2/CO_2 affects whether a plant undergoes more or less photorespiration, a process that competes with photosynthesis. Higher O_2 favors photorespiration and should result in greater carbon isotopic fractionation.

David and coworkers, Steve and I submitted a paper to Science on our results, but the reviewers insisted that we show that the O_2 fractionation effect would also affect marine photosynthesis. This led to my collaborating with oceanographic colleagues at the University of Hawaii who at that time were studying carbon isotopic fractionation by photosynthetic marine plankton. I asked Ed Laws and Brian Popp there to conduct isotopic fractionation experiments by varying the O_2/CO_2 ratio. They did and got results similar to those obtained for land plants by Beerling and co-workers. This settled the matter in our eyes. We resubmitted an expanded paper to Science, that included the results for both land plants and marine phytoplankton, and the paper was accepted. It was published (Berner and others, 2000) and also included our favorable comparison of values of O_2 over time via the isotopic method with those derived from the rock analysis method used much earlier by Canfield and myself. Including the co-workers from Sheffield and Hawaii, there were eleven co-authors. Results are shown in figure 12. Steve in the meantime got his Ph.D. and left Yale to become a post-Doc at Woods Hole oceanographic Institution followed by an assistant (now associate) professorship at the University of Massachusetts (Amherst).

The laboratory experiments proved only that changes in O_2 affect carbon isotopic fractionation. But what about our assumption of O_2 affecting sulfur isotope fractionation? Analogous experiments on sulfur could not be made because sulfur isotope fractionation is affected by many factors in the marine environment that are not easily reproduced in the laboratory. I made the assumption that greater sulfur isotopic fractionation should follow higher atmospheric O_2 levels based on findings at that time by Don Canfield and others. He found that unusually high fractionations between pyrite and sea water sulfate can result when there is a recycling process near the sediment-water interface where isotopically light sulfides, produced by bacterial sulfate reduction, are subsequently oxidized to intermediate sulfur oxidation states (those lying between sulfide and sulfate). Disproportionation of the intermediate sulfur oxidation states leads to sulfide that is further fractionated to lighter values than the original sulfide that underwent oxidation. My reasoning was that at higher atmospheric and oceanic O_2 there would be greater oxidation of sulfide near the sediment-water interface, due both to the higher O_2 and to greater mixing of O_2 into the sediment by increased bioturbation. This would lead, after disproportionation, to greater overall fractionation between sulfate and sulfide. This idea, however, needs independent confirmation.

Earth System Science and Founder Jacques Ebelmen

Having done a lot of work on the evolution of O_2 and CO_2, I realized that simple representations of the interaction of processes, including feedbacks, would be useful. I was impressed by the use of cause-effect or systems diagrams by my colleague, Barry Saltzman, to represent the interaction between CO_2, global climate, and ice sheet formation during the Pleistocene. I decided to apply the same approach, of systems

Fig. 1. Plot of carbon isotopic fractionation as a function of % O_2. $\Delta(\Delta_C) = \Delta_C - (\Delta_C)_O =$ change in fractionation from that for 21% O_2. Curves derived from Eq. 1 are shown for different values of J, with the experimental data fitted by $J = 2.5$. Solid squares represent the vascular plant results of Table 1; open circles are calculated from the data presented in Table 2 for *P. tricornutum* growth in seawater at 25°C equilibrated with 330 ppm CO_2 (*31*).
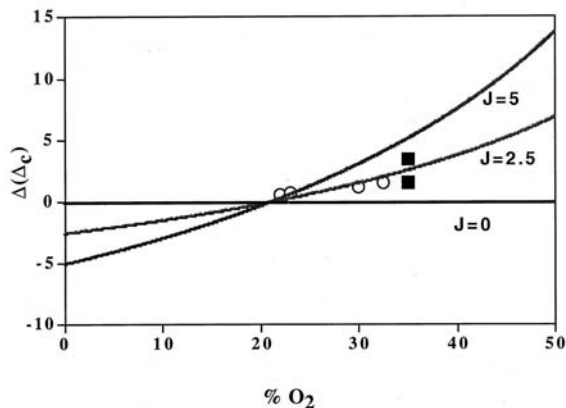
Fig. 2. Plot of O_2 versus time for the Phanerozoic calculated by isotope mass balance modeling (the present study) and by the abundance of organic carbon and pyrite sulfur in sedimentary rocks (*15*). The upper and lower lines represent the range of estimated errors for the results of the rock abundance modeling.
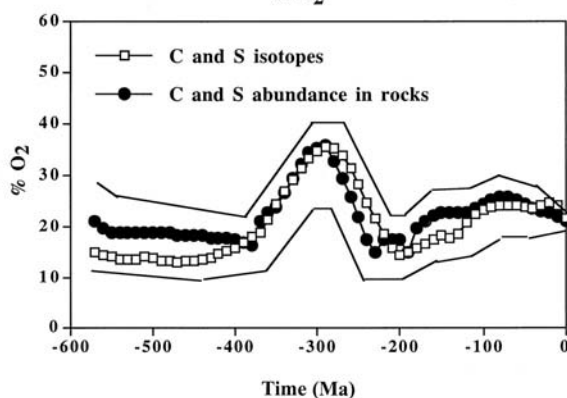
Fig. 12. Plots of (1) experimental carbon isotope fractionation during photosynthesis, as a function of atmospheric O_2 level (J is a measure of sensitivity) and (2) atmospheric O_2 versus Phanerozoic time (past 550 million years) calculated from carbon isotopic and rock abundance data (reproduced from Berner and others, 2000).

diagrams, to the factors affecting O_2 and CO_2 on a global basis and a million year geological time scale. This led to publication of a paper in GSA Today in 1999 entitled "A New Look at the Long Term Carbon Cycle." A slightly revised reproduction of a diagram from this paper (Berner, 1999) is shown in figure 13. (Expansion of the use of these diagrams to a number of separate diagrams has since been done—Berner and others, 2003). Arrows between one subject or substance and another represent causes leading to effects. Arrows with no attached bullseyes, represent direct causes and effects. For example, if CO_2 goes up, then temperature and rainfall go up (via the atmospheric greenhouse effect). Arrows with attached bullseyes represent inverse effects. For example, as weathering of silicates goes up, CO_2 goes down. Following a cycle around, if the sum of arrows with bullseyes is an odd number, this represents negative feedback. A cycle with one bullseye (labeled B-L-G) is: rise in $CO_2 \rightarrow$ higher temperature and more rainfall (climate) $\rightarrow$ more silicate weathering $\rightarrow$ drop in CO_2. This is the important negative feedback climate control that we used in the BLAG model. Another example of negative feedback (D-E-C) is: rise in $O_2 \rightarrow$ loss of land plants by fires $\rightarrow$ decreased organic carbon burial $\rightarrow$ drop in O_2. Most of the feedbacks in the diagram are negative leading to stabilization of conditions on the surface of the Earth. However, one can find an occasional positive feedback by following a cycle with an even number or no bullseyes. An example (B-J-K) is: increase in $CO_2 \rightarrow$ higher
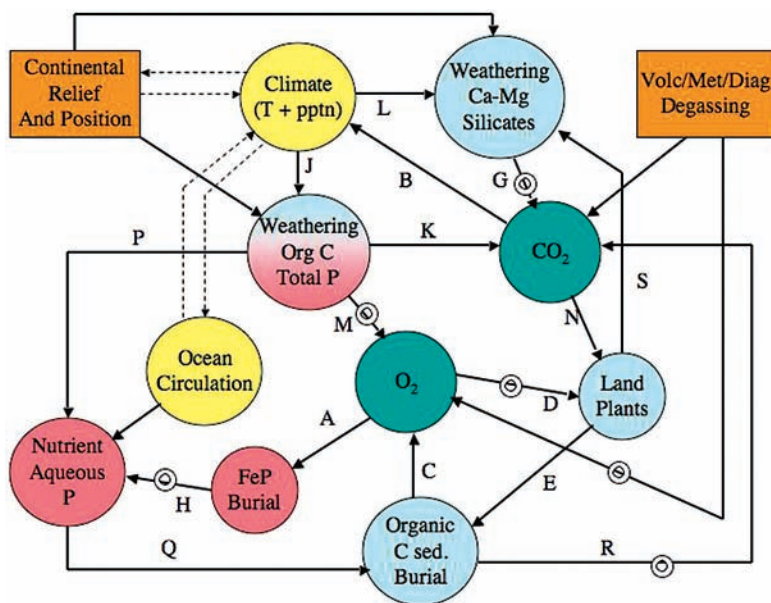
Fig. 13. Systems diagram for the long term (multimillion year) global carbon and phosphorus cycles. For explanation see text (after Berner, 1999).

temperature and more rainfall (climate) → faster oxidation (weathering) of organic matter → increase in CO_2. Geological forcing by changes in continental position and relief (as it affects erosion and silicate weathering), and degassing of CO_2 (plus reduced gases that react with O_2), are almost all independent processes that are not affected by the other subjects or substances. As a result no large arrows return to these geological factors. (Enhanced relief after plateau uplift, can lead to increases in erosion and weathering due to increased rainfall. This is an exception shown by light dotted lines.)

Phosphorus is an important nutrient for ocean productivity. Thus, the diagram also includes the phosphorus cycle. Organic carbon and total phosphorus are lumped together because much organic-rich sediment is accompanied by both organic P and carbonate fluorapatite-P. This means that weathering of organic matter in rocks consumes O_2 while weathering of the co-existing phosphorus leads via the loop (P-Q-C) to O_2 production. Also, the formation of phosphate associated with iron oxides (FeP) robs the ocean of nutrient P, which lowers organic matter production and burial and therefore, leads to a decrease in O_2. Lower O_2 should lead to less oxidized iron in sediments and less FeP. This loop illustrates another negative feedback (H-Q-C-A).

Although no systems diagrams existed at the time, the major processes affecting the concentrations of O_2 and CO_2 in the atmosphere were deduced long ago by Jacques Joseph Ebelmen. In a paper published in 1845, he correctly listed all of the major processes involving the long term cycles of both carbon and sulfur that affect atmospheric CO_2 and O_2. Ebelmen was so far ahead of his time that the same processes were deduced independently only much later in the period 1950–1980 by such eminent scientists as Harold Urey, Robert Garrels, and H. D. (Dick) Holland.

The discovery of Ebelmen's work is an interesting story in itself. A professor who was retiring from Yale had thrown out a bunch of old reprints. Kirk Maasch, a

climatology student of Barry Saltzman, found a reprint concerning CO_2 that referenced an old paper by T. Sterry Hunt that had been published in the American Journal of Science (AJS) in 1880. Since AJS is published at Yale, it was no difficulty for Maasch to find the Hunt 1880 paper. Hunt's theory for the origin of atmospheric CO_2 made little modern sense and Hunt takes issue with a much older paper by Ebelmen, published in the Bulletin of the French School of Mines in 1845. Kirk told me about the Ebelmen paper, and I wondered if we could find it. Fortunately Yale has a collection of very old journals and books stored in a special repository building. I went to the repository and was able to find the 1845 paper in a complete set of Bulletins of the School of Mines dating back into the 18th century. I translated essential parts of the paper from French into English. Upon reading Ebelmen's tabulation of the processes affecting CO_2 and O_2 over geologic time, the hair stood up on the back of my head. He had all the major processes figured out and expressed correctly! He even used the new chemical nomenclature devised recently by Berzelius and used by chemists ever since. I wrote up a paper with Kirk, about our discovery of Ebelmen's elucidation of the carbon and sulfur cycles as they affect CO_2 and O_2 (Berner and Maasch, 1996). I have recently (2012) written an unpublished paper about Ebelmen for the Comptes Rendus of the French Academy of Sciences and designated him as "The founder of earth system science." I realize that this is perhaps too much exuberance, but I feel that strongly about Ebelmen.

PART IV. CO_2 AND PLANTS, O_2 AND ANIMALS AND RETIREMENT
2001–2012

Collaboration on CO_2, Plants, and Evolution

During the period 2001 to 2011, I continued my research almost entirely on modeling CO_2 and O_2 over geologic time. My collaboration with David Beerling of Sheffield University continued and we published together several papers. To study the effect of varying O_2 on the fractionation of carbon isotopes during photosynthesis we determined the $^{13}C/^{12}C$ ratio of samples of carbonized fossil plant fragments, obtained from Leo Hickey at Yale. We found that in periods where I had calculated high O_2 levels, the fractionation between atmospheric CO_2 (the isotopic composition of which was calculated assuming equilibrium with marine carbonates) and plant carbon was higher and for low O_2 levels it was lower. This agreed with our experimental and theoretical studies done earlier and we published a paper along with Leo Hickey, Dana Royer and two others (Beerling and others, 2002).

David and I published a paper (Beerling and Berner, 2002) on the causes of the Triassic/Jurassic mass extinction based on his knowledge of paleobotany and my calculations of CO_2 and CH_4 levels over a 100,000 year time scale across the boundary using a BLAG-like time-dependent model. We found that CO_2 emissions by CAMP (Central Atlantic Magmatic Province) volcanism were insufficient to explain the rather large drop in oceanic $^{13}C/^{12}C$ across the boundary. We added methane degassing to the model and a reasonable methane value was sufficient to match the isotopic data. Our idea was that global warming accompanying the volcanic release of CO_2 resulted in the breakdown of methane hydrates with consequent emission of CH_4 to the atmosphere.

Later David and I published a paper in PNAS (Beerling and Berner, 2005) where we discuss feedbacks and the co-evolution of plants and atmospheric CO_2. Here was another opportunity to use systems diagrams for a complex problem. The interactions are best discussed by examining figure 14. The circles colored green represent plant physiological interactions whereas the circles colored blue recapture some of the atmospheric and geological processes discussed earlier in figure 13. Again the arrows with bullseyes represent inverse behavior and those with no bullseyes direct behavior.
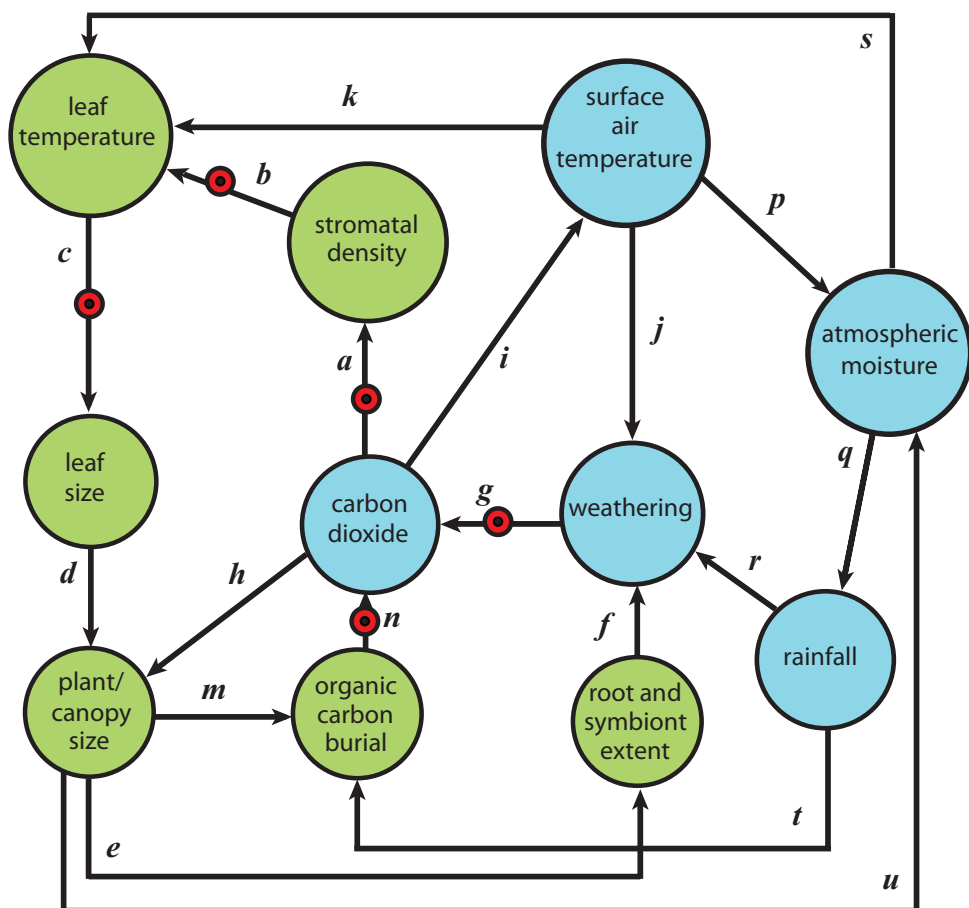
Fig. 14. Systems diagram for the interaction of CO_2 and land plants over geologic time scales. See text (after Beerling and Berner, 2005).

For example, a rise in CO_2 results both in a rise in air temperature (no bullseyes) and a reduction in stomatal density (one bullseye).

In 2009, David and I joined with a number of British air chemists and my old friend and colleague, Fred Mackenzie of the University of Hawaii, to publish a paper where the atmospheric concentration of methane, CH_4, over the Phanerozoic was calculated (Beerling and others, 2009). The key to being able to perform this calculation was the use of the abundance of coal basin sediments over time (the same data that was used by Canfield and myself in our 1989 O_2 modeling paper). We assumed that the main natural source of atmospheric CH_4 was swamps, as it is today, and that paleo-swamps and paleo-wetlands were indicated by coal basin sediments. We then normalized CH_4 emissions to calculated Pliocene values based on the relative abundance of paleo-swamps compared to those of the Pliocene. Methane has a short atmospheric lifetime and is oxidized to CO_2 at present in about ten years. To account for changing rates of CH_4 oxidation over time, already existing complex air chemistry models were employed and extrapolated back through time. Our results show that during the Carboniferous and Permian, when coal basin sediments (and coal itself) were the most abundant for all time, levels of atmospheric CH_4 were about 6 to 9 times
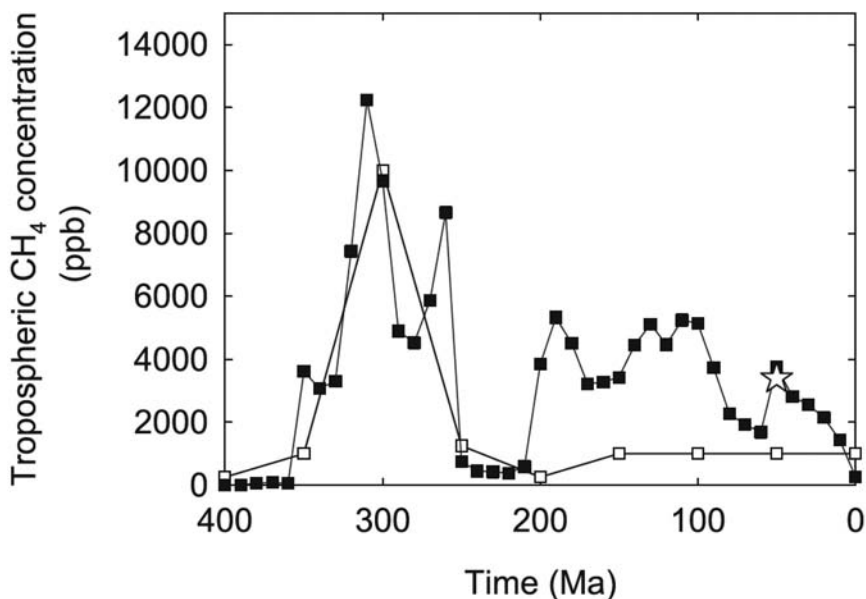
Fig. 15. Tropospheric CH_4 concentration over he past 400 million years (after Beerling and others, 2009).

higher than at present. This is shown in figure 15. Since CH_4 is a powerful greenhouse gas, this means that cooling at that time by low levels of atmospheric CO_2 should have been counterbalanced to some extent by CH_4 warming.

O_2, Fossils, and Evolution

I was attracted to the work of Peter D. Ward of the University of Washington upon reading his first book, coauthored with Don Brownlee, entitled "Rare Earth." This book proposes that intelligent life, as it exists on Earth, on a statistical basis is virtually impossible in the Universe. This appealed to me because of my reverence for intelligent life and so I contacted Dr. Ward. It turns out that he had just written another of his many popular science books "Gorgon" in which he cites my work on paleo-atmospheric composition to explain an evolutionary mystery. I found out quickly that he had also written other books on extraterrestrial life. We hit it off immediately. He proposed that we collaborate on the role of O_2 in evolution, using my just devised new model for O_2 over Phanerozoic time. In 2006, I published the new model (Berner, 2006a) for both CO_2 and O_2 by combining the GEOCARB model with my isotopic model for O_2. Because the calculations of O_2 involve the sulfur cycle, I named the new combined model GEOCARBSULF. A plot of GEOCARBSULF O_2, revised as of 2009, is shown in figure 16.

Since my initial contact Peter has written a book (Ward, 2006) on atmospheric O_2 and evolution entitled "Out of Thin Air" where he uses my GEOCARBSULF O_2 curve to describe important Phanerozoic evolutionary events, both on land and in the sea. He proposes that dinosaurs appeared during a period of low O_2 in the Triassic because they had a newly developed more efficient breathing system, better adapted to low O_2 than their competitors. This makes some sense because the descendents of the dinosaurs, birds, have an extremely efficient respiratory system that allows them to fly as high as Mount Everest in very thin air. To further the idea of the coevolution of animals and O_2, Peter and I and my student John VandenBrooks published a paper on
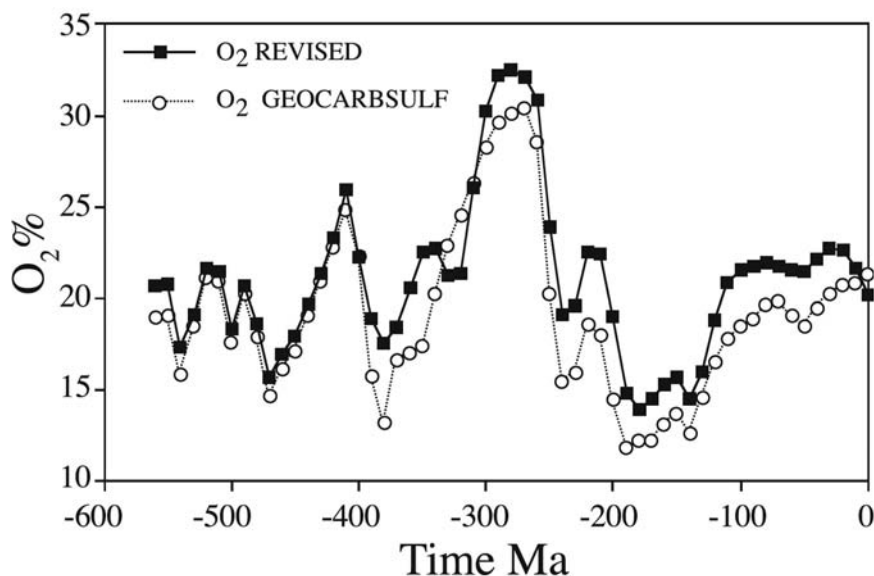
Fig. 16. Atmospheric O_2 over Phanerozoic time calculated by the GEOCARBSULF model and a revision of it to include new carbon isotopic data over time (after Berner, 2009).

this subject (Berner and others, 2007). Peter continues to pursue the idea of O_2 and evolution and is now working on a possible correlation between speciation and/or origination and atmospheric O_2 level.

During the 1990's, biologists noted that giant insects existed in the geological past during the Permian and Carboniferous Periods at the same time as that O_2 levels were much higher than at present according to my O_2 modeling. Since insects "breathe" through inlets (spiracles) on their body and have no lungs, their respiration should respond to the O_2 content of air. A giant fossil dragonfly *Meganeura* was described with a wingspan of about 80 cm, a real monster if he lived today. There were also 6 meter long millipedes making the whole thing sound like a monster movie. The idea of gigantism in the geological past correlating with O_2 level was proposed in a provocative paper by four biologists (Graham and others, 1995).

At about the same time Jon Harrison of Arizona State University was studying the effect of varying O_2 concentration on insects and he found enhanced flying ability in dragonflies with elevated O_2. After many requests I convinced another scientist, Robert Dudley, now at the University of California at Berkeley, to look at fruits flies (*Drosophila*). Fruit flies have a very short life span and as a result, one can see if changing the size of the flies grown under different O_2 levels could be inherited and not just a simple example of phenotypic plasticity. After raising five generations under elevated O_2 (23%) resulting in larger size, he placed the fifth generation in normal 21 percent air and their offspring retained the larger size. They had been selected for higher O_2 and they passed on their O_2-induced larger size genetically. These results and a review of Phanerozoic oxygen can be found in the paper by Berner and others (2003).

The idea of animal size and O_2 had occurred to Peter Ward and me and I wanted a graduate student to do some experiments to see if higher animals, not just insects, would grow larger under elevated O_2. Propitiously a new graduate student, John Vanden Brooks (mentioned earlier) arrived at Yale with an excellent background in chemistry, but he wanted to study paleontology. I took him on as an advisor. I hoped to

persuade him, with much help from Yale vertebrate paleontologists, Elisabeth Vrba and Jacques Gautier, to study the growth of alligator eggs under different levels of atmospheric O_2, as suggested by Elisabeth. He did agree to do this. But first he had to go to Louisiana and steal eggs from an alligator nest while the mother was away, grab some eggs and get back into his swamp boat before being eaten alive by the mother. He performed this feat admirably. Back in the lab he found that the alligator embryos grew faster and hatched sooner at elevated O_2 levels above the present value of 21 percent, and grew slower at lower O_2 levels. Now for reptiles, as well as insects, O_2 had an effect on body size. He has never published this work but a later study by others found that both alligator embryos and young live alligators grow faster under elevated O_2. Since leaving Yale with a Ph.D., John has worked with Jon Harrison on insects and, following Jon's earlier work, he has directly demonstrated that dragonflies grown under elevated O_2 in fact become distinctly bigger. The theory of high O_2 causing larger sizes I believe is now generally accepted.

The Phanerozoic Carbon Cycle

In 2004, I published a book (Berner, 2004) entitled "The Phanerozoic Carbon Cycle; CO_2 and O_2." In it I describe all the details of how I construct my GEOCARB and other models for CO_2 and O_2. An important aspect of the book is that in the first chapter I explain the differences between the short term and long term carbon cycles. The short term or earth-surface cycle, that which is normally thought of simply as the carbon cycle, involves the transfer of carbon between the atmosphere, life and the oceans on time scales ranging from days to centuries. The long-term cycle involves the removal of carbon from the short term cycle by its burial in sedimentary rocks. The carbon is ultimately returned to the atmosphere and oceans, after millions of years of burial, by volcanic and metamorphic degassing, resulting from the thermal breakdown of carbon-containing rocks, and by the oxidative weathering of old sedimentary organic matter. Unfortunately the book has sold very few copies, even though it is quoted often. I feel now that I could have sold more copies if I had used a more general title such as "The Geological Carbon Cycle," but I felt it misleading to use that title because I do not discuss the rest of geological time, the Precambrian. I have avoided applying my modeling to the Precambrian because the necessary geological and biological input data over that time I feel is either lacking or controversial.

O_2 and Burning

Elevated O_2 should cause an increase in the frequency of forest fires. Were there more and larger fires during the Permian and Carboniferous when O_2 was unusually high? Jennifer Robinson, of Murdoch University in Western Australia has stated that trees of this age show signs of having thick bark and other properties that would make them more fire resistant. Experiments with the effects of varying moisture and O_2 concentration on the flammability of paper was studied by the GAIA group in England and the conclusions were that at the high levels of O_2 that I had calculated for the Permo-Carboniferous (30-35% O_2), fires would burn, even when plants were wet. This would mean that my high Permo-Carboniferous paleo-O_2 values must be too high; otherwise there could not have been any Permo-Carboniferous forests and forests have existed continually since the Devonian Period over 400 million years ago.

I decided to fight back because I didn't believe that paper was a good representation of trees, which contained much more fire resistant lignin in their wood than cellulose, the major component of paper. I had a laboratory assistant, Richard Wildman, who had been my undergraduate advisee when he was in Yale's chemistry department. He is a most industrious and clever person and he accepted my challenge to come up with a better study of the burning of forest materials under varying conditions of moisture and atmospheric O_2 level. He took up the challenge and

performed incredible research. He went to a combustion engineering laboratory at Ohio State University and with their advice constructed a burning track over which air with different O_2 levels could be blown along the track. He lined the track with inch long wooden dowels or with pine needles and started burning at one end. The burning as it spread along the track was then followed with a series of thermocouples. He wetted the dowels or needles and then dried them to specific moisture levels before using them for burning. In this way, he controlled moisture content.

The results of Richard's ingenious experiment was that from 21 to 35 percent O_2 burning of wood and pine needles does not occur at a moisture level of 65 percent which is considerably lower that that of most living plant tissue. Thus, such high O_2 levels do not mean that forests under high O_2 conditions cannot exist. We feel that his experiments were far more realistic than the former study that used paper instead of plant materials. Richard got no degree for his work, but I considered that it was enough for a Ph.D. His work was published (Wildman and others, 2004). He could have been one of my best graduate students. He left me to go to the California Institute of Technology where he eventually received a Ph.D. in environmental engineering. I hated to see him leave.

CO₂ and Plants

<p>Dana Royer was accepted at Yale to be a graduate student, but it wasn't clear whether he should work in paleontology or geochemistry. He had a great undergraduate science record and I successfully grabbed him to become his advisor while the paleontologists and geochemists argued where he belonged. Having a paleobotanical background, I set him upon the problem of the use of the stomatal density of fossil leaves as an indicator of ancient CO_2 concentration. He took to this with aplomb. He got good advice from paleobotanist Leo Hickey and decided to study *Gingko* and *Metasequoia,* both of which have a long geologic history with sufficient fossils. The density of stomata, or leaf breathing holes where CO_2 passes inward and H_2O outward, has been shown to be inversely proportional to the concentration of atmospheric CO_2. To set up a standard reference calibration Dana collected modern Gingko and Metasequoia leaves that were stored in herbarium collections. The leaves ranged in age from 150 years old to the present. Since CO_2 has varied over this period by as much as 36 percent (280 ppm-385ppm), due to fossil fuel burning, the leaf collections are useable for ancient CO_2 levels within this range. The problem with this approach is that it cannot be extrapolated to the higher CO_2 values indicated by modeling and proxies for much of the geologic past. To remedy the problem, people working with David Beerling grew plants in the laboratory under higher CO_2 concentrations and measured their stomatal density. However, the correlation between stomatal density and CO_2 at higher CO_2 values was found to be non-linear, unlike the simple linear correlation found for the herbarium leaves. At very low stomatal densities the plot against CO_2 flattened out and gave indeterminate values for CO_2. A statistical best fit was done by Dana, Beerling and others to give the best possible calibration curve.</p>

Results from stomatal density analysis (Royer and others, 2001a) was applied by Dana to the Miocene and Eocene where fossils of *Gingko* and *Metasequoia* could be found. He found values for the Miocene of 300 to 400 ppm CO_2, in general agreement with the results of others using the stomatal density of fossil leaves of completely different species. His results for the Eocene fell in about this same range except for the Paleocene-Eocene boundary where a higher CO_2 value (with necessarily large errors) of about 800 ppm was calculated. This agrees with other studies that this boundary was at a time of very high CO_2 levels, deduced by other proxy methods.

Dana Royer, along with David Beerling and I published a review of all the methods used to deduce ancient (pre-Pleistocene) CO_2 levels (Royer and others, 2001b). This includes carbon cycle modeling, stomatal density measurements, determinations of

the carbon isotopic fractionation by paleo-plankton, as measured by the $^{13}C/^{12}C$ ratio of preserved organic photosynthate compounds, the carbon isotopic composition of carbonates in paleosols, and the use of boron isotopes to deduce paleo-pH (and with proper assumptions, paleo-CO_2). The assumptions and deficiencies of each method were discussed in detail. In general, we concluded that the paleosol method was best for high levels of CO_2 but could give results that are too high and the plankton and stomatal density methods have necessarily upper limits and generally give CO_2 values lower than obtained from paleosols. The boron isotope method has a problem because it assumes that the boron isotopic composition of seawater does not change with time and because one must make assumptions about oceanic dissolved bicarbonate in order to convert pH values to CO_2 values. Carbon cycle modeling has all the errors that go into the complex assumptions used in the modeling, but the range in error of the modeling results in generally good matches with the range of CO_2 values by the proxy methods.

In 2003, a paper was published in GSA Today by Nir Shaviv and Jan Veizer that purported to discredit the correlation of CO_2 with climate and offer an alternative explanation for climate over geologic time in terms of changes in the flux of cosmic rays to the earth. Dana and I and co-authors, Isabelle Montanez, Neil Tabor and David Beerling, attempted to defend the CO_2-greenhose warming theory for climate in terms of a follow-up paper (Royer and others, 2004) also published in GSA Today. We showed (see fig. 17) that, using GEOCARB III and all existing CO_2 proxies available at that time, that there is a good correlation between CO_2 and the existence or non-existence of continental glaciation and that the proxies agree rather well with the GEOCARB calculations. This provides geological evidence that the atmospheric greenhouse effect exerts a major effect on global climate, a subject that pertains to the present concerns over global warming.

Since leaving Yale, Dana Royer has distinguished himself as an expert on fossil leaves, not only as paleo-CO_2 indicators but also as indicators, based on their exterior margin shape, of paleo-temperature. After spending a few years working as a post-Doc with Beerling in Sheffield and with Peter Wilf at Penn State, he took up a position as assistant professor at Wesleyan University in Middletown, Connecticut. He later worked with me and Jeff Park of Yale to publish a paper (Royer and others, 2007) in Nature Magazine on climate sensitivity over the past 400 million years, based on varying the relation between global mean temperature and CO_2.

Megan Andrews was my last graduate student. In my GEOCARB modeling, I was always a bit hesitant to quantify changes in global weathering rate of Ca and Mg silicates due to trees as they evolved from a gymnosperm world to one with abundant angiosperms. Megan did a field thesis in the Cascade Mountains in the western U.S. where she found an area of mixed gymnosperms (conifers) and angiosperms both underlain by the same rock type in the same microclimate. (To examine the effects of plants on weathering, it is necessary to hold constant all other factors that affect weathering, as was done by Kathy Moulton in Iceland.) Megan collected soils from beneath each tree type and then did detailed analyses of their chemical and biological composition. She found that at shallow depths the loss of Mg and Fe under the gymnosperms was extensive. However, the release of Ca, and removal from the soil, was similar for both tree types. She also showed that in areas where roots from both tree types intersected, removal of Ca and Mg by weathering was intermediate between the values for each end member tree. After receiving her Ph.D. she went to work with David Beerling in Sheffield. There she did experiments growing seedlings under different levels of atmospheric CO_2. In a recent (2012) paper presented at an international meeting, she described how she uses radioactive ^{14}C labeling to follow the transfer of carbon from CO_2 to plants, to mycorrhizae and to the soil.
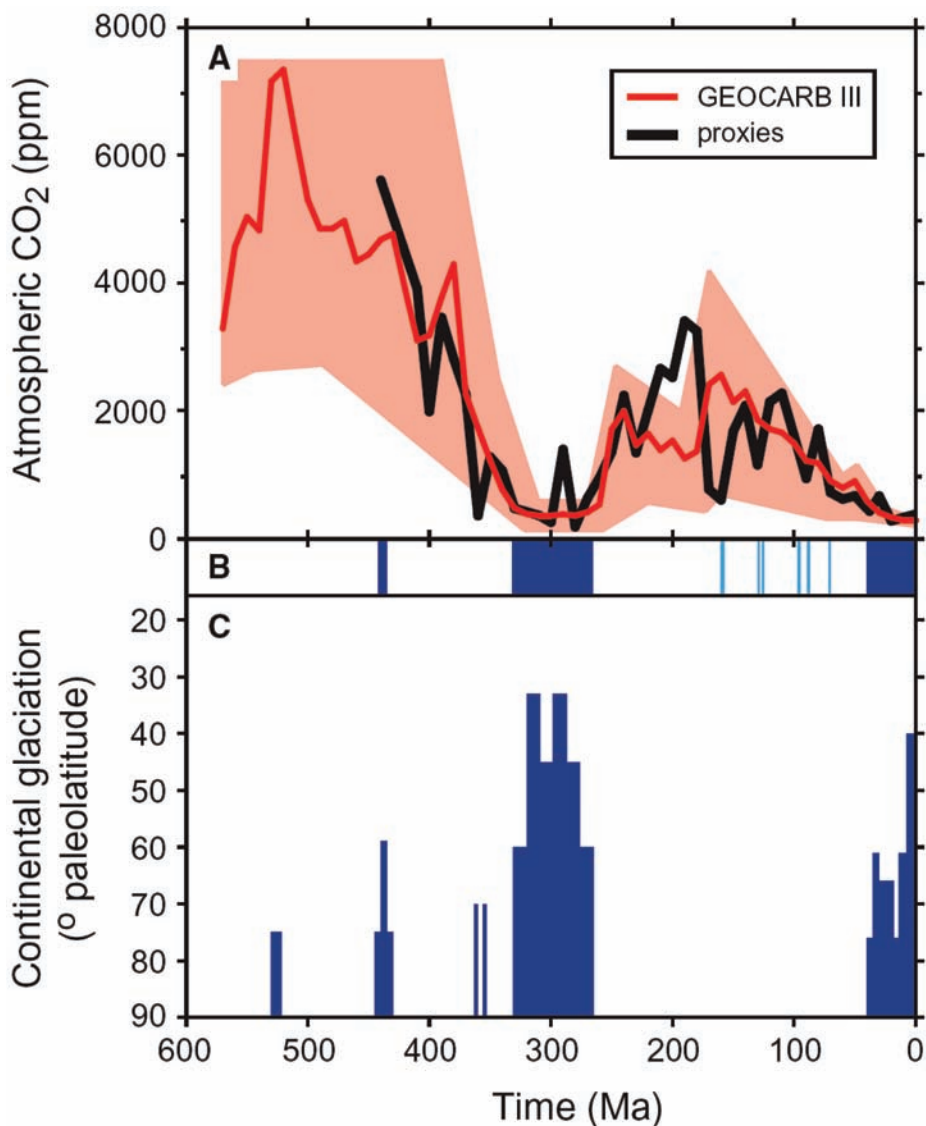
Fig. 17. Atmospheric CO_2 over Phanerozoic time from GEOCARB III calculations and paleo-CO_2 proxies. Duration and extent of continental glaciations are in blue. The pink area represents estimated errors of the GEOCARB III modeling (after Royer and others, 2004).

Retirement

I retired starting January 1, 2007. In December, 2006, the Yale Geology and Geophysics department organized a symposium in my honor with the speakers being my past graduate students and post-docs with a few former undergraduates and collaborators such as David Beerling. The talks were outstanding and I learned a lot from my former students. I was also proud of their many accomplishments since leaving Yale. I was especially impressed by the talk of Josh West, the undergraduate that had added soil analyses to the Iceland weathering study of Kathy Moulton. After
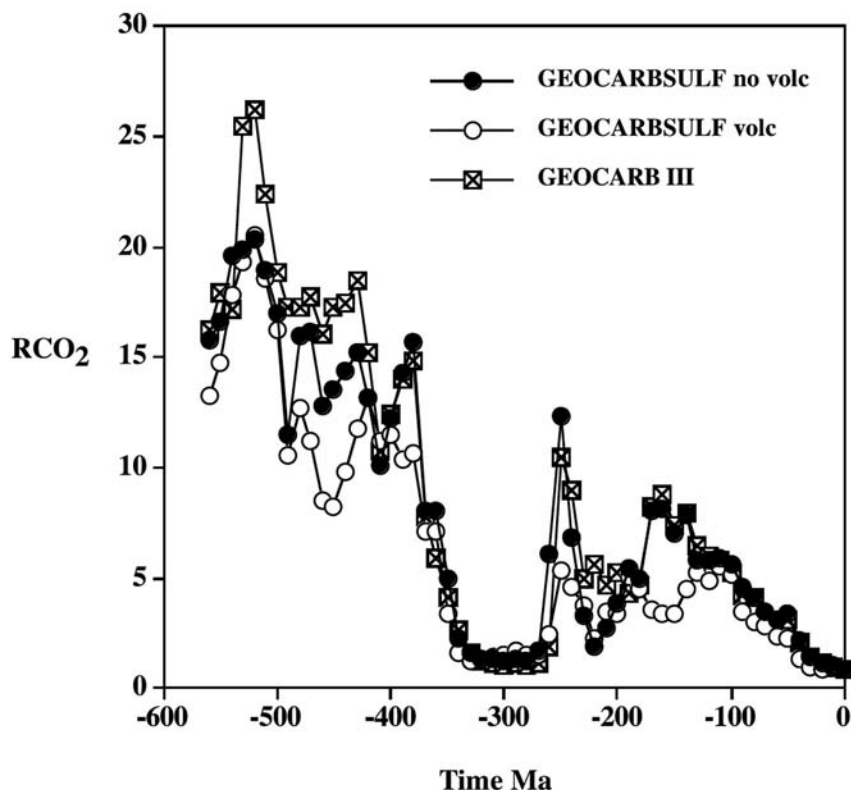
Fig. 18. Comparison of results for atmospheric CO_2 over Phanerozoic time via the GEOCARB III, GEOCARBSULF, and GEOCARBSULFvolc models. The subscript volc takes into effect the differential weathering rate of volcanics (basalt) versus plutonics (granite) (after Berner, 2006a).

leaving Yale he participated in the 2004 Olympic Games, placing 2nd in eight-man rowing, while obtaining a doctoral degree from Cambridge University (England). He is now considered a world expert on chemical weathering.

   Retirement left me free to try to finish up some lingering scientific problems, especially how to improve my GEOCARBSULF CO_2 modeling. By introducing the differences in the relative rates of weathering of plutonic rocks ("granite") and volcanic rocks ("basalt"), as guided by the strontium isotopic composition of seawater, I performed a recalculation of CO_2 over Phanerozoic time via the GEOCARBSULF model (Berner, 2006b). Results, compared to the original GEOCARBSULF model and GEOCARB III are shown in figure 18. Even with this I am still bothered by my treatment of the change in chemical weathering that results from the drift of continents into different climate zones. Because of this I have collaborated with Jeff Kiehl of NCAR (National Center for Atmospheric Research) and Yves Godderis of the University of Toulouse in France, but I have not been satisfied with my results. I know that there are still deficiencies in the GEOCARB model but I will probably never satisfy myself that I have done a complete job in producing a final version of the model.

   Being retired I had time to help my wife revise our book "Global Environment: Water, Air and Geochemical Cycles." A lot had occurred since our first edition, published in 1996. This applies especially to major advances in understanding the effects of the burning of fossil fuels on the global environment. For example, this
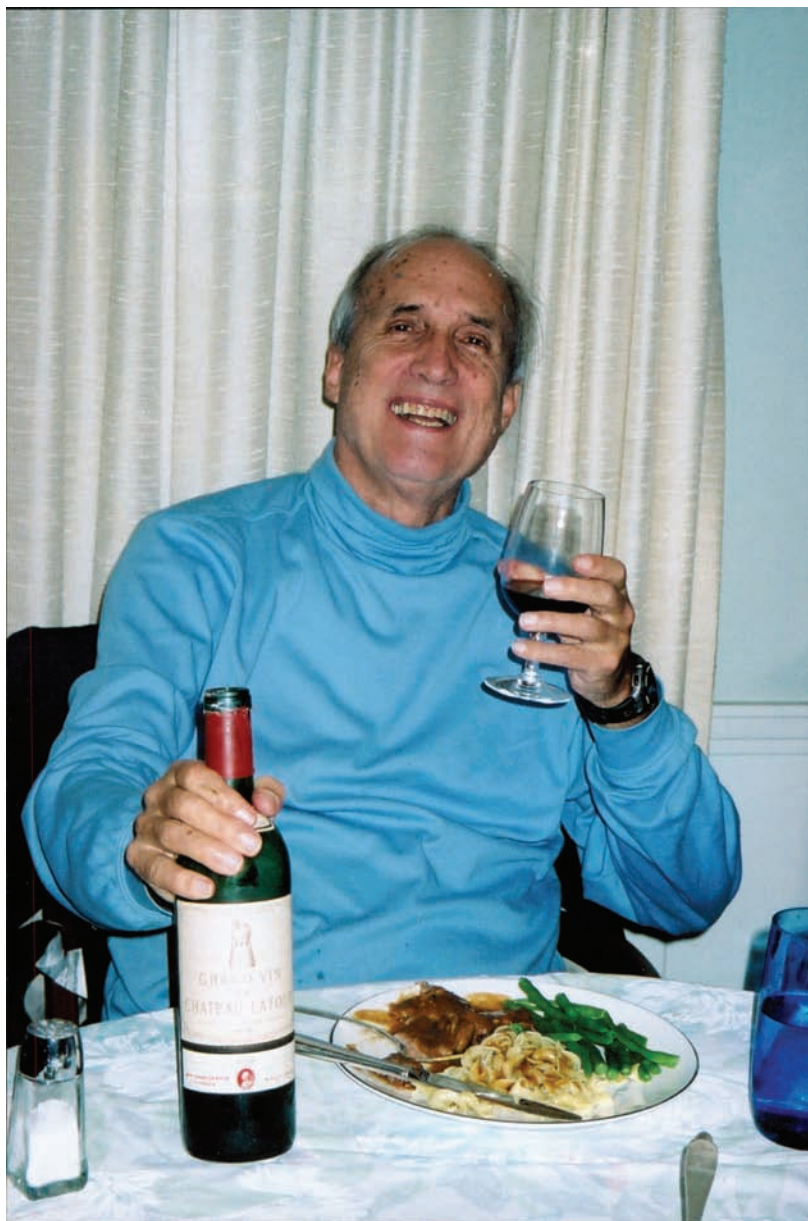
Fig. 19. Robert Berner at his 70th birthday.

includes global warming (we used the latest data from the IPCC or Intergovernmental Panel on Climate Change) and the new discovery of ocean acidification due to increases in atmospheric CO_2. Our second addition was published in May 2012 by Princeton University Press.

During retirement, I have returned to my favorite pastime (other than swimming, dining on French cuisine with fine old wines—see happy 70th birthday picture, figure 19, and watching the New York Yankees play baseball), which is musical composition. I

have been composing music since I was 5 years old and since retirement have taken advantage of a synthesizer to produce compositions for a variety of instruments including choral pieces. My musical web site can be found at: http://people.earth.yale.edu/profile/robert-berner/about/music.html.

   My last thoughts upon ending this autobiography are (1) that Earth system science has taught me that an interdisciplinary approach to science can bring about both self education and important results; it deserves a fruitful future. (2) Over the past 55 years I perhaps spread myself too thin working on so many, apparently disparate, subjects. However, there are many geological problems out there waiting to be addressed and I couldn't hold back my temptation to try to solve them. Following the example of Alfred C. Redfield, I learned long ago not to be afraid to enter new fields and stick your neck out. If I had concentrated on only one (for example sedimentary pyrite formation and the sulfur cycle), it would have been safer and I might be more easily classified. But, so be it, that is what I have done.

APPENDIX 1

MY MUSICAL BACKGROUND

   As a child I was told I had considerable musical talent. I found that I could pick out tunes on the piano from having heard them. After awhile, at about age 5, I composed my own tunes. My mother insisted that I take music lessons, but I didn't like them because I had to do finger exercises with boring sounding melodies. After a few months I quit. However, I never lost my interest in creating new tunes and melodies.

   Years later, during my late teenage years, I continued my interest in composing pieces for the piano. Certain chordal structure especially impressed me. I became enraptured by minor ninth chords, such as appear in the song "Laura," part of Debussy's "Claire de Lune" and, especially, the theme music from the movie "Invitation." At the age of 17, I wrote a piece that starts out with the standard "Blue Moon" chordal progression, but is interrupted suddenly by a dramatic shift to a minor ninth chord. I dedicated it at that time to a high school girl friend. I have since rededicated it to my wife, Betty.

   During the summer of 1955, I was enrolled in the summer Music School of Albion University, which was located near Petoskey in northern Michigan. My mother insisted I go there after a restaurant job I had near Petoskey fell apart. I again was forced to do finger exercises but now under the guidance of F. Dudleigh Vernor, who was best known as the composer of the Sweetheart of Sigma Chi. I did learn to play, for my mother when she came to visit, Debussy's Reverie which I performed in an empty concert hall, together with Vernor on the organ. The piano and organ combination sounded gorgeous. This reinforced my love of the impressionist composers. (I had already fallen in love with the music of Maurice Ravel.)

   To relieve the boredom of finger exercises, I worked on my own compositions, that were several at that time. I was especially interested in composing a piano concerto. I performed some of it for Vernor but he showed no interest and told me to go back to my finger exercises. Not much encouragement for (I thought) a budding composer.

   In 1956, I spent the summer working in Salt Lake City for an oil company. I lived on the University of Utah campus in an almost deserted fraternity house that had a grand piano. I also gained access to the music practice rooms at the university. In these two places I spent most of my spare time working on my piano concerto. I even composed a second piano part to take the place of an orchestral accompaniment. Between working and composing I did some mountain climbing in the beautiful surrounding Wasatch Mountains. When I returned to my home in Cincinnati, Ohio, I wrote down my compositions and dedicated a romantic piece to my girl friend at that time, Annette who came from Toledo and whom I had met earlier in Cincinnati. She loved it and I gave her the original score. (After we broke up, I got the score back.)

   For the next 50 years I dabbled from time to time with new piano compositions, some of which I wrote down, but my interests were almost entirely consumed by geology and geochemistry. Then a miracle occurred. I discovered in 2006 that I could compose music on a synthesizer and could add the other

instruments that I so badly wanted for my concerto. I bought an expensive one that allowed me to reproduce almost anything, from flutes, to pianos, to full sets of strings to choral voices. Since I was retired, I could return to my old love of musical composition. This has led from 2006 to date (2012) to 45 separate pieces for a variety of instrumental and vocal combinations that I have placed on the net free for anyone to listen. As I did as a youth, all this is done "by ear" since my familiarity with musical notation was never good and now has been almost completely forgotten. My music compositions can be reached at: http://people.earth.yale.edu/profile/robert-berner/about/music.html.

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