

**A GEOCHEMIST
IN HIS
GARDEN OF EDEN**

**WALLY BROECKER
2016**

ELDIGIO PRESS

Table of Contents

Chapter	Pages
Chapter 1	
Introduction.....	1-13
Chapter 2	
Paul Gast and Larry Kulp	14-33
Chapter 3	
Phil Orr.....	34-49
Chapter 4	
²³⁰ Th Dating	50-61
Chapter 5	
Mono Lake	62-77
Chapter 6	
Bahama Banks	78-92
Chapter 7	
Doc Ewing and his <i>Vema</i>	93-110
Chapter 8	
Heezen and Ewing	111-121
Chapter 9	
GEOSECS.....	122-138
Chapter 10	
The Experimental Lakes Area	139-151

Table of Contents

Chapter 11	
Sea Salt.....	152-165
Chapter 12	
Redfield Ratios.....	166-176
Chapter 13	
The Great Ocean Conveyor	177-191
Chapter 14	
The Paleo Ventilation Rates.....	192-203
Chapter 15	
Calcite Dissolution.....	204-216
Chapter 16	
Biosphere 2	217-230
Chapter 17	
Rock Varnish	231-241
Chapter 18	
Gary Comer.....	242-253
Chapter 19	
Fossil Fuel CO ₂	254-267
Appendices.....	268-313

Chapter 1

Introduction

Having nearly finished this book, I turn my attention to why I undertook such a project. Although there is no simple explanation, to be honest, it's because I love to write. Having run out of new things to say, I decided to summarize what I consider to be the major scientific accomplishments of my long career. In order to maintain the reader's interest, I have added anecdotes to illustrate the context in which my research was conducted.

As someone whose career has paralleled the evolution of my field of isotope geochemistry, and of my scientific home, Lamont-Doherty, I feel an obligation to record how I fit into these two enterprises. I must caution the reader that this book is neither a review of my field nor of my institution. Rather, it is based on my recollections. As recollections often become blurred with time, I include only those things that remain clear in my mind.

The first two chapters deal with three people who had enormous impacts on me. The first is Paul Gast who was assigned to be my 'big brother' when I entered Wheaton College. He not only got me through registration, he became a self-appointed mentor and also a friend. It was Paul who introduced me to Lamont. It was Paul who helped me through graduate school. It was Paul who joined me in directing Lamont's geochemistry program. Were it not for cancer which snuffed out his life in his mid-forties, I'm sure that we would still be close friends and colleagues.

The second person is J. Laurence (Larry) Kulp. From my arrival at Lamont on June 15, 1952, until he gave up his professorship in 1967, Larry opened one door after another, providing me with incredible opportunities. He also did wonders to build up my self-confidence. Were it not been for his persuasive skills, I would not have gotten into Columbia College without an official transcript on one day's notice, nor would I have been appointed to the faculty immediately after receiving my PhD. Although a flawed man, as a professor, Kulp was superb.

The third is Phil Orr. After listening to my first-ever scientific lecture, he realized correctly that I knew little about the world around me. On the spot, he offered a remedy. He would take me on a field trip which would open my eyes to the huge opportunities were I to choose my own samples for ^{14}C dating rather than merely providing a service by analyzing samples submitted by others. As one who had spent his entire life within 50 miles of downtown Chicago, seeing Pyramid Lake (near Reno, Nevada) and Santa Rosa Island (off Santa Barbara, California) made me realize that there were wonderful places with interesting histories awaiting study. My collaboration with Phil Orr went on for about five years. I realized along the way, however, that his motivation was not entirely pure. For by capturing me, he also captured a radiocarbon-dating laboratory at a time when there were few such facilities. Each existing lab had a large backlog and charged around 300 dollars per analysis. In connection with our research on the archeologic and climatic histories of the Pyramid Lake and Santa Rosa Island locales, Phil obtained over 100 radiocarbon ages – for free. I don't fault him for this as I got more out of my time with him than he did from the radiocarbon dates. In addition to introducing me to the world around me, he also taught me to loosen up a bit and enjoy life.

To this list of three, I must add three others: Taro Takahashi, George Kukla, and Gary Comer. One day in 1958, I walked into one of our labs and was surprised to see a young Japanese man building a vacuum system. He introduced himself as Taro Takahashi and explained that he had just returned from eight months at sea on Columbia's research vessel *Vema*. Kulp had obtained International Geophysical Year (IGY) funds to measure the partial pressure of CO_2 in surface water on a long traverse extending the length of the Atlantic Ocean. This program was designed to complement measurements of the atmosphere's pCO_2 content being conducted by Charles David Keeling. Kulp had latched onto Taro after he had just received a Columbia PhD in economic geology. Although Taro and I were both graduate students in the same department, he was one of the 'Schermerhorn group' and I was one of the 'Lamont group'. In those days interaction between the two groups was minimal. Hence my surprise as I was unaware of his existence. Little did I realize that Taro would become a life-long companion in

science. Upon completing his Lamont post-doctoral fellowship, Taro served in succession as a faculty member at Alfred College, Rochester University and Queens College (in NYC). Lured by the excitement of Lamont and bored with life at Queens, Taro gave up a Distinguished Professor position there and joined Lamont as a research scientist. At 84, he remains a full-time employee of Columbia University. Our collaboration includes research on the Bahama Banks, Green Lake (near Syracuse, NY), Biosphere 2 (in Arizona), and at Mono Lake (in California). We were both heavily involved in the GEOSECS survey and, based on the data collected, we struggled to sort out Redfield ratios. I regret that a result of my deep interest in abrupt climate change and his in the ocean's carbon cycle we have, of late, not been involved in any joint investigations.

In 1969 at a meeting in Paris, I met George Kukla, a Czech who would become a life-long family friend. I was alerted that he had made an important discovery that I should know about. When I found him, I immediately realized that he was the product of a different cookie cutter. Instead of the conventional name badge, he had pinned to his lapel a corner torn off the cardboard backing of a yellow tablet. On it, written with black magic marker, it said "Kukla". His scientific surprise was that he had put together a continental loess record which showed that, instead of the long-standing four-fold European glacial sequence, there were eight cycles since the last magnetic reversal. Further, their spacing was consistent with that for glacial to interglacial ^{18}O cycles recorded in marine sediments. I was so impressed that two years later when Columbia announced that it could invite one scientist from an Iron-Curtain country for a two-year stay in the U.S., I nominated Kukla. He was Columbia's choice and in 1971, he arrived at Kennedy Airport with his wife and two young children. His planned two-year stint lasted for the rest of his life. He remained a Lamont-Doherty staff scientist until his death in 2014. I could do a whole chapter on Kukla's exploits, but will say only a few words here. George loved the woods, the wilder the better; he loved to swim, no matter how cold the water; he loved to drink and cook sausages over bonfires. As a busy man with a large family, I had little time for close friendships. George was the exception. Our families spent many weekends together in the vast Harriman State Park.

During George's lifetime, I made several attempts to get samples of what he called 'markers'. They were several inch-thick layers of fine-grained white loess which capped each of the three soil horizons formed during the last interglacial period. George viewed each as the product of a single wind storm. Despite promises, he never fulfilled my request. However, since his death, we have obtained samples and are busily looking for clues regarding their origin.

I should add that my friendship with George was somewhat strained by his ardent denial that fossil fuel CO₂ was warming the planet. Our compromise was that this subject would not be a topic of discussion at our Friday evening get-togethers.

Late in my career, I was 'adopted' by a man named Gary Comer. I say 'adopted' because he came to me with questions about Arctic sea ice cover and almost immediately became extremely interested in abrupt climate change. Within two weeks he decided to provide twenty-five researchers with sizable monetary grants to push forward their climate research. He asked me to select the recipients (see list in the Appendices).

It didn't take me long to realize that Comer was an extremely unusual man. With no formal education beyond high school, he had launched Lands' End mail-order clothing company. At the time he came to see me, he was in the process of retiring. It was clear that he wanted to use a portion of the fortune he had accumulated to promote things he deemed important. Rather than hiring a staff to do this, he took the helm. He funded a children's hospital at the University of Chicago and a youth center in the south Chicago neighborhood where he grew up. And he found particular pleasure in working with his abrupt climate change mentors. He held meetings. He deployed his private 'air force' in support of our field efforts. He was our cheerleader, always helpful, but never meddlesome. He bragged that he was taking Paleo-Climate 101.

Unfortunately, our honeymoon with Gary lasted only four years, for he succumbed to a battle with prostate cancer. But he made sure that we were provided for. He had a special room built on his 'farm' where we could hold meetings. He donated money for a modern geochemistry building at Lamont. He left funds in his foundation for the launching of field projects. His daughter Stephanie makes it possible for us to hold abrupt climate-change meetings at the Comer

farm each year. And most important of all, Gary inspired us to work together in our quest to understand the intricacies of the Earth's climate system.

I could add many, many names to this list of people who have been important to me. However, as I can't include them all, I will stop with these six special people for each of them played a unique role in my career. I do, however, list the names of the 51 people who received PhD degrees under my mentorship (see Appendices). From Ed Olsen, my first, to Yoni Goldsmith who is about to finish, they have been my inspiration. Not listed here are the 40 or so postdocs who worked with me over the years. Needless to say, I owe much of my success to their efforts.

I must also thank the many people who have served as my life support group. As a dyslexic who can't type or use a computer, others have carried out these tasks for me. Early on it was Mary Lou Zickle and Ellen Cox. In mid-course, it was Sandy Glass, Nancy Majer and Moanna St. Claire. Currently Patty Catanzaro puts together the figures for my journal articles and lectures; Joan Totton converts my penciled drafts into typed manuscripts. My wife, Elizabeth Clark, a wonderful companion, also does my correspondence and makes appointments. I should also mention Tsung-Hung Peng who over the years conducted innumerable box model calculations in connection with our joint research and Ross Horowitz who organized a number of my field investigations.

In addition to the people who helped me along the way, I owe a tremendous debt of gratitude to Lamont-Doherty. It has been my Garden of Eden. Located across the Hudson River 15 miles to the north of Columbia's campus, it is perched on the Palisades Sill overlooking the river. Originally one of the estates owned by financier, Thomas Lamont, it was donated to Columbia upon his death. There is a photo in Lamont Hall of Dwight Eisenhower, then Columbia's president, receiving the deed from Mrs. Lamont.

The Lamont campus is 138 acres in size, about half is woodland and half research campus. Although over the years new buildings have been constructed, they are spaced in a way that preserves much of the beauty of the Lamont estate (see campus map). Below us is a small

enclave (Palisades, NY) which has served as hideaway residences for actors. Such notables as Bill Murray, Ellen Burstein, Mikhail Baryshnikov, and Al Pacino have lived there.

Although physically isolated, over the years Lamont-Doherty has become ever more closely linked to the Columbia's campus (on Manhattan's Upper West Side). Almost all of our courses are taught in the city. Currently we have a free hourly bus service to and from the main campus. Also, a large fraction of our students, postdocs and staff live in Columbia-subsidized apartments in the Morningside Heights area. Thus, we city dwellers spend our days sharing a rural space with deer, turkeys, turtles and now and then a coyote or a copperhead.

Aside from its natural beauty, the Lamont Campus serves as one of the premiere intellectual centers in the earth sciences. It attracts excellent graduate students and the best post-doctoral fellows out there. Our cast of 80 or so PhD-level scientists allows us to teach an amazing breadth of courses and provide top-notch mentorship for students and postdocs. Most importantly, it's a friendly environment. Compared to many places, over the years we have experienced little internal bickering and the extent of cooperation is unparalleled.

One aspect of Lamont-Doherty that merits special attention is our research staff. Were we to function with only the 25 or so people who have full-time faculty positions, we would rank with 50 other earth science departments. But from the very beginning Lamont has been able to retain scientists with superb credentials in soft money positions for major portions of their careers. To name a few: Taro Takahashi, Bill Ryan, Neil Opdyke, Dennis Kent, Bob Anderson, Walter Pitman, Joerg Schaefer, Gisela Winkler, Richard Seeger, Mark Langseth, Maureen Raymo and Gerard Bond – these people receive no paid sabbatical leaves and must raise a significant portion of their salaries. Despite many attempts to better their financial lot, we still have a long way to go. In the late 1970s, the University allowed us to appoint Adjunct Professors. We now have roughly one for every regular faculty member. In the early 1980s we created Doherty Fellowships for several of them. A few years ago, Director Mike Purdy got permission to use the title Lamont Research Professor. But the core problem remains. They still have to raise much of their salary from outside sources. As competition for these funds becomes

ever larger, they have to spend too much of their time writing proposals. I'm amazed that we've been able to retain such a high fraction of our staff scientists. Despite frequent offers for hard money positions, they remain at Lamont-Doherty. The lure of scientific excitement trumps that of a less stressful life. But for how long will Lamont-Doherty be able to maintain its large and excellent scientific staff?

Over the years I have paid a lot of attention to the conduct of the Lamont directors. As I treasure the place, I have had high expectations for each of them. For three of them, I became a harsh critic and supported movements designed to see them ousted. This being the case, I will write a bit about my relationship to each of the seven: Ewing, Talwani, Raleigh, Eaton, Eisenberger, Purdy and Solomon.

As two of these 19 chapters deal with aspects of Ewing's long term as director, I won't say anything further here. I'll start with Manik Talwani. Initially, I was highly impressed with him. At a young age, on short notice, he stepped into Ewing's giant shoes. It was a breath of fresh air. For me this honeymoon lasted a number of years. It began to deteriorate when we had a disagreement regarding the way we were to select what were to be called Doherty Scholars. A small number of Lamont's research staff would be given this title and with it several months of hard-money salary. The disagreement was that Talwani felt the director alone should make the selections. As we had more than a dozen imminent research scientists and were to appoint only five of them to the special position, I felt that we had to be very careful to avoid accusations of favoritism. To do this would require that the selections be done by a committee. But Talwani was adamant. As it turned out, the initiation of this program stalled and didn't go forward until Barry Raleigh took over as director. But our argument led me to speak with others regarding how Talwani was doing. What emerged was a strong sentiment that, as Talwani couldn't accept criticism, he was becoming ever more isolated from his scientific staff. An outside review committee was convened. To me, their report was disappointing for it didn't address the core problem. Rather, it criticized aspects of how our library and computer facility were being run. To my surprise, Talwani wrote an eleven-page reply to the six-page review committee report.

Manik's inability to deal with criticism triggered his removal. Although I fully agreed that Talwani should be replaced, and pushed to have it implemented, I much regret that it had to happen, for I viewed Manik as a highly intelligent and honest man and I liked him. But he had a fatal flaw.

Manik was replaced by Barry Raleigh, a seismologist from the U.S. Geological Survey. He had a quite different style than his predecessors. He was relaxed, friendly and open. It is my opinion that he did a fine job of running Lamont-Doherty. We had only one rather serious disagreement. It concerned debt money owed to the United States by Argentina and Uruguay. In connection with forgiving portions of this debt, someone got the idea of coupling it with the creation of research institutes in South America. The amounts of money talked about were staggering. My take on this was that the fights over managing the money constituted a huge tar baby. Fortunately, before this initiative could be implemented, someone pulled the plug. When Barry decided to accept a deanship at the University of Hawaii in 1989, I worried that it would prove difficult to find someone nearly as capable to replace him.

During the course of the search for Raleigh's replacement an interesting name turned up. Gordon Eaton, President of Iowa State University, made it clear that he was interested in the Lamont job. But he warned us that if word got back to his university, he would have to deny his candidacy and would be forced to withdraw from consideration. The reason he gave was that it would endanger an important Iowa State fund drive. We bought this and offered him the directorship. A huge mistake! In my view what Eaton wanted was an easy job with no stress. So he shoved his unopened mail into the bottom drawer of his desk, had nice lunches and pretty much let Lamont run itself. He wasn't a bad man. Rather, he was old and worn out. Fortunately, the Clinton Administration saved the day by hiring him away as director of the U.S. Geological Survey. As no one at Lamont was asked to comment on Eaton's suitability, I can only assume that he pulled a stunt similar to the one he pulled with us.

Despite his inadequacies, Eaton did one very important thing for Columbia University. He brought with him from Iowa State a young advisor named Michael Crow. Within a few years,

Crow had worked his way up to the number three person in Columbia's central administration (after President George Rupp and Provost Jonathan Cole). Bubbling with ideas, Crow made things move! For one thing, he made it clear that as Lamont-Doherty was a gem in Columbia's crown, we should no longer be treated as rural orphans. Crow remained on until 2001 when Rupp retired. At that point, Crow was offered the presidency of Arizona State University. Now 15 years later he remains at ASU, proud that he is creating the New American University. He is widely regarded as one of the top university presidents in America. His name pops up in the chapters which follow.

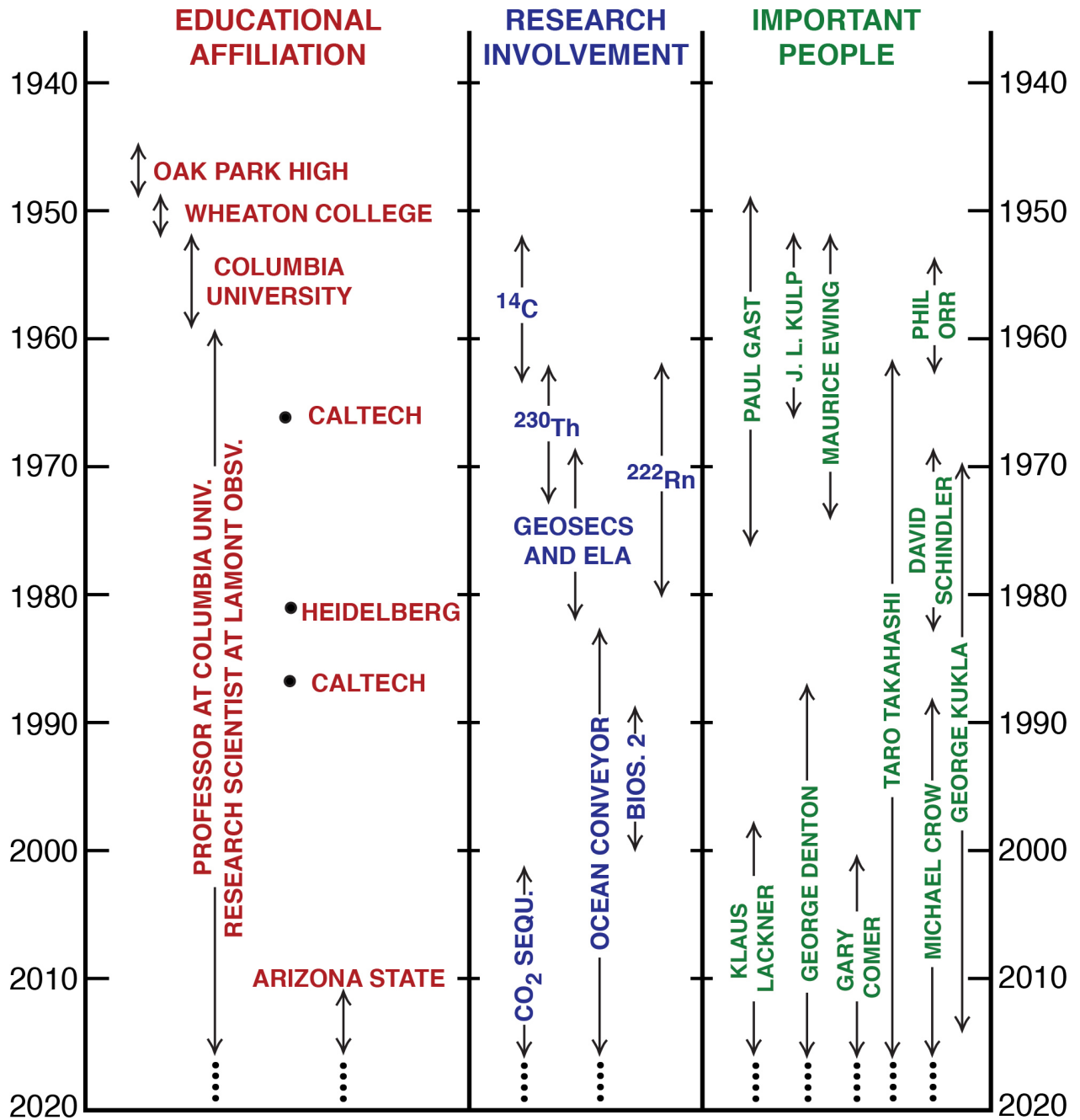
Did we learn from the Eaton debacle? No, we didn't. We turned around and offered the job to a brilliant physicist named Peter Eisenberger. In fact we compounded our mistake by offering him the chairmanship of our academic department as well. The result was unfortunate for Eisenberger didn't have the foggiest idea of how to run our place. He quickly annoyed a sizable portion of both the faculty and research scientists. In short order, he was asked to step down. I think he was probably relieved to be rid of this complex responsibility for he has remained at Columbia as professor in our department and doesn't appear to hold what happened against any of us.

Our next choice was Mike Purdy who at the time was head of the Ocean Science Division of the National Science Foundation. For the most part, he did a good job. However, as he wanted to be thorough and fair, he created many committees. In so doing, he launched us on a bureaucratic path. It was clear that he held me at arms-length. Perhaps this was because I was too old. Or maybe because I had a reputation as a fly in previous directors' ointments. While my isolation hurt my pride a bit, I was content to give up the self-appointed role as the director's watchdog. Purdy's directorship lasted 10 years. He surprised us all by accepting the position of Vice-President for Research in Columbia's central administration.

Our present director is Sean Solomon, one of the world's foremost geophysicists and a man with extensive administrative experience. I give him good marks. I have stayed out of his hair and he never asks me to do anything. So we are both happy campers.

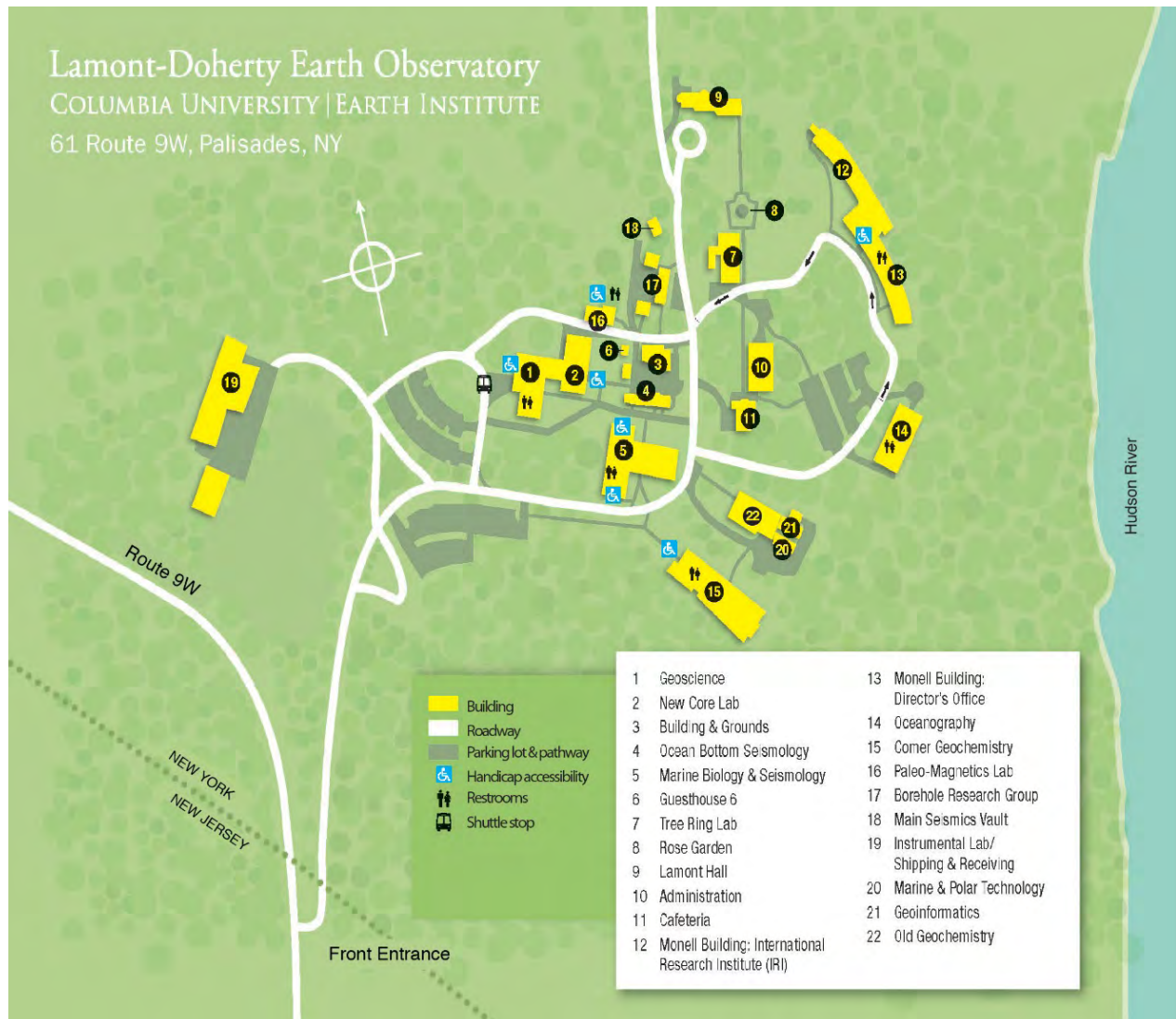
Lamont-Doherty has been good to me. I've never been burdened with administrative tasks. I've taught only classes which challenged me. I've had abundant time for research. I've always been more of an idea person than a hands-on experimenter. Over my career, I've published about 500 journal articles and written 15 books (see lists in the Appendices). In recognition, I have received a number of rewards (see Appendices) and been elected to membership in the U.S. National Academy of Sciences and the British Royal Society. I have also received honorary doctorates from Penn State, Southern Methodist, Cambridge, Harvard, Waterloo and Oxford.

MY SCIENTIFIC LIFELINE





Columbia University President Dwight Eisenhower, accepting the deed for the Lamont Estate from Thomas Lamont's widow.



Columbia University's Lamont-Doherty Earth Observatory campus.

Chapter 2

Paul Gast and Larry Kulp

My scientific career began with a series of very lucky occurrences. As a freshman at Wheaton College (a small religion-oriented, academically excellent school west of Chicago), I was befriended by a sophomore named Paul Gast. Although I did well in my classes, he realized that I had no ‘life plan.’ Despite his urgings, for two years I did nothing to remedy this deficiency. Then, at the beginning of my junior year, Paul made me promise I would make a plan. One month later, we passed on a campus walkway and he again asked what I had decided. Having done nothing, I blurted out that I would become an actuary. He was stunned and said, “Do you know how boring that would be?” Rather than giving up on me as a hopeless case, Paul made one more attempt. He alerted me to the possibility of spending the coming summer as an intern at Columbia University’s Lamont Geological Observatory in the laboratory of a former Wheatonite, Professor J. Laurence Kulp. Paul had spent the previous summer there and had much enjoyed it. Not having any other options, I agreed to apply. A week later, I was invited to New York for an interview during Christmas break.

I will never forget my flight to LaGuardia Airport. It was on what was then called a “non-scheduled” airline. The ‘El Cheapo’ flight did not go well: turbulence, spilled coffee... Because of fog in New York, we were forced to spend the night in a Columbus Ohio hotel. By morning, the weather had improved and upon arrival I hailed a taxi saying I wanted to go to Palisades, NY. Twenty minutes later, the driver stopped, saying, “Here we are.” I looked out and saw a sign reading ‘Palisades Amusement Park’. I pleaded that this couldn’t be the right place. The driver said this was the only Palisades he knew of. Fortunately I had a phone number for the Lamont lab, but as it was a Saturday morning, I feared no one would be there. To my relief, someone answered and I asked whether any of Professor Kulp’s people were around. A couple of minutes later a graduate student named Walter Eckelmann picked up the phone. When I told him where I was he laughed and said that I wasn’t even in the right state! Rather, I was in New Jersey. He then rescued me and we drove to the Lamont campus. As an Illinois flatlander, I was amazed as

we drove up the curving driveway to the rocky crest of the Palisades. He parked in front of Lamont Hall, a former residence of J. P. Morgan's protégé Thomas Lamont. Walter explained that upon Lamont's death, his widow donated the estate to Columbia University. Maurice Ewing, a seismologist, begged Dwight Eisenhower, then Columbia's President, to allow him to establish a geophysics laboratory on the property. He said that the truck traffic on Amsterdam Avenue was disturbing his seismometers. Ewing received permission and in 1949 the Lamont Geological Observatory came into being. He invited Kulp to join him. Little did I know that this estate would become my scientific home for the next 64 years.

Soon after I returned to Wheaton, I received a letter from Kulp offering me a summer job. So, when the spring semester ended, my wife of two months and I drove to Camp Shanks located about three miles from the Lamont campus. Paul Gast, who was to start as Kulp's graduate student, had arranged for the three of us to share a barracks apartment. The next day, June 15, 1952, I arrived at what would be my geochemical Garden of Eden.

Kulp assigned me to help out in his newly established radiocarbon-dating laboratory. It was being operated by three technicians who, while competent, did not go beyond their stated duties, while I, the eager-beaver summer helper, did. A whole new world had been opened up to me. I loved it!

In mid-July, I did something that in hindsight very likely made my career. The device used to measure the electron shot out when a ^{14}C atom changed itself into a ^{14}N atom (i.e., underwent radioactive decay) was malfunctioning. The center wire, maintained at several thousand volts, was intermittently arcing to the metal housing. As these tiny arcs masqueraded as ^{14}C decays, they could not be tolerated. I realized that the problem was in the narrow pass-through where the wire entered the chamber. The wire was insulated from the surrounding steel by a piece of Pyrex tubing used in vacuum systems. I suspected that when handled in summer humidity (the lab had no air conditioning), sweat stains left on the Pyrex were responsible for the arcing. One day, while passing a small electronics area shared by those in Kulp's group, I spied a spool of high voltage wire. I cut pieces the same length as the Pyrex tubes, stripped off the

orange fabric wrap, pulled out the wire and rounded the ends of the Teflon insulation. I took them to the lab and suggested that they be used in place of the Pyrex. The arcs disappeared. Suddenly I was Kulp's hero for he was able to get the ^{14}C measurements he so desperately needed.

A month before I was to return for my senior year at Wheaton College, Kulp invited me to his office. He asked whether my wife Grace would be willing to take care of his two-year-old son, Jimmy, while the rest of the family went on a cross-country vacation. We would live in his house and use his car. Eager to leave dreary Camp Shanks, we agreed. As Paul Gast was also leaving to get married, it worked out for him as well.

On the Kulp family's return, Grace and I were to stay the night and then head back to Wheaton. At dinner, Kulp said, "You know, Wally, as Wheaton doesn't have any worthwhile advanced science courses, perhaps you should transfer to Columbia College." Stunned, I replied that I would be thrilled but could such a thing be arranged on short notice. Wheaton's registration was only five days off. I assumed Columbia's was as well. He said, "Let's try," and then he said, "By the way, I will need a copy of your transcript." Of course I didn't have one so he said, "Well, write one for me." I did this and the next morning Kulp headed off to see what he could do. We had delayed our departure by one day. During the afternoon, Kulp returned, beaming "You're in. They accepted all your credits except those for a sociology course called "Criminology." So it was that I entered Columbia College.

Kulp was a handsome man with a broad smile. He dressed as a campus professor rather than in Lamont's casual style. As an ex-baseball player, he was physically fit. We, his students, held him in the highest regard for he treated us extremely well. Only later did we learn that he had feet of clay.

My senior year at Columbia turned out to be, effectively, my first year of graduate school. I took the same courses as Paul Gast. One of them was my first in geology. It was given by Professor Walter Bucher who taught a course in structural geology. He used a text by Robert Shrock titled "Sequence of Layered Rocks." He started by discussing ways to tell whether a

sequence of tectonically-disturbed sediments was upside down or right side up. All I remember is that rain drop imprints could be used. While to me the material was dull as dust, Bucher, who was absent-minded and spoke with a thick German accent, made it tolerable. Gast, Bruno Gilletti and I, as geochemists, shared the struggle to learn the stereonet (whatever that was), and at the end of the semester received B+ grades.

As this was a full-year course, registration was required for the second semester. I was told that as an undergraduate I had to get Bucher's signed permission. When I walked into his office, he took one look at my record and stated bluntly, "I don't teach undergraduates." I replied that I had already taken the first semester and had passed with a B+. "Well, you shouldn't have and I will not permit you to continue." He then ushered me out. When I related this to Kulp, he said that he would see what he could do. The next day Bucher signed. But he later got his revenge. Gilletti and Gast got B+ grades. I received a C-. Years later when I was inducted as an honorary member of Columbia's Phi Beta Kappa Chapter, I told this story and added that justice was done for Bucher's C- had very likely prevented me from receiving this honor in 1953.

Even though now a graduate student with a life plan, Paul Gast was always there to make sure that I didn't stumble. I remember my desperate attempt to learn French from scratch in two weeks in order to complete one of the two language requirements. Paul encouraged me to read something scientific. I insisted that my priority was to master the basic stuff. One day in our Geology Library, he handed me a book and made me promise to translate at least a couple of pages. I picked a random page and struggled through what turned out to be a description of manganese nodules. As was my habit, I kept a list of new French words and then memorized them. Two days later, I took the French language exam. I was stunned. The page I was given to translate was about manganese nodules. I passed. Then, as rapidly as I had learned French, it disappeared from my mind.

During my fourth year in graduate school, Kulp took a sabbatical leave at Oxford. He asked me to teach his class called 'Physical Chemistry for Geologists.' Although I had taken a course in thermodynamics, in Columbia's Physics Department, I had never taken one in physical

chemistry. So I learned a lot that semester. Once on the faculty, it became my course and the subject of my first book.

During a recent visit to Arizona State University, Peter Buseck, a senior professor there, reminded me that he had taken this course. He recalled that when he entered the classroom, there was no Professor Kulp. Rather, up front there was someone who looked like a high school student, erasing the blackboard. Then, to his surprise, the 'high school student' began to lecture. So at the end of my career, when at age 84 I can pass for 75, I have decided that the frequent indignities I encountered as a grad student when I was mistaken for a high school student, has paid off at the other end of my life.

A side benefit of Kulp's sabbatical was that he convinced the university to use his salary to bring in a series of prominent visitors. This turned out to be a good thing for his graduate students. The reason was that Kulp was despised by a number of important geochemists. They accused him of stealing ideas. This being the case, we were concerned that we would be shunned. However, we were pleasantly surprised by their friendliness and by their willingness to help us. Harmon Craig, one of Kulp's chief detractors, appeared to accept us at face value.

As our Geochemistry group of 15 or so was crammed into one end of Lamont Hall, Kulp campaigned vigorously for a geochemistry building. In early 1954, he got the go ahead and construction of a one-story, rectangular brick building soon began. Thanks to an inventive contractor, Bill Hans, the total cost was only \$110,000. (In 2008, we moved into a new building which cost 40 million dollars!)

Kulp had a plan to hold a grand opening in connection with a major meeting called "The Crust of the Earth Symposium," organized by Lamont's director, Maurice "Doc" Ewing. It was to be held at Casa Italiana on Columbia's campus. His idea was to have a Lamont dinner under a tent in the field facing our new building. The day before the dinner a tent was put in place. The fall weather appeared to be ideal. However, during the night the unexpected tail end of a hurricane swept through our area. The tent was blown far into the adjacent woods. The sit-down

dinner became a buffet held in the, as yet, unfurnished building. As there were no chairs, our renowned guests sat on the floor.

For me, the opening of this building presented a huge opportunity. The reason was that we were poised to change the way we measured radiocarbon. Until that point we had used Willard Libby's black carbon method, a carbon paste spun onto the inside of a steel cylinder. It was then dried by blowing warm air through the cylinder. The problem was that now and then an air mass passed over our lab bearing tiny amounts of fission products released during above-ground nuclear tests conducted in far off Nevada. Carbon black served as an excellent absorbent for aerosols. Hence we observed extra counts in our blanks attributable to fission products. As clean labs were a thing of the future, our only choice was to switch to a gas. Two ^{14}C laboratories had already gone to carbon dioxide and one to acetylene.

When Hessle De Vries, who operated a radiocarbon lab at Groningen in the Netherlands, passed through New York, he recommended that we switch to carbon dioxide. But he warned that it had to be purified of nitrous oxides which interfered with the operation of the counters. We also heard rumors that Hans Suess who operated a radiocarbon lab at the U.S. Geological Survey in Washington, D.C. was using acetylene. While it was an excellent counting gas, it was reputed to be tricky to synthesize.

Kulp decided to pay a visit to the Suess lab in order to get a first-hand briefing on acetylene. We took an early morning flight and upon arrival in the Suess lab, Kulp excused himself for a trip to the men's room. Left with a famous Austrian physicist, I was speechless. Fortunately, Dr. Suess was not. He bemoaned the fact that science loses many of its best people to administration. "It's a one way street," he said, and warned me not to fall into this trap. "To avoid it you must be a dynamic incompetent." When I asked what this involved, he replied, "Do at least three outrageous acts each year and no one will want you as an administrator." I have followed his advice. The extent of my administrative efforts was to serve one three-year term as chair of our academic department.

We decided to try acetylene. Charles Tuseck, a chemist in our group, duplicated the Suess acetylene synthesis apparatus. The critical step was to heat magnesium hydrate to the point where it reacted with CO₂ converting it to C₂H₂ (and Mg O). On Tuseck's first try, the reaction vessel exploded. Fortunately, he was not injured, but he was badly shaken and his eye brows were singed. That terminated our interest in acetylene and we decided to go the CO₂ route.

By a fortunate coincidence, I was invited to Argonne National Laboratory to see how they were doing gas counting. The coincidence was that Professor Kulp had gotten the idea that we could measure the ⁸⁵Kr produced by the atomic bombs exploded in New Mexico, Hiroshima and Nagasaki. The strength of the explosions (each equivalent to 20 tons of TNT) and the yield of the fission product ⁸⁵Kr were known (i.e., not classified). Kulp calculated that if we used krypton as the filling gas for our ¹⁴C counter, one liter would produce about ten ⁸⁵Kr decays per minute. So I ordered a liter of krypton from Lindy Air Reduction Co. in Buffalo, New York. When it arrived, I transferred it to the counter and lo and behold, I measured eight decays per minute.

Hoping to use this measurement to garner research funds, the next morning Kulp flew to Washington, D.C. to confer with people at the Atomic Energy Commission. That same afternoon, two FBI agents surprised me in the lab. "Are you the kid who did the ⁸⁵Kr measurements?" they asked. When I said I was, they informed me that I should burn any notes and never speak of it to anyone.

When Kulp returned, also chastened by the FBI, we tried to figure out why the huge fuss. It took a few months to find the answer. As it turned out, Professor Tony Turkevich at the University of Chicago had made a case that ⁸⁵Kr measurements could be used to determine whether the USSR had produced plutonium. If so, they could have nuclear weapons. As the krypton gas could not be captured when the fuel rods in a reactor were opened for plutonium recovery, the ⁸⁵Kr would leak to the atmosphere. The troposphere mixes top to bottom and pole to pole in a little more than one year so the atmosphere's ⁸⁵Kr inventory could be determined with a limited number of measurements. If this inventory exceeded the amount released by the

U.S. and Great Britain, then the extra would be Russian. Hence we had endangered the secrecy surrounding this clever method of espionage. Or so the thinking went.

It was because of this that I received an invitation to visit Argonne National Laboratory located outside Chicago in Naperville, Illinois. While there, I was given blueprints of their gas counters and their electronic circuitry. Dick Janes, an engineer in Kulp's group, was able to use this information to create the electronics for the gas counting system we installed in the new geochemistry building. Fred Gwinner, a machinist in Kulp's employ, constructed the gas counter. This facility would be mine to operate! Good fortune for a first-year graduate student.

One of the first things I did when the lab was up and running was to check an assumption made by Kulp in connection with ^{14}C measurements being made on carbon extracted from seawater. To get enough carbon for a measurement required 200 liters of seawater. As there was no way to store these large samples on a small research vessel, the carbon had to be removed at sea. This was done by acidifying the seawater (i.e., converting its $\text{CO}_3^{=}$ and HCO_3^- ions to CO_2 gas) and then circulating air round and round through the seawater and through Ascarite, a commercial CO_2 absorber. As the Ascarite was contaminated with a bit of CO_2 , before it was sent to sea an aliquot was taken from each bottle for CO_2 measurements. Kulp assumed that this CO_2 contamination was from the air and thus had a ^{14}C to C ratio the same as that in atmosphere CO_2 . But this had never been confirmed.

So, I took eight bottles of Ascarite and acidified it to release the CO_2 it contained. It was enough for a ^{14}C measurement. When I placed the CO_2 in the counter and turned it on, to my surprise, I got the same number of decays as I did from radiocarbon-free CO_2 . As the correction was sizable, the answer obtained assuming the contaminant CO_2 was 'modern' was very different than if it were 'dead'. When the proper correction was applied, the large ^{14}C ages published by Kulp became quite small. Instead of being replaced on a millennial timescale, the deep water in the Atlantic was being replaced on a centennial timescale!

At the time I made this measurement, Kulp was away and I asked his secretary to make sure he spoke with me at the first possible opportunity. While I was waiting, Lamont's Director,

Doc Ewing, called me into his office and asked how the radiocarbon measurements on seawater carbon were going. As he had built the water sampler and provided the ship time and technician for the at sea processing, in a sense he had half ownership of the project. So, I told him about my Ascarite measurement. I knew that he was already angry over Kulp's publication of the early results, so I probably shouldn't have done this. But I suspect it didn't change the way things turned out.

When Kulp returned, I renewed my plea to meet with him. I was told that he was extremely busy and would be leaving for a Geological Society of America (GSA) meeting in Mexico City in just three days. Finally, on the afternoon before his departure, Kulp came to my lab and asked what was so important. I told him about the Ascarite measurement. He thought about it for a moment and then said that, as it couldn't possibly be correct, I should repeat the measurement. I tried to tell him that there was no way it could be wrong, but he was already out the door.

A week later, I ran into someone who had attended Kulp's GSA lecture. He said that Kulp had presented the existing ocean water results with great confidence and pride. I asked whether he had mentioned problems with the Ascarite correction. He hadn't. Then, he dropped the bomb. Ewing had attended the lecture. Kulp's feet of clay were beginning to crumble.

About this time, Kulp and several members of his group launched a company named Isotopes Incorporated. Using funds provided by Texas oilmen, DeGolyer and MacNaughton, they were planning to construct an off-campus building in which to house it. In the meantime, they ran it from our Lamont lab. The company building was Kulp's fourth project with Bill Hans. First his home, second, the Lamont Geochemistry Lab, third, his church, and fourth, Isotope Inc. Kulp was a builder.

The launch of Isotopes Inc. led to a major change in Kulp's work habits. He put about half of his energy into his company and seemed to lose much of his interest in his Lamont research group. Part of this I'm sure was the result of the harsh treatment he received from his detractors.

By 1958, I had completed my PhD thesis and in 1959, I was appointed to the faculty of our Geology Department. With Kulp's diminishing interest, I was forced to pick up much of the slack. As it had from its beginning, the new radiocarbon lab was humming along. Kulp had a number of large grants that kept us going. Because of this, my new responsibilities didn't burden me.

Then, in 1965, I was invited to spend the spring semester at Caltech. I took a leave of absence, and moved my family to La Canada, California. I soon realized that I was being given a 'tryout.' If I passed muster, Caltech would offer me a faculty position. This brought two things to mind. First, with a growing family, Grace and I were stumbling along financially. Second, I could see that the lure of Isotopes Inc. was pulling Kulp ever further from Lamont. So, I wrote a letter to Ewing explaining that if I were to stay at Lamont, I would have to be promoted to Full Professor with a corresponding increase in salary. Also, we would need another isotope geochemist on the faculty. My choice was Paul Gast, who at that time was a professor at the University of Minnesota.

As a result, I was asked to fly back to New York. I vividly remember the meeting with Provost Jacques Barzun, Dean Ralph Halford and Director Maurice Ewing. At one point Ewing asked me why we needed to hire Gast. Was it because of Kulp's interest in his company? Clearly, Ewing wanted to make big trouble for Kulp. Caught by surprise, I tried to defend Kulp. I said that while he was no longer a 16-hour a day Lamont enthusiast, he did spend roughly the same amount of time on the job as my next door neighbor who was a professor in Columbia's English Department. After a few minutes of this back and forth, the provost brought it to a halt. The next day just before leaving for my return to Caltech, I learned that I would be promoted and Paul Gast would be offered a faculty position. In one sense, I had won but in another, I had lost. My once warm relationship with Doc Ewing became a frosty one.

Within a year, the situation with Kulp had clarified. A split occurred in the Isotopes Inc. group. One faction backed DeGolyer and MacNaughton, who wanted Kulp ousted as president.

The other backed Kulp but only if he agreed to leave Columbia and spend full-time running the company. Kulp chose Isotopes Inc. and resigned his professorship.

Gast accepted our offer and together we ran the Geochemistry group until he took a leave of absence at the Johnson Space Flight Center in Texas where he was to help plan the sampling and analysis program for rocks to be collected during the forth-coming lunar landing. While there, Gast learned that he had mesothelioma and that he was given only about a year to live. He remained in Texas until his death.

As Paul had never been a smoker, the question arose as to what triggered the cancer. His wife, Joyce, suspected that it was asbestos. All of Kulp's students (except me) were accomplished glass blowers. In those days vacuum systems were made entirely of Pyrex glass. When fusing together the elements of such a system, it was necessary to protect the stopcocks from the heat of the torch flame. This was done by wrapping them with wet asbestos tape. But I question this as the cause of Gast's mesothelioma. We had a lab cat named Skipper who, despite spilled mercury, airborne asbestos, and a host of other bad stuff, survived for 17 years.

There was what I consider a better explanation. As a child Gast had a serious asthma problem. Despite many attempts, his parents were not able to find a doctor who could provide relief for their son. When his mother heard of a Florida doctor, who claimed to have a unique cure, she went for it. The cure involved treatment with doses of arsenic (an illegal procedure). As is often the case with carcinogens, it took tens of years before the cancer appeared.

In order to learn what had killed her husband, Joyce Gast sent Paul's biopsy sections to Art Langer, one of our mineralogy PhDs. He worked with Dr. Selecop at Mt. Sinai Hospital, the first to put his finger on asbestos. But Art found that the biopsy material was inadequate for asbestos detection.

Regardless of the cause for Paul's premature death, it was a huge loss, not only for me personally, but also to the geochemical community. As he had pioneered the importance of large lithophile elements in the differentiation of magmas, he was on the brink of becoming a super star. But it wasn't to be.

Kulp moved on to become Director of Research at Weyerhaeuser Timber Co. in Tacoma, Washington. His successor in this position told me that Kulp had great ideas regarding plant cloning, laser cutting and Chilean forest acquisition that, if followed, would have greatly benefited Weyerhaeuser. But because of his constant bickering with management, most of Kulp's ideas were not implemented. Kulp then moved on to become Ronald Reagan's acid rain administrator. Although his decisions regarding existing coal-burning power plants infuriated environmentalists, strict regulations on new plants brought large dividends. Sulfur dioxide emissions have halved.

Kulp had never returned to Lamont. But when he retired, he decided not only to pay us a visit, but also asked to give a lecture. I was pleased to see him but his lecture was a disaster. He proposed to ease the buildup of fossil fuel CO₂ in the atmosphere by cutting down half of the Amazon trees and replacing them with loblolly pine!

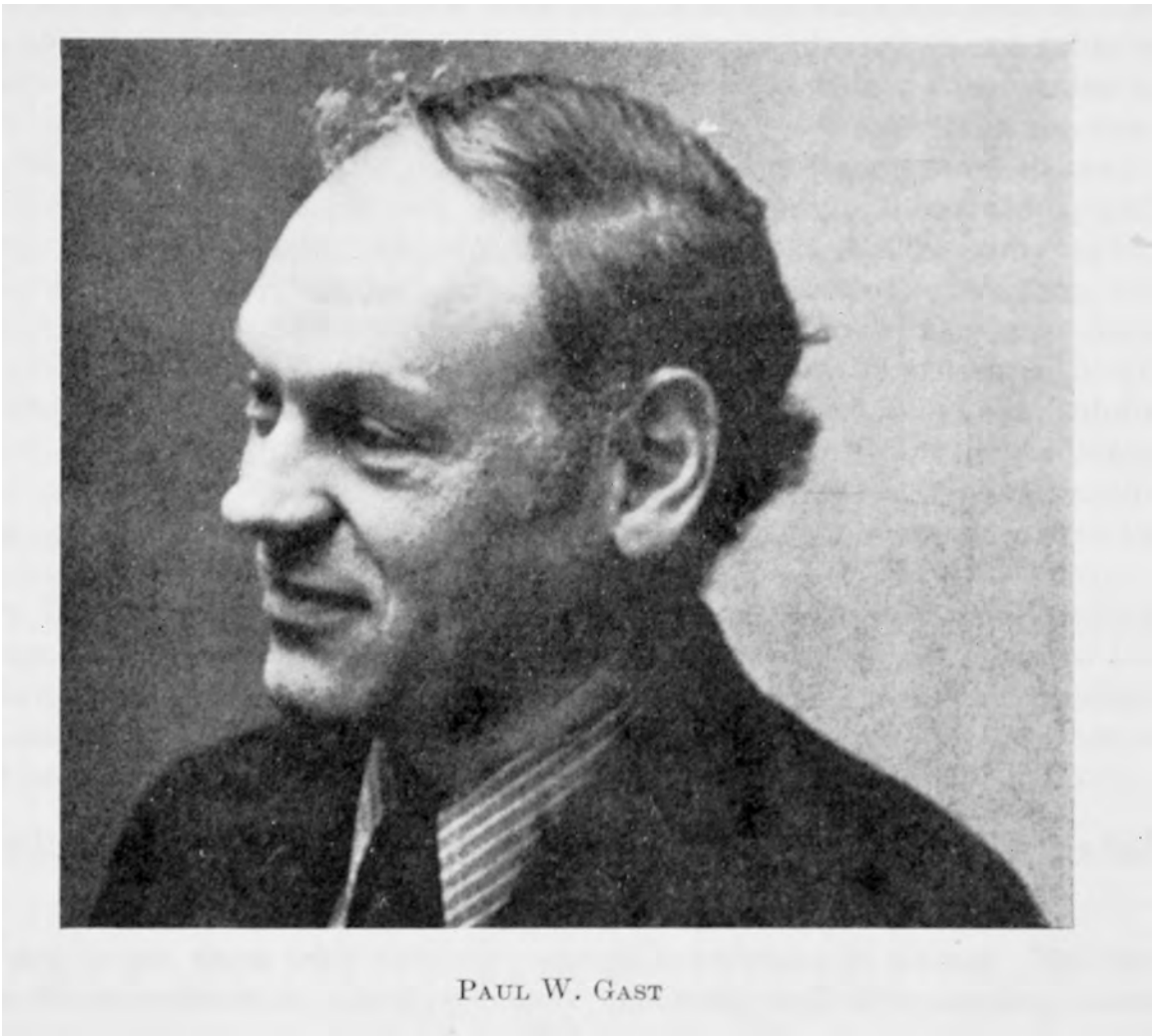
Were it not for Kulp, I would never have gained the self-confidence required to be a first-rank scientist. He rescued me with a summer job, he got me into Columbia College, he gave me a radiocarbon-dating facility to run, and he fought to secure my faculty position. As with us all, he had both great strengths and great weaknesses.



Wally as business manager of Wheaton College's 1952 yearbook. Borrowed jacket?



Mug shot of Wally as a new graduate student in Columbia University's Geology Department.



Paul Gast who took upon himself the task of directing the launch of my career. He remained my friend and colleague until his death in 1974.



Picture of Kulp's group in front of Lamont Hall (circa 1954). Kulp (with a tie) is in the middle of the first row. Karl Turekian is at his left. Bruno Giletti is behind Kulp. Walt Eckelmann is to the far left by the post. Paul Damon with a hand in his pocket is above him. Paul Gast was away making Sr isotope measurements. Where's Waldo?



My mentor, J. Laurence Kulp in the early 1950s, holding a steel housing containing the cylinder on which the carbon for ^{14}C dating is coated. He is about to insert it into the shield which kept out gamma radiation from the surroundings.



Kulp's original ^{14}C dating lab was housed in the basement of Lamont Hall. In October 1954, the lab was moved to a brand new Geochemistry Building.



J. Laurence Kulp and his wife, Helen, at the dinner held in his honor as he departed Columbia to become full-time head of Isotopes Incorporated.

References

Broecker, W.S., and J.L. Kulp (1957), Lamont Natural Radiocarbon Measurements IV, *Science*, 126(3287), 1324-1334.

Chapter 3

Phil Orr

A year after my arrival at Lamont, Prof. Kulp asked me to serve as his last minute substitute for a talk on radiocarbon dating at the Great Basin Archeological Society Meeting being held at the Southwest Museum in Los Angeles. I well remember my cross-country flight on United Airlines. In those pre-jet days, planes flew much lower and, of course, much slower. A friend lent me a copy of Arthur Strahler's book on the geomorphology beneath the NYC to LA flight path. It made the long flight quite enjoyable. I was welcomed in Los Angeles by a heat wave. The afternoon temperature reached 104°F.

This would be my first-ever lecture. It resurrected memories of the panic I experienced in my college speech class. But, as radiocarbon dating was in its infancy, I knew that I was in the driver's seat. Yes, my palms did sweat, but I got through it o.k. Even enjoyed it. Mine was the last lecture of the session and after a few questions, the room began to empty. Then I saw one attendee walking up the aisle toward the podium (and me). He was 55ish, partly bald, with a bit of a belly. His pants were tucked into cowboy boots and he had the stub of a cigar sticking out of his pipe. It didn't take me long to find out what he was about. As he approached, he looked me straight in the eye and said: "Look, kid, I can see that you know a lot about math and physics, but you don't know a goddamn thing about the Earth. Come with me for two weeks and I will change your life." Stunned, I recovered enough to ask who he was. His reply was "Phil Orr. I'm curator of archeology at the Santa Barbara Museum of Natural History." When I asked where we would go, his reply was, "Pyramid Lake in Nevada and Santa Rosa Island off the coast of California." I told him that, as a poor graduate student, I couldn't afford such a trip. He replied, "No problem; I'll pay for everything". After clearing it with my wife, I accepted his offer. The next morning we left LA in Phil's aging Ford station wagon headed for Carson City which would serve as our Nevada base of operations. As Orr had once been a curator at the museum there, for him it was a familiar stomping ground. For me, it was a whole new world.

The next day we drove north to Reno and from there northeast to Pyramid Lake. I got my first look when Phil pulled off the road onto a ridge overlooking the lake. I will never forget it. Stunningly beautiful!! Phil pointed out that during the last ice age, the lake was much larger; so large that only the very top of Anaho Island poked above the water. He said the ridge we were standing on was sculpted during the lake's highest stand. We walked to a rocky outcrop covered by a several-inch-thick lichen-coated CaCO_3 rind. Orr said it was tufa which had been deposited on the lake's ancient shoreline. It was here that I collected my first ever sample.

Phil explained that there was an ongoing debate concerning the relative ages of Pyramid Lake's elevated shorelines. In his 1899 report, Israel Cook Russell concluded that it was the youngest. But over the next half century, those who studied the shoreline history concluded that it was the oldest. I obtained a radiocarbon age of 11,500 years, a result which demonstrated that Russell was correct in his assessment.

That evening Phil took me to Harold's Casino in Reno for food and an introduction to Nevada gambling. At one point we encountered a security guard who wanted to know if I was old enough to be in the casino. Phil beamed "Not only is he old enough, he is an important atomic scientist who deals with radiocarbon." By the time Phil finished, the guard was in awe. He said that he would tell us something most patrons didn't know about, "On the 7th floor hot ovaries are being served and you are welcome to partake." Off we went only to find that the offering was hors d'oeuvres – not ovaries.

Later in the week, Phil took me to Lake Winnemucca, once a near twin to Pyramid Lake, but as a result of agricultural diversions of the Truckee River it was now dry. Our destination was a series of wave-cut caves on the lake's eastern side. To get there, we had to drive north on a highway which followed Winnemucca's western shoreline all the way to the lake's northern end. There Phil turned off onto a rarely-used dirt road which took us around the dry lake's north end and then back south on the remote east side. At one point in a sandy stretch, we got stuck, really stuck. The rear tires were six inches deep in dry sand. I envisioned a five-mile hike back to the main highway. But Phil said "never fear, we will get out." He proceeded to let most of the air out

of both of the rear tires and then with no trouble, drove out of the sand. So what now, I thought, one spare, two flats. But Phil knew what he was about. He pulled out a long hose and a wrench. The wrench was used to remove one of the sparkplugs. One end of the hose had a fitting which screwed into the plug hole and the other a fitting which screwed onto the tire valve. Once in place, Phil turned on the engine and used its compression to pump air into first one tire and then the other. I couldn't believe what I was seeing. Once done, he said, "it's time for a cool drink". He then unhooked the canvas water bag which was draped over the hood ornament and we took turns guzzling cold water.

When we finally reached our destination, I was in for yet another surprise. At the elevated level where the lake had stood during most of glacial time was a row of wave-cut caves, each about 10-meters deep with large openings facing the lake. First, we visited Phil's favorite, Fishbone Cave. He had excavated it and found human remains dating back 7500 years. Not just artifacts, but also a human skeleton, a mummy he called 'Whiskey Lil'. He showed me a picture of her propped in a chair at his desk with a bottle of Dewar's cradled in her arm.

A surprise to me was an 'attic' separated from the rest of the cave by an inch-thick layer of tufa. Apparently at one point the cave had been filled with sand upon which the CaCO_3 had precipitated. Then, at some later time, wave action removed the sand. A broken out section of the tufa ceiling allowed access to the attic. Coating the ceiling and walls was a dark brown resin which Orr referred to as 'amber-rat'. 'Amber' because it was resinous. 'Rat', (or maybe 'bat'), because it smelled like urine.

After a week of sampling adventures and casino exploits, we left Nevada and drove over the Sierra Nevada Mountains to Phil's home base in Santa Barbara, California. The only photo I have of Phil was taken in front of the Santa Barbara Museum of Natural History.

From there, we were picked up by a small vessel operated by Scripps Oceanographic. It ferried us 30 miles across the channel to Santa Rosa Island. Except for a small Coast Guard base, the entire island belonged to a man named Al Vail. As are the other of the Channel Islands, Santa

Rosa is quite dry. It was sparsely inhabited by Vail's ranch workers, a small number of cattle, wild boar brought in by the Spanish, and evil-smelling endemic foxes about the size of cats.

Phil was interested in the Paleo-Indians who had once inhabited the island. He had uncovered abundant evidence for mid-Holocene occupation. However, the primary goal of his current research was to find evidence for occupation by what he referred to as 'early man'. At the Southwest Museum meeting, I had witnessed a heated debate on this subject. The museum curators were adamant that humans were present in the Americas during the peak of the last glacial period. On the other side, university professors scorned the evidence put forward in support of this early arrival.

So on this trip and one other which followed, Phil and I scouted the arroyos and sea cliffs for evidence. At one point, I spotted a glisteningly white leg bone sticking out of the alluvium. It appeared to be extremely well preserved. On closer inspection, I spotted rib bones. They looked as if they had been thoroughly charred. I shouted for Phil to have a look. When he saw them, he danced a jig of joy. He declared that the bones were those of an endemic-dwarf mammoth and that it had been 'barbecued'. At that point, he told me that during an earlier visit he had found a human bone in deposits he deemed to be similar in age. He referred to it as Arlington Man.

Of course, in short order upon my return to Lamont, I performed radiocarbon measurements on both of these bones. The human bone yielded an age of 11,500 radiocarbon years (now that the radiocarbon time scale has been calibrated, this age becomes 13,000 calendar years). As it turns out, this age falls within the range for the oldest ages for human occupation found elsewhere in the Americas.

Phil was disappointed. He wanted it to be older. As was later made clear, carbon in porous bone was often contaminated with more recent carbon. Perhaps he was right. However, when collagen isolated from the Arlington Man bone was dated, the age came out quite close to that I had obtained. As sites of human occupation in this age range have been found throughout the Americas, archeologists puzzle at the rapidity at which humans spread. The idea is that as the ice sheets of the last glaciation melted away, humans living in Siberia managed to reach the

Americas by walking across the then dry Bering Straits. During the next millennium, they fanned out to the east coast of North America and to the southernmost tip of South America. And somehow, they crossed 30 miles of ocean to Santa Rosa Island. One idea is that these early arrivals were big game hunters. After killing off the mammoths, saber-tooth tigers and other large animals in one area, they moved on to another. Most archeologists believe this accounts for the extinction of these animals. I find it particularly interesting that these early humans reached Santa Rosa Island, for it supports the view of some that rafts were used as part of the migration strategy.

The radiocarbon date on the blackened mammoth rib gave an age which delighted Orr. It came out to be 29,500 radiocarbon years (about 32,500 calendar years). This was toward the end of what is now called marine-isotope stage 3: a time interval of intermediate climate preceding the onset of the last glacial maximum. Over the years, I have pondered the origin of the charred ribs. As Phil's barbecue theory appears to run afoul of everything we know about human history, there must be some other explanation for how the mammoth was killed and how its leg bones remained perfectly white while the rib bones turned jet black. However, I have yet to come up with a satisfactory one. Perhaps those who once pushed for a much earlier human occupation were correct. If so, the population of migrants must have been quite small and their way of life extremely primitive. Otherwise, after all this time, firm evidence of their presence would surely have been found.

In the years I worked with Orr, I learned a lot about the Earth. So, as promised, he changed my life. He also taught me how to enjoy life. During my second visit to Santa Rosa Island, he told a story which to me encapsulated this side of him. He said that he was a member of a group called 'E Clampus Vitus.' Phil said that it was a group that mocked the Free Masons. But I never could quite understand what this meant. He did, however, relate a bit of their high jinx. One Memorial Day, his cronies rented a hearse and donned frock coats and tall hats. They parked next to a large field where many picnickers were enjoying the holiday and carried a casket to the center of the field. They put it on the ground and with considerable reverence,

opened it. To the surprise of the crowd, it did not contain a body. Rather, it was loaded with beer and ice!

While writing this chapter, I had a close look at the ^{14}C ages I had obtained on samples Phil and I had collected from both Lake Lahontan and Lake Bonneville. As they were published long before we were aware of the sizable offset between radiocarbon ages and calendar ages, I have corrected them (see figures).

I have always worried about the reliability of ^{14}C dates on tufas for, during their long exposure to rain and lichens, partial recrystallization could have led to the incorporation of more recent carbon making the ^{14}C ages too young. I was surprised that the results fell into two groups, those which are consistent with more recent age dating and those which are far too young. The anomalously young group consists entirely of tufas from Lahontan's high shoreline. Back in the 1960s, I thought this shoreline was Younger Dryas in age (~12,000 calendar years). But now we know that the highstand of the lake occurred 15,500 calendar years ago. This older age is based on the radiocarbon collagen from a camel bone found by geologist Ken Adams while digging a trench in a high-shoreline beach deposit. As bone collagen has proven immune to secondary contamination and as camels eat terrestrial rather than lacustrine food, the age cannot be challenged. This being the case, my high-shoreline tufa ages are a whopping three thousand or so years too young. On the other hand, the ages for shells from the mid-elevation shoreline all fall nicely within the age limits of the last glacial maximum. So, what is the difference? My guess is that since the high shoreline tufas were plastered on rock outcrops, their exposure to rain and to lichen cover led to the incorporation of younger carbon. By contrast, the glacial-age samples were buried beneath layers of overlying sediment and hence were protected against the ravages of chemical weathering.

There is one more aspect of the tufa story which must be recounted. When it was realized that the isotope ^{230}Th (a decay product of long-lived ^{238}U) could be used to determine the ages of corals, one of my graduate students, Aaron Kaufman, decided to apply it to carbonate shells associated with Lake Lahontan's elevated shorelines. It turned out, however, that unlike marine

coral which formed free of any initial thorium, the Lahontan samples did not. The way he knew this is that the tufas and shells contained long-lived ^{232}Th . This was bad news, because the ^{232}Th would have been accompanied by ^{230}Th . Although the ^{232}Th content can be used to make a correction for initial ^{230}Th , a range of 230 to 232 ratios could be used. Hence, although Kaufman's ^{230}Th ages were in the right range, some were a thousand or so years greater than companion ^{14}C ages while others were a thousand or so years younger. A nice attempt but no cigar.

Years later, another graduate student, Jo Lin, took an alternate approach to the initial ^{230}Th correction. It involved analyzing several samples known to be the same age. The assumption was made that the initial ratio of ^{230}Th to ^{232}Th would be the same in all of them. If so, she could pin down the initial ^{230}Th correction. But she found there were two sources of common thorium. She assumed that one of these was detrital material (soil debris) trapped in the tufa and the other was thorium dissolved in the lake water. While her ages were more reliable than Kaufman's, they still lacked the desired accuracy.

An exciting event occurred during Jo Lin's struggle to write her thesis. Frustrated that I was more of a hindrance than a help, she took action with a dozen raw eggs! She stood on the lawn in front of our building and tossed them, one at a time, at my office window. My assistant, Nancy Majer, saw this and ran for help. She got my colleague, Bob Anderson, to go out and put a stop to the egg barrage. He calmed Jo down and suggested that she apologize to me. She came into my office with a smile saying that she felt better. I told her that, as neither Bob, Nancy, nor Building and Grounds were going to clean my windows, she would have to be the one. I also said that the longer she waited, the harder it would be to get the egg off. She said no problem and within a half hour the windows were as clean as a whistle.

Another advance came when Jay Quade and David McGee showed that so-called 'white carbonates' contained far less ^{232}Th than tufas. Why this is the case remains an open question. I suspect that the rusty color of tufa is caused by the deposition of the same stuff that creates rock varnish. All white carbonates were deposited at sites protected from rain and lichens. In any case,

precise ^{230}Th ages can now be obtained on ‘white carbonates’ deposited in closed basin lakes. As I write this, one of Sidney Hemmings graduate students, Guleed Ali, is writing up his PhD research involving a new record from Mono Lake based on thorium-230 dating of white carbonates. So, the project that Phil Orr initiated 63 years ago continues today.

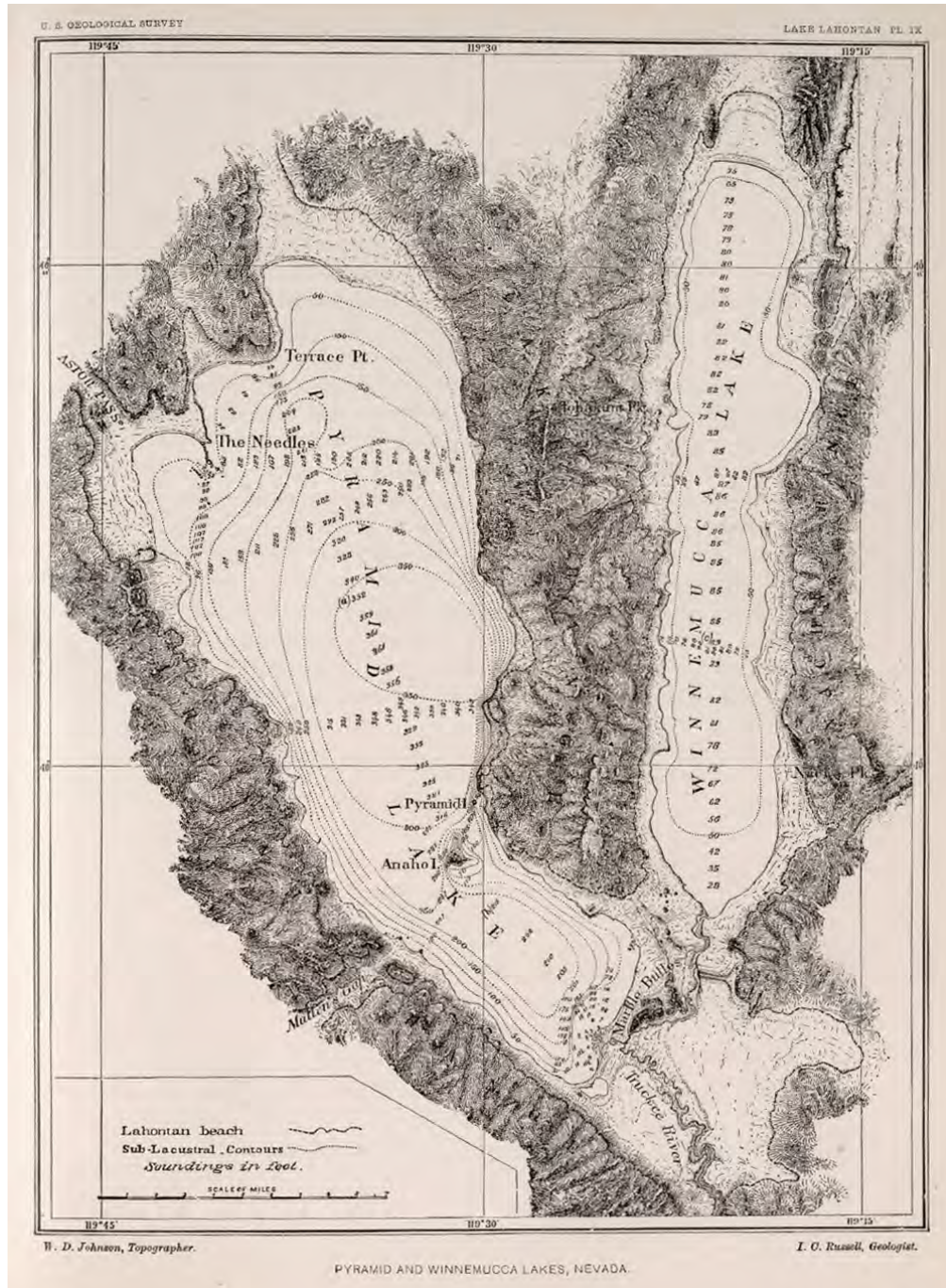
From the earliest days, I was aware that changes in the area covered by a closed basin lake constituted our best paleo-rainfall proxy. But only recently has interest picked up. One reason is that the ability to produce reliable ages has greatly improved. The other is that the ^{18}O record kept in stalagmites has added a new dimension to paleohydrology research. But it remains unclear as to how these records relate to rainfall. The solution appears to be pairing stalagmite records with those for closed basin lakes as a means of clarifying this situation.



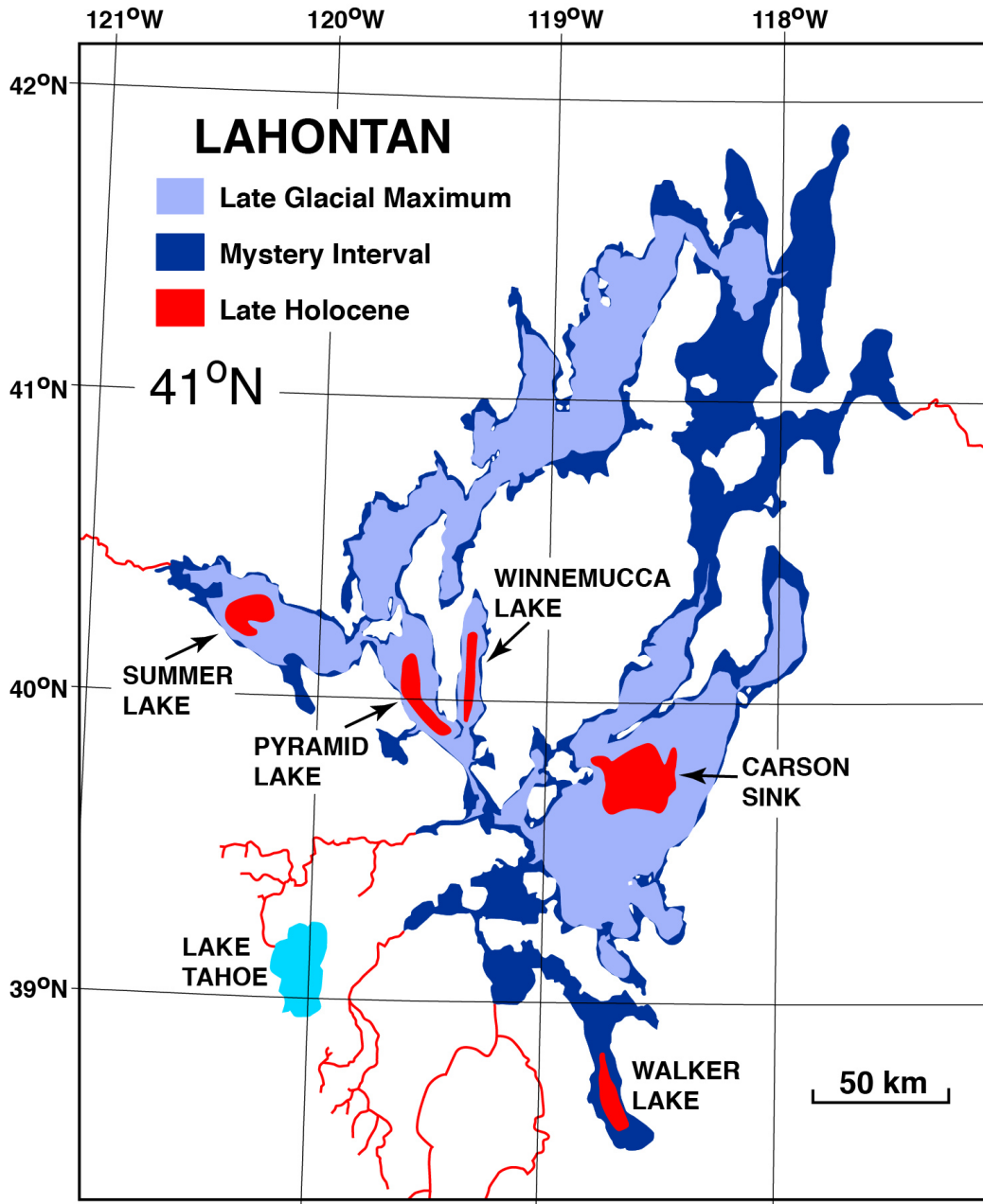
The only picture I have with Phil Orr. We were in front of the Santa Barbara Museum where he was employed as curator.



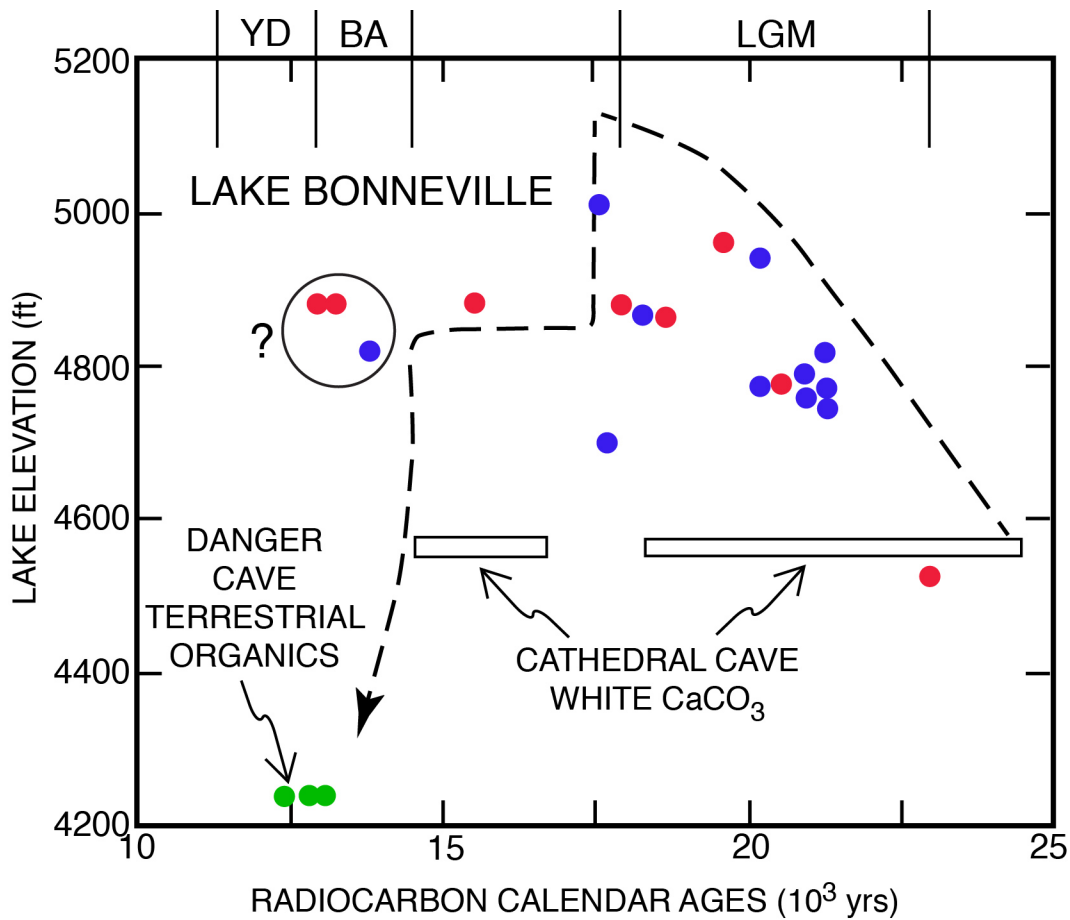
Pyramid Lake is named for one of its islets (see foreground) which formed over a hot spring vent when the lake was much larger. During the lakes highest stand (15.5 kyrs ago), only the tip of Anaho Island (see background) projected above the water. It is puzzling that CaCO_3 deposition, so common during high-water periods, ceased during the Holocene.



Bathymetric maps of Pyramid and Winnemucca Lakes as they existed in the late 1800s. When I first visited the area in 1954, as the result of diversions of the Truckee River for agricultural use, Winnemucca was dry. The locations of the famous Pyramid and of Anaho Island are shown. This map was published in a U.S. Geological Survey memoir authored by Israel Cook Russell.



Only four small remnants of once huge Lake Lahontan (Pyramid, Winnemucca, Summer and Walker) survived the Holocene desiccation. Winnemucca succumbed to agricultural diversions from the Truckee River. Carson Sink is more of a swamp which periodically dries out. Walker Lake was a separate basin except during the Mystery Interval (~15.5 kyrs) when Lahontan stood at its highest level. The city of Reno, Nevada through which the Truckee River flows.



Under Phil Orr's guidance, I also collected and radiocarbon dated shells from the elevated shorelines of Lake Bonneville located on the eastern side of the Great Basin. Lake Bonneville is the glacial age cousin of Great Salt Lake. At some time between 16 and 19 kyrs ago, it overflowed and cut a channel which stabilized at about 4850 feet (its Provo level) and remained there until the onset of the Bølling Allerød (BA) when the Great Basin underwent a major desiccation. As dated early on, by Willard Libby, wood and dung from Danger Cave which is only 50 meters above today's Great Salt Lake level (i.e., 4200 feet) suggesting that the lake remained low during the Younger Dryas (YD).

My early ^{14}C ages on shells (blue) are broadly consistent with more recent measurements which show that between 23 kyrs and 19 kyrs, the lakes became progressively larger and deeper. However, the two tufa ages at about 13 kyrs are certainly too young.

The dashed curve represents the current consensus view of Bonneville's elevation history.

David McGee, while a postdoctoral fellow at Lamont, obtained a series of precise ^{230}Th ages on a several-inch-thick layer of white CaCO_3 formed beneath the lake surface in Cathedral Cave. This CaCO_3 contained no ^{232}Th . His results suggest that the lake stood above 4560 feet between 24.5 kyrs and 14.5 kyrs. He views the gap between 16.7 kyrs and 18.8 kyrs as a time of non-deposition related to the lake's overflow (and hence undersaturation with respect to CaCO_3 deposition).

It should be noted that the elevations of the Broecker-Orr samples are not corrected for the warping of shorelines which occurred when the load of excess water was removed.



Coastal cliffs and stream channels cut into Santa Rosa Island's alluvial sediment deposited during the low sea stands of the last glacial period. These deposits originally extended out to the shorelines of the glacial-age low sea stand.

References

- Broecker, W.S., and P.C. Orr (1958), Radiocarbon chronology of Lake Lahontan and Lake Bonneville, *Geol. Soc. Am. Bull.*, 69, 1009-1032.
- Broecker, W.S., and A. Kaufman (1965), Radiocarbon chronology of Lake Lahontan and Lake Bonneville II, Great Basin, *Geol. Soc. Am. Bull.*, 76, 537-566.
- Kaufman, A., and W.S. Broecker (1965), Comparison of Th-230 and C-14 ages for carbonate materials from lakes Lahontan and Bonneville, *J. Geophys. Res.*, 70, 4039-4054.
- Orr, P.C. (1968), *Prehistory of Santa Rosa Island*, Santa Barbara Museum of Natural History, Santa Barbara, California.
- Lin, J.C., W.S. Broecker, R.F. Anderson, S. Hemming, J.L. Rubenstone, and G. Bonani (1996), New $^{230}\text{Th}/\text{U}$ and ^{14}C ages from Lake Lahontan carbonates, Nevada, USA, and a discussion of the origin of initial thorium, *Geochimica et Cosmochimica Acta*, 160(15), 2817-2832.
- McGee, D., J. Quade, R.L. Edwards, W.S. Broecker, and H. Cheng (2012), Lacustrine cave carbonates: Precisely dated recorders of paleohydrologic change in Lake Bonneville, *Earth and Planet. Sci. Lett.*, 351-352, 182-194.

Chapter 4

²³⁰Th Dating

During the early 1960s I became aware of efforts to harness isotopes in the ²³⁸U decay chain for dating. The focus was on ²³⁰Th, the fourth member of the ²³⁸U series. It has a half-life close to 75 kyrs and hence is ideal for late Quaternary dating. Further, the elements uranium and thorium have widely different aqueous chemistries. Uranium is highly soluble and thorium is extremely insoluble. The difference is that under oxidizing conditions in its +6 valence state uranium is strongly complexed with carbonate ion. Thorium makes no ionic complexes. Rather, it gloms onto particulate matter.

In seawater the ²³⁰Th produced by the decay of ²³⁸U is rapidly removed to the sediment. Hence, in core-top sediment there is a large excess of ²³⁰Th. With time, this excess ²³⁰Th decays away. Ed Goldberg, geochemist at Scripps Oceanographic, was the first to make use of this isotope for sediment dating. However because the magnitude of the initial ²³⁰Th excess is dependent on accumulation rate and hence on climate, the ²³⁰Th decay method was put aside.

Herbert Potratz and his student, Bill Sackett, at Washington University in St. Louis were the first to use the ²³⁰Th ingrowth method. They showed that corals incorporate uranium but, as there is so little in seawater, no measureable ²³⁰Th. Instead of measuring the disappearance of ²³⁰Th, they measured its buildup toward equilibrium with its ²³⁸U parent. Three of my early students took an interest in the Potratz-Sackett method. The first was David Thurber, a young man from upstate New York. Perhaps because of his tendency to stutter, he was quiet and somewhat shy. As I came to know him, I got a sense of the origin of the stuttering. I learned that when David was 10 years old, on the first day of spring vacation, his father berated him for failing to take out the garbage. As punishment, David was forced to drag a chain of tin cans behind himself. The second student was Aaron Kaufman, brought up in a Jewish family in New York City. Before deciding on a career in science, he had received full rabbinical training. The third was Teh-Lung Ku from Taiwan. The letters of recommendation from his National Taiwan University's professors proclaimed Teh-Lung to be their best geology student ever. All three of

these students produced highly significant theses and went on to successful careers: Thurber, as a professor at Queens College in NYC, Kaufmann, as a scientist at the Weizmann Institute in Israel, and Ku, as a professor at the University of Southern California.

Thurber got us started by adopting a new and far better way to measure the uranium series isotopes. It involved alpha-particle spectrometry. Thurber's initial interest was following up on a discovery made by a Russian physicist named Cherdyntsev, who had shown that in ground water ^{234}U was enriched with respect to its parent ^{238}U . He proposed that the recoil experienced by ^{238}U atoms when they emitted an alpha particle knocked them loose making ^{234}U more susceptible to release during chemical weathering. Thurber reasoned that if the Russians were correct, then there should be an excess of ^{234}U in seawater. To check this, using his alpha-particle spectrometer, he showed that in recent coral the radioactivity of ^{234}U was 15 percent higher than that of ^{238}U . He published a paper on this in 1962.

A few years later, in 1966, I attended an international oceanographic congress held in Moscow. As this was at the height of the Cold War, it was exciting to visit the 'enemy'. But, of course, there was no animosity. After all, we were fellow scientists. While there, Ed Goldberg and I arranged to visit Cherdyntsev's laboratory. He showed us around and he kindly provided me with acetone to mend a break in the plastic frames of my glasses. All I needed was one drop, but it had to be taken from a ten-liter bottle using a foot-long pipette!

As we were leaving, Cherdynstev asked if he could join us in our taxi. Along the way, he asked the driver to take a small detour. A few blocks later Cherdynstev pointed to a large building which, he said, housed the Russian National Academy of Sciences. Then he said he knew of someone who should be a member – but was not. When we asked who, he said “me.” When we returned to the U.S., Ed and I wrote a letter to the Russian Academy praising Cherdynstev's discovery of the ^{234}U anomaly. As we heard nothing back, I was concerned that we might have gotten him in trouble with the KGB. A few years later, I received two books in Russian from Cherdynstev's wife. By the time they were published, he had died, but she knew he would want me to have them.

The big payback came from the dating of corals. One day I got a phone call from Robley Matthews, a sedimentologist at Brown University. He had heard we were working on coral dating and he wanted us to generate ages for corals from two raised terraces on the Island of Barbados. He said he had a grant from an oil company to determine the rate at which the porosity in coral reefs was reduced by diagenesis. I agreed and when the samples arrived, Dave Thurber offered to analyze them. A week or two later with great excitement he announced that the coral from the upper terrace had an age close to 124,000 years and that from the lower one an age close to 82,000 years. His excitement (and mine as well) stemmed from our knowledge that both were from times of maximum summer insolation in the Northern Hemisphere. As each of these coral terraces represented a time when sea level crested, Thurber's results supported the idea that seasonality changes produced by cycles in Earth's orbital characteristics (i.e., tilt and precession) were driving glaciation. The stronger the summer insolation, the smaller the Northern Hemisphere ice sheets and the higher sea level.

I got on the phone with Matthews and told him the news. He replied, "I hate to tell you this, Wally, but there is a third coral terrace half way between the two you dated." He promised to send us a sample. Thurber found it to be 103,000 years old. This puzzled us because in Milankovitch's insolation record, there was no 103,000-year warm summer peak in the Northern Hemisphere.

Before divulging our solution to this problem, a few words about the origin of these terraces is in order. The island of Barbados sits behind a subduction zone. A piece of ocean crust is being thrust under it. As a result, the island is being pushed up out of the sea. We were at that time already quite sure that when the 124,000-year old terrace was formed, sea level stood a few meters above its present level. Matthews' coral terrace was about 40 meters above sea level. This suggested that Barbados was being pushed up at the rate of about 30 centimeters per thousand years. So, in a sense, the Island of Barbados was acting as a strip-chart recorder of sea level. Based on this uplift rate, we calculated sea level at both 103,000 and 82,000 years ago. At both times the sea stood about 16 meters below present level. As during the last glacial maximum sea

level stood about 120 meters below its present level, these were relatively warm times. Further, as these reefs were formed during sea level maxima, Thurber's ages provided dramatic evidence that the volume of ice tied up in the northern ice sheets was being modulated by summer insolation. In other words, Milankovitch was correct in proposing that the changes in summer insolation in the Northern Hemisphere were driving the size of ice sheets.

I struggled to figure out what the 103,000-year-old terrace was telling us. As of the early 1960s we had only Milankovitch's hand-calculated summer insolation chronologies. I realized that the shape of this record was strongly influenced by the ratio of the seasonality changes induced by the tilt of the Earth's spin axis (~40,000-year cycle) and those induced by precession of the Earth's spin axis (~20,000-year cycle). I made a set of graphs showing how the summer insolation record depended on this ratio. As the influence of the precession cycle increased, sure enough, a summer insolation peak emerged at 103,000 years. Years later when the summer insolation record was rigorously calculated, it showed that the magnitude of Northern Hemisphere summer insolation 103,000 years ago was about the same as that 82,000 years ago.

Thurber also helped to pioneer a quite different application of uranium series isotopes. It involved dating of phenocrysts contained in lavas. We gave this project to Adriano Taddeucci, a NATO-supported postdoctoral fellow from Rome. While researching Mono Lake, I became interested in the Mono Craters, a chain of explosive volcanoes extending south from the lake. A talk with Brent Dalrymple, geochronologist at the U.S. Geological Survey, led to a joint effort. Brent would conduct potassium argon analyses and we would do the uranium series analyses.

As no clear-cut separation between U and Th takes place during the formation of phenocrysts, our approach was to analyze mineral separates. As each mineral had a somewhat different ratio of ^{232}Th to ^{238}U , it was possible to back calculate the time when the various minerals had the same ^{230}Th to ^{238}U ratio. We were pleased to find that a reasonable match was achieved between our ^{230}Th dates and Dalrymple's ^{40}K - ^{40}Ar dates. However, the question remained; how long before the eruption had the phenocrysts formed? In any case, Taddeucci's

postdoctoral research launched a whole new field of petrologic investigation which continues today.

The success with corals suggested that we might be able to date marine mollusks. Aaron Kaufman took this on. He measured ^{238}U , ^{234}U and ^{230}Th in samples from raised marine terraces. It soon became clear that the uranium present in these shells could not be primary, for the ^{234}U excess was always larger than that in today's seawater. Further, when Kaufman analyzed living shells, he found no uranium whatsoever. Taken together, these two observations made clear that the uranium in the shells was secondary in origin. Our hope was that this uranium was added shortly after death of the mollusk as a result of the oxidation of organic material contained in the shell matrix. If so, once the organic matter had been depleted, the addition of uranium would cease and the secondary uranium would be sealed in place. Or so we hoped!

While a visitor at Caltech, I collected shell samples from raised shorelines along the west coast of the United States and Mexico. Kaufman's results provided hope that these assumptions might be largely fulfilled, for many of them yielded ages in the same range as those for the Barbados raised terraces. However, when Kaufman analyzed shells I collected in Italy, one result made it clear that this assumption was not always correct. That was the age obtained on a large cardium shell from a deposit thought to be near the Pliocene-Pleistocene boundary and hence about two million years old. The locale was in Rome, very near the Vatican. It gave a ^{230}Th age of only 5000 years. I joked with Kaufman that we should write to the Pope telling him we had found evidence which verified Bishop Ussher's (1581-1656 AD) estimate of the age of the Earth... This result chastened us. Instead of publishing our uranium series results on marine shells as ages, we listed only the actual measurements emphasizing that, as the uranium they contained was secondary, converting them to ages was not appropriate.

Teh-Lung Ku initially focused on uranium series isotopes in marine sediments. Soon after his arrival at Columbia, a paper was published by Ewing and Donn in which they proposed an entirely new explanation for glacial cycles. The central idea was that the Arctic Ocean was ice-free during glacial periods and it supplied the moisture needed to create the large Northern

Hemisphere ice sheets. As sea level dropped, the Arctic became isolated from the heat supplied from the Atlantic Ocean and froze over, ending the ice age.

At that time, there were no records from Arctic sediments. Ken Hunkins, using a floating ice island as an oceanographic vessel, made a point of securing such cores. The idea was that if the Arctic were ice-free during glacial time, the sedimentation rate would have been far higher than now. Teh-Lung Ku made measurements of ^{230}Th on the sediments in one of Ken's cores. He found that, as expected, during the Holocene the sediment accumulation rate was a measly $0.05 \text{ cm}/10^3\text{yrs}$ (compared to rates on the order of $1.5 \text{ cm}/10^3\text{yrs}$ for the rest of the world ocean). However, the important finding was that during glacial time, the sedimentation rate was even lower indicating that, as one might expect, the ice cover in the Arctic was even more extensive during glacial time than today.

When Ku finished a paper describing his results, I sent the preprint to Ewing. I altered the title to "The Nnod – Gniwe Theory" (Ewing and Donn spelled backward). To me, it was a joke. To Ewing it was a huge insult. I remember holding the phone at arms-length as he roared "Wally, you do not make fun of the director of this institution."

In papers published in 1967 and 1969, Ku used ^{230}Th to show that manganese nodules grow at the miniscule rate of about $0.3 \text{ cm}/\text{million years}$, i.e., a 3-cm radius nodule began its growth 10 or so million years ago. During this time a meter or two of red clay would have accumulated, so what kept the nodules afloat? Some years earlier, summer student Mike Bender made a case that, indeed, nodules grow very slowly. To do this, he compared records for the abundance of nodules in Lamont piston cores from the abyssal South Pacific with bottom photos showing their abundance on the sea floor. If the nodules remained afloat for several million years before being swallowed up by the sediment, then, based on the sediment accumulation rate, one could calculate the probability of finding one in a sediment core. When Michael did the arithmetic, his result was consistent with a slow growth rate.

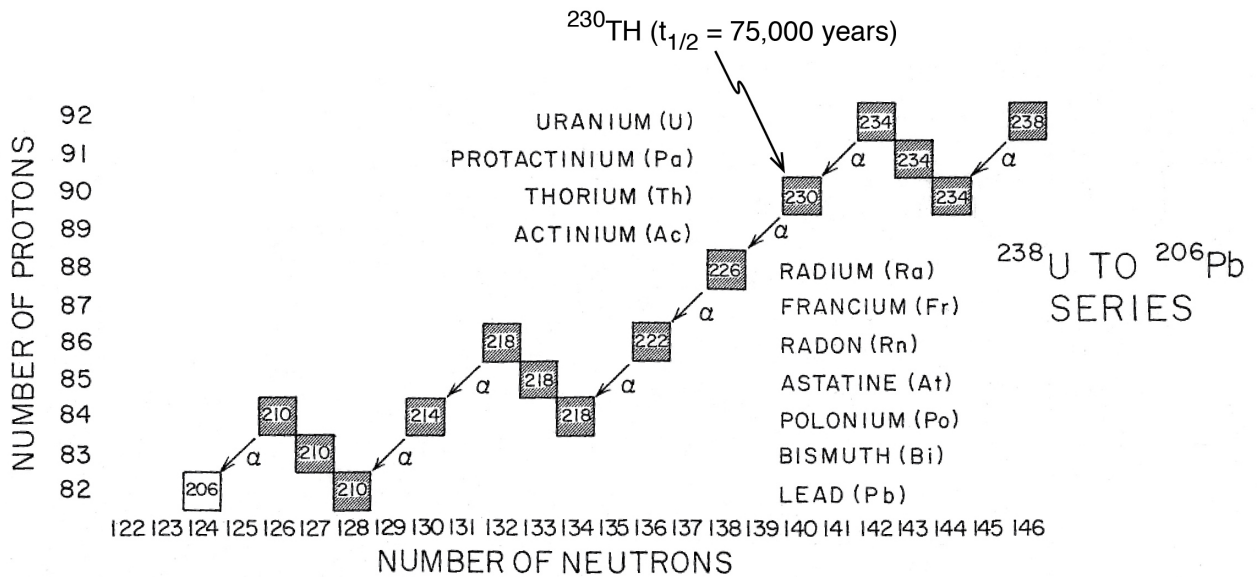
After we had published our paper, I received one to review. Its author, Claude Lalou, was a scientist at a geochemistry lab south of Paris. Based on radiocarbon dates on a shark's tooth

which had nucleated the growth of a manganese nodule, she claimed that the nodule had grown in just about 20,000 years (instead of a few million years as we claimed). At the end of my review, I added as a joke for the editor, Harmon Craig, “This is a beautiful example of French Provincial science”.

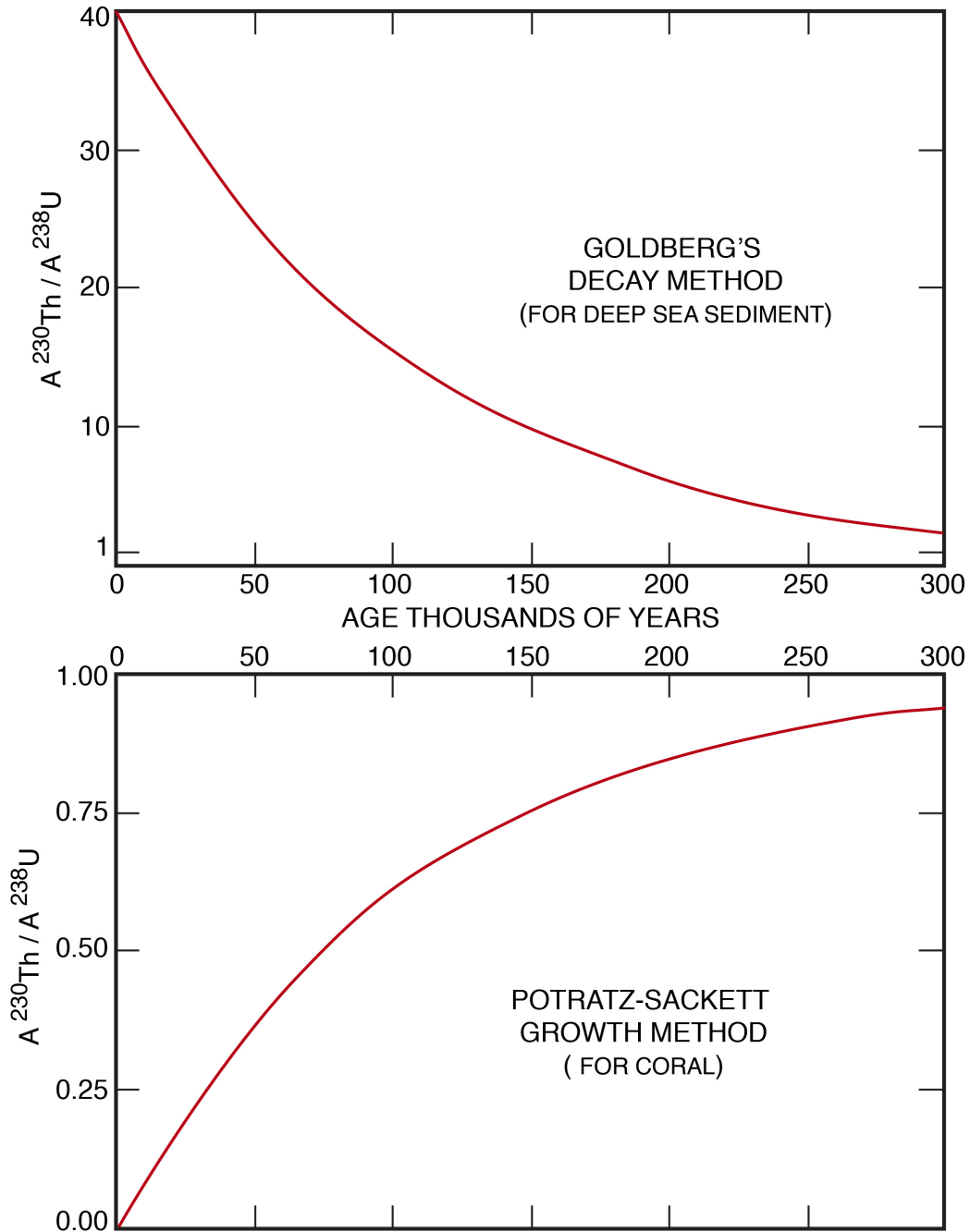
Some months later, one of Lalou’s colleagues, Laurent Labeyrie, visited Lamont. He begged me to hear Lalou’s case at an upcoming meeting in Grenoble. He also said that contrary to my wishes, the ‘French Provincial’ line had been included in the review. By process of elimination, the French had figured out that I must have written the review. I met with Claude and after apologizing for my rude remark we had our discussion about the growth rate of manganese nodules. As an expression of hospitality, Claude and Laurent took me to what they claimed was the best restaurant in the Grenoble area. I wasn’t disappointed. I remember it as one of my best meals ever.

Over the years, the ^{230}Th method has become the most important of those in our geochronology tool kit. In the mid 1980’s, Larry Edwards, a graduate student at Caltech, made a huge advance by demonstrating that ^{230}Th could be measured with a mass spectrometer. Not only are the results of atom counting far more accurate than those by decay counting, this method can be applied to far smaller samples. Over the years, Larry and his colleague, Hai Cheng, have achieved incredible precision. For example, they produced a stalagmite ^{18}O record extending back 600 thousand years.

One last thing. Of the isotopic dating methods we use in climate studies of the last few hundred thousand years, ^{230}Th is the only one that does not have to be calibrated. Dates obtained using the cosmogenic isotopes ^{14}C and ^{10}Be must be calibrated by comparison with ^{230}Th ages (or tree ring counts). The reason is that the flux of neutrons which produce these isotopes has changed with time. Even the chronologies for ice cores obtained by layer counting have been tuned by ^{230}Th dating of stalagmites. While pretty much on the sidelines, I pay close attention to the method I helped launch some 50 years ago.



Long-lived ^{238}U ($t_{1/2} = 4.5$ billion years) decays, through a chain of radioactive daughter products. This chain ends in stable ^{206}Pb . If this series has reached a steady state, as is the case for very old rocks, then the decay rate of each of the daughter products matches that of ^{238}U . Of particular interest for geochronologists is the isotope ^{230}Th . Not only is its half-life (75,000 years) ideal for dating, its very different chemistry creates ways to employ it.



The isotope ^{230}Th can be used in two quite different ways in marine geochronology. One involves the decay of the excess ^{230}Th present in marine sediments, and the other, the build of ^{230}Th in corals. The curves here are idealized in that the contribution of excess ^{234}U is not included.

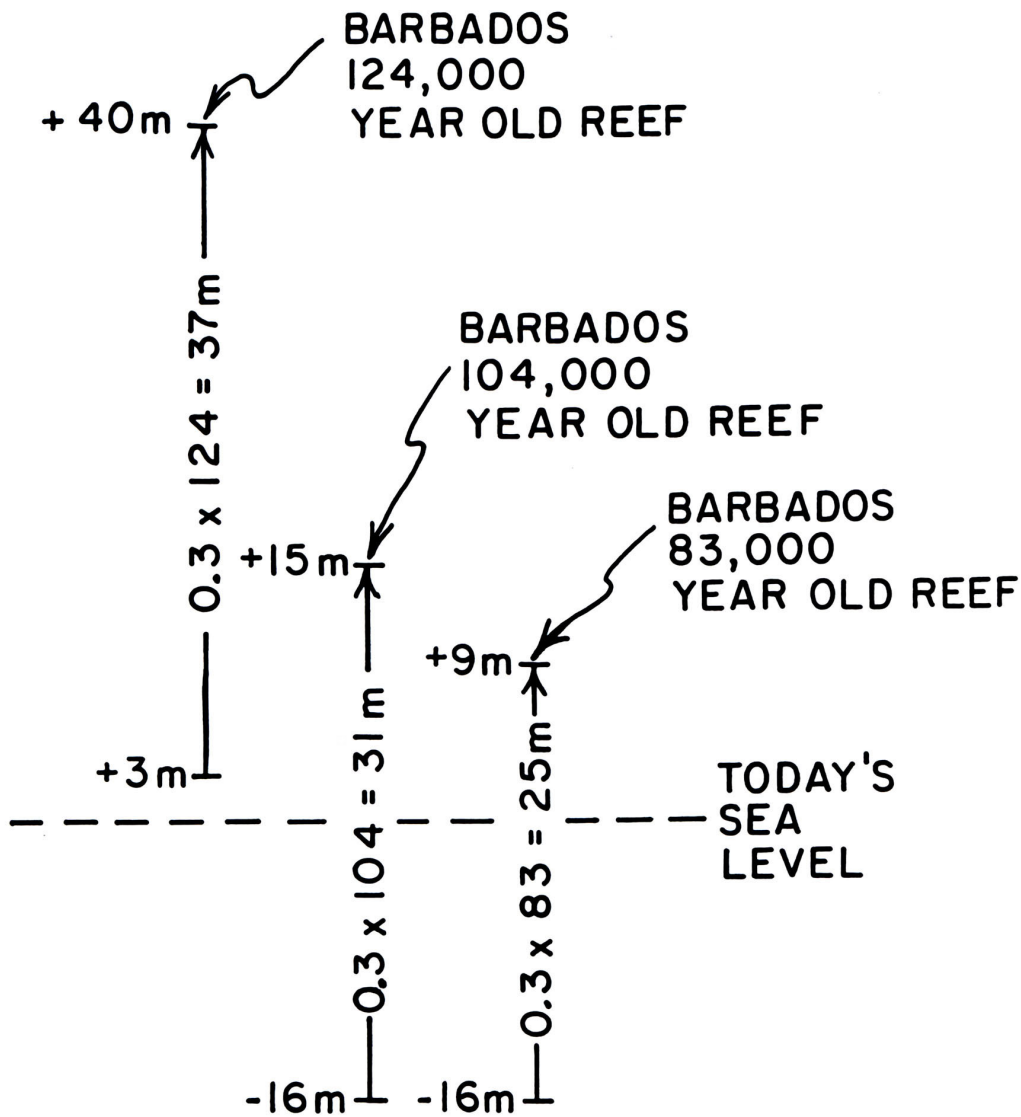
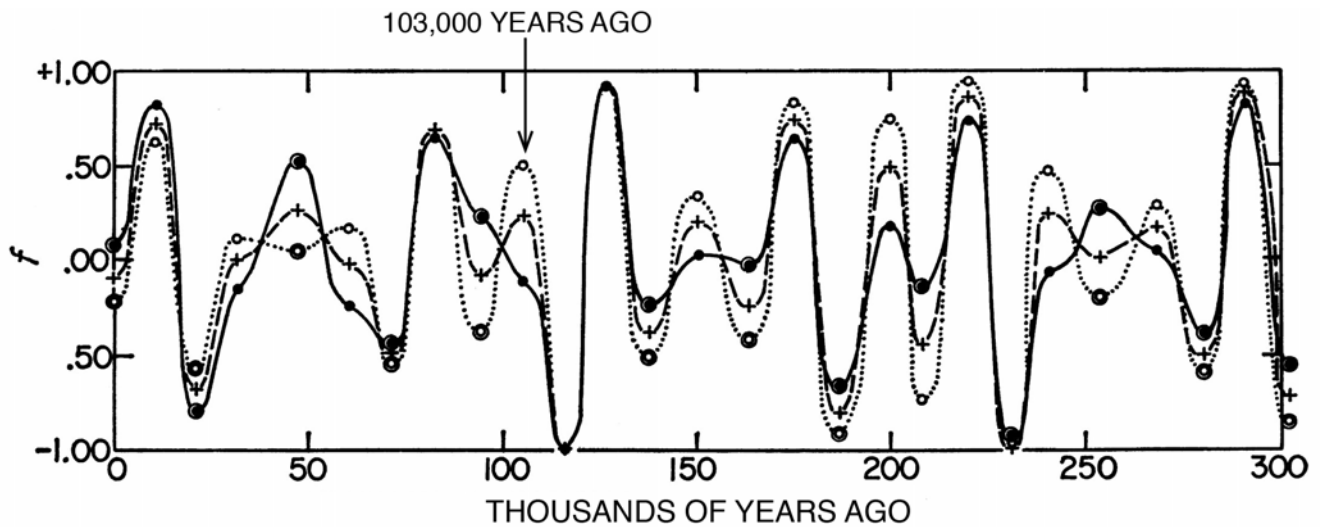


Diagram showing the relationship between the elevations of the crests of coral reefs on Barbados and sea level at the time they formed. A knowledge of the true sea level (+3 meters) at the time the 124,000 year old reef formed allows the uplift rate (0.3 meters per 1000 years) for Barbados to be established. This permits the elevations of the sea reconstructed for the times when the 104,000 and 83,000 year-old reefs formed on Barbados, to be reconstructed. Both formed about 16 meters below present-day sea level.



Milankovitch's original summer insolation record (solid line) was dominated by the 40,000-year-duration cycle in Earth tilt. Our finding that 103,000 years ago sea level was close to that at 82,000 years ago, suggested that Milankovitch had underestimated the importance of the 20,000-year-duration cycle. In a 1962 paper, I showed that if the 20,000-year cycle were given more weight, this mismatch could be explained (dotted line). Much later, when a precise summer insolation record became available, this turned out to be the case.

References

- Ewing, M. and W.L. Donn (1958), A Theory of Ice Ages II, *Science*, 127, 1159-1162, doi: 10.1126/science.127.3307.1159.
- Cherdyntsev, V.V., D.P. Orlov, E.A. Isabaev, and V.I. Ivanov (1961), Isotopes of uranium in natural conditions, 2, Isotopic composition of uranium in minerals, *Geokhimiya*, 13, 840-843.
- Thurber, D.L. (1962), Anomalous U^{234}/U^{238} in nature, *J. Geophys. Res.*, 67, 4518-4520.
- Ku, T.L., W.S. Broecker (1967), Rates of sedimentation in the Arctic Ocean, pp. 95-104, In: *Progress in Oceanography*, 4, Pergamon Press, Oxford and New York,.
- Ku, T.L., and W.S. Broecker (1967), Uranium, thorium and protactinium in a manganese nodule, *Earth Planet. Sci. Lett.*, 2, 317-321.
- Taddeucci, A., W.S. Broecker, and D.L. Thurber (1967), Th-230 dating of volcanic rocks, *Earth Planet. Sci. Lett.*, 3, 338-342.
- Broecker, W.S. (1968), In defense of the astronomical theory of glaciation, *Meteorological Monographs*, 8, 1339-1411.
- Broecker, W.S., D.L. Thurber, J. Goddard, T.L. Ku, R.L. Matthews, and K.J. Mesolella (1968), Milankovitch hypothesis supported by precise dating of coral reefs and deep-sea sediments, *Science*, 159, 297-300.
- Ku, T.L., and W.S. Broecker (1969), Radiochemical studies on manganese nodules of deep-sea origin, *Deep Sea Res.*, 16, 625-637.
- Kaufman, A., W.S. Broecker, T.L. Ku, and D.L. Thurber (1971), The status of U-series methods of mollusk dating, *Geochim. Cosmochim. Acta*, 35, 1155-1183.

Chapter 5

Mono Lake

During my graduate student days, I got the idea that the buildup of bomb test ^{14}C in closed basin lakes could be used to constrain the rate of invasion of atmospheric CO_2 . To this end, I chose two such lakes in the Great Basin: Pyramid and Mono. I took my first samples for radiocarbon measurement in 1954. As I needed a gram of carbon for the beta counting method then in use, I filled a 25-gallon drum with lake water. After acidification I extracted the CO_2 by circulating air round and round through the water and a small volume of KOH absorbent. This worked beautifully for Pyramid Lake. But when I poured acid into the Mono Lake sample, there was a violent reaction which blew off the hoses and sprayed hot water all over the place. I later learned that not only was there ten times more dissolved HCO_3^- and CO_3^{2-} in Mono water than in Pyramid water, its conversion to CO_2 was highly exothermic. Phil Orr, who introduced me to research on desert lakes, sat on the steps of our motel room watching my performance. He remarked, "Isn't chemistry wonderful." Foiled by this first attempt, it wasn't until 1958 that I got the first Mono Lake sample.

When I measured the ^{14}C to C ratio in that Mono Lake sample, I encountered another surprise. It was considerably lower than I had expected. Expressed as an apparent radiocarbon age it was 1700 years. But when I took into account that Mono Lake water has a dissolved inorganic carbon (DIC) content 150 times that in seawater, I realized that an old age was to be expected. The mean depth of the lake is about 20 meters, hence there are about 6000 moles of DIC residing beneath each square meter of its surface. By comparison, for an ocean water column of 4000 meters, there is about 8000 moles/ m^2 . If it is assumed that the 1700-year radiocarbon age of Mono Lake's DIC represents the time required to exchange its CO_2 with that in the overlying atmosphere, then the CO_2 invasion rate would have to be about 4 moles/ m^2yr . This is the rate I obtained for Pyramid Lake. This suggested that the buildup of bomb test radiocarbon in Mono would be far too slow to be of use. However, this simple picture fell apart

when I became aware that CO₂ was coming up from beneath the lake. As this CO₂ would surely be free of ¹⁴C, it must contribute to the large apparent radiocarbon age of the lake's dissolved inorganic carbon.

The first clue that there is a source of carbon from beneath the lake was a hot tub which had been dug into the sediment close to Mono's shoreline. At first look, the water in the pit appeared to be violently boiling. But, as no steam was coming off, this couldn't be the case. A dip of my finger found it to be pleasantly warm. The bubbles turned out to be CO₂. An analysis showed that indeed the CO₂ was ¹⁴C free.

Scott Stine, an expert on Mono Lake, informed me that Mono Lake sits on top of a volcanic vent. As evidence, he showed me blocks of porous lava which had floated across the lake and become stranded along its shoreline. He also pointed out that Mono's Paoha Island had to have been pushed above the lake's surface sometime during the last 250 years. He based this conclusion on the observation that a 250-year-old shoreline present around the lake's perimeter was absent on the island. An aborted volcanic event? As Mono Lake lies at the northern end of a line of late Quaternary-age explosive volcanoes, this made sense.

Another piece of evidence supporting a sub-lake CO₂ source came as the result of a seismic survey commissioned by Los Angeles Water and Power. Although the objective of this survey was to construct a highly detailed water-depth map, as a byproduct, it also yielded information about the underlying sediments. Of interest to me was that about one third were loaded with bubbles. As with those in the hot tub, these bubbles are likely filled with ¹⁴C-free CO₂.

Finally, measurements of the partial pressure of CO₂ in Mono Lake surface water showed that more CO₂ is being lost by evasion than is being gained by invasion. The supply for this evasion is the CO₂ coming up from beneath the lake. However, as the partial pressure of CO₂ (pCO₂) in Mono's surface waters is a strong function of salinity, the diversion of streams feeding the lake led to a large increase in salinity. Also, as the CO₂ partial pressure depends on water

temperature, our summer-time measurements were biased on the high side. Hence it is not possible to harness the pCO₂ excess to constrain the flux of CO₂ from beneath the lake.

It came as a big surprise when a ¹⁴C measurement made on a Mono Lake sample collected in 1977 showed that the Δ¹⁴C for the dissolved inorganic carbon (DIC) had jumped from -178 per mil in 1966 to -148 per mil. This jump was an order of magnitude greater than expected if the CO₂ invasion rate was 4 moles/m²yr. In order to check this result, measurements were conducted on four samples collected between 1978 and 1980. The average of -136 per mil confirmed that indeed the lake's ¹⁴C to C ratio was building up far faster than expected. Only after 1990 did this rise level off. And, if explained by invasion of atmospheric CO₂, the rise over the last 60 years would require a whopping CO₂ invasion rate of about 30 moles/m²yr. (a rate eight times higher than one early estimate of 4 moles/m²yr.). In addition, were the invasion rate that high, the pre-nuclear ¹⁴C age of Mono Lake carbon should have been only 200 years. In order to explain both the low pre-nuclear ¹⁴C to C ratio and the steep rise would require an input of 6 moles/m²yr. of ¹⁴C-free CO₂ from beneath the lake.

Attempts to find an explanation for this unexpected ¹⁴C to C ratio increase continue today. Most of this research has been conducted by Rik Wanninkhof who came to Lamont-Doherty in the early 1980s as a graduate student. Upon receiving his Columbia Ph.D., he accepted a job at NOAA's Laboratory in Miami, Florida. We still work together on this problem. I arrange the Mono sampling and the ¹⁴C measurements. Rik conducts the modeling.

But before discussing Rik's contributions, one other possible explanation must be mentioned. Because of its very large inorganic carbon content, Mono Lake would constitute an ideal place for clandestine disposal of the enriched radiocarbon waste. So suppose, between 1966 and 1977, one or more such illegal disposals were carried out. The total amount of ¹⁴C required is large (i.e., about 5 curies). At that time amounts of waste radiocarbon of this magnitude were being generated in large medical research facilities. However, our inquiries turned up no hint that such disposals had occurred at Mono Lake or for that matter anywhere else. But had it been

done, of course the perpetrators would have kept it a deep, dark secret. So while unlikely, this explanation remains a dark horse.

Wanninkhof's first contribution to unraveling this conundrum was to conduct a tracer experiment designed to establish the gas exchange rate for a chemically inactive gas. CO_2 is special because its invasion rate can be enhanced by isotope exchange with the far more abundant HCO_3^- and CO_3^{2-} . Normally this isotope exchange is far too slow, but it can be enhanced by either OH^- ion or the enzyme carbonic anhydrase. Working together with Jim Ledwell, then a scientist at Lamont, Wanninkhof decided to add sulfur hexafluoride (SF_6) to Mono Lake. SF_6 is an ideal choice for it can be measured at extremely low concentrations and is chemically inert. In order to eliminate the possibility that the unusual chemistry of Mono Lake water was somehow enhancing the invasion rates of all gases, Rik conducted an identical tracer experiment in Mono's neighboring fresh water Crowley Lake. For both, he bubbled in SF_6 , let it spread laterally, and then did repeated depth profiles of its concentration. Over a one month period, in each water body, the SF_6 concentration decreased by more than a factor of two. Further, the evasion rates calculated for both of these water bodies turned out to be as expected from the regions mean wind speed ($\sim 4\text{m/sec.}$). So it became clear that, if the increase in the lakes ^{14}C to C ratio was the result of the invasion of bomb test ^{14}C , then the invasion rate of CO_2 would have to be enhanced by about eight-fold over that of other gases.

Wanninkhof then set out to determine the extent to which its rate of CO_2 exchange was enhanced by hydroxyl ion (OH^-). As Mono Lake water has a pH of 9.8, it has an extremely high OH^- concentration. Thus enhancement is to be expected. Because the Mono water he used had been stored for several weeks, Rik assumed that the highly labile carbonic anhydrase it might have initially contained would have been destroyed. Wanninkhof carried out two sets of laboratory experiments. In one, he created surface agitation by stirring. In this way, he achieved a low SF_6 evasion rate (i.e., equivalent to a CO_2 exchange rate of about $2\text{ moles/m}^2\text{yr}$). He found a threefold enhancement of CO_2 evasion over that for SF_6 . In the other, he created surface agitation using a 'waterfall'. The SF_6 evasion rate was high (equivalent to a CO_2 exchange rate

of about 15 moles/m²yr). In this case, he saw no measureable enrichment of CO₂ evasion compared to that for SF₆. This difference was as expected (the OH⁻ enhancement should not depend on invasion rate). Based on these experiments, Rik concluded that for the mean wind speed experienced at Mono Lake (~4m/sec), the enhancement of the invasion rate induced by the OH⁻ was about a factor of two.

Although a step in the right direction, something else was needed to explain the large ¹⁴C increase. Putting aside clandestine radiocarbon disposal, the only candidate which could explain the rest is the enzyme carbonic anhydrase. In our lungs this catalyst speeds up the CO₂ – HCO₃⁻ isotope exchange reaction by several orders of magnitude, thus allowing us to exhaust the CO₂ released into the blood as the result of combining O₂ with organic matter. Without it, no oxygen-breathing organism could exist. Salty Mono Lake teems with tiny brine shrimp. As their only predator is migrating birds, their abundance is incredibly large. Were these creatures to ‘leak’ some of their carbonic anhydrase into the surrounding water, it would catalyze the exchange of CO₂ between Mono Lake and the overlying atmosphere.

I first became aware of this possibility in 1965 during a semester leave at Caltech. I was invited to lunch by Willard Libby, inventor of the radiocarbon-dating method. At that time, he was a professor at neighboring UCLA. I was flattered, but couldn’t figure out why a Nobel Prize winner would want to meet with me. At lunch I found out. Libby said he planned to determine whether the CO₂ exchange with seawater is enhanced by carbonic anhydrase. The idea was to compare the CO₂ exchange rate for seawater from a highly productive site with that for water from a low productivity site. He sought a high productivity site. I suggested the eastern equatorial Pacific. As he didn’t mention his choice of a low productivity site, I asked what it was. He said that it was off Baja, California. I told him that as it was adjacent to a zone of upwelling, it was likely to be quite productive, and hence not the best choice. His reply stunned me. He said that during his tenure as head of the U.S. Atomic Energy Commission, he had flown over this site immediately after an underwater atomic bomb test and there were no dead fish! I thought to myself, “Yeah, they were all vaporized”, but held my tongue.

Demonstrating that it is indeed carbonic anhydrase that is the villain in Mono Lake has so far proven beyond our capability. One brief attempt was made. It yielded negative results. When CO_2 and CH_4 were added to a 'helmet' floating in Mono Lake, the rate of drawdown of both gases was measured. No evidence for enhancement of the invasion rate of CO_2 over that for CH_4 was observed. Not even that by OH^- . I suspected that the gases had somehow leaked to the atmosphere instead of invading the lake. Clearly more such experiments should be conducted.

A knowledge of the invasion rate of CO_2 allows the rate of upwelling of CO_2 from beneath the lake to be determined. If the invasion rate were as low as $4 \text{ moles/m}^2\text{yr}$, then very little input from beneath the lake would be required. On the other hand, if the rate is about $30 \text{ moles/m}^2\text{yr}$, as suggested by buildup of the ^{14}C produced during hydrogen bomb tests, then 1500 of the 1700-year apparent ^{14}C age of pre-nuclear Mono Lake carbon would have to be explained by ^{14}C -free CO_2 seeping up from beneath the lake. In this case, the input of CO_2 from beneath the lake would have to be about $6 \text{ moles/m}^2\text{yr}$.

Rik Wanninkhof struggled to see if perhaps there was a third possible explanation for the large ^{14}C increase in Mono Lake. In desperation, he showed that were the input of CO_2 from beneath the lake to have been abruptly reduced, the rise in ^{14}C could be explained without resorting to either clandestine ^{14}C disposal or carbonic anhydrase enhancement. As a reason for why such a shutdown might have occurred, Rik invoked the diversion of mountain runoff via the aqueduct to Los Angeles which began in 1940. Perhaps the resulting reduction of ground water recharge somehow shut down the upwelling of water from beneath the lake. A clever but unlikely idea.

One way in which this dilemma might be resolved is to continue to monitor Mono Lake's ^{14}C to C ratio. The decline of bomb ^{14}C in the atmosphere and the continuing addition of fossil fuel CO_2 will lower the atmosphere's ^{14}C to C ratio. The rate at which the lake's ^{14}C to C drops will depend on the CO_2 evasion rate.

During the 1980s, a large number of automobiles in the West had bumper stickers saying 'Save Mono Lake'. Because mountain water was a valuable resource, Los Angeles Water and

Power resisted the pleas to allow more water to reach the lake. Not only did it supply 15 percent of the water used in L.A., the company made eight times more money by selling the electrical power generated by the water as it descended from 8000 feet to sea level.

Eventually court cases were initiated by both environmentalists and by trout fishermen to force Los Angeles Water and Power to release more water to the lake. Such a ruling would reverse the trend of increasing salt content. The environmentalists' case rested on two threats to avian wildlife. The drop in lake level posed a threat to California gulls for it would allow coyotes to reach their island rookeries. Further, the increase in salinity, if continued, would eventually kill off the brine shrimp and in so doing, eliminate a fueling stop for hundreds of thousands of migrating birds. It was, however, the trout fishermen rather than the environmentalists who succeeded in convincing the court. Mono Lake was saved!

Chemical composition of Mono Lake water

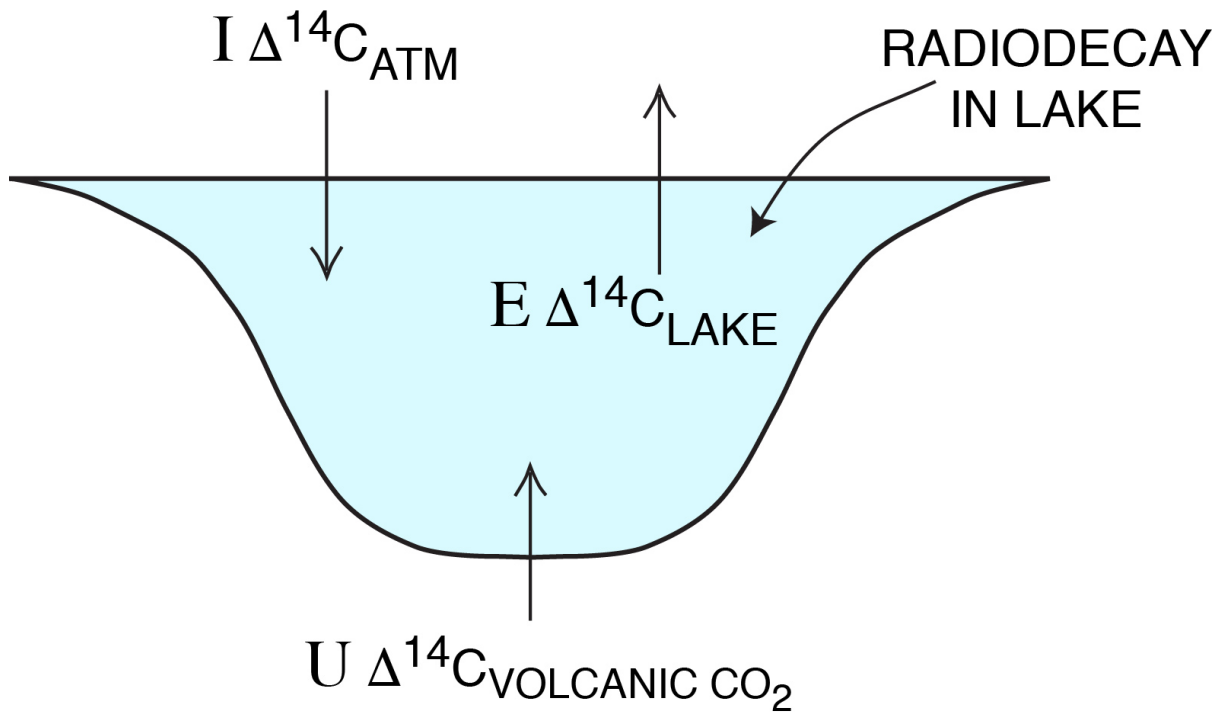
Plus Charge	<i>equiv/m³</i>	Minus Charge
Na ⁺ = 1190		Cl ⁻ = 515
K ⁺ = 37		SO ₄ ⁼ = 206
Mg ⁺⁺ = 3.8		H ₃ BO ₄ ⁻ = 15
Ca ⁺⁺ = 0.2		HCO ₃ ⁻ = 115
<u>Σ+ = 1231</u>		<u>CO₃⁼ = 380</u>
		Σ- = 1231

pH 9.8

DIC = 305 moles/m³

ΣSalt = 76 g/liter*

*As the water budget for the lake has varied widely, so also has its salinity. However, these salinity changes did not change the ratios of the individual contributors, one to another.



Terms in the radiocarbon budget for Mono Lake: **I** is the invasion rate of CO₂ from the atmosphere. **E** is the evasion rate of CO₂ from the lake. **U** is the upwelling rate of CO₂ from beneath the lake. At steady state **E** must equal **U + I**. The radioactive decay of ¹⁴C within the lake (one percent every 82 years) must be taken into account.

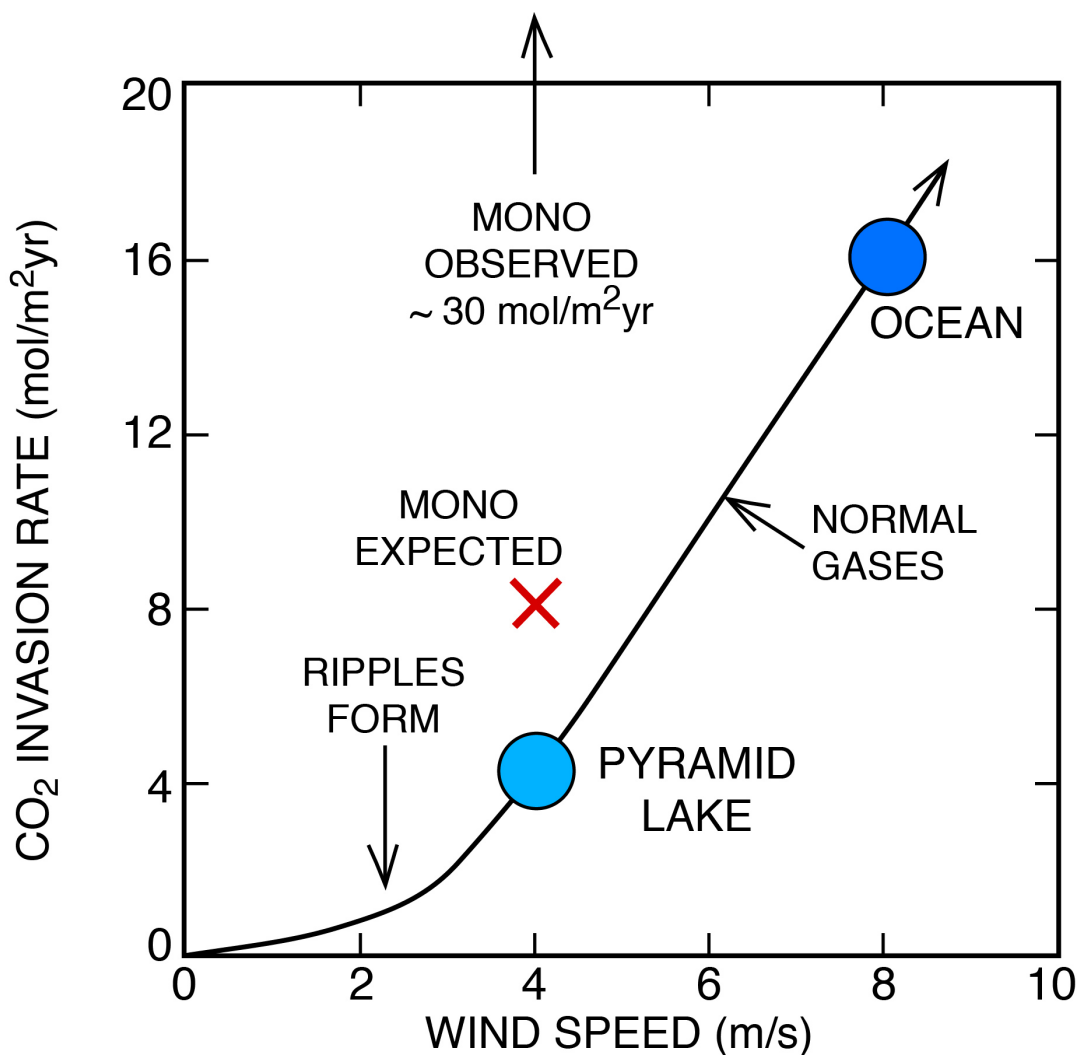
Mono Lake DIC Residence Times

Mean Depth ~20 m

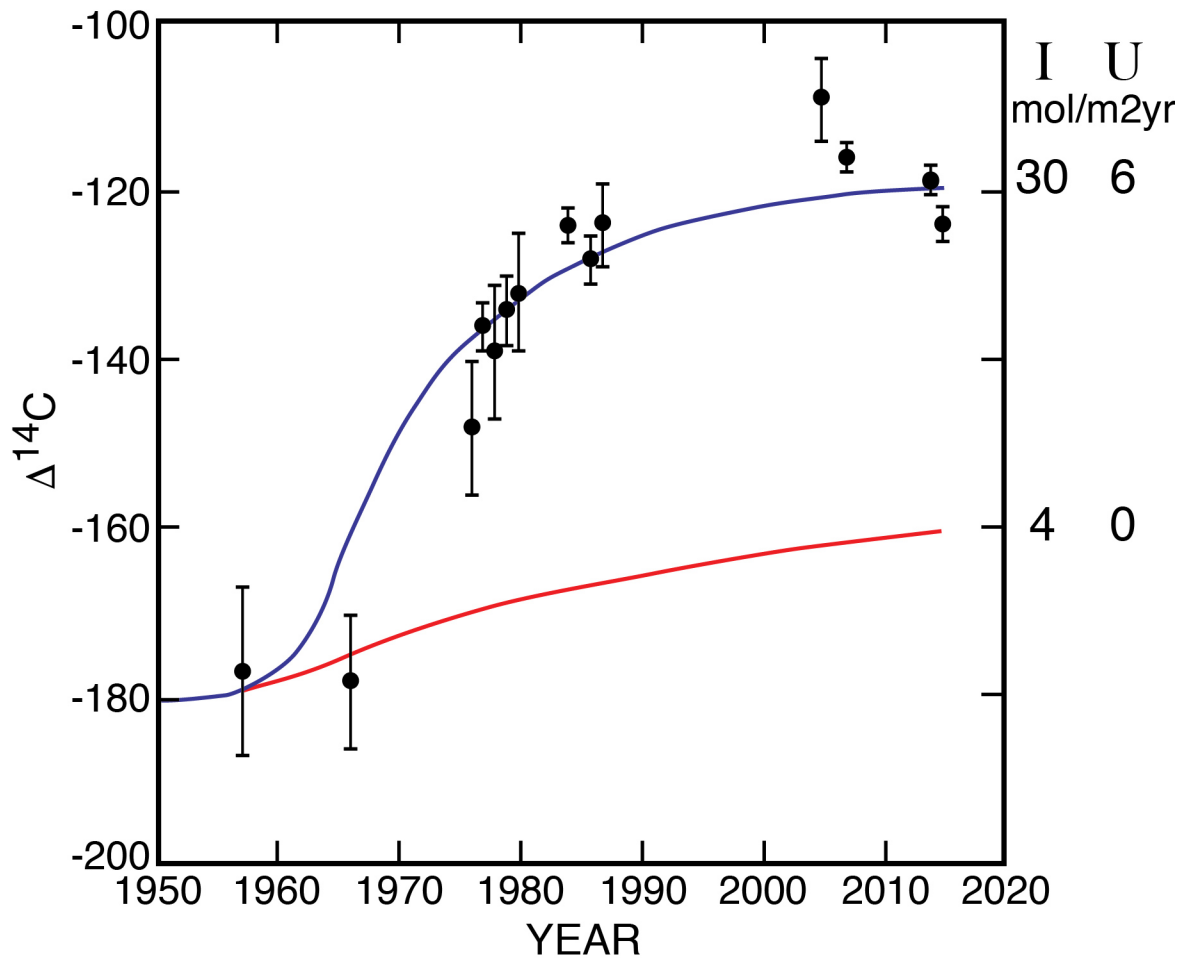
DIC* ~6000 moles/m²

Invasion Rate CO ₂ mol/m ² yr.	¹⁴ C age DIC In 1958 yrs.	Radio-Decay Contribution yrs.	Upwelling Contribution yrs.	Upwelling Rate mol/m ² yr.
4	1700	1500	200	<1
30	1700	200	1500	~6

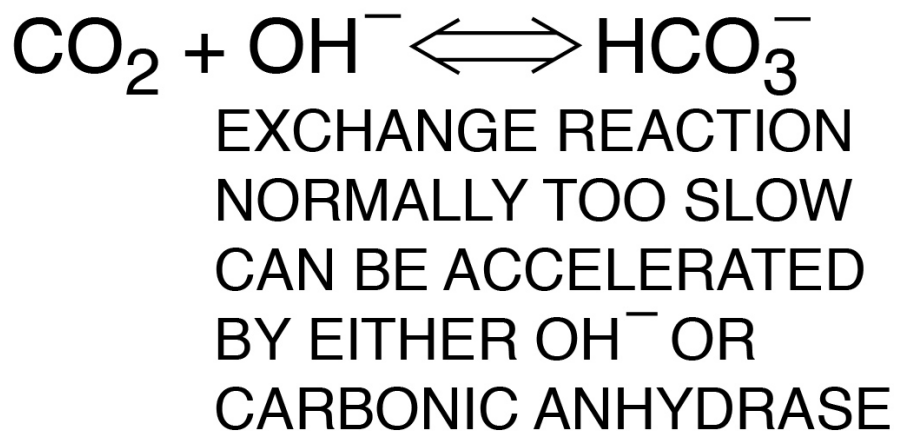
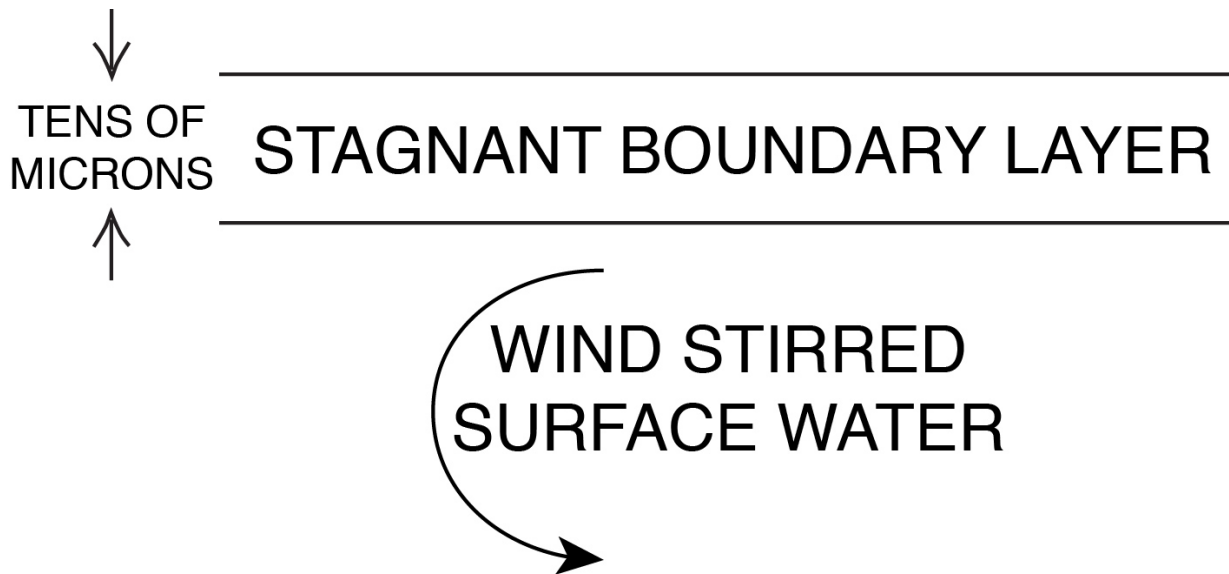
*Water column inventory of dissolved inorganic carbon.



Gas exchange rates increase with wind speed: Based on the uptake of H bomb-produced ¹⁴C, average rates have been established for Pyramid Lake and for the ocean. Because of its exceedingly large OH⁻ concentration, Mono Lake is expected to have a CO₂ invasion rate about twice that for neighboring Pyramid Lake. However, the uptake of bomb ¹⁴C appears to require a far higher invasion rate (~30 moles/m²·yr). In the absence of ripples, the exchange rate of gases is very small.



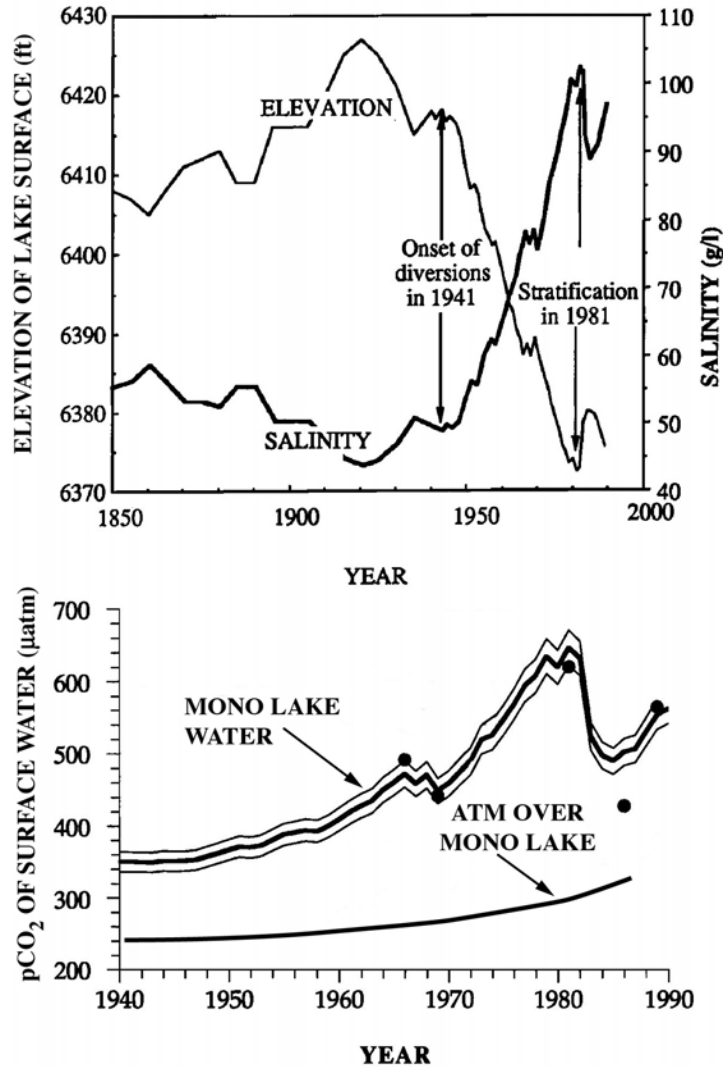
Radiocarbon time series for Mono Lake dissolve inorganic carbon: If it is assumed that there has been no clandestine disposal of enriched ¹⁴C, then in order to explain the large post 1957 increase in Δ¹⁴C a very high CO₂ invasion rate (I) is required (i.e., 30 ± 4 moles/m²yr). The red curve shows the expected Δ¹⁴C trend if Mono Lake CO₂ invasion rate were ~4 moles/m²yr. If the CO₂ invasion rate is 30 moles/m²yr, then in order to explain the low pre-H bomb Δ¹⁴C, an upwelling of CO₂ from beneath the lake (U) would have to be about 6 moles/m²yr. On the other hand, were it as low as that for Pyramid Lake (~4 moles/m²yr), then almost no CO₂ from beneath the lake would be required.



The exchange of gases between the atmosphere and a water body is limited by a tens of micron-thick 'stagnant' boundary layer. Passage through this layer is by molecular diffusion. The thickness of the layer decreases with increasing wind speed. To the extent that isotope exchange between CO_2 and HCO_3^- occurs within the stagnant boundary layer, the rate of invasion transfer of ^{14}C is enhanced. The reason is that the concentration of HCO_3^- is far larger than that of CO_2 .



Brine shrimp typically teem in lakes with high salt content. Their only predators are migrating birds. The brine shrimp from Great Salt Lake are sold for aquarium food. Those in Mono Lake fuel birds migrating to the Galapagos. However, even brine shrimp can't survive salt contents more than 110 g/liter. For this reason, the Dead Sea has none.



Dependence of CO₂ partial pressure in Mono Lake surface water on salinity: During the 1940- to 2005-time interval, diversions of the fresh water feeding Mono Lake waters by Los Angeles Water and Power led to a twofold increase in the lake's salinity (and also lowered its surface elevation by 40 meters). Heavy rains associated with the 1982 El Niño temporarily eased the situation, but in its aftermath, the salinity rise resumed and continued until 2005 when a court order forced LAWP to release water to the lake.

For her senior thesis, Rachael Oxburgh, an Oxford undergraduate, spent time at Lamont determining the salinity dependence of the partial pressures of CO₂ in Mono water. Assuming that the pre-diversion surface water CO₂ partial pressure was 350 µatm compared to that of 240 in the atmosphere (i.e., 80 percent of the sea level pressure), she demonstrated that except for one of the five measurements, she could fit the time trend of observed values. The anomalous point represents a time when the lake was stratified.

Her result that the pCO₂ in lake water prior to 1940 was about 45 percent higher than that in the air must be viewed as an upper limit. The reason is that all five measurements were made during the summer when the water temperature is higher than its annual average.

References

- Broecker, W.S., and A.F. Walton (1959), The geochemistry of C 14 in fresh-water systems, *Geochim. et Cosmochim. Acta*, 16, nos. 1-3, 15-38.
- Thurber, D.L., and W.S. Broecker (1971), The behavior of radiocarbon in the surface waters of the Great Basin, pp. 379-400, In: Nobel Symposium 12, *Radiocarbon Variations and Absolute Chronology*, I.U. Olsson, Ed., John Wiley and Sons, Inc.
- Peng, T-H., and W.S. Broecker (1980), Gas exchange rates for three closed-basin lakes, *Limnol. Oceanog.* 25, 789-796.
- Wanninkhof, R., J.R. Ledwell, W.S. Broecker and M. Hamilton (1987), Gas exchange-wind speed relationship on Mono and Crowley Lake, California, *J. Geophys. Res.*, 92, 14,567-14,580.
- Broecker, W.S. and S. Stine (1988), Mono Lake's radiocarbon budget: An unsolved enigma, *EOS*, 69, No. 23, June 7.
- Broecker, W.S., R. Wanninkhof, A. Herczeg, T.-H. Peng, G. Mathieu, S. Stine, and M. Stuiver (1988), The radiocarbon budget for Mono Lake; an unsolved mystery, *Earth and Planet. Sci. Lett.*, 88, 16-26.
- Oxburgh, R., W.S. Broecker, and R.H. Wanninkhof (1991), The carbon budget of Mono Lake, *Global Biogeochem. Cycl.*, 5(4), 359-372.
- Broecker, W.S., and R. Wanninkhof (2007), Mono Lake radiocarbon: The mystery deepens, *EOS, Trans., AGU*, 88(12), 141-148.

Chapter 6

Bahama Banks

In early 1963, John Imbrie, a colleague in Columbia's Geology Department, invited me to join his research expedition to the Bahama's banks, the submerged carbonate platforms which make up the Bahama Archipelago. He had rented a house on Frazer's Hog Cay that would be used as his base of operations. Imbrie planned to conduct a study of the carbonate sediments which coat these shallow banks. He said I could share the use of a small research vessel operated by the marine biology laboratory on Bimini Island and that perhaps there was some interesting geochemistry to be done.

Eager to explore the use of radon gas as a tracer for the rate of air-sea gas exchange, I jumped at the opportunity. Realizing that I needed help, I invited Taro Takahashi to join me. Perhaps we could also learn something of the rates of CaCO_3 precipitation on the banks which would link well with Imbrie's sediment studies. Taro agreed. We then asked Ross Horowitz, a resourceful young man who had been helping out in our labs since his high school days, to be chief of operations. Of course he was delighted and excited. It was agreed that we would ship our gear to Miami where it would be loaded aboard an LST (one of the surviving D-Day landing craft), and then taken by Imbrie across the Florida Straits to Bimini.

Taro and I arrived in Bimini without incident and awaited the LST's arrival. We waited and waited, and waited some more. No LST and no word from Imbrie. At midnight we gave up and turned in for the night. Hours later, Imbrie burst into our motel room asking us to quickly rinse out his portable radio with fresh water. This done, we sat Imbrie down and got the story. The LST had arrived off Bimini at about sunset and Imbrie had tried without success to radio the harbor authorities announcing their arrival in Bahaman waters. Thinking that the noise made by the LST's engine was interfering, they shut the radio down and then tried again. After several unsuccessful tries, they gave up and decided to land unannounced. But alas, the LST's batteries were dead and they couldn't restart the engine. Still offshore in the clutches of the Gulf Stream, they drifted to the north. Darkness fell, a storm kicked up. About midnight, a huge freighter

passed them heading south. Imbrie sent SOS signals with his flashlight. The ship turned out to be Russian, likely bound for Cuba. Jumper cables were lowered 25 feet or so from the bow and the LST was brought back to life. Captain George, a young man employed by the LST's owner, then headed back south arriving in Bimini at 4 a.m.

At breakfast, it was agreed that Horowitz would charter a sea plane and take the Broecker-Takahashi equipment to Frazer's Hog Cay. Imbrie and his students would take the LST to a neighboring shallow bank and test the coring gear. Taro and I would go to Bimini's marine lab and check out their small research vessel. We would meet again at dinner.

Once again, no Imbrie. But this time the wait was much shorter. The LST chugged back into Bimini's harbor. Again, bad news. The plan had been to open the LST's big forward door and use it as a platform for the coring winch. While setting up the coring system, they encountered a glitch which could only be remedied back in port. So they pulled up the door and started back. Only then did they realize the LST was taking on water. One of the chains that held the door had gotten caught leaving a gap through which the water was pouring in. The more water, the deeper the LST floated and the faster the water flowed in. Before they could free the chain, the LST had settled to the bottom. Fortunately, the bottom was so shallow that the boat was not totally submerged. Once the chain was freed and the water was pumped out, they were able to make port.

But there remained a problem. The LST had towed a small runabout across from Miami. It was to be used for bottom surveys. Unbeknownst to Imbrie and his helpers, while rescuing the LST, the rope tethering the runabout had severed. No runabout was to be seen. The next morning Imbrie chartered a sea plane to search for it. He brought along one of the marine lab's seamen, 'The Deacon'. From the plane's window Imbrie looked and looked through his powerful field glasses. No runabout. He was about to give up when The Deacon pointed and said "der it is boss". With naked eye, he had spotted a dot on a distant beach.

During another breakfast confab, it was agreed that Taro and I would fly across the banks to Frazier's Hog Cay to join Horowitz. During our flight, we spotted long comet-shaped white

patches in the otherwise clear blue water. The pilot informed us that they were called ‘whitings’ and that on most such flights, he spotted at least one of them. He went on to say that while most scientists he had flown with thought they were CaCO_3 precipitates, others favored sediment stirred up from the bottom. This triggered my quest to understand the origin of ‘whitings’.

As our plane taxied up to the pier in front of surgeon Leroy Tolcott’s Bahaman getaway home, we spotted Ross Horowitz waving and slapping himself like some sort of wild man. Only when we deplaned, did we realize he was trying to fend off a myriad of mosquitoes.

After this rather eventful introduction to marine fieldwork, we prepared to start our first project, namely, the use of radon gas as a tracer for rate of exchange of gases between the atmosphere and Bahaman bank water. My ultimate goal was to use the rates obtained in this way to calculate the isolation time of water on the banks by its burden of excess ^{14}C formed during the testing of hydrogen bombs. Then Taro could use this information to calculate the rate of precipitation of CaCO_3 from the water. An ambitious undertaking!

We knew the time history of bomb-produced radiocarbon in the water passing through the Florida Straits. So any extra ^{14}C in the water on the shallow banks must have been added by gas exchange. In order to convert this excess into a residence time, I needed to know the rate of CO_2 invasion. My strategy was to use the radon that was produced by the decay of the radium dissolved in the water. The ratio of the radioactivity of radon to that of its parent radium would tell me how much radon was lost to the overlying air and hence the rate of gas exchange.

As radon has a half-life of only 3.65 days, we could not return the samples to Lamont for analyses because a new batch of radon would have been produced in the interim. We had to do it in the lab Horowitz put-together on Frazer’s Hog Cay.

In order to get enough radon for a reliable measurement, we used 20-liter bottles obtained from the Poland Springs Company. We made special tops which allowed them to be evacuated. Ready for sampling, I called Chalk Airlines and arranged to fly out over the banks. The pilot would land on the water; I would jump out and he would hand me one of the evacuated bottles. Then I would plunge it into the water and open a valve allowing seawater to rush in. Back at

Frazer's Hog Cay, Horowitz would bubble helium round and round through the water and through a trap cooled by liquid air, which would capture the radon. He would then flush the trapped radon into a scintillation cell. Each alpha particle shot out when a radon atom underwent radio-decay would make a flash of light when it hit the cell's phosphored walls.

These flashes were seen by a photomultiplier. Horowitz hooked the cell to the measurement apparatus and began to count the flashes from the first sample. It soon became clear that something was amiss. Instead of finding the expected deficiency of radon, there was a sizable excess. Puzzled by this, Horowitz prepared another of the samples. Again, excess radon. The third sample gave a similar result. After some frantic thinking, I came up with a possible explanation. Perhaps the radon produced by the radium contained in the sediments was diffusing into the overlying water. If the amount supplied in this way more than counterbalanced that lost to the atmosphere, it could explain our results.

The next day we took an evacuated bottle with a six-inch-long copper tube projecting from its top out onto the shallow sediment flat off the end of our pier. We inverted the evacuated bottle and pushed the copper tube into the sediment, opened the valve, and sucked in half a bottle of sediment water. Later when we turned on the counter, instead of getting several flashes a minute, we got a burst of hundreds. Point made: our radon project was dead on arrival.

But all was not lost. I soon realized that if we were to do the same thing in the open ocean, we wouldn't have to concern ourselves with radon leaking from the bottom. The deficiency in surface water would provide a measure of the rate of gas exchange. Further, we could harness the radon leaking up from the sediment to constrain the near-bottom vertical mixing rate. Years later, as part of the decade-long GEOSECS survey, both surface and bottom profiles were obtained at 80 stations worldwide. These results became the grist for Jorge Sarmiento's PhD thesis.

Having to abort my pet project, Taro and I prepared for his. The idea was to conduct a traverse across the Great Bahama Bank stretching from the 'Tongue of the Ocean' on the east to the Florida Straits on the west and then another one back to Frazer's Hog Cay. We would make

continuous measurements of the partial pressure of CO₂ in the water and take discreet water samples for salinity and ΣCO₂ measurements. Of course, we would also extract CO₂ from large water samples for radiocarbon measurement.

Having completed one phase of his sediment program, Imbrie brought the LST and the Bimini lab's research vessel to Frazer's Hog Cay. It was our turn. We put our equipment onboard the 'research' vessel and sailed off onto Great Bahama Bank. 'The Deacon' was in command. He was aided by a single crewman, 'Cornbread'.

We soon learned that our Bahamian seamen read neither charts nor stars. But they knew where we were by looking at the bottom. Thus it was up to us to navigate. We did so by a combination of compass and propeller speed. As Taro was towing an intake for his CO₂ partial pressure analyses, we had to keep the speed down. Hence, our crude navigation system was seriously compromised by the influence of tidal currents.

It was a beautiful and largely uneventful voyage. Only when we came back across the banks did we encounter a bit of trouble. We were supposedly headed toward the Northwest Channel Light and once we saw it, we could easily find our way back to Frazer's Hog Cay. But we weren't at all sure we would pass close enough to see it. As it was becoming dark, we felt a bump and then a minute later, another, and then a third. Clearly, we were bouncing off the crest of submerged dunes. We asked The Deacon where we were and after staring overboard he replied, Jolters. We grabbed our charts and sure enough, we found a dune field referred to as Jolters. It was well south of our planned course. The Deacon knew how to get us back on course. He turned the ship around, back-tracking until we were out of danger. Then he headed north and within a couple of hours, lo and behold, we sighted the Northwest Channel Light.

The results of this expedition excited us so much that we decided to do a repeat two-week expedition the next summer (1964). Rather than depending on Imbrie's 'navy', we chartered our own vessel, the Lord Rayleigh, from the Miami Company Imbrie had used. It was under the command of the same Captain George who, in 1963, had commanded the LST. We also added Fred Gwinner, a machinist at our Lamont lab, to our small team.

We had two objectives in mind. In 1963, we were not able to sample the high salinity (hence longest residence time) waters off Andros Island. Also, we had not encountered a single 'whiting'. In 1964, we did both.

When at last we encountered a whiting, Taro suggested something which would not have occurred to me. He said that if the CaCO_3 were being actively precipitated, it would cause an increase in the partial pressure of CO_2 in the water. So we made a CO_2 partial pressure traverse across the whiting. There was no change going in or out of it. Then I came up with a second test. If we could get 30 grams of the suspended CaCO_3 , we could measure its ^{14}C age. The extra hydrogen bomb radiocarbon test in the water would provide an elevated ^{14}C to C ratio. By contrast, the bioturbated sediment would provide a depleted ^{14}C to C ratio.

Fortunately, we had brought along a continuous centrifuge which passes water through a rapidly spinning chamber. Any particles in the water are plastered onto the chamber walls. By running whiting water through this device for about an hour, we were able to obtain enough CaCO_3 for a ^{14}C analysis. We also extracted CO_2 from water adjacent to the whiting. Back at Lamont, when the ^{14}C measurements had been made, sure enough, the particles were deficient in radiocarbon and the water had extra radiocarbon. So Taro was correct in his assessment that the whiting material must be stirred-up sediment. Okay, but what stirred it up? Many years passed before a satisfactory answer appeared and it was Captain George who had planted an important clue in my mind. He said that no one ever swam in the whittings because they were infested with sharks.

All went well on this second voyage across the banks. Captain George always knew where we were. We ate better, slept better and even had some entertainment. We took a short side trip to Brown's Cay on the eastern margin of the Grand Bahama Bank; this islet was flanked by unusual sediment. Instead of algal CaCO_3 , the bottom was covered with glistening white oolites. Luckily Horowitz and I were prepared for this by having taken scuba lessons at a YMCA. So we put on our air tanks, flippers and face masks, and down we went to see the beauty close up. After some time, I came up only to find myself several hundred yards from the

anchored Lord Rayleigh. As a poor swimmer, I quickly realized that I wouldn't be able to make it back on my own. Fortunately, Captain George was one step ahead of me. The Lord Rayleigh was promptly underway headed for my 'rescue'.

We had a couple more special treats when we took samples in the salty water off Andros Island. We experienced our first rain. It was a cloud burst. Afterwards an empty bucket sitting on the deck contained 6 inches of water! The second was that Horowitz had read that the east side of Andros had a wide stretch of mangrove inhabited by flamingos. So we waded in and sloshed around this isolated wilderness in awe before returning to the tasks at hand.

Upon our return to the Miami dock, we unloaded everything and packed it for shipping. Then we thanked Captain George for his excellent help and made our way back to Lamont. In the following months, Taro made many, many salinity and dissolved inorganic carbon measurements and I did a few tens of ^{14}C analyses.

It was my task to estimate the residence time on the banks for each of the water samples we had taken. Two approaches were available. As during the early summer there is relatively little rainfall, we could use the rate of evaporation. Knowing the depth of water on the banks (uniformly 4.5 meters) and the approximate rate of evaporation (~ 1.2 m/yr), the increase in salinity could be converted to a residence time. The other approach was to use the buildup of extra ^{14}C . Of course to do this required a knowledge of the CO_2 exchange rate. As our plan to employ radon didn't pan out, we had to make an educated guess. Based on an open ocean CO_2 exchange rate estimate of about 20 moles/m/yr (mean wind speed of 8 m/sec) and a CO_2 exchange rate of 4 moles/m²/yr for closed basin Pyramid Lake (mean wind speed 4 m/sec), I guessed that the rate for the Bahama Banks was about 8 moles CO_2 /m²/yr. When these two estimates were plotted one against the other, the points fell close to a straight line. While this agreement didn't verify our guesses, it did show that the uptake of extra $^{14}\text{CO}_2$ and the loss of water by evaporation nicely correlated. The spread of results for individual stations ranged from 10 days or less along the bank margin to 150 to 250 days for the waters sheltered by Andros

Island. Admittedly, the uncertainties were sizable, but to my knowledge no one has yet improved on our method.

Having the residence times, the ball moved to Taro's court. He used them to determine the average rate at which CaCO_3 had been precipitated from each of our water samples while it resided on the banks. Based on the dissolved inorganic carbon concentration and pCO_2 for each sample, he calculated its alkalinity. He then normalized this alkalinity for the change in salinity (i.e., back to the 36 g/liter Florida Straits value). As the decrease in salinity-normalized alkalinity was the result of calcium removal, he was able to convert the alkalinity decrease in each sample to the amount of CaCO_3 precipitated. Finally, based on my residence time estimates, he calculated the average rate of CaCO_3 precipitation. Most of the values fell within 50 to 70 $\text{mg/cm}^2\text{yr}$ range.

The thickness of soft sediment on the banks is about 5 meters. The banks were flooded about 7000 years ago, hence the mean sedimentation rate was about $0.7\text{m}/10^3\text{yr}$. Based on the dry density of these sediments ($\sim 1\text{g/cm}^3$), our result of about $0.6\text{m}/10^3\text{ yrs}$. looked good.

Our paper summarizing all this was published two years later (1966) in the *Journal of Geophysics Research*. Upon rereading it now, my only regret is that Taro wasn't the first author. What he teased out of his measurements was truly amazing.

But what about the origin of whittings. Our results made clear that they consist of stirred up sediment. There doesn't even appear to be any room for CaCO_3 overgrowths on the stirred up sediment. But what caused the stirring? One proposal was that the whittings formed above artesian springs. As the result of chance opportunity I obtained evidence that this is not the case. Herb Volchok, once a fellow graduate student, called me asking advice about installing a platform in the middle of Grand Bahama Bank. The idea was to collect the ^{90}Sr and ^{137}Cs fission products produced by nuclear bomb tests. After answering his questions, I asked one of my own. Could I choose the exact spot for the platform? I said that one of the explanations for whittings was that they formed above artesian springs. He agreed but was puzzled over how to find a whiting, so I said I would charter a small plane and be the guide. I charted the plane and,

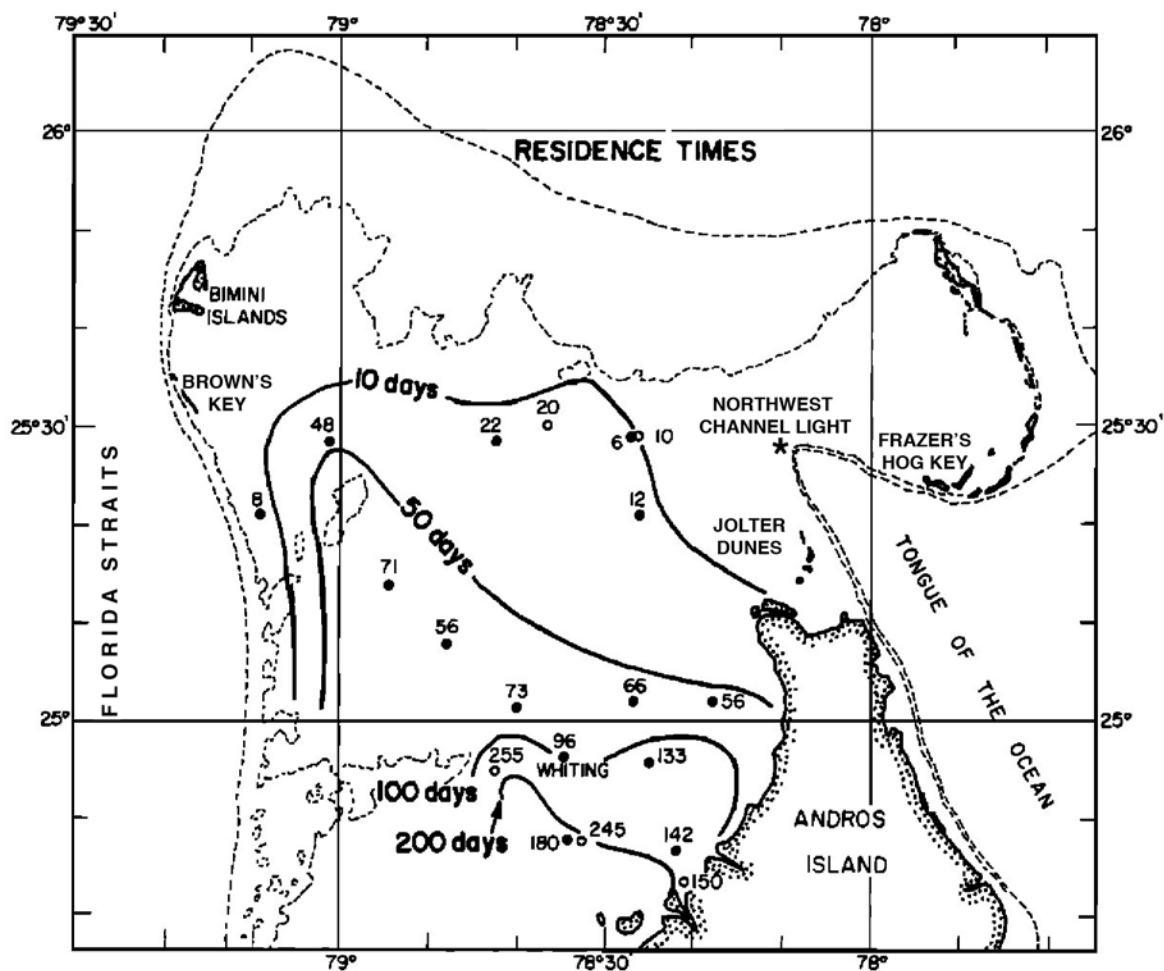
fortunately, was able to spot both a whiting and Volchok's ship. Our hasty preparations did not include radio communication, so I had the pilot swoop down to a level where Volchok could see my hand signals and he was able to place the platform a few tens of meters away from the nose of the whiting. During the two years the platform was in operation, Volchok's people made monthly visits to exchange collectors. Never again did a whiting appear. While never a serious contender, the artesian idea was dead. I should add that numerous birds used the platform as a rest stop and probably added ^{90}Sr and ^{137}Cs .

During a visit to Florida some years later, I learned that scientists at the USGS were claiming that whittings were formed by spontaneous crystallization of CaCO_3 from the supersaturated bank water. I was irate. How could this be when the evidence was so clear? During those discussions, Captain George's sharks came to mind. The USGS people agreed that sharks were indeed present in whittings. I asked why. The answer came back that as sharks could hunt electronically, they could 'see' the fish in the turbid water. But the fish couldn't see the sharks. One step in logic and I had the answer. Just as spiders make webs to capture bugs, sharks make whittings to capture fish. A great idea, but I've yet to make many converts.

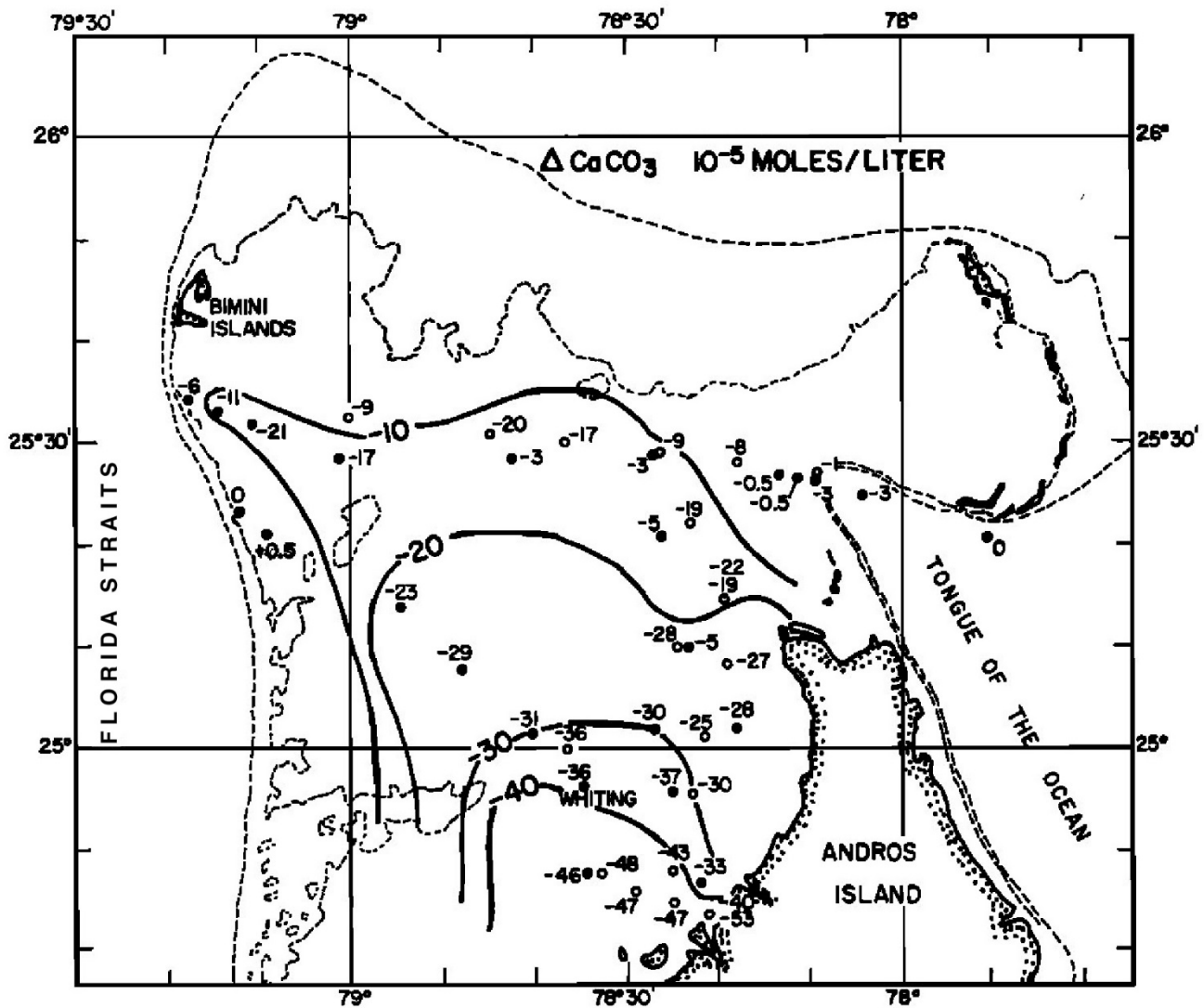
I made only one other visit to the Bahamas. This time as a tourist. While riding around on a motor scooter with a friend, we encountered a film crew. It turned out that they were filming the Beatles' movie "Help". We watched for a while sitting on top of a road cut. During a break, Ringo Starr wandered over and asked who we were. The result was his autograph, something that my daughters much prized.



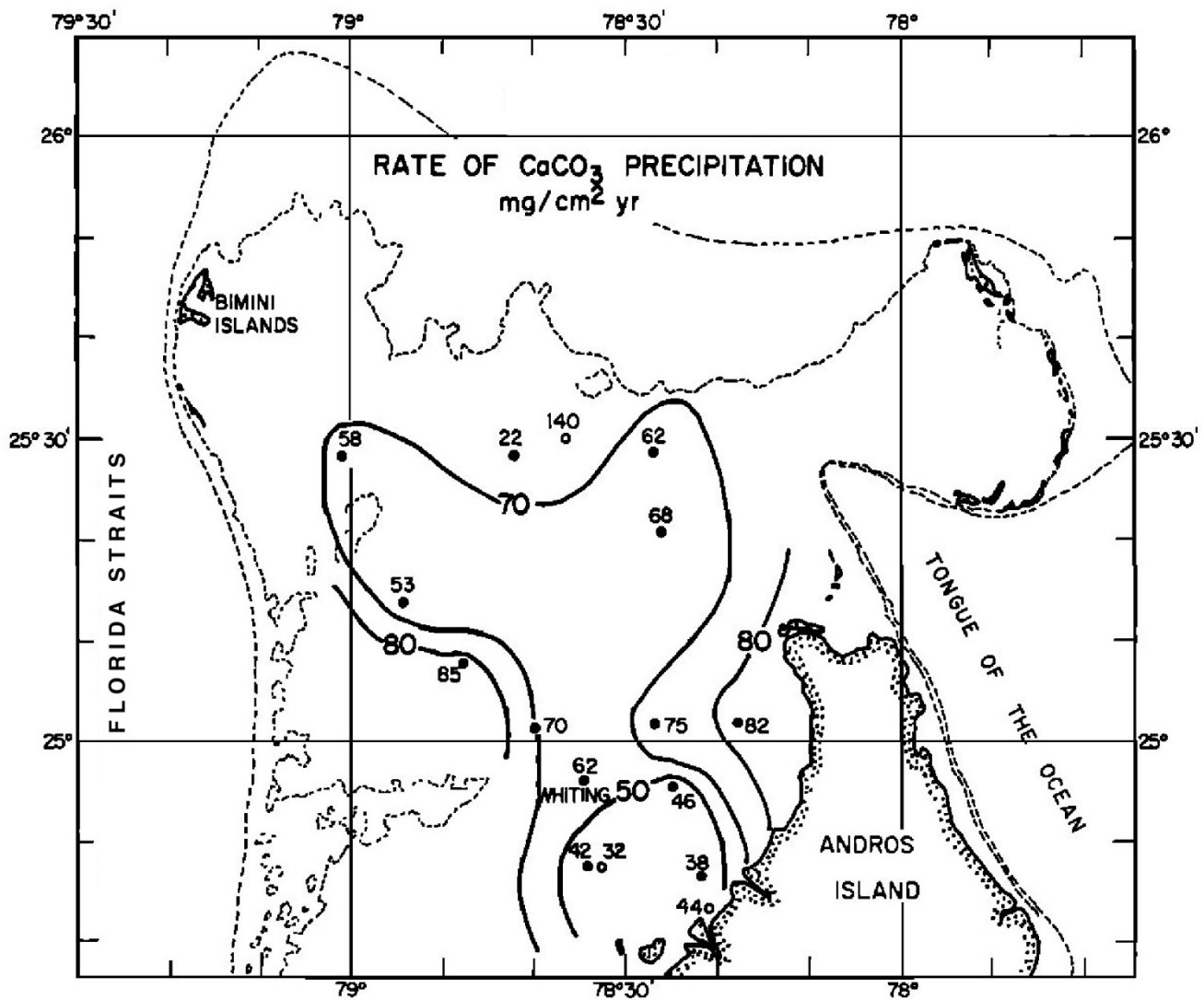
Air photograph showing white streaks in the water covering the shallow Bahama Bank. I am convinced that these so called 'whitings' are created by sharks. The water is so turbid that fish cannot see, allowing the sharks to feast on them.



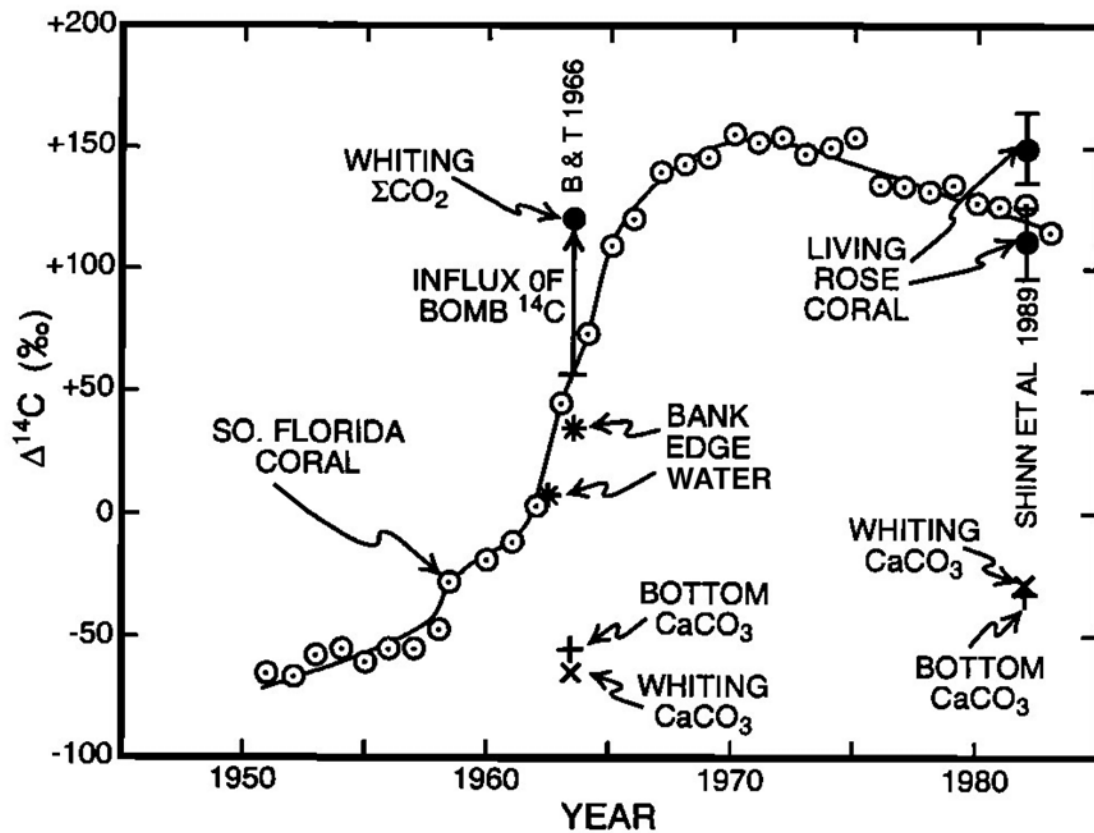
Residence time based from the salinity of individual water samples assuming an evaporation rate of 1.2 m/yr. As can be seen, Andros Island creates a barrier allowing residence times exceeding 100 days. The open circles are for samples taken in 1963 and the closed circles for those taken in 1964.



Magnitude of the amounts of CaCO_3 precipitated from the water during its residence on the Bahama Bank. The units are 10^{-5} moles CaCO_3 /liter. The open circles are for samples collected in 1963 and the closed for those from 1964.



Rate of CaCO₃ precipitation as a function of location on the Bahama Bank. As can be seen, they average about 60 mgCaCO₃/cm²yr. This translates to 0.6 meter of sediment per thousand years. If this rate has persisted for the last 7000 years, then about 4 meters of CaCO₃ must have accumulated since the banks were flooded at the end of the last glacial period. The open circles are for samples collected in 1963 and the closed for those collected in 1964.



Radiocarbon results (expressed as $\Delta^{14}\text{C}$) on whiting CaCO_3 published by Broecker and Takahashi (1966), and those published by Shinn et al. (1989). In both cases, the $\Delta^{14}\text{C}$ value is far below that for the dissolved inorganic carbon in bank water and nearly identical to that for bottom sediment. The circles are for samples of growth ring-dated coral obtained by Ellen Druffle.

References

Broecker, W.S., and T. Takahashi (1966), Calcium carbonate precipitation on the Bahama Banks, *J. Geophys. Res.*, *71*, 1575-1602.

Morse, J.W., F.J. Millero, V. Thurmond, E. Brown, and H.G. Ostlund (1984), The carbonate chemistry of Grand Bahama Bank waters: After 18 years another look, *J. Geophys. Res.*, *89*, 2604-3614.

Shinn, E.A., R.P. Steinen, B.H. Lidz, and P.K. Swart, (1989), Whitings, a sedimentologic dilemma, *J. Sed. Petrol.*, *59*, 147-161.

Broecker, W.S., A. Sanyal, and T. Takahashi (2000), The origin of Bahamian whitings revisited, *Geophys. Res. Letts*, *27*(22), 3759-3760.

Chapter 7

Doc Ewing and his *Vema*

Lamont's creator and first Director, Maurice Ewing, was an extremely unusual man. Large in stature with bushy eye-brows, he had presence, to say the least. I doubt that anyone else could have duplicated what he accomplished between 1949, when he convinced Dwight Eisenhower (then Columbia University's President) to allow him to take control of the Lamont estate and 1971, when at age sixty five, he was mandated to give up his administrative post. During these years, he put together a world class research organization. Much of this was accomplished by a combination of willpower and focus. Realizing that the sea floor was largely unexplored, Ewing moved quickly to secure an oceanographic vessel, to create a machine shop capable of equipping it, and to put together a pool of young scientists to man it.

His first ship, *Vema*, was purchased four years after Lamont opened. She was a three-masted schooner, *Hussar*, owned by the Hutton family and considered by many to be the most sumptuous private yacht in the world. In 1932, the *Hussar* was sold to George and Maude Vetlesen and renamed *Vema*. But, as happened to Anna Sewell's fictional horse, Black Beauty, her fate took a bad turn. During World War II, *Vema* was put into service as a Merchant Marine cadet training ship. Long time *Vema* Captain, Henry C. Kohler, told me that the first time he saw *Vema* was from his porch in Lunenburg, Canada. He remembered saying to himself, "What a wreck. I wonder who captain's her?" Two weeks later, he signed on to be that man.

Aware that the equipment required for his vessel had to be home built, Ewing managed to get funds to build a machine shop, and to assemble the full array of equipment needed for his purposes. Under the firm but friendly hand of Angelo Ludas, the Machine Shop became Lamont's hub. A number of young scientists had benches where they built apparatus necessary for their research. Although in those days, we had little time for socializing, there was what we now call TGIF with Angelo handing out small doses of Scotch whiskey to his guys and others drawn to this weekly event.

To man his ship, Ewing recruited young men eager to join him in exploring the sea floor. A number of them received Ph.D. degrees at Columbia and remained at Lamont as scientific staff members. In order to fend off more lucrative offers from other institutions, Ewing wrangled professorships for several of them in Columbia's Geology Department. In order to do this, he had to twist the arms of a succession of chairmen. Worn down by Ewing's overwhelming willpower, when their terms were over, each of these chairmen left the department. Arthur Strahler moved to Columbia's Geography Department, John Imbrie to Brown, Jack Oliver to Cornell, Chuck Drake to Dartmouth, and Tony Watts to Oxford. Meanwhile, Lamont became the dog and the Geology Department its tail. When I arrived, there were three Geology Department professors housed at Lamont (Ewing, Kulp, and Press). The rest were on the Manhattan campus. By the time Ewing's reign came to an end, all but one was housed at Lamont.

With these elements in place, Ewing took control. He sent the *Vema* on 25 globe-encircling expeditions. Each took about one year. Instead of doing a specialized research program on each month-long leg as we now do, Ewing prescribed a set program for all of the legs. Any specialized projects were treated as add-ons rather than centerpieces. While underway, topographic, gravity and magnetic measurements were made. At each daily station, a piston corer equipped with a series of outlying thermometers was deployed. A water sample for ^{14}C , a plankton tow, a nephelometer cast, and a series of bottom photos were taken. Each day, using a compact numerical code, Captain Kohler would telegraph Ewing a summary of the day's accomplishments. So, not only did Ewing create the facility, he supervised every aspect of its operation including the routes for each year's global expedition. As Lamont was block-funded by the Office of Naval Research (ONR), Ewing held the purse strings.

As a geochemist, during my first 8 years at Lamont I was not invited to go to sea aboard *Vema*. In fact, as most of us in Kulp's group shared his religious views (and those of Wheaton College's Billy Graham) we were largely shunned by Ewing's people. They referred to us as the "theo-chemists". Then in 1960 I got the nod. Georg Wüst, a world-renown hydrographer, recently retired from Keil, joined Lamont. He decided to check what he viewed as a downward

trend in the O₂ concentration in Caribbean deep water. The topographically-isolated deep Caribbean Sea is ‘ventilated’ by water from the Atlantic spilling in over an 1800-meter deep sill. In an attempt to explain the decline in its dissolved oxygen content, Wüst got the idea that the spill-over events occurred stochastically, separated in time intervals of many decades. In between each of these spills, the O₂ was steadily depleted by respiration. It later turned out that the actual explanation was very different. The metal Nansen bottles used in all hydrographic surveys were accumulating rust which consumed O₂ from the water they trapped. The more extensive the rust, the greater the extent of O₂ loss. Wüst didn’t know this, of course, so he was able to convince Ewing to allow him to use the *Vema* to resample the deep Caribbean. I was asked to go along. It was an eye-opening experience.

I joined the *Vema* at Grand Cayman Island. Now a tax haven, then it was a sleepy place with a magnificent crescent-shaped beach. As Wüst was unable to be there, Saul Friedman, a Columbia general studies student, was given responsibility for the O₂ measurements. My confidence in Saul plunged when I met him on the beach the day before we sailed. He had left his clothes unattended while he swam and he was extremely upset when he returned to find them missing, including his wallet containing \$500.

Our first station was to be just off the south side of Cuba. The *Vema* arrived there early in the morning. Karl Turekian, once my fellow grad student and at that time an assistant professor at Yale, and I had breakfast together. Afterward we went up on deck to see what was happening. It turned out there was a commotion over the approach of a Cuban light bomber complete with fore and aft gun turrets. As *Vema* carried a large load of dynamite used for seismic profiling, one bullet and we would have been blown to smithereens. The plane swooped over us about 100 feet above *Vema*’s mast. We were only nine miles offshore and it was the second year of Castro’s regime. We were apparently being told to get the hell out of Cuban waters. Captain Kohler acted quickly, running up the research flag and getting the ship underway. Noting that he had received our message, after buzzing us once more, the Cuban pilot flew back home.

But the real excitement came when we got to our next station. Karl and I watched with amazement as the crew prepared to lower wires from each of the ship's two winches. The piston corer was attached to a cable capable of hauling back the one-ton lead weight which drove the core pipe into the sediment. Once it was on its way down, they deployed a hydro wire from a second winch a scant 35 feet away. Puzzled, we were told that this was the standard mode of operation. The hydro wire kited away from the ship and the core wire went nearly straight down. It had been done hundreds of times without a problem, so we were told. At intervals, the thin hydro wire winch stopped and a Nansen bottle with its companion reversing thermometer was attached. This happened 20 times. The idea was to obtain a complete water column profile of O₂.

Then, all hands peeled their eyes on what was called the tension accumulator, a small metal arrow which registered the strain on the core cable. We were told that when the outlying trigger-weight touched bottom, the piston core would be released for a twenty meter free-fall. The sudden release of strain produced a blip in the position of the arrow. This blip signaled the winchman to stop. Everyone watched because the blip was over in the blink of an eye. The coring cable was attached to a piston which was rigged so the scope of the loop of extra wire would snap tight, thus stopping the piston just before it reached the bottom. This clever device was referred to as the Ewing piston corer. This brought howls from Scandinavia where Kuhlenberg claimed that it was only marginally different from a device he had invented years earlier.

When the crew had attached the last of the Nansen bottles on the wire, a messenger weight was placed on the wire and sent down. When it reached the uppermost Nansen bottle, it did three things. It closed the bottle which isolated water for the on-deck O₂ analysis. Second, it allowed the reversing thermometer to tip over sealing in the water temperature and pressure (i.e., depth). Third, it released a messenger that would trip the next Nansen bottle.

When adequate time had passed for the messenger to reach the last bottle, the winchmen began to reel in the two wires. All was going smoothly until someone yelled "the wires are tangled!" Sure enough, the hydro wire was wrapped around the coring cable. The crew tried

valiantly to pull them apart as they were being slowly reeled in. Then, someone shouted “asshole in the wire!” This was a nautical term indicating the wire had coiled in on itself. At the end of the coil was a tight loop (the asshole). One of the crew stuck a shiv through the loop and attempted to uncoil the ‘asshole’. As he was doing this, there was a sharp snap and 20 of Georg Wüst’s precious reversing thermometers (and their companion Nansen bottles) disappeared into the abyss.

Twenty more pairs remained. At the next station, Joe Worzel, who was Lamont’s Associate Director (and chief scientist on this *Vema* leg) decided the problem was that the trade winds were blowing one way and the current was flowing another. To compensate for this, he decided to hoist the *Vema*’s main sail. Once done, the two-wire operation was once again put in motion. The result was exactly the same; the wires tangled, an asshole developed, and down went the last of Wüst’s thermometers.

In hindsight, the problem was that the twenty Nansen bottles created a drag not present when only the camera and nephelometer were attached to the end of the wire. The *Vema* had never before deployed Nansen bottles nor had anyone aboard seen it done. Turekian and I wondered why Worzel took the chance. Had each cast been done sequentially rather than simultaneously, the cost would have been two hours of ship time. But “Doc” (as we affectionately called Ewing) wasn’t into wasting time. Years later, Turekian referred to this fiasco as Expedition Boo Boo.

This brought to an end the geochemical add-on to the leg for we had no more Nansen bottles or thermometers. This being the case, Karl and I were each assigned to a seismic profiling team. Each ‘shot’ required the release of a streamer of hydrophones coupled with the drop of a half-pound block of dynamite. As the fuse was set for about 30 seconds, to prevent it from sinking the dynamite block was attached to one end of a two-foot long string and a balloon to the other. The idea was to inject the sound produced by the explosion close to the sea surface. I well remember tucking these balloons under my arm pit, leaning over the side, dynamite block in my left hand, pulling the fuse igniter with my right.

The sound waves generated by the explosion would bounce off the sea floor and off 'layers' in the underlying sediment and basalt crust. These reflections were recorded by the hydrophones. Scary employment, especially when the seas were rough. I also remember that if the balloon came loose and the block was allowed to sink, the explosion would wake up all those in their bunks. It sounded as if someone had leaned over the side with a heavy hammer and clunked it against the ship's hull.

In addition to serving two four-hour daily shifts on a dynamite team, we took turns deploying a daily bathythermograph. This required lowering into the thermocline a brass cylinder from yet a third winch. The pressure and temperature were recorded on a small gold-coated glass plate. These measurements, mandated by the Navy, were presumably of use to submariners.

After one fifteen minute lesson, I was cleared to do these casts. My first attempt was at four in the morning. Alone on deck, I lowered the device with no problem. But raising it was a nightmare. Because of some mechanical fault, the winch would abruptly stop. This happened just as the device broke water, causing it to flip up above my head and over a cable stretched horizontally above the rail. Embarrassed at my ineptitude, I climbed up on the rail and tried to lift the bathythermograph back over the wire. I slipped and found myself suspended over the ocean hanging on the wire with one hand and holding the device in the other. I dropped it and was able to get my other hand on the wire. I then jumped back on deck. I still shudder when I think about it. Had I fallen overboard, no one would have missed me until breakfast time. Clearly, safety was not an issue on Ewing's ships. Had my mishap been observed from the bridge, I certainly would have heard about it. I didn't.

Three weeks later we arrived in Panama. Awaiting the canal transit I was able to spend another night on the *Vema* before releasing my bunk. The next morning while I was in line for breakfast, I encountered Howard Worzel, Joe's 16 year-old son who served as *Vema's* camera man. I had heard rumors that he had joined some of the crew members for a visit to the local red

light district. So I asked him if he had enjoyed himself. His reply was a classic, “Oh, it was o.k., but nowhere near as much fun as fighting for it in the back seat of the old man’s car.”

Although the seismic profiling on the Worzel leg went without incident, three months later a terrible, terrible disaster occurred. When the supply of the commercial half-pound dynamite blocks ran out, a switch was made to World War II surplus dynamite sticks. As half a stick was adequate, the procedure was to cut each one. One morning while Chief Scientist, John Hennion, was doing this, the dynamite stick exploded, killing him. Compounding the tragedy was that Hennion left behind four young children and a pregnant wife. This of course led to a temporary termination of the seismic profiling program. But, when the *Vema* reached Ushuaia, at the southern tip of Argentina, Ewing was there to make sure that the program was reinstated on the following leg. The son of Fritz Houtermans, a well-known European nuclear physicist, was onboard as a member of the technical staff. When he learned that the dynamiting was going to resume, he quit. Angered, Ewing refused to lend him any money. So he left the ship without nearly enough to get back to his home in Switzerland. It is said that he hitch-hiked to Buenos Aires. Ewing was tough!

I made three more voyages on the *Vema*: one in 1963, one in 1965 and the last one in 1976. Each was memorable. The first of these was a Bermuda to Bermuda leg and I well remember that our departure was delayed by the passing of a major storm. *Vema* was anchored in the middle of Hamilton Harbor waiting it out. At one point, she broke anchor and started to drift. The engines wouldn’t start. The steering was disabled. Our helpless ship was drifting toward a dock where, by sheer chance, Ewing’s newly acquired *R.V. Conrad* was tied up. A thought went through my mind that this might be the end of Lamont’s ‘navy’. Fortunately, before this could happen, the engine and also the steering apparatus came to life. The collision was avoided!

My reason for joining this leg was to test a device capable of obtaining water samples for radon measurement from just above the bottom. It had a foot which projected below the 25-liter water barrel. When it touched bottom, it was supposed to allow the lid to snap shut, sealing off

the water. But, alas, on each of the four tries, the device failed. So, I had to be content with measuring radon in surface water.

I was puzzled by the purpose of this expedition. Ewing had the idea that he could see evidence of a crater imprinted beneath the sediment in the basaltic crust. He was looking for evidence of an impact that occurred during the Earth's early days. I was baffled because both the thickness of the sediment cover and the sedimentation rate were known. It likely accumulated during a period encompassing only the last one percent of geologic time.

Further, this was the time when plate tectonics was being hatched. Evidence was emerging that the basaltic crust was being replaced once each 100 million years. The features Ewing envisioned to be circular were proved instead to be linear. It is said that Ewing never accepted plate tectonics. By the time he died in 1974, the evidence in support of this revolution was overwhelming. So the man who set out to study the ocean floor missed the most important evidence hidden there.

My next voyage on *Vema* was a leg from Hawaii to Tokyo. As chief scientist, one objective was to determine whether reversals in the Earth's magnetic field were recorded in deep sea sediments. Taro Takahashi, eager to visit his family in Japan, agreed to join me. We arrived in Honolulu a few days before we were to sail, so that we could take a side trip to the 'Big Island' to see the spectacular eruptions in the Kilauea fire pit and also to visit the observatory high up on the extinct volcano, Mauna Loa where Charles David Keeling's atmospheric CO₂ measurement facility was housed.

On the way back to Oahu, Taro and I calculated the steaming time to Tokyo and realized there was almost no time for our program. Early the next morning we located a pay phone and with fear and trembling, we called Ewing to ask for a 24-hour extension. Expecting a tirade, instead he welcomed our call and, in response to our request said, "No problem, boys – take two days." It was a few days later that we learned from Captain Kohler why we received such a warm reception. On the day that I phoned, Ewing and his administrative assistant, Harriet

Bassett, had gotten married. After a honeymoon lunch, they had returned to work at Lamont. In a sense, we had caught the bouquet!

Halfway to Tokyo, we took a core which consisted of red clay. We had planned to punch plastic vials (like those used for pills) into the red clay in order to get oriented samples for magnetic direction measurements (to be made by Lamont's John Foster). Little did we realize how sticky the red clay was. When we pulled the first tube out, there was more red clay sticking to its outside than was in the tube. Once the sampling was complete, half of the core was virtually destroyed. Ewing took note of this.

I saved the red clay scraped from the outside of these sample tubes for use in a prank. I molded pieces that looked like human excrement and placed them on the floor of Captain Kohler's private, newly-tiled shower. A few days later, the cook delivered the pie Taro and I had begged for. The crust was perfect, but instead of apples, inside was our red clay.

We entered Tokyo's estuary on a rainy and windy night. Little did we know that we were in for a huge treat. An algal bloom had occurred which created a phosphorescent glow on the ship's wake and on wave crests. Stunning! In the morning as we approached the dock, we saw a small group of people standing beneath umbrellas. It was Taro's family. They had not seen him since he left home for graduate school in 1952. They had waited 15 years for his return. I rarely cry. But Taro's 'welcome home' caused tears to flow.

My last voyage on the *Vema* was in 1976. By that time, I had spent several months on Woods Hole's *Knorr* and on Scripps' *Melville*. It was like jumping back a century in time. Kohler's *Vema* was operated like a British ship in the 1850s. The food was awful, the rooms were tiny, water was rationed, and Kohler was king. While on my first three *Vema* experiences, not knowing that a better world existed, I assumed that it was life at sea and didn't complain. But when I arrived in Singapore, things immediately began to unravel. At breakfast the first morning, I spotted a stainless steel bowl full of stewed rhubarb. As it is one of my favorites and was poised to dig in, I heard giggles from the others in line, then I heard why. "It's rancid; Kohler won't

remove it 'til we've eaten every bit." I responded, "Well, I'll fix that" and picked up the bowl, took it up on deck and poured it overboard.

I went below and realized that the only edible food was packaged dry cereal; all rice bubbles which I don't like. When I asked why no cornflakes, I was told that the ship's officers, who were served at tables, had first dibs and we, crew and scientists, got the rejects, i.e., rice bubbles. So I gathered a dozen or so packages of rice bubbles and threw them overboard. Needless to say, Kohler was furious, but as the leg's chief scientist, I was immune from reprimand.

Graduate student, Robbie Toggweiler, was one of the small scientific crew (4 in all). He was assigned one of the tiny rooms to be shared with a crew member. I asked if there wasn't a more suitable arrangement. Kohler said, "No." I said, "But what about the bridal suite?" This was a room added to the bridge which had been used by Kohler's daughter and his first mate as their honeymoon suite. Again "No". When I found that the reason was that Kohler was using the suite to store teak planks he had purchased along the way for his personal use, I raised the roof. Finally, Kohler relented and had the wood moved, so that Robbie could occupy it.

Our goal was to make ^{14}C , O_2 , dissolved silica, and radium measurements on the waters in the string of deep basins associated with the Indonesian passageway which connected the Pacific Ocean with the Indian Ocean. To get there from Singapore required a two-day eastward transit across the shallow shelf separating Borneo from Bali. On the way, my sixteen-year-old son, Scott, along as a helper, developed a very serious infection. It turned out that while skateboarding on the Singapore dock, he had fallen and cut his leg. Captain Kohler got in touch with shore-based medical people. Fortunately, *Vema* had a medical cabinet which contained what was prescribed. After a few days of soaking the wound, Scott recovered, much to my relief.

On our first attempt to recover our 20-liter Niskin bottle (the PVC replacement for Nansen bottles) from the hydro wire, we were stunned that the wire angle approached horizontal. We were aware of the very strong currents, but had no idea that because of this, the wire angle would be so great that we couldn't reach the Niskin bottle. As *Vema* had no thrusters, there was

no way to counter these currents. Rather, we had to live with them. The solution was to build a two-by-four platform. Even with this, Robbie, a tall man, had to use his foot to release the bottle's outboard clamp. Fortunately, we had a reversing thermometer which recorded the depth at which the sample was taken. For under these conditions, 'wire out' was useless. Once we mastered this complication, everything went smoothly. We sampled deep waters in a chain of deep basins: Celebes, Banda, Weber, Batjan and Morotai. When the analyses were completed, we found that the water in these basins has an apparent ^{14}C age about 250 years greater than that for the deep Pacific water which feeds them. Also, the O_2 , SiO_2 and ^{226}Ra concentrations matched those for the deep Pacific feed water.

Having said some negative things about *Vema*, I must end by praising the vast archive of information she retrieved. In her lifetime, she took more sediment cores, more miles of magnetic and gravity profiles, more pictures of the sea floor than any other oceanographic vessel before or since. This was accomplished under Spartan living conditions and a total disregard for safety.

It is puzzling that despite Ewing's tenacity in collecting data, to my knowledge, he never wrote a paper interpreting it. Yes, he put his name on many papers, but I suspect others produced the ideas and did the writing. However, were it not for Ewing there would be no Lamont and it would never have become the world's premier geoscience research center.

Faced with a University requirement then in force for Columbia's administrators, Ewing was scheduled to step down at age sixty-five. Facing this deadline, he sought a way to retain control of his creation. At that time, New York University was developing a large plot of land in the Ramapo Mountains, 40 miles northwest of the George Washington Bridge. It was to be a research complex combined with gardens and ski slopes. Ewing got the idea that Lamont could move out from under the Columbia umbrella and become an independent laboratory located in NYU's Sterling Forest complex.

I well remember a meeting held in Ewing's house on the Lamont campus. Few of us had ever been inside. The attendees consisted of all the senior people on the Lamont staff. About one third had faculty appointments. The rest were research scientists. Ewing presented a sketchy plan

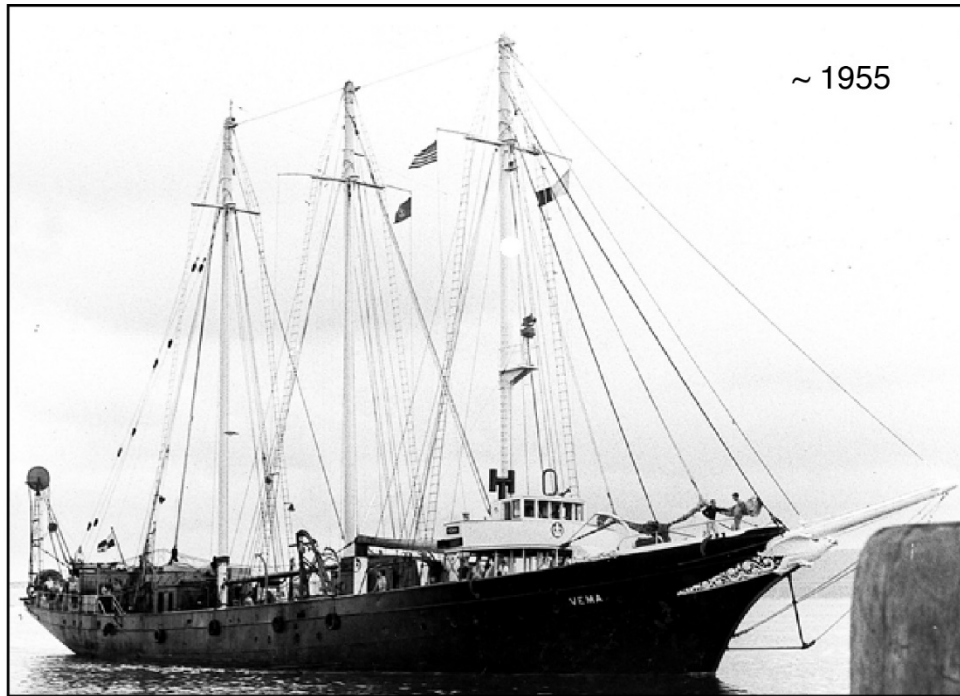
for the move to Sterling Forest. Then he asked for comments. I remember only one because I'm sure that it strongly influenced the vote. Someone asked Arnold Finck, Lamont's Administrator, how he viewed the plan. Although I don't remember Arnold's exact words, the gist of his answer was that from a financial point of view, it would be risky. As Columbia backed us against bankruptcy, were we to become independent, we would lose that security. Once the discussion wound down, Ewing asked for a vote. I suspect he felt those on the research staff would vote to move. The vote was done by raised hands. There was no need to count for at least three-quarters of the votes were nos. As we left the Ewing's living room, Associate Director, Joe Worzel, commented "you ungrateful bastards."

Realizing that the Sterling Forest plan was dead in the water, Ewing began negotiations with the University of Texas to move to their Galveston campus. Instead of having a meeting to discuss the plans, he invited us to join him in Galveston. Only five or six of our people chose to move. Ewing also attempted to transfer both Lamont ships (*Vema* and *Conrad*) to Galveston. Manik Talwani, who was appointed as Ewing's successor, conferred with the people at the National Science Foundation who funded the operation of the USA's oceanographic fleet. He was told that under no circumstances would they allow such a transfer.

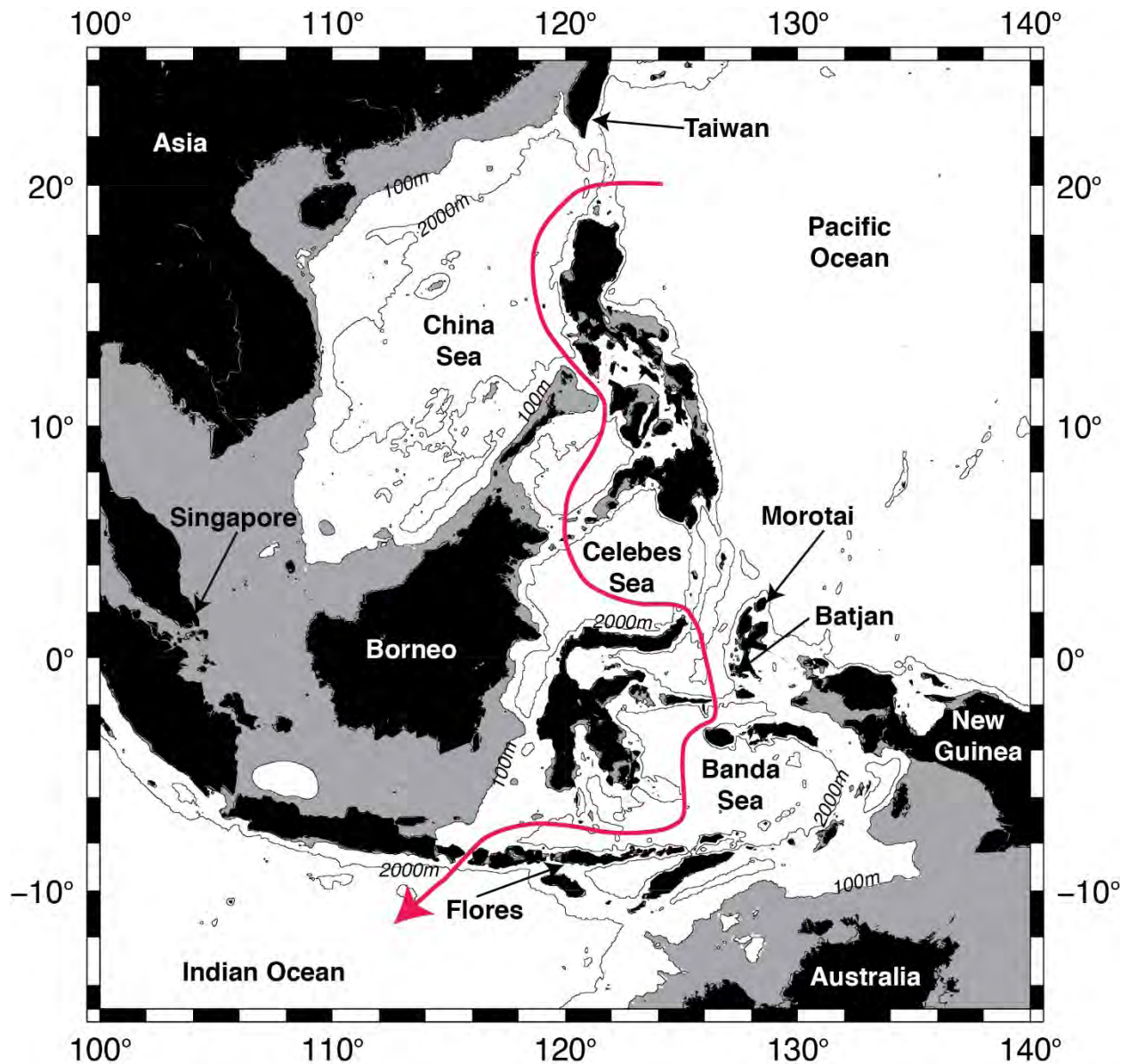
Ewing is buried in a cemetery a few miles north of the Lamont Campus. His gravestone overlooks the Hudson River where, between some of her annual round-the-world voyages, *Vema* made brief homeport landfalls. On Ewing's gravestone is imprinted a sketch of *Vema*. She remained a Lamont research vessel until 1981 (10 years after Ewing's departure). She was then sold to Windjammer Cruises to serve tourists in the Caribbean. Refurbished back to much of her original glory, she was renamed the *Mandalay*. She is still in service.



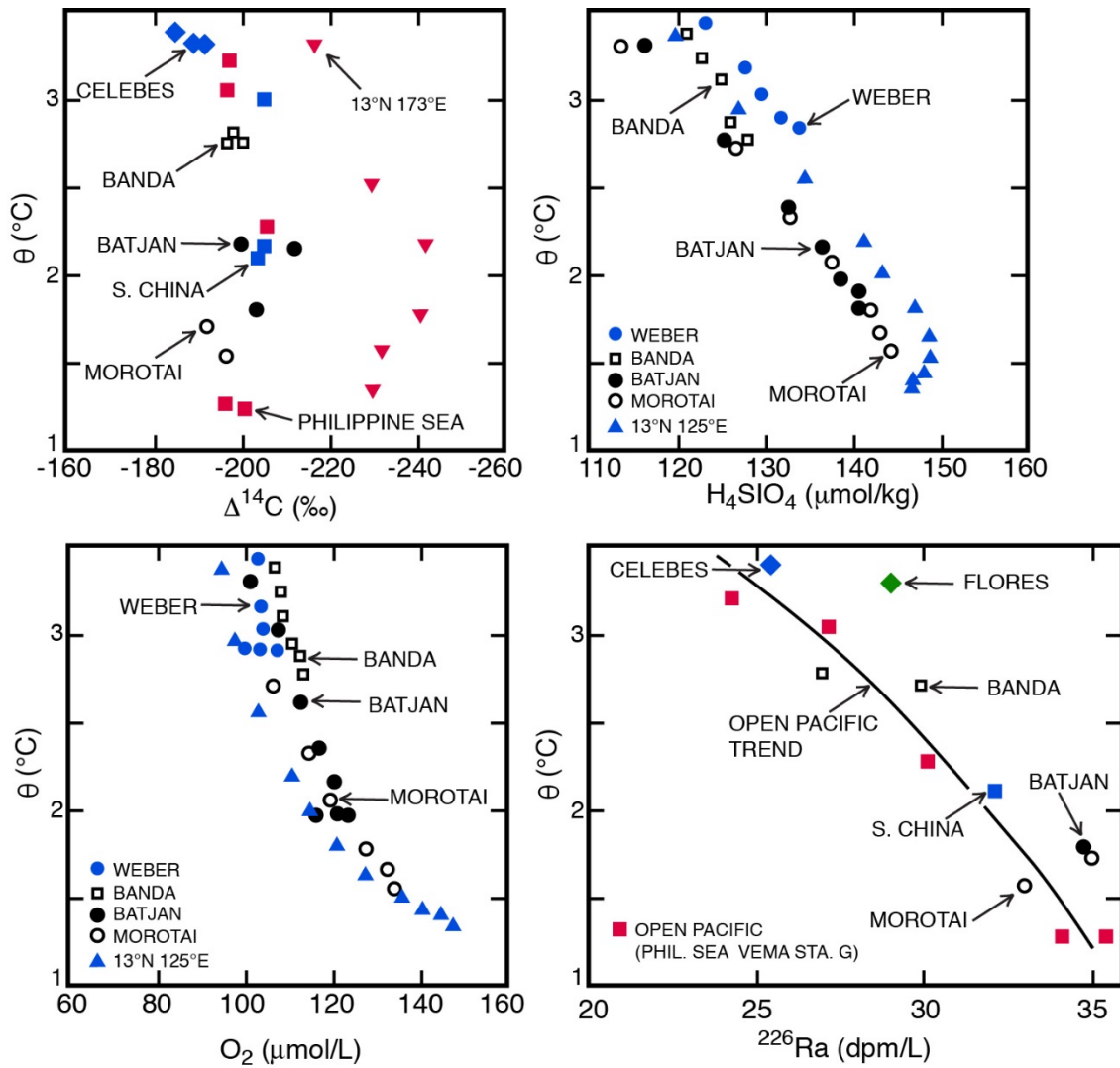
Portrait of Maurice Ewing who in 1949 created Lamont Geological Observatory. He directed it until his retirement in 1971. Behind him is depicted his beloved research vessel, *Vema*. It was the work horse of Lamont's oceanographic program from 1955 until 1981.



Although already diminished from its original sumptuous state in 1955, when Lamont refurbished *Vema* to become a research vessel, she retained much of her glory. But, by 1981, when she was decommissioned, she had lost her masts and bowsprit and she had gained a replacement bridge topped by an antiroll tank and 'bridal suite.' She also was equipped with aft labs.



A map showing the locations of the series of deep Indonesian Basins ventilated from the Pacific Ocean. With Robbie Toggweiler, Peter Katoris and my son, Scott, as scientific crew, we sampled all these basins. Our leg started in Singapore and finished in Taiwan.



Comparison of plots of radiocarbon, dissolved silica, O_2 and radium versus temperature for deep Indonesian Basins with that for the adjacent deep Pacific.



Ewing's gravestone, which in the 42 years since his death, has started to erode away. The sketch of the *Vema*, his name and an epitaph listing his accomplishments are barely legible. After his death, Harriet Bassett, Ewing's administrative assistant and wife, remarried and assumed her husband's name.

References

Broecker, W.S., W.C. Patzert, J.R. Toggweiler, and M. Stuiver (1986), Hydrography, chemistry and radioisotopes in the southeast Asian basins, *J. Geophys. Res.*, *91*, 14,345:14,354.

Chapter 8

Heezen and Ewing

Soon after I arrived at Lamont, I began to hear stories about Ewing's graduate students who had lived in Lamont Hall during the early days. One concerned Bruce Heezen who was starting out on a career in marine geology. It was said that each morning his breakfast consisted of two raw eggs and a bottle of beer. Years later when I was invited to his house for dinner, I realized that along the way Bruce had become both a gourmet and a wine connoisseur.

Although my contacts with Heezen were few and far between, I did publish a paper with him on what appeared in Atlantic sediment cores to be a very rapid ending of the last glacial period. Also, in connection with an international meeting on ocean science held at the United Nations in 1958, Bruce had a contribution to the abstract volume which concerned annual layering in Cariaco Basin sediments. As I did radiocarbon dating confirming his claim, I was listed as co-author.

At this meeting Heezen also presented an explanation for his globe-encircling ocean rift system. He postulated that as the result of a phase change in the Earth's mantle, the Earth had begun to expand and that this expansion created the ridge that runs down the middle of the Atlantic and extends from there through the other oceans. It was too bad he didn't realize that the extra crust being created at the ridge crests was compensated by subduction of old crust beneath trenches. Had he realized this, he would be remembered as the discoverer of plate tectonics.

Heezen is best known for the physiographic map of the sea floor created in cooperation with Marie Tharp. I'll never forget something that Mildred Rippey told me about Bruce and Marie's mode of operation. Mildred had once served as J. Laurence Kulp's secretary. But after a funding lapse, he had let her go. Fortunately, she was able to transfer to Heezen and Tharp. A while later when I encountered her on our campus, I asked how she liked her new job. "It is very interesting and I enjoy it. But, every now and then, Bruce and Marie have huge fights. They use sailor language and throw things at each other. I have to get under my desk and await the battle's end."

In the early 1960's I began to hear gossip that Ewing and Heezen, once like father and son, were no longer talking to each other. The reason appeared to be that Heezen had violated Ewing's firm rule that, upon arriving in port, *Vema's* chief scientist should immediately fly back to New York with the data in hand. Word had it that when Heezen arrived in Tahiti, instead of flying back, he bummed around the islands for a month (presumably with the precious data in hand).

Only recently, I heard that there was perhaps a more important reason behind their disenchantment. It had to do with an early version of the physiographic diagram of the sea floor (for the North Atlantic). As was the case for many of the papers written by members of his geophysical group, Ewing was added as a co-author. When he learned that the North Atlantic map was to be published, he asked that his name be added. Heezen refused.

I became involved in their war in 1966. As mentioned in the chapter titled "Ewing's *Vema*," Taro Takahashi and I had taken a red clay core in the Pacific Ocean in hopes of demonstrating that the reversals of the Earth's magnetic field were imprinted in ocean sediments. It turned out that our record was too noisy to prove this. A few months later, I learned that Billy Glass, one of Heezen's graduate students, had analyzed a core from the Southern Ocean which showed that indeed reversals were recorded. Just as I was leaving to attend the second (and last) International Oceanographic Conference in Moscow, I was given a preprint of the Glass *et al* paper. I put it in my briefcase and read it during the flight to Russia. Clearly, they had a solid record. The difference was that our core was from 20°N and theirs from 50°S. The higher the latitude, the stronger the magnetic signal.

One morning during the Moscow meeting I was having trouble finding talks that interested me. I settled on one which might fill the bill (a talk by a Russian scientist). I entered the lecture hall a few minutes after the talk had begun and was shocked to see that, instead of a Russian, it was Heezen giving the talk. It turned out that the Russian wasn't able to attend and Heezen was a last minute substitute. Even more surprising was the subject of his talk for he was presenting the Glass *et al* magnetic reversal paper. I pulled out the preprint and noted two things.

One was that Heezen was not an author and the other was that his projections matched those in the preprint.

When I returned to Lamont, I found that there was a huge uproar concerning Heezen's talk. Not only did he not have permission from any of the authors, he had held a press conference where he warned that yet another magnetic reversal was in the offing. Further, according to Heezen, as the last one had been accompanied by the extinction of planktonic organisms, perhaps man would be the next to go. The story appeared in newspapers around the world (including the *N.Y. Times*, *Time* and *Newsweek*). Making it worse, there was little mention of Billy Glass or the other authors. Rather, Heezen got the primary credit.

Ewing was irate and called for a meeting of our faculty. He asked us to vote to remove Heezen from the faculty citing his Moscow high jinx as the major reason. I regret to say that we all (yes, I as well) voted for Heezen's removal. Of course our vote was only the first step. As tenure is sacred, it can only be broken for 'grievous sins'. The next step was for the University to form an ad hoc committee to review Ewing's complaint. That would take months. Plus, as Heezen's sin wasn't grievous, the committee was unlikely to vote for his removal.

By the end of the summer, I had second thoughts about my vote. The fact that Glass was Heezen's graduate student made a difference. Many famous scientists are reputed to have swiped their students' research findings. Most paid no penalty. So one might say that Ewing's proposed punishment didn't fit the crime.

On Labor Day, I decided to confront Ewing. I picked that day because I knew that he would be in his office and that his administrator, Harriet Bassett, would not be there to fend off visitors. As it turned out, this was the case. So I went directly into Ewing's inner office. He asked why I was there. I told him that I was disturbed about the Heezen situation. He asked in what sense and I somewhat foolishly said, "It smells of a lynching." Ewing blew up. And reminded me that I had not undercut his attempt to get rid of Kulp. He went on to call me a "yellow, lily-livered bastard". My colleague Chuck Drake had only recently warned me, "As you have a big mouth Broecker, you should keep in mind that Ewing is the greatest verbal counterpuncher on

the planet.” He suspected that Ewing and I were due for a confrontation. Drake recommended that when it happened, I should keep my mouth shut and let Ewing simmer down. I heeded his advice. Ewing and I sat staring at each other across his desk for what seemed an eternity. Neither of us said a word. Finally, I said, “Well, Doc, if you feel that way about me, I guess I should resign and hope that Caltech’s offer is still open”. He mumbled that he didn’t want me to do that. I got up and left. That was the end of my friendly relationship with Ewing.

I remember leaving Lamont Hall somewhat dazed, until I remembered that I had left Corky, our beagle, running loose in Lamont’s apple orchard. He was nowhere to be found. When I reported this to my wife and kids, I received another set of incriminating stares. Two weeks later, we got a call from a family who lived along the Hudson River north of Lamont. Somewhat sheepishly, they said they had found Corky and renamed him George. Finally, their guilt built up to the point where they phoned the number on his tag.

As for Ewing and Heezen, I know only that a committee was formed. I saw the list of ‘sins’ Heezen had supposedly committed. One item sticks in my mind. He frequently parked his car in the circular drive directly in front of Lamont Hall – a no no. As Heezen was not dismissed, I assume the committee decided there were insufficient grounds for breaking his tenure.

Failing this attempt did not deter Ewing from doing everything possible to make life difficult for Heezen. The first step was to deny his use of Lamont’s administrative services. This being the case, his grants had to be handled through the Geology Department Office on the main campus. Further, one time when Heezen was away, Ewing instructed his administrator to hire a moving van and have everything removed from Heezen’s office. Someone reported to Columbia’s provost that this was about to happen. He called Harriet Bassett and told her in no uncertain terms not to touch one thing in Heezen’s office.

As all this was going on, I received a call from Polycarp Kusch, a Nobel Laureate who was serving as Columbia’s provost. I went to his office and he asked me what I thought about the Ewing–Heezen struggle, complaining that it was consuming thirty percent of his time. After

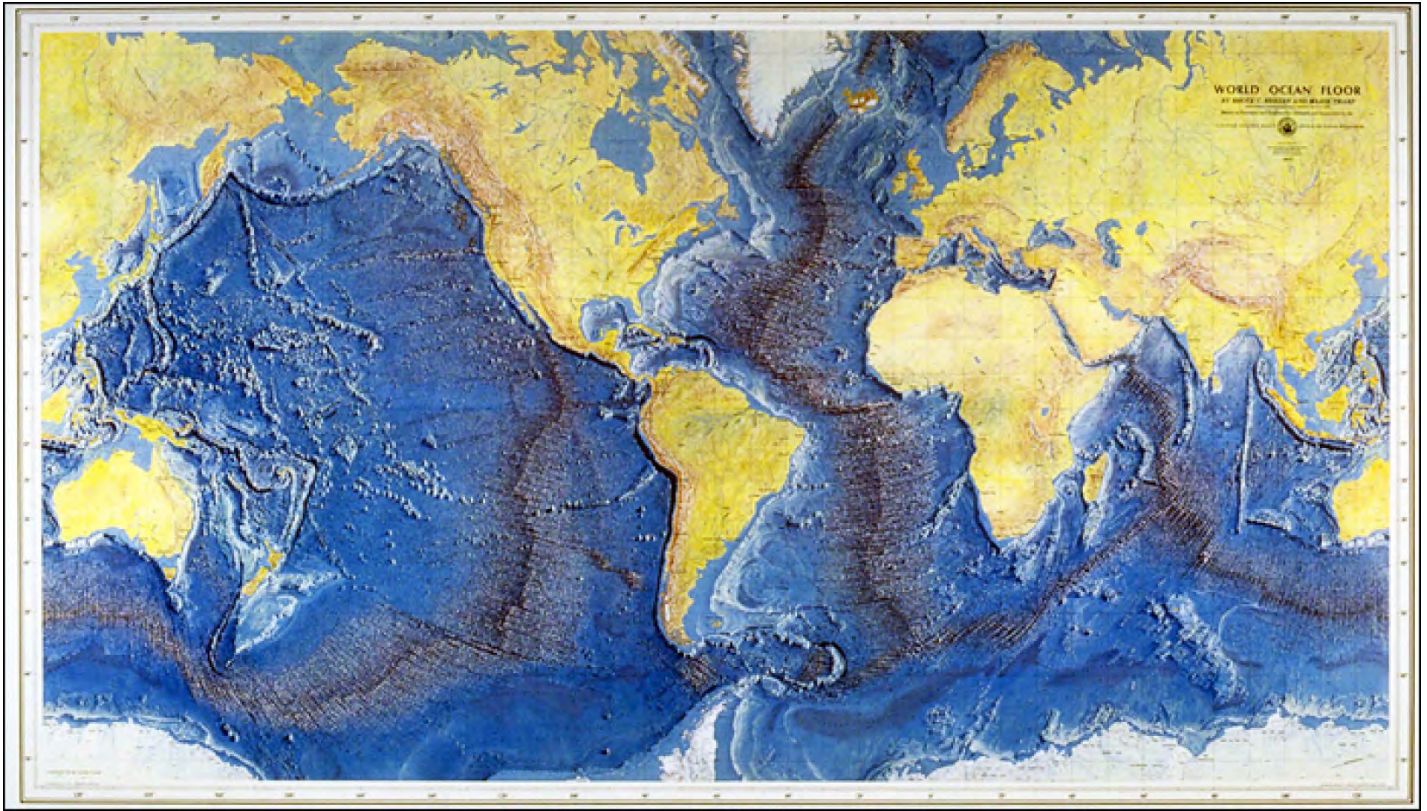
about a half hour, he wrapped up our conversation by saying, “Unlike my fellow nobelist who is a micromaniac, Ewing is a megalomaniac”.

The war continued until Ewing’s death in 1974. It is said that early on Heezen worshipped Ewing. Ewing, in turn, greatly valued Heezen’s advice. They were indeed like father and son. Then the war began and things deteriorated, putting both men under considerable stress. Both died prematurely of heart attacks (Heezen in 1977).

During my time as Geology chairman, a renovation of the hallway in our downtown classroom area was taking place. I asked Marie Tharp if she would place in a case on the wall a copy of the soon-to-be released National Geographic version of the global physiographic diagram of the sea floor. She agreed. A few weeks later, she came to my office and presented me with a press-run copy of the map. For some thirty years, it covered the top of my spare desk. I had long pondered what to do with it. A couple of years ago, Hali Felt, who wrote Marie Tharp’s biography, was invited to Lamont as speaker for our Friday afternoon colloquium. I asked to meet with her. During our visit, I showed her my Tharp-Heezen map. When I told her it was the first one printed, she oohed and aahed. I asked what she would do with it were it hers. She said she would place it on the wall in her living room. “Okay”, I said, “it’s yours.”



Marie Tharp and Bruce Heezen standing in front of their physiographic diagram of the North Atlantic sea floor.



The very widely-displayed National Geographic version of Tharp-Heezen global physiographic diagram of the sea floor.



The second International Oceanographic Congress was held in Moscow (May 30 to June 9, 1966). Shown here is Moscow State University where Bruce Heezen presented his graduate student's (Billy Glass) discovery of magnetic reversals in deep sea sediments.

EVOLUTION LINKED TO MAGNETIC FIELD

Extinction of Some Species Is Attributed to Reversals

Special to The New York Times

MOSCOW, June 1—The mutation and extinction of species in the evolution of life on earth may be attributable in part to periodic disappearances and reversals of earth's magnetic field, a scientist from Columbia University said here today.

The theory was advanced by Dr. Bruce Heezen in a report on the study of rock cores obtained by drilling in ocean beds around the world. The professor submitted his findings at the second International Oceanography Congress, which is holding a 10-day meeting at Moscow University.

Other members of the research team with Dr. Heezen were Dr. Neil Opdyke, Dr. Dragoslav Ninkovic, Dr. James Hays, Billy Glass and John Foster.

Dr. Heezen said that reversals of the earth's magnetic field, a phenomenon known through studies of lava rock, could be determined in dated cores of sedimentary rock containing fossils.

The reversals of the magnetic field, the scientist said, occur at intervals of from half a million to one million years and take as long as 10,000 years.

During the reversal process, he continued, the magnetic field diminishes in intensity until it reaches zero and then builds up again with opposite orientation. This decline in intensity, Dr. Heezen said, means the loss of the magnetic field as a shield helping to protect the earth from bombardment by cosmic rays. The cosmic rays thus strike species of life on earth with dangerous force.

"The result of this cosmic ray bombardment is the complete killing off of some species," the geologist declared.

"Other species are created through mutations, and some of these mutations are successful and create new, dominant species."

Dr. Heezen said that the theory was based on discoveries involving fossils of diatoms, a form of algae enclosed in a siliceous wall, and radiolaria and foraminifera, orders of protozoa.

"Six species of radiolaria, for example, became extinct in the southern ocean about 700,000 years ago, at the same time as the last major magnetic field reversal," the professor reported.

Several Shifts Noted

The magnetic field has reversed polarity several times over the last few million years, Dr. Heezen said, and added:

"Paleomagnetic studies of radiometrically dated subaerial lava flows have established that major semipermanent reversals of polarity took place 0.7 million years ago, 2.4 million years ago and 3.5 million years ago.

"Temporary reversals of short durations, called 'events,' took place 0.9 million and 1.9 million years ago."

Much remains to be learned about the relationship between magnetic field reversals and the evolution of life forms, he said, but some scientists are speculating that some major catastrophes in life history and periods of earth deformation may be related to the forces creating the magnetic field.

At the present time, Professor Heezen said, the magnetic field is decreasing in intensity and will reach zero in 2,000 years if the decrease continues at the present rate.

"I don't want to be an alarmist, but we may be next," he said with a smile.

[One of Dr. Heezen's colleagues in New York said Wednesday there was no real evidence that the earth's magnetic field was actually moving toward reversal but this could conceivably be the case.]

The Oceanographic Congress, which is sponsored by the Soviet Government and the United Nations Educational, Scientific and Cultural Organization, is being attended by close to 2,000 scientists, among them 200 Americans.

One of the many reports based on Bruce Heezen's 1966 Moscow press conference. Although he mentions Billy Glass, the reader would come away thinking that it was Heezen's finding. As Heezen was not an author of the preprint nor did he have permission from any of the authors to present this material, in a sense he stole the credit for his student's highly important discovery.

The idea that magnetic reversals caused extinctions was short lived, in light of more detailed studies which demonstrated that the extinctions and reversals did not take place at the same time.

**Excerpt from interview of Neil Opdyke by Ron Doel for the
Columbia Center for Oral History.**

“It was a concern of mine because I had a career to make. You know, I was 28 or something like that, and Bruce was already a famous oceanographer. And you know, this is my shot at it. You know, I wasn’t stupid. I know what was going, you know, I knew that I had to do and I didn’t want him going off and taking credit for this discovery, quite frankly. So I told him point blank not to give this talk, and he said he wouldn’t. Okay, so what happens, next thing I know is I’m reading the New York Times, and this is reported by (Walter) Sullivan in the New York Times. And then it was reported in Newsweek, Time magazine.”

And of course I went ballistic. And I was just really angry. And I discussed it with Jim Hays, who was the only other Ph.D., and Hays was a student of Heezen’s actually. Oh he was furious too so we, Hays and I, wrote a letter to Dr. Ewing accusing Bruce of unethical conduct.

It was like pouring gasoline on a fire. I didn’t realize it at the time, but there was already a lot of hard feelings between Dr. Ewing and Heezen, and so this --I didn’t realize what I had done when I did this essentially, because when I did this, Doc regarded this I think as the perfect opportunity to get rid of Heezen.”

Neil Opdyke headed Lamont’s paleomagnetism laboratory where the discovery that magnetic reversals were recorded in ocean sediments was made. In his oral-history, Neil recounts his anger concerning Bruce Heezen’s Moscow talk.

References

- Broecker, W.S., K. Turekian, and B. Heezen (1958), The relation of deep sea (Atlantic Ocean) sedimentation rates to variations in climate, *Am. Jour Sci.*, 256(7), 503-517.
- Felt, H. (2012), *Soundings: The Story of the Remarkable Woman Who Mapped the Ocean Floor*, Henry Holt and Co. Inc., New York, NY, 352 pp.

Chapter 9

GEOSECS

The birth of the GEOSECS (Geochemical Ocean Sections Study) survey was the result of a chance encounter I had with Henry Stommel, a legendary expert on the physics of ocean mixing. He pulled me aside during a meeting at Woods Hole Oceanographic and said, “Wally, your ^{14}C measurements on seawater are exceedingly important but unless they are done in a more systematic manner, most of their power will be wasted.” Stommel was alluding to the type of sampling carried out by *Vema*: one per day, at random depths and locations, i.e., the Ewing mode of operation. I asked what he meant by systematic. He said, “A transect of 20 stations, the length of the Atlantic’s western basin.” I asked, “How many samples at each?” he replied, “About 20.” I said, “To analyze 400 samples at \$400 each would cost \$160,000. Adding the ship cost would double that.” I added that for those of us doing geochemical research, a \$50,000 grant would be on the large side. He said, “Don’t worry about that because a new ocean initiative is about to be announced. It will be called the International Decade of Ocean Exploration (IDOE) and will fund large multi-investigator projects.” I asked, “How does one apply?” and he answered, “See Paul Fye, the Director of Woods Hole Oceanographic. He is a member of the planning group.”

Excited by this prospect, I called Harmon Craig at Scripps Oceanographic and asked him to join me in an attempt to get funding for the Stommel transect. He said, “If we are going to do ^{14}C measurements, we must back them with measurements of temperature, salinity, total CO_2 (i.e., $\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{=}$), nitrate, phosphate and silica.” To this list we eventually added radon, tritium and a few more exotic geochemical properties. Further, he said, “traverses should be run in both the western and eastern Atlantic”.

Armed with this plan, we made an appointment to meet with Paul Fye. I remember sitting in his outer office waiting for him to finish with another meeting. We spotted a fancy book of photos on the coffee table. Its pages were protected by transparent folders. There was a page which showed Fye holding out a palm-size leather case containing a medal he was about to

present. Harmon got the idea to insert a bubble on which was written, “I’m Paul Fye from the FBI.”

Our meeting with Fye turned out to be a success. He said that ours was exactly the kind of effort IDOE was designed to support. He told us to submit a proposal to Feenan Jennings at the National Science Foundation. We did and as a result, ours was the first of six such programs to be funded by IDOE.

As Woods Hole was an obvious third partner, we invited Derrick Spencer to join us. We also invited Arnold Bainbridge, geochemist at Scripps, to serve as the chief of operations. His task was to assemble a group of about 25 sea-going technicians and to pull together all the needed equipment. He turned out to be an extremely wise choice. I can’t think of another person from that era with Bainbridge’s combination of personal and technical skills. With him in charge, the program went like clockwork. In other hands it could well have been a fiasco.

We decided to hold a test cruise open to all. The group that made the best measurements for a given property would be invited to submit a proposal. In 1969 we sailed from San Diego to a site west of Baja, California. An important result of this competition was that Minze Stuiver of the University of Washington and Gote Ostlund of the University of Miami were chosen to share the radiocarbon analyses. They produced a superb set of measurements. Henry Stommel’s wish was fulfilled and more so. In addition to two traverses in the Atlantic, the program was extended to the Pacific Ocean and then to the Indian Ocean. My initial estimate of one third of a million dollars swelled to twenty-five million dollars. The global data set for so many properties became the grist for oceanographic research for the next two decades. Hence, it proved to be a bargain. For me, it was a gold mine which inspired me to write my text book “Tracers in the Sea.”

Lamont’s contribution to the program involved measurements of radon (half-life 3.65 days) in the upper 60 and lower 60 meters of the water column. The objective of the upper profiles was to measure the deficiency of radon in the surface mixed layer as a means of determining the gas exchange rate with the overlying atmosphere. The objective of the deep

profiles was to determine the vertical distribution of the radon which escaped from the sediment as a means of establishing the vertical mixing rate just above the ocean floor.

Over this decade-long program, I participated in two test cruises, two Atlantic legs, three Pacific legs and one Indian Ocean leg. The first of these legs was from Iceland to Barbados. When I arrived in Reykjavik, I was amazed to see the spanking new Woods Hole research vessel *Knorr*. Rather than being driven by a traditional propeller, she had fore and aft cycloids. Each had five blades extending vertically beneath the hull. The blades could be rotated allowing the ship to be pushed with equal force in any direction (or, if run in opposition, the ship would rotate). The idea was that this type of propulsion would help to maintain low wire angles. And so it did, but at the cost of ship speed. As about half of the time on our survey was spent getting from one station to the next, a reduction in speed from 9 to 6 knots was costly. Eventually the *Knorr* was cut in half, lengthened and switched to standard propulsion (i.e., propellers rather than cycloids). But this was a decade later.

The Icelanders who visited the *Knorr* were convinced that it must be a spy ship. She appeared far too fancy for mere oceanographers. No matter what we showed them or what we told them, they stuck with their view. I suspect they were influenced by the U.S. clandestine mission to raise a Russian submarine that sank off Hawaii. The claim was that the recovery ship was doing research aimed at mining sea-floor manganese nodules.

It turned out that the port stop in Iceland overlapped with the Fischer-Spassky chess tournament. Taro Takahashi and I were somehow able to get tickets to what turned out to be the last of their matches. The tournament was held in a field house. On one side was a balcony for spectators. On the other was a stage on which the chess table was placed. Fischer wore a garish maroon suit and sat in a chair capable of any desired mode of motion (employed to psyche Spassky). The end of the match was held over to the following day. We went back only to find that Spassky had resigned. Fischer's group, the press, and a few notables were celebrating with champagne in an area beneath the balcony. Most of the audience had left. I was standing alone in the large open area separating the balcony and stage. As the chess board remained unattended, it

occurred to me that I could walk over and pick up a pawn and then, if someone saw me, I could run through the crash doors which lined one end of the field house. From there, I could head for the *Knorr* and stash it in a foolproof hiding place.

I was considering this when I remembered Derrick Spenser's plea. He had reminded me that, as I was the first non-Woods Hole person to serve as chief scientist on one of their ships, I should not do any pranks that would embarrass his institution. Flashing before me were the headlines, "Woods Hole oceanographer nabbed with purloined Fischer-Spassky pawn." I didn't do it (something that I much regret).

At our first station, I was amazed to be able to view the data in real time. Attached above the rosette holding the PVC Niskin bottles (a space-age replacement for Nansen bottles and reversing thermometers), was a device that measured pressure (i.e., depth), temperature and salinity. This information was sent up a conducting cable and processed in our huge IBM computer (pre-pc days). This information was displayed on the operator's screen. The records for previous casts could be replayed for comparison. In addition, an electronic signal could be sent down the conducting cable to trigger the closure of a Niskin bottle. Also, by the time we reached the next station, we would have the results for onboard measurements of O₂, NO₃, PO₄ and radon. What is now routine was then revolutionary. All this, thanks to Arnold Bainbridge.

For entertainment we had a ping-pong table (in the ship's library) and a small swimming pool (in the stern ramp). The limited space and the ship's roll did not adversely influence ping-pong play. Several crew members fished while we were on station, catching pilot fish and dolphin fish (cousin of the Pacific's mahi-mahi) and put them in the ramp pool. Hence we were able to "swim with the fishes," as the mafia might say. As we approached Barbados, the pool was drained and we ate the fish for breakfast. Yum!

I found a use for the myriad of cards that fed information into our IBM computer. I would stand by the aft rail and deal them over the side. Within minutes they lined up in rows separated one from another by a few meters. After a half hour, they were all in two lines separated by half the length of the ship. I realized I was observing Langmuir cells. The cards accumulated at the

convergence of a pair of cells. With time, the smaller cells were eaten by the larger ones. By the time we left stations, they were aligned in neat rows separated by half the length of the ship.

In 1974, we moved our gear to the *Melville*, operated by Scripps Oceanographic. As *Melville* was *Knorr*'s twin, the move was straight forward. I served as chief scientist on the leg from Hawaii to Adak, an island in the Aleutian chain, and stayed aboard from Adak to Tokyo while Taro Takahashi took his turn as chief scientist.

The leg from Hawaii to Adak was uneventful except for our attempt to get samples for radiocarbon measurements deep in the Aleutian Trench. The stainless steel Gerard barrels used to get 200-liter water samples were deployed one above the other on the heavy wire. As the trench is 7300 meters deep we had to deploy almost all the wire on the drum. When we brought up the cast, we found that the messenger was caught on a splice in the cable. Because of this, the bottles failed to trigger and came up open. The boson suggested that we bore a bigger hole in the messenger so that it would be able to slide past the splice. This took a fair amount of time. But eventually we obtained a sample from 7322 meters depth. Surprisingly, it (and the other samples from within the trench) turned out to have slightly higher ^{14}C to C ratios than those in the overlying deep Pacific. This surprised us for the suspicion had been that the trench might be poorly ventilated and hence have an older radiocarbon age than the overlying deep water.

One day someone noticed a shark being sucked under the ship. It came out the other side chopped into many pieces. As one of the winches was located directly above the aft cycloid, a decision was made not to operate it on station for fear that someone might fall overboard and suffer the fate of the shark.

We then made a port stop at Adak, renowned for rainy weather. We were lucky that we arrived on one of its rare dry days. A group of us left the ship and walked up the hill to the navy base. At the top, we spotted an American eagle with a pigeon in its clutches. A short debate was held. Should we attempt to save the pigeon or let the eagle have its dinner? While this was going on, the eagle made the decision. It crunched into the pigeon.

When we left Adak, we headed north into the Bering Sea. I was surprised to find that the phosphate and nitrate contents of the deep water were far higher than in the deep open Pacific. The reason must be that the two are connected only by a narrow passage located at the far western end of the Aleutian chain. This deep gap marks the boundary between Russia and the United States. Its narrowness restricts the exchange of deep water between the deep Bering Sea and deep Pacific Ocean. One of my geochemistry graduate students, Robbie Toggweiler, explored the dynamics of this exchange as part of his PhD thesis. Interestingly, he went on to become the head of the ocean modeling group at NOAA's prestigious Geophysical Dynamics Laboratory in Princeton.

On the way out of the Bering Sea, we encountered by far the worst storm I have ever experienced. I remember standing on the bridge with Captain Phinney. The *Melville* was headed into the storm at a measly speed of three knots. Waves were breaking over the bow and splashing off the bridge windows. I was enjoying the excitement until Captain Phinney muttered, "I hope she holds together." As he was scared, I was too.

About halfway to Tokyo, Bill Reeburg and I deployed a rubber raft and rowed about a quarter of a mile away from the ship to collect a water sample for Exxon. The idea was to check if any petroleum compounds had found their way to this remote part of the ocean. We took precautions because oil is ubiquitous on ships and also on outboard motors. While we did the sampling, a dozen or so Albatross floated around the raft, curious to see why we had invaded their habitat. No sooner had we begun to row back than Bill's oarlock broke. A strong man, he was able to keep us on a straight course back to the ship using the oar as a paddle. As one of the wire casts was in progress, *Melville* couldn't have come to our rescue.

We arrived in Tokyo a day late. I realized that I had promised to give a seminar at the Oceanographic Institute. About an hour after our arrival, a limousine arrived to pick me up for the drive to the institute. When I arrived, an administrative assistant seated me in a small lounge and said that the director would see me shortly. As I waited, I paged through a book with pictures of their oceanographic vessel. One of the captions stated that the ship was equipped with a

million dollars worth of 'electronic' equipment. It reminded me of an off-color joke involving the Tokyo mayor's response to how long it was between elections. His answer was "once or twice a day."

I was stunned when an attractive young lady came in and said, "Hey, Professor Wally, it's good to see you again." It gradually dawned on me that she had taken one of my classes and I asked her what she was doing in Tokyo. "Don't you remember? I'm married to a well-known Japanese architect." Another of my students had written to alert her that I would be in Tokyo.

After the lecture and a brief reception, I was off to the airport to catch my flight to New York. I remember leaning against the wall of the extremely crowded waiting room. I was 'whipped.' The next thing I remember was that a man was lifting me back to my feet. I had fallen asleep and slid down the wall. Two months at sea takes its toll.

Some months later, I flew to Tahiti to join the last GEOSECS Pacific leg. The original plan was to go straight across the Pacific and refuel at a port in Chile, but that plan had to be scrapped. As oil prices were at an all-time high, the National Science Foundation decided that we should save money by heading back to San Diego. When I got to Tahiti and deplaned, Chuck Gallagher, a film maker, awaited me on the tarmac. As usual with photographers, I had to repeat my exit several times. Meanwhile, the pilot and passengers were becoming edgy. The Tahiti stop was supposed to be a brief one on the way to New Zealand.

Gallagher, a merry Irishman, turned out to be a delightful shipmate. He was a one-man film crew whose objective was to make a film documenting GEOSECS at NSF expense. It was to be titled "Rivers under the Sea". Of course, he charmed all of us into serving as his helpers.

Early one morning we heard a trumpet blast followed by a voice shouting "all pollywogs on deck." We, the pollywogs, soon learned that we were to be initiated in recognition of our first equator crossing (an old tradition among sailors). We were blindfolded and, in turn, sat in the barber's chair. It felt and sounded as if huge clumps of my hair were being cut. I was much relieved to find that instead of my hair, it was the shredded strands of rope. After kissing

Neptune's enormous grease-coated belly (probably the bosun's), we were treated to a barbeque fueled with lots of alcohol.

As we approached San Diego, I got the idea that we should sail in under the name *Vema*. This required painting over the raised *Melville* letters on both sides of the bow. As they were six or so feet below the rail, Guy Mathieu, one of the Lamont techs, used a roller mounted on a long pole to paint them out. He did this at 3:00 a.m. while Gallagher regaled the mate on the bridge with one of his many tales. There were also *Melville* designations on the stern. As they were within easy reach of the rail, we masked them with notebook covers painted *Melville* blue. As we approached the Scripps dock, we rechristened *Melville* as the *Vema*. Needless to say, Captain Phinney was not pleased with our shenanigans.

In 1977, the *Knorr* left Woods Hole for the final phase of the GEOSECS survey, the Indian Ocean. On the way through the Mediterranean samples were taken at one 'practice' station. Then, during a three-day port stop in Alexandria, Egypt, we celebrated the beginning of the end. The National Science Foundation sent me there to participate. After seeing the ship off for its traverse of the Suez Canal, I was able to spend time in both Cairo and Luxor. Never having been in Egypt, it was a memorable experience.

I was to join the ship in Fremantle, Australia, for the sixth Indian Ocean leg. On the way, I stopped in India to visit my friend and colleague Devendra Lal, who was at that time serving as Director of the Physical Research Laboratory (PRL) in Ahmedabad. As part of this visit, I wanted to sample a locale just south of the Rann of Kutch on India's west coast. It was where one of Lal's PhD students had obtained a ^{230}Th age of 45,000 years for a coral from an elevation close to that for a last interglacial sea-level maximum (a few meters above today's sea level). As this conflicted with everything we knew about the last glacial period, I wanted to collect a sample for a repeat analysis.

So, off we went in the Institute's Land Rover. There were four of us: the Institute's driver, a fellow geochemist named Soma, the student, Gupta, who made the measurement and me. Driving on Indian roads made the whole trip worthwhile. Every vehicle carried a large

surplus of people. Motorcycles carrying six people, trucks with fifteen people on top, buses with people sitting in the windows.... After staying the night in a hotel which had once been a Maharaja's palace, we reached our destination. I asked the student where he had collected the 45-kyr sample. He said he couldn't remember. We were, however, able to find outcrops of coral which likely formed during the last interglacial highstand. But, unlike Gupta's samples which he claimed showed no evidence of recrystallization from aragonite to calcite, all the coral we found was totally re-crystalized and hence useless for dating. The same was true for two other sites we visited. We decided to extend our search closer to the coast, but didn't know how best to get there. Soma suggested that we pick up a day laborer who would surely know the lay of the land. We found one and were taken to a broad field just inland from a set of coastal dunes. Once again, the coral was recrystalized. Then, our new guide beckoned me to follow him to the far corner of the field. He pointed to a hole about five feet in diameter and four feet deep. An abandoned or aborted well? We jumped in and he pointed to a layer of coral about two feet below the surface. Lo and behold, it had no visible calcite. I was amazed. This man, who spoke no English, had somehow realized what we were looking for. He had very likely seen well-preserved coral on the beach and had dug wells akin to the one in which we were standing. We subsequently dated this coral and got a last interglacial age (124,000 years). I can come up with no explanation other than that the results in the student's thesis were manufactured in his head. Chemists call it 'dry-labbing'. As PRL is known for the excellent quality of its research, if true, this was an unfortunate blot on their record.

When Lal took me to the airport for my flight to Freemantle, Australia, I found that I had no reservation. Further, the flight turned out to be fully booked. Ever resourceful, Lal asked around and found a passenger with a very young son. With a combination of charm and arm twisting, he convinced the man to hold his son on his lap and release his seat to me.

Freemantle reminded me of San Diego. None of the Victorian décor that dominates Sidney. After an all too short port visit, and thanks to the kind Indian man we were able to depart on schedule. For the first few days all went well. But when we had reached a point in the Indian

Ocean about 900 miles northwest of Australia, the assistant cook fell ill. It appeared that he had suffered a minor stroke. As we carried no medic, the captain got advice by radio to take him to Cocos-Keeling, an atoll not too far off our track. It housed an Australian airbase with a small hospital.

At the entrance to the atoll, we were met by a launch which took three of us and the cook to the airbase. Never having seen an atoll, I was stunned by the clarity of the lagoon water. Our host told us that the airbase controlled only part of the atoll. The rest was a copra plantation owned by a man named Cluines-Ross. There was no communication between the airmen and Ross. The suspicion was that Ross had several hundred Malaysian workers whom he treated pretty much as slaves. In the past when contact had been made, stories appeared in Australian newspapers that Ross's Malaysians were being mistreated.

It turned out that the cook had not had a stroke but was suffering from hypertension. We left him at the Cocos-Keeling hospital and returned to the *Knorr*. On the way, I noted that there was a golf course which crisscrossed a 2-mile-long runway used to refuel jet fighters in transit.

A few years later, I learned that Australia had conducted a referendum designed to release those Malaysians trapped on Cocos-Keeling. It passed and they were given the choice of transport to either Malaysia or Australia. If Australia was their choice, they would be given citizenship.

Our destination was Colombo, Sri Lanka. Several of the technicians were aware that the science fiction writer Arthur C. Clarke lived there. We cabled him with an invitation to visit the ship. He agreed but when we arrived (on April first) we were disappointed that Clarke was not there to greet us. Rather, he sent a message saying he was spending the morning on television and radio warning people not to look for a solar eclipse which had been announced in the newspaper. The report was intended to be an April Fool's joke, but no joke if people damaged their eyes searching for it.

Clarke did invite us to visit him at his compound. When our contingent arrived, he took us to his library. It was lined with shelves which contained only his books (including the many

translations of each). He showed us outtakes from commercials he had done for AT & T advertisements. He also took us to a huge tree around which was a chicken wire cage. Inside were a dozen or so small monkeys. Asked why he lived there, he said that Sri Lanka offered warmth and also tax relief. Our ship's agent told us another reason: Clarke liked young boys.

So for me this was the last hoorah. A decade after Stommel's invitation, the survey had been completed. GEOSECS was the Camelot of my career. After these years of working together, we had become a close knit family. Bainbridge had chosen well. Our technical staff, to a person, performed beautifully and cheerfully. Hardly a glitch and few complaints despite round-the-clock routine month after month. Readers should note that Gallagher's movie "Rivers under the Sea" provides a picture of our life at sea.



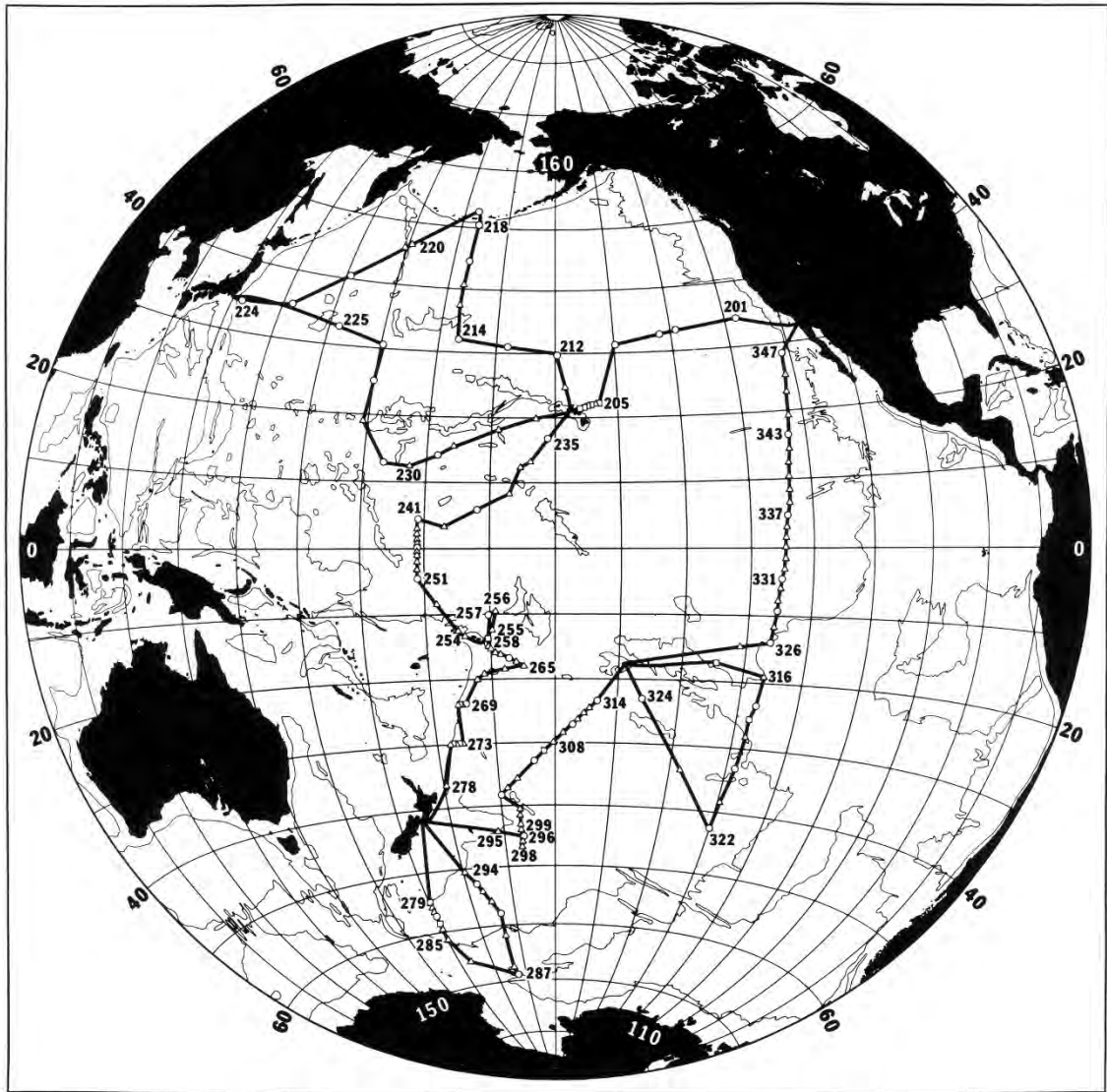
Arnold Bainbridge the man who made the GEOSECS survey click!



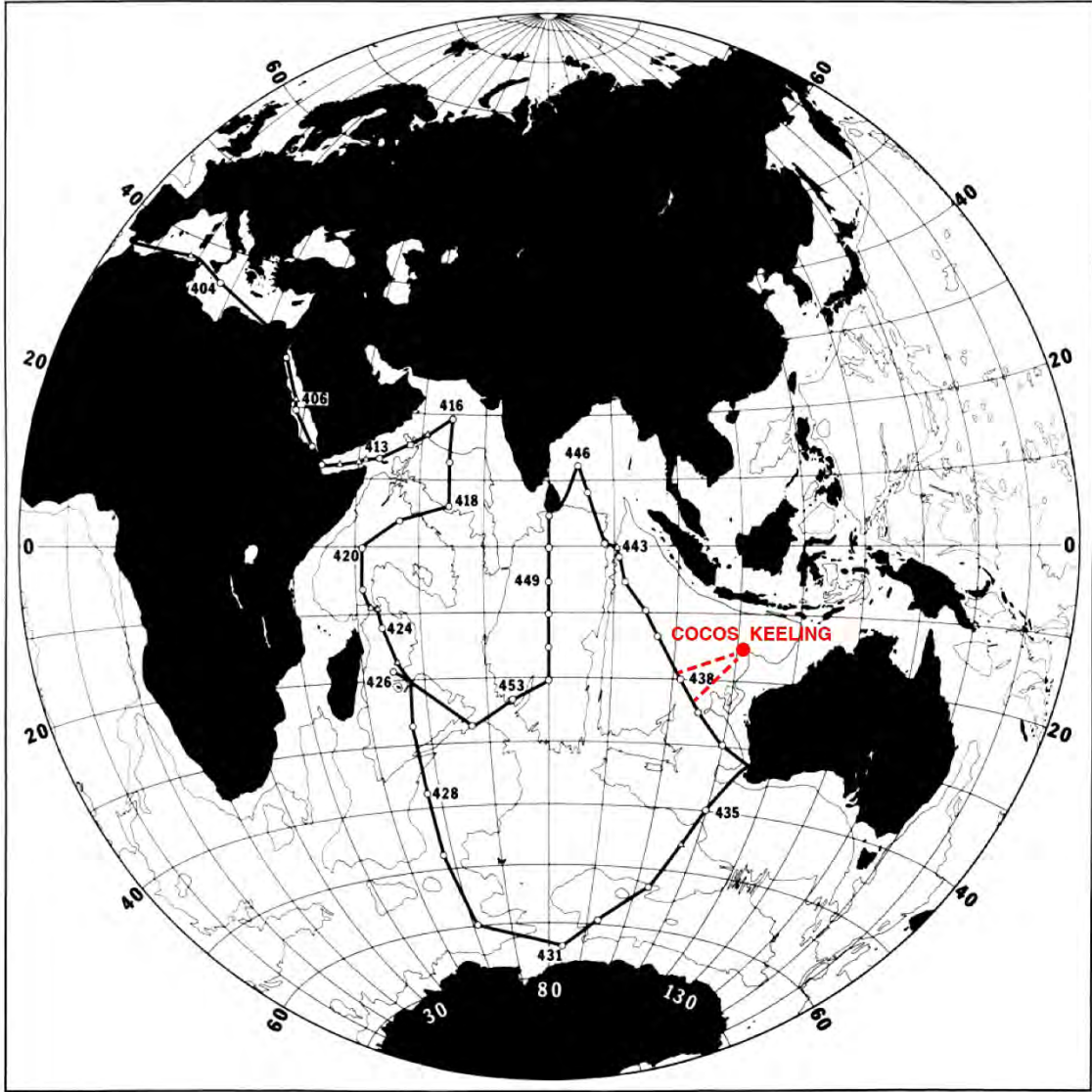
The crew of *R.V. Melville* and the GEOSECS gang on the leg from Tahiti to San Diego. Front and center: Chick Gallagher, the filmmaker, above him, Captain Phinney. In the van doorway, Guy Mathieu, a Lamonter. In the black sweater, me. And are those beads?



GEOSECS Atlantic track map. I was aboard for the leg from Iceland to Barbados (stn. 24 to 34), and the leg from Recife to Buenos Aires (stn. 54 to 63).



GEOSecs Pacific track map. I was aboard for the leg from Hawaii to Adak (stn. 212 to 218), for the leg from Adak to Japan (stn. 219 to 223), and for the leg from Tahiti to San Diego (stn. 326 to 347).



GEOSecs Indian Ocean track. I was aboard for the leg from Australia to Sri Lanka (stn. 436 to 446).

References

Broecker, W.S., and T.H. Peng (1982), *Tracers in the Sea*, 690 pp, Eldigio Press, Palisades, N.Y.

Chapter 10

The Experimental Lakes Area

My introduction to the Experimental Lakes Area (ELA) came as a complete surprise. Early in the 1970s, a Canadian limnologist by the name of Jim Valentine phoned me and asked for my help. He explained that the Fresh Water Institute in Winnipeg had established a field station in western Ontario, an area of forests and lakes. One of the missions of this facility would be to learn how to control the devastating pollution of lakes (eutrophication). He went on to say that a colleague named David Schindler had convinced him that the way to go about this was by manipulating rather than by merely observing. The institute had secured the exclusive use of a plot of isolated Crown Land containing a dozen or so lakes. In one of them, Lake 227, they were adding phosphate in order to learn how long it remained in solution before being removed to the sediment. They were convinced that phosphorous drives eutrophication. As green algae were fixing enough nitrogen to match the excess PO_4 , CO_2 had become the limiting ingredient for plant growth. The algae were drawing down the lake's CO_2 as fast as it was invading from the atmosphere. Valentine asked whether there was a way to assess this rate of invasion and if so, did I have a graduate student who could come to ELA and deploy it.

At the time, Steve Emerson was starting his graduate research at Lamont. We discussed Valentine's problem and hit on the idea to add radium to the lake. We could then measure the fraction of the radon gas generated by its decay that escaped to the atmosphere. As radon has a half-life of 3.65 days, the ^{222}Ra to ^{226}Ra ratio would reach a steady state value on the time scale of two weeks. Part of the radon gas would remain in the lake and part would escape to the atmosphere. Based on the fraction of radon lost to the atmosphere, we could calculate how fast atmospheric CO_2 was invading the lake.

Emerson was only the first student to be lured to ELA. Several others joined Schindler's ELA team. Good for me, as I was at that time heavily involved in the GEOSECS survey and good for them, as it afforded them personalized thesis projects. Over the next decade, about ten Lamont geochemistry students conducted part or all of their PhD research at ELA.

Together with Schindler, Steve Emerson arranged to get radium from the Canadian Atomic Energy Authority. I went to ELA to observe its addition to Lake 227. To do this, I had to fly to Winnipeg, rent a car, and drive east on the Trans-Canada Highway for some 100 miles to Kenora. Then 25 miles on local roads and finally 25 miles on unpaved logging roads. The research station was located on the shore of one of the larger lakes. We were greeted by Steve and the Schindler team and also by what seemed like a billion mosquitoes. Mr. Plunket, the government man with the radium was already there. The next morning we headed for Lake 227 where the PO_4 experiment was underway. This involved a series of boat trips separated by portages. Mr. Plunket carried the small radium canister dangling from his out-stretched finger. When we got to Lake 227, Schindler added the radium to 20 liters of lake water. Then he crisscrossed the small lake using the wake of the outboard motor to stir in the “radium cocktail” as it was poured into the lake. One couldn’t help but be impressed by Schindler, a handsome and highly intelligent man with a Charles Atlas physique. He had carried the outboard motor on his outstretched arm across each of the portages.

That evening, back in camp, we discussed PO_4 chemistry. Schindler explained to me that he was convinced that the excess PO_4 added to lakes in waste water was the primary cause of eutrophication (i.e., reduced water clarity, O_2 depletion, and rotting green algae floating on the surface). The biggest source of this phosphorus was laundry detergent. As the experiment in Lake 227 suggested that phosphorus was removed to the sediment on the timescale of a few years, were the phosphate in detergent to be replaced, lakes would revert to their original state on a short time scale (i.e., clear, oxic and with no blue-green algae).

I was surprised that phosphate was so rapidly removed from lakes, because I knew that it remained in the ocean for several tens of thousands of years before being removed to the sediment. We batted around possible explanations. The one that floated to the top was that the ocean has a far more efficient food web than lakes. Something like 99.9 percent of the organic matter produced by marine algae is consumed (releasing the PO_4). Another idea was that the

ocean water is rich in sulfate which serves as a backup oxidant. By contrast, fresh water has little SO_4 .

Just as cigarette companies played down the role of their product as a cause for lung cancer and, just as fossil fuel energy companies are currently playing down fossil fuel CO_2 as a cause for global warming, the detergent industry was attempting to counter the assertion that phosphorus was the cause of eutrophication. Scientific papers supporting the tie between PO_4 and eutrophication were rebutted by papers sponsored by the soap and detergent industry.

Frustrated by this, Schindler dreamed up a test which could not be rebutted. One of the ELA lakes had two basins separated by a bottleneck. Schindler took advantage of this shape and constructed a curtain which greatly restricted mixing between the two basins. To the upper basin, he added carbon and nitrogen, but no phosphorus. To the lower basin, he added the same amount of C and N and also P. He waited two weeks and then took an aerial photograph. The upper basin remained pristine blue. The lower basin looked like pea soup. When *Science* magazine published this photo, the war was over. Phosphorus soon disappeared from detergent.

Encouraged by Schindler's results, a University of Washington limnologist named Tommy Edmonson convinced the City of Seattle and its surrounding communities to divert the sewage plant effluent being added to Lake Washington directly into Puget Sound. Once this was accomplished, over a seven-year period the clarity of the lake's water returned to its pre-pollution level. The rapidity of its recovery confirmed Schindler's claim that phosphate was the villain. It also showed that this was the case for large lakes as well as tiny Lake 227. It is interesting to note that when Edmonson retired, Schindler's son, Daniel, was appointed in his place. Following his father, Daniel is in the midst of an illustrious career.

Although the research carried out by my graduate students did not directly contribute to Schindler's PO_4 crusade, they did discover things of importance. Andy Herczeg embarked on a project to determine whether the ELA lakes were drawing CO_2 in from the atmosphere or giving it off to the atmosphere. In other words, which was more important: storage of algal matter in

lake sediments (requiring CO₂ gain from the atmosphere) or the oxidation of labile organic compounds supplied from the surrounding land (requiring CO₂ loss to the atmosphere).

Andy's strategy was to compare the partial pressure of CO₂ (pCO₂) in lake surface water with that in the overlying atmosphere. As is conventional in limnology, he calculated the lake's pCO₂ from measurements of pH and alkalinity. He was surprised when surface water from the large lake (#239) next to the camp yielded a pCO₂ twice as large as that in the atmosphere. As this didn't seem possible, we decided to measure the lake pCO₂ directly. Ray Hesslein, a Lamonter who stayed on at the Fresh Water Institute after completing his PhD research, decided there was a simple way to do this. He filled a syringe half way with lake water, shook it to equilibrate the pCO₂ in the air with that in the water and then injected air from the syringe into an infra-red analyzer. When we used this technique to measure the pCO₂ in the camp lake, we found that it was very close to that in the atmosphere. As this made sense, what was the problem with the pH method?

I mentioned to Andy that Peter Brewer, a scientist at Woods Hole Oceanographic, showed that titrations used to determine alkalinity and total dissolved organic carbon in surface water using a pH electrode were biased. Brewer suspected the cause was that the pH electrode responded to dissolved organic matter as well as to hydrogen ions. Herczeg did a very clever thing. He pushed lake water through an ultrafilter and then compared the pH of the water that went through the filter with that in the water which was left behind. He found that the pH reading of the residual was higher than that for the filtrate. So the villain was large organic molecules, some of which were trapped by the filter.

At that time, the U.S. Environmental Protection Agency (EPA) was about to launch a survey of a large number of our nation's lakes. The concern was to establish a baseline for assessing the extent to which they were being acidified by airborne HNO₃ and H₂SO₄ acids. I alerted the EPA's chief scientist for this endeavor to the pH electrode bias and suggested that they instead measure pCO₂ and then calculate the pH. My advice went unheeded.

Another of our students, Sherry Schiff, who also did much of her research at ELA (and still does), conducted a study of three lakes located in New York State's Shawangunk quartzite belt. Lake Mohonk in front of Mohonk Mountain House had a near neutral pH and the other two had become quite acid (pH <5). Puzzled by the stark difference, she found that the lakes (Minnewaska and Awosting) with high acidity were underlain entirely by quartzite while Mohonk Lake was floored partly by a layer of shale. So, whereas two of the lakes had no source of cations (Ca^{++} and Mg^{++}) to neutralize the anthropogenic acids, the third did. If a layer of shale beneath a lake can neutralize acids, it's not surprising that Iceland's basalt quickly neutralized water acidified with CO_2 (see Chapter 19).

Yet another student, Paul Quay, decided that he would use a tritium tracer to determine how rapidly water was exchanged between warm summer surface waters and cold deep waters in one of ELA's small lakes. He injected tritium onto a mid-thermocline horizon and then monitored its vertical spread. He was surprised to find that the rate of spread was exceedingly slow (i.e., only a few times faster than molecular diffusion). He was in for a further surprise when he repeated the experiment in a second small lake and found that the mixing rate was an order of magnitude faster than in the first lake. His explanation involved the difference in hypsometry. The first lake was shaped more like a teacup and the second more like a saucer. This suggested that the mixing was driven by the frictional contact of internal waves with the sloping sediment surface. The gentler the slope, the larger the mixing rate.

In connection with Paul's research, we had the interesting case of the missing tritium. We placed an order for 50 curies with the Amersham facility in Great Britain. When the tritium failed to arrive, Paul checked with the railroads and airlines but could find no hint of its whereabouts. Eager to get the experiment going, we ordered a second shipment of 50 curies. It arrived promptly. A year later, one of the ELA people was waiting for a bus at the terminal in Kenora (the closest town to ELA). The manager asked him about the symbol on a box sitting in the corner. He had been told that it meant danger: radioactivity. Sure enough, it was our missing

tritium. There were no addresses on the box, only the warning label. To our surprise, it had been shipped from Toronto on a Greyhound bus!

I recruited undergraduate Tom Torgerson while visiting the University of Illinois. My host took me to the burger joint where he worked. There was Torgerson, all six feet-two inches, crowned with a foot-tall chef's hat. Within a year, he was a student doing a thesis at ELA. His project was to study the exchange of gases which occurred when the lake underwent seasonal overturn (i.e., the deep water mixed with that at the surface). This occurred at the time when the lake became ice free (early spring) and exposed the entire lake to gas exchange with the atmosphere. During overturn, the O₂ content of the isolated deep water (depleted by respiration) was partly replenished. In order to find out the extent of this replenishment, Torg, as we called him, decided to measure the ³He content of the water before and after overturn. Just as during the period of isolation O₂ was being consumed, ³He was being produced by the decay of its parent tritium (³H). The tritium had been produced by H bomb tests carried out mainly at the end of 1962. So, the fraction of the ³He released to the atmosphere during the interval of overturning allowed Torg to estimate the extent of O₂ uptake from the atmosphere.

For the experiment Torgerson chose Teggau, the deepest of the lakes in the ELA area. It owed its depth to its location on a major fault. An unexpected thing popped out: the pre-turnover deep water contained a very large excess of ⁴He. The only way the ⁴He could be explained was that it was produced by radioactive decay of ²³⁸U and ²³²Th in the underlying granite crust. The surprise was that the total amount of ⁴He held by the lake was equivalent to that produced each year in a granite cube 30 km on a side. Not only was there a fault zone beneath the lake, but it must serve as a 'chimney' venting helium from a very large volume of rock beneath the lake.

Each of these students has had a successful career at either a university or a government laboratory. Emerson and Quay spent their careers at the University of Washington. Schiff at the University of Waterloo, Torgerson at the University of Connecticut, Hesslein at the Fresh Water Institute in Winnipeg and Herczeg at a government lab in Adelaide, Australia. Except for Schiff and Torgerson, the others have retired, while I sit here writing about days past.

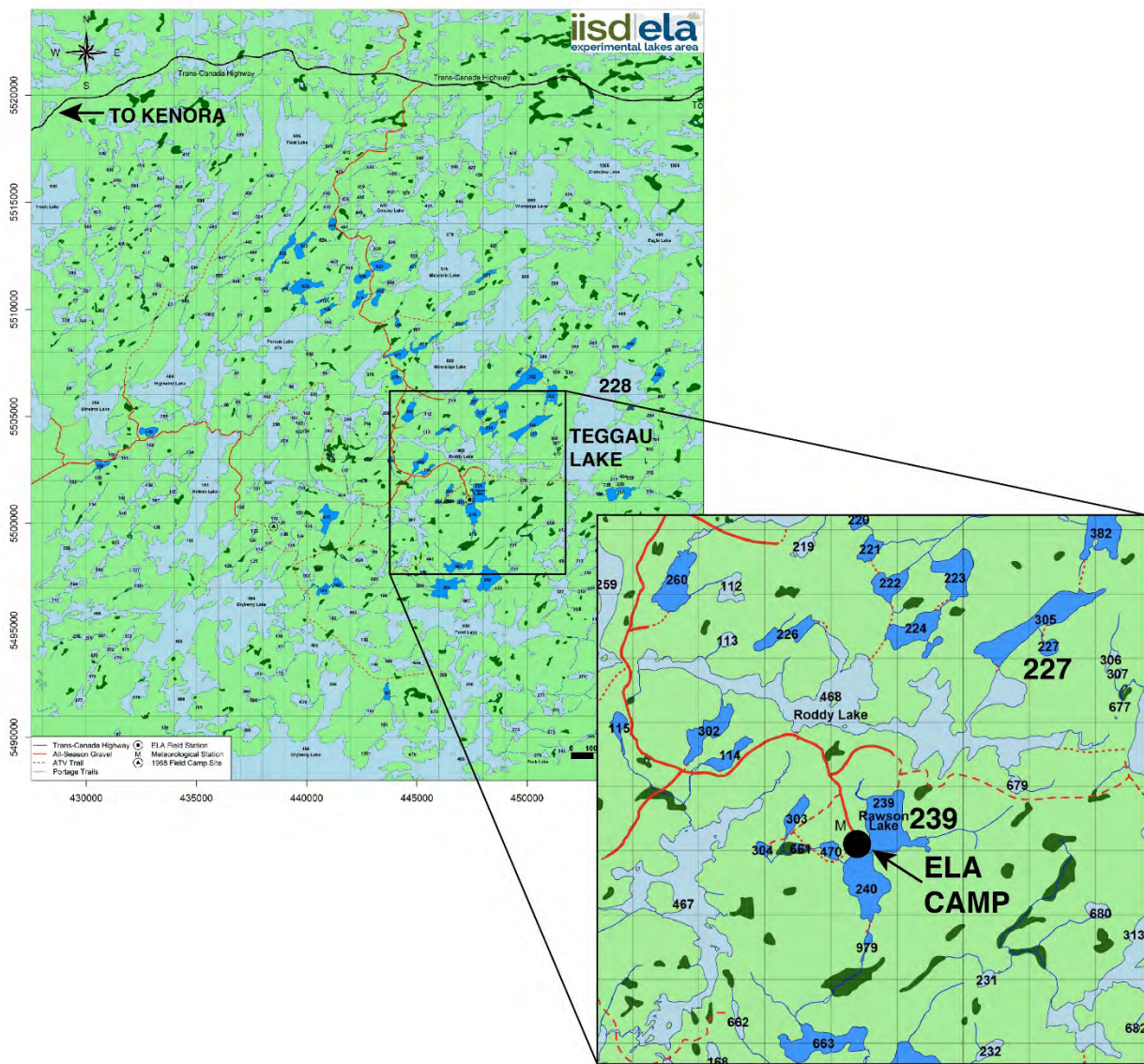
I haven't mentioned Richard Bopp, George Kipphut, John Crusius or Peter Bower. Each conducted a successful research project at ELA and went on to careers in academia.

Despite an attempt in 2013 by a conservative Canadian government to shut down ELA, as of 2016, the work continues. According to Sherry Schiff who still spends summers there, the quality of the research remains high. Schindler moved on to the University of Alberta in Edmonton. For his outstanding environmental research, he is and will be remembered as one of Canada's greatest scientists.

I can't end this chapter without mentioning a forest fire that came very close to burning down Schindler's camp. As he explained it, a severe windstorm blew down thousands of acres of trees. There was no way to harvest the wood, so it became ever drier until one day, two years later, it was ignited by lightning. The fire swept through much of the land south of Schindler's camp and had reached the edge of the camp before it was contained. To me it was a plus. I like to walk. But at ELA, mosquitoes made walking extremely unpleasant. So I found the recently denuded areas welcome havens. Schindler told me to listen for the sound of beetles chewing away at the fallen timber. Suspecting I was being teased, I was surprised that, indeed, the beetles could be heard.



David Schindler, who demonstrated that understanding lake biochemistry requires manipulation.



Map showing the lakes available for experimental research (dark blue). The logging road leading to ELA is also shown. Kenora, the nearest town, is about 50 road miles from the ELA camp.



Schindler's photo responsible for eliminating phosphorous from detergent.



Map showing the location of the three lakes studied by Sherry Schiff. All three are located on the Shawangunk conglomerate in an area about 90 miles west of New York City.

References

- Schindler, D.W., G.J. Brunskill, S. Emerson, W.S. Broecker, and T.H. Peng (1972), Atmospheric carbon dioxide: Its role in maintaining phytoplankton standing crops, *Science*, 177, 1192-1194.
- Emerson, S., W.S. Broecker, and D.W. Schindler (1973), Gas-exchange rates in a small lake as determined by the radon method, *J. Fish. Res. Bd. Canada*, 30, 1475-1484.
- Torgersen, T., Z. Top, W.B. Clarke, W.J. Jenkins and W.S. Broecker (1977), A new method for physical limnology-tritium-helium-3 ages-results for Lakes Erie, Huron and Ontario, *Limnol. & Oceanog.*, 22, 181-193.
- Hesslein, R., D. Schindler, G.W. Kipphut, W.S. Broecker, and P.H. Santschi (1978), Geochemical analysis of trace elements in lakes of the Experimental Lakes area, Ontario, Canada, *Intl. Cong. on Sedimentology 10, 1 (A-L)*, 304.
- Quay, P.D., W.S. Broecker, R.H. Hesslein, E.J. Fee, and D.W. Schindler (1979), Whole lake tritium spikes to measure horizontal and vertical mixing rates, *I.A.E.A., Panel Proc. Ser. STI/PUB/511*, 175-193.
- Hesslein, R.H., R.D. Quay, M. Thomas, and W.S. Broecker (1979), A whole lake gas exchange experiment using carbon-14 and radon-222 as tracers, *I.A.E.A., Panel Proc. Ser. STI/PUB/511*, 251-254.
- Hesslein, R.H., D.W. Schindler, W.S. Broecker, and G. Kipphut (1979), Fates of metal radiotracer additions in experimental enclosures in lakes and in a whole lake, *I.A.E.A., Panel Proc. Ser. STI/PUB/511*, 261-271.
- Quay, P.D., W.S. Broecker, R. Hesslein and D.W. Schindler (1980), Vertical diffusion rates determined by tritium tracer experiments in the thermocline and hypolimnion of two lakes, *Limnol. & Oceanog.*, 25, 201-218.
- Torgersen, T., G. Mathieu, R. Hesslein and W.S. Broecker (1982), Comparison of the Rn-222 and He-3 gas exchange methods in a small lake, *J. Geophys. Res.*, 87, 546-556.

Herczeg, A.L., W.S. Broecker, R.F. Anderson, S.L. Schiff, and D.W. Schindler (1985), A new method for monitoring temporal trends in the acidity of fresh waters, *Nature*, 315, 133-135.

Chapter 11

Sea Salt

While I was in college, I read somewhere that the chemical composition of human blood is related to that of the Ordovician ocean. I guess the idea referred to when our very distant ancestors emerged from the sea. It did, however, stir my curiosity. Has the composition of sea salt changed with time? If so, why? Thoughts about this have circulated through my head on and off during my entire career. I have read with interest papers purporting to have developed a means to reconstruct changes in the composition of sea salt. Most important are those which dealt with the composition of fluid inclusions in halite, the magnesium content of ridge crest calcites, and the concentrations of a range of elements in well-preserved aragonitic corals. I also have given thought to feedback loops that maintain a balance between the removal of a given constituent and its supply from continental weathering and volcanic emissions. Although a minor contributor to this subject, I did make a few early in my career.

The first of these was triggered in the late 1960s by a lecture given by L.G. Sillen, a Swedish chemist. It was his contention that the major ions in seawater were at thermodynamic equilibrium with bottom sediments. If so, the only way the composition of sea salt could have changed was by variations in the ocean's temperature. This didn't sit well with me. Although at that time, I didn't know very much about the major constituents of sea salt (i.e., Na, K, Mg, Ca, Cl and SO₄). I did, however, have an understanding of the constituents involved in life cycles (i.e., PO₄, NO₃, CO₃, and O₂). As their concentrations varied widely with water depth and also between the deep Atlantic and the deep Pacific, they couldn't be at thermodynamic equilibrium.

If it isn't thermodynamic equilibrium which sets the composition of seawater, then what is it? My idea was that there must be some sort of dynamic steady state. Every constituent of sea salt is being added to the sea from rivers and volcanoes. To the extent that the chemistry of the ocean is at steady state, the rate of removal of each constituent to the sediments must match this rate of supply. Hence, for each constituent there must exist a feedback loop which maintains this equality. Sillen would opt that this was accomplished through thermodynamic equilibrium with

sediments. In a paper published in 1971, I opted for a kinetic control rather than a thermodynamic one. One might ask doesn't this violate the laws of thermodynamics? No, because the concentrations of these constituents do tend toward thermodynamic equilibrium, but the time required to achieve this is long compared to the time any given constituent resides in the sea.

My favorite example is the control on what marine geologists refer to as the 'compensation' depth for CaCO_3 . It marks the mid-depth of the transition between those sediments rich in CaCO_3 and those devoid of CaCO_3 . Over the course of the Cenozoic, the average depth has remained within the range of 4 ± 1 km. Below this depth, the CaCO_3 -depleted sediments are referred to as red clays and above this depth, the sediments rich in CaCO_3 are referred to as carbonate oozes.

At that time many people were thinking, a la Sillen, that the compensation depth was controlled by temperature. But to my way of thinking, it had to involve the flow of Ca^{++} and $\text{CO}_3^{=}$ through the ocean. It turns out that the area of the sea floor covered by red clays is about four times that covered by oozes. Based on this, I reasoned that the rate at which CaCO_3 was being produced by marine organisms was about four times the rate at which the ingredients for CaCO_3 were being supplied from rivers and volcanoes. In order to balance the CaCO_3 budget, the $\text{CO}_3^{=}$ ion concentration in the deep sea is driven toward that value where the overproduction of calcite is compensated by sea floor dissolution. For example, if production of calcite were to increase and the ingredient input were to remain the same, then the $\text{CO}_3^{=}$ concentration would be driven down until a balance was restored. I say, $\text{CO}_3^{=}$ rather than Ca^{++} because there is roughly one hundred times more Ca^{++} than $\text{CO}_3^{=}$ dissolved in the ocean. So, at least on short time scales, it is $\text{CO}_3^{=}$ that undergoes changes in concentration.

At this point, one might ask why the deep ocean CaCO_3 is more susceptible to dissolution. The reason is that the solubility of calcite increases with pressure. One might also ask what controls the productivity of calcite in the upper ocean. The answer is that, as surface ocean water is highly supersaturated with CaCO_3 , marine organisms can produce as much calcite

as they need. Instead, the rate of calcite production is tied to the amount of photosynthesis taking place in the upper ocean. This sets the abundance of the organisms that produce calcite.

Over the years, I have pondered a number of the feedback loops which control the flow through the ocean of the constituents involved in life cycles. My latest thinking on this can be found in my book titled *Wally's Carbon World* (2014).

Early in my career, I also became interested in the record of ^{13}C to ^{12}C ratios for the carbon stored in marine limestones. As of 1970, there was a reasonably complete ^{13}C record for the Phanerozoic (i.e., the last 540 million years) and scattered results for the Precambrian. What struck me was the near constancy of these ratios. At that time, we already knew that CO_2 coming up in volcanoes had a $\delta^{13}\text{C}$ close to -5 per mil. The value for limestone averaged close to 0 per mil. Further, the 25 per mil difference between the $\delta^{13}\text{C}$ for terrestrial plants and that for marine CaCO_3 appears to have remained much the same over the course of the Phanerozoic. This being the case, if mantle CO_2 were the major source of the carbon entering the ocean, then on average 20 percent of the carbon removed from the ocean must be in the form of organic material and 80 percent in the form of calcite. What puzzled me was that, as limestone $\delta^{13}\text{C}$ remained nearly the same, there must be a feedback loop which maintains the 80 to 20 percent split.

In a paper titled "A Boundary Condition on the Evolution of Atmospheric Oxygen" (1970), I proposed that it was O_2 that exerted the control. If the burial of organic material became too large, the atmosphere's O_2 content would increase, thus raising the likelihood that the organic matter would be oxidized. But why a 20 – 80 mix?

Over the years, I have thought and rethought this problem. One way to ease the problem is to call on recycled limestone carbon as an important contributor. If so, the $\delta^{13}\text{C}$ value for the combined carbon input to the ocean shifts upward toward zero per mil. The closer it gets to zero, the smaller the contribution of organic material to the removal of carbon from the ocean; and the smaller the variation in the fraction preserved as organic matter for each per mil difference in the $\delta^{13}\text{C}$ for limestone. For example, were the contribution of limestone to be equal to that by volcanoes, then the required mix would be 10-90 instead of 20-80. Although there is no doubt

that the limestone recycling is an important contributor, neither the rate at which limestone carbon nor that at which volcanic carbon is being added to the ocean, is known to be better than a factor of two.

Another puzzle in this regard is that during the Cenozoic the major sediment sinks for CaCO_3 and for organic matter were very different than during the Paleozoic. Today CaCO_3 is deposited mainly in the deep ocean and organic material is deposited mainly in deltas. However, during the Paleozoic, CaCO_3 was stored largely in reefs and organic matter in shale. Yet no significant change in the $\delta^{13}\text{C}$ of CaCO_3 has occurred at the boundary between these eras.

In the late 1990s, I became aware of a large change (by ^{13}C standards) in carbon isotope ratio in limestone that occurred at the boundary between the Permian and Triassic. The $\delta^{13}\text{C}$ dropped from 0‰ to -3‰. This boundary marks the time of the Earth's greatest extinction event. Between 80 and 90 percent of the animal and plant species present at the end of the Permian disappeared. In the early Triassic, they were replaced by an entirely new set of organisms (including dinosaurs).

In a 1999 paper co-authored with a graduate student, Synte Peacock, we proposed that the most important environmental consequence was likely the demise of Permian trees. This reduced the storage of carbon in continental peats (these peats are now coal). Much of the continental organic matter was instead transported out to the sea. There is a major difference between carbon storage on land and carbon storage in the sea. It has to do with SO_4^- . Seawater is rich in this anion while continental waters have little. This has an important consequence regarding the fate of organic material. On the sea floor, if O_2 is depleted, organisms that use SO_4 as an oxidant come to fore. They reduce SO_4^- to S^- which precipitates as FeS . This can't happen on land for there is little sulfate. Instead, another set of organisms make methane. Hence in the early Triassic more FeS was produced and less carbon was stored as peat. We calculated that during the late Permian, 10 percent of the reduced material was stored as FeS and 90 percent as organic matter; during the early Triassic, the distribution shifted to 25 percent in FeS and 75 percent in organic

material. Although not well documented, the ^{34}S to ^{32}S ratio in marine sulfate appears to have shifted in the opposite direction. This is consistent with the increase in the importance of FeS.

It is interesting to note that during the late Precambrian (810 to 540 million years ago), there were a number of large swings in the carbon isotope ratio in limestones (and dolomites). After hovering around +5‰ for many million years, the $\delta^{13}\text{C}$ plunged to around -5‰ (and in one case to -10‰). As interpreted using the logic outlined above, the ratio of CaCO_3 to organic storage appears to have dropped from somewhere around a 50-50 mix to all CaCO_3 (i.e., 100 – 0). During two or three of these dips tropical glacial deposits at sea level formed, suggesting that both the land and the sea were covered with ice (i.e., the Earth had become a snowball). Something dramatic occurred during these so-called frozen-earth episodes which hasn't happened since. I suspect that it must have involved large dips in the atmosphere's CO_2 content which largely cut off photosynthesis. Whatever it was, the system appears to have been stabilized by the complex ecosystems which emerged at the close of this sequence of planetary freeze-ups.

In the early 1970s I decided to write a short book on chemical oceanography. It occurred to me that the easiest way to do this was to tape record the lectures I gave in my graduate class. To keep it simple, I asked the seven students to hold their questions until I had finished each lecture. As a reward, I offered them the possibility of a party instead of a final exam. I told them the exams were coiled up in seven yellow party favors and that one of the exams had a big black X on it. The others did not. I asked for a volunteer to pick one of the seven. If it had the X, then it was party time. If not, it was exam time. Facing 7 to 1 odds, Jim Simpson picked the one with the X and we enjoyed cake and ice cream. As they were all excellent students, I had no qualms about giving them top grades.

I then had the tapes transcribed. To my horror, when I read them, I realized how messed up my sentences were. As I couldn't bear to straighten them out, I hired a friend named Ellie Feltser, an editor for *Time and Life*, to do this task for me. Once this was done, I spent a fair amount of time tuning the manuscript. No problem for I enjoy revising. Harcourt Brace Jovanovich accepted it and *Chemical Oceanography* was published in 1974. Looking through it,

I was stunned to see that the labels on the x and y axes were reversed in several of the figures. It was only then that I realized when they redrafted the figures, they pasted on the axis labels. Whoever did this inadvertently made the switches. I had carefully proofed the text and captions, but not the figure labels. Live and learn.

As part of this book, I made my only significant contribution to reconstructing changes in sea salt composition. I proposed that the uranium content of fossil coral could be used as a proxy for the calcium concentration in seawater. Corals are inept chemists. They substitute U for Ca with little discrimination. By contrast, mollusks built no U whatsoever into their CaCO_3 . I assumed this was true in the past and noted that the U content of a set of Pliocene coral was about half that in recent corals. I was also aware that the uranium content of Mono Lake water was two orders of magnitude higher than that in ocean water. So also was the amount of dissolved inorganic carbon ($\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$). This made sense because U^{+6} and CO_3^{2-} form a stable ion complex. Based on this observation, I made the further assumption that the U content of ocean water was proportional to its carbonate ion content. Finally, I was aware that the product of Ca^{++} times CO_3^{2-} had remained roughly the same during the course of the Cenozoic. Taken together these three constraints suggested that the calcium content of seawater is proportional to the inverse of the square root of the U content of corals. Hence, as Pliocene corals have half the U content of recent corals, they must have formed when the calcium content of seawater was about $\sqrt{2}$ or 1.4 times larger than now.

My Lamont colleague, Bob Anderson, wouldn't buy into this. He felt that the uranium content was tied to the fraction of the sea floor which was anoxic (reflecting uranium's insolubility in plus four valence state). Because I valued Bob's judgement, I didn't pursue this idea any further.

But in the summer of 2015, I learned that Anne Gothmann, a PhD student working with Michael Bender at Princeton, had confirmed my idea. She measured the uranium content of well-preserved aragonitic corals extending back two hundred million years and found that since about 30 million years ago, the U content of corals has increased by a factor of about three. So, if my

idea is correct, the Ca content of seawater must have decreased by a factor of about 1.7. This made sense in light of the several-fold increase in Mg content she found in the same set of corals. In order to preserve the charge balance in seawater, the increase Mg⁺⁺ contribution with time was likely, at least in part, balanced by a decrease in the Ca⁺⁺ contribution. The uranium record preserved in corals suggests that the four-fold increase in their Mg content reflects a two-fold increase in seawater Mg⁺⁺ and a two-fold decrease in seawater Ca⁺⁺.

Gothmann also found a paper on the chemistry of Mongolian closed-basin lakes which showed a correlation between their U and ΣCO_2 contents over a range of two orders of magnitude. Perhaps my use of Mono Lake was appropriate after all.

I recently attempted to put together two observations. One is that over the last 50 million years the Mg to Ca ratio in seawater had been increasing. The other was that at 50 million years ago a long-term deep-ocean warming trend came to an end and was replaced by a steady cooling which continues today. As the deep ocean's temperature reflects that of polar surface waters, this meant that 50 million years ago, the warming of the polar regions gave way to a cooling. This cooling eventually allowed glaciers to form in both polar regions. I was also aware that changes in the isotopic composition of the elements lithium and sulfur in seawater occurred close to this time. The ⁷Li to ⁶Li in foraminifera shells began an upward climb and the ³⁴S to ³²S ratio jumped by 4 per mil and has remained there ever since.

Any explanation for the Mg/Ca and ⁷Li records requires global-scale changes in the environment. I suspect that a decrease in atmospheric CO₂ is responsible. It is my opinion that, unfortunately we have yet to find a reliable paleo CO₂ proxy. So, while this remains conjecture, it is difficult to come up with a better driver.

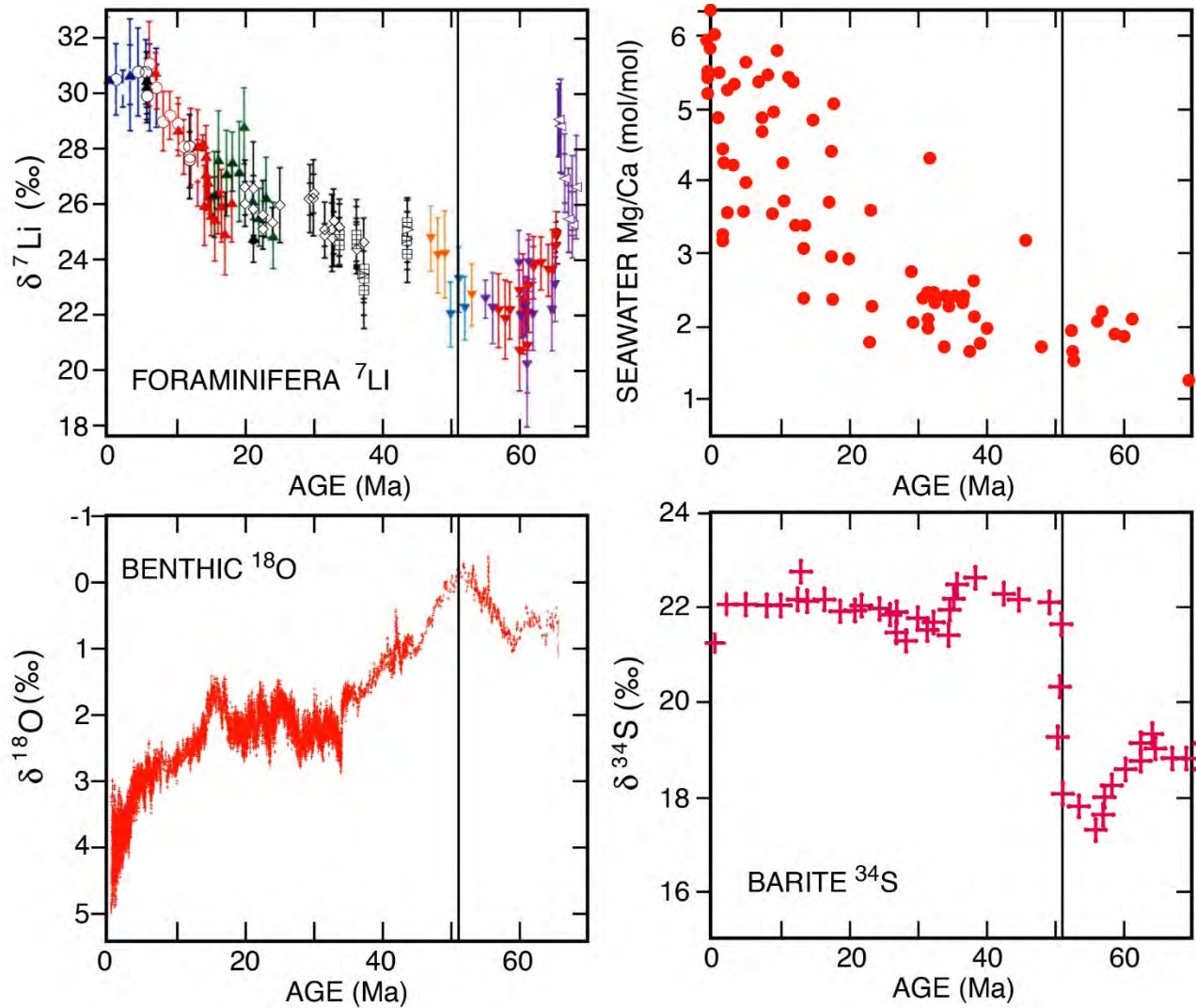
Regarding what triggered the global change, there is no doubt in my mind that it was the collision between the northward-drifting Indian continental block and the Asian continental block. The result was to push one 30 km-thick chunk of granitic crust under another. Not only did this create the Himalaya Mountain Chain and the Tibetan Plateau, it also disrupted the smooth flow of the Earth's crustal plates. For example, prior to 50 million years ago, the Pacific

plate was moving to the north at an average rate of about 10 cm per year. Then, very close to 50 million years ago, it started to move to the northwest at an average rate of 5 cm per year. We know this because it left behind a string of volcanoes. The mantle plume which created this trace now sits beneath the island of Hawaii. In a million or so years, there will be yet another island added to the chain. To the southeast of Hawaii lavas are already pouring out on the sea floor.

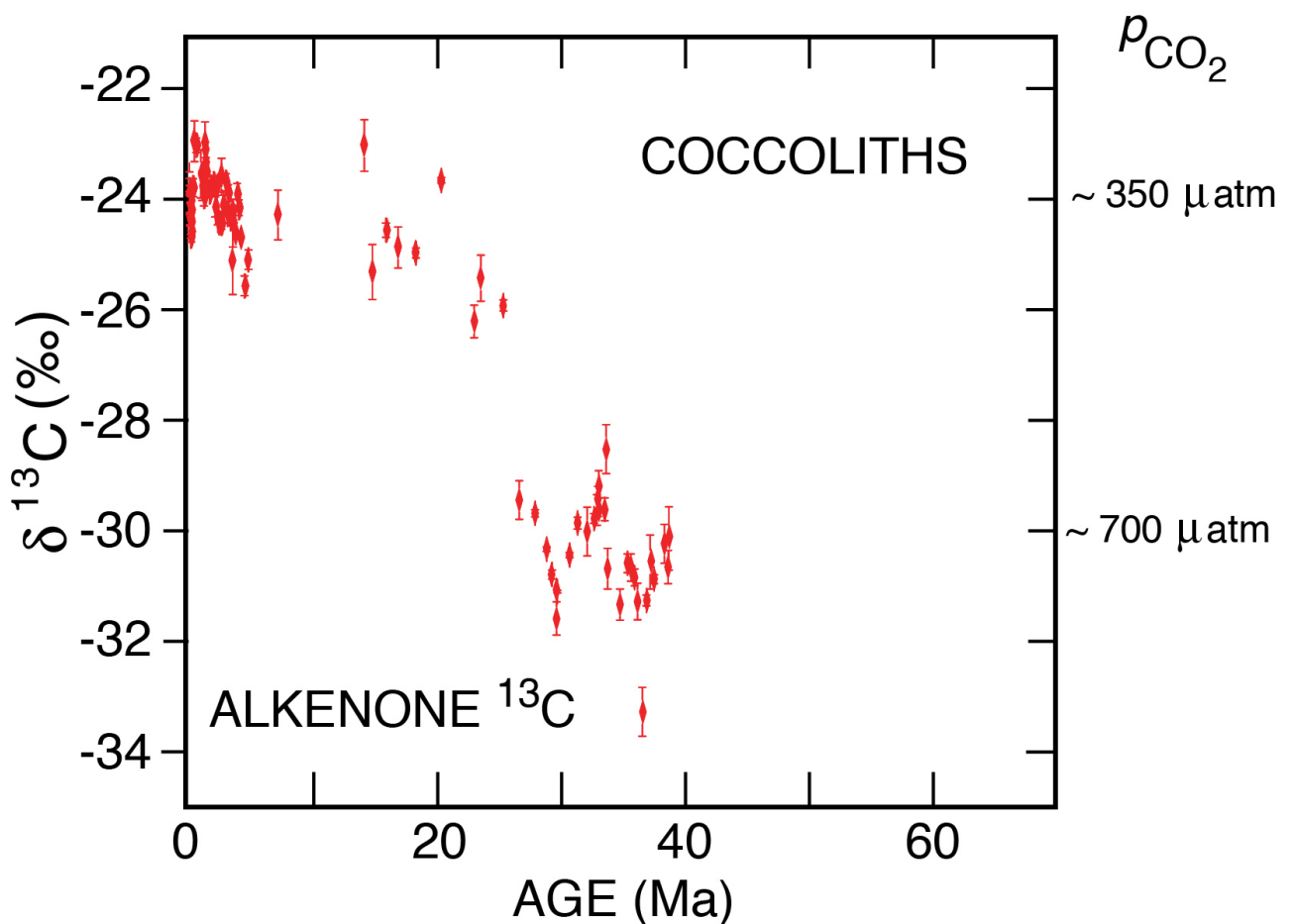
But why the changes in ocean chemistry? Prior to 50 million years, the Mg/Ca ratio in seawater remained more or less the same. Then it started to climb. I have a pet idea that the climb had to do with a fall in sea level which gradually drained the large inland seas that had occupied the low lying portions of the continents. Further, this fall of sea level gradually eliminated the locales where dolomite forms. As half the cations in dolomite are magnesium, when limestone is diagenetically converted to dolomite, for every calcium atom released a magnesium atom is added. Hence the diagenetic conversion of limestone to dolomite increases the rate of removal of Mg from the ocean and decreases the rate of removal of calcium. As there is very little dolomite formation today, the Mg added to the ocean by chemical weathering of the continents is being removed mainly by the circulation of seawater through the hot ridge crest basalts. So the demise of dolomite formation would have increased the ocean's magnesium inventory and decreased its calcium inventory (hence increased Mg to Ca in seawater).

Princeton's John Higgins and Anne Gothmann demonstrate that dolomitization leads to the fractionation of magnesium's isotopes. This being the case, the decrease in the rate of production of dolomite over the last 50 million years should have resulted in a shift in the isotopic composition of ocean magnesium. But Gothmann sees no such shift in her corals. Hence they reject the dolomite hypothesis. As they agree that the production of dolomite has undergone a large decrease, they are forced to conclude that dolomite formation has never been a big player in the global magnesium cycle. Hence, its demise did not significantly alter the ocean's Mg to Ca ratio.

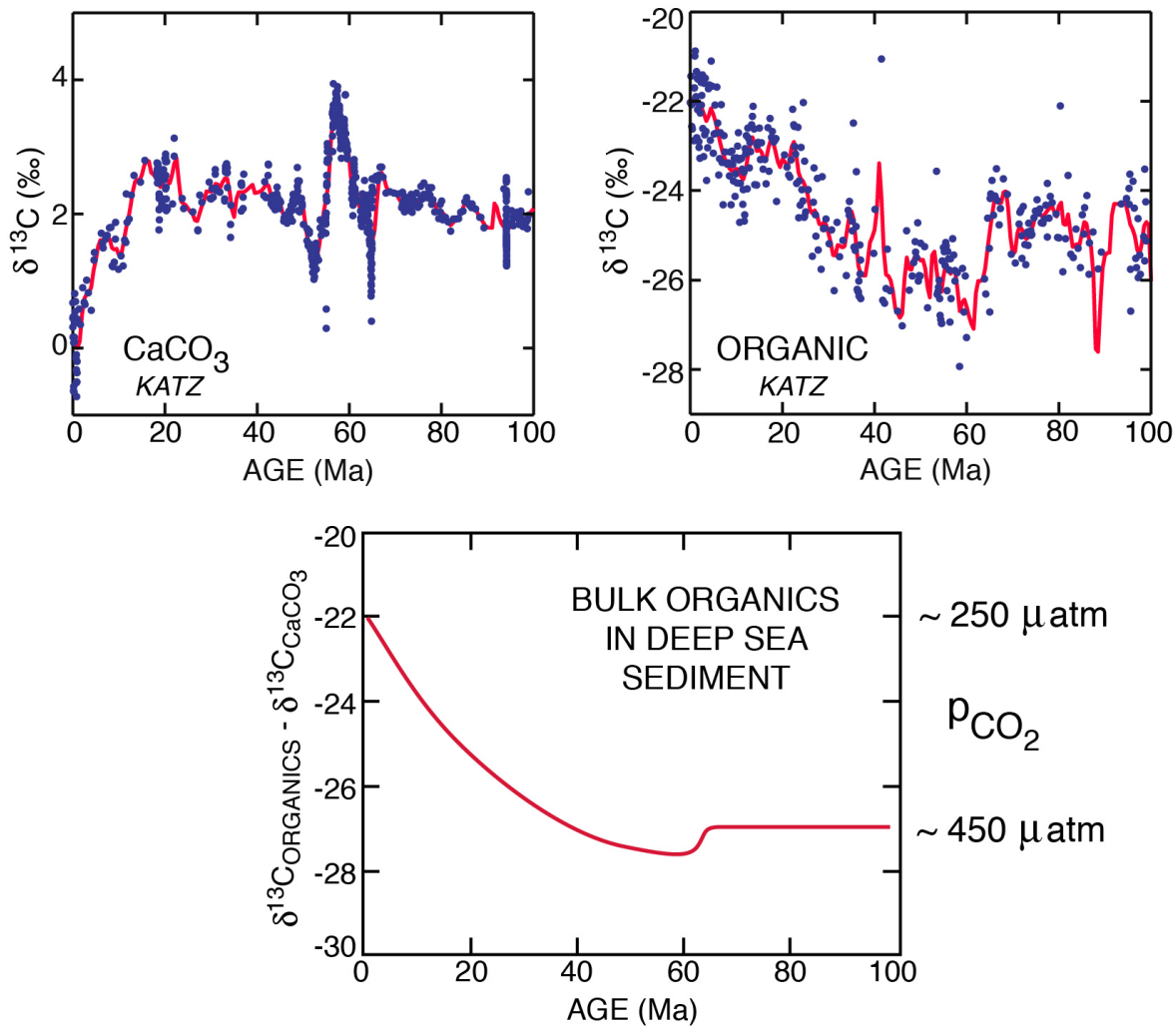
My 2015 paper titled “The collision that changed the world” published in *Elementa* has so far received little attention. Nor has my conclusion. I comment that if the cooling trend continues for another 200 or so million years, the Earth will once again become a snowball.



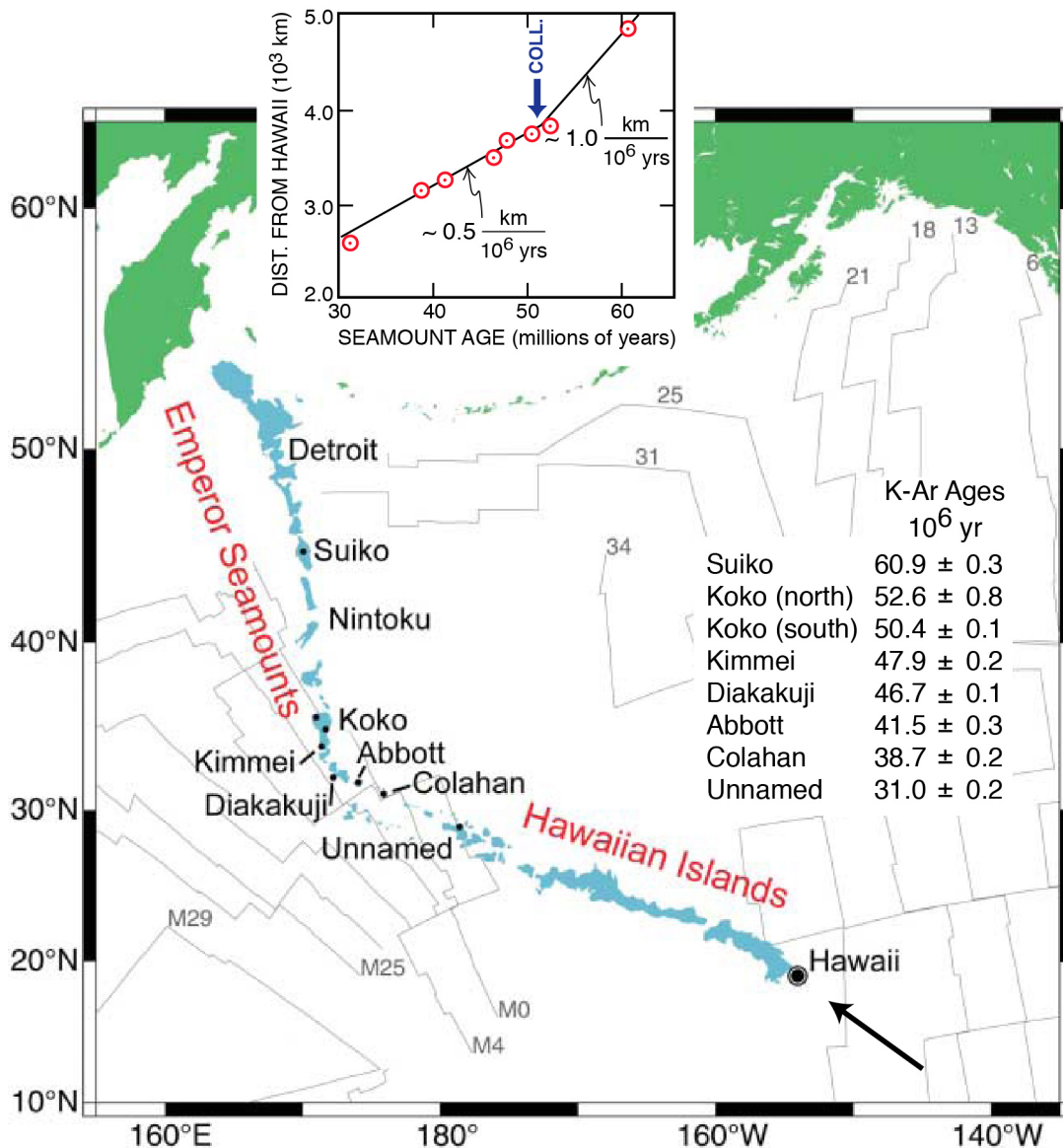
Three records of isotopic composition of seawater constructs suggest that something dramatic happened close to 50 million years ago. The decrease in $^{18}\text{O}/^{16}\text{O}$ ratio in the shells of benthic foraminifera came to an end and began an increase which continues today. This tells us that the polar regions have cooled by 12°C or so. The ^7Li to ^6Li record for planktonic foraminifera shells tells us that something happened close to 50 million years ago which caused the extent of fractionation between the lithium in igneous rocks and the lithium in the sea to begin a long term increase. Fifty million years ago, the difference was about 17 per mil and now it is about 26 per mil. Although we know that this separation occurs during the formation of clay minerals in soils, as yet we don't know why it underwent this progressive change. Barium sulfate records the ^{34}S to ^{32}S ratio in seawater. Fifty million years ago, the ratio jumped up 4 per mil and has remained there ever since. A graduate student working with Jess Atkins, has recently confirmed this record by analyzing trace amounts of sulfur contained in foraminifera shells. Although noisy, Ann Gothmann's measurements on the Mg content of well-preserved aragonitic coral have a trend which broadly parallels that for lithium isotopes. The vertical line marks the time of the collision between India and Asia.



The most widely accepted proxy for past atmospheric CO₂ contents is the ¹³C to ¹²C ratio in alkenones manufactured by a single species of *Coccolithophorids* (i.e., *Emiliani Huxley*). However, as this species which dominates *Coccolith* production came into being about 38 million years ago, this record goes no further back in time. It suggests that a twofold drop in pCO₂ occurred about 25 million years ago. This proxy has been criticized because it is thought that at low CO₂ partial pressures, *Coccoliths* might supplement their carbon supply by using bicarbonate. However, as it involves a single organic compound formed in the ocean's surface-mixed layer, it remains the favorite.



Not happy with the shape of the ^{13}C record kept by alkenones, I took an interest in an alternate record put together by Mimi Katz. She used measurements of the ^{13}C to ^{12}C ratio for bulk organic matter and bulk CaCO_3 in deep sea sediments. What struck my eye was that its shape is consistent with the idea that the CO_2 content of the atmosphere has steadily declined over the last 50 million years. But I must say that isotope geochemists would cringe at the idea that bulk organic matter reliably records the $\Delta\delta^{13}\text{C}$ of marine photosynthesis. The fact that organic matter makes up no more than one-half percent of the sediment and its origin is not known rules against the use of its ^{13}C to ^{12}C ratio as a CO_2 proxy. But the fact that it shows a distinct trend suggests that it might be telling us that we must find a more reliable proxy than alkenones.



The Island of Hawaii is the most recent of a chain of volcanoes that originated more than 60 million years ago. The idea is that a plume-carrying material from the core-mantle boundary to the surface has a fixed position. As the overlying crustal plate moves over the mantle, the plume creates a series of volcanoes. Of interest to me is that close to 50 million years ago, the motion of the plate changed from due north to northwest and its average speed dropped by a factor of two. This disruption was a consequence of the collision of India with Asia.

References

- Sillén, L.G. (1967), The ocean as a chemical system, *Science*, 156(3779), 1189-1197.
- Broecker, W.S. (1970), A boundary condition on the evolution of atmospheric oxygen, *J. Geophys. Res.*, 75, 3553-3557.
- Broecker, W.S. (1971), A kinetic model for the chemical composition of seawater, *Quaternary Res.*, 1, 188-207.
- Broecker, W.S. (1974), *Chemical Oceanography*, Harcourt Brace Jovanovich, Inc., NY.
- Broecker, W.S. and S. Peacock (1999), An ecologic explanation for the Permo-Triassic carbon and sulfur isotope shifts, *Global Biogeochem. Cycles*, 13(4), 1167-1172.
- Broecker, W. (2013), How to think about the evolution of the ratio of Mg to Ca in seawater, *American Journal of Science*, 313, 776-789, doi: 10.2475/08.2013.02.
- Broecker W (2015), The collision that changed the world. *Elem. Sci. Anth.* 3, 000061 doi: 10.12952/journal.elementa.000061.
- Gothmann, A.M. (2015), Fossil corals as archives of secular variations in seawater chemistry, PhD dissertation, Princeton University.

Chapter 12

Redfield Ratios

Before World War II, Alfred Redfield, a scientist at Woods Hole Oceanographic, set out to determine the average ratio of the elements phosphorus, nitrogen and carbon utilized by marine organisms and also the amount of O₂ consumed when it was 'eaten.' He did this by determining the changes in concentration of PO₄, NO₃, and O₂ along isopycnal horizons in the thermocline of the northern Atlantic. He concluded that for every additional P atom there were 16 N atoms and 100 C atoms and that for each extra P atom, 132 molecules of O₂ were utilized. His ratios have served as the standard for marine biologists ever since.

With the GEOSECS data set in hand, Taro Takahashi and I decided to redo what Redfield had done and to also extend it from the thermocline of the northern Atlantic to the rest of the world's ocean. The first thing we did was check Redfield's North Atlantic thermocline results for the 27.0 density horizon. We found that for each micromole increase in PO₄ there was a 138 ± 6 micromole decrease in O₂; a result which was consistent with Redfield's.

But when we did this for the same density horizon in the South Atlantic, we obtained a very different result. Instead of 138 ± 6 we found that 252 ± 20 micromoles of O₂ disappeared for every micromole of PO₄ added. A huge surprise! But it didn't take long to figure out the cause of this difference. The reason is that the water feeding the southern thermocline has a higher initial content of PO₄ than that feeding the northern thermocline. Further, these two water types mix with one another. However, as the northern waters have a higher salinity than those in the south, we were able to assess the extent of this mixing between these two sources of Atlantic thermocline water. This allowed us to correct the northern result for the intrusion of southern water and the southern result for the intrusion of northern water. When this was done, we obtained a ΔO_2 to ΔPO_4 ratio of -165 ± 7 for North Atlantic thermocline and -165 ± 6 for the South Atlantic thermocline. I suspect that if Redfield had had data from the entire Atlantic, he would have done what we did. I also like to think that if Redfield had lived in Buenos Aires and used measurements made in the South Atlantic, his ratios would have been very different.

I must add here that during the early phases of this effort, Sarah Langer, a graduate student at Lamont, worked with us. Sadly, she was diagnosed with brain cancer and she died in early 1983. Our paper on this was submitted to the *Journal of Geophysical Research* a year and a half later. In recognition of her contribution, she is an author. I should also mention that, as Sarah was much loved by everyone, our department gives an annual award in her honor.

One might ask why we focused on the ratio of oxygen lost to phosphate gained. We rejected NO_3 because it is being produced and destroyed within the ocean. We rejected ΣCO_2 (i.e., $\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$) because the dissolution of calcium carbonate adds ΣCO_2 . Although a correction can be made based on alkalinity measurements, there is a further complication which impacts thermocline water. It involves the uptake of fossil fuel CO_2 . Because the atmospheric burden of anthropogenic CO_2 is getting larger and larger, along any isopycnal horizon, there is a downstream decrease in its contribution. This decrease partially counterbalances the increase resulting from respiration. Of course, Redfield didn't face this problem, for in the 1930s, the amount of fossil fuel CO_2 in the atmosphere was rising ever so slowly.

Redfield likely calculated the amount of ΣCO_2 change along a density horizon from the O_2 and NO_3 changes. Oxidation of each carbon required one O_2 molecule and for each nitrogen, two O_2 molecules. Calculated in this way, the Redfield Ratio becomes:

ΔPO_4	ΔNO_3	$\Delta\Sigma\text{CO}_2$	ΔO_2	
1	16	100	-132	μmoles/Liter

However, there is a flaw in this reasoning for marine organic matter contains H. One O_2 is required to oxidize each hydrogen atom ($\text{H} + \text{O}_2 \rightarrow \text{H}_2\text{O}$). But there is no way to measure the increase in H_2O along a density horizon. Since Redfield's ratios must be revised, in order to avoid confusion one might suggest that they be called resource ratios. But, time honored terminology will win out. The term 'Redfield ratios' is here to stay.

Taro, Sarah, and I set out to determine these ratios elsewhere in the ocean. For the 27.0 density horizon in the Indian Ocean we obtained a $\Delta O_2/\Delta PO_4$ ratio of -169 ± 8 . For the deep Norwegian Sea and for the deep Red Sea, we obtained values of -170 ± 6 and -173 ± 6 . Finally, for the deep Pacific and deep Indian Oceans we obtained 183 ± 13 and -183 ± 8 . For two regions we could not recover Redfield ratio: the deep Atlantic Ocean and the thermocline of the Pacific Ocean. The reason is that for each there are more than two contributors, each with different initial PO_4 and O_2 contents. Although salinity can be used to separate the contributions of two sources, there is no way to reliably separate the contributions of three sources. As we've already seen, the failure to take into account the contributions of two sources in the thermocline of the Atlantic led to highly biased Redfield ratios.

We were amazed by the near identity of these results. A $\Delta O_2/PO_4$ ratio of -175 ± 10 covered them all. This led us to propose 'conservative property' useful for distinguishing contribution of deep water produced in the deep northern Atlantic and that produced in the Southern Ocean. We called this property PO_4^* . It is calculated as follows:

$$PO_4^* = PO_4 + O_2/175 - 1.95$$

We inserted the constant -1.95 to make deep sea PO_4^* values close to those for PO_4 . I regret this for it is a needless complication. As the choice of this constant is arbitrary, it would have been better to have made it zero.

PO_4^* was not my first attempt to find a conservative property. I had initially chosen a combination of NO_3 and O_2 . I called it NO . My decision to use NO_3 instead of PO_4 was that I felt the set of NO_3 measurements were analytically more sound than those of PO_4 . But, I eventually realized that NO_3 suffers from a bias not experienced by PO_4 . It is that NO_3 is being created and destroyed within the sea on a time scale of just a few cycles of ocean mixing. Further, sites of production and destruction were well separated. Cyanobacteria convert N_2 to NO_3 in the thermocline. Bacteria living in anoxic sediments beneath upwelling zones use NO_3 as an oxidant. This gives rise to small departures from the 16 to 1 ratio which characterize much of the ocean interior. Realizing that the creation and destruction of NO_3 in the ocean's interior violated my

conservative requirement, I switched to PO_4 . It is delivered by rivers. Further, it remains dissolved in the sea ten to thirty times longer than it takes the ocean to mix. So, its removal does not perturb its distribution within the sea's interior.

Early on I asked myself why the average NO_3 to PO_4 ratio in the sea was the same as the N to P ratio in the organic matter being oxidized in the sea's interior. I have come to realize that it is controlled demand by the organisms. Were the NO_3 to PO_4 in the ocean to fall below the 16 to 1 demand ratio, it would give an advantage to those organisms which are capable of fixing N_2 . In this way the ratio would be driven back toward 16.

Taro Takahashi once had a visitor from Australia who tried to convince us that the excess CO_2 in the atmosphere could be drawn down by adding NO_3 to the sea. It would, he said, increase plant productivity and thereby transfer carbon to the deep sea. I tried with no success to convince him that without matching PO_4 this wouldn't work.

If the coefficient 175 is indeed constant throughout the deep sea, then PO_4^* can be used as a conservative property. In any water mass it is set by the PO_4 and O_2 contents of the source water. During its residence in the ocean interior restoration increases the PO_4 content. This increase is balanced by the decrease in $\text{O}_2/175$.

Our interest lay in the large difference between the PO_4^* value of deep water produced in the northern Atlantic and that for the deep water produced in the Southern Ocean. In contrast to the range in temperatures and salinities for the northern source waters, they all have the same PO_4^* value i.e., 0.73 ± 0.03 . In contrast, Southern Ocean water descending to the abyss along the margins of the Weddell and Ross Seas have a PO_4^* value of 1.95 ± 0.07 . As both of these waters descend into the abyss carrying roughly the same amount of O_2 , the difference in PO_4^* primarily reflects the difference in the PO_4 content of source water in the Southern Ocean (i.e., $\sim 2.2 \mu\text{mol/liter}$) and that in the northern Atlantic (i.e., $\sim 0.9 \mu\text{mol/liter}$).

PO_4^* provides a first order picture of how waters mix in the deep sea. It depicts the extent to which Southern Ocean water diffuses northward into the Atlantic. It also shows how deep water produced in the northern Atlantic mixes into the deep water in the Southern Ocean. In a

section from Africa to Antarctica, the upper deep water has a lower PO_4^* value than the Southern Ocean average (i.e., $\text{PO}_4^* = 1.38$) and the lower deep water has a higher than average PO_4^* value. In a single traverse around the Antarctic continent these end members are mixed together. By the time they reach the Drake Passage, they have been completely homogenized.

We were amazed by the uniformity of PO_4^* values for deep Pacific and deep Indian Ocean waters. With two exceptions water at depths greater than 1500 meters have PO_4^* values of $1.38 \pm .02$. The exceptions are the far northern Pacific mid-depth water and the upper southwestern Indian Ocean deep water. In both cases the waters have slightly lower PO_4^* values. For the Indian, the reason is the influx of low PO_4^* water from the Atlantic. In the case of the northern Pacific I'm not sure. Or perhaps it reflects the downward mixing of overlying low PO_4^* water. But these zones constitute only five or so percent of the deep Pacific and Indian Oceans. The rest have the identical PO_4^* values.

If it is assumed that only deep waters formed in the northern Atlantic and along the margins of the Antarctic continent contribute to the deep Pacific and Indian Oceans, then 47 percent of this water is supplied from the northern Atlantic and 53 percent from the Antarctic margin. This might be termed the convective scenario. Two papers, one by Gebbie and Huybers and the other by Khatiwala, Primeau, and Holzer, take issue with this conclusion. They argue that diffusion along outcropping isopycnal horizons dominates the Southern Ocean contribution and they conclude that only about 25 percent of the water in the deep Pacific and Indian Oceans is produced in the northern Atlantic. We would have reached a similar conclusion were we to have chosen the lowest PO_4^* value observed in the interior of the deep Southern Ocean (i.e., $\text{PO}_4^* \sim 1.6$).

It is of interest to harness the radiocarbon budget for the deep ocean to mediate between these two scenarios. To balance the decay of radiocarbon in the deep sea requires the addition of about 220 moles of ^{14}C per year. Particles falling into the deep sea supply about 20 moles of ^{14}C . The remaining 200 moles are carried by water downwelling from the surface. Today, mean flux of North Atlantic Deep Water (NADW) is about 16 million cubic meters per second. It carries

about 130 moles of extra ^{14}C per year. The remainder (about 70 moles $^{14}\text{C}/\text{year}$) must come from the Southern Ocean. As the water descending in the Southern Ocean has only a slightly larger ^{14}C to C ratio than the water it is replacing, this requires a flux of roughly 40 million cubic meters per second. Were this the case, North Atlantic source water would supply 33 percent of the water in the deep Pacific and Indian Oceans, a fraction lying roughly half way between that based on the convective scenario (47 percent) and that based on the diffusive scenario (25 percent). The problem with this is the assignment of the amount of ^{14}C supplied by Southern Ocean sources. The uncertainty in this choice is large enough to allow either scenario.

One of the applications of PO_4^* is to determine how much of the decrease the ^{14}C to C ratio in waters deeper than 2 km in the Atlantic is the result of radiodecay and how much is the result of mixing with northward diffusing Southern Ocean water. The result came as a surprise. The gradient of the radio-decay component is west to east instead of north to south. However, we quickly realized how this reflected that the newly produced deep water was injected into western margin boundary currents moving equatorward from both ends of the Atlantic.

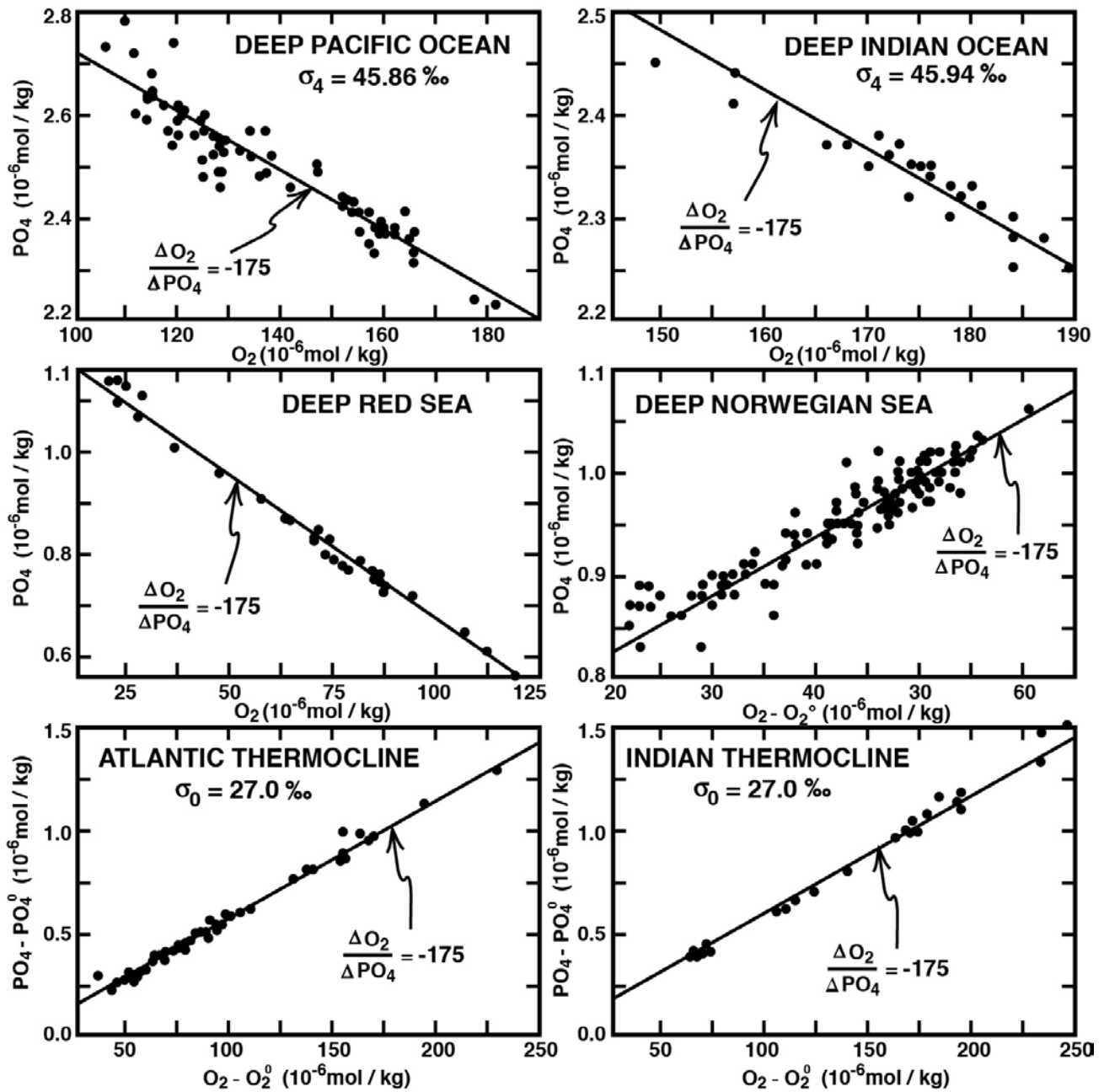
When we did a similar calculation for O_2 lost to respiration, we found an analogous pattern. The deficiency is smaller in the western Atlantic than in the eastern Atlantic. Further, when we plotted the loss of ^{14}C due to radiodecay against the loss of O_2 due to respiration, we obtained a slope of $0.9 \pm 0.1/\mu\text{molO}_2/\text{kg}$ per-mil drop in $^{14}\text{C}/\text{C}$. This yields an O_2 consumption rate of 11 ± 1 micromoles per century.

I should mention in closing this topic that it is clear that not all marine plankton have a composition consistent with our revised Redfield ratios. This being the case, one might think that the material sinking from the cold Norwegian Sea surface and the warm Red Sea surface would have different ratios, but for some reason, they do not. Somehow these organism-to-organism differences balance out.

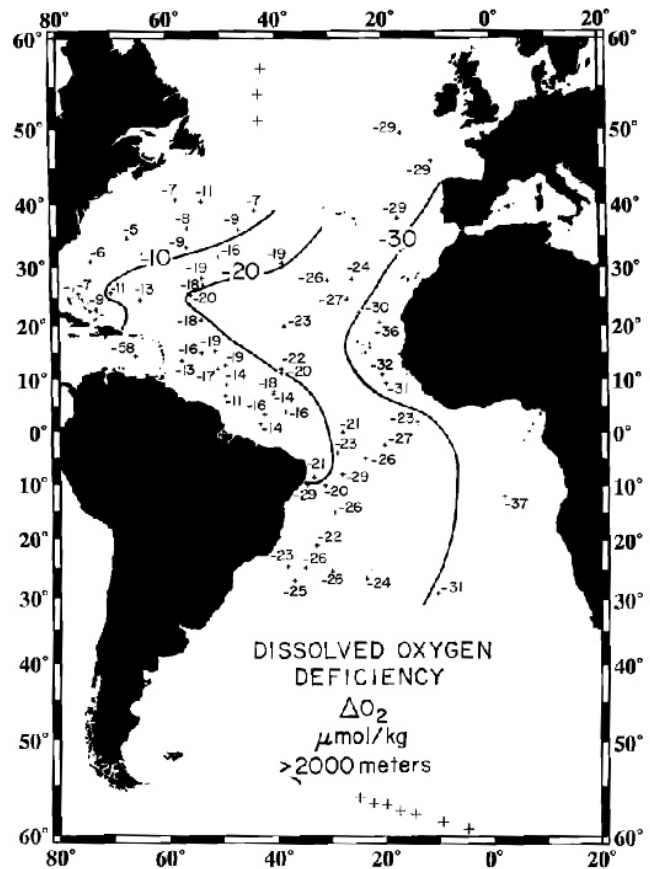
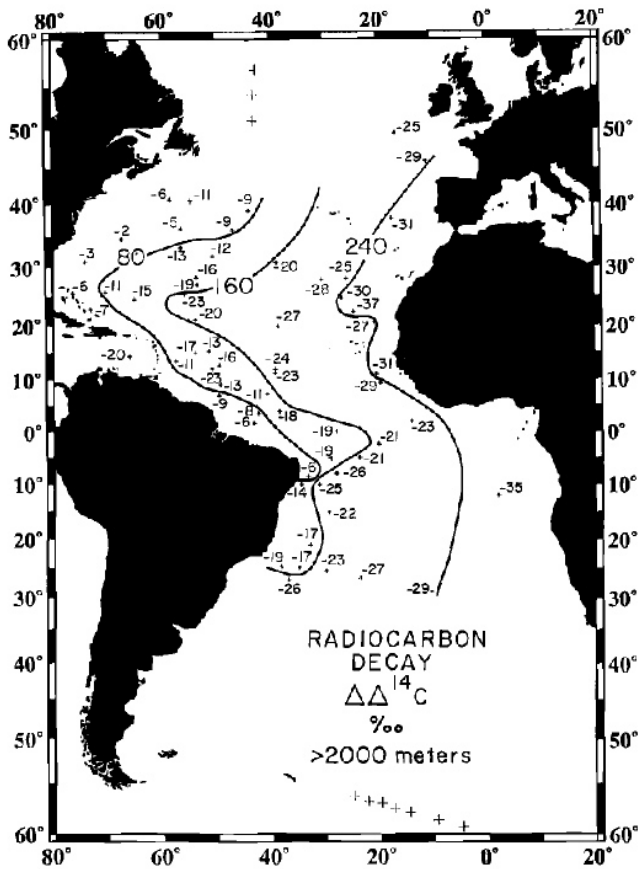
Working with Tsung-Hung Peng (who co-authored “Tracers in the Sea”), we tried to disentangle the contributions of carbon and hydrogen to the O_2 demand. Although uncertain, we

estimate carbon oxidation requires 125 moles of O_2 for P atom. If so, hydrogen oxidation must require about 16 moles O_2 . This yields the following set of revised Redfield ratios.

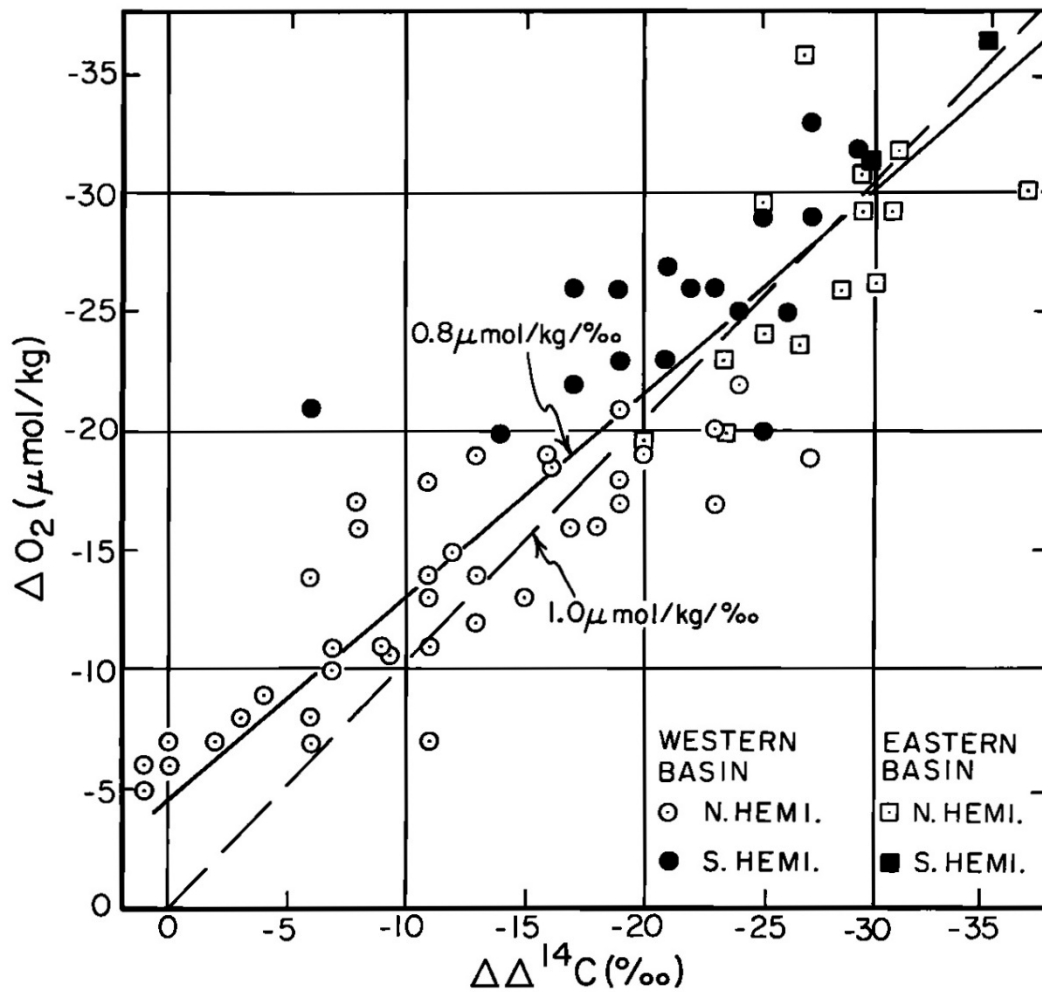
	P	N	C	H	O_2
Atom Ratio	1	16	125	16	
O_2 Demand	2	32	125	16	-175



Plots of PO_4 versus O_2 for six regions of the ocean. Note that for each, a line with a $\Delta O_2/\Delta PO_4$ slope of -175 moles per mole provides an adequate fit to the measurements. In three of the plots, the actual O_2 content is plotted. In the other three, it is the O_2 consumed (i.e., $O_2 - O_2^0$).



Maps showing the amount of ^{14}C lost to radiodecay and the amount of O_2 lost to respiration in the deep Atlantic. Note that for each, the gradient is from west to east reflecting ventilation by western boundary currents. As radiocarbon decays at a rate of about 80 per mil per hundred years, the oldest waters have remained in the Atlantic for about 300 years.



When plotted against ^{14}C loss by radiodecay, the O_2 utilization rate turned out to be about $0.8 \mu\text{mol/kg}$ per mil. This translates to an average respiration rate of about 10 micromoles of O_2 each century.

References

- Broecker, W.S., T. Takahashi and T. Takahashi (1985), Sources of flow patterns of deep waters as deduced from potential temperature, salinity and initial phosphate concentration, *J. Geophys. Res.*, *90*, 6925-6939.
- Takahashi, T., W.S. Broecker, and S. Langer (1985), Redfield ratio based on chemical data from isopycnal surfaces, *J. Geophys. Res.*, *90*, 6907-6924.
- Peng, T.-H., and W.S. Broecker (1987), C/P Ratios in Marine Detritus, *Global Biogeochemical Cycles*, *1*, 155-161.
- Broecker, W.S., S. Blanton, T. Takahashi, W. Smethie and G. Ostlund (1991), Radiocarbon decay and oxygen utilization in the deep Atlantic Ocean, *Global Biogeochemical Cycles*, *5*, 87-117.
- Broecker, W.S., S. Peacock, S. Walker, R. Weiss, E. Fahrbach, M. Schroeder, U. Mikolajewicz, C. Heinze, R. Key, T.-H. Peng, and S. Rubin (1998), How much deep water is formed in the Southern Ocean? *J. Geophys. Res.*, *103*, 15,833-15,843.
- Gebbie, G., and P. Huybers (2010), Total matrix intercomparison: A method for determining the geometry of water-mass pathways, *J. Phys. Oceanography*, *40*, 1710, doi: 10.1175/2010JP04272.1.
- Khatiwala, S., F. Primeau, and M. Holzer (2012), Ventilation of the deep ocean constrained with tracer observations and implications for radiocarbon estimates of ideal mean age, *Earth Planet. Sci. Letts*, *325-326*, 116-125, doi: 10.1016/j.epsl.2012.01.038.

Chapter 13

The Great Ocean Conveyor

My introduction to the record contained in Greenland ice came in 1971 at a meeting held at Yale. It was organized by Karl Turekian in honor of Richard Foster Flint's retirement. At that time, those of us interested in the climate record were thinking in terms of Milankovitch's orbital cycles. These variations in summer insolation were dominated by the 20-kyr precession cycle and the 40-kyr tilt cycle. There were, however, two things that didn't seem to mesh with orbital forcing. One was the abrupt endings of glacial cycles. I referred to them as 'terminations'. The other was the Younger Dryas, a short-lived cold snap which punctuated the most recent of these terminations. Both demonstrated that climate changed on shorter time scales. But, as our records came largely from slowly accumulating deep sea sediments, bioturbation had erased any evidence for millennial time scale changes including the Younger Dryas.

At Yale, when Willi Dansgaard stood up and presented the ^{18}O record from the Camp Century ice core (the first down-to-bed rock core taken in Greenland), we were in for a huge surprise. Instead of displaying the Milankovitch 'symphony,' it was dominated by millennial-duration cacophony. Rather than being unique, the Younger Dryas was only one of sixteen or so sharp-sided millennial-duration events. It was such a shock that most of us viewed Dansgaard's record as something strange related to Greenland's ice. Little did we dream that during the next 25 years, this cacophony would show up in records from everywhere on the planet.

During the 1970s my mind was focused mainly on the GEOSECS survey and on my graduate students' research at Canada's Experimental Lake Area. Because of this I didn't give Dansgaard's record much thought. Then, in the early 1980s, when I attended a meeting in Bern, Switzerland, I got a wake-up call. Results for a second ice core located in Southern Greenland were presented. The cacophony seen in the northern Greenland record was beautifully duplicated. In addition to their short duration, these events were very different in shape than in Milankovitch's insolation cycles. Instead, they were rectangular, suggesting that the air

temperature over Greenland had undergone sizable abrupt jumps. It was also shown that these sharp changes were accompanied by large changes in the dust content of the ice.

As part of his presentation of the Dye-3 ice core results, Hans Oeschger showed us records of the CO₂ content of air trapped in the ice. This preliminary effort focused on three events. Jumps in CO₂ content accompanied the jumps in ¹⁸O and dust! It was the CO₂ jumps which caught my attention. Based on the rate at which the extra ¹⁴C-tagged CO₂ (produced by testing H bombs) was being taken up by the ocean and terrestrial biosphere, it seemed impossible to explain the abrupt 50 ppm changes in atmosphere CO₂ content that Oeschger's people had found. How could this happen on time scales less than a few decades?

Back at Lamont, I put on my thinking cap and tried to figure out how these CO₂ changes could have been accomplished. The only plausible way I could see it happening was by turning on and off the production of deep water in the northern Atlantic. But, try as I may, I still couldn't see how such large changes in CO₂ content could be accomplished on such short time scales. While the on and off might account for a few ppm change in atmospheric CO₂ content, it surely couldn't account for 50 ppm. Foiled, I had to give up.

However, it dawned on me that turning on and off deep water formation in the northern Atlantic could produce sizable air temperature changes in Greenland. My reasoning was as follows. Deep water production in the northern Atlantic is fed by the Gulf Stream which currently is partly responsible for Norway's mild winters. During winters, cold air flowing off of Canada cools the water making it dense enough to sink to the bottom. It then flows down the Atlantic into the Southern Ocean. I termed this Atlantic branch of the global loop the Ocean Conveyor. Unhappy with my name, physical oceanographers have subsequently renamed it AMOC (Atlantic Meridional Overturning Circulation).

Were deep water production shut down, this ocean heat supply would also be cut off. I soon realized that a shutdown of deep water production in the northern Atlantic might have global repercussions. The reason is that the water which feeds deep water production comes from the Southern Ocean. This inflow is partly supplied by warm water from the Indian Ocean which

sneaks around Africa's tip. This outflow from the Indian Ocean is in turn balanced by inflow from the Pacific via the Indonesia passages. Further, this Pacific to northern Atlantic transport of surface water is balanced by the upwelling of deep water in the northern Pacific Ocean. The point is that if any part of this Earth-girdling loop is disrupted, it must have ocean-wide repercussions.

One of the first articles I wrote about the ocean conveyor was invited for the American Museum of Natural History's monthly magazine. The editor asked me to provide a diagram showing the global circuit. I made a sketch and the editor sent it to an artist in Hoboken, N.J. for formal drafting. He did this without any contact with me and as I deemed his creation adequate, I didn't request any changes. Had I known this simple diagram would become a logo for global change, I surely would have made some adjustments. For example, a postdoc from New Zealand complained that the conveyor belt ran right over her country. Needless to say, many others have made more detailed versions. But, as no such diagram can accurately display the features of the oceans' so-called thermohaline circulation, I like my simple one. It makes the point.

Of course, from the very beginning of my quest, I had to face the question of what caused the turn-on and turn-off of deep water formation in the northern Atlantic. At that time, Jim Teller, a Canadian scientist, was pushing the idea that glacial melt water stored in a large lake formed in front of the retreating ice sheet had catastrophically spilled through a weak point in the retreating ice front. Teller envisioned that this great flood rushed across the Great Lakes region and out through the St. Lawrence Valley into the Atlantic. Had this happened, the reduction in the salinity would have prevented winter cooling from making it sufficiently dense to sink to the bottom. Although in many ways appealing, despite intense searches no convincing evidence for the existence of such a flood has been found. Further, although ocean modelers have shown that such a flood could indeed shutdown deep water production, the amount of water they require is far larger than was stored in the lake.

To me, the most devastating argument against the flood was made by a physical oceanographer. He pointed out that while a flood of fresh water could shut down deep water

production, there is no such thing as an anti-flood which could have turned it back on. Further, the ice core record showed that the warming associated with the turn-on was even more abrupt than that associated with the turn-off.

Although there is no agreed-upon scenario to explain the off and on circulation change, I suspect that when there is, it will involve some sort of oscillation internal to the ocean. My reason for this is that the two dozen Younger Dryas-like Dansgaard-Oeschger events that punctuate the last glacial cycle have shapes and durations similar to that for the Younger Dryas. Hence it would be quite a stretch to explain the onset of each by a catastrophic event. Further, it would still be necessary to call on the ocean itself to trigger the abrupt rejuvenation of deep water formation at the end of each event.

One might ask why deep water forms in the northern Atlantic and not in the northern Pacific? The reason is that the surface waters in the northern Atlantic have about two grams per liter more salt than their Pacific equivalents. The density difference created in this way is large. It is equivalent to that produced by cooling the water by about 8°C. Hence, when cooled all the way to the freezing point, the surface waters in the northern Pacific are still not sufficiently dense to sink into the interior.

This raises a second question. What is responsible for this difference? The answer is vapor transport via the atmosphere from the Atlantic to the Pacific. Fritz Zaucker, a PhD student at Heidelberg University, did his thesis research at Lamont under my mentorship. He used global water budgets and ocean-atmosphere models to estimate the magnitude of this transport. He came up with 0.25 ± 0.12 million cubic meters a second. If not compensated by the export of salt from the Atlantic, this would result in a salinity increase of 0.6 ± 0.3 grams per liter per 1000 years. But if, as we believe, the ocean's thermohaline circulation has been more or less at steady state for the last 10,000 years, this extra salt must be exported. If the export is via the lower limb of the Atlantic's conveyor, then, as the flux is about 17 million cubic meters per second, the salt content difference between the departing water and the returning flow would have to be $0.25/17 \times 34$ or 0.5 grams per liter.

Another question which nagged me regarded the extent of the impacts of Y.D. cooling. My first thoughts were that they would have been confined to northern Europe (i.e., those areas benefiting from the Gulf Stream's warmth). However, in rapid succession, evidence poured in that they impacted a far larger area. The first came from my colleague, Dorothy Peteet. She found evidence for a Younger Dryas cooling in a pollen record for a core from a bog located less than a kilometer from my Lamont campus office. She also uncovered evidence for Younger Dryas impacts in southern Alaska. Then, Jim Kennett, a marine geologist at the University of California, Santa Barbara, startled me by showing that not only the Younger Dryas but all of Greenland's so-called Dansgaard-Oeschger events showed up prominently in a sediment core taken in the Santa Barbara coastal basin. And on it went: Persian Gulf sediment, Chinese stalagmites...

In 1987, I received a \$25,000 donation from Exxon. I decided to use it to finance a field trip to the Southern Andes. The motivation was that if the summer insolation changes produced by orbital cycles were driving glaciation, one would expect a different chronology for the advances of mountain glaciers in the Southern Hemisphere than those in the Northern Hemisphere. The reason is that the 20-kyr precession cycle is antiphased between the hemispheres. Yet the few existing radiocarbon measurements suggested that this was not the case. Rather, they appeared to be in phase.

I assembled a group of 22 scientists interested in Pleistocene glaciation to join me in a three-week tour of the southern Andes; eleven were from South American countries and eleven from elsewhere in the world. At the time, I was mentoring a postdoctoral fellow named Scott Stine. His wife, Mary, offered to organize the trip. This was fortunate because the logistics were complicated. She did a superb job. The trip was clockwork perfect.

I well remember our arrival in Buenos Aires. After a long day of flying and a big meal, I was bushed. So, I went to bed early. A couple of hours later, my friend George Kukla, whom I had chosen as my roommate, rolled in and promptly began to snore. I retreated to a couch in a neighboring lounge area. Next morning, I decided that I would not endure three weeks of his

snoring. So I switched to George Denton. This launched a collaboration which continues today. The trip also convinced Denton to terminate his streak of 17 consecutive field seasons in Antarctica and turn his attention to the glacial record in the Southern Andes (and later to that in New Zealand's South Island).

In 1989, a paper published by a young German scientist named Hartmut Heinrich caught my eye. While logging a core collected as part of a survey to evaluate the stability of sediment in an area off France (used for the disposal of low level radioactive wastes), he made what turned out to be a major discovery. Hartmut noted that there were six discrete layers of glacial debris spanning the cold part of the last glacial cycle. Although the sediment separating them was dominated by foraminifera shells, the debris layers had almost none. His interpretation was that the Hudson Bay lobe of Canada's Laurentide ice sheet had undergone a series of 'binge-purge' cycles. As the ice cap thickened (binge), heat from beneath eventually led to basal melting triggering a collapse (purge) which launched an armada of icebergs into the Atlantic. These bergs melted as they drifted across the Atlantic. As they melted, they released debris. A few icebergs must have reached as far as France. The time between these purges was about 7 thousand years. The melt water from each armada shut down the conveyor.

I was so captivated by these debris layers that I named them Heinrich events after the person who discovered them. I was pretty much alone in this view for his debris layers initially received almost no attention. George Denton did, however, share my enthusiasm. In order to make sure these layers were recognized by the broader community, I decided that George and I should make a presentation to a group called Spec Map. Supported by a large grant from the National Science Foundation, its purpose was to compare the frequency spectra of a wide range of well-dated climate records for the last half-million years. The hope was that the leads and lags in among these records would guide them to physics governing glacial cycles.

So we invited ourselves to a Spec Map meeting to be held in Edinburgh, Scotland. Not too eager for our spiel, we were scheduled for an after dinner hour following a long day of presentations. Each of us gave a twenty-minute talk. There were no questions, only yawns. The

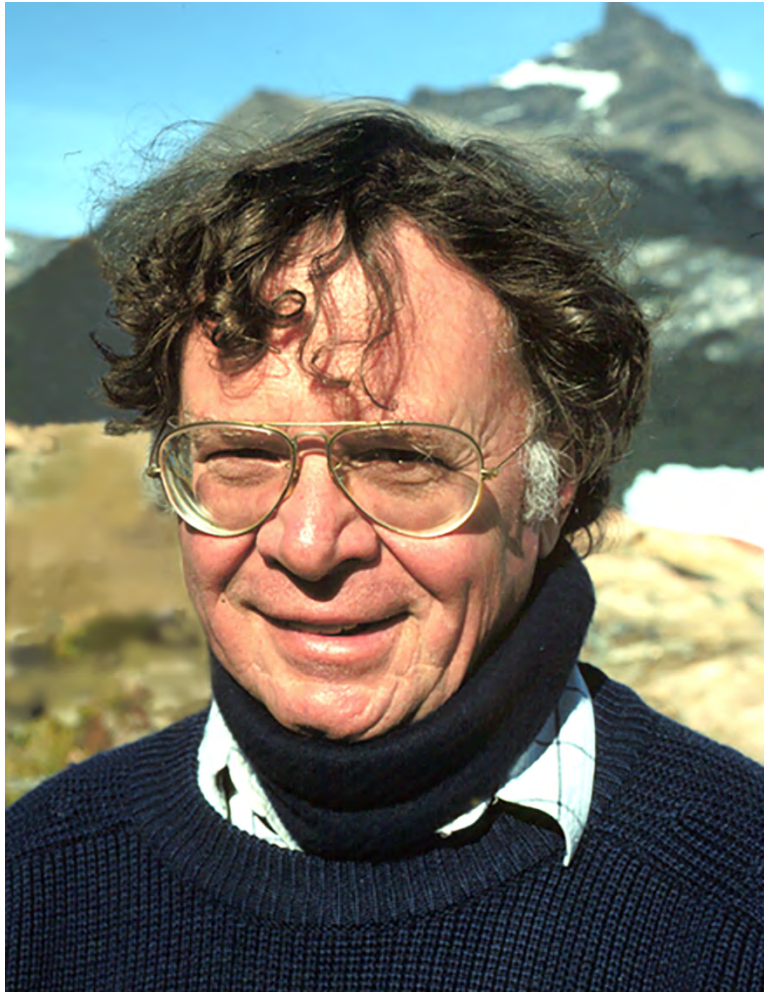
next morning, on our flight back to London, George expressed deep disappointment at the lack of interest. In order to cheer him up, I switched my flight to a Boston return. During our trip across the Atlantic, I eased George's pain by reminding him that all such first order paradigm shifts were initially resisted by the mainstream. I predicted that it could take as long as five years before the excitement of abrupt climate change caught on. And, once it did, it would become the rage. Further, it would lead us to the objective that Spec Map was chasing. Patience, George!

A turning point came in 2002, when Lands' End owner Gary Comer adopted some of us interested in abrupt-climate change research. Among many other things, he offered the use of his yacht, *Turmoil*, as a base for studies of the Younger Dryas record in Greenland. Spearheaded by George Denton and Tom Lowell, the idea was to determine the magnitude of the snowline lowering in the mountain glaciers surrounding Scoresby Sund (half way up the east coast of Greenland). The result was a demonstration that the summer warming at the end of the Younger Dryas could have been no more than about 5°C. This created a big problem, for based on measurements of nitrogen isotopes in the air trapped in the ice core from the summit of the Greenland cap, Jeff Severinghaus, a professor at U.C., San Diego, had shown that the magnitude of the mean annual warming at the end of the Younger Dryas was about 15°C. Why the large difference? It soon dawned on us that since the ice core recorded the mean annual temperature and snowlines the summer temperature, the explanation must be that winter temperature must have been extremely low during the Younger Dryas. Hence, it led to a major discovery. Seasonality was the key. Clearly the answer had to be that the Y.D. winters were a whopping 25 or so degrees colder. This led to the realization that during times when deep-water formation in the northern Atlantic was shut down, winter sea ice extended far to the south (i.e., perhaps as far as Ireland). Ice cover prevents ocean heat from escaping to the atmosphere and it also reflects sunshine back to space. Under these conditions, the climate in Norway would have resembled that in present day Siberia: fearfully cold winters and relatively warm summers. This finding opened up the understanding as to why these abrupt changes show up in records across the entire planet. They caused shifts in the latitude of the thermal equator. These shifts explained why both

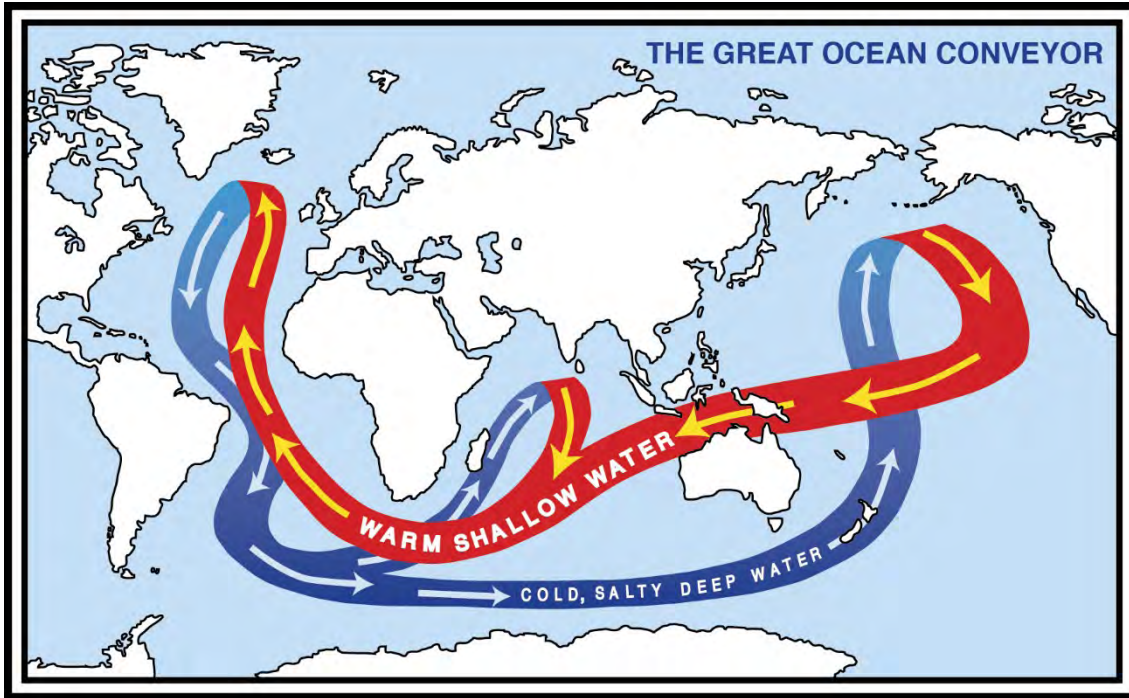
Dansgaard Oeschger and Heinrich events appeared so prominently in records influenced by precipitation, i.e., the ^{18}O to ^{16}O ratios in stalagmites, the size of closed basin lakes, and the contribution of river-borne debris to deep sea sediments. The results clearly demonstrate that the latitude of the world's rain belts is tied to that of the thermal equator. Hence, at times when the northern Atlantic was covered with massive sea ice, the thermal equator was pushed to the south and when the ice disappeared, it moved back to the north.

The best documented of these switches is the one that occurred 14,600 years ago. Before this time, as the result of the most recent Heinrich purge, the deep-water formation in the northern Atlantic was shut down and winter sea ice cover greatly expanded, pushing the thermal equator to the south. The consequences were spectacular. Closed basin lakes in the Great Basin of the western U.S. swelled by tenfold in size. The Chinese monsoons weakened. Amazonia shifted to the south and in Equatorial Africa, Lake Victoria dried up. Then 14,600 years ago, when the Atlantic's conveyor turned back on, expanded winter sea ice disappeared. The Great Basin lakes shrank, China's monsoons strengthened, Amazonia moved back to the north and Lake Victoria came back to life.

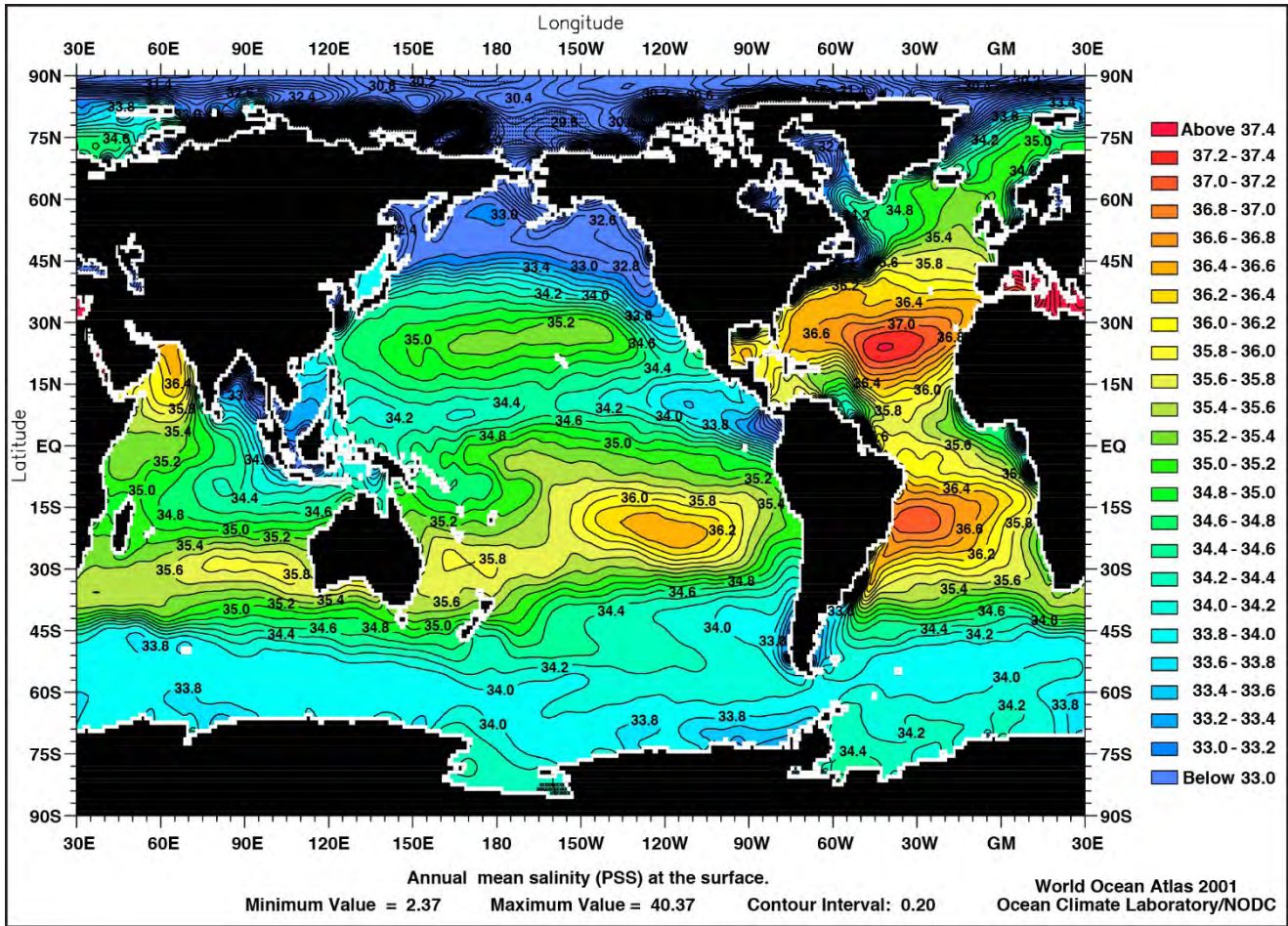
Aaron Putnam, once my postdoctoral fellow and now an a professor at the University of Maine, and I have a paper (in press) which suggests that something similar to what happened 14,600 years ago may be in progress today. The reason is that there is a large hemispheric difference in the extent of fossil fuel- CO_2 -induced global warming. Since 1950, the lands surrounding the Arctic have warmed by 1.8°C while the Southern Ocean has warmed by only about 0.3°C . If the rain belts were to react as they did 14.6 kyrs ago, then we will experience similar precipitation shifts. There has been a pronounced drying in the western U.S. and also on Bolivia's Altiplano. However, it is too soon to assign the cause of these changes for climate undergoes swings on decadal time scales. Hence, the rainfall changes we are seeing could be natural rather than the result of CO_2 warming. Time will tell.



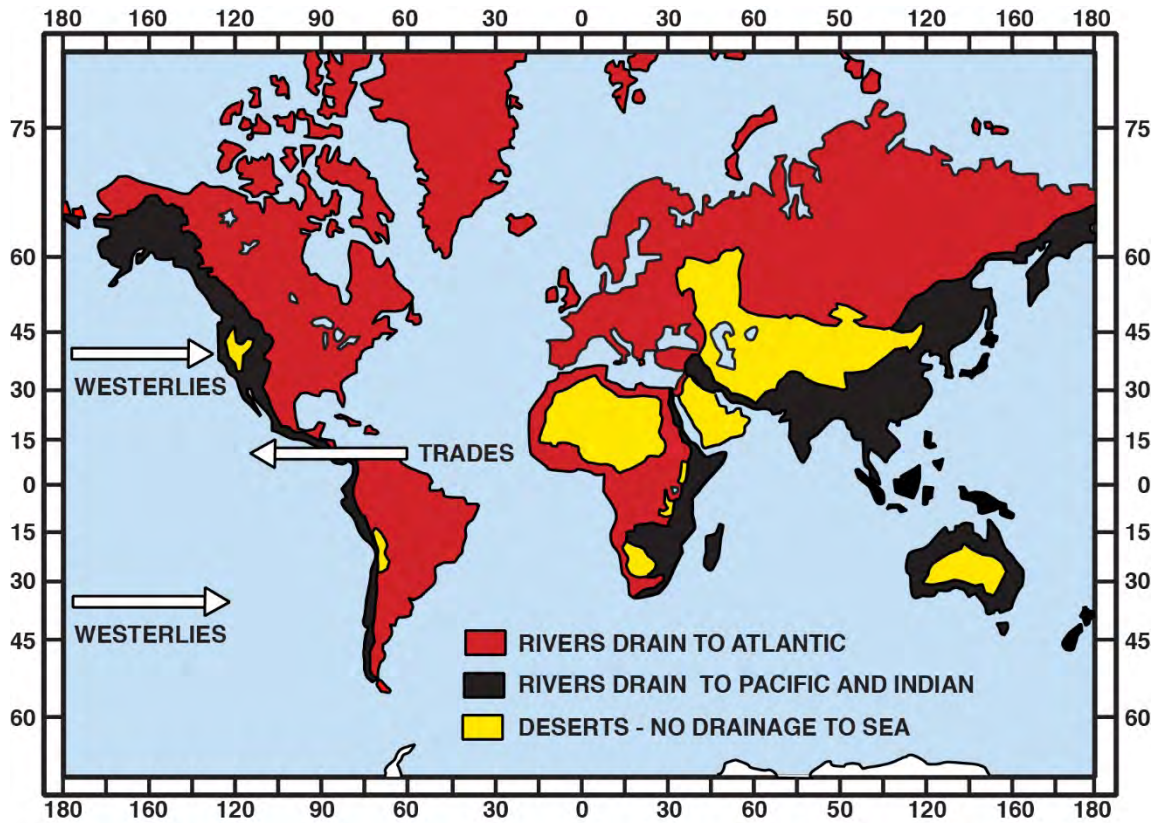
A picture of me at age 45 taken in the southern Andes by Steven Porter, one of the participants in our 1987 field trip.



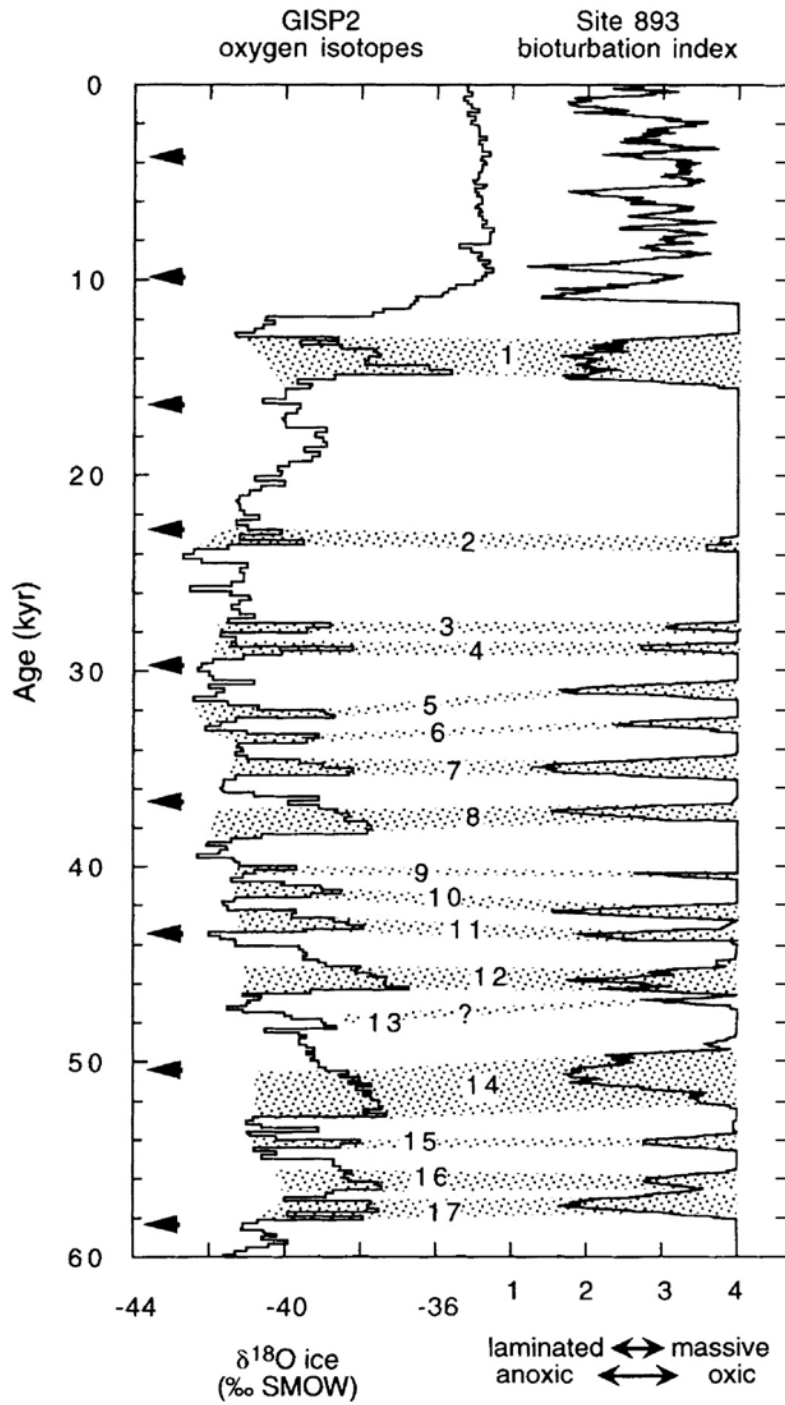
Cartoon depicting the global loop in the ocean's thermohaline circulation. It appeared in *Natural History Magazine* in 1987.



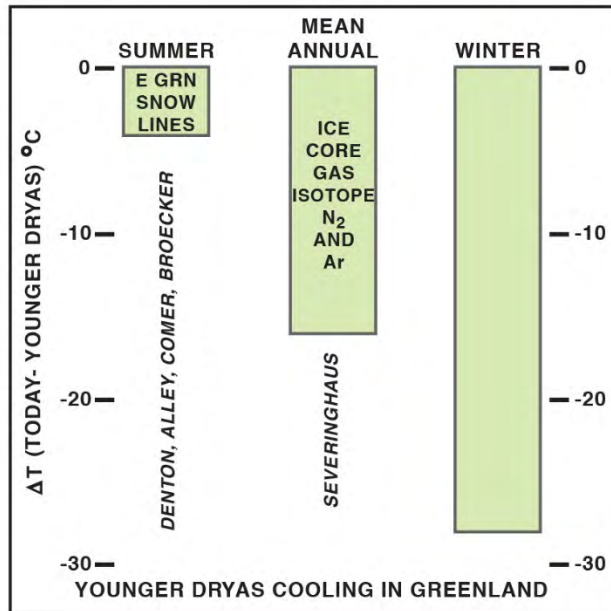
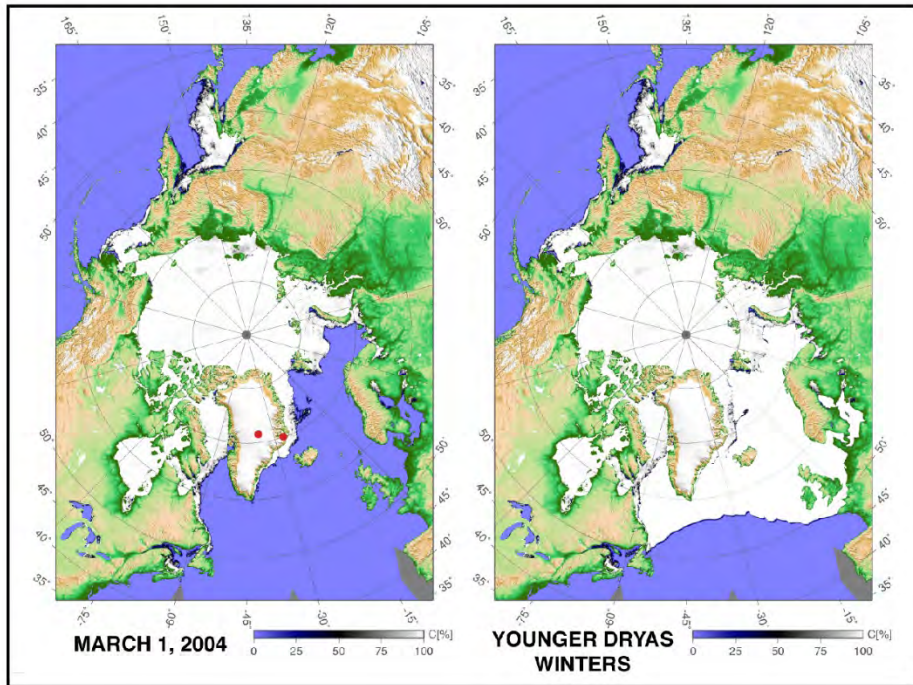
Map depicting the salinity of surface ocean water. Note that waters in the northern Atlantic are saltier than those in the northern Pacific.



Interocean water-vapor transport: The trade winds carry water vapor from the Atlantic to the Pacific across low elevation Panama. The American Western Cordillera prevents the westerlies from carrying water vapor from the Pacific to the Atlantic.



Comparison of the oxygen isotope record for Greenland ice with the bioturbation record for Santa Barbara Basin sediment. The former is a proxy for temperature and the latter for deep-water O₂ content.



The comparison of Younger-Dryas summer cooling temperature based on snowline lowering in the mountains for eastern Greenland with mean-annual cooling based on the isotopic composition of N₂ trapped in Summit Greenland ice. In order to explain the difference requires extremely cold Y.D. winter temperatures. This cooling is driven by a major expansion of winter sea ice.

References

- Broecker, W.S., D. Peteet and D. Rind (1985), Does the ocean-atmosphere have more than one stable mode of operation, *Nature*, 315, 21-25
- Broecker, W.S. (1987), Commentary, Unpleasant surprises in the greenhouse? *Nature*, 328, 123-126.
- Broecker, W.S. (1987), The Biggest Chill, *Natural History Magazine*, 74-82.
- Broecker, W.S., and G.H. Denton (1989), The role of ocean-atmosphere reorganizations in glacial cycles, *Geochimica et Cosmochimica Acta*, 53, 2465-2501.
- Broecker, W.S. (1991), The Great Ocean Conveyor, *Oceanography*, 4, 79-89.
- Broecker, W.S. (1994), Massive iceberg discharges as triggers for global climate change, *Nature*, 372, 421-424.
- Zaucker, F., T.F. Stocker, and W.S. Broecker (1994), Atmospheric freshwater fluxes and their effect on the global thermohaline circulation, *J. Geophys Res.*, Special Issue on North Atlantic Deep Water Formation: Observ. and Modeling, 99, 12,443-12,457.
- Denton, G.H., R.B. Alley, G.C. Comer, and W.S. Broecker (2005), The Role of Seasonality in Abrupt Climate Change, *Quaternary Science Reviews*, 24, 1159-1182.
- Broecker, Wally, and Aaron Putnam (2017), Man-induced changes in the distribution of rainfall, *Science Advances*.

Chapter 14

Paleo Ventilation Rates

During the late 1970s in my course on paleoclimate, I mentioned the possibility of using the radiocarbon age difference between co-existing benthic and planktic foram shells as a way to assess the rate of deep ocean ventilation during glacial time. But at the time this was just a dream for it couldn't be done. As foram shells weigh about 30 micrograms, in order to get the 3 grams of CaCO₃ required for ¹⁴C measurements would require 100,000 of these microscopic shells. And as they would have to be handpicked, doing this was unthinkable.

Then in the early 1980s, rumors began to circulate that it might be possible to make ¹⁴C measurements by counting atoms rather than by counting beta emissions. A huge advantage for this new method would reduce the required sample size by at least a factor of 1000. Suddenly the dream could become a reality, for it is easy to pick 100 foraminifera shells.

Checking into this, I found that my friend Hans Oeschger, a physicist in Bern, Switzerland had teamed up with Willy Wolfli in Zurich to do atom counting. The samples would be prepared in Bern and the measurements made in Zurich. So I called Hans and suggested that we work together to get age differences between benthic and planktic foraminifera. He agreed but said he needed an extra hand in the sample preparation lab but lacked funds. I agreed to send someone whose salary was paid from my Lamont-Doherty grants. One of our technicians, an adventurous sort named Nancy Ragano, offered to spend a year or two in Bern.

As no one in our geochemistry group was expert in identifying benthic foraminifera shells, Allen Mix, a graduate student in marine geology who was working on his PhD with Bill Ruddiman, offered to help. I should mention that, on average, there is only one benthic shell for every hundred or so planktic shells, so it was necessary to pick all the benthics regardless of species. As for planktics, each species has its own depth habitat, so we chose *G. sacculifer*. It is abundant and lives in the surface-mixed layer.

I should also mention that the radiocarbon measurements made as part of the GEOSECS program had just become available allowing us to calculate apparent age differences between

surface and deep waters in today's ocean. The complication introduced by the H-bomb radiocarbon in surface water was overcome by doing ^{14}C analyses on coral and shells formed before these tests were conducted.

In 1984, I attended a conference held in Zurich. It focused on the use of high energy accelerators to measure not only ^{14}C but also other radioisotopes produced by cosmic rays. After the meeting, I went to Bern to see how Nancy Ragano was doing. We went to dinner together in the Old Town and were seated at a table for four along with two elderly Swiss gentlemen. They conversed in their language and we in ours. Nancy and I finished first and were about to leave when one of the gentlemen said, "Don't leave. The night is young. Why don't you share a bottle of wine with us?" As we drank, they peppered us with questions, in English. In answer to who I was, I said "her father." Pressed further, I told them that I was visiting from New York and was flying back the next day. Nancy told them that she worked in the university physics department. When asked her last name, she said Andree (instead of Ragano). After we left, I asked her why Andree (the last name of Michael, the graduate student she worked with) and she said she had become uneasy with the nosiness of our table mates.

Sure enough, two weeks later, Oeschger's Administrator, Frau Reisen received a call from someone asking to speak with Nancy Andree. Big trouble. From the beginning Frau Reisen had been uneasy about the arrangement Hans and I had made. The phone call led her to believe that the arrangement was designed to facilitate a romance between Michael and Nancy. It took much talk to convince Reisen otherwise.

When Allen Mix finished his PhD, he secured a position at Oregon State University. We agreed to split the ^{14}C measurements on foraminifera shells. I would continue with the benthic-planktic pairs and he would use the ^{14}C to C gradient in the upper ocean generated by the invasion into the ocean of hydrogen bomb ^{14}C -tagged CO_2 to determine the water depth at which various organisms calcified. Our first try at this involved pteropods. Vicky Fabrei at the University of California, Santa Barbara agreed to provide us with samples she had collected from sediment traps. When the first of these was analyzed in Zurich, it had an enormous excess of ^{14}C .

Wolfli howled that we had contaminated his lab (and Oeschger's as well). He banned us from sending anymore samples. After a couple of weeks of running blanks, Wolfli quieted down. He agreed to accept samples for benthic-planktic age differences but not those from sediment traps. A blow to Alan Mix.

It was years later that Vicky figured out how her pteropods had been so badly contaminated with ^{14}C . She had inherited a refrigerator once used by marine biologists. It turned out they had used highly-enriched radiocarbon for plankton growth experiments. As sold, enriched radiocarbon bicarbonate has a ^{14}C to C ratio 10^{11} times larger than that in atmospheric CO_2 . I much regret that Allen Mix paid a price for contamination of samples he never touched.

As a means of evaluating the reliability of our benthic-planktic age differences, we made measurements on a number of planktic species. It turned out that *G. sacculifer* and *G. ruber* (species which lived in the surface-mixed layer) often had ages younger than those for *P. obliquiloculata* and *N. dutertrei* (species which lived in the thermocline). For small age differences one could call on the decrease in ^{14}C to C ratio with water depth. But, often the differences were larger than could be explained in this way. It was Steve Barker (a British postdoctoral fellow working with me) who put his finger on the cause. He attributed it to the greater susceptibility of the surface-dwelling species to dissolution-induced fragmentation when compared with their thermocline-dwelling brothers. As worms burrowing in deep-sea sediment homogenize the upper 8 or so centimeters, for a sediment accumulation rate of 2 cm per kyr, the residence time of entities in this layer averages about 4000 years. For a sediment with an accumulation rate of 10 cm/kyr, the residence time would be only 800 years. Steve reasoned that the unbroken shells would have younger ages, on average, than the shell fragments. The reason was that the longer a shell remained in the mixed layer, the greater the likelihood of breakage. So he predicted the offsets between the age of surface and thermocline-dwelling species would be larger in slowly accumulating sediments, than in rapidly accumulating sediments. It would also depend on the degree of undersaturation of the water which bathed the sediment. Looked at in this way, the data we had obtained for equatorial Pacific cores suddenly made sense. The higher

the sedimentation rate and the shallower the water depth, the smaller the planktic to planktic age offsets and hence, the more reliable the benthic-planktic age differences. In recognition of Steve's sharp thinking, Elizabeth Clark and I wrote a paper in which we called his finding the "Barker Effect."

Once we eliminated those results impacted by the Barker-effect, the picture became clear. The results showed that from 1.9 km to 4.4 km water depth in the equatorial Pacific, the benthic-planktic age differences for samples from the last glacial maximum were not significantly different than those obtained for water samples taken during the GEOSECS survey. In a sense we would have been happier were there a difference, for then we would have been challenged to figure out why. In fact, we did have a compelling reason to argue that the age differences should have been larger during the last glacial maximum. It has to do with the 15 percent decline in the ^{14}C to C ratio in the atmosphere which began at the onset of deglaciation, i.e. (17.8 kyrs ago) and the beginning of the Bølling Allerød (14.6 kyrs ago). In recognition of this large drop, I coined the name Mystery Interval.

The obvious explanation is that the ^{14}C production by cosmic rays dropped during this time interval. As the primary cosmic ray protons approach the Earth, they are deflected by its magnetic field. Hence, changes in the strength of this field change the extent of this deflection and hence, the number of these energetic particles that reach our atmosphere and produce ^{14}C . Although paleo proxies for the strength of the Earth's magnetic field are far from reliable, those who employ them conclude that the field has strengthened over the past 40 kyrs accounting for at least part of the decrease in the ^{14}C to C ratio in atmospheric CO_2 . However, our most reliable estimates come from the ^{10}Be record kept in polar ice cores. As this cosmogenic isotope is co-produced with ^{14}C , its accumulation ratio in ice serves as a proxy for radiocarbon. But the ice core record shows no significant decrease in ^{10}Be influx during the 17.8 to 14.6 kyr time interval. However, the fact that the drop in the ^{14}C to C ratio in the atmosphere begins at exactly the same time as the onset of post-glacial warming and rise in atmospheric CO_2 content suggests that it

isn't the flux of cosmic rays that changed. There is no way that a climate change at the Earth's surface could impact the strength of magnetic dynamo in its core. Or is there?

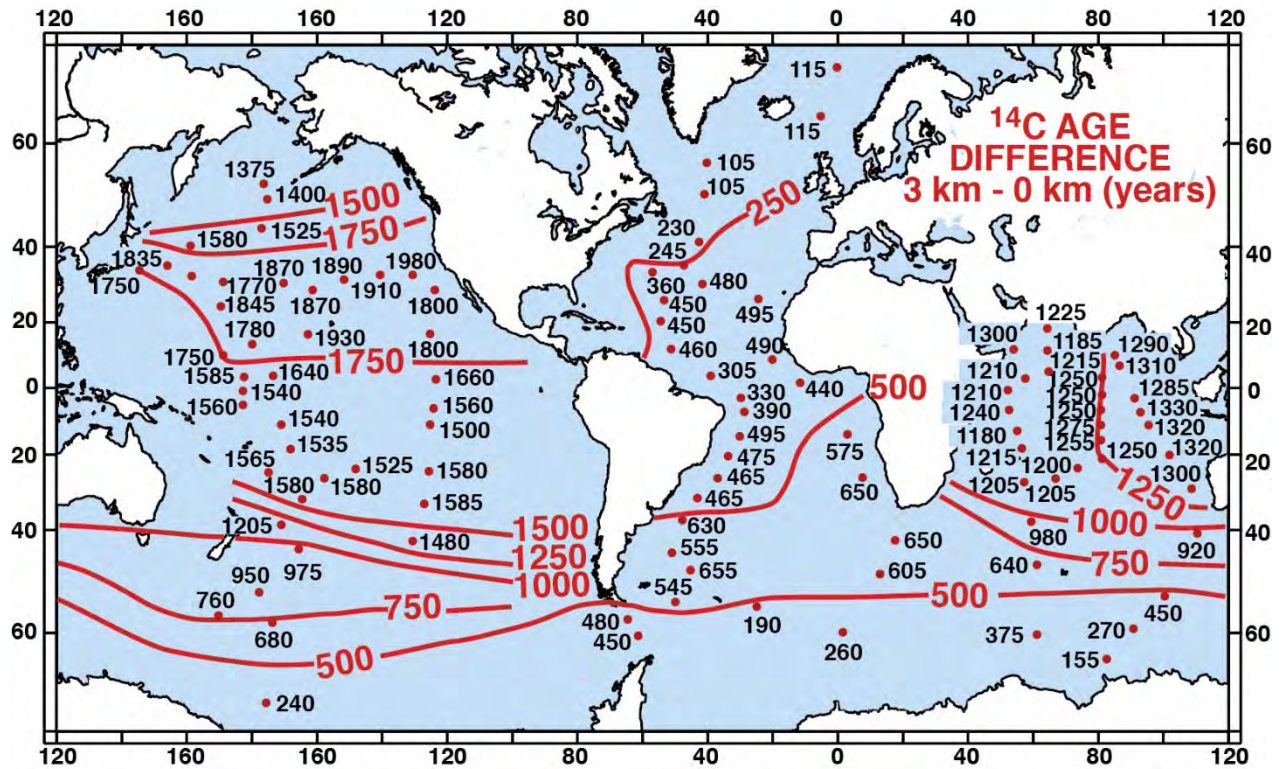
Another way to explain this large drop in atmospheric ^{14}C to C ratio is to call on a change in the isolation time of water in the ocean interior. For a given production rate the larger the isolation time, the larger the atmosphere's ^{14}C to C ratio. During the 18 kyrs since the end of the glacial maximum, the ^{14}C to C ratio in the atmosphere has decreased by 35 percent. Fifteen percent of this drop occurred during the Mystery Interval (3.2 kyrs). Although 60 percent of the total decline could be explained by a gradual strengthening of the Earth's magnetic field. The 40 percent drop that occurred during the Mystery Interval seemingly cannot. It must have to do with the ocean.

Perhaps some portion of the deep ocean was isolated from the rest during the Last Glacial Maximum. If at the onset of deglaciation this isolation began to break down, mixing the ^{14}C -depleted water into the remainder of the ocean-atmosphere's reservoir would drawdown its ^{14}C to C ratio. However, the observation that the planktic-benthic age difference for the deep equatorial Pacific (1.9 to 4.4 kyr) didn't change between the LGM and today appears to rule out the isolation scenario as the explanation for the drop in atmosphere's ^{14}C to C ratio during the Mystery Interval.

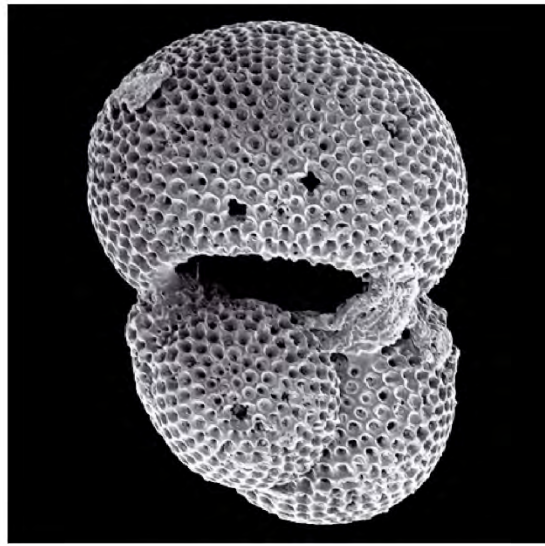
A simple scenario helps to understand this. Let's say some portion of the deep ocean was totally isolated from the rest of the ocean for the entire duration of glacial time (i.e., long enough for all its ^{14}C to decay away) and then beginning 17.8 kyrs ago it was mixed back into the whole. Were it to explain the Mystery Interval drop in the atmosphere's ^{14}C to C ratio, it would have to have occupied 15 percent of the ocean. Further, if the isolation time were only one ^{14}C half-life (i.e., 5800 years), then it would require 30 percent of the ocean. Seemingly, no matter how it was accomplished, it should show up in the benthic-planktic age differences for the deep equatorial Pacific Ocean. Not only does it not show up, but spot benthic-planktic age difference in the Atlantic and northern Pacific fail to show evidence in support of an ocean explanation. Others who have waded in on this problem share my frustration. After several decades of effort, we still

have no satisfactory explanation for the decline in atmospheric ^{14}C to C ratio during the Mystery Interval.

One explanation born of desperation comes to mind. As shown by David Lund, the flux of iron and manganese from the East Pacific Rise undergoes a dramatic rise during glacial terminations. Were this rise accompanied by the release of mantle CO_2 , then the ^{14}C to C ratio in the ocean would have been correspondingly reduced. However, the added carbon would have to have been largely in the form of bicarbonate ion. Otherwise it would have made a huge increase in the CO_2 content of the atmosphere. It would also have created a major CaCO_3 dissolution event in the deep sea sediment. Nice thought but no cigar.



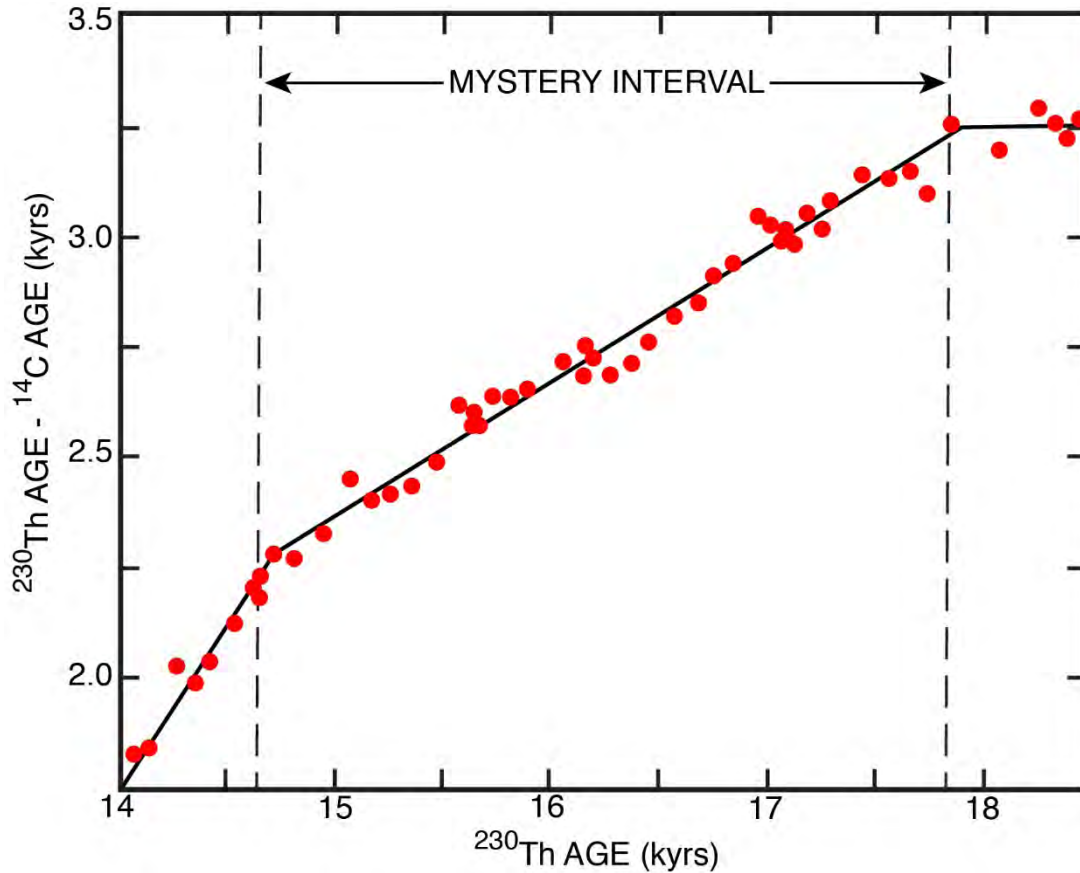
The apparent radiocarbon-age differences between water at 3000 meters and that in the surface-mixed layer as determined at stations occupied during the GEOSECS survey. Note that for the equatorial Pacific, this difference is about 1600 years.



On the left is a photo of a *Cibicides* shell (sea floor dweller) and on the right, photo of *G. sacculifer* (surface mixed-layer dweller).

Age difference between coexisting benthic (B) and planktic (P) foraminifera shells formed during the Last Glacial Maximum (~23 to 18 kyrs) for those free of the Barker effect. The average age difference for these 11 pairs is identical to that for today's ocean.

Latitude	Longitude	Depth km	Calendar Age kyrs	ΔB-P yrs
<i>Deep Equatorial Pacific</i>				
1°S	146°E	1.9		
	Broecker et al., 2004		21.5	1950 ± 220
			21.9	1640 ± 250
6°N	126°E	2.1		
	Broecker et al., 2004		19.1	1325 ± 200
			18.7	1170 ± 220
			19.6	1325 ± 200
1°N	130°E	2.8		
	Broecker et al., 2008		17.9	1790 ± 170
			18.6	1510 ± 120
			19.2	1700 ± 130
2°S	140°W	4.4		
	Broecker and Clark, 2010		17.2	1550 ± 300
			22.0	1500 ± 300
			24.2	<u>1700 ± 300</u>
			Mean	1575 ± 150



The differences between the ^{230}Th age and the ^{14}C age from for samples from a Hulu Cave stalagmite as a function of ^{230}Th age. The ^{14}C measurements were made by John Southon at the University of California, Irvine and the ^{230}Th measurements by Hai Cheng at the University of Minnesota. During the 3.2 kyrs duration of the Mystery Interval, the age difference decreased from 3.25 kyrs to 2.25 kyrs. This amounts to a 12.5 percent decrease in the atmosphere's ^{14}C to C ratio. One way to produce this drop would be to suddenly reduce the influx of cosmic rays by a whopping 40 percent. This explanation seems unlikely for many reasons. Rather, the drop must have been induced by either a redistribution of ^{14}C between the atmosphere and ocean or the addition of a large amount of ^{14}C bicarbonate.

References

- Broecker, W.S., A. Mix, M. Andree, and H. Oeschger (1984), Radiocarbon measurements on coexisting benthic and planktic foraminifera shells; potential for reconstructing ocean ventilation times over the past 20,000 years, In: *Proceedings of the Third Intl. Symp. on Accel. Mass Spectrometry*, Anderson, H.H., S.T. Picraux, eds., 331-339.
- Andree, M., J. Beer, H. Oeschger, W.S. Broecker, A. Mix, N. Ragano, P. O'Hara, G. Bonani, H. J. Hofmann, E. Morenzoni, M. Nesi, M. Suter, and W. Wolfli (1984), ^{14}C measurements on foraminifera of deep sea core V28-238 and their preliminary interpretation, In: *Proceedings of the Third Intl. Symp. on Accelerator Mass Spectrometry*, Anderson, H.H., S.T. Picraux, eds., 340-345.
- Andree, M., H. Oeschger, W.S. Broecker, N. Beavan, A. Mix, G. Bonani, H.J. Hofmann, E. Morenzoni, M. Nesi, M. Suter and W. Wolfli (1986), AMS radiocarbon dates on foraminifera from deep sea sediments, *Radiocarbon*, 28, 424-428.
- Andree, M., H. Oeschger, W. Broecker, N. Beavan, M. Klas, A. Mix, G. Bonani, M. Suter, W. Wolfli, T.H. Peng (1986), Limits on the ventilation rate for the deep ocean over the last 12,000 years, *Climate Dynamics*, 1, 53-62.
- Broecker, W.S., M. Andree, H. Oeschger, W. Wolfli, G. Bonani, M. Klas, A. Mix, and W. Curry (1988), Preliminary estimates of the radiocarbon age of deep water in the glacial ocean, *Paleoceanography*, 3, 659-669.
- Broecker, W.S., K. Matsumoto, E. Clark, I. Hajdas, and G. Bonani (1999), Radiocarbon age differences between coexisting foraminiferal species, *Paleoceanography*, 14, 431-436.
- Broecker, W.S. E. Clark, I. Hajdas, and G. Bonani (2004), Glacial ventilation rates for the deep Pacific Ocean, *Paleoceanography*, 19, PA2002, doi:10.1029/2003PA000974.
- Broecker, W.S., S. Barker, E. Clark, I. Hajdas, G. Bonani, and L. Stott (2004), Ventilation of glacial deep Pacific Ocean, *Science*, 306, 1169-1172.
- Broecker, W., S. Barker, E. Clark, I. Hajdas, and G. Bonani (2006), Anomalous radiocarbon ages for foraminifera shells, *Paleoceanography*, 21, PA2008, doi:10.1029/2005PA001212.

- Broecker, W., E. Clark, S. Barker, I. Hajdas, G. Bonani, and E. Moreno (2007), Radiocarbon age of late glacial deep water from the equatorial Pacific, *Paleoceanography*, 22, PA2206, doi:10.1029/2006PA001359.
- Barker, S., W. Broecker, E. Clark, and I. Hajdas (2007), Radiocarbon age offsets of foraminifera resulting from differential dissolution and fragmentation within the sedimentary bioturbated zone, *Paleoceanography*, 22, PA2205, doi:10.1029/2006PA001354.
- Broecker, W.S., E. Clark, and S. Barker (2008), Near constancy of the Pacific Ocean surface to mid-depth radiocarbon-age difference over the last 20 kyr, *Earth Planet. Sci. Lett.*, 274, 322-326, doi:10.1016/j.epsl.2008.07.035, 15.
- Broecker, W., and E. Clark (2011), Radiocarbon-age differences among coexisting planktic foraminifera shells: The Barker Effect, *Paleoceanography*, 26, PA2222, doi:10.1029/2011PA002116.

Chapter 15

Calcite Dissolution

Lamont-Doherty has the world's largest collection of marine piston cores. I once told a visitor that if he were to throw a dart at a world map and it hit an ocean basin, in all likelihood there would be at least one core in a circle of radius 100 miles from the dart. Further, as most of these cores were collected in the Ewing era (1960s and 1970s), this archive has been available to me during most of my career. Although over the years I have used this material in a wide range of projects, there has been one application that has repeatedly popped into focus. It involves proxies which have the potential to record changes in the deep ocean's carbonate ion content.

The changes I have been interested in are those related to glacial cycles and, in particular, the most recent of these cycles. The reason is that they offer clues regarding what drove the changes in atmospheric CO₂ content. One way this happens is if either the rate of input or the rate of withdrawal of CO₂ from the ocean-atmosphere reservoir changes. For example, the amount of carbon stored in the terrestrial biosphere (and in the soils in which plants are rooted) varies with climate. We know from the carbon isotope record kept by benthic foraminifera that the inventory of carbon in the reservoir was lower during times of glaciation than during times of interglaciation. This being the case, at the termination of each glacial cycle, CO₂ must have been removed from the ocean and stored as organic material on land. Such a withdrawal would lead to an increase in the carbonate ion content of ocean water and hence, reduce the extent of dissolution of CaCO₃ in the transition zone between foraminifera ooze (CaCO₃-rich) and red clays (CaCO₃-free).

Currently there is considerable interest in the relative contributions of two scenarios put forth to explain the glacial drawdown of the atmosphere's CO₂ content (280 to 185 ppm). The traditional scenario is that during times of glaciation, the ocean sucked CO₂ out of the atmosphere. However, recently a quite different scenario has been put forward. It postulates that during glacial time the release of CO₂ by volcanoes was greatly reduced. The cause of this

reduction was the buildup of ice on the continents. The weight of this ice raised the melting point of the rocks underlying volcanoes and in so doing, squelched melting.

The impact on calcite dissolution differs for the two scenarios. In the case of the ocean scenario, during glacial terminations CO_2 is released from the oceans creating an increase in carbonate ion and hence a preservation event. In the case of the volcano scenario, the opposite occurs. The release of pressure reactivates the volcanoes, adding CO_2 to the ocean. This creates a decrease in the carbonate ion and hence a dissolution event.

Questions of this type have led to the search for a proxy for dissolution extent. An obvious choice would be the CaCO_3 content of the sediment. Indeed it is used as a means of establishing past depths of the transition zone separating sediments which have lost little CaCO_3 to dissolution from those which have lost most of their CaCO_3 to dissolution. However in the case of glacial terminations (my interest) changes in the grain ratio of CaCO_3 to non CaCO_3 (i.e., silt and clay) confuse the situation.

Early on, people used the ratio of shell fragments to whole shells as an index of the extent of dissolution. The idea was that as the foraminifera shells dissolved, the links between their chambers weakened causing them to fall apart. As one can imagine, this method is labor intensive and is subject to a number of biases. This being the case, my colleague, Elizabeth Clark, and I sought a better one.

For some reason that I have forgotten, we stumbled upon one. It involved the ratio of CaCO_3 retained by a 63-micron sieve to that which passed through the sieve. We found that for sediments that had lost little CaCO_3 to dissolution this fraction was 50 ± 7 percent. As the extent of dissolution increased, this fraction went steadily down. This method was fast and easy. It involved sieving and weighing the two fractions, then measuring the CaCO_3 of the fine fraction (which contained all of the non CaCO_3).

During the time we were using this method, we thought the reason for this decrease was that the foram fragments were passing through the sieve. It was years later that Clara Chiu, a postdoctoral fellow working with me, discovered the primary reason for the drop. Elizabeth and I

had given little thought to coccoliths which make up about half the rain of calcite to the sea floor. Clara made a separation using a 20-micron sieve and showed that only coccoliths (and clay & silt) were able to pass through. She then compared results for an Ontong Java Plateau core from 2.3 km depth (little dissolution) with one from 4.0 km depth (much dissolution). To our surprise she found that although seventy percent of the foraminifer CaCO_3 had been lost from the deeper core, no more than seven percent of the coccolith carbonate had dissolved. Had we known this at the time we were using the 63-micron method, we would have switched to a 20-micron sieve. Using shallower cores in the same area as a reference, we could then have calculated the amount of CaCO_3 lost.

However, as we didn't realize that coccoliths were highly resistant to dissolution, we were lured into yet another method. At an AGU meeting, Pat Lohmann, a marine geologist at Woods Hole Oceanographic, took us aside and suggested that we switch to his shell-weight method. It involved picking 40 whole shells of a single foraminifera species from the 355 to 415 micron-size class and weighing them. Elizabeth took the plunge, and over a year or so, generated a host of results. By and large, they reproduced the features we had seen in our 63-micron results. But overall it wasn't an improvement.

Then, suddenly the whole ball game changed. Jimin Yu, a graduate student in Harry Elderfield's laboratory at Cambridge University, discovered a proxy for carbonate ion itself. It involved measuring the concentration of the element boron in benthic foram shells. He found that if he stuck with a single species, the concentration of boron decreased with the extent of calcite undersaturation. He noted that although the percentage change in boron content per unit supersaturation was similar, for two other benthic species, the absolute boron contents were much lower. He chose *Cibicides* because it is more common. Also, it has the highest boron content allowing the measurements to be made on only five shells.

Upon completing his PhD at Cambridge, Jimin joined me as a postdoctoral fellow. He currently is a research scientist at the Australian National University where he continues his

boron measurements. His proxy has proven to be not only highly precise, but unlike any other marine proxy now in use, it has not been shown to have ‘flaws’.

The events surrounding Jimin Yu’s arrival in New York are engraved in my mind. My wife Elizabeth and I drove to Newark Airport to pick him up. As we were a bit late, instead of parking, I pulled up to the terminal and Elizabeth got out to see if Jimin was already there. She dashed inside and a minute later came back out holding her head. In her rush she had run smack into a glass wall creating one of the worst black eyes I have ever seen. Frustrated, we parked the car and then found that Jimin’s flight had been diverted to another terminal. We rushed there only to find that his flight was delayed. We waited and waited. Finally, with Jimin in tow, we returned to Manhattan to the apartment of Sidney and Gary Hemming. As they were away, he was to stay there until he could move into his Columbia apartment. Alas, the doorman didn’t know anything about this plan. As our frustration grew to new heights, a second building employee arrived and showed Jimin to the apartment. By that time, it was well after midnight.

Jimin was married. His wife, Jingbo Wang had also obtained a PhD at Cambridge, in geophysics. Try as we may, we could not find a postdoc for her at Lamont or elsewhere in the New York area. Eventually she took matters into her own hands and landed a postdoctoral position at Livermore National Laboratory. She and their two very young children moved to California. After a few months Jimin realized that this arrangement wasn’t working, so he too moved to Livermore where he finished his postdoctoral fellowship. The situation they faced is all too common. It’s often called the two-body problem at universities.

So what have we learned from this foram dissolution quest? In our down-core records from the abyssal Atlantic, one thing stood out like a sore thumb. There was a profound dissolution event centered at 65,000 years ago (MIS stage 4). It was only when Yu did B/Ca measurements on the same core on which we had done both shell weights and 63-micron fractions, did it become clear what this dip in carbonate ion concentration was trying to tell us. Not only were his records less noisy, but he also did ^{13}C to ^{12}C measurements on the same shells. The results were eye opening.

In today's deep Atlantic, the $\text{CO}_3^{=}$ ion concentration is nearly constant with water depth. But based on shell weights and 63-micron fraction data, during the time of the last glacial maximum, there appears to have been a decrease with depth. I asked Jimin to check this out on a core from 3.4 km water depth on the Ceara Rise (off Brazil). He had already obtained a record from a core in the Caribbean Sea. As the deep Caribbean is 'ventilated' by the inflow over a 1.8 km-depth sill, this core provides a record of the carbonate ion content at 1.8 km depth in the open Atlantic. Hence, by comparing the Caribbean record with the Ceara Rise record we could check whether there was a decrease in carbonate ion content with water depth. Jimin went a step further and obtained a detailed record back 150,000 years (i.e., to the time of the penultimate glaciation).

What he found was amazing. Not only did he confirm the drop in carbonate ion content 65,000 years in the Ceara Rise core, he showed that it was matched by a small increase in the carbonate ion content in the Caribbean core. In addition, he found a similar feature during the last glacial maximum (centered at 22,000 years). Clearly during times of peak glacial cold, the deep Atlantic was strongly stratified.

Jimin went on to show that a similar pattern was seen for the carbon isotope ratios. Matching the carbonate ion minima at 65,000 and 22,000 years ago were minima in the ^{13}C to ^{12}C ratio. This raised the question as to what created this stratification. Two possibilities came to mind. One is that the inflow of abyssal water from the Southern Ocean (today's low ^{13}C , low $\text{CO}_3^{=}$ Antarctic Bottom Water) was enhanced to the point where it filled something like half of the deep Atlantic. As today this thin layer has a carbonate ion content and a carbon isotope ratio which are identical to those for the water flowing into the abyssal Pacific, it is reasonable to postulate that this was also the case during glacial times. And, of course, we know the composition of water entering the deep Pacific during these times of peak cold from measurements Jimin made on benthic forams from glacial-age sediments. Another way to generate the decreases in carbonate ion content and carbon isotope ratio would be to increase the rain of particulate organic material into the abyssal Atlantic. The respiration CO_2 released by the

oxidation of this organic matter would lower both the carbonate ion content and the carbon isotope ratio.

So, which did the job? The ratio of the magnitude of the carbonate ion change to that of the carbon isotope ratio at 63 kyrs and 20 kyrs provides the answer. It turns out that this ratio falls between those expected if it were the result of increased respiration and that expected if it were the result of the influx of Southern Ocean water. About one third of the change appears to have been the result of increased inflow of Pacific-like water and two thirds to an increased respiration contribution to deep water formed in the northern Atlantic.

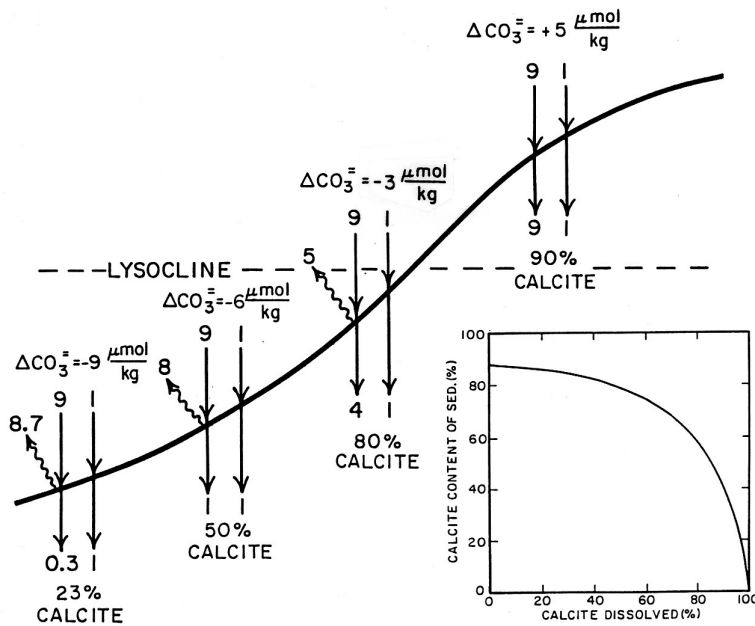
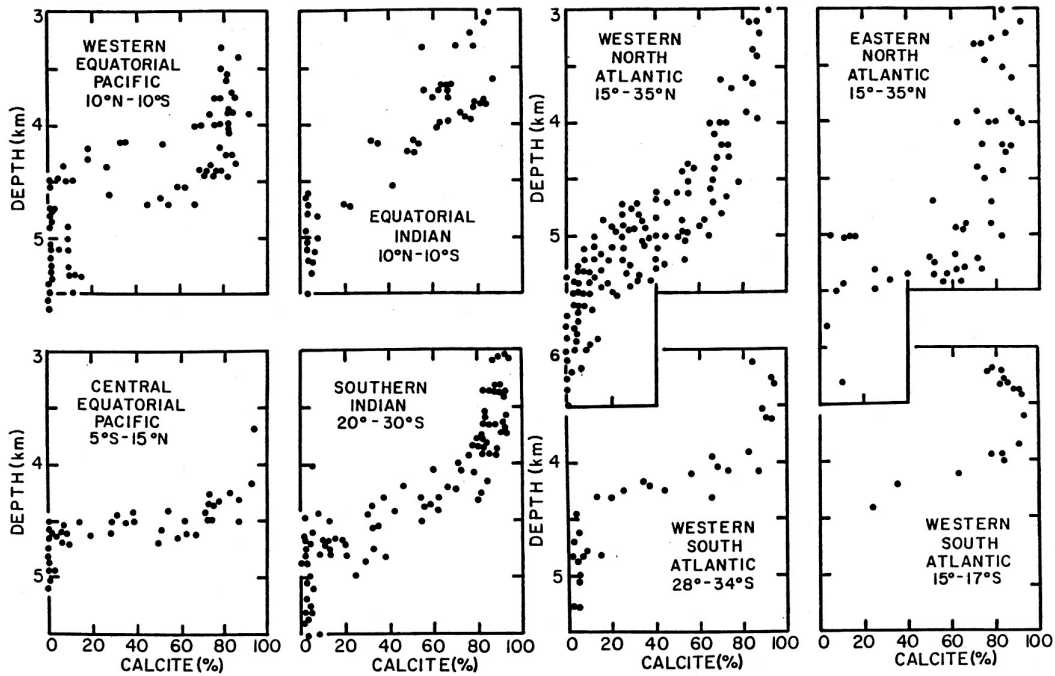
The next step is to ponder whether Jimin's method can help us distinguish between the two ways to explain the downward ramp in atmospheric CO₂ content which characterize each glacial cycle. Namely, is it suppression of the CO₂ supply related to the shutdown of volcanoes or is it uptake by the ocean? We have already seen how Jimin's method could be a help. One scenario calls for a CaCO₃ dissolution event during terminations and the other for a preservation event during terminations. However, this approach is complicated by the regrowth of forests during the same time interval. It would produce a preservation event. As the records in hand show neither a prominent dissolution event nor a prominent preservation event, one could postulate that the CO₂ added by the upsurge of volcanic activity is being partially balanced by the removal of CO₂ by forest regrowth. However, as the CO₂ content of the atmosphere rose during this time interval, forest compensation cannot by itself be the answer.

One important thing hasn't been mentioned. It has to do with the recovery time from such a perturbation. A thought experiment proves useful. Imagine that the carbonate ion content of the deep ocean were to be given a short-term push either up or down. Such a push would trigger a feedback loop causing the carbonate ion content to move back toward its initial level. The reason is that the push would create an imbalance between the burial of CaCO₃ and the supply of ingredients for the manufacture of CaCO₃. As a consequence, the carbonate ion content of deep water would move back toward its steady state value. The average carbonate ion content of deep ocean water (~100 μmol/liter) is about one-twentieth the concentration of

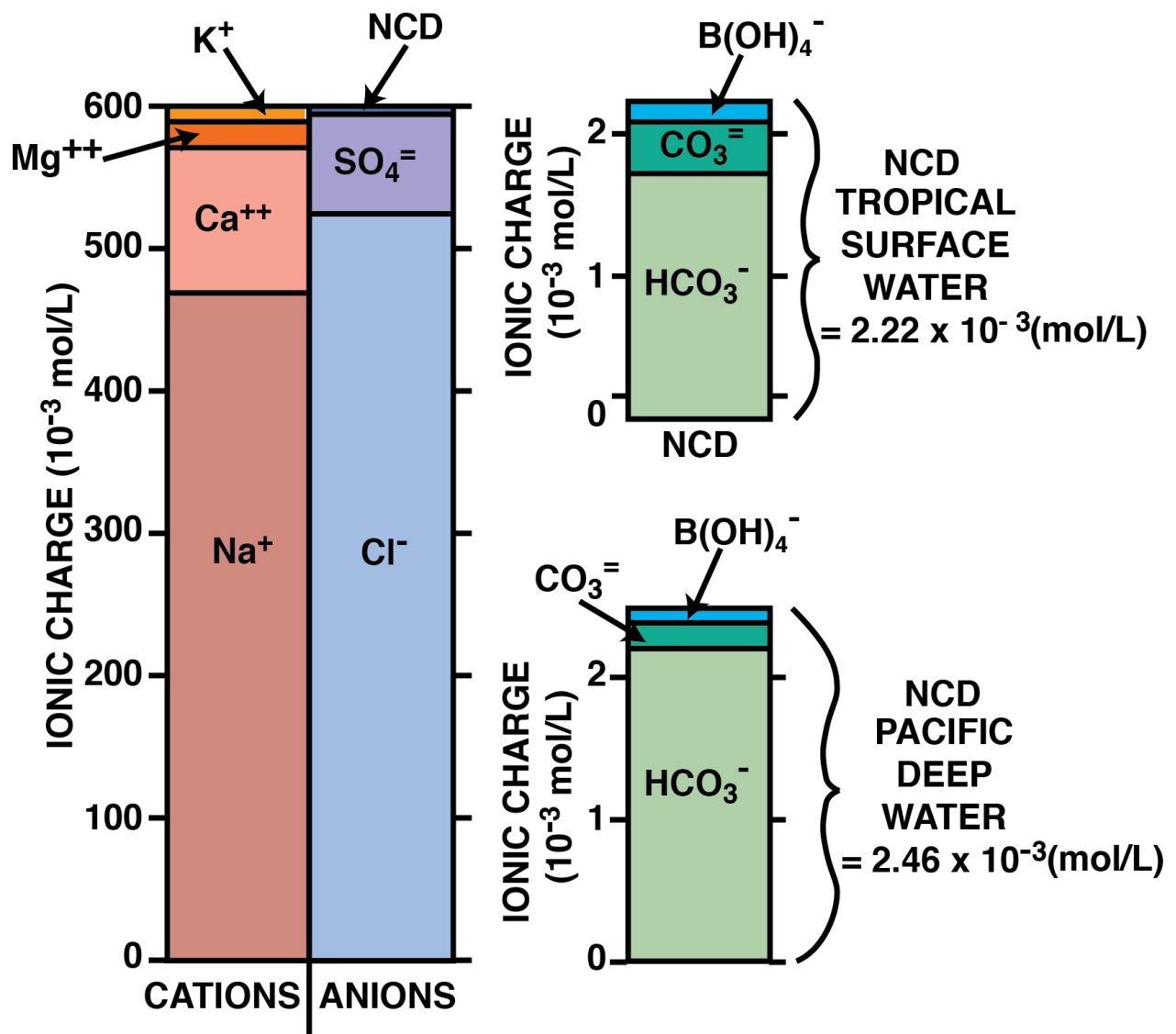
bicarbonate ($\sim 2000 \mu\text{mol/liter}$). Hence, the recovery time for an instantaneous perturbation of $\text{CO}_3^{=}$ content of the ocean should be about one-twentieth the replacement time of inorganic carbon in the ocean. As the replacement time is about 150,000 years, the recovery time from such an impulse would be 7500 years. Although short with respect to the length of a glacial cycle, the recovery time is comparable to the duration of terminations. This being the case, the imprints of forest regrowth and the resumption of CO_2 release by volcanoes would overlap.

One last thing about Jimin Yu. Soon after his arrival at Lamont, he spotted a bushy-tailed, tree climbing rodent that he had never seen before. He looked it up on the Web and proudly told me that he had seen a 'squeer-ule'. We chuckled, realizing that he had seen a squirrel. That pronunciation sticks with us.

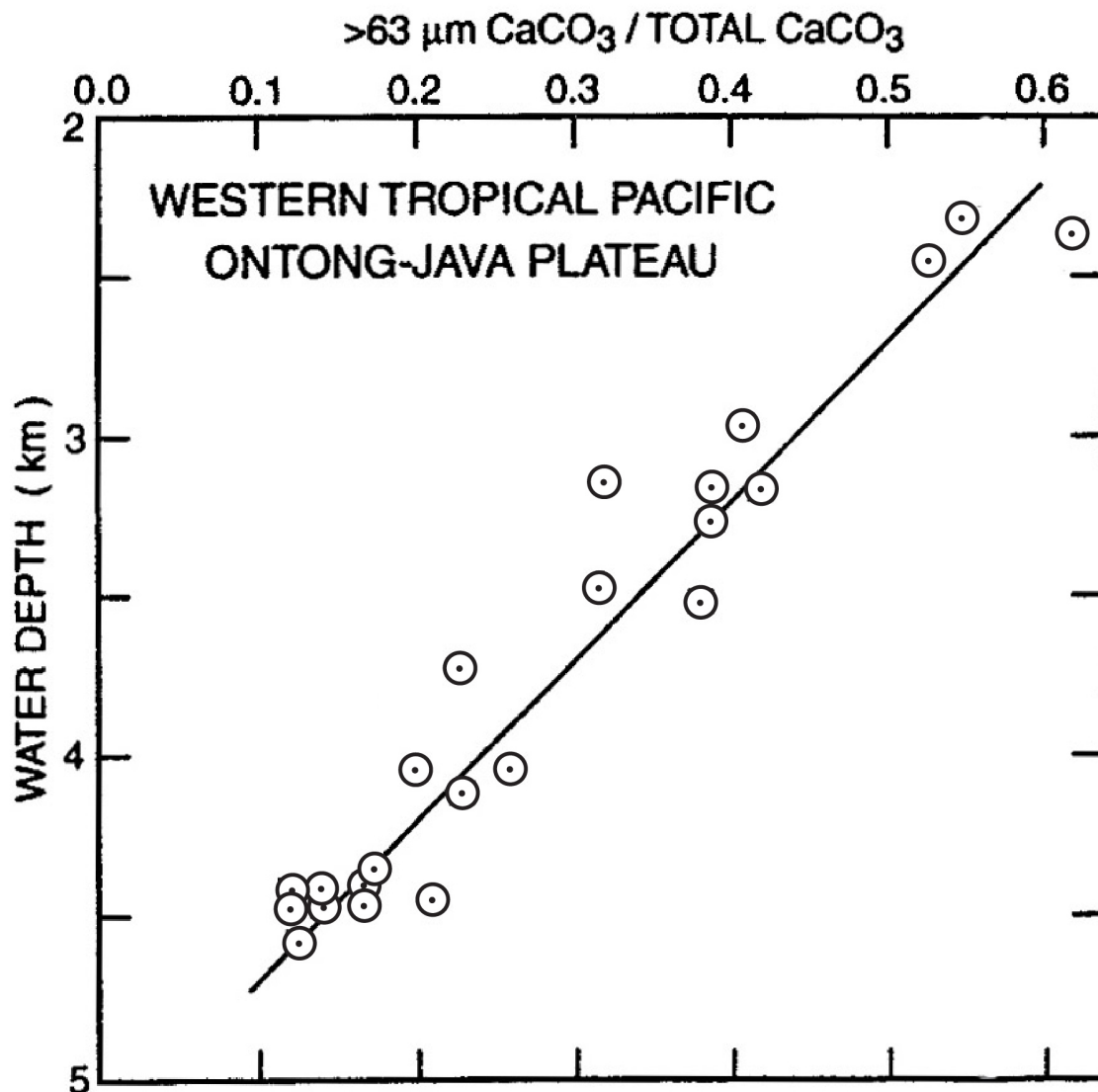
INFLUENCE OF DISSOLUTION ON CaCO_3 CONTENT OF SEDIMENTS



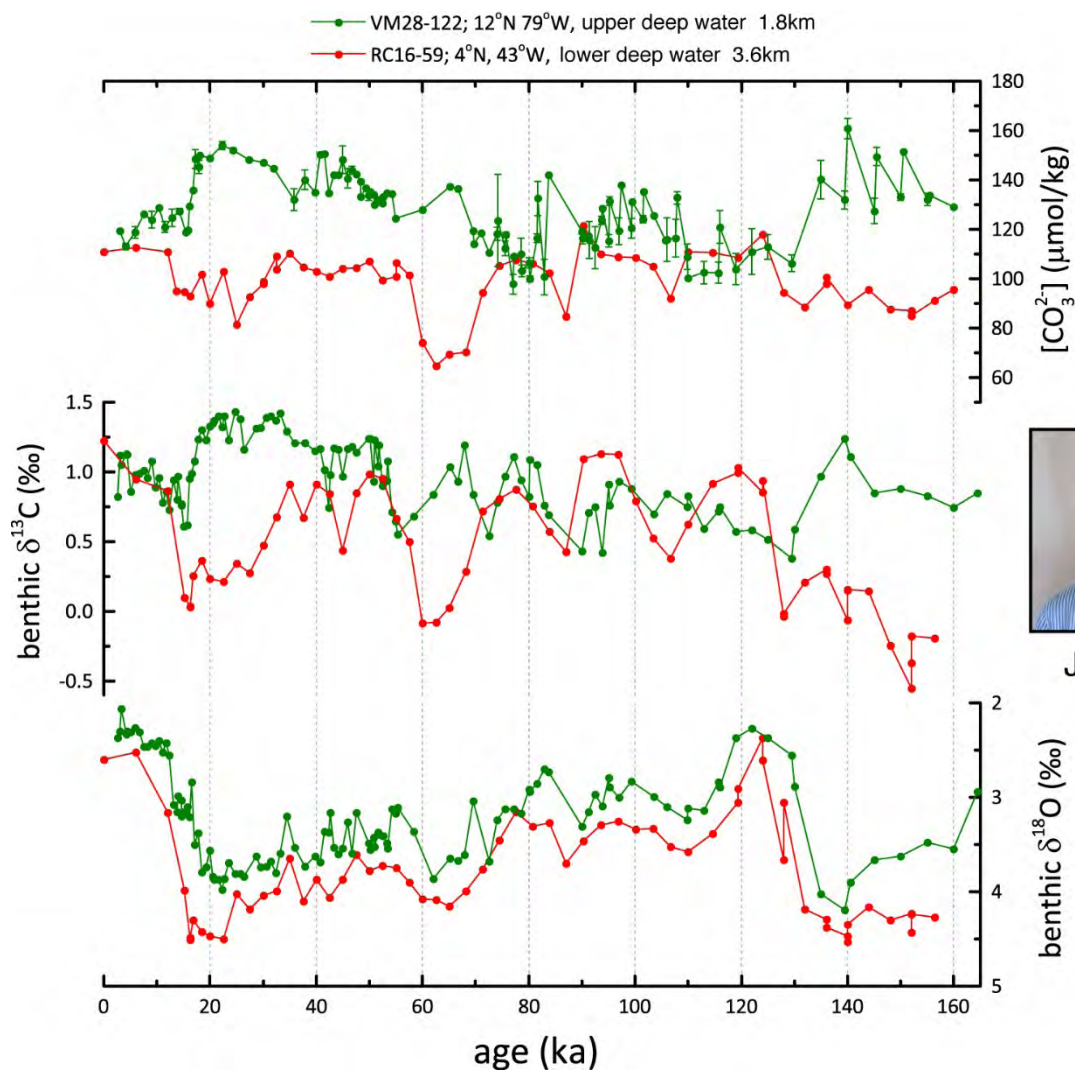
Plots of CaCO_3 content versus water depth in six regions of the ocean (see upper panel). The depth of the onset of dissolution is difficult to pinpoint. The reason is that the first 25 percent of the dissolution produces only a small change in CaCO_3 content (see lower panel).



Ionic constituents of seawater. As can be seen, there is only a tiny difference between the height of the positive ion column and that of the negative ion column. This 'negative charge deficit' (NCD) is balanced by some combination of HCO₃⁻, CO₃⁼ and B(OH)₄⁻ ions. Their proportions vary from place to place in the sea because of the uptake and release of CO₂ by plant matter and by the formation and dissolution of CaCO₃.



Plot of fraction of CaCO_3 in the greater than 63-micron-size fraction as a function of water depth in the western equatorial Pacific: At 2.4 kilometers depth little dissolution has occurred and foram shells and coccoliths each make up about half of the CaCO_3 . At 4.5 km depth almost all the foram CaCO_3 has dissolved and only coccoliths remain.



JIMIN YU

A comparison of the CO_3^{2-} and $\delta^{13}C$ records for the shells of the benthic foraminifer *Cibicides* from a core from the Ceara Rise with those for a core from the Caribbean. The Ceara Rise core from 3.4 km depth is representative of the lower portion of the deep Atlantic. The Caribbean core is representative of the water spilling over the 1.8 km depth sill which separates the deep Caribbean from the Atlantic. Hence it is representative of the upper Atlantic deep water. The time scales are based on the ^{18}O to ^{16}O records for the same benthics. These measurements were made by Jimin Yu.

References

- Li, T.Y., T. Takahashi, and W.S. Broecker (1969), The degree of saturation of a CO_3 in the oceans, *J. Geophys. Res.*, *74*, 5507-5525.
- Broecker, W.S., and T. Takahashi (1976), The solubility of calcite in sea water, *Thermodynamics in geology*, Oxford, UK.
- Takahashi, T., and W.S. Broecker (1977), Mechanisms for calcite dissolution on the sea floor, In: *The Fate of Fossil Fuel CO_2 in the Oceans*, (Neil Anderson and A. Malahoff, eds.), Plenum Press, NY, 455-477.
- Broecker, W.S. and E. Clark (1999), CaCO_3 Size Distribution: A paleo carbonate ion proxy, *Paleoceanography*, *14*, 596-604.
- Broecker, W.S. and E. Clark (2001), An evaluation of Lohmann's foraminifera-weight dissolution index, *Paleoceanography*, *16*, 531-534.
- Broecker, W.S. and E. Clark (2001), *A Dramatic Atlantic Dissolution Event at the Onset of the Last Glaciation*, *G³*, (*Geochemistry, Geophysics, Geosystems*), *2*, No. 2001GC000185.
- Broecker, W.S., R.F. Anderson, E. Clark, and M. Fleisher (2001), Record of sea-floor CaCO_3 dissolution in the Equatorial Pacific, *G³* (*Geochemistry, Geophysics, Geosystems*), *2*, No. 2001GC000151.
- Broecker, W.S. and E. Clark (2002), *A Major Dissolution Event at the Close of MIS 5e in the Western Equatorial Atlantic*, *G³* (*Geochemistry, Geophysics, Geosystems*) *3*, February 5.
- Broecker, W.S. and E. Clark (2003), Holocene Atmospheric CO_2 Increase as Viewed from the Seafloor, *Global Biogeochemical Cycles*, *17*, doi: 10.1029/2002GB001985.
- Broecker, W.S. (2003) The Oceanic CaCO_3 Cycle, 529-549. In: *The Oceans and Marine Geochemistry* (ed. H. Elderfield) *6 Treatise on Geochemistry* (eds. H.D. Holland and K.K. Turekian), Elsevier-Pergamon, Oxford.

Chiu, T.-C. and W.S. Broecker (2008), Towards Better Paleo-Carbonate Ion Reconstructions – A New Insight Regarding the CaCO₃ Size Index, *Paleoceanography*, 23, PA2216, doi:10.1029/2008PA001599.

Broecker, W., and E. Clark (2009), Ratio of coccolith CaCO₃ to foraminifera CaCO₃ in late Holocene deep sea sediments, *Paleoceanography*, 24, PA3205, doi:10.1029/2009PA001731.

Broecker, W. (2015), *What Drives Glacial Cycles?*, Eldigio Press, NY.

Broecker, W. S., J. Yu, and A.E. Putnam (2015), Two contributors to the glacial CO₂ decline, *Earth and Planet. Sci. Lett.*, 429, 191-196.

Chapter 16

Biosphere 2

One day in May 1992 I received a call from Jack Corliss, a fellow geochemist. He said he had been helping out at the recently completed Biosphere 2 in Southern Arizona. I knew from newspaper articles that the idea behind this project was to determine whether eight people could support themselves for two years in a sealed environment. Jack confirmed that this was correct and said John Allen, the group's leader, wanted to speak with me. As they were to spend a week in New York, he suggested that we meet for dinner.

At the agreed upon time I walked into the Santa Fe Restaurant (near Lincoln Center) and found John and Jack sipping margaritas. After a brief greeting, Allen, who reminded me a bit of an aging Indiana Jones, pulled out a folded piece of graph paper. After making sure that no one at the nearby tables was looking, he unfolded it. He clearly viewed it as highly confidential. It turned out to be a plot of the O₂ content of the Biosphere 2 atmosphere versus time. Eight months had passed since the two-year occupation had begun. The graph showed that the O₂ content had steadily declined. When sealed in September (1991), there was 21.5 percent oxygen which is characteristic of outside air and by May it had dropped to a bit below 19 percent. He asked me why this might have happened. The obvious answer was that the photosynthetic production of O₂ was not keeping pace with respiratory consumption of O₂. Allen said that if this was the case, why hadn't the CO₂ content of the atmosphere risen from 350 ppm, typical of outside air, to over 200,000 ppm? Yes, he admitted the Biospherians were scrubbing CO₂ out of the air but only a small fraction of the CO₂ that must have been created by 'burning' the O₂.

By chance, I had scheduled a trip to Tucson the following week to attend a meeting at the University of Arizona. So I offered to visit Biosphere 2. To get there, I drove north from the university around the west end of the Santa Catalina mountain range and then back east on the other side until I reached the Biosphere 2 approach road. Then there it was – a spectacular glass building located at the west end of a 'campus' lush with greenery. I parked in front of the administration building where I was met by John Allen. After a brief hello, he turned me over to

Bill Dempster, the chief engineer. Bill turned out to be a very friendly and extremely well informed man. He took me to the glass house and briefed me on how it functioned. Although matter-sealed, electricity was fed in from an on-site power station. Most of it went into air conditioning the sealed glass building which was subject to intense solar heating. The Biospherians had electronic access to the outside world. They grew their own food in the agriculture biome; they tended the ocean biome, the tropical biome and the desert biome. And, of course, they disposed of their waste.

Dempster made a big point of how the air-pressure inside Biosphere 2 was maintained at exact equality with that outside. Flanking the Biosphere 2 were two large circular ‘lungs’ which were connected to the glass house by underground tunnels. Each had an immense rubber diaphragm weighted down by an aluminum plate. If the outside air pressure went up, the diaphragm would be pushed down and vice versa. Bill told me that in this way, the air pressure in Biosphere 2 was kept equal to that outside. Without the lungs, a passing weather front could blow out the glass. He went on to tell me that the building was sealed from beneath by a welded stainless steel shell. An access tunnel ran beneath the shell with side ports which allowed helium checks to be conducted insuring that no leakage from below occurred.

The last part of my tour was a chat with two of the Biospherians, Tabor McCallum and Jane Poynter. Bill brought me to a window where I had a face to face with them. I was surprised that neither looked well. Apparently, low O₂ and sparse food were taking their toll. However, they were alert and seemed happy as they described their day to day life.

I was amazed by all this. Question: How much did it cost to build this grand facility? Answer: About 200 million dollars. Question: Where did the money come from? Answer: Ed Bass, son of a Texas oilman. Question: Why was it built? Answer: As a step toward colonizing the Moon and perhaps Mars.

Back in New York, I encouraged Jeff Severinghaus, who had just joined me as a graduate student, to help to solve Biosphere 2’s CO₂ mystery. I told him that if he agreed, it would be a ‘Saturday afternoon’ project, independent of his thesis research. He was up for it and back we

went to Arizona to plan a strategy. We focused on the soil, especially that in the agricultural biome. It was one-meter thick and contained three percent organic matter top to bottom. This was far more than in farm lands which have soil horizons averaging two tenths of a meter thick. Also, three percent organic carbon was on the high side. Clearly this vast food source allowed bacteria to consume oxygen faster than it was produced by the plants. At Jeff's request, Tabor McCallum probed the air at the base of the soil and found it to be devoid of O₂. This explained the declining O₂, but where was the CO₂?

Many months later, realizing that we needed help, Jeff's father, John, a high altitude physiologist at the University of San Francisco, suggested an answer. What about the concrete? It is made from calcium oxide (CaO) created by heating limestone (CaCO₃) to the point where CO₂ is driven off. As concrete is very basic (high pH), it protects the steel rebars, holding up the building, from corrosion. But cement absorbs CO₂ gradually converting it back to limestone. So Jeff asked Tabor MacCallum to take core samples from the concrete inside Biosphere 2 and Jeff took similar samples from the outside. Using a phenolphthalein indicator, Jeff showed that although the depth of carbonation for the outside samples was only about one millimeter; that for the inside samples was about one centimeter. The difference had to do with the high humidity and high carbon dioxide content of air inside Biosphere 2. Jeff calculated the surface area of concrete exposed inside Biosphere 2 and found that its uptake accounted for the missing CO₂.

John Allen and his team had given little attention to the interplay between the O₂ and CO₂ content of the air enclosed in Biosphere 2. As consumption of O₂ far outpaced the production, without the CO₂ removal provided by the concrete, the Biospherians would have faced medically unacceptable levels of CO₂. Allen didn't know this of course, so in this regard he was a lucky man.

During the course of our visits, we began to see the dark side of what went on there. My first indication came when Margaret Augustine, Allen's second-in-command asked me to sign a non-disclosure statement. In the last paragraph it warned that were I to disclose any of their secrets, I would be subject to a \$20,000 penalty. As I was not paid a consulting fee nor was I

reimbursed for my airfares and car rentals, I refused to sign. Jeff was asked to sign this document three separate times. He refused.

We came to realize that Allen's group of 25 or so people was a cult. It was patterned after that led by the Russian mystic, George Gurdjieff. Four of the eight Biospherians were cult members and four (including McCallum and Poynter) were not. It was said that the two groups rarely socialized during their long stay in the Biosphere. A few years later, I read an exposé in a Tucson newspaper claiming Allen ruled by intimidation and drugs and that he also considered it his duty to deflower the daughters of cult mothers.

Of course, Biosphere 2's oxygen continued to go down. When the O₂ partial pressure reached that at 17,000 feet elevation, Allen was forced to act. Not wanting to pull the plug on the isolation aspect of the mission, he had only one choice. He had to add O₂. Liquid O₂ was trucked in and fed into one of the lungs where it vaporized. While this was happening, the hatch in the connecting tunnel was closed. The oxygen-starved Biospherians clustered at the hatch waiting for it to be opened. When they were allowed to enter the lung, they danced around and did somersaults. In other words, the relief was immediate. Although John Allen had dodged the CO₂ bullet, the O₂ bullet got him.

One and a half years into their mission, on April 1, 1993, the Pima County Sheriff entered the Biosphere 2 campus with a court order to banish the cult. This ended a long struggle between the spend-thrift cult and the money-conscious Bass advisors. Allen was in Japan at the time. On learning of the ouster, he flew back to Arizona and commanded the eight Biospherians to abort their mission. They unanimously refused. They would stay inside for the full two years.

So the management had to change and Steve Bannon was brought in. The idea was that he would stay on until the Bass people could find a suitable organization to take over Biosphere 2 and operate it as a research facility. I was asked to serve as the interim science advisor. Realizing that this 'sealed box' had great potential as a laboratory to study the impacts of elevated CO₂, I encouraged Michael Crow (now President of Arizona State University), who was

at that time Executive Vice-Provost at Columbia University, to make a bid for it. He did this and in August 1994 Columbia accepted management.

I well remember meetings with Crow to decide what Columbia would do with the facility. His first priority was to establish an environmental science semester for college students. At a meeting attended by many Lamonters, he asked for a volunteer to develop and supervise this endeavor. Debbie Colodner, a postdoctoral fellow in our Geochemistry group, raised her hand. Crow appointed her on the spot. I am amazed at the exceptional job she did. Columbia and Barnard students, not known for their generosity in ranking courses, gave the Biosphere semester rave reviews. Some even said that it was the best of their college semesters.

I was given the task of building a research program. Fortunately, Joe Berry, a prominent plant physiologist at the Carnegie Lab in Palo Alto, California, was already interested. He took responsibility for research in the rainforest biome and hired Guanghui Lin, as a fulltime on-site scientist.

Concerned that we needed someone on our Columbia faculty to be involved in Biosphere 2 research, I convinced Michael Crow to fund a faculty position in our Earth Science Department. He agreed. A few weeks later, while attending a get-together of the newly appointed Department of Energy postdoctoral fellows, by chance I sat next to a young man named Kevin Griffin. He told me he was involved in operations of a plant microcosm facility at the Desert Research Laboratory in Reno, Nevada. Realizing that he was just the man for our job, I asked whether he could be persuaded to switch to research in a megacosm in the Sonoran Desert. A few months later, Kevin was appointed Assistant Professor of Columbia. He agreed to take responsibility for creating a tree growth experiment in Biosphere 2's agriculture biome. More than twenty years later, Kevin is still here. In recent years he has taken a key role in establishing a sustainability major for Columbia College students. He also serves as Chair of Columbia's Department of Ecology, Evolution and Environmental Biology.

My long-time colleague, Taro Takahashi, agreed to help with research in the Biosphere's ocean biome. He was joined by Chris Langdon, a member of Lamont's Marine Biology group.

They pulled in University of Hawaii's Marlin Atkinson to help them. These three pulled off the most significant piece of research conducted at Biosphere 2 during the time it was operated by Columbia University. They determined the dependence of CaCO_3 production on the carbonate ion concentration. Biosphere 2's ocean (the size of an Olympic swimming pool) was designed to mimic a coral lagoon. As such, most of the CaCO_3 was produced by benthic algae rather than coral. Because of the small volume of water compared to the size of the algal community, changes in the carbonate ion concentration of the ocean on the time scale of hours could be determined.

The plan was to manipulate (by either HCL or NaOH additions) the carbonate ion content of the water over a range corresponding to that for today's ocean, down to that if the atmosphere's CO_2 content reached several times its pre-industrial CO_2 value. What they found was extremely interesting. As expected, the rate of calcification decreased, but the magnitude of the decrease was twice as fast as had been estimated from small scale experiments.

Under the direction of Bill Harris (formerly head of the Physics and Chemistry Division of the National Science Foundation), the education program flourished and the research program stumbled along, gradually gaining momentum. In May 2000, Harris left to become the director of the newly created Irish National Science Foundation and work at Biosphere 2 began to deteriorate. Initially, I was delighted that Barry Osmond, a world-class plant physiologist, was appointed in his place. But it soon became clear that his vision of the research program was far different than what we had been striving to create. He soon squelched the weekly science phone meeting (a substitute for on-sight management) and Columbia people were pushed to the sidelines. It became Osmond's show. At the same time, enrollment in the teaching program began to plummet. Building it up had been the top item in Harris' agenda.

Then came the crowning blow. In 2001, Columbia President George Rupp retired and was replaced by Lee Bollinger. Rupp had been highly supportive of the effort at Biosphere 2 and, of course, Michael Crow paid close attention to the health of the operation. Bollinger seemed cool toward it. How could we operate a campus 3000 miles away? Discouraged by Osmond and

worried about a drop in the environment semester enrollment, I sent a long email to Bollinger stating my concerns and went as far as suggesting that we pull out of the Biosphere project. At the time, it was clear that Crow would accept the presidency of Arizona State University. It was decided to bring in a high level review committee to advise Bollinger regarding the wisdom of staying on at Biosphere 2. The committee made it clear that without a far better research plan, Biosphere 2 would not be able to pull in the research funding required were it to flourish. This was the death knell. Bollinger pulled the plug breaking the contract with the Bass organization. The upshot was a lawsuit that cost Columbia several tens of millions of dollars.

So once again Biosphere 2 was in limbo awaiting yet another group to operate it. This went on for ten years. I suspected that Crow would arrange for Arizona State University to take it on and was surprised when it was the University of Arizona that got the nod.

In 2012, I spent the first of five winter sabbaticals at ASU. Eager to learn what was happening at Biosphere 2 under its U of A management, I arranged a visit. The first thing I noticed was a reconfiguration of the original campus, half of which was closed and apparently abandoned. The new entrance to Biosphere 2 is now located in the dormitory complex built by Columbia, and, of course, the glass house is no longer sealed.

Budgetary considerations prohibited maintaining the dozen or so extra buildings and cooling the sealed glass house costs more than one million dollars a year. Further, instead of just looking in from outside, tourists can now tour the inside. In this way, income from tourism has remained close to the level of the Columbia years. I relate to this plan for it was our inability to attract adequate outside funding which held back progress in harnessing the potential of this incredible research facility.

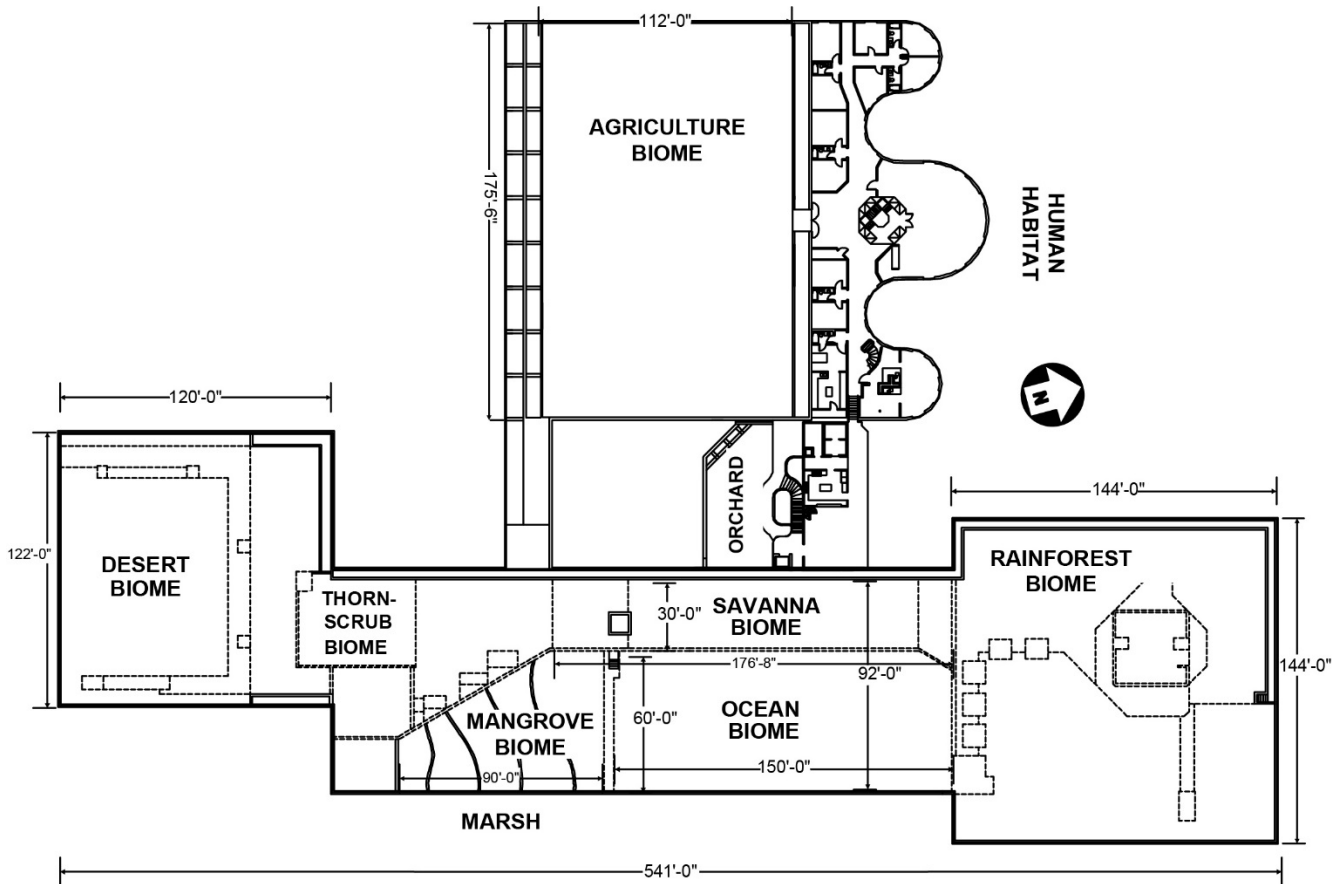
As the Biosphere 2 was no longer sealed, the University of Arizona's group had to take another research tack. They decided to focus on water rather than on carbon dioxide. The agricultural biome now houses three giant trays sloping downward from the balcony on its north side to the floor on its south side. The trays are filled with pulverized volcanic ash shipped in from northern Arizona. The trays are mounted on scales, so that the water content of the soils can

be precisely monitored. Several thousand sensors were buried in the soil. As any disturbance of the soil by walking on it or digging into it would impact the experiment, much sensor redundancy was built in.

Since my initial visit, I have gone back four more times. During the third of these visits we held a mini reunion of the Columbia group. Crow, Harris, Berry, Wright, Lackner, both Severinghaus' and me. During my 1996 visit, I was pleased to learn that John Adams, who had been hired as a junior staff member during the Columbia days, is now the on-site manager. I also learned that Julie Cole, once a Lamont-Doherty graduate student, and now a U of A professor, would step in and reestablish coral research in the long-neglected Biosphere 2 ocean.



Biosphere 2 in its beautiful mountain setting: Shown prominently are the two lungs which originally matched the air pressure inside the glass house with that outside. The tower which tops the living area serves as a library. The pyramid shaped glass structure contains the tropical rain forest.



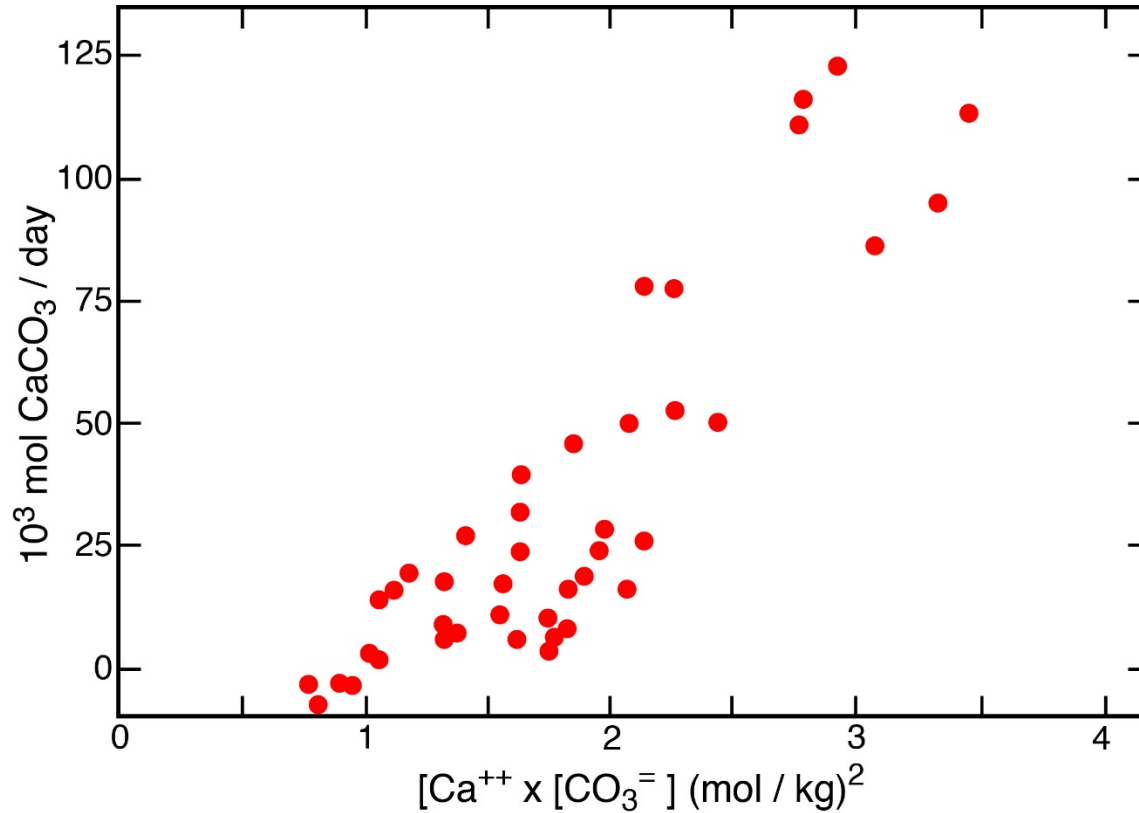
Floor plan of Biosphere 2: Beneath the biomes a basement houses the grant air handlers. At night it is a scary place for it also provides a home for a multitude of cockroaches which sit at the top of Biosphere 2's food chain. They feed on crazy ants which, in turn, eat plant aphids.



The Biosphere 2 coral lagoon. At the far end is a wave making device. During the occupation, the Biospherians had to spend a fair amount of time removing overgrowths of algae from the corals.



Ed Bass, the patron of Biosphere 2. His motivation for creating this facility reflects his love and respect for our planet's environment. Not only did he fund its construction, but also the efforts by Columbia University and the University of Arizona to conduct research in his glass house. Over the years, he has kept a close eye on its operation.



Dependence of the rate of calcification by algae (and coral) in the Biosphere 2 ocean as a function of the product of the concentrations of Ca⁺⁺ and CO₃⁻ ions. Over a range of a factor of three in the ionic product, the amount of calcite produced each day drops an order of magnitude. As the content of calcium is uniform throughout the world ocean, it is its carbonate ion concentration that matters. A doubling of the atmospheres CO₂ content will halve the carbonate content of surface waters, greatly reducing the rate of calcification in coral reefs and lagoons. The details of this are to be found in a paper by Langdon et al. (see references).

References

- Severinghaus, J, W.S. Broecker, W.F. Dempster, T. MacCallum and M. Wahlen (1994), Oxygen Loss in Biosphere 2, *EOS, Transactions, AGU*, 75 (3):33, 35-37.
- Broecker, W.S. (1996), The biosphere and me, *GSA Today*, 6, 1-7.
- Langdon, C., T. Takahashi, C. Sweeney, D. Chipman, and J. Goddard (2000), Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef, *Global Biogeochemical Cycles*, 14, 639-654.

Chapter 17

Rock Varnish

In 1996, I organized a field trip for a small group interested in the Quaternary history of Great Basin hydrology. We convened in Las Vegas and from there through Death Valley, Panamint Basin, Searles Basin, Owens Valley, Mono Lake and on to the Lahontan Basin. At each place, we were briefed on what was known and what might be done to learn more. Ron Dorn from Arizona State University brought along Tanzhuo Liu (TL), a graduate student conducting research on rock varnish. Along the way TL showed me thin sections of this resinous coating. He said that it thickened extremely slowly, a few microns per thousand years. He unrolled large blow-ups of photos he had taken of these ultrathin sections. He said that the yellow, orange, and black layers correlated with variations in its manganese (Mn) content. The more manganese, the darker its color. As the varnish formed during the dry Holocene was lighter in color than that formed during the less dry glacial time, TL felt that the Mn content increased with rainfall. I was captivated by rock varnish. One reason was that it shared several characteristics with manganese nodules formed on the ocean floor. Both have unusually high concentrations of what petrologists refer to as large lithophile elements (Rare Earths, U, Th, Pb...). Manganese nodules also grow at the rate of a few microns per thousand years. Further, manganese nodules nucleate on something hard (often on shark's teeth) but they grow for millions of years while varnish deposits, older than tens of thousands of years, are rare. Just as paint eventually peels off walls, varnish peels off rock.

I quickly realized that all sorts of geochemical measurements could be made on rock varnish and decided to take the plunge. On the spot, I offered TL a postdoctoral fellowship, hoping that Columbia's Executive Vice-Provost, Michael Crow, would be willing to put up one year's salary. If so, once at Lamont, TL and I would then write proposals to continue his support.

Our objective was to determine how varnish formed and what it was recording. The first step was to determine chemical composition. TL arranged with New York City's American Museum of Natural History to use their ion probe to make scans of his thin sections. It jumped

out that barium was highly correlated with the manganese and that the concentration of manganese (Mn) was anti-correlated with that of magnesium (Mg). Our working hypothesis was that Mg, K, A, and Si are delivered to the surface of the nodules bound in fine-grained dust and Mn and Ba are delivered in rain. This hypothesis is broadly consistent with the observation that the manganese content correlates with precipitation.

Recently, TL has measured the ratio of excess ^{40}Ar to that of its long-lived radioactive parent ^{40}K . The results demonstrate that the clay minerals carrying the radiogenic ^{40}Ar have existed for tens of millions of years. This eliminates the possibility that the clay minerals crystallize within the varnish. Rather, they must be brought in from the outside.

Bill McDonough, while a scientist at Harvard, kindly conducted a complete scan of the trace element composition of one of TL's varnish samples. He found that all the large lithophile elements were enriched by tenfold with respect to magnesium. He confirmed measurements made by Lamont's Marty Fleisher that the large separation between U and Th which occurs in aqueous systems does not take place during the formation of varnish. Rather, the Th to U ratio is within a factor of two of the 4 to 1 ratio which characterizes igneous rocks. I have yet to hear a plausible scenario explaining how this enrichment can occur without the large separation of Th and U.

Early on we showed that aerosols carried to the rock surface by rain or dew do indeed supply material to varnish. The first way in which this was done was by measuring ^{210}Pb in varnish. As this isotope has a half-life of 22 years, if present in varnish, it must have been added during the last 100 years. ^{210}Pb is produced in the atmosphere by radio-decay of the radon gas which leaks out of soil. Newly formed ^{210}Pb atoms glom onto aerosols and are carried to the varnish surface in rainfall and in 'dry' fallout. Marty Fleisher documented the presence of a large excess of ^{210}Pb in five varnish samples. In one of them, he measured ^{137}Cs , a radioactive fission product produced by atomic bomb tests. He also was able to document the presence of plutonium, an element produced in nuclear reactors.

While the presence of these isotopes demonstrated that they were delivered from the atmosphere, there was no way to distinguish between delivery by rainfall or 'dry fallout' rainfall. So, with the help of Willard Moore at the University of South Carolina, we designed a means by which this distinction could be made. It involved the radioisotope ^7Be (half-life 53 days). This isotope is produced in the atmosphere by cosmic ray neutrons which shatter the oxygen nuclei.

The first step was for TL to collect varnished rocks from two locales. He chose a site in Scottsdale, Arizona, and one in Panamint Valley, California. Then with the help of Allen Wright, chief engineer at Biosphere 2, he installed four rocks from each site in a fenced-in area in an outlying part of the Biosphere 2 campus. Wright built little carts which ran on tracks. When it rained, the carts were thus triggered to move over the varnished rock. When it stopped raining, the carts moved back. Four of the rocks had received cart cover and four did not. The rocks were left untouched for six months, i.e., long enough for its ^7Be to be largely replaced by that deposited at the Biosphere 2 site. The paired results indicated that 60 ± 10 percent of the ^7Be was delivered by rainfall. The rest was presumably carried by aerosols (perhaps captured in dew).

As part of this study, the ^{10}Be (a long-lived, radioisotope of beryllium, produced by cosmic rays) was also measured. As the production rate of ^{10}Be is known, we could estimate the fraction of ^{10}Be fallout which was captured by the varnish. For four samples from the western U.S., this fraction turned out to be very small ($2.5\pm 1.0\%$). This came as no surprise for the residence time of rain water on the varnish surface is very short. It promptly runs off. When making sections, TL focuses on dimpling in the rock surface. The varnish is thicker in these dimples.

Although most of the desert varnish TL has studied comes from Great Basin in the western U.S., his collection now includes samples from Africa, Israel, Mongolia, China and Argentina. Except for that in Africa, these locales are in drylands located in the 30° to 40° latitude zone (in both hemispheres). If he is correct that the color correlates with rainfall, then in all these places there was more rainfall during the last glacial period than during the Holocene. Of course, where available, records from closed basin lakes show that this is indeed the case.

In addition to the large glacial-to-Holocene color change, TL also sees finer-scale color layering that records millennial-duration climate changes. As varnish is subject to erosion, there is certainly a degree of subjectivity in comparing records with one another. But I'm convinced that these stripes characterize millennial-duration changes in rainfall.

The advent of ^{10}Be exposure dating for boulders has proven to be a huge boon to the study of rock varnish, for it provides the age for the onset of varnish deposition.

Lastly, rock varnish serves as a global environmental archive. We have shown, for example, that there is a large excess of anthropogenic lead in the upper micron of varnish. Isotopic composition of this lead can be used to distinguish between lead from gasoline and that from local smelters. With modern techniques, it should be possible to determine the geographic fallout pattern for a number of pollutants. Only the surface has been scratched in harnessing this wonderful archive.

I shouldn't finish this chapter without mentioning a hiatus in TL's rock varnish career. The publication of a paper in *Science* tarnished rock varnish research. Although this had nothing to do with TL, as a result, the Department of Energy decided not to renew his support. Without a source of salary, TL had to leave Lamont and needing a new career, he decided to get his MBA degree. Two years later, when he finished, the job market was at a low and he couldn't find employment. So he applied to the U.S. Post Office. After passing the written tests with flying colors, he was told he had to take a driving test which involved backing a large truck between two poles. With the poles on his left he succeeded. With the poles on the right he failed. No second try. He didn't get the job. Learning this, I scouted around Lamont to see if there was a technical position available. It turned out there was one in a group that analyzed the logs for deep sea drilling bore holes. TL took the job and quickly became the group's ace analyst. Although his weekdays are devoted to earning a living, nights, weekends, and vacations are available for varnish research. TL remains dedicated to learning more of the secrets hidden in this important archive.

When the Borehole group lost a portion of its funding, Professor Sidney Hemming offered to fill TL's salary gap. He helps her maintain the Ar isotope mass spectrometer. Only a month ago, he slipped in a few varnish samples and showed that the fine mineral grains have retained a major fraction of the ^{40}Ar produced in them over the last several tens of million years. Good work, TL!



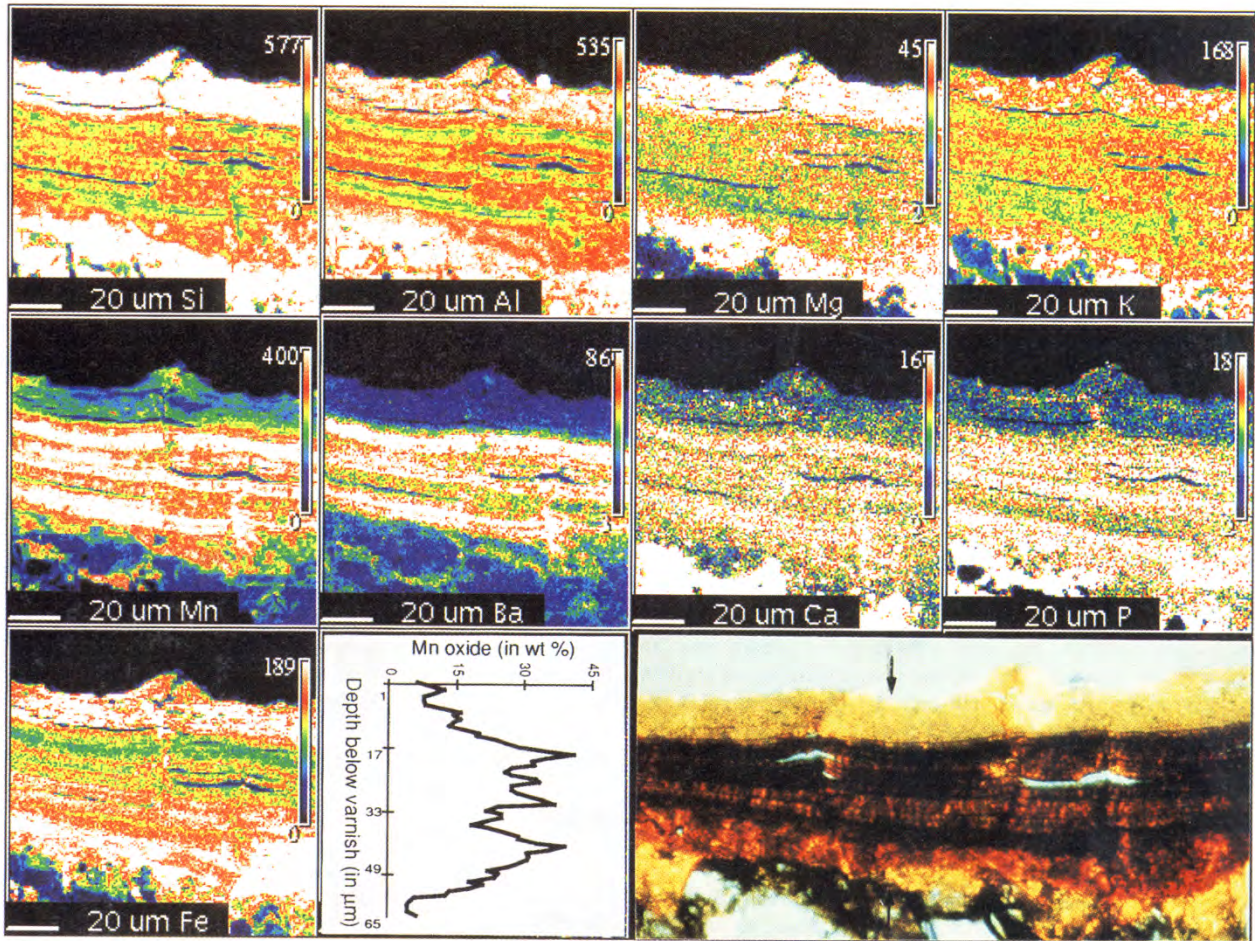
One of Tanzhuo Liu's ultrathin rock varnish sections. The yellow upper layer formed during the Holocene and the underlying dark layer during the latter part of the last glacial period. Crystals in the rock coated by the varnish are seen at the bottom. The thickness of the varnish is about 50 microns.



Rock varnish-coated clasts on late Pleistocene alluvial fan in Death Valley, California.



Tanzhuo Liu (TL) smiling and hard at work prying out a piece of varnish-coated rock.



Maps of the abundance of nine elements in one of TL's varnish thin sections. The upper band in each is for the Holocene, the middle band for the late glacial and the lower band for the rock which the varnish coats. Manganese, barium, calcium and phosphorus are more abundant during the glacial than during the Holocene. The opposite is the case for silicon, aluminum and magnesium. A traverse of Mn concentration is also shown. Note that the very bottom of the varnish section low Mn concentrations return, suggesting that the record extends back to the penultimate interglaciation. A photo of the section is also shown.

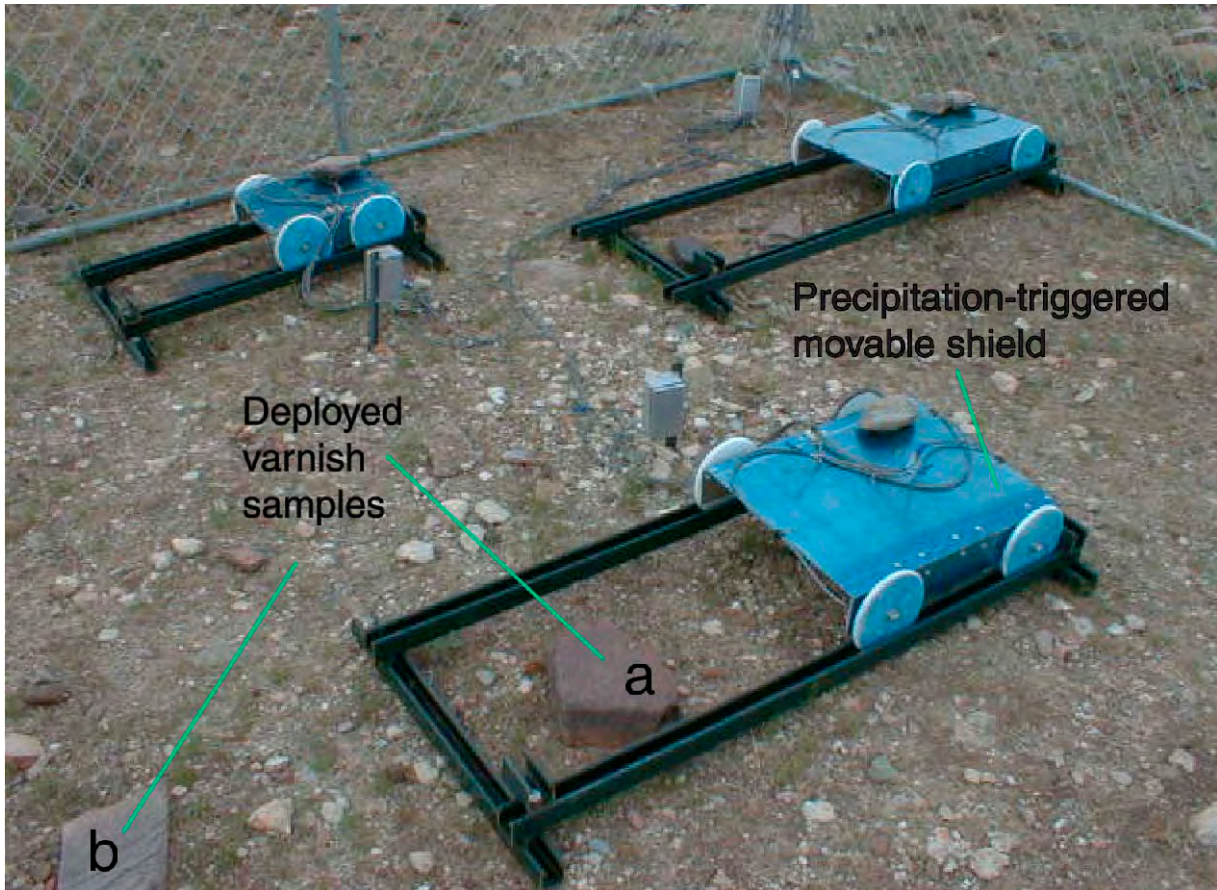


Photo of the carts Allen Wright made to cover the varnished rocks during periods of rainfall.

References

- *Beck, W., D.J. Donahue, A.J.T. Jull, G. Burr, W.S. Broecker, G. Bonani, I. Hajdas, and E. Malotki (1998), Ambiguities in direct dating of rock surfaces using radiocarbon measurements, *Science*, 280(5372), 2132-2139. doi:[10.1126/science.280.5372.2132](https://doi.org/10.1126/science.280.5372.2132).
- Fleisher, M., T. Liu, W.S. Broecker, and W. Moore (1999), A clue regarding the origin of rock varnish, *Geophys. Res. Lett.*, 26, 103-106.
- Liu, T., and W.S. Broecker (2000), How fast does rock varnish grow? *Geology*, 28, 183-186.
- Broecker, W.S. and T. Liu (2001), Rock varnish: recorder of desert wetness, *GSA Today*, 11, 4-10.
- Moore, W., T. Liu, W.S. Broecker, and A. Wright (2001), Factors influencing ^7Be accumulation on rock varnish, *Geophys. Res. Lett.*, 28, 4475-4478.
- Liu, T., and W.S. Broecker (2008), Rock varnish microlamination dating of late Quaternary geomorphic features in the drylands of western USA, *Geomorphology*, 93, 501–523.

*I have not discussed this paper in the text. The reason is that it was the subject of a law suit which was settled without trial. As part of the settlement, the parties agreed that the matter remain sealed. Although the courts can trump science, they cannot expunge the published record.

Chapter 18

Gary Comer

In mid-April 2002, I received a letter which in many ways changed my life. It was from a man named Gary Comer, written on Lands' End letterhead. It turned out that he wanted to meet with me about a trip he had taken through the Northwest Passage on his yacht *Turmoil*. As little ice was encountered, he suspected global warming was reducing sea ice cover in the Arctic. One of his friends recommended me as an expert on climate. He asked if I would meet with him.

I wrote him back and told him that I would be happy to meet with him. However, as the semester was drawing to a close, it would be best for me to delay the trip for two weeks so that I could give the remaining lectures in my class. He grumbled a bit and said that instead he would come to New York. We agreed that he would stay overnight at the Clinton Inn in Tenafly, New Jersey (one town over from my home in Closter). We would meet for breakfast at the Inn.

In the meantime, I did a bit of research on Comer. I found that he owned Lands' End, a very successful direct merchant enterprise. He was four years older than I and had grown up on the south side of Chicago not too far from my father's childhood home.

So it was with considerable anticipation that I entered the restaurant. As there were few people there, I had no problem spotting Comer. I was pleasantly surprised and relieved that, instead of a stern-faced man in a three-piece suit, he was dressed casually and had a warm and welcoming smile.

As I remember, one of the first things he said to me was "Wally, what can I do for you?" Stunned, I told him that I was there to answer his questions and expected nothing in return. I don't remember what we talked about as we ate, but I got the idea that he was thinking of something longer term than just my thoughts on Arctic ice. So, I invited him to visit the Lamont laboratory.

On our drive there, I remembered that my friend and colleague George Kukla had, by chance, scheduled one of his quarterly lunch time 'pignics' for that day. I asked Gary whether he was up for such an event and he said that would be fine. After a brief tour of the lab and grounds,

we hiked for a couple of hundred yards into the woods arriving at the rocky knob where Kukla had a fire pit and cooking tripod. About 25 other picnic regulars were already there. In addition to Kukla's pork, there was Rusti Lotti's black beans, cheese, and plenty of liquid refreshment. Gary made the rounds chatting with most everyone and taking photos. Afterward, Gary said that his limousine would pick him up and take him back to Teterboro Airport where his private plane was waiting. As he left, he reminded me "think of something that I can do for you", followed by "I'll be in touch with you soon." Three days later, I received a mailing tube. Rolled up inside was a montage of the photographs Comer had taken at the picnic. Framed, it now stands behind the telephone in my office.

I didn't have to wait long to find out what Comer was up to. He called me and asked for a favor. He wanted me to select 25 scientists involved in climate research. He would offer each of them \$350,000 to support their research. He made clear that his Foundation would not pay any institutional overhead. The first person I called was my former graduate student, Jeff Severinghaus, professor at the University of California, San Diego. I was stunned when he said he already had been given Comer support. Realizing my bewilderment, he explained that Sherry Rowland, a Nobel Prize recipient, had made the offer a few weeks earlier. It took me quite a while to figure out what was going on. Even now I'm not entirely sure. But, I suspect that Gary decided to switch horses. Concerned about global warming, he was captivated by abrupt climate change and only marginally interested in Rowland's work on trace gases. I also think that perhaps Rowland made a mistake by handing out four of Comer's research packages to people at his own institution (including himself). In any case, over the next several months, I chose 25 people from around the world to receive Comer research awards. In so doing, I made 25 friends.

Gary was a hands-on person. He had a strong desire to know us, to learn from us, and to participate in our field efforts. Yet he had a gentle touch and his involvement never bordered on control. It was our show. He would tag along.

When Comer became aware of the Younger Dryas (YD) and Jim Teller's idea that it was triggered by a flood of meltwater, he encouraged us to mount a field effort designed to evaluate

this proposal. We came up with a plan involving reconnaissance flights to search out evidence for Teller's flood and to collect samples for ^{10}Be dating of boulders perched on glacial moraines. The group consisted of Tom Lowell, George Denton, Joerg Schaefer, Sidney Hemming, Gil Hansen, Jim Teller, Elizabeth Clark and myself.

Gary set a time when we should be at the private plane terminal at Chicago's Midway Airport. From there he would take us in his jet to his 'farm' in western Wisconsin where we would have a planning meeting. From there we would fly to Thunder Bay at the western end of Lake Superior.

There were lots of oohs and ahs when we spotted Comer's jet on the tarmac. Not the standard corporate type, rather one of commercial caliber but with couches and easy chairs. It was a short hop to Soldiers Grave, Wisconsin, with Gary serving us pizza along the way. When asked if there was a local airport, he replied, "No, but I have my own". It turned out to be a 3800-foot concrete strip that crossed the northern edge of his wooded property.

At the beginning of our discussions, Gary told us that his nine-seat Cessna Caravan would be waiting in Thunder Bay along with a rental helicopter and pilot. We decided that while half of the group would use the helicopter to scout out sites for boulder sampling, the other half would use the Caravan for reconnaissance. (The jet would wait in Thunder Bay).

The search for evidence of a meltwater flood along Jim Teller's proposed route (i.e., from due west of Thunder Bay) came up dry—no channels, no boulders. There was, however, one prominent channel called Quimet, to the northeast of Thunder Bay. It had been featured in an environment program I saw on TV. It was approximately one hundred meters deep and a kilometer or so long, cut through a basaltic sill by a flood. It is now dry. I got excited. It must have been cut by the flood which initiated the Younger Dryas. But when I asked Teller about this, he was adamant that Quimet was a younger feature, cut on terrain which remained glaciated during the course of the Younger Dryas. The same was the case for the two fields of half-meter diameter boulders we visited. They were located even further to the north. Unfortunately, we could think of no way in which the creation of Quimet might be dated. However, Meredith Kelly

and Joerg Schaefer showed by ^{10}Be dating that the two boulder fields were created two thousand years after the end of the Younger Dryas. But, these features made clear that, if the flood initiating the Younger Dryas had passed through the Thunder Bay area, it would have left behind easily recognized evidence. It took only Gary's overflights to show there was none.

Convinced that he was wrong about the eastern flood route, Teller suggested that we check out a possible northward route. He explained that just south of Fort McMurray in northern Manitoba, there was a 20 mile-long, half-mile-wide channel created by a flood. The existing radiocarbon ages indicated that, like the ones north of Thunder Bay, this flood took place about 10,000 years ago; again, well after the Younger Dryas was over. But, perhaps there was also an earlier flood which took the same path.

Comer was up for another trip, so a year later, off we went. Jet to Fort McMurray, and the Cessna Caravan for reconnaissance (this time equipped with pontoons). As the channel itself offered no means of dating, we spent time looking at the apron of gravels and sand created by a flood. We could find no evidence for an earlier flood.

By coincidence, as I was working on this chapter, I received a preprint from Lloyd Keigwin at Woods Hole. He described measurements he had conducted on a core from the Arctic margin flanking the mouth of the Mackenzie River. It revealed a meltwater pulse Younger Dryas in age. So the case for a northern flood route will likely be reopened.

With the time remaining, we decided to do some tourism. We drove north to where an 'oil-rush' was taking place. The high price of gasoline had made it profitable to mine Canada's tar sands. 'Our' flood had stripped away the overburden exposing a portion of this huge reserve. When we arrived at the perimeter of the operation zone, we were told "no tourists allowed". So, after examining a ten-story-high dragline machine used during a previous incarnation of tar sand mining, Gary said, "If we can't drive in, we can fly."

It was an amazing site: huge bulldozers loading huge trucks which fed huge conveyor belts. The sands, black when they entered the processing plant, were clean as a whistle when they came back out. Of course, all this took a lot of water which ended up in equally huge

settling ponds. And, of course, the landscape was an eyesore. An entrepreneur's dream but an environmentalist's nightmare. As I write this, gasoline sells at two dollars a gallon. Fort McMurray is now somewhat of a ghost town.

In 2003, Gary invited his 35 Comer Fellows to a meeting at the IBM Conference Center in Palisades, NY, located just a mile from the Lamont campus. It was a meeting to remember. When Gary did something, he did it with style. His people had memorized our photos and names so there could be personal welcomes. In each of our rooms was a large basket filled with fruit and snacks. Gary made sure that he spoke with everyone personally. I was amazed by the presentations, mostly new work yet to be published. In many ways, this meeting changed the dynamic of those working on abrupt climate change. We realized that being open and friendly was far better than secrecy and bickering.

Gary Comer loved the Arctic. His yacht, *Turmoil*, made numerous trips to Inuit communities in northern Canada. So, when George Denton suggested that there was an important use for the *Turmoil* regarding the Younger Dryas, Gary jumped at it. The idea was that the summer temperature drop during the YD could be obtained by determining the snowline lowering in the mountains surrounding the Greenland ice sheet. It could then be compared to the 15°C mean annual temperature drop calculated by Jeff Severinghaus based on the neighboring ice core record. This resulted in three separate field efforts spearheaded by George Denton, Tom Lowell and Meredith Kelly. I was invited to one of them but some ailment or other prevented me from going. I suggested that Richard Alley be invited in my place.

Unlike the failure to find evidence for a YD triggering flood, the Greenland fieldwork led to a major discovery. The snowline reconstruction showed that the summer warming at the end of the YD was no more than 5°C. Taken together with the Severinghaus mean annual warming of 15°C, this suggested that the winter must have warmed by something like 25°C. The only way to explain this was to invoke winter sea ice cover during the YD extending perhaps as far south as Cornwall, England. This resulted in a landmark paper authored by Denton with Alley and Comer as second and third authors. I was an honorary fourth.

When I took Comer through our geochemistry building during his first visit to Lamont, he remarked that it was a bit of a pigsty, meaning worn-out. This hurt. But the dream occurred to me that he might help finance a new building to replace our 50-year-old one built on the cheap. I never mentioned this dream to Gary. Three years later, I got a call from him saying that he was aware of this need and would help to secure the building. After some serious bumps in negotiations with Columbia, Gary agreed to finance half of a new building. As the architects (Payette) and the contractor (Torcon) did fantastic jobs, I now do my work in what we think of as a palace. Unfortunately, Gary was not able to see his creation for he died before it was completed.

During much of the time Gary was doing all these good things for us, he was also fighting cancer. Perhaps as a goodbye to his closest confidants, Richard Alley, Philip Conkling, George Denton and me, he arranged for a two-week tour of southern Greenland. We stayed aboard *Turmoil* and took daily helicopter flights over the fiords, icebergs, steep-cut mountains. I have never experienced such beauty. I particularly remember a Sunday morning when we were taken to the ruins of Erik the Red's Hvalsey Cathedral. Made of rough-hewn basalt blocks, it was about the size of an average house. The roof was gone, but in the wall at one end was what was once its equivalent of a 'rose' window. We sat in the grass absorbing the morning sun. In front of us was a stretch of open water. We learned that the last wedding was held in the cathedral in 1409 A.D.

I saw Gary only once after that. It was in May 2006 at the grand opening of the youth center he created in the South Chicago neighborhood where he had grown up. To the residents of this desperately poor area, the Gary Comer Youth Center must have stood out like a Taj Mahal. The ceremony was attended by a host of important guests including Chicago's Mayor Daley. Gary arrived in a large maroon van equipped for his wheelchair. He appeared to be extremely weak, but nevertheless was able to read a well-thought-out speech. A few months later on October 4th he was no more.

Gone but hardly forgotten. All of us whom he touched remember him as a wonderful man who had his eye not only on the Earth's climate future, but also on the future of our nation's children. If only those fortunate enough to amass great wealth were as thoughtful as he was.

Dear Dr. Broecker:

I am interested in doing something constructive to further the World's understanding of climate change. Currently I'm supporting some science on the subject but am looking for larger ideas of things that can be done that will make a difference. Since sailing through an ice-free Northwest Passage last summer I have been reading everything I can find (and understand) on the subject. Whenever I ping the ocean's data base, your name invariably comes up.

The question is, would you be willing to spend some time counseling with me on things you see that need to be done and that the Government is not likely to do in a timely manner? I could meet on your turf, at my farm, aboard my boat—no one from the development office, just you and me.

Sincerely Yours,

Gary Comer

Above is the letter that started it all. I received it in mid-April, 2002. A week later, he flew to Teterboro Airport and we met the next morning for breakfast at the Clinton Inn in Tenafly, NJ.



Gary Comer (right) sitting beside my long-time friend George Kukla. The event was a ‘pignic’ held by chance on the day of Comer’s first visit to Lamont.



The Gary Comer Geochemistry Building. My spacious office projects out above the main entrance.



Gary's *Turmoil*. Shaped like a trawler, it has a luxurious interior.

References

Denton, G.H., R.B. Alley, G.C. Comer, and W.S. Broecker (2005), The Role of Seasonality in Abrupt Climate Change, *Quaternary Science Reviews*, 24, 1159-1182.

Conkling, P., R. Alley, W. Broecker, and G. Denton (2011), *The Fate of Greenland*, 219 pp., MIT Press.

Kelly, M., T. G. Fisher, T. V. Lowell, P. J. Barnett, and R. Schwartz (2016), ^{10}Be ages of flood deposits west of Lake Nipigon, Ontario: evidence for eastward meltwater drainage during the early Holocene Epoch, *Can. J. Earth Sci.*, 53, 1-10, [dx.doi.org/10.1139/cjes-2015-0135](https://doi.org/10.1139/cjes-2015-0135).

Chapter 19

Fossil Fuel CO₂

As a geochemist interested in the Earth's carbon cycle, about the time I received my PhD degree, I was excited to learn that Charles David Keeling had established an atmospheric CO₂ monitoring station high on Hawaii's extinct Mauna Loa volcano. Surprisingly, prior to this, measurements of atmospheric CO₂ scattered over a range of 5 percent. In the absence of an instrument which could make continuous measurements with an accuracy of 0.1 percent, it was not possible to track buildup of the CO₂ released by the burning of coal, petroleum and natural gas. Keeling was the man for the job. He kept the Mauna Loa device operating year after year without a glitch. He was also able to keep it funded despite the criticism that the National Science Foundation shouldn't be funding a monitoring effort. When NOAA was created in 2002, they put their support behind the effort. Trusting no one, Keeling kept an eye on this operation until his death in 2005.

Keeling's record soon made clear that a little more than half of the fossil fuel CO₂ was remaining in the atmosphere. Hence the remainder must be being taken up by the ocean and perhaps by the terrestrial biosphere. We had ways to assess the ocean's uptake, but not the biosphere's. So the only way to get at the biosphere's contribution was to establish the difference between the amount of fossil fuel CO₂ produced and the amount stored in the atmosphere and ocean. Several groups dug in, attempting to estimate the ocean's contribution. We all used simple one-dimensional models calibrated by the distribution of the extra radiocarbon produced by testing hydrogen bombs. The answer turned out to be that roughly half of that missing CO₂ from the atmosphere was being taken up by the ocean.

This led to the search for what we called the 'missing sink'. We oceanographers claimed that the remaining quarter was being taken up by the terrestrial biosphere. Following the lead of George Woodwell, a group of ecologists howled "impossible". They claimed that as the result of forest cutting, the amount of carbon stored on land was decreasing. Woodwell's intuition told him that in addition, pollutants were decreasing the productivity of the terrestrial biosphere.

Their solution was to claim that the ocean must be taking up a lot more CO₂ than indicated by our simple models.

I was senior author on a paper published in *Science* in 1979 in which we claimed that losses by forest cutting were more than offset by fertilization with manmade CO₂ and NH₃. With time, the Woodwell group's initial estimate of the rate of forest cutting came way down. Further, three-dimensional ocean models confirmed our box-model estimates. The atmosphere has been accumulating 57 percent of the CO₂ produced by fossil fuel burning. About half of the remaining 43 percent is going into the ocean and half into the terrestrial biosphere. As the ocean uptake estimate is subject to sizable uncertainties, a better way to put it is that the ocean is taking up 22 ± 5 percent and the terrestrial biosphere the remainder.

David Keeling's son, Ralph, developed an approach which made it clear that despite large-scale deforestation, the terrestrial biosphere was packing away more carbon than was being lost. He did this by developing the means to monitor the decline of the atmosphere's O₂ content. What he found was that the decrease in the O₂ content was less than that generated by the burning of fossil fuels. Hence, the biosphere must be producing more O₂ than it was losing to the oxidation of the cut-down forests.

In 1975, I was struck by the absence of any evidence that the Earth was warming. There were year to year fluctuations of a couple of tenths of a degree, but no significant upward trend. A few years earlier, an oxygen isotope record for the Camp Century ice core was published. Willi Dansgaard, a Dane, produced this record and showed that much of the variance in the last 1000 years could be explained by a combination of 80- and 180-year cycles. This record served as a proxy for air temperature over Greenland. Guessing that it might also be a stand-in for global temperature, I postulated that the lack of warming was being countered by a natural cooling. Further, if the pattern observed by Dansgaard was extrapolated forward in time, then we were due for a switch from a natural cooling to a natural warming. If so, nature would join forces with the ongoing fossil fuel CO₂ warming. My *Science* paper was published in 1975. In 1976, the planet began a warming which continues today.

But I'm embarrassed to admit that I was a very lucky puppy, for it turns out that my assumption that the Camp Century oxygen isotope record serves as a proxy for global temperature was incorrect. Rather, it is closer to a record for a regional temperature change associated with what is called the North Atlantic Multidecadal Oscillation. What appears to have happened is that in 1976-1977 the pattern of circulation in the Pacific Ocean's thermocline underwent a first order change. This shows up as a decrease in the strength of upwelling in the eastern equatorial Pacific, a northward penetration of warm species along the west coast of North America, a cooling in the South Pacific, and a jump in the rainfall in the Argentine Pampas. While we don't know why this reorganization initiated a warming trend, it likely has something to do with the heat budget of the Pacific Ocean.

In 1998, I attended a meeting called "Canada 2020". It was held near Ottawa. Its purpose was to consider the problems and opportunities the first two decades of the 21st century would present. Of course, one of the topics was the actions that should be taken to deal with ever increasing amounts of CO₂ produced by fossil fuel burning. I took particular interest in a short talk given by a physicist named Klaus Lackner, from Los Alamos National Laboratory (where the atomic bomb had been invented). Speaking with a slight German accent, he stressed the need to develop the means to capture and store CO₂. He went on to describe a storage scheme he and his colleagues were exploring. It involved mining ultrabasic rock and using the magnesium it contained to convert the CO₂ to solid form (i.e., MgCO₃). I was pleased to hear that our National Labs were giving the CO₂ problem attention. But the idea of mining and dissolving rock seemed to me to be an impractical way to go about it. A quick calculation indicated that roughly one cubic kilometer of rock per year would be needed to store the then annual CO₂ production. Today it would be two cubic kilometers.

It was a few years later that I encountered Lackner again. At the time, I was helping the Columbia group who had taken charge of Biosphere 2. Lackner was also intrigued by the research opportunities offered by this air-tight structure. I asked him how his CO₂ storage

research was progressing. He said he was attempting to put together a consortium of coal mining companies to build a pilot plant. Despite Klaus' efforts, this initiative faltered and then died.

He told me he was also working on a means to pull CO₂ back out of the atmosphere. He called it 'air capture'. He was convinced it was a necessary adjunct to what is referred to as 'stack capture'. He pointed out that it could be used to capture the 65 percent of fossil fuel CO₂ that isn't released through the stacks of electrical power plants (i.e., that from homes, autos, industry,...). Also, the air capture sites would be located in wastelands close to where the CO₂ would be stored. Air capture would avoid the creation of an extensive network of pipelines necessary to transport the captured CO₂ well away from urban areas. Further, he pointed out that the energy cost didn't scale with the CO₂ concentration (1×10^{-1} atm for stacks and 4×10^{-3} atm for air). Rather, it scaled with square root of the concentration. Further, in the case of stack capture, one would want to pull at least 90 percent of the CO₂ out of the smoke. For air capture, the optimum would be more like 35 percent. Taken together, all these factors suggested that air capture was competitive with stack capture. He also pointed out that the future transition from fossil fuel energy to renewable (and perhaps nuclear) energy would lead to a phase-out of coal burning plants. This being the case, why spend large sums of money to equip existing ones with the elaborate stack capture apparatus when they would likely be abandoned.

The more I learned about Lackner, the more I realized that he had a more powerful intellect than anyone I had known. Further, he was working on something I felt was an essential component of any long-term strategy for dealing with fossil fuel CO₂. Sooner or later, the CO₂ added to the atmosphere will have to be removed. For this reason, I decided that I would do everything I could to help him in his endeavors.

While in one sense Los Alamos was an ideal place for Lackner to conduct his research, in another way it was the wrong place. He had been promoted to Associate Director and was being sucked into ongoing espionage investigations. As others of my Columbia colleagues shared my views, we began a campaign to hire him. It took some doing because he had to be given tenure. The problem was that as part of the theoretical division at Los Alamos, almost everything

Lackner did was classified. Hence, his publication record was thin. But we prevailed and Lackner became a Professor in Columbia's newly created Earth and Environmental Engineering Department. He arrived in 2001 about a week before the 9-11 disaster.

Soon after his arrival, George Rupp retired as Columbia's President. Lee Bollinger, who took his place, was astonished that Columbia had taken on the responsibility for operating a research and teaching program 3000 miles away at Biosphere 2 in Oracle, Arizona. He considered it a bad idea and decided to back out of the contract with Ed Bass, the son of a very wealthy Texas oilman. Although I had put a big effort into this program, I agreed that for financial reasons both the science and education programs we had created at Biosphere 2 were in jeopardy.

The demise of Columbia's Biosphere 2 operation turned out to have a silver lining. We had hired Allen Wright, a very talented engineer who had given up operating submersibles in Hawaii and moved to Tucson to be close to his aging parents. I realized that he would be a perfect match for Lackner. I suggested that they start a company, based in Tucson, to develop an air capture device. I teased Allen saying that the Wright brothers had developed the first device to add CO₂ directly to the atmosphere, so another set of Wright brothers could develop the first device to remove CO₂ from the atmosphere. Allen's first reaction was "Sure Wally, but where will we get the money?" I told him about my new friend, Gary Comer, and his concern about the consequences of global warming.

So, a meeting was arranged: Lackner, Wright, (and his brother) and I met with Gary Comer and Bill Schleicher (administrator of the Comer Science and Education Foundation) at the private terminal at Teterboro Airport. The pitch was for Gary to put up 6 million dollars in venture capital to finance the company. After Gary agreed, Schleicher commented, "This is not venture capital, it's adventure capital."

So GRT (General Research Technologies) was born. Originally it was housed in Allen's brother's engineering firm, and then in one of Tucson's industrial parks. The first attempt involved the use of sodium hydroxide to capture the CO₂. In the original device it ran down a

series of baffles. But as some of it was carried away by the wind (expensive to replace and destructive to the surroundings) and as too much energy was required to free the captured CO₂, this approach was abandoned. Meanwhile, Allen learned of a commercial plastic peppered with solid amine islands. It was marketed for water purification. As amines pick up CO₂, Allen and Klaus gave it a try. They were amazed to find that it not only rapidly absorbed CO₂ but when it was dipped in water or treated with steam, the CO₂ was released. It took Klaus a while to figure out what was going on. As it is complicated, I won't attempt to explain it here. One advantage was that removal of the CO₂ from the plastic required five times less energy than removal from sodium hydroxide. Also, as a solid, it couldn't be carried away by the wind. Finally, exposure to a year of sun, wind, and rain did not lead to a deterioration of its CO₂ uptake capacity.

Having found the ideal absorbent, Allen and Klaus began to ponder how it would be deployed. Right away Klaus decided on modules that could be manufactured like automobiles, on assembly lines. Each unit would take up one ton of CO₂ per day. As the first phase of this research was complete and funding was almost gone, early in the summer of 2008, Klaus hit the road in search of financial backing for the next phase. He negotiated with investors throughout the country. But alas, the economic bubble burst and venture capital dried up. Out of funds, Klaus and Allen were forced to close down GRT. Out of a job, Allen moved to New York and joined Klaus at Columbia. Fueled by funds from the Lenfest Foundation, they were able to learn a lot more about the physical chemistry of the amine-loaded plastic. However, additional funds for creating a prototype module didn't materialize.

It occurred to me that Klaus might be able to move forward faster if he were to relocate to Arizona State University, again working in the southwest. During his years at Columbia, Michael Crow, the current President of Arizona State University, had become acquainted with Klaus' research on air capture and also with his genius. I approached Pres. Crow with the suggestion that Klaus might be movable. He set up a meeting which was attended by Jeff Severinghaus and me as advocates of air capture, and Klaus Lackner, the potential hire. It worked. For two years now Lackner and Wright have been hard at work developing a prototype module at ASU. Klaus

has been able to avoid the many administrative responsibilities he had been saddled with at Columbia and he has better facilities and funding. So things are now moving. Perhaps my colleagues here at Columbia view me as somewhat of a traitor. So be it.

I was also able to help in launching a project to determine whether disposal of CO₂ in basalt is feasible. In 2006, friends at the University of Iceland invited me to give a lecture. For some reason, they made it a big deal and invited Ragnar Grimsson, President of Iceland, to attend. I stressed how serious a problem fossil fuel CO₂ production was becoming and the importance of learning to capture and store CO₂. In private discussions with Grimsson, I mentioned Lackner's plan to construct modules for air capture. He promised to put the first one 'off the line' on display in downtown Reykjavik. When I mentioned storage in basalt, he encouraged me to help arrange a joint meeting between scientists from Columbia and Iceland Universities, with the people from Reykjavik Energy. There was no problem doing this for everyone was eager. Eight years later, as I am writing this book, a paper appeared in *Science*. Two of my colleagues, Martin Stute and Juerg Matter, demonstrated that within 100 days, the CO₂ which the group had pumped 500 meters down into Iceland basalt had been precipitated as carbonate minerals (CaCO₃, and possibly MgCO₃ and FeCO₃). They were able to show this because the CO₂ they added was tagged with ¹⁴C and was also mixed with a non-reactive tracer gas (SF₆). By monitoring the sampling well Matter and Stute showed that the ¹⁴C to SF₆ ratio dropped with time by a factor of more than ten thus demonstrating that at least 90 percent of the CO₂ had been mineralized. The advantage of basalt storage over sandstone storage is that basalt contains the Ca, Mg and Fe needed to mineralize CO₂. As sandstone is devoid of these cations, the CO₂ remains CO₂ and hence is subject to long-term leakage. Our University of Iceland cooperators obtained a host of details on the chemical changes which occurred. It should be mentioned that without Reykjavik Energy engineering skills and financial support, this project would never have happened.

Of course the solution to the CO₂ problem is to abandon fossil fuel energy and replace it with solar, wind, and nuclear energy. But this will take many decades to accomplish. In the

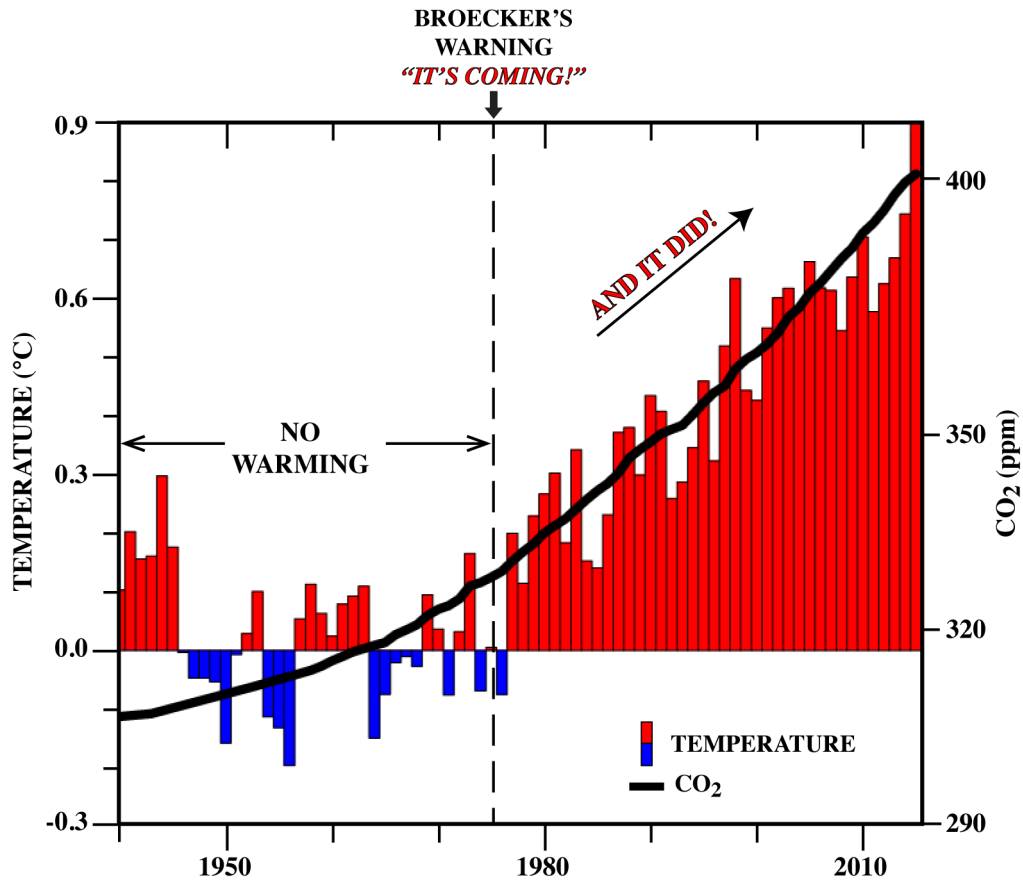
meantime the CO₂ content for the atmosphere will continue to climb. By the time a transition is complete, it will very likely have risen above 500 ppm. Although the ocean will eventually take up much of this CO₂, it will do so only on the time scale of centuries. Meanwhile, melting of the Greenland and Antarctic ice caps will create a several-meter rise in sea level.

One might ask, won't the extra CO₂ in the atmosphere be captured and stored? Likely yes, but doing so will be a huge and very expensive enterprise. Lackner estimates that each of his one-ton-a-day modules will, when mass produced, cost about as much as an automobile. In order to match today's CO₂ rate of increase would require 100 million such units. To bring down the CO₂ content 2 ppm a year would require an additional 100 million modules (to bring it down 4 ppm per year would require 400 million modules). Clearly removal will not only be expensive, but likely it will take fifty or so years to bring CO₂ down to its pre-industrial level. Meantime, we will have to cope with the myriad of consequences of the warming.

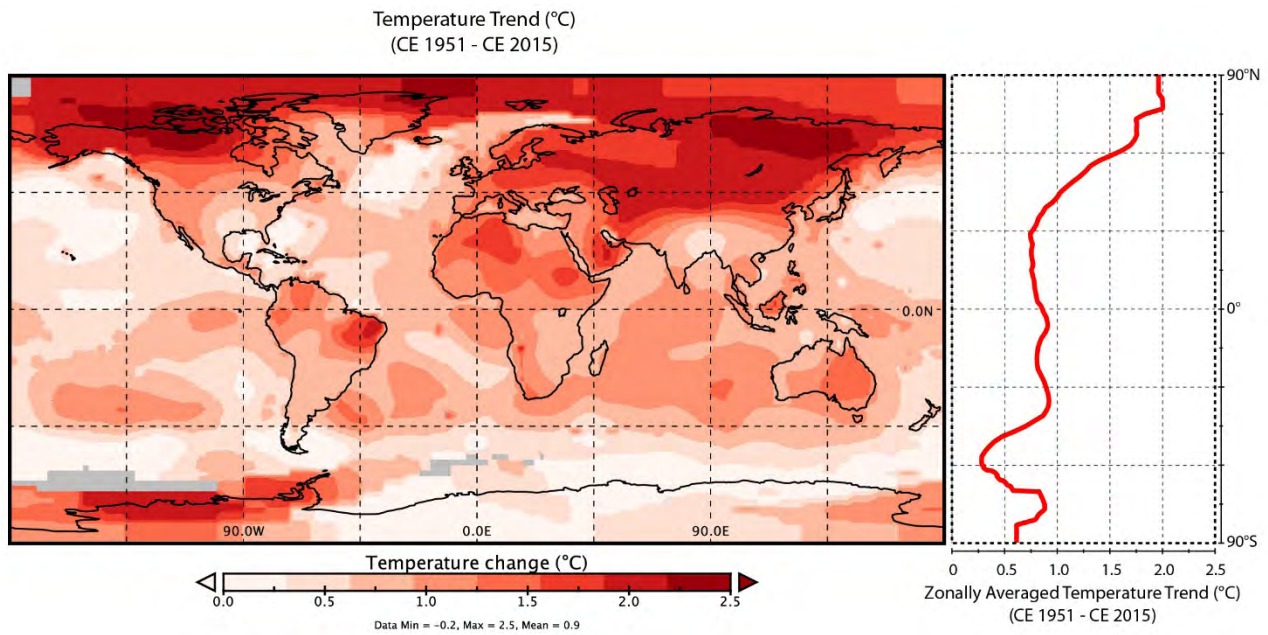
There is however, a Band-Aid that could be applied. It involves injecting SO₂ into the stratosphere. Once there, it is rapidly oxidized to tiny H₂SO₄ aerosols. These aerosols would back-scatter about 10 percent of the sunlight that strikes them. As doubling of atmospheric CO₂ content has a heating impact the same as dialing up the Sun's output by about two percent, to counter the warming, 20 percent of the Sun's rays would have to hit aerosols. This would require the input of 30 million tons of SO₂. Further, as the aerosols would remain in the stratosphere for one or two years, the dose would have to be repeated over and over.

Sounds scary. Yes it is. Sounds expensive. Yes, but the annual cost would be less than a tenth that for lowering the CO₂ content 2 ppm per year. Further, the cooling would occur within a decade. Deciding whether to go the Band-Aid route will require the most complex decision mankind has ever faced. Further, the consequences of its implementation could become a source of global discord. But, if our planet overheats, the temptation to use SO₂ to cool it will be enormous.

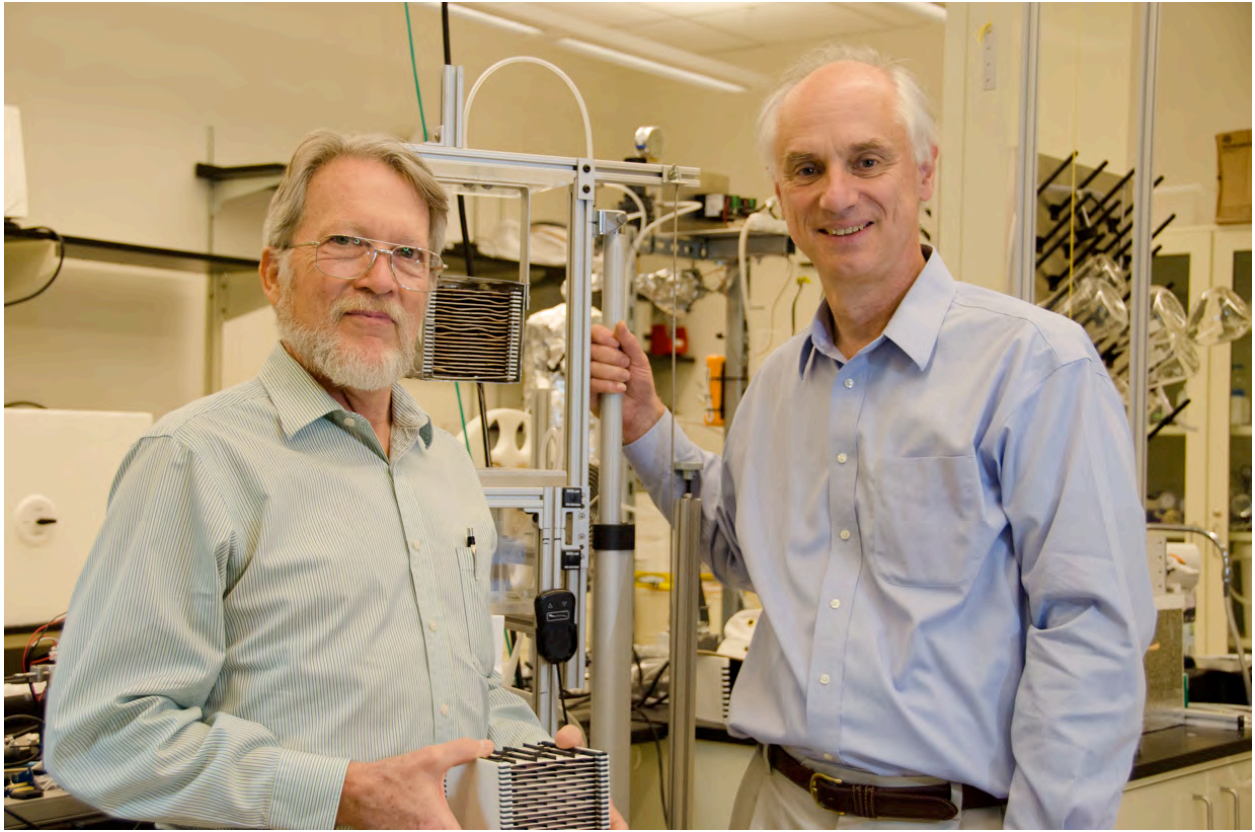
So I end this book warning that the world is on the brink of falling into the clutches of what I've called 'The Great Climate Beast.'



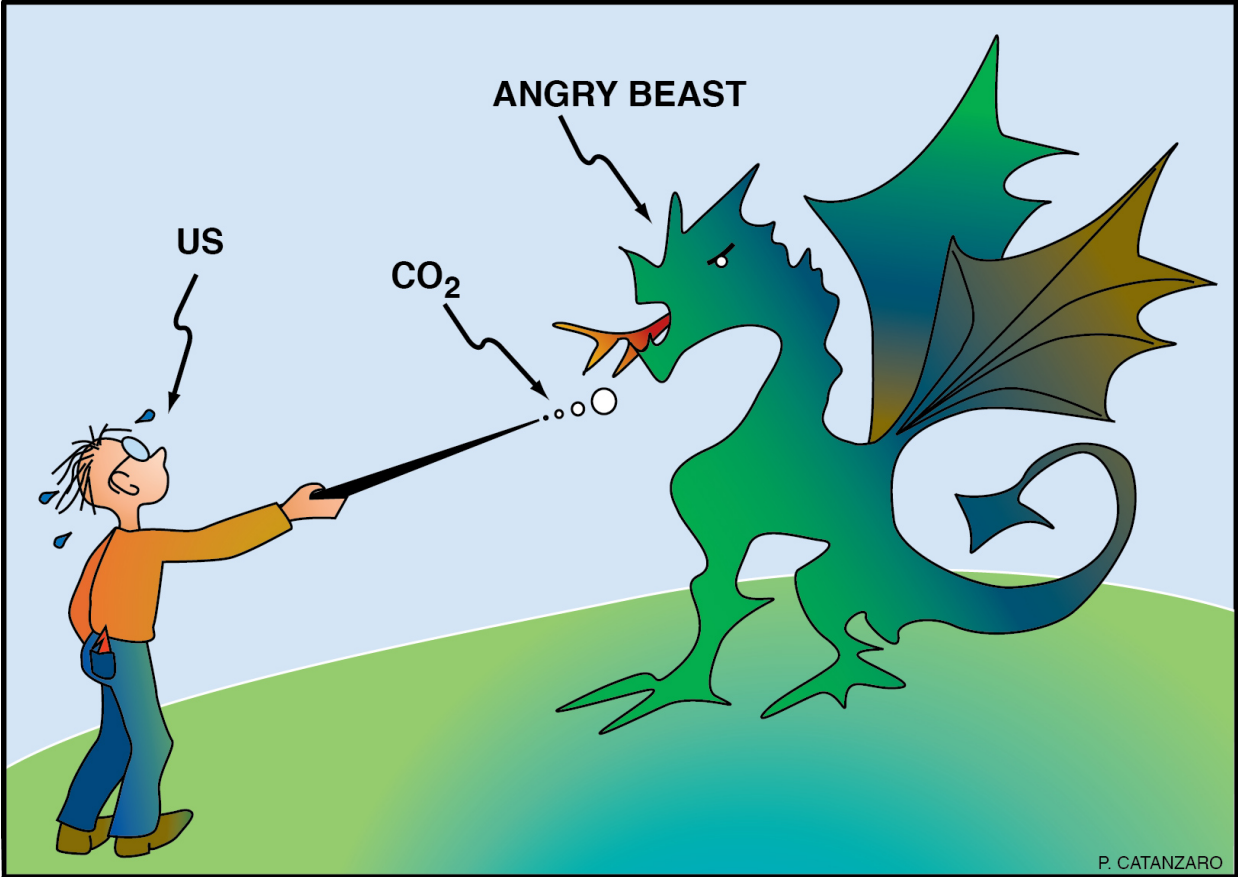
In 1975 in a paper published in *Science*, the line represents the atmospheric CO₂ content, and the bars the departure in global temperature from its pre-1950 mean. I predicted that we were on the brink of a pronounced global warming. My prediction was dead on. But alas, its basis has proven to be incorrect.



Not only is the world warming, the Northern Hemisphere is warming far more than the Southern Hemisphere. As a consequence, the planet's rain belts are being shifted to the north. The western United States will be strongly impacted by this shift. It will become even drier.



The heroes of CO₂ air-capture, Klaus Lackner (right) and Allen Wright (left).



The Angry Climate Beast



Yours truly at 83!

References

- Broecker, W.S. (1975), Climatic change: Are we on the brink of a pronounced global warming? *Science*, 189, 460-463.
- Broecker, W.S., T. Takahashi, H. Simpson, and T. Peng (1979), Fate of fossil fuel carbon dioxide and the global carbon budget, *Science*, 206, 409-418.
- Lackner, K.S., S. Brennan, J.M. Matter, A-HA. Park, A. Wright, and B. van der Zwaan (2012), The urgency of the development of CO₂ capture from ambient air, *PNAS*. 109 (33), 13,156-13162, doi: 10.1073/pnas.1108765109.
- Broecker W. (2013), Does air capture constitute a viable backstop against a bad CO₂ trip? *Elem. Sci. Anth. 1*: 000009 doi: 10.12952/journal.elementa.000009.
- Matter, J.M., M. Stute, S.O. Snaebjornsdottir, E.H. Oelkers, S.R. Gislason, E.S. Aradottir, B. Sigfusson, I. Gunnarsson, H. Sigurdardottir, E. Gunnlaugsson, G. Axelsson, H.A. Alfredsson, D. Wolff-Boenisch, K. Mesfin, D.F. de la Reguera Taya, J. Hall, K. Dideriksen, and W.S. Broecker (2016), Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions, *Science*, 352/6291, 1312-1314, doi: 10.1126/science.aad8132.

Appendices

	Page
1. Awards	269
2. Honorary Doctorates and Memberships	270
3. Comer Mentors I Selected	271
4. PhD Students.....	272
5. Books	274
6. Journal Articles.....	276

AWARDS

- 2014 Distinguished Achievement Award, Columbia University
- 2013 National Institute of Social Sciences Medalist
- 2009 BBVA Frontiers of Knowledge Award
- 2008 Balzan Prize
- 2008 Benjamin Franklin Medal
- 2006 Crafoord Prize
- 2002 Tyler Prize
- 2002 Arthur L. Day Prize
- 1999 State of Nevada Science Medal
- 1997 Distinguished Alumni Award, Oak Park High School
- 1996 Blue Planet Prize
- 1996 National Medal of Science
- 1995 Roger Revelle Medal
- 1990 Wollaston Medal
- 1990 Joseph Priestly Award
- 1987 Vetlesen Prize
- 1986 Alexander Agassiz Medal
- 1986 V. M. Goldschmidt Award
- 1985 A.G. Huntsman Award
- 1984 Arthur L. Day Medal
- 1982 Urey Medal
- 1979 Maurice W. Ewing Medal

HONORARY DOCTORATES AND MEMBERSHIPS

HONORARY DOCTORATES

- 2015 Harvard University
- 2015 Oxford University
- 2015 Waterloo University
- 2009 Cambridge University
- 2008 Southern Methodist University
- 2004 Penn State University

MEMBERSHIPS

- 2015 The Philosophical Society
- 2007 The Royal Society, Foreign Member, United Kingdom
- 1992 Fellow, European Geophysical Union
- 1982 Fellow, von Humboldt Society
- 1979 National Academy of Sciences
- 1976 Fellow, American Geophysical Union
- 1976 Fellow, American Academy of Arts and Sciences

LIST OF THE 25 COMER MENTORS I SELECTED

Name	University
Jess Adkins	California Institute of Technology
Richard Alley	Pennsylvania State University
Helge Arz	Leibniz-Institute for Baltic Sea Research, Warnemünde Germany
Edouard Bard	Collège de France, Laboratory located in Aix- en-Provence, France
David Batisti	University of Washington
Michael Bender	Princeton University
Ed Brook	Oregon State University
Isabel Cachs	Universitat de Barcelona, Spain
John Chiang	University of California, Berkeley
George Denton	University of Maine
Larry Edwards	University of Minnesota
Harry Elderfield	University of Cambridge
Graham Farquhar	Australian National University
Sidney Hemming	Columbia University
Gideon Henderson	Oxford University
Chris Hendy	University of Waikato, New Zealand
Ralph Keeling	University of California, San Diego
Jean Lynch-Stieglitz	Georgia Institute of Technology
Jochem Marotzke	Max Planck, Hamburg, Germany
Jerry McManus	Woods Hole Oceanographic
Ulysses Ninnemann	University of Bergen, Norway
Stefan Rahmstorf	Potsdam Institute, Germany
Julian Sachs	University of Washington
Jeff Severinghaus	University of California, San Diego
Lonnie Thompson	Ohio State University

PHDS MENTORED BY BROECKER

First Name	Last Name	Date of PhD
Edwin	Olson	1963
Aaron	Kaufman	1964
David L.	Thurber	1964
Teh-Lung	Ku	1966
Dennis M.	Adler	1967
Thomas F.	Anderson	1967
Yuan Hui	Li	1967
Harry James	Simpson Jr.	1970
Jan	Van Donk	1970
Michael Leslie	Bender	1971
Kenneth M.	Wolgemuth	1972
Tsung-Hung	Peng	1973
Steve R.	Emerson	1974
Darlene S.	Richardson	1974
Raymond H.	Hesslein	1976
John	Wehmiller	1976
Paul D.	Quay	1977
Thomas	Torgersen	1977
George W.	Kipphut	1978
Jorge L.	Sarmiento	1978
Peter M.	Bower	1981
Robert B.	Cook	1981
David C.	Kadko	1981
Michael	Amdurer	1983

PHDS MENTORED BY BROECKER (continued)

John Robert	Toggweiler	1983
James W.C.	White	1983
Andrew Leslie	Herczeg	1985
Sherry Line	Schiff	1986
Marilyn R.	Bucholtz	1987
Richard Paul	Cember	1988
Susan Elizabeth	Trumbore	1989
Yong	Lao	1991
John Frederick	Crusius	1992
Kevin Geyer	Harrison	1994
Robert Horacio	Gwiazda	1995
Jeffrey Peck	Severinghaus	1995
Jo Chiu-Fang	Lin	1996
Jerry F.	McManus	1997
Abhijit	Sanyal	1997
Randy Lee	Rutberg	2000
Synte Letitia	Peacock	2001
Arthur Mitchell	Greene	2002
Sean Michael	Higgins	2002
Allegra Nicole	LeGrande	2007
William David	McGee	2010
Yoni	Goldsmith	In 2017
Randal	Koster	*MIT 1988
Fritz	Zaucker	*Heidelberg 1992

*I supervised their theses.

BOOKS¹

- 1) **Chemical Equilibria in the Earth**, W.S. Broecker and V. Oversby, McGraw-Hill, NY, 1971.
An introduction to thermodynamics and its application to chemical and isotopic systems in the earth sciences.
- 2) **Chemical Oceanography**, W.S. Broecker, Harcourt Brace Jovanovich, Inc., NY, 1974.
This is a summary of the first-order chemical processes taking place within the sea that affect its chemistry.
- 3) **Tracers in the Sea**, W.S. Broecker and T.-H. Peng, Eldigio Press, NY, 1982.
A book covering ocean chemical cycles with particular emphasis on carbon and its fellow bioutilized elements. This book is based on results of the 1970s GEOSECS surveys.
- 4) **How to Build a Habitable Planet**, W.S. Broecker, Eldigio Press, NY, 1985.
(Japanese, German translations, 1993, Chinese translation, 1998)
An outgrowth of an undergraduate course. The approach is to trace the development of the Earth from its roots in the Big Bang to its future in man's hands.
- 5) **The Glacial World According to Wally**, W.S. Broecker, Eldigio Press, NY, 1992; Second Revised Edition, 1995; Third Revised Edition, 2002.
This is a book on glacial climates used to accompany his course on climate change at Columbia. It introduces the student to the basics of paleoclimate reconstruction of the Quaternary ice ages.
- 6) **Greenhouse Puzzles**, W.S. Broecker and T.-H. Peng, Eldigio Press, NY, 1992; Revised Edition, 1998.
This book treats three major questions: 1) How has fossil fuel CO₂ been partitioned among the atmosphere, ocean and terrestrial biosphere? 2) What caused the lowering of atmospheric CO₂ during glacial times? 3) What controlled the CO₂ content of the atmosphere over the last several hundred-million years?
- 7) **Fossil Fuel CO₂ and the Angry Climate Beast**, W.S. Broecker, Eldigio Press, NY, 2003.
Created as a companion to a Frontiers of Science lecture series at Columbia, this book discusses the fate and climatic consequences of the CO₂ produced by burning fossil fuels, and the effect tripled atmospheric CO₂ may have on our climate. It addresses the limitation of climate models, and looks at different approaches to reducing atmospheric carbon.
- 8) **The Role of the Ocean in Climate, Yesterday, Today and Tomorrow**, W.S. Broecker, Eldigio Press, NY, 2005.
This book presents the big picture regarding two subjects which dominate thinking with regard to our planet's climate during glacial times: the role of the Atlantic Ocean's conveyor circulation in the abrupt reorganizations of the Earth's climate system, and the cause for the large drop in the atmospheric CO₂ content which accompanies each major

¹ Several of these books were self-published under the label ELDIGIO PRESS, an acronym for LDGO (Lamont-Doherty Geological Observatory). The name of our laboratory has been changed to Lamont-Doherty Earth Observatory. A number of these books are available at no cost on-line.

glaciation. These same two subjects lie at the core of attempts to come to grips with man-induced global warming.

- 9) **A Business Executive's Guide to Global Warming**, W.S. Broecker, Eldigio Press, NY, 2005; Revised Edition, 2009.
This is a high level summary of the scientific evidence, effects, and possible responses to the problem of global warming. Required reading for decision and policy makers, and businessmen.
- 10) **Fixing Climate: What Past Climate Changes Reveal about the Current threat – and How to Counter It**, W.S. Broecker and R. Kunzig, Hill and Wang (a Division of Farrar, Straus, and Giroux Books), April 2008.
Deals with the consequences of global warming and the new technologies providing some hope for the future. *(This book was written entirely by Rob Kunzig. It was commissioned by philanthropist, Gary Comer. The publisher, Hill and Wang, refused to publish it unless Broecker was senior author. Under the circumstances Broecker gave in to this unfair demand. Fortunately, a British publisher (Profile Books) put out a paperback edition under the proper authorship (i.e., Kunzig and Broecker).*
- 11) **The Great Ocean Conveyor: Discovering the Trigger for Abrupt Climate Change**, W.S. Broecker, Princeton University Press, Princeton, 2010.
This book deals with the discovery of the link between ocean circulation and climate change. It introduces readers to the science of abrupt climate change while providing a first-hand account of the field's history and development.
- 12) **The Fate of Greenland: Lessons from Abrupt Climate Change**, Conkling, P., R. Alley, W. Broecker, and G. Denton, 291 pgs., MIT Press, 2011.
A documentation of Greenland's warming and investigation of the episodes in Greenland's climate history for clues about what happens when climate change is abrupt rather than gradual. Illustrated with photographs taken by Land's End founder, Gary Comer.
- 13) **The Carbon Cycle and Climate Change: Memoirs of my 60 Years in Science**, W.S. Broecker, Geochemical Perspectives, 2012.
Science mixed with personal experience.
- 14) **How to Build a Habitable Planet: The Story of Earth from the Big Bang to Humankind**. C.H. Langmuir and W.S. Broecker, 670 pgs., Princeton University Press, 2012.
An introduction to the origin and evolution of Earth, from the Big Bang through the rise of human civilization. It provides an understanding of Earth in its broadest context, as well as a greater appreciation of its possibly rare ability to sustain life over geologic time. *(This book was inspired by my much shorter 1987 book with the same title. However, it was written entirely by Charlie Langmuir using bits of the original. So, in a sense, Broecker is an honorary author.)*
- 15) **What Drives Glacial Cycles?** W. Broecker, Eldigio Press, NY, 2015.
Based on the observations that Southern Hemisphere mountain glaciers reached their LGM maximum at the same time as those in the Northern Hemisphere and that the snowline lowerings are about the same in both hemispheres, a case is made that orbital cycles somehow drive the atmosphere's CO₂ content and CO₂ drives glaciers.
- 16) **Wally's Carbon World**, Wally Broecker, Eldigio Press, NY, 2015.
The major climate changes experienced by the Earth over the last 4.5 billion years appear to involve changes in the atmosphere's greenhouse power. Prime examples are:

compensation for the weak young Sun, the snowball Earth episodes, the Paleocene-Eocene thermal maximum, the cooling over the last 50 million years and the glacial cycles of the last million years. We are now engaged in the world's greatest geophysical experiment, i.e., the addition of fossil fuel CO₂ to the atmosphere.

- 17) **A Geochemist in his Garden of Eden**, Wally Broecker, Eldigio Press, NY, 2016.
An autobiography of my scientific career at the Lamont-Doherty Earth Observatory.

JOURNAL ARTICLES

1953

- 1) Kulp, J.L., W.S. Broecker and W.R. Eckelmann, *Age determination of uranium minerals by the Pb-210 method*, Nucleonics, 11:191:21, 1953.
- 2) Kulp, J.L., G.L. Bates, and W.S. Broecker, *Present status of the lead method of age determination of uranium minerals by the Pb-210 method*, Nucleonics, 11:191:21, 1953.

1954

- 3) Grosse, A.V., A.D. Kirshenbaum, J.L. Kulp, and W.S. Broecker, *The natural tritium content of atmospheric hydrogen*, Phys. Rev., 93:250, 1954.

1956

- 4) Broecker, W.S., and J.L. Kulp, *The radiocarbon method of age determination*, Amer. Antiquity, 22:1-11, 1956.
- 5) Broecker, W.S., J.L. Kulp, and C.S. Tucek, *Lamont natural radiocarbon measurements III*, Science, 124:154-165, 1956.
- 6) Ericson, D.B., Broecker, W.S., J.L. Kulp and G. Wollin, *Late Pleistocene climates and deep-sea sediments*, Science, 124:3855-389, 1956.
- 7) Carr, Donald R., W.S. Broecker, P. Damon, J.L. Kulp, *The potassium-argon age method, (Chapt.) 16 of Nuclear processes in geologic settings*, Natl. Research Council, Comm. Nuclear Sci., Nuclear Sci. Ser. Rep. no.19, 109-113, 1956.

1957

- 8) Giletti, B. and W.S. Broecker, *A new look at the ocean*, Yale Sci. Mag., May, 1957.
- 9) Broecker, W.S., J.L. Kulp, *Lamont Natural Radiocarbon Measurements IV*, Science, v. 126, no. 3287, 1324-1334, 1957.

1958

- 10) Olson, Edwin A., W.S. Broecker, *Sample contamination and reliability of radiocarbon dates*, N.Y. Acad. Sci. Trans. ser. 2 v. 20, no. 7, p. 593-604, illus., May 1958.

- 11) Broecker, W.S., and Karl Turekian; Bruce Heezen, *The relation of deep sea (Atlantic Ocean) sedimentation rates to variations in climate*, Am. Jour Sci., v. 256, no.7, 503:517, illus., Summer, 1958.
- 12) Broecker, W.S., and P.C. Orr, *Radiocarbon chronology of Lake Lahontan and Lake Bonneville*, Geol. Soc. America Bull. v. 69, no. 8, 1009:1032, illus., Aug. 1958.

1959

- 13) Broecker, W.S., C.S. Tucek, E.A. Olsen, *Radiocarbon analysis of oceanic CO₂*, Intern. J. Appl. Radiation Isotopes, 7:1:8, 1959.
- 14) Broecker, W.S., E.A. Olson, J. Bird, *Radiocarbon measurements on samples of known age*, Nature, 183:1582, 1959.
- 15) Heezen, Bruce C., W.S. Broecker, M. Ewing, R.J. Menzies, *Stagnation of the Cariaco trench (Venezuela) (abs.)*, Int. Oceanog. Cong., 1st, preprints. 99:102, illus., 1959.
- 16) Broecker, W.S., E. Olson, *C 14 dating of cave formations*, Natl. Speleol. Soc. Bull. v. 21, pt. 1,43, Jan., 1959.
- 17) Broecker, W.S., A.F. Walton, *The geochemistry of C 14 in fresh-water systems*, Geochimica et Cosmochimica Acta v. 16., nos. 1-3, 15-38, 200, illus., May, 1959.
- 18) Broecker, W.S., A.F. Walton, *Re-evaluation of the salt chronology of several Great Basin lakes*, Geol. Soc. America Bull. v. 70, no. 5, 601-618, illus., with discussion by J.H. Feth, 637:640, tables, May, 1959.
- 19) Olson, Edwin A., W.S. Broecker, *Lamont natural radiocarbon measurements*, (Pt.) 5, Am. Jour. Sci. v. 257, no. 6, 464, June, 1959.
- 20) Broecker, W.S. and E.A. Olson, *Lamont Radiocarbon Measurements VI**, American Journal of Science Radiocarbon Supplement, **Vol. 1**, pp. 111-132, 1959.
- 21) Broecker, W.S., A. Schulert, E.A. Olson, *Bomb Carbon-14 in Human Beings*, Science, vol. 130, no. 3371, 331:332.
- 22) Broecker, W.S. and A. Walton, *Radiocarbon from Nuclear Tests*, Science, **Vol. 130**, No. 3371, pp. 309-314, August 7, 1959.

1960

- 23) Broecker, W.S., E.A. Olson, P.C. Orr, *Radiocarbon measurements and annual rings in cave formations*, Nature, 185:933-94, 1960.
- 24) Broecker, W.S., M. Ewing, B.C. Heezen, *Evidence for an abrupt change in climate close to 11,000 years ago*, Am. J. Sci., 258:429-448, 1960.
- 25) Eckelmann, W.R., W.S. Broecker, J.L. Kulp, *Half-life of Pb-210*, Physical Rev., 118:698-701, 1960.

- 26) Broecker, W.S., R. Gerard, M. Ewing, B. C. Heezen, *Natural Radiocarbon in the Atlantic Ocean*, J. Geophys. Res., 65:2903-2931, 1960.
- 27) Broecker, W.S., E.A. Olson, *Radiocarbon from nuclear tests II*. *Science*, 132:712-721, 1960.
- 28) Broecker, W.S., *Geochemistry of ocean water*, Am. Geophys. Union Trans. v. 41, no. 2, 259:260, June, 1960.

1961

- 29) Olson, E.A., W.S. Broecker, *Lamont natural radiocarbon measurements VII*, Radiocarbon, 3, 141-175, 1961.
- 30) Olson, E.A., W.S. Broecker, *Lamont natural radiocarbon measurements VIII*, Radiocarbon, 3, 176-204, 1961.
- 31) Broecker, W.S., R.D. Gerard, M. Ewing, B.C. Heezen, *Geochemistry and physics of ocean circulation*, Oceanography, AAAS, 301:322, 1961.
- 32) Broecker, W.S., *Radiocarbon dating of Late Quaternary deposits, South Louisiana: A discussion*, Bull. Geol. Soc. Am. 72:159:162, 1961.
- 33) Broecker, W.S., *Radium-uranium age determinations on marine shells, 3 in 2 problems related to interplanetary matter*, Natl. Acad. Sci., Natl. Research Council Pub. 845 (Nuc. Sci. Ser. Rept. 33) 96-101, illus., 1961.
- 34) Broecker, W.S., *Age determination on marine carbonate based on inequilibrium in the U^{238} decay series*, reprinted from: Report of the VIth International Congress on Quaternary Warsaw. Vol. I: Commission on the Absolute Age of Quaternary Deposits. 1961.

1962

- 35) Broecker, W.S., *The contribution of pressure induced phase changes to glacial rebound*, J. Geophys. Res., 67:4837-4842, 1962.
- 36) Skok, J., W. Chorney, W.S. Broecker, *Uptake of CO₂ roots of xanthium plants*, The Botanical Gazette, 124:118-120, 1962.
- 37) Eckelmann, Walter R., J.R. Allsup, W.S. Broecker, D.W. Whitlock, *Implications of carbon isotopic composition of total organic carbon of some recent sediments and ancient oils*, Am. Assoc. Petroleum Geol., b, v. 46, no. 5, 699:704, illus., 1962.

1963

- 38) Broecker, W.S., *Radioisotopes and large scale oceanic mixing*, THE SEA, v. II, Ch. 4, 88:108, John Wiley and Sons, Ltd., London, 1963.
- 39) Broecker, W.S., *Radiocarbon ages of Antarctic materials*, The Polar Record, 11:472-473, 1963.
- 40) Giffin, C., A. Kaufman, W.S. Broecker, *Delayed coincide counter for the assay of actinon and thoron*, J. Geophys. Res., 68:1749:1757, 1963.

- 41) Broecker, W.S., *A preliminary evaluation of uranium series in equilibrium as a tool for absolute age measurement on marine carbonates*, J. Geophys. Res. 68:2817-2834, 1963.
- 42) Broecker, W.S., W.R. Farrand, *The radiocarbon age of the Two Creeks Forest Bed*, Wisconsin, Bull. Geol. Soc. Am., 74:7955-802, 1963.
- 43) Rocco, G.G., W.S. Broecker, *The vertical distribution of cesium-137 and strontium-90 in the oceans*, J. Geophys. Res., 68:4501-4512, 1963.
- 44) Richards, H.G., W.S. Broecker, *Emerged Holocene South American shorelines*, Science, 141:1044-1045, 1963.
- 45) Broecker, W.S., *$^{14}\text{C}/^{12}\text{C}$ ratios in surface ocean water*, Natl. Acad. Sci., Nat. Res. Council Publ. 1075, 138-149.

1964

- 46) Broecker, W.S., *Radiocarbon dating: A case against the proposed link between river mollusks and soil humus*, Science, 143:596-597, 1964.

1965

- 47) Broecker, W.S., A. Kaufman, *Radiocarbon chronology of Lake Lahontan and Lake Bonneville II*, Bull. Geol. Soc. Am., 76:537-566, 1965.
- 48) Broecker, W.S., D.L. Thurber, *Uranium series dating of corals and oolites from Bahamian and Florida Key limestones*, Science, 149:58-60, 1965. series ages of Pacific atoll coral, Science, 149:55-68, 1965.
- 49) Thurber, D.L., Broecker, W.S., R.L. Blanchard, H.A. Potratz, *Uranium series ages of Pacific atoll coral*, Science, 149:55-68, 1965.
- 50) Broecker, W.S., *Isotope geochemistry and the Pleistocene climatic record*, Quaternary of the U.S., Rev. Vol. VIII INQUA Congress, Boulder, Col., 737:753, 1965.
- 51) Kaufman, A., W.S. Broecker, *Comparison of Th-230 and C-14 ages for carbonate materials from lakes Lahontan and Bonneville*, J. Geophys. Res., 70:4039-4054, 1965.
- 52) Broecker, W.S., *Isotope Geochemistry and the Pleistocene climatic record*, in the Quaternary of the U.S., Princeton Univ. Press, 737:753, 1965.
- 53) Broecker, W.S., *An application of natural radon to problems in ocean circulation, in symposium on diffusion in oceans and fresh waters*, Lamont Geol. Observatory of Columbia Univ., 116:145, 1965.

1966

- 54) Broecker, W.S., *Absolute dating and the astronomical theory of glaciation*, Science, 151:299-304, 1966.
- 55) Ku, T.L., W.S. Broecker, *Atlantic deep-sea stratigraphy: Extension of absolute chronology to 320,000 years*, Science, 151:448-450, 1966.

- 56) Broecker, W.S., *Glacial rebound and the deformation of the shorelines of pro-glacial lakes*, J. Geophys. Res., 71:4777-4783, 1966.
- 57) Broecker, W.S., T. Takahashi, *Calcium carbonate precipitation on the Bahama Banks*, J. Geophys. Res., 71:1575-1602, 1966.
- 58) Broecker, W.S., E.R. Bonebakker, G.G. Rocco, *The vertical distribution of cesium-137 and strontium-90 in the oceans*, 2, J. Geophys. Res., 71:1999-2003, 1966.
- 59) Broecker, W.S., G.G. Rocco, H.L. Volchok, *Strontium-90 fallout: Comparison of rates over ocean and land*, Science, 152:639-640, 1966.
- 60) Broecker, W.S., *Radioisotopes and the rate of mixing across the main thermoclines of the ocean*, J. Geophys. Res., 71:5827-5836, 1966.
- 61) Bender, M.L., T-L Ku, W.S. Broecker, *Manganese nodules--Their evolution*, Science v. 151, no. 3708, 325-328, illus., 1966.
- 62) Broecker, W.S., D.L. Thurber, *Ratio of total CO₂ to calcium in Tertiary and Quaternary oceans*, Geol. Soc. America Spec. paper 87,18-19, 1966.

1967

- 63) Ku, T.L., W.S. Broecker, *Rates of sedimentation in the Arctic Ocean*, 95-104; In: Progress in Oceanography, v.4, Pergamon Press, Oxford and New York, 1967.
- 64) Broecker, W.S., Y.H. Li, J. Cromwell, *Radium-226 and radon-222: Concentration in Atlantic and Pacific Oceans*, Science, 158:1307-1310, 1967.
- 65) Taddeucci, A., W.S. Broecker, D.L. Thurber, *Th-230 dating of volcanic rocks*, Earth Planet. Sci. Lett., 3:338-342, 1967.
- 66) Ku, Teh-Lung, W.S. Broecker, *Uranium, thorium and protactinium in a manganese nodule*, Earth & Planetary Sci. Letters v. 2, no.4, 317-321, 1967.

1968

- 67) Broecker, W.S., *In defense of the astronomical theory of glaciation*, Meteorological Monographs, 8:1339-1411, 1968.
- 68) Broecker, W.S., D.L. Thurber, J. Goddard, T.L. Ku, R.L. Matthews, K.J. Mesolella, *Milankovitch hypothesis supported by precise dating of coral reefs and deep-sea sediments*, Science, 159:297-300, 1968.
- 69) Ku, T.L., W.S. Broecker, N. Opdyke, *Comparison of sedimentation rates measured by paleomagnetic and the ionium methods of age determination*, Earth Planet. Sci. Lett., 4:1-16, 1968.
- 70) Takahashi, T., W.S. Broecker, Y.H. Li, D.L. Thurber, *Chemical and isotopic balances for a meromictic lake*, Limnology and Oceanography, 13: 272-292, 1968.
- 71) Broecker, W.S., J. Cromwell, Y.H. Li, *Rates of vertical eddy diffusion near the ocean floor based on measurements of the distribution of excess ²²²Rn*, Earth & Planetary Sci. Letters, v.5, no. 2, 101:105, 1968.

1969

- 72) Mesolella, K.J., R.K. Matthews, W.S. Broecker, D.L. Thurber, *The astronomical theory of climatic change: Barbados data*, J. Geol. 77:250-274, 1969.
- 73) Ku, T.L., W.S. Broecker, *Radiochemical studies on manganese nodules of deep-sea origin*, Deep Sea Res. 16:625-637, 1969.
- 74) Li, T.Y., T. Takahashi, and W.S. Broecker, *The degree of saturation of a CO₃ in the oceans*, J. Geophys. Res., 74:5507-5525, 1969.
- 75) Broecker, W.S., T.L. Ku, *Caribbean cores P6304-8 and P63044-9: New analysis of absolute chronology*, Science, 166:404-406, 1969.
- 76) Broecker, W.S., R.D. Gerard, *Natural radiocarbon in the Mediterranean Sea*, Limnol. And Oceano., 14:883-888, 1969.

1970

- 77) Broecker, W.S., J. van Donk, *Insolation changes, ice volumes and the 0-18 record in deep-sea cores*, Rev. of Geophys. & Space Physics 8:169-198, 1970.
- 78) Broecker, W.S., K. Wolgemuth, *Barium in sea water*, Earth Planet. Sci. Lett., 8:372-378, 1970.
- 79) Broecker, W.S., Y.H. Li, *Interchange of waters between the major oceans*, J. Geophys. Res., 75:3545-3552, 1970.
- 80) Broecker, W.S., *A boundary condition on the evolution of atmospheric oxygen*, J. Geophys. Res., 75:3553-3557, 1970.
- 81) Bender, M., T.L. Ku and W.S. Broecker, *Accumulation rates of manganese in pelagic sediments and nodules*, Earth Planet. Sci. Lett., 8:143-148, 1970.
- 82) Broecker, W.S., *Man's oxygen reserves*, Science, 168:1537-1538, 1970.
- 83) Broecker, W.S., A. Kaufman, T.L. Ku, Y.C. Chung, H. Craig, *Radium-225 measurements from the 1969 North Pacific GEOSECS station*, J. Geophys. Res. 75:7682-7685, 1970.
- 84) Broecker, W.S., A. Kaufman, *Near-surface and near-bottom radon results for the 1969 North Pacific GEOSECS Station*, Jour. Geophys. Research, v.75, no. 36, p. 7679-7681, 1970.
- 85) Thurber, D.L., W.S. Broecker, *The behavior of radiocarbon in the surface waters of the Great Basin, in radiocarbon variations and absolute chronology-Nobel Symposium*, 12th, Uppsala, 1969, New York and Stockholm, Almquist and Wiksell, p. 379-398, discussion, . 398:400, 1970.
- 86) Broecker, W.S., A. Kaufman, T-L. Ku, *Radium measurements on samples from the GEOSECS Station*, EOS, v. 51, no. 4, 324, 1970.
- 87) Crittenden, M.D., Jr., W.S. Broecker, A.L. Bloom, *Panel discussion on isostasy*, Can. J. Earth Sci. , v. 7, no. 2, pt 2,727:733, 1970.

- 88) Volchok, H.L., M. Feiner, H.J. Simpson, W.S. Broecker, V.E. Noshkin, V.T. Bowen, E. Willis, *Ocean fallout; the Crater Lake experiment*, J. Geophys. Res., v.75, no. 6, 1084:1091, 1970.

1971

- 89) Broecker, W.S., V.M. Oversby, *Chemical Equilibria in the Earth*, McGraw-Hill, N.Y., 319pp. 1971.
- 90) Thurber, D.L., W.S. Broecker, *The behavior of radiocarbon in the surface waters of the Great Basin*, 379-400, In: Nobel Symposium 12, *Radiocarbon Variations and Absolute Chronology*, (I.U. Olsson, ed.), John Wiley and Sons, Inc., 1971.
- 91) Broecker, W.S., *Calcite accumulation rates and glacial to interglacial changes in oceanic mixing*, The Late Cenozoic Glacial Ages (K.K. Turekian, ed.) Yale University Press, 1971.
- 92) Broecker, W.S., *A kinetic model for the chemical composition of sea water*, Quaternary Res., 1:188-207, 1971.
- 93) Broecker, W.S., T. H. Peng, *The vertical distribution of radon in the BOMEX area*, Earth Planet. Sci. Lett., 11:99-108, 1971.
- 94) Broecker, W.S., Y.H. Li and T.H. Peng, *Carbon dioxide - Man's unseen artifact, in: Impingement of Man on the Oceans*, (D. W. Hood, ed.), J. Wiley & Sons, Inc., pp. 287-324, 1971.
- 95) Kaufman, A., W.S. Broecker, T.L. Ku, D.L. Thurber, *The status of U-series methods of mollusk dating*, Geochim. Cosmochim. Acta, v. 35,1155:1183, 1971.
- 96) Bender, Michael, W.S. Broecker, V. Gornitz, U. Middel, R. Kay, S-S. Sun, P. Biscaye, *Geochemistry of three cores from the East Pacific Rise*, Earth Planet. Sci. Lett. vol. 12, no. 4, 425:433, 1971.

1972

- 97) Broecker, W.S., M. Bender, *Age determination on marine strandlines, In: Calibration of Homiloid Evolution*, (W.S. Bishop and J.A. Miller, eds.) The Wenner-Gren Foundation for Anthropological Res., N.Y, 19-35, 1972.
- 98) Trier, R.M., W.S. Broecker, H.W. Feely, *Radium-228 profile at the second GEOSECS intercalibration station*, 1970, in the North Atlantic, Earth Planet Sci. Lett. v. 16,141:145, 1972.
- 99) Schindler, D.W., G.J. Brunskill, S. Emerson, W.S. Broecker, T.H. Peng, *Atmospheric carbon dioxide: Its role in maintaining phytoplankton standing crops*, Science, v. 177, 1192:1194, 1972.
- 100) Gieskes, J.M., W.S. Broecker, *Interstitial water chemistry of sediments in the Caribbean Sea*, Caribb. Geol. Conf., Trans., no. 6, p. 493, 1972.

1973

- 101) Simpson, H. James, W.S. Broecker, *A new method for determining the total carbonate ion concentration in saline waters*, *Limnol. & Oceano.*, v. 18, 426:440, 1973.
- 102) Broecker, W.S., A. Kaufman, R.M. Trier, *The residence time of thorium in surface sea water and its implications regarding the rate of reactive pollutants*, *Earth Planet. Sci. Lett.*, v. 20, 35:44, 1973.
- 103) Anderson, T.T., M. Bender, W.S. Broecker, *Surface areas of biogenic carbonates and their relation to fossil ultrastructure and diagenesis*, *J. Sediment. Petrol.*, v.42, 471:477, 1973.
- 104) Kaufman, A., R.M. Trier, W.S. Broecker, *Distribution of ^{228}Ra in the world ocean*, *J. Geophys. Res.*, v.78, 8827:8848, 1973.
- 105) Broecker, W.S., *The marine chemistry of carbon and its role in oceanographic research*, in *Oceanography; the Last Frontier*, p. 56-66, Basic Books, NY, 1973.
- 106) *Interstitial water studies*, Leg 15 - Introduction and summary W.S. Broecker, *Initial Reports of the Deep Sea Drilling Project*, v. 15, Washington, (U.S. Government Printing Office), 1069:1073, 1973.
- 107) *Interstitial water studies*, Leg 15 - Introduction and summary W.S. Broecker, *Initial Reports of the Deep Sea Drilling Project*, v. 20, Washington, (U.S. Government Printing Office), 751:755, 1973.
- 108) *Interstitial water studies*, Leg 15 - *New Procedures and equipment*, R.M. Horowitz, L.S. Waterman, W.S. Broecker, *Initial Reports of the Deep Sea Drilling Project*, v. 20, Washington, (U.S. Government Printing Office), 757:763, 1973.
- 109) *Interstitial water studies*, Leg 15 - *Dissolved gases at site 147*, D.E. Hammond, M. Horowitz, W.S. Broecker, R. Bopp, *Initial Reports of the Deep Sea Drilling Project*, v. 20, Washington, (U.S. Government Printing Office), 765:771, 1973.
- 110) *Interstitial water studies*, Leg 15 - *Inert gases*, W. Brian Clarke, R.M. Horowitz, W.S. Broecker, *Initial Reports of the Deep Sea Drilling Project*, v. 20, Washington, (U.S. Government Printing Office), p. 777-781, 1973.
- 111) Broecker, W.S., *Environmental priorities*, *Science*, 182:435, 1973.
- 112) Emerson, S., W.S. Broecker, D.W. Schindler, *Gas-exchange rates in a small lake as determined by the radon method*, *J. Fish. Res. Bd. Canada*, v. 30, 1475:1484, 1973.
- 113) Broecker, W.S., *Factors controlling CO₂ content in the oceans and atmosphere*, U.S. A. E. C. Report, *Carbon and the biosphere*, 32-50, 1973.

1974

- 114) Chung, Y., H. Craig, T. Ku, J. Goddard, W.S. Broecker, *Radium-226 measurements from three GEOSECS intercalibration stations*, *Earth Planet. Sci. Lett.* v. 23, no 1, 116:124, 1974.
- 115) Hamza, M.S., W.S. Broecker, *Surface effect on the isotopic fractionation between CO₂ and some carbonate minerals*, *Geochem. Cosmochim. Acta*, v. 38, 669:681, 1974.

- 116) Peng, T.H., Takahashi and W.S. Broecker, *Surface radon measurements in the North Pacific Ocean station PAPA*, J. Geophys. Res., v. 79, 1772:1880, 1974.
- 117) Bloom, A. L., W.S. Broecker, J.M.A. Chappell, R.K. Matthews, K.J. Mesolella, *Quaternary sea level fluctuations on a tectonic coast: New $^{230}\text{Th}/^{234}\text{U}$ dates from the Huon Peninsula, New Guinea*, Quaternary Res., v. 4, 185:205, 1974.
- 118) Broecker, W.S., T.H. Peng, *Gas exchange rates between air and sea*, Tellus, v. 26, 21:35, 1974.
- 119) Broecker, W.S., *"NO", a conservative water-mass tracer*, Earth Planet. Sci. Lett., v. 23, 100:107, 1974.
- 120) Broecker, W.S., S. Broecker, *Carbonate dissolution on the western flank of the East Pacific Rise*, In: *Studies in Paleo-Oceanography, SEPM Memoir*, 20 (W.W. Hay, ed.), 44:57, 1974.
- 121) Broecker, W.S., *Chemical Oceanography*, Harcourt Brace Jovanovich, Inc., N.Y. (K.S. Deffeyes, ed.), 214.pp, 1974.
- 122) Chappell, J., W.S. Broecker, H.A. Polach, B.G. Thom, *Problem of dating upper Pleistocene sea levels from coral reef areas*, in: *Proceedings from the 2nd Intl. Coral Reef Symp.*, vol. 2; 563:571, The Great Barrier Reef Comm. Brisbane, Aust. , 1974.

1975

- 123) Lawrence, J.R., J.M. Gieskes, W.S. Broecker, *Oxygen isotope and cation composition of DSDP pore waters and the alteration of Layer II basalts*, Earth Planet. Sci. Lett. v. 27, no. 1, 1:10, 1975.
- 124) Broecker, W.S., *Floating glacial ice caps in the Arctic Ocean*, Science, v. 188, 1116:1118, 1975.
- 125) Broecker, W.S., *Climatic change: Are we on the brink of a pronounced global warming?* Science, v. 189, 460:463, 1975.

1976

- 126) Chan, L.H., J.M. Edmond, R.F. Stallard, W.S. Broecker, Y.C. Chung, R.F. Weiss, and T.L. Ku, *Radium and barium at GEOSECS stations in the Atlantic and Pacific*, Earth Planet. Sci. Lett., v. 32, 258:267, 1976.
- 127) Takahashi, T., P. Kateris and W.S. Broecker, *A method for shipboard measurement of CO_2 partial pressure in seawater*, Earth Planet. Sci. Lett., v. 32, 451:457, 1976.
- 128) Takahashi, T., P. Kateris, W.S. Broecker and A.E. Bainbridge, *An evaluation of the apparent dissociation constants of carbonic acid in seawater*, Earth Planet. Sci. Lett., v. 32, 458:467, 1976.
- 129) Broecker, W.S., T. Takahashi and Y. Li, *Hydrography of the Central Atlantic - I. The two degree discontinuity*, Deep-Sea Res., v. 23, 1083:1104, 1976.
- 130) Broecker, W.S., J. Goddard, J. Sarmiento, *The distribution of ^{226}Ra in the Atlantic Ocean*, Earth Planet. Sci. Lett. v. 32, 220:235, 1976.

- 131) Sarmiento, J., D. Hammond and W.S. Broecker, *The calculation of the statistical counting error for radon-222 scintillation counting*, Earth Planet Sci. Lett., v. 32, 351:356, 1976.
- 132) Sarmiento, J., H.W. Feely, W.S. Moore, A.E. Bainbridge and W.S. Broecker, *The relationship between vertical eddy diffusion and density gradient in the ocean*, Earth Planet. Sci. Lett., v. 32, 357:370, 1976.
- 133) Broecker, W.S., T. Takahashi, *The solubility of calcite in sea water*, *Thermodynamics in geology*, Oxford, UK, Sept. 17-27, 1976.

1977

- 134) Torgersen, T., Z. Top, W.B. Clarke, W.J. Jenkins and W.S. Broecker, *A new method for physical limnology-tritium-helium-3 ages-results for Lakes Erie, Huron and Ontario*, *Limnol. & Oceanog.*, v. 22, 181:193, 1977.
- 135) Broecker, W.S., *The Hazards of Coal Dependence*, *Natural History Magazine*, **Vol. 86**, No. 8, pp. 8-19, October, 1977.
- 136) Broecker, W.S. and T. Takahashi, *Neutralization of Fossil Fuel CO₂ by Marine Calcium Carbonate*, In: *The Fate of Fossil Fuel CO₂ in the Oceans*, (Neil Andersen and A. Malahoff, eds), 213-241, 1977.
- 137) Sundquist, E, D.K. Richardson, W.S. Broecker, T-H. Peng, *Sediment mixing and carbonate dissolution in the Southeast Pacific Ocean in: The Fate of Fossil Fuel CO₂ in the Oceans*, (Neil Anderson and A. Malahoff, eds.), Plenum Press, NY, 429:454. 1977.
- 138) Takahashi, T., W.S. Broecker, *Mechanisms for calcite dissolution on the sea floor, in: The Fate of Fossil Fuel CO₂ in the Oceans*, (Neil Anderson and A. Malahoff, eds.), Plenum Press, NY, 455:477, 1977.
- 139) Peng, T.-H., W.S. Broecker, G. Kipphut, N. Shackleton, *Benthic mixing in sea cores as determined by C-14 dating and its implications regarding climate stratigraphy and the fate of fossil fuel CO₂*, In: *The Fate of Fossil Fuel CO₂ in the Oceans*, (Neil Andersen and A. Malahoff, eds), Plenum Press, N.Y., 355:374, 1977.
- 140) Broecker, W.S., T. Takahashi, *The relationship between lysocline depth and in situ carbonate ion concentration*, *Deep-Sea Res.* v. 25, 65:95, 1977.

1978

- 141) Broecker, W.S. and A. Bainbridge, *An Abyssal Shear Zone*, *J. Geophys. Res.*, v. 83, 1963:1966, 1978.
- 142) Peng, T.H., J. Goddard, W.S. Broecker, *A direct comparison of C-14 and 230-Th ages at Searles Lake, Calif.*, *Quaternary Res.*, v. 9, 319:329, 1978.
- 143) Hoffert, M.I., W.S. Broecker, *Apparent vertical eddy diffusion rates in the pycnocline of the Norwegian Sea as determined from the vertical distribution of tritium*, *Geophys. Res. Lett.*, v. 5, 502:504, 1978.
- 144) Broecker, W.S., T.H. Peng and M. Stuiver, *An estimate of the upwelling rate in the Equatorial Atlantic based on the distribution of bomb radiocarbon*, *J. Geophys. Res.*, v. 83, 6179:6186, 1978.

- 145) Sarmiento, J., Broecker, W.S. and P.E. Biscaye, *Excess bottom radon-222 distribution in deep ocean passages*, J. Geophys. Res., v. 84, 1145:1154, 1978.
- 146) Broecker, W.S., *The cause of glacial to interglacial climatic change, in: Evolution of Planetary Atmospheres and Climatology of the Earth*. Centre National d'Etudes Spatiales (France), 165-177, 1978.
- 147) Peng, T.H. and W.S. Broecker, *Effect of sediment mixing on the rate of calcite dissolution by fossil fuel CO₂*, Geophys. Res. Lett., v. 5, 349:352, 1978.
- 148) Broecker, W.S., T-H. Peng, *Applications of atom counting to oceanography*, Conf. Radiocarbon Dating Accel., proc. 1, 294:313, 1978.
- 149) Hesslein, R., D. Schindler, G.W. Kipphut, W.S. Broecker, P.H. Santschi, *Geochemical analysis of trace elements in lakes of the Experimental Lakes area, Ontario, Canada*. Intl. Cong. on Sedimentology 10, vol. 1 (A-L), 304, 1978.

1979

- 150) Broecker, W.S., and H.G. Ostlund, *Property distributions along the $\sigma_t = 26.8$ isopycnal in the Atlantic Ocean*, J. Geophys. Res., v. 84, 1145:1154, 1979.
- 151) Peng, T.H., W.S. Broecker, G. Mathieu, Y.H. Li and A.E. Bainbridge, *Radon evasion rates in the Atlantic and Pacific Oceans as determined during the GEOSECS program*, J. Geophys. Res., v. 84, 2471:2486, 1979.
- 152) Bender, M., R. Fairbanks, F. Taylor, R. Matthews, J. Goddard, W.S. Broecker, *Uranium-series dating of the Pleistocene reef tracts of Barbados, West Indies*, Geol. Soc. Amer. Bull., Pt. 1, v. 90, 577:594, 1979.
- 153) Broecker, W.S., *Revised estimate for the radiocarbon age of North Atlantic Deep Water*, J. Geophys. Res., v. 84, 3218:3226, 1979.
- 154) Broecker, W.S., T. Takahashi, H. Simpson, T. Peng, *Fate of fossil fuel carbon dioxide and the global carbon budget*, Science, v. 206, 409:418, 1979.
- 155) Peng, T.H., W.S. Broecker and W.H. Berger, *Rates of benthic mixing in deep sea sediment as determined by radioactive tracers*, Quaternary Res., v. 11, 141:149, 1979.
- 156) Quay, P.D., W.S. Broecker, R.H. Hesslein, E.J. Fee, D.W. Schindler, *Whole lake tritium spikes to measure horizontal and vertical mixing rates*, I.A.E.A., Panel Proc. Ser. STI/PUB/511, 175-193, 1979.
- 157) Hesslein, R.H., R.D. Quay, M. Thomas, W.S. Broecker, *A whole lake gas exchange experiment using carbon-14 and radon-222 as tracers*, I.A.E.A., Panel Proc. Ser. STI/PUB/511, 251-254, 1979.
- 158) Hesslein, R.H., D.W. Schindler, W.S. Broecker, G. Kipphut, *Fates of metal radiotracer additions in experimental enclosures in lakes and in a whole lake*, I.A.E.A., Panel Proc. Ser. STI/PUB/511, 261-271, 1979.

1980

- 159) Sarmiento, J.L., W.S. Broecker, *Ocean floor 222 Rn standing crops in the Atlantic and Pacific oceans*, Earth Planet. Sci. Lett. v.49, no. 2, 341:350, 1980.
- 160) Broecker, W.S., T-H. Peng, *The distribution of bomb-produced tritium and radiocarbon at GEOSECS Sta. 347 in the eastern North Pacific*, GEOSECS collected papers, 1976:79, Earth Planet. Sci. Lett., v. 49, no. 2, 453:462,1980.
- 161) Broecker, W.S., T. H. Peng, and T. Takahashi, *A strategy for the use of bomb-produced radiocarbon as a tracer for the transport of fossil fuel CO₂ into the deep-sea source regions*, Earth Planet. Sci. Lett., v. 49, 463:468, 1980.
- 162) Broecker, W.S., T. Takahashi, and M. Stuiver, *Hydrography of the Central Atlantic-II Waters beneath the Two-Degree Discontinuity*, Deep Sea Res., v. 27, 397:419, 1980.
- 163) Broecker, W.S., T.H. Peng and T. Takahashi, *The Bay of Bengal - a major nutrient source for the deep Indian Ocean*, Earth Planet. Sci. Lett., v. 49, 506:512, 1980.
- 164) Broecker, W.S., *The distribution of 3-He anomalies in the deep Atlantic*, Earth Planet. Sci. Lett., v. 49, 513:519, 1980.
- 165) Broecker, W.S., T.H. Peng, G. Mathieu, R. Hesslein and T. Torgersen, *Gas exchange rate measurements in natural system*, Radiocarbon, v. 22, 676:683, 1980.
- 166) Peng, T-H., and W.S. Broecker, *Gas exchange rates for three closed-basin lakes*, Limnol. Oceanog. v. 25, 789:796, 1980.
- 167) Broecker, W.S., T.H. Peng, and R. Engh, *Modeling the carbon system*, Radiocarbon, v. 22, 565:598,1980.
- 168) Broecker, W.S. and T.H. Peng, *Seasonal variability in the ¹⁴C/¹²C ratio for surface ocean water*, Geophys. Res. Lett., v. 7, 1020:1022, 1980.
- 169) Broecker, W.S. and T. Takahashi, *Hydrography of the Central Atlantic-III. The North Atlantic deep-water complex*, Deep-Sea Res., v. 27, 591:613,1980.
- 170) Takahashi, T., W.S. Broecker, S.R. Werner and A. Bainbridge, *Carbonate chemistry of the surface waters of the world oceans, in: Isotope Marine Chemistry*, (E.D. Goldberg, Y. Horibe and K. Saruhashi, eds.) 291-326. Uchida Rokakuho Publ., Tokyo, 1980.
- 171) Quay, P.D., W.S. Broecker, R. Hesslein and D.W. Schindler, *Vertical diffusion rates determined by tritium tracer experiments in the thermocline and hypolimnion of two lakes*, Limnol. & Oceanog., v. 25, 201:218, 1980.
- 172) Santschi, P.H., W.S. Broecker, Y. Li, J. Bell and S. Carson, *Radioactive and stable trace metals in Narragansett Bay, R.I., in: Natural Radiation Environment III*, (T.F. Gesell and W.M. Lowder, eds.), 514-528, 1980.
- 173) Sarmiento, J. and W.S. Broecker, *Ocean floor Rn-222 standing crops in the Atlantic and Pacific Oceans*, Earth Planet. Sci. Lett., v. 49, 341:350, 1980.
- 174) Broecker, W.S., *Status of C 13/ C 12 research on tree rings, in: Proceedings of the Intl. meeting on stable isotopes in tree-ring research*, G. Jacoby, Ed.,69, 1980.

- 175) Santschi, P.H., W.S. Broecker, *228 Ra in the Central Indian and Wharton basins of the Indian Ocean*, EOS, v. 61, no. 46, 987:988, 1980.

1981

- 176) Broecker, W.S., *Geochemical tracers and ocean circulation*, in: *Evolution of Physical Oceanography*, eds., B.A. Warren and C. Wunsch, 434-460, MIT Press, Cambridge, MA, 1981.
- 177) Takahashi, T., W.S. Broecker and A. Bainbridge, *Supplement to the alkalinity and total carbon dioxide concentration in the world oceans*, Carbon Cycle Modeling, Scope 16, (B. Bolin, ed.) J. Wiley & Sons, 159:199, 1981.
- 178) Broecker, W.S. and T.H. Peng, *A strategy for the development of an improved model for the uptake of fossil fuel CO₂ by the ocean*, in: Carbon Cycle Modeling, Scope 16, (B. Bolin, ed.) J. Wiley & Sons, 223:226, 1981.
- 179) Takahashi, T., W.S. Broecker, A.E. Bainbridge, *The alkalinity and total carbon dioxide concentration in the world oceans*, in: Carbon Cycle Modeling, Scope 16, 271:286, 1981.
- 180) Broecker, W.S. and T. Takahashi, *Hydrography of the Central Atlantic-IV, Intermediate waters of Antarctic origin*, Deep-Sea Res., 28A:177:193, 1981.
- 181) Broecker, W.S., *Glacial to interglacial changes in ocean and atmosphere chemistry*, in: *Climatic Variations and Variability: Facts & Theories*, (A. Berger, ed.) 111:121, D. Reidel Pub. Co., Holland, 1981.
- 182) Stuiver, M, A. Rebellio, J.C. White, W.S. Broecker, *Radioisotopes; isotopic indicators of age/growth in tropical trees*, Bulletin, Yale University School of Forestry and Envl. Studies, 75:82, 1981.

1982

- 183) Broecker, W.S., *Glacial to interglacial changes in ocean chemistry*, Prog. Oceanogr., v. 11, 151:197, 1982.
- 184) Torgersen, T., G. Mathieu, R. Hesslein and W.S. Broecker, *Comparison of the Rn-222 and He-3 gas exchange methods in a small lake*, J. Geophys. Res., v. 87, 546:556, 1982.
- 185) Broecker, W.S., *Ocean chemistry during glacial time*, Geochim. Cosmochim. Acta, v. 46, 1689:1705, 1982.
- 186) Broecker, W.S. and T.H. Peng, *Tracers in the Sea*, Eldigio Press, Palisades, N.Y., 690 pp., 1982.
- 187) Torgersen, T., G. Mathieu, R. Hesslein and W.S. Broecker, *Gas exchange dependency on diffusion coefficient: direct Rn-222 and He-3 comparisons in a small lake*, J. Geophys. Res., v. 87, 546:556, 1982.
- 188) Sarmiento, J.L., C.G. Rooth, W.S. Broecker, *Radium 228 as a tracer of basin wide processes in the abyssal ocean*, Jour. Geophys. Research v. 87, no. 12, 9694:9698, 1982.

1983

- 189) Peng, T.-H., W.S. Broecker, H.D. Freyer and S. Trumbore. *A deconvolution of the tree ring based ^{13}C record*, J. Geophys. Res., v. 88(C6), 3609:3620, 1983.
- 190) Broecker, W.S., *The Ocean*, Scientific American, v. 249, no. 3, 146:161, 1983.
- 191) Santschi, P. H., P. Bower, U.P. Nyfeller, A. Azevedo, and W.S. Broecker, *Estimates of the resistance to chemical transport posed by the deep-sea boundary layer*, Limnol. Oceanogr., v. 28, no. 5, 899:912, 1983.
- 192) Bloom, A.L. W.S. Broecker, J.M. Chappell, R.K. Matthews, K.J. Mesolla, *Quaternary sea-level fluctuation on a tectonic coast; new $^{230}\text{Th}/^{234}\text{U}$ dates from the Huon Peninsula*, New Guinea, Intl. Geol. Correlation Programme, China Natl. Comm., 4:15, 1983.
- 193) Broecker, W.S., *El oceano*, Investigacion y Ciencia 86, 90-101,1983.

1984

- 194) Broecker, W.S. and T.-H. Peng, *Gas Exchange Measurements in Natural Systems; in "Gas Transfer at Water Surfaces"*, Eds., W. Brutsaert and G.H. Jirka, D. Reidel Pub. Co. Holland, 479:493, 1984.
- 195) Santschi, P.H., U.P. Nyfeller, P. O'Hara, M. Buchholtz and W.S. Broecker, *Radiotracer uptake on the sea floor: Results from the MANOP chamber deployments in the eastern Pacific*, Deep-Sea Res., v. 31, no. 5, 451:468,1984.
- 196) Broecker, W.S. *Terminations: in Milankovitch and Climate*, Part 2, Eds. A.L. Berger, et al., D. Reidel Pub. Co., Holland, 687-698, 1984.
- 197) Broecker, W.S. and T. Takahashi, *Is there a tie between atmospheric CO_2 content and ocean circulation? In "Climate Processes and Climate Sensitivity"*, Geophys. Monograph 29, Maurice Ewing v.5, Eds. J.E. Hansen and T. Takahashi, AGU, Washington, D.C., 314:325, 1984.
- 198) Broecker, W.S. and T.-H. Peng, *The Climate-Chemistry Connection: in "Climate Processes and Climate Sensitivity"*, Geophys. Monograph 29, Maurice Ewing V5, Eds. J.E. Hansen and T. Takahashi, AGU, Washington, D.C. 327:336,1984.
- 199) Li, Y.H., T.-H. Peng, W.S. Broecker and H.G. Ostlund, *The average mixing coefficient for the oceanic thermocline*, Tellus, 36B, 212:217, 1984.
- 200) Peng, T.-H. and W.S. Broecker, *Ocean Life Cycles and the Atmospheric CO_2 content*, J. Geophys. Res. v. 89, 8170:8180, 1984.
- 201) Broecker, W.S., *Carbon dioxide circulation through ocean and atmosphere*, Nature, v. 308, 602, 1984.
- 202) Broecker, W.S., A. Mix, M. Andree, H. Oeschger, *Radiocarbon measurements on coexisting benthic and planktic foraminifera shells; potential for reconstructing ocean ventilation times over the past 20,000 years*, in: Proceedings of the Third Intl. Symp. on Accel. Mass Spectrometry, Anderson, H.H., S.T. Picraux, Eds., 331:339, 1984.

- 203) Andree, M., J. Beer, H. Oeschger, W.S. Broecker, A. Mix, N. Ragano, P. O'Hara, G. Bonani, H. J. Hofmann, E. Morenzone, M. Nessi, M. Suter, W. Woelfli, *14 C measurements on foraminifera of deep sea core V28-238 and their preliminary interpretation*, in: Proceedings of the Third Intl. Symp. on Accelerator Mass Spectrometry, Anderson, H.H., S.T. Picraux, eds. ,340:345, 1984.
- 204) Peng, T-H., W.S. Broecker, *The impacts of bioturbation on the age difference benthic and planktonic foraminifera in deep sea sediments*, in: Proceedings of the Third Intl. Symp. on Accelerator Mass Spectrometry, Anderson, H.H., S.T. Picraux, eds.,346:352,1984.
- 205) Broecker, W.S., T-H. Peng, *The climate-chemistry connection*, in: Geophysical Monograph 29, 327:336,1984.

1985

- 206) Broecker, W.S., D. Peteet and D. Rind, *Does the ocean-atmosphere have more than one stable mode of operation*, Nature, v. 315, 21:25, 1985.
- 207) Broecker, W.S., T.-H. Peng, H.G. Ostlund and M. Stuiver, *The distribution of bomb radiocarbon*, J. Geophys. Res. v. 90, 6953:6970, 1985.
- 208) Broecker, W.S., T. Takahashi and T. Takahashi, *Sources of flow patterns of deep waters as deduced from potential temperature, salinity and initial phosphate concentration*, J. Geophys. Res., v. 90, 6925:6939, 1985.
- 209) Takahashi, T., W.S. Broecker and S. Langer, *Redfield ratio based on chemical data from isopycnal surfaces*, J. Geophys. Res., v. 90, 6907:6924, 1985.
- 210) White, J.W.C., E.R. Cook, J.R. Lawrence and W.S. Broecker, *The D/H ratios of sap in trees: Implications for water sources and tree ring D/H ratios*, Geochim. Cosmochim. Acta, v. 49, 237:246, 1985.
- 211) Wanninkhof, R., J.R. Ledwell and W.S. Broecker, *Gas exchange wind speed relation measured with sulfur hexafluoride on a lake*, Science, v. 227, 1224:1226, 1985.
- 212) Peng, T.-H. and W.S. Broecker, *The utility of multiple tracer distributions in calibrating models for uptake of anthropogenic CO₂ by the ocean thermocline*, J. Geophys. Res., v. 90, 7023:7035, 1985.
- 213) Broecker, W.S., C. Rooth and T.-H. Peng, *Ventilation of the deep northeastern Atlantic*, J. Geophys. Res., v. 90, 6940:6944, 1985.
- 214) Somayajula, B.L.K., W.S. Broecker and J. Goddard, *Dating Indian Corals by U-Decay-Series methods*, Quat. Res., v. 24, 235:239, 1985.
- 215) Herczeg, A.L., W.S. Broecker, R.F. Anderson, S.L. Schiff, and D.W. Schindler *A new method for monitoring temporal trends in the acidity of fresh waters*, Nature, v.315, no. 6015, 133:135, 1985.
- 216) Andree, M, J. Beer, H. Oeschger, A. Mix, W. S. Broecker, N. Ragano, P. O'Hara, G. Bonani, H.J. Hofmann, E. Morenzone, M. Nessi, M. Suter, W. Wolfli, in: *The carbon cycle and atmospheric CO₂; natural variations Archean to present*, Sundquist, E, W.S. Broecker, eds., Geophysical Monograph 32, 143:153, 1985.

- 217) Takahashi, T. J. Olafsson, W.S. Broecker, J. Goddard, D.W. Chapman and J. White, *Seasonal variability of the carbon-nutrient chemistry in the ocean area west and north of Iceland*, Rit Fiskideildar, no. 9, 20:36, 1985.
- 218) Andrée, M., J. Beer, H. Oeschger, A. Mix, W. Broecker, N. Ragano, P. O'Hara, G. Bonani, H.J. Hofmann, E. Morenzoni, M. Nessi, M. Suter, and W. Wölfli, *Accelerator Radiocarbon ages on foraminifera separated from deep-sea sediments*, reprinted from *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*, Geophysical Monograph 32, American Geophysical Union, 1985.

1986

- 219) Andree, M., H. Oeschger, W.S. Broecker, N. Beavan, A. Mix, G. Bonani, H.J. Hofmann, E. Morenzoni, M. Nessi, M. Suter and W. Wolfli, *AMS radiocarbon dates on foraminifera from deep sea sediments*, Radiocarbon, v. 28, 424:428, 1986.
- 220) Broecker, W.S., *Oxygen isotope constraints on surface ocean temperatures*, Quat. Res., v. 26, 121:134, 1986.
- 221) Clark, D.L., M. Andree, W.S. Broecker, A. Mix, et al., *Arctic ocean chronology confirmed by accelerator ¹⁴C dating*, Geophys. Res. Lett., v. 13, 319:321, 1986.
- 222) Koster, R., J. Jouzel, R. Suozzo, G. Russell, W. Broecker, D. Rind, and P. Eagleson, *Global sources of local precipitation as determined by the NASA/GISS GCM*, Geophys. Res. Lett., v. 13, 121:124, 1986.
- 223) Broecker, W.S. and T.-H. Peng, Carbon Cycle: 1985, *Glacial to interglacial changes in the operation of the global carbon cycle*, Radiocarbon, 28, No. 2A, 309:327, 1986.
- 224) Broecker, W.S., W.C. Patzert, J.R. Toggweiler, M. Stuiver, *Hydrography, chemistry and radioisotopes in the southeast Asian basins*, J. Geophys. Res., v. 91, 14345:14354, 1986.
- 225) Broecker, W.S., J.R. Ledwell, T. Takahashi, R. Weiss, L. Merlivat, L. Memery, T.H. Peng, B. Jahne and K.O. Munnich, *Isotopic versus micrometeorologic ocean CO₂ fluxes: A serious conflict*, J. Geophys. Res. v. 91, 10517:10527, 1986.
- 226) Andree, M., H. Oeschger, W. Broecker, N. Beavan, M. Klas, A. Mix, G. Bonani, M. Suter, W. Wolfli, T.H. Peng, *Limits on the ventilation rate for the deep ocean over the last 12,000 years*, Climate Dynamics, 1986, v. 1, 53:62.
- 227) Broecker, W.S., T.-H. Peng, and G. Ostlund, *The distribution of bomb tritium in the ocean*. J. Geophys. Res. v. 91, 14331:14344, 1986.
- 228) Broecker, W.S., *How to Build a Habitable Planet*, ELDIGIO Press, Palisades, New York, 291, 1986.
- 229) Rind, D., D. Peteet, W. Broecker, A. McIntyre, and W. Ruddiman, *The impact of cold North Atlantic sea surface temperatures on climate: Implications to the Younger Dryas cooling (11-10K)* Climate Dynamics v. 1, 3:33, 1986.
- 230) Ledwell, J.R., A.J. Watson, and W.S. Broecker, *A deliberate tracer experiment in Santa Monica Basin*, Nature, v. 323, 322:324, 1986.

- 231) Buchholtz, M.R., P.H. Santschi, W.S. Broecker, *Comparison of radiotracer K D values from batch equilibration experiments with in-situ determinations in the deep-sea using the MANOP Lander; the importance of geochemical mechanisms in controlling ion uptake and migration*, Elsevier Appl. Sci. Publ., 192:206, 1986.

1987

- 232) Broecker, W.S., Commentary, *Unpleasant surprises in the greenhouse?* Nature, v. 328, 123:126, 1987.
- 233) Peng, T.-H., and W.S. Broecker, *C/P Ratios in Marine Detritus*, Global Biogeochemical Cycles, v. 1, 155:161, 1987.
- 234) Broecker, W.S., and T.H. Peng, *The role of CaCO₃ compensation in the glacial to interglacial atmospheric CO₂ change*, Global Biochem. Cycles, v. 1, 15:39, 1987.
- 235) Peng, T.-H. , T. Takahashi, W.S. Broecker, and J. Olafsson, *Seasonal variability of carbon dioxide, nutrients and oxygen in the northern North Atlantic surface water: Observations and a model*, Tellus, 39b, 439:458, 1987.
- 236) Wanninkhof, R., J.R. Ledwell, W.S. Broecker and M. Hamilton: *Gas exchange-wind speed relationship on Mono and Crowley Lake, California*, J. Geophys. Res., v. 92, 14,567:14,580, 1987.
- 237) Broecker, W.S., T.-H. Peng, *The Oceanic Salt Pump: Does It Contribute to the Glacial-Interglacial Difference in Atmospheric CO₂ Content?* Global Biogeochemical Cycles, v. 1, 251:259, 1987.
- 238) Broecker, W.S., M. Andree, W. Wolfli, and H. Oeschger, *Timing of the Glacial-Holocene Transition in the South China Sea*, Nature, v. 333, 156:158, 1987.
- 239) Broecker, W.S., *The Biggest Chill*, Natural History Magazine, 74-82, Oct. 1987.
- 240) Jouzel, J., G.L. Russell, R.J. Suozzo, R. Koster, J.W.C. White and W.S. Broecker, *Simulations of the HDO and H₂O Atmospheric Cycles using the NASA GISS General Circulation model: The Seasonal Cycle for Present-Day Conditions*, J. Geophys. Res. v. 92, 14,739:144,760, 1987.
- 241) Broecker, W.S., *Paleocean circulation rates as determined from accelerator radiocarbon measurements on hand-picked foraminifera*, Terra Cognita v. 7, no.1, 43:44, 1987.
- 242) Broecker, W.S., *Beating the Big Battalions: Publishers are not Serving Some of their Authors or Student Customers as Well as They Might Think*, Nature, **Vol. 326**, p. 207, March 12, 1987.

1988

- 243) Broecker, W.S., M. Andree, G. Bonani, W. Wolfli, H. Oeschger and M. Klas, *Can the Greenland climatic jumps be identified in records from ocean and land?* Quaternary Res., v. 30, 1:6, 1988.
- 244) Broecker, W.S., R. Wanninkhof, A. Herczeg, T.-H. Peng, G. Mathieu, S. Stine, and M. Stuiver, *The radiocarbon budget for Mono Lake; an unsolved mystery*, Earth & Planet. Sci. Lett., v. 88, 16:26, 1988.

- 245) Broecker, W.S., M. Andree, W. Wolfli, H. Oeschger, G. Bonani, J. Kennett, and D. Peteet, *The chronology of the last deglaciation; Implications to the cause of the Younger Dryas event*. *Paleoceanography*, v. 3, 1:19, 1988.
- 246) Broecker, W.S., M. Andree, M. Klas, G. Bonani, W. Wolfli and H. Oeschger, *New Evidence from the South China Sea for an Abrupt Termination of the Last Glacial Period about 13,100 Years Ago*, *Nature*, v. 333, No. 6169, 156:158, 1988.
- 247) Broecker, W.S., M. Klas, N. Beavan, G. Mathieu, A. Mix, M. Andree, H. Oeschger, W. Wolfli, M. Suter, G. Bonani, H.J. Hofmann, M. Nessi, and E. Morenzoni, *Accelerator Mass Spectrometry Radiocarbon Measurements on Marine Carbonate Samples from Deep Sea Cores and Sediment Traps*, *Radiocarbon*, v. 30, 261:295, 1988.
- 248) Broecker, W.S., D. Oppo, W. Curry, M. Andree, W. Wolfli, and G. Bonani, *Radiocarbon based chronology for the $^{18}O/^{16}O$ record for the last deglaciation*, *Paleoceanography*, v. 3, 509:515, 1988.
- 249) Broecker, W.S., M. Andree, H. Oeschger, W. Wolfli, G. Bonani, M. Klas, A. Mix, and W. Curry, *Preliminary estimates of the radiocarbon age of deep water in the glacial ocean*, *Paleoceanography*, v. 3, no. 6, 659:669, 1988.
- 250) Broecker, W.S. and S. Stine, *Mono Lake's Radiocarbon Budget: An Unsolved Enigma*, *EOS*, **Vol. 69**, No. 23, June 7, 1988.
- 251) Broecker, W.S., M. Andree, G. Bonani, W. Wolfli, M. Klas, A. Mix, and H. Oeschger, *Comparison Between Radiocarbon Ages Obtained on Coexisting Planktonic Foraminifera*, *Paleoceanography*, **Vol. 3**, No. 6, pp. 647-657, December 1988.
- 1989**
- 252) Broecker, W.S., *Some thoughts about the radiocarbon budget for the glacial Atlantic*, *Paleoceanography*, v. 4, 213:220, 1989.
- 253) Koster, R., W.S. Broecker, J. Jouzel, B. Suozzo, G. Russell, D. Rind, J.W.C. White, *The global geochemistry of bomb produced tritium; general circulation models compared to the real world, accepted*, *Jour. Geophys. Res.*, v. 94, 18, 305:18,326, 1989.
- 254) Broecker, W.S., *The salinity contrast between the Atlantic and Pacific Oceans during glacial time*, *Paleoceanography*, v.4, 207:212, 1989.
- 255) Wahlen, M., N. Tanaka, R. Henry, B. Deck, J. Zeglen, J.S. Vogel, J. Southon, A. Shemesh, R. Fairbanks, and W. S. Broecker, *Carbon-14 methane sources and in atmospheric methane: The contribution from fossil carbon*. *Science*, v. 245, 286:290. 1989.
- 256) Broecker, W.S., J. Kennett, S. Trumbore, G. Bonani, and W. Wolfli, *The routing of Laurentide ice-sheet meltwater during the Younger Dryas cold event*, *Nature*, v. 341, 319:321, 1989.
- 257) Broecker, W.S., S. Trumbore, G. Bonani, W. Wolfli and M. Klas, *Anomalous AMS radiocarbon ages for foraminifera from high deposition rate ocean sediments*, *Radiocarbon*, v. 31, 157:162, 1989.

258) Broecker, W.S., and G.H. Denton, *The role of ocean-atmosphere reorganizations in glacial cycles*, *Geochimica et Cosmochimica Acta*, v. 53, 2465:2501, October, 1989.

259) Broecker, W.S., and T-H. Peng, *The Cause of Glacial to Interglacial Atmospheric CO₂ Change: A Polar Alkalinity Hypothesis*, *Biogeochemical Cycles*, v. 3 215:239, 1989.

1990

260) Broecker, W.S. and G.H. Denton, *What Drives Glacial Cycles?* *Scientific V. 262*, No. 1, 48-56, American, Jan. 1990.

261) Anderson, R.F., Y. Lao, W.S. Broecker, S.E. Trumbore, H.J. Hofmann, and W. Wolfli. *Boundary scavenging in the Pacific Ocean: a comparison of ¹⁰Be and ²³¹Pa*. *Earth & Planet. Sci. Lett.*, 96:287-304, 1990.

262) Peng, T.-H., T.L. Ku, J. Southon, C. Measures, and W. S. Broecker, *Factors Controlling the Distribution of ¹⁰Be and ⁹Be in the Ocean*. In: **From Mantle to Meteorites, A Garland of Perspectives: A Festschrift for Devendra Lal**, edited by K. Gopalan, V. K. Gaur, B. L. K. Somayajulu, and J. D. Macdougall, Indian Academy of Sciences, Bangalore, India. p.201-204, 1990.

263) Broecker, W.S., T.-H. Peng, J. Jouzel, and Gary Russell, *The magnitude of global fresh water transports of importance to ocean circulation*, *Climate Dynamics*, v. 4, 73:79, 1990.

264) Broecker, W.S., M. Klas, E. Clark, S. Trumbore, G. Bonani, W. Wolfli and S. Ivy, *Accelerator Mass Spectrometric radiocarbon measurements on foraminifera shells from deep sea cores*, *Radiocarbon* v. 32, no. 2, 119:133, 1990.

265) Broecker, W.S., *Salinity history of the Northern Atlantic during the last deglaciation*, *Paleoceanography*, v. 5, no. 4, 459:467, August 1990.

266) Broecker, W.S., G. Bond, M. Klas, G. Bonani, and W. Wolfli, *A salt oscillator in the glacial North Atlantic? 1. The Concept*, *Paleoceanography*, vol. 5, No. 4, 469:477, August 1990.

267) Broecker, W.S., T.-H. Peng, S. Trumbore, G. Bonani, W. Wolfli, *The distribution of radiocarbon in the glacial ocean*, *Biogeochemical Cycles* v. 4, 103:117, 1990.

268) Birchfield, G.E., W.S. Broecker, *A salt oscillator in the glacial northern Atlantic? Part II: A 'Scale Analysis' Model*, *Paleoceanography*, vol. 5, no. 6, 835-843, December 1990.

269) Broecker, W.S., Comment on "*Iron Deficiency Limits Phytoplankton Growth in Antarctic Waters*" by John H. Martin et al. *Global Biogeochemical Cycles*, v. 4, 3:4, 1990.

1991

270) Broecker, W.S., A. Virgilio, and T.-H. Peng, *Radiocarbon age of water in the deep Atlantic revisited*, *Geophys. Res. Lett.*, vol. 18, no. 1, 1:3, Jan. 1991.

271) Peng, T.-H., and Broecker, W.S., *Dynamical limitations on the Antarctic iron fertilization strategy*, *Nature*, v. 349, 227:229, 1991.

272) Broecker, W.S., S. Blanton, and T. Takahashi, W. Smethie and G. Ostlund, *Radiocarbon decay and oxygen utilization in the deep Atlantic Ocean*, *Global Biogeochemical Cycles*, v. 5, 87:117, 1991.

- 273) Jouzel, J., R.D. Koster, R.J. Suozzo, G.L. Russell, J.W.C. White, and W.S. Broecker, *Simulations of the H₂O and H₂¹⁸O atmospheric cycles using the NASA/GISS General Circulation Model: Sensitivity experiments for present-day conditions*, Journal of Geophys. Research, vol. 96, no. D4, 7495:7507, 1991.
- 274) Broecker, W.S., M. Klas, E. Clark, G. Bonani, S. Ivy and W. Wolfli, *The influence of CaCO₃ dissolution on core top radiocarbon ages for deep-sea sediments*, Paleoceanography, vol. 6, no. 5, 593:608, 1991.
- 275) Broecker, W.S., *Keeping Global Change Honest*, Global Biogeochemical Cycles, vol. 5, no. 3, 191:192, 1991.
- 276) Toggweiler, J.R., K. Dixon, and W.S. Broecker, *The Peru upwelling and the ventilation of the South Pacific thermocline*, Journal Geophys. Research, vol. 96, no. 20, 467:497, 1991.
- 277) Broecker, W.S., *The Great Ocean Conveyor*, Oceanography, v. 4, 79:89, 1991.
- 278) Peng, T.-H., and W.S. Broecker, *Factors limiting atmospheric CO₂ reduction by iron fertilization*, Limnology and Oceanography. vol. 36, no. 8. December 1991.
- 279) Oxburgh, R., W.S. Broecker, and R.H. Wanninkhof, *The Carbon Budget of Mono Lake*, Global Biogeochemical Cycles, v. 5, no. 4, 359:372, 1991.

1992

- 280) Broecker, W.S., G. Bond, M. Klas, E. Clark, J. McManus, *Origin of the Northern Atlantic's Heinrich events*, Climate Dynamics, v. 6, 265:273, 1992.
- 281) Broecker, W.S., *Global Warming on Trial*, Natural History, 6:11, April 1992.
- 282) Broecker, W.S. and T.-H. Peng, *Interhemispheric transport of CO₂ by ocean circulation*, Nature, v.356, 587:589, 1992.
- 283) Zaucker, F. and W.S. Broecker, *The influence of atmospheric moisture transport on the fresh water balance of the Atlantic drainage basin: GCM simulations and observations*, Jour. Geophys. Res. v. 97, 2765:2774, 1992.
- 284) Stute, M., P. Schlosser, J.F. Clark, and W.S. Broecker, *Paleotemperatures in the southwestern United States derived from noble gases in ground water*, Science, v. 256, 1000:1002, 1992.
- 285) Broecker, W.S., Thomas Stocker, *NADW Formation as a branch of the hydrological cycle*, EOS Transactions, American Geophysical Union, v. 73, no. 18, 202:203, 1992.
- 286) Broecker, W.S., *The strength of the Nordic heat pump, 13,500 to 9500 B.P.*, in *The Last Deglaciation: Absolute and Radiocarbon Chronologies*, ed., E. Bard and W.S. Broecker, NATO ASI Series, v. 12, Springer-Verlog, 173, 1992.
- 287) Broecker, W.S. and T.-H. Peng, *Dynamic constraints on CO₂ uptake by an iron-fertilized Antarctic*, *Modeling the earth system*, from OIES Global Change Institute, ed. Dennis Ojima, 77:105, 1992.

- 288) Broecker, W.S., *Defining the boundaries of the BOA warm and YD cold isotope episodes*, Quaternary Research, v. 38, 135:139, 1992.
- 289) Broecker, W.S., Bard, E., *The Last Deglaciation: Absolute and Radiocarbon Chronologies*, NATO ASI Series (Series 1: Global Environmental Change, Vol.2), 1992.
- 290) Lao, Y., R.F. Anderson, W.S. Broecker, S.E. Trumbore, H.J. Hofmann, W. Wolfli, *Increased production of cosmogenic ^{10}Be during the last glacial maximum*, Nature, v. 357, 576:578, 1992.
- 291) Broecker, W.S., F. Woodruff, *Discrepancies in the oceanic carbon isotope record for the last fifteen million years?* Garrels Memorial Collection, Geochimica et Cosmochimica Acta, v. 56, 3259:3264, 1992.
- 292) Peng, T.-H., W.S. Broecker and H.G. Östlund, *Dynamic constraints on CO_2 uptake by an iron-fertilized Antarctic, in modeling the Earth system*. Papers arising from the 1990 OIES Global Change Institute, ed. by Dennis Ojima, 77-105, UCAR, 1992.
- 293) Broecker, W.S. and E. Maier-Reimer, *The influence of air and sea exchange on the carbon isotope distribution in the sea*, Biogeochemical Cycles, v. 6, 315:320, 1992.
- 293) Lao, Y., R.F. Anderson, W.S. Broecker, S.E. Trumbore, H.J. Hofmann, W. Wolfli, *Transport and burial rates of ^{10}Be and ^{231}Pa in the Pacific Ocean during the Holocene period*, Earth and Planetary Science Letters, v. 113, 173:199, 1992.
- 294) Broecker, W.S., and Jeff Severinghaus, *Global Change: Diminishing oxygen*, Nature, v. 358, 710:711, 1992.
- 295) Broecker, W.S., *Upset for Milankovitch theory*, Nature, vol. 359, 779:780, 1992.
- 296) Bond, G., H. Heinrich, W. S. Broecker, L. Labeyrie, J. McManus, J. Andrews, S. Huon, R. Jantschik, S. Clasen, C. Simet, K. Tedesco, M. Klas, G. Bonani and S. Ivy, *Evidence for massive discharges of icebergs into the North Atlantic ocean during the last glacial period*, Nature, v. 360, 245:249, 1992.
- 297) Stocker, T.F., D.G. Wright and W.S. Broecker, *The influence of high-latitude surface forcing on the global thermohaline circulation*, Paleoceanography, v. 7, no.5, 529:541, 1992.
- 298) Bond, G., Broecker, W.S., R. Lotti and J. McManus, *Abrupt color changes in isotope stage 5 in North Atlantic deep sea cores: Implications for rapid change of climate-driven events*, in Start of a Glacial, NATO ASI Series, v. 3, ed. by G.J. Kukla and E. Went, Springer-Verlag, 1992.
- 299) Lao, Yong, R.F. Anderson, W.S. Broecker, *Boundary scavenging and deep-sea sediment dating: Constraints from excess ^{230}Th and ^{231}Pa* , Paleoceanography, v. 7 no. 6, 783:798, 1992.
- 300) Broecker, W.S., *Discovery of a large offset in the radiocarbon time scale*, Eos, vol. 73, no. 3, pg. 32, 1992.

- 301) Peng, T.-H., W.S. Broecker, *Reconstruction of radiocarbon distribution in the glacial ocean* (in *Radiocarbon after four decades: An interdisciplinary perspective*, Editors: R.E. Taylor, A. Long, and R. Kra. Springer-Verlag, New York, 1992), pgs. 75-92, 1992.

1993

- 302) Lao, Yong, R.F. Anderson, W.S. Broecker, H.J. Hofmann, W. Wolfli, *Particulate fluxes of ^{230}Th , ^{231}Pa and ^{10}Be in the northeastern Pacific Ocean*, *Geochimica et Cosmochimica Acta*, v. 57, no. 1, 205:217, 1993.
- 303) Harrison, K., W.S. Broecker and G. Bonani, *A strategy for estimating the impact of CO_2 fertilization on soil carbon storage*, *Global Biogeochemical Cycles*, v.7, no.1 69:80, 1993.
- 304) Broecker, W.S., *An oceanographic explanation for the apparent carbon isotope-cadmium discordancy in the glacial Antarctic?* *Paleoceanography*, v. 8, no. 2, 137:139, 1993.
- 305) Broecker, W.S., G. Bonani, C. Chen, E. Clark, S. Ivy, M. Klas, T.-H. Peng, *A search for an Early Holocene CaCO_3 Preservation Event*, *Paleoceanography*, v. 8, no. 3, 333:339, 1993.
- 306) Peng, T.-H., W.S. Broecker, E. Maier-Reimer, *The Distribution of ^{32}Si in the World Ocean; Model compared to observation*, *Global Biogeochemical Cycles*, v. 7, no. 2, 463:474, 1993.
- 307) Bond, G., W. Broecker, S. Johnsen, J. Jouzel, L. Labeyrie, J. McManus and G. Bonani, 220, 1995.
- 308) Broecker, W.S., and T.-H. Peng, *Does the ^{13}C Budget Provide a Useful Constraint on the Uptake of Fossil Fuel CO_2 by the Ocean?*, *Global Biogeochemical Cycles*, V. 7, No. 3, 619:626, 1993.
- 309) Oxburgh, R. and W.S. Broecker, *Pacific Carbonate Dissolution Revisited*, *Palaeogeography, Palaeoclimatology, Palaeoecology*, V. 103, No. ½, 31:40, 1993.
- 310) Harrison, K., W.S. Broecker, G. Bonani, *The Effect of Changing Land Use on Soil Radiocarbon*, *Science*, V. 262, 725:726, 1993.
- 311) Broecker, W.S. and T.-H. Peng, *Interhemispheric Transport of SCO_2 Through the Ocean*, *NATO SI Series, V. I 15, The Global Carbon Cycle*, ed. By M. Heimann, 551:570, Springer-Verlag, 1993.
- 312) Broecker, W.S. and T.-H. Peng, *What caused the glacial to interglacial CO_2 change?* *NATO SI Series, v. I 15, The Global Carbon Cycle*, ed. by M. Heimann, 94:115, Springer-Verlag, 1993.

1994

- 313) White, J.W.C., J. Lawrence, W.S. Broecker, *Modeling and interpreting D/H ratios in tree rings: A test case of white Pine in the northeastern United States*, *Geochim. Cosmochim. Acta*, v. 58, no 2, 851:862, 1994.
- 314) Stocker, T.F. and W.S. Broecker, *Observation and modeling of North Atlantic deep water formation and its variability. Introduction*, *Jour. Geophys. Research*, v. 99, no. C6, 12,317,1994.
- 315) Broecker, W.S., G. Bond, J. McManus, *Heinrich events: Triggers of ocean circulation*

change? Aussois -NATO volume, Springer-Verlag, 1994.

- 316) Zaucker, F., T.F. Stocker, and W.S. Broecker, *Atmospheric freshwater fluxes and their effect on the global thermohaline circulation*, Jour. Geophys Research, Special Issue on North Atlantic Deep Water Formation: Observ. and Modeling, v.99, no. C6,12,443:12,457,1994.
- 317) Broecker, W.S., T.-H. Peng, *The stratospheric contribution to the bomb radiocarbon inventory*, Global Biogeochemical Cycles, v.8, no. 3, 377:384,1994.
- 318) Broecker, W.S., *Ocean Circulation: An unstable superconveyor*, Nature, v. 367, 414:415,1994.
- 319) McManus, J.F., G.C. Bond, W.S. Broecker, S. Jobnsen, L. Labeyrie & S. Higgins, *High-resolution climate records from the North Atlantic during the last interglacial*, Nature, v. 371, 326:329,1994.
- 320) Stocker, T.F., W.S. Broecker and D.G. Wright, *Carbon uptake experiments with a zonally-averaged global ocean circulation model*, Tellus, 46B, 103:122, 1994.
- 321) Broecker, W.S., *Is Earth Climate Poised to Jump Again?* Geotimes, 16:18,1994.
- 322) Broecker, W.S., *Massive iceberg discharges as triggers for global climate change*, Nature, v. 372, 421:424,1994.
- 323) Severinghaus, J, W.S. Broecker, W.F. Dempster, T. MacCallum and M. Wahlen, *Oxygen Loss in Biosphere 2*, EOS, Transactions, AGU, v. 75, 33, 35:37,1994.
- 324) Gwiazda, R.H., and W.S. Broecker, *The separate and combined effects of temperature, soil pCO₂ and organic acidity on silicate weathering in the soil environment: Formulation of a model and results*, Global Biogeochemical Cycles, v. 8, no. 2, 141:155,1994.

1995

- 325) Heinze, C., and W.S. Broecker, *Closing off the southern ocean surface*, Paleoceanography, v.10, no.1, 49:58, 1995.
- 326) Peng, T-H, and W.S. Broecker, *Estimate of interhemispheric ocean carbon transport based on 211 92C02 and nutrient distribution*, (T.M. Powell and J.H. Steele, eds.), Chapman & Hall, NY, Ecological Time Series, 28:47, 1995.
- 327) Sanyal, A., N.G. Hemming, G.N. Hanson, W.S. Broecker, *Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera*, Nature, v. 373, 234:236, 1995.
- 328) Farley, K.A., E. Maier-Reimer, P. Schiosser and W.S. Broecker, and G. Bonani, *Constraints on mantle 3He fluxes and deep-sea circulation from an oceanic general circulation model*, Jour, Geophys. Res., v.100, no. B3, 3829:3839,1995.
- 329) Stute, M., J.F. Clark, P. Schlosser, and W.S. Broecker, *A 30,000 yr continental paleotemperature record derived from noble gases dissolved in groundwater from the San Juan Basin, New Mexico*, Quaternary Research, 43, 209:220, 1995.

- 330) Broecker, W.S., T.-H. Peng, S. Sutherland, G. Ostlund, and W. Smethie, *Oceanic radiocarbon: Separation of the Natural and Bomb Components*, Global Biogeochemical Cycles, v. 9, no. 2, 263:288, 1995.
- 331) Broecker, W.S., *Cooling the tropics*, Nature, 376, 212:213, 1995.
- 332) Stute, M., M. Forster, H. Frischkorn, A. Serejo, J.F. Clark, P. Schlosser, W.S. Broecker and G. Bonani, *Cooling of Tropical Brazil (5°C) During the Last Glacial Maximum*, Science, 269, 379:383, 1995.
- 333) Broecker, W.S., *Chaotic Climate*, Scientific American, V. 273, pgs. 62-68, Nov. 1995
- 334) Lynch-Stieglitz, J, T.F. Stocker, W.S. Broecker, and R.G. Fairbanks, *The influence of air-sea exchange on the isotopic composition of oceanic carbon: Observations and modeling*, Global Biogeochemical. Cycles, 9, 653-665, 1995

1996

- 335) Gwiazda, R.H., S.R. Hemming, and W.S. Broecker, *Tracking the sources of icebergs with lead isotopes: The provenance of ice-rafted debris in Heinrich layer 2*, Paleoceanography, vol. 11, no. 1 pgs. 77-93, 1996.
- 336) Broecker, W.S., *Paleoclimatology*, Geotimes, February 1996.
- 337) Gwiazda, R.H., Hemming, S.R., and W.S. Broecker, *Provenance of icebergs during Heinrich event 3 and the contrast to their sources during other Heinrich episodes*, Paleoceanographic Currents, vol. 11, no. 4 pgs. 371-78, 1996.
- 338) Broecker, W. S., *Glacial Climate in the Tropics*, Science, vol. 272, pgs. 1902-4, 1996.
- 339) Severinghaus, J., Bender, M. L., Keeling, R. F., and Broecker, W. S., *Fractionation of soil gases by diffusion of water vapor, gravitational settling, and thermal diffusion*, Geochimica et Cosmochimica Acta, Elsevier Science Ltd., Pergamon, vol. 60, no. 6, pgs. 1005-18, 1996.
- 340) Broecker, W.S., *The biosphere and me*, GSA Today, Vol. 6, No. 7, pp. 1-7, 1996.
- 341) Broecker, W.S., *The once and future climate*, Natural History, Vol. 105, No. 9, pgs. 30-39, 1996.
- 342) Sanyal, A., N.G. Hemming, W.S. Broecker, D.W. Lea, H.J. Spero, and G.N. Hanson, *Oceanic pH control on the boron isotopic composition of foraminifera: Evidence from culture experiments*, Paleoceanography, Vol. 11, No. 5, pgs. 513-517, 1996.
- 343) Lin, J.C., W.S. Broecker, R.F. Anderson, S. Hemming, J.L. Rubenstone, and G. Bonani, *New $^{230}\text{Th}/\text{U}$ and ^{14}C ages from Lake Lahontan carbonates, Nevada, USA, and a discussion of the origin of initial thorium*, Geochimica et Cosmochimica Acta, Vol. 160, No. 15, pp. 2817-2832, 1996.
- 344) Rutberg, R.L., D.S. Schimel, I. Hajdas, and W.S. Broecker, *The effect of tillage on soil organic matter using ^{14}C : A case study*, Radiocarbon, Vol. 38, No. 2, pp. 209-217, 1996.
- 345) Gwiazda, R.H., S.R. Hemming, W.S. Broecker, T. Onstott, C. Mueller, *Evidence from $^{40}\text{Ar}/^{39}\text{Ar}$ for a Churchill Province source of ice-rafted amphiboles in Heinrich Layer 2*, Journal of Glaciology, Vol. 42, No. 142, pp. 440-446, 1996.

- 346) Severinghaus, J.P., W.S. Broecker, T.-H. Peng, and G. Bonani, *Transect along 24°N latitude of ^{14}C in dissolved inorganic carbon in the subtropical North Atlantic Ocean*, Radiocarbon, Vol. 36, No. 3, pp. 407-414, 1996.
- 347) Broecker, W.S., *Et tu, O₂?*, 21st Century, Issue 2.1, pp. 7 and 14 Fall 1996.
- 348) Broecker, W.S., *The Coming Warmup: No Time for Complacency*, 21st Century Columbia University, Issue 1.3, pp.5-6, Winter 1996

1997

- 349) Broecker, W.S., *Will our ride into the greenhouse future be a smooth one?*, GSA Today, Vol. 7, No. 5, pp. 1-7, 1997.
- 350) Broecker, W.S. and A. Sanyal, *Magnitude of the CaCO₃ dissolution events marking the onset of times of glaciation*, vol. 12, No. 4, pp. 530-532, Paleoceanography, August, 1997.
- 351) Severinghaus, J.P., R.F. Keeling, B.R. Miller, R.F. Weiss, B. Deck, and W.S. Broecker, *Feasibility of using sand dunes as archives of old air*, vol. 102, No. D14, pp. 16,783-16,792, Journal of Geophysical Research, July 27, 1997.
- 352) Broecker, W.S., *Thermohaline Circulation, The Achilles Heel of our Climate System: Will Manmade CO₂ Upset the Current Balance?*, vol. 278, pp. 1582-1588, Science, Nov. 28, 1997.
- 353) Broecker, W.S., *Mountain Glaciers: Recorders of Atmospheric Water Vapor Content?*, vol. 11, No. 4, pp. 589-597, Global Biogeochemical Cycles, December, 1997.
- 354) Broecker, W.S., *Our burden of responsibility*, (essay) “A Better Future for the Planet Earth: Lectures by the Winners of the Blue Planet Prize”, pp. 208-210, The Asahi Glass Foundation, Japan, first edition, October, 1997.
- 355) Broecker, W.S., *Will our ride into the Greenhouse future be a smooth one?*, (lecture) “A Better Future for the Planet Earth: Lectures by the Winners of the Blue Planet Prize”, pp. 211-221, The Asahi Glass Foundation, Japan, first edition, October, 1997.
- 356) Broecker, W.S., *Future directions of paleoclimate research*, Quaternary Science Reviews, vol. 16, pp. 821-825, 1997.
- 357) Broecker, W.S., *Protection against excessive global warming*, Earth Matters, pp.4-5, Winter 1997-98.

1998

- 358) Lin, J.C., W.S. Broecker, S.R. Hemming, I. Hajdas, R.F. Anderson, G.I. F. Smith, M. Kelley, and G. Bonani, *A reassessment of U-Th and ^{14}C ages for late-glacial high-frequency hydrological events at Searles Lake, California*, Quaternary Research, vol. 49, pp. 11-23, 1998.
- 359) McManus, J.F., R.F. Anderson, W.S. Broecker, M.Q. Fleisher, and S.M. Higgins, *Radiometrically determined sedimentary fluxes in the sub-polar North Atlantic during the last 140,000 years*, Earth and Planetary Science Letters, vol. 155, pp. 29-43, 1998.

- 360) Broecker, W.S., *Paleocean circulation during the last deglaciation: A bipolar seesaw?*, *Paleoceanography*, vol. 13, no. 2, pp. 119-121, April 1998.
- 361) Broecker, W.S., S. Peacock, S. Walker, R. Weiss, E. Fahrback, M. Schroeder, U. Mikolajewicz, C. Heinze, R. Key, T.-H. Peng, and S. Rubin, *How much deep water is formed in the Southern Ocean?*, *JGR*, vol. 103, no. C8, pp. 15,833-15,843, July 15, 1998.
- 362) Donahue, D.J., W. Beck, W.S. Broecker, G. Bonani, A.J.T. Jull, I. Hajdas, E. Malotki, and G. Burr, *Ambiguities in direct dating of rock surfaces using radiocarbon measurements*, *Science*, June 26, 1998.
- 363) Broecker, W.S. and G. M. Henderson, *The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO₂ changes*, *Paleoceanography*, vol. 13, no. 4, pp. 352-364, August 1998.
- 364) Broecker, W.S., D. Peteet, and I. Hajdas, *Antiphasing between rainfall in Africa's Rift Valley and North America's Great Basin*, *Quaternary Research*, vol. 50, pp. 12-20, 1998.
- 365) Broecker, W.S. and A. Sanyal, *Does Atmospheric CO₂ Police the Rate of Chemical Weathering?* **Vol. 12**, No. 3, pp. 403-408, *Global Biogeochemical Cycles*, September, 1998.
- 366) Broecker, W.S., *The End of the Present Interglacial: How and When?* **Vol. 17**, pp. 689-694, *Quaternary Science Reviews*, 1998.
- 367) Broecker, W.S., *Flujos*, (in Spanish) pp. 89-93, *Atlantica Internacional*, 1998.
- 368) Hemming, S.R., P.E. Biscaye, W.S. Broecker, N.G. Hemming, M. Klas, and I. Hajdas, *Provenance change coupled with increased clay flux during deglacial times in the Western Equatorial Atlantic*, *Palaeogeography, Palaeoclimatology, Palaeoecology*, **V. 142**, pp. 217-230, 1998.
- 369) McCormac, F.G., A.G. Hogg, T.F.G. Higham, J. Lynch-Stieglitz, W.S. Broecker, M.G.L. Baillie, J. Palmer, L. Xiong, J.R. Pilcher, D. Brown, and S.T. Hoper, *Temporal Variation in the Interhemispheric ¹⁴C Offset*, *Geophysical Research Letters*, **V. 25**, No. 9, pp. 1321-1324, May 1, 1998.
- 370) Hemming, S.R., W.S. Broecker, W.D. Sharp, G.C. Bond, R.H. Gwiazda, J.F. McManus, M. Klas, and I. Hajdas, *Provenance of the Heinrich layers in Core V28-82, Northeastern Atlantic: ⁴⁰Ar-³⁹Ar ages of ice-rafted Hornblende, Pb Isotopes in feldspar grains and Nd-Sr-Pb Isotopes in the fine sediment fraction*, *EPSL*, v. 164, pp. 317-333, 1998.
- 371) Broecker, W.S., *The Reminiscences of Wallace S. Broecker (December 29, 1995)*, pp.1-124, in the Oral History Collection of Columbia University (hereafter OHCCU), 1998.
- 372) Beck, W., D.J. Donahue, A.J.T. Jull, G. Burr, W.S. Broecker, G. Bonani, I. Hajdas, and E. Malotki (1998), *Ambiguities in direct dating of rock surfaces using radiocarbon measurements*, *Science*, 280 (5372), 2132-2139. doi:[10.1126/science.280.5372.2132](https://doi.org/10.1126/science.280.5372.2132).
- 1999**
- 373) Fleisher, M., T. Liu, W.S. Broecker, and W. Moore, *A Clue Regarding the Origin of Rock Varnish*, *Geophysical Research Letters*, **vol. 26**, no. 1, pp. 103-106, January 1, 1999.

- 374) Broecker, W.S., *What if the Conveyor Were to Shut Down? Reflections on a Possible Outcome of the Great Global Experiment*, GSA Today, **vol. 9**, no. 1, pp. 1-6, January, 1999.
- 375) Broecker, W.S., *Climate Change Prediction* (letter to Science), Science, **vol. 283**, January 8, 1999.
- 376) Broecker, W.S., E. Clark, I. Hajdas, G. Bonani, and D. McCorkle, *Core-top ^{14}C Ages as a Function of Latitude and Water Depth on the Ontong-Java Plateau*, Paleoceanography, **vol. 14**, no. 1, pp. 13-22, February, 1999.
- 377) Greene, A.M. and W.S. Broecker, *Swiss glacier recession since the Little Ice Age: Reconciliation with climate records*, Geophysical Research Letters, **Vol. 26**, No. 13, pp. 1909-1912, July 1, 1999.
- 378) Broecker, W.S., K. Matsumoto, E. Clark, I. Hajdas, and G. Bonani, *Radiocarbon Age Differences between Coexisting Foraminiferal Species*, Paleoceanography, **Vol. 14**, No. 4, pp. 431-436, August, 1999.
- 379) Peacock, S., W. Jenkins, R. Key, and W.S. Broecker, *Assessing the importance of subtropical waters in ventilating the Equatorial Pacific thermocline: a combined transient-tracer approach*, International WOCE Newsletter, No. 35, pp. 18, 21, 23-24, June 1999.
- 380) Broecker, W.S. and E. Clark, *CaCO₃ Size Distribution: A Paleo Carbonate Ion Proxy*, Paleoceanography, **Vol. 14**, No. 5, pp. 596-604, October, 1999.
- 381) Broecker, W.S., S. Sutherland, and T.-H. Peng, *A Possible 20th-Century Slowdown of Southern Ocean Deep Water Formation*, Science, **Vol. 286**, p. 1132-1135, 5 November, 1999.
- 382) Higgins, S., W.S. Broecker, R.F. Anderson, D.C. McCorkle, and D. Timothy *Excess Sedimentation along the Equator in the Western Pacific*, Geophysical Research Letters, **Vol. 26**, No. 23, p. 3489-3492, December 1, 1999.
- 383) Broecker, W.S., *The Role of the Ocean in Climate Change: Past and Future*, Lecture given at Luso-American Development Foundation, Lisbon, Portugal, 30 pp., March 9, 1999.
- 384) Broecker, W.S., J. Lynch-Stieglitz, D. Archer, M. Hofmann, E. Maier-Reimer, O. Marchal, T. Stocker, and N. Gruber, *How Strong is the Harvardton Bear Constraint?*, Global Biogeochemical Cycles, **Vol. 13**, No. 4, p. 817-820, December, 1999.
- 385) Broecker, W.S. and S. Peacock, *An ecologic explanation for the Permo-Triassic carbon and sulfur isotope shifts*, Global Biogeochemical Cycles, **Vol. 13**, No. 4, p. 1167-1172, December, 1999.
- 386) Broecker, W.S., E. Clark, D.C. McCorkle, T.-H. Peng, I. Hajdas, and G. Bonani, *Evidence for a reduction in the carbonate ion content of the deep sea during the course of the Holocene*, Paleoceanography, **Vol. 14**, No. 6, p. 744-752, December, 1999.

- 387) Peacock, S., M. Visbeck, and W.S. Broecker, *Deep water formation rates inferred from global tracer distributions: An inverse approach*, in AGU Monograph entitled (2000) **Inverse Methods in Global Biogeochemical Cycles**, edited by Kasibhatla, P., Heimann, M., Rayner, P., Mahowald, N., Prinn, R. G., & Hartley, . Geophysical Monograph Series, Volume 114, approximately 324 pp., American Geophysical Union, Washington, D.C.114, p. 185-194, 1999.
- 388) Hofmann, M., W.S. Broecker, and J. Lynch-Stieglitz, *Influence of a [CO₂(aq)] Dependent Biological C-Isotope Fractionation on Glacial ¹³C/¹²C Ratios in the Ocean*, submitted to *Global Biogeochemical Cycles*, **Vol. 13**, No. 4, pp. 873-883, December, 1999.
- 389) Broecker, W.S., *Better Living Through Geochemistry: Tracking Chemical Clues to Investigate the Earth*, **Lamont-Doherty Earth Observatory: Twelve Perspectives on the First Fifty Years 1949-1999**, Laurence Lippsett, Editor, Office of Communications and External Relations, L-DEO of Columbia University, publishers, 1st Edition, Chapter 5, pp. 59-73, 1999.

2000

- 390) Broecker, W.S., *Was a Change in Thermohaline Circulation Responsible for the Little Ice Age?*, *Proceedings of the National Academy of Sciences (PNAS)*, Vol. 97, No. 4, pp. 1339-1342, February 15, 2000.
- 391) Broecker, W.S., *Poking the Angry Beast*, *Earth Matters*, pp. 7-9, Winter 1999/2000.
- 392) Liu, T. and W.S. Broecker, *How Fast Does Rock Varnish Grow?*, **V. 28**, no. 2, p. 183-186, *Geology*, February 2000.
- 393) Broecker, W.S., E. Clark, J. Lynch-Stieglitz, W. Beck, L.D. Stott, I. Hajdas, and G. Bonani, *Late Glacial Diatom Accumulation at 9°S in the Indian Ocean*, *Paleoceanography*, **vol. 15**, No. 3, pp. 348-352, June 2000.
- 394) Hemming, S.R., R.H. Gwiazda, J.T. Andrews, W.S. Broecker, A.E. Jennings, and T.C. Onstott, *⁴⁰Ar/³⁹Ar and Pb-Pb Study of Individual Hornblende and Feldspar Grains from Southeastern Baffin Island Glacial Sediments: Implications for the Provenance of the Heinrich Layers*, *Canadian Journal of Earth Sciences*, **Vol. 37**, No. 6, pp.879-890, 2000.
- 395) Liu, T, W.S. Broecker, J.W. Bell, and C.W. Mandeville, *Terminal Pleistocene Wet Event Recorded in Rock Varnish from Las Vegas Valley, Southern Nevada*, *Palaeogeography, Palaeoclimatology, Palaeoecology*, **Vol. 161**, pp. 423-433, 2000.
- 396) Broecker, W.S., *Abrupt Climate Change: Causal Constraints Provided by the Paleoclimate Record*, *Earth Science Reviews*, **Vol. 51**, pp. 137-154, 2000.
- 397) Broecker, W.S. and S. Sutherland, *The Distribution of Carbonate Ion in the Deep Ocean: Support for a Post-Little Ice Age Change in Southern Ocean Ventilation*, *G³*, **Vol. 1**, No. 2000GC000039, July 10, 2000.
- 398) Broecker, W.S., *Energy Prudence*. In: **Science for Survival and Sustainable Development, the Proceedings of the Study-Week of the Pontifical Academy of Sciences 12-16 March 1999**, Editors of the Proceedings: V.I. Keilis-Borok, and M. Sánchez Sorondo, Pontifical Academy of Sciences, pp. 145-159, 2000.

- 399) Broecker, W.S. and T.-H. Peng, *Comparison of ^{39}Ar and ^{14}C Ages for Waters in the Deep Ocean*. In: **Accelerator Mass Spectrometry: Proceedings of the Eight International Conference on Accelerator Mass Spectrometry, Palais Auersperg, Vienna, Austria, 6-10 September 1999**, Editors: W. Kutschera, R. Golser, A. Priller, and B. Strohmaier. Nuclear Instruments and Methods in Physics Research B, **172**, pp. 473-478, 2000.
- 400) Broecker, W.S., A. Sanyal, and T. Takahashi, *The Origin of Bahamian Whittings Revisited*, Geophysical Research Letters, **Vol. 27**, No. 22, pp. 3759-3760, November 15, 2000.
- 401) Hemming, S.R., G.C. Bond, W.S. Broecker, W.D. Sharp, and M. Klas-Mendelson, *Evidence from $^{40}\text{Ar}/^{39}\text{Ar}$ Ages of Individual Hornblende Grains for Varying Laurentide Sources of Iceberg Discharges 22,000 to 10,500 yr B.P.*, Quaternary Research, **Vol. 54**, No. 3, November 2000.
- 402) Archer, D., G. Eshel, A. Winguth, and W.S. Broecker, R. Pierrehumbert, M. Tobis, and R. Jacob, *Atmospheric ρCO_2 Sensitivity to the Biological Pump in the*, Global Biogeochemical Cycles, **Vol. 14**, No. 4, pp. 1219-1230, December, 2000.
- 403) Broecker, W.S., *Converging Paths Leading to the Role of the Oceans in Climate Change*, Annual Review of Energy and the Environment, 25:1-19, 2000.

2001

- 404) Greene, A.M. and W.S. Broecker, *Utility of Glacier Observations in Climate Change Detection and Attribution Studies*, Reprinted from the preprint volume of the **12th Symposium on Global Change Climate Variations**, 14-19 January 2001, Albuquerque, New Mexico by the AMS, Boston, Massachusetts.
- 405) Broecker, W.S., *A Dusty Past*, Reprinted from the preprint volume of the **12th Symposium on Global Change Climate Variations**, 14-19 January 2001, Albuquerque, New Mexico by the AMS, Boston, Massachusetts, pp. 175-176
- 406) Broecker, W.S., *Was the Medieval Warm Period Global?*, Science, **Vol. 291**, No. 5508, pp. 1497-1499, February 23, 2001.
- 407) Broecker, Wallace S., *Are We Headed for a Thermohaline Catastrophe?*, Chapter 4, **Geological Perspectives of Global Climate Change**, American Association of Petroleum Geologists Studies In Geology #47 (Lee C. Gerhard, William E. Harrison, and Bernold M. Hanson, Editors), pp. 83-95, 2001.
- 408) Broecker, W.S. and T. Liu, *Rock Varnish: Recorder of Desert Wetness*, GSA Today, **Vol. 11**, No. 8, pp. 4-10, August 2001.
- 409) Broecker, W.S., R.F. Anderson, E. Clark, and M. Fleisher, *Record of Sea-Floor CaCO_3 Dissolution in the Equatorial Pacific*, G^3 (Geochemistry, Geophysics, Geosystems), Vol. 2, No. 2001GC000151, June 28, 2001.
- 410) Broecker, W.S., C. Langdon, T. Takahashi, and T.-H. Peng, *Factors Controlling the Rate of CaCO_3 Precipitation on Great Bahama Bank*, Global Biogeochemical Cycles, **Vol. 15**, No. 3, pp. 589-596, September 2001.
- 411) Broecker, W.S., *Glaciers That Speak in Tongues*, Natural History Magazine, **Vol. 110**, No. 8, pp. 60-69, October 2001.

- 412) Broecker, W.S. and E. Clark, *An Evaluation of Lohmann's Foraminifera-Weight Dissolution Index*, *Paleoceanography*, **Vol. 16**, No. 5, pp. 531-534, October 2001.
- 413) Broecker, W.S., *The Big Climate Amplifier Ocean Circulation-Sea Ice-Storminess-Dustiness-Albedo*, in AGU's Geophysical Monograph Series The Oceans and Rapid Change: Past, Present, and Future Geophysical Monograph 126, 2001.
- 414) Matsumoto, K., W.S. Broecker, E. Clark, D.C. McCorkle, W.R. Martin, and I. Hajdas, *Can Deep Ocean Carbonate Preservation History Inferred from Atmospheric $p\text{CO}_2$ Account for ^{14}C and $\% \text{CaCO}_3$ Profiles on the Ontong-Java Plateau?*, *Earth & Planetary Science Letters*, **Vol. 192**, pp. 319-329, 2001.
- 415) Broecker, W.S., J. Lynch-Stieglitz, E. Clark, I. Hajdas, and G. Bonani, *What Caused the Atmosphere's CO_2 Content to Rise During the Last 8000 Years?*, *G³*, **Vol. 2**, No. 2001GC000177, October 2001.
- 416) Broecker, W.S. and E. Clark, *A Dramatic Atlantic Dissolution Event at the Onset of the Last Glaciation*, *G³*, **Vol. 2**, No. 2001GC000185, November 2001.
- 417) Moore, W., T. Liu, W.S. Broecker, and A. Wright, *Factors Influencing ^7Be Accumulation on Rock Varnish*, *Geophysical Research Letters*, **Vol. 28**, No. 23, pp. 4475-4478, December 1, 2001.
- 418) Broecker, W.S., *A Ewing Symposium on the Contemporary Carbon Cycle*, *Global Biogeochemical Cycles*, **Vol. 15**, No. 4, pp. 1031-1033, December 2001.
- 419) Broecker, W.S. and E. Clark, *Glacial to Holocene Redistribution of Carbonate Ion in the Deep Sea*, *Science*, **Vol. 294**, pp. 2152-2155, December 7, 2001.
- 420) Broecker, W.S. and S.R. Hemming, *Climate Swings Come Into Focus*, *Science*, **Vol. 294**, pp. 2308-2309, December 14, 2001.
- 421) Broecker, W.S. and E. Clark, *Reevaluation of the CaCO_3 Size Index Paleocarbonate Ion Proxy*, *Paleoceanography*, **Vol. 16**, No. 6, pp. 669-671, December 2001.
- 422) Sutherland, S.C., W.S. Broecker, and T. Takahashi, *Stability of the Boundary Separating Antarctic Bottom Water from North Atlantic Deep Water in the Western South Atlantic*, *Geophysical Research Letters*, **Vol. 28**, No. 22, pp. 4219-4222, November 15, 2001.
- 423) Wallace S. Broecker: *Carbon Futures*, Chapter 5 in: Geosphere-Biosphere Interactions and Climate; page 66 – 80, Lennart O. Bengtsson and Claus U. Hammer, eds., New York: Cambridge University Press. 2001.

2002

- 424) Broecker, W.S. and E. Clark, *A Major Dissolution Event at the Close of MIS 5e in the Western Equatorial Atlantic*, *G³*, **Vol. 3**, No. 2, February 5, 2002.

- 425) Hemming, S.R., C.M. Hall, P.E. Biscaye, S.M. Higgins, G.C. Bond, J.F. McManus, D.C. Barber, J.T. Andrews, and W.S. Broecker, ⁴⁰Ar/³⁹Ar Ages and ⁴⁰Ar* concentrations of Fine-Grained Sediment Fractions from North Atlantic Heinrich Layers, *Chemical Geology*, **Vol. 182**, pp. 583-603, 2002.
- 426) Broecker, W.S. and E. Clark, *Carbonate Ion Concentration in Glacial-Age Deep Waters of the Caribbean Sea*, *G³*, **Vol. 3**, No. 3, 10.1029/2000GC000231, March 27, 2002.
- 427) Broecker, W.S., *Dust: Climate's Rosetta Stone*, *Proceedings of the American Philosophical Society*, Vol. 146, No. 1, pp. 77-80, March 2002.
- 428) Greene, A.M., R. Seager, and W.S. Broecker, *Tropical Snowline Depression at the Last Glacial Maximum: Comparison with Proxy Records Using a Single-Cell Tropical Climate Model*, *Journal of Geophysical Research*, 10.1029/2001JD000670, April 19, 2002.
- 429) Kukla, G.J., M.L. Bender, J.-L. de Beaulieu, G. Bond, W.S. Broecker, et al, *Last Interglacial Climates*, *Quaternary Research*, Vol. 58, pp. 2-13, 2002.
- 430) Broecker, W.S., *Constraints on the Glacial Operation of the Atlantic Ocean's Conveyor Circulation*, *Israel Journal of Chemistry*, **Vol. 42**, pp. 1-14, 2002.

2003

- 431) Langdon, C., W. Broecker, D. Hammond, E. Glenn, K. Fitzsimmons, S. G. Nelson, T.-H. Peng, I. Hajdas and G. Bonani, *Effect of Elevated CO₂ on the Community Metabolism of an Experimental Coral Reef*, *Global Biogeochemical Cycles*, Vol. 17, No. 1, 1011, doi:10.1029/2002GB001941, 2003
- 432) Broecker, W.S. and E. Clark, *Pseudo Dissolution of Marine Calcite*, *Earth and Planetary Science Letters*, **Vol. 208**, pp. 291-296, 2003.
- 433) Broecker, W.S., *Does the Trigger for Abrupt Climate Change Reside in the Ocean or in the Atmosphere?*, *Science*, **Vol. 300**, No. 5625, pp. 1519-1522, June 6, 2003.
- 434) Broecker, W.S. and E. Clark, *Holocene Atmospheric CO₂ Increase as Viewed from the Seafloor*, *Global Biogeochemical Cycles*, **Vol. 17**, No. 2, doi: 10.1029/2002GB001985, 2003.
- 435) Broecker, W.S. and E. Clark, *Glacial-Age Deep Sea Carbonate Ion Concentration*, *Geochemistry, Geophysics, and Geosystems (G³)*, DOI number 10.1029/2003GC000506, **Vol. 4**, No. 6, June, 5 2003.
- 436) Broecker, W.S. E. Clark, and A. Droxler, *Shell Weights from Intermediate Depths in the Caribbean Sea*, *Geochemistry, Geophysics, and Geosystems (G³)*, **Vol. 4**, No. 7, doi:10.1029/2002GC000491, July 15, 2003.

- 437) Broecker, W.S. and E. Clark, *CaCO₃ Dissolution in the Deep Sea: Paced by Insolation Cycles*, *Geochemistry, Geophysics, Geosystems (G³)*, **Vol. 4**, No. 7, doi: 10.1029/2002GC000450, July 15, 2003.
- 438) Broecker, W.S. and E. Clark, *The Role of Sonification in Shell Weight Measurements*, *Geochemistry, Geophysics, Geosystems (G³)*, doi:10.1029/2003GC000569, **Vol. 4**, No. 11, November 7, 2003.
- 439) Broecker, W.S. (2003) The Oceanic CaCO₃ Cycle, pp.529-549. In *The Oceans and Marine Geochemistry* (ed. H. Elderfield) Vol. 6 *Treatise on Geochemistry* (eds. H.D. Holland and K.K. Turekian), Elsevier-Pergamon, Oxford.
- 440) Broecker, W.S. (2003) Radiocarbon, pp.245-260. In *The Atmosphere* (ed. R.F. Keeling) Vol. 4 *Treatise on Geochemistry* (eds. H.D. Holland and K.K. Turekian), Elsevier-Pergamon, Oxford.

2004

- 441) Broecker, W.S. and E. Clark, *Shell Weights from the South Atlantic*, *Geochemistry, Geophysics, Geosystems*, **Vol. 5**, No. 3, Q03003m DOI 10.1029/2003GC000625, 11 March 2004
- 442) Broecker, W.S. E. Clark, I. Hajdas, and G. Bonani, *Glacial Ventilation Rates for the Deep Pacific Ocean*, *Paleoceanography*, **Vol. 19**, PA2002, doi:10.1029/2003PA000974, 2004.
- 443) Broecker, W.S., S. Barker, E. Clark, I. Hajdas, G. Bonani, and L. Stott, *Ventilation of Glacial Deep Pacific Ocean*, *Science*, **Vol. 306**, p. 1169-1172, 12 November 2004.

2005

- 444) Denton, G.H., R.B. Alley, G.C. Comer, and W.S. Broecker, *The Role of Seasonality in Abrupt Climate Change*, *Quaternary Science Reviews*, **Vol. 24**, p. 1159-1182, 2005.
- 445) Lowell, T.V., T.G. Fisher, G.C. Comer, I. Hajdas, N. Waterson, K. Glover, H.M. Loope, J.M. Schaefer, V. Rinterknecht, W.S. Broecker, G. Denton, and J.T. Teller, *Testing the Lake Agassiz Meltwater Trigger for the Younger Dryas*, *EOS*, **Vol. 86**, No. 40, 4 October 2005.
- 446) Broecker, W.S., *Global Warming: Take Action or Wait?*, *Jökull*, No. 55, p. 1-16, 2005.

2006

- 447) Broecker, W.S. and T.F. Stocker, *The Holocene CO₂ Rise, Anthropogenic or Natural?*, *EOS*, **Vol. 87**, No. 3, p. 27, 17 January 2006.
- 448) Broecker, W., S. Barker, E. Clark, I. Hajdas, and G. Bonani (2006), Anomalous radiocarbon ages for foraminifera shells, *Paleoceanography*, 21, PA2008, doi:10.1029/2005PA001212.
- 449) Broecker, W.S., *Global Warming: Take Action or Wait?* *Chinese Science Bulletin*, **Vol. 51**, No. 9, p. 1017 – 1029, doi:10.1007/s11434-006-1017-4, May 2006 (co-publisher: Springer-Verlag GmbH, ISSN: 1001-6538).
- 450) Broecker, W.S., *Was the Younger Dryas Triggered by a Flood?*, *Science*, **Vol. 312**, pp. 1146 – 1148, 26 May 2006.

- 451) Denton, G.H., W.S. Broecker, and R.B. Alley, *The mystery interval 17.5 to 14.5 kyrs ago*, PAGES News, **Vol. 14**, No. 2, pp. 14 – 16, August 2006.
- 452) Broecker, W.S., *Abrupt Climate Change Revisited*, Global and Planetary Change, **Vol. 54**, Issues 3 – 4, pp. 211 – 215, December 2006.
- 453) Marchitto, T. M., and W. S. Broecker (2006), *Deep water mass geometry in the glacial Atlantic Ocean: A review of constraints from the paleonutrient proxy Cd/Ca*, *Geochem. Geophys. Geosyst.*, 7, Q12003, doi:10.1029/2006GC001323.

2007

- 454) Broecker, W., and E. Clark (2007), Is the magnitude of the carbonate ion decrease in the abyssal ocean over the last 8 kyr consistent with the 20 ppm rise in atmospheric CO₂ content?, *Paleoceanography*, 22, PA1202, doi:10.1029/2006PA001311.
- 455) Liu, T. and W.S. Broecker, *Holocene Rock Varnish Microstratigraphy and Its Chronometric Application in the Drylands of Western USA*, *Geomorphology*, Vol. 84, pp. 1 – 21, 2007.
- 456) Broecker, W. S., and S. Barker (2007), *Reply to comment by L. D. Stott on “Anomalous radiocarbon ages for foraminifera shells”: A correction to the western tropical Pacific MD9821-81 record*, *Paleoceanography*, 22, PA1212, doi:10.1029/2006PA001393.
- 457) Broecker, W.S., *CO₂ Arithmetic*, *Science*, **Vol. 315**, no. 5817, p. 1371, 9 March 2007.
- 458) Broecker, W.S. and S. Barker, A 190‰ drop in atmosphere’s $\Delta^{14}\text{C}$ during the “Mystery Interval” (17.8 to 14.5 kyrs), *Earth & Planetary Science Letters*, **vol. 256**, pp. 90 – 99, 2007.
- 459) W.S. Broecker and Rik Wanninkhof, *Mono Lake Radiocarbon: The Mystery Deepens*, *EOS*, **Vol. 88**, No. 12, pp. 141-142, 20 March 2007.
- 460) Broecker, W., E. Clark, S. Barker, I. Hajdas, G. Bonani, and E. Moreno (2007), Radiocarbon age of late glacial deep water from the equatorial Pacific, *Paleoceanography*, 22, PA2206, doi:10.1029/2006PA001359.
- 461) Barker, S., W. Broecker, E. Clark, and I. Hajdas (2007), Radiocarbon age offsets of foraminifera resulting from differential dissolution and fragmentation within the sedimentary bioturbated zone, *Paleoceanography*, 22, PA2205, doi:10.1029/2006PA001354.
- 462) Broecker, W.S., *Musings about the Connection Between Thermohaline Circulation and Climate*. In AGU Geophysical Monograph 173, *Past and Future Changes of the Oceans Meridional Overturning Circulation: Mechanisms and Impacts*, Andreas Schmittner, John C. H. Chiang, and Sidney Hemming, eds. AGU Volume on Thermohaline Circulation, 10.1029/173GM17, 2007.

2008

- 463) Liu, T. and W.S. Broecker, *Rock varnish microlamination dating of late Quaternary geomorphic features in the drylands of western USA*, *Geomorphology*, **93**, pp. 501 - 523, 2008.
- 464) Broecker, W. S. (2008), A need to improve reconstructions of the fluctuations in the calcite compensation depth over the course of the Cenozoic, *Paleoceanography*, 23, PA1204, doi:10.1029/2007PA001456
- 465) Broecker, W. (2008), Excess sediment ²³⁰Th: Transport along the sea floor or enhanced water column scavenging?, *Global Biogeochem. Cycles*, 22, GB1006, doi:10.1029/2007GB003057
- 466) Chiu, T.-C. and W.S. Broecker, *Towards Better Paleo-Carbonate Ion Reconstructions – A New Insight Regarding the CaCO₃ Size Index*, *Paleoceanography*, Vol. 23, PA2216, doi:10.1029/2008PA001599, 2008.
- 467) Liu, T. and W.S. Broecker, *Rock Varnish Evidence for Latest Pleistocene Millennial-Scale Wet Events in the Drylands of Western United States*, *Geology*, v. **36**, no. 5, p. 403-406, doi:10.1130/G24573A/1, May 2008.
- 468) Broecker, W.S., E. Clark, and S. Barker, *Near constancy of the Pacific Ocean surface to mid-depth radiocarbon-age difference over the last 20 kyr*, *Earth and Planetary Science Letters*, **Vol. 274**, Iss. 3-4, pp. 322-326, doi:10.1016/j.epsl.2008.07.035, 15 October 2008.
- 469) Denton, G. H. and W.S. Broecker, *Wobbly Ocean Conveyor Circulation During the Holocene?*, *Quaternary Science Reviews*, **Vol. 27**, Iss. 21 – 22, pp. 1939 – 1950, November 2008.

2009

- 470) Broecker, W.S., *Wally's Quest to Understand the Ocean's CaCO₃ Cycle*, *Annual Review of Marine Science*, Vol. 1: 1-18 , (doi:10.1146/annurev.marine.010908.163936), January 2009.
- 471) Barker, S., P. Diz, M.J. Vautravers, J. Pike, G. Knorr, I.R. Hall and W.S. Broecker, *Interhemispheric Atlantic seesaw response during the last deglaciation*, *Nature*, **Vol. 457**, pp. 1097 – 1102, (doi:10.1038/nature07770), 26 February 2009.
- 472) Broecker, W.S., *The Mysterious ¹⁴C Decline*, *The 50th Anniversary of Radiocarbon*, **Vol 51**, Nr 1, 2009, p 109 - 119.
- 473) Broecker, W., and E. Clark (2009), Ratio of coccolith CaCO₃ to foraminifera CaCO₃ in late Holocene deep sea sediments, *Paleoceanography*, 24, PA3205, doi:10.1029/2009PA001731.
- 474) Cheng, Hai, R.L. Edwards, W.S. Broecker, G. Denton, X. Kong, Y. Wang, R. Zhang and X. Wang, *Ice Age Terminations*, *Science*, **Vol. 326**, pp. 248-252, DOI: 10.1126/science.1177840, 9 October 2009.
- 475) Broecker, W. S. D. McGee, K. Adams, H. Cheng, R. L. Edwards, C. G. Oviatt, J. Quade, *A Great Basin-Wide Dry Episode During the First Half of the Mystery Interval?*, *Quaternary Science Reviews* 28 (2009) 2557–2563.

- 476) Quade, J. and W.S. Broecker, *Dryland Hydrology in a Warmer World: Lessons from the Last Glacial Period*, Eur. Phys. J. Special Topics 176, 21--36 (2009), EDP Sciences, Springer-Verlag 2009, DOI: 10.1140/epjst/e2009-01146-y.
- 477) Matter, J.M., W.S. Broecker, M. Stute, S.R. Gislason, E.H. Oelkers, A. Stefánsson, D. Wolff-Boenisch, E. Gunnlaugsson, G. Axelsson and G. Björnsson, *Permanent Carbon Dioxide Storage into Basalt: The CarbFix Pilot Project, Iceland*, Energy Procedia 1 (2009) 3641-3646, doi:10.1016/j.egypro.2009.02.160.
- 478) Broecker, W.S., *Man-Induced Climate Change*, In: The Multiple Faces of Globalization, Turner, Ed., BBVA, Series 2, pp. 174-183 (2009) Madrid, ISBN: 978-84-7506-909-8.

2010

- 479) Yu, J., G.L. Foster, H. Elderfield, W.S. Broecker and E. Clark, *An evaluation of benthic foraminiferal B/Ca and $d^{11}B$ for deep ocean carbonate ion and pH reconstructions*, Earth and Planetary Science Letters, 293 (2010) 114-120.
- 480) Broecker, W.S., G.H. Denton, R.L. Edwards, H. Cheng, R.B. Alley and A.E. Putnam, *Putting the Younger Dryas Cold Event into Context*, Quaternary Science Reviews, Volume 29, Issues 9-10, May 2010, Pages 1078-1081, ISSN 0277-3791, DOI: 10.1016/j.quascirev.2010.02.019.
- 481) Broecker, W., and E. Clark (2010), *Search for a glacial-age ^{14}C -depleted ocean reservoir*, Geophys. Res. Lett., 37, L13606, doi:10.1029/2010GL043969²
- 482) McGee, D., W.S. Broecker and G. Winckler, *Gustiness: The driver of glacial dustiness?*, Quaternary Science Reviews, Volume 29, Issues 17-18, August 2010, Pages 2340-2350, ISSN 0277-3791, DOI: 10.1016/j.quascirev.2010.06.009.
- 483) Yu, J. and W.S. Broecker, *Comment on "Deep-Sea Temperature and Ice Volume Changes Across the Pliocene-Pleistocene Climate Transitions"*, (18 June 2010) Science 328 (5985), 1480-c. [DOI: 10.1126/science.1186544].
- 484) Yu, J., W.S. Broecker, H. Elderfield, Z. Jin, J. McManus, and F. Zhang, *Loss of Carbon from the Deep Sea Since the Last Glacial Maximum*, Science, 19 November 2010: 330 (6007), 1084-1087. [DOI:10.1126/science.1193221].
- 485) Broecker, W.S., Long-Term Water Prospects in the Great Basin of the Western USA, *Journal of Climate*, 23, 6669-6683, doi: 10.1175/2010JCL13780.1, December, 2010.

2011

- 486) Thornalley, D.J.R., S. Barker, W.S. Broecker, H. Elderfield, and I.N. McCave (2011), The deglacial evolution of North Atlantic deep convection, *Science*, 331 (6014), 202-205, doi: 10.1126/science.1196812.
- 487) Broecker, W., and E. Clark (2011), Radiocarbon-age differences among coexisting planktic foraminifera shells: The Barker Effect, *Paleoceanography*, 26, PA2222, doi: 10.1029/2011PA002116.

²Click this link to access your article: <http://www.agu.org/journals/gl/gl1013/2010GL043969/>.
The following code is both the login ID and password: 35508728

- 488) Matter, J.M., W.S. Broecker, S.R. Gislason, E. Gunnlaugsson, E.H. Oelkers, M. Stute, H. Sigurdardottir, A. Stefansson, D. Wolff-Boenisch, G. Axelsson and B. Sigfusson (2011), The CarbFix Project-Storing Carbon Dioxide in Basalt, *Energy Procedia*, 4, 5579-5585.
- 489) Broecker, W., and J. Yu (2011), What do we know about the evolution of Mg to Ca ratios in seawater? *Paleoceanography*, 26, PA3203, 8 p., doi: 10.1029/2011PA002120.
- 490) Cartwright, A, J. Quade, S. Stine, K.D. Adams, W. Broecker, and H. Cheng (2011), Chronostratigraphy and lake-level changes of Laguna Cari-Laufquén, Río Negro, Argentina, *Quaternary Research*, 76, 430-440.

2012

- 491) Broecker, W. (2012), The Carbon Cycle and Climate Change: Memoirs of my 60 Years in Science, *Geochemistry Perspectives*, 1, No. 2, 221-339, editors: S.L.S. Stipp and E.H. Oelkers, European Association of Geochemistry.
- 492) McGee, D., J. Quade, R. L. Edwards, W. S. Broecker, and H. Cheng (2012), Lacustrine cave carbonates: Precisely dated recorders of paleohydrologic change in Lake Bonneville. *Earth and Planet. Sci. Lett.*, 351-352, 182-194.
- 493) Broecker, W. and A. E. Putnam (2012), How did the Hydrologic Cycle respond to the two-phase Mystery Interval? *Quaternary Science Reviews*, 57, 17-25.

2013

- 494) Liu, Tanzhuo and Wallace S. Broecker (2013), Millennial-scale varnish microlamination dating of late Pleistocene geomorphic features in the drylands of western USA, *Geomorphology*, 187, 38-60.
- 495) Broecker, W. (2013), The Impact of Global Warming on the Distribution of Rainfall: A Historical Perspective, chapter in BBVA volume entitled “*There’s a Future: Visions for a Better World*,” 223-247.
- 496) Broecker, W.S. and D. McGee (2013), The ¹³C record for atmospheric CO₂: What is it trying to tell us? *Earth and Planet. Sci. Lett.*, 368, 175-182.
- 497) Broecker, W. (2013), How to think about the evolution of the ratio of Mg to Ca in seawater, *American Journal of Science*, 313, 776-789, doi: 10.2475/08.2013.02.
- 498) Wang, X. and W. Broecker (2013), Long-term reworking of volcanic ash deposited in the abyssal ocean based on uranium and thorium isotope measurements, *Journal of Volcanology and Geothermal Research*, 264, 66-71.
- 499) Broecker, W.S., and A. Putnam (2013), Do the hydrologic impacts associated with shifts in the thermal equator offer insight into those to be produced by fossil fuel CO₂? *PNAS*, 110, no. 42, 16710-16715.
- 500) Broecker, W., Water Sustainability in a Warming World: A Paleo-Perspective, (2013) In: *Water Quality and Sustainability*, Volume 4 of “Comprehensive Water Quality and Purification,” 329-358, Elsevier Press.
- 501) Broecker W., (2013), Does air capture constitute a viable backstop against a bad CO₂ trip?

2014

- 502) Broecker, W., and L. Pena (2014) Delayed Holocene reappearance of *G. menardii*, *Paleoceanography*, 29, 291-295, doi: 10.1002/2013PA002590.
- 503) Matter, J. M., M. Stute., J. Hall., K. Mesfin, S.Ó. Snæbjörnsdóttir, S. R., Gislason, E.H. Oelkers, B. Sigfusson, I. Gunnarson, E. S. Aradottir, H. A. Alfredsson, E. Gunnlaugsson, W. S. Broecker (2014). Monitoring permanent CO₂ storage by in situ mineral carbonation using a reactive tracer technique..*Energy Procedia* 63, 4180-4185.
- 504) Gislason, Sigurdur R., W. S. Broecker, E. Gunnlaugsson, S. Snæbjörnsdóttir, K. G. Mesfin, H. A. Alfredsson, E. S. Aradottir, B. Sigfusson, I. Gunnarsson, M. Stute, J. M. Matter, M. Th. Arnarson, I. M. Galeczka, S. Gudbrandsson, G. Stockman, D. Wolff-Boenisch, A. Stefansson, E. Ragnheidardottir, T. Flaathen, A. P. Gysi, J. Olssen, K. Didriksen, S. Stipp, B. Menez, E. H. Oelkers (2014). Rapid solubility and mineral storage of CO₂ in basalt. *Energy Procedia*, 63, 4561-4574.

2015

- 505) Broecker W (2015). The collision that changed the world. *Elem. Sci. Anth.* 3, 000061 doi: 10.12952/journal.elementa.000061.
- 506) Broecker, W. S., Yu, J., Putnam, A.E. (2015). Two contributors to the glacial CO₂ decline. *Earth and Planet. Sci. Lett.*, 429, 191-196.
- 507) Steponaitis, E., A. Andrews, D. McGee, J. Quade, Y.-T. Hsieh, W. S. Broecker, B. N. Shuman, S. Burns, and H. Cheng (2015). Mid-Holocene drying of the U.S. Great Basin recorded in Nevada speleothems. *Quat. Sci. Rev.*, 127, 174-185.
- 508) Putnam, Aaron E., David E. Putnam, Laia Andreu-Hayles, Edward R. Cook, Jonathan D. Palmer, Elizabeth H. Clark, Chunzeng Wang, Feng Chen, George H. Denton, Douglas P. Boyle, Scott D. Bassett, Sean D. Birkel, Javier Martin-Fernandez, Irka Hajdas, John Southon, Christopher B. Garner, Hai Cheng, and Wallace S. Broecker (2015). Little Ice Age wetting of interior Asian deserts and the rise of the Mongol. *Quat. Sci. Rev.*, 131, 33-50.

2016

- 509) Anbar, A. D., S. J. Romaniello, B. R. Allenby, and W. S. Broecker (2016) Addressing the Anthropocene, *Environ. Chem.*, <http://dx.doi.org/10.1071/EN15115>.
- 510) Yu, J., L. Menviel, Z. D. Jin, D. J. R. Thornalley, S. Barker, G. Marino, E. J. Rohling, Y. Cai, F. Zhang, X. Wang, Y. Dai, P. Chen, and W. S. Broecker (2016). Sequestration of carbon in the deep Atlantic during the last glaciation. *Nature Geoscience*, doi: 10.1038.NGE02657.
- 511) Matter, J.M., M. Stute, S.O. Snaebjornsdottir, E.H. Oelkers, S.R. Gislason, E.S. Aradottir, B. Sigfusson, I. Gunnarsson, H. Sigurdardottir, E. Gunnlaugsson, G. Axelsson, H.A.

Alfredsson, D. Wolff-Boenisch, K. Mesfin, D.F. de la Reguera Taya, J. Hall, K. Dideriksen, W.S. Broecker (2016), Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions, *Science*, 352/6291, 1312-1314, doi: 10.1126/science.aad8132.