

# Geochemical Perspectives



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WALLY BROECKER

## The Carbon Cycle and Climate Change: Memoirs of my 60 years in Science



Each issue of *Geochemical Perspectives* presents a single article with an in-depth view on the past, present and future of a field of geochemistry, seen through the eyes of highly respected members of our community. The articles combine research and history of the field's development and the scientist's opinions about future directions. We welcome personal glimpses into the author's scientific life, how ideas were generated and pitfalls along the way. *Perspectives* articles are intended to appeal to the entire geochemical community, not only to experts. They are not reviews or monographs; they go beyond the current state of the art, providing opinions about future directions and impact in the field.

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## ABOUT THE COVER

Tufa towers in Mono Lake, Central California. These tufa towers are formed from  $\text{CaCO}_3$  that precipitates from the lake water as alkaline groundwater enters from springs; they have become exposed as the lake level dropped in response to natural processes and water diversion from the watershed.

Photo credit: Avraham Kushnirov/Veer



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# FOREWORD

*We are proud to present this issue of Geochemical Perspectives. It relates the personal odyssey of Wally Broecker, from his first days at university to his viewpoint now, looking back over a panorama of 60 years in science. Through his broad and deep experience and his ability to think analytically, he has played a central role in the development of our understanding of the carbon cycle. His narrative tells some of the events in perhaps the most riveting geoscientific story of our generation – the discovery of the interdependency of climate and the oceans.*

*In contrast with a classical scientific paper, that presents the results of a specific research study, in this issue, Wally relates the process of how his ideas were formulated. We are led to see that the path to scientific discovery is paved with ideas and hard work but the choice of the path depends on happenstance (i.e. luck). In one chapter, for example, Wally recounts that his start with radiogenic dating came from a chance encounter at a meeting of archaeologists in Los Angeles, which he had only attended as a last minute fill in for his professor. What he learned from the ensuing field trips led to radiogenic dating that showed past water levels in Mono Lake, sea level changes in the Mississippi delta and the ages of uplifted coral reefs in the Barbados. From these snapshots, Wally correlated the water level fluctuations to the orbital cycles of the Earth. His chance encounter made huge ripples through his life and the development of our science.*



*Over our careers, we have heard Wally giving talks on past climates, ocean circulation and more recently, CO<sub>2</sub>. We have heard his probing questions at our talks or those of others and we have read the papers he has coauthored with colleagues. Over the years, we learned the scientific story but we understood very little about how the story developed. Now in this issue, we get a glimpse inside. How does one set out to explore something as obscure as past climate? How can one even begin to discover the controls on climate? Can the geologic record reveal climate change over millions of years? Here, Wally tells us some of the rest of the story.*

*We hope you will find it as enlightening as we have – about isotope ratios, carbon, oceans and climate – but perhaps more important, about how a scientist struggles after the truth.*

Eric H. Oelkers and Susan L.S. Stipp



# THE CARBON CYCLE AND CLIMATE CHANGE: MEMOIRS OF MY 60 YEARS IN SCIENCE

## ABSTRACT

This manuscript presents the development of our current understanding of how the oceans operate and how past climates are reconstructed from the personal viewpoint of the author. It begins with the application of radiocarbon dating of carbonate rocks to deduce past climatic conditions. Age dating of carbonate sediments and microfossils provides a history of sea level rise and fall that closely matches fluctuations in temperature, which in turn correspond with cyclic changes in the Earth's orbit. The origins of our understanding of how ocean circulation can affect global climate are reviewed and the essential role of atmospheric carbon-dioxide content is explored. Central to this climate link is the rate of CO<sub>2</sub> flux between the various terrestrial reservoirs including seawater, glacial ice and the terrestrial biota. The manuscript concludes by describing how the collected knowledge about the carbon cycle provides insight into capture of CO<sub>2</sub> from the atmosphere with the aim of storing it and attenuating the potentially devastating effects of fossil fuel burning on global climate change.



## 1.

## INTRODUCTION

I summarise here my life as a scientist. Except for two six month sabbaticals at Caltech and one in Heidelberg, Germany, all 60 years have been spent here at Lamont. I say “Lamont” because when I arrived in June 1952, it was Lamont Geological Observatory. It then became Lamont-Doherty Geological Observatory and it is now Lamont-Doherty Earth Observatory. I am a lucky man to have been associated with this marvellous institution. Recently, I learned that our Earth science unit was ranked number one in the U.S. As far as I’m concerned, it has always been number one. During these 6 decades, I have published 480 papers and written 11 books. Along the way, I have worked with 50 graduate students and 35 post doctoral fellows. In this issue, I relate the accomplishments that stand out in my mind as meritorious and that hopefully will be of interest to at least some of the geochemistry community. At 80, it is not clear how long it will be before my memory becomes a fog so I’ve put aside two months to write it all down. Perhaps the product will inspire some young people to follow in my tracks. I hope so. It has been an exciting run. I wake up each day raring to pry loose more of nature’s closely guarded secrets.



PAUL W. GAST

Photo courtesy of Lamont-Doherty Earth Observatory Archives.

**Figure 1**

The late Paul Gast, my Wheaton College big brother, fellow Columbia graduate student and lifelong friend. If it had not been for Paul, I surely would not have become a geochemist! I owe him.

I confine this summary to my life as a scientist. Of course, the things I discuss here were intertwined with my home life. I helped to raise 6 children and now have 7 grandchildren and 5 great grandchildren. I say “helped” because the giant share of the effort was that of my late wife, Grace. Without her support and understanding, my wheels would likely have come off, but all that is another story that will surely never be told. Since Grace’s death five years ago, with the help of my daughters and my second wife, Elizabeth Clark, I have kept on track. My spirits remain high and, thanks to the wonders of modern medicine, my health is quite good. I dedicate this issue to the late Paul Gast (Fig. 1). Not only did he steer me to Columbia, but he helped me through graduate school, and also later in life, directing the Lamont Geochemistry Group.



## 2.

## WHEATON DAYS

In September of 1949, my high school buddy, Ernie Sandeen, and I drove our jointly owned 1934 Ford Coupe 30 miles west from our homes in Oak Park, Illinois. In the rumble seat were the possessions we needed for studies at Wheaton College (Fig. 2). Although academically strong, students at Wheaties, as we called it, were immersed in Christian Fundamentalism. First off, to get admitted, you had to sign a pledge not to smoke, drink, dance or attend movies. Further, each day we were required to attend a chapel service. Grade points were deducted for absence. To top it off, each class began with a brief period of “devotions”. Because I had been brought up by parents who conducted their lives in a similar fashion, I was accustomed to this heavy religious overprint.



**Figure 2** Wheaton College's Blanchard Hall, the scene of many of my college day pranks.

When I appeared at the college's gymnasium to register, I found that I had been assigned a sophomore big brother named Paul Gast. It was his task to guide me through the registration process. As it turned out, this was a lucky match, because Paul, realising that I was hopelessly naïve about matters academic, became my self appointed career counsellor. Although we moved in quite different circles (he, a serious academic, and I, a do what you have to



student), Wheaties had only 1,600 students, so we ran into each other now and then. As will become clear, these encounters ultimately led me to a career in isotope geochemistry at Columbia University.

Although I don't remember all that much about my three years at Wheaton, a few high points remain fixed in my mind. I was fortunate to have truly outstanding teachers in key classes. George Bate taught me basic physics. Periodically, he gave us what he called "bear problems." To do them, while a struggle, for the first time in my life presented a serious challenge. Rather than coasting along, I had to dig in and think deeply. More than anything else, these problem sets turned me toward a career in science. Angelline Brandt taught my calculus class. Unheard of today, it was held at 7:30 a.m. but she made her subject live. Each morning, I eagerly jumped out of bed and went through the often frigid Illinois cold to attend her class. By the end of the year, I had a solid understanding of this important subject.

Lacking many of the outlets characteristic of college life, my free time was filled with sports and pranks. Because I never amounted to much in the former, I don't have memories worth relating but I was a first class prankster so I will take a few paragraphs to relate a couple of my favourites. I do this because the inventiveness I pored into my college day pranks became the substance of my career as a scientist.

During the time I was at Wheaton College, its main library was housed in what was once the women's gymnasium. The tables at which we studied faced a vertical array of stacks in which the books were stored. Sitting at a desk located just in front of this archive was a stern faced librarian. Miss Ball not only served as guardian of our collection, she also as disciplinarian of those who entered her kingdom. To say the least, she was not well liked so I decided to send her a reminder that she was not, after all, in total control. With the help of roommate Ernie, I placed an open topped box of moth balls on the floor of the highest level in the stacks directly above Miss Ball's desk. A string attached to the bottom of the box was looped over the guard rail and then passed along the floor, out the window at the back of the stacks and down into the bushes below. We waited until Miss Ball was busy harassing a poor victim for not returning a book on time and we pulled on the string, tipping over the box and sending hundreds of moth balls raining down on Miss Ball and her desk. We continued to reel in the string until the empty box came through the window and fell to the ground. Perfect crime! Hoping to capture the perpetrator, Miss Ball sealed off the exit to the stacks, thereby trapping the students unlucky enough to be searching for books, but she had to release these innocent bystanders, when a note arrived explaining how the crime had been committed. Every time Miss Ball discovered yet another moth ball fragment, she redoubled her efforts to track down the pranksters – but she never succeeded.

For many years, there had been a tradition for members of the junior class to attempt to steal a limestone slab which served as the senior class bench. This was part of the high jinks which took place during what was known as



“activities week”. If the theft succeeded, the slab was eventually returned to its place. During their junior year, the class of ‘52 not only succeeded in carrying off the bench but they tossed it off a bridge into a murky river. Instead of recovering it, they offered to create a replacement. Rather than obtaining another limestone slab, they installed a concrete bench, whose heavy base was buried several feet underground. It must have weighed over a ton. We, the class of ‘53, were then faced with the challenge of removing and hiding this behemoth. Realising that this was impossible, we decided to dig a hole big enough to tip the bench over on its side but this would take hours of effort and during activities week, groups of students would be wandering about so we decided to do it during the wee hours of the Thursday preceding activities week. Sure enough, we had the campus to ourselves. Only the night watchman made his once an hour rounds. John Nuckolls (who subsequently became the Director of Lawrence Livermore National Laboratory) served as lookout and warned us of the approach of the watchman. We diggers would hide behind the growing dirt pile until he was safely past. As dawn approached, the hole was finally big enough to accommodate the bench, but try as we might, we were unable to push it over. It was stuck in what I later learned were the sticky clays deposited in a proglacial lake, so we ran and got a rope, looped it around the bench and attached one end to the ‘34 Ford and the other to a second car. After initially spinning wheels, we were able to make traction and pull the bench over. With first light, the hole was filled in and the ground smoothed – no more bench.

The story didn’t end here, however. By the middle of the same morning, an enterprising senior probed the disturbed ground with a steel rod and located the missing bench. The Dean intervened and threatened to cancel activities week if the guilty parties didn’t replace the bench. Faced with this threat, we developed a plan. At that time, the foundation for a new building was being dug. We explained our dilemma to the construction boss and asked him to send over his steam shovel to retrieve the bench. He agreed and we set the time to correspond to the end of Friday’s chapel when there would be a maximum presence on campus. We joined the crowd to watch the resurrection of the senior bench and refilling of the hole. The steam shovel operator even gingerly smoothed the ground around the bench. Victory for the class of ‘53! Defeat for the class of ‘52!

During my college years, I confronted my Christian roots. I had never been comfortable with my religion, but the fear of “burning in hell”, which had been instilled into me throughout my childhood, kept me in the fold. However, as I got older, the hypocrisy of the supposedly dedicated Christians began to take its toll on my acceptance. It seemed that a sizable number of so called Christians found it impossible to abide by the rigid way of life demanded of them, so they cheated – and often big time. It was a bizarre event that took place in Wheaton’s chapel that led to my break with Christianity. Each semester, one full week of our daily services was devoted to rededicating ourselves to the Lord. At the end of the first of these services, led by a guest minister, one of the students stood up and said that he wanted to confess his misdoings. He was followed by a second student and a third and soon the choir loft was filled not only with students, but





also many of the faculty, awaiting their turn. The parade of confessions went on night and day for 72 hours. It made the Chicago newspapers and even attracted psychology researchers from the neighbouring University of Chicago. I was torn. Should I join the line? Certainly I had my own set of failings but would I be sincere in my confession? Or would I just be yielding to social pressure? I not only decided to opt out – but also that I would abandon Christianity – and I did, cold turkey.

Throughout my time at Wheaton, big brother, Paul Gast, took a continuing interest in me. Early in my sophomore year, he asked what I planned to do when I graduated. I was taken by surprise. “No idea” was my answer. “What about graduate school?”, he asked. I had to admit that I didn’t know anything about graduate school. He patiently explained that it was a continuation of one’s education allowing specialisation in a particular area, leading to a Masters and then to a PhD degree. To get him off my back, I promised to ponder my future. Each time we met, he inquired about my progress. I would blush and admit that I hadn’t made any. In November of my junior year, came a turning point. Instead of admitting no progress, based on a magazine article I had read while waiting in my dentist’s office, I told Paul that I was going to be an actuary. He was stunned. “Do you know how boring that would be?” I replied, “but I’m good at math.” A couple weeks later, I learned that my revelation had sparked Paul into action. He recommended me to a certain J. Lawrence Kulp, a young geochemistry professor who carried out research at Columbia University’s Lamont Geological Observatory. To my surprise, I was invited for an interview during the 1951-2 Christmas break. So I purchased a ticket on what was then known as a “non-scheduled” airline.

My first plane trip was quite eventful. It left from Chicago’s Midway Airport headed for New York’s La Guardia. En route, we encountered severe turbulence which caught the stewardess by surprise. The plane dropped leaving a tray of coffee in paper cups momentarily suspended in mid air. Down they came, creating a river in the plane’s aisle. A few minutes later, the pilot announced that La Guardia was fogged in so we would have to stop off for the night in Columbus, Ohio and hope that morning would bring better weather. Fortunately, it did and after a night in a motel, I arrived at La Guardia. No one was there to meet me, so I decided to take a taxi. The driver assured me that there was no such place as Palisades, New York but rather, my destination must be Palisades, New Jersey. Not having a street address for Lamont, he dropped me off near the Palisades Amusement Park. Fortunately, I had the telephone number for the lab and called to ask the address. The phone was answered by one of the graduate students, Walter Eckelmann. He chuckled and said that indeed there was a Palisades, New York and that he would come and rescue me. I don’t remember my interview with Professor Kulp but it must have gone well because he offered me a summer job. I returned to Wheaton, finished out my junior year and on June 15, 1952, I arrived at Lamont. Little did I know that 60 years later, I would still be there, sitting at my desk in the Comer Building with pencil in hand, pondering the next section of this issue.





### 3. A PIECE OF TEFLON

Upon my arrival at Lamont (Fig. 3a), I was assigned to help out in the radiocarbon counting laboratory. In those days, there were only three or four labs in the world conducting such analyses and all used the method developed by Willard Libby, the inventor of this ever so important dating tool (Libby, 1955). Professor Kulp explained to me that the carbon in the sample to be dated was first converted to elemental carbon black. A slurry of this carbon was then spun onto the inside of a stainless steel cylinder. After drying, the cylinder was placed along side an identical blank cylinder inside what was referred to as a screen wall radiation Geiger counter. The idea was to count the electrons emitted as the result of decays of radiocarbon atoms in the sample. The older the sample was, the smaller was the number of these events. The air was then pumped out of the cylinder and replaced with a mixture of argon and ethylene gas. The cylinder was then placed in a massive iron box which served as a shield against the gamma rays emitted by radioactive sources in the surroundings, such as  $^{40}\text{K}$  from bricks and concrete blocks (Fig. 3b). Also inside this shield surrounding the sample counter was a ring of permanently sealed radiation detectors that acted to null the events created by the cosmic ray mesons which passed freely through the massive iron shield. Each time a meson passed through one of these guard ring counters, its electronic pulse was placed in anticoincidence with those from the sample counter. In this way, the meson induced events in the sample counter were eliminated. This was very important because the number of meson events greatly outnumbered those from radiocarbon in the sample.

In spite of these precautions, some additional “background” events not attributable to radiocarbon were recorded. These were corrected for by shifting the cylinders back and forth so that part of the time the cylinder containing the sample carbon faced the active counting area and part of the time the blank cylinder faced the active



Photo courtesy of Department of Earth and Environmental Sciences Archives, Columbia University.

**Figure 3a** Photo taken in 1953, when I registered for graduate study in Columbia's Geology Department.





Photo courtesy of Lamont-Doherty Earth Observatory Archives.

**Figure 3b** Professor J. Lawrence Kulp inserting a radiocarbon counting device into the massive iron radiation shield in the basement of Lamont Hall.

counting area. This was possible because the outer cylinder was half again as long as the combined length of the two inner cylinders. Once he had explained the principles, Kulp went on to say that was where I fitted in. At 8 a.m., noon, 4 p.m. and 8 p.m., someone had to manually shift the cylinders. From 8 a.m. to noon, the counter recorded background, from noon to 4 p.m., it recorded sample plus background, from 4 p.m. to 8 p.m., background, and overnight, sample plus background. That someone was to be me. Kulp hastened to point out that tilting the counter to allow the inner cylinder to shift had to be done gently because if it shifted too rapidly and smacked against the end of the chamber, the sample carbon could be dislodged and that was not to happen!

I was surprised when I encountered George Bate, my physics teacher, at Lamont that summer. He explained that he had only a Masters Degree so he had taken a leave of absence from Wheaton to be able to add a PhD to his *vita*e. Paul Gast was also there, preparing for his first year in graduate school at Columbia. Two other

Wheaton graduates, Walter Eckelmann and Karl Turekian, were also doing their research toward PhD degrees under Kulp's direction. The reason for the presence of this large Wheaton contingent became clear when I learned that Kulp was also a Wheaton College graduate. He made a point of latching on to promising science majors from his *alma mater* (group photo, Fig. 3c).

During a hot and very humid period in July, a serious problem developed in the counting lab. Electrical arcs occurred in the end seals of the counters causing spurious counts. The problem was associated with the Pyrex glass tubes used to insulate the high voltage centre wire from the metal housing in the counters. Despite careful cleaning and handling of these tubes, the arcing persisted. Each arc triggered the device, adding an unwanted spurious pulse. Kulp's dating program stalled but he was desperate to get results so we were urged to promptly



solve the problem. In a corner of our cramped quarters, in a wing of what was once the Lamont family's summer mansion, there was a small repair area. Passing by it one day, I spied a roll of Teflon insulated, high voltage wire. I cut off a piece, pulled the wire out and stripped off the orange silk wrap. I then cut two pieces of the Teflon to the length of the Pyrex tubes and trimmed the ends so that they looked nice. I then brought them to the counting lab and suggested that we give them a try as replacements for the Pyrex tubes. It was done and the problem went away. Kulp was delighted – and as it turned out, my career was launched.



Photo courtesy of Lamont-Doherty Earth Observatory Archives.

**Figure 3c**

Our geochemistry group in front of Lamont Hall in 1954. Karl Turekian is at Kulp's left (the only one with a tie). Bruno Giletti sits behind Kulp. George Bate is holding some papers. Paul Damon has his hand in his pocket. Walt Eckelmann sits with his knee bent up. Paul Gast was making measurements in Washington, D.C. Where's Waldo?

The revelation regarding my career didn't come, however, until the last day of my summer employment. I was planning to leave the next day and drive back to Wheaton for the start of my senior year but fate intervened. I went to Kulp's office to say goodbye and to thank him for an eventful summer. Out of the blue he said, "Wheaton has little more to offer you. You've taken all the basic science courses and they don't have any worthwhile advanced courses. Instead, you should transfer to Columbia College." I was stunned and replied "Only one



week remains until classes begin and I haven't even applied". Kulp replied, "No problem. Make me a list of your Wheaton courses and grades and I'll see to it that you are admitted." So that was that. Suddenly, thanks to Professor Kulp's magic, I was a senior transfer student. In addition to seeing to it that Columbia accepted me, Professor Kulp awarded me a Research Assistantship, which not only paid me a modest stipend but also covered my tuition. So during my senior year, I commuted back and forth between Columbia's main campus on Manhattan Island's upper west side and the Lamont research campus about 15 miles away, on the other side of the Hudson River. I remember that my sense of direction was confused by the fact that the Hudson River flows almost due south. I had difficulty dispelling my intuition that east coast rivers should flow to the east.

My senior year course work was mainly in physics but I also enrolled in my first ever geology course. It was taught by a world renowned structural geologist named Walter Bucher. He had a twinkle in his eye and rambled on with a delightful German accent and as professors are known to be, he was absent minded. Our text book, *"The Sequence of Layered Rocks"* by Robert Shrock (Schrock, 1949) was the most boring I have ever encountered. Only with the help of Paul Gast, was I able to master the material. Both of us received a grade of B+ but when I tried to register for the second semester of Bucher's course, I was told that as an undergraduate, I was not allowed to take his class. The rule was graduate students only, so I went to Professor Bucher and pleaded my case pointing out that I had already taken the first semester and received a respectable grade. He insisted, however, and told me that undergraduates were incapable of understanding his material. So I asked Larry (as I then called him) to intervene. He did and Bucher begrudgingly let me in. However, at the end of the semester, he proved his point by giving me a C-. Paul Gast, whom I studied with, received a B+.

In those days, it was important to be elected to the Phi Beta Kappa National Honor Society. Except for Bucher's C-, I had close to an A average. Needless to say, I wasn't elected. However, some 35 years later, the Columbia Chapter made me an honorary member and I received my "key". At the induction ceremony, I was able to tell my sad tale about my C- in Structural Geology from Walter Bucher, who by then was long dead.

One last point about my Columbia days: In memory of the American Revolution, when Washington's troops had to flee the British by swimming across the Harlem River, Columbia College had (and perhaps still does) a requirement that in order to graduate, each student must pass a test which required swimming a distance equal to the width of the Harlem River. As a terribly poor swimmer, I dreaded this test. Fortunately, my name somehow slipped through the cracks and I was never asked.





## 4.

## A LONG AGO BARBEQUE

A turning point in my young career came as the result of a change in Professor Kulp's plans. He had agreed to present a paper on radiocarbon dating at the Great Basin Archaeological Conference to be held at the Southwest Museum in Los Angeles, California. At the last minute, he decided not to go and asked me to take his place. I jumped at the opportunity and a few days later I was airborne headed west. I was greeted in LA by a record heat wave. On the day of my talk, the temperature reached 104 °F.

I listened with interest to papers dealing with the time of arrival of humans in the Americas. The speakers fell into two groups. While the contingent of university professors were convinced that humans first arrived in the Americas at the end of the last glaciation, the contingent of museum curators presented evidence for a much earlier arrival. As my turn to speak approached, thoughts of my panic in my Wheaton speech class came to mind and the sweat from my palms intensified but once I got going, my fears evaporated. I knew that my grasp of radiocarbon dating exceeded that of the audience. My talk was the last in the morning session, so after a couple of questions, the audience started to file out for lunch. However, a man wearing cowboy boots and smoking a cigar butt in his curved pipe approached the podium. He introduced himself as Phil Orr (Fig. 4a). I distinctly remember his first words to me: "Young man, I can see that you know a lot about math and physics, but obviously you don't know a god darn thing about the Earth. Come with me for three weeks and I'll change your life." I was stunned but had the presence of mind to ask where he would take me. The answer was, to dry Lake Winnemucca in Nevada and to Santa Rosa Island off the California coast.



Photo courtesy of Lamont-Doherty Earth Observatory Archives.

**Figure 4a**

Picture with Phil Orr taken in front of the Santa Barbara Natural History Museum, where he was employed as curator.



Who would pay? He would cover all my expenses. Although he didn't say it, he clearly wanted free radiocarbon dates at a time when it was difficult to even purchase them. I was to be his ticket.

I accepted, and the next day, we were on our way in his rickety Ford station wagon. After a night in a Carson City motel, we headed for Fishbone Cave. On the way, we passed Pyramid Lake, a jewel in the desert (Fig. 4b), and then on east to its sister valley where, before the building of diversion dams along the Truckee River, there had been a lake comparable in size to Pyramid. The water that once had evaporated from Lake Winnemucca, now evaporated from desert farm land. A paved highway took us to the north end of the dry lake bed, but from there to its eastern side, we followed a very rough track. The station wagon was like a vacuum cleaner, sucking in copious amounts of dust. Along the way, we got stuck in a sandy stretch and to get out, Phil had to deflate the rear tires. Once we had escaped, he removed a spark plug and in its place, screwed in a long hose. Using engine compression, he pumped the tires back up. This, combined with the burlap water bag that hung from the front of the station wagon and supplied us with cool drinking water, I was much impressed by Phil's desert savvy. At last, Phil parked and we climbed up to Fishbone Cave. It was about 50 feet deep and according to Orr, it had been created by wave action at a time when the lake was much larger than it had been when, during the 1850s, the first explorers arrived. One of Phil's charges to me was to use radiocarbon dating to determine when the Winnemucca watershed last occupied the cave.



**Figure 4b**

Pyramid Lake's namesake, a small islet near its eastern shore formed by seepage from an underlying hot spring.



Phil's primary interest in this cave was its archaeological record. It had been occupied by palaeo Indians on and off for at least 8,000 years. I obtained a  $^{14}\text{C}$  date of  $7830 \pm 350$  years on fragments of netting from the lowest habitation level (Broecker and Orr, 1958; Broecker *et al.*, 1960c). As a budding geologist, my interest was in the history of the lake itself. Desert lakes, such as Pyramid and Winnemucca, often occupy closed basins, i.e. they have no outlet to the ocean. Hence, the water that enters them from rivers and direct precipitation must be lost by evaporation. Thus, at times of increased rainfall, for evaporation to match input, the lakes would have become larger. I asked Phil where we could get samples for  $^{14}\text{C}$  dating representing the time when the lake reached its maximum size. He told me about tufa, the calcium carbonate deposited by algae, and recommended that we go to the top of Anaho Island in Pyramid Lake to collect samples. So, a couple of days later, one of the fisheries people ferried us out to the island. We climbed to near the top and found rock outcrops coated with beige coloured tufa several inches thick. With this experience, I began a continuing quest to understand the history of the climate changes that altered the hydrologic balance in the lakes in what is known as the Great Basin. It turns out that 56 years after collecting this first sample, I am busy using the histories of these and other of the world's closed basin lakes to aid in predicting how the distribution of precipitation is likely to change as the world is warmed by the build up of  $\text{CO}_2$  released from fossil fuel. More will be said about this in a subsequent section.

After a week of collecting samples in the Pyramid–Winnemucca area, we drove back to the coast, this time to Santa Barbara, where Phil was employed as a curator in the Natural History Museum. A small oceanographic vessel from Scripps Institution for Oceanography awaited us. We boarded and were off on the second leg of my geological education. Our destination was Santa Rosa, one of a series of Channel Islands located off the coast of California. We arrived at a dock associated with a small naval base and were taken by jeep to the home of the island's owner, Al Vale. It turns out that Phil Orr had exclusive archaeological access to the island. Vale operated a cattle ranch but Santa Rosa is a very dry place, so it could support only a small number of animals. The sole human occupants were a few ranch hands and the small staff at the navy base. Otherwise, the only inhabitants, other than the cattle, were wild boars left behind by the Spanish conquistadors and endemic foxes the size of house cats. Once again, Phil's interest lay in the archaeological remains and especially those left by early man. During a previous trip, he had found a human arm bone on which I subsequently did a radiocarbon date. Phil was disappointed that my result of 10,700  $^{14}\text{C}$  years was not as old as he had hoped. Rather than pushing back the arrival of man in the Americas, it matched that for other early sites. It did, however, raise the question as to how those early human arrivals were able to cross 30 miles of often quite rough seas.

Also on the island, a big surprise was in store for us. Sediments, formed during the time of the last glacial maximum and the period of deglaciation that followed, were well exposed both in wave cut shoreline cliffs and in the walls of arroyos cut by the runoff created by infrequent but intense rain showers. It



was in these exposures that Phil and I searched for radiocarbon datable material and signs of human occupation. After many hours of looking at walls of brown, largely featureless silt, I spotted some large bones sticking out of one of the arroyo walls. I yelled for Phil to come and have a look. When he arrived, he whooped “You’ve found the leg bones of a dwarf mammoth.” He explained that like the foxes, most animals isolated on islands evolve to smaller sizes. Soon he got even more excited when he spotted rib bones that had the appearance of being charred. While the leg bones were glistening white, the rib bones were a dull black. Phil’s excitement stemmed from his thought that the mammoth had been killed by man who then barbecued its ribs. This idea seemed to fit but when my radiocarbon date came out 29,500 years, the credibility of this interpretation became highly questionable because no other evidence for human occupation of the Americas dating even half this age had been found. As Phil promised, this trip changed my life. Many of my laboratory oriented contemporaries paid only scant attention to field observations. Phil taught me their value. So unlike many of my colleagues, I learned to put together apples and oranges, i.e. field and laboratory observations. Because of experience in both domains, I could often push ahead faster than others so I place Phil Orr beside Paul Gast and Larry Kulp as people who played key roles in my development as a scientist.

## 5.

## ESPIONAGE

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During my first year at Lamont, Professor Kulp got the idea that we should see if we could detect one of the A bomb fission products that remained airborne instead of being purged by rainfall. In particular, he focused on an isotope of the inert gas krypton,  $^{85}\text{Kr}$ , with a half life of about 10 years. Much of that produced by the Alamogordo, Hiroshima and Nagasaki A bombs (Fig. 5) would not yet have undergone radio decay. Further, during the seven or so years that had elapsed since these explosions took place, the  $^{85}\text{Kr}$  would have become well mixed throughout the atmosphere. Based on the published equivalent TNT tonnage of these three explosions and the fission yield of  $^{85}\text{Kr}$ , Kulp calculated that each litre of krypton gas should contain enough  $^{85}\text{Kr}$  to produce about 10 radioactive decay events per minute in the counters we used for  $^{14}\text{C}$  dating. So we purchased a litre of krypton from Linde Air Reduction in Buffalo, New York and I mixed it with ethylene as the filling gas for our  $^{14}\text{C}$  counter. We were amazed when we recorded 8 events per minute. The next day, Kulp, who had an eye not only for publicity but also for government research money, took a plane to Washington and went to the Atomic Energy Commission to see if he could get a grant to continue these measurements.







**Figure 5**

Picture of the mushroom shaped cloud created by an above ground atomic bomb test.

The same afternoon, back at Lamont, two men in suits and ties asked to see me. They flashed badges and announced that they were from the FBI. “Are you the kid who made  $^{85}\text{Kr}$  measurements?” I fessed up. “Well, tear up your notes and never say a word to anyone about what you did. And never again conduct such measurements!” It took us some months to figure out why the fuss. Finally, we got the answer. We had stumbled on an espionage scheme. There was at that time great concern that the Soviet Union was close to succeeding in creating its own nuclear weapons. To do this, they had to make plutonium. This required a nuclear reactor in which controlled fission of  $^{235}\text{U}$  took place, which released free neutrons that reacted with  $^{238}\text{U}$  to upgrade it to plutonium – and of course, these fissions would also produce  $^{85}\text{Kr}$ . When the fuel rods were processed to recover the plutonium, the  $^{85}\text{Kr}$  would escape to the atmosphere and join that produced by the US and British allies. Tony Turkevich, a physicist at the University of Chicago, realised that if we could accurately inventory the atmosphere’s  $^{85}\text{Kr}$  burden and subtract from it that produced by the allies, then any excess would provide a measure of Soviet plutonium production. Because I knew the facts and had been sworn to secrecy, I was subsequently invited to Argonne National Laboratory in Naperville, Illinois, to observe how they did the  $^{85}\text{Kr}$  measurements. Jim Gray, one of the team members, was assigned to be my mentor. I followed him around like a puppy! I was amazed to find that they had dozens of counters and were measuring hundreds of samples each year. During the three weeks I was there, I was able to get information about the design of their counters and the associated electronic circuitry. This information was not classified so I was

free to take it back to Lamont. It turned out to be very valuable because soon after my return, we set out to switch from black carbon to carbon dioxide for our  $^{14}\text{C}$  measurements.

## 6.

### ASCARITE

One of the research projects that was being conducted by Kulp involved measuring the amount of radiocarbon in the dissolved inorganic carbon ( $\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$ ) contained in seawater. The primary objective was to determine the water renewal rate in the deep Atlantic Ocean. This was to be done by comparing the  $^{14}\text{C}$  to total C ratio in deep

water with that in surface waters. The difference between these ratios could be converted to an isolation time. Assuming that the renewal rate had remained the same, this age could be converted to the renewal flux. We now know that this flux is about equal to the annual rainfall over the entire globe (i.e. 15 million cubic metres per second)! However, in the early 1950s, this flux was poorly constrained. Obtaining the 50 gallons of water required to get enough carbon for the measurement presented a challenge. Maurice Ewing, Lamont's Director, joined Kulp in this enterprise. He supervised the construction of the first large volume water sampler from an oil drum and a ship's porthole. On the way down, the porthole was propped open, allowing the barrel to be flushed. Once at the desired depth, a messenger weight was sent down the wire triggering a release that allowed a stretched elastic cord to pull the porthole shut. Subsequent generations of this device manufactured in Lamont's machine shop, although sleeker, were patterned after Ewing's original design (Fig. 6a). Because it was impractical to store these large samples of water onboard the research vessel, *Vema* (Fig. 6b), the carbon was



Photo credit: Treve Johnson Photography.

**Figure 6a**

A Gerard barrel used to collect the large volumes of water required for radiocarbon measurements by the decay counting method. With the advent of atom counting in the mid 1980s, the sample size was reduced by a factor of 1,000 and Gerard barrels were no longer needed.



extracted at sea by circulating air in a closed loop through the acidified seawater. Acid was added to convert  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions to  $\text{CO}_2$  gas. The  $\text{CO}_2$  gas was removed by circulating the air around and around through a commercial solid absorbent called ascarite. Then small bottles containing the ascarite were shipped back to Lamont for the radiocarbon analyses.



Photo courtesy of Lamont-Doherty Earth Observatory Archives.

**Figure 6b**

*Vema* under full sail. Over the years, the sleek yacht was modified stepwise for more efficient use as a research vessel. The sails were abandoned, the bowsprit was removed, the deck house was raised and finally, the masts were removed. This transition reminded me of a favourite childhood book *Black Beauty*, the story of a beautiful horse who fell on bad times.

Kulp was eager to publish the results that he obtained on the first set of deep Atlantic samples. Ewing was more cautious and urged Kulp to wait until they had confirming results. Kulp refused and, against Ewing's wishes, went ahead and published on his own. The early results indicated that the rate of renewal of deep waters in the Atlantic was much slower than oceanographers had estimated, so Kulp's paper received considerable press attention and ultimately led to his receipt of a prestigious award. Kulp was busy with several other geochemistry projects and as a first year graduate student, ever more responsibility fell on me for the operation of the radiocarbon lab and of course any problems that arose became mine to fix. Among these was a serious one. In addition to samples, we



ran frequent blanks (in other words, carbon black prepared from radiocarbon free material such as ancient coal or limestone). I noticed that now and then the blank carbon yielded more counts than its companion blank cylinder. This stopped us dead in our tracks. Finally, we realised that the source of these extra counts was radioactive fallout from above ground nuclear testing that was being conducted at the faraway Nevada Test Site. Our carbon black was very absorbent so as it dried, it would pick up particulates from the air, including small traces of bomb test fission products.

At that time, there were reports that several labs were switching from measuring carbon black to measuring carbon in a gaseous form. Hans Suess, who directed the U.S. Geological Survey laboratory in Washington, D.C., converted the carbon in his samples to acetylene gas ( $C_2H_2$ ). Realising we had to abandon the carbon black method, Kulp arranged for us to visit Suess to see how he generated acetylene. Soon after our arrival, Kulp excused himself to go to the men's room. Left alone with this famous Austrian scientist, I couldn't think of anything to say so I was relieved when he broke the silence. "Young man, too many of our best scientists are lost because they become administrators. It is a one way street; there is no return. You must in your career guard against this fate." I asked, "How does one do this?" The reply was, "be a dynamic incompetent and no one will ask you to become an administrator!" Not knowing what a dynamic incompetent was, I asked. Suess replied, "at least three outrageous acts each year." I took this advice and have lived by it. Except for a three year term as rotating chair person of our academic department, I have escaped administrative duty.

As it turns out, we did not switch to acetylene. Back to back visits by Hessel de Vries, the boss of a  $^{14}C$  lab in Groningen, Holland and by Gordon Ferguson from New Zealand convinced us that carbon dioxide was a better choice. Further, an attempt by Chuck Tucek, a chemist in our lab, to duplicate the Suess  $C_2H_2$  synthesis led to a nasty explosion which singed his eyebrows.  $CO_2$  generation posed no such threat.

At this time, in 1953, plans to build a building for geochemical research were firming up so it was decided that we would limp along with black carbon until a  $CO_2$  lab had been set up in this new facility. I was given the task of designing the lab. The building opened in October 1954, and several months later, the  $CO_2$  lab was up and running. One of the first things I did was to check out one of the assumptions Kulp had made regarding the use of ascarite. He was aware that ascarite contained a significant amount of absorbed  $CO_2$  so for every bottle that was sent to sea he had an aliquot analysed for its  $CO_2$  content but he had never measured the  $^{14}C$  to C ratio in this  $CO_2$ . He was convinced that its source must be the  $CO_2$  in ambient air and correspondingly corrected the radiocarbon measurements. Concerned that this might not be the case, I took 8 bottles of fresh ascarite and obtained enough  $CO_2$  for a radiocarbon measurement. I was shocked to find that instead of having the amount of radiocarbon equal to that in air, it had none at all. The upshot was that instead of raising the  $^{14}C$  to C ratio in the  $CO_2$  extracted from seawater, the correction for the  $CO_2$  initially



contained in the ascarite decreased it. So, instead of making the apparent age of deep Atlantic water older, the ascarite correction made it younger. When the proper correction was made, the deep water age came out to be only a couple of hundred years, instead of many hundreds of years. Hence it lay within range expected by oceanographers.

When I learned this, Kulp was away on vacation and hence out of contact. A few days later, Ewing called me in for an update on this project so I had to tell him about my finding. When Kulp returned two weeks later, I urged his secretary to make sure that I spoke with him. She promised to try but said that he was fearfully busy catching up from his absence and getting ready to go to Mexico City for the Geological Society of America (GSA) meeting. Finally, on the day before he left, he stopped by the lab looking harried. "So, what's so important?" he asked. I explained about the ascarite correction. He said "I can't believe it. You should do it again." I was about to say, "but Larry, there is simply no way that the CO<sub>2</sub> in ascarite has the <sup>14</sup>C content of today's atmospheric CO<sub>2</sub>." However, he was on his way out the door and that was the end of our brief conversation. A week later, I got another call to appear before Ewing. "Why the hell," he shouted, "didn't you tell Kulp?" I explained that I had. Ewing then told me that Kulp had, in his GSA talk, presented the same old results with no caveats or mention of the change in the ascarite correction. This incident deepened an already sizable rift between Ewing and Kulp. Years later, it would lead to a similar rift between Ewing and me.

## 7.

## TERMINATIONS

Part of my PhD thesis research dealt with radiocarbon dating of records extending back to the time of the last glacial maximum. Included were: the record of sea level contained in the sediments of the Mississippi River delta, the record of the reappearance of the planktonic foraminifera, *G. menardii*, in the Atlantic after an absence during glacial time and the record of the fluctuations in area of Nevada's closed basin, Lake Lahontan. In all three of these records, I noted that a marked transition from glacial to interglacial conditions occurred close to 11,000 <sup>14</sup>C years ago. This finding was reported in a paper entitled "Evidence for an Abrupt Change in Climate Close to 11,000 Years Ago," published in 1960 (Broecker *et al.*, 1960a). It was coauthored with Lamont Director, Maurice Ewing.

Time would tell that even though I had put my finger on something very important, the evidence was flawed. Twenty years later, Glen Jones, a scientist at Woods Hole, showed that *G. menardii* didn't reappear in the Atlantic until about 6,800 years ago. Although in many Atlantic sediment cores, *G. menardii* shells first appeared in sediment whose age was close to 11,000 years, these shells had <sup>14</sup>C age of 6,800 years. Fortunately, bioturbation had mixed them down to this much older level. In addition, my radiocarbon ages for algal tufas from Lahontan's





highest shoreline were later shown to be too young, because of the incorporation of secondary calcite. The correct date placed them at 13,500  $^{14}\text{C}$  years, or just before the onset of the profound Bølling Allerød warming. Finally, at the time, I failed to recognise that the Younger Dryas lapse back into cold conditions complicated the transition.

A decade later, in 1970, together with graduate student, Jon Van Donk, I made a point that the  $^{18}\text{O}$  to  $^{16}\text{O}$  ratio transitions marking the ends of each glacial cycle were quite abrupt (Fig. 7). We called these sharp transitions “Terminations” and numbered them I, II, III and so on, going back in time (Broecker and Donk, 1970). However, even then, we did not appreciate the complication posed by the Younger Dryas relapse into cold conditions. The reason was that the  $^{18}\text{O}$  records available at that time were all from sediments that accumulated at rates of a few centimetres per thousand years. As a result of stirring by worms to depths of 6 to 10 cm, core top radiocarbon ages ranged from 3 to 4 thousand years. Because the Bølling Allerød-Younger Dryas oscillation had a duration of only about 3 thousand years (Grootes and Stuiver, 1997), its presence had been obliterated by bioturbation in these sediment cores. It was only with the publication of the Camp Century ice core record (Dansgaard *et al.*, 1969), that the importance of the Younger Dryas became clear. Recognising terminations was one thing; explaining them was quite another. They have proven to be a thorn in the flesh for all those who have attempted to model glacial cycles. I remember the long discussion John Imbrie and I had about them in a hotel room in Atlantic City, in the early 1970s. He had become enamoured with the pacing of glacial cycles by Milankovitch orbital cycles but was stumped by the sharpness of terminations. Years later, in the 1980s, when he was leading an effort by the Specmap group, he got the idea that they occurred at times when the precession and tilt cycles came into alignment (Imbrie *et al.*, 1992).

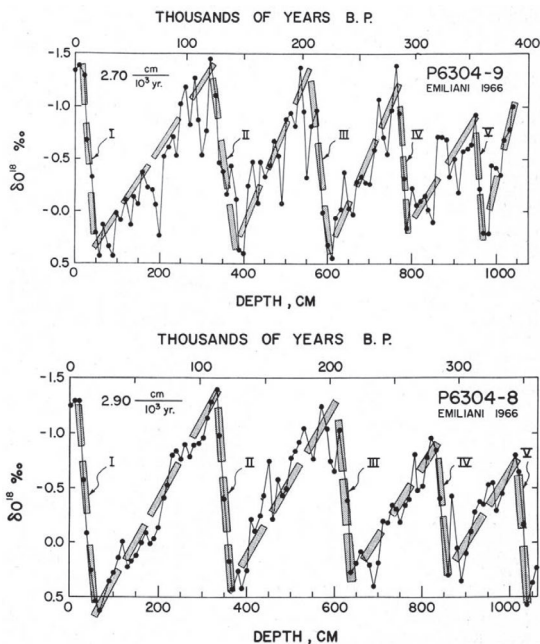
I remember when Andre Berger, in a Lamont seminar, presented a model study in which he claimed to have solved the problem. When questioned as to how it was that his model so nicely produced terminations, he admitted that he sprinkled a dark substance on the ice sheets, changing their albedo and hence made them melt. The failed attempts to unify cyclic Milankovitch pacing with sharp terminations continued until the discovery in ice cores that steep sided millennial temperature changes punctuated the Milankovitch cycles and that some of these events were triggered by Heinrich’s ice armadas. Jerry McManus took a big step forward when he showed that there was a Heinrich event associated with each of the last five terminations (McManus *et al.*, 1999). Clearly, ice armadas in the North Atlantic played a key role in bringing ice ages to a sharp close.

While a step forward, the McManus finding by no means solved the problem. Although the trigger for Termination I was a Heinrich event, the first indication that the glaciation had come to an end was in the Southern Hemisphere. This suggested that the message was transmitted from the north to the south through the deep ocean or perhaps by a shift in the location of the westerly wind belts.



Okay, but what triggered the Heinrich events? Maureen Raymo suggested that a prerequisite to creating a termination is the generation of a very large Northern Hemisphere ice sheet. Her evidence comes from the  $^{18}\text{O}$  record in benthic foraminifera which shows that terminations occur only after the  $^{18}\text{O}$  enrichment in the ocean reaches a certain level, i.e. the ice caps have reached a certain size. Heinrich events, which occurred at times when the ice caps were smaller, had impacts but they did not initiate terminations.

It is my feeling that until we understand how excess  $\text{CO}_2$  was stored in the glacial deep sea, and what triggered its release back to the atmosphere, we won't be able to close the case. This year, a group led by my close colleagues, George Denton and Bob Anderson, published a paper in *Science* that attempted to explain terminations (Denton *et al.*, 2010). They offered me coauthorship but I declined. My reason was that their argument involved shifts in the westerly wind belt. Although not opposed to this idea, my concern is that ocean atmosphere models have not succeeded in replicating the required shifts. Further, I'm convinced that the ocean could have done the job by itself. They got a bit closer to the answer but I feel that, until we understand what triggers Heinrich events and why, in the presence of large ice sheets, these events can in turn trigger a release of  $\text{CO}_2$  from the ocean, we can't close the book on terminations. It's been forty years since I coined the term, "terminations". It might be another forty before we have a firm understanding of what they involve.



**Figure 7**

Diagram showing the  $^{18}\text{O}$  to  $^{16}\text{O}$  ratio record for two sediment cores from the Caribbean Sea. John Van Donk and I were struck by the asymmetrical shape of these cycles. We coined the description "terminations" for the rapid warmings (i.e.  $^{18}\text{O}$  decreased) that marked the ends of each glacial cycle (from Broecker and van Donk, 1970).

I received my PhD degree from Columbia in 1958. Unlike several of Maurice Ewing's geophysicists, who put in 5 to 10 years on the Lamont research staff before being offered a faculty position, once again Kulp performed his magic and, upon graduation, I was granted an assistant professorship in Columbia University's Department of Geology. Nothing occurred during my first few years on the job that stands out in my memory so I'll skip to 1962. Early in that year, John Imbrie, a fellow faculty member, asked me if I would like to join his group doing field research in the Bahamas. He had rented a house on Fraser's Hog Key from Dr. Leroy Talcott, a young Miami surgeon. It was to serve as Imbrie's base of operation. He had also chartered a small vessel from the Lerner Marine Laboratory on the island of Bimini. Never having done any field work involving the ocean, I conferred with Taro Takahashi, once a fellow graduate student who was at that time teaching at New York State College of Ceramics in Alfred, New York. In 1958, during the IGY (International Geophysical Year), he had spent 9 months on Lamont's ocean going research vessel, *Vema*, measuring the partial pressure of CO<sub>2</sub> in surface water. He agreed to join me and together we developed a plan. I would take the lead in one project which involved measuring the radon gas content of the shallow bank water with an eye toward establishing the rate of gas transfer across the air-sea interface. Taro would direct a second project to establish the rate of CaCO<sub>3</sub> deposition on the Bahama shallow banks and its dependence on the degree of supersaturation.

The expedition was launched from Miami. Imbrie and two of his graduate students would go across the Florida Straits to Bimini aboard a World War II landing craft (i.e. a Landing Ship Tank, LST) owned by Miami Marine. Taro and I would fly to Bimini and join them. When we arrived, we fully expected the Imbrie group to be there but they were not, nor did the port authorities know their whereabouts. We waited 'til midnight – still no Imbrie – so, we retired to our motel room. The next thing I remember was Imbrie shaking me and yelling in my ear, "Wally, get up and rinse this radio in fresh water." It turns out that they had quite a voyage. After a delayed start from Miami, they had an uneventful trip across the straits. As they approached Bimini, they called in to report their arrival. However, because of engine noise, the Bimini authorities couldn't hear them so they cut the engine and were able to make their radio report but then the trouble began. The battery was too weak to restart the engine. The mighty Gulf Stream took hold and carried the LST rapidly northward. Night fell. A storm raged. They bailed and they prayed that their iron tub wouldn't swamp and sink like a rock. Finally, their salvation appeared in the form of a huge freighter. Using a flashlight, Imbrie sent an SOS.

The Russians aboard the freighter responded and after a difficult exchange, from the deck 40 feet above, down came a set of jumper cables. The engine started and they were able to limp back to Bimini. It turns out that their portable radio had received a dose of sea spray – hence, Imbrie's early morning command.





It was decided that Taro and I should fly across the banks to join Ross Horowitz, our technician, who was already there setting up our lab. The Imbrie group would stay behind and test their shallow water coring device to be deployed from the open door of the LST, but that's another story! I'll never forget that as the sea plane taxied up to the Fraser's Hog Key dock, we saw Ross jumping up and down like a banshee. Has he gone mad? When we stepped onto the dock, we realised why Ross was so animated. It was swarming with mosquitoes. After shaking hands, we all ran to the Talcott house and slammed the door. Ross sprayed us with RAID to kill any of the mosquitoes that came in with us. We were amazed to find that Ross had converted Talcott's hideaway into a laboratory. Radon extraction boards, alpha counters, liquid air, vacuum pumps, infra red analysers and so on filled the living room and one of the bedrooms.

The next day, the small sea plane returned. It was to serve as our water sampling platform. We loaded it with 20 litre evacuated glass bottles that we had purchased from a spring water company. I took the copilot seat and off we went out over the huge Grand Bahama Bank. I would point out a place to land and once we had coasted to a stop and the pilot had opened the cabin door, I would jump into the water. Then he would lower one of the bottles in its wooden crate and I popped the valve allowing seawater to be sucked in. The pilot then hauled the filled bottle (and me) back into the plane. Fortunately, as the plane landed on its belly rather than on pontoons, the cabin door was only a foot or so above the water.

We repeated this at five more locations and then headed back to Talcott's dock. The whole operation took only two hours. Enduring the myriad of mosquitoes, we hauled the bottles inside and started extracting the radon. This involved circulating helium gas round and round and freezing out the extracted radon in a trap cooled with liquid nitrogen. Once captured, the radon was transferred to a small cell that was coated inside with phosphor. Each alpha particle, shot out from a decaying radon atom and from radon's short lived daughter products, made a flash of light when it hit the phosphor and the flashes were recorded by a phototube.

To our amazement, we obtained more pulses than expected. Our idea was that some of the radon atoms produced in the water by the decay of its parent radium ( $^{226}\text{Ra}$ ) would have escaped to the overlying air. Hence, the radioactivity of radon in our samples was expected to be less than that of the radium dissolved in the water. Because radon has a half life of only 3.65 days, if the half time for escape to the atmosphere were, for example, also 3.65 days, then half of the radon would be lost and half would undergo radioactive decay in the water. The problem with our Bahamas measurements was that the radon content proved to be greater than that expected if none were lost to the atmosphere.

It didn't take long to figure out what was going on. Either during its residence on the banks, the water had accumulated excess dissolved radium over that present in open ocean surface water or radon was leaking out of the underlying sediments. We decided that the latter option was the more likely and checked



it by submerging one of our evacuated bottles in the shallow waters just off Talcott's dock and plunging an attached intake tube (equipped with a frit) into the carbonate sediment. We opened the valve and sediment pore water was sucked into the bottle, while the frit kept out the sediment. We processed this water in the same way as we had the bank water and soon had transferred the radon into the counting cell. We then turned on the counter. Instead of the ten or so events per minute produced by bank water samples, we got many hundreds. This, despite the fact that we had only filled the sampling bottle to about one tenth its capacity. Clearly, much of radon produced by the decay of the radium contained in the sediment was escaping into the surrounding pore water (Broecker, 1965).

So unfortunately, we had to terminate our gas exchange experiment but by serendipity, this finding led to much bigger game. In the open ocean, we could take advantage of the copious amounts of radon leaking out of the abyssal sediment by measuring its vertical distribution in the overlying water column. In this way, we could establish the rate of vertical mixing in the deep ocean. A decade later, in the 1970s, we made hundreds of measurements on water samples taken in the deep ocean in the zone extending 50 or so metres above the sea floor. This was done in connection with the global GEOSECS survey described in more detail, below.

Fortunately, the second project awaited us. It involved making traverses across the 40 mile wide Grand Bahama Bank. We had agreed to share the use of the Lerner Lab research vessel with the Imbrie team. Our time slot was scheduled to begin two days after our radon project came to its abrupt end. With the help of the Deacon, who captained the vessel, and his lone crew member, Cornbread (both native Bahamians), Taro, Ross and I loaded our gear and off we chugged. I say chugged because we were towing an intake pump that supplied a steady stream of water for our underway  $\text{CO}_2$  partial pressure measurements. We had to keep the speed down to three knots in order to prevent the intake pump from popping out of the water.

Our plan was to measure five properties of the bank water: temperature (T), salinity (S),  $\text{CO}_2$  partial pressure ( $\text{Pco}_2$ ), total dissolved inorganic carbon content ( $\Sigma\text{CO}_2$ ) and the  $^{14}\text{C}$  to C ratio in the dissolved inorganic carbon. Based on the salinity, we could calculate the calcium ( $\text{Ca}^{2+}$ ) content. The  $\text{Pco}_2$  and  $\Sigma\text{CO}_2$  (together with T and S) allowed Taro to calculate the  $\text{CO}_3^{2-}$  ion content of the water. The product of the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  yielded a measure of the extent of supersaturation and hence, of the drive for  $\text{CaCO}_3$  to precipitate. We knew from published surveys, that as a result of intense summer evaporation, the salinity of the bank water increased from its western side, which was open to the Florida Straits, to Andros Island, which formed its closed eastern boundary. This increase was important to us because it led to an increase in the concentration product ( $[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]$ ) and hence, the tendency to precipitate  $\text{CaCO}_3$ . Although we could presumably have used the across bank salinity increase as a rough measure of the isolation time of the water on the banks, evaporation rates were



approximate and there was no way to correct for salinity decreases produced by rain storms. Therefore, we decided a better approach was to use the across bank increase in  $^{14}\text{C}$  to C ratio.

To do this, we would take advantage of what I refer to as John Nuckoll's gift to environmental science. As you remember, John was a fellow Wheaton student who helped with the burial of the senior's bench. Along with Paul Gast, George Bate and me, John came to Columbia for graduate school but instead of joining us in geology, John went into physics. After his first year, he disappeared. Only years later, did I learn that he had been recruited by Edward Teller at Livermore National Laboratory. When we finally met again, Nuckolls told me that he was the primary architect of our first hydrogen bomb. He even admitted that he had peeked from under a lead blanket to watch his "baby" go off on the far side of Eniwetok Atoll. Although, thank heavens, hydrogen bombs were never used for their primary purpose, during H bomb tests, collisions between the stray neutrons and atmospheric nitrogen nuclei temporarily nearly doubled the amount of  $^{14}\text{C}$  in the atmosphere's  $\text{CO}_2$ . The passage of these extra  $^{14}\text{C}$  tagged  $\text{CO}_2$  molecules into the ocean and into the terrestrial biosphere constitutes an invaluable environmental tracer.

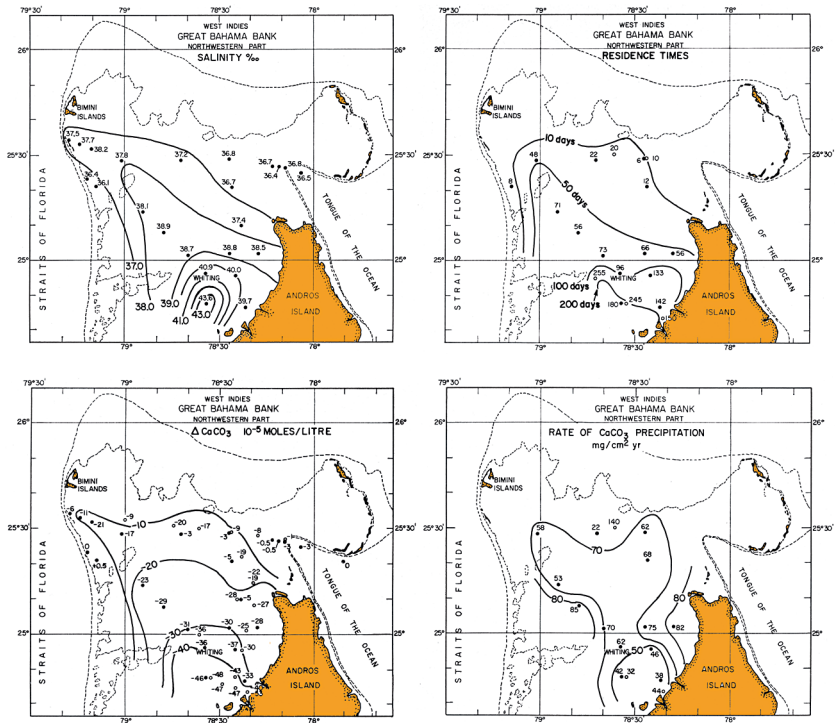
Taro and I took advantage of this tracer by measuring the across Bahama Bank increase in the  $^{14}\text{C}$  to C ratio in the dissolved inorganic carbon. This worked because the bank water was only 16 metres deep in contrast to the open ocean where the Nuckolls'  $^{14}\text{C}$  was stirred to depths averaging several hundred metres. Hence, the extent of dilution of this extra  $^{14}\text{C}$  on the banks was far smaller. The longer the water remained, the higher its  $^{14}\text{C}$  to C ratio became (Fig. 8, Broecker and Takahashi, 1966).

Unlike the radon strategy, which had backfired, our survey of the bank water yielded very nice results about the rate of  $\text{CaCO}_3$  formation and its dependence on the product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ion concentration. Years later, I went back to this study when questions arose regarding the impact of fossil fuel derived  $\text{CO}_2$  on calcification by marine organisms. The fossil fuel  $\text{CO}_2$  taken up by the ocean would decrease its  $\text{CO}_3^{2-}$  concentration and thus impede calcification. Although our  $\text{CaCO}_3$  study went well, we did experience a navigation problem. Our traverse from Fraser's Hog Key back across the bank took about a day and a half and the return trip another day and a half. During this time we saw no land, so we had only a rough idea where we were.

At our slow pace, tidal currents distorted any estimates we made from our speed through the water and our compass readings. We were headed (we hoped) toward the northwest channel light, a marker not too far from Fraser's Hog Key but because we could not see any of the low islands, our charts were of little use. Anyway, darkness had fallen. The Deacon was no help because he never used charts and said that he couldn't read ours. Then, all of a sudden, we bounced off the bottom and a couple minutes later, we bounced again. The Deacon grabbed a pole and leaned overboard to probe the bottom. Then he uttered the word "Jolters" and suddenly we, the scientists, and they, the crew, were on the same



page because we had seen this word on our chart. It denoted a series of under-water dunes. Clearly, we had struck on the crests of two of them. This placed us well to the south of our planned course. The Deacon promptly turned the research vessel around and gingerly retreated from danger. We decided to call off any remaining research objectives and to proceed back to Fraser's Hog Key. Not having heard from us for three days, Imbrie was in a dither. He was relieved to see us arrive safely at Talcott's dock.



**Figure 8**

Map of Great Bahama Bank showing the locations at which measurements were conducted. The map on the upper left shows the salinity distribution; that on the upper right shows water residence times calculated from the content of excess bomb test radiocarbon. The map on the lower left shows the amount of  $\text{CaCO}_3$  precipitated from the water during its residence on the banks and that on the lower right shows how the rate of  $\text{CaCO}_3$  precipitation changed with location on the banks (after Broecker *et al.*, 1988).

During my flight to obtain water samples for our radon measurements, I was struck by the white streaks in the bank water (Fig. 9). I asked the pilot what it was. He replied, "It's a whiting". When I asked what he meant, he said that it was made up of tiny calcium carbonate crystals which had spontaneously precipitated from the bank water. When we got back to New York, I asked around and found that there were two schools of thought regarding the origin of whittings. One school agreed with the pilot that they were spontaneous precipitates and the other viewed them as sediment stirred up from the bottom.

Intrigued by the results of the summer of 1962's survey, Taro and I decided to repeat it during the summer of 1963. As a result of an international treaty banning above ground nuclear tests, which was to take effect on January 1, 1963, Russia, Great Britain and the U.S.

each tested huge H bombs in the closing weeks of 1962. While we knew that the  $^{14}\text{C}$  produced by these tests had been carried up into the stratosphere, we also knew that much of it would be transferred down to the troposphere during the late spring of 1963. This would make the task of determining the isolation time of water on the Grand Bahama Bank much easier so we chartered the *Lord Raleigh*, a Miami Marine vessel and headed across the Florida Straits. Because of our interest in whittings, we brought along a continuous centrifuge. Our hope was that we would encounter a whiting and pass enough water through the centrifuge to recover about 30 grams of the suspended  $\text{CaCO}_3$  (i.e. the amount required for a radiocarbon analysis). If formed by spontaneous crystallisation, the  $^{14}\text{C}$  to C ratio in this  $\text{CaCO}_3$  would be equal to that in the bank water's dissolved inorganic carbon. On the other hand, if it was stirred up sediment, it would have a  $^{14}\text{C}$  to C

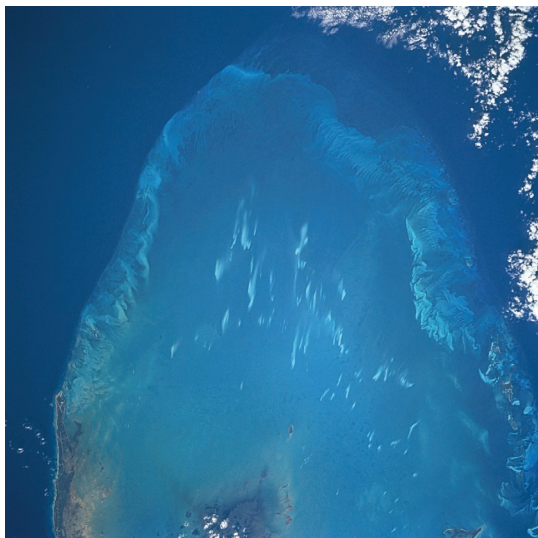


Photo courtesy of NASA.

**Figure 9**

Air photograph showing numerous whittings in the shallow waters of the Bahama Banks. The origin of the fine white particles that make up these plumes is  $\text{CaCO}_3$  sediment stirred up from the bottom.

ratio equal to that in the top most sediment. The measurements made on samples from the previous summer showed that these two ratios were quite different so we would be able to make a clear distinction between the two hypotheses.

Fortunately, we did encounter a whiting. Before stopping to do the centrifuging, Taro suggested that we do a couple of traverses across the whiting in order to measure the contrast in the partial pressure of  $\text{CO}_2$  between the water in the whiting and that outside the whiting. He explained to me that if  $\text{CaCO}_3$  precipitation was occurring, it would raise the  $\text{CO}_2$  content of the water (counterintuitive, but true). On the other hand, if the  $\text{CaCO}_3$  was stirred up from the bottom, then there would be no difference. Of course, there was a third possibility; the stirred up crystals might serve as nuclei for further  $\text{CaCO}_3$  precipitation. In this case, there would also be an increase in the  $\text{CO}_2$  content of the whiting water. Taro found no significant difference between the  $\text{CO}_2$  content of water in the whiting and that outside, so he predicted that the  $^{14}\text{C}$  to C ratio in the  $\text{CaCO}_3$  we recovered by centrifuging the whiting water would be identical to that in the underlying sediment. Months later, when we completed the  $^{14}\text{C}$  measurement, it turned out that Taro was correct. The  $\text{CaCO}_3$  was stirred up from the bottom (Broecker and Takahashi, 1966).

Decades later, I learned that despite our efforts, the debate still raged. The people involved had either forgotten or disregarded our publication. The argument was fed by the failure to come up with a believable mechanism for creating the sediment suspension. Faced with this, I put on my thinking cap. I remembered that Captain George of the *Lord Raleigh* had forbidden scuba dives into the whiting. "They're loaded with lemon sharks." In answer to my inquiry as to why they might be there, I was told that while fish in the whittings were blind (as are airplane pilots in clouds), the sharks used electric sensors to locate the fish. I took this one step further and proposed that it was the sharks that stirred up the sediment. Just as spiders spin webs to catch insects, the sharks stirred up sediment to catch fish but, as far as I know, there are still no converts to this explanation.

## 10. THE MONO MYSTERY

My first trip to Nevada's closed basin lakes was not my last. Many more were to follow. Nor did my association with Phil Orr come to an end after that ever so important three week training trip. During the summers that followed, I made trips west to join Phil for the collection of more samples for  $^{14}\text{C}$  dating. We expanded the scope of our investigations from Lake Lahontan, the glacial age predecessor of Pyramid and Walker Lakes to Lake Bonneville, the glacial age predecessor of Utah's Great Salt Lake (Broecker and Orr, 1958; Broecker *et al.*, 1960c). I decided that in addition to dating tufa and shells found on the shorelines of these once expanded lakes, I needed to determine the offset between the  $^{14}\text{C}$  to C ratio in the  $\Sigma\text{CO}_2$  of the present day lakes and in atmospheric  $\text{CO}_2$ . Geochemists





refer to this offset as the reservoir correction. It must be applied to radiocarbon ages on materials whose carbon was derived from the  $\Sigma\text{CO}_2$  in water as opposed to atmospheric  $\text{CO}_2$ . Because this correction differs from one water body to the next, it has to be measured in each so in 1957, I set out to do this for three of the Great Basin Lakes, Pyramid and Walker (remnants of glacial age Lake Lahontan) and Mono Lake (Fig. 10a; Broecker and Walton, 1959). I was aware that these lakes had higher dissolved inorganic carbon content than the ocean so I decided that I needed only 10 gallons of water. Phil and I used a bucket to fill a tank of this size with water obtained from a convenient beach and then transported it to our motel. There, we hooked up a system for recirculating air. In this case, we used liquid potassium hydroxide (KOH) instead of solid ascarite as the absorbent. The advantage was that KOH could be purified, avoiding the bothersome ascarite blank correction. Once set up, we added acid to the lake water and turned on the air circulation pump. All went well for the Pyramid and Walker samples but not for the sample from Mono Lake.



**Figure 10a**

Mono Lake sits immediately to the east of the steep front of California's Sierra Nevada mountain range. In the lower left is Panum Crater, created by the most recent of a series of explosive volcanic eruptions. The large island in the middle of the lake is thought to have been pushed up about 200 years ago by an abortive volcanic event beneath the lake.

By the time we got to the Mono Lake samples, we were confident that we had the system down pat so instead of helping, Phil sat on the steps to our motel room and watched. Out in the parking lot, after I had hooked everything up, I took the cap off the top of the tank of Mono water and poured in the acid. I was about to replace the cap when I heard a roar and watched the hoses blow off and hot water spurt out. Phil roared with laughter. "Chemistry is such wonderful entertainment," he shouted. It turned out that Mono Lake water had 10 times more dissolved inorganic carbon than Pyramid and Walker Lake water and 100 times more than seawater. The reaction between the acid and the carbonate and bicarbonate in the water was highly exothermic so the water became quite hot and, of course, an enormous amount of  $\text{CO}_2$  was released.

Not only was Mono Lake full of chemical surprises, it turns out that figuring out its carbon cycle has proven to be a geochemical nightmare. Our first hint of complications came when the radiocarbon measurements were completed. While the reservoir corrections for Walker and Pyramid proved to be only a few hundred years, the correction for Mono Lake was a whopping 1,500 years. With the advent of H bomb testing and the consequent rise in the  $^{14}\text{C}$  to C ratio in atmospheric  $\text{CO}_2$ , I got the idea that by doing a time series of measurements on Walker and Pyramid Lake  $\Sigma\text{CO}_2$ , I could pin down the rate of  $\text{CO}_2$  invasion for each. These results could then be compared with those we had obtained for the ocean. Because the invasion rate must depend on wind speed, the rate of invasion into these two lakes, which experienced wind velocities averaging four metres per second, could be compared with that for the ocean, which experienced on the average twice this wind speed (i.e. 8 m/sec). I decided to continue the measurements on Mono Lake as well. Because of its very high dissolved inorganic carbon content (and similar average wind speed), I expected that the increase in its  $^{14}\text{C}$  to C ratio would be negligible. Hence, in a sense, it would serve as a control. Five years later, when we resampled these three lakes, we found that the  $^{14}\text{C}$  to C ratio in Walker and Pyramid had increased more or less as expected. However, Mono Lake surprised us. It too showed a substantial  $^{14}\text{C}$  to C increase which translated to a  $\text{CO}_2$  invasion rate about five times what we expected (Broecker *et al.*, 1988). This rise was soon confirmed by measurements made at two other radiocarbon labs.

To constrain what was responsible for this anomalous increase, Rik Wanninkhof, a Lamont graduate student interested in gas exchange, carried out two tracer experiments, one in Mono Lake and the other in nearby Owens reservoir. For these experiments, he used as a tracer, sulphur hexafluoride ( $\text{SF}_6$ ), a nearly indestructible gas widely used as insulation in electrical transformers. Further, it had the advantage that as little as 100 million molecules could be detected by gas chromatography. The  $\text{SF}_6$  Rik added to the lake's surface waters spread rapidly and after a few days was homogeneously distributed. Rik then did daily surveys to determine how rapidly the  $\text{SF}_6$  was being lost to the atmosphere. This loss rate was then converted to an  $\text{SF}_6$  evasion flux. Based on their respective molecular diffusion rates, the  $\text{SF}_6$  flux could be used to calculate flux for any other gas. When Rik calculated the flux for  $\text{CO}_2$ , it was consistent with





that obtained for Walker and Pyramid. As an additional check, the evasion of  $\text{SF}_6$  from Mono Lake, which has quite a high salt content, came out to be nearly the same as the rate for neighbouring Owens reservoir, which has a very low salt content (Wanninkhof *et al.*, 1987).

There were three possible explanations for the much larger than expected increase in the  $^{14}\text{C}$  to C ratio in Mono Lake. One could have been a clandestine (and highly illegal) addition of waste  $^{14}\text{C}$  to the lake. Because it would have required many curies of  $^{14}\text{C}$ , this explanation seemed unlikely but not completely out of the question. The hospitals in New York City, for example, were at that time using this much  $^{14}\text{C}$  each year for experimental studies. However, the  $^{14}\text{C}$  in Mono Lake has continued its increase right up to the present, so it would have been necessary to postulate either a number of such clandestine additions or that the  $^{14}\text{C}$  was added in solid form and since then has slowly dissolved. The second possibility required a large enhancement of  $\text{CO}_2$  invasion relative to that for other gases. Such an enhancement occurs in our lungs where the relatively slow conversion rate of bicarbonate to  $\text{CO}_2$  gas is accelerated by several orders of magnitude through the activity of the catalyst, carbonic anhydrase. Leakage of this catalyst from the brine shrimp, which thrive in Mono's salty waters, might explain the anomaly, but we have been unable to produce evidence that this actually happens.

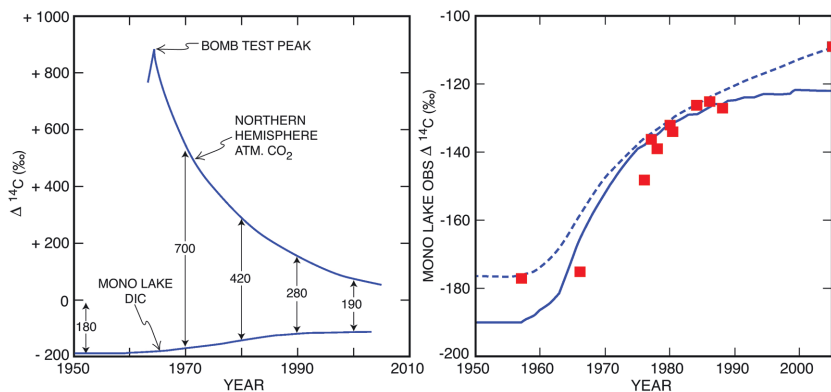


**Figure 10b**

Exotic tufa towers along the southern side of Mono Lake. They are made of  $\text{CaCO}_3$  precipitated when  $\text{Ca}^{2+}$  rich ground waters meet  $\text{CO}_3^{2-}$  rich lake water.

The third possibility was a very clever explanation dreamed up by Rik Wanninkhof. To explain the unusually large reservoir correction (i.e. 1,500 years), we invoked the delivery of  $^{14}\text{C}$  free  $\text{CO}_2$  from beneath the lake (Broecker and

Wanninkhof, 2007). Hot springs rich in  $\text{CO}_2$  (and  $\text{HCO}_3^-$ ) dot the Sierra Nevada front (Fig. 10b). Seismic surveys of the sediments beneath Mono Lake reveal large pockets of gas. Further, the excess  $\text{CO}_2$  partial pressure observed in Mono Lake water is best explained by the seepage of  $\text{CO}_2$  from beneath the lake. Wanninkhof showed that if for some reason this seepage had recently stopped, the invasion of atmospheric  $\text{CO}_2$  at the rate observed for Walker and Pyramid Lakes would explain the increase in  $^{14}\text{C}$  to C ratio. When asked why this shutdown might have occurred, he pointed to the installation of the aqueduct which, after 1941, diverted the mountain streams feeding Mono Lake to supply thirsty Los Angeles.



**Figure 10c**

Attempts to explain the unexpectedly large buildup of  $^{14}\text{C}$  in Mono Lake. As shown on the left during the last 45 years, the excess H bomb test radiocarbon content of atmospheric  $\text{CO}_2$  has been decreasing as the result of uptake by the ocean and by terrestrial vegetation. At the same time, the  $^{14}\text{C}$  to C ratio in Mono Lake's dissolved inorganic carbon content has been rising. On the right are two scenarios that could explain the unexpectedly large increase. The solid line is the expected trend if the  $\text{CO}_2$  exchange rate were five times that obtained from Wanninkhof's  $\text{SF}_6$  evasion experiment. The dashed line is that expected if the inflow of  $^{14}\text{C}$  free inorganic carbon from beneath the lake was shut down as a result of the interception of the streams feeding the lake by the Los Angeles aqueduct (after Broecker and Wanninkhof, 2007).

Perhaps in some way this diversion perturbed the ground water input beneath the lake and, in turn, the upwelling of  $\text{CO}_2$  rich water. Rik fortified his suggestion by showing that it could account for the shape of the increase in the  $^{14}\text{C}$  to C ratio time dependence curve as well as its magnitude (Fig. 10c). This mystery remains unresolved. Perhaps as time goes on and the excess  $^{14}\text{C}$  in the atmosphere is dissipated through uptake by the ocean, the shape of Mono Lake's  $^{14}\text{C}$  change will provide a better explanation. In any case, I am proud of the 50 year long  $^{14}\text{C}$  record that I have generated for Mono Lake.



Radon was not the only radioactive daughter product of uranium that captured my interest. Two more of these isotopes,  $^{230}\text{Th}$  (half life 75,000 years) and  $^{234}\text{U}$  (half life 250,000 years) dominated my research interests during the 1960s. Several graduate students also made their mark. Aaron Kaufman examined the possibility of using these isotopes to date shells and tufas from the Great Basin (Kaufman and Broecker, 1965). Tehlung Ku explored their use for dating deep sea sediments (Ku and Broecker, 1966). Michael Bender investigated their rise in determining the growth rate of the manganese nodules found on the abyssal sea floor (Bender *et al.*, 1966). David Thurber demonstrated that the uranium dissolved in seawater had a 15% excess of  $^{234}\text{U}$ . Finally, Adriano Taddeucci, a NATO post doc from Italy, applied them for dating phenocrysts in lava flows (Taddeucci *et al.*, 1967).

It was during this period that my problems with Maurice Ewing began. I took a leave of absence and visited Caltech in the spring term of 1964. Chair person, Bob Sharp and his colleagues there wanted to lure me away from Lamont. They chose a good time because I was overwhelmed by my growing responsibilities. Larry Kulp's interest was rapidly shifting to Isotopes Inc., a company he and several of his former students had spawned. This left me with an ever greater responsibility for the maintenance of the sizable empire he had created at Lamont. I was becoming too much of an administrator. Toward the end of my semester at Caltech, I made it known to the people back home that I was thinking of leaving Columbia.

Columbia flew me back and arranged a meeting with the provost and dean. Ewing was the only other Lamont person to attend. Asked what it would take to keep me at Columbia, I said I would consider staying only if another professor was added to our geochemistry group. I suggested Paul Gast, who at the time was a faculty member at the University of Minnesota. I explained that Kulp was splitting his time between Lamont and his fledgling company, thereby shifting too much responsibility my way. Ewing caught me totally by surprise by suggesting that Kulp be fired for dereliction of his Columbia duties. He asked if I agreed. I said "No, I do not," and added, "while once a 16 hour a day, 6 days a week person, Kulp was now more like an 8 hour a day, 4 days a week person. In this regard, he was no different than many other Columbia professors." Ewing glared at me. I could tell that he was angry and, knowing him, I realised that things would never again be quite the same between us but perhaps he sensed that Kulp was likely to leave on his own. He backed Gast's appointment and I agreed to turn down Caltech's overture. As it turned out, an internal battle for control of Isotopes Inc. forced Kulp to decide between remaining at Columbia or becoming the full time director of the company. He chose Isotopes Inc. So it was that Paul Gast and I came to share the direction of Lamont's geochemistry research group.

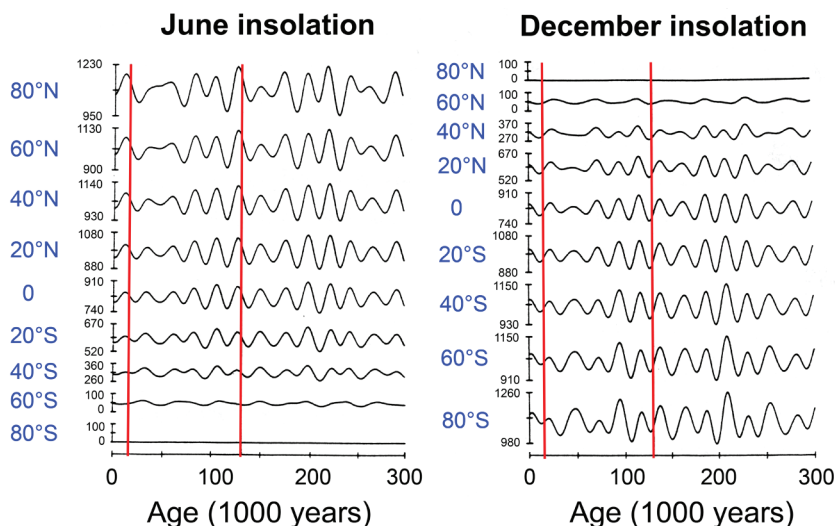


Soon after my return from Caltech, I received a phone call which led to a rekindling of my interest in palaeoclimate. It came from Robley Matthews, a professor at Brown University. He had learned that we were using uranium's decay series isotopes to determine the ages of fossil corals and asked if we would determine the ages of two corals from uplifted reefs on the island of Barbados. When I asked why, he said that he had a grant from an oil company to study how rapidly the porosity of fossil corals was reduced. He went on to explain that, because much petroleum was stored in ancient coral reefs, knowing what controlled their porosity was important.

The coral from the higher of the two Barbados terraces yielded an age of 124,000 years and for the one from the lower terrace, an age of 82,000 years (Broecker *et al.*, 1968). These ages rang a bell. They corresponded to times of prominent maxima in Northern Hemisphere summer insolation that had been determined by the Yugoslavian mathematician, Milutin Milankovitch (Fig. 11a). These shifts among the seasons of the proportion of the annual sunshine raining onto various regions of the planet are related to cyclic changes in the Earth's orbit induced by the gravitational attraction by the Sun, the Moon and the major planets, Jupiter and Saturn. Milankovitch postulated that it was changes in Northern Hemisphere summer insolation that modulated the extent of glacial cover in Canada and Scandinavia and, in turn, the level of the sea (Milankovitch, 1998). Milankovitch's hypothesis had remained highly controversial until the mid 1950s when Cesare Emiliani, a post doc of Nobel Laureate Harold Urey at the University of Chicago, produced a palaeotemperature record based on oxygen isotope measurements on foraminifera shells from deep sea sediments (Emiliani, 1956; 1957). Only when Emiliani's records were published did the tide of opinion begin to swing toward pacing by orbital cycles.

When I reported the results to Matthews and told him that they matched two prominent summer insolation maxima, he said, "but Wally, there is a third coral terrace half way between these two." So I asked him for a sample and the result turned out to be 107,000 years (Broecker *et al.*, 1968). I was initially puzzled because the Milankovitch reconstruction had no prominent summer insolation peak at this time so I went back to the primary material and noted that Milankovitch's insolation reconstruction was dominated by the 40,000 year cycle of the tilt of the Earth's spin axis, hence the peaks at 124,000 and 82,000 years. I recalculated the time sequence of Northern Hemisphere insolation, giving more weight to the influence of the 20,000 year cycles associated with the precession of the Earth's spin axis. In this way, I was able to produce a third peak in Northern Hemisphere summer insolation. It fell close to the 107,000 year date we had obtained on Matthew's third coral terrace. I emphasise Northern Hemisphere because unlike the cycle in Earth tilt that simultaneously increases and decreases summer insolation at high latitudes in both hemispheres, in the case of precession, the response is antiphased between the hemispheres. Thus, not only did this third analysis explain why there were three coral terraces rather than two, it also pointed to summer insolation in the Northern Hemisphere as the driver (Broecker *et al.*, 1968).



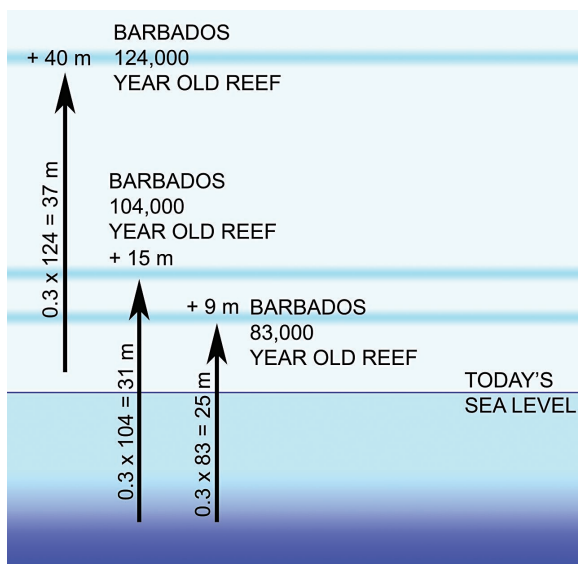


**Figure 11a**

Solar insolation for the last 300,000 years at a range of latitudes for the months of June and December. These cycles are generated by gravitational interactions between the Sun, Earth, Moon and the planets, Jupiter and Saturn. In recognition of the first person to make these calculations, they are referred to as Milankovitch cycles. Note that following the Northern Hemisphere summer insolation maximum corresponding to Termination II, there are two additional maxima, one centred at 104,000 years ago and the other at 82,000 years ago. Black numbers give the solar input in calories per centimetre squared per day OR  $\text{cm}^2/\text{day}$  (after Broecker, 2002).

These ages also demonstrated that the island of Barbados acted as a strip chart recorder of sea level. Tectonic uplift caused by the subduction of the Atlantic Ocean plate beneath the islands lifted the reefs, that formed by successive sea level maxima, out of the sea, allowing us to sample and date corals formed on them. It had been shown that along stable coastlines, such as those in Australia 124,000 years ago, sea level stood about 5 metres higher than it does today. Thus, assuming that Barbados was being pushed up out of the sea at a more or less constant rate, and based on the elevation on Barbados, we could establish its rate of uplift during the last 124,000 years. Then, based on this uplift rate, we could reconstruct the level of the sea 82,000 and 107,000 years ago. The result came out that at both of these times, Barbados stood about 16 metres lower than today (Fig. 11b). Using estimates of the volume of excess ice at the time of the last glacial maximum about 25,000 years ago, sea level must have stood about 120 metres below its present level. With this as a reference, all three of the Barbados coral terraces that we dated for Matthews must have formed during the time interval of the last interglaciation. Further, the timing of these crests in sea level was consistent with Milankovitch's claim that the glaciations were paced by Northern Hemisphere summer insolation.





**Figure 11b**

The ages of three uplifted coral reefs on the island of Barbados have been determined by the  $^{230}\text{Th}$  method. All three fall within the last major interglacial interval and occur at times of prominent Northern Hemisphere summer insolation maxima. Equivalents of the older of these three reefs located on geologically stable coast lines have crests lying about three metres above today's sea level. This allows the tectonic uplift rate of Barbados to be determined. Based on this rate, the elevation of sea level at the times when the other two reefs formed can be reconstructed (after Broecker *et al.*, 1968).

## 12. MAGNETIC REVERSALS

It was during this period that the second (and last) International Oceanographic Conference took place. The first one had been held in 1958 at the United Nations Headquarters in New York City. The second was held in Moscow in 1966. I was excited to attend and peek behind the Iron Curtain. On the third day of the meeting, I had planned to attend a lecture given by a Russian marine geologist but when I walked into the lecture hall, I saw that it was my Lamont colleague, Bruce Heezen (Fig. 12), who was being introduced. The chairman





explained that Heezen's lecture was in place of the one by the Russian who, at the last minute, was unable to attend the conference. Heezen's lecture discussed the discovery that reversals in the Earth's magnetic field were recorded in deep sea sediments. Further, they were associated with extinctions of marine organisms.

Heezen's projections came from a preprint of a paper coauthored by his student, Billy Glass, together with Lamont's John Foster and Neil Opdyke. I had been given a copy just before I left for Moscow and had it in my briefcase. At the end of his lecture, Heezen pointed out that there had not been a reversal for 750,000 years so we were due for another. He explained that previous reversals had been accompanied by extinctions of marine organisms so the next one might extinct us. This warning was repeated at a press conference held the same day and was picked up by newspapers and magazines across the world. As is often the case, only Heezen was given credit for the discovery of magnetic reversals in deep sea sediments and their association with extinctions of marine organisms. This created a huge uproar because Heezen was not an author of the paper, nor had he obtained permission from the authors to present their research at the Moscow meeting.

When they read the press accounts, the authors of the paper were angry and complained to Director Ewing that their research findings had been hijacked by Heezen. Ewing had a bone to pick with Heezen just as he had had with Kulp a year or two earlier. So he jumped at this opportunity and made a formal complaint to the University asking that Heezen's tenure be revoked. At first, I tended to agree with Ewing but as I thought more about it, I changed my mind. Billy Glass, the senior author on the paper, was Heezen's graduate student. This shed a somewhat different light on Heezen's seeming theft. While clearly wrong, it by no means merited dismissal from the university. Further, Heezen was certainly one of Lamont's most creative researchers, if not the most creative, so I suspected that his rising fame was a thorn in Ewing's side. Ewing had, since its beginning in 1949, dominated every aspect of Lamont. Hence he resisted the rising influence of Kulp and Heezen.



Photo courtesy of Lamont-Doherty Earth Observatory Archives.

**Figure 12**

The late Bruce Heezen, pointing to the Earth girdling midocean ridge which he discovered. I consider him as one of the top five scientists Lamont has produced.



My concern heated up as the summer progressed and on Labour Day, it boiled over. I suspected that as was his habit, Ewing would be at work in his office. I also suspected that Harriet Basset, his administrator (and gate keeper) would not. So, I took a chance and went to his office on the second floor of Lamont Hall. Sure enough, Ewing was at work and there was no gate keeper. I asked if I could speak with him about the Heezen situation. He said, "Okay, what about it?" I said that it was my opinion that while reprehensible, his actions in Moscow did not merit dismissal from the university and then added (big mistake), "It's being carried out like a lynching." Ewing exploded, "You lily livered bastard; you let me down with regard to Kulp and now you are doing the same in the case of Heezen." I was stunned but had the presence of mind to remember a warning given to me by Chuck Drake, a Lamont colleague. "You are on Ewing's list of irritants; I fear that a confrontation with him is in the offing. When it happens, keep your mouth shut because Ewing is one of the world's greatest verbal counter punchers." So, I said only, "If that's your opinion of me I guess that I should leave Columbia." I said no more. He said no more. We just sat and stared at each other. This stand off lasted a full 40 minutes. Finally, Ewing broke the silence and said that there was no need for me to leave. However, I could tell that he had written me off. I was now his foe. It turned out that the committee convened by Columbia's provost to decide Heezen's fate unanimously voted against his dismissal so Ewing and Heezen were forced to coexist at Lamont. Fortunately, I was able to steer clear of Ewing and thus escaped the harassment he rained on Heezen.

## 13. GEOSECS

Toward the end of the 1960s, two unique opportunities arose which led me to temporarily abandon my desire to plunge ever more deeply into palaeoclimate. One was the creation by the National Science Foundation of an initiative called IDOE (i.e. International Decade of Ocean Exploration) and the other was an invitation to participate in a limnological research program being launched in Canada. In 1968, during a visit to Woods Hole, Henry Stommel, a legendary figure in physical oceanography, took me aside and said "Wally, you guys measure radiocarbon here and there in the ocean, but if we are to properly use the results to pin down the rates of transport, we need a systematic survey along transects from one end of the ocean to the other." I asked, "how many stations along each transect and how many depths at each station?" He replied, "50 stations and 20 depths". I made a quick mental calculation that each such traverse would cost at least a half million dollars and pointed out that those of us doing such measurements operated on yearly grants of \$50,000 or so. Stommel then hinted that there would soon be big money available at NSF to do big money research. Intrigued by this possibility, I nosed around a bit and learned that the National Science Foundation had plans to launch a multimillion dollar program under the banner



International Decade of Ocean Exploration, or as it came to be known IDOE. The idea was to create 5 to 10 multi institutional projects aimed at accomplishing goals unachievable by single investigators.

I phoned up Harmon Craig, a high profile ocean oriented geochemist at Scripps, and told him about Henry Stommel's charge to us. I also told him that Stommel's proposed radiocarbon traverses would be a perfect fit to IDOE. Harmon, who liked to think big, jumped at the idea but he said we should also measure all the other geochemical properties of significance. Included were  $O_2$ ,  $NO_3$ ,  $SiO_2$ ,  $\Sigma CO_2$ , alkalinity, tritium and seven or eight other properties. We were told that Paul Fye, Director of Woods Hole Oceanographic Institution (WHOI), was the man to see. He was one of the inner circle laying the foundation for this enterprise. Harmon and I arranged a meeting with Fye. I remember waiting in the reception area outside his office. As we leafed through a photo album designed to extol the accomplishments of WHOI, we came upon a picture of Paul Fye in a suit and tie holding out a medal held in a leather case to the winner of some prize or other. I mentioned to Harmon that he looked just like the FBI agents who had warned me never to make any more  $^{85}Kr$  measurements. Harmon made a bubble with the words "I'm Paul Fye from the FBI," and we slipped it under the clear plastic which protected the picture.

We came away from the meeting elated, because Fye said that our program was just what IDOE was looking for. He told us to write a letter proposal to Feenan Jennings at NSF who would administer the program. He also made it clear that the program would have a much better chance if we added a WHOI person to the leadership group. So, Derek Spencer became the third partner.

Our first action was to offer Arnold Bainbridge, a Kiwi on the Scripps scientific staff, to join us as a head of the program's logistic group. This turned out to be a tremendously important and lucky choice, because without Bainbridge, we could never have successfully pulled off this program. We then struggled with the choice of a name. Craig came up with GEOSECS, which stood for Geochemical Ocean Sections Study. Although I have never liked acronyms, this one had a nice ring to it. NSF took us on as IDOE's pilot program and immediately provided funds for a test cruise. We opened it up to all comers with the challenge that the group that produced the best measurements for a given property would be selected to be part of the Atlantic survey. In 1969, this group of applicants sailed out into the Pacific Ocean from the Scripps facility in San Diego and occupied a station off Baja, California. It was agreed ahead of time that Bainbridge's team would perform the shipboard measurements (temperature, salinity, dissolved oxygen, nitrate, phosphate and silica) which would serve as the matrix for the measurements of the numerous stable and radio isotopes. Once the test cruise measurements were reported, we chose the investigators. At the top of the list were Minze Stuiver from the University of Washington and Gote Ostlund from the University of Miami who were to conduct the all important radiocarbon measurements. I had stepped aside from the operation of the Lamont radiocarbon laboratory in 1965, so we did not compete to be part of this action. Rather, Lamont people took responsibility for the radon, radium and barium measurements.



Bainbridge then took the next two years to assemble a group of 25 technicians and to accumulate all the necessary equipment. Included were nine 200 litre stainless steel water samplers built by a German company following the design created by Lamont's Sam Gerard. Each of these so called Gerard barrels cost about the same amount as a Mercedes automobile. He also purchased an IBM computer that filled a whole room on the ship.

Then in 1972, we were ready for the real thing. Bainbridge moved all the apparatus and people from California to Woods Hole where they equipped the RV *Knorr* for 9 months in the Atlantic Ocean. We agreed that the chief scientist on each one month duration leg would be one of the principal investigators. Derek Spencer took this job for the initial leg from Woods Hole to Iceland. I took over on the leg from Iceland to Barbados. Then Harmon Craig took command from Barbados to Recife, Brazil, and so forth.

A couple of events that occurred while I awaited our departure from Iceland remain vivid in my mind. One was that none of the Icelanders who came to the docks in Reykjavik could believe that such a beautiful and well equipped vessel could be for academic research. Instead, it was rumoured that we were doing some clandestine project for the CIA. The other was the Fischer-Spassky chess match. A few of us were able to get tickets for what turned out to be the final match. I will never forget Fischer in his maroon suit, twisting and turning in his specially constructed chair, and solemn Spassky never moving a muscle. When Spassky resigned, spectators dribbled out of the field house, leaving it nearly empty except for the group celebrating with Fischer under the balcony. On the far side, on a small stage, stood the table with the chess set. A plan began to build in my mind. I could walk casually across to the stage and snatch a pawn and then run to the series of emergency doors at the end of the field house and out into the streets of Reykjavik. I would head for the *Knorr* and, for safe keeping, drop the pawn into one of the Gerard barrels. I started the walk and then it hit me. Derek Spencer had warned me to be on especially good behaviour because I was to be the first person from the outside to serve as chief scientist aboard a Woods Hole Oceanographic vessel. I could see the headlines "Scientist purloins pawn!" So I stopped in my tracks. Forty-eight years later, I wish I had done the deed!

Our Atlantic survey proved to be a roaring success. The NSF authorised us for a similar survey of the Pacific so Bainbridge moved his equipment and people back to Scripps and made the necessary repairs and upgrades. In 1974, we were off again! The first leg was from San Diego to Honolulu with Ray Weiss from Scripps in charge. I took the second leg from Hawaii to Adak in the Aleutians and then joined Taro Takahashi who served as chief scientist from Adak to his homeland, Japan. Two events broke the tedium of doing the same set of things at every station. The first was the worst storm I ever experienced. After a station in the Bering Sea, we headed back toward the open Pacific. As we approached the Aleutian Island chain, we were hit by fierce winds and huge waves. The Scripps vessel, *Melville* (twin of WHOI's *Knorr*) was powered by two five bladed cycloids, one forward and the other aft. While excellent for maneuvering in port



or on station, they were not particularly good for traversing open ocean waters; eight knots was all the *Melville* could do in calm seas and much less in heavy ones. During the storm, we made only three or four knots. The captain was pale, fearing the ship would come apart. Those of us who were not sick in our bunks desperately struggled to make sure the equipment remained secure or, at times, just hung on for dear life as the waves tossed the *Melville* about.

The other event was a side trip that Bill Reeburgh, from the University of Alaska, Fairbanks, and I made in a rubber raft while the *Melville* was on station midway along the traverse to Japan. Bill and I rowed a half mile from the ship to get a clean water sample for scientists at Exxon who were checking to see whether hydrocarbons were building up in open ocean surface waters so we went far from any oil associated with the *Melville* and did so without an outboard motor. Keeping us company were a dozen or so “gooney” birds (albatross) floating on the ocean surface many hundreds of miles from any land. Awesome. We finished filling the sampling bottles and started to row back to the *Melville* but before we got very far, one of our oarlocks broke. Thanks to Bill’s very strong arms, we were able to struggle back – quite an experience.

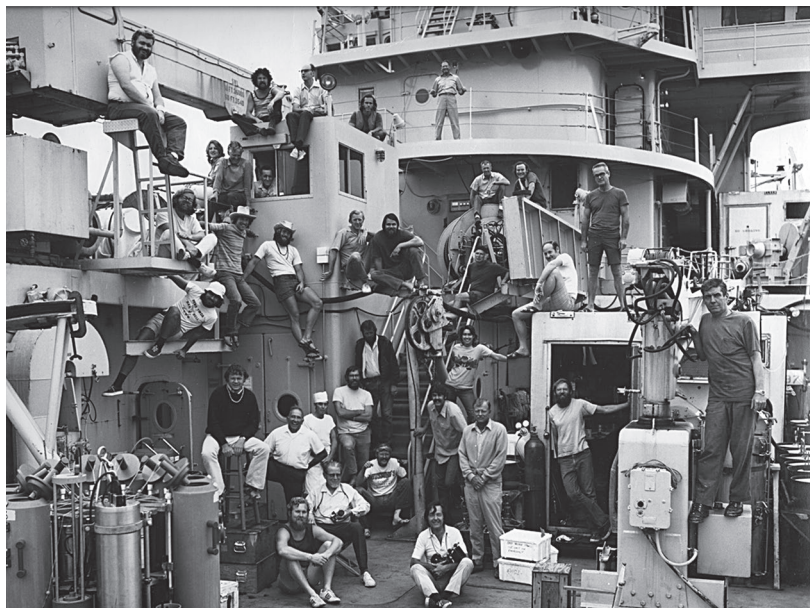
Once again, I was chief scientist on the last of the Pacific legs – Tahiti to San Diego. In addition to our usual tasks, we helped filmmaker, Chick Gallagher, document our expedition (Fig. 13a). It eventually came out as an NSF educational film entitled “Rivers in the Sea.” Chick shared my love of pranks, so we decided to rechristen the *Melville* giving her the name of the Lamont oceanographic vessel, *Vema*. It was easy to lean over the aft rail and cover *Melville* with the word, *Vema* but the raised letters “Melville” located about 8 feet below the rail on both sides of the bow posed a challenge so at three o’clock one morning while underway, using his Irish charm, Gallagher diverted the attention of the mate on bridge watch. Meanwhile, Guy Mathieu, a Lamont scientist who conducted the radon measurements, crept out on the dark forward deck carrying a paint roller mounted on a long pole and leaned over first one side and then the other covering the raised white letters, MELVILLE, with blue ship’s paint. As we sailed into San Diego harbour, the covers, which hid the word VEMA along the ship’s aft rail, were removed. To say the least, Captain Phinney was not pleased.

Pleading a shortage of funds, the NSF denied our request for a grant to survey the Indian Ocean but a year later they relented and in 1978, the *R. V. Melville* left Alexandria, Egypt and passed through the Suez Canal into the last of the great oceans (Fig. 13b). I served as chief scientist on one of the four legs (from Perth, Australia to Colombo, Sri Lanka). Our arrival was on April 1, 1978. We had cabled the science fiction author, Arthur Clarke, inviting him to visit the *Melville* but on our arrival at the dock, the ship’s agent apologised for Clarke, telling us that he was busy that morning countering an April fool’s story in the Colombo newspaper that announced that there would be an eclipse of the Sun that day. Clarke was appearing on television and the radio to warn people not to endanger their vision by staring at the Sun. Instead of coming to see us, he invited us to his Colombo estate. When we arrived that afternoon, we were given a tour





of Clarke's sizable estate. One of the large trees was surrounded by chicken wire to prevent the escape of a dozen small monkeys. Three of the walls in Arthur's study were lined ceiling to floor with books. "All of those were written by me." In answer to our amazed stares, he continued "Of course, each has been translated into twenty or so languages and I include copies of these as well."



**Figure 13a**

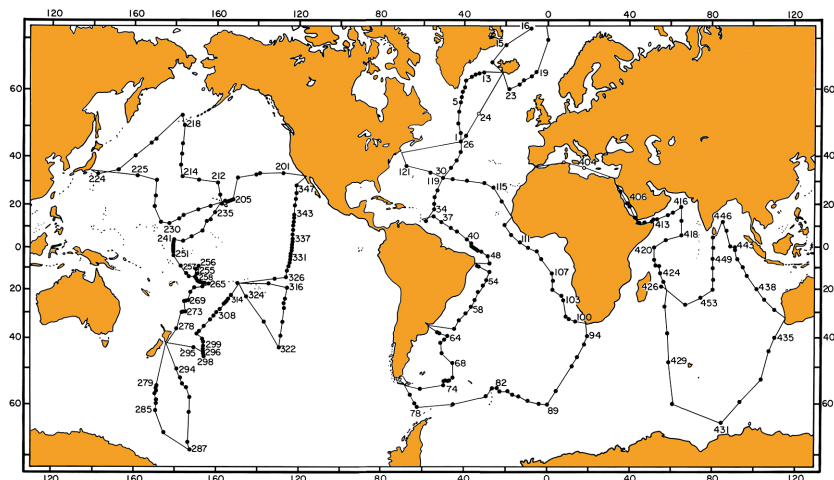
The GEOSECS scientific team aboard the *R.V. Melville*, enroute from Tahiti to San Diego. Chick Gallagher, the film maker, sits with his camera in his lap. To Gallagher's right, leaning on the door to his radon van, is Guy Mathieu. At the age of 43, I looked quite different than I now do at 80. Can you pick me out?

Although GEOSECS made no astounding discoveries, our superb global data set became the basis for a host of subsequent research projects. I benefited greatly; it became the grist for my tome "Tracers in the Sea" which, 30 years later, remains the book on the geochemistry of the oceans (Broecker and Peng, 1982). It was self published by ELDGIO Press (an Italianised acronym for Lamont-Doherty Geological Observatory). The Doherty had been added to the name of our institution in recognition of a large donation to our endowment made by the Doherty Foundation. I went the self publication route after the editor of the publishing company I had dealt with decided it needed stylistic editing. I was at the time fighting third stage lymphoma so I pulled the manuscript and created ELDGIO in order to get it printed and distributed while I was still alive. It particularly pleased me because of a side benefit. I was able to place a picture of my dog peeking out of a life ring. The title on the picture was "Woofier, the Tracer Dog." Published





in 1982 (Broecker and Peng, 1982) before the availability of computers, it gave the appearance of a set of old style preprints bound together and sandwiched between hard covers. A woman at Cambridge Press said that it would make an excellent doorstop but all 5,000 copies sold and offers ranging up to 450 dollars have been made on ebay for used copies.



**Figure 13b** Track map showing the locations of the 454 stations occupied as part of the GEOSECS program.

## 14. DAVID SCHINDLER

The offer to join the research team at the Experimental Lakes Area (ELA) in Canada's western Ontario came at just the right time. I resisted having my graduate students be involved in GEOSECS because I was afraid that they would get wrapped up in its routine and, as a consequence, fail to develop individuality. In contrast, ELA was made to order for graduate student research. Most of the Canadians involved were biologically oriented limnologists and David Schindler, the scientist in charge, realised the power of using isotopes as tracers of lake processes. He abandoned the old school, which was based on nonintrusive observations of lakes, and sought to replace it with a combination of purposeful manipulation and use of whole lake radio tracers. Thus, he welcomed my graduate students because their background nicely complemented the members of his core group. So while I was preoccupied with GEOSECS, my graduate students did their research at ELA, working closely with David Schindler.



Before I describe what they did, a few words must be said about the ELA facility and David Schindler. To get to ELA, one had to drive about 50 miles east from Kenora, Canada. The last 25 miles were on unpaved logging roads. One arrived at a small group of buildings that included two labs, sleeping units and a mess hall. The location was on the shore of one of the 10 or so lakes set aside by the Canadian government for limnological research. The lakes are surrounded by dense forests, carpeted with thick moss. They teem with mosquitoes and black flies. Rather than giving these lakes names, Schindler referred to them by number. For example, the lake by the camp was known as 239. I used to tease Schindler by bragging that I studied Lake 1, the world's largest water body, i.e. the ocean. Although difficult to get to, the isolation had its advantages. There were no residents or tourists who might tamper with the instruments placed in and around the lakes nor was there any pollution caused by people. Further, Schindler had "carte blanche" permission to manipulate the lakes and to use radioisotopes.

In many ways, Schindler was made for his job: handsome, soft spoken, highly intelligent, physically powerful and well trained. Further, he loved the wilderness and sought to preserve it. Realising that eutrophication and acidification threatened Canada's thousands of pristine lakes, he sought practical means to minimise the damage generated by the addition of algal nutrients and acids to lakes. My first contact with Schindler came during the early 1970s when his research was focused on eutrophication (Schindler 1971; 1974). Given the essential chemical ingredients (i.e.  $\text{CO}_2$ ,  $\text{NO}_3$  and  $\text{PO}_4$ ), the algae in water bodies flourish. In their natural state, most lakes are oligotrophic (i.e. nutrient limited). Under this condition, there is plenty of  $\text{O}_2$  in the deep water to consume the organic debris that falls from the surface. Further, the number of algal cells present in the upper waters is not great enough to significantly influence the water's clarity, nor do inedible bluegreen algae proliferate, forming a surface scum. Such lakes are ideal habitats for fish and for human recreation.

As the land surrounding a lake, however, becomes ever more densely populated, the  $\text{NO}_3$  and  $\text{PO}_4$  carried to the lake in domestic sewage and runoff from fertilised fields or lawns gradually increases the algal population and eutrophies the lake. Water clarity drops. In some cases, the deep waters become  $\text{O}_2$  depleted. Bluegreen algae often take over. Seeking inexpensive ways to minimise eutrophication, Schindler focused his attention on the element phosphorus. When I first went to ELA, he was adding  $\text{PO}_4$  to one of the smaller lakes. He had found that unlike the ocean, where  $\text{PO}_4$  is very efficiently recycled, allowing it to reside in the water for tens of thousands of years before being removed to the sediment, in fresh water lakes, Schindler demonstrated that the phosphorus was removed on a time scale of a year or two (Schindler, 1974; Schindler and Fee, 1974). Schindler focused on phosphorus because unlike N and C, P cannot be pulled in from the overlying air. Bluegreen algae convert atmospheric  $\text{N}_2$  into a form they can use and if algae decrease the  $\text{Pco}_2$  in surface water below that in air, atmospheric  $\text{CO}_2$  spontaneously flows into the lake. However, there is no equivalent way to get extra  $\text{PO}_4$ .



So why did Schindler need us? He wanted to quantify all aspects of the cycles of C, N and P in his lakes. His initial request was for someone from Lamont who could determine the rate of invasion of CO<sub>2</sub> gas into a lake that he had eutrophied by adding phosphorus. Graduate student, Steve Emerson, offered to try his hand. We decided the best approach was to add <sup>226</sup>Ra to the lake in large enough quantities so the radon it produced swamped that produced by the small amounts of radium dissolved in the lake water and that present in the underlying sediment. Based on the rate of the loss of the added radon, the rate of CO<sub>2</sub> gain could be calculated (Emerson *et al.*, 1973). Of course, in order to calculate the rate of CO<sub>2</sub> uptake by the lake, the difference between the CO<sub>2</sub> partial pressure in the surface lake water and that in the overlying air had to be determined. Traditionally, limnologists did this by measuring pH and alkalinity of the water. Schindler tried this in Lake 239, the large lake on whose shore the camp was located. The Pco<sub>2</sub> he calculated based on these traditional measurements was twice that in the atmosphere. This puzzled us because using Steve Emerson's radon based CO<sub>2</sub> exchange rate, the export of carbon from the lake greatly exceeded any inputs we could think of. Lamont's Ray Hesslein came to the rescue. He measured the Pco<sub>2</sub> directly and found that it was very close to that in the overlying air.

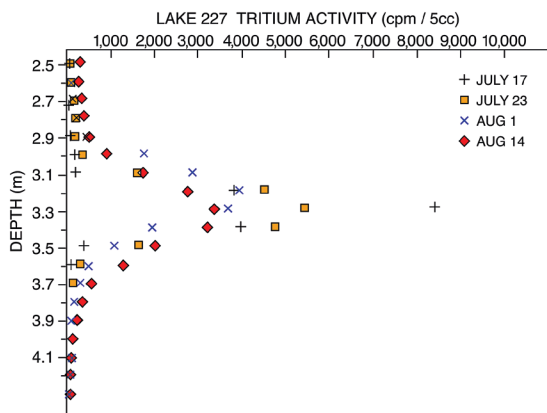
So, Andy Hertzog, another Lamont member, decided to find out why. Taro Takahashi, who was by then also a Lamont scientist, told him that he suspected that pH electrodes were sensitive to certain dissolved organic compounds as well as to the hydrogen ion. So Andy came up with an innovative way to check this. He passed Lake 239 water through an ultra filter, which blocked the passage of large organic molecules. He found that Pco<sub>2</sub> calculated from pH and alkalinity in the filtered water moved closer to the correct value, while that in the residual unfiltered water, moved further away. Clearly, some component of the large organic molecules blocked by the filter was perturbing the pH electrode (Herczeg *et al.*, 1985). At that time, the EPA (Environmental Protection Agency) was about to make a base line survey of hundreds of U.S. lakes. We shared our results and urged them to switch from using a pH meter to measuring the Pco<sub>2</sub> directly. They pleaded, "too much bother". We countered that all one had to do was to fill a syringe half full, shake it, and then inject one cubic centimetre of the air at the top of the syringe into a basic gas chromatograph. I am convinced that their survey conducted with pH meters would have been more useful, had they calculated pH from Pco<sub>2</sub> and ΣCO<sub>2</sub> measurements made without the use of electrodes.

Another of Schindler's questions was how rapidly did the warm summer surface waters mix with the cold deep waters. Paul Quay, another graduate student, took on this task. He carefully injected water tagged with tritium as a thin layer into the middle depths of the thermocline in one of the small ELA lakes. He waited until the tritium had spread laterally and was uniformly distributed in a narrow layer across the entire lake and then made weekly vertical profiles. He found that the rate of vertical mixing was extremely small, only four or five times the rate of molecular diffusion (Fig. 14a). Quay then repeated his experiment in a second lake and was surprised to find that the vertical mix rate was considerably larger than in the first. One difference between the two lakes was



clear. The sides of the first were on average much steeper than those of the second lake. In other words, one lake was shaped like a tea cup and the other, like a soup bowl. Quay reasoned that when the interval waves in the lake resembling the soup bowl broke against the sediment, the friction generated was larger than that created when they broke against the steep sides of the tea cup shaped lake (Quay *et al.*, 1980). However, by then the summer was almost over so Paul came back to Lamont and went on to a quite different research project. There were many other examples. A total of 10 graduate students did part or all of their PhD research with David Schindler at ELA. As I had hoped, the experiences they had there served them well!

Schindler convinced himself and many of his fellow limnologists that the key to fighting eutrophication lay in decreasing the input of phosphorus.



**Figure 14a**

To obtain a measure of the rate of vertical mixing in the thermocline of a small, strongly stratified ELA lake, Paul Quay, a Lamont graduate student, added tritium. The initial distribution is shown by the + signs. Four weeks later, the tracer had spread vertically by only a very small amount (after Quay *et al.*, 1980).

Tommy Edmondson, a highly respected limnologist at the University of Washington, was faced with cleaning up local Lake Washington. The problem was that much of the effluent from sewage plants in the Seattle metropolitan area went into the lake. While the sewage plants oxidised the offending organic matter, there was no tertiary treatment so  $\text{NO}_3$  and  $\text{PO}_4$  were not removed and added nutrients went into the lake. As a result, the lake that once had been transparent blue water had become highly clouded with algae. Edmondson told the town fathers that

all they had to do to clean up the lake was to divert the effluent of the sewage plants into the nearby Pacific Ocean. Of course, Edmondson was banking on Schindler's experiments, which demonstrated that  $\text{PO}_4$  already in the lake would be rapidly removed. The diversion was carried out and within five years, the lake's pristine clarity had been reestablished.

Meanwhile, Schindler was after bigger game. A considerable fraction of the phosphorus that entered lakes came from detergents. Schindler maintained that silica or some other equally inexpensive water softener could be substituted



for phosphorus but the detergent companies were unwilling to make a change. The Soap and Detergent Association did everything it could to discredit Schindler's claims. Put simply, they played dirty. Frustrated, Schindler came up with an ingenious idea. He placed a curtain across the narrow neck that separated the two halves of a dumbbell shaped ELA lake. While the curtain allowed water to flow from the upstream portion of the lake to the downstream portion, it prevented mixing between the two. He then added sugar and nitrate to the upper basin and sugar, nitrate and phosphate to the lower. After two weeks, he took an air photograph of the lake. While the upstream portion retained its pristine blue colour, the lower portion turned to green pea soup (Fig. 14b). Publication of this picture in *Science* did the trick. The soap and detergent people caved in, found a different way to make detergent effective and we no longer have phosphate in our detergent!



Photo from Dave Schindler.

**Figure 14b**

Air photo from David Schindler's research area in northern Ontario showing a dumbbell shaped lake, two weeks after the addition of C and N to one half and C, N and P to the other. Without P, the algae could not make use of the C and N so that water retained its clarity.

## 15. HOW TO COOL A PLANET

It has been known for over a century that the Earth has experienced repeated glaciations. Further, shortly after this discovery was made, it was proposed that these glaciations were paced by cyclic changes in the Earth's orbit. However, because modifications in the Earth's orbital characteristics do not change the amount of solar energy received annually at any location on the planet, but only its distribution among the seasons, it is difficult to understand how these modifications could drive glacial cycles. Could the reflectivity of the glaciers themselves be responsible for the 5 °C or so of glacial cooling of the Earth or is something else needed?

The prime candidate for the something else was the atmosphere's CO<sub>2</sub> content. Perhaps it underwent sizable ups and downs in synchrony with the glacial cycles. The CO<sub>2</sub> molecules in the ocean-atmosphere system are replaced on a time scale comparable to the length of a glacial cycle so the amount of CO<sub>2</sub> present in the atmosphere is susceptible to change on this time scale. However,



and even as late as 1980, no method existed for determining whether the content in the atmosphere of this powerful greenhouse gas was substantially different during times of peak glaciation than now.

Then, during the late 1960s, borings were made through the icecaps in both Antarctica and Greenland. The ice was shown to contain a sizable amount of air trapped in bubbles. I remember attending a meeting held in Grenoble, France, in the late 1970s, at which the first attempt to measure the CO<sub>2</sub> content of the air in these bubbles was reported. I came away discouraged because the measurements showed that the air extracted from the ice contained 30 times more CO<sub>2</sub> than that in the atmosphere. It appeared that snow flakes were somehow able to absorb large amounts of CO<sub>2</sub>. Discouraged by this finding, I began to think of possible indirect means of determining the amount of CO<sub>2</sub> in the glacial atmosphere. I came up with the idea that the ocean's biological pump might have been stronger during times of glaciation. In other words, the reduction of the CO<sub>2</sub> content of surface ocean water resulting from photosynthesis, coupled with settling into the deep ocean of a portion of organic matter that had formed, was greater during glacial time than now. Such a strengthening would have occurred if the ocean's inventory of the nutrients needed for plant growth (i.e. NO<sub>3</sub> and PO<sub>4</sub>) was larger during glacial time.

Of course, in order to make use of this idea, there had to be a way to determine the strength of the biologic pump. Fortunately, there was a proxy that seemed made to order for this task. It was the ratio of <sup>13</sup>C to <sup>12</sup>C contained in the CaCO<sub>3</sub> shells of planktonic (i.e. surface dwelling) and benthic (bottom dwelling) foraminifera. The key to the proxy was the fractionation of carbon isotopes that occurs during photosynthesis. Plants use isotopically light <sup>12</sup>CO<sub>2</sub> in slight preference to the heavier <sup>13</sup>CO<sub>2</sub>. Hence, organic remains that fall from the sunlit surface waters into the deep sea deplete surface water carbon species in <sup>12</sup>C slightly more than they do in <sup>13</sup>C. This results in an enrichment of <sup>13</sup>C relative to <sup>12</sup>C in surface waters relative to deep water. This difference is recorded in the foraminifera shells preserved in deep sea sediments. Planktonic organisms record the <sup>13</sup>C to <sup>12</sup>C in surface water and benthic organisms record this ratio in deep water. Hence, I reasoned that if the biologic pump were stronger during glacial time, then the planktonic-benthic difference in carbon isotope ratios would have been larger than today's.

At that time, there was only one published set of carbon isotope ratio measurements on coexisting planktonic and benthic foraminifera shells that extended back through the most recent glaciation cycle. Nicholas Shackleton of Cambridge University, who pioneered measurements of oxygen and carbon isotopes in the shells of benthic foraminifera, produced this record with the goal of estimating the glacial to interglacial change in the inventory of terrestrial biomass. The idea was that a reduction in biomass would add <sup>13</sup>C depleted CO<sub>2</sub> to the ocean. Deep water makes up most of the ocean so this addition would be best recorded by benthic foraminifera. Indeed, Shackleton found evidence for a decrease of forest biomass during glacial time. I looked at his record through different eyes. His data also showed that the difference between the <sup>13</sup>C to <sup>12</sup>C ratio for coexisting

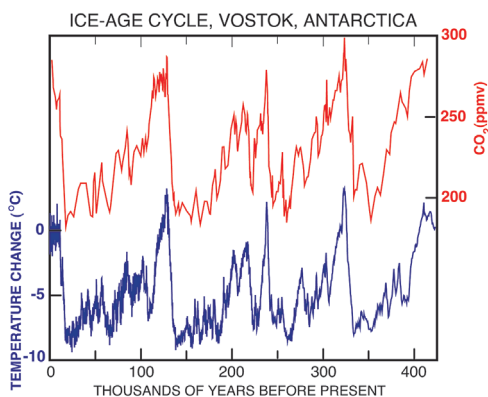




planktonic and benthic shells was larger during glacial than during interglacial time. Further, the direction of the change in the difference suggested that there was a reduction of CO<sub>2</sub> in the glacial atmosphere (Broecker, 1982).

Then a surprise came. Two years after the initial, very discouraging, ice core CO<sub>2</sub> results were reported, research groups in Grenoble, France and Bern, Switzerland, independently showed that these early measurements were incorrect. They demonstrated that air from ice formed during the Holocene contained an amount of CO<sub>2</sub> close to that thought to have been present in the preindustrial atmosphere but it was their measurements on ice formed during peak glacial time that created the excitement. Instead of the 280 parts per million (ppm) CO<sub>2</sub> found in ice formed prior to the onset of the Industrial Revolution, both groups got values close to 200 ppm. When these revised ice core CO<sub>2</sub> results appeared, I was poised to explain what might have caused the 30% reduction in CO<sub>2</sub> during the time of the last peak in glaciation. I say “poised” because I had yet to figure out a way to increase the ocean’s nutrient inventory during times of glaciation and reduce it again during times of interglaciation. The time interval over which the CO<sub>2</sub> content rose during the interval of deglaciation (~6,000 years) was far shorter than the residence time of phosphorus in the ocean (~40,000 years), so I concluded that changes in the delivery rate of phosphorus from the continents could not be the cause. Rather, the nutrients had to be moved back and forth, in and out of some oceanic storehouse. I postulated that this storehouse was the continental shelves. They were flooded during interglacial periods and laid bare during glacial periods. Hence organic matter produced by marine organisms living along continental margins would accumulate on the continental shelves during the interglacial stages and be eroded back into the sea during glacial times. Even though carbon itself was also removed, causing an opposing change, the impact of N and P removal would be far more important. A paper proposing this hypothesis was published in 1982, two years after the reports documenting the low glacial CO<sub>2</sub> appeared.

While perhaps ingenious, my hypothesis proved to have serious flaws. At the writing of this paper in 2011 (i.e. 30 years later), in spite of other ingenious ideas and



**Figure 15**

CO<sub>2</sub> and air temperature records for the last 400,000 years based on measurements made on ice from the Vostok, Antarctica core. Based on newer ice cores, this record now extends back to 800,000 years and there is a hope that it can be extended even further back in time (from Broecker, 2005, with permission from Eldigio Press).



reams of measurements, an acceptable solution has yet to be presented. Faced with this, David Archer suggests that there is no single dominant cause. Rather, several processes made significant contributions. If this proves to be the case, I fear that another 30 years might pass before the glacial to interglacial changes in atmospheric CO<sub>2</sub> are fully understood! There is, however, a hot clue. Thanks to the recovery of several new ice cores from Antarctica, the CO<sub>2</sub> record now extends back to 800,000 years (Fig. 15; Luthi *et al.*, 2008). Through the 8 major glacial-interglacial cycles recorded in this ice, the CO<sub>2</sub> content of the trapped air follows in beautiful detail the D/H and <sup>18</sup>O/<sup>16</sup>O records in the ice itself. The latter are proxies for the air temperature over the Antarctic plateau so the similarity with CO<sub>2</sub> points to the Southern Ocean as the conduit for the CO<sub>2</sub> drawn into the ocean during glacial times and released back to the atmosphere during interglacial times. There is also evidence that the extent of the winter sea ice apron around the Antarctic continent was anticorrelated with local air temperature and atmospheric CO<sub>2</sub> content. This last is discussed further, below.

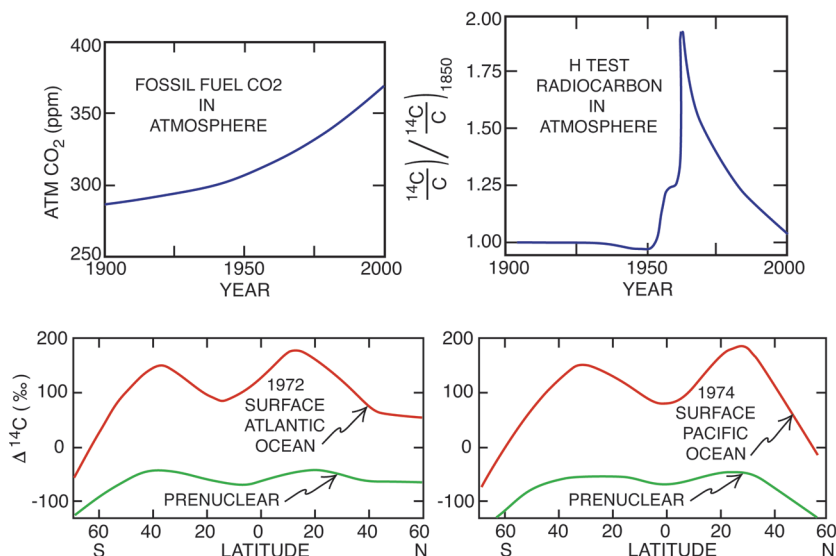
## 16. THE MISSING SINK

At the very end of 1957, Charles David Keeling commenced his monitoring of the atmosphere's CO<sub>2</sub> content at a lab located high on the extinct Mauna Loa Volcano, on Hawaii's Big Island (Harris, 2010). Not only were these measurements more accurate by far than any published previously, they were continuous – night and day, 24 hours a day, 7 days a week. After a few years, Keeling was able to determine the magnitude of the upward trend of CO<sub>2</sub> and compare it with that expected if all the CO<sub>2</sub> produced by fossil fuel burning were to have remained airborne. The answers came out to be a bit more than half. Clearly some of the remainder had been sucked up by the ocean, but how much? Ideally, this question would be answered by repeated inventories of the amount of total dissolved inorganic carbon ( $\Sigma\text{CO}_2 = \text{CO}_2, \text{HCO}_3^- \text{ and } \text{CO}_3^{2-}$ ) in the ocean but at the time, this approach proved to be impossible. Not only was the expected increase very small compared to the large background amount of  $\Sigma\text{CO}_2$  in the ocean but the fossil fuel component would drop off with water depth, becoming ever more difficult to quantify.

Therefore, the ocean uptake estimates had to be made indirectly. To do this, three things had to be known. One was the thermodynamic capacity of ocean water for CO<sub>2</sub> uptake. Another was the exchange rate of CO<sub>2</sub> gas between the atmosphere and the surface ocean and the third was the rate of vertical mixing in the ocean. Only the first of these was known. We geochemists set out to make estimates of the other two. Our strategy was to use the extra <sup>14</sup>C created by John Nuckolls and his British and Soviet counterparts during H bomb testing. The <sup>14</sup>C created from H bombs was rapidly converted to <sup>14</sup>CO<sub>2</sub> so even though the time histories for the production of Nuckolls <sup>14</sup>C and the production of fossil



fuel  $\text{CO}_2$  were quite different, the distribution in the ocean of H bomb test  $^{14}\text{C}$  provided a means to constrain the other two of the unknowns (Fig. 16a). I was one of the first to use simple box models calibrated with Nuckolls  $^{14}\text{C}$  to estimate the fraction of the  $\text{CO}_2$  produced by fossil fuel that was absorbed by the ocean. The result came out to lie between 30 and 35%. Taken together with the 50% that remained in the air, this left 15 to 20% unaccounted for. Hence, the term “missing sink” came into use.



**Figure 16a**

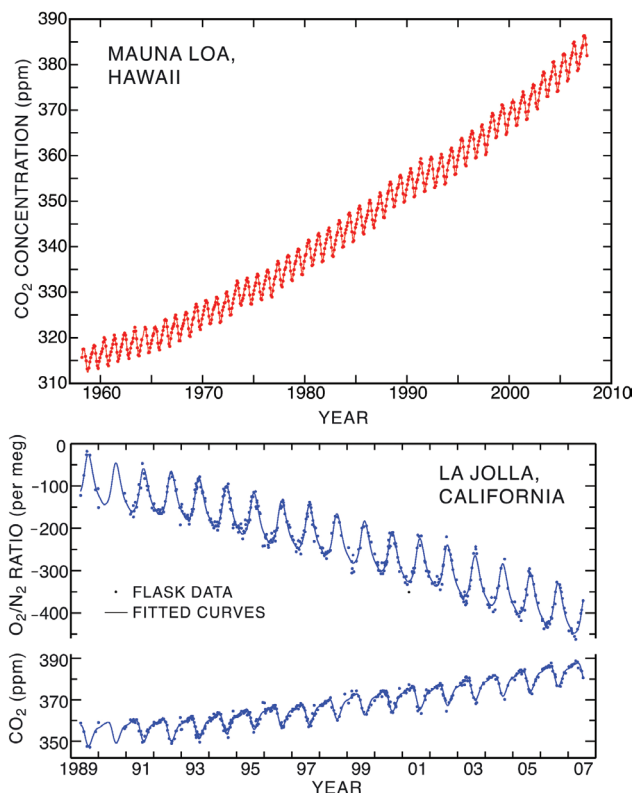
Even though the history of the excess radiocarbon produced by atmospheric H bomb tests (upper right panel) is quite different than that for the excess  $\text{CO}_2$  fossil fuel burning (upper left panel), H bomb  $^{14}\text{C}$  can be used to constrain the amount of this  $\text{CO}_2$  taken up by the ocean. The key is the documentation of the extent of build up of H test radiocarbon in the surface ocean as measured as part of the GEOSECS program (lower panels) (from Broecker, 2005, with permission from Eldigio Press).

The only other reservoir that could be capable of taking up appreciable amounts of  $\text{CO}_2$  was the terrestrial biosphere. It was at about this time that George Woodwell shocked the geochemical community by claiming that deforestation rivalled fossil fuel burning in adding extra  $\text{CO}_2$  to the atmosphere (Houghton *et al.*, 1998). Although Woodwell’s initial forest cutting estimate was shown to be far too high, the subsequent estimates still showed that forest cutting was delivering amounts of  $\text{CO}_2$  to the atmosphere that were somewhere in the range of 15 to 20%. So if the terrestrial biosphere was the missing sink, in order to compensate for deforestation, it would have to be taking up extra  $\text{CO}_2$  at a



rate comparable to that being taken up by the ocean so the argument raged. Ocean oriented people stood by their estimates. Biologically oriented people were convinced that ocean uptake was seriously underestimated.

It was not until Ralph Keeling developed a means of precisely measuring the  $O_2$  to  $N_2$  ratio in air that this debate was resolved to everyone's satisfaction. His monitoring began in 1989, 30 years after his father began to monitor  $CO_2$  (Keeling *et al.*, 1996). After a decade of  $O_2/N_2$  measurements, son Ralph was able to establish the downward trend of  $O_2$  resulting from its consumption by fossil fuel burning (Fig. 16b; Keeling and Garcia, 2002). Unlike  $CO_2$ , the dominant  $O_2$  reservoir is the atmosphere rather than the ocean. Hence the difference between the  $O_2$  consumption by fuel burning and its loss from the atmosphere was a direct measure of the contribution by the terrestrial biosphere. If the inventory of



**Figure 16b**

Son, Ralph Keeling, supplemented his father, Charles David Keeling's, measurements of the increase in atmospheric  $CO_2$  at Mauna Loa, Hawaii with measurements of the drawdown of atmospheric  $O_2$  at La Jolla, California (after Broecker, 2005).



wood and soil humus had increased during this ten year period, then the observed loss of atmospheric  $O_2$  would be less than that predicted by fossil fuel burning. Conversely, if the inventory of wood and humus had decreased, then the observed atmospheric loss of  $O_2$  would be larger than the expected. Keeling's  $O_2$  results clearly demonstrated that, despite forest cutting, the inventory of carbon stored in the continental biomass had steadily increased. The rate of this  $CO_2$  uptake by the terrestrial biosphere had been comparable to that by the ocean. This result was music to my ears, because it was consistent with the conclusions of a paper on this subject that I had published in *Science* in 1979 (Broecker *et al.*, 1979).

## 17. REDFIELD RATIOS

Basic to the understanding of ocean chemistry, is the chemical composition of the organic tissue manufactured by marine organisms. The key elemental ingredients are C, H, N and P. It is the ratio of these ingredients that sets the oxygen demand connected with their consumption by predators and bacteria in the deep sea. Although a very minor contributor to the  $O_2$  demand, phosphorus is important because it is the limiting nutrient. Hydrogen is, of course super abundant because it is easily available in  $H_2O$ . The carbon in  $\Sigma CO_2$  ( $CO_2$ ,  $HCO_3^-$  and  $CO_3^{2-}$ ), although not super abundant, never comes close to limiting algal productivity. As described in the experiments in the Canadian lakes, nitrate can be generated from  $N_2$  gas, which is 78% of the atmosphere, by organisms capable of nitrogen fixation but phosphorus is supplied only by weathering of rocks and transported to the oceans by runoff in rivers so it is the limiting nutrient.

In the 1930s, Alfred Redfield of Woods Hole Oceanographic Institution set out to determine what might be called the “stoichiometry” of marine organisms. Just as the mineral sanidine has the stoichiometric composition  $KAlSi_3O_8$ , as published in 1963, Redfield's measurements suggested that marine plankton had a stoichiometric composition of  $C_{106} N_{16} P$  (Redfield, 1934). Instead of obtaining this result solely by the analysis of the plankton itself, Redfield also used measurements on water samples taken along horizons of constant sea water density (i.e. isopycnals). The idea was that mixing along such horizons was many orders of magnitude faster than mixing between them. Hence, the ratios of the increases in  $\Sigma CO_2$ ,  $NO_3$  and  $PO_4$  away from the surface ocean “outcrops” of these isopycnals would yield the composition of the organic matter consumed on these horizons. Redfield was, of course, aware that all organisms would not have the same stoichiometry so his result represented an average composition. In addition to establishing the average composition of organic matter “eaten” in the Atlantic thermocline, in a similar manner, Redfield was able to determine the oxygen demand. He found that 138 molecules of  $O_2$  were consumed for every molecule of  $PO_4$  released by respiration. Each mole of carbon consumed would require



one mole of  $O_2$  and each mole of nitrogen would need two moles of  $O_2$ . So, for each mole of phosphorus,  $106 + 2 \times 16$  or 138 moles of  $O_2$  would be required. In so doing, Redfield neglected the hydrogen associated with fatty compounds.

When the GEOSECS data became available, Taro Takahashi and I decided to redo Redfield's calculations. The new data set was not only far more accurate but the measurements covered the entire world ocean. Redfield's ratios were based entirely on data from the thermocline of the Atlantic but we wanted to see if there would be differences for other parts of the ocean. Determination of the  $\Sigma CO_2$  increase resulting from respiration was difficult for several reasons. First, the increase was small compared with the large background concentration. Second, in deep water, the contribution of  $CaCO_3$  dissolution had to be considered. Third, in thermocline water, the invasion of fossil fuel  $CO_2$  had to be accounted for. It would counter the increase in  $\Sigma CO_2$  along the isopycnal. Therefore, we instead concentrated on determining the ratio of the phosphorus increase relative to the  $O_2$  decrease.

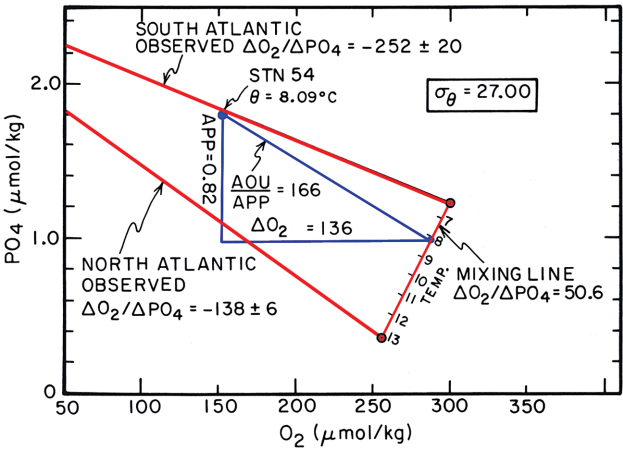
Our analysis of GEOSECS data in the North Atlantic yielded  $O_2$  to P ratios very close to those obtained by Redfield but when we analysed the measurements from the thermocline of the South Atlantic, we obtained a quite different result. Instead of a ratio of -138 moles  $O_2$ /mole P, we got -252 moles  $O_2$ /mole P (Takahashi *et al.*, 1985)! It did not take us long to realise that it was along isopycnal mixing between thermocline waters formed at northern outcrops and those formed at southern outcrops that produced the difference. The southern waters of a given density had lower temperatures and salinities than those formed in the north, so we were able to use salinity variations along each isopycnal surface to correct for the mixing of southern sourced waters into the North Atlantic thermocline and northern sourced waters into the South Atlantic thermocline. Lo and behold, when this was accomplished, we found that the corrected stoichiometries were very nearly the same. Both yielded a  $DO_2/DP$  ratio close to -165 moles/mole (Fig. 17a). It turned out that the reason was that the so called preformed content of  $PO_4$  (i.e. that at the surface ocean outcrop) was much higher for southern than northern waters.

We then did similar analyses of data from along isopycnal horizons in the thermocline of the Indian Ocean and along those in the deep Indian and deep Pacific Oceans. Because more than two end member sources contributed, we could not use our procedure in the thermocline of the Pacific Ocean but we were able to use measurements from the deep Red Sea and deep Norwegian Sea to get additional, independent estimates. We were pleased to see that all these estimates were in agreement with those obtained in the thermocline of the Atlantic. All gave  $DO_2$  to DP ratios of  $-175 \pm 10$  (Fig. 17b; Broecker *et al.*, 1985). We also found that Redfield's 16 to 1 ratio for N to P held for all quadrants of the ocean. Hence, if we assumed, as Redfield had done, that two moles of  $O_2$  were required to oxidise each mole of  $NO_3$ , then the  $O_2$  to P ratio of -175 would have corresponded to a C to P ratio of 143. However, analyses of deep waters free of fossil fuel  $CO_2$  suggested a ratio closer to 120. It is likely that the oxidation of the extra





hydrogen associated with the fatty component of organic matter is responsible for the difference. In any case, our best estimate of the stoichiometry of average marine organic matter is  $C_{120}N_{16}P$ .



The Observed and Corrected Property/Property Ratios						
	$\sigma_\theta$	$\Delta O_2/\Delta PO_4$	$\Delta O_2/\Delta NO_3$	$\Delta O_2/\Delta CO_2$	$\Delta O_2/\Delta TALK$	$\Delta O_2/\Delta Ca$
Observed Ratios						
North Atlantic	27.00	$-138 \pm 6$	$-8.1 \pm 0.4$	$-1.53 \pm 0.07$	$\infty$	—
South Atlantic	27.00	$-252 \pm 20$	$-13.5 \pm 0.8$	$-1.53 \pm 0.08$	$-8 \pm 2$	—
Ratios Corrected for Water Mixing						
North Atlantic	27.00	$-165 \pm 7$	$-9.4 \pm 0.3$	$-1.7 \pm 0.1$	—	$-11 \pm 3$
South Atlantic	27.00	$-165 \pm 6$	$-9.8 \pm 0.5$	$-1.53 \pm 0.07$	—	$-20 \pm 5$

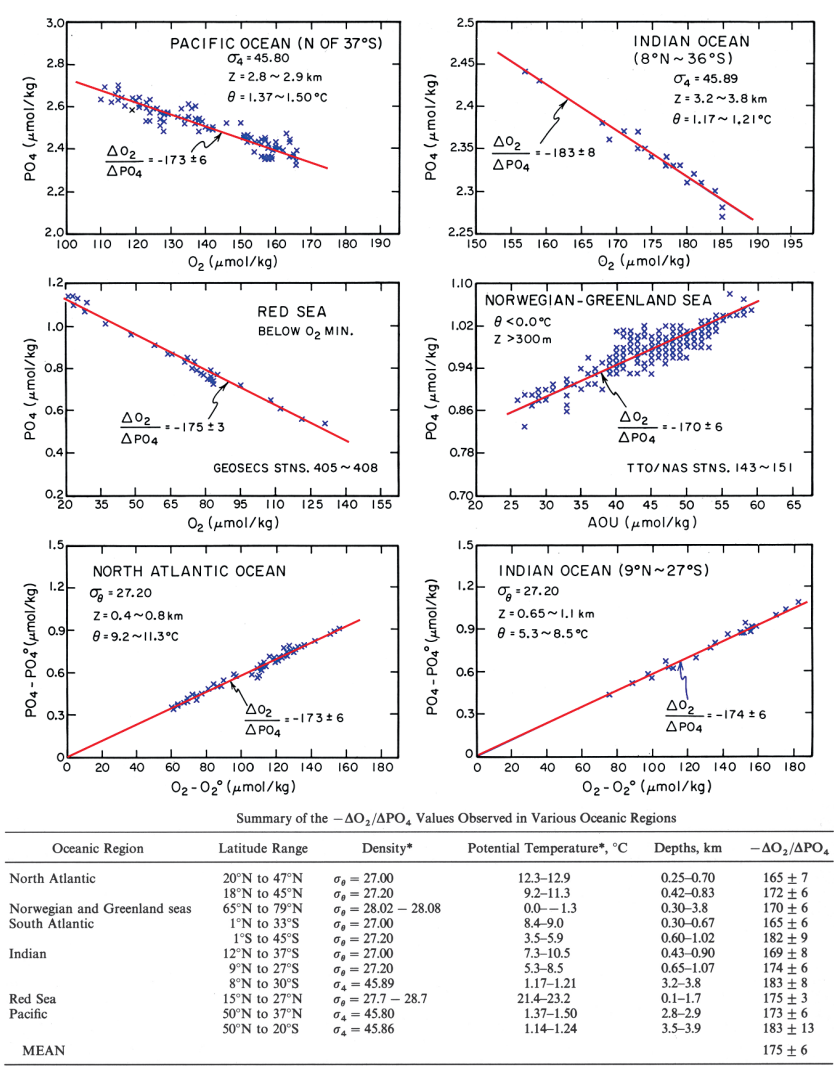
**Figure 17a**

Takahashi's graphical scheme for correcting for the intermixing of northern and southern source waters along the sigma,  $\theta$  27.0 isopycnal horizon in the Atlantic Ocean thermocline. It takes advantage of the temperature difference between the two end members. The northern waters on this isopycnal horizon are warmer and less salty than the southern waters. The example is for GEOSECS Station 54 in the South Atlantic Ocean. Although located in the Southern Hemisphere, it contains about 30% northern source water (after Takahashi et al., 1985).

The finding that the average stoichiometry of the organic matter respired in the subsurface ocean was nearly the same everywhere, led me to develop the source water tracer, phosphate star,  $PO_4^*$ . I was particularly interested in using it to distinguish the contributions of deep water formed in the northern Atlantic from those formed in the Southern Ocean. Even before Taro and I revised Redfield's ratios, in a 1974 paper published in *Earth and Planetary Science Letters*, I proposed a new conservative tracer defined as follows:  $NO = O_2 + 9NO_3$  (Broecker, 1974). The idea was that as  $O_2$  is consumed, extra  $NO_3$  would appear



in the water. Based on Redfield's original ratios, 9 moles of O<sub>2</sub> were consumed to produce each mole of nitrate released. Because of this, at that time, my friends called me Dr. NO, after the villain in one of the early James Bond movies.



**Figure 17b** Plots of PO<sub>4</sub> versus dissolved O<sub>2</sub> for two deep ocean isopycnals (top), two thermocline isopycnals (bottom), for the warm, deep waters in the Red Sea and the cold, deep waters in the Norwegian-Greenland Sea. The table summarises the DO<sub>2</sub>/DPO<sub>4</sub> ratios obtained in this way (after Broecker *et al.*, 1985).

A decade later, when Taro and I completed our revision of Redfield's ratio, it was clear that the coefficient had to be changed. Instead of 9, it should be closer to 11. We also became aware that  $\text{NO}_3$  was not conservative. In  $\text{O}_2$  free deep waters and sediment pore waters, organisms used  $\text{NO}_3$  as an oxidant, so we switched to  $\text{PO}_4$ . Our new conservative tracer, phosphate star, was defined as follows:

$$\text{PO}_4^* = \text{PO}_4 + \text{O}_2/175 + 1.95$$

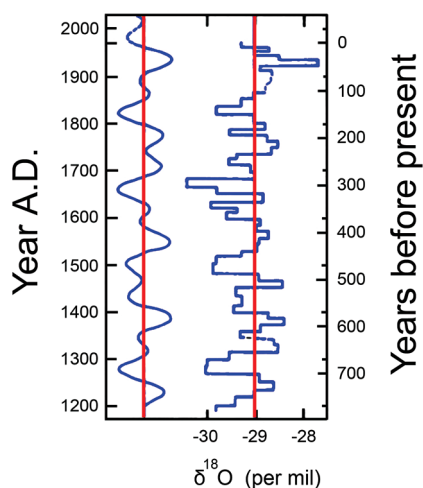
We introduced the arbitrary constant, 1.95, to bring the deep water values closer to those for  $\text{PO}_4$ . In hindsight, I wish we had not done this because it often confuses people. Based on  $\text{PO}_4^*$ , Taro and I, together with Taro's son, Tim, estimated that deep water in the Pacific and Indian Oceans consisted of nearly equal parts of deep water produced in the North Atlantic and deep water produced along the margins of Antarctica in the Weddell and Ross Seas (Broecker *et al.*, 1985).

## 18. GLOBAL WARMING

Although, during the first two decades of my scientific career, my involvement with  $\text{CO}_2$  produced by fossil fuel burning was pretty much confined to using radiocarbon measurements to constrain simple models designed to elucidate how much of it was being sucked up by the ocean, I also kept my eye out for the impacts of the  $\text{CO}_2$  that remained in the atmosphere. I was puzzled by the absence of any measurable rise in global temperature. The steady warming that had occurred prior to 1940 flattened and there was no subsequent rise. Each January, when the average Earth temperature for the previous year became available, I looked to see if there was any evidence that the stall in warming had come to an end but year after year it continued. In 1975, I decided to seek an explanation for this lack of response to rising  $\text{CO}_2$ . A publication by a Danish scientist, Willy Dansgaard caught my eye. It presented an oxygen isotope record from the first core to be drilled through Greenland's icecap (Dansgaard *et al.*, 1969). Because the ice is annually layered, with coarser crystals in summer snow than in winter snow, Dansgaard was able to generate a precise chronology. Further, changes in the  $^{18}\text{O}$  to  $^{16}\text{O}$  in the ice were thought to be mainly the result of changes in air temperature. Thus, for the first time, a detailed record of temperature fluctuations extending back thousands of years became available.

In their paper, Dansgaard and colleagues demonstrated that much of the variance in the record for the last couple of thousand years could be attributed to cycles of 80 and 180 years (Fig. 18a). I noticed that between about 1940 and 1968, when the coring was done, Dansgaard's record showed a cooling, so I extended the 80 and 180 year cycles into the future and found that the Greenland cooling trend would soon cease and a warming trend would set in. I then made a gigantic





**Figure 18a**

On the right is shown the oxygen isotope record for the last 800 years for the northern Greenland Camp Century ice core. Willy Dansgaard, who obtained this record, showed that much of the variance could be accounted for by cycles of 80 and 180 years (left). In the absence of any other temperature record of anywhere near this quality, I made the bold assumption that these cycles characterised the entire planet. How wrong I was! (after Broecker, 1975).

intellectual leap and asked myself, “What if Dansgaard’s record typifies the whole globe?” If so, could it be that a natural cooling has by chance cancelled the warming expected from increased CO<sub>2</sub>? If this were the case, then once the natural cooling cycle ended, nature would join forces with man made CO<sub>2</sub> and bring an end to the temperature plateau (Fig. 18b). Based on this, I submitted a paper to *Science* entitled “Climate Change: Are We on the Brink of a Pronounced Global Warming?” It was published on August 8, 1975 (Broecker, 1975).

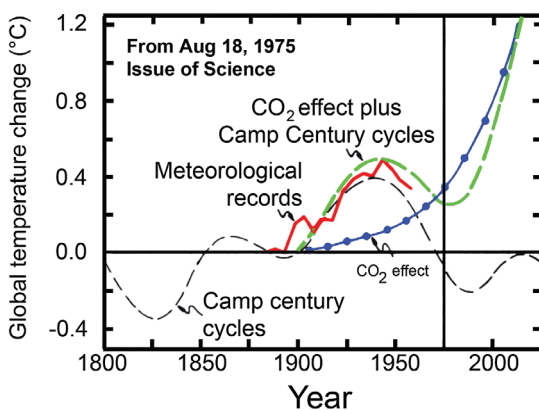
My prediction proved to be correct. One year later, in 1976, the warming resumed and has continued right up to the present but alas, since that time, many records of the quality of Dansgaard’s have been obtained. None, including those for ice cores from elsewhere in Greenland, contain significant contributions from either the 80 or the 180 year cycles. Hence, my prediction was based on the false premise that Dansgaard’s record typified the globe. In reality, it typified only the northern tip of Greenland. Three years ago in Rome, I received the Balsam Award. During the presentation ceremony and the accompa-

nying press conference, a big point was made that I was the “Father of Global Warming”. It took me a while to remember that I had used the words, “Global Warming” in the title of my 1975 *Science* paper. Apparently, I was the first to use them in the title of a refereed publication. I was sufficiently upset by this to offer a \$200 reward to anyone who could find an earlier use of the words “Global Warming” because I did not want to be remembered that way.

In August 2010, several articles appeared celebrating the 35th anniversary of my *Science* paper prediction and making a big point of my title as the “Father of Global Warming”. Each mentioned my offer of a reward. I received a number of suggestions but unfortunately, none fit the requirement that the use was in a refereed publication. The most interesting was something the late William Safire mentioned in a 2008 *New York Times* column where he discussed the word “change”. In one paragraph, Safire discussed climate change and global warming.



The first mention of global warming he could find was in a brief article published in November 1957, in the *Hammond* (Indiana) *Times*. It referred to a claim by southern California scientists (unnamed) that exhaust fumes were going to lead to global warming. Charles David Keeling spent his career at the University of California, San Diego, and in November 1957, was poised to launch his program to monitor the build up of CO<sub>2</sub> in our atmosphere, so I suspect that he was one of the unnamed scientists. Certainly, if anyone merits the title “Father of Global Warming”, it should be he, and not I, because it is his record on which our concern rests.



**Figure 18b**

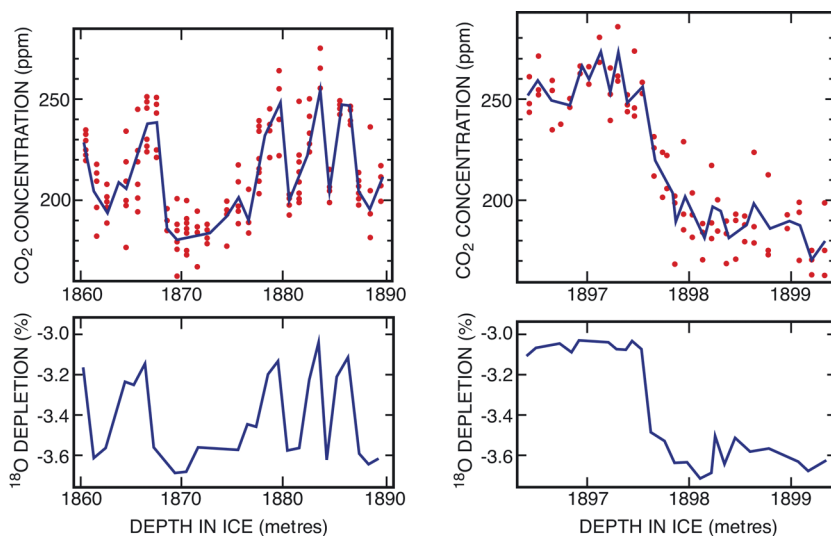
In a paper published in *Science* in the summer of 1975 (Broecker, 1975), I attributed the lack of a CO<sub>2</sub> driven warming between 1940 and the time I wrote the paper to be the result of an offset by a natural cooling associated with Dansgaard’s temperature cycles and went on to conclude that if this were so, we were on the brink of a pronounced warming. Once again, I was a lucky man because one year after my paper was published, the warming commenced and has continued until the present. However, the basis for my prediction proved to be invalid, because the 80 and 180 year temperature cycles have not been confirmed in any subsequent record, even those from elsewhere in Greenland (after Broecker, 1975).

## 19. THE CONVEYOR

If I remember correctly, it was in 1984 that I was hit by a thunderbolt that still reverberates. I was sitting in a lecture hall listening to my friend, Hans Oeschger, present the results that his group had obtained on the newly completed ice core from the Dye 3 site in southern Greenland. He showed that the oxygen isotope record reproduced all of the abrupt changes found previously in the Camp Century ice core from northern Greenland. These steep sided, repeated ups and downs had half the amplitude of the full glacial/interglacial oxygen isotope change. Spaced at millennium time intervals, rather than the 20 and 40 thousand year timing expected for orbital pacing, they were clearly a different breed of cat. Now that they had been reproduced in a second ice core, that had been taken a full length of Greenland away from the first one, they could no longer be passed off as a curiosity. They must be telling something quite new!



In his next projection, Oeschger showed CO<sub>2</sub> results obtained by his group on Dye 3 ice (Neftel *et al.*, 1985). Their preliminary measurements covered an interval including several of the abrupt <sup>18</sup>O shifts. Lo and behold, each time the <sup>18</sup>O to <sup>16</sup>O ratio underwent a sudden rise, the CO<sub>2</sub> content also sharply increased and each time the <sup>18</sup>O to <sup>16</sup>O ratio dropped, the CO<sub>2</sub> content also dropped (Fig. 19a). Just as the <sup>18</sup>O to <sup>16</sup>O shifts were half as large as the full glacial to interglacial changes, so also were the CO<sub>2</sub> changes. Based on my struggles to figure out what drove the glacial to interglacial CO<sub>2</sub> change, the speed and magnitude of these changes boggled my mind. Also, having thought hard about the uptake of fossil fuel CO<sub>2</sub> by the ocean, I realised how difficult it was to push the CO<sub>2</sub> content of the atmosphere up and down by 40 to 45 ppm on a time scale of less than a century.



**Figure 19a**

<sup>18</sup>O to <sup>16</sup>O ratios (red dots) and CO<sub>2</sub> concentrations in air (blue line) for the glacial age section of the Dye 3 Greenland ice core. In an attempt to understand the origin of the large and abrupt CO<sub>2</sub> changes shown here, I stumbled onto the idea that the turning on and off of the Atlantic Ocean's conveyor circulation was responsible for the large and abrupt temperature changes recorded in the oxygen isotope record. The elevated CO<sub>2</sub> content associated with the warm phases of the so called Dansgaard-Oeschger events proved to be artefacts of the *in situ* reaction between acids and CaCO<sub>3</sub> but I was again a lucky man. False evidence led me to a very important discovery (from Broecker, 2005, with permission from Eldigio Press).

My immediate impression was to pass off the high values as artefacts of summer melting. Much CO<sub>2</sub> would dissolve in the melt water and then be trapped when, during the following winter, the water refroze. I asked Oeschger about melt



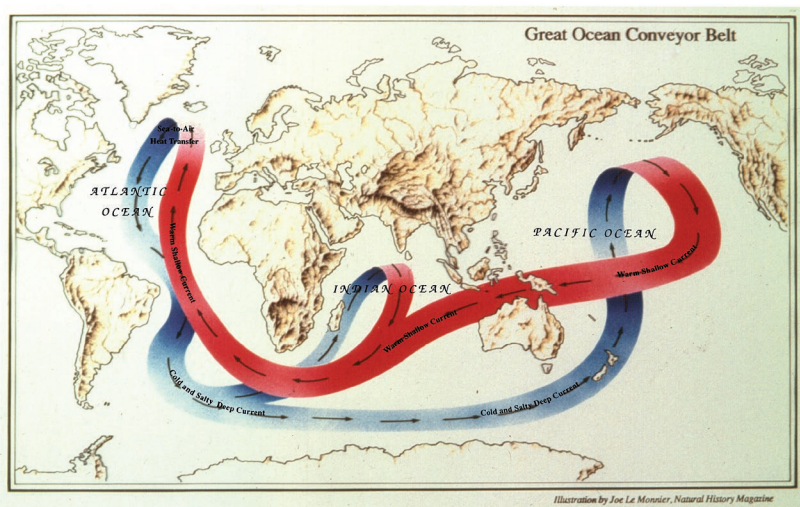


layers. He said that if melting had occurred, the refrozen layers would stand out dramatically. He assured me that no such changes could be seen and further, at those times, the summer temperatures were so far below the freezing point that no melting was to be expected. He also pointed out the consistency of the CO<sub>2</sub> measurements for these times when the air temperature was halfway between that for times of glaciation and times of interglaciation. This consistency ruled against melt layers which would have far higher CO<sub>2</sub> concentrations. I went home from that meeting, half believing that the measurements reflected the atmosphere and half believing that they were artefacts. In the days that followed, I tried to think of some mechanism by which these large and rapid CO<sub>2</sub> changes could have been made to happen. These mental struggles led me to the North Atlantic. Based on the radiocarbon measurements I had made on water samples from the Atlantic (Broecker *et al.*, 1960b) and the more complete set that Ostlund and Stuvier had produced on the GEOSECS samples, it was clear that an enormous amount of upper ocean water, that had been warmed during its northward passage through the tropics, was cooled off each winter in the northern reaches of the Atlantic. This cooling increased the water density to the point where it could sink to the abyss and commence its southward trip through the deep sea. Although this conveyor belt pattern of Atlantic circulation had been worked out during the 1930s by the German oceanographer, George Wüst, it was the <sup>14</sup>C results that allowed the amount of water moving through this loop to be quantified.

Desperate to find a way to push enough CO<sub>2</sub> in and out of the ocean to explain Oeschger's results, I considered an extreme case. What if the Atlantic's conveyor (Fig. 19b) were to be brought to a halt? As it turned out, although this idea proved to be just another CO<sub>2</sub> dead end, it proved to be a bonanza with regard to explaining Greenland's sharp temperature changes (Broecker, 2010a). As part of my CO<sub>2</sub> quest, I had calculated how much heat would be lost to the atmosphere over the northern Atlantic if the conveyor circulation were to be shut down. I estimated that the upper waters entering the region around Iceland had a temperature averaging about 10 °C and the deep water leaving this region had a temperature of about 2 °C. Hence, each cubic centimetre of deep water produced must have released about 8 calories of heat to the overlying air. When multiplied by the 16 million cubic metres per second of deep water production and the number of seconds in a year, the annual heat release associated with today's conveyor circulation turns out to be enormous. It was equal to the amount of solar heat received by the Atlantic north of 45 °N. Hence, were the current to be turned off, the atmosphere over the North Atlantic would undergo a major cooling.

Following this curious route, I got the idea that shutdowns and rejuvenations of the conveyor circulation in the Atlantic were responsible for the abrupt coolings and warmings recorded in the Greenland ice cores. It was years later that it was realised that these shutdowns would allow winter sea ice to cover the North Atlantic as far south as London. This sea ice would have entirely blocked the release to the atmosphere of ocean heat. Also, it would have reflected back to space much of the incident sunshine. The northern Atlantic and the surrounding lands would have become much like today's Siberia!





**Figure 19b**

An idealised diagram depicting the global sweep of the Great Ocean Conveyor Belt. The blue depicts the path followed by the deep water formed in the North Atlantic; and the red, the path followed by the returning upper ocean flow. This diagram was prepared for an article published in the popular *Natural History Magazine*. I never dreamed that it would become a logo for global change.

It turned out that Oeschger's colleagues soon had to admit that the large increases in  $\text{CO}_2$  associated with the sharp warmings were indeed artefacts. They showed this in two ways. First, they made detailed measurements on air trapped in Antarctic ice covering the same time interval. All the results were close to the 200 ppm value characteristic of the low  $^{18}\text{O}$  stadials in Greenland. No ice with 240 or so ppm  $\text{CO}_2$  in its air was found. Second, they carefully compared the timing of one of the sharp rises in  $\text{CO}_2$  with that for the  $^{18}\text{O}$  to  $^{16}\text{O}$  ratio. It occurred at exactly the same depth in the ice core. But because air bubbles close to the base of the firn, some 80 metres below the surface, if the  $\text{CO}_2$  rise were real, its depth in the ice core should have been offset from that of the  $^{18}\text{O}$  change.

The absence of a depth offset provided a clue regarding what might have produced the  $\text{CO}_2$  anomalies. The extra  $\text{CO}_2$  must have been generated within the ice by the interaction between  $\text{CaCO}_3$  dust and  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  acid in the ice. During times of interglaciation, the amount of acid deposited on the Greenland icecap greatly exceeded the amount of  $\text{CaCO}_3$  so all the  $\text{CaCO}_3$  dissolved in the acid and none was incorporated into the ice. During times of ultracold conditions, the amount of  $\text{CaCO}_3$  deposited on the icecap greatly exceeded the amount of acid so all of the acid was neutralised by  $\text{CaCO}_3$  and no acid was included in the ice. However, during the times of intermediate cold, the amount of  $\text{CaCO}_3$  and



acid deposited were similar so some of both were present in the ice. Subsequently, they reacted with one another releasing the  $\text{CO}_2$  bound in  $\text{CaCO}_3$  and it remained trapped in the ice.

It turned out that Antarctic ice proved to be a much better archive for the  $\text{CO}_2$  record. The reason is that Antarctica is so remote from land masses, that it receives almost no  $\text{CaCO}_3$  dust. Furthermore, while the Greenland record extends back only 110,000 years, the Antarctic record extends back 800,000 years. Therefore, just as the misleading 80 and 180 year cycles in the Camp Century ice core made me the “Father of Global Warming”, the anomalous  $\text{CO}_2$  content of Dye 3 ice led me to invent the concept of the Great Ocean Conveyor (Broecker, 2010a). Had I not been challenged to explain Oeschger’s  $\text{CO}_2$  results, I probably would not have been the first to realise what was responsible for the abrupt changes recorded in Greenland ice. Serendipity!

## 20. CRYING WOLF

In 1986, I was invited to testify before a U.S. Senate committee chaired by Al Gore. I was told that I would have five minutes but I had been warned by others who had appeared before congressional committees that after each Senator on the committee had his or her say, the time remaining for testimony by outsiders would be severely cut. This being the case, I decided to prepare something that could subsequently be published in a refereed journal. So it was that I submitted to *Nature* a paper entitled “Unpleasant Surprises in the Greenhouse”. It was accepted and published in July 1987 (Broecker, 1987a). In it, I warned that the changes in climate to be brought about by rising  $\text{CO}_2$  might well come in sudden jumps. This assessment was based on the Greenland ice core record coupled with my idea that the abrupt jumps in temperature were the result of stops and starts of the Atlantic Ocean’s conveyor circulation. I followed this up with an article entitled “The Biggest Chill” published in the October 1987 issue of *Natural History* magazine (Broecker,

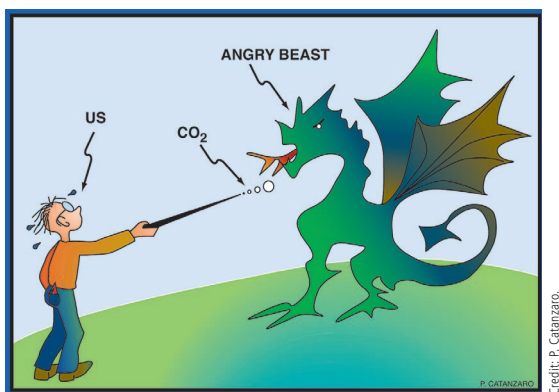
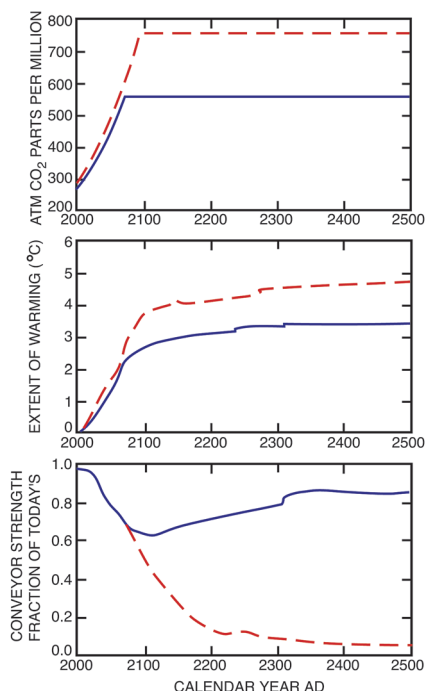


Figure 20a

Patty Catanzaro’s cartoon depicting the Angry Climate Beast, the world’s climate, being poked by the addition of fossil fuel  $\text{CO}_2$  to the atmosphere.





**Figure 20b**

Model response of the strength of the Atlantic Ocean's overturning circulation to forcing by fossil fuel CO<sub>2</sub>. A doubling of the atmosphere's CO<sub>2</sub> content, which warms the planet by a little over 3 °C, causes only a temporary sag, while a tripling, which warms the planet by about 4.5 °C, results in a near shutdown. However, rather than being abrupt as were those of the last glacial period, the change is gradual (after Stocker and Schmittner, 1997).

warming would lead to a conveyor shutdown was quite small. The only reasonable impetus for such a shutdown was a combination of an increase in water addition to the North Atlantic, by increased precipitation and increased river runoff. Model simulations suggested that a doubling of CO<sub>2</sub> would lead to only a temporary sag in conveyor strength (Fig. 20b), although in one such simulation, a quadrupling of CO<sub>2</sub> created a shutdown. However, rather than occurring suddenly, it took more than a century.

1987b). It was there that my Great Ocean Conveyor diagram first appeared. In this article, I mention that the Earth's climate system has proven itself capable of making large and sudden jumps but was careful not to warn that one might be in the offing. However, much to my dismay, the *Natural History* editor placed a sales "stimulator" on the issue's cover which stated "Europe beware; the big chill may be coming." I was much annoyed by this but nothing could be done to retract it. Unfortunately, most readers assumed that somewhere in the article, this warning had been issued.

A 1991 article entitled "The Great Ocean Conveyor" was published in the *Journal of Oceanography* (Broecker, 1991). In it, I pointed out my annoyance regarding the *Natural History* magazine "stimulator" and briefly discussed several scenarios by which the build up of CO<sub>2</sub> might either strengthen or weaken the conveyor but I must admit that in lectures on global warming, I frequently used a picture of a dragon being threatened by a boy with a sharp stick (Fig. 20a). I called the dragon "The Angry Climate Beast", and the little boy was "us", the producers of fossil fuel CO<sub>2</sub>. My point was that by adding large amounts of CO<sub>2</sub> to the atmosphere, we were poking our climate system without being sure how it would respond. As time went on, it became ever clearer that the likelihood that global



George Denton's discovery (described further below), that it was winter sea ice cover that produced the large and widespread consequences of the shutdown, greatly decreased the probability of future threats. In a warmer world, the chance that the North Atlantic would freeze over would be negligible. Rather, a shutdown would more likely only counter some of the CO<sub>2</sub> warming experienced in northern Europe. I cringe when I hear references to "tipping points", because I fear that they are an outgrowth of my warning of a possible conveyor shutdown. When asked about "tipping points", I often refer to an analogy used by my friend, Richard Alley. "It's as if a blind man is warned that he is approaching a cliff but, when queried, his informant isn't sure that the cliff exists and has no idea how far away it lies". In any case, *mea culpa*, I am guilty, I did cry wolf.

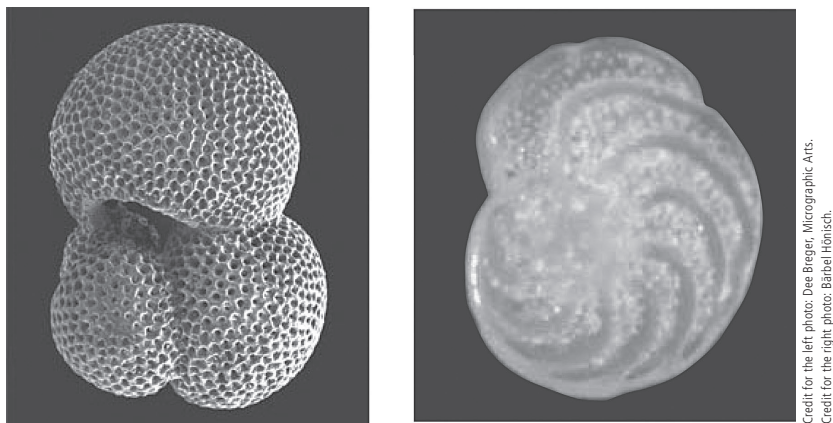
## 21. ATOM COUNTING

Throughout my career, two themes have dominated my research: one is to understand how today's oceans operate and the other is to reconstruct glacial climates. Initially these were quite separate tracks, but as time went on, it became clear that they intersected. To understand the changes in climate that occurred during the last million years, it is essential to come to grips with the reorganisations that have taken place in the ocean's mode of operation. Well before I grasped the importance of the role played by the ocean, I realised that the difference between the radiocarbon ages of coexisting benthic and planktonic foraminifera from sediment core must carry the same information as the difference between the <sup>14</sup>C to C ratio in deep and surface water and, of course, I also realised the potential of using <sup>14</sup>C measurements on coexisting shells to determine how the apparent radiocarbon age of deep water differed during glacial time.

Although an interesting concept at that time, it lay well beyond our experimental reach. To perform a <sup>14</sup>C analysis by the decay counting method required about 10 grams of CaCO<sub>3</sub> (i.e. about 1 gram of carbon). Foraminifera shells weigh between 20 and 50 micrograms each, so to get a large enough sample for radiocarbon analysis would have required picking several hundred thousand shells, which was impossible, so the idea of reconstructing deep ocean ventilation rates by this method remained a dream. Then in the early 1980s, the situation dramatically changed. Physicists at the University of Rochester demonstrated that it was possible to measure the <sup>14</sup>C atoms themselves, rather than their radio decays. The method was called accelerator mass spectrometry. Geochemists had for decades been using mass spectrometers to routinely measure the isotopic composition of the elements oxygen, carbon, strontium and lead. In these cases, the ratio of the more abundant to the less abundant isotope did not exceed a thousand (i.e. 10<sup>3</sup>). In the case of radiocarbon, the ratio of <sup>12</sup>C to <sup>14</sup>C for contemporary carbon is a staggering 10<sup>12</sup>. In an ordinary mass spectrometer, this tiny amount of <sup>14</sup>C would be swamped by its isobar <sup>14</sup>N and likely also by <sup>13</sup>CH. However, the Rochester



physicists overcame this difficulty by accelerating the carbon atoms to extremely high velocities so they were able to break up any  $^{13}\text{CH}$  strays and also to distinguish between  $^{14}\text{N}$  and  $^{14}\text{C}$  events in the collector. Further, the atom counting method had a huge advantage over the decay counting method in that only one milligram of carbon was needed for an analysis. Within a few years, this new way of measuring radiocarbon had been implemented in several laboratories. One of these was located in Zurich. With the help of my Swiss friend, Hans Oeschger, I was able to make an arrangement to have analyses done there, which opened the door to making measurements on hand picked benthic and planktonic shells (Fig. 21). Instead of 300,000 shells, we needed only 300 for each analysis (Andree *et al.*, 1986).



**Figure 21** Photos of a planktonic foraminifera shell (left) and a benthic foraminifera shell (right). The diameter of the shells picked for radiocarbon dating averages 250 micrometres. The weight of each shell averages about 30 micrograms.

I remember attending a meeting held in Zurich in 1984, where papers on this new method were presented. On the last day, a panel was convened to discuss the future of radiocarbon dating. Fears were expressed that the accelerator method would never achieve the accuracy attainable by decay counting. Proponents of this point of view felt that because of this, the labs doing decay counting would continue to operate. My view was that the decay counting labs would function only until their primary mentor retired. This is pretty much what happened. Currently, virtually all radiocarbon measurements are made by accelerator mass spectrometry. Furthermore, accuracy rivals that achieved in the best of the decay counting labs. During the late 1980s, I obtained  $^{14}\text{C}$  ages on coexisting benthic and planktonic shells from glacial age deep sea sediments (Broecker *et al.*, 1990). Surprisingly, for those from deep Pacific Ocean, there was no significant difference from today's. Because of this, I went on to other





things but as is discussed in the chapter entitled “The Mystery Interval”, a huge interest has recently developed in explaining why we did not, and still do not, see a big difference.

## 22. DIPLOMACY

After the completion of Dye 3, ice coring in Greenland stalled. Peter Wilkness, who was in command of Polar Research at the National Science Foundation, was angry that although the U.S. had paid most of the bills for the two Greenland ice cores, European scientists had reaped the giant’s share of the scientific glory. Because of this, he refused to fund further coring efforts. Lacking airplanes capable of transporting the heavy loads of equipment into Greenland’s interior, the Europeans found it difficult to continue on their own. So there were no plans for further coring.

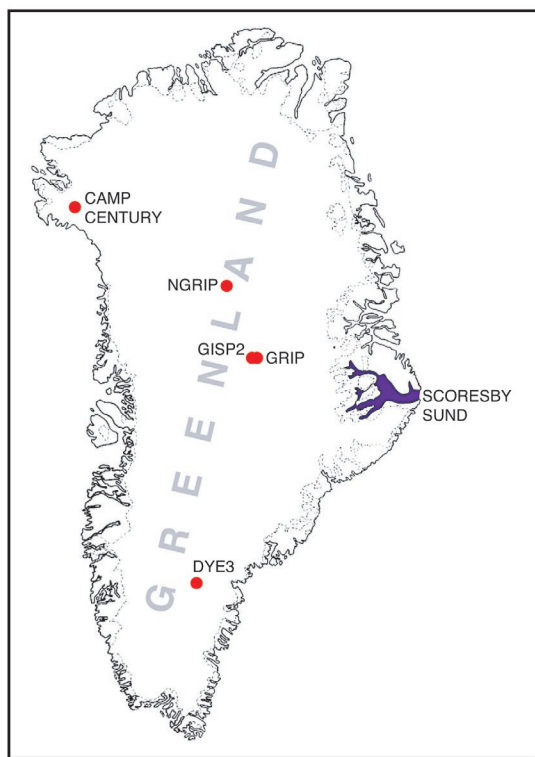
Disturbed by this impasse, I sought a way to break the jam. My idea was to bring together ice scientists from both sides of the Atlantic to create a plan that would ensure that the costs and scientific results would be equally shared. Because at that time, the Europeans had a larger number of scientists active in ice core research than we did, it would be necessary to establish an equivalent group of Americans. To this end, I arranged a weekend get together of several senior scientists from the U.S. (Minze Stuiver, Harmon Craig, Chet Langway and John Imbrie) and Europe (Willy Dansgaard, Hans Oeschger and Jean Jouzel). As a representative of the young Americans, I also invited Paul Mayewski. Our Lamont-Doherty Director, Barry Raleigh agreed to pay for the plane tickets to bring the European participants. The meeting was held at the Bostonian Hotel (in Boston) on the weekend of the Super Bowl. I remember this because my favourite team, the N.Y. Giants, was pitted against the Denver Broncos.

During the first morning, it was quickly agreed that the next core should be located at Greenland’s Summit but the discussion as to how to share the ice from a single hole bogged down. At that point, Denmark’s Willy Dansgaard, made a dramatic suggestion. There should be two holes, one paid for and drilled by a European team and the other paid for and drilled by an American team. Each group would have first call regarding the allocation of its ice. The enterprise would be a congenial one rather than a race. After quite a bit of discussion regarding this plan’s pros and cons, the Dansgaard proposal was unanimously accepted.

The American group asked Paul Mayewski to assemble a team of Americans to put together a proposal to NSF. Meanwhile, unknown to us, the American NSF was poised to put out an RFP (request for proposals) seeking three universities to jointly propose a new Greenland initiative. Only at the last minute, were we able to stop this RFP. Paul Mayewski was able to get almost all of the U.S. scientists who were interested in the ice record to join in the submission of one



proposal. Left with no other option, the NSF had to fund the Mayewski *et al.* proposal. The rest is history. The GISP II and GRIP cores (Fig. 22) were drilled 30 km apart and the measurements made on them led to a giant leap forward for palaeoclimate research (Johnsen *et al.*, 1992). Dansgaard's plan paid off handsomely. The extremely detailed electrical conductivity logs for the two cores were identical in every respect. The exception was the lowest 200 metres, where they were entirely different. These differences were shown to be the result of shearing and folding induced as the ice moved over the rough underlying topography. Although the European team was the first to reach bed rock, the agreement of congeniality was adhered to. The scientific credit was equally divided. While not being known as much of a diplomat, I am proud that I was able to bring together the two groups at the Bostonian Hotel. As a bonus, the N. Y. Giants won the Super Bowl.



**Figure 22**

Location of the GISP2 and GRIP Greenland ice cores. Also shown is the location of the Camp Century and Dye 3 ice cores and of Scoresby Sund. More details about Scoresby Sund are provided in the section entitled "Gary Comer."



## 23. THE CULT

In the late 1980s, I learned through newspaper articles, that a large, airtight enclosure was being constructed outside Tucson, Arizona. Its purpose was to house eight “Biospherians” who would be self sufficient, in a closed system, for a period of two years. They would grow their own food and dispose of their wastes. There would be no imports or exports of any material. I puzzled as to how the composition of the air in this enclosure would be managed. Plants produce  $O_2$  and consume  $CO_2$ . Bacteria in the soil consume  $O_2$  and release  $CO_2$ . Unless some means of maintaining a balance existed, there was certainly the possibility that the bacteria would out compete the plants and the Biospherians’ limited  $O_2$  supply would steadily shrink. I asked my sister who lives in Tucson whether she could find any more details. She could not. A year or so later, in September 1989, accompanied by considerable hoopla, Biosphere 2 (Fig. 23) was sealed. After that I heard little. Of course, there were rumours that the Biospherians snuck out at night for hamburgers and a report that one of them had cut off the end of her finger and had to be taken to the hospital for repairs. Then, in May 1990, eight months after the experiment began, I got a phone call from Jack Corliss, a geochemist I had brushed shoulders with. He said that John Allen, who was the leader of the group responsible for Biosphere 2, would be coming to New York and would like to meet with me so it was arranged that we three would have dinner together at the Santa Fe Restaurant near New York City’s Lincoln Center.

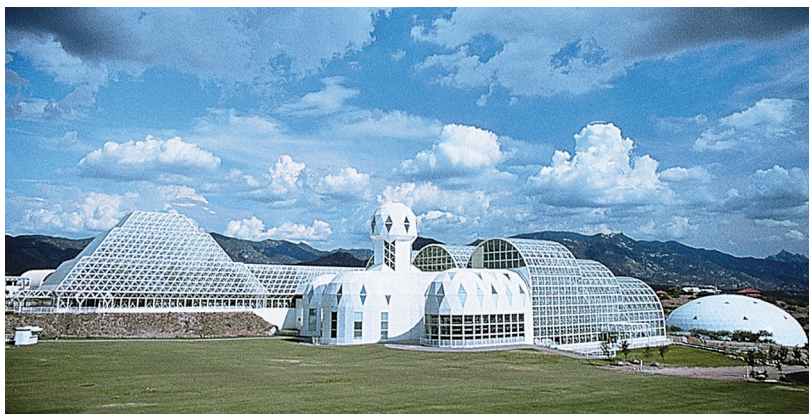


Photo credit: CDO Ranching and Development, L.P.

**Figure 23**

Biosphere 2, an airtight structure designed to house eight people for periods of two years. The colony was to be self sufficient, growing food and disposing of wastes. In 1993, Columbia University took over this facility and used it to study the impacts of elevated  $CO_2$  on planet growth and coral calcification. One of the two “lungs” which maintained a balance between the air pressure inside and that outside is shown to the far right.



I will remember the meeting. Allen had the appearance of an aging Indiana Jones. After our drinks arrived, he pulled out a piece of paper but before showing it to me, he pulled his chair closer to mine. He then held the paper out in such a way that no one else could see it. Then he said in a hushed voice, "This is a graph of the  $O_2$  content of Biosphere 2 air versus time. As you can see, it's steadily declining." I could see that it had reached about 18.5% (the atmosphere has 21%). Having already thought about it, I said, "Clearly the soil bacteria are consuming  $O_2$  faster than the plants are producing it." Allen replied, "but, if that were the case, why hasn't the  $CO_2$  content shot way up?" I did a quick calculation and agreed that it should be up to about 25,000 ppm (70 times that of the atmosphere outside). Allen responded, "But, it's never gone higher than 6,000 ppm." I was stunned and had to admit that this was indeed an intriguing geochemical mystery.

It turned out that I was scheduled to attend a meeting at the University of Arizona in Tucson the following week so I offered to have a look around to see if I could come up with any useful suggestions. On my arrival at Biosphere 2, I was astounded. The site itself was one of the most beautiful pieces of desert landscape I had come across and the glass structure that housed the Biospherians was an ideal match. In addition to the living quarters and a section for agriculture, it had a rain forest, a coral lagoon and a desert (referred to by Allen as biomes). Of course, I could not go inside but I could see quite a bit through the glass (and also in pictures in Allen's office). I spoke face to face (through the glass) with two of the Biospherians. They looked a bit worse for the wear but appeared to be in good spirits. John Allen turned me over to Bill Dempster, the chief engineer. While the other members of Allen's cult that I met during my visit appeared to be highly secretive and a bit scary, Dempster was friendly and open. He proved to be very helpful in sorting out the  $O_2$  mystery. He described to me how the two external "lungs" were able to maintain a precise balance between air pressure inside and outside the Biosphere. He took me to a tunnel beneath the Biosphere where he could perform tests to see whether leaks had developed in the welded stainless steel shell designed to prevent any transfer of air or ground water from beneath the structure. He also explained that during the lower light, winter months, the Biospherians pulled  $CO_2$  out of the air into sodium hydroxide but hastened to add that the amount recovered was quite small and could by no means be the answer to the  $CO_2$  mystery.

We agreed that we would work together to find a solution. It was also decided that no money would change hands. Except for onsite meals and lodging, I would cover all my own expenses. This arrangement was made because I refused to sign a release filled with threats about if I were to divulge any of their secrets. I said a gentleman's hand shake was adequate. They grumbled but dropped the subject when it became clear that otherwise they would not get any help from me. That summer, Jeff Severinghaus, a new graduate student, arrived at Lamont. I asked him whether he would help me try to figure out why  $CO_2$  was not building up in Biosphere 2. I assured him that it would be a separate "Saturday afternoon project", and would have nothing to do with his thesis research. Jeff agreed but



some months went by without any breakthrough. We did learn that the agricultural soils were loaded top to bottom with organic matter. While the organic matter in most natural soils is confined mainly to the upper 10 or 20 centimetres, in Biosphere 2's agricultural biome, it extended down the full 100 cm and indeed, bacteria were hard at work trying to consume it. O<sub>2</sub> measurements in air from the soil pores showed that it reached zero at the base of the soil! This confirmed our suspicion that the soil bacteria were out competing the above ground plants but where had the CO<sub>2</sub> gone?

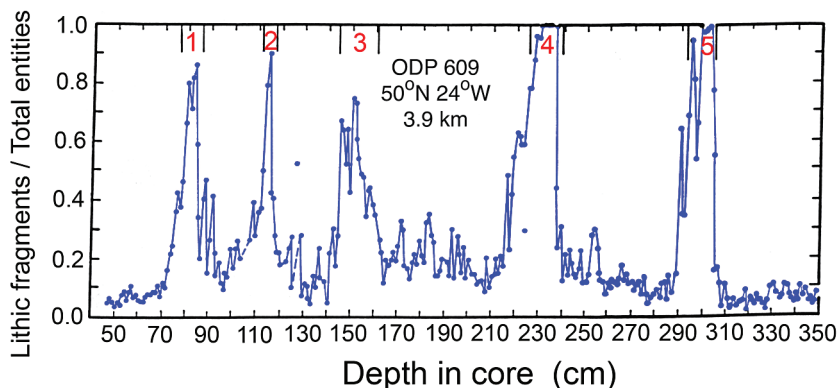
Thanks to a suggestion by Jeff's father, a high altitude physiologist at the University of California, San Francisco, we found the answer. "What about the concrete?" he asked. It turns out that the key ingredient in concrete is lime. The lime is produced from limestone by heating it to the point where the CO<sub>2</sub> is driven from the CaCO<sub>3</sub> leaving behind CaO. When mixed with water and aggregate and allowed to dry, the result is concrete (Severinghaus *et al.*, 1994). Concrete gradually takes up CO<sub>2</sub> from the air and in this way, it slowly converts back to limestone. Following Severinghaus Senior's suggestion, Jeff took plugs of concrete from the outside of Biosphere 2 and the Biospherians exported plugs from the inside. Using a pH indicator, Jeff was able to determine how far into the concrete the conversion back to limestone had progressed. He found that it was between one and two millimetres for plugs from the outside and between one and two centimetres for plugs from the inside. We reasoned that the difference reflected some combination of the higher CO<sub>2</sub> content and higher humidity inside Biosphere 2 but the important lesson was that there was an enormous area of concrete in Biosphere 2. It had a basement where all the mechanical equipment was located. The cement floor above the basement supported the soils of the various biomes. When Jeff multiplied the area of the concrete by the amount of CO<sub>2</sub> it had taken up, it turned out that the concrete nicely accounted for the missing CO<sub>2</sub>. Mission accomplished!

Of course, the O<sub>2</sub> continued to decrease. It got to the point where the eight Biospherians were gasping for breath and had difficulty climbing stairs. Something had to be done. Finally, John Allen agreed to add O<sub>2</sub>. A tank truck arrived. The door at the end of the tunnel connected to one of the lungs was sealed. Air was let out of the lung and replaced by O<sub>2</sub> from the tank truck. The door was opened and the panting Biospherians entered the lung. A few breaths of O<sub>2</sub> enriched air later, they were able to do summersaults! However, the story does not end here. In April 1, 1991, the county sheriff moved in and told the Allen group to leave. It turns out that the site was owned by Ed Bass, the son of a very wealthy Texas oil man. Bass had financed the construction of Biosphere 2 and its associated buildings and was footing the bill for the operational costs. Apparently Bass' managers convinced him that his money was being misused, so he agreed to pull the plug. A year and a half later, Columbia University took over the management of the site and I was once again involved (Broecker, 1996). This time, it was to try to convert Bass' glass house into a research facility dedicated to the study of the impacts of the ongoing build up of fossil fuel CO<sub>2</sub> on plant growth and coral calcification. That story comes later.



## 24. ARMADAS OF ICEBERGS

In 1988, I came across a journal article that caught my interest. It was authored by Hartmut Heinrich, a German scientist working in Hamburg (Heinrich, 1988). The article focused on six layers of detrital material in the glacial section of a sediment core from the north eastern Atlantic. Although the sediment surrounding these layers was typical of the deep sea, i.e. fine grained mud with abundant foraminifera shells, the six layers were rich in rock debris and nearly free of foraminifera (Fig. 24a). Heinrich concluded that the only way to form such a layer was to melt icebergs in the overlying surface water. Based on a comparison between potassium argon age of the rock debris and those for various terrains surrounding the North Atlantic, he concluded that the source of the icebergs must have been Canada's Hudson Bay region. If so, some of the icebergs must have drifted the width of the North Atlantic before melting above the site of Heinrich's core.



**Figure 24a** Ratio of the number of lithic grains to the number of foraminifera shells as a function of depth in Core 609 from the north eastern Atlantic Ocean. Five Heinrich layers, that are dominated by lithic fragments dropped from melting icebergs, stand out (after Bond *et al.*, 1992).

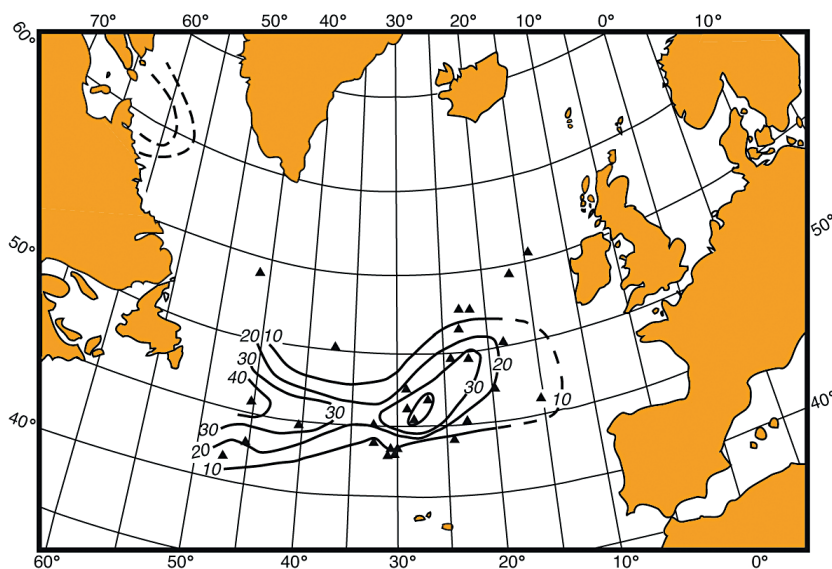
It was the timing of these events that puzzled me. Their ~7,000 year spacing did not match that of the steep sided millennial events nor the 20,000 year orbital cycles. Further, they had no obvious expression in the Greenland ice core record. I could not raise any interest among my fellow palaeoceanographers in Heinrich's layers of detritus but I could not get them out of my mind. I felt that Heinrich had stumbled onto something very important – but what?





Sometime later, Gerard Bond, a Lamont colleague, stopped in my office with a copy of a research proposal he planned to submit and asked for my opinion regarding its merit. A few days later, I got around to reading it. The thrust was a novel approach for documenting the periodicities associated with the Earth's orbital cycles in ancient sedimentary sequences. As an illustration of the method, Gerard had applied it to the record in a well dated Pleistocene marine sediment core that had been recovered from the north eastern Atlantic as part of the Ocean Drilling Program (ODP). The proposal included photographs of the core. I noted that several distinct narrow white bands stood out from the otherwise buff coloured sediment.

I ran over to Bond's office and pointed out the layers. "This core must record Heinrich events." Until that time, Bond had never dabbled in palaeoceanography so he had no idea what I was talking about. I explained what Heinrich had found and asked where the core was stored. "Right here at Lamont." Off we went to what was called the ODP archive and asked the technician to pull out the upper part of Core 609. We took a small sample from one of the white layers and sure enough, it was rich in mineral fragments and poor in foraminifera shells. We carefully analysed what we assumed to be the glacial section of the core and came up with a record identical to Heinrich's (Fig. 24b; Bond *et al.*, 1992). So it was that the discovery by a German graduate student became a big, big thing. Dozens of papers have been written about these layers and the global impacts associated with them.



**Figure 24b**

Contours showing the thicknesses of Heinrich Layer #4 based on measurements on cores from the sites indicated by the triangles (after Hemming, 2004).



It turns out that based on his single sediment core, young Heinrich had gotten the story just about right. Subsequent records from many other cores from the North Atlantic showed that the debris from these ice armadas forms a belt centred at 40 °N extending from North America to Europe. Consistent with a Canadian origin, the thickness of each of these layers diminishes from west to east. The  $^{18}\text{O}$  to  $^{16}\text{O}$  ratio in the sparse foram shells from within the layers attests to the addition of fresh water introduced by the melting of the icebergs as they drifted across the Atlantic. The isotopic composition of elemental lead in the detrital feldspars indicated that these grains originated in the Archean terrain to the north and west of Hudson Bay. Four of the six layers have exceedingly sharp bases indicating that deposition began abruptly. Measurements of  $^{230}\text{Th}$  in the layers show that they were deposited at a much higher rate than the surrounding sediment. This demonstrated that the scarcity of foraminifera reflects their dilution with rapidly deposited debris rather than a reduction in their production by the foraminifera in the overlying surface water.

A number of scenarios have been put forth regarding the mechanism responsible for the launch of these ice armadas. While to date, no agreement has been achieved, my favourite is that suggested by the University of Chicago's Doug McHale. He termed it the binge-purge hypothesis. Simply put, during the binge phase, ice built up over Hudson Bay and trapped heat diffusing up from the Earth below. After several thousand years, this trickle of geothermal energy raised the temperature at the base of the growing icecap to its melting point. The melt water lubricated the base of the ice initiating the purge phase, allowing the ice to slide through Hudson Strait, into the sea.

A puzzle remaining to be solved was why the geographic pattern of climate impacts induced by Heinrich's ice armadas was quite different from that of the more numerous steep sided millennial events. The fresh water lid produced by the melting of the armada of icebergs would have brought the conveyor circulation to a halt and allowed winter sea ice to form over the North Atlantic so one might conclude that the impacts of the six Heinrich events would be similar to those of the 16 or so sudden coolings which punctuate the glacial section of the Greenland record. However, global maps of these two sets of impacts look quite different. A couple of examples make the point. A record kept in rapidly deposited sediment in the Santa Barbara Basin off the coast of California beautifully replicates the record from Greenland's ice. As is the case for the Greenland ice, no imprint of Heinrich events is to be seen. At the other extreme, is the record from Antarctic ice. It has muted features related to the Heinrich events but no hint of the steep sided millennial events. Similarly, a record in continental margin sediments in the Atlantic Ocean off Brazil contains evidence for pronounced increases in river runoff at the times of Heinrich events but there is no evidence of impacts associated with the steep sided millennial events. There are, however, records that show both. One of these is in the Indian Ocean off Pakistan. At the time of each Heinrich event, there is a reduction in the sedimentation of organic matter



to the seafloor, suggesting a reduction in the strength of upwelling, which would supply nutrients to marine plankton. The largest reductions are seen at the times of the six Heinrich events and smaller ones are observed at the times of the 16 steep sided millennial events.

Unfortunately, Hartmut Heinrich has not been able to directly participate in this follow up research. After receiving his PhD degree, he was employed by the German Hydrographic Service and spends his energy trying to sort out the numerous anthropogenic environmental problems experienced by the Baltic Sea. I do, however, see him from time to time. Last time, he told me that while attending a scientific meeting, someone had looked at his name badge and said “My, my, you have the same name as the man who discovered Heinrich events.” Hartmut blushed and responded, “I am that man.” He also told me that his 16 year old daughter looked forward to pursuing graduate studies at Lamont. So my hunch that the layers of detritus described by Hartmut Heinrich had something important to tell us was correct. In a later chapter on global rainfall, I return to them.

## 25. OCEAN ACIDIFICATION

In 1994, Columbia University signed a contract with Ed Bass to take over the operation of Biosphere 2. Michael Crow, our Vice Provost, who carried out the negotiations, put in place two key programs. One was a semester long education program for college students. Debbie Colodner, a research scientist in Lamont-Doherty’s geochemistry group, offered to take charge of its development. Because I had advised Biosphere 2’s interim management group on possible scientific research projects, I offered to continue in this role.

It certainly was a great opportunity and a number of Lamont scientists worked very hard to make something of it. Although in the end we failed, along the way we were able to do some important things. Our students, who spent a semester there, gave the education program very high grades. A few even said that it ranked as their best Columbia semester. By elevating the CO<sub>2</sub> level in the rain forest biome, important things were learned about the short term photosynthetic response of its various plants. Toward the end, experiments were conducted at lower CO<sub>2</sub> concentrations. The interest was to replicate glacial conditions when the atmosphere’s CO<sub>2</sub> content had fallen to 190 parts per million. Unfortunately, the affiliation ended before these experiments could be completed.

My interest and that of Lamont colleagues, Taro Takahashi and Chris Langdon, was to use Biosphere 2’s coral lagoon (Fig. 25a) to assess the impact of acidification that would occur as fossil fuel CO<sub>2</sub> built up in the surface ocean, shifting the distribution of carbonate species and driving down its CO<sub>3</sub><sup>2-</sup> concentration. Our plan was to manipulate the coral lagoon’s carbonate ion



concentration. The objective was to determine how the rate of calcification for the aggregate of algae and coral in the lagoon changed with the extent of supersaturation with respect to aragonite (the mineral form of the  $\text{CaCO}_3$  precipitated in coral lagoons). By daily additions of either HCl or NaOH, the carbonate ion concentration in Biosphere 2's tiny ocean could be maintained at any desired level. Further, through precise measurements of  $\text{Pco}_2$  and  $\Sigma\text{CO}_2$ , the amount of  $\text{CaCO}_3$  produced each day could be determined and correlated with the amount of soft tissue produced. Chris and Taro found that going from carbonate ion concentrations of 125 to 425 micromoles per litre (corresponding to an atmospheric  $\text{CO}_2$  range from 110 to 800 ppm), there was an eight fold decrease in calcification rate (Fig. 25b) but no measureable change in the rate of photosynthesis (Broecker *et al.*, 2001a). As an indication that Biosphere 2's little ocean was replicating the real world, Chris and I showed that the dependence of calcification rates on carbonate ion concentration satisfactorily matched that found by Taro and me thirty years earlier on the Bahama Banks (Broecker *et al.*, 2001a).



Photo credit: CDO Ranching and Development, L.P.

**Figure 25a**

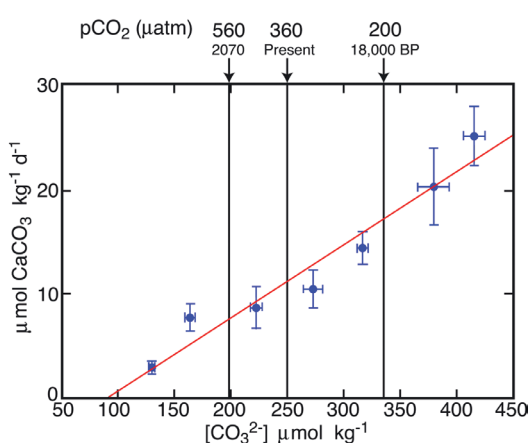
Biosphere 2's coral lagoon. Through daily additions of either acid or base, the carbonate ion concentration of the water would be maintained at any desired level. Further, precise measurements of the  $\text{Pco}_2$  and  $\Sigma\text{CO}_2$  in the water allowed the daily amount of calcification and net photosynthesis to be determined.

Pleased by our success, we submitted a proposal to the National Science Foundation to support a continuation of this research. In addition to the whole lagoon studies, Chris Langdon planned to measure the carbonate ion dependence



of the growth rate of small corallites shipped to him from Hawaii by Marlin Atkinson. His approach was to make highly precise measurements of their increase in length. Our hopes that this proposal would be funded were dashed when it was soundly rejected. One reviewer declared categorically that Biosphere 2's lagoon was in no way representative of the real world and graded the proposal as "poor", a devastating mark for any NSF proposal. Chris' proposal was, in my estimation, about as solid as any we could generate so its rejection played a big role in my decision that our uphill battle to raise the government contract funds we needed if we were to make proper use of this wonderful facility, was futile. The checkered reputation achieved by the cult hung over us like an albatross.

So in the end, it was a lack of funding that did us in. Columbia's very high tuition put our educational program beyond the grasp of most students and our inability to supplement the funds made available by Ed Bass and by Columbia, with government grants, doomed our research mission. This is unfortunate, because this \$200 million, beautifully engineered structure had much to offer as the world grapples with evaluating the coming impacts of what the late Roger Revelle referred to as a man's greatest geophysical experiment.



**Figure 25b**

Through chemical manipulation, the dependence of the rate of calcification in the Biosphere 2 coral lagoon on carbonate ion concentration, and hence also CO<sub>2</sub> partial pressure, could be quantified. As can be seen, the difference in calcification rate between an atmospheric CO<sub>2</sub> partial pressure equal to that of glacial time (i.e. 200 μatm) and that expected by the end of this century (i.e. 560 μatm) is a bit more than a factor of two (figure by Taro Takahashi).

## 26. ROCK VARNISH

In 1995, during a field trip to Death Valley, I encountered Tanzhou Liu, a graduate student at Arizona State University. His specialty was rock varnish. While I had heard of these coatings, I had never given them more than passing attention. T.L.,



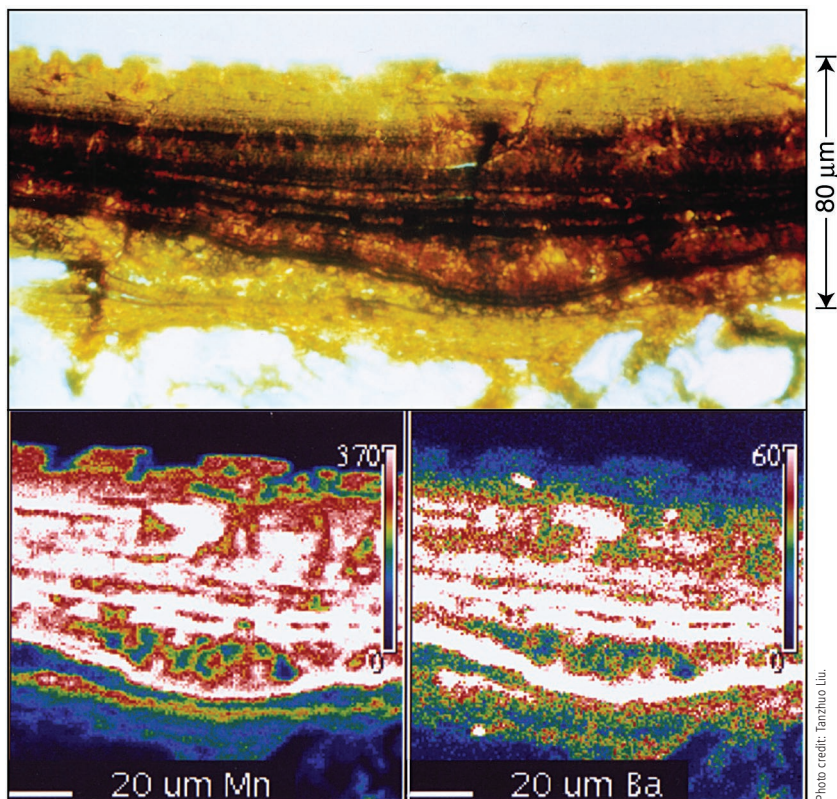
as I came to know him, made sure that my state of ignorance did not persist. He not only showed me varnished rocks, but also blowups, in colour, of thin sections he had made. They were spectacular. Each section was capped by a yellow band that was underlain by a series of orange and black stripes. He explained that the colour reflected the manganese content of the varnish (ranging from low in the yellow to high in the black). He further explained that the yellow layer had formed during the Holocene and the orange and black striped varnish had formed during the last glacial period. He even had one blow up where the layers extended all the way back to the time of the last interglacial period, as indicated by the return to yellow colour. During the Holocene, rainfall was much lower than during glacial time, so T.L. attributed the colour to the amount of rainfall.

T.L. told me that two ways existed to determine the time when varnish accumulation began. One was to recover carbon trapped between the outermost mineral grains in the host rock and the other was to use cosmogenic dating to determine when the host rock was first exposed on an alluvial fan, a lake shoreline or a glacial moraine. All of this fascinated me. In addition to its possible use as a palaeomoisture recorder, the geochemistry of varnish needed to be explored. So I asked T.L. what his plans were. He said that he was about to defend his thesis and would like to continue his research on varnish as a post doc. So, I told him to hold off accepting any jobs until I had a chance to see if I could wrestle up some money for a position at Lamont. He agreed and a week later, thanks to the foresight of Columbia's vice provost, Michael Crow, I was able to come up with one year's salary.

So it was that T.L. and I joined forces to learn more about rock varnish. He handled the geological aspects and I twisted the arms of friends in geochemistry to make analyses that would provide clues about how varnish formed. At the American Museum of Natural History, we got element microprobe scans which not only confirmed that the manganese content of the varnish varied with the colour but also that the concentration of barium underwent even larger variations, matching those of manganese (Fig. 26). At Harvard University, we obtained trace element analyses that showed that all the large lithophile elements were highly enriched over the rock forming elements: calcium, magnesium and silicon. Of particular interest, were thorium and uranium which, although highly enriched, retained the 4 to 1 ratio characteristic of igneous rocks. This came as a surprise because the behaviour of these two elements in aqueous systems is totally different; thorium is very insoluble and uranium is quite soluble. As a bonus, we found that the outermost few micrometres of the varnish were highly enriched in the elements lead and copper. So large are these excesses over the ambient Holocene concentrations, that they must be anthropogenic in origin. One possibility is that they reflect emissions from smelters.







**Figure 26**

Photograph of light that passed through a 5  $\mu\text{m}$  thick thin section of rock varnish from California's Mohave Desert. The upper yellow band is low manganese content varnish formed during the dry Holocene. The lower yellow band is varnish formed during the latter part of the dry Eemian interglacial period. The orange and black striped middle portion consists of intermediate to high manganese content varnish formed during the moderately wet last glacial period (~70 to ~10 thousand years ago). Below are electron microprobe maps over a portion of this section. The one on the left shows the manganese content and the one on the right, the barium content. The highest concentrations are shown in white, intermediate concentrations in red, and low concentrations in blue. The white bars give the scale in micrometres (i.e.  $\mu\text{m}$ ).

This finding led us to look for the presence of excesses of  $^{210}\text{Pb}$ . This isotope is produced in the atmosphere by the decay of radon. It is incorporated into aerosols and purged from the atmosphere by rain. With help from Willard Moore at the University of South Carolina, we documented that indeed, the outer portion of varnish contained a large excess of  $^{210}\text{Pb}$ . This led us to look for  $^7\text{Be}$  in varnish. The advantage of this cosmogenic isotope was that it has only a 57 day half life.

Hence, we could learn things from it that were not possible with the 22 year half life of  $^{210}\text{Pb}$ . Working together with Biosphere 2's Chief Engineer, Allen Wright, T.L. installed varnished rocks he had collected elsewhere in Arizona in a fenced in area on the mesa adjacent to the glass dome. Half of the rocks were equipped with shields that were automatically put in place when it rained and then retracted when the rain stopped. The other half had no shields. We then left them there for 6 months, a time long enough for most of the  $^7\text{Be}$  initially present on the varnish to decay away and a new batch to be emplaced. What we found was that the shielded rocks accumulated half the amount of  $^7\text{Be}$  as the unshielded ones. This suggested that the varnish gained material not only from rain but also from aerosols or dew (Moore *et al.*, 2001).

During the period that these geochemical measurements were being conducted, T.L. was comparing varnish from a number of other sites in the Great Basin. He was pleased to find the same sequence of orange and black layers at each locality. This demonstrated that the climate changes that produced the varnish stratigraphy were the same over the width of the Great Basin. Further, because the varnish rocks represented a variety of lithologies, it demonstrated that its constituents came from the atmosphere and not from the host rock.

Unfortunately, our progress came to a halt when it was shown that it was not possible to obtain radiocarbon dates on carbon from beneath the varnish. There is no carbon in the mineral interstices. This finding tarnished varnish research and led to a nonrenewal of T.L.'s Department of Energy research grant even though he had not been involved in the radiocarbon dating scandal. Because he was supported on "soft" (i.e. grant) money, he was forced to leave Lamont but thankfully, the story did not end there. Some years later, T.L. was reemployed at Lamont to work with the borehole logging group. Although his week days are taken with his new job, many of his weekend and vacation days are devoted to his first love, rock varnish. The application of exposure dating, employing the in situ production of  $^{10}\text{Be}$ , provided him with a number of well dated rocks. Slowly his efforts are paying off (Liu and Broecker, 2008). The papers he published are gaining attention and researchers elsewhere are joining his quest!

## 27. CALCITE DISSOLUTION

An alternate to my 1982 hypothesis about the driver for the atmosphere's  $\text{CO}_2$  content reduction during glacial time was proposed by Wolf Berger, a scientist at Scripps Oceanographic Institution (Berger, 1982). His hypothesis also involved carbon storage in the shallow parts of the ocean but there was a major difference. While I proposed storage in organic matter, he proposed storage of  $\text{CaCO}_3$ . His became known as the coral reef hypothesis. The formation of  $\text{CaCO}_3$ , from waters where  $\text{HCO}_3^-$  dominates the inorganic carbon species, releases protons. This increases the concentration of  $\text{H}_2\text{CO}_3$ , thus releasing  $\text{CO}_2$ . In other words,



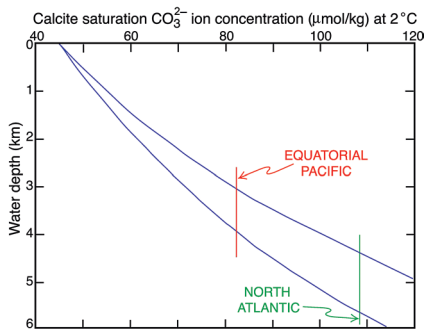
the removal of  $\text{CO}_3^{2-}$  upsets the balance among the three species that make up the ocean's  $\Sigma\text{CO}_2$  (i.e.  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ). At chemical equilibrium, the concentrations of these three must satisfy the relationship:

$$K = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}] [\text{CO}_2]}$$

Because the concentration of bicarbonate ion in seawater is much greater than that of the other two species, to a close approximation, the concentration product of  $[\text{CO}_3^{2-}]$  and  $[\text{CO}_2]$  remains constant. Hence, if the concentration of carbonate ion is decreased by incorporation into  $\text{CaCO}_3$ , then in order to reestablish chemical equilibrium, the concentration of  $\text{CO}_2$  must increase.

Berger realised that deposition on shallow banks was important only during times of interglaciation, when the sea flooded the world's vast system of continental shelves so during these times, the  $\text{CO}_2$  content of ocean water, and hence of the atmosphere as well, would rise. Then, when the sea level dropped during the next glacial cycle, this shallow water  $\text{CaCO}_3$  would be eroded back into the sea, where it would dissolve. Just as the formation of  $\text{CaCO}_3$  from seawater raises the  $\text{CO}_2$  content, its dissolution lowers its  $\text{CO}_2$  content.

Akin to my nutrient hypothesis, which made a prediction about changes in the difference between the  $^{13}\text{C}$  to  $^{12}\text{C}$  ratio for planktonic and benthic foraminifera, Berger's hypothesis made the prediction that the so called  $\text{CaCO}_3$  compensation depth would be substantially deeper during times of glaciation than during times of interglaciation. The reason is that the concentration of carbonate ion would be higher during times of glaciation ( $\text{CO}_2$  decreases so  $\text{CO}_3^{2-}$  increases). To understand the term "compensation depth", one has to be aware that the solubility of calcite (the mineral form of  $\text{CaCO}_3$  in foraminifer shells) increases with pressure and hence with water depth (Fig. 27a). Although the upper ocean waters are supersaturated with respect to calcite, because of the pressure dependence of calcite's solubility, the deepest waters everywhere in the ocean are undersaturated with respect to calcite. The depth at which the crossover from saturation to undersaturation occurs depends on both the calcium and carbonate ion content. So, if the carbonate ion



**Figure 27a**

The solubility of the mineral calcite increases with pressure, i.e. with water depth in the ocean. Although the solubility in surface water is well established, the increase with water depth is less certain. Hence only upper and lower bounds are shown. Depths of the transition between supersaturated and undersaturated water with respect to calcite in the northern Atlantic and in the equatorial Pacific are indicated.



content increased during times of glaciation, the crossover from saturated to undersaturated water must have shifted deeper. This shift would be reflected in the sediment composition because the deeper one goes below the crossover depth, the greater the degree to which the calcite is eaten away by dissolution. At very great depth in today's Pacific Ocean, the calcite is entirely consumed. For convenience, the compensation depth is defined as the depth at which dissolution decreases the normally very high  $\text{CaCO}_3$  content of the sediment to only 20%.

Thus, the way to test Berger's hypothesis was to determine whether the sections of sediment cores deposited during glacial time suffered less intense dissolution than their interglacial sections. Early on, these tests were based on measurements of  $\text{CaCO}_3$  content. If Berger was correct, the idea was that as a result of the deepening of the boundary, glacial age sediment would have a higher  $\text{CaCO}_3$  content than that of Holocene sediment. However, the use of  $\text{CaCO}_3$  content for this purpose is tricky because the quantity also depends on the ratio of delivery of calcite to the sea floor on the one hand and the delivery of silicate debris on the other. However, it was adequate to test Berger's hypothesis. The reason is that if the entire 90 ppm swing in atmospheric  $\text{CO}_2$  content was to be attributed to shallow water  $\text{CaCO}_3$  deposition during glacial periods (coupled with erosion during interglacial times), then the boundary would have been a huge 2 km deeper during the glacial than during the interglacial periods. Such a large change would stand out as dramatic in the  $\text{CaCO}_3$  record. However, because it does not, Berger's  $\text{CaCO}_3$  hypothesis soon was forgotten. We can remember that David Archer made the case that no single process could be responsible for the 30% drop in atmospheric  $\text{CO}_2$  content during the glacial period. Rather, it was likely the result of contributions by several processes. If so, then each potential contributor has to be closely examined. By how much did the surface ocean cool? By how much did the strength of the ocean's biological pump increase? By how much did the concentration of carbonate ion in the deep sea rise?

During the 1990s, I devoted a lot of effort to finding a reliable way to reconstruct the changes in the carbonate ion concentration that the deep ocean experienced over the course of the last glacial cycle. Such a proxy would have a number of applications, so it was a worthwhile quest. Over a period of years, with the help of Elizabeth Clark, I looked into three possible proxies. As it turned out, none of the three panned out. The first attempt involved the isotopes of the element boron. It began when I took on Gary Hemming as a post doc. During the course of his PhD research, Gary had shown that the ratio of  $^{11}\text{Be}$  to  $^{10}\text{Be}$  in marine  $\text{CaCO}_3$  depended on the pH of the water in which they grew. Assuming that the  $\Sigma\text{CO}_2$  content of seawater did not change very much over the course of the last glacial cycle, one could calculate the partial pressure of  $\text{CO}_2$  and the concentration of carbonate ion from the reconstructed pH. One of my graduate students, Abhijit Sanyal, decided to work under Gary's supervision to see if he could obtain palaeo  $\text{CO}_2$  partial pressures for glacial age surface water that would be consistent with that reconstructed from measurements on ice cores. He determined the ratio of boron isotopes in planktonic foraminifera shells from a core from the Atlantic and a core from the Pacific Oceans. He was excited to



find that both yielded a Holocene glacial pH difference consistent with a 30% lower CO<sub>2</sub> content in the glacial atmosphere. Encouraged by this, he turned to benthic shells in the same two sediment cores. His objective was to determine the glacial to Holocene change in deep water carbonate ion concentration. When the answers came in, we were stunned to find that they supported Berger's coral hypothesis (Sanyal *et al.*, 1995) but, by this time, we had several lines of evidence that demonstrated that Berger's hypothesis could not be correct so something must be wrong with the boron results.

Sanyal received his PhD and continued his boron isotope research as a post doc. His hope was that he could get a teaching job. He applied to 33 universities and in spite of strong letters of recommendation from me and two very prominent geochemists, he was not invited for a single interview. Discouraged, he applied and was accepted for an elite one year MBA program at Cornell. He now has an executive position at Johnson and Johnson. He laughs with pride that he is the only oceanographer in the company.

Our second attempt to reconstruct the changes in carbonate concentration involved what we called the size index method. It was quite simple in that it involved determining the fraction of CaCO<sub>3</sub> in the cores that was greater than 63 micrometres. Based on measurements at the top of cores taken from tropical ocean sediment, we showed that there was a tight correlation between the <63 µm fraction and the present day extent of calcite undersaturation in the bottom water at the core sites (Broecker and Clark, 1999). My thought was that this correlation reflected the progressive breakup of the foraminifera shells as they dissolved. So the greater the extent of fragmentation, the lower was the >63 µm fraction. Based on this calibration, we began a program of down core studies. At first, we were encouraged by the discovery of three pronounced dissolution events (Broecker and Clark, 2001a) during the last interglaciation and also of a decrease in carbonate ion during the course of the Holocene but then, when we obtained some contradictory results for sediment representing the last glacial period (Broecker and Clark, 2001b), I worried that we were being misled by a change in the contribution of coccolith calcite.

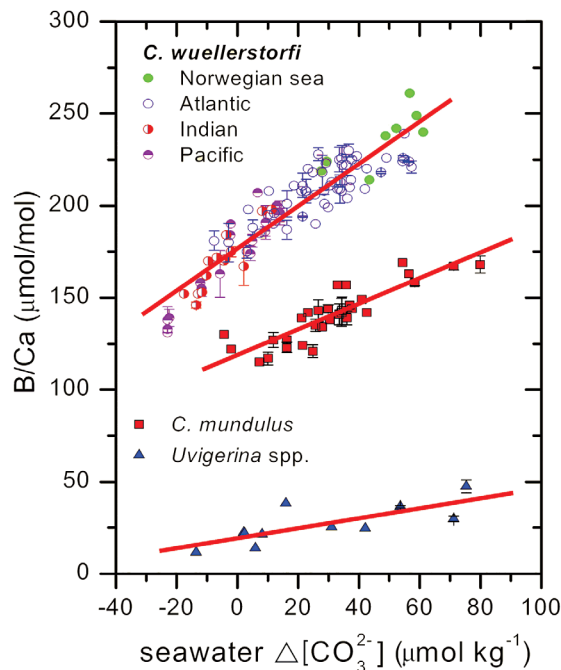
While I was pondering how I might deal with the coccolith question, I ran into Woods Hole's Pat Lohmann at the San Francisco AGU meeting. He took me aside and told me about his palaeocarbonate ion proxy. It involved sieving the foraminifera shells of his samples to isolate the 250 to 350 µm size class. Then, out of this split, he picked 50 shells of a given foraminifera species and weighed them. The idea was that as the shells dissolved, they became thinner. As we had done with our size index results, he regressed the weights for core top samples against the extent of undersaturation, thereby calibrating his method.

So, we took the plunge. The first step was to repeat Pat's calibration using core top samples covering a range of undersaturations. We also obtained a nice correlation (Broecker and Clark, 2001c). We then made down core measurements on the same set of cores on which I had done size index measurements and we were able to reproduce the three dissolution events in Atlantic cores and the



Holocene decline in carbonate ion concentration. However, before I had done much on samples representing the last glacial maximum, some disturbing news appeared. Stephen Barker, a graduate student in Harry Elderfield's Cambridge lab, found that the initial weight of foraminifera shells depends on the carbonate ion concentration in the surface water in which they grew. I looked into this and convinced myself that not only Barker was correct but that the situation was even more complicated. Initial shell mass also appears to depend on growth rate and perhaps other environmental factors.

Because of these setbacks, I became discouraged about finding a reliable palaeo carbonate ion proxy and turned my attention to other subjects. Then a few years later, Clara Chiu, who had done an outstanding PhD thesis with Lamont's Rick Fairbanks involving  $^{230}\text{Th}$  dating of corals, came to me looking for a one year post doc before her return to Taiwan. I said that if she was interested in coccoliths, I would take her on. My goal was to see how the ratio of the amount of coccolith calcite to the amount of foraminifera calcite settling onto the sea floor changed with climate.



**Figure 27b**

Jimin Yu, as part of his PhD thesis at Cambridge University, demonstrated that the boron to calcium ratio in benthic foraminifera correlates with the extent of calcite undersaturation. There is a unique slope and intercept representing each benthic species (after Yu and Elderfield, 2007).

Clara signed on and soon demonstrated that, using a 20  $\mu\text{m}$  sieve, she could separate coccoliths from the foraminifera. None of the foram shells or fragments of these shells were small enough to pass through this sieve and none of the coccoliths were large enough to get caught above the sieve. In this way, she achieved a clean separation. One of the things Clara did was to compare the results for two cores taken at different depths on the Ontong-Java Plateau in the western equatorial Pacific Ocean. Both core sites were located on the equator. This comparison was conducted because from previous studies, we had shown that the core from 4.0 km had experienced





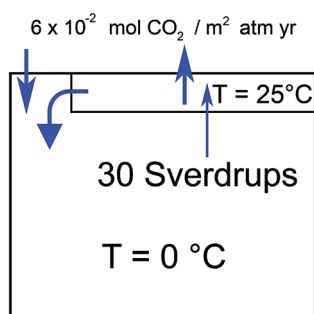
considerably more dissolution than the one from a depth of 2.3 km. Its shell weights and content of  $\text{CaCO}_3$  were lower. Based on down core radiocarbon dating, it was shown that the rate of accumulation of  $\text{CaCO}_3$  at the deeper site was about half that at the shallower site. Yet, the rate of non  $\text{CaCO}_3$  accumulation (mainly clays) was the same in both cores. Hence, we could assume that the lower  $\text{CaCO}_3$  accumulation rate at the deeper site reflected excess dissolution. To our surprise, there was no measurable difference in the accumulation rate of coccolith  $\text{CaCO}_3$ . Rather, the deficiency of  $\text{CaCO}_3$  in the deeper core appeared to be entirely the result of the dissolution of foraminifera shells. Apparently something about the coccoliths made them immune to dissolution (Chiu and Broecker, 2008).

This shed a different light on the meaning of our so called size index. It was misnamed because it had nothing to do with fragmentation. Rather, it reflected the differential dissolution of foraminifera shells and coccoliths. Although an extremely interesting discovery, it did nothing to salvage our futile efforts to come up with a reliable palaeocarbonate ion concentration proxy. I gave up my attempts to find a carbonate ion proxy, but Cambridge's Harry Elderfield persisted and hit the jackpot. Together with graduate student Jimin Yu, he looked into a chemical proxy and found the boron to calcium ratio for benthic foraminifera. They showed that using a single species, *wuellerstorfi*, they got a very tight correlation between the B to Ca ratio and the extent of undersaturation of calcite in the bottom water in which the foraminifera formed their shells (Fig. 27b). Jimin, currently a Lamont post doc under my mentorship, is busily establishing the carbonate ion concentration record for the last 30,000 years at a number of deep ocean localities. So far, no glitches have appeared. I keep my fingers crossed that at last we have the long sought after, carbonate ion proxy (Yu *et al.*, 2010).

## 28. THE HARVARDTON BEARS

I was taken by surprise by the simultaneous publication in 1985 of three separate papers that presented a nearly identical finding. One was by Harvard's McElroy and Knox, another by Princeton's Toggweiler and Sarmiento and the third by Bern's Wenk and Siegenthaler. As a shorthand, I refer to them as the Harvard-ton Bears. The surprise was that, using simple three box ocean models, these authors made a case that it was the surface waters of the cold Southern Ocean that controlled the partial pressure of  $\text{CO}_2$  in the atmosphere (Fig. 28). This came as a shock to me. I had always thought that, because the warm part of the surface ocean was so much greater in area, its  $\text{CO}_2$  partial pressure must dominate. However, what these three papers showed is that, at least in their three box world (i.e. a deep ocean, a warm surface ocean and a cold surface ocean), if the warm ocean deviated in  $\text{Pco}_2$  from that in the cold surface ocean,  $\text{CO}_2$  would flow through the atmosphere alleviating much of the difference. The warm ocean's  $\text{Pco}_2$  was a slave to that in the cold "outcrop" of the deep ocean.





**Figure 28**

A simplified abiotic two box version of the Harvardton Bear effect. The competition between the flux of water (thin arrows) and the flux of CO<sub>2</sub> (thick arrows) determines the degree to which the outcrop of the deep ocean dictates the atmosphere's CO<sub>2</sub> content.

This, of course, made a big difference in thinking about the cause of the drawdown of CO<sub>2</sub> during glacial times. If the Harvardton Bears were correct, only changes in the Southern Ocean surface waters count and because today's Southern Ocean is loaded with available NO<sub>3</sub> and PO<sub>4</sub>, the Harvardton Bears were quick to point out that if the extent of availability of these nutrients were greater during glacial time, then the CO<sub>2</sub> question would be solved. This idea picked up steam when a few years later, John Martin demonstrated that the availability of the element iron limited NO<sub>3</sub> and PO<sub>4</sub> utilisation. Coupled with the finding that glacial age ice in Antarctic cores had a far higher dust content than interglacial age ice, the claim was made that the delivery of this excess dust resulted in iron fertilisation of the glacial Southern Ocean and in this way drove down the atmosphere's CO<sub>2</sub> content.

Problem solved? Unfortunately, the answer is "no". Despite much effort, no one has provided convincing evidence that the use of the nutrients in the Southern Ocean was greater during glacial time than it is today. Perhaps the

most damaging bit of evidence is the finding that no significant increase occurred in the difference between the <sup>13</sup>C to <sup>12</sup>C ratios in coexisting glacial age planktonic and benthic foraminifera. The other disconcerting result was that full scale ocean circulation models do not give the same answer as the simple three box models employed by the Harvardton Bears. In the full scale models, although the influence of the Southern Ocean is greater than would be expected from its area, it does not dominate. At one point, I organised an intercomparison of a range of models and the result came out that the greater the complexity of the model, the less important its Harvardton Bear effect (Broecker *et al.*, 1999). However, I must admit that the final answer is not yet in. Direct iron fertilisation experiments in the Southern Ocean show that indeed John Martin was correct. It works and, of course, the dust falling on the Southern Ocean was much greater during the last glacial period than during the Holocene. A variety of proxies are being explored that might shed new light on whether or not utilisation of NO<sub>3</sub> and PO<sub>4</sub> in the Southern Ocean was greater during glacial time than it is today and of course, just because models are more complex, does not necessarily mean that they give better answers.



The atmospheric CO<sub>2</sub> content record for the Holocene, as preserved in Antarctic ice, has a puzzling feature. The steep rise during the Younger Dryas time is followed by a small drop during the early Holocene. Then, about 8,000 years ago, this decline bottomed out and the CO<sub>2</sub> rise resumed and continues to the present. An earlier and less precise version of this record, which had an even more pronounced CO<sub>2</sub> oscillation, caught my eye. In 1993, I published a paper attempting to explain it. I proposed that the dip was the result of regrowth, during the early Holocene, of forests destroyed during glacial time (Broecker *et al.*, 1993). The removal of CO<sub>2</sub> from the ocean supporting this increase in terrestrial biomass resulted in a rise in deep ocean carbonate ion concentration. In so doing, it disrupted the match between the burial of CaCO<sub>3</sub> in sediments and the supply to the ocean of the ingredients required for the production of CaCO<sub>3</sub> hard parts. Too much CaCO<sub>3</sub> accumulated, leading to a reduction in carbonate ion and a consequent downward displacement of the boundary between supersaturated and undersaturated water. In this way, the ocean's CO<sub>3</sub><sup>2-</sup> ion concentration was drawn down until the match between output and input was reestablished. As a result, there was an increase in the atmosphere's CO<sub>2</sub> content.

In 2001, a second paper on this subject provided direct evidence for the proposed post 8,000 year decline in deep ocean carbonate ion concentration (Broecker *et al.*, 2001b). It also provided evidence that the <sup>13</sup>C to <sup>12</sup>C ratio in equatorial surface water had not changed during the last 8,000 years. This finding reinforced my explanation based on CaCO<sub>3</sub>. If instead,

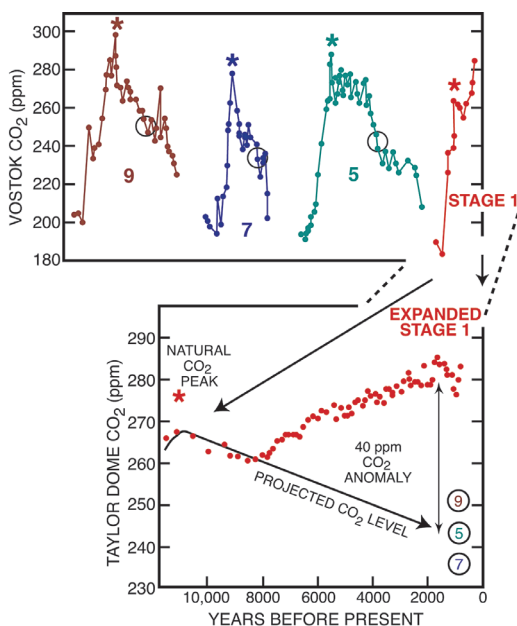
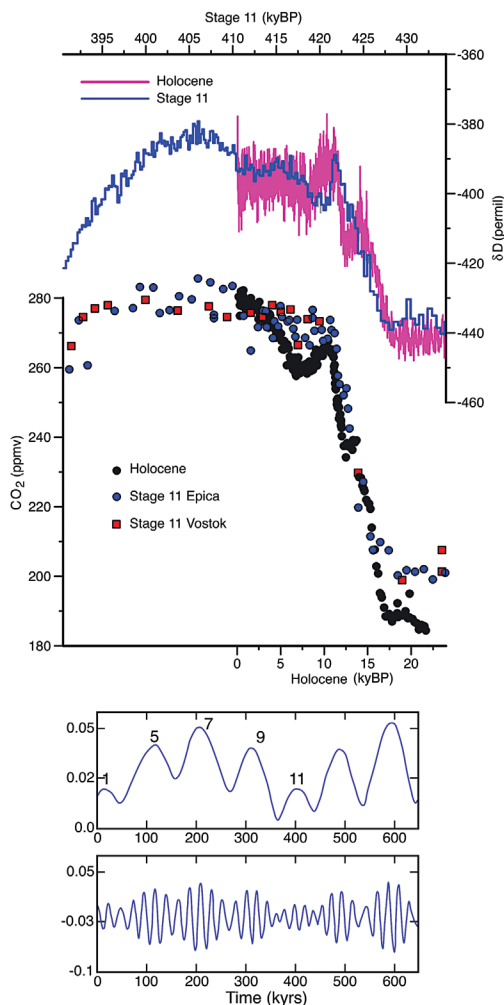


Figure 29a

As pointed out by Ruddiman, the CO<sub>2</sub> record kept in Antarctic ice for the present interglacial period shows an increase not present in the records for the previous three interglaciations. He attributes this increase to deforestation by humans (after Ruddiman, 2003).





**Figure 29b**

Unlike the previous three interglaciations, the  $CO_2$  record for Stage 11 is quite similar to that for the Holocene (i.e. Stage 1). Because stages 1 and 11 are characterised by weak precessional forcing associated with the low eccentricity of the Earth's orbit, Thomas Stocker and I concluded that the Holocene  $CO_2$  rise was caused by natural forces rather than intervention by man (after Broecker and Stocker, 2006).

the rise had been the result of a decrease in terrestrial biomass, then there would have been a corresponding decrease in the  $^{13}C$  to  $^{12}C$  ratio in atmospheric  $CO_2$  and ocean  $\Sigma CO_2$ .

In 2003, Bill Ruddiman, of the University of Virginia, published a paper claiming that the 20 ppm increase in  $CO_2$  was instead the result of deforestation carried out by humans (Ruddiman, 2003). He pointed out that no equivalent oscillation of  $CO_2$  had occurred during the previous three interglacial periods. Rather, after  $CO_2$  peaked, it began a steep decline (Fig. 29a). So, Ruddiman attributed the past 8,000 year rise to early man and claimed that in the absence of this human intervention,  $CO_2$  would have declined and the world would have been plunged into another glacial period. Ruddiman's claim was well received by the press. He has lectured in many, many places and expanded his ideas in a book. When I pointed out to him that the massive deforestation he required did not show up in the  $^{13}C$  record, he replied, " $^{13}C$  never proved anything".

In 2006, Thomas Stocker and I published a short paper in *EOS* pointing out that if Ruddiman had gone back one more interglaciation, he would have found that  $CO_2$  did the same thing as it did in the Holocene



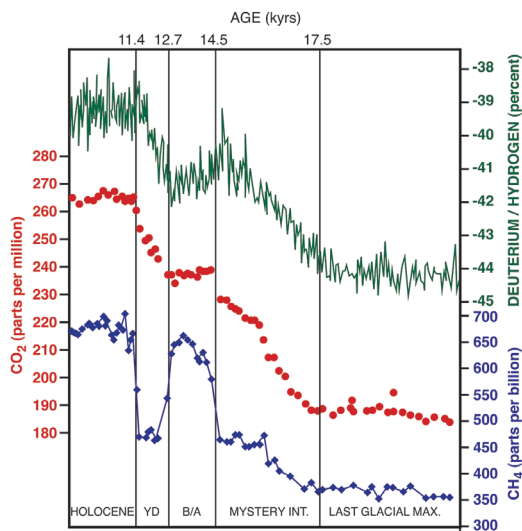
(Broecker and Stocker, 2006). Further, as the result of a 400,000 year orbital cycle, the eccentricity of the Earth's orbit at that time was quite small, as is the case for the Holocene (Fig. 29b). Hence, we concluded that it constituted the proper analogue! We also emphasised that were Ruddiman correct, humans would not only have to deforest an area the size of the Amazon, they also would have had to prevent forest regrowth on this vast area. Further, about half of this deforestation would have had to occur prior to 4,000 years ago, a time when man lacked the tools to cut down large trees and, of course, we stressed the lack of any evidence for the consequent  $^{13}\text{C}$  change. Despite what to me appears to be overwhelming evidence against Ruddiman's hypothesis, it persists. In an attempt to get around the criticisms, he now says that only part of the 20 ppm loss was the result of forest cutting and the rest was the result of some ill defined feedback. This year the final spike was driven into the coffin of the Ruddiman hypothesis. The group in Bern, Switzerland, after a long struggle, finally found a way to produce a reliable  $^{13}\text{C}/^{12}\text{C}$  record for  $\text{CO}_2$  trapped in polar ice. They confirmed my finding, based on measurements on foraminifera shells, that there was no significant downward trend in  $^{13}\text{C}$  during the last 8,000 years.

## 30. THE MYSTERY INTERVAL

After being locked in the jaws of peak glacial cold for ten or so thousand years, a Heinrich event jarred the system, initiating the transition back toward interglacial conditions (Heinrich, 1988). Surprisingly, while this impetus occurred in the North Atlantic, the first indications that a thaw was underway appeared in the south. As recorded in Antarctic ice, starting 17.5 ka (thousand years) ago, the air temperature commenced a steady climb that continued for 3 ka (i.e. until 14.5 ka ago), bringing the temperature about halfway back to its interglacial level (Augustin *et al.*, 2004). At this point, a pause occurred and 2 ka elapsed before the temperature rise resumed. By contrast, conditions in the north remained cold until 14.5 ka ago. Only then did a warming in the north finally take place but instead of undergoing a gradual rise, the temperature took a sudden jump, reaching close to that of the Holocene. Early on, I realised that this series of events must have been induced by changes in ocean circulation. I referred to it as the bipolar seesaw. I also gave a name to the time interval from 17.5 to 14.5 ka ago. I called it the Mystery Interval (Fig. 30a).

The Mystery Interval rise in southern temperature was accompanied by two other changes. As recorded in bubbles of air trapped in Antarctic ice (Barnola *et al.*, 1987), the  $\text{CO}_2$  content of the atmosphere began a steady rise and, as recorded in stalagmites in caves, the  $^{14}\text{C}$  to C ratio in atmospheric  $\text{CO}_2$  began a steady decline. As was the case for southern temperature, both of these steady drifts continued until 14.5 ka years ago, when they flattened. During the Mystery Interval, the atmosphere's  $\text{CO}_2$  content rose halfway back to its interglacial level





**Figure 30a**

D to H ratio and CO<sub>2</sub> and CH<sub>4</sub> concentration from trapped air bubbles from an Antarctic ice core for the time interval of the last deglaciation. At close to 17.5 kyrs, the Antarctic air temperature and the atmosphere's CO<sub>2</sub> content began to rise. These changes continued for about 3,000 years, at which point the warming and CO<sub>2</sub> rise paused. This time period is referred to as the Mystery Interval. The methane record is quite different. It reflects conditions in the Northern Hemisphere where the warming did not kick in until 14.5 ka (i.e. the onset of the Bølling Allerød). YD means Younger Dryas (from Broecker, 2005, with permission from Eldigio Press).

and its <sup>14</sup>C to C ratio dropped by 15%. Of these changes, the most difficult to understand is the rapid decline in radiocarbon. The most obvious explanation is that the production of <sup>14</sup>C by cosmic rays was dramatically reduced during the Mystery Interval but this explanation was eliminated based on the record of <sup>10</sup>Be in ice cores. <sup>10</sup>Be is produced by the same cosmic rays as <sup>14</sup>C. However, unlike <sup>14</sup>C, which largely remains in the ocean-atmosphere reservoir until it undergoes radiodecay, <sup>10</sup>Be is rapidly removed from the atmosphere by incorporation into rain and snow. Some of it ends up in polar ice. Hence, if the explanation for the <sup>14</sup>C decline were a drop in its production, this same drop should be seen in the record of <sup>10</sup>Be in ice cores. In order to explain the 15% drop in <sup>14</sup>C, the <sup>10</sup>Be content would have had to drop by more than a factor of two. However, no significant dip in <sup>10</sup>Be concentration is seen

in Mystery Interval ice. Instead, the explanation has to be that the distribution of <sup>14</sup>C within the ocean underwent a major change. Specifically, during peak glacial time, the contrast in radiocarbon between the upper and the deep ocean must have been considerably greater during peak glacial time than now. Then, during the Mystery Interval, this contrast must have been significantly decreased (Fig. 30b).

Documenting the greater isolation of glacial age deep water proves to be a perfect task for accelerator mass spectrometry because a difference should be recorded by the age difference between coexisting benthic and planktonic foraminifera. I had made a few such measurements on cores from the Pacific Ocean early on and had found that the age difference between coexisting benthic



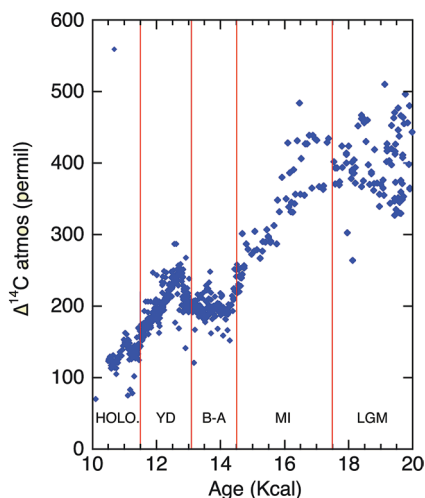


and planktonic foraminifera was no different than that measured on GEOSECS water samples. However, because I had measured only a few pairs, a more thorough job needed to be done. Starting in 2003, aided by Elizabeth Clark and Post Doc, Steve Barker, I set out to find what we termed the isolated glacial reservoir. This reservoir must have occupied a large fraction of the deep ocean so we focused on cores from the vast Pacific. Further, in order to avoid complications created by bioturbation (i.e. the mixing of sediment by worms), we concentrated on cores with high sedimentation rates.

The first core we chose was from the western equatorial Pacific just south of Morotai Island. Its depth was 2.1 km (Broecker *et al.*, 2004). The sediment accumulation rate averaged close to 70 cm/ka so the impacts of bioturbation were certainly negligible. Three samples that were deposited before the onset of the Mystery Interval yielded benthic-planktonic age differences averaging 1.3 ka. For today's surface at 2.1 km,  $^{14}\text{C}$  to C difference corresponds to an apparent age of 1.5 ka. Hence this core yielded no hint of greater isolation (Broecker, 2009).

In addition to the benthic-planktonic difference, we got a bonus in that Elizabeth Clark found a wood fragment in one of the samples. Its age came out to be 0.56 ka younger than that of the coexisting planktonic species. This was encouraging because it matched expectations based on the contemporary  $^{14}\text{C}$  to C difference between atmosphere and surface water.

We then analysed paired foraminifera from a second western equatorial Pacific core located at a depth of 1.9 km just north of Admiralty Island. Its average sediment accumulation rate was 10 cm/ka. Two samples, that were deposited several thousand years before the onset of the Mystery Interval, yielded a mean benthic-planktonic age difference of 1.8 ka. Although a bit larger than today's 1.5 ka, the difference was nowhere large enough to account for the Mystery Interval decline in  $^{14}\text{C}$ . Failing to find any evidence at a depth of 2 km, we tracked down a western equatorial Pacific core from 2.8 km water depth. It has a sediment



**Figure 30b**

By measuring the  $^{14}\text{C}$  to C ratio in corals and stalagmites for which calendar ages have been determined through  $^{230}\text{Th}$ - $^{234}\text{U}$  dating, the temporal changes in the  $\Delta^{14}\text{C}$  for the atmosphere have been reconstructed. As can be seen, during the Mystery Interval, it dropped from about 40% higher to about 20% higher than today's values.



accumulation rate averaging 50 cm/ka. Two samples that were deposited a thousand or so years before the onset of the Mystery Interval yielded a mean benthic-planktonic age difference of 1.6 ka. Again, there was no hint of a glacial age, isolated, ocean reservoir. Interestingly, six samples from the Mystery Interval itself also yielded benthic-planktonic age differences averaging 1.6 ka.

Frustrated, we decided to go deep but the abyssal parts of the Pacific lie far from sources of detritus derived from continents, so we could not locate a site with a large accumulation rate. Further, below 4 km depth, most Pacific sediment is nearly devoid of  $\text{CaCO}_3$  because these sediments are bathed with water highly undersaturated with respect to calcite. We were, however, able to find a core from a depth of 4.4 km with high  $\text{CaCO}_3$  content. It was located 2°S of the equator, beneath a zone of intense upwelling. The high productivity supported by this rich supply of nutrients led to such a rapid precipitation of  $\text{CaCO}_3$  that it exceeded the rate of dissolution. Even so, the sediment accumulation rate was only 2 cm/kyr. Worms stir deep sea sediments to a depth of 6 to 8 cm, so we had to hope that this mixing did not produce anomalies in the benthic-planktonic age differences. We got lucky. Four samples, ranging in age from 18 to 26 ka yielded excellent results. The mean age difference between benthic and planktonic samples turned out to be 1.2 ka. Once again, there was no hint of the existence of an isolated glacial age reservoir (Broecker and Clark, 2010).

As a bonus, we confirmed something Steve Barker had predicted. The *G. sacculifer* shells from these four samples had ages averaging 1.4 ka younger than those for three other planktonic species and also the coccoliths. It is important to note that *G. sacculifer* is the preferred species for palaeoceanographic studies because it calcifies in the surface mixed layer. The other planktonic species calcify beneath the mixed layer and hence could conceivably have somewhat lower  $^{14}\text{C}$  to C ratios. However, the fact that coccoliths that form in the surface mixed layer have the same age as the other planktonic species demonstrates that this is not the explanation for the younger *G. sacculifer* ages. Steve reasoned that because *G. sacculifer* shells are more susceptible to dissolution and breakup than the other foraminifera (and also, as we have seen, coccoliths), the few shells remaining unbroken in the sediment must have, by luck, passed through the mixed layer more quickly than the average. Instead of going round and round for about 3 ka, as did the other planktonic and benthic shells and coccoliths, the unbroken *G. sacculifer* shells escaped to the underlying sediment in about half this time. Had we been able to identify and pick *G. sacculifer* fragments, they would likely have yielded a radiocarbon age older than that for the coccoliths and other planktonic forms, because they would be the representatives of the unlucky *G. sacculifer* that resided in the stirred layer for a longer than average time (Broecker and Clark, 2011).

So the search goes on. Because there appears to be no other explanation for the Mystery Interval  $^{14}\text{C}$  decline, the isolated reservoir must be hiding somewhere in the deep sea. Although we haven't been able to find the mother lode, evidence for its demise during the Mystery Interval appears recorded in cores



at intermediate water depth. Further, suggestive evidence for its existence has been found in both the North Atlantic and the Southern Ocean source regions. So, we won't give up!

## 31. GARY COMER

In April 2002, I received a letter from a man named Gary Comer. In it, he described his puzzlement that, during the previous summer, he had been able to sail his yacht, *Turmoil*, through the Northwest Passage without being blocked by ice. No other vessel of *Turmoil's* class had been able to do this, so he wondered whether his success had something to do with global warming. He requested that I come to Chicago to meet with him, but added that none of Columbia's "development" people were to accompany me. I replied that I certainly would meet with him but because I was teaching, it would be best to delay my visit for two weeks until the semester was over. He responded that he was eager to get an answer so he would come to New York on a one day visit. Comer's private jet would take him to Teterboro Airport and he would stay the night at the Clinton Inn located a couple of miles from my New Jersey home. He suggested that we meet for breakfast.

I well remember this first encounter. Comer was dressed casually, open collared shirt and sleeveless pullover sweater. Once seated, he said to me, "Wally, what can I do for you?" Aware that his company, Lands End, had made him a billionaire, I was stunned. After an embarrassing pause, I was only able to say that I would have to think about it. Once our orders were in, our conversation turned to the Arctic. I explained that my expertise lay in the area of palaeoclimate. I went on to explain that it was centred on the role of the ocean in provoking the abrupt climate changes that had punctuated the last ice age. Hence, I could only say that CO<sub>2</sub> derived from fossil fuel burning was surely warming the Earth. While by no means expert on Arctic sea ice, I was aware of evidence that it was shrinking and that model simulations suggested that if the rise in CO<sub>2</sub> was not stopped, in a few decades, ice free summers were a possibility.

After getting answers to a bevy of questions about my research, Comer asked me if he could visit the Lamont campus. Once there, he was clearly impressed with the setting but after a brief tour of our 50 year old geochemistry building, he remarked that it was a bit of a pig sty. As lunch time approached, I told him that my friend, George Kukla, was, by chance, hosting a "pignik" out in the adjacent woods and that if he was agreeable, we could attend. So it was that Comer joined about 30 of us as we chatted and chewed on roast pork. I remember Gary (as he instructed me to call him) sitting on a log with a big smile on his face. A week later, I received a collage of photos he had taken at this event.



Clearly, he had captured the spirit of Lamont! After lunch, he said that he had best be getting back to Chicago. He thanked me and promised to keep in touch. As a parting shot he asked me whether I had come up with anything that I needed. I said that the greenhouse Columbia inherited as part of the Lamont estate was in ill repair and that one of our young professors sought to have it renovated for his CO<sub>2</sub> research. So it was that we received \$7,500 from the Comer Science and Education Foundation. Little did I realise that it was just the tip of the iceberg.

Some weeks later, Gary called me and asked if I would help him to create a network of scientists who were expert in the area of abrupt climate change. His idea was to provide \$300,000 to each of these people as a means of speeding up their research. The only restriction was that each host institution would have to waive its usual overhead. I asked, "How many investigators he was thinking of?" He replied, "25". So it was that I became Santa Claus to the palaeoclimate scientific community. The following October, the newly installed climate fellows and their post docs (and Gary) met together at the IBM Conference Center in Palisades, New York. This meeting marked a turning point in our community. Rather than competing in our often dog eat dog fashion, we realised that friendly cooperation not only produced better science but it was also more fun.



Photo credit: Philip Conkling.

**Figure 31a** Gary Comer at the controls of his single engine Caravan aircraft.

By this time, Gary had sold his Lands End clothing business and was free to pursue his philanthropic interests. Realising that one of the important aspects of our abrupt climate change research involved field work, he was eager to participate. Our first venture was to explore the proposed eastern outlet of proglacial Lake Agassiz. Jim Teller, of the University of Manitoba, had postulated that this was the route taken by the catastrophic flood thought to have triggered the onset of the Younger Dryas (the name associated with the last of Greenland's steep sided, millennium long, cold temperature intervals). So, I assembled a group and we gathered at Chicago's Midway Airport where we boarded Gary's large private jet and flew to his "farm" in western Wisconsin. We spent a day in this Shangri-La, planning our expedition

and then, it was off to Thunder Bay on the shore of Lake Superior where Gary's single engine Caravan (Fig. 31a) and a rented helicopter awaited us.



Our mission was two fold. First, we wanted to explore boulder fields and channels created by floods and second, we wanted to collect samples for  $^{10}\text{Be}$  dating. With this in mind, half the group, using the Caravan, did aerial reconnaissance and the other half, using the helicopter, searched for and sampled large granite boulders (so called glacial erratics). Although to the north of Teller's pathway there were two spectacular now dry channels cut through an Archean diabase and two fields of thousands of granite boulders, to the west of Thunder Bay, along Teller's proposed flood course, neither channels nor boulders were to be seen. Further, the results of  $^{10}\text{Be}$  exposure dating showed that the boulder fields to the north of Thunder Bay were emplaced a millennium or so after the end of the Younger Dryas. Thus we were forced to conclude that the water that escaped from Agassiz must have followed some other route.

Frustrated by the absence of evidence for a flood to the east, we decided to look for one to the north. Indeed, a deep and wide channel had been cut through sediments near Fort McMurray but radiocarbon ages suggested that it formed two millennia after the Younger Dryas. We decided to have a look for evidence that the channel was occupied twice, once during the Younger Dryas and then a second time two millennia later. Once again, Gary's air force provided the transport but our search and subsequent dating provided no evidence in support of an earlier flood. We did, however, get a glimpse of one of the consequences of the flood waters that had passed through this area. North of the channel, they had stripped away the sediment overburden, exposing what is known as the Athabasca tar sands. From the Caravan, we could see huge bulldozers dumping these tar laden sands into equally huge trucks. The trucks carried the tar laden sand to a conveyor belt which transported it the rest of the way to the processing plant. There, we were told, it was treated with hot water to release the hydrocarbons. By combining it with hydrogen, the hydrocarbons were transformed into gasoline – a bonanza for Canada rivalling the Arabian oil fields!

George Denton, who participated in both of these field trips, had an even grander idea as to how Gary might push forward abrupt change research. He suggested that our group take advantage of Gary's vessel, *Turmoil*, and look into the Younger Dryas advance of Greenland's ice sheet. Gary agreed and plans were made to head for Scoresby Sund, halfway north on Greenland's east coast. Much to my disappointment, a last minute health crisis prevented me from participating. Richard Alley took my place. Denton wanted to compare the Younger Dryas temperature reduction derived from the extent of snowline descent with that obtained by Jeff Severinghaus based on an anomaly in the isotopic composition of nitrogen gas trapped in the ice core that had been recovered from Greenland's summit. What he found turned out to be exceedingly important. While the Scoresby snowline lowering suggested a Younger Dryas cooling of about 5 °C, the nitrogen isotope based estimate suggested a whopping 15 °C. Puzzled by the difference, Denton realised that, while the Severinghaus result reflected mean annual temperature, his snowline elevation reflected only summer conditions. Thus, the implication was that winter temperatures must have been about 25 °C colder than now (Denton *et al.*, 2005). This could only have been the case if, during



the Younger Dryas, winter sea ice cover had expanded southward all the way to the British Isles. As shall be discussed in the section on water, this proved to be the key to understanding the large tropical impacts associated with the Younger Dryas and with Heinrich events. So, although our Canadian field trips failed to find the trigger that launched the Younger Dryas, the trips to Greenland showed why its consequences were so widespread.

When Gary first asked me what we needed, the first thing that entered my mind was a new geochemistry building but I did not want him to think that I was an agent representing Columbia's development office so I didn't bring it up. However, his mention that our building was something of a pig sty gave me hope that he would eventually offer help on his own initiative and indeed, one day Gary called me and said he had been thinking that we should have a new building and that he was ready to help us get one. Thus began the long process of getting Columbia's approval, hiring an architect and making a budget. All appeared to be going well until I saw the budget. The total was \$65 million: 45 million for the building itself and 20 million for contingencies and internal costs. As I suspected, Gary was furious. Eventually, just when I thought things had been worked out, I got a call from Gary saying that he was so angry with Columbia that he was going to pull the plug. I was stunned and begged him to reconsider. At last, he backed off, but said that he was going to reduce his contribution from 20 million (half the cost) to 18 million dollars. I realised that unless we came up with half the cost, Columbia would call the deal off, so I called Jerry Lenfest, one of Columbia's trustees, and explained the situation to him. He made my day by offering to put in the missing \$2 million. So it was, that in 2008 we got our fantastic Gary Comer Geochemistry Laboratory (Fig. 31b).

It was during this period that Gary Comer's health began to deteriorate. His prostate cancer had spread to his bones and despite the efforts of experts at Sloan Kettering Hospital here in New York, nothing could be done to arrest it. Realising that death was coming, in his last days, Gary put aside \$5 million dollars in his family foundation for the support of abrupt climate change research. He empowered George Denton, Richard Alley and me to decide how it was to be spent. Gary also initiated the construction of what he called the Center for Abrupt Climate Research on his Wisconsin farm. Each year, those of us who benefit from Comer start up grants meet there to discuss our progress. Unfortunately, there are very few Gary Comers in the world. He decided to make a difference and he did. Not only did he provide money, but he enthusiastically acted as cheerleader. He was curious and paid close attention to what we were doing and in this way, he inspired us all. We miss him.







**Figure 31b**

I am lucky to have as my office an area originally designed as a small conference room situated above the entrance to the Gary C. Comer Geochemistry Building.

## 32. WATER

I began this story with a description of my first geological field trip to Pyramid Lake. Since then, I have revisited the Great Basin many times but it was only three years ago that it dawned on me that the records kept in the world's closed basin lakes might offer guidance regarding how water availability in the Earth's dry lands will change as fossil fuel CO<sub>2</sub> warms our planet. Currently, 40% of the world's grains are produced on irrigated land. Much of the water supporting this growth is pumped from underlying aquifers. Even in the absence of climate change, water will become ever more scarce, because there will be more mouths to feed and the aquifers beneath dry lands are being depleted. Climate change will certainly aggravate this situation.

The geologic record tells us that changes in climate generate changes in water availability. During glacial time, not only were Lake Lahontan (Pyramid Lake's predecessor) and Lake Bonneville (Great Salt Lake's predecessor) as much as 10 times larger than their late Holocene remnants but dozens of lakes occupied now dry playas throughout the Great Basin and over the rest of the globe.



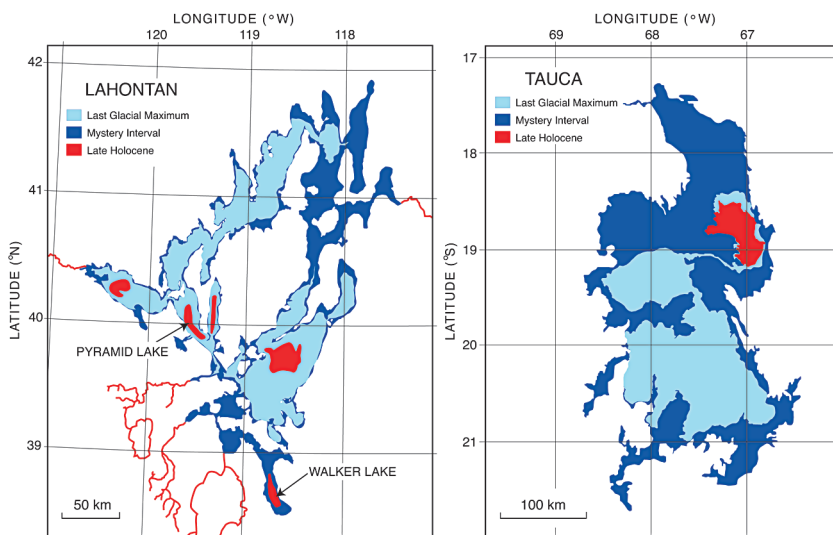
If much more water was available during times of colder climate, is it safe to predict that less will be available as CO<sub>2</sub> warms the Earth? The obvious way to approach this question would be through simulations carried out in global ocean-atmosphere models. All such simulations agree that global warming will increase precipitation in the already wet tropics and decrease it in the already dry extra tropics (15 to 25 ° latitudes) but unfortunately, these simulations yield no consensus regarding the temperate dry lands (30 to 40 ° latitudes). Thus, they make no consistent prediction for the western USA.

This being the case, George Denton, Richard Alley and I decided to focus some of our Comer Foundation funds on the creation of a group of scientists who would explore the record of past changes in water availability with an eye toward using it to say something about the future. The core group consists of Minnesota's Larry Edwards, who pioneered the <sup>18</sup>O record in stalagmites as an indicator of monsoon strength, Arizona's Jay Quade, who concentrates on the reconstruction of closed basin lake sizes, U.C. San Diego's Jeff Severinghaus, who uses the <sup>18</sup>O to <sup>16</sup>O record in the O<sub>2</sub> trapped in ice core bubbles to reconstruct changes in the Earth's hydrologic cycle and Hayward State's Scott Stine, who documents Holocene droughts in the Sierra Nevada. I coordinate the effort. Our first project was the evaluation of the hypothesis that the proximity to the great Laurentide ice sheet was responsible for the large glacial age expansion of the lakes in the Great Basin. This huge topographic feature split the jet stream, forcing half to loop around its southern edge. If this were the case, then the value of past lake size as a predictor of the response to the ongoing global warming would be nullified. In an attempt to decide whether this was the case, our approach was to examine the response of closed basin lakes elsewhere in the same latitude belt.

Closed basin Lago Cari Laufquen at 41 °S in Argentina's Patagonian dry lands posed an obvious target. In October 2008, Jay Quade, Scott Stine and I spent a week collecting tufa from shorelines that Stine's reconnaissance <sup>14</sup>C measurements had shown to have formed during the time of the last glacial maximum. Indeed, extensive <sup>14</sup>C ages obtained by Quade confirmed this. At that time the lake was about four times larger than it is today so this weakened the claim that the Laurentide ice sheet was responsible for the enlargement of the Great Basin lakes during glacial time. I say "weakened" because although there was no large, land based ice cap in the Southern Hemisphere, winter sea ice in the Southern Ocean extended 8 °C further north than it does today so there is an important difference between the cooling of the glacial world and the warming that is to come. Only about half of the 5 °C glacial cooling is attributable to reduced CO<sub>2</sub>. The rest appears to have resulted from reflection of incoming sunlight from the greatly expanded ice and snow cover. It is possible, for example, that the presence of this extra ice was responsible for a shift in the position of the westerly wind belts in both hemispheres and it was this shift that caused the increase in lake size. Because there would be no comparable decrease in sea ice cover associated with global warming, the answer to whether global warming will dry the western U.S. can only be a qualified "yes".



Our indicators of hydrologic change tell us that during the 6,000 year time interval during which the Earth's climate reverted from its cold glacial state to its warm interglacial state, the availability of water in dry lands underwent very large fluctuations. Lake Lahontan became even larger during the Mystery Interval than it was during the last glacial maximum. The same is true for the lakes in the southern part of Bolivia's Altiplano (Fig. 32a). These wet episodes were followed by very dry ones, during the so called Bølling Allerød (i.e. the time interval of the pause in the CO<sub>2</sub> rise and the near Holocene Northern Hemisphere warmth). Then water availability increased once again during the Younger Dryas.

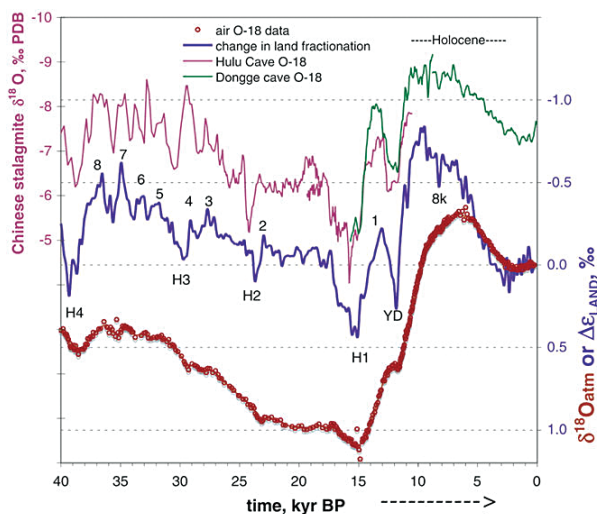


**Figure 32a** Comparison of the sizes of Lakes Lahontan, Nevada and Tauca, Bolivia, during the last glacial maximum (24 to 18 ka) and the latter half of the Mystery Interval (16 to 15 ka) with that of the late Holocene remnants (after Broecker, 2010b).

Of course, if some regions of the world got wetter during the Mystery Interval, others must have become correspondingly drier. One of these was equatorial east Africa's Lake Victoria. It was dry during the latter part of the Mystery Interval and then came back into existence during the Bølling Allerød. Another area was China, where monsoon rains underwent a major weakening during the Mystery Interval. Unfortunately, we don't know what happened at Lago Cari Laufquen. It has a higher shoreline, which matches that for Lake Lahontan, but a thorough search by Jay Quade turned up no datable material so we don't know its age. The only hint we have is that soils on the shoreline have experienced only a small extent of lithification by CaCO<sub>3</sub>, suggesting that the soil formed during the last 30,000 years. Further evidence comes from Jeff Severinghaus' record of the <sup>18</sup>O to <sup>16</sup>O ratio in O<sub>2</sub> gas trapped in bubbles in Greenland ice. As depicted

in Figure 32b, it closely parallels the record of  $^{18}\text{O}$  to  $^{16}\text{O}$  in Chinese stalagmites, suggesting that monsoons over the entire Northern Hemisphere strengthened and weakened, in unison with those in China.

What might have orchestrated these hydrologic shifts? It appears to have been a seesawing of sea ice cover in the North Atlantic and Southern Oceans. As Denton demonstrated from his Scoresby snowline reconstruction, it appears that during the Younger Dryas cold, and also following the invasion of Heinrich ice armadas, the North Atlantic experienced extensive winter sea ice cover. Lamont's Bob Anderson has shown that during these same times, increases in the deposition of opal in the Southern Ocean peaked, likely as the result of strong upwelling that reduced sea ice cover. Thus, it appears that at times of maximum sea ice cover in the north, minimum sea ice cover existed in the south. If so, this would have caused the Earth's thermal equator to shift southward, carrying with it the tropical rain belts. Such a shift would nicely explain the weakening of the Northern Hemisphere monsoons and also the increase in rainfall on the southern portion of the Altiplano, documented by Jay Quade. However, it is not clear why Lake Lahontan reached its largest size during the Mystery Interval. Perhaps changes



**Figure 32b**

Comparison of  $^{18}\text{O}$  to  $^{16}\text{O}$  record for  $\text{O}_2$  trapped in ice core bubbles with that in  $\text{CaCO}_3$  of stalagmites in Chinese caves. While the caves record the instantaneous oxygen isotope ratio in Chinese rainfall, the ice cores record the millennial average for Northern Hemisphere monsoonal precipitation. The slope of the  $\text{O}_2$  record reflects the instantaneous composition of this precipitation. The similarity of the two records is striking (after Severinghaus *et al.*, 2009)!



in the extent of sea ice cover caused a shift in the westerly wind belts. A test of this would be to determine how the size of Lago Cari Laufquen changed during the Mystery Interval (Broecker, 2010b).

We think of the Holocene as a time of relatively quiescent climate. Changes did occur but they are for the most part lost in the noise associated with our palaeoproxies. We do, however, have some regional information concerning the last millennium. During its first 300 years, the north polar region was a bit warmer. We know this from the poleward shift in tree lines and in upward shift in snow lines (Denton and Broecker, 2008). Consistent with these changes is the occupation of Greenland by the Vikings. This period, known as the Medieval Warm Period, was followed by a cooling. Snowlines dropped in elevation. Northern forests retreated southward. Sea ice was more prevalent around Iceland and the Vikings disappeared from Greenland. This cold snap, known as the Little Ice Age, came to a halt about 150 years ago. Since then, there has been a steady warming.

This Northern Hemisphere temperature cycle was accompanied by sizable hydrologic changes. Scott Stine has documented a pair of century long megadroughts in the drainage basins of the western Great Basin (Stine, 1994). They took place late in the Medieval Warm Period. His evidence is based on the remains of trees and other woody plants that are now covered by water, in river beds, lake shore zones and swamps. These plants were killed by root submergence so they must have grown during times when the water was not there. Radiocarbon dating fixes the time of growth and the number of rings records the duration of growth.

During a 2010 field trip to westernmost China, Aaron Putman, a graduate student working with our Comer group, happened upon stumps of trees now covered by desert sand and shells from the shoreline of a once large lake. He was surprised to find that (as indicated by  $^{14}\text{C}$  ages) both date from the Little Ice Age. Since then, the large lake has shrunk to a small swamp and the forest has become a sand desert. Aaron located a report by Marco Polo that during what we now know to have been the latter part of the Medieval Warm Period, the lake was only a small swamp, as it is today. It is my opinion that we do not know what caused the Medieval Warm-Little Ice Age climate swing but I suspect that it was associated with small variations in the ocean's vast heat inventory. Two lines of evidence point in this direction. Georgia Tech's Jean Lynch-Stieglitz has shown that the Atlantic's conveyor circulation weakened by about 15% during the Little Ice Age (Lund *et al.*, 2006) and Lloyd Keigwin has shown that the tongue of Antarctic Bottom Water, that penetrated into the North Atlantic during the Medieval Warm Period, retreated during the Little Ice Age and then returned during the last 150 years.

There is also evidence that the thermal equator shifted in parallel with the Medieval Warm-Little Ice Age oscillation. Julian Sachs, of the University of Washington, has shown from the record in lake sediments in the north-south chain of islands in the central equatorial Pacific, that during the Little Ice Age, the rain belt was positioned 5° latitude further south than it is today (Sachs *et al.*, 2009). This is of interest because the Northern Hemisphere, with its much greater



land area, will, as the result of the ongoing build up of fossil fuel CO<sub>2</sub>, warm twice as fast as the Southern Hemisphere. This will push the thermal equator to the north and likely also the position of the tropical rain belt. Although spotty, this type of evidence suggests that even during the quiet Holocene, water availability in dry lands underwent substantial shifts. This being the case, it seems likely that the much larger warming to be brought about by the build up of fossil fuel CO<sub>2</sub> will bring about even larger shifts. Our group will continue the study of past changes in hopes that we can use this information to say something useful about what is likely to transpire.

### 33. AIR CAPTURE OF CO<sub>2</sub>

I first encountered Klaus Lackner (Fig. 33a) at a meeting held in Ottawa titled “Canada 2020.” In a session on energy, he gave a very brief talk on carbon capture and storage. His idea was to mineralise CO<sub>2</sub> by reacting it with magnesium derived from ultrabasic rock (Lackner *et al.*, 1995). It struck me that this was a wild idea and I wrote Lackner off in my mind as just another guy from our national laboratories looking for a way to justify his continuation. It wasn’t until a year later, when Lackner visited Biosphere 2, that I began to revise my assessment. Here was one very bright man. We encouraged him to join us in our struggle to convert the glass house into a first class research facility. Further dealings with Klaus strengthened my realisation regarding his brilliance. Hence when he gave an in depth presentation of his research on CO<sub>2</sub> mineralisation, I realised that, far from being crazy, it made good sense. At that time, Los Alamos was undergoing upheavals over supposed security leaks. Klaus was serving as an Associate Director and was caught up in these witch hunts. So, Peter Schlosser, who pioneered the establishment of a Department of Earth and Environment Engineering in Columbia’s Engineering School, and I saw a possibility that he might be lured to Columbia. This proved difficult because, while Klaus was tired of the bureaucratic entanglements at the lab, his family (Klaus included) loved the town of Los Alamos and its beautiful surroundings. Fortunately for us, the lure of university life won out and the Lackner family came to New York.

Our interest in Klaus centred more on his ideas about capturing CO<sub>2</sub> than those associated with storing it. He was convinced that direct capture from the atmosphere was feasible and that his plan could compete financially with capture from power plant exhaust (Lackner, 2009). However, no one had tried to pull CO<sub>2</sub> out of the atmosphere so any such effort would have to start from scratch. Shortly after Lackner’s arrival at Columbia, our administration changed hands. George Rupp retired as President and Lee Bollinger took up the reins. One of the first actions of the new management group was to reevaluate the situation at Biosphere 2. Although its semester long immersion environmental education program had been extremely successful, during the previous two years, largely





because of Columbia's high tuition, enrolment had sagged. Further, the highly promising research programs in Biosphere 2's rain forest and in its coral lagoon had failed to garner federal support. So Bollinger decided to pull the plug and abandon our effort there. This left Allen Wright, who served as Biosphere 2's engineering chief, without a job. Allen had come to Tucson from Hawaii where he had led NOAA's (National Oceanic and Atmospheric Association) submersible program. Highly recommended by the University of Hawaii's Marlin Atkinson, who was a member of our coral lagoon team, I had hired Allen. So, I felt somewhat responsible for his layoff. It occurred to me that he would be a perfect match for Klaus in his struggle to develop a means to capture  $\text{CO}_2$  from the atmosphere.



Photo credit: Kimberly Martineau.

**Figure 33a**

Klaus Lackner, now a professor in Columbia University's Department of Earth and Environmental Engineering, received his PhD in particle physics in Heidelberg, Germany. He is shown here with a glove box designed to demonstrate his amazing solid absorber for  $\text{CO}_2$  capture from air.

I suggested to Klaus that he and Allen start a company dedicated to developing a device capable of capturing  $\text{CO}_2$  from the atmosphere. "Good idea, but where will we get the money?" was his reply. I had my answer ready. "Gary Comer!" So, once again, Gary made the trip to Teterboro Airport in his big jet. He brought along Bill Schleicher who managed his family foundation. They arranged for us to meet in a conference room in the private plane terminal. So it was that General Research Technologies (GRT) was born. Allen and Klaus convinced Gary to put up 5 million dollars in venture capital to support the enterprise. After the deal was set, Schleicher commented that rather than being venture capital, it was

“adventure” capital. Allen, who was to serve as president of this new enterprise, immediately began the process of renting the required space, purchasing the equipment and hiring the personnel. Klaus remained a Columbia employee and commuted to Tucson as time permitted.

Sodium hydroxide was the logical choice as the CO<sub>2</sub> absorbent, so the first two years were spent experimenting with it. In one apparatus, NaOH was recycled by allowing it to flow down plastic strips. This strategy was rejected because tiny droplets of this highly corrosive liquid were entrained in the air stream. In another, NaOH filled the pores in the spongy material employed by florists. This strategy was rejected when no method could be found to reduce the large energy penalty associated with getting the CO<sub>2</sub> back off the NaOH. In the meantime, Klaus and Allen searched for a suitable solid absorber. After some false tries, they hit upon a commercial plastic with imbedded solid amine “islands”. It came in thin sheets used for water purification. Allen cut the sheets into spaghetti sized fibres and mounted these on a stiff wire making something resembling a bottle brush. To their amazement, these brushes absorbed enormous amounts of CO<sub>2</sub>. Then, when either bathed in water or exposed to water vapour, the CO<sub>2</sub> came off. This CO<sub>2</sub>-H<sub>2</sub>O cycle could be repeated hundreds of times, with no loss in uptake capacity. Most important, the energy expenditure associated with the removal of the CO<sub>2</sub> was only one fifth that for NaOH.

Having found a suitable absorbent, the next step was to design the basic unit. Lackner is a proponent of modules (Fig. 33b). Unlike major power plants, which are designed to last 50 years, modules can be replaced with improved versions as they become available, as are automobiles and computers. Klaus envisions a module capable of capturing one ton of CO<sub>2</sub> a day (i.e. the average amount produced by 20 U.S. automobiles). All the module’s pieces would be designed to fit into a standard shipping container. When assembled, a ring of 30 mattress shaped absorbers would be placed in a rotating ring above the container. Thirty more absorbers would reside in a series of iron chests placed in the container. Each mattress would spend about an hour in the uptake mode exposed to the wind and then an hour in the removal mode in the chambers. An elevator would serve to move them back and forth.

The extraction would be accomplished by spraying the mattress with liquid water. Of course, prior to this treatment, the chamber would have to be evacuated. Once the CO<sub>2</sub> was released from the fibres, the remaining liquid water would be pumped out of the chamber. The CO<sub>2</sub> and water vapour mixture would then be compressed. Most of the water vapour would condense and be recycled. The CO<sub>2</sub> would be dried and further compressed until it liquefied and then would be piped to a nearby storage site. Lackner projects that the price of each unit would be about the same as an automobile. Hence, the modules could be financed by placing a 5% surcharge on the purchase of automobiles. The cost of operating these devices would add 10 to 15% to the cost of U.S. gasoline. Of course, in order to compensate for CO<sub>2</sub> emissions by the 70 million automobiles presently on our



planet, 3.5 million of these modules would have to be deployed. With 20 or so million autos manufactured each year in the U.S., constructing these modules would lie well within our industrial capacity.



**Figure 33b**

Lackner's device for capturing CO<sub>2</sub> directly from the atmosphere. The air that passes through the ring of mattress-shaped filters loses about 30% of its CO<sub>2</sub> to a solid absorber. The mattresses are traded one at a time for recycled equivalents that have had their CO<sub>2</sub> removed by water in the sealed chambers. The CO<sub>2</sub> captured in this way is liquefied and piped to storage. Each of these modules is designed to capture one ton of CO<sub>2</sub> per day (i.e. the amount produced by 20 automobiles). The cost to manufacture each unit is expected to be about that for an automobile. The cost for capturing and storing the CO<sub>2</sub> would require an increase in U.S. gasoline prices of about \$0.30 per gallon.

Klaus has a long range vision. He realises that once the CO<sub>2</sub> rise has been stemmed, there would be a desire to bring its level in the atmosphere back down. His units could do the job. He also has thoughts about how to fuel our transportation fleet once our petroleum reserves run out. He envisions the manufacture of inorganic "gasoline", by combining hydrogen separated from water (using solar energy) with CO<sub>2</sub> captured from the atmosphere. Late in the summer of 2008, Klaus hit the road seeking \$20 million of venture capital to construct prototypes of his module. Realising that in order to attract this capital he needed interim uses for his device before the world woke up to the need to use it for CO<sub>2</sub> capture and storage, so he sought other markets. At that time, energy costs were at an all time high so he envisioned a first use of his device to produce CO<sub>2</sub> for the soft drink industry. Further, he had his eye on supplying CO<sub>2</sub> to be used to flush residual petroleum from oil fields but before he could sell his idea, the great financial implosion of October 2008 occurred and venture capital disappeared.



GRT ran out of Comer money and had to shut down. Klaus and Allen went into hibernation. Allen moved to New York and took a job at Columbia in Lackner's Lenfest Energy Center. Two years later the search for venture capital took a new turn. With reduced energy costs, Lackner's device could no longer compete with conventional sources for soft drink CO<sub>2</sub> but a new industry had appeared, growing algae to be used as a source of liquid fuel. In the ponds in which algae are grown, CO<sub>2</sub> becomes the limiting nutrient. Klaus, to the rescue! Armed with venture capital, a new company called Kilimanjaro was born.

There is something bizarre about this. It is clear that we must stem the rise of CO<sub>2</sub> and that it will be a long time before we can substitute other sources of energy for fossil fuels. Hence, in the interim, CO<sub>2</sub> capture and storage will be required. Lackner has found a very promising means of capturing CO<sub>2</sub> from the atmosphere. Yet as of 2011, no government or industry or major foundation has seen fit to finance its development. So far only about \$8 million has been spent. This is what a New York Yankee pitcher makes in a single season. It's interesting how wrong first impressions can be. When I encountered Klaus in Ottawa, I wrote him off as a nut. I now consider him far and away the most brilliant person I've ever known! I wonder how long it will take for others to reach the same conclusion.

## 34. ICELAND

In 2005, at the University in Reykjavik, I gave a lecture on global warming and the need for carbon capture and storage. Iceland's President, Olafur Ragnar Grimsson, was in the audience. Afterward, he told me that he wanted his country to be the first in the world to become CO<sub>2</sub> neutral. Building on this interest, a group of us suggested that an experiment be conducted in Iceland to determine whether it was feasible to dispose of CO<sub>2</sub> by injecting it into basalt. This mode of disposal would have the advantage that the CO<sub>2</sub> would be chemically fixed, rather than merely stored, as would be the case if it were injected into sandstone. In basalt, the CO<sub>2</sub> would react with Mg and Ca bearing minerals, transforming the CO<sub>2</sub> from gaseous to mineral form, preventing escape to the atmosphere and totally immobilising the carbon.

So it was that scientists from the University of Iceland and the University of Toulouse joined forces with several of us at Lamont to design a pilot experiment. At Grimsson's encouragement, Reykjavik Energy Company offered to join in this enterprise. Our first problem was to locate a source of CO<sub>2</sub>. Purchase from abroad was quickly ruled out as too expensive. We were aware that in Iceland's aluminium plants, the oxygen in the ore was removed by reacting it with charcoal to form CO<sub>2</sub> but it proved impractical to capture and transport this CO<sub>2</sub> to the injection site. So we settled on the small amount of CO<sub>2</sub> present in the high temperature steam that fuelled the electricity generating plants in the rift zone.



Reykjavik Energy Company offered to isolate this CO<sub>2</sub> and pipe it to a 500 metre deep well that they had drilled into the underlying basalt two kilometres away from one of their power plants (Fig. 34; Gislason *et al.*, 2010).

The next question was whether to inject the CO<sub>2</sub> “dry” or dissolved in water. It was quickly agreed that because we wanted to get answers in the shortest possible time scale, we would dissolve the CO<sub>2</sub> in water. If the CO<sub>2</sub> were injected dry, it would not react with the basalt until it had dissolved in the formation water. We decided to inject the CO<sub>2</sub> at a pressure of 25 atmospheres into water piped in from a nearby reservoir because at the low pH this would generate, the Mg bearing minerals (pyroxene and olivine) would preferentially dissolve. This was advantageous because the basalt’s Ca bearing feldspars would provide aluminium which would form clay minerals. We feared that these clays would coat the surfaces of the unreacted basalt, slowing down the reaction.



Photo credit: Sigfrús Már Pétursson.

**Figure 34**

Air photo of one of the two geothermal power plants located in Iceland’s rift valley. The 300 °C steam that fuels these plants contains about 1% CO<sub>2</sub>. This CO<sub>2</sub> is being separated from the steam and also from the CH<sub>4</sub> and N<sub>2</sub> that it also contains. It is then piped 2 km to the northwest and injected into basalt at a depth of 500 metres. The purpose of this experiment is to evaluate the suitability of basalt for the storage of CO<sub>2</sub> removed from the atmosphere.

Our strategy to monitor reaction progress was to inject the carbonated water in one well and then sample the water from downstream wells as it moved through the aquifer. In order to assess the flow rate, we conducted a preliminary injection of water tagged with SF<sub>6</sub>, a gas that could be detected by gas chromatography at extremely low concentrations. We found that the flow rate was an





order of magnitude lower than expected, so our plan had to be modified to include pumping water out of one of the downstream wells. One more innovation was decided upon. We would tag the injected CO<sub>2</sub> with radiocarbon, so we could distinguish the bicarbonate formed as a result of the injection from that initially present in the aquifer (Matter *et al.*, 2011).

There was an additional challenge before injection could begin. In addition to CO<sub>2</sub>, the geothermal steam contains H<sub>2</sub>S, N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>. The aim was to remove these gases from the CO<sub>2</sub>. In the case of H<sub>2</sub>S, the fear was that it would become oxidised to H<sub>2</sub>SO<sub>4</sub> and then we would be dissolving basalt with a strong acid instead of with CO<sub>2</sub>. N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> are far less soluble in water than CO<sub>2</sub>, so if they were not removed, we would be forced to use a far higher ratio of H<sub>2</sub>O to gas. The separation plant was built, and troubles with the distillation unit delayed its implementation, but injection began in 2012. Together with a multitude of laboratory experiments done by the Reykjavik, Toulouse and Lamont teams and their associates, these field tests will point to ways to optimise the system. However, without the \$10 million of financial support and the world class expertise and equipment supplied by the Reykjavik Energy Company, this experiment could never have begun. Thanks to the foresight of President Grímsson, this small country of 300,000 people has stepped forward to accept a common responsibility and leads the world in per capita contributions to stemming the build up of CO<sub>2</sub> in our atmosphere.

## 35. WHAT'S LEFT TO DO?

I was lucky to have entered the field of Earth science at a very special time. The use of isotopes, which had gained traction during the 1930s, stalled with the onset of World War II. Then, during the late 1940s, armed with technology developed during the war years, isotope research once again picked up with a vengeance so in 1952, when I came to Columbia, it was going full blast. However, there were only a few professionals involved. It was the first wave of PhD students that reaped the initial harvest of new discoveries. We and our graduate students picked the glut of low hanging fruit. Now, almost 60 years later, you might ask, "What's left to be done?" The answer is "plenty." Even though the once unified field of geochemistry has been subdivided into many specialties, in each, just as many important questions remain to be answered as we, the pioneers, had before us. Research creates more new questions than it answers. My research has been centred on two main topics: how the Earth's carbon cycle operates and how the Earth's climate responds to forcing. Atmospheric CO<sub>2</sub> content is one of the main climate drivers so these two subjects are strongly linked. I see, in the near future, several extensions of my research. One has to do with the glacial to interglacial changes in atmospheric CO<sub>2</sub> content. Despite much thought and a host of measurements, we still have not come up with a satisfactory explanation





for these swings. Because of this, those attempting to simulate glacial cycles are forced to estimate the atmosphere's CO<sub>2</sub> content. This is unsatisfactory because CO<sub>2</sub> has driven much of the climate change (Stocker and Schmittner, 1997; Severinghaus *et al.* 2009). Until we have models that can generate the CO<sub>2</sub> changes, instead of prescribing them, it will not be possible to fully understand how the cyclic changes in the Earth's orbital climate pace glaciation.

The late Roger Revelle referred to the build up of fossil fuel CO<sub>2</sub> in the atmosphere as man's greatest geophysical experiment (Revelle, 1982). It will impact everything that takes place on the Earth's surface. We scientists will have the opportunity to observe these impacts. One such impact will probably be a slow down in ocean circulation because as the upper ocean is warmed, the vertical gradient in density will steepen, thus impeding the movement of surface waters into the ocean's depths. Although simulations carried out in ocean-atmosphere models will provide clues regarding what will happen, it will be necessary to verify them with observations. Key will be following the invasion of bomb test <sup>14</sup>C and of man made CFCs (chlorinated fluorocarbon) compounds as they penetrate ever deeper into the ocean.

Another area of research looming on the horizon is the development of means to verify the treaties designed to slow the ongoing build up of CO<sub>2</sub> in our atmosphere. No matter how this slowdown is accomplished, it will cost money and this will give rise to incentives to cheat. Thus, one of the prerequisites for the implementation of a comprehensive treaty will be the ability to verify that each nation is fulfilling its promises. A key element in verification will be the creation of a means to deconvolve CO<sub>2</sub> emissions from individual regions through measurements of the spatial distribution of CO<sub>2</sub> in the atmosphere. This poses a huge challenge. The major emitters are arrayed in a belt across the temperate zone of the Northern Hemisphere so it is the longitudinal gradients that carry the required information. These gradients are quite small and tend to be obscured by much larger vertical gradients over the continents. Further, the records in hand reveal that year to year variations in the photosynthetic uptake of CO<sub>2</sub> introduce noise that could easily be confused with deviations from agreed upon emission limits. To monitor correctly and fairly will require an array of CO<sub>2</sub> sensing satellites, ocean buoys equipped to measure CO<sub>2</sub> partial pressure, flux towers to monitor continental fluxes. All this information will have to be fed into a new generation of atmosphere models. You, the scientists of the future, will have to create these observational networks and evaluate the output of the computer simulations used to deconvolve the geographic distribution of CO<sub>2</sub> fluxes – a daunting task.

It will be many decades before society's reliance on fossil fuels to power the planet can be replaced by renewable energy. During this transition period, CO<sub>2</sub> will have to be pulled out of electrical power plant exhaust and directly removed from the atmosphere. The captured CO<sub>2</sub> will have to be stored. How to both capture and store CO<sub>2</sub> safely, economically and verifiably will require much research. Geochemists will have an important role in storing CO<sub>2</sub>. While initially



CO<sub>2</sub> will likely be liquefied and pumped into pores in subsurface sandstones, in the future, it would be better to react the CO<sub>2</sub> with igneous rocks rich in Mg and Ca. If stored in sandstone, there is little for the CO<sub>2</sub> to react with because the bulk of sandstone is quartz, which has no cations (Oelkers *et al.*, 2008). Hence there is a possibility that the stored CO<sub>2</sub> could escape either slowly or perhaps even catastrophically. If instead, the CO<sub>2</sub> were injected into basalt or other reactive, porous rock, it would react with the magnesium and calcium bearing minerals and be converted to carbonate minerals, such as MgCO<sub>3</sub> and CaCO<sub>3</sub>, immobilising the carbon for geological timescales (Matter and Kelemen, 2009). However, because it takes time for weathering reactions to occur, the possibility for CO<sub>2</sub> escape would be reduced but not eliminated. An even better solution would be to mine and crush rock rich in magnesium and perform the reaction with CO<sub>2</sub> above ground. In this case, the target would be ultrabasic rock which is rich in olivine (Mg<sub>2</sub>SiO<sub>4</sub>) and pyroxene (MgSiO<sub>3</sub>). While this mode of storage would eliminate the threat of leakage, it currently requires too much energy.

Allocation of water for agriculture, already a major issue, will become ever more important. There will be more mouths to feed and grain yields will likely decrease as the world warms. Further, the availability of subsurface water will dwindle as ever more is pumped from aquifers (Schwartz and Ibaraki, 2011). The demand for better understanding about how the Earth's hydrologic system operates will increase. The heavy isotopes of water have much to offer in this regard. Not only do they offer insight into how water is currently cycled but they also shed light on how this cycle changed during past times when climate differed. Incredible improvements in the techniques for measuring isotope ratios have recently become available. No longer does this require mass spectrometers. Rather, a laser based technique allows *in situ* measurements of the isotopic composition of water vapour (Kerstel *et al.*, 1999). The archives of oxygen in stalagmites and ice core allow us to collect remarkably detailed and chronologically correct records of past changes (Groote *et al.*, 1993).

One thing is clear. There will be a shift in emphasis in the directions of research. Less and less resources will be available to conduct research for its own sake, to find out why. Rather, scientists will be pushed more and more to do research that has a direct impact on societal problems, i.e. that is considered "strategic" by policy makers and funding bodies. Sustainability will be a central theme, as we humans continue to push the Earth system to its very limits.



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