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# Threads: A Life in Geochemistry

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0084-6597/06/0530-0001\$20.00 I returned and saw under the sun, that the race is not to the swift, nor the battle to the strong, neither yet bread to the wise, nor yet riches to men of understanding, nor yet favour to men of skill; but time and chance happeneth to them all. Ecclesiastes 9:11

(King James version)

# BEGINNINGS

My father and mother were Armenian, survivors of the events of 1915 in Turkey that destroyed most of both their families. My father, while in his teens, had been sent by his family to the United States before World War I to be with his older brother, who had become an American citizen. With his family destroyed in 1915, including his American brother who had returned to Turkey to discover the fate of his family, he was "adopted" by Yankee families of New Bedford, Massachusetts. When the United States entered the war, he became a naturalized citizen, enlisted in the army, and went to fight in France—returning as an infantry sergeant. Several years after the war, some of the few living survivors of the events of 1915 made their way westward, often through Cuba, to the United States. While on a mission to Cuba to bring the widow and children of his deceased oldest brother to the United States, my father met and married my mother—herself a survivor, thanks to the protection of American and Danish missionaries.

Two years after my birth, almost to the day, the great crash on Wall Street occurred, but another more ominous cloud had settled on our family—my father began to develop, bit by bit, the features of an unrelentingly disabling disease we now know as multiple sclerosis. This may not have seemed to be a great way for a young boy to start his life, but the strength of the family preserved the image of America as a land of boundless opportunity for the person willing to strive after it.

My mother traded on her childhood skills of needlework to become a seamstress; all her sewing was done at home so she could care for both her incapacitated husband and growing son. My memories of those days focus on my carrying boxes of unfinished ties from a Union City (New Jersey) factory to our apartment in West New York and returning the excellently crafted work from my mother's hand for which a small sum of money was given. My father fought hard against the ultimate weakening that was overcoming him. He forced himself to thread the needles for my mother. He insisted on reading *The New York Times* to be aware and keep his intellect sharp. The dedication of my mother and father to learning and intellectual matters influenced me deeply. (My greatest relief came when the old Ralph Ingersoll newspaper, PM, became part of our family reading because there, at last, was a comic strip—Barnaby!)

Listening to the radio with my father was one of the high points of my evenings especially on Wednesday nights when the Cavalcade of America was broadcast under the sponsorship of DuPont. The one message that program transmitted over and over to me was, "Better things for better living through chemistry." This vision competed heavily with the dream of my devout Christian mother whose highest aspiration for me was to become a minister—perhaps to certify the faith she felt so many Armenians had died for.

When the United States entered World War II, I had just turned 14. I had been advanced in school so I finished high school just as I became 17 and I was ready to join the Navy. Parental permission was required. My mother said she would sign the permission form only if I went to college for one semester, in the hope, I suspect, that that would start me on my path to the ministry. So I went off to Wheaton College in Illinois—most famous in the past few years as the school attended by the Reverend Billy Graham.

I obeyed and my mother kept her word, which I knew she would, and her only child went off to the war on July 4, 1945. Well, almost to war but not quite—VJ day was August 14, 1945, just as I was finishing boot camp! Anyway, the Navy had taken me on to train me as a radio technician because I had passed the "Eddy test" (a test devised by a Captain Eddy responsible for identifying potential enlistees for training as radar technicians) on enlisting, and by March I was a petty officer—aviation electronic technician's mate third class, and about 14 months after my enlistment I was discharged and returned to college at the tender age of 18.

The GI bill, credits earned in the Navy, wages earned working at school and during the summer, and merit scholarships got me through college financially. My Navy experience convinced me that I could not be a minister, but perhaps I could make up for the personal deficiency by becoming a medical missionary. By that rationalization, I accepted my fate as a chemistry major with the relish of a sinner—the words of the serpent in my Garden of Eden echoing, "Better things for better living through chemistry."

My taste for medicine was not very strong except for its obvious good to humankind endorsed by my mother. It was made less strong by the senseless memorization in a comparative anatomy class taught by a teacher who could not believe in evolution!

Salvation takes many forms. For me, it was my inability to make the sine-qua-non Grignard reaction work in organic chemistry laboratory because the postwar stoppers were of terrible quality. My professor said he would let me off the hook if I worked with him synthesizing sulfa compounds—a project he had started during the war.

As I worked on these compounds—remembering that they and penicillin had literally saved my life in a Navy hospital when I had contracted a very bad case of pneumonia—I realized that helping humankind meant not only hands-on helping but also more detached helping such as discovering ways to improve the human weal—"better things for better living through chemistry"—Eureka, the answer was there!

I must bring another thread to my story at this point. My third grade teacher, Miss Robertori, instilled in me a love for the geography of far-off places. She reinforced my father's Sunday morning yarns about France, Cutty Hunk Island, Prince Edward Island, and other places that were real only in my imagination. With every penny I earned I sent away for topographic sheets from around the United States. I looked to these maps to describe places I had heard of but had not seen as a boy growing up in Brooklyn, Hudson County (New Jersey), and ultimately the Bronx.

## **COLUMBIA**

I didn't take a geology course at Wheaton, but I did go along on a field trip on glacial features in Illinois with my then girlfriend one day when I was visiting from the Navy. I was all set to go to graduate school in organic chemistry when J. Laurence Kulp, a Wheaton chemistry alumnus, Princeton PhD, and an instructor at Columbia

University, wrote the chairman of the Wheaton Chemistry Department to ask if there were any promising chemistry majors graduating who would like to enter a new program in geochemistry at Columbia University.

Somehow it seemed the right thing for me. The subject I loved mixed with the interest I had developed unconsciously since third grade and a chance to return home to New York all worked together to make me accept the offer.

As it turned out, I was the first of a long string of Wheaton College students who were serially recruited for geochemistry at Columbia by Larry Kulp. Walter Eckelmann, Paul Gast, and Wallace Broecker soon followed me to the then new and idyllic Lamont Geological Observatory of Columbia University in the tiny town of Palisades, New York.

When I joined the nascent geochemistry group at Columbia in 1949, the Lamont Geological Observatory (now the Lamont-Doherty Earth Observatory) was just inaugurated. The geophysics and geochemistry groups were divided between Schermerhorn Hall on the Columbia Morningside Campus and Lamont Hall. My lab and the machine shop, among other things, remained at Schermerhorn Hall until adequate space was constructed on the Palisades facility.

I was given a new emission spectrograph and told to make it work. My ultimate assignment was to initiate a program for dating limestones by the presumed monotonic increase <sup>87</sup>Sr/<sup>86</sup>Sr in seawater over time. This idea was proposed by Franz Wickman (Wickman 1948), a creative Swedish geochemist, on the basis of an average Rb/Sr for the crust of Earth undergoing weathering while <sup>87</sup>Sr was continuously generated by the decay of <sup>87</sup>Rb( $\lambda = 1.42 \times 10^{-10}$  years<sup>-1</sup>).

My initial task was to survey all the limestones and fossils I could gather from collections at Columbia and from elsewhere (Kulp et al. 1952) and to develop a method of isolating milligram quantities of Sr for the ultimate isotopic measurement yet to be developed.

Developing the spectro-analytical technique was aided by spending the summer of 1950 at the United States Geological Survey (USGS) laboratory in Washington, DC, under the tutelage of Jack Murata—an extraordinarily kind and patient man who taught me more than emission spectrography. I met a lot of the Survey crowd, so my respect for that organization and its scientists has always remained with me.

My attention to tracking strontium isotope growth in limestones for dating purposes was part of the drive at several institutions to develop geochronometric methods for dating a variety of rocks by a variety of methods. The three major competing universities were the University of Chicago, MIT, and Columbia. But two components of the Carnegie Institution of Washington had also entered the fray—the Geophysical Laboratory and the Department of Terrestrial Magnetism. There was also serious mass spectrometer development going on at the University of Minnesota under Alfred Nier, who was the godfather of much of this effort when it first developed. Along the way, a strong presence in mass spectrometry developed at the Bureau of Standards in Washington (now NIST).

When Paul Gast, also from Wheaton College, joined the Lamont group, Larry Kulp sent him to the Department of Terrestrial Magnetism to learn the thermal ionization mass spectrometric techniques necessary for geochronometry using the <sup>87</sup>Rb-<sup>87</sup>Sr system as well as the U,Th/Pb systems.

When Paul was in Washington he ran three limestone samples of a wide range of geological ages for <sup>87</sup>Sr/<sup>86</sup>Sr and found that the values did not form a monotonically increasing trend with time (Gast 1955). This remarkable set of measurements turned my thesis away from developing a limestone chronometer to trying to find out what Rb and Sr were behaving like in the vast geologic realm. Because Rb was being studied by a group at the University of Minnesota, I put all my attention on Sr. As in the case of limestones, I analyzed every rock I could put my hands on and many minerals for their Sr concentrations.

This grand, comprehensive study became my thesis: "The Geochemistry of Strontium" (Turekian & Kulp 1956). With the rapid development of interest in the Sr isotope systematics, including dating, the amount of mass spectrometric Sr data has grown with time, but when I made the survey it provided not only the first exploration but also shaped a lot of my future research interests. Indeed, the threads to a number of problems I became enthralled by were established by this seminal experience as a graduate student. These include paleoecology, magmatic evolution, deep-sea sediments and paleoceanography, planetary history, and geochemical archaeology.

A second component of life as a graduate student at Columbia was the intense interaction with fellow students. On Saturday afternoons (so designed so that our work in the lab through Saturday morning would not be interfered with) we met for seminars to discuss the ongoing developments in geochemistry both in the literature and our individual laboratories. The sessions were always intense and long but the breadth of geochemistry was hammered into all our heads. Many future ideas at Columbia and wherever we each ended up came from these rumbles. The corridors of the geochemistry labs reverberated with the sounds of debate long after the seminars.

Life at Columbia was exciting. The Saturday geochemistry seminars at Lamont honed our skills and made us aware of the great field of geochemistry then coming into existence. The descriptive mineralogy and petrology of the past was giving way to the experimental and theoretical approaches of the present led by the Geophysical Laboratory of the Carnegie Institution of Washington. We thought all of this to be the legitimate area of geochemistry. The quest for the age of Earth and the ages of rocks was also an important aspect of geochemistry. Even the origin of ore deposits was considered to be nothing but a special case of concentrating elements in Earth and therefore also geochemistry. As I think back, I realize that geochemistry had come to mean understanding how Earth and other planets operated. That view has controlled my life since. Most of us have applied our geochemical thinking and methodology to broad problems such as climatology or the origin of Earth. I am eternally grateful that I had been given the opportunity to develop these insights at Columbia. My thesis was a great education both in patience and geology. The latter led me from the Bahamas to Montana and focused my interest on unusual places in the world I never would visit.

In all of this pursuit I was being well educated by my professors at Columbia. Walter Bucher taught me that thinking was more important than being right; Norman Newell and John Imbrie showed me how to understand shallow marine environments of carbonate systems in the Bahamas and ultimately provided my approach to ecology and paleoecology. Marshall Kay taught me how to extract history from sedimentary rocks, and by his lectures provided me with notes for the beginning historical geology class I taught later on at Yale. (Yale was the home of the classic book Historical Geology by Schuchert & Dunbar, and there I was, teaching the geosynclinal heresies of my teacher at Columbia. My historical geology teaching assistants used to chant on the way to coffee, "All the way with Marshall Kay," in recognition of this rebellious act of mine.) Arie Poldervaart taught me the ways of a field petrologist as I explored the Beartooth Range and collected from the Stillwater Complex in Montana as part of my thesis research into the geochemistry of strontium. Larry Kulp, my advisor, always encouraged me to benefit from all these men and did not constrain me to a simple narrowly prescribed geochemistry training. For this wisdom I am beholden to him. My last act at Columbia in transition to Yale was to sample the Greenland ice cap at the classified early warning location known as Site 2 for snow samples for tritium analyses by Bruno Giletti, a fellow student. The traverse of the entire west coast of Greenland, after my descent into a 100-ft hole in the cap for sampling (in 1956 the drilling of the ice caps had not yet been achieved), provided me not only with a good idea of Greenland geography and civilization but also let me collect rocks, which influenced the career of one of my future students, Richard L. Armstrong.

At Columbia the organized (?) and disorganized encounters with my geochemical colleagues led to papers outside my general pursuit of the geochemistry of strontium that were published after I had arrived at Yale. I give two examples below.

I had developed a rapid method for analyzing sediments and sedimentary rocks for total carbonate. Wally Broecker and I decided to analyze an Atlantic equatorial core raised by Bruce Heezen aboard the Atlantis (A180-74) for radiocarbon (Wally Broecker's thesis interest) and carbonate to determine the change in accumulation rates of clay and carbonate across the glacial-postglacial boundary determined by David Ericson using Globorotalia menardii as the index foram. We established that the boundary was at about 11,000 years BP and that the accumulation rates of both clay and carbonate were higher during glacial times than postglacial times, with the clay fraction showing the largest change (Broecker et al. 1958). We found intermediate rates in the so-called interstadial from 26,000 years to about 44,000 years. By combining those clay accumulation rate histories we inferred that the end of the penultimate glaciation was about 150,000 years BP. Later, by the <sup>238</sup>U-<sup>230</sup>Th dating method, the actual date was inferred to be about 130,000 years BP. One problem we didn't quite understand was why the extrapolation to the topmost part of the core yielded a value of about 2000 years BP. We guessed that either the top part of the core was missing or that some sort of mixing had occurred. Not until we obtained a core with a submersible (the Alvin) did we at Yale solve the problem. It was indeed mixing and the depth and rate could be determined with <sup>210</sup>Pb (mixing) and <sup>14</sup>C (depth). Nozaki et al. (1977) solved the problem. Indeed based on our work in estuarine deposits and other types of deep-sea deposits, an average depth of mixing of about 8 cm seemed to be universal (Turekian et al. 1978).

The other example is based on a challenge I made to the rate of degassing of rare gases estimates made by another fellow student, Paul Damon (Damon & Kulp 1958). I wrote a separate interpretation and this led to an interest not only in planetary degassing but also the origin and composition of Earth on one side and cosmic ray and solar interactions in the atmosphere on the other (Turekian 1959). The work on the degassing of the planet led to the recognition that our knowledge of the composition of Earth was not at all complete. This led to a series of explorations, starting with the proposal of a nonhomogeneous accumulation of planets during condensation and accretion (Turekian & Clark 1969).

Both of these early engagements influenced my thinking and interests thereafter.

# YALE

I was offered an Assistant Professorship at Yale to start on July 1, 1956. I turned down several other posts (geochemists were in big demand that year) in part because Yale was close to New York where my father languished in a Veteran's Administration hospital and my mother was alone taking care of herself with complete self-confidence (after all, she was willing to see her son go off to war and then to a far away college and possibly to a far off land as a medical missionary!). Yale was the right place for these reasons among others, although at that time Yale was all male and the coeds at the University of Texas, another job possibility, held a great charm for a young bachelor.

I arrived at Yale and started a geochemistry program there. I startled everyone, I think, when I offered to teach the beginning "tough" course in geology. It may have been arrogant on my part but I did want to firm up my background in geology as a geochemist. I had the opportunity to do this first as a Lecturer in Columbia College during my graduate student days. This was a position that allowed me to teach a major part of the undergraduate program at Columbia College for the year because of the sudden illness of the primary professor, Armin K. Lobeck. What an opportunity and what a lot of work! I figured Yale couldn't be any worse than that, and anyway, I would show that a geochemist could do anything—such moxie!

I recruited three undergraduates to be fledgling geochemists. One, Richard L. Armstrong, set up a dating lab using neutron activation analysis to measure argon isotopes for potassium-argon dating and applied it to the ensemble of rocks I had collected from Greenland, as we shall see later. My first graduate student was a Yorkshireman named Michael Carr. He started life at the University of London as a regional geologist and took on the geochemistry banner at Yale. He subsequently became chief of the Astrogeology Branch of the USGS and wrote a definitive book, *The Surface of Mars*, based on the Viking project for the exploration of Mars in 1976. Another graduate student who was recruited to geochemistry during my first year at Yale was Rama Murthy. He was transported (literally, in my car) to Caltech to work with Claire Patterson after graduation and has followed a distinguished career in academia since then.

All in all, my initial experiences at Yale were very exciting and my influence for geochemistry was evident. My undergraduate and graduate students brought excitement to my life at Yale then and this has continued to the present day.

My first experience in open-ocean oceanography occurred in the winter of 1961. Maurice Ewing, the director of the Lamont Geological Observatory, did not like the idea of geochemists going aboard the Vema, the Columbia research vessel, but Wally Broecker and I convinced him in a weak moment that we should go aboard. His acquiescence started the enterprise that arguably was the predecessor to the Geochemical Ocean Section Study (GEOSECS) program several years later.

In 1962, in what was considered to be a very low probability event according to Paul Gast and Wally Broecker, I met and married Roxanne. The probability argument ran as follows. I said I was waiting for a beautiful intelligent girl of Protestant Armenian extraction who would be willing to marry me. Because the Protestants make up only ten percent of all Armenians (including William Saroyan and Ara Parseghian) and because Armenians were so sparse, especially after the 1915 massacres, the pool was obviously quite small. The beautiful and intelligent conditions obviously also put constraints on the search, but the greatest constraint had to be the willingness of that person to link up with a rambunctious geochemist. I beat the odds as anyone who has met Roxanne will attest.

I was living, when I got married, in one of the residence houses (called Colleges at Yale and Houses at Harvard, but both the consequences of the largesse of Harkness who wanted to establish Oxford and Cambridge in the New World). It was an all male environment with no women except the Master's wife living in the college. Only by a special act of the Yale Corporation was Roxie allowed to move in with me in my quarters after we got married! She could be said to have been the first to have broken the gender barrier at Yale and I guess I had then, in effect, married a feminist icon.

Before we could fully exploit this new standing we went off to Cambridge University on a Guggenheim Fellowship. There I was formally associated with the Geophysics Department run by Teddy Bullard but I spent time at the Mineralogy and Petrology, Geology, and Botany Departments doing research on eclogites, coccoliths, and trace elements. I also hung around with my old Columbia classmate Dick Chorley, who was in the Geography Department. I guess, as an American I was permitted the luxury of penetrating the walls that literally separated these groups. Not until Ron Oxburgh became king of Earth sciences at Cambridge were some of these walls toppled! Geophysics at Cambridge was on Maddingly Rise, away from the central campus. Space was very limited. It turned out that Walter Munk, Bill Menard, and I were all visiting Cambridge at the same time and we were all at Maddingly Rise. Teddy Bullard said that the three of us would have to share a small map room. Luckily, Walter left soon for the Soviet Union and Bill and I worked out a time-sharing routine because I had a few other places I was going to anyway. That was the year of the Cuban missile crisis. We worried about Walter driving through the Russian countryside and how he would be treated. He reported on his return, with family in tow, that the hinterlands didn't know anything about the crisis and it didn't affect the way they were treated (nicely) anyway.

While we were in Cambridge, a small rebellion began brewing in our department at Yale that came to a head the following year. The issue was how our department was going to grow, if at all. The chairman, Richard Foster Flint, had stated that no new appointments were going to be made in our department. Syd Clark (whom I had helped to recruit so we could make an entry into the field of geophysics) and I asked the Provost if that were indeed true because if it were (especially so far as the fields of geochemistry and geophysics were concerned) it would mean it was a good time to leave Yale. We were assured that that was not the intention of the Provost but rather the areas in which appointments were to be made and how they were to be made were at issue. Until then, chairmanships were without term. This meant that a change in policy involved a change in chairman. Thus came into being the rotating chairmanship at Yale, and our department was the first to follow that pattern.

The department changed dramatically after the new pattern was established. Three senior faculty left and several people in new fields were brought in. The department was now changing to a broader one with new disciplines and new approaches to old disciplines. After the turmoil (or as one person described it—the contained explosion) the department grew into its present recognizable form. Richard Foster Flint retired with full honors and a fine colloquium on "The Late Cenozoic Glacial Ages," which I organized with much help and edited the Yale University Press book of the same title.

## **TRACE ELEMENTS**

"When all you have is a hammer everything becomes a nail." So said Harmon Craig (and he probably got some variant of this from someone else). I had an emission spectrograph and a massive collection of deep-sea sediments as well as rocks of all types at my disposal because of where I was as a graduate student and what my thesis was.

Analysis of deep-sea cores for elements other than Sr resulted in an appreciation of the value of coupled studies. An example of this was the case of Atlantic equatorial cores that Broecker and I had analyzed for rates of accumulation of various components. This approach arose from the test of an experiment that Hans Pettersson had done to determine the meteorite dust flux to Earth's surface by measuring the Ni concentration of air samples in Hawaii (Pettersson 1958). Analyses of the Atlantic Equatorial cores for accumulation rates logically led to measuring the Ni flux. The fact that the Ni concentration of the clay fraction of these cores was constant across the large variation in accumulation rates indicated that Ni as well as many other trace metals were of terrestrial origin and did not provide an estimate of cosmic matter accumulation rate (Turekian 1958). Many years later Esser & Turekian (1988) used Os isotopes and sediment accumulation rates in the Pacific Ocean to determine the meteorite dust flux.

I did not publish most of the trace element data on cores that I had accumulated at Lamont until I went to Yale and set up an emission spectrograph there. By then I realized how poor data were for many of the elements in rocks. I decided to make a table of element concentrations in major units of Earth's crust based on work that had been done to date. I used the model of Suess and Urey, who constructed a table of cosmic abundances from acceptable meteorite data (assisted in no small part by Craig and Urey as they established the criteria for reliable analyses and discovered the diversity of chondritic classes). I discovered that Hans Wedepohl at Gottingen (the home of V.M. Goldschmidt, the "father of geochemistry") was attempting the same thing, so we pooled our resources and published a table with sources and modes of extrapolation and interpolation in the *Geological Society of America Bulletin* in 1961 (Turekian & Wedepohl 1961). This table was used for many years by many geochemists in their work until the quality and quantity of analyses resulted in more comprehensive tables. This work did result in the commissioning of the *Handbook of Geochemistry* by Springer Verlag for publication from 1968 through 1971 under the chief editorship of Hans Wedepohl, with me and a couple of others as associates.

As attempts to understand the geochemistry of the elements evolved, new techniques also were developing. Aside from isotope dilution mass spectrometry, used extensively for the geochronometrically important nuclides, such as Rb, Sr, U, Th, Pb, and their isotopes, it was obvious that other elements could be determined under proper conditions. But the most productive direction seemed to be in the direction of neutron activation analysis.

At first, using sodium iodide detectors, total chemical separation was required after irradiation because of the poor resolution of gamma ray energies with the detectors. Our original work on cobalt (Mike Carr's thesis) was done this way (Carr & Turekian 1961). Indeed, the principle of "If all you have is a hammer..." began to operate. As Mike Carr, my first graduate student at Yale; Dick Armstrong, my first undergraduate advisee at Yale; and I drove to Brookhaven, Oak Ridge, and Argonne National Laboratories to explore the methodology of neutron activation analysis, we talked about determining <sup>40</sup>Ar for dating purposes by the same procedure. Dick Armstrong took on the procedure for his senior thesis. It involved releasing the argon from the rock or mineral into a sealable tube and irradiating the gas to form <sup>41</sup>Ar and <sup>37</sup>Ar from <sup>40</sup>Ar and <sup>36</sup>Ar, respectively. (Potassium was determined separately by atomic absorption spectrophotometry.) The method was applied to the rocks from Greenland that I had collected earlier, and the results when compared to ages of Canadian rocks across Baffin Bay arguably showed that continental splitting could have occurred (Armstrong 1963). Dick later went on to analyze igneous rocks from the cordillera for his PhD thesis by the same method!

Aside from rocks, there was a paucity of reliable data for aqueous systems as well. I had developed a technique for the emission spectrographic analysis of lake waters. When our results were published for Maine lakes (Turekian & Kleinkopf 1956), G. Evelyn Hutchinson was just completing his *Treatise on Limnology* and was seeking trace element data on lakes and found that he could use these, the only data available at that time, for his book.

Later on, using our developing methods in neutron activation and freeze-drying sea water samples, we proceeded to analyze sea water profiles for a number of elements for which the procedure seemed to apply. This was Donald Schutz's thesis (Schutz & Turekian 1965). Although much better results were obtained as methods improved later, the elaborate chemical separations after irradiation but prior to counting not only taught us all to do very hot environment geochemistry (an irradiated sea salt sample produced a curie of <sup>35</sup>S and <sup>32</sup>P—luckily both short-lived and soft beta emitters) but also not to bite our fingernails ever again! The methods were applied to stream waters and provided the first entry into the analysis of streams. The summary of our data as well as those few available in the literature were used to construct tables of streams and sea water compositions for Volume I of the *Handbook of Geochemistry* (Turekian 1969).

By the time the first lunar samples were brought to Earth in July 1969 the scientific community was ready to analyze the rocks for virtually every element and most isotopic properties. Our task at Yale was to use the newly developed technique of instrumental neutron activation analysis to determine about 30 elements on sample sizes of 20 mg. This method of neutron activation analysis was possible because of the development of Ge(Li) detection with unique analyzers of high-energy photons (both gamma rays and X-rays). We wanted standards to certify our procedures so I contacted Isadore Perlman and Frank Asaro at Lawrence Berkeley Laboratory, who were busy analyzing archeological pottery and had created a standard pot.

The lunar program took off and there were many active participants, so our laboratory took some new directions to which I shall return later.

#### THE BOTTOM OF THE SEA

It is safe to say that there was not a unanimous agreement after World War II on what chemistry went on in the oceans to control its composition as well as the deposits on its floor. One idea was that the oceans were an arena in which a sort of "reverse weathering" was going on to reconstitute the detritus from the land to conform to an equilibrium product in contact with sea water. I associate Bob Garrels and Lars Sillen with these ideas.

There were several ways to address this problem. One was to map the mineralogy of the finest grained, and therefore presumably most reactive, sediments. These were the clay minerals that had been extensively studied in sedimentary rocks closely tied to oil exploration. When Pierre Biscaye came to Yale for graduate work, I suggested that only a detailed study of the clay mineralogy of the Atlantic Ocean basin sediments could tell us what controlled the make-up of the final repository of sediments derived from land. The skeptics were rife, but the late Bill Bradley, then of the Illinois Geological Survey and arguably the dean of clay mineralogy, encouraged us when we visited his hot attic office in Champaign, Illinois. Pierre's thesis was a landmark publication (Biscaye 1965) and clearly showed that source, in part controlled by climate, was the control on the mineralogy of the ocean sediments and not any putative "reverse weathering."

The next step was to determine the <sup>87</sup>Sr/<sup>86</sup>Sr of the deep-sea clays to see if any chemical exchanges had occurred. Soon after I arrived at Yale I decided that emission spectrography and neutron activation (even where used for the measurement of argon isotopes) were insufficient to attack the problems I had long been aware of. Brashly, with a \$15,000 grant from the (then) Esso Educational Foundation, I undertook to build a thermal ionization mass spectrometer. I went to Al Nier at the University

of Minnesota, and he had his machinist fabricate the flight tube. He also gave me the plans for the magnet assembly. Local commercial machine shops fabricated the magnets and the coils. We tried to build our own electronics (pure folly!) but eventually bought the high-voltage power supply and current regulator and recorders from the growing available stocks. It was a heroic and probably foolish venture because I knew nothing about running a mass spectrometer, let alone building one. There were charitable auras surrounding us, however, and by a series of good fortunes our machine eventually actually became functional and useful. Based on a friendship with a student, Alan Hills, who was a petrology student studying the Adirondacks, I encouraged him to take a postdoc with Paul Gast who was then at the University of Minnesota. He learned well from Paul and then came back to Yale and made sure our instrument was working by 1966.

Julius Dasch came up from Texas to work with me, recruited by the older finishing graduate students who had overlapped with Alan when he was a graduate student. Julius attacked the problem of retention of strontium isotope signatures by clay minerals transported to the sea from the weathering profiles on land. He showed that provenance age determined the isotopic signature in deep-sea clays and exchange with seawater Sr was undetectable (Dasch et al. 1966, Dasch 1969).

At about the same time, Jim Lawrence and Sam Savin, working with Sam Epstein, showed that the oxygen isotope signature of clays from weathering profiles was established under local climatic conditions and retained that record even after deposition on the ocean floor.

It was evident that the cold dark deep was not an area of mineral equilibration. Rather, the arenas of such activity were ones later identified as hydrothermal events and coastal zones and during high-temperature diagenesis.

Deep-sea sediments also provide another important recorder in the carbonate component. Aside from the source for radiocarbon dating and oxygen isotope climate tracing, the record of <sup>87</sup>Sr/<sup>86</sup>Sr is also preserved. Here I return to the original attempt at using marine <sup>87</sup>Sr/<sup>86</sup>Sr change with time as a possible geochronometric tool. Since it was shown that the simple idea was not valid and that the variation with time was undoubtedly an expression of the contributions of the more radiogenic and less radiogenic components of Earth's crust, further explorations were called for. Peterman et al. (1970) of the USGS had determined the variation of marine <sup>87</sup>Sr/<sup>86</sup>Sr using fossil clam shells from coastal deposits and deposits from interior seaways.

When I was at Columbia I analyzed crinoids and brachiopods from the Permian Florena shale in Kansas being studied by John Imbrie (Turekian 1955). I thought that we might find variations in the Sr/Ca ratio representing changes in open ocean versus basin deposition. The results did not show a clear pattern. The perfectly reasonable alternative to an environmental record was that variations were strictly diagenetic in origin and did not record the environment at all.

When I reached Yale I met up with Karl Waage, who was working on ammonites from the Cretaceous interior seaway as seen in the Dakotas. When I analyzed what I thought were preserved aragonitic remains in concretions, I found that the Sr/Ca increased at incipient alteration to calcite. From then on I doubted that one would ever be able to see through the most subtle diagenetic alteration to arrive at the true environmentally determined property (Turekian & Armstrong 1961). Only recently, through the careful identification of unaltered parts of ammonite shells by Neil Landman, was the study of the ancient record of the <sup>87</sup>Sr/<sup>86</sup>Sr and the  $\delta^{18}$ O as environmental indexes properly retrieved (Cochran et al. 2003).

This implied to me that the Peterman et al. (1970) curve for <sup>87</sup>Sr/<sup>86</sup>Sr during the Cenozoic should be tested from a system not exposed to groundwater and therefore free of diagenetic alterations. Obviously, deep-sea carbonate deposits were the answer. For that reason, I was excited when Julius Dasch and Pierre Biscaye analyzed forams from deep-sea sediment cores for <sup>87</sup>Sr/<sup>86</sup>Sr. Their curve was the first deep-sea sediment record of <sup>87</sup>Sr/<sup>86</sup>Sr for the Cenozoic (Dasch & Biscaye 1971). The record was refined by a number of other workers later on but the certification had been done by them.

Garry Brass made additional <sup>87</sup>Sr/<sup>86</sup>Sr measurements to confirm the variability over a longer period of time (Brass 1976). The work was done just before hydrothermal vents had been discovered and analyzed but he recognized that a mixing of a radiogenic and a less radiogenic component was required to explain the data and he posited that basalts were the less radiogenic component. We now know that Sr from hydrothermal vents with a very low <sup>87</sup>Sr/<sup>86</sup>Sr (~0.703) and Sr from the continents with a high <sup>87</sup>Sr/<sup>86</sup>Sr (~0.720) mix in the oceans to yield the value for the oceans (present day about 0.709).

In 1967, even as new procedures were being developed for the trace element assay of rocks in anticipation of the arrival of the moon rocks in 1969, we ventured into two new areas addressing problems involving deep-sea deposits. This was due to the arrival of D.P. Kharkar from Devendra Lal's lab. He brought some low-level beta counters (in swap, if I remember, for sponges) so that we could begin our work on the measurement of natural cosmogenic <sup>32</sup>Si in deep-sea sediments. In addition, we set up an alpha spectrometer system for the determination of the U isotopes and Th isotopes. All this was used to determine the accumulation rate of siliceous deposits around Antarctica. The initial results showed that silica was accumulating rapidly on the short timescale (<1000 years) but much less rapidly on the longer (<sup>220</sup>Th-<sup>238</sup>U) timescale (Kharkar et al. 1969). This clearly meant the deposition was faster than accumulation and there was removal of sediments by dissolution or bottom transport. The whole issue of the fate of <sup>32</sup>Si and silica was later addressed in depth by Dave DeMaster for his doctoral dissertation.

The issue of apparent excess <sup>230</sup>Th over <sup>231</sup>Pa in deep-sea sediments, reported by Richard Ku in his PhD thesis at Lamont (for which I was an external reader), was addressed by Martha Scott, a postdoc working with me, by considering the river sediment ratio of these two nuclides. It was later clear that the deficiency of <sup>231</sup>Pa (or apparent excess of <sup>230</sup>Th) was due to the fact that these two nuclides did not behave the same chemically in the water column. Turekian & Chan (1971) later addressed this problem. Later, the different behavior of the two isotopes produced in ocean water, relative to open ocean removal and ocean margin removal, was established by DeMaster and subsequently by Bob Anderson at Woods Hole.

# LOOKING AT CONNECTICUT FROM THE BOTTOM OF THE OCEAN

When Dick Armstrong joined our faculty, one of the first things he did was to get a mass spectrometer suitable for argon isotope analysis. He ran all the rocks he had measured for his thesis by neutron activation of the separated argon. After Dick left for the University of British Columbia it remained to David Seidemann, who had arrived from Stony Brook to work with Dick and me, to make the instrument work for his thesis. That was the measurement of oceanic basaltic rocks obtained in the ocean drilling program for potassium-argon ages (Seidemann 1978). It was evident that the glassy basalts, although looking fresh, had retained <sup>40</sup>Ar from the mantle at the time of eruption. Only from the holocrystalline basalts, having reacted at the time of emplacement to release their inherited <sup>40</sup>Ar, could a reasonable age be obtained. But Dave had another goal when he finished his thesis and that was to establish the age of the Triassic-Jurassic boundary that was the gift that Connecticut provided with the basalts of the region. It had been pursued by Dick Armstrong first but there were a lot of uncertainties and the <sup>40</sup>Ar/<sup>39</sup>Ar method would help solve them with the proper choice of samples (Seidemann et al. 1984). In the process, several undergraduates received their training in mass spectrometric analysis of argon for their senior theses. Among them was Bob Poreda, whom I had recruited from a seminar on geochemical archaeology I taught in my residential college. He was thinking of an archaeology/anthropology major until he took the course, and for his senior thesis applied the argon dating method to volcanics from East African hominid sites excavated by David Pilbeam, then of Yale and now at Harvard. This orientation led him to go to work with Harmon Craig at Scripps specifically on <sup>3</sup>He in Icelandic rocks and then on to other related rocks to help establish the remarkable <sup>3</sup>He story of mantle-derived rocks for which the Craig laboratory became famous.

#### **GEOSECS, THE MOON, AND PLANETARY MATERIALS**

By 1969 the GEOSECS program was firmly established. North-South traverses of each of the major oceans were to be made. The group at Yale had the responsibility of making measurements on the concentrations of Sr and <sup>210</sup>Pb in the ocean profiles. The variation of Sr showed a control by the nutrient elements, the first discovery of the nutrient control on a cation concentration that was later replicated for many other elements (Brass & Turekian 1974). <sup>210</sup>Pb was clearly controlled by the particle scavenging in the water column. But more about this later. The short mean residence time of Pb so inferred put constraints on the extent of lead isotope signatures in marine deposits. I went on the first Pacific leg of the expedition on which the late Harmon Craig was Chief Scientist and I was Associate Chief Scientist. Our voyage out of San Diego was uneventful until we ran into a storm that belied the word "pacific" for the ocean we were steaming across. Despite many difficulties, the expedition was successfully completed in Honolulu.

The GEOSECS planning sessions were some of the most dynamic ever encountered by the National Science Foundation. They quickly abandoned their idea of what a management plan should be and left it to Feenan Jennings to deal with the motley crew without further intrusions. One could argue that this was one of the most productive and scientfically rewarding enterprises of the International Decade of Ocean Exploration, under whose aegis this program was supported. The two new sister ships, the *Knorr* and the *Melville*, were the agents of this massive sampling program. A new generation of marine geochemists was trained in this venture.

The year GEOSECS began also saw the first manned landing on the moon. I was involved in the analysis of returned lunar samples using neutron activation analyses on 20-mg-sized samples for about 20 elements (Turekian & Kharkar 1970a,b; Kharkar & Turekian 1971). This work went hand in hand with the development of an idea of planetary condensation based on thermodynamic expectations mentioned earlier. When Larry Grossman showed up at Yale as a student I talked him into working out, for his thesis, the thermodynamics of condensation and sequence of phases formed. It was a fortuitous time. The first manned lunar landing and sample return were set for July 1969, and NASA had the wisdom to outfit geochemical laboratories everywhere to be ready to analyze the samples when they returned. But before the moon samples arrived aboard a space capsule, an unusual meteorite, Allende, landed in Mexico in sufficient quantities that it could be distributed to the laboratories that were waiting for another type of cosmic sampler. Allende was a carbonaceous chondrite with grains of high temperature condensate minerals that Larry Grossman had modeled in his condensation calculations (Grossman 1972, 1973).

Later, when Larry went off to the University of Chicago as a faculty member he took his calculations and knowledge of the mineralogy of Allende with him and posed the problem of certifying temperatures of condensation to Bob Clayton, his new colleague. The oxygen isotope data did not conform to the simple temperature sequence of Grossman's calculations. Luckily, Clayton was worried enough about that to determine the relative abundance of three isotopes of oxygen, <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O, instead of just <sup>16</sup>O and <sup>18</sup>O as was usually done on the assumption of mass-dependent fractionation. The discovery of non-mass-dependent oxygen isotope fractionation started there and revolutionized the fields of cosmochemistry and planetary accretion. It was a strange nonlinear path from questions of the composition of Earth for one reason to questions of the relationship of the composition of Earth to other planetary objects on the other.

When Andy Davis arrived on the scene as a graduate student he got embroiled in our group, as the whole idea of planetary formation was being pursued. He was the son of my friend Ray Davis, who was at Brookhaven National Laboratory. In a naïve moment (maybe one of many) I thought that perhaps pallasites, composed of an intergrowth of olivine and metallic iron-nickel, belonged to the meteorite type that most closely resembled the accumulation of the early condensates free of the more oxidized and more volatile phases. As Andy could "go home" to Brookhaven across the Long Island Sound, he attacked the problem of the chemistry of pallasites using the reactor at Brookhaven for his analyses. Pallasites, as it turned out, best represented the situation at a core-mantle boundary of small planetesimals rather than an original condensation sequence (Davis 1977). These results were only published as extended abstracts but they influenced our thoughts on planetary reactions. When Andy was at Yale his father was searching for the solar neutrino flux in Homestake Mine, South Dakota (that I had gone down into earlier when I first came to Yale and taught a course on the Geology of the United States and needed the experience of seeing the geology of the United States for myself!). Anyway, Ray never found solar neutrinos (or almost never) no matter how he refined his counting procedures. I told Andy that his father would get a Nobel Prize for not finding anything. Sure enough, that prophesy came true! As for Andy, he went on to Chicago where he has distinguished himself looking at, among other things, the isotopic signatures of Mo and W in meteorites to determine the types of stars involved in the nuclear synthetic mix.

#### SUBMARINE PATROL

When I was at Cambridge, one laboratory that I worked in was the radiocarbon laboratory run by Eric Willis. The lab housed, in addition to the counting equipment, a lightstable isotope set-up and some elemental analytical equipment. There I met Nick Shackleton who was doing his seminal study on oxygen isotopes in benthic and planktic forams for his PhD thesis. Eric and I had developed a friendship and the following year he arrived in the United States. After a start at Columbia and labs associated with Larry Kulp, he took a job with the Advanced Research Projects Agency ARPA (now DARPA, Defense Advanced Research Projects Agency) in the Washington area. ARPA dealt with advanced projects having to do mainly with military preparedness.

One project supported by ARPA was dedicated to detecting nuclear submarines. A suggestion was made to mount a giant NaI detector on the bow of a hunter submarine and detect the stray radiation from a target nuclear sub. When the test of this proposed system was done the system did not behave as expected. The contractors said that it was due to plankton patches with natural radioactive nuclide concentrations.

Eric asked if I could assay plankton for the members of the U and Th decay chains. Because we had set up alpha spectrometry and were equipped with Li-Ge detectors for gamma rays, I said we could do the job. So, with Kharkar and John Thomson, newly arrived from Glasgow, we analyzed plankton. The results for <sup>210</sup>Pb and <sup>210</sup>Po were particularly interesting and that started a major enterprise at Yale involving these nuclides in the oceans (Turekian et al. 1974).

As Yale does not allow classified contracts, I presented the results, which clearly showed that plankton could not provide the radiation detected by the deployed detectors, to the security-cleared contractors at ARPA. As I was ushered out of the secured room in which the meeting was held, I heard the gasps of the contractors as they realized that plankton were not going to save their precious (and I bet expensive) propositions.

Plankton concentrated <sup>210</sup>Po over its grandparent <sup>210</sup>Pb, and this suggested the idea that separation could take place in the ocean water column and possibly by bursting bubbles in the atmospheric aerosols. When this latter idea was tested by a number of people it was evident that volcanoes and old air descending from the stratosphere influenced the <sup>210</sup>Po/<sup>210</sup>Pb more than bursting bubbles, thereby bursting

my bubble. Oh well, nobody is perfect (as Cesare Emiliani said in his response to a critic of one of his papers).

Yoshiyuki Nozaki, from Shizuo Tsunogai's laboratory in Hokkaido, was working on <sup>210</sup>Pb and <sup>210</sup>Po in the shallow oceans for his thesis. I invited him to join us at Yale as the GEOSECS enterprise was extending into the Pacific Ocean. Combining the results of GEOSECS profiles in the Pacific and the data from Yoshi's thesis, we made a detailed map of the ocean surface (Nozaki et al. 1976) and later a three-dimensional display of the behavior of <sup>210</sup>Pb in the Pacific Ocean basin (Nozaki et al. 1980). We entered the arena at the time that Harmon Craig, Somayajulu, and Krishnaswami at Scripps had shown that <sup>210</sup>Pb activity was deficient relative to <sup>226</sup>Ra in the deep ocean, contrary to what had previously been assumed.

When Krishnaswami joined the Yale laboratory the cycle was complete, and through Krishnaswami's study of <sup>230</sup>Th in Indian Ocean profiles and the large amount of <sup>210</sup>Pb data, the idea of particle scavenging was quantified (Cochran et al. 1983).

There is another thread to this story. A young man, Ken Farley, a chemistry undergraduate major at Yale, inquired if there were a way for him to enter the field of geochemistry. Thanks to Glen Shen at MIT, we had a collection of ocean water profiles from the Atlantic side of the Southern Ocean (the Ajax expedition). These samples supplemented the GEOSECS profiles from the other oceans. I suggested analyzing these profiles for 210Pb for Ken's senior thesis (Farley & Turekian 1990). But I also sent Ken aboard ship with Harmon Craig for a short expedition north of Hawaii. It was a perverse act on my part. Chung and Craig had reported very low <sup>210</sup>Pb concentrations in this region based on samples collected during GEOSECS. Our numbers were significantly higher. I decided that if Ken sampled on Harmon's expedition then Harmon would be convinced of our correct values. Indeed, Ken's results showed that the high values were right. (The reason was that Chung had measured <sup>210</sup>Pb in the water samples collected for radiocarbon and adsorption of <sup>210</sup>Pb had occurred in the steel samplers.) Ken then went on another expedition with Harmon in the South Pacific in the winter of his senior year and was recruited thereby for the Craig lab. There, Ken was introduced to the world of <sup>3</sup>He and ultimately <sup>4</sup>He. The rest, as they say, is history.

On the eastern Indian Ocean GEOSECS legs Yale was responsible for supplying the <sup>210</sup>Pb-free lead carrier for separations at sea. With the help of Karen Von Damm, who had just graduated from Yale and was deferring for a year before she would go to MIT to work with John Edmond, we assayed every lead compound available commercially and discovered that all of them had a high <sup>210</sup>Pb background. The reason was that commercially available lead had a large component of recycled lead that was enriched in <sup>210</sup>Pb, probably from exposure to atmospheric precipitation. We finally settled on separating lead from galena that was totally <sup>210</sup>Pb free.

Later, using these observations, we resolved the authenticity problems for lead containing bronzes from Los Angeles County Museum and the Metropolitan Museum of Art. If the artifact was truly made before 100 years ago, it would not have <sup>210</sup>Pb (half-life = 22 years). If it were fraudulently manufactured recently, it would be high in <sup>210</sup>Pb if commercially available lead were used, as would almost certainly be the case. Virtually all the artifacts and works of art we analyzed were fraudulent!

#### THE SKY IS FALLING!

The other side of the <sup>210</sup>Pb story was the atmosphere. The source of <sup>210</sup>Pb in the atmosphere is <sup>222</sup>Rn escaping from soils. Radioactive nuclides in the air had been measured ever since the interest in the radioactive debris from nuclear bombs and tests had begun. In addition to <sup>137</sup>Cs and <sup>90</sup>Sr from these sources, laboratories supported by the federal government also measured the natural radionuclide <sup>210</sup>Pb. There were heroic studies being performed by the group under Ed Martell at the National Center for Atmospheric Research (NCAR). I had become friends with Ed when I was editor of the newly separated "Oceans and Atmospheres" section of the *Journal of Geophysical Research* (commonly called "Green" *JGR*). Ed and Christian Junge had organized an "International Symposium on Atmospheric Trace Constituents and Atmospheric Circulation" in 1969 at Heidelberg. I asked him to be one of my board of very distinguished Associate Editors, with his first task being to gather the papers from this meeting to publish in "Green" *JGR*. The publication as a separate collection of reprints was funded by the (then) U.S. Atomic Energy Commission.

From then on I learned to follow the work that was coming from the Martell lab on the <sup>222</sup>Rn daughters in the atmosphere. When I thought that the radionuclide data in plankton was coupled to the atmosphere, our interest in atmospheric radioactivity became progressively more intense. Thus an incorrect assumption led to a productive area of study.

With time, our pursuit of natural radioactivity in the atmosphere as a way of determining processes there became an obsession. This obsession was flamed by the development of an atmospheric sampling program led by Bob Duce and Joe Prospero called SEAREX (Sea/Air Exchange). The aim was to study the air and precipitation over the Pacific with an eye also to the Asian dust flux. As I remember it, I was invited to one of the organizing meetings as a reviewer and my query was how was flux to be determined with the risks of island dust contamination. I proposed <sup>210</sup>Pb as the cure-all and they signed me up. The atmospheric concentration and flux of <sup>210</sup>Pb at each Pacific Island of the SEAREX network provided a measure of the fluxes of other components measured, including Pb—Claire Patterson's love. The greatest triumph for me was to convince Pat that the major supply of contaminant Pb to the oceans was atmospheric and not by streams. So we published a paper (Settle et al. 1982) to that end, and I think it influenced other work on detecting human-caused Pb transport to the ocean.

In anticipation of our study of the SEAREX sites, we published a paper in the *Annual Review of Earth and Planetary Sciences* (Turekian et al. 1977) on what we thought we should expect based on a few data obtained by several people (including Martell's group) and a naïve approach to atmospheric transport and aerosol scavenging. The paper was very important to the development of sampling and certification and proved what I learned from Walter Bucher at Columbia, that thinking was more important than being right even as our SEAREX results became evident (Turekian et al. 1989).

One of the important consequences of our entry into the atmospheric radioactivity venture was the realization that we could use soil profiles to determine <sup>210</sup>Pb fluxes. Our first measurements were made in a laborious fashion, the <sup>210</sup>Pb by alpha spectrometry via its granddaughter <sup>210</sup>Po (assuming that secular equilibrium had been obtained) and <sup>226</sup>Ra via scintillation counting of <sup>222</sup>Rn in secular equilibrium (Nozaki et al. 1978). On proving the feasibility, and with Bill Graustein joining the group after completing his thesis on soils in the Tesuque Watershed in New Mexico, a campaign of soil sampling throughout the United States was undertaken, only this time all measurements of <sup>210</sup>Pb and <sup>226</sup>Ra were done by gamma spectrometry on sealed cans of the soils from profiles. The differential between <sup>210</sup>Pb and <sup>226</sup>Ra activities provided a measure of <sup>210</sup>Pb addition from the atmosphere. We quickly realized that we also could get the flux of <sup>222</sup>Rn from the same soil profile tracking the deficiency of <sup>210</sup>Pb at depth in the soil profile (Graustein & Turekian 1986, 1990).

Bill and I were able to construct a map of the atmospheric <sup>210</sup>Pb flux and the <sup>222</sup>Rn flux from soil profiles. These results were published in a number of papers and recently summarized in a paper in the *Treatise on Geochemistry* (Turekian & Graustein 2003).

We had started to collect precipitation data for the determination of cosmogenic <sup>7</sup>Be as well as <sup>210</sup>Pb at Bermuda and New Haven to see the variations with geography and time (Turekian et al. 1983). It was expected, for example, that<sup>7</sup>Be would show seasonal variations owing to the history of tropopausal folding, and the <sup>210</sup>Pb flux in Bermuda was supposed to be lower than the more continental New Haven site. Neither of these expectations was met, requiring a better understanding of the behavior of these nuclides—one from the ground surface (<sup>210</sup>Pb) and the other from the upper troposphere (<sup>7</sup>Be).

The opportunity to exploit these processes was provided through the Atlantic equivalent of SEAREX called AEROCE (Atmosphere/Ocean Chemistry Experiment). With towers deployed throughout the Atlantic Ocean basin, measurements of the geographic and temporal variations of <sup>7</sup>Be and <sup>210</sup>Pb could be tracked in aerosols and precipitation. The former was done elegantly with gamma ray spectrometry; the latter still requires the tedious chemistry developed earlier.

We could now see what controlled <sup>7</sup>Be and <sup>210</sup>Pb—it was the constraints on convective mixing. We also could relate these radioisotope measurements to the origins of tropospheric ozone (Graustein & Turekian 1996) and nitrate.

Nori Tanaka also came to Yale from the Tsunogai laboratory. Nori had the knack for making even the most obsolete instruments yield valuable results. Using our old liquid scintillation counter, initially obtained for radiocarbon measurements, we developed a program for the measurement of cosmogenic <sup>35</sup>S (half-life = 87 days) in aerosols, gaseous SO<sub>2</sub>, and precipitation. Combined with our <sup>7</sup>Be and <sup>210</sup>Pb measurements we could make sense of the kinetics of the oxidation and deposition of SO<sub>2</sub> (Tanaka & Turekian 1995). The measurement of cosmogenic <sup>35</sup>S has been pursued by Mark Thiemens and his group at UCSD to differentiate S from the stratosphere from lower troposphere S to track non-mass-dependent isotopic fractionation. Incidentally, the Thiemens group has used the three isotope method for oxygen in sulfate to determine the relative importance of homogeneous oxidation and in-cloud oxidation—something we had attempted from cosmogenic and radon-produced radionuclides in the studies mentioned above.

#### LONG ISLAND SOUND

We were lucky at Yale to have an arm of the sea in our backyard, so to speak. New Haven's status as a seaport never really recovered after the Jefferson administration Embargo Act, yet now it provided a scientific gateway to Long Island Sound. An estuarine basin with defined inputs of "fresh" water (the East River, one of its most important inputs, is hardly fresh), subject to human assaults both from the surrounding land and air and subject to natural and artificial modification of its boundaries, would be an ideal object of study. The late Gordon Riley led a group of Yale scientists, mainly biologists, in the first scientific campaign in the Sound. A second generation of Yale scientists started a new campaign with different tools and insights. Four groups, led by Bob Berner, Bob Gordon, Don Rhodes and myself, each with specific orientations, worked closely in this enterprise. Several government agencies supported the groups, but we were excited by the prospect of broad support by the establishment of a new unit in the National Science Foundation called Research Applied to the Nation's Needs (RANN). We dutifully submitted a multiauthor proposal including participation in the areas of systems analysis from the newly constructed Department of Engineering and Applied Science. The results were catastrophic. Our grand proposal was rejected because, of all reasons, we didn't have an obvious policy component! Enough for RANN! It was with a great deal of pleasure that I noted that RANN was ultimately destroyed on the rocks of scientific ignorance.

Anyway, we all did what we wanted, thanks to individual components of the federal government that were not constrained by the folly generated by political administrators. The behavior of reactive species in the water column was tracked by Larry Benninger for his thesis using <sup>210</sup>Pb. Its absence in the dissolved state in Long Island Sound indicated that the atmospherically supplied <sup>210</sup>Pb had a very short lifetime in the water before removal to the estuarine bottom (Benninger 1978). Using intrinsically produced<sup>234</sup>Th and <sup>230</sup>Th in the New York Bight, the relationship of removal efficiency to particle density was established by Archie Kaufman, visiting from the Weizmann Institute of Science in Israel (Kaufman et al. 1981).

The transport of these nuclides provided a way of studying the behavior of sediments as the result of biological activity. The isotopes <sup>210</sup>Pb, <sup>234</sup>Th, <sup>228</sup>Th, <sup>7</sup>Be, and even <sup>14</sup>C provided evidence for mixing at different rates and depth scales. This provided Bob Aller as well as Kirk Cochran and Larry Benninger the tools to investigate the biologically driven chemistry of estuarine deposits. A summary of the different scales of bioturbation in Long Island Sound sediments was published by the consortium (Benninger et al. 1979). These three men have continued the studies, first tested in a convenient basin, in many parts of the world.

The records in salt marshes fringing Long Island Sound were studied for their upward growth rates (and therefore rise in sea level) using <sup>210</sup>Pb by Dick McCaffrey and John Thomson, who also determined the fluxes of atmospherically derived contaminants in recent times.

Many of these studies were published in a volume of the *Advances in Geophysics* (Volume 22, 1980) edited by Barry Saltzman entitled "Estuarine Physics and Chemistry: Studies in Long Island Sound."

One of our latest sorties into Long Island Sound involved a collaborative study with a group at the Avery Point campus of the University of Connecticut led by Tom Torgersen. I deployed my son, Vaughan, on the old rusting University of Connecticut research vessel, a converted 1952 U.S. Army tug (since replaced by a shiny new research vessel), to collect water in traverses across the Long Island Sound. The aim was to measure the concentration of radium isotopes ( $^{224}$ Ra,  $^{226}$ Ra, and  $^{228}$ Ra) along these traverses. The daily delivery of the samples concentrated on manganese oxide–coated acrylic fibers was accomplished, like surreptitious contraband deliveries, by Zodiac or occasional docking at Connecticut marinas. This rapid transfer was done so that the samples could be processed and counted right away for the short-lived  $^{224}$ Ra (half-life = 3.6 days)—that was my job.

We determined the flushing time of Long Island Sound and transport rates within the Sound using all three isotopes (Turekian et al. 1996, Torgersen et al. 1996).

# READING SEA SHELLS, VOLCANOES, AND GROUNDWATER

With the capacity to measure virtually all of the U and Th decay series nuclides using alpha and gamma counting, low-level beta counting, and radiocarbon through liquid scintillation counting as described above, our lab turned to novel systems that could be approached with these tools. One was the growth rates of marine organisms through the analysis of minerals deposited and the record inherent in the deposited tests, another was contemporary volcanic materials, and another was groundwater. All three came from unusual contexts and relationships. The common thread was our ability to make measurements on low-level concentrations of natural radionuclides and the availability of light-stable isotope ratio determinations by mass spectrometry, thanks to Danny Rye who had joined our faculty.

# Sea Shells

As I remember it, in a casual conversation with the late Howard Sanders of the Woods Hole Oceanographic Institution (WHOI), who had been part of the original biological gang studying Long Island Sound at Yale, I learned that he and Fred Grassle were studying a tiny (~1 cm) deep-sea benthic clam, *Tindaria callistiformis*. They knew the growth rate must be slow because food supply to 3800 m depth had to be limited but they were not sure how slow except for what appeared to be periodic bands on the shell surface. We figured we might be able to help in determining the ages of the clams recovered by using <sup>228</sup>Ra (5.7 year half-life). Billy Moore (Moore 1969) had started to look at <sup>228</sup>Ra in ocean water as part of his thesis (the first for the new department at Stony Brook, on which I was an external examiner). Further work on profiles in the Atlantic Ocean, as part of the GEOSECS campaign at Lamont under Wally Broecker, affirmed the high concentration of <sup>228</sup>Ra in the ocean bottom, and other studies indicated high values in deep-sea sediment pore waters (Trier et al. 1972). So, brashly, we determined the growth rate of *Tindaria* using the bands and the <sup>228</sup>Ra-based age (Turekian et al. 1975). The largest clam (8 mm) was about 100 years old and, on the basis of comparison with shallow water clams, probably reached puberty at about 40 years. When the Emperor of Japan, an avid marine biologist, visited WHOI in the late 1970s, Sus Honjo gave him a specimen of *Tindaria* with this information. I understand that the aging Emperor was quite pleased with the old age that was reported.

Among the original investigators in this project was Kirk Cochran, who was just finishing his thesis on radium isotopes in the ocean. When the first dives on hydrothermal vents on the Galapagos Ridge occurred in 1977, we obtained, through the courtesy of John Edmond, Jack Dymond, and Jack Corliss (who spent some time at Yale), a sample of an approximately foot-long vesicomyid clam for which we (Cochran, Nozaki, and I) proceeded to determine a growth rate. Using the uranium and thorium decay chain nuclides and radiocarbon, we established that for the clam to grow to 22 cm in length it took 6.5 years (Turekian et al. 1979). This age had a very large error so we later analyzed a freshly procured 1979 dive clam shell, which we analyzed systematically and arrived at a growth rate of about 4 cm per year (Turekian & Cochran 1981). We later showed that at the 21°N East Pacific Rise hydrothermal area the growth rate of vesicomyid clam was 0.27 cm per year, about a factor of ten slower than at the Galapagos vent (Turekian et al. 1983).

With our ability for determining how fast marine organisms grow, using variants of the techniques developed, we addressed how fast the ocean quahog (*Arctica islandica*) grows—very slow despite what some people thought (Turekian et al. 1982). Later, Doug Jones, who was working on *Arctica* at Princeton for his thesis (and a coauthor on our paper) continued to extract environmental history from the annual bands deposited by *Arctica*.

The question of the age of fishes was raised by George Boehlert, then of the National Oceanic and Atmospheric Administration (NOAA), because his way of counting bands in aragonitic otoliths on a rock fish species (*Sebastes diploproa*) gave an older age than was generally presumed. We established not only that the rock fish had longevity, the larger specimens more than 100 years, but also that "puberty" was reached at about 14 years of age (Bennett et al. 1982).

For his thesis, Dick Dodge had taken on the project of understanding the record in contemporary and fossil corals to interpret climate and environmental imprints. John Thomson determined that the layers in a "brain" coral were indeed annual using <sup>210</sup>Pb (Dodge & Thomson 1974). Using one of these corals from Bermuda, we determined the annual variation in  $\delta^{18}$ O,  $\delta^{13}$ C, and radiocarbon. The coral was "captured" in 1976 and we dubbed it the bicentennial coral because there were about 200 layers. This was the first detailed study of changes over the past 200 years of a coral from the Sargasso Sea. Using the carbon isotopes we established that in the nineteenth century there was a period of increased upwelling (Nozaki et al. 1978). This fact makes corals indicators of changes in local upwelling history. Since then, others have discovered the same thing in the Pacific tied to the onset of the El Niño Southern Oscillation. The precaution that corals may not record temperatures of the regional surface ocean uniquely meant that their record need not track the record in land-based detectors such as tree rings.

#### Volcanoes

Another application of our capabilities in measuring many of the radionuclides in the U and Th decay chains came when Mt. St. Helens erupted in May 1980. President Carter charged the National Science Foundation to support, without delay, research on the event. I could not believe that the National Science Foundation could act quickly even in response to a presidential edict, so I wrote a proposal to analyze the Mt. St. Helens eruptives for the U and Th decay chain nuclides to infer the timescales of magma formation and the fractionation of elements during the process. Working on rocks studied petrologically by Bill Melson and Cliff Hopson, we analyzed the nuclides of interest as we had done for plankton and marine organisms. We discovered that <sup>226</sup>Ra and <sup>210</sup>Pb were concentrated in the magma that gave rise to the effusives and that this magma formation occurred between 30 and 10<sup>4</sup> years with a probable time of 150 years (Bennett et al. 1982).

This experience indicated that much could be learned from recent volcanic eruptions using the abundance of members of the U and Th decay chains. Two other events involving volcanics occurred at about the time of the Mt. St. Helens eruption. One was increasing exploration of hydrothermal vents and associated volcanism, especially along the northern part of the East Pacific Rise. The other was the sampling on the big island of Hawaii where flank eruptions of Kilauea started in earnest in 1984 and continue to the present.

Ilene Reinitz, with a bachelor's degree from Caltech, accompanied her husband to Yale where he had a postdoc in biology. She at first worked as a technician in our lab, but then I suggested she should become a graduate student and continue the work on volcanic rocks for her thesis. That indeed is what she did and we looked at freshly formed rocks from divergent plate boundaries, convergent plate boundaries, and hot spots. In virtually all cases excess <sup>226</sup>Ra was observed and variable levels of disequilibrium in the <sup>230</sup>Th/<sup>238</sup>U was observed. In our summary paper we tried, with the help of theorist Neil Ribe, to determine the major parameters of magna formation, rate of movement, and fractionation factors for U, Th, and Ra (Turekian et al. 1997).

#### Ground Water

The third area in which the tool of exploitation of the U and Th decay chain nuclides was used was ground waters. Originally, I proposed to my colleagues Krishnaswami and Graustein that we should be able to determine flow rates of ground water using the U and Th decay chain nuclides. Instead, we learned about the retardation factors affecting the elements represented by the critical radionuclides. <sup>222</sup>Rn in ground water provided the recoil flux measurement for all nuclides that were the product of alpha decay. The relative abundances of the isotopes of the elements with different half-lives, such as Ra, Th, U, and Pb, provided measures of retardation efficiency

for different aqueous systems. Conditions such pH, salinity, and Eh set the matrix controlling the "stickiness" of the various nuclides. Although we tried this first on Connecticut ground waters (Krishnaswami et al. 1982), we quickly realized the value of this procedure to apply to Long Island aquifers, especially those impacted by the Brookhaven National Laboratory, and the Yucca Mountain (Nevada) site chosen for long-term nuclear waste disposal. Although our measurements were to be made from well water used mainly to hose down dirt roads at the Yucca Mountain site, the State of Nevada, in those litigious times, would not allow us to use the water for our measurements with the argument that measurements meant endorsement. After the legal issues were resolved, we could address the scientific problem of retardation of ions. This study was done as a master's thesis by Sally Copenhaver in cooperation with Henry Shaw of the Lawrence Livermore National Laboratory—the place her future husband, Brad Esser, who was working on Os isotopes at Yale for his PhD, later went (Copenhaver et al. 1992).

The blend of volcanism and ground water occurred in the study of the hot springs of Yellowstone Park. Jordan Clark as an undergraduate sampled the waters and dispatched them to Yale by FedEx so we could count the short-lived <sup>224</sup>Ra. Using all three radium isotopes with different half-lives we were able to determine the flow rate/reaction time for one of the major geyser basins (540 years), with a water/rock ratio of 250 (Clark & Turekian 1990). We had earlier determined the same parameters for oceanic hydrothermal vent systems with a reaction time of 40 years and a water/rock ratio of 5 (Turekian & Cochran 1986). The difference could be ascribed to the nature of the heat sources and the differences in salinity and pH between the two domains.

#### **Cosmic Rays**

The work of Devendra Lal was the inspiration for our entry into the field of environmental uses of the cosmogenic nuclides. Indeed, through the arrival of D.P. Kharkar and later S. Krishnaswami from his lab, the transfer of knowledge was effected.

Kharkar was responsible for the initiation of our program using <sup>32</sup>Si in marine deposits as previously mentioned. Dave DeMaster later exploited the methods of low-level beta counting of <sup>32</sup>Si (via <sup>22</sup>P) in his thesis to explore a way of determining its half-life based on varved deposits in the Gulf of California, rates of deposition (again) in the Antarctic and bioturbation rates in the Pacific. I will return to the problem of <sup>32</sup>Si in sea water as part of GEOSECS later on but it was spearheaded by the PRL group under Lal with Somayajulu as a key investigator. (The grant for this effort was channeled through Yale for pragmatic reasons at least for some of the effort.)

I have alluded to our measurement of <sup>7</sup>Be (half-life = 54 days) in atmospheric precipitation and aerosols, but we also analyzed shallow ocean profiles for determining <sup>7</sup>Be flux to the oceans as well as sediments of Long Island Sound for rates of accumulation and bioturbation studies.

Our most dramatic excursion into measuring cosmogenic nuclides was the development of the method of measuring <sup>10</sup>Be (half-life =  $1.5 \times 10^6$  years) in natural

materials using accelerator mass spectrometry. Although Krishnaswami had come to Yale one year when we measured <sup>10</sup>Be by low-level counting, I realized that the suggestion made by the University of Rochester group that <sup>10</sup>Be could be measured on the tandem van de Graff accelerator could be tested at Yale. So Peter Parker of the Physics Department and I began to explore the use of the accelerator of the Wright Nuclear Structure Laboratory under the direction of the late Allan Bromley. We could not interfere with the ongoing physics experiments, so we sneaked in on Saturdays and experimented with the best procedure and mounting to use to get a measurable beam. At first we packed ground manganese nodules into the target cone and got nowhere. I realized that we had to separate the <sup>10</sup>Be, using a Be carrier, to get proper results. We were the first to measure a marine deposit (manganese nodule profile) for <sup>10</sup>Be with a tandem van de Graff accelerator (Turekian et al. 1979), although Grant Reisbeck had begun to do the same in Paris using a cyclotron.

When Marc Monaghan showed up as a student, he accepted the challenge of determining the <sup>10</sup>Be flux in precipitation throughout the United States using large collectors for annual samples (Monaghan et al. 1985). He also measured the <sup>10</sup>Be concentrations in soil profiles and discovered that <sup>10</sup>Be was not retained efficiently therein.

Augusto Mangini came to Yale from Heidelberg and put himself to the task of measuring a <sup>10</sup>Be profile in a Pacific deep-sea sediment core (actually GPC-3-Grant Piston Core-3 of the Long Lines expeditions collected by the late Charlie Hollister at WHOI). The actual measurements were made in Zurich because our use of the Yale accelerator had ended (Mangini et al. 1984). Clearly, an accelerator dedicated to accelerator mass spectrometry was the hope for the future.

I have already referred to our measurement of <sup>35</sup>S in addressing the study of the fate of SO<sub>2</sub> in the atmosphere. I close with our work on the <sup>32</sup>Si data set collected aboard the GEOSECS expeditions and analyzed at PRL (Physical Research Laboratory in Ahmedabad, India), mainly by Somayajulu. The data appeared to be a random number table and was diminished in importance by some of the GEOSECS participants. One day as Harmon Craig and I were sitting around his dinner table, overseen by Valerie Craig, we had an epiphany. The data were being viewed incorrectly. The fibers were collecting both adsorbed silica and also diatom frustules. All the measured <sup>32</sup>Si specific activity was on mixing curves between these two end members. When this was deconvoluted the <sup>32</sup>Si profiles in the three ocean profiles made clear sense. This was the last paper that Harmon Craig wrote (with Somayajulu and me) before his death (Craig et al. 2000).

At Lal's 75th birthday party in 2004, I met Michael Paul of the Hebrew University. He had been measuring cosmogenic <sup>59</sup>Ni (half-life = 77,000 years) in meteorites. I wanted to know how much meteoritic material dissolved in sea water to estimate the contribution to the osmium isotope signature there. I will discuss this later. This and the analysis of ancient Ni-bronze are avenues of research now being pursued at Argonne National Laboratory. Stay tuned!

#### **OSMIUM**

In 1980 two papers appeared that were destined to change the orientation of my lab up to the present day. There appeared a paper by Louis Alvarez, Walter Alvarez, Frank Asaro, and Helen Michel that reported a massive imprint of Ir at several clay layers at the Cetaceous-Tertiary (K/T) boundary (Alvarez et al. 1980). This remarkable discovery at the time horizon when the dinosaurs and many other species became extinct led to the idea that the impact of a massive extraterrestrial body, probably a meteorite, was the cause of the extinctions. In the same year, Jean-Marc Luck working with Claude Allegre revitalized the prospect of measuring variations of <sup>187</sup>Os in the ensemble of Os isotopes with variations possible owing to the decay of <sup>187</sup>Re (half-life ~4.5 × 10<sup>10</sup> years). This was accomplished with the ion microprobe analysis of Os. The earlier method using normal thermal ionization techniques did not provide the ease of measurement that the ion probe did because of the method of excitation.

Allegre and Luck sent their paper to me as one of the six editors of *Earth and Planetary Science Letters* for possible publication. I was excited by the paper and was pleased to publish it with all dispatch (Allegre & Luck 1980).

As Os and Ir are almost in equal abundance in virtually all meteoritic and Earth materials, I saw the way to verify if the Ir at the K/T boundary clays was of meteoritic or terrestrial origin. Meteorites have a lower Re/Os than the crust of Earth, therefore the <sup>187</sup>Os/<sup>186</sup>Os (the ratio used by Luck and Allegre) at present was about 1 for meteorites and should be between 10 and 20 for the crust, depending on age and recycling.

I proposed this test at a meeting at Snowbird, Utah, which was convened to discuss the Alvarez et al. results and hypothesis (Turekian 1982). The usually garrulous Louis Alvarez sat silently through my talk.

I invited Jean-Marc Luck to join our group specifically to test this idea about Os isotopes. This was only possible because MIT had just acquired an ion microprobe of the kind used by Jean-Marc in Paris. Stan Hart, who was then at MIT, made the instrument available as a "regional" facility, and with the help of Nobu Shimizu we were able to effect the plan we had in mind. Subsequently, other members of the Yale group were given access to the instrument. It was an act of extraordinary generosity on behalf of Stan, something he continued even after he moved to WHOI.

Because no data were available for the crust, we decided to use the great integrating reservoir on Earth, the oceans, for a sampling of the crust. And in the oceans I thought manganese nodules were the best samplers because there were a few measurements on the platinum group composition of manganese nodules together with those for Ni, Cu, and Co.

Jean-Marc and I measured <sup>187</sup>Os/<sup>186</sup>Os in several manganese nodules from a number of ocean sites and discovered the high value (though not as high) we expected from the weathering of the crust. Finally, we analyzed the Ir-rich K/T boundary clays. The results clearly showed that the high-Ir layers had Os of meteoritic composition and not crustal (Luck & Turekian 1983)!

When I called Louis Alvarez immediately on obtaining our results he said, in his characteristic rough voice, "Karl, I have to admit I didn't understand what you

were saying at Snowbird, but now that I see the results, I think it was the most important measurement that could be made." I realize that the overstated enthusiasm was because it confirmed his hypothesis. There would have been blood on the floor if the K/T clays had a crustal <sup>187</sup>Os/<sup>186</sup>Os!

Our analyses of manganese nodules from the different parts of the world ocean did not all yield a constant value, neither were the values as high as we expected from a simple weathering of continental crust model. Martin Palmer joined our group and the baseline of our Mn nodule study was increased considerably. The variability did not seem to be due to regional differences. Because we were not careful how we sampled the nodules and because we and others had shown that they grew at a rate of a millimeter per million years, obviously we were sampling a range of layers deposited over tens of millions of years. If the Os isotope composition of the oceans varied with time like <sup>87</sup>Sr/<sup>86</sup>Sr, which was well documented, then the variability in <sup>187</sup>Os/<sup>186</sup>Os was most likely due to what ages of each nodule we sampled.

With the arrival of three new graduate students, Brad Esser, Candace Martin, and Greg Ravizza, a small club of Os aficionados was established. Brad took on the task of understanding what the crustal Os isotope and concentration imprint were really like and what the flux of extraterrestrial dust to the ocean bottom was (as alluded to earlier). He also recognized that our coastal ocean sediments could be imprinted by the release, mainly from hospital research facilities, of Os from mantle-derived platinum group ore deposits (Esser & Turekian 1993). So we were getting an idea of the continental and extraterrestrial source terms with a hint that if nature was also supplying mantle-type Os to the oceans, the lowered value of sea water could be understood.

Candace Martin went after the mantle sources of Os in the form of abyssal peridotites and basalts from oceanic plumes such as Hawaii. She was the first to recognize differences within those various sources. The study of basaltic rocks has since continued in many labs and added to the diversity of signatures of mantle sources (Martin 1990).

Greg Ravizza explored how Os was removed from sea water into anoxic sediments, and ultimately was able to determine both ages of black shales and Paleozoic oceanic <sup>187</sup>Os/<sup>186</sup>Os values from them (Ravizza & Turekian 1989).

So the sources and sinks had been identified. The next step was to look precisely at variability of <sup>187</sup>Os/<sup>186</sup>Os with time. Because we had worked on dating GPC-3 with <sup>10</sup>Be, we turned to that core—a quintessential, slowly accumulating "red clay" sediment pile from the area around Hawaii. In addition, this core had been studied geochemically by Frank Kyte and his associates.

With B.J. Pegram, Krishnaswami, and Ravizza, we created the first curve of variation of <sup>187</sup>Os/<sup>186</sup>Os over the Cenozoic with the KT boundary clearly demarked by the lowest <sup>187</sup>Os/<sup>186</sup>Os value in the entire record (Pegram et al. 1992).

Indeed, there was variation similar but not identical to the <sup>87</sup>Sr/<sup>86</sup>Sr curve. Similar because both ratios increased dramatically from 35 million years to the present. Dissimilar because although <sup>87</sup>Sr/<sup>86</sup>Sr was effectively low and constant throughout the Paleogene, the <sup>187</sup>Os/<sup>186</sup>Os showed large fluctuations with time.

We decided that we had better home in on the causes of the variation. The first task was to ascertain the texture of river supply around the world. Here the role of rock type being weathered would be important. We approached the problem by measuring the available Os by acid hydrogen peroxide leaches of river sediments, as we did for deep-sea sediments. In the absence of stream water values, we felt this was the best way to assay the world streams (Pegram et al. 1994). The results seem self-evident now. Streams draining normal continental crust were lower than those draining sediments with black shales in their section. The lowest values were from those streams draining ophiolite sections and islands like the Philippines. The variability observed over the Cenozoic could be explained by the relative importance of these three components.

We had a chance to see this when Franco Marcantonio joined our group and measured a core on the 90°E Ridge in the Indian Ocean (Marcantonio et al. 1999). There the detrital source of Os clearly changed with the glacial cycle. During glacial time with lowered sea level the lands to the east, such as Indonesia, similar to the Philippines, the Os concentration was relatively higher and the <sup>187</sup>Os/<sup>186</sup>Os more mantle-like. During nonglacial times with higher sea level, the Os concentration was considerably lower and the <sup>187</sup>Os/<sup>186</sup>Os resembled the sediments of the Ganges that we had previously analyzed.

Although we are still trying to understand the relationship of time, tectonic history, and climate, an attempt has been published (Turekian & Pegram 1997).

The role of atmospheric transport and the record in coastal deposits, where both natural variations and human-induced variations occurred, were pursued by Gwyneth Williams (Williams 2002). She was the last of the Wizards of Os at Yale.

#### AN UNUSUAL DIVERSION

In 1997 and 1998 several events occurred that made some changes in my life. The more mundane was quadruple coronary bypass surgery followed by several surgeries to accommodate the massive infections resulting from the original operation. The more poetic was the arrival in sequence of a student from Harvard, Albert Colman, who had worked as an undergraduate with Dick Holland on the role of phosphate in ocean history; and soon thereafter Ruth Blake, who had worked with Jim O'Neil at the University of Michigan and came to Yale first as an NSF postdoc and then as a faculty member; and finally Yeshu Kolodny of the Hebrew University at Yale on sabbatical. Arguably, Kolodny was one of the founders of the environmental record in oxygen isotopes in phosphates. This convergence brought two different enterprises to the fore in an unexpected way. One involved GEOSECS and the other the record in GPC-3, which we had studied for Os isotopes and <sup>10</sup>Be.

Longinelli, another of the primary workers in the  $\delta^{18}$ O record in phosphates as possible paleothermometers, measured the  $\delta^{18}$ O of the phosphate adsorbed on the iron oxide–coated fibers used to capture <sup>32</sup>Si in ocean water profiles of GEOSECS. His results showed invariance of  $\delta^{18}$ O in phosphate at all depths sampled. Because ocean water profiles are not isothermal in most of the oceans, this result was a surprise. The most reasonable explanation was that the containers holding the fibers sat on deck and inherited bacteria equilibrated phosphate oxygen with associated sea water at the temperature of the deck so that all phosphate  $\delta^{18}$ O values would end up being the same—the high temperature value typical of equilibration at surface temperature.

To test this, Albert developed a scheme to analyze small amounts of phosphate from sea water in oceanic profiles by freezing and transporting them to Yale for analysis. The two profiles studied were off Hawaii and Bermuda. The results showed the expected results—the phosphate at each depth effectively was in equilibrium with sea water at the temperature change in the thermocline (Colman et al. 2005). Slight diversions from equilibrium were the consequence of other biological effects that were ultimately resolved by Ruth Blake and her student, Yuhong Liang, and Albert.

The other use of  $\delta^{18}$ O in phosphates was in trying to work out the chronostratigraphy of GPC-3. This core was composed only of hydrogenous deposits, detrital material, and fish debris, so Ruth Blake and I decided to measure the  $\delta^{18}$ O of the fish debris (mainly teeth) to see if the pattern with depth replicated the well-dated established pattern derived from foraminifera. Our initial results showed that the two patterns were effectively the same, thereby providing confirmation of the chronology we had used in our Os isotope study.

## **EPILOG**

In October 1997 when I reached my 70th birthday most of my former students, postdocs, and coinvestigators arrived at Yale to talk for two days on the remarkable things they were doing. Each brought me, as a birthday present, a coffee mug from the institution each was at (all except Jean-Marc Luck who could not find a coffee mug with the University of Montpellier crest—so he and Dalilah ben Othman brought a coffee table book called "Café" instead). In addition, the group presented me with a corporate gift, a small slate blackboard that they had all signed on the back. There was a small meteorite piece pasted on the blackboard and the brass label above the blackboard that read, "All you need is one point and a good idea."

These captured the essence of life at Yale. The morning coffee hour became the no-holds-barred exchange of data and ideas. Indeed one can legitimately argue that the blackboard could have been coauthor on all our papers. Certainly, it deserves a belated acknowledgment. I have to confess that one point arriving on the blackboard with a bunch of good ideas was the fuel to drive the research into the future. Nick Shackleton probably would not have liked this, but he was the inspiration for that comment. When I saw his thesis at Cambridge he had carefully chosen a few coexisting benthic and planktic forams along a 50,000-year traverse in a core to solve the question of how much of the variation of  $\delta^{18}$ O was temperature related and how much reservoir related. He showed the effect was primarily reservoir related. Of course, since that thesis Nick probably made more measurements on  $\delta^{18}$ O in forams than anyone in the world. But his frugal attitude toward his thesis was a great inspiration.

Aside from the Yale coffee hour, the other sources of inspiration were my colleagues external to Yale. I have already mentioned the late Harmon Craig, Wally Broecker, and Devendra Lal. Added to this list are Claude Allegre, Thure Cerling, the late John Edmond, the late Sam Epstein, Stan Hart, Dick Holland, Frank Richter, and Jerry Wasserburg. Our lives have intersected in a number of ways and I have come away richer for the encounters. Of course, there have been many others, including my other former students Eric Dion, Kathy Bertine, Michaele Kashgarian, Dale Lewis, and Peter Rona. All of these participants in the "blackboard" encounters I gratefully acknowledge for their significant contributions to our science and to me.

All the threads identified in this little essay have been responsible for the construction of the fabric of my scientific life.

#### LITERATURE CITED

- Allegre C, Luck J-M. 1980. Osmium isotopes as petrogenetic and geologic tracers. *Earth Planet. Sci. Lett.* 48:148–54
- Alvarez LW, Alvarez W, Asaro F, Michel HV. 1980. Extraterrestrial cause for the Cretaceopus-Tertiary extinction. *Science* 208:1095–108
- Armstrong RL. 1963. K-Ar dates from West Greenland. *Geol. Soc. Am. Bull.* 74:1189– 92
- Benninger LK. 1978. <sup>210</sup>Pb balance on Long Island Sound. Geochim. Cosmochim. Acta 42:1165–74
- Benninger LK, Aller RC, Cochran JK, Turekian KK. 1979. Effects of biological sediment mixing on the <sup>210</sup>Pb chronology and trace metal distribution in a Long Island Sound sediment core. *Earth Planet. Sci. Lett.* 43:241–59
- Bennett JT, Krishnaswami S, Turekian KK, Melson WG, Hopson CA. 1982. The uranium and thorium decay series nuclides in Mt. St. Helens effusives. *Earth Planet. Sci. Lett.* 60:61–69
- Bennett JT, Boehlert GW, Turekian KK. 1982. Confirmation of longevity in Sebastes diploproa (Pisces: Scorpaenidae) from <sup>210</sup>Pb/<sup>226</sup>Ra measurements in otoliths. Mar. Biol. 71:209–15
- Biscaye PE. 1965 Mineralogy and sedimentation of recent deep-sea clays in the Atlantic Ocean and adjacent seas and oceans. *Geol. Soc. Am. Bull.* 76:803–32
- Brass GW. 1976. The variation of the marine <sup>87</sup>Sr/<sup>86</sup>Sr ratio during Phanerozoic time: interpretation using a flux model. *Geochim. Cosmochim. Acta* 40:721–30
- Brass GW, Turekian KK. 1974. Strontium distribution in GEOSECS oceanic profiles. *Earth Planet. Sci. Lett.* 23:141–48
- Broecker WS, Turekian KK, Heezen BC. 1958. The relation of deep-sea sedimentation rates to variations in climate. Am. J. Sci. 256:503–17
- Carr MH, Turekian KK. 1961. The geochemistry of cobalt. *Geochim. Cosmochim. Acta* 23:9–60
- Clark JF, Turekian KK. 1990. Time scale of hydrothermal water-rock reactions in Yellowstone National Park, based on radium isotopes and radon. *J. Volcan. Geotherm. Res.* 40:169–80
- Cochran JK, Bacon MP, Krishnaswami S, Turekian KK. 1983.<sup>210</sup>Po and <sup>210</sup>Pb distributions in the central and eastern Indian Ocean. *Earth Planet. Sci. Lett.* 65:51–60
- Cochran JK, Landman NH, Turekian KK, Michard A, Schrag DP. 2003. Paleoceanography of the Late Cretaceous Western Interior Seaway of North America: evidence from Sr and O isotopes. *Paleogeogr. Paleoclim. Paleocol.* 191:45–64

- Colman AS, Blake RE, Karl DM, Fogel ML, Turekian KK. 2005. Marine phosphate oxygen isotoes and organic matter remineralization in the oceans. *Proc. Natl. Acad. Sci. USA* 102:13023–28
- Copenhaver SA, Krishnaswami S, Turekian KK, Shaw H. 1992. <sup>238</sup>U and <sup>232</sup>Th series nuclides in groundwater from the J-13 well at the Nevada test site: implications for ion retardation. *Geophys. Res. Lett.* 19:1383–86
- Craig H, Somayajulu BK, Turekian KK. 2000. Paradox lost: silicon 32 and the global ocean silica cycle. *Earth Planet. Sci. Lett.* 175:297–308
- Damon PE, Kulp JL. 1958. Inert gases and the evolution of the atmosphere. *Geochim. Cosmochim. Acta* 13:280–92
- Dasch EJ. 1969. Strontium isotopes in weathering profiles, deep-sea sediments, and sedimentary rocks. *Geochim. Cosmochim. Acta* 15:1521–52
- Dasch EJ, Biscaye PE. 1971. Isotopic composition of strontium in Cretaceous-torecent, pelagic foraminifera. *Earth Planet. Sci. Lett.* 11:201–4
- Dasch EJ, Hills FA, Turekian KK. 1966. Strontium isotopes in deep-sea sediments. *Science* 153:295–97
- Davis AM. 1977. *The cosmochemical history of the Pallasites*. PhD thesis. Yale Univ., New Haven, CT. 285pp.
- Dodge RE, Thomas J. 1974. The natural radiochemical and growth records in contemporary hermatypic corals from the Atlantic and Caribbean. *Earth Planet. Sci. Lett.* 23:313–22
- Esser BK, Turekian KK. 1988. Accretion rate of extraterrestrial particles determined from osmium isotope systematics of Pacific pelagic clay and manganese nodules. *Geochim. Cosmochim. Acta* 52:1383–88
- Esser BK, Turekian KK. 1993. Anthropogenic osmium in coastal deposits. *Environ. Sci. Technol.* 27:2719–24
- Farley KA, Turekian KK. 1990. Lead-210 in the Circumpolar South Atlantic. Deep-Sea Res. 37:1849–60
- Gast PW. 1955. Abundance of Sr<sup>87</sup> during geologic time. *Geol. Soc. Am. Bull.* 66:1449–54
- Graustein WC, Turekian KK. 1986. <sup>210</sup>Pb and <sup>137</sup>Cs in air and soils measure the rate and vertical distribution of aerosol scavenging. *J. Geophys. Res.* 91:14:355–66
- Graustein WC, Turekian KK. 1990. Radon fluxes from soils to the atmosphere measured by <sup>210</sup>Pb-<sup>226</sup>Ra disequilibrium in soils. *Geophys. Res. Lett.* 17:841–44
- Graustein WC, Turekian KK. 1996. <sup>7</sup>Be and <sup>210</sup>Pb indicate an upper troposphere source for elevated ozone in the summertime subtropical free troposphere of the eastern North Atlantic. *Geophys. Res. Lett.* 23:539–42
- Grossman L. 1972. Condensation in the primitive solar nebula. *Gecochim. Cosmochim.* Acta 36:597–619
- Grossman L. 1973. Refractory trace elements in Ca-Al-rich inclusions in the Allende meteorite. *Geochim. Cosmochim. Acta* 37:1119–40
- Kaufman A, Li Y-H, Turekian KK. 1981. The removal rates of <sup>234</sup>Th and <sup>228</sup>Th from waters of the New York Bight. *Earth Planet. Sci. Lett.* 54:385–92
- Kharkar DP, Turekian KK. 1971. Analyses of Apollo 11 and 12 rocks and soils by neutron activation. *Proc. 2nd Lunar Conf.*, 2:1301–5. Cambridge, MA: MIT Press

- Kharkar DP, Turekian KK, Scott MR. 1969. Comparison of sedimentation rates obtained by Si<sup>32</sup> and uranium decay series determinations in some siliceous Antarctic cores. *Earth Planet. Sci. Lett.* 6:61–68
- Krishnaswami S, Graustein WC, Turekian KK, Dowd JW. 1982. Radium, thorium and radioactive lead isotopes in groundwaters: application to the *in situ* determination of adsorption-desorption constants and retardation factors. *Water Resour*: *Res.* 18:1663–75
- Krishnaswami S, Mangini A, Thomas JH, Sharma P, Cochran JK, et al. 1982. <sup>10</sup>Be and Th isotopes in manganese nodules and adjacent sediments: nodule growth histories and nuclide behavior. *Earth Planet. Sci. Lett.* 59:217–34
- Kulp JL, Turekian KK, Boyd DW. 1952. Strontium content of limestones and fossils. Geol. Soc. Am. Bull. 63:701–16
- Luck J-M, Turekian KK. 1983. <sup>187</sup>Os/<sup>186</sup>Os in manganese nodules and the Cretaceous-Tertiary boundary. *Science* 222:613–15
- Mangini A, Segl M, Bonani G, Hofmann HJ, Morenzoni E, et al. 1984. Massspectrometric <sup>10</sup>Be dating of deep-sea sediments applying the Zurich tandem accelerator. *Nucl. Instr. Meth. Phys. Res. B* 5:353–58
- Marcantonio F, Turekian KK, Higgins S, Anderson RF, Stute M, Schlosser P. 1999. The accretion rate of extraterrestrial <sup>3</sup>He based on oceanic <sup>230</sup>Th flux and the relation to Os isotope variation over the past 200 thousand years in an Indian Ocean core. *Earth Planet. Sci. Lett.* 170:157–68
- Martin CE. 1990. *Rhenium-osmium isotope geochemistry of the mantle*. PhD thesis. Yale Univ., New Haven, CT. 170 pp.
- Monaghan MC, Krishnaswami S, Turekian KK. 1985. The global-average production rate of <sup>10</sup>Be. *Earth Planet. Sci. Lett.* 76:279–87
- Moore WS. 1969. Oceanic concentrations of radium and a model for its supply. PhD thesis. SUNY Stony Brook. 135 pp.
- Nozaki Y, Thomson J, Turekian KK. 1976. The distribution of <sup>210</sup>Pb and <sup>210</sup>Po in the surface waters of the Pacific Ocean. *Earth Planet. Sci. Lett.* 32:304–12
- Nozaki Y, Cochran JK, Turekian KK, Keller G. 1977. Radiocarbon and <sup>210</sup>Pb distribution in submersible-taken deep-sea cores from Project FAMOUS. *Earth Planet. Sci. Lett.* 34:167–73
- Nozaki Y, DeMaster DJ, Lewis DM, Turekian KK. 1978. Atmospheric Pb-210 fluxes determined from soil profiles. *7. Geophys. Res.* 83:4047–51
- Nozaki Y, Rye DM, Turekian KK, Dodge RE. 1978. A 200 year record of carbon-13 and carbon-14 variations in a Bermuda coral. *Geophys. Res. Lett.* 5:825–28
- Nozaki Y, Turekian KK, Von Damm K. 1980. Pb-210 in GEOSECS water profiles from the North Pacific. *Earth Planet. Sci. Lett.* 49:393–400
- Palmer MR, Turekian KK. 1986. <sup>187</sup>Os/<sup>186</sup>Os in marine manganese nodules and the constraints on the crustal geochemistries of Re and Os. *Nature* 319:216–20
- Pegram WJ, Krishnaswami S, Ravizza GE, Turekian KK. 1992. The record of seawater <sup>187</sup>Os/<sup>186</sup>Os variation through the Cenozoic. *Earth Planet. Sci. Lett.* 113:569– 76
- Pegram WJ, Esser BK, Krishnaswami S, Turekian KK. 1994. The isotopic composition of leachable osmium from river sediments. *Earth Planet. Sci. Lett.* 128:591–99

Peterman ZE, Hedge CE, Tourtelot HA. 1970. Isotopic composition of strontium in sea water throughout Phanerozoic time. *Geochim. Cosmochim. Acta* 34:105–20

Pettersson H. 1958. Rate of accretion of cosmic dust on the Earth. Nature 181:330

- Ravizza G, Turekian KK. 1989. Application of the <sup>187</sup>Re-<sup>187</sup>Os system to black shale geochronometry. *Geochim. Cosmochim. Acta* 53:3257–62
- Schutz DF, Turekian KK. 1965. The investigation of the geographical and vertical distribution of several trace elements in sea water using neutron activation analysis. *Geochim. Cosmochim. Acta* 29:259–313
- Seidemann DE. 1978. 40Ar/39Ar studies of deep-sea igneous rocks. Geochim. Cosmochim. Acta 42:1721-34
- Seidemann DE, Masterson J, Dowling MP, Turekian KK. 1984. K-Ar dates and <sup>40</sup>Ar/<sup>39</sup>Ar age spectra for Mesozoic basalt flows of the Hartland Basin, Connecticut and the Newark Basin, New Jersey. *Geol. Soc. Am. Bull.* 95:594–98
- Settle DM, Patterson CC, Turekian KK, Cochran JK. 1982. Lead precipitation fluxes at tropical oceanic sites determined from <sup>210</sup>Pb measurements. *J. Geophys. Res.* 87:1239–45
- Tanaka N, Turekian KK. 1995. The determination of the dry deposition flux of SO<sub>2</sub> using cosmogenic <sup>35</sup>S and <sup>7</sup>Be measurements. *7. Geophys. Res.* 100:2841–48
- Torgersen T, Turekian KK, Turekian VC, Tanaka N, DeAngelo E, O'Donnell J. 1996.
  <sup>224</sup>Ra distribution in surface and deep water of Long Island Sound: sources and horizontal transport rates. *Cont. Shelf Res.* 16:1545–59
- Trier RM, Broecker WS, Feely HW. 1972. Radium-228 profile at the second GEOSECS intercalibration station 1970 in the North Atlantic. *Earth Planet. Sci. Lett.* 16:141–45
- Turekian KK. 1955. Paleoecological significance of the strontium-calcium ratio in fossils and sediments. *Geol. Soc. Am. Bull.* 66:155–58
- Turekian KK. 1958. Rate of accumulation of nickel in Atlantic equatorial deep-sea sediments and its bearing on possible extra-terrestrial sources. *Nature* 182:1728– 29
- Turekian KK. 1959. The terrestrial economy of helium and argon. Geochim. Cosmochim. Acta 17:37-43
- Turekian KK. 1969. The ocean, streams and atmosphere. In *Handbook of Geochem-istry*, ex. ed. KH Wedepohl, et al., pp. 297–323. Berlin, Heidelberg, New York: Springer-Verlag
- Turekian KK. 1982. Potential of <sup>187</sup>Os/<sup>186</sup>Os as a cosmic versus terrestrial indicator in high iridium layers of sedimentary strata. In *Geological Implications of Impacts* of Large Asteroids and Comets on the Earth, ed. LT Silver, PH Schultz, Spec. Pap. 190, Geol. Soc. Am., pp. 243–49. Boulder, CO: Geol. Soc. Am.
- Turekian KK, Armstrong RL. 1961. The composition of fossil shells from the Fox Hills formation, South Dakota. *Geol. Soc. Am. Bull.* 72:1817–28
- Turekian KK, Benninger LK, Dion EP. 1983. <sup>7</sup>Be and <sup>210</sup>Pb total deposition fluxes at New Haven, Connecticut and Bermuda. *J. Geophys. Res.* 88:5411–15
- Turekian KK, Chan LH. 1971. The marine geochemistry of the uranium isotopes, Th<sup>230</sup> and Pa<sup>231</sup>. In Activation Analysis in Geochemistry and Cosmochemistry, ed. A Brunfelt, E Steinnes, pp. 311–20. Oslo: Oslo Univ. Press

- Turekian KK, Clark SP Jr. 1969. Inhomogeneous accumulation of the earth from the primitive solar nebula. *Earth Planet. Sci. Lett.* 6:346–48
- Turekian KK, Cochran JK. 1981. Growth rate of a vesicomyid clam from the Galapagos spreading center. *Science* 214:909–911
- Turekian KK, Cochran JK. 1986. Flow rates and reaction rates in the Galapagos spreading center hydrothermal system as inferred from <sup>228</sup>Ra/<sup>226</sup>Ra in vesicomyid clam shells. *Proc. Natl. Acad. Sci. USA* 83:6241–44
- Turekian KK, Cochran JK, Bennett JT. 1983. Growth rate of a vesicomyid clam from the 21°N East Pacific Rise hydrothermal area. *Nature* 303:55–56
- Turekian KK, Cochran JK, DeMaster DJ. 1978. Bioturbation in deep-sea deposits: rates and consequences. *Oceanus* 21:34–41
- Turekian KK, Cochran JK, Kharkar DP, Cerrato RM, Vaisnys JR, et al. 1975. The slow growth rate of a deep-sea clam determined by <sup>228</sup>Ra chronology. *Proc. Natl. Acad. Sci. USA* 72:2829–32
- Turekian KK, Cochran JK, Krishnaswami S, Lanford WA, Parker PD, Bauer KA. 1979. The measurement of <sup>10</sup>Be in manganese nodules using a tandem Van de Graaff accelerator. *Geophys. Res. Lett.* 6:417–20
- Turekian KK, Cochran JK, Nozaki Y. 1979. Growth rate of a clam from the Galapagos Rise hot spring field using natural radionuclides. *Nature* 280:385–87
- Turekian KK, Cochran JK, Nozaki Y, Thompson I, Jones DS. 1982. Determination of the shell deposition rates of *Arctica islandica* (Mollusca: Bivalvia) from the New York Bight using natural <sup>228</sup>Ra and <sup>228</sup>Th and bomb-produced <sup>14</sup>C. *Limnol. Oceanogr.* 27:737–41
- Turekian KK, Graustein WC. 2003. Natural radionuclides in the atmosphere. In *Treatise on Geochemistry*, ed. HD Holland, KK Turekian, Vol. 4. *The Atmosphere*, ed. RF Keeling, pp. 261–79. Oxford: Elsevier-Pergamon
- Turekian KK, Graustein WC, Cochran JK. 1989. Lead-210 in the SEAREX program: an aerosol tracer across the Pacific. In *Chemical Oceanography*, ed. JP Riley, 10:51– 81. New York/London: Academic
- Turekian KK, Kharkar DP. 1970a. Neutron activation analysis of milligram quantities of lunar rocks and soils. *Science* 167:507–9
- Turekian KK, Kharkar DP. 1970b. Neutron activation analysis of milligram quantities of Apollo 11 lunar rocks and soils. Geochim. Cosmochim. Acta, Suppl. I, Proc. Apollo 11 Lunar Sci. Conf. 2:1659–64
- Turekian KK, Kharkar DP, Thomson J. 1974. The fates of Pb<sup>210</sup> and Po<sup>210</sup> in the ocean surface. *J. Rech. Atmos.* 8:639–47
- Turekian KK, Kleinkopf D. 1956. Estimates of the average abundance of Cu, Mn, Pb, Ti, Ni and Cr in surface waters of Maine. *Geol. Soc. Am. Bull.* 67:1129–31
- Turekian KK, Kulp JL. 1956. The geochemistry of strontium. *Geochim. Cosmochim.* Acta 10:245–96
- Turekian KK, Nozaki Y, Benninger LK. 1977. Geochemistry of atmospheric radon and radon products. Annu. Rev. Earth Planet. Sci. 5:227–55
- Turekian KK, Pegram WJ. 1997. Os isotope record in a Cenozoic deep-sea core: its relation to global tectonics and climate. In *Tectonic Uplift and Climate Change*, ed. W Ruddiman, pp. 383–97. London, New York, San Francisco: Plenum

- Turekian KK, Tanaka N, Turekian VC, Torgersen T, DeAngelo EC. 1996. Transfer rates of dissolved tracers through estuaries based on <sup>228</sup>Ra: a study of Long Island Sound. *Cont. Shelf Res.* 16:863–73
- Turekian KK, Wedepohl KH. 1961. Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Am. Bull.* 72:175–92
- Wickman FE. 1948. Isotope ratios: a clue to the age of certain sediments. J. Geol. 56:61–66
- Williams GA. 2002. *The transport of osmium from the continents to the oceans*. PhD thesis. Yale Univ., New Haven, CT. 154 pp.