INFORMATION TO USERS

The negative microfilm copy of this dissertation was prepared and inspected by the school granting the degree. We are using this film without further inspection or change. If there are any questions about the content, please write directly to the school. The quality of this reproduction is heavily dependent upon the quality of the original material.

The following explanation of techniques is provided to help clarify notations which may appear on this reproduction.

1. Manuscripts may not always be complete. When it is not possible to obtain missing pages, a note appears to indicate this.
2. When copyrighted materials are removed from the manuscript, a note appears to indicate this.
3. Oversize materials (maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left hand corner and continuing from left to right in equal sections with small overlaps.
4. Most photographs reproduce acceptably on positive microfilm or microfiche but lack clarity on xerographic copies made from the microfilm. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to the Dissertations Customer Services Department.

U·M·I Dissertation
Information Service

University Microfilms International
A Bell & Howell Information Company
300 N. Zeeb Road, Ann Arbor, Michigan 48106

Order Number 9203903

Extraterrestrial organic molecules, the heavy bombardment, and the terrestrial origins of life

Chyba, Christopher Frank, Ph.D.

Cornell University, 1991

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

EXTRATERRESTRIAL ORGANIC MOLECULES, THE HEAVY BOMBARDMENT, AND THE TERRESTRIAL ORIGINS OF LIFE

A Dissertation
Presented to the Faculty of the Graduate School
of Cornell University
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

by
Christopher Frank Chyba
August 1991

Biographical Sketch

Christopher Frank Chyba was born in Baltimore, Maryland, on October 28, 1959, the fourth child of Mary Santora and Herman Joseph Chyba. He attended Saint Ursula Elementary School in Parkville, and Calvert Hall College High School, in Towson, Maryland. In 1977, Mr. Chyba was very fortunate to enter Swarthmore College, in Pennsylvania. He graduated from Swarthmore with the degree of Bachelor of Arts with Honors in 1982, having majored in Physics and minored in Mathematics and Philosophy.

While an undergraduate at Swarthmore, Mr. Chyba was sole author of a number of scholarly papers. These included such diverse topics as black hole evolution (published in *The Journal of Mathematical Physics*), and a historical comparison between the genetic engineering (recombinant DNA) controversy of the late 1970s with attempts during the 1930s to keep nuclear fission research secret from the Nazis (in *Science and Ethical Responsibility*, Addison-Wesley/Advanced Book Program). His senior thesis at Swarthmore, "U.S. military-support equipment sales to the People's Republic of China," was in the department of political science, and appeared in the journal *Asian Survey*. Upon leaving Swarthmore, Mr. Chyba accepted a Marshall Scholarship from Her Majesty's Government for study at Trinity College, at the University of Cambridge, England.

As a Marshall Scholar, Mr. Chyba published work in Kaluza–Klein theory, an attempt to unify the four known fundamental forces of nature via postulating certain symmetries within an eleven–dimensional universe. He was awarded the "Yeats and Rouse Ball Mathematical Essay Prize" from Trinity College for his monograph on claims to faster–than–light communication arising within quantum theory. Mr. Chyba received the degrees of Bachelor of Arts in Mathematics and Master of Philosophy in History and Philosophy of Science (for his dissertation, "Determining the role of consciousness in quantum measurement: Indistinguishability, uncertainty, and the reduced density matrix formalism") from Cambridge in 1984 and 1985, respectively.

In 1985, Mr. Chyba accepted a Sage Fellowship to do research under Dr. Carl Sagan in the Laboratory for Planetary Studies in the Department of Astronomy at Cornell University. From 1988 to 1991 at Cornell, he was a NASA Graduate Student Researcher's Program Fellow.

At the Laboratory for Planetary Studies, Mr. Chyba's research interests broadened, to include a wide range of topics in planetary and space science. Much of his work centered around conditions in the early inner Solar System relevant to the origins of life, and the role that terrestrial collisions of comets and asteroids may have played in that process. This work has appeared in *Icarus*, *Science*, and the British journal *Nature*, and was the topic of Mr. Chyba's invited lecture at the August 1990 Gordon Conference on the Origin of Life.

Mr. Chyba has also observed at the 1000 foot Arecibo radiotelescope observatory in Puerto Rico, and worked with the *Voyager* imaging team during that spacecraft's encounters with Uranus in Neptune in 1986 and 1989, respectively.

He is a coauthor of the imaging team's Neptune ninety day report in *Science.*

In addition to his strictly scientific pursuits while at Cornell, Mr. Chyba maintained an interest in foreign affairs. He served as one of ten delegates on the Science and Technology Commission at the U.S.–U.S.S.R. Emerging Leaders Summit in Philadelphia, December 1988, and was one of a dozen members of a delegation of the American Center for International Leadership to the Chernobyl nuclear power plant in July 1989.

Mr. Chyba received a Master of Arts degree in Astronomy from Cornell University in 1988. In June of 1991, he successfully defended his Ph.D. dissertation, and was awarded the degree of Doctor of Philosophy from Cornell in August 1991. Mr. Chyba spent July of that summer above the Arctic Circle in northeast Siberia, as a member of a joint Soviet–U.S. team investigating tundra lakes and evidence for viable bacteria in ancient (three million year old) permafrost. These topics will comprise part of Dr. Chyba's investigations at the NASA Ames Research Center in Moffett Field, California, where he will take up a National Research Council Fellowship in October 1991.

To my parents, Mary Santora and Herman Joseph Chyba, and my brothers and sister, David, Michele, and Tom. *Si valetis, valeo.*

Acknowledgments

Certain acknowledgments are of a primordial nature. This dissertation is dedicated to my sister, brothers, and parents. No one who has completed the years of study and research necessary for a Ph.D. thesis could doubt the help that a family's support brings, or the importance of all that happened in the many years prior to university. How can one express gratitude for events that stretch continuously over all of one's memories and, more daunting still, prior even to those? One could do worse than to recall Alasdair MacIntyre's acknowledgment of a similarly fundamental debt, in the preface to his *After Virtue*: In this, as in so much else, *sine qua non.*

I decided to come to Cornell to do planetary science one Saturday morning in the spring of 1984, while sitting in my room in Fisher House, Cambridge. At the time, I was studying field theory in the Department of Applied Mathematics and Theoretical Physics, under a Marshall Scholarship from the British Government. My years at Cambridge, at least after my first Michaelmas term, were wonderful. But I had realized that I needed a change. I loved the elegance of field theory, but I disliked the idea of spending the next few years of my life sitting behind a desk doing only Lie Algebras. There were too many other areas of science I had always been interested in. And I had noticed that my time in Heffers bookshop, when spent amongst the science shelves, was spent mostly in the biology section, and especially with those few books on the origins of life.

So that morning I began to dig through the university brochures that I had carried across the Atlantic with me. At some point in my undergraduate years, I had sent for information to various astronomy, biology, foreign affairs (you name it) programs around the country. I leafed through a few of these. I picked up the little Cornell Astronomy and Space Sciences booklet. I saw the picture of the Arecibo radiotelescope. Gosh that looked interesting, even if I had no relevant background in electrical engineering. (Only later, in planetary science, was I to coin the ironic phrase, "never let ignorance of all relevant fields prevent you from publishing." In Cambridge, though, I hadn't yet realized how that remark really is half —if only half—true.) I turned a few more pages, past various pictures of faculty, and came to Carl Sagan's photo. Underneath there was a description of research in the planetary group at Cornell: ". . . broad range of research . . . using theoretical, laboratory, and observational techniques . . . ."

Breadth of techniques, I thought, almost certainly implied breadth of interests, an attitude disposed to addressing a variety of topics—all the science I couldn't see while doing Lie Algebras, elegant though they were. Then I found the description of Carl's research: ". . . investigations of the organic clouds of Titan . . . the chemistry of comets and interstellar grains, aeolian [I looked the word up] processes and seasonal changes on Mars, and several subjects connected with exobiology . . . ." Bingo. A way to segue towards the origins of life for someone with a physics, not a biology, background. And maybe get to work with spacecraft and radiotelescopes to boot!

What did I know about Dr. Carl Sagan? Very little. I had never seen any of *Cosmos*; it had come out while I was in college, and somehow not much TV got watched during those years. In high school I had read *The Cosmic Connection*, and I remembered its enjoyable willingness to grapple with problems that were tough (if not impossible) to make progress with, and to see how far we could push our answers to them. Somehow, from the little I had read, I had the impression that Carl was probably a nice guy. (I had long previously decided, while watching others battle their way through grad school, that I would work only in a friendly department, and only for someone I could get along with.) It was time to write letters, and visit the department.

I visited the department that summer, where Dr. Phil Nicholson helped swing things in Cornell's favor by making time for a long, thoughtful chat with me in his office. It was around this time that I also talked with my old friend Steve Palumbi. Steve happened to be visiting his parents in Baltimore when I passed though, taking time out from his marine biological explorations to travel with his infant son. One afternoon, as he swung in the swing of his parents' front porch, bouncing Tony in his lap, I mentioned misgivings about leaving one graduate career, and switching to another. Steve remarked, "Just remember the Concorde Fallacy." "The Concorde Fallacy?" "The Concorde fallacy says that once you've put enough money, effort, but above all *time* into something, you should stick with it, no matter what." I remembered his remark. And I wrote to Carl, and to Dr. Joseph Veverka, who was then graduate field representative for the department. Both got in touch with me.

It was early in 1985 when I first heard from Carl. By that time I had moved to a flat at 3 Portugal Place, less than a block (Cambridge is like this) from where Francis Crick had lived in a home with a golden helix mounted on the front wall. My flat didn't have a phone, so getting in touch with me was a problem. Carl's executive staff assistant, Eleanor York, tried calling my home in Baltimore, to find out how to reach me. My sister took the call, and passed it to my mother. My Mom explained how I called home pretty regularly; Eleanor requested that they ask me to call Carl the next time they heard from me.

Never someone to loiter when action calls, my Dad decided not to wait. Thus the first thing I learned of any of this was when a telegram arrived out of the blue:

CHRIS CHYBA FLAT 1 3 PORTUGAL PL CAMBRIDGECB58A5ENGLAND PHONE COLLECT DOCTOR CARL SAGAN 607-555-1234 AFTER 3 PM BALTIMORE TIME. DAD

In subsequent communications, both Carl and Joe were extremely encouraging about the breadth of topics I could have a look at while at Cornell. Joe promised I could take a course in "e.g., Chinese history" if I wanted to. I decided to come.

I really can't thank Carl enough for all he did for me as a thesis advisor. We had fascinating, free-wheeling discussions in his office, over lunch, in restaurants, in cars. He encouraged me to enroll in his graduate seminar my first semester at Cornell, despite my initial objection that I was ignorant of all relevant fields . . . . He encouraged me—and funded me—to go to many conferences, to go observing at Arecibo, and to join the imaging team during the *Voyager* spacecraft's encounters with Uranus and Neptune. (Thus I was a participant in the first exploration of two whole new systems of worlds; either experience alone justified my decision to come to Cornell.) He enthusiastically took up my suggestion that he teach a graduate seminar in the origins of life, which may have been the best course I took at Cornell. He suggested both broad lines of research and specific problems, but also let me chase down my own projects. Even in the latter cases, he carefully critiqued my work. He has scrupulously respected—no, encouraged—my right to disagree with him. He has given me wise advice; he has been my friend. And he threw the best parties I've ever been to, anywhere.

I must also thank the other members of my Special Committee; Drs. Joe Burns, Phil Nicholson, Martha Haynes, and Steve Squyres. Many people don't believe me when I tell them that every member of my committee read my thesis, but the tall pile of marked copies on my desk attests to it. Joe Burns especially deserves to be thanked here, as I gave him a copy of the dissertation while forgetting to mention that my reference list was not yet complete. Joe checked off whole chapters of citations that he did not find in the bibliography: Sorry, Joe!

Joe also taught two excellent courses in Theoretical and Applied Mechanics and, as described in Chapter 1 of this thesis, got me started thinking about the heavy bombardment. His "Mechanics of the Solar System" course showed me over and over again how exciting planetary science is. Phil patiently helped me through Kaula perturbation theory and the theory of Cassini states, so that we could attack Triton's orbital evolution around Neptune. He also gave an excellent, top-notch "Physics of the Planets" course my first semester at Cornell. (I needed this course badly, as at the time I came to the Department of Astronomy at Cornell, I scarcely knew what a "planet" was.) Steve worked with me on a number of problems related to Mars, and over the years kept dangling new projects before my eyes. He also helped instill an enthusiasm for field work. Martha (and Dr. Jim Cordes) taught me radio astronomy, or rather, as much of it as I know. Martha has also been a good friend, joining me for lunches and dinners, and listening to some of my exaggerated woes.

Many good friends helped me through Cornell. I would especially like to thank Ann Blythe, Paul Thomas, and Andy Clegg. You three got me through this alive, and I'll never forget it. Enough said.

I've enjoyed many talks with Gene McDonald, Friday afternoon and otherwise. Bill Bohrer has selflessly shared his reminiscences from the Peace Corps and the EPA, and his honed taste in scotch. Neil Rowlands and Lu Nan–Yao were especially pleasant people to share a first–year office with. Tony Phillips, *inter alia*, joined Andy and me for a night in a tiny "Visiting Scientists' Quarters" (VSQ) room at Arecibo Observatory as Hurricane Hugo blew past, and we broke out the hardhats, machetes, short–wave radios, beer, and first–aid kits. Andy showed me the ropes of observing at Arecibo, and also rode me around the island of Puerto Rico in an observatory car that he wouldn't let me drive. Kristen Clegg kept Andy Clegg sane, if only barely, and snuck off with me for dinners when Andy was out of town.

Pete Thomas upheld the traditions of Astro$cam, and gave wonderful dinner parties. Bishun Khare and Reid Thompson were always there when I needed them scientifically, and were terribly helpful people to share a floor with. Jules Goldspiel and Mike Smith somehow put up with me as an officemate, and took innumerable phone calls when I was away from my desk, which must have seemed like always. Several times, especially early on, Joe Veverka gave me excellent advice. Dave Chernoff showed a concern for grad students that I shall not soon forget. Steve Beckwith, along with Andy Clegg, Tony Phillips, and Reid Thompson, all helped me to understand radiative transfer theory. Jim Houck taught me a few things about teaching.

Eleanor York, Nancy Struckman, and Susan Bohuslav, Carl's executive and research aids, helped me so often and so well that it's hard to know what to say. Things would have been much, much, more difficult without them. And much less fun.

One of the wonderful things about studying planets at Cornell is the Spacecraft Planetary Imaging Facility (SPIF); Margaret Dermott, Rick Kline, and Meghan Brundage: *ex libris ad astra.*

To Gerry Hoffman, with whom I lived my first two years here, and who regularly rolled his eyes over my ignorance of organic chemistry (thanks for the tutoring, Gerr), and to Barbara Bowman, with whom I've had many long, fascinating, and enjoyable conversations about molecular biology: I'm glad I'll see much more of you in California.

Bob "Boss" Kolvoord roomed with me at nearly all of my DPS meetings, and was a regular morale–booster. "Illogique, Capitaine." Joel Schwartz somehow became a very good friend only after we lived thousands of miles away from one another. Some of the finest restaurant conversations (and certainly the highest bills) I've ever had have been with Joel. I shall always remember going to "Le Caveau" in Paris with Joel and Bob, and jitterbugging there with Ann "Bo" Verbiscer. Bo, thank you for everything. Joel, thanks for the rides around L.A. in your big red convertible, and for helping me learn how to get in and out without opening the door.

Back again at Cornell, Slava Paperno taught a lot of Russian classes with me as a student, and put up with my perennial lack of time and choppy schedule. Hope D'Amore tried to keep me from becoming too one–dimensional. Cheryl Hall has always helped me stay calm *and* provided countless cookies. Frank Cooper has just been his usual ornery, good–natured self. Jayaram Chengalur has been a quiet voice for reason. Paul Helfenstein *always* made time to help. Dave and Tracy Jankowski threw great superbowl and presidential debate parties. Mary Roth has always given me conversations to look forward to. Tami Hall and Sue Clark have brightened many days. Tom Megeath has steered me towards good literature. Max ("The sky above the port was the color of television, tuned to a dead channel") has also steered me, though it's harder to say where.

I hope that Elizabeth Bilson and Yervant Terzian feel they've gotten something back, considering all the problems I've caused. Thanks.

The penultimate word here goes to Barbara Boettcher. Most of the graphics, and many of the tables, in this dissertation and in my papers, have been made ready for publication by Barb. Both Barb and Janice Ricardo were looking out for us from the moment we all came in as first year grad students. Thank you.

The Cornell Shorinji Kempo club helped me keep things in perspective. Joe Arcail, Liz Carr, Gary Dolce, Chris Kjellmark, Todd Olson, Iva Wong, and Kam Ming Wong: It's not your fault if perspective sometimes eluded me nonetheless.

Finally, I have to say a special thank you to Jim Cordes. Jim was standing in his workroom one morning and witnessed one of the dumbest moments of my graduate career. I came walking by while Andy typed away at the keyboard of Jim's brand-new workstation. Only minutes earlier, Andy had bought the biggest cup of coffee he'd ever purchased in his life and, unusual for him, had it sitting right next to the keyboard. Before even noticing the cup, I had knocked it over. As I watched the resulting tsunami of coffee roll over Jim's brand-new keyboard, I wondered: Is Jim going to scream? Much to his credit, he did not; rather he seemed to find my embarrassment amusing. Note to the reader: Coffee really does destroy computer keyboards—right before your eyes.

If the number of people I have to thank at Cornell are too many to list *in toto*, the numbers away from Cornell are impossible. Leigh Brookshaw was a first-rate collaborator who became a good friend. Carolyn Porco and Dave Grinspoon are two more people who somehow have become good friends while living thousands of miles away from me. Mike Mumma, Humberto Campins, Bill McKinnon, Paul Weissman, Jay Melosh, Kevin Zahnle, Chris McKay, Jim Pollack, Dave Stevenson, Norm Sleep, Stanley Miller, Juan Oró—all have been very helpful to a newcomer in their fields. Jim Kasting invited me to the Gordon Conference, which he chaired. This conference remains the best conference I have ever attended, a model of excited, enthusiastic people eager to learn from one another.

Lou Friedman was pivotal in The Planetary Society's decision to fund my trip to Chernobyl. Cornell University, then NASA, provided fellowships supported me for five of my six years at Cornell.

During the *Voyager* encounters, Mert Davies, Larry Soderblom, and Candy Hansen all helped me get on my feet. But I especially have to thank Bob Hamilton Brown and his wife Priscilla. Not only did they make me feel at home, but Bob went out of his way to give me special opportunities, such as inviting me to go observing with him on Mauna Kea.

My friend Dave DeBeer has taught me perspective for over a decade now, and took me through one of the craziest "holidays" I've ever been on in Ecuador and the Galápagos. Thanks, I think, Dave.

As explained elsewhere, I came to Cornell from the University of Cambridge, where I was funded by a Marshall Scholarship. I'd like to thank the Marshall Aid Commemoration Commission, and the British Government, for making this possible. Gil Stott at Swarthmore played a big role in helping me win the Marshall. Thanks again, Gil. I'm sure my many good friends at Cambridge will forgive me for picking out just one of their number, Dave Randell, for indirectly helping me go into planetary science. In Cambridge, Dave and I attended all sorts of colloquia together: Freeman Dyson on the origins of life, Stephen J. Gould on evolution, talks on the caves of Java, Mesozoic reptiles, even exobiology. Then a cup of tea or a pint and a good chat. Note that all these topics could loosely be described as "natural history". Clearly, this was telling me something.

I began these acknowledgments with some remarks about primordial debts. My debt to Swarthmore College may not be primordial, but it is vast. Going to Swarthmore may be the best decision I ever made; even now I think of all else flowing from that one choice. I shall not try to name all the professors, students, and administrators who made that school a place of amazing intellectual ferment, a place where you would read Roberto Unger's "Knowledge and Politics" not because you were taking it in a course, but because your friends were, and they were spending their dinners in the cafeteria talking about it. But with respect to my being a scientist, I owe a special debt to Jim England, Paul Mangelsdorf, Rush Holt, and John Boccio. Aside from my thesis advisor here at Cornell, my training as a scientist probably owes more to John Boccio than to anyone. Thanks again, John.

No one becomes a space scientist who can't read and write, or who can't do math. I was fortunate to be sent to good schools as a child, but I was also fortunate to have parents who helped me every step of the way. I have not forgotten my mother reading me Donald Duck comic books at lunch, pointing to the words, while my brothers and sister scowled because *they* were trying to read their Donald Duck comics in peace. I have not forgotten my mother working through the multiplication tables with me as we walked to school together in fourth grade, at a time when long multiplication and division seemed impossible, and my test scores seemed to confirm that it was. I haven't forgotten sitting at the kitchen table the nights before tests in (of all things) Earth Science, while Mom, at my request, quizzed me on the chapters I was supposed to know. (Of course, I understand better now than I did then how much this all meant.) Less tangible, but just as important, was the sense my Dad conveyed to me of science as an exciting adventure: Exploration, and maps, and mysteries, and flashes of wonder and sudden understanding. He was right.

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1 Ever Since Berzelius

Since the Swedish chemist Baron Jöns Jacob Berzelius first analyzed the Alais CI carbonaceous chondrite for organic molecules in 1834 (Berzelius 1834), attempts to forge a link between extraterrestrial organic materials and terrestrial life have remained alluring, but often deceptive. Two distinct investigations are demanded in exploring such links (Chyba 1990b): accurately characterizing the organics present in extraterrestrial bodies; and evaluating possible mechanisms for delivering these molecules intact to Earth. This thesis hopes to carry both these investigations a few steps further along.

Something must be said immediately about the word "organic". It was Berzelius who introduced the term, using it to delineate the domain of compounds seemingly unique to living systems. Twenty-one years later, in 1828, one of Berzelius' own students, the German chemist Friedrich Wöhler, showed that the supposed barrier between biological and non-biological compounds was a false one. Beginning with an inorganic salt, Wöhler produced in the laboratory the organic molecule urea. (This history has been summarized by, for example, Day 1979, 1984.)

In modern usage, the word "organic" refers simply to molecules in which carbon is covalently bonded to hydrogen, and perhaps to other atoms such as nitrogen, oxygen, or sulfur. By this definition, methane (CH_4) or hydrogen cyanide (HCN) are simple organics, but carbon dioxide (CO_2) or calcium carbonate ($CaCO_3$) are not. "Hydrocarbons" are molecules consisting entirely of carbon and hydrogen. All hydrocarbons are organics, but even as simple (and prebiotically important) an organic as HCN is not a hydrocarbon. HCN appears to be abundant in comet Halley (see Chapter 5). Therefore Halley is "organic-rich", and not merely "hydrocarbon-rich".

Organic molecules are of distinct prebiotic interest, but the word carries no implication of biological origin. Perhaps because it once did, however, the word makes some planetary scientists nervous (it does not have this effect on chemists, who are entirely nonchalant about the term). Dr. Steven Squyres of Cornell University likes to call to mind the effect the term "organic" sometimes has by referring to it as "the O-word". Other planetary scientists, less ironically, have adopted the acronym "CHON", for "carbon-hydrogen-oxygen-nitrogen". "CHON" is meant to be a more dignified way of saying "the O-word".

1.2 The Christmas of 1908

In the December 25, 1908 issue of the journal *Science*, two Univeristy of Chicago geologists, T.C. Chamberlin and R.T. Chamberlin, suggested that infalling planetesimals may have played a role in setting the stage for life on Earth (Chamberlin and Chamberlin 1908). This strikingly prescient paper[1] relied on an accreting planetesimal model for planetary formation (similar to the models favored today). Chamberlin and Chamberlin knew that hydrocarbons had been extracted from meteorites, and that the carbonaceous chondrite Orgueil had been shown to contain organic matter similar in composition to terrestrial humus. Speculating

---

[1] I am grateful to Roscoe Stribling and Stanley Miller for first bringing this paper to my attention, at the Prague meeting of the International Society for the Study of the Origin of Life, in July 1989.

on the fate of such material if brought to the Earth in accreting planetesimals, they wrote (pp. 902–903): "The chief point of interest here is not simply the presence, but the close intergrowth, of compounds of the organic elements in states of combination which, while stable in the cosmic regions surrounding the earth from which the planetesimal material was gathered, are pronouncedly unstable in the presence of the air and water, even at the ordinary temperatures at which organic synthesis takes place. On reaching the surface of the earth, these compounds would therefore have been no longer stable, but must have sought new relations." Sources of energy that may have been important for ensuing chemical reactions, they noted, could have included (p. 906) "the electrolytic action of earth–currents", as well as (p. 907) "the agitations of radioactivity, and the states of ionization to which it gives rise, [which] may have played a slightly more active part in the chemical processes of early times than they do to–day . . . ." Chamberlin and Chamberlin thus anticipated later investigations of both *in situ* prebiotic organic synthesis by electrical discharge or radiation (first brought to experimental fruition a half–century later, again at the University of Chicago), and direct organic delivery from extraterrestrial bodies.

1.3 The Miller–Urey Experiment: Its Antecedents, and its Aftermath

Since the middle of the nineteenth century, chemists had been experimenting with the production of ammonia (NH_3) by electrical discharge acting on mixtures of hydrogen and nitrogen, early work later summarized by Briner and Mettler (1908). By about the time of that review, it had been recognized that hydrogen cyanide (HCN), recognized today as a key prebiotic molecule, was also produced in similar experiments, and the nature of the mechanism by which electrical discharge led to molecular synthesis was being debated (Briner 1914). (A modern incarnation of one aspect of this debate may be found in Section 8.4 of this thesis.) By 1919, the details of HCN production were being investigated (Briner and Baerfuss 1919). However, perhaps because these investigations were motivated by maximizing production for industrial purposes, no connection appears to have been made with the speculations of Chamberlin and Chamberlin (1908), concerning a possible role for electrical discharges in prebiotic organic chemistry.

In 1953, however, results were published for a set of organic synthesis experiments that had been undertaken explicitly because of their implications for the origins of life (for an engrossing first–person account of the genesis and execution of these first experiments, see Miller 1974). In 1953 Stanley Miller, a University of Chicago graduate student working with the cosmochemist Harold Urey, showed that amino acids, the building blocks of proteins, would form naturally in what was then believed to have been the likely atmosphere of the early Earth (Miller 1953). Simulating this primitive atmosphere with a gas mixture of methane, ammonia, and water, Miller introduced an electrical spark (representing, for example, lightning) and obtained a high yield of amino acids.

It has since been shown that in such a reducing atmosphere, a variety of energy sources (Miller and Urey 1959, Bar–Nun *et al.* 1970) will lead to the creation not only of amino acids but to the precursors of other important biological molecules. In the traditional view of primitive Earth, these precursor molecules collected in the oceans, forming a warm, dilute "organic soup", on the surface or shorelines of which life somehow evolved. (The contemporary debate over this "somehow" has recently been sketched by Marcus and Olsen 1991.)

Starting in the 1960s, however, the model of an early reducing terrestrial atmosphere began to be called into question on geological and geochemical grounds (Abelson 1966). There is now a new, still somewhat tentative, consensus among Earth scientists (see Chapter 5) that the early atmosphere probably consisted not of reducing gases, but mainly of carbon dioxide and nitrogen (see Walker 1977, 1986). Under these conditions, production of organic molecules is much more difficult (Chang *et al.* 1983, Schlesinger and Miller 1983a,b).

By no means do the new atmospheric models require us to look to exogenous sources to explain the early Earth's supply of prebiotic molecules. However, these models do suggest that present investigators would do well to quantify as well as possible prebiotic organic production from the variety of sources that have been proposed. Much of this thesis is devoted to this project, extensively for exogenous sources, and less completely for endogenous ones. As complete a quantitative comparison as currently possible of exogenous with endogenous sources is underway (Chyba and Sagan 1990, and in preparation). Inevitably, though, a given investigator may always invoke some as-yet unquantified source of prebiotic organics as the *deus ex machina* which will render, for example, the exogenous sources considered here superfluous. The challenge to that investigator is to quantify the importance of his or her favorite source at least to the extent that it may be compared with the sources considered here.

Of course, one ultimately wants to characterize the nature of the organics supplied by the various sources. Certain quantitatively less important sources might provide especially important molecules in amounts greater than those sources that dominate in a crude "total mass of organics" sense. This program remains almost entirely unfulfilled.

1.4 Extraterrestrial Organics Come of Age

Shortly after the early reducing atmosphere model for prebiotic organic synthesis began to be called into question, extremely good samples of organic-rich meteorites became available for study. Earlier identifications of amino acids in meteorites (Degens and Bajor 1962, Kaplan *et al.* 1963) had failed to survive objections concerning terrestrial contamination (Hamilton 1965, Oró and Skewes 1965), and were made in the midst of an acrimonious controversy over claims for microfossils (Claus and Nagy 1961, Fitch *et al.* 1962, Briggs and Kitto 1962, Nagy *et al.* 1962, Fitch and Anders 1963) and biogenic organic molecules (Nagy *et al.* 1961, Anders 1963) in meteorites (for reviews see Urey 1966, and Day 1979, 1984). In 1970, Kvenvolden *et al.* published the first of a series of studies that unequivocally demonstrated that amino acids in the Murchison meteorite, which had fallen the previous year, were extraterrestrial and probably abiogenic (Kvenvolden *et al.* 1970, 1971).

The evidence was threefold: Murchison's amino acids were nearly racemic (equal) mixtures of the D and L enantiomers (see Figure 1.1), whereas terrestrial organisms use almost exclusively the L enantiomer (known mechanisms of abiological chemical production produce both in equal quantities, however); extractable Murchison organic compounds had δ^{13}C values (which measure the carbon isotope ratio ^{13}C/^{12}C) that were greater than those in any naturally occurring terrestrial organics; and Murchison contained non-biological amino acids—those not among the 26 or so commonly found in terrestrial organisms. At least 74 amino acids have now been identified in Murchison extract (Cronin *et al.* 1988).

There is no difficulty in the non-destructive delivery of organic molecules to Earth in objects the size of the Murchison fragments (see Chapter 7). The bulk of the mass in potential terrestrial impactors, however, is concentrated in much larger bodies. For extraterrestrial material to have had a substantial influence on prebiotic chemistry, it would seem that this reservoir must somehow be tapped.

1.5 Infrared Emission by Organic Grains in Comets

Before turning to discussions of delivering organic molecules intact to Earth, this thesis concerns itself with cometary organic molecules. As discussed in Chapter 5, spacecraft exploration of comet Halley has confirmed comets to be much richer in organics than carbonaceous chondrites. Spectroscopic observations allow us to reliably extrapolate some of the discoveries found by the Giotto and Vega probes

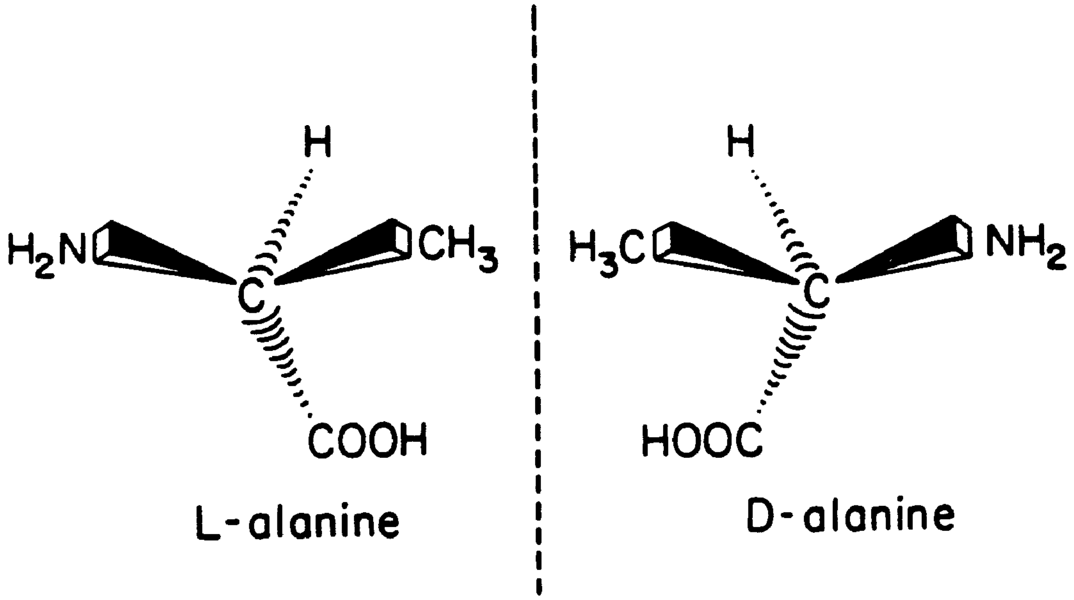

Figure 1.1 The L and D enantiomers (from the Greek *enantios*: opposite) of the amino acid alanine. The two molecules are mirror images; no rotation through three dimensions can superimpose them. The enantiomers rotate the plane of polarization of light in opposite directions; unequal mixtures are therefore optically active. A mixture consisting of equal numbers of each is said to be racemic. Terrestrial life uses almost exclusively the L-amino-acid enantiomers (Chyba 1990b).

at comet Halley to other comets. In particular, the 3.4μm emission feature, indicative of C–H stretching in hydrocarbons, has now been definitely observed in some five comets (Brooke *et al.* 1991).

Clearly, then, understanding the origin of the 3.4μm feature is important to our knowledge of cometary organics in general. Chapters 2 and 3 of this thesis pursue a model of the feature as due to thermal emission by hot submicron grains in the cometary coma. Chapter 2 is based on two papers, in *Nature* (Chyba and Sagan 1987b), and in a NASA conference volume (Chyba and Sagan 1989). (The original submission to *Nature* included what became the two papers, but had to be substantially shortened for publication. In the event, our description of the comet Halley pre– and post–accretion irradiation environments, which we argue are responsible in varying degrees for the observed cometary organics, was shortened to a single paragraph for *Nature*. The details eventually appeared as the conference publication.)

In the spring of 1986, we began an extensive literature review of spectroscopic features around 3.3μm and 3.4μm in the interstellar medium. Simultaneously, spectra from the Vega 1 spacecraft in the comet Halley coma (Combes *et al.* 1986), and a number of ground-based spectral observations (for a summary, see Chyba, Sagan, and Mumma 1989) became available. We began to compare these cometary emission features with transmission spectra from the organic residue of irradiated candidate cometary ices, which had been determined prior to these encounters (eventually published in Thompson *et al.* 1987, and Khare *et al.* 1988). By early autumn 1986, we had realized that a simple, direct comparison would not be reliable (though such comparisons were common in the interstellar medium literature). This was because the blackbody spectra relevant to micron and submicron grains at one astronomical unit from the Sun peak close to emission features of interest. Therefore the strength of cometary infrared emission features would be a strong function of the temperature of the grains. Clearly this was an important dependence that is simply not present in laboratory transmission spectra. Returning to first-principles radiative-transfer theory (a paper by Léger and Puget (1984) was most helpful here), we constructed a simple model to transform the laboratory-determined transmission spectrum into a model thermal grain emission spectrum. By early February 1987, we had recognized that a three-component model was a necessary minimum: one component to represent reflected sunlight, one to represent large grains emitting like blackbodies, and one to represent the hot, submicron organic grains responsible for the 3.4μm emission feature. Only the latter component employed the laboratory transmission data.

Finally, in April 1987, Dr. George Helou, then of the California Institute of Technology, gave a Department of Astronomy colloquium on galactic dust and the IRAS survey. One particular viewgraph of blackbody spectra of dust at successive temperatures led to my sudden realization that the three-component model described above requires that cometary emission features of different wavelengths would come in and out of high contrast with the continuum as the comet changed its distance from the Sun (thereby altering grain temperatures). (I heard not another word of Dr. Helou's seminar.) This phenomenon was used in our original *Nature* paper to explain the observed absence of any feature in comet Halley's *emission* spectrum near 6 microns, a result that otherwise would be extremely puzzling, since features near this wavelength are common in laboratory *transmission* spectra of many organic compounds (Chyba and Sagan 1987b).

The heliocentric evolution of cometary infrared emission features was addressed in detail in a subsequent paper in *Icarus* (Chyba, Sagan, and Mumma 1989). The idea of cometary spectral evolution with heliocentric distance was presented as a poster at the August 1987 workshop on infrared observations of comets Halley and Wilson, held at Cornell Univeristy (Hanner 1988). Dr. Robert Gehrz of the University of Minnesota, a conference organizer, noted the poster, and invited me to give an oral presentation. In the discussion following this presentation, Dr. Michael Mumma of the NASA Goddard Space Flight Center remarked that the heliocentric evolution of spectral features would, at least in principle, differ in the cases of thermal emission from small grains and gas–phase fluorescence. Dr. Mumma reminded us of these remarks in his solicited comments on the first draft of the *Icarus* paper, leading us to invite him to join us as a third author. Chapter 3 of this thesis presents the spectral evolution work in detail. Section 3.6 is based on Dr. Mumma's interesting remarks. An effort to test whether the 3.4μm feature is due primarily to grain thermal emission (as we have suggested) or to fluorescence has recently been attempted by combining observations of a number of different comets (Brooke *et al.* 1991). Unfortunately, the results appear inconclusive. Clearly a broader data base is needed; most valuable would be an extensive data base for one particular comet. (The CRAF mission would, for example, provide these data. A dedicated series of ground observations could probably do so as well, though with much poorer signal–to–noise, and therefore undoubtedly only to smaller heliocentric distances.) Perhaps most importantly, a search for emission features near 6μm , at cometary heliocentric distances $\gtrsim$ 2 AU, would not only test our model (see Chapter 3), but potentially provide valuable spectroscopic information about the composition of cometary organics.

1.6 Life on Comets?

In the midst of our work on cometary infrared spectroscopy, we became embroiled in a controversy with Drs. F. Hoyle, N.C. Wickramasinghe, their colleagues, and others, over whether the Halley 3.4μm feature could plausibly be construed as implying the existence of cometary bacteria or viruses (in chronological order, the relevant references are Hoyle and Wickramasinghe 1987, Kissel and Krueger 1987, Chyba and Sagan 1987a, Hoyle and Wickramasinghe 1988a, Greenberg and Zhao 1988, Hoyle and Wickramasinghe 1988b, Chyba and Sagan 1988b, Wallis *et al.* 1989). While Hoyle and Wickramasinghe have argued that resistance to the ideas of interstellar or cometary microorganisms are due to a cultural bias against the existence of extraterrestrial life on the part of the scientific community in general (Hoyle and Wickramasinghe 1986), or on the part of Chyba and Sagan in particular (Hoyle and Wickramasinghe 1988a), their suggestions have in fact been criticized on specific spectroscopic (Davies *et al.* 1984, 1985, 1988, Chyba and Sagan 1987a, 1988b), chemical (Kissel and Krueger 1987), and biological (see Marcus and Olsen 1991, and references therein) grounds. Although the possibility cannot be entirely ruled out, comets seem to offer a poor setting for the origins of life (Bar–Nun *et al.* 1981, Marcus and Olsen 1991).

1.7 Delivery of Biogenic Elements to a Volatile–Poor Early Earth

Throughout the autumn of 1985, I attended the Department of Astronomy seminar, "Scientific Findings by Spacecraft in the Outer Solar System", given by Dr. Carl Sagan and Dr. W. Reid Thompson. I had had only the vaguest ideas of what comets were prior to this seminar. Towards the end of Dr. Sagan's first few lectures, however (during which he delivered his "comet primer"), I for the first time heard the provocative speculation that comets may have provided a late–accreting veneer early in Earth history and thereby supplied the water in the terrestrial oceans. The following semester, spring 1986, I took Dr. Joseph Burns' course, "Mechanics of the Solar System". It was in this course that, *inter alia*, I first obtained anything beyond the vaguest understanding of the existence of the "heavy bombardment" of the early inner Solar System. Immediately I was excited by the idea that the two ideas—cometary water and the heavy bombardment—could somehow be combined. Shortly thereafter, I discovered a remarkable paper by Dr. Herbert Frey, written in partial fulfillment of his Ph.D. requirements at the University of Maryland, and published in *Icarus* in 1977 (Frey 1977). The paper, "Origin of the Earth's Ocean Basins", suggested the provocative (and almost certainly entirely wrong) idea that the Earth's ocean basins were due to giant impacts analogous to those responsible for the lunar impact basins. This paper first introduced me to the idea of mass–diameter scaling laws for lunar craters, and it first suggested to me the idea of extrapolating from the lunar cratering record to the Earth. Regardless of the veracity of Frey's ocean basins–origins speculation, the paper was tremendously important to my initial thinking and subsequent research. To me, Frey's paper provides an excellent example of the value of *Icarus'* embracing of speculative ideas, as summarized by that journal's frontispiece quote from Sir Arthur Eddington.

I initially attempted to use lunar crater scaling to normalize a seemingly uncertain absolute cometary mass flux predicted by a model due to Fernández and Ip (1983) to have impacted Earth early in Solar System history. This idea was initally written up as a paper for Dr. Burns' course. Dr. Burns, in his comments on the paper, encouraged the author to publish the idea, with his remark, "I don't believe it of course but . . . who knows? With work it might be worth trying to publish or present somewhere." Recognizing that this was almost ecstatic praise, coming from Dr. Burns, I did just that, presenting it under the intentionally provocative title, "Are the Earth's Oceans Extraterrestrial?" as a paper at the Paris 1986 meeting of the Division for Planetary Sciences of the American Astronomical Society (Chyba 1986).

It is perhaps a credit to the congeniality of the planetary science community that I drew more encouragement than discouragement from the reception accorded this paper. The most important criticism I received after my presentation was a remark by Dr. George Wetherill of the Carnegie Institution. This remark proved to be perhaps the single most valuable comment made to me at the meeting. In essence, it convinced me that numerical models for the early cometary flux through the inner Solar System would simply not be considered sufficiently reliable to answer a question as important as the origins of the Earth's oceans. I therefore reconsidered my work, hoping to base it more firmly on empirical data (i.e., the lunar cratering record). This led to my first paper in *Nature* on the topic (Chyba 1987). This paper was largely superseded by a later paper in the same journal (Chyba 1990a). Chapter 4 combines the two papers, reproducing only those parts of the earlier paper which were not rendered obsolete by the second publication.

The difficulty in all this work, as emphasized in Chapter 4, remained the unreliability of extrapolations from the lunar cratering record prior to ~4 Gyr ago. I recalled that Dr. Wetherill had also pointed this out in Paris. Chapter 6 represents an attempt to use lunar regolith and terrestrial mantle geochemistry to exclude certain models of this bombardment. Moreover, Chapter 6 considers the implications of the heavy bombardment not just for delivery of planetary oceans, but also for the delivery of other volatile elements, especially the key "biogenic" elements, carbon, nitrogen, and sulfur.

1.8 Exogenous Sources of Prebiotic Organic Molecules

In addition to delivering volatile elements to the early Earth, comets and volatile-rich asteroids might also have provided intact organic molecules of prebiotic interest. As discussed in Section 1.2 above, such speculations had existed at least since 1908. Could the work on the heavy bombardment be used to address this problem more quantitatively?

This possibility was first brought to my attention by Dr. Sagan in the summer of 1986. In a lengthy memo dated 23 July, Dr. Sagan outlined what in effect became the central problem of this thesis, concluding: "So what I imagine, if this interests you, is an updating of the Urey/Miller table for the primitive Earth (cf. Miller and Urey 1959), and some necessarily cruder attempt to estimate energy sources elsewhere in the Solar System in the same epoch as well as today. I think the result would be broadly useful to workers in a number of fields. Also it might help us estimate whether the organic matter that led to the origin of life on Earth was mainly exogenous or endogenous. What do you think?"

The greatest difficulty with this suggestion lay in the fact that the bulk of organic matter reaching the early Earth clearly resided (on the basis of the lunar impact record; see Chapter 6) in the largest impactors. But these are precisely the impactors that should be too large to be decelerated by the Earth's atmosphere, and whose organics one would therefore be expected to be incinerated on impact. Yet if only a small percentage of these survived, they could dominate one's conclusions. Therefore the exogenous part of the problem remained unaddressed for almost two years.

In early April 1988 Dr. Paul Thomas (then at Cornell, now at the University of Wisconsin, Eau Claire) and I first spoke about the cometary organic survival problem. The two of us were, quite frankly, casting about for some problem to work on together. With his usual enthusiasm, Dr. Thomas quickly realized that a hydrodynamic code called smoothed particle hydrodynamics (SPH) might allow the problem to be attacked. He also realized that to do so reliably would require collaborating with an SPH expert. Thus Dr. Leigh Brookshaw, then of Yale University, now at Lawrence Livermore National Laboratory, was drawn into the problem. This wonderfully successful (in my opinion) collaboration eventually led to the extended abstract by Thomas, Chyba, Brookshaw, and Sagan in *Lunar and Planetary Science XX* (Thomas *et al.* 1989), and to the paper by Chyba, Thomas, Brookshaw, and Sagan in *Science* (Chyba *et al.* 1990). The latter forms the basis of Chapter 5.

The *Science* paper acknowledged the ambiguities due to the variety of plausible fits to the lunar cratering record that had been emphasized by Chyba (1990a), summarized here in Chapter 4. The research in Chapter 6 was undertaken largely in the hope of reducing these ambiguities. As argued in that chapter, there was then reason to believe that one particular fit to the lunar cratering record was, in fact, to be preferred, as it was best in accord with geochemical data. Thereafter the problem of exogenous delivery of organics could be addressed with a bit more certainty. Moreover, additional delivery mechanisms, such as interplanetary dust particles and catastrophic airbursts, could also be better quantified. Finally, shock–generation of organics in the terrestrial atmosphere due to bolide passage and subsequent impact could also be addressed. This is discussed in Chapter 7, which is based on a paper currently being revised for publication in *Nature.*

Finally, Chapter 8 begins the process of re–evaluating terrestrial energy sources for the *in situ* production of prebiotic organics. This program is currently being pursued, with the intention of submitting a paper in which the relative quantitative importance of exogenous vs. endogenous prebiotic organics may finally be weighed. Preliminary results (Chyba and Sagan 1990, 1991) suggest that exogenous sources will in fact prove to be of comparable importance to endogenous ones.

1.9 There Are Certainly Uncertainties

Chapter 9 presents a concise review of the uncertainties that currently beset attempts to evaluate the exogenous contribution to the terrestrial prebiotic inventory. While the uncertainties are indeed large, they are comparable to the uncertainties that have long existed in efforts to quantify endogenous contributions. Despite the uncertainties, I believe Chapters 4 through 7 move the broad question of the possible extraterrestrial contribution to the origins of life to a new plane, one on which simple assertions of plausibility are no longer sufficient. The investigation has now matured to evaluations of specific and, in most cases, quantifiable entities.

Chapter 2

Infrared Emission by Organic Grains in Comet Halley[1]

2.1 The Halley 3.4 Micron Feature

Spacecraft (Combes *et al.* 1988) and ground-based (Baas *et al.* 1986, Danks *et al.* 1986, Knacke *et al.* 1986, Wickramasinghe and Allen 1986, Tokunaga *et al.* 1987) observations of comet Halley in the near-infrared reveal an emission feature peaking near $3.36\mu m$, characteristic of C–H stretching in hydrocarbons ($-CH_3$ and $-CH_2-$ alkanes; see, e.g., Allamadola 1984, or Khare *et al.* 1989). Transmission spectra of organic residues produced by laboratory irradiation of candidate cometary ices allow the modelling of emitting cometary dust. As one such candidate, we consider a low-occupancy methane (CH_4) hydrate clathrate. The laboratory synthesis of solid organic residue from this ice simulates the radiation processing experienced by comet Halley. The transmission spectrum of this residue, convolved with a simple two-component thermal emission model based

---

[1] This chapter is based on two papers: Chyba, C. and C. Sagan (26 November 1987), Infrared emission by organic grains in the coma of comet Halley, *Nature* **330**, 350–353 [copyright 1987 by MacMillan Magazines Ltd.]; and Chyba, C. and C. Sagan (1989), The pre- and post-accretion irradiation history of cometary ices, in *Interstellar Dust: Contributed Papers* (A.G.G.M. Tielens and L.J. Allamandola, Eds.), pp. 433–435, NASA CP-3036.

on the spacecraft-determined dust distribution in the Halley coma, fits the 3.4μm feature, provides optical depths in good agreement with those observationally determined, and accounts for the absence of features at longer wavelengths, despite their presence in transmission spectra of typical ice irradiation residues (Chyba and Sagan 1987a,b, 1988a,b).

The 3.4μm feature has the broad, structureless character expected for a solid phase origin, although the best resolution available (Baas *et al.* 1986), $\lambda/\Delta\lambda$ $\sim$400, is insufficient to rule out blending of a variety of lines from gas phase molecules. If due to infrared fluorescence, a production rate for CH–X molecules in the gas phase $\sim$20% that for H_2O seems sufficient to account for the observed flux in the 3.4μm feature in ground-based spectra (Baas *et al.* 1986), in agreement with results from the Vega fly-by (Combes *et al.* 1988). Some contribution to the 3.4μm feature by gaseous emission is therefore expected (Crovisier and Encrenaz 1983). However, a simple model based on thermal emission from small, hot, organic or organic-coated grains in the Halley coma can readily account for this feature. Such a model is given credence by the fact that Vega mass spectrometry shows that $\sim$80% of the dust encountered in the Halley coma is richer in carbon and nitrogen than CI carbonaceous chondrites (Kissel *et al.* 1986). The Vega results have also been interpreted—perhaps over-interpreted—as showing many particles to consist of a predominantly chondritic core surrounded by a complex organic mantle (Kissel and Krueger 1987a). Therefore there is direct evidence for small organic grains in the coma, with typical particle size $\sim$0.1μm (Sekanina 1986).

2.2 Irradiation of Cometary Ices

In cometary ices, clathrate hydrates are thermodynamically favored (Delsemme and Swings 1952, Delsemme 1976), and the most probable unprocessed form of hydrocarbons is the methane hydrate clathrate. Proton (Calcagno *et al.* 1985) or

γ–ray (Davis *et al.* 1966) irradiation of pure CH_4 ice produces an organic residue that shows a 3.4μm absorption feature, as does charged particle irradiation of CH_4 hydrate clathrate and other hydrocarbon/H_2O ices (Thompson *et al.* 1987, Khare *et al.* 1989). (This feature is by no means present in all organic solids; it is absent, e.g., in the solid irradiation products of simulated Uranian and Neptunian atmospheres (Khare *et al.* 1987).) The transmission spectrum for one such irradiated ice residue, that of a low–occupancy (1:200) CH_4/H_2O clathrate, is shown in Figure 2.1. As comet Halley approaches the sun, icy grains are ejected from its surface or jetted from its interior, and the ice sublimes. The refractory organic residue, probably stable to temperatures of 500–1000 K (Sagan *et al.* 1984), remains largely in solid form (though some evaporation may contribute to gas phase fluorescence) and, heated by solar radiation, emits in the infrared. This process is well modelled in our laboratory experiments, where the ice is first irradiated, then completely evaporated by high–vacuum pumping at temperatures $\sim$425 K before the transmission spectrum of the residue is determined (Thompson *et al.* 1987).

A number of regimes can be distinguished for the irradiation of C–rich ices in comet Halley (Chyba and Sagan 1989). The irradiation environments experienced by comet Halley (summarized in Table 2.1) may be divided into four categories: (1) Pre–accretion irradiation of interstellar dust by ultraviolet (UV) light and cosmic rays; (2) Post-accretion irradiation of cometary interiors by incorporated radionuclides; (3) Cosmic ray irradiation over 4.6 Gyr of a comet's outer $\sim$10 m; and (4) Solar wind and UV irradiation to a depth < 1 μm during a comet's typically $\sim$1 Gyr residence in the inner Oort cloud (Ip 1977, Fernández 1985), $\sim$3.5 Gyr residence in the outer Oort cloud, and eventual passage(s) through the inner Solar System.

In its present short-period (SP) orbit, comet Halley's charged particle radiation environment is dominated by the solar wind. At a heliocentric distance

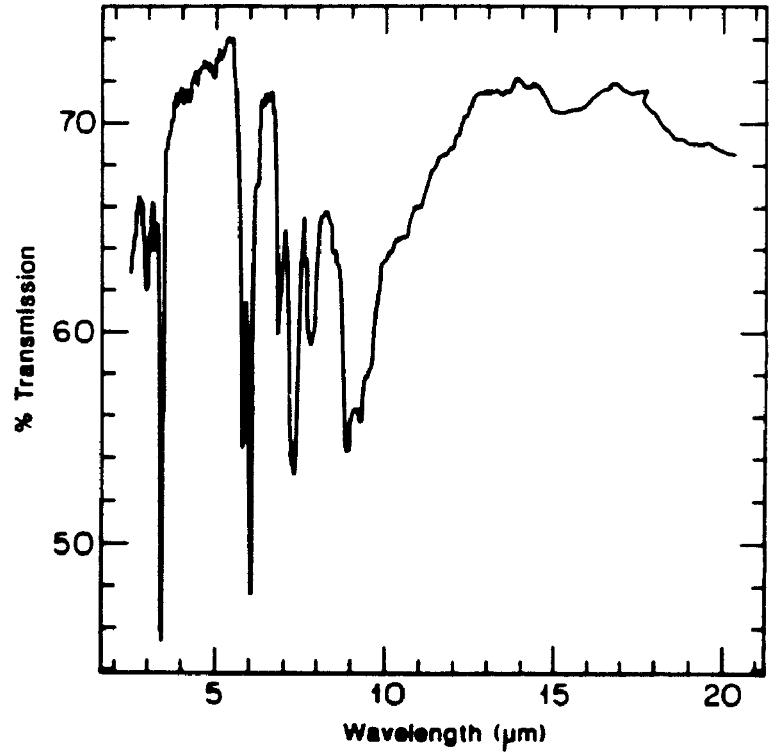

Figure 2.1 The 2–20 μm transmission spectrum of the organic residue of irradiated methane hydrate clathrate. After Thompson *et al.* (1987).

TABLE 2.1

COMET HALLEY IRRADIATION HISTORY

ENVIRONMENT	DOSE (Mrad)[a]	PROCESSING DEPTH	REMARKS
Inner Solar System			
Solar Wind, 1 Orbit	10^3	$<1\,\mu m$	Nucleus Shielded within ~ 5 AU
Solar Wind, 10^2 - 10^3 Orbits	10^5 - 10^6	$<1\,\mu m$	
Residence in Oort Cloud			
Solar Wind, 4.6 Gyr	10^4	$<1\,\mu m$	
Cosmic Rays, 4.6 Gyr [b]	10^4 - 10^5 10^3	~ 1 m ~ 10 m	Flux May Increase Beyond Heliosphere
Radionuclides, 4.6 Gyr [b]	10^3	Entire Nucleus	Assumes no Differentiation ^{26}Al ~ 80%
Inner Oort Cloud			
Solar Wind, ~ Gyr	10^9	$<1\,\mu m$	
Pre - Accretion			
Low Energy Cosmic Rays[c] 10^7 - 10^8 yr	10^4 - 10^5	~ 100 μm	All C - containing Ices Polymerized
Interstellar UV, 10^8 yr [d]	10^7 - 10^8	$<1\,\mu m$	

[a] 1 Mrad = 10^6 rad = 10^8 erg g^{-1} = 10^4 J kg^{-1} = 6.24×10^{16} keV g^{-1} = 2.39 cal g^{-1}

[b] Draganić et al. 1984

[c] Strazzulla et al. 1983

[d] Greenberg and Grim 1986

of 1 AU, the solar wind flux is $\sim 3 \times 10^8$ kev cm^{-2} s^{-1} (Thompson *et al.* 1987). What is the energy flux experienced by the nucleus of comet Halley integrated over one orbit? Close to the Sun, the nucleus is shielded by magnetized plasma in the coma. The Vega 2 spacecraft found that $\lesssim 1.5 \times 10^5$ km from the nucleus, the solar wind ion population disappeared (Gringauz *et al.* 1986). While the heliocentric distance at which this mechanism becomes effective is uncertain, it seems reasonable to assume that the nucleus begins to be protected at the onset of sublimation, estimated for comet Halley to have begun with CN emission at $\sim$5 AU (Wyckoff *et al.* 1985). Only beyond this distance is the nucleus subject to irradiation by solar wind ions. In Figure 2.2, we show the total solar wind flux that would be experienced by an unshielded object in Halley's orbit. Between aphelion and 5 AU, the cometary nucleus actually experiences a flux $\sim 2 \times 10^{15}$ kev cm^{-2} per orbit, representing only $\sim$20% of the flux that it would absorb were it not shielded by its coma. This result is insensitive to the heliocentric distance at which shielding of the nucleus begins, changing by less than a factor of two if the shielding begins at any distance between 2 and 15 AU.

From an evaluation of the statistics of cometary disappearances, Kresák (1985) estimates that a Halley-like SP comet should make $\sim$100 perihelion passages before disruption. Weissman (1987), however, estimates that Halley must have made 600–900 returns just to get into its current orbit. As a rough estimate, then, the Halley nucleus should have experienced a solar wind flux $\sim 10^{17}$–10^{18} kev cm^{-2} over its lifetime as an SP comet.

The mean penetration depth of 1 kev solar wind particles into the nucleus is small: In an ice lattice it is only 0.05 μm (Rössler *et al.* 1985), although this depth may rise to as much as 0.5 μm if cometary ice is extremely underdense (Johnson and Lanzerotti 1986). Therefore the outer $\lesssim 1$ μm of the comet experiences a radiation dose $\sim 10^{20}$ kev cm^{-3} per orbit (or, for a density $\sim$1 g cm^{-3}, $\sim 10^3$ Mrad per orbit; 1 Mrad $= 6.24 \times 10^{16}$ kev g^{-1}). However, integration of the production

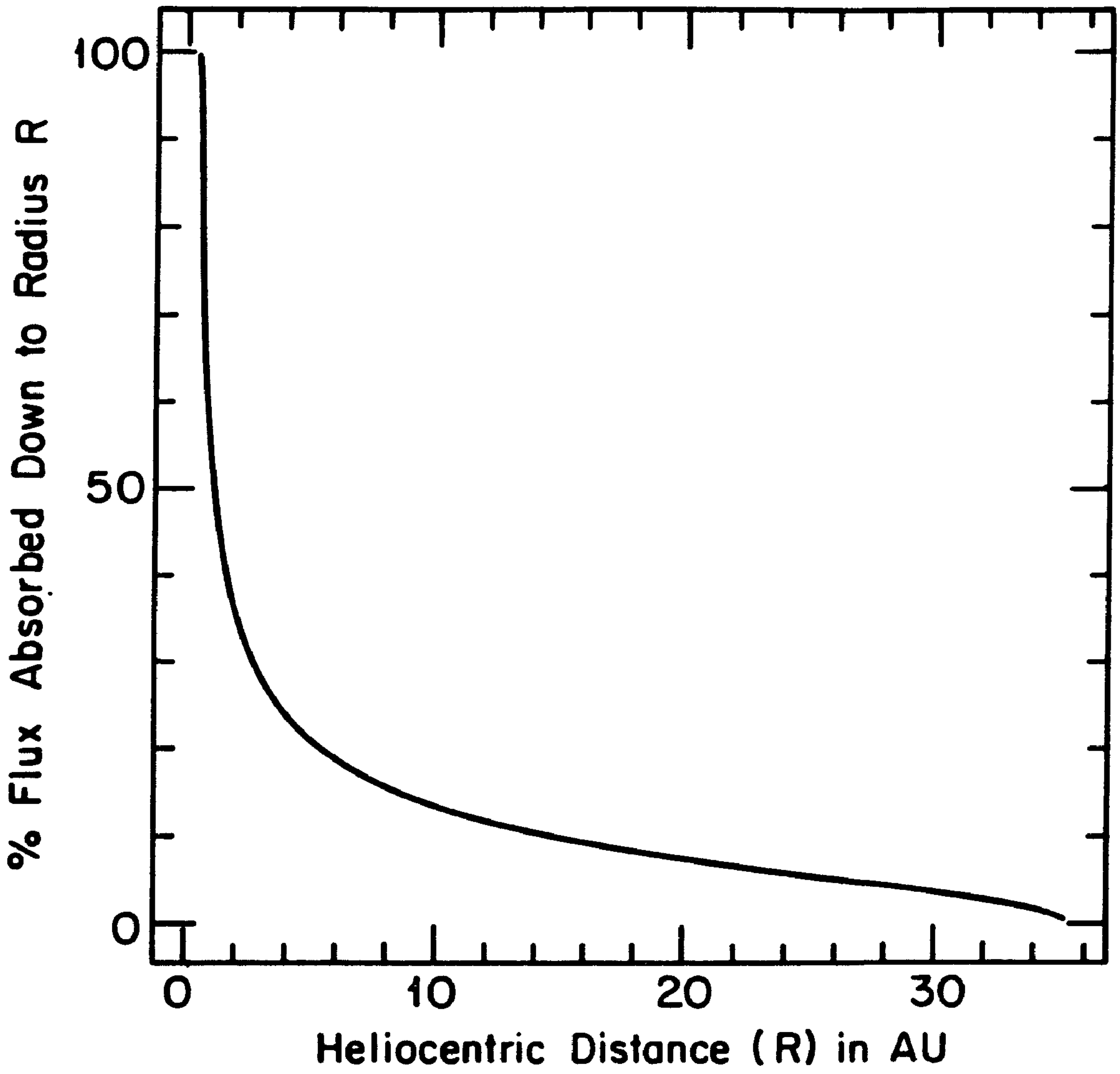

Figure 2.2 Fraction of total solar wind flux absorbed during passage from aphelion to perihelion for an unshielded object in the orbit of comet Halley, as a function of decreasing heliocentric distance.

rates of OH and dust suggests a cometary mass loss $\sim 2\times10^{15}$ g per orbit (Ferrin and Gil 1986). Approximating Halley as a ~5 km radius sphere (Keller *et al.* 1987) means that a depth ~5 m is lost from the nucleus each orbit, so that most of the ice irradiated by solar wind during any given perihelion passage is lost during that passage. (Some of the organics produced during any given orbit might, however, be retained as a lag deposit. Indeed, only ~10% of the surface area of comet Halley was actively outgassing during its last perihelion passage, a result that appears crudely typical of other comets as well (Sekanina 1991). Irradiation–products on non–active regions might well be retained over many perihelion passages.)

Prior to its perturbation into the inner Solar System, comet Halley was subject to a solar wind and cosmic ray flux during its ~4.6 Gyr residence in the Oort cloud at $\sim 5\times10^{4}$ AU. The solar wind flux integrated over this time yields a dose $\sim 10^{4}$ Mrad, extending to a depth < 1 μm . Draganić *et al.* (1984) have estimated the total absorbed cosmic ray dose experienced by a cometary nucleus over 4.6 Gyr; the uppermost meter of the comet experiences an average dose $\sim 10^{4}$–10^{5} Mrad, with significant irradiation extending to depths of 10 m ($\sim 10^{3}$ Mrad) or more. Typical particle energies are ~1 Gev. Again, after only a few perihelion passages, most of the heavily irradiated layers will be lost from the comet, although conversion by thermal processing into a dark crust of organic residue may also occur (Johnson *et al.* 1987), and some organic lag deposit will be retained.

Current scenarios for cometary formation (Fernández 1985) hold that comets form in the vicinity of Uranus and Neptune and remain in this region for timescales ~1 Gyr before being raised to Oort cloud orbits or ejected from the Solar System altogether. During this time, the outer $\lesssim 1$ μm of the Halley nucleus should have received 10^{9} Mrad in solar wind flux, or perhaps much more if the Sun's T–Tauri phase is taken into account (Zahnle and Walker 1982). Most of this layer would probably be lost during the comet's first perihelion passage.

During the first $\sim 10^6$–10^7 yr of the comet's lifetime, the nucleus would have been subjected to irradiation by decaying radionuclides which had been incorporated into the comet during its formation. Draganić *et al.* (1984) have estimated these radionuclides to have been responsible for a dose $\sim 10^3$ Mrad, with $\sim 80\%$ of this due to the extinct radionuclide ^{26}Al. Typical particle energies are ~ 3 Mev (Urey 1955). The radionuclides are distributed throughout the nucleus, so that the entire volume of the comet is subject to this radiation dose. This conclusion could change if the comet underwent significant differentiation in a time about equal to the 7.4×10^5 yr half-life of ^{26}Al; in this case only the inner ~ 1 km core of the comet would experience a highly concentrated radiation flux. Such calculations take $^{26}\mathrm{Al}/^{27}\mathrm{Al} \approx 5 \times 10^{-5}$, as implied by isotopic analysis of meteorites (Wasserburg 1987), and assumes essentially cosmic abundances for most other elements. There is reason to believe this ^{26}Al abundance to be typical of bulk interstellar dust composition, as three independent γ-ray measurements (by HEAO 3 (Mahoney *et al.* 1984), the Solar Maximum Mission Satellite (Share *et al.* 1985), and a balloon flight (Von Ballmoos *et al.* 1987)) find $^{26}\mathrm{Al}/^{27}\mathrm{Al} \approx 1 \times 10^{-5}$ in the interstellar medium (Wasserburg 1987). A ratio $^{26}\mathrm{Al}/^{27}\mathrm{Al} \approx 10^{-5}$ would melt only the inner core of a comet ~ 5 km in radius (Irvine 1980, Wallis 1980).

Both UV and cosmic ray irradiation should significantly process volatile ices on grains in the interstellar medium. Over a $\sim 10^8$ yr molecular cloud residence, interstellar grains experience $\sim 10^7$–10^8 Mrad due to UV photons (Greenberg and Grim 1986), and $\sim 10^5$ Mrad due to low-energy cosmic rays (Strazzulla *et al.* 1983). Both doses may increase substantially for those grains cycled between diffuse and dense clouds, although optically-thick clouds will shield dust from ultraviolet light.

Strazzulla *et al.* (1983) have experimentally measured polymerization cross-sections for 0.1–2 Mev protons incident on C–rich ices; they conclude that, at the cosmic ray doses cited above, C–containing molecules in interstellar grains will be totally polymerized in times less than typical cloud lifetimes. Therefore the fact that a grain's UV dose may be ~10^2–10^3 times that due to low–energy cosmic rays is not decisive for the two mechanisms' importance to the formation of interstellar organics. Even in the total absence of UV processing (as in an optically thick cloud), complete polymerization of C–containing ices would occur.

Comets must contain both solar nebula and interstellar condensates; the former may well be non–negligible (Geiss 1987). C–containing solar nebula condensates will be irradiated by incorporated cometary radionuclides; the resulting dose ~10^3 Mrad should polymerize more than half of the C atoms present (Strazzulla *et al.* 1983). Therefore it appears that both pre– and post–accretion environments may be of importance for the formation of cometary organics. Clearly what is needed is a well–characterized study of the infrared spectral evolution of candidate ice residues, with irradiation extending from radionuclide to interstellar doses. These experiments might exclude one or more radiation environments, in the event that only certain doses were to yield spectra providing good fits to cometary 3.4 μm features.

2.3 Thermal Emission from Dust in the Halley Coma

Figure 2.3 shows the spectrum of comet Halley observed by Wickramasinghe and Allen (1986) on 31 March 1986 (heliocentric distance R=1.16 AU, geocentric distance Δ=0.549 AU), and our best fit (see below) to their data. The overall shape of the spectrum is that of a continuum which is well–fit by the sum of scattered sunlight (known from observations made that night at shorter wavelengths) and a 350±10 K black body. The emission feature at 3.4μm is evident. In addition, there is an absorption feature between 3.0μm and 3.1μm, which is apparent in

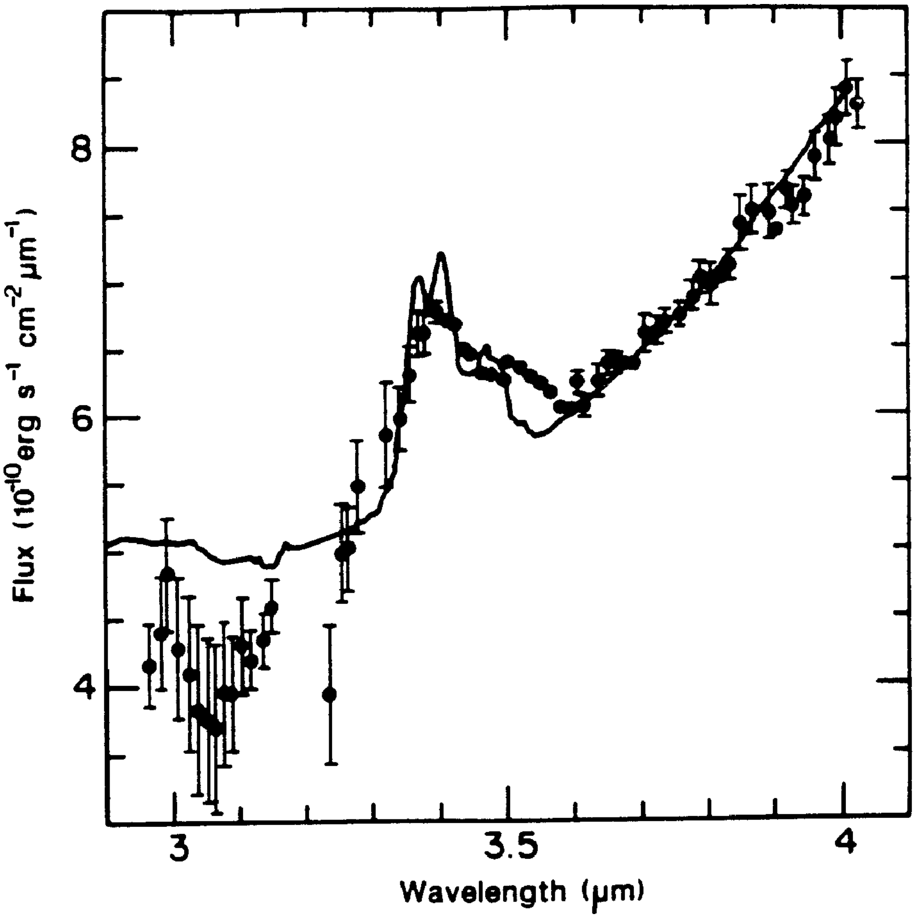

Figure 2.3 Best fit (solid curve) to 3–4 μm spectrum of comet Halley. The possible absorption feature at ~3.05 μm is not modeled.

other ground-based (Danks *et al.* 1986) and spacecraft (Combes *et al.* 1988) observations; it has been tentatively identified as due to H_2O ice (Combes *et al.* 1988). We have not incorporated such absorption into our model.

At a heliocentric distance R=1.16 AU, a black body would be expected to have a temperature ~280 K. The fact that the shape of the continuum is best fit for 350±10 K indicates the presence of small (submicron) grains which, being inefficient emitters in the infrared, heat to temperatures well above black body equilibrium. In reality, of course, no single temperature can be ascribed to the dust responsible for the continuum emission: the observed flux is an integral over emission from grains of all sizes, each at different temperatures. In the optically thin case (an assumption justified below), we have

$$F_\lambda = \Omega \int \tau(\lambda, a) B_\lambda[T(a)] da, \tag{2.1}$$

where $B_\lambda[T(a)]$ is the Planck function per μm wavelength per particle radius a, Ω is the solid angle subtended by the source, and the wavelength– and radius–dependent optical depth $\tau(\lambda, a)$ is given by

$$\tau(\lambda, a) = \int n(a) \pi a^2 Q(a) dl. \tag{2.2}$$

Here $n(a)$ is the number density, πa^2 is the geometrical cross section, and $Q(a)$ is the extinction efficiency factor for a particle of radius a. The integral is taken along the line of sight through the source.

Modelling dust emission from an actual comet is a matter of making sufficient approximations to allow Eqs.(2.1) and (2.2) to be computed. $Q(a)$ is not only a function of particle radius, but of chemical composition and frequency as well; $T(a)$ depends on the absorptivity of the grain near the peak of the solar spectrum; and $n(a)$ is in general unknown.

Hanner (1983) has fit cometary continuum emission with a two–parameter model for $n(a)$, calculating $T(a)$ via Mie theory. For $\lambda \gg a$, $Q(a) \propto 2\pi a/\lambda$, with the proportionality factor composition–dependent (Greenberg 1978). The Giotto spacecraft measured the mass spectrum of dust along its trajectory through the Halley coma (McDonnell *et al.* 1986). Using the Divine *et al.* (1986) pre–encounter model of the density-radius relationship, this mass spectrum yields either the geometrical filling factor (cross section per unit area) or number density of dust along the Giotto trajectory as a function of particle radius (McDonnell *et al.* 1986). Unfortunately, we cannot hope to use the resulting distribution in more than a crude way to model infrared emission from Comet Halley, due to its extreme time–variability. Most comets exhibit a R^{-4} brightness dependence in heliocentric distance R, indicating a R^{-2} dependence for dust production. This general trend is observed for Comet Halley as well, although the comet varies by as much as a factor of 7 from this trend over several days (Gehrz and Ney 1986). Indeed, over a period of just 3 nights' observations, Wickramasinghe and Allen (1986) found a 4-fold variation in overall flux, and an uncorrelated variation of a factor of 4.5 in the emission feature. Similarly, 5–13μm observations show that the 10μm silicate dust feature varies by as much as a factor of 2 relative to the continuum (Bregman *et al.* 1987). Thus the composition and/or $n(a)$ of the emitting dust is highly time-variable. There are two weeks between the Giotto and Vega fly-bys and the Wickramasinghe and Allen (1986) observations. To evaluate Eqs.(2.1) and (2.2) for the ground-based spectra therefore requires the introduction of free parameters to describe the dust distribution, or else a much simpler model. Here we use a simple two-component model to explain the spectrum shown in Figure 2.3.

The simplest model for dust emission from the Halley nucleus—constant velocity outflow for particles of a given radius—predicts that dust number density $n(a,r)$ should vary as r^{-2} where r is the nuclear distance. This model is roughly confirmed by spacecraft observations (McDonnell *et al.* 1986). The trajectory of the Giotto spacecraft defines a chord through the Halley coma, with closest approach to the nucleus $r_G \approx 600$ km. With the r^{-2} relation, the geometrical filling factor $A_G(a)$ integrated along the Giotto trajectory for particles of radius a can be determined:

$$A_G(a) = 2\int_{r_G}^{R_c} n(a,r)\pi a^2 dr \approx 2n(a,r_G)r_G\pi a^2, \tag{2.3}$$

where $R_c \equiv 5 \times 10^4$ km is the radius of the coma. Combining the Divine *et al.* (1986) density-radius model for the Halley dust with the empirical formula for dust fluence as a function of mass experienced by Giotto (McDonnell *et al.* 1986), we find the total filling factor summed over all particles to be $A_G = 8.3 \times 10^{-4}$.

Individual dust grains with $a \gg \lambda$ are optically thick at wavelength λ, and contribute an optical depth to emission at that wavelength (at which they emit as black bodies) appropriate for their geometrical cross section. Taking particles with $a \gtrsim 10\mu$m to be optically thick at the wavelengths of interest here, we find such particles comprise ~77% of the geometric cross section in the Halley coma.

Wickramasinghe and Allen (1986) observed using a rectangular aperture measuring 10×5 arc seconds, centered on the position of greatest infrared flux. Taking this as the nucleus, we can integrate A_G, correcting for its variation with r^{-2}, to find the total geometric cross section, A_{tot}, of all dust in their field of view. We find $A_{tot} \propto$ aperture size; i.e., we recover the usual result that observed thermal flux is proportional to aperture size (Gehrz and Ney 1986). Incorporating the R^{-2} dependence of dust production on heliocentric distance (for 14 March 1986, the day of the Giotto fly-by, $\Delta = 0.96\ AU$ and $R = 0.90\ AU$), integration gives $A_{tot} = 1.4 \times 10^3$ km^2, which is the total geometric emitting area of the dust in the Wickramasinghe and Allen (1986) aperture. With a radius ~5 km, the nucleus contributes ~80 km^2, or about 5% of the total emitting area. Thus the observed continuum radiation is due almost entirely to the dust in the coma. Yet this dust is optically thin: dividing A_{tot} by $\Omega\Delta^2$, we find a geometrical filling factor $A_{\mathrm{WA}} = 1.9 \times 10^{-4}$.

The simplest approximation to Eq.(2.1) for the continuum radiation is to treat $\tau(\lambda, a) = A_{\mathrm{WA}}$, and the Planck function to be that appropriate for T=350 K. Such an approximation crudely averages together the effects of the small, hot particles with the larger, optically thick particles at 280 K. This approximation mitigates the need to "fine tune" several parameters, and we will demonstrate that it works extremely well.

In our model, the emission feature at 3.4μm is due to small, hot, optically thin organic or organic-coated grains. The transmission spectrum of the organic residue of irradiated CH$_4$ hydrate clathrate allows us to model the wavelength-dependent optical depth of such grains directly. We have $\tau_\lambda = N_1\sigma_\lambda$, where N_1 is the column density of the residue in the coma and $\sigma_\lambda = N_2^{-1} ln(t_\lambda^{-1})$ is the wavelength-dependent cross section derived from the laboratory-measured transmission. Here N_2 is the column density through the residue sample in the laboratory, and t_λ is the transmissivity of the sample (given by Figure 2.1, with maximum transmissivity set equal to 1).

Using the optical constants (Khare *et al.* 1984) for an organic residue formed by sparking 10% CH_4 in a nitrogen atmosphere, both Hanner (1986) and Lamy and Perrin (1988) have found that 0.1 μm grains will reach temperatures ~500 K at ~1 AU; 0.1μm grains composed of magnetite or glassy carbon will have somewhat higher temperatures (~600 K) at this heliocentric distance (Hanner 1983). None of these compositions is an appropriate choice for cometary organics; however, they are currently the only optical constants available in the literature that are even remotely appropriate. As the optical constants of irradiated ice residues are at present unknown, we adopt ~500 K as a temperature for the emitting organic grains.[2] We therefore have the following expression for the 3–4μm flux measured by Wickramasinghe and Allen (1986) : $F_\lambda = C_\lambda + \Omega\tau'_\lambda B_\lambda(T = 500\ K) + \Omega\tau B_\lambda(T = 350\ K)$, where C_λ is the scattered solar flux and $\tau'_\lambda = \beta(a/\lambda)ln(t_\lambda^{-1})$. Here β and τ are parameters varied to provide a best χ^2 fit to the data. In practice τ is constrained by the Giotto–determined filling factor in the Halley coma, and an upper bound is placed on τ'_λ (hence β) by the filling factor represented by the optically thin grains.

Our best fit is shown in Figure 2.3. χ^2-minimization yields $\tau = 1.4 \times 10^{-4}$ and β=3.7$\times$10^{-4} (giving $\tau'_\lambda = 3.6 \times 10^{-6}$ at $\lambda = 3.4\mu$m). τ compares very well with the value predicted by a simple geometric filling factor model: τ is within 25% of the value A_{WA} found by integrating the Giotto-determined dust distribution (adjusted for heliocentric distance) over the aperture used by Wickramasinghe

---

[2] Optical constants for an ethane/water ice mixture became available (Carl Sagan and Bishun Khare, 1991, personal communications) as this thesis was being finalized. Preliminary results indicate that the imaginary part of the ice tholin optical constants is ~50% larger than that for Titan tholin near 3.4μm, suggesting the former material does provide a better analogue material to comet Halley organics.

and Allen (1986) . This agreement is much closer than the highly variable nature of Halley dust emission allows us to expect.

The optical depth found for the small organic grains, $\tau'_\lambda = 2.6 \times 10^{-2}\tau$, is roughly consistent with the upper bounds placed by the Giotto–determined dust distribution. Combining the Divine *et al.* (1986) density–radius relationship with the Giotto mass spectrum (McDonnell *et al.* 1986) we find that dust particles with $a \leq 0.1\mu$m contribute a filling factor $\sim 1.0 \times 10^{-3} A_G$; particles $\leq 1.0\mu$m contribute $\sim 2.2 \times 10^{-2} A_G$, and particles $\leq 10\mu$m contribute $\sim 0.23 A_G$, where A_G is the total filling factor found by Giotto.

2.4 Suppression of Longer–Wavelength Spectral Features

The emission feature predicted by the laboratory-measured transmission spectrum is seen (Figure 2.3) to be slightly too narrow to match perfectly the observed Halley spectrum. The width of the laboratory feature is, however, somewhat influenced by radiation dose and temperature, dependencies which needs to be explored in future experimental work. Finally, we must address the question of other emission features predicted by our model. The transmission spectrum in Figure 2.1 exhibits a variety of features at $\lambda > 3.4\mu$m, not present in a set of 5–13μm spectra of Halley's comet taken by Bregman *et al.* (1987). However, if the parameters determined above in modelling the 3–4μm spectrum are used to model the Halley spectrum out to 20μm (Figure 2.4), it is found that all higher–wavelength features evident in Figure 2.1 are greatly suppressed relative to the continuum. The continuum optical depth $\tau \sim 10^2$ times the optical depth due to the emitting organics (τ'_λ), so that only near the minimum in the continuum radiation can an organic emission feature make a significant contribution. The 3.4μm feature is the sole feature near that minimum, lying at the intersection of the scattered solar and 350 K black body curves.

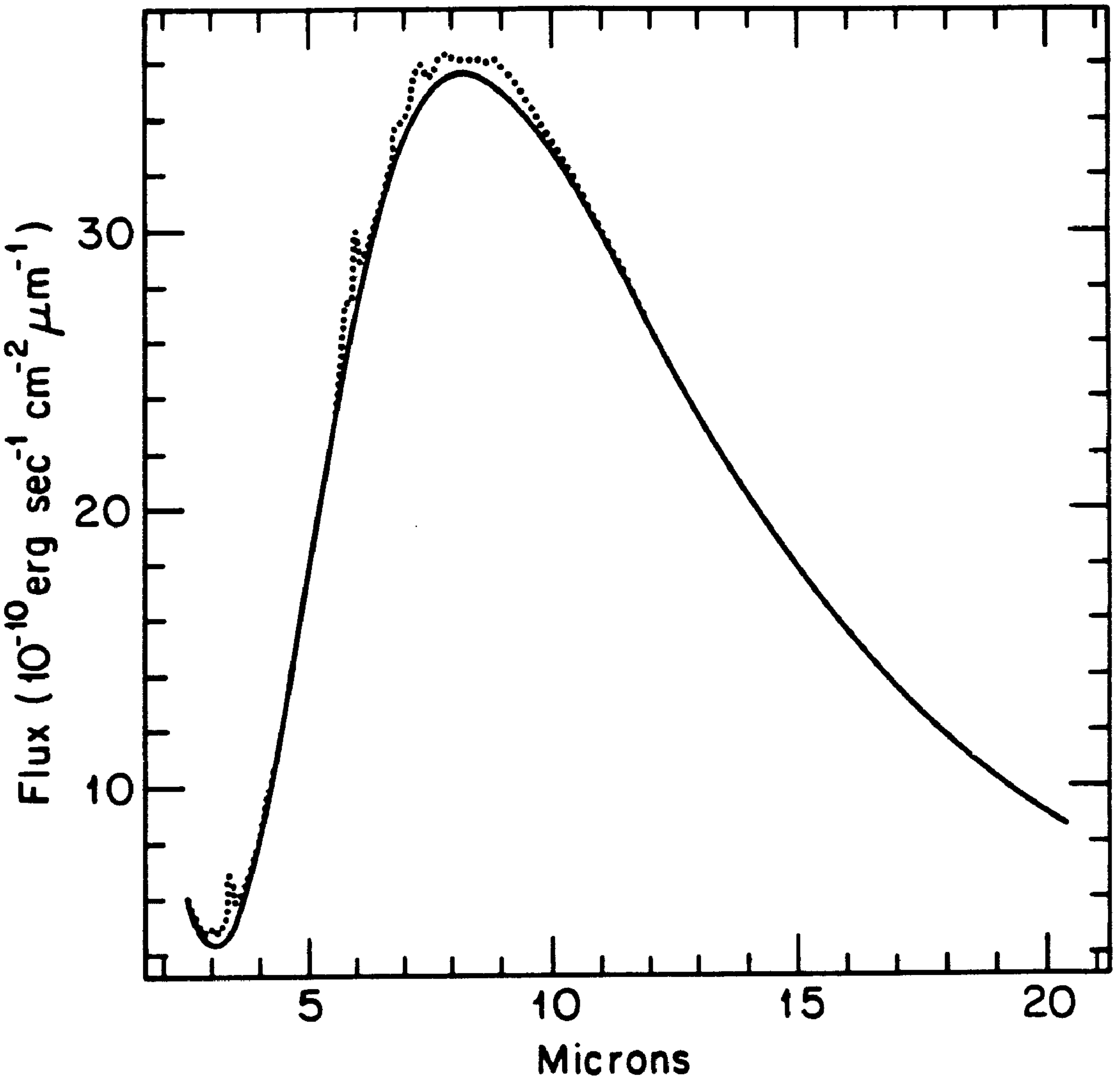

Figure 2.4 The comet Halley 2-20 μm spectrum predicted by our model (dotted curve), taking T ~500 K for the small organic emitters, compared to that of a 350 K blackbody (solid curve).

In Figure 2.5 we divide out the continuum to examine the strength of the individual emission features. Only the 3.4μm feature rises over the level 10% above continuum, and the peaks at ~6μm are too narrow to be detectable at the wavelength resolution ($\Delta\lambda/\lambda \sim 0.02$) of the Bregman *et al.* (1987) observations above the ~6% over background level. Although these observations show no 6μm feature to the 2% level (L. Allamandola, 1987, personal communication), we consider the predictions of our model to be in sufficient agreement with this limit of detectability, as the optical depths appropriate for fitting the 3.4μm feature for March 31, 1986 cannot be exactly appropriate for other dates (indeed, had we fitted the observations of Wickramasinghe and Allen (1986) of March 30, the predicted 6μm feature would be resolvable only below ~3% above continuum). Among other uncertainties, the strength of the 6μm feature relative to that at 3.4μm is expected to vary with radiation dose; CH_4 hydrate clathrate is certainly not the only C- or N-containing ice initially present in comet Halley; the temperature 500 K calculated from optical constants for a gas-phase N-rich product may not be correct for an ice residue (indeed, taking T~600 K for the organic emitters, the temperature appropriate for glassy carbon grains (Hanner 1983), reduces the strength of the 6μm feature by a factor of 2); and most importantly, the simple two-component model used here is too crude to expect precise agreement with observation. Nevertheless, even this simple model demonstrates a physical mechanism for the suppression of higher-wavelength features relative to that at 3.4μm.

As the comet moves away from perihelion, the intersection of the scattered solar spectrum and the comet's thermal emission spectrum will move to longer wavelengths. Thus, relative to the continuum, we expect the 3.4μm feature to be suppressed and those at longer wavelengths progressively enhanced—as long as the comet retains a coma. Future comet rendezvous missions will be well placed to test this prediction of our model, which is investigated in detail in Chapter 3.

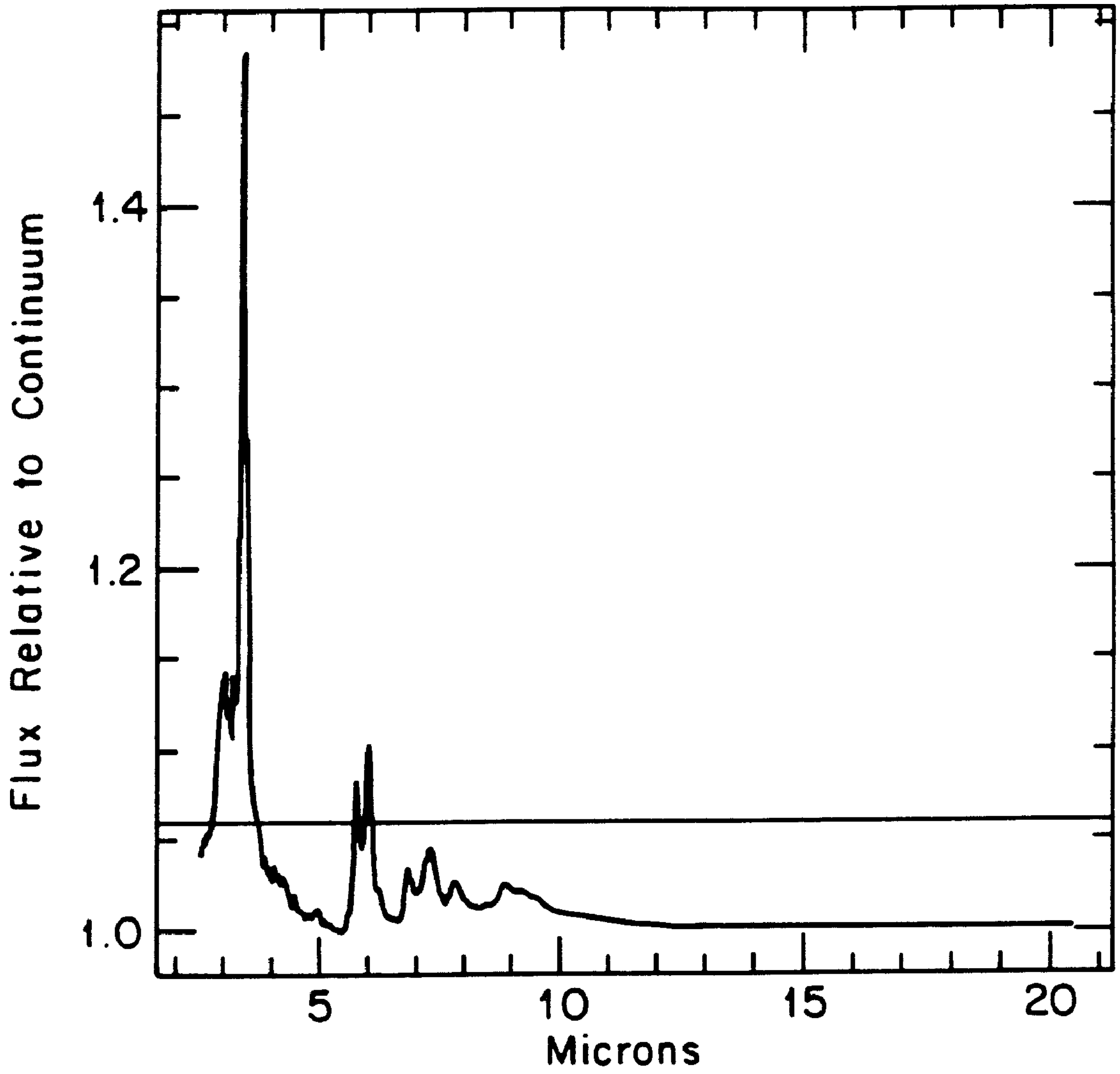

Figure 2.5 The comet Halley 2–20 μm spectrum predicted by our model after dividing out the continuum. Only the 3.4 μm feature is resolvable above the 6%-above-continuum level (indicated by the horizontal solid line).

We note that the continuum temperature in the 5–13μm range (Bregman *et al.* 1987), adjusted for heliocentric distance, agrees to within the uncertainty with the 350±10 K continuum temperature found by Wickramasinghe and Allen (1986) . That is, approximating continuum emission by a 350 K temperature averaged over all dust sizes remains valid through the wavelength region of interest. Herter *et al.* (1986) have shown, however, that the continuum emission cannot be fit by a single black body temperature to 30μm, where the more rapid fall–off of high–temperature emission by small grains evidently begins to render our approximation invalid.

Finally, subsequent to the completion of our modelling of dust emission for comet Halley, Allen and Wickramasinghe (1987) reported observations of a 3.4μm emission band in the long period comet Wilson, closely matching the comet Halley feature for approximately the same heliocentric distance. It is surprising that two comets with such evidently different histories should display such nearly identical infrared spectra: Apparently the characteristics of cometary organics are remarkably similar for both dynamically new and old comets, strengthening the case made here for the primordial origin of these molecules.

Chapter 3

Heliocentric Evolution of Cometary Infrared Spectra[1]

3.1 The Near–Infrared Spectra of Comets Halley and Wilson

As discussed in Chapter 2, the 3.4μm feature observed in the spectrum of comet Halley has been interpreted as thermal emission from organic grains in the Halley coma (Wickramasinghe and Allen 1986, Chyba and Sagan 1987b, 1989), although some contribution to the 3.4μm feature by gaseous emission is expected (Crovisier and Encrenaz 1983, Combes *et al* 1988). However, Drapatz *et al.* (1987) observed the ~3.2–3.4μm region of the Halley spectrum and found no prominent line structure, typical of gas–phase emission, at high resolution ($\lambda/\Delta\lambda \sim 1.1 \times 10^4$). Moreover, mass spectrometric observations by spacecraft flying through the coma directly demonstrate the presence of organic–rich grains (Kissel and Krueger 1987a, Clark *et al.* 1987), although there remains ample room for debate on the detailed composition.

---

[1] This chapter is based on the paper: Chyba, C.F., C. Sagan, and M.J. Mumma (June 1989), The heliocentric evolution of cometary infrared spectra: Results from an organic grain model, *Icarus* 79, 362–381 [copyright 1989 by Academic Press, Inc.].

Observations of comet Wilson (Allen and Wickramasinghe 1987, Brooke *et al.* 1987) also reveal a 3.4μm emission band which closely resembles the comet Halley feature for approximately the same heliocentric distance. Again, high resolution ($\lambda/\Delta\lambda \sim 3.3 \times 10^4$) observations in the 3.2–3.3μm region reveal no prominent line structure in comet Wilson, although a possible (3σ) detection of methane has been reported (Larson *et al.* 1989). It is remarkable that dynamically old (Halley) and new (Wilson) comets should display such a nearly identical emission feature, a similarity which strengthens the case (Greenberg and Grim 1986, Chyba and Sagan 1987a,b, 1989, Brooke *et al.* 1987, Johnson *et al.* 1987) for the primordial, although not necessarily the interstellar, origin of cometary organics.

Any proposed identifications of the molecules responsible for the 3.4μm feature must take into account the absence of organic emission features in cometary infrared spectra at longer wavelengths. The peak position of the 3.4μm feature itself is indicative of alkanes ($-CH_3$, $-CH_2-$), while substructure indicates the presence of other organics (e.g., aldehydes ($-CHO$) emit near 3.5μm) (see, e.g., Allamandola 1984, or Khare *et al.* 1989); naively one might expect the presence of these or other plausible classes of organic molecules to result in observable spectral features in the 4.5–8μm region. For example, alkanes exhibit prominent deformation bands in the 6.8–8μm region; alkenes and aromatics exhibit ($C{=}C$) bands in the 6–7μm region; and ketones and aldehydes have a carbonyl ($C{=}O$) feature near 5.8μm. Such features are typically present in the transmission spectra of the organic residue of irradiated candidate cometary ices (Thompson *et al.* 1987; Khare *et al.* 1989), for example in that of the residue of irradiated methane ice clathrate (Figure 3.1). Organic solids produced by irradiating N_2/CH_4 gas mixtures exhibit a prominent nitrile ($C{\equiv}N$) feature at 4.6μm (Khare *et al.* 1984). Yet observations of both comet Halley (Combes *et al.* 1988, Bregman *et al.* 1987) and comet Wilson (Lynch *et al.* 1988) in the 5–13μm range have shown such features to be absent at the $\gtrsim$2% level.

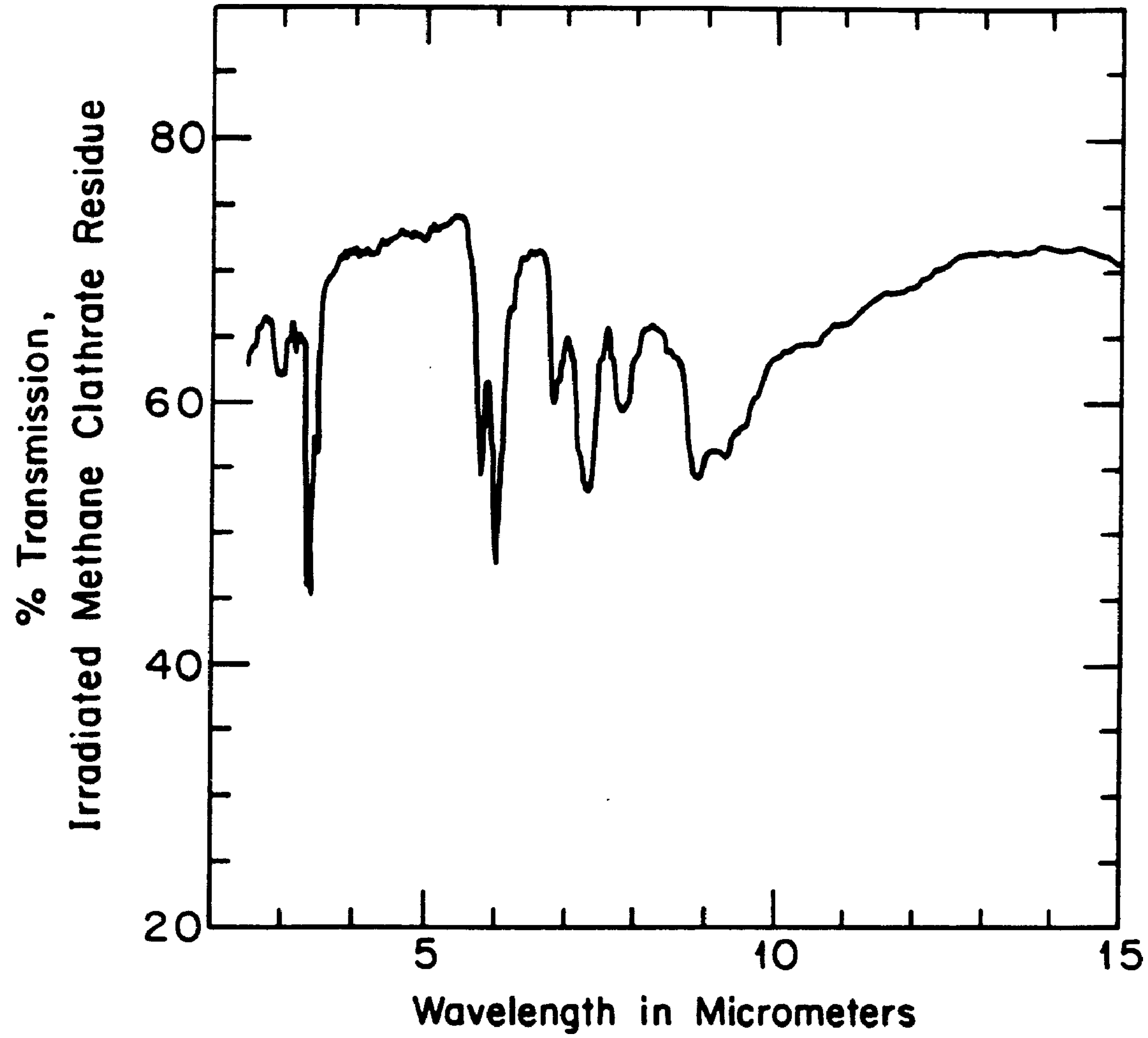

Figure 3.1 The 2–12μm transmission spectrum of the organic residue of irradiated methane hydrate clathrate. See Thompson *et al.* 1987, and Khare *et al.* 1988, for the transmission spectrum of this and other irradiation-produced residues presented on a scale linear in wavenumber.

In the model for infrared emission by organic grains in the Halley coma described in Chapter 2 (Chyba and Sagan 1987b), we have explained the absence of these longer wavelength bands as due to the dilution of spectral features by the continuum when such features do not lie near the intersection of the scattered solar and thermal emission curves of the dust in the cometary coma. At the heliocentric distances of the 5–13μm observations (~1.3 AU and ~1.2 AU for comets Halley (Bregman *et al.* 1987) and Wilson (H. Campins, 1988, personal communication), respectively), the 3.4μm band is the sole feature near the minimum in the continuum. Our model quantitatively demonstrates that it is the only organic feature likely to be observable at these distances. Therefore attempts to rule out the presence of certain organic functional groups or polycyclic aromatic hydrocarbons in comets Wilson or Halley (Bregman *et al.* 1987) appear premature. The presence of absorption features in laboratory transmission spectra does not necessarily require them to be observable in cometary emission, even if the corresponding molecular functional groups are present in substantial abundance.

However, with changing heliocentric distance, the intersection of the scattered solar and thermal emission flux will sweep through the infrared spectrum. Thus, for a comet moving away from perihelion, Chyba and Sagan (1987b) predicted that the contrast between the 3.4μm feature and the continuum would be gradually suppressed, and spectral features at longer wavelengths progressively revealed, as this intersection moves towards longer wavelengths. In this chapter (Chyba *et al.* 1989b), we present quantitative results of a model for the heliocentric evolution of the comet Halley infrared spectrum. We expect any comet that displays organic emission features in the infrared to exhibit an analogous evolution with heliocentric distance, although the details of such evolution will vary according to the precise composition of a given comet's organics (see below). Such spectral evolution should be testable by Earth–based observations and, especially, by future comet rendezvous missions.

3.2 An Improved Model for Halley Dust Emission

A variety of plausible cometary materials exhibit C–H stretching features near 3.4μm, including the organic residue of candidate cometary ices irradiated by charged particles. Higher resolution spectroscopic observations will be required in the future to understand the nature of the organic material responsible for cometary emission. For now, tentative identifications must rest on additional evidence, including a plausible account of the origins of the organic material, a plausible model for the infrared emission of this material, and a demonstration that this conjunction of material and model not only matches the 3–4μm spectrum, but also does not yield additional emission features where none is observed (Chyba and Sagan 1987a).

We have embarked on an experimental survey of diagnostic spectral features for the organics produced by irradiation of a variety of hydrocarbon and ammonia-bearing ices (Thompson *et al.* 1987, Khare *et al.* 1988). An examination of other (e.g., CO and CO_2) ices is clearly needed as well. In Chapter 2, we argued that the laboratory synthesis of the organic residue well simulates certain types of pre- and post-accretion radiation processing experienced by cometary ices (Chyba and Sagan, 1989). As an example of one such organic residue, we considered the residue of irradiated low-occupancy CH_4 hydrate clathrate. There is evidence from the Giotto ion mass spectrometer for CH_4 in the Halley coma with a production rate ~2% that of water (Allen *et al.* 1987), and in cometary ices, clathrates are thermodynamically favored (Delsemme 1976). A possible 3σ spectroscopic detection of CH_4 in comet Wilson has been reported (Larson *et al.* 1989), equivalent to $[CH_4]/[H_2O] \sim 0.04$. However, by no means do we insist on CH_4 hydrate clathrate as the only plausible candidate ice yielding radiation–

processed organics. Rather, a comparison of experimentally determined spectra with observed cometary emission features may allow certain otherwise plausible ices to be excluded as candidates for the origins of cometary organics (Khare *et al.* 1989).

Deriving a simple two-component model for emission from dust in the Halley coma (Chyba and Sagan 1987b), we used the laboratory-determined transmission spectrum (Thompson *et al.* 1987) of the organic residue of irradiated CH_4 hydrate clathrate to fit the Halley spectrum in the 3–4μm range, as observed by Wickramasinghe and Allen (1986) for 31 March 1986 (heliocentric distance R=1.16 AU, geocentric distance Δ=0.549 AU; all heliocentric and geocentric distances cited here are from the ephemeris of Yeomans (1986)). Our model predicted an observed infrared flux given by

$$F_\lambda = C_\lambda + \Omega\tau'_\lambda B_\lambda(T_r) + \Omega\tau B_\lambda(T_c), \tag{3.1}$$

where C_λ was the scattered solar flux, Ω the telescope solid angle, τ the optical depth of the blackbody continuum emitters (at temperature T_c), $\tau'_\lambda = \beta(a/\lambda)ln(t_\lambda^{-1})$ the optical depth of the submicron (radius $a \sim 0.1\mu$m) organic emitters (temperature T_r), and t_λ the transmissivity of the laboratory sample (given by Figure 2.1, with maximum transmissivity set equal to 100%). β and τ were free parameters varied to provide a best (χ^2) fit to the data. β and τ have clear physical interpretations and are tightly constrained (see below) by spacecraft and ground-based data.

Several improvements may be made to the model summarized by Eq.(3.1). For purposes of comparison with the Wickramasinghe and Allen observations of 31 March 1986, Chyba and Sagan (1987b) took the scattered solar flux C_λ to be given directly by the flux measured that night in two wavelength windows between 1.5 and 2.5μm. This procedure slightly overestimates the solar contribution to F_λ, as there is also a minor contribution to the flux measured at these short wavelengths by the final two B_λ terms in Eq.(3.1). We therefore now adopt the following procedure. For each value of β and τ examined in the χ^2 minimization, we subtract from C_λ at $0.1\mu m$ intervals over the 1.5–2.5μm range the two small B_λ contributions. We then perform a linear regression ($log(F_\lambda)$ vs. $log(\lambda)$) to obtain the scattered solar curve (i.e., with the B_λ contributions removed) for this choice of β and τ. This avoids a double counting of the B_λ contributions at short wavelengths and also results in a better fit to observations in the $3\mu m$ region (Figure 3.2). No attempt is made to model a possible band at $3.05\mu m$, which may be due to O–H absorption (Combes *et al.* 1988). Thus, we now write

$$F_\lambda = S_\lambda + \Omega\tau_\lambda B_\lambda(T_r) + \Omega\tau B_\lambda(T_c), \tag{3.2}$$

where S_λ, the scattered solar continuum, is given at any λ via the above regression. We also now set $\tau_\lambda = \gamma(2\pi a/\lambda)ln(t_\lambda^{-1})$, where γ differs from the previously employed β by a factor 2π, so that the usual $2\pi a/\lambda$ Mie theory dependence is explicitly displayed.

Eq.(3.2) requires a choice of temperatures T_c and T_r. T_c may be determined empirically from observations of continuum emission in the Halley coma. Wickramasinghe and Allen (1986) find that the Halley spectrum in the 3–4 μm range (exclusive of the emission feature at 3.4 μm, and the possible absorption feature at $3.05\mu m$) is best fit by $T_c = 350 \pm 10K$. This temperature is ~25% hotter than the temperature of a blackbody at that heliocentric distance, presumably due to the presence of submicron grains in the coma. The temperature T_r of the submicron organic emitters, as a function of heliocentric distance and grain size, may be found via Mie theory calculations using the optical constants of laboratory-produced organic residue or other candidate materials. Hanner (1986) and Lamy and Perrin (1988) have performed such calculations for an organic residue ("Titan tholin") produced by sparking 10% CH_4 in a nitrogen atmosphere (Khare et al. 1984). (We stress that Titan tholin is an unlikely material for cometary grains; it was selected by these authors because it is an organic irradiation residue whose optical constants are well-characterized (Khare *et al.* 1984).) Taking a typical

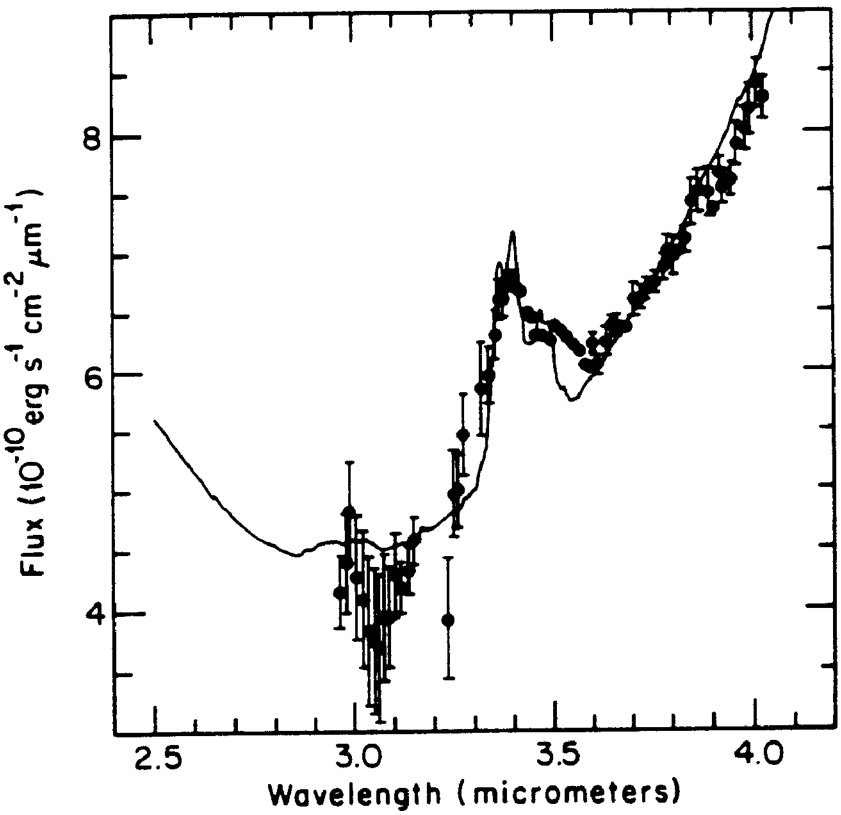

Figure 3.2 Our best fit (continuous curve) to the 3–4μm 31 March 1986 spectrum of comet Halley (Wickramasinghe and Allen 1986), using a temperature T_r=450 K appropriate to Titan tholin optical constants, and the spectrum of Figure 3.1. The 3.4μm feature lies almost at the minimum of the scattered solar flux (declining from the left) and blackbody thermal emission (rising to the right). The best fit for T_r=560 K, appropriate to glassy carbon optical constants, is nearly identical to that shown here.

particle size for presumed spherical emitting organic grains in the Halley coma to be $\sim 0.1\mu$m then gives $T_r = 450K$ at 1.16 AU. By contrast, Mie calculations for 0.1μm glassy carbon grains (Hanner 1983) yield T_r=560 K at 1.16 AU. T_r=560 K is also close to the temperature given by Mie calculations for biologically-derived organic grains of radius 0.1μm (Wallis *et al.* 1987). If cometary grains are highly porous and non-spherical these temperatures would be higher, and particles as large as tens of microns in size might be much hotter than expected for a blackbody (Greenberg and Hage 1990).

3.3 Comparison with Spacecraft Results

Given choices for T_c and T_r, we vary τ and γ in Eq.(3.2) to minimize χ^2; our improved best fit to the 31 March 1986 observations is shown in Figure 3.2. The resulting values of τ and τ_λ may then be compared with spacecraft-determined filling factors for the Halley coma. For T_r=560 K (glassy carbon), we find $\tau = 1.5 \times 10^{-4}$ and $\gamma = 2.4 \times 10^{-5}$, giving $\tau_\lambda = 1.5 \times 10^{-6}$ at λ=3.36μm, or $\tau_\lambda/\tau = 1.0 \times 10^{-2}$. τ_λ is sensitive to the choice of T_r; at a temperature appropriate for Titan tholin, T_r=450 K, we find $\tau = 1.5 \times 10^{-4}$ and $\gamma = 1.5 \times 10^{-4}$, giving $\tau_\lambda = 9.1 \times 10^{-6}$ and $\tau_\lambda/\tau = 6.1 \times 10^{-2}$. It must be emphasized that neither the optical constants for glassy carbon nor those of Titan tholin are necessarily appropriate for the organic residue of an irradiated carbon-bearing ice, so that these temperatures and τ_λ/τ ratios should be thought of only as indicators of a plausible range of values. In particular, irradiated ice residues typically show a strong absorption in the 3.4μm region (Khare *et al.* 1989), which Titan tholin and glassy carbon do not.

In Chapter 2, we compared τ to the geometrical filling factor $A_{\rm WA} = 1.9\times10^{-4}$ for the dust in the field of view of the Wickramasinghe and Allen (1986) aperture. $A_{\rm WA}$ is calculated by integrating over the telescope aperture the dust fluence as a function of mass and nucleocentric distance determined by the spacecraft Giotto

(McDonnell *et al.* 1986, 1987), convolved with a model for the density–radius relationship for Halley dust (Divine *et al.* 1986), correcting for heliocentric distance. The interim assessment of the Halley dust distribution (McDonnell *et al.* 1986) used for this calculation by Chyba and Sagan (1987b), was subsequently finalized in a slightly different form (McDonnell *et al.* 1987), so that A_{WA} must be reassessed. Best values for the Giotto–observed dust fluence indicate a mass distribution index $\alpha \approx -0.85$ (where the number of particles having mass greater than m is given by $N(>m) \propto m^{\alpha}$] for $m < 10^{-8}$ kg, above which the exponent changes to $\alpha \approx -0.54$. McDonnell *et al.* (1986, 1987) consider two upper limits to which the mass integration may be extended, 10^{-3} and 1 kg. The first of these corresponds to the upper limit needed to give a total mass sufficient to account for the observed deceleration of the Giotto spacecraft. The second is chosen to yield a dust/gas ratio of 1:1; it is not an observation–based quantity, although larger dust particles than those encountered by Giotto may well exist in the Halley coma. Depending on which choice is made, one finds $A_{\mathrm{WA}} = 9.4 \times 10^{-5}$ (for 10^{-3} kg) or $A_{\mathrm{WA}} = 1.5 \times 10^{-4}$ (for 1 kg). As cometary dust emission is known to be highly time variable (emission from Halley has been observed to deviate from an overall R^{-4} law for infrared flux by as much as a factor of 7 over a few days (Gehrz and Ney 1986), and there were two weeks between the Giotto flyby and the Wickramasinghe and Allen (1986) observations), the agreement between A_{WA} and the optical depth τ required by our model is excellent.

It is more difficult to compare quantitatively the optical depth τ_{λ} found for the emitting organic grains with the spacecraft results. Submicron grains in the Halley coma certainly contribute to the 3.4μm feature, but much larger particles might also contribute if the grains are sufficiently fluffy (Greenberg and Hage 1990). The Giotto–determined dust distribution can be integrated to find the percentage of the coma filling factor due to grains smaller than a certain radius. Using the latest (McDonnell *et al.* 1987) results for the distribution observed along the Giotto trajectory, one finds that dust particles with radii $\leq 1\mu$m contribute between 2.8% and 4.4% of the total filling factor, depending upon whether the integration is continued to 1 or 10^{-3} kg, respectively. Similarly, grains with radii $\leq 10\mu$m contribute between 25% and 40% of the total filling factor. More recently, however, Perry, Green, and McDonnell (1988) have re-examined the Giotto data, in light of discrepancies between the spacecraft results and ground-based observations made shortly before encounter. Taking into account the dependence of grain outflow velocity with size, they conclude that the change in the value of the exponent α at 10^{-8} kg may have been an artifact of variations in the level of dust production at the nucleus. They therefore recommend that modelling of the Halley coma should not include the large mass excess actually observed by Giotto, but rather that the small-particle exponent ($\alpha \approx -0.85$) should be extended through the larger sizes. If this recommendation is followed, one finds that that submicron grains contribute ~6% of the filling factor, while grains $\leq 10\mu$m contribute ~50%. These results are independent of whether the integration range extends to 10^{-3} or 1 kg, as the large negative exponent α in this case guarantees that particles larger than 1 g contribute almost negligibly to the coma filling factor. Finally, it should be noted that these results make use of the Divine *et al.* (1986) density-radius distribution, which assumes that the smallest coma particles have densities approaching 3 g cm^{-3}, with density dropping with increasing size up to a large-particle limit of 0.8 g cm^{-3}. To test the sensitivity of the above results to alternate density-radius models, we have convolved the Giotto-measured mass fluence with a dust particle density 0.8 g cm^{-3}, taken to be independent of particle size. We find that the resulting filling factors differ little from those cited above.

The range of optical depths τ_λ found above for the emitting organic grains, τ_λ/τ=0.01–0.06, may be compared with upper bounds placed on this ratio by the fraction A_f of the total coma filling factor determined from Giotto data for dust grains with radii less than 1 and 10μm, *viz.* $A_f(\leq 1\mu\mathrm{m})$=0.03–0.06 and $A_f(\leq 10\mu\mathrm{m})$=0.25–0.5. Only some portion of A_f is due to organic grains, but this component appears large: Some 84% of Halley's dust contains carbon (Jessberger *et al.* 1988), and Kissel and Krueger (1987) have interpreted Vega mass spectrometer data to mean that most Halley dust consists of a chondritic core coated with an organic mantle. Subsequent analysis by these authors led to the conclusion that Halley's dust is fully one–third organic by mass (Krueger and Kissel 1987).

τ_λ and A_f cannot be directly compared, however. In general, the absorption optical depth of the organic emitters at a wavelength λ is given by

$$\tau_\lambda = \int \tau(\lambda, a) da, \qquad (3.3)$$

with

$$\tau(\lambda, a) = \int n(a) \pi a^2 Q_{abs}(\lambda, a) dl, \qquad (3.4)$$

where $n(a)$ is the number density for particles of radius a, and $Q_{abs}(\lambda, a)$ is the dimensionless absorption efficiency factor for these particles at wavelength λ. The integral in Eq.(3.4) is taken along the line of sight through the coma. For optically thick grains, $Q_{abs}(\lambda, a) \approx 1$, so that the optical depth is just the geometrical filling factor. Thus τ can be compared directly to A_{WA}, as was done above. For grains with $a \lesssim \lambda$, however, Q_{abs} may be either greater or less than 1, typically becoming very small for $a \ll \lambda$. To compare τ_λ with the Giotto–determined filling factors A_f, we need Q_{abs} at λ=3.4μm throughout the range of interest in a. Most simply, τ_λ could be approximated by the expression $\tau_\lambda \approx \bar{Q}_{abs} A_f$, where $\bar{Q}_{abs}$ is some "typical" value of Q_{abs} for the emitting organic grains over the appropriate range of grain radii.

Q_{abs} may be calculated from Mie theory if the optical constants (complex refractive index $n_c = m - ik$, where m is the real and k the imaginary refractive index) are given. Although such constants are not known for ice residues

TABLE 3.1

APPROXIMATE EFFICIENCY FACTORS FOR TITAN THOLIN AND GLASSY CARBON AT 3.4 μm

Particle radius a(μm)	$x \equiv 2\pi a/\lambda$ [a]	Q_{abs}, Titan tholin[b]	Q_{abs}, glassy carbon[c]
0.1	0.2	0.009	0.1
0.25	0.5	0.05	0.5
0.5	0.9	0.1	1.7
1.0	1.9	0.4	1.5
2.0	3.7	0.8	1.2
2.7	5.0	0.9	1.1

[a] x evaluated at $\lambda = 3.4$ μm.

[b] At 3.4 μm, Titan tholin has $n_c = 1.65 - 0.041i$ (Khare *et al.* 1984); Wickramasinghe (1973) lists $n_c = 1.7 - 0.05i$.

[c] At 3.4 μm, glassy carbon has $n_c = 2.93 - 1.01i$ (Edoh 1983); Wickramasinghe (1973) lists $n_c = 3.0 - 1.01i$.

at 3.4μm, we can delineate a plausible range of values by considering m and k for Titan tholin and glassy carbon. At $\lambda = 3.4\mu$m, n_c for Titan tholin (interpolated from Khare *et al.* 1984) is given by m=1.65 and k=0.041; glassy carbon at this wavelength (interpolated from Edoh 1983) has m=2.93 and k=1.01. Wickramasinghe (1973) has compiled Mie theory results for extinction and scattering efficiencies, Q_{ext} and Q_{sca}, over a wide variety of m and k values. Employing the relation $Q_{abs} = Q_{ext} - Q_{sca}$, we use his tables for m=1.7 and k=0.05, and m=3.0 and k=1.0, to approximate the efficiency factors for Titan tholin and glassy carbon, respectively, over a range of values for x$\equiv 2\pi a/\lambda$. At $\lambda = 3.4\mu$m, these x–values correspond to particles of definite radii a. Our results are summarized in Table 3.1. We see that Q_{abs} for glassy carbon is typically >1 for particles with radii in the range $\sim 0.3-3\mu$m, whereas Q_{abs} for Titan tholin ~0.1–1. We can thus conclude that the values $\tau_\lambda/\tau \sim 10^{-2}$ required by our model are consistent with the spacecraft determined values $A_f \sim 0.03 - 0.5$, at least given the large range of uncertainty in A_f and Q_{abs}. Agreement is more easily obtained with glassy carbon optical constants than with those appropriate for Titan tholin. Optical constants for an actual ice residue over the crucial wavelength range, as well as a better knowledge of the fluffiness of cometary grains, are critical to performing this calculation more definitively.

3.4 Heliocentric Evolution of Cometary Emission Features

Green et al. (1986) have shown that the Halley continuum spectrum over the range 1–20 μm as a function of heliocentric distance R (measured in AU) is well fit by a combination of scattered sunlight and blackbody emission at a temperature

$$T_c = 329R^{-0.53}, \tag{3.5}$$

a relation derived from observations of a number of comets. This value of T_c is ~15% lower than that found both by Wickramasinghe and Allen (1986) for the 3–4 μm region, and by Bregman *et al.* (1987) for the range 5–13μm. This discrepancy may be explained as due to the different wavelength ranges being fit: as increasingly longer wavelengths are considered, the contribution due to small, hot grains in the coma becomes less and less significant. Indeed, Tokunaga *et al.* (1988) have also recently determined a relation similar to Eq.(3.5) for comet Halley, finding that color temperatures defined by the flux ratio 4.8μm/7.8μm are ~15% higher than those derived for 7.8μm/12.5μm data, which are in turn ~15% hotter than equilibrium blackbody temperatures. Thus the continuum over the range 2–12μm is expected to be best fit by a temperature higher than that given by eq.(3.5). Indeed, our own numerical investigations show that our model cannot fit the Wickramasinghe and Allen (1986) observations well for temperatures outside the range 350±10 K. Therefore, for consistency with the results of Wickramasinghe and Allen (1986) and Bregman *et al.* (1987), we take the temperature of the continuum emitters at 3–4 μm to be given by

$$T_c = 350(R/1.16)^{-0.53}. \tag{3.6}$$

The exponent is close to that (−0.50) expected for a gray body in thermodynamic equilibrium.

Thus it is possible to model Halley emission over the range 2–12μm using the model given by eq.(3.2). The continuum optical depth $\tau \sim 10^2$ times the optical depth due to the emitting organics (τ_λ), so that only near the minimum in the continuum radiation can an organic emission feature achieve good visibility relative to the continuum. At 1 AU, the 3.4μm feature is the sole feature near that minimum, lying near the intersection of the scattered solar and 350 K blackbody curves. However, as the comet moves away from perihelion, the intersection of the scattered solar spectrum and the comet's thermal emission spectrum will move to longer wavelengths. Thus, relative to the continuum, we expect the 3.4μm feature to be diluted and those at longer wavelengths progressively revealed, as the minimum in continuum emission sweeps through the infrared spectrum towards longer wavelengths.

Of course, this evolution is only relevant at those heliocentric distances R at which the comet retains its coma. Water ice is expected to vaporize in the solar radiation field for $R \lesssim 3$ AU (Delsemme 1982), and indeed, it is at this distance that comets typically develop an obvious, extended coma. However, some comets develop comae at larger distances. Comet Bowell 1980b exhibited an extended dust coma (but no detectable gaseous emission spectrum) for R as large as 7.2 AU (Cochran and McCall 1980). In the case of comet Halley, there is evidence for a gaseous coma beginning at $R \sim 6$ AU (Green and Morris 1987), and for a coma of dust grains within R=5.4 AU (Hanner 1986).

Using the values of the parameters found in Eq.(3.2) to provide the best fit to the 3–4 μm emission of comet Halley at 1.16 AU, we can predict the spectrum of the comet at all wavelengths in the range 2–12μm as a function of heliocentric distance R. We simply evaluate the flux given by Eq.(3.2), with T_c given by Eq.(3.6) and T_r taken to be the temperature of 0.1μm spherical grains found by Mie theory for either glassy carbon (Hanner 1983) or Titan tholin (Hanner 1986, Lamy and Perrin 1988) optical constants at the appropriate R. The temperature of these grains as a function of R is shown in Figure 3.3. In addition, it is known that dust production by comet Halley exhibited an approximate R^{-2} dependence on heliocentric distance (Gehrz and Ney 1986). Thus the two B_λ terms in Eq.(3.2) are further reduced by this amount. S_λ falls off as R^{-4}, one R^{-2} factor due to reduced dust production, and one due simply to the decreasing angle subtended by each dust particle as a function of increasing R. Note that our model describes the spectral evolution of organic features only; it does not, for example, include emission due to silicates (observed in both comets Halley (Bregman *et al.* 1987) and Wilson (Lynch *et al.* 1988)) or carbonates (tentatively identified in comet

Halley (Bregman *et al.* 1987)).

Our results are displayed in Figures 3.4 and 3.5. In each we present parallel results for both glassy carbon and Titan tholin optical constants, over the spectral range 2.5–12μm. Beginning at ~8μm, however, silicate emission should begin substantially to alter the results predicted here (see below), and beyond ~10μm the assumption of constant T_c will begin to fail.

Figure 3.4 shows the predicted spectrum of comet Halley for six different representative heliocentric distances. (Halley's perihelion distance was 0.59 AU; we have however extended our calculations to 0.3 AU, in anticipation of observations of comets with perihelion distances within several tenths of an AU of the Sun. Our 0.3 AU spectra may serve as predictions for such comets only if their 3.4μm spectrum near 1 AU resembles that of comet Halley, however.) The decrease in overall flux from the comet due to decreased dust production is evident. No account is taken of changing geocentric distance in calculating the overall magnitude of the flux. Thus, the magnitude of the flux in Figure 3.4 changes in the manner that would be observed by a co-orbiting spacecraft that maintained a fixed distance from the cometary nucleus.

As seen in Figure 3.4, as the continuum minimum sweeps to longer wavelengths, the ~ 6μm feature (present at the level of the 3.4μm feature in the transmission spectrum of Figure 3.1, but greatly suppressed in emission relative to the continuum at ~ 1 AU) becomes progressively enhanced. We have exaggerated the strength of the emission features in Figure 3.4 by a factor of 10, in order to make this evolution more apparent. Note the evolution of the continuum underlying the 3.4μm feature from thermal emission to scattered solar continuum as the comet moves from $R = 0.3$ to 2.0 AU. Such an evolution has been observed by Knacke *et al.* (1986) in ground-based observations for comet Halley moving between $R = 1.08$ and 1.54 AU. The movement of the continuum minimum towards longer wavelengths with increasing R found in Figure 3.3 is in quantitative

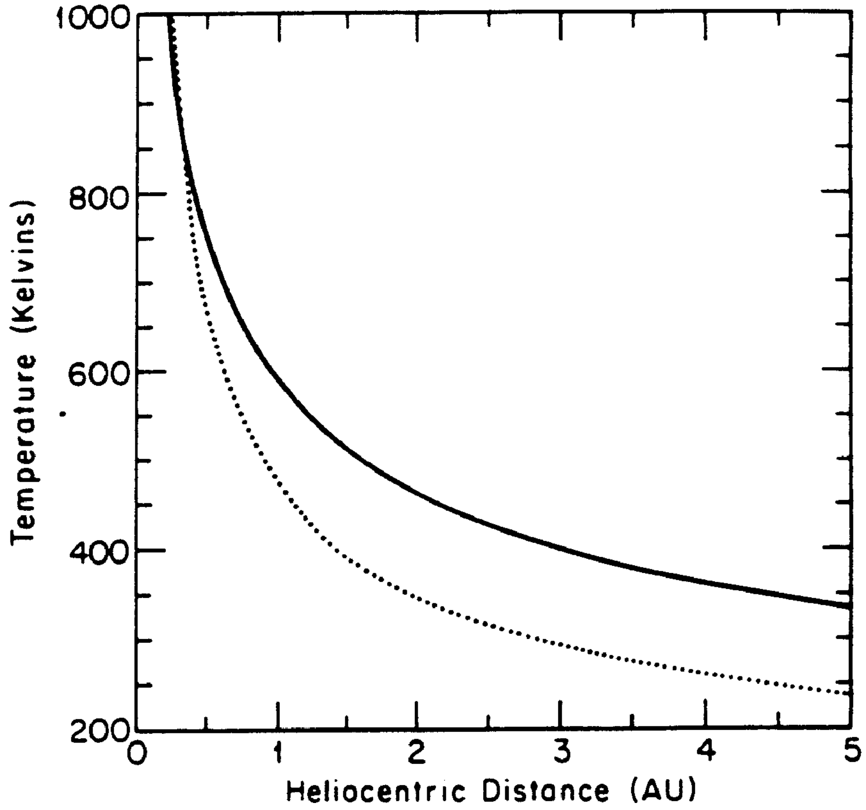

Figure 3.3 The temperature of 0.1μm grains as a function of heliocentric distance for glassy carbon (solid line) and Titan tholin (dotted line) optical constants. Titan tholin results are from Lamy and Perrin (1988) and Hanner (1986). Glassy carbon results are given by Hanner (1983), for $R < 2$ AU, and are extremely well fit by the relation $log(T) = 2.77 - 0.355\ log(R)$. This relation is then used to extrapolate out to 5 AU.

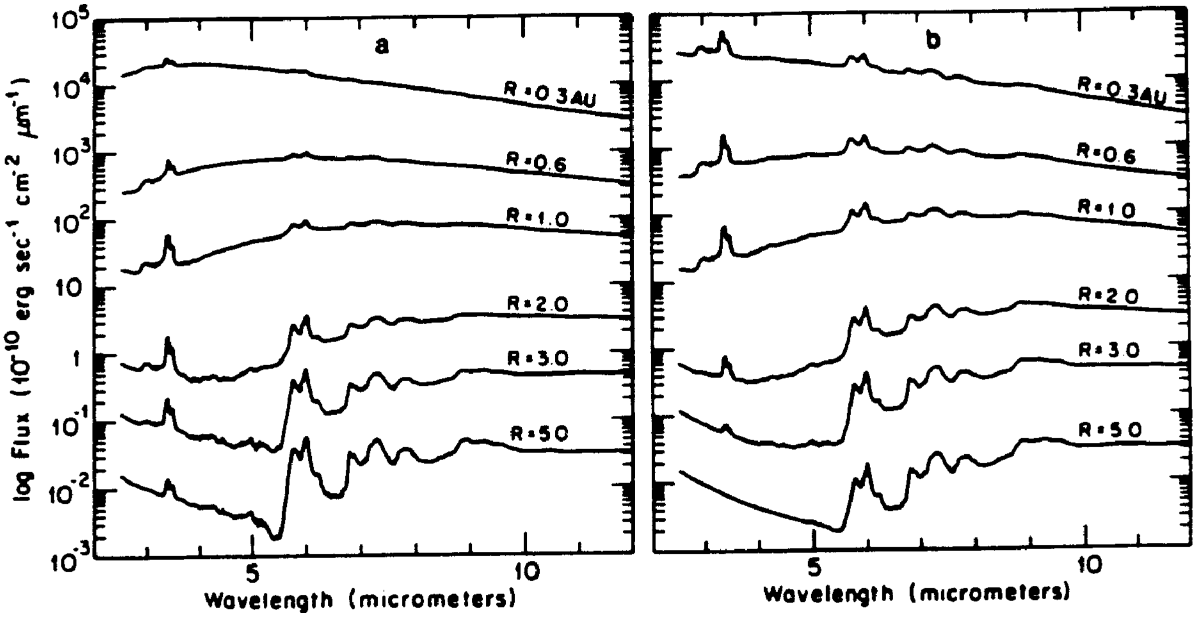

Figure 3.4 (a) The 2–12μm spectrum of comet Halley predicted by our model for T_r given by glassy carbon optical constants (solid line in Figure 3.3) at six different heliocentric distances. Emission features have been exaggerated by a factor of 10 for clarity. The prominence given to successive organic emission features by the minimum in the continuum spectrum as the comet moves to larger heliocentric distances is evident. (b) The same as (a), but for T_r given by Titan tholin optical constants (dotted line in Figure 3.3).

agreement with continuum measurements for comet Halley made by Tokunaga *et al.* (1986) over the heliocentric range 0.9–2.8 AU.

In Figure 3.5, we divide out the continuum from the predicted cometary emission spectra in order to make evident the evolving strengths of the features relative to the continuum. No exaggeration of emission features is made here. There are important similarities and contrasts between the heliocentric evolution predicted by glassy carbon (solid line) and Titan tholin (dotted line) optical constants. In both cases, the strength of the 3.4μm feature increases from a low level at 0.3 AU out to a maximum between 1 and 2 AU, then becomes nearly negligible by the time the comet is 5 AU from the Sun. (Of course, the cometary coma may have already disappeared by this heliocentric distance.) Simultaneously, the features at $\sim$6μm grow from only a few percent above continuum at $\sim$ 0.3 AU to $\sim$100% over continuum at 5 AU. For best visibility relative to the continuum, observations of the 6μm or longer wavelength features should evidently be conducted at heliocentric distances greater than 2 AU.

Finally, we note that the 3.4μm feature increases in strength between 1 and 2 AU in the case of glassy carbon optical constants, whereas it decreases in strength over the same range of distances for Titan tholin optical constants. This is immediately explicable in terms of the differing heliocentric temperature dependence for these materials as displayed in Figure 3.3. Glassy carbon, with a much larger imaginary refractive index, is more highly absorbing than Titan tholin, so that grains of this material reach higher temperatures. The resulting differences in spectral feature heliocentric evolution provide an observational diagnostic of cometary organic composition, as will be addressed in the following section.

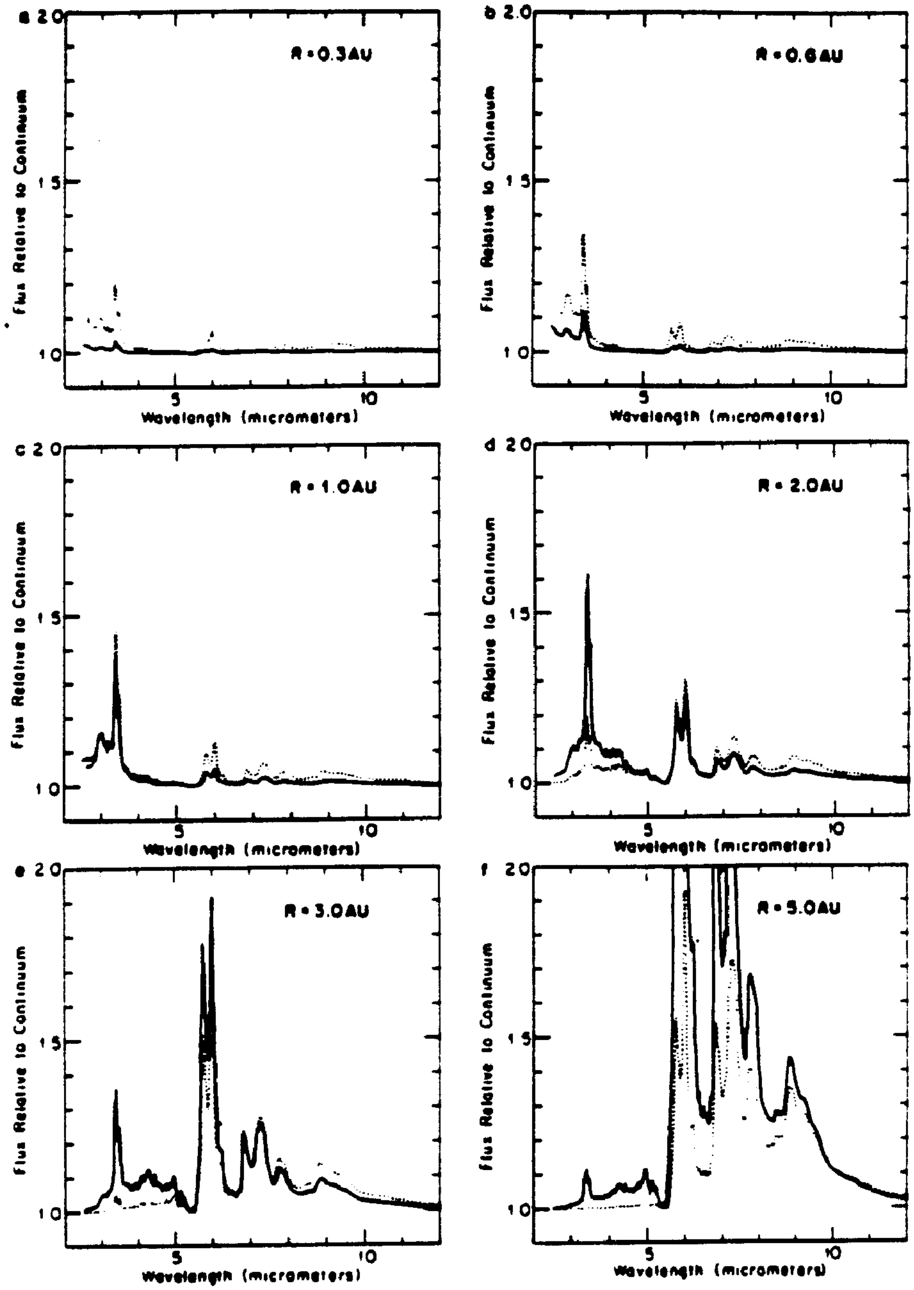

Figure 3.5 (a) The 2–12μm spectrum of comet Halley predicted by our model at heliocentric distance R=0.3 AU, after dividing out the continuum. The solid line depicts a model in which the 0.1μm emitting organics are assigned a temperature T_r appropriate to glassy carbon optical constants. The dotted line assumes a T_r appropriate to Titan tholin optical constants (see Figure 3.3). (b) The same as (a) for the case R=0.6 AU. (c) The case R=1.0 AU. (d) The case R=2.0 AU. (e) The case R=3.0 AU. (f) The case R=5.0 AU. Note the great suppression of the 6μm feature (compared to its strength in the transmission spectrum shown in Figure 3.1) within R ~2 AU, and the peaking of the 3.4μm feature in the 1–2 AU range.

3.5 Comparison with Airborne and Ground–Based Observations

Observations of comet Halley in the 5–13μm range (Bregman *et al.* 1987) at heliocentric distance R ~1.3 AU show a band rising to ~40% above continuum near 9μm and to ~80% above continuum near 10μm. This feature is usually attributed to Si–O stretching in small siliceous grains. Figure 3.5 shows that organic features predicted by our model in the vicinity of 9μm from 0.3 to 2 AU rise to no more than ~10% above continuum, so Si emission is expected to swamp these features at these heliocentric distances. However, the 10μm feature in comets typically disappears at larger heliocentric distances (Hanner 1986). At sufficiently large heliocentric distances (e.g., $R \gtrsim 3$ AU) it is therefore possible that organic spectral features near 9μm could become visible (Figures 3.5e and f).

Hanner (1986) and Lamy and Perrin (1988) have suggested that the Si feature may not be visible at large heliocentric distances because the Si is embedded in more volatile material which begins to evaporate only close to the sun. Especially from the point of view of a Greenberg (1982) core–mantle interstellar grain model for cometary dust, it is interesting to speculate that the silicate material is embedded in a more volatile organic matrix. The correlation, if any, between the 3.4μm feature and silicate emission in comets is unclear, however. For example, comets West and IRAS–Araki–Alcock showed Si features in the absence of the 3.4μm feature (Tokunaga and Brooke 1988). In addition, while comets Halley and Wilson showed quite similar 3.4μm organic features, their Si features differed significantly: Halley had an 11.3μm feature which Wilson lacked, whereas Wilson displayed a 12.3μm feature absent in the Halley spectrum (Lynch *et al.* 1988, Campins and Ryan 1988). Moreover, preliminary results for the PIA experiment in Giotto (Clark *et al.* 1987) indicate that ~30% of the "CHON" dust particles encountered by the Giotto spacecraft were, to the limits of detectability, purely organic in composition, rather than organics enclosing a silicate core. In addition, the similarity between the core-mantle interstellar dust model and interplanetary dust particles ("IDPs") of possible cometary origin is at best ambiguous. The only "ground truth" we have for cometary dust is the cometary fraction of the IDPs collected by high altitude aircraft in the Earth's stratosphere. But Walker (1988) has concluded that "nothing resembling the Greenberg model has been seen in the study of several hundred IDPs. We therefore doubt that it is a valid picture for typical cometary particles . . . . Some interstellar material is present but the volume fraction is small . . . ." (See also Walker 1987, and Brownlee 1988.)

The results of our model presented in Figures 3.4 and 3.5 assume a greatly idealized regularity in the parameters necessary to predict cometary emission spectra. As previously noted, comet Halley is in fact known to be highly time variable, both deviating from a simple R^{-4} law for infrared flux by as much as a factor of 7 over a few days (Gehrz and Ney 1986), and showing great variability of emission features relative to continuum on successive nights' observations. Similarly, Weaver *et al.* (1987) observed a 40% variation in Halley water molecule production over a space of only two hours on March 24, 1986. Thus heliocentric evolution of organic spectral features may well be indiscernible due to stochastic cometary variability, at least in the absence of sufficiently comprehensive observational statistics.

Given this variability, as well as the many uncertainties in our model, it is evident that one can at best make general predictions on the basis of Figures 3.4 and 3.5. Uncertainties in the model include, among others, that the τ_λ/τ ratio appropriate for fitting the 3.4μm feature on the date of Wickramasinghe and Allen's 31 March 1986 observation cannot be exactly appropriate for other dates; the strength of the 6μm feature relative to that at 3.4μm in the transmission spectrum used in the model is expected to vary with radiation dose; CH_4 hydrate clathrate is certainly not the only C– or N–containing ice initially present in a comet; the temperatures 450 K and 560 K calculated from optical constants for a gas–phase N–rich product or glassy carbon can only be an approximation to the temperature appropriate to an ice residue; and finally, the simple two–component model used here is obviously crude. These uncertainties need to be addressed by further experimental work (see also Khare *et al.* 1989, for an initial exploration of some of the relevant experimental parameters).

Nevertheless, it is instructive to compare quantitatively the predictions of our model with actual observations of the heliocentric evolution of the 3.4μm feature in comet Halley. In Table 3.2, we summarize the observations made of this feature for heliocentric distances between 1.08 and 1.96 AU. Column 3 of Table 3.2 lists the ratios $F_\lambda^{em}/F_\lambda^{cont}$ of the peak flux F_λ^{em} of the emission feature to the continuum flux F_λ^{cont}. These results are to be compared with the model predictions listed in columns 4, 5, and 6. Quantifying the error associated with $F_\lambda^{em}/F_\lambda^{cont}$ in column 3 is difficult, as a determination of this ratio requires fitting an underlying continuum to the observed emission feature and a typically small number of neighboring points. However, we estimate typical uncertainties in our determinations of the ratios given in column 3 to be ± 0.1.

The observed flux ratios given in column 3 make the extent of time–variability in cometary emission clear. The pre–perihelion observation of Danks *et al.* (1986) made at R=1.11 AU found *no* 3.4μm feature at the 1σ level. (Note that Danks *et al.* (1987) present the observations described by Danks *et al.* (1986) in refereed form. However, the December observing date and corresponding heliocentric and geocentric distances listed in Danks *et al.* (1987) are in error, whereas those given in Danks *et al.* (1986) remain correct (A. Danks, 1988, personal communication). We therefore use the results of Danks *et al.* (1986) here.) Observations by Wickramasinghe and Allen (1986) on 31 March and 1 April 1986 show a jump in $F_\lambda^{em}/F_\lambda^{cont}$ of ~35% between the two nights. Since T_c and T_r in

TABLE 3.2

COMPARISON BETWEEN MODEL AND OBSERVED FLUX RATIO AT $\lambda = 3.4\ \mu m$[a]

Observation date		Heliocentric distance R (AU)[b]	Observed flux ratio ($F_\lambda^{em}/F_\lambda^{cont}$)	Predicted flux ratio ($F_\lambda^{em}/F_\lambda^{cont}$)		
				Grains for Which T = 900 °K at 1.16 AU	Glassy carbon optical constants	Titan tholin optical constants
25 December	1985[c]	1.11	~0[h]	1.5	1.5	1.5
26 March	1986[d]	1.08	1.4	1.5	1.4	1.5
27 March	1986[d]	1.10	1.6	1.5	1.5	1.5
28 March	1986[c]	1.12	1.4	1.6	1.5	1.5
29 March	1986[d]	1.13	1.4	1.6	1.5	1.5
30 March	1986[e]	1.15	1.4	1.6	1.5	1.5
31 March	1986[e]	1.16	1.4	1.6	1.5	1.5
1 April	1986[e]	1.18	1.9	1.6	1.5	1.5
25 April	1986[d,f]	1.54	1.7	1.9	1.7	1.3
19 -20 May	1986[g]	1.90	2.2	2.0	1.6	1.2
24 May	1986[f]	1.96	~2[i]	2.0	1.6	1.2

[a] It is shown in Section 3.5 that discrepancies between model predictions in columns 4 and 5 and observations lie within the stochastic variability of $F_\lambda^{em}/F_\lambda^{cont}$ observed for comet Halley.

[b] Ephemeris from Yeomans (1986).

[c] Danks *et al.* (1986).

[d] Knacke *et al.* (1986).

[e] Wickramasinghe and Allen (1986).

[f] Baas *et al.* (1986)

[g] Tokunaga *et al.* (1987).

[h] Feature observed at the 1σ level.

[i] $F_\lambda^{em}/F_\lambda^{cont}$) is difficult to quantify, as the placement of the continuum baseline cannot be made with confidence.

Eq.(3.2) are virtually unchanged as a comet moves from R=1.16 to R=1.18 AU, this jump must be due to a change in the ratio τ_λ/τ. From Eq.(3.2), we have $F_\lambda^{em} = S_\lambda + \Omega\tau_\lambda B_\lambda(T_r) + \Omega\tau B_\lambda(T_c)$ and $F_\lambda^{cont} = S_\lambda + \Omega\tau B_\lambda(T_c)$, so that

$$F_\lambda^{em}/F_\lambda^{cont} - 1 = (\tau_\lambda/\tau)A_\lambda, \tag{3.7}$$

where

$$A_\lambda \equiv B_\lambda(T_r)/[(S_\lambda/\Omega\tau) + B_\lambda(T_r)]. \tag{3.8}$$

(Note that Eqs.(3.7) and (3.8), provided S_λ is known, serve to check the consistency of the result τ_λ/τ found by minimizing χ^2 in Eq.(3.2)). Since $S_\lambda \propto \tau$, A_λ in Eq.(3.8) is independent of τ, depending only on T_c and T_r; A_λ for the dates 31 March and 1 April 1986 is thus approximately constant. Dividing both sides of Eq.(3.7) for 1 April by Eq.(3.7) for 31 March, A_λ cancels out and we find that the change in $F_\lambda^{em}/F_\lambda^{cont}$ between the two observations by the factor 1.9/1.4≈1.4 requires that τ_λ/τ change by a factor $(1.9-1)/(1.4-1) \approx 2.3$. Thus we discover that the optical depth of the emitting organic grains may change stochastically relative to the continuum optical depth by a factor of a least 2.3 on timescales of one day. Such a sudden increase in τ_λ/τ requires either a sudden increase in the number or the absorption coefficient of the organic grains in the coma; either result seems to imply significant nuclear heterogeneity. Such an outburst of small organic grains implies a change in the exponent α of the Halley dust distribution. This result should therefore also caution cometary modellers against drawing strong conclusions on the basis of the dust mass distribution measured by the Giotto or Vega spacecraft, as these may also be highly time variable.

We remark that the evident outburst of emitting organic particles on 1 April 1986 coincided with an unusually strong CN-shell expansion at that date (Schlosser *et al.* 1986). This coincidence lends support to the suggestion of A'Hearn *et al.* (1986) that CN jets in comet Halley form as the CN dissociates directly from submicron organic dust particles in the coma (see also Lamy and Perrin 1988).

In addition to CN jets, Halley exhibited OH outbursts between 24 and 29 March 1986, and 30 March and 4 April 1986 (Silva and Mirabel 1988). These outbursts also coincide with evident outbursts of emitting organics seen in Table 3.2.

The greatest discrepancies between our model results and observations are for 25 December 1985, and for the period from 25 April to 24 May 1986. The lack of an observed 3.4μm feature on 25 December is a further warning that comparisons between model predictions and observations for comet Halley infrared emission cannot be expected to be exact when only a small number of observations are available for this highly time-variable object. We know from the dates 31 March and 1 April 1986 that variations in $F_\lambda^{em}/F_\lambda^{cont}$ of a factor ~1.4 occur unpredictably; the observed flux ratio for 25 April is just consistent with the model predictions for Titan tholin (column 6) to within this factor. Model predictions for glassy carbon (column 5) are in perfect agreement with observations on this date. The 19–20 May observations, however, appear to require an increase in $F_\lambda^{em}/F_\lambda^{cont}$ over that predicted by our model by a factor ~1.4 in the case of glassy carbon, and ~1.8 in the case of Titan tholin. In light of the time variability exhibited by Halley, it is clear that, at least in the case of glassy carbon, changes of this magnitude (equal to that observed between 31 March and 1 April) in $F_\lambda^{em}/F_\lambda^{cont}$ are entirely possible. Therefore we conclude that both the general evolutionary trend and quantitative values predicted by our model for glassy carbon optical constants are consistent with observations. Model predictions for Titan tholin optical constants, however, are more evidently discrepant with observations in both qualitative and quantitative respects. Thus the observed heliocentric evolution of the 3.4μm feature provides information on the optical constants, and by extension the nature of the organic material, in comet Halley.

Although the predictions shown in column 5 of Table 3.2 for our model with glassy carbon optical constants are consistent to within observed stochastic variability with the observational results listed in column 3, the match is far from perfect. In particular, $F_\lambda^{em}/F_\lambda^{cont}$ for glassy carbon optical constants peaks at ~1.5 AU, whereas the observed $F_\lambda^{em}/F_\lambda^{cont}$ for comet Halley appears to continue rising out to ~1.9 AU. Glassy carbon optical constants provide a closer fit to these observations than do those of Titan tholin because of the higher temperatures reached by the former. An obvious question, then, is what temperature emitting organic grains must attain at 1.16 AU in order to reach a peak $F_\lambda^{em}/F_\lambda^{cont} \sim 2$ at ~1.9 AU. Numerical experiments show that, for particles whose temperature falls off with heliocentric distance as a blackbody, T_r ~900 K at 1.16 AU best matches the observational data. Results for a model with these temperatures are shown in column 4 of Table 3.2. T_r ~900 K gives $\tau_\lambda/\tau \sim 5.8 \times 10^{-4}$ for a χ^2 minimum fit to the 3.4μm feature at 1.16 AU.

In fact, T_r ~900 K is probably an overestimate of the temperature required at 1.16 AU to match the data of column 3. For submicron particles, temperature is expected to fall off with heliocentric distance more slowly than that of a blackbody, because the long wavelength emissivity of small particles relative to that of a blackbody decreases with decreasing particle temperature (Greenberg 1971). Thus the temperature of submicron grains is expected to fall off as

$$T_r = T_r(R = 1.16AU)(R/1.16AU)^{-\xi}, \tag{3.9}$$

where ξ <0.5. Dumont and Levasseur-Regourd (1988) find ξ ~0.33 from IRAS data on zodiacal dust; if this choice of ξ were appropriate for comet Halley submicron emitting organics (Greenberg and Hage 1990), $T_r(R = 1.16AU)$ ≈825 K would fit the observational results listed in column 3. Such temperatures, higher than those expected for 0.1μm glassy carbon spheres, may be due in part to a fluffy or fractal grain structure to comet dust (Meakin and Donn 1988). In such particles, flash heating of individual fractal elements by UV photon absorption may lead to temperatures well above those expected for a blackbody (Sellgren *et al.* 1983, Sellgren 1984).

3.6 Thermal Emission from Grains vs. Gas–Phase Fluorescence

It was first suggested by M.J. Mumma at the workshop *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. Hanner, Ed. 1988) that the heliocentric evolution of organic spectral features will differ in the cases of thermal emission from small grains and gas–phase fluorescence. The observed intensity of a cometary emission feature will be proportional to the total number N of emitters present in that part of the coma subtended by the telescope aperture. N is in turn dependent upon the lifetime of the emitters. Using Mie theory, Wallis *et al.* (1987) have calculated lifetimes for biologically–derived organic grains of radius $\sim 0.1 \mu$m. Assuming the range of bond energies of terrestrial Type II kerogen to be appropriate for cometary organics, they find that, at 1 AU, the grains experience almost no evaporation within a cometary coma of radius 5×10^4 km, the "nominal" size (McDonnell *et al.* 1987) of the Halley dust coma. (At these heliocentric distances, 0.1μm grain lifetimes are well in excess of $10^6 - 10^7$ s; with an outflow velocity ~ 350 m s^{-1} (McDonnell *et al.* 1987), such a grain will travel $\sim 10^6$ km prior to evaporation). Organic molecular bonds with activation energies $\lesssim 50$ kcal mol^{-1} will be disrupted on shorter timescales, but $\lesssim 5\%$ of the bonds in kerogen have strengths below this level. Significant evaporation of 0.1μm grains on timescales $\sim 10^4$ s will begin only for heliocentric distances <0.64 AU or at grain temperatures >680 K (Wallis *et al.* 1987). Similarly, Combi (1987) has concluded that grain lifetimes are as short as $\sim 10^5$ sec only for grains that are very small ($\sim 10^{-3} \mu$m, $\sim 10^{-21}$g).

These results are in rough agreement with thermogravimetric analyses of the involatile organic residue produced by electron, spark, or UV irradiation of cosmically abundant gases; typical results indicate that the residues are 50% stable at temperatures ranging from ~600–1200 K (Sagan and Khare 1979, Sagan *et al.* 1984). Since ground–based observations of comet Halley at heliocentric distances

$\sim$1–2 AU typically subtend $\sim 10^3$–10^4 km across the coma, particle evaporation is evidently of little importance to evaluating N in the case where organic spectral features are due to thermal emission from grains. Of course, those most volatile organics which do evaporate should themselves contribute to gas-phase fluorescence.

If the organic spectral features are due primarily to fluorescence, however, limits on molecular lifetimes due to dissociation by solar ultraviolet light are of great significance. For example, at 1 AU, unshielded CH_4 and NH_3 lifetimes against UV dissociation are $\sim 10^5$ sec and $\sim 10^4$ sec, respectively (see Allen *et al.* 1987). CH_4 would contribute prominently to fluorescence near 3.3μm, and NH_3 near 6μm (Crovisier and Encrenaz 1983). With a typical gas outflow velocity from the nucleus $\sim$1 km s^{-1} (Allen *et al* 1987), CH_4 and NH_3 molecules should experience significant UV dissociation within a 5×10^4 km dust coma radius. Ground-based observations conducted with aperture sizes large enough to include this molecular dissociation, but small enough to exclude significant organic grain evaporation, are in principle capable of determining which mechanism, grain thermal emission or gas-phase fluorescence, is primarily responsible for observed cometary organic spectral features. In the simplest approximation, the lifetimes of gas-phase fluorescing molecules will increase as the square of the heliocentric distance R, whereas the lifetimes of thermally emitting organic grains ("infinite" for the purposes of these observations) will remain unchanged. Thus the band strengths predicted by these two mechanisms for the 3.4μm emission feature differ by a factor R^2 in their heliocentric evolution. To observe this evolution, a sequence of observations over a range of heliocentric distances, with appropriately chosen aperture sizes, would be required.

Of course, the situation is in practice much more complex. For example, the fluorescing of daughter products of dissociated parent molecules (among other complications) must be taken into account. In addition, lifetimes of evaporating grains depend both on grain size and on the binding energy of the relevant organics. For example, Lamy and Perrin (1987), choosing a uniform bond energy of 34.5 kcal mol^{-1}, find that 0.2μm grains have lifetimes at 1 AU of $\sim 2\times10^5$ s, travelling $\sim 7\times10^4$ km before being completely destroyed. If grain lifetimes are indeed on the order of molecular UV–dissociation lifetimes, heliocentric spectral evolution will not allow a choice between gas–phase fluorescence and solid particle thermal emission. However, given independent reasons to accept the thermal emission model, such evolution would put constraints on grain evaporation lifetimes, and hence, on the nature of the organic bonds present. Finally, it must again be noted that the stochastic variability of a comet's dust emission, if as great as that exhibited by comet Halley, might well overwhelm the differences between fluorescent and thermal emission described here.

3.7 Discussion and Future Observations

In spite of the many uncertainties discussed above, certain broad conclusions may be drawn. We have demonstrated quantitatively that in the vicinity of 1 AU, spectral features in the 5–8μm range should be overwhelmed by the continuum while the 3.4μm feature should be apparent, whereas between 1.5 and 3 AU this relationship will reverse. Thus, for best visibility relative to the continuum, observations which hope to identify organic spectral features beyond 4μm are preferably conducted at these larger heliocentric distances, placing a premium on early spectral observations of comets as soon as their comae develop—or late observations, as they recede from the Sun (subject, of course, to signal–to–noise limitations). Observations within $\sim$2 AU potentially face the dilemma of yielding an uninterpretable null result: no spectral features may indicate a true paucity of molecules with emission features at these wavelengths, or the absence of such features may simply be a result of poor visibility relative to the continuum, the effect described here. The absence of organic spectral features at greater heliocentric distances, however, would begin significantly to constrain the organic composition of the comet in question. In the context of our model, such results would constrain the composition of the ices that are precursors to the organic grains (Khare *et al.* 1989).

Future comet rendezvous missions will be ideally placed to test the predictions of our model. Airborne and ground-based observations are also clearly of great importance. For example, spectral observations in the 5–8μm range of a cometary coma as the comet moves from 1 to 3 AU would be especially valuable. In addition, observations of a comet approaching perihelion within several tenths of an AU of the Sun could serve to check the near–Sun evolution of the 3.4μm feature predicted here.

Chapter 4

Impact Delivery and Erosion of Planetary Oceans in the Early Inner Solar System[1]

4.1 A Cometary Contribution to the Terrestrial Oceans?

In its classical formulation, the Oort cloud (Oort 1950) comprised 10^{11} – 10^{12} comets orbiting the Sun in a spherical shell extending from 10^4 to 10^5 AU. Perturbations by passing stars and, we now know, by molecular clouds and galactic tides (see Weissman 1985 for a review), would send some of these comets into the inner Solar System where collisions with Earth could occur, leading to a terrestrial accretion of cometary material. An early estimate by Oró (1961) suggested Earth could have acquired 10^{11} – 10^{15} kg in this way. (This early work, which pre–dated Apollo and Luna sample returns from the Moon, did not make

---

[1] This chapter is based on two papers: Chyba, C.F. (17 December 1987), The cometary contribution to the oceans of primitive Earth, *Nature* 330, 632–635 [copyright 1987 by MacMillan Magazines Ltd]; and Chyba, C.F. (11 January 1990), Impact delivery and erosion of planetary oceans in the early inner Solar System, *Nature* 343, 129–133 [copyright 1990 by MacMillan Magazines Ltd.].

allowance for a possible higher early comet flux.)

In comparison, Earth's mass $M_\oplus = 5.98 \times 10^{24}$ kg, and the terrestrial oceanic mass $M_{\mathrm{oceans}} = 1.4 \times 10^{21}$ kg H_2O (Walker 1977). The total near-surface quota of water is greater, but quantifying it is difficult; typical estimates of water in Earth's crust range from 2.0 to 3.3×10^{20} kg (Carr 1984). Of course much more water could possibly be present deep in the interior. Here we take M_{oceans} as a reference, as it is the only certain figure. Taking comets to be ~50% water ice (Delsemme 1988), Oró's result gives a cometary contribution of at most 10^{-6} to M_{oceans}. More recent estimates (Pollack and Yung 1980, Oró *et al.* 1980, Wetherill 1981) increased this number, but still allowed only $\lesssim$ 4% of M_{oceans} to be cometary. (This conclusion would change dramatically if the interpretation of atmospheric dayglow emissions apparently observed by the Dynamics Explorer satellite as representing a $\sim 10^{12}$ kg yr^{-1} influx of ~10 meter comets (Frank *et al.* 1986a, Frank and Huyghe 1990) were correct. Such a flux would deliver $\sim M_{oceans}$ over the age of the Earth. But this interpretation has faced severe objections, including that the proposed flux of small comets is inconsistent by five (Davis 1986) or six (Nakamura *et al.* 1986) orders of magnitude with Apollo lunar seismic data (but see the reply by Frank *et al.* 1986b). A host of other objections, and an argument that the Dynamics Explorer satellite data actually represent instrumental artifacts, are summarized by Dessler 1991.)

In the past few years, difficulties with the classical Oort picture and improved models of planetary formation have suggested an inner Oort cloud (sometimes called the "Kuiper belt", as an inner Oort cloud was first suggested as a natural consequence of cometary formation in the outer Solar System by Kuiper 1951), with $\sim 10^{14}$ comets, beginning near the orbit of Neptune in the plane of the ecliptic, and slowly deforming outward into the classical Oort sphere (Weissman 1985). Such models indicate that proto-Uranus and Neptune should have ejected from their vicinities planetesimals totalling many times their own final masses;

the resulting flux of comets through the inner Solar System early in its history may have been $10^4 - 10^5$ times greater than that currently observed (Whipple 1976, Wetherill 1981, Fernández and Ip 1983, Shoemaker and Wolfe 1984). These results have led to renewed speculation that comets may indeed have brought vast quantities of water to the primitive Earth (Fernández and Ip 1983, Shoemaker and Wolfe 1984, Chyba 1987).

In addition to comets, carbonaceous asteroids may also have been important sources of Earth's oceans, as well as other surface volatiles (Anders and Owen 1977, Chyba 1990a). An objection to this hypothesis has been that large impacts might erode as much or more of the terrestrial volatile inventory as they deliver (McKinnon 1989). Analytical fits to the lunar cratering record, appropriately scaled to Earth's larger gravitational cross section, allow estimates of the terrestrial bombardment history. By convolving these estimates with quantitative models for impact erosion of planetary atmospheres (Melosh and Vickery 1989) and condensed oceans, we will show in this chapter that Earth probably accreted a net (after impact erosion) amount of water $\gtrsim$ 0.2–0.7 oceanic masses during the period of heavy bombardment 4.5 to 3.5 Gyr ago (Chyba 1990a). Venus should have collected approximately as much water as Earth, whereas Mars, more subject to impact erosion, should have accreted an ocean equivalent to a layer ~10–100 meters deep distributed over the planet.

4.2 Uncertainties in the Lunar Cratering Record

Ironically, one of the greatest uncertainties in these results arises from that part of the calculation which is based most strongly on empirical data. Differing lunar crater counts, as well as disparate acceptable fits to even the same lunar cratering data sets, lead to cumulative bombardment history models which differ by $\sim 10^3$ when extrapolated back to 4.5 Gyr. (However, lunar geochemical data, discussed below, do allow a firm lower limit to be placed on total incident impactor mass, a limit which yields the 0.2–0.7 M_{oceans} figure cited above.) An ancillary result of this investigation is that calculations of the impact frustration of the origins of life (Maher and Stevenson 1988, Oberbeck and Fogleman 1989a) that rely on such bombardment models may also suffer from correspondingly great uncertainties.

Attempts to estimate the impact environment of early Earth typically begin with an analytical fit to the lunar cratering record. One such fit is that found by Melosh and Vickery (1989) in their recent work on impact erosion of atmospheres. They give

$$N(>4\ \text{km},\ \mathrm{T}) = 2.68 \times 10^{-5}[\mathrm{T} + 4.57 \times 10^{-7}(e^{\mathrm{T}/\tau_a} - 1)]\ \text{km}^{-2} \qquad (4.1a)$$

as an analytical fit to empirical data (from the Basaltic Volcanism Study Project (BVSP) 1981, Table 8.4.2) relating surface density of lunar craters with diameters D >4 km, N(>4 km), to the radiogenic age, T, of the cratered surface. Melosh and Vickery (1989) choose τ_a=220 Myr. The BVSP (1981) data, and the fit given by Eq.(4.1a), are shown in Figure 4.1.

It is not clear that τ_a=220 Myr is the correct time constant for the decay of the early impactor flux. Other authors have made different choices. For example, Maher and Stevenson (1988) modelled the impactor flux with τ = 70 Myr, while Neukum (1983) favors τ = 144 Myr (corresponding to a 100 Myr half-life). Fundamentally, imprecision is inevitable because, as Wetherill (1977), Hartmann (1980), and Grinspoon (1988) have emphasized, the impactor flux cannot actually have decayed at a constant rate. Rather, the flux must initially have been dominated by objects in nearly circular Earth-like orbits (for which τ ∼10- 20 Myr); as this population was swiftly swept up, different, more slowly-decaying populations (with τ ∼100–300 Myr; e.g. comets or Mars-exchanged asteroids) would have become predominant. Thus fitting a decay "constant" to the lunar data is a crude approximation at best. Nevertheless, the actual data (∼15 points) may not justify a more sophisticated treatment (see, however,

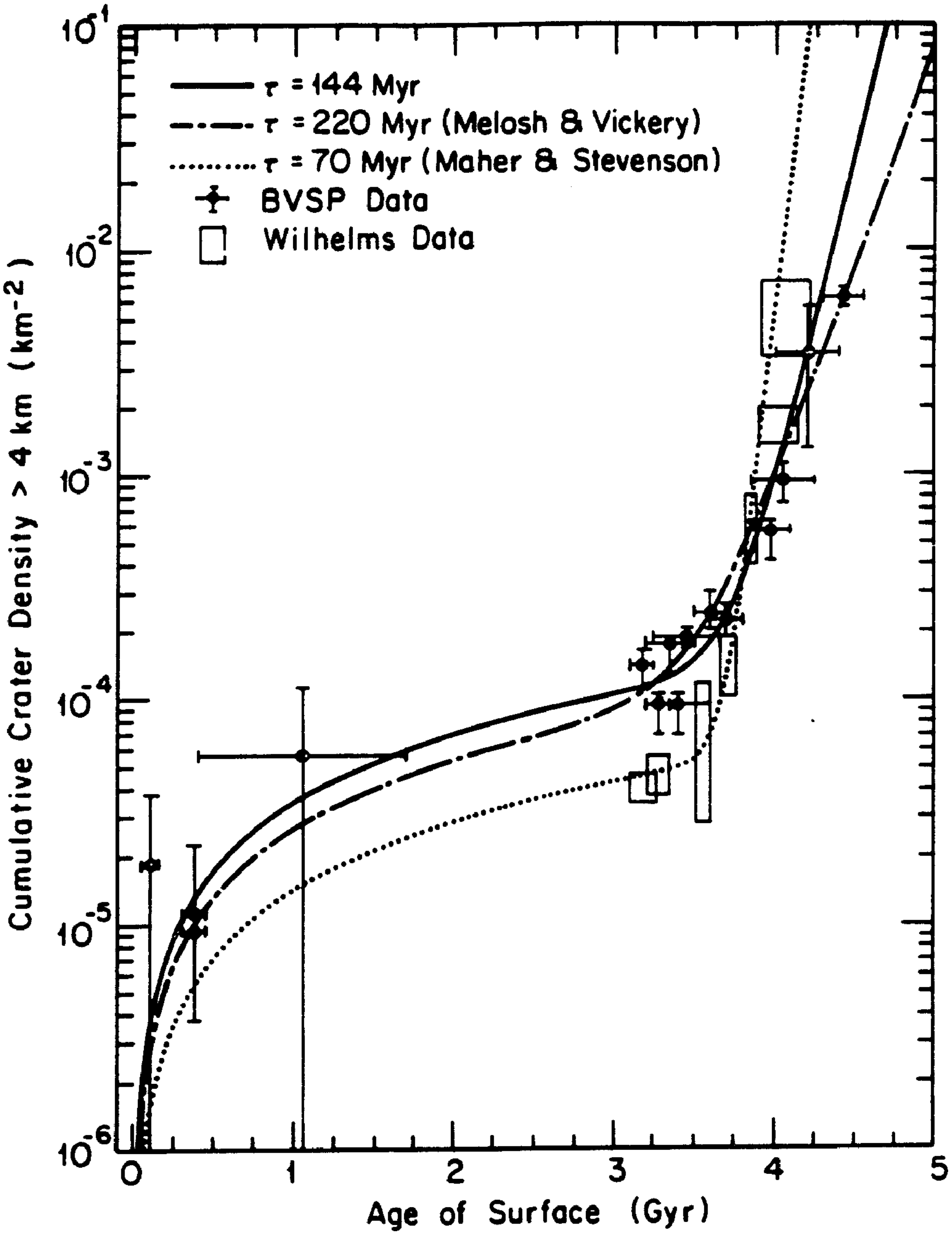

Figure 4.1 Cumulative lunar crater density as a function of surface age, for the data of Wilhelms (1984) (boxes) and BVSP (1981) (crosses), fit by analytical formulae with 70 (dotted line; Maher and Stevenson 1988), 144 (solid line; Chyba 1990a), and 220 (dashed line; Melosh and Vickery 1989) Myr decay constants.

Grinspoon 1988, for such an attempt).

To demonstrate the range of decay rates permitted by the BVSP (1981) data, we have fit these data, using two-dimensional χ^2 minimization, with an equation of the form (4.1a), using τ =144 Myr. Such a decay constant is of intrinsic interest, as a 100 Myr half-life has been demonstrated for the decline of the primordial cometary flux through the inner Solar System by independent numerical simulations of the formation of Uranus and Neptune (Fernández and Ip 1983, Shoemaker and Wolfe 1984). Our fit, shown in Figure 4.1 as the solid curve, is given by:

$$N(>4\text{ km, T}) = 3.5\times10^{-5}[\text{T} + 2.3\times10^{-11}(e^{\text{T}/\tau_b}-1)]\text{ km}^{-2}, \qquad (4.1b)$$

with τ_b=144 Myr. Both Eqs.(4.1a) and (4.1b) provide moderately good fits to the BVSP (1981) data, with χ^2 values of 8.06 and 10.6, respectively (for 15–2=13 degrees of freedom). Eq.(4.1a) is formally a better fit by ~25%, but this comparison is of little significance. First, as just discussed, fitting any single decay "constant" to the cratering flux is a procrustean exercise. Second, note that the two fits are most discrepant for the point at ~4.4 Gyr in Figure 4.1. However, there is no true radiogenic date for this "uplands" point; rather its age is simply estimated (BVSP 1981). Furthermore, if the lunar uplands are saturation cratered, the crater density plotted for this point could be a considerable underestimate.

Recent work on the impact frustration of the origins of life (Maher and Stevenson 1988, Oberbeck and Fogleman 1989a) uses a cumulative lunar crater density given by

$$N(>4\text{ km, T}) = 1.4\times10^{-5}[\text{T} + 5.6\times10^{-23}(e^{\text{T}/\tau_c}-1)]\text{ km}^{-2}, \qquad (4.1c)$$

with τ_c=70 Myr. Eq.(4.1c) provides a reasonable fit to the lunar cratering data (for D >20 km) given by Wilhelms (1984, Figure 6.49). Maher and Stevenson (1988) adopt a number-diameter scaling law $N \propto D^{-1.8}$ for lunar cratering, which they explicitly consider to hold at least to diameters as small as D=1 km.

In Eq.(4.1c), we have used this scaling law to convert Wilhelm's (1984) data (and Maher and Stevenson's (1988) fit) to D=4 km so that it may be compared directly (Figure 4.1, dotted line) with the BVSP (1981) results. (Melosh and Vickery (1989) implicitly adopt a -1.8 scaling as well, in their conversion from cumulative crater density to heavy bombardment flux.) This conversion is of course perfectly consistent with Maher and Stevenson's (1988) model, although not quite with Wilhelm's (1984) data, which are based on combining crater counts at D >20 km and D >1 km, via an empirical law (derived from Imbrium basin counts) that is *not* consistent with -1.8 scaling. The D >1 km counts are drawn from Neukum (1983) whose small crater counting methodology is incompatible with that adopted by BVSP (1981). It is not surprising that the results given by Eq.(4.1c) differ so markedly from those of Eqs.(4.1a) and (4.1b).

Note that each model gives similar results for ages ~3.8 Gyr, since the data at these dates are in rough agreement. (It is the requirement that the models approximately agree at ~3.8 Gyr, despite differing time constants, that leads to the vastly different coefficients, 10^{-7} vs. 10^{-23}, in Eqs.(4.1a)–(4.1c).) However, at dates $\gtrsim$ 3.8 Gyr, the models diverge: extrapolation back to 4.5 Gyr leads to cumulative crater densities which differ by $\sim 10^3$.

Another question that arises in comparing the BVSP (1981) and Wilhelms (1984) data sets is the role of secondary craters. BVSP (1981) generally include only craters with D > 2.8 km, to minimize contamination by secondaries. However, basin secondaries as large as $D \sim$ 20–30 km may substantially contaminate crater counts in the lunar highlands (Wilhelms *et al.* 1978, BVSP 1984). Nevertheless, the slopes of the crater diameter distributions used by BVSP (1981) for the oldest lunar surfaces show no steepening at small D, suggesting they have successfully excluded most secondaries from these counts. If this is not the case, then the crater densities plotted for the two oldest BVSP (1981) data points in Figure 4.1 are overestimates, and the difference between models based on the

BVSP (1981) and Wilhelms (1984) data are even *greater* than those described here.

4.3 Early Terrestrial Impact Environment

Given Eqs.(4.1), we may compute the total mass incident upon Earth during heavy bombardment. N in Eqs.(4.1) scales as $D^{-1.8}$; we may convert this crater diameter scaling to impactor mass scaling through the use of a mass–diameter equation. Following Melosh and Vickery (1989), we use Melosh's (1989) version of the Schmidt–Housen (1987) relation, assuming a typical impact angle to be 45° and a crater collapse factor c_f of 30% (Shoemaker 1983):

$$m_p = (0.11)\rho_t^{19/15}\rho_p^{-1/4}g^{21/25}v_p^{-5/3}(1.3/c_f)^{19/5}(\sin 45^\circ/\sin\theta)^{5/3}D^{19/5}. \qquad (4.2)$$

Here m_p is the mass of the impactor in kg, ρ_t=2900 kg m^{-3} is the lunar crustal density (Haines and Metzger 1980), ρ_p=2500 kg m^{-3} is the density of a typical impacting asteroid (Shoemaker *et al.* 1979) g=1.61 m s^{-2} is the gravitational acceleration at the lunar surface, $v_p = 1.3 \times 10^4$ m s^{-1} is a typical impact velocity of asteroids with the Moon (discussed below), and D is measured in meters. Melosh and Vickery (1989) choose c_f=1.25 in Eq.(4.2), a choice which would increase m_p by ~16% over the values found here. Inserting Eq.(4.2) into the implicit (4 km/D)$^{-1.8}$ scaling in Eqs.(4.1) yields three equations for the cumulative number, $n(> m, T)$, of impactors > mass m which have been incident on a lunar surface of age T. The total mass, M(T), incident in impactors with masses in the range m_1 to m_2 is then:

$$M(\mathrm{T}) = \int_{m_2}^{m_1} m[\partial n(> m, \mathrm{T})/\partial m]dm, \qquad (4.3)$$

which yields

$$M(\mathrm{T}) = 0.76[\mathrm{T} + 4.6 \times 10^{-7}(e^{\mathrm{T}/\tau_a} - 1)]m_2^{1-b}\ \mathrm{kg^b\ km^{-2}} \qquad (4.4a)$$

$$M(\mathrm{T}) = 0.99[\mathrm{T} + 2.3 \times 10^{-11}(e^{\mathrm{T}/\tau_b} - 1)]m_2^{1-b}\ \mathrm{kg^b\ km^{-2}} \qquad (4.4b)$$

$$M(\mathrm{T}) = 0.40[\mathrm{T} + 5.6 \times 10^{-23}(e^{\mathrm{T}/\tau_c} - 1)]m_2^{1-b}\ \mathrm{kg^b\ km^{-2}}, \qquad (4.4c)$$

for Eqs.(4.1a) to (4.1c), where b=(1.8/3.8)≈0.47, T is in Gyr, and we assume $m_2 \gg m_1$.

What is the appropriate value in Eqs.(4.4) for m_2? An N vs. D power law for lunar cratering is well-obeyed in both the lunar frontside highlands and heavily cratered uplands (i.e., the oldest lunar surfaces) through histogram bins in D up to D=$512\sqrt{2}$ km =724 km (BVSP 1981, Figures 23 & 26, Sec. 8.11). D=724 km in Eq.(4.2) corresponds to $m_p = 1.5 \times 10^{18}$ kg, which we take for m_2 in Eqs.(4.4). It is true that larger basins appear to be present on the Moon (see, e.g., Wilhelms 1984, Table 6.4), but the existence of the largest of these is problematic. (See Chapter 5, however, for a review of the most recent evidence for the existence of the South Pole–Aitken basin.) Therefore our calculation of M(T) in Eqs.(4.4) is a conservative underestimate. Note that $M(\mathrm{T}) \sim D^2$, so the effect of a different choice for the largest basin included in Eqs.(4.4) is easily deduced.

To calculate the total mass incident on Earth since T=4.5 Gyr ago, we must multiply M(T) by the lunar surface area and scale to the larger gravitational cross section of Earth. (We choose 4.5 Gyr because the possible Moon-forming impact of a Mars-sized object with Earth is typically dated (Melosh 1989) at ~4.5 Gyr; volatiles previously accreted by the outer layers of Earth would probably be lost in this event. The oldest lunar rocks have ages consistent with crystallization 4.5–4.6 Gyr ago (Swindle *et al.* 1986).) A body's gravitational cross section $\sigma = \pi r^2[1 + v_{esc}^2/v_\infty^2]$ where r is the body's physical radius, v_{esc} is its escape velocity, and v_∞ is the relative velocity at infinity of the approaching impactor. As discussed below, we take 17 km s^{-1} as a typical asteroidal impact velocity with Earth, corresponding to $v_\infty \approx$13 km s^{-1} $\approx v_p$. v_∞=13 km s^{-1} gives σ for Earth ~23 times bigger than that of the Moon. However, ~4.5 Gyr ago, the Moon was much closer to Earth than now. In this case, gravitational focussing by Earth leads to both an increased lunar gravitational cross section (v_{esc}^2 is replaced with the sum of the squares of the lunar escape velocity and the escape velocity of Earth at the Moon's orbital radius, thereby decreasing ξ, the terrestrial/lunar gravitational cross section ratio), and a larger average lunar impact velocity (v_p in Eq.(2)). Dynamical calculations of the evolution of the lunar inclination may exclude accretion of the Moon in Earth's equatorial plane within about 10 $R_\oplus$ (Earth radii) (Boss and Peale 1986). At 10 $R_\oplus$, the effects of terrestrial gravitational focussing on both ξ and v_p are <10%, negligible compared to other uncertainties in the problem. If the Moon did in fact form near the terrestrial Roche limit, ~3 $R_\oplus$, its orbital evolution out to ~10 $R_\oplus$ was almost certainly so rapid ($<10^{-5}$ of the time required to evolve from 10 to 60 $R_\oplus$, in a model with constant Q; see, e.g., Chyba *et al.* 1989, Eq.(8)) that we may take $T \approx 4.5$ Gyr as that time when the Moon was at 10 $R_\oplus$, recognizing that the resulting $M(T)$ is once again a lower limit.

We thus find that the total mass incident on Earth since 4.5 Gyr ago is $M_{tot} = 9.9 \times 10^{20}$kg, 3.2×10^{21}kg, or 6.9×10^{23}kg, respectively, according to which of Eqs.(4.4a)-(4.4c) is used. This range is similar to the lower limit (7.6×10^{20}–2.3×10^{23}kg) found by summing the masses implied by all extant lunar craters and basins (Chyba 1987). In comparison, Earth's mass $M_\oplus = 5.98 \times 10^{24}$kg, and the terrestrial oceanic mass $M_{oceans} = 1.4 \times 10^{21}$ kg H_2O.

These results may also be compared with a recent determination by Sleep *et al.* (1989). These authors use iridium and nickel abundances found in lunar highland rocks, together with estimates of the mixing depth of the meteoritic component of the lunar crust, to calculate a lower limit to the total amount of material impacting the Moon since the solidification of the lunar crust ~4.4 Gyr ago. They conclude that the Moon has accreted an equivalent meteoritic thickness 0.7 km, with an estimated uncertainty of a factor of two. Scaling to Earth with the parameters used in this paper, and multiplying by a factor ~exp[(4.5-4.4) Gyr/100 Myr], gives $M_{tot} = 4.8 \times 10^{21}$ kg as a lower limit for the total mass incident on Earth subsequent to 4.5 Gyr ago. Therefore the value $M_{tot} = 1.0 \times 10^{21}$ kg, derived via a $\tau_a = 220$ Myr fit to the lunar cratering record, is evidently an underestimate of the total impacting flux. This conclusion is even stronger when one takes into account impact models which suggest the Moon should have lost much material in the ejecta (O'Keefe and Ahrens 1982) and vapor plumes (Melosh and Vickery 1989) resulting from high-velocity impacts. While some of this material would have been trapped in Earth orbit and reaccreted by the Moon, much may have been lost from the Earth–Moon system altogether, since even as close as 10 $R_\oplus$, Earth escape velocity is only 3.5 km s^{-1}, comparable to that of the Moon (2.4 km s^{-1}).

4.4 Frustration of the Origins of Life

Certain conclusions of recent work on the impact frustration of the origin of life may be called into question by the uncertainties in the lunar (and hence, terrestrial) early impact environments described above. Maher and Stevenson (1988) have compared proposed timescales (10^5–10^7 yr) for the origin of life to timescales for globally sterilizing impacts, and argued that life could not have originated prior to 4.2 Gyr ago. Oberbeck and Fogleman (1989a) corrected an error in the calculation, and found that life could have first originated between 3.7 and 4.0 Gyr ago. However, both these investigations rely on the cratering time constant τ_c= 70 Myr. Figure 4.1 cautions that their conclusions may depend strongly upon this choice for τ.

$^{13}C/^{12}C$ isotope ratios in 3.8 Gyr Isua metasediments have been interpreted as evidence for biologically-mediated carbon isotope fractionation, suggesting that life originated prior to 3.8 Gyr ago (Schidlowski 1988). It is clear from Figure 4.1 that, subsequent to ~3.9 Gyr ago, all three fits to the lunar cratering record provide approximately equal fluxes, and hence must give about the same results for impact frustration (V. Oberbeck, 1989, personal communication). However, prior to this time, conclusions drawn from the different models dramatically diverge. For example, at 4 Gyr, Eq.(4.1c) gives a cumulative cratering flux, N_c, which is ~5 times greater than that given by Eq.(4.1a), N_a. Timescales for devastating impacts will be proportional not to cumulative fluxes, but to differential fluxes. The relevant ratio is therefore $(\partial N_c/\partial T)/(\partial N_a/\partial T) \approx 5(\tau_a/\tau_c) \approx 15$. That is, the frequency of impacts at 4 Gyr for a τ_c=70 Myr model is ~15 times greater than that for a τ_a=220 Myr model. The frequency of impacts sufficient to frustrate the origin of life at 4 Gyr in the τ_c model is only achieved in the τ_a model at a time Δt prior to 4 Gyr, where Δt is given by exp(Δt/220 Myr)≈15, or Δt≈600 Myr—prior to terrestrial accretion. That is, frustration of life at 4 Gyr in the τ_c model implies there is no time in the τ_a model at which frustration occurs. These uncertainties emphasize the advantage of impact frustration models which calculate annihilation of assumed already-extant ecosystems (Sleep *et al.* 1989) or give as a result (rather than assume) a timescale for the origin of life (Oberbeck and Fogleman 1989b).

4.5 Impact Erosion of the Hydrosphere

Melosh and Vickery (1989) find that large impacts may cause atmospheric erosion when two criteria are met. The first is that the impactor must strike the planet at a velocity high enough for a vapor plume to form and expand at a speed $> v_{esc}$. Second, the mass of the plume must exceed the airmass above the plane tangent to the impact. In effect, these criteria are a momentum balance requirement (McKinnon 1989). In the following discussion, we treat an impactor which satisfies these two criteria to be entirely lost as an escaping vapor plume from the target planet. Not only will that impactor's volatiles not contribute to the target world, but atmospheric mass will be lost as well. As shown below for the case of the oceans, those volatiles present in a condensed state prior to an eroding impact will be largely immune to such erosion, providing a means of preferentially removing some planetary volatiles (e.g. noble gases, N_2, and carbon as CO_2), while leaving others relatively unaffected.

Melosh and Vickery (1989) find the threshold impact velocity v_{min} for most of a vapor plume to exceed v_{esc} to be given by $v_{min}^2 = 4(v_{esc}^2 + 2H_{vap})$, where H_{vap} is the vaporization energy, taken to be 13 MJ kg^{-1} for silicates and 3 MJ kg^{-1} for ice (1 MJ kg^{-1} = 1 km^2 s^{-2}). For the Moon, $v_{min} \approx 11$ km s^{-1} for silicate projectiles (asteroids), and $v_{min} \approx 7$ km s^{-1} for ice impactors (comets), so that virtually all vapor plumes resulting from cometary impacts (for comets of any mass, as there is no atmospheric airmass to be overcome), and most resulting from asteroidal impacts, will be lost. This no doubt helps to explain why the Moon, although battered by carbonaceous chondrites and comets throughout its history, remains so volatile-poor. For Earth, however, $v_{min} \approx 25$ km s^{-1} for asteroids, and $v_{min} \approx 23$ km s^{-1} for comets. These threshold values are analytical approximations to numerical work in preparation by Melosh and Vickery (1989, personal communication); however, the results of this paper do not depend strongly on the exact values chosen.

Short period (SP) comets have v_{rms}=28.9 km s^{-1} (Weissman 1982), which has led to the suggestion that "the idea that the Earth owes its oceans to cometary bombardment long ago may have to be abandoned" (McKinnon 1989). However, rms calculations of most probable impact velocities assign greatest weight to those objects with exceptionally high values of v_∞, skewing the velocity distribution towards high velocities. In fact, many SP comets will hit Earth with velocities below 23 km s^{-1}. We may use Weissman's (1982) compilation of SP comet velocities and collision probabilities to calculate the percentage of cometary collisions with Earth that occur at a given velocity (Figure 4.2). The statistics are poor, but Figure 4.2 visually demonstrates that a small number of high-inclination and retrograde comets pulls v_{rms} towards high values. In fact, some ~30% of cometary collisions with Earth occur at or below 20 km s^{-1}, and another ~45% occur just at ~22–23 km s^{-1} (the critical velocity for escape of the resulting vapor plume). If we take half of the latter collisions to cause atmospheric erosion, we still have the conclusion that a full ~50% of SP cometary collisions with Earth do not create vapor plumes with sufficient velocity to reach escape speed. Since models of the early cometary bombardment of the inner Solar System (Fernández and Ip 1983, Shoemaker and Wolfe 1984) indicate that the flux of comets scattered directly from the Uranus–Neptune region (i.e., following SP–like orbits) dominated by several orders of magnitude the flux of those (long period) comets first scattered out to the Oort cloud, we may take ~50% of the early cometary flux incident on Earth to have impacted with velocities low enough for their volatiles to have been retained. An analogous calculation using data for Earth–crossing asteroids (BVSP 1981, Table 8.5.1) shows that ~90% of asteroidal collisions with Earth occur at velocities below 25 km s^{-1}. Yet these data also give a comet–like asteroidal rms impact velocity ~25 km s^{-1}. Again, a small number of high-inclination objects skew the rms value. In fact, >50% of the terrestrial collisions of the Earth-crossing asteroids in this compilation will occur at velocities <17 km s^{-1}, the value chosen as "typical" in the calculations above.

To determine the total mass of water accreted by Earth due to asteroidal and cometary impacts, we must combine the calculation of M_{tot} above with an estimate of the division of M_{tot} into cometary and asteroidal fractions, with an estimate of the average H_2O content of these bodies, and with the results of impact erosion in cometary and asteroidal collisions. The fraction ψ of the total ancient impacting flux that was cometary is at present an unknown, free parameter. There are a variety of data pertaining to this question, none of which appears to be conclusive (Chyba 1987). We briefly review these here:

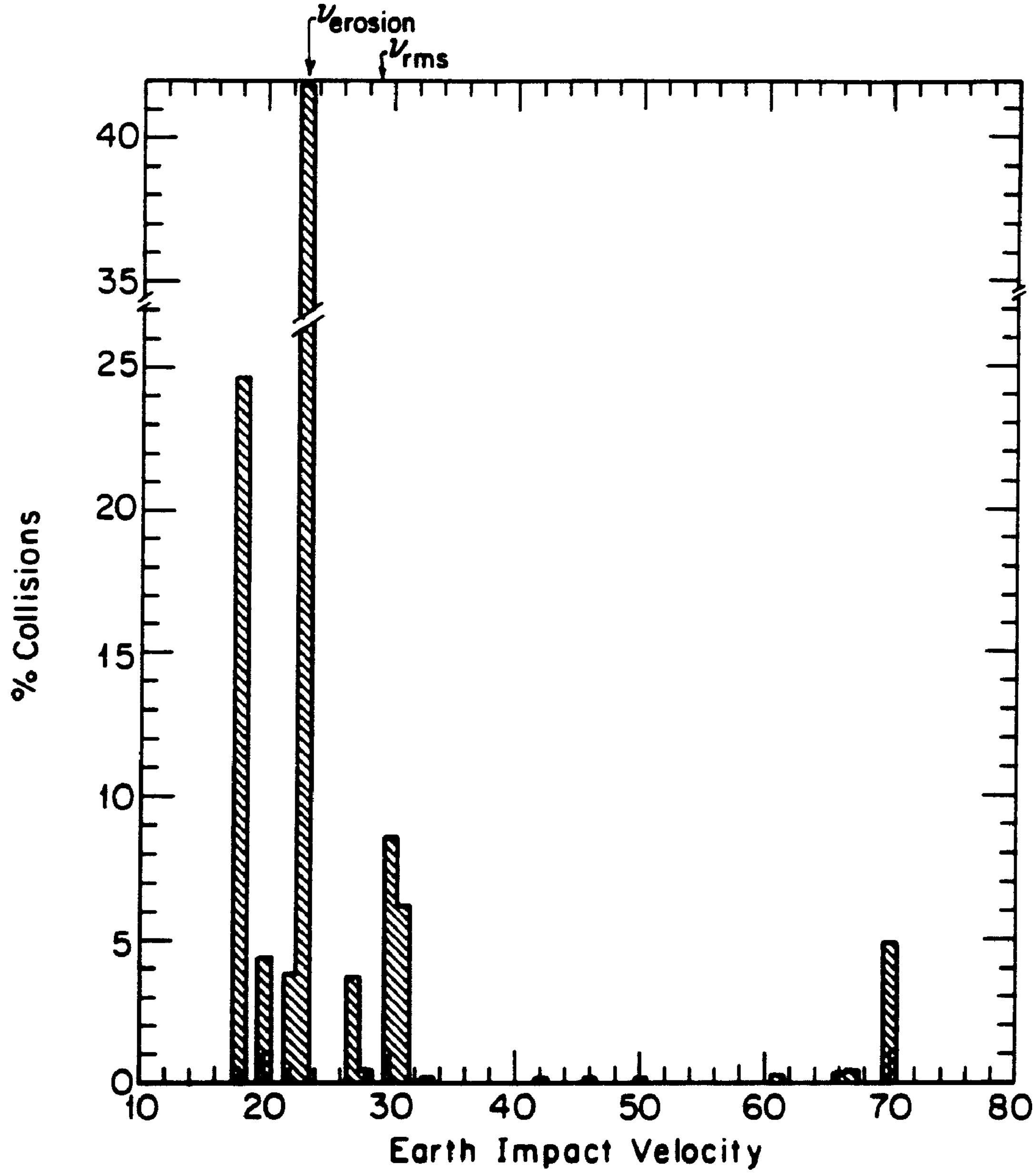

Figure 4.2 The percentage of short period comet collisions with Earth as a function of impact velocity. Data from Weissman (1982).

4.5.1 The H_2O Inventory of the Other Terrestrial Planets

Comets should have delivered water to the other terrestrial bodies as well as to Earth. Study of lunar samples is consistent with *no* measureable "lunar water", apart from terrestrial contamination (Epstein and Taylor 1971, 1972, 1973). But on the Moon, most impacting cometary or asteroidal H_2O would be lost in vapor plumes and ejecta, with the remainder susceptible to photodissociation and destruction by the solar wind. Several sources of lunar H_2O during the past 2 Gyr (including recent cometary impacts) probably each supplied $10^{13} - 10^{14}$ kg of water; its complete absence testifies to the high efficiency of these destructive mechanisms, although some water may remain in polar cold traps (Watson 1961, Arnold 1979). Mars, with a smaller cross section and a smaller v_{esc} (5.0 km s^{-1}) than Earth, would be expected to acquire and retain less impact-delivered H_2O. Many martian landforms suggest the former presence of considerable ground ice or water (Squyres 1989, Goldspiel and Squyres 1991), and there appears at present to be ice-rich terrain poleward of ±30° latitude (Squyres and Carr 1986). Finally, the deuterium-hydrogen (D/H) ratio in the Venus atmosphere suggests the former presence of much water on Venus (Donahue *et al.* 1982), though these data have also been interpreted as indicators of recent cometary impacts (Grinspoon 1987, Grinspoon and Lewis 1988), an interpretation that has in turn been disputed (De Bergh *et al.* 1991). These observations are consistent with (but do not independently require) a significant cometary source of H_2O.

4.5.2 Morphological and Compositional Characteristics of Lunar Impacts

Can we distinguish between asteroidal and cometary impact features? Certain magnetized lunar swirl patterns have been interpreted as results of recent ($\lesssim$ 100 Myr) cometary impacts (Schultz and Srnka 1980). But it has been argued that the features are in fact the antipodal effects of ancient basin-forming impact events, so that no cometary origin need be invoked (Hood 1987). In any case, the associated craters do not appear to be anomalous.

Enrichment of siderophile trace elements in some lunar highland breccias may indicate sampling of basin-forming projectile remnants (Gros *et al.* 1976, Hertogen *et al.* 1977), although interpretation remains controversial (see, e.g., Wetherill (1981) for a review). Ternary plots indicate that, whereas the siderophile composition of most of the nine putatively-identified impactors is distinct from the composition of carbonaceous chondrites (the meteoritic class most likely to resemble comets), at least one (represented by the group 5L clasts) does have CI proportions (Hertogen *et al.* 1977). The CI are the most primitive and volatile-rich (presumably, the most "comet-like") of the chondrites. All impactor remnants, however, are depleted in volatiles by factors of 2–100 relative to carbonaceous chondrites (Gros *et al.* 1976). However, this may be a poor diagnostic, as these elements might be preferentially lost at the high post-impact temperatures.

4.5.3 Isotopic Data

It has been argued (Anders and Owen 1977) that hydrogen and carbon isotopic data require an exogenous source of surface volatiles for Earth and Mars. It is suggestive that the oceanic D/H ratio (1.6×10^{-4}) and that of comet Halley (0.6–4.8×10^{-4}) are both an order of magnitude above cosmic abundance ($2.0 \pm 1.0 \times 10^{-5}$) (Eberhardt *et al.* 1987). Some authors have also interpreted findings that apparently juvenile water in certain igneous rock inclusions contains $\sim$15% less deuterium than the oceans (Kokubu *et al.* 1961) as evidence for an extraterrestrial source of surface H_2O (Anders and Owen 1977). However, this interpretation has been challenged on the grounds that the supposedly "juvenile" D/H ratio found was in good agreement with local rainfall values, and so might represent contamination (Friedman and O'Neil 1978).

4.5.4 The Cratering Record Throughout the Solar System

Estimates of current asteroidal and cometary cratering rates suggest that comets account for 10–30% of the recent production of terrestrial impact craters $\gtrsim$ 10 km in diameter (Shoemaker 1983), although the inclusion of 'extinct' comets or possible comet showers (Shoemaker and Wolfe 1986) could raise this fraction to above 50%. How to extrapolate this result back to the early Solar System is not clear, however. A recent model of outer planet formation implies a cometary flux through the inner Solar System declining with an approximate 150 Myr half-life between 4.5 and 3.8 Gyr (before levelling off to its current relatively low value), possibly delivering as much as ~100 M_{oceans} to the Earth (Fernández and Ip 1983). Any such enormous influx of water would have to be largely lost; possible mechanisms would include photodissociation or destruction by transportation to Earth's interior and subsequent destruction by reaction with metallic iron (National Research Council 1990). Other models for cometary flux and mass spectrum may be inconsistent with the delivery of so much H_2O (Wetherill 1981). The empirically-based approach taken here serves as an observational diagnostic for such theoretical models.

Crater diameter-density distributions for the terrestrial planets imply a common heliocentric impactor population for the heavy bombardment of the inner Solar System (Woronow *et al.* 1982). But the great disparities between the cratering records of the Moon and those of some outer planet satellites strongly suggests that comets were not the major component of this population (Strom 1987). Any scenario in which Earth receives many tens of oceans of water or more must explain this contradiction between the cratering record implied by such an influx and that which is in fact observed. Admittedly, as long as only the lunar cratering record can be assigned absolute ages, such an objection may remain indecisive.

In light of these constraints, it seems likely that ψ, the cometary mass fraction of the heavy bombardment, is $\lesssim$10–20%, but clearly this conclusion may be questioned. In the following discussion, we let ψ range from 10^{-3} to 1, and find that our results vary by less than an order of magnitude over this range.

Comets are ~50% H_2O ice (Delsemme 1988). It has been estimated on the basis of albedos and UBV colors of Earth–crossing asteroids, that the asteroidal flux at Earth is an equal mix of S and C–types; only types CI and CII carbonaceous chondrite meteorites on Earth match the spectra of C–type asteroids (Shoemaker *et al.* 1979). Here we take C–type asteroids to be an equal mix of these. CI and CII meteorites are ~20% and 13% H_2O by mass, respectively (Mason 1971). (The question of the H_2O content of carbonaceous chondrites will be further discussed in Chapter 6.) We take S–type asteroids to be 0% H_2O.

Finally, we must ask if impactors could erode a significant quantity of condensed H_2O from Earth's surface. Consider an impactor with velocity and mass sufficient to cause atmospheric erosion. For a 1 bar terrestrial atmosphere, such an impactor has a minimum mass $m_* = 3.5 \times 10^{15}$ kg, or a diameter $2r_p \approx 14$ km (Melosh and Vickery 1989, Eq.(2)). The primordial terrestrial ocean would have accumulated over time to its current surface–averaged depth $d_{oc} \approx 3$ km; the following calculation maximizes impact erosion of this ocean by assigning it d_{oc} beginning 4.5 Gyr ago. An eroding impactor of diameter $2r_p$ or greater deposits nearly all its impact energy at a depth $\sim 2r_p$; i.e. it penetrates a 3 km ocean and continues many km into the seabed (Melosh 1989). The ocean water in the cylinder underlying the impactor is rammed into the seabed and severely shocked; this cylinder will enter the escaping vapor plume. For hypervelocity impact, the shock pressure in the ocean around this cylinder falls off as $\sim r^{-3}$ (Melosh 1989), so that little additional water is sufficiently shocked to contribute to the escaping vapor plume (H.J. Melosh, 1989, personal communication)— of course, much more H_2O is vaporized, but not lost from the planet.

Thus, the mass of ocean water eroded by an impactor of mass m, diameter $2r_p$ is given by

$$M(m) = \pi r_p^2 d_{oc}\rho_{oc} = \pi(3/4\pi\rho_p)^{2/3} m^{2/3} d_{oc}\rho_{oc}, \tag{4.5}$$

where ρ_{oc} and ρ_p are the densities of the ocean and impactor, respectively. The total mass $M_{lost}(\mathrm{T})$ of condensed ocean eroded by impactors of mass $> m_*$ is then

$$M_{lost}(\mathrm{T}) = \int_{m_2}^{m_*} M(m)[\partial n(> m, \mathrm{T})/\partial m]dm. \tag{4.6}$$

Performing this integration, and taking into account that only ~10% of asteroids and ~50% of comets have v_{min} large enough to cause erosion, we find that $\lesssim$ 5% and $\lesssim$ 15% of the H_2O delivered by asteroids and comets, respectively, is subsequently eroded by incorporation of condensed water into vapor plumes.

The fractional volume of atmosphere removed by an eroding impact is $\sim 3\times10^{-4}$. With $\sim10^{-5}$ M_{oceans} residing in the present atmosphere (Walker 1977), a calculation analogous to that above shows that loss by erosion of vapor-phase H_2O is negligible. This result holds even in hypothesized 10 bar CO_2 early atmospheres, with ~ 0.5 bar H_2O in the vapor phase (Durham and Chamberlain 1989). Finally, certain earlier models (Walker 1986) of impact erosion suggested that erosion could not occur for worlds with $v_{esc} \gtrsim$ 10 km s^{-1}; in this case Earth would have retained all incident volatiles.

4.6 Volatile Inventories in the Inner Solar System

Combining all of these considerations, the total amount of water accreted by Earth due to impacts over the past 4.5 Gyr is given by

$$M_{H_2O} = [(1-\psi)(0.95)(0.9)(0.5)(0.17) + \psi(0.85)(0.5)(0.5)]M_{tot}, \tag{4.7}$$

where the first term is the asteroidal contribution (5% of condensed oceans eroded, 90% of impactors accreted, 50% type C, which are ~17% H_2O by mass), and the second is cometary (15% of oceans eroded, 50% accretion, 50% H_2O by mass). Note M_{H_2O} scales erosion appropriately for the case $d_{oc} > 3$ km (as for Eq.(4.4c)). M_{H_2O} is plotted as a function of ψ in Figure 4.3, for M_{tot} calculated from both Eqs.(4.4) and the geochemically-based determination of Sleep *et al.* (1989). Since this latter determination represents a lower limit, it appears from Figure 4.3 that Earth accreted a net (after impact erosion) amount of water $\gtrsim$0.2–0.7 M_{oceans} during the period of heavy bombardment.

Even taking impact erosion into account, the cratering decay constant τ_c=70 Myr requires Earth to have accreted ~30–100 M_{oceans} of water subsequent to 4.5 Gyr ago. Barring creative, and ad hoc, mechanisms to bury this much water in Earth's mantle, this result suggests either that this choice of τ considerably overestimates the severity of the early terrestrial impactor flux, or that the assumptions used above regarding the H_2O content of heavy bombardment asteroids are incorrect. For example, if S–types were in fact responsible for 90% of terrestrial collisions, and if the cometary contribution were negligible, net H_2O accretion would be reduced by a factor ~25, so that τ_c=70 Myr would deliver only ~1.2 M_{oceans}. It could also be that early in Solar System history, the impacting flux was dominated by water-poor objects in Earth-like orbits. However, the flux of such short half-life objects would have been superimposed over the flux of longer-lived objects represented by Eqs.(4.1) (see, e.g., Grinspoon 1988, pp. 73–85).

If ψ were as large as ~20%, the water accreted by Earth would be dominated by comets. Is such a result consistent with the terrestrial inventory of other volatile elements, especially carbon and nitrogen? The elemental abundance ratios found for comet Halley (Delsemme 1988) suggest that Earth, were its carbon primarily cometary in origin, should have ~5 times as much nitrogen than is in fact the case (Walker 1977). However, both the preferential impact erosion of N_2, and the likelihood that comets supplied only a fraction of the terrestrial volatile

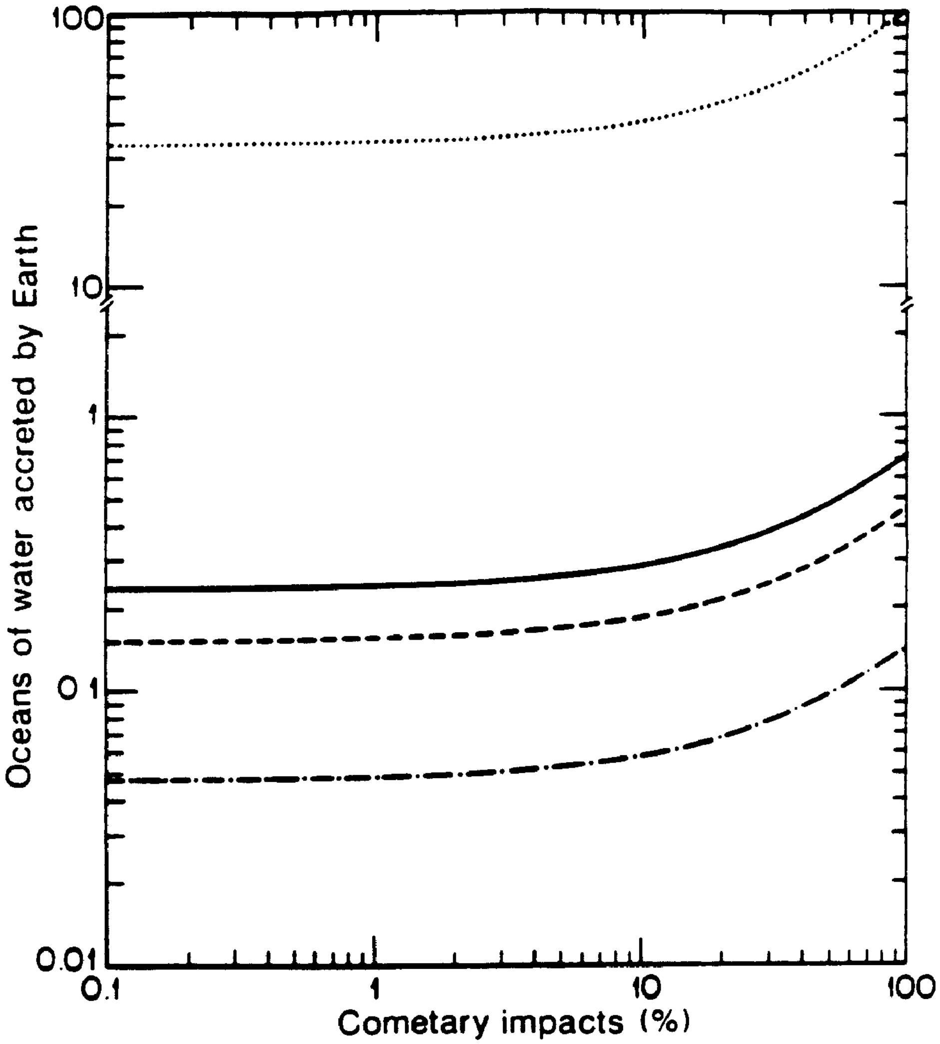

Figure 4.3 Oceans of water accreted by Earth (in units of $M_{oceans} = 1.4 \times 10^{21}$ kg), as a function of the cometary percentage of impactor mass. Dot-dashed curve from Eq.(4.4a), dashed from Eq.(4.4b), dotted from Eq.(4.4c), and the solid curve is derived from Sleep *et al.* (1989). These results assume C-type asteroids are ~17% H_2O by mass (Mason 1971); see Chapter 6 for a further discussion of the H_2O content of carbonaceous chondrites.

inventory, defuse this dilemma. These questions will be addressed in much greater detail in Chapter 6.

Finally, these calculations have implications for the volatile inventories of the other terrestrial planets. For reasons noted above (Chyba 1987), the Moon probably did not retain more than an insignificant fraction of the volatiles incident upon it. Delivery of volatiles to Venus and Mars depend on these bodies' impact rates relative to the Moon, but the analysis presented above suggests that Venus should have accreted approximately as much water as Earth. Mars, more subject to impact erosion (Melosh and Vickery 1989) should have accreted an ocean equivalent to a layer of water ~10–100 meters deep uniformly distributed over the planet. This result is in rough agreement with other estimates (McKay and Stoker 1989), based on different methods, of the martian water inventory.

Chapter 5

Cometary Delivery of Organic Molecules to the Early Earth[1]

'Some theories, he [Stanley Miller] asserts, do not merit serious attention. He calls the organic-matter-from-space concept "a loser," the vent hypothesis "garbage" and the pyrite theory "paper chemistry." Such work, he grumbles, perpetuates the reputation of the origin-of-life field as being on the fringe of science and not worthy of serious pursuit.' (Horgan 1991)

5.1 Sources of Prebiotic Organics on Early Earth

A significant fraction of the Earth's volatile inventory may have been acquired as a late-accreting veneer from impacts of C-type asteroids (Anders and Owen 1977) and comets (Chyba 1987, 1990) during the period of heavy bombardment of the inner solar system 4.5 to 3.8 Gyr ago (see also Chapters 4 and 6). In addition to

---

[1] This chapter is based on the paper: Chyba, C.F., P.J. Thomas, L. Brookshaw, and C. Sagan (27 July 1990), Cometary delivery of organic molecules to the early Earth, *Science* **249**, 366–373 [copyright 1990 by the AAAS].

simple volatile molecules such as H_2O and short-chain hydrocarbons, C-type asteroids and comets are also rich in complex organics. In the case of asteroids, this is known from direct analysis of carbonaceous chondrite meteorites (Wilkening 1978, Cronin *et al.* 1988) plus the observation that these meteorites are spectroscopically similar to C-type asteroids (Shoemaker *et al.* 1979), believed to represent their parent bodies (Chapman 1974). As long ago as 1908, this organic component in carbonaceous meteorites led Chamberlin and Chamberlin (1908) to suggest that infalling "planetesimals" may have been an important source of prebiotic organic material on early Earth. In 1961, Oró (1961) suggested, on the basis of spectroscopic observations of carbon and nitrogen-containing radicals in cometary comae, that comets may have played a similar role. Since then, the possible relevance of cometary organics to the terrestrial origins of life has received considerable attention (Chang 1977, Ponnamperuma 1980, Greenberg 1989, Thomas *et al.* 1989, Delsemme 1991)

Over the last decade, this potential cometary source of prebiotic organics has taken on new importance, as an emerging consensus in planetary science has replaced previous models of a primordial reducing (CH_4/NH_3-rich) terrestrial atmosphere with that of a neutral (CO_2/N_2-rich) one. Such early CO_2-rich atmospheres are implied by "hot" accretion scenarios for the Earth, in which core formation takes place quickly, leaving the upper mantle (and hence, outgassed carbon) in an oxidized state (Walker 1977, Chang *et al.* 1983, Stevenson 1983). The short photodissociation lifetimes of CH_4 and NH_3 in model paleoatmospheres reinforces this conclusion (Kuhn and Atreya 1979, Levine and Augustsson 1985). If subduction-resistant continental platforms were largely or entirely absent on Earth prior to 3.8 Gyr ago, the ~60 bars of CO_2 currently sequestered in continental platforms would have led to a dense, 10 to 20 bar CO_2 early terrestrial atmosphere (Walker 1986), a conclusion that is consistent with solutions to the early faint sun "paradox", and arguments based on comparative inner solar system planetology (Kasting *et al.* 1988, Kasting and Toon 1989, Durham and Chamberlain 1989). Early Earth atmospheres with CO_2 pressures as high as 100 bars appear to be stable against a runaway greenhouse effect, and are therefore consistent with oceans of liquid water (Kasting and Ackerman 1986, Kasting 1989).

Syntheses of key prebiotic molecules (such as HCN and H_2CO, precursors to purines, pyrimidines and amino acids, and to sugars, respectively) in CO_2 atmospheres would have been much more difficult than in reducing ones (Abelson 1966, Chang 1983). Experiments with CO_2 gas mixtures demonstrate that, relative to CH_4 or CO–rich atmospheres, yields of HCN and H_2CO, as well as amino acids themselves, drop precipitously by many orders of magnitude as the ratio H_2/CO_2 falls below unity (Schlesinger and Miller 1983a,b). However, while these results are suggestive, there is certainly at present no requirement to invoke impactor–delivered organics to account for the evolution of life on Earth. Many other speculative mechanisms for terrestrial prebiotic synthesis have been proposed, including production of HCN via photolysis of N_2 and CH_4 in a hypothesized weakly–reducing atmosphere (Zahnle 1986), reduction of CO_2 to CO by impactor–delivered iron (Kasting 1990), volcanic production of H_2 via H_2O decomposition, or reduction of CO_2 in solution or in the presence of clays (see Chang *et al.* 1983 for a review). The goal of investigators at present must be to quantify as best as possible prebiotic organic production from the various proposed sources, so that their comparative importance may be weighed. Our purpose here is to extend this compilation to the case of cometary delivery of organics.

5.2 Pyrolysis of Cometary Organics by Impact

A long-standing objection to cometary delivery of intact organic molecules to Earth is that these compounds would be totally dissociated by the heat of cometary atmospheric passage and the ensuing impact. This has led Clark (1988, p. 209) to suggest "an improbable, fortuitous soft-landing of a cometary nucleus" as a mechanism for the origin of life. While such unlikely events cannot be entirely ruled out, they are also extremely difficult to quantify. However, a closer examination of the claim that cometary organics will be pyrolyzed at impact reveals that this conclusion is uncertain. Consider a comet colliding with Earth at a velocity 18 km s^{-1}. (Some ~25% of short-period (SP) comet/Earth collisions should occur at or below this velocity (Chyba 1990a).) If we assume that upon impact all of the comet's kinetic energy goes into heating the comet, treat the comet as composed of water ice, and choose a specific heat of water appropriate to the resulting high temperatures and pressures (~4 kJ kg^{-1} K^{-1} (Shurshalov 1967)), we find the comet to be shocked to an average temperature ~40,000 K. This temperature is certainly too high for any organics to survive. However, it is only a factor 20 to 40 too high. Since most of the kinetic energy of a 1 g cm^{-3} comet will be partitioned not into heating the impactor, but into kinetic energy of ejecta and target heating (O'Keefe and Ahrens 1982), it is possible that aerobraking and uneven distribution of shock energy throughout the impacting projectile will conspire to yield some region of the comet for which temperatures remain low enough for at least the hardier organics to survive. This possibility can only be quantified via detailed numerical modeling of cometary atmospheric passage and surface collision. But before pursuing such models, we must first review what is known about the abundance and volatility of cometary organics.

5.3 Cometary Organics: Results from the Halley Apparition

Laboratory analysis of CI and CII carbonaceous chondrite meteorites reveal them to be 3 to 5% by mass organic heteropolymer (Wilkening 1978). *In situ* mass spectroscopy in the coma of comet Halley by the Giotto and Vega spacecraft revealed Halley dust to be fully one–third organic by mass (Krueger and Kissel 1987). The volatile (gas) fraction of the comet appears to be ~14% by mass organic (Delsemme 1988); assigning a standard gas/dust mass ratio of 1:1 gives an overall cometary organic component ~25% by mass. This may seem extraordinary, but it should be remembered that Halley has approximately cosmic abundance of carbon and nitrogen—an elemental abundance more than an order of magnitude higher than that of CI chondrites (Delsemme 1988, Jessberger *et al.* 1988, Anders and Grevesse 1989). Spectroscopic observations of Halley suggest that the production rate of H_2CO is about 2% by mass that of H_2O. (Production of H_2CO in comet Halley was observed from one of about four vents only, at ~4.5% that of H_2O by number. This corresponds to about 2% H_2CO by mass overall (Mumma and Reuter 1989, Reuter *et al.* 1989).) *In situ* ion mass spectrometry for comet Halley (Allen *et al.* 1987) and spectroscopy of comet Wilson (Larson *et al.* 1989) suggest CH_4 is present at 1–4 % H_2O by mass. We therefore take H_2CO and CH_4 to account for 4 and 5 mass % of cometary organics, respectively. Perhaps ~7% by mass is HCN (Delsemme 1988). Such estimates should be treated as rough at best. (Indeed, Boice *et al.* (1990) have reconsidered the Giotto data in light of evidence that CO, H_2CO, and CH_n^+ observed in the coma largely originate from organic rich dust particles, rather than representing volatiles released directly from the nucleus. They conclude that H_2CO, HCN, NH_3, and CH_4 are present at about 1%, 0.07%, 1%, and 0.02% H_2O by number, respectively, corresponding to roughly 1%, 0.1%, 0.6%, and 0.01% of the comet by mass. The mass of organic polymer would then be correspondingly increased. Boice *et al.* (1990)

suggest polymerized formaldehyde as a likely source.)

Approximately 3% of the organic carbon in carbonaceous chondrites is in the form of amino acids (Cronin *et al.* 1989). It is not known if comets contain comparable (or indeed any) amounts of such compounds. However, the discovery that amino acids from the Murchison meteorite are as a group highly enriched in deuterium (δD=1370%) strongly suggests that the amino acids or their precursors were formed at low temperatures in interstellar clouds (Epstein *et al.* 1987, Cronin *et al.* 1989). If amino acids formed in interstellar clouds, they should be at least as abundant in comets as in carbonaceous chondrites. However, this conclusion need not hold if only amino acid precursors are present in interstellar dust. Despite dedicated searches, free amino acids remain undetected in interstellar clouds (Snyder *et al.* 1983, and references therein), although amino acids in dust would remain undetectable.

Finally, although we cannot entirely rule out the possibility that cometary organics are biological in origin (Hoyle and Wickramasinghe 1987, 1988a,b, 1990), we believe that there is no persuasive evidence for this claim, and that much more plausible alternatives exist (Chyba and Sagan 1987a, 1988a, 1989). The problem we address here is whether abiotic cometary organics may have played a role in stocking the terrestrial prebiotic inventory. We do not concern ourselves in the following with panspermia theories (for a critical discussion of the latter, see Davies 1988).

5.4 Volatility of Cometary Organics

Most organic material in carbonaceous chondrites is in the form of high-molecular weight, "intractable" heteropolymer (Wilkening 1978, Cronin *et al.* 1988). Laboratory experiments under conditions meant to simulate radiation processing of interstellar dust and cometary ices suggests that cometary organics are similar (Sagan and Khare 1979, Greenberg 1982, Sagan *et al.* 1984, Thompson *et al.*

1987, Khare *et al.* 1989) a result supported by the success of such materials in modeling organic spectral features in a number of comets, as discussed in Chapters 2 and 3 (Chyba and Sagan 1987b, Chyba *et al.* 1989b). As a well-investigated analogue to such intractable organics, we use terrestrial kerogens, which are both compositionally similar to meteoritic carbonaceous material (Wilkening 1978), and provide reasonable spectroscopic fits to certain asteroids and outer solar system objects (Gradie and Veverka 1980, Cruikshank *et al.* 1983). The optical constants of Type II kerogens and an organic extract from the Murchison carbonaceous chondrite are also in good mutual agreement (Arakawa *et al.* 1989). Note that terrestrial kerogens are biological in origin; our use of them as structural analogues to presumably abiotic (Chyba and Sagan 1987a, 1988a) cometary organics carries no implication of a biological origin for the latter.

Kinetic parameters from pyrolysis experiments with Types I and II kerogens indicate that such material can survive temperatures ~850 K for one second. We calculate 1 second survival temperatures from the Arrhenius equation in the form $T=(E_a/R)[\ln(\tau A)]^{-1}$, where temperature T is in Kelvins, R is the gas constant, τ is the duration of shock heating (taken to be 1 second), and A (in s^{-1}) and E_a are the pre-exponential and activation energy kinetic parameters. For type I kerogen, $A=1.7\times10^{14}$ s^{-1} and $E_a=55.19$ kcal mol^{-1}; for type II, $A=6.7\times10^{12}$ s^{-1} and $E_a=48.82$ kcal mol^{-1} (Burnham *et al.* 1987). As will be described in Sec. 5.7, in the impacts of relevance to this discussion one second is an overestimate for the duration of the most intense shock heating cometary organics will endure. Well before this time, shock temperatures will have peaked and begun quickly to decline.

However, about 50% of the resulting kerogen pyrolysate is composed of *n*-alkanes up to C_{30}, as well as such aromatics as benzene, toluene, and *m*, *p*-xylene (Arnosti and Müller 1987). Therefore, to understand the ultimate fate of kerogen-like organics in the impactor, we must examine the fate of their components, e.g.

short–chain hydrocarbons and simple aromatics (and their O– and N– analogues and substitutions). Kinetic parameters derived from shock–tube pyrolysis of such compounds (e.g., ethane or benzene) at temperatures ~1000 to 3000 K, the best laboratory analogue we have to organic destruction in large impacts, show that these basic organic units will survive ~1200 K for 1 second. (For benzene, $A=5\times10^{16}$ s^{-1} and $E_a=88.2$ kcal mol^{-1} (Khandelwal and Skinner 1981). For ethane, $A=3.2\times10^{16}$ s^{-1} and $E_a=88.0$ kcal mol^{-1} (Tsang 1978).)

These temperatures are probably severe underestimates of the thermal stability of at least the hardiest of cometary organics. Thermogravimetric analyses of the involatile organic residue produced by electron, spark, or UV irradiation of cosmically abundant gases show that the residues are typically 50% stable at temperatures ranging from 600 to 1200 K; timescales for such analyses are far in excess of 1 second (Sagan and Khare 1979, Sagan *et al.* 1984). Similar material produced in analogous ice irradiation experiments provides a good match to observed cometary organic emission features (Chyba and Sagan 1987b, Chyba *et al.* 1989b). Therefore, we expect there is some (probably polycyclic) component of cometary organics which is much more thermally stable than the compounds being explicitly considered here.

Kinetic parameters from shock–tube experiments with CH_4 show it to survive temperatures ~1500 K for 1 second. (Shock experiments with CH_4 yield $A=1.3\times10^{15}$ s^{-1} and $E_a=104$ kcal mol^{-1} (Khandelwal and Skinner 1981).) Numerous shock–tube experiments with H_2CO (H_2CO experimental results have been compiled by Warnatz 1984) and HCN (HCN shock–tube experiments are summarized in Szekely *et al.* 1984) have been performed; we estimate from these results that these compounds will withstand shock temperatures ~1200 and ~1800 K, respectively. (We know of no shock–tube pyrolysis experiments for HCN or H_2CO conducted at sufficiently high pressures to yield first–order rate constants. Shock tube pyrolysis of these compounds at low (~1 bar) pressures have provided second-order rate constants (Warnatz 1984, Szekely *et al.* 1984), giving decomposition half-lives dependent on the concentration of background gas (usually Ar), which cannot be reliably extrapolated to cometary impacts. We take activation energies for HCN and H_2CO decomposition from those shock pyrolysis experiments with temperatures most appropriate for the impacts considered here: E_a=76.5 kcal mol^{-1} for $H_2CO+Ar \rightarrow H+HCO+Ar$ with 1000 K < T < 3000 K (Warnatz 1984), and E_a=117 kcal mol^{-1} for $HCN+Ar \rightarrow H+CN+Ar$ with 2200 < T < 2700 (Roth and Just 1976). First-order kinetic parameters for breaking C–H bonds in simple hydrocarbons give A in the range 2.0×10^{13} to 1.0×10^{15} s^{-1}, with typical values $\sim 10^{14}$ s^{-1}. We therefore adopt $A=10^{14}$ s^{-1} for HCN and H_2CO. Altering this choice by a factor ~10 results in a change in the 1 second survival temperature by only about 7%. We consider the choice of these parameters for HCN to be conservative, in the sense that they may underestimate HCN survival in impacts. HCN spectra consistent with temperatures as high as 2800 K have been observed in carbon stars; see, e.g., Gobel *et al.* 1980.)

To our knowledge, kinetic parameters for the pyrolysis of amino acids have been measured only in solution. The results of such experiments are of questionable applicability to shock pyrolysis, but until gas phase results become available, we approximate impact survival of amino acids using these results. Alanine should withstand temperatures ~700 K for 1 second. (Thermal degradation of alanine in dilute solution yields the first-order parameters $A=2.2 \times 10^{11}$ s^{-1} and E_a=44 kcal mol^{-1} (Abelson 1959), while other amino acids fall in the range 600 to 800 K. (This temperature range has as its end members the amino acids threonine, with $A=2 \times 10^{12}$ s^{-1} and E_a=33.8 kcal mol^{-1}, and phenylalanine, with $A=1.7 \times 10^{8}$ s^{-1} and E_a=30.8 kcal mol^{-1} (Vallentyne 1964). The major primary decomposition step for α-amino acids is decarboxylation (Ratcliff *et al.* 1974); a vapor phase study of decarboxylation in 3-butenoic acid gives $A=2.2 \times 10^{11}$ s^{-1} and E_a=40.6 kcal mol^{-1}, or survival for 1 second at 780 K (Smith and Blau 1964, Benson and O'Neal 1970).)

5.5 Impact Environment of Early Earth

The existence of complex terrestrial microorganisms by 3.5 Gyr ago, and evidence for biologically-mediated carbon isotope fractionation in 3.8 Gyr Isua metasediments (Moorbath 1983, Schidlowski 1988), suggest choosing the period prior to 3.8 Gyr ago to assess cometary delivery of organics. As described in Chapter 4, attempts to estimate the impact environment of early Earth typically begin with an analytical fit to the lunar cratering record. The impactor flux thus derived can then be scaled to Earth's larger gravitational cross section. Following such a procedure for several published lunar cratering data sets and choices of time constant for the decay of the early impactor flux, we found three possible values, spanning the current uncertainties:

$$M(\mathrm{t}) = 0.76[\mathrm{t} + 4.6 \times 10^{-7}(e^{\mathrm{t}/\tau_a} - 1)](m_2^{1-b} - m_1^{1-b})\ \mathrm{kg^b\ km^{-2}} \tag{5.1a}$$

$$M(\mathrm{t}) = 0.99[\mathrm{t} + 2.3 \times 10^{-11}(e^{\mathrm{t}/\tau_b} - 1)](m_2^{1-b} - m_1^{1-b})\ \mathrm{kg^b\ km^{-2}} \tag{5.1b}$$

$$M(\mathrm{t}) = 0.40[\mathrm{t} + 5.6 \times 10^{-23}(e^{\mathrm{t}/\tau_c} - 1)](m_2^{1-b} - m_2^{1-b})\ \mathrm{kg^b\ km^{-2}} \tag{5.1c}$$

for the total mass, M(t), that has been incident in impactors with masses in the range m_1 to m_2 on a lunar surface of age t. Here $b \approx 0.47$, t is in Gyr, and τ_a=220, τ_b=144, and τ_c=70 Myr. Performing the appropriate gravitational scaling, Eqs.(5.1) yield a total cometary mass incident on Earth since 4.5 Gyr ago of M_{tot}= 1×10^{21}, 3×10^{21}, or 7×10^{23} ψ kg, respectively, where ψ is the fraction of the ancient impacting mass flux that was cometary (see Chapter 4). Nearly all of this mass was collected prior to 3.8 Gyr ago, i.e. during the period of heavy bombardment, which is also the time of interest for the origins of life.

As discussed in Chapter 4, the parameter ψ is not well constrained. Estimates of current asteroidal and cometary cratering rates suggest that comets account for 10–30% of the recent production of terrestrial impact craters >10 km in diameter, although "extinct" comets or possible comet showers could raise this fraction to over 50% (Shoemaker 1983, Shoemaker and Wolfe 1986). How to extrapolate this result back to the early solar system is not clear, however. None of the data pertaining to this question is conclusive (Chyba 1987, 1990). For definiteness, we set ψ=0.1 in the following. Our results scale linearly, so the effect of a different choice of ψ will be evident.

Comets are ~18% carbon by mass (Delsemme 1988), so Eqs.(5.1) imply Earth has collected 2×10^{19}, 6×10^{19}, or 1×10^{22} $(\psi/0.1)$ kg of cometary carbon, respectively, which may be compared to the total terrestrial surface (ocean, atmosphere, and sedimentary column) carbon inventory $\sim 9\times10^{19}$ kg (Walker 1977, Hayes *et al.* 1983). Clearly, there is a discrepancy between the terrestrial carbon inventory predicted by Eq.(5.1c), and that actually present on Earth. A similar discrepancy exists for H_2O (Chyba 1990a). Impact erosion by sufficiently large and fast-moving comets and asteroids could reduce this discrepancy for carbon (which may have been eroded as atmospheric CO_2), but appears incapable of doing so for condensed volatiles such as H_2O (Chyba 1990a). It therefore appears that the volatile flux predicted above by Eq.(5.1c) for ψ=0.1 is a factor ~100 too large.

Conversely, the mass flux predicted by Eqs.(5.1a) and (5.1b) is probably too small. Sleep *et al.* (1989) have used lunar highland iridium and nickel abundances, to calculate the total amount of material impacting the Moon since the solidification of the upper lunar crust ~4.4 Gyr ago. Scaling to Earth yields a value $M_{tot} = 5\times10^{21}\ \psi$ kg as a lower limit for the total cometary mass incident on Earth subsequent to 4.5 Gyr ago (Chyba 1990a).

Taking these limits into account, and recalling comets to be about 25% organic by mass, suggests that $\sim 10^{20}$ kg of cometary organics have impacted Earth over geological time. Clearly, as many authors have noted, Earth may have acquired a vast quantity of extraterrestrial organics. The key question, however, is what fraction of these organics actually survived atmospheric passage and impact shock heating. We now turn to models of these two processes.

5.6 Atmospheric Entry and Ablation[2]

We model atmospheric entry by a finite difference numerical scheme incorporating aerobraking and ablation. In this model, both atmospheric drag and ablation rate are functions of cross-sectional area, which in turn changes due to ablation (Öpik 1958, Melosh 1989). As a conservative assumption, we treat all organic molecules in ablated material as completely pyrolyzed.

Impactor ablation is determined by the drag coefficient, C_D, the heat of ablation, ζ, and the heat transfer coefficient, C_H. These parameters are functions of impactor shape, composition, mass, and velocity. From aerodynamic theory for hypervelocity impactors in the terrestrial atmosphere, we set $C_H=0.01$ (Allen *et al.* 1963, Liu 1978, O'Keefe and Ahrens 1982), and $C_D=0.92$ (O'Keefe and Ahrens 1982). These values are consistent with typical estimates (Melosh 1989). The exact value of ζ is a function of material type and the specific process of ablation. Passey and Melosh (1980) suggest taking ζ for an iron meteorite to be the average of the heats of fusion and vaporization, 5 MJ kg^{-1}. The same procedure using the heats of fusion and vaporization of ordinary chondrites (Baldwin and Shaeffer 1971) also yields 5 MJ kg^{-1}. Given this chondritic value for ζ, we scale to cometary and carbonaceous chondritic values via observed ablation coefficients $\sigma=C_H/C_D\zeta$ for cometary, carbonaceous chondritic, and ordinary chondritic meteors, taking C_H/C_D to be the same for all three types. (Values of σ for different meteor types have been determined from luminosity observations of some 3000 small meteors of varying compositions, densities, and orbital elements (Ceplecha 1977, Bronshten 1983).) We find ζ for carbonaceous chondrites and comets to

---

[2] The finite difference code described in this section (which is based on Chyba *et al.* 1990) was written by Dr. Paul J. Thomas; Figure 5.1 is largely his work.

be 3.2 and 1.6 MJ kg^{-1}, respectively. This cometary value is within 25% of the average of the heats of vaporization and fusion of ice (Atkins 1986), an encouraging agreement between observations of cometary meteors and laboratory data. Even models with detailed self-consistent calculations of the above parameters (Baldwin and Shaeffer 1971) produce values that are nearly constant throughout atmospheric passage.

As initial conditions for atmospheric entry, we need typical cometary impact velocities with Earth. Statistics for SP comet velocities and impact probabilities may be used to calculate the percentage of cometary collisions with Earth that occur at a given velocity (Chyba 1990a). As seen in Figure 4.3, some 25% of SP cometary collisions with Earth occur at or below 18 km s^{-1}, and another 50% occur between 18 and 23 km s^{-1}. Since models of the early cometary bombardment of the inner solar system (Fernández and Ip 1983, Shoemaker and Wolfe 1984) indicate that the flux of comets scattered directly from the Uranus–Neptune region (that is, following SP-like orbits) dominated by several orders of magnitude the flux of those (long period) comets first scattered out to the Oort cloud, we may use SP velocities as typical for cometary collisions with Earth during the heavy bombardment.

Calculations using our atmospheric entry model show that, for a cometary impactor (density $\delta = 1$ g cm^{-3}, initial velocity 23 km s^{-1}, and ζ=1.6 MJ kg^{-1}), even impactors of initial radius $r_0 \approx 100$ m have their speeds reduced $\lesssim 10\%$ by aerobraking, assuming an atmospheric density similar to that of the present-day Earth ($P_0 = 1$ bar). Impactors with $\delta = 2.5$ g cm^{-3}, an initial velocity of 18 km s^{-1}, and ζ=3.2 MJ kg^{-1} (parameters appropriate for chondritic asteroids (Shoemaker *et al.* 1979, Chyba 1990a)) are aerobraked less than cometary impactors of the same size, due to their greater density. Large objects, with $r_0 \gtrsim 1$ km, impact Earth's surface with their speeds essentially unchanged.

However, aerobraking in a primordial dense CO_2 terrestrial atmosphere may have been much more effective than in the present one. For a primordial atmosphere with P_0 = 10 bar CO_2 (Walker 1986, Durham and Chamberlain 1989), with consequent (Kasting and Ackerman 1986, Kasting 1989) greenhouse–enhanced surface temperature and H_2O abundance (0.6 bar), 0.8 bar N_2, and resulting scale height (7.3 km), 100 m comets striking the atmosphere at a typical incidence angle 45° with velocities 23 or 18 km s^{-1} are aerobraked to final impact speeds 5.9 km s^{-1}. (For comparison, at 0° incidence angle, an 18 km s^{-1} comet would be aerobraked under such conditions to a final velocity 8.1 km s^{-1}). Asteroidal impactors are not slowed to below ~10 km s^{-1}. Mass loss due to ablation is 65 to 83% for cometary impactors and $\lesssim$ 25% for chondrites with r_0 = 100 m. (Reducing ζ tends to reduce impact speed and increase ablation. For example, an impactor with r_0=100 m, δ=1 g cm^{-3}, initial velocity 23 km s^{-1}, and an impact angle 45° in a 10 bar CO_2 atmosphere will impact with velocities 5.9, 7.9, and 8.4 km s^{-1}, and experience 83, 56, and 40% ablation, for values of ζ appropriate to comets, carbonaceous chondrites, and ordinary chondrites, respectively.) Larger objects will be less ablated, due to their smaller area to volume ratio. In a primordial atmosphere with P_0 = 20 bar CO_2, final velocities for 100 m comets at 45° and 23 km s^{-1} are ~ 1 km s^{-1}. While the results of these self-consistent 10 and 20 bar early atmospheres will be used for all subsequent calculations, we have used a simplified model in Figure 5.1 to provide graphic intuition of cometary and chondritic aerobraking in terrestrial atmospheres ranging from 1–100 bars, for impactors of 100, 500, and 1000 m radii.

Throughout the calculations presented here, we have taken the cometary density $\delta \equiv 1.0$ g cm^{-3}. Calculations of the density of comet Halley based on non-gravitational forces suggest a large range of possible densities, 0.2–1.5 g cm^{-3} (Sagdeev 1988; see also Peale 1989). How will a different choice for δ affect the above results? In the aerobraking model used here (Öpik 1958, Melosh 1989), deceleration in the atmosphere is, to a good approximation, proportional to $\rho/\delta r$,

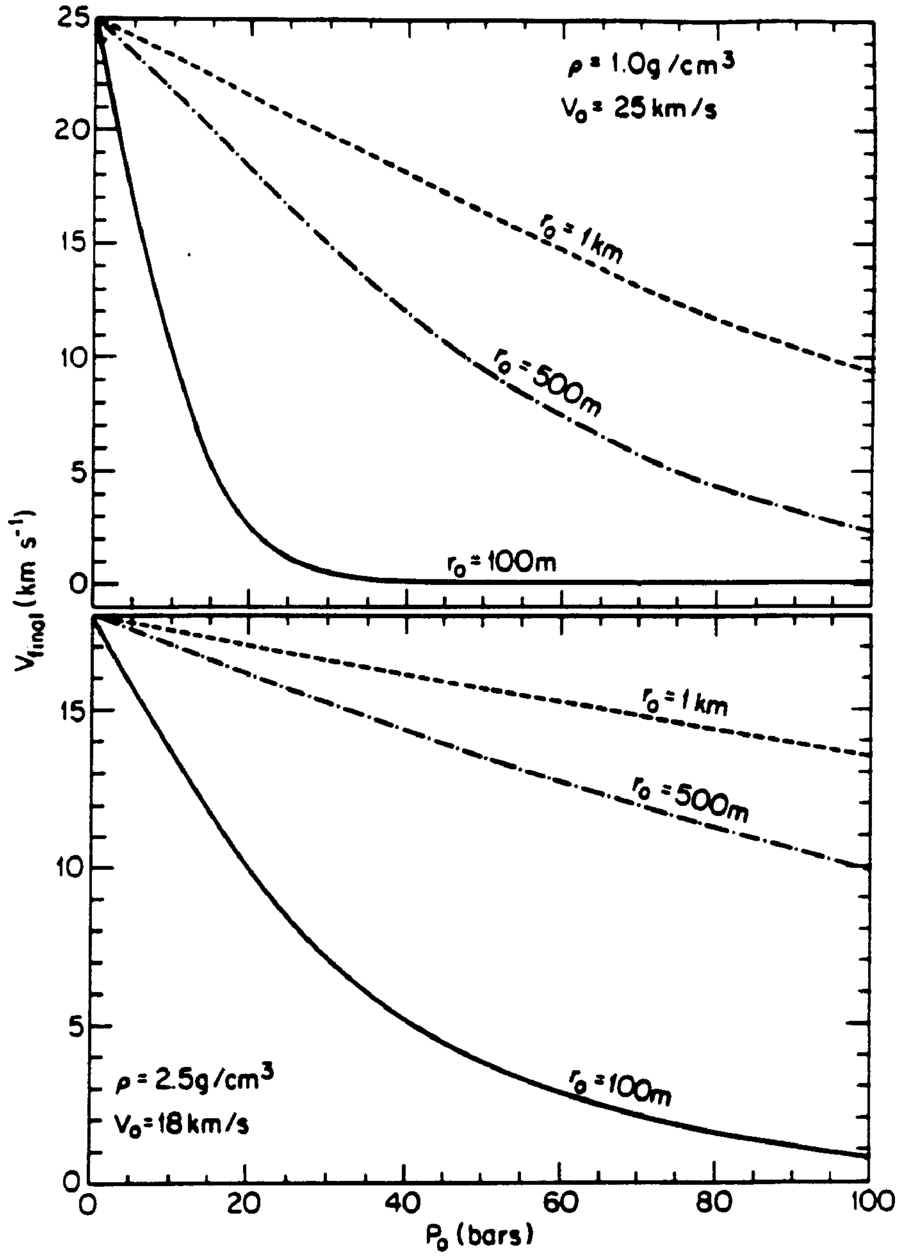

Figure 5.1 Impact velocities as a function of surface atmospheric pressure for generic cometary and chondritic impactors at 0° incidence angle with radii 100, 500 and 1000 m. In this illustrative model, the atmosphere is equivalent to the contemporary terrestrial one, with a surface pressure increased to P_0.

where ρ is the atmospheric density, and δ and r are the density and radius of the impactor, respectively. Thus, for a given r, the results found above for aerobraking a 1 g cm^{-3} comet in a 10 bar atmosphere will be approximately the same as those for a 0.5 g cm^{-3} comet in a 5 bar atmosphere. This approximation is imperfect, as ablation (which changes r) does not obey this simple inverse relationship between δ and ρ, and a 5 bar CO_2 atmosphere will not have exactly the same greenhouse temperature or proportional H_2O abundance (and hence, scale height) as required for the approximation to be exact.

Are radii of 0.1 to 1.0 km reasonable values for short period comets? Using a cometary radius–absolute magnitude (H_{10}) relation derived from comet Halley, Hughes (1987, 1988) finds that about 6, 45, and 75% of SP comets have radii $r < 0.1$, 0.5, and 1.0 km, respectively. Provided Halley's r–H_{10} relation is roughly representative, SP comets with radii of several hundred meters are not uncommon.

We have not attempted to model the effects of impactor fragmentation due to aerodynamic stresses. At present our understanding of this process is incomplete, and existing models make many simplifying assumptions (Baldwin and Shaeffer 1971, Passey and Melosh 1980). Neglecting this process renders our estimates of survivable organic material conservative, as fragmentation greatly increases the effective surface area of an impactor, enhancing aerobraking and reducing impact velocity. This effect, of importance only for impactors with radii $\lesssim$ 1 km, will be discussed further below. Catastrophic fragmentation of a comet or comet fragment appears to have occurred in Tunguska, Siberia, in 1908 (Levin and Bronshten 1986, and references therein). Fragmentation of a CI carbonaceous chondrite occurred over Revelstoke, Canada, in 1965; photomicrographs of resulting fragments up to 0.5 cm in size showed no heat damage within an exterior layer $\lesssim$ 0.7 mm thick (Folinsbee *et al.* 1967), suggesting such airbursts would indeed allow organic inclusions to survive. Fragmentation of

"Sun-grazing" and "Jupiter-grazing" comets, presumably due to tidal stresses, also suggests that some comets are loosely cohesive (tensile strengths $\lesssim 10^3$ to 10^5 dyne cm^{-2} (Sekanina 1982)), and subject to fragmentation upon entry into Earth's atmosphere.

5.7 Hydrodynamic Simulation of Cometary Impact[3]

Given appropriate post-aerobraking collision speeds with the Earth, we then calculate resulting shock temperatures throughout the impactor, via a numerical scheme called the Smoothed Particle Hydrodynamics (SPH) method (Monaghan 1985, Pongracic 1988). A hydrodynamic model is acceptable because typical shock pressures ($\sim 10^{12}$ to 10^{13} dyne cm^{-2} $\sim 10^2$ to 10^3 GPa) are much higher than material strengths of rock or ice (~Gpa). The advantage of SPH in impact simulations is that motion of material is represented by motion of mass points, avoiding problems with complex or tangled grids, boundaries, or multiple materials. SPH allows us to calculate (via equations for continuity, momentum, and energy, applied at the mass points) the density, pressure, their derivatives, and the internal energy of the material, using known statistical methods based on smoothing kernels.

SPH is based on the interpolation of a function f such that

$$\langle f(\mathbf{r}, h)\rangle = \int_V f(\mathbf{r}')W(\mathbf{r} - \mathbf{r}', h)\,\mathrm{d}\mathbf{r}', \tag{5.2}$$

where $\mathbf{r} = \mathbf{r}(x, y, z)$, W is the interpolating, or 'smoothing' kernel, h is the smoothing length and V is the solution domain. The smoothing length defines the resolution of the calculation. Any feature in f that has a length scale $\ll h$ will be smoothed out and will not appear in $\langle f\rangle$. This is an important consideration

---

[3] This section (based on Chyba *et al.* 1990) was written primarily by Dr. Leigh Brookshaw; the SPH results described here are almost entirely the work of Drs. Brookshaw and Paul J. Thomas; Figure 5.2 is largely the work of Dr. Thomas.

for impact calculations, as the width of the shock front can never be smaller than h and is normally $\sim 2h$. Derivatives of f can be estimated in a similar fashion; with the assumption $fW \rightarrow 0$ on the boundary (satisfied for most problems, since $W \rightarrow 0$ as $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$), we have

$$\left\langle \frac{\partial f}{\partial x} \right\rangle = - \int_V f \frac{\partial}{\partial x'} W(\mathbf{r} - \mathbf{r}', h)\, \mathrm{d}\mathbf{r}', \tag{5.3}$$

so that derivatives of f are replaced by derivatives of W. If f is known at the points $\mathbf{r}_i, i = 1, 2, ..., N$, the equations above can be approximated by summations. The summation equations produced from the equations of motion of the particles may then be solved numerically. As each point has a mass and a smoothed density, it may be viewed as a particle. The calculation is advanced forward in time by calculating pressure forces at each mass point, and moving the points accordingly.

The SPH formulation allows 1, 2, or 3–dimensional simulations to be done with almost equal facility. For constant resolution, however, the number of mass points increases as the power of the dimension. Due to computing constraints, the SPH simulations reported here are 2–dimensional, with a resolution of 8% of the radius of the comet.

An important problem in modeling shock transitions with particle schemes is particle interpenetration at the shock interface. Simple dimensional arguments show that particle interpenetration will occur when the relative velocity of particles is on the order of the local sound speed. To overcome this difficulty when modeling supersonic flows, an artificial viscosity is added to the momentum equation. In the continuum limit, the artificial viscosity terms reduce to standard viscous terms in the Navier-Stokes equation. The effect of these terms is to broaden the shock front while reducing post–shock oscillations. The magnitude of the viscous coefficients are reduced to the minimum consistent with ensuring that particle penetration will not exceed the resolution of the calculation. (The need to restrict the interpenetration of particles at a shock interface places a lower limit on the magnitude of the artifical viscosity. All results quoted here use this lower limit. No constraint is placed on the upper limit of the artifical viscosity. Tests done to examine the effect of increasing the artificial viscosity show that variations $\sim 10\%$ occur in the results, insignificant relative to other uncertainties in the calculation. In most problems the inclusion of an artificial viscosity gives satisfactory results. However, spurious heating occurs when materials collide supersonically. This effect (called wall heating) has been shown to be greatly reduced, and the shock fronts sharpened (Noh 1987), by the inclusion of an artificial thermal diffusion. We include an artificial thermal diffusion along the lines of Monaghan 1988.)

SPH allows us to calculate the density and internal energy of every particle at each time step. We ignore radiative heat transfer in our calculations, as it has a negligible effect on calculated temperatures ($\lesssim 0.01\%$). To calculate pressures and particle temperatures, we need an equation of state (EOS) for each material. We employ two independent methods to calculate temperature and pressure from density and internal energy, the Tillotson EOS (Tillotson 1962), and the Los Alamos Sesame II EOS data base (Los Alamos National Laboratory 1983).

The Tillotson EOS (TEOS) is based on a set of analytic equations that can be used over a wide range of pressures, densities and materials. The parameters incorporated in the analytic equations are fixed for each material by experimental data. TEOS has been widely used (O'Keefe and Ahrens 1982, Benz *et al.* 1987, 1989), although it is incapable of representing material strength (by negative pressures), and does not adequately represent two-phase media (Benz *et al.* 1987, 1989). The advantages of TEOS are its computational simplicity and its calculation of pressure as a function of density and internal energy, both in turn easily calculable in SPH. The major disadvantage of TEOS is that temperature is not explicitly determined. Fortunately, the specific heat of H_2O is known over a wide range of thermodynamic parameters (Shurshalov 1967). For our purposes, it is adequate to take the specific heat of water to be a constant (4 kJ kg^{-1} K^{-1} (Shurshalov 1967)), as we will use TEOS only as a check on results given by the Sesame II data base.

The latter is a library of some 100 materials. Pressures and thermal energies for each material are tabulated over a wide range of densities and temperatures; programs are supplied to invert and interpolate from these tables, so that pressure and temperature can be found as a function of density and thermal energy. We have used Sesame II together with our SPH code to trace the evolution of temperature throughout the bodies of comets and asteroids during impact on basalt and ocean surfaces. A wide variety of impact velocities and angles, as well as impactor sizes, has been investigated. Throughout, we have been guided by the conservative requirement that only those collisions resulting in some fraction of the impactor remaining heated to $T \lesssim 1800$ K for $\lesssim 1$ s are possible contributors to the terrestrial organic inventory. (For projectiles small enough to be sufficiently aerobraked for temperatures to remain under ~2000 K, shock temperatures peak and begin to decline in well under 1 second; in calculating organic survivability, we conservatively treat the peak temperature reached by any given particle to extend for this length of time.) For both chondrites and comets, impacting basalt surfaces at all plausible impact speeds for bodies with $r_0 > 100$ m, none of the impactor experiences $T < 1800$ K. However, comets impacting the ocean surface at velocities $\lesssim 10$ km s^{-1} do have some fraction heated to a maximum temperature below this level. (For example, comets with impact speeds of 5.9 km s^{-1}, as found above for aerobraking in a 10 bar CO_2 atmosphere, have 100, 87, and 40% of their mass exposed to temperatures < 1800, 1200, and 1000 K, respectively. Substantial quantities of HCN, CH_4, H_2CO, and even kerogen-like heteropolymers and amino acids would survive this impact intact.) This is because the greater specific heat and lower density of water results in a smaller fraction of the kinetic energy of the impactor converted into impactor thermal energy. In these calculations, neither the depth of the ocean nor the absolute size of the impactor is important, provided the ocean is at least several impactor radii deep. These results are essentially independent of impact angle for the cases calculated (up to 45° to the normal). Figure 5.2 shows the resulting maximum, mean, and minimum temperatures experienced for an ocean–impacting comet as a function of impact velocity.

5.8 Cometary Delivery of Organics to Early Earth

To determine the flux of cometary organics delivered intact to the early Earth, we must convolve the incident cometary mass flux, the cometary organic mass fraction, ablative loss during atmospheric passage, and pyrolysis of organics on impact. The relevant incident cometary mass flux is that corresponding to objects 100 to 200 m in size, since our simulations show that in a 10 bar CO_2 atmosphere, only these will be aerobraked to impact velocities low enough for organics to survive.

Eqs.(5.1) will yield the total mass incident on Earth in comets in a given size range since time t. A much more useful quantity is the mass flux (kg yr^{-1}) at a particular time in Earth's past, which both facilitates comparison with photochemical or other production rates of prebiotic organics (Bar–Nun *et al.* 1970a,b, Pinto *et al.* 1980, Chang *et al.* 1983, Fegley *et al.* 1986, Stribling and Miller 1987), and allows us to state our conclusions contingent on particular models for early terrestrial atmospheric evolution and the origin of life—e.g. "*If* the time of interest for stocking the prebiotic inventory was 4.2 Gyr ago, and *if* the atmospheric density at that time was 10 bars, *then* the flux of intact cometary organics was $\dot{m}$ kg yr^{-1}." (For example, it may be that delivery of organic molecules prior to some time t was useless to the origins of life, due to subsequent surface pyrolysis of organics by giant impacts (Sleep *et al.* 1989).) In order to present our results

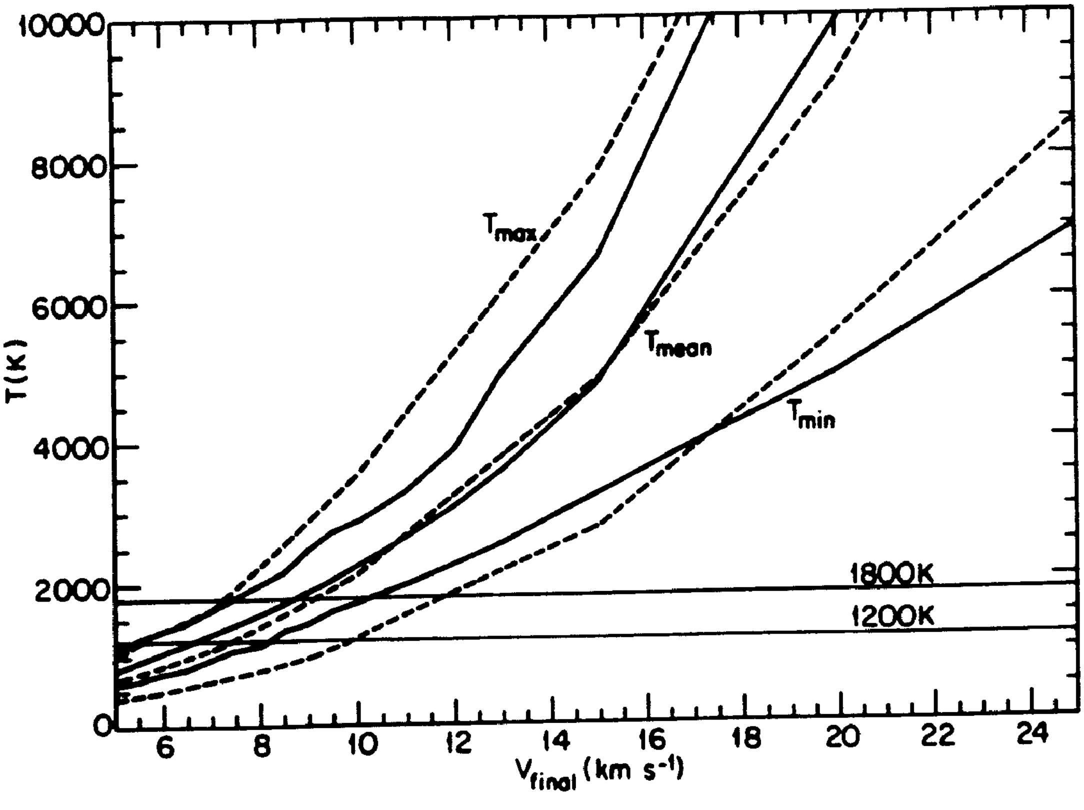

Figure 5.2 Maximum, minimum and mean temperatures for a comet impacting a 3 km ocean. The results here are independent of comet radius, provided the ocean is at least several radii deep. The dotted lines denote temperatures obtained from the Tillotson EOS with an assumed constant specific heat capacity for ice. The solid lines represent temperatures from Sesame EOS. 1800 K and 1200 K are the temperatures for which HCN and simple organics (such as short-chain aliphatics, C_6H_6, and H_2CO), respectively, survive shock heating for timescales comparable with those of impact. Note that, for impact velocities $\lesssim$ 10 km/s, some fraction of the organic inventory survives impact.

in this form, we find $\dot{m}(t) = \partial M(\mathrm{t})/\partial \mathrm{t}$, with $M(\mathrm{t})$ from Eqs.(5.1) and scale to Earth. We calculate ablation, aerobraking, and subsequent shock-heating and pyrolysis over mass bins for m_1 and m_2 corresponding to comets with radii from r_1 and r_2, taking radial bin sizes of 50 m.

Eqs.(5.4) then give $\dot{m}_{org}(t)$, the rate of organic accretion by Earth as a function of time:

$$\dot{m}_{org}(t) = 420\ (1 + 2.1 \times 10^{-6} e^{\mathrm{t}/\tau_a})\ (\psi/0.1)\ \mathrm{kg\ yr}^{-1} \tag{5.4a}$$

$$\dot{m}_{org}(t) = 540\ (1 + 1.6 \times 10^{-10} e^{\mathrm{t}/\tau_b})\ (\psi/0.1)\ \mathrm{kg\ yr}^{-1} \tag{5.4b}$$

$$\dot{m}_{org}(t) = 220\ (1 + 8.0 \times 10^{-22} e^{\mathrm{t}/\tau_c})\ (\psi/0.1)\ \mathrm{kg\ yr}^{-1}. \tag{5.4c}$$

Note these equations require a choice of ψ only for objects with radii ~100 m; since larger objects do not contribute to $\dot{m}(t)$, the cometary percentage of these impactors is irrelevant to our results. Eqs.(5.4) imply that in a 10 bar CO_2 atmosphere 4.5 Gyr ago, Earth was accreting 7×10^5, 3×10^6, and 1×10^9 kg yr^{-1} of organics, respectively. (The 25% lowest-velocity comets account for $\gtrsim$ 50% of these.) This flux thereafter declined with time-constants τ_a, τ_b, or τ_c (Figure 5.3). Using the empirical constraints on the impact record described above, we find that the most likely range of organic accretion is ~10^6–10^7 kg yr^{-1}. (Of course, both UV photolysis of organics settling and raining out of the atmosphere, and thermal and cosmic ray decomposition of those accumulating on the surface, would lower this total.) Intact heteropolymer and its pyrolysates each represented ~40%, and HCN, CH_4, and H_2CO about 9, 6, and 4%, of this *surviving* organic mass fraction. Amino acids, if present at carbonaceous chondrite abundances, were ~1% of the total. (There is a kind of impact selection of the thermodynamically most stable species, but significant amounts of comparatively labile organics also survive impact.) For a 20 bar atmosphere 4.5 Gyr ago, Earth would have accreted only several times as much cometary organics, although these would have experienced considerably less shock heating. These results may be put in context by comparison with terrestrial oceanic and total biomasses $\sim 3 \times 10^{12}$ kg, and $\sim 6 \times 10^{14}$ kg, respectively (Hayes *et al.* 1983).

We have not treated the possibility of delivery of intact organics by efficient fragmentation or airburst. We estimate the magnitude of this effect in the following way. A bolide will airburst when the differential pressure between its leading and trailing hemispheres exceeds its tensile strength. But for comets with radii $r_o \gtrsim 1$ km, an atmospherically-induced pressure wave would not have time to traverse the comet prior to terrestrial impact, so that only impactors with $r_o \lesssim 1$ km may airburst. (This does not require all comets with radii $\lesssim 1$ km to airburst, however. Weissman (1985) cites two terrestrial impact craters of diameters 8.5 and 14 km, for which impactor compositions are known to have been either carbonaceous chondritic or cometary. These craters are consistent with impacts by either intact bolides or tightly clustered fragments (Passey and Melosh 1980), but are certainly inconsistent with a Tunguska-like airburst. Applying a standard impactor mass-diameter scaling law (Chyba 1990a) for either a C-chondrite or comet impacting Earth at ~20 km s^{-1} yields radii ~ 200 and 600 m for the two impactors.)

From Eqs.(5.1), the incident mass ratio between comets in the ranges 200–1000 m and 50–200 m is about 13. If all comets in the range 200–1000 m were to airburst, and if all their organics were to reach the surface intact, then our previous estimates of terrestrial organic accretion are low by a factor ~50. (A more careful treatment would treat cometary fragments following an airburst using the methods outlined in this paper. One way to calculate the mass fraction of fragments in a given size range is to assume a power-law distribution of fragment sizes (Turcotte 1986). One such distribution is $N(m) = Cm^{q/3}$, where $N(m)$ is the number of fragments with mass $> m$, C is a constant fixed by the total mass, and q is a material-dependent constant. This equation can be used to calculate the mass fraction of fragments in the range 50–200 m, which may then

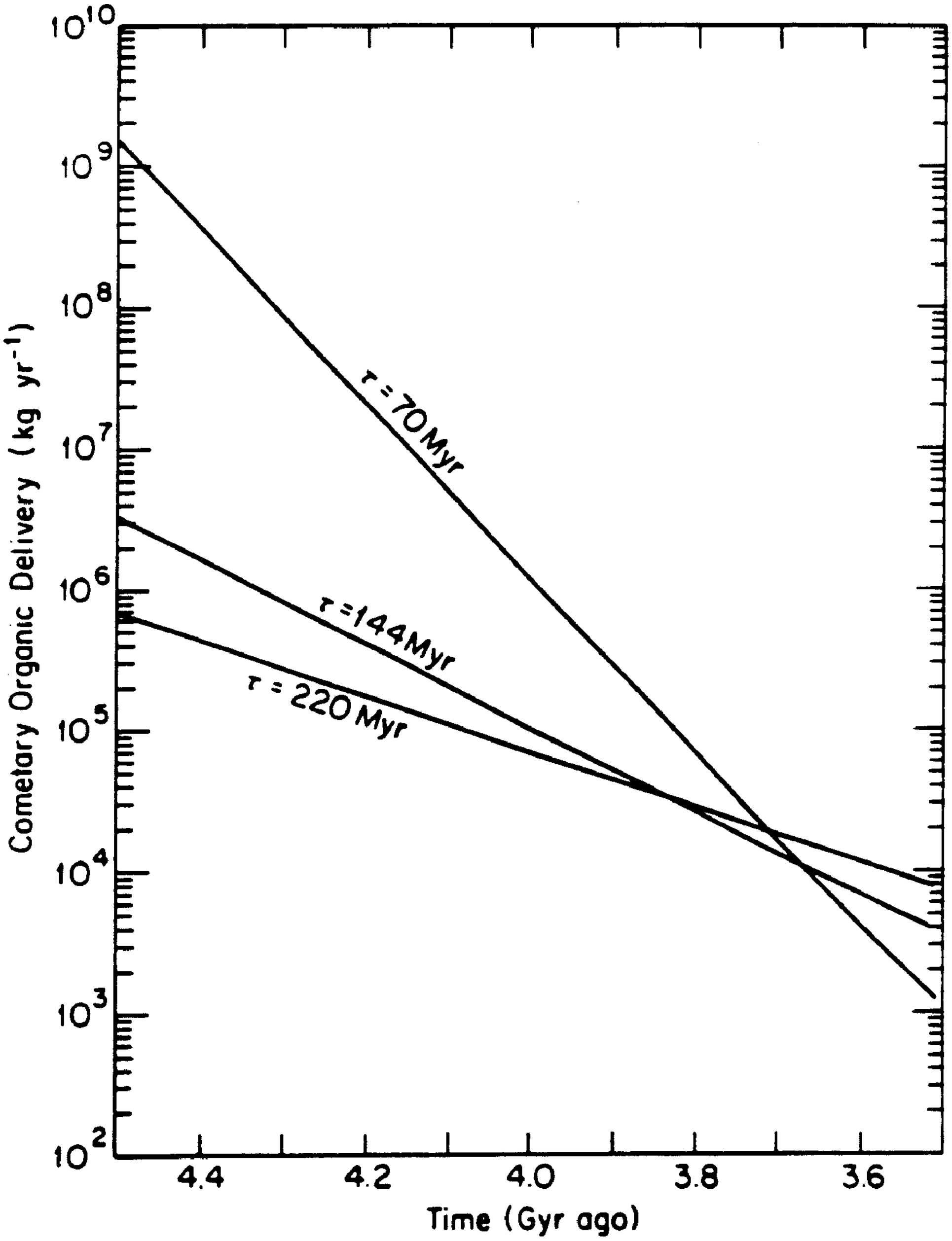

Figure 5.3 Cometary delivery of organics to Earth as a function of time (from Eqs.(5.4)), for a 10 bar CO_2 atmosphere and a typical cometary density $\delta \sim 1$ g cm^{-3}. If comets instead have $\delta \sim 0.5$ g cm^{-3}, the results shown would correspond approximately to 5 bar CO_2 atmospheres.

be combined with Eqs.(5.1) to calculate the mass of surviving organics. q for geological materials is typically ~2.5, with more fragile materials having smaller values. Assuming q in the range 2.2–2.8, we find that our neglect of fragmentation underestimates terrestrial organic accretion by a factor 4–9.)

Zhao and Bada (1989) have recently identified large quantities of apparently extraterrestrial non-protein amino acids, α-amino-isobutyric acid (AIB) and racemic isovaline, in Cretaceous/Tertiary (K/T) boundary sediments. Since Ir abundances require the K/T bolide (assuming a single object was responsible) to have been ~ 10 km in radius, by our results amino acids (or any other organics) could not have survived the resulting impact in a presumptive 1 bar atmosphere 65 Myr ago. As just argued, a 10 km diameter bolide is unlikely to have airburst, so it appears the claimed extraterrestrial amino acids cannot be the result of intact delivery by a comet or asteroid. It has been suggested that dust evolved from a large comet trapped in the inner solar system may have provided the source (Zahnle and Grinspoon 1990). This suggestion, while promising, nevertheless faces several difficulties (Chyba 1990b). Alternatively, the K/T amino acids may be the result of post-impact quench synthesis. Barak and Bar-Nun (1975) have found efficient production of AIB (at levels ~ 10% that of glycine and alanine) in shock tube experiments with initial mixtures 10% C_2H_6 + 10% NH_3 in Ar + air + H_2O. Production efficiency seems to be unaffected by the background air, at least up to ratios $O_2/C_2H_6 = 2.5$. Therefore the quench synthesis explanation for K/T amino acids is not yet ruled out.

Anders (1989) has recently suggested that interplanetary dust may have been an important source of prebiotic organics for the early Earth. He calculates the current infall rate of organic carbon in interplanetary dust to be $f \approx 3 \times 10^5$ kg yr^{-1}. If we assume f scales proportionally to the impactor flux in the inner solar system, the time dependencies of Eqs.(5.4) may be used to extrapolate f into the past. We then find a terrestrial infall rate 4.5 Gyr ago of organic carbon from interplanetary dust $\sim 10^8$ to 10^{10} kg yr^{-1}.

Even in ~10 bar early terrestrial atmospheres, this rate exceeds the conservative estimates we have derived here for ~100 m comets. However, we have left almost entirely unquantified likely augmentations to the latter estimate, including those arising from ablated material, airbursts, a possible extremely thermally stable fraction of cometary organics, a relaxation of our approximation that peak shock heating extends over the full 1 second of the impact simulation, and lower temperatures implied by 3-D impact simulations. (Results reported here are taken entirely from 2-D simulations. Preliminary 3-D models of cometary impacts indicate that our estimates of the fraction of the comet exposed to $T < 1200$ K may be underestimates, in some cases by as much as a factor ~10 (Thomas *et al.* 1990). This is consistent with work reported by Brown (1981), who found pressure reductions by factors ~2 for 3-D codes over 2-D approximations. These differences will be further explored in future work.) Moreover, the role of (small) carbonaceous asteroids is yet to be determined. In any case, the nature of the organics provided by interplanetary dust and impacting comets would have been radically different: Comets could deliver extremely volatile molecules, such as CH_4 or non-polymeric HCN and H_2CO, whereas the organics in interplanetary dust are almost certainly highly processed and refractory (Anders 1989, Chyba 1990b).

Finally, we emphasize that we have ignored a host of possible mechanisms for impact generation of organics, including production by shock waves in reducing or neutral atmospheres (Bar-Nun *et al.* 1970a,b, Barak and Bar-Nun 1975, Fegley *et al.* 1986), or even by vaporization and recombination of target material (Mukhin *et al.* 1989). Moreover, substantial organic recombination may take place via the quenching of the vaporized cometary projectile itself (McKay *et al.* 1989, Oberbeck *et al.* 1989). However, efficient organic synthesis in dense background CO_2 atmospheres via such recombination is problematic. These mechanisms will be considered in greater detail in Chapter 7.

Typical estimates of photochemical production rates for HCN and H_2CO in terrestrial CO_2 atmospheres (taking into account rainout efficiencies) are $\sim 10^9$ kg yr^{-1} (Pinto *et al.* 1980, Stribling and Miller 1987) But these rates drop precipitously as H_2/CO_2 levels fall below ~ 1 (Schlesinger and Miller 1983a,b). It is intriguing that it is exactly these dense CO_2 atmospheres, where photochemical production of organic molecules should be the most difficult, in which intact cometary organics would be delivered in large amounts.

Chapter 6

Terrestrial Mantle Siderophiles and the Lunar Impact Record[1]

6.1 Introduction

In light of the length of this chapter, is seems prudent to begin with a summary of the the key arguments to be presented.

A simple analytical fit to the lunar cratering record, scaled from final to transient crater diameters, then to impactor masses, implies a total mass $\sim 1.0 \times 10^{20}$ kg incident on the Moon subsequent to the solidification of the lunar crust ~4.4 Gyr ago. About half this mass would be retained, and comparable lunar mass would be eroded. These results are in good agreement with geochemical estimates of the meteoritic component mixed into the lunar crust, which give $(0.4\text{–}1.5) \times 10^{20}$ kg. Gravitationally scaling to Earth, and taking account of the statistical probability that the largest impactors incident on Earth were more massive than the largest incident on the Moon, gives an estimate of 1.5×10^{22} kg of material accumulated by Earth subsequent to 4.4 Gyr ago. This result is in excellent accord

---

[1] This chapter is a lengthier version of Chyba, C.F. (August 1991), Terrestrial mantle siderophiles and the lunar impact record, *Icarus* **92**, 217–233 [copyright 1991 by Academic Press, Inc.].

with geochemical estimates of post–core formation terrestrial meteoritic input. These estimates, based on abundances of highly siderophile elements in the terrestrial mantle, lie in the range (1–4)$\times 10^{22}$ kg. The close agreement of the lunar cratering model with available lunar and terrestrial geochemical constraints suggests the model may credibly be used to estimate exogenous volatile and prebiotic organic delivery. (We proceed to the latter estimates in Chapter 7.)

In order for the comparisons between cratering record extrapolations and geochemical data just discussed to be as reliable as allowed by the admittedly sparse data, this chapter begins with a number of improvements to our scaling from the lunar impact record, and updates previous work on likely impact velocities. We then proceed to a discussion of the geochemical data.

6.2 Terrestrial Volatiles: A Late–Accreting Veneer?

The role of impacts in the delivery of volatile elements and prebiotic organic molecules has a speculative history extending back at least to the beginning of this century (Chamberlin and Chamberlin 1908). Such speculation has, over the last two decades, received support from inhomogeneous terrestrial accretion models (Wasson 1971, Turekian and Clark 1975, Anders and Owen 1977, Chou 1978, Sun 1984, Wänke *et al.* 1984, Dreibus and Wänke 1987, 1989, Newsom 1990) as well as dynamical models for outer planet formation (Fernández and Ip 1983, Shoemaker and Wolfe 1984), in which Earth receives the bulk of its surface volatiles as a late-accreting impactor veneer. Moreover, chemical equilibrium models predict one-to-several orders of magnitude less water and nitrogen on Earth than is in fact present (Prinn and Fegley 1989), indicating that some terrestrial accretion of volatile-rich material from greater heliocentric distances must have occurred (see, e.g., Wetherill 1990), or that nonequilibrium models must be considered. However, independently of solar nebula chemistry or planetary formation models, we may ask what the observed lunar cratering record tells us about terrestrial accretion of volatiles (Chapter 4) and organics (Chapter 5) during the period of heavy bombardment (Chyba 1987, 1990a, Grinspoon 1988, Chyba *et al.* 1990). Such an approach intends to minimize the model-dependence of the conclusions, by basing the calculations as much as possible on the available data.

In practice, this procedure is much less successful in narrowing the uncertainties of the problem than one might hope. The oldest lunar province for which a radiometric date actually exists (the Apollo 16 and 17 uplands) is only 3.85–4.25 Gyr old; the ages of more heavily cratered provinces can at present only be estimated (BVSP 1981). For that matter, the entire interpretation of the late heavy bombardment as representing exponentially-decaying remnants of planetary formation is occasionally questioned by those favoring a lunar cataclysm (e.g., Ryder 1989). In Chapters 4 and 5, we cautioned that a range of impactor decay rates are permitted by the extant lunar data, and that different choices for these rates can lead to substantially different conclusions about terrestrial mass influx during the heavy bombardment (Chyba 1990a). In Chapter 4, we suggested—but did not pursue in detail—the possibility that lunar siderophile abundances might be used to constrain fits to the cratering record. This chapter (Chyba 1991) extends the procedure for generating simple analytical fits to the lunar data, to include recent work (Croft 1985, McKinnon and Schenk 1985, McKinnon *et al.* 1990) in the scaling of transient to final crater diameters, and considers constraints imposed by both lunar and terrestrial geochemical data. These constraints are complicated by impact erosion of both the lunar surface and the terrestrial atmosphere, which therefore must be quantified to the extent allowed by current theory. We consider a first-order treatment of these effects, employing the Melosh and Vickery (1989) model for erosion by rapidly-expanding post-impact vapor plumes, and scaling relationships (Housen *et al.* 1983) for ejecta speeds greater than escape velocities. The discussion concludes with an account of volatile delivery and erosion during the heavy bombardment that provides a best fit to the variety of data presently available to constrain the problem.

6.3 Procrustean Fits to the Lunar Impact Record

Figure 6.1 shows cumulative lunar crater density as a function of surface age, from the Basaltic Volcanism Study Project (BVSP 1981). Also shown is an analytical fit to these data, which is discussed below. In Chapter 4, we compared other authors' fits to this, as well as an alternate lunar data set (Chyba 1990a). The data, for craters bigger than a diameter D, are well modeled by the equation

$$N(t,D) = \alpha[t + \beta(e^{t/\tau} - 1)](D/4 \text{ km})^{-1.8} \text{ km}^{-2}, \qquad (6.1)$$

where t is in billions of years (Gyr), and α and β are determined by two-dimensional χ^2 minimization. (Eq.(6.1) is just the mathematical statement of the observation that cratering has been roughly constant for the past 3.5 Gyr, while increasing exponentially into the past prior to that time. Since Figure 6.1 is a cumulative crater plot, its data are fit by the integral (over time t) of this constant plus exponential, giving a sum of a linear and exponential term. The logarithmic ordinate in Figure 6.1 results in the term linear in t extrapolating to $-\infty$ as t goes to 0.) Choices of the decay constant τ in the literature have ranged from 70 Myr to 220 Myr (Chyba 1990a). Fundamentally, however, fitting any single decay 'constant' to the cratering flux is a procrustean exercise, as the impactor flux cannot actually have decayed at a constant rate, but must rather have made a transition from rapidly swept-up objects in Earth-like orbits, to objects from comparatively long-lived, slowly-decaying orbits (Wetherill 1977, Hartmann 1980, Grinspoon 1988). The fit derived in this section should therefore represent the impactor flux subsequent to the time after which the flux of those impactors with very short ($\tau \sim 20$ Myr) sweep-up timescales has decayed to a negligible level, compared with that of more slowly ($\tau \sim 100$ Myr) decaying populations (Grinspoon 1988, Chyba 1990a).

We argued in Chapter 4 for choosing a heavy bombardment decay half-life of 100 Myr, or τ=144 Myr (which gives $\alpha = 3.5 \times 10^{-5}$ and $\beta = 2.3 \times 10^{-11}$ in Eq.(6.1) by two-dimensional χ^2 minimization). This choice is attractive because a ~100 Myr half-life has been demonstrated for the decrease of the primordial comet flux through the inner Solar System by independent numerical simulations of the formation of Uranus and Neptune (Fernández and Ip 1983, Shoemaker and Wolfe 1984). Therefore it might at least correctly represent the time-dependence of the cometary fraction of the inner solar system heavy bombardment flux. (As previously discussed, however, comets may have represented only a small fraction of that flux.) In addition, this choice has the advantage of lying in the middle range of the values of τ with which the observed lunar cratering record is reasonably consistent. Finally, an independent estimate of τ by Oberbeck and Fogleman (1989b, 1990), that correlates absolute age estimates for lunar impact basins from a crustal viscosity model (Baldwin 1987a) with crater counts for these basins (Baldwin 1987b), yields τ=150 Myr. However, the most compelling reason for a choice of τ roughly consistent with a 100 Myr decay half-life is the discovery that such a choice not only well-models the lunar cratering data, but is in excellent agreement with lunar and terrestrial geochemical constraints. This will be demonstrated below in Sec. 6.5.

The initially-excavated (or transient) crater diameter D_{tr} (in meters; MKS units are used throughout) is related to the mass m of the incident impactor via an equation of the form (Schmidt and Housen 1987):

$$m = \gamma v^{-1.67} D_{tr}^{3.80}, \tag{6.2}$$

where v is impactor velocity, and γ is a constant that depends on surface gravity, impactor and target densities, and impactor incidence angle θ (taken here to be

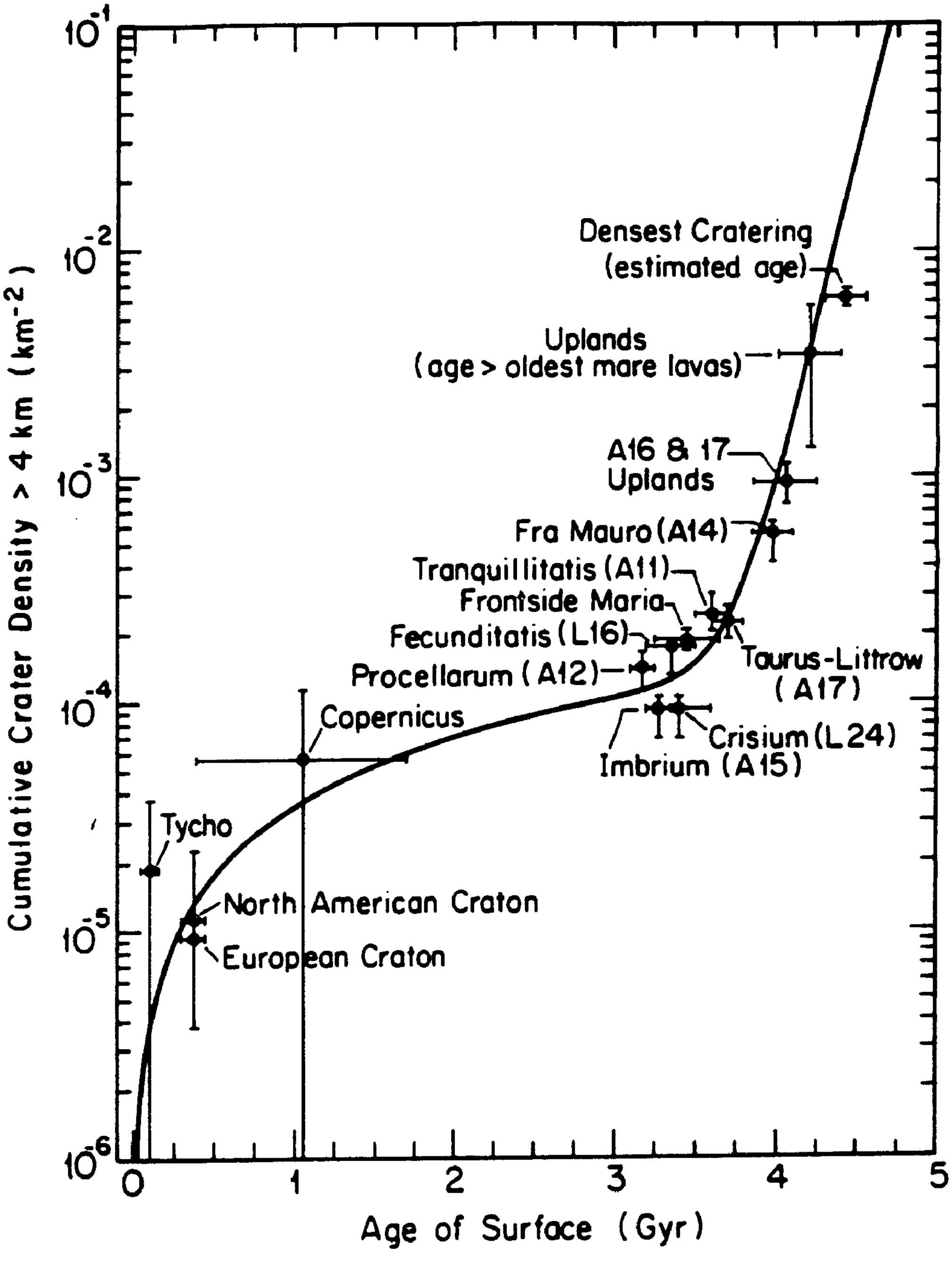

Figure 6.1 Analytical fit (Eq.(6.1)) to cumulative lunar crater density as a function of surface age (BVSP 1981), with a decay time constant τ=144 Myr (100 Myr half-life).

45°):

$$\gamma = 0.3 g^{0.84} \rho^{-0.27} \rho_t^{1.27} (\sin 45° / \sin \theta)^{1.67}. \tag{6.3}$$

$\rho_t = 2,900$ kg m^{-3} is the lunar crustal density (Haines and Metzger 1980), ρ=2,200 kg m^{-3} is the density of a typical impacting asteroid, and g= 1.67 m s^{-2} is the gravitational acceleration at the lunar surface (Melosh 1989). These values give $\gamma = 1.4 \times 10^3$ kg s$^{-1.67}$ m$^{-2.13}$.

In Chapter 4, we cited investigations of wall collapse for craters in the 3–100 km range, showing final crater diameters enlarged over initial excavation (transient) diameters by ~30% (Shoemaker 1983). We therefore related final to transient crater diameter via $D_f = c_f D_{tr}$, where the collapse factor c_f=1.3. This treatment of the transient to final crater transition is a typical approximation (see, e.g., Melosh and Vickery (1989), who set c_f=1.25), but more extensive empirical studies show that D_f cannot be related to D_{tr} by a simple proportionality factor (Croft 1985, McKinnon and Schenk 1985, McKinnon *et al.* 1990). Rather, D_f scales as D_{tr} to a power greater than one. Croft (1985) has suggested the relation

$$D_f \approx D_Q^{-0.18} D_{tr}^{1.18}, \tag{6.4}$$

where D_Q is the diameter of the simple–to–complex crater transition. For the Moon, Croft takes D_Q = 15 km, so $D_f = D_{tr}$ for crater diameters of 15 km. Eq.(6.4) is not applicable to diameters smaller than 15 km; formally it gives $D_f < D_{tr}$ for such craters, an evident absurdity. Rather, Eq.(6.4) is applicable only for complex craters, with $D_f > D_Q$.

McKinnon *et al.* (1990), following McKinnon and Schenk (1985), present a somewhat different treatment, arguing that simple craters on the Moon near the simple–complex transition (which they define, on the basis on depth–diameter data, to be $D_c \approx$11 km) are in fact ~15-20% wider than their original transient craters. McKinnon *et al.* (1990) write

$$D_f = k D_{tr}^{1.13}, \tag{6.5}$$

where

$$k = \kappa D_c^{-0.13}. \tag{6.6}$$

The requirement that D_f is 17.5% (the average of 15% and 20%) larger than D_{tr} when $D_f = D_c$, combined with Eqs.(6.5) and (6.6), allows κ to be determined; one finds $\kappa = (1.175)^{1.13} = 1.2$, whence

$$D_f = 1.2 D_c^{-0.13} D_{tr}^{1.13}, \tag{6.7}$$

with D_c=11 km.

Eq.(6.7) may be taken together with Eq.(6.2) to relate impactor mass and velocity to final (collapsed) crater diameter D_f:

$$m = 0.54 \gamma v^{-1.67} D_c^{0.44} D_f^{3.36}. \tag{6.8}$$

D_f is, of course, what one actually observes on the Moon. Eq.(6.1), with D properly interpreted as D_f, may then be combined with Eq.(6.8) to give the number of objects with mass > m that have impacted the Moon as a function of time t:

$$n(>m,t) = \alpha[t + \beta(e^{t/\tau} - 1)][m/m(4\text{ km})]^{-b}\text{ km}^{-2}, \tag{6.9}$$

where b=(1.8/3.36)=0.54, and m(4 km) is given by Eq.(6.8) with D_f=4 km. The total mass, $M(t)$, incident in impactors with masses in the range m_{min} to m_{max} on a lunar surface of age t is then:

$$M(t) = \int_{m_{max}}^{m_{min}} m[\partial n(>m,t)/\partial m]dm, \tag{6.10}$$

which yields

$$M(t) = \alpha[t + \beta(e^{t/\tau} - 1)][b/(1-b)][m(4\text{ km})]^b m_{max}^{1-b}\text{ km}^{-2}, \tag{6.11}$$

where we have assumed $m_{max} \gg m_{min}$. Note that

$$M(t) \sim m_{max}^{0.46}[m(4\text{ km})]^{0.54} \sim v^{-1.67} D_{max}^{1.55}; \tag{6.12}$$

that is, $M(t)$ depends much more weakly upon D_{max}, the largest crater diameter used in the calculation, than one might have anticipated from either Eq.(6.8), or from the Schmidt–Housen scaling, Eq.(6.2). As discussed in Secs. 6.3 and 6.4 below, uncertainties in D_{max} and v lead to final uncertainties in $M(t)$ of a factor of a few.

$M(t)$ from Eq.(6.11) may be gravitationally scaled to determine the total mass incident on Earth during the heavy bombardment, subsequent to a time t. Several variables must first be determined, however: the mass, m_{max}, of the largest impactor (or, equivalently, D_{max}), and a 'typical' impactor velocity v. These choices are the topic of the next two sections.

6.4 Impact Velocities on the Earth and Moon

Eq.(6.8), and therefore Eq.(6.11), require a choice of a "typical" lunar impact velocity v for the long-lived component of the heavy bombardment. A common approach (BVSP 1981, Melosh and Vickery 1989) has been to use the root-mean-square (rms) impact velocity v_{rms} for the known Earth-crossing asteroids. Such an approach can at best provide a "snapshot" of asteroid-Earth collisions, as evolution of orbits (mainly due to Jovian perturbations) will alter perihelia (q), which strongly influence collision probabilities and velocities. For example, collision probabilities reach a strong maximum when $q \approx 1$ AU (Olsson-Steel 1987). Note, however, that the calculations cited below (Kessler 1981, Steel and Baggaley 1985) do average over simple secular precession of asteroid perihelia, which occurs on timescales of $\sim 10^4 - 10^5$ yr (Shoemaker *et al.* 1979), short compared to typical asteroid dynamical lifetimes in the inner solar system. For the Earth-crossing asteroids these lifetimes are only $\sim 10^7 - 10^8$ yr (Steel and Baggaley 1985), so the current Earth-crossing asteroid swarm is in any case no better than a "snapshot" on Solar System history timescales. The implicit assumption of this approach, then, is that the resulting "snapshot" is approximately representative of a "typical" distribution of Earth-crossing impactor velocities. These objects appear to provide the best contemporary velocity analogues to the impactors primarily responsible for the heavy bombardment, which, as attested by the similarities in the cratering records of Mercury, Mars, and the Moon (Strom 1987), crossed the orbits of all the terrestrial planets.

We argued in Chapter 4 that the use of rms velocities in impact calculations is inappropriate, as rms calculations of most-probable impact velocities assign great weight to those few objects with exceptionally high relative velocities at infinity (v_∞), skewing "typical" velocities towards misleadingly high values. Previous work (Melosh and Vickery 1989, Sleep *et al.* 1989, Chyba 1990a) has employed velocity values calculated from the 20 Earth-crossing asteroids known in 1981 (BVSP 1981). But the orbits of 65 such objects were known by May 1989 (Olsson-Steel 1990), so velocity calculations may now be updated, with a substantial improvement in statistical reliability.

Figure 6.2(a) shows the percentage of asteroid-Earth collisions that occur at a given velocity, using Olsson-Steel's recent (1990) compilation of Aten and Apollo asteroids. (Aten asteroids have semi-major axes $a < 1$ AU, and aphelion distances $Q > 0.9833$ AU, the perihelion distance of the Earth; Apollos have $a > 1$ AU, and perihelion distances $q < 1.0167$, the aphelion distance of the Earth.) The method used by Olsson-Steel to calculate individual asteroid collision probabilities and velocities (Kessler 1981, Steel and Baggaley 1985) results in minimum (v_{min}) and maximum (v_{max}) possible velocities at infinity for a given mean collision probability. We have averaged these extremes to find the values of v_∞ used here. In fact this procedure slightly underestimates impact velocities, as for any given asteroid, the higher collision velocities have slightly higher collision probabilities (Kessler 1981, Steel and Baggaley 1985). However, the uncertainty in v_∞ introduced by my simple averaging procedure is less than $v_\infty - v_{max} = v_\infty - v_{min}$; in the "worst case", that of asteroid 1954 XA, this value is just 0.75 km s^{-1}. The standard deviation of this uncertainty for all 65 impactors is <0.5 km s^{-1}. These uncertainties are unimportant compared with other unknowns in the problem.

Given values of v_∞ and probabilities of terrestrial collisions for each object, it is a simple matter to calculate the percentage of Earth–crossing asteroid collisions with Earth as a function of impact velocity v, where

$$v^2 = v_\infty^2 + v_{esc}^2, \tag{6.13}$$

and the escape velocity $v_{esc} = 11.2$ km s^{-1} for Earth. The results are shown in Figure 6.2(a). For asteroid–Earth collisions, these data yield $v_{rms} = 18$ km s^{-1}, and an average velocity $v_{av} = 17$ km s^{-1}. However, about 50% of collisions occur at velocities below $v_{med} = 15$ km s^{-1}, which we therefore take to be the "typical" value in the median sense. These values are well below those calculated from the much smaller BVSP (1981) data set, for which $v_{rms} = 25$ km s^{-1}, $v_{av} = 20$ km s^{-1}, and $v_{med} = 17$ km s^{-1}.

These calculations may be easily extrapolated to the Moon, as shown in Figure 6.2(b). This extrapolation is not merely a case of replacing $v_{esc} = 11.2$ km s^{-1} in Eq.(6.13) for the Earth with v_{esc}=2.4 km s^{-1} for the Moon, because collision probabilities, which depend on the quantity $[1 + (v_{esc}/v_\infty)^2]$, also change relative to one another. For lunar collisions, we find $v_{rms} = 16$ km s^{-1}, $v_{av} = 14$ km s^{-1}, and $v_{med} = 12$ km s^{-1}; this last value is also, to within 2%, the median value of v_∞. Note that throughout this chapter, the effects of the Moon's orbital velocity (~1 km s^{-1}) with respect to Earth are neglected; this approximation never introduces an error >1% in any of the following calculations.

4.5 Gyr ago, the Moon should have been much closer to Earth than now. In this case, gravitational focussing by the Earth leads to both a larger lunar gravitational cross-section (discussed in Sec. 6.4 below), and a larger average lunar impact velocity (v_{esc}^2 in Eq.(6.13) is replaced with the sum of the squares of the lunar escape velocity and the escape velocity of Earth at the Moon's orbital

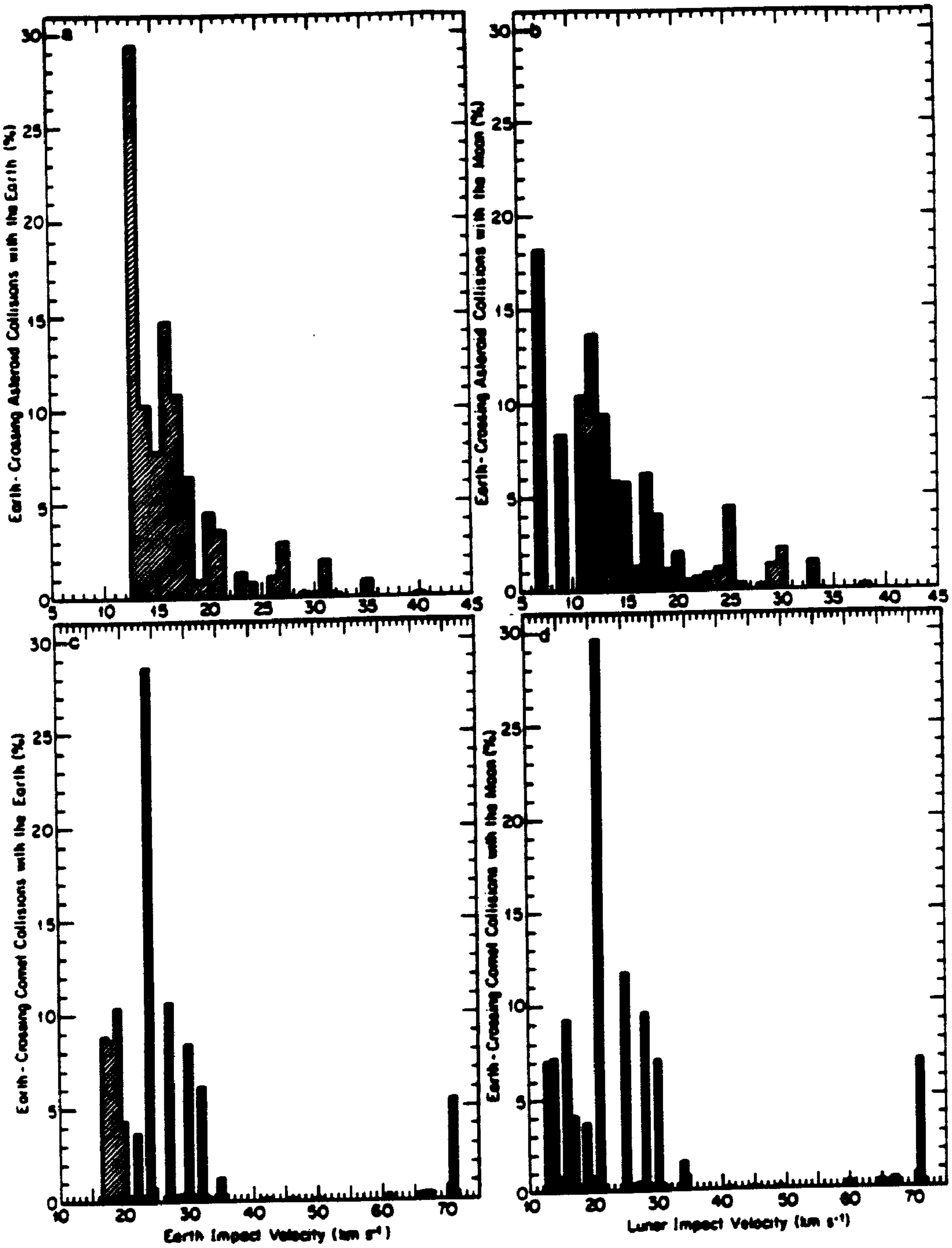

Figure 6.2 Percentage of Earth-crossing asteroid and short-period (SP) comet collisions with the Earth and Moon as a function of impact velocity. Percent collisions of asteroids with (a) Earth, and (b) the Moon, based on data from Olsson-Steel (1990). Percent collisions of SP comets with (c) Earth, and (d) the Moon, based on data from Olsson-Steel (1987).

distance). At the current lunar distance, 60.3 Earth radii ($R_\oplus$), terrestrial gravity increases v in Eq.(6.13) by <1%. Dynamical calculations of the evolution of the lunar inclination may exclude accretion of the Moon in Earth's equatorial plane within ~10 $R_\oplus$ (Boss and Peale 1986). At 10 $R_\oplus$, the effects of terrestrial gravitational focussing on v, given $v_\infty = 12$ km s^{-1}, are only ~4%, or an increase of ~0.5 km s^{-1}, negligible compared to other uncertainties in the problem. If the Moon did in fact form near the terrestrial Roche limit, ~3 $R_\oplus$, its orbital evolution out to 10 $R_\oplus$ would have been extremely rapid. In a model with constant terrestrial specific tidal dissipation Q, the time needed for the lunar orbit to evolve from an initial (a_i) to final (a_f) semi-major axes is given by (Chyba *et al.* 1989):

$$\tau \approx (2/39)(a_i^{13/2} - a_f^{13/2})(M_\oplus/m_m)(Q/R_\oplus^5 k)(GM_\oplus)^{-1/2}, \qquad (6.14)$$

where $M_\oplus$ and m_m are the terrestrial and lunar masses, respectively, G is the gravitational constant, and k is the terrestrial second-order Love number. Using Eq.(6.14), it is easy to show that the timescale for the Moon to evolve from 3 to 10 $R_\oplus$ was $< 10^{-5}$ of the time required to evolve from 10 to 60.3 R$_\oplus$, or only $10^4 - 10^5$ yr. As (see Sec. 6.5 below) we will be concerned only with the impactor flux subsequent to the first 10^8 yr of terrestrial and lunar history, we may ignore this possible very early near-Earth stage of lunar history. Therefore, it seems sufficient to approximate typical lunar impact velocities during heavy bombardment by those of the contemporary Earth-crossing asteroids.

What of the Earth-crossing short-period (SP) comets? In Chapter 4, we followed a procedure analogous to that just used for the asteroids, to compute typical impact velocities for SP comets. Because models of the early cometary bombardment of the inner Solar System (Fernández and Ip 1983, Shoemaker and Wolfe 1984) indicate that the flux of comets scattered directly from the Uranus–Neptune region (that is, following SP-like orbits) dominated by several orders of magnitude the flux of those (long-period) comets first scattered out to the

Oort cloud, it is appropriate to use contemporary SP comet orbits as analogues to those of the cometary component of the heavy bombardment.

In Chapter 4 (Chyba 1990a), we used Weissman's (1982) compilation of 20 SP comet impact velocities and probabilities. These statistics may now be slightly improved, with the addition of comets Tuttle, Schwassmann–Wachmann 3 and Wilk; however, comet Giacobini–Zinner's perihelion has evolved to $q = 1.028$ AU, so it is no longer an Earth-crosser and must be dropped from Weissman's list (Olsson-Steel 1987). Figures 6.2(c) and 6.2(d) show the results of using Olsson-Steel's (1987) compilation for 22 SP comets, following a procedure identical to that used above for asteroids. Obviously the statistics for SP comets are considerably worse, however. The results are nearly identical to those found using Weissman's (1982) data: For collisions with the Earth, we find v_{rms}=30 km s^{-1} and v_{av}=27 km s^{-1}; whereas for lunar collisions, v_{rms}=30 km s^{-1} and v_{av}=26 km s^{-1}. (The effects of terrestrial gravitational focussing are relatively minor for SP comet orbits, due to their high values of v_∞.) Median collision velocities are a bit more difficult to define than for asteroids, however, because of the poorer cometary statistics. For terrestrial collisions, ~36% of cometary collisions occur at velocities <22 km s^{-1}, whereas ~64% of collisions occur under 24 km s^{-1}. (The velocity bin for 23 km s^{-1} in the histogram of Figure 6.2(c) is empty.) Thus we choose v_{med} to lie half-way between 22 and 24 km s^{-1}, or v_{med}=23 km s^{-1}, with an evident uncertainty of ~1 km s^{-1}. Similarly for cometary collisions with the Moon, for which v_{med}=20 km s^{-1}. For the Moon, the median value of v_∞ is equal to v_{med} to within 1%.

Finally, note that the asteroidal distribution of % collisions vs. impact velocity appears very different from the cometary one. Crudely speaking, the cometary distribution has a "bell-shaped" appearance, whereas the asteroidal has a "decaying-exponential" one. This difference may be rationalized as follows. The more elliptical cometary orbits have greater values of v_∞, so the resulting % collisions vs. impact velocity distribution reflects the "intrinsic" distribution of cometary orbits. In the case of Earth–crossing asteroids, however, the orbits are far more circular, with resulting much smaller values of v_∞ (the lowest asteroid values are ~7 km s^{-1}, half that for the slowest SP comet), so that there are comparatively slow (and long) overlaps with the Earth's orbit. Objects with sufficiently small values of v_∞ therefore acquire large collision probabilities. It is possible that the "bell-shaped" appearance of the cometary curve reflects the poor SP comet statistics, and that the addition of more cometary orbits would also yield an "exponential"-shaped curve. However, the analogous asteroid distribution for the 20 Earth–crossers contained in the BVSP (1981) list, a number comparable to that of the SP comets used here, shows the same distinctly "exponential"-type distribution as that found for the 65 asteroids plotted in Figures 6.2(a) and 6.2(b). In any case, note that in order to be consistent with observations, asteroid orbits in any model for the origin of Earth–crossing asteroids must either begin in, or evolve into, a similar "exponential" distribution of collision probability vs. impact velocity.

We take the value $v_{med} = 12$ km s^{-1} for asteroid impacts on the Moon to be the most appropriate value for v in Eqs.(6.8) and (6.11). (In Chapter 4, as in some earlier work (Sleep *et al.* 1989, Chyba 1990a), we used a lunar impact velocity of $v = 13$ km s^{-1}, based on the limited BVSP (1981) compilation of Earth–crossing asteroids.) With $v = 12$ km s^{-1}, Eq.(6.8) yields $m(4 \text{ km}) = 8.9 \times 10^9$ kg. How sensitive are the results of Eq.(6.11) to different choices of v? Using Eq.(6.12), we see that, were we to use the asteroidal v_{rms} instead of v_{med} in Eq.(6.11), $M(t)$ would decrease by $(16/12)^{1.67} = 1.6$. If we used the cometary value of v_{med}, instead of the asteroidal one, $M(t)$ would decrease by $(20/12)^{1.67} = 2.3$. The range of values for v, then, seems to introduce an error at most a factor of a few into $M(t)$.

6.5 Maximum–Mass Impactors

Calculating $M(t)$ in Eq.(6.11) requires a value for m_{max}. For the Moon, m_{max} will be the mass of the impactor that excavated the largest lunar basin, taken here to be South Pole–Aitken. This ancient lunar farside basin was first tentatively identified photogeologically (see Wilhelms 1987); its existence has now been clearly demonstrated by Galileo observations (Head *et al.* 1991). Wilhelms (1987) suggests a pre–Nectarian age for South Pole–Aitken of 4.1 Gyr, and identifies (his Table 4.1) an average ring diameter of 2200 km (or, possibly, two rings of 1800–2000 km and 2500 km). It is true that other giant, highly–degraded lunar basins have been suggested, both on the basis of photogeological evidence (Wilhelms 1987), and subsurface mass concentrations (Campbell *et al.* 1969, O'Leary *et al.* 1969), but their existence remains controversial. In particular, Spudis *et al.* (1988) have recently argued that the reality of the proposed giant "Procellarum" basin is called into question by these authors' conclusion that the large–scale, concentric structural pattern on the lunar near side probably represents Imbrium rings (ranging up to 3200 km in diameter), rather than a "Procellarum" signature. Impacts larger than Imbrium would probably have excavated lunar mantle material, but no lunar mantle samples have ever been found on the lunar nearside (Sleep *et al.* 1989). Indeed, Head *et al.* (1991) have suggested, on the basis on Galileo multispectral imaging, that the South Pole–Aitken basin may show excavated lunar mantle material.

Sleep *et al.* (1989) have argued that lunar impacts similar to or larger than Imbrium must have been rare after 4.4 Gyr ago, or else the lunar regolith would be more stirred than it appears to be. If South Pole–Aitken is taken as the largest lunar basin, with D_f=2200 km, how many basins as large or larger than Imbrium are implied? The observed number of lunar craters larger than some diameter D falls off as $D^{-1.8}$, a power law that is well obeyed in both the lunar frontside highlands and heavily cratered uplands, for histogram bins in D up to

$D = 512\sqrt{2} = 724$ km (BVSP 1981; Figs. 23, 26, Sec. 8.11). Assuming this N vs. D power law to hold for the largest objects (an assumption examined further below), we may write:

$$N(> D_f) \propto D_f^{-1.8}. \tag{6.15}$$

This equation allows the number of basins as large or larger than Imbrium, which has a diameter ~1160 km (see below), to be calculated from $N(> 1160 \text{ km}) = N(> 2200 \text{ km})[(1160 \text{ km})/2200 \text{ km})]^{-1.8}$. Taking $N(> 2200 \text{ km})$ to mean the number of basins as large or larger than South Pole–Aitken, $N(> 2200 \text{ km}){=}1$ so that $N(> 1160 \text{ km}) \approx 3$. Of these three basins, South Pole–Aitken is one; if we consider Imbrium to represent a second, there remains only one other giant. The statistics here are of such small numbers that this object could easily not exist. (Of course, *a priori*, the poor statistics also allow several to exist.) It seems that regolith stirring arguments do not exclude $D_f{=}2200$ km for the South Pole–Aitken basin.

What is the mass of the South Pole–Aitken impactor? Choosing $D_f{=}2200$ km in Eq.(6.7) corresponds to an initial excavation (transient) diameter for the basin of $D_{tr}{=}1020$ km. Eq.(6.2) (or Eq.(6.8) directly) then yields a south Pole–Aitken object mass of 1.4×10^{19} kg. Should Eqs.(6.2), (6.7), and (6.8) be trusted for giant basins? The answer appears to be yes, based on analogous calculations for the masses of the Orientale and Imbrium objects, which may be checked against independent estimates. For example, Sleep *et al.* (1989) obtain a mass for the Orientale object from a thermal contraction estimate of the heat buried by this impact, and then scale the result to the Imbrium impactor. They conclude that the Orientale object had an impact kinetic energy of 1.2×10^{26} J, with an uncertainty of about a factor of 3. Choosing an impact velocity $v = 13$ km s^{-1}, they find an Orientale impactor mass of 1.4×10^{18} kg. An estimate of Orientale ejecta mass of 2.4×10^{19} kg then yields a ratio of ejected mass to projectile mass of about 17. Imbrium ejected about 3.6×10^{19} kg of material

(Spudis *et al.* 1988), so by this method (Sleep *et al.* 1989), the Imbrium object had a mass of about 2.1×10^{18} kg, with an evident uncertainty of a factor of $\sim$3. These estimates may be compared to the results of calculating Orientale and Imbrium object masses from Eq.(6.8). Choosing D_f for these basins to be 930 km (Wilhelms 1987, Baldwin 1987a) and 1160 km (Wilhelms 1987, Baldwin 1987a, Spudis *et al.* 1988), respectively, Eq.(6.8) yields impactor masses of 8.1×10^{17} kg and 1.7×10^{18} kg. Both estimates agree with the independent calculations of Sleep *et al.* to better than a factor of two. Finally, Baldwin (1987b) has also estimated a mass for the Imbrium object, relying on his own crater diameter–impactor energy scaling argument, finding a mass of 2.3×10^{18} kg. All three Imbrium estimates for this mass agree to within $\sim$40%. Since Eq.(6.8) appears reliable for calculating impactor masses for those giant basins where its results may be compared with independent estimates, I will employ it as well for the South Pole–Aitken object, and take $m_{max} = 1.4 \times 10^{19}$ kg in Eq.(6.11).

Eq.(6.11) may now be used to calculate the total mass incident upon the Moon subsequent to some time t, and this result may then be extrapolated to Earth. In Section 6.5, we will compare these results with constraints imposed by lunar and terrestrial geochemical evidence. For the Moon, this evidence depends on the meteoritic component (determined from Ir and, possibly, Ni abundances) retained in lunar samples; Ir and Ni would have been retained in the lunar regolith subsequent to that date when a mostly solid crust first existed (Sleep *et al.* 1989). These authors cite samarium–neodymium (Sm–Nd) isotopic evidence that the upper lunar crust, ferroan anorthosite, solidified as early as 4.44 ± 0.02 Gyr ago (Carlson and Lugmair 1988), whereas the age of KREEP basalt (Carlson and Lugmair 1979) implies 4.36 ± 0.06 Gyr ago as the solidification of the base of the crust. We therefore take 4.4 Gyr as the approximate time t to use in Eq.(6.11) for the Moon. Since $\tau = 144$ Myr, an error in this choice of $\sim$40 Myr will change $M(t)$ by $\lesssim 30\%$.

Inserting these values into Eq.(6.11) gives $M(4.4\text{ Gyr}) = 2.7 \times 10^{12}$ kg km^{-2}, or, with a lunar radius r_m=1738 km, $M(4.4\text{ Gyr}) = 1.0 \times 10^{20}$ kg delivered to the Moon since 4.4 Gyr ago. (The mass of the South Pole–Aitken object was ~14% of this total.) This mass flux is the appropriate value to scale to the larger gravitational cross-section of Earth. It is not, however, the net amount of mass actually accreted by the Moon since 4.4 Gyr ago: As we will argue in Sec. 6.6 below, probably only ~50% of the objects striking the Moon during heavy bombardment were moving slowly enough for their mass to be accreted, rather than ejected into space. Moreover, significant impact erosion of the Moon should also have taken place.

Scaling from the Moon to Earth requires accounting for Earth's larger gravitational cross-section. A planet's gravitational cross-section is $\sigma = \pi R_g^2$, where the gravitational radius R_g for a planet of physical radius R and escape velocity v_{esc} is given by

$$R_g = R[1 + (v_{esc}/v_\infty)^2]^{1/2}. \tag{6.16}$$

With v_∞=12 km s^{-1}, the ratio of the Earth's gravitational cross-section to that of the Moon is then

$$\sigma_\oplus/\sigma_m \equiv \xi = 1.8(R_\oplus/r_m)^2. \tag{6.17}$$

The Earth's equatorial and polar radii are 6378 km and 6357 km, respectively; the Earth's volume is equivalent to a sphere of radius $R_\oplus$=6371 km (Stacey 1977). Therefore, Eq.(6.17) yields $\xi \approx 24$. Simply multiplying $M(4.4\text{ Gyr})$ for the Moon by 24 gives 2.4×10^{21} kg of meteoritic material accreted by Earth subsequent to 4.4 Gyr ago.

However, this simple scaling does not fully account for the role of Earth's larger gravitational cross-section. Because $\xi \approx 24$, it is likely that the largest impactors in the Earth–Moon system were collected by the Earth. Therefore, $M(4.4\text{ Gyr})$ for the Earth will be larger than implied by simply scaling Eq.(6.11) for the Moon by ξ, with the assumption that m_{max} is the mass of the South

Pole–Aitken object.

To try to quantify this effect, we follow the approach of Sleep *et al.* (1989), and write the probability P that the Moon is not hit by any of the largest n impactors:

$$P = (24/25)^n. \tag{6.18}$$

Taking the logarithms of both sides of Eq.(6.21) shows $P \approx 50\%$ provided $n \approx 17$. Thus if South Pole–Aitken is the largest lunar impactor subsequent to 4.4 Gyr ago, 17 larger objects are expected to have hit Earth since that time. We take the sizes of these objects to be distributed according to Eq.(6.15) from South Pole–Aitken–sized up to the largest object in the population.

Eq.(6.8) implies $D_f \propto m^{0.30}$, so Eq.(6.15) may be transformed into an equation for the number of impactors with masses $> m$:

$$N(> m) \propto m^{-0.54}. \tag{6.19}$$

If Earth collected 17 objects with masses greater than that of the South Pole–Aitken object, 1.4×10^{19} kg, Eq.(6.19) shows Earth should also have been struck by 1 object with mass $m > 2.6 \times 10^{21}$ kg, the maximum-mass impactor on Earth subsequent to 4.4 Gyr ago. How much larger than 2.6×10^{21} kg was this impactor? Any such "statistics-of-one" question can only be answered probabilistically, and with concomitant caution. One approach to this question is to begin with Eq.(6.19), and ask: What mass must an impactor have had such that Earth would have collected 0.5 such objects? Eq.(6.19) then yields:

$$(17/0.5) = [(1.4 \times 10^{19}\ \mathrm{kg})/m]^{-0.54}, \tag{6.20}$$

giving $m = 9.5 \times 10^{21}$ kg ($\sim$13% the mass of the Moon) as the mass of the largest impactor incident on the Earth. The total mass, M, of all 17 impactors is, analogously, given by the sum:

$$M = \sum_{i=1}^{17} (1.4 \times 10^{19}\ \mathrm{kg})[(i - 0.5)/17]^{-1.85}. \tag{6.21}$$

Evaluating this sum yields $M = 1.2 \times 10^{22}$ kg. (Clearly there is great uncertainty in this result. Even formally, the number of larger–than–South Pole–Aitken impactors is uncertain to $\sqrt{17} \sim 4$, and the real uncertainty is of course much worse, given our empirical ignorance of the mass distribution of these largest impactors.) Summing the mass incident on Earth in the largest impactors with that previously found, yields a total incident mass during the heavy bombardment of 1.5×10^{22} kg.

Sleep *et al.* (1989) find that an impact energy of 2×10^{28} J is sufficient to evaporate the entire terrestrial ocean by the formation of a globe–encircling rock vapor atmosphere; such impacts may possibly have globally sterilized the early Earth. With a typical Earth impact velocity 15 km s^{-1}, a kinetic energy 2×10^{28} J corresponds to an impactor of mass 1.8×10^{20} kg. If 17 larger–than–South Pole–Aitken impactors are taken to have hit Earth during the heavy bombardment, Eq.(6.21) shows that, statistically, Earth should have sustained ~4 such impacts between ~4.4 and 3.8 Gyr ago.

Is $\xi \approx 24$ appropriate for the Earth–Moon system prior to ~4 Gyr ago? In fact, ξ for a Moon as close to the Earth as 10 $\mathrm{R}_\oplus$ is only ~8% smaller than the contemporary value. As this effect—whose temporal applicability is in any case unknown—is less than those arising from uncertainties in m_{max} or v, it shall be neglected here.

The derivation of the maximum-mass terrestrial impactor found here relies on the number–mass ($N - m$) relationship shown in Eq.(6.19), i.e., on the exponent s in the relationship $N(>m) \propto m^{-s}$. Eq.(6.19), with $s = 0.54$, has the clear advantage of consistency with the ancient lunar cratering record and crater diameter-mass equations adopted throughout this chapter. Nevertheless, one may ask to what extent our results would differ had some other plausible value for s been chosen. For example, theoretical treatments of collisionally evolved planetesimal systems predict s=0.83 when fragmentation dominates, 0.67 with both fragmentation and coagulation present, and 0.5 for coagulation in the absence of comminution (Greenberg 1989, and references therein). Empirically, contemporary Solar System asteroids with diameters $D < 260$ km approximately follow a distribution with $s = 1.0 \pm 0.1$, and those with $D > 260$ km have $s = 0.83 \pm 0.25$ (Donnison and Sugden 1984). Short–period comets with magnitudes $H_{10} < 10.8^m$ (i.e., those with radii $\gtrsim 1$ km (Hughes 1990)) have $s = 0.50$. (Unfortunately, the situation is less clear–cut than these citations imply. For example, in an earlier treatment of asteroidal $N - m$ distributions than that cited above, Hughes (1982) found that asteroids with $D > 260$ km had $s = 0.58 \pm 0.25$. And it is certainly the case (Gradie *et al.* 1989) that values of s differ between different asteroid classes, as well as between different size ranges within given classes.) In any case, evidently s in Eq.(6.19) does not lie outside the range of size distributions for known Solar System objects. Suppose that instead of Eq.(6.19) for the largest impactors ($s = 0.54$), we were to adopt $s = 1.0$, the empirical distribution differing the greatest from Eq.(6.19). Then the total mass collected by the Earth would be reduced by a factor ~4, compared with the values found above.

6.6 Lunar and Terrestrial Geochemical Constraints

The preceding sections have shown that the lunar cratering record, fit by a simple analytical formula with an exponential decay half–life of 100 Myr (e–folding time $\tau = 144$ Myr), and with consistent estimates of the size of maximum–mass impactors on the Moon and Earth, predicts the net mass incident on these bodies subsequent to 4.4 Gyr ago by the slowly–decaying population of the heavy bombardment to have been $\sim 1.0 \times 10^{20}$ kg for the Moon, and $\sim 1.5 \times 10^{22}$ kg for the Earth, with evident uncertainties of a factor of at least a few. As will be argued in Sec. 6.6 below, probably about half the mass incident on the Moon, and nearly all the mass incident on Earth, was accreted by these bodies. However, the values of total accreted mass for these two objects depends strongly on the choice of τ one uses when fitting the cratering record. We will now show that the mass estimates just cited, resulting from the choice $\tau = 144$ Myr, are in excellent agreement with lunar and terrestrial geochemical data. Therefore, it seems likely that broad conclusions regarding volatile and prebiotic organic delivery in the early inner Solar System, based on the treatment developed here, should be reliable. At the least, one may say that this treatment is in good accord with those (admittedly sparse) data that are available.

What constraints are provided by lunar and terrestrial geochemistry? In the case of the Moon, one may use Ir, and possibly Ni, abundances in lunar highland breccias to obtain an estimate of the meteoritic component retained in lunar samples. (Strictly, as discussed in Sec. 6.6 below, this estimate provides only a lower limit to the extra-lunar component, as some material must have been impact eroded off the lunar surface.) Sleep *et al.* (1989) have recently summarized these results. They estimate a meteoritic component mixed into the upper half of the lunar crust (35 km) of between 1% and 4%, with 2% their preferred value. This corresponds to a total meteoritic thickness of 0.7 km of material, or, using our previous estimate for the density of the lunar crust (Haines and Metzger 1980), a total extra-lunar mass of 7.7×10^{19} kg ($\sim$0.2% of the current lunar mass), with an uncertainty of a factor of two. This mass would have been accreted subsequent to the solidification of the lunar crust $\sim$4.4 Gyr ago.

In the case of the Earth, one may use siderophile abundances in ultramafic xenoliths (more–or–less unaltered solid mantle material brought to the surface by volcanic eruptions of basaltic magmas), as well as basalts, peridotites, and other mantle–derived rocks, to estimate the meteoritic component mixed into the Earth's mantle (Chou 1978, BVSP 1981, Sun 1984, Wänke *et al.* 1984, Dreibus and Wänke 1987, 1989, Newsom 1990). Amongst the xenoliths, apparently unaltered (or nearly unaltered) mantle samples have been found only among the spinel–lherzolites, which represent upper mantle material from depths up to 70 km (Wänke *et al.* 1984). The observed near–chondritic proportions of siderophile elements in these samples are evidently not the result of metal–silicate fractionation processes, as it is unlikely that the partitioning of all of these elements upon fractionation is similar (BVSP 1981). This conclusion is supported by detailed modeling of various core formation theories (Newsom 1990). It has therefore been suggested that the highly siderophile "noble metals", Ru, Rh, Pd, Re, Os, Ir, Pt, and Au, were added to the upper mantle during the heavy bombardment, subsequent to terrestrial core formation (Chou 1978, BVSP 1981, Sun 1984, Newsom 1990). (During core formation, virtually all noble metals present in the mantle should have been incorporated into the core (Sun 1984, Newsom 1990).) The nearly–chondritic ratios of the noble metals excludes fractionated impactors (such as eucrites) as sources (Chou 1978).

Noble metal abundances in upper mantle samples can be explained by ~1% of CI carbonaceous chondrite input subsequent to core formation (Chou 1978, BVSP 1981, Sun 1984, Dreibus and Wänke 1989). How much total extraterrestrial mass does this represent? This depends on whether one takes the post–core formation input to have been mixed throughout the entire, or only the upper, mantle. The upper mantle appears to be well–mixed, as indicated by studies of isotope ratios and distributions of rare earth elements in mid–ocean ridge basalts; convective mixing in the upper mantle greatly reduces heterogeneities on a timescale of several hundred million years (Turcotte and Kellogg 1986). Therefore it certainly appears reasonable to take the CI chondrite abundances implied by available samples to correctly represent typical upper mantle abundances. If one assumes that the CI input is mixed only until this depth (Chou 1978), the CI abundance may be multiplied by the mass of the upper mantle to obtain the total mass accreted by Earth during the heavy bombardment.

The depth of Earth's upper mantle is defined by the seismic discontinuity at 670 km (Stacey 1977, Turcotte and Kellogg 1986). Virtually no earthquake activity occurs below this depth; it remains controversial whether subducted lithospheric slabs ever penetrate this layer (Frohlich and Grand 1990). However, even if a barrier to mantle convection exists at 670 km depth on the contemporary Earth (Turcotte and Kellogg 1986), it nevertheless remains possible that a vigorously–convecting early Earth would have experienced whole mantle convection, and therefore mixed the extraterrestrial component throughout the entire mantle (Wänke *et al.* 1984).

We estimate a mass for the terrestrial upper mantle from an Earth interior model in which density is a simple analytic function of depth (Dziewonski *et al.* 1975, Stacey 1977). Integrating from a radius of 5701 km (670 km depth) up to 6352 km (the base of the crust, for an "average structure" model), gives the mass of the upper mantle as 1.1×10^{24} kg. Assuming this to be $\sim$1% CI chondritic then gives $\sim 1.1 \times 10^{22}$ kg as an estimate of the total mass accreted by Earth during the heavy bombardment, subsequent to core formation. This value is a lower limit, as it assumes mixing occurred only throughout the upper mantle. An upper limit should be given by taking mixing to occur throughout the entire mantle, which yields 4.0×10^{22} kg total accreted mass (taking the mass of the whole mantle to be 4.0×10^{24} kg (Stacey 1977)). Therefore the actual value is likely to be bracketed by the range $\sim (1 - 4) \times 10^{22}$ kg.

Wänke *et al.* (1984), and Dreibus and Wänke (1987, 1989) have argued that mixing should have occurred throughout the entire mantle, and find a total CI component equivalent to 0.44% the mass of the Earth, or 2.6×10^{22} kg. (Given the mass of the Earth, $M_{\oplus} = 5.98 \times 10^{24}$ kg, these authors have effectively taken the CI component of the mantle to be 0.65%.) A detailed model recently presented by Newsom (1990) requires a late veneer chondritic component equivalent to 0.2% $M_{\oplus}$, or 1.2×10^{22} kg. Again, this value falls within the range, $(1 - 4) \times 10^{22}$ kg, considered here.

Terrestrial core formation is believed to have taken place within $\sim 10^8$ yr of the formation of the Earth (Stevenson 1983, 1990, Sun 1984). The Earth's age may be determined by Iodine–Plutonium–Xenon (I–Pu–Xe) dating of the Earth's atmosphere and mantle, which suggests formation 75–100 Myr after t_o, the time of formation of primitive meteorites (Swindle *et al.* 1986). I–Pu–Xe dating of lunar samples suggests a lunar age of 63±42 Myr after t_o, between 80 Myr before and 30 Myr after the terrestrial formation date. (Therefore, if the impact–trigger hypothesis for the formation of the Moon is correct, the Moon–forming event occurred no more than 30 Myr subsequent to terrestrial accretion.) A period of 75–100 Myr for the formation of the Earth subsequent to meteorite formation is in excellent agreement with dynamical models for the formation of the terrestrial planets, which yield $\sim 10^8$ yr timescales for the accretion of the Earth from an initial population of planetesimals (Wetherill 1977, Greenberg 1989; see also Grinspoon 1988). A recent study by Wetherill (1990) yields 99% accretion of the Earth after 77 Myr.

What is the value of t_o, the time of formation of primitive meteorites? The oldest high-precision meteorite date comes from calcium-aluminum-rich inclusions of the CV chondrite Allende, which give a ^{207}Pb/^{206}Pb model age of 4.559±0.004 Gyr (Tilton 1988). This value of t_o in turn implies that terrestrial formation was virtually complete (∼99%, say, following Wetherill's (1990) simulation results) by 4.49–4.46 Gyr ago. The formation of Earth's core would then have taken place by ∼4.4 Gyr ago.

Therefore, it is appropriate to compare the extraterrestrial mass input implied by terrestrial geochemical data with that found by extrapolating from the lunar cratering record to the Earth, using $t \approx 4.4$ Gyr in Eq.(6.11). The agreement between the two techniques is excellent. The value found via the lunar cratering extrapolation, 1.5×10^{22} kg, lies within the range $(1 - 4) \times 10^{22}$ kg implied by the geochemical data. Moreover, the extrapolation is reasonably robust against a different choice for the time of terrestrial core formation; for example, changing the time of core formation by 100 Myr will change the result by only a factor of two.

6.7 Impact Erosion of the Earth and Moon and Origins of the Bombarding Population

In Sec. 6.4, we used the lunar cratering record to derive the total impactor mass incident on the Earth and Moon subsequent to $\sim$ 4.4 Gyr ago. In Sec. 6.5, these results were compared with those implied by terrestrial and lunar geochemical data. In order for these comparisons to be appropriate, however, an account must be made of the erosion of the Earth and Moon by high–speed impacts. This section presents a first–order treatment of this problem for both worlds, considering erosion due both to loss of high–velocity crater ejecta, and to atmospheric erosion by expanding post–impact vapor plumes.

To treat the latter effect, we follow the treatment of Melosh and Vickery (1989). These authors find that large impacts may cause atmospheric erosion when two criteria are met. The first is that the impactor must strike the planet at a velocity high enough for a vapor plume to form and expand at a speed $> v_{esc}$. Second, the mass of the plume must exceed the air mass above the plane tangent to the impact. Here we consider an impactor that satisfies these two criteria to be entirely lost as an escaping vapor plume from the target planet. The Melosh and Vickery (1989) treatment takes a mass of the target equal to that of the impactor to be incorporated into the plume, and similarly lost. (This should be considered as an extremely rough–and–ready approximation, whose uncertainty should be remembered throughout the following discussion.) Thus, not only will that impactor's mass not contribute to the target world, but in this simple model, an equal mass of the target's surface (as well as some atmospheric mass) will be lost as well.

Melosh and Vickery (1989) show that the threshold impact velocity v_{min} for most of a vapor plume to exceed v_{esc} is given by

$$v_{min}^2 = 4(v_{esc}^2 + 2H_{vap}), \tag{6.22}$$

where H_{vap} is the vaporization energy, taken to be 13 MJ kg^{-1} for silicates and 3 MJ kg^{-1} for ice (1 MJ kg^{-1} = 1 km^2 s^{-2}). For the Moon, v_{min} is a bit over 11 km s^{-1} for silicate projectiles ("asteroids") and about 7 km s^{-1} for ice impactors ("comets"). As may be seen from Figure 6.2(d), virtually all vapor plumes resulting from cometary impacts on the Moon (for comets of any mass, as there is no atmosphere to be overcome) would be lost. In the case of asteroids, as Figure 6.2(b) illustrates, nearly 40% of lunar collisions occur at velocities below 11 km s^{-1}, and about 50% below 12 km s^{-1}. Recognizing that published treatments of impact erosion remain approximate at best, we may therefore take 50% as a rough estimate of the fraction of asteroidal collisions with the Moon that result in escaped vapor plumes.

For Earth, v_{min} $\approx$25 km s^{-1} for asteroids, and about 23 km s^{-1} for comets. As seen in Figures 6.2(a) and 6.2(c), ~90% of Earth-colliding asteroids, and ~50% of Earth-colliding comets (recall we found v_{med}=23 km s^{-1} for these bodies in Sec. 6.3), impact Earth with velocities below the appropriate v_{min}. Therefore Earth retains nearly all asteroid-delivered volatiles, and about half of those brought in by comets; comets erode about as much terrestrial mass as they deliver. Atmospheric volatiles might be significantly eroded, as discussed in Sec. 6.7 below.

In addition to erosion by expanding vapor plumes, we must also consider loss of target material in that fraction of crater ejecta propelled at velocities $> v_{esc}$. Quantitative treatments of this effect, like those of atmospheric erosion, remain at an early and uncertain stage (Melosh 1989). Housen *et al.* (1983) have used dimensional analysis and scaling arguments to derive the functional form of an expression for the volume of ejecta, $V_e(>v_e)$, with velocity equal to or greater than some velocity v_e. For cratering in the gravity regime (where material strength is unimportant), they find:

$$V_e(>v_e)R^{-3} = K(v_e/\sqrt{gR})^{-\nu}, \qquad (6.23)$$

where $R = D_{tr}/2$ is the radius of the transient (initially-excavated) crater, and K and ν are (in general, target-dependent) constants. Experiments with targets of Ottawa sand yield $K = 0.32$ and ν=1.2 (Housen *et al.* 1983, and references therein). Cratering equations previously employed in this chapter (e.g., Eq.(6.2)), in Chapter 4, and elsewhere (Melosh and Vickery 1989, Chyba 1990a) make use of results for cratering in competent rock, rather than sand—the former presumably providing a better model for cratering in the lunar crust than the latter. However, the only experiments available for crater ejecta velocities are for sand targets, so that the only experimentally-derived values for K and ν are those appropriate for sand. (In fact, ν may be theoretically related to crater-diameter or volume exponents arising in crater size-impactor mass experiments, and may thereby be derived for competent rock targets. However, these experiments do not determine K.) We will therefore model ejecta loss using exclusively parameters for sand targets. A treatment for competent rock must await relevant experimental data.

Eq.(6.23) may be combined with a crater diameter-impactor mass scaling law to determine how much ejecta is propelled at velocities $> v_e$ for a projectile of a given mass and velocity incident upon a certain target world. A general form for the crater diameter-impactor mass relation is (Schmidt 1980, Schmidt and Housen 1987, Melosh 1989):

$$\pi_D = C_D \pi_2^{-\beta}, \qquad (6.24)$$

where

$$\pi_D = D_{tr}(\rho_t/m)^{1/3}, \qquad (6.25)$$

and

$$\pi_2 = 3.22gr/v^2. \qquad (6.26)$$

Here C_D and β are constants, g is surface gravity, and m, r, and v are the incident impactor's mass, radius, and velocity, respectively. The crater diameter–impactor mass scaling law employed in this chapter, Eq.(6.2), is just Eq.(6.24) with parameter values appropriate to competent rock, *viz.* $C_D = 1.6$ and $\beta = 0.22$. To be consistent with Eq.(6.23) above, in the following treatment only, we must employ parameters for Ottawa sand: C_D=1.68 and β=0.17 (Schmidt 1980, Schmidt and Housen 1987). Combining Eqs.(6.23) through (6.26), assuming a spherical impactor, then yields:

$$M_e(> v_e) = 0.11(\rho/\rho_t)^{0.2}(v/v_e)^{1.2}m, \tag{6.27}$$

where $M_e(> v_e)$ is the mass of ejecta with velocity greater than some velocity v_e, and ρ and ρ_t are the impactor and target densities, respectively (so that $M_e = \rho_t V_e$). Using parameters appropriate to asteroidal collisions with the Moon (in particular, choosing v=12 km s^{-1}), and taking v_e to equal v_{esc}= 2.4 km s^{-1}, the lunar escape velocity, Eq.(6.27) becomes $M_e(> v_{esc}) \approx 0.7\ m$. Thus, a "typical" asteroid incident on the Moon erodes in ejecta alone ~70% as much mass (m) as it delivers. From Figure 6.2(b) and Eq.(6.27), it may be seen that nearly 20% of incident asteroids will erode about half as much as this, whereas the few objects in the high-velocity tail may erode considerably more. As a very rough approximation, it seems we may say that a net mass M of asteroids incident upon the Moon will erode about a mass M worth of lunar material in the form of ejecta. In addition, the Moon will lose mass due to escaping impact vapor plumes. Therefore the Moon appears to have experienced a net impact erosion due to "asteroid" collisions subsequent to ~4.4 Gyr ago.

Comets, with higher typical velocities, will tend to erode in high-speed ejecta slightly more lunar material than they deliver. Moreover, as previously argued, it appears that virtually all cometary collisions will result in vapor plumes that expand away from the Moon at velocities greater than v_{esc}. These plumes will carry away not only the impactor mass, but a comparable target mass as well

(Melosh and Vickery 1989). Thus a typical collision of a comet of mass m will add no mass to, and erode a mass $\sim 2m$ from, the Moon. While this may not have been an important effect for an early Moon, whose impact environment was probably dominated by non-cometary impactors, the current lunar cratering flux may be anywhere from 10% to $\gtrsim$50% cometary, where the higher percentages require the inclusion of "extinct" comets (Shoemaker 1983) or possible comet showers (Shoemaker and Wolfe 1986).

What of the Earth? Simply inserting the appropriate terrestrial values, v=15 km s^{-1} and $v_e \equiv v_{esc}$=11.2 km s^{-1}, into Eq.(6.27), gives $M_e(> v_{esc}) \approx 0.1\ m$, suggesting terrestrial erosion by high-speed ejecta is at most a small effect. This conclusion is reinforced by the likelihood that much of the ejecta escaping from the Earth will be reaccreted from their resulting Earth-crossing heliocentric orbits. (Note that in the lunar case, while some ejecta would be trapped in Earth orbit and re-accreted by the Moon, Eq.(6.27) may be used to show that the majority would escape from geocentric orbit into a heliocentric one. This is because even when the Moon was as close as 10 $R_\oplus$, Earth's escape velocity was only 3.5 km s^{-1} at the lunar orbit, scarcely bigger than the Moon's 2.4 km s^{-1}. Hence, perhaps most of the material eroded from the Moon would eventually be collected by Earth, rather than reaccreted by the Moon.)

In Sec. 6.5, we cited siderophile abundances in the lunar regolith that suggest the Moon accreted 7.7×10^{19} kg of extra-lunar material (with a factor of 2 uncertainty) subsequent to $\sim$4.4 Gyr ago. In Sec. 6.4, we used a fit to the lunar cratering record to argue that $\sim 1.0 \times 10^{20}$ kg of material was incident upon the Moon in the slowly-decaying component of the heavy bombardment. This value must be reduced by a factor $\sim$2, since $\sim$50% of asteroids incident on the Moon are expected to contribute no mass, as they are immediately lost in post-impact vapor plumes. The result is clearly in agreement with lunar geochemical estimates. Must the net amount of extra-lunar material added to the Moon be significantly further reduced due to erosion of the lunar surface in vapor plumes and ejecta?

A rough treatment of this problem, presented below, argues the answer is no. While a more sophisticated model could be considered, such a model seems unjustified in light of the preliminary nature of the impact erosion models themselves. Nevertheless, because of the uncertainties in all these models, the following conclusions should be treated with caution. Consider the result of a total mass M of asteroids incident on the Moon. Half this mass, $0.5M$, is accreted, while the remainder, $0.5M$, is lost. The latter fraction also results in $\sim 0.5M$ of lunar regolith lost in vapor plumes. Also, for an incident mass M, a regolith mass $\sim M$ is lost in high-speed ejecta. Therefore, the Moon experiences a net mass loss of $\sim M$. Subsequent to ~4.4 Gyr ago, taking $M \approx 1 \times 10^{20}$ kg, this represents ~1 km of material eroded from the lunar surface.

This result does not, however, contradict the presence of ~2% extra-lunar siderophiles in the lunar crust. There are two reasons for this. The first is that, while a typical impactor, taken to be a CI chondrite, will deliver 100% CI siderophile abundances, the resulting eroded lunar regolith material will be only ~2% CI material. Therefore the Moon will accrete a net mass $\sim(0.5M-0.02M) \sim 0.5M$ of CI siderophile-abundance material—even as it experiences a net mass loss. That is, efficient regolith mixing (Sleep et al. (1989) take the extra-lunar material to be mixed through the megaregolith, extending to a depth of 35 km) would guarantee that impact erosion will have little effect on extra-lunar abundances found in the crust.

A second reason that impact erosion by asteroid-like projectiles does not contradict regolith siderophile abundances is that we have so far neglected to take into account those lunar impactors that derive from the residual long-lived "tail" of bodies remaining in the region of the terrestrial planets after the growth of the Earth and Venus have been completed (~99%, say; see, e.g., Wetherill

(1990)). These bodies will have much lower velocities at infinity than bodies in asteroid–type orbits; typical values of v_∞ for the former should be ~8 km s^{-1} (Wetherill 1977). The terrestrial impact rate of the residual Earth–crossers will initially decay with a 15–20 Myr half life, but this half-life will lengthen after ~100 Myr (Wetherill 1977). If 1% of the terrestrial mass remains to be accreted from this population subsequent to 4.5 Gyr ago, numerical experiments show some 0.02%, or $\sim 2 \times 10^{21}$ kg, would remain in Earth-crossing orbits ~4.3 Gyr ago (Wetherill 1980). For $v_\infty = 8$ km s^{-1}, the Moon's gravitational cross-section (see Eq.(6.15)) is ~31 times smaller than Earth's, giving $\sim 6 \times 10^{19}$ kg of material delivered to the Moon after 4.3 Gyr ago. This is approximately equal to the amount of accreted extra–lunar material implied by lunar regolith Ir abundances. Moreover, most of this material would have been accreted: $v_\infty = 8$ km s^{-1} results in a lunar impact velocity of only 8.4 km s^{-1}, which by Eq.(6.22) is too low for the formation of an escaping vapor plume. Eq.(6.25) suggests that a typical impactor of mass m striking the Moon at 8.4 km s^{-1} would have eroded a mass of less than $0.5m$ in ejecta: The residual Earth–crossers collected by the Moon would therefore have yielded a net accretion of lunar mass, for as long as this population persisted.

Note that it appears extremely unlikely that residual bodies from the Moon–forming circumterrestrial disk (whether this disk was formed by a giant impact or otherwise) could have accounted for any significant influx of mass to the Moon subsequent to 4.4 Gyr ago. As Stevenson (1987) has emphasized, the characteristic sweep–up time for such a disk is extremely short, perhaps as brief as ~500 yr, due to the rapidity of tidal orbital evolution of Moon–sized bodies near the Earth's Roche limit.

The story we have presented in this section is one in which two populations of objects, short-lived (~15-20 Myr half-life) residual Earth-crossers, and longer–lived (~100 Myr half-life) bodies that are eventually fed into orbits similar to those of Earth–crossing asteroids or short–period comets, both contribute to the heavy bombardment on the Earth and Moon. About 4.4 Gyr ago, both populations would have contributed roughly equally, but after only a few short (15–20 Myr) half–lives, the longer–lived population would dominate. This account is similar to that suggested by Hartmann (1980) and Grinspoon (1988). It is complicated by the fact that some fraction of the residual Earth–crossers will evolve into Mars–crossing orbits with $\sim$ 200 Myr half–lives (Wetherill 1975). Therefore the various populations are not cleanly distinguishable by orbital decay times alone.

From the point of view of total mass accreted by the Earth and Moon, the origin of the impactors is of little importance. However, this question is of critical importance in estimating the quantity of volatiles or organics delivered to the early Earth. Throughout the remainder of this discussion, this uncertainty remains, and is fundamental. It could be (Wetherill 1980) that the bulk of heavy–bombardment impactors were residual bodies from the initial Earth– and Venus–forming swarm, passed through Mars–crossing storage orbits. If this were true, these bodies might deliver roughly chondritic abundances of refractory elements, while making little contribution to the terrestrial volatile inventory. On the other hand (see Sec. 6.7 below), if a substantial fraction of these impactors were CI chondrites or comets, Earth could have thereby acquired the bulk of its surface volatile inventory.

As discussed in Chapter 4, there appears at present to be no decisive evidence for the composition of the population responsible for the heavy bombardment (Chyba 1987), beyond the inference from terrestrial noble metal abundances that the bulk of the population had roughly chondritic abundances of highly siderophile elements (Chou 1978). What inferences may be drawn from lunar geochemical evidence remains highly controversial. Some authors (Gros *et al.* 1976, Hertogen *et al.* 1977, Anders 1978) have argued that enrichment of siderophile trace elements in some lunar highland breccias indicates sampling of basin–forming projectile remnants, and that independent statistical tests agree in the identification of nine distinct meteoritic component clusters, corresponding to remnants of nine distinct parent bodies. These claims have been disputed on a number of grounds, including the possibilities that clusters identified by certain elemental ratios merely reflect indigenous lunar variations (Wänke *et al.* 1978, Delano and Ringwood 1978), procedure–dependent artifacts (Delano and Ringwood 1978), or regional heterogeneities due to large–scale impact gardening (Wetherill 1980). Rebuttals to most of these objections have been offered (Anders 1978). Most recently, Attrep *et al.* (1991) have cited observations of siderophile elements in impactites from Australian meteorite craters to argue that strong impact fractionation of siderophile elements can, in fact, occur, and that one should therefore be cautious in attempting to deduce the nature of impacting projectiles from siderophile element patterns in impact melt rocks. This controversy seems unlikely to be resolved soon. Here we wish only to emphasize that, if the nine putatively–identified impactors are real, only one has a siderophile composition similar to CI chondrites, and even this cluster (the group 5L clasts) is depleted in volatiles relative to CI abundances by as much as $\sim 10^{-2}$. Therefore, if these data may be correctly interpreted as representing the composition of nine large heavy–bombardment impactors, they imply that no more than a small percentage of this population could have been CI chondrites. (There seems to be no contradiction here with terrestrial upper mantle noble metal element ratios, which lie within the ranges found in the lunar highland breccias, and are closest to lunar group 1H (Chou, 1978).) It is important to note, however, that essentially no restriction is placed by the lunar highland samples on the fraction of the heavy bombardment that may have been cometary. Virtually all comets incident on the Moon should have been lost as vapor plumes expanding with velocities greater than v_{esc}, and therefore should have made little contribution to the extra–lunar component of highland rocks.

6.8 Impact Delivery of Volatiles and Terrestrial Abundances

As discussed in Sec. 6.4, mantle abundances suggest Earth collected (1–4)$\times 10^{22}$ kg of extraterrestrial material subsequent to core formation, in agreement with lunar cratering data. If so, what quantity of accreted volatile elements is implied?

The answer to this question depends on the fraction of the heavy bombardment population composed of volatile-rich objects such as CI chondrites or comets. Table 6.1 shows two candidate heavy bombardment compositions which, given a net accreted mass of 2.5×10^{22} kg (chosen as the midpoint of the range allowed by the geochemical data), yield an approximately terrestrial abundance of water. (The mass of the terrestrial oceans, lakes, and icecaps is 1.4×10^{21} kg. Of this, some 97% resides in the oceans (Walker 1977). Estimates of the mass of water residing in the terrestrial crust, deep crust, or even mantle are obviously uncertain (see, e.g., Yardley 1986).) Implied abundances of certain other volatiles are also listed. Two questions of obvious interest are: If volatile-rich CI asteroids or comets delivered a substantial fraction of the ~1% of the mantle mass thought to have been accreted subsequent to core formation, what fraction of the terrestrial volatile inventory is then also due to the heavy bombardment? Also, if the bulk of the Earth's oceans were derived from such a heavy bombardment source, would this imply a terrestrial abundance of any other element so far in excess of known terrestrial inventories as to rule the possibility out?

What if the entire ~100% were accreted from CI chondrites? This possibility is considered in Column 4 of Table 6.1. Wänke *et al.* (1984) have compiled a list of the abundances of some 56 elements in the terrestrial crust and mantle, based on geochemical data, and normalized these to CI abundances. Given the resulting numerical values for noble metals, their list may be readily scanned for

Table 6.1 Estimated Terrestrial Volatile Inventories vs.
Accretion from Candidate Heavy Bombardment Fractions

Element or Compound	Terrestrial Inventory (kg) in Mantle and Crust	Terrestrial Surface Inventory (kg)[e]	100% CI Chondrite (H_2O content 6%)[f]	25% Cometary (H_2O content 50%)[g]
Carbon[a]	2.7×10^{20}	8.7×10^{19}	9.7×10^{20}	5.3×10^{20}
Nitrogen[b]	6.1×10^{19}	5.2×10^{18}	4.0×10^{19}	1.4×10^{20}
Sulfur[c]	1.4×10^{21}	2.1×10^{19}	1.5×10^{21}	8.8×10^{19}
Chlorine[c]	4.7×10^{19}	4.5×10^{19}	1.6×10^{19}	9.4×10^{17}
H_2O[d]	1.9×10^{21}	1.6×10^{21}	1.5×10^{21}	1.6×10^{21}

[a] C terrestrial abundance estimates from Turekian and Clark (1975) and Hayes *et al.* (1983), respectively.

[b] N terrestrial abundance estimates from Schidlowski *et al.* (1983).

[c] S and Cl terrestrial abundance estimates from Dreibus and Wänke (1989).

[d] H_2O terrestrial abundance estimates from Dreibus and Wänke (1989) and Turekian and Clark (1975), respectively. Terrestrial oceanic mass comprises 1.4×10^{21} kg H_2O (Walker, 1977).

[e] Terrestrial surface abundances taken to include atmosphere, hydrosphere, sedimentary rocks, and crustal estimates.

[f] Chondritic abundances, exclusive of H_2O, from Dreibus and Wänke (1989). See text for discussion of CI H_2O abundances.

[g] Cometary abundances from Delsemme (1991); Cl value assumes CI chondritic S/Cl ratio. Only ~50% of cometary impacts occur at sufficiently low velocities for terrestrial accretion.

any elements which are present in the terrestrial mantle + crust in CI-relative abundances below these values. Only these elements would be provided by a putative ~1% CI chondrite accretion in quantities in excess of the known terrestrial inventories.

In fact these limits are exceeded for almost no elements. All noble metal normalized abundances are within ~50% of the Ir value. In the Wãnke *et al.* (1984) compilation, only selenium (Se), sulfur (S), and carbon (C) would appear to be delivered in quantities greater than the known terrestrial inventories for these elements if the heavy bombardment were 100% CI chondrite. A more recent estimate of the sulfur inventory on the Earth by these same authors (Dreibus and Wãnke 1989) substantially increases the estimate of S in the terrestrial mantle, and the apparent discrepancy is virtually removed. Se is explicitly identified by Wãnke *et al.* (1984) as an element whose abundance, inferred from mantle samples, is suspect. Excluding this element, only C is delivered by a 100% CI chondrite heavy bombardment in excess of its estimated terrestrial abundance, and only by a factor of ~3. Note, however that estimates of terrestrial mantle abundances vary greatly from author to author (see also Sec. 6.9). Along these lines, Dreibus and Wãnke (1989) have argued that discrepancies of factors of 4 between predicted and known C and N inventories are "not really disturbing, considering the poor knowledge on the mantle and even the crustal concentrations of these elements", so it is unclear whether the discrepancies shown in Table 6.1 should be considered real. Column 3 of Table 6.1 lists estimates of terrestrial surface (atmosphere, hydrosphere, sedimentary rocks, and crust) volatile inventories. These estimates are, of course, on a firmer basis than the mantle estimates included in Column 2; the former may therefore be viewed as reasonably firm lower limits for the terrestrial inventories.

In addition to C and N, Table 6.1 also lists abundances for water, sulfur and chlorine (Cl). The latter two elements are included as some previous authors

(Clark 1987, Dreibus and Wänke 1989) have suggested using these elements to constrain the chondritic or cometary fraction of the heavy bombardment. Table 6.1 shows that neither S nor Cl terrestrial inventories are smaller than those expected to be delivered by either a comet- or CI asteroid-delivered ocean of water. We have not included noble gas abundances in Table 6.1. While Sill and Wilkening (1978) have argued that cometary ice clathrate could explain the observed terrestrial abundances of Ar, Kr, and Xe, it appears that noble gas isotope ratios are incompatible with any simple "veneer" scenario (Pepin 1989). Evidently some form of mass fractionation must be invoked to explain these data (Pepin 1989, Zahnle *et al.* 1990), mechanisms that lie beyond the scope of this discussion.

Column 5 of Table 6.1 considers the possible role of a cometary fraction in the heavy bombardment. A comparison of cratering curves between the inner and outer Solar System seems to imply that comets did not comprise the bulk of the heavy bombardment (Strom 1987). Table 6.1 shows that comets could have supplied about a terrestrial ocean of water if they comprised as little as ~25% of the heavy bombardment. Note that Table 6.1 incorporates the result (see Sec. 6.6 above) that only ~50% of comets incident on Earth actually contribute their volatiles, as the remainder are lost to space in post-impact vapor plumes. (The conclusions of this paper are roughly consistent with those of Chyba (1987), taking into account that this earlier study did not include erosion effects.) Given the way the heavy bombardment impactor population's mass peaks in the largest objects, comets could have comprised 25% of this population only if very large comets existed. However, some giant comets are known to exist: The trans-saturnian comet Chiron appears to have a diameter of at least 180 km, and possibly as large as 372 km (Sykes and Walker 1991) (as well as an orbit that may evolve into an Earth-crossing one (Hahn and Bailey 1990)), and the Great Comet of 1729 was a naked-eye object at a perihelion of about 4 AU (Kronk

1984).

The masses of accreted volatiles in Table 6.1 are calculated subsequent to 4.4 Gyr ago. What of volatiles delivered prior to this time? (For example, Hartmann (1987, 1990) has argued that the first $\lesssim 10^8$ years of Solar System history witnessed an intense scattering of C asteroid materials, as evidenced by the fact that most Solar System satellites thought to be captured appear to be spectral class C (Hartmann 1987), and by the preponderance of CM clasts among the foreign fragments in polymict meteoritic breccias (Hartmann 1990).) Terrestrial atmospheric volatiles present prior to the hypothesized Moon-forming impact might be lost in this event (Cameron 1986). Moreover, terrestrial water prior to core formation (~4.4 Gyr) should have been efficiently destroyed by reacting with metallic iron: $Fe + H_2O = FeO + H_2$; large quantities of H_2 produced in this way may have effectively removed other degassed volatiles by hydrodynamic escape (Dreibus and Wänke 1987, 1989). Some volatiles may also have been incorporated into Earth's core. In any case, the 100 Myr half-life of the slowly-decaying population considered here means that even if we were to integrate back to the time of Earth's accretion, our results would change by only about a factor of two.

6.9 Uncertainties in CI Chondrite Water Content

It is a surprising fact of the carbonaceous chondrite literature that water abundances (wt%) commonly cited for CI chondrites vary by a factor of nearly three (~7% vs. ~20%), and that one or the other value is typically cited without reference to the other. Both results derive from experiments done in Harold Urey's laboratory at the University of Chicago in the mid 1950s, first by Boato (1954), then by Wiik (1956). Kaplan (1971) has summarized and briefly compared the two sets of results.

Wiik (1956) reported determinations for the H_2O abundance of three CI chondrites. Two of these values were his own; one was taken from Christie (1914). Each determination yielded ~20% H_2O. Mason's (1971) commonly referenced *Handbook of Elemental Abundances in Meteorites* lists the mean value of these three measurements, 20.08%. Many recent textbooks on meteorites (e.g., Dodd 1981, Wasson 1985) reproduce the petrologic classification of Van Schmus and Wood (1967), which follows Wiik (1956) and gives the bulk water content of CI chondrites as "~20%". In Chapter 4 (Chyba 1990a), we used a carbonaceous chondrite bulk water content given by the average of Mason's (1971) values for CI and CII chondrites.

However, two years prior to Wiik (1956), Boato (1954) had published H_2O abundance results for some eight CI chondrites, finding values substantially below those later found by Wiik. This discrepancy is particularly striking, as the two CI chondrites analyzed by Wiik, Orgueil and Ivuna, were two of the eight used by Boato. For Orgueil and Ivuna, the latter author had found net water abundances of 11.3% and 11.7%, but argued convincingly on the basis of deuterium/hydrogen (D/H) ratios that 4.0% and 4.7%, respectively, of this water was terrestrial contamination. Wiik (1956) noted the discrepancy between his and Boato's abundances, saying that "The material for analyses was the same as Boato's. . . . and the reason for the disagreement of the results is not clear." Dreibus and Wänke (1987, 1989) have advocated an H_2O abundance for CI chondrites of either 7.15% (1987) or 7.29% (1989), following Boato's (1956) results for the indigenous H_2O fraction.

Boato used a step-heating method of his sample, involving evaporation under vacuum at a sequence of temperatures. He found that H_2O liberated at temperatures <180 °C had a strikingly different D/H ratio than that of H_2O liberated above these temperatures, and that the D/H ratio of the loosely-bound H_2O correlated with the "ambient" D/H ratio in Chicago—meteorites analyzed at different times of the year had D/H ratios below 180 °C that tracked the D/H ratio of the dominant precipitation for that season. H_2O liberated at temperatures above 180 °C had D/H ratios that were unquestionably extraterrestrial. (However, Boato's highest experimental temperatures (800–900°C) may have been insufficient to guarantee release of all the hydrogen bound in hydrated silicates (Friedman and O'Neil 1978).) Kaplan (1971) experimentally corroborated (using, however, a very different experimental protocol, without a D/H determination), to within 2%, Boato's determination of the percentage of terrestrial water contamination in Orgueil and Ivuna. Wiik (1956) employed the Pennfield method for determining his samples' water content, a technique that apparently neither involved stepwise heating, nor tested D/H ratios. (Wiik does not describe his procedures in detail; a recent description of the Pennfield method may be found in Skoog and West (1982).) However, his compilation includes Christie's (1914) determination that the water in the Tonk CI chondrite was half lost after drying at 106°C, suggesting that ~50% of Wiik's measured water content is due simply to adsorption of terrestrial water.

Kerridge (1985) has summarized more recent determinations of hydrogen in some 30 carbonaceous chondrites. Kerridge's experimental protocol first crushes and outgasses samples at 200°C overnight to eliminate hygroscopic water. This includes water adsorbed by the sample subsequent to its fall; however, it might also include some water indigenous to the meteorite (Kerridge, 1991, personal communication). Therefore Kerridge's (1985) results may best be viewed as lower limits to CI water content. Averaging the results from the CI chondrites Orgueil and Ivuna gives a hydrogen content of 0.66% H, or 5.9% H_2O. Attempting to subtract the effect of H originally present in organics reduces this figure to about 4.7% (J. Kerridge, 1991, personal communication). On the other hand, in an impact, much of the organic H might be pyrolized into H_2O.

For definiteness, Table 6.1 uses a CI water abundance of 6%. If meteorites reach Earth with substantial hygroscopic water content, this number could be a considerable underestimate. Since CI and CM chondrites consist mainly of a variety of clay-like hydrous sheet silicates (Sears and Dodd 1988), a reasonable upper limit to CI water abundance should be given by considering the water content of terrestrial clays (J. Cronin, N. Sleep, personal communications 1991). Water abundance in clay minerals ranges as high as ~25%; hygroscopic (H_2O^-) and combined (H_2O^+) water content are known to range individually as high as ~16% and ~18%, respectively, depending on the sample (Grim 1968). Several CM chondrites (Kerridge 1985) have hydrogen abundances that imply they are ~9% H_2O^+.

6.10 Impact Erosion of Volatiles

Melosh and Vickery (1989) have proposed a simple analytical approximation to their more detailed numerical work treating impact erosion of planetary atmospheres (see Sec. 6.6 above). Their treatment indicates that an atmospheric cap of mass

$$m_{cap} = 2\pi P_o H R_{\oplus}/g \qquad (6.28)$$

above the plane tangent to the point of impact will be removed by impactors with masses above some threshold, m_*. In Eq.(6.28), P_o is the terrestrial surface atmospheric pressure, H is the atmospheric scale height, 8.4 km for the contemporary Earth (Walker 1977), and g is terrestrial surface gravity. The threshold mass $m_* \approx m_{cap}$, which for the contemporary 1 bar terrestrial atmosphere is 3.5×10^{15} kg.

It is easy to show from Eqs.(6.9) and (6.28) that the heavy bombardment should have resulted in substantial atmospheric erosion for the Earth. In fact, the heavy bombardment should have removed about as much atmospheric mass as it delivered. Eq.(6.9) may be used to calculate how many atmosphere-eroding impacts were suffered by Earth subsequent to 4.4 Gyr. With m in Eq.(6.9) set equal to m_* from Eq.(6.28), scaling to the Earth yields $n(> m_*, 4.4\ \mathrm{Gyr}) = 1.3 \times 10^4$. (Parenthetically, taking comet Halley to have the mass of a 1000 kg m^{-3} density sphere of 5 km radius, Eq.(6.9) predicts Earth was struck by $\sim 3 \times 10^4$ objects the size of Halley or larger subsequent to this date.) For the purposes of illustration, take comets to have represented a negligible fraction of the impactors, so that only ~10% of the latter had sufficient velocity to cause erosion. Conservatively, then, about 10^3 atmosphere-eroding impacts occurred on Earth subsequent to 4.4 Gyr ago. Again for illustration, take the mass of the early atmosphere to equal that of the contemporary one, 5.3×10^{18} kg (Walker 1977). Then each eroding impact removed about 6.6×10^{-4} of the total atmospheric mass. Multiplying this result by 1.3×10^3 eroding impacts yields about 0.9 atmospheres of mass eroded by the heavy bombardment. A denser atmosphere would lead to more eroded atmospheric mass.

To treat the problem more quantitatively, the net effect of erosive impacts during the heavy bombardment may be calculated from integrals similar to Eq.(6.10), of the form:

$$M(t) = \int_{m_{max}}^{m_*} Q(m)[\partial n(> m, t)/\partial m]dm. \tag{6.29}$$

In Chapter 4, we argued that the oceanic mass eroded by impacts could be estimated from an integral like Eq.(6.29), with $Q(m) = f\pi(3/4\pi\rho)^{0.67}m^{0.67}d_{oc}\rho_{oc}$, where ρ_{oc} and d_{oc} are the density and depth of the terrestrial ocean, and f is that fraction of the incident impactors arriving with sufficient velocity to cause erosion (Chyba 1990a). Erosion of condensed oceans appears to be an unimportant effect, amounting to $\lesssim$10% of the mass of the ocean (Chyba 1990a). Eq.(6.29) also gives the mass of atmosphere eroded, by setting $Q(m) = fm_{cap}$, where m_{cap} is from Eq.(6.28). Performing the integral gives

$$M_{lost} = f\alpha[t + \beta(e^{t/\tau} - 1)]m_{cap}[m(4\ \mathrm{km})/m_*]^b\ \mathrm{km}^{-2}. \tag{6.30}$$

A long-standing concern about cometary volatile delivery scenarios is that a cometary source for Earth's water may imply an abundance of nitrogen in excess of known terrestrial inventories (C.P. McKay, personal communication 1989, Chyba 1990a). The gravity of this concern remains unclear in light of vast disagreement over the size of the relevant terrestrial inventories. For example, Turekian and Clark (1975) suggest 1.1×10^{19} kg N resides in the Earth's atmosphere, crust, and upper mantle. Dreibus and Wänke (1989) tabulate the terrestrial mantle N inventory as "?". Schidlowski *et al.* (1983) give as their preferred mantle estimate 5.6×10^{19} kg N (used in Table 6.1), but cite other estimates as high as 2.0×10^{20} kg. Here, we intend simply to show, using Eq.(6.30), that impact erosion could remove a substantial quantity of whatever "excess" N may have been delivered.

Consider, then, the case of cometary delivery of the bulk of terrestrial volatiles (Column 5, Table 6.1). About half of the 25% of the collisions that were cometary, and about 10% of the remaining collisions, should have caused erosion of the atmosphere for masses $> m_*$. Hence $f \approx 0.2$ in Eq.(6.30). We consider a very simple model in which half of all the N delivered by comets remains in the early terrestrial atmosphere. Obviously, however, the exact quantity eroded depends on details of the early terrestrial atmosphere, in particular what fraction of N delivered to the early Earth remained as atmospheric N_2 (or ammonia, NH_3), and what fraction was incorporated into the sedimentary column. Detailed models could be pursued, although so much is uncertain about the early terrestrial atmosphere (see, e.g., Walker 1986) that it seems unwise to consider any but the simplest models. In any case, our purpose here is only to demonstrate the existence and possible magnitude of an effect.

To approximate cometary delivery and simultaneous atmospheric erosion, we have used Eq.(6.30), with m_* and m_{cap} scaled by Eq.(6.28) to an atmosphere with a mass equal to one in which half of the total nitrogen delivered, 7×10^{19} kg, is present in the atmosphere. Eq.(6.30) then shows that some 3×10^{19} kg of atmospheric N_2 may thereby be removed from Earth by impact erosion. This represents about one–half of the "excess" cometary nitrogen predicted by comparing Column 5 with Column 2 of Table 6.1. Considering the uncertainties of the various factors in Eq.(6.30), this result is perhaps fairly summarized by saying that atmospheric impact erosion can remove a quantity of N_2 about equal to that which is delivered in excess. Nevertheless, this result is far from a demonstration that erosion of exactly that needed to reconcile nitrogen delivery by comets with the (uncertain) terrestrial inventory did, in fact, occur.

Chapter 7

Exogenous Sources of Organic Molecules on the Early Earth[1]

'Others find the impact scenarios inherently implausible. "It's too much like manna from heaven," says Sherwood Chang of NASA Ames, an authority on extraterrestrial organic compounds. . . . Theories giving impactors a role in genesis "are very trendy right now," he adds, "but they are also very speculative."' (Horgan 1991)

7.1 Sources of Extraterrestrial Organics on Contemporary Earth

A variety of exogenous sources are known to be delivering organic molecules more–or–less intact to Earth at the present time. These include those interplanetary dust particles small enough to be gently decelerated by the atmosphere (An-

---

[1] As this dissertation is finalized, Chapter 7 is being rewritten, in light of referees' remarks, for publication in late 1991 as a review article in *Nature* by C. Chyba and C. Sagan. The reader is strongly urged to refer to that paper for the most recent treatment of the questions addressed in this chapter.

ders 1989), and meteorites large enough to avoid complete ablation, but small enough to be substantially decelerated during their fall (Wasson 1985, Anders 1989). Some impactors catastrophically fragment during atmospheric passage, as appears to have occurred with a comet or comet fragment over Tunguska, Siberia, in 1908 (Levin and Bronshten 1986). Fragmentation of a CI carbonaceous chondrite took place over Revelstoke, Canada, in 1965; photomicrographs of recovered millimeter-sized fragments reveal unheated interiors (Folinsbee *et al.* 1967) within which organics should have survived (Chyba *et al.* 1990). Finally, the discovery of apparently extraterrestrial amino acids in Cretaceous–Tertiary (K/T) boundary sediments at Stevns Klint, Denmark, has been taken to suggest that a large fraction of cometary organics might in fact survive giant impacts (Zhao and Bada 1989), although other delivery mechanisms appear more plausible (Zahnle and Grinspoon 1990, Chyba 1990b).

Each of these contemporary exogenous sources of organics should also have been present on the early Earth. In addition to direct delivery of intact exogenous organics, at least two other broad sources of prebiotic organics would have existed. One of these would have been impact-induced organic shock-synthesis, whether in the terrestrial atmosphere (Bar-Nun *et al.* 1970a,b, Fegley *et al.* 1986) or the vaporized material of surface rocks (Freund *et al.* 1986, Mukhin *et al.* 1989) or the impactor itself (McKay *et al.* 1989, Oberbeck *et al.* 1989). These latter sources may also be loosely referred to as "exogenous", as their importance declined with the ~100 Myr half-life of the heavy bombardment. In addition, a host of energy sources for *in situ* terrestrial synthesis of organics are known, as first summarized in 1959 by Miller and Urey (1959). In the years since this landmark paper, our understanding of some of these sources has advanced sufficiently to require their quantitative re-evaluation, an investigation we will begin in Chapter 8 (Chyba and Sagan 1991). Here we quantify the magnitude and time-dependence of the variety of exogenous sources of prebiotic organics. As this quantification relies strongly on our current understanding of the early terrestrial impact environment, we begin with a very brief review of the key results of Chapter 6.

7.2 Early Terrestrial Impact Environment

Attempts to estimate the impact environment of early Earth typically begin with analytical fits to the lunar cratering record. Such an approach intends to minimize the model-dependence of the conclusions, by basing the calculations as much as possible on available data. In practice, however, this procedure has remained quantitatively ambiguous, as the lunar cratering data are sufficiently imprecise to allow a broad range of choices of exponential decay constants (Chyba 1990a). However, in Chapter 6, we demonstrated that one particular fit both models adequately the cratering data, and also is in excellent agreement with terrestrial mantle and lunar regolith geochemical estimates of total meteoritic accretion by the Earth and Moon (Chyba 1991). We therefore employ this fit throughout this paper.

Data for the cumulative surface density of lunar craters with diameter $> D$, as a function of surface age t in billions of years (Gyr), are well modelled by the equation

$$N(t, D) = \alpha[t + \beta(e^{t/\tau} - 1)](D/4000 \text{ m})^{-1.8} \text{ km}^{-2}, \qquad (7.1)$$

where τ=144 Myr, corresponding to a 100 Myr decay half-life for the impactor population, $\alpha = 3.5 \times 10^{-5}$, and $\beta = 2.3 \times 10^{-11}$. The crater diameter D (in m) observed on the Moon is related to the mass m (in kg) and collision velocity v (in m s^{-1}) of an impactor by

$$m = 0.54\gamma v^{-1.67} D_c^{0.44} D^{3.36}, \qquad (7.2)$$

where $D_c \approx 1.1\times10^4$ m is the transition diameter at which lunar craters change morphology from simple to complex forms, and $v = 1.2 \times 10^4$ m s^{-1} for typical impacts on the Moon. The constant $\gamma = 1.4\times10^3$ kg s$^{-1.67}$ m$^{-2.13}$ depends on target and impactor densities, surface gravity, and impactor incidence angle. Eqs.(7.1) and (7.2) may be combined to give the number of objects of mass $> m$ that have impacted the Moon as a function of time t:

$$n(>m,t) = 3.1 \times 10^{8}[t + 2.3 \times 10^{-11}(e^{t/\tau} - 1)]m^{-b}\ \mathrm{kg}^{b}, \tag{7.3}$$

where b=0.54. The total mass, $M(t)$, incident on the Moon subsequent to some time t in impactors with masses in the range m_{min} to m_{max} is given by the integral:

$$M(t) = \int_{m_{max}}^{m_{min}} m[\partial n(>m,t)/\partial m]dm, \tag{7.4}$$

which yields

$$M(t) = 3.7 \times 10^{8}[t + 2.3 \times 10^{-11}(e^{t/\tau} - 1)](m_{max}^{1-b} - m_{min}^{1-b})\ \mathrm{kg}^{\mathrm{b}}. \tag{7.5}$$

To scale to the Earth, $M(t)$ must be multiplied by $\xi \approx 24$, the ratio of the terrestrial to the lunar gravitational cross sections at typical asteroid approach velocities.

Taking m_{max} to equal the mass of the lunar impactor that excavated the South Pole–Aitken basin ($D \approx$2200 km), or about 1.4×10^{19} kg by Eq.(7.2), and m_{min} to be negligible, Eq.(7.5) yields a total mass of 1.0×10^{20} kg incident on the Moon subsequent to the solidification of the lunar crust ~4.4 Gyr ago. About half this mass would actually have been retained by the Moon. This result is in good agreement with geochemical estimates (Sleep *et al.* 1989) of the meteoritic component mixed into the lunar crust, which yield $(0.4\text{–}1.5)\times10^{20}$ kg. Similarly, scaling Eq.(7.5) to Earth, and taking proper account of the statistical probability that the largest impactors incident on Earth were more massive than the largest incident on the Moon, gives an estimate of 1.5×10^{22} kg of material accumulated by Earth subsequent to 4.4 Gyr ago. This result is in excellent accord with terrestrial mantle geochemistry estimates (BVSP 1981) of post-core formation meteoritic input, which lie in the range $(1\text{–}4)\times10^{22}$ kg. The close agreement of Eq.(7.5) with both the lunar cratering record and the available lunar and terrestrial geochemical constraints suggests that it provides a reliable model for terrestrial mass accretion during the heavy bombardment. It may therefore serve as a basis for estimates of exogenous organic delivery.

7.3 Delivery of Intact Exogenous Organic Matter

Eq.(7.5), multiplied by ξ, gives the total mass incident on Earth in impactors within a certain size range, subsequent to some time t. A more useful quantity is the mass flux (kg yr^{-1}) at a particular time in the Earth's past. Combined with estimates of the organic mass fraction surviving delivery, this allows a quantitative comparison of these sources with photochemical or other *in situ* production rates of prebiotic organics (Miller and Urey 1959, Chyba and Sagan 1991) as a function of time. To this end, we define $\dot{M}(t) \equiv \xi[\partial M(t)/\partial t]$, the terrestrial mass flux from objects within a given mass range (m_{min} to m_{max}) being accreted by Earth at a time t. From Eq.(7.5),

$$\dot{M}(t) = 8.9 f(t)(m_{max}^{1-b} - m_{min}^{1-b}) \text{ kg}^b \text{ yr}^{-1}, \tag{7.6}$$

where $f(t) \equiv (1 + 1.6 \times 10^{-10} e^{t/\tau})$. The following discussion will also require $\dot{n}(t) \equiv \xi[\partial n(> m, t)/\partial t]$, the number flux of objects within a given mass range being accreted by Earth as a function of time. From Eq.(7.3),

$$\dot{n}(t) = 7.4 f(t)(m_{max}^{-b} - m_{min}^{-b}) \text{ kg}^b \text{ yr}^{-1}. \tag{7.7}$$

The existence of 3.5 Gyr–old microfossils and stromatolites, and evidence for biologically mediated carbon isotope fractionation in 3.8 Gyr–old Isua metasediments (Schidlowski 1988), suggest choosing the period prior to 3.5–3.8 Gyr ago to assess exogenous delivery of prebiotic organics. On the other hand, the treatment of the terrestrial impact environment cited above is certainly not reliable prior to

4.4 Gyr ago (Chyba 1991). Moreover, delivery of organic molecules before ~4.4 Gyr ago was probably useless to the origins of life, because of subsequent surface pyrolysis of organics by giant impacts (Sleep *et al.* 1989). Such "impact frustration" may also have occurred much more recently than 4.4 Gyr ago. We therefore give our results as an exogenous organic mass flux subsequent to 4.4 Gyr ago (see Figure 7.1), to allow the influx to be readily determined for whatever epoch a particular model for the origin of life suggests is appropriate.

7.3.1 Interplanetary Dust Particles (IDPs)

Anders (1989) has recently estimated the flux of intact organic matter reaching the contemporary Earth due to IDPs and meteorites. The bulk of the mass in IDPs is in the 100μm to 300μm size range, or, for a typical initial density ~1 g cm^{-3} (Love and Brownlee 1991), in particles with masses $\sim 10^{-5}$ g. The mass scaling shown in Eq.(7.6) leads one to expect most incident mass to lie in the largest particles, but in fact this scaling breaks down for particles with masses $\lesssim 10^2$ g, probably due to dust production from larger bodies (Kyte and Wasson 1986). The global mass flux in particles below 10^2 g is observed to increase with decreasing size until it peaks at $\sim 10^{-5}$ g.

Anders (1989) takes IDPs to be ~10% organic carbon by mass, a mean carbon content determined from 30 IDPs by X-ray analysis (Schramm *et al.* 1989). He takes IDPs in the 10^{-12}–10^{-6} g (~0.6–60μm) range to be sufficiently gently decelerated during atmospheric entry to deliver their organics intact. Anders' 60μm upper limit is in good agreement with results of both theoretical modelling (Love and Brownlee 1991) and direct examination of IDPs (Brownlee 1985). His lower limit is based on an estimate of the size below which IDP organics would be destroyed by ultraviolet photolysis; this choice could vary considerably without significant quantitative effects on the final result. It remains unclear whether the more fragile organic species would survive IDP atmospheric passage (Chyba

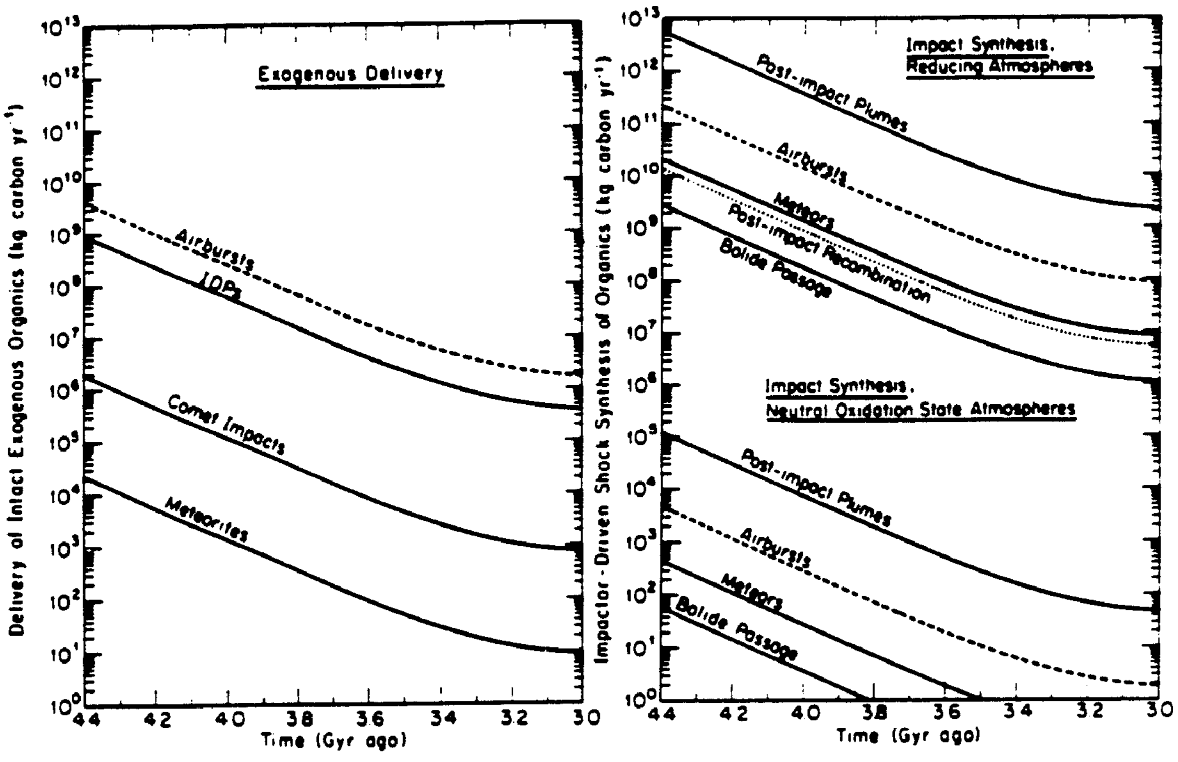

Figure 7.1 Exogenous organic carbon provided to Earth as a function of time, from (a) sources delivering intact extraterrestrial organic molecules, and (b) impactor-driven shock synthesis of organics in the terrestrial atmosphere or post-impact vapor plume. Labels correspond to the appropriate section of the text. In (b), the upper curves are for CH_4+(N_2 or NH_3)+H_2O reducing atmospheres, and the lower curves are for CO_2+N_2+H_2O neutral oxidation state atmospheres. Solid lines represent the more secure estimates; the relative importance of these is unlikely to be altered by uncertainties in the calculations. Dashed lines indicate upper bounds, and the dotted line denotes an estimate that is especially poorly understood, although perhaps largely independent of the oxidation state of the atmosphere.

1990b), especially at the high velocities appropriate to cometary-derived particles (Flynn 1989, Love and Brownlee 1991); there is probably a kind of deceleration heating natural selection of the thermodynamically most stable species.

Earth is currently accreting (Kyte and Wasson 1986) $\sim 3.2\times 10^6$ kg yr^{-1} of 10^{-12}–10^{-6} g IDPs, or $\dot{m}(0) \approx 3.2\times 10^5$ kg yr^{-1} of intact organics (Anders 1989). This quantity may be scaled to the early Earth using Eq.(7.7) to relate $\dot{m}(0)$, the IDP organic carbon accretion rate at present, to $\dot{m}(t)$, the accretion rate at some earlier time t. Using Eq.(7.7), we find $\dot{m}(t) = \dot{m}(0)[\dot{n}(t)/\dot{n}(0)]$, or

$$\dot{m}(t) = \dot{m}(0)f(t), \tag{7.8}$$

shown as a function of time in Figure 7.1(a).

7.3.2 Meteorites

Anders (1989) also estimates the contemporary terrestrial accretion rate of intact organic matter from meteorites. This calculation requires an estimate of the mass range (10^1–10^8 g) over which meteorites are both sufficiently decelerated by atmospheric passage for their organics to survive, yet not completely ablated away. Also required is an estimate of the percentage of meteorites incident on Earth which are either carbonaceous or non-carbonaceous. Anders chooses a 50% contribution from each type, giving an overall mean organic carbon content of 1.3%, and a total contemporary organic carbon accretion rate of 7.6 kg yr^{-1}. Taking this value as $\dot{m}(0)$ in Eq.(7.8) allows the meteoritic organic carbon input through time to be calculated, as shown in Figure 7.1(a). This source is clearly so negligible compared to IDPs that even large errors in calculated ablation rates or other parameters would not transform meteorites into a quantitatively important source of prebiotic organics.

7.3.3 Asteroid and Comet Impacts

What is the fate of organics incident on Earth in bodies larger than the 10^8 g (~5 m diameter) meteorites considered above? Such objects are insufficiently aerobraked by the current 1 bar terrestrial atmosphere for their organics to survive (Chyba *et al.* 1990). However, certain plausible early-Earth models suggest that Earth may have had a dense, ~10 bar CO_2 atmosphere sometime prior to 3.8 Gyr ago (Walker 1986, Kasting and Ackerman 1986). Under these conditions, comets with radii as large as ~100 m would have been sufficiently aerobraked (after as much as ~80% ablation during atmospheric passage) for most remaining organics to have survived impact with the terrestrial ocean. Carbonaceous asteroids of similar size would not have been sufficiently aerobraked (Chyba *et al.* 1990).

In Chapter 5, we considered a broad range of possible early terrestrial impact environments, due to uncertainties in lunar cratering data. Since then, as discussed in Chapter 6, these uncertainties appear to have been considerably reduced by appealing to lunar and terrestrial geochemical constraints (Chyba 1991). Following Delsemme's analysis of comet Halley data (Delsemme 1991), we take ~83% of cometary carbon to be present in organic form, and comets to be ~17% carbon by mass, so that comets are ~14% organic carbon by mass (carbon therefore accounting for more than half of the total organic mass of ~25% noted in Chapter 5). Analogously to Eqs.(5.4), the mass flux of cometary organic carbon surviving impact at time t is given by Eq.(7.8), with $\dot{m}(0) = 6.6 \times 10^2(\psi/0.1)$ kg yr^{-1}. Here ψ, chosen to be 0.1, is the mass fraction of the ancient impacting flux that was cometary. As discussed in Chapter 4, none of the data pertaining to the value of ψ is conclusive, although it seems likely (Chyba 1987) that $\psi \lesssim 10$–20%. Our results, labeled "comet impacts" in Figure 7.1(a), scale linearly, so the effect of a different choice for ψ is evident. More recent numerical modelling, extending earlier two-dimensional hydrodynamic impact models (Chyba *et al.* 1990) to a full three dimensions, suggests the two-dimensional results used here may underestimate organic delivery from cometary impacts by a factor ∼3 (Thomas *et al.* 1990, P.J. Thomas and L. Brookshaw, 1991, personal communications).

7.3.4 Catastrophic Airbursts

Photometric observations of Earth–crossing asteroids imply that the current asteroidal flux at Earth is ∼50% C–type (Shoemaker *et al.* 1979). Yet of 17 terrestrial craters for which impactor type may be identified, only two appear to be due to carbonaceous chondrites (Grieve 1982). Similarly, the latter constitute only ∼5–6% of stony meteorite falls (Wasson 1985, Anders 1989), although they represent over one–third of $10^2 - 10^6$ g Prairie Network fireballs (with another one–third seemingly having cometary origins) (Ceplecha 1977). It therefore appears that carbonaceous chondrites have material strengths so low that they are typically unable to survive atmospheric passage without breakup (Baldwin and Sheaffer 1971). Evidence from meteorite falls (Baldwin and Shaeffer 1971, Levin and Bronshten 1986) seems consistent with a compressive strength for carbonaceous chondrites of $\sigma_c \approx 10^6$ Pa (10 bars), orders of magnitude below typical rock strengths. In this case, the catastrophic fragmentation of the Revelstoke object (Folinsbee *et al.* 1967) may be a typical fate for carbonaceous impactors. Because of the increased surface area to volume ratio of the resulting fragments, such airbursts might then provide an efficient mechanism for exogenous organics to reach Earth (Chyba *et al.* 1990).

We estimate the magnitude of this source in the following way. A bolide will airburst when the differential pressure between its leading and trailing edges exceeds its material strength (Baldwin and Shaeffer 1971, Passey and Melosh 1980, Levin and Bronshten 1986, Chyba *et al.* 1990). Since the pressure in the bolide's wake is nearly zero, this differential pressure is simply equal to the stagnation pressure ρv^2 (where ρ is atmospheric density) experienced by the bolide's leading hemisphere. For a typical carbonaceous asteroid with $\sigma_c \approx 10^6$ Pa and atmospheric entry velocity $v = 15$ km s^{-1}, $\rho = \sigma_c/v^2$ at an altitude just under 40 km (see Walker 1977, Table 1-1). However, only those impactors small enough such that the pressure wave atmospherically induced at this altitude has time to traverse the bolide before terrestrial impact may undergo airburst. Therefore the bolide diameter d must obey $d \lesssim ch/v$, where $h \approx 40$ km, and c is the sound speed within the bolide. (For weak shock waves (Zel'dovich and Raizer 1967), as is the case here, the shock traverses the body at c.)

What value of c is appropriate for a carbonaceous asteroid? Typical sound speeds for granite, diabase, or basalt are in the 4–5 km s^{-1} range (Touloukian *et al.* 1981). However, carbonaceous asteroids are expected to have lower densities (~2.2 g cm^{-3} (Melosh 1989)), and so should have lower values for c. Porous terrestrial rocks, such as dry sandstones with densities of 2.0 to 2.6 g cm^{-3}, have c ranging from 3.0 to 5.0 km s^{-1}, respectively (Touloukian *et al.* 1981). Permafrost clays have c between 2.0 and 3.9 km s^{-1}, and polycrystalline ice has $c \approx 3.2$ km s^{-1} (Christensen 1989). We choose c=3.0 km s^{-1} as a reasonable value for a typical carbonaceous bolide, giving $d \lesssim 8$ km. Clearly variations in v and c could change this value by as much as several km. Note that d is approximately equal to the terrestrial atmospheric scale height (Walker 1977) $H \approx 8.4$ km, in agreement with the intuition that bolides with $d \gtrsim H$ are too large to "see" the atmosphere. $d \approx 8$ km is about the diameter of the bolide required to explain the K/T boundary iridium layer (Alvarez *et al.* 1980); it may therefore not be out of the question that the K/T bolide catastrophically disrupted in the atmosphere (Chyba *et al.* 1990, Chyba 1990b).

An approximate upper limit to organic delivery via airbursting asteroids and comets may be obtained by taking m_{max} in Eq.(7.6) to be that appropriate to a 4 km radius chondrite or comet. In this calculation, we take 10% of the impacting mass to be cometary, with the remainder split evenly between carbonaceous and ordinary chondrites. Eq.(7.6) then becomes $\dot{M}(0) = (1.4 \times 10^6 \text{ kg yr}^{-1}) f(t)$, and is shown in Figure 7.1(a). Clearly this value is an upper limit, as it ignores organic destruction in the airburst event itself (the Tunguska object exploded with an energy of $\sim 10^{16}$ J, or several kilotons of high explosive (Levin and Bronshten 1986)), or in subsequent ablation of the resulting fragments. Moreover, not all carbonaceous asteroids with $d \lesssim 8$ km airburst while traversing the atmosphere: Scaling Eq.(7.2) to the Earth, we find that two terrestrial craters known to have resulted from impacts of carbonaceous chondrites, Lappajärvi and East Clearwater (Grieve 1982), required impactors of diameters just over 1 km and 3 km, respectively (we assume the Clearwater object fragmented to excavate both East and West Clearwater craters). This latter object had a size close to that calculated here for disruption. However, while these craters are consistent with impacts by either intact bolides or tightly clustered fragments (Passey and Melosh 1980), they are inconsistent with a Revelstoke–like airburst.

Suppose that early Earth did indeed have a $\sim$10 bar CO_2 atmosphere at the time of the origins of life (Walker 1986). How would the above results differ? We have already noted that in this case, organics in comets as large as $\sim$100 m could survive impact. Delivery by IDPs should remain unchanged, as these particles would simply decelerate at a higher altitude. Finally, airbursting impactors would first experience critical stagnation pressures at altitudes $\sim \log_e(10)$ scale heights higher than in a 1 bar atmosphere, but the magnitude of this effect is no greater than uncertainties already present due to σ_c and c.

7.4 Impactor–Driven Shock Synthesis of Organic Molecules

In 1963, Gilvarry and Hochstim suggested that shock waves from meteoroids traversing the terrestrial atmosphere may have synthesized organics on early Earth (Gilvarry and Hochstim 1963). It was demonstrated in 1970 that shock heating of laboratory reducing gas mixtures yielded amino acids in high yield

(Bar–Nun *et al.* 1970a,b), although more recent results (Bar–Nun and Shaviv 1975) suggest that the experimental efficiency (molecules J^{-1}) first reported (Bar–Nun *et al.* 1970a,b) for amino acid synthesis in $CH_4/C_2H_6/NH_3/H_2O$ atmospheres appears to be overestimated by a factor ~30. However, while previous studies have suggested that atmospheric shock synthesis may have been an important source of terrestrial organics (Bar–Nun *et al.* 1970a,b, Fegley *et al.* 1986), estimates of both the early terrestrial impact environment and the coupling efficiency of an impactor's energy with the atmosphere may now be considerably updated and extended.

The mass of organics shock-synthesized in the atmsophere by an impactor of mass m is given by $\eta e_c \Delta E(m)$, where $\Delta E(m)$ is the energy the object delivers to the atmosphere, e_c is the efficiency with which this energy is converted to shock energy, and η is the organic synthesis efficiency (kg organic carbon produced per joule of shock energy); η is strongly dependent on atmospheric composition. To indicate its range of possible values, we consider here two oxidation state end–members of plausible early–Earth atmospheres (Walker 1986, Chyba *et al.* 1990).

A thermochemical model of shock synthesis in reducing $CH_4+N_2+H_2O$ atmospheres (Chameides and Walker 1981) gives a hydrogen cyanide (HCN) production efficiency of $\sim 10^{17.5}$ molecules J^{-1}, in excellent agreement with laboratory results (Rao *et al.* 1967, Bar–Nun and Shaviv 1975) of $\sim 2 \times 10^{17}$ molecules J^{-1}. These experiments also show simultaneous formation of very simple hydrocarbons, such as C_2H_2 and C_2H_4, as well as carbon soot (Rao *et al.* 1967). While these results are temperature–dependent, typical organic C yields, ignoring soot, are ~3 times that of HCN alone (Rao *et al.* 1967).

Because of the strength of the N_2 bond, we might expect efficiencies to increase in atmospheres where N is present as NH_3, rather than N_2. In fact, this effect is unimportant at the high shock temperatures appropriate here. Both high–

power laser simulation, and theoretical high-temperature–equilibrium modelling, of shocks in NH_3/CH_4 atmospheres give HCN production yields (McKay *et al.* 1988) of $\sim 3 \times 10^{17}$ molecules J^{-1}. Hydrocarbons at least up to pentane (C_5H_{12}) are also produced. Using the experimental yields reported for all C-containing organic species gives a total efficiency for organic C production $\eta \approx 1.2 \times 10^{-8}$ kg J^{-1} for a reducing atmosphere (McKay *et al.* 1988), a result virtually identical with that found for N_2/CH_4 atmospheres (Rao *et al.* 1967, Bar-Nun and Shaviv 1975, Chameides and Walker 1981). Efficiencies for HCN production in neutral oxidation state, CO_2+N_2+H_2O atmospheres, are $\sim 10^{7.5}$ times smaller (Chameides and Walker 1981). In this case, formaldehyde (H_2CO) production is comparable (Fegley *et al.* 1986) to that of HCN, giving $\eta \approx 2.5 \times 10^{-16}$ kg J^{-1} for CO_2 atmospheres.

7.4.1 Shocks from Bolide Passage Through the Atmosphere

An impactor of mass m loses kinetic energy $\Delta E(m)$ while traversing the terrestrial atmosphere, some fraction e_c of which is converted into atmospheric shock waves. $\Delta E(m)$ is given by

$$\Delta E(m) = \left(\frac{1}{2}\frac{dm}{dt}v^2 + mv\frac{dv}{dt}\right)\left(\frac{H}{v}\right). \tag{7.9}$$

The first factor on the right hand side is the sum of energy losses due to ablation and deceleration, respectively, and the second is the time spent traversing the lower atmosphere, given by the scale height H divided by the impactor's velocity v. The ablation and deceleration terms in Eq.(7.9) are, from standard aerodynamic theory (Baldwin and Shaeffer 1971, Melosh 1989):

$$dm/dt = -C_H \rho v^3 A(2\zeta)^{-1} \quad \text{and} \quad dv/dt = -C_D \rho A v^2 m^{-1}. \tag{7.10}$$

Here $C_H = 0.01$ is the heat transfer coefficient (Chyba *et al.* 1990), ρ=1.23 kg m^{-3} is the current atmospheric density at the Earth's surface (Walker 1977),

$A = S_F(m/\delta)^{2/3}$ is the frontal area of an impactor of density δ and shape factor S_F (1.92 for a hemisphere (Baldwin and Shaeffer 1971)), $C_D = 0.92$ is the drag coefficient (O'Keefe and Ahrens 1982), and $\zeta = 3.2\,\mathrm{MJ\ kg^{-1}}$ is the heat of ablation appropriate to a carbonaceous chondrite (Chyba *et al.* 1990). In principle, v in Eq.(7.9) is a function of time t, so that $\Delta E(m)$ should be determined by numerical integration over dt, decrementing v according to Eq.(7.10) at each step. In practice, $\Delta E(m)$ is dominated (see Eq.(7.12) below) by large objects for which dv/v is sufficiently small that Eq.(7.9) provides a good approximation.

The total mass of organics shock-synthesized due to impactor passage through the terrestrial atmosphere as a function of time is then given by

$$\dot{\mu}(t) = \eta e_c \frac{\partial}{\partial t} \int_{m_{min}}^{m_{max}} \Delta E(m) \xi [\partial n(> m, t)/\partial m] dm. \tag{7.11}$$

Evaluating the integral yields

$$\dot{\mu}(t) = 2.6 \eta e_c \xi H \rho \delta^{-2/3} v^2 [C_H v^2 (4\zeta)^{-1} + C_D] f(t) (m_{max}^{2/3-b} - m_{min}^{2/3-b})\ \mathrm{kg}^b\ \mathrm{yr}^{-1}. \tag{7.12}$$

Pollack *et al.* (1986) and McKay *et al.* (1988) have selected a value $e_c \approx 0.3$ for the efficiency of converting impactor kinetic energy into atmospheric shock heating, based on analyses of meteorite ablation in the contemporary atmosphere (Bronshten 1983). Adopting this value, Eq.(7.12) for an atmosphere with ρ=1.23 kg m^{-3} becomes

$$\dot{\mu}(t) = \eta (8 \times 10^{13}\ \mathrm{J\ yr^{-1}}) f(t). \tag{7.13}$$

$\dot{\mu}(t)$ is shown in Figure 7.1(b) for both CH_4+(N_2 or NH_3)+H_2O and CO_2+N_2+H_2O atmospheres. In Eq.(7.13), we have used $v = 15$ km s^{-1}; at this velocity, impactor deceleration deposits five times as much energy in the atmosphere as does ablation.

There is a strong velocity-dependence in Eq.(7.12); an obvious concern is that a small number of unusually fast impactors (Chyba 1991) could dominate $\dot{\mu}(t)$, but have been ignored here. This concern is mitigated, however, by the fact that impactors with velocities $\gtrsim 24$ km s^{-1} and masses $\gtrsim 10^{15}$ kg will erode the entire atmospheric cap above the tangent plane to the point of impact (Melosh and Vickery 1989). Organics synthesized by such impactors would be blown away into space, so would not contribute to $\dot{\mu}(t)$. Only ~10% of asteroid, and ~50% of comet, collisions with Earth occur at velocities sufficient to cause erosion (Chyba 1991), effects small (unless comets comprised the bulk of heavy bombardment impactors) compared with other uncertainties in the problem.

7.4.2 Shocks from Meteors

Eq.(7.12) scales extremely weakly with m ($\dot{\mu}(t) \propto m^{0.13}$) because large impactors are so little decelerated or ablated (per unit mass) by the atmosphere. Indeed, Eq.(7.13) implies, via division by $\dot{M}(t)v^2/2$ from Eq.(7.6) above, that only ~0.04% of the total kinetic energy of all impactors striking Earth is lost traversing the atmosphere. However, Eq.(7.12) assumes a power-law number-mass distribution of impactors, given by Eq.(7.3), that holds to arbitrarily small sizes. In fact, there is a mass peak (Kyte and Wasson 1986) in infalling meteoritic matter below $\sim 10^2$ g. Remarkably, objects below this mass deposit more kinetic energy in the terrestrial atmosphere than the passage of all impactors with $m > 10^2$ g combined, as given by Eq.(7.13). Approximately 1.6×10^7 kg yr^{-1} strikes the Earth's atmosphere in $10^{-14} - 10^2$ g meteors. These objects lose 100% of their kinetic energy in the atmosphere. Assuming an average velocity of 15 km s^{-1}, about midway between those typical for asteroidal and cometary IDPs (Love and Brownlee 1991), meteors deposit 1.8×10^{15} J yr^{-1} into the present atmosphere, or ~8 times more energy, albeit at higher altitudes, than do all the larger objects. Again taking $e_c \approx 0.3$, total organic production in the atmosphere by meteors (Figure 7.1(b)) is given by $\dot{m}(t) = \eta(6 \times 10^{14}\ \mathrm{J\ yr^{-1}})f(t)$.

7.4.3 Shocks from Airbursts

Eq.(7.13) ignores the possibility that objects as large as ~4 km in radius may airburst, thereby coupling their entire kinetic energy to the atmosphere (Lewis *et al.* 1982). Eq.(7.6) may be used to put an upper limit on the importance of this effect. Assuming that 100% of all objects with radii < 4 km do airburst, Eq.(7.6), for this choice of m_{max}, multiplied by $v^2/2$, becomes $\dot{m}(t) = \eta(6.2 \times 10^{15}\ \mathrm{J\ yr^{-1}})f(t)$. This upper limit is shown in Figure 7.1(b).

7.4.4 Post–Impact Shocks

So far we have considered coupling the impactors' kinetic energy to the atmosphere during flight. However, for large impactors, the total energy imparted to the atmosphere by the rapidly-expanding post-impact plume is much greater than that lost by the bolide during atmospheric passage (O'Keefe and Ahrens 1982, Prinn and Fegley 1987). Since the bulk of impactor kinetic energy incident on Earth lies in the largest impactors (see Eq.(7.6)), this will be the dominant energy source for atmospheric shock processing, if the energy of these objects couples efficiently to shocks from post-impact vapor plumes.

We estimate the magnitude of this effect following a simple thermodynamic treatment of vapor plume expansion (Melosh and Vickery 1989, Melosh 1989). We take the mass of the plume to be approximately twice that of the impactor mass (Melosh and Vickery 1989). The plume mass-averaged expansion velocity is $[2(E - H_{vap})]^{1/2}$, where, for an impactor incident at velocity v, $E \approx v^2/8$ is the specific energy of the vaporized projectile and target material, and H_{vap} is the vaporization energy, about 13 MJ kg^{-1} for silicates. The plume kinetic energy is then $2m[(v^2/8) - H_{vap}]$. Dividing this by the kinetic energy of the impactor shows that the expanding vapor plume has about 25% of the incident impactor's kinetic energy, a result consistent with typical approximations in the literature (Prinn and Fegley 1987). This energy couples extremely efficiently

($\sim$100%) to the atmosphere (O'Keefe and Ahrens 1982). Multiplying Eq.(7.6) by $0.25(v^2/2)$, post-impact vapor plume processing of the atmosphere is then given by $\dot{m}(t) = \eta(1.6 \times 10^{17}\ \mathrm{J\ yr^{-1}})f(t)$. As seen in Figure 7.1(b), this is by far the dominant source of atmospheric shock energy.

The resulting timescale at 4.4 Gyr ago for complete shock processing of a 1 bar CH_4 atmosphere is $\sim 10^6$ yr. Even if all impactor-delivered carbon predicted by Eq.(7.6) were immediately put into the atmosphere as CH_4, this exogenous source could not resupply the atmosphere as quickly as CH_4 was processed to more complex organics. Therefore, a 1 bar CH_4 atmosphere on early Earth could only have been sustained if terrestrial volcanism or other endogenous sources re-supplied CH_4 to the atmosphere at a rate $\sim 2 \times 10^9 f(t)$ kg yr^{-1}, or 6×10^{12} kg yr^{-1} 4.4 Gyr ago. Terrestrial volcanoes are estimated (Walker 1977) to currently release as much as $\sim 4 \times 10^{10}$ kg yr^{-1} of carbon into the atmosphere, mostly in the form of CO_2. If carbon were released on a reducing primitive Earth as CH_4, early terrestrial volcanism would need to have been $\sim$150 times more intense than today to maintain an early reducing atmosphere against impactor shock-processing. In the absence of such heightened volcanic recycling of carbon, early terrestrial sediments should be so organic-rich as to represent a *reductio ad absurdum* of the reducing atmosphere model for early Earth (Abelson 1966). This constraint is inapplicable to the geologic record subsequent to 3.5 Gyr ago, where microorganisms would be expected to metabolize abiotically-produced organics (Schidlowski *et al.* 1983, Stoker *et al.* 1990). Organic carbon in the 3.8 Gyr old Isua metasediments may represent metamorphosed biologically-mediated material; however, it is intriguing that $^{13}C/^{12}C$ ratios here are distinct from those of later sediments, and at least marginally consistent with fractionations observed in abiotic organic synthesis (Schidlowski *et al.* 1983).

7.4.5 Post–Impact Recombination

Several authors have suggested that organic molecules may have formed on early Earth by recombination from reducing mixtures resulting from the shock vaporization of impacting bolides (McKay *et al.* 1989, Mukhin *et al.* 1989, Oberbeck *et al.* 1989). Others have suggested organic molecules might be similarly produced by impact shocks of terrestrial rocks (Freund *et al.* 1986, Mukhin *et al.* 1989). McKay *et al.* (1989) have attempted to simulate the former process using a thermochemical model. Their preliminary results show evidence for post–impact organic shock synthesis. However, these simulations assumed as initial conditions a reducing mixture equivalent to the elemental composition of comets. In an actual impact, as much target material (oxygen–rich surface rocks) as impactor would be incorporated into the expanding and cooling vapor plume (Melosh and Vickery 1989), and background atmosphere, possibly CO_2–rich, might also be entrained. The applicability of results for an initially reducing ($[O]<[H_2]$) vapor mixture is therefore unclear.

At the same time, there are some relevant experimental data. Barak and Bar–Nun (1975) have demonstrated amino acid shock synthesis even when initial gas mixtures contain large quantities of H_2O and air. Amounts of oxygen as large as $[O_2]/[C_2H_6]=2.5$ did not significantly lower amino acid yields. Mukhin *et al.* (1989) have simulated shock vaporization and organic recombination using laser–pulse heating of a variety of terrestrial rocks and meteorite samples, and report a wide range of products of varying oxidation states. Unfortunately, their experiments vaporized only a fraction of the target, so organics may have been released from melted and heated target material, as well as synthesized in post–vaporization recombination. Experiments in which the entire target is vaporized seem called for.

Mukhin *et al.* (1989) performed their experiments in the presence of both He and H_2 background atmospheres. The ratio of produced ($CO+CO_2$) to hydrocarbons decreased by factors 2–5 for the H_2 atmosphere, suggesting entrainment of some background gas. (Of course, how to scale this result to giant terrestrial impacts is unclear.) We recommend that experiments be attempted using CO_2 and air as background gases, so the effect of non-reducing background atmospheres can be explored. Experiments in air would be of particular interest (Chyba *et al.* 1990) with respect to the apparently non-biological amino acids found at the K/T boundary (Zhao and Bada 1989).

Nevertheless, we may ask what results Mukhin *et al.* (1989) found for their vaporization experiments. Firstly, most carbon was incorporated into CO and CO_2, but typically several % (He atmosphere) went into hydrocarbons, and smaller amounts of HCN and aldehydes. This was true for terrestrial rocks such as basalt, peridotite, and gabbro, as well as samples of ordinary and carbonaceous chondrite. This suggests that oxygen in vaporized surface rock does not prevent the formation of hydrocarbons. The resulting ratio of ($CO+CO_2$) to hydrocarbons was roughly constant, even as initial C wt% of the sample varied over more than an order of magnitude; this seems to be consistent with post-shock recombination, rather than escape of unshocked organics. Hydrocarbon production (like that of CO and CO_2) scaled with the carbon content of the sample.

Consider the result of directly scaling the Mukhin *et al.* (1989) experiments up to impacts of comets and asteroids with early Earth. First note that organic production from surface rocks is unimportant (~10%) compared with that for the C-rich impactors, so we henceforth ignore the former. Assuming 10% of the impacting mass to be cometary (~17% carbon), of which 50% is blown out into space (Chyba 1991), and the remainder asteroidal (~1.3% C) and taking the Mukhin *et al.* (1989) result that ~4% of impactor carbon is incorporated into organics, we find post-impact recombination produced organic carbon at a rate $\dot{m}(t) = (4.6 \times 10^6 \text{ kg yr}^{-1})f(t)$ on early Earth. To the extent that recombination occurs without significant entrainment of atmosphere, this result is independent of terrestrial atmosphere oxidation state. We emphasize the uncertanities in the preceding calculation by displaying post-impact recombination results as a dotted line in Figure 7.1(b).

At the time of the origins of life ~4 Gyr ago, IDPs (and, possibly, efficient airbursts and post-impact recombination) were delivering or producing $\gtrsim 10^8$ kg yr^{-1} of organic carbon (or more than one contemporary terrestrial biomass (Hayes *et al.* 1983) of organics every 10 Myr), regardless of the oxidation state of the terrestrial atmosphere. Typical estimates (Stribling and Miller 1987) of *in situ* production rates for terrestrial CO_2 atmospheres are $\sim 10^9$ kg yr^{-1} for H_2/CO_2 ratios near unity. However, the rates drop precipitously by orders of magnitude as this ratio falls. Therefore it appears that in such CO_2 atmospheres, exogenous sources of organics were at least as important as endogenous ones. Organic production in CH_4 atmospheres from endogenous sources may be as high as $\sim 10^{11}$ kg yr^{-1} if a long-wavelength ultraviolet photon receptor (Sagan and Khare 1971) that produces superthermal atomic hydrogen, such as H_2S, is present. However, as shown in Fig. 7.1(b), impactor-driven shock synthesis in such atmospheres appears to produce roughly equal quantities of organics. Therefore it seems that exogenous sources were of comparable quantitative importance to endogenous production, regardless of which oxidation state end-member for the early atmosphere is considered. A substantial, possibly dominant, fraction of the prebiotic organic molecules from which terrestrial life arose appears to have been exogenous in origin.

Chapter 8

Electrical Energy Sources for Organic Synthesis on the Early Earth[1]

8.1 Introduction

The comparative importance of various energy sources for the production of prebiotic organic molecules on early Earth was first assessed by Miller and Urey (1959). While these authors identified ultraviolet light (UV) as the most abundant energy source contributing to organic synthesis in a reducing atmosphere, they also noted that electrical discharge sources (lightning and corona) were second to UV in total power (energy per unit time averaged over Earth's surface), and would act closer to the surface, leading to more efficient transfer of products to the oceans. Recent work for "neutral" oxidation state, largely carbon dioxide atmospheres, now generally viewed as more likely candidates for the atmosphere of early Earth (Walker 1986), has suggested that organic synthesis due to electri-

---

[1] This chapter is based on the paper, Chyba, C. and C. Sagan (1991), Electrical energy sources for organic synthesis on the early Earth, *Origins of Life*, accepted for publication [copyright 1991 by Kluwer Academic Publishers].

cal discharge would have been comparable in importance to any other terrestrial source (Stribling and Miller 1987). These estimates have helped to reassure experimenters of the relevance of electrical discharges (convenient laboratory energy sources) to terrestrial prebiological organic chemistry. However, such calculations are based upon Miller and Urey's original estimates of global lightning and coronal sources of energy, now over thirty years old. Although their values remain those typically cited in the origins of life literature (Bar–Nun *et al.* 1970, Fox and Dose 1972, Miller and Orgel 1974, Miller *et al.* 1976, Day 1984, Stribling and Miller 1987, Oró *et al.* 1990), and in biology textbooks (e.g., Darnell *et al.* 1990, Strickberger 1990), more recent work in terrestrial lightning and point discharge research suggests that they are overestimates by factors of about 20 and 120, respectively. Calculated concentrations of amino acids (or other prebiological organic products) in the early terrestrial oceans due to electrical discharge sources may therefore have been equally overestimated.

To our knowledge, all attempts to estimate electrical sources of energy available for early terrestrial organic synthesis have assumed that lightning and coronal energy discharge rates on early Earth were the same as those today. While we examine this assumption more carefully below, there appears to be no better way to attack the problem, and we adopt it here. We note, however, that this assumption could be the dominant source of uncertainty in our conclusions.

8.2 Lightning Discharges

Before proceeding to quantitative estimates, we briefly review terminology from lightning research (detailed presentations may be found in Schonland 1953, Chalmers 1967, Uman 1969, Dawson 1980, and Uman and Krider 1989). Lightning can take place entirely within a cloud (intracloud discharges), between a cloud and the earth (cloud–to–ground discharges), between two clouds (cloud–to–cloud discharges), or between a cloud and the surrounding air (air discharges). The latter two types of discharge are comparatively rare. Although intracloud discharges are more common than cloud-to-ground discharges, cloud-to-ground discharges are by far the better studied of the two. (Differences in frequency and discharge energies between the two will be further discussed below.) A typical cloud-to-ground discharge develops roughly as follows (Uman 1969, Dawson 1980, Uman and Krider 1989): As a result of poorly-understood processes of charge separation in a thundercloud, local electrical breakdown occurs, mobilizing electric charges that were previously attached to ice and water particles. The resulting negative charge concentration at the cloud base initiates a negatively charged column, the "leader", which then propagates downward. For reasons that remain unclear, this initial leader grows towards the ground in a stepwise fashion. Once sufficiently close to the ground, the high negative potential results in an electric field sufficient to cause upward-moving discharges to be launched from the ground to the leader tip. The leader then acts as a transmission line, emptying its charge to ground, first from its tip, and then from successively more distant points. This creates the "return stroke", a wave of luminosity moving from ground to cloud. Most of the energy of the discharge is released in this first stroke. The first stroke is often followed by successive leader/return-stroke sequences (successive leaders are termed "dart leaders", and travel in a smooth, rather than stepwise, pattern), along the original channel, at intervals of $\sim$40 msec. This complete sequence, which appears to the eye as a flickering, jagged chain, typically extends for $\sim$0.2 sec, and is termed the flash.

Miller and Urey (1959) based their estimates of global energy dissipation from lightning and corona discharges on the best data available in 1959, those summarized by Schonland (1953). Schonland (his Secs. 30,31) cited estimates that about 100 flashes of lightning occur over the surface of the Earth each second. (Of these, he took 1 in 4 to be a cloud-to-ground discharge. Schonland made no distinction between cloud-to-ground and intracloud flashes in his estimates

Table 8.1 Estimates* of Lightning Flash Discharge Energy (J flash^{-1})

Reference	Energy
Schonland (1953)	6×10^9
Hill et al. (1980)	8×10^7
Borucki & Chameides (1984)	4×10^8

*See text for discussion of uncertainties.

of energy dissipation.) He then reviewed (his Sec. 34) estimates of current discharges and potential differences in typical flashes. With a choice for a typical lightning flash discharge energy of 6×10^9 J, Schonland's results yield 2×10^{19} J yr^{-1} of electrical energy from terrestrial lightning, which is the value given by Miller and Urey.

The largest source of error in this result comes from an overestimate of the energy dissipated per lightning flash. Various estimates for this value are summarized in Table 8.1. Both Hill *et al.* (1980) and Borucki and Chameides (1984) based their values on extensive reviews of measurements of the energy dissipated in cloud-to-ground return strokes.

Hill *et al.* (1980) calculated terrestrial annual energy dissipation by lightning using a review by Hill (1979a), who examined four independent methods of estimating the energy dissipated along a cloud-to-ground first return stroke. One of these methods, acoustical measurements, yielded numerical values ranging over three orders of magnitude (10^2 to 10^5 J m^{-1}). Two others, electrical and theoretical estimates, ranged from 5×10^3 to 8×10^4 J m^{-1}, and from 3×10^3 to 2×10^4 J m^{-1}, respectively. (A more recent theoretical estimate of lightning energy dissipation gave a value $\sim 4 \times 10^3$ J m^{-1} (Paxton *et al.* 1986), smaller by a factor ~2.5 than that preferred by Hill (1979a); this result remains controversial, however (Hill 1987).) The sole determination of electrical energy dissipation per unit length by an optical method gave a result of 2×10^5 J m^{-1}; Hill (1979a) argued that this value should be revised downward by a factor of ~ 20. Hill (1979a) and Hill *et al.* (1980) gave a preferred value for the electrical, optical, and theoretical estimates of $\sim 10^4$ J m^{-1}. (Note that optical measurements of lightning return strokes indicate that stroke luminosity, and therefore probably energy dissipation, decays with height (Guo and Krider 1982). All estimates of lightning energy dissipation per unit length must therefore be understood to represent average values only.) Hill (1979a) gave the range of lengths for lightning strokes as 1 to 12 km, in agreement with other authors (for example, Uman (1969) gives a typical range to be 2 to 12 km). The upper value is roughly the thickness of the troposphere. Hill *et al.* (1980) chose 5 km as an average value, again a typical selection (Uman 1969). This gives the total energy dissipated by a first stroke along its length to be 5×10^7 J.

The number of strokes in an individual lightning flash has been observed to range from 1 to 26 (Uman 1969). Some 20% of flashes appear to be single strokes (Hill 1979a). Estimates in the literature for the average number of strokes per flash vary from 3 to 5 (Uman 1969, Berger 1977, Chameides *et al.* 1977, Hill 1979a, Hill *et al.* 1980, Borucki and Chameides 1984). However, subsequent strokes are typically less energetic than the first (Hill 1979a, Hill *et al.* 1980, Dawson 1980, Borucki and Chameides 1984). Dawson (1980) has argued that for this reason, the best approximation for molecular synthesis calculations is simply to count only the first stroke. Other authors, however, have incorporated the energy discharged in subsequent strokes. Hill *et al.* (1980), for example, used measurements of the charge transferred by the first and subsequent strokes, to conclude that the ratio of energies of successive strokes is approximately 2:1. Taking a three-stroke flash as typical, they concluded that a typical flash dissipates 1.5 ± 0.5 times as much energy as the first return stroke alone, giving about 8×10^7 J dissipated per flash.

What is the frequency of lightning flashes over the Earth? The modern estimate (Hill *et al.* 1980, Borucki and Chameides 1984) for the global flash rate, 100 $\sec^{-1}$, remains the same as the historical value (Schonland 1953). Satellite observations of nighttime thunderstorms from the OSO–B satellite, reported in 1970 by Vorpahl *et al.* , suggested a global nighttime average of $\sim$30 $\sec^{-1}$; however, these authors noted that some nighttime flashes may have been missed due to a combination of cloud cover and threshold limits. More recent results from the Defense Meteorological Satellite Program confirm the historical value. Orville and Spencer (1979) found a global frequency of 96 flashes s^{-1} for dusk observations, and 123 flashes s^{-1} for observations made at midnight. Turman and Edgar (1982) found 80±40 flashes s^{-1}, with 10% variation through the seasons. From an entirely different direction, Prentice (1977, Sec 2.3.2) reviewed results from visual, flash counter, and power transmission–line performance studies of cloud–to–ground flash frequencies; rates were observed to vary from 0.2 to 12.1 flashes km^{-2} yr^{-1}, bracketing the historical observations cited by Chalmers (1967, Sec. 14.34). Extrapolating these results globally, while incorporating the observation (Vorpahl *et al.* 1970) that 10 times as many lightning flashes occur over land areas as over the sea ($\sim$70% of Earth's surface area), yields a flash frequency of 1.2 to 71 cloud–to–ground flashes s^{-1}. In temperate climates, the frequency of intracloud flashes is $\sim$3, and in tropical climates, $\sim$6, times that of cloud–to–ground flashes, respectively (Prentice 1977). This observed latitudinal variation (Chalmers 1967, Prentice 1977) yields a globally averaged intracloud/cloud–to–ground flash ratio of $\sim$4 (Chameides *et al.* 1977). Scaling the observed cloud–to–ground flash frequency by this factor yields (very) rough agreement with the satellite observations, which are clearly the more reliable. It is unclear how the value of 100 flashes s^{-1} would have differed on an early Earth which may have had very little continental mass, and a possible dense CO_2 atmosphere (Walker 1986).

Table 8.2 Estimates* of Electrical Energy Available for Organic Synthesis on Early Earth (J yr^{-1})

Reference	Lightning	Coronal Discharge
Miller & Urey (1959)	2×10^{19}	6×10^{19}
Hill et al. (1980)	2×10^{17}	—
Chameides & Walker (1981)	2×10^{18}	—
Borucki & Chameides (1984)	1×10^{18}	—
This Work	1×10^{18}	5×10^{17}

*See text for discussion of uncertainties.

With 100 flashes s^{-1}, and an average energy of 8×10^7 J per flash, Hill *et al.* 's (1980) values yield a global lightning energy dissipation rate of 2×10^{17} J yr^{-1}, a value some 100 times below that suggested by Miller and Urey. (Results are summarized in Table 8.2.)

However, Borucki and Chameides (1984) have recently reviewed optical and electrical measurements of lightning energy dissipation, supplementing the measurements cited by Hill (1979a) with additional data, while excluding some of the more extreme determinations. Moreover, these authors employ the results of field measurements that give the total energy dissipated by the entire first return stroke, rather than an energy dissipation per unit length. Therefore, estimates of the length of the discharge column need not be made. In fact, for measurements of lightning energy dissipation, only rarely are estimates of the height of the discharge available. For this reason, Borucki and Chameides (1984) are able to average over many more optical and electrical measurements than is Hill (1979a). Borucki and Chameides choose 4 strokes per flash as typical, and argue that subsequent strokes dissipate about one quarter as much energy as the first return stroke. They thereby find an average energy dissipation for optical and electrical measurements of 4×10^8 J per flash with an uncertainty of a factor of 2.5. Choosing a global frequency of 100 flashes s^{-1}, they find a global energy dissipation rate of 1×10^{18} J yr^{-1}, a factor 5 greater than that of Hill *et al.* (1980), and a factor of 20 smaller than that found by Miller and Urey (1959).

Hill's (1979a) estimate for energy dissipation by a typical return stroke was given only to a certainty of "on the order of" 10^8 J m^{-1}, leading to an estimate of lightning flash discharge energy $\sim 8 \times 10^7$ J per flash. We adopt in this paper the more recently determined value (4×10^8 J per flash) preferred by Borucki and Chameides (1984), recalling that this value is uncertain to a large factor (~3). The lower end of the Borucki and Chameides error bar overlaps the uncertainties in the value preferred by Hill (1979a) and Hill *et al.* (1980). Similar considerations obviously also hold for these authors' estimates of the global energy dissipation rate.

The energy of an individual lightning flash is partitioned primarily into ohmic dissipation and shock–wave passage (thunder). An important uncertainty is the relative importance of these two mechanisms, as calculations of prebiotic organic production rely on extrapolations from experimental efficiencies derived from simulating one or the other process. Dawson (1980) argues that nearly instantaneous energy release would be well–modeled by ideal shock heating, whereas in a slower and more diffuse release, ohmic heating would be the more important dissipation mechanism. Real lightning evidently lies between these two extremes; Dawson (1980) holds that intracloud strokes are poorly modeled by an instantaneous release model, as they differ from cloud–to–ground strokes in that they generate only weak return strokes (see also Uman and Krider 1989). Hill (1979b) has argued that no more than ~10% of lightning energy dissipation goes into shock heating. Even if we were to assume 100% efficiency in converting the energy discharge of all strokes into shocks, previous estimates (Bar–Nun *et al.* 1970, Miller *et al.* 1976, Oró *et al.* 1990) that 2×10^{19} J yr^{-1} were available for shock processing by thunder on the early Earth must be revised. Moreover, these researchers' conclusion that shock waves from lightning were more important by a factor of 10 than were atmospheric shocks from asteroid and comet impacts during the heavy bombardment of early Earth no longer stands. Rather, the relative importance of the two sources for terrestrial atmospheric shocks now appears to have been roughly comparable (Chyba and Sagan 1991).

Chameides and Walker (1981) employed an average rate of dissipation of energy by lightning for the early Earth of $\sim 2 \times 10^{18}$ J yr^{-1}, a value ~3 times greater than that we advocate here. Unfortunately, these authors did not present the calculations leading them to this value, but we have included it in Table 8.2 for completeness. An earlier calculation by Chameides *et al.* (1977) yielded 3×10^{19} J yr^{-1}, a value higher than Miller and Urey's (1959) result. However, Chameides *et al.* 's (1977) choice for energy dissipation in a single lightning flash (2×10^9 J per flash), as well as their argument for a global flash rate of 400 flashes s^{-1}, are now agreed to have been in error (Dawson 1980, Borucki and Chameides 1984), so we have not included these estimates in Tables 8.1 and 8.2.

Finally, we note that an alternative approach to calculating global lightning energy dissipation on the early Earth would be by analogy to Borucki *et al.* 's (1984) attempt to estimate the lightning dissipation rate, E_L, on the saturnian moon Titan. These authors calculated E_L via the equation $E_L = RE_C$, where R, the ratio of Titan's lightning energy-dissipation rate to its convective energy rate, was taken to lie between that of Earth and Jupiter. E_C, the convective energy rate, depends linearly on both the solar flux, and the fraction of that flux, f, which reaches the layer of the atmosphere in which lightning occurs. Unfortunately, trying to estimate the lightning discharge rate for the early Earth through this method seems to provide no advantages over simply setting the rate for early Earth equal to that of today. R must be taken from the contemporary Earth, so E_L will differ from a direct extrapolation from lightning discharge rates on the present-day Earth only if E_C differs. E_C, however, is proportional to f (which for the early Earth can only be guessed at), and to the solar flux. While it is true that the early Sun would have been less luminous than the Sun of today (Sagan and Mullen 1972), the magnitude of this difference was $\lesssim$30% (see, for example, Zahnle and Walker 1982) around the time of interest for the origins of life, $\sim$ 4 Gyr ago. This difference is small compared with the uncertainties in the problem.

8.3 Coronal Discharges

Miller and Urey (1959), again relying on Schonland (1953), estimated that coronal discharge was a more important source of electrical energy for organic synthesis than lightning by a factor of $\sim$3. How does their estimate of 6×10^{19} J yr^{-1} fare in light of more recent research into terrestrial point discharges? To answer this question, we first review the physical nature of such discharges, discuss Schonland's results, and summarize subsequent critiques of his work. We conclude with a new estimate, based on recent data.

Historically, there was agreement in the atmospheric electricity literature that coronal discharges from pointed objects were the dominant mechanism for transfer of charge between thunder clouds and the Earth (Schonland 1928, 1953, Chalmers 1951, 1967, Stromberg 1971). Such discharges are also often called point discharges. (See Sec. 4 below for a review and clarification of the variety of terminology used in electrical discharge research.) The mechanism of point discharge is well-understood (Schonland 1953, Chalmers 1967, Latham and Stromberg 1977); the tip of any sharp object will act to concentrate a local electric field, causing breakdown and an electron avalanche (coronal discharge) for sufficiently high field values. "Sharp" in this context may mean objects as seemingly "blunt" as water droplets or wave crests, provided electric fields of sufficient magnitude are present (Latham 1975, Toland and Vonnegut 1977, Latham and Stromberg 1977), a complication discussed further below. Nevertheless, it is thought that by virtue of their relative height, pointed geometry, and large numbers, trees may be the main terrestrial objects for which point discharge occurs today (Schonland 1953, Chalmers 1967, Stromberg 1971, Ette and Utah 1973).

Schonland's (1953) quantitative treatment of point discharge was based on his pioneering earlier work in South Africa (Schonland 1928). In these studies, Schonland took an actual tree, supported it on insulators, and connected it to the Earth through a galvanometer. Once the tree withered, fresh twigs and leafy branches were occasionally wired to it. Schonland then measured currents through the tree during thunderstorms, when electric field strengths were high enough to cause point discharge. By estimating the average spacing of live trees beneath the storm, Schonland extrapolated his measurement for a single tree to an estimate of an upward point discharge current density 3.3×10^{-8} A m^{-2} beneath a typical thunderstorm, or 2.1 A beneath an estimated effective storm radius of 4.5 km. (In the SI system of units, one ampere (A) is defined as the flow of one coulomb (C) of charge per second.) Multiplication of this current by the potential below the thundercloud prior to discharge yields the total energy dissipated by point discharge beneath the storm. Schonland (1953, Sec. 34) considered simple spherical cloud models, and calculated the maximum potential reached prior to discharge for different estimates of thundercloud electric fields. His first model suggested potentials of around 4.2×10^8 V, with subsequent estimates varying by factors of 1/3 to 10 about this value. The choice 4.2×10^8 V gives a value for energy dissipation in a thunderstorm due to point discharge of $(4.2\times10^8 \text{ V})(2.1 \text{ A}) \approx 9\times10^5$ kW, about 3 times higher than Schonland's estimate of 3×10^5 kW dissipated by lightning discharges in the storm. As noted above, Miller and Urey (1959) gave a global coronal energy discharge rate $\sim$3 times greater than that due to lightning.

It is only to be expected that Schonland's measurements have been criticized and improved upon in the 60 years subsequent to his initial work. Chalmers (1967, Sec. 9.8) noted that the tree Schonland employed in his experiments was not in natural surroundings, and that the trees nearest to it were considerably more distant than the average 5 m separation that Schonland assumed. Chalmers suggested that Schonland's experiment may therefore have overestimated average currents, perhaps by a factor ~4. Over the past 30 years, considerable progress has been made in the ability of experimenters to accurately measure point discharge currents from living trees—an important improvement as the sap of a living tree may be its most important conductor of electricity (see Latham and Stromberg (1977) for a review). Moore and Vonnegut (1977) conducted experiments with a small forest of potted trees under thunderstorms, and found current densities "of up to" 10^{-8} A m^{-2}, a maximum value several times smaller than Schonland's result. The best recent measurements give an average value an order of magnitude smaller. Careful measurements on a living spruce tree plantation (Stromberg 1971) found a net charge transferred through a tree on the inside of the plantation of -156 μC in 31 min, giving a current density 2.3×10^{-9} A m^{-2} for an average tree spacing of 6 m (Stromberg 1971, Ette and Utah 1973, Latham and Stromberg 1977). Extensive measurements (Ette and Utah 1973) with palm trees, metal points, and grass yield mean discharge current densities of $(1.2 \pm 0.2) \times 10^{-9}$ A m^{-2}, in approximate agreement with the spruce plantation result. Choosing a typical effective storm cloud area to be 50 km^2 (Ette and Utah 1973, Latham and Stromberg 1977) then gives total currents of 0.12 and 0.06 A for the two sets of results (note that Latham and Stromberg (1977, p.107) list the latter value incorrectly as 0.6 A, an error that has unfortunately been propagated in the literature (e.g., Hill *et al.* 1984, Sec. 5.2)); we therefore take 0.09 A as a mean contemporary estimate for the current that flows beneath a typical thunderstorm. This value is ~20 times smaller than that found by Schonland.

An objection to the use of such contemporary thunderstorm point discharge measurements for calculations pertaining to early Earth is the obvious one that no trees, or any of the other pointed objects used in the measurements cited, existed prior to the origins of life. This objection may not be as important as it initially appears, however, due to the theoretical argument (Chalmers 1951, Moore and Vonnegut 1977) that the total point discharge current below a cloud is nearly independent of the nature of the points beneath it. Electric field intensity over "blunt" surfaces will simply build to the threshold level necessary for discharge from these surfaces (Toland and Vonnegut 1977). This argument receives support from observations that electric field intensities over water during storms reach values as high as 130 kV m^{-1}, a factor ~10 higher than those needed for discharges from trees and metal points (Stromberg 1971, Moore and Vonnegut 1977), and in good agreement with laboratory determinations of the field strengths (~200 kV m^{-1}) necessary to produce coronal discharges in splashes, water droplet collisions, and bubble bursts (Latham 1975, Latham and Stromberg 1977).

What, then, is the energy dissipated by point discharge by an average thunderstorm on contemporary Earth? This calculation requires knowing the potential difference between the thundercloud and ground. Uman (1969) estimates a typical potential difference of 1×10^8 V, which lies at the lower end of the range given by Schonland. Moore and Vonnegut (1977) give electric field strengths below thunderstorms ranging from 10^4 V m^{-1} over land to 10^5 V m^{-1} over oceans, bracketing Uman's (1969) value, for a cloud-ground separation of 5 km. Toland and Vonnegut (1977) list seven measurements of electric fields at lake surfaces during thunderstorms; their value of $(6 \pm 4) \times 10^4$ V m^{-1} corresponds to a potential of $(3 \pm 2) \times 10^8$ V for a 5 km separation. As ~90% of lightning flashes occur over land (Vorpahl *et al.* 1970), we choose 1×10^8 V for our calculations, with an uncertainty given by the ranges cited above of a factor ~5. Then, given a typical point discharge current of 0.09 A beneath a thundercloud, we find 9×10^3 kW energy dissipated by coronal discharge. How does this compare with the energy dissipated by lightning for a typical storm? Prentice (1977, Sec. 2.3.3) has reviewed recent measurements of flash rates during storms; a good global average value appears to be 3 flashes min^{-1}, in excellent agreement with historical estimates (Schonland 1953). Taking an average flash to dissipate 4×10^8 J, a typical storm dissipates energy by lightning at a rate 2×10^4 kW, so that energy dissipation by coronal discharge is roughly comparable to that of lightning. The global coronal discharge energy rate is then approximately 5×10^{17} J yr^{-1} (with a factor ~5 uncertainty), or 120 times less than the original estimate of Miller and Urey (1959).

8.4 Electrical Discharge Terminology: Hot and Cold Plasmas

Before proceeding to a discussion of energy yields for organic synthesis of laboratory simulations of lightning and coronal discharges, we first review electrical discharge terminology. Different laboratory simulations provide reasonable analogues to either lightning or coronal discharges, whereas some do not appear to provide unambiguous representations of either naturally-occurring energy source. Some clarification of the terminology used to describe, and the basic physics of, different electrical discharge sources used in the laboratory therefore seems necessary.

Laboratory discharges depend upon creating a potential between a cathode an anode that is sufficiently high to achieve the breakdown voltage of the background gas. Upon breakdown, the gas is transformed from an insulator to a conductor. Penning (1957) and Bell (1967) have reviewed the variety of ways this transformation may take place. For parallel flat plate electrodes in ordinary air at atmospheric pressure, as soon as the breakdown voltage is reached, a current of high intensity and short duration (that is, a spark) will occur. At lower gas pressures, however, a self-sustaining "glow discharge" may be produced, in which the cathode continuously emits electrons due to ion bombardment. Typical currents in laboratory glow discharges are in the range $10^{-2} - 10^{2}$ mA. Thermal effects are negligible and not necessary for sustaining the discharge. At higher currents, however, the cathode temperature rises rapidly, and the cathode gives off electrons by thermionic emission. This form of discharge is therefore known as a thermionic arc, or simply as an arc discharge. Typical currents are above $\sim$0.1 A.

Glow discharges create "cold plasmas", in which the electrons are highly superthermal, but the ions, neutral molecules, and molecular fragments in the background gas remain near the ambient temperature. What we have previously referred to as "point discharges" are the natural-world analogues of laboratory glow discharges, but which occur at atmospheric pressure. As Darrow (1932) has explained, sparking may be avoided (and glow discharges produced) at atmospheric pressure, provided that one or both of the experimental electrodes is sufficiently curved. In practice, at least one of the electrodes must have a radius of curvature smaller than the distance between the two electrodes.

Historically, the appellation "coronal discharge" has been used by some authors to mean a glow discharge in the case where the sharply-curved electrode was a wire (Darrow 1932, McTaggart 1967). However, Chalmers (1967, p. 239) defined "coronal discharge" to mean any point discharge "when investigated in the laboratory". At least as early as Darrow (1932), however, "coronal discharge" was sometimes also being used as a simple synonym for "glow discharge". In a similar inconsistent usage, the name "point discharge" has not always referred exclusively to discharges outside the laboratory: McTaggart (1967) used this term to denote a specific experimental geometrical configuration, *viz.* one where at least one electrode was a point, or at least sharply curved. Because of these various conflicting usages, we must define our own convention. We take "coronal discharge" to be synonymous with "glow discharge", whether in the natural world or laboratory; no specific electrode geometry is connoted. We take "point discharge" to have a more restricted meaning, *viz.* a coronal discharge where one or both (natural or laboratory) electrodes has a high radius of curvature.

The common physical characteristic of all these discharges is that each creates a cold plasma. We may therefore expect other discharges that similarly create cold plasmas to provide adequate simulations of the chemical effects of naturally-occurring point discharges (see Sec. 5 below). Such laboratory discharges include radio-frequency cold plasma discharges induced by either capacitative or inductive coupling (Bell 1967, Thompson *et al.* 1991).

Arc discharges may also produce cold plasmas, provided that pressures and currents are sufficiently low (Brown 1966, Bell 1967). Sufficiently high current arcs, however, create "hot plasmas", in which the kinetic and excitation temperatures of all species—electrons, ions, molecules, and molecular fragments—are very high (Bell 1967, Thompson *et al.* 1991). Arc discharges operating at pressures at or above one atmosphere typically create hot plasmas, although at sufficiently low currents, an appreciable difference between the electron temperature and that of the other species may still exist (Brown 1966, Bell 1967). In the natural world, lightning is a hot plasma process (Thompson *et al.* 1991), so that sufficiently-high-pressure arc discharges may provide adequate simulations. Laser-induced hot plasmas will also provide good laboratory simulations of lightning (Borucki *et al.* 1988, Scattergood *et al.* 1989).

8.5 Relative Organic Production from Lightning and Coronal Discharges

As shown in Table 8.2, our preferred estimates of electrical energy available for organic synthesis on the early Earth give comparable values for net energy dissipation by lightning discharges and coronal discharges. However, the physics of lightning and coronal discharges is quite distinct, and the efficiency of organic synthesis from the two energy sources appears to differ substantially. As just discussed, coronal discharges create cold plasmas of superthermal electrons, whereas high voltage, high current arcs such as lightning create hot plasmas, in which the kinetic and excitation temperatures of all species are very high. It would not be surprising if energy yields for molecular synthesis varied according to whether the plasmas were hot or cold, and in fact this is found to be the case experimentally: Hot plasmas appear to be much more efficient for organic synthesis than cold plasmas.

Thompson *et al.* (1991) have summarized recent work on the energy yields for organic synthesis (e.g., nmole product per joule of energy in the discharge) from a variety of laboratory discharges. For production of HCN in CH_4/N_2 atmospheres, they find energy yields from a variety of cold plasma experiments to lie typically in the range ~10–20 nmole J^{-1}. Spark discharge experiments by Stribling and Miller (1987) reported yields of ~10 nmole J^{-1}, in good agreement with cold plasma results from coronal discharges and inductively-coupled plasma discharges. The Stribling and Miller spark discharge experiments took place at a pressure of 267 mbar, a pressure sufficiently low so that we might expect the plasma created to have been a cold one. The fact that three different mechanisms for generating cold plasmas yielded synthesis efficiencies identical to within a small factor suggests that any laboratory-created cold plasma will provide a reasonable simulation of natural point discharges. It is true that a low efficiency, ~3 nmole J^{-1}, was found (Thompson *et al.* 1991) for an inductively-coupled plasma at very low pressures (0.24 mbar). However, efficiencies of other experiments appear to be pressure-independent over the range 13 to 267 mbar.

Organic synthesis in hot plasmas, by contrast, appears to be more efficient by about one order of magnitude. HCN production by laser-induced hot plamas ranges from 93 to 249 nmole J^{-1} (Scattergood *et al.* 1989). A thermochemical-hydrodynamic model by Chameides and Walker (1981) of HCN production by lightning gives just over 10^{17} molecules J^{-1}, or ~200 nmole HCN J^{-1}, consistent with the experimental results.

Lying between these efficiencies for hot and cold plasmas are a set of high-voltage arc experiments at pressures of approximately one atmosphere (summarized in Thompson *et al.* 1991), with efficiencies ranging from 47 to 78 nmole J^{-1}. It is possible that these efficiencies lie between the results for coronal discharges and lightning because these arcs create plasmas where the ion and molecular temperatures are almost, but not quite, as high as that of the electrons. One set of arc discharge experiments have sometimes yielded efficiencies comparable to those of laser-induced hot plasmas. In an extensive set of experiments by Briner *et al.* (1919, 1938), HCN production efficiencies were found to vary from 49 to 361 nmole J^{-1} in CH_4/N_2 atmospheres at atmospheric pressure. Analogous experiments at pressures ranging from 155 to 328 mbar gave yields in the range 49 to 426 nmole J^{-1}. Experimental yields appeared to depend strongly on the frequency of the arc discharge, with a maximum efficiency achieved at $\sim 10^7$ Hz (Briner *et al.* 1938).

HCN production seems to be approximately one order of magnitude more efficient for hot plasma discharges than for cold plasmas. The discrepancies of efficiencies for C_2H_2 production are even more pronounced: Hot plasmas appear nearly two orders of magnitude more efficient for C_2H_2 production than cold plasmas (see Thompson *et al.* 1991, Table III). These comparisons carry an evident implication for the relative importance of lightning versus coronal discharge on the early Earth: Although the total energy dissipation on the early Earth from both sources appears to have been about equal, production of HCN and C_2H_2 by lightning apparently would have considerably overshadowed that by coronal discharge, perhaps by nearly an order of magnitude.

However, there are a variety of sources of coronal discharge energy that are included neither in our estimate here, nor in the earlier estimate by Miller and Urey

(1959). These include coronal emission from highly deformed or colliding raindrops, as well as from the surfaces of cloud ice crystals (Latham and Stromberg 1977). In addition, typical lightning stroke channels are probably surrounded by a coronal region (Hill *et al.* 1984, Bhetanabhotla *et al.* 1985).

This latter source of coronal discharge energy appears to be negligible compared with the point discharge sources evaluated in Sec. 3. Hill *et al.* (1984, see also Bhetanabhotla *et al.* 1985) calculate the energy dissipated in the coronal sheath of a lightning stroke, and find it to be only 3×10^{-4} to 5×10^{-3} of that dissipated in the stroke itself. Table 8.2 shows that coronal sheath energy dissipation can therefore equal no more than 10^{-2} of that dissipated in terrestrial point discharges.

Upper limits on the importance of intracloud coronae have been placed by direct airborne observation of enhanced nitric oxide (NO) levels in the anvils of two cumulonimbus clouds (Ridley *et al.* 1987, Chameides *et al.* 1987). In these daylight flights, no direct observations of lightning flashes were made, although secondary evidence (e.g., radio static) indicated some electrical activity. It remains uncertain whether synthesis of the observed NO was primarily due to lightning or coronal discharges within the cloud. However, observed NO production extrapolated from the two clouds yields a global production rate of nitrogen oxides from electrified clouds of 7×10^9 kg N yr^{-1}, with an uncertainty of a factor of 3. As pointed out by Chameides *et al.* (1987), this result is in good agreement with entirely independent estimates (via an approach analogous to that used in Sec. 2 above) of global production of NO from lightning alone, which yield a range $(0.8\text{–}8) \times 10^9$ kg yr^{-1} (Borucki and Chameides 1984). This suggests that coronal production of NO within clouds cannot exceed that by lightning by more than a small factor.

Ridley *et al.* (1987) have proceeded along slightly different lines than Chameides *et al.* (1987), and found an upper limit of NO production by coronal discharge within the clouds by assuming that all observed NO is due to coronae. This approach yields a net NO production of ~20 kg N hr^{-1}. As these authors point out, this is approximately half the rate expected by assuming a lightning discharge frequency within the cloud of 1 min^{-1} (see Sec. 3 above, where it was argued that the best contemporary value is about 3 flashes min^{-1} in a storm), and the Borucki and Chameides (1984) estimate of NO yield per lighning flash. Once again, we find that NO production by coronal discharge appears to be at most comparable to that due to lightning. This is unsurprising, since laboratory yields for NO due to coronae have been found to be 23$\pm$12 nmole J^{-1} (Hill *et al.* 1988), a value considerably below that found for production by lightning, 149$\pm$33 nmole J^{-1} (Borucki and Chameides 1984). (In both absolute and relative terms, these values are similar to those found for HCN production.) On the basis of the very limited data base (two clouds) provided by the airborne observations cited here, it seems unlikely that coronal discharges within clouds could provide a source of organic molecules which outweighs that due to lightning.

However, the data base clearly needs to be broadened. Both with respect to coronal sources within clouds, and regarding better estimates of global energy dissipation by lightning and point discharges, the origins of life community needs assistance from those scientists specializing in atmospheric electricity. Nevertheless, it now appears that those lightning and coronal energy discharge rates currently employed in the origins of life literature need to be substantially reduced.

Chapter 9

Uncertainties in Estimates of the Contribution of Exogenous Organics to the Origins of Life

9.1 Introduction

The central issue which this dissertation has attempted to address is an evaluation of the role of exogenous sources of organics to the prebiotic inventory of the early Earth. As discussed in Chapter 1, this question has haunted speculations on the origins of life for nearly a century. Here we have identified the key physical and chemical questions that must be answered in order to give a quantitative answer to this question. Previous work in this field typically went little further than noting that comets seemed to be organic-rich, organics were needed for the origins of life, comets fell on the early Earth, so maybe they were important (see, e.g., papers in Ponnamperuma 1980). Indeed, some work has continued to imply that one simply needs to estimate the total organic content of all infalling planetesimals, and take this as the exogenous contribution to the origins of life (see, e.g., Greenberg 1989). This dissertation demonstrates that such plausibility arguments, while valuable, are no longer sufficient: Substantial progress may be made, first in *ruling out* the importance of certain potential mechanisms for a wide range of early Earth conditions, and second, in quantifying (within broad uncertainties) the possible contribution of those mechanisms that remain plausible. In particular, the organics in those impactors too large to be substantially aerobraked or to airburst—representing the vast bulk of the potential exogenous source—should have been pyrolyzed on impact, and did not contribute to the origins of life on Earth.

Throughout this dissertation, we have taken pains to emphasize—and attempt to quantify—the uncertainties associated with each step in our calculations. It may be valuable, however, to assemble and review those uncertainties here (recently summarized in Chyba 1991c).

Chapter 7 attempted to summarize the variety of possible exogenous sources for prebiotic organics. Some uncertainties are fundamental to the approach taken here in evaluating any of these sources; in particular, the analytical fit to the lunar cratering record, and the velocities used in the crater diameter–impactor mass equation. In the case of mechanisms for the delivery of more–or–less intact exogenous organics, our lack of knowledge of the fraction of the heavy bombardment composed of volatile– or organic–rich impactors is also critical. In addition, each individual mechanism has its associated specific uncertainties. We review these in turn.

9.2 Procrustean Fits to the Lunar Impact Record, Encore Une Fois

As emphasized in Sections 4.2, 5.5, 6.3, 6.4, 6.5, and 7.2, there are a number of important uncertainties in attempting to pursue simple analytical fits to the lunar impact record. While these uncertainties are now sometimes explicitly acknowledged in the literature, prior to work by Chyba (1990a), they were commonly ignored (as discussed in Chapter 4), with different authors making particular choices without acknowledgment of alternative possibilities (see, for example, Maher and Stevenson 1988, Oberbeck and Fogleman 1989, and Melosh and Vickery 1989).

As discussed in Chapters 4 and 5, different fits to the lunar cratering record lead to estimates of terrestrial mass accretion as a function of time varying by a factor of ~800 at 4.4 Gyr ago, the time at which the discrepancies are greatest. In Chapter 4, it was first argued that the most extreme (the highest) of these results (that employed by Maher and Stevenson 1988) could probably be ruled out on the grounds of its implications for the terrestrial water inventory. This argument is certainly not decisive, however, because one may always take the view that the heavy bombardment impactors were simply extremely water–poor (see below). Therefore, an initial appeal was made to the work of Sleep *et al.* (1989), who used lunar regolith siderophile abundances to estimate meteoritic infall subsequent to the formation of the lunar crust. In Chapter 4, it was argued that such an appeal seemed to reduce the uncertainty in early influx from nearly three to only one order of magnitude.

The central point of Chapter 6 was to pursue this question more thoroughly, for both the Moon and the Earth. There it was found that one particular fit to the cratering record, subsequent to ~4.4 Gyr ago, was in good agreement with both lunar and terrestrial geochemical requirements. The terrestrial mantle siderophile abundances appear to reduce the uncertainty in total accreted post–core formation mass to a factor of ~4, with most of this uncertainty stemming from the possibility of whole–mantle mixing. Note that the geochemical constraint provides only a constraint on the *integral over time* of the heavy bombardment flux. Therefore, while it certainly may be used to rule out those flux models whose integrals exceed the geochemically–derived value, it cannot speak to the details of the time rate of change of the bombarding flux. However, it does decisively rule out the 70 Myr half-life fit to the cratering record. The remaining simple analytical fits consistent with that record differ at 4.4 Gyr by a factor of ~4. Numerical experiments show that a much broader range of fits is not consistent with the cratering data. However, precisely because the geochemical constraint is an integral constraint, and the cratering data are so sparse, a more elaborate fit with a varying decay "half-life" can certainly not be excluded (to the contrary, some version of the latter is likely to ultimately prove correct, though more lunar data will first need to be available). Over time, however, all fits must deliver about the same amount of mass to Earth, to be in agreement with the geochemical constraints.

Chapter 6 also examined uncertainties in the key variable parameters, impactor velocities and masses, that go into the crater diameter—impactor mass relation. Letting the uncertainty for lunar impact velocity range from that appropriate to the slowest plausible impactors (residual Earth-crossers), with $v_\infty \approx$ 8 km s^{-1}, to SP comets, with $v_\infty \approx 20$ km s^{-1}, introduces an uncertainty of a factor of ~4 into the final results. Treating this error and that introduced by our different fits to the cratering record as independent, the net error introduced by these uncertainties together is less than a factor of 6.

There are also great uncertainties in the largest object that struck the Earth subsequent to 4.4 Gyr ago; as emphasized in Chapter 6, the mass of this object can at present only be evaluated via the statistics of small numbers. However, this question is a red herring for the uncertainties relevant here. Consider the exogenous sources of organics identified in Chapter 7. The contributions of airbursts and comet impact survival employ values of maximum-mass impactors, m_{max}, orders of magnitude smaller ($\lesssim$ 4 km in radius) than the largest impactors striking the Earth. The contributions of IDPs and meteorites make no reference to m_{max} at all. The choice of the latter is irrelevant to all these results. Our calculations of post-impact recombination of organics relies on the value of m_{max}

appropriate for the Moon—we have been explicitly conservative in ignoring any possible contribution from the difficult–to–quantify small set of larger objects that reached the Earth. The uncertainty in m_{max} for the Moon lies somewhere between the masses of the Imbrium and "Procellarum" objects. (As discussed in Chapter 6, the latter may well not have existed, but we include it here in order to maximize our stated error.) This range in basin sizes, 1160 km to 3200 km, introduces a range of error in m_{max} of a factor $(3200/1160)^{3.36} \approx 30.2$. This in turn introduces an error into our estimates of mass flux of a factor $(30.2)^{0.47} \approx 5.0$. Combining uncertainties in fits to the cratering record, velocities, and m_{max} then gives an overall uncertainty to post–impact recombination of a factor of ~8.

9.3 Delivery of Intact Exogenous Organics

As previously discussed in this thesis (see especially Sections 4.5, 4.6, and 6.7), a key uncertainty in evaluating the organic influx to the early Earth is the question of the fraction of the heavy bombardment composed of organic–rich bodies (comets and carbonaceous chondrites). None of the data currently available decisively, or even very persuasively, resolves this question. (We have demonstrated, however, that only a fraction of the heavy bombardment on Earth need have been cometary for the bulk of the terrestrial oceans to derive from a cometary source.) The fraction of the heavy bombardment composed of comets or carbonaceous asteroids is ultimately a free parameter. As stated in Section 6.7, "this uncertainty remains, and is fundamental."

Throughout this thesis, we have been explicit about this uncertainty, introducing it as the free parameter ψ. In Figure 7.1, for example, the "airbursts" and "comet impact" sources were evaluated with the assumption that ψ=0.1. The "airburst" source was otherwise assumed to be 50% CI chondrite, and 50% ordinary chondrite (the latter making a negligible contribution). Different choices would lead to proportionately different results.

In the case of meteorites and IDPs, we have simply extrapolated into the past their current organic fraction. The contribution of meteorites is so negligible that there seems little point in discussing the associated uncertainties. IDPs, however, are potentially the most important source of intact exogenous organics on the early Earth, so we examine uncertainties in their contribution in some detail.

9.4 Interplanetary Dust

In Chapter 7, we estimated the contribution of IDPs to the early terrestrial inventory via three key assumptions. The first was that the organic composition of IDPs in the past was that of IDPs today. The second was that the IDP number–mass distribution in the past was the same as that of IDPs today. The third was that IDP flux through time scaled like the lunar cratering record. Each of these assumptions is the most "natural" to make, but each is an assumption based on ignorance. Let us examine each in turn.

9.4.1 The IDP Organic Component

In Chapter 7, we followed the evidence cited by Anders (1989) that the current influx of IDPs is ~10% organic by mass. This is a value midway between what one might expect for cometary and carbonaceous chondritic particles; whether comets or asteroids are the primary souce of IDPs remains unclear (Brownlee 1985). As typical IDP survival lifetimes in the inner solar system due to collisions and Poynting–Robertson drag are only $\sim 10^4$–10^5 yr (Grün *et al.* 1985, Brownlee 1985), it is also unclear whether the present organic fraction of IDPs is typical of the past. This question may well turn on past relative abundances of comets, organic-rich asteroids, and organic-poor objects.

9.4.2 The IDP Number–Mass Distribution

The bulk of the mass in the current population of IDPs peaks around 10^{-6} to 10^{-4} g, a result that is now widely accepted in the IDP literature (Hughes 1978, Kyte and Wasson 1986, Anders 1989, Flynn 1990). However, as the existence of this mass peak sometimes causes confusion, it may be worthwhile to review briefly the reasons for its existence.

A plot of global IDP mass influx per mass interval (in which the mass peak around 10^{-5} g is apparent) derives immediately (Hughes 1978) from a plot, based on observation, of IDP cumulative number flux versus mass (see, for example, Dohnanyi 1972, 1978, Hughes 1978). The latter curve is of the form (Hughes 1978, Eq.(4)):

$$\theta(m) \propto m^{1-s_m} \qquad (9.1),$$

where $\theta(m)$ is the cumulative flux of IDPs with mass greater than m, and s_m is the mass index. Over the mass range 10^{-13}g to 10 g, this curve is well known, from a combination of spacecraft, radio, and photographic data (Dohnanyi 1972, 1978, Hughes 1978, Grün *et al.* 1985). The curve may be extended up to 10^6 g by observations of meteorite fireballs (Dohnanyi 1972, Hughes 1978), and to higher masses by observations of Earth-crossing asteroids and the lunar impact record (Kyte and Wasson 1986).

Uncertainties in IDP absolute cumulative fluxes are about one order of magnitude (Hughes 1978, Section 7). At particle masses below about 10^{-6} g, $s_m \approx 1.55$, between 10^{-6} g and 10^{-4} g s_m passes through the value 2, and then climbs to nearly 3 by 10 g (Hughes 1978, and references therein). This slope change is important when considering global IDP mass influx per mass interval. This distribution is given by integrating Eq.(9.1) over mass, giving a mass flux proportional to m^{2-s_m}. On a log-log scale, the slope of this curve changes from positive to negative as s_m passes through 2; there is therefore a peak in the IDP mass input where this transition occurs (around 10^{-5} g).

If one simply extended the power–law distribution of larger impactors down below ~ 10 g, the mass influx predicted for IDPs would be 5 to 6 orders of magnitude smaller than it is in fact observed to be. Should the change in s_m from 1.6 to 3 over the relevant mass range be expected to have persisted in time? In the absence of an understanding of the origins of IDPs, this question cannot be answered *a priori.* An important constraint, however, is placed by lunar and terrestrial siderophile abundances.

9.4.3 IDP Flux Through Time

The current terrestrial mass influx from IDPs found by Hughes (1978) on the basis of meteor observations is in excellent agreement with accretion rates inferred from terrestrial and lunar data. In the case of the Earth, these data are based on siderophile abundances found in deep sea sediments. These observations have now been extended from the past million years (Barker and Anders 1968; these authors' estimate of sedimentation rate should be (Kyte and Wasson 1986) corrected by the results of Ku *et al.* 1968) to the period between 33 and 67 million years ago (Kyte and Wasson 1986). Similarly, the current net accretion of siderophiles from IDPs is consistent with the micrometeorite component in the lunar regolith (Dohnanyi 1971, Anders *et al.* 1973). Results from three Apollo missions for mare soils vary by only 25% (Anders 1973); the present net IDP mass flux therefore appears to have been remarkably constant over the past 3.5 Gyr.

Because these data take the form of an integral over the IDP size distribution, they cannot be used to prove that the current shape of the IDP flux curve has remained unchanging through time. Moreover, there is no evidence for or against the claim that, prior to 3.5 Gyr ago, the IDP population would have increased proportionally to the cratering flux. If IDPs are the product of cometary evaporation or of asteroid–asteroid collisions, one would expect their number roughly to scale linearly, or as the square, respectively, of the number of such objects in the inner solar system. (In Chapter 7 we have scaled IDP flux linearly with the flux of large cratering objects.) This is by no means certain, however. A safe lower limit for the IDP flux on Earth prior to 3.5 Gyr would seem to be a simple extension of the current flux back into the past. At 4 Gyr ago, the time of relevance to the origins of life, this introduces an uncertainty of about two orders of magnitude into the relevant IDP mass flux.

9.5 Impact Synthesis of Organics

Section 9.2 examined a number of uncertainties in the contribution by impact synthesis to organics on the early Earth. To these must be added the absolutely fundamental uncertainty in the oxidation state of the early terrestrial atmosphere. As detailed in Chapter 7, plausible end-members of this oxidation state introduce some 7.5 orders of magnitude uncertainty into one's conclusions. This uncertainty is directly analogous to the standard uncertainty in estimates of endogenous production of organics in the early terrestrial atmosphere. That is why we considered the two standard end-members explicitly in Chapter 7.

In addition, there is the question of the importance of post-impact recombination by the material of the projectile itself. As discussed at length in Section 7.4, results of laboratory experiments relevant to this question are, so far, highly suspect. This is explicit in Figure 7.1, where the possible contribution of this source is shown as a dotted line. There are a variety of experiments in the impact and orgins of life communities just initiated that hope to better resolve this issue.

9.6 Comparison with Uncertainties in the Endogenous Contribution to the Origins of Life

To put the uncertainties just detailed into context, it may be valuable to consider the magnitude of some uncertainties typical in estimates of the endogenous contribution to the prebiotic organic inventory. In effect, Chapter 8 provides one measure of these uncertanties. Firstly, new estimates of energy dissipation by lightning and coronal discharge suggest that for the past 30 years, the origins of life community has been overestimating the importance of these sources by one to two orders of magnitude. Even now, a number of key quantities are inferred from a very limited number of observations, suggesting that the possible contemporary error may remain comparably large. In addition, however, there remains a potentially grave and virtually unquantifiable source of error in these results: One can do no better, at present, than assume that the rate of electrical discharges on the early Earth equalled that of the Earth today.

Similar uncertainties exist for the second key early endogenous energy source, ultraviolet light. The evolution of ultraviolet luminosity of G class stars is poorly understood (Zahnle and Walker 1982). However, this evolution appears to increase ultraviolet fluxes at 4 Gyr ago by about an order of magnitude over those of the present-day Sun (Chyba and Sagan, in preparation; this effect coexists with the decrease in overall solar luminosity as one goes back in time). Decreasing ultraviolet luminosity with time of the main-sequence Sun has not previously been considered by the origins of life community.

It can be seen that order-of-magnitude uncertainties are typical in the origins of life field. Worse, some uncertainties are, at present, nearly impossible to quantify. This does not mean we have learned nothing from the past 30 years of research. It does mean key facts about the primordial terrestrial environment remain poorly understood. But this, after all, is exactly the contribution that planetary science can make to our understanding of the origins of life: In the absence of an extant terrestrial record, we must look outward for knowledge of conditions on the early Earth.

References

Abelson, P.H. 1959. Geochemistry of organic substances. In *Researches in Geochemistry* (P.H. Abelson, Ed.), pp. 79–103. John Wiley & Sons, New York.

Abelson, P.H. 1966. Chemical events on the primitive Earth. *Proc. Nat. Acad. Sci.* **55**, 1365–1372.

A'Hearn, M.F., S. Hoban, P.V. Birch, C. Bowers, R. Martin, and D.A. Klingesmith 1986. Cyanogen jets in comet Halley. *Nature* **324**, 649-651.

Allamandola, L.J. 1984. Absorption and emission characteristics of interstellar dust. In *Galactic and Extragalactic Infrared Spectroscopy* (M.F. Kessler and J.P. Phillips, Eds.), pp. 5–35. D. Reidel, New York.

Allen, D.A., and D.T. Wickramasinghe 1987. Discovery of organic grains in comet Wilson. *Nature* **329**, 615-616.

Allen, H.J. 1960. On the motion and ablation of meteoric bodies. In *Aeronautics and Astronautics* (N.J. Hoff and W.G. Vincenti, Eds.), pp. 378–416. Pergamon, New York.

Allen, H.J., A. Seiff, W. Winovich 1963. Aerodynamic heating of conical entry vehicles at speeds in excess of Earth parabolic speed. NASA Technical Report TR R–185.

Allen, M., M. Delitsky, W. Huntress, Y. Yung, W.-H. Ip, R. Schwenn, H. Rosenbauer, E. Shelley, H. Balsiger, and J. Geiss 1987. Evidence for methane and ammonia in the coma of comet P/Halley. *Astron. Astrophys.* **187**, 502-512.

Alvarez, L.W., W. Alvarez, F. Asaro, and H.V. Michel 1980. Extraterrestrial cause for the Cretaceous–Tertiary extinction. *Science* **208**, 1095–1108.

Anders, E. 1963. Meteoritic hydrocarbons and extraterrestrial life. *Ann. N.Y. Acad. Sci.* **93**, 649–664.

Anders, E. 1978. Procrustean science: Indigenous siderophiles in the lunar highlands, according to Delano and Ringwood. *Proc. Lunar Planet. Sci. Conf.* **9**, 161–184.

Anders, E. 1989. Pre–biotic organic matter from comets and asteroids. *Nature* **342**, 255–257.

Anders, E. and N. Grevesse 1989. Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta* **53**, 197–214.

Anders, E. and T. Owen 1977. Mars and Earth: Origin and abundance of volatiles. *Science* **198**, 453–465.

Anders, E., R. Ganapathy, R. Krähenbühl, and J.W. Morgan 1973. Meteoritic material on the Moon. *Moon* **8**, 3–24.

Arakawa, E.T., C. Meisse, B.N. Khare, W.R. Thompson, C. Sagan, I. Gilmour, and E. Anders 1989. Optical constants of kerogen from 0.15 to 40 μm. *Bull. Am. Astron. Soc.* **21**, 940.

Arnold, J.R. 1979. Ice in the lunar polar regions. *J. Geophys. Res.* **84**, 5659–5668.

Arnosti, C. and P.J. Müller 1987. Pyrolysis–GC characterization of whole rock and kerogen–concentrate samples of immature Jurassic source rocks from NW–Germany. *Org. Geochem.* **11**, 505–512.

Ashwal, L.D., Ed. 1988. *Workshop on the growth of continental crust.* LPI Tech. Rpt. 88–02. Lunar and Planetary Institute, Houston. 174 pp.

Atkins, P.W. 1986. *Physical Chemistry.* W.H. Freeman, New York.

Attrep, M., C.J. Orth, L.R. Quintana, C.S. Shoemaker, E.M. Shoemaker and S.R. Taylor 1991. Chemical fractionation of siderophile elements in impactites from Australian meteorite craters. In *Reports of Planetary Geology and Geophysics Program–1990*, pp. 375–376. NASA Technical Memorandum 4300.

Baas, F., T.R. Geballe, and D.M. Walther 1986. Spectroscopy of the 3.4 micron emission feature in comet Halley. *Ap. J. Lett.* **311**, L97-L101.

Baldwin, B. and Y. Sheaffer 1971. Ablation and breakup of large meteoroids during atmospheric entry. *J. Geophys. Res.* **76**, 4653–4668.

Baldwin, R.B. 1987a. On the relative and absolute ages of seven lunar front face basins. I. From viscosity arguments. *Icarus* **71**, 1–18.

Baldwin, R.B. 1987b. On the relative and absolute ages of seven lunar front face basins. II. From crater counts. *Icarus* **71**, 19–29.

Barker, J.L. and E. Anders 1968. Accretion rate of cosmic matter from iridium and osmium contents of deep-sea sediments. *Geochim. Cosmochim. Acta* **32**, 627–645.

Barak, I. and A. Bar-Nun 1975. The mechanisms of amino acids synthesis by high temperature shock-waves. *Origins of Life* **6**, 483–506.

Bar-Nun, A. 1975. Shock synthesis of amino acids II. *Origins of Life* **6**, 109–115.

Bar-Nun, A. and A. Shaviv 1975. Dynamics of the chemical evolution of Earth's primitive atmosphere. *Icarus* **24**, 197–210.

Bar-Nun, A., N. Bar-Nun, S.H. Bauer, and C. Sagan 1970a. Shock synthesis of amino acids in simulated primitive environments. *Science* **168**, 470–473.

Bar-Nun, A., N. Bar-Nun, S.H. Bauer, and C. Sagan 1970b. Amino acid synthesis in simulated primitive environments. *Science* **170**, 1000–1002.

Bar-Nun, A., A. Lazcano-Araujo, and J. Oró 1981. Could life have evolved in cometary nuclei? *Origins of Life* **11**, 387–394.

Basaltic Volcanism Study Project (BVSP) 1981. *Basaltic Volcanism on the Terrestrial Planets.* Pergamon, New York.

Bell, A. 1967. In *The Application of Plasmas to Chemical Processing* (R.F. Baddour and R.S. Timmins, Eds.), pp. 1-12. M.I.T. Press, Cambridge, MA.

Bell, A.T. 1974. In *Techniques and Applications of Plasma Chemistry* (J.R. Hollahan and A.T. Bell, Eds.), pp. 1–56. John Wiley, New York.

Benson, S.W. and H.E. O'Neal 1970. *Kinetic data on gas phase unimolecular reactions.* Publication NSRDS-NBS 21, U.S. Government Printing Office, Washington DC.

Benz, W., W.L. Slattery, and A.G.W. Cameron 1987. The origin of the Moon and the single impact hypothesis II. *Icarus* **71**, 30–45.

Benz, W., A.G.W. Cameron, and H.J. Melosh 1989. The origin of the Moon and the single impact hypothesis III. *Icarus* **81**, 113–131.

Berzelius, J.J.. 1834. Ueber meteorstein. *Ann. Phys. Chem.* **33**, 113.

Bhetanabhotla, M.N., B.A. Crowell, A. Coucouvinos, R.D. Hill, and R.G. Rinker 1985. Simulation of trace species production by lightning and corona discharge in moist air. *Atmospheric Environment.* **19**, 1391–1397.

Boato, G. 1954. The isotopic composition of hydrogen and carbon in the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **6**, 209–220.

Boice, D.C., W.F. Huebner, M.J. Sablik, and I. Konno 1990. Coma sources of organic molecules and CH_4/CO in comet Halley. *Geophys. Res. Lett.*, submitted.

Borucki, W.J. and W.L. Chameides 1984. Lightning: Estimates of the rates of energy dissipation and nitrogen fixation. *Rev. Geophys. Space Phys.* **22**, 363–372.

Borucki, W.J., C.P. McKay, and R.C. Whitten 1984. Possible production by lightning of aerosols and trace gases in Titan's atmosphere. *Icarus* **60**, 260–273.

Boss, A.P. and S.J. Peale 1986. Dynamical constraints on the origin of the Moon. In *Origin of the Moon* (W.K. Hartmann, R.J. Phillips, and G.J. Taylor, Eds.), pp. 59–101. Lunar and Planetary Inst., Houston.

Bregman, J.D., H. Campins, F.C. Witteborn, D.H. Wooden, D.M. Rank, L.J. Allamandola, M. Cohen, and A.G.G.M. Tielens 1987. Airborne and Ground-based Spectrophotometry of Comet P/Halley from 5-13 micrometers. *Astron. Astrophys.* **187**, 616-620.

Briggs, M.H. and G. B. Kitto 1962. Complex organic micro–structures in the Mokoia meteorite. *Nature* **193**, 1126–1127.

Briner, E. 1914. Recherches sur le mécanisme de l'action chimique des décharges électriques. *J. Chimie Phys.* **12**, 526–563.

Briner, E. and A. Baerfuss 1919. Sur la fixation de l'azote sous forme d'acide cyanhydrique au moyen de l'arc électrique. *Helv. Chim. Acta* **2**, 663–666.

Briner, E. and E. Mettler 1908. Recherches sur la formation du gaz ammoniac à partir de ses éléments sous l'action des décharges éléctriques. *J. Chimie Phys.* **6**, 137–178.

Briner, E., J. Desbaillets, and H. Paillard 1938. Recherches sur l'action chimique des décharges électriques. XII. Production de l'acide cyanhydrique par l'arc électrique à différentes fréquences. *Helv. Chim. Acta* **21**, 115–131.

Bronshten, V.A. 1983. *Physics of Meteoric Phenomena.* D. Reidel, Dordrecht.

Brooke, T.Y., R.F. Knacke, T.C. Owen, and A.T. Tokunaga 1987. Detection of infrared emission features in comet Wilson. *Bull. Am. Astron. Soc.* **19**, 893.

Brooke, T.Y., A.T. Tokunaga, and R.F. Knacke 1991. Detection of the 3.4μm emission feature in comets P/Brorsen–Metcalf and Okazaki–Levy–Rudenko (1989R) and an observational summary. *Astron. J.* **101**, 268–278.

Brown, S.C. 1966. *Introduction to Electrical Discharges in Gases.* John Wiley and Sons, New York.

Brownlee, D.E. 1985. Cosmic dust: Collection and research. *Annu. Rev. Earth Planet. Sci.* **13**, 147–173.

Brownlee, D.E. 1988. A comparison of Halley dust with meteorites, interplanetary dust and interstellar grains. In *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. S. Hanner, Ed.), pp. 66-67. NASA Conference Publication 3004.

Burnham, A.K., R.L. Braun, H.R. Gregg, and A.M. Samoun 1987. Comparison of methods for measuring kerogen pyrolysis rates and fitting kinetic parameters. *Energy Fuels* **1**, 452–458.

Calcagno, L., G. Foti, L. Torrisi, and G. Strazzulla 1985. Fluffy layers obtained by ion bombardment of frozen methane: Experiments and applications to saturnian and uranian satellites. *Icarus* **63**, 31–38.

Cameron, A.G.W. 1986. The impact theory for origin of the Moon. In *Origin of the Moon* (W.K. Hartmann, R.J. Phillips, and G.J. Taylor, Eds.), pp. 609–616. Lunar and Planetary Inst., Houston.

Campbell, M.J., B.T. O'Leary and C. Sagan 1969. Moon: Two new mascon basins. *Science* **164**, 1273–1275.

Campins, H., and E.V. Ryan 1988. The identification of crystalline olivine in cometary silicates. *Ap. J.*, in press.

Carlson, R.W. and G.W. Lugmair 1979. Sm–Nd constraints on early lunar differentiation and the evolution of KREEP. *Earth Planet. Sci. Lett.* **45**, 123–132.

Carlson, R.W. and G.W. Lugmair 1988. The age of ferroan anorthosite 60025: Oldest crust on a young Moon? *Earth Planet. Sci. Lett.* **90**, 119–130.

Carr, M.H. 1984. Earth. In *The Geology of the Terrestrial Planets* (M.H. Carr, Ed.), pp. 79–105. NASA SP–469.

Ceplecha, Z. 1977. Meteoroid populations and orbits. In *Comets, Asteroids, and Meteorites* (A.H. Delsemme, Ed.), pp. 143–152. Univ. Toledo Press, Toledo.

Chalmers, J.A. 1951. Point discharge currents. *J. Atmos. Terr. Phys.* **2**, 301–305.

Chamberlin, T.C. and R.T. Chamberlin 1908. Early terrestrial conditions that may have favored organic synthesis. *Science* **28**, 897-911.

Chameides, W.L. and J.C.G. Walker 1981. Rates of fixation by lightning of carbon and nitrogen in possible primitive atmospheres. *Origins Life* **11**, 291–302.

Chameides, W.L., D.H. Stedman, R.R. Dickerson, D.W. Rusch, and R.J. Cicerone 1977. NO_x production in lightning. *J. Atmos. Sci.* **34**, 143–149.

Chameides, W.L., D.D. Davis, J. Bradshaw, M. Rodgers, S. Sandholm, and D.B. Bai 1987. An estimate of the NO_x production rate in electrified clouds based on NO observations from the GTE/CITE 1 fall 1983 field operation 1987. *J. Geophys. Res.* **92**, 2153–2156.

Chang, S. 1977. Comets: Cosmic connections with carbonaceous meteorites, interstellar molecules and the origin of life. In *Space Missions to Comets* (M. Neugebauer, D.K. Yeomans, J.C. Brandt, and R.W. Hobbs, Eds.), pp. 59–111. NASA Conference Publication 2089.

Chang, S., D. DesMarais, R. Mack, S.L. Miller, and G.E. Strathearn 1983. Prebiotic organic syntheses and the origin of life. In *Earth's Earliest Biosphere* (J.W. Schopf, Ed.), pp. 53–92. Princeton Univ. Press, Princeton.

Chapman, C.R. 1974. The asteroids as meteorite parent–bodies. *Meteoritics* **9**, 322–324.

Chou, C.-L. 1978. Fractionation of siderophile elements in the earth's upper mantle. *Proc. Lunar Planet. Sci. Conf.* **9**, 219–230.

Christensen, N.I. 1989. In *Physical Properties of Rocks and Minerals* (R.S. Charmichael, Ed.), pp. 431–546. CRC Press, Boca Raton, FL.

Christie, W.A.K. 1914. A carbonaceous aërolite from Rajputana. *Records of the Geological Survey of India* **44**, 41–51.

Chyba, C.F. 1986. Are the Earth's oceans extraterrestrial? *Bull. Am. Astron. Soc.* **18**, 782.

Chyba, C.F. 1987. The cometary contribution to the oceans of primitive Earth. *Nature* **330**, 632–635.

Chyba, C.F. 1990a. Impact delivery and erosion of planetary oceans in the early inner solar system. *Nature* **343**, 129–133.

Chyba, C.F. 1990b. Extraterrestrial amino acids and terrestrial life. *Nature* **348**, 113–114.

Chyba, C.F. 1991. Terrestrial mantle siderophiles and the lunar impact record. *Icarus* **92**, 217–233.

Chyba, C. and C. Sagan 1987a. Cometary organics but no evidence for bacteria. *Nature* **329**, 208.

Chyba, C., and C. Sagan 1987b. Infrared emission by organic grains in the coma of comet Halley. *Nature* **330**, 350-353.

Chyba, C. and C. Sagan 1988a. A two-component model for thermal emission from organic grains in comet Halley. In *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. S. Hanner, Ed.), pp. 83-84. NASA Conference Publication 3004.

Chyba, C. and C. Sagan 1988b. Cometary organic matter still a contentious issue. *Nature* **332**, 592.

Chyba, C. and C. Sagan 1989. The pre- and post-accretion irradiation history of cometary ices. In *Interstellar Dust: Contributed Papers* (A.G.G.M. Tielens and L.J. Allamandola, Eds.), pp. 433–435. NASA Conference Publication 3036.

Chyba, C. and C. Sagan 1990. Cometary and asteroidal delivery of prebiotic organics vs. *in situ* production on early Earth. *Bull. Am. Astron. Soc.* **22**, 1097.

Chyba, C. and C. Sagan 1991. Electrical energy sources for organic synthesis on the early Earth. *Origins of Life*, in press.

Chyba, C.F., D.G. Jankowski, and P.D. Nicholson 1989a. Tidal evolution in the Neptune–Triton system. *Astron. Astrophys.* **219**, L23–L26.

Chyba, C.F., C. Sagan, and M.J. Mumma 1989b. The heliocentric evolution of infrared cometary spectra: Results from an organic grain model. *Icarus* **79**, 362–381.

Chyba, C.F., P.J. Thomas, L. Brookshaw, and C. Sagan 1990. Cometary delivery of organic molecules to the early Earth. *Science* **249**, 366–373.

Clark, B.C. 1987. Comets, volcanism, the salt-rich regolith, and cycling of volatiles on Mars. *Icarus* **71**, 250–256.

Clark, B.C. 1988. Primeval procreative comet pond. *Origins Life* **18**, 209–238.

Clark, B.C., L. Mason, and J. Kissel 1987. Systematics of the "CHON" and other light element particle populations in comet P/Halley. *Astron. Astrophys.* **187**, 779-784.

Claus, G. and B. Nagy 1961. A microbiological examination of some carbonaceous chondrites. *Nature* **192**, 594–596.

Cochran, A.L., and McCall, M.L. 1980. Spectrophotometric observations of comet Bowell (1980b). *Publ. Astron. Soc. Pacific* **92**, 854-857.

Combes, M., V.I. Moroz, J.F. Crifo, J.M. Lamarre, J. charra, N.F. Sanko, A. Soufflot, J.P. Bibring, S. Cazes, N. Coron, J. Crovisier, C. Emerich, T. Encrenaz, R. Gispert, A.V. Grigoryev, G. Guyot, V.A. Krasnopolsky, Yu.V. Nikolsky, and F. Rocard 1986. Infrared sounding of comet Halley from Vega 1. *Nature* **321**, 266–268.

Combes, M., V.I. Moroz, J. Crovisier, T. Encrenaz, J.P. Bibring, A.V. Grigoriev, N.F. Sanko, N. Coron, J.F. Crifo, R. Gispert, D. Bockelée-Morvan, Yu.V. Nikolsky, V.A. Krasnolpolsky, T. Owen, C. Emerich, J.M. Lamarre, and F. Rocard 1988. The 2.5–12μm spectrum of comet Halley from the IKS–Vega experiment. *Icarus* **76**, 404–436.

Combi, M.R. 1987. Sources of cometary radicals and their jets: Gases or grains. *Icarus* **71**, 178-191.

Crichton, M. 1969. *The Andromeda Strain.* Dell, New York.

Croft, S.K. 1985. The scaling of complex craters. *Proc. Lunar Planet. Sci. Conf.* **15**, C828–C842.

Cronin, J.R., S. Pizzarello, and D.P. Cruikshank 1988. Organic matter in carbonaceous chondrites, planetary satellites, asteroids and comets. In *Meteorites and the Early Solar System* (J. Kerridge and M.S. Matthews, Eds.), pp. 819–857. Univ. Arizona Press, Tucson.

Crovisier, J., and Encrenaz, Th. 1983. Infrared fluorescence of molecules in comets: the general synthetic spectrum. *Astron. Astrophys.* **126**, 170-182.

Cruikshank, D.P., J.F. Bell, M.J. Gaffey, R.H. Brown, R. Howell, C. Beerman, and M. Rognstad 1983. The dark side of Iapetus. *Icarus* **53**, 90–104.

Danks, A., Th. Encrenaz, P. Bouchet, T. Le Bertre, A. Chalabaev, and N. Epchtein 1986. Observation of an emission feature at 3.4μ in the spectrum of comet Halley. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **3**, pp. 103-106. ESA SP-250.

Danks, A.C., T. Encrenaz, P. Bouchet, T. Le Bertre, and A. Chalabaev 1987. The spectrum of comet P/Halley from 3.0 to 4.0μm. *Astron. Astrophys.* **184**, 329–332.

Darnell, J., Lodish, H. and Baltimore, D. 1990. *Molecular Cell Biology.* 2nd ed., Freeman, New York, p. 1051.

Darrow, K.K. 1932. *Electrical Phenomena in Gases*, Williams & Wilkins, Baltimore.

Davies, R.E. 1988. Panspermia: Unlikely, unsupported, but just possible. *Acta Astr.* **17**, 129–135.

Davies, R.E., A.M. Delluva, and R.H. Koch 1984. Investigation of claims for interstellar organisms and complex organic molecules. *Nature* **311**, 748–750.

Davies, R.E., A.M. Delluva, and R.H. Koch 1985. No valid evidence for interstellar proteins, bacteria, etc. In *The Search for Extraterrestrial Life: Recent Developments* (M.D. Papagiannis, Ed.), pp. 165–169.

Davis, D.R., W.F. Libby, and W.G. Meinschein 1966. Chemistry of positive ions. VI. Positive–ion chemistry in solid methane. *J. Chem. Phys.* **45**, 4481–4492.

Davis, P.M. 1986. Comment on the letter "On the influx of small comets into the Earth's upper atmosphere". *Geophys. Res. Lett.* **13**, 1181–1183.

Dawson, G.A. 1980. Nitrogen fixation by lightning. *J. Atmos. Sci.* **37**, 174–178.

Day, W. 1979. *Genesis on Planet Earth.* House of Talos, East Lansing, MI.

Day, W. 1984. *Genesis on Planet Earth.* 2nd ed., Yale University Press, New Haven.

De Bergh, C., B. Bézard, T. Owen, D. Crisp, J. Maillard, B.L. Lutz 1991. Deuterium on Venus: Observations from Earth. *Science* **251**, 547–549.

Degens, E.T. and M. Bajor 1962. Amino acids and sugars in the Bruderheim and Murray meteorite. *Naturwiss.* **49**, 605–606.

Delano, J.W. and A.E. Ringwood 1978. Siderophile elements in the lunar highlands: Nature of the indigenous component and implications for the origin of the moon. *Proc. Lunar Planet. Sci. Conf.* **9**, 111–159.

Delsemme, A.H. 1976. Chemical nature of the cometary snows. *Mem. Soc. Roy. Sci. Liège* **9**, 135-145.

Delsemme, A.H. 1982. Chemical composition of cometary nuclei. In *Comets* (L.L. Wilkening, Ed.), pp. 85-130. Univ. Arizona Press, Tucson.

Delsemme, A.H. 1988. The chemistry of comets. *Phil. Trans. R. Soc. Lond. A* **325**, 509–523.

Delsemme, A.H. 1991. Nature and history of the organic compounds in comets: An astrophysical view. In *Comets in the Post-Halley Era* (R.L. Newburn, M. Neugebauer, and J. Rahe, Eds.), pp. 377–428. Kluwer, Dordrecht.

Delsemme, A.H. and P. Swings 1952. Hydrates de gaz dans les noyaux cometaires et les grains interstellaires. *Ann. Astrophys.* **15**, 1–6.

Dessler, A.J. 1991. The small-comet hypothesis. *Rev. Geophys.*, in press.

Divine, N., H. Fechtig, T.I. Gombosi, M.S. Hanner, H.U. Keller, S.M. Larson, D.A. Mendis, R.L. Newburn, R. Reinhard, Z. Sekanina, and D.K. Yeomans 1986. The comet Halley dust and gas environment. *Space Sci. Rev.* **43**, 1-104.

Dodd, R.T. 1981. *Meteorites: A petrologic–chemical synthesis.* Cambridge Univ. Press, Cambridge.

Dohnanyi, J.S. 1971. Flux of micrometeoroids: Lunar sample analyses compared with flux model. *Science* **173**, 558.

Dohnanyi, J.S. 1972. Interplanetary objects in review: Statistics of their masses and dynamics. *Icarus* **17**, 1–48.

Dohnanyi, J.S. 1978. Particle dynamics. In *Cosmic Dust* (J.A.M. McDonnell, Ed.), pp. 527–605. John Wiley & Sons, New York.

Donahue, T.M., J.H. Hoffman, R.R. Hodges, and A.J. Watson 1982. Venus was wet: A measurement of the ratio of deuterium to hydrogen. *Science* **216**, 630–633.

Donnison, J.R. and R.A. Sugden 1984. The distribution of asteroid diameters. *Mon. Not. R. astr. Soc.* **210**, 673–682.

Draganić, I.G., Z.D. Draganić, and S. Vujosević 1984. Some radiation-chemical aspects of chemistry in cometary nuclei. *Icarus* **60**, 464-475.

Drapatz, S., H.P. Larson, and D.S. Davis 1987. Search for methane in comet P/Halley. *Astron. Astrophys.* **187**, 497-501.

Dreibus, G. and H. Wãnke 1987. Volatiles on Earth and Mars: A comparison. *Icarus* **71**, 225–240.

Dreibus, G. and H. Wãnke 1989. Supply and loss of volatile constituents during the accretion of terrestrial planets. In *Origin and Evolution of Planetary and Satellite Atmospheres* (S.K. Atreya, J.B. Pollack, and M.S. Matthews, Eds.), pp. 268–288. Univ. Arizona Press, Tucson.

Dumont, R. and A.-C. Levasseur-Regourd 1988. Properties of interplanetary dust from infrared and optical observations. *Astron. Astrophys.* **191**, 154-160.

Durham, R. and J.W. Chamberlain 1989. A comparative study of the early terrestrial atmospheres. *Icarus* **77**, 59–66.

Dziewonski, A.M., A.L. Hales, and E.R. Lapwood 1975. Parametrically simple Earth models consistent with geophysical data. *Phys. Earth Planet. Inter.* **10**, 12–48.

Eberhardt, P., U. Dolder, W. Schulte, D. Krankowsky, P. Lämmerzahl, J.H. Hoffman, R.R. Hodges, J.J. Berthelier, and J.M. Illiano 1987. The D/H ratio in water from comet P/Halley. *Atron. Astrophys.* **187**, 435–437.

Edoh, O. 1983. *Optical Properties of Carbon from the Far Infrared to the Far Ultraviolet.* Ph.D. dissertation, Dept. of Physics, U. Arizona. Cited by M. Hanner (1988). Grain optical properties. In *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. S. Hanner, Ed.), pp. 22-49. NASA Conference Publication 3004.

Epstein. S. and H.P. Taylor 1971. O^{18}/O^{16}, Si^{30}/Si^{28}, D/H, and C^{13}/C^{12} ratios in lunar samples. *Proc. Lunar Sci. Conf.* **2**, 1421–1441.

Epstein, S. and H.P. Taylor 1972. O^{18}/O^{16}, Si^{30}/Si^{28}, C^{13}/C^{12}, and D/H studies of Apollo 14 and 15 samples. *Proc. Lunar Sci. Conf.* **3**, 1429–1454.

Epstein, S. and H.P. Taylor 1973. The isotopic composition and concentration of water, hydrogen, and carbon in some Apollo 15 and 16 soils and in the Apollo 17 orange soil. *Proc. Lunar Sci. Conf.* **4**, 1559–1575.

Epstein, S., R.V. Krishnamurthy, J.R. Cronin, S. Pizzarello, and G.U. Yuen 1987. Unusual stable isotope ratios in amino acid and carboxylic acid extracts from the Murchison meteorite. *Nature* **326**, 477–479.

Ette, A.I.I. and E.U. Utah 1973. Measurement of point-discharge current density in the atmosphere. *J. Atmos. Terr. Phys.* **35**, 785–793.

Fegley, B., R.G. Prinn, H. Hartman, and G.H. Watkins 1986. Chemical effects of large impacts on the Earth's primitive atmosphere. *Nature* **319**, 305–308.

Fernández, J.A. 1985. The formation and dynamical survival of the comet cloud. In *Dynamics of Comets: their Origin and Evolution* (A. Carusi and G.B. Valsecchi, Eds.), pp. 45–70. D. Reidel, Dordrecht.

Fernández, J.A. and Ip, W.-H. 1983. On the time evolution of the cometary influx in the region of the terrestrial planets. *Icarus* **54**, 377-387.

Ferrin, I. and C. Gil 1986. Sizes, aging rates and extinction dates of comets Halley and Encke. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **2**, pp. 427–432. ESA SP-250.

Fitch, F.W. and E. Anders 1963. Observations on the nature of the "organized elements" in carbonaceous chondrites. *Ann. N.Y. Acad. Sci.* **108**, 495–513.

Fitch, F., H.P. Scharcz, and E. Anders 1962. "Organized elements" in carbonaceous chondrites. *Nature* **193**, 1123–1125.

Flynn, G.J. and D.S. McKay 1990. An assessment of the meteoritic contribution to the martian soil. *J. Geophys. Res.* **95**, 14,497–14,509.

Folinsbee, R.E., J.A.V. Douglas, and J.A. Maxwell 1967. *Revelstoke, a new Type I carbonaceous chondrite. Geochim. Cosmochim. Acta* **31**, 1625–1635.

Frank, L.A. and P. Huyghe 1990. *The Big Splash.* Birch Lane Press, Secaucus.

Frank, L.A., J.B. Sigwarth, and J.D. Craven 1986a. On the influx of small comets into the Earth's upper atmosphere. II. Interpretation. *Geophys. Res. Lett.* **13**, 307–310.

Frank, L.A., J.B. Sigwarth, and J.D. Craven 1986b. Reply to Davis and Nakamura *et al.* . *Geophys. Res. Lett.* **13**, 1186–1189.

Freund, F., J.T. Dickinson, C.H. Becker, M.M. Freund, and S. Chang 1986. Organic molecules released from olivine by impact fracture. *Origins Life* **16**, 291-292.

Frey, H. 1977. Origin of the Earth's ocean basins. *Icarus* **32**, 235–250.

Friedman, I. and O'Neil, J.R. 1978. "Hydrogen", in *Handbook of Geochemistry*, Vol II/1, Sec. 1-C. Springer–Verlag, Berlin.

Frohlich, C. and S.P. Grand 1990. The fate of subducting slabs. *Nature* **347**, 333-334.

Gehrz, R.D., and E.P. Ney 1986. Infrared temporal development of P/Halley. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **2**, pp. 101-106. ESA SP-250.

Geiss, J. 1987. Composition measurements and the history of cometary matter. *Astron. Astrophys.* **187**, 859-866.

Gilvarry, J.J. and A.R. Hochstim 1963. Possible role of meteorites in the origin of life. *Nature* **197**, 624–626.

Goebel, J.H., J.D. Bregman, D. Goorvitch, D.W. Strecker, R.C. Puetter, R.W. Russell, B.T. Soifer, S.P. Willner, W.J. Forrest, J.R. Houck, and J.F. McCarthy 1980. The infrared spectrum of the carbon star Y Canum Venaticorum between 1.2 and 30 microns. *Astrophys. J.* **235**, 104–113.

Goldspiel, J.M. and S.W. Squyres 1991. Ancient aqueous sedimentation on Mars. *Icarus* **89**, 392–410.

Gradie, J. and J. Veverka 1980. The composition of the Trojan asteroids. *Nature* **283**, 840–842.

Gradie, J.C., C.R. Chapman, and E.F. Tedesco 1989. Distribution of taxonomic classes and the compositional structure of the asteroid belt. In *Asteroids II* (R.P. Binzel, T. Gehrels, and M.S. Matthews, Eds.), pp. 316–335. Univ. Arizona Press, Tucson.

Green, D.W.E., and Morris, C.S. 1987. The visual brightness behavior of P/Halley during 1981-1987. *Astron. Astrophys.* **187**, 560-568.

Green, S.F., J.A.M. McDonnell, G.S.A. Pankiewicz, and J.C. Zarnecki 1986. The UKIRT infrared observational program. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **2**, pp. 81-86. ESA SP–250.

Greenberg, J.M. 1971. Interstellar grain temperatures. Effects of grain materials and radiation fields. *Astron. Astrophys.* **12**, 240-249.

Greenberg, J.M. 1978. Interstellar dust. In Cosmic Dust (J.A.M. McDonnell, Ed.), pp. 187–294. John Wiley & Sons, New York.

Greenberg, J.M. 1982. What are comets made of? A model based on interstellar dust. In *Comets* (L.L. Wilkening, Ed.), pp. 131-163. Univ. Arizona Press, Tucson.

Greenberg, J.M. 1989. Synthesis of organic compounds in interstellar dust and their transport to Earth via comets. *Adv. Space Res.* **9(6)**, 15–23.

Greenberg, J.M. and R. Grim 1986. The origin and evolution of comet nuclei and comet Halley results. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **2**, pp. 255-263. ESA SP–250.

Greenberg, J.M. and J.I. Hage 1990. From interstellar dust to comets: A unification of observational constraints. *Astrophys. J.* **361**, 260–274.

Greenberg, J.M. and N. Zhao 1988. Cometary organics. *Nature* **331**, 124.

Greenberg, R. 1989. Planetary accretion. In *Origin and Evolution of Planetary and Satellite Atmospheres* (S.K. Atreya, J.B. Pollack, and M.S. Matthews, Eds.), pp. 137–164, Univ. Arizona, Tucson.

Grieve, R.A.F. 1982. The record of impacts on Earth: Implications for a major Cretacous/Tertiary event. In *Geological Implications of Impacts of Large Asteroids and Comets on the Earth* (L.T. Silver and P.H. Schultz, Eds.), pp.25–38. Geol. Soc. Am. SP–190.

Grim, R.E. 1968. *Clay Mineralogy.* McGraw–Hill, New York.

Gringauz, K.I., T.I. Gombosi, A.P. Remizov, I. Apáthy, I. Szemerey, M.I. Verigin, L.I. Denchikova, A.V. Dyachkov, E. Keppler, I.N. Klimenko, A.K. Richter, A.J. Somogyi, K. Szegö, S. Szentrö, M. Tátrallyay, A. Varga, and G.A. Vladimirova 1986. First *in situ* plasma and neutral gas measurements at comet Halley. *Nature* **321**, 282–285.

Grinspoon, D.H. 1987. Was Venus wet? Deuterium reconsidered. *Science* **238**, 1702–1704.

Grinspoon, D.H. 1988. *Large Impact Events and Atmospheric Evolution on the Terrestrial Planets.* Ph.D. thesis, Univ. Arizona.

Grinspoon, D.H. and J.S. Lewis 1988. Cometary water on Venus: Implications of stochastic impacts. *Icarus* **74**, 21–35.

Gros, J., H. Takahashi, J. Hertogen, J.W. Morgan, and E. Anders 1976. Composition of the projectiles that bombarded the lunar highlands. *Proc. Lunar Sci. Conf.* **7**, 2403–2425.

Grün, E., H.A. Zook, H. Fechtig, and R.H. Giese 1985. Collisional balance of the meteoritic complex. *Icarus* **62**, 244–272.

Guo, C. and E.P. Krider 1982. The optical and radiation field signatures produced by lightning return strokes. *J. Geophys. Res.* **87**, 8913–8922.

Hahn, G. and M.E. Bailey 1990. Rapid dynamical evolution of giant comet Chiron. *Nature* **348**, 132–136.

Haines, E.L. and A.E. Metzger 1980. Lunar highland crustal models based on iron concentrations: Isostasy and center-of-mass displacement. *Proc. Lunar Planet. Sci. Conf.* **11**, 689–718.

Hamilton, P.B. 1965. Amino acids on hands. *Nature* **205**, 284–285.

Hanner, M.S. 1983. The nature of cometary dust from remote sensing. In *Cometary Exploration II* (T.I. Gombosi, Ed.), pp. 1-22. Hungarian Acad. Sci., Budapest.

Hanner, M.S. 1986. A preliminary look at the dust in comet Halley. *Adv. Space Res.* **5**, 325-334.

Hanner, M.S., Ed. 1988. *Infrared Observations of Comets Halley and Wilson and Properties of the Grains*, NASA Conference Publication 3004.

Hartmann, W.K. 1980. Dropping stones in magma oceans: Effects of early lunar cratering. In *Proceedings of the Conference on the Lunar Highland Crust*, pp. 155–171. Lunar and Planetary Institute, Houston.

Hartmann, W.K. 1987. A satellite–asteroid mystery and a possible early flux of scattered C–class asteroids. *Icarus* **71**, 57–68.

Hartmann, W.K. 1990. Additional evidence about an early intense flux of C asteroids and the origin of Phobos. *Icarus* **87**, 236–240.

Hayes, J.M., I.R. Kaplan and K.W. Wedeking 1983. Precambrian organic geochemistry, preservation of the record. In *Earth's Earliest Biosphere* (J.W. Schopf, Ed.), pp. 93–134. Princeton Univ. Press, Princeton.

Head, J.W., M. Belton, M. Carr, C. Chapman, M. Davies, F. Fanale, E. Fischer, R. Greeley, R. Greenberg, R. Kolvoord, L. Dose, P. Helfenstein, H. Hoffmann, R. Jaumann, T. Johnson, K. Klaasen, A. McEwen, T. Becker, S. Murchie, G. Neukum, J. Oberst, C. Pieters, C. Pilcher, J. Plutchak, M. Robinson, R. Sullivan, J. Sunshine, J. Veverka 1991. Orientale and South Pole–Aitken basins: Preliminary Galileo imaging results. *Lunar Planet. Sci. XXII*, 547-548.

Herter, T., G.E. Gull, H. Campins 1986. Airborne spectrophotometry of P/Halley from 16 to 30 microns. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **2**, pp. 117-120. EAS SP-250.

Hertogen, J., M. Janssens, H. Takahashi, H. Palme, and E. Anders 1977. *Proc. Lunar Sci. Conf.* **8**, 17–45.

Hill, R.D. 1979a. A survey of lightning energy estimates. *Rev. Geophys. Space Phys.* **17**, 155–164.

Hill, R.D. 1979b. On the production of nitric oxide by lightning. *Geophys. Res. Lett.* **6**, 945–947.

Hill, R.D. 1987. Comments on "Lightning return stroke. A numerical calculation of the optical radiation" [Phys. Fluids 29, 2736 (1986)]. *Phys. Fluids* **30**, 2585–2587.

Hill, R.D., I. Rahmim, and R.G. Rinker 1988. Experimental study of the production of NO, N_2O and O_3 in a simulated atmospheric corona. *Ind. Eng. Chem. Res.* **27**, 1264–1269.

Hill, R.D., R.G. Rinker, and A. Coucouvinos 1984. Nitrous oxide production by lightning. *J. Geophys. Res.* **89**, 1411- 1421.

Hill, R.D., R.G. Rinker, and H.D. Wilson 1980. Atmospheric nitrogen fixation by lightning. *J. Atmos. Sci.* **37**, 179–192.

Hochstim, A.R. 1963. Hypersonic chemosynthesis and possible formation of organic compounds from impact of meteorites on water. *Proc. Nat. Acad. Sci.* **50**, 200–208.

Hood, L.L. 1987. A model for the formation of magnetic anomalies antipodal to lunar impact basins. *Lunar Planet. Sci. XVIII*, 433–434.

Horgan, J. 1991. In the beginning . . . . *Sci. Am.* **264(2)**, 116–125.

Housen, K.R., R.M. Schmidt, and K.A. Holsapple 1983. Crater ejecta scaling laws: Fundamental forms based on dimensional analysis. *J. Geophys. Res.* **88**, 2485–2499.

Hoyle, F. and N.C. Wickramasinghe 1986. The case for life as a cosmic phenomenon. *Nature* **322**, 509–511.

Hoyle, F. and N.C. Wickramasinghe 1987. Organic dust in comet Halley. *Nature* **328**, 117.

Hoyle, F. and N.C. Wickramasinghe 1988a. Cometary organics. *Nature* **331**, 123–124.

Hoyle, F. and N.C. Wickramasinghe 1988b. Cometary organics. *Nature* **331**, 666.

Hughes, D.W. 1978. Meteors. In *Cosmic Dust* (J.A.M. McDonnell, Ed.), pp. 123–185. John Wiley & Sons, New York.

Hughes, D.W. 1982. Asteroidal size distribution. *Mon. Not. R. astr. Soc.* **199**, 1149–1157.

Hughes, D.W. 1987. Cometary magnitude distribution: The tabulated data. In *Symposium on the Diversity and Similarity of Comets*, pp. 43–48. ESA SP–278.

Hughes, D.W. 1988. Cometary magnitude distribution and the ratio between the numbers of long- and short-period comets. *Icarus* **73**, 149–162.

Hughes, D.W. 1990. Cometary absolute magnitudes, their significance and distribution. In *Asteroids, Comets, Meteors III* (C.-I. Lagerkvist, H. Rickman, B.A. Lindblad, and M. Lindgren, Eds.), pp.327–342. Uppsala universitet, Uppsala.

Hulett, H.R. 1970. Amino acid synthesis in simulated primitive environments. *Science* **170**, 1000–1002.

Irvine, W.M., Leschine, S.B., and F.P. Schloerb 1980. Thermal history, chemical composition and relationship of comets to the origin of life. *Nature* **283**, 748–749.

Jessberger, E.K., A. Christoforidis, and J. Kissel 1988. Aspects of the major element composition of Halley's dust. *Nature* **332**, 691-695.

Johnson, R.E. and L.J. Lanzerotti 1986. Ion bombardment of interplanetary dust. *Icarus* **66**, 619–624.

Johnson, R.E., J.F. Cooper, L.J. Lanzerotti, and G. Strazzulla 1987. Radiation formation of a non–volatile comet crust. *Astron. Astrophys.* **187**, 889-892.

Kaplan, I.R. 1971. Hydrogen. In *Handbook of Elemental Abundances in Meteorites* (B. Mason, Ed.), pp. 21–27. Gordon and Breach, New York.

Kaplan, I.R., E.T. Degens and J.H. Reuter 1963. Organic compounds in stony meteorites. *Geochim. Cosmochim. Acta* **27**, 805–834.

Kasting, J.F. 1987. Theoretical constraints on oxygen and carbon dioxide concentrations in the precambrian atmosphere. *Precamb. Res.* **34**, 205–229.

Kasting, J.F. 1989. Long-term stability of the Earth's climate. *Palaeogeog. Palaeoclim. Palaeoecol.* **75**, 83–95.

Kasting, J.F. 1990. Bolide impacts and the oxidation state of carbon in the Earth's early atmosphere. *Origins Life* **20**, 199–231.

Kasting, J.F. and T.P. Ackerman 1986. Climatic consequences of very high carbon dioxide levels in the Earth's early atmosphere. *Science* **234**, 1383–1385.

Kasting, J.F. and J.B. Pollack 1984. Effects of high CO_2 levels on surface temperature and atmospheric oxidation state of the early Earth. *J. Atmos. Chem.* **1**, 403–428.

Kasting, J.F. and O.B. Toon 1989. In *Origin and Evolution of Planetary and Satellite Atmospheres* (S.K. Atreya, J.B. Pollack, and M.S. Matthews, Eds.), pp. 423–449. Univ. Arizona Press, Tucson.

Kasting, J.F., O.B. Toon, and J.B. Pollack 1988. How climate evolved on the terrestrial planets. *Sci. Am.* **256(2)**, 90–97.

Keller, H.U., C. Arpigny, C. Barbieri, R.M. Bonnet, S. Cazes, M. Coradini, C.B. Cosmovici, W.A. Delamere, W.F. Huebner, D.W. Hughes, C. Jamar, D. Malaise, H.J. Reitsema, H.U. Schmidt, W.K.H. Schmidt, P. Seige, F.L. Whipple, and K. Wilhelm 1986. First Halley Multicolour Camera imaging results from Giotto. *Nature* **321**, 320–326.

Kerridge, J.F. 1985. Carbon, hydrogen and nitrogen in carbonaceous chondrites: Abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta* **49**, 1707–1714.

Kessler, D.J. 1981. Derivation of the collision probability between orbiting objects: The lifetimes of Jupiter's outer moons. *Icarus* **48**, 39–48.

Khandelwal, S. and G. Skinner 1981. In *Shock Waves in Chemistry* (A. Lifshitz, Ed.), pp. 1–57. Dekker, New York.

Khare, B.N., C. Sagan, E.T. Arakawa, F. Suits, T.A. Calcott, and M.W. Williams 1984. Optical constants of organic tholins produced in simulated Titanian atmospheres: From soft X-ray to microwave frequencies. *Icarus* **60**, 127-137.

Khare, B.N., W.R. Thompson, B.G.J.P.T. Murray, C.F.Chyba, C. Sagan, and E.T. Arakawa 1989. Solid organic residues produced by irradiation of hydrocarbon-containing H_2O and H_2O/NH_3 ices: infrared spectroscopy and astronomical implications. *Icarus* **79**, 350–361.

Kissel, J. and F.R. Krueger 1987a. The organic component in dust from comet Halley as measured by the PUMA mass spectrometer on board Vega 1. *Nature* **326**, 755-760.

Kissel, J. and F.R. Krueger 1987b. Organic dust in comet Halley. *Nature* **328**, 117.

Kissel, J., R.Z. Sagdeev, J.L. Bertaux, V.N. Angarov, J. Audouze, J.E. Blamont, K. Buchler, E.N. Evlanov, H. Fechtig, M.N. Fomenkova, H. von Hoerner, N.A. Inogamov, V.N. Khromov, W. Knabe, F.R. Krueger, Y. Langevin, V.B. Leonas, A.C. Levasseur-Regourd, G.G. Managadze, S.N. Podkolzin, V.D. Shapiro, S.R. Tabaldyev, and B.V. Zubkov 1986. Composition of comet Halley dust particles from Vega observations. *Nature* **321**, 280–282.

Knacke, R.F., T.Y. Brooke, and R.R. Joyce 1986. Observations of 3.2-3.6 micron emission features in comet Halley. *Ap. J. Lett.* **310**, L49-L53.

Kokumbu, N., T. Mayeda, and H.C. Urey 1961. Deuterium content of minerals, rocks and liquid inclusion from rocks. *Geochim. Cosmochim. Acta* **21**, 247–256.

Kresák, Ľ. The aging and lifetimes of comets. In *Dynamics of Comets: Their Origin and Evolution* (A. Carusi and G.B. Valsecchi, Eds.), pp. 279–302. D. Reidel, Dordrecht.

Kronk, G.W. 1984. *Comets: A Descriptive Catalogue.* Enslow, Hillside, New Jersey.

Krueger, F.R. and J. Kissel 1987. The chemical composition of the dust of comet P/Halley as measured by "PUMA" on board VEGA–1. *Naturwiss.* **74**, 312–316.

Ku, T., W.S. Broecker, and N. Opdyke 1968. Comparison of sedimentation rates measured by paleomagnetic and the ionium methods of age determination. *Earth Planet. Sci. Lett.* **4**, 1–16.

Kuhn, W.R. and S.K. Atreya 1979. Ammonia photolysis and the greenhouse effect in the primordial atmosphere of the Earth. *Icarus* **37**, 207–213.

Kuiper, G.P. 1951. On the origin of the Solar System. In *Astrophysics: A Topical Symposium* (J.A. Hynek, Ed.), pp. 357–424. McGraw–Hill, New York.

Kvenvolden, K., J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I.R. Kaplan, and C. Moore 1970. Evidence for extraterrestrial amino–acids and hydrocarbons in the Murchison meteorite. *Nature* **228**, 923–926.

Kvenvolden, K.A., J.G. Lawless, and C. Ponnamperuma 1971. Nonprotein amino acids in the Murchison meteorite. *Proc. Nat. Acad. Sci.* **68**, 486–490.

Kyte, F.T. and J.T. Wasson 1986. Accretion rate of extraterrestrial matter: Iridium deposited 33 to 67 million years ago. *Science* **232**, 1225–1229.

Lamy, P.L. and J.M. Perrin 1988. Optical properties of organic grains: Implications for interplanetary and cometary dust. *Icarus* **76**, 100-109.

Larson, H.P., H.A. Weaver, M.J. Mumma, and S. Drapatz 1989. Airborne infrared spectroscopy of comet Wilson (1986*l*) and comparisons with comet Halley. *Astrophys.. J.* **338**, 1106–1114.

Latham, J. 1975. Possible mechanisms of corona discharge involved in biogenesis. *Nature* **256**, 34–35.

Lederberg, J. 1965. Signs of life: Criterion-system of exobiology. *Nature* **207**, 9–13.

Leger, A. and J.L. Puget 1984. Identification of the "unidentified" IR emission features of interstellar dust? *Astron. Astrophys.* **137**, L5–L8.

Levin, B.Yu. and V.A. Bronshten 1986. The Tunguska event and the meteors with terminal flares. *Meteoritics* **21**, 199–215.

Levine, J.S. and T.R. Augustsson 1985. The photochemistry of biogenic gases in the early and present atmosphere. *Origins Life* **15**, 299–318.

Lifshitz, A., A. Bar-Nun, P.C.T. de Boer, and E.L. Resler 1970. Boundary layer effects on chemical kinetics studies in a shock tube. *J. Chem. Phys.* **53**, 3050–3055.

Liu, V.C. 1978. A test of the comet hypothesis of the Tunguska meteor fall: Nature of the meteor "thermal" explosion paradox. *Geophys. Res. Lett.* **5**, 309–312.

Los Alamos National Laboratory 1983. *Sesame '83: Report on the Los Alamos Equation-of-State Library.* LALP-83-4, Los Alamos National Laboratory, Los Alamos, NM.

Love, S.G. and D.E. Brownlee 1991. Heating and thermal transformation of micrometeoroids entering the Earth's atmosphere. *Icarus* **89**, 26–43.

Lynch, D.K., R.W. Russell, F.C. Witteborn, J.D. Bregman, D.M. Rank, M.C. Cohen, and H. Campins 1988. 5-13μm airborne observations of Comet Wilson 1986*l*: Preliminary results. In *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. S. Hanner, Ed.), p. 165. NASA Conference Publication 3004.

MacIntyre, A. 1981. *After Virtue: A Study in Moral Theory.* Univ. Notre Dame Press, Notre Dame, IN.

Maher, K.A. and D.J. Stevenson 1988. Impact frustration of the origin of life. *Nature* **331**, 612–614.

Mahoney, W.A., J.C. Ling, Wm. A. Wheaton, and A.S. Jacobson 1984. HEAO 3 discovery of ^{26}Al in the interstellar medium. *Astrophys. J.* **286**, 578–585.

Marcus, J.N. and M.A. Olsen 1991. Biological implications of organic compounds in comets. In *Comets in the Post-Halley Era* (R.L. Newburn, M. Neugebauer and J. Rahe, Eds.), pp. 439–462. Kluwer Academic, Dordrecht.

Mason, B. 1971. *Handbook of Elemental Abundances in Meteorites.* Gordon and Breach, New York.

Maurette, M., C. Olinger, M.C. Michel-Levy, G. Kurat, M. Pourceht, F. Brandstätter, and M. Bourot-Denise 1991. A collection of diverse micrometeorites recovered from 100 tonnes of Antarctic blue ice. *Nature* **351**, 44–47.

McDonnell, J.A.M, J. Kissel, E. Grün, R.J.L. Grard, Y. Langevin, R.E. Olearczyk, C.H. Perry, and J.C. Zarnecki 1986. Giotto's dust impact detection system DIDSY and particulate impact analyser PIA: Interim assessment of the dust distribution and properties within the coma. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **2**, pp. 25-38. ESA SP–250.

McDonnell, J.A.M., W.M. Alexander, W.M. Burton, E. Bussoletti, G.C. Evans, S.T. Evans, J.G. Firth, R.J.L. Grard, S.F. Green, E. Grun, M.S. Hanner, D.W. Hughes, E. Igenbergs, J. Kissel, H. Kuczera, B.A. Lindblad, Y. Langevin, J.-C. Mandeville, S. Nappo, G.S.A. Pankiewicz, C.H. Perry, G.H. Schwehm, Z. Sekanina, T.J. Stevenson, R.F. Turner, U. Weishaupt, M.K. Wallis, and J.C. Zarnecki 1987. The dust distribution within the inner coma of comet P/Halley 1982i: Encounter by Giotto's impact detectors. *Astron. Astrophys.* **187**, 719-741.

McKay, C.P. 1991. Urey Prize lecture: Planetary evolution and the origin of life. *Icarus* **91**, 93–100.

McKay, C.P. and C.R. Stoker 1989. The early environment and its evolution on Mars: Implications for life. *Rev. Geophys.* **27**, 189–214.

McKay, C.P., T.W. Scattergood, J.B. Pollack, W.J. Borucki, and H. T. Van Ghyseghem 1988. High-temperature shock formation of N_2 and organics on primordial Titan. *Nature* **332**, 520–522.

McKay, C.P., W.R. Borucki, K.R. Kojiro, and F. Church 1989. Shock production of organics during cometary impact. *Lunar Planet. Sci. Conf.* **20**, 671–672.

McKinnon, W.B. 1989. Impacts giveth and impacts taketh away. *Nature* **338**, 465–466.

McKinnon, W.B. and P.M. Schenk 1985. Ejecta blanket scaling on the Moon and Mercury—and inferences for projectile populations. *Lunar Planet. Sci.* **16**, 544–545.

McKinnon, W.B., C.R. Chapman, and K.R. Housen 1990. Cratering of the uranian satellites. In *Uranus* (J.T. Bergstrahl, E.D. Miner, and MS. Matthews, Eds.), in press.

McTaggart, F.K. 1967. *Plasma Chemistry in Electrical Discharges.* Elsevier, New York.

Meakin, P. and B. Donn 1988. Aerodynamic properties of fractal grains: implications for the primordial solar nebula. In *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. S. Hanner, Ed.), pp.166-171. NASA Conference Publication 3004.

Melosh, H.J. 1988. The rocky road to panspermia. *Nature* **332**, 687–688.

Melosh, H.J. 1989. *Impact Cratering: A Geologic Process* (Oxford Univ. Press, New York).

Melosh, H.J. and A.M. Vickery 1989. Impact erosion of the primordial atmosphere of Mars. *Nature* **338**, 487–489.

Miller, S.L. 1953. A production of amino acids under possible primitive Earth conditions. *Science* **117**, 528–529.

Miller, S.L. 1974. The first laboratory synthesis of organic compounds under primitive Earth conditions. In *The Heritage of Copernicus: Theories "Pleasing to the Mind"* (J. Neyman, Ed.), pp. 228–242. MIT Press, Cambridge, MA.

Miller, S.L. and J.L. Bada 1991. Extraterrestrial synthesis. *Nature* **350**, 387–388.

Miller, S.L. and L.E. Orgel 1974. *The Origins of Life on Earth.* Prentice-Hall, Englewood Cliffs, New Jersey.

Miller, S.L. and H.C. Urey 1959. Organic compound synthesis on the primitive Earth. *Science* **130**, 245–251.

Miller, S.L., H.C. Urey, and J. Oró 1976. Origin of organic compounds on the primitive Earth and in meteorites. *J. Mol. Evol.* **9**, 59–72.

Monaghan, J.J. 1985. Particle methods for hydrodynamics. *Comput. Phys. Rep.* **3**, 71–124.

Moorbath, S. 1983. The dating of the earliest sediments on Earth. In *Cosmochemistry and the Origin of Life* (C. Ponnamperuma, Ed.), pp. 213–233. D. Reidel, Dordrecht.

Moreno, M.A. 1988. Microorganism transport from Earth to Mars. *Nature* **336**, 209.

Mukhin, L.M., M.V. Gerasimov, and E.N. Safonova 1989. Origin of precursors of organic molecules during evaporation of meteorites and mafic terrestrial rocks. *Nature* **340**, 46–48.

Mumma, M.J. and D.C. Reuter 1989. On the identification of formaldehyde in Halley's comet. *Astrophys. J.* **344**, 940–948.

Nagy, B., W.G. Meinschein, and D.J. Hennessy 1961. Mass spectroscopic analysis of the Orgueil meteorite: Evidence for biogenic hydrocarbons. *Ann. N.Y. Acad. Sci.* **93**, 25–35.

Nagy, B., G. Claus, and D. Hennessey 1962. Organic particles embedded in the minerals in the Orgueil and Ivuna carbonaceous chondrites. *Nature* **193**, 1129–1133.

Nakamura, Y., J. Oberst, S.M. Clifford, and B.G. Bills 1986. Comment on the letter "On the influx of small comets into the Earth's upper atmosphere II. Interpretation". *Geophys. Res. Lett.* **13**, 1184–1185.

National Research Council 1990. *The Search for Life's Origins.* Nat. Acad. Press, Washington.

Neukum, G. 1983. *Meteoritenbombardement und Datierung Planetaren Oberflächen.* Habilitationsschrift, Univ. Munich.

Newsom, H.E. 1990. Accretion and core formation in the Earth: Evidence from siderophile elements. In *Origin of the Earth* (H.E. Newsom and J.H. Jones, Eds.), pp. 273–288. Oxford Univ. Press, New York.

Newsom, H.E. and K.W.W. Sims 1991. Core formation during early accretion of the Earth. *Science* **252**, 926–933.

Noh, W.H. 1987. Errors for calculations of strong shocks using an artificial viscosity and an artificial heat flux. *J. Comput. Phys.* **72**, 78–120.

Oberbeck, V.R. and G. Fogleman 1989a. Impacts and the origin of life. *Nature* **339**, 434.

Oberbeck, V.R. and G. Fogleman 1989b. Estimates of the maximum time required to originate life. *Origins Life* **19**, 549-560.

Oberbeck, V.R. and G. Fogleman 1990. Impact constraints on the environment for chemical evolution and the continuity of life. *Origins of Life* **20**, 181–195.

Oberbeck, V.R., C.P. McKay, T.W. Scattergood, G.C. Carle, and J.R. Valentin 1989. The role of cometary particle coalescence in chemical evolution. *Origins Life* **19**, 39–55.

O'Keefe, J.D. and T.J. Ahrens 1977. Impact-induced energy partitioning, melting, and vaporization on terrestrial planets. *Proc. Lunar Sci. Conf.* **8**, 3357–3374.

O'Keefe, J.D. and T.J. Ahrens 1982. Cometary and meteorite swarm impact on planetary surfaces. *J. Geophys. Res.* **87**, 6668–6680.

O'Leary, B.T., M.J. Campbell and C. Sagan 1969. Lunar and planetary mass concentrations. *Science* **165**, 651–657.

Olsson-Steel, D. 1987. Collisions in the solar system—IV. Cometary impacts upon the planets. *Mon. Not. R. astr. Soc.* **227**, 501–524.

Olsson-Steel, D. 1990. The asteroidal impact rate upon the terrestrial planets: An update. *Proc. Astron. Soc. Australia* **8**, 303–307.

Oort, J.H. 1950. The structure of the cloud of comets surrounding the solar system, and a hypothesis concerning its origin. *Bull. Astronom. Inst. Neth.* **11**, 91–110.

Öpik, E.J. 1958. *Physics of Meteor Flight in the Atmosphere.* Interscience, New York.

Oró, J. 1961. Comets and the formation of biochemical compounds on the primitive Earth. *Nature* **190**, 389–390.

Oró, J. and H.B. Skewes 1965. Free amino-acids on human fingers: The question of contamination in microanalysis. *Nature* **207**, 1042–1045.

Oró, J., G. Holzer, and A. Lazcano-Araujo 1980. The contribution of cometary volatiles to the primitive Earth. In *COSPAR: Life Science and Space Research XVIII* (R.M. Holmquist, Ed.), pp. 67–82. Pergamon, New York.

Owen, T., R.D. Cess, and V. Ramanathan 1979. Enhanced CO_2 greenhouse to compensate for reduced solar luminosity on early Earth. *Nature* **277**, 640–642.

Passey, Q.R. and H.J. Melosh 1980. Effects of atmospheric breakup on crater field formation. *Icarus* **42**, 211–233.

Peale, S.J. 1989. On the density of Halley's comet. *Icarus* **82**, 36–49.

Penning, F.M.. 1957. *Electrical Discharges in Gases.* Macmillan, New York.

Pepin, R.O. 1979. The formation interval of the Earth. *Lunar Sci VII*, 682–684.

Pepin, R.O. 1989. Atmospheric compositions: Key similarities and differences. In *Origin and Evolution of Planetary and Satellite Atmospheres* (S.K. Atreya, J.B. Pollack, and M.S. Matthews, Eds.), pp. 291–305. Univ. Arizona Press, Tucson.

Perry, C.H., S.F. Green, and J.A.M. McDonnell 1988. A possible explanation for the inconsistency between the Giotto grain mass distribution and ground-based observations. In *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. S. Hanner, Ed.), pp. 178-179. NASA Conference Publication 3004.

Pinto, J.P., G. Randall Gladstone, and Y.L. Yung 1980. Photochemical production of formaldehyde in Earth's primitive atmosphere. *Science* **210**, 183–185.

Pollack, J.B. and Y.L. Yung 1980. Origin and evolution of planetary atmospheres. *Annu. Rev. Earth Planet. Sci.* **8**, 425–487.

Pongracic, H. 1988. *Numerical Modelling of Large Body Impacts.* Ph.D. thesis, Monash University, Clayton, Australia.

Ponnamperuma, C., Ed. 1980. *Comets and the Origin of Life.* D. Reidel, Dordrecht.

Ponnamperuma, C. and E. Ochiai 1982. Comets and origin of life. In *Comets* (L.L. Wilkening, Ed.), pp. 696–703. Univ. Arizona Press, Tucson.

Prinn, R.G. and B. Fegley 1987. Bolide impacts, acid rain, and biosphere traumas at the Cretaceous–Tertiary boundary. *Earth Planet. Sci. Lett.* **83**, 1–15.

Prinn, R.G. and B. Fegley 1989. Solar nebula chemistry: Origin of planetary, satellite and cometary volatiles. In *Origin and Evolution of Planetary and Satellite Atmospheres* (S.K. Atreya, J.B. Pollack, and M.S. Matthews, Eds.), pp. 78–136. Univ. Arizona Press, Tucson.

Rao, V.V., D. Mackay, and O. Trass 1967. A shock tube study of the high temperature reactions of nitrogen with hydrocarbons. *Can. J. Chem. Eng.* **45**, 61–66.

Ratcliff, M.A., E.E. Medley, and P.G. Simmonds 1974. Pyrolysis of amino acids. Mechanistic considerations. *J. Org. Chem.* **39**, 1481–1490.

Reuter, D.C., M.J. Mumma, and S. Nadler 1989. Infrared fluorescence efficiencies for the ν_1 and ν_5 bands of formaldehyde in the solar radiation field. *Astrophys. J.* **341**, 1045–1058.

Ridley, B.A., M.A. Carroll, G.L. Gregory 1987. Measurements of nitric oxide in the boundary layer and free troposphere over the Pacific Ocean. *J. Geophys. Res.* **92**, 2025–2047.

Rössler, K. and G. Eich 1985. Computer calculation of collision cascades by energetic particles penetrating dust grains. In *Properties and Interactions of*

Interplanetary Dust (R.H. Giese and P. Lamy, Eds.), pp. 351–356. D. Reidel, Dordrecht.

Roth, P. and Th. Just 1976. Messungen zum thermischen Zerfall von HCN hinter Stoßwellen. *Ber. Bunsenges. Phys. Chem.* **80**, 171–172.

Ryder, G. 1990. Lunar samples, lunar accretion and the early bombardment of the Moon. *Eos* **71**, 313, 322–323.

Sagan, C. 1977. Reducing greenhouses and the temperature history of Earth and Mars. *Nature* **269**, 224–226.

Sagan, C., and B.N. Khare 1971. Long-wavelength ultraviolet photoproduction of amino acids on the primitive Earth. *Science* **173**, 417–420.

Sagan, C., and B.N. Khare 1979. Tholins: Organic chemistry of interstellar grains and gas. *Nature* **277**, 102-107.

Sagan, C. and G. Mullen 1972. Earth and Mars: Evolution of atmospheres and surface temperatures. *Science* **177**, 52–56.

Sagan, C., B.N. Khare, and J.S. Lewis 1984. Organic matter in the Saturn system. In *Saturn* (T. Gehrels and M.S. Matthews, Eds.), pp. 788-807. U. Arizona Press, Tucson.

Scattergood, T.W., C.P. McKay, W.J. Borucki, L.P. Giver, H. Van Ghyseghem, J.E. Parris, and S.L. Miller 1989. Production of organic compounds in plasmas: A comparison among electric sparks, laser–induced plasmas, and UV light. *Icarus* **81**, 413–428.

Schidlowski, M. 1988. A 3,800–million–year isotopic record of life from carbon in sedimentary rocks. *Nature* **333**, 313–318.

Schidlowski, M., J.M. Hayes and I.R. Kaplan 1983. Isotopic inferences of ancient biochemistries: Carbon, sulfur, hydrogen, and nitrogen. In *Earth's Earliest Biosphere* (J.W. Schopf, Ed.), pp. 149–186. Princeton Univ. Press, Princeton.

Schlesinger, G. and S.L. Miller 1983a. Prebiotic synthesis in atmospheres containing CH_4, CO, and CO_2. I. Amino Acids. *J. Mol. Evol.* **19**, 376–382.

Schlesinger, G. and S.L. Miller 1983b. Prebiotic synthesis in atmospheres containing CH_4, CO, and CO_2. I. Hydrogen cyanide, formaldehyde and ammonia. *J. Mol. Evol.* **19**, 383–390.

Schlosser, W., Schulz, R., and P. Koczet 1986. The cyan shells of comet P/Halley. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **3**, pp. 495-498. ESA SP-250.

Schonland, B.F.J. 1928. The interchange of electricity between thunderclouds and the Earth. *Proc. R. Soc. A* **118**, 252-262.

Schonland, B.F.J. 1953. *Atmospheric Electricity.* Methuen, London.

Schmidt, R.M. 1980. Meteor crater: Energy of formation—Implications of centriruge scaling. *Proc. Lunar Planet. Sci. Conf.* **11**, 2099-2128.

Schmidt, R.M. and K.R. Housen 1987. Some recent advances in the scaling of impact and explosion cratering. *Int. J. Impact Engng.* **5**, 543-560.

Schramm, L.S., D.E. Brownlee, and M.M. Wheelock 1989. Major element composition of stratospheric micrometeorites. *Meteoritics* **24**, 99-112.

Schultz, P.H. and L.J. Srnka 1980. Cometary collisions on the Moon and Mercury. *Nature* **284**, 22-26.

Sears, D.W.G. and R.T. Dodd 1988. Overview and classification of meteorites. In *Meteorites and the Early Solar System* (J.F. Kerridge and M.S. Matthews, Eds.), pp. 3-31. Univ. Arizona Press, Tucson.

Sekanina, Z. 1982. The problem of split comets in review. In *Comets* (L.L. Wilkening, Ed.), pp. 251-287. Univ. Arizona Press, Tucson.

Sekanina, Z. 1986. Dust environment of comet Halley. In *20th ESLAB Symposium on the Exploration of Halley's Comet* **2**, pp. 131-143. ESA SP-250.

Sekanina, Z. 1991. Cometary activity, discrete outgassing areas, and dust-jet formation. In *Comets in the Post-Halley Era* (R.L. Newburn, M. Neugebauer, and J. Rahe, Eds.), pp. 769-823. Kluwer, Dordrecht.

Sellgren, K. 1984. The near-infrared continuum emission of visual reflection nebulae. *Astrophys. J.* **277**, 623-633.

Sellgren, K., M.W. Werner, and H.L. Dinerstein 1983. Extended near-infrared emission from visual reflection nebulae. *Astrophys. J.* **271**, L13-L17.

Share, G.H., R.L. Kinzer, J.D. Kurfess, D.J. Forrest, E.L. Chupp, and E. Rieger 1985. Detection of galactic ^{26}Al gamma radiation by the SMM spectrometer. *Astrophys. J.* **292**, L61-L65.

Shaviv, A. and A. Bar-Nun 1975. The oxidation of hydrocarbons by water vapor behind high-temperature shock-waves. *Int. J. Chem. Kin.* **7**, 661-677.

Shock, E.L. and M.D. Schulte 1990. Amino–acid synthesis in carbonaceous meteorites by aqueous alteration of polycyclic aromatic hydrocarbons. *Nature* **343**, 728–731.

Shoemaker, E.M. 1983. Asteroid and comet bombardment of the Earth. *Ann. Rev. Earth Planet. Sci.* **11**, 461–494.

Shoemaker, E.M. and R.F. Wolfe 1984. Evolution of the Uranus–Neptune planetesimal swarm. *Proc. Lunar Planet. Sci. Conf.* **15**, 780-781.

Shoemaker, E.M. and R.F. Wolfe 1986. Mass extinctions, crater ages and comet showers. In *The Galaxy and the Solar System* (R. Smoluchowski, J.N. Bahcall, and M.S. Matthews, Eds.), pp. 338–386. Univ. Arizona Press, Tucson.

Shoemaker, E.M., J.G. Williams, E.F. Helin, and R.F. Wolfe 1979. Earth–crossing asteroids: Orbital classes, collision rates with Earth, and origin. In *Asteroids* (T. Gehrels, Ed.), pp. 253–282. Univ. Arizona, Tucson.

Shurshalov, I.V. 1967. Expressions for the internal energy and entropy of water over a wide range of thermodynamic parameters. *Izv. AN SSSR Mekhanika Zhidkosti i Gaza* **2**, 184–186; English translation 1967. Fluid Dynamics **2**, 133–134.

Sill, G.T. and L.L. Wilkening 1978. Ice clathrate as a possible source of the atmospheres of the terrestrial planets. *Icarus* **33**, 13–22.

Silva, A.M. and I.F. Mirabel 1988. Gaseous outbursts in comet P/Halley. A model for the dissociation of the OH radical. *Astron. Astrophys.* **201**, 350-354.

Skoog, D.A. and D.M. West 1982. *Fundamentals of Analytical Chemistry.* Saunders College Publishing, New York.

Sleep, N.H., K.J. Zahnle, J.F. Kasting, and H.J. Morowitz 1989. Annihilation of ecosystems by large asteroid impacts on the early Earth. *Nature* **342**, 139–142.

Smith, G.G. and S.E. Blau 1964. Decarboxylation. I. Kinetic study of the vapor phase thermal decarboxylation of 3–butenoic acid. *J. Phys. Chem.* **68**, 1231–1233.

Snyder, L.E., J.M. Hollis, R.D. Suenram, F.J. Lovas, L.W. Brown, and D. Buhl 1983. An extensive galactic search for conformer II glycine. *Astrophys. J.* **268**, 123–128.

Spudis, P.D., B.R. Hawke, and P.G. Lucey 1988. Materials and formation of the Imbrium basin. *Proc. Lunar Planet. Sci. Conf.* **18**, 155–168.

Squyres, S.W. 1989. Urey prize lecture: Water on Mars. *Icarus* **79**, 229–288.

Squyres, S.W. and M.H. Carr 1986. Geomorphic evidence for the distribution of ground ice on Mars. *Science* **231**, 249–252.

Stacey, F.D. 1977. *Physics of the Earth.* John Wiley & Sons, New York.

Steel, D.I. and W.J. Baggaley 1985. Collisions in the Solar System—I. Impacts of the Apollo–Amor–Aten asteroids upon the terrestrial planets. *Mon. Not. R. astr. Soc.* **212**, 817–836.

Stevenson, D.J. 1983. The nature of the Earth prior to the oldest known rock record: The Hadean Earth. In *Earth's Earliest Biosphere: Its Origin and Evolution* (J.W. Schopf, Ed.), pp. 32–40. Princeton Univ. Press, Princeton.

Stevenson, D.J. 1987. Origin of the Moon—The collision hypothesis. *Ann. Rev. Earth Planet. Sci.* **15**, 271–315.

Stevenson, D.J. 1990. Fluid dynamics of core formation. In Origin of the Earth (H.E. Newsom and J.H. Jones, Eds.), pp. 231–249. Oxford Univ. Press, New York.

Strazzulla, G., L. Calcagno, and G. Foti 1983. Polymerization induced on interstellar grains by low-energy cosmic rays. *Mon. Not. R. astr. Soc.* **204**, 59p-62p.

Stribling, R., and S.L. Miller 1987. Energy yields for hydrogen cyanide and formaldehyde syntheses: The HCN and amino acid concentrations in the primitive oceans. *Origins Life* **17**, 261–273.

Strickberger, M.W. 1990. *Evolution.* Jones and Bartlett, Boston.

Strom, R.G. 1987. The Solar System cratering record: Voyager 2 results at Uranus and implications for the origin of impacting objects. *Icarus* **70**, 517–535.

Sun, S.-S. 1984. Geochemical characteristics of archaean ultramafic and mafic volcanic rocks: Implications for mantle composition and evolution. In *Archean Geochemistry* (A. Kröner, G.N. Hanson, and A.M. Goodwin, Eds.), pp. 25–46. Springer–Verlag, Berlin.

Swindle, T.D., M.W. Caffee, C.M. Hohenberg, and S.R. Taylor 1986. I-Pu-Xe dating and the relative ages of the Earth and Moon. In *Origin of the Moon* (W.K. Hartmann, R.J. Phillips, G.J. Taylor, Eds.), pp. 331–357. Lunar and Planetary Institute, Houston.

Sykes, M.V. and R.G. Walker 1991. Constraints on the diameter and albedo of 2060 Chiron. *Nature* **251**, 777–780.

Szekely, A., R.K. Hanson, and C.T. Bowman 1984. Thermal decomposition of hydrogen cyanide behind incident shock waves. *J. Phys. Chem.* **88**, 666–668.

Thomas, P.J., C.F. Chyba, L. Brookshaw, and C. Sagan 1989. Impact delivery of organic molecules to the early Earth and implications for the terrestrial origins of life. *Lunar Planet. Sci. XX*, 1117–1118.

Thomas, P.J., L. Brookshaw, C.F. Chyba, and C. Sagan 1990. Numerical models of comet and asteroid impact on the early Earth: Implications for the delivery of organic molecules. *Eos* **71**, 1429.

Thompson, W.R., B.G.J.P.T. Murray, B.N. Khare, and C. Sagan 1987. Coloration and darkening of methane clathrate and other ices by charged particle irradiation: Applications to the outer solar system. *J. Geophys. Res.* **92**, 14,933-14,947.

Tillotson, J.H. 1962. *Metallic equations of state for hypervelocity impact.* General Atomic Corp. Rep. GA–3216.

Tilton, G.R. 1988. Age of the Solar System. In *Meteorites and the Early Solar System* (J.F. Kerridge and M.S. Matthews, Eds.), pp. 259–275. Univ. Arizona Press, Tucson.

Tokunaga, A.T., and T. Brooke 1988. Comparison of the 3.36μm feature to the ISM. In *Infrared Observations of Comets Halley and Wilson and Properties of the Grains* (M. S. Hanner, Ed.), pp. 79-82. NASA Conference Publication 3004.

Tokunaga, A.T., W.F. Golisch, D.M. Griep, C.D. Kaminski, and M.S. Hanner 1986. The NASA infrared telescope facility comet Halley monitoring program. I. Preperihelion results. *Astron. J.* **92**, 1183-1189.

Tokunaga, A.T., T. Nagata, and R.G. Smith 1987. Detection of a new emission band at 2.8μm in comet P/Halley. *Astron. Astrophys.* **187**, 519-522.

Tokunaga, A.T., W.F. Golisch, D.M. Griep, C.D. Kaminski, and M.S. Hanner 1988. The NASA infrared telescope facility comet Halley monitoring program. II. Postperihelion results. *Astron. J.* **96**, 1971–1976.

Touloukian, Y.S., W.R. Judd, and R.F. Roy 1981. *Physical Properties of Rocks and Minerals.* McGraw–Hill, New York.

Tsang, W. 1978. Thermal stability of primary amines. *Int. J. Chem. Kin.* **10**, 41–66.

Turcotte, D.L. 1986. *J. Geophys. Res.* **91**, 1921.

Turcotte, D.L. and L.H. Kellogg 1986. Isotopic modelling of the evolution of the mantle and crust. *Rev. Geophys.* **24**, 311–328.

Turekian, K.K. and S.P. Clark 1975. The non-homogeneous accumulation model for terrestrial planet formation and the consequences for the atmosphere of Venus. *J. Atmos. Sci.* **32**, 1257-1261.

Uman, M.A. 1969. *Lightning.* McGraw–Hill, New York.

Unger, R.M. 1975. *Knowledge and Politics.* Macmillan, New York.

Urey, H.C. 1955. The cosmic abundances of potassium, uranium, and thorium and the heat balances of the Earth, the Moon, and Mars. *Proc. Nat. Acad.* **41**, 127–144.

Urey, H.C. 1966. Biological material in meteorites: A review. *Science* **151**, 157–166.

Vallentyne, J.R. 1964. Biogeochemistry of organic matter—II. Thermal reaction kinetics and transformation products of amino compounds. *Geochim. Cosmochim. Acta* **28**, 157–188.

Van Schmus, W.R. and J.A. Wood 1967. A chemical-petrologic classification for the chondritic meteorites. *Geochim. Cosmochim. Acta* **31**, 747–765.

Von Ballmoos, P., R. Diehl, and V. Schönfelder 1987. Map of the galactic center region in the 1.8 MeV ^{26}Al gamma-ray line. *Astrophys. J.* **318**, 654–663.

Walker, J.C.G. 1977. *Evolution of the Atmosphere.* Macmillan, New York.

Walker, J.C.G. 1986. Carbon dioxide on the early Earth. *Origins Life* **16**, 117–127.

Walker, R.M. 1987. Are IDPs and Halley dust similar and, if so, so what? *Lunar Planet. Sci. XVIII*, 1048-1049.

Walker, R.M. 1988. Comparison of laboratory determined properties of interplanetary dust with those of comet Halley particles: What are comets made of? In *Infrared Observations of Comets Halley and Wilson and Properties of the Grains*, (M. S. Hanner, Ed.), pp. 53-63. NASA Conference Publication 3004.

Wallis, M.K. 1980. Radiogenic melting of primordial comet interiors. *Nature* **284**, 431–433.

Wallis, M.K., Rabilizirov, R., and N.C. Wickramasinghe 1987. Evaporating grains in P/Halley's coma. *Astron. Astrophys.* **187**, 801-806.

Wallis, M.K., N.C. Wickramasinghe, F. Hoyle, and R. Rabilizirov 1989. Biologic versus abiotic models of cometary grains. *Mon. Not. R. astr. Soc.* **238**, 1165–1170.

Wänke, H., G. Dreibus, and H. Palme 1978. Primary matter in the lunar highlands: The case of the siderophile elements. *Proc. Lunar Planet. Sci. Conf.* **9**, 83–110.

Wänke, H., G. Dreibus, and E. Jagoutz 1984. Mantle chemistry and accretion history of the Earth. In *Archean Geochemistry* (A. Kröner, G.N. Hanson, and A.M. Goodwin, Eds.), pp. 1–24. Springer–Verlag, Berlin.

Warnatz, J. 1984. In *Combustion Chemistry* (W.C. Gardiner, Ed.), Chap. 5. Springer–Verlag, New York.

Wasserburg, G.J. 1987. Isotopic abundances: Inferences on Solar System and planetary evolution. *Earth Planet. Sci. Lett.* **86**, 129–173.

Wasson, J.T. 1971. Volatile elements on the Earth and the Moon. *Earth Planet. Sci. Lett.* **11**, 219–225.

Wasson, J.T. 1985. *Meteorites: Their Record of Early Solar–System History.* W.H. Freeman, New York.

Watson, K., B.C. Murray, and H. Brown 1961. The behavior of volatiles on the lunar surface. *J. Geophys. Res.* **66**, 3033-3045.

Weaver, H.A., M.J. Mumma, and H.P. Larson 1987. Infrared investigation of water in comet P/Halley. *Astron. Astrophys.* **187**, 411-418.

Weissman, P.R. 1982. Terrestrial impact rates for long and short–period comets. In *Geological implications of impacts of large asteroids and comets on the Earth* (L.T. Silver and P.H. Schultz, Eds.), pp. 15–24. Geological Society of America, Boulder.

Weissman, P.R. 1985. Cometary dynamics. *Space Science Rev.* **41**, 299–349.

Weissman, P.R. 1987. How typical is Halley's comet? In *Symposium on the Diversity and Similarity of Comets*, pp. 31–36. ESA SP–278.

Wetherill, G.W. 1975. Late heavy bombardment of the moon and terrestrial planets 1975. *Proc. Lunar Sci. Conf.* **6**, 1539–1561.

Wetherill, G.W. 1977. Evolution of the earth's planetesimal swarm subsequent to the formation of the earth and moon. *Proc. Lunar. Sci. Conf.* **8**, 1–16.

Wetherill, G.W. 1980. Nature and origin of basin-forming projectiles. In *Multi-ring Basins, Proc. Lunar Planet. Sci.* (P.H. Schultz and R.B. Merrill, Eds.), pp. 1–18. Lunar and Planetary Institute, Houston.

Wetherill, G.W. 1981. Nature and origin of basin-forming projectiles. In *Multi-Ring Basins, Proc. Lunar Planet. Sci.* **12A**, pp. 1–18. Pergamon, New York.

Wetherill, G.W. 1990. Formation of the Earth. *Annu. Rev. Earth Planet. Sci.* **18**, 205–256.

Whipple, F.L. 1976. A speculation about comets and the Earth. *Mém. Soc. R. Sci. Liège, 6ème série* **9**, 101–111.

Wickramasinghe, D.T., and D.A. Allen 1986. Discovery of organic grains in comet Halley. *Nature* **323**, 44-46.

Wickramasinghe, N.C. 1973. *Light Scattering Functions for Small Particles, with Applications in Astronomy.* Halsted Press, New York.

Wiik, H.B. 1956. The chemical composition of some stony meteorites. *Geochim. Cosmochim. Acta* **9**, 279–289.

Wilhelms, D.E. 1984. Moon. In *The Geology of the Terrestrial Planets* (M.H. Carr, Ed.), pp. 107–205. NASA SP–469.

Wilhelms, D.E. 1987. The Geologic History of the Moon. U.S. Geological Survey professional paper 1348. U.S. Government Printing Office, Washington D.C.

Wilhelms, D.E., V.R. Oberbeck, and H.R. Aggarwal 1978. Size-frequency distributions of primary and secondary lunar impact craters. *Proc. Lunar Planet. Sci. Conf.* **9**, 3735–3762.

Wilkening, L.L. 1978. Carbonaceous chondritic material in the Solar System. *Naturwiss.* **65**, 73–79.

Woronow, A., R.G. Strom, and M. Gurnis 1982. Interpreting the cratering record: Mercury to Ganymede and Callisto. In *Satellites of Jupiter* (D. Morrison, Ed.), pp. 237–276. Univ. Arizona Press, Tucson.

Wyckoff, S., R.M. Wagner, P.A. Wehinger, D.G. Schleicher, and M.C. Festou. 1985. Onset of sublimation in comet P/Halley (1982i). *Nature* **316**, 241–242.

Yardley, B.W.D. 1986. Is there water in the deep continental crust? *Nature* **323**, 111.

Yeomans, D.K. 1986. The comet Halley ephemeris development effort. In *Space Missions to Halley's Comet*, pp. 179-197. ESA SP–1066.

Zahnle, K.J. 1986. Photochemistry of methane and the formation of hydrocyanic acid (HCN) in the Earth's early atmosphere. *J. Geophys. Res.* **91**, 2819–2834.

Zahnle, K. and D. Grinspoon 1990. Comet dust as a source of amino acids at the Cretaceous/Tertiary boundary. *Nature* **348**, 157–159.

Zahnle, K.J., and J.C.G. Walker 1982. The evolution of solar ultraviolet luminosity. *Rev. Geophys. Space Phys.* **20**, 280–292.

Zahnle, K., J.F. Kasting, and J.B. Pollack 1990. Mass fractionation of noble gases in diffusion–limited hydrodynamic hydrogen escape. *Icarus* **84**, 502–527.

Zel'dovich, Ya.B. and Yu.P. Raizer. *Physics of Schock Waves and High–Temperature Hydrodynamic Phenomena* (Academic Press, New York, 1967), Ch. 11, Sec. 11.

Zhao, M. and J.L. Bada 1989. Extraterrestrial amino acids in Cretaceous/Tertiary boundary sediments at Stevns Klint, Denmark. *Nature* **339**, 463–465.