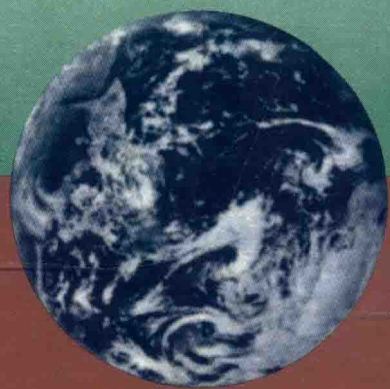


BIOGEOCHEMISTRY OF GLOBAL CHANGE

Radiatively Active Trace Gases



EDITED BY
R. S. OREMLAND

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Radiatively Active Trace Gases

SELECTED PAPERS FROM THE TENTH INTERNATIONAL
SYMPOSIUM ON ENVIRONMENTAL BIOGEOCHEMISTRY,
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BIOGEOCHEMISTRY OF GLOBAL CHANGE

Preface

Public awareness has increased about the prospect of global climatic change occurring in the coming century. Whereas broad changes in the Earth's climate have taken place in the geologic past, they have, with some significant exceptions, been of a gradual nature. Gradual change allows time for plants and animals to evolve via natural selection and to produce species capable of thriving in the new climate. Additionally, the geographic range of species already present will either expand or contract with an altered climate, depending on their ability to establish themselves in new environment.

It is now possible that anthropogenic activity may induce such a change and that this may occur at a rate too rapid for present ecosystems to adapt to or be replaced by systems suited for the new climate. Of even greater concern is whether agricultural production can be sustained to meet human needs in the face of such broad environmental change. Although there is a great disparity of views among climatologists with regard to the extent, significance, and potential disruptive effects of climate change, there is general agreement that some degree of change will occur.

The basis for this type of climatic change is directly related to the increased abundance of radiatively active trace gases in the atmosphere. "Radiatively active" refers to the capacity of certain gases, such as CO_2 , CH_4 , N_2O , and chlorofluorocarbons (CFCs), to absorb infrared energy reflected from sunlight incident on Earth's surface. The increased abundance of these gases derives from expanded human industrial and agricultural activities occurring over the past two centuries. Because many of these heat-trapping gases have demonstrated continuously increasing patterns of atmospheric mixing ratios over time periods ranging from decades to centuries, a "greenhouse effect" has occurred as a consequence of their buildup. In addition, some of these gases, such as CFCs and N_2O , pose a threat to the integrity of the stratospheric ozone layer. Still others, such as dimethylsulfide, although not "radiatively active," nonetheless influence climate because their oxidation products induce cloud condensation. Hence, these gases act in complex, interdependent patterns that affect atmospheric chemistry and physics. The sum of their influences on these processes, as well as on global change, is difficult to predict. In addition, their sources and fates are not well-known.

With the exception of only a few cases (e.g., CFCs), most of these gases arise from mixed sources, that is, from industry as well as agriculture, biomass-burning, and emissions from unperturbed ecosystems. Similarly, recognized sinks are diverse and include atmospheric photochemical reactions, dissolution into the oceans, and biological uptake by soil and plant communities. Under-

standing the relative importance of these sources and sinks to the past, present, and future global balance of these gases, as well as their influence on the biota and global habitability, poses a difficult and interdisciplinary challenge to environmental scientists and managers. Clearly, this topic encompasses significant aspects of numerous disciplines, including atmospheric chemistry, oceanography, paleoclimatology, geochemistry, soil and plant sciences, and microbiology, to name but a few. In short, this falls under the general discipline of "environmental biogeochemistry," with the scope of the problem being beyond the expertise of any individual investigator. It follows that no single conference or book can hope to cover adequately the breadth of this rapidly moving field. Nonetheless, because of the diverse and disparate perspectives of the disciplines listed above, it is essential for individual researchers to gain an appreciation of the breadth of the field. One mechanism to achieve this is by holding interdisciplinary conferences that allow a free exchange of experimental results on the topic of the biogeochemistry of radiatively active trace gases. This volume consists of invited and contributed papers presented at the Tenth International Symposium on Environmental Biogeochemistry (ISEB), held in San Francisco during the week of 19–25 August 1991. There are 45 chapters in this volume, with diverse topics ranging from geologic temporal scales of mass transfer to aspects of microbial biochemistry related to the formation of CH_4 . Most of the chapters deal with experimental assessments of the fluxes of trace gases or the biological formation (or consumption) of trace gases in various ecosystems.

I conceived the idea of hosting such a meeting when I attended the Ninth ISEB in Moscow in 1989. I previously organized a meeting devoted to atmospheric methane at the 1987 American Chemical Society meeting in Denver, but I was interested in conducting a meeting having a broader theme. Inasmuch as the ISEB is an international scientific organization and because "radiatively active" trace gases are truly a problem of global concern, the ISEB would be an appropriate forum for an expanded conference. My offer was accepted, and as the ISEB meets on alternate, odd-numbered years, I returned home thinking that two years was more than sufficient to put it all together. I soon realized that time was already quite short and that I would be working on this project for the next three years, if you include editing this volume. My life was occupied with worrying about where to hold the conference, what agencies were willing to support it, mailing lists and flyers, bank accounts and bills, session topics and chairpersons, reservations and cancellations, abstracts, manuscripts, publishers, receptions, tours, banquets, and, of course, whether the San Francisco Giants would play a home game that week. (They did!) So much for my naiveté!

There are many individuals and institutions to thank for bringing this conference and book to fruition, but as the result of space restrictions, I can acknowledge only some of them. First of all, the scientific agencies of the United States Government that provided generous financial support for the event: The Geo-

logical Survey, the National Aeronautics and Space Administration, the National Oceanic and Atmospheric Administration, the Department of Energy, the Environmental Protection Agency, the Department of Agriculture, and the National Science Foundation. In particular, the National Science Foundation acted as a funding/clearinghouse for several of the above agencies, in addition to providing its own share of funds. I am indebted to the efforts of Dr. Jarvis Moyers, who successfully guided the various ISEB funds through the bureaucratic maze, and did so in a timely fashion. If for nothing else, I wish to thank him for being able to achieve all this, even in the face of my many annoying, panic-stricken phone calls! I wish to thank Jo Ann Glennon and her staff at the Cathedral Hill Hotel for making the meeting go so smoothly, and the members of the ISEB 10 National Committee for the programmatic work, and the ISEB 10 Local Committee for numerous arrangements. As all the manuscripts in this volume received two anonymous peer reviews, I thank these nameless souls for their efforts. Most important, I am deeply grateful to my associate, Ms. Francis Strohmaier, who was involved in every facet of this undertaking, and whose attention to detail and tireless secretarial efforts not only helped me to retain my sanity, but made both the conference and the publication of the book possible.

Ronald S. Oremland
Chairman, ISEB
Menlo Park, California
September 22, 1992

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Paleoatmospheres and Climates

Biogeochemical Cycles of Carbon on a Hierarchy of Time Scales

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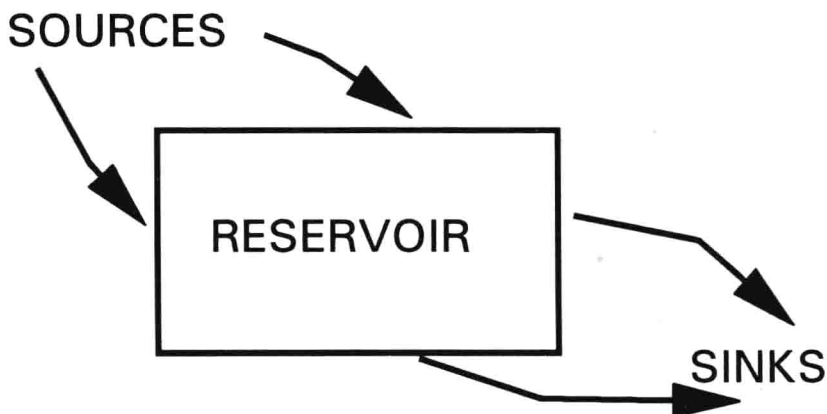
ABSTRACT

The carbon dioxide content of the atmosphere affects life, climate, and the chemistry of oceans and sedimentary rocks. The processes that control atmospheric carbon dioxide can be analyzed in terms of biogeochemical cycles that transfer carbon between reservoirs. The small atmospheric reservoir is closely linked to other small reservoirs, shallow sea and biota. Transfer of carbon between these small reservoirs is rapid; residence times are short. The small reservoirs are connected by slower transfers to a much larger deep sea reservoir, and the coupled reservoirs of ocean, atmosphere, and biota are coupled, in turn, to very much larger reservoirs in sedimentary rocks. The exogenic reservoirs of sedimentary rocks, ocean, atmosphere, and life are coupled, in turn, by the very slow exchange of carbon with a large mantle reservoir. This hierarchy of interacting reservoirs controls atmospheric carbon dioxide on all time scales. Particular problems with restricted time scales can be analyzed in terms of a subset of the total system. Observations that illustrate interactions on different levels of the hierarchy include the seasonal change of carbon dioxide partial pressure, the glacial to interglacial change, and the evolving distribution of carbonate sediments.

Introduction

What controls the amount of carbon dioxide in the atmosphere? How has this amount changed in the past? How might it change in the future? To answer these questions, we must examine the biogeochemical cycles of carbon on various time scales. In terms of the evolution of environmental composition, there is probably no other constituent as interesting and important as carbon. Carbon dioxide is the substrate for photosynthesis and, thus, for all life. As a greenhouse gas, it has a great effect on climate. It leaves a record of change in sedimentary rocks because dissolved carbon affects marine chemistry, the pH of sea water, and the formation of carbonate sediments. In addition, there is a close relationship between the

CONSERVATION OF MATTER



$$\text{Residence time} = \text{Amount/Rate}$$

Rate laws

Figure 1. Terms used in studies of biogeochemical cycles.

biogeochemical cycles of carbon and those of oxygen, so the study of the carbon cycles improves our knowledge of possible changes in atmospheric oxygen.

Basic Concepts

We approach the geochemical cycles of constituents of the environment from the point of view of conservation of matter.^{102,112} This approach underlies all work in the field.⁸² Imagine a reservoir that contains a certain amount of matter, carbon for instance. The reservoir might be the ocean or the atmosphere or perhaps some smaller slice of the environment. As shown in Figure 1, sources add material to the reservoir; sinks remove material from the reservoir. The biogeochemical cyclist constructs a computational system coupling a number of reservoirs with

specified amounts of material in them and specified rates of transfer of material between them. The cyclist then solves the system of differential equations that equates the rate of change of the amount of material in a reservoir to the difference between the sum of the sources and the sum of the sinks. Appropriate computational techniques have been described with examples by Walker.¹¹⁰

In the examination of biogeochemical cycles, it is convenient to consider a residence time, which is the average length of time that material spends in a reservoir. The residence time is simply the amount of material in the reservoir divided by the rate at which material is added to or removed from the reservoir. But, for quantitative analysis, we need also to know the rate laws. We need to know how the rates of transfer of material between reservoirs depend on the parameters of the system. How, for example, does the rate of removal of material from a particular reservoir depend on the amount of material in the reservoir, or the date, or biological activity, or the weather. Rate laws are great sources of uncertainty. In Figure 1, as in most of the figures, uncertainty increases rapidly from top to bottom. It is a fairly easy matter to establish the amount of carbon dioxide in the atmosphere or dissolved carbon in the ocean. Information about reservoir sizes is generally good, at least for the present time: Measurement of rates is more difficult. It requires a different observational technology. Therefore, rates are usually not known as well as amounts, although rates can, in principle, be established to any degree of accuracy by hard work.

Rate laws are quite different. No amount of assiduous observation of the global system will reveal a global rate law. There is, for example, no way to conduct a controlled experiment to learn how the globally integrated rate of weathering of silicate rocks depends on the amount of carbon dioxide in the atmosphere. We can guess rate laws and we can test the consequences of those guesses against the geological record or direct observations of global change, but rate laws are inherently less knowable than amounts or rates.

Lacking information about global rate laws, geochemical cyclists frequently find it convenient to assume that a rate law is first order in reservoir amount.¹⁵ Such an assumption is a matter of convenience in ignorance only. There is no computational requirement to limit consideration to first-order rate laws, and there is no reason to believe that global rate laws are linear. Indeed, it is already clear that many rate laws are definitely not linear. What my modeling colleagues and I use for rate laws depends on our understanding of the system we are simulating. Most of us put into our simulations the best assumptions that we can devise, but these assumptions are hard to test on a global scale. Components of some rate laws can be tested in the laboratory or in a particular ecosystem or river, but there remains the problem of extrapolation of local findings to the entire globe. How does the global rate of precipitation of calcium carbonate minerals, for example, depend on the evolutionary state or even the health of corals?