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HOW LIFE AFFECTS THE GEOCHEMICAL CYCLE OF CARBON

REPORT ON THE SECOND YEAR OF RESEARCH AND REQUEST FOR CONTINUATION
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Research under this grant has been concerned with the influence of life on the global carbon cycle, the influence of changes in the carbon cycle on global climate, and the affect of evolving climate back on life. Results of the research have been described in several papers published or submitted for publication.

In "Biogeochemical Cycles of Carbon on a Hierarchy of Time Scales" I analyzed the processes that control atmospheric carbon dioxide in terms of a hierarchy of cycles that couples small reservoirs by rapid exchange processes, these cycles being embedded in other cycles that couple large reservoirs by slow exchange processes. The smallest, most rapid, inner cycle couples atmosphere to biota by means of photosynthesis and respiration. Larger, slower cycles successively involve the ocean, sedimentary rocks, and the mantle. All of these cycles act together to control the concentration of atmospheric carbon dioxide on geological time scales, but any particular process or event can be analyzed in terms of a subset of the whole system, depending on the time scales involved. The paper was presented at the Tenth International Symposium on Environmental Biogeochemistry and should appear soon in the proceedings of that conference.

This approach to the study of the history of carbon dioxide has been applied in two papers concerned with change on shorter time scales. "The Return of the Coral Reef Hypothesis: Basin to Shelf Partitioning of Calcium Carbonate and Its Effect on Atmospheric Carbon Dioxide" describes how biological processes influenced by changing climate may have caused the large change in atmospheric carbon dioxide between glacial and interglacial periods in the Pleistocene. Observations of the composition of air in bubbles in Antarctic Ice have shown that the concentration of carbon dioxide in the atmosphere declined gradually from 280 parts per million to 200 parts per million during the last advance of the ice sheets, and then climbed rapidly back to 280 parts per million when the ice melted between 20 and 10 thousand years ago. In a paper published in Geology, Bradley Opdyke and I argue that this change in atmospheric composition is a response to changing oceanic composition caused by varying rates of deposition of calcium carbonate by corals and other carbonate-secreting organisms living in shallow water. These organisms flourish when sea level is rising as a result of melting ice, because rising sea level gives them space into which to grow without growing out of the water. When sea level is falling, due to expanding continental ice, the rate at which organisms deposit calcium carbonate on the continental shelves decreases markedly. These expectations are sustained by careful studies of Holocene deposits of calcium carbonate on the continental shelves. Excess precipitation of calcium carbonate on the shelves extracts

alkalinity, in the form of dissolved calcium ions, from sea water, making the ocean more acidic, and driving up the equilibrium partial pressure of carbon dioxide in air in contact with the ocean. Our published paper shows how this mechanism can plausibly explain the glacial to interglacial change in atmospheric carbon dioxide.

In "Effects of Fuel and Forest Conservation on Future levels of Atmospheric Carbon Dioxide", James Kasting and I apply the carbon cycle model to change on the historical time scale. The simulation is tuned to reproduce the observed radiocarbon record resulting from atomic weapons testing. It is tuned also to reproduce the distribution of dissolved phosphate and total dissolved carbon between the oceanic reservoirs as well as the carbon isotope ratios for both 13C and 14C in ocean and atmosphere. The simulation reproduces reasonably well the historical record of carbon dioxide particle pressure as well as the atmospheric isotope ratios for 13C and 14C over the last 200 years as they changed in response to fossil fuel burning and forest clearance. The agreement between observation and calculation is achieved with the assumption of a carbon dioxide fertilization affect in which the production of biomass increases with increasing carbon dioxide partial pressure. At present, the fertilization effect of increased carbon dioxide outweighs the effect of forest clearance, so the biota is an over all sink of atmospheric carbon dioxide sufficiently large to bring the budget into balance.

This simulation is used to examine the future evolution of carbon dioxide and its sensitivity to assumptions about the rate of fossil fuel burning and of forest clearance. Over times extending up to thousands of years, the results are insensitive to the theoretical description of the rock cycle and to the dissolution of deep sea carbonate sediments. Atmospheric carbon dioxide continues to increase as long as fossil fuel is burned at a significant rate, because the rate of fossil fuel production of carbon dioxide far exceeds the rate at which geochemical processes can remove carbon dioxide from the atmosphere. The maximum atmospheric concentration of carbon dioxide depends on the total amount of fossil fuel burned, but only weakly on the rate of burning. The future course of atmospheric carbon dioxide is, however, very sensitive to the fate the forests in this simulation because of the important role assigned to carbon dioxide fertilization of plant growth. Forest clearance drives up atmospheric carbon dioxide not only by converting biomass into atmospheric carbon dioxide but more importantly by reducing the capacity of the biota to sequester fossil fuel carbon dioxide. In this simulation, atmospheric carbon dioxide levels could be sustained indefinitely below 500 parts per million if fossil fuel combustion rates were immediately cut by a factor of 25 and if further forest clearance

were immediately halted. If neither of these conditions is met and if we consume most of the world's fossil fuel reserves, peak carbon dioxide concentrations in excess of 1,000 parts per million are probable within the next few centuries.

Interest in the carbon cycle is high, of course, because of the likely effect of carbon dioxide on climate through the atmospheric greenhouse. We have been involved in research on paleoclimate in the effort to understand how climate may change in response to changing carbon dioxide concentrations. A time of particular interest is the early Eocene, some 55 million years ago. The global climate at that time was markedly different from that of our time. The polar regions were more than 15 degrees C warmer than at present, but the tropics were not warmer and were possibly even cooler by a few degrees. There were no extensive ice sheets, and flora and fauna intolerant of cold were wide spread at high latitudes. As far as we can tell, however, this was not a world of markedly increased greenhouse effect. Partial pressures of atmospheric carbon dioxide can be deduced from the carbon isotope fractionation between coexisting carbonate and organic carbon deposits. Recent publications suggest that the carbon dioxide partial pressure was only twice its present value, a conclusion that is consistent with carbon cycle models, including that of Francois and Walker (1992). Global average temperature was only a few degrees higher than at present, entirely consistent with the expected greenhouse effect from a doubling of carbon dioxide concentration.

The problem with the Eocene climate was how to transport enough heat to high latitudes to keep the polar regions warm. In "Something is Wrong With Climate Theory ", Lisa Sloan and I provided a short, non-technical discussion of this problem in an effort to bring it more forcefully to the attention of researchers in climate change and Earth history. We argued that there is a real conflict between our understanding of climate and the observations for the Eocene, a conflict that can not be readily explained away by anticipated changes in albedo, or transport of heat by ocean or atmosphere.

In "Possible Methane-induced Polar Warming in the Early Eocene", I joined with Sloan, Moore, Rea, and Zachos to suggest a possible resolution of the Eocene climate problem. We speculated that the geological conditions at this time were appropriate for much enhanced fluxes of methane produced by microorganisms in swamps and wetlands. Transport of this methane into the stratosphere, were it is oxidized to water vapor, might have made the Eocene stratosphere much wetter. A moist stratosphere would promote the formation of polar stratospheric clouds during the polar winter, when stratospheric temperatures fall to their minimum values. Polar stratospheric clouds can trap infrared

radiation if the cloud droplets are large enough, keeping the underlying troposphere and surface warm during the polar winter. At the same time, polar stratospheric clouds during the winter do not cool the Earth by reflecting sunlight off to space because there is very little sunlight at polar latitudes during the winter. The overall effect, then, of polar stratospheric clouds would be to keep the high latitudes warm during winter. We regard this wildly speculative mechanism as an example of the kind of unusual and unexpected climatic process that may be needed to explain the unfamiliar global climate of the Eocene. Although unfamiliar to us, the Eocene climate has not been unusual in Earth history. The earlier, Cretaceous period showed similar climatic features. In general, warm poles seem to be more common in earth history then cold poles.

Because we are far from understanding what kept the Eocene poles warm, we are also far from understanding what caused the climate to change in the direction of colder poles during the last 50 million years of Earth history. If this change in climate was a consequence of the observed decrease in atmospheric carbon dioxide by just a factor of 2, from about 600 parts per million to about 300 parts per million, the implications for future climate change are severe. There is every reason to suppose that we will drive atmospheric carbon dioxide concentration above 600 parts per million during the course of the 21st century (Walker and Kasting, 1992).

Recent Publications

Francois, L. M., and J. C. G. Walker, Modelling the Phanerozoic carbon cycle and climate: Constraints from the $^{87}Sr/^{86}Sr$ isotopic ratio of seawater, *American J. Sci., 292*, 81-135, 1992.

Kasting, J. F., and J. C. G. Walker, The geochemical carbon cycle and the uptake of fossil fuel CO_2, in *AIP Conference Proceedings 247, Global Warming: Physics and Facts*, edited by B. G. Levi, D. Hafemeister, and R. Scribner, pp. 175-200, American Institute of Physics, New York, 1992.

Opdyke, B. N., and J. C. G. Walker, Return of the coral reef hypothesis: Basin to shelf partitioning of $CaCO_3$ and its effect on atmospheric CO_2, *Geology, 20*, 733-736, 1992.

Sloan, L. C., J. C. G. Walker, T. C. Moore, D. K. Rea, and J. C. Zachos, Possible methane-induced polar warming in the early Eocene, *Nature, 357*, 320-322, 1992.

Walker, J. C. G., Degassing, in *Planetary Sciences, American and Soviet Research*, edited by T. M. Donahue, K. K. Trivers, and D. M. Abramson, pp. 191-202, National Academy Press, Washington, D. C., 1991a.

Walker, J. C. G., Feedback processes in the biogeochemical cycles of carbon, in *Scientists on Gaia*, edited by S. H. Schneider, and P. J. Boston, pp. 183-190, MIT Press, Cambridge, Mass., 1991b.

Walker, J. C. G., Biogeochemical cycles of carbon on a hierarchy of time scales, *Environmental Biogeochemistry, in press*, 1992.

Walker, J. C. G., and J. F. Kasting, Effects of fuel and forest conservation on future levels of atmospheric carbon dioxide, *Palaeogeography, Palaeoclimatology, Palaeoecology (Global and Planetary Change Section), 97*, 151-189, 1992.

Walker, J. C. G., and L. C. Sloan, Something is wrong with climate theory, *GeoTimes*, 1992.

Research Plans

I plan to continue the study of paleoclimate, and in particular the climate of the early Eocene. My present thinking is that the solution to the Eocene climate puzzle must lie in the dynamics of oceanic circulation, with enhanced transport of heat to high latitudes being a consequence of reduced vertical stratification of the ocean, but I am not sure that this is a viable mechanism, nor am I sure how to work out its implications quantitatively. On the other hand, the unusual climate may turn out to be the response to changing chemistry, most likely involving the carbon cycle, and probably driven by the biota. We will continue to develop ideas concerning possible chemical and biological influences involving the greenhouse effect and cloud distributions.

I also plan to develop in more detail the coral reef hypothesis for glacial-to-interglacial changes in atmospheric carbon dioxide. This model can be tested and refined using data on deep sea carbonate sediments. The Pleistocene records of atmospheric carbon dioxide and pelagic carbonate sedimentation cycles provide much the best data we have concerning the behavior of the global biogeochemical cycle of carbon on a time scale of thousands to hundreds of thousands of years. We need to interpret and understand these records in order to predict the long-term consequences of fossil fuel burning. Uncertainty in evolution of fossil fuel carbon on time scales beyond a few hundred years derives largely from uncertainty about the response of pelagic carbonate sediment. This response can be calibrated on the appropriate time scale from the observations of Pleistocene change. The simulations that successfully represent the Pleistocene can be applied also to the study of global change.

Opdyke and I plan to explore theoretically the consequences of varying rates of shelf carbonate deposition using coupled computer simulations of the global carbon cycle, ocean chemistry, and sediment diagenesis. Our goal is to see what aspects of the observed Pleistocene history of atmospheric carbon dioxide and of pelagic carbonate sedimentation might have been caused by varying rates of shelf carbonate deposition. Carbonate deposition removes both alkalinity and dissolved carbon from sea water in a ratio by moles of two to one. Carbonate decomposition therefore drives up the acidity of the water, shifting carbonate solution equilibria toward a high partial pressure of carbon dioxide. In the process, sea water becomes more corrosive with respect to calcium carbonate, so that previously deposited sediments, for example, those in the deep sea, become more susceptible to dissolution.

We plan to compare the results of our calculations with various observations and to adjust the undetermined parameters that are inevitable in a global model to improve agreement between the theory and the observations. In this way we expect to arrive at a model that is consistent, but not necessarily unique. This model can then be applied to studies of other time periods in Earth history and to the exploration of possible future changes in carbon dioxide.

The goal of this research program is to develop a quantitative understanding of the biogeochemical cycles of carbon as they have worked throughout Earth history on various time scales, how they have been affected by biological evolution, and how changes in the carbon content of ocean and atmosphere may have affected climate and the evolution of life. In pursuit of this goal we develop theoretical simulations that can be tuned to reproduce such data as exist and, once tuned, can be used to predict properties that have not yet been observed. This is an ongoing process, in which models and results are refined as new data and interpretations become available, and as understanding of the global system improves.