

Introduction

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In a decade or so, the human race will enter the 21st century. A major task facing the Earth's growing population will be to overcome the threat of anthropogenic change to the biosphere and human survival. In historical times the largest changes seem to have arisen from the development of agriculture, but now a primary focus of concern is acid rain; the result of perturbed flows of nitrogen and sulphur to the biosphere. The interest of scientists and politicians in the true health of our environment has led to scientific coordinating centres such as the SCOPE/UNEP International Sulphur Unit being established in the 1970s. The objectives of such units are to investigate the global biogeochemical cycles of essential elements.

The first monograph prepared by the sulphur unit was published as a SCOPE report in 1983 and titled *The Global Biogeochemical Sulphur Cycle*. This report was devoted to constructing a simulation model for the modern sulphur cycle. It also included an important body of experimental material on sulphur masses in the lithosphere in Phanerozoic times. A second monograph *Stable Isotopes in the Assessment of Natural and Anthropogenic Sulphur in the Environment* attempts, as indicated by the title, to separate the contributions of natural and anthropogenic sulphur to the global cycle using sulphur isotopic composition in various reservoirs, fluxes and ecosystems. The current volume, *Evolution of the Global Biogeochemical Sulphur Cycle* is the third in this series. The term evolution, deriving from the Latin *evolvere*, to unroll, embodies the notion of development. Evolutionary concepts have become important in the natural sciences since the 19th century. The past decade has witnessed an increased interest in evolutionary processes taking place on a global scale. Space research has eliminated all but the faintest hopes for the existence of life in our solar system apart from the Earth. The uniqueness of life on Earth and the need to assess its tolerance to changes imposed by human activity compels scientists to better understand the changes in the sulphur cycle throughout the entire length of the geological record.

In the modern biosphere substantial variations in sulphur concentration are found in similar ecosystems at different geographical locations. Consequently we also need to understand the variability and distribution of sulphur in the past. This calls for knowledge of the mechanisms which control the

transformation of sulphur compounds on the Earth's surface. An overview of long-term geological and geochemical investigations of rocks from the Archaean to the Neogene, including the determination of sulphur concentrations and isotopic composition, has been the object of Part I of this book. Here authors have modelled parts of the global sulphur cycle that have been subject to major changes throughout the Earth's history. The large changes of the past are useful in assessing the ability of the biosphere to cope with the stress currently imposed as a result of human activities.

The evolution of the sulphur cycle began with high temperature volcanic emissions of reduced and sulphur gases to the atmosphere of the Archaean Earth. Chapter 1, written by M. Schidlowski, reviews the blurred record left in Precambrian rocks. These rocks have been attracting increasing attention, because they cover the period in which the Earth's earliest biosphere emerged. In terms of the sulphur cycle it is important to establish the appearance of sulphate-reducing bacteria, whose activities gave rise to an effective large-scale fractionation of sulphur isotopes during its exogenic cycling. Over the last 1.2 Ga the fractionation has acquired a clearly defined pattern. Some key questions arise about the Precambrian Earth: at what moment in Earth history was the sulphur flux split into reducing and oxidizing pathways and is the evolution of the sulphur cycle on the Precambrian Earth the result of microbial activity and is there a correspondence between ancient and modern microbial activity?

Schidlowski gives 2.75 Ga before the present (BP) as the date for the initiation of sulphate reduction based on the isotopic composition of sulphide in the Canadian Shield. However, the record has been so degraded by time that assigning a biological origin to this sulphur cannot be entirely certain. These sulphides may have arisen as the result of hydrothermal activity. Regardless of these arguments, though, the lack of apparently biogenic sulphur in most rocks of the Canadian Shield for the ensuing 0.5 Ga argues against widespread distribution of sulphate reduction at 2.75 Ga BP.

Chapter 1 also raises the question of the interactions between rocks of the mantle and the early ocean in the light of current understanding of the processes that occur at the basalt-seawater interface in the oceanic rift zones (see Chapter 7).

To some extent, Chapter 2 is a continuation of Chapter 1, considering the sulphur fluxes of the Phanerozoic when biological processes controlled the fractionation of sulphur isotopes. The authors of this chapter, Holser, Maynard and Cruikshank, propose a simple multi-box model of exogenic sulphur which derives from the Soviet work of Ronov and his colleagues on the volumes and composition of crustal rock and more recent publications of isotopic data. The model presented is novel in including erosion coefficients, updated reservoir sizes and the flux of exogenic sulphur.

Variation in fluxes are assessed by comparing the changes in isotopic composition of oxidized and reduced sulphur on an isotope age curve. Correct interpretation of the results from the model and more specifically the application to the sulphur cycle requires good estimates for the input parameters, primarily the data concerned with evaporite isotopy in various regions. Quite often such data are not consistent with existing geological interpretations and Chapter 3, written by H. Nielsen, one of the most experienced researchers in the field of sulphur isotopes, examines a number of specific examples of departures from the isotope age curve which are difficult to interpret unequivocally.

Models of exogenic sulphur are usually taken as 'closed' systems and do not account for influx and efflux of sulphur to deep layers of the terrestrial crust and mantle. The model presented in Chapter 2 is no exception. The SCOPE 19 volume, *The Global Biogeochemical Sulphur Cycle*, provided a rather approximate estimate of the flux which withdraws sulphur from the exogenic cycle among marine sediments in the subduction zones of the modern biogeochemical sulphur cycle. This is comparatively small and may be neglected in models. It is not as easy to disregard volcanic and hydrothermal fluxes that supply sulphur to exogenic reservoirs. In Chapter 4, Lein and Ivanov attempt, for the first time, to introduce endogenic sulphur fluxes, modelling the evolution of the sulphur cycle in the Phanerozoic.

Overall Part I presents a picture of the sulphur cycle in the Precambrian and some dynamic models of the cycles from the Cambrian through to the Neogene. The quantitative nature of the models makes it possible to single out unusual periods in the history of the sulphur cycle which appear to be related to evolutionary changes in the biosphere.

The second part of the book is devoted to considering the evolution of the sulphur cycle in the Holocene, i.e. the last ten thousand years. The authors of this part (Chapter 5—Brimblecombe, Hammer, Rodhe, Ryaboshapko and Boutron) are interested in atmospheric aspects of the sulphur cycle and quite naturally concentrate on this component of the exogenic sulphur cycle. The bias is not accidental; the low mass of the atmosphere makes it very sensitive to change. As in *The Global Biogeochemical Sulphur Cycle*, the authors consider the basic fluxes of the global atmospheric balance of sulphur (Section 5.1) and update a few of the 1983 flux estimates. The contribution of anthropogenic emissions to the continental atmosphere is assessed as some 55% in the updated sulphur balance. In Section 5.2 the changes in sulphur fluxes through the Holocene are examined using ice cores from polar regions of the Earth remote from important centres of human population: e.g. glaciers of central Antarctica and the Greenland ice plateau. The background concentrations of sulphur in ice cores ranges from 6 to 35 ng (S) g⁻¹. Prior to the 20th century, variations

in sulphur concentration were due to volcanic eruptions. Over the past hundred years the concentration of anthropogenic sulphur in the middle troposphere of the northern hemisphere has been as much as 2–4 times that of the natural background. No such clear increase is found in the Antarctic ice cores.

Section 5.3 attempts to reconstruct the natural sulphur flux of the Holocene, prior to human intervention. The authors infer that the continental and marine atmosphere were balanced with regard to sulphur fluxes in the pre-industrial period. Their scenario for the next 50 years does not anticipate a substantial increase in global anthropogenic emissions of sulphur, but suggests possible shifts in the geographical distribution of anthropologically induced sulphur stress. There may be increases in emissions from tropical and developing countries while industrialized countries of Europe and North America are expected to abate the present level of anthropogenic emissions through control practices.

Throughout the evolutionary history of the biosphere the sulphur cycle has been and remains closely linked with the cycles of other essential biogenic elements, most notably the carbon cycle. The only criteria available for assessing this interrelation through past geological epochs derive from studies of rock composition. In some instances this is illustrated by the correlation between C_{org} and sulphide-sulphur. Another approach uses a comparison of the isotope age curves of sulphate-sulphur and carbonate-carbon (as seen in Chapter 2). The inverse correlation that is observed between the curves for carbon and sulphur can be explained by the compensation that occurs during the reduction processes in the sulphur cycle (i.e. $SO_4^{2-} \rightarrow S^{2-}$) and the oxidative reactions in the carbon cycle (i.e. $C_{org} \rightarrow CO_2 \rightarrow CO_2^{2-}$).

The interrelation of the sulphur and carbon cycles may be clearly demonstrated in modern ecosystems, such as microbial mats of inland water bodies, marshes and marine sediments. Peculiar microbial communities were discovered in deep hydrothermal systems in 1977. Researchers are currently giving a great deal of attention to microbial mats in the volcanic regions of the Earth, as these fascinating ecosystems show how chemosynthetic and photosynthetic processes interact with the sulphur system. Such systems appear to be among the most ancient on the Earth, being present in the earliest biosphere. Thus studies of these special communities are of great interest for those concerned with the interactions between the sulphur and carbon cycles. The extensive experimental work on these systems is reviewed in Part III of the book.

The role of sulphur bacteria, especially the sulphur-reducing bacteria, in the C, N and P cycles has been emphasized during investigations of modern anaerobic marine systems; e.g. organic matter of sediments is oxidized to CO_2 during bacterial reduction of sulphate in marine interstitial water and

re-enters the biosphere. Under some conditions this CO_2 is precipitated as isotopically light carbonate minerals—metabolites which are paragenic to pyrite sulphides in sediments. In 1975 Lein and Ivanov proposed a method of estimating C_{org} consumption during anaerobic biogeochemical processes in the early stages of marine diagenesis. Widespread use of labelled compounds (^{14}C and ^{35}S) over the past decade has allowed the C and S interactions in marine sediments to be assessed quantitatively.

In Chapter 6 (Section 6.1) Skyring reviews the data available on sulphate reduction and carbon metabolism in marine sediments, underlining the complicated dependence of quantitative estimates on radio-experimental conditions. He argues that the amount of carbon oxidized on reduction of sulphate is dependent on the specific organic acid in the substrate. This differs from the arguments of Lein and may arise from results obtained with pure cultures of sulphate-reducing bacteria under rather special conditions. Section 6.1 also attempts a mass balance of C_{org} in the global oceanic sediments using the available evidence on the rates of biogeochemical processes. It appears that about 15% of the organic carbon reaching the sea-bottom is mineralized under anaerobic conditions.

During anaerobic mineralization of C_{org} , anaerobic oxidation of methane apparently occurs in parallel to sulphate reduction. This explains the fact that the final parts of the chapter focus on methane production, a topic which might have seemed rather removed from the central theme of the book. In Section 6.3 Reeburgh discusses the evidence he has found for this process and provides a quantitative estimate of the portion of C_{org} consumed. In the concluding section of the chapter Ivanov and Lein examine the interrelation between sulphate reduction, methane production and methane oxidation.

It is only recently that techniques have become available to examine the fluxes and chemistry of sulphur compounds in deep sea hydrothermal vents. H. Jannasch summarizes some of the findings of this research in Chapter 7. As our knowledge of these particular sources increases we should be able to introduce them into models of the evolution of the sulphur cycle. It is probable that hydrothermal activity was particularly important in controlling ocean composition in the very earliest stages of the evolution of the Earth.

Chapter 8 examines the all-important bacterial mats which produce laminated sediments that are evident in sedimentary rocks of great antiquity. Thus it examines, in a different way, some of the areas of interest in the first chapter of the book. Yehuda Cohen describes the role sulphur plays as an electron donor in oxygenic and anoxygenic photosynthesis for these microorganisms which may display a remarkable tolerance to sulphide, which is normally toxic. V.M. Gorlenko and E.A. Bonch-Osmolovskaya discuss microbial mat communities in hot springs, paying attention to their importance in the sulphur cycle. They also examine the importance of

environmental variables, such as salinity, temperature and pH in influencing these communities. Their work provides some estimates of productivity and the intensity of sulphate reduction in these communities. While the processes seen in these rather specialized ecosystems do not contribute significantly to the overall fluxes on the Earth of the present day, they do give important information about the biogeochemistry of sulphur on the ancient Earth.

The papers in this volume in no way complete the story of the evolution of the sulphur cycle: rather they map out areas that continue to yield valuable results. It is hoped that they will not only foster these research areas, but also help initiate investigations into topics that have been mentioned only in passing.

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