

MINERALOGICAL ASSOCIATION OF CANADA



**Short Course
In
Environmental
Geochemistry**

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Editor: M. E. Fleet

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ENVIRONMENTAL GEOCHEMISTRY

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London

May 1984

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P R E F A C E

Chemical pollution of biospheric environments by human activity has developed into a problem of regional and even global proportions in recent decades. Defining the extent of this problem and estimating its long-term effects on life-forms presents a formidable challenge to contemporary science. Geochemists can make important contributions to this effort in defining background concentrations, in mapping and accounting for dispersion patterns, in understanding the chemical interaction of pollutants with natural dissolved constituents and mineral matter, in estimating residence times, and, particularly, in estimating the extent to which geochemical processes will remove pollutants from the environment.

This MAC Short-Course Handbook is a comprehensive and up-to-date instructional text on environmental geochemistry. The authors and I hope that it will further communication between earth scientists, chemists and biologists on environmental concerns.

Many thanks go to the authors and lecturers for their time and effort, to W.S. Fyfe and J.R. Kramer for organizing the content of the Handbook, and to H.W. Nesbitt and W. Shotyk for editorial assistance.

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CHAPTER 1

THE GEOCHEMICAL CYCLE

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INTRODUCTION

The concept of the geochemical cycle was developed to focus attention on the pathways of any chemical element or isotope of the earth system during geologic history. In a sense it involves the ultimate objective of geochemistry. The data necessary to achieve the objective are rarely available. If they were, there would be little necessity for holding this short course. In this introductory paper I wish to focus attention on some recent developments which have, or are showing, the inadequate state of present knowledge.

Urey (1956) drew attention to the importance of geochemical cycling in his classic discussion of the carbon dioxide system. He used the simple reaction:



to describe atmosphere-crust reactions at low temperatures which fix carbon dioxide, reactions which later may be reversed during metamorphism and magmatism. A system which dramatically shows the influence of cycling on a much shorter time scale is provided by the biosphere. As stressed by Allegre and Michard (1974), the ratios of the mass of the hydrosphere, atmosphere and biosphere are 70000:300:1. The biosphere appears insignificant but when the production rate of organic material is considered at about 10^{17} g a^{-1} , and if this number is integrated over the 3 billion years or more for which there is clear evidence for abundance of life, the integrated sum of biomass approaches the mass of the earth as was first pointed out by Abelson (1957). As living matter contains a significant fraction of elements other than O-C-N-H, and normally metals make up 10,000 ppm or so, the mass of such species recycled through the biomass ($\sim 10^{24} \text{ g}$) is similar to the mass of the earth's crust. Thus the geochemical significance of any of the classic geospheres (lithosphere,

core, mantle, etc.) is not simply a function of its mass at any given time, but is also a function of the fluxes in and out of the given part of the earth we choose to study.

During this present age of plate tectonics it perhaps should be noted that the carbon cycling rate of 10^{17} g a^{-1} should be compared with the rate of mantle volcanism ($3 \times 10^{16} \text{ g a}^{-1}$) which creates new crust and is associated with the driving forces of plate tectonics.

The classical concept of the geochemical cycle is described by Mason (1966) as follows: "In the lithosphere the geochemical cycle begins with the initial crystallization of a magma, proceeds through the alteration and weathering of the igneous rock and the transportation and deposition of the material thus produced, and continues through diagenesis and lithification to metamorphism of successively higher grade until eventually, by anatexis and palingenesis, magma is regenerated". This classic cycle of the 60's is shown in Fig. 1. It is important to note that while Mason clearly recognized the biosphere as a significant part of the major cycle, there is little connection to the deep earth. The emphasis on near surface processes partly shows the state of knowledge of 1966. Magma generation was put at the Verhoogen (1960) figure of $3 \times 10^{15} \text{ g a}^{-1}$, a figure we now know is more than an order of magnitude too low. Before the great sea floor discoveries of the past two decades, most data was drawn from continental observations and in fact, Verhoogen's figure is about correct for andesite generation rates.

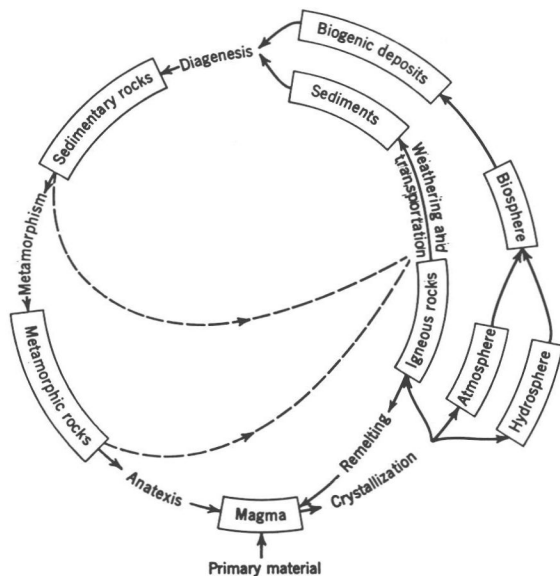


Fig. 1. The geochemical cycle (after Mason, 1966).

Most recent workers concerned with geochemical cycles have tended to focus on "box models". Each box can be chosen to represent that part of the planet (the core, the biosphere, the Baltic Sea, etc.) which is to be described. The chemistry of a given box is normally considered to be in an essentially steady state with constant mass fluxes in and out. The task of describing the given region then becomes one of defining the species in the box and their chemical reactions, and defining the steady state fluxes. The box model leads to the concept of a "residence time" for a given species in the chosen box. In terms of environmental geochemistry, the concept is of critical importance (e.g. the residence time of a radioactive element in the human body, or of a species in the groundwater reservoir). For many parts of the earth the approximation of a steady state is reasonable for short time scales but some degree of caution is needed as the mass of a given box becomes small. For example, recent studies of Chesapeake Bay (Orth and Moore, 1983) show that for this large estuarine region, biomass has diminished dramatically over the last ten years probably because of an increased influence of human activity.

In recent years major gaps in large scale geochemical models of the Earth have become increasingly evident. There is increasing evidence that fluxes between the atmosphere-hydrosphere-crust system with the mantle have been greatly underestimated. Recent data largely derived from the study of rare gas isotopes indicate that there is significant interaction from the lower mantle or even the core region (O'Nions and Oxburgh, 1983; Allegre et al., 1983). Exchange across all the major geosphere boundaries is being recognized on a scale not quite appreciated previously. There is also increasing evidence that the concept of steady state ocean chemistry is a little shaky and that the time constants of fluctuations may not necessarily be long.

Interaction between the ocean floor crust and ocean system has attracted much recent attention. The recognition that about 50% of the total heat production of the planet is vented at the ocean ridges, and that half of this energy is removed by convective circulation of sea water has had a profound influence on our thinking about the history of the oceans. It is becoming clear that ocean chemistry, and sediment chemistry, is not entirely controlled by near surface processes. There is exchange with the deeper parts of the igneous ocean crust and the time scales of the exchange are relatively short.

Box models of geochemical cycling assume a steady state within the box. But it is obvious that no planetary object which is cooling can be in a perfect steady state; all fluxes must reflect available energy. For major parts of the earth, the steady state may be reasonable on human time scales.

But today, as parts of this workshop show, there is increasing concern with human perturbations of local steady states. Human

activity is drastically changing the fluxes in major parts of the surface environment as the most simple calculations will show (see Fyfe, 1981). Thus modern western man uses about 20 tons a^{-1} of mineral materials for his needs. This flux of $4 \times 10^{16} \text{ g a}^{-1}$, exceeds the rate of ocean crust formation. Man burns more than 3 billion tons of coal per year, a mass ($3 \times 10^{15} \text{ g}$) which exceeds the rate of subduction zone volcanism. Burning fossil carbon fuels is perturbing the atmosphere at easily observable rates but as coal and hydrocarbon fuels contain other species the local perturbations by sulphur and nitrogen acids and some trace metals can be extreme. For metals such as Fe, Mn, Cu, Zn, Pb, Sn, the man made flux to the oceans is now at least 10x the pre-man levels.

The human impact on sediment transport is perhaps the most dramatic perturbation. As shown by Toy (1983) conversion of forest to farm land can increase sediment transport by a factor of 1000x, a forest fire can increase erosion by 7000x, changing grassland to row crops can lead to 100x increase in erosion. In parts of Iowa (see also Risser, 1981) top soil erosion rates are now 444 tons $\text{ha}^{-1} \text{ a}^{-1}$ or represent land surface removal at a rate of 2 cm a^{-1} .

Such perturbations greatly complicate predictions of environmental influences of toxic materials based on sediment core data. A change in erosion patterns which changes light penetration into, and chemistry of waters, can dramatically perturb the biomass (see Orth and Moore, 1983). In what follows I wish to briefly mention some areas where there have been major changes in our views concerning geochemical cycles.

THE OCEAN RIDGES AND OCEAN CHEMISTRY

Recent data principally derived from studies of oceanic heat flow patterns and age have shown that about 50% of earth's internal energy is vented near the ocean ridge system ($10^{20} \text{ cal a}^{-1}$). For a comprehensive review of ocean floor observations see Emiliani (1981). Wolery and Sleep (1976) analysed the difference between theoretical and observed heat flow patterns and showed that about $4 \times 10^{19} \text{ cal a}^{-1}$ was not recorded by measurements of conductive heat flow but was removed by circulation of cold sea water onto the oceanic crust (see also Edmond and von Damm, 1983). Given these energy fluxes it follows that the ocean water circulation rate through the ridges is of the order of 10^{18} g a^{-1} , a figure which implies that the entire ocean mass ($1.4 \times 10^{24} \text{ g}$) is processed through the ridges every few million years (see Fyfe and Lonsdale, 1981). Recent studies of heat flow in older ocean crust indicates that convective circulation continues in ocean crust almost to the point of subduction and influences sediment chemistry. It has been shown that sea water penetrates to depths corresponding to the oceanic Moho and it is possible that exothermic hydration reactions such as serpentinization may provide some of the energy to maintain the circulation far from the igneous thermal input at the ridges.

It is now certain that the sea water which enters the convective system is dramatically modified by the time it vents back to the sea floor and the oceanic lithosphere is correspondingly modified.

In particular the highly reduced discharged ocean water carries trace metals at much larger concentrations than the normal marine waters. Edmond and Von Damm (1983) show that species like iron occur at the 100 ppm level while copper, zinc, nickel, etc., occur at the ppm level in hot vent waters. As better analytical data become available exotic gas phases are being detected (CH_4 , H_2 , CO , N_2O) some of which may have inorganic source reactions but others may imply biological processes by populations of thermophilic bacteria living in the hot porous rocks of the discharge zones (Baross et al., 1982; Lilley et al., 1982).

The importance of these discoveries can be shown by a few examples. Thus for copper, the average content in river water is about 5 ppb. Given a river flux to the oceans of $3.6 \times 10^{19} \text{ g a}^{-1}$, the copper flux is about $1.8 \times 10^{11} \text{ g a}^{-1}$. Given a hydrothermal flux of 10^{18} g a^{-1} with copper at 1 ppm, the hydrothermal copper transport is near 10^{12} g a^{-1} , about 10 x the continental runoff flux. When we note that the present man made flux is of the order of $4.5 \times 10^{12} \text{ g a}^{-1}$, we see that the two presently largest fluxes into the oceans and sediments, were not considered in geochemical cycles a decade ago! This conclusion is probably true for most heavy metals. For some species like uranium which is present at low levels in basalts, sea water circulation actually removes uranium from the water and enriches the basalts (the same is true for Rb, K, Na, Mg, S, etc.). It is clear that until all the fluxes are well quantified, the presently available residence times of many elements are likely to be in serious error and these parameters are of great importance for environmental considerations.

There is presently great interest in the general problem of the constancy of sea water composition on various time scales. A most instructive case is provided by studies of the strontium isotope systematics of sediments. At the present time rivers feed $^{87}/^{86}\text{Sr}$ to the oceans at a ratio of 0.711. Modern sea water has a ratio of 0.7091. Clearly there must be other Sr sources influencing sea water and the obvious source is hydrothermal fluids moving through basalts with a ratio 0.702. Recent data (Faure, 1982; Burke et al., 1982) clearly show that there have been large fluctuations in the $^{87}/^{86}\text{Sr}$ ratio during the past 600 Ma (a range of at least 0.709-0.7067). The causes of these fluctuations can be complex as stressed by Faure, but there is a clear suggestion that continental runoff inputs and volcanogenic inputs may fluctuate. The same factors which influence strontium isotopes may also influence other critical trace metals, critical in the sense that trace metals may dramatically influence the biosphere population (Ortner et al., 1983). Such observations for recent times must certainly make us a little concerned about ocean chemistry constancy back into Archean times when volcanism and hydrothermal influences could have been an

order of magnitude more intense.

It is also becoming clear that as well as multimillion year fluctuations in ocean chemistry, small scale fluctuations are also possible. Thus recently Brewer et al. (1983) report a salinity decrease in parts of the deep Atlantic over the past 20 years, probably a response to climate fluctuations. The fact is that our significant record of changes in ocean masses is very short and generally quite inadequately chemically.

The consequences of changes in ocean chemistry on short time scales may be of great environmental importance (cf. atmospheric perturbations caused by volcanic eruptions such as the recent El Chichon event). Ortner et al. (1983) have shown that trace metals such as copper and zinc can greatly influence carbon fixation in marine phytoplankton. Van Andel (1983) has stressed the rapid increase in knowledge and the surprises in our knowledge of "states of past oceans".

It is now clear that any detailed "box model" of large ocean water masses must consider at least three major fluxes, continental runoff, volcanic influences and human influences. The latter, largely ignored a decade ago have profound influences on both major (e.g. S, Mg, K) and trace metal (e.g. Cu, Zn, Li, Rb, U) fluxes. More improved sampling and monitoring of such systems is needed before adequate models of such large bodies is possible. I would note that while oceans present such problems, the situation with the atmosphere is even more critical and complicated (see Baum, 1982).

SUBDUCTION, MANTLE RECHARGE

It is interesting to consider the older geochemical cycle of Fig. 1 and to note that no mantle recycling is shown. But there certainly were those who believed in deep convection and return flow and I am always impressed by the ideas and diagrams of Holmes (1928). Uyeda (1977) considered the subduction process as one of the great remaining questions of plate tectonics. In the past five years or so knowledge of trench environments and the subduction process have greatly increased due to more detailed seismic, drilling and topographic studies in trench environments. Some of the more recent data are summarized in Hilde and Uyeda (1983).

Plate tectonic theory requires that for a steady state earth, the creation of new oceanic lithosphere at ridges must be balanced by its removal in the subduction process. The mass of oceanic lithosphere and continental lithosphere is approximately conserved (Hallam, 1976). But clearly such conservation is an approximation for a cooling planet. One of the great problems regarding the subduction process is to define the exact nature of what is subducted.

All would agree today that new ocean crust added from the