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Element Cycling in Bottom Sediments [and Discussion]

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Element cycling in bottom sediments

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Significant cycling of trace elements can occur during early diagenesis of oceanic sediments. For some elements this leads to a benthic flux at the water–sediment interface which influences their distributions in the water column. In other cases, redistribution occurs within the sediment column, leading to metal-enriched horizons within sediments. Element cycling in bottom sediments is an important factor in the flow of elements within the oceans.

A useful theoretical framework for understanding metal diagenesis is to consider that the early diagenetic reactions involving organic-matter oxidation occur in the sequence of decreasing free-energy yield thus; aerobic oxidation > denitrification ⩾ iodate reduction > manganese oxide reduction > ferric oxide reduction > sulphate reduction > methanogenesis:

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\begin{aligned}
&CH_2O + O_2 \rightarrow CO_2 + H_2O\\
&5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O\\
&3CH_2O + 2IO_3^- \rightarrow 2I^- + 3CO_2 + 3H_2O\\
&CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-\\
&CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O\\
&2CH_2O + SO_4{}^{2-} \rightarrow H_2S + 2HCO_3^-\\
&2CH_2O \rightarrow CH_4 + CO_2.
\end{aligned}
$$

This sequence is frequently inferred to have occurred via measurement of pore-water solutes, although historical changes in sedimentation can seriously affect element transport described by steady-state models that are based on this framework.

Three factors are considered to be of particular importance in controlling diagenetic reactions in the deep sea: the rate of supply of organic matter, the rate of sediment mixing, and diffusion. Thus, in pelagic sediments at sites where the organic carbon flux to the sediments are similar, contrasting pore-water profiles can occur because enhanced mixing rates can lead to less pre-burial aerobic oxidation and consequent manganese mobilization within the sediment column. Nevertheless, the organic carbon flux to deep-sea sediments (for example, *ca.* 12–13 μmol C cm^{-2} a^{-1}) is oxidized dominantly by oxidation by O_2 (for example, *ca.* 12 μmol C cm^{-2} a^{-1}) compared with denitrification (for example, *ca.* 0.1 μmol C cm^{-2} a^{-1}) and MnO_2 reduction (for example, *ca.* 0.05–0.1 μmol cm^{-2} a^{-1}) with a burial flux of organic carbon (for example, *ca.* 0.1–0.4 μmol cm^{-2} a^{-1}) of the order of 1 % of the flux to the sediment interface.

Such factors influence the cycling of certain metals in addition to Mn in bottom sediments because they are coupled with Mn. Thus, Co and Ni show enrichments in pore waters at redox boundaries because they are released with the dissolution of Mn oxides. Other elements (such as Cu and I) show strong interfacial enrichments in pore waters that appear to reflect the breakdown of labile organic material at the water–sediment interface followed by scavenging of some of the released elements.

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† This extended abstract by Dr Elderfield replaces the contribution of Dr M. Whitefield (Marine Biological Association, Plymouth), who was obliged to withdraw from the Discussion Meeting at very short notice.

Therefore, the pore-water gradients are supported by active diagenetic recycling at the interface, which sets limits on the release of the elements to the oceanic water column.

Discussion

A. S. Mackenzie (*BP Geochemistry Branch, Sunbury-on-Thames*). The flux of copper and other metals across the sediment–water interface could be the result of the formation of organometallic compounds. Copper porphyrins have been found in ancient deep-sea sediments, which are supposed to have been formed under oxidizing conditions. Some of the other elements Dr Elderfield mentioned have the correct atomic radii for chelation by the porphyrin macrocyle. At the sediment–water interface the copper porphyrins may form parts of enzymes or may have been formed by a reaction that does not involve any organism. Once formed, the metal porphyrins and related compounds are relatively unstable, and the metal can be separated from the porphyrin by oxidation and in this way recycled.

H. Elderfield. Such transfer could well occur, but it is then somewhat difficult to understand why porphyrins are preserved at depth in sediments.

A. S. Mackenzie. The occurrence of copper porphyrins in sediments has not yet been widely investigated. It is generally believed that they principally occur in more oxidized sediments, but it is not clear how well founded this belief is.

H. Elderfield. If the transfer of metals by porphyrins does take place under oxidizing conditions, the process might resemble those involved in the movement of iodine. The surficial enrichment of iodine is only found in oxidizing sediments. Though the mechanism by which this enrichment occurs is unclear, it is believed to involve the oxidation of iodide to iodate ions.

R. A. Berner (*Department of Geology and Geophysics, Yale University, U.S.A.*). A considerable amount of organic matter is transported downwards by bioturbation, especially in near-shore sediments like those in Long Island Sound. The importance of this process is evident from the rate of sulphate reduction, which is more rapid than would be expected from the rate of decrease of organic material with depth.

H. Elderfield. In most deep-sea studies it is difficult to separate the effect of bioturbation from other processes affecting element transport because of the problem of sampling. Sporadic coring at widely spaced intervals is not a satisfactory technique for investigating biological activity. What is needed is a detailed investigation of the sediments beneath a region where there is a steady influx of organic matter, to discover whether increased bioturbation affects the zones in which different elements are remobilized.

P. S. Meadows (*Zoology Department, Glasgow University*). I was interested in Dr Elderfield's comments on differing rates of bioturbation at different sites. Could he tell me if rates of bioturbation were actually measured, or were they inferred by visual observation? The reason I ask this is because I do not know of any easy way of measuring bioturbation rates. One can certainly obtain estimates of bioturbation by measuring numbers of burrows per square metre for example, but this is not a rate process. The analogy I would draw here is between the standing crop of phytoplankton (grams C per square metre) and primary productivity of phytoplankton (grams C per square metre per day). There is also an important distinction to be made between bioturbation rate and microbial activity; the latter being a rate process that is relatively easy to measure by radioactive methods.

H. Elderfield. The bioturbation rates at these sites were measured by using ^{210}Pb, and are therefore the integrated rates resulting from all processes. It is not possible to use these measurements to determine what type of organism is responsible for the sediment transport, or even to decide whether biological activity is responsible. Furthermore it is likely that whatever process is responsible also transports the pore water. Indeed, at the Mediterranean sites I mentioned, the ^{210}Pb inventories suggest that the mechanism is physical, rather than biological.

J. G. Jones (*Freshwater Biological Association, The Ferry House, Ambleside, Cumbria*). Bioturbation may also increase the area of the anoxic–oxic interface and hence the activity of bacteria, particularly the nitrifiers. This process will in turn stimulate the nitrogen cycle. Because nitrifiers have extensive internal membranes, this process should increase the abundance of the lipids that form part of the membrane and which will remain as biological markers in the sediment. These bacteria are also autotrophic and produce organic matter by the reduction of carbon dioxide.

H. Clemmey (*Department of Earth Science, Leeds University*). An alternative explanation of the position of the oxidation front within the turbidite is that it is a primary depositional feature. The lower part of the turbidite should retain carbon, because it is rapidly deposited and poorly sorted. However the upper units are commonly formed from reworked sediment which has been winnowed and oxidized. The increased concentration of metal ions found near the contact between the oxidized and reduced sediment could have been produced from sea water and from the water expelled from the turbidite as it is compacted.

H. Elderfield. There could well have been an initial variation of carbon content with depth in the turbidite, which may account for some of the variation which is still present. But I believe that the main features are controlled by the rate at which oxygen can diffuse into the upper part of the turbidite and that this rate has decreased with time as the turbidite has become more deeply buried by overlying sediment. As the boundary between oxidized and reduced sediments moves downward, manganese and nickel are transported upwards, whereas uranium moves downward because it is more soluble in its oxidized than in its reduced form. It is this behaviour which leads to the association of uranium and carbon in sediments. As the turbidite is oxidized from the top the uranium becomes steadily more concentrated in basal layer as this becomes thinner. The same type of behaviour is common in uranium ores. The opposite behaviour occurs in the case of manganese and nickel, which become concentrated in the most oxygen-rich part of the sytem, at the contact between the turbidite and the overlying sediments.

D. G. Murchison (*Organic Geochemistry Unit, The University, Newcastle-upon-Tyne*). Near the sediment–water interface some organic compounds are likely to be more reactive than others.

The products of the rapid degradation of lignin and cellulose are likely to be particularly important. Could the reactions Dr Elderfield has discussed account for the high concentration of certain trace elements which are found in the derivatives of lignin and cellulose in coal?

H. Elderfield. The more reactive organic compounds certainly are removed from the sediment at an early stage. A good example of such a process occurs in coastal sediments where the top 10–20 cm are disturbed by biological processes. The organic material beneath this layer is much less reactive than it is where such bioturbation is absent. But inorganic geochemists do tend to treat organic matter as a black box, with little concern for the compounds present. On the other hand, organic geochemists tend to be interested in characterizing individual compounds of particular interest. Such studies provide little information about the reactions that are occurring in the bulk of the organic matter.

D. G. Murchison. Dr Elderfield suggested that bioturbation could act as a concentrating mechanism, but I did not understand how he believed this to occur.

H. Elderfield. Because bioturbation removes the most reactive organic material it will produce a concentration of the less reactive material in the sediments below the zone involved. But even in the absence of bioturbation, the more reactive organic material will be removed at the sediment–water interface, especially if the sedimentation rate is slow. These reactions are presumably linked to the anomalous metal concentrations found in the porphyrins. Though these reactions are not associated with the classical redox boundary, they still involve oxidation and reduction and mobilization can occur.

R. A. Berner. Bioturbation is often modelled as a diffusive process, but it is important to treat the particles and pore water separately. The water moves more rapidly than the solid material. For instance, in Long Island Sound the sulphate concentration varies little in the top 150 cm even though extensive sulphate reduction is taking place. We believe that this layer is being flushed by sea water, which is being pumped into burrows in the sediment.

P. S. Meadows. I would like to follow Professor Berner's interesting comments on bioturbation with one or two general points about biological activity.

Biological activity in sediments is caused by two contrasting groups of organisms on two very different scales. Bioturbation is produced by the burrowing activities of macrobenthic invertebrates whose sizes range from *ca.* 0.5 cm to *ca.* 1 m in length. Their burrows are relatively large structures on a microscale. Microbiological activity, on the other hand, is mainly produced by bacteria, which are orders of magnitude smaller, ranging in size from 1 to 5 μm. These organisms do not produce any burrow structures, but modify the sediment biochemically.

There are also large differences between the relative importance of bioturbation and microbiological activity in continental shelf and abyssal plain sediments. Bioturbation structures are very common on the continental shelf but rare in the deep sea (mean benthic biomass is about 200 g dry mass animal m^{-2} on continental shelves, but only about 0.2 g m^{-2} on the abyssal plains). Microbiological activity remains relatively high in both environments, although slightly reduced in great depths of water.

B. DURAND (*Institut Français du Pétrole, Rueil Malmaison, France*). There are many more mineral geochemists than there are organic geochemists. It would certainly be helpful if the two groups worked together on the same sediments more often. But the tools of the organic geochemist are in some ways more primitive. He has no equivalent to the X-ray camera.

G. EGLINTON (*Organic Geochemistry Unit, School of Chemistry, University of Bristol*). The techniques for examining small organic molecules have been available for some time and most organic geochemists have, for this reason, studied such compounds. Mass spectrometers, which can be used to study molecules with a molecular mass of a few thousand, are now becoming available. The insoluble precursors of kerogen are of great interest but must first by broken down by chemical methods. Once the fragments have been characterized, the original molecule can be 'reconstructed' on paper. Yet another new microanalytical method is rapid pyrolysis, which can determine how much lignin and cellulose are present. These methods can potentially provide information about the chemical structure of the bulk of the organic matter.

Bioturbation is used by chemists to describe any transport due to biological activity and I have often wondered how important the ciliated micro-organisms are. Though they are small they are very abundant.

Bacteria can, in principle, live at any depth where their metabolic processes can repair thermal or other environmental damage. The necessary water is present at all depths and, as recent work on the hot springs in the deep ocean has shown, high temperature by itself is not fatal. At a depth of a kilometre it is not clear whether bacteria can metabolize fast enough to repair chemical damage and to reproduce.

M. SARNTHEIN (*Geolisches Palaontisches Institut, Universität Olshausenstrasse, F.R.G.*). In the deep sea the macrobenthic activity depends on the nutrient supply. Below those regions of high surface productivity the bioturbation is vigorous and much more organic meterial will be preserved than usual.

J. G. JONES. Decomposition rates in deep-sea sediments are much slower than those in shelf sediments. The faecal material is also very important in the recycling of organic material, and is rapidly colonized by bacteria. Some anaerobic bacteria are now known that live on very simple substrates, reducing ferric iron with hydrogen and using carbon dioxide as their carbon source. Such metabolism is, however, extremely slow.

R. A. BERNER. If the sulphate profiles from D.S.D.P. holes are fitted to a simple diagenetic model, the resulting half-life of the organic carbon in such sediments is about a million years. It is not clear whether the reaction is organic or inorganic.