

TREADING IN MORTIMER'S FOOTSTEPS: THE GEOCHEMICAL CYCLING OF IRON AND MANGANESE IN ESTHWAITE WATER**(W. DAVISON & E. TIPPING)****Introduction**

Clifford H. Mortimer's ideas about the environmental redox chemistry of iron have had a worldwide influence. His classic work (Mortimer 1941, 1942) was largely based on observations of seasonal cycles in Esthwaite Water in 1939. The onset of a World War and his imminent recruitment to the Navy stimulated the swift transfer of his ideas to paper. Forty years on we tried to amplify Mortimer's work on iron and also to see if the same concepts could explain the behaviour of manganese in lakes. Our work was stimulated by the NERC Special Topics Programme on Geochemical Cycling.

To give the reader a perspective from which to view our additional information we will summarize Mortimer's findings.

Mortimer's description of the iron cycle

Although the following description of the seasonal cycle of iron in Esthwaite Water is in our own words, it is based entirely on Mortimer's ideas.

During the winter months the surface of the sediment in the deeper parts of the lake is covered by a red-brown layer, the colour of which is due to ferric (hydr)oxide. Underlying this red-brown layer is a strongly reducing black mud containing ferrous iron – Fe(II) – in solution in the interstitial water. The Fe(II) diffuses upwards and on encountering the overlying oxic waters is oxidized and precipitated at the sediment-water interface. The net result is that no iron is released from the sediment. When the lake becomes thermally stratified in early summer the oxygen in the bottom waters is progressively consumed, largely by processes occurring in the highly reducing sediments. The sediment surface becomes devoid of oxygen prior to complete deoxygenation of the overlying waters. This leads to reductive dissolution of the ferric hydroxide causing release of soluble Fe(II). The latter is re-oxidized in the bottom waters of the lake which become cloudy due to re-precipitation of insoluble ferric iron. Once these bottom waters become completely reducing, ferrous iron is stable (i.e. does not re-oxidize) and present in measurable amounts. Its release from the sediment continues throughout the summer. The bottom waters become more transparent as the maximum of the particulate iron migrates to shallower water. This precipitation of ferric iron at the thermocline is caused by the continuous oxidation of ferrous iron. As these processes occur the concentration

of ferrous iron in the bottom waters progressively increases so that by the end of the summer most of the iron is in this lower oxidation state (Fig. 1). In early autumn when the lake waters become completely mixed the ferrous iron is rapidly oxidized and precipitated, most of it returning to the sediment surface. Relatively high concentrations of iron are maintained in the surface waters at this time, the element probably being present as colloidal ferric hydroxide, or as soluble or colloidal ferric-organic complexes similar to those found in waters and soils in the presence of humic material.

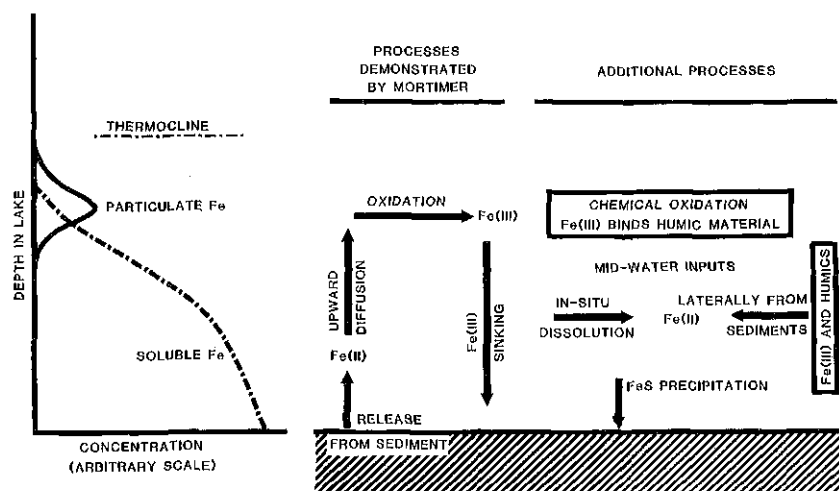


FIG. 1. The iron cycle in the lake during late summer. Concentration-depth profiles of particulate and soluble iron are shown on the left. On the right are shown interpretations of the profiles in terms of processes identified by Mortimer and additionally by ourselves. The soluble iron is exclusively in the ferrous form. The particulate iron is present as Fe(III) , except for the small amount of ferrous sulphide which has little influence on the profiles.

Advances in understanding

Mortimer's work contained many speculative ideas concerning the iron cycle in lakes. His interpretation (Fig. 1) of the situation during late summer had to be based on examination of the depth-dependence of the concentrations of ferrous iron and total iron. The particulate peak shown in Fig. 1 was deduced from the turbidity of the water. Therefore his work only provided evidence for release of iron from the sediment and its subsequent oxidation in the water column. Although he mentioned, as possibilities, several additional processes (Fig. 1) he was unable to provide proof of their existence.

Our work has provided quantitative information about the summer cycling of iron (Davison et al. 1981). In a stratified lake, the movements of water in horizontal directions are about 100 times faster than in vertical directions and so lateral interactions with the sediment are important. The lake basin was therefore modelled as a series of horizontal layers of different volumes overlying one another. Thus our concept of the lake was quite different from Mortimer's simpler idea of a cylinder with sediment at the bottom. Fluxes of iron to and from each layer were calculated by analysing the shape of the concentration-depth profile of soluble iron. It transpires that similar amounts of iron are supplied laterally, from sediments at the sides of the basin, as are supplied vertically, from the underlying layers. Moreover there was evidence for an additional flux of iron in those layers of water below the peak in particulate matter. This was attributed to the sinking iron particles being reduced and re-dissolved in the water column. Support for this view was obtained by using sediment traps, at different depths in the lake, to measure directly the sinking material. The direct measurement agreed with the calculated values from profile shapes (Davison et al. 1982).

Further details concerning the summer cycle emerged. There has been considerable speculation about the possible role of bacteria in the oxidation of ferrous iron (Jones 1981). Ferrous iron in samples of lake water collected throughout the summer from different depths is oxidized at different rates. However, when variations in pH and initial concentration of ferrous iron are considered the oxidation is found to obey one simple rate law with a single constant (Davison & Seed 1983). There is no evidence for biological mediation of the reaction.

We have studied the product of the oxidation reaction, the ferric oxide which comprises the peak of particulate matter in the water column (Fig. 1). The material (Fig. 2) consists of amorphous particles which are approximately spherical or ellipsoidal with mean diameters in the range 0.05–0.5 μm (Tipping et al. 1981). The particles contain 30–40% by weight Fe with the following elements accounting for up to 8% of the weight: P, N, Mn, Si, S, Ca, Mg. As much as 36% by weight is organic matter, about one third of which consists of humic substances. The latter are present as the result of adsorptive interactions with the precipitating oxide (Tipping 1981a) and have a profound influence on the properties of the particles. The humics dominate the surface chemistry of the oxide (Tipping 1981a, b; Tipping & Cooke 1982), affecting trace metal uptake (Tipping et al. 1983) and the aggregation rate of the particles (Tipping & Higgins 1982; Tipping & Ohnstad 1984).

A noteworthy feature of the iron oxide particles from Esthwaite Water is that they show no sign of being composed of smaller, primary units. In contrast, iron oxides of similar composition formed when anoxic,

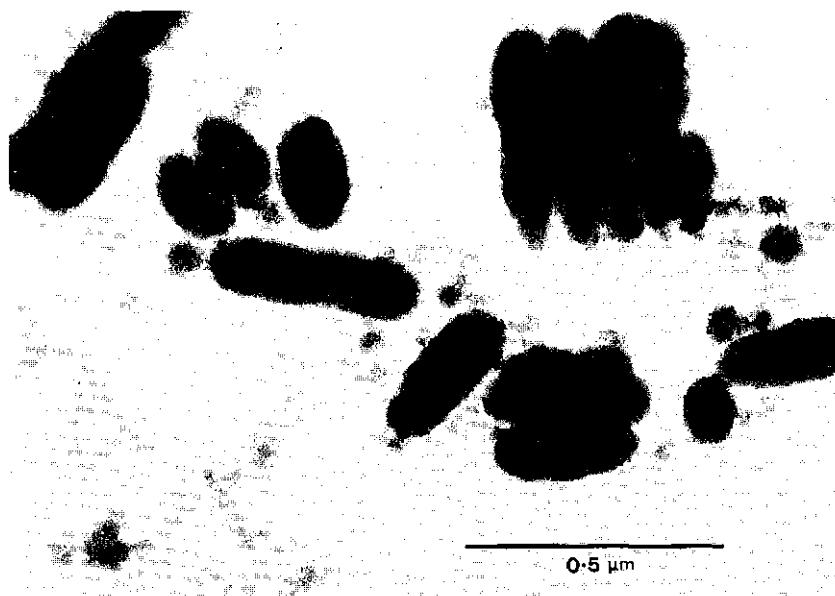


FIG. 2. Transmission electron micrograph of iron oxide particles from Esthwaite Water. The sample was taken from the bottom water of the lake in the early stages of seasonal anoxia. The electron microscopy was carried out in collaboration with Dr D. W. Thompson, University of Bristol.

ferrous-rich, soil-borne waters encounter the atmosphere do consist of such units, which are of the order of 5 nm in diameter (Coey & Readman 1973; Schwertmann & Fischer 1973). The difference is possibly explained by the slower oxidation of Fe(II) in the lake water resulting in only slight supersaturation with respect to the oxide phase, so that nucleation centres for oxide formation are supplied by pre-existing particles, allowing growth to relatively large sizes. Development of a recognizable crystal structure is inhibited by the adsorbed humic substances. The maintenance of the oxide in an amorphous state makes it sufficiently labile to be reduced in the water column (see above and Fig. 1). Even though the particles are rather large by comparison with the primary units of the soil-derived material, they are none the less too small for individual particles to sink at an appreciable rate in the water column. Their sedimentation thus depends on aggregation processes.

The detailed characterization of the particulate ferric oxide has provided evidence in support of Mortimer's suppositions concerning the importance of humic uptake and of phosphate transport by the iron

cycle. In addition, his observations of increased colour in the bottom waters in late summer have been confirmed and shown to be due to humic substances, which accumulate following their co-transport with iron (Tipping & Woof 1983a, b).

The formation of iron sulphide can literally cloud the observations of colour. Towards the end of the summer ferrous iron builds up to very high concentrations and sulphide starts to accumulate in the bottom waters. When the solubility of ferrous sulphide is exceeded an intense black precipitate is formed (Davison & Heaney 1978). Results obtained by using sediment traps have shown that relatively little iron is removed from the lake by this mechanism. Moreover examination of the black particles reveals that they may consist largely of iron oxide with only a surface coating of ferrous sulphide (Davison & Dickson 1984). Because the concentration of ferrous iron far exceeds that of sulphide the shape of the concentration-depth profile of soluble iron is virtually unaffected. The sulphide profile is determined by this precipitation process, however, and so develops a peaked shape. As Mortimer suspected, it is this interaction which restricts sulphide to low concentration.

Whole-lake cycling

Mortimer's interest in iron chemistry was prompted by its role in supplying nutrients. From this biological standpoint it is most appropriate to consider the concentration of a chemical species at any one point in time – the "chemical standing crop". Therefore his work was focused on the largest of such crops, that in the hypolimnion during the summer months. By contrast the geochemist is primarily concerned with fluxes and the ultimate fate of an element. This necessitates consideration of the whole lake.

Annual budgets to and from the lake have revealed that most iron enters the lake in the autumn and winter months and c. 70–90% of it is ultimately accumulated in the sediment. Of this annual loading only a small fraction (3–18%) is released back into the water as ferrous iron. This immobility was explained by examination of the iron in the sediment which showed that c. 80% of it is present in the clay mineral, chlorite (Davison & Dickson 1984; Ochsenein et al. 1983). As this iron forms an integral part of the crystal lattice of chlorite it is not available for participation in redox reactions.

The rapid transport of chlorite through the lake illustrates the importance of distinguishing concentrations and fluxes. Consider two types of particle, one which sinks quickly and the other slowly. The former will contribute more significantly to the flux whereas the latter will determine the standing crop. Chlorite and amorphous iron (hydr)oxide respectively fill these roles. Confirmation of the nature of the standing

crop was provided by showing that c. 90% of the iron in the surface waters is in a chemically reactive form (Tipping et al. 1982). Electron microscopy showed that the particles were similar to those from the oxic/anoxic boundary, although they had a wider range of morphologies and contents of other elements.

Similarities of manganese and iron

Mortimer did not study manganese to anything like the same extent as iron. He observed that hypolimnetic accumulation of Mn(II) occurred slightly before that of Fe(II), and that Mn(II) persisted in the lake for a longer period after overturn. Its potential importance, possibly in the elemental phosphorus cycle was noted, however.

Iron and manganese are transition metals which occupy adjacent positions in the periodic table of the elements. They have many things in common. Both are particularly abundant in the Earth's crust. Each is a micronutrient. Their higher oxidation states, Fe(III), Mn(III) and Mn(IV), are stable in the presence of oxygen and occur as insoluble oxide particles which adsorb organics, trace elements and biological nutrients. Once conditions become anoxic these oxides are readily reduced to the lower oxidation states, Fe(II) and Mn(II). The latter both occur as soluble ions which are relatively free from complexation and are hence highly mobile.

The amorphous oxide form of manganese is the major contributor to the downward flux of the element in the lake. On the face of it this manganese behaves in the same way as amorphous iron (hydr)oxide. In the anoxic hypolimnetic waters of lakes such as Esthwaite Water the reduced forms accumulate to very high concentrations. Thus their standing crops are very similar. However, our work has considered manganese geochemically and shown that where fluxes are concerned its behaviour differs markedly from that of iron.

The manganese cycle

Figure 3 shows how, in midsummer, the dissolved components of iron and manganese vary with respect to the distance from the sediment. Whereas the concentration of iron decreases rapidly with distance from the sediment, that of manganese changes only very little. This indicates that the supply of manganese differs from that of iron and is not dominated by release from the mud. Calculations (Davison 1981) support this qualitative observation. All of the iron which accumulates in the bottom waters during the summer can be accounted for by diffusion from the sediment. Very little of the manganese can be supplied in this way. The near vertical profile shape of manganese indicates that Mn(II)

is supplied by reduction of the particulate manganese which sinks through the water. As soon as this sinking particulate matter encounters the reducing conditions below the oxycline it must be converted to its soluble reduced form. Support for this hypothesis comes from analysis of the manganese in sediment traps (Davison et al. 1982). Very little manganese reaches traps located in the anoxic bottom waters. Analysis of the interstitial waters of the sediments also indicates that manganese probably diffuses into the sediments from the overlying water, rather than being supplied by the sediment (J. Hamilton-Taylor, person. comm.).

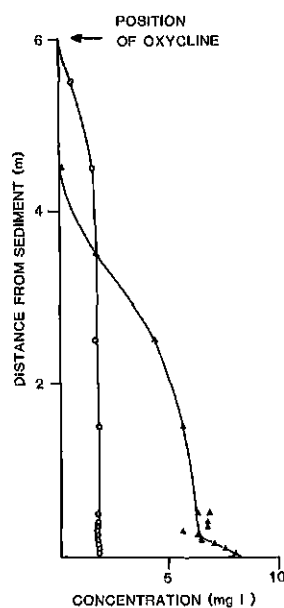


FIG. 3. Concentrations of soluble Fe(II), ▲, and soluble Mn(II), O, versus distance from the sediment on 14 August 1980. Adapted from Davison (1981).

A small amount of Mn(II) is released from the sediment during the early summer and undergoes oxidation in the bottom waters to form particulate manganese. In this respect manganese behaves like iron. However, as mentioned in the previous paragraph, the great bulk of the Mn(II) which builds up in the hypolimnion is supplied by the reductive dissolution of sedimenting particles originating in the lake's catchment. Thus the first appreciable accumulation of manganese is in the bottom waters as soluble Mn(II), with particulate manganese formed by re-

oxidation of the Mn(II) only occurring in substantial amounts at shallower depths. This behaviour contrasts with that of iron which, as we have seen, accumulates in the bottom waters first as ferric (hydr)oxide and subsequently as soluble Fe(II).

The behaviour of manganese during the winter, when the lake waters are well oxygenated, is also different from that of iron. Ratios of the concentrations of iron and manganese in sediment traps and in inflows show that most of the metal which enters the lake is transported to the sediment. However, whereas iron is retained in the sediment manganese is not (Davison et al. 1982). On contacting the reducing sediment manganese is immediately re-released to the overlying waters and during the course of the winter most of it is flushed out of the lake. In contrast to iron most of the manganese which enters the lake is ultimately discharged via the outflow. Before discharge, however, it participates in a redox cycle at the oxic/anoxic boundary.

Differences in the properties of iron and manganese

Why are the geochemical cycles of these two similar elements so different? The answer lies in a fundamental difference in their chemistry. In the presence of oxygen ferrous ions are oxidized quickly whereas manganous ions are relatively stable. At pH 7.0 in air-saturated lake water, the concentration of ferrous iron decreases to half its initial concentration in less than 40 minutes (Davison & Seed 1983). This reaction is chemically controlled and thus identical kinetics are found in synthetic media. In the same synthetic media, Mn(II) takes years to oxidize. In lake water the reaction is speeded by microorganisms but still takes several days (Tipping et al 1984). There is strong evidence to suggest that microorganisms play a role in catalysing the oxidation of Mn(II).

These different reaction rates control the winter release of the elements from the sediment surface. Amorphous iron and manganese are both reduced in the anoxic sediment and diffuse up towards the well-oxygenated overlying water. When they encounter oxygen in the thin layer of oxidizing surface sediment they both tend to be oxidized and precipitated. However, the much slower oxidation rate of Mn(II) permits it to diffuse through this layer prior to oxidation, whereas the rapidly oxidized Fe(II) has much less chance of escaping. By this mechanism the release of manganese and the permanent incorporation of iron is realized.

Supply of manganese to anoxic hypolimnetic summer waters by reduction in the water column clearly cannot be explained in terms of the rates of oxidation. The reduction of manganese is thermodynamically favoured over that of iron. According to our water column results it is

also kinetically favoured. Indeed the dynamic reduction and release of manganese in the vicinity of the redox boundary occurs throughout the year.

Examination by electron microscopy of the manganese particles which occur in the lake water during the summer shows that they differ markedly from iron particles (Fig. 4) (Tipping et al. 1984). They are usually much larger ($1\text{--}5\text{ }\mu\text{m}$), with an undefined amorphous structure. Elemental analysis shows that they sometimes contain large concentrations of iron and so they may possibly be associated with iron particles. Appreciable amounts of calcium are present and Mg, Si, P, S, Cl, K and Ba have also been identified. Little organic matter appears to be incorporated into the oxide phase, although the small amount of humic material present could be important with regard to the surface chemistry. Some, but not all, of the particles examined had the gross morphology of *Metallogenium*, a putative manganese-depositing bacterium.

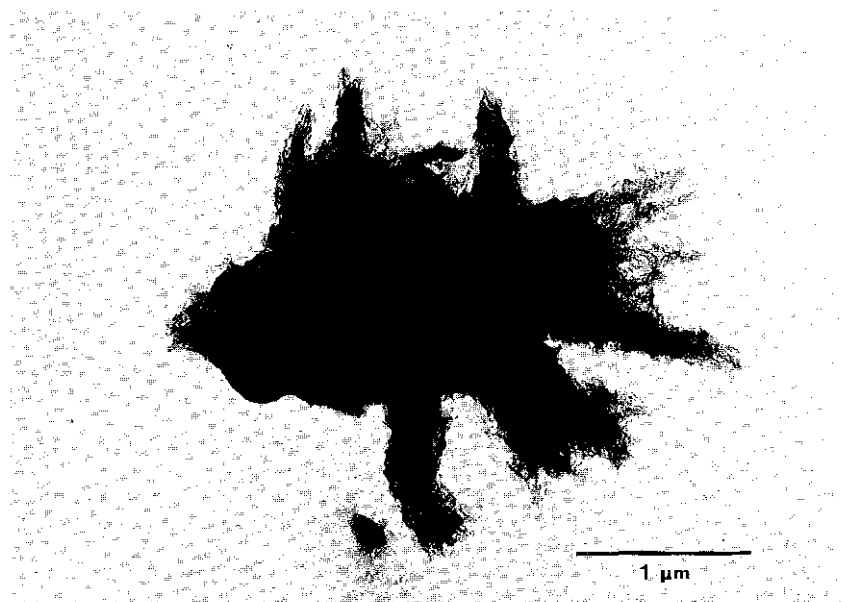


FIG. 4. Transmission electron micrograph of oxidized manganese formed on the exposure to oxygen of a manganese(II)-rich sample of Esthwaite Water. The electron microscopy was carried out in collaboration with Dr D. W. Thompson, University of Bristol.

It is relatively easy to collect manganese particles during the summer because of the peak in particulate manganese which forms above the

oxycline. No such natural concentration mechanism operates in the well-mixed winter waters and so it is difficult to find manganese particles. The ones which have been examined have a different morphology from the summer particles in that they have some recognizable crystal structure.

Conclusion

Our study of iron and manganese has verified Mortimer's observations and has confirmed some of his speculations. Undoubtedly the greatest advances have been the new understanding of the manganese cycle, and the detailed information on the particulate forms of both elements. Significant details concerning the mechanisms and transformations of iron have also emerged. The story is still not complete however, and refinements will continue to be made. Clifford Mortimer's work has undoubtedly stood the test of time during the past four decades. Perhaps, in the 2020's an Annual Report will show whether our contribution has done the same.

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