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ORGANIC CONTROLS ON THE SEDIMENTARY GEOCHEMISTRY OF MANGANESE*

D. A. CRERAR, R. K. CORMICK and H. L. BARNES

The sedimentary behavior of the element Mn is influenced by a wide variety of organic reactions and processes. In this discussion, we shall trace the sedimentary cycle of Mn, noting at each step some of the more important of these organic controls. To provide the necessary background, we first review the predominant inorganic controls on Mn solubility.

During weathering, Mn is leached typically after the mobile alkalis and alkaline earths, and just before or directly with the relatively immobile metals Fe and Al. This sequence is illustrated on the first figure which gives the solubilities of quartz and the simple oxides of Mn, Fe, and Al as a function of pH. The Mn curve has been calculated for three separate values of Eh. Note that Mn solubility exceeds that of Fe and Al by six or seven orders of magnitude for any given Eh and acid pH. Raising soil acidity markedly increases leaching capability and metal oxide solubility. Similarly, solubility is far greater in reducing than in oxidizing environments. Compare the position of the Mn oxide curves at the different Eh values shown. At any one pH, Mn solubility will increase by seven orders of magnitude on reducing Eh from 0.7 to 0.3 volts. Note that Al solubility changes only with acidity, not Eh.

Obviously, any agent capable of acidifying and/or reducing a weathering zone will increase mobility of Fe and Mn. Simplified reactions are given on the second figure. With the free electrons on the left side, these reactions indicate reductions. The hydrogen ion for such reactions is commonly contributed in nature by the organic oxy-acids of sulfur, nitrogen, phosphorus and carbon dioxide.

(1) $Al(OH)_3(C) + 3H^+ \rightarrow Al^{3+} + 3H_2O$

(2) $Fe(OH)_3(\text{amorph.}) + e^- + 3H^+ \rightarrow Fe^{2+} + 3H_2O$

(3) $MnOOH(C) + 3H^+ + e^- \rightarrow Mn^{2+} + 2H_2O$

(4) $2H_2O + CH_2O \rightarrow HCO_3^- + 5H^+ + 5e^-$

Fig. 2. Solvation reactions involving Al, Fe and Mn oxyhydroxides and simple carbohydrates in weathering environments

In addition to these simple inorganic controls on Mn solubility, there are even more important organic reactions. Take, for example, simple organic decay reactions such as number *4* on this figure. Here, the decay of one mole of the simplified

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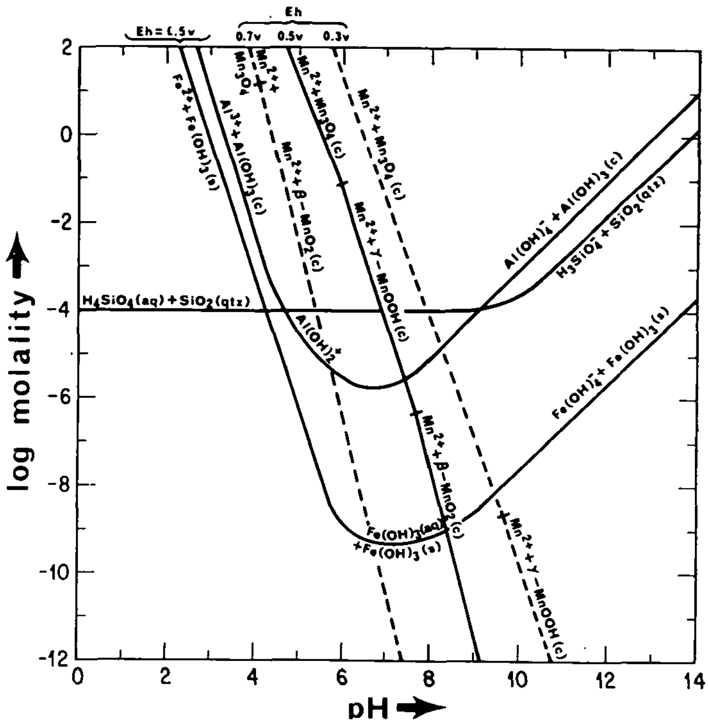

Fig. 1. Solubilities of Fe, Al, and Mn oxyhydroxides in weathering environments as a function of pH. Mn solubilities contoured in Eh.

carbohydrate, CH_2O, produces a sufficient number of electrons to reduce and dissolve five moles of manganite, and sufficient hydrogen ion to dissolve almost two moles. With more realistic complex hydrocarbons, this efficiency is dramatically increased. Organic decay, such as reaction *4*, is catalytically accelerated by simple oxidizing bacteria which thereby indirectly increase Mn dissolution. It is also possible that Mn-specific soil bacteria might directly solubilize the element in much the same manner as those known to corrode Fe. Perkins and Novielli [1962] for example, have isolated a Mn-specific soil bacterium capable of leaching most of the element from manganiferous rocks.

In densely vegetated regions, a significant quantity of Mn may be mobilized by simple plant accumulation and decay. Much of the Mn held within plant tissue may be returned to the soil in an immediately water-soluble form. Levanidov [1957] for example, has found that birch leaves of the Southern Ural Steppes annually deposit about 2 Kg Mn per acre, some 50% of this being water-soluble. In such organic-rich weathering environments, both soluble and insoluble Mn complexes may form with many of the common organic constituents of soils. Chemical processes involved here include surface adsorption, ion exchange, chelation, and the formation of protective colloids. Organic reactants include amino and fatty acids, polysaccharides, amino sugars, porphyrins, and humic and carboxylic acids. In *figure 3* we have outlined a generalized humic acid reaction scheme first proposed by Ong, Swanson and Bisque [1970]. In part *A* of the reaction Mn^{2+} ions are bound chemically to suitable organic ligands. Physical aging of the resultant complex and the possible adsorption of additional Mn^{2+} ions result in the flocculation and eventual precipitation of Mn humates shown by steps *B* and *C*.

$$\text{ORGANIC ACID} + 2Mn^{2+} \xrightarrow[\text{(chelation)}]{A} \underset{\text{(hydrophilic)}}{\underset{\text{COMPLEX}}{\text{Mn-ORGANIC}}} + Mn^{2+}$$

$$\overset{B}{\rightleftharpoons} \underset{\text{(hydrophobic)}}{\underset{\text{COMPLEX}}{\text{Mn-ORGANIC}}} \xrightarrow{C} \text{Mn-HUMATES} \downarrow$$

Fig. 3. Manganese and humic acid reaction mechanism

K	$Mn^{2+} + L^- = MnL^+$
$10^{3.9}$	DIGALLIC (TANNIC) ACID
$10^{2.16}$	GALLIC ACID
$10^{2.15}$ $10^{3.7}$	FULVIC ACID
$10^{2.55}$	OXALIC ACID
$10^{3.29}$	MALONIC ACID

Fig. 4. Equilibrium constants for organic Mn complexes. $Mn^{2+} + L = MnL^+$

Compiled data on Mn organic complexes of geological interest are summarized in *figure 4*. These complexes form by reaction with the indicated organic acids, all of which occur in natural surface waters. Note that numerical values of all complexing constants are relatively high, showing a strong tendency towards complex formation. The fact that all constants agree to within an order of magnitude probably indicates similar bonding mechanisms by phenol, amide or carboxyl functional groups, and permits generalizing these data to high molecular weight organic compounds. Consequently, we may use these data to approximate soubility of naturally occuring organic Mn complexes in general. The results are shown in *figure 5* which compares concentrations of organic complexes and simple inorganic Mn ions in surface waters. Mn solubilities are plotted for typical conditions at $Eh = 0.5$ V and total carbonate $= 10^{-3}$ m; total soluble organic concentrations of 10^{-2}, 10^{-4}, and 10^{-6} m have been used as estimates of the range expected in natural waters. When organic concentrations approach saturation levels of 10^{-2} to 10^{-4} molal characteristic of humate-rich soils, bogs and swamps, organic complexing may exceed other dissolution mechanisms by as much as several orders of magnitude. Add to this the further possibility of Mn transport by poly-nuclear and multi-ligand complexes or suspended organic colloids, and the pre-eminence of organic agents in weathering Mn from rocks becomes quite apparent.

With this chemical background, let us take a brief look at Mn behavior in certain soil types. Because acidity, total organic content, and rate of organic decay are predominant weathering controls, it is not surprising to find characteristically high Mn mobility in the humate-rich podzols and tundras of the northern temperature and subarctic climatic zones, as shown in *figure 6a*. Bog, lake ,and stream-bed deposits of both Fe and Mn are thus common in these regions and are not, as a rule, found under other climate conditions.

In tropical and subtropical humid climates, chemical weathering is greatly accelerated and soil profiles frequently exceed 100 m in depth. See *figure 6b*. Here however, total organic content is diluted by the actual bulk of soil. In addition, true laterites and bauxites do not support dense vegetation as soil fertility is reduced by effective leaching of essential alkali and alkaline-earth nutrients. As a rule then, Mn mobility is reduced, while Fe and Al commonly remain *in situ*. Residual Mn deposits, though not as common as bauxites and laterites, do form under tropical conditions. In general, the element may be leached or accumulated, thereby acting as a sensitive indicator of subtle variations in Eh, pH or total organic content.

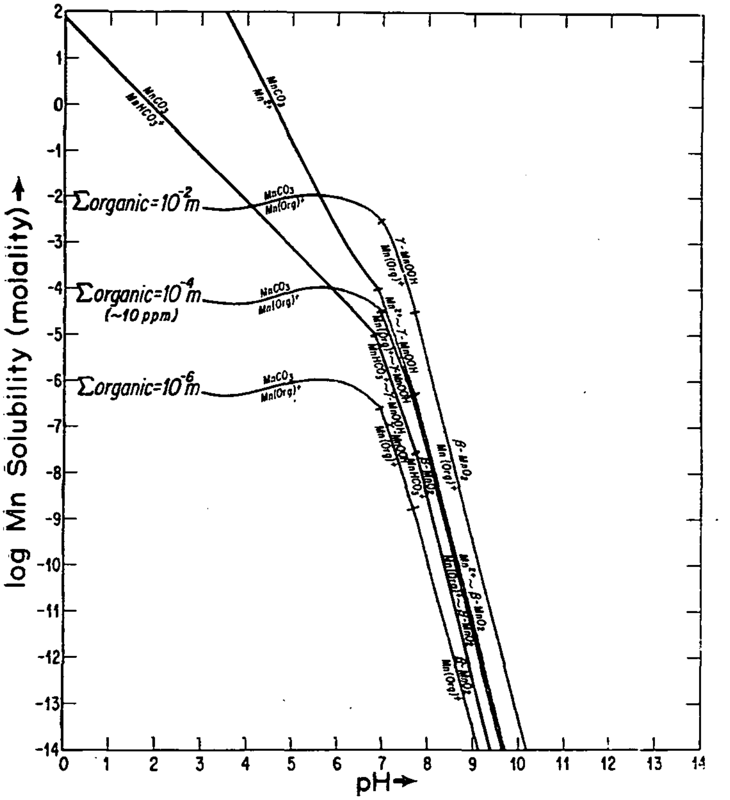

Fig. 5. Typical inorganic and organic complexing of manganese at 25°C. Eh. 0,5 *v*, and total carbonate activity at 10^{-3} molal.

In the arid regions illustrated by *figure 6c*, organic activity is minimized and Mn mobility is limited by simple inorganic mechanisms. Consequently, most Fe and Al remains in place and Mn only migrates locally resulting in surface deposits such as "desert varnish". An estimated 75% of Southern California desert bedrock is coated with a thin layer of amorphous material of this type, compositionally similar to marine Mn nodules [ENGEL and SHARP, 1963].

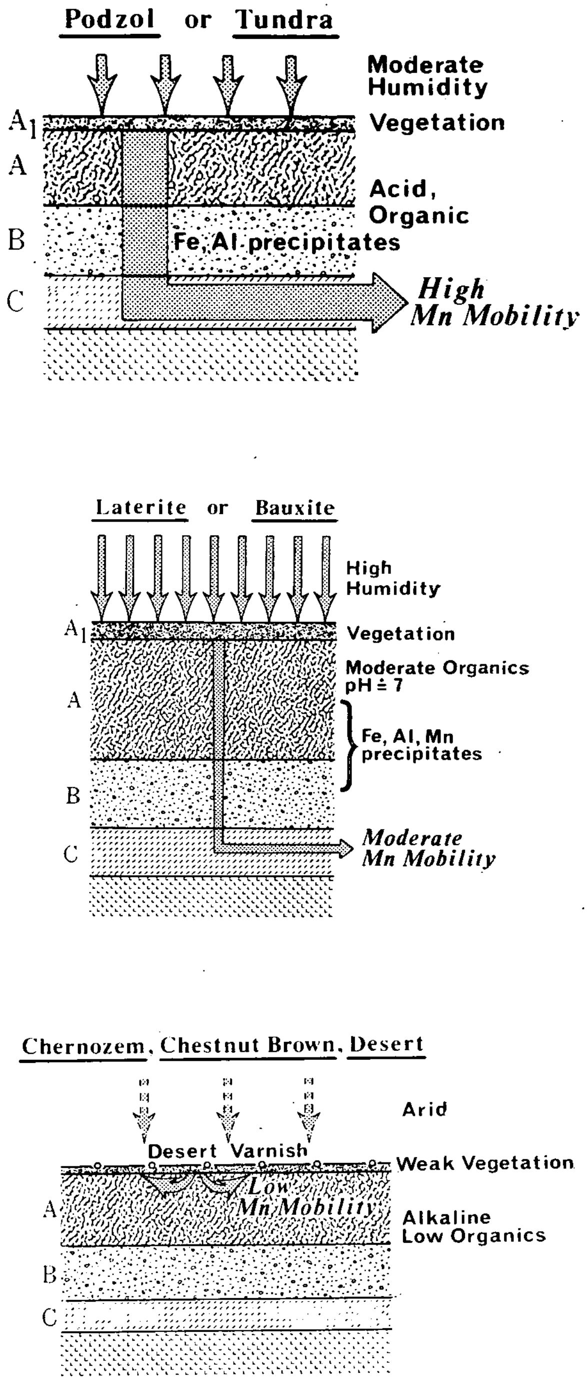

Fig. 6a, b, c. Manganese mobility in generalized soil profiles

Let us now combine these aspects of Mn behavior, considering their effect during transportational and depositional stages of the sedimentary cycle. Despite the fact that natural waters are nearly always undersaturated with respect to inorganic Mn species, there is good reason to believe that important concentrations may be transported as soluble or particulate organics. STRAKHOV [1967] for example, has found that over 50% of the total Mn dissolved in the Dneper R. travels as soluble humic acid compounds or complexes. He also finds that much of the Mn particulate fraction is associated with suspended organics. The situation is similar in the open oceans. Here, approximately 10% of the total Mn in seawater is colloidal or particulate, and only about 78% exists as simple inorganic ions. An additional 12% is complexed organically, or is at least, chemically associated with a sub-colloidal organic fraction [GOLDBERG and ARRHENIUS, 1958, RONA *et al,* 1962, HOOD and SLOWEY, 1964, SLOWEY, 1966, HOOD, 1967, SAXBY 1969]. The observed decrease in organic association on approaching marine environments, indicates that settling basins enroute to terminal marine outlets act as filters, effectively scavenging the larger, predominantly organic species.

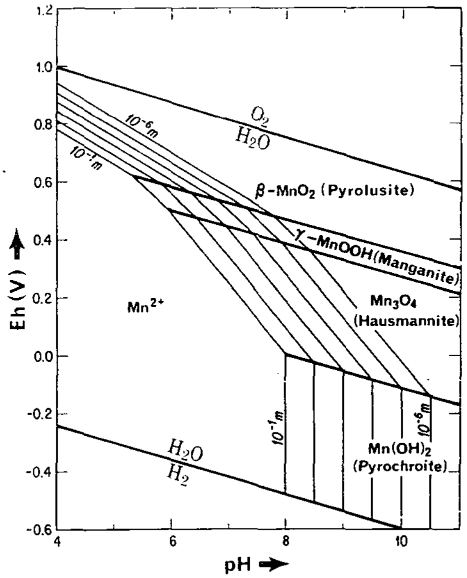

Fig. 7. Eh-pH diagram for system Mn-H_2O at 25°C, 1 atm. pressure. Contours represent Mn^{2+} molality.

Within any single depositional basin, marine or continental, sedimentary accumulation of Mn is primarily controlled by the effects of acidity and oxidation potential whether Mn is transported in inorganic or organic forms. *Figure 7* presents the Eh-pH relationships of common stable Mn oxyhydroxides. Note that solubility of any one phase given by the contours separating that phase from the Mn^{2+} ion field, decreases exponentially with increasing Eh and pH. Mn is thus most mobile in acid, reducing environments. Given two neighboring environments, one acid and/or reducing, the other basic and/or oxidizing, Mn will migrate from the former to the latter.

Precisely such a mechanism is provided during diagenesis on modern ocean floors, where the decay of buried organic detritus creates acid, reducing conditions at depth within the sediment. Refer to reaction *4, figure 2. Figure 8* presents a generalized chemical profile drawn from measurements on sediments in the Atlantic, Arctic, and Pacific Oceans [VAN DER WEIJDEN *et al.,* 1970, LI *et al.,* 1969, LYNN and BONATTI, 1965, BEZRUKOV, 1960, STRAKHOV, 1966, PRESLEY *et al.,* 1967]. Dissolved Mn and CO_2 increase with depth, Mn reaching a maximum while Eh and pH show a correlative decrease. The increased CO_2 at depth represents oxidation products of organic decay. Total Mn, constituting precipitated mineral phases, increases towards the surface. Assuming a roughly constant rate of Mn deposition, this data demonstrates that there must be an upward diagenetic migration of the element. Recent experimental studies support this conclusion [SHANKS, 1972]. Such a diagenetic migration can account for the large-scale surface accumulations of Mn characteristic of virtually all modern ocean basins.

An interesting corollary here is that too high an "active" or oxidizable sedimentary carbon content will effectively dissolve Mn right out of a deposit. Thus the thickness of marine surface oxidizing zones and associated Mn crusts correlates negatively with total oxidizable carbon in carbon-rich environments [PRICE and CALVERT, 1970, STRAKHOV, 1966, LYNN and BONATTI, 1965]. Oxidizing crusts of near-shore carbon-rich sediments are generally much thinner than deep-water equivalents where carbon has been previously oxidized during the long descent, or has been filtered out near river mouths. Similarly, highly organic stagnant conditions are capable of quantitatively leaching Mn from bottom sediments. For example, MANHEIM [1961, 1964, 1965] has shown that Mn migrates laterally away from stagnant reducing deeps of the Baltic Sea, forming oxide accumulations only in peripheral aerated regions. In the Black Sea, organic bottom waters and sediments are so reducing that, despite high dissolved concentrations of Mn, the metal will not accumulate as oxide crusts or concretions. Instead, Mn is carried as dis-

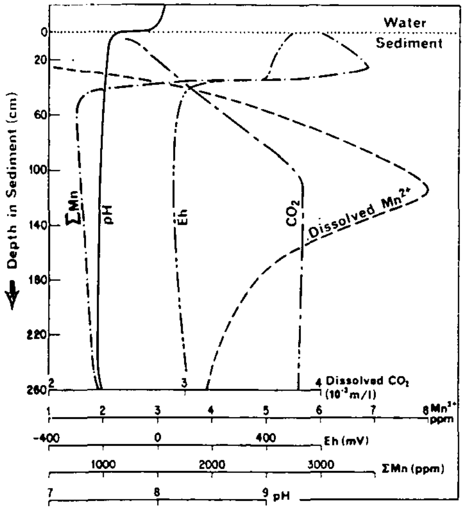

Fig. 8. Generalized geochemical profile of a marine sediment showing dissolved and total Mn variation with depth, Eh, pH and dissolved CO_2.

solved species in all but the uppermost aerated levels of sea water. STRAKHOV [1966] has estimated that 10^8 metric tons of dissolved Mn are borne by the lower, reducing waters of the Black Sea.

Similar diagenetic behavior occurs in manganiferous lake deposits, with the qualification that here the catalytic effects of Mn-specific bacteria vastly accelerates reaction times. PERFIL'EV and co-workers [1965] have found that lacustrine Fe—Mn ores commonly develop the layering shown in *figure 9*. An uppermost Mn-oxide zone is underlain by a similar Fe oxide crust. Im the lowermost reducing zone, total Mn and Fe are impoverished, but pore solutions commonly contain relatively high dissolved concentrations of both metals. Bacterial strains specific to either Fe or Mn occupy each of the three zones, oxidizing or reducing the metals as a necessary metabolic function. The net effect again is an accelerated upward migration of both Fe and Mn during diagenetic stages of sedimentation.

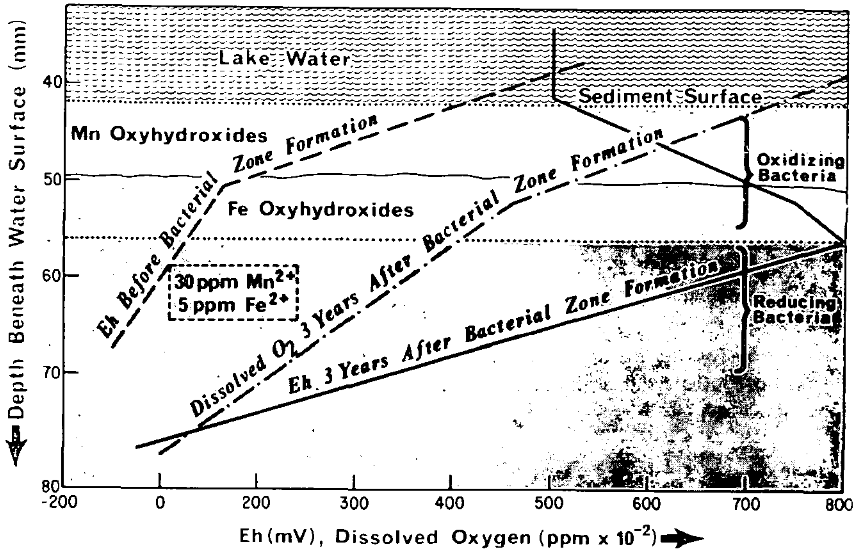

Fig. 9. Generalized geochemical profile of a lacustrine sediment showing Mn distribution, dissolved O_2, and Eh.

Interestingly enough, no comparable Mn-specific bacteria have yet been discovered in the marine environment despite the many similarities between continental and marine deposits. Such strains should be investigated, particularly in view of the current interest in marine Mn nodules. However, several preliminary investigations to date have produced only limited or negative results [GOLDBERG, 1961, GRAHAM, 1959, GRAHAM and COOPER, 1959].

In lacustrine, as in marine environments, a little bit of carbon goes a long way. Should total oxidizable carbon exceed specific limits, Mn mobility increases to the point where it is effectively washed away. STRAKHOV [1966] has proposed a theory relating the origin of Mn and Fe deposits to lateral variations in chemistry during the three major stages of lacustrine evolution. See *figure 10*. In youngest, oligotrophic lakes, waters are fresh, Eh and pH high, and total oxidizable carbon low. Ultrafine particles and suspensions are carried by waves out to quietest and deepest

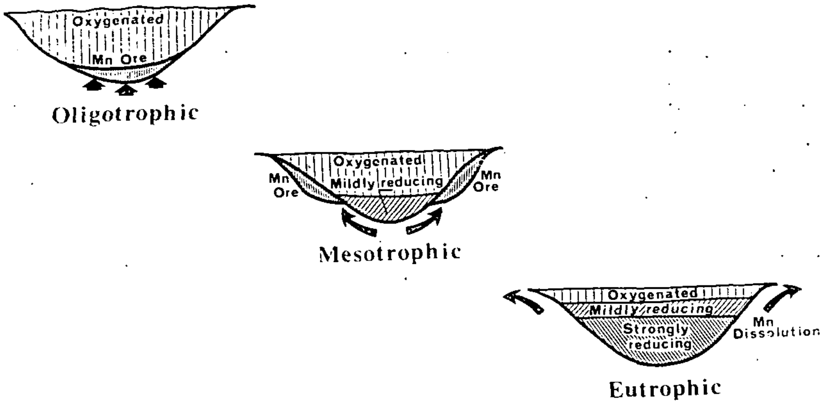

Fig. 10. Mn accumulation versus lacustrine evolution. Arrows indicate direction of diagenetic Mn migration.

reaches, where ferromanganese deposits readily accumulate. With increasing age and eutrophication, both Mn and Fe migrate to the margins of the reduced zone near aerated lake outlets.

In closing, we emphasize again that organic processes exert major and often predominant controls on the geochemical distribution of Mn at every phase of the sedimentary cycle. Inanimate processes include the formation of Mn-organic complexes, often outweighing inorganic ion concentrations by orders of magnitude in many soil and surface-water environments. Life forms such as bacteria contribute directly to the diagenetic behavior of Mn in lake deposits. Primary chemical variables such as Eh and pH are typically controlled by bacterially induced decay reactions of buried organic materials. The influence of organic processes on Mn behavior extends from weathering to depositional environments and must be given due weight in any consideration of Mn geochemistry.

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D. A. CRERAR, R. K. CORMICK
and H. L. BARNES
Ore Deposits Research Section, The Pennsylvania State University, 208 Deike Building, University Park, Pennsylvania 16802,
U. S. A.