A MODEL FOR THE DIFFUSION-CONTROLLED GROWTH OF DEEP-SEA MANGANESE NODULES

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ABSTRACT. The source of metals in manganese nodules and the anomalous growth rates of nodules continue to defy unequivocal explanation after years of study. In response to these debates, we have employed mathematical models to evaluate the potential source roles of interstitial waters and seawater to a manganese nodule. This approach has allowed the calculation of the maximum possible fluxes of metals from these reservoirs and, consequently, an upper limit to nodule accretion rates.

The results of a simple one-dimensional diffusion-reaction model applied to the diagenetic remobilization of manganese in sediments indicate that even under the most optimum conditions porewater cannot supply sufficient manganese for nodule growth, when the oxidizing layer of the sediment column exceeds 40 cm, a conclusion that has been reached by a number of previous studies. As the oxic layer of sediments underlying many manganese nodule fields commonly exceeds this limit, seawater must predominate as a source in these areas.

We have developed a model that accounts for the finite rate of mass transfer across the benthic boundary layer, and we have used the model to assess the capability of seawater to act as a source of metals. The diffusion-controlled flux of manganese through the benthic boundary layer was calculated not only to be completely adequate to account for all the manganese in deep-sea nodules but also to match surprisingly well the observed radiometric rates. This has been interpreted to indicate that mass transfer of Mn is important, and may indeed control, nodule growth. With the exception of perhaps cobalt, the results of this model have suggested further that seawater can supply the other metals (Fe, Cr, Cu, Mo, Ni, U) at rates vastly exceeding their observed accumulation rates in nodules.

INTRODUCTION

Deep-sea manganese nodules begin their growth by a heterogeneous reaction: the precipitation of dissolved manganese, iron, and other metals on the surface of preexisting solid phases. This is attested by the almost invariable presence of foreign nuclei at the center of nodules. Growth continues by reaction of these same metal ions on the surface of the newly formed oxide. The rate of these reactions and so the rate of accumulation will be a function of (1) the available supply of dissolved metals, (2) the rate of mass transfer of this dissolved material to the reacting sites on the growing nodule (diffusive resistance), and (3) the kinetics of adsorption and reaction of the metals to form the nodule (kinetic resistance). Given an adequate supply of metals, the rate of accretion will, however, be determined by the relative speed of the last two steps.

The first problem in understanding nodule genesis lies in identifying the sources of the metals. Although seawater is an obvious source of Mn, Fe, Co, Ni, Cu, et cetera these metals are present in very minute concentrations (<$10^{-6}$ g/cm$^3$), and there has been considerable debate about the mechanisms that could concentrate them by a factor of $>10^8$ to form manganese nodules. Because of this difficulty, many in the scientific community believe that the ambient concentrations must be greatly increased by volcanic activity or that the interstitial waters must be the
source. These hypotheses are not without their own problems (Glasby, 1973, 1974; Broecker, 1974).

The second difficulty arises from the observed growth rates. Application of various radiometric dating techniques such as $^{230}$Th, $^{231}$Pa (Bender, Ku, and Broecker, 1966; Ku and Broecker, 1969; Somayajulu, Heath, and Moore, 1971), $^{238}$U (Ku and Broecker, 1967), $^{10}$Be (Krishnaswami, Somayajulu, and Moore, 1972), $^{26}$Al (Reyes and Yokoyama, 1976), and $\alpha$-fission track (Heye, 1975) to measure the rate of deep-sea manganese nodule accretion has consistently yielded growth rates in the range of 1 to 10 mm/10$^6$ yrs. Dating of nodule nuclei by $^{40}$K (Barnes and Dymond, 1967) and study of magnetic reversals in nodules (Crecelius, Carpenter, and Merrill, 1978) have lent support to these results. These measured rates are fully two to three orders of magnitude lower than the accumulation rates of the associated pelagic sediment, which has caused some workers to question the validity of these methods and to postulate rapid nodule accretion rates (Lalou and Brichet, 1972; Lalou, Brichet, and Ranque, 1973).

In order to help resolve the source problem and the accumulation rate controversy we have modeled mathematically the accretion reactions by accounting for diffusive and kinetic resistances for each of the possible sources and have attempted to predict the limits of nodule accretion rates.

**The Source of Metals**

The overwhelming abundance of nodules at the sediment-seawater interface strongly suggests that accretion occurs at this interface; consequently, the nodules are in a position to receive dissolved metals from both interstitial waters and seawater. Recently Murray and Brewer (1977) have summarized the varied and mounting evidence indicative of a seawater source for the nodule metals. This evidence includes consideration of the rare earth distribution in nodules and seawater (Piper, 1972; Glasby, 1972; Dymond and others, 1973), the variations in isotopes such as $^{87}$Sr/$^{86}$Sr (Bender, 1972), $^{238}$U/$^{234}$U (Ku and Broecker, 1969), lead isotopes (Chow and Patterson, 1962), and also the surface activity of $^{10}$Be (Somayajulu, Heath, and Moore, 1971). Although there is evidence that submarine hydrothermal activity (Scott and others, 1974; Moore and Vogt, 1976) and accumulations of organic-rich reduced sediment (Ku and Glasby, 1972) provide large local fluxes of dissolved Mn into the ocean, the majority of hydrogenous deep-sea nodules cannot be directly associated with these sources. From the above considerations, it seems reasonable to suggest that the low ambient concentrations of metals in seawater must form an important source for the metals in nodules, keeping in mind, of course, that other sources can contribute to these background concentrations.

On the other hand, the possibility of metal fluxes from the underlying sediments to the bottom of nodules cannot be ignored. This is
especially true in regard to "flat" nodules which could only be rolled
with great difficulty.

It is fairly well established that the availability of Mn, Fe, Co, Cu,
and Ni for diffusion is dependent on Eh and pH conditions existing
within the sediment (Lynn and Bonatti, 1965; Bonatti and others, 1971).
Generally the reduced forms of these elements are soluble, whereas their
oxidized states tend to precipitate. Thus if gradients of Eh or pH exist
within sediments, these elements should migrate along the chemical
potential gradients from regions of reducing or acid conditions to regions
of oxic or basic conditions where they should precipitate. Although pH
gradients in oceanic sediments are generally small (Van de Weijden,
Schuiling, and Das, 1970; also see the Initial Reports of the Deep Sea
Drilling Project, 1967-1971), appreciable Eh gradients have frequently
been observed that have the potential of generating concentration gra-
dients of these elements.

If the redox potential determines the mobility of the above elements,
that is to say, elements with higher redox potentials are more readily
reduced to their mobile state, then one would expect the mobility in
sediments to increase in the order,

$$Fe < Cu < Mn < Co < Ni.$$ 

This would imply that Fe precipitates at depth within the sediment
under relatively low Eh conditions and that each of the above elements
would successively precipitate in accordance with the above sequence as
the Eh increased toward the surface. In reality, however, Mn exhibits the
strongest tendency to migrate (Bonatti and others, 1971). This phenom-
enon results from the fact that Co and Ni do not form their own min-
erals but are incorporated in Fe and Mn phases within the sediment.
Therefore, as Fe and Mn precipitate, they can effectively remove Co
and Ni from the interstitial solutions giving Mn the appearance of being
the most mobile element.

This mobilization model has been used successfully to explain the
manganese distribution in a number of lacustrine and oceanic cores
where the oxidizing layer for Mn has been relatively thin (Presley,
Brooks, and Kaplan, 1967; Li, Bischoff, and Mathieu, 1969; Bischoff and
Ku. 1971; Bischoff and Sayles, 1972; Calvert and Price, 1972; Robbins
and Callender, 1975). Deep-sea manganese nodules grow on pelagic sedi-
ments in which the oxic layer (where Mn precipitates) is measurably
thicker than observed in the above studies. Consequently, there has been
considerable debate about whether or not sufficient manganese for nod-
ule growth can be supplied by diffusion through the oxic layer of oceanic
sediments. Bender (1971) has employed a simple diffusion model that
ignored any precipitation reaction to show that the large amounts of
manganese oxide present in the upper part of pelagic sediments cannot
be accounted for by upward migration of manganese.
To assess more accurately the magnitude of the possible flux of dissolved manganese to the sediment-seawater interface (and the bottom of a nodule), we will use a one dimensional diagenetic equation. Berner (1975, 1976) has developed a general equation that described the effects of diffusion, advection, reaction, adsorption, and time variations on a solute concentration in pore-water. Because the adsorption of Mn onto a nodule is essentially irreversible and actually forms part of the heterogeneous manganese (II) oxidation process, the effects of adsorption are, in this case, accounted for in the reaction term. The resulting equation, modified from Berner (1975), is:

$$\frac{\partial \phi C}{\partial t} = \frac{\partial}{\partial \xi} \left( \phi D' \frac{\partial C}{\partial \xi} \right) - \frac{\partial \phi v C}{\partial \xi} + \phi R$$  \hspace{1cm} (1)

where $C =$ concentration of dissolved interstitial manganese ($\text{g/cm}^3$)

$\xi =$ distance from the sediment-seawater interface referenced to the interface ($\xi = 0$) and increasing downward, that is, negative $z$ direction (cm)

$t =$ time (sec)

$\phi =$ porosity (dimensionless)

$v =$ velocity of the pore water relative to the interface (cm/sec)

$R =$ rate of manganese oxidation in the oxic layer ($\text{g/cm}^3 \cdot \text{sec}$)

$D' =$ diffusion coefficient for manganese in the sediment corrected for tortuosity ($\text{cm}^2$/sec).

To simplify the solution of eq (1) we make the following assumptions: (1) that the velocity of the porewater, the diffusion coefficient, and the porosity are independent of depth and time; (2) that the advective term is very small compared to diffusion and reaction terms; (3) that the reaction term can be represented by an expression of the form

$$R = -k_{ox} (C - C_s)$$

where $C_s$ is the saturation concentration ($\text{g/cm}^3$), and $k_{ox}$ is the apparent homogeneous precipitation rate constant (sec$^{-1}$), also assumed independent of depth and time; and finally (4) that steady state diagenesis occurs. As a consequence of these assumptions, eq (1) reduces to,

$$D' \frac{d^2 C}{d\xi^2} - k_{ox} (C - C_s) = 0$$  \hspace{1cm} (2)

The following boundary conditions for eq (2) are introduced,

$C = 0$ at $\xi = 0$

$C = C_L$ at $\xi = L$

where $L$ is the thickness of the oxic layer. The condition that the concentration goes to zero at the interface insures calculation of the greatest possible flux but also requires that the saturation concentration of Mn
with respect to manganese oxide, $C_s$, is essentially equal to zero. This may be a reasonable assumption if one considers the fact that hydrogenous manganese crusts on exposed rock material clearly form from the very low Mn concentration of seawater, suggesting that the saturation concentration of the precipitating phase is even smaller than this ambient concentration of seawater ($C_s < C_w$).

Elderfield (1976) developed an expression similar to eq (2) to describe the transport of manganese through the oxic layer. Unfortunately by following Anikouchine (1967), he arrived at an incorrect solution. The correct solution for the above boundary conditions and assuming $C_s \approx 0$ is given by eq (3),

$$C = \frac{C_L \sinh \left( \frac{k_{ox}}{D'} \right)^{\frac{1}{2}} \xi}{\sinh \left( \frac{k_{ox}}{D'} \right)^{\frac{1}{2}} L}$$

(3)

which was derived earlier in a different form by Michard (1971). The flux at the surface is, therefore, given by,

$$\text{Flux } \xi = 0 = \frac{\phi \left( D' k_{ox} \right)^{\frac{1}{2}} C_L}{\sinh \left( \frac{k_{ox}}{D'} \right)^{\frac{1}{2}} L}$$

(4)

By inserting optimum values of the parameters in eq (4) we can estimate the maximum flux of dissolved manganese at the surface of pelagic sediments. This is illustrated in figure 1 (A and B) where the flux of Mn at the surface is plotted against the thickness of the oxic layer (L) for various values of the oxidation rate constants ($k_{ox}$) and at set values of the diffusion coefficient in the sediment ($\phi D' = D_{sed}, \phi = 0.7$) and dissolved manganese concentration at the base of the oxic layer ($C_L$). The stippled area represents the observed rate of Mn accretion in nodules.

Figure 1A represents an optimum situation for diffusion of Mn out of the sediment where $C_L$ has been assigned a value equal to the highest observed interstitial concentration of manganese (Elderfield, 1976) and where a moderately high value of $D_{sed}$ has been employed. In actuality such high concentrations of dissolved manganese occur well within reducing zones, and values in the vicinity of 1 ppm for $C_L$ are more reasonable (Li, Bischoff, and Mathieu, 1969). Further, many authors (Li Bischoff, and Mathieu, 1969; Michard, 1971, 1975; Robbins and Callander, 1975; Elderfield, 1976) believe that $D_{sed}$ for manganese is more on the order of $4 \times 10^{-7}$ cm$^2$/sec. These less than optimum but perhaps more realistic conditions have been used to generate figure 1B.

The final parameter that must be specified in order to evaluate the possible flux of Mn is the oxidation rate constant ($k_{ox}$). There is still some uncertainty associated with the value of this constant in sediments. Results of experimental studies by Hem (1963, 1964) on sand center around $k_{ox} = 10^{-5}$ to $10^{-6}$ sec$^{-1}$ at pH = 8. These same experiments
Fig. 1A and B. Diagrams illustrating the potential flux of manganese to the surface of pelagic sediments (bottom of a nodule) as a function of the thickness of the oxic layer for given values of the oxidation rate constant ($k_{ox}$), the effective diffusion coefficient of manganese in the sediments ($D_{sed}$) and the dissolved manganese concentration at the base of the oxic layer ($C_L$) as predicted by eq (4). The limiting diagonal line represents diffusion without reaction and the stippled area represents radiometric observed rates of manganese accumulation in nodules.
showed that the rate constant for deposition on previously formed Mn oxide was considerably faster and autocatalytic, $k_{ox} = 10^{-2}$ to $10^{-3}$ sec$^{-1}$. Michard (1969) confirmed these autocatalytic rates and found that the rate constant for oxidation on hydrous iron oxide was in this same range. Later, Michard (1975) indicated that $k_{ox}$ was on the order of $\sim 10^{-5}$ sec$^{-1}$ in argillaceous carbonates. Elderfield (1976) calculated that $k_{ox}$ was slightly greater than $10^{-7}$ sec$^{-1}$ from data on dissolved manganese in Loch Fyne sediments.

In fact, $k_{ox}$ in sediments is probably not a constant, since it is a function of the substrate and Eh conditions. Because the amount of Mn oxide in sediments (probably present as coatings and micronodules) increases toward the interface, the availability of autocatalytic surface also increases. One would thus expect the rate constant to exhibit a similar trend, although the precise functional relationship is unknown. From the previous discussion a lower limit of $k_{ox} = 10^{-7}$ sec$^{-1}$ appears reasonable, and the adoption of this value provides for the calculation of the maximum flux.

Using the above estimate of $k_{ox}$ it can be seen from figure 1A that for this optimum case, the oxide layer (L) cannot exceed $\sim 40$ cm, if a flux equal to the slowest observed manganese nodule growth rate is to be obtained. Under the more moderate conditions defined by figure 1B, this layer must be no more than 20 cm thick if even the minimum Mn flux for nodule growth is to be supplied by diffusion from sediments. Chester and Hughes (1969) and Bender (1971) have noted that the oxic layer exceeds 10 m in thickness over a large extent of the Pacific Ocean, parts of which are over lain by manganese nodule fields. In such areas, the above model would predict that diagenetic remobilization of Mn is not an important source for deep-sea nodule growth. This would probably also be true of highly oxidizing sediments in the Atlantic and Indian Oceans.

On the other hand there are deep-sea areas in the Atlantic (Van de Weijden, Schuiling, and Das, 1970), Arctic (Li, Bischoff, and Das, 1969), and Equatorial Pacific Oceans (Arrhenius, 1952; Hartmann and others, 1973), and also on the continental borderlands (Lynn and Bonatti, 1965), where the oxic layer has been determined to be less than half a meter thick and where nodules have been observed. In these areas diffusion from the sediments may be a source of manganese for nodule accretion, but these areas are of limited extent and deep-sea sediments are sufficiently oxidizing that diagenetic manganese mobilization is only a secondary source. Similar conclusions have been reached by Morganstein (1972), Crerar and Barnes (17974), Glasby (1974), Elderfield (1976), and many others. It is evident, however, that the accuracy of this conclusion is limited by our present understanding of the processes controlling manganese mobilization in the sediments (and the availability of good porewater data).
As we have discussed previously, iron is much less mobile than manganese, and consequently diagenesis of this element should contribute negligibly to nodule accretion. Whether or not interstitial water can supply any of the other metals depends primarily on the efficiency of the removal by precipitated Fe and Mn oxides within the sediment. Cobalt is particularly subject to removal by this mechanism (Murray, Healy, and Fuerstenau, 1968). Calvert and Price (1977) have used this fact to explain the low Fe and Co concentrations on the underside of some nodules (Raab, 1972). However, any attempt to quantify possible Co, Cu, and Ni fluxes from the sediments would at this time be highly speculative.

In summary, seawater is probably the principal source of manganese and the other trace elements accreting on the nodule face exposed to seawater. The seawater concentrations of metals in the vicinity of nodules will be maintained by river runoff, underwater decomposition of biogenic material, advection of material diffused from nearshore sediments, and hydrothermal activity. The concentrations need not be constant geographically nor temporally. We shall now develop a model to test if seawater can indeed be a primary source of manganese and the other elements in nodules.

DIFFUSION AND KINETICALLY-CONTROLLED REGIMES

Let us assume that the rate of accumulation of metals on the surface of a nodule can be described by an expression of the form:

$$\frac{dm}{dt} = k' (C_o - C_s) \quad (5)$$

where $\frac{dm}{dt}$ = rate of accumulation per unit area and per unit time (g/cm²/sec)

$k'$ = apparent heterogeneous kinetic rate constant (cm/sec)

$C_o$ = concentration of metal at the surface of the nodule (g/cm³)

$C_s$ = saturation concentration (g/cm³).

A first order dependence of the rate on reactant concentration is justifiable for manganese in view of past experimental results (Hem, 1963, 1964; Morgan, 1967; Graveland and Heertjes, 1975; Murray and Brewer, 1977). Although this assumption for the other metals has not been justified experimentally, it can easily be shown that the exact order of the surface reaction is of little consequence to the outcome of this model (Birchumshaw and Riddiford, 1952; Frank-Kamenetskii, 1969; Plummer, ms; Konak, 1974; Plummer and Wigley, 1976).

If the source reservoir is large enough, and given sufficient time, a steady state can be attained within the diffusive boundary layer such that the diffusional supply balances kinetic uptake (Frank-Kamenetskii, 1969):
\[
\frac{dm}{dt} = \beta (C_x - C_o) = k' (C_o - C_s)
\]  \hspace{1cm} (6)

where \( \beta = \) mass transfer coefficient = \( \frac{D}{\delta_D} \) (cm/sec)

\( D = \) diffusion coefficient (cm²/sec)

\( \delta_D = \) thickness of the diffusive boundary sublayer, the diffusive length (cm)

\( C_x = \) bulk concentration of reactant (g/cm³)

and where \( C_s < C_o < C_x \) if precipitation is to occur.

Solving eq (6) for \( C_o \) gives,

\[
C_o = \frac{\beta C_x + k'C_s}{k' + \beta}
\]  \hspace{1cm} (7)

Substitution of (7) into (5) gives,

\[
\frac{dm}{dt} = \frac{k'\beta (C_x - C_s)}{k' + \beta} = k^* (C_x - C_s)
\]  \hspace{1cm} (8)

where \( k^* \) is the observed rate constant.

In the case where the kinetic rate constant is much smaller than the mass transfer coefficient (\( k' << \beta \)), then \( k^* = k' \), and the concentration at the surface \( (C_o) \) is approximately that of the bulk solution (that is, \( C_x >> k'C_s/\beta \) in eq 7). The actual kinetics of the surface reaction control the observed rate (kinetic-controlled regime). The observed rate will vary with concentration in a manner described by the rate expression but will in no way depend on the flow rate of the surrounding fluid (Chambers and Boudart, 1966) or any other hydrodynamic property.

Conversely, when diffusive resistance is greater than kinetic resistance (\( \beta << k' \)), the rate is controlled by the transfer of reactant material to the nodule-fluid interface (diffusion-controlled regime). The concentration of reactant at the surface must be very near the saturation concentration \( (C_o \approx C_s) \) if the equality in eq (6) is to be maintained. The reaction will always be first order with respect to the reactant species (even for higher order surface reactions). Further, the observed rate will be strongly dependent on the fluid velocity, because the diffusive length and consequently the mass transfer coefficient are functions of the free stream velocity. Increasing the velocity should increase the rate.

There exists also a transitional regime intermediate to these two limiting cases for which \( k' \) and \( \beta \) are of the same order of magnitude, and the observed kinetics can only be explained by solving eq (8). In this situation, major changes in the fluid velocity can cause transition to either of the two limiting regimes.

From the analysis above it can be concluded that if the rates of mass transfer of metals from seawater are very much greater than the observed (radiometric) rates of accretion, then either nodule growth is kinetically controlled or the radiometric rates are in error. If, however, the calcu-
lated mass transfer of material matches the observed rates, the nodules must be slow growing and diffusion or intermediate controlled, since under no circumstances can kinetics alone induce faster rates (Plummer, ms). Therefore the evaluation of mass transfer characteristics of the nodule-seawater system becomes imperative in any attempt to evaluate the nodule growth rates.

**MASS TRANSFER MODEL.**

Mass transfer from seawater to nodules is regulated by the chemical and physical hydrodynamics of the benthic boundary layer. The benthic boundary layer results from viscous “wall” interactions between moving seawater and the ocean floor. This interaction strongly influences the mode of mass and momentum transport both tangential and normal to the sea floor.

The benthic boundary layer has generally been considered turbulent (Wimbush and Munk, 1970; Wimbush, 1976). Because of the complexity of the turbulent transport processes, prediction of transport rates is made by conceptual models which include many simplifications (Sideman and Pinczewski, 1975). The models can be divided into two categories: (1) those based on eddy or turbulent diffusivity (for example, Deissler, 1954), which are macro-scale investigations of transport phenomena, and (2) those based on surface renewal concepts (penetration theory), which are micro-scale analyses of the same processes, but limited to the viscous transport region (Sideman and Pinczewski, 1975). Most studies of mass transport in the benthic boundary layer use eddy diffusivity models (Morse, 1974; Schink and Guinasso, 1977), and that approach is used here.

The benthic boundary layer can be subdivided into three sublayers on the basis on the mode of momentum and mass transfer: (1) a logarithmic sublayer, (2) a viscous sublayer, and (3) a diffusive sublayer (fig. 2).

![Fig. 2. Schematic representation of the various mass and momentum sublayers within the benthic boundary layer at large values of Sc. Included are typical velocity (line a) and concentration (line b) profiles (not shown to scale).](image)
diffusion-controlled growth of deep-sea manganese nodules

In the logarithmic sublayer the tangential velocities can be described by the logarithmic expression (Wimbush and Munk, 1970):

$$\frac{U_z}{u_*} = \frac{1}{\kappa} \ln \frac{z}{z_o}$$  \hspace{1cm} (9)

where $U_z$ = the velocity in cm/sec at some height within the logarithmic sublayer ($U_z = U_x$ at $z \geq 100$ cm where $U_x$ is the free stream velocity)

$u_*$ = the friction velocity (cm/sec)

$\kappa$ = von Karman’s constant (0.4, dimensionless)

$z$ = height above the bottom (cm)

$z_o$ = the characteristic roughness of the sea floor (cm).

For a smooth bottom the parameter $z_o$ is a function of the hydrodynamics of the sea floor (Sternburg, 1970; Wimbush and Munk, 1970):

$$z_o = \frac{0.11 \nu}{u_*}$$

where $\nu$ is the kinematic viscosity (cm$^2$/sec). Within this logarithmic sublayer, momentum and mass are dominantly transferred toward (or away from) the “wall” by eddies that decrease in intensity as the surface is neared.

Below this sublayer there exists a zone where viscous stresses become appreciable in momentum transport and turbulent stresses increasingly less so. This is commonly referred to as the viscous sublayer. An analysis by Deissler (1954) indicated that viscous effects first become significant at a distance $Z+ \approx 26$ from the “wall,” where the dimensionless distance $Z+$ is defined as

$$Z+ = \frac{z u_*}{\nu}$$  \hspace{1cm} (10)

In some treatments this sublayer is itself divided into a buffer (or transition) zone and a zone of “laminar” flow (Levich, 1962; et cetera) at $Z+ \lesssim 10$.

Unlike momentum transport, mass transfer will continue to be dominated by turbulent stresses up to the point near the “wall” where the eddy and molecular diffusion coefficients become equal. This marks the beginning of the diffusive (concentration) sublayer. The thickness of this sublayer relative to the viscous sublayer is determined by a unique parameter called the Schmidt number which is constant for any given system:

$$Sc = \frac{\nu}{D}$$  \hspace{1cm} (11)

where $Sc$ = Schmidt number (dimensionless)

$\nu$ = kinematic viscosity of the transportation medium (that is, for water: $1.8 \times 10^{-2}$ cm$^2$/sec)

$D$ = (ionic) diffusion coefficient (cm$^2$/sec).
For Schmidt numbers of the order of one (1) the diffusive boundary layer occupies the entire viscous sublayer. In systems with greater Schmidt numbers the thickness of this resistance layer occupies a proportionately smaller part of the viscous sublayer so that at very large values of Sc the diffusive resistance is located in a thin layer adjacent to the ocean floor.

Table 1 lists the ionic diffusion coefficients for some of the elements of interest in nodule growth and their corresponding Schmidt numbers. It is clear that the diffusive boundary layer for these elements will be quite thin in comparison to the thickness of the viscous sublayer.

The surface of the sea floor is not a perfect flat plate but deformed by many irregularities including ripples, biologically produced roughness, manganese nodules, and the intrinsic roughness due to the finite grain size of the sediment. It is generally agreed (Schlichting, 1968; Dawson and Trass, 1972; Hinze, 1975) that if the height of the roughness elements is smaller than the laminar layer of the viscous sublayer (typically < 1 cm) then they will have only a negligible effect on the flow pattern or the mass transfer characteristics of the system. Consequently the presence of grain roughness, minor biological structures, and small nodules can be ignored except perhaps for their effect in increasing the surface area. Similarly if the nodules are very widely spaced the surface can be considered hydrodynamically smooth (Levich, 1962).

Generally, however, the presence of manganese nodules on the sea floor should increase the dynamic roughness of the surface. This influences the velocity profile in the logarithmic sublayer by making $z_o$ in eq (9) independent of the flow conditions and related solely to the height of the roughness elements (k), that is, $z_o = k/30$. Figure 3 shows the effect of nodules on the shear velocity ($u_*$) letting $k = \text{height of the nodules (cm)}$ above the interface (Sternberg, 1970).

Although studies of the effects of surface roughness on boundary layer transfer of a scalar quantity (heat or mass) can be found in the literature, the results of these investigations sometimes disagree either

<table>
<thead>
<tr>
<th>Ion</th>
<th>$D \times 10^{-14}$</th>
<th>$Sc$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$</td>
<td>3.05</td>
<td>5900</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$\sim 5.00^*$</td>
<td>$\sim 3600$</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>3.41</td>
<td>5300</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>3.11</td>
<td>5800</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>3.41</td>
<td>5800</td>
</tr>
<tr>
<td>CrO$_4^{-2}$</td>
<td>5.12</td>
<td>3500</td>
</tr>
<tr>
<td>MoO$_4^{-2}$</td>
<td>$\sim 5.00^*$</td>
<td>$\sim 3600$</td>
</tr>
<tr>
<td>UO$_2^{2+}$</td>
<td>4.26**</td>
<td>4200</td>
</tr>
</tbody>
</table>

* extrapolation

** at 25°C

$\dagger$ cm$^2$/sec
Fig. 3. A plot of the friction velocity ($u_*$) as a function of the free stream velocity ($U_\infty$) for various values of the roughness height $k$ (in cm). Curves are based on eq (9) with the assumption that $z_0 = k/30$.

partly or totally; that is to say, some investigations indicate an increase in the transport rate (coefficient) with increasing roughness (Nunner, 1956; Dipprey and Sabersky, 1963; Dawson and Trass, 1972) while others show the opposite effect (Levich, 1962; Hughmark, 1972, 1975). The complex manner in which the roughness elements interact with the fluid and the differences in geometry of the systems studied are partly responsible for this divergence in results. Another contributing factor is the large variation (100 percent) in the predicted mass transfer rates (coefficients) from smooth surfaces (fig. 3; Boudreau and Guinasso, in preparation).

To obtain a working range of mass transfer coefficients we will first adopt as a lower limit the semi-theoretical correlation proposed by Deissler (1954) for flat plates at high Schmidt numbers ($Sc > 200$),

$$\beta_{(stl)} = \frac{0.11 \, u_*}{Sc^{3/4}}$$

(12)
where $\beta_{(stli)} = \text{mass transfer coefficient for a smooth surface (cm/sec)}$

$u_* = \text{the shear velocity (cm/sec)}$

$Sc = \text{Schmidt number (dimensionless)}$.

The correlation determined experimentally by Dawson and Trass (1972) for rough surfaces at high Schmidt numbers ($Sc > 400$) will be used to set an upper limit on the mass transfer coefficient,

$$\frac{\beta_{(rgh)}}{\beta_{(stli)}} = 1.94 Sc^{0.09} \left( \frac{k u_*}{\nu} \right)^{-0.10}$$  \hspace{1cm} (13)

where $\beta_{(rgh)} = \text{mass transfer coefficient to a rough surface (cm/sec)}$

$k = \text{height of the roughness elements (cm)}$

This correlation predicts the largest increase in the mass transfer rate with the appearance of roughness that we could find in the literature. It is valid in the range,

$$25 < \frac{k u_*}{\nu} < 120$$

![Graph](image-url)

Fig. 4. Plot illustrating the dependence of the manganese mass transfer coefficient ($\beta$) and the thickness of the diffusive subayer ($\delta_D$) on the friction velocity ($u_*$). The smooth surface curve is based on eq (12). The curves for the rough surfaces, where $k$ indicates the roughness height (in cm), are from eq (13). The dashed portions of these curves are extensions of eq (15) below its zone of validity ($ku_*/\nu < 25$) and where the true value of $\beta$ approaches that for the smooth surface.
below which the transfer coefficient approaches that for a smooth surface. Nodule-produced roughness on the sea floor will virtually always fall within or below this range.

Values of the mass transfer coefficient for manganese calculated from eqs (12) and (13) are plotted on figure 4. Similar diagrams could be constructed for iron and the other elements.

DIFFUSION-CONTROLLED GROWTH MODEL

A diffusion-controlled model to determine the maximum possible flux of metals from seawater through the benthic boundary layer to an "average" deep-sea manganese nodule can now be evaluated. In this limiting case, the rate of metal accumulation is solely a function of the rate of mass transfer through the diffusive sublayer ($\beta << k'$); consequently eq (8) becomes,

$$\frac{dm}{dt} = \beta(C_\infty - C_s)$$  \hspace{1cm} (14A)

Because we are interested only in the potential of seawater to supply metals, we will assume that the saturation concentration is negligibly small ($C_\infty >> C_s \approx 0$) in order to maximize the flux calculations. Eq (14A) then simplifies to

$$\frac{dm}{dt} = \beta C_\infty$$  \hspace{1cm} (14B)

The most recent values of the dissolved seawater concentrations of manganese and the other elements ($C_\infty$) are listed in table 2 and will be used in the following calculations. Based on this data a range of 0.02 to 0.4 x 10^{-9} g/cm^3 was selected for manganese.

Next the mass transfer equations of the previous section will be used to calculate a representative value of $\beta$. The first parameter necessary in these formulations is the average height of the nodules above the bottom. The vast majority of nodules are in the 1 to 4 cm diameter size class (J. D. Craig, in Margolis and Burns, 1976). A value of $k = 2$ cm seems appropriate. Secondly, DOMES current meter data (D. Horne, personal commun.) and other baseline data (Amos, Roels, and Paul, 1976) suggest a time average bottom current of approximately $U_\infty = 6$ cm/sec over some Pacific nodule fields. Although this estimate appears high (Earle, 1975; Hayes, 1977), it leads to conservative estimates of the thickness of the diffusive boundary layer. With this value of $U_\infty$ and the roughness size, eq (9) and then (12) and (13) can be solved to yield values of $\beta$ (in the range of 4 to 15 x 10^{-8} cm/sec for manganese).

This information permits solution of eq (14B). The resulting potential fluxes are tabulated in table 3, along with the radiometric accumulation rates. These radiometric rates were calculated by use of eq (15) below,

$$\frac{dm}{dt} \text{ (radiometric)} = \rho \cdot C_m \cdot V / 3.156 \times 10^{13}$$  \hspace{1cm} (15)
where \( \rho \) = nodule density (g/cm\(^3\))
\( C_m \) = metal content in the nodule (g/g)
\( V \) = radiometric growth rate (cm/10\(^6\) yrs).

The numerical factor in the denominator is necessary to convert the radiometric rate (\( V \)) to units of cm/sec. The radiometric accumulation

### Table 2

Seawater trace element concentration data used in calculating potential fluxes to nodules

<table>
<thead>
<tr>
<th>Element</th>
<th>Area</th>
<th>Concentration (ppb)</th>
<th>Source of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>North Atlantic</td>
<td>0.02 – 0.2</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>North Pacific</td>
<td>0.07 – 0.3</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>Northwest Pacific</td>
<td>0.02 – 0.07</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>Northeast Atlantic</td>
<td>&lt;0.04</td>
<td>[2]</td>
</tr>
<tr>
<td>Fe</td>
<td>—</td>
<td>( \sim 2.0 ) (variable)</td>
<td>[3]</td>
</tr>
<tr>
<td>Co</td>
<td>—</td>
<td>0.05</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td>Northeast Atlantic</td>
<td>0.01 – 0.05</td>
<td>[2]</td>
</tr>
<tr>
<td>Cu</td>
<td>Sargasso</td>
<td>0.2 – 0.3</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>North Pacific</td>
<td>0.3 – 0.4</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>Northeast Atlantic</td>
<td>0.3 – 0.6</td>
<td>[2]</td>
</tr>
<tr>
<td>Ni</td>
<td>North Atlantic</td>
<td>0.16 – 0.53</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>North Atlantic</td>
<td>0.15 – 0.4</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>North Pacific</td>
<td>( \sim 0.6 )</td>
<td>[4]</td>
</tr>
<tr>
<td>Cr</td>
<td>—</td>
<td>0.3</td>
<td>[3]</td>
</tr>
<tr>
<td>Mo</td>
<td>Northeast Atlantic</td>
<td>2.1 – 19</td>
<td>[5]</td>
</tr>
<tr>
<td>U</td>
<td>—</td>
<td>3.2</td>
<td>[3]</td>
</tr>
</tbody>
</table>

[1] Bender, Klinkhammer, and Spencer (1977)

### Table 3

Comparison of predicted metal fluxes to nodules with accumulation rates measured by radiometric methods

<table>
<thead>
<tr>
<th>Element</th>
<th>Assumed form</th>
<th>Predicted flux* eq (14B)</th>
<th>Radiometric flux* eq (15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>( \text{Mn}^{2+} )</td>
<td>0.8 – 52.5</td>
<td>0.8 – 48.0</td>
</tr>
<tr>
<td>Fe</td>
<td>( \text{Fe}^{2+} )</td>
<td>120 – 340</td>
<td>0.6 – 32.0</td>
</tr>
<tr>
<td>Co</td>
<td>( \text{Co}^{2+} )</td>
<td>0.5 – 7.0</td>
<td>0.008 – 2.5</td>
</tr>
<tr>
<td>Cu</td>
<td>( \text{Cu}^{2+} )</td>
<td>10.0 – 87.6</td>
<td>0.005 – 2.5</td>
</tr>
<tr>
<td>Ni</td>
<td>( \text{Ni}^{2+} )</td>
<td>6.0 – 71.0</td>
<td>0.2 – 3.2</td>
</tr>
<tr>
<td>Cr</td>
<td>( \text{CrO}_2^{2-} )</td>
<td>18 – 35</td>
<td>( 4 \times 10^{-5} – 8 \times 10^{-3} )</td>
</tr>
<tr>
<td>Mo</td>
<td>( \text{MoO}_4^{2-} )</td>
<td>125 – ( 3 \times 10^3 )</td>
<td>( 8 \times 10^{-4} – 8 \times 10^{-2} )</td>
</tr>
<tr>
<td>U</td>
<td>( \text{UO}_4^{2-} )</td>
<td>170 – 500**</td>
<td>( 2 \times 10^{-4} – 8 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

* \( 10^{-7} \text{g/cm}^2 \cdot \text{sec} \\
** at 25°C
rates are then calculated using $\rho = 2.5$ g/cm$^3$, $V = 0.1 - 2$ cm/10$^6$ yrs, and using the observed range of concentration of manganese (that is, $C_m = 0.1 - 0.3$ g/g) and other metals in manganese nodules (Cronan, 1972; Margolis and Burns, 1976; et cetera).

**DISCUSSION**

*Deep-sea manganese nodules.*—The results displayed in table 3 are very informative. The predicted flux of manganese to a nodule surface, assuming diffusion-controlled transfer from seawater, matches the radiometric rates surprisingly well and proves that the ambient concentration of manganese is sufficient to account for all the manganese in nodules. This agreement is even better illustrated when a larger range of free stream velocities is considered (fig. 5). Experimental evidence from Michard (1969) suggests that the assumption $C_x >> C_s \approx 0$ used in the above model is valid for dissolved Mn$^{2+}$ with respect to manganese oxide even at the low ambient seawater concentrations. Thus the concurrence of predicted and observed rates not only lends strong support to the concept of slow nodule growth but also indicates either a diffusional or transitional-controlled growth regime ($\beta \approx k'$). This conclusion agrees with Hem’s (1977) assertion that in well oxygenated environments the rate of oxide accumulation may be principally governed by the rate at which reactants (that is, Mn$^{2+}$) are brought into the system. If a slower kinetic step is to produce the slow radiometrically determined manganese accretion rates in nodules, then the ambient Mn concentration ($C_x = C_0$) must be no less than 1 ppb, which is considerably higher than the values in table 2.

Because manganese oxides are commonly the dominant constituent of hydrogenous nodules, the accumulation of manganese is an important step in controlling their growth. If, as shown above, boundary layer mass transfer controls Mn incorporation then the rate of nodule growth is a function of the hydrodynamics of the environment. Fast bottom currents would encourage nodule growth, not only by producing low net sedimentation rates through erosion but also by increasing the flux of manganese to the nuclei. The intimate association of nodule development with high current activity as noted by Watkins and Kennett (1971) and Kennett and Watkins (1975) for the Southeast Indian Ocean is thus of a two fold nature.

A number of authors (Kraemer and Schornick, 1974; Heye, 1975; Harada and Nishida, 1976) have produced evidence indicating that the growth rate of a given nodule can change during its accretionary history. This same data also suggests that periods of rapid growth can occur, sometimes as much as 5 to 6 times higher than the upper limit of the usually accepted range. Such changes are within the scope of this model and can be attributed to temporal variations in ambient Mn concentrations or current velocities or both (not to mention variations in available iron). For example, under moderate hydrodynamic conditions the
ambient Mn concentrations may need only rise to 1 to 2 ppb to induce rates of 50 to 60 mm/10^6 yrs in Mn rich nodules if diffusion of Mn controls nodule growth.

In addition to manganese, cobalt also shows appreciable overlap in the ranges of the predicted and radiometric fluxes. Although the agreement is not as good as that observed for manganese, it nevertheless suggests that mass transfer across the benthic boundary layer may play some role in determining the rate of cobalt uptake.

More specifically the nodules in which Co incorporation rates agree with rates predicted by a diffusion-controlled model are almost exclusively those rich in δ-MnO₂ and birnessite, originating from topographic

---

**Fig. 5.** Plot comparing the predicted diffusion-controlled flux of manganese to a nodule surface as a function of free stream velocity to the observed radiometric accretion rates. The lower limit of radiometrically determined incorporation rates is represented on the diagram by the line marked X (1 mm/10^6 yrs, 10 percent Mn). The possible upper limits are given by the lines marked Y (10 mm/10^6 yrs, 30 percent Mn) and Z (20 mm/10^6 yrs, 30 percent Mn).
diffusion-controlled growth of deep-sea manganese nodules

highs (Barnes, 1967; Cronan, 1972, 1975). Conversely, todorokite-rich nodules, typical of deep oceanic basins, have low Co concentrations (Cronan, 1972, 1975), and consequently Co incorporation rates are somewhat less than those expected for diffusion control alone.

The apparent trend toward diffusion-controlled rates for cobalt may, in this case, be purely an artifact of the model resulting from higher concentrations of available Co on topographic highs (Burns, 1965) and may not actually reflect a change in the rate controlling step. Conversely, if this shift is real, then it must result from an increase in the apparent kinetic rate constant of the uptake reaction in the more oxidizing environment of the topographic highs. Regardless of which of the above possibilities is true, the model illustrates that transfer of dissolved cobalt from seawater could account for all the cobalt in deep-sea manganese nodules.

The remaining results of table 3 clearly indicate that seawater can supply Fe, Cr, Cu, Mo, Ni, and U at rates vastly higher than their rates of accumulation observed in deep-sea manganese nodules. In arriving at this conclusion we have used the wrong species for iron and uranium in seawater, because diffusion coefficients for the other species are not available (Brewer, 1975; Byrne and Kester, 1976). Fortunately, because the diffusion coefficients of the actual species present are probably within a factor of two of the values used, the error introduced by these assumptions should not be serious. Evidently manganese nodules are not an efficient sink for the metals in seawater.

The pronounced difference between the calculated diffusion-controlled accumulation rate and the observed accumulation rate of iron in manganese nodules suggests that a slower, kinetically controlled step limits its rate of accretion. Goldberg and Arrhenius (1958), Stumm and Morgan (1970), Burns and Brown (1972), Crerar and Barnes (1974), Glasby (1974), and Burns and Burns (1975) have previously discussed the importance of the precipitation of hydrous ferric oxides for the initial formation and continued growth of manganese nodules. Some of these same authors have proposed that the ferric oxides present in nodules result from the heterogeneous oxidation of Fe$^{2+}$ on exposed surfaces. However, Kester and Byrne (1972), Crerar and Barnes (1974), and Kester, Byrne, and Liang (1975) have shown that the concentration of ferrous iron in seawater is insignificant compared to ferric iron (perhaps as much as 8 orders of magnitude less abundant) and that the most abundant species of iron is Fe(OH)$_3$$^{0}$, > 90 percent of total dissolved Fe (Byrne and Kester, 1976). This means that deposition of iron in nodules must be controlled not by the rapid oxidation of Fe$^{2+}$ but by the precipitation of Fe(OH)$_3$. Because this reaction involves primarily an uncharged species, the incorporation rate of iron should not be significantly enhanced by electrostatic adsorption. Further, although the precipitation of Fe(OH)$_3$ appears to be intimately associated with nodule growth, it certainly is not a necessary step in the continued formation as witnessed
by the low iron content of nodules from the Gulf of Aden (Glasby, Tooms, and Cann, 1971), from the continental borderlands off California (Cronan and Tooms, 1969; Cronan, 1972), and especially in hydrothermal crusts (Scott and others, 1974).

Microprobe measurements and statistical analysis of other geochemical data have established that Cu and Ni are predominately incorporated into the manganese oxide phases of nodules and preferentially in the mineral todorokite (Burns and Brown, 1972; Sorem and Foster, 1972; Cronan, 1975, 1977; Calvert and Price, 1977). The incorporation rate of these two minor elements should therefore be controlled by three factors. First is the amount of Cu and Ni that can be accommodated in the precipitating oxide phases. As indicated above this is primarily a function of mineralogy which in turn appears to be controlled by the redox potential of the environment. Consequently both the amount of todorokite and the Cu and Ni content of manganese nodules increase with depth (Cronan, 1977).

The second factor is the ability of Cu and Ni to occupy the available sites in the oxide structure. This reflects not only the affinity of these ions for the sites but also their absolute concentration in seawater and their concentration relative to other competing ions (Mn²⁺, Co²⁺, Zn²⁺, et cetera). Because the concentration of both Cu and Ni in seawater may be controlled by biological processes (Sclater, Boyle, and Edmond, 1976), bottom waters overlain by high productivity zones may be enriched in these metals. This may partly explain their enrichment in nodules from the Equatorial Pacific (Cronan, 1977) and perhaps the general increase in the Cu–Ni content of nodules going from the Atlantic to the Pacific (Cronan, 1977).

Finally, because Cu and Ni are incorporated principally in manganese oxide phases, their accretion rate must be a function of the rate at which manganese accumulates in the possible oxide phases.

The incorporation scheme for the minor elements Cu and Ni into manganese nodules can be greatly complicated by the post-depositional recrystallization of the manganese oxides within the nodules. If the recrystallizing minerals have access to a supply of Cu and Ni from seawater by diffusion through pores and cracks in the nodule structure or by solid state diffusion or from degrading and dissolving biogenous material included into the nodule, then the newly formed phases may be appreciably enriched over the original oxides (Burns and Burns, 1976; Burns and Burns, 1977).

The elements that are present in anionic forms in seawater (Cr, Mo, and U) are incorporated in nodules at rates strikingly slower than those predicted by the diffusion-controlled model. This probably reflects the aversion of these species for the negatively charged nodule surface.

*Manganese crusts.*—Hydrous manganese oxides precipitate on exposed volcanic rocks and other exposed surfaces in the ocean to form crusts, sometimes reaching tens of centimeters in thickness. Based on the
compositional, mineralogical, structural, and textural similarities, it is probable that many of the same processes operate to form both nodules and crusts. Moreover, radiometric dating has shown that hydrogenous crusts grow at rates nearly identical to those observed for manganese nodules, 0.1 to 2.0 cm/10^6 yrs (Moore, 1973; Kraemer and Schornick, 1974; Scott and others, 1974; Burnett and Morgenstein, 1976).

The above evidence indicates, though not totally unequivocally, that seawater supplies the metals for the formation of manganiferous crusts. We should then be able to apply a diffusion controlled model to arrive at some upper limit to their growth. Because the roughness of crusts is difficult to characterize, we have used the equation developed by Deissler (1954) to describe fluxes across the benthic boundary layer (see fig. 4). Not too surprisingly, the results show good agreement between predicted and observed rates of manganese accumulation and indicate that transfer from seawater is more than sufficient to account for the observed concentrations of the other metals (Fe, Cr, Cu, Ni . . .) in hydrogenous crusts.

Microbial effects.—Some authors have attributed the formation of manganese nodules to microbial activity (Thiel, 1925; Graham, 1959; Monty, 1973), while others have proposed a more modest role, that of catalytically increasing the rate of reaction (Ehrlich, 1963, 1966, 1968, 1972, 1975; Crerar and Barnes, 1974; Greenslate, 1974). The evidence accumulated to date has been ambiguous and so has not clarified the importance of bacteria to nodule genesis. Ehrlich's data (1972) showed that there were 3 to 4 times as many manganese reducing as oxidizing bacteria in and on nodules collected from the East and Central Pacific. Ehrlich believes, however, that this observation cannot be taken to mean that nodules are undergoing active MnO_2 reduction.

In a preceding section we implemented a diffusion-controlled model that indicated that mass transfer resistance across the diffusive sublayer may be important in determining the growth rate of nodules. If this is true then it is logical that the catalytic effect of bacteria cannot increase the depositional rate of manganese beyond this rate. To illustrate this point we have mathematically modelled the influence of a microbial film on a nodule. It will be assumed that the film is thin enough not to offer any transport resistance.

Atkinson and Davies (1974) state that the growth rate of microorganisms can be described algebraically in terms of the available nutrients, including inorganic salts, by Michaelis-Menten or Monod kinetics (Monod, 1949),

\[ R = \frac{k_B \cdot C_r \cdot C_o}{C_1 + C_o} \]  \hspace{1cm} \text{(16)}

where 
\[ R = \text{rate of growth or uptake of Mn (g/cm}^2 \cdot \text{sec)} \]

\[ k_B = \text{apparent biological rate constant (cm/sec)} \]

\[ C_r = \text{critical concentration (g/cm}^3) \]
\[ C_1 = \text{concentration of Mn (or nutrient) at which the rate is half the maximum (g/cm}^3) \]

\[ C_\infty = \text{interfacial concentration (g/cm}^3). \]

At steady state the flux from seawater must be equal to the microbial uptake. Defining a new rate constant \( k'_B = k_B (C_\infty)/(C_1 + C_\infty) \), we get,

\[ \beta (C_\infty - C_\infty) = k'_B C_\infty \]

where \( \beta = \text{mass transfer coefficient (cm/sec)} \)

\[ C_\infty = \text{concentration of Mn in seawater (g/cm}^3) \]

If eq (17) is solved for \( C_\infty \), then by substitution eq (16) becomes,

\[ R = \frac{k'_B \beta C_\infty}{k'_B + \beta} \]

(18)

It is obvious from eq (18) that if the catalytic ability of bacteria is great, then \( k'_B \) becomes very much larger than \( \beta \), eq (18) reduces to eq (14B), and diffusion controls the rate of Mn accretion. If the inorganic precipitation is under transfer control then it follows that the catalytic biological reaction is similarly controlled.

It could be argued that the concentration of manganese available to bacteria is greater than for an inorganic reaction, because organisms can use complexed manganese in addition to freely dissolved \( \text{Mn}^{2+} \). Bender, Klinkhammer, and Spencer (1977) have concluded that the organically complexed manganese is only a small fraction of the dissolved manganese and therefore should not constitute an important new source.

**SUMMARY AND CONCLUSIONS**

Our mathematical approach to the problems of manganese nodule growth, although at times simplistic, has allowed us to gain insight into the mechanisms that control accretion and has permitted us to place limits on the rates at which these processes can operate. By applying a one-dimensional diffusion-reaction equation to describe the diagenetic remobilization of metals in sediments, we have shown, as many have previously proposed, that interstitial waters may not form an important source of manganese in highly oxidizing pelagic sediments.

We have evaluated the capability of seawater to supply the necessary metals by developing a model that accounts for the mass transfer resistance of the benthic boundary layer. The results indicate that not only does seawater have the ability to provide the required manganese flux for nodule accretion but that the predicted diffusion controlled rates correspond remarkably well with the observed radiometric rates. This is not an absolute proof for growth under a diffusion-controlled or intermediate regime, but it does strongly suggest the possibility. Furthermore, our model predicts that iron and the trace elements \( \text{Co, Cr, Cu, Mo, Ni, and U} \) can be furnished by seawater at rates much greater than exhibited in deep-sea manganese nodules, so that a slower kinetically controlled step may regulate their concentrations in nodules.
ACKNOWLEDGMENTS

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