

THE MIGRATION OF MANGANESE IN THE ARCTIC BASIN SEDIMENT*

Yuan-Hui LI

Department of Geological Sciences, Harvard University, Cambridge, Mass. 02138, USA

James BISCHOFF

Department of Geological Sciences, University of Southern California, Los Angeles, California, USA

Guy MATHIEU

Lamont Geological Observatory, Columbia University, Palisades, New York, USA

Received 9 October 1969

A relatively high content of manganese at the top of an arctic sediment core and a smooth exponential increment of manganese concentration in its interstitial water down to one meter have been found. The data strongly support the idea that manganese may be remobilized after burial by local reducing conditions. The thermodynamic calculation shows that the interstitial water is reaching chemical equilibrium with respect to $MnCO_3$ precipitate in the deeper part of the sediment.

1. Introduction

One of the continuing controversies in marine geology concerns the primary origin of manganese oxide in marine sediment, whether ultimately from submarine volcanism or continental weathering. Many proponents of both sides of this controversy have, however, recognized that manganese may be remobilized after burial by local reducing conditions. Murray and Irvine [1] first suggested such post-depositional migration. Brujevicz [2] suggested such a model to explain his observation in the Barents and Kara seas of oxidizing red clays rich in Fe and Mn overlying grey reducing clays. He concluded that organic matter in the sediment reduces Mn and Fe oxides to divalent bicarbonates which diffuse upward to re-oxidize upon contact with the oxygen-rich bottom waters. Mortimer [3] concluded a similar process from his observations in lakes. Hartman [4] found a decrease of Mn oxide with depth in sediment cores from the Baltic Sea. He also detected dissolved Mn in the pore water but discerned no clear diffusion

gradients. Berzukov [5] noted oxidizing top layers rich in Fe and Mn oxide underlain by reducing sediments in the western Pacific, finding that the thickness of oxidizing layers increased the open ocean to the point where piston cores could no longer penetrate to reducing sediments. His Eh measurements strongly support the model of solution and upward migration of manganese.

Manheim [6] has concluded that such a process is central in explaining the relatively rapid accumulation of Mn oxide in shallow marine environments.

Quantitative treatments of the post-depositional remobilization model have been presented by Anikouchine [7] and Lynn and Bonatti [8]. As shown by these authors, such a post-depositional process will result in a diffusion-controlled gradient of dissolved Mn, accompanied by an inverted gradient of total solid Mn oxide in the sediment. This present paper reports on such an observation on a core taken from the Arctic Ocean.

2. Methods

A three meter gravity core of clay sediment at

* Woods Hole Oceanographic Institution Contribution.

water depth of 3800 m was taken at ice station T-3 (latitude 82°N, longitude 156°W, in April 1968). The sediment is characterized by a 20 cm oxidizing zone underlain by a dark gray reducing zone. The core was cut into 10 cm sections for pore water sampling. Pore water was extracted at the station using a passivated stainless steel sediment squeezer [9], and sealed in air-tight polyethylene bottles. The pore water was then analyzed in the laboratory for Mn and some other major elements (atomic absorption spectrometry), pH, total dissolved CO₂ (infrared technique [10, 11]), and Cl⁻ and SO₄²⁻ (high-frequency titration [12]). Two splits were made of the remaining squeezed sediment, one for mineralogical analysis and the other for analysis of solid Mn (dissolution by HF and aqua regia, analysis by atomic absorption). The split for mineralogy was subjected to X-ray analysis.

3. Data

X-ray analysis of the bulk sediment samples indicates a very homogeneous mineralogy for the entire core, with illite accounting for approximately 50% of the sediment followed by about 20% each for chlorite and kaolinite, and 10% mixed layer illite-montmorillonite.

lonite. Trace amounts of quartz and feldspar were noted in each sample, but no carbonate minerals were detected.

The manganese content of the sediment (fig. 1) is characterized by a general, if somewhat erratic, decrease with depth. Manganese in the pore water, however, (fig. 1) displays a remarkably continuous increase with depth, being below the detection limit (0.05 ppm) for the top 20 cm, then increasing steadily to a maximum of 9.2 ppm at 120 cm and dropping to 4 ppm for the remaining depth. Dissolved total inorganic CO₂ (ΣCO_2 , fig. 1) also displays a continuous increase with depth, reaching a maximum at the same point as the dissolved Mn. pH (table 1) appears to follow a similar pattern, reaching 8.5 at about 100 cm and staying constant below that depth. The salinity of pore water is 35.0 ± 0.1 ‰ and SO₄²⁻, 2.7 ± 0.2 mg/cm³ from top to bottom.

4. Discussion

The increase of manganese concentration of pore water with depth, ΔMn^{2+} , can be explained by the oxidation of organic carbon and reduction of solid

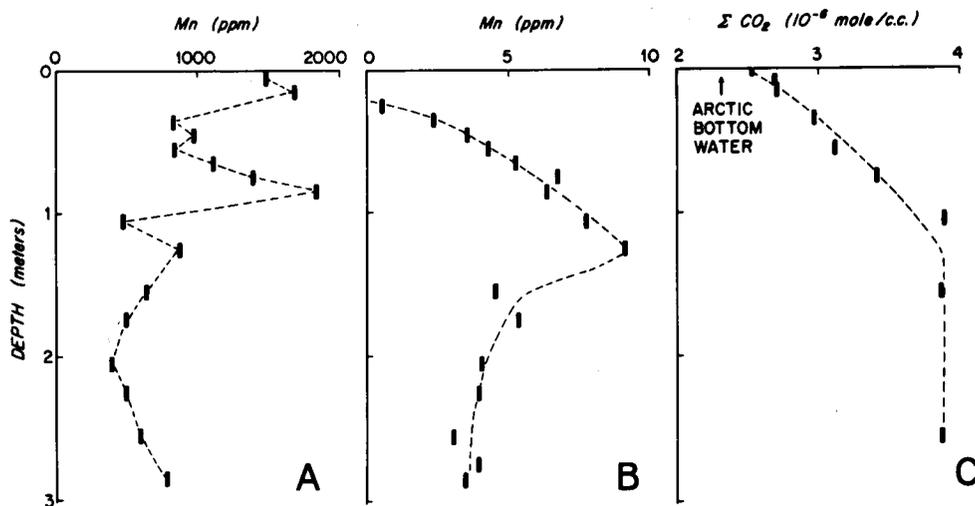


Fig. 1. (A) Content of manganese in the sediment, (B) concentration of manganese in the pore water and (C) total inorganic carbon concentrate in the pore water.

Table 1

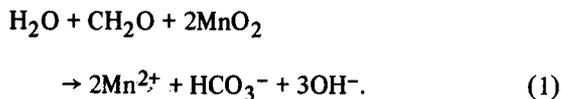
Chemical analysis of arctic sediment and its interstitial water (core position = latitude 82°N, longitude 156°W, water depth = 3800 m and water temperature above the core = 0°C).

Core depth (cm)	Mn (ppm)		ΣCO_2 (10^{-6} mole/cm ³ pore water)	pH <i>in situ</i> * pore water	
	Sediment	Pore water			
		Observed			Calculated
0-5	1500 ± 20	<0.05		2.53 ± 0.01	7.99
5-10	1500	<0.05		2.70	8.07
10-20	1700	<0.05		2.71	8.06
20-30	—	0.6	(7.9)**	(2.85)**	8.12
30-40	830	2.38	7.5	2.98	8.11
40-50	970	3.56		(3.10)	7.95
50-60	830	4.36	7.3	3.12	8.13
60-70	1120	5.34	(5.6)	(3.30)	8.19
70-80	1400	6.84	5.4	3.42	8.19
80-90	1850	6.40	—	—	—
100-110	470	7.80	2.5	3.90	8.52
120-130	890	9.20	(3.3)	(3.89)	8.36
150-160	650	4.60	4.7	3.88	8.22
170-180	500	5.38	(2.5)	—	8.57
200-210	380	4.06	(2.5)	—	8.53
220-230	500	4.02	(2.5)	—	8.51
250-260	610	3.12	2.5	3.87	8.50
270-280	—	4.00	—	—	—
280-288	780	3.62	(2.5)	—	8.53

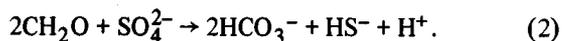
* The pH at *in situ* is obtained by adding 0.19 pH unit to the pH measured at 25°C and one atmosphere pressure (temperature correction: 0.011 pH/°C; pressure correction: -0.232 pH/1000 bars [15]).

** The parentheses are extrapolated values.

manganese dioxide in the core. A generalized hypothetical reaction is:



The increase of total dissolved inorganic carbon of pore water with depth, $\Delta\Sigma\text{CO}_2$, cannot be accounted for by reaction (1) only, since $\Delta\Sigma\text{CO}_2$ is in the order of 10^{-3} M as compared to 10^{-4} M of ΔMn^{2+} . The other possible reaction accounting for $\Delta\Sigma\text{CO}_2$ is the bacterial reduction of sulfate, i.e.



For $\Delta\Sigma\text{CO}_2$ of 10^{-3} M, ΔSO_4^{2-} should be in the order of 0.5×10^{-3} M or 0.05 mg $\text{SO}_4^{2-}/\text{cm}^3$. It is too small a change to be detected by the present study.

Also it is unlikely that a considerable amount of $\Delta\Sigma\text{CO}_2$ is contributed from the solution of CaCO_3 detritus, since the pore water throughout the core is supersaturated with respect to both calcite and aragonite, except the very top at 20 cm is undersaturated with respect to aragonite [13]. The increase of pH with depth is discussed elsewhere [13].

Though the amount of MnCO_3 in the core is too small (< 1%) to be detected by the present X-ray analysis, one can investigate whether the manganese concentration of pore water represents a saturation value with respect to MnCO_3 or not. In other words, is the pore water in chemical equilibrium with MnCO_3 ?

The pertinent reaction is



The solubility product of MnCO_3 , K_{sp} is defined as:

$$\begin{aligned}
 K_{sp} &= a_{Mn^{2+}} \cdot a_{CO_3^{2-}} \\
 &= \gamma_{Mn^{2+}} \cdot [Mn^{2+}] \cdot \gamma_{CO_3^{2-}} \cdot [CO_3^{2-}] \quad (4) \\
 &= \gamma_{Mn^{2+}}^T \cdot [Mn^{2+}]^T \cdot \gamma_{CO_3^{2-}}^T \cdot [CO_3^{2-}]^T
 \end{aligned}$$

where $[M]^T = [M] (l + f)$ = total concentration of M including both free ion and complex ion forms,

$$\gamma_M^T = \gamma_M / (l + f),$$

f = fraction of M in complex ion form. K_{sp} at 25°C and one bar pressure is 5×10^{-11} [14]. From the partial molar volume data of $\bar{V}_{CO_3^{2-}}^\circ = 2.0 \text{ cm}^3/\text{mole}$ [15], and $\bar{V}_{Mn^{2+}}^\circ = -15.5 \text{ cm}^3/\text{mole}$ (obtained from the density data of $MnCl_2$ solution given in International Critical Table, vol. 3) and assuming that the molar volume of $MnCO_3$ precipitate is same as Rhodochrosite i.e. $\bar{V}_{MnCO_3} = 31.1 \text{ cm}^3/\text{mole}$ [16] and the heat capacity change of reaction (4) is negligible, the K_{sp} at *in situ* condition, i.e. at 0°C and 380 bars, is estimated as equal to 2×10^{-10} . As in the case of $CaCO_3$, the solubility of $MnCO_3$ increases with increasing pressure and decreasing temperature.

Using Garrels and Thompson's sea water model [17] and the dissociation constants of manganese ion complexes given by Hem [18], it is estimated that about 80% of Mn^{2+} in pore water is in free ion form and 20% in complex with sulfate, bicarbonate and chloride ions. Therefore, $\gamma_{Mn^{2+}}^T = 0.8 \gamma_{Mn^{2+}}$. One assumes that $\gamma_{Mn^{2+}} \approx \gamma_{Ca^{2+}}$ (since both Mn^{2+} and Ca^{2+} have the same effective diameter in solution [14]), and $\gamma_{Ca^{2+}}$ in sea water equal to 0.28 [17] and quite insensitive to temperature and pressure [11], then $\gamma_{Mn^{2+}}^T \approx 0.22$. $\gamma_{CO_3^{2-}}^T$ at 0°C and 380 bars is equal to 0.039 [11]. $[CO_3^{2-}]^T$ *in situ* can be calculated from ΣCO_2 and pH data. (The detail calculation procedure of $[CO_3^{2-}]^T$ in sea water at *in situ* condition is given elsewhere [19].) Therefore, the concentration of total Mn^{2+} of pore water in equilibration with $MnCO_3$ (ppt) at *in situ* condition can be calculated from eq. (4). The calculated results are given in column 4 of table 1. Comparing columns 3 and 4 of table 1, it is clear that the pore water from the top down to around 60 cm is undersaturated with respect to $MnCO_3$ and between 60 cm to 130 cm, ranging from saturation to supersaturation. Though

the pore water below 130 cm seems supersaturated, in fact it may represent a saturation or equilibrium condition, if one takes into account the uncertainty involved in the theoretical calculation. Especially in the present calculation the effect of the possible formation of strong complex ion between Mn^{2+} and organic acid [20] is neglected.

The average concentration gradient of Mn^{2+} of pore water, $\frac{dC}{dX}$, in the core above one meter is about

$$\frac{9 \times 10^{-6} \text{ g Mn/cm}^3}{100 \text{ cm}} = 9 \times 10^{-8} \text{ g Mn/cm}^3/\text{cm}.$$

(By chance, this value coincides with Lynn and Bonatti's estimation [8].) If the diffusion coefficient of Mn^{2+} , $D_{Mn^{2+}}$ is known, then simply from Fick's law i.e.

$$\frac{-dC}{dX} \cdot D_{Mn^{2+}} = F_{Mn^{2+}}, \quad (5)$$

the Mn^{2+} flux, $F_{Mn^{2+}}$, from depth to the water-sediment boundary can be estimated. (Since the diffusion of ions in sediment is much faster than the accumulation rate of sediment, the accumulation of sediment would not effect the direct application of Fick's first law. Anikouchine [7] and Lynn and Bonatti [8] also have quantitatively shown that at steady state, the transportation of Mn^{2+} by relative upward flow of interstitial water due to the compactness of sediment is negligible.)

Lynn and Bonatti [8] assumed that $D_{Mn^{2+}}$ in sediment is the same order of magnitude for that of several electrolytes in sea water. Accordingly they adopted $D_{Mn^{2+}} = 2 \times 10^{-5} \text{ cm}^2/\text{sec}$. In so doing, they got one to two orders of Mn, more than enough to account for Mn at the top of sediment. Their assumption is not justified because the diffusion coefficient of ion in a water-clay mixture system is drastically affected by the water content of the mixture and by adsorption of ions on the diffuse layer of clay minerals. For example, from the data given by von Schaik et al. [21], $D_{Ca^{2+}}$ in aqueous solution is about $8 \times 10^{-6} \text{ cm}^2/\text{sec}$, and in 74% water-calcium clay system, it is reduced to $4 \times 10^{-7} \text{ cm}^2/\text{sec}$. If it is assumed that $D_{Mn^{2+}} \approx D_{Ca^{2+}} = 4 \times 10^{-7} \text{ cm}^2/\text{sec}$, then, $F_{Mn^{2+}} \approx 10^{-3} \text{ g Mn/cm}^2 \cdot 10^3 \text{ yr}$ as comparing to the accumulation rate of excess Mn at the top of core, i.e. about $10^{-4} \text{ g Mn/cm}^2 \cdot 10^3 \text{ yr}$. (The latter is calculated from the sedimentation rate of the core,

i.e. 10^{-1} g/cm² 10³ yr [22] and the excess Mn content at the top of core i.e. 1000 ppm. The excess Mn is defined as the concentration of Mn in the sediment minus the concentration of Mn in the detrital silicate fraction of sediment. In this core, the concentration of detrital Mn is assumed to be 500 ppm.) Therefore, the manganese flux by diffusion is still more than enough to account for the manganese at the top of the core.

On the other hand, Duursma determined the diffusion coefficient of many ions in sediments by an indirect method [23]. He gives $D_{Ca^{2+}} = 0.9 \times 10^{-8} \sim 1.5 \times 10^{-8}$ cm/sec [23] and $D_{Mn^{2+}} = 10^{-9} \sim 10^{-10}$ cm²/sec (personal communication) in various sediments. If $D_{Mn^{2+}}$ given by Duursma is in right order, then the transportation of manganese by diffusion in deep sea sediments is too small to be important. Unfortunately the validity of Duursma's indirect method has never been checked by some other independent methods. A direct measurement of $D_{Mn^{2+}}$ is still in demand.

In summary, we conclude that the observed pattern in fig. 1 can only be explained by reduction of manganese oxide after burial, diffusion toward the surface, and reprecipitation of the oxidizing surface. This maintains an enrichment of manganese in surface sediments.

Now, if such a process can be shown to operate universally throughout the oceans, and that the large areas of red clays are underlain by reducing sediments at depth (Berzukov [5]), then estimates of Mn in marine sediments based on surface samples may be greatly exaggerated, as pointed out by Bonatti and Nayudu [24]. This could explain the calculated "excesses" of manganese in marine sediments indicated by geochemical balance calculations (see, for example, Horn and Adams [25] and Boström [26]) and tend to support the concept that continental weathering is sufficient to account for the manganese in marine sediments.

Acknowledgements

We wish to thank Drs. W.S.Broecker, E.D.Goldberg, T.L.Ku, F.Manheim and R.Siever for their suggestions and criticisms in reviewing the manuscript. Also, we

are indebted to Drs. J.Hunt and D.Spencer for the constant encouragement and help.

The research was supported by the Office of Naval Research contract Nonr 266 (82), and NSF Grant Ga-4239 and Ga-1419.

References

- [1] J.Murray and R.Irvine, On the manganese oxides and manganese nodules in marine deposits, *Trans. Roy. Soc. Edinb.* 37 (1895) 721.
- [2] S.W.Bruevich, Oxidation reduction potential and the pH of sediments of the Barentz and Kara seas, *Dokl. Akad. Nauk. SSSR* 19(1938) 637.
- [3] C.Mortimer, The exchange of dissolved substances between mud and water in lakes, *J. Ecol.* 30 (1942) 147.
- [4] M.Hartman, *Sur Geochemie con Mangan und Eisen in der Ostsee*, *Meyniana* 14 (1964) 3.
- [5] P.L.Berzukov, Sedimentation in the Northwestern part of the Pacific Ocean. Reports 21st Internatl. Geological Congress, Copenhagen, pt. 10 (1960) 39.
- [6] F.T.Manheim, Manganese-iron accumulations in the shallow marine environment. *Symp. on Marine Geochemistry Occ. publ. No. 3* (Narragansett Marine Lab. Univ., Rhode Island, 1965) p. 217.
- [7] W.A.Anikouchine, Dissolved chemical substances in compacting marine sediments, *J. Geophys. Res.* 72 (1967) 505.
- [8] D.C.Lynn and E.Bonatti, Mobility of manganese in diagenesis of deep sea sediments, *Marine Geol.* 3 (1965) 457.
- [9] F.T.Manheim, A hydraulic squeezer for obtaining interstitial water from consolidated and unconsolidated sediments, *U.S. Geol. Survey Prof. Paper* 550-C (1966) C256.
- [10] W.S.Broecker and T.Takahashi, Calcium carbonate precipitation on the Bahama Banks, *J. Geophys. Res.* 71 (1966) 1575.
- [11] Y.H.Li, The degree of saturation of CaCO₃ in the oceans. Ph. D. Thesis, Columbia University (1967).
- [12] G.S.Bien, High-frequency titration of micro quantities of chloride and sulfate, *Anal. Chem.* 5 (1954) 909.
- [13] J.Bischoff, Y.H.Li and G.Mathieu, The diagenetic change of pore water in arctic basin sediment, in preparation.
- [14] R.M.Garrels and C.L.Christ, Solutions, minerals and equilibria (Harper and Row, 1965).
- [15] A.Disteche and S.Disteche, The effect of pressure on the dissociation of carbonic acid from measurements with buffered glass electrode cells, *J. Electrochem. Soc.* 114 (1967) 330.

- [16] R.A.Robie and D.R.Waldbaum, Thermodynamic properties of minerals and related substances at 25°C and one atmosphere pressure and at higher temperature, Geol. Surv. Bull. 1259 (1968).
- [17] R.M.Garrels and M.E.Thompson, A chemical model for sea water at 25°C and one atmospheric total pressure, Am. J. Sci. 260 (1962) 57.
- [18] J.D.Hem, Chemical equilibria and rates of manganese oxidation, Geol. Survey water-supply paper 1667-A (1963).
- [19] Y.H.Li, W.S.Broecker and T.Takahashi, The degree of saturation of CaCO₃ in the oceans, J. Geophys. Res., in press.
- [20] C.P.C.Poon and F.J.DeLuise, Manganese cycle in impoundment water, Water Res. Bull. 3 (1967) 26.
- [21] J.C.Von Schaik, W.D.Kemper and S.R.Olsen, Contribution of adsorbed cations to diffusion in clay-water system, Soil Sci. Soc. Am. Proc. 30 (1966) 17.
- [22] T.L.Ku and W.S.Broecker, Rates of sedimentation in the Arctic Ocean, in: Progress in Oceanography, vol. 4 (Pergamon Press, 1967) p. 95.
- [23] E.K.Duursma, Disposal of radioactive wastes in seas, oceans and surface waters (International Atomic Energy Agency, Vienna, 1966).
- [24] E.Bonatti and V.R.Nayudu, The origin of manganese nodules on the ocean floor, Am. J. Sci. 263 (1965) 17.
- [25] M.K.Horn and J.A.S.Adams, Computer derived geochemical balances and element abundance, Geochim. Cosmochim. Acta 30 (1966) 279.
- [26] K.Boström, The problem of excess manganese in pelagic sediments, Res. Geochem., ed. Abelson, vol. 2 (1967).