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Neoformation of hydrotalcite due to industrial inputs in marine sediments

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Abstract

Authigenic formation of hydrotalcite [$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$] and calcite in a sediment core from Krause Lagoon, St. Croix, Virgin Islands, is due to industrial inputs of waters rich in $NaHCO_3$ and NaOH from a nearby bauxite factory into the sediment-pore water system. This occurrence of hydrotalcite is the first reported for the mineral in marine sediments. Calcite and hydrotalcite are found in the sediment at a depth corresponding to maxima in the carbonate alkalinity and pH profiles, and minima in the Ca and Mg concentration profiles of the interstitial waters. These inflections are due, respectively, to pollutional inputs of $NaHCO_3^-$ and NaOH-enriched waters into the sediment and to precipitation of the minerals. This study represents one of the first quantitatively-documented cases of chemical modification of pore-water profiles of major constituents from man's activities. Furthermore, the results emphasize the fact that instantaneous modification of interstitial water chemistry can result in long-term changes in pore-water concentration profiles.

Introduction

During the past decade chemical inputs into natural water systems from anthropogenic activities have been extensively studied. However, little quantitative documentation of modifications of pore-water profiles of major dissolved constituents induced by man's activities is available. This paper is concerned with pollutional inputs into a sediment/pore-water system, and their effects on the vertical distribution of minerals and major dissolved constituents.

During the summer of 1973, a 150-cm core was obtained from the mangrove tidal flat in Krause Lagoon, St. Croix, Virgin Islands. Interstitial waters were extracted from the sediment core by pressure squeezing or centrifugation immediately after collection. The waters at ambient temperature were analyzed for pH, titration alkalinity, dissolved sulfide, and Ca within 24 hours after collection. Na, K, Mg, SO_4, and Cl in water samples preserved in polyethylene containers were determined about two months after obtaining the core. Only those pore-water data relevant to this study are discussed here. Mineralogy of the sediments was determined by X-ray diffractometry. Detailed methods and analytical techniques are summarized in Thorstenson and Mackenzie (1974).

Analytical results

X-ray diffraction shows that the sediments are principally an admixture of calcite, aragonite, and magnesian calcite (Fig. 1). However, at a depth of 17 to 40 cm in the core, hydrotalcite [$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$] was observed. This is the first reported occurrence of hydrotalcite in marine sediments. The depth zone in which hydrotalcite is found corresponds to a maximum in carbonate alkalinity, pH, and Na concentration of the pore waters (Fig. 2). This zone is also coincident with a minimum in the Ca and Mg concentrations of the pore waters (Fig. 3). In the hydrotalcite zone, the sediment is composed of 70 weight percent calcite, whereas in the rest of the core, aragonite and magnesian calcite (Fig. 1) are the principal minerals.

The ratio of Cl/Na in the pore waters compared to that of sea water (Table 1) shows that at a depth of 15–80 cm there is an excess of Na. Simple evaporation would produce waters with Cl/Na ratios similar to that found in sea water. This excess Na in the pore waters is due to the fact that a nearby bauxite factory sporadically released waters rich in $NaHCO_3$ and NaOH into Krause Lagoon during the years 1966–72 (Thomas W. Darrow, written communication). These waters mixed with the lagoon waters and were

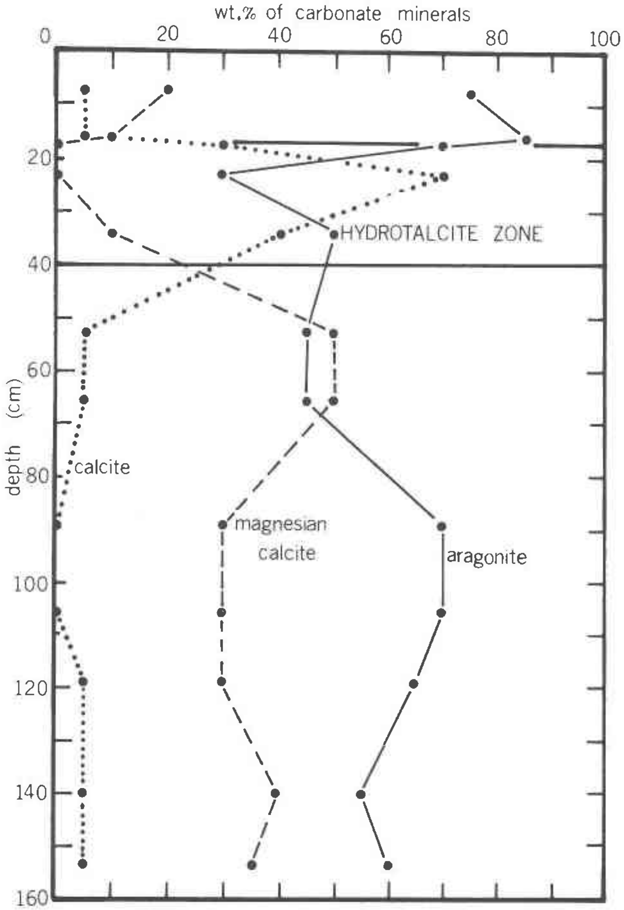

Fig. 1. Variation of carbonate minerals with depth in Krause Lagoon sediments. Carbonate minerals content in each core segment is normalized to 100 weight percent. Depths are mean values of the core sections.

incorporated in the sediment during deposition. Their input accounts not only for the excess Na but also the high carbonate alkalinity and pH observed in the pore waters at this depth.

Table 1 shows, however, that in about the upper 17 cm of the core the Cl/Na ratio is that of sea water. The Na and Mg (Fig. 3b) concentrations, which at these depths are higher than those of sea water, are a result of the evaporation of water from the tidal flats. On the other hand, Ca concentrations at these depths are less than that of sea water (Fig. 3a). This deficiency of Ca is a result of the precipitation of aragonite during evaporation of sea water. Thin crusts of aragonite were observed at the surface of the sediment, and aragonite-cemented layers of sediment were found at depths less than about 17 cm in the core. The upper 17 cm of sediment were deposited after the pollutional inputs from the bauxite factory ceased (*i.e.*, 1972). Furthermore, no bioturbation structures or organisms were observed in this portion of the core. The strong concentration gradients of Mg, Ca, Na, pH and carbonate alkalinity (Figs. 2 and 3) also suggest that the sediment was not significantly affected by bioturbation, which would tend to eliminate any existing concentration gradients.

We will show that the increased carbonate alkalinity and pH, caused by the pollutional inputs, induced precipitation of calcite and hydrotalcite. Furthermore, this precipitation caused the observed minima in the Ca and Mg concentrations. Concentration gradients developed between the hydrotalcite-zone waters and the rest of the sediment pore waters owing to precipitation of these two minerals; thus the resultant diffusion led to more Ca and Mg entering the hydrotalcite zone and to the diffusion-controlled profiles of Ca and Mg that we observe today.

Discussion

The calcite and hydrotalcite observed in the hydrotalcite zone are not of detrital origin. If the calcite were of detrital origin it would have to have been derived from the operation of the bauxite factory, because the natural detrital carbonates are predominantly bioclastic aragonite and magnesian calcite, as seen in the rest of the core (Fig. 1). However, most calcite present in the bauxite ore would be dissolved during the ore treatment before being released into the lagoon waters. Therefore, very little detrital calcite could have been derived from the bauxite factory. The hydrotalcite observed in the hydrotalcite zone can not be of detrital origin because there is no hydrotalcite found either on the island of St. Croix (Whetten 1966) or in the bauxite processed by the factory. Therefore, the presence of these minerals within the hydrotalcite zone must be due to neoformation within the sediments or within the lagoon waters.

We calculated the mass of calcite and hydrotalcite that could be formed by diffusion of Ca and Mg into the hydrotalcite zone, with subsequent precipitation owing to the high carbonate alkalinity and pH of this zone. The mass that diffused into the hydrotalcite zone can be estimated from a diagenetic equation (Berner, 1971), expressing the concentration of Ca or Mg in the sediment pore waters as a function of depth for the sediment zones above and below the hydrotalcite zone. To obtain a diagenetic equation, we assumed that the system is at steady state and advection is neglibible. Thus the basic diagenetic equation becomes (Lerman, 1975, 1976)

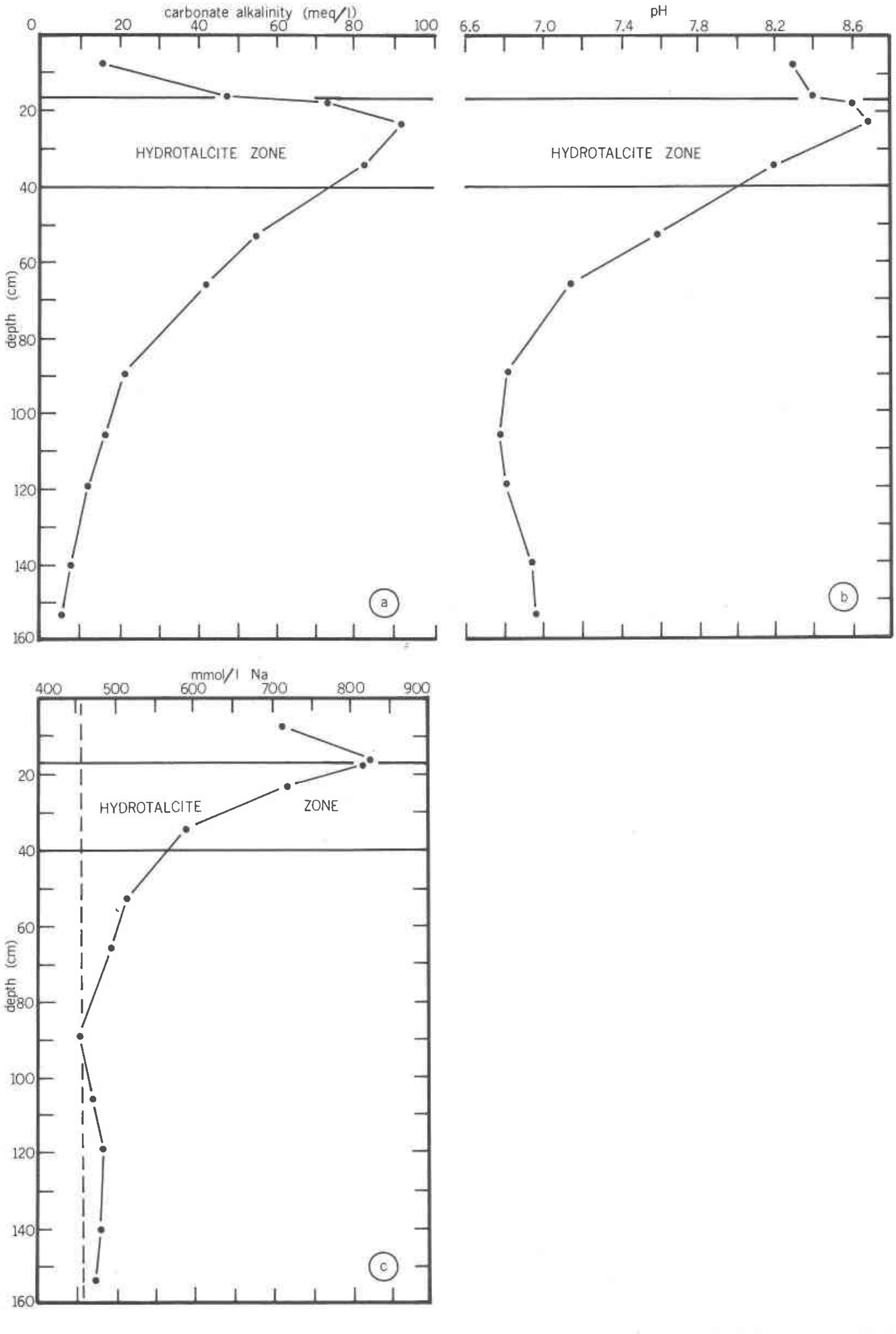

Fig. 2. (a) Variation of carbonate alkalinity with depth in the Krause Lagoon pore waters. (b) Variation of pH with depth in the Krause Lagoon pore waters. (c) Variation of Na with depth in Krause Lagoon pore waters; ---- average sea water concentration (after Turekian, 1969).

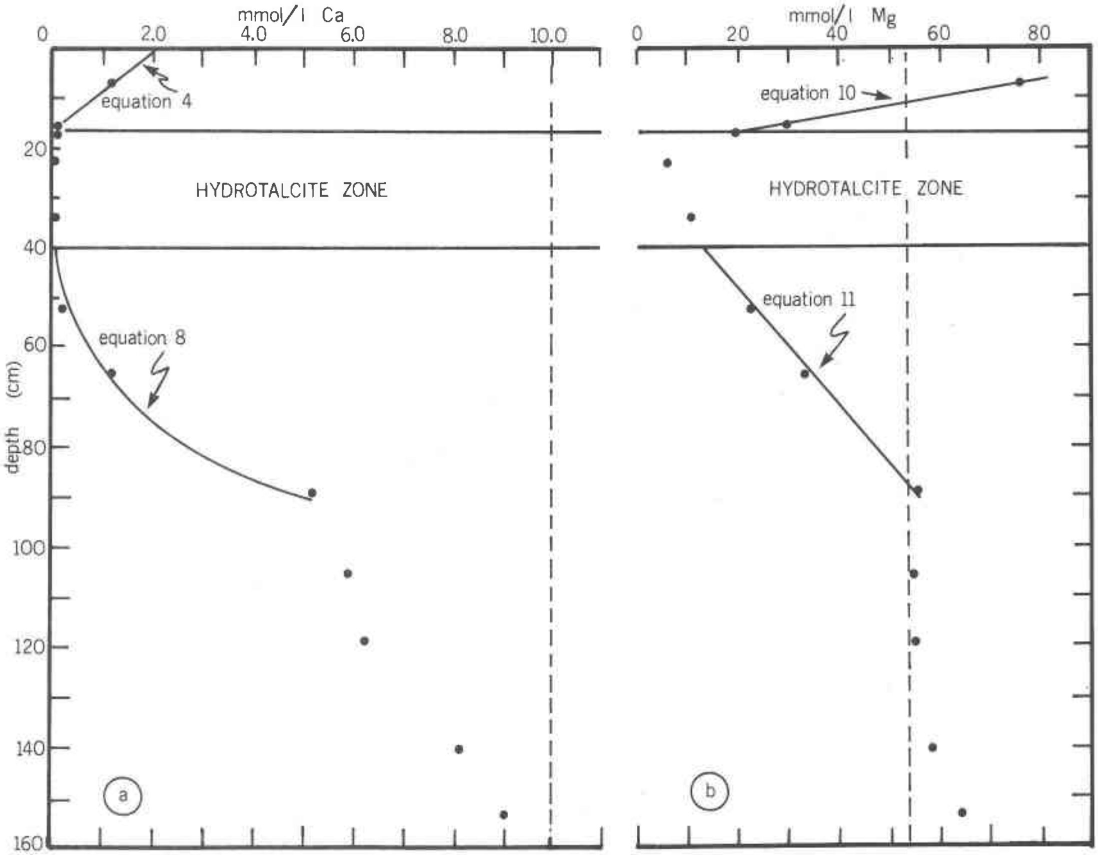

Fig. 3. (a) Variation of Ca with depth in Krause Lagoon pore water. Dots represent observed data points; solid curves represent calculated diffusion profile; ---- average sea water concentration (after Turekian, 1969). (b) Variation of Mg with depth in Krause Lagoon pore waters, legend as in Fig. 3a.

$$D(d^2C)/(dZ^2) - kC + J = 0, \qquad (1)$$

where k = net removal or precipitation rate constant
J = net production or dissolution rate,
D = diffusion coefficient = 3.15×10^2 cm^2 yr^{-1} (Berner, 1971),
C = concentration in mol cm^{-3},
Z = depth in cm.

Then by applying Fick's law (Equation 2), we can obtain the flux of Ca or Mg into the hydrotalcite zone from the sediment above and below.

$$F = -\phi D(dC)/(dZ), \qquad (2)$$

where F = flux in mol cm^{-2} yr^{-1},
ϕ = porosity of the sediment = 0.7.

Calcium transport and calcite precipitation

The concentration profile of Ca in the sediment above the hydrotalcite zone (0–17 cm depth) can be reproduced by a diagenetic equation which assumes that only diffusion operates in the system. This zone is supersaturated with respect to calcite and aragonite, and authigenic aragonite was observed in thin crusts and layers within this depth zone. Only two data points are from this zone, consequently it is difficult to include the reaction terms of Equation 1 in modeling of this portion of the core. Conclusions drawn using the simple diffusion model for this zone, however, would not be significantly modified by a better knowledge of the dissolved Ca distribution. Equation 1 reduces to

$$(d^2C)/(dZ^2) = 0. \qquad (3)$$

By integrating (3) and substituting in the appropriate data, we obtain

$$C = -0.129 \times 10^{-6}Z + 2.17 \times 10^{-6}, \qquad (4)$$

where $Z = 0$ at the sediment-water interface and increases in value with depth. From Equations 2 and

4 the flux of Ca into the hydrotalcite zone is calculated as 2.84×10^{-5} mol cm^{-2} yr^{-1}.

The concentration profile of Ca in the zone below the hydrotalcite zone, 40–90 cm depth, can be modeled by use of equation 1 in which $J = 0$. The pore waters are in equilibrium with respect to calcite throughout this portion of the sediment. In Figure 3a, the convexity to the left of the plotted data points shows that there is a net removal of Ca caused by calcite precipitation (Lerman, 1976). If calcite is assumed to be the only phase controlling Ca concentration in the pore waters, then there is no net production term and J is equal to zero. Thus equation 1 becomes

$$D(d^2C)/(dZ^2) - kC = 0. \qquad (5)$$

In this case, $Z = 0$ is taken as the lower boundary of the hydrotalcite zone (40cm depth) and increases downward. Two boundary conditions are needed to obtain an explicit solution to Equation 5. These conditions are obtained from the measured Ca concentrations at the boundaries of the zone:

$$C = C_0 \quad \text{at} \quad Z = 0 \qquad (6)$$

$$C = C_h \quad \text{at} \quad Z = h. \qquad (7)$$

The solution of Equations 5–7 is

$$C = \frac{C_0 \sinh[(h - z)(k/D)^{1/2}] + C_h \sinh[(k/D)^{1/2} Z]}{\sinh[(k/D)^{1/2} h]} \qquad (8)$$

where $C_0 = 5.0 \times 10^{-8}$ mol cm^{-3},

$C_h = 5.2 \times 10^{-6}$ mol cm^{-3}, and

h = thickness of zone = 50 cm.

A value of k is found which gives the best fit to the observed data. The calculated curve shown in Figure 4a is for $k = 1.15$ yr^{-1}. This rate is relatively fast (half life $\simeq$ 0.6yr) if compared to the deep-sea sediment reaction rates of calcite removal ($\sim 10^{-7}$ yr^{-1}) determined by Lerman (1975). However, reaction rates for silica removal in sediments of Kaneohe Bay, Hawaii, were also found to be much higher than in deep-sea sediments (Lerman 1975). Higher reaction rate constants are to be expected in young sediments at shallow depths as compared to older deeper sediments, in which concentration gradients are measured on a scale of hundreds of meters instead of several tens of centimeters.

Table 1. Cl/Na ratio in Krause Lagoon pore waters

Depth (cm)	Cl/Na*
0-15	1.16
15-17	0.98
17-18	0.92
18-28	0.84
28-40	0.83
40-47	0.89
47-58	0.96
58-73	1.03
73-80	1.06
80-98	1.17
98-113	1.19
113-125	1.17
125-133	1.20
133-147	1.20
147-160	1.20
Sea Water**	1.17

*ratio as determined from molar concentrations
**calculated using average sea water values from Turekian, 1969.

The flux of Ca into the hydrotalcite zone from below can be evaluated using Equation 2, and the value of dC/dZ at $z = 0$ derived from Equation 8. The resultant flux is 6.1×10^{-6} mol cm^{-2} yr^{-1} into the hydrotalcite zone. Thus the total flux of Ca into this zone results in the formation of $\sim 1.5 \times 10^{-4}$ g cm^{-3} yr^{-1} of calcite according to:

$$\frac{\text{(Total flux) (Molecular wt calcite)}}{\text{(Thickness of hydrotalcite zone)}}$$

$$= \frac{(2.84 \times 10^{-5} + 6.1 \times 10^{-6})(100)}{23}$$

$$\simeq 1.5 \times 10^{-4} \text{ g cm}^{-3} \text{ yr}^{-1}.$$

It would take about 3800 years for this flux to produce the mass of calcite observed in the hydrotalcite zone. Because the hydrotalcite zone has existed only since 1966, diffusion alone is not the cause of the observed calcite content. Furthermore, incongruent dissolution of magnesian calcite resulting in formation of calcite (Thorstenson and Mackenzie, 1974) would not be adequate to explain the high calcite content, because there is substantially less magnesian calcite in the other zones of the sediment than there is calcite in the hydrotalcite zone. Also, if calcite had been formed by incongruent dissolution of magnesian calcite the percentage of aragonite would be constant throughout the hydrotalcite zone. The aragonite content, however, shows a sharp decrease in the hydrotalcite zone (Fig. 1).

The fact that neither diffusion nor incongruent dissolution of magneisan calcite can account for the quantity of calcite in the hydrotalcite zone suggests that a major part of the calcite was chemically precipitated in the water column at the time of pollutional inputs of the very high carbonate alkalinity and pH waters, and at that time sedimented to the lagoon floor. This conclusion is in agreement with the observation that there is no noticeable porosity change within the hydrotalcite zone. If all the calcite in the hydrotalcite layer had precipitated in a preexisting sediment of similar mineralogy and porosity as that of adjacent zones, the layer would be completely cemented. Furthermore, it is likely that during mixing of the high-alkalinity waters from the bauxite factory with sea water of Krause Lagoon, the solubility product of calcite would be exceeded. A degree of supersaturation of only four times is sufficient to induce rapid heterogeneous nucleation and growth of calcite crystals (Wollast, 1971).

In summary, it is probable that at the time of pollutional inputs a large quantity of calcite precipitated in the water column and sedimented to the bottom. The occluded waters of the sediment thus formed were low in Ca concentration, owing to precipitation of calcite; subsequent diffusion from the underlying sediment then began and produced the concentration profile observed today.

Magnesium transport and hydrotalcite precipitation

The concentration profile of Mg in the sediment above and below the hydrotalcite zone can be modeled by a diagenetic equation which includes only the diffusion term. This argument is substantiated by the straight-line trend of the data points for Mg concentrations *vs.* depth (Fig. 3b). Also, because these parts of the sediment column are undersaturated with respect to hydrotalcite, and contain none, there is no need to include a reaction term. By integration of Equation 3 and finding the best fit to the data, we obtain the following equation for the Mg concentration in the sediment above and below the hydrotalcite zone:

$$C \text{ above} = -5.56 \times 10^{-6} Z + 1.18 \times 10^{-4} \quad (10)$$

$$C \text{ below} = 9.11 \times 10^{-7} Z - 2.57 \times 10^{-5}, \quad (11)$$

where $Z = 0$ at the sediment-water interface and increases in value with depth. From Equation 2 the flux of Mg into the hydrotalcite zone can be calculated, and is equal to 1.23×10^{-3} mol cm^{-2} yr^{-1} from the upper layer and 2.01×10^{-4} mol cm^{-2} yr^{-1} from the lower layer. Because the base of the hydrotalcite zone probably corresponds to the first pollutional inputs, it can be dated as 8 years B.P. at the time of coring (first pollutional inputs were in 1966, and the core was taken in 1973). The base of the hydrotalcite zone is at 40 cm, giving an average sedimentation rate of 5 cm yr^{-1}. Thus, Mg has diffused into the hydrotalcite zone from the upper layer for approximately 3 years (17 cm of sediment have accumulated above the hydrotalcite zone), and from the lower layer for about 8 years. An estimate of the total amount of Mg transferred into the hydrotalcite zone can be arrived at as follows:

$$\frac{[(3)(1.23 \times 10^{-3}) + (8)(2.01 \times 10^{-4})]}{23 = \text{thickness of zone}} = 2.30 \times 10^{-4} \text{ mol cm}^{-3}. \quad (12)$$

If all the Mg diffusing into the zone precipitated as hydrotalcite, 2.32×10^{-2} g cm^{-3} of hydrotalcite would have been formed. At an average dry sediment density of 2.7 g cm^{-3} and a porosity of 70 percent, 2.9 weight percent of dry sediment would be hydrotalcite formed from Mg diffusing into the hydrotalcite zone at the steady-state fluxes calculated above. However, the water trapped in the sediments during their formation probably had a concentration Mg very close to that of sea water. This conclusion is applicable to sediment above, below, and within the hydrotalcite zone. Therefore, to the 2.9 weight percent of hydrotalcite formed by the steady flux of Mg into the zone must be added the quantity of hydrotalcite formed by the depletion, from sea-water concentration to its present observed concentration, of original Mg trapped in the pore waters. Thus, the area between the sea-water concentration line (assumed to be the original profile) and the actual observed profile in Figure 3b is the amount of Mg depletion that occurred. This area represents a depletion of about 1.88×10^{-3} mol of Mg per cm^2 of sediment. If all the depleted Mg is assumed to have been removed from the pore-water system by precipitation of hydrotalcite, it would account for the formation of 8.23×10^{-3} g cm^{-3} of this mineral in the hydrotalcite zone. This quantity is equivalent to the formation of 1 weight percent of hydrotalcite in the dry sediment. Therefore, diffusion of Mg in the hydrotalcite zone and precipitation there owing to the high carbonate alkalinity and pH can account for the formation of a total of 3.9 weight percent of hydrotalcite. This amount is sufficient to be detected by X-ray methods, as was done in this study.

If we calculate the ion activity product for hydrotalcite in sea water that has its carbonate alkalinity raised to about 90 meq l^{-1}, as observed in the pore waters, we find that 5ppb Al are needed to attain saturation with respect to hydrotalcite ($k_{\text{hydrotalcite}} = 2.51 \times 10^{47}$; Couture, 1975, personal communication). This concentration is not an unusually high Al concentration for sea water (Sackett and Arrhenius, 1962; Shigematsu *et al.*, 1970), particularly near a bauxite factory; however, supersaturation with respect to hydrotalcite was probably never excessive during pollutional inputs, so that precipitation of major amounts of this mineral probably did not occur at this time. Instead, the hydrotalcite precipitated slowly in the sediment pore waters rich in carbonate alkalinity, and continued formation of the mineral was assured by diffusion of Mg into the hydrotalcite zone.

The above conclusions leave unexplained the problem of the source of the mass of Al necessary for the formation of hydrotalcite. Because about 5 ppb Al in solution are needed for hydrotalcite to be precipitated in the hydrotalcite zone and sea water contains only about 1–5 pbb Al in solution (Sackett and Arrhenius 1962), it seems unlikely, because of the probable lack of a strong concentration gradient for Al, that Al could have diffused in significant quantities into the hydrotalcite zone. A possible explanation is that a sodium–aluminum carbonate, such as dawsonite [$NaAl(CO_3)(OH)_2$], precipitated in the water column at the time of the pollutional inputs and sedimented contemporaneously with the calcite. This precipitation could have been caused by the high carbonate alkalinity and high Na concentration of the pollutional inputs. Once in the sediment, the diffusion of Na and carbonate out of the hydrotalcite zone would result in the dawsonite becoming unstable and dissolving. The Al released by the dissolution could then be available for the formation of hydrotalcite. Unfortunately, there are no solubility data for dawsonite and the mineral was not observed in the core; therefore, we can not substantiate this possible explanation for the source of Al.

Conclusions

This study shows that an initial change in water chemistry, owing to industrial inputs, has altered markedly the mineralogy and concentration profiles of major constituents of a sediment pore-water system. Pollutional input probably caused the mass precipitation of calcite, thereby depleting the Ca content of the pore waters in a section of the core and setting up concentration gradients that now control the profile of Ca. The high carbonate alkalinity resulted in supersaturation with hydrotalcite, and its precipitation substantially modified the Mg profile in the pore waters. The conditions leading to hydrotalcite neoformation are very specific and not likely to be attained in most marine environments.

Acknowledgments

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