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Observations on the diagenetic behavior of arsenic in a deep coastal sediment

HARRY M. EDENBORN,[1,2] NELSON BELZILE,[1] ALFONSO MUCCI,[3] JEAN LEBEL[1] and NORMAN SILVERBERG[1]

[1] Département d'Océanographie, Université du Québec à Rimouski, 310, avenue des Ursulines, Rimouski, Quebec G5L 3A1, Canada
[2]Present address: Oak Ridge Research Institute, 113 Union Valley Road, Oak Ridge, TN 37830, USA
[3]Present address: Department of Geological Sciences, McGill University, 3450 University Street, Montreal, Quebec H3A 2A7, Canada

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Abstract. Vertical profiles of total dissolved arsenic, manganese and iron, pH, Eh and rates of sulfate reduction were determined in a freshly-collected box core from a 335 m depth station in the Laurentian Trough. The relationships observed between the profiles were further examined in the laboratory by measuring these same parameters with time in surficial sediment slurries as the Eh decreased in response to biological activity or chemical alteration.

Both field and laboratory observations have shown that arsenic is released predominantly as As(III) into reducing sediment porewaters. This occurs after the dissolution of manganese oxides and at the same time as the dissolution of iron oxyhydroxides and the onset of sulfate reduction. Laboratory experiments indicated that sulfate reduction and the production of sulfide ions are not solely responsible for the release of arsenic to the porewaters, although this process is necessary to create and maintain a highly reducing environment conducive to rapid iron dissolution.

The diagenesis of arsenic in Laurentain Trough sediments involves the simultaneous release of arsenic and iron at a subsurface depth, followed by its removal from porewaters by precipitation and adsorption reactions after migration by diffusion along concentration gradients. A qualitative model is presented to describe the behavior of arsenic in coastal marine sediments.

Introduction

Arsenic is found ubiquitously in nature due to its introduction via the weathering of igneous rocks and geothermal activity. In addition, the use of arsenical herbicides in agriculture, the combustion of fossil fuels, and the production of arsenic during mining and smelting operations have contributed to elevated concentrations of this element in some environments (Manahan, 1975).

Arsenic is toxic to most living organisms. It may inhibit metabolic reactions by combining with the sulfhydryl groups of key enzymes (White *et al.*, 1973), or uncouple oxidative phosphorylation by substituting for phosphate (Stryer, 1981). Langston (1980) observed that organisms living in estuaries where the concentration of arsenic in sediments was high contained significantly higher concentrations of arsenic than those living in less polluted estuaries. It is known that marine organisms are able to bioconcentrate far more arsenic than terrestrial organisms, but the subsequent biological effects of the consumption of this arsenic by man are

unknown (Lunde, 1977). An accurate assessment of both the long and short-term biological hazards associated with arsenic pollution therefore requires detailed knowledge of the geochemical cycling of this element.

The chemical and biological processes that influence the distribution and speciation of arsenic in marine waters have been relatively well-documented (Andreae, 1979; Sanders, 1980; Holm *et al.*, 1980; Windom and Sanders, 1981). Arsenic in oxygenated seawater is found primarily as arsenate, As(V), the stable oxidation state, although lesser concentrations of reduced arsenite, As(III), and methylated arsenicals are also found (Andreae, 1978; Sanders, 1980; Sanders and Windom, 1980). Marine organisms contain only a small fraction of the total arsenic in seawater ($>0.1\%$; Sanders, 1980) but have a considerable impact upon arsenic speciation. Phytoplankton take up large quantities of arsenic and release it in reduced and methylated forms (Sanders and Windom, 1980). Bacteria have likewise been implicated in arsenic reduction (Johnson, 1972), oxidation (Scudlark and Johnson, 1982) and demethylation reactions (Sanders, 1979).

Less is currently known about the fate of arsenic in the underlying sediments. Coastal marine sediments are the natural depositories for arsenic associated with particles carried by river runoff or incorporated in organic detritus settling through the water column (Crecelius *et al.*, 1975; Waslenchuk, 1978). Some investigators have presented convincing evidence for a specific correlation between the dissolution of iron oxides and the release of arsenic in freshwater sediments (Clement and Faust, 1981; Aggett and O'Brien, 1985) and in flooded soils (Deuel and Swoboda, 1972). Both iron and manganese oxides have been suggested to be important components regulating arsenic distribution in marine porewaters (Andreae, 1979; Peterson and Carpenter, 1986). Langston (1980) likewise reported that 60% of the total arsenic in a United Kingdom estuarine sediment was associated with an acid-soluble fraction that included both iron and manganese oxides. In the present paper, we report the distribution of total dissolved arsenic in a deep coastal marine sediment and demonstrate that iron exerts a major influence on the biogeochemical cycling of arsenic.

Materials and methods

Field sampling

Relatively undisturbed sediment samples were collected using a box corer at about 335 m depth in the landward part of the Laurentian Trough, near Rimouski, Quebec, in August and October 1984 (Figure 1, Station 23). The bottom water at this station is well-oxygenated, cold (4 °C), and of relatively constant salinity (34.6‰; El-Sabh, 1979). The box core taken in August was subsampled immediately upon recovery under a low-oxygen

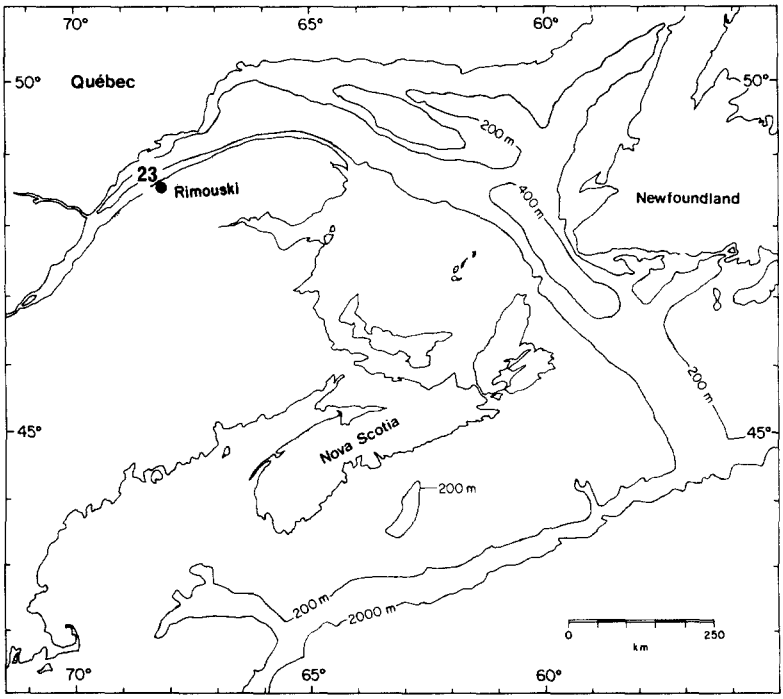

Figure 1. Map of the St. Lawrence Estuary and Gulf of St. Lawrence, showing the location of sampling station 23.

atmosphere in a specially-constructed glove box (Edenborn et al., 1986a). Redox potential (Eh) and pH were measured by punching electrodes directly into the sediment at each sampling depth. Eh was measured with platinum-calomel electrodes (Radiometer P1312-K4112) calibrated using a ferricyanide-ferrocyanide solution (precision ± 10 mV). The pH was measured using a glass-calomel combination electrode (Orion 8102000) calibrated with NBS buffers at the *in situ* temperature (precision ± 0.1 units). Sediment porewaters were extracted under nitrogen by centrifugation for 20 min at 2,500 rpm, filtered through a 45 μm Millipore membrane filter, acidified with Ultrex nitric acid, and kept cold until analysis. Acid was not added to subsamples to be analyzed for As(III).

Analytical procedures

Total dissolved iron and manganese in acidified porewaters were analyzed without preconcentration using a flame atomic absorption spectrophotometer, calibrated with aqueous standards. The precision of these analyses was $\pm 5\%$. Total dissolved arsenic was determined by atomic absorption analysis of the hydride (Aggett and Aspell, 1976) using a Perkin-Elemer MHS-10-hydride generator; detection limit = 0.3 $\mu g\, L^{-1}$.

Arsenite (As(III)) was determined as the arsenite hydride in samples maintained at pH 4–5 with acetate buffer (Aggett and Aspell, 1976). Total arsenic content of the surface sediment and the plankton material used in the laboratory experiments was determined following an oxidizing acid digestion of the samples (Agemian and Bedek, 1980). The precision of arsenic analysis was $\pm 5\%$.

Pore water sulfate concentrations were determined gravimetrically by the precipitation of $BaSO_4$, using a modification of the method of Presley and Claypool (1971); the analytical precision was $\pm 1\%$.

Sediment porosity was calculated based on percent water loss after freeze-drying, assuming interstitial water density of $1.03\,g\,cm^{-3}$, sediment density of $2.65\,g\,cm^{-3}$, and correcting for the precipitation of salts (Berner, 1971).

Sulfate reduction rates in box core sediments were measured using a modification of the radiotracer method of Jorgensen (1978). Four cm^3 sediment mini-cores were collected at selected depths using 5 cm^3 syringes with the distal ends removed. The syringes were plugged with single-hole rubber stoppers sealed with silicone rubber cement. After subsampling of the box core was completed, the mini-cores were transferred from the glove box to a nitrogen-filled glove bag. Each mini-core was then injected with 10 μL of a $Na_2{}^{35}SO_4$ solution (approx. 22 μCi) as a single-line source along the center of each enclosed syringe-sediment core. The inoculated mini-cores were then incubated in the dark at 4 °C for 48 h, followed by freezing (−25 °C) to stop the reactions. Controls were incubated by freezing some mini-cores immediately following inoculation with the radioisotope. Acid-volatile sulfides were distilled from the frozen sediment samples by thawing them in anoxic 3 N HCl and flushing the slurry with oxygen-free nitrogen gas for 1 h. The sulfides were trapped as ZnS in two traps in series, each containing 5 mL of a 3% zinc acetate solution and 1 drop of an antifoaming solution (Antifoam B; BDH Chemicals). Gels containing the ZnS precipitate were prepared following the addition of liquid scintillation cocktail (Scintiverse; Fisher Scientific) and these were radioassayed in a Beckman LS5801 liquid scintillation spectrometer. Sulfate reduction rates were calculated using the formula of Jorgensen (1978). The precision of analysis was approximately $\pm 8\%$ (Edenborn *et al.*, 1986b).

Fresh plankton material for use in laboratory studies was collected by plankton tow, washed free of salt with fresh water, and freeze dried. Total organic carbon and nitrogen content were determined by the total combustion of finely-ground and homogenized samples in a Perkin-Elmer model 249 C-H-N Analyzer.

Laboratory studies

Two 40 cm^3 aliquots of homogenized oxidized surface sediment (0–5 mm), from the box core collected in October 1984, were placed in separate 1 L

polycarbonate flasks containing 960 mL of artificial seawater (ASW; 23.48 g NaCl, 10.63 g $MgCl_2 \cdot H_20$, 3.92 g Na_2SO_4, 1.46 g $CaCl_2 \cdot 2H_20$ and 0.66 g KCl per liter of demineralized water; final pH 7.8) and 300 mg of freeze-dried plankton material (33% carbon by weight; C/N ratio = 6.5). The surface sediment and plankton material contained 22 and 1.8 $\mu g\, g^{-1}$ dry wt of total arsenic, respectively. Mercuric chloride was added to one flask (final concentration 0.3 mM) to inhibit bacterial activity. The flasks were then incubated at room temperature (20 °C) and were only disturbed by shaking prior to each sampling. Samples were taken at regular intervals over the following two weeks. No special precautions were taken to maintain an anaerobic atmosphere within the flasks during sampling. The pH and Eh of the slurries were determined using electrodes as described previously. Five mL aliquots of sediment slurry were removed from each flask and filtered through 0.45 μm Millipore membrane filters. A 1 mL aliquot of this volume was taken for As(III) analysis. The remainder of the filtrate was acidified with Ultrex nitric acid, followed by the analyses of total dissolved iron, manganese, and arsenic as described previously.

Sulfate reduction rates in the experimental flasks were measured using a method similar to that described by Hardy and Syrett (1983). Five mL aliquots of sediment slurry were removed by pipette and added under nitrogen to sterile 60 mL serum bottles, each containing approximately 10 μCi of $Na_2{}^{35}SO_4$. Each bottle was sealed immediately with a gas-tight rubber cap including a small plastic bucket. The bucket was suspended above the sediment slurry inside the bottle and held a pleated piece of filter paper. A 0.2 mL volume of 5% zinc acetate solution was then added to the bucket through the rubber cap by needle and syringe to saturate the filter paper wick. After the slurries had been incubated at room temperature for 6 h, 1 mL of 3 N HCl was added to each sediment slurry through its rubber cap to stop microbial activity and release acid-volatile sulfides. The slurries were shaken gently for one hour. The filter papers were then removed, added to 10 mL of liquid scintillation cocktail and radioassayed. Sulfate reduction rates were then calculated as described previously.

The effect of the chemical alteration of redox potential on the release of total dissolved manganese, iron and arsenic from surface sediment slurries was investigated. One gram aliquots (wet weight) of freshly-collected oxidized surficial sediment from station 23 were added to glass bottles containing 40 mL ASW and 0–14.4 mM sodium hydrosulfite. The sulfite-dithionite redox couple,

$$2SO_3^{-2} + 2H_2O + 2e^- \longleftarrow\!\!\!\!\!\!\longrightarrow S_2O_4^{-2} + 4OH^-,$$

$$E^0 = -1.12\,V, \qquad (1)$$

established by this compound, appeared to have the least interference with iron, manganese and arsenic chemistry among the numerous chemical reductants tested. A small volume (< 0.5 mL) of a 1 M ammonium

Table 1. Physical and chemical characteristics of sediments and porewaters sampled at station 23

Depth Interval (mm)	Porosity	Eh[a] (mV)	pH	Sulfate (mM)
0–20	0.888	+16	7.61	28.3
20–30	0.864	−57	7.76	28.5
30–40	0.850	−105	7.92	28.0
40–50	0.827	−157	7.84	28.5
50–60	0.808	−128	7.70	28.1
60–70	0.801	−168	7.82	28.6
80–90	0.793	−174	7.74	28.4
100–110	0.790	−183	7.70	27.9
130–140	0.788	−160	7.69	27.2
160–170	0.774	−160	7.71	27.3
190–200	0.771	−138	7.61	26.7
220–230	0.780	−168	7.57	26.4
250–260	0.762	−170	7.54	25.9
280–290	0.765	−171	7.52	26.5
310–320	0.769	−135	7.51	25.7
340–350	0.771	−160	7.47	25.0

[a] Relative to saturated calomel electrode.

chloride/ammonium hydroxide buffer was used to maintain the pH of each slurry between 7.4 and 8.0. The buffered slurries were then incubated for 4 h at room temperature (22 °C), after which subsamples were taken, filtered, and analyzed for total dissolved manganese, iron and arsenic as described previously.

Results

Distribution of chemical species and sulfate reduction rates in station 23 sediment

Some physical and chemical characteristics of the sediments and porewaters sampled at station 23 are presented in Table 1. The vertical profiles for total dissolved manganese, iron, arsenic and arsenite in the interstitial water are shown in Figures 2a–2c. The profiles for each of these elements were similar, with concentration maxima located between 100–200 mm depth. The sediment core, which consisted of silty clay, was characterized by a surficial oxidized zone 30–40 mm thick, of positive or slightly negative Eh, in which low or undetectable concentrations of dissolved Mn, Fe and As were found. Recent measurements of dissolved oxygen concentrations using microelectrodes indicate that oxygen does not penetrate more than 8–10 mm below the surface at this station (Silverberg, unpublished data). Total dissolved arsenic present in the upper 40 mm was composed of species other than arsenite (Figure 2c). Sediment redox potential decreased almost linearly from +16 mV to −157 mV between the surface and the

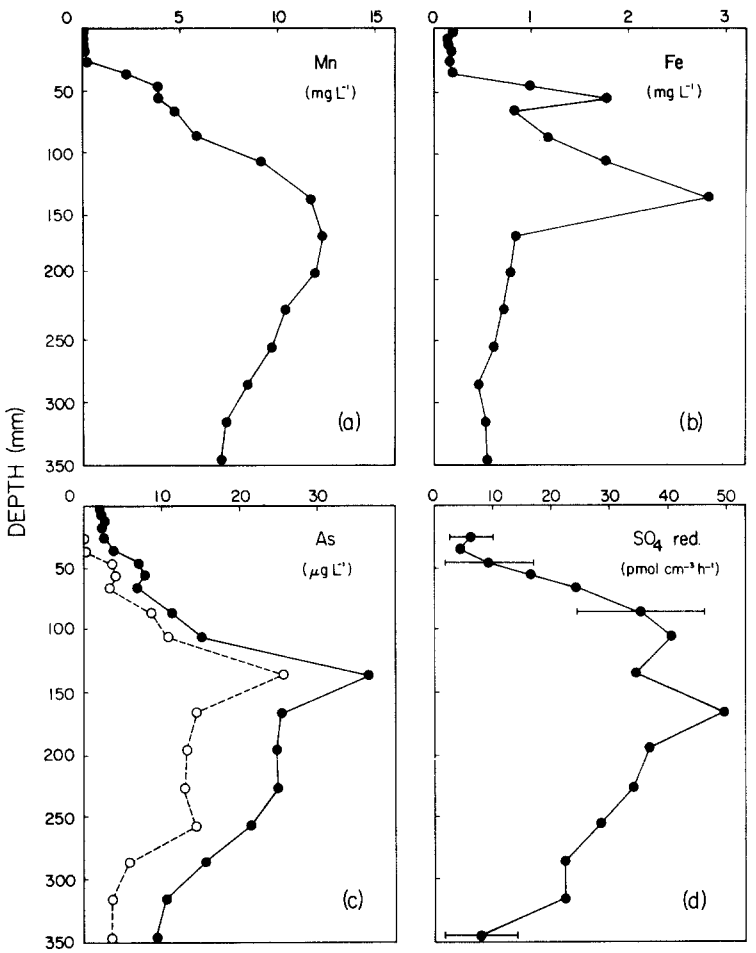

Figure 2. Porewater profiles of (a) total dissolved manganese, (b) total dissolved iron, and (c) total dissolved arsenic (solid line) and arsenite (dashed line) in the sediment of station 23 (August 1984). Sulfate reduction rates (d) are also shown for whole wet sediment over the same depth interval; error bars indicate standard deviation about the mean at selected depths.

40–50 mm depth interval (Table 1). Below this depth, the Eh remained near −160 mV and arsenite made up a consistent percentage (65–70%) of the total dissolved arsenic pool. This is in agreement with other studies that indicate that inorganic arsenic in oxidized aquatic systems is present primarily as arsenate (Waslenchuk, 1978; Sanders, 1980), whereas arsenite becomes the dominant arsenic species in anoxic environments (Andreae and Froelich, 1984).

Sulfate reduction rates measured in the sediment were extremely low (Figure 2d). The integrated rate over 350 mm was 23.2 nmol SO_4 cm^{-2} d^{-1}.

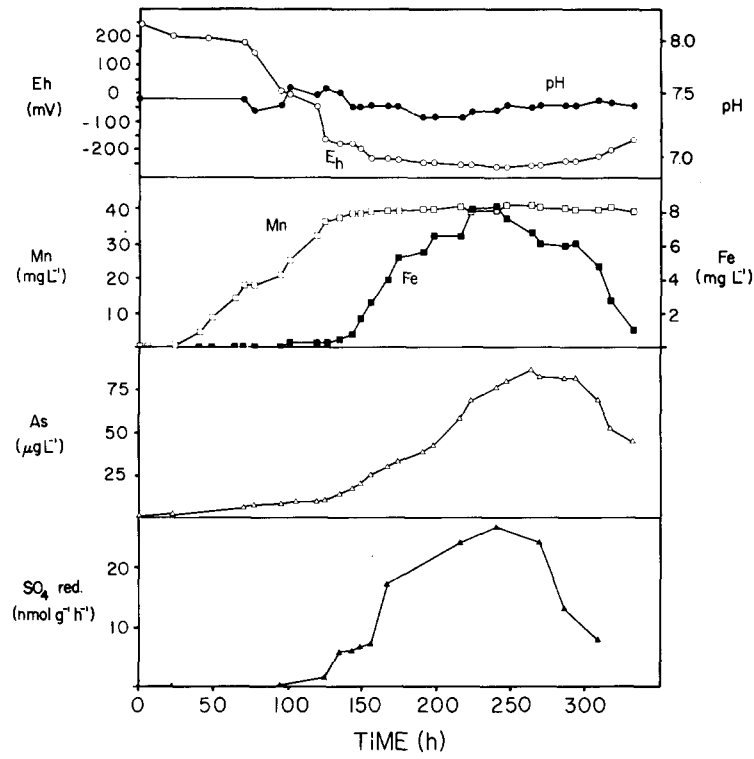

Figure 3. Changes in pH, Eh, total dissolved manganese, iron and arsenic, and sulfate reduction rates in an experimental flask containing oxidized surficial sediment, artificial seawater and freeze-dried plankton material. Greater than 95% of the As measured was in the form of As(III).

The measured rates increased with depth to approximately 165 mm, below which they decreased slowly to the base of the core. The rates are low compared to those measured in other coastal sediments (Edenborn *et al.*, 1986b). Sulfate reduction rates were not corrected for the production of pyrite, which made up approximately 17% of sulfate reduction end-products (Edenborn *et al.*, 1986b). The apparent relationship between the sulfate reduction rate profile and the distribution of dissolved Mn, Fe and As is examined in the Discussion.

Laboratory experiments

The results of an experiment in which a slurry of oxidized surface sediment and seawater was incubated with added plankton material are shown in Figure 3. The presence of fresh planktonic material accelerated the microbial activity, resulting in a rapid decrease of Eh. The experiment was done in an attempt to mimic the sequential depletion of oxidants that occurs during early sedimentary diagenesis, with time of incubation replacing the

variable of time of burial in the core. At zero time, the Eh measured in the slurry was high (+245 mV), and the water contained undetectable amounts of dissolved manganese, iron or arsenic. After 46 h of incubation, dissolved manganese began to be released into solution and reached a maximum concentration plateau after 143 h. During this period of manganese release, a small amount (6–14% of the final maximum concentration) of total dissolved arsenic was released. Throughout the entire experiment, greater than 95% of the total dissolved arsenic measured was in the form of As(III). Rapid release of dissolved iron and arsenic occurred when the redox potential of the sediment slurry dropped below −150 mV, and concentrations of both elements increased over the next 96 h. The maximum contribution of dissolved arsenic due to the complete degradation of the added plankton material (0.5 $\mu g\ L^{-1}$) was negligible. Sulfate reduction was first detectable when the redox potential dropped below −150 mV, and the measured rate increased concurrently with the increase in dissolved iron and arsenic concentration. All three parameters decreased simultaneously after approximately 250 h incubation. This presumably reflects the exhaustion of labile organic carbon and the subsequent inability of the bacterial population to maintain a low redox potential in competition with the diffusion of oxygen from the ambient atmosphere in the flask.

In an identical sediment slurry system treated with 0.3 mM $HgCl_2$, the Eh only dropped to −80 mV after 10 days, and neither manganese, iron nor arsenic were released into solution during the course of the experiment (data not shown). No sulfate reduction activity was detected in this experimental sediment slurry. We also attempted to assess the influence of sulfate reduction on the solubilization of arsenic in a replicate slurry containing 20 mM ammonium molybdate, a specific inhibitor of sulfate reduction activity (Nedwell, 1982). Unfortunately, the analysis of dissolved arsenic was unsuccessful due to the complexation of molybdate ions with arsenic.

Chemical alteration of the redox potential of oxidized surface sediment slurries had a significant effect upon the release of manganese, iron and arsenic. The addition of chemical reductant lowered both the pH and Eh of the sediment slurries. This was accompanied by the sequential release of manganese, iron and arsenic, but made it impossible to distinguish which parameter was responsible for the release. Since the pH of the natural sediment porewaters at station 23 does not vary significantly in the top 30 cm (Table 1), a pH-buffered experiment was conducted. It confirmed the predominant effect of Eh on the observed sequential release (Table 2) and provided evidence that sulfate reduction and the production of sulfide ions are not solely responsible for the solubilization of arsenic, even though this process is necessary to create and maintain a highly reducing environment in the presence of organic matter. It is interesting to note that at an extremely low Eh (−670 mV) an additional fraction of

Table 2. Effect of redox potential on the release of manganese, iron and arsenic from oxidized surface sediment slurries incubated for 4 h at room temperature

Final Eh (mV)[a]	Final pH	Mn ($mg\,L^{-1}$)	Fe ($mg\,L^{-1}$)	As ($\mu g\,L^{-1}$)
+209 (0.0)	7.9	—[b]	—	—
+15 (1.4)	8.0	0.9	—	—
−20 (1.7)	7.9	3.2	—	—
−60 (2.2)	7.6	11.7	2.3	2.9
−150 (2.9)	7.4	12.8	18.0	26.3
−160 (2.9)	7.4	12.1	22.7	29.0
−670 (14.4)	7.7	13.7	32.4	30.0

[a] Eh was adjusted using sodium hydrosulfite; final concentration (mM) is shown in parentheses. The pH was maintained between 7.4 and 8.0 using ammonium chloride/ammonium hydroxide buffer.
[b] — = none detected.

soluble iron was released which was associated with little or no arsenic release.

Discussion

Few arsenic concentration profiles have been reported for marine sediments. Andreae (1979) determined arsenite and arsenate concentrations in the porewaters of three different stations in the NE Pacific and off the southern California coast. Arsenate was much more abundant than arsenite in all porewaters analyzed. Arsenic concentrations were extremely low and generally increased with increasing depth in the sediments. In contrast, arsenic in the sediment porewaters of Puget Sound, Saanich Inlet and along the Washington coast is predominantly arsenite, and the concentration profiles observed commonly exhibit subsurface maxima just below the sediment-water interface (Peterson and Carpenter, 1986). These latter profiles and the concentrations of dissolved arsenic measured at unpolluted stations in their study closely resemble those measured in Laurentian Trough sediments.

Arsenic-mineral association

The dissolved arsenic profile in Laurentian Trough sediment porewaters correlated closely with profiles for total dissolved iron and manganese, suggesting the concomitant release of arsenic with the dissolution of one or both of these elements. This is in agreement with the observations of several other investigators (Andreae, 1979; Neal *et al.*, 1979; Maher, 1984/85; Peterson and Carpenter, 1986). However, none of these studies could clearly distinguish between iron and manganese as factors that might influence arsenic distribution in porewaters.

The sequential release of manganese and iron that occurred as the redox potential of experimental sediment slurries was lowered in our

laboratory studies revealed that arsenic (III) was released to porewaters at the same time as iron, after the dissolution of almost all of the reducible manganese. A similar release pattern was observed when the change in redox potential was either chemically or biologically induced. Under our experimental conditions, however, it could not be determined if significant amounts of arsenic adsorbed onto or incorporated into manganese oxides were released and then rapidly readsorbed by iron oxyhydroxides. If some arsenic transfer of this type occurs in natural sediments during early diagenesis, iron oxyhydroxides would still ultimately control the release of arsenic into porewaters, since they should be reduced after manganese oxides. A similar mechanism has been suggested by Peterson and Carpenter (1986). Evidence presented in other studies suggests that arsenic may be associated primarily with iron throughout the water column and sediments. Langston (1983) showed that the co-precipitation of arsenic with colloidal hydrous iron oxides and hydroxides in the water column was an important mechanism of arsenic removal and transport to the sediment in a United Kingdom estuary. Likewise, it is known that arsenate is strongly adsorbed by hydrated iron oxides (Gulens *et al.*, 1979), but much less so by manganese oxides (Oscarson *et al.*, 1981b). Therefore, the arsenic associated with manganese oxides may only constitute a small percentage of the particulate arsenic inventory in marine sediments.

Redox considerations

The application of standard potentials to complex natural solutions such as sediment porewaters is often questionable because of the lack of information on the speciation of redox sensitive components and the kinetics of redox reactions in such solutions. Berner (1963) discovered that the Eh of many sediments containing H_2S is controlled by the reversible half-cell:

$$S_{(s)} + 2e^- \longleftarrow\!\!\!\!\longrightarrow S^{2-}. \tag{2}$$

He then derived the following direct relation between Eh and the logarithm of the activity of the sulfide ion, pS^{2-}:

$$Eh = -0.485 + 0.0295pS^{2-}. \tag{3}$$

If we assume that porewaters below a depth of 15 cm in the sediment are in equilbrium with amorphous FeS (pK = 16.9; Berner, 1967), which corresponds to a dissolved Fe(II) concentration of approximately 1 ppm, or 1.8×10^{-5} M, we can calculate an equilibrium S^{2-} ion activity of 3.6×10^{-12}, or a pS^{2-} of 11.45 ($\gamma_t(Fe^{2+}) = 0.195$; Davison, 1979, 1980). Using this calculated value and equation (3), we obtain an Eh value of -0.147 V. Despite the large uncertainities in the activity coefficient (γ_t) estimate of Fe(II) and the equilbrium assumption, this value corresponds

closely to our measured field values of -0.140 to -0.170 V. The close agreement between calculated and measured Eh values indicates that electrode potential measurements may accurately reflect the activity of the S^0/S^{2-} redox couple in these sediments. However, because of kinetic constraints, other redox couples in the system may not be in equilbrium with the S^0/S^{2-} couple.

Our field and laboratory data indicated that most of the arsenic released to anoxic porewaters along with the dissolution of iron oxyhydroxides was in the form of As(III). However, at a pH of approximately 7.5, significant reduction of As(V) to As(III) should not occur prior to iron oxide reduction, according to the standard redox reactions listed in Table 3. These equations predict that the release of arsenic as As(V) would result from the dissolution of any iron oxyhydroxide carrier phase, whereas As(III) should become the dominant inorganic arsenic species (As(III)/As(V) > 1) only after the Eh had fallen to -0.274 V, relative to the saturated calomel electrode. Under the redox conditions found in the reducing sediments at station 23 (Eh = -0.140 to -0.170 V, relative to the saturated calomel electrode), less than 0.1% of the As(V) would be expected to be chemically reduced to As(III) at the same time and following Fe(III) reduction to Fe(II). The bacterial reduction of free or bound As(V) to As(III) may explain its relative abundance in the sediment porewaters. Johnson (1972) demonstrated that arsenate reduction by bacteria in oxygenated seawater resulted in a much lower arsenate/arsenite ratio than predicted under equilibrium conditions. Other laboratory studies have also shown that As(III) is metastable in oxidizing solutions (Gulens *et al.*, 1979; Oscarson *et al.*, 1981b), which probably accounts for the persistence of high arsenite concentrations under the existing redox conditions in sediment porewaters.

The results of the present study and others (e.g. Balzer, 1982) indicated that the onset of sulfate and iron reduction can occur simultaneously in some sediments, contrary to thermodynamic predictions (Table 3) and published data from the deep sea (Froelich *et al.*, 1979). This diagenetic behavior is most probably a function of the high sedimentation rate and rapid burial of easily metabolizable organic matter that occurs in coastal environments. The rapid consumption of organic matter near the sediment-water interface in these sediments makes it difficult to distinguish depths at which the reduction of specific oxidants begins. Furthermore, sulfate reduction activity may take place in anoxic microenvironments within the upper oxidized sediments (Jorgensen, 1977), and heterogeneous redox conditions persist to considerable depths in natural sediments. Also, the slow reduction kinetics of various Fe(III) mineral phases may result in continued iron dissolution at redox values far lower than expected from thermodynamic calculations.

Table 3. Half reactions of pertinent redox couples

Half reaction		E^0 (V)[a]	Ref.
(1) $MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	$p\varepsilon = 20.42 - 2pH - \frac{1}{2}\log\{Mn^{2+}\}$	+0.320 (+0.076)[b]	Stumm and Morgan (1981)
(2) $FeOOH + 3H^+ + e^- = Fe^{2+} + 2H_2O$	$p\varepsilon = 26.3 - 3pH - \log\{Fe^{2+}\}$	+0.225 (−0.019)	Stumm and Morgan (1981)
(3) $HAsO_4^{2-} + 4H^+ + 2e^- = H_3AsO_3 + 2H_2O$	$p\varepsilon = 14.50 - 2pH + \frac{1}{2}\log\frac{\{HAsO_4^{2-}\}}{\{H_3AsO_3\}}$	−0.030 (−0.274)	Ferguson and Gavis (1972)
(4) $SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O$	$p\varepsilon = 4.25 - \frac{9}{8}pH + \frac{1}{8}\log\frac{\{SO_4^{2-}\}}{\{HS^-\}}$	−0.248 (−0.492)	Stumm and Morgan (1981)

[a] E^0 were calculated from standard equilibrium constants at pH = 7.5 and unit activities.
[b] E^0 in parentheses are relative to the saturated calomel electrode.

A close relationship was observed between sulphate reduction rates and arsenic concentrations in porewaters of the Laurentain Trough sediments. In the upper sediments, this relationship is due to the apparently simultaneous onset of sulfate reduction and iron dissolution as the redox potential falls. The lowered Eh leads to the dissolution of iron oxides and the release of associated arsenic to the porewaters. Alternatively, sulfide may participate directly in the dissolution of iron hydroxides (Pyzik and Sommer, 1981) and result in some arsenic release. At greater depth in the sediment, sulfate reduction rates decrease due to the progressive depletion of available organic matter. However, higher concentrations of dissolved sulfide at these depths result in the net precipitation of iron and arsenic. The laboratory experiments also indicated that Eh, rather than the rate of sulfate reduction itself, controlled the release of arsenic to the porewaters.

A relationship between sulfate reduction and the release of phosphate in a coastal sediment has been reported by Watanabe and Tsunogai (1984). This agrees with a proposed mechanism for phosphate release in sediments that also involves the dissolution of an iron oxide carrier phase at a lowered redox potential (DeLaune *et al.*, 1981; Krom and Berner, 1981). The chemical similarities between arsenic and phosphorus and their affinities for iron oxyhydroxide surfaces suggest that the processes involved in their adsorption and release to coastal marine sediment porewaters may be identical.

Descriptive diagenetic model

A simple model is proposed to explain the interaction between arsenic and iron in coastal marine sediments (Fig. 4). A similar model has been suggested for lacustrine sediments by Aggett and O'Brien (1985). In this model, iron oxides and hydroxides in surficial sediments adsorb arsenic diffusing upwards from the reduced zone. Laboratory results (Yoshida *et al.*, 1976; Gulens *et al.*, 1979) indicate that As(V) is adsorbed much more strongly than As(III) by the hydrated iron oxide. This suggests that one mechanism of As(III) removal from the porewaters near the sediment-water interface may be its oxidation to As(V) prior to rapid adsorption onto freshly precipitated iron oxyhydroxides. Alternatively, the oxidation of As(III) to As(V) by Fe(III) may occur after its adsorption (Gulens *et al.*, 1979). More recently, Oscarson *et al.* (1981a, 1981b) have shown that iron oxides in freshwater systems do not oxidize As(III) to As(V) within 72 h, although this process can be carried out by MnO_2.

Diagenetic iron oxide-arsenic complexes, along with detrital arsenic deposited at the sediment-water interface, are eventually buried to a depth in the sediment where the low redox potential favors the dissolution of iron (Figure 4). This results in the simultaneous release of dissolved iron and arsenic into the porewaters. Diffusion of dissolved arsenic and iron would then occur both upwards and downwards along concentration

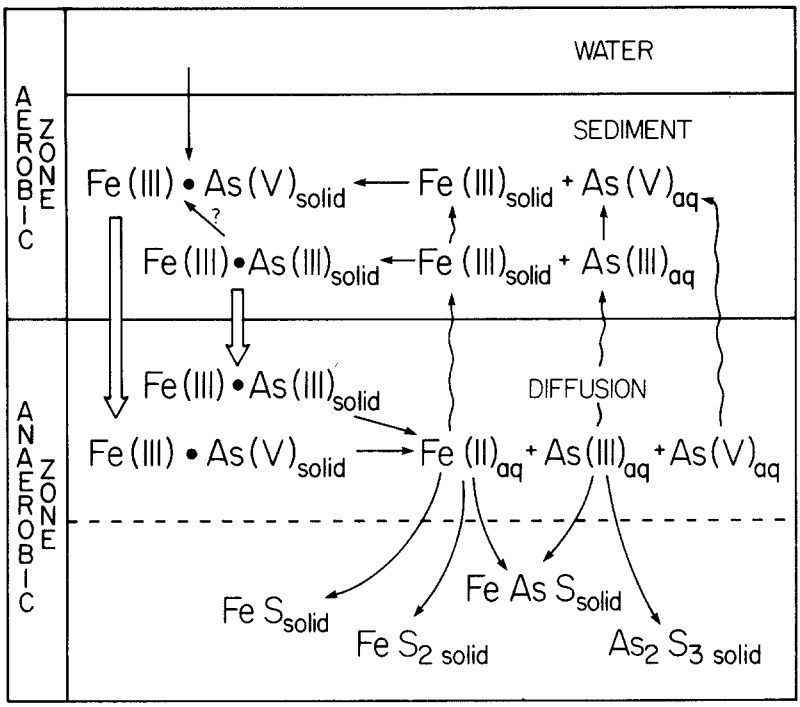

Figure 4. Proposed model for the biogeochemical cycling of arsenic in coastal marine sediments (after Aggett and O'Brien, 1985). The dashed line indicates sediment below which free sulfide favors sulfide precipitation. Solid iron species above the line are presumed to contain oxide and hydroxide groups.

gradients. Arsenic is either trapped by iron oxides in the oxidized zone or escapes into the overlying water column. At depth, arsenic may precipitate with iron (eg.. arsenopyrite) or form distinct arsenic sulfide minerals (eg. orpiment). Additional work is needed to determine the precise chemical associations between arsenic and iron in marine sediments.

Based upon the above model, arsenic would be expected to be internally cycled in sediments maintaining an oxic surficial layer. However, diffusion of arsenic from sediments into the overlying water column has been observed in several environments (Carpenter *et al.*, 1978; Andreae, 1979; Aggett and O'Brien, 1985; Butler and Smith, 1985). This may occur when the oxic zone becomes too thin to effectively trap all of the upward diffusing arsenic, or when the concentration gradient between porewaters and overlying water is enhanced by the presence of polluted sediments (Aggett and O'Brien, 1985). Although relatively pristine sediments are generally considered to be a negligible source of the arsenic found in coastal marine waters (Sanders, 1980), arsenic release may occasionally occur in environments where the sedimentation rate of organic matter is

periodically high. Sedimentation rates at station 23, for example, vary annually by a factor of 4 (Silverberg *et al.*, 1985), and preliminary evidence suggests that the depths at which both manganese and iron dissolution occur change accordingly. High levels of organic matter input, either natural or anthropogenic, would be expected to erode the thickness of the oxic layer of sediment and allow arsenic diffusion upwards into the water column. Additional research is necessary to determine if our current appraisal of coastal marine sediments as efficient arsenic sinks is warranted.

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