

YALE PEABODY MUSEUM

P.O. BOX 208118 | NEW HAVEN CT 06520-8118 USA | PEABODY.YALE. EDU

JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research*, one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at <https://elischolar.library.yale.edu/>.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research*.

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License.
<https://creativecommons.org/licenses/by-nc-sa/4.0/>



The geochemistry of iodine and bromine in sediments of the Panama Basin

by T. F. Pedersen^{1,2} and N. B. Price¹

ABSTRACT

The areal and vertical distribution of iodine, bromine and organic carbon has been examined in a suite of sediment cores from the Panama Basin. Both halogens are approximately correlative with organic carbon in surface sediments. The concentrations of all three elements vary sympathetically but considerably with depth, especially in equatorial carbonate oozes where a distinct mid-depth (40-80 cm) concentration maximum is observed.

Iodide is the dominant iodine species in interstitial water. Detailed pore water profiles of two cores display iodine increases at depth; in one of the cores the mid-depth halogen enrichment is clearly a major locus of dissolved iodine production.

All cores characteristically show a first-order decrease in the sediment I/C_{org} ratio with depth. In contrast, Br/C_{org} profiles show considerable variation; subsurface peaks in the ratio roughly reflect the sediment Br distribution. The contrastive diagenetic behavior of the two halogens implies bonding by different organic ligands.

The coincident carbon, iodine and bromine peaks at depth in biogenic equatorial sediments are temporally related to the maximum of the Wisconsin glacial advance. Simple calculations suggest that a minor proportion of the Pacific iodine reservoir could have been removed to carbon-rich equatorial Pacific sediments during the Wisconsin maximum, implying that climatic fluctuations may indirectly have a minor importance in regulating the oceanic iodine balance.

1. Introduction

Sediments are known to play an active role in determining the concentrations of a great number of elements in the sea, but for many of these the geochemical processes involved are poorly known. The geochemistry of iodine and bromine, for example, has been investigated in some shelf and marginal sea deposits but little is known about the behavior or distribution of either element in hemipelagic facies.

The occurrence of high concentrations of iodine in near-shore and continental margin sediments has been reported in several studies (e.g. Vinogradov, 1939; Shishkina and Pavlova, 1965; Price *et al.*, 1970; Pavlova and Shishkina, 1973;

1. Grant Institute of Geology, West Mains Road, Edinburgh, EH9 3JW, Scotland.

2. Present address: Department of Oceanography, The University of British Columbia, 6270 University Boulevard, Vancouver, B.C., Canada, V6T 1W5.

Price and Calvert, 1973). In oxidized surface sediments the concentration of this element has been found to be directly proportional to the organic carbon content. Thus, oxic sediments underlying areas of high primary productivity are characteristically enriched in iodine.

Similar enrichments for bromine associated with organic carbon have been noted in Barents Sea (Vinogradov, 1939; Price *et al.*, 1970) and Namibian Shelf surface sediments (Price and Calvert, 1977). Unlike iodine, however, the linear relationship $[Br] = k [C_{org}]$ appears to be independent of the surface sediment redox potential.

Iodine and bromine concentrations have been shown to generally decrease with increasing depth of burial in sediments undergoing early diagenesis (Shishkina and Pavlova, 1965; Pavlova and Shishkina, 1973; Price and Calvert, 1977). The iodine decrease is accompanied by a more gradual fall in the organic carbon content and by an increasing iodine concentration in interstitial water (Pavlova and Shishkina, 1973). A similar increase might be expected for bromide in pore water; however the screening effect of the relatively high concentration of sea water bromide would render it difficult to detect such an enrichment.

In this paper the distributions of iodine and bromine in hemipelagic Panama Basin area sediments and the iodine distribution in the pore waters of two Basin cores are discussed. Historical variations in organic carbon content are characteristic of sediments of the Galapagos Islands area, as described below, and will be used in this work to assist in resolving contrasts in the post-depositional behavior of the two halogens. In addition, possible effects of Pleistocene climatic variations on the iodine balance in the sea will be briefly considered.

2. Environmental setting

The Panama Basin is defined by the Cocos Ridge to the west, the Carnegie Ridge to the south, and the continental margins of Central and South America to the north and east (Fig. 1). The sediments consist largely of rapidly accumulating organic-rich hemipelagic clays in the northeast and radiolarian- and diatom-bearing foraminiferal oozes in the large sub-basin to the southwest (Moore *et al.*, 1973).

Sub-surface upwelling along the equatorial divergence (supplemented by the emergence of Cromwell Current water around the Galapagos Archipelago), and domal upwelling in the Panama Bight and Costa Rica Dome areas, support exceptionally high primary productivity in Panama Basin surface waters. In the northeastern sub-basin, the combination of high euphotic zone production and rapid sediment accumulation is reflected in the sediments by a high organic carbon content. Slower accumulation of the biogenic sediments in the Galapagos area permits more efficient bacterial metabolization of organic material during deposition and, as a result, these sediments generally contain less organic carbon (Pedersen, 1979). The biogenic facies does, however, exhibit pronounced temporal variations in the organic carbon concentration, as initially described by Arrhenius (1952). Arrhenius

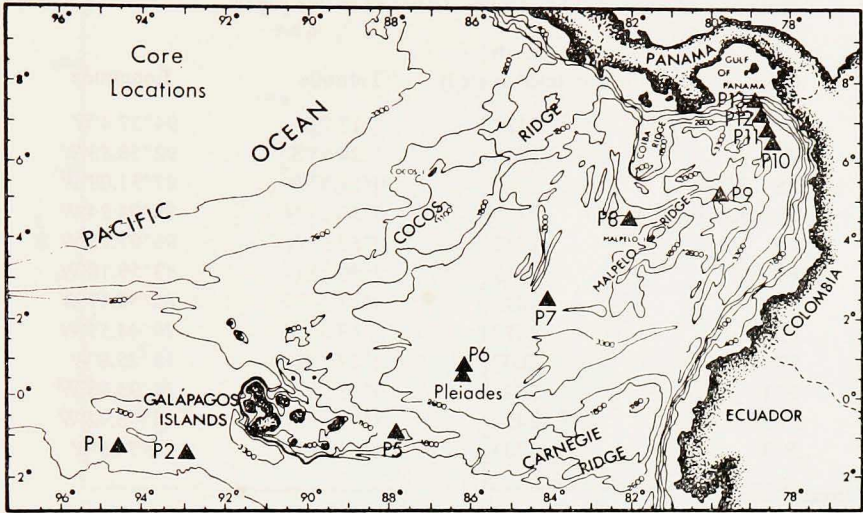


Figure 1. Physiography of the Panama Basin and locations of cores discussed in this paper.

postulated that variations in carbon concentration with depth in Galapagos-area sediments to some degree reflect historical changes in primary productivity in equatorial surface waters. He linked increased carbon concentrations to greater productivity, which was thought to be a direct result of enhanced upwelling during Pleistocene glacial maxima.

3. Sampling and analytical methods

Sediments were collected in the Panama Basin by gravity coring from R.R.S. *Shackleton* during May, 1976. The cores collected during that cruise have been supplemented by a surface sample from a box core collected in the Panama Basin during Leg II (1976) of the Pleiades Expedition of Scripps Institution of Oceanography. Core locations are shown in Figure 1 and the positions listed in Table 1.

Interstitial water from cores P6 and P8 was sampled on board ship using a water-jacketed PVC-Teflon hydraulic squeezer. Sediment samples were extruded from the cores in air and squeezed at *in situ* temperatures (2-3°C). The expressed pore waters were stored in acid-cleaned glass vials and refrigerated, while the squeezed sediments and the remaining cores were frozen. All samples were transported to Edinburgh for analysis.

The distributions with depth of I, Br and C_{org} have been determined in detail for the four cores P1, P2, P6 and P8. For the remaining eight cores, only surface sediment analyses are considered here.

Sediment samples were oven-dried at 50°C (which does not affect the halide content) and ground in a tungsten-carbide disc mill to pass 200 mesh. Carbonate was

Table 1. Locations and water depths of cores discussed in this paper.

Core	Depth (m, uncorrected)	Latitude	Longitude
P1	3422	1° 17.7'S	94° 37.4'W
P2	3510	1° 24.65'S	92° 58.83'W
P5	1540	0° 54.57'S	87° 51.08'W
Pleiades Box Core	2716*	0° 36.13'N	86° 08.24'W
P6	2712	0° 52.34'N	86° 07.73'W
P7	3085	2° 36.26'N	83° 59.18'W
P8	4093	4° 37.24'N	82° 59.17'W
P9	3075	5° 15.67'N	79° 44.51'W
P10	4007	6° 27.5'N	78° 25.8'W
P11	3847	6° 48.28'N	78° 35.35'W
P12	3491	7° 08.66'N	78° 43.92'W
P13	1803	7° 31.3'N	78° 54.5'W

* Corrected depth.

removed from sediment sub-samples by repeated dropwise addition of 10% H_3PO_4 until effervescence had totally ceased; loss of organic carbon by hydrolysis was prevented by very slowly adding the acid to sediment samples previously weighed into Leco ceramic crucibles. Organic carbon was analyzed on a Leco carbon analyzer by dry combustion of the carbonate-free samples followed by measurement by hydroxide absorption of the CO_2 produced. Analytical precision was $\pm 4\%$ (1σ , $n = 11$) at 1% C_{org} and about $\pm 10\%$ for C_{org} concentrations less than 0.5%.

Total I and Br were determined by x-ray fluorescence on a Philips PW 1450 automatic x-ray spectrometer using a tungsten anode, a LiF (200) analyzing crystal, and a scintillation counter (flow proportional and scintillation counters for Br). A series of synthetic standards utilizing potassium bromide and barium iodate (both nonvolatile in the presence of x-rays) were used for calibration. Analytical precision in each case was $\pm 4\%$ (1σ). An additional error arises in the analysis of Br because of the necessity to correct for large quantities of seasalt bromine. The bromine content contributed by salt was estimated by analyzing (by XRF) each sample for total Cl and assuming that the pore waters had a salinity of 35‰ and that the Br/Cl ratio in salt was equivalent to its value in sea water. Analyses are reported here on a salt-free basis. The estimated overall precision for salt-free Br is $\pm 8\%$.

Total dissolved iodine was determined in core P8 by autoanalysis following the method of Truesdale and Chapman (1976). Analytical precision was $\pm 2.0\%$ (1σ , $n = 9$). Pore water samples from core P6 were analyzed for total iodine and iodate using the method of Truesdale and Spencer (1974), as modified for interstitial waters by Dr. A. Leonard of Liverpool University. To determine total iodine, H_2SO_4 and bromine water are added to the sample to oxidize I^- to IO_3^- . Formic acid is then added to discharge the yellow bromine colour, followed by the addition of 1%

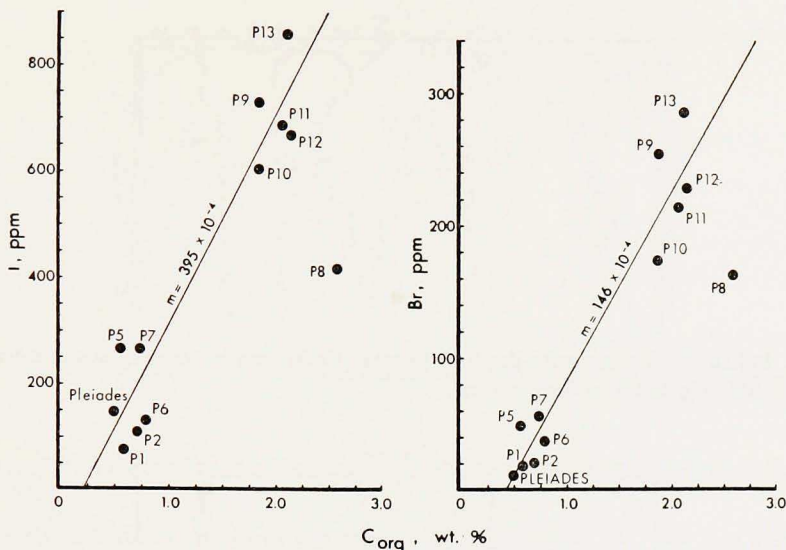


Figure 2. The relationship between salt-free iodine, bromine and organic carbon in Panama Basin area surface sediments. The surface sample for core P8 was omitted from the regression calculations since it deviates strongly from linearity. This deviation may be due to the presence of reworked, relatively refractory carbon in the core. The zeolite clinoptilolite occurs throughout the core (Pedersen, 1979); since this mineral is invariably of Pleistocene age in marine sediments, it indicates input of reworked sediment which would contain "old" unreactive carbon.

sulphamic acid and 10% KI. The former suppresses interference from nitrite (Chapman and Liss, 1977) while the latter reacts with IO_3^- under acid conditions to form I_3^- which is measured colorimetrically at 3550 Å. Iodate is determined in the same fashion except that the initial oxidation step is deleted. Standards for calibration were prepared by dissolving Analar KI and KIO_3 in iodine-free artificial sea water. Analytical precision was $\pm 8\%$ (1σ , $n = 6$).

4. Iodine and bromine distribution in Panama Basin area sediments

Iodine concentrations vary considerably in Panama Basin area surface sediments, ranging from 76 to 861 ppm while bromine values range from 11 to 278 ppm. Surficial organic carbon levels range from 0.50 to 2.58 wt. %. The concentrations of both halogens are plotted against organic carbon in Figure 2. Of the two well-segregated clusters of points on the graphs, one corresponds to the biogenic sediments of the Galapagos Platform area and Western Basin, which are relatively depleted in halogens and organic carbon, while the other represents the organic carbon and halogen-enriched sediments of the Eastern Basin.

The sediment accumulation rate in the Eastern Basin is relatively high (van Andel

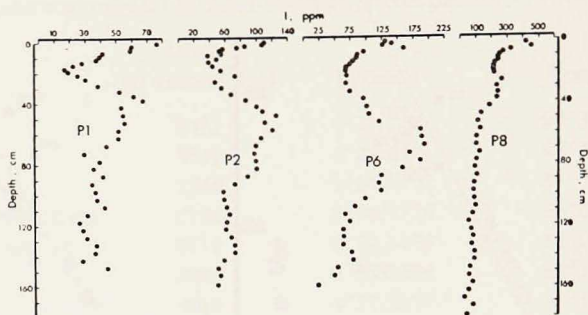


Figure 3. Iodine distributions with depth in Panama Basin area sediments, on a salt-free basis. Note the differing scales on the abscissae.

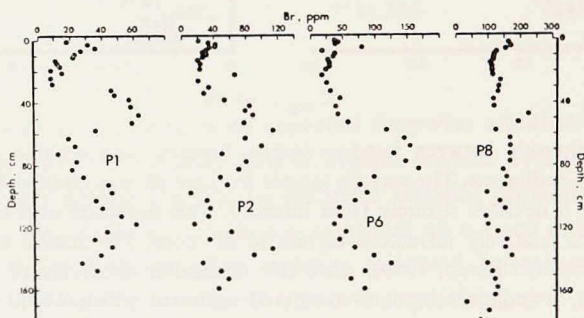


Figure 4. Bromine distributions in Panama Basin area sediments. Note the differing scales on the abscissae. The increased scatter compared to the iodine profiles is probably due to the large corrections applied for salt bromine.

et al., 1971; Pedersen, 1979), thereby preserving a greater fraction of the carbon input which, in turn, appears to be associated with higher halogen contents in the sediments. Unfortunately, the lack of data points in the 1-2% C_{org} range in Figure 2 reduces, to some extent, confidence in the halogen- C_{org} correlations. Even so, regression lines for both elements have slopes which are very similar to those for Barents Sea surface sediments (Price *et al.*, 1970): Panama Basin, $I/C_{org} = 395$, $Br/C_{org} = 146$; Barents Sea, $I/C_{org} = 380$, $Br/C_{org} = 120$ (all $\times 10^{-4}$). This consistency demonstrates that the relationships previously observed for shelf sediments probably apply equally to hemipelagic areas.

Salt-free iodine, bromine and organic carbon distributions with depth in cores P1, P2, P6 and P8 are profiled in Figures 3, 4 and 5, respectively. Both halides are enriched in the surface sediments of all cores, relative to underlying minima, although the magnitude of the iodine enrichment is considerably greater. The extent of the iodine enrichment relative to bromine can be gauged by comparing the I/Br ratio in surface sediments (~ 3) with that in sea water (8.5×10^{-4}). On this basis the addi-

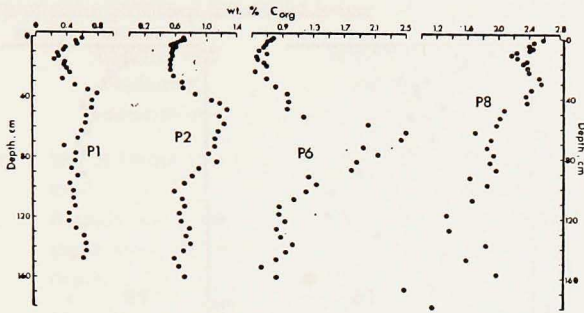


Figure 5. Organic carbon profiles in Panama Basin area sediments. The data are on a salt-free basis.

tion of iodine to the sediments from sea water is favored over bromine by a factor of 3.5×10^3 .

A striking feature common to the three carbonate cores (P1, P2 and P6) is the sharp three-fold increase in iodine and the nearly six-fold increase in bromine contents at 40-80 cm depths in the sediments, relative to the minima seen at ~ 20 cm in each case. Less obvious increases in the iodine content occur lower in the cores at depths of 110-145 cm. Iodine peaks here are subtle, but the opposite is true for bromine; concentrations of this element in the lower horizons (110-145 cm) are nearly equal to those seen between 40 and 80 cm in each core. In all three cores, variations in the concentrations of both halogens broadly parallel the organic carbon profiles (Fig. 5).

Core P8 differs from the others in lacking well-defined carbon, iodine and bromine maxima at depth. Nevertheless, a minor iodine increase at ~ 30 cm is associated with a similar increase in carbon content. Variations in bromine concentrations in this core are clouded by some scattering of the data which has been mainly introduced by the large interstitial salt correction.

5. Dissolved iodine distribution

Iodine in sea water exists almost entirely as iodate and iodide (Sugawara and Terada, 1957). Thermodynamic calculations show that iodate is the stable ion at the pE (~ 12.5) of normal oxygenated sea water (Sillén, 1961) but recent work has demonstrated that iodide predominates in anoxic conditions (Wong and Brewer, 1977).

In this study, pore waters from core P6 and some samples from P8 were analyzed for both iodine species. At a detection limit of $\sim 0.06 \mu\text{M IO}_3^-$, no iodate was found in either core, even in the core top interstitial water samples. Hence, "total dissolved iodine" as used here denotes the analyzed iodide concentration. The analyses are plotted in Figure 6.

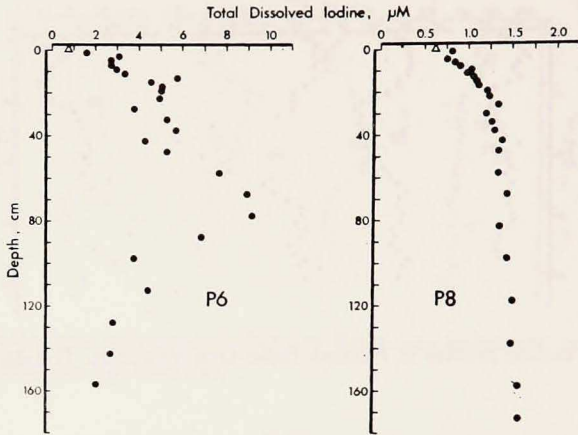


Figure 6. Total dissolved iodine profiles for two Panama Basin cores. Δ = supernatant water. Precision: P6 = \pm 8% (1σ , $n = 6$); P8 = \pm 2% (1σ , $n = 9$).

Interstitial waters of both cores are enriched over the average deep ocean total iodine concentration of $0.44 \mu\text{M}$ (Tsunogai, 1971; Wong and Brewer, 1974) by a maximum factor of ~ 20 for core P6 and ~ 3.6 for P8.

The profiles differ sharply. Core P6 is characterized by a broad linear increase in total iodine concentration to a maximum $9.2 \mu\text{M}$ between 60 and 80 cm depth followed by an exponential decrease to the bottom of the core. In contrast, the dissolved iodine concentration in P8 increases rapidly in the upper 20 cm and appears to gradually approach an equilibrium value with increasing depth. A maximum concentration of $1.58 \mu\text{M}$ is reached at the base of the core.

6. Uptake and diagenesis of the halogens

A possible mechanism of iodine uptake by organic matter has been outlined by Price and Calvert (1977), but little is known about bromine absorption. It is well known that marine organisms concentrate iodine and bromine from sea water, often to levels of 200-300 ppm (e.g. 300 ppm I in diatoms; Bowen, 1966). Some algae such as *Laminaria* sp. contain up to 10,000 ppm I. The consensus of most workers is that iodine is absorbed as iodide and the degree of uptake is limited by the available iodide concentration (Shaw, 1962; Tsunogai and Sase, 1969). The reaction appears to be mediated by a soluble enzyme, "iodide-oxidase" (Kylin, 1930). According to Shaw (1962), iodide, possibly produced by the reducing action on iodate of nitrate-reducing organisms (Tsunogai and Sase, 1969), is oxidized to I_2 by the enzyme which is present on the surface of many algae. The molecular iodine is hydrolyzed to HOI which diffuses through the cell wall and is subsequently reduced back to iodide. This reaction apparently occurs only in the presence of free oxygen; it is strongly inhibited in anoxic conditions (Shaw, 1959; Price and Calvert, 1977).

Table 2. Summary of some published interstitial iodine concentrations in marine sediments.

Reference	Locality and sediment description	Interstitial iodine concentration	Comments
Vinogradov (1939)	Sea of Okhotsk, green mud Barents Sea, grey-green mud, 300 m depth	4.7 μM to 873 μM	Range of seven analyses from various localities. The Barents Sea concentration would appear to be unacceptably high.
Shishkina and Pavlova (1965)	Mediterranean carbonate clayey mud Black Sea sulphide-bearing clay	0.94 μM to 63 μM	Range of reported values for Indian Ocean, Mediterranean and Black Seas. Authors noted a general increase in dissolved iodine content with depth in sediments.
Bojanowski and Paslawska (1970)	Southern Baltic Sea, sandy muds	29-150 μM	Sediments mainly anoxic with high C_{org} contents.
Pavlova and Shishkina (1973)	North Pacific Peruvian continental margin	1.26-180 μM 1.6-7.3 μM	Highest concentrations found in sulphate-depleted oozes of the northern Japan Trench, lowest in oxic (?) brown clays. A regular increase of dissolved iodine with depth was noted where C_{org} in the sediments exceeded 1%.
Wakefield (1978)	Bauer Basin, East Pacific Rise, metaliferous clays	0.5-2.5 μM	Range of several profiles. Very little increase over sea water concentration in highly oxidized clays.
This study	Panama Basin	0.72-9.2 μM	Range of analyses from two cores.

Comparative studies of the iodine and bromine concentrations in oxic and anoxic sediments of the Namibian shelf led Price and Calvert (1977) to postulate that uptake occurs to a much higher degree on plankton seston on the seabed rather than by incorporation into living organisms. They suggested that as much as 80% of the total iodine in oxidized sediments is sorbed by seston.

The detailed pore water profiles of P6 and P8 show clearly that sorbed iodine is subject to diagenesis during burial. From this data and several previously published analyses (Table 2), it is apparent that the magnitude of the pore water iodine enrichment in marine sediments is broadly a function of the organic matter content in the sediments. As a general rule, coastal and continental margin deposits are considerably more enriched in dissolved iodine than organic carbon-poor pelagic clays;

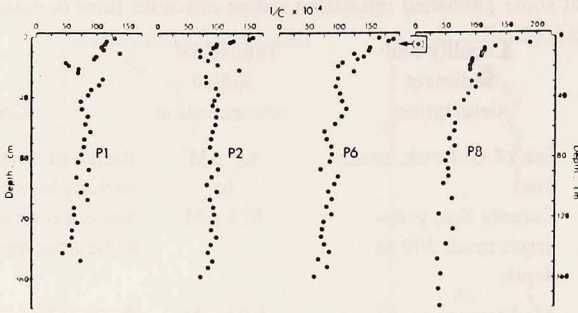


Figure 7. I/C_{org} ratios in Panama Basin area cores. All four surface samples lie considerably below the regression line calculated in Figure 2 and therefore have surface I/C ratios considerably lower than the mean for the Basin.

interstitial waters in hemipelagic sediments fall between these end-members.

The dissolved iodine distribution in core P8 implies that much of the iodine is released near the sediment-water interface and that an equilibrium level is approached at depth. In contrast, the carbon and iodine-enriched horizon at about 60-80 cm depth in P6 acts as the dominant locus of dissolved iodide production in the core so that iodide diffuses along concentration gradients both upward and downward from that band.

Variations in halogen/ C_{org} ratios in the sediments can also provide evidence of the mechanism of halogen diagenesis at depth. Unlike the elemental distributions, the I/C_{org} (Fig. 7) and Br/C_{org} (Fig. 8) ratios differ markedly in the sediments. I/C_{org} ratios decrease exponentially in all four cores to values less than 100×10^{-4} .

The absence of I/C_{org} peaks at depth, irrespective of the iodine and organic matter-enriched horizons in the biogenic cores, indicates that, relative to carbon, the rate of loss of iodine is independent of the concentration at any point in the sediment column. Where organic matter oxidation is most severe near the sediment-sea water interface, the relative rate of loss of iodine is greatest. The rate decreases exponentially upon burial, presumably because bacterial destruction of organic matter becomes progressively less efficient at depth and the remaining iodine becomes increasingly less labile. The first-order decrease in the I/C_{org} ratio is consistent with the observations of Price *et al.* (1970) for shelf sediments.

The absence of a regular decrease in the Br/C_{org} ratio is the most important indicator of the markedly different post-depositional behavior of bromine compared to iodine. In fact the overall *increase* with depth suggests that during diagenesis organically-bound bromine is released at an apparently slower rate than that at which the bulk of organic matter itself is mineralized. This clearly contrasts with the preferential rate of loss of iodine relative to organic carbon. Of the two halogens bromine must be bound much more strongly to organic material.

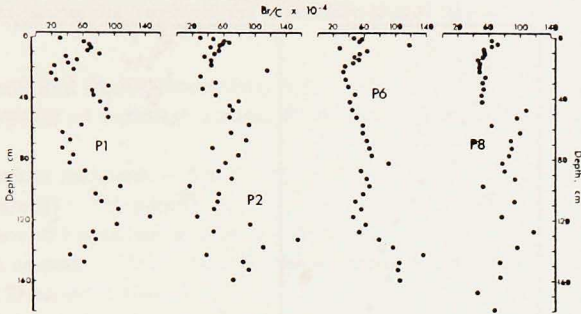


Figure 8. $\text{Br}/\text{C}_{\text{org}}$ ratios in Panama Basin area cores. As for I/C , surface Br/C ratios in these four cores are all less than the mean for Basin surface sediments.

Some insight into the possible halogen binding sites can be gained by using pore water chemistry to compare the relative reactivities of nitrogenous organic substances and iodine within the sediments. The dissolved ammonium profiles for cores P6 and P8 are shown in Figure 9. In core P6, little evidence of increased ammonia production at the 60-80 cm deep halogen and organic carbon-rich horizon exists, in contrast to dissolved iodine. Since iodide and ammonium ions have nearly identical diffusion coefficients (Li and Gregory, 1974), the absence of ammonium enrichment here cannot be due to physical factors. Instead, the contrasting NH_4^+ and I profiles in this core suggest that iodine is much more labile than organic nitrogen during diagenesis. This apparent greater lability of iodine relative to nitrogen suggests that iodine may not be associated with the proteinaceous fraction of organic matter as has been previously postulated (e.g. Price and Calvert, 1973). In addition the contrast between the post-depositional behavior of iodine and bromine discussed above implies that different binding sites for the two elements exist. It is possible, for example, that iodine may react principally with unsaturated carbon to produce such forms as labile halohydrins (March, 1968) whereas bromine may become bonded to a more refractory carbohydrate phase. An experimental investigation of the organic geochemistry of iodine and bromine in marine sediments is clearly required to resolve these diagenetic contrasts.

The evidence presented here has demonstrated that organically-bound iodine is more susceptible to diagenetic remobilization in hemipelagic sediments than the more refractory bromine. The data can also be used to assess whether changes in the long-term rate of uptake of iodine might affect the content of the element in sea water.

In the foraminiferal oozes of the equatorial Pacific (represented in this work by cores P1, P2 and P6) iodine is enriched in historic horizons of high organic carbon content which are believed to be a result of enhanced surface biological productivity during glacial maxima. Radiocarbon dating has clearly shown (Pedersen, 1979)

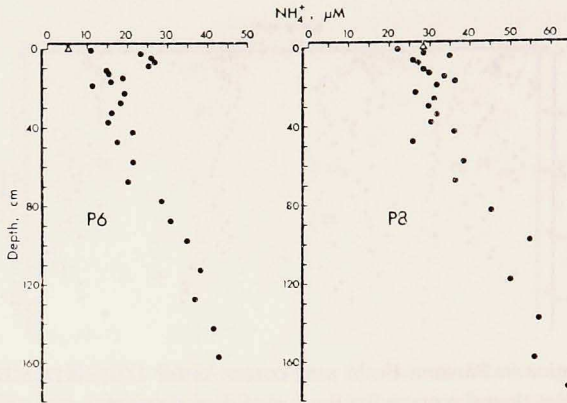


Figure 9. Dissolved ammonium profiles for cores P6 and P8, analyzed by the method of Solorzano (1969), adapted for pore water. Δ = NH_4^+ concentration in supernatant water.

that the carbon peak found at depths of 40-70 cm in P1, P2 and P6 corresponds very closely to the period of maximum advance of the Wisconsin glaciation in the northern hemisphere (about 19,000-14,000 years ago) as originally suggested by Arrhenius (1952). In the central Panama Basin, represented by core P6, the rate of removal of iodine from sea water during the Wisconsin maximum must have been at least twice as high as at present, assuming an invariant $\text{I}/\text{C}_{\text{org}}$ ratio in surface sediments during the past 20,000 years. Simple calculations summarized in Table 3 suggest that if climatically-induced increased production occurred over the entire equatorial productivity belt of the Pacific for a period of several thousand years, a minimum of 0.3 per cent of the Pacific iodine reservoir could have been removed to the sediments by organic matter sorption. This quantity has some significance, especially considering that the assumed organic carbon concentration and sedimentation rate used in the calculations are probably minimum estimates. The calculations suggest that climatic fluctuations may well have a small but measurable importance in regulating the iodine balance in the oceans on a time scale of several mixing cycles.

7. Summary and conclusions

Iodine and bromine correlate positively with organic carbon in Panama Basin surface sediments. Mean $\text{I}/\text{C}_{\text{org}}$ and $\text{Br}/\text{C}_{\text{org}}$ ratios (395×10^{-4} and 146×10^{-4} , respectively) are similar to those in Barents Sea sediments (380×10^{-4} and 120×10^{-4}), demonstrating that the halogen-carbon relationship observed previously for shelf and marginal sea deposits probably applies equally to hemipelagic facies. The congruent distribution of the two halogens and carbon at depth in biogenic eastern equatorial Pacific sediments is well illustrated by distinct mid-depth maxima of all three elements in Galapagos-area cores P1, P2 and P6.

Table 3. Estimate of the proportion of the Pacific iodine reservoir removed by equatorial Pacific sediments during the height of the Wisconsin glacial stage.

Assume:

- i) Areas of equatorial Pacific productivity belt = 1.5×10^7 km².
- ii) Avg. C_{org} content of sediment accumulating during Wisconsin maximum was 1% (dry wt.).
- iii) I/C_{org} in surface sediments = 350×10^{-4}
Therefore [I] = 350 ppm.
- iv) Avg. thickness of I-enriched sediments = 5 cm.
- v) Avg. $CaCO_3$ content = 50%. Then avg. bulk density = 0.43 (calculated from equations of Lyle and Dymond, 1976).
Therefore volume of enriched sediment is
 7.5×10^{11} m³ containing 11×10^{13} g iodine.
- vi) Pacific Ocean vol. = 7.2×10^{20} l (Riley & Chester, 1971). Avg. iodine concentration = 0.44 μ M
Therefore Pacific contains 4×10^{19} g I.

Hence during the Wisconsin maximum, about

$$\frac{11 \times 10^{13}}{4 \times 10^{19}} = 0.3\%$$

of the Pacific iodine reservoir could have been removed to the sediments.

Iodide appears to be the principal dissolved species in interstitial water in Panama Basin sediments; at a detection limit of 0.06 μ M, no iodate was found. As a consequence of post-depositional metabolization of organic matter the interstitial iodine concentration is enriched over the sea water iodine level by a maximum factor of ~ 20 . In core P6, the iodine-rich band at mid-depth is clearly the major contributor of dissolved iodine in the core.

A smooth exponential decrease of the I/C_{org} ratio with depth is characteristic of Panama Basin sediments. The decrease is independent of concentration and indicates a regular preferential loss of iodine relative to carbon during diagenesis.

In considerable contrast to iodine, peaks at depth in Br/C_{org} profiles suggest that bromine is relatively refractory during post-depositional alteration of organic matter. The dissimilar behavior of the two halogens implies bonding by different organic ligands, with iodine being diagenetically more labile than bromine.

Calculations, based on extrapolation of the iodine distribution reported here, suggest that a small fraction of the Pacific iodine inventory could be removed to equatorial Pacific sediments during glacial maxima. At such times, higher euphotic zone productivity results from enhanced upwelling along the equatorial divergence, and the underlying sediments are subject to an increased input of iodine-sorbing organic detritus. Pleistocene climatic fluctuations may therefore be of some minor importance in regulating the iodine balance in the sea.

Acknowledgments. We are very grateful to the officers and crew of R.R.S. *Shackleton* for their assistance and cooperation during Leg II of cruise 2/1976 in the eastern Pacific. Dr. Victor

Truesdale of the Institute of Hydrology, Wallingford, generously made available his autoanalyzer facilities for dissolved iodine determination, and Dr. Joris Geiskes kindly provided samples from the Pleiades Box Core collected by SIO in 1976.

One of us (T.F.P.) gratefully acknowledges the receipt of an Edinburgh University Post-graduate Studentship over the years 1975-1978.

This work was supported by the Natural Environment Research Council, under grant GR3/2716.

REFERENCES

- Arrhenius, G. O. 1952. Sediment cores from the East Pacific, in Repts. Swedish Deep-Sea Exped., H. Pettersson, ed., Vol. 5, Fasc. 1. 227 pp.
- Bojanowski, R. and S. Paslawska. 1970. On the occurrence of iodine in bottom sediments and interstitial waters of the southern Baltic Sea. *Acta Geophys. Pol.*, 18, 177-286.
- Bowen, H. J. M. 1966. Trace elements in Biochemistry. Academic Press, London. 241 pp.
- Chapman, P. and P. S. Liss. 1977. The effect of nitrite on the spectro-photometric determination of iodate in seawater. *Mar. Chem.*, 5, 243-249.
- Kylin, H. 1930. Über die jodidsaltende Fähigkeit der Phaephycean. *Z. Physiol. Chem.*, 191, 200-210.
- Li, Y. H. and S. Gregory. 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta*, 38, 703-714.
- Lyle, M. W. and J. Dymond, 1976. Metal accumulation rates in the Southeast Pacific—errors introduced from assumed bulk densities. *Earth Planet. Sci. Lett.*, 30, 164-168.
- March, J. 1968. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 1st edition. McGraw-Hill, New York. 1098 pp.
- Moore, T. C. Jr., G. R. Heath and R. O. Kowsmann. 1973. Biogenic sediments of the Panama Basin. *J. Geol.*, 81, 458-472.
- Pavlova, G. A. and O. V. Shishkina. 1973. Accumulation of iodine in interstitial water during metamorphism in relation to the iodine distribution in Pacific sediments. *Geochem. Int.*, 10, 804-813.
- Pedersen, T. F. 1979. The geochemistry of sediments of the Panama Basin, eastern equatorial Pacific Ocean. Unpubl. Ph.D. Thesis, Univ. of Edinburgh, 235 pp.
- Price, N. B., S. E. Calvert and P. G. W. Jones. 1970. The distribution of iodine and bromine in the sediments of the Southwestern Barents Sea. *J. Mar. Res.*, 28, 22-34.
- Price, N. B. and S. E. Calvert. 1973. The geochemistry of iodine in oxidized and reduced Recent marine sediments. *Geochim. Cosmochim. Acta*, 37, 2149-2158.
- 1977. The contrasting geochemical behaviours of iodine and bromine in Recent sediments from the Namibian shelf. *Geochim. Cosmochim. Acta*, 41, 1769-1775.
- Riley, J. P. and R. Chester. 1971. *Introduction to Marine Chemistry*. Academic Press, London. 465 pp.
- Shaw, T. I. 1959. The mechanism of iodide accumulation by the brown sea weed *Laminaria digitata*. I. The uptake of ¹³¹I. *Roy. Soc. London, Proc.*, B150, 356-371.
- 1962. Halogens in algae, in *Physiology and Biochemistry of Algae*, R. A. Lewin, ed., Academic Press, London, 922 pp.
- Shishkina, D. V. and G. A. Pavlova. 1965. Iodine distribution in marine and oceanic bottom muds and in their pore fluids. *Geochem. Int.*, 2, 559-565.
- Sillén, L. G. 1961. The physical chemistry of sea water, in *Oceanography*, M. Sears, ed., Amer. Ass. Adv. Sci., Washington, D.C.
- Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolphthorite method. *Limnol. Oceanogr.*, 14, 799-801.

- Sugawara, K. and K. Terada. 1957. Iodine distribution in the western Pacific Ocean. *J. Earth Sci. Nagoya Univ.*, 5, 81–102.
- Truesdale, V. W. and C. P. Spencer. 1974. Studies on the determination of inorganic iodine in sea water. *Mar. Chem.*, 2, 33–47.
- Truesdale, V. W. and P. Chapman. 1976. Optimisation of a catalytic procedure for the determination of total iodine in sea water. *Mar. Chem.*, 4, 29–42.
- Tsunogai, S. 1971. Determination of iodine in sea water by an improved Sugawara method. *Anal. Chim. Acta*, 55, 444–447.
- Tsunogai, S. and T. Sase. 1969. Formation of iodide-iodine in the ocean. *Deep-Sea Res.*, 16, 489–496.
- Van Andel, Tj. H., G. R. Heath, B. T. Malfait, D. F. Heinrichs and J. I. Ewing. 1971. Tectonics of the Panama Basin, eastern equatorial Pacific. *Geol. Soc. America Bull.*, 82, 1489–1508.
- Vinogradov, A. P. 1939. Iodine in marine muds. To the problem of the origin of iodine-bromine waters in petroliferous regions (in Russian). *Tr. Biogeokhim. Lab. Akad. Nauk SSSR*, 5, 19–32 (English, pp. 33–46).
- Wakefield, S. J. 1978. The iodine content of sediments and pore waters from the region of the East Pacific Rise (Abstract). *Quart. J. Geol. Soc. London*, 135, p. 478.
- Wong, G. T. F. and P. G. Brewer. 1974. The determination and distribution of iodate in South Atlantic waters. *J. Mar. Res.*, 32, 25–36.
- 1977. The marine chemistry of iodine in anoxic basins. *Geochim. Cosmochim. Acta*, 41, 151–159.