

Natural organobromine in marine sediments: New evidence of biogeochemical Br cycling

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[1] Organobromine (Br_{org}) compounds, commonly recognized as persistent, toxic anthropogenic pollutants, are also produced naturally in terrestrial and marine systems. Several enzymatic and abiotic bromination mechanisms have been identified, as well as an array of natural Br_{org} molecules associated with various marine organisms. The fate of the carbon-bromine functionality in the marine environment, however, remains largely unexplored. Oceanographic studies have noted an association between bromine (Br) and organic carbon (C_{org}) in marine sediments. Even so, there has been no direct chemical evidence that Br in the sediments exists in a stable form apart from inorganic bromide (Br_{inorg}), which is widely presumed conservative in marine systems. To investigate the scope of natural Br_{org} production and its fate in the environment, we probed Br distribution and speciation in estuarine and marine sediments using in situ X-ray spectroscopy and spectromicroscopy. We show that Br_{org} is ubiquitous throughout diverse sedimentary environments, occurring in correlation with C_{org} and metals such as Fe, Ca, and Zn. Analysis of sinking particulate carbon from the seawater column links the Br_{org} observed in sediments to biologically produced Br_{org} compounds that persist through humification of natural organic matter (NOM). Br speciation varies with sediment depth, revealing biogeochemical cycling of Br between organic and inorganic forms as part of the burial and degradation of NOM. These findings illuminate the chemistry behind the association of Br with C_{org} in marine sediments and cast doubt on the paradigmatic classification of Br as a conservative element in seawater systems.

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1. Introduction

[2] Organobromine (Br_{org}) chemicals are synthesized industrially for various uses and have gained notoriety as persistent environmental toxins. Polybrominated diphenyl ether (PBDE) flame retardants, for instance, are widely used in

consumer products and now have a global environmental distribution, with bioaccumulation through the food chain [Darnerud, 2003; Norstrom *et al.*, 2002; Santillo and Johnston, 2003]. Environmental bromine (Br) is thought to exist as inorganic bromide (Br_{inorg}), in the $-I$ oxidation state. Br_{inorg} is presumed sufficiently unreactive for use as a conservative tracer in hydrological studies [Simmons *et al.*, 1992; Tanner and Sukias, 1995; Weaver *et al.*, 2003].

[3] However, Br_{inorg} can convert to Br_{org} via natural mechanisms, through abiotic [Keppler *et al.*, 2000; Pelizzetti and Calza, 2002] and enzymatic [Butler and Carter-Franklin, 2004; Theiler *et al.*, 1978] pathways. Marine organisms in particular are known to synthesize a variety of low molecular weight Br_{org} molecules, including bromoalkanes, bromo-ketones, bromopyrroles, bromophenols, bromophycolides, and PBDE analogs, as probable means of chemical defense [Dembitsky, 2002; Gribble, 2000; La Barre *et al.*, 2010; Lane *et al.*, 2009; Laturmus *et al.*, 2000; Wever *et al.*, 1991]. Several naturally produced volatile bromocarbons have been linked to stratospheric ozone depletion [Carpenter and Liss, 2000; Quack *et al.*, 2004]. Approximately 2000 natural Br_{org}

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compounds have been identified, the majority of marine origin [Gribble, 2003], but the fate of natural Br_{org} in the water column and sedimentary environment remains largely unexplored. In fact, the classification of Br as a conservative element in seawater [Morris and Riley, 1966] has endured for decades.

[4] Several studies have provided clues that Br does not exist exclusively as Br_{inorg} in marine sediments by revealing strong correlations between total Br and organic carbon (C_{org}) concentrations in sediment columns [Mayer *et al.*, 1981; Price *et al.*, 1970; Pruyssers *et al.*, 1991; Tenhaven *et al.*, 1988; Ziegler *et al.*, 2008]. Tellingly, total Br has been found to be enriched in the upper portions of sediment cores from the Antarctic coast [Santos *et al.*, 2007]. These oceanographic studies did not explore the chemical speciation of Br in the sediments and drew no clear conclusions about the molecular basis for the observations. Few efforts have been made to probe the dynamics of Br in the environment, and thus, the paradigmatic classification of marine Br as conservative Br_{inorg} persists. The scarcity of research in this area may be partly attributable to the disciplinary disconnect between the oceanographic studies that examine elemental profiles in sediments and the natural products chemistry or ecological studies that typically report discoveries of biogenic Br_{org} molecules.

[5] Elucidating the chemical speciation of Br associated with C_{org} in environmental samples presents exceptional challenges due to the complex macromolecular structure of natural organic matter (NOM). The existence of high molecular weight brominated NOM in sediments has been proposed based on detection of brominated degradation products [Johansson *et al.*, 1994] and the “adsorbable organohalogen” (AOX) sum parameter, following reaction with activated carbon [Müller *et al.*, 1996]. A recently developed technique relies on combustion followed by ion chromatography to measure the concentrations of organohalogens in peat samples [Putschew *et al.*, 2003]. This method was used to demonstrate the formation of Br_{org} during humification in terrestrial peat bogs and show that more than 90% of Br in these environments is bonded to carbon [Biestler *et al.*, 2006, 2004]. Degradative techniques, however, are prone to induce chemical alterations in natural samples, while the AOX assay does not distinguish among halogens and is subject to interferences from inorganic halides and nonhalogenated organic molecules [Berger, 1984; Harper, 1984].

[6] In order to investigate the role of different sedimentary systems as sinks of naturally produced Br_{org} , we used synchrotron-based X-ray spectroscopic and spectromicroscopic techniques to probe Br distribution and speciation in coastal and deep marine sediments. These element-specific methods remove the risks of incomplete extraction or chemical alterations of samples. Br_{org} was detected at various concentrations in all sediments examined, including those from (1) deep marine systems [Bower’s Ridge, Bering Sea; northern continental shelf, Bering Sea; the Antarctic Zone in the west Pacific sector of the Southern Ocean] and (2) coastal and estuarine systems [Barnegat Bay, NJ, USA; Cape Cod, MA, USA]. For several of the coastal and marine systems, chemical profiles were established as a function of sediment

column depth, shedding light on the biogeochemical cycling of Br.

2. Materials and Methods

2.1. Sample Details

2.1.1. Coastal and Deep Sea Sediments

[7] Sediment cores (30.5 cm depth, 5.1 cm diameter; stainless steel AMS soil core sampler, American Falls, ID) were taken from coastal sites in Barnegat Bay, NJ, and Cape Cod, MA. Cores were collected in removable butyrate plastic retaining liners and secured with polyethylene liner caps. In the laboratory, cores were stored horizontally at 4°C until further processing. For quantitative analysis of Br_{org} and Br_{inorg} species, intact cores were divided into horizontal sections of 3–5 cm in height using a Dremel™ saw. Portions of these sediment sections were set aside at 4°C, still wet, for Br speciation analysis by X-ray absorption spectroscopy. For total Br quantification, the remainder of the sediment material was air-dried over several days before pulverization with a mortar and pestle. The resulting powder was mixed with a cohesive matrix material, NaNO_3 (~150 mg sediment + ~250 mg NaNO_3). Pellets were formed from this mixture using a 13 mm die with tungsten carbide anvils beneath 10 tons of pressure in a standard hydraulic laboratory press. For X-ray spectromicroscopic analysis of elemental distributions, cores were brought intact to the synchrotron beamline, where the butyrate plastic core liner was sliced open vertically with the Dremel™ saw and sections of the core were delicately removed and mounted with minimal disturbance of the sediment grains.

[8] Wet, presectioned, mixed sediment subsamples from Bering Sea and Southern Ocean cores were provided courtesy of D. Sigman (Department of Geosciences, Princeton University; refer to Lehmann *et al.* [2005] for geographical and sampling details on the Bering Sea northern continental shelf “MC5” and Bower’s Ridge “MC24” samples and Robinson *et al.* [2004] for details on the Southern Ocean “MC4” samples). These sediments were analyzed in situ for Br speciation by X-ray absorption spectroscopy and elemental distribution by X-ray spectromicroscopy. For total Br quantification, sediments were freeze-dried, pulverized, and pelletized as described previously [Leri *et al.*, 2006]. To assess the solubility of Br species, two MC24 samples (2–3 cm and 18–19 cm) were analyzed before and after vigorous rinsing with deionized water.

2.1.2. Sinking Particulates From Water Column Sediment Traps

[9] Dry, elutriated particulates from the water column in the Sea of Okhotsk were provided by D. Sigman (Department of Geosciences, Princeton University). This material was collected in sediment traps deployed at 258 and 1061 m every few months over the course of a cruise in 1990–1991 [Honda *et al.*, 1997]. Dry, elutriated particulates from the water column in the Ligurian Sea were provided by C. Lee (Marine Sciences Research Center, SUNY Stony Brook). This material was collected in sediment traps deployed at 200 m in May 2004 [Goutx *et al.*, 2007]. In both cases, the quantities of sediment trap material available were insuffi-

cient to allow total Br quantification, but the samples were subjected to qualitative Br speciation and elemental distribution analyses.

2.2. Quantification of Br_{org} and Br_{inorg}

[10] A novel quantitative method described previously [Leri *et al.*, 2006] was used to measure absolute Br_{org} and Br_{inorg} concentrations in sediment samples through a combination of X-ray fluorescence (XRF) and Br 1s X-ray absorption near-edge structure (XANES) spectroscopies. Br 1s XANES spectroscopy was performed at beamline X23A2 at the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, Upton, NY) and at beamline 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL, Stanford Linear Accelerator Center, Menlo Park, CA). For total Br concentration measurements, Br K α emission spectra were collected at NSLS beamline X26A.

2.3. X-ray Microanalysis and Br 1s μ m-XANES Spectroscopy

[11] The micron (μ m) scale distribution and speciation of Br were established in heterogeneous natural samples using synchrotron-based X-ray spectromicroscopic techniques involving (1) μ m-scale X-ray fluorescence (μ -XRF) imaging of elemental distributions and (2) establishment of Br speciation through μ -XANES spectroscopy using a focused beam [Bertsch and Hunter, 2001]. X-ray spectromicroscopic studies were performed on beamline 10.3.2 [Marcus *et al.*, 2004] at the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory, Berkeley, CA).

[12] Sediment samples were analyzed with no chemical preparation, mounted between X-ray clean polyfilm and Kapton tape on metal alloy sample holders designed to fit the movable stage in the X-ray beam path. The polyfilm-covered side of the sample was exposed to the incoming beam at a 45° angle. The seven-element Ge detector was oriented at 90° from the X-ray beam in the plane of the sample. Micro-XRF elemental distribution maps were acquired at 16 μ m² resolution by training the microfocussed X-ray beam on the sample while the stage moved in the horizontal and vertical directions. The X-ray beam was set to the maximum size available at the focus of the beamline, 16 (horizontal) \times 7 (vertical) μ m². Fluorescence counts were collected exciting at 14 keV, producing image “maps” of select elemental distributions, including Br, Zn, Cu, Ni, Co, Fe, Mn, Ti, and Ca. Micro-XRF maps were processed using the XY-mapping software associated with beamline 10.3.2. Cross correlations between Br and other elements were deduced quantitatively through Pearson-like, pixel-by-pixel comparison of the two elements’ μ -XRF maps. The resulting Pearson *r* correlation coefficient quantifies the degree to which two elemental distributions are related, either inversely or directly, with a range of -1.00 to $+1.00$.

[13] To explore the spatial variability of Br speciation, areas of interest on the μ -XRF maps were probed via Br 1s μ -XANES spectroscopy. For Br 1s μ -XANES spectra, sample fluorescence was measured over an energy range of 13,415 to 13,550 eV. Spectra were acquired using a 0.6 eV step size around the *K* absorption edge and 0.9–2.5 eV step

sizes above and below the edge. Dwell times at each point were set to at least 3 s; the monochromator was allowed to settle for 0.5 s between steps. The energy of the monochromator was calibrated to the inflection point in the Br 1s XANES spectrum of solid KBr, defined at 13,474 eV. The precise value of the inflection point was determined from the maximum of the first derivative of the spectrum.

[14] Br 1s μ -XANES data were processed using EXAFS Editor and WinXAS version 2.0 [Ressler, 1998]. EXAFS Editor, a data analysis utility associated with beamline 10.3.2, was used for preliminary inspection, dead time correction, and averaging of fluorescence scans. Averaged scans were imported into WinXAS for energy calibration, background subtraction, and normalization. A smooth background was obtained by fitting a first-order polynomial to the preedge region, and the edge jump was normalized to 1.0 with another first-order polynomial fit to the postedge region. This normalization allows for comparative analysis of spectral features in the near-edge region, where absorption intensity is dependent on Br speciation. WinXAS was also used for nonlinear least squares fitting of sample spectra with data from Br-containing standards to establish the speciation of Br.

2.4. Quantification of C_{org}

[15] C_{org} concentrations in sediment samples were measured using an autosampler-equipped Carlo Erba NA-1500 Elemental Analyzer (CE Elantech, Lakewood, NJ). Carbonate was removed from preweighed sediments prior to analysis by acidification with excess 5% H₂SO₃. Acidified samples were weighed into precombusted tin boats with excess tin powder to promote oxidation. Acetanilide (C₈H₉NO) was used as a calibration standard.

3. Results and Discussion

3.1. Br 1s XANES Spectroscopy

[16] Drawing on synchrotron radiation, XANES spectroscopy is sensitive to the bonding state of Br, allowing distinctions to be drawn between Br_{inorg} and Br_{org} species in natural samples without subjecting them to procedures that amplify the risk of inadvertent bromination or incomplete recoveries.

[17] The intense increase in X-ray absorption around 13,474 eV (the Br *K* absorption edge) and the spectral features in the near-edge region correspond to electronic transitions from the Br-1s shell to empty atomic and molecular orbitals of Br-4*p* character. For Br_{inorg} compounds, the energy of the Br transition shifts to higher values with an increase in Br oxidation state. For example, Br(V) in sodium bromate (Figure 1, spectrum d) exhibits an absorption maximum at 13,478.1, whereas Br(-I) in aqueous KBr (Figure 1, spectrum c) absorbs at 13,477.3 eV. (Energy values are arbitrary, quoted for illustration of relative differences.) By contrast, Br_{org} compounds give rise to discrete low-energy peaks around 13,473 eV, as in 4-bromophenol (Figure 1, spectrum a) and 1-bromoeicosane (Figure 1, spectrum b). These sharp features correspond to the 1s \rightarrow π^* or σ^* transitions associated with the C-Br bonds and differ slightly in absorption

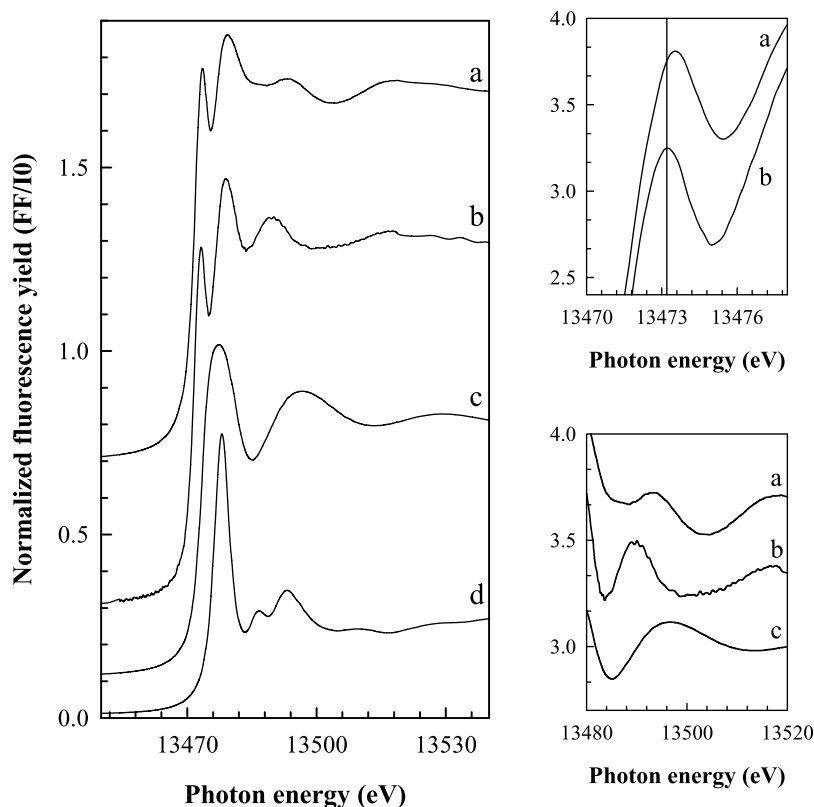


Figure 1. (left) Normalized Br 1s X-ray absorption near-edge structure (XANES) spectra of model compounds: spectrum a, 4-bromophenol; spectrum b, 1-bromoeicosane; spectrum c, KBr (aq), amplitude $\times 0.7$; spectrum d, sodium bromate, amplitude $\times 0.25$. (top right) Amplitudes enhanced 3X. (bottom right) Amplitudes of spectra a and b enhanced 3X.

energy depending on the C-Br bond length, as becomes evident through comparison of the aliphatic (bromoeicosane) and aromatic (bromophenol) Br_{org} standards (Figure 1, top right). Postedge features also vary depending on the coordination environment of Br (Figure 1, bottom right). X-ray absorption fine structure features have been theoretically modeled to shed light on the molecular structure of brominated pollutants [Bergknut *et al.*, 2008].

[18] The substantial spectral variations depending on the oxidation state and coordination environment of Br allow the relative contributions of Br_{inorg} and Br_{org} to total Br in natural sample spectra to be estimated via least squares fitting with spectra of representative model compounds. However, while Br 1s XANES spectroscopy illuminates the *local* coordination environment of Br, it offers little information on the comprehensive size and structure of Br-containing molecules in the natural samples.

3.2. Geochemistry of Br as a Function of Sediment Depth and C_{org} Content

[19] Chemical profiles of coastal and marine sediment cores reveal the variation of Br_{org} concentration as a function of sediment depth and NOM content (Table 1). In opal-rich Southern Ocean Antarctic sediments composed of Holocene

diatomaceous ooze [Robinson *et al.*, 2004], Br speciation changes from Br_{org^-} to Br_{inorg} -dominated going from 0 to 16 cm down the sediment column (Figure 2). This transformation is signaled in the spectra by the narrowing and amplification of the main Br 1s XANES transition, with the disappearance of the Br_{org} shoulder (Figure 2a). The Br_{inorg} appears in aqueous form, resembling the KBr (aq) standard (compare Figure 2a, spectrum e, with Figure 1, spectrum c). The absolute Br_{org} concentration decreases sharply below the sediment-water interface, falling below the detection limit (<1 ppm) by 14–16 cm (Figure 2b). The C_{org} concentration also declines with depth, though less precipitously than Br_{org} (Figure 2b). The decrease in the $\text{Br}_{\text{org}}:\text{C}_{\text{org}}$ ratio with sediment depth (Table 1) suggests that the Br_{org} in these sediments constitutes a relatively labile fraction of NOM.

[20] Comparable trends appear in sediments from the Bering Sea sampling site located at the base of the northern continental shelf, at a water depth of 3349 m (Figure 3). Total Br concentrations at this location are lower than those in the Antarctic sediments (Table 1), possibly because the Bering Sea is less saline than the open ocean and/or because the sediments have a larger fraction of terrestrially derived NOM, which originates under lower background Br concentrations. The sediments are rich in C_{org} , likely owing to

Table 1. Br Speciation, Concentration, and Total Organic Carbon in Sediments^a

Depth Below Sediment-Water Interface (cm)	Br _{inorg} (ppm)	Br _{org} (ppm)	Total [Br] (ppm)	Total [C _{org}] (g/kg)	Br _{org} :C _{org} Ratio/10 ⁻³
<i>Antarctic Pacific</i>					
0–0.5	201	108	309	ND	ND
0.5–1	108	36	144	5.5 ± 0.1	6.5
2–2.5	126	14	140	4.3 ± 0.2	3.3
7–8	190	10	200	3.3 ± 0.2	3.0
14–16	130	<1	130	2.6 ± 0.1	UD
<i>Bering Sea (Northern Continental Shelf)</i>					
2	91	59	150	13.1 ± 0.1	4.5
7	79	60	139	12.0 ± 0.3	5.0
13	66	28	94	11.7 ± 0.3	2.4
19	83	28	111	10.8 ± 0.1	2.6
<i>Bering Sea (Bower's Ridge)</i>					
2–3	162	8	170	ND	ND
4–5	118	6	124	7.2 ± 0.1	0.8
8–9	52	42	94	8.9 ± 0.1	4.7
18–19	29	16	45	8.7 ± 0.9	1.8
28–29	27	33	60	18.0 ± 0.8	1.8
34–35	71	47	118	10.9 ± 0.4	4.3
<i>Cape Cod, MA, Estuary</i>					
0–3.5	12	18	30	4.3 ± 0.8	4.2
4–9	7	3	10	0.9 ± 0.2	3.3
9–16	8	3	11	1.1 ± 0.3	2.7
16–20	7	3	10	0.4 ± 0.1	7.5
20–25	8	<1	8	0.3 ± 0.1	UD
<i>Barnegat Bay, NJ</i>					
7–9 cm (organic lens included)	4	2	6	0.7 ± 0.1	2.9

^aND, not determined; UD, undefined.

the high biological productivity characteristic of the Bering Sea continental shelf, in combination with the physical characteristics of the steep slope channeling large quantities of NOM into the sediments below [Lehmann *et al.*, 2005]. The C_{org} concentration decreases steadily with sediment depth but remains high even at >10 cm, which may account for the greater Br_{org} concentrations relative to the Antarctic sediments at similar depths (Table 1). At the Bering Sea northern continental shelf site, the Br_{org}:C_{org} ratio plunges dramatically at deeper depths, again suggesting that the Br_{org} component is a comparatively labile form of NOM.

[21] These observations resonate with recent findings in sediments from coastal Louisiana, where increasing total Br concentrations were used as a proxy for increasing content of marine (as opposed to terrestrially) derived NOM [Mayer *et al.*, 2007]. In the Louisiana sediments, the total Br:C_{org} ratio decreases with sediment depth, which the authors interpreted as enhanced degradation of the marine fraction of NOM during diagenesis.

[22] Sediments from Bower's Ridge in the Bering Sea (water depth ~714 m) deviate from the Br geochemical patterns described above. In these sediments, Br speciation is dominated by Br_{inorg} near the sediment-water interface and Br_{org} at sediment depths of >8 cm (Figure 4a). In these sediments, Br_{org} concentration fluctuates and increases

overall down the 35 cm sediment column, as does C_{org} concentration (Figure 4c). The increasing NOM content with depth is most likely attributable to the low sedimentation rates at this location, which make the effects of past deglaciation apparent at shallow depths in relation to other cores [Cook *et al.*, 2005].

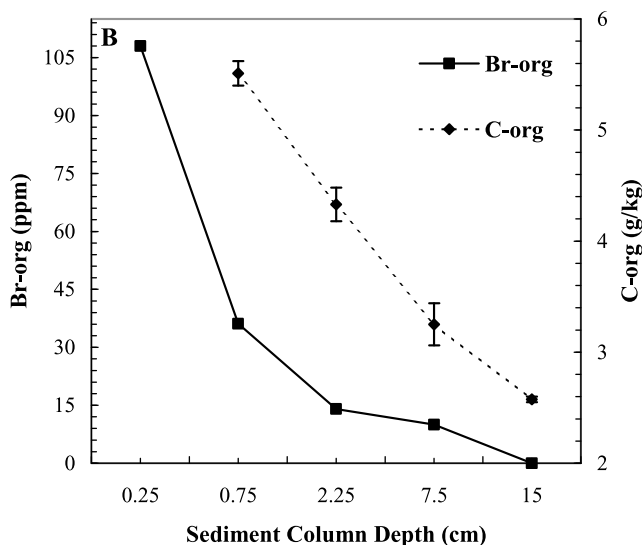
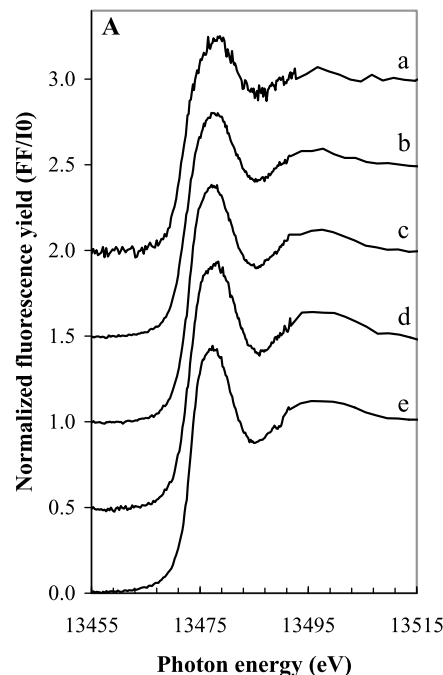


Figure 2. Data from homogenized Antarctic Pacific sediment sections. (a) Variation in Br speciation with sediment column depth. Normalized Br 1s bulk XANES spectra: spectrum a, 0–0.5 cm; spectrum b, 0.5–1 cm; spectrum c, 2–2.5 cm; spectrum d, 7–8 cm; spectrum e, 14–16 cm. (b) Relationships between depth, Br_{org} and C_{org} concentrations.

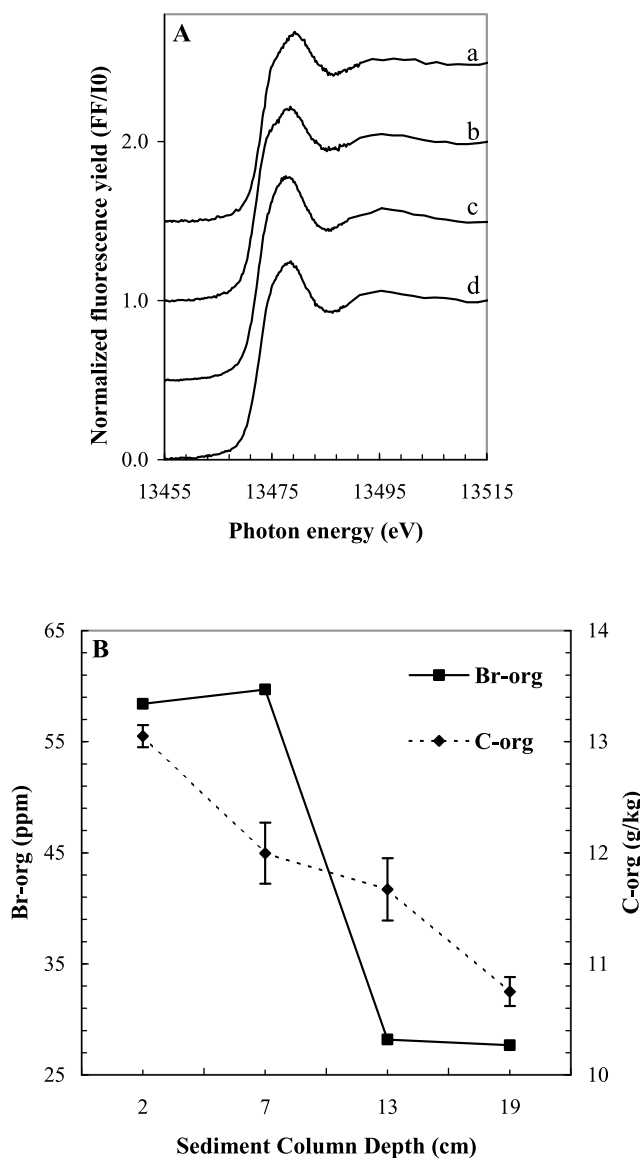


Figure 3. Data from homogenized Bering Sea (northern continental shelf) sediment sections. (a) Variation in Br speciation with sediment column depth. Normalized Br 1s bulk XANES spectra: spectrum a, 2 cm; spectrum b, 7 cm; spectrum c, 13 cm; spectrum d, 19 cm. (b) Relationships between depth, Br_{org} , and C_{org} concentrations.

[23] Rinsing Bower's Ridge sediments with deionized water easily removes Br_{inorg} , revealing strong Br_{org} transitions in samples from shallow and deep sections of the core (Figure 4b). This indicates that Br_{inorg} exists in a soluble form, probably inhabiting sediment pore waters. The Br_{org} revealed in the XANES signal after rinsing may form part of macromolecular sediment NOM or else undergo strong sorption interactions in the sediments, making it resistant to removal by vigorous aqueous rinsing.

[24] In estuarine sediments from Cape Cod, MA, Br displays geochemical trends similar to those observed in the

Antarctic and Bering Sea continental shelf sediments. Br_{inorg} accounts for an increasing proportion of total Br with depth in the 25 cm sediment column (Figure 5a). Br_{org} concentration decreases sharply below the sediment-water interface, closely paralleling the drop in C_{org} (Figure 5b).

[25] This investigation of Br geochemistry as a function of depth and NOM content reveals a general correlation between Br_{org} and C_{org} in estuarine and marine sediments. In most of the locations examined, Br speciation changes with sediment depth from Br_{org} - to Br_{inorg} -dominated, and both Br_{org} and C_{org} concentrations decrease with depth. In the anomalous case of the Bower's Ridge sediments, Br speciation changes from Br_{inorg} - to Br_{org} -dominated with depth. However, the resemblance in fluctuation patterns of Br_{org} and C_{org} concentrations with depth in the Bower's Ridge sediments appears sufficient to uphold the general correlation between Br_{org} and C_{org} . In the marine environments, the C_{org} - Br_{org} correlations are imperfect, which could be attributable to variable sources of NOM in the sediments, with multiple types of Br_{org} produced through different biotic and abiotic pathways.

3.3. Spatial Distribution of Br and Correlations of Br With Other Elements

[26] High-resolution spectromicroscopic images of Br distribution in undisturbed sediment core sections reveal a spatial correlation between C_{org} and Br_{org} that reinforces the association apparent in the bulk measurements. Sediment cores from shallow waters in Barnegat Bay, NJ, exhibit distinct "lenses" of dark-colored NOM approximately 8 cm below the sediment-water interface. The organic lenses coincide with areas of radically elevated Br concentration (Figure 6a). Br 1s μ -XANES spectra reveal the Br associated with NOM to exist as Br_{org} , with strong Br_{org} transitions characterizing spectra acquired within the region of the organic lens (Figure 6c, spectra b and c). By contrast, in areas of dilute Br concentration in the sediment, spatially removed from the organic lens, Br speciation is inorganic (Figure 6c, spectrum a). Such images provide a dramatic illustration of Br enrichment and fractionation in areas of high NOM content. Homogenization of the sediment section analyzed in Figure 6 resulted in a bulk Br speciation measurement of 65% Br_{inorg} and 35% Br_{org} (Figure 6c, spectrum d).

[27] The correlation of C_{org} and Br_{org} is substantiated by the coincidence of NOM and Br_{org} with metal cations. An example of such associations becomes qualitatively manifest through comparison of the fluorescence images of Br and Fe/Mn in the New Jersey bay sediment section (Figures 6a and 6b). The coincidence of elevated Fe/Mn concentrations with the organic lens could result from sorption interactions between metal cations and NOM. The μ -XRF maps do not indicate whether these metals are in the mineral phase, but in principle they could form authigenic oxide phases in decaying organic aggregates during diagenesis. Strong cross correlations between Br and numerous cations, including Zn, Fe, Mn, Ni, and Ca, were calculated through Pearson-like analysis of spatial elemental distributions in the sediment, though the calculations likely exhibit some bias toward

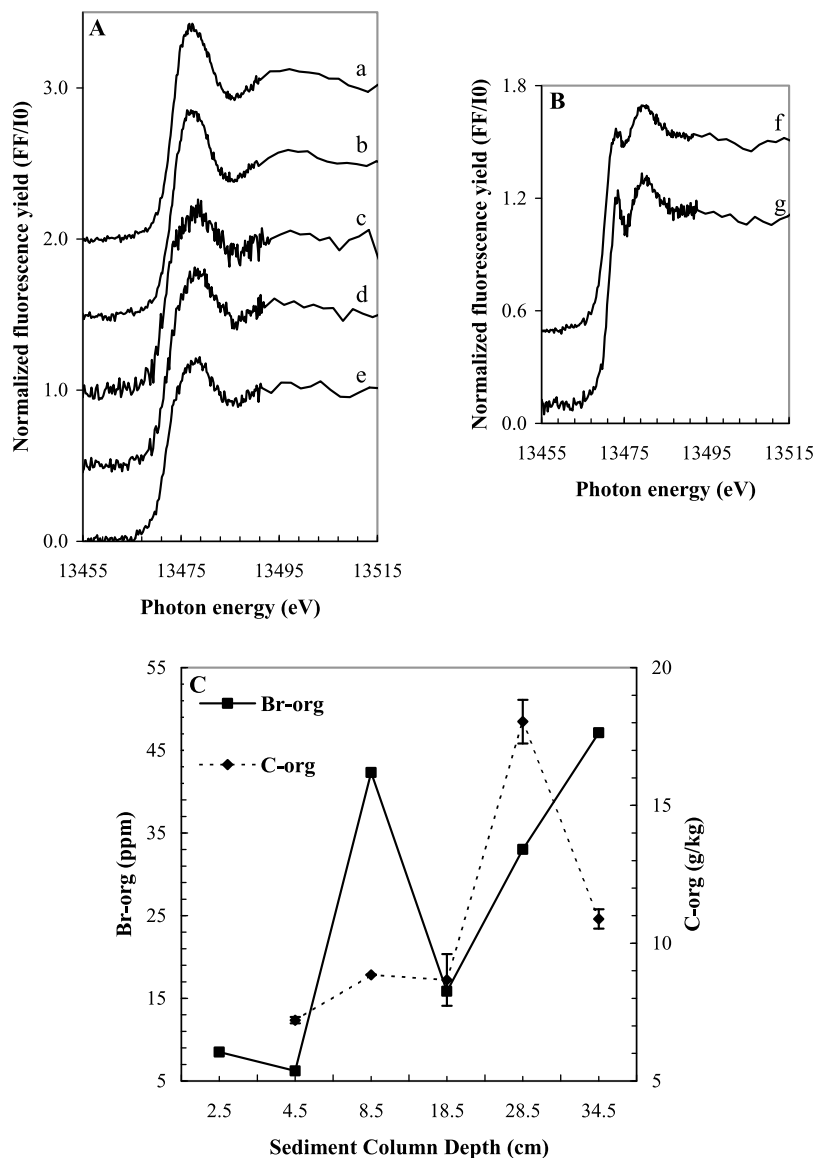


Figure 4. Data from homogenized Bering Sea (Bower's Ridge) sediment sections. (a and b) Variation in Br speciation with sediment column depth. Normalized Br 1s bulk XANES spectra: spectrum a, 2–3 cm; spectrum b, 4–5 cm; spectrum c, 8–9 cm; spectrum d, 18–19 cm; spectrum e, 34–35 cm; spectrum f, 2–3 cm (rinsed); spectrum g, 18–19 cm (rinsed). (c) Relationships between depth, Br_{org} and C_{org} concentrations.

positive correlations due to the irregular density of the sediment surface (see auxiliary material).¹

[28] The spatial distribution and μ -speciation of Br in sediments undergo striking changes with depth. Close to the sediment-water interface in undisturbed Cape Cod estuarine sediments, Br distribution is highly heterogeneous, concentrated in nebulous aggregates spanning several mm^2 (Figure 7a). Br appears most concentrated in such clusters at least as far as 10–13 cm down the sediment column

(Figure 7b). Br μ -speciation in these aggregates is predominantly organic (Figure 7c).

[29] By contrast, at 23–25 cm below the sediment-water interface, Br appears in a more uniform and diffuse distribution, concentrated between mineral grains, in areas of low Fe concentration (Figures 8a and 8b). The speciation of Br in these interstitial spaces is chiefly inorganic (Figure 8c, spectra b–d). Reducing conditions at deeper depths in the sediment column could encourage reductive debromination of Br_{org} moieties by microorganisms, with consequent release of Br_{inorg} ion into pore waters [Ahn *et al.*, 2003; Biester *et al.*, 2006; Müller *et al.*, 1996]. Studies of element

¹Auxiliary materials are available in the HTML. doi:10.1029/2010GB003794.

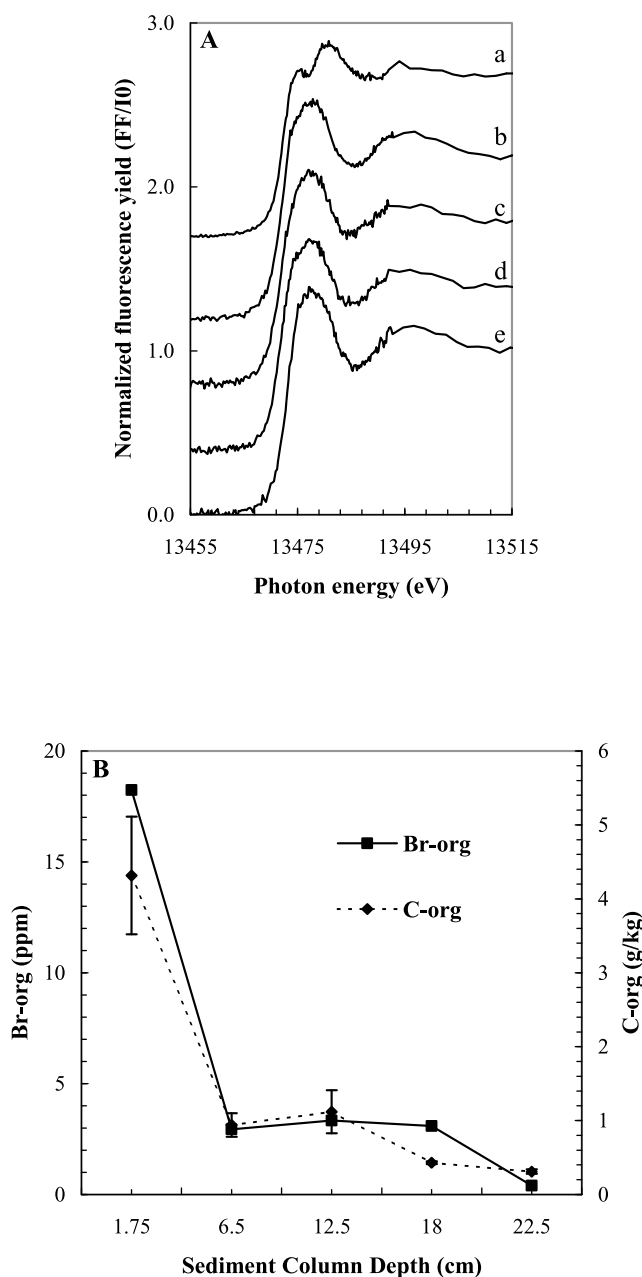


Figure 5. Data from homogenized Cape Cod (MA) estuarine sediment sections. (a) Variation in Br speciation with sediment column depth. Normalized Br 1s bulk XANES spectra: spectrum a, 0–3.5 cm; spectrum b, 4–9 cm; spectrum c, 9–16 cm; spectrum d, 16–20 cm; spectrum e, 20–25 cm. (b) Relationships between depth, Br_{org}, and C_{org} concentrations.

cycling in marine sediments have interpreted increasing Br_{inorg} concentrations in sediment pore waters with depth as evidence that the anion is regenerated as a result of the decomposition of NOM during diagenesis [Mahn and Gieskes, 2001; Martin et al., 1993]. Concentrated Br_{org} occurs at 23–25 cm at sparsely distributed, localized hot

spots, which coincide with areas of elevated Fe concentration (Figure 8c, spectrum a). These Br_{org} hot spots may represent remnants of the brominated NOM aggregates observed at shallower depths (Figure 7).

[30] In the Cape Cod sediments, associations between Br and most metal cations are pronounced at the sediment-water interface and decrease significantly with depth. The values of Pearson *r* correlation coefficients for the relationship between Br and other elements decrease by as much as 75% down the 25 cm column (see auxiliary material). The strong correlations between Br and metal cations at shallower depths likely reflect sorption reactions between the metals (or their oxides) and C_{org}, which comprises Br_{org}. In the deeper sediments, in which correlations between Br and metal cations are not as pronounced, Br is present mainly as Br_{inorg} in interstitial spaces rather than being present as Br_{org} bound to NOM. These results suggest that Br_{org} is correlated with metals in the sediments, while Br_{inorg}, with its low binding affinity, is not.

[31] Taken together, the phenomena described in this section and the trends in Br speciation and concentration outlined in section 3.2 hint at bromination and debromination mechanisms related to the cycling of NOM.

3.4. Sources of Sediment Br_{org}

[32] The previous sections demonstrate that marine and estuarine sediments potentially act as a locus for the transformation of Br between inorganic and organic forms. This phenomenon of Br cycling in the sediments is supported by the dramatic decrease of Br_{org} with depth in most of the samples investigated here (Table 1) and also strikingly depicted in the μ -XRF images of Br distribution at various depths in undisturbed Cape Cod sediments (Figures 7 and 8).

[33] Before we can adequately describe the marine Br cycle, the different biotic and abiotic sources of Br_{org} in the sediments must be illuminated. A major mechanism of C-Br bond production in marine systems is apparent in the bromoperoxidative capabilities common to diverse aquatic organisms [Butler and Carter-Franklin, 2004]. The estuarine sediments from Cape Cod, for example, play host to the bromoaromatic-producing hemichordate worm *Saccoglossus kowaleskii* [King, 1986]. Benthic organisms such as this have been regarded as indicators of low molecular weight Br_{org} in sediments [Fielman et al., 2001]. Br_{org} may also form abiotically in sediments during early diagenetic processes as insoluble Fe(III)-oxides are reduced [Keppler et al., 2000; Schöler and Keppler, 2003].

[34] Much of sediment NOM, however, originates in surface waters, as detrital matter from organisms in the euphotic zone that ultimately settles on the sediment surface. Sinking particles represent the major means of transport of NOM from surface waters to the seafloor [Boyd and Trull, 2007]. In search of Br_{org} in sinking particulate matter, we probed Br speciation and distribution in solid phase material from sediment traps deployed at 258 and 1061 m down the water column in the Okhotsk Sea [Honda et al., 1997] and at 200 m in the Ligurian Sea [Goutx et al., 2007].

[35] The Okhotsk Sea is characterized by a rich supply of nutrients and high biological productivity. The Br in Okhotsk sediment trap material was revealed to be exclu-

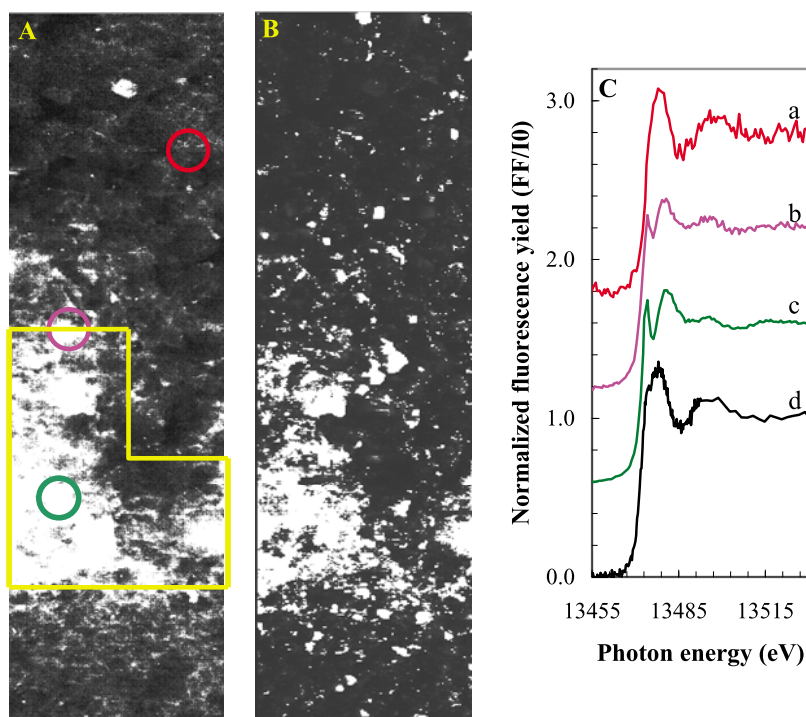


Figure 6. Undisturbed sediment core section from coastal New Jersey bay waters, 7.2–8.5 cm below sediment-water interface. The sediment core contained a distinct “lens” of dark-colored NOM ~8 cm below the sediment-water interface. The core was sectioned for X-ray analysis with minimal disturbance of the sediment grains, and the position of the organic lens was recorded by microscopic observation (yellow outline) once the sample was mounted in the sample chamber, prior to fluorescence map acquisition. (a) Micro-X-ray fluorescence (μ -XRF) image map at Br $K\alpha$ emission energy. Lighter shade corresponds to greater intensity. Map dimensions: $1.3 \times 0.45 \text{ cm}^2$. (b) A μ -XRF map for Fe $K\alpha$ /Mn $K\beta$ (these emission energies could not be resolved). (c) Normalized Br $1s$ μ -XANES spectra, where the color of spectral lines corresponds to that of the circled areas in Figure 6a. Least squares fitting with model compounds reveals the speciation of spectrum a to be 100% Br_{inorg} and spectra b and c are both 100% Br_{org} . Spectrum d, bulk Br $1s$ XANES spectrum of homogenized sediment from 7 to 9 cm, inclusive of organic lens; 65% Br_{inorg} , 35% Br_{org} .

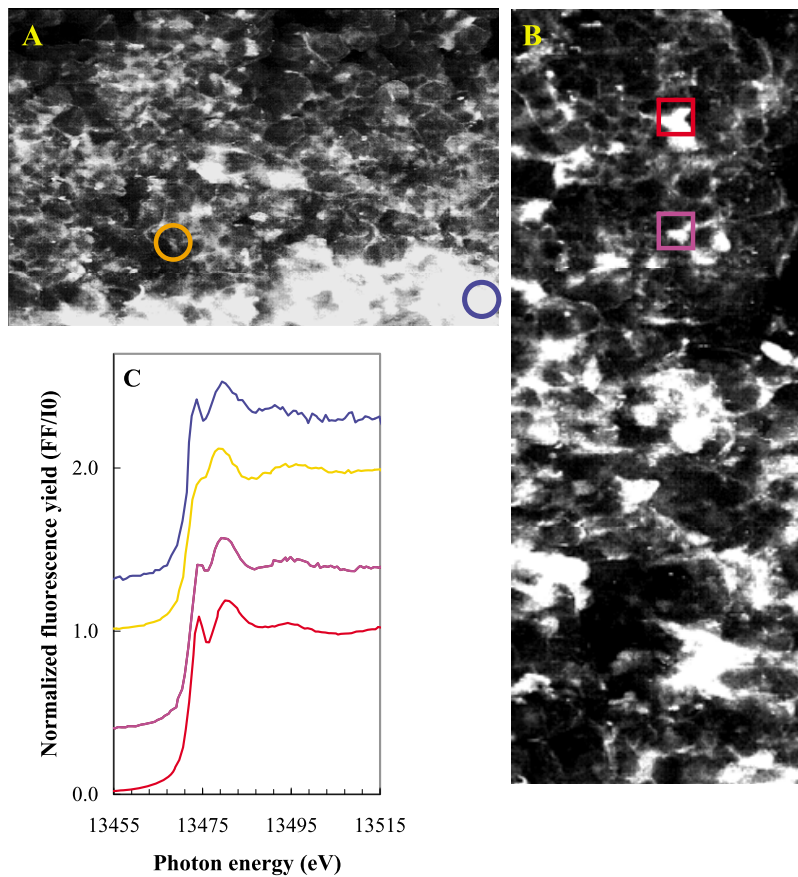


Figure 7. Br distribution and μ -speciation in upper portions of Cape Cod (MA) estuarine sediment (undisturbed core sections). Br $K\alpha$ μ -XRF maps: (a) 0–1 cm (10×7 mm²) and (b) 10–13 cm (5×13 mm²). Lighter shade corresponds to greater fluorescence intensity, i.e., greater Br concentration. (c) Normalized Br 1s μ -XANES spectra. Colors of open shapes in Figures 7a and 7b match colors of associated μ -XANES spectra in Figure 7c.

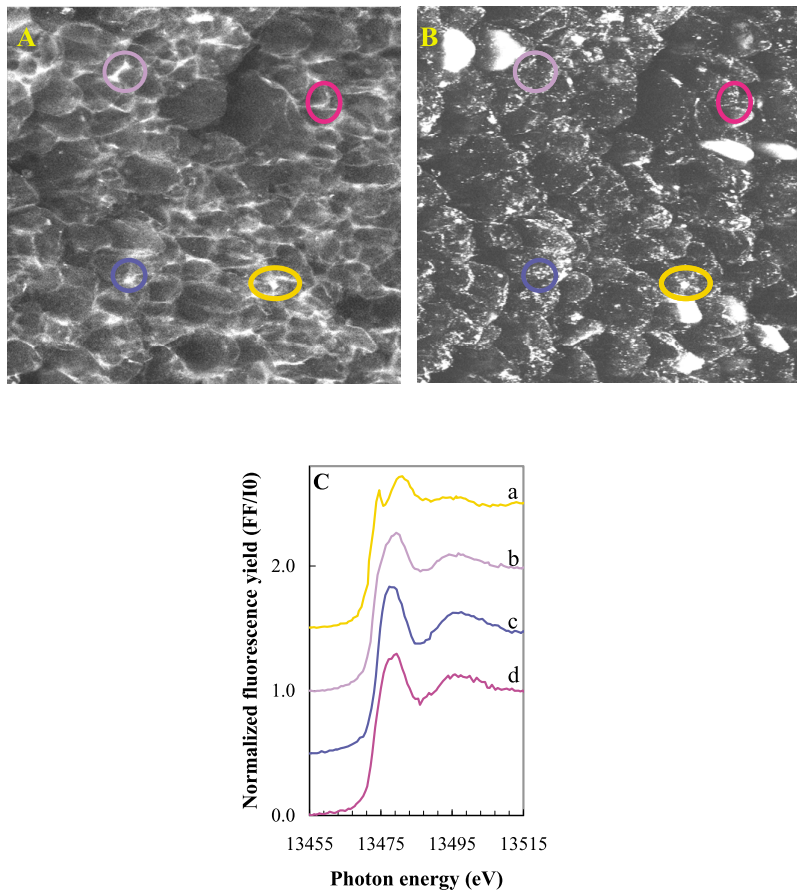


Figure 8. Br distribution and μ -speciation in lower depths (23–25 cm) of Cape Cod (MA) estuarine sediment (undisturbed core section). Shown are μ -XRF maps ($8 \times 8 \text{ mm}^2$): (a) Br K α and (b) Fe K α /Mn K β . Lighter shade corresponds to greater fluorescence intensity, i.e., greater elemental concentration. (c) Normalized Br $1s$ μ -XANES spectra. Colors of open circles in Figures 8a and 8b match colors of associated μ -XANES spectra in Figure 8c.

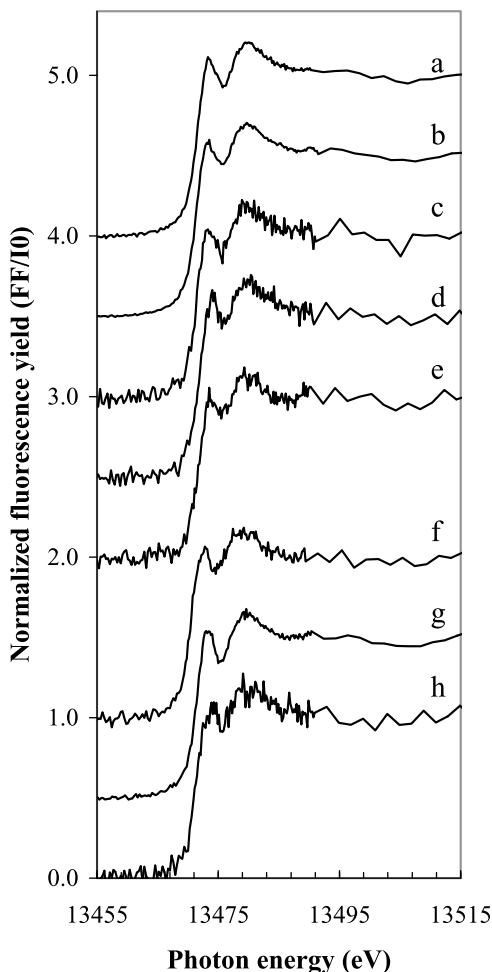


Figure 9. Normalized Br 1s bulk XANES spectra of particulate sediment trap material from the Sea of Okhotsk. Sediment traps deployed at 258 m (spectra a–e) and 1061 m (spectra f–h) down the water column. Dates of collection: spectrum a, August 1990; spectrum b, October 1990; spectrum c, December 1990 to February 1991; spectrum d, April 1991; spectrum e, June 1991; spectrum f, August 1990; spectrum g, October 1990; spectrum h, December 1990 to February 1991.

sively organic, at both depths and through all seasons (Figure 9). In Br $K\alpha$ μ -XRF maps of Okhotsk sediment trap material, Br distribution is heterogeneous, with prominent areas of high Br concentration (Figure 10a). The Ca distribution is similarly heterogeneous, with calcareous shells of coccolithophores clearly evident in Ca $K\alpha$ maps (Figure 10b). Comparison of the Ca $K\alpha$ and Br $K\alpha$ distributions suggests that the areas of highest Br concentration are not correlated with coccolithophore shells. By contrast, Fe and Mn (Figures 10c–10e) coincide spatially with Br.

[36] In sediment trap material from the Ligurian Sea, Br is again correlated with Fe and Mn more than Ca (see auxiliary material). Once more, Ca appears most prominent in cal-

careous fragments, and Br does not appear at high concentrations in these areas. Br 1s μ -XANES spectra reveal that the areas of highest Br concentration in the sediment trap material correspond to Br_{org} , while areas of low Br concentration and high Ca concentration correspond to Br_{inorg} (see auxiliary material). These results suggest that Br_{org} is either associated with the lithogenic fraction of the sinking particulates or with a fraction of NOM unrelated to biogenic $CaCO_3$, possibly a diatomaceous fraction. Br has been found in high concentrations in the frustules of many diatom species and has been used as a proxy of paleoproductivity [Kerfoot *et al.*, 1999; Phedorin *et al.*, 2000]. The μ -XRF beamline does not allow for detection of low-Z elements like Si, so we were unable to measure Si-Br correlations in our samples. If diatoms are significant sources of sedimentary Br_{org} , it could partly explain the observation of the highest Br_{org} concentrations in the opal-rich Southern Ocean Antarctic sediments (Table 1).

[37] The observed correlations between Br_{org} and metals such as Fe and Mn in sediment trap material could arise due to sorption interactions between these metal cations and sinking NOM. This association may also relate to the causality of Br_{org} formation, since abiotic reactions between NOM, halides, and redox-active metals have been shown to be environmentally feasible modes of Br_{org} production [Keppler *et al.*, 2000]. In the euphotic zone, Br_{org} compounds may form abiotically through radical photochemical reactions between Fe species, NOM, and Br_{inorg} ions [Pelizzetti and Calza, 2002].

[38] The high Br_{org} concentrations found in sinking particulate material suggest that a portion of the stable Br_{org} observed in marine sediments originates as Br_{org} compounds produced in surface waters by biota, such as macroalgae and phytoplankton, or through abiotic processes, such as photochemical reactions. The simple molecules arising from the decomposition of biological and other organic material polymerize to form macromolecular NOM that ultimately undergoes sedimentation, mineralization, or degradation to dissolved species. Thus, it seems feasible that detrital matter from Br_{org} -producing organisms and abiotic Br transformations contain C-Br bonds that persist through the formation of polyfunctional geomacromolecules and sedimentation. This would account for the ubiquity of Br_{org} in estuarine and marine sediments and point to the sediments as sinks of naturally produced Br_{org} , which is ultimately debrominated through the degradation of NOM. Decreasing $Br_{org}:C_{org}$ ratios with sediment depth at two of our locations imply that Br_{org} is preferentially degraded during diagenesis, a rich topic for further investigation.

4. Summary and Implications for the Geochemical Br Cycle

[39] These results show that stable Br_{org} constitutes the dominant form of Br in the organic fraction of estuarine and marine sediments from various geological environments. By extension, the documented associations between Br and C_{org} in marine sediments [Mayer *et al.*, 1981; Price *et al.*, 1970; Pruyssers *et al.*, 1991; Tenhaven *et al.*, 1988; Ziegler *et al.*,

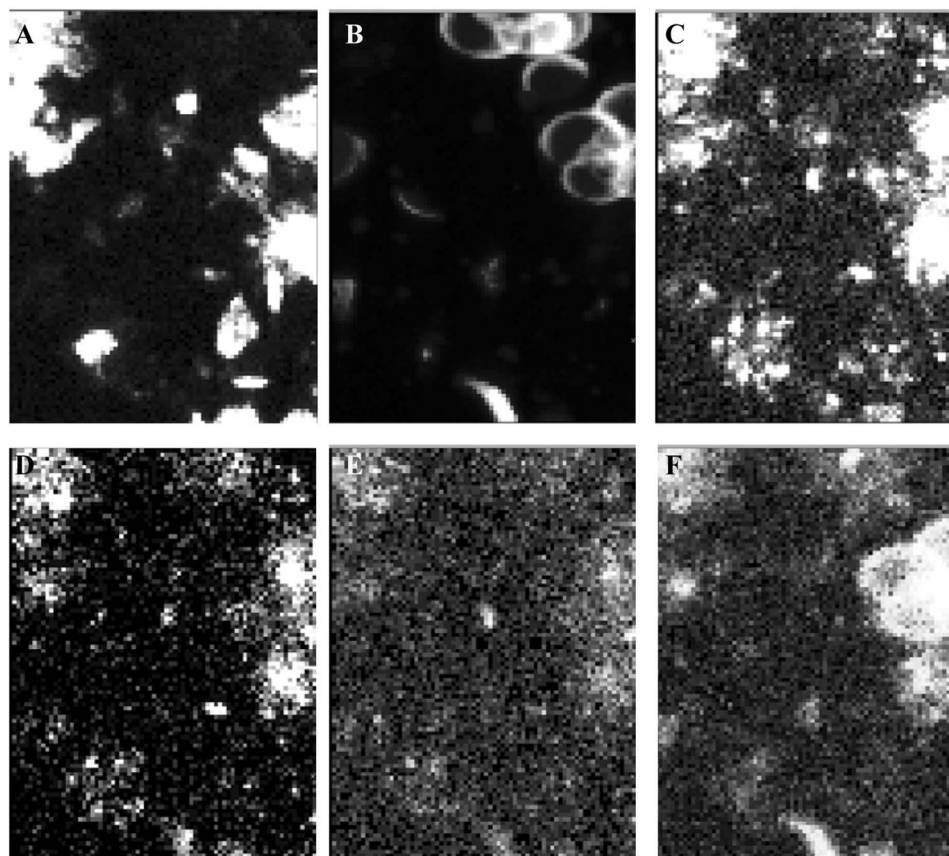


Figure 10. Elemental distributions in particulate sediment trap material from the Sea of Okhotsk. Shown are μ -XRF maps ($0.5 \times 0.3 \text{ mm}^2$): (a) Br $K\alpha$, (b) Ca $K\alpha$, (c) Fe $K\alpha$ /Mn $K\beta$, (d) Co $K\alpha$ /Fe $K\beta$, (e) Mn $K\alpha$, and (f) Zn $K\alpha$. Lighter shade corresponds to greater fluorescence intensity, i.e., greater elemental concentration.

2008] are probably attributable to covalent C-Br bonds. It appears therefore that Br incorporated into geomacromolecules (e.g., humics) as Br_{org} accounts for a major reservoir of this halogen in the pedosphere, in line with recent observations of terrestrial peat bogs [Biestler *et al.*, 2006, 2004]. The omnipresence of Br_{org} in the environmental samples examined and the changing Br speciation with sediment column depth suggest that the Br_{org} functionality not only affects the chemistry of specific microenvironments but participates in a complex, universal biogeochemical cycle involving formation of the C-Br bond, humification, and ultimate regeneration of Br_{inorg} through the degradation of NOM. The magnitude of Br cycling must now be evaluated in the context of the global marine Br budget to reassess the classification of Br as a conservative element in seawater [Morris and Riley, 1966]. The relative contributions of biotic and abiotic bromination pathways in the environment require further exploration as well. Ultimately, discovering how ecosystems accommodate Br_{org} produced naturally on such a wide scale may influence the assessment of environments polluted by anthropogenic chemicals with analogous chemical properties.

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