



Bromine counts from XRF scanning as an estimate of the marine organic carbon content of sediment cores

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[1] XRF sediment core scanning technology is increasingly used to quantify sediment composition. The overall good correlation between biophilic halogen bromine (Br) and sedimentary total organic carbon (TOC) potentially allows the fast estimation of down core TOC profiles by XRF scanning. In order to test this approach we present data from the Arabian Sea and a Mediterranean brine basin, comparing XRF core scanning Br data with discrete sample TOC analyses. Overall, Br counts and TOC show a clear correlation, except when stable carbon isotope and C/N data indicate intervals characterized by enhanced input of terrestrial organic matter. Hence, solid phase Br is exclusively associated with marine organic matter (MOC) and can be used as a direct estimate of this parameter after a calibration is established. High pore water Br in the brine core steepens the Br/TOC correlation but after salt correction shows a nearly identical gradient to that of the Arabian Sea core.

Components: 3189 words, 3 figures.

Keywords: X-ray fluorescence; XRF core scanner; sediment chemistry; bromine; sedimentary organic carbon.

Index Terms: 1051 Geochemistry: Sedimentary geochemistry; 3094 Marine Geology and Geophysics: Instruments and techniques; 3036 Marine Geology and Geophysics: Ocean drilling.

Received 20 December 2007; **Revised** 11 February 2008; **Accepted** 24 March 2008; **Published** 15 May 2008.

Ziegler, M., T. Jilbert, G. J. de Lange, L. J. Lourens, and G.-J. Reichart (2008), Bromine counts from XRF scanning as an estimate of the marine organic carbon content of sediment cores, *Geochem. Geophys. Geosyst.*, 9, Q05009, doi:10.1029/2007GC001932.

1. Introduction

[2] Recent advances in XRF sediment core scanning technology [Richter *et al.*, 2006; Thomson *et al.*, 2006; Tjallingii *et al.*, 2007] have paved the way for the use of elemental counts as tracers of variability in less readily quantified sediment constituents. Profiles of sedimentary total organic carbon (TOC) and marine organic carbon (MOC) are widely used in reconstructions of the balance between sea surface productivity and preservation in a range of oceanic environments [Rühlemann *et al.*, 1999], notably the Arabian Sea [Reichart *et*

al., 1998; Schulz *et al.*, 1998] and Mediterranean [Rohling, 1994, and references therein]. The origin (marine or terrestrial) of organic matter in sediments is furthermore an important parameter in global carbon budget calculations. However, existing procedures to establish down core TOC profiles, and to differentiate between the two sources (e.g., $\delta^{13}\text{C}$, TOC:N_{total}, or the newly developed biomarker-based Branched and Isoprenoid Tetraether (BIT) index [Hopmans *et al.*, 2004]), require the analysis of discrete sample series. Sedimentary Br/TOC can be employed as an alternative tracer for marine versus terrestrial organic carbon [Mayer *et al.*, 2007], using the principle that

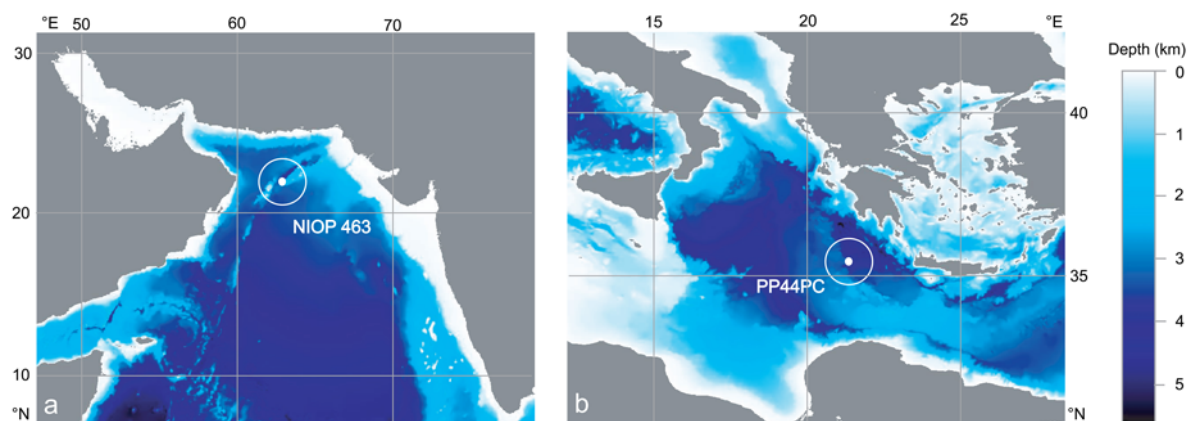


Figure 1. Coring locations of (a) NIOP 463 and (b) PP44PC.

the terrestrial environment, and hence terrestrial organic matter, is comparatively poor in bromine. Details of the relationship between Br and marine organic matter are still debated [see Mayer *et al.*, 2007, and references therein] and will form the subject of further investigation. Here we investigate the potential of XRF Br counts/s as an estimate for MOC.

[3] We show that a correlation exists between XRF Br counts/s and sedimentary MOC in two sediment cores from contrasting marine environments. Alongside the XRF scanning data of the two cores, we performed conventional discrete sample analyses for TOC, water content, partitioning between organic Br (Br_{org}) and salt Br (Br_{salt}), and Br/Cl ratios in the Br_{salt} component. The results allow us to estimate core-specific functions relating XRF bromine counts to MOC. In doing so, we extend the potential of XRF scanning as a fast, efficient method to establish sedimentary composition beyond the information yielded by elemental counts alone.

2. Material and Methods

[4] XRF core-scanning measurements were obtained directly at the split core surface of the archive half of each core, using the Avaatech XRF core scanner at the Netherlands Institute for Sea Research (NIOZ). The split core surface was covered with 4 μ m thickness SPEXCerti Prep Ultralene1 foil to avoid contamination of the XRF measurement unit and desiccation of the sediment. A Pd filter was placed in front of the incoming X-ray beam and measurements were taken at 1 cm resolution with a slit size of 1×1.5 cm, generator setting of 30 kV and a sampling

time of 30 s. Further technical and practical details about the XRF core scanner are described by Richter *et al.* [2006]. While Tjallingii *et al.* [2007] showed that measurement of light elements can be affected (due to their limited response depth) by the development of a water film on the core surface, the atomic weight of bromine (80) ensures that it is not affected by these problems.

[5] Piston core NIOP 463 ($22^{\circ}32.9'N$, $064^{\circ}02.8'E$, 920 mbss) was collected at the base of the modern Oxygen Minimum Zone (OMZ) on Murray Ridge, Arabian Sea (Figure 1a). The sediments show organic carbon variations of between one and six wt% TOC, related to changing OMZ intensity on orbital timescales [Reichart *et al.*, 1998]. Pore water salinity is assumed to remain constant at the bottom water value of 38‰ throughout the core. Piston Core PP44PC Section 8 ($35^{\circ}14.2'N$, $21^{\circ}29.8'E$, 3378 mbss) was recovered from the Urania basin in the Eastern Mediterranean (Figure 1b). The basin is filled with a brine of 165‰ salinity, and dissolved Br is elevated to 0.315‰. However, the seawater Br/Cl mass ratio of 0.0034 is maintained. Brine and pore waters are entirely anoxic, and the core section contains a well preserved example of the TOC-rich Holocene Sapropel S1.

[6] A series of discrete samples (1 cm stratigraphic thickness) was taken at 10 cm resolution from the working half of each section of NIOP 463, and at 1 cm resolution in the working half of PP44PC Section 8. Water content was estimated by weight loss on freeze drying. Organic carbon and total nitrogen contents were measured with a CNS analyzer (Fisons NA 1500). Carbonate was extracted prior to CNS analysis by mechanical shaking with 1M HCl for 12 h, and rinsing with deionized water to remove $CaCl_2$. This sequence

was repeated with a 4 h HCl shake to guarantee dolomite removal, after which the samples were again rinsed and finally oven dried. Replicate analyses of samples and comparison with international (Atropine, Acetanilide) and in-house (F-TURB and MM-91) standards were used to establish analytical precision and accuracy, which were both better than 3%. In addition, we performed a sequential extraction on limited series of dried subsamples representing the full range of XRF Br counts, organic carbon and water content from each core. Assuming all Br, in both cores, to be partitioned between organic carbon and salt fractions [Mayer *et al.*, 1981], we rinsed the samples first with deionized water (to extract Br_{salt}) and subsequently with hydrogen peroxide in an 80°C water bath (to extract Br_{org}). Repeat rinses confirmed complete removal of extractable Br during the two steps. The deionized water rinses were subsequently analyzed using an Ion Chromatograph to calculate Br/Cl ratios. These were always within 5% of the seawater value, indicating negligible removal of Br_{org} during pore water rinsing. Both deionized water and hydrogen peroxide rinses were analyzed by ICP-MS (precision <1%) for determination of extracted Br.

3. Results

[7] Comparison of discrete sample TOC measurements with high-resolution XRF Br counts/s shows that the two parameters covary in both cores (Figures 2a and 2b). Maxima in organic carbon are consistently reproduced in the bromine data series. However, in the intervals 600–800 cm and 1100–1200 cm in NIOP 463 and the “early Sapropel S1” interval in PP44PC, the amplitude of individual bromine peaks is lower than predicted by the corresponding TOC peaks (note that the TOC peak in NIOP 463 around 420 cm is not reproduced due to missing XRF data).

3.1. Influence of Terrestrial Organic Matter

[8] To explain the mismatch between XRF Br counts/s and TOC in these intervals, a comparison was made with down core variations in $\delta^{13}\text{C}_{\text{TOC}}$ and the $\delta^{13}\text{C}_{\text{TOC}}$ -estimated terrestrial organic carbon content of NIOP 463 (Figure 2a), assuming end-members of -20 (marine) and -26 (terrestrial) [Fontugne and Duplessy, 1986]. Terrestrial organic carbon content records maxima in the mismatched intervals, most clearly in the last interglacial period

(Marine Isotope Stage 5), which was characterized by strong Indian summer monsoon intensity [e.g., Emeis *et al.*, 1995] and hence possible increased Indus river discharge. Therefore, we conclude that the mismatch between XRF Br counts/s and TOC in the intervals of heavily depleted $\delta^{13}\text{C}_{\text{TOC}}$ values is caused by the addition of low-Br terrestrial organic carbon.

[9] Subsequently, a (semi) quantitative estimate of MOC can be achieved for NIOP 463 by performing a regression analysis between the TOC values of the samples least affected by terrestrial contribution (i.e., $\delta^{13}\text{C}_{\text{TOC}} < -20$) and their respective XRF Br counts/s (Figure 2c). The resulting Br/TOC correlation coefficient of 0.89 ($n = 18$) (Figure 2c) is higher than that for the entire sample set (0.50, $n = 144$) and effectively represents Br/MOC. Both correlations are significant at the 99% confidence level.

[10] Carbon isotope data was not available for PP44PC, and its Br/TOC correlation is therefore presented without correction for terrestrial organic matter (Figure 2c). The low Br/TOC of early Sapropel S1 suggests, however, that the input of terrestrial organic carbon was relatively high at this time. This conclusion is supported by a higher TOC:N_{total} ratio of this interval (13.8) relative to the later stage of S1 (13.0).

3.2. Influence of Brine Salt

[11] The Br/TOC gradient is clearly steeper in PP44PC than in NIOP 463 and has a higher intercept at zero TOC (Figure 2c). Our sequential extraction results show that the brine core PP44PC has a Br_{salt}:Br_{org} ratio far higher than that of NIOP 463 (Figure 3a). Assuming the larger Br_{salt} component of PP44PC to be responsible for the different intercepts, a salt correction was performed on the XRF Br counts of both cores. For this purpose all Br XRF counts were first normalized to water content, and plotted against TOC (Figure 3b). For NIOP 463, again only those samples with a minimum terrestrial organic matter contribution were used. The number of Br_{salt} counts/s per wt% water was subsequently derived from the intercept at zero TOC (Figure 3b). Using this relationship and the water content of each sample, the Br_{org} component (or Br_{salt} corrected XRF Br counts) can be calculated (Figure 3c). The resulting Br_{org}:TOC regression of NIOP 463 passes through the origin. The regression for PP44PC, if samples from the early sapropel interval are excluded, shows a nearly

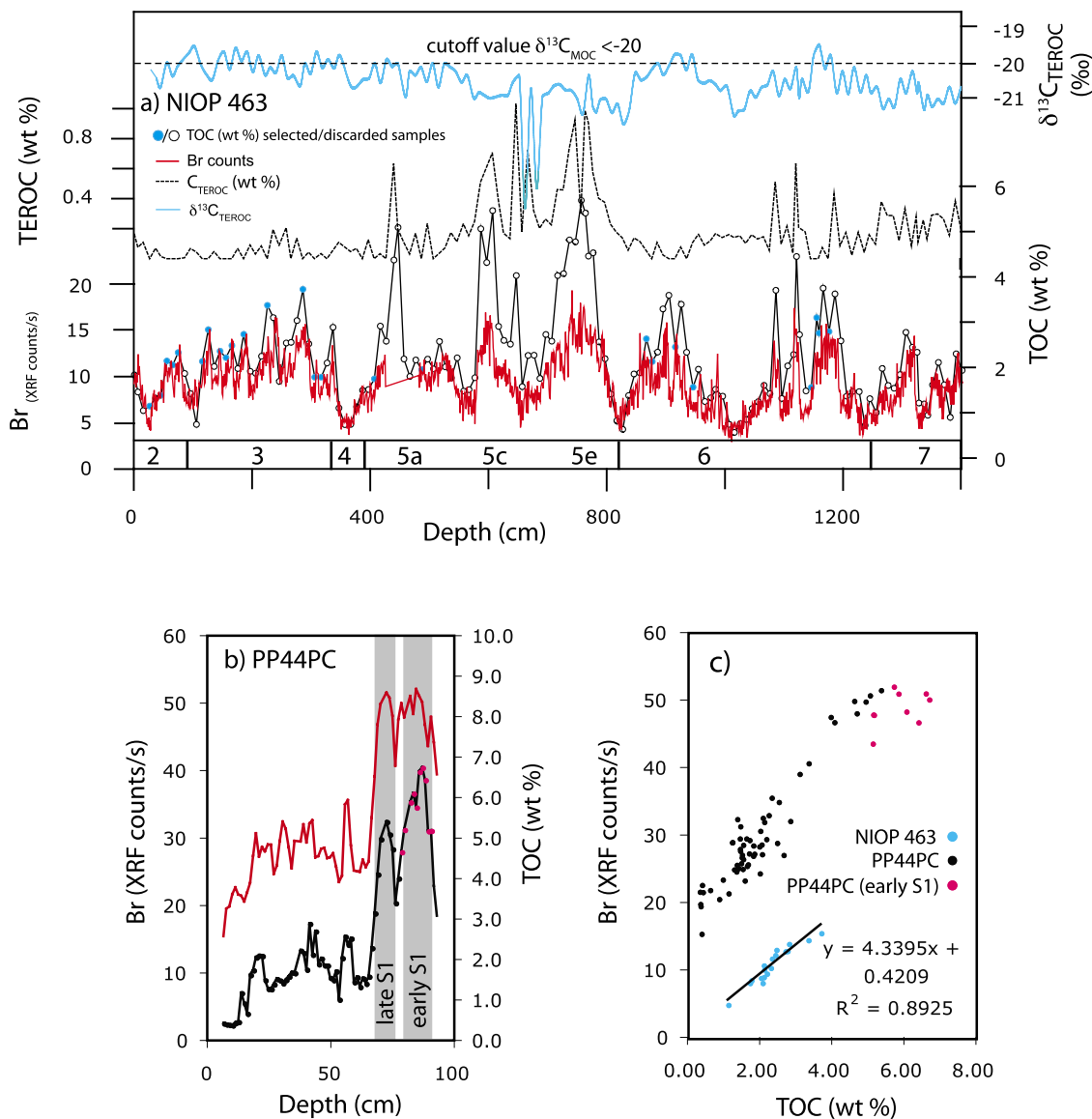


Figure 2. (a) Arabian Sea core NIOP 463. Depth profiles of $\delta^{13}C_{TOC}$, and the estimated terrestrial organic carbon (TEROC) content based on $\delta^{13}C_{TOC}$ (using $TEROC = TOC * [(\delta^{13}C_{MOC} - \delta^{13}C_{TOC}) / (\delta^{13}C_{TOC} - \delta^{13}C_{TOC})]$, end-members $\delta^{13}C_{MOC} = -20$, and $\delta^{13}C_{TEROC} = -26$ [e.g., Fontugne and Duplessy, 1986]). Below are depth profiles of TOC (%) and XRF Br total raw counts. Open symbols represent samples with $\delta^{13}C_{TOC} < -20$, which have been removed from subsequent regression. Numbers in the bar at the bottom indicate marine isotope stages according to the age model for NIOP 463 from Sinnighe Damste et al. [2002]. (b) Depth profiles of TOC (%) and XRF Br counts/s for Mediterranean brine core PP44PC ($\delta^{13}C$ data not available). (c) Scatterplots of XRF Br counts/s versus total organic carbon content for the two cores. NIOP 463 data were selected on the basis of $\delta^{13}C$ of organic carbon, excluding samples with a potential contribution of terrestrial organic matter.

identical gradient to that of NIOP 463 and also passes through the origin (Figure 3c).

4. Discussion and Conclusions

[12] The common gradient of the two cores after salt correction implies that no post-depositional sorption of Br to organic matter occurs in the brine,

a conclusion also drawn by Ten Haven et al. [1988] from another Mediterranean brine core. Therefore, the Br/MOC ratio observed in our two cores is apparently fixed in the water column, and thus must be related to the initial association of Br with marine organic matter. Ambient salinity at the time of Br association may play a role; indeed, the lack of Br in terrestrial organic matter is caused by the

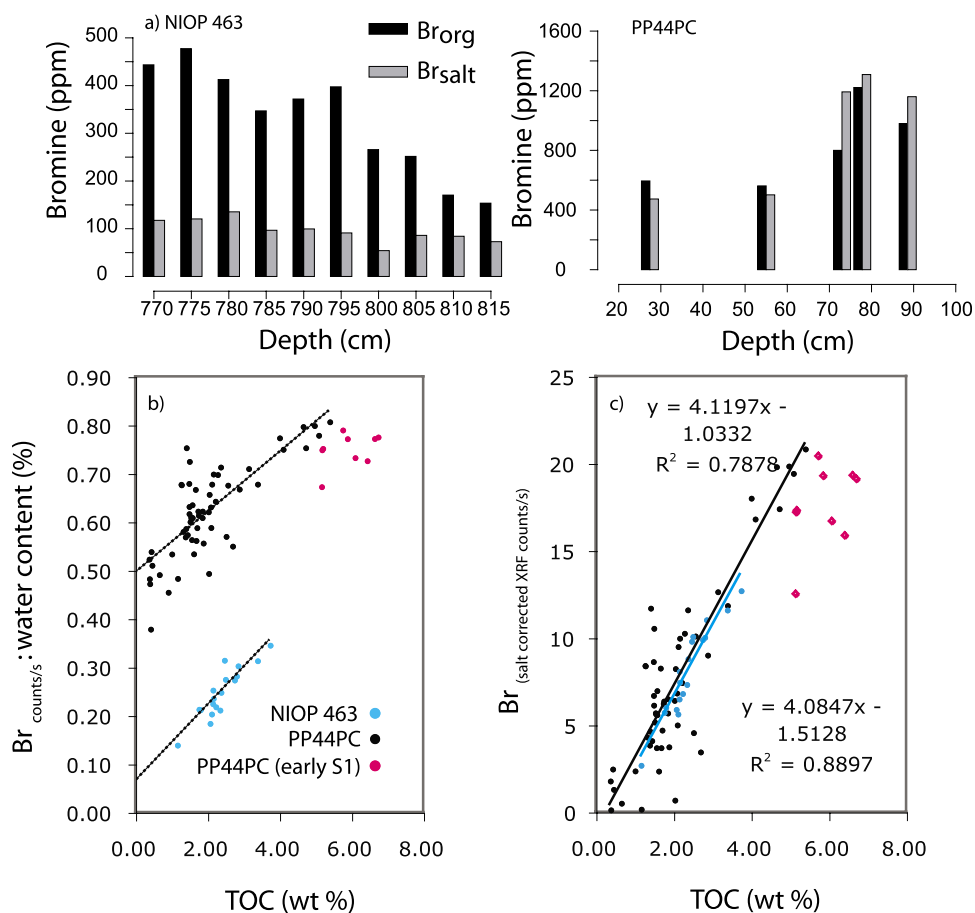


Figure 3. (a) Results of the sequential extraction, showing the partitioning of organic and salt bromine in Arabian Sea core NIOP 463 and Mediterranean brine core PP44PC (data in ppm water-free sediment; note different y axis scales). (b) XRF Br counts/water content (%) plotted versus TOC. Intercept with y axis gives a measure of XRF Br counts/s per 1% water content for NIOP 463 and PP44PC. (c) Salt contribution corrected XRF Br counts/s plotted versus TOC.

low salinity of the terrestrial environment. Therefore, the similar surface water salinities of the Eastern Mediterranean and Arabian Sea could explain the common gradient. By extension, the drop in Mediterranean surface water salinity [Van der Meer *et al.*, 2007] during the onset of sapropel formation might be evoked as an alternative explanation for the low Br/TOC of early Sapropel S1. However, further study is required to improve our understanding of the potential paleosalinity information stored in sedimentary Br/MOC ratios.

[13] Although our two cores yield a common function for estimating MOC from XRF Br counts/s, such data remain sensitive to the settings of the XRF apparatus. Thus, when applying the method it is necessary to analyze a short series of discrete samples for TOC and $\delta^{13}\text{C}_{\text{TOC}}$, to establish a quantitative Br/MOC calibration for the core in question. Salt correction of the XRF data, requiring

a full series of water content measurements, is not a prerequisite for the calculation of MOC from XRF Br counts/s, since a linear empirical relationship exists in salt-uncorrected data (Figure 2c). However, significant salt contribution affects the gradient of this relationship.

[14] The advantages of the XRF scanning approach are clear: data is acquired quickly, and at high resolution, allowing the identification of short-timescale changes in sedimentary (paleoenvironmental) archives. MicroXRF scanning [e.g., Böning *et al.*, 2007] potentially allows the determination of changes in sedimentary MOC on the submillimeter scale, facilitating the investigation of sedimentary microfabrics and interannual accumulation variability. In addition, recently developed handheld XRF scanning devices [e.g., Moore, 2006] offer the possibility to analyze the organic carbon content of land-based marine deposits in geologic sections

in the field. Since the standard procedure of XRF scanning involves measurements of most other major elements, Al or Ti counts can be used to normalize Br in order to estimate the relative input of sedimentary components.

[15] To conclude, Br XRF scanning counts can be used as a quick and nondestructive, high-resolution, semiquantitative estimate of sedimentary TOC. Deviations from the overall linear relationship between Br and TOC can be explained by the influence of low-Br terrestrial organic matter, and after removal of these samples a strong linear relationship, representing Br/MOC, is observed. Records from two contrasting regions display, after correction for the contribution from dissolved Br, common Br/MOC regression slopes.

Acknowledgments

[16] We are grateful for technical and scientific help by Thomas Richter, Helen de Waard, Rineke Giles, Aad Vaars, Bertil van Os, and Erik van Vilsteren. Helpful comments by Phillip Böning and an anonymous reviewer are acknowledged. This work was supported by the Netherlands Organization for Scientific Research (NWO).

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