9. SULFUR-IRON-CARBON GEOCHEMISTRY IN SEDIMENTS OF THE DEMERARA RISE¹

Michael E. Böttcher,^{2, 3} Almut Hetzel,⁴ Hans-Jürgen Brumsack,⁴ and Andrea Schipper²

ABSTRACT

The geochemical composition of sediments (squeeze cake samples) from five drill sites (Ocean Drilling Program Sites 1257-1261) on the Demerara Rise in the tropical Atlantic was determined, with special regard to a sequence of Cretaceous black shales. Sediments were analyzed for different iron (total, pyrite, Na dithionite, and HCl leachable) and sulfur (total, pyrite, acid volatile, and organic bound) fractions, in addition to total organic carbon (TOC) and total inorganic carbon. The relative abundance of highly reactive iron (Fe_{HR}/Fe_T) in the investigated black shale samples indicates that pyrite was formed both in the water column and the sediment. This corresponds to euxinic paleoenvironmental conditions, a situation similar to the modern deep Black Sea. This geochemical approach is independent of a possible minor contribution from ongoing sulfate reduction which is triggered by anaerobic methane oxidation above the black shale sequence. Pyrite sulfur in black shales makes up between 30% and 100% of total sulfur. In addition to fixation of sulfide with iron, organic matter (OM) acted as an important sulfur trap during early diagenesis, with organic sulfur composing between 5 and 10 atom% of TOC. The relative importance of OM sulfurization is increasing with its content.

INTRODUCTION

The paleoenvironmental conditions during organic matter (OM)-rich black shale formation have been an important scientific issue in the field of global and regional biogeochemical element cycling for a con-

¹Böttcher, M.E., Hetzel, A., Brumsack, H.-J., and Schipper, A., 2006. Sulfuriron-carbon geochemistry in sediments of the Demerara Rise. In Mosher, D.C., Erbacher, J., and Malone, M.J. (Eds.), Proc. ODP, Sci. Results, 207: College Station, TX (Ocean Drilling Program), 1-23. doi:10.2973/odp.proc.sr.207.108.2006 ²Department of Biogeochemistry, Max Planck Institute for Marine Microbiology, Celsiusstrasse 1, D-28359 Bremen, Germany. ³Present address: Marine Geochemistry-Geology, Leibniz Institute for Baltic Sea Research, Seestrasse 15, D-18119 Rostock, Germany. michael.boettcher@iowarnemuende.de

⁴Institute of Chemistry and Biology of the Marine Environment, Carl-von-Ossietzky University of Oldenburg, PO Box 2503, D-26111 Oldenburg, Germany.

Initial receipt: 20 July 2005 Acceptance: 30 December 2005 Web publication: 17 November 2006 Ms 207SR-108

siderable period of time (e.g., Gauthier, 1987; Arthur et al., 1988; Arthur and Sageman, 1994; Brumsack, 2006, and references therein) but are still far from being completely understood. A number of different geochemical approaches have been applied to approach these questions, including trace element, biomarker, and stable isotope studies. As examples of more recent analogs for OM-rich sediment deposition, the formation of sapropels in the Black Sea and the eastern Mediterranean has been investigated in detail (e.g., Brumsack, 1986; Calvert et al., 1996; Lyons, 1997; Arthur and Dean, 1998; Emeis et al., 2000; Rinna et al., 2002; Lourens et al., 2001; Brumsack and Wehausen, 1999; Böttcher et al., 2003).

Accumulation of OM in sediments is often associated with the enrichment of sulfur and iron. The systematics behind the combined (bio)geochemistry of sulfur, iron, and organic carbon have been evaluated for the modern Black Sea (e.g., Leventhal, 1983; Arthur and Dean, 1998; Canfield et al., 1996; Raiswell and Canfield, 1998; Anderson and Raiswell, 2004) and successfully applied by analogy to the ancient depositional environments of OM-rich sediments (e.g., Dean and Arthur, 1989; Raiswell et al., 2001; Shen et al., 2003; Grice et al., 2005). Interpretation of ancient black shales is often complicated because of the modification by deeper burial and associated geochemical overprints. Close to the Earth's surface, modification of the geochemical composition of black shale can take place by weathering that may be induced by flow of rain and ground water (Petsch et al., 2000, 2001, 2005). Black shale sequences as well as corresponding pore water gradients obtained by deep sea drilling, on the other hand, have seldom been analyzed at a resolution sufficient for a detailed interpretation of past environmental change and possible diagenetic overprints. First analyses of pore waters associated with frequent sapropel layers from the Mediterranean gave no indication for a contribution of OM-rich zones to the shapes of present pore water profiles (Böttcher et al., 1998, 2003).

Widespread black shale formation took place during the global ocean anoxic events of the Cretaceous period (e.g., Schlanger and Jenkyns, 1976; Jenkyns, 1980), the causes still being a matter of intense debate (e.g., Arthur and Sageman, 1994; Arthur et al., 1988; Brumsack, 1986; Sinninghe Damstae and Koester, 1998). In the present study, we carried out a detailed geochemical investigation on Cretaceous black shale samples from the southern North Atlantic not previously affected by surface weathering. Expanded, shallowly buried Cretaceous sediments were recovered during Ocean Drilling Program (ODP) Leg 207 from the Demerara Rise off Suriname, South America, including multiple sequences of Cretaceous black shales. By means of a solid phase geochemical approach we aimed to characterize the sulfur-iron-carbon (S-Fe-C) systematics of these sediments and their use as indicators for the depositional paleoenvironment. Results are compared to the composition of the overlying younger organic-poor sediments. This communication is accompanied by reports on the bulk inorganic geochemistry including trace element contents (Hetzel et al., this volume), a high-resolution geochemistry study of Cretaceous black shales (Hetzel et al., unpubl. data), and the biogeochemistry of stable sulfur and oxygen isotope fractionation in pore waters and authigenic sulfur phases (Böttcher et al., unpubl. data).

MATERIALS AND METHODS

During Leg 207, sediments on the Demerara Rise were cored at ~9°N in the tropical Atlantic (Fig. F1; Table T1). The rise stretches ~380 km along the coast of Suriname and reaches a width of ~220 km from the shelf break to the northeastern escarpment, where water depths increase sharply from 1000 to >4500 m. Although most of the plateau lies in shallow water (700 m), the northwest margin is a gentle ramp that reaches water depths of 3000–4000 m. Nearly uniform, shallowly buried stratigraphically expanded sections of Cretaceous and Paleogene age exist with good stratigraphic control. Five drill sites (Sites 1257–1261) constitute a depth transect ranging in water depths from 1900 m to 3200 m (Fig. F1). The recovered sediments include multiple sequences of Cretaceous black shales (Erbacher, Mosher, Malone, et al., 2004; Erbacher et al., 2005) pointing to varying levels of bottom water dysoxia and/or enhanced surface water productivity. Five units were identified:

- Unit I: consisting of modern, Pleistocene, and Pliocene sediments.
- Unit II: consisting of Oligocene and Eocene sediments.
- Unit III: consisting of late Paleocene–Campanian sediments.
- Unit IV: consisting of Santonian–Cenomanian black shales.
- Unit V: consisting of Albian sediments.

Interstitial waters from 152 samples from Sites 1257–1261, covering a depth range from the sediment/seawater interface to 648 meters composite depth (mcd), were collected and processed using standard ODP methods. Interstitial water samples were squeezed from sediment samples immediately after retrieval of the cores using titanium squeezers, modified after the standard ODP stainless steel squeezer (Manheim and Sayles, 1974). Results for dissolved species relevant to the present study are summarized in Figure F2. On board the ship, splits of all squeeze cakes were taken, freeze-dried, and stored in polyethylene bags. In the shore-based laboratory, the samples were ground and homogenized in an agate mill. X-ray fluorescence analysis for main elements (Philips PW 2400 X-ray spectrometer) using fused glass beads were conducted as described by Schnetger et al. (2000). Detailed results are presented in Hetzel et al. (this volume); the present communication only refers to the total iron (Fe_T) measurements. Total sulfur (S_T) and total carbon (TC) were analyzed using a LECO SC-444 infrared analyzer for squeeze cake samples. Total inorganic carbon (TIC) was determined coulometrically using a UIC CM 5012 CO₂ coulometer coupled to a CM 5130 acidification module. Total organic carbon (TOC) was calculated as the difference between TC and TIC (e.g., Babu et al., 1999). Different sedimentary sulfur fractions, acid volatile sulfur (S_{AVS}), chromium-reducible sulfur (S_P, essentially pyrite), OM (essentially kerogen)-bound organic sulfur (S_{ORG}), and residual sulfur (S_{RFS}) were separated quantitatively on freeze-dried powdered samples. S_{AVS} was obtained using anaerobic distillation with 6-M HCl (1 hr). Because FeS is not expected to survive the diagenetic pyritization and laboratory-based freeze-drying process in the black shale samples, the S_{AVS} fraction is assumed to dominantly represent water column– derived ZnS and/or CuS (Brumsack, 1980). SAVS contents (data not shown) in the investigated black shale samples are <270 mg/kg. These results will be discussed in the light of trace element enrichments in more detail in a later contribution. Pyrite sulfur, S_P, was extracted using hot acidic Cr(II)Cl₂ (2 hr) (Zhabina and Volkov, 1978; Canfield et al., 1986).

F1. Positions of the sites cored during Leg 207, p. 13.









Liberated H_2S was precipitated quantitatively in Zn acetate traps and measured spectrophotometrically (Cline, 1969). The residue was washed, dried, and weighed and analyzed for CNS contents by elemental analysis using a Fisons elemental analyzer. This fraction represents the sum of S_{ORG} and S_{RES} . The Cr(II) residue was then tempered in a porcelain cruicible for several hours at 550°C to remove OM, weighed, and again analyzed for CNS (Böttcher and Schnetger, 2004). This fraction is considered to mainly represent residual barite sulfur. The S_{ORG-1} fraction was calculated from the difference of the two sulfur fractions. Additionally, the organic sulfur fraction was calculated from the difference of total sulfur and the sum of chromium-reducible sulfur and the sulfur content of the tempered Cr residue:

$$S_{ORG-II} = S_T - S_P - S_{RES}.$$

Organic sulfur results from both approaches agree well (Fig. F3). Stillreactive iron (Fe_D) was extracted from sediment samples using a buffered solution of Na dithionite (Canfield, 1989), which removes iron (oxyhydr)oxide phases (ferrihydrite, goethite, lepidocrocite, and hematite) but only small amounts of iron from silicates (Canfield, 1989; Haese, 2000). The iron concentration was determined spectrophotometrically (at 562 nm) with ferrozine in N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES) buffer at pH 7 (Stookey, 1970). The amount of pyrite iron (Fe_P) was calculated from the content of S_P. The highly reactive iron fraction Fe_{HR} is calculated as the sum of extractable and pyrite iron:

$$Fe_{HR} = Fe_{D} + Fe_{P}$$

The range of geochemical results in the Fe-S-C system for Unit IV sediments is summarized in Table T2. Finally, the iron fraction extractable by cold 0.5-M HCl (Fe_{HCl}) was determined in all samples (data not shown). Maximum dry weight contents of Fe_{HCl} are 140 mg/kg (Unit V, Site 1257), 70 mg/kg (Unit I, Site 1258), 199 mg/kg (Unit V, Site 1259), 83 mg/kg (Unit I, Site 1260), and 302 mg/kg (Unit I, Site 1261). Fe_{HCl} and Fe_D contents are positively correlated. Scanning electron microprobe analysis of gold-coated nonground sediment samples was carried out using a Hitachi S-3200N scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Lithologic Units, Pore Waters, Sulfate Reduction, and Anaerobic Methane Oxidation

The depth profiles of the contents of different sedimentary carbon, sulfur, and iron fractions measured at all sites recovered during Leg 207 are presented in Figure F4. The geochemical data demonstrate the occurrence of highly OM rich (Cretaceous) black shales (Unit IV) with TOC contents as high as 18 wt%. The black shales were deposited on synrift clastic sediments (Unit V). Units IV and V are overlain by organic-poor open-marine chalk and calcareous claystones (Units I–III) (Erbacher, Mosher, Malone, et al., 2004). Downcore variations of the pore water sulfate (Fig. F2) clearly indicate that deep-seated microbial sulfate reduction at slow rates is occurring in the sediments above Unit IV. Anaerobic oxidation of upward diffusing methane (AOM), which is derived from the black shale sequence, is the process associated with

F3. Comparison of the two approaches to measure S_{ORG}, p. 16.



T2. Range of geochemical parameters, p. 23.

F4. Downcore variations of geochemical parameters, p. 17.



the microbial sulfate reduction process (Erbacher, Mosher, Malone, et al., 2004). AOM has been found to be carried out in marine sediments by a consortium of archaea and sulfate-reducing bacteria (Hoehler et al., 1994; Hinrichs et al., 1999; Boetius et al., 2000). The mechanistic, gualitative interpretations from the pore water profiles are additionally confirmed by quantitative modeling (Arndt et al., 2006). The reaction zone is currently positioned at Sites 1257-1260 above the black shale sequences and is triggered by a flux of biogenic methane from the OMrich shales, where it is produced by methanogenesis. At Site 1261, sulfate reduction already goes to completion within the upper 200 mcd, indicating that OM degradation takes place in the rapidly deposited Pliocene nannofossil clay of Unit I (Erbacher, Mosher, Malone, et al., 2004). Whereas OM mineralization at depth is reflected by the continuous increase in ammonium concentrations, alkalinity data are partly superimposed by carbonate precipitation. Accumulation of dissolved barium concentrations in the pore waters (Fig. F2) originates from the dissolution of biogenic barites and only takes place where pore water sulfate was completely exhausted. Enhanced dissolved iron concentrations, on the other hand, exclude significant sulfide concentrations.

Sedimentary Iron and Sulfur Species

The burial of OM in the black shale sequence is associated with an enrichment of all analyzed sulfur fractions: total, pyrite, and organicbound sulfur (Fig. F4). This is due to the coupling of OM deposition to microbial sulfate reduction and the associated formation of sedimentary sulfur compounds. Dissimilatory sulfate reduction leads to the formation of hydrogen sulfide that may further react with reactive iron to precipitate iron sulfides (essentially pyrite, FeS_2) and with OM to form organic sulfur compounds (e.g., Aizenshtat et al., 1983, 1995; Sinninghe Damsté and De Leeuw, 1990; Bein et al., 1990; Rullkötter, 2000; Werne et al., 2004). Other metal sulfides (e.g., ZnS) that may have been formed in a sulfidic paleowater column (Brumsack, 1980), although found in investigated black shale samples (A. Hetzel, unpubl. data), are quantitatively only of trace importance.

Reactive Iron Phases and Pyrite Formation

Pyrite typically occurs in marine sediments in framboidal and euhedral occurrence, depending on the physicochemical boundary conditions (Wilkin et al., 1996; Wang and Morse, 1996). As shown in Figure F5, framboidal pyrite was found in black shale samples from Site 1260. This occurrence is typical for pyrite that is formed in a euxinic water column or in sediment close to the sediment/water interface during early diagenesis (Wilkin et al., 1996). Besides sulfur, the iron contents are also enhanced in sediments of Unit IV (Fig. F4), in particular, the Fe_P and Fe_D fractions. The only exception is Site 1261. The formation of pyrite is ultimately limited by the availability of iron minerals that are able to react with dissolved sulfide (Canfield, 1989). The amount of socalled highly reactive iron (Fe_{HR}) in marine sediments consists of the sum of the iron fraction that already reacted to pyrite (Fe_P) and sedimentary iron that is still able to react with sulfide. This still-reactive iron fraction (Fe_D) is extracted with buffered Na dithionite solution (Canfield, 1989). The relationship between Fe_{HR} and Fe_{T} has been shown to be indicative for the redox conditions characterizing the sediment-

F5. SEM photographs of framboidal pyrite, p. 19.



forming environment, with Fe_{HR}/Fe_T ratios < 0.38 in normal marine environments with oxic bottom waters (Raiswell and Canfield, 1998; Anderson and Raiswell, 2004). In euxinic systems, on the other hand, the clastic and reactive iron fluxes to the sediment may be decoupled, which may lead to Fe_{HR}/Fe_T ratios > 0.38. This corresponds to an excess of reactive sedimentary sulfur in euxinic compared to oxic sediments. Below oxic bottom waters, pyrite formation takes place exclusively in the sediment. An additional fraction of iron sulfide may be formed in the water column of euxinic systems, as found in the modern Black Sea (Raiswell and Berner, 1985; Canfield et al., 1996). It has been shown for modern environments that the geochemical indicators in the iron-sulfur system, such as the Fe_{HR}/Fe_T ratio and the degree of pyritization, mostly lead to the same paleoredox interpretations (e.g., Shen et al., 2003).

The downcore variations of the relative fraction of highly reactive iron (Fe_{HR}/Fe_T) for the Leg 207 samples are presented in Figure F4. Reactive iron was enriched in virtually all black shale samples with Fe_{HR}/Fe_{T} values > 0.38, indicating euxinic conditions during deposition of the organic-rich sediments of Unit IV (Fig. F4). Differences between the sites, as well as downcore variations of the relative enrichment of reactive iron, indicate that environmental conditions and/or associated transport processes were not constant with time. Besides water column iron sulfide formation, the enrichment of reactive iron also requires the presence of a paleoshelf situation where an extended oxygen minimum zone (OMZ) led to the liberation of dissolved iron from shelf areas into a suboxic water column and, after further transport, to precipitation when reaching the sulfidic deeper waters (Canfield et al., 1996; Lyons, 1997; Wijsman et al., 2001; Anderson and Raiswell, 2004). Alternatively, such an enrichment may have been caused by a fluctuation of a chemocline on the shelf slope, leading to a pumping of dissolved iron into suboxic waters with subsequent fixation in areas of higher sulfide accumulation. The latter mechanism is similar to a model proposed by Lepland and Stevens (1998) for the formation of Mn(II) carbonates in an anoxic deep of the Baltic Sea. Additionally, an excess of Fe_{HR} is also found below the black shales in Unit V at Sites 1257, 1258, and 1260. In contrast, euxinic conditions were limited to Unit IV at Site 1259, based on the present sampling resolution. Besides an onset of euxinic conditions already occurring during clastic sediment deposition of Unit V, a later sulfidization of underlying sediments as described for sediments below sapropels of the Kau Basin (Middelburg, 1991), the Eastern Mediterranean (Passier and de Lange, 1998; Passier et al., 1996, 1997, 1999), the Baltic Sea (Böttcher and Lepland, 2000), or the Black Sea (Jørgensen et al., 2004) may also have caused this iron sulfide enrichment. A similar diagenetic sulfidization mechanism was identified in Mesoproterozoic marine sediments of the Belt Supergroup (Lyons et al., 2000).

 Fe_{HR}/Fe_{T} ratios in Units I–III are below the threshold value for euxinia, indicating an essentially nonsulfidic water column during sediment formation. When the different sites are compared, however, it becomes obvious that Fe_{HR} is relatively enriched in the sediments at Site 1261, which is positioned closest to the paleocoastline and at the lowest paleowater depth. An import of iron from shallower shelf sediments according to the (suboxic) OMZ model is consistent with this observation.

The covariation of S_P with TOC data is presented in a Berner plot (Fig. **F6**) and compared to the relationship proposed for "normal marine sediments" (Berner and Raiswell, 1983). Only a few data points coincide





with the relation found for clastic sediments below an oxic water column. A number of data points plot above the regression line, indicating an excess of sulfur that may coincide with a euxinic depositional environment (Leventhal, 1983; Raiswell and Berner, 1985). At highest TOC contents, however, most data show a relative excess of OM. This indicates a certain degree of iron limitation during black shale deposition (Leventhal, 1983) as also found for the Black Sea and Mediterranean sapropels (Fig. F6) or Albian black shales from the North Atlantic (Hofmann et al., 2000). Iron limitation upon black shale formation is also indicated from the sedimentary sulfur speciation (Fig. F4). S_P in the investigated black shale samples makes up between 30% and 100% of $S_{T_{\nu}}$ with a decrease of the relative importance with increasing OM content (Fig. F7). This indicates the importance of the balance between OM and the syngenetic metal flux to the surface sediments. In addition to fixation of sulfide by the reaction with iron, OM acted as the second important sulfur trap during early diagenesis.

Organic Sulfur Formation

Sulfur can react with OM via a number of different pathways, where sulfide and polysulfides are the most likely reaction partners (Aizenshtat et al., 1983, 1995). This requires a decreased availability of reactive iron and leads to a modification of reactivity of the remaining OM (Sinninghe Damsté and De Leeuw, 1990). Organic sulfur incorporation is found in the high-TOC black shale samples at all sites (Fig. F4). From the nearly linear variation of organic sulfur and organic carbon contents (Fig. F6), essentially constant atomic C/S ratios are obtained. Quantitatively, the samples with TOC contents exceeding ~2 wt% have as much as 10 atom% organic sulfur. Most of the atomic S/C ratios fall in the range of 0.04 to 0.06. A similar linear relationship has been observed previously for Mediterranean sapropels by Passier et al. (1999). The fraction of S_{ORG}, however, is relatively more enriched in the Cretaceous black shale samples, probably due to a higher abundance of reactive sulfur species or a higher reactivity of the OM toward sulfurization. From a comparison with literature data it is obvious that OM in the black shales is significantly enriched in sulfur when compared to marine planktonic material (S/C of ~0.008) (Francois, 1987). This is due to the reaction of reduced sulfur species with OM upon early diagenesis (Aizenshtat et al., 1983, 1995; Bein et al., 1990; Raiswell et al., 1993; Sinninghe Damsté and de Leeuw, 1990; Passier et al., 1999; Werne et al., 2004). Stable sulfur isotope measurements have shown that the original seawater-derived sulfur in the OM was superimposed by the addition of diagenetic sulfur species (Bein et al., 1990; Passier et al., 1999). The relative importance of OM sulfurization compared to the bonding to pyrite increases with OM contents (Fig. F7). Deviations of atomic S/C ratios from the mean value of 0.056 (TOC > 2 wt%) may be caused by different extents of dissolved sulfur species availabilities and/or different sulfur sink capacities of OM. In Creaceous carbonates, Bein et al. (1990) observed maximum S/C ratios as high as 0.38. On the other hand, Jurassic black shales, anoxic Peru margin upwelling sediments, and Mediterranean sapropels had maximum S/C ratios of 0.019, 0.056, and 0.038, respectively (Raiswell et al., 1993; Mossmann et al., 1991; Passier et al., 1999).

F7. Covariation of sulfur fraction in pyrite with TOC, p. 21.



CONCLUSIONS

A detailed geochemical analysis of iron and sulfur speciation in sediments recovered during Leg 207 on the Demerara Rise show that the paleoenvironment was euxinic during Cretaceous black shale deposition with iron sulfides being formed in the sulfidic part of the water column and the sediment. This requires the transport of iron to the place of iron sulfide formation, for instance, via an intense but not sulfidic OMZ. In addition, OM acted as an important early diagenetic sink for dissolved reduced/intermediate sulfur species at (present) OM contents exceeding ~2 wt%. Results from the five different sites demonstrate that environmental redox conditions were not constant with time. A more detailed analysis of iron-sulfur speciation during black shale deposition at Sites 1258 and 1260 together with sulfur isotope partitioning between sulfur species is needed and is currently being carried out to identify the frequency of changes in water column euxinia during black shale deposition with time in relation to the availability of iron.

ACKNOWLEDGMENTS

We thank the scientific and technical crew of Leg 207 for support during onboard sampling and R. Kort (Institute of Chemistry and Biology of the Marine Environment, Oldenburg) for technical support during SEM measurements. This research used samples and data provided by the Ocean Drilling Program (ODP). ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc. Research was funded by Deutsche Forschungsgemeinschaft (grants BO 1584/2-1,2 and BR 775/16-1,2 and 17-1,2) and Max Planck Society, Germany. Work on sediments from the Black Sea was funded by Deutsche Forschungsgemeinschaft to MEB and BBJ during DFG-SPP (RV Meteor cruise M51-4; grant JO 307/6-1). M.E. Böttcher wishes to thank E. Clapton, R. Gilbert, G. Harrison, and J. Lennon for their influence on the atmosphere during manuscript preparation. The manuscript is dedicated to E.O. Böttcher on the occasion of his 80th birthday. Constructive comments by editor M. Malone, reviewer T.J. Algeo, and an anonymous reviewer helped to improve the manuscript.

REFERENCES

- Aizenshtat, Z., Krein, E., Vairavamurthy, M., and Goldstein, T., 1995. Role of sulfur in the transformation of sedimentary organic matter: a mechanistic overview. *ACS Symp. Ser.*, 612:378–396.
- Aizenshtat, Z., Stoler, A., Cohen, Y., and Nielsen, H., 1983. The geochemical sulphur enrichment of recent organic matter by polysulfides in the Solar Lake. *In Bjorøy*, M., Albrecht, C., Cornford, C., de Groot, K., Eglinton, G., et al. (Eds.), *Advances in Organic Geochemistry*, 1981. Proc. Int. Meet. Org. Geochem., 10:279–288.
- Anderson, T.F., and Raiswell, R., 2004. Sources and mechanisms for the enrichment of highly reactive iron in euxinic Black Sea sediments. *Amer. J. Sci.*, 304:203–233.
- Arndt, S., Brumsack, H.-J., Hetzel, A., and Wirtz, K., 2006. Cretaceous black shales as active bioreactors: a biogeochemical model for the deep biosphere encountered during ODP Leg 207 (Demerara Rise). *Geochim. Cosmochim. Acta*, 70 (2): 480–425. doi:10.1016/j.gca.2005.09.010
- Arthur, M.A., and Dean, W.E., 1998. Organic-matter production and preservation and evolution of anoxia in the Holocene Black Sea. *Paleoceanography*, 13:395–411. doi:10.1029/98PA01161
- Arthur, M.A., Dean, W.E., and Pratt, L.M., 1988. Geochemical and climatic effects of increased marine organic carbon burial at the Cenomanian/Turonian boundary. *Nature (London, U. K.)*, 335:714–717. doi:10.1038/335714a0
- Arthur, M.A., and Sageman, B.B., 1994. Marine black shales: depositional mechanisms and environments of ancient deposits. *Annu. Rev. Earth Planet. Sci.*, 22:499– 551. doi:10.1146/annurev.ea.22.050194.002435
- Babu, C.P., Brumsack, H.-J., and Schnetger, B., 1999. Distribution of organic carbon in surface sediments along the eastern Arabian Sea: a revisit. *Mar. Geol.*, 162:91–103. doi:10.1016/S0025-3227(99)00047-X
- Bein, A., Almogi-Labin, A., and Sass, E., 1990. Sulfur sinks and organic carbon relationships in Cretaceous organic-rich carbonates: implications for evaluation of oxygen-poor depositional environments. Am. J. Sci., 290:882–911.
- Berner, R.A., and Raiswell, R., 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. *Geochim. Cosmochim. Acta*, 47:855– 862.
- Boetius, A., Ravenschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gieseke, A., Amann, R., Jørgensen, B.B., Witte, U., and Pfannkuche, O., 2000. A marine microbial consortium apparently mediating the anaerobic oxidation of methane. *Nature* (*London, U. K.*), 407:623–626. doi:10.1038/35036572
- Böttcher, M.E., Brumsack, H.-J., and de Lange, G.J., 1998. Sulfate reduction and related stable isotope (³⁴S, ¹⁸O) variations in interstitial waters from the Eastern Mediterranean. *In* Robertson, A.H.F., Emeis, K.-C., Richter, C., and Camerlenghi, A. (Eds.), *Proc. ODP, Sci. Results*, 160: College Station, TX (Ocean Drilling Program), 365–373. doi:10.2973/odp.proc.sr.160.002.1998
- Böttcher, M.E., and Lepland, A., 2000. Biogeochemistry of sulfur in a sediment core from the west-central Baltic Sea: evidence from stable isotopes and pyrite textures. *J. Mar. Sys.*, 25:299–312.
- Böttcher, M.E., Rinna, J., Warning, B., Wehausen, R., Howell, M.W., Schnetger, B., Stein, R., Brumsack, H.-J., and Rullkötter, J., 2003. Geochemistry of sediments from the connection between the western and eastern Mediterranean Sea (Strait of Sicily, ODP Site 963). *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 190:165–194. doi:10.1016/S0031-0182(02)00604-1
- Böttcher, M.E., and Schnetger, B., 2004. Direct measurement of the content and isotopic composition of sulfur in black shales by means of combustion-isotope-ratiomonitoring mass spectrometry (C-irmMS). *In* de Groot, P. (Ed.), *Handbook of Stable Isotope Analytical Techniques:* Amsterdam (Elsevier), 597–603.

- Brumsack, H.-J., 1980. Geochemistry of Cretaceous black shales from the Atlantic Ocean (DSDP Legs 11, 14, 36, and 41). *Chem. Geol.*, 31:1–25. doi:10.1016/0009-2541(80)90064-9
- Brumsack, H.-J., 1986. The inorganic geochemistry of Cretaceous black shales (DSDP Leg 41) in comparison to modern upwelling sediments from the Gulf of California. *In* Summerhayes, C.P., and Shackleton, N.J. (Eds.), *North Atlantic Palaeoceanography*. Spec. Publ.—Geol. Soc. London, 21:447–462.
- Brumsack, H.-J., 2006. The trace metal content of recent organic carbon-rich sediments: implications for Cretaceous black shale formation. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* doi:10.1016/j.palaeo.2005.05.011
- Brumsack, H.-J., and Wehausen, R., 1999. A geochemical record of precessioninduced cyclic eastern Mediterranean sedimentation: implications for northern Sahara humidity during the Pliocene. *Naturwissenschaften*, 86:281–286. doi:10.1007/s001140050615
- Calvert, S.E., Thode, H.G., Yeung, D., and Karlin, R.E., 1996. A stable isotope study of pyrite formation in the Late Pleistocene and Holocene sediments of the Black Sea. *Geochim. Cosmochim. Acta*, 60:1261–1270. doi:10.1016/0016-7037(96)00020-8
- Canfield, D.E., 1989. Reactive iron in marine sediments. *Geochim. Cosmochim. Acta*, 53:619–632. doi:10.1016/0016-7037(89)90005-7
- Canfield, D.E., Lyons, T.W., and Raiswell, R., 1996. A model for iron deposition to euxinic Black Sea sediments. *Am. J. Sci.*, 296:818–834.
- Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., and Berner, R.A., 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shale. *Chem. Geol.*, 54:149–155. doi:10.1016/0009-2541(86)90078-1
- Cline, J.D., 1969. Sectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.*, 14:454–458.
- Dean, W.E., and Arthur, M.A., 1989. Iron-sulfur relationships in organic-carbon-rich sequences, I. Cretaceous western interior seaway. *Am. J. Sci.*, 289:708–743.
- Emeis, K.-C., Sakamoto, T., Wehausen, R., and Brumsack, H.-J., 2000. The sapropel record of the Eastern Mediterranean Sea—results of Ocean Drilling Program Leg 160. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 158:371–395. doi:10.1016/S0031-0182(00)00059-6
- Erbacher, J., Friedrich, O., Wilson, P.A., Birch, H., and Mutterlose, J., 2005. Stable organic carbon isotope stratigraphy across Oceanic Anoxic Event 2 of Demerara Rise, western tropical Atlantic. *Geochem., Geophys., Geosyst.,* 6(6):Q06010. doi:10.1029/2004GC000850
- Erbacher, J., Mosher, D.C., Malone, M.J., et al., 2004. *Proc. ODP, Init. Repts.*, 207: College Station, TX (Ocean Drilling Program). doi:10.2973/odp.proc.ir.207.2004
- Francois, R., 1987. A study of sulfur enrichment in the humic fraction of marine sediments during early diagenesis. *Geochim. Cosmochim. Acta*, 51:17–27. doi:10.1016/ 0016-7037(87)90003-2
- Gauthier, D.L., 1987. Isotopic composition of pyrite: relationship to organic matter type and iron availability in some North American Cretaceous shales. *Chem. Geol.*, 65:293–303.
- Grice, K., Cao, C., Love, G.D., Böttcher, M.E., Twitchett, R.J., Grosjean, E., Summons, R.E., Turgeon, S.C., Dunning, W., and Jin, Y., 2005. Photic zone euxinia during the Permian–Triassic superanoxic event. *Science*, 307:706–709. doi:10.1126/science.1104323
- Haese, R.R., 2000. The reactivity of iron. *In* Schulz, H.D., and Zabel, M. (Eds.) *Marine Geochemistry:* Berlin (Springer), 233–261.
- Hinrichs, K.-U., Hayes, J.M., Sylva, S.P., Brewer, P.G., and DeLong, E.F., 1999. Methane consuming archaebacteria in marine sediments. *Nature (London, U. K.)*, 398:802– 805. doi:10.1038/19751
- Hoehler, T.M., Alperin, M.J., Albert, D.B., and Martens, C.S., 1994. Field and laboratory studies of methane oxidation in an anoxic sediment—evidence for methano-

gen-sulfate reducer consortium. *Global Biogeochem. Cycles*, 8:451–464. doi:10.1029/94GB01800

- Hofmann, P., Ricken, W., Schwark, L., and Leythäuser, D., 2000. Carbon-sulfur-iron relationships and δ^{13} C of organic matter for late Albian sedimentary rocks from the North Atlantic Ocean: paleoceanographic implications. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 163:97–113. doi:10.1016/S0031-0182(00)00147-4
- Jenkyns, H.C., 1980. Cretaceous anoxic events: from continents to oceans. J. Geol. Soc. (London, U. K.), 137:171–188.
- Jørgensen, B.B., Böttcher, M.E., Lüschen, H., Neretin, L.N., and Volkov, I.I., 2004. Anaerobic methane oxidation and a deep H₂S sink generate isotopically heavy sulfides in Black Sea sediments. *Geochim. Cosmochim. Acta*, 68:2095–2118. doi:10.1016/j.gca.2003.07.017
- Lepland, A., and Stevens, R.L., 1998. Manganese authigenesis in the Landsort Deep, Baltic Sea. *Mar. Geol.*, 151:1–25. doi:10.1016/S0025-3227(98)00046-2
- Leventhal, J.S., 1983. An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition. *Geochim. Cosmochim. Acta*, 47:133–137. doi:10.1016/0016-7037(83)90097-2
- Lourens, L.J., Wehausen, R., and Brumsack, H.-J., 2001. Geological constraints on tidal dissipation and dynamical ellipticity of the Earth over the past three million years. *Nature (London, U. K.)*, 409:1029–1033. doi:10.1038/35059062
- Lyons, T.W., 1997. Sulfur isotopic trends and pathways of iron sulfide formation in upper Holocene sediments of the anoxic Black Sea. *Geochim. Cosmochim. Acta*, 61:3367–3382. doi:10.1016/S0016-7037(97)00174-9
- Lyons, T.W., Luepke, J.J., Schreiber, M.E., and Zieg, G.A., 2000. Sulfur geochemical constraints on Mesoproterozoic restricted marine deposition: lower Belt Supergroup, northwestern United States. *Geochim. Cosmochim. Acta*, 64:427–437. doi:10.1016/S0016-7037(99)00323-3
- Manheim, F.T., and Sayles, F.L., 1974. Composition and origin of interstitial waters of marine sediments, based on deep sea drill cores. *In* Goldberg, E.D. (Ed.), *The Sea* (Vol. 5): *Marine Chemistry: The Sedimentary Cycle:* New York (Wiley), 527–568.
- Middelburg, J.J., 1991. Organic carbon, sulphur, and iron in recent semi-euxinic sediments of Kau Bay, Indonesia. *Geochim. Cosmochim. Acta*, 55 (3):815–828. doi:10.1016/0016-7037(91)90344-5
- Mossmann, J.R., Aplin, A.C., Curtis, C.D., and Coleman, M.L., 1991. Geochemistry of inorganic and organic sulphur in organic-rich sediments from the Peru margin. *Geochim. Cosmochim. Acta*, 55:3581–3595. doi:10.1016/0016-7037(91)90057-C
- Passier, H.F., Böttcher, M.E., and de Lange, G.J., 1999. Sulphur enrichment in organic matter of Eastern Mediterranean sapropels; a study of sulphur isotope partitioning. *Aquat. Geochem.*, 5:99–118. doi:10.1023/A:1009676107330
- Passier, H.F., and de Lange, G.J., 1998. Sedimentary sulfur and iron chemistry in relation to the formation of Eastern Mediterranean sapropels. *In* Robertson, A.H.F., Emeis, K.-C., Richter, C., and Camerlenghi, A. (Eds.), *Proc. ODP, Sci. Results*, 160: College Station, TX (Ocean Drilling Program), 249–259. doi:10.2973/odp.proc.sr.160.020.1998
- Passier, H.F., Middelburg, J.J., de Lange, G.J., and Böttcher, M.E., 1997. Pyrite contents, microtextures and sulphur isotopes in relation to formation of the youngest Eastern Mediterranean sapropel. *Geology*, 25:519–522. doi:10.1130/0091-7613(1997)025<0519:PCMASI>2.3.CO;2
- Passier, H.F., Middelburg, J.J., Van Os, B.J.H., and de Lange, G.J., 1996. Diagenetic pyritization under Eastern Mediterranean sapropels caused by downward sulphide diffusion. *Geochim. Cosmochim. Acta*, 60:751–763. doi:10.1016/0016-7037(95)00419-X
- Petsch, S.T. Berner, R.A., and Eglinton, T.I., 2000. A field study of the chemical weathering of ancient sedimentary organic matter. *Org. Geochem.*, 31:475–487. doi:10.1016/S0146-6380(00)00014-0

- Petsch, S.T., Edwards, K.J., and Eglinton, T.I., 2005. Microbial transformations of organic matter in black shales and implications for global biogeochemical cycles. *Palaeogeogr., Palaeoclimatol., Palaeoecol.,* 219:157–170. doi:10.1016/ j.palaeo.2004.10.019
- Petsch, S.T., Eglinton, T.I., and Edwards, K.J., 2001. ¹⁴C-dead living biomass: evidence for microbial assimilation of ancient organic carbon during shale weathering. *Science*, 292:1127–1131. doi:10.1126/science.1058332
- Raiswell, R., and Berner, R.A., 1985. Pyrite formation in euxinic and semi-euxinic sediments. *Am. J. Sci.*, 285:710–724.
- Raiswell, R., Bottrell, S.H., Al-Biatty, H.J., and Tan, M.Md., 1993. The influence of bottom water oxygenation and reactive iron content on sulfur incorporation into bitumens from Jurassic marine shales. *Am. J. Sci.*, 293:569–596.
- Raiswell, R., and Canfield, D.E., 1998. Sources of iron for pyrite formation in marine sediments. *Am. J. Sci.*, 298:219–245.
- Raiswell, R., Newton R., and Wignall, P.B., 2001. An indicator of water-column anoxia: resolution of biofacies variations in the Kimmeridge Clay (Upper Jurassic, UK). *J. Sediment. Res.*, 71:286–294.
- Rinna, J., Warning, B., Meyers, P.A., Brumsack, H.J., and Rullkötter, J., 2002. Combined organic and inorganic geochemical reconstruction of paleodepositional conditions of a Pliocene sapropel from the eastern Mediterranean Sea. *Geochim. Cosmochim. Acta*, 66:1969–1986. doi:10.1016/S0016-7037(02)00826-8
- Rullkötter, J., 2000. Organic matter: the driving force for early diagenesis. *In* Schulz, H.D., and Zabel, M. (Eds.), *Marine Geochemistry:* Berlin (Springer), 129–172.
- Schlanger, S.O., and Jenkyns, H.C., 1976. Cretaceous oceanic anoxic events: causes and consequences. *Geol. Mijnbouw*, 55:179–184.
- Schnetger, B., Brumsack, H.-J., Schale, H., Hinrichs, J., and Dittert, L., 2000. Geochemical characterization of deep-sea sediments from the Arabian Sea: a high-resolution study. *Deep-Sea Res., Part II*, 47:2735–2768. doi:10.1016/S0967-0645(00)00047-3
- Shen, Y., Knoll, A.H., and Walter, M.R., 2003. Evidence for low sulphate and anoxia in a mid-Proterozoic marine basin. *Nature (London, U. K.)*, 423:632–635. doi:10.1038/nature01651
- Sinninghe Damstae, J.S., and Koester, J., 1998. A euxinic southern North Atlantic Ocean during the Cenomanian/Turonian oceanic anoxic event. *Earth Planet. Sci. Lett.*, 158:165–173. doi:10.1016/S0012-821X(98)00052-1
- Sinninghe Damsté, J.S., and De Leeuw, J.W., 1990. Analysis, structure and geochemical significance of organically-bound sulfur in the geosphere: state of the art and future research. *Org. Geochem.*, 16:1077–1101. doi:10.1016/0146-6380(90)90145-P
- Stookey, L.L., 1970. Ferrozine—a new spectrophotometric reagent for iron. *Anal. Chem.*, 42:779–781. doi:10.1021/ac60289a016
- Wang, Q., and Morse, J.W., 1996. Pyrite formation under conditions approximating those in anoxic sediments, I. Pathways and morphology. *Mar. Chem.*, 52:99–121. doi:10.1016/0304-4203(95)00082-8
- Werne, J.P., Hollander, D.J., Lyons, T.W., and Sinninghe Damsté, J.S., 2004. Organic sulfur biogeochemistry: recent advances and future research directions. *Spec. Pap.—Geol. Soc. Am.*, 379:135–205.
- Wilkin, R.T., Barnes, H.L., and Brantley, S.L., 1996. The size distribution of framboidal pyrite in modern sediments: an indicator of redox conditions. *Geochim. Cosmochim. Acta*, 60:3897–3912. doi:10.1016/0016-7037(96)00209-8
- Wijsman, J.W.M., Middelburg, J.J., and Heip, C.H.R., 2001. Reactive iron in Black Sea sediments: implications for iron cycling. *Mar. Geol.*, 172:167–180. doi:10.1016/S0025-3227(00)00122-5
- Zhabina, N.N., and Volkov, I.I., 1978. A method of determination of various sulfur compounds in sea sediments and rocks. *In* Krumbein, W.E. (Ed.), *Environmental Biogeochemistry and Geomicrobiology* (Vol. 3): Ann Arbor (Ann Arbor Sci. Publ.), 735–746.

Figure F1. Positions of the investigated five sites cored during Leg 207 in the tropical Atlantic on the Demerara Rise, off Suriname. A. Map modified from Erbacher, Mosher, Malone, et al. (2004). B. Map was created using the Generic Mapping Tools (GMT) program (www.aquarius.geomar.de).



Figure F2. Onboard measurements of selected constituents in pore waters at Sites (A) 1257, (B) 1258, (C) 1259, (D) 1260, and (E) 1261 (from Erbacher, Mosher, Malone, et al. [2004] and ODP database). TA = total alkalinity. (Continued on next page.)



M.E. BÖTTCHER ET AL. SULFUR-IRON-CARBON GEOCHEMISTRY IN SEDIMENTS

Figure F2 (continued).



M.E. BÖTTCHER ET AL. SULFUR-IRON-CARBON GEOCHEMISTRY IN SEDIMENTS

Figure F3. Comparison of the results of two analytical approaches to measure organic sulfur (S_{ORG}) contents in black shale samples (see "Materials and Methods," p. 3).



Figure F4. Downcore variations of selected geochemical parameters for Sites (A) 1257, (B) 1258, (C) 1259, (D) 1260, and (E) 1261. Definition of lithological units according to Erbacher, Mosher, Malone, et al. (2004). TOC = total organic carbon, TIC = total inorganic carbon, Fe_T = total iron, Fe_D = still-reactive iron, Fe_P = pyrite iron, S_T = total sulfur, S_P = pyrite sulfur, S_{ORG} = OM (essentially kerogen)-bound organic sulfur. Dashed line in the relative abundance of highly reactive iron (Fe_{HR}/Fe_T) plots indicates boundary to euxinic conditions (see "**Reactive Iron Phases and Pyrite Formation**," p. 5). (Continued on next page.)



M.E. BÖTTCHER ET AL. SULFUR-IRON-CARBON GEOCHEMISTRY IN SEDIMENTS



Figure F4 (continued).

Figure F5. A–B. SEM photographs of framboidal pyrite found in a foraminifer shell in a black shale sample (Sample 207-1260B-40R-4, 140–150 cm). B is an extension from A.



10 µm



3 µm

Figure F6. Covariation of (A) pyrite (S_P) and (B) organic sulfur (S_{ORG}) contents as a function of total organic carbon (TOC) contents. Dashed line marks the relationship derived for normal marine sediments as defined by Berner and Raiswell (1983). o = Leg 207, this study. x = data for Holocene and Pleistocene sediments from the Black Sea (Core BS4-14GC; Calvert et al., 1996; Core GeoB 7620-2, M. Böttcher and B. Jørgensen, unpubl. data). + = data for sapropelic sediments from the Mediterranean Sea (Böttcher et al., 2003).



Figure F7. Covariation of the sulfur fraction in pyrite with total organic carbon (TOC) in black shale samples.



Table T1. Drilling locations of Leg 207 with geo-graphical positions and water depths.

Hole	Latitude	Longitude	Water depth (mbsl)
1257A	9°27.230′N	54°20.518′W	2951.0
1257B	9°27.218′N	54°20.508′W	2951.0
1257C	9°27.206′N	54°20.495′W	2951.0
1258A	9°26.000′N	54°43.999′W	3192.2
1258B	9°26.000′N	54°43.982′W	3192.2
1258C	9°26.000′N	54°43.966′W	3192.2
1259A	9°17.999′N	54°11.998′W	2353.8
1259B	9°18.048′N	54°11.945′W	2353.8
1259C	9°18.024′N	54°11.969′W	2353.8
1260A	9°15.984′N	54°32.633′W	2548.8
1260B	9°15.931′N	54°32.652′W	2548.8
1261A	9°2.917′N	54°19.038′W	1899.7
1261B	9°2.918′N	54°19.049′W	1899.7

Note: mbsl = meters below sea level.

Table T2. Range of geochemical parameters in the Fe-S-C system measured on squeeze cake samples of Unit IV sediments from Leg 207.

Fe-S-C (wt%)	Site 1257	Site 1258	Site 1259	Site 1260	Site 1261
тос	3.5–7.7	5.7–15.1	7.6–18.6	2.7–6.0	9.2–12.0
TIC	5.3-6.3	2.4–6.9	4.9–7.1	8.1–10.4	4.4-6.4
Fe _T	0.6–4.6	1.1-3.1	0.7–1.7	0.6–1.2	0.8–1.5
Fe _P	0.4–1.4	0.5-2.3	0.4–1.2	0.4-0.9	0.6–1.3
Fe _{HR}	0.4–1.5	0.6–2.6	0.4–1.3	0.4-0.9	0.6–1.3
S _T	1.3-2.0	1.7–4.7	1.3-4.5	0.8–1.5	2.0-3.3
Sp	0.5–1.6	0.6-3.0	0.4–1.4	0.4–1.0	0.7–1.5
S _{ORG}	0.3–1.0	1.2–2.9	0.8–3.1	0.4–0.8	1.4–1.9

Notes: Fe_P was calculated from S_P measurements considering the stoichiometric composition of pyrite. Corresponding main, minor, and trace elements are found in **Hetzel et al.** (this volume). TOC = total organic carbon, TIC = total inorganic carbon, Fe_T = total iron, Fe_P = pyrite iron, Fe_{HR} = highly reactive iron, S_T = total sulfur, S_P = pyrite sulfur, S_{ORG} = organic matter (essentially kerogen)-bound organic sulfur.