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Trace metal signatures of Jurassic/Cretaceous black shales from the Norwegian Shelf and the Barents Sea

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Abstract

Black shale samples of Jurassic to Cretaceous age recovered during the ‘Norwegian Shelf Drilling Program’ between 1987 and 1991 from Sites 7430/10-U-01 (Barents Sea), 6814/04-U-02 (Norwegian Shelf near the Lofoten) and 6307/07-U-02 (Norwegian Shelf near Trondheim) were analyzed for major and trace elements. These laminated black shales are characterized by high total organic carbon (TOC) and total sulfur (TS) contents as well as by significant enrichments in several redox-sensitive and/or sulfide-forming trace metals (Ag, Bi, Cd, Co, Cr, Cu, Mo, Ni, Re, Sb, Tl, U, V, and Zn). Enrichment factors relative to ‘average shale’ are comparable to those found in Cenomanian–Turonian boundary event (CTBE) black shales and Mediterranean sapropels. The Re content is high in the studied black shales, with maximum values up to 1221 ng/g. Re/Mo ratios averaging 2.3×10^{-3} are close to the seawater value. High trace metal enrichments and Re/Mo ratios close to the seawater value point to a dominantly anoxic and sulfidic water column during black shale formation. Interbeds with higher Re/Mo ratios, especially in high-resolution sampled core sections, point to brief periods of suboxic conditions. Additionally, enhanced Zn concentrations in the black shales from the Barents Sea support the assumption that hydrothermal activity was also high during black shale deposition. Trace metal signatures of black shales at different drill sites on a transect along the Norwegian Shelf are not only influenced by water depth but also by their location in the boreal realm. Metal enrichments are higher in the northern compared to the southern sites. Volgian (= Tithonian 151–144 Ma BP) black shales exhibit elevated trace metal contents in comparison to their Berriasian (144–137 Ma BP) counterparts. This probably reflects a change in the circulation pattern during periods of black shale formation. Therefore different paleoceanographic conditions, probably controlled by climatic change linked to the transgression of the paleo-sealevel and the North Atlantic opening, may have developed from the Volgian to the Berriasian.

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1. Introduction

The earlier notion of the Jurassic and Creta-

ceous being times of monotonously warm, equable conditions with sluggish ocean circulation has given way to much more varied views of changing paleoclimatic and oceanographic conditions, especially during the Late Jurassic and Early Cretaceous (Barrera and Johnson, 1999; Huber et al.,

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2000). Global paleoenvironmental changes should be most clearly reflected in high latitudes, but because of the paucity of outcrops and drill core material, most studies have concentrated on low latitudes, in particular south of 40°N in the Tethys region (Kollmann and Zapfe, 1992). In order to obtain a better understanding of the Cretaceous paleoenvironment of the northern hemisphere (the ‘boreal realm’), information from higher paleolatitudes is needed. We have chosen sediment samples of Kimmeridgian (~154 Ma) to Barremian (~121 Ma) age from cores on the Norwegian Shelf. The paleolatitudes of these sites were 42–67°N during the Late Jurassic/Early Cretaceous in a narrow seaway between Greenland and Norway connecting the Tethyan with the northern polar ocean. The geological settings of these sites are discussed by Århus (1991), Leith et al. (1992), Smelror (1994), Smelror et al. (1994, 1998, 2001a,b), Jongepier et al. (1996), Dypvik et al. (1996), and Mutterlose and Kessels (2000).

Numerous dark-colored, often laminated, organic-rich sediment layers are intercalated with Kimmeridgian to Barremian organic carbon-poor claystone/clayey sandstone and limestone. Layers >1 cm thick and containing >1% total organic carbon (TOC) are defined as ‘black shales’ by Pettijohn (1957). Black shales are further characterized by high Fe and S contents and significant enrichments in various trace elements (Nijenhuis et al., 1998). The geochemical behavior of trace metals in modern organic carbon-rich sediments, such as upwelling areas and anoxic basins, has been frequently discussed (e.g. Jacobs et al., 1987; Brumsack, 1989; Calvert and Pedersen, 1993). Similar studies have focussed on ancient black shales (e.g. Brumsack, 1980, 1986; Arthur et al., 1990). Enrichments of redox-sensitive elements should reflect the depositional environment of ancient TOC-rich sediments and sedimentary rocks and may therefore be used to elucidate the paleoceanographic conditions leading to their formation (Brumsack, 1980, 1986; Hatch and Leventhal, 1992; Piper, 1994). The trace element Re seems to reflect paleo-redox conditions with particular sensitivity (Colodner et al., 1993, 1995; Crusius et al., 1996).

In this paper we present trace element data of

black shales in samples of Kimmeridgian to Barremian age originating from different locations along the Norwegian Shelf. Through high-resolution sampling (~10 ka for cores 6814/04-U-02 and 6307/07-U-02, ~20 ka for core 7430/10-U-01) we hope to discern even small changes in water column redox conditions during the Late Jurassic and Early Cretaceous. The purpose of our contribution is to use Re/Mo ratios in connection with trace metal enrichments as proxies to distinguish between oxic, suboxic, and anoxic/sulfidic depositional conditions and to provide new data on the temporal and spatial distribution of specific trace metals in Norwegian black shales.

2. Material and methods

660 samples were collected during the ‘Norwegian Shelf Drilling Program’ from Sites 7430/10-U-01 (Barents Sea), 6814/04-U-02 (Norwegian Shelf near Tromsø) and 6307/07-U-02 (Norwegian Shelf near Trondheim) (e.g. Århus, 1991). Black shale subsamples (445 total), each comprising 2 cm intervals, were collected from the three drill sites. The samples of Kimmeridgian to Barremian age form a transect along the Norwegian–Greenland seaway on the Norwegian Shelf (Fig. 1). The northernmost site (7430/10-U-01) is located in 335 m water depth in the Barents Sea near Svalbard (Spitsbergen) on a wide bathymetric plain, the Bjarmeland Platform. This site contains black shales (139 samples) of Kimmeridgian to Barremian age. Site 6814/04-U-02 was drilled on the central Norwegian Shelf at 233 m water depth at the base of the Lofoten Ridge. Black shales of Volgian to Barremian age were identified in this core (135 samples). Site 6307/07-U-02 is located in the Hitra Basin at a water depth of 290 m on the southern portion of the Norwegian Shelf near Smøla. At this location 171 discrete black shale samples from Volgian to Valanginian age were recovered. In this study the term ‘black shale’ is used in reference to all organic-rich layers containing >2.0% TOC.

The samples were ground and homogenized in an agate ball mill. For X-ray fluorescence (XRF)

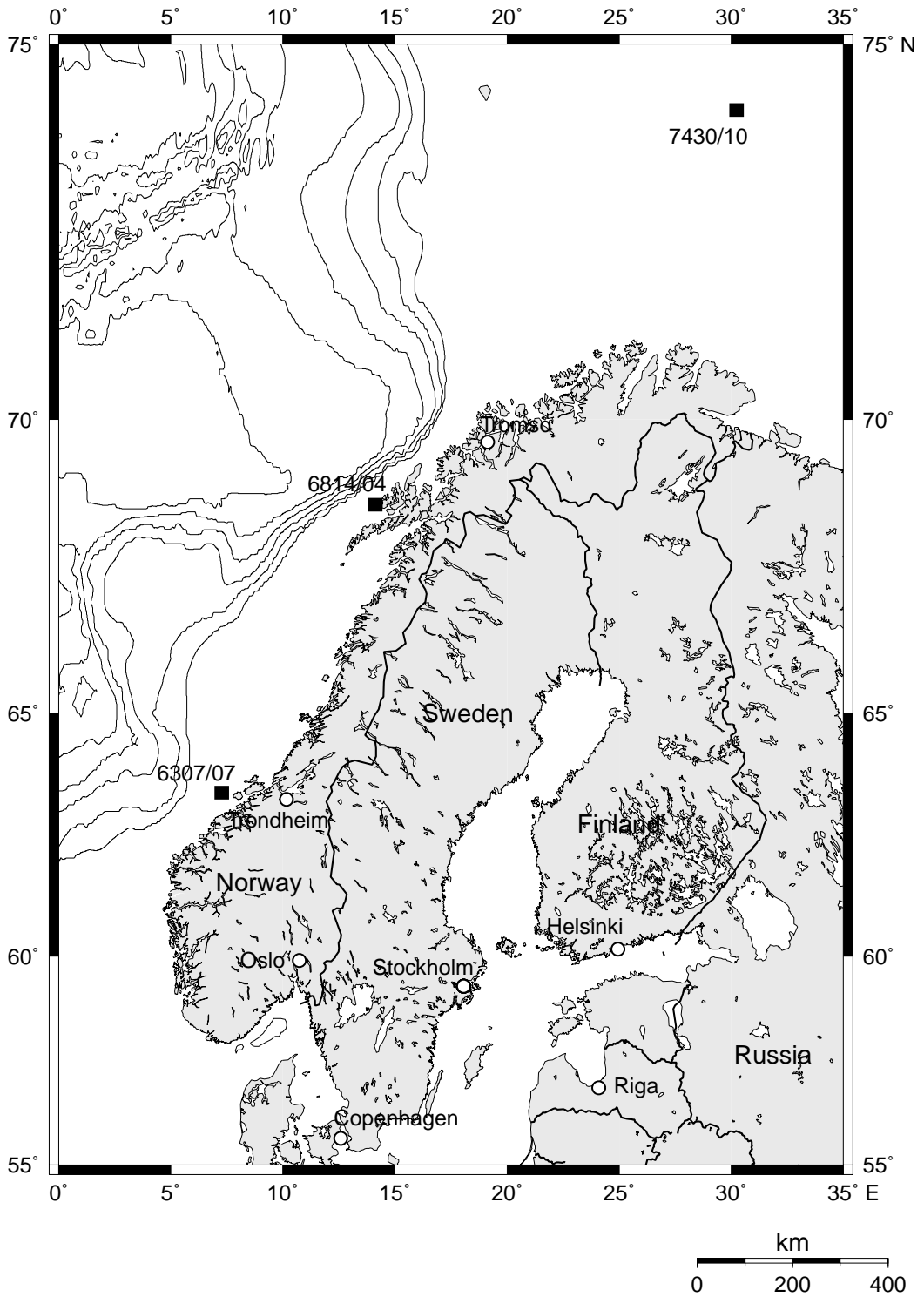


Fig. 1. Norwegian Shallow Drilling Program sampling locations along the Norwegian Shelf and the Barents Sea.

analysis on a Philips® PW 2400 X-ray spectrometer, 600 mg of sample was mixed with 3600 mg lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$, Spektromelt®), ashed at 500°C, preoxidized at 500°C with NH_4NO_3 (p.a.) and fused into glass-beads. Analytical precision was better than 8% for minor elements Co, Cr, Cu, Mo, Ni, V, Zn.

Total carbon and total sulfur were determined with a LECO® SC-444 instrument by IR-detection following combustion at 1400°C. Analytical precision was better than 2.2% for carbon and better than 5.1% for sulfur. Inorganic carbon was measured with an UIC® CM 5012 CO_2 -coulometer by coulometric titration following release of CO_2 with 2 N HClO_4 . Precision of this method was better than 1.5%. TOC was calculated as the difference between total and inorganic carbon. For detailed information see [Prakash Babu et al. \(1999\)](#).

We selected 445 black shale samples from Sites 7430/10-U-01, 6814/04-U-02 and 6307/07-U-02 for inductively coupled plasma mass spectrometry (ICP-MS) analysis. For acid digestions 50 mg of sample was preoxidized with 2 ml HNO_3 (65%) in polytetrafluoroethylene (PTFE) vessels overnight and then heated with 3 ml HF (40%) and 3 ml HClO_4 (70%) in closed PTFE autoclaves (PDS-6) for 6 h at 180°C. The acids were then evaporated on hot plates at 180°C to incipient dryness. Afterwards, four times 3 ml 6 N HCl aliquots were added and evaporated at 180°C. The wet residue was dissolved in 1 ml HNO_3 (65%) and diluted to 10 ml with deionized water and heated once again in closed PTFE autoclaves (PDS-6) for 2 h at 180°C. The acid digestions were diluted to 50 ml and one drop of HF was added for stabilization of LREE. HNO_3 , HCl and HClO_4 were purified by sub-boiling distillation. HF of Suprapure® (Merck) quality was used. Prior to analysis the clear solutions were diluted 1:5 with 2% v/v HNO_3 . Measurements of Ag, Bi, Cd, Mo, Re, Sb, Tl and U were carried out using the double-focusing magnetic sector mass spectrometer 'Element' (Finnigan MAT, Germany). Analytical precision was better than 7.8% (for detailed information see [Schnetger, 1997](#)). Procedures and accuracy of all methods were checked with international (AVG-1, GSD-7, GSR-3, SCO-1, SDO-1

and SGR-1) and in-house (TW-TUC, Loess, PS-S) reference materials (see [Appendix](#)).

3. Results and discussion

Black shales from the Norwegian Shelf of Kimmeridgian to Barremian age are characterized by high TOC, TS, and Fe contents. Concentrations of up to 37.2 wt% TOC and up to 25.8 wt% TS were determined in the black shales recovered during the 'Norwegian Shelf Drilling Program' between 1987 and 1991 ([Table 1](#)). These concentrations are significantly higher than those reported for Mediterranean sapropels ([Warning and Brumsack, 2000](#)). Sulfur is largely present as pyrite in the black shales, indicating anoxic, sulfate-reducing sedimentary conditions ([Langrock et al., submitted](#)).

Calcium carbonate contents between 0.2 and 53.2% (average 3.4%) were determined for all 666 investigated samples. The carbonate content is consistently lower in TOC-rich and higher in TOC-poor samples due to dilution effects. Compared to the surrounding sediments (4–76% CaCO_3 ; [Mutterlose et al., in press](#)), the carbonate content decreases drastically (average 2.7%) in the 455 black shales samples.

Samples from the southern site (Hitra Basin) differ from the more northerly sites (Lofoten Ridge and Barents Sea) in their major element ratios. For example, Ti/Al ratios at the individual sites are significantly different. Samples from the Hitra Basin (0.037) and the Barents Sea (0.046) exhibit Ti/Al ratios lower than those at the Lofoten Ridge (0.050). If we use Zr as a proxy for heavy minerals such as zircon, the lower Zr/Ti ratios in samples from the Hitra Basin (93.3) and Barents Sea (174.8) compared to samples from the Lofoten Ridge (205.6) suggest that the sediments at the latter site must have been transported from shallower and more energetic depositional environments. Shallower water depths or stronger bottom water currents causing winnowing, possibly due to the presence of an oceanic plateau, are indicated by elevated concentrations of elements that are typically enriched in heavy minerals.

Table 1

Comparison of average and maximum (in brackets) contents of organic carbon (TOC), sulfur, trace metals and element/Al ratios of Norwegian black shales, Mediterranean sapropels, TOC-rich sediments and 'average shale'^a

	Norwegian black shales (Mutterlose et al., in press, and this study) <i>n</i> = 445	Mediterranean sapropels (Warning and Brumsack, 2000) <i>n</i> = 240	Black Sea sapropels (Brumsack, 1989) <i>n</i> = 12	CTBE black shales (Arthur et al., 1990; Warning and Brumsack, 2000, Warning, unpubl.) <i>n</i> = 123	Average shale (Wedepohl, 1971, 1991)
TOC	7.6 (37.2)	5.5 (28)	6.5 (14.7)	8.9 (37.4)	0.2
S	3.8 (25.8)	2.8 (17)	1.28 (2.50)	2.1 (8.3)	0.2
Ba	492 (2238)	1015 (3514)	624 (1240)	645 (3882)	580
Ag	2.7 (12.9)	0.5 (2.8) ^b		2.9 (12.9) ^d	0.07
Bi	261 (912)	200 (460) ^c		303 (820) ^d	130
Cd	17 (128)	14 (52)	1.04 (2.1)	16 (201)	0.13
Co	17 (76)	64 (400)	27 (51)	33 (564)	19
Cr	158 (447)	108 (441)	70 (105)	137 (367)	90
Cu	106 (337)	114 (604)	87 (175)	188 (610)	45
Mo	62 (1233)	76 (523)	80 (185)	145 (585)	1.3
Ni	138 (924)	190 (843)	96 (150)	162 (1074)	68
Re	100 (1221)	330 (1000) ^c		210 (2556) ^d	0.5 ^c
Sb	10.5 (62.0)	14.2 (147) ^c		15.4 (82.3) ^d	1
Tl	3.5 (21.6)	3.0 (9.3) ^c		3.5 (25.5) ^d	0.68
U	13 (46)	17 (47) ^c		18 (185) ^d	3
V	864 (4474)	440 (3180)	173 (415)	739 (3575)	130
Zn	944 (7063)	91 (615)	93 (108)	1213 (7763)	95
TOC/Al	0.69	1.41	1.37	3.1	0.02
S/Al	0.45	0.72	0.27	0.60	0.02
Ba/Al	68	265	130	202	65
Ag/Al	0.17	0.14		0.44	0.008
Bi/Al	0.04	0.05		0.05	0.015
Cd/Al	0.9	3.9	0.22	4.6	0.015
Co/Al	2.1	16	5.6	12.6	2.1
Cr/Al	20	26	14	40	10
Cu/Al	9	28	18	63	5.1
Mo/Al	5	20	16	54	0.15
Ni/Al	16	27	20	48	7.6
Re/Al	0.01	0.08		0.01	6 × 10 ⁻⁵
Sb/Al	0.77	3.7		5.3	0.11
Tl/Al	0.24	0.77		0.99	0.08
U/Al	1.7	4.5		2.1	0.34
V/Al	74	112	35	214	15
Zn/Al	57	22	16	423	11

^a TOC and S concentrations in wt%, trace metals in µg/g, Bi and Re in ng/g. TOC/Al and S/Al ratios expressed as weight ratios; trace metal/Al ratios as weight ratios × 10⁻⁴.

^b Value from Warning, unpublished.

^c *n* = 45.

^d *n* = 38.

^e Value from Crusius et al. (1996).

3.1. Trace metal enrichments

The organic carbon-rich layers are significantly enriched in sulfide-forming and/or redox-sensitive trace elements (Table 1). Trace metal enrichments

in black shales have been reported for CTBE black shales (Brumsack, 1980; Arthur et al., 1990; Warning and Brumsack, 2000; Warning, unpublished). The average trace metal contents of black shales studied in this work are compara-

ble with those found in CTBE black shales (>2% TOC) recovered during DSDP/ODP Legs 11, 14, 36, 41, 103, and 122 (Arthur et al., 1990; Warning and Brumsack, 2000; Warning, unpublished; Table 1). Compared to recent TOC-rich sediments from the Black Sea (Kiratli and Ergin, 1996; Brumsack, 1989; Table 1), Norwegian black shales are characterized by more pronounced trace metal enrichments (except for Co and Mo). The Volgian and Early Berriasian black shales have accumulated Co, Cu, Cr, and Ni as well as the rarer trace metals Ag, Bi, Cd, Mo, Re, Sb, Tl, U and, to a larger extent, V very efficiently. These elements can be fixed in high amounts in sediments under reducing conditions (Brumsack, 1980, 1989; Jacobs et al., 1985, 1987; Hatch and Leventhal, 1992; Calvert and Pedersen, 1993). They are either bound to organic matter, precipitated as autonomous sulfides or co-precipitated with Fe-sulfides (Kremling, 1983; Calvert et al., 1985; Jacobs et al., 1985). The direct interaction of Mo with Fe via S bridges led to the concept of a geochemical switch which transfers Mo from a conservative to a particle-reactive element in sulfidic waters without reduction as the initial step (Helz et al., 1996; Adelson et al., 2001). For several trace elements, a reduction step at the redox boundary is necessary to become immobilized in reducing environments (e.g. Cr, Re, Sb, U, and V; Anderson et al., 1989; Cutter, 1991; Emerson and Husted, 1991; Crusius et al., 1996; Rue et al., 1997). Some of the metals (Mo, U, V) may also be enriched during early diagenesis by diffusion into the sediment and fixation after a reduction step (Brumsack and Gieskes, 1983; Shaw et al., 1990).

Barium concentrations of up to 2200 µg/g were measured in the Norwegian black shales. Barium has often been discussed as an indicator for paleoproductivity (e.g. Dehairs et al., 1980; Dymond et al., 1992). Wehausen and Brumsack (1998) showed that Ba is indeed a useful paleoproductivity indicator in the eastern Mediterranean. In shallow marine environments, however, this indicator is not always reliable owing to barite dissolution in sulfate-depleted pore waters (Brumsack and Gieskes, 1983; McManus et al., 1998).

Little has been published about the behavior of

Ag, Tl, and Bi in reducing water columns and sediments. Thallium behaves conservatively in oxic seawater (Flegal and Patterson, 1985) and can be enriched in pyrites (Heinrichs et al., 1980) and reducing sediments (Brumsack, 1980; Thomson et al., 1995), but little is known about the detailed enrichment mechanisms operating in anoxic waters and sediments. The high concentrations found in Norwegian black shales in this study may confirm the preferential Tl accumulation under sulfidic conditions.

Bismuth is only moderately enriched by a factor of 2.7 in the black shales compared to 'average shale' (Wedepohl, 1971, 1991). A similar value was reported for Mediterranean sapropels by Warning and Brumsack (2000). This fact possibly indicates fixation of Bi in anoxic waters and sediments owing to the formation of sulfides. Heinrichs et al. (1980) found Bi (as well as Cd and Tl) enrichments to be more related to sulfur than to organic carbon contents in black shales. Therefore, the enrichment of Bi compared to 'average shale' can be explained due to higher sulfur values. In CTBE black shales Bi is comparably enriched relative to crustal levels as in Mediterranean sapropels and Norwegian black shales. The moderate Bi enrichment may result from the low abundance and very short residence time of this element in seawater owing to its reactivity and involvement in scavenging processes. Bismuth concentrations range between only 5–20 pg/kg in deep waters and 500 pg/kg in surface waters (Lee et al., 1986).

Silver is significantly enriched in black shales from the Barents Sea and shows the same concentration range as CTBE black shales. Silver behaves like a nutrient type element. Concentrations of Ag range between 50 and 3800 pg/kg in seawater (Bruland, 1983). The high Ag enrichment may result from its involvement in the biogeochemical cycle of silica (Ndung'u et al., 2001).

High enrichments of redox-sensitive and sulfide-forming elements (e.g. Mo, V, U, Ag, Cd, and Zn) in various sediments have been related to anoxic bottom water conditions during deposition (Bruland, 1983; Brumsack, 1980, 1986; Jacobs et al., 1985, 1987; Breit and Wanty, 1991; Hatch and Leventhal, 1992; Piper, 1994; Nijen-

huis et al., 1998). For example, in recent sediments of euxinic basins like the Black Sea or the Framvaren Fjord, Mo concentrations are significantly higher than in suboxic sediments like those of the Gulf of California or the Arabian Sea (Brumsack, 1986; Jacobs et al., 1987; Crusius et al., 1996). Piper (1994) proposed that the accumulation rate by diffusion from an oxic or suboxic water column probably is much lower than by precipitation or adsorption of the reduced species in an anoxic water column.

Using organic geochemistry, Langrock et al. (submitted) have recently demonstrated that the water column was likely anoxic during the formation of black shales in the Barents Sea. The expansion of the oxygen minimum zone due to an elevated nutrient supply and phytoplankton flux led to higher preservation of total organic carbon.

Brumsack (1980) showed through budget calculations that seawater represents the most important source for trace metals (except for Zn) in CTBE black shales. The same conclusion was drawn by Nijenhuis et al. (1998) for the trace metal content of Eastern Mediterranean sapropels. Thus, the high concentrations of trace metals in Norwegian black shales most likely are related to water column anoxia, which is responsible for the effective removal of elements from seawater. Hydrothermal activity as a supplementary source could account for high Zn values in the Barents Sea samples, as proposed for CTBE black shales (Brumsack, 1980).

3.2. Rhenium and Re/Mo ratios

Rhenium is regarded as one of the most promising paleo-redox indicator elements as its concen-

tration is extremely low in the continental crust (0.5 ng/g; Crusius et al., 1996) and in oxic sediments (<0.1 ng/g; Koide et al., 1986). It may be significantly enriched in TOC-rich sediments deposited under reducing conditions in the water column (Koide et al., 1986; Colodner et al., 1993, 1995; Crusius et al., 1996).

The Re content of the Norwegian black shales studied is lower than in Mediterranean sapropels or CTBE black shales. Concentrations average 100 ng/g, with maxima of up to 1220 ng/g Re. With a mean enrichment factor of 200 relative to 'average shale', Re, along with Cd (mean enrichment factor of 60), shows the most pronounced enrichment in Norwegian black shales of all elements investigated. In Table 2, the average Re content of the studied black shales is compared to literature values of recent suboxic and anoxic sediments. These values are significantly lower than the concentrations found in Mediterranean sapropels.

In contrast to Re, Mo is rapidly scavenged by Mn-oxyhydroxides (Koide et al., 1986; Colodner et al., 1995). Their stable oxyanions (ReO_4^- , MoO_4^{2-}) are the cause for relatively high seawater concentrations of Mo (10.3 ng/g; Collier, 1985) and Re (8.2 pg/g; Colodner et al., 1993). Their conservative behavior in oxic seawater documents that both elements are only marginally involved in biological cycles. Their effective accumulation mechanism in TOC-rich sediments is still under discussion (e.g. Helz et al., 1996). It is proposed that Re is finally incorporated into sulfides like pyrite (Koide et al., 1986; Colodner et al., 1993), as is the case for Mo. The similar behavior of both elements is confirmed by the fact that Re contents correlate with lower Mo concentrations

Table 2

Average Re and Mo contents and Re/Mo ratios of Norwegian black shales, Mediterranean sapropels, and recent anoxic and suboxic sediments

	Norwegian black shales			Mediterranean sapropels ^a	Black Sea ^b	Japan Sea ^b	Pakistan Margin ^b
	Site 6307/07	Site 6814/04	Site 7430/10				
Re (ng/g)	83	20	200	330	43	12	31
Mo (μg/g)	48	8	133	76	29	1.3	1.7
Re/Mo × 10 ⁻³	1.9	4.1	2.6	2.9	1.5	9	19

^a Warning and Brumsack (2000).

^b Crusius et al. (1996).

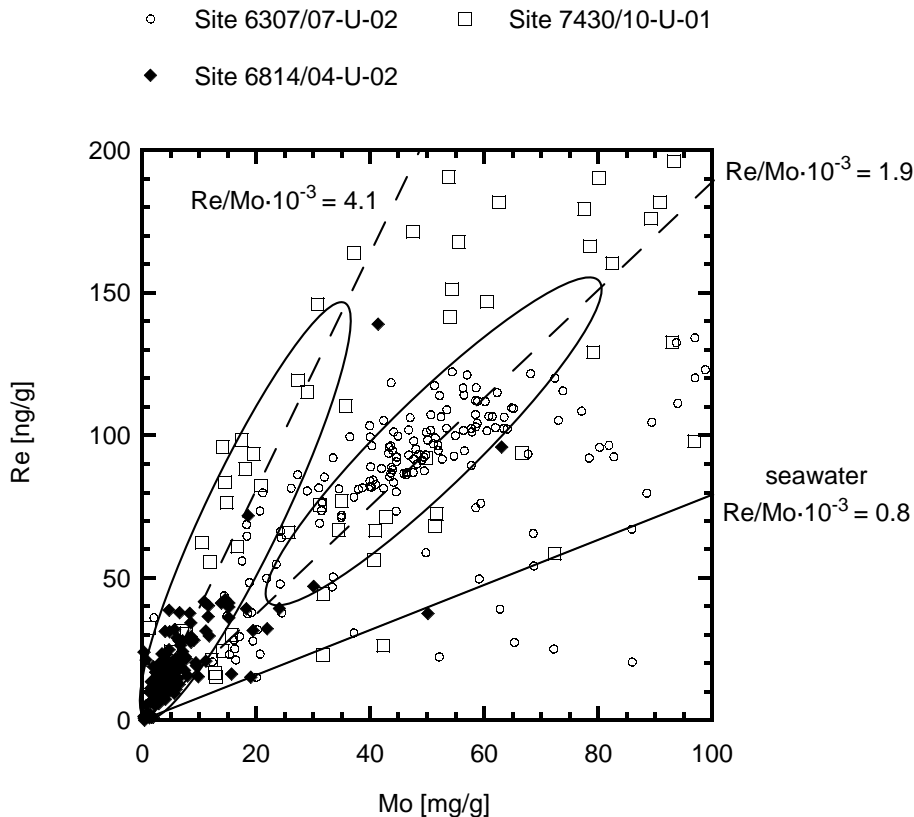


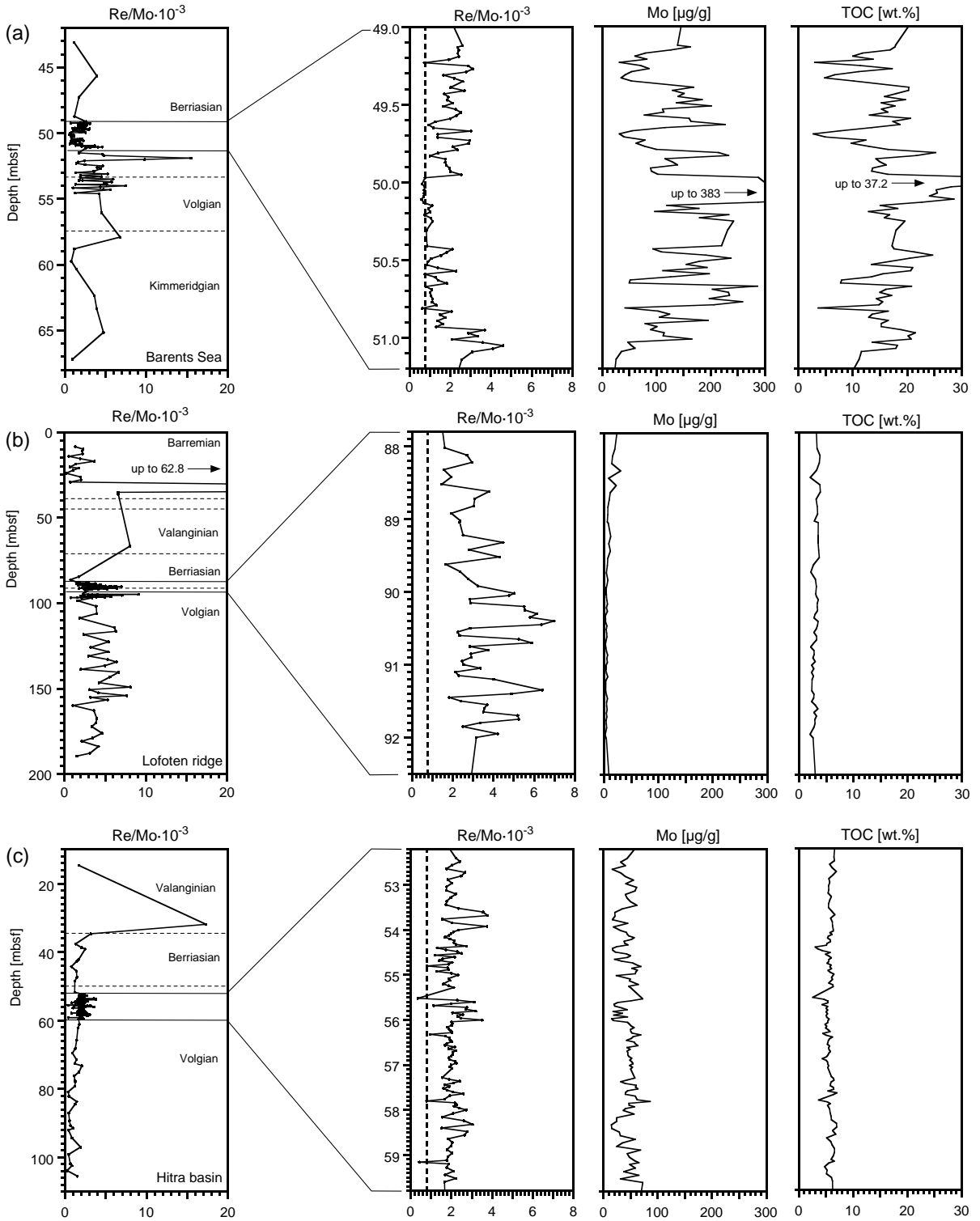
Fig. 2. Re versus Mo plot for all sapropel samples analyzed by ICP-MS. Average Re/Mo ratios for the two sets of data points and the seawater ratio (solid line) are also given.

in the investigated black shales, particularly from the Hitra Basin and Lofoten Ridge sites (Fig. 2). Two correlation trends with Re/Mo ratios of 1.6 and 3.1×10^{-3} are found. Most samples from the Hitra Basin site (6307/07-U-02) show lower Re/Mo ratios of approximately 1.6×10^{-3} , whereas samples from the Lofoten Ridge (Site 6814/04-U-02) are characterized by higher Re/Mo ratios. Rhenium and Mo concentrations found in black shales from the Barents Sea site are as high as in black shales from the other sites, but their ratios scatter over a wider range. The difference in the Re/Mo ratio therefore seems to depend mainly on

the location of the drill site. But it should be kept in mind that the paleoenvironmental significance of Re may be compromised in low sedimentation rate environments (Crusius and Thomson, 2000). The relationship between site location and trace metal composition will be discussed in Section 3.4.

Re/Mo ratios were used by Crusius et al. (1996) to distinguish between anoxic and suboxic conditions during sedimentation. The mean Re/Mo ratio of the Norwegian black shales and literature values are given in Table 2. High ratios presumably indicate suboxic conditions (e.g. Japan Sea,

Fig. 3. Re/Mo ratios, Mo, and TOC contents for all black shale samples analyzed by ICP-MS. Average Re/Mo ratio for the seawater (dotted line) is also given. (a) Site 7430/10-U-01 (Barents Sea), (b) Site 6814/04-U-02 (Lofoten ridge), and (c) Site 6307/07-U-02 (Hitra Basin).



Arabian Sea) owing to the preferential enrichment of Re over Mo in low-sulfide environments (Cru-sius et al., 1996), whereas low ratios close to the recent seawater value of 0.8×10^{-3} likely indicate anoxic and sulfidic conditions (e.g. Black Sea). In black shales from the Lofoten site, the Re/Mo ratios of all samples investigated average 4.1×10^{-3} , which is closer to the ratio of 9×10^{-3} seen in recent suboxic sediments from the Japan Sea than to the seawater value (Table 2). Though today's seawater composition may have been different from the Mesozoic, the Re/Mo ratio of these black shales still seems to indicate anoxic conditions during black shale formation. In contrast to black shales from the Lofoten Ridge, samples from the Hitra Basin and Barents Sea with Re/Mo ratios of 1.9×10^{-3} and 2.6×10^{-3} point towards the seawater value, indicating euxinic depositional conditions.

The advantage of high-resolution analysis is shown in the Mo concentration and Re/Mo ratio versus core depth plots from the different drill sites (Fig. 3). The Lofoten Ridge site (Fig. 3b) is characterized by low Mo (and U, not shown here) values. Re/Mo ratios show a large scatter and vary between 1.8 and 7.2×10^{-3} , which supports the assumption that the water column was dominated by oxic to suboxic conditions. In the Hitra Basin (Fig. 3c) and most pronounced in the Barents Sea (Fig. 3a) Mo concentrations are significantly higher. This points to more oxygen-deficient and intermittently euxinic conditions, which is also reflected in lower Re/Mo ratios (from 0.8 to 4.6×10^{-3}). The near-absence of Re/Mo-ratio variation between 49.96 and 50.41 m in the Barents Sea core seems to indicate that anoxic conditions must have prevailed continuously in this time interval.

3.3. Norwegian black shales, Mediterranean sapropels and CTBE black shales

High organic carbon and trace element contents have frequently been reported for Cretaceous, Mesozoic and Paleozoic black shales (e.g. Brum-sack, 1980; Arthur et al., 1990; Hatch and Leven-thal, 1992). The basic mechanisms that were proposed for their formation are quite similar to

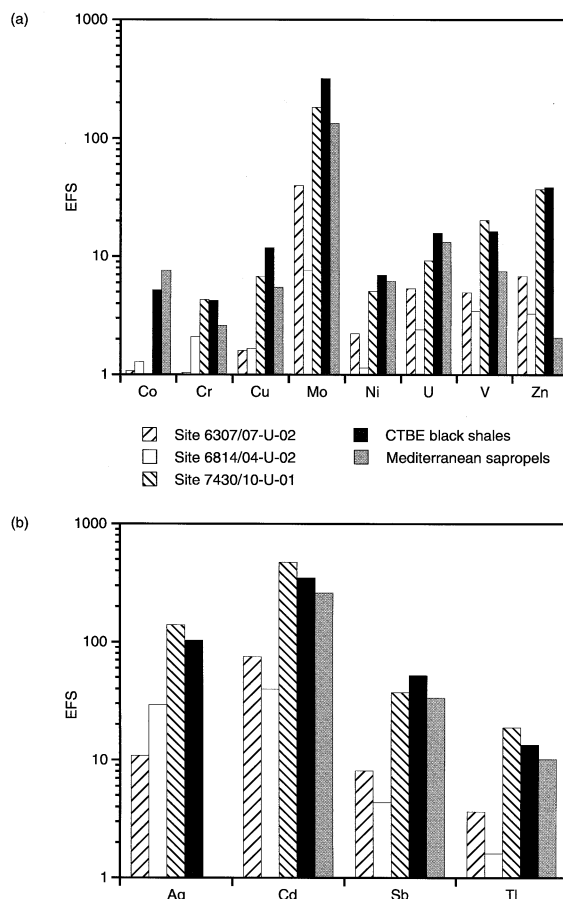


Fig. 4. Comparison of mean enrichment factors relative to 'average shale' (Wedepohl, 1971, 1991) for Norwegian black shales (this study), Mediterranean sapropels and CTBE black shales (Arthur et al., 1990; Brumsack, unpublished; Warning, unpublished). Enrichment factor = $\text{element}/\text{Al}_{(\text{sample})} / \text{element}/\text{Al}_{(\text{average shale})}$.

those assumed for the investigated Norwegian black shales. In Fig. 4, average trace element enrichment factors relative to 'average shale' (Wedepohl, 1971, 1991) for Norwegian black shales are compared with those determined for Mediterranean sapropels (Warning and Brumsack, 2000; Warning, unpublished) and Cenomanian–Turonian black shales (Brumsack, 1980; Arthur et al., 1990). Except for Co, which is only weakly enriched in Norwegian black shales but moderately enriched in sapropels and CTBE black shales, trace element signatures are quite similar

for these three types of TOC-rich sediments. Conspicuously, black shales from the Lofoten Ridge are less enriched in trace metals compared to the other Norwegian black shales, in accordance with low Mo concentrations as stated above. Zinc, an element that is only moderately enriched in recent sapropels, is significantly enriched in Barents Sea and in CTBE black shales.

Whereas average V contents are slightly higher in the black shales from the Barents Sea, CTBE black shales are more enriched in Co, Cr, Cu, Mo, Ni, Sb and U. For the trace metals Ag, Cd, and Tl (Fig. 4b), which are slightly more enriched in Barents Sea black shales than in CTBE black shales, the similarity of the enrichment factors is also evident.

Results of 38 CTBE black shale samples from the Atlantic show that their Re content may be more comparable to the high Re concentrations found in sapropels than in Norwegian black shales (Warning and Brumsack, 2000). The average Re/Mo ratio of 1.62×10^{-3} is close to the present-day seawater value and probably reflects anoxic conditions during black shale deposition.

Because of the similar trace metal contents, comparable mechanisms are likely to have been responsible for the trace metal enrichments in Norwegian black shales, sapropels and black shales. CTBE black shales accumulated trace metals under anoxic conditions mainly from seawater (Brumsack, 1980), but, based on mass balance calculations, for some elements additional sources like fluvial and hydrothermal input have to be considered (Arthur et al., 1990). We presume that an additional hydrothermal input may be responsible for the high enrichment of Zn in Norwegian and in CTBE black shales (Brumsack, 1980). Hydrothermal solutions are often enriched in Zn (Campbell et al., 1988; Philpotts et al., 1987) and during the Late Jurassic/Early Cretaceous the breakup of the North Atlantic, possibly associated with mantle plumes (Larson, 1991), may have provided elevated hydrothermal Zn input. For other trace metals seawater represents the most important source in black shales from Norway, as is the case for CTBE black shales. Sedimentation rates of the Norwegian black

shales are comparable to those found for CTBE black shales, which accumulated within a time period of at least 10^5 years (Arthur et al., 1990). Based on their similar trace metal signatures, Norwegian black shales may be regarded as roughly analogous to CTBE black shales. Moreover, the Norwegian black shale formation was limited to a more restricted depositional area, especially for black shales from the Barents Sea.

3.4. Norwegian black shales from different locations

One of the objectives of our investigation is to show how black shale formation and trace metal composition depend on location from within the Barents Sea and on the Norwegian Shelf. We will therefore compare the trace metal signatures of black shales originating from different sites on a transect along the Norwegian Shelf up to the Barents Sea (Fig. 4). Trace metal enrichments are generally most pronounced at the Barents Sea and Hitra Basin sites, whereas trace element, TOC and S contents are significantly lower at the Lofoten Ridge site. Rhenium, Cd, Sb and Tl concentrations are, despite this bias, significantly higher for samples from the Barents Sea and Hitra Basin compared to the Lofoten Ridge. Only Co in samples from the Lofoten Ridge shows higher enrichments. Silver and Cr are slightly enriched at this site compared to samples from the Hitra Basin.

The Barents Sea and Hitra Basin sites are located in relatively deep basins. The anoxic conditions prevailing during black shale formation probably influenced sediments at both sites similarly. Therefore, the different trace metal compositions of black shales from both sites may largely be the result of the difference in water column conditions. The enrichment of Mo, for example, suggests that stronger anoxic depositional conditions prevailed in the Barents Sea, whereas in the Hitra Basin lower contents of H_2S in the water column occurred (see Fig. 3).

The shallower Lofoten Ridge location might have been situated in an oxygen minimum layer. The lower enrichments of trace metals (except Co, Cr, Cu, and Ag compared with Site 6307/07-U-02)

and the higher Re/Mo ratios, especially in the high-resolution core section, confirm this assumption.

The idea that the Barents Sea and Hitra Basin formed one contiguous depositional area with comparable paleoenvironmental conditions from Late Jurassic to Early Cretaceous time (Volgian to Berriasian), that was developed by Mutterlose et al. (in press), is supported by our observations. If the high Zn enrichment in the Barents Sea samples reflects hydrothermal activity, this basin may have been more restricted. This assumption seems to be supported by organic geochemical investigations like maceral analysis (Langrock et al., submitted).

For the much studied sediments of the Black Sea, for example, it is still under debate whether anoxic conditions started to develop in the deeper parts or simultaneously all over the basin (Glenn and Arthur, 1985; Jones and Gagnon, 1994). Our results suggest that in the Barents Sea anoxic conditions may have persisted more continuously and therefore led to a higher enrichment of trace metals, TOC and S. This is supported by the fact that at the shallower location investigated (Lofoten Ridge), bioturbation and reoxidation effects are more regularly observed in the black shale sequence than at the deeper sites (Mutterlose et al., in press; Mutterlose and Kessels, 2000). In this respect the situation seems to be comparable to eastern Mediterranean sapropels (ODP Sites 966 and 967; Warning and Brumsack, 2000). Since seawater is the most important source for trace elements (Nijenhuis et al., 1998), the larger anoxic water volume above the sediments provided a larger reservoir and/or lower sedimentation rates may have caused a longer exposure time for trace element accumulation in the deeper basins. The residence time of the water will determine the flux of metals to the sediment surface and the sedimentation rate governs the dilution of the authigenic water column metal contribution. At the northernmost Barents Sea location sedimentation rate is lower than in the Hitra Basin (Mutterlose et al., in press). It is therefore indicated that sedimentation rate (i.e. dilution with terrigenous detrital or biogenic matter) has influenced the trace metal enrichment.

When discussing water depth in the Norwegian black shales, it has to be considered that water depth may have changed significantly since the mid-Volgian. Results from benthic foraminifers suggest that the water depth at different sites was comparatively low in the Volgian and increased to the Valanginian (Mutterlose and Kessels, 2000).

Sedimentary cyclicity, governed by orbital parameters, is pronounced at all sites. The eccentricity and precession signals were prominent in the southern part of the Greenland–Norwegian Seaway, and the obliquity signal became prominent poleward of 50°N (Mutterlose et al., in press). The shallow Lofoten Ridge may have divided the Greenland–Norwegian Seaway into two ‘restricted basins’. The decline in organic matter content of sediments in the Valanginian–Hauterivian indicates enhanced ventilation and more active water flow through the seaway when the sealevel rose (Mutterlose et al., in press). Intermediate waters were probably enriched in specific trace metals and nutrients owing to the bio-cycling of these elements (e.g. Ag and Cu). Consequently, black shales from the Lofoten Ridge site show slightly elevated Ag and Cu enrichments compared to those from the Hitra Basin.

In Section 3.2 we have shown that Re/Mo ratios differ between the individual locations (Fig. 3), i.e. they are lower at the deeper sites (Hitra Basin and Barents Sea). Since both elements probably accumulated from seawater under anoxic/sulfidic conditions at these two sites, the higher ratios at the Lofoten Ridge site can only be attributed to a different (more oxic) paleoredox environment. Bioproductivity should also not have altered the Re/Mo ratio because both elements behave conservatively in seawater (Collier, 1985; Colodner et al., 1993). Like most trace elements investigated, Mo concentrations are highest at the Barents Sea site leading to low Re/Mo ratios.

Warning and Brumsack (2000) assumed that despite varying bioproductivity similar sulfate reduction rates in different investigated Mediterranean sapropels led to high Mo contents, pointing towards a preferential incorporation of Mo into sulfides (Koide et al., 1986). By contrast, the Re

concentration seems to be more influenced by the TOC content of the sediment.

3.5. Comparison of Volgian and Berriasian black shales

During the ‘Norwegian Shallow Drilling Program’, black shale sequences of early Kimmeridgian to Barremian age were recovered from several drill sites. Based on biostratigraphy (Fjordingstad et al., 1985; Århus et al., 1987; Skarbø et al., 1988; Bugge et al., 1989; Hansen et al., 1991; Mutterlose et al., in press), the samples were divided into Volgian and Berriasian black shales.

Volgian Norwegian black shales are characterized by increased trace metal/Al ratios, higher TOC/Al- and slightly lower S/Al ratios compared to the Berriasian ones (Fig. 5). The enhanced accumulation of trace elements and TOC during the Volgian at all sites may record different paleoceanographic conditions developing during this time period compared to the Berriasian. Circulation in the Greenland–Norway Seaway may have changed in some parts, and therefore anoxic con-

ditions leading to black shale formation and high trace metal enrichments were possibly less pronounced during the Berriasian. The elevated values of TOC point to a higher productivity of organic matter during the Volgian. The preservation of organic matter owing to an oxygen-depleted water column is similar in both time periods (U. Langrock, personal communication). Since concentrations of TOC and redox-sensitive trace metals are significantly lower in Berriasian black shales (Mutterlose et al., in press) than in the older black shales investigated in our study, the sedimentary environment was probably more reducing during Volgian black shale formation due to higher bioproductivity. Nevertheless, in this case TOC may still be the most reliable paleoproductivity indicator (Langrock et al., in press).

As black shale formation is closely connected to climatic variation (e.g. Schlanger and Jenkyns, 1976; Arthur et al., 1990), a climatic cause for the change in paleoceanography can be assumed. Whereas several studies (e.g. Brumsack, 1980; Arthur et al., 1990) have dealt with the climatic control of black shale formation during the late Cretaceous (e.g. Cenomanian and Turonian), only little attention has been paid to the Late Jurassic to Early Cretaceous paleoclimatic record of higher northern latitude sediments (Mutterlose et al., in press).

Black shale occurrence was influenced by cyclic climatic variation induced by orbital forcing (Mutterlose et al., in press). Our results suggest that due to enhanced bioproductivity the paleoredox conditions in the water column changed from strongly anoxic/sulfidic during the Volgian to less anoxic in the Berriasian. Therefore, climatic and oceanographic conditions leading to black shale formation were possibly different in the Berriasian compared to the Volgian. Black shale formation may largely have been controlled by the long-term climatic change throughout the whole investigated time interval and may additionally be influenced by changes in orbital parameters.

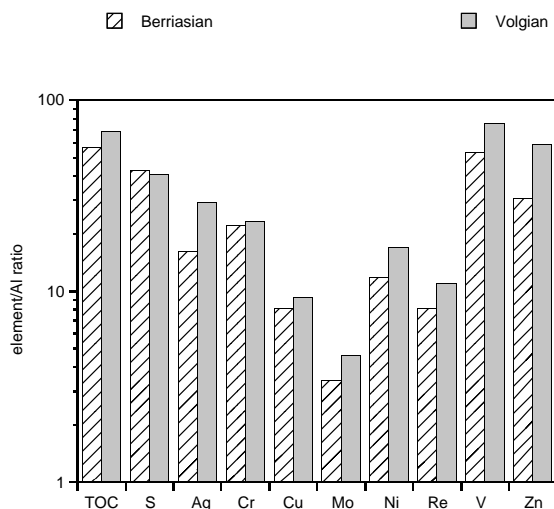


Fig. 5. Element/Al ratios of organic carbon (TOC), sulfur and trace metals for Berriasian and Volgian Norwegian black shales. TOC, S: element/Al ratios as weight ratios $\times 10^{-2}$, Cr, Cu, Mo, Ni, V, and Zn: element/Al ratios as weight ratios $\times 10^{-4}$. Ag/Al ratios as weight ratios $\times 10^{-6}$, and Re/Al ratios as weight ratios $\times 10^{-7}$.

4. Conclusions

Norwegian black shales are characterized by

high contents of several redox-sensitive and sulfide-forming trace elements (e.g. Ag, Cd, Co, Cu, Mo, Ni, Re, Sb, Tl, U, V). Trace metal enrichment factors relative to ‘average shale’ are comparable to those found in Cenomanian–Turonian black shales. Therefore, Norwegian black shales can be regarded to a certain degree as older analogs of CTBE black shales.

Rhenium contents are not as high as in the CTBE black shales studied which show maximum values up to 1220 ng/g. Results from Cretaceous black shale samples indicate that Re concentrations are comparably low in these TOC-rich sediments. Re/Mo ratios close to the seawater value probably reflect anoxic conditions during black shale deposition. Higher Re/Mo ratios point to suboxic depositional conditions for the black shales from the Lofoten Ridge.

High trace metal enrichments and Re/Mo ratios close to the seawater value point to an anoxic water column operating as an effective removal mechanism for trace metals from seawater during periods of black shale formation, as is the case for Mediterranean sapropel formation (Warning and Brumsack, 2000). Additionally, the high TOC concentrations in the black shales support the enhanced bioproductivity scenario which has been proposed to promote e.g. sapropel formation in the Mediterranean.

Trace metal signatures of black shales originating from different drill sites on a transect along the Norwegian Shelf to the Barents Sea depend on their location and reflect paleoenvironmental differences. Trace metal enrichments are significantly lower on the Lofoten Ridge site. This may reflect a change in circulation pattern during black shale formation. The circulation might not have been totally restricted, because otherwise the amount of trace metals provided to the Barents Sea from seawater would not have been sufficient to account for the black shale metal signal.

Volgian black shales are characterized by elevated trace metal contents in comparison to those from the Berriasian. This fact presumably documents different paleoceanographic conditions persisting during the two time intervals. Paleoceanographic conditions may have been controlled by

long-term climatic change throughout the time period investigated.

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Appendix 1

Precision and accuracy of analyzed elements

Element	Method	Precision S.D. 2σ [%]	Accuracy [%]
TS	IR-analyzer	5.1	4.0
TC	IR-analyzer	2.2	2.3
TIC	Coulometry	1.5	0.4
Ba	XRF	4.5	5.1
Ag	ICP-MS	6.5	8.8
Bi	ICP-MS	2.1	15.3
Cd	ICP-MS	6.2	8.7
Co	XRF/ICP-MS	7.8/1.6	5.7/4.5
Cr	XRF/ICP-MS	4.2/7.5	8.3/36.4
Cu	XRF/ICP-MS	7.1/3.4	17.0/5.0
Mo	XRF/ICP-MS	6.5/3.8	14.5/3.9
Ni	XRF/ICP-MS	7.6/3.2	4.8/6.4
Re	ICP-MS	7.8	26.7 ^a
Sb	ICP-MS	6.7	7.2
Tl	ICP-MS	4.9	12.3
U	ICP-MS	4.5	3.3
V	XRF	3.6	4.5
Zn	XRF	3.4	2.6

^a Determinated from JB-1.

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