

# Anoxic vs dysoxic events reflected in sediment geochemistry during the Cenomanian–Turonian Boundary Event (Cretaceous) in the Umbria–Marche Basin of central Italy

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## Abstract

One of the most spectacular expressions of global “Oceanic Anoxic Events” (OAEs) of the Cretaceous is the *Livello Bonarelli* of central Italy, deposited during the Cenomanian–Turonian Boundary Event (CTBE or OAE2) at around 93.5 Ma. At Furlo in the Umbria–Marche Basin in Italy, the Bonarelli consists of approximately 1 m of  $C_{org}$ -rich shales interbedded with radiolarian-rich layers, and contrasts sharply with the extensive over- and underlying siliceous limestones. Several minor  $C_{org}$ -rich intervals (herein termed *black levels*; average thickness=4.5 cm) are interbedded within the Scaglia Bianca beneath the Bonarelli. X-ray fluorescence and ICP-MS analyses show that these sediments consist of different mixing systems with three end-members: 1)  $SiO_2$ – $CaCO_3$  (Scaglia Bianca); 2) “average shale”– $CaCO_3$  (black levels); and 3) “average shale”– $SiO_2$  (Bonarelli). Given the sharp lithologic contacts and the little geochemical mixing between the groups, these are thought to represent rapid switching events between sedimentary modes. Major element concentrations are generally low, except for Si and P, owing to dilution by silica (up to 96%) and carbonates. As Al-normalised ratios for elements such as Ti or Zr, taken as proxies for higher energy environments, are close to average shale values, excess  $SiO_2$  is most likely linked to biogenic processes rather than quartz. Element/Al ratios of Ti, Mg, K, Rb, and Zr are fairly constant, pointing to a mostly homogeneous source area. The black levels and Bonarelli are characterised by lower Mg/Al ratios compared to the Scaglia Bianca sediments, suggesting variability in chlorite input, which could be linked with short-term sea level drops indicated by Ti/Al ratios. The Bonarelli sediments are severely depleted in Mn, which is indicative of oxygen-depleted bottom water conditions and an open marine environment, while the black levels appear to have been deposited in a much more restricted setting. A model involving partial physical isolation of the Furlo site by a sill, coupled to OMZ variations by extra-basinal forcing mechanisms is proposed to account for these conflicting data. Based on Re/Mo ratios, the Bonarelli sediments were deposited under varying oxygen-depletion levels (from suboxic to anoxic), while Re/Mo ratios in the black levels show deposition under less oxygen-deficient conditions. Most minor elements, many of them redox-sensitive or sulphide-residing, are strongly enriched in the  $C_{org}$ -rich sediments, further documenting the absence of oxygen and potential availability of hydrogen sulphide in the water column at times, while high Zn concentrations suggest elevated submarine hydrothermal activity during this time interval. Ba is also present in very high concentrations (up to 1.4%, with an average weighed concentration of 0.6% for the entire Bonarelli), and is probably indicative of high paleoproductivity in this area. This is further supported by high P concentrations, hinting at nutrient availability at this site.

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## 1. Introduction

The Cretaceous stratigraphic record is punctuated with several important  $C_{\text{org}}$ -rich intervals representing “Oceanic Anoxic Events” (OAEs; Schlanger and Jenkyns, 1976). Although the exact depositional mode of OAE black shales is still under debate, several “trigger” mechanisms attempting to account for the observed organic matter sequestration have been proposed, including enhanced preservation of organic matter owing to anoxic bottom waters (Schlanger and Jenkyns, 1976), increased productivity (Calvert, 1983; Pedersen and Calvert, 1990), and submarine volcanism (Larson, 1991). The Cenomanian/Turonian (C/T; ca. 93.5 Ma) event is the most extensive of the Cretaceous OAEs, with global temperatures apparently the highest of the last 115 Ma (Clarke and Jenkyns, 1999; Huber et al., 2002; Wilson et al., 2002). The C/T OAE (OAE2), or Cenomanian/Turonian Boundary Event (CTBE), is characterised by a positive global carbon-isotope excursion in both carbonates (2.5 to 3.0‰) and organic matter (2.6 to 6.0‰), most probably due to the widespread removal of isotopically light organic carbon into black shales during the C/T event, leading to  $^{13}\text{C}$  enrichments of the oceanic and atmospheric  $\text{CO}_2$  reservoirs (Scholle and Arthur, 1980; Arthur et al., 1987, 1988). The similarity of bulk carbonate and organic matter  $\delta^{13}\text{C}$  curves at distant locations (Schlanger and Jenkyns, 1976; Summerhayes, 1981; de Graciansky et al., 1984; Herbin et al., 1986; Pratt et al., 1986; Schlanger et al., 1987; Kuhnt et al., 1990; Gale et al., 1993; Kuhnt and Wiedmann, 1995) hint at the global nature of this event. Duration estimates for the  $\delta^{13}\text{C}$  excursion vary between 220 (Lamolda et al., 1994) and 800 kyr (Meyers et al., 2001).

One of the most spectacular expressions of the OAE2 is the *Livello Bonarelli* in the Umbria–Marche Basin of central Italy. There, the C/T boundary consists of between 50 and 200 cm of  $C_{\text{org}}$ -rich sediments, interspersed with radiolarian-rich beds, and contrasts sharply with the extensive over- and underlying siliceous limestones of the Scaglia Bianca Formation. The Bonarelli is contained well within the  $\delta^{13}\text{C}$  isotope excursion (Harilaos Tsikos, pers. com.), hence the duration of the  $C_{\text{org}}$  sequestration in the Umbria–Marche Basin is assumed to be shorter than the  $\delta^{13}\text{C}$  isotopic excursion duration estimates. At several sites within the Umbria–Marche Basin,  $C_{\text{org}}$ -rich shale and/or chert beds and laminae (the “black levels” of Beaudoin et al., 1996) are discretely and unevenly inter-layered with the beds of the Scaglia Bianca every few tens of cm, down to approximately 20 m below the Bonarelli. These are generally thought to be precursor events related to the Bonarelli and, given their thickness, perhaps comparable to Mediterranean sapropels which were formed

during events lasting less than 10 kyr (Wehausen and Brumsack, 2000).

Although some studies have focussed on the inorganic geochemistry of the Bonarelli sediments (i.e. Brigatti and Poppi, 1991; Kuroda et al., 2002; Scopelliti et al., 2004), we are aware of no study that has looked at the black levels in order to determine causal or genetic links between these groups of  $C_{\text{org}}$ -rich sediments based on geochemical arguments. Given that under oxygen-depleted conditions, several trace elements are enriched within modern sediments owing to either the redox-sensitivity of many transitional elements, association with organic matter, incorporation into sulphides, or to “bioconcentration” of elements from seawater (Brumsack, 1980; Bruland, 1983; Jacobs et al., 1985; Brumsack, 1986; Jacobs et al., 1987; Breit and Wanty, 1991; Hatch and Leventhal, 1992; Piper, 1994; Nijenhuis et al., 1998), elemental enrichments should reflect the original depositional environments of ancient sedimentary rocks and can thus be used to gain insight into the paleoceanographic conditions at the time of their deposition.

In this paper, we present inorganic geochemical data for the Bonarelli, as well as for several meters of sediments from both above and below the Bonarelli in the Umbria–Marche Basin. The purpose of this paper is three-fold: 1) to provide information relating to the origin of the sediments and water column conditions such as level of oxygenation and productivity (Schmitz, 1987; Dymond et al., 1992; Francois et al., 1995; Paytan et al., 1996); 2) to compare the inorganic geochemistry of the black levels to that of the Bonarelli, in order to determine genetic links between these two groups of sediments; and 3) to contribute an extended data set relating to the inorganic geochemistry of Cretaceous black shales as these are scarce in the literature. It is not our intent to provide a comprehensive review of the processes affecting the geochemistry of sediments, as several syntheses are available (see for example Morford and Emerson, 1999, or Brumsack, 2006, and references therein). Rather, our aim is to highlight certain aspects of our data relating to paleoenvironmental reconstructions of the events associated with the OAE and attempt to provide a general depositional model for this setting.

## 2. Samples

For this paper, we have studied sediments from the Furlo section (Figs. 1 and 2), located approximately 25 km SE of Urbino. The outcrop consists of tens of meters of siliceous carbonates of the Scaglia Bianca. Thirty black levels, ranging in thickness from a few mm up to 15 cm (average=4.5 cm), punctuate this section below the

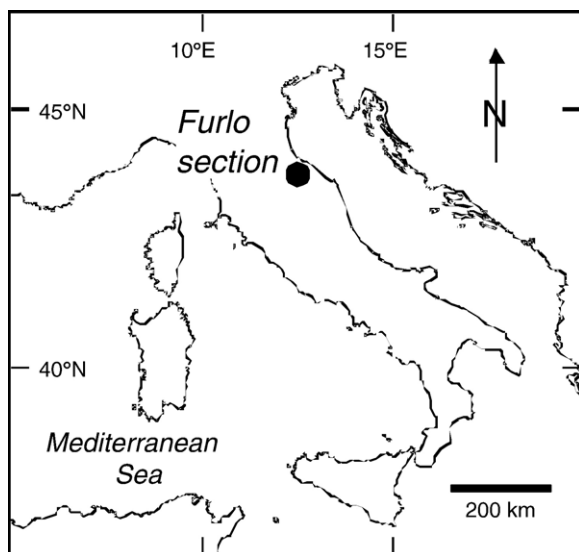


Fig. 1. Location of the Furlo section in central Italy.

Bonarelli. The Bonarelli itself (paleodepth approximately 1000 to 2000 m; Elisabetta Erba, pers. com.), is 108 cm thick and consists of several dark coloured, fissile  $C_{org}$ -rich beds and laminae of radiolarian-rich shales and cherts. Within the Bonarelli, several pyrite lenses composed of euhedral crystals occur parallel to bedding planes. Several samples ( $n=201$ ) of 5–10 vertical cm were taken from the Scaglia Bianca down to 20 m below the Bonarelli. A further 73 samples were taken from a 4 m interval of Scaglia Bianca immediately above the Bonarelli. In addition to 38 samples taken from the Bonarelli (average thickness  $\sim 3$  cm), 17 out of the 30 black levels present at Furlo were sampled. Sampling was done on fresh surfaces in order to minimise present-day weathering effects.

### 3. Methodology

Samples were air-dried, ground and homogenised in an agate ball-mill. Total carbon ( $C_{tot}$ ) and total sulphur ( $S_{tot}$ ) were measured on the  $C_{org}$ -rich samples using a LECO® SC-444 IR-analyser following combustion at 1400 °C. Typical precision, calculated by replicate analysis of standards, is  $<1\%$  for  $C_{tot}$  and  $<2\%$  for  $S_{tot}$ . Total inorganic carbon ( $C_{min}$ ) values were obtained by coulometric titration using a UIC® Coulometrics CM 5012  $CO_2$  coulometer coupled to a CM5130 acidification module. Samples were acidified using 2N  $HClO_4$  in order to release  $CO_2$  and determine  $C_{min}$ . Precision for  $C_{min}$  measurements is 2%. Total organic carbon ( $C_{org}$ ) is taken as the difference between  $C_{tot}$  and  $C_{min}$ .

Major and minor elements were determined by X-ray fluorescence (XRF). 600 mg of the powdered sample

was mixed with 3600 mg of lithium borate ( $LiBO_2$  or  $Li_2 B_4O_7$ ) and pre-oxidised at 500 °C in porcelain crucibles for 5 h. After cooling, approximately 1 g of ammonium nitrate ( $NH_4NO_3$ ) was added and the samples were heated again to 500 °C for 4 h in order to further oxidise the samples. The samples were then melted at 1200 °C in Pt–Au crucibles and cooled in Pt–Au disk moulds. The disks were analysed with a Philips® PW2400 XRF spectrometer for several major and minor elements. Analytical precision was verified by the preparation and analysis of several in-house standards. Precision and accuracy was found to be better than 5% for all major elements (reported as oxides), and better than 7.6% for minor elements except for Zr (better than 12%).

All of our Bonarelli and black level samples were analysed for minor and trace elements using inductively coupled plasma-mass spectrometry (ICP-MS). Acid digestions were prepared using approximately 50 mg of powdered sample, preoxidised overnight with 1 ml  $HNO_3$  (65%) in PTFE vessels, and subsequently heated to 180 °C for six hours in PTFE autoclaves (PDS-6) with 3 ml HF (40%) and 3 ml  $HClO_4$  (70%). Acids were removed by evaporation at 180 °C on hot plates, and the wet residues were redissolved and reevaporated using  $3 \times 1$  ml of half-concentrate HCl. After the final HCl treatment, wet residues were dissolved in 1 ml  $HNO_3$  (65%) and diluted to 50 ml with distilled and deionised water.  $HNO_3$ ,  $HClO_4$  and HCl acids were prepared by sub-boiling distillation. Suprapure® (Merck) quality HF was used. For analysis, the acid digestions were diluted (1:5) with  $HNO_3$  (2%) and spiked with In and Be as internal standards. Measurements of several trace elements (including Ag, Bi, Cd,

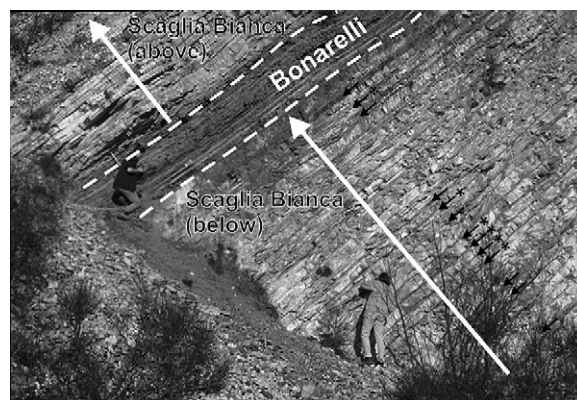


Fig. 2. Photo of outcrop at Furlo showing Scaglia Bianca, the Livello Bonarelli (approximately 1 m thick), and position of the uppermost black levels (indicated by black arrows). Arrows with asterisks indicate the black level was sampled.

Table 1  
Geochemical parameters of the different sediment groups at Furlo, Italy

Element/ oxide	Scaglia Bianca (above)			Livello Bonarelli		
	<i>n</i> = 73			<i>n</i> = 38		
	conc. (1 $\sigma$ , max)	–/Al (1 $\sigma$ )	EF	conc. (1 $\sigma$ , max)	–/Al (1 $\sigma$ )	EF
C <sub>org</sub>	--	--	--	4.1 (4.1, 16)	2.6 (2.9)	--
CaCO <sub>3</sub> <sup>(b)</sup>	63 (24, 86)	--	--	3.3 (6.3, 28)	--	--
S <sub>tot</sub>	--	--	--	1.3 (1.1, 5.5)	0.81 (0.84)	27
SiO <sub>2</sub>	30 (22, 83)	22 (20)	6.9	72 (7.3, 85)	20 (11)	6.4
SiO <sub>2(excess)</sub> <sup>(c)</sup>	25 (20, 78)	18 (17)	--	57 (12, 80)	17 (52)	--
TiO <sub>2</sub>	0.061 (0.047, 0.29)	0.048 (0.003)	0.90	0.19 (0.13, 0.71)	0.048 (0.006)	0.91
Al <sub>2</sub> O <sub>3</sub>	1.5 (1.1, 6.8)	[1.00]	--	4.2 (2.3, 11)	[1.00]	--
Fe <sub>2</sub> O <sub>3</sub>	0.45 (0.29, 1.7)	0.43 (0.088)	0.79	2.3 (1.4, 6.3)	0.8 (0.58)	1.5
MgO	0.44 (0.17, 1.3)	0.40 (0.11)	2.2	0.71 (0.40, 2.0)	0.19 (0.029)	1.1
CaO	36 (14, 48)	46 (24)	254	1.9 (3.5, 16)	0.93 (1.8)	5.2
Na <sub>2</sub> O	0.038 (0.10, 0.75)	0.038 (0.16)	0.29	0.091 (0.078, 0.28)	0.031 (0.024)	0.24
K <sub>2</sub> O	0.42 (0.31, 1.9)	0.45 (0.050)	1.3	1.2 (0.77, 4.1)	0.45 (0.057)	1.3
P <sub>2</sub> O <sub>5</sub>	0.031 (0.014, 0.10)	0.020 (0.005)	2.5	0.34 (0.60, 2.5)	0.12 (0.29)	14
As	1.9 (1.4, 12)	2.9 (1.5)	2.6	16 (14, 81)	8.8 (9.7)	7.8
Ba	1963 (2414, 13874)	2394 (1476)	36	6097 (1964, 9711)	3520 (2142)	54
Co	4.2 (3.5, 12)	5.8 (4.8)	2.7	7.9 (6.4, 27)	4.7 (5.3)	2.2
Cr	19 (6.6, 67)	31 (10)	3.0	57 (50, 220)	28 (23)	2.8
Cu	21 (15, 82)	29 (13)	5.7	113 (55, 234)	64 (47)	13
MnO	0.064 (0.026, 0.14)	848 (415)	8.8	0.003 (0.010, 0.047)	15 (52)	0.16
Ni	6.9 (6.4, 25)	8.6 (6.8)	1.1	42 (39, 225)	26 (31)	3.4
Rb	14 (10, 64)	18 (2.3)	1.1	38 (22, 94)	17 (2.0)	1.0
Sr	636 (427, 3113)	930 (320)	27	1600 (667, 2964)	972 (803)	29
V	15 (13, 70)	20 (4.6)	1.4	424 (279, 1123)	220 (152)	15
Y	16 (3.3, 24)	26 (9.0)	5.6	18 (18, 91)	12 (20)	2.6
Zn	22 (19, 153)	33 (24)	3.0	369 (391, 2204)	229 (342)	21
Zr	17 (8.7, 57)	23 (4.6)	1.3	42 (15, 82)	21 (7.2)	1.2
Ag	--	--	--	2.0 (1.6, 5.8)	1.1 (1.1)	138
Bi	--	--	--	0.41 (0.19, 0.9)	0.19 (0.035)	13
Cd	--	--	--	2.8 (3.4, 17)	1.9 (2.9)	127
Cs	--	--	--	4.7 (2.9, 11)	2.2 (1.2)	3.5
Li	--	--	--	41 (9.8, 76)	22 (11)	3.0
Mo	--	--	--	9.2 (8.5, 40)	5.6 (5.6)	38
Nb	--	--	--	3.2 (1.9, 8.1)	1.4 (0.25)	0.67
Pb	--	--	--	14 (7.3, 38)	6.9 (3.8)	2.8
Re	--	--	--	0.053 (0.055, 0.26)	0.026 (0.043)	456
Sb	--	--	--	4.0 (5.0, 27)	2.5 (3.9)	15
Sc	--	--	--	6.2 (3.3, 18)	2.4 (1.6)	1.6
Tl	--	--	--	1.5 (1.3, 5.2)	0.88 (0.86)	11
U	--	--	--	4.3 (2.2, 12)	2.5 (2.1)	6.0

ICP-MS values reported for Ag, Bi, Cd, Cs, Li, Mo, Nb, Pb, Re, Sb, Sc, Tl, and U. All others measured using XRF. All oxides and bulk parameters are reported as %, minor and trace elements in  $\mu\text{g/g}$ , except for Re ( $\text{ng/g}$ ). Standard deviation (1  $\sigma$ ) and maximum values are shown in parentheses. All trace element/Al and Mn/Al ratios are expressed as  $\times 10^{-4}$ , except for Re ( $\times 10^{-9}$ ). Shaded areas represent elemental mean values below the quantitation limits of Wehausen (1999) for specific sediment groups.

<sup>(a)</sup> Average shale values from Wedepohl (1971, 1991), except Re (Crusius et al., 1996).

<sup>(b)</sup> Calculated from the CaO values using an oxide conversion factor of 1.7751.

<sup>(c)</sup> Calculated assuming  $(\text{Si}/\text{Al})_{\text{detrital}}=3.11$  from Wedepohl (1971; see text for explanation).

Mo, Re, Sb, Tl and U) were carried out using a Finnigan Mat Element double focussing magnetic sector ICP-MS. Measurements with relative standard deviations (RSDs) values greater than 7% were discarded. Accuracy of the analyses was verified using several in-house reference materials calibrated

to international standards. The Scaglia Bianca samples were not analysed by ICP-MS owing to preliminary tests indicating that many trace elements (e.g. Ag, Cd, Mo, Re) are present in concentrations too low to measure adequately without preconcentration or elemental separation.

Table1 (continued)

Black levels			Scaglia Bianca (below)			Average shale <sup>(a)</sup>	
n = 17			n = 201				
conc. (1 $\sigma$ , max)	-/Al (1 $\sigma$ )	EF	conc. (1 $\sigma$ , max)	-/Al (1 $\sigma$ )	EF	conc. (1 $\sigma$ , max)	-/Al (1 $\sigma$ )
2.8 (2.4, 9.4)	1.9 (1.2)	--	--	--	--	--	--
57 (28, 88)	--	--	67 (28, 94)	--	--	3.9	--
0.41 (0.37, 1.2)	0.25 (0.22)	8.4	--	--	--	0.24	0.03
23 (30, 58)	5 (3.3)	1.6	28 (18, 96)	44 (74)	14	58.9	3.11
6.8 (30, 47)	1.9 (3.2)	--	25 (12, 96)	41 (74)	--	--	--
0.23 (0.023, 0.66)	0.056 (0.003)	1.1	0.035 (0.21, 0.22)	0.045 (0.008)	0.85	0.78	0.053
4.7 (0.49, 15)	[1.00]	--	0.87 (4.6, 4.4)	[1.00]	--	16.7	[1.00]
2.6 (0.46, 4.5)	0.99 (0.42)	1.8	0.41 (1.3, 6.4)	0.7 (0.96)	1.3	6.9	0.55
1.0 (0.13, 2.9)	0.27 (0.049)	1.5	0.33 (0.83, 0.97)	0.46 (0.18)	2.6	2.6	0.18
32 (17, 50)	21 (18)	117	38 (16, 53)	68 (40)	376	2.2	0.18
0.088 (0.044, 0.24)	0.025 (0.025)	0.19	0.037 (0.091, 0.18)	0.07 (0.093)	0.54	1.6	0.13
1.6 (0.16, 4.8)	0.52 (0.026)	1.5	0.25 (1.5, 1.4)	0.43 (0.10)	1.3	3.6	0.34
0.23 (0.053, 0.55)	0.049 (0.015)	6.1	0.030 (0.15, 0.56)	0.027 (0.029)	3.3	0.16	0.008
19 (2.0, 58)	11 (7.3)	10	2.5 (14, 20)	7.1 (11)	6.3	10	1.1
473 (874, 970)	369 (293)	5.6	531 (220, 7972)	1586 (2819)	24	580	66
61 (4.1, 147)	37 (21)	17	4.4 (36, 27)	11 (10)	5.0	19	2.1
161 (15, 380)	98 (58)	9.7	15 (103, 98)	39 (54)	3.8	90	10
142 (22, 485)	76 (46)	15	14 (113, 170)	31 (44)	6.0	45	5.1
0.026 (0.032, 0.067)	172 (167)	1.8	0.058 (0.013, 0.13)	1104 (704)	11	0.11	96
149 (12, 311)	91 (37)	12	10 (71, 100)	23 (26)	3.0	68	7.7
42 (5.3, 143)	15 (2.1)	0.97	8.2 (47, 49)	17 (4.0)	1.1	140	16
946 (247, 1668)	670 (412)	20	594 (241, 2163)	1482 (703)	44	300	34
386 (37, 1308)	241 (149)	16	18 (300, 470)	41 (71)	2.8	130	15
27 (5.4, 76)	13 (2.9)	2.7	11 (20, 50)	26 (10)	5.6	41	4.6
466 (102, 1958)	302 (224)	28	52 (431, 1024)	113 (171)	10	95	11
46 (4.7, 118)	21 (3.6)	1.2	14 (35, 46)	35 (12)	1.9	160	18
1.9 (1.3, 4.2)	1.1 (1.0)	142	--	--	--	0.07	0.008
0.34 (0.32, 1.0)	0.13 (0.027)	9.0	--	--	--	0.13	0.015
5.6 (6.0, 22)	3.8 (4.2)	261	--	--	--	0.13	0.015
3.6 (3.7, 12)	1.4 (0.42)	2.2	--	--	--	5.5	0.62
22 (21, 68)	8.9 (2.9)	1.2	--	--	--	66	7.5
3.2 (2.3, 7.5)	2.0 (1.6)	13	--	--	--	1.3	0.15
3.8 (4.5, 14)	1.4 (0.46)	0.68	--	--	--	18	2.0
22 (13, 55)	10 (6.7)	4.2	--	--	--	22	2.5
0.042 (0.034, 0.12)	0.023 (0.023)	407	--	--	--	0.5	5.7
1.8 (1.1, 4.0)	1.1 (0.77)	6.5	--	--	--	1.5	0.17
7.4 (5.7, 20)	3.2 (1.4)	2.2	--	--	--	13	1.5
0.94 (0.55, 2.0)	0.55 (0.38)	7.2	--	--	--	0.68	0.077
3.1 (2.1, 9.3)	1.9 (1.3)	4.4	--	--	--	3.7	0.42

Elemental values were normalised to Al in order to account for dilution effects by potential biogenic components such as carbonates, silica, and phosphorites. Concentrations are compared to the average shale values (AS) of Wedepohl (1971, 1991) and expressed as enrichments factors ( $EF_{\text{element}}$ ) relative to AS (except for

Re which has been compared to the continental crust value given by Crusius et al., 1996). Enrichment factors were calculated using:

$$EF_{\text{element}} = (\text{element}/\text{Al})_{\text{sample}} \div (\text{element}/\text{Al})_{\text{AS}} \quad (1)$$

Hence an element with the same Al-normalised ratio as AS would yield an EF of 1. Based on the elemental concentrations within the sediments, we use the term “enrichment” for  $EF_{\text{element}} \geq 5$ , while we consider the samples “depleted” when  $EF_{\text{element}} \leq 0.5$ . Given correlation problems associated with using normalised data in some cases (Van der Weijden, 2002), we will also present and interpret some unmodified data.

## 4. Results and discussion

### 4.1. Furlo sediment geochemistry

A summary of the geochemical parameters is provided in Table 1, while bulk parameters ( $C_{\text{org}}$ ,  $S_{\text{tot}}$ ,  $\text{CaCO}_3$ ,  $\text{SiO}_2$  and Mn/Al ratios) are plotted in Fig. 3. Generally, the sediments are characterised by low concentrations of major elements such as Ti, Al, Fe, Mg, Na, K, and Mn, although many of the elemental/Al ratios (Ti/Al, Fe/Al, Mg/Al, and K/Al) are relatively close to AS values, except for Na/Al, which is well below the XRF quantitation limit provided by Wehausen (1999) in all sediment groups.  $C_{\text{org}}$  and  $S_{\text{tot}}$  concentrations are high in the Bonarelli and the black levels

( $C_{\text{org}}=4.1\%/S_{\text{tot}}=1.2\%$  and  $C_{\text{org}}=2.8\%/S_{\text{tot}}=0.55\%$  on average, respectively). These  $C_{\text{org}}$  and  $S_{\text{tot}}$  concentrations are comparable to those found in Mediterranean sapropels (Warning and Brumsack, 2000), as well as in other sediments at the Cenomanian/Turonian boundary (Brumsack, 1980; Arthur et al., 1990).  $EF_S$  values average 27 and 12 for the Bonarelli and black level sediments respectively. Although many minor elements (Sr, Ag, Bi, Cd, Mo, Re, Sb, Tl) are found in high concentrations in the sediments, others (Pb, Rb, Y, Zr, Cs, Li, Sc) are present in concentrations lower than AS values. When normalised to Al however, most elements are present in ratios similar to (Rb, Zr, Cs, Li, Sc) or above (Ba, Cu, Sr, Ag, Bi, Cd, Mo, Re, Sb, Tl) AS. The following three sections present the major geochemical differences between the sediment groups.

#### 4.1.1. Scaglia Bianca

The sediments of the Scaglia Bianca Formation from both above and below the Bonarelli will be discussed jointly owing to their overall geochemical similarity (Table 1). Concentration values presented here are the thickness-weighted averages between the two Scaglia groups. In the limestones, all major elements, except for

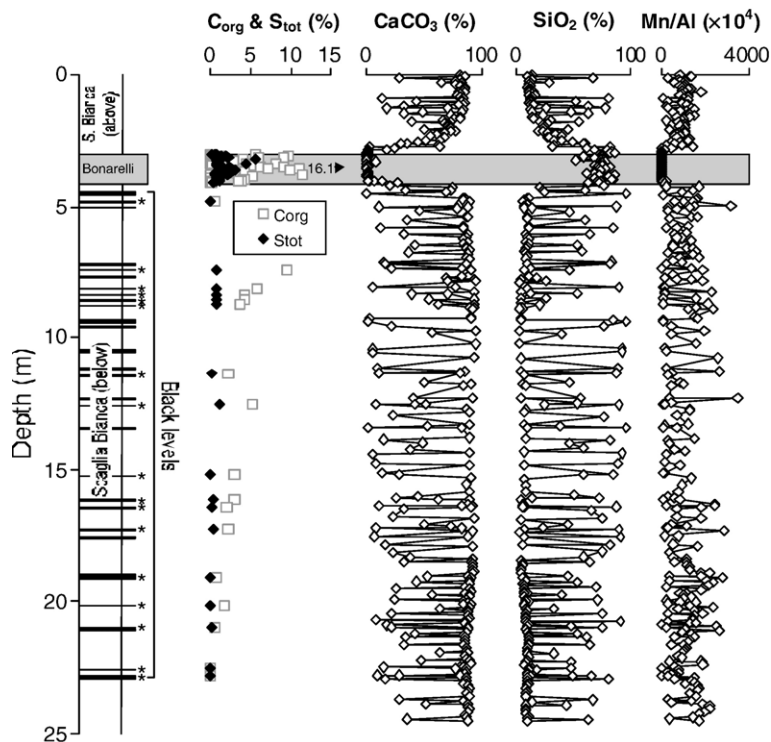


Fig. 3. Stratigraphic section of Furlo outcrop along with bulk  $C_{\text{org}}$  and  $S_{\text{tot}}$  data, as well as  $\text{CaCO}_3$ ,  $\text{SiO}_2$  and Mn/Al ratios. Sampled black levels are denoted with asterisks.

Ca, are present in low concentrations owing in part to a dilution effect by either carbonates (up to 94% CaCO<sub>3</sub>) or SiO<sub>2</sub> (up to 96%). Only two of the major elements (Si and Mn) are significantly enriched relative to AS ( $EF_{Si} \approx 12$  and  $EF_{Mn} \approx 11$ ). The average phosphorus enrichment factor ( $EF_P$ ) of 3.1, although slightly above AS values, is the lowest of the sediment groups. Several redox-sensitive or sulphide-residing elements (i.e. As, Co, Cr, Cu, Ni, V, Zn) are present in low concentrations. Al-normalised values are close to AS values (i.e. Co, Cr, Ni, V), although other elements are enriched ( $EF_V = 5.6$ ;  $EF_{Zn} = 8.5$ ). Ba concentrations are high (908 µg/g on average and up to 1.4%;  $EF_{Ba} = 27$ ) in the Scaglia Bianca.

#### 4.1.2. Bonarelli

The sediments of the Livello Bonarelli are characterised by high Si concentrations (average SiO<sub>2</sub> of 72%, with a maximum of 86%) and phosphorus (P<sub>2</sub>O<sub>5</sub> = 0.34%), while Ca (3.3% CaCO<sub>3</sub> on average) and Mn concentrations (below the quantitation limit) are low. However, the Al-normalised data show that most elements are close to or slightly above AS values, with the exception of the few elements noted earlier ( $EF_{Si} = 6.4$ ;  $EF_P = 14$ ) which are enriched and Mn, which is significantly depleted relative to AS. Calcium values ( $EF_{Ca} = 5.2$ ) are the lowest within the three groups of sediments but still enriched relative to AS. While elements such as Cu (113 µg/g;  $EF_{Cu} = 13$ ), V (424 µg/g;  $EF_V = 15$ ), and Zn (369 µg/g;  $EF_{Zn} = 21$ ) are found in concentrations significantly higher than AS values within the Bonarelli sediments, Co (7.9 µg/g) is found in lower concentrations. In addition, the Ba concentrations within the Bonarelli are truly striking (6100 µg/g on average, compared to 580 µg/g for AS;  $EF_{Ba} = 54$ ). Other elements with enriched Al-normalised values are As ( $EF_{As} = 7.8$ ) and U ( $EF_U = 6.0$ ).

#### 4.1.3. Black levels

The black levels follow the same general pattern as the Bonarelli sediments, except for lower concentrations of most elements. Major differences are found in the higher Ca (57% CaCO<sub>3</sub> on average) and Mn contents (MnO = 0.026%). Furthermore, Si values (SiO<sub>2</sub> = 23%) and P (P<sub>2</sub>O<sub>5</sub> = 0.23%) are lower than those found in the Bonarelli sediments. These differences relative to Bonarelli sediments are also reflected in the enrichment factors of Ca ( $EF_{Ca} = 117$ ) Mn ( $EF_{Mn} = 1.8$ ), Si ( $EF_{Si} = 1.6$ ), and P ( $EF_P = 6.1$ ) of the black level sediments. Elements such as As, Co, Cr, Cu, Ni, V, and Zn are found in high concentrations within the black levels compared to AS, while Ba is present in concentrations slightly below AS (473 µg/g). When normalised to Al, several elements (As, Ba, Co,

Cr, Ni, V, and Zn) show significant enrichments, while others (Pb, U, and Y) have enrichment factors varying between 0.5 and 5.

#### 4.2. Sedimentation rate estimates

To estimate the sedimentation rates for the different sediments groups, we compared the studied Furlo section to the Contessa Quarry at Gubbio as stable isotope data has been published for this site (Tsikos et al., 2004). This allows the direct comparison with Tarfaya deposits for which an orbital chronology has been established using geochemical parameters (Kolonin et al., 2005). A duration of 500 kyr has been proposed for the entire OAE, defined as ranging from the base of the isotopic excursion to the first occurrence of *Q. gartneri* (Kolonin et al., 2005), at Tarfaya. This interval contains the entirety of the Livello Bonarelli at Gubbio. Based on the thickness and Al contents of the Bonarelli (86 cm, 5.72 wt.% Al<sub>2</sub>O<sub>3</sub>) and the Scaglia Bianca from both below (65 cm, 0.64 wt.% Al<sub>2</sub>O<sub>3</sub>) and above (75 cm, 1.27 wt.% Al<sub>2</sub>O<sub>3</sub>) the Bonarelli within the OAE at Gubbio, we have determined a duration of 375 kyr for the Bonarelli. Assuming that the Bonarelli at Gubbio and Furlo are coeval, a sedimentation rate of 2.9 m/Myr is calculated for the Bonarelli at Furlo. Based on the Al contents at Furlo, we have determined that the Scaglia Bianca from below has a sedimentation rate of 14 m/Myr, while the Scaglia Bianca from above has a sedimentation rate of 8.1 m/Myr. The values for the Scaglia Bianca are somewhat higher than the rate of 5.3 m/Myr determined for the Scaglia Bianca on the basis of planktonic foraminifera (Premoli Silva et al., 1977). The black levels have an average sedimentation rate of 2.6 m/Myr, which is comparable to the estimated rate for the Bonarelli. Based on the average sedimentation rate, the duration of the individual black level events range from <3900 years (1 cm thickness) to approximately 50 kyr (15 cm thickness), with an average duration of 17.5 kyr.

#### 4.3. Nature of sediments

Results indicate that many of the common conservative lithogenic elements (i.e. Ti, K, Mg, Rb, Zr) trend close to “average shale” lines (lines formed from origin to the AS point) when plotted against Al<sub>2</sub>O<sub>3</sub>, and generally have good correlation coefficients ( $r^2$  between 0.90 for MgO and 0.99 for K<sub>2</sub>O), pointing to homogenous source area material. In addition, the enrichment factors of many of these elements relative to AS are close to 1, indicating that this “background”

detrital sedimentation is relatively close to AS in bulk composition. Also, given the low Al contents of these sediments, we assume that the terrigenous detrital input was relatively low, perhaps owing to the distance of the sampling locality relative to the paleoshoreline, as Al in marine sediments can generally be assigned to fine-grained detrital aluminosilicates (Calvert, 1976). The samples are Na-poor (often below the quantitation limit), indicating either plagioclase-poor source material or weathering effects preferentially removing Na in solution.

In Fig. 4, all data points from the Furlo section have been plotted on a triangular diagram with axes representing three of the major chemical components in sedimentary rocks, namely  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and CaO representing clays, quartz and/or biogenic silica, and calcium carbonate respectively. The diagram shows that the sediments from the Scaglia Bianca from both above and below the Bonarelli show very similar arching trends from the CaO to the  $\text{SiO}_2$  poles. In contrast, the majority of the Bonarelli data points plot along the  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  line, but below the AS point (Fig. 4), indicating a simple two component (AS– $\text{SiO}_2$ ; little or no carbonates) mixing for these sediments. Sediments from the black levels show a distinct distribution pattern along the carbonate dilution line (from AS to CaO pole), indicating that they represent a simple background sedimentation (AS) diluted by carbonates

and in this way significantly differ from the  $\text{C}_{\text{org}}$ -rich sediments of the Bonarelli.

#### 4.3.1. Excess silica

The sediments at Furlo contain high amounts of  $\text{SiO}_2$  leading to correspondingly high Si/Al ratios.  $\text{SiO}_2$  excess values ( $\text{Si}_{\text{xs}}$ ), i.e.  $\text{SiO}_2$  levels above “normal” detrital background, were determined using the general formula:

$$\text{element}_{\text{xs}} = \text{element}_{\text{sample}} - [(\text{element}/\text{Al})_{\text{background}} \times \text{Al}_{\text{sample}}] \quad (2)$$

where  $(\text{element}/\text{Al})_{\text{background}}$  is the ratio between the element and Al in detrital material. For Si, a first order approximation is provided using the AS Si/Al value of 3.11 (Wedepohl, 1971). According to this calculation, up to 96% of  $\text{SiO}_2$  is excess (i.e. not accounted for by the background AS component). In the Bonarelli, on average 57% of the sediment is excess  $\text{SiO}_2$ , while approximately 7% of the silica is not accounted for by background sedimentation in the black levels. Although other detrital sources of  $\text{SiO}_2$  cannot be discounted entirely, we ascribe this excess Si to biosiliceous accumulations (opal), or possibly by filling by chalcedonic quartz, owing to the very high abundance, and excellent preservation, of radiolarian taxa within the sediments (Elisabetta Erba, pers. com.).

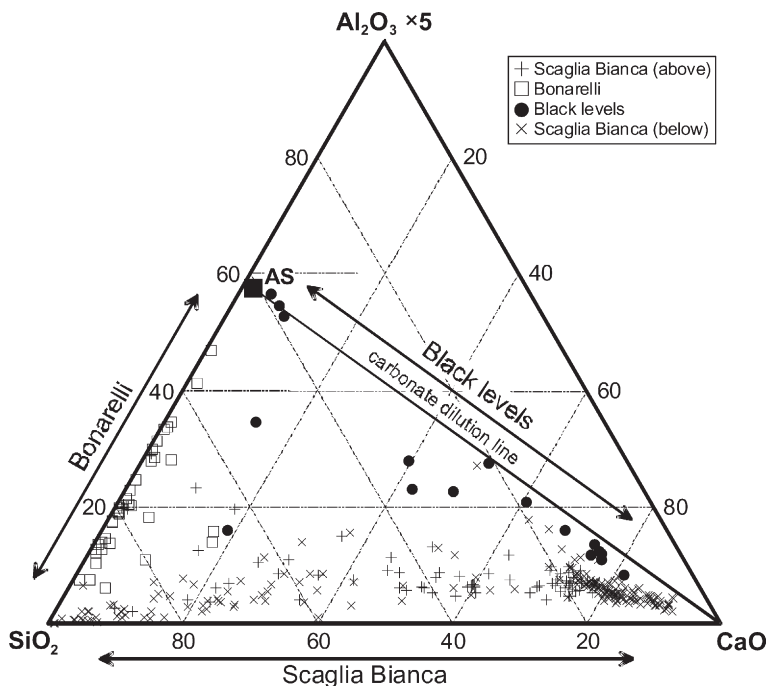


Fig. 4. Ternary diagram of relative proportions of  $\text{Al}_2\text{O}_3$  ( $\times 5$ ),  $\text{SiO}_2$ , and CaO. An arbitrary multiplier of 5 is used for  $\text{Al}_2\text{O}_3$  in order to better distribute the data points within the graph. “Average shale” (AS) composition is also shown (Wedepohl, 1971).



#### 4.3.2. Changes in clay mineralogy

Fig. 5 shows a plot of Mg/Al versus K/Al. This graph shows distinct distributions between the Scaglia, Bonarelli and black level sediments of the Furlo section. For example, the Bonarelli sediments have relatively low Mg/Al ratios, clustered around 0.2, and medium to high K/Al ratios (0.36 to 0.65). Similarly, the black level sediments show a high degree of clustering around Mg/Al=0.3 and K/Al=0.5. The Scaglia Bianca sediments show much higher variations in both Mg/Al (up to 0.97, generally higher than both the Bonarelli and black level sediments, and significantly higher than the average shale ratio) and K/Al. We attribute these differences to variations in the nature of the clay fraction. For example, illite has been considered as a primary source of K (Yarincik et al., 2000), and could therefore account for horizontal distribution of the samples (along the K/Al axis) along with K-feldspars. The higher Mg contents found in the clay mineral chlorite could likewise be responsible for the high Mg/Al seen in the Scaglia Bianca sediments. Little Mg is assumed to be in the carbonate phase, even though the Mg/Al ratios are higher in the Scaglia Bianca, as MgO correlates well with Al<sub>2</sub>O<sub>3</sub>. This could indicate that there is a source of detrital chlorite to the Umbria–Marche Basin that is cut-off or severely reduced during the deposition of the C<sub>org</sub>-rich sediments. Furthermore, a distinction between the two C<sub>org</sub>-rich groups can be seen in the K/Al ratios, which indicate a greater variability in the illite supply to the basin during deposition of the Bonarelli. Conversely, the lower ratios of Mg/Al and K/Al could be associated with clay minerals containing little or no Mg and/or K such as kaolinite.

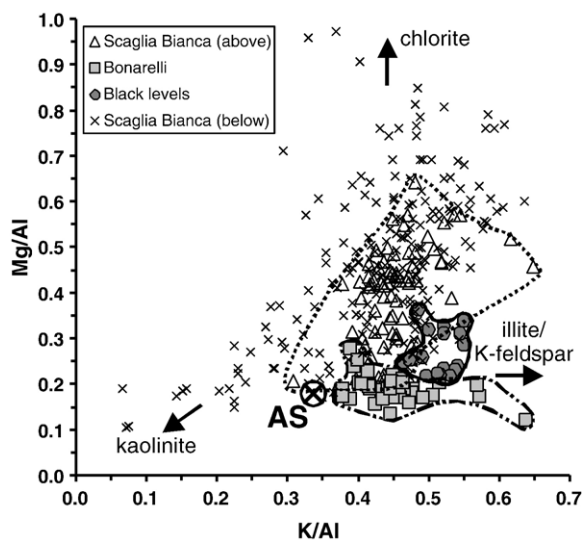


Fig. 5. Plot of Mg/Al vs. K/Al.

#### 4.4. Bottom water oxygenation indicators: Mn and Re/Mo ratios

Low Mn contents can be indicative of dysoxic bottom water conditions given that, under reducing conditions at the sediment/water interface, soluble Mn<sup>2+</sup> (as opposed to the much less soluble Mn<sup>4+</sup>) diffuses from the sediments into the oxygen-depleted bottom waters (Landing and Bruland, 1980; Bruland, 1983; Landing and Bruland, 1987). Thurow et al. (1992) present a model postulating that Mn originating from C<sub>org</sub>-rich reducing sediments is transported through an oxygen minimum zone (OMZ) and deposited as Mn<sup>4+</sup> oxide/hydroxide in deeper oxic waters. The Mn could then be incorporated as Mn-rich carbonate coatings beneath the redox boundary (Boyle, 1983). This transport mechanism through the water column implies an open marine environment. At Furlo, Mn is depleted in the Bonarelli, slightly above AS values in the black levels, and enriched in the Scaglia Bianca (Fig. 3 and Table 1). Frakes and Bolton (1984) and Force and Cannon (1988) have also reported the coexistence of Mn-rich sediments and black shales. The low EF<sub>Mn</sub> of the Bonarelli sediments indicates that the Mn is lost from the sediments during or shortly after deposition owing to the presence of strongly oxygen-depleted waters, while the black levels seem to have been deposited under slightly less oxygen-deficient conditions or in a more restricted environment owing to the observed Mn trapping, with Mn/Al values comparable to those found in the Black Sea (129 × 10<sup>-4</sup>; Lüschen, 2004) and in Mediterranean sapropels (202 × 10<sup>-4</sup>; Birgit Warning, pers. com.). The high enrichment factors shown by the Scaglia Bianca sediments hint at oxic water conditions, while an association of Mn/Al and Ca/Al shows that the Mn resides in the carbonate phase (as in the black levels), most likely as Mn coatings. This model, proposed by Thurow et al. (1992), could also apply to the Furlo sediments, with a Mn accumulation area located in deeper waters during deposition of the Bonarelli sediments under oxygen-depleted conditions in an expanded OMZ.

Rhenium is regarded as a powerful paleo-redox proxy element owing to its extremely low concentration in the continental crust (0.5 ng/g; Crusius et al., 1996) and in oxic sediments (<0.1 ng/g; Koide et al., 1986) compared to its high accumulation potential under even slightly reducing conditions (Koide et al., 1986; Colodner et al., 1993, 1995; Crusius et al., 1996). This is potentially the case in our sediments as the Re content of the C<sub>org</sub>-rich sediments at Furlo is high, containing up to 260 ng/g of Re (53 ng/g of Re on average; EF<sub>Re</sub>=456) in the Bonarelli and up to 120 ng/g of Re (average concentration=42 ng/g; EF<sub>Re</sub>=407) in the black levels, making Re the most

enriched element in the Furlo sediments. Rhenium forms a stable oxyanion ( $\text{ReO}_4^-$ ), and Re enrichment occurs via diffusion across the sediment–water interface, subsequent reduction of porewater Re, and formation of a solid phase where Re is incorporated into sulphides (pyrites) (Koide et al., 1986; Colodner et al., 1993).

Molybdenum is another element behaving somewhat similarly to Re, as it is also conservative in oxic seawater ( $[10.3 \text{ ng/g}]_{\text{seawater}}$ ; Collier, 1985) and forms stable oxyanions ( $\text{MoO}_4^{2-}$ ). Mo generally diffuses from the water column into porewaters along a concentration and redox gradient until it is reduced and removed from solution (e.g. Shaw et al., 1990; Emerson and Huested, 1991). Mo is very efficiently accumulated in sulphides (Koide et al., 1986; Colodner et al., 1993) under anoxic conditions through very rapid molybdenum scavenging onto manganese oxyhydroxides (Koide et al., 1986; Colodner et al., 1995), as well as in sulphur-rich organic matter under high  $\text{H}_2\text{S}$  concentrations and reactive iron-limited systems (Tribovillard et al., 2004). In contrast with Re, Mo is not significantly enriched in sediments under oxic or even suboxic bottom waters. For example, Mo values in recent sediments of anoxic basins such as the Black Sea or anoxic fjords are significantly higher than in suboxic sediments from the Arabian Sea or the Gulf of California (Brumsack, 1986; Jacobs et al., 1987; Emerson and Huested, 1991; Crusius et al., 1996; Nijenhuis et al., 1998). The Livello Bonarelli at Furlo contains up to  $40 \mu\text{g/g}$  of Mo ( $9.2 \mu\text{g/g}$  on average;  $\text{EF}_{\text{Mo}}=38$ ), while the black levels contain up to  $7.5 \mu\text{g/g}$  (average =  $3.2 \mu\text{g/g}$ ;  $\text{EF}_{\text{Mo}}=13$ ).

Crusius et al. (1996) have proposed the use of Re/Mo ratios to distinguish between anoxic and suboxic sedimentary conditions. They postulated that Re/Mo ratios close to the present-day seawater value of  $0.8 \times 10^{-3}$  ( $[\text{Re}]_{\text{sw}}=8.2 \text{ pg/g}$ , Colodner et al., 1993;  $[\text{Mo}]_{\text{sw}}=10.3 \text{ ng/g}$ , Collier, 1985) indicate anoxic conditions, while higher ratios hint at suboxic conditions owing to the low Mo enrichments in the absence of  $\text{H}_2\text{S}$ . In the  $\text{C}_{\text{org}}$ -rich sediments of Furlo, most samples lie within Re/Mo ratios between approximately  $0.8 \times 10^{-3}$  (the value for present-day seawater) and  $15 \times 10^{-3}$  (Fig. 6). Within these limits, the samples seem to be either grouped relatively close to the seawater Re/Mo line (some Bonarelli samples only) or trend along the  $15 \times 10^{-3}$  Re/Mo line (including all of the black level samples and approximately the 40% lowermost Bonarelli samples; Fig. 6). We interpret this bi-modal distribution as indicating deposition under conditions ranging from suboxic (the  $15 \times 10^{-3}$  Re/Mo trendline; low dissolved  $\text{O}_2$ , no  $\text{H}_2\text{S}$ ) to fully anoxic (present-day seawater line).

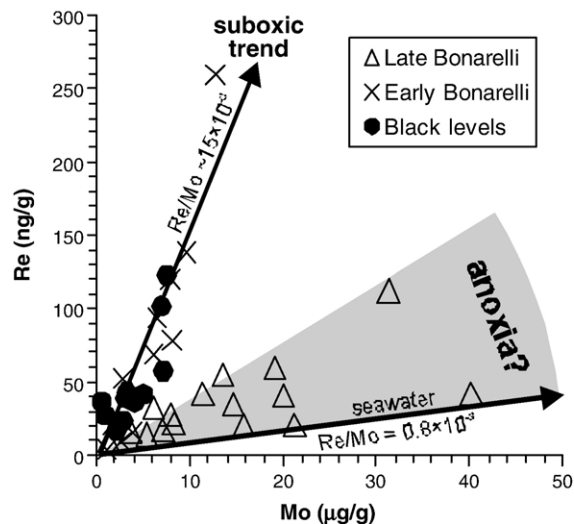


Fig. 6. Re vs. Mo diagram for Bonarelli and black level sediments (analysed by ICP-MS). Shaded area represents potential deposition under anoxic (0 mg/l dissolved  $\text{O}_2$ , presence of  $\text{H}_2\text{S}$ ) conditions. Trendlines are given for suboxic ( $\sim 15 \times 10^{-3}$ ) conditions as well as for the present-day seawater Re/Mo ratio ( $0.8 \times 10^{-3}$ ). Only 27 Bonarelli and 14 black level samples are plotted owing to the 7% RSD cut-off on Re and/or Mo.

levels were probably deposited from suboxic bottom waters, the distribution of the Bonarelli sediments suggests that bottom waters conditions became more anoxic (0 mg/l dissolved  $\text{O}_2$ , presence of  $\text{H}_2\text{S}$ ) in the upper 60% of the Bonarelli.

#### 4.5. Other redox-sensitive and sulphide-residing minor elements

Many redox-sensitive and/or sulphide-residing minor and trace elements are significantly enriched in the Furlo sediments (Fig. 7 and Table 1). Trace metal enrichments are commonly reported for  $\text{C}_{\text{org}}$ -rich sediments such as black shales (Brumsack, 1980, 1989; Arthur et al., 1990; Hatch and Leventhal, 1992; Lipinski et al., 2003), Mediterranean sapropels (Sutherland et al., 1984; Pruyssers et al., 1991; Van der Weijden, 1993; Thomson et al., 1995; Nijenhuis et al., 1996; Van Santvoort et al., 1996; Nijenhuis et al., 1998; Warning and Brumsack, 2000), and recent Black Sea sediments (Brumsack, 1989; Lüschen, 2004). Synsedimentary enrichments of redox-sensitive and sulphide-residing elements in various sedimentary environments have often been related to oxygen-depleted bottom waters conditions (Brumsack, 1980; Jacobs et al., 1985; Brumsack, 1986; Jacobs et al., 1987; Breit and Wanty, 1991; Hatch and Leventhal, 1992; Calvert and Pedersen, 1993; Piper, 1994; Nijenhuis et al., 1998). For example, high amounts of elements such as As,

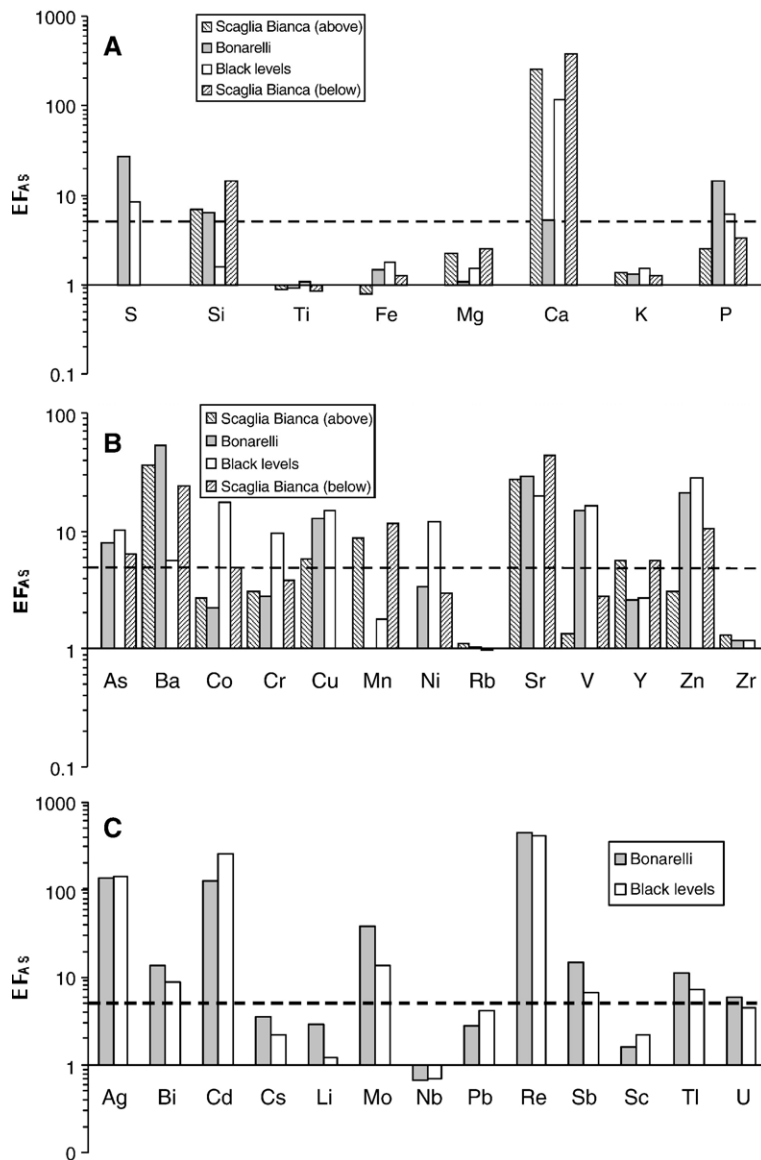


Fig. 7. Enrichment factors (relative to average shale of Wedepohl, 1971, 1991) of analysed elements in the Furlo section: A) Major elements analysed by XRF; B) Minor and trace elements analysed by XRF; C) Minor and trace elements analysed by ICP-MS. Dashed lines represent  $EF_{\text{element}} \geq 5$  enrichment cut-offs.

Co, Cr, Cu, Mo, Ni, Pb, Sb, U, and V can be fixed under reducing conditions in sediments either by precipitation as sulphides, coprecipitation with Fe-sulphides (Kremling, 1983; Jacobs et al., 1985), scavenged on sulphurised organic matter (Tribovillard et al., 2004), or precipitated as metallo-organic complexes like porphyrins during early diagenesis (Simoneit, 1978).

The redox-sensitive/sulphide-residing elements can be supplied to the sediments following several pathways: for example, some elements (Mo, U, V) can diffuse into the sediments during early diagenesis (Brumsack and Gies-

kes, 1983; Shaw et al., 1990), while others can be delivered owing to scavenging by sinking particles, binding to organic matter (Calvert et al., 1985; Brumsack, 1986), or even “bioconcentration” by plankton in high productivity settings (for elements such as Ag, Cd, Cu, Ni, and Zn) and released to the sediments during organic matter decomposition (Boyle et al., 1976; Bruland, 1980, 1983; Martin et al., 1983). This seems to be the case for some of the elements (Co, Cr, Ni) which are more enriched in the black levels, although they appear to be associated with both  $C_{\text{org}}$  and  $Al_2O_3$  in the black levels along with several

other elements, strongly suggesting a bioconcentration effect and/or adsorption of organic matter onto clays particles. No other clear associations between redox-sensitive/sulphide-residing elements and  $C_{\text{org}}$  or  $\text{Al}_2\text{O}_3$  can be distinguished. Additionally, Co behaves similarly to Mn in seawater (Knauer et al., 1982; Bruland, 1983) and in sediments (Klinkhammer, 1980; Hem et al., 1989), hence Co can diffuse out of sediments under reducing conditions (Heggie and Lewis, 1984), although it can be fixed as a stable sulphide under sulfidic conditions (Luther, 1991; Huerta-Diaz and Morse, 1992). This diffusion out of the sediments could also in part explain the lower Co enrichments observed in the Bonarelli sediments (anoxic) compared to the black levels (suboxic).

Several studies have also focused on the behaviour of trace elements Ag, Bi, Cd, and Tl in reducing water columns and sediments (Heinrichs et al., 1980; Thomson et al., 1995; Nathan et al., 1997; McKay and Pedersen, 2002; Crusius and Thomson, 2003). Tl behaves conservatively in oxic seawater (Flegal and Patterson, 1985), but can accumulate in pyrites (Heinrichs et al., 1980) as well as in reducing sediments (Brumsack, 1980; Thomson et al., 1995), although the detailed mechanisms leading to these enrichments in anoxic sediments are poorly known. The high Tl concentrations (up to 5.2  $\mu\text{g/g}$  in the Bonarelli and up to 2.0  $\mu\text{g/g}$  in the black levels) found in our sediments further indicate that sulphidic conditions were more likely to have been prevalent during Bonarelli sediment deposition. Bi is enriched by a factor of 13 in the Bonarelli and 9 in the black levels, although Bi enrichments in other CTBE black shales are not significant when compared to surrounding sediments (Brumsack, 1980). Bi enrichments have been related to sulphur contents in black shales with high Cd and Tl concentrations (Heinrichs et al., 1980). Both Ag and Cd are nutrient-type elements and show significant enrichments in the Bonarelli sediments ( $EF_{\text{Ag}}=138$ ;  $EF_{\text{Cd}}=127$ ) and in the black levels ( $EF_{\text{Ag}}=142$ ;  $EF_{\text{Cd}}=261$ ). High Ag accumulations may result from its involvement in the silicate biogeochemical cycle (Martin et al., 1983; Ndung'u et al., 2001), high Ag concentrations in bottom waters and scavenging onto settling particles (McKay and Pedersen, 2002), or by fixation in sulphides or diagenetic selenides (Crusius and Thomson, 2003). Cd can also be accumulated in phosphorites (Baturin and Oreshkin, 1984; Nathan et al., 1997) or sulphides as it precipitates even in the presence of trace amounts of  $\text{H}_2\text{S}$  (Rosenthal et al., 1995), which might explain why the Cd enrichment pattern is different from Bi, Sb, Tl, and U (higher  $EF_{\text{Cd}}$  in the black levels compared to the Bonarelli sediments; Fig. 7).

Although an increased detrital flux to the basin or a change in source area could be reflected in minor and trace

elements, mass balance calculations have suggested that seawater is the main source for trace metals supplied to  $C_{\text{org}}$ -rich sediments such as CTBE black shales (Brumsack, 1980) and Mediterranean sapropels (Nijenhuis et al., 1998) although additional sources, such as fluvial, hydrothermal, and biogenic inputs have to be considered at times (Arthur et al., 1990). This is perhaps the case for Zn, as it is highly enriched in the studied sediments ( $EF_{\text{Zn}}=22$  in the Bonarelli and 28 in the black levels) and other CTBE (Arthur et al., 1990) and Jurassic/Cretaceous black shales (Lipinski et al., 2003), but only moderately accumulated in Mediterranean (Warning and Brumsack, 2000) and Black Sea sapropels (Brumsack, 1989) in spite of overall similar trace element signatures of most  $C_{\text{org}}$ -rich sediments. The high Zn enrichments observed in the pre-Pliocene black shales could be due to increased hydrothermal activity during the Cretaceous as proposed by Brumsack (1980, 2006).

#### 4.6. Barium as a paleoproductivity indicator

Barium is present in very high concentrations (up to 1.4% in the Scaglia Bianca compared to 580  $\mu\text{g/g}$  in AS) at Furlo, and is possibly indicative of high paleoproductivity in this area. A high productivity scenario during the Cenomanian/Turonian transition is supported by the elevated P concentrations (up to 2.5%  $\text{P}_2\text{O}_5$  in the Bonarelli sediments), which hint at increased nutrient availability at this site, as well as the high levels of excess Si. Barium has often been discussed as a paleoproductivity proxy (Goldberg and Arrhenius, 1958; Dehairs et al., 1980; Schmitz, 1987; Lea and Boyle, 1990; Dymond et al., 1992). It is arguably one of the most reliable paleoproductivity indicators in older sediments owing to its preservation potential related to porewater saturation with respect to barite ( $\text{BaSO}_4$ ), thought to be the main carrier phase of Ba. However, sedimentary barite might undergo diagenetic changes and should be used cautiously (Van Os et al., 1991; McManus et al., 1998). For example, Ba migration is possible under severe sulphate depletion due to microbial sulphate reduction in porewaters (Brumsack and Gieskes, 1983; Brumsack, 1986; Brumsack et al., 1992), giving rise to the development of barite fronts or nodules (von Breyman et al., 1992; Torres et al., 1996; Br  h  ret and Brumsack, 2000). But given the abundance of small barite crystals typically on the order of tens of microns (Elisabetta Erba, pers. com.) throughout the Furlo outcrop thought to be of biogenic origin (Gingele and Dahmke, 1994), we suggest that Ba can be used as a reliable paleoproductivity indicator for this site.

Barium contents can thus be used to estimate paleo-productivity by calculating excess Ba ( $Ba_{xs}$ ; the proportion of Ba unsupported by detrital fluxes) as given by Eq. (2), although excess Ba can overestimate Ba related to biological activity owing to additional Ba-bearing phases such as carbonates, organic matter, opal, Fe–Mn oxides, and hydroxides (Eagle et al., 2003). According to detrital fluxes in modern upwelling areas (Philipp Böning, pers. com.), we use a  $(Ba/Al)_{background}$  ratio of  $27 \times 10^{-4}$ . Based on this assumption, the Bonarelli and Scaglia Bianca sediments contain up to 99% excess Ba, with slightly lower (86%) values found in the black levels, pointing to continuously high productivity at this site, even during carbonate deposition.

## 5. Summary of Furlo geochemistry

This section presents a summary of the main geochemical features of the Scaglia Bianca, black levels and the Bonarelli sediments, as well as a depositional model synthesising the events surrounding the Cenomanian–Turonian Boundary at Furlo. Beneath the Bonarelli, the lithology at Furlo abruptly and repeatedly changes from a biosiliceous–carbonate dominated system (Scaglia Bianca) to a mode of clay–carbonate deposition (black levels), and eventually to the biosiliceous–clay sediments of the Bonarelli. The very low  $C_{org}$  (Luca Bombardiere, pers. com.) and elevated Mn contents, in addition to the biogenic (both  $SiO_2$  and  $CaCO_3$ ) nature of the Scaglia Bianca sediments, suggest deposition under oxic water column conditions. Hence the generally high concentrations of trace elements found in these sediments are at least in part due to bioconcentration by organisms in the water column as proposed by Brumsack (1986) for sediments located under high productivity areas.

From a geochemical perspective, the main differences between the  $C_{org}$  sediments and the sediments of the Scaglia Bianca are the higher Mn contents and Mg/Al ratios as well as lower P, Cu, and V contents of the Scaglia sediments. While the lower P contents (albeit still above AS values) suggest lower nutrient availability or more intense nutrient regeneration during the deposition of these sediments, the higher Mg/Al ratios could indicate a variation in clay mineralogy (perhaps relating to a change in chlorite input) or provenance. In order to supply Mn to the sediments, the presence of an oxygen-minimum zone above the Furlo area is needed (see Section 4.4). The frequency and sharpness of the lithologic contacts between the black levels, Bonarelli and Scaglia Bianca sediments, as well as the relatively low level of geochemical mixing between sediment groups, as seen on

Fig. 4, suggest a rapid “on–off” type switching between these different sedimentary modes.

Compared to the Bonarelli, the black levels have high Re/Mo ratios and high Co, Cr, Ni, and Cd contents, as well as lower  $SiO_2$ , Ba, and U concentrations (Table 1). Their higher Re/Mo ratios point to a more oxygenated environment relative to the later Bonarelli conditions. The triggering mechanism for oxygen depletion in the water column during black level deposition is poorly understood, but does not appear to be related to an increase in productivity as Ba concentrations in the black levels are lower than in the Bonarelli sediments. Some of the redox-sensitive/sulphide-residing trace elements, however, are enriched probably owing at least in part to  $C_{org}$  adsorbed onto clay particles (for Co, Cr, Ni, and possibly other elements).

### 5.1. Carbonate “crisis” during the Bonarelli

The major features of the Livello Bonarelli are the general absence of carbonate, low Mn concentrations, and low Re/Mo ratios (in the upper 60% of the unit). While the low Mn levels and low Re/Mo ratios both point to strong oxygen deficiency during deposition, the absence of carbonate in the sediments reflects an important ecosystem change in the water column compared to both the Scaglia Bianca and the black levels. A similar scenario has been reported by Van Os et al. (1994) for Mediterranean sapropels where the lower carbonate content could have resulted from a decrease in carbonate production owing to the dominance of siliceous plankton, indicated by the high excess silica, during periods of high nutrient input. The high P content of the Bonarelli sediments would support such an interpretation, and is consistent with the high excess Si values calculated for the Bonarelli samples. Other scenarios include a carbonate drop during the Bonarelli that may result from the difficulty for organisms to produce carbonate under conditions of locally elevated  $pCO_2$  in the water column and/or eutrophic conditions, as is the case for coccolithophorids, planktic foraminifers, and coral reefs in the extant ocean (Elisabetta Erba, pers. com.).

In addition, we should also consider the low carbonate preservation potential in high alkalinity anoxic waters and carbonate corrosion in upwelling environments, where alkalinity build-up occurs at a certain depth within anoxic sediments. This could be the case here as, in addition to an upward decrease in the abundance and diversity of calcareous organisms towards the Bonarelli, severe microfossil corrosion has been observed (Ben Walsworth-Bell, pers. com.), either suggesting that the Furlo site was constantly close to or beneath the Carbonate Compensation Depth (CCD) or that the site has a lower carbonate

preservation potential. This latter scenario is supported by the general association between Sr and  $\text{CaCO}_3$  for the Scaglia Bianca, in addition to the high Sr content (up to 3000  $\mu\text{g/g}$ ) in the Bonarelli which point to the possible presence and subsequent dissolution of carbonate microfossils in the sediments. Alternatively, the Sr could have been supplied to the sediment in a phase other than carbonate, such as celestite ( $\text{SrSO}_4$ ) for which associations and even solid solutions with barite have been reported (Bernstein et al., 1992).

### 5.2. Depositional model for the Furlo site

In order to account for these geochemical features, we propose that during Cenomanian/Turonian times the Furlo site was located in a sub-basin, of local to regional extent, separated from either the rest of the Umbria–Marche Basin or the Tethyan Sea by a sill (Fig. 8). This interpretation is supported by the absence of black levels at several sites within the Umbria–Marche Basin (Beaudoin et al., 1996), which could be indicative of topographical features isolating sub-basins from one another. A semi-restricted environment, in addition to acting as a potential trap for continental detritus, would also have

prevented Mn escape during times of black level formation. For example, during these times the oxygen-depleted zone of the Furlo sub-basin water column could have been cut-off from the OMZ of the main basin by the sill (Fig. 8B). This would allow the fixing of  $\text{Mn}^{2+}$  (supplied from the sediments owing to bottom water reducing conditions) in carbonates or sulphides and elevate Mn/Al ratios in the sediments to slightly above average shale values as seen in the black levels (Table 1), a situation similar to present-day Black Sea conditions (Brumsack, 1989). This situation, however, differs from that of the Black Sea as bottom waters appear to have been slightly oxygenated during black level formation, as shown by the elevated Re/Mo ratios in these sediments.

During Bonarelli deposition, the expanded OMZ was probably shallower than the sill (relative to sea level), forming an oxygen-depleted connection between the sub-basins and the main basin. This would have led to a net export of Mn to deeper (and possibly still oxic) parts of the Umbria–Marche Basin or Tethyan Sea, and explain the low Mn/Al values seen in the Livello Bonarelli sediments. In addition, the transition between high Re/Mo ratios, which are comparable to ratios in the black levels below, to

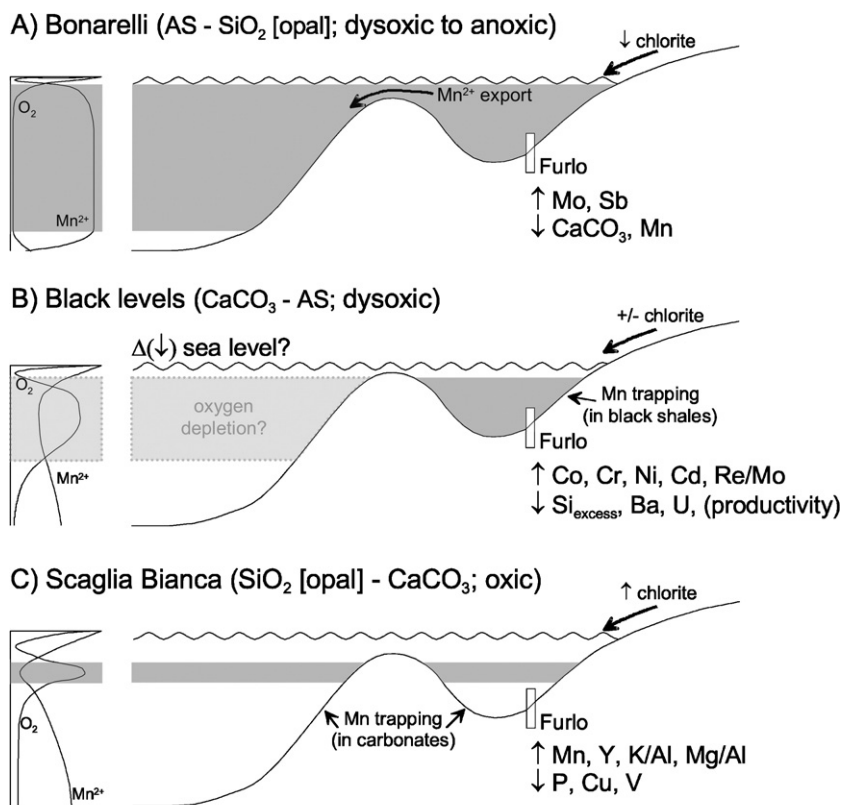


Fig. 8. Summary of geochemical parameters and depositional model for the Furlo outcrop: A) Livello Bonarelli; B) Black level; C) Scaglia Bianca.

much reduced ratios in the upper part of the Bonarelli, indicates a switch from generally dysoxic to anoxic conditions during Bonarelli deposition. Although speculative at this stage, the exact switching mechanism from high to low Re/Mo ratios within the Bonarelli could be linked to an anoxic feedback mechanism owing to the extended duration of the Bonarelli event compared to the black levels.

#### 5.2.1. Evidence for high-frequency eustasy during black level deposition?

Normalised Ti ratios of the lower and upper Scaglia Bianca, along with the Bonarelli, are fairly similar, but appear to increase in the black levels and, except for the Bonarelli sediments, the Ti/Al ratios of the black levels are statistically higher (at  $1\sigma$ ; Table 1). Ti/Al ratios have been shown to correlate well with the coarser component of the fine fraction in sediments (Bertrand et al., 1996). They have thus been used to reconstruct changes in detrital fluxes to distal depositional sites either as a proxy for sea level fluctuations or for the aeolian input of very fine Ti-bearing sand grains (Sageman et al., 2003). If sea level variations are presumed, then the Ti/Al ratios would indicate that the sea level was lower during the black level events, while wind pattern variations (i.e. an increase in wind strength) could affect ocean circulation patterns, namely local upwelling sites during times of black level formation. However, given that paleoproductivity (based on Ba contents and excess Si) appears to be lower during black level formation, the Ti/Al ratios are more likely to represent sea level variations.

A model calling only for episodic sea level drops resulting in black level formation provides an attractive alternative to OMZ variability as sub-basins could be physically cut-off from the main basin. The repetitious nature of the black levels would suggest high-frequency sea level changes on orbital-band time scales (Beaudoin et al., 1996), a plausible scenario given the remarkable similarity (both physically and geochemically) of the black levels with Pliocene–Pleistocene Mediterranean sapropels (Waming and Brumsack, 2000).

Rapid (<1 Myr) global eustatic sea level cycles for this time frame have recently been identified (Gale et al., 2002; Miller et al., 2003). However, given the estimated depth of the basin during the Late Cretaceous (~1500 m; Elisabetta Erba, pers. com.), a sea level drop of a few tens of meters (Gale et al., 2002; Miller et al., 2003) is probably insufficient to physically isolate the basin. Rather, we suggest that these high-frequency sea level variations could have provided a trigger mechanism for black level formation, even during a time of generalised high sea levels proposed for the CTBE (Erbacher et al., 1996).

In addition, sea level variations (and associated wavebase fluctuations) could explain changes in clay influx to the basin associated with the different sediments groups. Indeed, if different strata are eroded in response to sea level change, different clay minerals could be supplied to the basin at those times. This situation seems plausible as Brigatti and Poppi (1991) have already shown that clay mineralogy supplied to parts of the Umbrian–Marche basin was highly variable during Bonarelli deposition, suggesting a heterogeneous clay distribution in source rocks.

## 6. Conclusions and future research

The geochemical parameters of the different sediment groups of the Furlo outcrop highlight differences in depositional environments. Major elements show that the sediments of the Furlo outcrop are characterised by rapid switching between faunal assemblages, with silica forms virtually absent from the black levels, whereas carbonate remains appear to be lacking in the Bonarelli. Most redox-sensitive or sulphide-residing trace elements are strongly enriched in the  $C_{org}$ -rich sediments, indicating periodic depletion of oxygen and potential availability of hydrogen sulphide in the water column.

The Mn depletion in the Bonarelli sediments shows that bottom waters were oxygen-depleted during this time and that open marine conditions permitted the export of Mn. This contrasts with the elevated Mn/Al ratios in the black levels which indicate that Mn was trapped during these times and that the (sub-)basin or the oxygen minimum zone was more restricted. Furthermore, Re/Mo ratios show that conditions were largely dysoxic during black level formation and the earlier part of the Bonarelli, and changed to fully anoxic during the Bonarelli. Elevated Ba concentrations are indicative of high paleoproductivity in this area, which is further supported by the high P concentrations, while high Zn concentrations suggests an increase in submarine hydrothermal activity during this time interval. Evidence for ephemeral sea level drops during black level deposition is provided through Ti/Al ratios: these sea level fluctuations could be the controlling factor in Mg/Al variations seen between the sediments groups, as a change in erosion locus could provide different clay types to the basin.

This research leaves many outstanding questions and research opportunities regarding the CTBE. Namely, further research into the timing of the black levels would shed light on the mechanisms, such as orbital-band forcing and sea level fluctuations, which could modulate and control these events. Direct radiometric dating of these deposits, as well as a good integration of sequence

stratigraphy and an analyses of geochemical parameters in a stratigraphic context, would provide good tools for such studies and evaluate the role of sea level on the rapid faunal switching and the supply of different clay types (which could be studied using XRD) to the basin over time.

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