

# Comparative high-resolution chemostratigraphy of the Bonarelli Level from the reference Bottaccione section (Umbria–Marche Apennines) and from an equivalent section in NW Sicily: Consistent and contrasting responses to the OAE2

Giovanna Scopelliti <sup>a</sup>, Adriana Bellanca <sup>a</sup>, Rodolfo Neri <sup>a,\*</sup>,  
Francois Baudin <sup>b</sup>, Rodolfo Coccioni <sup>c</sup>

<sup>a</sup> *Dipartimento di Chimica e Fisica della Terra ed Applicazioni alle Georisorse e ai Rischi Naturali (CFTA),*

*Università di Palermo, Via Archirafi 36, 90123 Palermo, Italy*

<sup>b</sup> *Département de Géologie Sédimentaire et CNRS-FR 32/UMR 5143, UPMC, 4 place Jussieu, 75252 Paris Cedex 05, France*

<sup>c</sup> *Istituto di Geologia e Centro di Geobiologia dell'Università, Campus Scientifico, Località Crocicchia, 61029 Urbino, Italy*

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## Abstract

The Bonarelli Level (BL) from the upper Cenomanian portion of the reference Bottaccione section (central Italy) is characterized by the presence of black shales containing high TOC concentrations (up to 17%) and amounts of CaCO<sub>3</sub> near to zero. In the absence of carbonate and, consequently, of relative carbon- and oxygen-isotopic data, the elemental geochemistry revealed to be a very useful tool to obtain information about the palaeoclimatic and palaeoceanographic evolution of the Tethys Ocean during the OAE2. Based on several geochemical proxies (Rb, V, Ni, Cr, Si, Ba), the BL is interpreted as a high-productivity event driven by increasingly warm and humid climatic conditions promoting an accelerated hydrological cycle. The enrichment factors of peculiar trace metals (Zn, Cd, Pb, Sb, Mo, U) provide further insight about the H<sub>2</sub>S activity at the seafloor during the organic-rich sediment deposition and permitted us to evaluate the use of Ba as palaeoproductivity tracer in conditions of high rate of sulphate reduction.

By comparing geochemical records from the reference Bottaccione section (central Italy) with those previously obtained for the coeval Calabianca section (northwestern Sicily), different degrees of oceanic anoxia were delineated and ascribed to different abundance and type (degradable or refractory) of organic matter, which are limiting factors in the bacterial sulphate reduction reactions and in subsequent euxinic conditions at seafloor in the Tethys realm. Based on a cyclostratigraphic approach, consistent fluctuations at 100 ky scale in the chemostratigraphic signals from the two sections are inferred to be expression of a strong orbital-climatic forcing driving changes in the oceanic environment during the BL deposition.

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## 1. Introduction

During greenhouse conditions in the mid-Cretaceous, marine environments were characterized, for

\* Corresponding author. Tel.: +39 91 6161574; fax: +39 91 6168376.

E-mail address: neri@unipa.it (R. Neri).

short time intervals, by massive accumulation of organic carbon ( $C_{org}$ ) on a global scale. The widespread deposition of  $C_{org}$ -rich sediments, which can be correlated between different basins and oceans, was referred to as “Oceanic Anoxic Events” (OAEs) by Schlanger and Jenkyns (1976). The Bonarelli Level (Scisti ittoliolici of Bonarelli, 1891) is one globally recognized period of  $C_{org}$ -rich sediment accumulation occurring

at the Cenomanian–Turonian boundary and is considered to be the sedimentary expression of the Oceanic Anoxic Event 2 (OAE2 or Bonarelli Event: Schlanger and Jenkyns, 1976; Jenkyns, 1980; Arthur et al., 1990). To explain the special geochemical conditions existing during the OAEs various models have been proposed. They rely mainly on changes in sea-surface productivity (e.g. Pedersen and Calvert, 1990; Weissert and Lini,

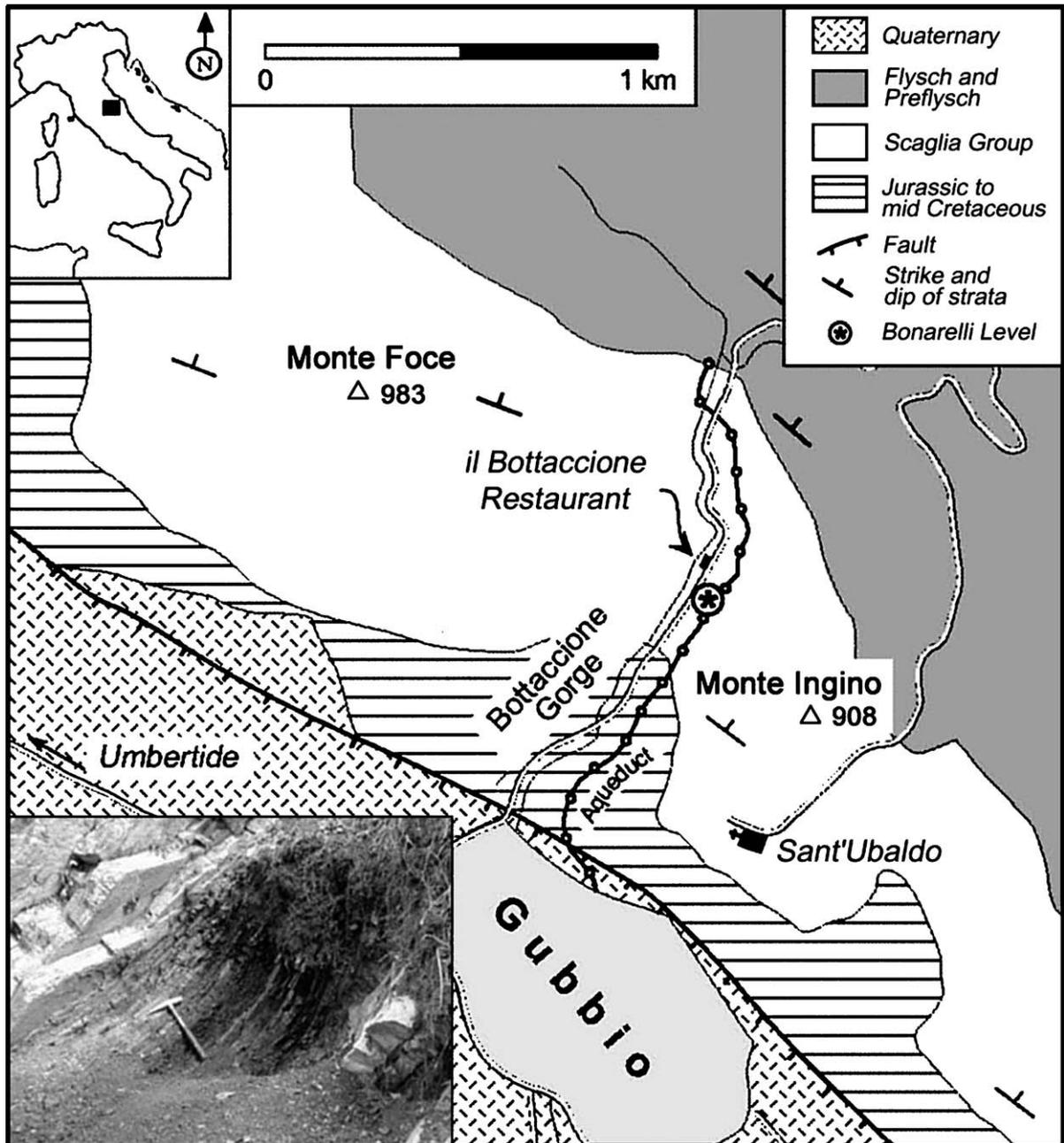


Fig. 1. Location of the Bottaccione section, a geological sketch map of the Gubbio area (central Italy) and view of the Bonarelli Level exposure (modified after Coccioni and Luciani, 2004).

1991) and/or  $C_{org}$  preservation conditions (e.g. Bralower and Thierstein, 1984; Tyson, 1995). However, it is indisputable that the OAE2, even if a short-lived event, induced both major oceanographic changes in the marine environment and severe disturbance of the biosphere which, in turn, triggered the ecological stress forcing one of the larger biotic crises of the Mesozoic Era (see Hallam and Wignall, 1997, and references therein).

Carbon-rich shales, which characterize the late Cenomanian stratigraphic interval, have been recognized in different regions of the globe including northern and southern Europe, Africa, North and South America, the western margin of Australia and the Pacific and Atlantic basins (Schlanger and Jenkyns, 1976; Jenkyns, 1980, 1991; Kuhnt et al., 1986, 1990; Schlanger et al., 1987; von Rad et al., 1989; Crumière et al., 1990; Lipson-Benitah et al., 1990; Baudin, 1995).

In Italy, the Bonarelli Level (BL) has been studied in different settings (e.g. Bosellini et al., 1978; Arthur and Premoli Silva, 1982; Coccioni et al., 1991, 2001; Bellanca et al., 1996, 1998; Scopelliti et al., 2001; Coccioni and Luciani, 2004; Scopelliti et al., 2004a,b). In its type area (Umbria–Marche Apennines) the Bonarelli Level was identified on the basis of lithology and calcareous plankton biostratigraphic investigations (Arthur and Premoli Silva,

1982; Piergiovanni, 1989; Coccioni et al., 1991; Premoli Silva and Sliter, 1994; Premoli Silva et al., 1999; Coccioni and Luciani, 2004). Recently, it has been object of an isotopic study based on TOC and phytane  $\delta^{13}C$  profiles (Tsikos et al., 2004) and of a lamina-scale compositional mapping (Kuroda et al., 2005) concerned with this area and other key localities. With the aim to provide a contribution to the understanding of the palaeoceanographic conditions during the anoxic event in the Tethyan realm and considering that the lack of carbonate in the Bonarelli Level inhibits the possibility to analyse trends of the carbon- and oxygen-isotopes in the carbonate record, we have carried out a high-resolution geochemical study of the Bottaccione section centred on the Bonarelli Level Event inside a stratigraphic interval well-constrained by a detailed biostratigraphic study on planktonic foraminifera (Coccioni and Luciani, 2004). Furthermore, we propose a comparison between geochemical proxies of the reference Bottaccione section and those previously obtained for the coeval Calabianca section in northwest Sicily (Scopelliti et al., 2004a,b). We discuss and evaluate possible differences in the elemental distribution patterns of the two sections in terms of different geochemical response to the basin-wide palaeoceanographic changes through the OAE2. Consistent variations across the

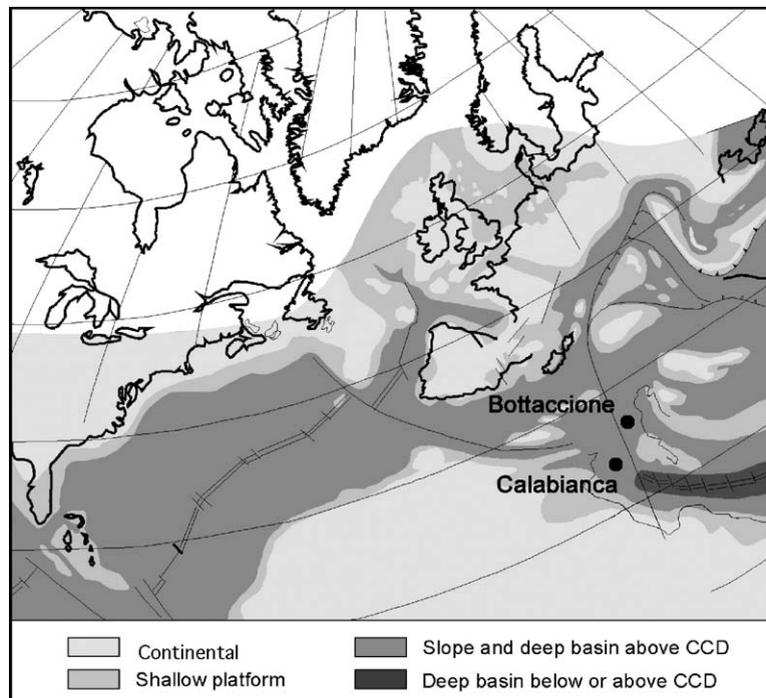


Fig. 2. Location of the Bottaccione and Calabianca (NW Sicily) sections inside the map of Western Tethys and North Atlantic paleoenvironments for the mid-Cretaceous (adapted from Dercourt et al., 1993). CCD=calcite compensation depth.

geochemical records from the Bottaccione and Calabianca sections were used to constrain the influence of orbital-climatic forcing in relation to oceanic environmental conditions during the BL deposition.

**2. Geologic and stratigraphic context**

The Cretaceous pelagic sequence of the Umbria–Marche Basin (central Italy) is well exposed in the classic Tethyan reference section of the Bottaccione

Gorge (Gubbio area; Fig. 1). The studied section, about 2.5 m in thickness, is located about 1 km northeast of the Gubbio town, along the road S.S. 298. The segment sampled comprises a stratigraphic interval of the Upper Cretaceous “Scaglia Bianca” Formation enclosed in a pelagic sequence deposited at an estimated water depth of 1500–2500 m (Arthur and Premoli Silva, 1982; Kuhnt, 1990) in a complex basin along the continental margin of the Apulian block (Fig. 2) that moved together with Africa rela-

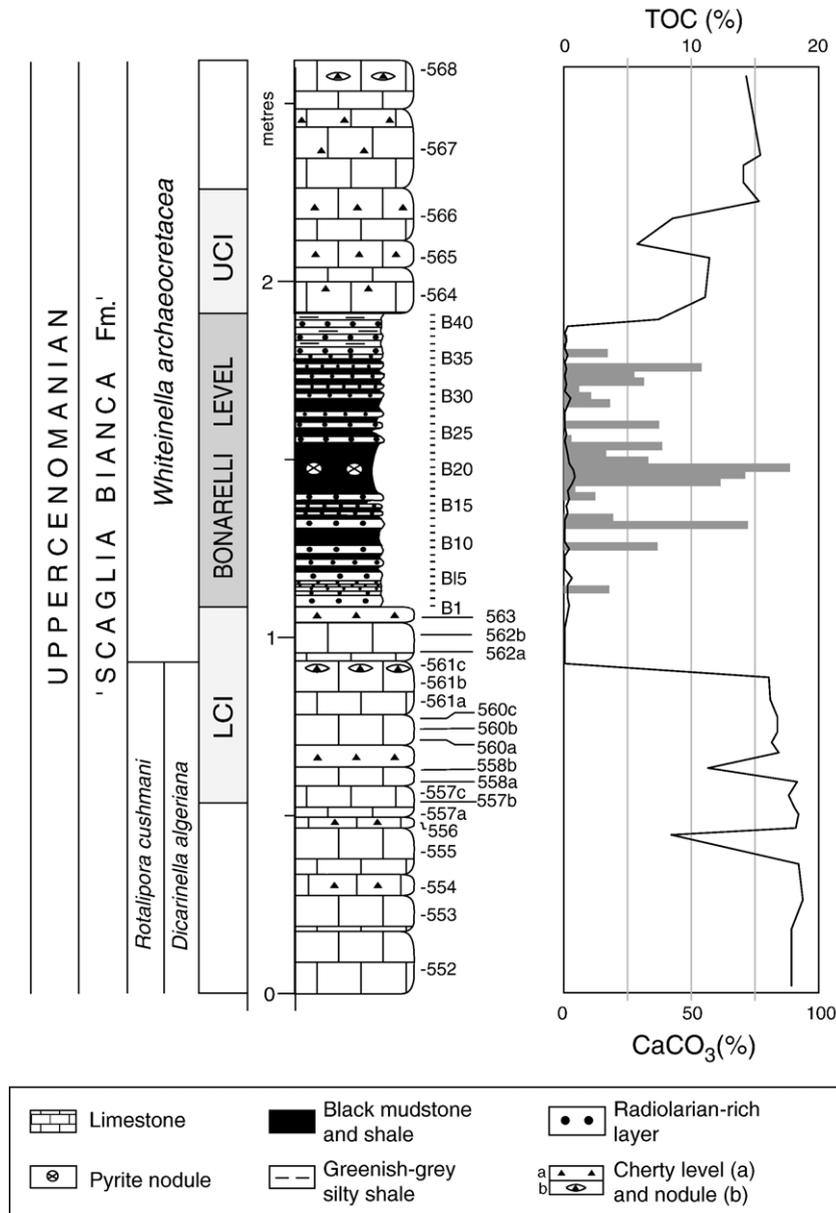


Fig. 3. Lithologic and biostratigraphic log of the Bottaccione section (reported from Coccioni and Luciani, 2004) plotted against TOC (grey bands) and CaCO<sub>3</sub> (solid line) values. LCI and UCI are lower and upper critical intervals (see text).

tively to northern Europe (Channell et al., 1979; Centamore et al., 1980).

The Bonarelli Level (OAE2) is a prominent ichthyolithitic-bituminous-radiolaritic regional marker bed, about 1 m thick on average (Fig. 3), occurring near the top of the latest Cenomanian–earliest Turonian “Scaglia Bianca” Formation (greyish member of Coccioni et al., 1992, and member W4 of Coccioni, 1996). It falls in the lowermost part of the planktonic foraminiferal *Whiteinella archaeocretacea* Zone (Premoli Silva and Sliter, 1994, 1999) and is referable to the uppermost part of the Cenomanian stage.

The portion of the “Scaglia Bianca” Formation, inside which the Bonarelli Level is sandwiched, consists mostly of yellowish–grey to greyish limestones (CaCO<sub>3</sub> up to 90%) with a siliceous component occurring mainly as chert nodules and lenses. The Bonarelli Level consists of olive-green to black mudstones and black, organic carbon-rich, finely laminated shales, often with abundant fish remains, pyrite nodules and/or radiolaria, alternating to radiolarian-rich layers. Black shales and other silica-rich lithologies of the BL show calcium carbonate contents close to zero (Fig. 3).

The features of the pre- and post-Bonarelli Level planktonic foraminiferal assemblages allowed Coccioni et al. (1991) to recognize two transitional intervals which were defined as ‘lower’ (LCI) and ‘upper’ (UCI) critical intervals. Both these intervals, respectively ~50 and ~22 cm thick, are characterized by unstable planktonic foraminiferal structure and show marked and abrupt fluctuations of the relative abundance, ‘eclipse’ of larger forms, dominance of small hedbergellids and schackoinids, drop in genus and species diversity, and dwarfing (Coccioni and Luciani, 2004).

The Bonarelli Level equivalent from the Calabianca section (northwestern Sicily), proposed here for a comparison, covers a stratigraphic interval of the Upper Cretaceous “Scaglia” Formation. It is part of a more complete succession mainly constituted by shelf carbonates (“Trapanese” domain) which were deposited in a more proximal palaeogeographic setting of the African continental margin (see Fig. 2). For more complete information about this section see the paper of Scopelliti et al. (2004b).

### 3. Materials and methods

The Bottaccione section is represented by 65 samples. Across the Bonarelli Level each lithology was collected with a sampling interval of 2 cm.

Twenty-two samples were studied for their total organic carbon (TOC) contents by using a LECO IR-

212 analyser. Precision for this analysis is  $\pm 0.1\%$ . The source and thermal maturation of the organic matter were estimated using a Rock-Eval instrument, Oil Show Analyser or Rock-Eval 6 device (Espitalié et al., 1985–86; Lafargue et al., 1998). Standard notations are used: S<sub>1</sub> and S<sub>2</sub> are in mg hydrocarbons (HC) per gram of dry sediment and  $T_{\max}$  is expressed in °C. The hydrogen index (HI = S<sub>2</sub>/TOC × 100) is expressed in mg HC per gram of TOC.

Major- and minor-element concentrations were determined respectively on 65 and 53 samples by X-ray fluorescence spectrometry (XRF) on pressed, boric-acid backed pellets of bulk rock. Data reduction was achieved using the method described by Franzini et al. (1975). Certified reference materials were used as monitors of data quality. Analytical errors were below 1% for Si and Al; below 3% for Ti and Ca; and below 10% for trace elements.

In some selected samples of the Bonarelli Level Zn, Cd, Sb, Pb, Mo, Th and U were determined via Induced Coupled Plasma Mass Spectroscopy (ICP-MS) at European Geochemical Facility of Bristol (European Commission contract HPRI-1999-CT-00008). Samples underwent an acid digestion using a mixture of concentrated HNO<sub>3</sub>, HClO<sub>4</sub>, and HF. Samples were diluted to 1:1000 by mass and aliquots of this solution were mixed with an internal standard and analysed by comparing them to a calibration curve constructed using multi-element standards. ICP-MS used was a VG Elemental Plasma Quad II. Precision is reported as percent relative standard deviation (RSD) and is <2% for Zn, Pb, Th, U and 4–10% for Cd, Sb, Mo.

## 4. Results

### 4.1. Organic geochemistry

The organic carbon content of samples from the Bottaccione Bonarelli Level is high (average TOC value of 6.1%) with a fourth of samples reaching up to 10% TOC (Fig. 3). Samples B18 to B20 are very rich in organic matter (TOC up to 17%) and are enclosed in a 15-cm-thick interval lacking of radiolarian-rich layers.

Information on thermal evolution and origin of organic matter was obtained from pyrolytic measurements (Espitalié et al., 1985–86). Relatively low  $T_{\max}$  values (422 °C in average, Fig. 4) suggest that organic matter has not experienced strong thermal maturation.

The hydrogen index (HI) parameter provides a further tool to assess the source of organic matter. The organic-rich samples, according to their relatively high range of HI-values (300 to 416 mg HC/g TOC), are

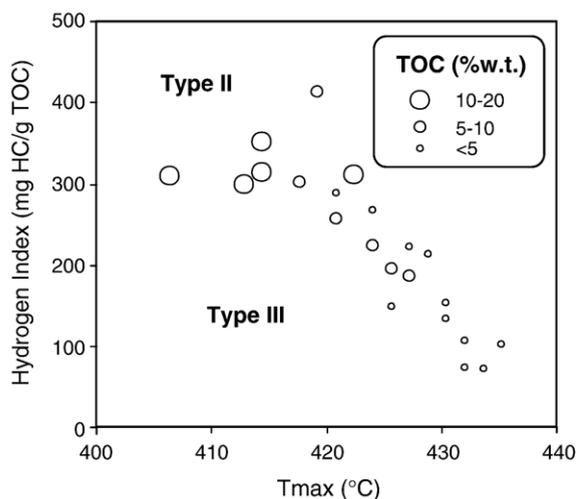


Fig. 4. Rock-Eval Hydrogen Index versus  $T_{max}$  values. Type II and Type III indicate approximate evolution areas for different end-member types of sedimentary organic matter as defined by Tissot and Welte (1984).

located in the Type II area of the modified van Krevelen diagram (Fig. 4). Type II is usually related to marine organic matter, more or less reworked by bacteria (Tissot and Welte, 1984). Samples with lower organic carbon content show lower HI-values, and plot at the boundary between Type II and III. Type III derives from higher plant biomass which is hydrogen-lean compared to bacteria and phytoplankton but it may also be explained by the oxidation of hydrogen-rich organic matter, which results in a decrease of the hydrogen content while its oxygen content increases.

#### 4.2. Elemental geochemistry

Depth profiles of some geochemical markers used for the Bottaccione section are presented in Fig. 5 and interpreted in terms of changes in detrital delivery to the sediment, surface primary productivity, and basin-bottom redox conditions during the time of the Bonarelli Level deposition. To avoid the influence of variable organic carbon, biogenic carbonate and silica contents, element concentrations were normalized to Al. Although removal of some Al amount from seawater by the oxide components cannot be ruled out (Kryc et al., 2003), this element is generally assumed to represent a reliable measure of the terrigenous load in marine sediments. Another reason for using Al is that this element is typically not diagenetically labile.

The enrichment factor (EF) for each trace metal in selected samples was calculated as  $(\text{Element}/\text{Al})_{\text{sample}} / (\text{Element}/\text{Al})_{\text{shale}}$ , using concentration values for the

average shale from Wedepohl (1978) for Zn, Mo, Sb, Cd, Pb and from Gromet et al. (1984) for Al.

##### 4.2.1. Detrital flux variations

A common approach to evaluate the amount and source of detrital components into the sedimentary basin is to interpret the Ti/Al record. Based on studies of recent sediments (Emelyanov and Shimkus, 1986), titanium tends to be enriched in fine-silty detritus and fluctuations in Ti/Al stratigraphic profiles are generally thought to indicate variations in the aeolian source strength (Bertrand et al., 1996; Rachold and Brumsack, 2001). In the Bottaccione section, Ti/Al depth profile displays values fluctuating around 4.5 in the underlying limestones, a clear decrease across the Bonarelli Level down to a minimum of 2.9 and higher ratios in the overlying limestones ranging around 5.2. This pattern could indicate dilution of wind-transported material due to enhanced runoff rate. Intriguingly, the decreasing trend in the BL is interrupted by an interval of high Ti/Al ratios that corresponds to  $C_{\text{org}}$ -rich, Si poor layers (Figs. 3 and 5). Possible associations between Ti and organic matter have been indicated to be responsible for removal of the metal from the seawater column (Kryc et al., 2003). Similarly, scavenging processes of dissolved Ti by settling particulate matter at times of intensive deposition of organic matter could have promoted Ti accumulation in the BL, thus obscuring the effect of decreased Ti aeolian input. This could be the reason of elevated Ti/Al observed in the middle part of the BL.

Fig. 5 also displays the Rb/Al depth profile. Because Rb is mainly fixed in illite, its content is related to the finest fraction (Rachold and Brumsack, 2001). Values of Rb/Al ratio widely fluctuate across the BL and averagely are higher than those of the underlying and overlying limestones, suggesting repeated episodes of enhanced fluvial discharge through the OAE event.

##### 4.2.2. Bottom-water redox conditions

Indications about redox conditions during the Bonarelli Level deposition are deduced from the proportionality of vanadium to nickel, Cr/Al ratio, and Zn, Cd, Sb, Pb, Mo enrichment factors (EFs) in the Bottaccione section (Figs. 5 and 6). Under euxinic conditions, although large amounts of vanadium and nickel are associated to metallo-organic complexes (Lewan and Maynard, 1982; Breit and Wanty, 1991), a substantial presence of bacterially generated  $H_2S$  limits the availability of nickelous cations because of the formation of NiS complexes, whereas vanadyl or trivalent vanadium are available (Lewan, 1984). From the V/(V+Ni) curve (Fig. 5) it is evident that most of the data from the

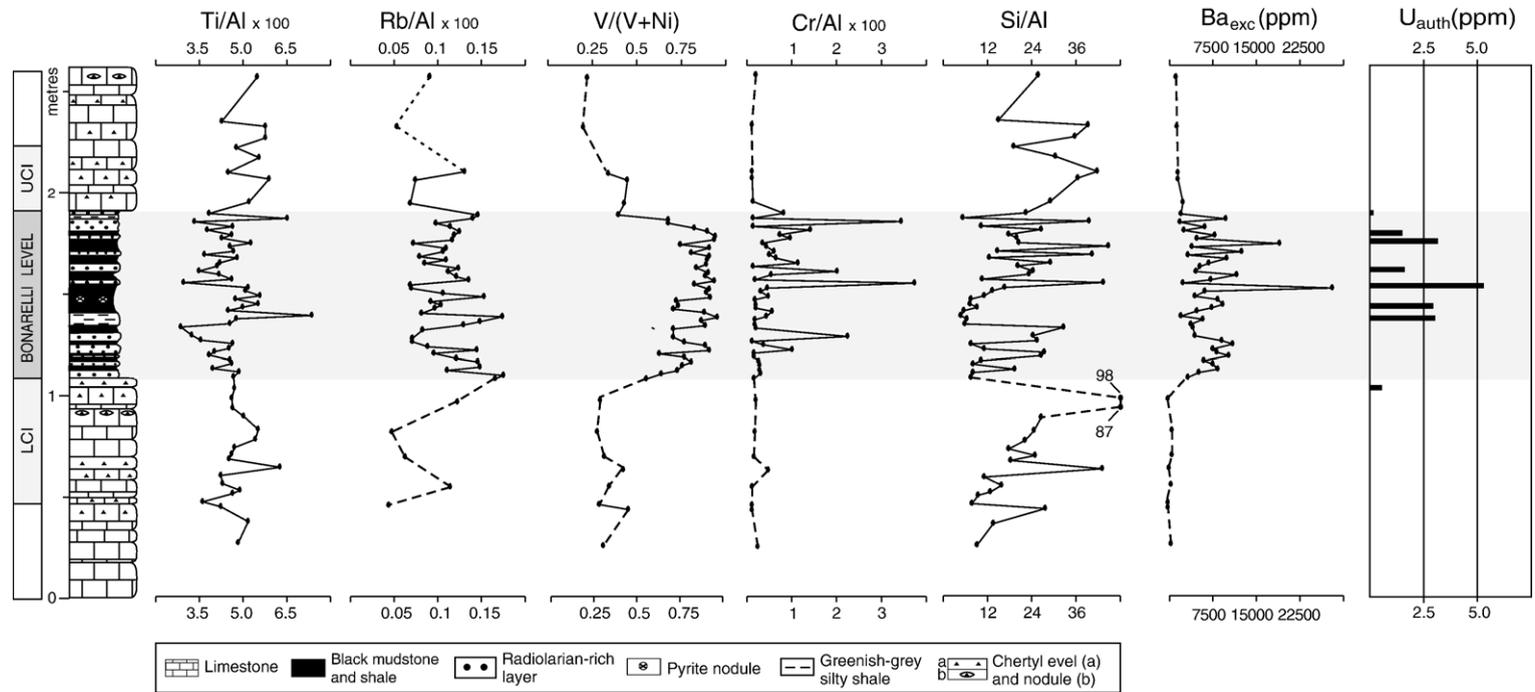


Fig. 5. Distribution of values of geochemical proxies throughout the Bottaccione section; light grey band is the Bonarelli Level, LCI and UCI as in Fig. 3.

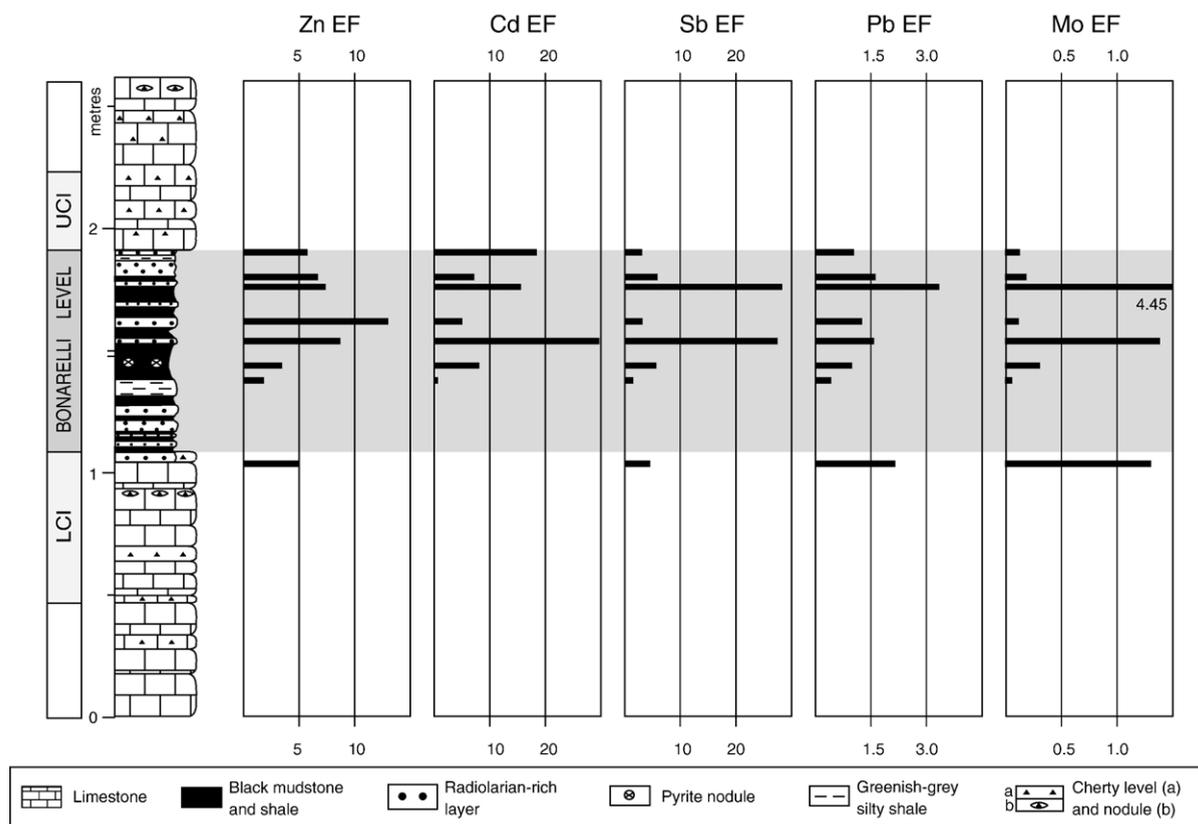


Fig. 6. Variation of trace metal enrichment factors (black bands) throughout the Bottaccione Bonarelli Level; light grey band as in Fig. 5, LCI and UCI as in Fig. 3.

Bonarelli Level fall in the range of 0.54–0.80, proposed by Hatch and Leventhal (1992) as indicative of anoxic conditions, with many values greater than 0.80 suggestive of euxinic conditions, while the underlying and overlying limestones show ratios lower than 0.54 which are related to oxic conditions at the seafloor.

Cr/Al depth profile (Fig. 5) displays for the BL an average value of the ratio equal to 0.65 with a maximum of  $\sim 4$ . The majority of values are markedly higher than the ratio of the average shale (0.14; Gromet et al., 1984). Strong Cr enrichments can be indicative of an algal source of the organic matter, which preferentially concentrates Cr, or, more likely, of relatively higher redox potentials favouring, consequently, the availability of reduced Cr ( $\text{Cr}^{3+}$ ) for reaction with organic matter (Hatch and Leventhal, 1992). Some authors, however, suggest an entirely detrital origin for Cr (e.g. Wignall, 1994; and references therein); thus, combining both these interpretations, the increased values in Cr/Al profile throughout the BL suggest a strong relation between the development of oxygen-depleted bottom-waters and an enhanced riverine discharge.

Enrichments of Zn, Cd, and Sb characterize the Bonarelli Level with EF average values of 6.62 (max = 12.95), 12.02 (max = 29.60), and 10.63 (max = 28.20), respectively (Fig. 6). Pb is only slightly enriched showing an average value of 1.45 (max = 3.33), while as to Mo only three samples have EF higher than 1. This different behaviour is related to the different mechanisms determining the enrichment of these metals in organic-rich sediments by (i) syngenetic precipitation of sulphide minerals and (ii) interaction between metals dissolved in seawater and organic matter, during sedimentation and early diagenesis (Coveney, 1979; Holland, 1979; Coveney and Martin, 1983). Morse and Luther (1999) reported that  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sb}^{2+}$ , and  $\text{Pb}^{2+}$ , existing in oxic seawater as cations, have faster water exchange reaction kinetics than  $\text{Fe}^{2+}$ , thus forming their own sulphide minerals; differently,  $\text{Mo}^{6+}$ , present in seawater as oxyanion  $\text{MoO}_4^{2-}$ , must be reduced to  $\text{Mo}^{4+}$  prior to incorporation into pyrite. These considerations imply that where euxinic conditions at seafloor are prevalent, beyond the formation of pyrite, Zn, Cd, Sb and, to a lesser extent, Pb form own sulphides as a consequence of high  $\text{H}_2\text{S}$  activity. In this stage, Mo is

not trapped in sediments but undergoes reduction to be incorporated into pyrite only during early diagenesis (Crusius et al., 1996; Algeo and Maynard, 2004; Piper and Perkins, 2004; Sundby et al., 2004). In concordance with this, elevated enrichment factors for Zn, Cd, and Sb in the Bottaccione samples confirm H<sub>2</sub>S availability at the seafloor during the C<sub>org</sub>-rich level deposition, while Mo EF seldom greater than 1 is indicative of poor incorporation into pyrite, probably during an early diagenetic stage.

#### 4.2.3. Primary productivity-sensitive elements

As potential proxies for primary productivity we have used the Si/Al ratio and Ba<sub>exc</sub> index together with U<sub>auth</sub> values (Fig. 5).

In this work, the biogenic carbonate content, generally assumed to be a primary productivity indicator, will be neglected because of values of CaCO<sub>3</sub>% near zero in the Bonarelli Level (Fig. 3). Beyond the decrease of calcareous organisms related to anoxia in the euphotic zone, absence of carbonate in C<sub>org</sub>-rich intervals is very common and thought to be linked to a temporary rise of CCD due to an increase of the water acidity as a

consequence of enhanced oxidation of the organic matter sinking at the seafloor.

In the Bottaccione section, the Si/Al ratio displays a trend characterized by wide fluctuations without apparent enrichment in the Bonarelli Level. High Si/Al ratios in the BL correspond to radiolarian-rich layers exhibiting under the microscope well preserved spherical to elliptical tests generally filled with fan chalcedonic quartz (Fig. 7A–B). According to Kuroda et al. (2005), who investigated the Bonarelli Level at Gorgo Cerbara (Umbria, Italy) by image processing of compositional mapping, we assume that chalcedonic quartz replacing radiolarian fossils is representative of biogenic silica. Therefore, Si/Al can be considered a reliable proxy of surface productivity. By contrast, very high Si/Al ratios in the underlying and overlying limestones are a diagenetic artefact due to pervasive silicification resulting in microquartz cement and filling of calcareous fossils (Fig. 7C–D). Source of silica is ascribed to radiolarians recognizable as scattered moulds in limestones of the critical intervals (LCI and UCI).

Further indications of enhanced surface productivity have been provided by the Ba<sub>exc</sub> record (Fig. 5) compu-

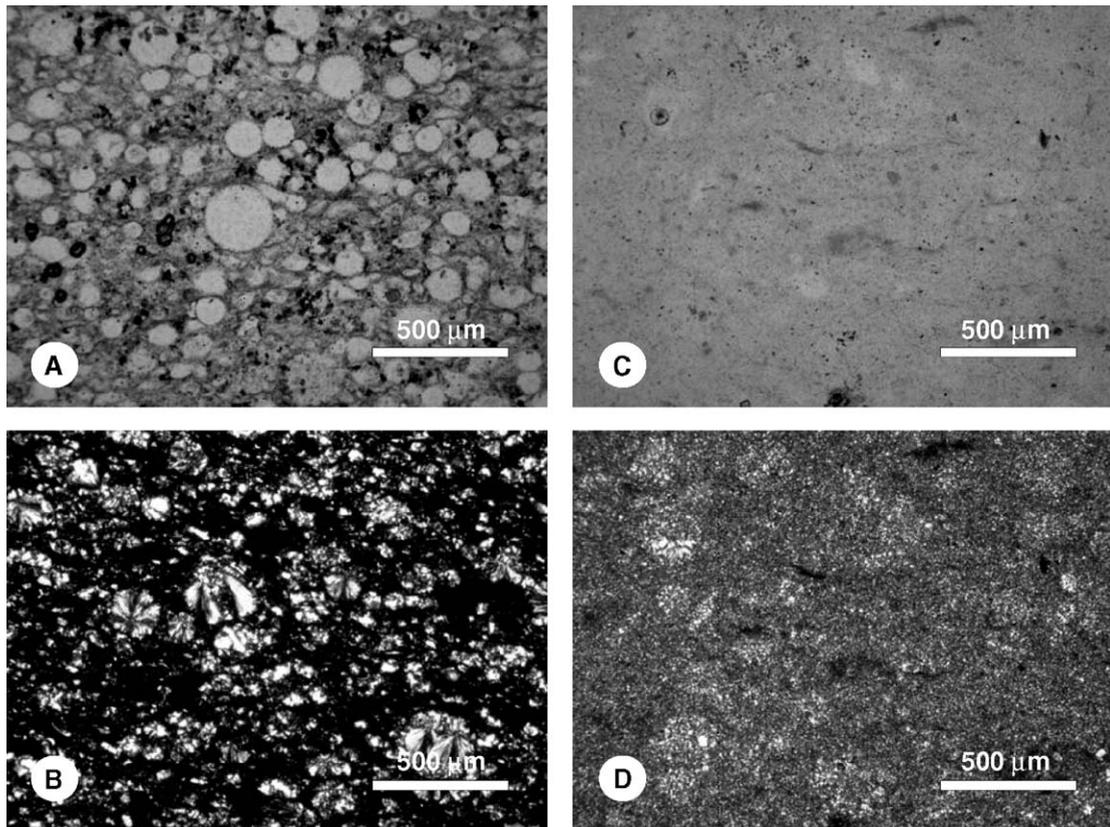


Fig. 7. A–B. Micrographs of a radiolarian-rich layer from the Bottaccione Bonarelli Level showing chalcedonic quartz replacing radiolarian fossils; A: PPL, B: XPL. C–D. Micrographs of a cherty level from the LCI (see Fig. 3) due to pervasive silicification of a limestone; C: PPL, D: XPL.

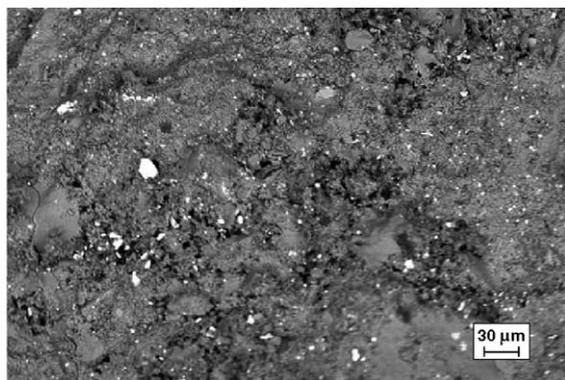


Fig. 8. Backscattered SEM image of disseminated barite (white crystals) in the Bottaccione Bonarelli Level.

ted by using the algorithm of Dymond et al. (1992) based on which  $Ba_{exc} = Ba_{sample} - [Al_{sample} \times (Ba_{shale} / Al_{shale})]$ , where  $Ba_{shale}$  and  $Al_{shale}$  are those reported by Gromet et al. (1984). Formation of biogenic barite is thought to occur as a process accompanying the decay of organic matter on its pathway through the water column once it left the biologically productive surface layer of the ocean. In this model, the sulphate of decaying proteins in organic aggregates, such as faecal pellets, and dissolved barium in sea water can combine and precipitate to form, at first, amorphous aggregates of barium sulphate within oxic microenvironments. The barium sulphate aggregates then recrystallize to barite and grow further on their sinking through the water column (Dehairs et al., 1980; Stroobants et al., 1991; Gingele and Dahmke, 1994).  $Ba_{exc}$  for the Bottaccione section shows particularly high values in the BL with a mean value of 7397 ppm against 477 and 1920 ppm in the underlying and overlying limestones, respectively. SEM observations showed the presence of barite crystals with size mostly lesser than 10  $\mu\text{m}$  (Fig. 8), which supports the interpretation of enhanced  $Ba_{exc}$  values across the BL in terms of increased surface productivity.

Preservation of barite in the Bottaccione organic-rich sediments testifies moderate rate of sulphate reduction at the water-sediment interface. To evaluate the palaeo-redox conditions at the bottom water during the early diagenesis, following McManus et al. (1998), we coupled our  $Ba_{exc}$  data with authigenic U values (computed through the algorithm of Myers and Wignall, 1987, based on which  $U_{auth} = U_{total} - (Th_{total} / 5)$  assuming that the detrital fraction contains all Th and has a Th/U ratio of 5, close to crustal values). Uranium is removed from seawater and pore waters into organic-rich sediments (Anderson et al., 1989; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991) but U reduction probably does not occur by simple inorganic reactions in

solution, because reduction of soluble U(VI) to insoluble U(IV) is not reported in sulphide-containing water columns of anoxic marine basins, despite thermodynamically favourable conditions. The limiting factors in the reduction of U(VI) to U(IV) could be linked to the requirement of particle surfaces to catalyse the inorganic reaction and/or the presence of enzymes associated with iron and sulphate reducing bacteria which are able to reduce U (Zheng et al., 2002; McManus et al., 2005).

The Bottaccione Bonarelli Level shows a  $U_{auth}$  mean value of 2.26 with a maximum reaching up to 5.27 ppm (Fig. 5).  $U_{auth}$  enrichment with respect to the average shale value (0.2 ppm; Gromet et al., 1984) testifies anoxic conditions at the water–sediment interface. However, these values are much lower than in coeval sections that do not exhibit particular enrichments of  $Ba_{exc}$  (Scopelliti et al., 2004a; see discussion below). Overall, the results obtained for the Umbrian section give indication of moderate sulphate-reduction reactions at the water–sediments interface, which allowed barite to be preserved across the Bonarelli Level interval.

#### 4.3. Time series analyses

In the last decades the Milankovitch orbital perturbations have been recognized as one of the most important periodic forcing mechanisms in driving cyclicity at ky scale of investigation. Their duration in the Cenozoic has the following variability ranges: 23–19 ky, 54–41 ky and 123–95 ky (e.g. Berger and Loutre, 1994). The duration of the orbital cycles can be normalised and tuned to the shortest periodicities (precession cycles; Table 1), and the resulting ratios used as a tool to interpret the periodicity ratios obtained in the frequency spectrum. This approach has been widely employed providing valuable results (see Fischer et al., 1991; Hinnov and Goldhammer, 1991; Claps and Masetti, 1994; Bellanca et al., 1996; Negri et al., 2003).

For the Bottaccione section, spectral analyses have been performed on Rb/Al, Si/Al, and Cr/Al data from the Bonarelli Level. We excluded the Ti/Al ratio be-

Table 1  
Time duration of the Milankovitch orbital cycles normalized and tuned to the shortest periodicities of the orbital perturbations (precession cycle)

Orbital perturbation ratios	Milankovitch orbital cycles		
	Eccentricity	Obliquity	Precession
Corresponding duration	123–95 ky	54–41 ky	23–19 ky
Ratios (relative to precession)	6.5–4.2	2.8–1.8	1

cause of the anomalous increase of this element in the middle portion of the organic-rich horizon (see above) and the V/(V+Ni) ratio because this is characterized by moderate fluctuations (see Fig. 5). The composite power spectra (Fig. 9) exhibit four statistical significant peaks at ~29.6, ~12, ~5.6 and ~4.6 cm. The obtained wavelengths are normalised to the shortest periodicity (4.6 cm) and the relative ratios (Table 2) are compared with those calculated for the classic Milankovitch periodicity with respect to the eccentricity/precession and obliquity/precession ratios (see Table 1). This comparison shows that: (i) if we consider that the 21 ky precessional cyclicity (P) is a mean between two modes at 19 (P1) and 23 ky (P2) and their ratio is 1.21, then the periodicities in our spectra, at 5.6 and 4.6 cm (ratio=1.22; Table 2), are likely related to P1 and P2; (ii) as the hierarchical pattern of the remaining peaks is very similar to that calculated for the classic Milankovitch periodicity, it is possible to associate the wavelengths at 12 and 29.6 cm with obliquity and eccentricity cyclicity, respectively.

To identify possible correspondences between the lithological or geochemical variations in the stratigraphic succession and the frequency band individuated by spectral analyses, the recognized periodicity have been extracted from the raw data of the considered proxies by band-pass filters (Priestley, 1981). Fig. 10 shows the filtered signals for Rb/Al compared with its depth profile. It is evident that the fluctuation in the geochemical signal (evidenced by the 5-point moving average) clearly corresponds to the short-term eccentricity period (~110 ky). The same figure highlights a probable linkage between the lithological alternations (black shale/radiolarian-rich layer couplets) and the precessional period (~21 ky). Periodic variations attributable to orbital parameters are also recognizable in Si/Al (with

Table 2

Wavelengths evaluated from the power spectra in Fig. 9

Spectral peak ratios	Peaks			
Wavelengths	29.6 cm	12 cm	5.6 cm	4.6 cm
Wavelengths ratios	6.4	2.6	1.22	1

Peaks are normalized to the highest periodicity.

a specular pattern) and Cr/Al depth profiles (Fig. 11). An explanation for the chemostratigraphic signals not matching the obliquity signal (Fig. 10) may be that this orbital forcing influences the organic-rich layer thickness as a consequence of the precession/obliquity interference and affects negligibly the solar radiation at low latitude (de Boer, 1991).

The cyclostratigraphic approach is very useful to estimate the organic-rich interval duration in the Bottaccione section. An accurate evaluation of the OAE2 duration may result difficult either on a biostratigraphic basis, because OAE2 is a short-term event, and on a magnetostratigraphic basis, as a consequence of its occurrence within the Cretaceous Long Normal Polarity Chron. The OAE2 duration was originally estimated based on biostratigraphic evidence and interpolation of geological time-scale data points between 0.5 and 0.8 Ma (Arthur et al., 1987) and 0.4 Ma (Caron et al., 1999). Recently, orbital cyclicity has been used to estimate the duration of the event. The relative estimates range from 720 ky in Colorado (Meyers et al., 2001), to ~400 ky (Kuhnt et al., 1997) in the Tarfaya Basin (Morocco) and to 320 ky in western Canada (Prokoph et al., 2001).

By averaging the ratios of each found wavelength with the associated orbital cyclicity in the Bottaccione Bonarelli Level (e.g. 29.6/110) we obtain a transformation of space domain (cm/cycles) in time domain (cm/ky). On this basis, we have estimated a sedimentation

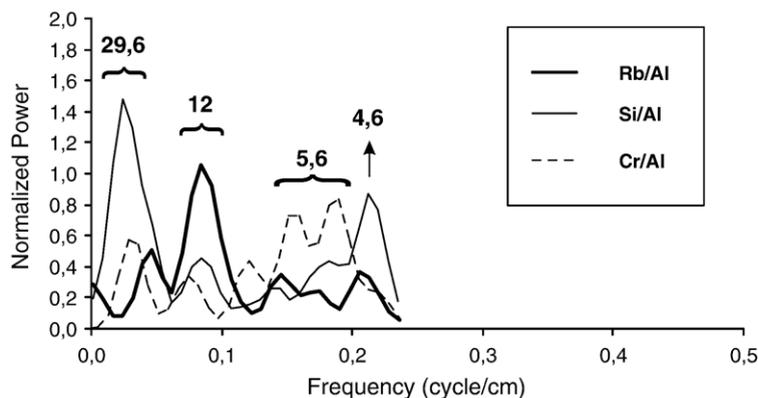


Fig. 9. Power spectra of Rb/Al, Si/Al, and Cr/Al for the Bottaccione Bonarelli Level. Spectra are normalized (Rb/Al power  $\times 10^5$ ; Cr/Al power  $\times 10^{-2}$ ) to obtain a suitable representation.

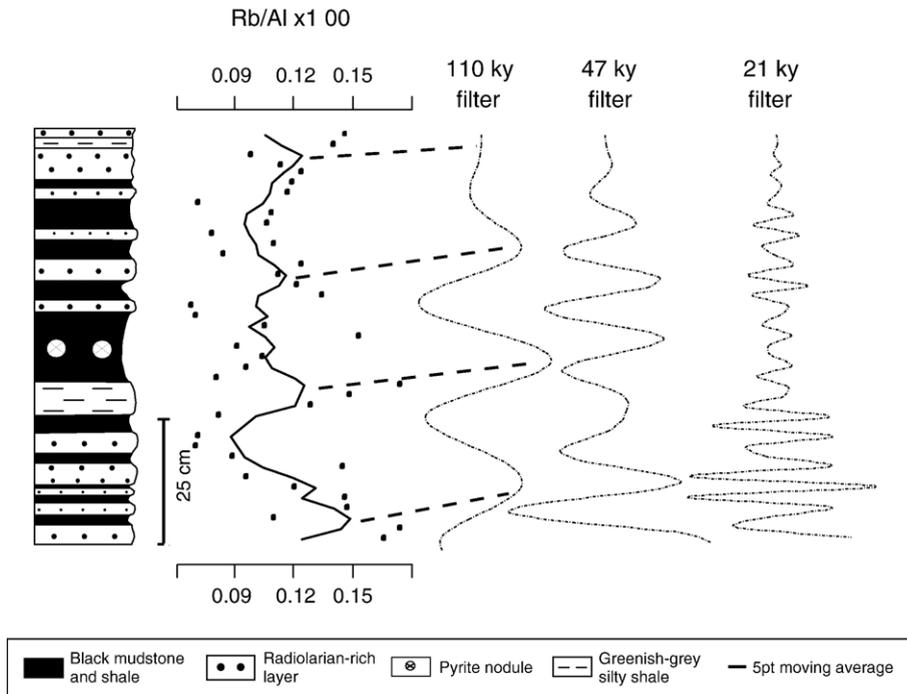


Fig. 10. Comparison between Rb/Al filtered signals and the same ratio depth profile for the Bottaccione Bonarelli Level.

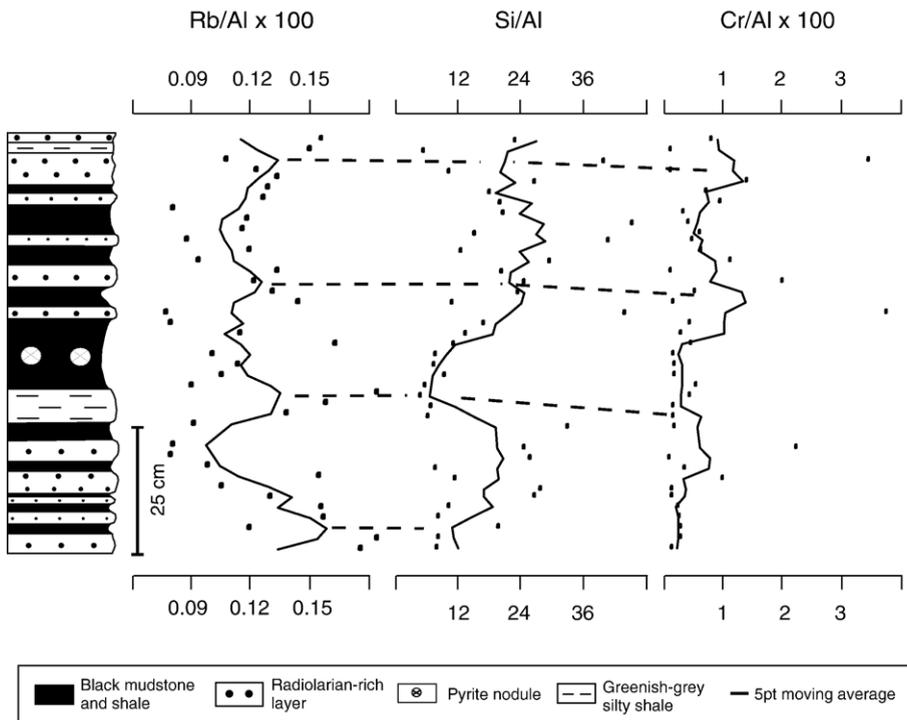


Fig. 11. Fluctuations of the 5-point moving average in the Rb/Al, Si/Al, and Cr/Al depth profiles for the Bottaccione Bonarelli Level related to variations of the orbital parameters (see text).

rate of  $\sim 0.25$  cm/ky and a duration of  $\sim 320$  ky for the anoxic event. This estimated sedimentation rate falls in the range of 1.3 to 2.6  $\text{m my}^{-1}$  recently proposed by Kuroda et al. (2005) for an analogous section in the Umbrian Apennines.

## 5. Discussion

### 5.1. Palaeoceanographic conditions during the Bonarelli Level deposition

The geochemical results obtained for the Bottaccione section provide useful information about the palaeoceanographic and palaeoenvironmental conditions in the Tethys during deposition of the Bonarelli Level and of limestones belonging to the lower and upper critical intervals (Figs. 3–8).

During the mid-Cretaceous, the atmospheric  $\text{CO}_2$  content was higher than at present and the poles were free of ice. In such a context, the anoxic event can be regarded as a pathway by which the ocean–atmosphere system returns to a pre-existing equilibrium sequestering large organic carbon amounts. As a consequence of enhanced atmospheric  $\text{CO}_2$ , the mean temperature was presumably 6–14°C higher than today (Barron, 1982; Arthur et al., 1985; Barron and Washington, 1985; Herbert and Fischer, 1986). It has been suggested that, due to equable climate, the oceans were characterized by “sluggish” water circulation (Bralower and Thierstein, 1984; de Graciansky et al., 1984). In the absence of significant ice and with an ocean basin configuration different than at present, bottom, deep, and/or intermediate water masses may have become the major bottom water source (Arthur and Natland, 1979; Brass et al., 1982; Wilde and Berry, 1982). Such warm, saline bottom water (WSBW) probably formed in the Tethys, on adjacent broad shelves or in epicontinental seas characterized by a negative water balance (evaporation > precipitation + inflow).

The WSBW production rates were modulated by low-latitude shelf areas determined by sea level (Brass et al., 1982). Rapid and pronounced sea level/shelf area changes may have conditioned the oceanic deep-water circulation and surface-water biological productivity. This is in accord with the extensive late Cenomanian–early Turonian transgression well-documented in the Western Interior Seaway of North America (e.g. Kauffman, 1977), Northwest Europe (Hancock, 1975; Cooper, 1977), and Africa (van Houten, 1980; Reyment and Mörner, 1977; Matsumoto, 1980; Einsele and Wiedmann, 1982; Petters and Ekweozor, 1982). The upwelling of WSBW, particular-

ly along the continental margins, would have increased the sea surface fertility and productivity. In the Bottaccione section, a biostratigraphic study (Coccioni and Luciani, 2004) highlighted biotic evidence for high surface productivity during the OAE2 event consisting in very low species richness, species dwarfism, near absence of deeper dwellers, and dominance of surface dweller hedbergellids. From the geochemical point of view, the high productivity event is supported by elevated Si/Al ratios, accounting for radiolarian proliferation, as well as by very high  $\text{Ba}_{\text{exc}}$  values (Fig. 5).

Additional amounts of nutrients from continent might have been contributed by an intensified hydrologic cycle due to increase of global precipitation rates consequent, in turn, to the global warming. For the BL of the Bottaccione section, this is inferred by decreased Ti/Al values and increased Rb/Al ratios. Enhanced productivity and, subordinately, high rates of riverine runoff may have induced oxygen level depletion in bottom water and an expanded OMZ (oxygen minimum zone) improving  $\text{C}_{\text{org}}$  preservation, as indicated by high  $\text{V}/(\text{V}+\text{Ni})$  and Cr/Al ratios, and elevated Sb, Cd, and Zn enrichment factors in the Bonarelli Level (Figs. 5 and 6).

### 5.2. New insights on the different geochemical response to paleoredox conditions in the Tethyan realm

In this work, we propose a comparison between the above discussed geochemical data and those previously obtained for the Bonarelli Level equivalent from the Calabianca section (NW-Sicily) by Scopelliti et al. (2004a,b). Most significant discrepancies concern geochemical indicators of the flux of biogenic material to the sediment (Table 3). Although high Si/Al ratios measured for both the Bonarelli Levels indicate enhanced surface-water productivity in the two sites of the Tethys basin, the Bottaccione section exhibits very low  $\text{CaCO}_3$  contents and markedly higher  $\text{Ba}_{\text{exc}}$  values compared to the coeval Calabianca organic-rich horizons. Values of  $\text{CaCO}_3$  near zero for the Bottaccione section are interpreted in terms of temporary rise of CCD linked to increased water acidity as a consequence of enhanced oxidation of organic matter sinking at the seafloor and probably are related to a deeper depositional setting of the Umbrian Bonarelli Level with respect to that of Sicily. Different deposition bathymetries of these sections could also explain their different Ba concentrations, because it has been demonstrated that shallow sediments receive relatively more labile Ba compared to deep traps (Dymond and Collier, 1996; Dehairs et al., 2000) where, upon settling, barite particles partly recrystallize becoming less

Table 3

Mean values and variation range of geochemical proxies for the Bottaccione Bonarelli Level (this work) and the Calabianca Bonarelli Level equivalent (data from Scopelliti et al., 2004a,b)

	Bottaccione Bonarelli Level			Calabianca Bonarelli Level equivalent		
	Mean	Min	Max	Mean	Min	Max
Rb/Al × 100 (a)	0.11	0.06	0.17	0.13	0.02	0.21
Ti/Al × 100 (a)	4.47	2.86	7.33	5.21	3.96	7.45
V/(V+Ni) (a)	0.80	0.40	0.96	0.80	0.43	0.95
Cr (ppm) (a)	134	11	413	171	26	419
CaCO <sub>3</sub> (%) (a)	1.39	0.33	4.18	18.68	0.49	81.96
Si/Al (a)	17.29	4.80	43.46	29.31	2.92	181.65
Ba <sub>exc</sub> (ppm) (a)	7397	2251	27,984	185	0	537
U <sub>auth</sub> (ppm) (b)	2.26	0.14	5.27	12.26	0.72	34.12
Zn EF (b)	6.62	1.76	12.95	20.40	3.87	90.50
Cd EF (b)	12.02	0.61	29.60	23.37	1.27	63.29
Sb EF (b)	10.63	1.41	28.20	19.29	3.20	69.23
Pb EF (b)	1.45	0.41	3.33	1.45	0.71	2.32
Mo EF (b)	0.94	0.05	4.45	0.94	0.20	4.53
TOC (c)	6.08	0.21	17.64	14.41	1.42	26.31
HI (c)	227	75	416	409	233	569

(a)=All samples (Bottaccione: 41, Calabianca: 58).

(b)=Selected samples (Bottaccione: 7, Calabianca: 16).

(c)=Selected samples (Bottaccione: 22, Calabianca: 23).

soluble (McManus et al., 1998). Further information is provided by coupling Ba<sub>exc</sub> and U<sub>auth</sub> values (Fig. 12), which allows us to evaluate the use of barium as palaeoproductivity marker in conditions of elevated fluxes of organic matter and high rates of sulphate reduction (Prakash Babu et al., 2002). Because reduction of uranium and its uptake into sediments seem to be initiated by microbially mediated sulphate reduction (Klinkhammer and Palmer, 1991), we would expect that, in places having high authigenic U concentrations, barite preservation should be compromised and barium could be mobilized. Following this hypothesis, Ba<sub>exc</sub> values for the Bottaccione section much higher than those of the BL equivalent from Calabianca and U<sub>auth</sub> mean value more than five times lower than in the Sicilian section (Fig. 12) give indication that the two basins experienced at different extents sulphate reduction reactions occurring at the expenses of organic matter during the organic-rich sediments deposition and/or early diagenesis.

Stronger H<sub>2</sub>S activity at the seafloor during the deposition of the Bonarelli Level equivalent at Calabianca is also testified by Zn, Cd, and Sb enrichment factors that are from two to three times higher than in the Bottaccione organic-rich sediments (Table 3). In accordance with the above considerations, these elements reveal particular affinity with hydrogen sulphide being incorporated in pyrite and/or forming own sulphides. Different extents of euxinic conditions can be explained considering that bacterial sulphate

reduction and subsequent fixation of H<sub>2</sub>S-sulphur in sediments can be theoretically limited by (1) deficiency of dissolved sulphate, (2) low concentrations of dissolved metals, or (3) scarcity of degradable organic carbon which is required by sulphur-reducing bacteria as an energy source for their metabolism (e.g. Cook and Kelly, 1992). We suppose that the abundance and type (degradable or refractory) of organic matter are limiting factors in determining the onset of euxinic conditions at seafloor. As to the abundance, the Calabianca section shows (Table 3) more elevated paleoproductivity indicators (i.e. mean Si/Al ratio of 29.31 against 17.29 in the Bottaccione section) and TOC percentages (mean value of 14.41 against 6.08% in the Umbrian section). Information about the type of organic matter can be derived from HI values in the two sections. Generally, the hydrogen index tends to decrease from shallow to mid-deep-water marine environment (Tissot and Welte, 1984; Littke and Sachsenhofer, 1994) because a number of biological, chemical and physical processes alter the organic matter as it is transported through the water column (Wakeham and Lee, 1993). Thus, lower HI values of the Bottaccione section could be consistent with a deeper depositional setting accounting for a decreased reactivity of organic matter. A lesser supply of organic matter, which was becoming more refractory during its deposition in the deeper Umbrian basin, may be responsible for limited sulphate reduction reactions with respect to those in the Sicilian basin.

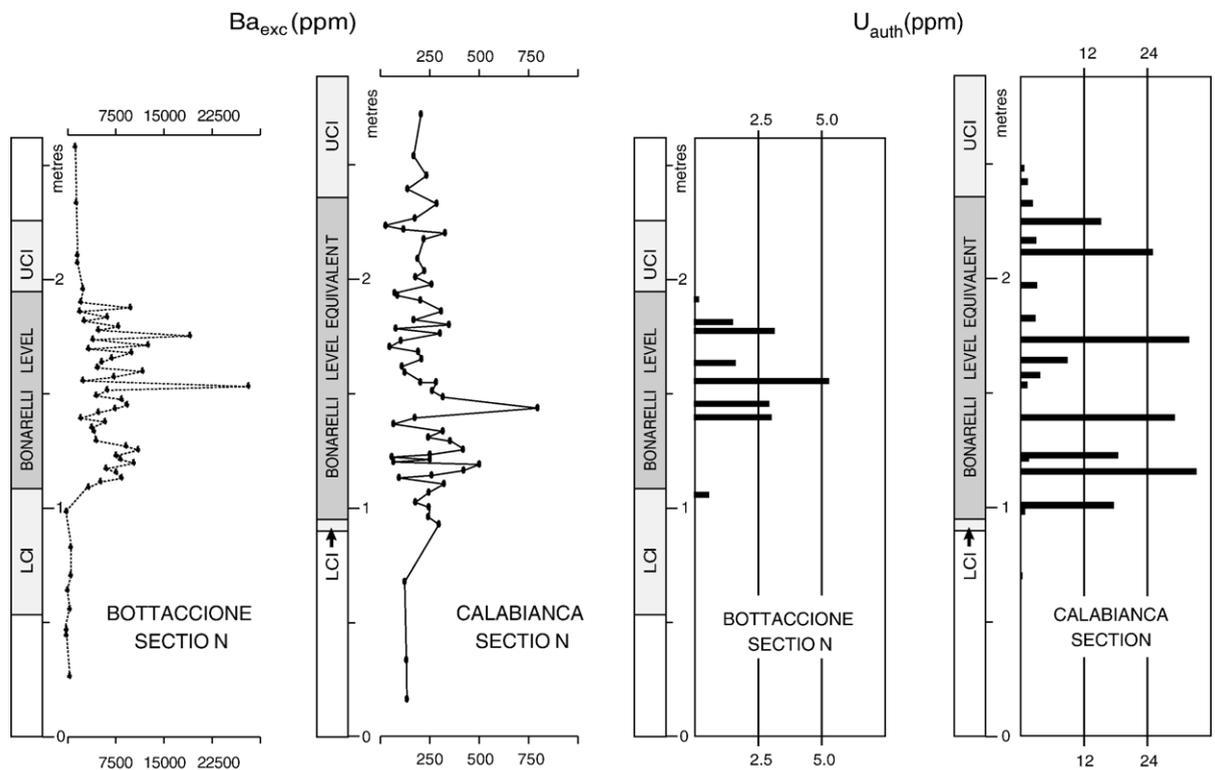
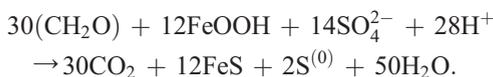


Fig. 12. Comparison of  $Ba_{exc}$  and  $U_{auth}$  values throughout the Bottaccione (this work) and Calabianca (data from Scopelliti et al., 2004b) sections. LCI and UCI as in Fig. 3. Note the different scale for the same proxies in the two sections.

All previous considerations can be also used to justify the anomalously high carbonate content in the Bonarelli Level equivalent of Calabianca (see Table 3). According to Fauville et al. (2004), during bacterial sulphate reduction, sulphate is used as terminal electron acceptor in the oxidation of organic carbon (or hydrogen). The produced hydrogen sulphide can react with reduced forms of metals, such as iron (Fe II), to form sulphide minerals following the generalized reaction:



The reduction of sulphate and iron (III) (or other metals) by carbohydrates and subsequent formation of sedimentary pyrite (or other sulphide minerals) result in the generation of alkalinity (e.g. Cook et al., 1986; Schindler, 1986; Anderson and Schiff, 1987) and, potentially, in an effective neutralization of the water column. Therefore, the anomalous presence of carbonate registered in the Sicilian Bonarelli Level equivalent may be related to particularly intense sulphate reduction resulting in increased pH values.

### 5.3. Influence of orbital-climatic forcing on the oceanic environment

A cyclostratigraphic approach and smoothing of the raw data in the Bottaccione Bonarelli Level allow us to recognize a marked influence of orbital-climatic forcing on the oceanic environment during the organic-rich level deposition. We used the produced fluctuations in the geochemical proxies to correlate black shale horizons from different marine settings (Fig. 13).

The maxima of the Rb/Al oscillations, steered by eccentricity forcing, have been used to define the boundaries of stratigraphic intervals inside the Bonarelli Level (Fig. 13). In accordance with what observed in the Calabianca section (Scopelliti et al., 2004b), changes in concentrations of detrital-flux indicative elements are thought to reflect periodically increased riverine influxes triggered by enhanced humidity and resulting in a sluggish circulation mode and consequent reduced bottom-water ventilation that, in turn, promoted a higher preservation rate of organic matter. This scenario accounts for the concurrence of highs in the Rb/Al, Cr/Al and V/(V+Ni) curves in correspondence

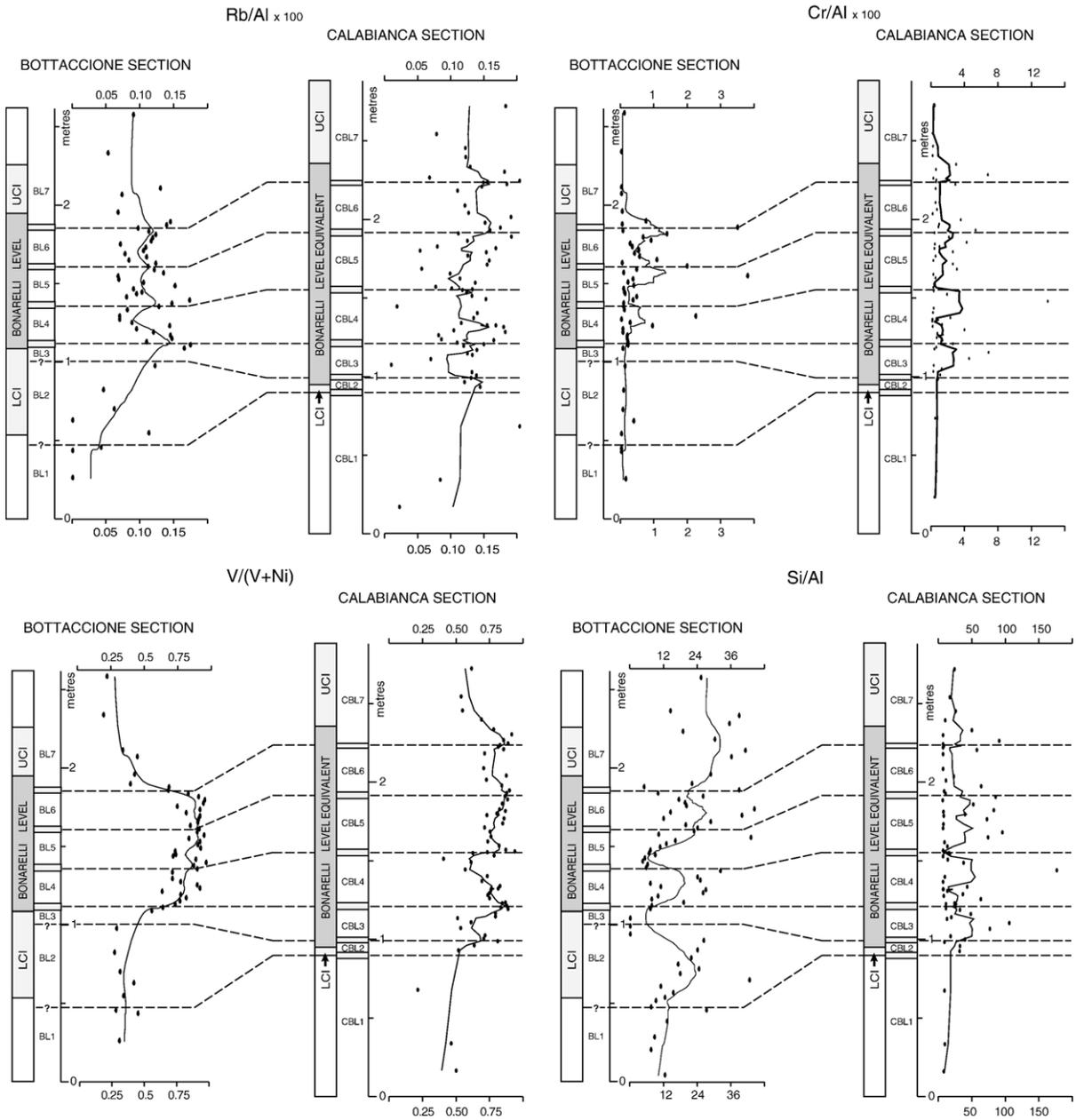


Fig. 13. High-resolution stratigraphic correlation between main geochemical proxy records of the Bottaccione (this work) and Calabianca (data from Scopelliti et al., 2004b) sections. Correlation lines connect stratigraphic intervals individuated by elemental geochemistry (see text). LCI and UCI as in Fig. 3.

of the interval boundaries defined for the two sections (Fig. 13). Conversely, periodic reductions of humidity caused a renewal of circulation with overturn of stratified water masses resulting in a recycling of nutrients from deeper waters that could have been more marked in coincidence with enhanced siliceous biogenic production, as testified by higher Si/Al inside the same intervals (Fig. 13). Contemporaneously, an increase in the supply of oxygen to deep waters induced more of

the sinking organic matter to be oxidized, which can be reasonably inferred by associated lower Cr/Al and V/(V+Ni) ratios.

A discrepancy between two sections is the number of complete intervals constituting the Bonarelli Level. In the Calabianca section, Scopelliti et al. (2004b) have recognized four intervals (coded as CBL3 to CBL6), while in the Bottaccione section the interval at the base of the organic-rich level appears to be incomplete. It is

possible that, in the last section, this first interval (coded as BL3) covers part of the Lower Critical Interval characterized by wider thickness than in the Calabianca section. We suppose that in the deeper Umbrian setting the onset of anoxia was shifted in time; thus, the preservation of organic matter might have begun later than in the Sicilian section, deterioration of the seafloor environmental conditions being expressed by the persistence of LCI.

## 6. Conclusions

Major element and trace metal distributions from the Bottaccione section are consistent with the Bonarelli Level being expression of an enhanced productivity event and high rates of riverine runoff inducing anoxic/euxinic conditions in bottom water and consequently a high  $C_{org}$  preservation rate.

The geochemical comparison proposed between the data obtained from this study and those relative to a Bonarelli Level equivalent from the southern Tethys (Calabianca section) allowed us to evaluate differences in palaeoceanographic conditions of the Tethyan realm at the time of  $C_{org}$ -rich sediments deposition. Increase in the surface productivity less important in central Tethys than in southern Tethys might be explained by that the latter was interested by a more efficient coastal upwelling affecting the African margin. A deeper bathymetric depositional setting of the Umbrian section was also responsible for relatively moderate sulphate reduction reactions occurring at the expenses of organic matter.

Consistent variations inside the trends of principal geochemical proxies from the two sections give indication about periodic fluctuations in the palaeoceanographic conditions during the  $C_{org}$ -rich sediment deposition and reveal within the Bonarelli Event a strong orbital-climatic forcing.

The recognition of four main intervals in  $C_{org}$ -rich sediments from both sections addresses towards a new pathway to assess correlations for spatial comparisons among coeval sections, overall in the compulsory absence of the carbonate  $\delta^{13}C$  record.

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