

STRATIGRAPHY AND GEOCHEMICAL ANOMALIES OF THE EARLY TOARCIAN OXYGEN-POOR INTERVAL IN THE UMBRIA-MARCHE APENNINES (ITALY)

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ABSTRACT - A multidisciplinary approach is used to demonstrate the occurrence of oxygen-poor sediments in the Tenuicostatum Zone (Early Toarcian) within the clayey-marly pelagic sediments of Marne del Monte Serrone Formation (Umbria-Marche basin). This approach involves examination of some geochemical anomalies (trace elements), measurement of Total Organic Carbon and observation of benthic foraminifera and trace fossils. A distinction between "**black shale facies**" (BSF1) and "**black shale-like sediments**" (BSF2) allows better identification of the variable anoxic conditions present within the same basin. A high degree of organic matter preservation and major anoxia extensions occur in the middle-upper part of the Tenuicostatum Zone (Early Toarcian) probably related to maximum flooding - high stand of the global Early Toarcian sea-level rise. Several subenvironments showing pelagic conditions and high primary productivity of planktonic organisms (mainly radiolarians and calcareous nannofossils), have been defined on the basis of organic matter content and positive geochemical anomalies. The diversified physiography of the Umbria-Marche basin, related to synsedimentary tectonic activity and circulation patterns, probably determined different intensities of ventilation conditions on the sea-floor.

KEYWORDS : OXYGEN-POOR SEDIMENTS, STRATIGRAPHY, GEOCHEMICAL ANOMALIES, UMBRIA-MARCHE BASIN, EARLY TOARCIAN.

RÉSUMÉ - Une étude pluridisciplinaire est utilisée pour démontrer la présence de sédiments pauvres en oxygène dans la Zone à Tenuicostatum (Toarcien inférieur) inclus dans des sédiments argilo-marneux de la Formation des Marnes del Monte Serrone (Bassin de Umbria-Marche). Cette étude implique l'examen de certaines anomalies géochimiques (éléments traces), la mesure du Carbone Organique Total et l'observation de foraminifères et de traces fossiles. La distinction entre "**facies des black shales**" (BSF1) et "**sédiments semblables à des black shales**" (BSF2) permet une meilleure identification des conditions anoxiques variables dans le même bassin. Dans la partie moyenne et supérieure de la Zone à Tenuicostatum (Toarcien inférieur) il y a une importante préservation de la matière organique et des extensions anoxiques, probablement en relation avec la montée la plus forte du niveau de la mer durant le Toarcien inférieur. Nous avons identifié, à partir de la teneur en matière organique et des anomalies géochimiques, plusieurs environnements pélagiques avec une grande productivité d'organismes planctoniques (principalement radiolaires et nannofossiles calcaires). La physiographie diversifiée du bassin de Umbria-Marche, mise en relation avec des processus d'activité tectonique synsédimentaire et avec les modèles de circulation, a probablement déterminé des intensités différentes des conditions de ventilation sur le fond océanique.

MOTS-CLÉS : SÉDIMENT PAUVRES EN OXYGÈNE, STRATIGRAPHIE, ANOMALIES GÉOCHIMIQUES, BASSIN UMBRIA-MARCHE, TOARCIEN INFÉRIEUR.

INTRODUCTION AND PREVIOUS STUDIES

Early Jurassic marly-clayey sediments were deposited in the Umbria-Marche basin (UMB, Central Italy) with variable thickness (from several decimeters to 60 m) depending on the palaeomorphology of

the basin area inherited from the break-up and flooding of the Early Jurassic carbonate platform (Channell *et al.* 1979 ; Colacicchi *et al.* 1988). Late Domerian/Middle Toarcian sedimentation is represented by the marly and marly-clayey "Marne del Monte Serrone" (MS) Formation (Pialli 1969a ; Pialli 1969b). This formation is interposed between

a calcareous unit (Corniola = COR) and a reddish nodular calcareous marly one (Rosso Ammonitico Umbro-Marchigiano = RAUM) (Colacicchi *et al.* 1988 ; Cresta *et al.* 1988). Organic-rich black shale intervals formed during the Early Toarcian in the MS formation. Jenkyns & Clayton (1986) and Jenkyns (1988) found this organic-rich interval in the Umbria-Marche area (Valdorbia section) and in other parts of the Mediterranean Tethys. These authors defined the interval as the "Oceanic Anoxic Event " (OAE) dating it as Early Toarcian (early Falciferum or Serpentinus Zones). Baudin *et al.* (1990a, 1990b) studied the OAE in the Mediterranean area including northern and central Italy. These authors suggested that the OAE is located between the Tenuicostatum/Falciferum Zones in northern Italy (Lombardia and Belluno area, see also Claps *et al.* 1995), and in the upper part of the Tenuicostatum Zone in central Italy (Valdorbia section). Bassoulet & Baudin (1994) believe that the Toarcian anoxic event was caused in the Tethys by several periods of biological crises that could span from the Domerian/ Toarcian boundary to the top of the Serpentinus Zone. According to these authors, the preservation of organic matter can be explained by the concurrence of several factors, depending on the palaeogeography: variation of sea-level, organic productivity, anoxia of the water, tectonization of margins and degree of clay sedimentation.

Recently, other authors have investigated black shale facies in several areas of the Umbria-Marche basin using calcareous nannofossils, ammonite biostratigraphy, palynology and organic-matter geochemistry (Bucefalo-Palliani & Cirilli 1993 ; Cresta *et al.* 1989 ; Mattioli 1993 ; Nocchi 1992 ; Reale *et al.* 1991 ; Bartolini *et al.* 1992).

Oxygen-poor deposits often occur during deposition of the MS formation (see also Nini *et al.* 1995), although the black shale facies were not found in all the examined portions of the UMB, as proposed by Bartolini *et al.* (1992).

Furthermore, during a preliminary study on clay minerals from Late Domerian to Early Aalenian, positive geochemical anomalies were detected in black shale episodes during the Early Toarcian (Tenuicostatum Zone) (Ortega-Huertas *et al.* 1993 ; Monaco *et al.* 1994).

The aim of this paper consists in determining and constraining relationships among some trace elements geochemical anomalies, Total Organic Carbon (TOC), benthic foraminifera, trace fossils and sediment types, during MS deposition.

Data presented in this paper intend to contribute to the understanding of factors causing deposition of oxygen-poor sediments and organic-rich ones in the Umbria-Marche area.

LITHOLOGY OF THE STUDIED SECTIONS

Many Jurassic stratigraphic sections have been drilled in the central part of the Umbria-Marche Apennines, but only five have been examined to study their geochemistry (Fig. 1). These sections consist of various lithologies represented mainly by limestones, marly-limestone, shales and clay deposits that are sometimes bioturbated, vary widely in thickness (Fig. 2, 6) and correspond to a differentiated palaeodepositional setting in Jurassic time: "condensed", "intermediate" and "extended" successions (Colacicchi *et al.* 1988 ; Cresta *et al.* 1989 ; Monaco 1992).

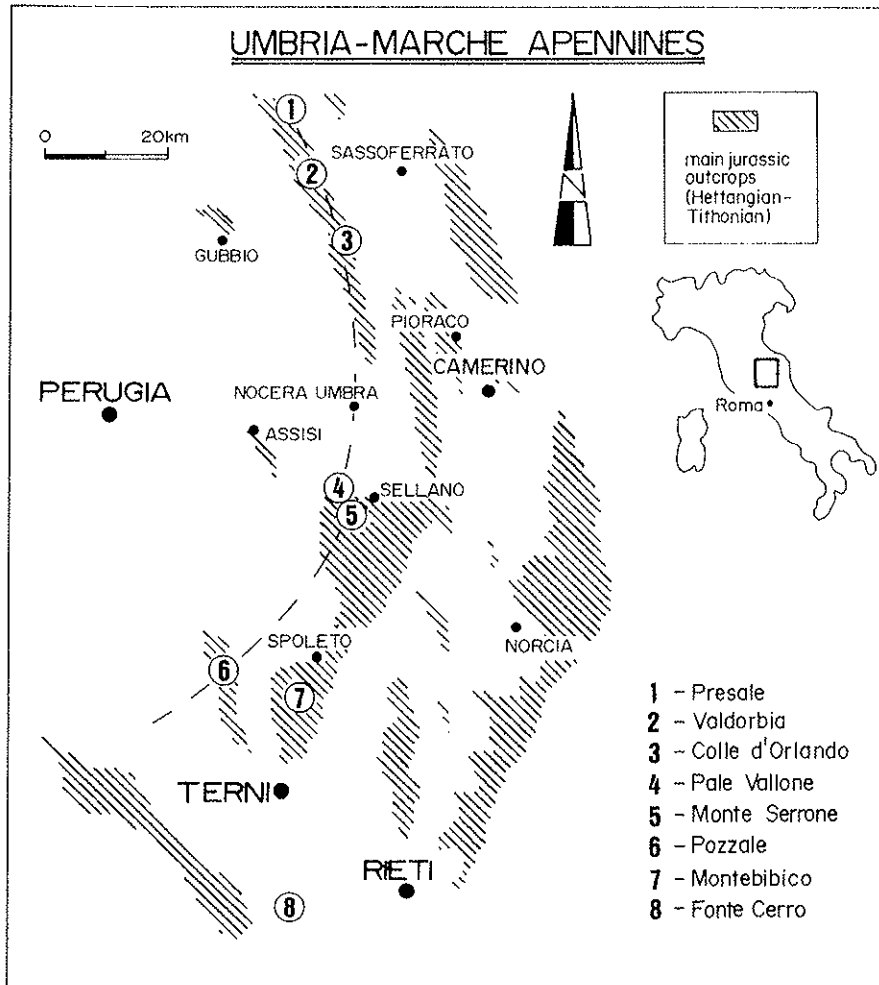
This paper considers the Early Toarcian portions of the Valdorbia (VD), Colle d'Orlando (CO), Pale Valdorbia (PLV), Monte Serrone (MS) and Pozzale (PO) sections. The stratigraphic intervals concerned in the study belong to the Tenuicostatum and Serpentinus Zones ; age is determined by ammonites and calcareous nannofossils (Baldanin *et al.* 1992a ; Mattioli 1992a ; Cresta *et al.* 1989 ; Reale *et al.* 1991 ; Benedetti *et al.* in press).

The lower boundary of the Tenuicostatum Zone has been identified with *Dactyloceras* FO (first occurrence) and *Calyculus* FO, while the upper boundary is marked by *Hildaites* FO indicating the base of the Serpentinus Zone. This last event occurs slightly above the *Discorhabdus ignotus* FO (Baldanin *et al.* 1992a). The FO of *Lotharingius crucialis* represents an important event for oxygenation and falls approximately in the middle part of the Tenuicostatum Zone. On the basis of macroscopic and microscopic observations, two groups of facies have been recognized: a) oxygenized deposits (BSF1 and OF2) ; b) poorly-oxygenized deposits (BSF2).

OXYGENIZED DEPOSITS

Facies 1 (OF1) is made up of white mudstones and wackestones, generally well stratified and moderately bioturbated with cherty lenses (COR unit) and highly bioturbated mudstones to wackestones of reddish colour (RAUM unit). The abundant macrofauna of this last unit contains ammonites, echinoderm remains, and thin-shelled bivalves. Foraminifera associations belong to assemblage units BC, F, G and H recording the occurrence of oxygen on the sea-floor (Nocchi 1992). Assemblage BC is characterized by the occurrence of both *Glomospira-Glomospirella* and high structured large *Lagenina* with a Pliensbachian affinity. In the F assemblage the characteristic benthic foraminifers of BC assemblage are disappearing while *Eoguttulina* and *Prodentalina* (medium

FIGURE 1 - Geological map and location of the studied sections. Geochemical anomalies were only analyzed in sections 2, 3, 4, 5 and 6. A discontinuous line links the selected sequences showed in Figure 7. Carte géologique et localisation des coupes étudiées. Les anomalies géochimiques ont été analysées dans les coupes 2, 3, 4, 5, et 6 seulement. La ligne en tirets réunit les coupes sélectionnées en Figure 7.



size) prevail. G and H assemblages are characterized by the abundance of large *Vaginulinidae* and by the occurrence of small gastropods, brachiopods, ammonite nuclei and bivalve lumachellas. Bioturbation is abundant and pervasive (both horizontal and vertical trace fossils are noted) throughout RAUM, displaying a diversified trace fossil association: *Chondrites*, *Planolites*, *Zoophycos*, *Thalassinoides*, *Ophiomorpha*, *Skolithos*, *Paleophycus*, *Helminthopsis* and *Trypanites* (Monaco 1995; Monaco *et al.* 1994). Penetration depths, burrow diameters, trace fossils density and species diversity emphasize well oxygenated conditions both on the sea-bottom and in the sediment column (Monaco 1995; Monaco *et al.* 1994).

Facies 2 (OF2) is characterized by wackestones, mudstones and packstones varying in colour from violet to reddish and from green to light grey. These sediments are generally not laminated and show scattered nodules. The scarce macrofaunal content

consists of thin-shelled bivalves and few ammonites; the foraminifera belong to the assemblage unit D (characterized by small and tiny *Eoguttulina* and *Prodentalina*) which is indicative of moderate oxygenation on the sea-floor (Nocchi 1992). Trace fossils are scattered and not pervasive: *Chondrites* and *Planolites* are prevalent, while *Zoophycos* rare (see assemblages of Savrda & Bottjer 1989).

In the sediments of OF1 and OF2 the Total Organic Carbon (TOC) is very low (0 to 0.05 %) (Figs. 2-6). Pyrite is absent or scattered; moreover, geochemical anomalies are lacking indicating the absence of organic matter deposition.

POORLY-OXYGENIZED DEPOSITS

Oxygen-poor sediments can be characterized by positive geochemical anomalies, by colour, by the presence of laminated sediments, as regards underlying and overlying sediments (lower MS form

tion). Oxygen-poor deposits can basically be subdivided into two different groups characterized as follows: III) "black shale facies" (BSF1) already well known in the literature, and IV) "black shale-like sediments" (BSF2). The TOC values generally range from 0.5 to 2.7% in both facies and maximum values are recorded in BSF1.

BSF1 consists of dark gray to black very fine (mm) laminated shales, containing pyrite crystals, sulphate-rich horizons (mainly secondary gypsum microcrystals probably due to pyrite alteration), carbon fragments and bituminous sapropels with fish remains. Macrofaunal content is absent or very rare (thin-shelled bivalves and rare ammonites in the Colle d'Orlando and Pozzale sections). Trace fossils are rare and poorly diversified. Only sporadic *Chondrites* are present at Valdorbis, Colle d'Orlando and Pozzale sections. Microfauna is characterized by the dominance of *Paralingulina* gr. *tenera* (Bartolini *et al.* 1992), which is an oligotypical and r-selected form. This taxon flourishes in organic-rich sediments since the greatest abundance coincides with the highest TOC values. The occurrence of *Paralingulina* gr. *tenera* indicates dysaerobic to anaerobic conditions with low availability of CaCO_3 ; such conditions are still bearable by benthic assemblages. *P. tenera* is associated to small (<500 μm) pyritized bivalve prodissoconchs, juvenile or dwarf gastropods, ornated ostracods and tiny, transparent echinoderm spines. In this facies (dysaerobic to anaerobic conditions with low availability of CaCO_3) other Lagenina, such as tiny *Eoguttulina* (*E. metensis*) and *Prodentalina* (*P. gracilis*) can be found, but often *P. gr. tenera* is almost the only surviving foraminifer species. In fact, when TOC values are highest the other foraminifers are very rare (few tiny *Eoguttulina*, e.g. sample CO 204.20 with TOC=2.69). The microfauna is attributable to the E assemblage unit, characterized by the abundance of *Paralingulina* gr. *tenera* (Nocchi 1992).

BSF2 consists of grey, green to dark-brown, yellowish or ochre mm- to cm-laminated, locally stratified silty levels. Pyrite always occurs abundantly. Ammonites are rare, trace fossils are scarce, very small and represented by *Chondrites* 0.3-0.5 mm in diameter; very rare *Planolites* 3-6 mm in diameter are present only at the BSF2/OF2 transition. When benthic microfauna is poor, pyrite is not always present and geochemical data show fluctuation in the anomalies, sediments are interpreted as transitional between BSF2 and OF2 facies. The microfauna is characterized by the occurrence of *Paralingulina* gr. *tenera*, but this form is not dominant, being associated to *Prodentalina*, *Eoguttulina*, *Astacolus* and *Lenticulina* representing the transition between assemblage unit D and assemblage unit E (Nocchi 1992). Other invertebrate remains are rare and there are no pyritized organisms.

DESCRIPTION OF THE OXYGEN-POOR INTERVAL IN THE STUDIED SECTIONS

LITHOLOGICAL CHARACTERISTICS

Figures 2 to 6 represent the five studied sections. Pyrite abundance, trace fossil content, TOC values, positive geochemical anomalies and *Paralingulina tenera* occurrences are all plotted together with lithological characteristics. Diagrams allow a comparison between the most significant parameters and vertical trends, representative of oxygen-poor conditions.

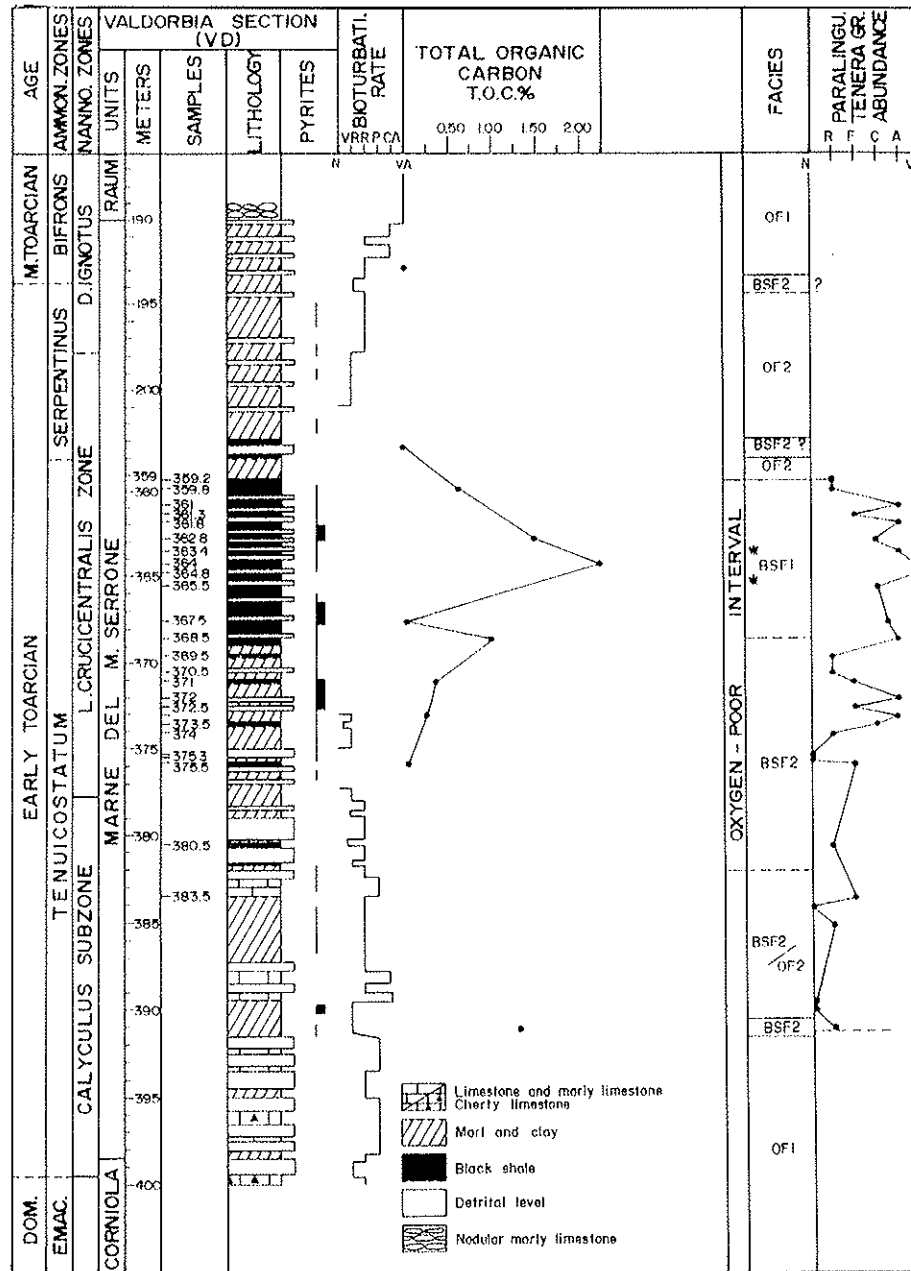
Valdorbis. The oxygen-poor interval in the Valdorbis section is about 23 m thick. BSF1 and BSF2 are easily recognizable in the field (Fig. 2). The former occurs throughout all the Tenuicostatum Zone, except for the base, while the latter represents the only poorly-oxygenated facies in the upper part of the Tenuicostatum Zone. Moreover, there are small intervals of BSF2 although uncertain and absent at the base of the Serpentinus Zone and intercalated with oxygenated facies (Fig. 2).

During the Early Toarcian low-density, fine-grained (muddy to silty) calcareous turbidites show a fining-upward trend are interbedded with oxygen-poor sediments. These calciturbidites are associated with gravity-flow deposits at the Dome of the Toarcian transition (Monaco 1992; Monaco 1994).

Colle d'Orlando. In the Colle d'Orlando section (Benedetti *et al.* in press) the oxygen-poor interval is 16 m thick, but the lower part does not outcrop and no data are available below sample CO-20 (Fig. 3). From samples CO-200 to CO-204 the oxygen-poor interval shows a rhythmic alternation of couplets of mm-laminated BSF1 sediments 1-2 cm thick and brownish-yellowish BSF2 silty-sapropelic deposits of the same thickness (Fig. 3). This rhythmic alternation begins above the *L. crucicera* zone (FO) and corresponds to the middle part of the Tenuicostatum Zone. On the other hand, the lower part of the Tenuicostatum Zone is represented by BSF1. Intercalated within poorly-oxygenated deposits are 20-40 cm thick calcarenitic beds consisting of planar-bedded, densely packed echinoid and peloidal fine-grained packstones, or siltstone-based hummocky cross-stratified (HCS) calcarenites. A short BSF2? interval occurs at the top of the Tenuicostatum Zone where oxygenated sediments are present.

Pale Vallone. This section is a condensed succession and the MS Formation is very thin (1 m thick). The oxygen-poor interval is 0.90 m thick (Fig. 4). The lower part of the Pale Vallone section is

FIGURE 2 - Valdorbria stratigraphic section (VD). Abbreviations : N = none ; VR = very-rare ; R = rare ; F = few ; P = present ; C = common ; A = abundant ; VA = very abundant. Asterisks indicate levels with maximum anoxic conditions. Pyrites : thinline = present ; thickline = abundant. *Coupe stratigraphique de Valdorbria (VD)*. N = nul ; VR = très rare ; R = rare ; F = quelques spécimens ; P = présents ; C = communs ; A = abondants. VA = très abondant. Les astérisques indiquent les niveaux avec le maximum de conditions anoxiques. Pyrite : ligne mince = présente ; ligne épaisse abondante.

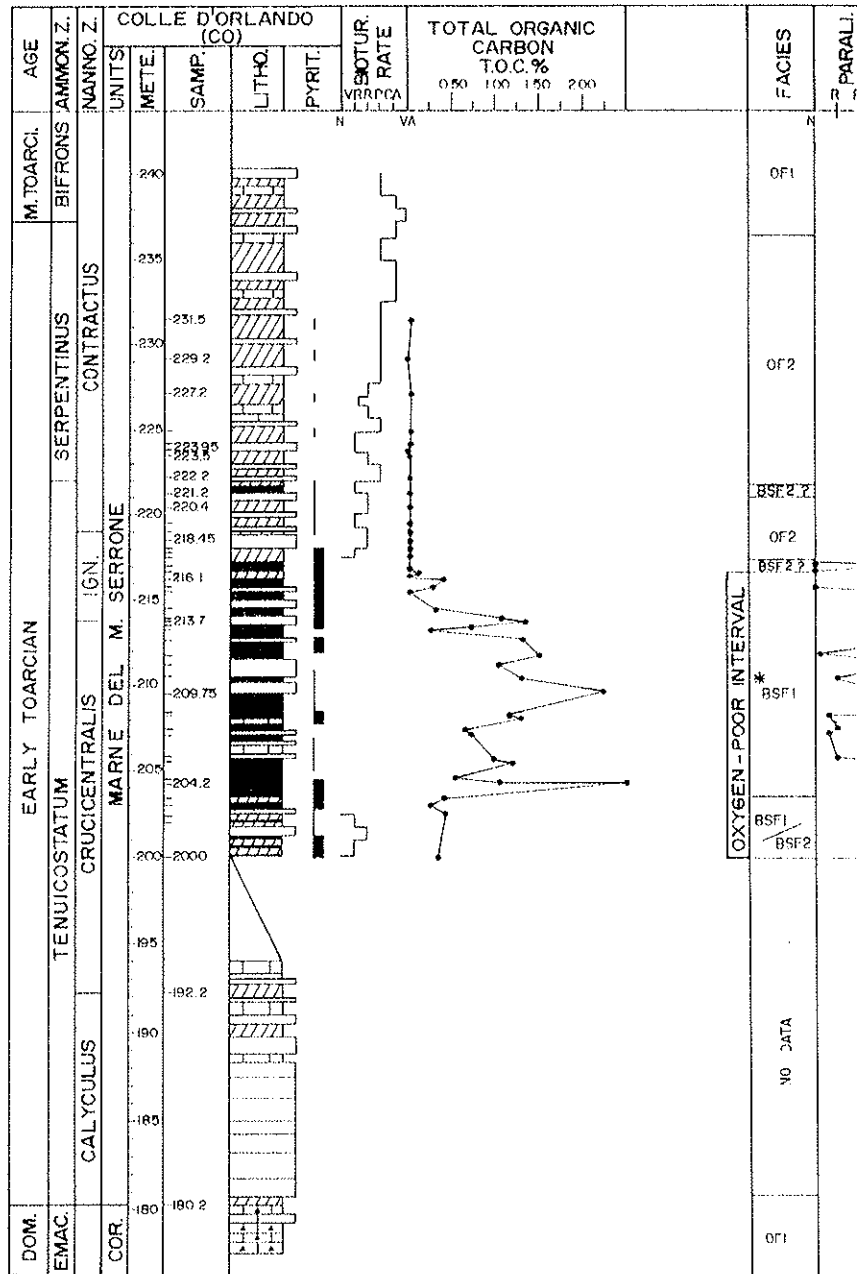


up of limestones of COR unit spanning the lower part of the Tenuicostatum Zone (Bartolini *et al.* in press). Clay levels appear suddenly within MS formation (middle-upper part of the Tenuicostatum Zone, immediately below the *L. crucicentralis* FO) and are represented by BSF2-type sediment 0.70 m thick. However, BSF1-type sediment is 0.20 m thick. The transition from BSF1 and BSF2 falls around the *L. crucicentralis* FO.

Monte Serrone. Previous authors dealing with black shale deposits in the Umbria-Marche basin did not mention the occurrence of oxygen-poor depo-

sits in the Monte Serrone section (Baudin *et al.* 1990b ; Bartolini *et al.* 1992). The Early Toarcian part of this succession is 50 m thick with a high rate of clay sedimentation. Further research has indicated the predominance of oxygenized sediments within the Tenuicostatum Zone (OF2-type), but also rare and thin (2-3 cm) intercalations of BSF2-type sediments ; only one horizon showing BSF1-type lenses (5-10 cm thick) was observed in the middle upper part of the Tenuicostatum Zone, above the *L. crucicentralis* FO. The oxygen-poor interval has not been plotted in Figure 5 because the poorly-oxy-

FIGURE 3 - Colle d'Orlando stratigraphic section (CO). Asterisk indicates level with maximum anoxic conditions. Lithology and abbreviations as Figure 2. *Coupe stratigraphique de Colle d'Orlando (CO). Lithologie et abréviations les mêmes que pour la Figure 2. L'astérisque indique le niveau de conditions anoxiques.*



nized facies are rare, discontinuous and mixed with reworked Domerian/Toarcian microfauna (BC foraminifer assemblages).

Pozzale. The oxygen-poor interval in the Pozzale section is 5.5 m thick (Fig. 6) and belongs to the middle-upper part of *Tenuicostatum* Zone. In the lower part of the MS formation, a 10 cm thick level with BSF2 characteristics occurs within oxygenized sediments (OF2). A thin-shelled bivalve-bearing bed (30 cm thick), overlying 1.70 m of bioturbated, polychrome marls, occurs immediately below the

poorly-oxygenized interval. BSF2 prevails lower part of the oxygen-poor interval, above *crucicentralis* FO (Mattioli 1993) and occurs between 7.45 and 8.50 m. BSF1 prevails between 7.45 and 8.50 m. From 8.50 m upwards sediments become oxygenized, progressively bioturbated and the reddish colour becomes more defined (OF1 of this unit).

GEOCHEMICAL DATA

X-ray fluorescence, neutron activation, induced gamma-ray emission, coupled plasma and atomic absorption spec-

FIGURE 4 - Pale Vallone stratigraphic section (PLV). Lithology and abbreviations as Figure 2. *Coupe stratigraphique de Pale Vallone (PLV). Lithologie et abréviations, voir Figure 2.*

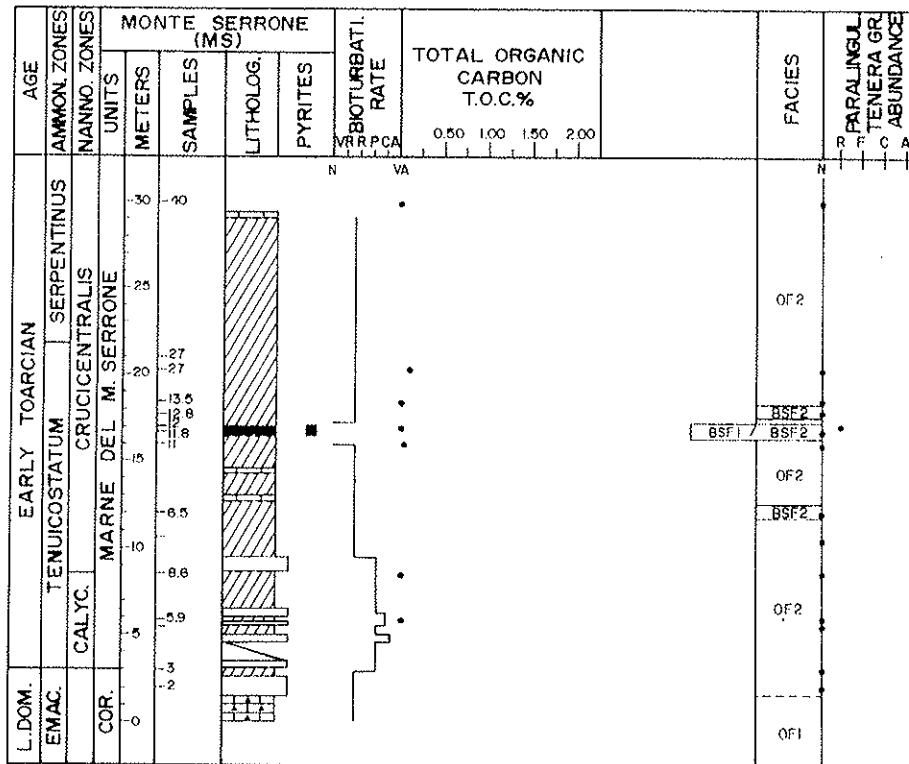
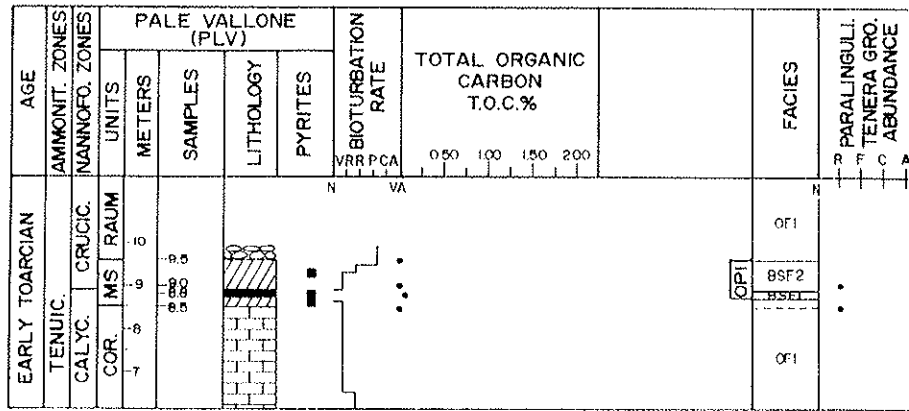


FIGURE 5 - Monte Serrone stratigraphic section (MS). Lithology and abbreviations as Figure 2. *Coupe stratigraphique de Monte Serrone (MS). Lithologie et abréviations, voir Figure 2.*

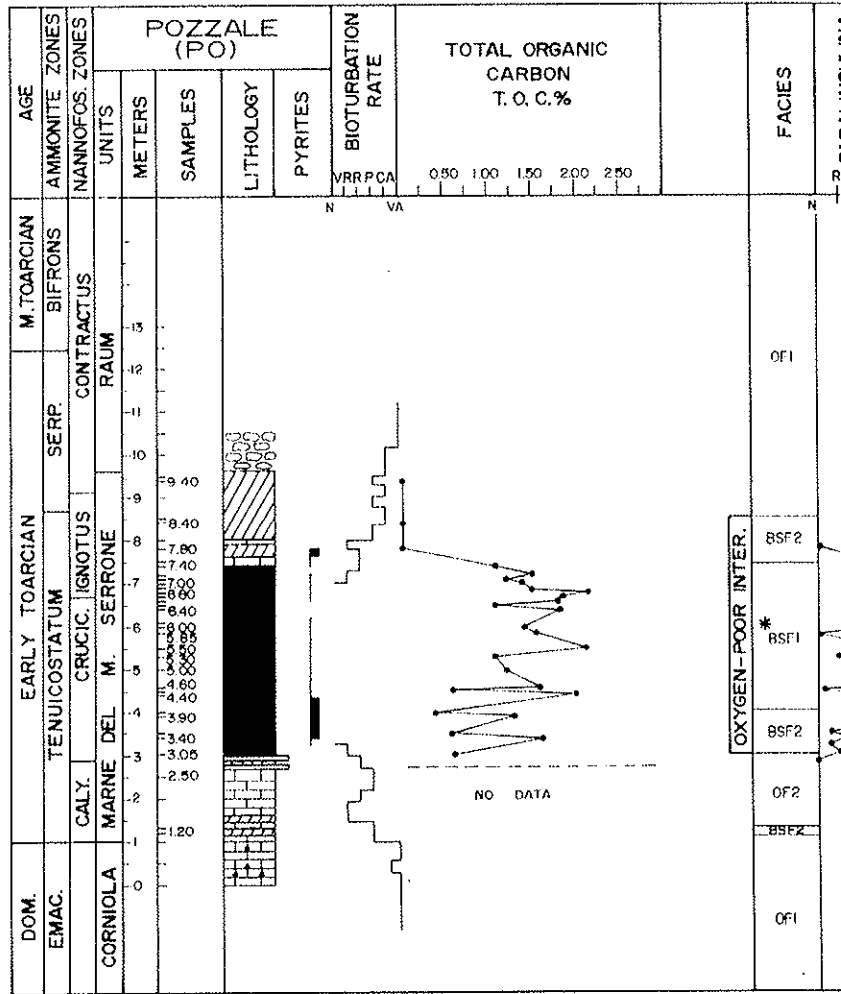
try techniques were used for the geochemical studies. Table 1 summarises the most significant results obtained in the studied sections, and includes a border indicating samples with geochemical anomalies by which they can be classified as BSF1 or BSF2 facies. An asterisk indicates layers corresponding geochemically to maximum anoxia conditions.

MINERALOGY, GEOCHEMISTRY AND MAXIMUM OXYGEN-POOR CONDITIONS

The whole mineralogy of the BSF1 and BSF2 facies consists of calcite, feldspars, quartz and clay mine-

erals; gypsum, dolomite, celestite and barite were detected exceptionally in some sections. The clay minerals found were illite, smectites and kaolinite. In percentage terms the illite contents vary from 70%-76% in the VD sequence, 52%-69% in CO, 65%-90% in PO, 80%-90% in PLV and 65%-75% in MS. Smectite proportions vary from 17%-25% in VI, 26%-46% in CO, 10%-30% in PO, 0%-10% in PLV and 20%-30% in MS. Kaolinite, which is not always present, reaches a maximum of 10% in PLV, with most frequent value of 5%. To summarize, the BSF1 and BSF2 facies are characterized by an illite-smectite-quartz association as predominant mineralogy with lower contents of feldspars, kaolinite and calcite.

FIGURE 6 - Pozzale stratigraphic section (PO). Lithology and abbreviations as Figure 2. Asterisk indicates level with maximum anoxic conditions. *Coupe stratigraphique de Pozzale (PO). Lithologie et abréviations voir Figure 2. L'astérisque indique le niveau avec le maximum de conditions anoxiques.*



cite. This mineral association coincides both quantitatively and qualitatively with that proposed by Weissert (1981) for Cretaceous black shale and similar facies in the region of the Western Tethys, deposited in rhythmic alternation with limestones, marls and silts. The lithological differences visible in the field between typical "black shale facies" (BSF1) and "black shale-like sediments" (BSF2) do not correspond to different mineralogical compositions. Similar conclusions were reached by Palomo (1987) and Ortega-Huertas *et al.* (1991) for Early Jurassic pelagic sediments in the Betic Cordilleras (S Spain).

The maximum oxygen-poor levels can also be distinguished mineralogically, as they are characterized by an important increase in smectite content (50%-60%) in comparison to the other BSF1 and BSF2 levels, where the proportions of this mineral are no higher than 35%, which agrees with the data of Ortega-Huertas *et al.* (1993). Another distinguishing feature of these black shale levels is the low

CaCO₃ content. X-ray diffraction data and the percentages included in Table 1 show the contents to be as follows: 12% (VD-364.15 and 362.8 layers), 16% (CO-209.75 and PO-6.40), 29% (PLV-8.80 layer). These proportions are very different to those presented by the BSF1 levels, where the contents vary as follows (12%-27%), CO (21%-39%), PO (19%-35%).

The geochemical studies differentiate the two types from other Early Toarcian sediments, because the black shale facies present important geochemical variations as they are mainly made of fine particles with a high adsorption capacity such as oxy-hydroxide, clays and organic matter (Murdmaa *et al.* 1977). The horizons richest in organic material correspond to a reductive environment in which the relation between the organic matter and an enrichment in certain trace elements (especially, those included in Table 1) has been established by several authors (e.g. Tardy & Klinkhammer & Palmer 1991; Hatch & Le

SAMPLE	%			ppm													FACIES
	SiO ₂	CaO	Fe ₂ O ₃	Ba	V	Cr	Ni	Co	Cu	Zn	As	Sb	Pb	U	REE		
VD-194	25.80	30.80	3.47	137	47	35	26	6	16	47	9	0.4	7	1.1	79.98	BSF2?	
VD-203.3	30.10	27.00	3.19	162	76	46	19	7	16	37	<2	0.4	4	1	91.24	BSF2?	
VD-361.8	54.20	5.37	5.75	314	112	74	54	19	56	59	10	1.4	13	2.3	133.8	BSF1	
VD-362.8*	51.10	6.83	5.11	752	140	83	53	18	47	92	11	1.7	8	2.5	146.9	BSF1	
VD-364.15*	48.50	6.83	5.11	989	160	85	41	19	46	69	12	1.8	8	2.5	140.58	BSF1	
VD-368.50	41.70	14.90	5.10	166	100	68	49	19	46	71	11	1.3	4	1.8	167.95	BSF1	
VD-371	29.10	29.10	2.98	157	76	42	22	10	22	37	4	0.8	2	1.1	103.45	BSF2	
VD-375.8	39.20	19.50	3.81	69	66	58	40	14	32	32	10	0.6	8	1.9	119.78	BSF2	
VD-380.5	25.40	33.50	2.39	103	46	53	33	7	24	125	11	0.7	8	1.4	62.67	BSF2	
VD-382	24.90	34.80	2.07	119	43	29	24	7	21	37	10	0.5	<2	1.4	64.67	BSF2	
VD-384	17.30	40.50	1.85	42	32	21	22	6	14	23	11	0.3	<2	0.7	43.93	BSF2/OF2	
VD-391	20.00	37.00	2.09	85	38	30	23	7	23	32	10	0.3	<2	1.2	58.96	BSF2	
CO-227.20	14.00	42.60	1.87	114	26	20	17	6	11	18	3	0.3	2	1.3	49.64	OF2	
CO-221.20	18.40	38.40	1.92	64	25	24	18	5	15	30	2	0.3	6	1.0	55.01	BSF2?	
CO-216.10	37.70	20.70	1.87	194	62	49	35	13	21	41	3	0.4	9	1.6	97.61	BSF1	
CO-213.70	44.40	13.70	5.61	819	85	59	67	18	37	63	9	1.0	9	1.8	117.36	BSF1	
CO-209.75*	49.90	9.25	5.10	390	115	60	47	15	53	74	11	1.3	11	2.8	123.09	BSF1	
CO-204.20*	46.90	11.80	5.15	171	107	66	67	19	50	106	10	1.3	14	2.1	125.48	BSF1	
CO-200	37.60	21.80	3.44	64	68	50	33	11	27	46	4	0.5	8	2.0	125.70	BSF1	
PLV-9.50	25.70	31.40	2.59	153	72	51	43	21	18	130	6	1	4	1	101.54	BSF2	
PLV-8.80*	40.10	16.70	4.88	114	96	75	83	50	25	64	7	1.3	16	1.1	144.24	BSF1	
PO-8.40	32.00	25.80	2.63	109	68	41	39	13	28	46	<2	0.3	5	1.2	88.24	BSF2	
PO-7.40	42.30	14.30	4.33	145	140	76	49	18	41	88	11	1.5	6	1.9	160.85	BSF1	
PO-7	46.40	10.80	4.35	194	150	79	40	15	45	72	14	2	10	2.6	166.87	BSF1	
PO-6.40*	49.00	9.05	5.13	314	113	67	52	13	47	82	9	1.4	9	2	131.01	BSF1	
PO-4	36.60	19.40	3.33	450	100	60	29	14	37	69	5	0.7	2	1.6	127.33	BSF1	
PO-1.20	34.40	21.30	4.74	173	67	52	77	15	28	89	<2	0.8	8	1.4	82.94	BSF2	

□ Samples with geochemical anomalies.

* level with maximum anoxic conditions.
BSF1, BSF2 and OF2: see text.

TABLE 1 - Selected chemical analyses of the whole samples. *Analyses géochimiques sélectionnées pour l'ensemble des échantillons.*

1992). In particular, the BSF1 and BSF2 facies are characterized by an important positive geochemical anomaly in certain trace elements, such as Ba, V, Cr, Ni, Co, Cu, Zn, As, Sb, Pb, U and rare-earth elements (REE) (Table 1). Similarly, the percentages of SiO₂ and Fe₂O₃ are quite different to those in the oxygenized Toarcian sediments (OF2).

Detailed study of the geochemical contents (Table 1) also permits differentiation of the BSF1 and BSF2 facies separately and, therefore, geochemical differences can be established between them which complement the macroscopic criteria in the field. Thus, the samples with a lower CaO content, higher SiO₂ and Fe₂O₃ contents, and the highest trace element values (Table 1) correspond to the BSF1 facies.

levels presenting a less intense geochemical anomaly in trace elements correspond to the BSF2 facies (Table 1). In the broad anoxic layer (Table 1 and Figs. 2-6), the maximum anoxic conditions invariably correspond to BSF1 layers (see samples marked by asterisks in Table 1).

The relative richness in MgO is often taken as characteristic of black shale facies. In the case studied here, the BSF1 facies present mean values ranging from 2.10% to 2.34%, with the exception of the PLV sequence, where the content of the BSF1 level is 2.80%. This facies is clearly richer in MgO than the BSF2 facies, whose mean values range from 1.30% to 2.07%, which also indicates the more anoxic nature of the BSF1 facies. In fact, as these percentages are similar to those detected by Brosse (1982), the maximum values coincide with the most anoxic levels in all the sequences (VD-362.8 = 2.11%, CO-209.75 = 2.10%, PO-6.40 = 2.40%, PLV = 2.80%).

The Monte Serrone section is a case apart, as some of its levels can be geochemically characterized as similar to BSF2 facies. Specifically, the samples in question are MS-6.50, MS-12.80 and MS-43, belonging to the Early Toarcian.

The geochemical results obtained in these Toarcian black shale facies are very similar to those of Gavshin (1991) for Jurassic black shales and the geochemical anomalies shown in Table 1 present a trend similar to that of the Cretaceous black shale facies studied by other authors (Debrabant *et al.* 1979; Chamley *et al.* 1979; Brosse 1982). Likewise, the studies by Turekian & Wedepohl (1961) and Lyons & Gaudette (1979), in which a connection is established between trace elements and clayey facies, coincide with our results.

Finally, we should point out that the absence of important diagenetic effects is common to all the sections. This is confirmed by the abundance of smectite, which X-ray diffraction shows to contain illite layers in all cases. The illite proportions are lower than 15%, as quantified by the methods of Reynolds & Hower (1970) and Srodon (1984), i.e. it is $R=0$, following the terminology of Reynolds (1980).

DISCUSSION

PALAEOENVIRONMENTAL INFERENCES

Authors that have studied Jurassic sedimentation in the Mediterranean domain (García Hernández *et al.* 1980; Vera 1981; Jenkyns & Clayton 1986; Palomo 1987; Ortega-Huertas *et al.* 1991, 1993; Hallam 1988; Baudin *et al.* 1990a; Baudin *et al.* 1990b) agree that the Early Toarcian was a period of important transgression, characterized by the

input of a marly-argillaceous deposition, as in the UMB area, where the marly-argillaceous sediments abruptly replace the predominant calcareous sedimentation typical of the Domerian (Farinacci 1981; Bartolini *et al.* 1992; Baudin *et al.* 1990; Monaco *et al.* 1994; Bucefalo-Palliani & 1993). These facies were deposited in a clearly anoxic environment and are similar to those of the Betic Cordilleras (SE Spain), given by rhythmic alternations of marls and marly limestones (Palomo 1987; Ortega-Huertas *et al.* 1991; Palomo 1994).

Reductive conditions of different intensity, to which the BSF1 and BSF2 facies are related, can be referred to different subsidence conditions leading to the individualization of subenvironments: troughs and swells. The Early Toarcian mineral association in the VD, CO, MS and PLV sequences consists of illite-smectite-(kaolinite) facies and is characteristic of a pelagic environment with low influence from emerged reliefs. On the other hand, the BSF1 and BSF2 facies in the PLV sequence must have been deposited under the influence of nearby emerged areas (perhaps islands), as suggested by the greater abundance of kaolinite and the considerable decrease in smectite (Fig. 7). The values of the Ce/Ce* ratio (0.80-1, Fig. 7) (Ce* corresponds to the concentration obtained by extrapolation between La and Nd, as described by Coe & Hoffert 1977), which is a parameter indicating the degree of detrital influence in a basin (Coe & Hoffert 1977), indicate considerable detrital influence in all the studied sequences. These conclusions agree with the high values (0.65-0.90) for the detrital index ($D = Al/(Al+Fe+Mn)$, Boström 1969) found by Ortega-Huertas *et al.* (1993; Monaco *et al.* 1994) in some of these sequences, also with the high concentration of REE, particularly in the BSF1 facies (Table 1). Similar values for the D parameter (0.65-0.81) were found in Cretaceous black shale facies by Brosse (1982). Detrital influence is important as it may have caused some resedimented layers. In this sense, the TiO₂ values (0.42%-0.86%) are in accordance with those indicated for the D parameter and the Ce/Ce* ratio, and are also similar to those given by Vignati & Tourtelot (1970), Chamley *et al.* (1979) and Hower (1982) for black shale facies. On the other hand, oceanic influence was detected in the sequence studied here, as indicated by the low MnO content (0.05%-0.19%).

Several authors (e.g. Ronov *et al.* 1967; Cullis *et al.* 1975) established that the La/Lu ratio normalized to chondrites presents values of 21.8, 14.9 and 9.4 as respectively characteristic of sediments deposited in continental, nearshore marine and pelagic environments. In the sections studied here, the values obtained correspond to sediments deposited

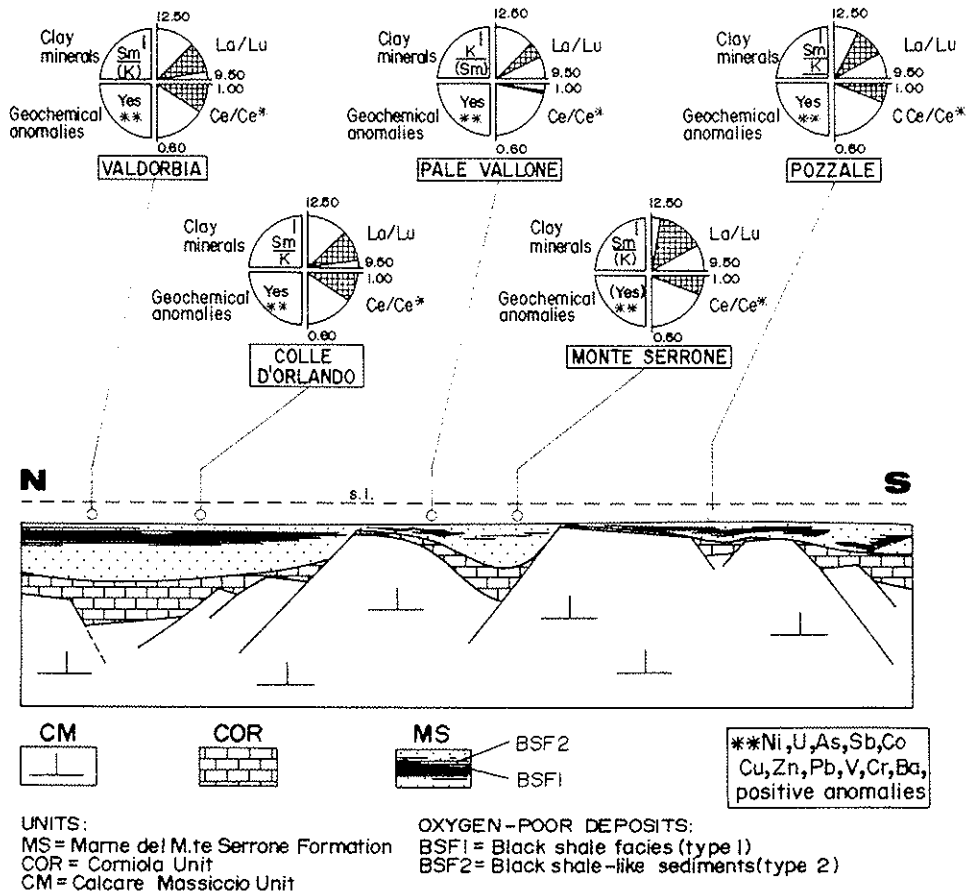


FIGURE 7 - Mineralogical and geochemical data and schematic palaeoenvironmental interpretation of the oxygen-poor deposits dated as Tenuicostatium Zone (Early Toarcian) (not in scale). Clay minerals: I=illite; Sm=smeectites; K=kaolinite. *Données minéralogiques géochimiques et interprétation des dépôts pauvres en oxygène datés de la Zone à Tenuicostatium (Toarcien inférieur).*

in a clearly pelagic environment, although some levels present values more representative of environments intermediate between pelagic and near-shore marine characteristics. This geochemical parameter shows that there are no differences between the BSF1 and BSF2 facies as regards their pelagic conditions. Thus, the variation ranges of the La/Lu ratio are similar in all the studied sections: VD (BSF1: 9.90-11; BSF2: 9.70-11.20), CO (BSF1: 10.45-11.96; BSF2: not present), PO (BSF1: 10.52-11.51; BSF2: 9.83-10.97), PLV (BSF1 and BSF2: 10.97). Consequently, the geochemical differences between both facies are due to their different degrees of anoxia. To be more specific, we can say that the levels with maximum oxygen-poor conditions present the lowest values of the La/Lu ratio (VD = 9.90, CO = 10.45, PO = 10.67, PLV = 10.97).

Together with the greater intensity of the geochemical anomaly (Table 1) and the greater abundance of smectites in these levels, this suggests that we

should interpret these levels as having been deposited in more pelagic and perhaps even deeper marine conditions. According to this criterion, the depositional conditions of the most oxygen-poor levels evolved towards less pelagic and/or shallower conditions as follows: VD-CO-PO-PLV. Since even the most anoxic levels contain calcite in the proportions indicated above (see also the CaO values in Table 1), we can say that they were deposited above the calcite compensation depth (CCD).

The BSF1 deposits are generally preceded by BSF2, which indicates that the anoxic conditions became gradually established in the depositional basin. Similarly, after the anoxic maximum, the near-surface conditions in which oxygenized sediments were deposited also became established gradually. These features can be clearly observed in the Valdorbis and Pozzale sections (Figs. 2, 6), where the BSF1 facies correspond to levels VD-368.50 to VD-368.50 and PO-4 to PO-7.40. In the case of the Colle d'Orlando section, the samples taken correspond

BSF1 facies (CO-200 to CO-216.10), although level CO-221.20 presents geochemical characteristics intermediate between the BSF2 facies and the overlying, Early Toarcian oxygenized sediments (OF2).

According to the hypothesis of Hatch & Leventhal (1992), the $V/(V+Ni)$ ratio (0.63-0.79) indicates that the BSF1 facies were deposited in a less strongly stratified water column, whereas the low $V/(V+Ni)$ values in the BSF2 facies (0.46-0.62) suggest that these were deposited in a weakly stratified, primarily dysoxic water column.

On the basis of geochemical analyses both BSF1 and BSF2 represent poorly-oxygenized sediments which are differentiated by different degrees of anoxic intensity. Therefore, sediments can also be attributed to BSF2 that do not have features characteristic of black shales, but which are grey-green or yellowish in color, not completely laminated, slightly bioturbated, with a low TOC value and microfaunal assemblage D (*Eoguttulina*, *Prodentulina*, flat vaginulids and more or less abundant *Paralingulina* gr. *tenera*). It has thus been possible to recognize in the field poorly-oxygenized sediments that were not identified. This in turn has led to the extension in both time and space of the development of environments characterised by oxygen deficiency even for a short interval of time. In fact, in the Pale Vallone and Monte Serrone sections and in the lower part of MS formation in the VD and PO sections signals of poor oxygenation were not recorded before the geochemical analyses were carried out.

Consequently a multidisciplinary approach to the study of more or less organic-rich levels in the Early Toarcian can be useful to detect subenvironments with different degrees of anoxic intensity in the UMB. Information can be obtained on both the causes of deposition and preservation of a variable amount of organic matter and on its post-depositional oxidation.

The presence of BSF2 and very rare BSF1 facies in the MS section should be interpreted as a consequence of a less restricted depositional environment (Bartolini et al., 1992). However, as in the other sections studied here, the depositional conditions of the BSF2 facies corresponded to an environment intermediate between pelagic and nearshore marine characteristics (La/Lu range = 9.80-11.17).

The recognition of two types of poorly-oxygenized sediments and the scarcity of benthic life leads us to consider that the poorly ventilated conditions on the sea-floor and the consequent biological crisis started as early as the lower part of the Tenuicostatum Zone and lasted till the upper part of this Zone. Only rare BSF2 levels have been found in the Serpentinus Zone, indicating the possible occurrence of scarce oxygenation episodes in the areas where

the MS deposition persists. However, different trends in deposition and accumulation of organic matter, together with development of reducing environments during the Tenuicostatum Zone, have been detected also considering TOC values and microfaunal assemblages from other sections (Bartolini et al. 1992; Nini et al. in press) (Fig. 6).

Presale, M. Bibico and F. Cerro sections have been investigated by geochemical analyses and therefore, the detailed logs are not shown. More detailed study of M. Bibico and F. Cerro sections is reported in Nini et al. (1995), and in Storti & Baldanza (in prep.).

On the basis of the preservation of organic matter and the preservation, the present state of research has reached the following environmental distinctions:

- Depressed areas with long lasting black shales (Valdorbica, Colle d'Orlando, Pozzale and F. Cerro) or troughs: such areas may or may not contain calcareous detrital discharges; rare levels appear in the lower part of the Tenuicostatum Zone below the *Lotharingius crucicentralis* FO. The maximum development of poorly-oxygenized sediments occurs above the FO of *Lotharingius crucicentralis*, within the middle-upper part of the Tenuicostatum Zone. Parameters indicative of oxygen conditions and rich-organic sedimentation, show a trend that coincides in section CO and PO; curves representative of these sections show an acme of maximum anoxia in the upper part of the Tenuicostatum Zone (Fig. 2, Fig. 3, Fig. 6).
- Depressed areas with discontinuous and poorly-oxygenized sediments (Monte Serrone Section); here the MS formation is very thick and characterized by rare, brief episodes of oxygenation above the *L. crucicentralis* FO (Bartolini et al. 1992) (Fig. 5).
- Depressed areas with short lasting black shales (Monte Bibico, Nini et al. in press): these areas show black shales at the base of the Tenuicostatum Zone while oxygen-rich sediments occur above the *L. crucicentralis* FO. In each depressed area the timing of clay discharge coincides approximately with the Domerian/Toarcian boundary.
- Swell areas: Presale (Monte Nerone area) and Pale Vallone. These correspond to areas represented by very condensed sections; here BSF1 and BSF2 facies display different TOC high values; the highest values are found in the Presale section (Bartolini et al. 1992). Oxygen-poor deposits are found just above the FO of *L. crucicentralis* in the Pale area, and above it in the Presale section. In these areas the thickness of MS formation is less than 1 m, and the lower boundary with the Corniola unit falls in the lower part of the Tenuicostatum Zone. The TOC values that occur in different subenvironments such as Colle d'Orlando, Pozzale and F. Cerro are unrelated to sea-floor depth.

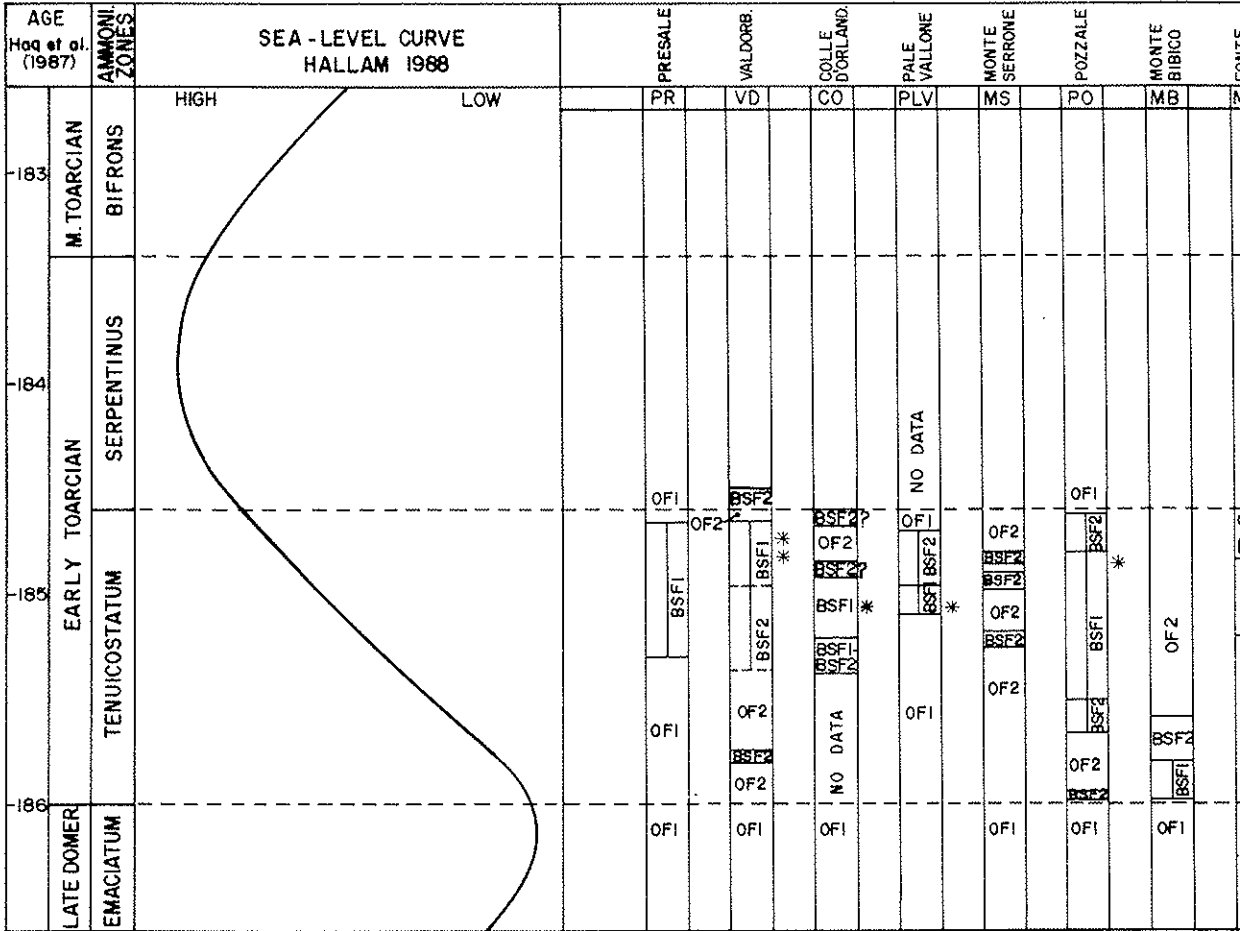


FIGURE 8 - Correlation of the oxygen-poor deposits to the sea-level curve (Hallam 1988). Asterisks indicate levels with maximum anoxic conditions. *Corrélation entre les dépôts pauvres en oxygène et la courbe du niveau de la mer. Les astérisques indiquent les niveaux maximum de conditions anoxiques.*

Discussion on factors affecting the degree of anoxia and organic matter preservation in the different subenvironments as now defined must take into account the possibility of post-depositional oxidation or a thermal maturation effect on the organic matter. However, mineralogy reveals that the analyzed succession seems to lack diagenetic overprinting ; the occurrence of abundant *Paralingulina gr. tenera* and positive geochemical anomalies, related to the TOC value, show that organic matter was both accumulated and preserved here. The concurrence of the two parameters can not be verified when organic matter is not preserved (low TOC values).

The identification of different types of subenvironments shows that the evolution of anoxic conditions

and organic matter preservation occurred differently in the UMB and has varied through time (Bibico area). Parameters such as clay input and planktonic productivity do not account for the differentiation of these subenvironments during the Early Toarcian. Clay sedimentation, necessary for organic matter preservation, was in fact spread and not specifically localized, in the UMB (Ortiz Huertas *et al.* 1993) ; at the same time, the widespread abundance of planktonic organisms (radiolarians and nannoplankton, Bartolini *et al.* 1993) through the entire Tenuicostatium Zone, indicates an equally high primary productivity of surface water. Factors that must instead be taken into account are : a) persistence in some areas of restricted environments with sea-floor stagnant water

that allowed maximum anoxia development in the middle-upper part of the Tenuicostatum zone ; **b**) oxygenation of the sea bottom in other less restricted areas (M. Serrone) ; **c**) at M. Bibico anoxic conditions began to develop at the base of the Tenuicostatum Zone, and the environment only became oxygenated later, when other areas display maximum anoxia (Fig. 8).

Circulation patterns were therefore slightly different in the various subenvironments, thus causing differentiated distribution of poorly-oxygenized sediments. Anoxic conditions seem independent from sea-floor depth. Restricted conditions and organic-rich sediments might occur in any situation, and their vertical distribution is probably affected by the physiography of the UMB, inherited from an earlier phase of extensional tectonics and modified by a synsedimentary one. The existence of physical barriers probably determined differentiated current circulation and differentiated oxygen supply reaching the various subenvironments. These last factors can be of fundamental importance in controlling anoxic facies development, since primary productivity is not locally affected because of the pelagic nature of the UMB.

RELATIONSHIPS WITH SEA-LEVEL FLUCTUATIONS

The Early Toarcian global transgression modified the sedimentary regime of the Tethyan realm into differentiated types of environment.

The sea-level rise determined an increase both in clay input and in primary productivity, thereby establishing conditions favorable for development of anoxia and preservation of organic matter (Bassoulet & Baudin 1994). This global transgression and more or less extended anoxia are associated with a biological crisis and faunal changes (Hallam 1988 ; Bassoulet & Baudin 1994). In the UMB this biological crisis is recorded by scarcity of ammonites, reduced sizes and low generic and specific diversity of benthic microfauna. Such parameters occur within the Tenuicostatum Zone even in oxygenized subenvironments, while microfauna abundance, size and species diversity are observed to increase from the base of the Serpentinus Zone on.

Maximum anoxia occurs in the middle-upper part of the Tenuicostatum Zone, above the FO of *L. crucicentralis*, when suitable organic matter preservation conditions occurred in the different UMB subenvironments. The development of anoxic conditions has also been observed in structural highs or swells, when clay sedimentation reached the most elevated areas of the UMB.

In this paper, clayey sedimentation including poorly-oxygenized levels is related to the Hallam curve

(1988), corresponding to the Early Toarcian level rise. The anoxia maximum, identified multidisciplinary approach for the different sections reported here, falls slightly above the inflection point of the eustatic curve (Fig. 8). Recent studies on the composition and preservation of organic matter in the Pozzale section (Bucefalo-Palliani-Cirilli 1993) distinguished differently oxygenized organic intervals within the Tenuicostatum Zone related to the Early Toarcian eustatic rise. The oxygenated interval (anaerobic condition) is related to the maximum flooding event and the overlying intervals, showing conditions ranging from dysbiotic to aerobic, have been assigned to the high stand phase. Consequently, the anoxia maximum recorded here coincides with the maximum flooding event-high stand phase inferred by Bucefalo-Palliani & Cirilli (1993).

However, interferences with regional tectonics have during the Early Jurassic probably led to similar expansion of the anoxia maximum in the different subenvironments developed after flooding an Early Jurassic platform. The depth of these subenvironments was such that eustatic variations have affected sea-floor sedimentation.

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