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THE EARLY TOARCIAN (JURASSIC) ANOXIC EVENT: STRATIGRAPHIC, SEDIMENTARY, AND GEOCHEMICAL EVIDENCE

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ABSTRACT. Detailed stratigraphic studies of Jurassic deep-marine Tethyan organic-rich shales and manganoan carbonates from Austria-Germany, Italy, Greece, Hungary, and Tunisia suggest they are principally of early Toarcian, *falciferum*-Zone age. Carbon-isotope stratigraphy from non-carbonaceous Tethyan sections indicates a positive $\delta^{13}C$ excursion in the early part of the *falciferum*-Zone (*exaratum* Subzone) suggesting accelerated extraction of organic carbon from the ocean reservoir at this time, and it is likely that most, if not all, Tethyan Jurassic black shales are confined to this interval: they can thus be used as a stratigraphic index. These facies are of exactly equivalent age to the more renowned equivalents in epicontinental northern Europe such as the Jet Rock, Schistes Cartons, and Posidonienschiefer. Epicontinental *falciferum*-Zone black shales are also known from western Canada, the Arctic Slope, Japan, Madagascar, Argentina, and possibly offshore western Australia. It is thus clear that synchronous deposition of these facies occurred in diverse parts of the globe which allows interpretation of the phenomenon as an Oceanic Anoxic Event, whose duration is estimated as approximately half-a-million years.

Detailed paleogeographic studies in the Southern Alps suggest that an oxygen-minimum model is appropriate for interpreting conditions on Tethyan continental margins. Advection of manganese in this low-oxygen layer may explain the local occurrence of carbonate ores of this element. Carbon-sulfur and iron-sulfur ratios, although showing considerable scatter, suggest that bottom waters at this time were locally euxinic, containing free hydrogen sulfide.

This Oceanic Anoxic Event was preceded by significant faunal turnover of ammonites in Tethys and accompanied by widespread extinction of benthos in northern Europe in response to the lateral spread of anoxic bottom waters during transgression. Similar changes may be recognized in other parts of the world. Other anoxic events may have taken place during the Jurassic, but documentation is as yet meager. Furthermore, models for such phenomena remain largely speculative, although upwelling and increased planktonic productivity, commencing in pre-Toarcian time, are favored for the *falciferum*-Zone event documented here.

INTRODUCTION

The concept of an Oceanic Anoxic Event was introduced by Schlanger and Jenkyns (1976) to delineate a period of time characterized by abnormally high depositional and preservational rates of organic carbon in favorable marine environments in many parts of the globe. This concept, with particular respect to the Cretaceous, has since been discussed, elucidated, and refined by Jenkyns (1980), Schlanger and others (1987), and Arthur, Schlanger, and Jenkyns (1987). Critiques of the hypothesis have been given by Thiede, Dean, and Claypool (1982) and Waples (1983). Justification for the anoxic-event model hinges on a stratigraphy with sufficient resolution to demonstrate the depositional synchroneity of anomalously organic-carbon-rich laminated shale across a wide area. The purpose of this paper is to show that a period of preferred "black-shale" deposition existed during the Early Toarcian (Early Jurassic) across much of Europe and elsewhere. This interval of Mesozoic time has already been suggested as a possible candidate for an Oceanic Anoxic Event (Hallam and Bradshaw, 1979; Jenkyns, 1980, 1985; Hallam, 1981). The major part of this study has been carried out on Jurassic pelagic sediments in North Italy and Greece, but outcrops have also been studied in Austria, Germany, Hungary, and Yugoslavia. Given that Mesozoic sediments in the Tethyan belt closely resemble those cored in the Atlantic Ocean (Bernoulli, 1972; Bernoulli and Jenkyns, 1974; Ogg, Robertson, and Jansa, 1983) it is suggested that the development of Alpine-Mediterranean Jurassic facies was influenced by regional oceanographic changes. As the Lower Jurassic pelagic record of the oceans is currently limited to one Deep Sea Drilling core taken from off Morocco (Hinz, Winterer, and others, 1985) it may be that the Toarcian of the Tethys is as close as one currently comes to having a window on the World Ocean.

STRATIGRAPHIC SCHEME FOR THE TOARCIAN

Suggested zonal subdivisions for the Toarcian are shown in figure 1, based primarily on the work of Géczy (1984) on Tethyan facies in the Gerecse Mountains of Hungary. Here very detailed collecting has enabled recognition of enough key northwest European ammonite genera to apply much of the stratigraphical scheme devised in the type locality for the stage. The exposure at Valdorbia, commonly used as a reference section for the Alpine-Mediterranean Toarcian, is considered to contain a major stratigraphic gap as suggested by Guex (1975) and implied by Géczy (1984). Guex suggested the absence of the *insigne* Zone at Valdorbia, and the correlation of the *erbaense* Zone with the *variabilis* Zone by Géczy implies that the *thouarsense* Zone is also missing.

Some authors (for example, Kottek, 1966; Géczy, 1984) use the term "Serpentinus" or "Serpentinum" after *Hildaites serpentinus* for the *falciferum* Zone in the Tethyan region as the index species *Harpoceras falciferum* may be rare and relatively wide-ranging (Donovan, 1958; Fischer, 1966). However, in the recent work of Wiedenmayer (1980) on

British Isles	Thouars, France	Valdorbia, Italy	Gerecse Mountains, Hungary
LEVESQUEI	AALENSIS	MENEGHINII	LEVESQUEI
	PSEUDO-RADIOSA		
THOUARSENSE	INSIGNE	▨	INSIGNE
	THOUARSENSE		THOUARSENSE
VARIABILIS	VARIABILIS	ERBAENSE	VARIABILIS
BIFRONS	BIFRONS	BIFRONS	BIFRONS
FALCIFERUM	SERPENTINUS	FALCIFERUM	SERPENTINUS
TENUICOSTATUM	TENUICOSTATUM	TENUICOSTATUM	TENUICOSTATUM

Fig. 1. Stratigraphic scheme for the Toarcian stage. Zonal division in British Isles after Cope and others (1980); Thouars, France after Mouterde and others (1971) and Gabilly (1976); Valdorbia, Italy after Gallitelli-Wendt (1969); Gerecse Mountains, Hungary after Géczy (1984). Additional data from Guex (1975). The Valdorbia section is assumed to contain a substantial stratigraphic gap.

the Pliensbachian-Toarcian of the Southern Alps, the "*falciferum* Zone" is retained, and since this aids comparison with northern Europe such usage is employed in this paper.

TOARCIAN BLACK SHALES IN NORTHERN EUROPE

In the shelf regions of northern Europe deposition of organic-rich shales took place at numerous times during the Jurassic. Favored intervals include parts of the Early Jurassic, particularly the Sinemurian and Toarcian as well as the Callovian-Oxfordian (Oxford Clay, Terres Noires, and equivalents) and Kimmeridgian (Artru, 1968: Morris, 1980: Hallam, 1987a). Of all these horizons it is the Lower Toarcian Jet Rock and Bituminous Shales of Yorkshire, England and their equivalents in the North Sea, France (Schistes Cartons), Germany, and Switzerland (Posidonienschiefer) that show the most widespread distribution in northern Europe (fig. 2) where they may represent important petroleum source rocks (Barnard and Cooper, 1981); organic-carbon contents commonly range between 5 and 15 percent (Bitterli, 1960; Demaison and Moore, 1980: Küspert, 1982: Raiswell and Berner, 1985). The fine fraction is dominated by quartz, kaolinite, illite, illite-smectite, chlorite, pyrite, and calcite with lesser dolomite, feldspar, and carbonate fluorapatite (Pye and Krinsley, 1986). Calcareous and pyritic concretions are common (for example, Raiswell, 1976: Raiswell and Plant, 1980; Coleman and Raiswell, 1981). The sediments, typically millimeter-lami-

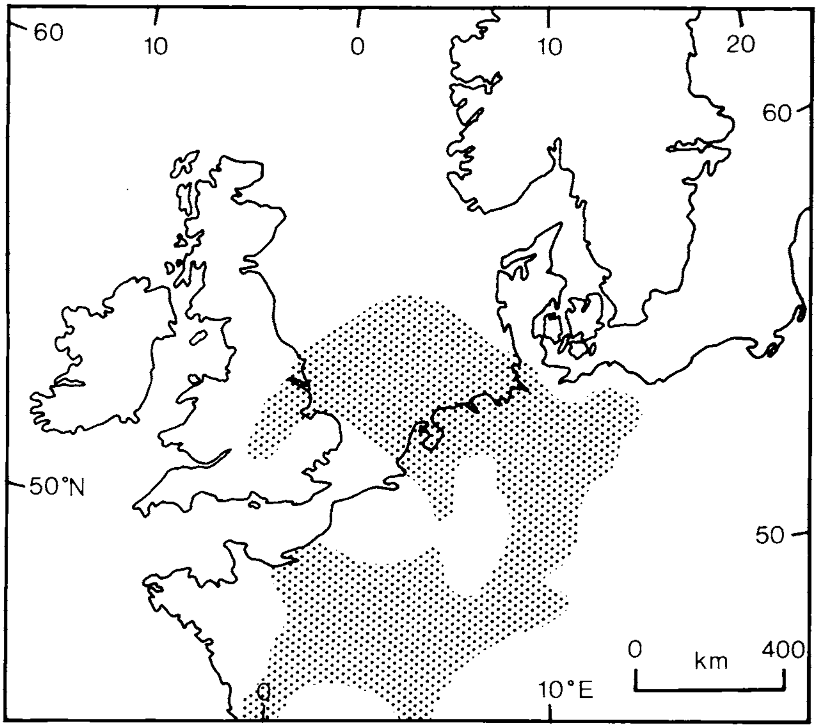


Fig. 2. Distribution (outcrop and subcrop) of the Jet Rock, Schistes Cartons, and Posidonienschiefer in epicontinental northern Europe. The organic-rich facies are of *falciferum*-Zone age. After Morris (1979) and Riegraf (1985). Such deposits also occur patchily in areas south of that illustrated here, for example in the Swiss and French Jura and on the southwestern edge of the Massif Central in southern France (Bitterli, 1960; Broquet and Thomas, 1979; Cubaynes and others, 1984).

nated, are characterized by abundant remains of the thin-shelled bivalve *Posidonia alpina* (= *Bositra buchi*), thought by some to be nekto- or pseudoplanktonic (Jefferies and Minton, 1965; Sturani, 1971; compare Kauffman, 1981). Other macrofauna locally include ammonites, typically flattened, belemnites, nautiloids, brachiopods, gastropods, echinoderms plus remains of fish and other vertebrates. The microfauna include Foraminifera, ostracods, radiolarians, and dinoflagellates; calcareous nannofossils, particularly coccoliths, and the larger problematic form *Schizosphaerella* are important rock-forming constituents (Müller and Blaschke, 1969; Goy, Noël, and Busson, 1979; Riegraf, Werner, and Lörcher, 1984; Riegraf, 1985). The Jet Rock and Bituminous Shales, Schistes Cartons, and Posidonienschiefer are all of *falciferum*-Zone age (Weitschat, 1973; Morris, 1979; Howarth *in* Cope and others, 1980; Riegraf, 1982, 1985; Riegraf, Werner, and Lörcher, 1984), although organic-carbon-rich sedimentation was locally of greater duration than this, extending into the *tenuicostatum* Zone below and the *bifrons* Zone above. Thicknesses of the organic-rich facies are typically in the range of 10 to 30 m. In northern Spain the exact age of the Lower Toarcian organic-rich shales is unclear (Dahm, 1965). In Portugal the *falciferum* Zone is represented by gray-blue sandy marls with pyritized ammonites: more bituminous facies occur in the *tenuicostatum* Zone (Mouterde, 1955, 1967; Exton and Gradstein, 1984). Generally, however, the most organic-carbon-rich facies (for example, the Jet Rock itself) occurs as finely laminated shales in the lower part of the *falciferum* Zone: in the so-called *exaratum* Subzone. Much interest and controversy has centered on the nature and bottom conditions of the floor of the Posidonienschiefer Sea during the *exaratum* Subzone, and recent and opposing views are given by Kauffman (1981) and Seilacher (1982). Recent paleoecological studies of this carbon-rich "fecal-pellet mud" are given by Bandel and Knitter (1986) and Loh and others (1986).

In parts of Alpine Switzerland (Valais Trough) the graphitic phyllites of the Bündnerschiefer have yielded a specimen of *Harpoceras falciferum* suggesting that these rocks are a metamorphosed equivalent of the Posidonienschiefer (Bernoulli, 1942).

AGE AND LITHOLOGY OF TOARCIAN BLACK SHALES IN TETHYS

Toarcian organic-rich shales occur sporadically throughout the Alpine-Mediterranean region (fig. 3), although they have nothing like the lateral extent of those in northern Europe. In this section of the paper such occurrences are briefly described, and their stratigraphy examined. The level of treatment varies according to whether or not the area has been studied personally. With two exceptions, in Hungary and Czechoslovakia, of north Tethyan derivation the carbon-rich levels occur in pelagic-limestone facies deposited on what was or what became the southern continental margin of Tethys (Bernoulli and Jenkyns, 1974; Laubscher and Bernoulli, 1977).

The fundamental philosophy here has been to search for sedimentary anomalies in sections through the Lower Toarcian. Particularly striking in many localities is a dramatic change in lithology during part of the Toarcian in that a clay-rich sequence is developed within a dominantly calcareous section. Such changes may be observed in stratigraphically condensed red nodular limestones or Ammonitico Rosso facies (Jenkyns, 1974); however, in many localities the clays are dark brown to black, organic-rich, millimeter-laminated, and therefore suggestive of deposition in anoxic or near-anoxic conditions on benthos-free sea floors (for example, Rhoads and Morse, 1971; Savrda, Bottjer, and Gorsline, 1984). Dissolved oxygen contents in the bottom waters may have been as low as <0.1 ml/l (compare Thompson and others, 1985). Less direct evidence of oxygen-depleted bottom-water conditions may be furnished by the presence of abundant well-preserved fish faunas typically associated with organic-rich deposits. Taxonomic papers on such fossils commonly provide a guide to the location of organic-rich

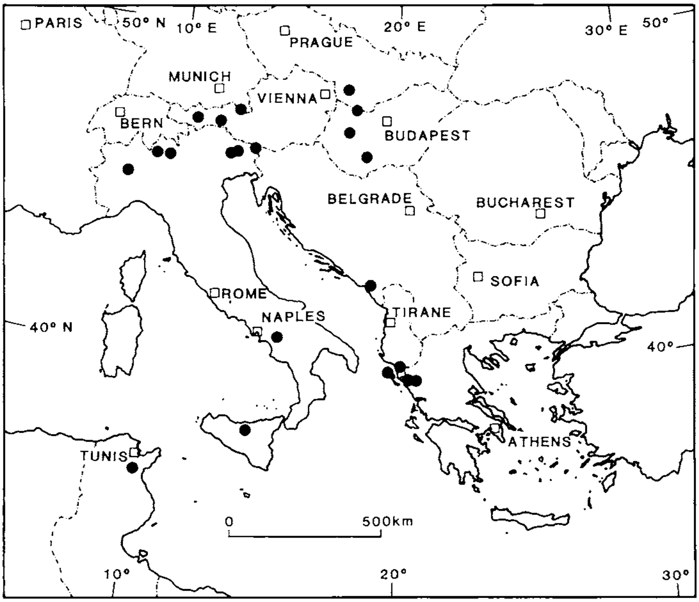


Fig. 3. Distribution of Lower Toarcian organic-rich shales and/or manganoan carbonates in the Alpine-Mediterranean domain. (Data are taken from Andrusov, 1965; Bernoulli, 1964; Cousin, 1981; Fülop, 1971; Gaetani and Poliani, 1978; Gaudant, Rakus, and Stranik, 1972; Géczy, 1966a,b, 1971; Germann and Waldvogel, 1971; Germann, 1972; Jenkyns and others, 1985; Renz, 1907, 1910; Schmidt di Friedberg, Barbieri, and Giannini, 1960; Szabo-Drubina, 1962; Walzebuck, 1982 and ms; and personal observations.) Many other localities undoubtedly exist and information is particularly meager for Bulgaria and Romania.

facies even if the sediments are not described as such in the literature. The abundance of fish in laminated black shales is probably dependent on a number of factors: when falling into anoxic waters after death, the fish are not destroyed by scavengers and thus enter the burial stage intact; the reducing environments within the sediment ensure considerable preservation of the body matter; the elevated phosphate concentrations typically found in organic-rich sediments tend to retard dissolution of the skeletal apatite (compare Soutar and Isaacs, 1974; Diester-Haass, 1978; DeVries and Pearcy, 1982). In areas of upwelling and high plankton productivity fish may also be particularly abundant.

Another sedimentary feature locally associated with organic-rich shales is the presence of replacive manganoan/ferroan carbonates. Only divalent iron and manganese can readily enter the carbonate lattice, and high concentrations of these cations are not stable in oxidizing environments. Such carbonates are forming today in the stagnant anoxic deeps of the Baltic Sea and elsewhere (Manheim, 1961; Hartmann, 1964; Suess, 1979): there is also a substantial record found in temporal and

Fig. 4. Map giving positions of Alpine-Mediterranean localities mentioned in the text. A = Abriola, B = Biella, Ba = Bar, Bg = Bergamo, BG = Breggia Gorge, Bl = Belluno, Bu = Budva, Ch = Chionistra, CP = Col Pedrino, Dk = Dubrovnik, E = Elbigenalp, Fl = Feltre, K = Kouklessi, L = Lábatlan, Le = Lecco, Lo = Lonno, Lok = Lókút, Lon = Longarone, LM = Lago Maggiore, MB = Monte Brughetto, MMn = Monte Mangart, MM = Mecsek Mountains, MS = Monte Serrone, N = Nembro, O = Obersdorf, P = Petalia, Pi = Pignale, PF = Pont du Fahs, Pr = Pradalunga, R = Rizapol, S = Sachrang, Sa = Salzburg, Sc = Scillato, Si = Sirako, Sn = Siniais, T = Titograd, U = Úrkút, V = Viglatzuri, VaVa = Val Varea, Val = Valdorbia, VC = Val Ceppelline, VG = Vajont Gorge, VV = Val de Vesa, Z = Zoldo.

TABLE 1

Geochemical data from Toarcian organic-rich shales of the Alpine-Mediterranean domain

	%TOC	%$CaCO_3$	%S	%Fe	%Mn
JULIAN BASIN, ITALY					
Monte Mangart	1.62	1.0	0.10	7.02	0.22
	1.48	10.3	0.06	3.78	0.69
	1.70	14.5	0.13	3.68	1.12
	1.35	2.0	0.32	3.64	0.54
	0.96	28.6	1.32	2.08	0.72
	0.48	22.2	0.78	1.36	1.31
	0.65	15.9	0.10	2.35	8.76
	1.21	13.3	0.40	3.63	9.27
BELLUNO BASIN, ITALY					
Rizapol	3.67	0.7	0.12	4.00	0.62
	3.21	37.6	0.15	2.61	0.62
	2.96	37.0	0.09	2.29	0.59
	1.53	39.3	0.64	2.31	10.52
	2.13	36.1	2.06	2.98	0.44
TRENTO PLATEAU, ITALY					
Val di Vesa	2.45	42.7	0.87	2.54	0.09
	5.12	23.2	0.33	2.97	0.10
	2.44	19.3	0.54	3.22	0.07
LOMBARDY BASIN, ITALY					
Monte Brughetto	2.00	17.3	1.81	4.43	0.33
	0.53	27.1	0.79	2.80	0.44
	2.61	0.2	0.05	6.10	0.18
	1.18	0.1	0.03	3.94	0.44
	1.09	12.5	0.02	4.33	0.41
	1.14	24.2	0.58	2.36	0.39
	1.33	20.5	2.86	4.81	0.54
Col Pedrino	2.84	30.7	1.71	3.76	0.46
	1.95	8.3	0.06	5.24	0.33
	0.42	49.5	0	2.98	0.89
Val Varea	2.78	32.8	2.44	4.11	0.50
	3.69	27.1	2.07	3.52	0.45
	1.12	64.3	2.33	4.66	8.87
LOMBARDY BASIN, ITALY					
Nembro	1.47	13.6	2.95	4.59	0.16
Pradalunga	0.26	0.7	0.02	5.21	21.35
IONIAN ZONE, GREECE					
Kouklessi	2.74	9.8	3.24	6.05	0.03
	3.64	6.9	1.07	3.59	0.03
	2.19	5.3	1.19	3.85	0.04
	1.26	7.0	1.99	4.29	0.05
	2.21	0.2	2.40	4.47	0.01
Petalia	0.99	51.5	0.03	1.63	0.03
	0.45	51.9	0.05	2.20	0.03
Viglatzuri	2.09	47.0	1.60	1.98	0.02
	1.51	23.8	2.27	2.85	0.02
PINDOS ZONE, GREECE	3.64	0.5	0.16	3.68	0.01
SCLAFANI ZONE, SICILY	0.73	3.2	1.10	2.63	0.02
LAGONEGRO ZONE, ITALY	0.51	-	-	1.45	0.01
EASTERN ALPS, AUSTRIA-GERMANY					
Sachrang	4.77	27.4	5.07	5.98	0.54
	2.72	33.4	2.26	4.51	7.16
	3.66	38.5	0.31	4.49	11.62
Elbigenalp	0.93	16.0	1.22	3.99	0.09
	8.13	25.9	2.34	3.66	0.61

Samples in stratigraphic sequence. Note the local enrichment in manganese; ores of this metal have been economically significant in Austria-Germany, Czechoslovakia, and Hungary. Carbon and sulfur were determined by a direct combustion and automatic titration method using a Strohlein Coulomat 702. Duplicate samples were taken, one of which was roasted at 450°C overnight to remove organic carbon. Both samples were then combusted at 1300°C to decompose the calcium carbonate. In a separate operation samples were roasted at 1400°C to decompose sulfur-bearing compounds, principally pyrite. The gaseous products of combustion (CO_2 and SO_2) were fed into solutions (barium perchlorate for the "C" analysis; sodium sulfate for the "S" analysis) with resultant change in pH. Back titration to the original pH was performed using an electrolytically produced reagent; the quantity of electricity required for this purpose gave an absolute determination of the amounts of carbon and sulfur present. The difference between the samples that had and had not been roasted at 450°C gave a measure of the value of TOC. As the quantity of CO_2 given off from the pre-roasted samples has been recalculated as if it all derived from calcite, the values are overestimates for those samples containing substituted Mn and Fe in the carbonate lattice. Analytical reproducibility by this method was such that repeat analyses for carbon generally differed by no more than 0.02 percent and by no more than 0.03 percent for sulfur. Fe and Mn were determined by atomic-absorption flame photometry on solutions derived by acid digestion (HNO_3, HF, HCl) of whole-rock samples.

spatial association with Cretaceous black shales (Pomerol, 1983). Stratiform primary manganese-carbonate ores in Toarcian sections are thus indicative of very specific sedimentary and early diagenetic conditions, although they do not necessarily provide direct evidence on the oxygen levels of the bottom waters.

Austria-Germany-Switzerland

Organic-carbon-rich shales are well documented from numerous outcrops in the Lower Toarcian of the Eastern (Allgäu and Lechtal) Alps of Austria and southernmost Germany in the region between Obersdorf and Salzburg (fig. 4). Typically they are associated with manganoan carbonates (more properly carbonates belonging to the system $CaCO_3$–$MgCO_3$–$MnCO_3$–$FeCO_3$) which have, in the past, been economically exploited (Germann and Waldvogel, 1971; Germann, 1972); manganese and iron contents average 6.4 and 4.5 percent respectively. Fragments of quartz, plagioclase, hornblende, muscovite, biotite, and chorite are recognizable in thin section where they may attain sand-size; illite dominates the fine-fraction. These sediments belong to the middle unit of the Allgäu-Schichten or Fleckenmergel and are typically represented by interbedded manganoan carbonates and finely laminated black shales (Jacobshagen, 1965). As the manganoan carbonates are typically superficially oxidized they too are dark-colored at outcrop. The more bituminous facies usually occur higher in the sections. Thicknesses of the manganese-bearing and organic-rich shales are commonly a few tens of meters. In the more Mn-rich shales, organic-carbon contents average less than 1 percent, whereas in the bituminous levels they locally rise to 16.5 percent (Bitterli, 1962). Organic-rich samples collected in this study gave values of 2.72, 3.66, and 4.77 percent TOC from a southern German section (Sachrang profile) and 0.93 and 8.13 percent from an Austrian locality (Elbigenalp) (table 1). These sections (fig. 4) are described by Bitterli (1962) and Germann and Waldvogel (1971).

Ammonites from the middle unit of the Allgäu-Schichten suggest the presence of the *falciferum* and at least part of the *bifrons* Zone, although little of the fauna has been collected *in situ* (Jacobshagen, 1965). Although it cannot be conclusively demonstrated that the organic-rich shales pertain exclusively to the *falciferum* Zone, they were certainly deposited during this interval, and both Jacobshagen and Bitterli consider the Austrian sediments to be of identical age with the German Posidonienschiefer. These Austrian organic-rich sections occur in relatively expanded sequences associated with syn-sedimentary breccias and redeposited limestones, and their setting was clearly that of a topographic basin (Bernoulli and Jenkyns, 1974).

The Allgäu Formation, with interbedded manganese shales, also occurs in Graubünden in eastern Switzerland, but stratigraphic documentation is poor (Eberli, 1987).

Italy

Organic-rich shales are not uncommon in the Southern Alps of northern Italy, and some examples are described by Jenkyns and others (1985). These sediments occur in the Lombardy Basin, on the Trento Plateau, in the Belluno Trough and the Julian Basin, and the paleogeographic significance of these occurrences is discussed in a later section. The Jurassic history of the region has been ably summarized by Winterer and Bosellini (1981).

Lombardian Basin.—Some 20 km east of Chiasso, on the Swiss-Italian frontier, black shales are exposed in two adjacent gulleys north of the village of Suello: the Val Varea and the Val Ceppelline (fig. 4) (for example Bernoulli, 1964; Cantaluppi and Montanari, 1969). The Val Varea section contains 5.2 m of black to gray, partly millimeter-laminated micaceous shales interbedded with gray limestones. These shales contain quartz, illite, and calcite in the fine fraction. Abundant sand-sized quartz, commonly showing undulose extinction, muscovite, biotite, and rare plagioclase are seen in thin sections of these shales and adjacent strata: the quartz and feldspar grains are typically etched. Organic-carbon analyses of shale samples gave a maximum value of 3.69 percent (table 1). Much of the black coloration of this unit is due to the presence of finely disseminated manganese oxides.

No detailed geochemistry has been carried out on these interbedded limestones, but one sample from Val Varea analyzed in this study (atomic absorption flame photometry) gave Mn and Fe values of 8.87 and 4.66 percent respectively and contained rhodochrosite or a closely related mineral (table 1). Microprobe analyses of the carbonate of the same sediment gave sample compositions of $Ca_{0.861}Mg_{0.019}Mn_{0.101}Fe_{0.019}CO_3$, $Ca_{0.871}Mg_{0.023}Mn_{0.065}Fe_{0.041}CO_3$, and $Ca_{0.879}Mg_{0.021}Mn_{0.084}Fe_{0.016}CO_3$. Such manganese values are lower than those reported from the Toarcian carbonates of the Eastern Alps in Austria (compare Germann and Waldvogel, 1971). Underneath the black shales in Val Varea are poorly dated Upper Pliensbachian gray and pink pelagic limestones; a few centimeters above the organic-rich level fossiliferous Ammonitico Rosso appears, containing fauna indicative of basal *bifrons* Zone (Bernoulli, 1964). The organic-rich shales are thus of *falciferum*-Zone age, possibly extending down to the *tenuicostatum* Zone.

Greater paleontological constraints are available at Val Ceppelline lying less than 1 km to the west (Cantaluppi and Montanari, 1969). Although no stratigraphic interpretations are given, their faunal lists, interpreted with the data of Wiedenmayer (1980), suggest that the *tenuicostatum* Zone is present immediately below the black shale (the base of which is taken to coincide with the appearance of the first *Dactylioceras*) and that the basal subzone of the *bifrons* Zone is present above (Jenkyns and others, 1985). It is thus clear that the shales, which are very poorly exposed at this locality, pertain to the *falciferum* Zone and possibly part of the *tenuicostatum* Zone as well. Etched sand-sized quartz, muscovite, and biotite are also common in the sediments above and below these shales.

Organic-rich millimeter-laminated shales, lacking interbedded limestone, are also exposed some 15 km farther east between Lecco and Bergamo. The best section, comprizing some 6.5 m of millimeter-laminated shales and marly limestones, is exposed in a road cut on Monte Brughetto (fig. 4) where an abundant and well-preserved fish fauna has been collected (Tintori, 1977). Carbonized wood fragments are also common. Minerals identified in the shales include quartz, calcite, illite, and smectite; sand-sized material includes angular quartz, plagioclase, muscovite, and biotite. Gaetani and Poliani (1978) record an organic-carbon value of 1.29 percent from these shales; the analyses of Jenkyns and Clayton (1986) give values up to 2.5 percent, and further analyses are reported in table 1. Paleontological data from this locality are a little confusing. Gaetani and Poliani (1978) record *Dactylioceras polymorphum* and *Hildaites* one meter above the fish-bearing level, the former being indicative of *tenuicostatum* Zone, the latter typical for the *falciferum* Zone. There is evidence of slumping in this section, suggesting that the *Dactylioceras* may have been reworked, particularly as Kälin (personal commun., 1982) has found the identical species some 12 m below the base of the black shales themselves and just below the level where the sequence becomes suddenly argillaceous. Thus it seems as if the organic-rich shales, indeed the whole argillaceous part of the section, represents the *falciferum* Zone and possibly part of the *tenuicostatum* Zone as well.

Millimeter-laminated brown shales (maximum TOC found = 2.84 percent, table 1) are also exposed by the roadside at Col Pedrino, close to Monte Brughetto (fig. 4). Exposure here is more patchy; Gaetani and Poliani (1978) record *bifrons*-Zone ammonites a little way above the top of the shales. Elsewhere in the Lombardy Basin, particularly in the region of the so-called Sebino Trough (Gaetani, 1975), black shales and interbedded limestones (6–8 m thick) are present in the area around Pradalunga, Lonno, and Nembro (fig. 4) and are attributed to the basal Toarcian by Kälin (personal commun., 1982). Organic-carbon values of a shale sample from Nembro gave 1.47 percent TOC, a sample from Pradalunga gave 0.26 percent TOC (table 1). This latter specimen is black in color and particularly rich in manganese (table 1), here interpreted as an oxide-hydroxide formed by secondary oxidation of an original carbonate.

In the western part of the Lombardy Basin between Biella and the Lago Maggiore (fig. 4) there are patchy outcrops of Jurassic pelagic sediments which include black shales of probable Toarcian age (Rasetti, 1897; Carraro and Sturani, 1972).

Trento Plateau.—The Trento Plateau was a former topographic high delineated by Mesozoic faults from adjacent basins, and its paleogeographic significance is discussed in more detail below. On the eastern side of the Plateau, in the Feltre Alps, Toarcian organic-rich shales are exposed not far from the Rifugio Dal Piaz in the Val di Vesa (fig. 4) (Dal Piaz, 1907). The sediments are described as fissile, black, bituminous argillaceous shales containing abundant teeth and scales of fish and are attributed by Dal Piaz to the Lower Toarcian, more precisely the oldest level of the stage. These shales pass laterally, over less than 1 km, into gray-green limestones containing ammonites of *falciferum*-Zone age, no *tenuicostatum*-Zone forms being recognized (Dal Piaz, 1907: Clari and Pavia, 1980). Of note, therefore, is the extremely local occurrence of the organic-rich shales. Where I have examined them the sediments, of which 1.4 m are tolerably well exposed, are mostly brown, partly millimeter-laminated and interbedded with limestones containing abundant carbonate-replaced radiolarians: overlying sediments are red fossil-rich limestones containing ferromanganese nodules, typical condensed facies of the Tethyan Jurassic (compare Jenkyns, 1971). Dal Piaz remarks on the remarkable similarity of the shales with the "Posidonomyenschichten" of Wüttemberg, Southern Germany. The organic-carbon content of these shales ranges between 2.44 and 5.12 percent (table 1). Their mineralogy is dominated by quartz and calcite with illite and chlorite.

Belluno Trough.—The Belluno Trough, lying to the east of the Trento Plateau, contains Toarcian organic-rich shales with the best exposures close to the village of Longarone, near Belluno (fig. 4). The only prior mention known to me of these sediments is that of Boyer (1913) who produced a general account of this region. Jenkyns and others (1985) discuss the stratigraphy and depositional context of the black shales in the area. Typically some 6 to 12 m of dark-brown millimeter-laminated white-weathering shales, rich in fish remains, are interbedded with brown-weathering manganoan limestones containing calcite-replaced radiolarians: minerals identified in the shales are calcite, quartz, and illite. The laminated shales locally contain tiny ovoid calcareous bodies (fig. 5) whose shape and dimensions suggest an interpretation as fecal pellets of planktonic organisms (compare Hattin, 1975). Some current-sorted layers are particularly rich in fish remains, bivalves, echinoids, and Foraminifera (fig. 5). The outcrops are well seen on the road from Longarone to Zoldo and in the Vajont Gorge underneath the redeposited oolites of the Vajont Limestone described by Bosellini, Masetti, and Sarti (1981). Organic-carbon values of the shales range between 1.53 and 3.67 percent (table 1); microprobe analyses of an interbedded brown-weathering limestone gave sample compositions of $Ca_{0.946}Mg_{0.018}Mn_{0.036}Fe_{0.0}CO_3$; $Ca_{0.971}Mg_{0.021}Mn_{0.008}Fe_{0.0}CO_3$; $Ca_{0.926}Mg_{0.016}Mn_{0.054}Fe_{0.001}CO_3$. In the Val di Grisol at Rizapol (fig. 4) the organic-rich level fingers out completely, apparently influenced by underlying slump-induced topography. The stratigraphy of the organic-rich shales is indicated by the presence of upper *falciferum*-Zone ammonities immediately above the shales and manganoan limestones at one locality in the Vajont Gorge (Jenkyns and others, 1985).

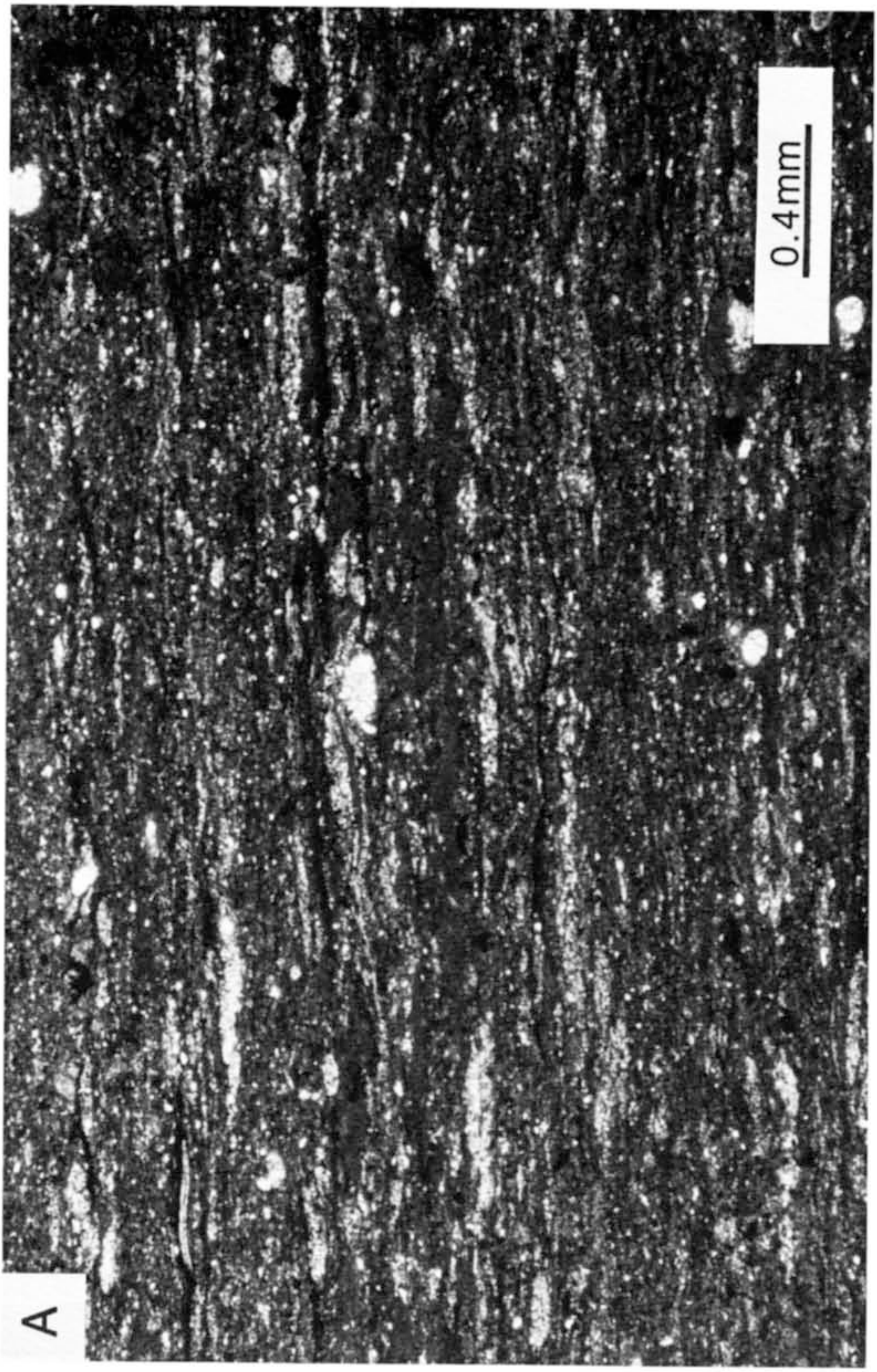
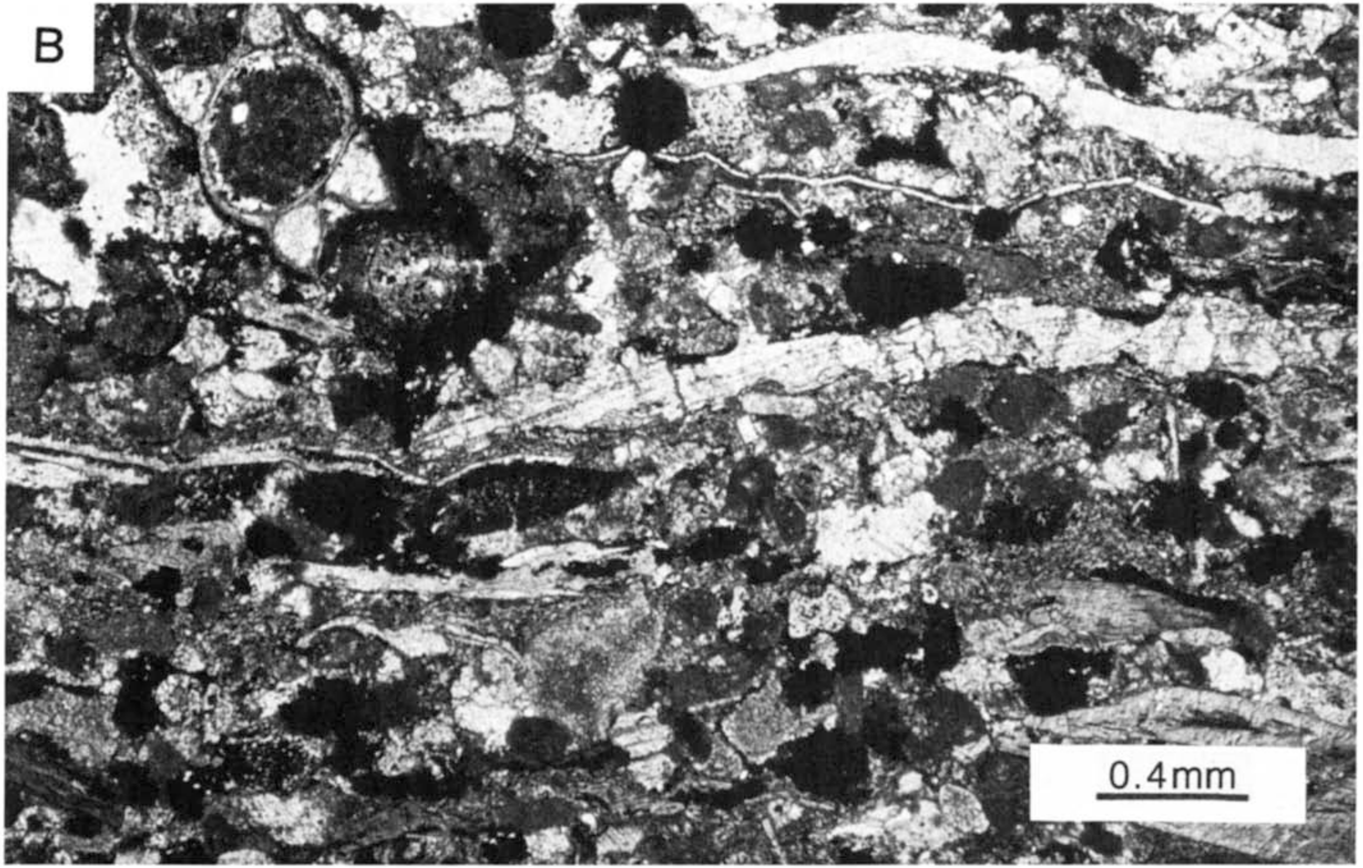
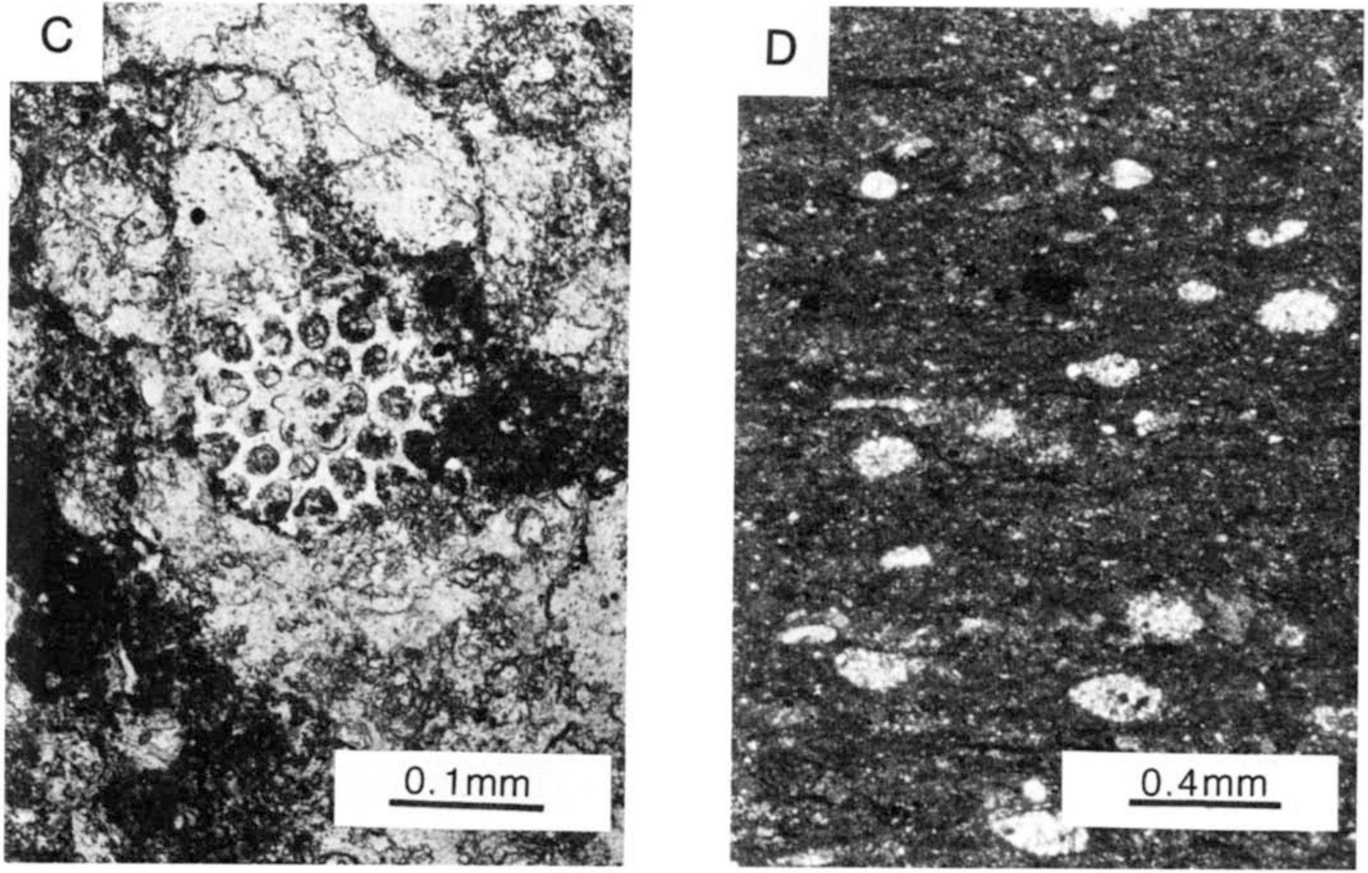


Fig. 5(A) A typical example of a laminated organic-rich shale, showing sparse calcareous fecal pellets. This represents the most commonly occurrring lithology in the sections studies. Toarcian, Rizapol, Belluno Trough, Italy.

Fig. 5 (continued)



(B) Sample from cross-bedded sand composed of mollusc shells, fish teeth, echinoderm fragments, radiolarians, and pyrite. This unit is 1 to 5 cm thick, contains clay lenticles, and is intercalated within millimeter-laminated shales. It clearly attests to some, albeit infrequent, current activity in the basin. Toarcian, near Longarone on the road to Zoldo, Belluno Trough, Italy.



(C) Carbonate layer, intercalated between organic-rich shales, containing abundant carbonate-replaced and occasional siliceous radiolarians: a well-preserved skeleton is visible in the photograph. The limestone is manganese-rich. ?Toarcian, Monte Mangart, Julian Basin, Italy-Yugoslavia border.

(D) Faintly laminated shale containing abundant carbonate blebs interpreted as fecal pellets. Toarcian, Rizapol, Belluno Trough, Italy.

Julian Basin.—The Julian (or Tolmino) Basin, generally considered to be an extension of the Belluno Trough, contains sediments that are well exposed on either side of the Italian-Yugoslav frontier (for example Cavalin and Pirini Radrizzani, 1983). A substantial exposure exists on Monte Traunig on Monte Mangart (fig. 4) just on the Italian side of the border (Cousin, 1981). Some 26.5 m of black, laminated calcareous shales, manganiferous at base, and brown marls rich in pollen are interbedded with limestones containing abundant radiolarians, both siliceous and replaced by carbonate (fig. 5). This outcrop recalls those in the Eastern Alps of Austria-Germany. Minerals identified in these shales are quartz, smectite, and illite. Organic-carbon values range between 0.48 and 1.7 percent, and the manganese contents are high (up to 9.27 percent) in the basal parts of the section (table 1). Microprobe analyses of a dark-weathering carbonate in the central part of the section gave sample compositions of $Ca_{0.918}Mg_{0.024}Mn_{0.053}Fe_{0.005}CO_3$; $Ca_{0.886}Mg_{0.037}Mn_{0.058}Fe_{0.018}CO_3$; $Ca_{0.887}Mg_{0.037}Mn_{0.069}Fe_{0.007}CO_3$. The dating is poor, but a Toarcian age is consistent with what is known of the stratigraphy.

Northern Apennines.—In parts of the Apennines of Marche-Umbria-Abruzzi there is a distinct clay-rich level developed in the Lower Jurassic that passes laterally into Ammonitico Rosso. In Marche-Umbria, these clay-rich sediments have been termed the "Marne di Monte Serrone" by Pialli (1969) and obtain a maximum thickness of 64 m (fig. 4). They include numerous redeposited beds. The central portion, some 24 m thick, is the most clay-rich and is chiefly constituted by gray-green marls. Faunal data show clearly that these marls are of Toarcian age, and the central portion is likely to be just older than the *bifrons* Zone. In the Abruzzi similar greenish-yellow marls occur (Cantelli, Castellarin, and Praturlon, 1978), but, despite careful search, millimeter-scale lamination has not been observed at outcrop: there is no evidence therefore for bottom-water anoxia. Poorly preserved hildoceratids suggest a Toarcian age for this facies. Of note, however, is the description by Dufour and Wenz (1972) of a fossil fish from the Marne di Monte Serrone of Umbria. The fossil is preserved as an impression in blue-gray and red marls and overlain by a turbidite. This occurrence could conceivably be of little significance, but it is nonetheless but one more example of the preservation of a Toarcian fossil fish in clay-rich sediments from the Tethyan region and possibly suggestive of poorly oxygenated depositional conditions.

Correlatives of the Marne di Monte Serrone include the largely redeposited gray limestones and marls exposed at Valdorbia in Marche-Umbria (Donovan, 1958; Bernoulli, 1967; Gallitelli-Wendt, 1969; Elmi, 1981). The clay-rich level at Valdorbia (fig. 4), containing modest amounts of silt-grade quartz, includes both the *falciferum* and *bifrons* Zones, but it is only in the former zone that a positive carbon-isotope anomaly is developed, thought to be related to storage of unusually high quantities of organic matter in the World Ocean at this time (see below;

Jenkyns and Clayton, 1986). Fish remains have also been found in *falciferum*-Zone limestones at this locality. The carbon-isotope stratigraphy for the Valdorbia section, together with an "acid-soluble" manganese, iron, and magnesium profile for that part of the section in gray-limestone facies, is given in figure 6. Unlike some Cretaceous sections (Pomerol, 1983; Schlanger and others, 1987) the manganese peak does not correspond with the highest values of the carbon isotopes. The Mn and Fe profiles co-vary sympathetically to some extent, and both tend to be antipathetic to Mg. Incorporation of Mn and Fe into the lattice was presumably a function of local diagenetic conditions, whereas the carbon isotopes reflect regional storage patterns of organic carbon.

In the Toarcian of the Tuscan Apennines there is a notable enrichment of manganese in the basal levels of a pelagic-carbonate facies known as the Marne a Posidonia (Bencini and Turi, 1974); little stratigraphic detail is available, but the data of Kälin, Patacca, and Renz (1979) indicate the presence of the *bifrons* Zone a few meters above the base of the formation.

Southern Apennines.—In the Lagonegro Zone of the Southern Apennines the pelagic succession ranges from the Triassic to the Cretaceous, although dating is poor (Scandone, 1967; Wood, 1981). In the higher parts of the gray pelagic limestones of the Sirino Formation, classically attributed to the Triassic but now known to extend locally into the mid-Jurassic (de Wever and Miconnet, 1985), shale becomes more abundant and is partly black and millimeter laminated. One sample collected along the roadside between Abriola and Pignola (fig. 4), south of Potenza, has an organic-carbon content of 0.51 percent (table 1). It is possible that this clay-rich unit correlates with the *falciferum*-Zone shales developed elsewhere in Italy, but the complete lack of stratigraphically useful fossils prevents verification of this.

Sicily

A very similar Mesozoic pelagic succession to that at Lagonegro is developed in the Sclafani or Imerese Zone in central Sicily (Broquet, Caire, and Mascle, 1966; Mascle, 1970; Bernoulli and Jenkyns, 1974; Catalano and D'Argenio, 1978). In the section described by Schmidt di Friedberg, Barbieri, and Giannini (1960) from the Crisanti Valley close to Scillato (fig. 4) black shales and siltstones of the basal Crisanti Formation are developed stratigraphically above a sequence of brecciated platform-carbonates (dolomites and dolomitic limestones of Fanusi Formation) which are intercalated in the pelagic succession. The top of these derived platform carbonates is probably attributable to the Early Jurassic, and a Toarcian age for the dark shales is thus consistent with the known stratigraphy. An organic-carbon determination of a black laminated siltstone from this locality gave 0.73 percent (table 1).

Yugoslavia

No undisputed Toarcian organic-rich shales have been recognized in Yugoslavia, but a dark argillaceous interval lying stratigraphically

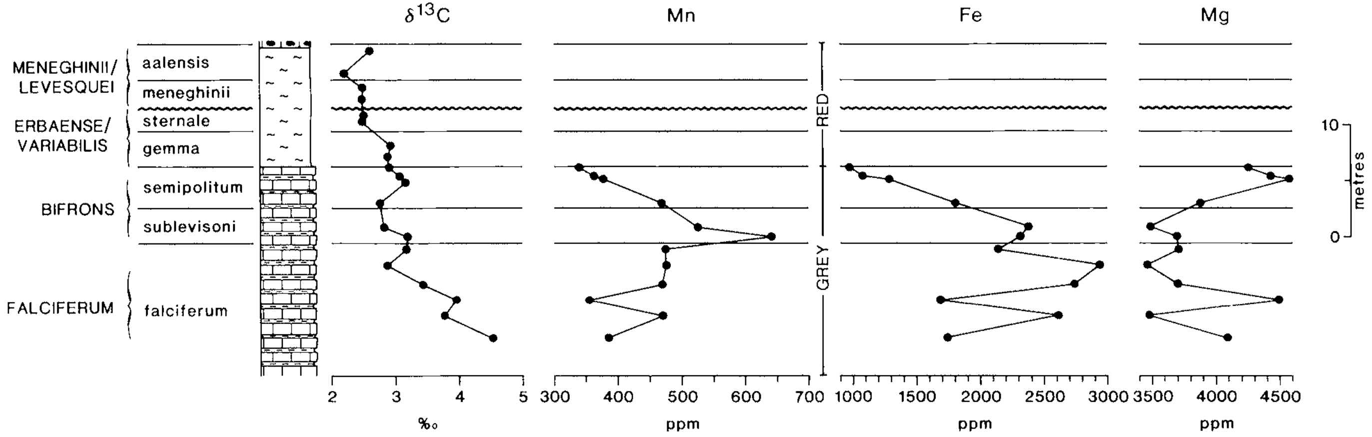


Fig. 6. Geochemical data for the Valdorbia section, Marche-Umbrian Apennines, Italy (fig. 4). Stratigraphic data after Gallitelli-Wendt (1969). Part of the positive $\delta^{13}C$ spike in the *falciferum* Zone is well displayed. Acetic-acid soluble values of Mn, Fe, and Mg have been determined by atomic-absorption flame photometry for that part of the section in gray-limestone facies, where the elements are likely to reside in the carbonate phase. Higher parts of the section are red and contain substantial quantities of manganese-oxide dendrites on bedding planes; these sediments were presumably laid down under oxidizing conditions. The abundances of Fe and Mn in the carbonate lattice covary closely and are generally antithetic to Mg. There is no exact correlation between the carbon-isotope profile and that of iron and manganese.

above a red nodular limestone and below a redeposited oolite occurs, on the main road south of Dubrovnik, a few kilometers east of the junction of the routes to Bar, Budva, and Titograd (fig. 4). Such redeposited oolites typically pertain to the Middle Jurassic and appear to be a reliable, albeit generalized, stratigraphic marker in the Tethyan region (compare Bosellini, Masetti, and Sarti, 1981). The argillaceous interval is thus probably of Early Jurassic age, but no detailed stratigraphy is known to me. The sequence belongs to the Budva Basin, usually thought to be an extension of the Pindos Zone of Greece, and whose pelagic history extends back into the Trias (Aubouin and others, 1970).

Greece-Albania

Lower Jurassic black shales were documented by Renz (1907, 1910) from Greece and southern Albania and have recently been described in great detail by Walzebuck (1982 and ms). The sediments occur in different zones or facies domains (fig. 4) which are defined and described by Aubouin (1959, 1965).

Ionian Zone.—Within the Grecian Ionian Zone (fig. 4) two coeval facies exist in the Toarcian: an organic-rich black shale and the pelagic red nodular limestone known as Ammonitico Rosso (Inst. de Géologie et cetera, 1966). The Ammonitico Rosso is stratigraphically condensed, cut by lacunae, and is attributed to an environment of paleotopographic high or seamount, whereas the stratigraphically expanded black shales are referred to basins. However, the two facies may occur in the same section as at Kouklessi in western Greece (Bernoulli and Renz, 1970) and in parts of Corfu (for example, Petalia, fig. 4). Walzebuck (1982) includes a number of different lithogies under the sack term "black shales" including black limestones made up largely of parallel-laminated shells of the supposed planktonic or pseudoplanktonic bivalve *Bositra buchi;* the lamination has thus been imparted by redeposition and is dissimilar to that found in typical anoxic black or brown shales undisturbed by bioturbation. True organic-rich millimeter-laminated shales are less well developed but are exposed near Chionistra in mainland Greece (black shales about 40 m thick) and on Corfu (Viglatzuri and Siniais, figs 4, 7) where some 20 to 25 m are developed (Walzebuck, 1982 and ms). Organic-carbon contents of these facies from Corfu range up to 2.09 percent (table 1). Typical minerals present are illite and mixed-layer illite-montmorillonite; the locally high quartz contents can be traced to the presence of abundant radiolarians which may constitute up to 50 percent of the sediment. The age of the organic-rich argillaceous section is early Toarcian, although Walzebuck (1982 and ms) suggests that dark-colored sediments extend down into the Pliensbachian and up into the upper Toarcian. In the absence of a detailed ammonite stratigraphy and with the possibility of reworked faunas it is difficult to arrive at a more accurate zonation. In the Viglatzuri section on Corfu the black shales are capped by a redeposited layer containing mostly elements of the *bifrons* Zone and one ammonite of *variabilis* Zone age (Walzebuck, ms); this suggests that the organic-rich facies pertain to the *falciferum* Zone.

At Kouklessi in mainland Greece (fig. 4) one of the best sections of the Ionian Zone is exposed (Kouklessi, sec. A; Bernoulli and Renz, 1970). Locally, above Pliensbachian gray pelagic limestones, 9.3 m of black, green, and gray partly laminated shales containing fish remains occur (fig. 7): quartz, feldspar, calcite, illite, and smectite constitute the fine fraction. Organic-carbon contents are in the range of 1.26 to 3.64 percent (table 1). The shales are interbedded with gray limestones, one of which contains derived grains and is clearly redeposited. The shaly interval is capped by red nodular limestones of Ammonitico Rosso facies containing numerous redeposited horizons. Some 10 m above the shales Bernoulli and Renz (1970) record *Hildoceras* sp., suggestive of a *bifrons*-Zone age. The black shales are thus likely to lie between the top Pliensbachian and *bifrons* Zone, that is, *falciferum*- or *tenuicostatum*-Zone age. From their regional study of the pelagic Jurassic facies in this part of the Ionian Zone both the Institut de Géologie et cetera (1966) and Kottek (1966) concluded that the earliest Toarcian sediments developed in the region are of *falciferum*-Zone age, and it is thus reasonable to attribute the black shales at Kouklessi to this interval. The *tenuicostatum* Zone is either very thin or missing in much of the Alpine-Mediterranean region (Fischer, 1966; Wiedenmayer, 1980; Géczy, 1984).

Pindos Zone.—The Pindos Zone (fig. 4), like the Lagonegro and Sclafani Zones of southern Italy and Sicily, contains deep-marine sediments ranging in age from Triassic to Cretaceous (for example Aubouin, 1965; Baltuck, 1982). Much of the Jurassic is developed as radiolarian chert completely lacking in macrofossils, and high-resolution stratigraphy is hence impossible. However, within or below the main radiolarite sequence in the Pindos Zone, a 15 to 20 m-thick sequence of gray to brown shales containing occasional beds of limestone is typically developed: these are the "Pelites de Kastelli" or Kastelli Mudstones. I have examined this unit along a dirt road near the hamlet of Sirako some 25 km southwest of Ioanina in Epirus, Greece (fig. 4) where parts of the marly succession are millimeter-laminated: quartz, smectite, and illite make up the fine fraction. An analysis for organic carbon in this sequence gave 3.64 percent (table 1). Detailed palynological work by French geologists dates this horizon as pertaining to the late Pliensbachian-Toarcian, and analogies are drawn with similar floras from a horizon in the Southern Alps (Lyberis, Chotin, and Coubinger, 1980). It is herewith suggested that the Kastelli Mudstones are correlative with the "black shales" of the Ionian Zone and are of *falciferum*-Zone age. Such a putative correlation is shown in figure 7. This correlation is at odds with the assignment by de Wever and Origlia-Devos (1982a) of the Kastelli Mudstones to the mid-Jurassic, based on foraminiferal evidence. However, since there is no evidence of mid-Jurassic organic-rich shales anywhere else in the Tethyan region a Toarcian age is deemed more likely.

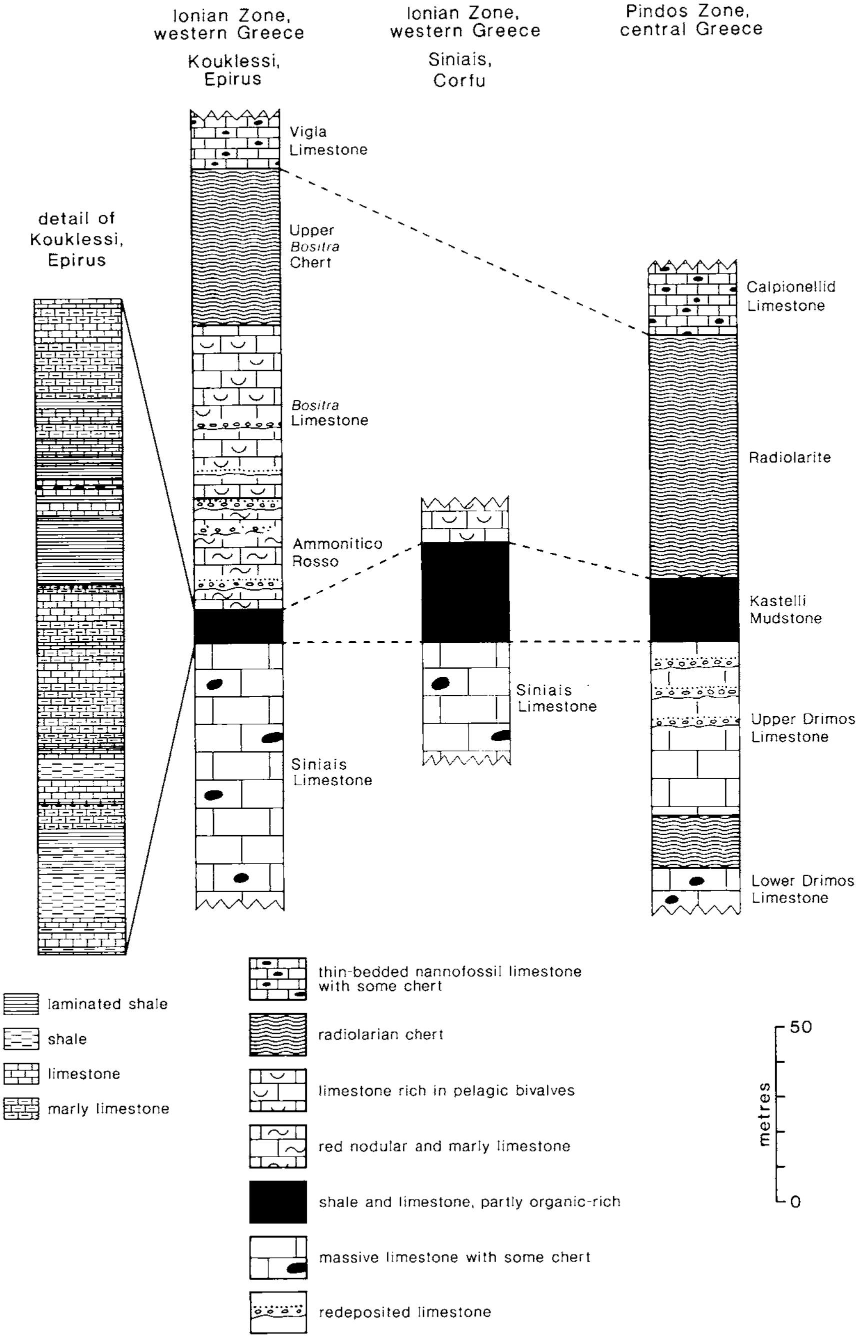


Fig. 7. Suggested correlation scheme of Toarcian organic-rich shales in the Ionian Zone (Kouklessi and Siniais) and Pindos Zone. Data from Bernoulli and Renz (1970), Lyberis, Chotin, and Coubinger (1980), Walzebuck (1982), and personal observations. It is hypothesized that the organic-rich shales are, in both zones, of *falciferum*-Zone age, and that consequently deposition of radiolarian cherts probably began substantially earlier in the Pindos than in the Ionian Zone; radiolarian ages confirm this (Baumgartner, 1984; de Wever and Dercourt, 1985). The Siniais Limestone is of late Pliensbachian age, the Ammonitico Rosso of Toarcian-Aalenian age, the *Bositra* Limestone of Bajocian age, the Upper *Bositra* chert Mid- to Late-Jurassic age, and the Vigla Limestone of Tithonian and lesser age (Bernoulli and Renz, 1970). The Lower Drimos Limestone is of probably Norian or lesser age; the Upper Drimos Limestone of probable Pliensbachian-Toarcian age; the Pindos radiolarite is ?Bajocian-early Tithonian age, and the Calpionellid Limestone of late Tithonian to early Valanginian age (Lyberis, Chotin, and Coubinger, 1980; de Wever and Origlia-Devos 1982 a,b).

As in Austria-Germany, the Toarcian of the Bakony Mtns of northern Hungary contains stratiform manganese carbonates intercalated in dark gray radiolarian-rich shale; the ores have been extensively quarried and mined at Úrkút (fig. 4), and a considerable literature exists on their geology and mineralogy (for example, Grasselly and Cseh Németh, 1961; Szabo-Drubina, 1959, 1962; Cseh Németh and Grasselly, 1966). Where fresh the primary manganese ore is finely laminated, although much of it has been secondarily oxidized at outcrop and in the subsurface. An ammonite fauna from Úrkút, investigated by Geczy (1966a, b), derives from the brown and greenish-gray clay directly overlying the manganese ore; this includes abundant elements of the basal *bifrons* Zone and one genus, *Nodicoeliceras,* formerly thought to be typical of the *falciferum* but now known also to extend up into the *bifrons* Zone (Wiedenmayer, 1980). The presence of *Hildaites,* typical of the *falciferum* Zone but similarly known to extend into the overlying subzone, also provides stratigraphic assignment. The manganese carbonates are thus likely to be of *falciferum*-Zone age or older. A *falciferum*-Zone age is most likely (Géczy, personal commun., 1984).

Presumed correlatives of this manganese and clay-rich horizon occur at Lókút, a classic profile in the Bakony Mtns, and at Tölgyhat Quarry near Lábatlan, Gerecse Mtns (Konda, 1970; Fülop, 1971: fig. 4). At Lókút the exposure virtually fails where the 5 m-thick manganese-bearing marls are present, but excavation reveals a yellow-weathered millimeter-laminated leached shale in parts of the section. Ammonite control is poor here; below the manganiferous clays, and apparently separated by a hiatus, there is a crinoidal limestone containing ammonites of latest Pliensbachian age (*spinatum* Zone: Géczy, 1971). In the Tölgyhat Quarry a similar gray and altered yellow laminated shale, some 50 cm thick and containing secondarily oxidized manganiferous material, is underlain by red limestone of *spinatum*-Zone age and overlain by red nodular limestone containing abundant Toarcian ammonites. Vigh (1961) places the clay seam at the top of the Pliensbachian, but there is no detailed faunal evidence yet available. If the correlation with Úrkút is correct, and there is no other comparable manganiferous clay seam at Tölgyhat Quarry, then this level must also be of *falciferum*-Zone age. Clay-mineral analysis of this clay showed dominant illite with much lesser amounts of kaolinite and chlorite; quartz and albite were accessories (Bernoulli and Peters, 1970).

In the Mecsek Mtns of central Hungary (fig. 4) the Lower Jurassic is of very different character in terms of facies and fauna to that exposed in the Bakony and Gerecse Mountains and apparently derives from the northern margin of Tethys (Géczy, 1973). Typical organic-rich north-European-type Posidonienschiefer, containing abundant fossil fish, are developed in the Toarcian (Fülöp, 1971).

Czechoslovakia

In the Tatrides of Czechoslavakia, attributed to the northern margin of Tethys (Laubscher and Bernoulli, 1977), thinly bedded organic-rich facies are locally developed in the Toarcian (Marianka or Mariatal shales: Andrusov, 1965, p. 145). Ammonites collected from this sequence prove the presence of the basal subzone of the *bifrons* Zone, but no information is available on the ammonite faunas. Within these dark shales there are sporadic occurrences of stratiform manganese carbonates that are secondarily oxidized and concentrated to form ore bodies with typical average Mn values of 20 to 24 percent.

Tunisia

Tunisia provides an example of fossil fish indicating the presence of probable organic-rich shales. From the Tunisian Dorsal, some 15 km south of Pont du Fahs (fig. 4), Gaudant, Rakus, and Stranik (1972) describe a well-preserved fish from sediments dated as Toarcian. The facies are described as gray white-weathering laminated marls interbedded with brown-weathering limestones, a description that recalls similar facies in the Belluno Trough of the Southern Alps. Fish fossils are abundant, and rare ammonites (*Harpoceras*) occur, probably indicative of the top Pliensbachian (*spinatum* Zone) to *bifrons* Zone. However, lateral correlatives of these marls contain a *Dactylioceras anguinum* suggestive of the *falciferum* Zone (Biely and Rakus, 1972: compare Wiedenmayer, 1980), indicating the fossiliferous level may be of this age.

CARBON-ISOTOPE DATA FROM TETHYAN TOARCIAN PELAGIC LIMESTONES

An independent criterion for accurately dating the period of deposition of Toarcian organic-rich facies is offered by carbon isotopes. Following the hypothesis of Scholle and Arthur (1980), it is assumed that an interval of geological time characterized by abnormally high depositional and burial rates of organic carbon (Oceanic Anoxic Event of Schlanger and Jenkyns, 1976) will be characterized by a disturbance in the carbon-isotope reservoir. Organic matter containing reduced carbon is relatively enriched in the lighter isotope ^{12}C over oxidized carbon found in the ocean-atmosphere reservoir: thus abnormally high rates of sedimentation and storage of organic carbon in black shales would withdraw the lighter isotope selectively from the global reservoir, rendering it richer in ^{13}C (for example Schidlowski, 1982). Such a "heavier" isotopic composition would be transmitted to planktonic skeletal carbonates secreted in approximate isotopic equilibrium with ocean water. Thus, if deposition of organic-rich shale was essentially confined to the *falciferum* Zone, this interval should be characterized by a positive carbon-isotope excursion. Analyses of Tethyan pelagic limestones from Hungary, Italy, and Switzerland (fig. 8) show that this is indeed the case (Jenkyns and Clayton, 1986), and the positive shift occurs in the *exaratum* Subzone. Exactly similar phenomena are

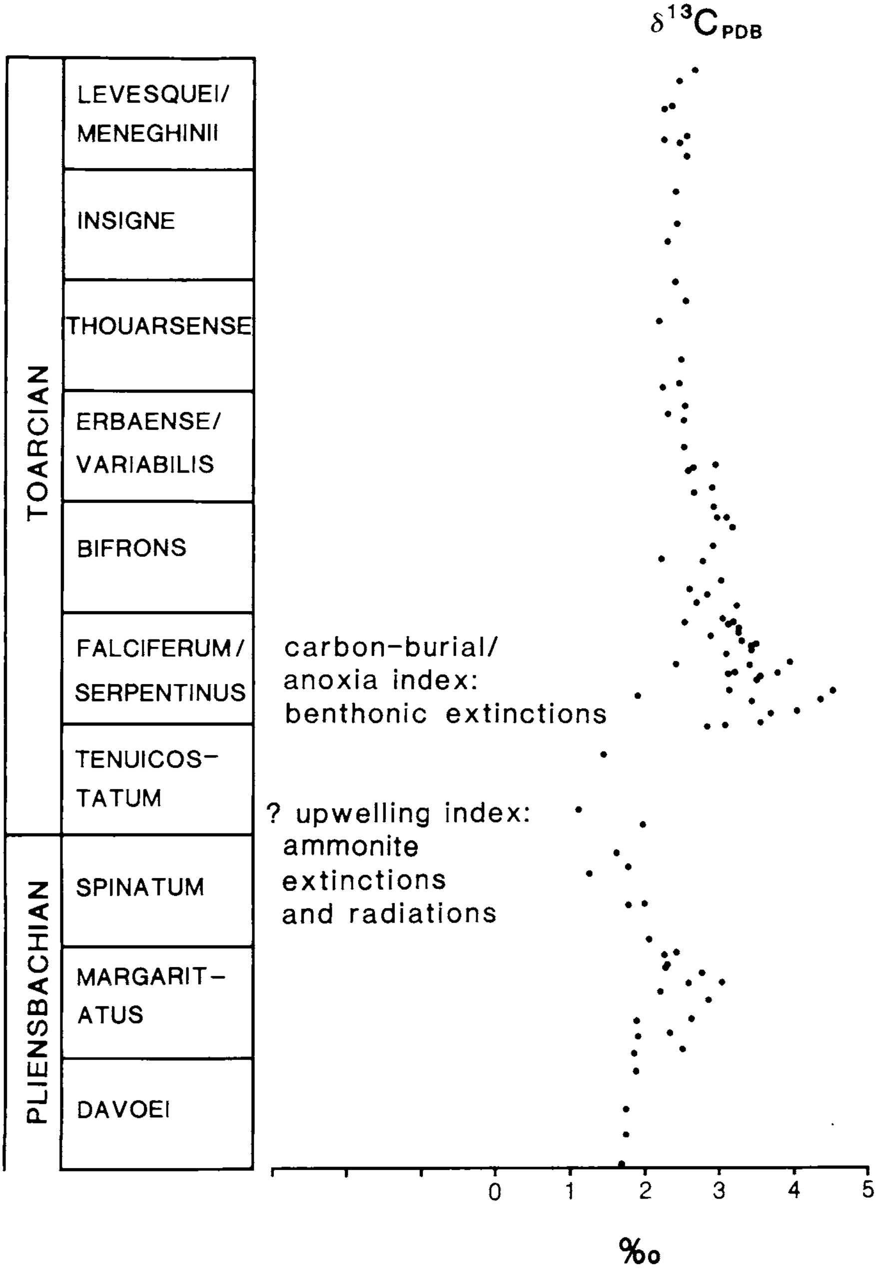


Fig. 8. Carbon-isotopic stratigraphy, across the Pliensbachian-Toarcian boundary, after Jenkyns and Clayton (1986). This composite curve is based on data from four different pelagic-carbonate sections in Italy, Hungary, and Switzerland. Note the positive carbon-isotope shift in the early *falciferum* Zone or *exaratum* Subzone, interpreted as a response to unusually high rates of burial of organic carbon. The correlation with faunal change is discussed later in the paper.

recorded from the Cenomanian-Turonian boundary in the Cretaceous, and the magnitude of the isotopic excursion is similar in both cases (Jenkyns, 1985; Schlanger and others, 1987).

It is important to realize that there are many places where the *falciferum*-Zone is not developed in laminated carbon-rich facies. For example, certain limestones of this age, both in Tethyan and northern Europe, are colored pink to red (Hallam, 1967; Jenkyns, 1985). Indeed the isotopic data in figure 8 have been deliberately assembled from such carbonates in order to eliminate the diagenetic overprint deriving from the presence of organic matter (Jenkyns and Clayton, 1986). Any suspicion, however, that the preceding catalogue of *falciferum*-Zone organic-rich shales constitutes a selective data set is dispelled by the carbon-isotope curve that unambiguously shows that excess organic carbon entered the burial stage during this time. Furthermore, the *falciferum*-Zone black-shale record is not confined to northern Europe and the Tethyan region as detailed below.

TOARCIAN BLACK SHALES IN EXTRA-ALPINE AREAS

Organic-rich shales of *falciferum*-Zone age have been recognized in a number of places outside the north European and Tethyan domains. None of them, however, occurs in pelagic facies; typically they resemble the Posidonienschiefer of Germany in both lithology and, to some extent, in fauna. They are plotted on a global reconstruction for the stage in figure 9.

Alaska, U.S.A.

On the Arctic Slope of northern Alaska the Kingak Shale is developed as a dark gray mudrock of Early Jurassic and younger age (Imlay, 1952). Organic-carbon values rise to about 3.5 percent in the Prudhoe Bay area (Magoon and Claypool, 1984). In this region, a number of fossils were collected from pyritic concretions in thin-bedded black shales by de Leffingwell (1919). The fauna included two specimens of *Harpoceras* suggestive of the top Pliensbachian (*spinatum* Zone) to *bifrons* Zone. From a borehole in the Barrow region, farther to the west, Imlay (1952) recorded the presence of *Dactylioceras* and *Peronoceras* in the basal levels of the Kingak Shale, similarly indicating an early Toarcian age.

Support for the presence of the *falciferum* Zone in the Kingak Shale comes from the unlikely source of carbon-isotope ratios in kerogens. Such values from organic matter in the Prudhoe Bay are extremely negative (-33 to -31 permil$_{\mathrm{PDB}}$: Magoon and Claypool, 1984). Study of carbon isotopes in kerogens from a range of marine Phanerozoic sedimentary rocks shows such values to be extraordinarily rare, except in the Lower Jurassic (Lewan, 1986). Isotopic ratios as low as -32 and -33 permil are, however, typical for organic matter of *falciferum*-Zone age in northern and Tethyan Europe (Küspert, 1982; Jenkyns and Clayton, 1986). Where stratigraphic refinement is possible the most negative values can be shown to derive from organic matter of *exaratum*-

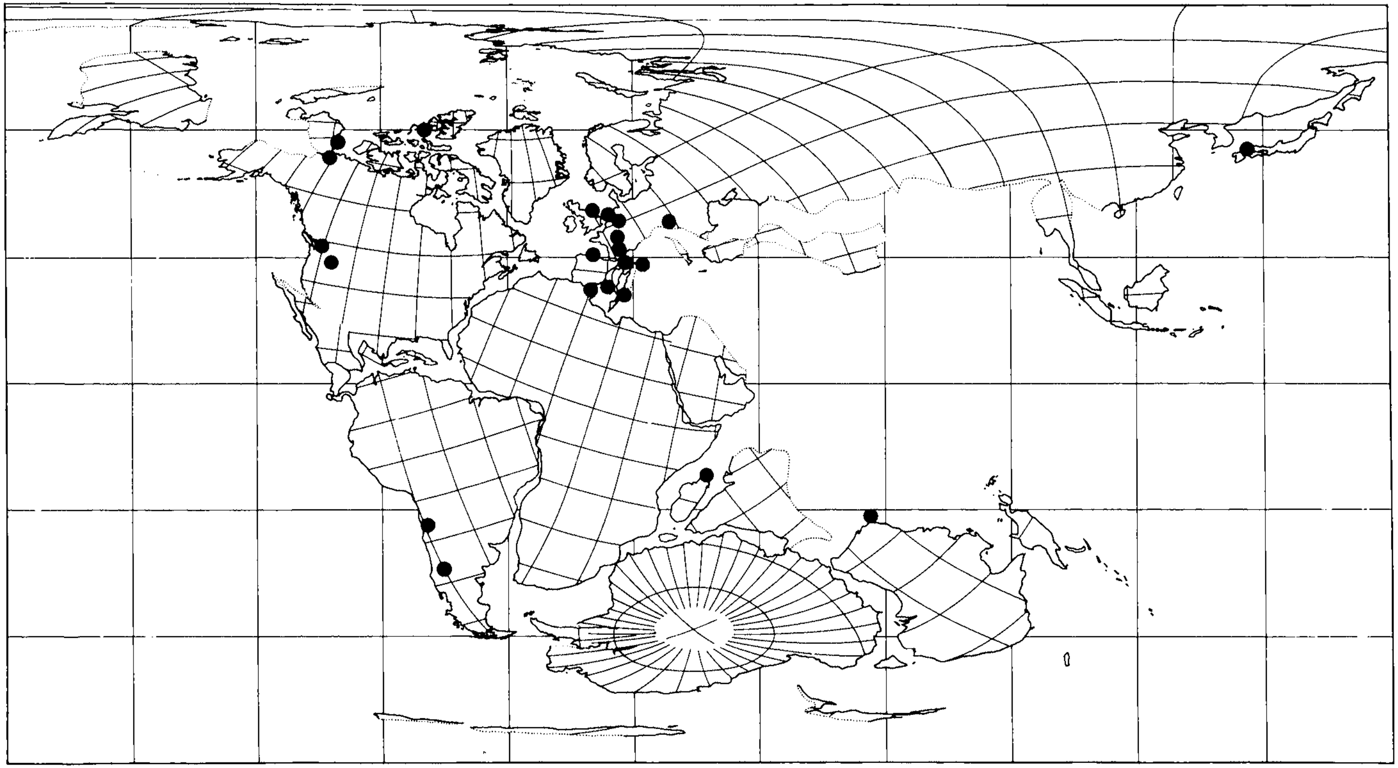


Fig. 9. Occurrences of Toarcian organic-rich shales set in a Smith-Hurley-Briden-type (1981) world matrix, generalized for Europe. Data are given in text. Toarcian map at 190 my BP courtesy of A. G. Smith. The global spread of such facies, in many cases shown to be of *falciferum*-Zone age, is notable. Further study will undoubtedly reveal other localities. Except for Tethyan examples, all organic-rich shales are of epicontinental Posidonienschiefer facies. The known distribution of these sediments shows limited correlation with the postulated Pliensbachian upwelling centers of Parrish and Curtis (1982).

Subzone age. If, as suggested here, these anomalously low values are uncommon enough to have stratigraphic use, they also indicate the presence of lower *falciferum*-Zone carbon-rich facies in the Prudhoe Bay area of Alaska.

Canada

The Fernie Group of the Canadian Rocky Mountains and Foothills (Alberta and British Columbia) includes a Toarcian facies described as "dark thin-bedded commonly papery shales, not unlike the German *Posidonomya* shale of the Toarcian" (Frebold, 1957). This black shale, the so-called Poker-Chip Shale, includes fossils suggestive of the *falciferum, bifrons* and *variabilis* Zones (Frebold, 1976; Hall, 1984). This unit, some 10 to 38 m thick, is one of the most extensive in the Fernie Formation. It is gray to black in color, finely laminated, and, in the most faunally restricted facies, organic-carbon contents vary between 1.3 and 4.9 percent (Stronach, 1984). The macrofauna consists of belemnites, flattened ammonites, and the bivalve *Bositra;* the microfauna comprises radiolarians and rare agglutinated Foraminifera. This description certainly recalls the Posidonienschiefer of Germany.

Similar facies are exposed in southern British Columbia close to the international boundary with Washington State (Frebold, 1959).

In the Yukon and adjacent Northwest Territories the Manuel Creek Formation of the Bug Creek Group includes Lower Toarcian black organic-rich shales containing calcareous and pyritic concretions (Poulton, Leskiw, and Audretsch, 1982; Poulton, 1984): the presence of the *falciferum* Zone has been proved (Frebold, 1975). In the Sverdrup Basin of the northwest Canadian Arctic Archipelago the Toarcian Savik Formation (= Jameson Bay Formation of Embry, 1984) is partly in dark gray to green shale facies, locally papery and thinly laminated; pyrite, phosphate, and glauconite are accessory minerals (Balkwill, 1983). The sediments are carbon-rich with values of 5 percent TOC recorded locally. The basal levels of the Savik (or Jameson Bay) Formation are thought to be of *falciferum*-Zone age in the central part of the basin.

The total lateral extent of this North American Toarcian black shale is considerable, extending intermittently over much of western Canada from its border with the United States to north of the Arctic Circle (fig. 10). Such a distribution is greater than that of the Posidonienschiefer in northern Europe.

Japan

Lower Jurassic black shales are represented in the Nishinakayama Formation of the Toyara Group of southwest Japan, the stratigraphy and fauna of which have been described by Hirano (1971–73). The lower and middle part of the Formation is finely laminated, contains pyrite, and is certainly equivalent in age to the *falciferum* and adjacent Zones, although correlation of Japanese ammonite stratigraphy with that of northern Europe presents some difficulties. Tanabe and others (1982, 1984) and Tanabe (1983) have commented on the great similar-

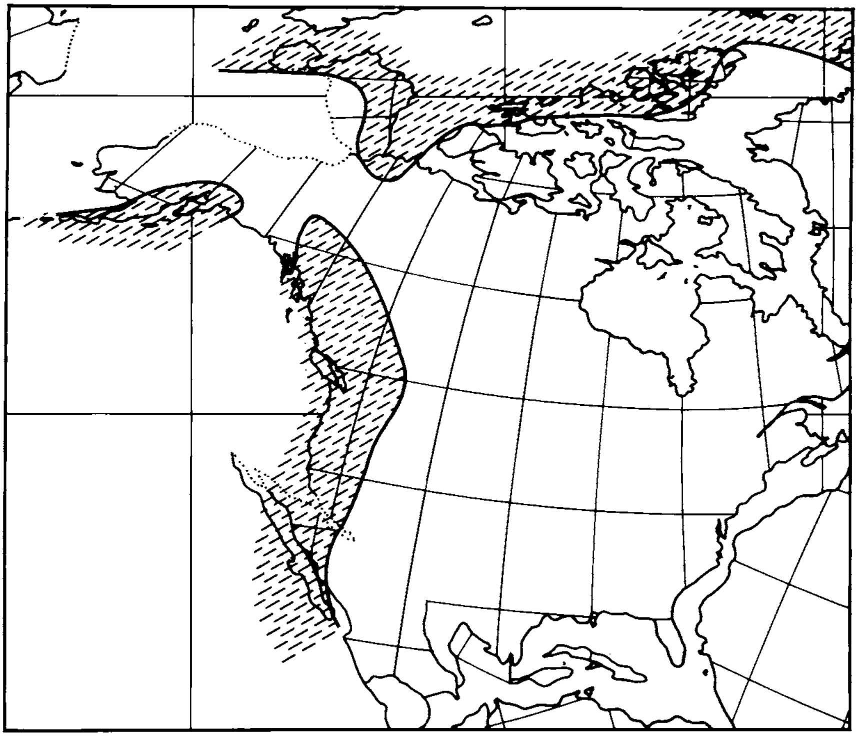


Fig. 10. Extent of Toarcian shelf seas in western North America, after Imlay (1984). Base map as in figure 9. Posidonienschiefer-type facies occur from the Canadian-United States frontier to north of the Arctic Circle.

ity of the Nishinakayama Formation, in terms of facies, fauna, and geochemistry, to the Posidonienschiefer of southern Germany: they refer to certain of the Japanese facies as oil shales and suggest deposition locally under euxinic conditions.

Madagascar

In northern Madagascar the Lower Toarcian is locally represented by laminated black shales rich in lignite (Besairie and Collignon, 1972). The descriptions of these facies suggest the sediments are extremely similar to those of equivalent age in northern Europe. In particular the mention of abundant calcareous nodules and pyrite recalls descriptions of the Jet Rock and Posidonienschiefer. The ammonites described from the Diégo Basin (for example, *Harpoceras* cf *serpentinum*) include forms of early *falciferum*-Zone age; the bivalve *Posidonia alpina* (= *Bositra buchi*) has also been recorded. In the Majunga Basin a rich fauna of varied species of *Bouleiceras* accompanied by *Programmoceras* is indicative of the *tenuicostatum* or early *falciferum* Zone (compare Howarth, 1973).

Australia

Drilling in the offshore basins of northwest Australia has revealed substantial thicknesses of marine Lower Jurassic sediments that are not dissimilar to those of epicontinental northern Europe. In the so-called Dampier Sub-Basin, the Toarcian part of the section locally contains marine black shales, and the microfaunal assemblages indicate their deposition under poorly oxygenated bottom-water conditions (Crostella and Barter, 1980). The Lower Jurassic section has probable correlatives in the Dingo Claystone cored from onshore Western Australia (McWhae and others, 1956). Unfortunately there is no record of the black shales having been dated to the zonal level.

Argentina

In the Lower to Mid-Jurassic Los Molles Formation of southwest Argentina (Nequén) marine black shales and limestones are recorded (Riccardi, 1983). From the basal levels of this Formation, von Hillebrandt (1973) has recorded ammonites, including *Bouleiceras,* of *tenuicostatum* or *falciferum*-Zone age from a finely bedded claystone. The presence of organic-rich sediments and the bivalve *Posidonia alpina* (= *Bositra buchi*) in closely associated strata is confirmed by Volkheimer (1973). Bituminous pyritic limestones of Sinemurian, Pliensbachian, and Toarcian age are also recorded from adjacent parts of Argentina and Chile (Biese, 1957; Volkheimer, 1970; von Hillebrandt and Schmidt-Effing, 1981).

Other Areas

Other areas flooded by Early Toarcian seas include parts of Asia, and *Posidonienschiefer* facies might be expected to occur there (for example, Hallam, 1981). Records, however, are poor, although Lefeld (1978) does refer to a Lower Jurassic black shale from northern Mongolia.

TOARCIAN ZONATION AND DURATION OF THE OCEANIC ANOXIC EVENT

The conventional and isotopic stratigraphy described above is taken as suggesting that a period of anomalously rapid sedimentation and burial of organic carbon took place during the *falciferum*-Zone. The global spread of *falciferum*-Zone black shales, embracing several continents and affecting not only shelf seas but deeper-water continental margins allows interpretation of this phenomenon as an Oceanic Anoxic Event (OAE). Such phenomena have been documented for the Cretaceous by Schlanger and Jenkyns (1976), Jenkyns (1980), and Schlanger and others (1987).

Attempts to date the duration of the *falciferum* Zone OAE hinge on the assumption that an ammonite zone represents approx 1 my. Rigid adherence to this simple-minded idea leads to a remarkable flexible duration for the Toarcian stage itself. Adopting the antiquated scheme of Arkell (1956) for the Jurassic, which split the Toarcian into only four zones, van Hinte (1976) arrived at a duration of 4 my for the Toarcian. Following the scheme of Mouterde and others (1971) and Gabilly (1976), which gives twice as many zones for the stage, Kennedy and Odin (1982) suggested a duration of 8 my. Using the modified scheme of Howarth *in* Cope and others (1980), six zones spanning 6 my are preferred by Harland and others (1982). Greater sophistication and accuracy may perhaps be obtained by recourse to the summation of subzones, but problems arise when successions between northern and Tethyan Europe are compared. For example, the *tenicostatum* Zone contains four subzones in northeast England, yet this horizon is vanishingly thin over the whole of the Tethyan region. Does it in fact represent a relatively short period of time, as suggested by Géczy (1984), or was a regional unconformity developed across the Tethyan continental margins during this interval? Great uncertainty exists over the absolute duration of zones.

The *falciferum* Zone is readily split into two or more subzones in Northern Europe, whereas resolution is generally only possible to the zonal level in the Tethyan region. Thicknesses of strata representing this interval in the Alpine-Mediterranean domain suggest that it constitutes an "average" type of zone: it is not anomalously thin like the *tenuicostatum* Zone or excessively thick as the *bifrons* and *levesquei* Zones may be (Géczy, 1984). For the purposes of this discussion I thus conventionally assume a duration of 1 my for the *falciferum* Zone.

The focus of early Toarcian organic-rich sedimentation certainly lay within this zone. If we assume furthermore that the Tethyan outcrops are of identical age to those in northern Europe, as demonstrated at one locality in the Belluno Trough, northeast Italy (Jenkyns and others, 1985), then the most organic-rich sedimentation was concentrated in the lower half (*exaratum* Subzone) of the *falciferum* Zone (Morris, 1979; Küspert, 1982). The carbon-isotope data from the Tethyan region (fig. 8) also suggest that the maximum withdrawal rate of isotopically light carbon from the marine reservoir took place during the earlier half of the *falciferum* Zone, although this could be simply reflecting depositional patterns in northern rather than Tethyan Europe, or even global events. However, given that these sedimentary and isotopic anomalies, within the present level of stratigraphical resolution, are apparently confined to the period of time represented by half an ammonite zone, the duration of the early Toarcian OAE is suggested as approx 500,000 yrs. A comparable figure has been suggested by Arthur, Schlanger, and Jenkyns (1987) for the Cenomanian-Turonian Oceanic Anoxic Event.

EARLY JURASSIC PALEOGEOGRAPHY OF THE SOUTHERN ALPS AND DEPOSITION OF BLACK SHALES

Most instructive in terms of depositional models for Toarcian organic-rich facies are the ancient "starved" continental margins of the Alps where pelagic deposition took place, and a wide range of relative paleobathymetric levels may be reconstructed. The known distribution and detailed stratigraphy of lower Toarcian organic-rich shales in the Southern Alps are plotted in a paleogeographic framework in figure 11. The paleogeographic scheme, valid for much of Jurassic-Cretaceous time, is reconstructed using fault-lines known to have been active during the Mesozoic and the differing stratigraphies of the regions (for example, Bernoulli and others, 1979; Winterer and Bosellini, 1981; Bosellini, Masetti, and Sarti, 1981). Basinal successions are very thick (for example, ~4 km pelagic Jurassic in part of the Lombardy Basin, Bernoulli, 1964) and contain numerous slumps and turbidites, whereas the Trento Plateau is characterized by stratigraphically condensed sequences lacking evidence of redeposition and commonly containing ferromanganese nodules and subtidal cyanobacterial stromatolites (Drittenbass, 1979; Massari, 1981; Ogg, 1981). There seems little doubt, therefore, that the Trento Plateau lay in shallower water than the surrounding basins. Thus it is of particular interest that *falciferum*-Zone organic-rich shales were deposited on the eastern edge of this edifice: they were not confined to the basins. The western edge of the Plateau was still accumulating oolitic sediments at this time and hence lay in water too shallow to experience oxygen starvation. A parallel phenomenon is apparent with the Cenomanian-Turonian Anoxic Event which left a black-shale record on both the western and eastern edge of the Plateau (Jenkyns, 1980, 1985; Arthur and Premoli-Silva, 1982).

Distribution of the organic-rich shales within the Lombardian Basins is also intriguing. In the Breggia Gorge section (fig. 4) and adjacent areas of the Generoso Trough (fig. 11) the *falciferum* Zone is represented by red Ammonitico Rosso facies (Wiedenmayer, 1980). Some 25 km to the east, black shales of identical age are exposed in the Val Cepelline and Val Varea in the Brianza region (fig. 4). The Pliensbachian-Toarcian stratigraphy in this area is more condensed than that of the Breggia Gorge (Bernoulli, 1964; Jenkyns and Clayton, 1986), and the sediments were presumably deposited on less subsident and possibly topographically higher ground. Thus it is probable that black shales were not deposited in what was the deepest part of the Lombardian Basin. In the case of the black shales exposed around Albenza (Monte Brughetto, Col Pedrino, and related sections, fig. 4) relative bathymetry is not so apparent. Gaetani and Poliani (1978) place these black shales in the area of relative maximum sedimentation rate and probable deepest water in the Albenza region. However, this area subsided relatively little compared with the Generoso Trough in Hettangian-Pliensbachian time and may have lain at shallower depth during the early Toarcian. A geochemical correlation between the carbon isotopes in the kerogen and the calcium-carbonate content of the sediments at Monte Brughetto has been interpreted as indicating a change in the relative abundance of calcareous and non-calcareous plankton during the *falciferum* Zone, with the latter exhibiting a different pattern of carbon-isotope fractionation (Jenkyns and Clayton,

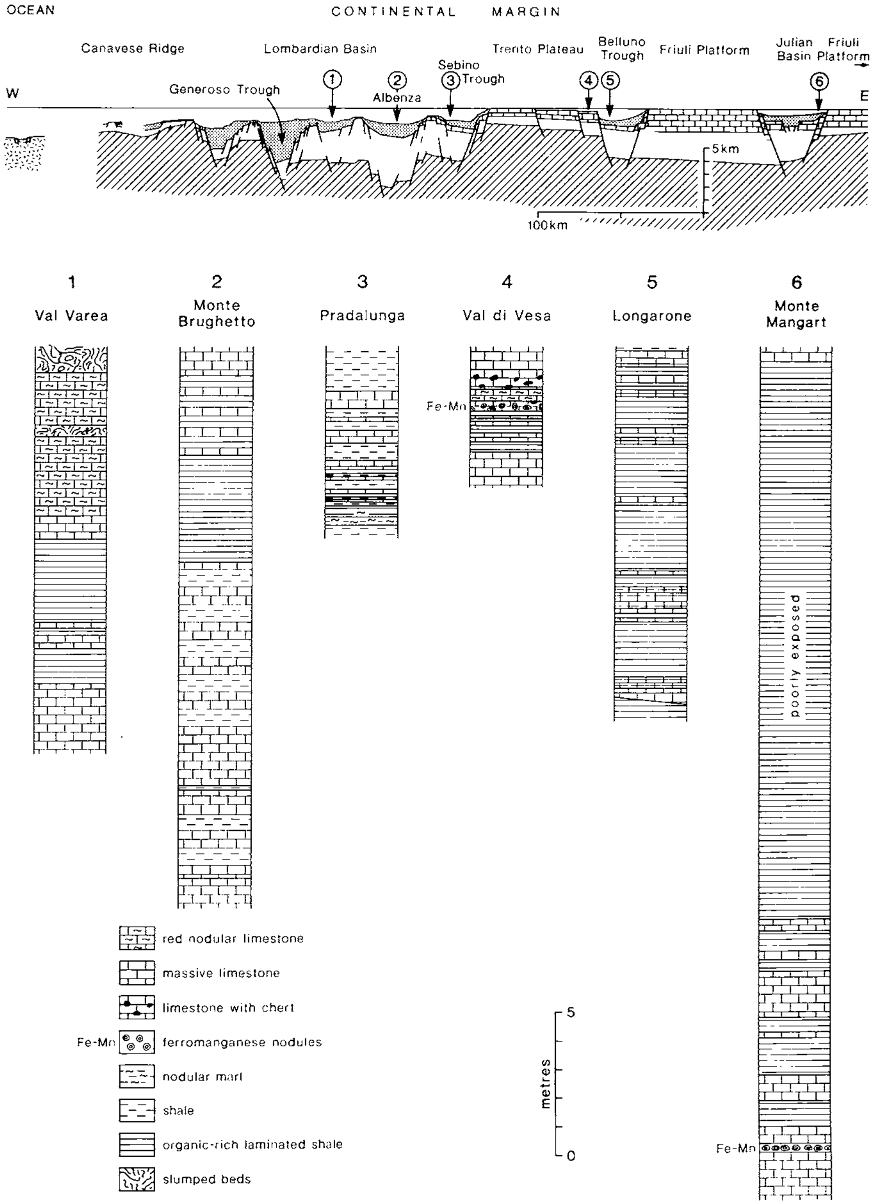


Fig. 11. Sections measured in the Southern Alps, Italy, related to a tentative paleogeographic scheme. This scheme is modified after Bernoulli and others (1979) and Kälin (personal commun., 1983). *Falciferum*-Zone organic-rich shales may have formed preferentially on paleotopographic highs (for example Trento Plateau) and on the flanks of basins; they are absent in the Generoso Trough where red nodular limestones (Ammonitico Rosso) are developed. Such a configuration is suggestive of an oxygen-minimum model for this sector of the Tethyan continental margin.

1986). Such a correlation would not be found if redeposition of calcitic ooze had taken place at this site, hence implying an area of relative paleotopographic high. Relative bathymetry is less clear in the Sebino Trough represented by the black shales around Lonno, Nembro, and Pradalunga (figs 4, 11).

The lack of evidence for *falciferum*-Zone anoxic waters in the presumed deepest reaches of the Generoso Trough coupled with positive indications of their having impinged on the eastern edge of the Trento Plateau implies that the mid-part of the water column was primarily affected by oxygen depletion. This suggests that the oxygen-minimum model is best suited to explain the distribution of these black shales and implies a locus of high plankton productivity producing, via bacterial degradation of organic matter, intense oxygen demand in the water column (compare Demaison and Moore, 1980).

A possible model is given in figure 12A with the North European shelf acting as a locus of particularly high productivity and, consequently, as the fount of poorly ventilated waters. The relatively high values of organic carbon in north European *falciferum*-Zone shales (typically 5–15 percent TOC) versus those in Tethyan Europe (typically 0.5–3 percent TOC) are consistent with this hypothesis. Longer transport paths of organic matter falling through a deeper Tethyan water column, oxygenated in its upper layers, may explain the generally low values found in these areas. The viability of this overall model is illustrated by recent quasi-horizontal seaward transport of oxygen-depleted water masses from the fertile shelf off Peru (Pak, Codispoti, and Zanefeld, 1980). Deepening of the Toarcian epicontinental sea to allow upwelling may explain the coincidence in time noted between transgression and the Oceanic Anoxic Event (Hallam, 1981): changes in climate and the paths of major current-systems, influenced by rifting in the Tethyan-Atlantic System, may also have played a role (Jenkyns, 1985; compare Southam, Peterson, and Brass, 1982; Summerhayes, 1987). In the global scheme for the Pliensbachian reconstructed by Parrish and Curtis (1982), upwelling is predicted for western North and South America, Madagascar, and western Australia, but not Europe and Japan (compare fig. 9).

An alternative model (fig. 12B) envisages a modest increase in productivity during *falciferum*-Zone time in both epicontinental and Tethyan Europe with production of an extensive oxygen-minimum zone; in this case, however, the preservation of organic matter is enhanced on the north European shelf by salinity stratification effected by southward-draining major fluvio-deltaic systems. The recognition of Lower to mid-Jurassic deltaic successions in the North Sea and adjacent regions shows this to be a viable hypothesis (Hancock and Fisher, 1981; Fleet and others, 1987). The two models encapsulate the "productivity versus preservation" dilemma which affects interpretation of many organic-rich shales (Demaison and Moore, 1980).

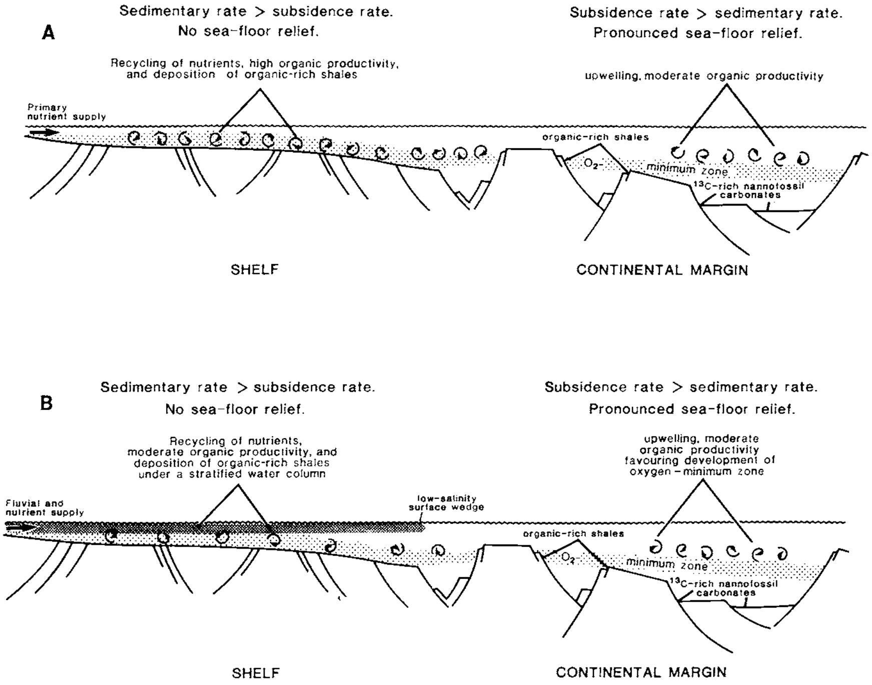


Fig. 12(A) Tentative model, after Jenkyns (1985), for generation of an oxygen-minimum zone in the north European shelf and proximal continental-margin regions of Tethys. Nutrient supply was presumably abundant in shelf regions to allow high productivity and deposition of organic-rich muds in many areas. On the block-faulted margin, deposition of organic-rich facies was favored on the edge of topographic highs and on the flanks of basins. Above and below the oxygen-minimum zone, red limestones were deposited; such facies carry a positive δ^{13}C isotopic signature.

(B) Model showing uniform generation of an oxygen-minimum zone in epicontinental and Tethyan Europe due to modest increase in productivity but enhanced preservation on the shelf due to water stratification effected by a deltaically derived fresh-water wedge.

The first model (fig 12A) is, however, favored, as the relative rise in sealevel documented for the *falciferum*-Zone (Hallan, 1981) would have caused northward retreat of the deltaic systems, and it is difficult to understand why salinity stratification should have been intensified at this time particularly in areas as distant from the North Sea as the southwest border of the Massif Central, France where organic-rich shales are well developed (Cubaynes and others, 1984).

GEOCHEMICAL IMPLICATIONS

The implications of the oxygen-minimum model may be discussed in the context of the geochemistry of manganese. As stated above, Mn–Fe–rich carbonates are associated with many Toarcian organic-rich shales and are locally present in economic quantity, as in Hungary (table

1). Toarcian volcanicity, for which there is evidence in the Tethyan region, has been suggested as a source of manganese (Jenkyns, 1970; Germann, 1972). However, recent oceanographic studies suggest that it may not be necessary to appeal to a special local source of manganese (such as a hydrothermal spring) to explain these deposits, for this element is relatively concentrated in recent oxygen-minima of the Pacific (Klinkhammer and Bender, 1980). Detailed studies suggest that 70 percent of dissolved manganese in the northeast Pacific oxygen minimum is rapidly supplied by lateral advection from the continent (Martin and Knauer, 1984, 1985).

Manganese is also concentrated immediately below the oxic-anoxic interface in the Black Sea: the dissolved Mn in the anoxic layer diffuses and is advected upward where it precipitates as MnO_2 in the oxygenated water (Brewer and Spencer 1974). The particles then sink and redissolve in the reducing environment. Thus waters particularly rich in dissolved manganese may characterize the upper boundaries of intense oxygen minima. And, where such minima intersect the sediment-water interface, the distinctive geochemical signature may be transmitted into early diagenetic carbonate. Were anoxic conditions to exist at the sea floor, manganoan carbonates would presumably form both at and below the sediment-water interface (compare Suess, 1979; Berner, 1981a,b). The possible relationship between deposition of manganese carbonates and impingement of oxygen minima during the Cenomanian-Turonian Oceanic Anoxic Event has been explored by Stamm and Thein (1982), Frakes and Bolton (1984), and Force and others (1986) and is relevant to an understanding of Toarcian metalliferous deposits.

Determining whether or not the oxygen-minimum was ever completely devoid of oxygen by geochemical means is a delicate enterprise. An attempt in this direction was made by Leventhal (1983) who examined geochemical data from the Black Sea and suggested that ancient organic-rich sediments containing a critical quantity of excess sulfur could be identified as having been deposited within euxinic waters containing free hydrogen sulfide. One important limiting factor to this simple relationship would appear to be the availability of iron, which can govern the extent of pyrite formation (Berner, 1984; Gibson, 1985). The extent and influence of diagenetic mobilization of pyrite is also unknown. Relevant data from Toarcian organic-rich shales are shown in table 1 and figures 13 and 14. All samples are millimeter-laminated and lack benthos. Figure 13 demonstrates that, above a sulfur content of ~0.5 percent, there is good correlation of Fe and S, suggesting that availability of reactive iron may have been a limiting factor in the formation of iron sulfides: such a relationship is typical of euxinic shales and those limestones and cherts that contain negligible iron (Berner, 1984; Raiswell and Berner, 1985, 1986). Although a certain variable quantity of non-reactive iron is locally present in the Toarcian samples, and some sulfur may have been lost during weathering, the slope suggests that pyrite is the dominant phase; indeed its presence can be

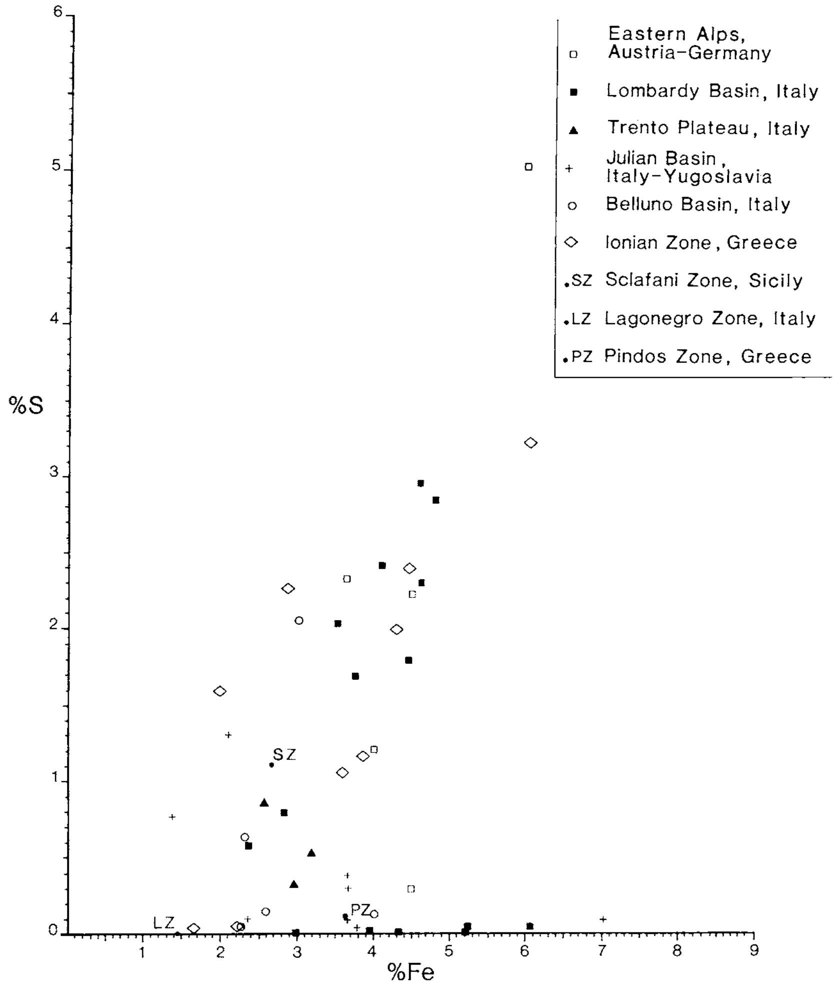


Fig. 13. Plot of total iron (determined by atomic absorption flame photometry) against sulfur (determined by a Ströhlein Coulomat: details given under table 1) for Toarcian organic-rich shales. Correlation is good above a sulfur content of 0.5 percent; iron may have been a limiting factor in iron sulfide formation. Such a relationship is typical for euxinic sediments (Raiswell and Berner, 1985). Fe and S correlate in a ratio consistent with the presence of pyrite.

confirmed by x-ray diffractometry. The excess iron may perhaps be held in clay minerals or carbonates, as is presumably the case with those samples containing negligible sulfur and substantial iron. The local presence of such carbonate phases is confirmed by microprobe analysis of samples from Italy (Belluno, Julian, and Lombardy Basins) and those described from Austria-Germany, although the quantities of substituted

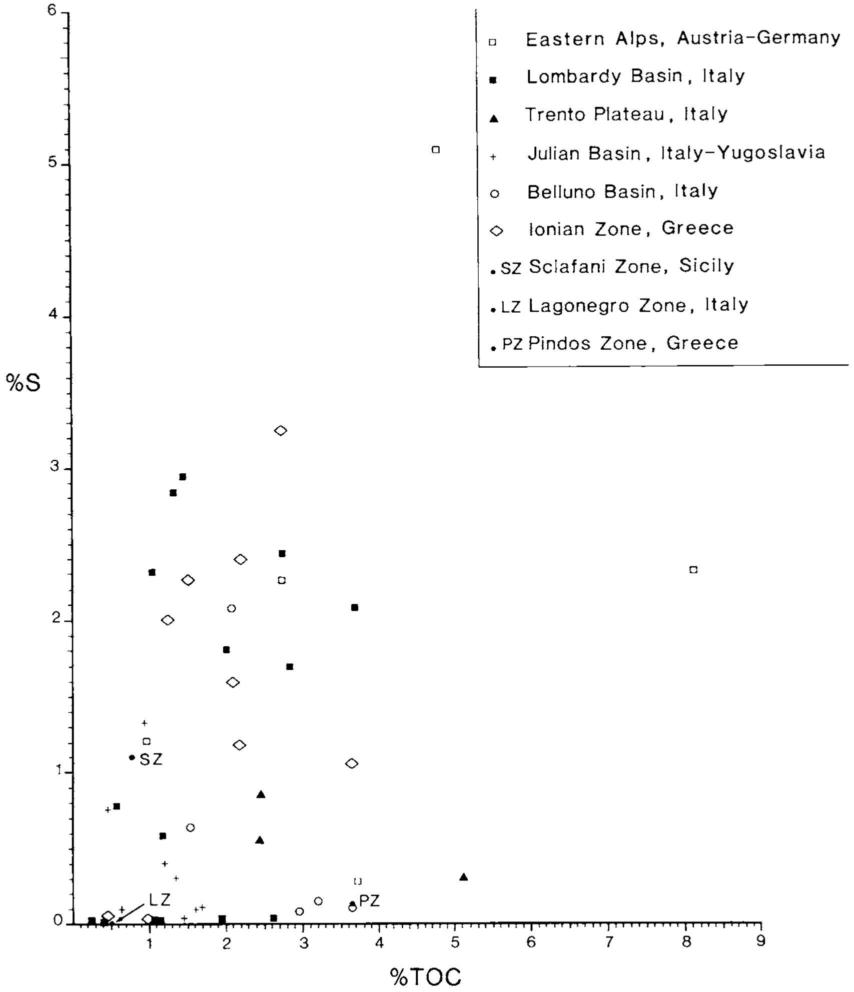


Fig. 14. Plot of total organic carbon (TOC) against sulfur for Toarcian organic-rich shales; no apparent trend is recognizable, even within any one basin, and, interpreted at face value, such data could suggest deposition in anoxic, normally oxygenated and even fresh-water environments (Berner and Raiswell, 1983; Leventhal, 1983). The latter interpretation is clearly untenable and indicates that carbon-sulfur ratios, without consideration of other factors, such as carbonate content, cannot be used as a universal indicator of paleosalinity. A general lack of correlation between TOC and sulfur is, however, typical of many euxinic sediments (Berner, 1984).

Fe are not large. Those samples containing abundant Mn in the carbonate lattice may have formed in an anoxic non-sufidic diagenetic environment (Froelich and others, 1979; Berner, 1981a,b; Coleman, 1985). As the more manganiferous levels generally occur in the basal portions of the black-shale sections, and the more organic-rich sediments higher up, the implication is that the intensity of oxygen-depletion increased after the onset of the Toarcian event. Such increased oxygen depletion could have resulted from the expansion or migration of the oxygen-minimum zone such that the sediment-water interface was no longer bathed in the Mn-rich waters concentrated in the upper boundary layers.

The plot of TOC against sulfur (fig. 14) when superposed against the 'anoxic' and 'oxic' fields of Leventhal (1983) shows a remarkable scatter of values. Such lack of correlation is typical for euxinic shales (Berner, 1984). Some samples with low sulfur values even fall into the "lacustrine" or non-marine field for recent sediments given by Berner and Raiswell (1983). Such low values may be explicable in terms of weathering and, in some cases, elevated carbonate contents (Berner and Raiswell, 1984). Certainly there is no consistent pattern between the sulfur and TOC values in any one basin. In summary, these data are in harmony with the view that an oxygen-minimum zone, of variable intensity in space and time, existed in Tethyan continental margins during the *falciferum* Zone. It is probable that some of these waters were euxinic, containing free hydrogen sulfide, and diagenesis proceeded accordingly; equally some waters were anoxic but had not reached the sulfate reduction stage and non-sulfidic diagenetic minerals could form.

Relevant to the concept of an oxygen-minimum zone are the generally higher levels of organic carbon and hydrogen indices (compare Tissot and Welte, 1984) in north European Toarcian shales versus those (Eastern Alps excepted) in the Tethyan region (Jenkyns, 1985). Organic productivity was presumably high in northern Europe at this time, and oxygen-depleted waters could have been exported to the Tethyan continental margins from shelf-sea sites (fig. 12A). A substantial increase in productivity in the Tethyan region is also likely, probably triggered by the onset of upwelling in *tenuicostatum*-Zone times, a conclusion fostered by isotopic evidence (fig. 8).

Examination of the carbon-isotope curve shows a pronounced minimum in the *spinatum* and *tenuicostatum* Zones followed by the *falciferum*-Zone positive excursion. This minimum has been interpreted by Jenkyns and Clayton (1986) to reflect initial upwelling and recycling of excess isotopically light organic matter within the north European and Tethyan regions before the onset of widespread *falciferum*-Zone anoxia, large-scale storage of organic-carbon in the World Ocean, and a positive carbon-isotope shift. Local occurrences of organic-rich shale in the *tenuicostatum*-Zone of northern Europe are consistent with this hypothesis (Mouterde, 1955, 1967; Riegraf, Werner, and Lörcher, 1984).

In this context the change to clay-rich sedimentation during *falciferum*-Zone times may be related to replacement of calcareous by siliceous and/or organic-walled plankton in response to increasing productivity of near-surface waters; carbon-isotopic evidence is again suggestive in this respect (Jenkyns and Clayton, 1986). It is important to stress that this zone of Toarcian time registers a clay-dominated period as well as one characterized by enrichment in organic matter. The relative enrichment in clay is also seen in red oxidized Ammonitico Rosso facies of Toarcian age in many Tethyan areas (Jenkyns, 1974), suggestive of changes in productivity across the whole region. If these conclusions are correct they imply that the planktonic-carbonate influx was temporarily switched off, rather than excess clay being suddenly supplied. Such a decrease in the rate of supply of planktonic carbonate would have caused elevation of the calcite compensation depth (Berger and Winterer, 1974), although deciphering this effect from that attendant on a rise in sealevel would clearly be difficult.

Using the equations of Schidlowski (1982) and Holland (1984, p. 524) some rough estimates may be made of the relative increase of organic carbon buried during the early *falciferum* Anoxic Event. During *spinatum-tenuicostatum* time the carbon-isotope signature recorded in figure 8 probably reflects the composition of near-surface waters affected by upwelling and is not representative of the ocean as a whole. The background carbon-isotope value is hence taken as approx 2 permil. The maximum $\delta^{13}C$ value at the height of the event is taken as 4.5 permil. The difference between the $\delta^{13}C$ of Toarcian carbonates and organic matter is taken as approx 33.5 permil (Küspert, 1982; Jenkyns and Clayton, 1986). The isotopic mass balance equation is expressed thus:

$$\overline{\delta^{13}C} = f\,\delta^{13}C_{org} + (1-f)\,\delta^{13}C_{carb}$$

where $\overline{\delta^{13}C}$ = the isotopic composition of all carbon deposited from the oceans and f = the fraction leaving the oceans as a constituent of organic matter. This fraction, f_1, prior to the *falciferum*-Zone event was:

$$f_1 \approx \frac{-\overline{\delta^{13}C_1} + 2}{33.5}$$

At the acme of the event, the fraction, f_2, had the value:

$$f_2 \approx \frac{-\overline{\delta^{13}C_2} + 4.5}{33.5}$$

If the value of $\overline{\delta^{13}C}$ did not change during the interval in question, then:

$$f_2 - f_1 = \Delta f \approx \frac{2.5}{33.5} = 0.075$$

Thus some 7 to 8 percent more of the total carbon buried per unit time was buried as a constituent of organic matter during the *exaratum* Subzone than during the preceding zone, a figure that is probably an overestimate, as there is evidence for a fall in the carbon-isotope ratios of kerogens during this time (Küspert, 1982; Moldowan, Sundararaman, and Schoell, 1986). Calculations using a change in $\delta^{13}C_{org}$ from -28 to -31 permil during the early *falciferum* Zone and assuming $\delta^{13}C$ of -5 to -3.7 permil (Holland, 1984, p. 362; Garrels and Lerman, 1984) indicate the increase may have been as low as 3 to 4 percent. Whatever the figure, burial of the excess organic carbon, which otherwise would have been oxidized to carbon dioxide, would have led to an increase in atmospheric oxygen. This additional oxygen may have rapidly reacted with available organic carbon in the marine and terrestrial reservoirs to introduce ^{12}C into the oceans, hence explaining the rapid return to isotopic equilibrium, by *bifrons*-Zone time, after the anoxic event itself (fig. 8). This type of mechanism, and the possible role of the global sulfide-sulfate reservoirs in controlling atmospheric and oceanic oxygen levels, is discussed by Shackleton (1985), Berger and Vincent (1986), Kump and Garrels (1986), and Berner (1987). Such relationships would, however, be more complex if the carbon buried was largely derived from juvenile sources, that is released as CO_2 during a period of vigorous volcanic degassing (Arthur, Dean, and Schlanger, 1985).

Similar mass-balance calculations for the Cenomanian-Turonian Oceanic Anoxic Event, using data from Jenkyns (1985) and Dean, Arthur, and Claypool (1986), suggest a relative increase of 8 to 9 percent in the amount of carbon buried per unit time as a constituent of organic matter during this part of the Cretaceous: the particularly broad expanses of epicontinental seas developed during this latter part of the Mesozoic may have provided more sites for organic-rich sedimentation than existed during the Early Jurassic.

FAUNAL CHANGE ACROSS THE PLIENSBACHIAN-TOARCIAN BOUNDARY

The dramatic faunal changes that took place amongst diverse groups during the early Toarcian have been amply documented by Hallam (1967, 1976, 1977, 1987b) with particular respect to the bivalves. Generally *tenuicostatum*-Zone faunas are similar to those of the late Pliensbachian whereas *bifrons*-Zone forms have a mid-Jurassic aspect. A similar turnover has been suggested for the ostracods (Lord, 1974; Riegraf, 1984). Equally the *falciferum* Zone was a time of transition of the dinoflagellate population (Wille, 1982; Loh and others, 1986); gastropods, brachiopods, and particularly Foraminifera also show major extinctions and radiations. Indeed the *falciferum*-Zone is probably the most important faunal boundary in the European Jurassic for bottom-dwelling species, presumably reflecting the impact of widespread anoxic bottom waters in destroying benthonic habitats (Riegraf, 1985; Hallam, 1987b). Significant faunal change at this time may also be recognized in other continents. For necktonic/planktonic biota such as ammonites, however, the major changes took place in the *spinatum* Zone (latest Pliensbachian) and the *tenuicostatum*-Zone (Hallam, 1967, 1987b; Wiedenmayer, 1980). Both ammonites and belemnites are represented by very few genera in the *tenuicostatum* Zone of southwest Germany (Riegraf, Werner, and Lörcher, 1984).

A correlation between extinction of planktonic Foraminifera and anoxic events has been suggested for the Cenomanian-Turonian boundary where oceanographic factors have been used to explain faunal change (Hart, 1980; Wonders, 1980; Caron and Homewood, 1983; Hart and Ball, 1986; Kuhnt and others, 1986). Such interpretations may also be applied to the Pliensbachian-Toarcian boundary (Jenkyns, 1985). Major disturbances in the higher levels of the water column, potentially affecting necktonic and planktonic biota, probably began in boreal and Tethyan Europe during latest Plienbachian-earliest Toarcian time (fig. 8). Initial upwelling of nutrient-rich oxygen-poor waters would have produced expanded planktonic populations in near-surface waters generating the oxygen-minimum zone by bacterial oxidation of descending organic matter and perhaps excluding certain ammonites from those bathymetric levels that became poorly ventilated (fig. 12A).

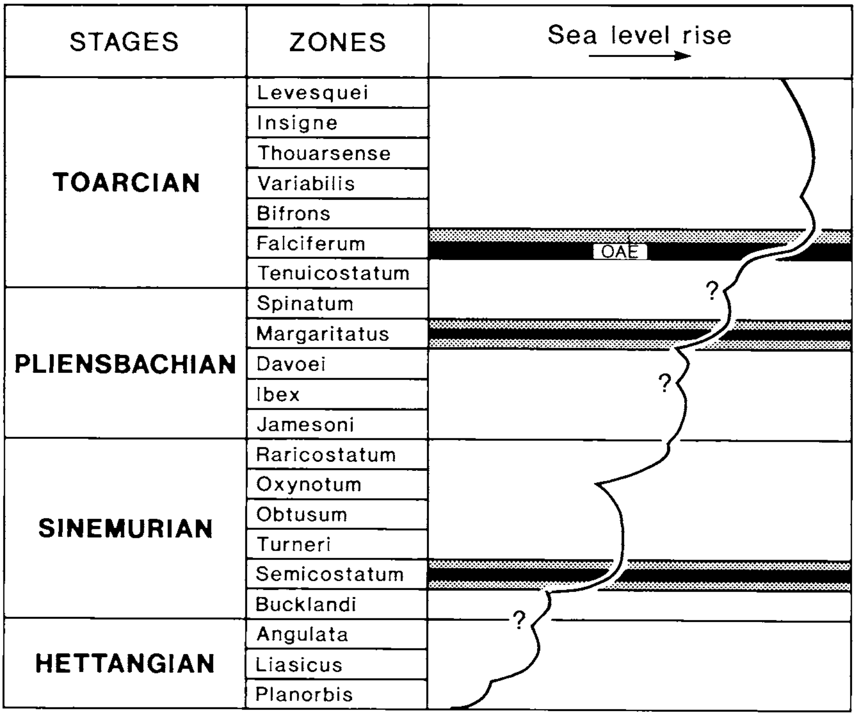


Fig. 15. Periods of preferred Early Jurassic organic-carbon deposition on a regional scale set against the sealevel curve of Hallam (1981); foci of events shown in black. Only the early *falciferum* event is sufficiently well documented at present to deserve the status of an Oceanic Anoxic Event (OAE). The core of this event is dated exactly as *exaratum* Subzone, based on stratigraphic and carbon-isotope evidence. The *margaritatus*-Zone event, suggested by Hallam (1981), is probably localized in the *subnodosus* Subzone, following the isotopic data of Jenkyns and Clayton (1986). The *semicostatum*-Zone event is largely confined to the *scipionanum* Subzone as shown by ammonite stratigraphy (Hallam, 1981). Periods of regional black-shale deposition correlate well with transgression, and there is probably a causal link between the two phenomena.

Such a phenomenon could have significantly pre-dated the onset of *falciferum*-Zone bottom-water anoxia that affected many benthonic habitats in both northern and Tethyan Europe, with concomitant deposition of organic-rich muds.

CONCLUSIONS

It is concluded that during the early part of the *falciferum* Zone (*exaratum* Subzone) certain levels of the world ocean, namely the oxygen-minimum zone, were particularly poorly ventilated and deposition of organic-rich shales was widespread; such periods of rapid chemical change have been termed Oceanic Anoxic Events. Although the major sedimentary record stems from Europe, other occurrences around the Pacific Rim and Indian Ocean spot-light the global distribution of organic-rich facies of this age. Carbon-isotope anomalies in Tethyan pelagic limestones reinforce the interpretation of the *exaratum* Subzone and the preceding *spinatum* and *tenuicostatum* Zones as times of significant sedimentary and faunal change. In Europe, the major sources of oxygen-depleted waters were probably fertile shelf regions, where much organic matter was deposited, although upwelling, commencing in *spinatum-tenuicostatum*-Zone time, also affected Tethyan continental margins. Regional deepening of the shelf to allow upwelling provides a plausible link with transgressions.

Whether or not this anoxic event is unique in the Jurassic is not established; however, other possible times of anomalously high depositional rates of organic-carbon on a regional scale are illustrated in figure 15. Further studies will doubtless elucidate their relative importance.

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