Organic-rich deposits from the Callovian of the Sierra de la Demanda, Northern Spain.

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ABSTRACT

The Middle-Upper Callovian is mostly absent in Northern Spain due to truncation beneath Late Jurassic unconformities. However, tectonic conditions in parts of the southern Sierra de la Demanda permitted local preservation of a 140 m thick sequence of Callovian marine organic rich deposits at Villavelayo (La Rioja Province), the upper part of which is probably of Middle to Late Callovian age. Sedimentological and faunal evidence, as well as the presence of pyrite, are consistent with intermittently low bottom-water oxygen levels. Interbedded dark marly shales and silty limestones show low to moderate TOC values of up to 2% (mean TOC = 0.7%). Organic maturity determinations reveal that outcrop samples are overmature for hydrocarbon generation and have suffered loss of much of their original organic carbon during deep burial (> 6 km). Pre-burial organic carbon contents may have reached 4% at some horizons. Thus the Middle-Upper Callovian sequence may be a potential hydrocarbon source rock.

RÉSUMÉ

Le Callovien moyen et supérieur est généralement absent au nord de l'Espagne en raison de la troncature sous les discordances du Jurassique supérieur. Cependant, 140 m de dépôts marins riches en matière organique ont été préservé dans une partie de la Sierra de la Demanda en raison de conditions tectoniques particulières. La partie supérieure de cette séquence est probablement d'âge Callovien moyen à supérieur. Tant les données sédimentologiques et fauniques que la présence de pyrite reflètent un appauvrissement intermittant en oxygène des eaux de fond. Les marnes sombres et calcaires silteux interstratifiés ont des valeurs de TOC faibles à modérées pouvant atteindre 2% (TOC moyen: 0.7%). Le degré de maturation de la matière organique montre que les échantillons à l'affleurement sont «surmatures» (overmature) et ont subi la perte de beaucoup de leur carbone organique originel pendant la diagenèse d'enfouissement profond (> 6 km). Avant l'enfouissement, le pourcentage de carbone organique pourrait avoir atteint 4% dans certains horizons. Ainsi, les dépôts du Callovien moyen et supérieur pourraient être une roche mère potentielle.

Introduction

The Sierra de la Demanda lies in the provinces of Burgos, Soria and La Rioja, approximately 200 km to the north of Madrid (Fig. 1). The Demanda lies to the north of the Cameros Basin, which forms the northwestern continuation of the Iberian Chains. The Demanda consists mostly of Palaeozoic rocks, but its southern part also displays a thick sequence of Mesozoic marine and continental carbonates and clastics similar to those of the Cameros Basin to the south. The tectonics, sedimentology and stratigraphy of this area have recently been reviewed by Platt (1986, 1990).

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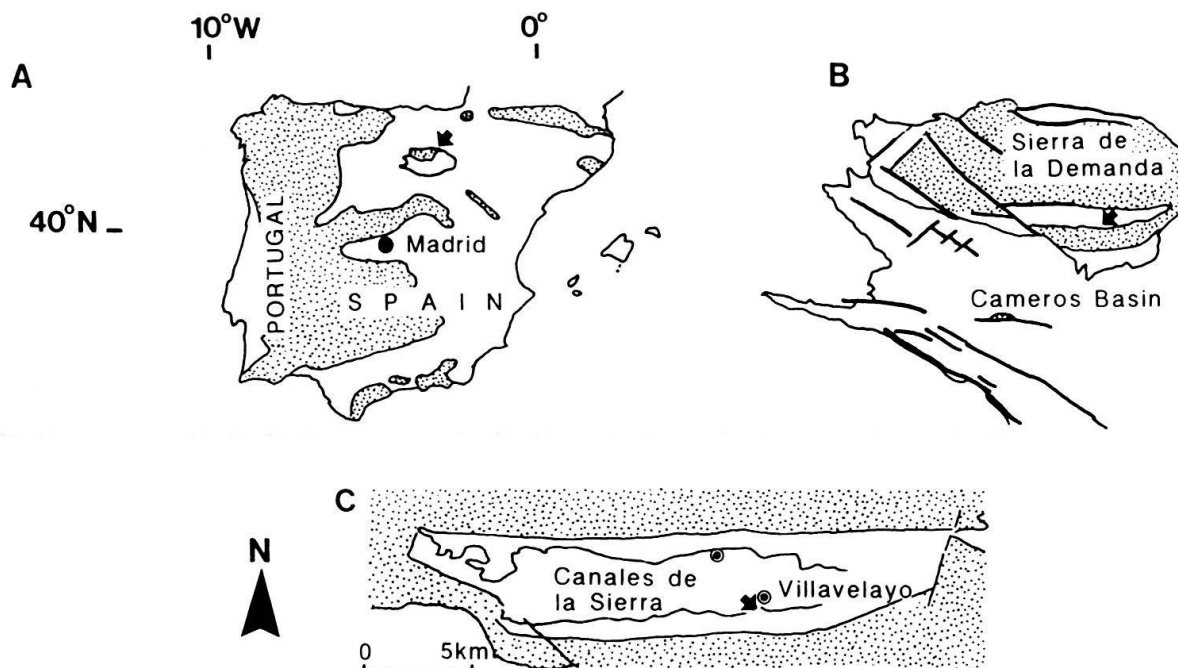
Fig. 1. Location maps. A: Location of the study area in Northern Spain. B: Detail of the Sierra de la Demanda and part of the Cameros Basin. C: Location of the studied section at Villavelayo (arrow). Precambrian and Palaeozoic basement stippled.

Rocks of Middle-Late Callovian age are absent in many parts of northern Iberia, so that the outcrops in parts of the southern Sierra de la Demanda provide a rare opportunity to study these strata in this area. No sedimentological or geochemical studies have been carried out on the Middle-Upper Callovian to date. However, the characterisation of these organic-rich deposits and their depositional environment is of considerable importance in view of exploration interest for hydrocarbons in Northern Iberia. The limited success of this exploration programme to date is probably partly linked with the scarcity of prospective source rock horizons in the area.

Characterisation of Organic-rich Sediments

Organic-rich deposits are common in the Jurassic of western Europe (HALLAM 1987). Those of Britain, France and Germany have received particular attention, partly reflecting the interest generated through hydrocarbon exploration in the North Sea (see e.g. BRAND & HOFFMANN 1963; TISSOT et al. 1971; BROOKS & FLEET 1987; CORNFORD 1990).

Integration of palaeontological and sedimentological data has permitted the classification of organic-rich facies into three groups (see e.g. RHOADS & MORSE 1971; DUFF 1975; MORRIS 1979, 1980). In descending order of faunal diversity, these groups are: *normal shales, restricted shales,* and *bituminous shales.* HALLAM (1987; see his Fig. 2) proposed an alternative classification of four depositional facies: *shelly mudstone, shelly shale, shelly laminite* and *barren laminite.* These classification schemes allow the features of organic-rich deposits to be related to the oxygen content of marine bottom waters (see e.g. RHOADS & MORSE 1971; THOMPSON et al. 1985; SAVRDA & BOTTJER

1987; WIGNALL & MEYERS 1988). Geochemical studies can further understanding of the chemical conditions at and below the sediment surface during deposition and early diagenesis (see e.g. BERNER 1981, RAISWELL & BERNER 1985; RAISWELL et al. 1988).

This paper adopts a multi-disciplinary approach; an outline of the Jurassic stratigraphy and palaeogeographic evolution of the area is followed by discussion of the sedimentology, palaeontology and geochemistry of the Callovian succession. This approach provides a better understanding of the depositional setting of the sequence and discussion of its hydrocarbon prospectivity.

Stratigraphy

Early and Middle Jurassic

The Jurassic facies evolution of the northwestern Iberian Chains (see ERRENST et al. 1984) is broadly comparable with that of the central and southeastern Iberian Chains (GOMEZ 1979), of the southern part of the Vasco-Cantabrian Basin (DAHM 1966; SBETA 1985; ROBLES et al. 1989), of Asturias (DUBAR et al. 1971; Valenzuela et al. 1986) as well as of Portugal (WILSON et al. 1989; WATKINSON 1990; HISCOTT et al. 1990), Southern Britain and the Jura Mountains (see e.g. ANDERTON et al. 1979; TRÜMPY 1980; ZIEGLER 1982, 1990; PETRIE et al. 1989). The relatively thin sequences and the predominance of near-shore, shallow-water facies in the northwestern Iberian Chains, however, suggest that sedimentation took place in shallower water and on a less rapidly subsiding shelf than in these other areas (PLATT 1986). This difference reflects the proximity of the Iberian Chains to the Meseta, a major basement massif which acted as a palaeogeographic high throughout the Mesozoic (PLATT 1990).

The "marine Jurassic" sequence of the northwestern Iberian Chains (Fig. 2) is an 800 m thick carbonate succession of Rhaetian to Early Kimmeridgian age, deposited on a differentially subsiding, north-east facing marine shelf (MENSINK 1966; BULARD 1972; VALLADARES 1976, 1980; BENKE 1981; ERRENST et al. 1984; MERTMANN 1986; PLATT 1986; ALONSO et al. 1987; WILDE 1988, 1990; ALONSO & MAS 1990). Jurassic extensional pulses led to the development of minor discordances (PLATT 1986; 1990), which punctuate the sequence at the Rhaetian ("Early Cimmerian"), Lower Toarcian, Lower Bajocian ("Mid Cimmerian"), and Middle Oxfordian ("Lusitanian"; MOUTERDE 1971).

Middle and Upper Callovian

The upper part of the Callovian sequence at Villavelayo comprises black marly shales interbedded on a 20–100 cm scale with dark grey limestones. The age of these strata is problematic, since ammonites are scarce. Some authors (e.g. DIETL 1974) have dated the youngest marine Jurassic rocks in the study area as Bajocian or Bathonian in age. More recently, SCHUDACK (1979, 1987), MENSINK & SCHUDACK (1982) and CONZE et al. (1984) have reported occurrences of Middle and Upper Callovian rocks in the area. The youngest dated ammonites reported by MENSINK & SCHUDACK (1982) were *Hecticoceras (Lunuloceras)* cf. *compressum* (Quenstedt 1887) and *Hecticoceras (Putealiceras)* ? *robustum* (De Tysovitch 1911), which indicate a Middle Callovian age.
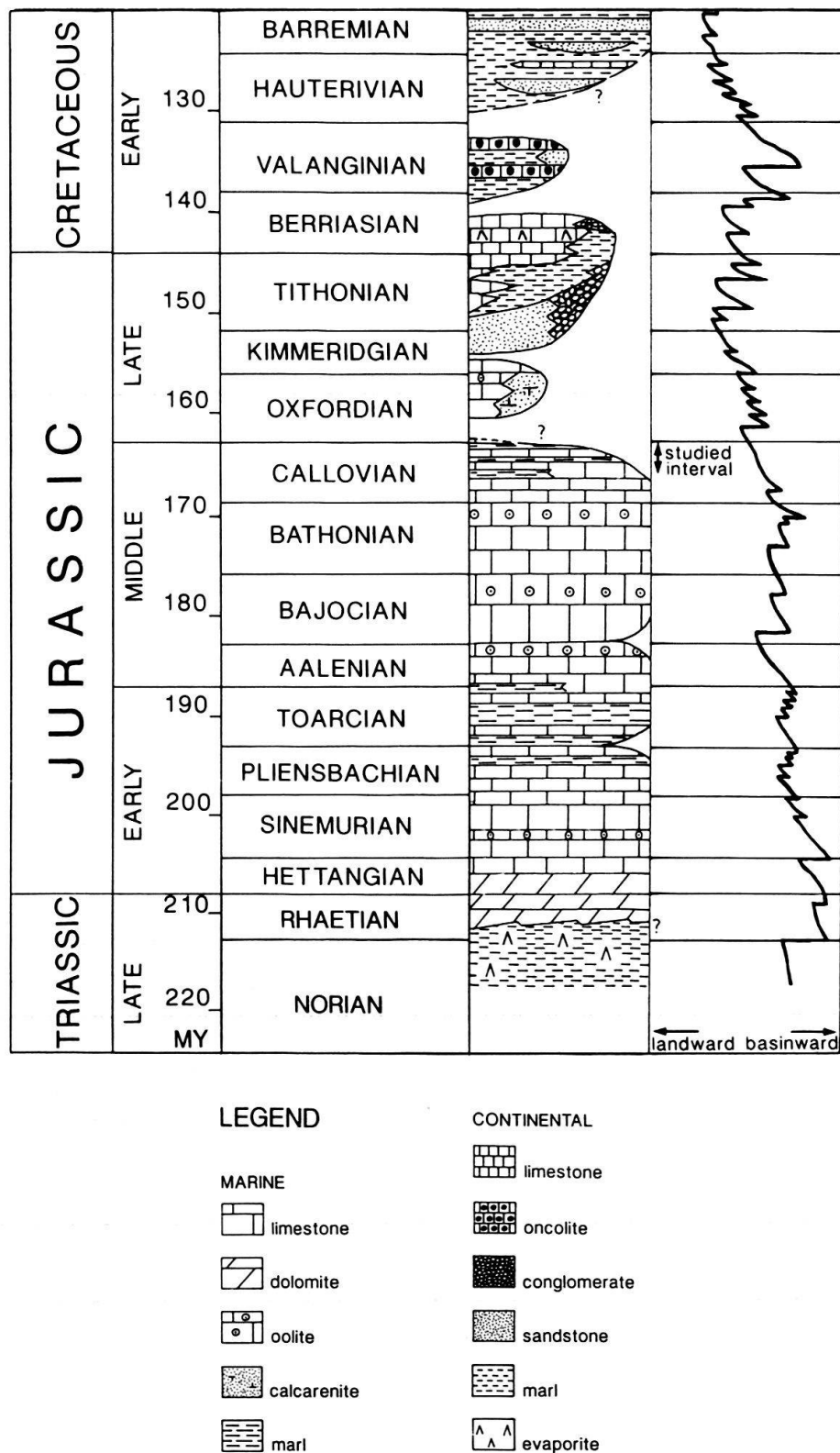
Fig. 2. Jurassic stratigraphy of the northwestern Iberian Chains. Compiled and modified from a variety of sources including: ERRENST et al. (1984); VISSER (1984); MENSINK & MERTMANN (1984a, 1984b); ERRENST (1984); SCHUDACK (1984); MERTMANN (1986); PLATT (1986, 1990); ALONSO et al. (1987); KISSLING (1989); THALMANN (1989); ALONSO & MAS (1990); WILDE (1990); FORRER (1991).

Global Coastal Onlap Curve (based on HAQ et al. 1987) shown alongside for comparison.

During the course of this study, ammonites of the genus *Garantiana* similar to those described by DIETL (1974), and probably of Late Bajocian age, were collected from more than 180 m below the top of the marine sequence at Villavelayo (see Fig. 3). Ammonites of the genus *Choffatia* were found between 100 m and 120 m below the top of the marine succession. Comparison of these with examples collected from laterally equivalent strata in the Jura Mountains (MANGOLD 1970), points to a Early Callovian age, possibly from within the *macrocephalus* zone (RIEBER pers. comm. 1988). This is consistent with a Middle to Late Callovian age for at least part of the overlying marine Jurassic sequence. SCHUDACK (pers. comm. 1988) and WILDE (pers. comm. 1990) consider that the occurrence at Villavelayo of Middle Callovian strata is proved, and that presence of Upper Callovian rocks is also possible, although not certain.

Data from bivalves collected during the course of this study strongly supports this view. The occurrence of *Gryphaea (Bilobissa) dilobotes* (DUFF 1975) 120 m below the top of the sequence is consistent with a Early Callovian age for that part of the succession. The presence near the top of the section of the bivalve *Gryphaea lituola* (LAMARCK 1819), which is transitional to *Gryphaea dilatata* (SOWERBY 1816, 1822) see below), probably indicates strata close to the Callovian-Oxfordian boundary; the transition between the two species occurs at the stage boundary.

Upper Jurassic – Lower Cretaceous

The uppermost Callovian – Lower Oxfordian is commonly absent or condensed. Oxfordian and Kimmeridgian strata are missing at Villavelayo, but have been described from the eastern Sierra de la Demanda, where they consist of black Oxfordian limestones and Lower Kimmeridgian coralliferous carbonates (see e.g. BENKE 1981; ERRENST 1984; ALONSO et al. 1987; ALONSO & MAS 1990). Rocks of this age have also recently been described from the southern Cameros Basin, where cross-bedded shoreface arenites of ?late Oxfordian age are overlain by Kimmeridgian lagoonal limestones (DIAZ-MOLINA et al. 1983, 1988; THALMANN 1989; PLATT 1990).

The onset of a major rifting phase during the Late Jurassic led to block faulting and erosion. Faulting was followed by rapid subsidence, and was associated with the deposition of a thick sequence of Upper Jurassic – Lower Cretaceous continental deposits resting unconformably upon the Marine Jurassic (BULARD et al. 1973; SALOMON 1982; SCHUDACK 1984; PLATT 1986; PLATT 1989a).

The widespread absence of Callovian strata below these continental deposits has in the past been interpreted as the result of retreat of the sea from the west of the basin beginning as early as the Callovian. However, the presence of Oxfordian and Kimmeridgian marine strata in neighbouring areas and sedimentological analysis of the Mid-Jurassic sequence both point to continued transgression during Callovian times. Thus Bathonian lagoonal and oolitic limestones are overlain by shallow marine, sandy, fossiliferous limestones of Lower Callovian age, while the upper part of the Callovian sequence at Villavelayo (see Figs. 1 and 3) comprises grey to black, organic-rich marine deposits. This evidence for Late Callovian transgression is supported by consideration of HAQ et al.'s (1987) global coastal onlap curve (see Fig. 2).

The common absence of the Callovian-Kimmeridgian marine sequence in fact results from truncation beneath the Late Jurassic unconformity. This unconformity has

a complex geometry, reflecting the supperposition of Middle Oxfordian (minor) and mid-Kimmeridgian (major) discordances (PLATT 1986, 1990; see Fig. 2). As a result of these Late Jurassic erosion phases, the Middle and Upper Callovian, as well as the marine Oxfordian-Kimmeridgian, are missing from much of the western Cameros Basin (see MENSINK 1966; PLATT 1990). Preservation of these strata occurred only in those areas (such as the southern and eastern Sierra de la Demanda) which formed structural lows not subject to such severe Late Jurassic erosion.

Methods

Field and laboratory work enabled the detailed description of the Callovian sequence through sedimentological logging of the best outcrop section (140 m in thickness) at Villavelayo, La Rioja Province (see Fig. 1). Systematic sampling was carried out at this locality, a road section on the east side of a stream, 1.5 km south of Villavelayo village, between IGME co-ordinates 65798357 (base) and 65768360 (top) (see GIL SERRANO et al. 1978).

Petrographic and laboratory investigations were carried out on representative samples. Palaeontological data were obtained from macrofossils collected at outcrop and from identification of the microfaunal elements present in thin section.

The samples collected for this study were all obtained from outcrops. Oxidation during weathering may affect both total organic carbon (TOC) and sulphur (S) values (see RAISWELL & BERNER 1986). TOC values, for example, may be reduced by up to 25% (LEYTHAUSER 1973; CLAYTON & SWETLAND 1978). Every attempt was made to minimise the effects of weathering on our analyses by sampling from as far beneath the outcrop surface as practicable.

Geochemical analyses were carried out on whole rock powder samples. Inorganic and total carbon determinations performed on a Coulomat machine enabled calculation of organic carbon content. Sulphur contents were also measured on this machine. After removal of organic matter in a plasma asher, stable isotope analyses for $\delta^{13}C$ and $\delta^{18}O$ in carbonate were carried out using a VG Prism-II mass spectrometer equipped with an on-line reaction system. Samples were reacted at 90 °C in 100% H_3PO_4 (McCREA 1950), and all results are reported relative to the PDB standard (CRAIG 1957) in δ (per mil) units. Vitrinite reflectance determinations are averages of approximately 20 readings per sample.

Sedimentology and Microfacies

Figure 3 presents a sedimentological section of the Villavelayo sequence, while Figure 4 shows a field view (A) and a detailed sketch map (B). Two main facies can be recognised (Figs. 5A and 5B). The sequence mainly comprises a rhythmic alternation of calcareous shales (black or dark grey) and shaly limestones (dark grey to mid-grey). Intercalated 0.5–2 cm thick lenticular shelly lags occur within the limestones, and dark shales with oysters occur near the top of the section.

These rocks are largely unlaminated, with 1 cm diameter burrows locally discernible. However, weak lamination is preserved at some horizons. Detrital content is

VILLAVELAYO: SEDIMENTOLOGICAL SECTION
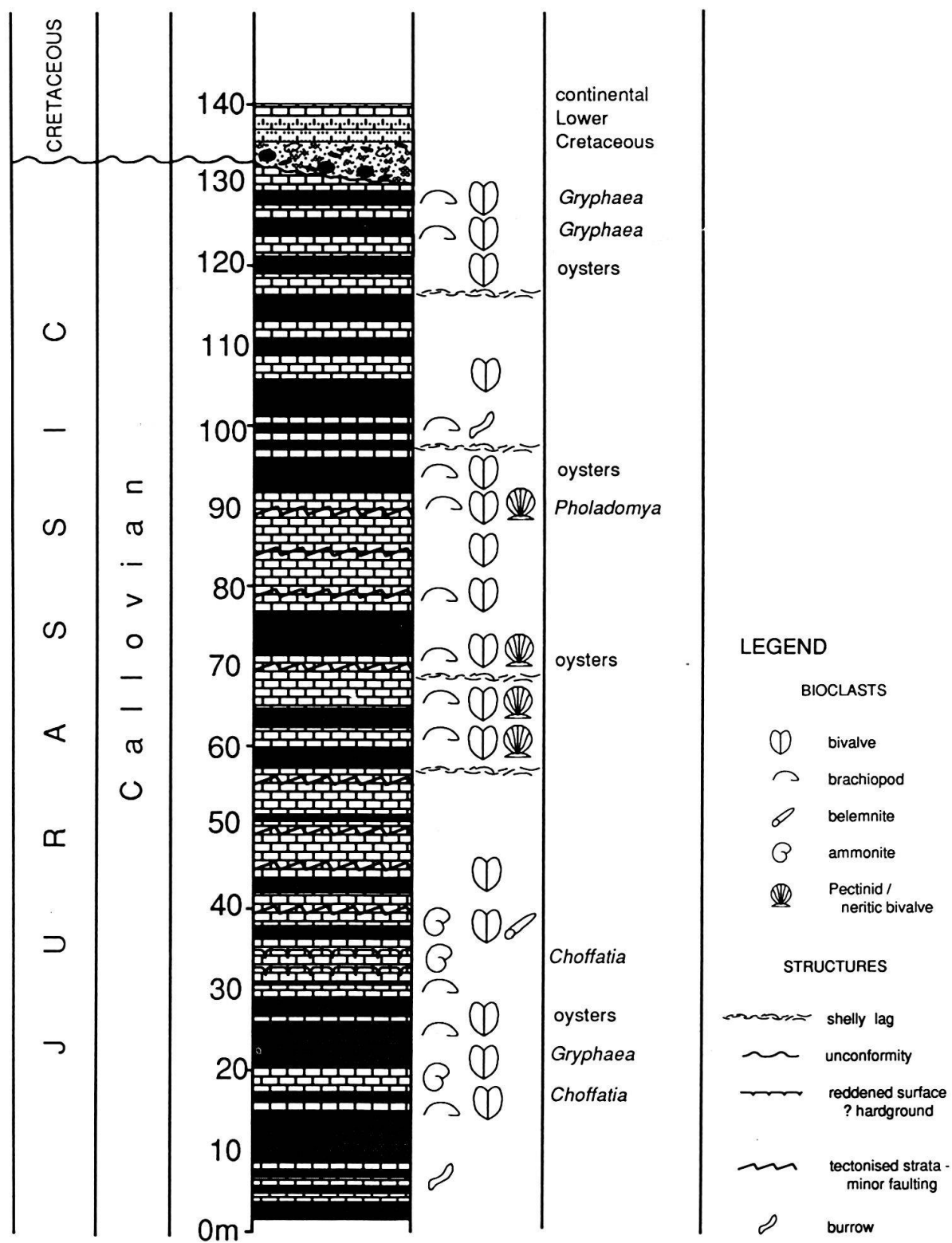
Fig. 3. Sedimentological profile of the Villavelayo section. Data are simplified. Although the entire sequence consists of 20–100 cm-bedded alternations of limestones and shales, these are commonly arranged in limestone-rich and shale-rich packages, as indicated by limestone and shale signatures on the section.
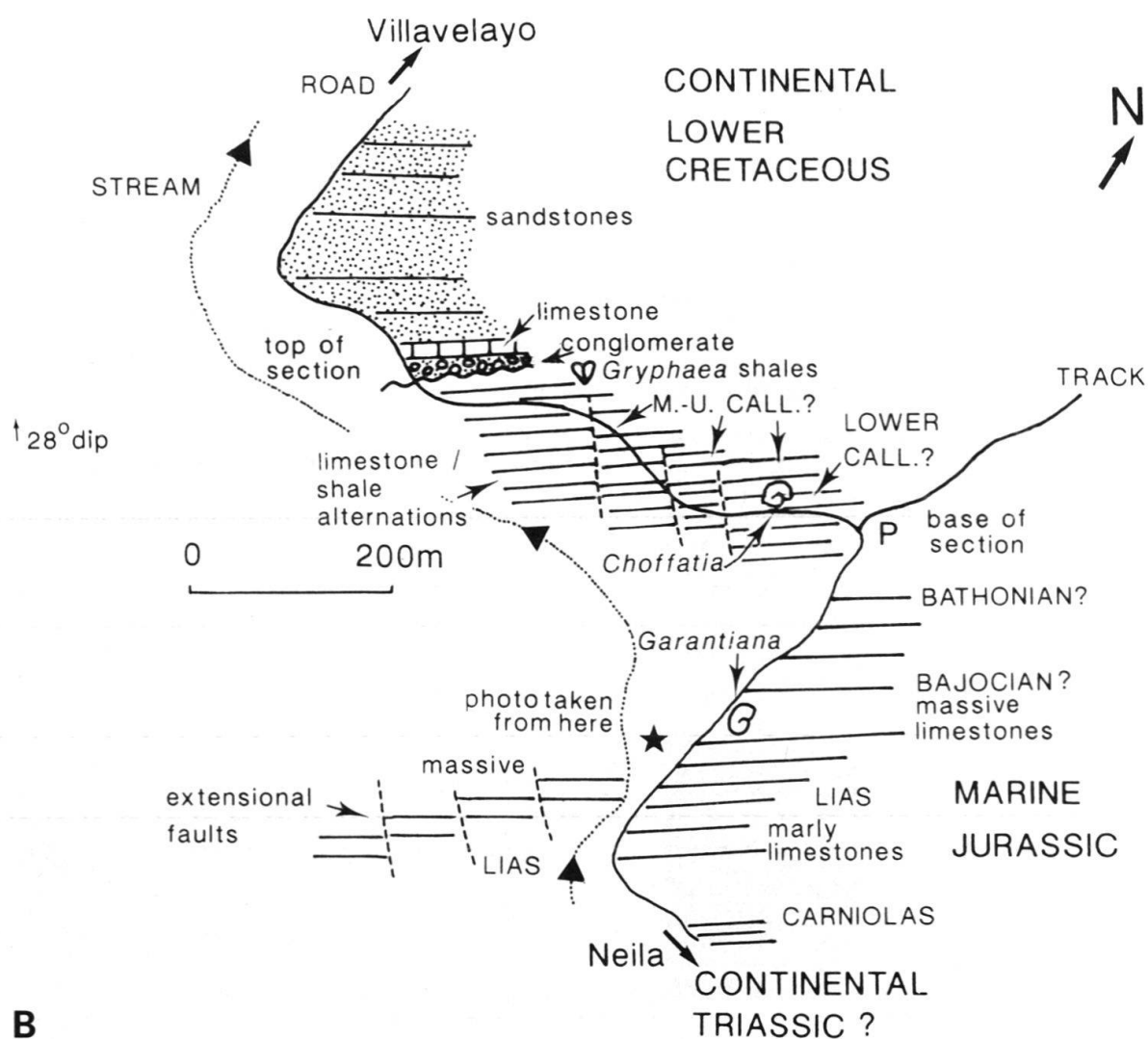
Fig. 4. A: Field photograph of the Callovian section at Villavelayo. Looking west. The continental Lower Cretaceous is visible at the top of the section: limestone conglomerate (c); alluvial sandstones above (s). B: Sketch map of the Villavelayo section showing area of photograph and additional stratigraphic details. P = car parking place.

generally high; these rocks contain significant quantities of detrital quartz, with muscovite and rare quartzite lithoclasts.

This facies assemblage is reminiscent of other reported Jurassic limestone-mudrock alternations (see e.g. MORRIS 1980; HALLAM 1987). The low faunal diversity of these successions is thought to reflect deposition under low-oxygen conditions. The shelly lags suggest occasional storm events (see below).

Mid-grey micritic or microsparry limestones (Fig. 5C) contain subangular detrital quartz grains 0.05 to 0.1 mm in size, 0.1 mm pellets and a fauna including echinoderm fragments (plates up to 2 mm in size), bryozoan débris, bivalves, rhynchonellids, rare gastropods, foraminifera, cadosinids and rare radiolaria. Pyrite occurs both in the form of rare cm-scale nodules and as small spherical framboids 10 to 50 microns across. Framboids are ubiquitous in thin section, but are commonly concentrated in clusters within intragranular porespace in bioclasts, particularly in foraminifera tests and the small fenestrae within porous echinoderm plates (Fig. 5C). Traces of glauconite are also present. Lenticular shelly lags from 2–5 cm thick occur within the limestones at several horizons in the sequence. The lags show concentrations of fragmented and whole shells, mostly bivalves.
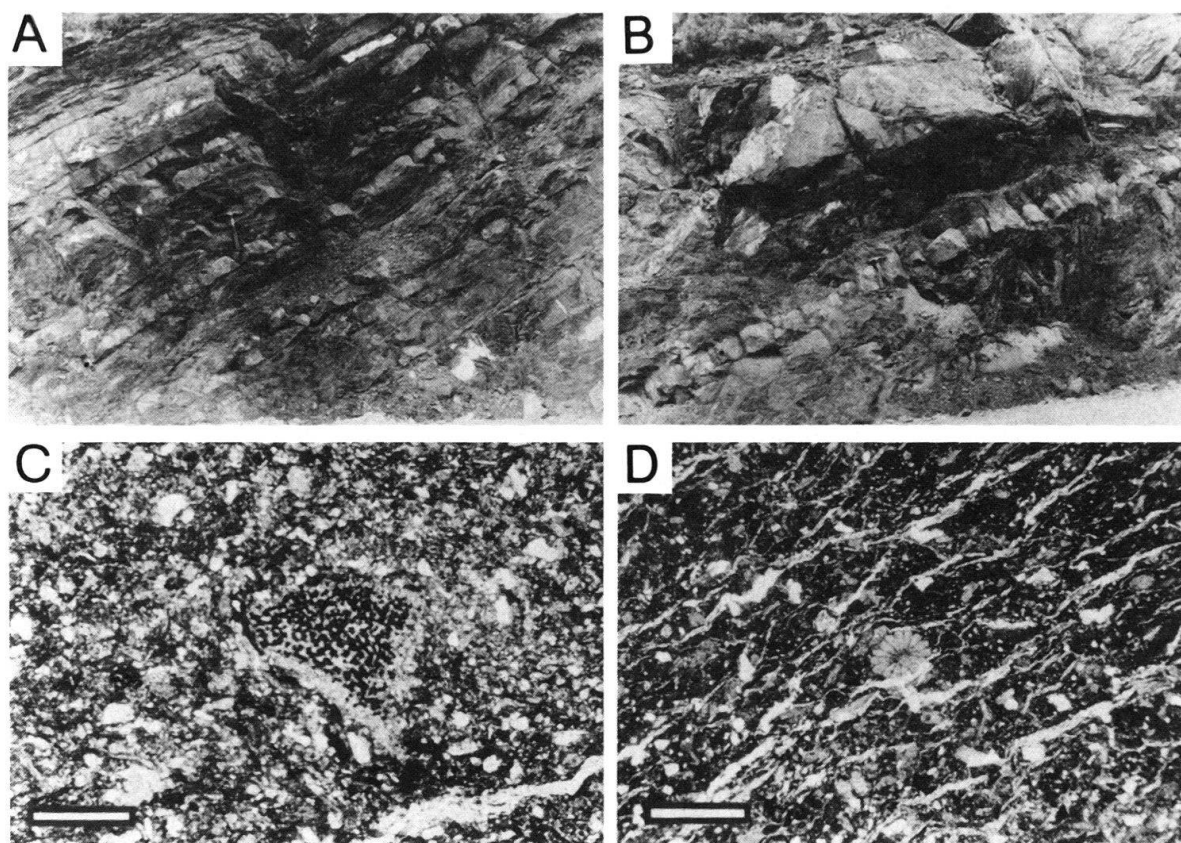
Fig. 5. A: Typical outcrop showing rhythmic alternation of black marly shales and dark grey silty limestones. Villavelayo section, 40 m (see Fig. 3). Hammer for scale (35 cm long). B: Outcrop showing thicker, organic-rich marly shale unit. Villavelayo section, 107 m (see Fig. 3). Hammer for scale (35 cm long). C: Shaly limestone showing partially pyritised echinoderm fragment and abundant sand-sized quartz grains. Villavelayo section, 118 m (see Fig. 3). Scale bar = 0.2 mm. D: Calcareous shale showing echinoderm spine and fine detrital quartz grains. Villavelayo section, 37 m (see Fig. 3). Scale bar = 0.5 mm.

Dark grey to black calcareous shales show a sparse macrofauna, with pyrite framboids as above, rare micritic pellets, partially recrystallised echinoderm fragments up to 0.5 mm in size, and fine quartz grains 0.05–0.1 mm in size (Fig. 5D). A weak, commonly disrupted, mm-scale lamination is locally present.

Interpretation

Both the bioclast assemblages and the presence of minor glauconite within bioclasts testify to open marine conditions. The abundance of fragmented bioclasts supplies evidence of sedimentary reworking. The relatively high detrital content in the limestones seems to indicate significant terrigenous input from a not-too-distant land source area. The fine silt grains in the shales record continued, although more distal, terrigenous input. Thin section study of the shales shows that the darker colour reflects higher contents of clay matrix.

The presence of pyrite and organic matter suggests poor oxygenation of sediment pore fluids at the time of deposition. The combined presence of macroscopic and microscopic pyrite and a moderate- to low-diversity fauna is characteristic of upper dysaerobic conditions. The limestones are bioturbated, but the local presence of lamination in the shales suggests periods when bottom waters were poorly oxygenated and bioturbation consequently incomplete.

The rare lags appear similar to storm beds described from the Upper Jurassic Kimmeridge Clay of southern Britain (WIGNALL 1989) and northern France (FÜRSICH & OSCHMANN 1986). Such storm events are capable of causing physical reworking of shelf material. Storm events may also result in periodic bottom oxygenation, permitting colonisation by benthic fauna and leading to bioturbation of the sediment. The remainder of the sequence shows mudstone-wackestone textures, indicating low depositional energies.

Macrofauna

The fauna of the Callovian sequence at Villavelayo is sparse and scattered. Reworked echinoderm fragments occur throughout the sequence and rare bryozoan fragments also occur. Bivalves, brachiopods and shell fragments occur at certain horizons (see Table 1). The bivalve assemblage collected is similar to that of the British Lower Oxford Clay (DUFF 1978). Examples are present from each of the various bivalve feeding groups, namely the infaunal suspension feeders, epifaunal suspension feeders and infaunal deposit feeders.

Shales occurring 6–8 m below the top of the sequence contain abundant entire oysters of the free-lying genus *Gryphaea*. These were assigned to the species *Gryphaea dilatata* (strictly, an Oxfordian species) by MENSINK & SCHUDACK (1987); the specimens collected during the course of this study resemble examples of *G. lituola*, a form normally encountered in Late Callovian strata.

Brachiopods found include common examples of a terebratulid species characterised by numerous, weak radial striae. These individuals probably belong to the genus *Ornithella*. Other brachiopods found were examples of *Torquirhynchia astieriformis*, a characteristic rhynchonellid with an asymmetric suture. *Torquirhynchia* was

MACROFAUNAL ELEMENTS

metres TOP	GENUS / SPECIES	MODE OF LIFE / FEEDING HABIT
133	*Gryphaea* sp.	free-lying suspension feeder
132	*Gryphaea* sp.	free-lying suspension feeder
	terebratulids *(Ornithella?)*	
132	*Gryphaea (Bilobissa) lituola*	free-lying suspension feeder
131	*Torquirhynchia astieriformis*	
125	*Gryphaea* sp.	free-lying suspension feeder
	terebratulids *(Ornithella?)*	
123	*Torquirhynchia astieriformis*	
115	*Pholadomya (Pholadomya)*	deep infaunal suspension feeder
	c.f. *hemicardia*	
95	*Lopha* sp.	cemented, epifaunal susp. feeder
	poorly preserved terebratulids	
70	*Entolium (Entolium) orbiculare*	free-lying, swimming susp. feeder
61	*Palaeonucula triangularis*	infaunal deposit feeder
	Radulopecten scarburgensis	epibyssate suspension feeder
	Palaeonucula sp. nov.	infaunal deposit feeder
58	*Chlamys (Chlamys) textoria*	epibyssate suspension feeder
	Plagiostoma sp. nov.	vertical epibyssate susp. feeder
41	*Palaeonucula?*	infaunal deposit feeder
35	*Entolium (Entolium) orbiculare*	free-lying, swimming susp. feeder
31	terebratulids *(Ornithella?)*	
21	*Choffatia*	planktonic (ammonite)
20	*Gryphaea (Bilobissa) dilobotes*	free-lying suspension feeder
17	*Choffatia*	planktonic (ammonite)
15	poorly-preserved terebratulids	
	Lopha sp.	cemented, epifaunal susp. feeder
13	poorly-preserved terebratulids	
10	*Entolium (Entolium) orbiculare*	free-lying, swimming susp. feeder

Table 1: Macrofaunal elements from the Callovian section at Villavelayo.

previously thought to have arisen in the earliest Kimmeridgian (see CHILDS 1969), although a few doubtful specimens have been recorded from the latest Oxfordian of Russia.

Interpretation

The occurence at some horizons of terebratulids, echinoderm fragments, thick-shelled bivalves and deep infaunal bivalves indicates normal benthic oxygen levels. The presence of each of the bivalve feeding groups suggests classification of these horizons as "normal shales" according to the scheme of DUFF (1975). Finds of some quite deep infaunal bivalves (see Table 1) argue against the permanent establishment of anoxia within the sediment, as they point to the periodic presence of oxygen even some centimetres below the sediment surface.

Nevertheless, the occurrence of lower diversity horizons suggests that periods of lower oxygenation also occurred. The rare presence of disrupted or diffuse lamination defines these horizons predominantly as "shally shales" and "shelly mudstones" according to the classification scheme of HALLAM (1987). This is consistent with oxygen contents in bottom waters >1.0 ml O_2/l of between 0.5 and 1 mg O_2/l respectively. The absence of finely laminated strata indicates that bottom water oxygenation was never as low, for example, as during deposition of the bituminous shales of the Upper Jurassic Kimmeridge Clay in England (see AIGNER 1980; OSCHMANN 1988; WIGNALL 1989).

The dominance of oysters to the practical exclusion of other faunal groups at the top of the sequence may indicate increased fresh-water influence. *Gryphaea* oysters occur in many Jurassic shale sequences (see e.g. DUFF 1975), commonly as opportunistic colonisers of soft substrates. Studies in progress on the Middle and Upper Oxford Clay of Britain (WIGNALL, unpublished data) show that *Gryphaea* species are able to inhabit very soft substrates churned by deposit-feeding bivalves. The forms found here have relatively thick shells. Thick-shelled taxa are rarely, if ever, found in low oxygen conditions, so that the horizons with *Gryphaea* probably record moderately oxygenated waters.

Microfauna

The microfauna is sparse and mostly pyritised, but comprises a number of different foraminiferal families (see Table 2). Among the benthic forms are *Miliolina, Textulariina, Lagenina* and *Robertinina*. Planktonic ogranisms include cadosinids and some radiolaria. This association points to an outer shelf or external platform environment. All of the foraminifera represented are very small. Low abundances of foraminifera may reflect periods of low benthic oxygenation (compare MORRIS 1979), while small test size in the foraminiferal assemblages of many marine shale sequences was related by BERNHARD (1986) to low oxygen environments. Small tests provide a relatively greater surface area and thus may permit more efficient respiration. In addition, small tests are more easily supported by soft substrates; this is likely to have been the dominant control on organism size in this case.

FORAMINIFERA

Genera:
>   *Lenticulina*
>   *Conorboides*
>   *Cornuspira*
>   *Ammodiscus*
>   *Bolivinopsis textularia*
>   *Gaudryina*
>   *Bigenerina?*
>   *Quinqueloculina*
>   *Planinvoluta*
>   *Spiroplectammina*
>   *Dentalina*
>   *Valvulina?*
>   *Glomospira*
>   *Opthalmidium*
>   *Astacolus*

Morphological types:
(After Classification of BERNHARD, 1986):

All of the forms represented are very small. According to the classification of BERNHARD (1986), the following morphological types may be recognised:

Morphological Type	Interpretation
Elongate flattened	Dysaerobic
Flattened planispiral	Dysaerobic
Lenticular	Aerobic
Cylindrical	Aerobic

Table 2: Foraminiferal groups collected from the Callovian section at Villavelayo, showing morphological classification and probable environmental significance after BERNHARD (1986).

Vitrinite Reflectance Data

Vitrinite reflectance provides a measure of the degree of thermal maturation (see TISSOT & WELTE 1984). Values of vitrinite reflectance obtained during the course of this study lie in the range R_0 = 2.3–3.3% (Table 3), with a weak trend to higher R_0 down section (Fig. 6).

Interpretation

Such values indicate a high degree of organic thermal maturity, equivalent to anthracite grade (HEROUX et al. 1979). Most determinations were obtained from phytoclasts. Although the general downward increase in R_0 is consistent with increasing thermal maturity with depth, some of the absolute values may be unreliable. The most reliable determinations were obtained from vitrinite and inertinite particles in a sample

metres	lithology	$\delta^{13}C_{carb}$ ‰ PDB	$\delta^{18}O_{carb}$ ‰ PDB	TOC %	S %	C_{inorg} %	R_0 %
136.8	limestone	-2.57	-5.41	0.6	0.2	8.9	-
136.5	shale	-0.61	-6.18	0.2	0.6	4.6	-
135.4	limestone	0.31	-5.94	0.4	0.3	9.1	-
134.2	limestone	0.55	-6.15	0.8	0.3	8.6	-
133.9	shale	-0.27	-6.27	0.3	0.7	5.3	-
132.7	limestone	0.54	-5.98	-	-	-	-
132.0	limestone	0.94	-6.01	0.6	0.2	9.2	-
131.7	shale	0.90	-6.25	0.7	0.5	6.4	-
130.3	limestone	0.55	-6.23	0.2	0.2	10.4	2.59
128.9	shale	0.87	-6.14	0.3	0.2	7.2	2.32
128.3	limestone	1.12	-6.03	0.4	0.2	9.2	-
126.9	shale	0.85	-6.01	0.6	0.3	5.7	-
125.9	limestone	0.81	-5.86	0.5	0.2	9.8	-
124.8	limestone	0.85	-6.39	0.5	0.0	7.8	-
123.1	limestone	0.99	-5.88	0.5	0.4	10.1	-
122.4	limestone	1.44	-5.49	0.6	1.4	9.5	-
121.4	shale	1.32	-5.90	0.4	0.5	6.9	-
120.4	limestone	1.01	-5.86	0.7	0.3	9.8	-
119.4	shale	0.79	-6.07	0.3	0.9	6.4	2.38
117.8	limestone	1.16	-5.83	0.7	0.5	9.2	-
117.6	limestone	1.23	-5.64	0.9	0.5	9.1	-
116.3	shale	1.03	-5.98	0.9	1.3	6.1	-
115.9	limestone	1.36	-5.38	0.6	0.3	9.3	-
115.6	limestone	1.16	-5.64	0.3	0.1	9.4	-
114.9	shale	0.81	-5.98	0.4	0.2	6.3	-
114.2	limestone	1.43	-5.56	0.8	0.1	9.1	-
107.1	limestone	1.21	-5.56	1.1	0.6	9.0	2.67
105.3	shale	1.17	-5.90	0.9	0.2	6.4	3.07
95.8	limestone	0.33	-5.58	0.9	0.5	9.4	2.76
94.7	shale	1.12	-5.31	1.5	1.2	7.1	3.34
93.4	limestone	1.03	-6.14	1.8	1.1	7.9	2.54
79.3	limestone	0.33	-5.97	1.4	0.5	9.7	2.54
65.3	shale	0.83	-5.07	0.7	1.6	6.6	-
56.8	limestone	1.09	-5.21	1.3	0.7	8.6	-
48.2	limestone	0.98	-5.83	0.7	0.7	7.9	-
36.9	limestone	1.10	-5.26	0.6	1.3	9.7	-
36.0	shale	1.29	-5.01	0.6	0.5	7.2	2.91

Table 3: Geochemical and vitrinite reflectance data for the Callovian section at Villavelayo.
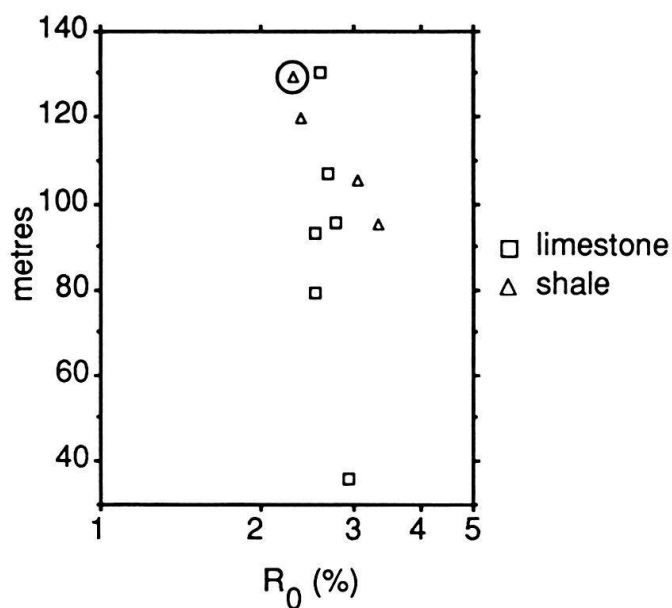
Fig. 6. Vitrinite reflectance data for the Callovian section at Villavelayo. Most values obtained from phytoclasts; circled value (128.9 m) was obtained from vitrinite and inertinite and is thus probably the most reliable.

taken at 128.9 m. These indicate R_0 of around 2.3% (average of 20 readings; 40% inertinite, 60% vitrinite). Thermal maturity reflects both temperature and geological time; however, R_0 values of 2.3% suggest peak burial temperatures in the order of 200 °C (HEROUX et al. 1979). Assuming a geothermal gradient of 30–35 °C km^{-1}, this suggests maximum burial depths of 5–6 km.

Total Organic Carbon (TOC), Sulphur

The TOC values obtained vary between 0.2 and 1.8%, with a mean of 0.69% (Table 3; see Fig. 7). Such values are typical of "normal shale" facies (MORRIS 1980; HALLAM 1987).
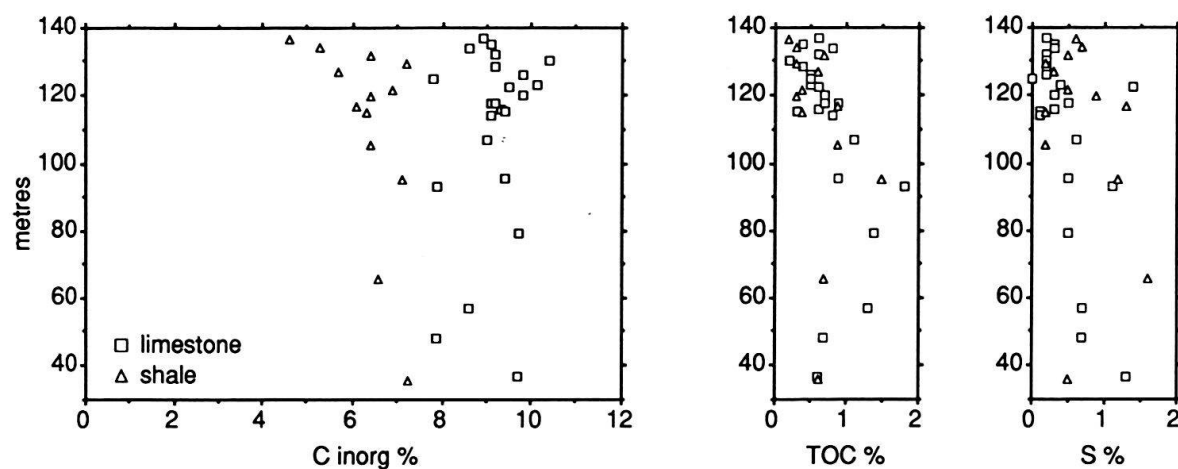

Fig. 7. C_{inorg}, TOC and S data plotted stratigraphically for the Villavelayo section.

Sulphur is present in the form of pyrite. Sulphur contents vary from 0 to 1.6% (Table 3; see Fig. 7), with a mean of 0.54%. Thin section petrography shows that some pyrite formation was localised in intragranular porosity within bioclasts, such as for-
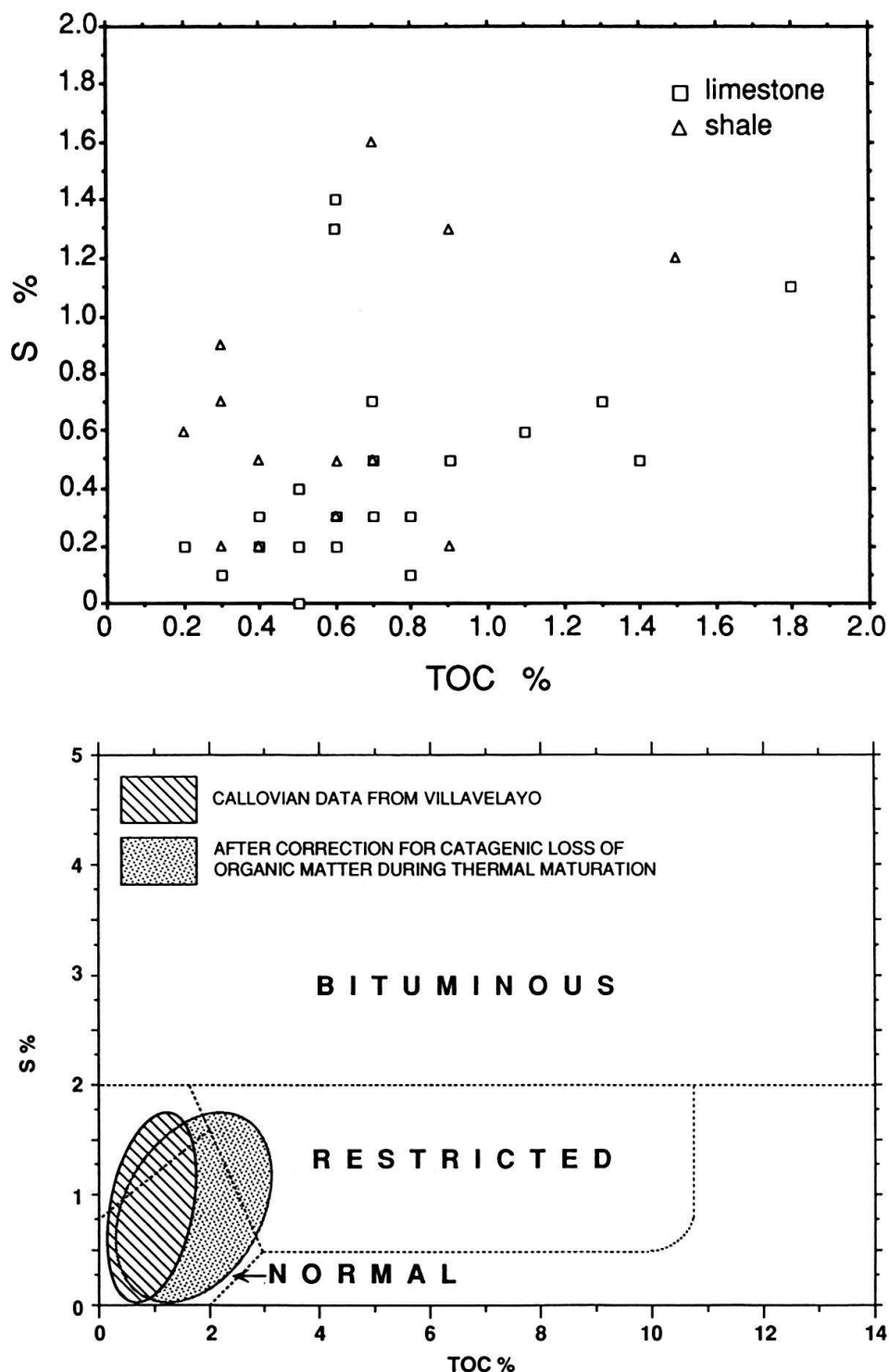

Fig. 8. A: TOC/S plot, showing data for limestones and shales. B: TOC/S plot, showing field occupied by data from this study, before and after correction for extensive organic carbon loss on burial (see text), against a background showing the typical C/S fields occupied by the respective shale biofacies (after FISHER & HUDSON 1987).

aminiferal tests and echinoderm plates, where sulphate reduction may have taken place in reducing micro-environments (compare HUDSON 1982).

A plot of TOC/S for all data shows no well-defined trend (Fig. 8A; see also Table 3). Nevertheless, the data plot broadly into two groups: limestone samples generally show TOC > S, while the shales show TOC < S. Thus although the mean C / mean S ($\overline{C/S}$) for the sequence is 1.28, there is a strong distinction between the limestones ($\overline{C/S}$) = 1.59) and the shales ($\overline{C/S}$) = 0.90).

Discussion: C/S data

The measured TOC and S contents, averaging 0.69% and 0.54% respectively, are not especially high, and the $\overline{C/S}$ ratio of 1.28 is lower than those reported from many normal marine shales. Shales in the British Jurassic, for example, commonly show C/S values in the range of 1.8 ± 0.2 (compare BERNER & RAISWELL 1984; FISHER & HUDSON 1987). The relatively low C/S ratios encountered in this study probably reflect the high maturity of the rocks, as explained below.

LEVENTHAL (1983) was able to relate C/S ratios of recent sediments in the Black Sea with environments of deposition. A similar method was outlined by BERNER & RAISWELL (1984) for distinguishing ancient and recent sediments from freshwater and marine settings. Euxinic or semi-euxinic shales may show higher C/S values than those of normal marine shales, which show a steady original mean of around 2.8 near the sediment-water interface (compare LEVENTHAL 1979; BERNER 1982; BERNER & RAISWELL 1983).

The C/S ratios of marine shales are thought to decrease during the first metres of burial from a mean of 2.8 to around 1.8, probably reflecting bacterial oxidation of organic carbon (RAISWELL & BERNER 1986). Thermal maturation leads to catagenetic loss of organic carbon at temperatures in excess of 150 °C, (RAISWELL & BERNER 1987), resulting in a steady decline in the C/S ratio on deeper burial. By the time anthracite grade is reached, as much as 70% of the original organic carbon may be lost; depressing C/S values to as low as 0.6 (RAISWELL & BERNER 1987).

The $\overline{C/S}$ value of the shales here is 0.90, approximately 30% of the likely original value of 2.8. This value is consistent with loss of 70% of the original organic carbon. The mean TOC for the sequence at outcrop is 0.69%; we may thus calculate an original mean TOC of around 2.1%. Those horizons now displaying TOC values of up to 1.8% may have had original values reaching as high as 5.5%. Bacterial action prior to burial would probably have reduced the mean TOC values to around 1.4%, with maxima of 4% for some horizons.

Thus although the shales now show C/S ratios plotting in the field of normal marine shales (FISHER & HUDSON 1987), restoration to their pre-burial organic carbon contents would suggest a classification as normal to restricted marine shale facies (see Fig. 8B), consistent with the faunal evidence (see above).

Discussion; pyrite

The presence of pyrite points to diagenetic sulphate reduction (BERNER 1970, 1984; GOLDHABER & KAPLAN 1974). Pyrite may be produced either syngenetically, i.e.

before burial (as in euxinic environments, where bottom waters contain H_2S), or diagenetically, i.e. below the sediment-water interface, when anoxic conditions develop within the buried sediment (compare RAISWELL & BERNER 1985). The general absence of lamination in these deposits indicates that the sediments were bioturbated, and therefore that the surface conditions were oxidising, at least intermittently. Thus sulphate reduction most probably occurred just below the surface during early diagenesis.

According to BERNER (1970), the three major limiting factors in the formation of pyrite are: the concentration of sulphate in the water body; presence of reactive (bacterially decomposable) organic matter; and availability of reactive (reducible) iron (for a discussion of this topic see DAVIS et al. 1988).

Pyrite formation in carbonates ($CaCO_3 > 65\%$; $C_{inorg} \geqslant 7.8\%$) is commonly "iron-limited" (BERNER 1984; BERNER & RAISWELL 1986) due to the relatively low contents of potentially reactive iron-bearing detrial minerals present. Iron-limitation on pyrite production within carbonates permits only low concentrations of pyrite sulphur per unit of buried organic carbon in the sediment. Thus limestones commonly show higher C/S ratios than shales.

Although the organic carbon contents of both lithologies are reduced during burial, the C/S ratios of carbonates are likely to remain rather higher than in shale facies of equivalent thermal maturity (RAISWELL & BERNER 1987). In this case, the C/S values are generally low ($\overline{C/S} = 1.28$), reflecting high thermal maturity, while the limestones ($\overline{C/S} = 1.59$) show higher values than those of the shales ($\overline{C/S} = 0.90$), suggesting that pyrite formation in the limestones was indeed iron-limited.

Stable Isotopes

37 carbonate samples were analysed for $\delta^{13}C$ and $\delta^{18}O$; these included 11 samples from the lower part, and 26 samples taken from the upper part of the sequence. The
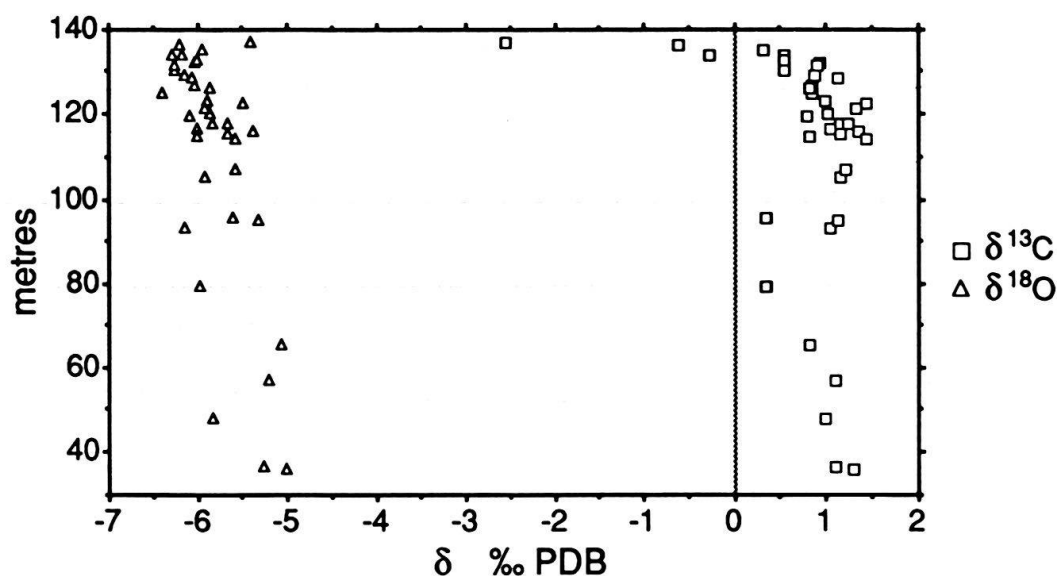

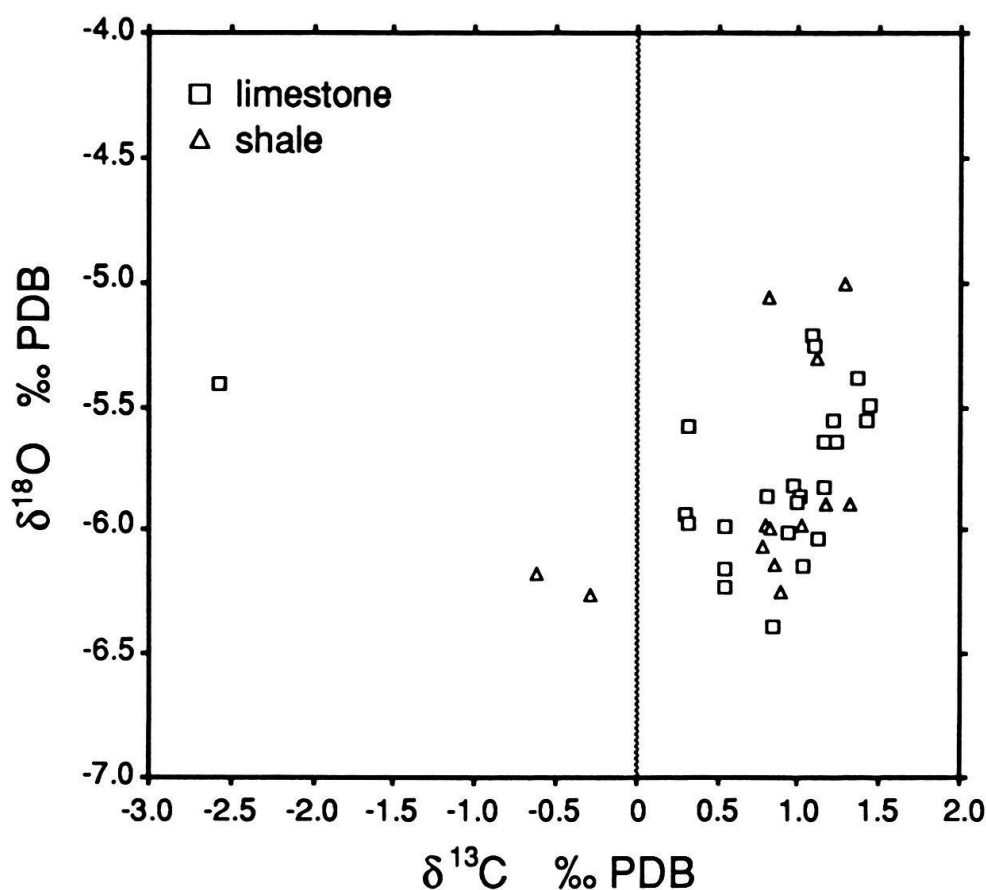Fig. 9. $\delta^{13}C/\delta^{18}O$ (carbonate): plotted stratigraphically for the Villavelayo section.

Fig. 10. $\delta^{13}C/\delta^{18}O$ (carbonate): graphic plot showing values for limestones and shales.

results obtained were remarkably constant (see Table 3). Most of the $\delta^{13}C$ values range between 0 and $+1.5\%$o (PDB), with a few negative values down to -2.6%o occurring at the top of the sequence. The $\delta^{18}O$ values range from -6.4 to -5%o (PDB). The results are presented on a vertical section (Fig. 9) as well as graphically (Fig. 10).

Interpretation

The vertical section (see Fig. 9) shows a pronounced negative shift in $\delta^{13}C$ just beneath the top of the sequence. Lower $\delta^{13}C$ values from this part of the section are attributed to the effects of weathering at the Late Jurassic unconformity surface. The $\delta^{13}C$ and $\delta^{18}O$ values otherwise show only small-scale variations, with no positive excursions in $\delta^{13}C$ similar to those reported from organic-rich facies deposited during times of widespread anoxia (see e.g. SCHOLLE & ARTHUR 1980; JENKYNS & CLAYTON 1986; SCHLANGER et al. 1987; JENKYNS 1988). This is consistent with the faunal and other geochemical evidence (see above) that these deposits were not laid down under truly anoxic conditions.

The graphic plot (Fig. 10) emphasises the close grouping of the data points. Although there is no discernible difference in stable isotopic composition between the limestones and shales, many samples analysed from the top of the succession show

slightly heavier $\delta^{18}O$ values (by approximately 0.5 per mil) than those from the lower part of the sequence (see Fig. 9).

$\delta^{13}C$ values are broadly similar to those reported by SCOTCHMAN (1989) from the Kimmeridge Clay Formation of onshore Britain, although the $\delta^{18}O$ values lie near the lighter end of Scotchman's data range. The close grouping of the results from this study suggests a very similar diagenetic history for the entire section studied. In particular, the carbon isotope values are well-clustered, with the exception of a few negative values, implying that the calcite has essentially retained its original values with very little input of organically-derived, isotopically-light carbon during diagenesis.

The oxygen isotope values are too light to reflect only their original composition, since Jurassic sea-water was probably only 1–2‰ lighter than modern sea-water (e.g. early marine cements and ooids from the Middle Jurassic of eastern England studied by MARSHALL & ASHTON (1980) have $\delta^{18}O$ values of −1 to −3‰).

The $\delta^{18}O$ values are quite heavy, however, for rocks which have seen temperatures in the range of 150–200 °C. For example, using the palaeotemperature equation of CRAIG (1965), if the formation fluids had a $\delta^{18}O$ composition of −2‰ SMOW (Standard Mean Ocean Water; CRAIG 1961) at 150 °C, a calcite in equilibrium with the fluid would have a $\delta^{18}O$ value of approximately −21‰ PDB. Thus either the diagenetic alternation and recrystallisation of the rocks ceased well before maximum burial was achieved, or, if any recrystallisation did take place during deeper burial, this occurred in an essentially closed system.

This is supported by thin section observation; although the limestones show abundant neomorphic microspar, there is virtually no later ferroan calcite cement present.

Prospective Source Rocks in Northern Iberia

Low-oxygen marine facies are commonly oil source rocks (DEMAISON & MOORE 1980; BROOKS et al. 1987; TYSON 1987). The principal prospective hydrocarbon source rocks in Northern Spain are the limestone-marl rhythms of the Lias, which show TOC values up to 1 or 2%. Potential may exist in the Pliensbachian *margaritatus* and *davoei* zones, but the marine open shelf carbonate facies of the Lias in the study area were generally deposited in shallower water and show lower TOC values than their equivalents in the Vasco-Cantabrian Basin to the north (see e.g. SBETA 1985; ROBLES et al. 1989). Source rock potential is likely to be further limited by the reported absence in the area (MENSINK 1966) of the basal Toarcian *falciferum* zone black shales (c.f. JENKYNS 1985; JENKYNS & CLAYTON 1986; JENKYNS 1988).

Possible source rock horizons in the Cretaceous include rare dark lacustrine carbonate beds in the Berriasian Rupelo Formation ("Purbeck" facies; TOC locally up to 1.4%, PLATT 1986, 1989b, c), and thin lignitic horizons in the alluvial deposits of the ?Aptian Salas Group (PLATT 1989a); however, both of these show very localised distribution. Potential may also exist in outer shelf marls of the Turonian Picofrentes Formation, although unlike in Cantabria to the north (HINES 1988), organic-rich hemipelagic marls do not occur in the Upper Cretaceous of the study area.

The Callovian strata studied here may thus provide some of the best prospective source rocks in the area. Their high organic thermal maturity makes accurate reconstruction of original organic carbon contents difficult, but consideration of C/S values

suggests original TOC values of 1–4%, indicating moderate to good potential to generate hydrocarbons (c.f. CORNFORD 1990). Laterally equivalent Middle-Upper Callovian strata provide locally important source rock horizons in southern England (HALLAM 1987). However, their prospectivity in Northern Spain is probably limited by their localised distribution, which is restricted to those areas where pre-Cretaceous erosion was less severe.

Sedimentological and palaeontological evidence from the Callovian succession of normal to restricted shale deposition in a low-oxygen (but not anoxic) marine setting suggests that the organic matter originally present in these rocks was mostly of algal/bacterial origin (Types I and II) with added input of spores and terrigenous organic material (Types II and III). Thus this succession is probably a potential oil source rock.

The presence of these deposits at outcrop in an isolated graben structure hinders confident reconstruction of burial history and heat flow, making accurate timing of possible oil generation difficult. In view of the great thickness of Lower Cretaceous continental deposits laid down in the area (locally up to 5 km according to SALOMON 1982), burial into the oil window (approximately 2.5–4 km, assuming a geothermal gradient of 30–35 °C km^{-1}) probably took place by the Mid – Late Cretaceous.

Although potential reservoirs are abundant in the alluvial sandstones of the Lower Cretaceous (see PLATT 1989a), suitable seals are absent and thrusting accompanying strong regional tectonic inversion in the Oligocene (PLATT 1990) may have resulted in breaching of any earlier accumulations. Nevertheless, the local occurrence of the Middle-Upper Callovian remains an interesting possibility within less intensely deformed areas of the Cameros or the neighbouring Vasco-Cantabrian Basin. In an area with few potential hydrocarbon source horizons, these strata are certainly worthy of consideration in future hydrocarbon exploration.

Conclusions

The Callovian of Villavelayo (southern Sierra de la Demanda, La Rioja Province, Northern Spain) comprises a 140 m thick series of thinly-bedded limestones and marly shales. These rocks contain a sparse fauna of bivalves, brachiopods and foraminifera, with reworked echinoderm fragments. Ammonite and bivalve finds are consistent with a Middle to Late Callovian age for the upper part of this sequence.

The generally low faunal diversity and the occurrence of weak lamination suggests deposition under low benthic oxygen levels. The autecology of the bivalves and foraminifera represented suggests generally soft substrate conditions. Periodic oxygenation probably took place during storms, which led to deposition of thin shelly lags at intervals throughout the sequence. This interpretation is supported by consideration of TOC and S analyses, which suggests classification of these rocks in the "normal shale" to "restricted shale" groups.

The Middle-Upper Callovian is only locally preserved, its limited distribution reflecting the effects of Late Jurassic erosion. However, where present, this sequence may provide an alternative hydrocarbon source rock horizon in this area of Northern Spain, where the remainder of the marine Jurassic succession is relatively thin, probably incomplete and developed in generally shallow-water shelf facies. Although TOC values are moderate (mean TOC = 0.7%), vitrinite reflectance data obtained from out-

crop material indicate a high degree of thermal maturity. Consideration of current C/S values suggests that pre-burial organic carbon contents may have reached 4% at some horizons.

Acknowledgments

REFERENCES

AIGNER, T. 1980: Biofabrics and stratinomy of the Lower Kimmeridge Clay (U. Jurassic, Dorset, England). N. Jb. Geol. Paläont. Abh. 159, 324–338.

ALONSO, A. & MAS, R. 1990: El Jurásico superior marino en el Sector Demanda-Cameros (La Rioja-Soria). Cuadernos de Geología Ibérica 14, 173–198.

ALONSO, A., MAS, J.R. & MELENDEZ, N. 1987: Los arrecifes coralinos del Malm en la Sierra de los Cameros (La Rioja, España). Acta geológica Hispánica 21–22, 293–306.

ANDERTON, R., BRIDGES, P.H., LEEDER, M.R. & SELLWOOD, B.W. 1979: A Dynamic Stratigraphy of the British Isles. A Study in Crustal Evolution. George Allen & Unwin, London.

BENKE, K. 1981: Die Dogger/Malm-Wende in den NW-Keltiberischen Ketten (Spanien) und angrenzenden Gebieten – Sedimentologie, Stratigraphie und Paläogeographie. Fazies 4, 95–164.

BERNER, R.A. 1970: Sedimentary pyrite formation. Amer. J. Sci. 268, 1–23.

— 1981: A new geochemical classification of sedimentary environments. J. sedim. Petrol. 51, 359–365.

— 1982: Burial of organic carbon and pyrite sulphur in the modern ocean: its geochemical and environmental significance. Amer. J. Sci. 282, 451–473.

— 1984: Sedimentary pyrite formation – an update. Geochim. Cosmochim. Acta 48, 605–615.

BERNER, R.A. & RAISWELL, R. 1983: Burial of organic carbon and pyrite sulphur in sediments over Phanerozoic time: a new theory. Geochim. Cosmochim. Acta 47, 855–862.

— 1984: C/S method for distinguishing freshwater from marine sedimentary rocks. Geology 12, 365–368.

BERNHARD, J.M. 1986: Characteristic assemblages and morphologies of benthic foraminifera from anoxic, organic-rich deposits: Jurassic through Holocene. J. foram. Res. 16, 207–215.

BRAND, E. & HOFFMANN, K. 1963: Stratigraphy and facies of the North-west German Jurassic and genesis of its oil deposits. In: Proceedings of the 6th World Petroleum Congress, Frankfurt. Section 1, Paper 7, 223–246.

BROOKS, J., CORNFORD, C. & ARCHER, R. 1987: The role of hydrocarbon source rocks in petroleum exploration. In: Marine Petroleum Source Rocks (Ed. by BROOKS, J. & FLEET, A.J.). Spec. Publ. geol. Soc. Lond. 26, 17–46.

BROOKS, J. & FLEET, A.J. 1987: Marine Petroleum Source Rocks (Eds.). Spec. Publ. geol. Soc. Lond. 26.

BULARD, P.-F. 1972: Le jurassique moyen et supérieur de la Chaîne Ibérique sur la bordure du bassin de l'Ebre (Espagne). Thèse Fac. Sc. Nice.

BULARD, P.-F., SALOMON, J. & THIERRY, J. 1973: Le substratum anté-wealdien dans le Sierra de los Cameros (Espagne). Essais de paléogéologie C. r. Séances Acad. Sci. Paris 276, 2493–2496.

CHILDS, A. 1969: Upper Jurassic rhynchonellid brachiopods from north-western Europe. British Museum of Natural History Bulletin (Geology) Supplement 6.

CLAYTON, J.L. & SWETLAND, P.J. 1978: Subaerial weathering of sedimentary organic matter. Geochim. Cosmochim. Acta 42, 305–342.

CONZE, R., ERRENST, C. & MENSINK, H. 1984: Die Ammoniten des Ober-Callovium bis Unter-Kimmeridgium in den Nordwestlichen Keltiberischen Ketten. Palaeontographica, Abt. A 183, 162–211.

CORNFORD, C. 1990: Source rocks and hydrocarbons of the North Sea. In: Introduction to the Petroleum Geology of the North Sea (3rd Edition) (p. 294–361) (Ed. by GLENNIE, K.W.). Blackwell Scientific Publications, Oxford.

CRAIG, H. 1957: Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. Geochim. Cosmochim. Acta 12, 133–149.

— 1961: Standards for reporting concentrations of deuterium and oxygen 18 in natural waters. Science 133, 1833–1834.

— 1965: The measurements of oxygen isotope paleotemperatures. In: Stable Isotopes in Oceanographic Studies and Paleotemperatures (p.1–24) (Ed by TONGIORGI, E.). Spoleteo, July 26–27, Consiglio Nazionale delle Richerche, Laboratorio die Geologia Nucleare, Pisa.

DAHM, M. 1966: Stratigraphie und Paläogeographie im Kantabrischen Jura (Spanien). Beih. geol. Jahrb. 44, 13–54.

DAVIS, H.R., BYERS, C.W. & DEAN, W.E. 1988: Pyrite formation in the Lower Cretaceous Mowry Shale: Effect of organic matter type and reactive iron content. Amer. J. Sci. 288, 873–890.

DEMAISON, G.J. & MOORE, G.E. 1980: Anoxic environments and oil source bed genesis. Bull. amer. Assoc. Petroleum Geol. 64, 1179–1209.

DIAZ MOLINA, M., GOY, A. & YEBENES, A. 1983: Un complejo de isla barrera-lagoon del Jurásico superior (Talveila, Soria). Libro de Abstracts del X Congreso Nacional de Sedimentología, 2.58–2.62.

— 1988: Sedimentos de isla barrera – «lagoon» del Jurásico medio-superior (Talveila, Soria). III Coloquio Estratigrafía y Paleogeografía del Jurásico. Ciencias de la Tierra (Geología) 11, 197–209.

DIETL, G. 1974: Zur Stratigraphie und Ammoniten Fauna des Dogger, insbesondere des Oberbajocium des westlichen Keltiberischen Ketten (Spanien). Stuttgarter Beitr. Naturk., Ser. B 14, 1–21.

DUBAR, G., MOUTERDE, R., VIRGILI, C. & SUAREZ, L.C. 1971: El Jurásico de Asturias (Norte de España). Cuadernos de Geología Ibérica 2, 561–580.

DUFF, K.L. 1975: Palaeoecology of a bituminous shale – the Lower Oxford Clay of Central England. Palaeontology 18, 443–483.

— 1978: Bivalvia from the English Lower Oxford Clay (Middle Jurassic). Palaeontogr. Soc. Monogr.

ERRENST, C. 1984: Der marine Malm in den nordwestlichen Keltiberischen Ketten (Spanien). Z. dt. geol. Ges. 135, 45–55.

ERRENST, C., MENSINK, H., MERTMANN, D., SCHUDACK, M. & VISSER, H. 1984: Zum Jura der nordwestlichen Keltiberischen Ketten. Z. dt. geol. Ges. 135, 23–25.

FISHER, I. ST. J. & HUDSON, J.D. 1987: Pyrite formation in Jurassic shales of contrasting biofacies. In: Marine Petroleum Source Rocks (Ed. by BROOKS, J. & FLEET, A.J.). Spec. Publ. geol. Soc. Lond. 26, 69–78.

FORRER, A. 1991: Geologische Betrachtungen insbesondere der unteren Oberkreide entlang der San Leonardo-Überschiebung bei Hontoria del Pinar (NW Keltiberische Ketten, Provinz Burgos, Spanien). Unveröff. Dipl.-Arb., Universität Bern (in prep.).

FÜRSICH, F.T. & OSCHMANN, W. 1986: Storm shell beds of Nanogyra in the Upper Jurassic of France. N. Jb. Geol. Paläontol., Abh. 155, 137–161.

GIL SERRANO, G., JIMENEZ, S. & ZUBIETA, J.M. 1978: Mapa geológico de España, 1:50 000. Hoja 278, Canales de la Sierra, IGME.

GOLDHABER, M.B. & KAPLAN, I.R. 1974: The marine sulphur cycle. In: The Sea, Volume 5, (p. 569–655) (Ed. by GOLDBERG, E.D.). John Wiley & Son.

GOMEZ, J.J. 1979: El jurásico en facies carbonatadas del sector levantino de la cordillera ibérica. Sem. Estrat., Ser. Monograf.

HALLAM, A. 1987: Mesozoic marine organic-rich shales. In: Marine Petroleum Source Rocks (Ed. by BROOKS, J. & FLEET, A.J.). Spec. Publ. geol. Soc. Lond. 26, 251–261.

HAQ, B.U., HARDENBOL, J. & VAIL, P.R. 1987: Chronology of fluctuating sea levels since the Triassic. Science 235, 1156–1166.

HEROUX, Y., CHAGNON, A. & BERTRAL, A. 1979: Compilation and correlation of major thermal maturation indicators. Bull amer. Assoc. Petroleum Geol. 63, 2128–2144.

HINES, F.M. 1988: The Sedimentation, Tectonics and Stratigraphy of the Cretaceous/Tertiary Sequence of Northwestern Santander, Northern Spain. Unpubl. D. Phil. Thesis, Univ. of Oxford.

HISCOTT, R.N., WILSON, R.C.L., GRADSTEIN, F.M., PUJALTE, V., GARCIA-MONDEJAR, J., BOUDREAU, R.R. & WISHART, H.A. 1990: Comperative stratigraphy and subsidence history of Mesozoic rift basins of Northern Atlantic. Bull. amer. Assoc. Petroleum Geol. 74, 60–76.

HUDSON, J.D. 1982: Pyrite in ammonite-bearing shales from the Jurassic of England and Germany. Sedimentology 29, 639–667.

JENKYNS, H.C. 1985: The Early Toarcian and Cenomanian-Turonian anoxic events in Europe: comparisons and contrasts. Geologische Rundschau 74, 505–518.

—   1988: The Early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary and geochemical evidence. Amer. J. Sci. 288, 101–151.

JENKYNS, H.C. & CLAYTON, C.J. 1986: Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic. Sedimentology 33, 87–106.

KISSLING, O. 1989: Die Geologie entlang der San Leonardo-Überschiebung zwischen San Leonardo de Yagüe und Cubilla (NW-Keltiberische Ketten, Provinz Soria/Spanien). Unveröff. Dipl.-Arb., Universität Bern. Teil A, 1–125.

LEVENTHAL, J.S. 1979: The relationships between organic carbon and sulfide sulfur in recent and ancient marine and euxinic sediments. Eos 60, 282.

—   1983: An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition. Geochim. Cosmochim. Acta 47, 133–137.

LEYTHAUSER, D. 1973: Effects of weathering on organic matter in shales. Geochim. Cosmochim. Acta 37, 113–120.

McCREA, J.M. 1950: Isotopic chemistry of carbonates and a paleotemperature scale. J. chem. Phys. 18, 849–857.

MANGOLD, C. 1970: Les perisphinctidae (Ammonitina) du Jura méridional au Bathonien et au Callovien. Docum. Lab. Géol. Fac. Sci. Lyon 41/2.

MARSHALL, J.D. & ASHTON, M. 1980: Isotopic and trace element evidence for submarine lithification of hardgrounds in the Jurassic of eastern England. Sedimentology 27, 271–291.

MENSINK, H. 1966: Stratigraphie und Paläogeographie des marinen Jura in den nordwestlichen Iberischen Ketten (Spanien). Beih. geol. Jahrb. 44, 55–102.

MENSINK, H. & MERTMANN, D. 1984a: Diskontinuitäten im Unter-Callovium der nordwestlichen Keltiberischen Ketten (Spanien). N. Jb. Geol. Paläontol., Abh. 167, 189–223.

—   1984b: Regressionen/Transgressionen während des Unter-Callovium in den nordwestlichen Keltiberischen Ketten (Spanien). Z. dt. geol. Ges. 135, 37–44.

MENSINK, H. & SCHUDACK, M. 1982: Caliche, Bodenbildungen und die paläogeographische Entwicklung in der westlichen Sierra de los Cameros (Spanien). N. Jb. Geol. Paläontol., Abh. 163, 49–80.

MERTMANN, D. 1986: Die regressive Faziesentwicklung im Ober-Toarcium/Aalenium der NW-Iberischen Ketten, Spanien. N. Jb. Geol. Paläont., Abh. 173, 1–46.

MORRIS, K.A. 1979: A classification of Jurassic marine sequences: an example from the Toarcian (Lower Jurassic) of Great Britain. Palaeogeogr., Palaeoclimatol., Palaeoecol. 26, 117–126.

—   1980: Comparison of major sequences of organic-rich mud deposition in the British Jurassic. J. geol. Soc. Lond. 137, 157–170.

MOUTERDE, R. 1971: Esquisse de l'évolution biostratigraphique de la Péninsule Iberique au Jurassique. Cuadernos de Geología Ibérica 2, 21–31.

OSCHMANN, W. 1988: Kimmeridge Clay sedimentation – a new cyclic model. Palaeogeogr., Palaeoclimatol., Palaeoecol. 65, 217–251.

PETRIE, S.H., BROWN, J.R., GRANGER, P.J. & LOVELL, J.P.B. 1989: Mesozoic history of the Celtic Sea Basins. In: Extensional Tectonics and Stratigraphy of the North Atlantic Margins (Ed. by TANKARD, A.J. & BALKWILL, H.R.). Mem. amer. Assoc. Petroleum Geol. 46, 433–444.

PLATT, N.H. 1986: Sedimentology and Tectonics of the Western Cameros Basin, Province of Burgos, Northern Spain: Unpubl. D. Phil. Thesis, University of Oxford.

—   1989a: Continental sedimentation in an evolving rift basin: the Lower Cretaceous of the western Cameros Basin (northern Spain). Sedim. Geol. 64, 91–109.

—   1989b: Lacustrine carbonates and pedogenesis: Sedimentology and origin of palustrine deposits from the Early Cretaceous Rupelo Formation of the W Cameros Basin, N Spain. Sedimentology 36, 665–684.

—   1989c: Climatic and tectonic controls on sedimentation of a Mesozoic lacustrine sequence: The Purbeck of the west Cameros Basin, N Spain. Palaeogeogr., Palaeoclimatol., Palaeoecol. 70, 187–197.

—   1990: Basin evolution and fault reactivation in the western Cameros Basin, northern Spain. J. geol. Soc. Lond. 147, 165–175.

RAISWELL, R. & BERNER, R.A. 1985: Pyrite formation in euxinic and semi-euxinic sediments. Amer. J. Sci. 285, 710–724.

—   1986: Pyrite and organic matter in normal marine shales. Geochim. Cosmochim. Acta 50, 1967–1976.

—   1987: Organic carbon losses during burial and thermal maturation of normal marine shales. Geology 15, 853–856.

RAISWELL, R., BUCKLEY, F., BERNER, R.A. & ANDERSON, T.F. 1988: Degree of pyritization of iron as a paleoenvironmental indicator of bottom-water oxygenation. J. sedim. Petrol. 58, 812–819.

RHOADS, D.C. & MORSE, I.W. 1971: Evolutionary significance of oxygen-deficient marine basins. Lethaia 4, 413–428.

ROBLES, S., PUJALTE, V. & VALLES, J.C. 1989: Sistemas sedimentarias del Jurásico de la cuenca Vasco-Cantábrica. Cuadernos de Geología Ibérica 13, 185–198.

SALOMON, J. 1982: Les formations continentales du Jurassique supérieur – Cretacé inférieur (Espagne du Nord, Chaines Cantabrique et NW Ibérique). Mém géol. Université de Dijon 6.

SAVRDA, C.E. & BOTTJER, D.J. 1987: The exaerobic zone, a new oxygen-deficient marine biofacies analysis. Nature 327, 54–56.

SBETA, A.M. 1985: Sedimentology of the marine and lacustrine Jurassic – basal Cretaceous carbonates in the SW Cantabrian mountains of north Spain. Abstracts, 6th Eur. Reg. Mtg., Int. Assoc. Sedimentol., 420–423.

SCHLANGER, S.O., ARTHUR, M.A., JENKYNS, H.C. & SCHOLLE, P.A. 1987: The Cenomanian-Turonian Oceanic Anoxic Event, I. Stratigraphy and distribution of organic carbon-rich beds and the distribution of the marine $\delta^{13}C$ excursion. In: Marine Petroleum Source Rocks (Ed. by BROOKS, J. & FLEET, A.J.). Spec. Publ. geol. Soc. Lond. 26, 371–399.

SCHOLLE, P.A. & ARTHUR, M.A. 1980: Carbon-isotope fluctuation in Cretaceous pelagic limestones: potential stratigraphic and petroleum exploration tool. Bull. amer. Assoc. Petroleum Geol. 64, 67–87.

SCHUDACK, M. 1979: Die Grenze mariner Jura/Wealden in der westlichen Sierra de los Cameros (Spanien). Unveröff. Dipl.-Arb., Universität Bochum.

— 1984: Die Jura/Wealden Grenzschichten in der nordwestlichen Iberischen Ketten (Spanien). Z. dt. geol. Ges. 135, 57–65.

— 1987: Charophytenflora und fazielle Entwicklung der Grenzschichten mariner Jura/Wealden in den Nord-westlichen Iberischen Ketten (mit Vergleichen zu Asturien und Kantabrien). Palaeontographica Abt. B 204, 1–180.

SCOTCHMAN, I.C. 1989: Diagenesis of the Kimmeridge Clay Formation, onshore UK. J. geol. Soc. Lond. 146, 285–303.

THALMANN, C. 1989: Die Geologie entlang der San Leonardo-Überschiebung zwischen San Leonardo de Yagüe und Cubilla (NW-Keltiberische Ketten, Provinz Soria/Spanien). Unveröff. Dipl.-Arb., Universität Bern. Teil B, 126–270.

THOMPSON, J.B., MULINS, T.H., NEWTON, C.R. & VERCOUTERE, T.L. 1985: Alternative biofacies model for dys-aerobic communities. Lethaia 18, 167–179.

TISSOT, B., CHALIFET-DEBYSER, Y., DEROO, G. & ODIN, J.L. 1971: Origin and evolution of hydrocarbons in early Toarcian shales, Paris Basin, France. Bull. amer. Assoc. Petroleum Geol. 55, 2177–2193.

TISSOT, B. & WELTE, D.M. 1984: Petroleum Formation and Occurrence. 2nd Edition, Springer-Verlag, New York.

TRÜMPY, R. 1980: Geology of Switzerland: a Guide Book. Part A: an Outline of the Geology of Switzerland. Schweiz. Geol. Komm., Wepf & Co., Basel.

TYSON, R.V. 1987: The genesis and palynofacies characteristics of marine petroleum source rocks. In: Marine Petro-leum Source Rocks (Ed. by BROOKS, J. & FLEET, A.J.). Spec. Publ. geol. Soc. Lond. 26, 47–67.

VALENZUELA, M., GARCIA-RAMOS, J.C., GONZALEZ LASTRA, J. & SUAREZ DE CENTI, C. 1986: The Jurassic sedimentation in Asturias. Trabajos de Geología, Univ. de Oviedo 16, 121–132.

VALLADARES, I. 1976: Estratigrafía del Jurásico marino en el sector suroccidental de la provincia de Burgos. Stud. Geol. Salamanticensia 11, 151–161.

— 1980: Evolución de facies en el Jurásico calcareo del sector suroriental de la provincia de Burgos. Stud. Geol. Salamanticensia 16, 37–57.

VISSER, H. 1984: Meeresspiegelschwankungen an der Trias/Jura-Wende in Nordspanien. Z. dt. geol. Ges. 135, 27–36.

WATKINSON, M. 1990: Postrift carbonate sequences from the Lusitanian Basin, Portugal. Abstract, 13th Interna-tional Sedimentological Congress, Nottingham, England, 1990, 592.

WIGNALL, P.B. 1989: Sedimentary dynamics of the Kimmeridge Clay: tempests and earthquakes. J. geol. Soc. Lond. 146, 273–284.

WIGNALL, P.B. & MYERS, K.J. 1988: Interpreting benthic oxygen levels in mudrocks: a new approach. Geology 16, 452–455.

WILDE, S. 1988: Das Bathonium und Callovium der Nord-West Iberischen Ketten (Jura-Spanien). Diss. Univ. Bochum; Bochumer Geol. u. Geotechn.

— 1990: The Bathonian and Callovian of the northwest Iberian Range: stages of facial and paleogeographical dif-ferentiation on an epicontinental platform. Cuadernos de Geología Ibérica 14, 113–142.

WILSON, R.C.L., HISCOTT, R.N., WILLIS, M.G. & GRADSTEIN, F.M. 1989: The Lusitanian Basin of west-central Portugal: Mesozoic and Tertiary tectonic, stratigraphic and subsidence history. In: Extensional Tectonics and Stratigraphy of the North Atlantic Margins (Ed. by TANKARD A.J. & BALKWILL, H.R.). Mem. amer. Assoc. Petroleum Geol. 46, 341–361.

ZIEGLER, P.A. 1982: Geological Atlas of Western and Central Europe, Elsevier, Amsterdam.

—   1990: Geological Atlas of Western and Central Europe, Second and Completely Revised Edition, Shell Internationale Petroleum Maatschappij B.V.