Total organic carbon and pyrolysis analysis of the Lower Cretaceous in Compton Bay and Atherfield, Isle of Wight (England)

Ricardo L. Silva[1,2*], Grant D. Wach[1], Stephen P. Hesselbo[3], Darragh E. O'Connor[1]

[1] Basin and Reservoir Lab, Department of Earth and Environmental Sciences, Dalhousie University, Nova Scotia, Canada

[2] iCRAG, Department of Geology, School of Natural Sciences, Trinity College Dublin, The University of Dublin, Dublin, Ireland

[3] Camborne School of Mines and Environment and Sustainability Institute, University of Exeter, Penryn, Cornwall, TR10 9FE, UK

*corresponding author: ricardo.silva@tcd.ie

current address: Department of Geology, School of Natural Sciences, Museum Building, Trinity College Dublin, 1 Park Ln E, Dublin 2, Ireland

Abstract

The Wessex Basin (United Kingdom) includes hundreds of meters of Lower Cretaceous clays, silts, and sands deposited in a wide range of depositional environments. Studies have investigated these depositional systems from the organic matter (OM) perspective. However, questions remain concerning the composition, source, and the overall depositional constraints on the distribution of sedimentary OM in this area. Elemental (carbonate % and total organic carbon - TOC) and pyrolysis analyses were conducted on representative lithofacies of the Lower Cretaceous from the Wessex Basin at the Compton Bay and Atherfield sections, Isle of Wight. The highest TOC contents were determined in the upper part of the Ferruginous Sands and Sandrock formations. These elevated TOC intervals are associated with predominantly estuarine deposition. Except for one sample from the Vectis Formation, Hydrogen Index (HI) in all studied units is low and indicates Type IV kerogen assemblages, interpreted to be linked with strongly variable climates (with pronounced dry periods) and significant water table fluctuations in the source area and during transport. The one sample with a Type II-III kerogen assemblage from the lagoonal Vectis Formation supports previous studies which suggested that OM in the Vectis Formation varied vertically as a function of fluvial sediment and terrestrial organic matter input to the lagoonal environment with changes in salinity, sediment resuspension, and turbulence as a result controlling the abundance of dinoflagellate cysts.

Keywords: Total organic carbon, pyrolysis analyses, sedimentary organic matter, coastal environments, Wessex Basin, Lower Cretaceous.

1. Introduction

The Lower Cretaceous in the Wessex Basin (United Kingdom) records a complex array of depositional environments associated with tectonic, climatic, and sea-level changes (Batten, 1982; Wach, 1991; Wach and Ruffell, 1991; Stewart et al., 1991; Insole and Hutt, 1994; Ruffell and Rawson, 1994; Allen et al., 1998; Gröcke et al., 1999; Ruffell and Worden, 2000; Ruffell et al., 2002; Robinson and Hesselbo, 2004; Akinlotan, 2018). The Isle of Wight includes hundreds of meters of Lower Cretaceous clays, silts, and sands deposited in terrestrial to marine environments (fluvial, lacustrine, lagoonal, estuarine, and marine shelf) and are subdivided into the Wessex and Vectis formations of the Wealden Group, the Atherfield Clay, Ferruginous Sands, Sandrock, and Monk's Bay Sandstone formations of the Lower Greensand Group, and the Gault Clay Formation of the Selborne Group (Casey, 1961; Ruffell and Wach, 1991; Wach, 1991; Wach and Ruffell, 1991; Hopson et al., 2008, 2011; Radley and Allen, 2012) (Figs 1 and 2).

Several studies have investigated the Wessex Basin Lower Cretaceous depositional systems from the organic matter (OM) perspective (e.g. Batten, 1982; Ruffell and Batten, 1994; Harding and Allen, 1995 and the review in Radley and Allen, 2012). However, questions remain concerning the composition and source of sedimentary OM and the overall depositional constraints on the distribution of sedimentary organic matter during deposition. To address these questions, elemental analysis (carbonate and total organic carbon, TOC) and pyrolysis analysis (Rock-Eval) were performed on samples from the Upper Barremian–Middle Albian (Lower Cretaceous) sedimentary succession cropping out along the western margin of the Isle of Wight at Compton Bay and Atherfield (Fig 1). The main goal was to characterise (amount and type) kerogen assemblages (fossil sedimentary organic matter, Tyson, 1995) of representative Lower Cretaceous lithofacies.

2. Geological background

The Wessex Basin, southern England, developed initially through subsidence in the Permian-Triassic, followed by Jurassic–Cretaceous rifting and thermal subsidence, and then by Cenozoic basin inversion (Whittaker, 1985; Karner et al., 1987) (Figs 1 and 2). The Isle of Wight is the continuation of the coastal topography of Dorset to the west and Sussex to the east and exposes a thick sedimentary succession that includes an almost complete record of the Lower Cretaceous, i.e. the Wealden, Lower Greensand, and Selborne groups. The Wealden and Lower Greensand groups are separated by a major erosional surface. Another large-scale erosional surface is observed between the Sandrock and Monk's Bay Sandstone formations, near the top of the Lower Greensand Group (Hopson et al., 2008, 2011) (Fig. 2).

The Compton Bay and Atherfield sections are located on the southwest side of the Isle of Wight, cropping out along several hundreds of metres of beach cliffs. Modern slope failure and minor faults affect the continuous observation of this outcrop (Fig 3). In Compton Bay, sampling was focused on the Barremian–Middle Albian succession, i.e. the Vectis, Atherfield Clay, Ferruginous Sands, Sandrock, Monk's Bay Sandstone, and Gault Clay formations (Figs 1–4). In Atherfield, sampling was focused on the Atherfield Clay Formation (Table 1). Below is a succinct description of the studied lithostratigraphic units in the Isle of Wight based on previously published works (Casey, 1961; Owen, 1975; Batten, 1982; Ruffell and Batten, 1994, 1990; Ruffell and Wach, 1991, 1998b, 1998a; Stewart et al., 1991; Wach, 1991; Wach and Ruffell, 1991; Harding and Allen, 1995; Gröcke et al., 1999; Gröcke, 2002; Robinson and Hesselbo, 2004; Wilkinson, 2008; Hopson et al., 2008, 2011).

The Vectis Formation (Barremian–Lower Aptian) comprises a succession of dark grey siltstone and mudstone with smaller-scale beds and laminae of fine-grained sandstone, shelly limestone, clay ironstone, and ironstone beds. This formation corresponds to an oxic-dysoxic paralic (mostly lagoonal) environment with varying salinity and progressively more marine influence upwards. The Vectis Formation includes the Cowleaze Chine, Barnes High Sandstone, and the Shepherds Chine members (Batten, 1982; Ruffell and Wach, 1991; Stewart et al., 1991; Wach, 1991; Harding and Allen, 1995; Hopson et al., 2008).

The Lower Greensand Group on the Isle of Wight, comprising the Atherfield Clay, Ferruginous Sands, Sandrock, and Monk's Bay Sandstone formations, record an overall marine transgression during the Aptian–Albian, interrupted by periods of static and falling relative sea level (Casey, 1961; Batten, 1982; Ruffell and Wach, 1991; Wach, 1991; Gröcke et al., 1999; Robinson and Hesselbo, 2004; Hopson et al., 2008) (Fig. 2). Blocky brown and blue-grey silty clays with some phosphatic and calcareous nodules characterise the Atherfield Clay Formation (*P. fissicostatus–D. deshayesi* ammonite zone). Bioturbation obscures many sedimentary structures, but these include starved wave ripples, thin coarser grained lag deposits, and erosional gutter casts infilled with cross-laminated silts and shell debris, interpreted to represent storm features. This unit is interpreted as a mud-dominated shelf or broad, open estuary (Wach, 1991; Wach and Ruffell, 1991). The Ferruginous Sands Formation (*D. deshayesi–P. nutfieldiensis* ammonite zone) comprises several heavily bioturbated coarsening-upward units each made up of dark grey sandy mud or muddy sand passing upward into fine- to medium-grained grey to green glauconitic sand. These units are interpreted to have been deposited in a mixed energy shelf setting (Wach, 1991; Wach and Ruffell, 1991; Ruffell and Wach, 1998a). Variations in relative sea level produced corresponding higher energy conditions winnowing fines from the coarser sand fraction, followed by abrupt flooding of the shelf, depositing finer-grained mud representing a deeper shelf facies. Firmground horizons with condensation of fauna are often bioturbated, including *Thalassinoides*, and cap these cycles (Ruffell and Wach, 1998b). The unconsolidated glauconitic and white quartzose sands with clay drapes are interpreted to be estuarine in origin and are typical of the estuarine cycles found in the Aptian-Albian Sandrock Formation above. The Sandrock Formation (*H. jacobi?–L. tardefurcata?* ammonite zone) comprises laterally extensive sand bodies separated by thick intervals of mud. The sandstone beds generally coarsen upward and contain evidence of erosional surfaces, flaser, wavy, and lenticular bedding, uni- and bi-directional crossbedding, trough and planar cross-bedding, ripple forms, intra-formational clasts, and lag deposits. The physical sedimentary structures preserved in these successions could represent several depositional environments including barrier ridges, shallow shelf deposits, deltaic sediments, mouth bars, or tidal deposits of shoals and sand ridges (Wach and Ruffell, 1991). The dark grey to black, often glauconitic muds, have few physical sedimentary structures and are either finely laminated or extensively bioturbated. The presence of brackish microfauna suggests marginal marine conditions, i.e. muddy shelf deposits, estuary mud fill or intertidal flats (Wach, 1991; Wach and Ruffell, 1991; Ruffell and Wach, 1998a). The Lower Albian Monk's Bay Sandstone Formation (*D. mammillatum–H. dentatus* ammonite zones) consists of interbedded units of highly ferruginous, generally coarse-grained, weakly consolidated quartz-rich sandstone, fine-grained pebbly sandstone (gritstone), and ironstone (Hopson et al., 2011). The dark red sediments comprise oxidized coarse-grained consolidated sandstone with iron oxide/oxyhydroxide cement, perhaps derived from glauconite-rich sediments deposited on a shallow shelf (Wach, 1991; Wach and Ruffell, 1991; Ruffell and Wach, 1998a).

The clay-dominated Gault Clay Formation (Albian, Selborne Group) corresponds to a low-energy open marine facies (Owen, 1975).

3. Material and methods

Twenty-four (24) samples from the Lower Cretaceous succession in Compton Bay (Fig. 3) and Atherfield (Isle of Wight, UK) were analysed for carbonate and TOC content and several Rock-Eval pyrolysis parameters (Table 1 and 2 and Figs 4 and 5) at GeoMark Research, Ltd (USA).

TOC was measured using a LECO C230 instrument, calibrated with internal standards having known carbon contents. After weighing and decarbonation with concentrated HCl for at least two hours, the samples were rinsed with water and flushed through a filtration apparatus to remove the acid. The filter was then removed, the sample weighed, and placed into a LECO crucible and dried in an oven (110 °C) for a minimum of four hours. Carbonate content (%) is calculated from the sample weight loss after decarbonation. The LECO C230 uses an induction furnace to combust samples and standards to a temperature of ~ 1200 °C in an oxygen-rich atmosphere. Both CO and CO_2 are generated; CO is converted to CO_2 by a catalyst. CO_2 is then measured by an infrared cell and converted to TOC %. GeoMark Standards were analysed as unknowns every ten samples to check precision and accuracy. Laboratory acceptable standard deviation for TOC is 3%.

For Rock-Eval pyrolysis determinations (Rock-Eval II) approximately 100 mg of crushed sample was heated (in a pyrolysis oven) in an inert atmosphere (helium) to 550 ºC, per the analytical procedures outlined in (Espitalié et al., 1977, 1985) and (Peters, 1986). Standards were analysed as unknowns for every ten samples to check precision and accuracy. In addition to

TOC, direct measurements obtained by this procedure include S1 (mg HC/g rock), S2 (mg HC/g rock), S3 (mg CO_2/g rock), and T_{max} (ºC). The acceptable standard deviation for T_{max} is ± 2 °C, 10% for S1 and S2, and 20% for S3. The pyrolysis oven was programmed as follows: for 5 min the oven is kept isothermally at 300 °C and the free hydrocarbons are volatilized and measured as the S1 peak (detected by Flame Ionization Detector - FID). The temperature is then increased from 300° to 550 °C (at 25 °C/min). The released hydrocarbons are measured as the S2 peak (by FID). The temperature at which S2 reaches its maximum is called T_{max} (°C) and depends on the nature and maturity of the kerogen. The CO_2 released from kerogen cracking is trapped between 300-390 °C. The trap is heated; CO_2 is released and detected on a Thermal Conductivity Detector during cooling (S3 peak). Other parameters derived were Hydrogen Index (HI = S2/TOCx100) and Oxygen Index (OI = S3/TOCx100) (Espitalié et al., 1977, 1985; Peters, 1986). Kerogen type classification follows guidelines in Tissot et al. (1974), Espitalié et al. (1977, 1985), Harwood, 1977), and Peters (1986).

4. Kerogen assemblages from the Lower Cretaceous successions cropping out at Compton Bay and Atherfield

4.1. Kerogen characterization: TOC and Rock-Eval pyrolysis

The obtained carbonate, TOC and Rock-Eval datasets from the Lower Cretaceous successions cropping out at Compton Bay and Atherfield are presented in tables 1 and 2 and Figures 4 and 5. Carbonate and TOC contents range between 1.4–83.5 and 0.04–2.93 % respectively. Pyrolysis S1, S2, and S3 vary between 0.01–0.12 mg HC/g rock, 0.01–5.40 mg HC/g rock, and 0.02–2.28 mg CO_2/g rock, respectively. HI and OI varies between 2–338 mg

HC/g TOC and 12–317 mg CO2/g TOC respectively (an OI value of 1594 mg CO2/g TOC from sample CB-R-1 is considered not valid) (Table 1). Valid T_{max} vary between 425–432 °C.

Sample IOWR-RS-1m (1m above the Perna Bed) presents a *low-temperature S2 shoulder* on the Rock-Eval pyrogram. This is thought to occur because heavier, free hydrocarbons and non-hydrocarbons, such as resins and asphaltenes, vaporise or crack only at higher temperatures and are included in the S2 peak, resulting in reduced S1, artificially elevated S2, and potentially suppressed T_{max} values (Clementz, 1979). The *low-temperature S2 shoulder effect* may be more expressive in samples with low TOC and low S2 peak, as is the case of sample *IOWR-RS-1m*. Remaining T_{max} values < 435 °C (Table 1) indicate that the Lower Cretaceous is thermally immature (Tissot and Welte, 1984; Law, 1999).

It is known that the rock matrix (mainly clay minerals) adsorbs some of the hydrocarbons liberated during the pyrolysis experiment, possibly resulting in depressed HI values and incorrect kerogen type identification (Espitalié et al., 1980, 1985), i.e. the 'matrix effect' (Langford and Blanc-Valleron, 1990). Figure 5 illustrates that the regression trends of the Vectis (excluding the high HI sample *Shepherds Chine*) and Atherfield Clay formations have regression slopes close to the hypothetical regression line HI = 50 mg HC/g TOC. The Ferruginous Sands and Sandrock formations have lower HI trends, approximately HI = 20 mg HC/g TOC. Adsorption of hydrocarbons via the matrix effect is visualised by a positive x-intercept of the regression trend on the S2 vs TOC diagram, and the magnitude of this effect is related to the position of the intercept (Langford and Blanc-Valleron, 1990). The regression equation calculated for the Sandrock Formation has an x-intercept of 0.55 % TOC. However, the slope of the regression line falls below the hypothetical regression line HI = 50 mg HC/g TOC and even high TOC samples fall in the kerogen Type IV field (Fig. 5). The observations above suggest that the matrix effect, despite the x axis-intercept of 0.55 % TOC determined in the Sandrock Formation, does not explain the overall low HI (see Langford and Blanc-Valleron, 1990) and, therefore, HI data reflect the composition and preservation state of the kerogen assemblages (Table 1).

The variable TOC and low HI values (≤ 50 mg HC/g TOC) classify the kerogen assemblages as Type IV, excepting the higher HI sample *Shepherds Chine*, which is classified as Type II-III (Tissot and Welte, 1984; Tyson, 1995). These interpretations are consistent with the overall depositional setting of the Lower Cretaceous in the Wessex Basin (Casey, 1961; Ruffell and Wach, 1991, 1998b; Wach, 1991; Wach and Ruffell, 1991; Hopson et al., 2008, 2011), published palynological, palynomaceral, and palynofacies studies (Batten, 1982; Ruffell and Batten, 1994; Harding and Allen, 1995; Allen et al., 1998; Stead and Eyers, 2017).

4.2. Depositional constraints on the distribution of sedimentary OM during the Lower Cretaceous in the Isle of Wight, Wessex Basin

Type IV kerogens are usually dominated by oxidised wood and coaly particles and charcoal and with subordinate amounts of sporomorphs (a collective term for all terrestrial spores and pollen), aquatic marine and non-marine palynomorphs (e.g. dinoflagellate cysts, *Botryococcus* sp.), and amorphous organic matter (Tissot et al., 1974; Harwood, 1977; Tyson, 1995). Opaque phytoclasts (oxidised wood) are thought to be formed by desiccation, oxidation, and fungal mouldering of woody material in aerobic conditions in the upper part of soils and peats (Styan and Bustin, 1983; Tyson, 1995). Charcoal is the product of the natural pyrolysis of terrestrial macrophyte material in high temperatures and under conditions of oxygen starvation (Cope, 1980; Chaloner, 1989). It was suggested that the occurrence of opaque phytoclasts *s.l.* is favoured by strongly variable climates (with pronounced dry periods) and with significant water table fluctuations (Diessel, 1986; Tyson, 1995; Lamberson et al., 1996). Also, in coarser-grained rocks (sands and siltstones), the thick oxic layer below the sediment surface and exposure to oxygenated groundwaters may result in Type IV kerogens (Peters, 1986; Tyson, 1995). Type IV kerogens may also consist of highly oxidised amorphous organic matter (Ebukanson and Kinghorn, 1985), but the overall depositional environment and known palynological data suggest this is not the case in the studied section. The exception is the relatively high HI sample *Shepherds Chine* (Vectis Formation) indicating Type II-III kerogen (see below).

The dominantly lagoonal Vectis Formation (Wealden Group, Barremian) is characterised by low carbonate and TOC contents, 7.1±4.5 (sd) % and 0.42±0.54 (sd) %, respectively. HI is highly variable, 74±108 (sd) mg HC/g TOC, indicating the presence of one sample with Type II-III kerogens while the rest comprise Type IV kerogens (Fig 5). OI averages at 91±92 (sd) mg CO_2/g TOC (Table 2). The low TOC contents of the Vectis Formation confirm the oxic-dysoxic character of the depositional environment. The highly variable HI contents of the Vectis Formation reflect changes in kerogen assemblages, driven by variation in depositional and paleoenvironmental conditions which modulated sedimentary organic matter composition and preservation conditions (Tyson, 1995). Harding and Allen (1995) demonstrated that the palynomaceral assemblages of the Vectis Formation range from being dominated by terrestrial particles (kerogen assemblages with low HI) to being dominated by aquatic particles (kerogen assemblages with higher HI, i.e. *Shepherds Chine* sample). The kerogen assemblage of the *Shepherds Chine* sample is likely dominated by dinoflagellate cysts, saccate pollen, and unknown amounts of amorphous organic matter, phytoclasts, and sporomorphs. Findings from this study supports Harding and Allen (1995) interpretation that the variability of the kerogen assemblages in the Vectis Formation was a function of fluvial sediment and terrestrial organic matter input into the lagoonal environment with changes in salinity, sediment resuspension, and turbulence, which controlled the abundance of dinoflagellate cysts.

The Atherfield Clay Formation (Lower Aptian, Lower Greensand Group, Atherfield section) has the highest carbonate content of all studied units, with an average of 44.4±39.0 (sd) %. Average TOC is the lowest of all studied units, 0.32±0.22 (sd) %. Average HI and OI are 23±12 (sd) mg HC/g TOC and 173±144 (sd) mg CO_2/g TOC respectively (Table 2). In the Wessex Basin, the Early Aptian OAE 1a corresponds to most of the Atherfield Clay Formation (Gröcke et al., 1999; Gröcke, 2002). The base of this unit represents a widespread transgressive episode, overlying the dominantly lagoonal Vectis Formation. Despite the marine nature of the studied interval, TOC and HI in the studied samples are low, suggesting that OM preservation potential was low in this shallow marine setting (likely due to oxidization) and preserved sedimentary OM is characterised by Type IV kerogen assemblages (Table 1). However, some organic matter enrichment (although not detected in our dataset) accompanies the major negative $\delta^{13}C$ excursion recorded at the base of OAE 1a (Gröcke et al., 1999; Gröcke, 2001). A detailed discussion regarding the record of OAE1a in the Wessex Basin (Isle of Wight, Chale Bay section) can be found in Gröcke (2002).

Carbonate and TOC average contents of the Ferruginous Sands Formation (Lower Greensand Group, Lower–Upper Aptian) are 14.3±16.5 (sd) % and 1.04±0.77 (sd) %, respectively. Average HI and OI are 8±4 (sd) mg HC/g TOC and 41±11 (sd) mg CO_2/g TOC, respectively (Table 2). TOC contents of the Ferruginous Sands Formation are highly variable (Tables 1 and 2 and Fig 4). As in the previous units, HI is low, indicating Type IV kerogens and that preservation was very low. The variable TOC contents of the Ferruginous Sands Formation are interpreted to reflect depositional variation (estuary–shelf) associated with this unit and the differing ability of each system to entrap and store organic matter (Tyson, 1995) (Fig. 4).

Carbonate and TOC average contents of the Sandrock Formation (Lower Greensand Group, Upper Aptian–Lower Albian) are 3.7±1.0 (sd) % and 1.55±1.03 (sd) %, respectively. Average HI and OI are 9±7 (sd) mg HC/g TOC and 27±5 (sd) mg CO_2/g TOC, respectively (Table 2). Except for its extreme base, representing a major flooding interval (Wach and Ruffell, 1991), high TOC contents (TOC > 2 %) in the Sandrock Formation at Compton Bay were determined in black mudstones interpreted as estuary mud fill/subtidal flats and in thin black mudstone bands interpreted as tidal bundles within poorly consolidated white quartzose sandstone (Table 1 and Figs 4 and 5). Rock-Eval pyrolysis indicates Type IV kerogen assemblages, again suggesting marked climatic variation (with pronounced dry periods) and large variations of the water table in the source area and during transport (Diessel, 1986; Tyson, 1995; Lamberson et al., 1996) (Fig. 4).

5. Conclusions

Elemental analysis (carbonate and TOC) and pyrolysis of kerogen assemblages (pyrolysis Rock-Eval) from the upper Barremian–Lower Albian sedimentary successions cropping out in Compton Bay and Atherfield (Isle of Wight, UK) allow us to conclude that:

-The variable TOC and low HI contents, overall depositional setting, and published palynological, palynomaceral, and palynofacies studies classify the kerogen assemblages of the analysed samples as Type IV. One sample from the Vectis formation is classified as Type II-III.

-Type IV kerogen assemblages (immature rocks) are interpreted to be dominated by oxidised wood and coaly particles and charcoal, with variable amounts of sporomorphs, aquatic marine and non-marine palynomorphs, and amorphous organic matter. The dominance of oxidised wood, coaly particles, and charcoal suggest marked climatic variations (with pronounced dry periods) along with significant water table fluctuations.

-The Type II-III kerogen assemblage determined in the lagoonal Vectis Formation comprises a mixture of terrestrial and aquatic particles. This study's findings support previous studies that have suggested that kerogen assemblages in the lagoonal Vectis Formation varied as a function of fluvial sediment and terrestrial organic matter input into the lagoonal environment with changes in salinity, sediment resuspension, and turbulence controlling the abundance of dinoflagellate cysts.

Acknowledgements

This research was supported by the Source Rock and Geochemistry of the Central Atlantic Margins consortium (Dalhousie University, Basin and Reservoir Lab, PI-Grant Wach). Ricardo L. Silva was also partially supported by iCRAG (project: Temporal and spatial variability in Lower Jurassic hydrocarbon source rock quality in Irish off-shore marine basins, PI-Dr Micha Ruhl). We gratefully acknowledge Maya Soukup, Philip Sedore, and Charlie Carlisle for their help with sample collection and preparation; and the Editor-in-Chief Malcolm Barrie Hart and two anonymous referees for their insightful comments that greatly benefited the manuscript.

References

Akinlotan, O., 2018. Multi-proxy approach to palaeoenvironmental modelling: the English Lower Cretaceous Weald Basin. Geological Journal 53, 316–335.

Allen, P., Alvin, K.L., Andrews, J.E., Batten, D.J., Charlton, W.A., Cleevely, R.J., Ensom, P.C., Evans, S.E., Francis, J.E., Hailwood, E.A., Harding, I.C., Horne, D.J., Hughes, N.F., Hunt, C.O., Jarzembowski, E.A., Jones, T.P., Knox, R.W.O., Milner, A., Norman, D.B., Palmer, C.P., Parker, A., Patterson, G.A., Price, G.D., Radley, J.D., Rawson, P.F., Ross, A.J., Rolfe, S., Ruffell, A.H., Sellwood, B.W., Sladen, C.P., Taylor, K.G., Watson, J., Wright, V.P., Wimbledon, W.A., Banham, G.H., 1998. Purbeck–Wealden (early Cretaceous) climates. Proceedings of the Geologists' Association 109, 197–236.

Batten, D.J., 1982. Palynofacies and salinity in the Purbeck and Wealden of southern England, in: Banner, F.T., Lord, A.R. (Eds.), Aspects of Micropalaeontology. Springer Netherlands, Dordrecht, pp. 278–308.

British Geological Survey, 2014. Isle of Wight (B&S) Special Sheet E330, 331, 344 & 345.

Casey, R., 1961. The stratigraphical palaeontology of the Lower Greensand. Palaeontology 3, 487–621.

Chaloner, W.G., 1989. Fossil charcoal as an indicator of palaeoatmospheric oxygen level. Journal of the Geological Society 146, 171–174.

Clementz, D.M., 1979. Effect of Oil and Bitumen Saturation on Source-Rock Pyrolysis: Geologic notes. American Association of Petroleum Geologists Bulletin 63, 2227–2232.

Cope, M.J., 1980. Physical and chemical properties of coalified and charcoalified phytoclasts from some British Mesozoic sediments: An organic geochemical approach to palaeobotany. Physics and Chemistry of the Earth 12, 663–677.

Diessel, C.F.K., 1986. On the correlation between coal facies and depositional environments, in: Proceedings of the 20th Symposium on Advances in the Study of the Sydney Basin. Department of Geology, University of Newcastle, New South Wales, pp. 19–22.

Ebukanson, E.J., Kinghorn, R.R.F., 1985. Kerogen Facies in the Major Jurassic Mudrock Formations of Southern England and the implications on the Depositional Environments of their Precursors. Journal of Petroleum Geology 8, 435–462.

Espitalié, J., Deroo, G., Marquis, F., 1985. La pyrolyse Rock-Eval et ses applications. Deuxième partie. Revue de l'Institut Francais du Petrole 40, 755–784.

Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mètres, de leur potentiel pétrolier et de leur degré d'évolution. Revue de l'Institut Français du Pétrole 32, 23–42.

Espitalié, J., Madec, M., Tissot, B., 1980. Role of mineral matrix in kerogen pyrolysis: influence on petroleum generation and migration. American Association of Petroleum Geologists Bulletin 64, 59–66.

Gröcke, D.R., 2002. The carbon isotope composition of ancient CO2 based on higher-plant organic matter. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 360, 633–658.

Gröcke, D.R., 2001. Isotope stratigraphy and ocean–atmosphere interactions in the Jurassic and Early Cretaceous. University of Oxford.

Gröcke, D.R., Hesselbo, S.P., Jenkyns, H.C., 1999. Carbon-isotope composition of Lower Cretaceous fossil wood: Ocean-atmosphere chemistry and relation to sea-level change. Geology 27, 155-158

Harding, I.C., Allen, R.M., 1995. Dinocysts and the palaeoenvironmental interpretation of non-marine sediments: an example from the Wealden of the Isle of Wight (Lower Cretaceous, southern England). Cretaceous Research 16, 727–743.

Harwood, R.J., 1977. Oil and Gas Generation by Laboratory Pyrolysis of Kerogen. American

Association of Petroleum Geologists Bulletin 61, 2082–2102.
Hopson, P.M., Wilkinson, I.P., Woods, M.A., 2008. A stratigraphical framework for the Lower Cretaceous of England, British Geological Survey Research Report RR/08/03.
Hopson, P.M., Wilkinson, I.P., Woods, M.A., Farrant, A.R., 2011. The Lower Albian (Lower Cretaceous) Monk's Bay Sandstone Formation (formerly the Carstone) of the Isle of Wight: Its distribution, litho- and biostratigraphy. Proceedings of the Geologists' Association 122, 816–830.
Insole, A., Hutt, S., 1994. The palaeoecology of the dinosaurs of the Wessex Formation (Wealden Group, Early Cretaceous), Isle of Wight, Southern England. Zoological Journal of the Linnean Society 112, 197–215.
Karner, G.D., Lake, S.D., Dewey, J.F., 1987. The thermal and mechanical development of the Wessex Basin, southern England, in: Coward, M.P., Dewey, J. F., Hancock, P.L. (Eds.), Continental Extensional Tectonics. Geological Society, London, Special Publications Vol 28. pp. 517–536.
Lamberson, M.N., Bustin, R.M., Kalkreuth, W.D., Pratt, K.C., 1996. The formation of inertinite-rich peats in the mid-Cretaceous Gates Formation: implications for the interpretation of mid-Albian history of paleowildfire. Palaeogeography, Palaeoclimatology, Palaeoecology 120, 235–260.
Langford, F.F., Blanc-Valleron, M.-M., 1990. Interpreting Rock-Eval pyrolysis data using graphs of pyrolizable hydrocarbons vs. total organic carbon. American Association of Petroleum Geologists Bulletin 74, 799–804.
Law, C.A., 1999. Evaluating Source Rocks, in: Beaumont, E.A., Foster, N.H. (Eds.), Treatise of Petroleum Geology/Handbook of Petroleum Geology: Exploring for Oil and Gas Traps. The

American Association of Petroleum Geologists, pp. 6-1-6–41.
Owen, H.G., 1975. The stratigraphy of the Gault and Upper Greensand of the Weald. Proceedings of the Geologists' Association 86, 475–498.
Peters, K.E., 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. American Association of Petroleum Geologists Bulletin 70, 318–329.
Radley, J.D., Allen, P., 2012. The Wealden (non-marine Lower Cretaceous) of the Wessex Sub-basin, southern England. Proceedings of the Geologists' Association 123, 319–373.
Robinson, S.A., Hesselbo, S.P., 2004. Fossil-wood carbon-isotope stratigraphy of the non-marine Wealden Group (Lower Cretaceous, southern England). Journal of the Geological Society 161, 133–145.
Ruffell, A., Worden, R., 2000. Palaeoclimate analysis using spectral gamma-ray data from the Aptian (Cretaceous) of southern England and southern France. Palaeogeography, Palaeoclimatology, Palaeoecology 155, 265–283.
Ruffell, A.H., Batten, D.J., 1994. Uppermost Wealden facies and Lower Greensand Group (Lower Cretaceous) in Dorset, southern England: correlation and palaeoenvironment. Proceedings of the Geologists' Association 105, 53–69.
Ruffell, A.H., Batten, D.J., 1990. The Barremian-Aptian arid phase in western Europe. Palaeogeography, Palaeoclimatology, Palaeoecology 80, 197–212.
Ruffell, A.H., McKinley, J.M., Worden, R.H., 2002. Comparison of clay mineral stratigraphy to other proxy palaeoclimate indicators in the Mesozoic of NW Europe. Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences 360, 675–693.
Ruffell, A.H., Rawson, P.F., 1994. Palaeoclimate control on sequence stratigraphic patterns in

the late Jurassic to mid-Cretaceous, with a case study from Eastern England. Palaeogeography, Palaeoclimatology, Palaeoecology 110, 43–54.

Ruffell, A.H., Wach, G.D., 1998a. Estuarine/Offshore Depositional Sequences of the Cretaceous Aptian-Albian Boundary England, in: Graciansky, P.-C. de, Hardenbol, J., Jacquin, T., Vail, P.R. (Eds.), Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. Vol 60. SEPM (Society for Sedimentary Geology), pp. 411–421.

Ruffell, A.H., Wach, G.D., 1998b. Firmgrounds - key surfaces in the recognition of parasequences in the Aptian Lower Greensand Group, Isle of Wight (southern England). Sedimentology 45, 91–107.

Ruffell, A.H., Wach, G.D., 1991. Sequence stratigraphic analysis of the Aptian-Albian Lower Greensand in southern England. Marine and Petroleum Geology 8, 341–353.

Stead, D., Eyers, J., 2017. The palynology and geology of the Lower Cretaceous (Aptian–Albian) of Munday's Hill Quarry, Bedfordshire, UK. Proceedings of the Geologists' Association 128, 599–612.

Stewart, D.J., Ruffell, A., Wach, G., Goldring, R., 1991. Lagoonal sedimentation and fluctuating salinities in the Vectis Formation (Wealden Group, Lower Cretaceous) of the Isle of Wight, southern England. Sedimentary Geology 72, 117–134.

Styan, W.B., Bustin, R.M., 1983. Petrographyof some fraser river delta peat deposits: Coal maceral and microlithotype precursors in temperate-climate peats. International Journal of Coal Geology 2, 321–370.

Tissot, B., Durand, B., Espitalie, J., Combaz, A., 1974. Influence of Nature and Diagenesis of Organic Matter in Formation of Petroleum. American Association of Petroleum Geologists Bulletin 58, 499–506.

Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence, Springer-Verlag Berlin Heidelberg. Springer Berlin Heidelberg, Berlin, Heidelberg.

Tyson, R. V., 1995. Sedimentary organic matter: organic facies and palynofacies. Springer Netherlands.

Wach, G.D., 1991. Sedimentology and Stratigraphy of the Lower Cretaceous of the Channel Basin. D.Phil. dissertation, University of Oxford.

Wach, G.D., Ruffell, A.H., 1991. Sedimentology and sequence stratigraphy of a Lower Cretaceous tide and storm-dominated clastic succession, Isle of Wight and S.E. England. British Sedimentological Research Group Field Guide 4.

Whittaker, A., 1985. Atlas of onshore sedimentary basins in England and Wales : post-Carboniferous tectonics and stratigraphy. Blackie, Glasgow.

Wilkinson, I.P., 2008. The effect of environmental change on early Aptian ostracods faunas in the Wessex Basin, southern England. Revue de Micropaléontologie 51, 259–272.

Figure captions

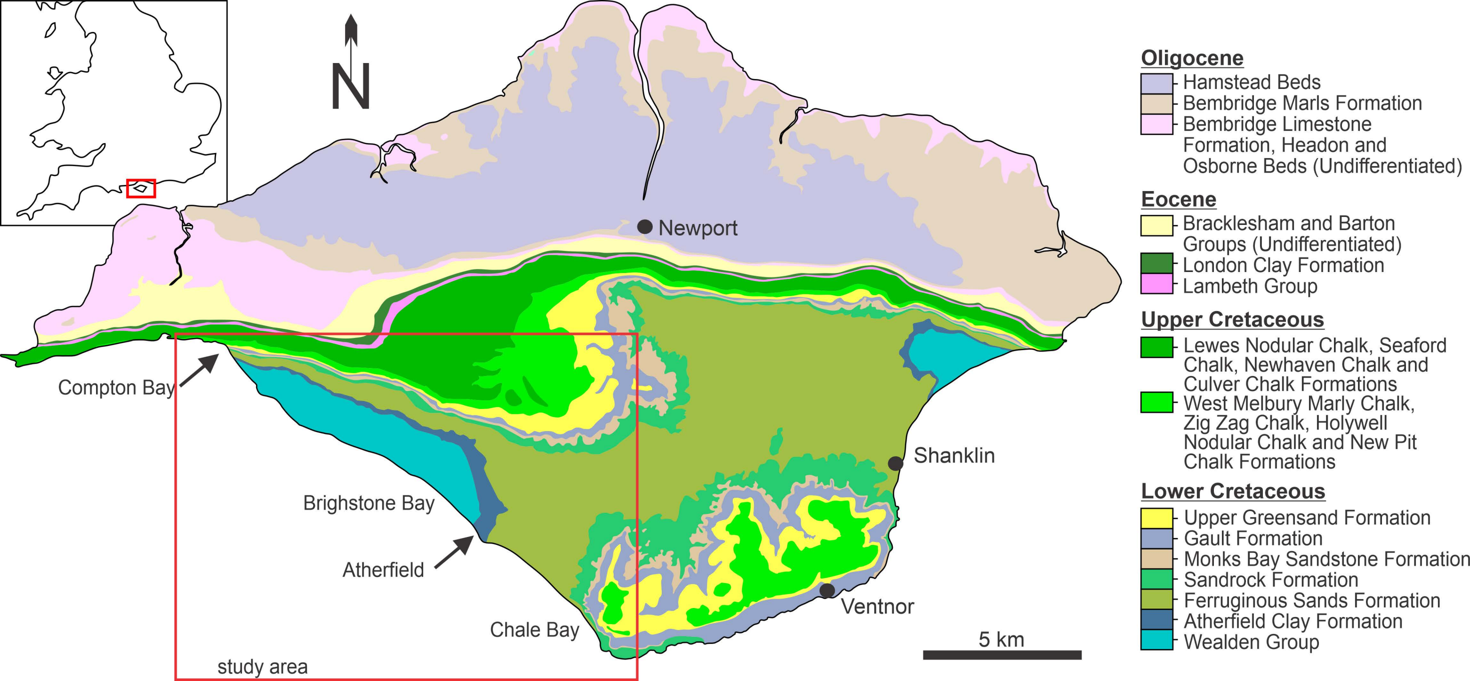
Figure 1. Simplified geological map of the Isle of Wight, Wessex Basin, UK (modified from BGS, 2014).

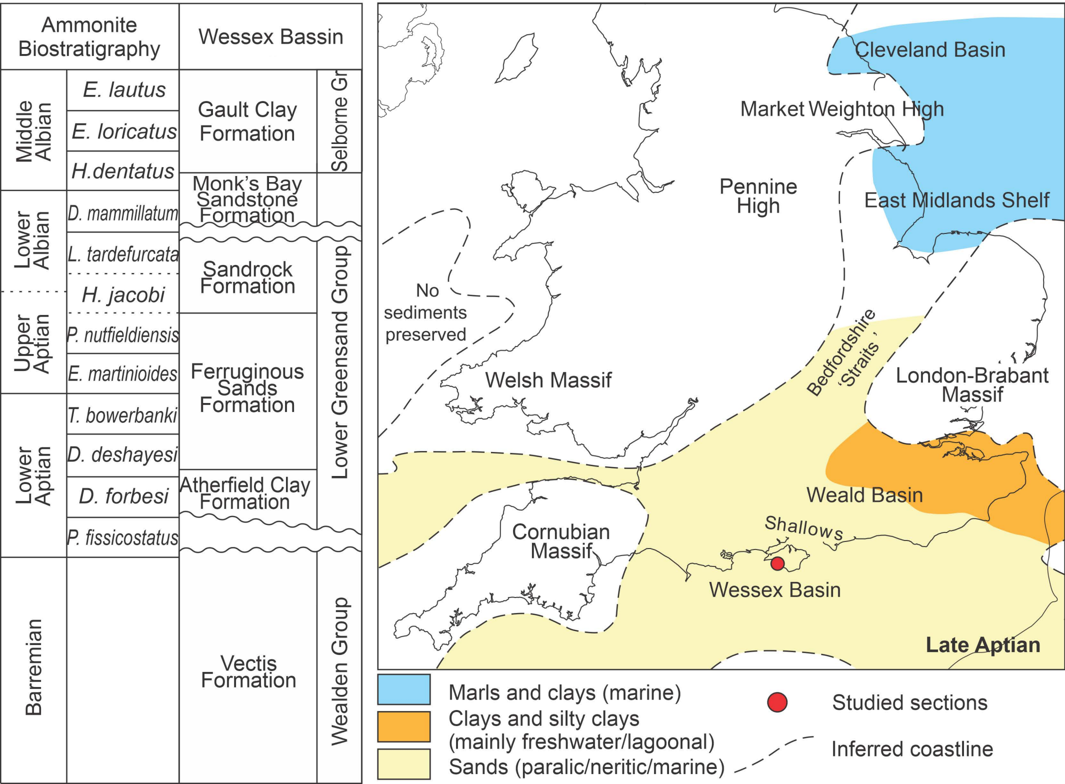
Figure 2. Lithostratigraphy of the Wealden, Lower Greensand, and Selborne groups in the Wessex Basin (UK) and simplified paleogeographic setting of the studied area during the Late Aptian (modified from Casey, 1961; Wach, 1991; Hopson et al., 2008, 2011). This study is focussed on the Vectis, Atherfield Clay, Ferruginous Sands, Sandrock, and Gault Clay formations.

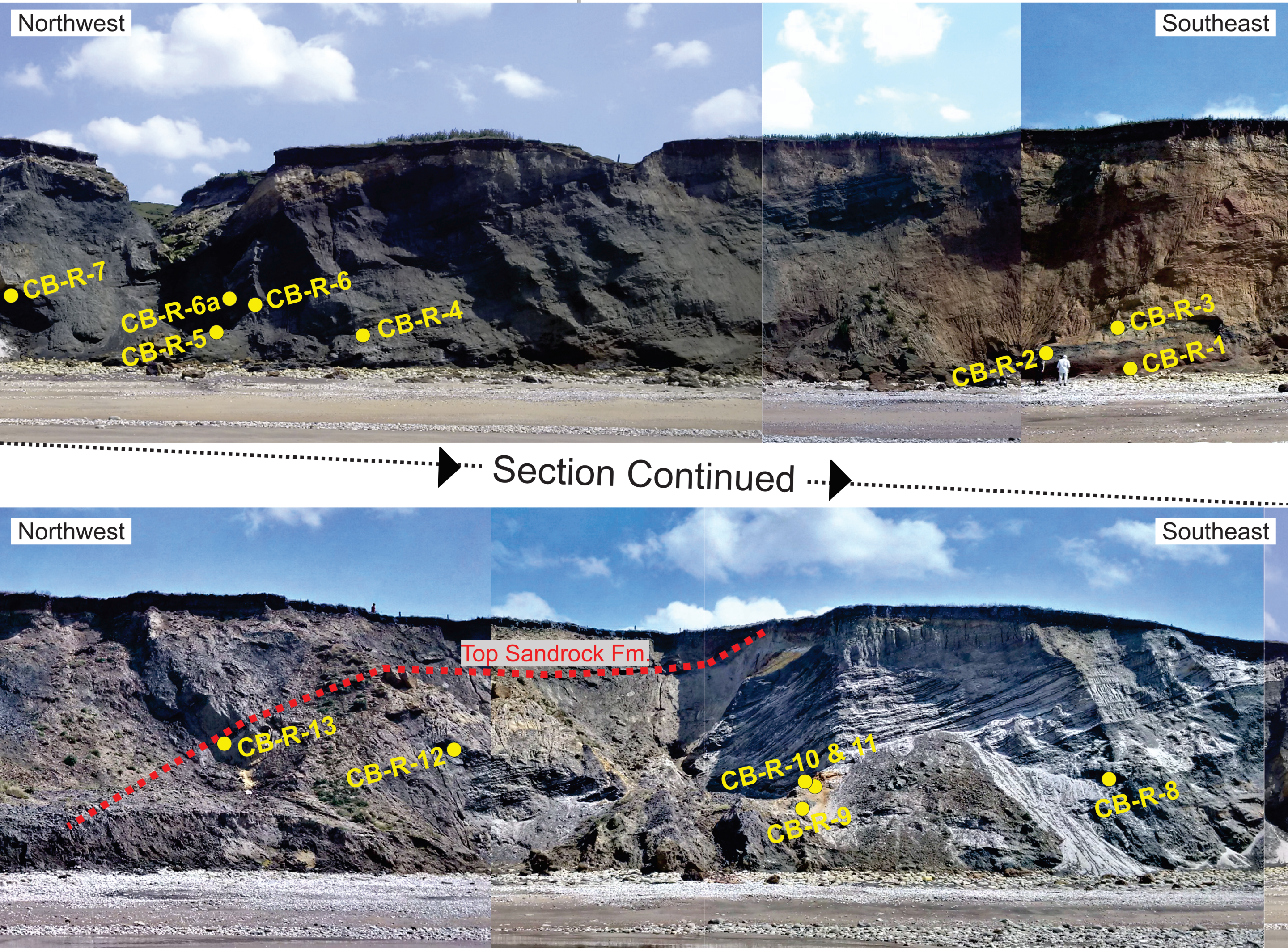
Figure 3. Photomontage of the CB-R sample suite from Compton Bay, Isle of Wight, Wessex Basin, UK (see also Fig. 4).

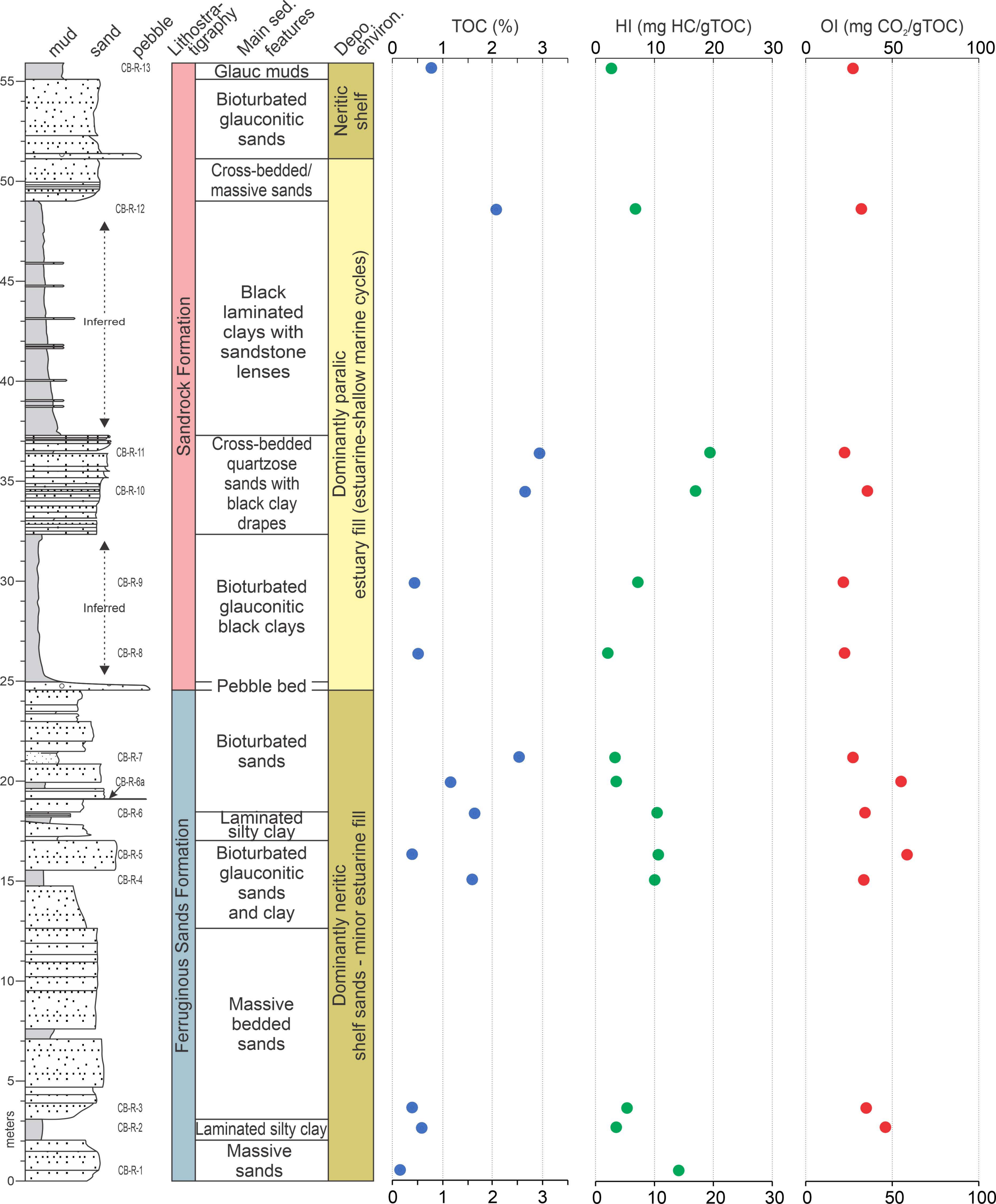
Figure 4. Sedimentological log and TOC, Hydrogen Index (HI), and Oxygen Index (OI) data analysed from the Ferruginous Sands and Sandrock formations at Compton Bay, Isle of Wight, Wessex Basin, UK. Sed. – sedimentary; depo – depositional; environ – environment.

Figure 5. S2 vs TOC plot (Langford and Blanc-Valleron, 1990) of the studied samples from the Vectis, Atherfield Clay, Ferruginous Sands, Sandrock, and Gault formations in the Compton Bay and Atherfield sections, Wessex Basin (UK).

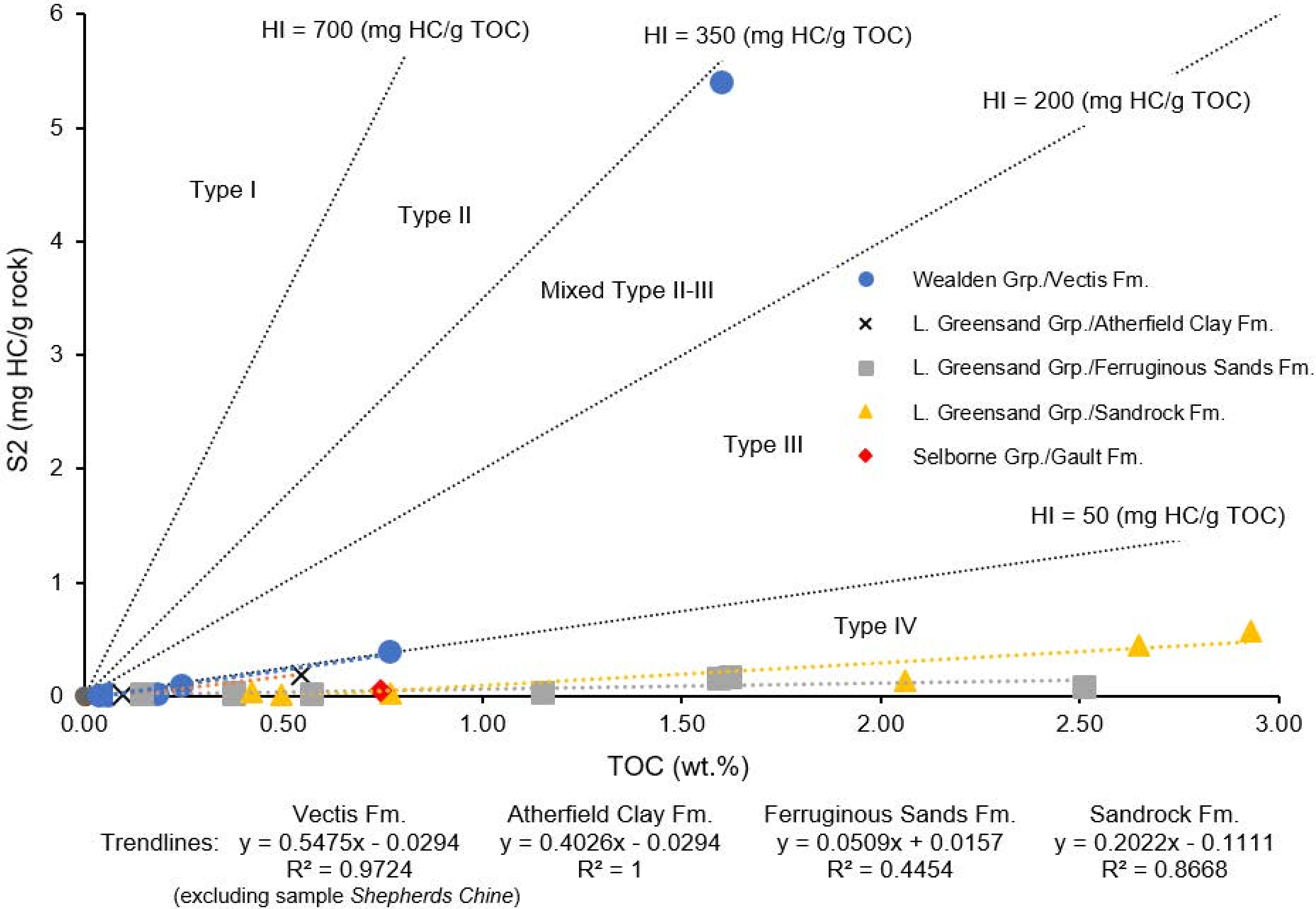

N
Newport
Shanklin
Ventnor
Compton Bay
Brighstone Bay
Atherfield
Chale Bay
study area
5 km
Oligocene
Hamstead Beds
Bembridge Marls Formation
Bembridge Limestone Formation, Headon and Osborne Beds (Undifferentiated)
Eocene
Bracklesham and Barton Groups (Undifferentiated)
London Clay Formation
Lambeth Group
Upper Cretaceous
Lewes Nodular Chalk, Seaford Chalk, Newhaven Chalk and Culver Chalk Formations
West Melbury Marly Chalk, Zig Zag Chalk, Holywell Nodular Chalk and New Pit Chalk Formations
Lower Cretaceous
Upper Greensand Formation
Gault Formation
Monks Bay Sandstone Formation
Sandrock Formation
Ferruginous Sands Formation
Atherfield Clay Formation
Wealden Group


Ammonite Biostratigraphy
Wessex Bassin
Middle Albian
E. lautus
E. loricatus
H.dentatus
Lower Albian
D. mammillatum
L. tardefurcata
H. jacobi
Upper Aptian
P. nutfieldiensis
E. martinioides
Lower Aptian
T. bowerbanki
D. deshayesi
D. forbesi
P. fissicostatus
Barremian
Gault Clay Formation
Monk's Bay Sandstone Formation
Sandrock Formation
Ferruginous Sands Formation
Atherfield Clay Formation
Vectis Formation
Selborne Gr
Lower Greensand Group
Wealden Group
Cleveland Basin
Market Weighton High
Pennine High
East Midlands Shelf
No sediments preserved
Welsh Massif
Bedfordshire 'Straits'
London-Brabant Massif
Weald Basin
Shallows
Cornubian Massif
Wessex Basin
Late Aptian
Marls and clays (marine)
Clays and silty clays (mainly freshwater/lagoonal)
Sands (paralic/neritic/marine)
Studied sections
Inferred coastline


Northwest
Southeast
CB-R-7
CB-R-6a
CB-R-6
CB-R-5
CB-R-4
CB-R-3
CB-R-2
CB-R-1
Section Continued
Northwest
Southeast
Top Sandrock Fm.
CB-R-13
CB-R-12
CB-R-10 & 11
CB-R-9
CB-R-8



mud
sand
pebble
Lithostratigraphy
Main sed. features
Depo. environ.
TOC (%)
HI (mg HC/gTOC)
OI (mg CO2/gTOC)
meters
CB-R-13
CB-R-12
CB-R-11
CB-R-10
CB-R-9
CB-R-8
CB-R-7
CB-R-6a
CB-R-6
CB-R-5
CB-R-4
CB-R-3
CB-R-2
CB-R-1
Inferred
Inferred
Sandrock Formation
Ferruginous Sands Formation
Glauc muds
Bioturbated glauconitic sands
Cross-bedded/ massive sands
Black laminated clays with sandstone lenses
Cross-bedded quartzose sands with black clay drapes
Bioturbated glauconitic black clays
Pebble bed
Bioturbated sands
Laminated silty clay
Bioturbated glauconitic sands and clay
Massive bedded sands
Laminated silty clay
Massive sands
Neritic shelf
Dominantly paralic estuary fill (estuarine-shallow marine cycles)
Dominantly neritic shelf sands - minor estuarine fill



HI = 700 (mg HC/g TOC)
HI = 350 (mg HC/g TOC)
HI = 200 (mg HC/g TOC)
HI = 50 (mg HC/g TOC)
Type I
Type II
Mixed Type II-III
Type III
Type IV
Wealden Grp./Vectis Fm.
L. Greensand Grp./Atherfield Clay Fm.
L. Greensand Grp./Ferruginous Sands Fm.
L. Greensand Grp./Sandrock Fm.
Selborne Grp./Gault Fm.
S2 (mg HC/g rock)
0
1
2
3
4
5
6
0.00
0.50
1.00
1.50
2.00
2.50
3.00
TOC (wt.%)
Trendlines:
Vectis Fm.
y = 0.5475x - 0.0294
R² = 0.9724
(excluding sample Shepherds Chine)
Atherfield Clay Fm.
y = 0.4026x - 0.0294
R² = 1
Ferruginous Sands Fm.
y = 0.0509x + 0.0157
R² = 0.4454
Sandrock Fm.
y = 0.2022x - 0.1111
R² = 0.8668

Table 1. Carbonate, TOC, and Rock-Eval datsets of the studied samples from the Vectis, Atherfield Clay, Ferruginous Sands, Sandrock, and Gault formations cropping out at the Compton Bay section, Wessex Basin, UK.

sample ID	Location	Group/Formation	Stratigraphic position (m) (Fig. 4)	Carbonate (%)	TOC (%)	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg CO2/g rock)	Tmax (°C)	Hydrogen Index (mg HC/g TOC)	Oxygen Index (mg CO2/g TOC)
GW-IOWR-1	Compton Bay	Wealden Grp./Vectis Fm.	n.d.	6.69	0.06	0.12	0.02	0.05	n.d.	33	82
GW-IOWR-2	Compton Bay	Wealden Grp./Vectis Fm.	n.d.	16.62	0.04	0.04	0.01	0.09	n.d.	28	252
GW-IOWR-3	Compton Bay	Wealden Grp./Vectis Fm.	n.d.	4.44	0.06	0.04	0.01	0.02	n.d.	17	34
GW-IOWR-4	Compton Bay	Wealden Grp./Vectis Fm.	n.d.	1.38	0.24	0.04	0.1	0.04	n.d.	41	17
GW-IOWR-5	Compton Bay	Wealden Grp./Vectis Fm.	n.d.	6.67	0.18	0.04	0.02	0.38	n.d.	11	210
GW-IOWR-6	Compton Bay	Wealden Grp./Vectis Fm.	n.d.	4.76	0.77	0.07	0.4	0.23	432	52	30
Shepherds Chine	Atherfield	Wealden Grp./Vectis Fm.	single sample	8.88	1.60	0.08	5.4	0.19	432	338	12
Perna Bed RS-1	Atherfield	L. Greensand Grp./Atherfield Clay Fm./Perna Bed Member	0.8 cm above the base of Perna Bed Member	83.48	0.10	0.07	0.01	0.31	n.d.	10	317
IOWR-RS-1m	Atherfield	L. Greensand Grp./Atherfield Clay Fm/Chale Clay Member	1 m above the top of the Perna Bed Member	5.38	0.55	0.05	0.19	0.16	428†	35	29
CB-R-1	Compton Bay	L. Greensand Grp./Ferruginous Sands Fm.	0.5	56.23	0.14	0.05	0.02	2.28	n.d.	14	1594*
CB-R-2	Compton Bay	L. Greensand Grp./Ferruginous Sands Fm.	2.7	10.45	0.57	0.02	0.02	0.26	n.d.	4	46
CB-R-3	Compton Bay	L. Greensand Grp./Ferruginous Sands Fm.	3.7	5.46	0.38	0.04	0.02	0.13	n.d.	5	35
CB-R-4	Compton Bay	L. Greensand Grp./Ferruginous Sands Fm.	15.1	2.13	1.59	0.05	0.16	0.53	n.d.	10	33
CB-R-5	Compton Bay	L. Greensand Grp./Ferruginous Sands Fm.	16.3	3.83	0.38	0.01	0.04	0.22	n.d.	11	59
CB-R-6	Compton Bay	L. Greensand Grp./Ferruginous Sands Fm.	18.4	13.38	1.62	0.02	0.17	0.55	n.d.	10	34
CB-R-6a	Compton Bay	L. Greensand Grp./Ferruginous Sands Fm.	20.0	17.08	1.15	0.02	0.04	0.63	n.d.	3	55
CB-R-7	Compton Bay	L. Greensand Grp./Ferruginous Sands Fm.	21.2	5.83	2.51	0.02	0.08	0.68	n.d.	3	27
CB-R-8	Compton Bay	L. Greensands Grp./Sandrock Fm.	26.4	4.16	0.50	0.02	0.01	0.11	n.d.	2	22
CB-R-9	Compton Bay	L. Greensands Grp./Sandrock Fm.	30.0	4.44	0.42	0.02	0.03	0.09	n.d.	7	21
CB-R-10	Compton Bay	L. Greensands Grp./Sandrock Fm.	34.6	1.56	2.65	0.04	0.45	0.93	432	17	35
CB-R-11	Compton Bay	L. Greensands Grp./Sandrock Fm.	36.5	4.61	2.93	0.05	0.57	0.65	425	19	22
CB-R-12	Compton Bay	L. Greensands Grp./Sandrock Fm.	48.7	3.72	2.06	0.02	0.14	0.66	n.d.	7	32
CB-R-13	Compton Bay	L. Greensands Grp./Sandrock Fm.	55.7	3.83	0.77	0.04	0.02	0.21	n.d.	3	27
CB-R-14	Compton Bay	Selborne Grp./Gault Fm.	n.d.	5.19	0.75	0.05	0.05	0.28	n.d.	7	38

n.d. - not determined; * - not valid; † - low temperature S2 shoulder; Grp. - Group; Fm. - Formation

Table 2. Average carbonate, TOC, HI and OI contents of the studied samples from the Vectis, Atherfield Clay, Ferruginous Sands, Sandrock, and Gault formations cropping out at the Compton Bay section, Wessex Basin, UK.

	Wealden Grp.	L. Greensand Grp		
	Vectis Fm.	Atherfield Clay Fm.	Ferruginous Sands Fm.	Sandrock Fm.
Carbonate (wt%)				
n	7	2	8	6
average	7.1	44.4	14.3	3.7
sd	4.5	39.0	16.5	1.0
TOC (%)				
n	7	2	8	6
average	0.42	0.32	1.04	1.55
sd	0.54	0.22	0.77	1.03
Hydrogen Index (mg HC/gTOC)				
n	7	2	8	6
average	74	23	8	9
sd	108	12	4	7
Oxygen Index (mg CO2/g TOC)				
n	7	2	7	6
average	91	173	41	27
sd	92	144	11	5