Intermittent euxinia: Reconciliation of a Jurassic black shale with its biofacies

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ABSTRACT
Isorenieratane, a molecular fossil derived from the brown strain of the green sulfur bacteria Chlorobiaceae, is ubiquitous in the organic carbon–rich, argillaceous, fossiliferous Peterborough Member (Callovian, UK) of the Oxford Clay Formation, indicating a temporal overlap of the euphotic and sulfidic zone in the water column. The presence of euxinic conditions in the water column is inconsistent with the abundant benthic fauna in that formation, which indicates bottom-water oxygenation. These conflicting geochemical and paleontological data suggest intermittent euxinia during deposition. The duration of oxic-dysoxic events can be estimated by considering the life mode, life span, and colonization time of the benthic fauna incorporated in these sedimentary rocks. As previously proposed, the preservation of sedimentary organic matter, based on Rock-Eval parameters, is directly related to the frequency and/or duration of oxic bottom-water conditions.

Keywords: green sulfur bacteria, biofacies, Oxford Clay Formation, Peterborough Member, anoxia, isorenieratane.

INTRODUCTION
The Peterborough Member of the Oxford Clay Formation (south-central England) is an organic carbon–rich mudrock (black shale), containing to 16.6 wt% organic carbon (Kenig et al., 1994), that was deposited during the middle Callovian in an epeiric sea joining the Tethys to the Boreal Sea (e.g., Hudson and Martill, 1994; Fig. 1). Abundant benthic and nektonic fauna (ammonites, belemnites, and some of the largest fish and marine reptiles known) inspired many paleontological studies (summarized in Martill and Hudson, 1991; Wilby et al., 2004). The organic matter is essentially composed of microscopic remains of well-preserved marine phytoplankton with occasional macroscopic wood fragments (Kenig et al., 1994; Belin and Kenig, 1994). The Peterborough Member is an excellent example of an oil-prone source rock, although it is thermally immature, having never been exposed to temperatures greater than ~50 °C (Green et al., 2001).

The relative roles of organic carbon flux, redox conditions of bottom waters, and rate of sediment accumulation on organic carbon preservation and concentration are still debated (e.g., Arthur and Sageman, 1994; Wignall, 1994; Tyson, 1995; Hudson, 2001). However, few deny that oxygen deficiency at the sediment-water interface and in the water column is a major factor in the formation of organic carbon–rich sediments (e.g., Demaison and Moore, 1980; Tyson, 1995).

Rhoads and Morse (1971) published the first model relating biofacies to ranges of oxygenation of benthic environments. Duff (1975) applied this biofacies approach to the Peterborough Member and concluded, on the basis of the distribution of benthic fauna, that bottom-water conditions were never anaerobic during deposition. Faunal reconstruction of the Oxford Clay sea (e.g., Duff, 1975; Hudson and Martill, 1991; Martill et al., 1994) indicates a diversity of benthic and pelagic organisms not encountered in modern oceanic environments with anoxic bottom waters. These works raised questions about the role of anoxia in the preservation of organic matter in the Oxford Clay and other organic carbon–rich shales.

To understand the paleoceanographic conditions associated with the origin of these organic-matter and fossil-rich sedimentary rocks, we determined the distribution of molecular fossils in 11 samples representing 5 of the major benthic biofacies identified by Duff (1975) in the Peterborough Member of south-central England.

The molecular fossil isorenieratane, and
other isorenieratene derivatives, provide strong constraints on water-column structure. Isorenieratene is a pigment biosynthesized by the brown strain of green sulfur bacteria, Chlorobibaceae (Liaaen-Jensen, 1978). These photosynthetic bacteria grow in strictly anoxic environments and require H$_2$S as an electron donor. Isorenieratene can be preserved in sedimentary rocks in slightly altered forms and isoprenoids, including isorenieratane I. Note that isorenieratene derivatives are absent in the Stewartry Member sample where II [2-methyl-2-(4,8,12-trimethyltridecyl)monoaryl isoprenoids], including isorenieratene I. Isorenieratene derivatives in aromatic fraction of representative Peterborough Member samples analyzed contain isorenieratene derivatives (structures shown and labeled in the text), internal standard, is dominant.

**SAMPLES AND METHODS**

All 11 samples were collected from the Peterborough, Stewartry, and Weymouth Members of the Oxford Clay Formation in south-central England (Fig. 1). Samples were collected at the Dogsthorne brick pit of the London Brick Company at Peterborough and at the Stewartry, Bletchley, and Calvert brick pits (Hudson and Martill, 1994). Additional samples were also collected at the Cleveland farm pit, Ashton Keynes. Bulk geochemical parameters of the samples analyzed were given in Kenig et al. (1994).

Powdered samples were Soxhlet extracted and fractionated following the procedure described in Simons and Kenig (2001). Organic compounds were identified using a Hewlett Packard 6890 gas chromatograph (GC) coupled to a mass-selective detector (HP-5973) operated in electron ionization mode at 70 eV. The GC was equipped with an injector operated in splitless mode and with an HP-5MS fused-silica capillary column (30 m x 0.25 mm, film thickness 0.25 μm). The oven temperature was programmed from 60 °C, held for 1.5 min, to 130 °C at 20 °C/min, and at 4 °C/min to 315 °C, at which it was held for 60 min. Major isorenieratene derivatives, including isorenieratene, were monitored using the summed mass chromatogram m/z 133 + 134 + 237 + 287 (Koopmans et al., 1996).

The isotopic compositions of individual compounds were measured by isotope-ratio monitoring–gas chromatography–mass spectrometry (irm-GCMS) following the method of Hayes et al. (1990). The δ$^{13}$C values are averages of duplicate analyses and are reported in permil relative to the Vienna Peedee belemnite (VPDB) standard. Uncertainties reported in the text are 1 standard deviation to the average of duplicate analysis.
Molecular Record of Euxinia

The aromatic fraction and desulfurized polar fractions of all analyzed shales and shell beds from the Peterborough Member contain isorenieratene derivatives, including isorenieratane (I, Fig. 2). These compounds were all identified on the basis of their mass spectra, their retention times, and comparison to published mass spectra (Koopmans et al., 1996). Isorenieratane isolated from the desulfurized polar fraction is enriched in $^{13}$C ($^{13}$C$_{iso}$ ranging from $-16.2\%e \pm 0.5\%e$ to $-17.0\%e \pm 0.5\%e$) by ~15% relative to molecular fossils of upper water column primary producers (e.g., phytane, derived from the side chain of chlorophyll a; $^{13}$C$_{phy}$ ranging from $-30.7\%e \pm 0.5\%e$ to $-32.0\%e \pm 0.5\%e$). This enrichment confirms that isorenieratane in the Oxford Clay is derived from Chlorobiaceae (e.g., Koopmans et al., 1996) as green sulfur bacteria assimilate carbon via the reverse tricarboxylic acid cycle (Sirevåg et al., 1977). On the contrary, isorenieratane derivatives were not observed in the aromatic fractions and desulfurized polar fractions of samples of the Stewartby (Fig. 2) and Weymouth Members (Middle Member and Upper Member of the Oxford Clay, respectively).

Dynamic Water Column: Intermittent Euxinia

Identification of isorenieratane indicates that water-column euxinia with a chemocline reaching into the euphotic zone was recurrent during deposition of the Peterborough Member. The presence of fossils of benthic organisms throughout the Peterborough Member argues for the presence of variable amounts of oxygen in bottom waters. Very few benthic species are suspected of having the ability to adapt to the presence of sulfide (e.g., Oschmann, 1994; Fenchel and Finlay, 1995). We therefore suggest that periodic alternation of euxinic and oxic-dysoxic bottom-water conditions must have occurred during deposition of the Peterborough Member (cf. van Kaam-Peters et al., 1997; Röhl et al., 2001; Simons and Kenig, 2001). In our model, accumulation of organic matter and isorenieratane is associated with periods of strong stratification of the water column with euxinic conditions periodically reaching into the euphotic zone. Benthic fossils, on the contrary, must have accumulated at times of dysoxic and oxic bottom waters.

Given the characteristics of their surviving relatives, many of the bivalve species found in the Peterborough Member are suspected of being adapted to soft substrates and/or reduced oxygen levels, or are suspected of being partially independent of bottom conditions during part of their life cycle (Oschmann, 1994). Several of Duff’s “pendent” bivalves, such as Melagrinella, have the “flat clam” morphology that is often associated with both soft substrates and dysoxia (Wignall, 1994; Oschmann, 1994). They have planktonic larvae, so could opportunistically colonize temporarily oxygenated seafloors. Protobranch bivalves, abundant throughout the Peterborough Member, are adapted to deposit feeding in soft muds and contribute to their “soupiness” by near-surface bioturbation. They can live in dysoxic waters. However, they cannot survive sulfidic waters and have benthic larvae, so the maintenance of viable populations demands long periods during which Chlorobiaceae could not have lived in the water column (Oschmann, 1994; Hudson, 2001). The most oxic faeces were the Gryphaea shell beds. These demand both a firm substrate, usually provided by a winnowed shell pavement, and fully oxic bottom waters. We can form a crude estimate of the duration of these conditions from estimates of the life span of Gryphaea.

Timing of Anoxic-Oxic Events

Jones and Gould (1999) measured the growth rings of $>200$ Gryphaea specimens from the Oxford Clay in central England. In the Kosmoceras medea and K. jason ammonite subzones (Fig. 1), Gryphaea dilobotes (48 samples) and Gryphaea “lituola” (77 samples; probably also $G$. dilobotes) were never found to exceed 8 years of age (80% died before reaching age 7). This result contrasts with $G$. lituola of the Athleta ammonite zone (K. proniae subzone) of the Stewarty Member (Middle Member of the Oxford Clay), in which the life span extended to 17 yr. The life expectancy of $G$. lituola in the Stewarty member, where no isorenieratane derivatives were observed (Fig. 2), is approximately twice that observed in the Jason zone, which contains abundant isorenieratane derivatives. It can thus be speculated that the life span of Gryphaea in the Jason zone was limited by the recurrence of lethal euxinic bottom waters. For the sake of discussion, and because we have no measure of colonization time, we will consider duration of oxic periods associated with Gryphaea in the Peterborough Member to be ~10 yr or more. Most shell beds contain several generations of Gryphaea, so the total accumulation time of the bed would probably be centuries. However, we have no means to determine the duration of euxinic events.

At the other extreme, in bed 10 at Peterborough, the dominant bivalve is Bosittra, and protobranchs are absent. If Bosittra had a prolonged planktonic larval stage (teleplanic life cycle), as proposed by Oschmann (1994), it can be speculated that stratification of the water column with euxinic bottom waters was frequent enough to prevent colonization by true benthic fauna. However, the common occurrence of foraminifera, and the sporadic occurrences of benthic gastropods and bivalves, such as Pinna and Protocardia, shows that oxic or dysoxic events occurred even in this facies. They did not lead to macroscopic bioturbation, however, until the burrowed top to bed 10 developed beneath the succeeding shell bed. Wilby et al. (2004) have given an analogous description of the equally organic carbon–rich “squid bed” at Ashton Keynes.

It can thus be concluded that the Peterborough Member was deposited under recurrent anoxic bottom-water conditions. The longest or most frequent anoxic periods can be ascribed to bed 10 and the squid bed, explaining partly why bed 10 is a prolific source of well-preserved vertebrate fossils and the squid bed contains soft-preserved coleoids. During deposition of deposit-feeder shales, these recurrent euxinic events were separated by longer oxic-dysoxic (decennial?) periods than during deposition of Bosittra shale facies. Even longer and/or probably more oxic periods interrupted anoxia during deposition of Gryphaea shell beds.

Organic-Matter Preservation

If this model is valid, organic-matter degradation must be greater for Gryphaea shell beds and other shell beds than for Bosittra shale facies and other shales. Belin and Kenig (1994) and Kenig et al. (1994) showed that the organic-matter type in all biofacies is dominantly algal marine with significant differences in the level of organic-matter degradation. The distribution of samples on a van Krevelen-type diagram between type II and type III kerogen (Fig. 3) is the result of differential degradation of organic matter (Pratt, 1985; Holland and Keil, 1990; Kenig et al., 1994; Simons and Kenig, 2001). Samples located closer to a type III kerogen are relatively depleted in hydrogen and enriched in oxygen, and are thus oxidized compared to samples of type II kerogen. The organic matter associated with Gryphaea shell beds and other shell beds is on average more oxidized than organic matter of deposit-feeder shales and other shales (Fig. 3). Bed 10 at Peterborough and other Bosittra shale beds have the highest hydrogen index values and thus the least oxidized, best preserved, organic matter. Thus, variations in organic-matter preservation, as determined from Rock-Eval data, are concordant with our model of variable duration of bottom-water aeration.

Conclusions

The deposition of the Peterborough Member of the Oxford Clay was associated with
successions of oxic-dysoxic and anoxic-euxinic bottom waters. The occurrence of the molecular fossil isorenieratene indicates that sulfidic conditions existed in the euxthic zone during sediment and organic-matter accumulation. On the contrary, benthic fossils indicate periods of bottom-water aeration, and were thus deposited in a water column not representative of the conditions conducive to accumulation of high concentrations of sedimentary organic matter. The duration of oxic bottom-water periods can be crudely estimated from the benthic fossil assemblages and probably varied from an annual to a decadal time scale. The preservation of organic matter is inversely proportional to the duration of oxic-dysoxic bottom-water conditions. Thus, we speculate that the water-column structure of the Callovian epeiric sea was changing dynamically. At this point, the mechanisms at the origin of these changes are not well understood. One implication of our results is that benthic biofacies alone may not reveal the level of oxygen in bottom waters during the entire deposition of organic carbon–rich shales.

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REFERENCES CITED


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