Basinal restriction, black shales, Re-Os dating, and the Early Toarcian (Jurassic) oceanic anoxic event

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Received 8 February 2008; revised 20 July 2008; accepted 17 September 2008; published 24 December 2008.

[1] Profiles of Mo/total organic carbon (TOC) through the Lower Toarcian black shales of the Cleveland Basin, Yorkshire, United Kingdom, and the Posidonia shale of Germany and Switzerland reveal water mass restriction during the interval from late *tenuicostatum* Zone times to early *bifrons* Zone times, times which include that of the putative Early Toarcian oceanic anoxic event. The degree of restriction is revealed by crossplots of Mo and TOC concentrations for the Cleveland Basin, which define two linear arrays with regression slopes (ppm/%) of 0.5 and 17. The slope of 0.5 applies to sediment from the upper *semicelatum* and *exaratum* Subzones. This value, which is one tenth of that for modern sediments from the Black Sea (Mo/TOC regression slope 4.5), reveals that water mass restriction during this interval was around 10 times more severe than in the modern Black Sea; the renewal frequency of the water mass was between 4 and 40 ka. The Mo/TOC regression slope of 17 applies to the overlying *falciferum* and *commune* subzones: the value shows that restriction in this interval was less severe and that the renewal frequency of the water mass was between 10 and 130 years. The more restricted of the two intervals has been termed the Early Toarcian oceanic anoxic event but is shown to be an event caused by basin restriction local to NW Europe. Crossplots of Re, Os, and Mo against TOC show similar trends of increasing element concentration with increase in TOC but with differing slopes. Together with modeling of $^{187}Os/^{188}Os$ and $\delta^{98}Mo$, the element/TOC trends show that drawdown of Re, Os, and Mo was essentially complete during upper *semicelatum* and *exaratum* Subzone times (Mo/TOC regression slope of 0.5). Drawdown sensitized the restricted water mass to isotopic change forced by freshwater mixing so that continental inputs of Re, Os, and Mo, via a low-salinity surface layer, created isotopic excursions of up to 1.3‰ in $\delta^{98}Mo$ and up to 0.6‰ for $^{187}Os/^{188}Os$. Restriction thereby compromises attempts to date Toarcian black shales, and possibly all black shales, using Re-Os chronology and introduces a confounding influence in the attempts to use $\delta^{98}Mo$ and initial $^{187}Os/^{188}Os$ for palaeo-oceanographic interpretation.

Citation: McArthur, J. M., T. J. Algeo, B. van de Schootbrugge, Q. Li, and R. J. Howarth (2008), Basinal restriction, black shales, Re-Os dating, and the Early Toarcian (Jurassic) oceanic anoxic event, *Paleoceanography*, *23*, PA4217, doi:10.1029/2008PA001607.

1. Introduction

[2] It is commonly held that Early Toarcian time was one of climatic upheaval and the deposition of organic-rich sediment worldwide [e.g., *Pearce et al.*, 2008, and references therein]. The period of organic-rich deposition is often termed the Early Toarcian oceanic anoxic event (OAE) [*Jenkyns*, 1988]. A negative excursion in $\delta^{13}C_{(org)}$ through the organic-rich interval in Europe (mostly the *exaratum* Subzone) is taken to reflect the effects of global, synchronous, black shale deposition, without synchroneity being demonstrated. Indeed, the epitome of correlative methods, ammonite biostratigraphy, may be rejected in pursuit of chemostratigraphic synchroneity, despite evidence that the onset of Toarcian black shale deposition in NW Europe was diachronous biostratigraphically [*Wignall et al.*, 2005].

[3] Interpretations that invoke whole-Earth catastrophes as the driving force for black shale deposition in the Early Toarcian (and, by implication, at other times) necessarily require a whole-ocean response to the driving force. Most of the data used to underpin these interpretations for the Early Toarcian derive from black shales (in a broad sense hereinafter; the term is seldom defined) of NW Europe (Figure 1). The data are often force fitted to hypotheses invoking catastrophe, rather than being used to critically test them, and contrary data and interpretations, such as those of *Wignall et al.* [2005] and *van de Schootbrugge et al.* [2005], are sometimes ignored.

[4] Other palaeoenvironmental interpretations of European black shales hold that they formed in response to water mass restriction in, for example, silled basins, in which anoxic or euxinic bottom water was separated by a pycnocline from a surface water mass of low salinity that isolated the underlying water from atmospheric oxygen

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0883-8305/08/2008PA001607

[*Küspert*, 1982; *Sælen et al.*, 1996, 1998, 2000; *Röhl et al.*, 2001; *Schmid-Röhl et al.*, 2002; *Schmid-Röhl and Röhl*, 2003; *Schwark and Frimmel*, 2004; *Frimmel et al.*, 2004; *van de Schootbrugge et al.*, 2005]. These models invoke local processes, such as basin restriction via salinity stratification, as the driving force for deposition of these shales: their formation is thus detached from global events. The models account for all phenomena associated with the deposition of Toarcian black shales, and do so without invoking global drivers.

[5] It is possible to envisage mixed scenarios, in which a combination of local and global events operated together to cause widespread, global deposition of black shales in Toarcian times; for example, reduced levels of atmospheric O_2 might have reinforced local factors to precipitate the onset of diachronous anoxia in semienclosed basins that had a spectrum of sensitivities to an anoxic-inducing tipping point. But any scenario involving global events assumes that the deposition of organic-rich sediments was indeed widespread (and synchronous) in Early Toarcian times and, implicitly, that they constituted an unusual proportion of Toarcian sediments. Such assumptions are often preferred over objective data. Organic-rich (i.e., black) shales certainly appear from literature sources to be common in the Toarcian, but it is not clear whether this is because they have been reported on assiduously because of their intrinsic interest, or because they really do represent a high proportion of all Toarcian strata, or because the definition of black shale is stretch beyond breaking point. There is certainly some of the latter: documenting shales as black shales when more than half of those reported have less than 2% total organic carbon (TOC) [*Jenkyns*, 1988, Table 1] does not clarify discussion. Correlating organic-rich units to the putative OAE (*exaratum* Subzone) of Yorkshire because they have a δ^{13}C(org) of −31‰ (Alaskan samples of *Jenkyns* [1988]) may have been acceptable when formulating an interesting hypothesis, but requires revision in the light of negative excursions in δ^{13}C now found at many stratigraphic boundaries.

[6] Nevertheless, some of the organic-rich shales deposited across NW Europe in Toarcian times contain more than 5% of TOC (i.e., are true black shales) [*Neuendorf et al.*, 2005, p. 72]:

> A black shale is a dark, thinly laminated carbonaceous shale, exceptionally rich in organic matter (5% or more carbon content) and sulfide (esp. iron sulfide, usually pyrite), and more commonly containing unusual concentrations of certain trace elements (U, V, Cu, Ni).

According to *Kearey* [2001, p. 30], "A black shale is a black/dark grey mudstone rich in organic carbon (>5% by weight) generally formed in anoxic marine bottom waters." They occur widely across NW Europe, and are dated to Early Toarcian time, although their onset and decline are diachronous [*Wignall et al.*, 2005]. Understanding how they formed is important to interpreting depositional environments of other black shales (do they all form as a result of basin restriction?) for which data may be less abundant and geological interpretation more difficult. We therefore address the question as to whether environmental signals in European organic-rich sediments reflect regional or global drivers. We do so using profiles of environmental proxies through Lower Toarcian sediments of NW Europe, especially the relation of Mo to TOC, and by isotopic modeling of δ^{98}Mo and initial ^{187}Os/^{188}Os.

2. Working Model

[7] Molybdenum is removed from euxinic waters by reduction to the thiomolybdate complexes ($MoO_xS_{4-x}^{2-}$) in the presence of free H_2S and subsequent sequestration in either sedimenting organic matter, sedimenting pyrite formed in the water column, or both [*Helz et al.*, 1996; *Erickson and Helz*, 2000; *Vorlicek and Helz*, 2002; *Tribovillard et al.*, 2004a, 2006, 2008]. Because of this removal, the renewal time i.e., degree of restriction, of the subpycnoclinal water mass in modern, euxinic, marine basins, can be estimated from the slope of the regression line between Mo and TOC (*rs*Mo/TOC hereinafter, to distinguish it from raw Mo/TOC ratios) in a crossplot of TOC against Mo in sediments [*Algeo and Lyons*, 2006]. The method works only where euxinic conditions exist(ed) both in the sediment and the overlying water column. Such water column euxinia is well documented for the Early Toarcian seas of northwestern Europe beneath which black shales (in a strict sense) are deposited (see section 6.1).

[8] The *rs*Mo/TOC value of a sediment reflects the balance of fluxes into and out of a restricted parcel of overlying seawater from which the nonclastic component of the sedimentary Mo is derived; i.e., the frequency of deepwater renewal [*Algeo and Lyons*, 2006]. Molybdenum concentrations in euxinic bodies of seawater decline if the removal rate of Mo into underlying sediments exceeds the rate of replenishment of Mo to the water column; under such conditions, the Mo/TOC of depositing sediment declines as the Mo reservoir in solution is drawn down. Complete isolation of a water body leads to total drawdown of Mo and, thereafter, the accumulation of organic-rich sediments with very low *rs*Mo/TOC (<4). Conversely, under conditions of seasonal euxinia that is yearly destroyed by seasonal overturn of the water mass, Mo is removed to the sediment from an annually replenished store in the water column, so *rs*Mo/TOC is high in sediments deposited under such a regime e.g., sediments of Saanich Inlet, where *rs*Mo/TOC is around 45. Thus, in modern settings, values of *rs*Mo/TOC are low in very restricted basins and increase to a maximum of around 45 as restriction decreases to be seasonal i.e., the frequency of deepwater renewal increases. This maximum value of ~45 presumably reflects the concentration of Mo in modern seawater (105 nM) [*Collier*, 1985; *Morford and Emerson*, 1999]; a different maximum *rs*Mo/TOC would apply had seawater a different Mo concentration, as it may have had in past times. If renewal becomes too frequent, i.e., the environment too open, *rs*Mo/TOC decreases to low values as open marine conditions are reestablished and euxinia retreats into the sediments or disappears [*Algeo and Lyons*, 2006], thereby removing the primary source of Mo, which is euxinic seawater.

[9] The range of *rs*Mo/TOC found today is from 4.5 ± 1 in the Black Sea (severe restriction and a body of euxinic water 2000 m thick), through 9 ± 2 for Framvaren Fjord,

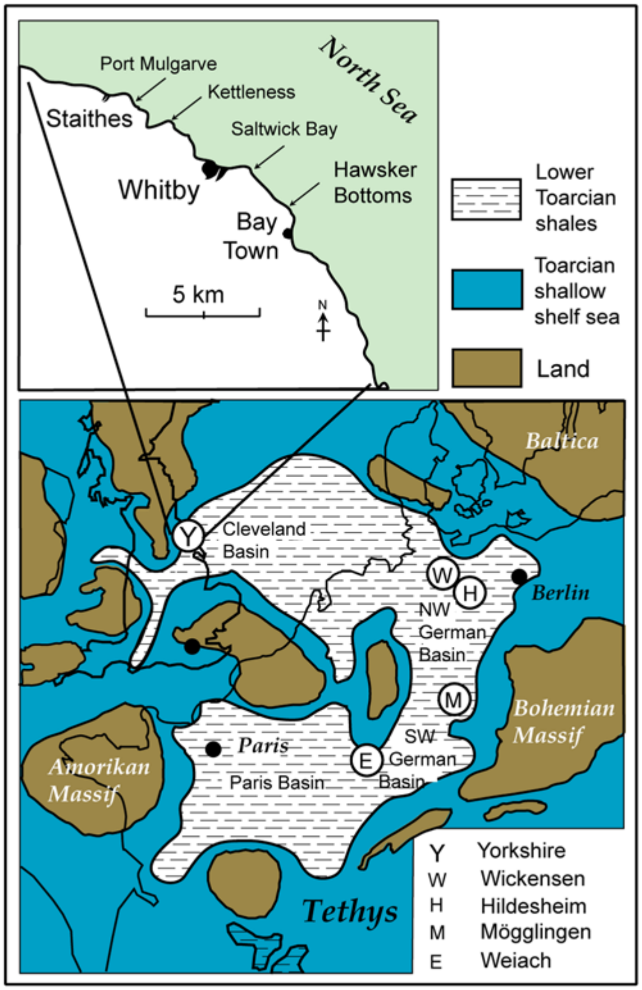

Figure 1. Extent of organic-rich sediment defined loosely in the Lower Toarcian of northwestern Europe, 51°50′N, 6°15′E. The top map shows location of sampling sites in Yorkshire, United Kingdom: Witby (54°29′N, 0°37′W).

25 ± 2 for the Cariaco Basin, to 45 ± 5 for Saanich Inlet (seasonal euxinia in a water body ~ 100 m thick). A special case occurs on the Namibian Shelf, where *rs*Mo/TOC is around 6 ± 3. The Namibian Shelf is not hydrographically restricted. Accumulation of Mo above clastic background concentrations (<5 ppm Mo) occurs there, presumably by diffusion of Mo into sediments, but the degree of enrichment is limited by the fact that euxinic conditions rarely occur above the sediment-water interface because of the hydrographically unrestricted nature of the environment: deep and bottom water typically contain up to 22 μM of dissolved oxygen. As a consequence, the opportunity for sequestration of Mo from large volumes of euxinic seawater is rarely present and *rs*Mo/TOC is low [*Algeo and Lyons*, 2006].

[10] The Namibian example demonstrates a subtlety of the model: for different reasons, the accumulation of Mo is modest, and *rs*Mo/TOC is low, both in severely restricted euxinic basins, and in open-ocean environments where redox conditions in the water column are oxic to suboxic and euxinic conditions exist in the underlying sediments [*Algeo and Lyons*, 2006]. When examining premodern black shales, it is necessary to use criteria other than Mo/TOC or *rs*Mo/TOC to establish which end-member is dealt with. For the Toarcian sediments considered here, a wide range of reasons that we document hereinafter show that the environment was not open ocean but was restricted, and was euxinic because of that water mass restriction.

[11] Our work here on Toarcian events also reinterprets the δ^{98}Mo from *Pearce et al.* [2008]. Mo in seawater has a δ^{98}Mo of zero; that incorporated into oxic sediments, particularly Mn oxides, has a δ^{98}Mo around −3‰; that incorporated into euxinic sediments is unfractionated because removal from seawater is quantitative. The δ^{98}Mo of seawater sequestered into euxinic shales is therefore hypothesized to reflect the δ^{98}Mo of seawater, and variations in that δ^{98}Mo with stratigraphic level through a black shale section is assumed to reflect a changing balance of sequestration globally into oxic and euxinic sediments. In reality, the controls on δ^{98}Mo are poorly known, and caution is needed in applying this palaeoproxy, as we shall show later, a need for caution emphasized by *Nägler et al.* [2005], *Poulson et al.* [2006] and *Reitz et al.* [2007].

3. Geological Setting

[12] Upper Pliensbachian and Lower Toarcian sedimentary rocks of the Cleveland Basin, Yorkshire coast, United Kingdom, are well exposed in coastal sections (Figure 1), have been zoned with ammonites, and been subdivided biostratigraphically and lithologically (Figure 2) [*Howarth*, 1955, 1962, 1973; *Powell*, 1984; *Howard*, 1985]. The *Harpoceras falciferum* zone is now the *H. serpentinum* Zone, and the *commune* Subzone of the *bifrons* Zone is now the *H. laticosta* Subzone [*Page*, 2004], but older names are retained here to provide a link to the primary literature of most relevance (*Howarth* [1955] and subsequent authors). As zero datum, we take the base of the Toarcian as the base of the *tenuicostatum* Zone [*Howarth*, 1973] (Figure 2).

[13] The sediments analyzed are part of the Whitby Mudstone Formation. The lithostratigraphic units are, in ascending order, the Grey Shale Member (beds 1 to 32 inclusive, Figure 2) between 0.66 and 14.22 m above datum (mad); the Mulgrave Shale Member (beds 33 to 48) between 14.22 to 31.0 mad, and the Alum Shale Member above that (beds 49 to 72). The top of the Grey Shale Member, and the base of the *falciferum* Zone (*exaratum* Subzone) was placed at the base of bed 33 by *Howarth* [1973]. Correlation between sections of Lower Toarcian strata on the Yorkshire coast is possible to decimeter level over kilometers because of the numerous distinctive marker beds of (mostly) carbonate and (rare) sideritic concretions (e.g., beds 46, 50 [*Howarth*, 1955, 1962, 1973]).

[14] Much of the Lower Toarcian sediment contains calcite, either cryptically as nannofossil debris and dispersed diagenetic cement, or as discrete carbonate concretions. The concretions typically occur in discrete horizons. Upsection from the *exaratum* Subzone, concretion horizons

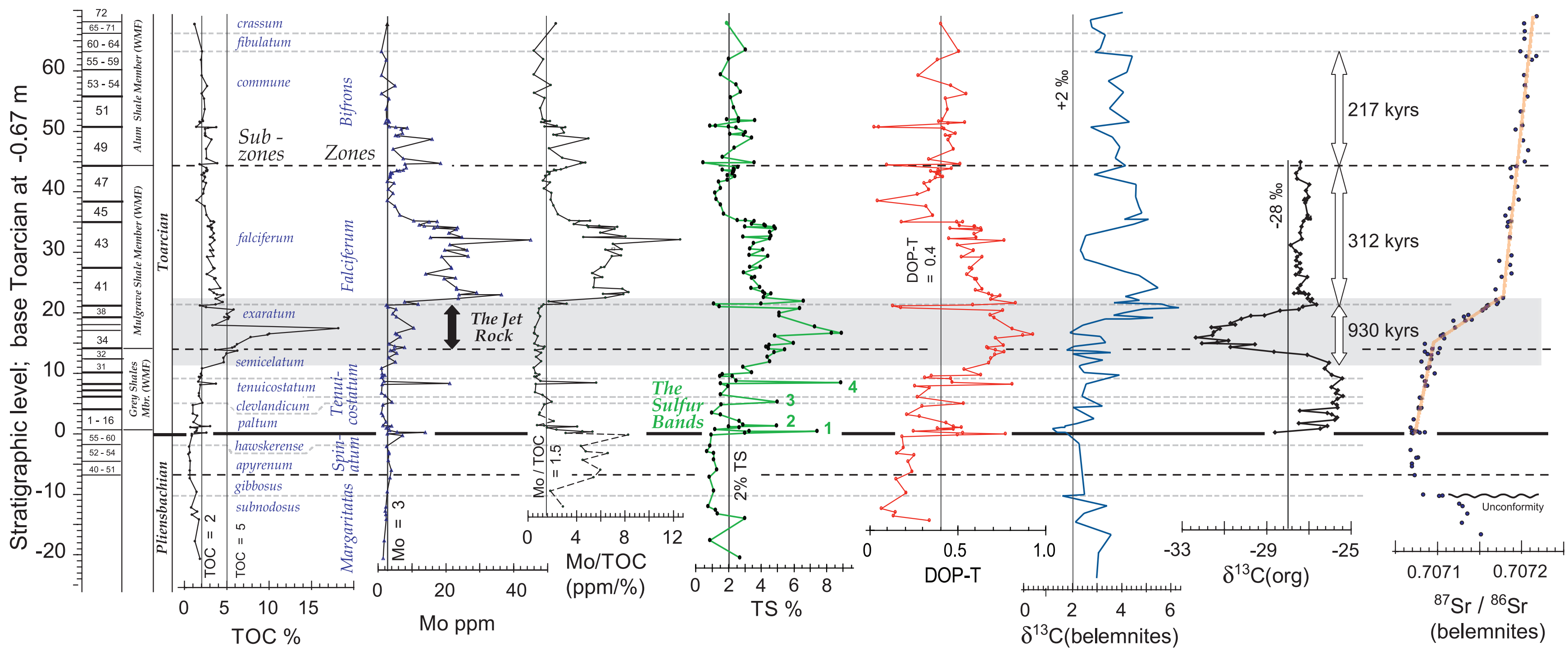

Figure 2. Biostratigraphy, outline lithostratigraphy, and profile of concentrations TOC, Mo, Mo/TOC, TS, and DOP-T (this work); $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ of belemnite calcite (data of *McArthur et al.* [2000]); and $\delta^{13}C$ of the organic matter ($\delta^{13}C_{(org)}$) (data from *Cohen et al.* [2004]), through the Upper Pliensbachian and Lower Toarcian strata of Yorkshire, United Kingdom. In the lithological crossplot, bed numbers are from *Howarth* [1955, 1962, 1973], and the thick horizontal lines represent the more prominent carbonate concretions and cemented horizons. The four Sulfur Bands are numbered on the TS profile (see text). The negative $\delta^{13}C_{(org)}$ excursion in the upper *semicelatum* Subzone and the *exaratum* Subzone was around 900 ka in duration [*Suan et al.*, 2008].

are less common and the sediments comprise monotonous, dark gray, mudstones. Downsection from the *exaratum* Subzone, toward the Pliensbachian/Toarcian boundary, in the interval commonly interpreted as a sea level lowstand [*Hallam*, 1997; *Wignall et al.*, 2005], concretionary horizons are more common and more sideritic, while the intervening shales become less rich in organic matter and greyer in color. The base of a pyritic shale that is 15 cm thick, coincides with the base of the Toarcian and three other decimeter-thick, pyritic units occur at 1.2, 5.1, and 8.2 m above the base of the grey shales (Figure 2 and Table 1) (R. J. Newton, personal communication, 2006). The four pyritic units are termed here collectively the Sulfur Band and the second, third, and fourth Sulfur Bands, from the base upward.

4. Methods

4.1. Sampling

[15] Samples were from exposures at Hawsker Bottoms, Staithes, Port Mulgrave, Saltwick Bay, and Kettleness, on the coast of Yorkshire within a few kilometers of Whitby (Figure 1) [*Howarth*, 1962]. The stratigraphic levels of samples collected from Pliensbachian strata (below 0 mad) are referred to Hawsker Bottom [*Howarth*, 1955]; levels from 0 to +24 mad are referred to the section at Port Mulgrave [*Howarth*, 1973]. Levels above 24 mad (upper part of bed 41) relate to the section at Saltwick Bay [*Howarth*, 1962].

[16] Samples were collected from beneath a surface layer of weathered paper shale some 5 cm deep, at a depth where the rocks were homogenous, compact, and without structure. That the samples are well preserved is attested to by their content of percentage amounts of pyrite, both as microscopic disseminated framboids and as uncommon millimeter size cubic pyrite.

4.2. Chemical Analysis

[17] Analysis for Mo, and Fe was done by X-ray fluorescence (XRF) on pressed-powder pellets at the University of Cincinnati, and by inductively coupled plasma emission spectroscopy (ICP-AES) (Mo, Fe) and inductively coupled plasma mass spectrometry (ICP-MS) (Mo) at University College London (UCL) after dissolution of the samples in mixed strong acids. Analysis for total sulfur (TS), total carbon (TC), and total organic carbon (TOC) was done using an Eltra C/S Analyzer (at the University of Cincinnati) or a Leco C/S Analyzer (at University College London). For TOC analysis, samples were decarbonated with dilute (10% vol/vol) hydrochloric acid. The results of the chemical and isotopic analyses are given in Table 1. The uncertainty of the analyses lie within the size of the symbols used to plot concentrations on our figures. We calculated degree of pyritization based on total Fe (DOP-T) as 0.95TS/(Total Fe) to allow for organic S. For the *exaratum* Subzone, we supplemented our data with the Mo, TOC, δ^{98}Mo, Re, and TOC data of *Pearce et al.* [2008] who sampled at a higher density than we did in that interval. The methods of analysis used by *Pearce et al.* [2008] are documented in their paper and its Supplementary Information.

[18] Data for northern Germany derive from the Wickensen and Hildesheim cores [*Jochum*, 1993; *Brumsack*, 1988]: the biostratigraphy of the Wickensen core is given by *Littke et al.* [1991] and that for the Hildesheim core by *Loh et al.* [1986]. Data for the Mögglingen core in southern Germany are from *Brumsack* [1988], whose biostratigraphic assignments were from *Riegraf et al.* [1984]. The TOC data from the Weiach core from Switzerland were reported by *Feist-Burkhardt* [1992] and the Mo data are unpublished (A. Quigg, Rutgers University, personal communication, 2008).

[19] Diagenetic carbonate is present through much of the section in the Cleveland Basin (Table 1) as calcite or, at rare levels, subordinate siderite (beds 46, 50; Table 1). Our data profiles with stratigraphic level (Figures 2 and 3) are not shown on a carbonate-free basis because doing so has a negligible effect on their interpretation. Recalculation to a carbonate-free basis did clarify the Mo-TOC crossplot (Figure 5 only; see section 5.2), which is therefore shown on a carbonate-free basis.

4.3. Timescale

[20] In order to estimate the duration of units discussed here, we use the timescale of *Suan et al.* [2008], coupled with the Sr isotope stratigraphy of *McArthur et al.* [2000] (Figure 2). The cyclostratigraphic analysis by *Suan et al.* [2008] assigned a duration of ~900 ka (from their detailed discussion, it is 930 ± 40 ka) to the well-defined negative isotopic excursion in δ^{13}C(org) seen in the *exaratum* Subzone and the uppermost few meters of the underlying *semicelatum* Subzone (Figure 2). This excursion is often termed the Early Toarcian CIE. These authors also estimated that the deposition of the *tenuicostatum* and *falciferum* Zones (the Lower Toarcian) occupied 2.05 ± 0.15 Ma, a duration close to that of 2.3 Ma estimated independently by *Ogg* [2004, Figure 18.1 and Table 18.2], taking the base of the *H. variabilis* Zone as the base of the Upper Toarcian. The duration of the Early Toarcian derived by *McArthur et al.* [2000] from an earlier timescale was 2.17 Ma.

[21] That three linear regressions describe the ^{87}Sr/^{86}Sr profile of belemnite calcite through all the Toarcian strata of Yorkshire [*McArthur et al.*, 2000, Figure 2] is good evidence that sedimentation rates were different within each regression interval. The linearity and slope of each regression shows that *exaratum* Subzone and overlying 30 cm of the *falciferum* Subzone of the Toarcian are stratigraphically condensed by a factor of 7 relative to underlying strata and by a factor of 12 relative to overlying strata (Figure 2) [*McArthur et al.*, 2000; *McArthur and Wignall*, 2007]. The rates of change of ^{87}Sr/^{86}Sr with stratigraphic level (see *McArthur et al.* [2007] for a graphic explanation), and an Early Toarcian duration of 2.17 Ma, were used to determine zonal and subzonal durations [*McArthur et al.*, 2000] and these durations, and the zonal and subzonal thicknesses, have been used to derive sediment accumulation rates and so approximate durations for discrete packages of sediment, such as the decimeter-thick Sulfur Bands. Such durations are tentative, and systematic uncertainty of around ±10% in the durations of the events we calculate arises simply from the range of the Lower Toarcian durations noted above (1.9 to 2.3 Ma). Sedimentation rate changes that occurred at a scale irresolvable with ^{87}Sr/^{86}Sr must also introduce unquantifiable uncertainty. Nevertheless, we speculate that the

Table 1. Elemental Compositions, Pyrite-Fe, and DOP-T in Upper Pliensbachian and Lower Toarcian Sediments From the Coastal Sections of Yorkshire, United Kingdom[a]

Stage	Bed Number	Sample Locality	Stratigraphic Level (m)	TC (%)	TOC (%)	TS (%)	Mo (ppm)	Fe (%)	Pyrite Fe (%)	DOP-T
Toarcian	70	SB	67.66	0.8	1.2	1.90	2.7	3.9	1.7	0.41
Toarcian	61	SB	63.17	2.2	2.1	3.06	1.0	5.0	2.7	0.51
Toarcian	57	SB	61.79	2.1	2.0	2.03	2.4	4.3	1.8	0.39
Toarcian	53	SB	59.21	2.1	2.1	1.50	1.0	4.4	1.3	0.28
Toarcian	53	SB	57.47	2.4	2.7	2.48	5.0	4.4	2.2	0.47
Toarcian	53	SB	56.20	2.0	2.0	2.72	1.0	4.1	2.4	0.56
Toarcian	51	SB	55.34	2.2	2.3	2.14	3.2	4.1	1.9	0.44
Toarcian	51	SB	53.64	2.1	2.4	2.31	2.4	4.3	2.0	0.45
Toarcian	51	SB	51.87	2.1	2.1	2.63	2.5	5.2	2.3	0.42
Toarcian	51	SB	51.67	2.2	2.2	1.91	3.1	4.0	1.7	0.40
Toarcian	51	SB	51.52	2.0	1.8	3.62	3.3	5.5	3.2	0.55
Toarcian	51	SB	51.37	2.0	1.9	2.61	2.1	4.8	2.3	0.45
Toarcian	50	SB	50.72	7.7	1.4	0.88	3.3	22.2	0.8	0.03
Toarcian	50	SB	50.64	8.1	3.8	1.21	5.2	17.1	1.1	0.06
Toarcian	49	SB	50.50	2.9	2.8	2.01	8.6	4.0	1.8	0.42
Toarcian	49	SB	50.36	2.6	2.5	2.47	6.9	4.8	2.2	0.43
Toarcian	49	SB	49.63	2.5	2.4	3.05	7.2	5.1	2.7	0.49
Toarcian	49	SB	49.29	2.4	2.4	2.08	5.1	4.0	1.8	0.44
Toarcian	49	SB	49.19	2.7	2.5	2.91	6.0	5.2	2.5	0.46
Toarcian	49	SB	48.64	3.9	3.2	3.41	15.9	6.2	3.0	0.45
Toarcian	49	SB	47.02	2.6	2.6	2.35	4.4	4.0	2.1	0.48
Toarcian	49	SB	45.44	2.7	2.6	1.65	7.4	4.0	1.4	0.34
Toarcian	49	SB	44.66	4.2	3.9	3.58	18.4	5.7	3.1	0.52
Toarcian	48	SB	44.53	9.9	1.8	0.46	7.9	3.6	0.4	0.11
Toarcian	47	SB	43.90	2.7	2.6	2.57	8.3	4.5	2.2	0.47
Toarcian	47	SB	43.53	2.8	2.7	2.30	7.4	4.8	2.0	0.40
Toarcian	47	SB	43.46	2.6	2.6	2.36	5.6	4.9	2.1	0.40
Toarcian	47	SB	43.39	2.8	2.7	1.64	6.3	3.8	1.4	0.36
Toarcian	47	SB	43.12	2.3	2.3	2.33	3.7	4.9	2.0	0.39
Toarcian	47	SB	43.01	2.3	2.3	2.27	4.2	4.9	2.0	0.39
Toarcian	47	SB	42.77	2.2	2.1	2.26	3.7	4.6	2.0	0.41
Toarcian	47	SB	42.49	2.4	2.4	1.94	3.5	3.8	1.7	0.42
Toarcian	47	SB	42.40	2.4	2.5	2.41	3.6	5.3	2.1	0.38
Toarcian	47	SB	41.67	2.4	2.2	1.93	2.8	4.6	1.7	0.35
Toarcian	47	SB	41.39	2.4	2.6	1.43	4.7	3.8	1.2	0.32
Toarcian	47	SB	40.39	2.3	2.3	1.53	3.0	3.7	1.3	0.34
Toarcian	47	SB	39.67	2.2	2.3	1.19	4.4	3.5	1.0	0.28
Toarcian	46	SB	38.53	7.5	1.5	1.24	2.7	19.8	1.1	0.05
Toarcian	45	SB	37.57	2.4	2.4	1.51	5.0	3.8	1.3	0.33
Toarcian	45	SB	36.12	2.6	2.6	1.73	6.4	3.9	1.5	0.37
Toarcian	45	SB	35.12	5.9	3.1	2.55	10.5	11.2	2.2	0.19
Toarcian	44	SB	35.04	4.0	3.4	3.05	17.4	4.7	2.7	0.53
Toarcian	44	SB	35.00	4.2	3.6	3.59	15.0	5.9	3.1	0.50
Toarcian	43	SB	34.48	3.7	3.2	3.42	12.1	5.5	3.0	0.52
Toarcian	43	SB	34.28	4.0	2.8	4.20	13.7	5.8	3.7	0.60
Toarcian	43	SB	34.21	3.9	3.0	4.28	17.5	5.9	3.7	0.61
Toarcian	43	SB	34.01	3.9	3.2	4.77	23.5	6.2	4.2	0.64
Toarcian	43	SB	33.97	4.0	3.3	2.99	16.5	5.4	2.6	0.46
Toarcian	43	SB	33.71	4.2	3.2	4.87	23.0	6.3	4.3	0.64
Toarcian	43	SB	33.10	4.3	3.5	4.53	20.8	6.3	4.0	0.60
Toarcian	43	SB	32.45	4.0	3.1	4.61	24.7	6.3	4.0	0.61
Toarcian	43	SB	32.37	4.0	3.4	2.89	15.5	5.3	2.5	0.46
Toarcian	43	SB	31.97	4.1	3.6	4.53	45.0	4.9	4.0	0.77
Toarcian	43	SB	31.22	3.0	3.0	3.54	21.1	5.8	3.1	0.51
Toarcian	43	SB	30.30	4.6	3.4	3.32	26.3	4.6	2.9	0.60
Toarcian	43	SB	30.27	4.0	3.1	4.10	19.7	5.7	3.6	0.60
Toarcian	43	SB	29.30	4.2	3.5	3.29	26.6	5.2	2.9	0.53
Toarcian	43	SB	29.20	3.4	2.7	4.42	18.7	5.7	3.9	0.65
Toarcian	43	SB	27.40	4.3	3.4	3.31	21.5	4.8	2.9	0.57
Toarcian	43	SB	27.32	4.4	3.6	3.96	21.6	5.6	3.5	0.59
Toarcian	41	SB	26.37	3.3	2.6	2.93	14.0	4.4	2.6	0.56
Toarcian	41	PM	25.68	3.9	3.7	3.62	22.8	4.9	3.2	0.61
Toarcian	41	SB	25.57	3.6	3.5	3.42	19.4	4.7	3.0	0.60
Toarcian	41	HB	24.02	4.8	4.3	3.93	23.1	5.1	3.4	0.64
Toarcian	41	HB	23.80	4.0	3.0	3.39	23.2	4.6	3.0	0.61
Toarcian	41	HB	23.25	4.2	3.5	4.12	29.0	5.0	3.6	0.68
Toarcian	41	PM	22.95	4.4	3.8	4.22	23.8	5.0	3.7	0.70
Toarcian	41	PM	22.90	6.4	4.6	4.59	36.3	5.1	4.0	0.75
Toarcian	41	PM	22.30	5.3	3.7	4.16	23.6	5.0	3.6	0.69

Table 1. (continued)

Stage	Bed Number	Sample Locality	Stratigraphic Level (m)	TC (%)	TOC (%)	TS (%)	Mo (ppm)	Fe (%)	Pyrite Fe (%)	DOP-T
Toarcian	41	PM	21.73	6.8	4.6	6.59	7.8	6.6	5.8	0.83
Toarcian	41	PM	21.33	9.0	3.7	4.01	11.8	5.6	3.5	0.59
Toarcian	40	PM	21.20	11.9	1.9	1.09	2.4	6.5	1.0	0.14
Toarcian	39	PM	20.88	11.6	2.6	1.45	2.9	6.5	1.3	0.19
Toarcian	38	PM	20.50	8.6	5.8	6.36	5.4	6.9	5.6	0.76
Toarcian	38	PM	19.77	6.2	5.0	5.11	4.3	6.2	4.5	0.69
Toarcian	38	PM	19.24	6.5	5.3	5.09	5.4	5.9	4.5	0.71
Toarcian	35	PM	17.41	19.3	18.2	7.25	10.5	7.4	6.3	0.82
Toarcian	34	HB	16.49	12.4	10.1	8.89	5.1	7.9	7.8	0.93
Toarcian	34	PM	16.36	11.4	9.8	8.29	5.6	7.9	7.3	0.87
Toarcian	34	PM	15.95	8.7	7.8	4.82	6.5	5.6	4.2	0.72
Toarcian	34	K	14.75	6.6	6.2	5.96	3.2	6.5	5.2	0.76
Toarcian	34	K	14.39	6.5	5.9	4.48	4.9	5.5	3.9	0.67
Toarcian	33	PM	14.22	6.5	5.7	4.29	7.8	5.3	3.8	0.68
Toarcian	32	PM	13.88	4.9	3.7	4.46	4.7	5.2	3.9	0.72
Toarcian	32	K	13.67	6.7	6.3	5.42	3.6	5.8	4.7	0.77
Toarcian	32	K	13.22	6.1	5.0	4.78	5.5	5.5	4.2	0.72
Toarcian	32	K	12.52	4.8	4.6	4.39	3.1	5.3	3.8	0.69
Toarcian	31	K	11.78	5.1	4.7	4.52	5.1	5.5	4.0	0.68
Toarcian	29	K	9.86	2.2	2.0	3.43	1.2	4.5	3.0	0.64
Toarcian	29	PM	9.60	2.2	2.1	1.65	2.0	3.8	1.4	0.36
Toarcian	29	K	9.34	2.1	1.7	1.50	1.3	3.9	1.3	0.32
Toarcian	27	PM	8.55	1.8	1.6	2.46	1.7	4.3	2.1	0.48
Toarcian	26	PM	8.24	3.9	3.7	8.86	21.1	9.0	7.8	0.81
Toarcian	25	PM	8.05	2.4	1.9	1.51	1.2	4.8	1.3	0.26
Toarcian	20	PM	6.22	2.4	1.7	1.52	2.1	4.5	1.3	0.28
Toarcian	19a	HB	5.11	2.9	2.1	4.97	4.1	7.7	4.4	0.54
Toarcian	18	PM	4.67	1.2	1.0	1.56	1.4	4.2	1.4	0.31
Toarcian	8	HB	3.31	1.6	1.0	1.00	1.0	3.8	0.9	0.22
Toarcian	8	PM	2.95	1.7	1.5	1.51	1.4	4.3	1.3	0.29
Toarcian	4	PM	1.89	1.6	1.1	2.66	2.3	5.0	2.3	0.44
Toarcian	2	HB	1.25	2.0	1.9	2.87	1.4	5.0	2.5	0.48
Toarcian	2	HB	1.19	3.4	3.0	4.94	4.1	7.8	4.3	0.53
Toarcian	1	PM	1.02	1.3	0.7	2.02	3.0	4.3	1.8	0.39
Toarcian	1	HB	0.86	1.0	1.5	2.66	2.4	4.6	2.3	0.48
Toarcian	43	HB	0.48	1.1	1.4	1.18	3.4	3.8	1.0	0.26
Toarcian	43	HB	0.20	1.5	1.3	3.27	5.6	5.1	2.9	0.54
Toarcian	43	HB	0.15	2.7	2.6	7.41	13.9	7.9	6.5	0.78
Pliensbachian	43	HB	−0.09	0.6	0.9	3.00	2.7	4.9	2.6	0.50
Pliensbachian	57	PM	−0.36	0.8	0.9	0.95	7.2	4.1	0.8	0.19
Pliensbachian	40	HB	−2.19	0.6	0.6	0.86	2.5	3.6	0.8	0.20
Pliensbachian	38	HB	−3.13	0.7	0.7	0.70	3.2	3.6	0.6	0.16
Pliensbachian	38	HB	−3.39	0.5	0.5	1.12	3.2	3.6	1.0	0.26
Pliensbachian	38	HB	−4.51	0.8	0.7	1.12	3.0	4.1	1.0	0.22
Pliensbachian	34	HB	−6.13	0.8	0.7	1.30	3.9	4.3	1.1	0.25
Pliensbachian	32	HB	−7.39	0.8	0.6	0.82	3.5	4.3	0.7	0.16
Pliensbachian	28	HB	−9.65	0.8	1.5	1.12	2.7	4.3	1.0	0.21
Pliensbachian	38	PM	−12.22	1.3	0.8	0.76	2.3	8.4	0.7	0.07
Pliensbachian	38	PM	−12.90	1.7	1.5	1.23	2.1	6.7	1.1	0.15
Pliensbachian	38	PM	−13.43	1.3	0.9	1.33	2.3	7.7	1.2	0.14
Pliensbachian	36	PM	−14.23	1.8	1.7	3.02	2.4	7.3	2.6	0.35
Pliensbachian	34	PM	−17.78	1.6	1.2	0.86	1.8	6.3	0.8	0.11
Pliensbachian	30	PM	−20.72	1.9	1.9	2.68	1.5	4.2	2.3	0.53

[a]Stratigraphic levels are in meters from the base of the base of the Toarcian (base of the *Tenuicostatum* Zone) [*Howarth*, 1973]. Sample numbers: S, Saltwick Bay; St, Staithes; HB, Hawsker Bottom; K, Kettleness; PM, Port Mulgrave. Bed numbers from *Howarth* [1955, 1962, 1973] are location specific and may repeat.

event durations we calculate are unlikely to be in error by more than a factor of three, an error that has no impact on our conclusions.

5. Results

5.1. Stratigraphic Profiles of Environmental Proxies

[22] In Figure 2 we profile through the composite section data for TOC, Mo, Mo/TOC (ppm/%; note, not *rs*Mo/TOC), TS, DOP-T, a proxy for degree of pyritization, the $\delta^{13}C$ of organic matter ($\delta^{13}C_{(org)}$; data of *Cohen et al.* [2004]), and the $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ of belemnite calcite ($\delta^{13}C_{(bel)}$) from *McArthur et al.* [2000]. In Figure 3 we profile through the *exaratum* Subzone and upper part of the *semicelatum* Subzone our data for $\delta^{13}C$ of belemnite calcite, and the data of *Pearce et al.* [2008] for Re/Mo, $\delta^{98}Mo$, Mo/TOC, $\delta^{13}C_{(org)}$, Re/TOC, TOC, and initial $^{187}Os/^{188}Os$. In Figure 4,

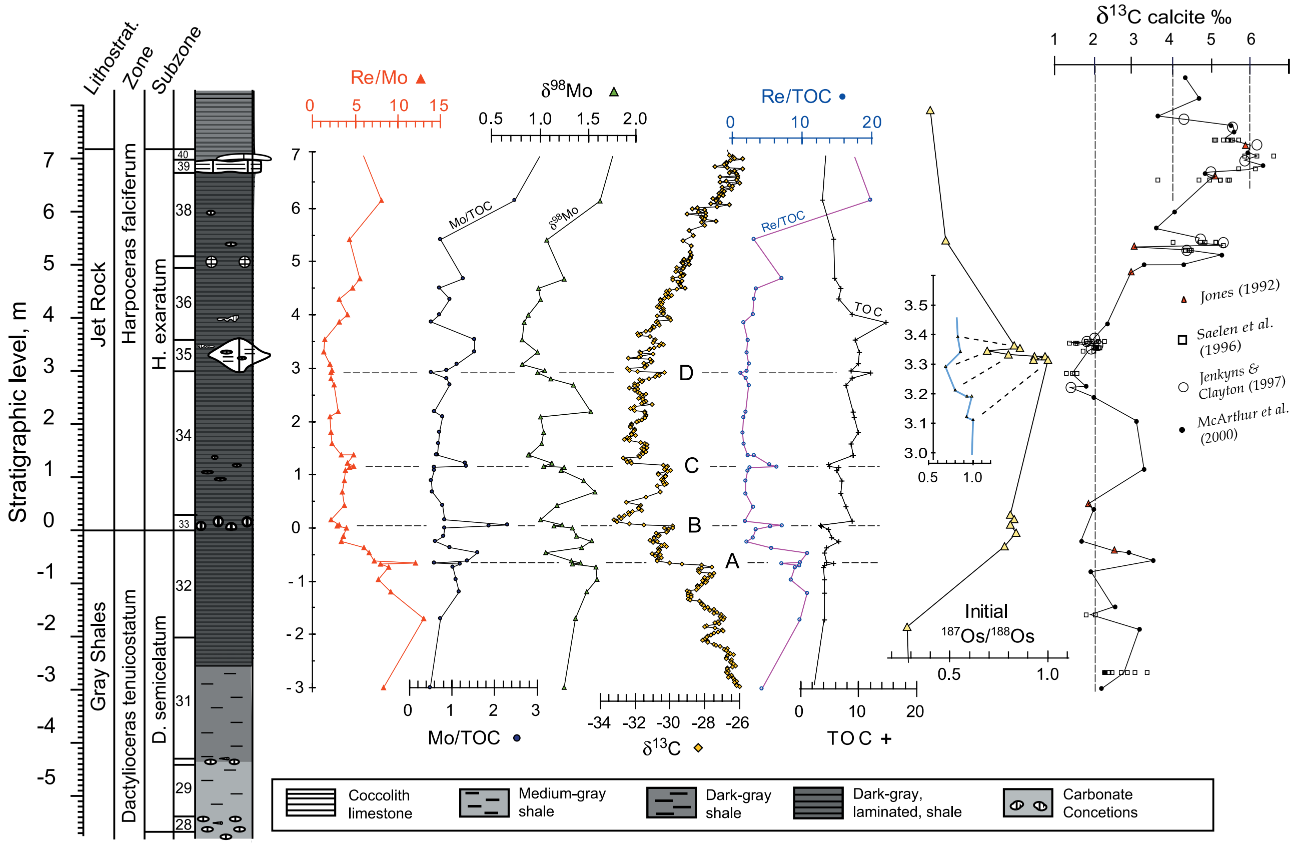

Figure 3. Lithology, biostratigraphy, and profile of concentrations Re/Mo, Mo/TOC, δ^{98}Mo, $\delta^{13}C_{(org)}$, Re/TOC, TOC, and δ^{13}C of belemnite calcite through the upper *semicelatum* Subzone and *exaratum* Subzone of Yorkshire. Data are from *Pearce et al.* [2008] except δ^{13}C of belemnite calcite, which is from sources listed on the plot.

we show Mo/TOC profiles for the Lower Toarcian Posidonia shale of Germany and Switzerland.

[23] Pliensbachian and Toarcian sediments below the middle of the *semicelatum* Subzone of the Cleveland Basin have TOC concentrations less than 2%, excepting for the Sulfur Bands (Figure 2) which range from 2.1 to 3.7% TOC. Upward from the mid-*semicelatum* Subzone of the Toarcian, concentrations of TOC exceed 3% and increase to peak at 18% in bed 35 of the *exaratum* Subzone (the whale stones of *Howarth* [1962]). Above that level, TOC concentrations decrease abruptly to around 4% and then decline upsection until stabilizing around 2% in the upper *falciferum* subzone. DOP-T values, and TS concentrations, are high between the mid-*semicelatum* Subzone and the mid-*falciferum* Subzone. For the *exaratum* Subzone, degree-of-pyritization (DOP) values of 0.84 were reported by *Raiswell and Berner* [1985] and values between 0.8 and 0.9 reported by *Pearce et al.* [2008]. Our values for DOP-T are similar, even though our calculation of DOP-T includes iron that may not be diagenetically available.

[24] In the Pliensbachian, Mo/TOC is high because TOC is low; the profile is dominated by detrital Mo and is not discussed further. In the Toarcian below the mid-*semicelatum* Subzone, Mo concentrations are <3 ppm except in the Sulfur Bands where concentrations reach between 4 and 21 ppm (Figure 2). Concentrations are ≈ 10 ppm where TOC is highest in the interval between the mid-*semicelatum* Subzone and the top of the *exaratum* Subzone, and are ≈20 ppm in the lower half of the *falciferum* Subzone where TOC is lower. Concentrations decline to be around 3 ppm above that level, although the lower *commune* Subzone is marked by two higher spikes to around 15 ppm which are accompanied by only small changes in TOC. In the upper *semicelatum* Subzone and the *exaratum* Subzone (the putative OAE in a wider sense), Mo/TOC is exceptionally low while TOC is high (>5%). In the *falciferum* and *commune* Subzone, Mo/TOC is high but TOC is only 3–4%. All the patterns noted here have significance for interpretation of palaeoenvironmental conditions and are discussed later.

[25] Values of Mo/TOC show sharp changes in several parts of the profile. The rapidity of the changes can be calculated from sediment thickness, the duration of ammonite subzones as deduced from a Sr isotope profile (Figure 2) *McArthur et al.* [2000] and the cyclostratigraphic timescale of *Suan et al.* [2008]. Working up from the base of the Toarcian, four examples illustrate this. First, the spikes of Mo/TOC in the Sulfur Bands occur over stratigraphic intervals of 12–22 cm, which equate to durations of 5–10 ka. Second, four excursions in Mo/TOC within the upper *semicelatum* and *exaratum* Szs. (A–D in Figure 3)

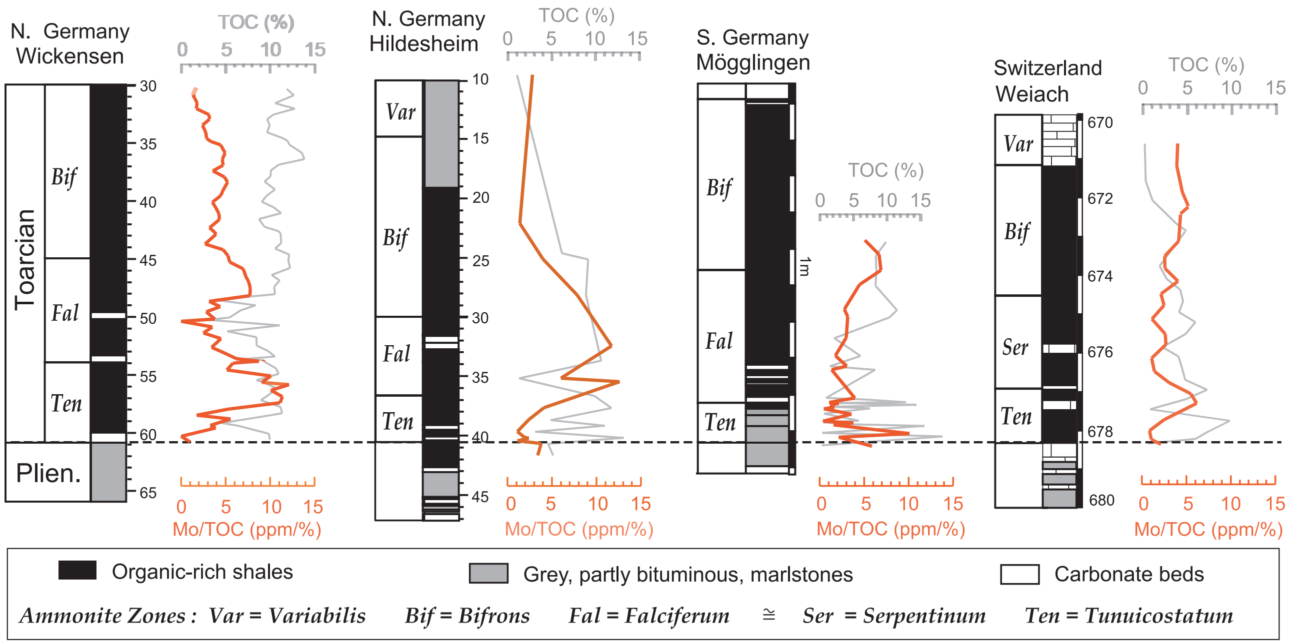

Figure 4. Profiles of Mo/TOC through sections of the Posidonia shale in Germany. Data for Wickensen Mo and TOC are from *Jochum* [1993], data for Mögglingen and Hildesheim Mo and TOC are from *Brumsack* [1988]; data for Weiach Mo are from A. Quigg (personal communication, 2008), and data for Weiach TOC are from *Feist-Burkhardt* [1992]. Assignment of ammonite biostratigraphy relies on the respective authors. Heights are indicated as meters below drill floor except for Mögglingen.

have durations of around <9 ka. Third, in the base of the *falciferum* Subzone, Mo/TOC values increases sharply (Figure 2) over 57 cm of sediment that represents around 10 ka; sampling at this level was not dense, so the signal of change may be aliased and, in reality, be sharper. Finally, across 3.7 m of strata bracketing, and including, bed 48 (the Ovatum Band of *Howarth* [1962]), values of Mo/TOC rise from <2, peak at 4.7, and then decline to 1.7; the thickness represents a time of around 65 ka (Figure 2). The key element of these durations is that they are all small fractions of the residence time of Mo in the modern ocean (800 ka [*Emerson and Huested*, 1991; *Colodner et al.*, 1995]) and, in the absence of contrary evidence, presumably also in the Toarcian ocean.

[26] A subdued positive excursion in both $\delta^{13}C_{(org)}$ and $\delta^{13}C_{(bel)}$ occupies the Toarcian *tenuicostatum* Zone (Figure 2). From the mid-*semicelatum* Subzone, values of $\delta^{13}C_{(org)}$ decline steeply to around −32‰ before recovering to a stable baseline of around −27‰ in the upper *exaratum* Subzone. The carbon isotopic composition of belemnite calcite does not show this negative excursion, but does show a positive isotopic excursion (max +6.5‰) in the upper *exaratum* Subzone and the lower *falciferum* Subzone (Figure 2). Thus, profiles of $\delta^{13}C_{(org)}$ and $\delta^{13}C_{(bel)}$ are decoupled.

[27] Trends in environmental proxies through the *exaratum* Subzone are shown in more detail in Figure 3, where data derive from four literature sources for $\delta^{13}C$ of belemnite calcite, and the data of *Pearce et al.* [2008] for most other parameters. The four excursions in Mo/TOC, Re/TOC and TOC are accompanied by the larger of many sharp changes in $\delta^{13}C_{(org)}$. The $\delta^{13}C$ data is denser than data for other palaeoproxies, which may therefore be aliased. Comparison of the trends in $\delta^{13}C_{(org)}$ and $\delta^{13}C$ of belemnite calcite in Figure 3 shows more clearly than in Figure 2 the different trends in the isotopic profiles of calcite and organic matter. There is a broad negative excursion in $\delta^{13}C$ of organic matter through the *exaratum* Subzone but belemnite calcite shows no such excursion.

[28] Our Mo/TOC profiles for Germany and Switzerland differ between localities (Figure 4). At Wickensen, TOC remains above 10% over most of the Toarcian; at Dotternhausen [*Schouten et al.*, 2000; *Röhl et al.*, 2001] it is above 6% through most of the Toarcian. At Mögglingen and Weiach, TOC frequently dips below 5%. Profiles of Mo/TOC also differ between localities. The profile at Hildesheim bears some resemblance to the profile in Yorkshire while at Weiach Mo/TOC remains <5 through the entire interval in which black shale (loosely defined) was deposited.

5.2. Crossplots of Environmental Proxies

[29] Samples from levels below the mid-*semicelatum* Subzone have low concentrations of TOC. Their Mo concentration represents clastic contributions and they are therefore not considered further. For the remaining samples from Yorkshire, crossplots of Mo-TOC define two data arrays (Figure 5). Samples from the mid-*semicelatum* to upper *exaratum* Szs. (beds 31 to 38) define a regression line of slope 0.5 (regression A, Figure 5) that intercepts the Mo axis at a concentration of around 2 ppm. Samples from levels above bed 38 define a regression line of slope 17 (regression B, Figure 5) that intercepts the TOC axis around

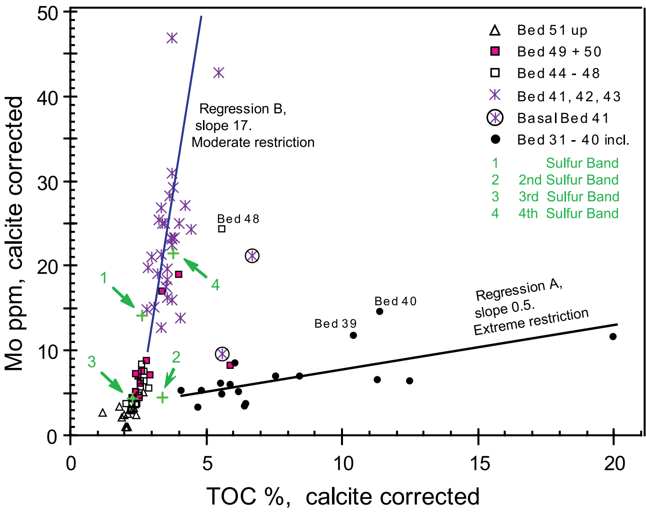

Figure 5. Crossplot of Mo and TOC concentrations in Lower Toarcian sediments of Yorkshire, United Kingdom. Samples from most of the *exaratum* Subzone and the upper *semicelatum* Subzone define regression line A, with a slope of 0.5 (*rs*Mo/TOC in ppm/%) that represents severe water mass restriction. Samples from the overlying *falciferum* Subzone and above define regression line B, with a slope of 17, that represents moderate water mass restriction. Samples from strata above the *falciferum* Subzone plot toward the lower end of regression line B and approach background (silicate) values of Mo (around 1–2 ppm) and TOC. A few samples with intermediate Mo/TOC represent intermediate states of restriction (e.g., beds 39 and 40 and the basal part of bed 41). The Sulfur Bands represent four brief periods of restriction and pyrite formation in the earliest Toarcian. Note that *rs*Mo/TOC (the slope of the regression line between Mo and TOC) is not Mo/TOC, which is the direct ratio of Mo to TOC in ppm/% and which takes no account of nonzero axial intercepts of the Mo versus TOC regressions.

a value of 2.0 to 2.5%. Samples from beds 39, 40, and the basal part of bed 41, fall between these regressions. As stratigraphic level increases above bed 45, concentrations of Mo and TOC decrease and are mostly <8 ppm Mo and <3% TOC. Nevertheless, the samples still define a remarkably tight regression around the slope of 17 defined by more Mo-rich samples; we comment of this below.

6. Interpretation of the Palaeoproxies

6.1. Euxinia and Aliasing

[30] The model of *Algeo and Lyons* [2006] works only where euxinic conditions exist(ed) in the water column: such euxinia is well documented for the Lower Toarcian black shales of NW Europe. The "degree of pyritization" (DOP) [*Raiswell and Berner*, 1985] through both the *exaratum* Subzone in Yorkshire and the Posidonia shale of Germany was shown by those authors to be around 0.85, a value attesting to long-term euxinic conditions in both basins. Similar values (0.8 to 0.9) for DOP were reported for the *exaratum* Subzone of Yorkshire by *Pearce et al.* [2008]. *Wignall et al.* [2005] document anoxia and euxinia through the upper *semicelatum* Subzone and lower *exaratum* Subzone in Yorkshire on the basis of the size of pyrite framboids, and DOP. Our values of TS exceed 2%, and values of DOP-T (Figure 2) exceed 0.5, in the interval from the mid-*semicelatum* Subzone to the mid-*falciferum* Subzone. Such values confirm the general euxinic nature of the interval. In the upper *falciferum* Subzone values are less than 0.4, suggesting euxinic conditions no longer affected the water column, but they recover to between 0.4 and 0.5 above that level. Exceptionally low DOP-T is seen at the levels of two thin sideritic mudstones, beds 46 and 50.

[31] In Germany, *Röhl et al.* [2001] showed that euxinia was prevalent throughout deposition of the Posidonia shale from the mid-*semicelatum* Subzone into the upper *bifrons* Zone. Photic zone euxinia was also documented by *Schouten et al.* [2000] to be present at each of the seven levels that were examined through the same stratigraphic interval, but was shown to be absent at three lower stratigraphic levels. *Schwark and Frimmel* [2004] broadly confirmed those findings using a higher sample density.

[32] Despite the prevalence of long-term euxinia over a substantial part of the time represented by the section in the Cleveland Basin, the presence of fossil "event communities" at uncommon, discrete, horizons within the sections in Yorkshire and the Posidonia shale of Germany [*Howarth*, 1962; *Röhl et al.*, 2001] show that conditions were occasionally oxygenic, if only for periods of a few weeks to a few years at a time. The geochemical signal of oxygenation is aliased because sampling has not been undertaken (even by *Pearce et al.* [2008] or *Röhl et al.* [2001]) at a resolution high enough to capture the short periods when euxinia was interrupted and life flourished, briefly, in the Toarcian seas of NW Europe. We discuss this below.

6.2. Faunas

[33] The palaeobiology of the Yorkshire sections has been presented by *Little and Benton* [1995], *Little* [1996], and *Harries and Little* [1999]. These authors note that organisms that inhabited the upper water column suffered little from these extinction events, and that epifaunal bivalves were also largely unaffected. The last work recognized the latest Pliensbachian and the earliest Toarcian (*tenuicostatum* Zone) as an interval in which extinction was most pronounced at four levels, the last occurring at the end of the interval (top of bed 32, i.e., top of the Grey Shale Member, Figure 6). During the time of deposition of the upper part of the *semicelatum* Subzone, species diversity and richness declined to low levels and remained low until the lower part of the *commune* Subzone (*bifrons* Zone). Above bed 50, in the *commune* Subzone, species diversity increased as populations recovered.

[34] While presenting a good synopsis of Early Toarcian biotas in Yorkshire, the work of *Harries and Little* [1999, Figure 6] nevertheless aliases the faunal data by joining adjacent sample points with a line. This disguises the fact that significant parts of the stratigraphic interval between the upper *semicelatum* Subzone to mid-*commune* Subzone; that is, the intervals between those levels where faunas were recorded, are devoid of macrofossils of any type. For the

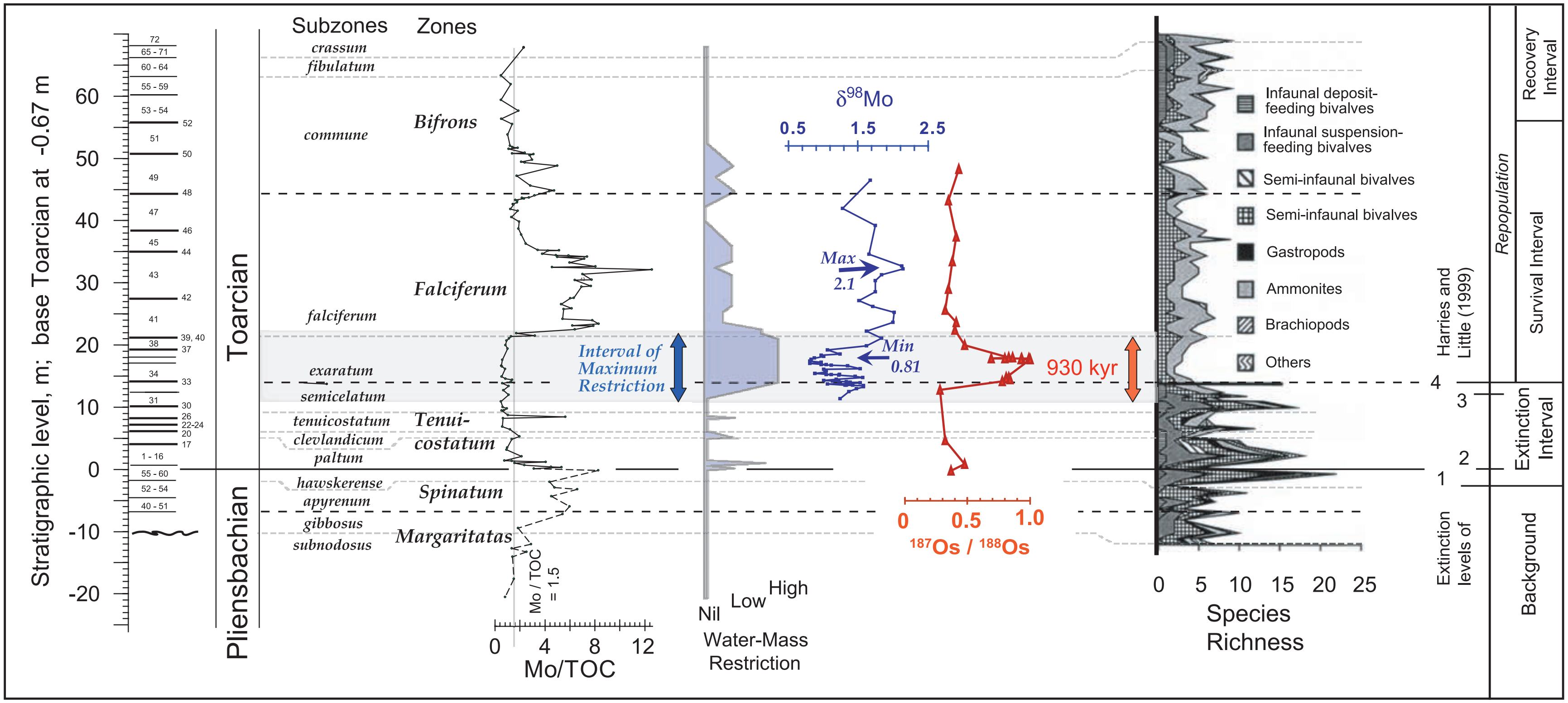

Figure 6. Comparison with species abundance from *Harries and Little* [1999] with Mo/TOC, interpreted degree of restriction, δ^{98}Mo (data of *Pearce et al.* [2008]), and $^{187}Os/^{188}Os$ (data of *Cohen et al.* [2004]) through the Upper Pliensbachian and Lower Toarcian of Yorkshire, United Kingdom. Faunal diversity drops when restriction begins and recovers above bed 50, the level at which restriction had ceased.

Posidonia shale of Germany this point of aliasing was noted by *Röhl et al.* [2001] and *Schmid-Röhl and Röhl* [2003]. Documenting faunal and geochemical parameters at near centimeter-scale resolution through some 12 m of section at Dotternhausen in S Germany, they showed that the macrofossils are present at discrete horizons and represent "event communities," i.e., opportunistic recolonizations of the seafloor that lasted only a few weeks to a few years [*Röhl et al.*, 2001]. Such periods were rarely captured in geochemical parameters, such as C/S crossplots, probably because the sampling resolution, although exceptionally high, was still not high enough to do so. From faunal evidence, they noted around 30 such oxygenation events [*Röhl et al.*, 2001, Figure 10] during the German equivalent of the United Kingdom's *exaratum* Subzone, with a higher density being recorded above that level.

[35] The pertinent point about such "event communities," in which we include the uncommon belemnite horizons within the *exaratum* Subzone of Yorkshire (Figure 2), is that they record conditions only during the geologically brief moments when the fossils were alive [*van de Schootbrugge et al.*, 2005; *Wignall et al.*, 2005]. Their presence in Yorkshire and Germany attests to occasional brief periods when the general euxinic conditions were briefly interrupted and these periods have an importance far beyond their duration: into a long-term euxinic geochemical signal they interleave a short-term oxic geochemical signal (e.g., δ^{13}C in belemnite calcite). The oxic signals were captured either during the brief periods of normal (open-ocean) conditions in the Cleveland Basin or, because belemnites were mobile, in the open (oxic) ocean outside the euxinic Cleveland Basin, into which the belemnites occasionally strayed to die [*van de Schootbrugge et al.*, 2005; *Wignall et al.*, 2005]. The chemical signatures of belemnites in the Cleveland Basin (or Posidonia shale) do not record the chemical signature of the euxinia generally prevalent within it, which is why they do not show the negative isotopic excursion shown by organic matter and (presumably?) nonmobile phytoplankton trapped in the basin and able to survive within the upper oxic interval of the water column.

6.3. Crossplot of Mo Versus TOC for the Cleveland Basin

[36] The Mo versus TOC crossplot (Figure 5) defines two data trends to which regression lines A and B have been fitted. Regression A has a slope of 0.5 and applies to samples collected from the upper half of the *semicelatum* Subzone and most of the *exaratum* Subzone (beds 31 to 38). This interval encompasses the putative Early Toarcian OAE, and the local negative excursion in δ^{13}C of organic matter (Figure 2). The value of 0.5 is around 10 times less than that for Holocene sediments from the Black Sea (*rs*Mo/TOC of 4.5 ± 1 [*Algeo and Lyons*, 2006]). It implies that almost complete restriction occurred during this interval, so we term it the interval of maximum restriction (IMR). The frequency of deepwater renewal in a restricted basin scales linearly with *rs*Mo/TOC [*Algeo and Lyons*, 2006], so an *rs*Mo/TOC of 0.5 implies a renewal frequency of deep water of 5 to 40 ka. Over a period of around 930 ka (Figure 2), renewal therefore occurred between 23 and 186 times. It is interesting that *Röhl et al.* [2001] identified around 30 brief events of oxygenation during the equivalent time period in Germany, and ascribed them to the occurrence of tropical storms. The renewal frequency estimated by *Röhl et al.* [2001] and here is much lower than is implied by the annual flushing model of *Schwark and Frimmel* [2004] and *Frimmel et al.* [2004], which, with today's concentration of marine Mo, would give *rs*Mo/TOC around the 45 (cf. Saanich Inlet [*Algeo and Lyons*, 2006]).

[37] The infrequency of renewal implies that the concentration of Mo in the seawater of the basin was drawn down to concentrations well below those currently seen below 200 m in the Black Sea, where they are only 2–3% of that in open ocean water [*Algeo and Lyons*, 2006], so a mass balance of Mo is of interest here. For the 10 m of sediment in the IMR, the mean Mo concentration is 5.1 mg/kg (Table 1), a value that equates to 10 mg/cm^2, using a sediment density of 2 g/cm^2. This amount of Mo is contained within column of modern seawater (Mo 105 nM) that is 1000 m thick. This figure leaves little room for much replenishment of Mo during the IMR, were the Toarcian sea indeed 1000 m deep, so it implies that the Toarcian sea was very much less than 1000 m in depth, or that scavenging efficiency for Mo was nonlinear and declined at low concentrations of Mo in seawater.

[38] Within the IRM, sharp, albeit small, excursions in Re/Mo, Re/TOC, Mo/TOC, δ^{98}Mo, and TOC coincide with the abrupt decreases in $\delta^{13}C_{(org)}$ (A–D in Figure 3). The Mo/TOC excursions are defined by either one datum (A and D) or two (B and C), where the sampling interval was 3 cm. As the major negative excursion in $\delta^{13}C_{(org)}$ occupies 10 m of strata from the mid-*semicelatum* Subzone to the basal *falciferum* Subzone (Figure 2), and endured over a period of 930 ± 40 ka [*Suan et al.*, 2008], excursions A and D occupied <3 ka, while B and C occupied >3 ka but less than 9 ka. These durations are around one hundredth of the residence time of Mo in seawater today. Another subtlety of the excursions is that the middle pair (B, C) move to higher Mo/TOC, Re/TOC, and lower TOC, while the outer pair (A, D) move to lower Mo/TOC, Re/TOC, and higher TOC. At A and B, the decline in δ^{98}Mo is briefly interrupted, while at C and D, the decline in δ^{98}Mo is briefly strengthened, although these effects are small.

[39] These subtle changes must relate to changes in the rate of deepwater renewal. The importance of these excursions lies in their short duration, which provides good evidence that they are driven by changes in a reservoir of small size: they are consistent with control by a varying degree of restriction and inconsistent with any interpretation of the signals in terms of whole-ocean events, owing to the large mass of the ocean. The data defining the excursions plot on regressions of Mo versus TOC that have slopes of 0.4 to around 3.4, confirming that the variations in restriction they imply was small. It is not known whether these excursions coincide with oxygenic events identifiable by the presence of event faunas. The low frequency of water mass renewal accords with the faunal observations of only brief intervals of reoxygenation in this interval in Germany (the density of faunal event horizons has not been measured in the Cleveland Basin). Such intervals of oxygenation may

represent the effects of 10 or 50 ka events, i.e., events of such severity that they occur only at those frequencies, that briefly overturned the water column. They are, perhaps, the tropical storms of *Röhl et al.* [2001].

[40] Samples from above the IMR (beds 41 and above) fall along regression B (Figure 5), which has a slope of around 17. For modern sediments, this slope would imply a degree of restriction that is intermediate between that seen now for Framvaren Fjord (*rs*Mo/TOC of 9 ± 2), where water mass renewal is around 50 to 130 years, and that seen in the Cariaco Basin (*rs*Mo/TOC of 25 ± 2) where renewal times are around 50 to 100 years [*Algeo and Lyons*, 2006]. Restriction above the IMR was therefore less than it was in it. Excepting bed 49, both Mo concentrations (<8 ppm) and TOC concentrations (<3 %) are low in most strata above bed 45, where DOP-T is around 0.4 to 0.5, and TS around 2%. The Mo and TOC data nevertheless define a tight curvilinear regression (Figure 5) that suggests sulfidic sequestration of Mo was still happening. The data suggest that sediments above bed 45 were sulfidic, but that euxinic conditions had retreated to be close to the sediment-water interface in the Cleveland Basin, expanding briefly through bed 49.

[41] We speculate that a small part of the water column remained euxinic in much of this interval because of two factors: first, the recovery of faunal diversity did not begin until bed 50, in the lower part of the *bifrons* Zone, a matter which attests to the continued inhospitable nature of the environment until *bifrons* zone times. Second, the distribution of data along regression line B in Figure 5 may be interpreted roughly as reflecting the proportion of the overlying water column that was euxinic during times of moderate restriction. The position of a sample on the regression may therefore indicate the size of the reservoir available to supply Mo, and be a proxy for the depth of the chemocline. The faunal trends shown in Figure 6 therefore broadly reflect the geochemical trends through the entire composite section and confirm our interpretation of the profile of Mo/TOC as a proxy for degree of deepwater restriction.

6.4. Mo/TOC Profiles for Continental Europe

[42] Our Mo/TOC profiles for Germany and Switzerland differ between localities, the differences likely arise from differing degrees of restriction at differing times and places within the NW European Basin (loosely defined). In all four continental localities, values of Mo/TOC rise in, or below, the lower part of the *tenuicostatum* zone as restriction begins and intensifies, this is at a lower stratigraphic level than is found in The Cleveland Basin. At Dotternhausen, four thin units of organic-rich shale occur in the *paltum* and uppermost *clevelandicum* Szs. [*Röhl et al.*, 2001] and it is tempting to equate those units with the four Sulfur Bands of Yorkshire. Across Germany and Switzerland, the onset of permanent restriction was therefore both earlier and less sudden than it was in the Cleveland Basin. This is no surprise; *Wignall et al.* [2005] clearly documented diachroneity in the onset of black shale deposition across Europe. Although the application of the Mo/TOC proxy for Toarcian palaeoceanography in Germany and Switzerland would certainly benefit from more detailed sampling, and improved biostratigraphic calibration of existing Mo/TOC profiles, the existing data are significant in the sense that they corroborate the overall conclusions drawn from the detailed record of the Cleveland Basin in Yorkshire, and confirm the diachroneity of the onset of deepwater restriction across NW Europe in Early Toarcian time.

7. Local or Global Cause for Variations in Mo/TOC and *rs*Mo/TOC?

[43] The interpretation presented above appears to offer good evidence that the basin restriction model applies to the formation of the Lower Toarcian black shales of NW Europe. For several reasons, we discount explanations of the data that invoke global events, or variations in the Mo concentration of open-ocean seawater (the global drawdown scenario), or variations in the area of anoxic sedimentation on the seafloor [*Barling et al.*, 2001; *Pearce et al.*, 2008].

[44] First, the diachroneity of the onset of extinction patterns associated with anoxia in the Early Toarcian of Europe [*Wignall et al.*, 2005] (Figures 3 and 4) and beyond [*Wignall et al.*, 2006] is not consistent with the operation of a global process, which must act at the same time worldwide.

[45] Second, environmental proxies as diverse as TOC, δ^{13}C, Mo/TOC and *rs*Mo/TOC, and Re/TOC, have a range of response times to whole-ocean perturbations, yet they show simultaneous perturbations in the Lower Toarcian records of Yorkshire. Such fast and simultaneous response times for both initiation and, crucially, relaxation, of such excursions can occur only when the reservoir size is small and so decoupled from the whole ocean. It is important to emphasize that the most diagnostic point about such excursions is their rate of relaxation. Having been drawn down to low Mo concentrations, any observable recovery of oceanic Mo concentrations via normal weathering processes (and so the development of high Mo/TOC in sediments) would occupy a period equal to at least several residence times of Mo (800 ka). The fast excursions and relaxations, over timescales of a few thousand years we document in Yorkshire in Mo/TOC (and Re/TOC) were too rapid to reflect whole-ocean events. They prove that, throughout the time interval examined, drawdown and replenishment of Mo must have occurred within a small (local) reservoir. Similar, short, excursions (that, by definition, incorporate relaxations) are also found in the Sulfur Bands, where elevated Mo/TOC indicates brief periods of euxinia (Figure 2): these excursions and their relaxation are consistent with the operation of a local, not a global, process.

[46] Third, drawdown of oceanic Mo requires it be sequestered in organic-rich sediments. But the amount of Mo in European black shales is extremely low, so the fate of oceanic Mo is obscure if a whole-ocean explanation is invoked for low Mo/TOC and *rs*Mo/TOC in the interval. Only 0.3% of the total flux of Mo to the Early Toarcian ocean was captured in NW Europe during the IMR: this calculation assumes a duration for the IMR of 930,000 years [*Suan et al.*, 2008], a riverine flux of Mo to the ocean during the IMR equal to that of today (18.2 × 10^6 kg/a [*Algeo*, 2004, Table 1], an area of European black shale of 500,000 km^2 (from Figure 1); and a mean concentration

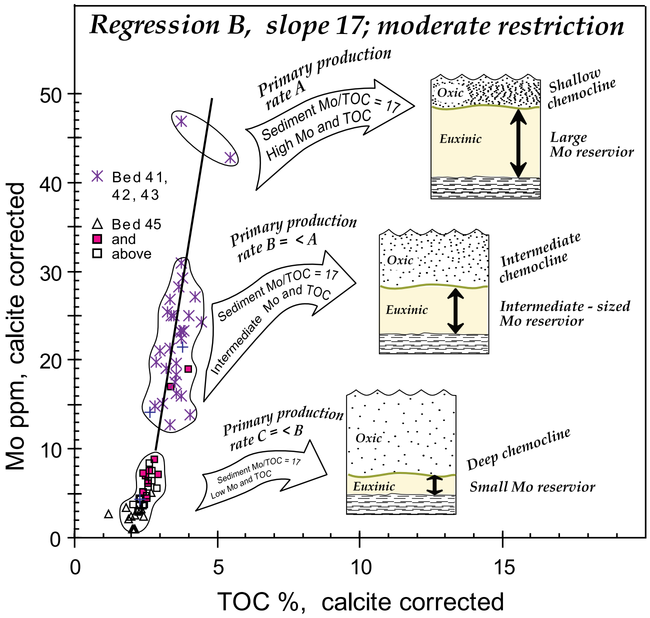

Figure 7. Postulated control on Mo and TOC concentrations at constant *rs*Mo/TOC (regression line B of Figure 5) in the Lower Toarcian sediments of the Cleveland Basin.

of Mo in the IMR of 5.1 mg/Kg (from Table 1). The figure of 0.3% is too small to be much affected by uncertainties in the estimates of input parameters; it therefore mitigates against global drawdown of seawater as a cause of the low Mo/TOC in that interval.

[47] Finally, a restricted basin scenario is consistent with the range of Mo and TOC concentrations seen at *rs*Mo/TOC values of both 0.5 and of 17 (Figures 5 and 7). We speculate that such ranges may have arisen through drawdown of Mo from a reservoir in which the depth to the chemocline, and so the size of the euxinic reservoir able to supply Mo, varied with time, and we illustrate this using regression B, of *rs*Mo/TOC 17, as the example (Figure 7). For regression B, the spread in TOC is from 2 to 5% TOC and in Mo from 2 to 47 ppm. The depth to the chemocline would have depended on the rate of primary production, other things being constant, and would have controlled the depth of euxinic water available to supply Mo to sediments i.e., reservoir size. In bed 45 and above, where Mo and TOC are low but still define a tight regression, the oxic/euxinic interface would have been close to, or at, the sediment-water interface. In this speculative model, the slope of the regression line indicates the degree of water mass restriction, while the position on the regression line indicates the depth of the chemocline.

8. Case for a Pycnocline

[48] Many previous models for the formation of the organic-rich sediments in the Lower Toarcian of NW Europe have postulated that they accumulated as a response to restriction imposed by isolation of a subpycnoclinal water mass beneath a lower-salinity surface layer, a model often termed the Küspert model [*Küspert*,1982; *Sælen et al.*, 1996, 1998, 2000; *Röhl et al.*, 2001; *Schmid-Röhl et al.*, 2002; *Bailey et al.*, 2003; *Frimmel et al.*, 2004; *Schwark and Frimmel*, 2004; *van de Schootbrugge et al.*, 2005]. This model works, for several reasons.

[49] First, *Sælen et al.* [1996] and *Bailey et al.* [2003] argued that δ^{13}C, δ^{18}O, and Mg/Ca values in belemnites from Yorkshire and Germany, profiled through the transition from the mid-*tenuicostatum* zone through the *exaratum* Subzone (in the UK sense), record a reduction of salinity of up to 5 psu, and an increase in temperature of up to 7°C. Second, for the Posidonia shale of Germany, *Prauss et al.* [1991] noted the wholesale replacement of dinocysts and acritarchs by praesinophytes (e.g., *Tasmanites*) across the *tenuicostatum-falciferum* zone boundary and attributed the change to decreasing salinity in the photic zone as a result of density stratification and eutrofication. Third, such a scenario is able to succinctly explain isotopic excursions in both δ^{98}Mo and ^{187}Os/^{188}Os through the interval (documented in Figure 6), as we explain in later sections. Finally, a problem with whole ocean interpretations of *rs*Mo/TOC is that low values in sediments imply drawdown of Mo in the oceans, a drawdown that might limit primary production and make continued black shale deposition impossible to sustain [*Zerkle et al.*, 2006; *Scott et al.*, 2008]. This limitation does not apply to a restricted basin scenario because the more dominant role of the low-salinity surface layer can provide both nutrients and Mo for primary production. Mixing of deeper waters into the surface layer can then generate C-isotopic anomalies while not lowering production despite supplying low-Mo water.

[50] Lowered surface salinity may have been driven by enhanced precipitation and runoff within the basin's watershed as a consequence of a warmer climate and more evaporation and rainfall (Figure 8). Increased surface runoff would have strengthened the pycnocline and led to greater isolation of the deepwater mass, allowing more rapid and sustained depletion of dissolved oxygen within it [*Hay*, 1995; *Sælen et al.*, 1996; *Röhl et al.*, 2001; *Bailey et al.*, 2003; *Wignall et al.*, 2005] as well as suppressing vertical mixing within the water column. We postulate (Figure 8) that the transition from nil to extreme restriction involved such a strong development of a pycnocline, which effectively blocked exchange of water with the surrounding seas because of the large flux of freshwater ensuing from warming.

[51] The black, organic-rich shales of the Lower Toarcian have long been associated with a transgression [*Hallam*, 1997]. A rise in global sea level elevations would usually lead to enhanced deepwater exchange across a restricted marginal marine or intracontinental basin (other factors being equal), as when the modern Baltic and Black seas were transformed from freshwater lakes to marine basins during the eustatic transgression that followed the last glacial maximum [*Jones and Gagnon*, 1994; *Sohlenius et al.*, 2001]. But the hydrographic effects of a sea level rise depend on basin geometry and concurrent climatic changes. An increase in surface water outflow across a basin's marginal sill during a sea level rise can, when large enough, cause the deepwater flux into the basin to remain constant or decrease despite an increase in water depth over the sill [cf. *Ehlin*, 1981].

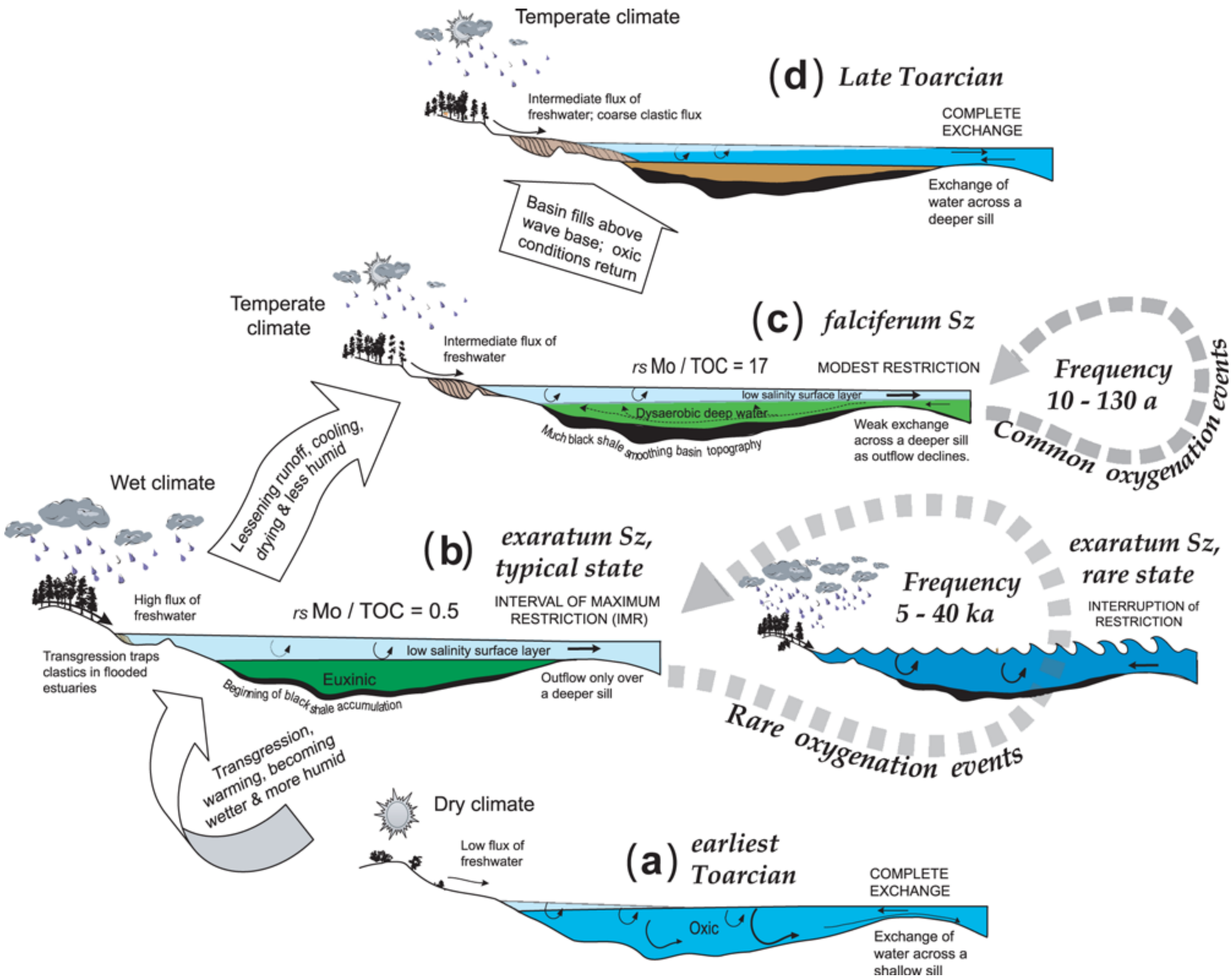

Figure 8. Development of salinity stratification and its effect on exchange with open-ocean seawater. (a). The earliest Toarcian; low-to-mid *Tenuicostatum* Zone. Complete exchange with open-ocean seawater, little or no salinity stratification; sediment deposited with low concentrations of Mo and TOC. (b). The *exaratum* Subzone, upper *semicelatum* Subzone, and IMR. Mo/TOC regression slope of 0.5. Deposition of organic-rich sediments. Warm, wet, climate. High runoff of freshwater created a deep pycnocline, which interested local sills and prevented exchange with the open ocean, despite higher sea level. Rare oxygenation events destroyed stratification and brought macrofauna into the seaway for short periods. (c). The lower *falciferum* Subzone; Mo/TOC regression slope of 17. Runoff lessened, pycnocline shallowed; weak exchange occured with the open ocean allowing more frequent invasions of fauna during more frequent oxygenation events. (D). The upper Toarcian Basin fill brought sediment near to wave base; return of fully marine conditions. Coarser clastics encroached into the basin (Fox Cliff Siltstone Member, Blea Wyke Sandstone Formation).

[52] In discussing Early Toarcian events recorded in the Cleveland Basin, the focus of others has been largely on the 3 m interval in the lower *exaratum* Subzone where TOC concentrations are highest (the putative OAE in the strict sense), or the 7 m of the *exaratum* Subzone itself (the putative OAE in the wider sense). Here, we revisit older literature [e.g., *Hallam and Bradshaw*, 1979], and emphasizes more recent literature [e.g., *Harries and Little*, 1999; *Wignall et al.*, 2005] and German literature that places the black shales deposition and restriction into a longer temporal context. In conjunction with the timescale of *Suan et al.* [2008], our data confirm that restriction in the shallow shelf seas of NW Europe was presaged by organic-rich intervals in the *tenuicostatum* Zone of Germany and the United Kingdom (the Sulfur Bands in the latter), then developed in around 150 ka through the upper *semicelatum* Subzone, was extreme for around 750 ka, and persisted in intermittent, or lesser form over the ensuing 500 ka into mid *bifrons* time. This interval of euxinia in Yorkshire is therefore now demonstrated to occupy approximately the same stratigraphic interval as does the Posidonia shale of Germany.

[53] Our Mo versus TOC crossplots show that samples fall on one of two regression lines with very different slopes. The real conundrum, at least for the Cleveland

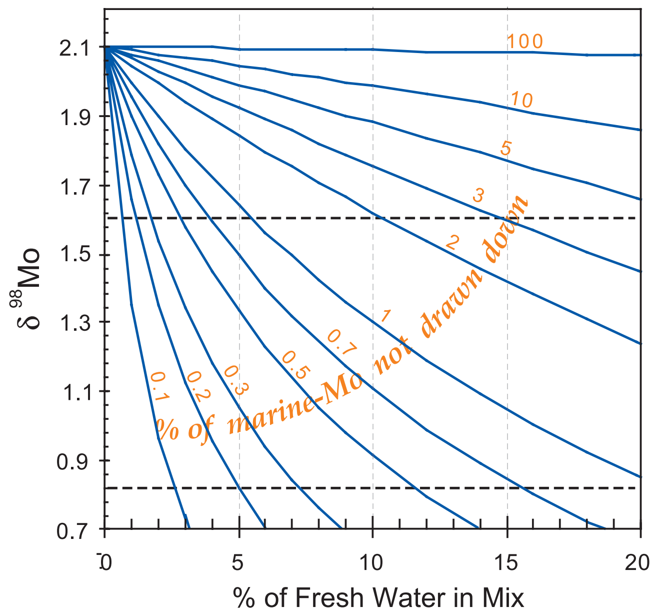

Figure 9. Modeled δ^{95}Mo in the Early Toarcian sea of the Cleveland Basin as a function of salinity and drawdown of marine Mo. End-member values for isotopic composition and concentration are from Table 2. Plot shows the percentage of typical continental runoff required in a mix of freshwater and seawater to generate an isotopic composition of the mix, given on the ordinate. In the current Black Sea, Mo drawdown is below 200 m to 2–3% of its open-ocean value.

Basin, may lie in why samples define only two regression lines, i.e., reveal a two-state system of restriction, rather than variable restriction. Do other black shales do the same? Our data preclude open-ocean models, e.g., those based on enhanced upwelling (e.g., a Namibian shelf model), as viable explanations of Toarcian events because of the low faunal diversity demonstrated by *Harries and Little* [1999] for the Cleveland Basin and by *Röhl et al.* [2001] for Germany, and the event communities documented by the latter. Explanations for Toarcian condition must reckon with the longer time frame we demonstrate, which requires driving forces operating over the entire Early Toarcian, but not in such overwhelming strength that they could not be briefly interrupted. Given these considerations, it seems inappropriate to designated the interval of separation of the Early Toarcian sea of NW Europe from the ocean as an oceanic anoxic event, and more appropriate, especially today, to term it a regional anoxic event (RAE).

9. Local or Global Expression for δ^{98}Mo Variations?

[54] The data of *Pearce et al.* [2008] show that δ^{98}Mo ranges between 0.8 and 1.6 (Figures 3 and 6) within the IMR (Figures 2 and 6). In the overlying *falciferum* Subzone, where restriction was less, values are higher and reach 2.1‰ where the Mo/TOC profile peaks at 31.3 m in the section. These data are consistent with restriction and euxinia being imposed by a low-salinity surface layer. During the IMR, the δ^{98}Mo of the restricted water mass within the Cleveland Basin would have been sensitized to such freshwater inputs for two reasons. First, because drawdown of Mo was nearly total during that time; second, because the concentration of Mo in seawater (105 nM) is only about twenty times that in continental runoff (5 nM) [*Hem*, 1978; *Nägler et al.*, 2005, and references therein].

[55] Development of a low-salinity cap as a driver for restriction would have allowed Mo in continental-derived freshwater to override the marine isotopic composition of drawn-down Mo in the Cleveland Basin. We model such changes in Figure 9. We assume that the Mo concentration in Toarcian seawater was 105 nM (as it is today) and had an isotopic composition of 2.1‰, the maximum recorded in the section [*Pearce et al.*, 2008] (Figure 6). The model results show that lowering δ^{98}Mo to a value of 0.8 from 2.1‰ requires salinity to decline by around 7% (2.3 psu) if Mo is drawn down to be 0.3% of its original concentration. This drawdown is around ten times more than seen today in the Black Sea below 200 m depth. The *rs*Mo/TOC of regression A of Figure 5 is around one tenth of that for Black Sea sediments. The comparison suggest that drawdown of Mo to 0.3% of the oceanic value was possible; the required percentage drawdown would have been less if the Mo concentration in the Toarcian ocean was lower than it is in the modern ocean. To drive marine δ^{98}Mo down from 2.1 to around 1.6‰ would have required a lowering of salinity of only 2% (around 0.7 psu) on a drawdown of Mo to 0.3% original. *Nägler et al.* [2005], *Poulson et al.* [2006] and *Reitz et al.* [2007] emphasized the present uncertainty that attends interpretation of Mo isotopic composition as a palaeoproxy; we confirm that caution is required in the interpretation of δ^{98}Mo in all black shales sequences.

10. Impact of Restriction on Re-Os Dating

[56] Our Mo and TOC data demonstrate that the model of a restricted basin, lidded by a low-salinity surface layer (the Küspert model), applies to much of Early Toarcian time of NW Europe. As Mo was drawn down in the waters beneath the pycnocline in the Cleveland Basin, organophile elements such as Re, and Os would also have been drawn down into organic matter accumulating on the seafloor. The resulting low concentrations of dissolved Re and Os would have sensitized the water column to isotopic change caused by small inputs of elements from the mixed, low-salinity surface layer. We examine below the implications of this sensitization on the attempts to date black shales using the Re-Os geochronology, because such attempts have not always been successful.

[57] A minority of Re/Os isochrons yield large uncertainties on the date derived. Drawdown of Os following restriction explains why. The assumption of the method is that radiogenic ^{187}Os accumulated in a suite of samples in which the initial ^{187}Os/^{188}Os was uniform. This assumption is violated if drawdown of Os, following restriction, sensitized the isolated water mass, and so the sediments, to fluctuating inputs of continental Os. The sensitization occurs because, assuming modern values applied, the con-

Table 2. Isotopic and Elemental Data for Seawater and Continental Runoff Pertinent to Early Toarcian Times[a]

	River		Seawater	
Element	Concentration	IR	Concentration	IR
Os, aM	48	1.4	53	0.4
Mo, nM	5	0.0	105	2.1

[a]IR is isotope ratio, $^{188}Os/^{187}Os$ and $\delta^{98/95}Mo$. Data are from *Hem* [1978], *Peucker-Ehrenbrink and Ravizza* [2000], and *Cohen et al.* [2004].

centration of Os in seawater (53 aM) was about the same as that in continental runoff (48 aM) but their isotopic compositions were very different; values of $^{187}Os/^{188}Os$ are around 1.1 to 1.2 for continental inputs to seawater, and around 0.12 for extraterrestrial and MOR inputs [*Peucker-Ehrenbrink and Ravizza*, 2000] (Table 2). This problem appears to have compromised attempts to date the *exaratum* Subzone in Yorkshire using the Re-Os isochron method [*Cohen et al.*, 1999]. The date obtained was imprecise because the initial $^{187}Os/^{188}Os$ for their suite of samples was not constant. In the *exaratum* Subzone initial $^{187}Os/^{188}Os$ values are high and variable (0.8 to 1.0, Figure 6) [*Cohen et al.*, 1999, 2004], values well above the 0.4 derived for higher stratigraphic levels (Figure 6).

[58] We model the effect on the isotopic composition of drawdown of Os and resupply by dilution with a freshwater end-member (Figure 10) using model parameters given in Table 2 that are appropriate to the Toarcian. The value of 0.4 for initial $^{187}Os/^{188}Os$ is that for organic-rich sediments above the *exaratum* Subzone (Figure 6) [*Cohen et al.*, 2004]; even that value may have been affected by the restriction. From Figure 10, it can be seen that to drive $^{187}Os/^{188}Os$ to the value of 0.8 seen in the *exaratum* Subzone from 0.4 required only 4% dilution of seawater by freshwater, i.e., a lowering of salinity by 1.3 psu, if the seawater Os had been drawn down to 5% of its original value by restriction and rainout to sediments. Given the salinity reduction in the surface layer calculated by *Sælen et al.* [1996] of 5 psu, and that of 2.5 psu calculated by *Bailey et al.* [2003] using Mg/Ca and $\delta^{18}O$, the Os isotopic anomaly in the *exaratum* Sz is thus explained.

[59] The anomaly was interpreted by *Cohen et al.* [2004] as reflecting a 400–800% increase in continental weathering, communicated to the whole ocean. This explanation is unlikely to be correct and not only for the reason given here: the isotopic anomalies are recorded in a section that is condensed [*McArthur et al.*, 2000; *McArthur and Wignall*, 2007], rather than expanded, and the increased sediment flux that increased weathering would entail have not been identified. Our interpretation, that the elevated initial $^{187}Os/^{188}Os$ reflect a signal of riverine input that was magnified by marine isolation and consequent drawdown of Os into sediments, is compatible with both condensation and with restriction.

[60] *Cohen et al.* [1999] also found that the isochrons for other organic-rich sediments from the United Kingdom (Table 3) including the Kimmeridge Clay, had unexpectedly large uncertainties in calculated age. We postulate that this was for the same reason as given above; drawdown and sensitization of Os isotopic composition in the respective overlying water masses to modification by small freshwater inputs, leading to variable initial $^{187}Os/^{188}Os$. Such drawdown is evident from crossplots of Mo, Re, and Os, against TOC (Figure 11). The regression slopes have a range of slopes, but many are low. The *rs*Re/TOC and *rs*Os/TOC for the Kimmeridge Clay (*wheatleyensis* Zone of Dorset) are particularly low and seem extreme, while the *rs*Mo/TOC for the Kimmeridge Clay (*hudlestoni* and *wheatleyensis* Zones of the Cleveland Basin [see *Tribovillard et al.*, 1994, 2004b] is around 3, which is low but not as extreme as the 0.5 for the Toarcian sediments of the Cleveland Basin. We interpret all of these the low slopes to be diagnostic of water mass restriction. Drawdown and sensitization consequent on restriction explains why the initial $^{187}Os/^{188}Os$ ratios are variable (Table 3) and Re-Os dating compromised.

[61] Similar problems of imprecision were encountered by *Turgeon et al.* [2007] when applying Re-Os to date black shales across the Frasnian-Femennian boundary. Four isochrons obtained for four levels close to the boundary showed a range of mean square weighted deviation (MSWD) from 0.51 to 11.7. The level with the poorest precision on age (WVC777, 476 ± 140 Ma for the boundary age that is around 370 Ma) is aberrant in

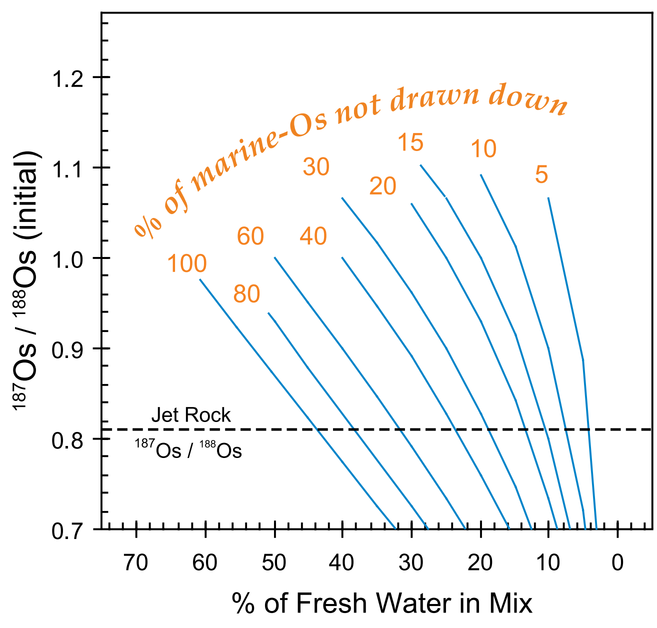

Figure 10. Modeled $^{187}Os/^{188}Os$ (initial) in the Early Toarcian sea of the Cleveland Basin as a function of salinity and drawdown of marine Os. End-member values for isotopic composition and concentration are from Table 2. Value of $^{187}Os/^{188}Os$ (initial) of 0.81 for the jet rock was taken from *Cohen et al.* [1999]. Plot shows the percentage of typical continental runoff required in a mix of freshwater and seawater to generate an isotopic composition of the mix, given on the ordinate. In the current Black Sea, Mo drawdown is below 200 m to 2–3% of its open-ocean value.

Table 3. Organic-Rich Sediments From the UK Used for Dating via the Re-Os Geochronometer[a]

Units of Sediment	Calculated Age	MSWD	Number of Analyses	$^{188}Os/^{187}Os_{(i)}$
Kimmeridge clay	155 ± 4.3	11	11	0.65 ± 0.38
Toarcian	181 ± 13	17	9	0.81 ± 0.09
Sinemurian	No isochron	None	4	0.18 ± 1.23
Hettangian	207 ± 12	88	13	0.18 ± 0.20

[a]Data are from *Cohen et al.* [1999].

several respects compared to the other levels. It has the most restricted range of $^{187}Re/^{188}Os$, the lowest *rs*Os/TOC and *rs*Re/TOC, and the highest concentration of TOC (Figure 12). We suggest that the imprecise isochron for WVC777 arises from drawdown locally of Os consequent on ephemeral basin restriction and enhanced primary production that sensitized the basin to freshwater inputs. Given these considerations, future attempts to date black shales using the Re-Os geochronometer should be made bearing in mind that sediments showing well-defined,

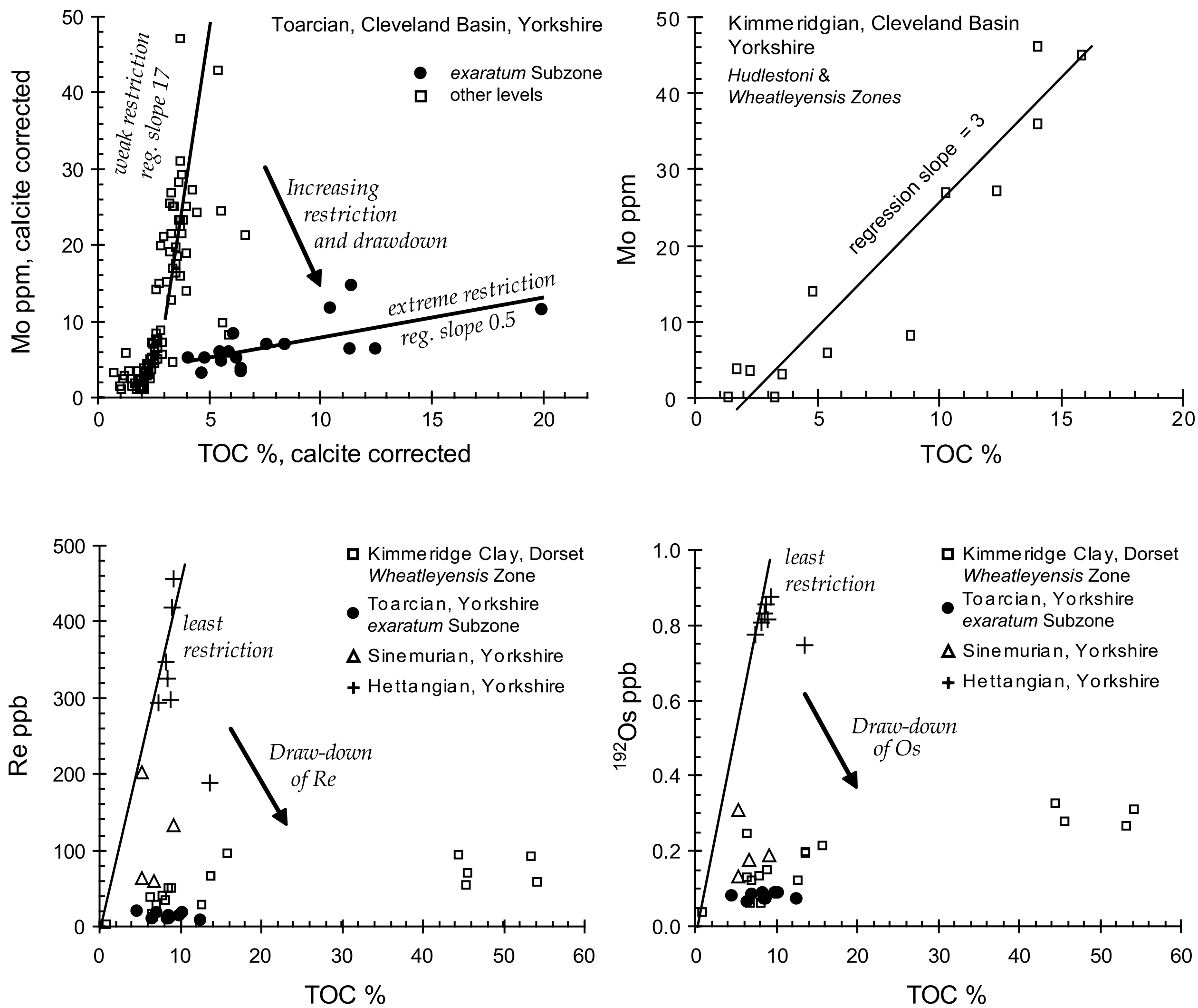

Figure 11. Crossplots of Mo versus TOC for this study and Re and ^{192}Os versus TOC for the data of *Cohen et al.* [1999] for organic-rich sediments of Toarcian, Hettangian, and Sinemurian age from coastal sections in Yorkshire and organic-rich sediments of Kimmeridgian age (*wheatleyensis* zone) from Dorset, United Kingdom. Data for the Kimmeridge Clay Formation for Mo and TOC are from *Tribovillard et al.* [1994, 2004b] and are for samples from the *hudlestoni* and *wheatleyensis* Zones of the Cleveland Basin, as no Mo data is given by *Cohen et al.* [1999]; a strict comparison of Mo with either Re or Os is therefore not possible. Drawdown of elements from a restricted water mass had exhausted the local element reservoir in the Toarcian and Sinemurian. The sedimentary content of Mo, Re, and Os was low compared to Hettangian organic-rich sediments from the same sequence and localities nearby, where restriction was less. Depletion of Re and Os in the Kimmeridge Clay seems extreme, and *rs*Mo/TOC is around 3, slightly lower than that in modern sediments of the Black Sea.

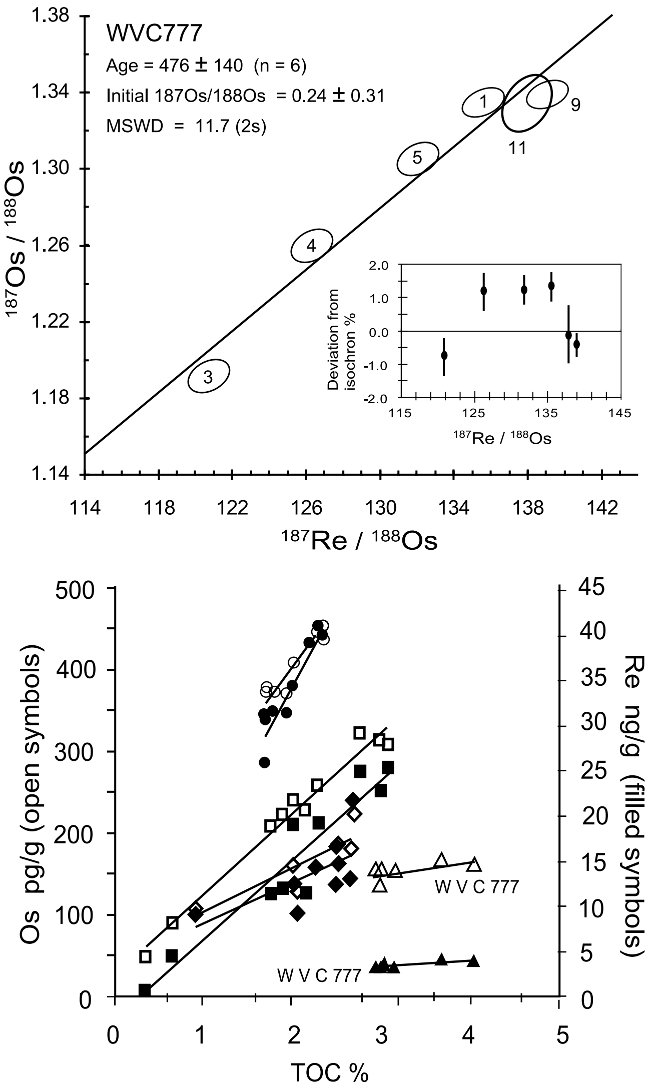

Figure 12. Relation of Re, Os, and TOC in samples across the Frasnian-Famennian boundary (Late Devonian), and Re-Os isochron for aberrant level WVC777, for the data from *Turgeon et al.* [2007]. Level WVC777 is the least enriched in Re or Os because of restriction and drawdown of these elements from an anoxic water mass in a restricted basin, which was therefore sensitized to changes in Os isotope composition through freshwater inputs. This level therefore provided the worst isochron. See text for fuller account.

linear, relationships between TOC and Re, Os, and Mo, might have been affected by water mass restriction, and that the best sediments to sample are those that are not the most organic rich.

11. An Eocene Equivalent of the Toarcian Sea?

[62] Previous workers have proposed that the Early Toarcian seas of northwestern Europe had a low-salinity surface layer [*Sælen et al.*, 1996, 1998, 2000; *Röhl et al.*, 2001; *Schmid-Röhl et al.*, 2002; *Frimmel et al.*, 2004; *Schwark and Frimmel*, 2004, and references therein]. Younger analogs of the restricted Early Toarcian sea might be the eastern Mediterranean, where sapropels formed in response to surface freshening and nutrient supply [*Rohling*, 1994], or the Arctic, high-latitude, Azolla Ocean of middle Eocene time. Examining the latter, the freshwater/brackish water fern *Azolla* flourished in the Arctic Ocean in a low-salinity surface layer that extended over an 800,000 year period, depositing sediments that reach up to 5% TOC [*Brinkhuis et al.*, 2006]. According to *Brinkhuis et al.* [2006, p. 607], the Arctic sediments show cyclic oscillations that “may reflect orbital forcing of the 100-ka eccentricity cycle, suggesting that the periodical freshening of the Arctic Ocean was astronomically modulated.” The abundance of *Azolla*, and its occurrence together with the remains of other brackish/marine organisms, suggested that the salinity of surface seawater in the *Azolla* Ocean was low as a result of high precipitation and restricted exchange with surrounding seas [*Brinkhuis et al.*, 2006]. The demonstration of freshening has relevance for similar suggestions applied to the Toarcian.

[63] The *Azolla* sediments show alternating laminations composed of dark, organic-rich, and lighter, siliceous, microlayers that are interpreted to reflect annual, seasonal, influences [*Brinkhuis et al.*, 2006]. Similar laminations occur in the Toarcian black shales of Yorkshire, United Kingdom, and were taken to be annual varves [*Hallam*, 1997]. They are reinterpreted by *Wignall et al.* [2005] as silt laminae event beds recording a much more aperiodic style of deposition than varves. Indeed he states that varves are not present. Laminations that are superficially similar to varves also occur in the time-equivalent Posidonia shale of Germany. They were interpreted by *Röhl et al.* [2001] specifically not to be varves but to represent events happening at intervals of several tens to hundreds of years.

12. Conclusions

[64] 1. The slopes of two Mo versus TOC regression lines for the Lower Toarcian sediments of the Cleveland Basin in Yorkshire, United Kingdom, define two periods of water mass restriction. In the upper half of the *semicelatum* Subzone (*tenuicostatum* Zone) and most of the *exaratum* Subzone (*falciferum* Zone), data define a regression line between Mo and TOC that has a slope (*rs*Mo/TOC) of 0.5, a value around ten times lower than in modern sediments from the Black Sea, where *rs*Mo/TOC is 4.5. The value of 0.5 shows that restriction was extreme. The frequency of deepwater renewal was around 10 times less than in the modern Black Sea and occurred at intervals of 5–40 ka. In the overlying strata of the *falciferum* Subzone the deepwater renewal frequency was 10–130 years on the basis of an *rs*Mo/TOC of 17, a value comparable to that for the Cariaco Trench and Framvaren Fjord of today. In the Cleveland Basin, open marine conditions were reestablished by mid-Toarcian times (lower *bifrons* Zone times).

[65] 2. The comparison of Mo/TOC profiles through Lower Toarcian sections in the Cleveland Basin, United

Kingdom, and in Germany and Switzerland, shows that some geographical variability existed in the degree of restriction of the Toarcian sea. Across Europe, the onset of restriction was diachronous.

[66] 3. The time of the most extreme restriction of the local water mass in Yorkshire coincided with the interval over which a negative excursion in $\delta^{13}C_{(org)}$ is recorded in the sediments. The isotopic anomaly, and deposition of Lower Toarcian black shales, reflect a local, or regional, response of a coastal seaway to restriction, rather than a response to a global catastrophe. The period of black shale deposition is therefore defined as a regional anoxic event (RAE). Our recognition of restriction provides support for the silled-basin (Küspert) model of black shale deposition in Early Toarcian times in northwestern Europe.

[67] 4. Drawdown of marine Mo, Os, and Re into sediments during the upper-*semicelatum* and *exaratum* Subzone times was almost complete. Drawdown sensitized the restricted water mass to isotopic changes driven by small inputs from riverine sources and drove large excursions in $^{187}Os/^{188}Os$ and $\delta^{98}Mo$ that were recorded in sediments. The use of $\delta^{98}Mo$ and initial $^{187}Os/^{188}Os$ as palaeoredox indicators is thus made more complex.

[68] 5. Drawdown of Os, in restricted anoxic basins may pose a problem for the application of the Re-Os geochronometer to black shales. Such dating should consider whether samples showing strong covariance between Re and TOC, and between Os and TOC, might have been affected by restriction, and so sensitized to natural change in background marine $^{187}Os/^{188}Os$ to a degree that might compromise the methods usefulness.

[69] **Acknowledgments.** We thank Ryan Wilson, Nick Bose, and Tony Osborn for assistance with the analysis for Mo and TS/TC/TOC and Robert Newton, Leeds University, for providing additional samples from the Yorkshire sections. Assistance with Mo analysis from Benoit Disch and Kim Jarvis, of the late NERC ICP-MS Facility, is gratefully acknowledged. We thank Antonietta Quigg (Texas A&M) for providing us with her unpublished Weiach trace element data; Hans-Jürgen Brumsack for Mo and TOC data for the Mögglingen and Hildesheim, Germany; Nicholas Tribovillard for Mo and TOC data for the Kimmeridge Clay; and Tim Lyons and an anonymous reviewer for making many constructive suggestions in review that led to improvements in the script.

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