Environmental conditions during the Toarcian Oceanic Anoxic Event (T-OAE) in the westernmost Tethys: influence of the regional context on a global phenomenon

FRANCISCO J. RODRÍGUEZ-TOVAR & MATIAS REOLID

A geochemical analysis has been conducted in the Fuente de la Vidriera section of the External Subbetic (Betic Cordillera, southern Spain) in order to interpret the incidence of the Toarcian Oceanic Anoxic Event (T-OAE) in the westernmost end of the Tethys. The obtained values of detrital, redox and palaeoproductivity proxies throughout the succession show minor fluctuations, but only punctual significant changes. Detrital input is nearly constant during the studied interval, except punctually in the lower part of *serpentinum* Zone, characterized by an increase in both fluvial and eolian detrital transport. Associated to this local higher fluvial and eolian activity, a comparatively higher concentration of organic matter is punctually registered, as revealed by the comparatively highest total organic carbon (TOC) value (0.99 wt.%). The remaining part of the section shows TOC values in the lower range of those registered in the Tethyan Toarcian sections (< 0.4 wt.%). The obtained ratios of redox-sensitive trace metals lead to the interpretation of oxic to dysoxic bottom-waters, with a singular sharp decrease in oxygenation corresponding to a short interval within the *serpentinum* Zone (sample FV-18) correlated to the T-OAE. The minor incidence of the T-OAE registered in this westernmost end of the Tethys, in which punctual dysoxic conditions are restricted only to a decimetre-scale interval reveals the importance of regional context and local oceanic-atmosphere dynamics on the local record of this phenomenon.
• Key words: T-OAE, geochemical proxies, palaeoxygenation, palaeoproductivity, Jurassic, Betic Cordillera.

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The Early Toarcian Oceanic Anoxic Event (T-OAE) is recognized as one of the most important environmental perturbations during the Mesozoic, with a dramatic impact on marine biota revealed by a significant mass extinction event (MEE) in benthic and pelagic groups (Hallam 1996, Wignall *et al*. 2005). The sedimentary record of the T-OAE is characterized by organic-rich sediments "black shales" associated with a distinctive negative excursion in the $\delta^{13}C$ recorded in organic matter, biomarkers, marine carbonates, and fossil wood from marine and continental sections (*e.g.* Jenkyns & Clayton 1997, Jenkyns *et al*. 2002, Cohen *et al*. 2004, Hesselbo *et al*. 2007, Suan *et al*. 2008, Hermoso *et al*. 2009a, Sabatino *et al*. 2009, Bodin *et al*. 2010, Gómez & Arias 2010, Littler *et al*. 2010). In this sense, is significant and widely debated the absence of this excursion in the $\delta^{13}C$ in the belemnite data (van de Schootbrugge *et al*. 2005, McArthur 2007, Metodiev *et al*. 2012).

The T-OAE has been extensively studied in the past three decades (from Jenkyns 1985, 1988 to recent). Still, questions regarding the mechanisms involved, the major environmental changes affecting biota, the global scale and the synchronism remain unresolved. There is no general consensus about the causes or triggering mechanisms of the T-OAE, including the massive enrichment of isotopically light carbon and its transfer between the different reservoirs (*e.g*., Hesselbo *et al*. 2000, Kemp *et al*. 2005), or the production of thermogenic methane during the concomitant intrusive eruption of the Karoo-Ferrar province (*e.g*., McElwain *et al*. 2005). Several environmental changes may have been involved in the mass extinction event, mainly affecting benthic organisms, such as generalized anoxia, the enhancement of greenhouse conditions and a warming trend, or the incidence of sea-level changes (*e.g*., Hallam 1986, 1987; Elmi 1996; McArthur *et al*. 2000;

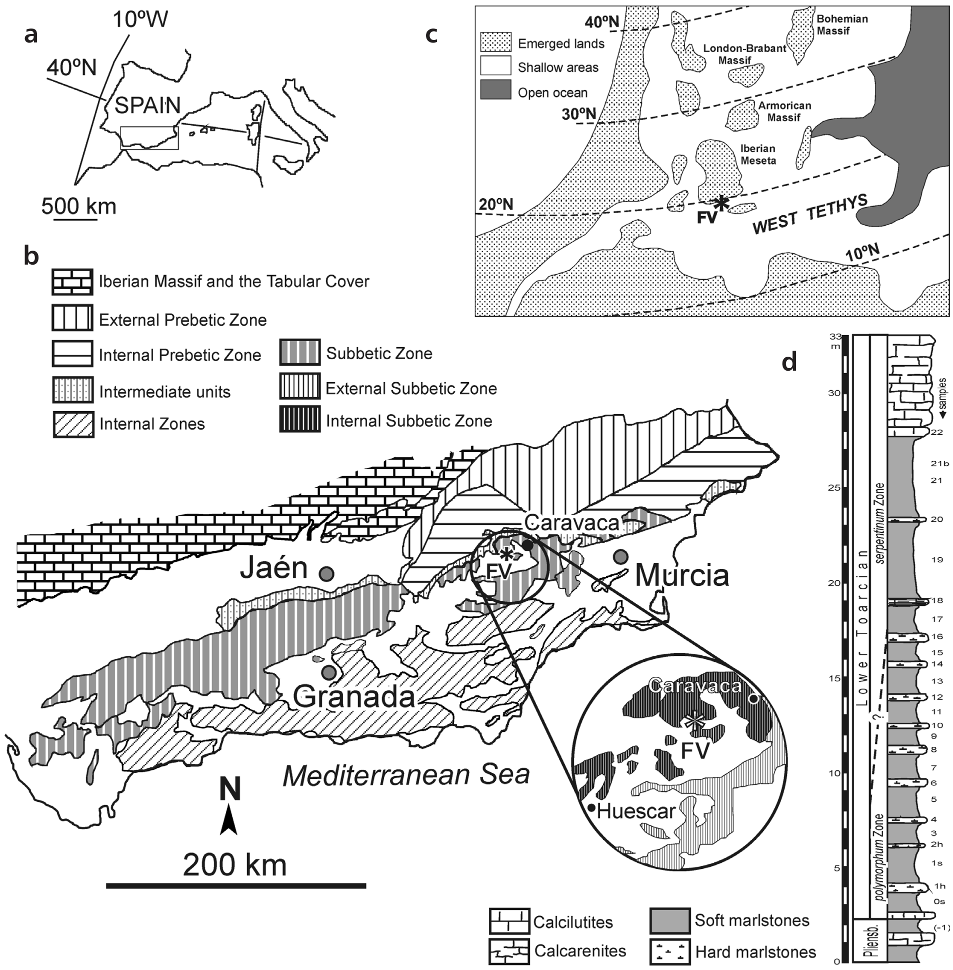

Figure 1. Geographical (a) and geological (b) location of the Fuente de la Vidriera (FV) section (start); palaeogeography (c) of the western Tethys in the Toarcian (modified after Bassoulet *et al.* 1993); and (d) synthetic column including studied samples.

Bailey *et al.* 2003; Ruban & Tyszka 2005; Wignall *et al.* 2005; Ghadeer & Macquaker 2011; Gómez & Goy 2011; Reolid *et al.* 2012a; Trabucho-Alexandre *et al.* 2012). Originally, the T-OAE was considered as a global phenomenon based on the apparently simultaneous deposition of organic-rich facies identified in many parts around world, associated to anoxic bottom waters (Jenkyns 1988). However, recent studies point to geographical variability and the incidence of local or regional scale processes (McArthur *et al.* 2008, Rodríguez-Tovar & Uchman 2010).

To improve our characterization of the T-OAE, one promising strategy is an integrative analysis, including data from biotic and abiotic components, especially in exceptional sections. This is the case of the Fuente de la Vidriera section (Betic Cordillera, southern Spain), which belongs to the westernmost Tethys and is affected by the singular ocean dynamics occurring at the Hispanic Corridor in the connection between the Western Tethys and the Proto-Atlantic seaway, at an approximate palaeolatitude of 20° N (Fig. 1; from fig. 6 in Jiménez *et al.* 1996). In this paper, an analysis of elemental geochemical proxies for the Fuente de la Vidriera section is presented, with the aim to improve characterization of the environmental effects of the T-OAE in this setting, and correlate new findings with previous interpretations based on the ichnological research (Rodríguez-Tovar & Uchman 2010).

Geological setting

The study was carried out at the Fuente de la Vidriera (FV) section, located on a valley slope (N 38° 03´ 19.8˝; E 02° 07´ 01.7˝; ± 9 m), 15 km west of the village of Barranda (Murcia Province), near Caravaca de la Cruz (Fig. 1). The study section pertains to the Upper Pliensbachian to uppermost Toarcian of the Zegrí Formation, and contains alternating marls and marly limestones in the lower part with nodular marly limestones in the upper part (J. Rey, unpublished PhD thesis, Univ. Granada, 1993, Rey & Delgado 2002). The FV section belongs to the eastern External Subbetic (Betic Cordillera, southern Spain). In the Betic Cordillera, the External Zones comprise the Prebetic and Subbetic, consisting of thick successions of Triassic to Miocene strata (García-Hernández *et al.* 1980, Vera 2004 and references therein). The Jurassic and Cretaceous deposits of the Prebetic are shallow marine, coastal plain, and continental. During the Toarcian the Subbetic was a pelagic distal setting, featuring two strings of swells with low subsidence (External and Internal Subbetic, respectively), located north and south of a more rapidly subsiding central trough called the Median Subbetic. Jurassic sedimentation in the External Subbetic is characterized by shallow shelf deposits of the lowermost Jurassic, overlain by hemipelagic facies of marls and marly limestones dating Pliensbachian-Aalenian, along with pelagic cherty limestones and nodular limestones of Middle-Late Jurassic age. In the Subbetic region overall, the External Subbetic represents swell areas produced by fragmentation of large carbonate platforms during the middle Early Jurassic (García-Hernández *et al.* 1989).

The studied Lower Toarcian section contains an approximately 30-m-thick succession of alternating soft and hard marlstones, from a calcilutite bed containing *Dactylioceras* (*Eodactylioceras*) *polymorphum* (Fucini) to a succession of limestone beds just below the *Hildoceras bifrons* Biozone of the Middle Toarcian. Biostratigraphic zonation within the Lower Toarcian of the FV section was mainly obtained based on stratigraphic correlation, due to the scarcity of index fossils (A.P. Jiménez, unpublished PhD thesis, Univ. Granada, 1986, Jiménez & Rivas 2007). Thus, at the FV section the *Dactylioceras polymorphum* (approx. correlated with the *Dactylioceras tenuicostatum*, or *Dactylioceras semicelatum* Biozone) and *Harpoceras serpentinum* (approx. correlated with the *Harpoceras serpentinus*, or *Harpoceras falciferum* Biozone) biozones could be distinguished, although their boundaries are imprecise (A.P. Jiménez, unpublished PhD thesis, Univ. Granada, 1986, Jiménez *et al.* 1996, see Rodríguez-Tovar & Uchman 2010, for a detailed review of the Lower Toarcian subdivisions and correlations).

Materials and methods

Bed-by-bed geochemical analysis was conducted in the alternating soft and hard marlstones with 30-m thickness. A total of 24 sampling levels were selected for a geochemical analysis and a preliminary mineralogical study. For a precise correlation of the samples here obtained with those from the previous trace fossil analysis (Rodríguez-Tovar & Uchman 2010) we have used the same numbering.

Mineral grains were analysed under stereoscopic microscope on sieved samples, the rinsing procedure involving a column of standard stainless steel sieves with mesh openings of 250, 125, and 65 μm, and a gentle jet of water from the top. Residues were oven-dried at 40 °C.

Elemental geochemistry analysis provides results for major (Al, K, Fe, Mg, Mn, P, Si, and Ti) and trace elements (Ba, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sr, U, V and Zr). Whole-rock analyses of major elements were carried out using X-ray fluorescence (XRF) in a Philips PW 1040/10 spectrometer. Trace elements were analysed using an inductively coupled plasma-mass spectrometer (ICP-MS Perkin Elmer Sciex-Elan 5000) at the *Centro de Instrumentación Científica* (CIC, Universidad de Granada). The instrumental error was ± 2% and ± 5% for elemental concentrations of 50 ppm and 5 ppm, respectively (Bea 1996).

Total organic carbon was analysed by leaching in the laboratories of SGS Canada Inc. (Ontario). Total carbon (C) contents were measured as mg and calculated as percentages of the sample weight. Precision and accuracy of the method are approximately 0.01% and 92%, respectively.

In order to compare trace-element proportions in samples with variable carbonate and clays contents, it is usual to normalize trace-element concentrations to aluminium content (Calvert & Pedersen 1993). Such normalization enabled us to avoid any lithological effect on trace or major element concentrations, assuming that Al content in sediments is contributed by aluminosilicates (*e.g.*, Calvert 1990). In the last years, diverse geochemical proxies have been applied to interpret palaeoenvironmental conditions, being specially recommended the use of an integrative multi-proxy approach to characterize depositional and ecological conditions. In our case study, geochemical proxies have been used to reconstruct the terrigenous input, and the palaeoproductivity and palaeoxygenation conditions, based on the differentiation of three main groups:

a) Together with the mineral composition of the studied succession, some element/Al ratios (Si/Al, K/Al, Rb/Al, Ti/Al, and Zr/Al), have been used as proxies for the reconstruction of detrital input, with the differentiation between fluvial contribution (K/Al and Rb/Al, Chester *et al.* 1977), and eolian transport (Zr/Al, Si/Al and Ti/Al, Pye 1987).

b) The palaeoproductivity group includes Ba/Al, Sr/Al, P/Ti, and Total Organic Carbon (TOC). The most extensively used geochemical proxy for palaeoproductivity reconstructions is Ba enrichment in marine sediments (*e.g.*, Dehairs *et al.* 1987, Bishop 1988, Dymond *et al.* 1992, Van Os *et al.* 1994, Francois *et al.* 1995, Paytan *et al.* 1996, Martínez-Ruiz *et al.* 2000, Turgeon & Brumsack 2006, Gallego-Torres *et al.* 2007, Reolid & Martínez-Ruiz 2012), but the Ba excess as a palaeoproductivity proxy must be applied with caution because the Ba concentrations can be significantly modified by secondary processes. Others geochemical proxies commonly used to interpret relative fluctuations in productivity are P/Ti ratio (Latimer & Filippelli 2001, Robertson & Filippelli 2008, Reolid & Martínez-Ruiz 2012, Reolid *et al.* 2012a, b) and Sr/Al ratio (Niebuhr 2005, Sun *et al.* 2008, Reolid *et al.* 2012a). The P/Ti ratio reflects excessive phosphorous delivery to the sea-bottom not supported by terrigenous components. For

Table 1. Analysed geochemical proxies (element/Al ratios) and TOC in the Fuente de la Vidriera section.

Sampling level	Detrital proxies					Redox proxies									
	Rb/Al	Zr/Al	Si/Al	K/Al	Ti/Al	V/Al	Pb/Al	Cu/Al	Ni/Al	Cr/Al	Co/Al	Mo/Al	U/Th	Fe/Al	Mn/Al
FV-21	12.488	14.725	2.852	0.349	0.073	13.459	2.348	4.649	6.673	12.466	2.133	0.153	0.210	0.611	0.015
FV-20	14.604	14.221	2.933	0.374	0.064	12.831	2.152	6.936	5.643	11.856	0.943	0.080	0.235	0.634	0.011
FV-19	14.880	13.643	2.922	0.371	0.064	12.504	1.587	4.708	5.476	11.622	1.452	0.049	0.225	0.594	0.009
FV-18	14.603	15.907	3.514	0.355	0.088	15.060	1.532	3.978	12.436	20.611	2.178	0.065	0.441	0.783	0.031
FV-17	14.676	13.393	2.932	0.370	0.063	13.027	1.933	4.787	6.237	11.904	1.489	0.062	0.232	0.611	0.010
FV-16	14.334	13.370	2.949	0.367	0.066	13.047	2.155	5.725	6.827	12.448	1.871	0.069	0.255	0.660	0.011
FV-15	14.052	13.407	2.798	0.392	0.063	13.556	1.798	5.517	6.040	11.324	2.324	0.066	0.238	0.528	0.006
FV-14	14.826	13.302	3.057	0.367	0.067	12.990	2.836	5.847	6.862	12.981	1.446	0.113	0.245	0.634	0.011
FV-13	14.524	13.189	2.966	0.388	0.063	12.407	1.436	6.751	5.067	10.528	1.848	0.044	0.213	0.568	0.007
FV-12	14.769	14.242	3.094	0.367	0.071	13.119	2.665	4.953	6.812	12.841	1.211	0.076	0.275	0.600	0.012
FV-11	14.066	13.143	2.935	0.403	0.063	12.011	1.958	4.348	4.793	10.105	1.039	0.047	0.222	0.525	0.006
FV-10	15.107	13.506	3.122	0.386	0.070	13.050	1.746	3.659	6.410	12.011	2.303	0.050	0.261	0.591	0.012
FV-9	15.225	13.014	2.929	0.409	0.063	13.349	1.584	6.647	5.204	11.531	1.259	0.058	0.200	0.576	0.006
FV-8	14.890	13.958	3.114	0.439	0.061	14.762	7.516	24.209	14.278	14.076	6.715	0.270	0.294	0.848	0.012
FV-7	15.345	13.936	3.104	0.373	0.063	13.761	2.375	14.124	8.469	14.222	2.018	0.080	0.284	0.630	0.014
FV-6	15.331	13.440	2.970	0.400	0.066	11.624	1.485	4.971	5.321	10.606	2.621	0.043	0.211	0.508	0.006
FV-5	14.987	13.921	2.948	0.396	0.062	13.092	1.794	4.940	5.969	12.122	1.593	0.044	0.221	0.554	0.008
FV-4	15.137	13.866	3.099	0.380	0.074	12.521	1.763	4.292	6.313	13.097	1.597	0.046	0.269	0.609	0.011
FV-3	15.459	15.702	3.162	0.411	0.069	13.777	1.650	8.072	5.826	11.932	2.020	0.040	0.210	0.566	0.007
FV-2h	14.933	13.899	3.151	0.380	0.065	12.835	2.626	4.174	7.640	12.756	2.943	0.070	0.280	0.719	0.012
FV-1s	14.514	15.255	3.051	0.400	0.064	11.890	2.072	4.027	5.302	10.618	1.949	0.051	0.227	0.537	0.006
FV-1h	15.399	15.572	3.133	0.402	0.064	12.767	1.866	4.394	6.312	12.453	1.935	0.051	0.240	0.574	0.010
FV-0s	16.415	16.804	3.260	0.490	0.069	12.818	1.943	5.083	5.696	11.274	2.324	0.049	0.199	0.576	0.006
FV-(-1)	14.385	14.638	3.241	0.380	0.064	13.777	1.793	8.537	7.276	13.072	1.144	0.067	0.234	0.605	0.005

this reason, an increase in the P/Ti ratio implies higher phosphorous sedimentation to the sea-bottom from biological processes (Latimer & Filippelli 2001, Flores *et al.* 2005, Sen *et al.* 2008). Of additional importance is the relationship of uranium with organic matter in the sediment; high values of U/Al ratio would be congruent with high values in other palaeoproductivity proxies (Nagao & Nakashima 1992, Baturin 2002).

Total Organic Carbon content has been used as an indirect palaeoproductivity proxy (*e.g.*, Calvert & Fontugne, 2001, Gupta & Kawahata, 2006, Plewa *et al.* 2006, Su *et al.* 2008), being specially informative when compared with the results obtained from the rest of selected palaeoproductivity proxies. However, enhanced TOC contents may result from low bottom-water ventilation and oxygen depletion, and are not necessarily related to high surface productivity. However, the TOC is generally proportional to surface-water productivity and constitutes a useful palaeoproductivity proxy (Tribovillard *et al.* 2006).

c) Diverse element/Al ratios have been extensively used as redox proxies to interpret palaeoxygenation conditions at time of sediment deposition (Wignall & Myers 1988; Nagao & Nakashima 1992; Calvert & Pedersen 1993; Jones & Manning 1994; Powell *et al.* 2003; Siebert *et al.* 2003; Jiménez-Espejo *et al.* 2007; Gallego-Torres *et al.* 2007, 2010; Yilmaz *et al.* 2010; Reolid *et al.* 2012a, b). We selected several proxies (Co/Al, Cu/Al, Cr/Al, V/Al, Ni/Al, Mo/Al, Pb/Al, Mn/Al, and U/Th), focusing on those, which tend to be less soluble under reducing conditions. Some redox-sensitive metals are delivered to the sediment in association with organic matter (Ni, Cu, and Zn). These redox-sensitive elements tend to co-precipitate with sulphides (mainly pyrite) and are not usually remobilized during diagenesis in the absence of post-depositional replacement of oxidizing agents (Tribovillard *et al.* 2006). In the case of the manganese, high concentrations indicate an oxidation front that penetrates the sediments (*e.g.*, Martínez-Ruiz *et al.* 2000, 2003).

Results

Obtained results from the analysed geochemical proxies and TOC are presented in Figs 2 to 6 and Table 1.

Table 1. continued.

Sampling level	Palaeoproductivity proxies				TOC (wt.%)
	U/Al	P/Ti	Sr/Al	Ba/Al	
FV-21	0.234	0.106	112.230	27.156	0.239
FV-20	0.308	0.124	157.118	32.326	0.246
FV-19	0.296	0.100	127.365	32.206	0.194
FV-18	0.552	0.194	370.607	38.225	0.987
FV-17	0.303	0.110	155.187	33.966	0.263
FV-16	0.324	0.124	175.997	32.832	0.282
FV-15	0.258	0.097	82.020	26.474	0.243
FV-14	0.323	0.132	190.476	42.873	0.346
FV-13	0.256	0.109	105.682	33.760	0.302
FV-12	0.356	0.133	262.931	38.453	0.304
FV-11	0.259	0.090	121.344	28.479	0.331
FV-10	0.308	0.125	223.690	34.525	0.247
FV-9	0.209	0.082	85.870	28.567	0.179
FV-8	0.317	0.117	288.583	38.897	0.271
FV-7	0.330	0.160	201.834	29.854	0.188
FV-6	0.255	0.068	114.114	30.248	0.237
FV-5	0.241	0.091	127.252	27.930	0.301
FV-4	0.334	0.131	162.752	32.184	0.261
FV-3	0.246	0.111	92.848	27.635	0.267
FV-2h	0.310	0.113	161.417	27.610	0.386
FV-1s	0.250	0.094	83.371	26.355	0.367
FV-1h	0.280	0.108	140.059	26.156	0.313
FV-0s	0.243	0.091	81.302	28.267	0.374
FV-(-1)	0.248	0.225	162.360	31.563	0.307

Detrital proxies. – Preliminary mineralogical analysis reveals a similar composition in any of the marlstone levels through the FV section, consisting essentially of calcite, quartz and clay minerals (illite, smectite and interstratified illite/smectite). The element/Al ratios used for the reconstruction of detrital input (Rb/Al, Si/Al, and K/Al) show only minor changes (Fig. 2, Table 1). Conversely, the Zr/Al and Ti/Al ratios temporarily manifest some increases. The Zr/Al ratios exhibit high values in the upper part of the section, around sample FV-18, though other significant increases are noted in the middle (samples FV-7 and FV-8; K/Al), and lower parts (samples FV-1 and FV-2; Zr/Al, Ti/Al).

Redox proxies. – The stratigraphic evolution of the analyzed ratios used as redox proxies shows some fluctuations along the succession (Figs 3 and 4, Table 1), the most significant ones being found in samples FV-8 and FV-18. In FV-8, relatively high values are registered for V/Al, Pb/Al, Cu/Al, Ni/Al, Co/Al, and Mo/Al but without changes in Mn/Al. In this level, analysis of grains from sieved samples revealed Cu and Fe sulphides including pyrite, chalcopyrite and covellite. In FV-18, high values are recognized for V/Al, Ni/Al, Cr/Al, Mn/Al, and U/Th, while other redox proxies do not increase (Pb/Al, Cu/Al, Co/Al, and Mo/Al). A maximum in Mn/Al, together with an increase in Fe/Al, are registered at this sample level (Fig. 4, Table 1). Analysis of grains from sieved samples reveals common goethite grains in sample FV-18; whereas in sample FV-19 pyrite is totally absent, and goethite grains are very common in the > 200 μm fraction.

Palaeoproductivity proxies. – Stratigraphic distribution of these proxies indicates peaks with relatively high values of U/Al, P/Ti, Sr/Al, and Ba/Al ratios, as well as a comparatively higher TOC (Figs 5, 6, Table 1). The Ba/Al ratio shows a slightly increasing trend, with a maximum value in FV-14 and two secondary peaks at FV-8 and FV-18, while U/Al, P/Ti, Sr/Al, and TOC clearly increase in FV-18 (Fig. 5, Table 1). In the case of the Sr/Al ratio, the trends seen for soft and hard marlstones levels differ, with values generally higher in hard marlstones than in soft marlstones (Fig. 6, Table 1). In both cases, maximum values are in FV-8 and FV-18. In the case of P/Ti, no significant differences exist between the highest values with respect to the background. Total organic carbon content manifests minor fluctuations throughout the section. Its values are lower than 0.4 wt.% (usually ranging between 0.18 wt.% in sample FV-9 and 0.39 wt.% in sample FV-2h), with the exception of sample FV-18 (Fig. 5, Table 1), which shows an increase in TOC, nearly 1% (0.99 wt.%).

Palaeoenvironmental changes and the T-OAE event

The selected Lower Jurassic section represent a pelagic-marine setting in the Hispanic Corridor in a passage between the Western Tethys and the Proto-Atlantic seaway (Aberhan 2001, Bailey *et al*. 2003), revealing of special interest to interpret the Early Toarcian Oceanic Anoxic Event at the westernmost end of the Tethys. The External Subbetic is characterized by the complex palaeogeography and relatively isolated from open oceanic influences during the Early Toarcian.

Jiménez *et al*. (1996) studied the stable isotopes and recorded the characteristic negative excursion on $\delta^{13}C$ values located in the *serpentinum* Zone. Trace fossil analysis was recently conducted in the FV section (Rodríguez-Tovar & Uchman 2010). A well-developed endobenthic multitiered community was interpreted based on the presence of a relatively abundant, diverse, and continuous trace-fossil assemblage in the section, composed by *Alcyonidiopsis*, *Chondrites*, *Nereites*, *Palaeophycus*, *Planolites*, *Teichichnus*, *Thalassinoides*, and *Trichichnus*, with only local lamination (FV-18). Oxic or slightly dysoxic bottom waters

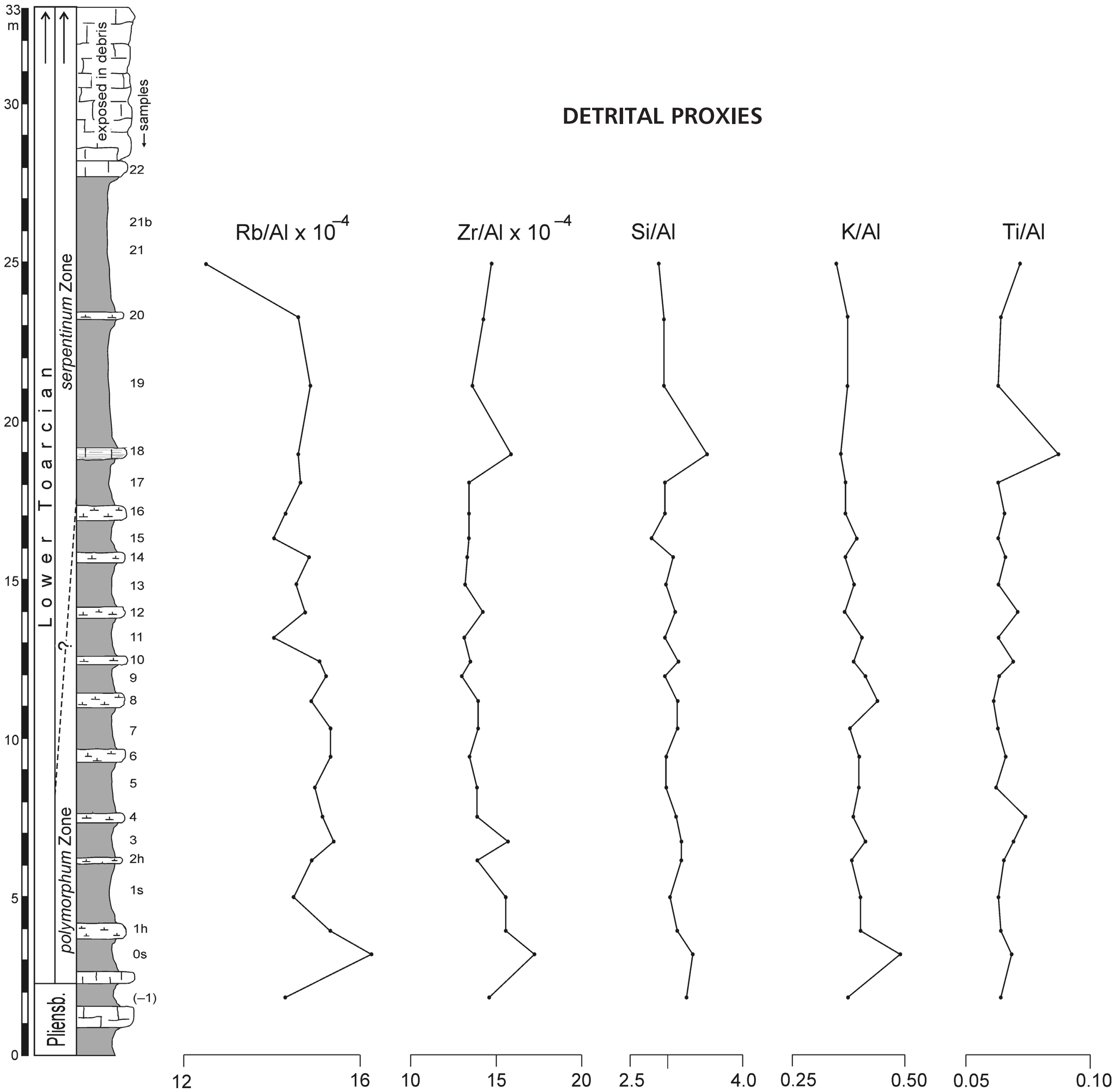

Figure 2. Stratigraphic distribution of detrital proxies throughout the Fuente de la Vidriera section.

were inferred, as well as the absence of anoxic conditions by these authors. Thus, in view of ichnological evidence, minor incidence of the T-OAE on the macro-endobenthic environment in this part of the westernmost Tethys was interpreted, and the worldwide anoxic phenomena related with the T-OAE, determining significant biotic changes, including global mass extinctions, was not recognized.

The geochemical data obtained and described here lead us to a more precise characterization of the palaeoenvironmental conditions in this area during the development of the T-OAE, and underline its particular incidence (Fig. 7).

Detrital input; eolian and fluvial contributions

Data obtained from the ratios of the detrital proxies Si/Al, K/Al, Rb/Al, Ti/Al, and Zr/Al through the Fuente de la Vidriera section allow the interpretation of the incidence of the detrital input, and the main source of detrital material, as eolian (Zr/Al, Si/Al and Ti/Al, Pye 1987) or fluvial (K/Al and Rb/Al, Chester *et al*. 1977) contribution.

According to the absence of significant variations in the K/Al, Rb/Al, and Si/Al ratios, a context of uniform detrital input could be inferred. This interpretation accords with the generalized homogeneous lithology through the studied

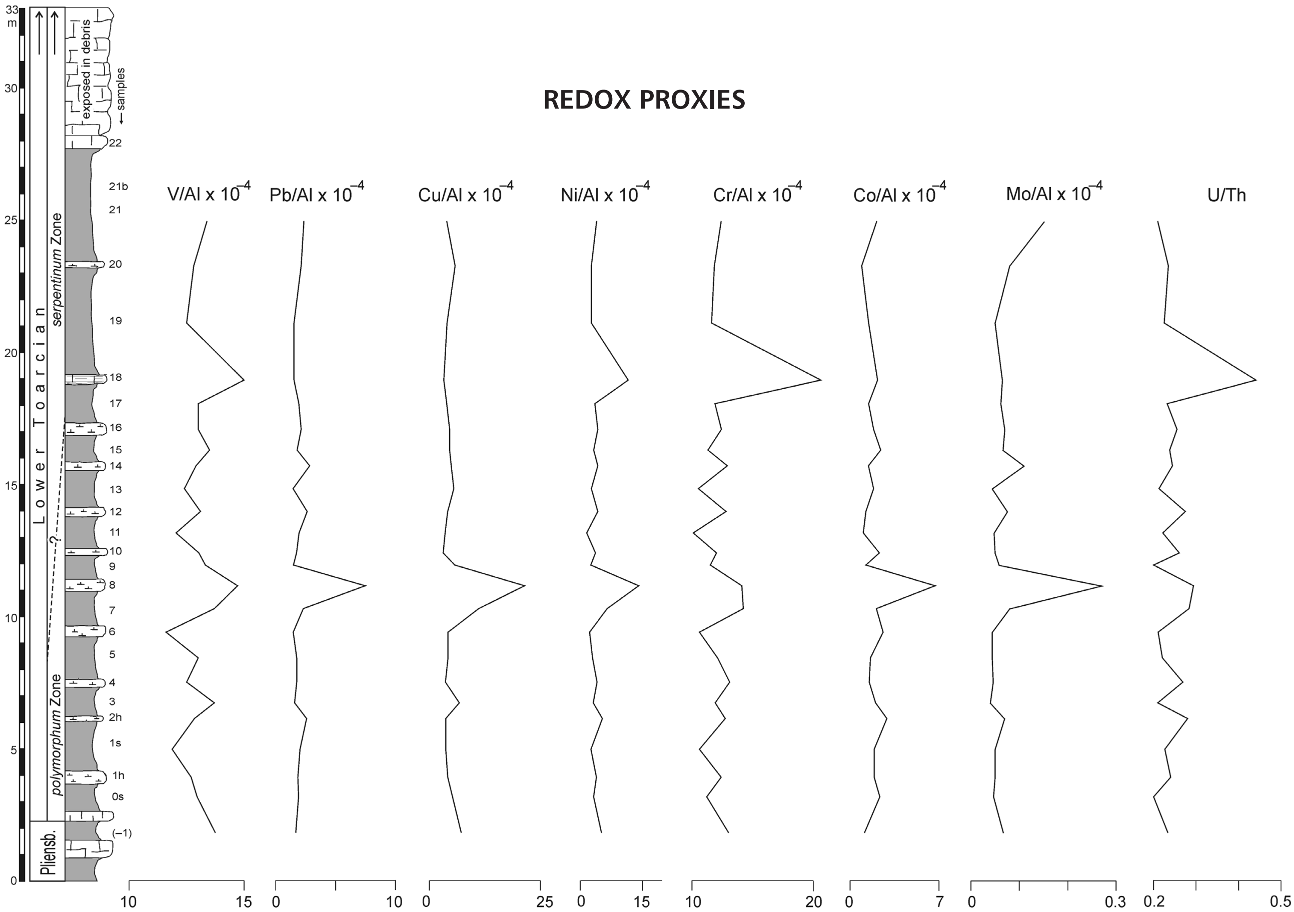

Figure 3. Stratigraphic distribution of geochemical proxies of elements which tend to be less soluble under reducing conditions, indicating redox conditions during deposition of the earliest Toarcian sediments of the Fuente de la Vidriera section.

succession, mainly consisting of the alternation of soft and hard marlstones, and the absence of significant sedimentary structures (except for bed FV-18 characterized by the presence of primary lamination). However, the punctual but simultaneous significant increases in the Ti/Al and Zr/Al ratios registered at the upper part of the section (FV-18) may be associated to short periods of intensification in the eolian supply of siliciclastic material to the basin. This could be understood as the response to climatic changes increasing the input from the source area.

Palaeoproductivity proxies and nutrient availability

Reconstruction of nutrient availability during the studied interval has been approached based on the integrative analysis of selected palaeoproductivity proxies as Ba/Al, Sr/Al, U/Al, P/Ti, and TOC. Although the Ba excess is extensively used as a marine palaeoproductivity proxy, the Ba concentrations can be modified by secondary processes (dissolution, remobilization, *etc*.). In our case study, the absences of any trend in the Ba/Al ratio from bottom to top or vice versa allow discard the alteration by diagenesis (see also Fig. 6). However, to be the most conservative as possible the Ba/Al results will be finally integrated with those from the rest of the palaeoproductivity proxies to approach nutrient availability.

Stratigraphic fluctuations on the selected geochemical palaeoproductivy proxies reveal a similar pattern, with a generalized increase from sample FV-8 to FV-14 (in Ba/Al) and FV-18 (in Sr/Al, U/Al, and P/Ti). This increase is not constant in the interval, but showing notable oscillations. This fluctuated increase suggests a local addition of nutrients in the middle part of the section with respect to the sediments below and above this interval, associated with intermittent processes.

The overall TOC values for the entire succession (except for sample FV-18), lower than 0.4 wt.%, would lie in the lower range of those registered in the Tethyan Toarcian sections. In northern European sections, TOC values typically range from 5 wt.% to 15 wt.% (Sælen *et al*. 2000, Röhl *et al*. 2001, Bucefalo-Palliani *et al*. 2002, Mailliot *et al*. 2006, McArthur *et al*. 2008); in southern European sites

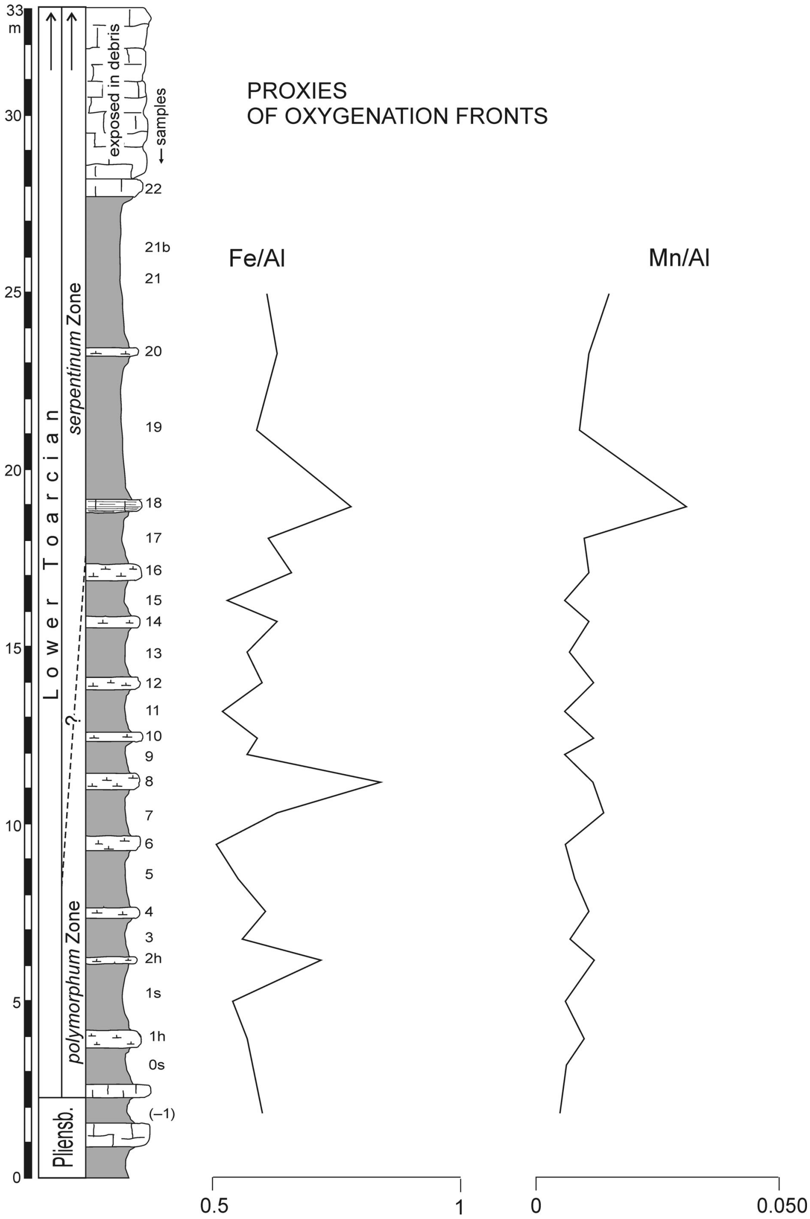

Figure 4. Stratigraphic distribution of iron (which precipitates as Fe^{3+} or Fe^{2+} depending on oxygenation) and manganese (less soluble under oxidizing conditions) represented as Fe/Al and Mn/Al ratios.

(Tethyan region) the usual values are some 0.5–3 wt.% TOC (Jenkyns 1985, 1988; Jenkyns *et al*. 2002; Hesselbo *et al*. 2007; Bodin *et al*. 2010; Tyszka *et al*. 2010; García-Joral *et al*. 2011), at any rate higher than those registered in the studied succession. As McArthur *et al*. (2008) affirm that black shales are exceptionally rich in organic matter (5 wt.% or more carbon content), the sediments studied here should not be considered true black shales. Yet most shales documented from southern European sites have less than 5 wt.% TOC and are nonetheless considered to constitute black shales. Recently, black shales showing relatively low total organic carbon concentrations (TOC general values lower than 2 wt.%, with data < 0.1 wt.% TOC), are described from several sections in Italy (Sabatino *et al*. 2009).

However, regardless of whether the studied succession corresponds to real black shales, what is clear is that the low overall TOC values here presented suggest lower concentrations of organic matter in the westernmost end of the Tethys than in other settings within the Tethyan Realm (see also Bodin *et al*. 2010, García-Joral *et al*. 2011, Reolid *et al*. 2012a). This may reflect geographical variations in the signals of the Toarcian Oceanic Anoxic Event, with a local diminution of the organic matter reaching the sea floor at the westernmost Tethys.

In this context of low overall TOC values, of special interest is the TOC maximum registered in sample FV-18, with a value (0.99 wt.%) over 3 times the mean of the rest of the section (Fig. 5). Such increase in TOC underlines punctual and abrupt concentrations in organic matter with

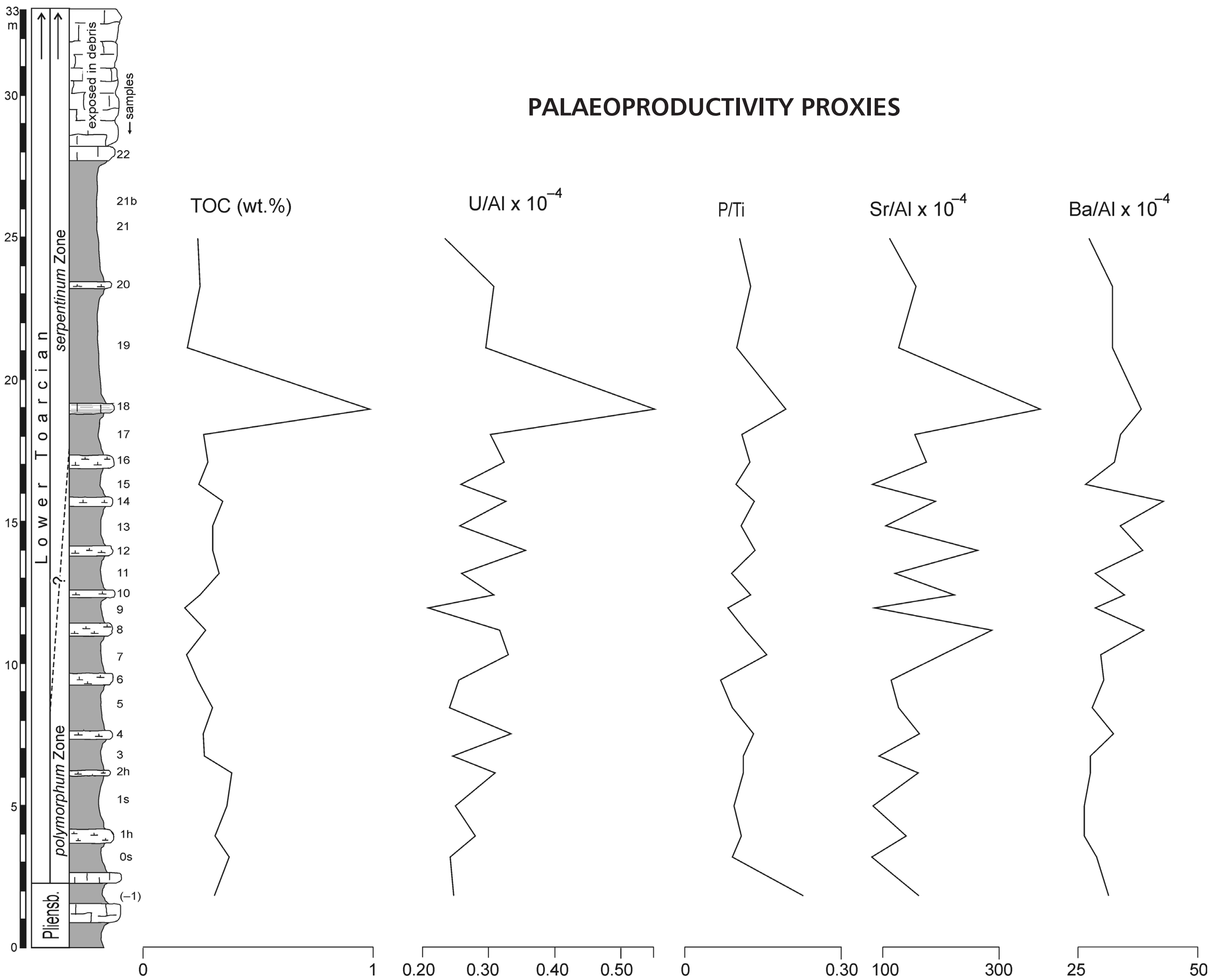

Figure 5. Stratigraphic distribution of palaeoproductivity proxies throughout the Fuente de la Vidriera section.

respect to the sediments just above and below the record, suggesting that a brief phenomenon occurred suddenly in the *serpentinum* Zone. Moreover, the Mn/Al ratio indicates that the oxidation front penetrates this potentially high productivity level, consuming part of the organic matter originally present in the sediment.

Palaeoxygenation conditions during the T-OAE

As presented in Figs 3 to 5 and in Table 1, the selected ratios of redox-sensitive trace elements (Co, Cu, Ni, Cr, V, Mo, Pb, U, and Th), used to interpret redox conditions in the water column and the sea-bottom, show similar patterns throughout the studied interval, with generalized low values and the absence of significant fluctuations or any observable trend. The generalized absence of high values in the ratios of the selected redox-sensitive trace metals through the studied interval suggests predominating oxic to slightly dysoxic bottom waters, discarding anoxic conditions. However, occasionally, punctual enrichments in redox sensitive elements are observed in levels FV-8 (V/Al, Pb/Al, Cu/Al, Ni/Al Cr/Al, Co/Al, and Mo/Al ratios) and FV-18 (V/Al, Ni/Al, Cr/Al, U/Th and U/Al ratios). These local concentrations would point to decreasing oxygen conditions. U-based proxies suggest that the deposition of the bed FV-18 was in comparatively lower oxygen conditions (Figs 3 and 5).

Especially relevant is the interpretation of the Fe/Al and Mn/Al ratios (Fig. 4). Fe can precipitate under either reducing (as sulphides) or oxidizing conditions (as oxy-hydroxides); whereas Mn precipitates as oxy-hydroxides at the sediment-water interface when oxygen is available, and constitutes a clear mark of the oxidation front (Thomson *et al*. 1995, 1999; Powell *et al*. 2003). The enrichment of Fe in FV-8 is congruent with the dysoxic conditions indicated by other redox proxies, given that the Mn/Al ratio is low. Analysis of grains from sieved samples allows us to ob-

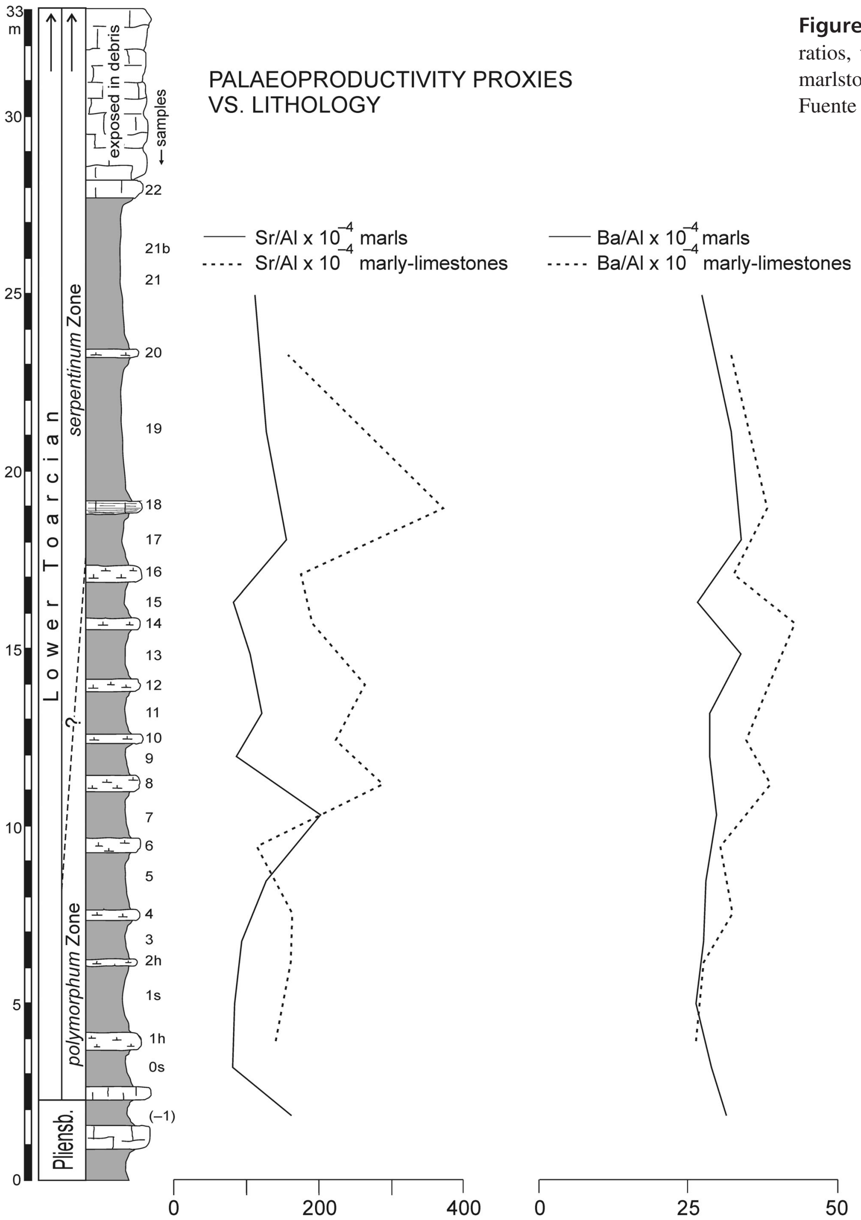

Figure 6. Stratigraphic distribution of Sr/Al and Ba/Al ratios, with differentiation of trends in soft and in hard marlstones from lowermost Toarcian deposits of the Fuente de la Vidriera section.

serve Cu and Fe sulphides in the form of pyrite, chalcopyrite and covellite, congruent with reducing conditions.

An abrupt return to oxic conditions below the sediment-water interface after sample FV-18 could be indicated by the high Mn/Al ratio, which may reflect the input of well-oxygenated waters to the basin or bottom water ventilation. The oxidation front could have removed the Co, Cu, Mo and Pb, which would explain the absence of maximum of these elements in the FV-18. The Fe/Al ratio in FV-18 is related to the presence of grains of goethite from sieved samples. The oxidation front may have consumed the organic matter originally present in the sediment (Thomson *et al.* 1995, 1999) meaning that TOC values would be reduced with respect to the initial sedimentary conditions.

Hermoso *et al.* (2009b) described Mn enrichment in black shales from Sancerre section (Paris Basin) section interpreted as Mn^{4+} and Mn^{3+} species reduced to Mn^{2+} under strongly anoxic conditions, and then incorporated into carbonate lattice. This is not the case in FV section due the presence of goethite and the absence of sulphides as pyrite.

Detrital input, nutrient supply and palaeoxygenation at the sea-floor and the incidence of the T-OAE

The bulk analysis of the obtained data, together with the integration of ichnological information (Rodríguez-Tovar & Uchman 2010), allows us to interpret the ecosedimentary

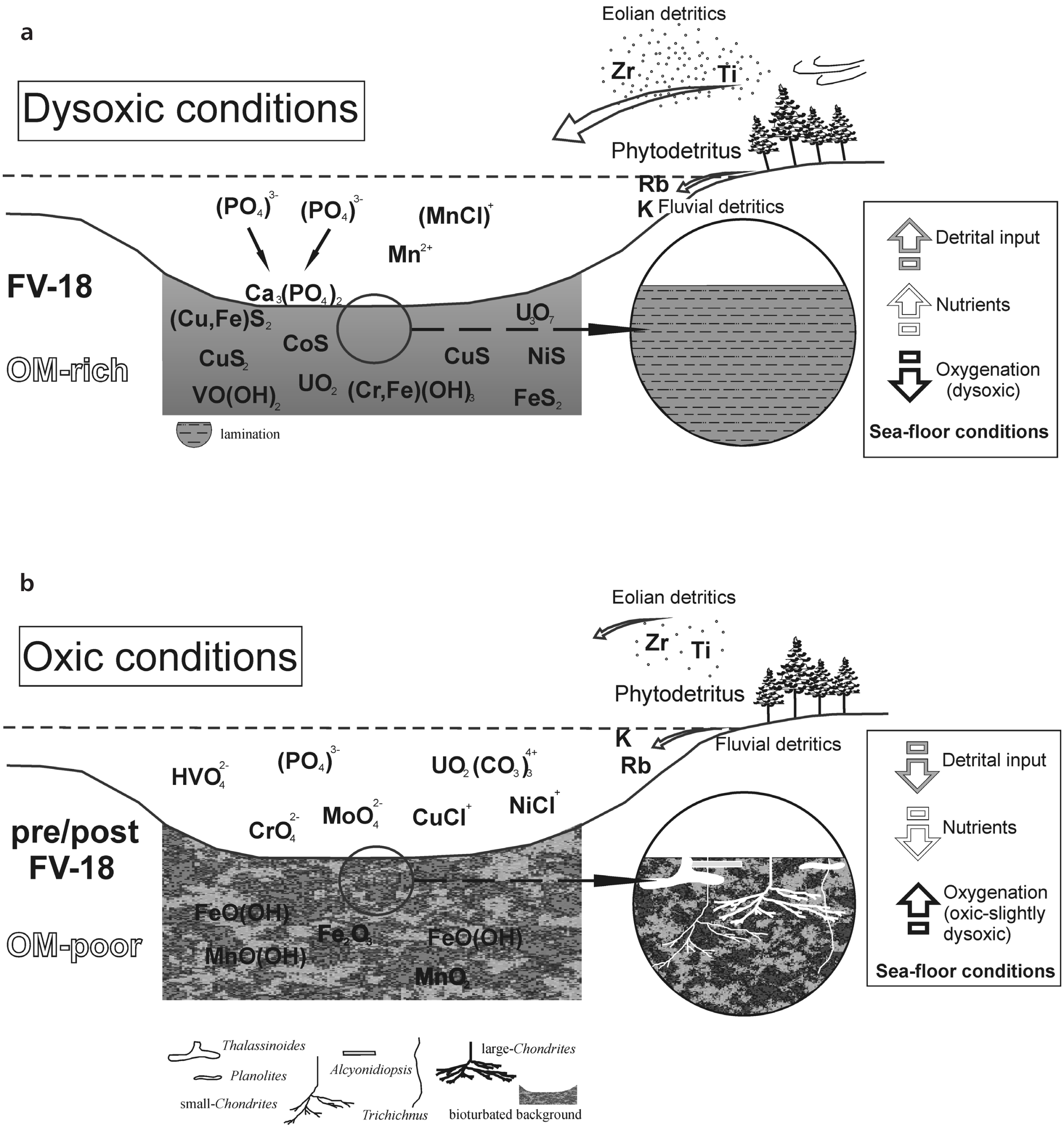

Figure 7. Palaeoenvironmental changes during deposition of FV-18 (a) and pre/post FV-18 (b) sediments, showing distribution of some trace elements studied. Note that in FV-18, under dysoxic conditions (a) trace elements sensitive to redox conditions are precipitated mainly as sulphides, the laminated sediment is organic matter-rich (OM-rich) and the detrital and phytodetritus input from emerged areas increase. In normal conditions at FV section (b), the main species in oxic seawater are in oxidation state and oxides and oxy-hydroxides of Mn and Fe precipitate in a bioturbated sediment, organic matter is scarce (OM-poor, probably oxidized) and detritals and phytodetritus are scarcer.

conditions in this westernmost end of the Tethys during the development of the T-OAE.

In a context of uniform detrital input determining a very homogeneous succession of soft and hard marlstones, minor increases in the detrital proxies reveal several short periods of accentuation in the transport of siliciclastic material to the basin. Among these, the most significant increase in fluvial and eolian detrital proxies is registered in the upper part of section FV-18. This finding can be related to a significant variation in the palaeo-depositional context, probably involving climatic changes. Associated with the higher fluvial and eolian activity, a comparatively higher concentration in organic matter is punctually registered, as derived from the comparatively higher TOC values of sample FV-18. In the rest of the succession, minor inputs of detrital material are registered in conditions of low concentration, without significant variations, in organic matter content. This generalized low concentration of organic matter content is associated to oxic or slightly dysoxic bottom-waters, sufficient to maintain a fairly abundant and moderately diverse endobenthic multitiered community (Rodríguez-Tovar & Uchman 2010), as is corroborated by the absence of high concentrations of the selected redox-sensitive trace metals.

The comparatively higher concentration of organic matter registered in sample FV-18 would be associated with a sharp decrease in oxygenation, as revealed by increasing values of redox proxies, the absence of bioturbation and the presence of lamination (Rodríguez-Tovar & Uchman 2010). In NW Europe, evidence to support marine anoxia is represented by millimetre-scale sedimentary lamination and the absence of bottom-dwelling fauna (see Hermoso *et al*. 2009). The highest concentrations of organic matter in the sediment associated with high values of certain element ratios support a link among TOC, palaeoxygenation conditions and the concentration of these elements. The highest values of TOC at FV-18 can be interpreted in the framework of a complex interaction of processes. Organic matter deposition was most likely related to: a) phytodetrital inputs from emerged areas correlated to increasing detrital proxies; b) an increase in marine surface productivity as indicated by high Sr/Al and P/Ti values; and c) oxygen depletion at the sea-bottom favouring the preservation of organic matter. The FV-8 level probably represents less accentuated oxygen depletion than in FV-18. Sample FV-18 corresponds to the lower part of the *serpentinum* Zone, and its geochemistry could prove useful for correlation with other sections offering the same trends in the geochemical proxies and better biostratigraphic resolution as happen in the Ratnek El Kahla section from Saharan Atlas of Algeria (Reolid *et al*. 2012a).

During the development of the T-OAE worldwide, in the westernmost end of the Tethys, local conditions would have assuaged the impact of this global phenomenon as reflected by the obtained geochemical data and the correlation with the ichnological information.

We cannot discard that the restricted oxygen conditions occurred in a phase of generalized transgression that involved water stratification. According to Hallam (1986, 1987) and Haq *et al*. (1987), among others, during the Early Toarcian a sea-level rise took place, causing maximum confinement of bottom waters of the deep sub-basins in the Western Tethys. The configuration of the Subbetic in troughs and swells, with an intricate physiography, resulted in different sub-basins, disfavouring bottom water circulation.

Conclusions

Geochemical analysis conducted in the Fuente de la Vidriera section (External Subbetic, Betic Cordillera, southern Spain) allow us to interpret the incidence of the Toarcian Oceanic Anoxic Event (T-OAE) in the westernmost end of the Tethys. Detrital, palaeoproductivity, and redox proxies reveal a significant change in the lower part of the *serpentinum* Zone (bed FV-18).

Simultaneous and significant increases in the detrital proxies Ti/Al and Zr/Al ratios registered throughout the section – and especially in FV-18 – could be related with locally significant variations in the ocean-atmosphere dynamics due to climatic or sea-level changes affecting both fluvial and eolian processes. Increases in palaeoproductivity proxies Ba/Al, Sr/Al, and P/Ti ratios, along with TOC values, mainly in sample FV-18, reveal the punctually higher addition of nutrients, and relatively high palaeoproductivity. This is followed by a generalized low concentration of organic matter content in the rest of the studied interval. According to the redox proxies, oxic to slightly dysoxic bottom waters prevail throughout the section, decreasing to dysoxic conditions in FV-18 as revealed by the enrichment in V/Al, Ni/Al, Cr/Al, U/Th and U/Al. The return to a normal oxygenation degree at sea-bottom was probably abrupt, as suggested by the high Mn/Al ratio.

In the westernmost end of the Tethys, the local configuration of the Subbetic features troughs and swells with an intricate physiography. This resulted in a series of sub-basins where the incidence of the T-OAE was less abrupt, and there is a lack of evidence of the global anoxia inferred in many other studied successions, here represented instead by a decimetre level with dysoxic conditions.

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