



The Valanginian $\delta^{13}\text{C}$ excursion may not be an expression of a global oceanic anoxic event

Stéphane Westermann^{a,*}, Karl B. Föllmi^a, Thierry Adatte^a, Virginie Matera^b, Johann Schnyder^c, Dominik Fleitmann^d, Nicolas Fiet^{e,f}, Izabela Ploch^g, Stéphanie Duchamp-Alphonse^e

^a Institute of Geology and Paleontology, University of Lausanne, Anthropôle, 1015 Lausanne, Switzerland

^b Institute of Geology, University of Neuchâtel, Emile Argand 11, CP 158, 2009 Neuchâtel, Switzerland

^c UPMC Univ. Paris 6, CNRS, UMR 7193, ISTEP, case 117, 4, pl. Jussieu, 75252 Paris Cedex 05, France

^d Institute of Geological Sciences, University of Bern, Baltzerstrasse 1-3, 3012 Bern, Switzerland

^e UMR 8148 – I.D.E.S., Bât. 504, University of Paris XI Orsay, 91405 Orsay Cedex, France

^f AREVA, 33 rue La Fayette, 75009 Paris, France

^g Polish Geological Institute, 4 Rakowiecka, 00-975 Warsaw, Poland

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ABSTRACT

Marine and terrestrial sediments of the Valanginian age display a distinct positive $\delta^{13}\text{C}$ excursion, which has recently been interpreted as the expression of an oceanic anoxic episode (OAE) of global importance. Here we evaluate the extent of anaerobic conditions in marine bottom waters and explore the mechanisms involved in changing carbon storage on a global scale during this time interval. We assess redox-sensitive trace-element distributions (RSTE; uranium, vanadium, cobalt, arsenic and molybdenum) and the quality and quantity of preserved organic matter (OM) in representative sections along a shelf-basin transect in the western Tethys, in the Polish Basin and on Shatsky Rise. OM-rich layers corresponding in time to the $\delta^{13}\text{C}$ shift are generally rare in the Tethyan sections and if present, the layers are not thicker than several centimetres and total organic carbon (TOC) contents do not surpass 1.68 wt.%. Palynological observations and geochemical properties of the preserved OM suggest a mixed marine and terrestrial origin and deposition in an oxic environment. In the Polish Basin, OM-rich layers show evidence for an important continental component. RSTE exhibit no major enrichments during the $\delta^{13}\text{C}$ excursion in all studied Tethyan sections. RSTE enrichments are, however, observed in the pre- $\delta^{13}\text{C}$ excursion OM-rich “Barrande” levels of the Vocontian Trough. In addition, all Tethyan sections record higher Mn contents during the $\delta^{13}\text{C}$ shift, indicating rather well-oxygenated bottom waters in the western Tethys and the presence of anoxic basins elsewhere, such as the restricted basins of the North Atlantic and Weddell Sea. We propose that the Valanginian $\delta^{13}\text{C}$ shift is the consequence of a combination of increased OM storage in marginal seas and on continents (as a sink of ^{12}C -enriched organic carbon), coupled with the demise of shallow-water carbonate platforms (diminishing the storage capacity of ^{13}C -enriched carbonate carbon). As such the Valanginian provides a more faithful natural analogue to present-day environmental change than most other Mesozoic OAEs, which are characterized by the development of ocean-wide dysaerobic to anaerobic conditions.

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1. Introduction

Global oceanic anoxic events (OAEs) represent exceptional episodes in Earth's history, which are marked by widespread dysoxic to anoxic conditions in the world oceans. These events are characterized by extensive organic carbon deposition in marine sediments and associated perturbations in the global carbon cycle. The Valanginian stage is considered to include the oldest Cretaceous OAE (“Weissert” anoxic event; Erba et al., 2004) and effectively, it

witnessed a pronounced excursion in marine carbonate- and marine and terrestrial organic carbon-isotope records with amplitudes of 1.5‰ and 4–5‰, respectively (Lini et al., 1992; Föllmi et al., 1994; Weissert et al., 1998; Hennig, 2003; Erba et al., 2004; Gröcke et al., 2005). However, in contrast to other Cretaceous OAEs, such as the Early Aptian OAE1a and the end-Cenomanian OAE2 (Schlanger and Jenkyns, 1976; Jenkyns, 1980; Jenkyns et al., 1994; Leckie et al., 2002; Berseozio et al., 2002; Erba, 2004; Kuypers et al., 2004; Mort et al., 2007), marine sediments deposited during the Valanginian carbon-isotope event lack the widespread occurrence of well-developed organic carbon rich levels (van de Schootbrugge et al., 2003; Reboulet et al., 2003; Gröcke et al., 2005), and the presence of centimetric organic-rich deposits is limited to a few localities (Erba et al., 2004).

* Corresponding author.

E-mail address: stephane.westermann@unil.ch (S. Westermann).

Table 1
Characteristics of the studied sections.

Section	Localisation	Paleogeography	Paleoenvironment	Lithology	Age	Numbers of samples ¹	Ref ²
Capriolo	Northern Italy (45°38'40" N; 09°57'26" E)	Lombardian basin	Open ocean, pelagic setting	Micritic limestone, some chert and marl	Valanginian (CM 14 to CM 10n)	88, (22)	1, 2, 3
Breggia	Southern Switzerland (45°52'43" N; 09°01'53" E)	Lombardian basin	Open ocean, pelagic setting	Micritic limestone with chert	Valanginian (CM 11n to CM 10n)	60, (10)	4, 5
Angles	SE France (43°58' N; 6°37' E)	Vocontian Trough	Epicontinental sea, hemipelagic setting	Marl-limestone succession	Valanginian (Pertransiens to Furculata zone)	(10)	6
Vergol	SE France (44°13' N; 5°32' E)	Vocontian Trough	Epicontinental sea, hemipelagic setting	Marl-limestone succession	Valanginian (Campylotoxus zone)	20, (20)	7
Malleval	E France (45°08'55" N; 05°27'13" E)	Northern Tethyan shelf	Outer shelf	Limestone	Valanginian (Campylotoxus to Verrucosum zone)	80	8
Alvier	E Switzerland (47°06'46" N; 09°24'56" E)	Northern Tethyan shelf	Outer shelf	Limestone and marly limestone	Valanginian	85	9, 10
Wawal	Central Poland (51°30'00" N; 20°04'21" E)	Poland basin	Shallow epicontinental sea environment	Silty clay with phosphate nodules	Valanginian (Verrucosum zone)	(7)	11
Hole 6814/04-U02	Ribban Basin (68°09'45" N; 14°09'47" E)	Norwegian–Greenland Seaway	Shallow seaway	Calcareous siltstone	Valanginian	(2)*	12, 13
Hole 6307/07-U02	Hitra Basin (63°27'54" N; 07°14'44" E)	Norwegian–Greenland Seaway	Shallow seaway	Red and grey marl	Valanginian	(2)*	12, 13
Poykin	Siberia (60°45' N; 71°22' E)	Western Siberian basin	Hemipelagic setting	Clayey mudstone and sandstone	Valanginian	(2)*	14, 15
Leg 198, site 1213B	Shatsky Rise (Pacific Ocean, 31°34.64' N; 157°17.86' W)	Pacific	Open marine pelagic environment (> 1000 m)	Micritic limestone with chert	Valanginian	10, (10)	16
Leg 93, site 603	Hatteras Rise (35°29.71' N; 70°01.71' W)	North Atlantic	Pelagic setting	Micritic limestone	Valanginian	(5)*	17
Leg 44, site 391C	Blake–Bahama Basin (28°13.61' N; 75°37.00' W)	North Atlantic	Pelagic setting	Calcareous claystone, nannofossil chalk	Valanginian	(2)*	18
Leg 76, site 534A	Blake–Bahama Basin (28°20.6' N; 75°22.9' W)	North Atlantic	Pelagic setting	Bioturbated nannofossil-radiolarian limestone	Valanginian	(8)*	18
Leg 77, site 535	Gulf of Mexico (23°42.48' N; 84°30.97' W)	North Atlantic	Pelagic setting	Limestone and marly limestone	Valanginian	(12)*	19
Leg 101, site 638B	Galician Margin (42°09.2' N; 12°11.8' W)	North Atlantic	Pelagic setting	Sandstone and claystone	Late Valanginian	(2)*	20
Leg 113, site 692B	Weddell Sea (70°43.43' S; 13°49.19' W)	Southern Ocean	Open ocean, pelagic setting	Clayey mudstone	Valanginian/Hauterivian	(29)*	21

¹Number of samples analysed by ICP-MS; the numbers of sample analyses for organic matter determination are indicated in parentheses; numbers with * correspond to published data.

²References: 1 = Lini et al., 1992, 2 = Channel et al., 1987, 3 = Channel and Erba, 1992, 4 = Bersezio et al., 2002, 5 = Channel et al., 1993, 6 = Duchamp-Alphonse, 2006, 7 = Reboulet et al., 2003, 8 = Blanc, 1996, 9 = Briegel, 1972, 10 = Föllmi et al., 1994, 11 = Lesniak et al., 2003, 12 = Langrock et al., 2003, 13 = Mutterlose et al., 2003, 14 = Peters et al., 1993, 15 = Vyssotski, et al., 2006, 16 = Bralower et al., 2002, 17 = van Hinte et al., 1987, 18 = Katz, 1983, 19 = Herbin et al., 1983, 20 = Stein and Rullkötter, 1988, 21 = O'Connell, 1990.

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