



The mid-Valanginian Weissert Event as recorded by calcareous nanoplankton in the Vocontian Basin



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ABSTRACT

The mid-Valanginian Weissert Event represents one of the most significant paleoceanographic events of the Early Cretaceous and is characterized by a major perturbation of the carbon cycle testified by a positive carbon isotope shift, a crisis of both neritic and pelagic carbonate producers, and climatic fluctuations. Here we propose a paleoreconstruction of paleoenvironmental changes that occurred in the reference Vergol and La Charce sections (Vocontian Basin, SE France) during the Weissert Event based on the analysis of calcareous nanofossil absolute abundance and assemblages. These latter are compared to newly acquired and already published sedimentological and organic geochemical analyses. Our approach is novel for the time interval considered. Indeed, Principal Component Analysis was applied for the first time to the entire nanofossil assemblage to reconstruct environmental conditions, instead of using paleoecological preferences of single species. The comparison of calcareous nanofossils and biomarker analyses indicates that a phase of severe sea–water stratification occurred prior to the carbon positive excursion of the Weissert Event in the Vocontian Basin. This was followed by a raise in fertility of surface waters, as attested by increased nanofossil abundances, in particular, of meso–eutrophic taxa, and biomarkers likely produced by dinoflagellates. This increase in fertility was likely triggered by a humid climate and enhanced continental input of clays and nutrients to surface oceanic waters. Calcareous nanofossils also proved to react to sea-level changes that occurred in the Valanginian, as inferred by previous works. Species likely inhabiting proximal areas were recorded in higher proportions during a major sea-level drop in the Peregrinus Ammonite Zone, Late Valanginian. The results of this study also permit to revise previously proposed paleoecological affinities of some nanofossil species. We suggest that *Watznaueria barnesia*, one of the most-widely used species in the literature, should be used cautiously because of its high plasticity with respect to environmental conditions. Also, nannoconids that are usually regrouped in papers with paleoceanographic purposes should be analyzed separately because they show distinct species-specific ecological preferences.

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1. Introduction

The Valanginian (139.4–133.9 Ma; Gradstein et al., 2012) records the earliest major perturbation of the global carbon cycle of the Cretaceous System: the mid-Valanginian Weissert Event (Erba et al., 2004) reflected by $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ positive excursions. The major positive carbon isotope shift of the Valanginian occurred after a long-lasting period of relative quiescence during the Late Jurassic–earliest Cretaceous (Erba et al., 2004; Föllmi et al., 2006). The Cretaceous shifts in $\delta^{13}\text{C}$ are commonly associated with an enhanced deposition of organic matter in marine sediments, possibly linked to the development of oceanic dysoxic or anoxic conditions. However, the mid-Valanginian Weissert Event appears to be different from the other Cretaceous $\delta^{13}\text{C}$ perturbations because significant organic matter-rich deposits did not occur in

the oceanic realm, and no clear evidence of anoxia is recorded (Westermann et al., 2010; Kujau et al., 2012). The positive shift in $\delta^{13}\text{C}$ during the Valanginian is possibly linked to the deposition of organic matter as coals in various continental areas (Budyko et al., 1987; Ziegler et al., 1987; McCabe and Totman Parrish, 1992; Rees McAllister et al., 2004; Westermann et al., 2010), although the age of these deposits is controversial. These deposits were favored by humid climate conditions (Frakes and Francis, 1988; Frakes et al., 1992; Price et al., 1998; Fesneau et al., 2009) starting a few thousands years before the carbon isotope shift (Gréselle et al., 2011; Kujau et al., 2012). Such conditions occurred in a period of low sea level probably triggering subaerial exposure of large epicontinental areas (Gréselle and Pittet, 2010) where vegetation could develop. Humid conditions could have thus favored ^{12}C sequestration by plants, and organic matter storage in continental environments (Westermann et al., 2010; Kujau et al., 2012). In addition, higher trophic levels in shallow seas favored biotic assemblages producing less carbonate than tropical communities (Funk

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et al., 1993; Föllmi et al., 1994; Gréselle and Pittet, 2010; Bonin et al., 2012), thus implying a decrease in the storage capacity of ^{13}C -enriched carbonate carbon on platforms (Föllmi et al., 2006; Westermann et al., 2010). The positive shift in $\delta^{13}\text{C}$ of the Valanginian occurred simultaneously to a cooling of marine waters (Podlaha et al., 1998; Pucéat et al., 2003), with the highest $\delta^{13}\text{C}$ values reached when the temperature was the lowest (McArthur et al., 2007; Gréselle et al., 2011; Barbarin et al., 2012). These conditions likely also played a role in the observed changes of carbonate producing biota in shallow water environments (Gréselle et al., 2011; Bonin et al., 2012).

Climate changes throughout the Valanginian and the development of more humid conditions have probably impacted weathering intensity on lands and enhanced the delivery of nutrients to surface oceanic waters (Erba et al., 2004; Duchamp-Alphonse et al., 2007, 2011; Gréselle et al., 2011; Barbarin et al., 2012). Since diatoms did not diversify significantly until the Late Cretaceous (Round et al., 1990), calcareous nannoplankton and dinoflagellates were among the main primary producers in the oceans during the studied time interval. Fluctuations of trophic conditions in surface waters deeply affected the calcareous nannoplankton community. Changes in nannoplankton assemblages can thus be used as a proxy to reconstruct paleoenvironmental conditions in marine surface waters (Williams and Bralower, 1995; Melinte and Mutterlose, 2001; Bersezio et al., 2002; Reboulet et al., 2003; Erba and Tremolada, 2004; Erba et al., 2004; Kessels et al., 2006; Duchamp-Alphonse et al., 2007; Bornemann and Mutterlose, 2008).

The paleoecology of a few selected species of calcareous nannofossils of the Early Cretaceous is relatively well assessed, and fluctuations in relative abundance of these species served as indicators of paleoceanographic conditions (Williams and Bralower, 1995; Melinte and Mutterlose, 2001; Bersezio et al., 2002; Reboulet et al., 2003; Erba and Tremolada, 2004; Erba et al., 2004; Duchamp-Alphonse et al., 2007; Bornemann and Mutterlose, 2008). However, entire calcareous nannofossil assemblages have been rarely considered in studies of Early Cretaceous (Mutterlose, 1996; Herrle et al., 2003; Watkins et al., 2005; Browning and Watkins, 2008). In the present study, changes in the entire nannofossil assemblage preserved in sediments from the Vocontian Basin were investigated. Stratigraphical variations in nannofossil assemblages combined with absolute nannofossil abundances and fluxes, clay accumulation rates and $\delta^{13}\text{C}_{\text{carb}}$ data available for the studied sections were used to infer changes in productivity in marine surface waters during the mid-Valanginian Weissert Event and to characterize the impact of climate changes on primary paleoproductivity in the Vocontian Basin. The analysis of lipid biomarkers (namely, sterane/hopane and pristane/phytane ratios) in selected samples together with already available data of organic biomarkers helped to support changes in primary productivity and redox conditions at this site.

2. Geological setting

The Vocontian Basin was a relatively small (about 150 km in width; Cotillon et al., 1980), eastward gulf located along the NW margin of Tethys in the Jurassic and Cretaceous. The basin was bounded to the West by the Paleozoic “Massif Central” and it was surrounded by carbonate platforms where carbonate mud was produced and exported offshore (Reboulet et al., 2003; Gréselle and Pittet, 2010) (Fig. 1A). The Vocontian Basin has been considered as analogous of the present European margin of the Atlantic Ocean, composed of a series of tilted blocks deepening eastwards to the deeper Tethyan Ocean (Lemoine, 1984, 1985). Ferry (1990) suggested that the evolution of the area was linked to an aborted rift basin. In this view, the Vocontian Basin may be considered as a sort of pull-apart basin. The basin probably attained its maximum bathymetry (~500–800 m) in the Early Cretaceous (Hauterivian–Barremian; Wilpshaar et al., 1997; Mattioli et al., 2008).

The studied successions of Vergol and La Charce were located in the central part of the Vocontian Basin (Fig. 1B), and are well-dated by ammonite and calcareous nannofossil biostratigraphy (Reboulet et al., 1992, 2003; Reboulet, 1996; Reboulet and Atrops, 1999; Gardin, 2008; Barbarin et al., 2012). These two successions can be correlated to each other, but also to the well-studied parastratotypic section of Angles located ca. 100 km south of the analyzed localities (Gréselle et al., 2011). In order to obtain a continuous record of the Valanginian interval and to avoid local sedimentary perturbations such as slumps, the two sections were combined in a composite section.

The lower Valanginian is characterized by carbonate-rich marl-limestone alternations. A decrease of the carbonate content is observed in the Fuhri horizon of the Biassalense ammonite Subzone (AS) (Fig. 1C). This interval is also characterized by the occurrence of four centimeter-thick levels enriched in organic matter, the Barrande layers (Reboulet et al., 2003). These levels, although relatively thin, are recorded in several sections of the Vocontian Basin and can be considered as stratigraphical marker beds (Reboulet et al., 2003). The lower–upper Valanginian boundary is identified as the limit between the Campylotoxus and Verrucosum ammonite Zones (AZ), and lays ca. 4 m above the NK3A/NK3B nannofossil subzones. The clay-rich upper Valanginian interval is interrupted by a 10 m thick carbonate-rich bundle, the “Faisceau Médian”, which is present throughout the Vocontian Basin (Cotillon et al., 1980). Sampling of the lower part of the succession is in Vergol, starting from the Nicklesi AS, the logging and sampling were effectuated in the La Charce succession (Fig. 1C).

3. Material and methods

Samples for calcareous nannofossil analysis were taken in marl-limestone alternations starting from the base of the lower Valanginian Campylotoxus AZ up to the lowermost levels of the lower Hauterivian Radiatus AZ. Sample spacing was irregular. Contiguous limestone beds and marly interbeds were sampled at a low frequency (each couple of samples taken every meter to 10 m spaced) all along the composite section (Fig. 1C), but two intervals were sampled with a higher resolution (1 sample every 5 cm), namely: 1) the transition between the carbonate-rich and the carbonate-poor marl-limestone alternations (Campylotoxus and Biassalense ASs; ~15 m), and 2) the “Faisceau Médian” in the Peregrinus AS (~10 m).

A total of 174 microscope slides were prepared according to the random-settling technique (Beaufort, 1991; Williams and Bralower, 1995; Geisen et al., 1999), slightly modified as described in Olivier et al. (2004). This technique allows absolute quantification of nannofossils per gram of rock. Briefly, a homogeneous suspension is made with ~20 mg of dried rock-powder and water. The suspension is let in a settling device during 24 h. After decantation of the powder on a glass slide, water is very slowly evacuated. Once dried, slides are mounted on microscope slides using Rhodopass. Slides were observed under a ZEISS AXIOSKOP 40 polarizing light microscope at a magnification of 1000×. On average, 320 nannofossils per sample (from 200 up to 516 specimens depending on the richness of the sample), both coccoliths and nannoliths, were counted over a variable surface area (0.001 to 0.023 cm²) according to the richness of nannofossils in the slide. In one single sample, only 123 specimens could be counted, due to the paucity of nannofossils. After counting, a larger surface of the slide was analyzed in order to retrieve very rare species and have a correct estimation of species richness. A total of 110 different taxa were taxonomically determined. Three preservation classes (relatively poor, moderate and good) were recognized on the basis of etching and overgrowth of the specimens, as established by Roth (1981).

Principal Component Analysis (PCA) was used to treat and interpret nannofossil assemblages. PCA allows interpreting complex data sets and reducing a large data matrix composed of several variables to a small number of factors representing the main modes of variations (Beaufort and Heussner, 2001). In order to avoid the closed-sum

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