



Organic-geochemical characterization of sedimentary organic matter deposited during the Valanginian carbon isotope excursion (Vocontian Basin, SE France)

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Terrestrial and marine sedimentary archives covering the Valanginian interval (136.8-133.9 Ma, Ogg et al., 2004) display a distinct positive $\delta^{13}\text{C}$ -isotope excursion (CIE) of ~ 2.5 permil (Lini et al., 1992; Gröcke et al., 2005). The carbon isotope shift spans ~ 2.0 Ma and has been interpreted to reflect severe perturbations of the Early Cretaceous carbon cycle and paleoenvironmental conditions. According to different authors, the Valanginian CIE was accompanied by enhanced volcanic activity of the Parana-Etendeka large igneous flood basalts, enhanced $p\text{CO}_2$ (Lini et al., 1992; Weissert et al., 1998), widespread biocalcification crisis (Erba et al., 2004) and a distinct climatic cooling as evidenced by ice-rafted debris and glendonites from high-latitude sites. In addition, the positive CIE was assigned to be the result of an anoxic event, named the Weissert OAE (Erba et al., 2004).

In this study, we investigate the composition and distribution of sedimentary organic matter (OM) deposited in a hemipelagic setting before, during, and after the Valanginian CIE. The aim of this study is to provide a detailed view on possible changes in OM deposition during a time of major paleoenvironmental and climatic stress. The chosen approach combines sedimentological and chemostratigraphical information ($\delta^{13}\text{C}_{\text{carb}}$) with geochemical analysis of the bulk OM (incl. TOC, C/N, $\delta^{13}\text{C}_{\text{org}}$, Rock-Eval) and biomarker data. For this study, hemipelagic deposits located in the basinal part of the Vocontian Trough (SE France) covering the late Valanginian to early Hauterivian (Campylotoxus Zone to Radiatus Zone) (Gréselle 2007) have been sampled on a high resolution (sampling spacing of ~ 2 m). A total of three sections has been logged (La Charce, Vergol, Morenas), which consist of hemipelagic marl-limestone alternations and which allow for the construction of a composite succession.

The $\delta^{13}\text{C}_{\text{carb}}$ values range between ~ 0.1 and 2.7 permil and show a characteristic stratigraphic trend typical for this time interval, including a prominent positive CIE. The high-resolution $\delta^{13}\text{C}_{\text{carb}}$ record allows for detailed correlation and comparison with existing chemostratigraphic records across this event. TOC values fluctuate between 0.20 and 4.05%, Rock-Eval pyrolysis results depict HI values of 134 to 383 mgHC/g TOC and OI values of 19 to 160 mg CO_2 /g TOC indicating the predominance of marine OM with only minor terrestrial inputs in all investigated samples. The aliphatic fraction of the OM extractable by organic solvents is dominated by n-alkanes, isoprenoids, and a variety of hopanes and steranes. No distinct changes during the CIE in the abundances of biomarkers specific for Dinoflagellates and methanotrophic bacteria are observed, pointing to no significant response of the marine biota in this basin to the carbon cycle perturbation. There is no indication for an anoxic water column during the CIE.

Steranes show slightly enhanced values for the plateau phase of the excursion, and increasing values during the decline of the $\delta^{13}\text{C}$ shift (e.g. dinosterane) what may just as well be due to the cooling episode or a change in sea-level (Melinte and Mutterlose, 2001).

At this stage, the detailed analysis of the sedimentary OM does not provide evidence for the existence of an OAE or enhanced accumulation/preservation of OM associated with the Valanginian CIE. These findings point to paleoenvironmental changes on continents rather than in marine settings as causes for the isotope shift.

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