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Palaeoceanographic change involved with the Valanginian carbon excursion: Evolution of trace-metal and phosphorus contents along a shelf-basin transect in the Tethyan realm

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The Early Cretaceous Valanginian stage is marked by a pronounced increase in the marine carbonate 13C record, which has commonly been interpreted as the expression of a global anoxic event (Erba et al., 2004). Here we propose to evaluate changes in paleoredox and paleoclimatic conditions, which occurred during the Valanginian carbon event by investigating phosphorus (P) and redox-sensitive trace-metal (TM) contents. We complement our geochemical analyses by an evaluation of organic-matter contents. We selected a series of representative sections along a basin-shelf transect in the western Tethys with the sections of Capriolo (northern Italy), Breggia (southern Switzerland), Vergol (southeastern France), Alvier (northeastern Switzerland) and Malleval (eastern France). We also analysed samples of Valanginian age from the Shatsky Rise (leg ODP 198, site 1213B).
The onset of the carbon excursion is marked by maximal values in phosphorus accumulation rates (0.7, 0.4 and 4.1 mg P/cm2/kyr in the sections of Capriolo, Breggia and Alvier, respectively) and minimal values during the 13C positive shift (0.3, 0.1 mg and 0.5 mg P/cm2/kyr in the sections of Capriolo, Breggia and Alvier, respectively). The trends in P accumulation observed are comparable to the global long-term trend established from the Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) (Föllmi, 1995), which indicate that the phosphorus enrichment observed in the western Tethyan has to be sought in general changes in the marine phosphorus cycle related to changes in the phosphorus delivery rate from the continent. TOC contents in the dark marly layers present in the sections of Capriolo and Breggia are characterized by values lower than 2 wt% and the HI/OI obtained suggest a terrestrial origin of the preserved organic matter. At Vergol, the organic matter of the “Barande” levels appears predominantly of marine origin. At Shatsky Rise, three of the analysed samples show TOC values of up to 4 w% and HI/OI indicate a type-II origin. The stratigraphic distribution of TM in the analysed sections shows no major excursions during the 13C excursion in all studied sections. The only possible correlation is observed for the pre-13C event “Barande” levels, in which U, V, Co, As and Mo contents show maxima. At Shatsky rise, the organic-rich levels indicate higher TM values compared to the organic-lean samples of the site.
Our results show that the onset of the shift is marked by an increase in P content, indicating an increase in continental runoff. This change is coeval with a change in clay-mineral assemblages with the disappearance of kaolinite. We also show that sediments of the western Tethyan realm lack evidence for the persistence of dys- to anaerobic conditions during the Valanginian positive 13C excursion and that preserved organic matter from this time interval is largely of continental origin. Dysoxic to anoxic zones seem to be restricted to marginal seas of Atlantic (Meyers, 1987) and also to the Pacific. We suggest that the Valanginian 13C shift is the consequence of an increase in continental carbon storage (as a sink of 12C-enriched organic carbon), coupled with the demise of shallow-water carbonate platforms (diminishing the storage capacity of 13C-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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