

## **SECULAR VARIATIONS OF ALGAL STEROID BIOMARKERS AT THE UPPERMOST DEVONIAN KELLWASSER- AND HANGENBERG EVENTS**

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The Devonian was characterised by profound global changes. The spread of vascular plants was met by an unusual accumulation of mass extinction events in the marine realm. Two of the uppermost Devonian mass extinctions, the Kellwasser- and Hangenberg events, are presumably among the most severe mass extinction events. However, these mass extinctions are not reflected adequately in the phytoplanktonic fossil record, possibly due to the fact that only few marine algae produce hard parts that can be fossilised. Molecular fossils or biomarkers can add complementary information to the fossil palynomorph record.

Grantham and Wakefield (1988) investigated the secular variation of the  $C_{28}/C_{29}$ -sterane ratio in oils throughout the Phanerozoic and Schwark and Empt (2006) determined a trend for Paleozoic sediments. This ratio shows a gentle and continuously increasing trend in the Devonian, due to a smoothing effect of an averaging of the values in 50 ma steps. This contrasts with profound changes in environmental regimes known to occur during this period (Algeo et al., 2001; Joachimski et al., 2001).

Sections of the Kellwasser Event (Kowala, Poland) and the Hangenberg Event (Appalachian Basin) show sharp, but short-lived, increases of the  $C_{28}/C_{29}$ -sterane ratio at the extinction pulses of the events, attributed to an episodic change in the green algae community from primitive  $C_{29}$ -sterane producing algae to opportunistic (disaster species)  $C_{28}$ -sterane producing prasinophyte algae. Initiated by the Hangenberg-Event, in the outgoing Devonian to lowermost Carboniferous, a profound and irreversible change in the algal community occurred indicated by a shift in  $C_{28}/C_{29}$ -sterane ratios to values in excess of 0.7. This evolutionary progress was possibly triggered by the cumulative effects of several Upper Devonian mass extinctions, reorganization of the nutrient budget in the oceans due to the terrestrialization of the continents (Algeo et al., 2001), or the climate changes in the early Carboniferous. The  $C_{28}/C_{29}$ -sterane ratios reflect excursions in the algal assemblage during the extinction events and an evolutionary progress in the Lower Carboniferous, predating the Mesozoic bloom of fossilising algae.

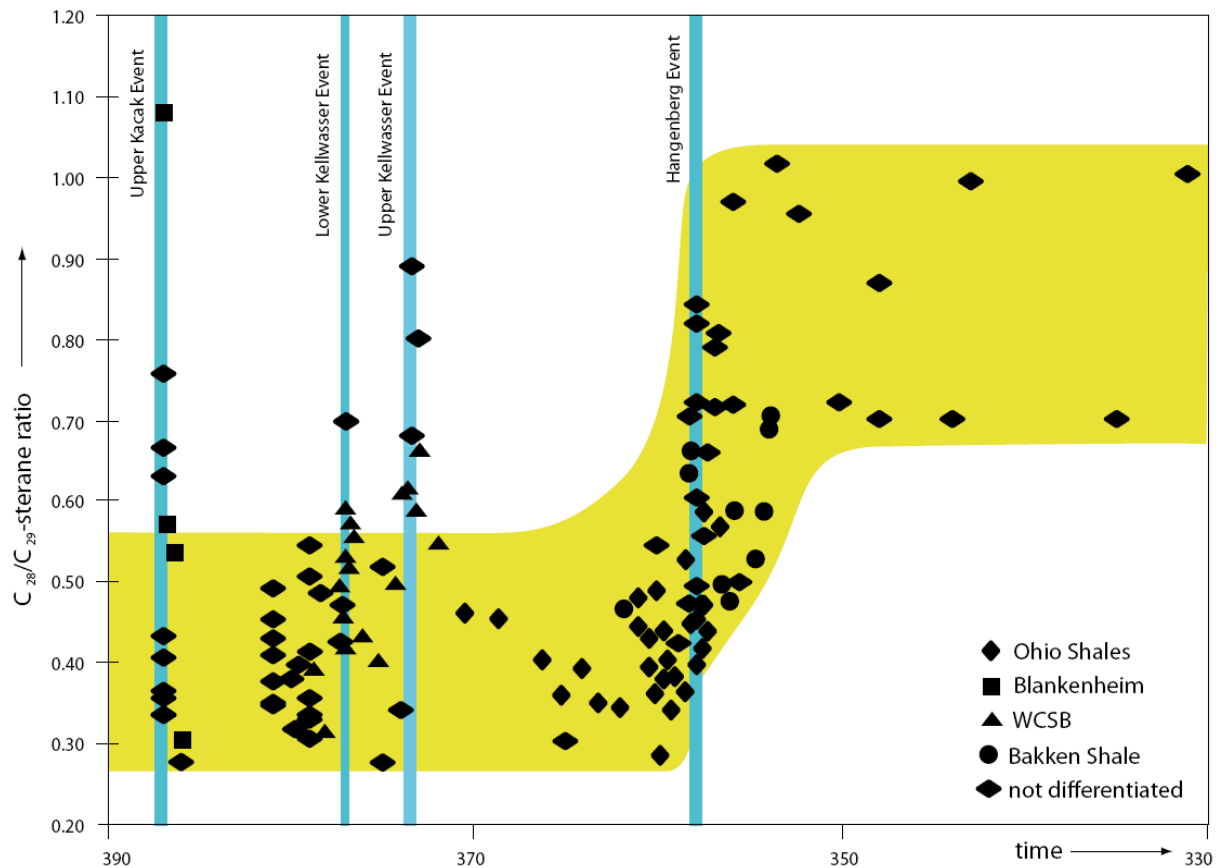


Figure 1. Variations in  $C_{28}/C_{29}$ -sterane ratios of sediment samples during the Upper Devonian to Lower Carboniferous. WCSB = Western Canada Sedimentary Basin, Blankenheim = Eifel Mountains in Western Germany. A stepwise increase in the  $C_{28}/C_{29}$ -sterane ratios occurs at the D/C-boundary, likely caused by a fundamental change in the algal community. Before the D/C-boundary the ratios lie below a threshold value of 0.55. Only major extinction events yield exceptionally high ratios. After the D/C-boundary  $C_{28}/C_{29}$ -sterane ratios consistently exceed the threshold value of 0.55.

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