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Latest Sinemurian to Earliest Toarcian $\delta^{18}O$ and $\delta^{13}C$ fluctuations in belemnite rostra from the Aubach section of Wutach area, South Germany

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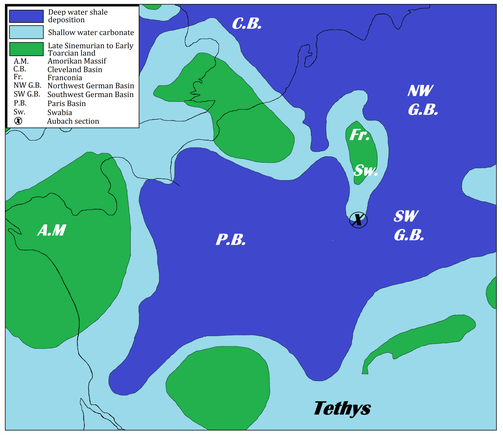


Palaeogeograpic map of Late Sinemurian to Early Toarcian.
The map shows the Laurasian Seaway between the Tethys Ocean to the south and the Boreal Sea to the north. The samples measured in this study were taken from the Aubach section (marked with and X) in the Swabo-Franconian Basin. The map is modified from Coward et al., (2003) and McArthur et al., (2008).

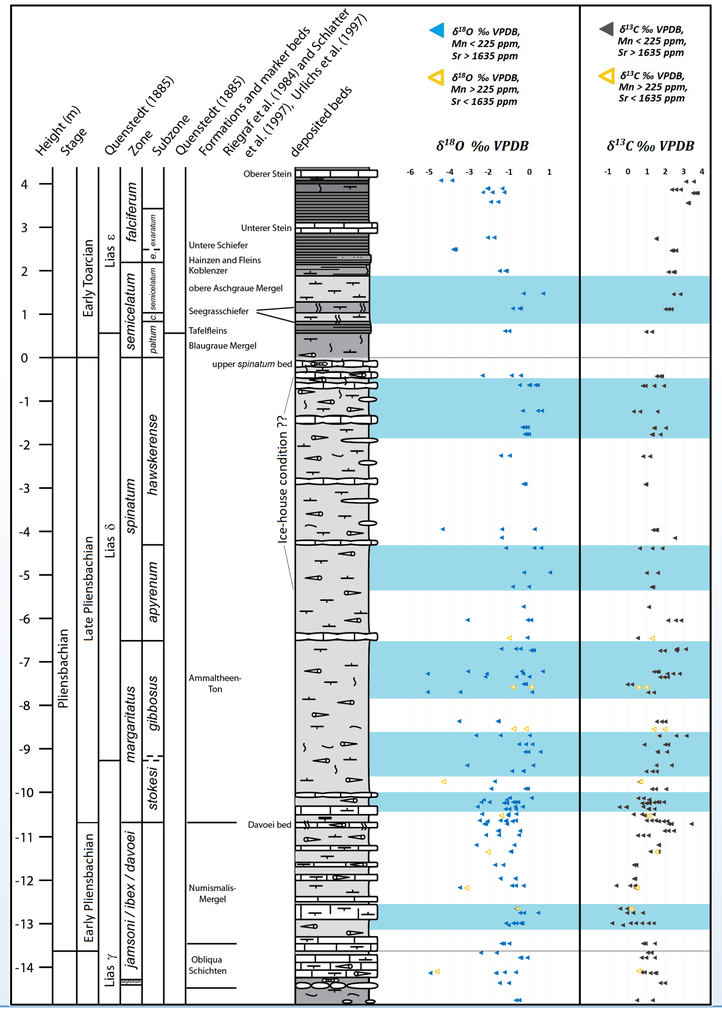
Early Jurassic (Late Sinemurian—Early Toarcian) siliciclastic and carbonate sediments, now exposed in the Aubach section in SW Germany, were deposited in the Swabo-Franconian Basin. This basin then situated at mid-latitudes in a relatively shallow marine environment of the Laurasian seaway. The present study is based on analyzes of carbon and oxygen isotopes derived from belemnite rostra.

The $\delta^{13}C$ data show a negative excursion in the Latest Sinemurian and are compatible with an injection of isotopically light carbon into the atmosphere-ocean system. The positive oxygen isotope excursion from this study in the Latest Sinemurian supports previous data from Lusitanian Basin and Cleveland Basin.

Three intervals of relatively heavy $\delta^{13}C$ values are observed in the Early Pliensbachian supporting the hypothesis that the burial of organic carbon and increased carbon-rich marl deposition is combined with a decline in the atmospheric carbon dioxide. Five cooling phases are observed during Late Pliensbachian, and lend further support to the existence of at least one pronounced Late Pliensbachian 'cooling' Event (LPE) in SW Germany. Based on supportive data from Cleveland Basin and Lusitanian Basin we point to its superregional nature. In the *spinatum* zone heavy oxygen isotope values (up to +1 ‰) indicate continuing ice-house conditions in the Swabo-Franconian Basin supported by sedimentary regressive-transgressive cycles.

A brief negative oxygen isotope excursion at the Pliensbachian—Toarcian boundary parallel to a positive carbon excursion indicates a short warming followed by a cooling interval for Laurasian Seaway with increasing carbon isotopes at the upper *semicelatum* zone, Earliest Toarcian.

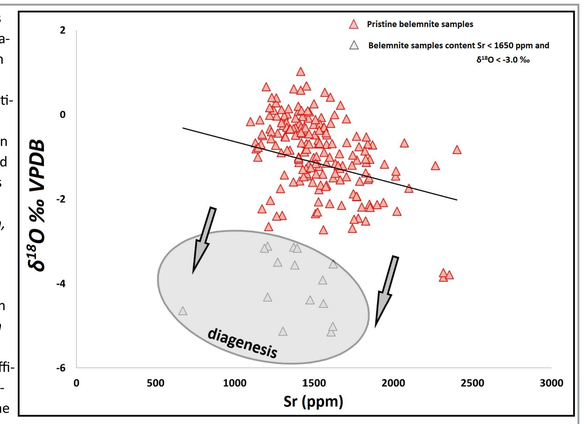
Keywords: $\delta^{18}O$ and $\delta^{13}C$ fluctuation, belemnite rostra, Late Pliensbachian Event (LPE), long-term cooling, ice-house conditions



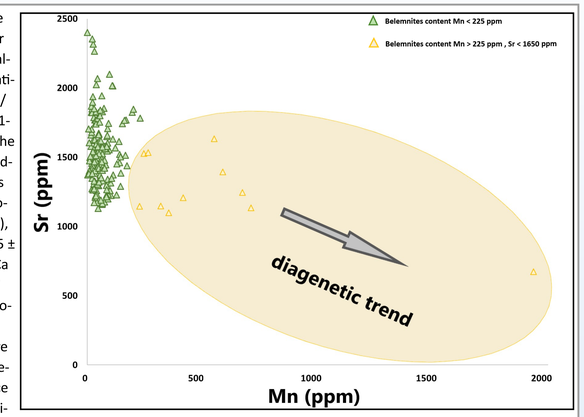
Late Sinemurian to Early Toarcian oxygen and carbon isotope record plotted against the stratigraphic sedimentological units and the ammonite biozones of the Aubach section. Data from 77 belemnite calcitic fossils from the Aubach section in southern Germany of the paleo mid-latitude epi-continental Swabo-Franconian Basin in north-western most part of Tethys Ocean. The vertical left axis shows the heights of the Aubach section. The horizontal left axis of the data shows the measured and corrected $\delta^{18}O$ ‰ VPDB marked with blue triangles. The right horizontal axis of the data diagram shows the $\delta^{13}C$ ‰ VPDB marked with dark grey triangles. The orange open triangles represent altered samples with Mn concentrations larger than 225 ppm. The oxygen isotope fluctuations during Pliensbachian show an increasing trend in the heavy isotope of the belemnite calcite. Through Pliensbachian six cooling periods are highlighted in light blue. The $\delta^{13}C$ values have a decreasing trend during Pliensbachian stage with strong fluctuations and a positive trend entering Toarcian.

Examples of specimen and cross-sections of belemnite rostra.
Elleven different samples of Jurassic belemnites with– or without drill holes. The rostra varies in colours, sizes, shapes, architecture and species. Some of the samples are in scale of wideness or lenght and one in scale of a 0.5 mm pencil lead.

For strontium concentrations depletion may also be associated with diagenetic alteration and might be assented with depletion in $\delta^{18}O$. Concentrations of Sr in biogenic calcium carbonates is usually higher in pristine samples and depleted in diagenetic altered samples caused by thermodynamics (e.g. *Carpenter and Lohmann, 1992; Tang et al., 2008; De-Paolo, 2011*). In general, the Sr/Ca-ratios decrease in the state of progressive alteration in the fossils (e.g. *Bruckschen and Veizer, 1997; Korte et al., 2003*). However, it may be difficult to use strontium as an alteration indicator, because the concentration is dependent on temperature of the seawater and the individual fossils at the time of precipitation (*Veizer, 1974; Steuber and Veizer, 2002, Wierzbowski and Joachimski, 2009; Korte et al., 2011; Li et al., 2012*).



The analyzed elements of the present study will be used for interpretation of diagenetic alteration. The results of the ratios vary from 0.67-2.40 mmol/mol for Sr/Ca, and from 0.001-1.94 mmol/mol for Mn/Ca. The measurements were repeatedly assessed by measurements of the JLs-1 reference limestone material (*Imai et al., 1996*), yielding a Sr/Ca ratio of 0.345 ± 0.007 mmol/mol and a Mn/Ca ratio of 0.029 ± 0.006 mmol/mol (2 sd, n = 37) with a reproducibility of 2.0 % for Sr.
Strontium and manganese are well related to diagenetic alteration, and thus the only trace elements which will be examined in this study. In most of the investigated belemnite subsamples with depleted Sr/Ca ratio are assented to Mn/Ca enrichment. The most Sr-depleted subsample with a ratio of 0.67 mmol/mol is the most Mn-enriched with a ratio of 1.94 mmol/mol and is assented to a very low $\delta^{18}O$-value of -4.65 ‰ VPDB.
The concentration of manganese in calcitic external and internal shells is commonly used as an indicator for the degree of diagenetic alteration as the Mn-enriched samples are frequently depleted in heavier stable isotopes (e.g. *Veizer et al., 1974; Veizer et al., 1999; Korte et al., 2003*). The threshold often used for identifying diagenetic alteration refers to concentrations greater than 250 ppm (e.g. *Veizer et al., 1999; Korte et al., 2003*), despite the threshold for alteration differs from each locality and type of specimen (*Ullmann and Korte, 2015*). The threshold may in this study be 225 ppm and the primary indicator for diagenetic alteration in these low-Mg calcitic belemnite rostra. The examined belemnite rostra with minor depletion or enrichment of Sr and less than 225 ppm Mn concentration is assumed to be pristine fossils.



Early Jurassic analyzed data of well-preserved fossilized nektobenthic belemnite rostra from Southern Germany Aubach section show results oxygen and carbon isotopes with large fluctuations. Oxygen isotopes near the S/P-boundary in Swabo-Franconian Basin show an earlier shift from heavy isotopes to light isotopes in comparison to previously studied Cleveland Basin. The drop of carbon isotopes of 2 ‰ near the S/P-boundary is related to a significance global event.

$\delta^{18}O$ signals from the investigated dataset represent five regional cooling periods in the Late Pliensbachian Swabo-Franconian Basin and give rise to suggest an interpretation of temporary icehouse-conditions. A long-term positive oxygen isotope excursion parallel to long-term negative excursion of carbon isotopes is characterized by a long-termed cooling trend during Late Pliensbachian *spinatum* zone. Combined with previous studies it is concluded that the Late Pliensbachian 'cooling' Event (LPE) is a superregional event for the northwestern Tethys Laurasian Seaway area. The Earliest Toarcian *semicelatum* zone includes a significant cooling interval characterized by increasing oxygen and carbon isotopes also suggested by studies from Cleveland and Lusitanian Basins.

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