



# Organic carbon isotope stratigraphy of Devonian-Carboniferous boundary sections in the Rhenish Mountains

Dieter Korn<sup>1</sup> · Franziska E. Schmid<sup>1,2</sup> · Ulrich Struck<sup>1,3</sup>

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## Abstract

The boundary between the Devonian and the Carboniferous has been drawn using ammonoids, conodonts and miospores, while geochemical data have only rarely been used. The sampling of eight sections (Aprath, Apricke, Effenberg, Wocklum, Stockum, Drewer WJ, Drewer WA, Marsberg) at the northern margin of the Rhenish Mountains demonstrates the potential of the isotope ratio of organic carbon to regionally correlate sections in different facies areas. With the help of the carbon isotopes, a distinct stratigraphic succession is documented, which is characterised by several positive and negative excursions; this succession was recorded in all examined sections. The carbon isotopes can therefore make a significant contribution to the stratigraphic subdivision of sections and complement the biostratigraphic methods.

**Keywords** Devonian-Carboniferous boundary · Hangenberg Event · Rhenish Mountains · Organic carbon isotopes · Stratigraphy

## Introduction

The Hangenberg Event at the Devonian-Carboniferous boundary caused one of the greatest crises in the evolutionary history of the biosphere. Although it is not usually counted among the “Big Five” (e.g. Jablonski 1994, 2001; Alroy et al. 2008; Fan et al. 2020), it is one of the most massive reductions in diversity, particularly in the marine

realm. For example, it is a major extinction event for some marine groups such as the conodonts (e.g. Ziegler and Sandberg 1984; Corradini et al. 2017), ammonoids (e.g. Price and House 1984; Korn 1993; Klein and Korn 2016) and trilobites (e.g. Brauckmann et al. 1993).

Analyses of the ratio of the two stable carbon isotopes <sup>12</sup>C and <sup>13</sup>C have become standard methods for stratigraphic investigations of sedimentary successions (e.g. Saltzman et al. 2012; Cramer and Jarvis 2020). They have been carried out in numerous sections spanning the Devonian-Carboniferous boundary, such as the Rhenish Mountains (Kaiser 2005; Kaiser et al. 2008; Hartenfels et al. 2022), Belgium (Buggisch and Joachimski 2006; Kumpan et al. 2014a), Moravia (Kumpan et al. 2014b), the Holy Cross Mountains (Trela and Malec 2007; Pisarzowska et al. 2020; Matyja et al. 2021), the Carnic Alps (Kaiser 2007; Kaiser et al. 2008), the Montagne Noire (Buggisch and Joachimski 2006), the American Midcontinent (Cramer et al. 2008; Clark et al. 2009; Day et al. 2013; Myrow et al. 2013; Heath et al. 2021), Bolivia (Lakin et al. 2021), the Tien Shan of Uzbekistan (Rakociński et al. 2021), Vietnam (Paschall et al. 2019; Shizuya et al. 2020) and South China (Bai et al. 1987; Wei and Ji 1989; Qie et al. 2015, 2019, 2021). However, most of these studies were based on the analysis of the carbon isotope ratio in the carbonates; analyses of the carbon ratio in the organic material were only occasionally carried out. In some studies, decoupling of organic and carbonate carbon isotope records was postulated (e.g. Heath et al. 2021).

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✉ Dieter Korn  
dieter.korn@mf.n.berlin

Franziska E. Schmid  
franziska.schmid@igb-berlin.de

Ulrich Struck  
ulrich.struck@mf.n.berlin

- <sup>1</sup> Leibniz Institute for Evolution and Biodiversity Science, Museum für Naturkunde Berlin, Invalidenstraße 43, Berlin 10115, Germany
- <sup>2</sup> Leibniz Institute of Freshwater Ecology and Inland Fisheries, Müggelseedamm 310, Berlin 12587, Germany
- <sup>3</sup> Institute of Geological Sciences, Freie Universität Berlin, Maltheser Straße 74–100, Berlin 12249, Germany

The Devonian–Carboniferous boundary was defined by the successive occurrence of conodonts (Paproth et al. 1991). With increasing demands on the precision of the boundary definition between the Devonian and the Carboniferous, the application of additional stratigraphic methods will become necessary. It is already clear that biostratigraphy alone is hardly capable of satisfactorily defining the boundary between these periods. The far greater problem, however, is the practical applicability of the biostratigraphically defined boundary; with increasing geographic distance from a selected index section or GSSP, the reliability of the stratigraphic correlation decreases.

In recent years, almost all period and stage boundaries in the younger Palaeozoic have been defined with the help of conodonts. At least for the shelf sediments, this has probably been a good choice, simply because the conodonts are much easier to recover than macrofossils and are therefore at an advantage because of their larger number of specimens. However, hypotheses about the almost global distribution of conodont species are generally cited as a reason for preferring conodonts as most relevant index fossils. Indeed, other fossil groups, such as the ammonoids, show a sometimes very pronounced provincialism. In the late Viséan and Serpukhonian, for example, it is not possible to correlate stage divisions or zonation across province boundaries (Korn et al. 2012).

Despite the probably greater reliability of stratigraphic correlation of successions of Devonian and Carboniferous sedimentary rocks using conodonts, some difficulties remain. Since conodonts are largely extracted from carbonate rocks, clastic successions are often difficult or even impossible to correlate. Furthermore, conodonts also show

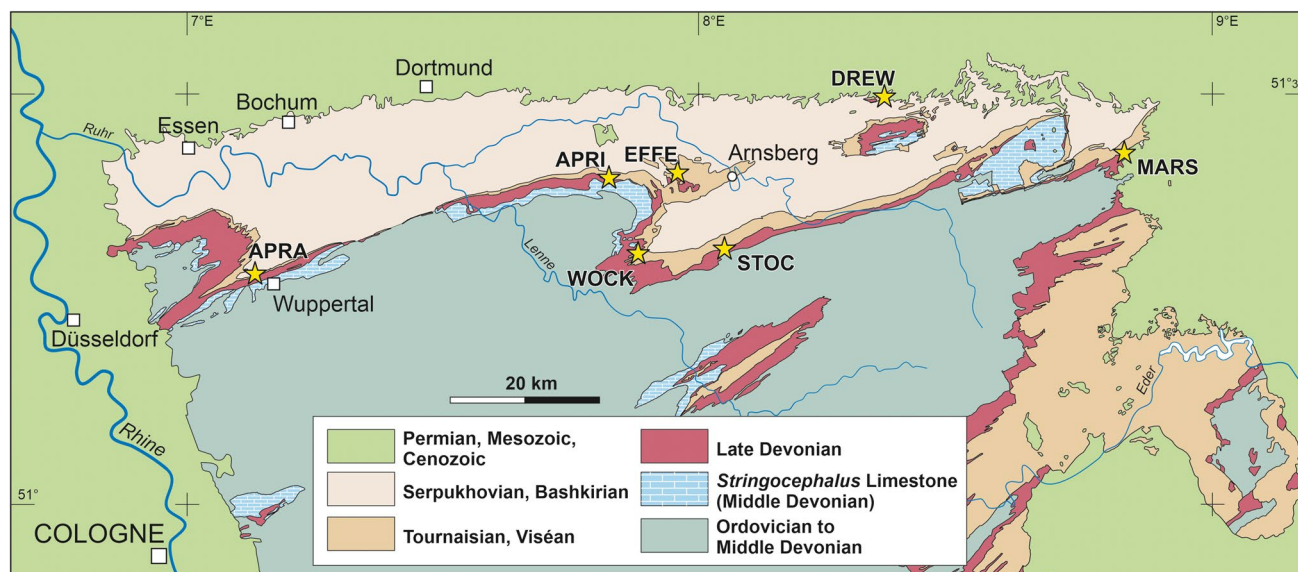
some facies dependence; assemblages of the shallow shelf often differ considerably from those of the deep shelf.

Another major drawback in the application of the conodonts, though also to an even greater extent in the macrofossils, lies in a scientific-logical aspect: the biostratigraphic subdivisions for the Devonian and Carboniferous mostly use the traditional method of the lowest occurrence of a certain index species as a criterion. This means that the absence and presence of the index species are accepted as equally important data. Of course, it must be taken into account that the absence of a certain species in a sample, a section or a geographic area can have various and partly unknown reasons.

By analysing the geochemical properties of sedimentary rocks, this epistemological problem can be at least partially overcome. However, there are also limitations in this method: Investigations of the carbon isotope values of carbonate material may be imprecise when the carbonate content of the sediments is too low (black shales, sandstone). For this reason, we examined the organic material of the sediments, which was available in all examined samples.

A stratigraphic subdivision based on geochemical features obviously has a major disadvantage compared to biostratigraphy: the lack of index characters. Geochemical data can usually only be interpreted in the context of a succession; boundaries with an either/or criterion are not usually present because isotope trends tend to be continuous rather than showing sudden changes.

Here we present organic carbon isotope records measured in sections in the Rhenish Mountains (Fig. 1) across the Devonian–Carboniferous boundary and point out the



**Fig. 1** Geological map of the northern Rhenish Mountains with the geographic position of the investigated sections (yellow stars). APRA Aprath, APRI Apricke, EFFE Effenberg, WOCK Wocklum, STOC Stockum, DREW Drewer, MARS Marsberg

potential application and support of this method for an interdisciplinary study of the period boundary.

### Stratigraphic framework

There is no generally accepted biostratigraphic subdivision that would allow for a correlation of all sections examined here. The conodont stratigraphy that provides the best correlating zonation is currently the subject of intense debate (e.g. Corradini et al. 2017; Becker et al. 2021). For this reason, the traditional scheme of Sandberg et al. (1978) is used in the following. However, as some of the sections have not been studied for conodonts, the principal lithological succession of sections was used (Fig. 2).

To facilitate the correlation of lithostratigraphy and biostratigraphy, we subdivide the sedimentary succession of interest into units, for each of which we present the characteristic variations in isotope values. These are, in ascending order:

**(A)** Upper part of the Wocklum Limestone and its argillaceous equivalents. – The Wocklum Limestone has, in the typical sections such as Wocklum and Apricke, a thickness of about four metres. It is composed of an alternation of nodular, usually dark grey, usually micritic limestone beds 2 to 10 cm thick in alternation with grey shales up to 30 cm thick. At some places, the shale content decreases towards the top and the nodular beds are amalgamated to thicker beds. The carbonate content of the limestone nodules and beds is usually between 70 and 90 wt. %.

Our sampling start varies from section to section because of the lack of strict stratigraphic control, but the top of the Wocklum Limestone is unambiguously defined by the base of the Hangenberg Black Shale. The Wocklum Limestone belongs, according to conodonts, to only one zone (*Siphonodella praesulcata* Zone or expanded *Bispathodus ultimus* Zone sensu Corradini et al. 2017). A subdivision is possible with ammonoids (Schindewolf 1937; Korn 2002b; Klein and Korn 2016; Korn and Weyer 2023), however, species-rich assemblages were not recovered in the sections studied here.

**(B)** Hangenberg Black Shale. – The distinctive unit is present in all sections, except Aprath (which begins at a higher level), but the thickness varies considerably between sections from one millimetre (Effenberg) to 80 cm (Marsberg). The most distinctive feature of the unit is its markedly higher organic carbon content. One has to bear in mind, however, that this content depends on the degree of weathering of the rocks. Samples from deep outcrops that expose the rocks below the weathering zone (Marsberg, Drewer WA) show total organic carbon (TOC) levels of up to 5%, while near-surface and heavily weathered outcrops (Apricke, Wocklum) have significantly lower levels (about 0.5%).

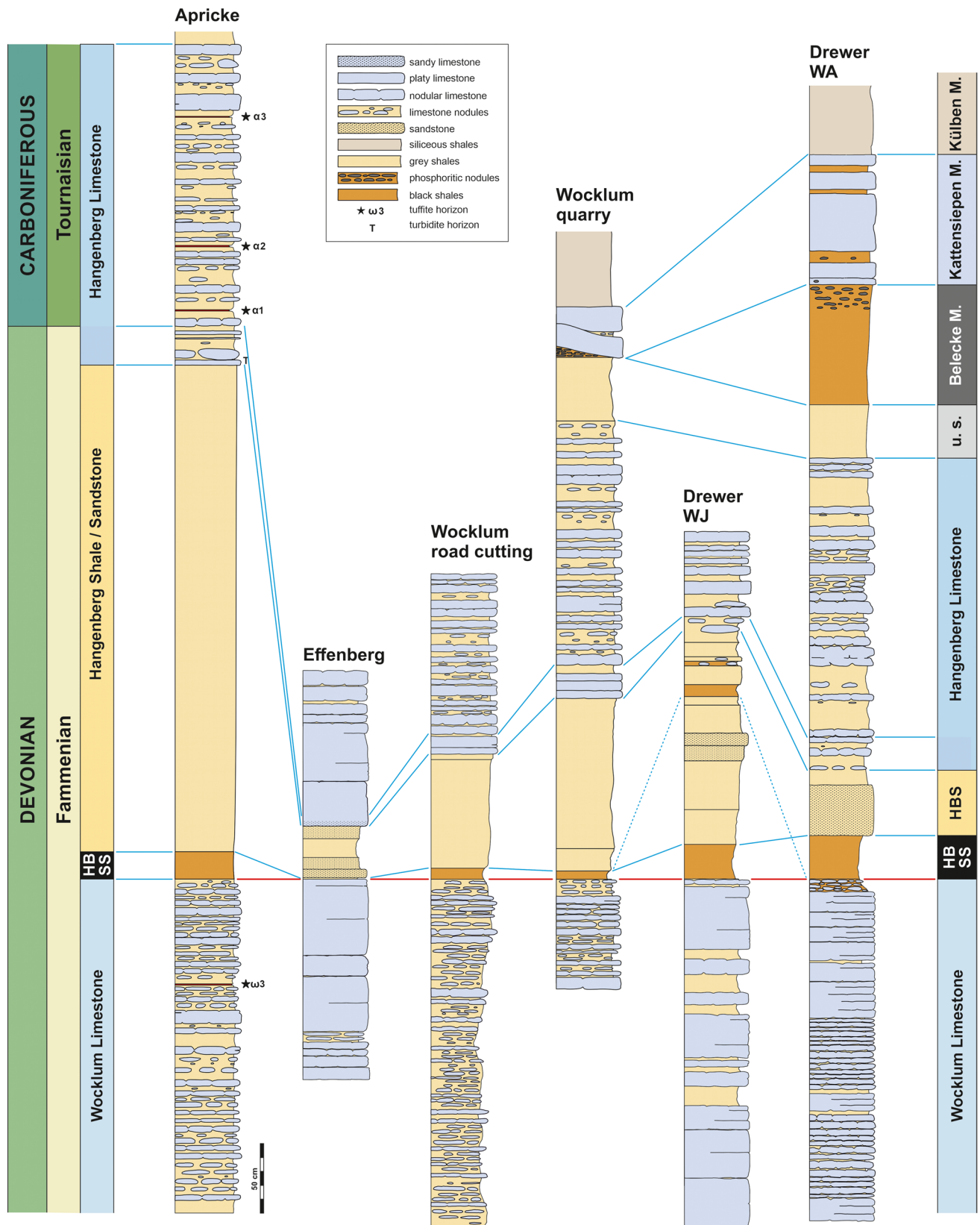
The unit is difficult to define biostratigraphically. Conodonts have only been found in small nodules in the upper part of the Hangenberg Black Shale from two complementary sections in the abandoned Drewer quarry (Korn et al. 1994); they provided a small assemblage with *Protognathodus kockeli*. A revision of this small assemblage is necessary because of the advanced knowledge on the taxonomy and phylogeny of the genus *Protognathodus* (Corradini et al. 2011, 2017; Hartenfels et al. 2022). Ammonoids from the same nodules yielded *Postclymenia evoluta* and *Cymaclymenia nigra* (Korn 1991). In terms of ammonoids, the Hangenberg Black Shale belongs to the *Cymaclymenia nigra* Zone (Korn 2000).

**(C)** Hangenberg Shale and Hangenberg Sandstone. – The Hangenberg Black Shale passes upwards into the Hangenberg Shale without a sharp boundary, but the transition is characterised by the rather rapidly decreasing organic carbon content. The Hangenberg Sandstone is locally embedded in the Hangenberg Shale (Effenberg), but may also represent them (Drewer WA) or being absent or represented by silty shales (Apricke, Wocklum, Marsberg). The unit has, in the studied sections, a thickness between 0.35 m (Effenberg) and about 12 m (Stockum). The shales as well as the siltstones and sandstones show a fairly regular carbonate content of 20–30%.

An unambiguous placement in the conodont stratigraphy scheme is not possible for this unit; according to Becker et al. (2021) it belongs to the “*Bispathodus costatus* – *Protognathodus kockeli* Interregnum” and according to Corradini et al. (2017) to the expanded *Bispathodus ultimus* Zone. However, these assignments are not based on empirical data but rather on theoretical correlations.

**(D)** Stockum Limestone and lateral equivalents (basal part of the Hangenberg Limestone). – Some of the sections in the Rhenish Mountains show a few centimetres thick unit of marly shales and turbiditic limestone beds with high sand content between the Hangenberg Shale and the typical Hangenberg Limestone, built up of nodular limestone beds. The thin unit (usually less than 20 centimetres) can also be laterally represented by nodular limestone beds similar to the Hangenberg Limestone. For this reason, only the base of this unit can be defined lithostratigraphically; the upper boundary is defined with the first occurrence of the conodont *Siphonodella sulcata* or species of the ammonoid genus *Gattendorfia*.

The Stockum Limestone is a very characteristic, only one metre thick lithological unit of dark grey limestone beds with high sand content and fossiliferous lenses in a coarse-grained clastic rock succession. It has, in this characteristic lithology, so far only become known from the type locality. A transfer of the term to other facies and especially to sedimentary rocks with rather different lithology (basal part of the Hangenberg Limestone



**Fig. 2** Lithological succession of six selected sections of the Devonian-Carboniferous boundary beds in the Rhenish Mountains. *HBSS* Hangenberg Black Shale; *HBS* Hangenberg Shale/Sandstone; *u.s.* unnamed shale; *M* Member

or platy limestone beds at Wocklum), as proposed by Becker et al. (2021) and Hartenfels et al. (2022), is not adopted here. An equivalent stratigraphic position and conodont biofacies cannot be the sole argument for the universal application of the name.

**(E)** Main part of the Hangenberg Limestone and lateral argillaceous equivalents. – The Hangenberg Limestone is very similar in most sections and consists of alternating nodular limestone beds and grey shales; it thus closely resembles the Wocklum Limestone that was deposited before the Hangenberg Event, but the carbonate content of the nodules in the Hangenberg Limestone is slightly lower, usually between 70 and 80%. The thickness of the shale interbeds is determined by the bathymetric position of the sections. The basal Aprath and Marsberg sections consist exclusively of shales. The Hangenberg Limestone has been intensively investigated in numerous studies for ammonoid and conodont stratigraphy; the biostratigraphic division is therefore rather well known. The competing classification schemes are not so much based on different data sets, but rather on a different interpretation of these data. Using conodonts, the unit can be divided into four (Sandberg et al. 1978) or six (Becker et al. 2021) zones or subzones defined by species of *Siphonodella*; with ammonoids four well distinguishable zones can be separated (Korn 2000; Klein and Korn 2016; Korn and Weyer 2023).

**(F)** Unnamed shales between the Hangenberg Limestone and the Kahlenberg Formation. – The unit is, where clearly identified (Wocklum, Drewer), about 0.50 metres thick and contains no nodular limestones, even in sections on submarine elevations. It appears impossible to assign it biostratigraphically.

**(G)** Kahlenberg Formation and lateral equivalents (Belecke Member). – The formation is built up by siliceous black shales; its base is considered isochronous. Phosphoritic nodules occur particularly in the upper part. The unit is less than 0.90 metres thick in the Drewer WA section (Korn et al. 1994; Siegmund et al. 2002).

**(H)** Kattensiepen Member and lateral equivalents. – Some of the sections (e.g. Drewer, Wocklum) show a succession of some siliceous limestone beds with a total thickness between 0.40 and 1.00 metres. At Drewer, this unit was dated by conodonts to belong in the late Tournaisian *Scaliognathus anchoralis* Zone (Clausen and Leuteritz 1984; Hartenfels et al. 2022).

The application of lithostratigraphy is based on some basic assumptions:

**(1)** Two of the studied lithological units (Hangenberg Black Shale, Kahlenberg Formation and lateral equivalents) are isochronous with respect to their bases. This hypothesis is now generally accepted. However, there

is only indirect evidence for an isochronous base of the Hangenberg Black Shale. Particularly the very frequent occurrence of specimens of the ammonoid genus *Wocklumeria* in the uppermost centimetres of the Wocklum Limestone immediately below the base of the Hangenberg Black Shale is regarded as evidence.

**(2)** Two lithostratigraphic units (Hangenberg Shale, Hangenberg Limestone) have a base, which, although not necessarily exactly isochronous, is suitable for a correlation between adjacent sections.

**(3)** Within some lithostratigraphic units (Wocklum Limestone, Hangenberg Limestone), an internal correlation can be carried out using rock sequences. Such a lithostratigraphic correlation was carried out by Korn and Weyer (2003) for the sections between Hasselbachtal and Apricke; that study showed that even a bed-by-bed correlation is possible. This also allows to transfer the conodont stratigraphy of one section (e.g. Hasselbachtal) to neighbouring sections (e.g. Apricke).

### Studied sections

All sections examined have a geographic position on the northern margin of the Rhenish Mountains between Wuppertal and Marsberg (Fig. 1). Palaeogeographically, they were located on the southern shelf of Laurussia. (e.g. Scotese 2014). All sections are predominantly built up of fine clastics; depending on the bathymetric position, limestone nodules and, particularly on the submarine elevations, compact limestone beds are intercalated.

The investigated sections differ in their thermal maturity. Paproth and Wolf (1973) and especially Wolf and Braun (1994) demonstrated that the Drewer area shows, due to a regional anomaly, the highest vitrinite reflection values of 5–6%  $R_{max}$ . Both to the west and to the east the values decrease; all other sections show values of 3–4%  $R_{max}$ .

#### Aprath

**Location:** The investigated section was only temporarily accessible in 1998 during the construction of the WEDAL gas pipeline. It was located about 4.5 km north-west of the centre of Wuppertal-Elberfeld, 700 m north-east of Aprath and about 200 m east of the federal road B224n. The geographical coordinates are 51.27676° N, 7.08769° E.

Previous investigations: Sections in the vicinity of Aprath have been known for a long time and have been recognised as important fossil deposits due to their rich late Viséan assemblages, especially consisting of trilobites (Brauckmann 1973; 1988). In contrast, the stratigraphic succession at the Devonian-Carboniferous boundary has been studied only very rarely. Reasons for this could be the monotony of the

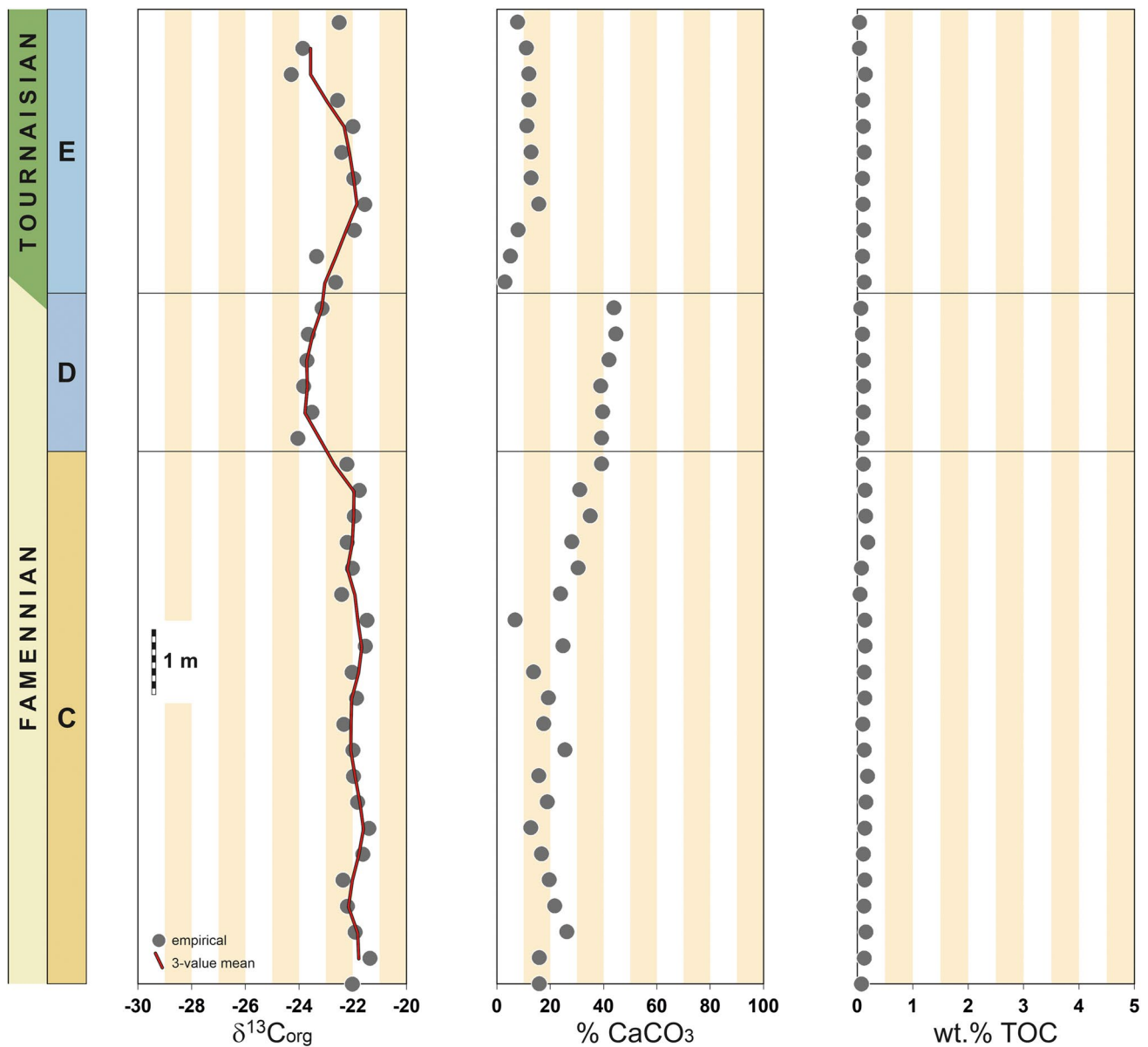
rock succession, the poor fossil content, and poor outcrop conditions.

A more intensive investigation was carried out by Thomas and Zimmerle (1992) during the construction work for the B224n federal road. They named the Devonian-Carboniferous boundary layers as “Schichtgruppe 05–07” (layer group 05–07); the 14.30 m thick layer group 05 is separated from the 9.00 m thick layer group 07 by a 0.90 m thick section (layer group 06) with carbonate nodules and an ammonoid assemblage with prionoceratids described by Korn (1992).

Lithological succession: The entire section examined (Grewing et al. 2000) was 111 metres thick; of this, the lower 90 metres belong to the Velbert Formation and the Hangenberg Formation. In the Velbert and Hangenberg formations,

mica containing shales and siltstones alternate with layers that have an increased sand or carbonate content. The shales and siltstones weather greenish-brown, while the layers with increased limestone content largely retain a bluish colour. Occasionally, grey pure limestone nodules are also included.

Our samples were taken at intervals of 0.40 metres by Anke Grewing (formerly University of Münster): A 15 metres thick succession was sampled, of which 10 m come from below and 5 m above the fossil horizon with prionoceratid ammonoids. This interval probably belongs entirely to the Hangenberg Formation. Most of the samples have a very similar lithology, but there is a trend towards a higher carbonate content of the shales that ends abruptly between the two samples 40 and 80 cm above the fossil horizon (Fig. 3). The



**Fig. 3** The Aprath section and its  $\delta^{13}\text{C}_{\text{org}}$  dynamics, carbonate content and total organic carbon content

Hangenberg Black Shale or an equivalent was not recorded; probably the studied section starts at a higher level.

**Biostratigraphy:** A black shale layer, which would correspond to the Hangenberg Black Shale, could not be recorded. The only index horizon is the ammonoid-bearing layer of the “Stockum fauna” with prionoceratids but without *Gattendorfia*, which can be correlated with the sections further east (Effenberg, Stockum, Drewer). Further index fossils were not investigated.

Apricke

**Location:** There are several outcrops that expose the Devonian-Carboniferous boundary beds in the vicinity of Apricke and Riemke, but most of them were only temporarily accessible. A single permanent outcrop is located in the small stream one kilometre north of Apricke (51.39629° N, 7.81169° E); here the Wocklum and Hangenberg limestones, separated by the Hangenberg Black Shale and Hangenberg Shale, are exposed in a small outcrop on both banks of the stream.

Previous investigations: The Apricke section was already briefly described by Schmidt (1924) and re-examined by Paproth (in Paproth and Streel 1982) and Luppold et al. (1994). The outcrop area proved to be relatively poor in macrofossils;

only the uppermost part of the Wocklum Limestone yielded ammonoids (Luppold et al. 1994) and trilobites (Feist et al. 2000). Korn and Weyer (2003) examined the section in greater detail with regard to its lithological succession and correlated it with the neighbouring Hasselbachtal and Oese sections.

Lithological succession (Fig. 2): The Wocklum Limestone consists of an alternation of nodular, dark grey, mostly micritic limestone beds 2 to 5 cm thick and greenish grey shales up to 10 cm thick. In the upper half metre, the shale interbeds are somewhat thinner; the limestone beds are often amalgamated to more compact beds. The Wocklum Limestone is strikingly similar to that in the Hasselbachtal and Oese sections (Korn and Weyer 2003); it contains a meta-bentonite horizon 0.75 m below the top (bed ω3).

The Hangenberg Black Shale is 0.20 m thick and strongly weathered; it appears dark grey with rusty spots and is split into fine layers. Due to weathering, the shale has obviously lost a large part of the organic material. It is overlain by 3.60 m of silty Hangenberg Shale with low carbonate content.

The Hangenberg Limestone is lithologically similar to the Wocklum Limestone; it consists of up to 10 cm thick micritic nodular limestone beds. The base of the Hangenberg Limestone is marked by a turbiditic, weakly laminated, non-nodular bed. Two other very thin turbiditic beds are located near the

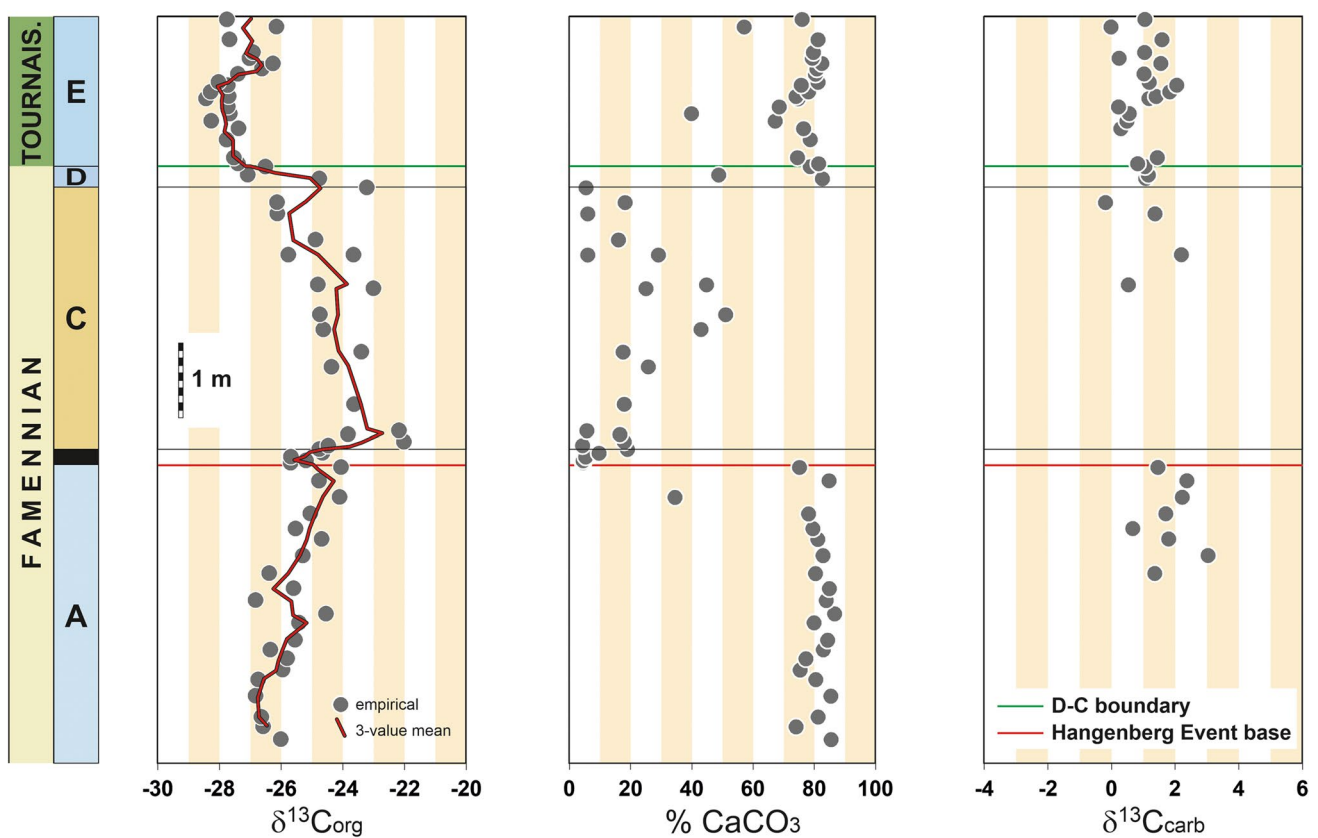


Fig. 4 The Apricke section and its  $\delta^{13}\text{C}_{\text{org}}$  dynamics, carbonate content and  $\delta^{13}\text{C}_{\text{carb}}$  dynamics

base. This lower portion of the Hangenberg Limestone was named Stockum Limestone by Becker et al. (2021). However, this attribution is misleading, because the term Stockum Limestone refers to  $C_{org}$ -rich, partly very sandy limestone nodules and beds within the clastic basinal facies (Fig. 4).

The Hangenberg Limestone has a thickness of 2.30 m; three metabentonite horizons are located in this unit 0.40, 0.85 and 1.80 m above the base (Korn and Weyer 2003), respectively (index beds  $\alpha 1$ ,  $\alpha 2$  and  $\alpha 3$ ). They can directly be correlated with the three metabentonite horizons at Hasselbachtal that yielded geochronological data (Trapp et al. 2004).

**Biostratigraphy:** The Devonian-Carboniferous boundary can be drawn rather accurately with the help of conodonts. Luppold et al. (1994) found the first *Siphonodella sulcata* in a bed 30 cm above the base of the Hangenberg Limestone; the underlying beds only yielded assemblages with several species of *Protognathodus*. Well-preserved ammonoids have not been found in the boundary interval. However, the section has not yet been intensively examined for macrofossils.

#### Effenberg

**Location:** Devonian-Carboniferous boundary sections have been repeatedly exposed in the large active quarry on the Effenberg summit, 3.8 km south of Herdringen, since the 1970s; these sections vary particularly in the interval between the Wocklum and Hangenberg limestones. The section studied here is located at the south-eastern margin of the large quarry at 51.38929° N, 7.95993° E.

Previous investigations: Exposures on the Effenberg are mainly known for the late Famennian ammonoid succession (Price and Korn 1989). Luppold et al. (1994) studied a section that included the Devonian-Carboniferous boundary with respect to the carbonate microfacies and conodont content. That outcrop has since disappeared due to rock mining. Hartenfels (2011) and Hartenfels and Becker (2016) gave an overview of the research history of the Effenberg section and provided detailed data on the conodont succession around the *Annulata* and Effenberg black shales.

Lithological succession (Fig. 2): In the deep quarry on the Effenberg, a presumably complete Famennian rock succession is exposed. While the older strata of the Famennian are represented in shaly facies, the carbonate content increases during the middle Famennian part of the section. From about the *Prolobites delphinus* Zone upwards to the Hangenberg Event, the succession consists of nodular limestones. There are three black shale marker beds, the two-fold *Annulata* Black Shale and the Effenberg Black Shale (Korn 2004), the latter subsequently called Dasberg Black Shale by Hartenfels and Becker (2009, 2016), Hartenfels (2011) and Myrow et al. (2011). Becker et al. (2021) gave a further overview of the exploration of the Effenberg section with special focus on the Devonian-Carboniferous boundary.

The Wocklum Limestone consists of three rather clearly separable lithological units. It starts with a unit 1.90 m thick consisting of partly very fossil-rich nodular limestone beds up to 5 cm thick and shaly interbeds. The middle unit is composed of denser, hard nodular limestone beds with lower fossil content; it has a thickness of 1.70 m. Finally, the upper unit is an almost compact, hard limestone bed with 1.05 m thickness. This bed is exceptionally rich in fossils, especially in the upper part. The uppermost part of the Wocklum Limestone is affected by re-deposition, as can be seen from the numerous intraclasts (Fig. 5). There is a sharp boundary with the overlying Hangenberg Shale.

The interval of the Hangenberg Black Shale and the Hangenberg Shale in the newly investigated section is only about 40 cm thick and consists mostly of sandy and silty layers. The Hangenberg Black Shale is represented only by an irregularly occurring millimetre-thick layer above the Wocklum Limestone. It is overlain by a 1 cm thick dark grey shale layer. The following finely laminated sandstone bed of 6 cm thickness has a rather high carbonate content (45%  $CaCO_3$ ); it also has a much higher organic carbon content (up to 0.5%) than the other sediments in the section (TOC usually below 0.05%); the lowest sample from this sandstone bed has a TOC content of 0.5%. Further up in the Hangenberg Shale, the TOC content decreases and the sediments are more fine-grained.

In the newly investigated section, the Hangenberg Limestone begins with two 32 cm and 42 cm thick, compact beds. At the base, the lower bed has a higher sand content; towards the top, the intercalations of millimetre-thick shales increase. The carbonate content of these two beds is between 65 and 85%. The higher part of the Hangenberg Limestone consists of nodular limestone layers; the limestone nodules contain more clay material and therefore have a lower carbonate content, which is between 45 and 70% (Fig. 6).

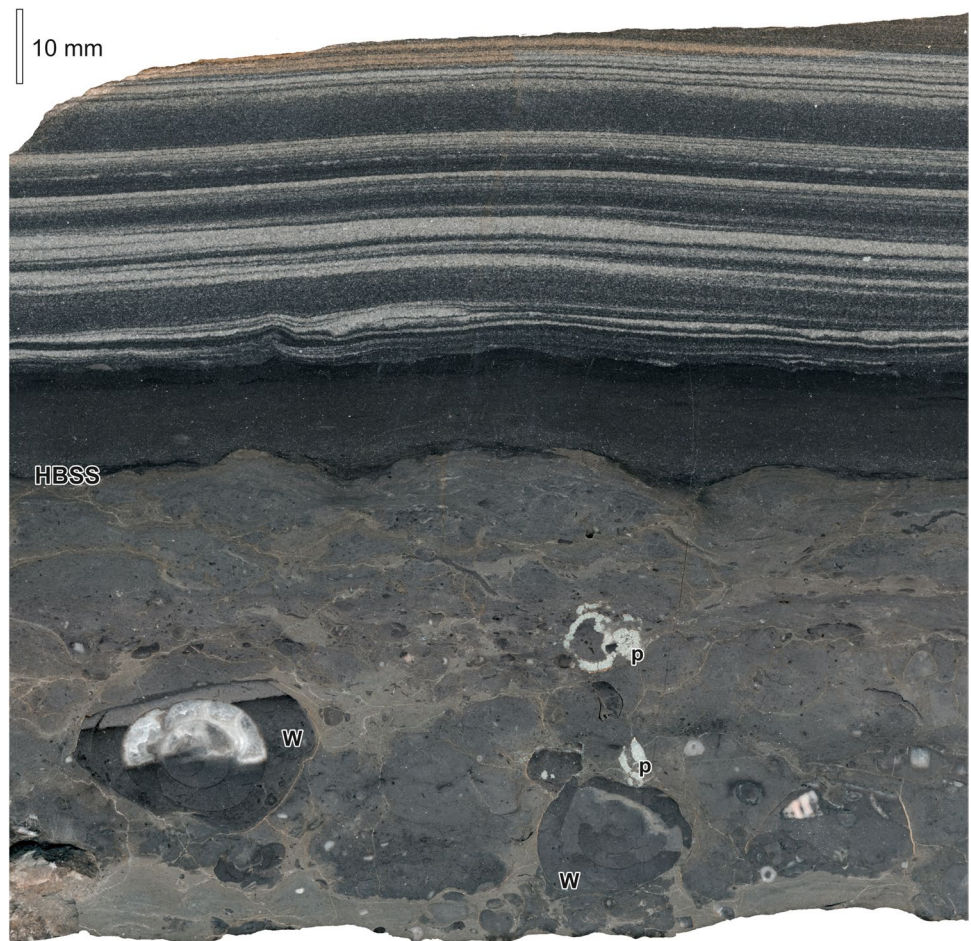
**Biostratigraphy:** The Effenberg section yielded rather diverse conodont assemblages from the Devonian-Carboniferous boundary interval (Luppold et al. 1994). The boundary, recorded by the lowest occurrence of *Siphonodella sulcata* has a position fifteen centimetres above the base of the Hangenberg Limestone. These basal 15 cm yielded assemblages dominated by *Protognathodus*. As for the Apricke section, Becker et al. (2021) referred this lower 15 cm of the Hangenberg Limestone to the Stockum Limestone. As this differs from the Hangenberg Limestone solely in terms of biostratigraphy, this practice is not followed here.

#### Wocklum

**Location:** South-western foot of the Burgberg, 1.7 km south-southwest of the Wocklum castle; the



**Fig. 5** Polished slab of the transition from the Wocklum Limestone to the Hangenberg Shale/Sandstone. Note the transported clasts of *Wocklumeria* (W) and other ammonoids, pyrite aggregates (p) and the near-complete lack of the Hangenberg Black Shale (HBSS)

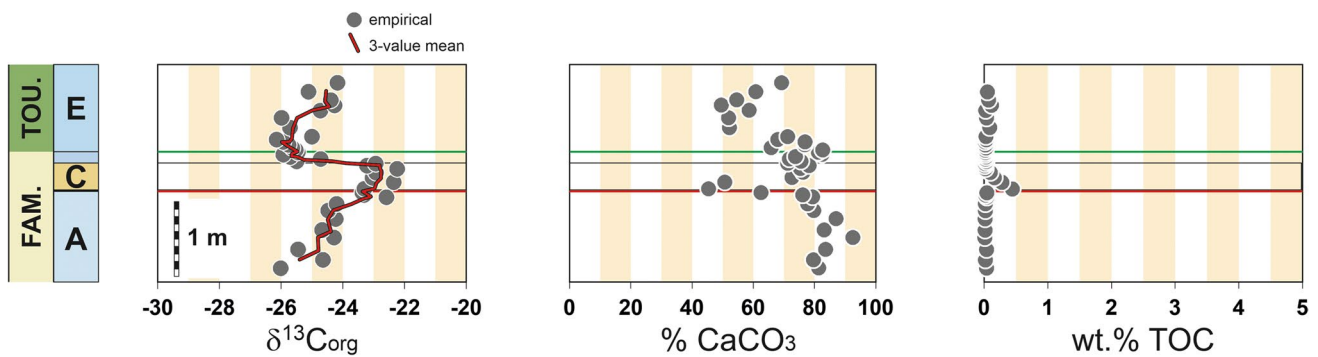


Devonian-Carboniferous boundary beds are exposed at two places:

(1) The small quarry that has been abandoned for a long time. In this quarry, the section begins with the upper 0.80 m of the Wocklum Limestone; upwards it continues through Hangenberg Black Shale, Hangenberg Shale/Sandstone and Hangenberg Limestone into siliceous

Viséan rocks. The geographic coordinates are 51.32731° N, 7.88096° E.

(2) The road embankment in the area of the entrance to the old quarry, 15 metres away from the quarry section. The uppermost parts of the Famennian nodular limestones (Wocklum Limestone), the Hangenberg Black Shale and the Hangenberg Shale/Sandstone are exposed here; the section ends in the Hangenberg Limestone.



**Fig. 6** The Effenberg section and its  $\delta^{13}C_{org}$  dynamics, carbonate content and total organic carbon content

**Previous investigations:** The outcrop is represented in the literature under various names such as “Borkewehr”, “Burg bei Wocklum”, “Burgberg” and “An der Borke”. For the latest Famennian limestone unit exposed here, Denckmann (1902) introduced the term Wocklum Limestone. Wedekind (1918) noted strange triangularly coiled clymeniids at this locality and named them *Wocklumeria*. This genus and closely related other genera became the most important ammonoid index forms for the latest Famennian (Schindewolf 1937).

Hartenfels and Becker (2018) suggested the Wocklum section as a possible stratotype for the Devonian-Carboniferous boundary. An overview of literature on the Wocklum section was provided by Becker et al. (2021). A detailed description of the section, including a range chart of conodonts as well as carbon isotopes of carbonates and organic material was carried out by Hartenfels et al. (2022). They paid particular attention on the road embankment section, which they called the “main section”.

**Lithological succession (Fig. 2):** The lithology of the Wocklum Limestone and the Hangenberg Limestone corresponds to that in the Apricke area: both units are composed of dark grey nodular limestones with shale interbeds of varying thickness. Ammonoid assemblages were found only in some of the nodular limestone beds, mainly in the upper part of the Wocklum Limestone. The Wocklum Limestone appears to be rather uniform; a change in the ratio of the thickness of limestone layers and shale interbeds is apparently not as clear as near Apricke. The nodular limestone beds of the uppermost 1.70 m in the Wocklum Limestone are very uniform in composition; they are almost exclusively micrites. The carbonate content is between 83 and 86% and the TOC content between 0.06 and 0.09%. The uppermost 12 cm

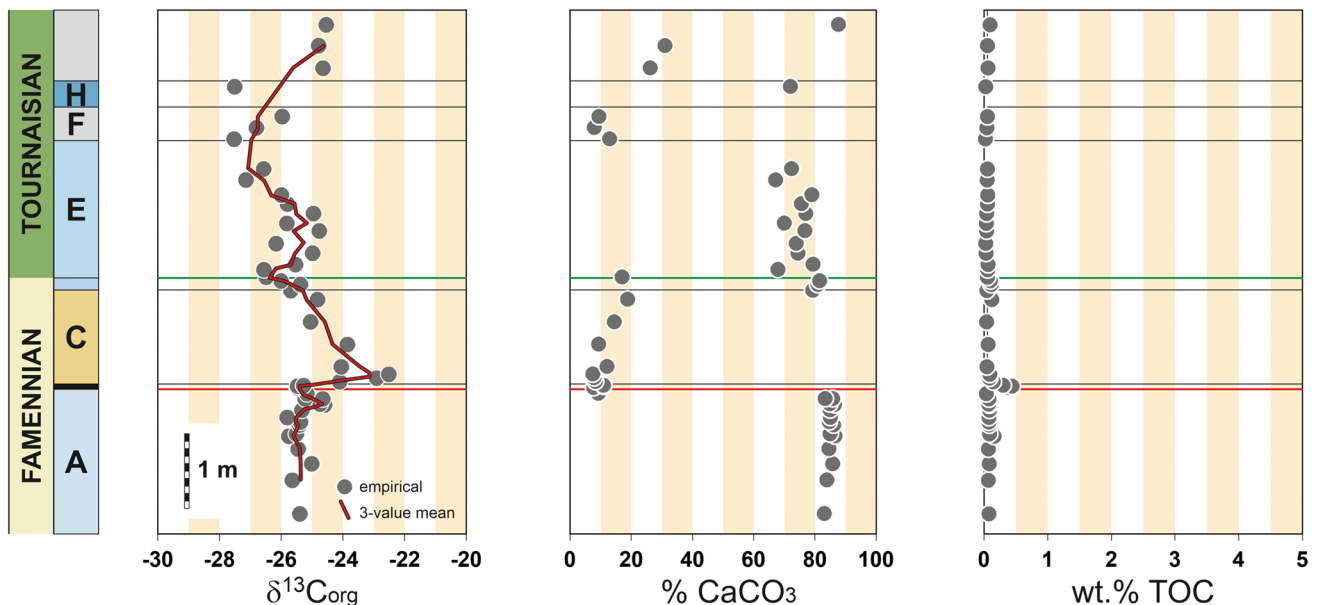
of the Wocklum Limestone are strongly weathered and almost completely decalcified, both in the quarry and in the road embankment. This layer was wrongly interpreted as part of the Hangenberg Black Shale by Becker et al. (2016a; text-fig. 3) and Hartenfels et al. (2022, text-figs 3, 17, 19, 22).

The Hangenberg Black Shale has a thickness of 8 cm. It is also strongly weathered and has lost most of the organic carbon, as the TOC content is only up to 0.05% (Fig. 7). Above this follow the Hangenberg Shale/Sandstone with a thickness of 1.20 m (quarry) and 0.85 m (road embankment); it is very silty at the base and fine-grained with increased carbonate content in the upper 5 cm.

The Hangenberg Limestone is almost exactly two metres thick. At the base, there are three micritic, non-nodular, internally stratified layers in the quarry section, which together are 18 cm thick (in the road embankment section, there are only two beds with a total thickness of about 13 cm). This thin unit has been regarded as belonging to the “Stockum Limestone” by Becker et al. (2016a) and Hartenfels et al. (2022).

Most of the Hangenberg Limestone consists of nodular limestone layers 1 to 12 cm thick; they are separated by greenish-grey shales. Although the cyclicity is quite clearly developed, a bed-by-bed correlation, as was possible between the Hasselbachtal and Apricke sections (Korn and Weyer 2003), cannot be carried out here. The Hangenberg Limestone is only completely exposed in the old quarry; only the basal 1.40 m are present in the road embankment.

The Hangenberg Limestone is overlain by grey shales with 45–60 cm thickness; the varying thickness is caused by an oblique truncation at the top. This unit cannot be assigned with biostratigraphic data. Based on its lithology, this unit can probably be correlated with the very similar shales above



**Fig. 7** The Wocklum section and its  $\delta^{13}\text{C}_{\text{org}}$  dynamics, carbonate content and total organic carbon content

the Hangenberg Limestone at Drewer. Hartenfels et al. (2022) correlated it with the Kahlenberg Formation, but at the same time indicated the significantly lower organic carbon content.

Above this follow up to 15 centimetres of black shales with phosphoritic and carbonatic limestone lenses and then two dense, compact, weakly siliceous limestone layers, both about 15–20 cm thick. The upper part of the section consists of siliceous shales and some siliceous limestone layers. Unfortunately, this part of the section is affected by faults that are almost parallel to the bedding planes and, therefore, does not show its original succession. The upper part of the section consists of siliceous shales and some thin tuffitic horizons and siliceous limestone turbidite layers.

**Biostratigraphy:** Latest Famennian ammonoids were described already shortly after the first investigation of the section (Wedekind 1918). It can be assumed that these species originate from the highest 0.80 m of the Wocklum Limestone. In contrast, no significant finds of ammonoids have yet been reported from the Hangenberg Limestone.

Pioneering conodont investigations were carried out by Bischoff (1957) and Voges (1959; 1960), but only a few samples were examined in these studies. The horizon with the phosphoritic nodules and the lower of the two highest, 20 cm thick limestone beds was placed in the *Scaliognathus anchoralis* Zone by Voges (1959; 1960). This would mean that there is extreme condensation or sedimentary or tectonically caused gaps between the Hangenberg Limestone and this unit.

Recently, Hartenfels et al. (2022) have intensively studied the section of Wocklum and presented a detailed succession of conodont species from both sides of the Devonian-Carboniferous boundary. In one of the micritic limestone beds at the base of the Hangenberg Limestone they found their new conodont species *Protognathodus semikockeli*, which was considered by the authors to be a descendent of *Pr. collinsoni* and an ancestor of *Pr. kockeli*. Hartenfels et al. (2022) correlated these beds with the “basal Stockum Limestone”, a term earlier introduced by Becker et al. (2021) for black limestone nodules occurring in black shales in some of the Drewer sections (Korn 1991; Korn et al. 1994).

## Stockum

**Location:** Outcrops of interest are located about 900–1000 m east-southeast of the church of Stockum. Three sections were investigated:

- (1) The embankment of the forestry road, which yielded the first ammonoids from this locality, but the Devonian-Carboniferous boundary beds were rarely well exposed (51.29189° N, 7.99828° E).
- (2) A trench immediately north of the forest road (trench I of Alberti et al. 1974).

- (3) A vegetation-poor slope 80 metres further east, which was extended northwards by two trenches (trench II of Alberti et al. 1974; Clausen et al. 1994).

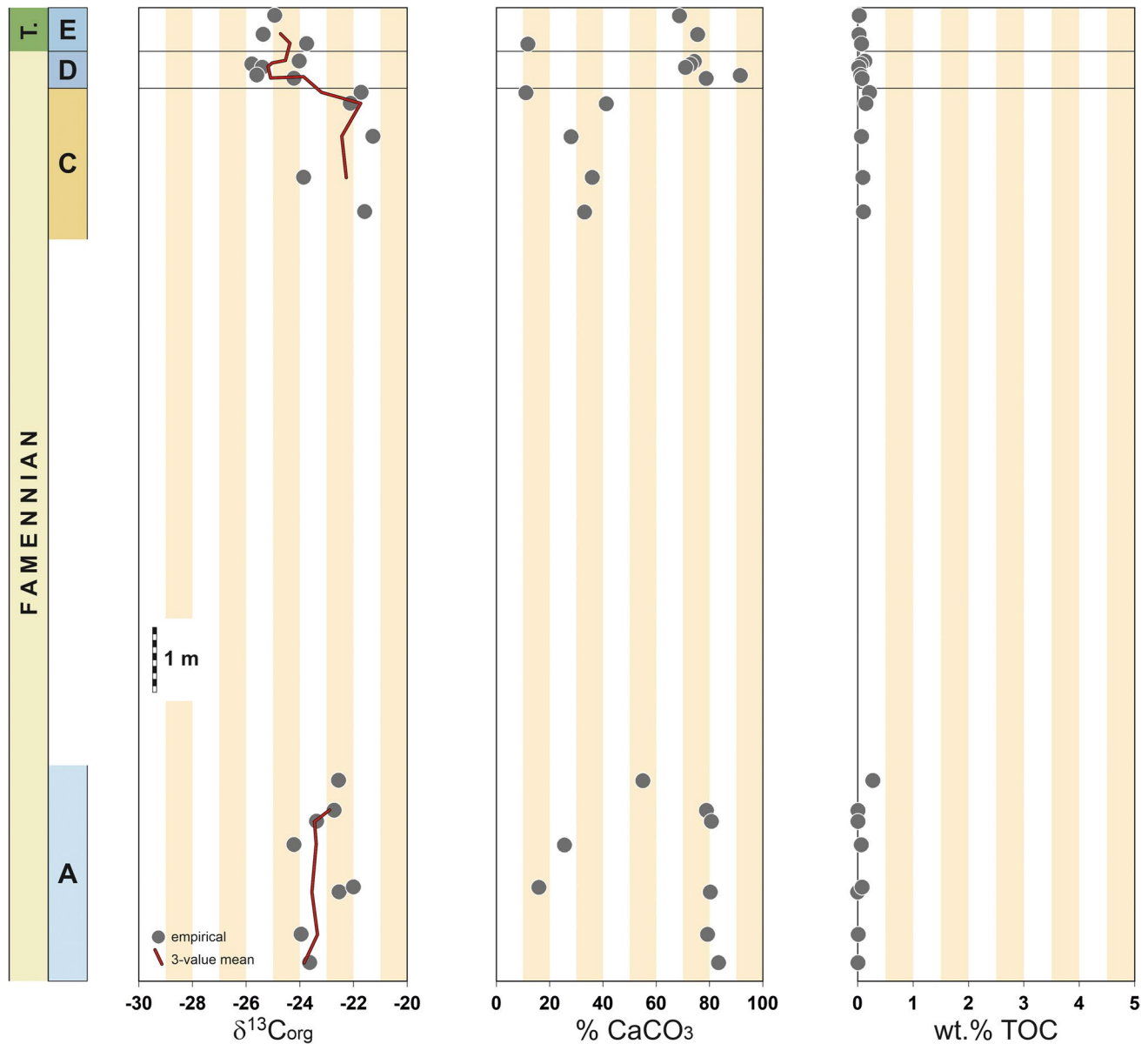
**Previous investigations:** Since the discovery of fossil-bearing black limestone lenses within an otherwise largely clastic succession by the assistant geologist Caesar in 1917 (Schmidt 1924), the ammonoid assemblage contained therein has repeatedly been the starting point of speculation and discussion. While Schmidt (1924) interpreted the assemblage as time-equivalent with the Hangenberg Limestone, Vöhringer (1960) considered it to be somewhat older. A newly discovered conodont fauna consisting of species of *Protognathodus* in the nodules was considered by Ziegler (1969) to be latest Devonian in age. Paproth and Streel (1970) analysed the miospore succession of the section and postulated that the Stockum Limestone must be stratigraphically younger than the uppermost part of the Hangenberg Shale but older than the Hangenberg Limestone in the famous Oberrödinghausen section.

The first coherent description of the section including the position of the fossil-rich limestone lenses was published by Alberti et al. (1974). Simultaneous investigations of trilobites, ostracods, miospores and ammonoids led the authors to the statement that the limestone lenses, which they gave the new term “Stockum Limestone”, should be placed in the Carboniferous. New records of ammonoids from the road cutting section were described by Korn (1984); the nodules were named there “Stockumer *Imitoceras*-Kalklinsen”.

A partial exposure of the slope at the forest road as well as a renewal of trench II allowed a more intensive study of the sections, where the content of conodonts, ammonoids, ostracods and miospores was studied simultaneously (Clausen et al. 1994). Becker et al. (2021) summarised the data published so far from the Stockum outcrops.

**Lithological succession:** The rock succession across the Devonian-Carboniferous boundary in the vicinity of Stockum is characterised by an alternation of fine clastic and coarse clastic sediments and the occasional intercalation of limestone beds and lenses.

At the base of the succession, light grey shales about twelve metres thick are exposed with some layers of 1 to 5 cm thick limestone nodules. This part of the section corresponds to the Dasberg and Wocklum limestones. It is overlain, in the former trench II section, by the approximately 35 cm thick, strongly weathered Hangenberg Black Shale. Above this follows an 11.40 m thick series of mostly micaceous, grey shales with a few intercalations of dark shales and thin sandstone beds. The following 3.20 m show then an alternation of grey shales, which are partly very crumbly, and sandstones, which can reach a bed thickness of up to 55 cm. Particularly the highest of these sandstone beds have a higher carbonate content up to 40% (Fig. 8).



**Fig. 8** The Stockum section and its  $\delta^{13}\text{C}_{\text{org}}$  dynamics, carbonate content and total organic carbon content

Above the last thick sandstone bed follows another series (2.30 m thick) of predominant shales, in which a number of mostly very dark, more or less nodular limestone beds are intercalated. Most of these contain a high content of sand. Embedded in the lowest part of this series are several layers of isolated dark grey limestone lenses, which yielded the so-called Stockum Fauna (Schmidt 1924; Korn 1984, 1994; Clausen et al. 1994). The section is completed by a series of 3.30 m thick grey shales with about 25 intercalated, 2–8 cm thick, uneven, sideritic carbonate beds, which yielded no macrofossils.

**Biostratigraphy:** Biostratigraphic data are available from conodonts, ostracods and miospores; in addition, there are ammonoids from the Stockum Limestone. According to the

conodonts, the lower part of the section is an equivalent of the Wocklum Limestone and yielded mainly species of the genera *Bispathodus* and *Palmatolepis*, while the upper part with black limestone beds and lenses yields the so-called *Protognathodus* Fauna. *Siphonodella sulcata* was not recorded, possibly for facies reasons. The Devonian-Carboniferous boundary can, based on this index species, thus not be drawn based on empirical data.

Drewer

The outcrop investigated is the eastern one of two abandoned quarries at the eastern side of the road between Belecke and Drewer. We sampled two sections:

- (1) The complete section at the former northern entrance to the quarry (= Drewer WA; 51.49424° N, 8.35675° E); here a succession from the Dasberg Limestone (late Famennian) to siliceous rocks of the late Tournaisian is exposed.
- (2) The steep face on the north-western flank of the quarry (= Drewer WJ; 51.49380° N, 8.35619° E), about 40 m south-west of the northern entrance. This section is partly accessible only by rope descent; it exposes a section from the Dasberg Limestone to basal Hangenberg Limestone.

**Previous investigations:** The so-called eastern Provinzial quarry of Drewer, which was abandoned in the late 1950s, is one of the most frequently visited outcrops in the Rhenish Mountains by geologists. There are several reasons for this: the excellent outcrop conditions, the fossil content and numerous interesting sedimentary structures and phenomena. Hardly any other of the European Devonian-Carboniferous boundary sections allows such a deep insight into the temporal development of the sedimentation area. Hardly any other has yielded as many fossil groups in continuous succession. Therefore, the outcrop is particularly important for stratigraphic classification and correlation.

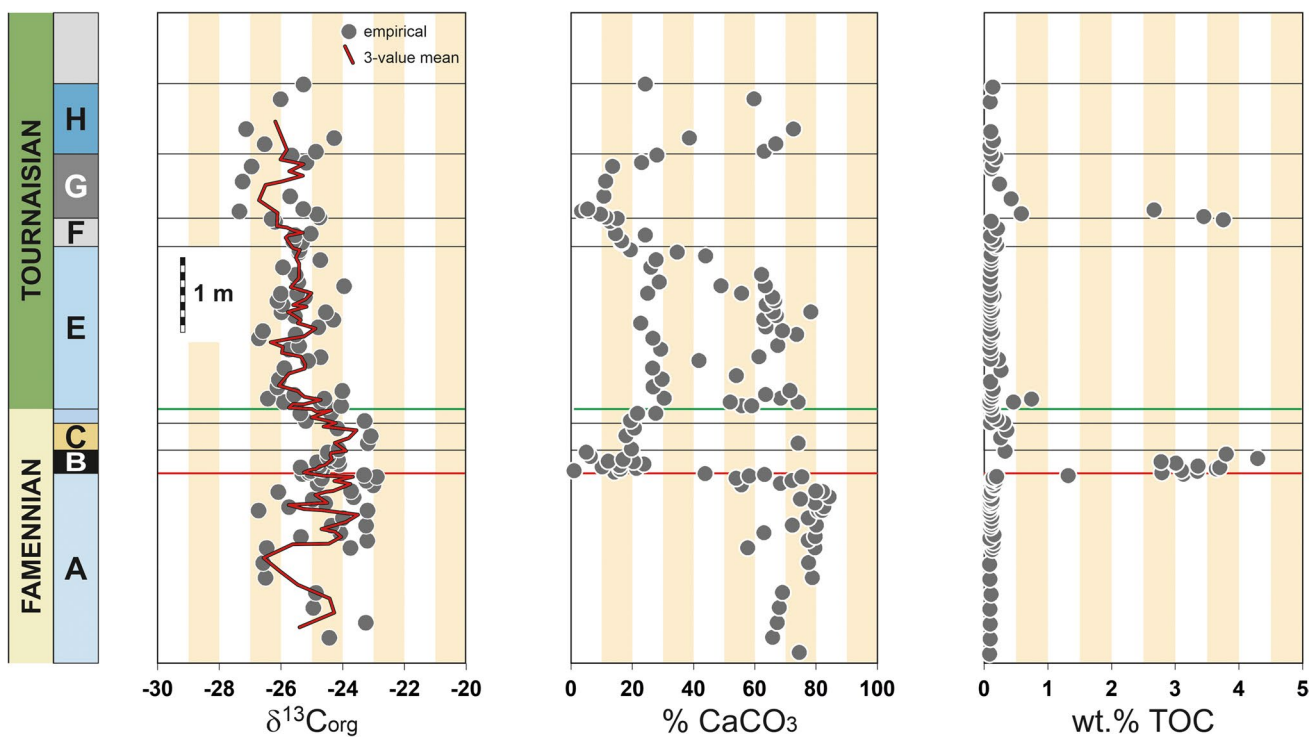
Becker et al. (2016b) gave a comprehensive overview of the research history of the Drewer outcrops; this review also includes studies with individual fossil descriptions. The long list illustrates the intensity of research dedicated to the outcrops, which began in the late 19th and early 20th centuries (Denckmann 1895; Schmidt 1922). However, systematic

section logs were rarely published. A first detailed description of the Devonian-Carboniferous boundary section was apparently given by Staschen (1968) and Ziegler (1971). Further detailed descriptions of the section, including the presentation of conodont data, were provided by Clausen and Leuteritz (1984), Ziegler (1988), Clausen et al. (1989) and Clausen and Korn (2008).

Korn et al. (1994) examined 16 parallel sections along the western (WA to WJ) and northern (NA to NF) faces in this outcrop and made a lateral correlation of these. This showed that the Wocklum Limestone and the Hangenberg Limestone are relatively well correlated along the entire outcrop, but that the interval between the two rock units shows considerable lateral differences. These differences are mainly evident in the varying occurrences of black shales and sandstones.

Kumpan et al. (2015) investigated the Drewer section using various petrophysical (gamma-ray spectrometry, magnetic susceptibility) and geochemical (X-ray fluorescence spectrometry and inorganic carbon isotope geochemistry) methods; they emphasised the potential of these methods for detailed regional correlation.

**Lithological succession (Fig. 2):** Above a 25 to 30 cm thick, dark grey shale layer, which can be interpreted as equivalent to the *Annulata* Black Shales, follow about eight metres of late Famennian, grey nodular limestone beds of 4 to 8 cm thickness. These beds are usually separated by 2 to 5 cm thick shale interbeds, which become less important in the higher part (Dasberg and Wocklum limestones).



**Fig. 9** The Drewer WA section and its  $\delta^{13}C_{org}$  dynamics, carbonate content and total organic carbon content

The carbonate content of the limestone nodules is usually between 65 and 80%; the TOC content is usually less than 0.05% (Fig. 9). Starting from the section at the former northern quarry entrance (WA section), it can be seen that the thickness of the interbedded shales increases towards the south-west, but that the shales become thinner towards the east and almost wedge out. Indications of a palaeotopography with an elevation located in the east are provided by several synsedimentary slip folds, which affect small areas of a few centimetres thickness but also rock packages more than 1 m thick (Clausen and Leuteritz 1984, p. 91). The differences between the individual sections are not easy to explain and are probably related to the particular palaeotopography of the depositional area. For the interpretation of the various sections that were measured in the outcrop, it is important to keep these synsedimentary displacements of sediment bodies in mind.

A unique feature in the section is a 50 m long, lenticular intercalation of a mica- and clay-rich sandstone lens up to 40 cm thick, which is intercalated between the highest beds of the Wocklum Limestone. It was termed Drewer Sandstone by Becker et al. (2016b). Such a sandstone is not known from any other Devonian-Carboniferous boundary section in the Rhenish Mountains and it is only known from the western quarry face. It yielded numerous deformed specimens of *Postcymenia evoluta* (Korn et al. 1994) and is thus clearly separated from the ammonoid content of the higher sandstone beds, which contain assemblages with prionoceratids.

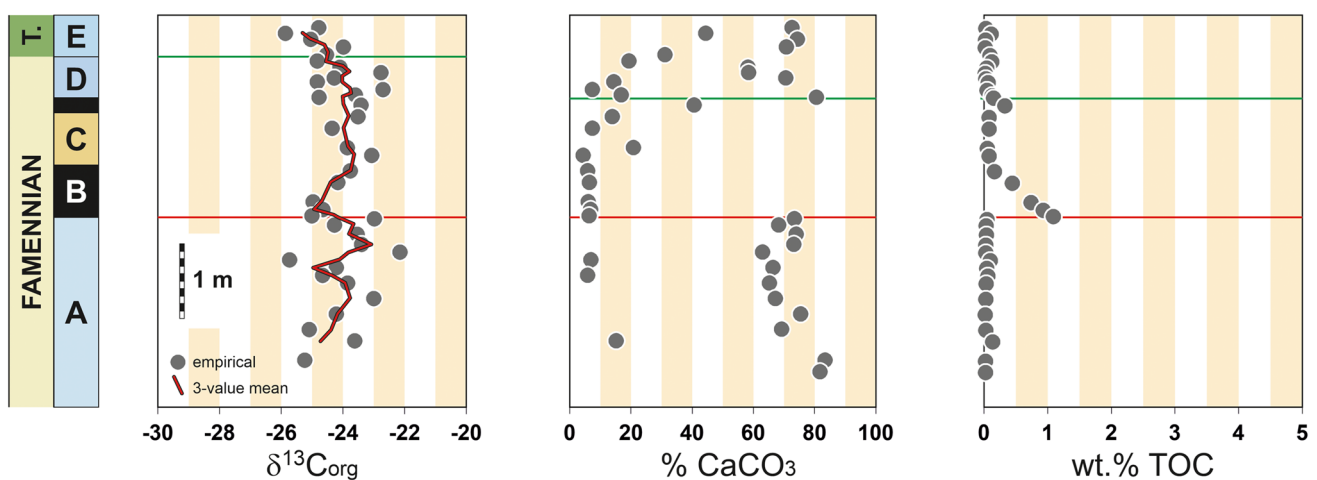
Above this sandstone lens follows an interval of Wocklum limestone only about 10 cm thick. This horizon consists mostly of small, dark grey, slightly silicified and often pyrite-bearing limestone nodules embedded in black shales. Compared to the main part of the Wocklum Limestone, the carbonate content in this layer is reduced (to 40–75%) and

the TOC content is increased (1.0–1.3%). It may be possible that this comparatively high TOC content is an indication of beginning hypoxic conditions already at the time with continuing carbonate production. The limestone nodules are quite fossil-rich and contain the typical ammonoid assemblage of the *Wocklumeria denckmanni* Zone.

The overlying Hangenberg Black Shale varies in thickness; in the WA section it has a thickness of 32 cm. Here it appears to be unweathered; it is a pitch-black, crumbly disintegrating shale layer with a TOC content between 2.7 and 4.3%. It is increasingly weathered and bleached in the parallel sections of the same outcrop when exposed closer to the surface, losing most of the organic carbon. In section WJ (about 60 m southwest of section WA), the TOC content at the base of the black shale is 1.35% and decreases steadily upwards to 0.1% (Fig. 10).

The Hangenberg Black Shale wedges out completely from the northern entrance towards the east after 25 metres. Towards the south-west, on the other hand, it becomes increasingly thicker and contains an intercalation of grey shales and a micaceous, coarse-grained and in places obliquely layered sandstone. This irregular lenticular sandstone differs from the sandstone between the uppermost layers of the Wocklum Limestone in that it contains a lower clay content. It yielded only prionoceratid ammonoid remains.

The black shale above this sandstone bed is, in the parallel sections, very irregular in its thickness and composition. In the WA section, it is just visible as a millimetre-thick dark horizon and in the WB section 20 metres towards the south-west, it has a thickness of four centimetres. Further towards the south-west, it becomes up to 60 cm thick but varies in the content of sand and silt. Important for the stratigraphic interpretation of the Hangenberg Black Shale is the occurrence of small, bituminous limestone nodules in the uppermost part of



**Fig. 10** The Drewer WJ section and its  $\delta^{13}\text{C}_{\text{org}}$  dynamics, carbonate content, and total organic carbon content

this unit. These occur in three layers in the southern sections of the north-western quarry wall (WF to WJ); they contain low-diverse but distinct ammonoid assemblages with *Cymaclymenia nigra* (Korn 1991; Korn et al. 1994). Walliser (1996) criticised the previous assumption of an undisturbed succession; he explained the occurrence of two black shale layers with ductile deformation of the black shale sediment caused by sediment load with subsequent sliding and resulting in a mixture of sediments. As can be impressively seen at the northern quarry face, slump faults of various size suggest a westward (probably downslope) displacement of sedimentary bodies. They may be responsible for a duplication of the sedimentary succession. As a result of this critics, Clausen and Korn (2008) published a modified synthetic section of the Devonian-Carboniferous boundary beds at Drewer, including only one black shale horizon.

For the interpretation of the succession of rocks and fossils at the Devonian-Carboniferous boundary at this locality, it is crucial to know the original sedimentary context in this outcrop. The main question here is whether this is a normal, undisturbed succession or whether there is a doubling of the black shale horizon. It is also particularly important for gaining insight into the interpretation of other, mostly much smaller, outcrops of the Devonian-Carboniferous boundary layers. In their review paper on the Drewer section, Becker et al. (2016b) modified the synthetic section previously published by Clausen and Korn (2008) in adding the putative second black shale layer. They followed thus the primary hypothesis (Korn 1991; Korn et al. 1994) that there is a continuous succession of sediments with two different black shales. Becker et al. (2016b, 2021) were probably not aware of the critical statement by Walliser (1996) and used the sections for outlining a Hangenberg Event scenario including two black shales, which were putatively caused by repeating transgressive phases.

In the WA section there is a fairly compact sandstone bed almost 40 cm thick. This has a lenticular extent of about 40 m and wedges out in both south-western and also eastern direction. It is likely that the sandstone bodies embedded in black shales further to the south-west belong to this unit. It is remarkable that, in the south-western sections, the sandstone bed is much less clearly separated from the shales below and above.

Above the black shale and sandstone units, 10 cm of hard, partly silty shales follow in all measured sections; ammonoids were only found in two places (section WB: *Postclymenia evoluta*; section WG: *Stockumites* sp.).

The Hangenberg Limestone has a thickness of 2.25 m and consists of a rhythmic succession of grey, brownish weathered nodular limestone beds with mudstone interbeds of up to 20 cm thickness. The carbonate content is between 55 and 75% and the TOC content is usually below 0.05%.

The base of the Hangenberg Limestone is heterochonous in the studied sections. Ideally (in sections WA and WB), the unit begins with four thin limestone layers, which lie approximately in the middle of a 60 cm thick shale package. However, the nodular beds gradually wedge out in a south-westerly direction, starting with the lowest of the four. The lowest bed is not present in the sections on the northern quarry wall. The fourth limestone layer of profile WA, which is always surrounded by shale layers about 15 cm above and below, is clearly visible in almost all sections and serves as an important correlation horizon. The succession of the higher parts of the Hangenberg Limestone is quite uniformly formed in all measured sections (Korn et al. 1994).

Above the uppermost three limestone nodule layers of the Hangenberg Limestone follow 40 cm of brittle shales with low carbonate and organic carbon content (12–25% CaCO<sub>3</sub>; 0.02–0.13% TOC). Separated by a sharp boundary, 85 cm of brittle alum shales follow, containing masses of phosphoritic nodules in the upper 16 cm (Siegmond et al. 2002). The content of organic carbon is particularly high at the base of the unit and varies greatly between the sampled horizons; it reaches a maximum of 3.8%.

Overlying the alum shales follows a package 95 cm thick, which is built up by five 5–42 cm thick, very hard, brittle limestone beds. These beds are separated by dark grey siliceous shales. They were usually called Erdbach Limestone (e.g. Clausen and Leuteritz 1984); Korn (2006) reduced this term to the limestones locally deposited on dead Devonian reefs and, therefore, introduced the new term Kattensiepen Member.

**Biostratigraphy:** The Drewer section can probably be considered as one of the most intensively studied sections at the Devonian-Carboniferous boundary in terms of biostratigraphy. The succession of conodonts is well known, at least as far as the Wocklum Limestone and the Hangenberg Limestone are concerned; however, data are lacking for the clastic interbeds (e.g. Korn et al. 1994; Clausen and Korn 2008). Ammonoids occur quite frequently, but are usually poorly preserved and do not allow a clear identification. However, they support the conodont stratigraphy and partly allow an insight into the fossil record of the clastic strata (e.g. Korn 1991; Korn et al. 1994).

#### Marsberg

**Location:** The stratigraphic section is a subsurface outcrop in the abandoned copper ore mine of Marsberg. It is exposed in the so-called 680 m crosscut of the Kilianstollen (Kilian gallery; geographic data of the gallery entrance = 51.45361° N, 8.81876° E).

**Previous investigations:** The copper ore mine of Marsberg was one of the three most important copper deposits in Germany and had been in operation since the 10th century

(Slotta 1983). Therefore, it was intensively studied, at least with regard to the deposit characteristics and the general geological frame (Stribrny 1989; Farrenschon and Oesterreich 2008). A detailed investigation of the sedimentary succession and the geochemical properties was carried out by Stribrny (1989) and recently comprehensively presented by Stribrny et al. (in press).

The Devonian-Carboniferous boundary strata (Wocklum and Hangenberg shales) at Marsberg are quite monotonous and consist mainly of grey shales, interrupted by the Hangenberg Black Shale (Stribrny et al. in press). Carbonate nodules are rarely embedded in the shales; such micritic limestone nodules occur in the upper part of the Wocklum Shale; they are particularly frequent in the range 0.40–0.20 m below the base of Hangenberg Black Shale. Two thin tuffite horizons occur 1.20 and 0.70 m below the Hangenberg Black Shale; three further tuffite horizons follow in the Hangenberg Shale 5.00, 5.35, and 5.40 m above the base of the Hangenberg Black Shale.

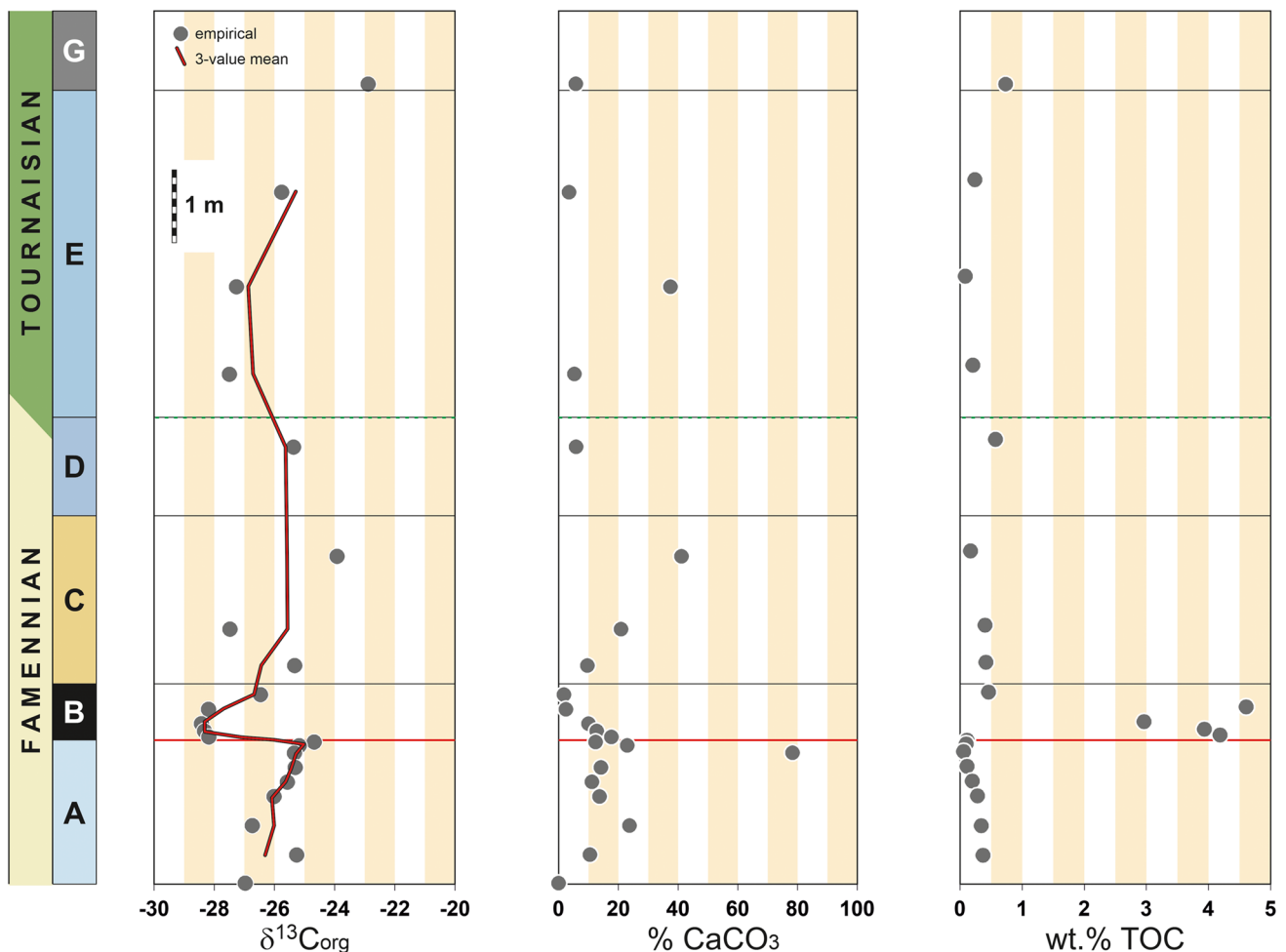
The shales have usually a carbonate content of 10–15% and the organic carbon content is less than 1% (Fig. 11).

About 8 m below the top, the conspicuous 0.8 m thick Hangenberg Black Shale is intercalated. This layer is demarcated by a sharp lithological boundary with a conspicuous colour change from dark grey to black at the base, while upwards there is a rather continuous transition into the grey shales. Occasionally, the Hangenberg Black Shale reaches an organic carbon content of 8% (Stribrny et al. in press).

**Biostratigraphy:** Biostratigraphic data are not available for the section.

## Methods

We sampled fresh rock material from eight sections (at seven localities) across the Devonian-Carboniferous boundary described above. A total of about 360 samples were taken. In the limestone-dominated sections, we sampled each nodular limestone horizon (and additionally the shale interbeds in the Drewer section); in the shale-dominated sections, we took samples at 0.20–0.50 m intervals.



**Fig. 11** The Marsberg section and its  $\delta^{13}\text{C}_{\text{org}}$  dynamics, carbonate content, and  $\delta^{13}\text{C}_{\text{carb}}$  dynamics



We used the standard lab procedures for processing and analysing the samples. Each sample was first cleaned and visually examined for mineral veins and weathered surfaces. Only clean samples were powdered; one to two grams of this powder was weighed and decalcified with dilute hydrochloric acid. From the residue, 50–70 mg was taken for  $\delta^{13}\text{C}_{\text{org}}$  measurement. Stable isotope analysis and concentration measurements of carbon were performed simultaneously with a THERMO Fisher Delta V isotope ratio mass spectrometer, coupled to a THERMO Flash EA 1112 elemental analyser via a THERMO Fisher ConFlo IV-interface in the stable isotope laboratory of the Museum für Naturkunde, Berlin. Stable isotope ratios are expressed in the conventional delta notation ( $\delta^{13}\text{C}$ ) relative to VPDB (Vienna Pee-Dee Belemnite standard). Standard deviation for repeated measurements of lab standard material (peptone) is generally better than 0.15 per mill (‰) for carbon. Standard deviations of concentration measurements of replicates of our lab standard are <3% of the concentration analysed.

Carbonate contents were determined by the loss of weight during the decarbonisation process with hydrochloric acid and is given in weight percent. TOC has been analysed by combustion of the decalcified samples in a Thermo 1112 Flash EA elemental analyser during the TOC isotopic measurements.

## Results and discussion

### Geochemical dynamics in the Devonian-Carboniferous boundary beds

All geochemical data assembled in the present study are shown in the supplementary material (Online Resource 1). The lithostratigraphic units distinguished by us show in parts very characteristic trends in their carbonate content, content of organic carbon and carbon isotope values ( $\delta^{13}\text{C}_{\text{org}}$ ), which allow to record a stratigraphic succession (Fig. 12):

**(A)** Upper part of the Wocklum Limestone and its argillaceous equivalents. – The carbonate beds and nodules usually have a carbonate content of 80–85%; the organic carbon content lies between 0.04 and 0.16% (mean value = 0.08; Wocklum) or between 0.01 and 0.05% (Effenberg, Drewer). In the Drewer section occurs an increase in organic carbon content in the uppermost centimetres of the Wocklum Limestone; 1 cm below the top of the formation, the TOC content rises to 1.26%, which is ten times the value just one centimetre below. A similar pattern has not yet been demonstrated in any other section. However, this could also be due to near-surface weathering in most of the sections; in the Wocklum section, for

example, the top 12 cm of the Wocklum Limestone are intensively weathered and decalcified.

In the time-equivalent shale-dominated section of Marsberg, the carbonate content of the shales is usually between 10 and 15%. The TOC contents of the shales are not fundamentally different from the carbonate beds of other sections; they usually oscillate between 0.01 and 0.1%.

All examined sections of the Wocklum Limestone show an enrichment in  $^{13}\text{C}$  carbon isotope. At Apricke, a  $\delta^{13}\text{C}_{\text{org}}$  increase from  $-27\text{‰}$  to  $-24\text{‰}$  can be seen in the upper 2.00 m of the Wocklum Limestone, but the value drops back to  $-25.7\text{‰}$  in the highest sample 2 cm below the top.

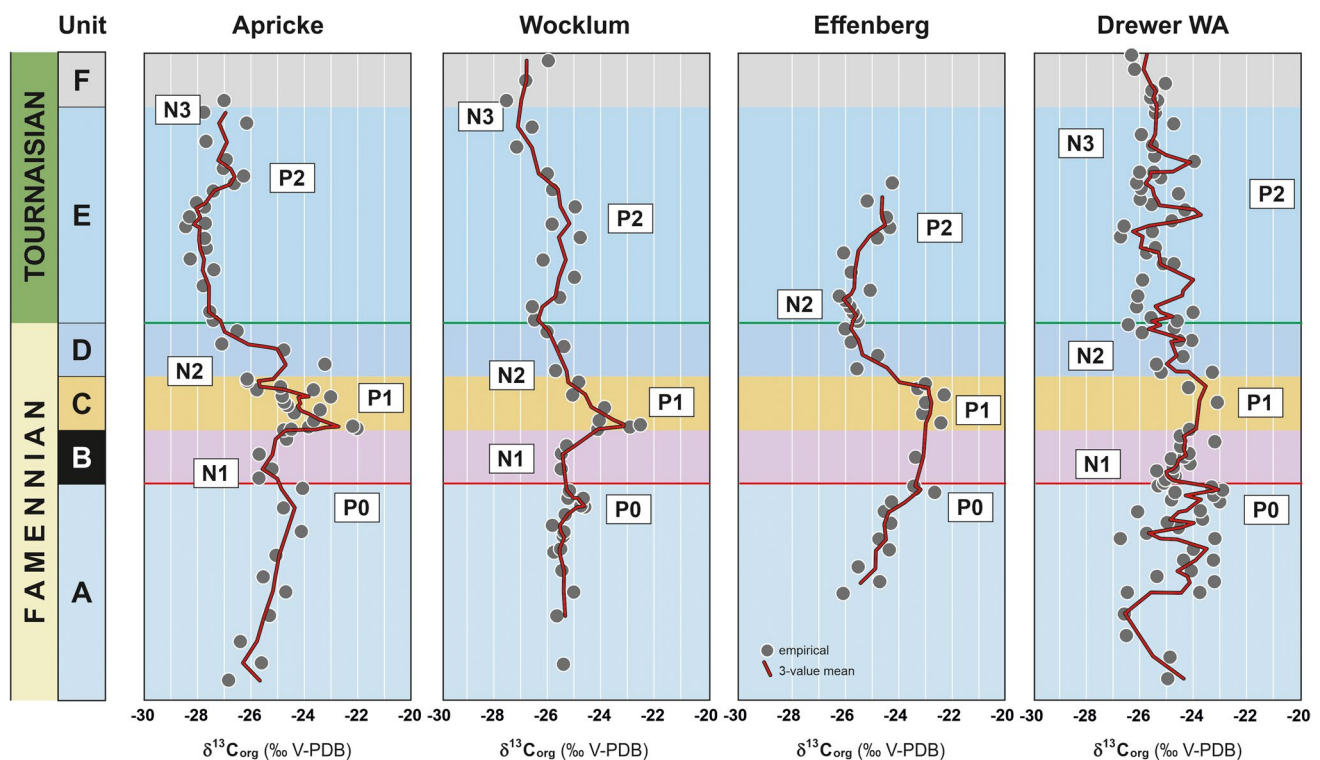
At Wocklum this pattern is less evident; the values rise discontinuously from  $-25.6\text{‰}$  to  $-24.6\text{‰}$  in the uppermost 2.00 m of the Wocklum Limestone. Although less conspicuous, a decrease can also be seen in the highest sample of this section.

The Drewer WA section shows a stronger oscillation of the values within the Wocklum Limestone, but there is also a general trend towards heavier values; the sample 4 cm below the top shows the heaviest value with  $-22.9\text{‰}$ . As in the Apricke section, there is also a very rapid decrease immediately below the top of the Wocklum Limestone. The two samples at 2 and 1 cm below the top yielded values of  $-23.3\text{‰}$  and  $-25.3\text{‰}$ , respectively. At Effenberg, the positive excursion means an increase from  $-26\text{‰}$  (one metre below the top) to  $-22.5\text{‰}$  (8 cm below the top); in the highest two samples from the Wocklum Limestone (5 and 2 cm below the top) the value goes back to  $-23.3\text{‰}$ .

The positive excursion can also be seen in Marsberg; however, the drop directly below the Hangenberg Black Shale has not been recorded so far.

**(B)** Hangenberg Black Shale. – Depending on the degree of weathering, the unit can have a colour ranging from pitch black to light brown; the colour reflects the organic carbon content. In outcrops below the weathering zone, the organic carbon content in the fresh material normally reaches about 5% (Drewer, Marsberg); however, near-surface weathering in some sections (Apricke, Wocklum) has reduced the content to one tenth or even less, and the original black colour has turned into a grey-brown.

The influence of weathering on the TOC content can even be studied in lateral sections in the Drewer quarry. While the TOC content in section WA (at the former north entrance) oscillates between 2.7 and 4.3% and shows no vertical trend, it is clearly below this in section WJ (60 m southwest of WA), which is closer to the surface. At the base of the largely bleached black shale, it has a value of 1.3% and decreases to a value of 0.11% towards the top. In the Marsberg section, the lower 0.50 m of the



**Fig. 12** Schematic correlation of four of the investigated sections and their  $\delta^{13}\text{C}_{\text{org}}$  curves. P0, N1 etc. refer to positive and negative excursions

Hangenberg Black Shale has TOC contents of 3.0–4.5%; upwards the content decreases rapidly, although a further 0.30–0.40 m is dark grey in colour. In this section, the reduced decrease in the TOC towards the top is not caused by weathering but represents an almost continuous decrease of organic carbon in the sediments.

The Hangenberg Black Shale is characterised by light  $\delta^{13}\text{C}_{\text{org}}$  values; the lowest values occur usually at the base of the unit. These values are very similar in most of the sections; it is  $-25.7\text{‰}$  at Apricke,  $-25.5\text{‰}$  at Wocklum,  $-25.1\text{‰}$  at Drewer WA and Drewer WJ; however, Marsberg deviates significantly with  $-28.2\text{‰}$  and thus shows the by far lightest values of the studied sections.

**(C)** Hangenberg Shale and Hangenberg Sandstone. – It is the unit with the greatest lateral changes in lithology, which range from calcareous shales (Aprath, Marsberg) to silty shales (Apricke, Wocklum) to an alternating bedding of shales and sandstone (Effenberg, Stockum, Drewer). Despite these differences, the TOC contents are quite similar; the mean values of the localities range between 0.08% (Wocklum) and 0.24% (Drewer WA). However, weathering near the surface could have led to partial depletion at least in some of the sections.

The  $\delta^{13}\text{C}_{\text{org}}$  curve of this rock unit is characterised by a strong positive excursion, which continues the trend that has already started in the Hangenberg Black Shale. The

total increase, compared to the base of the Hangenberg Black Shale, is  $+3.7\text{‰}$  at Apricke,  $+3.0\text{‰}$  at Wocklum and  $+2.0\text{‰}$  at Drewer. The top of this interval shows a drop of the  $\delta^{13}\text{C}_{\text{org}}$  to values similar to the base. A similar record was published by Shizuya et al. (2020) for north-eastern Vietnam.

In the Aprath section, the lower 8 metres belong to this rock unit. The  $\delta^{13}\text{C}_{\text{org}}$  curve of this interval shows a remarkably low variation (slightly more than  $1\text{‰}$ ) when compared to Apricke, where variation between  $22.1\text{‰}$  and  $26.2\text{‰}$  was recorded.

**(D)** Stockum Limestone and lateral equivalents (basal part of the Hangenberg Limestone). – The limestone beds and lenses of the Stockum Limestone usually contain a lot of sand material, so the carbonate content usually only reaches about 70–80%. However, in the ammonoid lenses with lower sand content, the carbonate content can exceed 90%. The TOC content in the five studied samples ranges from 0.03% to 0.16% (mean = 0.09%), which is about the same as in the Wocklum Limestone. The three thin, platy limestone beds at Wocklum show a similar picture; their TOC content, with a mean value of 0.085%, is about twice as high as in the typical Hangenberg Limestone above.

In the Stockum Limestone and lateral equivalents, there is a clear drop in the  $\delta^{13}\text{C}_{\text{org}}$  curve in all sections, which

can be as low as  $-5‰$  in some sections. The lightest values are mostly in the upper range and the trend continues upwards.

This negative excursion is also clearly pronounced in the clastic sections. At Stockum the decrease in the curve at the base of the Stockum Limestone is about  $-3.5‰$ . This drop is much smaller at Aprath with about  $-1.8‰$ .

**(E)** Main part of the Hangenberg Limestone and lateral argillaceous equivalents. – The Hangenberg Limestone is a fairly uniform unit, occurring in very similar lithology in many sections. The carbonate content of the limestone beds and nodules is somewhat lower than in the Wocklum Limestone and usually ranges between 70 and 80%. When compared to the Wocklum Limestone, the Hangenberg Limestone shows higher organic carbon contents. They are between 0.02% and 0.07% (mean = 0.05%) at Wocklum and between 0.015% and 0.075% (mean = 0.036%) at Effenberg.

In the Drewer sections, the carbonate content is lower than in the other sections and mostly range between 60 and 70%. The shale interbeds at Drewer usually have a carbonate content of 20–30%. The TOC content in the carbonate beds and nodules is on average 0.025%; in the shale interbeds it is twice as high.

The main part of the Hangenberg Limestone shows a continuation of the decrease of the  $\delta^{13}\text{C}_{\text{org}}$  curve. The curve is not uniform in the sections of the Hangenberg Limestone, but the largest, lower part of the unit is characterised by very light values ( $-28‰$  at Apricke,  $-26‰$  at Wocklum,  $-25.5‰$  at Effenberg). Only in the upper part of the Hangenberg Limestone a weak positive excursion of the curve occurs.

**(F)** Shales between the Hangenberg Limestone and the Kahlenberg Formation. – The unit could only be studied in the Wocklum and Drewer sections. The average carbonate content of the shales is low, namely 10% (mean TOC = 0.04) at Wocklum and 17% (mean TOC = 0.08) at Drewer.

**(G)** Kahlenberg Formation and lateral equivalents. – The alum shales of the Külben Member (time equivalent to the Kahlenberg Formation) have a low carbonate content, which increases in the Drewer section from about 10% at the base to about 28% at the top of the member. Almost diametrically, the TOC content decreases from the base (3.7%) upwards to 0.03–1.03%. These values are consistent with the time-equivalent Kahlenberg Formation values from the Eisenberg borehole (Ghazwani et al. 2018). A single sample from the base of the Kahlenberg Formation of Marsberg is comparable to Drewer, although with a lower TOC content. The carbonate content is 6% and the TOC content is 0.88%. At Drewer, there is another negative excursion of the  $\delta^{13}\text{C}_{\text{org}}$  curve within the Külben Member, which goes back to a value of  $-27‰$ .

Previously published  $\delta^{13}\text{C}_{\text{org}}$  data for the Devonian–Carboniferous boundary

Kaiser et al. (2006) investigated three sections, Haselbachtal on the northern margin of the Rhenish Mountains as well as Grüne Schneid and Kronhofgraben in the Carnic Alps, but only with a rather small number of samples.

The data presented by Kaiser et al. (2006) for the Haselbachtal section show similarities but also differences to the Apricke section studied by us. It should be noted that these two sections, which have a lateral distance of only 17 km, are very similar in their lithological succession and even a bed-by-bed correlation is possible (Korn and Weyer 2003). Kaiser et al. (2006) had two samples from the Hangenberg Black Shale; the lower one shows a value of  $-26‰$ , while the upper value jumps up to  $-22‰$ . Such a steep increase within the Hangenberg Black Shale was not found in any of the sections studied by us; the steep increase only occurs in the grey Hangenberg Shale above.

Another discrepancy exists at the transition from the Hangenberg Shale to the Hangenberg Limestone. According to Kaiser (2005) and Kaiser et al. (2006), the lower limestone bed in the Hasselbachtal section shows a very high value of  $-22‰$ , while the basal carbonates of the Apricke and Wocklum sections in our study already show light values ( $-24.8‰$  and  $-25.5‰$ , respectively). In both sections the negative excursion starts already in the upper part of the Hangenberg Shale.

The two sections in the Carnic Alps also seem to show a positive excursion at the Devonian–Carboniferous boundary interval, but the rough sample density, only 13 samples from the Grüne Schneid and 10 samples from the Kronhofgraben, does not allow a clear statement. However, it is remarkable that for the Grüne Schneid section a decrease in  $\delta^{13}\text{C}_{\text{org}}$  values is directly at the base of the *Siphonodella sulcata* Zone, whereas in the Kronhofgraben section this only starts within this zone. However, this contradiction was not discussed by Kaiser et al. (2006) and Kaiser (2007).

Zhang et al. (2020) showed a  $\delta^{13}\text{C}_{\text{carb}}$  curve for the Long'an section (southern China). In parallel, they studied  $^{238}\text{U}$  isotopes and showed a curve that has some similarities with the  $\delta^{13}\text{C}_{\text{carb}}$  curve, but is in some aspects also similar to the  $\delta^{13}\text{C}_{\text{org}}$  curve in the Rhenish Mountains. They named the negative and positive peaks in the  $\delta^{238}\text{U}$  curve with the symbols N and P.

Possible reasons for the  $\delta^{13}\text{C}_{\text{org}}$  fluctuations across the Devonian–Carboniferous boundary

Main processes involved in the formation of organic matter in sediments are primary biological productivity, decomposition of organic matter and final diagenesis. Many of these processes show isotope effects resulting in the carbon isotopic composition, but it is widely believed that  $\delta^{13}\text{C}_{\text{org}}$

in sedimentary rocks originates mainly from primary production of organic matter (e.g. Westerhausen et al. 1994). However, the bulk  $\delta^{13}\text{C}_{\text{org}}$  in sedimentary rocks is often formed from a mixture of organic matter from different origin (terrestrial versus marine) and it is therefore hard to distinguish what the main source of the  $\delta^{13}\text{C}_{\text{org}}$  values is (e.g. Mook 2000). The  $\delta^{13}\text{C}_{\text{carb}}$  in bulk sedimentary rock samples is often thought to represent the carbon isotopic composition in the dissolved inorganic carbon of the concomitant aquatic environment (Mook 2000).

Therefore, the interpretation of the  $\delta^{13}\text{C}$  curves spanning the Devonian-Carboniferous boundary must consider changes in the sedimentary regime from limestone/shale alternation to black shale, to shale with sandstone intercalation and back to limestone/shale alternation. This succession is usually interpreted to be related to eustatic sea-level fluctuations at the beginning of a glaciation on Gondwana (e.g. Streele et al. 2000; Bábek et al. 2016).

It is remarkable that the positive excursion with the largest amplitude largely coincides with the deposition of the Hangenberg Shale (incl. Hangenberg Sandstone). Especially the sandstone beds are sometimes rich in plant debris (Keupp and Kompa 1984). It is therefore possible that the isotope curve was influenced by the terrigenous input in a time of increasing vegetation on land and soil formation (e.g. Algeo et al. 1995). However, the positive excursion has been found in all investigated sections in the Rhenish Mountains, regardless of their lithology. Therefore, it is at least a basin-wide phenomenon. The results of Kaiser et al. (2006) from the Carnic Alps, however, demonstrate far-reaching similarities with another sedimentary basin and sections that are almost free of clastic material. This may be an indication for a global phenomenon driven by climate changes.

Analyses of  $\delta^{13}\text{C}_{\text{org}}$  have rarely been carried out on Devonian-Carboniferous boundary sections; therefore, only limited data is available for a comparison of  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  curves. Kaiser et al. (2006) noticed somehow resembling courses of the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  curves in the Grüne Schneid section that is entirely built up of carbonates; however, the amplitude of the positive excursion in the  $\delta^{13}\text{C}_{\text{org}}$  curve is significantly higher than in the  $\delta^{13}\text{C}_{\text{carb}}$  curve. In the other two sections, this could not be examined because of the intercalation of clastic sediments and lack of  $\delta^{13}\text{C}_{\text{carb}}$  data. Kaiser et al. (2006) excluded a significant contribution from terrestrial organic material, pointing to the amorphous structure of the organic material in the Hangenberg Black Shale. The higher TOC content was attributed to a marine origin and increased primary production. However, their interpretation of the two  $\delta^{13}\text{C}$  curves was based on the assumption that the positive excursion already begins in the Hangenberg Black Shale. This was not confirmed by our investigations; we only found significantly higher values in the  $\delta^{13}\text{C}_{\text{org}}$  curve above this horizon, which itself yielded

the most negative values. Hartenfels et al. (2022) have also shown this in the Wocklum section; the  $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{13}\text{C}_{\text{org}}$  and TOC curves for the section in the road embankment; these curves largely agree with those we found in the section in the old quarry.

A composite  $\delta^{13}\text{C}_{\text{org}}$  curve for the Devonian-Carboniferous boundary

The eight sections under study vary in their lithological succession and can therefore be assigned to different bathymetric positions on the shelf. The probable bathymetric succession of the sections Effenberg – Drewer – Wocklum – Apricke – Stockum – Marsberg – Aprath represents positions on a deep submarine rise along the slope into the basin. This diversity of sections allows to correlate geochemical data of various facies and to create a composite  $\delta^{13}\text{C}_{\text{org}}$  curve. This curve can be correlated with the lithostratigraphy and biostratigraphy of the individual sections (Fig. 13).

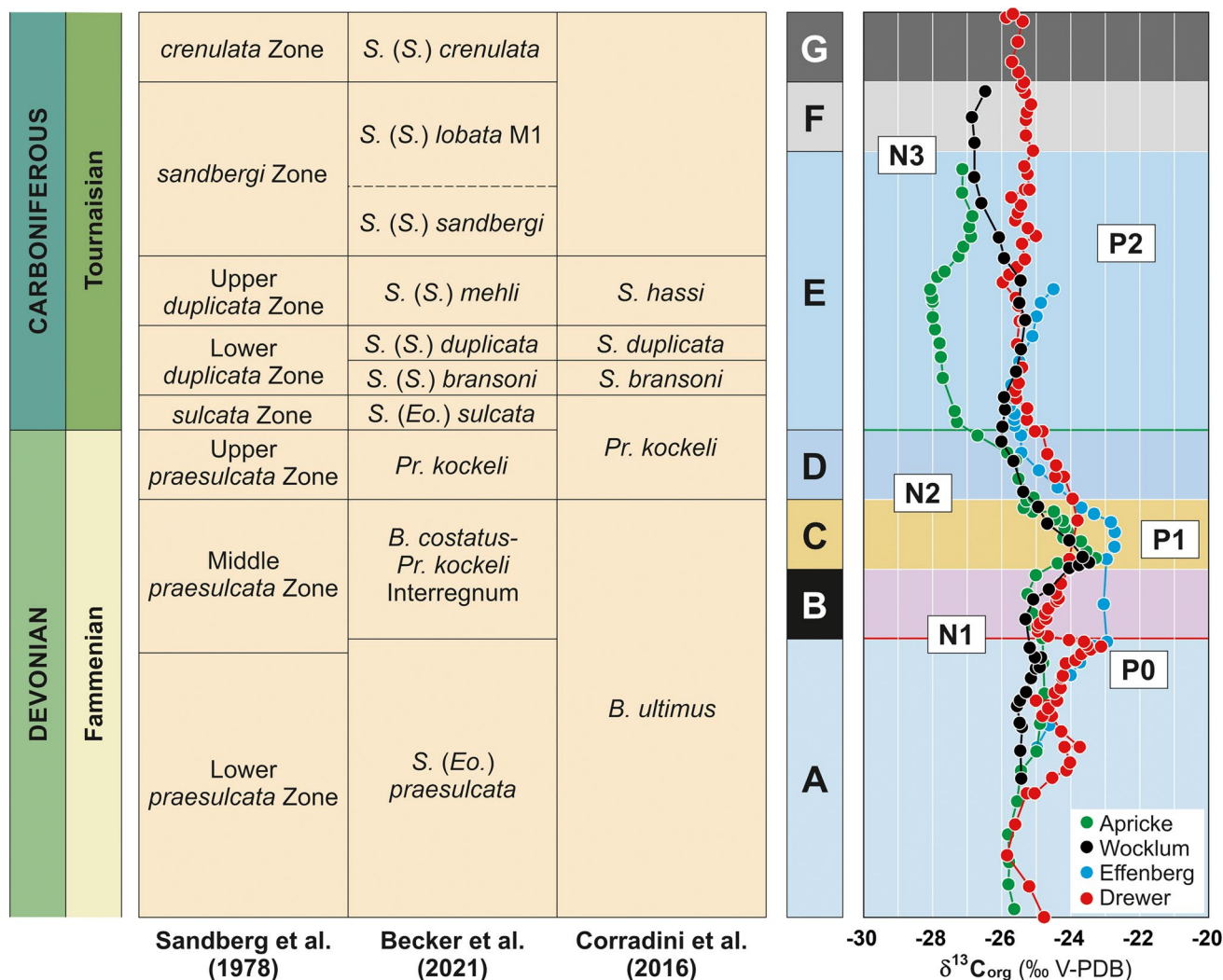
The  $\delta^{13}\text{C}_{\text{org}}$  curves of the examined sections show a distinct variation with values ranging between  $-22$  and  $-28\text{‰}$ . Several successive positive and negative excursions can be recorded, which, in case of completeness, occur in each of the sections.

Following the terminology proposed by Zhang et al. (2020) to describe the  $\delta^{238}\text{U}$  curve in the Lang'an section in South China, we propose here a terminology for the  $\delta^{13}\text{C}_{\text{org}}$  curve across the Hangenberg Event. This terminology proposed here names the positive (P) and negative (N) excursions in the  $\delta^{13}\text{C}_{\text{org}}$  curve as follows in ascending order:

P0 – A slow increase in the  $\delta^{13}\text{C}_{\text{org}}$  curve can be observed in the upper part of the Wocklum Limestone and its time equivalents; the maximum values occur about 20–10 centimetres below the top of the unit (upper part of the Lower *praesulcata* Zone in old terminology).

N1 – The sudden and rapid decrease beginning in the uppermost 10–20 centimetres of the Wocklum Limestone reaches the minimum values at the base of the Hangenberg Black Shale (highest part of the Lower *praesulcata* Zone). This decrease of 1.0–1.5‰ can be detected in all sections with fully preserved Hangenberg Black Shale (Apricke, Wocklum, Drewer); at Effenberg this negative excursion is not preserved because of the condensation of the Hangenberg Black Shale.

P1 – A steep increase beginning in the upper part of the Hangenberg Black Shale and continuing into the Hangenberg Shale and Hangenberg Sandstone (Middle *praesulcata* Zone) is preserved in all of the continuous sections. In the Apricke section as well as the Wocklum section, the highest values occur already at the base of the Hangenberg Shale (20–30 cm above its base); they show an increase of 3.0–3.5‰ higher than in the Hangenberg



**Fig. 13** Schematic correlation of four of the investigated sections, based on conodonts and  $\delta^{13}\text{C}_{\text{org}}$  curves. *S.*: *Siphonodella*; *Eo.*: *Eosiphonodella*; *Pr.*: *Protognathodus*; *B.*: *Bispathodus*. Lithological units: **A** Wocklum Limestone; **B** Hangenberg Black Shales; **C**

Hangenberg Shales and Sandstone; **D** Stockum Limestone and lateral equivalents (basal part of the Hangenberg Limestone); **E** Hangenberg Limestone; **F** unnamed shale; **G** Belecke Member

Black Shale. In sections with condensed succession of the Hangenberg Shale and Hangenberg Sandstone (Effenberg, Drewer), the positive excursion is less clearly developed, but nevertheless well recognisable.

**N2** – A sudden decrease occurs at the transition from the Hangenberg Shale (and Hangenberg Sandstone) into the basal part of the Hangenberg Limestone and its time equivalents such as the Stockum Limestone (Upper *praesulcata* Zone and lower part of the *sulcata* Zone). The decrease in values occurs immediately below the ammonoid assemblage known as the “Stockum Fauna”. Normally, very negative values continue upwards into the Hangenberg Limestone. The negative excursion shows, in the investigated sections, a drop in the  $\delta^{13}\text{C}_{\text{org}}$  values between 1.5 and 2.5 ‰.

**P2** – A weak positive excursion occurs in the middle of the Hangenberg Limestone, but a precise correlation in the investigated profiles is not yet possible.

**N3** – In the uppermost part of the Hangenberg Limestone a weak negative excursion is visible, which continues in the sections of Wocklum and Drewer also into the shales between the Hangenberg Limestone and the siliceous shales above.

An interdisciplinary stratigraphy for the Devonian-Carboniferous boundary

The Devonian-Carboniferous boundary is considered a boundary that is difficult to define with biostratigraphic methods. This circumstance is mainly due to the fact that

the boundary was originally placed at a significant facies change. In numerous sections of the deeper shelf, for example in the Rhenish Mountains, there occurs a clastic succession with very limited fossil content between the two carbonate formations Wocklum Limestone (latest Devonian) and Hangenberg Limestone (earliest Carboniferous).

When the Devonian-Carboniferous boundary was first defined with *Gattendorfia subinvoluta* and the selection of the standard section at Oberrödinghausen, this facies change did not play any particular role (Jongmans and Gothan 1937; Paeckelmann and Schindewolf 1937). However, in the course of redefining this limit with higher demands on precision, it was recognised that neither the previously selected index fossil nor the standard section are particularly well suited. Therefore, a new definition for the Devonian-Carboniferous boundary was proposed with “the first appearance of the conodont *Siphonodella sulcata* within the evolutionary lineage from *Siphonodella praesulcata* to *Siphonodella sulcata*” (Paproth and Streele 1984a, b).

To precisely define the Devonian-Carboniferous boundary, considerable effort was expended to find a more accurate and better to correlate boundary since the 1970s and numerous sections in the Rhenish Mountains had been studied (for more complete reference lists of the localities, see Becker et al. 2021). The most important of these are Hasselbachtal (Becker et al. 1984; Higgs and Streele 1984, 1994; Becker 1985, 1988; Claoué-Long et al. 1992, 1993; Becker and Paproth 1993; Higgs et al. 1993; Korn 1993; Kürschner et al. 1993; Luppold et al. 1994; Korn and Weyer 2003; Trapp et al. 2004; Kaiser 2005; Kaiser et al. 2006; Korn et al. 2010), Oese (Higgs and Streele 1984; Keupp and Kompa 1984; Becker et al. 1993; Kürschner et al. 1993; Luppold et al. 1994; Korn and Weyer 2003; Kumpan et al. 2015), Apricke (Paproth and Streele 1982; Higgs and Streele 1984; Luppold et al. 1994; Feist et al. 2000; Korn and Weyer 2003), Oberrödinghausen (Higgs and Streele 1984, 1994; Korn 1993; Kürschner et al. 1993; Korn and Weyer 2003; Kumpan et al. 2015), Effenberg (Luppold et al. 1994), Müsenberg (Korn 1981, 1984, 1993; Clausen et al. 1990; Luppold et al. 1994), Wocklum (Luppold et al. 1994; Hartenfels et al. 2022), Stockum (Alberti et al. 1974; Higgs and Streele 1984, 1994; Korn 1984; Higgs et al. 1993; Clausen et al. 1994), and Drewer (Clausen and Leuteritz 1984; Clausen et al. 1989; Korn 1991, 1993, 2002a; Korn et al. 1994; Clausen and Korn 2008; Kumpan et al. 2015; Becker et al. 2016b). The long, but by no means complete, list illustrates the intensive investigations at these localities. There are also other sections that have played a less important role in defining the Devonian-Carboniferous boundary (Becker et al. 2016b, 2021).

More recent biostratigraphic studies on Devonian-Carboniferous boundary sections mainly aim to replace the previously chosen index species *Siphonodella sulcata*

with another conodont species; for a detailed review of the discussions regarding this issue, see Aretz and Corradini (2021) and Hartenfels et al. (2022). Following a proposal by Corradini et al. (2011), the evolution within the genus *Protognathodus* was regarded as the more precise criterion for defining the boundary. Therefore, in recent years, the main focus has been on *Pr. kockeli* as the possible index fossil.

With the preliminary vote of the working group at the XIX. ICCP in Cologne 2019 to define the boundary with the first appearance of *Pr. kockeli* and the “top of the major regression (top of the Hangenberg Sandstone)” (Hartenfels et al. 2022), the taxonomic problem of the *Siphonodella* species was put aside. However, the fundamental problem with the facies changes and the associated poor availability of index fossils was not eliminated, but even intensified. The problem lies even in the definition itself; the boundary would be placed at the transition from sandstones with few available fossils to shales, which also yielded only few fossils. Furthermore, it appears not clear if the “top of the major regression” is isochronous in the section on a regional and a global scale.

Carbon isotopes can make an important contribution to correlate sections in different lithology. The disadvantage of this method, of course, is that there is no specific data comparable to the occurrence of index fossils; only isotope curves can be compared for sections in which a lithostratigraphic or biostratigraphic age determination has taken place at the same time. The carbon isotopes offer the great advantage that an analysis is always based on empirical data. The absence of data, as is usual in biostratigraphy, does not pose a problem.

Carbon isotopes provide particularly important data for the precise definition of the boundary between the Devonian and the Carboniferous, because very marked changes in the ratio of  $^{12}\text{C}$  and  $^{13}\text{C}$  have taken place near the biostratigraphically defined boundary. However, these changes only seem to affect the isotope ratio in organic carbon and not the ratio in the carbon of the carbonates.

There are several theoretical possibilities to define the Devonian-Carboniferous boundary in terms of carbon isotopes: (1) at the first negative excursion (CN1), which would correspond to the onset of the Hangenberg Black Shale; (2) at the first positive excursion (CP1) and thus at the transition from the Hangenberg Black Shale to the Hangenberg Shale; (3) to the second negative excursion (CN2) and thus to the transition from the Hangenberg Shale (and Hangenberg Sandstone) to the lower part of the Hangenberg Limestone and its lateral equivalents (e.g. Stockum Limestone). The latter comes closest to fulfilling the wish of the majority in the preliminary vote during the XIX. ICCP in Cologne 2019. The negative excursion CN2 can be seen very clearly in all sections examined. It has a different amplitude in the sections; normally it is about 2 ‰. It is important to note that this negative excursion always begins below the horizon

with the so-called “Stockum Fauna” (Aprath, Effenberg, Stockum, Drewer); the lowest values occur near the base of the Hangenberg Limestone in the *Siphonodella sulcata* Zone.

## Conclusions

While the boundary between the Devonian and the Carboniferous has been drawn using ammonoids, conodonts and miospores, geochemical data have only rarely been used to assist the biostratigraphic schemes. With the help of the isotopes of the organic carbon, a distinct stratigraphic succession is documented for selected sections across various facies in the Rhenish Mountains. The  $\delta^{13}\text{C}_{\text{org}}$  curves are characterised by several positive and negative excursions; these were, with some differences, recorded in all examined sections.

The sampling of eight sections (Aprath, Apricke, Effenberg, Wocklum, Stockum; Drewer WJ, Drewer WA, Marsberg) at the northern margin of the Rhenish Mountains revealed a pattern of the following positive and negative trends in the  $\delta^{13}\text{C}_{\text{org}}$  curve:

CP0 – Positive excursion of 1–3‰ in the upper part of the Wocklum Limestone.

CN1 – Negative excursion of about 1–1.5‰, beginning in the topmost part of the Wocklum Limestone; with the most negative values at the base of the Hangenberg Black Shale.

CP1 – Positive excursion beginning in the Hangenberg Black Shale, reaching the maximum values (about 3–3.5‰ higher) in the Hangenberg Shale (and Sandstone).

CN2 – Negative excursion of about 1.5–2.5‰ during the upper part of the Hangenberg Shale (and Sandstone) and the Stockum Limestone interval. The decrease in the  $\delta^{13}\text{C}_{\text{org}}$  values ends in an interval close to the Devonian-Carboniferous boundary drawn with *Siphonodella sulcata*.

CP2 – Positive excursion of up to 2‰ in the middle of the Hangenberg Limestone.

CN3 – Negative excursion at the top of the Hangenberg Limestone and following shales.

The organic carbon isotopes can therefore make a significant contribution to the stratigraphic subdivision and regional correlation of sections in various facies and weathering status; it can complement the biostratigraphic methods.

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**Data availability** All data generated or analysed during this study are included in the supplementary information files. All sample materials are stored in the collection of the Museum für Naturkunde, Berlin.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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