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# Exceptional cameral deposits in a sublethally injured Carboniferous orthoconic nautiloid from the Buckhorn Asphalt Lagerstätte in Oklahoma, USA

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The cameral and intrasiphonal deposits of a Pennsylvanian straight nautiloid (Pseudorthoceratidae) are studied in order to understand the formation of these deposits. The specimens from the Buckhorn Asphalt deposit (Oklahoma) are exceptionally preserved including original aragonite and microstructures. The specimen investigated survived a predation attempt and shows bite marks on the phragmocone. This is the second report of an ectocochleate cephalopod and first report of an orthoconic nautiloid which survived massive damage of conch and siphuncle. For the first time, a high-magnesium calcitic mineralogy of cameral deposits is documented. These deposits were formed in alternation with aragonite in a chamber which was perforated during the unsuccessful predation attempt. The animal formed the chamber deposits throughout its entire lifetime and the siphuncle played a major role in formation of the cameral deposits.

**Key words:** Nautiloidea, Pseudorthoceratidae, predation, sublethal damage, cameral deposits, high Mg-calcite (HMC), Carboniferous, Buckhorn Asphalt, Oklahoma, North America.

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## Introduction

The formation of cameral and intrasiphonal deposits in nautiloid phragmocones has been discussed repeatedly (e.g., Fischer and Teichert 1969; Blind 1991) as their interpretation is of great importance for the understanding of habitat, palaeobiology, and mode of life of Palaeozoic nautiloids. Recently collected well-preserved orthoceratid specimens from the Middle Pennsylvanian Buckhorn Asphalt Fossil Lagerstätte (Oklahoma, USA) reveal fine details of these deposits. The fossil record is incomplete and, as a rule of thumb (which always has exceptions), the older fossils are, the more poorly they are preserved (e.g., Newell 1959; Durham 1967; Koch 1978; Valentine and Grubb 1990; Foote 1996). The Middle Pennsylvanian Buckhorn Asphalt Quarry in Oklahoma is one of the very few Palaeozoic occurrences of mollusk shell material with preserved original mineralogy (especially aragonite) and microstructures (e.g., Brand 1982, 1987; Seuss et al. 2009). Hydrocarbons intruded during or

shortly after deposition and impregnated the fossils in the deposits (e.g., Ham 1969; “Impregnation Fossil Lagerstätte” sensu Seuss et al. 2009).

This study mainly focuses on a single specimen of an orthoconic nautiloid consisting of two chambers of the phragmocone and with abnormal marks on the outside of the shell. It is assigned to the ectocochleate cephalopod-family Pseudorthoceratidae. This general identification is tentative because the cephalopod systematics of the Buckhorn Fossil Lagerstätte has not been updated for almost 50 years and the features of the outer shell of the specimen are not preserved which would allow a more detailed determination.

*Institutional abbreviation.*—BSPG, Bayerische Staatssammlung für Paläontologie und Geologie, Munich, Germany.

*Other abbreviations.*—EDX, energy dispersive X-ray microanalyzer; GADDS, general area detection diffraction system; HMC, high-Magnesium-calcite; SEM, scanning electron microscopy; XRD, X-ray diffraction.

## Geological setting

The Buckhorn Asphalt Quarry is situated about 10 km to the South of Sulphur, Oklahoma, on the northern edge of the Arbuckle Mountains in south-central Oklahoma near the Texas-Oklahoma state boundary (Fig. 1A, B). Today, the outcrop is about 150 m long, 21 m wide, and 6 m deep. The stratigraphic succession exposed in the quarry was formed during a transgressive-regressive (T-R) cycle in the Middle Pennsylvanian. The asphalt-impregnated lithic units belong to the Boggy Formation, which is an early to mid-Desmoinesian (Middle Pennsylvanian/Moscovian) unit of the Deese Group (Ham 1969; Sadd 1991).

Sediments in the Buckhorn Asphalt Quarry consist of a mixture of siliciclastic-carbonatic (bioclastic) deposits with varying grain-size (from coarse conglomerate to silty mudstone; Seuss et al. 2009). Shallow water deposits of the T-R cycle that represent the near-shore environment are dominated by gastropods and bivalves. Cree (1984) assumed a water depth of only 3 metres for the shallow water deposits and the endolithic ichnocoenosis found in these sediments indicates a palaeoenvironment in the shallow euphotic zone II to III (Wisshak et al. 2008). Plant remains and a significant amount of quartz reflect strong terrigenous input. Squires (1973) reported channel fills (see also Seuss et al. 2009), which provide evidence for recurrent high run-off from a nearby terrestrial source. Poor sorting in some units in the quarry documents periodic mass flow deposition (Seuss et al. 2009). Deeper water deposits of the T-R cycle are rich in cephalopods (“cephalopod coquina”; Seuss et al. 2009), especially of orthoconic forms which are represented by the genera *Michelinoceras*, *Pseudorthoceras*, *Mooreoceras* (Unklesbay 1962), and *Thoracoceras* (RHM personal observation). These cephalopod-rich deposits were probably formed in an off-shore environment as indicated by the fauna and the sediment succession. Their fossil content, addressing various topics, was repeatedly studied by e.g., Smith (1938), Stehli (1956), Unklesbay (1962), Fischer and Teichert (1969), Ristedt (1971), Brand (1987, 1989a, b), Blind (1987, 1991), Grégoire (1988), Mutvei (2002), Kulicki et al. (2002), and Wisshak et al. (2008).

## Material and methods

**Material.**—The studied specimen of the *Pseudorthoceratidae* (BSPG 2011 0002; Fig. 2) was recovered from the cephalopod coquina beds. It is well preserved and displays two complete phragmocone chambers with thick cameral deposits. Due to the saturation of sediments and fossils with hydrocarbons in the quarry (Fig. 1C, D) the specimen preserves original nacreous luster. The specimen is about 3 cm long and has a diameter of 2 cm. On both, the ventral and the dorsal sides two distinct shell abnormalities are present.

Twenty thin sections of additional orthoconic nautiloid specimens (Fig. 3; BSPG 2011 0003–BSPG 2011 0010)

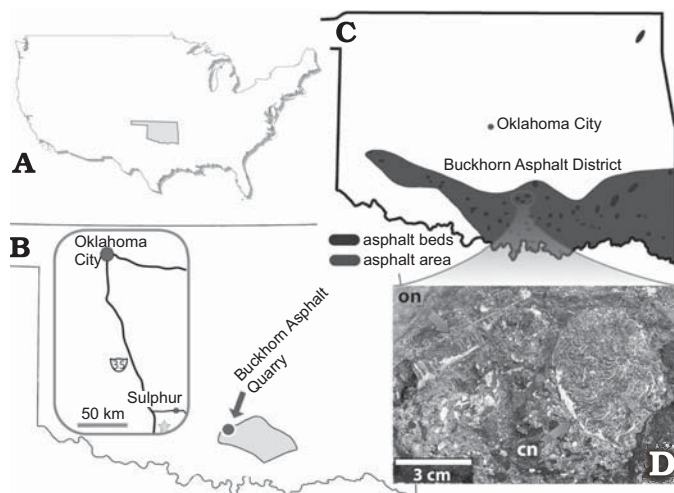


Fig. 1. Setting and features of Oklahoma and the Buckhorn Asphalt Quarry. **A.** Geographical position of Oklahoma (modified after [www.stepmap.de](http://www.stepmap.de)). **B.** Section of Oklahoma with the Buckhorn Asphalt Quarry northeast of the Arbuckle Mountains (indicated with the arrow and the dot); inserted sketch of the geographical position of Sulphur and the Buckhorn Asphalt Quarry area (marked with a star). **C.** Main section of Oklahoma with the “asphalt belt” of Oklahoma and the Buckhorn Asphalt Quarry within this belt (marked with the oval); modified after Hutchinson (1911: 5). **D.** Hydrocarbon-soaked cephalopod coquina with an orthoconic (on) and a coiled nautiloid (cn) specimen.

from the Buckhorn Asphalt Quarry were prepared to compare their cameral deposits with those present in the specimen BSPG 2011 0002. These additional nautiloids were collected from the same cephalopod coquina that yielded specimen BSPG 2011 0002.

**Methods.**—The specimen BSPG 2011 0002 was studied using scanning electron microscopy (SEM), an energy dispersive X-ray microanalyzer (EDX), a general area detection diffraction system (GADDS) combined with X-ray diffraction (XRD), and in a series of longitudinal serial thin sections. To prevent disintegration of the specimen the asphalt was not removed during processing. After photographing the

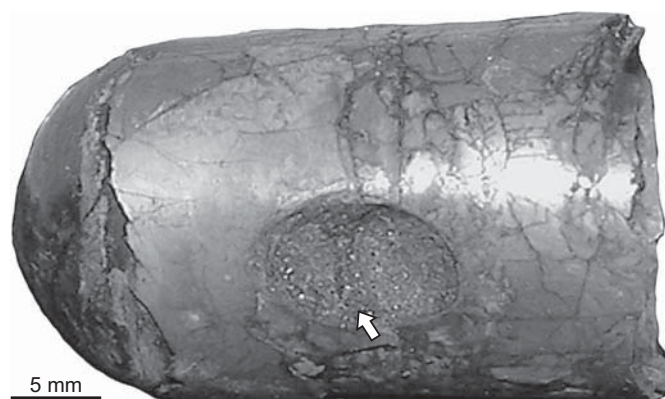


Fig. 2. Investigated orthoconic nautiloid specimen BSPG 2011 0002 from the Carboniferous Buckhorn Asphalt Quarry, Oklahoma, USA with nacreous shine and one of the marks on the conch (dorsal side of the phragmocone). In the middle of this mark a septum is visible (marked with an arrow).



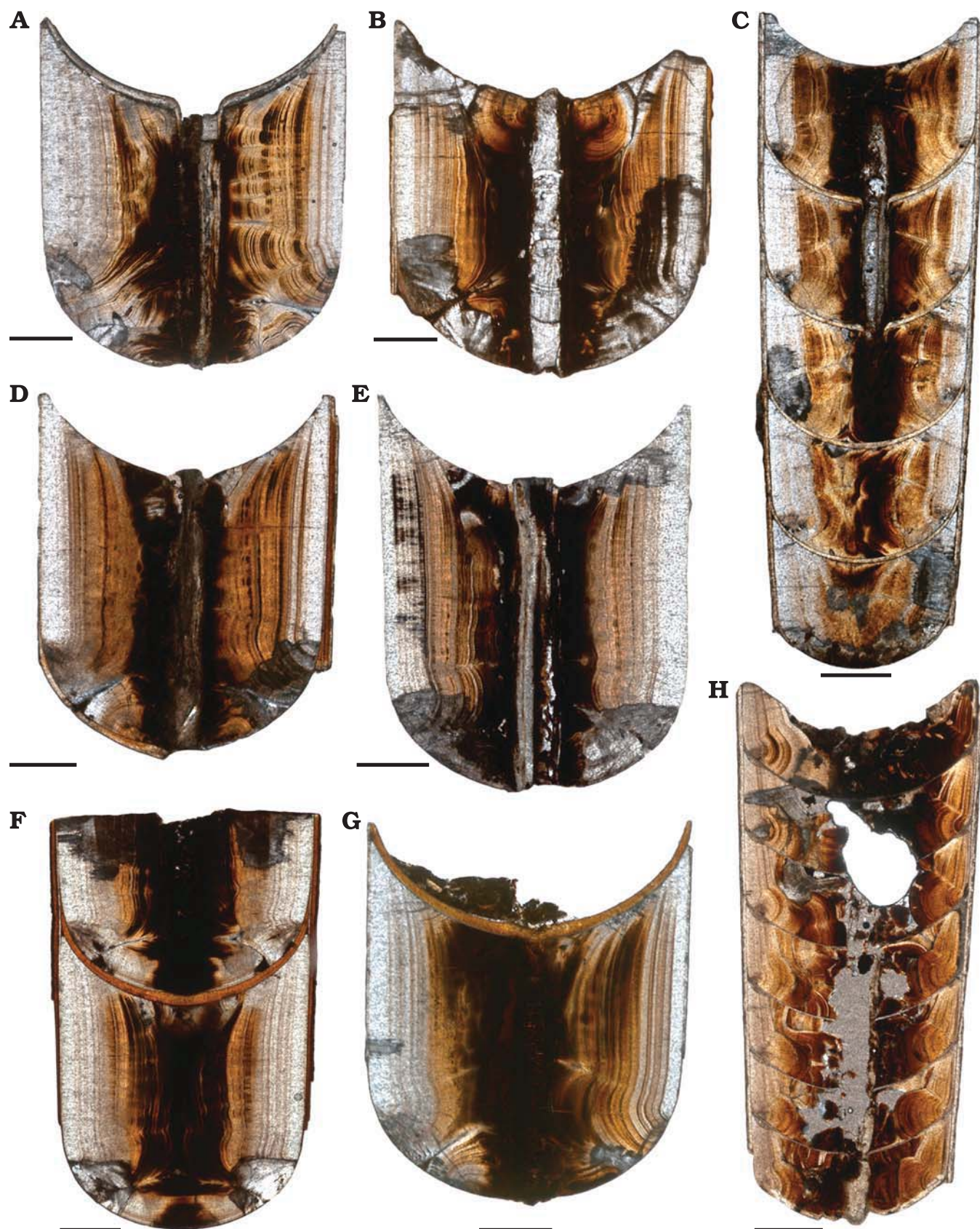


Fig. 3. Various orthoconic nautiloid specimens from the Carboniferous Buckhorn Asphalt Quarry, Oklahoma, USA: BSPG 2011 0003 (A), BSPG 2011 0004 (B), BSPG 2011 0005 (C), BSPG 2011 0006 (D), BSPG 2011 0007 (E), BSPG 2011 0008 (F), BSPG 2011 0009 (G), and BSPG 2011 0010 (H) representing at least two different undetermined genera with normal, but in part diagenetically altered cameral deposits. Generic determination is difficult because the outer test is missing and the siphuncle is not well preserved or absent and is not aim of this study. Scale bars 1 mm.

specimen, it was embedded in epoxy resin (Araldite BY158 + Aradur<sup>21</sup>) and longitudinally sectioned. The section was oriented in such way that it cut both holes in the external shell. This resulted in a section that is near the dorsal-ventral plane of symmetry and cuts the siphuncle. The distribution of the cameral deposits indicates the section is nearly parallel to the dorsal-ventral plane. Both halves of the specimen were polished and affixed to glass plates with their interior sides using the epoxy resin Biresin L84.

One part of the specimen was used for serial sectioning using a MPS 2 300 grinding device (G&N GmbH). The sample was abraded in 100 µm steps. After every step the specimen was photographed. From the final slide a thin section was prepared. The other half of the specimen was used for geochemical sampling (micromill-drilling for isotope samples) and mineralogical investigations (XRD-GADDS; SEM-EDX), and additional thin sections were prepared (Seuss et al. 2012).

A two-dimensional XRD-GADDS-detector was used to determine the shell mineralogy of the specimen. The measurements with XRD-GADDS are carried out on surfaces of objects and are site-specific and non-destructive. For this analysis, one half of the specimen BSPG 2011 0002 was fixed on a glass plate (see above), polished, and cleaned with acetone. The section was placed in the equipment and irradiated with x-rays. The emitted spectrum from the sample was transferred to a computer and reproduced as a spectrum illustrating the diffraction pattern of the reflected irradiation. This spectrum was then converted into a peak diagram. From this diagram, the present mineral phases were identified (see also Seuss et al. 2012).

Mineralogy and shell structure of the specimen were additionally investigated with EDX and SEM, respectively. The samples affixed to the glass plates (see above) were etched with EDTA (ethylenediaminetetraacetic acid) for 5 minutes in order to achieve a structured surface, rinsed with distilled water, and dried. To remove as much hydrocarbon as possible, the samples were cleaned with acetone before sputter-coating them for the investigation with the SEM and the attached EDX-detector.

For comparison with the peculiar specimen BSPG 2011 0002, additional twenty thin sections of orthoconic nautiloids (Fig. 3) from samples of the cephalopod coquina were produced. The preparation method for the thin sections was the same as that described above. These thin sections were also investigated with SEM and EDX to determine their mineralogy and shell structure.

## Results

The shells of the 20 additional specimens (Fig. 3) show no signs of damage or uncommon marks. Generally the outer tests are missing and only the inner nacreous layer is preserved. The loss of the outer shell layers is probably a result of mechanical splitting of the outer test when the conchs are

separated from the hydrocarbon impregnated matrix that surrounds the individual specimens in the coquina. The number of preserved chambers of each specimen varies. Preservation of the individual samples is variable. These specimens are presumably younger than the specimen BSPG 2011 0002 because of their smaller conch size. The septa at the adapical and adoral ends of some conchs are not preserved. Cameral deposits are preserved in all specimens. Their organic origin is suggested because of their uniform and symmetric arrangement (Fig. 3).

The pore space in the specimen with the abnormal marks on its phragmocone (BSPG 2011 0002) had been completely saturated with a complex mixture of hydrocarbons (i.e., oil). Light hydrocarbon fractions devolatilised during burial and diagenesis transforming the original hydrocarbons into asphaltic material. Sealing with hydrocarbons produced a lustrous specimen (Fig. 2) with parts of the original mineralogy and shell structure being well preserved (Figs. 4–7A<sub>1</sub>).

Specimen BSPG 2011 0002 consists of two phragmocone chambers (Figs. 2, 7). The external prismatic layer of the test is missing, leaving the inner nacreous shell layer exposed (Fig. 2). Septa are exposed on each end of the specimen (Fig. 7A). On the dorsal and ventral exterior surfaces at the position of the septum dividing the two chambers, there are two abnormalities in the form of oval openings measuring 9.5 × 6.8 mm and 6.9 × 5.2 mm, respectively (Figs. 2, 7). There are no crushed shell fragments in the interior of the holes, and no fragments were found within the sections of the chambers. The analysis of the cameral deposits of the specimen underlies thin and serial sections. The main description is based on the thin section shown in Fig. 7A<sub>1</sub> combined with the information achieved from other sections.

The connecting rings of the siphuncle of the punctured specimen are damaged in both chambers on the dorsal side (Figs. 4D, 7). In the adapical chamber, the connecting ring is dorsally broken into several fragments (Figs. 4D, 7). There is a relatively small ventral siphuncular deposit. However, siphuncular deposits are absent on the dorsal side. Cameral deposits on the outside of the connecting ring are well preserved but are only present on the ventral side of the chamber. In the adoral chamber, the dorsal side of the connecting ring is fragmented as is the cameral deposit directly attached to the outside of the connecting ring. Ventrally, cameral deposits are present on the inside and outside, and well preserved on the outer surface of the undamaged connecting ring. Small siphuncular deposits are present dorsally and at its adapical end. On the ventral side of the connecting ring, thick lenticular deposits are situated on both, the adapical and adoral, ends of this chamber. The siphuncular deposits are thicker in the adoral chamber compared with the adapical chamber. According to observations of siphuncle and deposits Björn Kröger (personal communication 2011) tentatively assigned the specimen to *Hebetorthoceras unicamera* (see also Kröger and Mapes 2005). In both chambers the cameral deposits adjacent to the connecting ring are beige (Figs. 4D, 5C, 7A<sub>1</sub>) and EDX-analyses indicate a high magnesium content (Seuss et al. 2012). Inside the con-



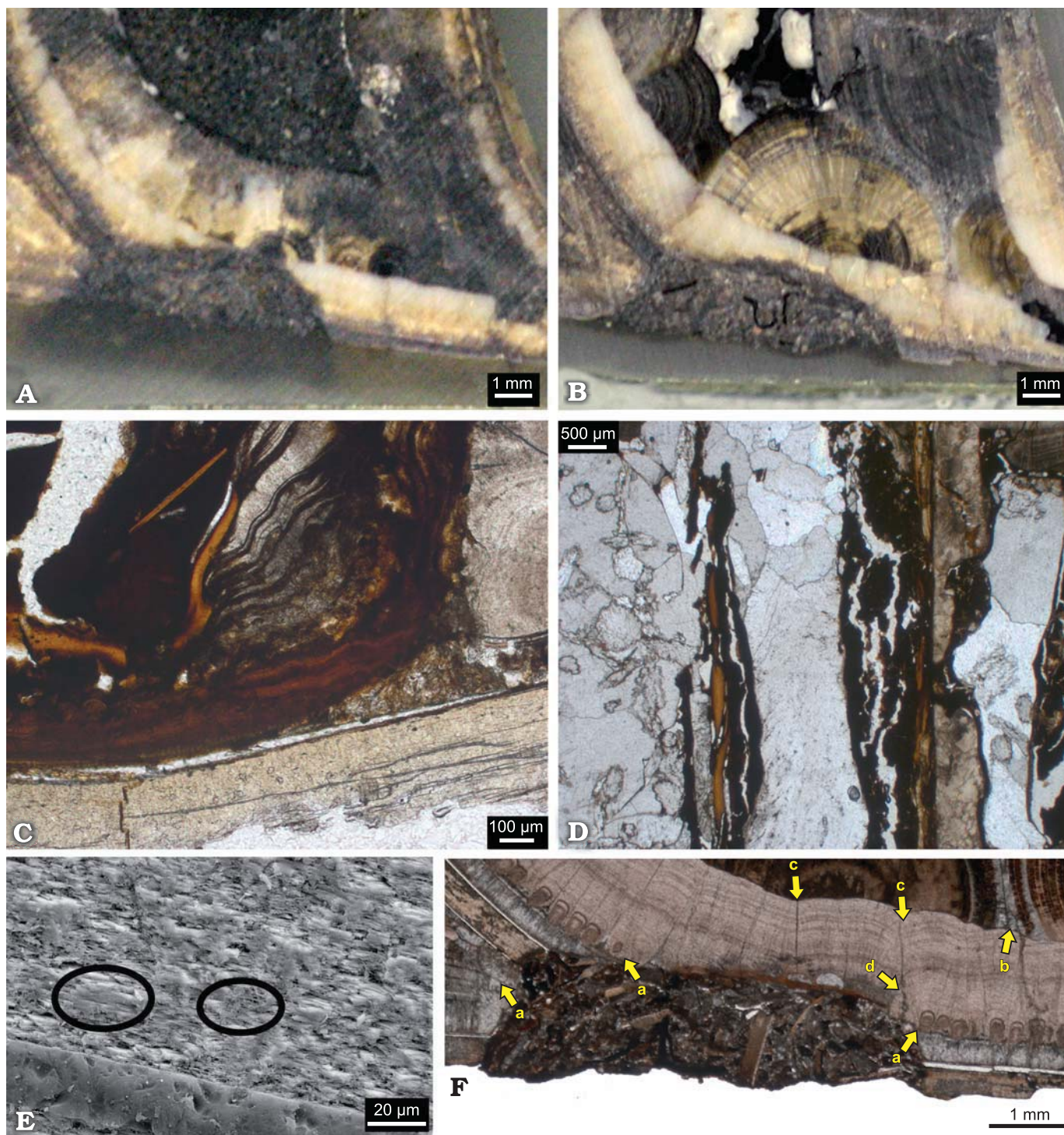


Fig. 4. Details of shell wall of the orthoconic nautiloid specimen BSPG 2011 0002 from the Carboniferous Buckhorn Asphalt Quarry, Oklahoma, USA. **A.** Venter showing the damage on the shell filled with sediment and proving that the damage extends through layer 1, thus opening the chamber for seawater, this establishes that alteration of the original cameral fluid was possible. **B.** Large spherical dark brownish deposits (layer 6; that the deposit directly above the bite mark appears whitish is an effect of the imaging technique; compare with thin section in Fig. 7A<sub>1</sub>). **C.** Siphuncular and cameral deposits in the adapical chamber; siphuncular deposits are best preserved at the adoral end of the chamber inside the connecting ring and adjacent to the ventral side of the septal neck. **D.** Fragmented siphuncle in the apical chamber with late post-mortem cement filling. Within the connecting ring there are blocky cements, hydrocarbons and some sediment, on the outside outer surface of the connecting ring cameral deposits are present. **E.** Preserved (circle on the right) and diagenetically altered (circle on the left) aragonite of the middle septum. Hydrocarbons partly cover the nacreous structure. **F.** Sector of the thin section in Fig. 7A<sub>1</sub> illustrating the area of the ventral hole. In the upper right, the boundary between the dark brown cameral deposits is visible (arrow b). On the left and right of the hole the cauliflower-like layer 3 is present, identical structures are missing directly above the bite. On the left and right of and above the hole the black deposit is present, but this layer is missing within the hole (arrows a). Vertical cracks (arrows c) through the whitish layer (layers 3 and 4) indicate that external pressure was exerted from the outside of the shell. On the right above the bite the whitish deposits shows a structure suggesting that the part left of the crack was moved upward (arrow d).



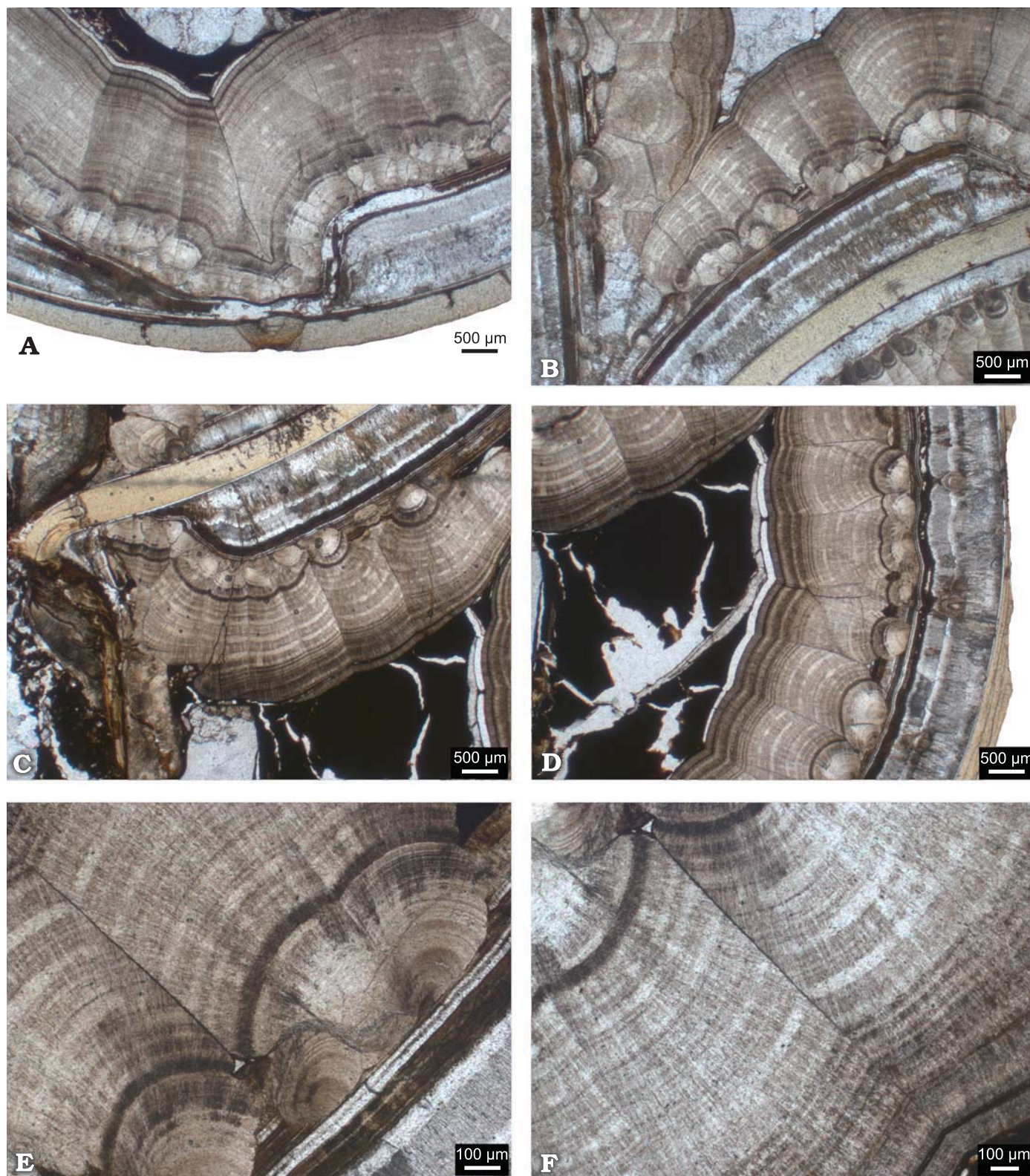


Fig. 5. Thin sections of the orthoconic nautiloid specimen BSPG 2011 0002 from the Carboniferous Buckhorn Asphalt Quarry, Oklahoma, USA illustrating the whitish cameral deposits (layers 3 and 4) in adoral and adapical chambers. **A.** Adapical septum, altered early deposits and black deposit overlain by the cauliflower-shaped and laminated whitish cameral deposits in the older chamber. **B.** Ventral side of the conch with the middle septum, early cameral deposits, the black deposit and the whitish deposits. **C.** Middle septum with ventral side of the siphuncle of the adapical and adoral chambers; hypo- and episepal deposits and the black deposit; in the siphuncle sediment and siphuncular deposits are present; in the adapical chamber the filling with hydrocarbons is obvious. **D.** Ventral side of the adapical chamber with cameral deposits and hydrocarbon filling. **E.** Whitish cameral deposits and black deposit in the adapical chamber. **F.** Whitish cameral deposit illustrating the alternation of lighter and darker layers and the grading into darker later deposits of layer 4.



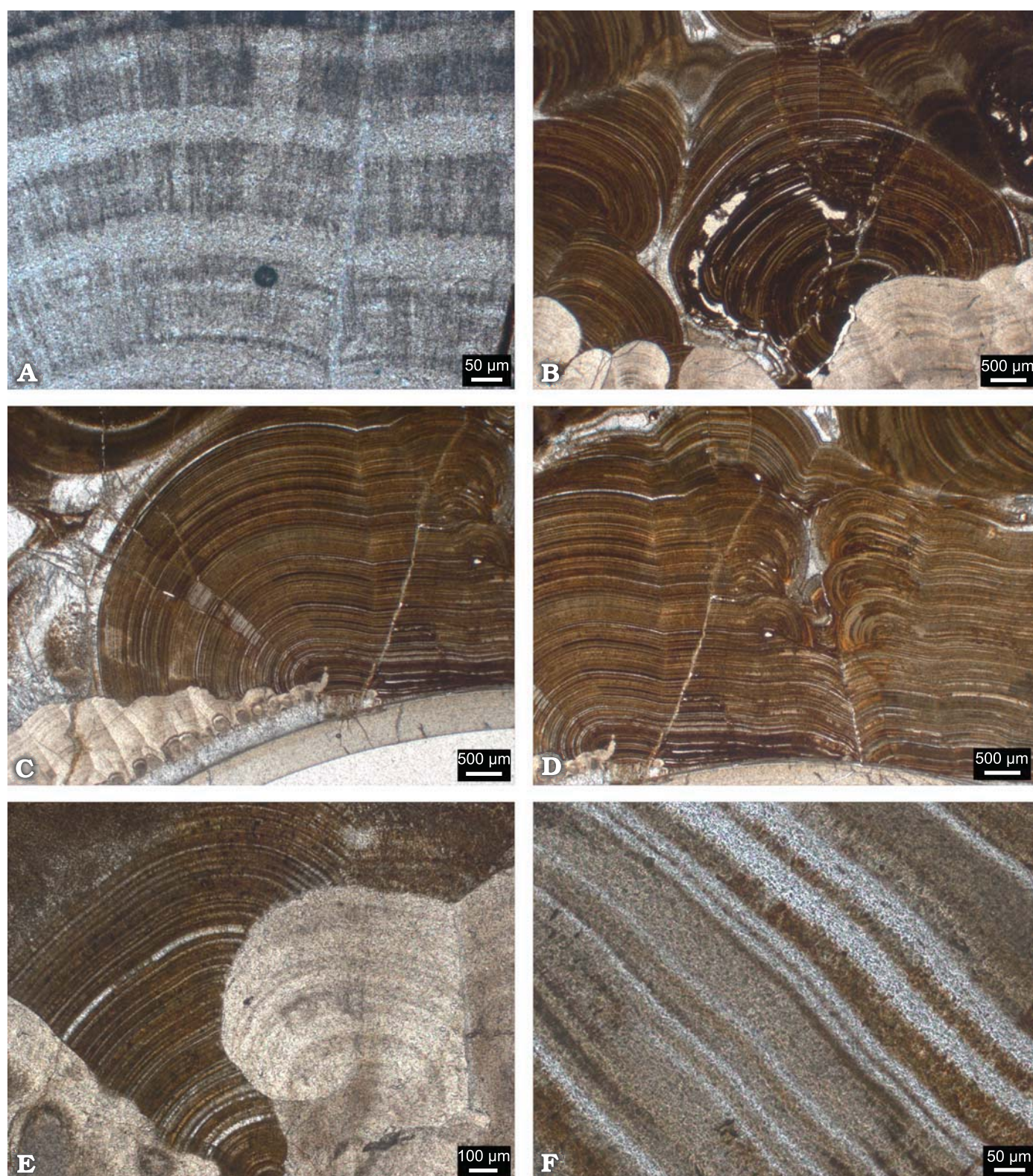


Fig. 6. Thin sections of the orthoconic nautiloid specimen BSPG 2011 0002 from the Carboniferous Buckhorn Asphalt Quarry, Oklahoma, USA illustrating the whitish (layers 3 and 4) and dark brown deposits (layer 6). **A.** Layer 4 illustrating the alternation of lighter granular and darker fibrous layers. **B.** Cauliflower-like to semi-spherical dark brown deposits (layer 6) in the adoral chamber overlying the whitish deposits illustrating the abrupt change in cameral deposition. **C.** Adoral septum with early deposits, whitish deposits and the dark brown deposits. **D.** Layered dark brown deposits in the orad chamber. **E.** Whitish and dark brown deposits in the adoral chamber illustrating the abrupt change in deposition. **F.** Dark brown deposits showing the alternation of light mineral layers and darker more organic layers.



necting ring at the septal necks in both chambers, not only lenticular siphuncular deposits are preserved (Figs. 4C, 5C), but the siphuncle void was partially filled with sediment, coarsely crystalline calcite, and hydrocarbons. The latter are mainly present in the adapical chamber, whereas sediment is concentrated in the adoral chamber (Fig. 7).

Three septa are preserved in the specimen BSPG 2011 0002 (Fig. 7). All are composed of densely packed, platy aragonite crystals as is typical for nacre (Fig. 4E). We examined the mineralogy and microstructure with XRD-GADDS (aragonite) and EDX (distinct amount of Sr). In all of the three septa the nacre has, in places, been diagenetically altered and is best preserved in the septum separating the adoral and the adapical chamber (Figs. 4E, 7). The well preserved nacre plates are about 10  $\mu\text{m}$  in diameter and 1  $\mu\text{m}$  thick, whereas recrystallised crystals measure up to 20  $\mu\text{m}$  in diameter and 3 to 4  $\mu\text{m}$  in thickness.

Episeptal, hyposeptal, and mural cameral deposits, calcite cements, and hydrocarbons fill the interior of the cameral space in both chambers of the specimen BSPG 2011 0002 (Figs. 4A–D, 4F, 5A–D, 6E, 7). The deposits in the two chambers are complex and variable. There is variation in colour, structure, mineralogy, and position of the cameral deposits in each chamber as well as on the dorsal and ventral sides of the specimen. The cements are formed by coarsely crystalline calcite and together with hydrocarbons they fill the chamber voids that were not filled by cameral deposits or sediment. In the following, all parts of the phragmocone fillings including cameral deposits as well as diagenetic cements, sediment, and hydrocarbon fillings are described according to their structure and mineralogy in their assumed chronological order of formation. The following descriptions are mainly based on the cameral deposits seen in the thin section illustrated in Fig. 7A<sub>1</sub> but also include information from SEM images, as well as other thin and serial sections. The spatial distribution of primary mineralogies/materials in the chambers is illustrated in Fig. 7B.

**Combined cameral deposits** (layer 1; Figs. 4A, B, 4F, 5A–E, 6C, 7A<sub>1</sub>).—These white/translucent deposits are relatively thin, approximately 1–3 mm thick on the ventral side of the adapical chamber and thinner on the dorsal side of the chamber. They are developed on the hyposeptal, mural, and episeptal parts on the inner surface of the septa and shell representing the earliest visible deposits in the chamber. They are present on both, the dorsum and venter of both chambers and are thicker in the adapical chamber. EDX-data indicate the presence of Sr at a low Mg-content. All deposits of this type are altered and show a granular structure in the SEM. In thin sections, they appear to be partly fibrous and also contain some blocky calcite crystals. The mural deposits were affected by the damage on the dorsal side and were penetrated on the ventral side of the adoral chamber.

**Black deposit** (layer 2; Figs. 4F, 5A–E, 7A<sub>1</sub>).—A thin black organic-aragonitic layer, about 0.1 mm thick, immediately overlies the initial episeptal, mural, and hyposeptal deposits.

It is black only in the adapical chamber on its ventral side but is present dorsally as well as in the adoral chamber. Where it is not preserved in black, the structure is still visible and the layer appears to be bleached and altered. A small-scale internal lamination is visible in the dark parts of this layer. The altered parts of this thin layer appear to be granular. In the adapical chamber a laminated structure seems to overly parts of the black deposit and fills space between the initial crystals of the whitish deposits (layer 3; see below). Whether this represents a part of layer 2 or not cannot be determined. GADDS- as well as EDX-measurements evidence the presence of Sr and organic remains in this deposit. Layer 2 is disrupted by the hole on the ventral side of the adoral chamber (Figs. 4F, 7).

**Cauliflower-like deposit** (layer 3; Figs. 4A, B, 4F, 5, 6A–C, 6E, 7A<sub>1</sub>).—This is a relatively thin layer of cauliflower-shaped hyposeptal and combined creamy white, mural as well as episeptal deposits with radial laminated structures of variable thickness overlying the thin black deposit. These deposits appear to be precipitated from “origins of mineralisation” or nuclei (Figs. 4F, 5B–E, 6C). They are present dorsally and ventrally in both chambers. The cauliflower-like structures are separated from the overlying deposit in structure and by a thin darker layer. The deposit consists of lighter and darker layers. The internal structure is fibrous. Layer 3 is absent directly above the hole in the adoral phragmocone segment but present on its left and right sides. In this chamber, it contains vertical cracks perpendicular to the damage in the conch. In the dorsal half of the adoral chamber these deposits built up small semi-spherical deposits following the dark brown deposits (layer 5; see below; Fig. 7A<sub>1</sub>).

**Light brown deposits** (layer 4; Figs. 4F, 5A–D, 7A<sub>1</sub>).—This cameral deposit is relatively thick on the ventral side of both chambers and distinctly thinner dorsally. It consists of fine, wavy, lighter and darker alternating deposits of light brownish colour, merging into a medium brown in the adapical chamber. Internally, the darker layers of the deposits are fibrous whereas the light layers are granular. The deposits are emplaced directly on the sites of the cameral deposits of layer 3 and the cracks noticed in layer 3 continue into these deposits, ending abruptly at the border to the dark brown deposits (layer 6) (Figs. 4A, B, 4F, 5A–D, 6B–E, 7A<sub>1</sub>). In the adapical chamber, layer 4 is thicker and tends to begin with darker brownish deposits in some places (Figs. 5B–D, 7A<sub>1</sub>). In the adoral chamber, the progress was immediately stopped by the dark brown deposits in a state in which layer 4 only consisted of the light brown and slightly darker layers. In the adapical chamber close to the siphuncle, the deposits appear to have been immediately terminated.

Together, the layers 3 and 4 (combined referred to as “whitish deposits”) are up to 3 mm thick. Their thickness depends on the position of the section and on the progress of development at a specific position in the chamber. They are less prominent in the adoral chamber. An alteration of the layers by diagenetic effects can be identified with GADDS- and



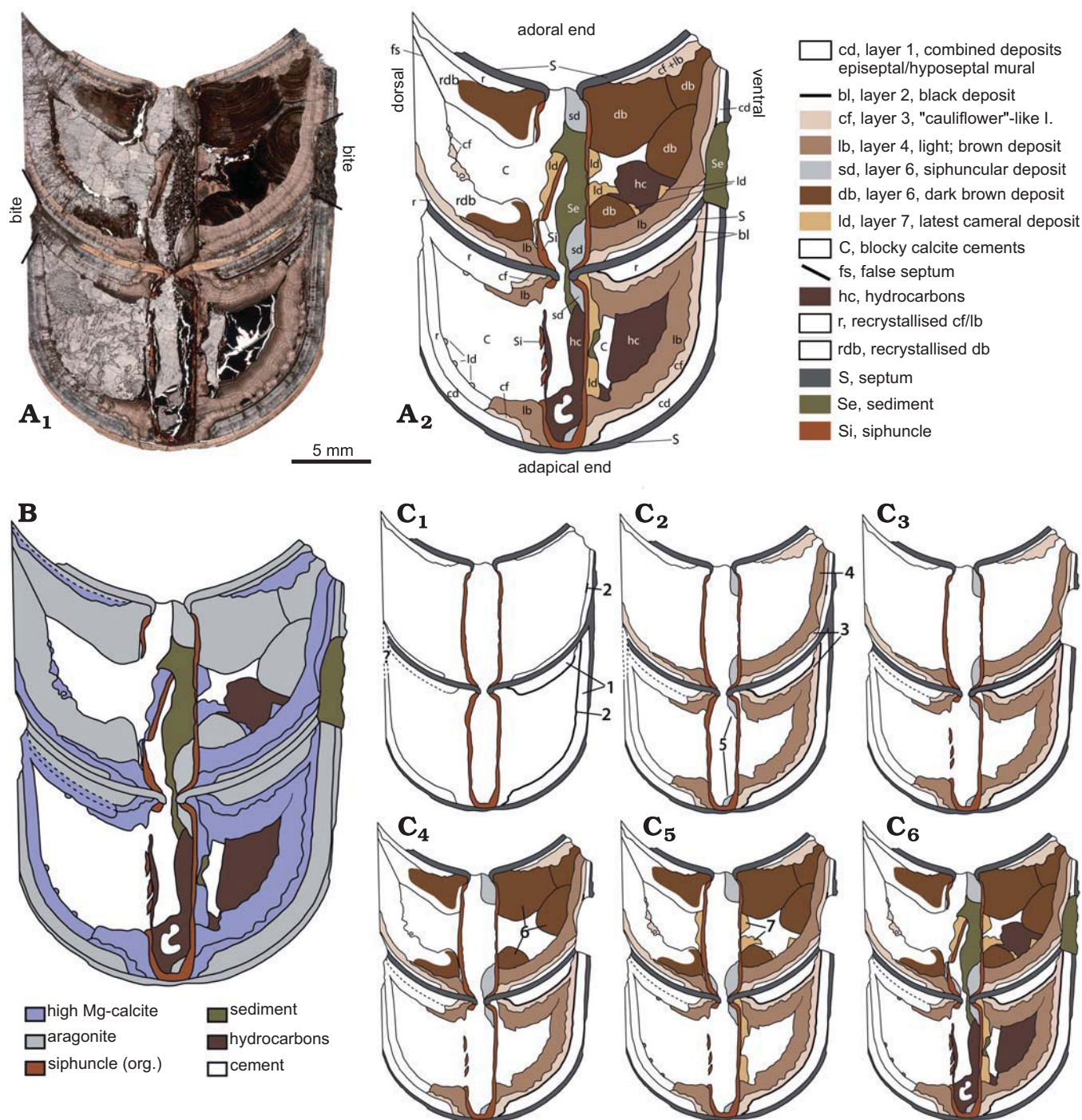


Fig. 7. Sketches of the orthoconic nautiloid specimen BSPG 2011 0002 from the Carboniferous Buckhorn Asphalt Quarry, Oklahoma, USA illustrating the distribution and formation of cameral deposits. **A**. Thin section illustrating the bite marks on the dorsal (left) and ventral (right) sides of the conch, the pre- and post-attack cameral deposits, and the post-mortem deposits. The dorsal septum was partly cut off during sectioning. **A<sub>1</sub>**, photograph, **A<sub>2</sub>**, explanatory sketch drawing. **B**. Sketch drawing illustrating the distribution of the several mineralogies/materials (HMC, aragonite, siphuncle, hydrocarbons and sediment). **C**. Hypothetical precipitation of the cameral deposits. **C<sub>1</sub>**, **C<sub>2</sub>** before, **C<sub>3</sub>** at the time, and **C<sub>4</sub>-C<sub>6</sub>** after the attack. For abbreviations and colours used see **A**. Note that the drawing is prepared from the thin section illustrated in **A<sub>1</sub>** and thus, effects of the cut through the specimen also play a role in the distribution of deposits and the individual parts of the specimen. The interpretation of the precipitation is based on thin sections, serial sections and observation in SEM. Before the attack: **C<sub>1</sub>**, the two chambers of the specimen with layers 1 and 2 (black deposit) and an intact siphuncle; the "?" denotes the suggested trend of the deposit in this area; **C<sub>2</sub>**, layers 3 (cauliflower-like deposits) and 4 (light brown deposits) are deposited and in the siphuncle the first deposits (layer 5) are precipitated. The attack: **C<sub>3</sub>**, damage marks on both sides of the specimen; on the right (ventral) the mark penetrates the cameral deposits layer 1 to 4 (see Fig. 4A). After the attack: **C<sub>4</sub>**, deposition of the unusual dark brown cameral deposits (layer 6) in the orad chamber; further growth of the deposits in the orad siphuncle (note: whether these deposited had grown further same time as the dark brown deposits were precipitated cannot be stated without doubt); **C<sub>5</sub>**, precipitation of the latest deposits in the chambers (layer 7), mainly at the siphuncle (layer 7) and in the siphuncle (note: the deposits might have started growing in this stage, see also comment on **C<sub>4</sub>**). Post-mortem: **C<sub>6</sub>**, intrusion of hydrocarbons and sediment; precipitation of calcite cements and diagenesis.



EDX-measurements, with calcite and dolomite detected by the GADDS and a relatively high Mg-content measured with the EDX.

**Siphuncular deposits** (layer 5; Figs. 4C, 5C, 7A<sub>1</sub>).—These layered lenticular deposits are present in both chambers. In the adoral chamber, the deposits are distinctly thicker than in the adapical chamber. They are present on both the dorsal and the ventral sides of the adoral siphuncle whereas in the adapical chamber they are only developed on the ventral side of the connecting ring. In both chambers they are mainly concentrated at the septal necks. EDX-measurements indicate the presence of Mg, Sr, and organic remains.

**Dark brown deposits** (layer 6; Figs. 4B, 6B–F, 7A<sub>1</sub>).—These deposits are present in the adoral chamber exclusively and nearly completely fill the ventral part of this chamber. Dorsally they are less massive. The deposits abruptly follow the whitish deposits. Both, ventral and dorsal deposits form well-developed hyposeptal and combined mural and epi-septal deposits. They are built up by a dark brown, relatively large, finely laminated structure resulting in an overall cauliflower-like to semi-spherical shape on the ventral side of the adoral chamber. On the dorsal side they appear slightly laminated. The internal alternation of light and dark layers in the deposits is caused by more mineral-rich and more organic layers. Generally, the internal structure is granular, but in some darker areas, fibre-like structures are present. Ventrally the formation of the dark deposits advanced to the point where there are distinct crystal boundaries between the single deposits (Fig. 4F: upper right: arrow b). In places, the deposits are heavily altered. EDX- and GADDS-analyses indicate the presence of Sr.

**Late cameral deposits attached to the siphuncle** (layer 7; Figs. 4D, 5C, 7A<sub>1</sub>).—These deposits likely represent the latest deposits precipitated in the chambers before the death of the animal. They are medium brown (“caramel”-coloured) and have an irregular non-laminated structure. They are irregularly distributed on the outer surface of the connecting rings of the siphuncle in both chambers. In the adapical chamber, they are only visible on the ventral side of the siphuncle. In the adoral chamber, the deposit on the dorsal side is broken at the same position as is the connecting ring. They also fill the space between the dark brown cameral deposits in the damaged chamber. Measurements with EDX indicate the presence of high amounts of magnesium.

**Heavy fractions of hydrocarbons** (hc; Figs. 4C, D, 5C, D, 7A<sub>1</sub>).—The hydrocarbons filled the remaining voids in both chambers between the cameral deposits and in the siphuncle after death. These hydrocarbons were injected into the cephalopod-bearing sediments of the Buckhorn Lagerstätte during early diagenesis of the sediment. In the adapical chamber a geopetal structure is present, indicating the approximate post-mortem shell orientation prior to tectonic movements. Cracks in the hydrocarbons are caused by outgasing of volatiles transforming the liquid hydrocarbons into asphalt.

**Sediment** (Se; Figs. 4A, B, 7A<sub>1</sub>).—Most sediment is concentrated in the siphuncle of the adoral chamber with a reduced amount in the adapical connecting ring and the adoral chamber. The sediment is only present on the ventral side of the chambers and in the connecting ring where it is overlain by blocky calcite, filling the remaining chamber space.

**Cements** (C; Figs. 4D, 7A<sub>1</sub>).—In both chambers the remaining chamber and siphuncle space is filled with cements of blocky and coarse crystalline calcite (Figs. 4D, 7A<sub>1</sub>). The even surface of the calcite in contact with the hydrocarbon infilling forms a geopetal structure.

All other 20 orthoconic nautiloid remains used for comparison show no signs of irregular cameral deposit precipitation (Fig. 3). In some cases, recrystallisation and diagenetic effects altered the cameral deposits. The deposits in these specimens also conform well to those described previously from the Buckhorn Lagerstätte by Fischer and Teichert (1969) and Blind (1987, 1991). Thus, these specimens provide a base line for the normal state of cameral and siphuncular deposit deposition in several genera. They can be compared very well with the deposits described and illustrated herein for the abnormal specimen BSPG 2011 0002 and represent our reference for the normal arrangement and composition of the cameral deposits.

## Discussion

The studied well preserved phragmocone fragments of straight nautiloids and especially the specimen with shell damage during life time facilitate to infer when and how cameral deposits were formed. Claims that such deposits were formed post-mortem (e.g., Mutvei 2002) can now be refuted. The external prismatic shell layers are lacking in all studied specimens. This can be the result of exfoliation when the specimens were removed from the matrix when collected. In theory, it is also possible that the absence of this shell layer occurred prior to burial, i.e., during transportation when the cephalopod coquina was formed. All specimens illustrated in Fig. 3 show no signs of unusual cameral deposition or any shell damage. This is different in specimen BSPG 2011 0002. Numerous cracks are apparent in the nacreous shell layer. These cracks, which are filled with hydrocarbons, are probably due to lithostatic compression after burial. If this hydrocarbon “glue” was removed, the shell would probably begin to disintegrate. There are two oval openings in the shell, one on the dorsal and the other one on the ventral side of the conch. The slightly crushed edges at their margins might have originated from diagenetic crushing of the specimen due to lithostatic load and possibly tectonic forces that have occurred in the area. In the following discussion will be on the abnormal nautiloid specimen only.

**The marks in the conch.**—A critical point in understanding the unusual sequence of cameral deposit formation is in determining what caused the holes in the nautiloid phragmocone. We suggest the following interpretation: It is well known that,



with the rise of fishes, reptiles, and cephalopods, predation among animal species in the marine realm became increasingly important as a driving force on evolutionary and macro-ecological development during the Palaeozoic and Mesozoic (Vermeij 1987). Predator and prey interactions in the Mollusca forced the evolution of defence mechanisms and methods of shell repair (e.g., Vermeij 1977; Mapes et al. 1995; Kröger 2002a; Kelley et al. 2003 and references therein; Mapes and Chaffin 2003; Nützel and Frýda 2003; Klug 2007; Ebbestad and Stott 2008; Klug et al. 2010). Some of these authors reported cases where cephalopods were attacked by larger marine animals, specifically sharks and other fish. Cephalopods represented a valuable food source for marine predators including jawed fish and aquatic reptiles (e.g., crocodiles, turtles, mosasaurs, and other aquatic reptiles) in the Mesozoic (Mapes et al. 1995; Kauffman and Kesling 1960; Kase et al. 1998; Kauffman 2004), for gnathostome fish in the Devonian (Klug 2007; Klug et al. 2010) or other cephalopods perhaps as far back as the Ordovician (Mapes et al. 1995; Kröger 2002b, c, 2004; Kröger and Keupp 2004; Klug 2007; Slotta et al. 2011 and references therein). Some of the ammonoids and bactritoids examined by Mapes (1979), Bond and Saunders (1989), and Mapes et al. (1995), as well as the cephalopods investigated by Klug (2007) show intensive shell repair, indicating the animals had survived attacks and were able to repair their conch. The conch and the siphuncle of a cephalopod are essential for the animal's buoyancy. In contrast to endocochleate cephalopods which cover the shell with tissue, the conch of ectocochleate cephalopods is exposed to the environment and thus more likely damaged. Kröger and Keupp (2004) stated that only where a mantle covers the shell, damage can be repaired. These authors suggest that surviving an injury of the phragmocone and siphuncle is nearly impossible. Anyhow, in a re-study of the ectocochleate cephalopod *Trocholites depressus* (Eichwald, 1840) with injured conch and siphuncle, they found first evidence ever of an individual surviving such a severe damage.

As already mentioned above, there are two distinct holes in the phragmocone of specimen BSPG 2011 0002, one on the ventral and one on the dorsal side. Position, preservation, sediment-filling, and shape of the holes make it unlikely that they are a result of the sampling technique or compaction. There are no shell fragments within the holes, indicating that the holes were formed during sampling or compaction. The holes were obviously present at the time of burial. Figure 4F (also see Fig. 4A, B) illustrates the hole on the ventral side of the specimen. It shows that the septum, layer 1, and the thin black deposit (layer 2) are missing in the area of damage (arrows a in Fig. 4F). On the left and right sides of the hole, the cauliflower-like deposits are present, whereas directly above the hole, the cauliflower-like structure is missing (note: the grey bubble left of arrow d is a result of dissolution processes, e.g., by pore waters infiltrating through the sediment or along the sediment-specimen boundary). Based on the section through the ventral hole seen in Fig. 4F, the cameral deposits from layers 1 to 3 were present at the time of damage. Another section

through the ventral hole (Fig. 4A) shows that layer 4 (the light brownish layer) was also present and perforated at the time when the hole was formed. Assuming the dark brown deposits (layer 6), which overly the whitish layer, were not present at the time of perforation, the hole would have opened the chamber and seawater could intrude. The chemical composition of a possible cameral fluid would have been altered, and cameral gas, if present, could have been released. The whitish deposits must have been present at the time of the injury which is corroborated by the vertical cracks marked by arrows c in Fig. 4F. These cracks are present in only this layer and probably caused by the predator. Similar cracks are also observed at other positions in this layer in the adoral chamber. None of these cracks continues into the dark brown deposits. The whitish deposits are more developed in the adapical chamber compared to those in the adoral chamber as would generally be the case for the precipitation of cameral deposits in nautiloids (Teichert 1964). Thus, the pre-damage deposits include at least layers 1 to 4 and post-damage deposits probably started with the dark brown deposits (layer 6). Another structure, which would not be expected if the whitish layers were formed as a reaction to the damage is the displaced wedge-like fragment of cameral deposit (marked with arrow d in Fig. 4F) which was probably displaced in the moment of damage. If the whitish layers were formed as a reaction to the damage, a smooth base between layer 2 and layer 3 should be present. One possibility to explain the presence of the displaced wedge could be that the whitish layer cracked and the wedge-like fragment was pushed into the chamber by the external pressure, i.e., the predatory attack. Another possibility would be that the object causing the hole did not have a smooth surface (e.g., the shark teeth described by Mapes and Hansen [1984] or other fish teeth with serrations or ornament illustrated by Mapes and Chaffin [2003]).

The damage of the siphuncle documents two different events. The siphuncle in the adapical chamber ruptured first as is suggested by the presence or absence of the siphuncular deposits (layer 5) and latest cameral deposits (layer 7) that were formed on the exterior of the connecting ring. Siphuncular deposits are present on the dorsal side of the connecting ring in the adoral chamber but are absent in the adapical chamber. On the ventral side of the connecting ring, layer 7 deposits are present in both chambers. This indicates that the deposit could be precipitated but that the rupture of the dorsal side of the siphuncle in the adapical chamber inhibited further formation of cameral deposits in this area of the adapical chamber. There are latest deposits on the outside of the connecting ring in the adapical chamber. This suggests that in this area the siphuncle broke apart in a later phase. The deposits inside the siphuncle at the position of the septal neck support the hypothesis that the adapical connecting ring broke first. The ventral siphuncular deposits in the adoral chamber are thicker than those at the same position in the adapical chamber. Usually this is rather the other way round according to the mode for precipitation of cameral deposits in nautiloids (Teichert 1964; Ristedt 1971). Cameral deposits

are formed first near the apex and continue to grow and spread. Therefore, deposit thickness decreases towards the aperture. The question of when the rupture of the connecting ring happened can be estimated in accordance with the cracks in the whitish deposits. Assuming that the cracks were caused by a certain pressure, we suggest that this pressure was transferred onto the siphuncle. The pressure first would have occurred in the adoral chamber (i.e., the chamber with the distinct marks) causing the cracks and squeezing its siphuncle. The pressure in the siphuncle would have been transferred to the connecting rings of the neighbour-chambers. When the pressure was too high the siphuncle in the adapical chamber—maybe also in the other adjacent which is not preserved—would have been torn apart. By that the siphuncle would have stayed intact in the adoral chamber. In the progress of cameral deposit precipitation on both sides of the siphuncle in the adoral chamber deposits were formed before the siphuncle broke because it is evident that the cameral deposits broke at the same position where the connecting ring cracked. The siphuncle in the adoral chamber likely broke after intrusion of the sediment because otherwise it would have been buried beneath.

The two significant features on the phragmocone are morphologically similar to the bite marks described and documented by Mapes and Hansen (1984) on a coiled nautiloid from the Lower Pennsylvanian Kendrick Shale. It is very likely that the holes in the studied conch of the specimen BSPG 2011 0002 were the result of a predatorial attack because the holes were filled with sediment (i.e., they were formed prior to burial in the sediment) and because of the peculiar cameral deposits, which were formed after the attack as a reaction to the injury. It is possible that a predator, such as a fish, had caught the nautiloid and that the dorsal and ventral holes in the cephalopod shell are the bite marks made by a pair of opposing teeth in the maxilla and the mandible which penetrated the phragmocone. The chewing pressure of the jaw of the predator would then have caused the rupture of the adapical siphuncle (see above) and also of the cracks in the whitish deposits of the adoral chamber. Presuming the cephalopod had achieved an approximately horizontal orientation of the elongated shell in the water column because of the counterweights of the cameral deposits (e.g., Teichert 1964), the localisation of the holes would coincide with a horizontal position of the predator's mouth.

**The cameral deposits.**—Organic precipitation of cameral deposits in orthoconic nautiloids was first proposed by Woodward (1851). Soon thereafter, Sandberger and Sandberger (1852) suggested an inorganic post-mortem origin via infiltrating fluids. Teichert (in Fischer and Teichert 1969) suggested the presence of a cameral tissue which formed the deposits in orthoconic nautiloids. Blind (1987, 1991) concluded that there must have been some pallial liquid filling the empty spaces of the chambers. According to his explanation, the deposits would have precipitated from this liquid (containing  $\text{Ca}^{2+}$  and  $\text{HCO}_3^{2-}$ ). He also suggested that the liquid was se-

creted by siphuncular tissues because the chambers were sealed off otherwise and thus, no other material exchange or supply was possible. The majority of studies assumes a biogenic origin of the cameral deposits (e.g., Fischer and Teichert 1969; Blind 1987, 1991; Björn Kröger, personal communication 2009). Some other researchers (e.g., Mutvei 2002), however, still favour an inorganic, post-mortem origin.

The specimen with supposed bite marks (BSPG 2011 0002) shows that at least some of the cameral deposits were precipitated during lifetime. There are two primary mineralogies indicated by GADDS and EDX, which are aragonite and HMC (Fig. 7B). Aragonite is present in the septum, the early deposits (layer 1), the black deposit (layer 2) and the dark brown deposits (layer 6). The GADDS- and EDX-data for the whitish and light brown (layer 3 and 4) as well as the latest deposits (layer 7) suggest a primary HMC-mineralogy (see also Seuss et al. 2012). An alternation of the two different mineralogies in the cameral deposits of orthoconic nautiloids has not been described previously to our knowledge. This mineralogical alteration is probably not the result of diagenesis because the deposits were sealed by hydrocarbons very early in its diagenetic history and generally, cements are dependent on the substrate they grow on. The complex changes from aragonite (layer 2) to HMC (layer 3), then HMC (layer 4) back to aragonite (layer 6), and again back to HMC (layer 7) argue strongly against diagenetic overprint. Because of their symmetric arrangement, their peculiar shape, and the abnormal composition, we are convinced that these deposits are primary and were precipitated during the animal's lifetime. The deposits inside the connecting ring contain Sr as well as a low amount of Mg, and we suggest that they were primarily aragonitic. However, due to the direct contact to sediment and calcite cement in the siphuncle, a diagenetic alteration of aragonite in these siphuncular deposits to calcite is likely. Therefore the only post-mortem deposits in specimen BSPG 2011 0002 consist of asphalt, sediment, and sparry calcite cements.

**Possible scenario.**—Summarising the information available on cephalopod predation and the information gathered during this study (holes in the phragmocone of specimen BSPG 2011 0002, development and mineralogy of its cameral deposits) a realistic scenario of the development of the cameral deposits prior and after the predatory attack can be constructed. This scenario presents the second report of an ectocochleate cephalopod surviving damage of the phragmocone and the siphuncle, and is as follows:

The specimen had already precipitated the first biologically induced cameral deposits (layers 1 and 2; Fig. 7C<sub>1</sub>). There is a slight variation in the thickness of the cameral deposits but we consider this to be biological effects of both, simple intraspecific and individual variability. Both layers are primarily aragonitic. Following these initial cameral deposits further cameral deposits were precipitated (Fig. 7C<sub>2</sub>), as represented by the cauliflower-like (layer 3) and light brown deposits (layer 4). Both, layers 3 and 4, have a HMC-



mineralogy. Presumably some siphuncular deposits were present already (layer 5).

A predator, probably a shark or other fish, attacked the specimen (Fig. 7C<sub>3</sub>). The teeth of the predator caused heavy damage on the ventral side of the conch and less severe damage dorsally. The teeth penetrated all deposits (layers 1–4) in the adoral chamber and opened a minute passageway into the chamber to the seawater (Fig. 4A). This chemical mixing of cameral fluid with the seawater would have caused disequilibrium of the fluids in the chamber and deranged deposition of cameral deposits. The siphuncle was torn apart in the adapical chamber due to hydrostatic pressure from the siphuncle in the adoral chamber (Fig. 4D). Precipitation of the whitish deposit of layer 4 immediately stopped. The breakage of the connecting ring would also have influenced but not completely inhibited precipitation of the siphuncular deposits (layer 5; these deposits are less developed in the adapical chamber and the latest cameral deposits are not present on the dorsal side of the connecting ring, but on the healthy ventral side). Damage on the dorsal side of the phragmocone was less intense as only some of the external shell, part of the septum and layer 1 were penetrated.

As a reaction to the massive damage (and the change of the cameral fluid composition) the nautiloid precipitated the dark brown cameral deposits (layer 6) (Fig. 7C<sub>4</sub>). These are aragonitic but also have a high amount of organic matter, which is typical for cephalopod animals under some kind of distress (compare, e.g., Ward 1987; Keupp and Riedel 1995; Klug 2004; Klug et al. 2007). There is a massive build-up directly above the hole on the ventral side of the conch (Fig. 4B). Speculatively this could have helped to strengthen the damaged area of the shell or, alternatively (and maybe more likely), carbonate precipitation was increased due to the influence of seawater seeping into the damaged chamber. The dark brownish deposits are absent in the adapical chamber. This could indicate that the damage in the adoral chamber was much higher, causing an immediate reaction to the attack.

The last biologically induced cameral deposits (layer 7) in the chambers were deposited (Fig. 7C<sub>5</sub>). These are present on the outsides of the connecting ring in both chambers, except on the dorsal side of the siphuncle in the adapical chamber, which we interpret to have been damaged in the initial attack. This indicates that after precipitation of the dark aragonitic deposits, the specimen was able to precipitate further cameral deposits. These late deposits have primary HMC-mineralogy, suggesting that the nautiloid was capable to precipitate HMC-deposits. These late deposits are a sign that the connecting ring played a major role in the precipitation of carbonate deposits in the phragmocone. The damage of the adapical siphuncle indicates that siphonal deposits could not be precipitated anymore when there was a rupture or injury of the connecting ring. The deposits on the outside of the siphuncle in the adapical chamber point to the possibility that an intact outside of the siphuncle also is a prerequisite for the precipitation of cameral deposits.

The last stage of deposition inside the phragmocone (Fig. 7C<sub>6</sub>) was not biological. At this point asphalt, sediment, and calcite cements filled the remaining void of the chambers of specimen BSPG 2011 0002. This was a taphonomic process that took place after burial in the sediment. Initially, hydrocarbons intruded the chamber, followed by the sediment before compaction had occurred. The remaining space was filled with calcitic blocky cements.

For the formation of intrasiphonal and cameral deposits, the siphuncle must have been at least partly functional up to the point where these secondary deposits were formed. Several hypotheses have been introduced to explain the formation of the organically induced cameral deposits (e.g., Barrande 1859; Blake 1882; Flower 1955; Grégoire 1962, 1988; Mutvei 1964, 2002; Schindewolf 1967; Fischer and Teichert 1969; Ristedt 1971; Blind 1987, 1991). For instance, Schindewolf (1967) suggested that cameral organic sheets were involved in the formation of the cameral deposits (see also Teichert in Fischer and Teichert 1969) and Blind (1987, 1991) concluded that there must have been a pallial liquid filling the empty spaces of the chambers. In the Buckhorn orthoconic cephalopod shells presented here, the bilaterally symmetric arrangement of most of the deposits under consideration corroborate their organic origin and *syn vivo*-formation because they were deposited in accordance with the animals plane of symmetry (Blind 1991). It can also be considered as a fact that liquid was involved in the deposition of these organogenic carbonates.

**Open questions.**—Was there living cephalopod tissue within the chambers outside of the siphuncle? In the specimens from the Buckhorn Asphalt, we could not find clear evidence for this hypothesis. Anyhow, a living tissue is one possible explanation for the lasting process of precipitation. The tissue would have been damaged by the attack and in a first step the tissue would need some regeneration and might have behaved abnormally. This tissue would then, after some recovery, have sealed the hole caused by predation and inhibited further intrusion of seawater. From this tissue, the dark brown (aragonitic, organic-rich) deposits (layer 6) could have been precipitated. The siphuncle would then have played a major role to restore the equilibrium of the initial cameral fluid by exchanging ions. Accordingly, at the moment when the cameral fluid was renewed, normal cameral deposition could have been restored and the latest deposits (layer 7) precipitated. In any case, it appears plausible that the localisation of carbonate precipitation was influenced by the orientation of the shell and local differences in ion concentration, which might have been controlled by the siphuncle's differential intensity of ion segregation. By contrast, Blind (1991) correctly stated that the shape of intracameral deposits evokes the impression of being formed without organic control. It basically looks superficially like the filling of an agate.

Were the chambers completely filled with liquid? The chambers could have been filled with chamber liquid ("Pallialflüssigkeit" of Blind 1991), like Blind (1991: 44) suggested. Since the deposits dominate on the ventral side, it is

conceivable that there also was some gas in the chambers, at least in those places where no carbonate was deposited. In the case of a cameral tissue lining the entire inner surface of the chamber, the presence of some gas in the phragmocone cannot be excluded, assuming the tissue was accountable for the precipitation of cameral deposits. The tissue would have worked even without a liquid when it was supplied with the necessary ions to build up cameral deposits. Thus, not only deposits on the venter would have been precipitated but also dorsal deposits could have been precipitated independent of a complete filling with chamber liquid and of gravity. Gas being concentrated dorsally would probably not have been lost through the ventral injury, unless the assumed tissue was damaged and cracks in the cameral deposits would have released some or all the gas.

What caused the alternation of HMC and aragonite in the damaged chamber? Blind (1991) did not report the presence of HMC in the phragmocone chambers of the specimens he studied nor did any other author. The specimens Blind illustrated (Blind 1991: pls. 1, 2, 4) show much more uniformly coloured and shaped cameral deposits like those illustrated in Fig. 3. Our study (GADDS, EDX, isotope data, microscopical observations) suggests that there was a primary deposition of both, HMC and aragonite, in the chambers (Fig. 7B; Seuss et al. 2012). It appears likely that BSPG 2011 0002 first secreted an aragonitic phragmocone and that early endocameral deposits also were aragonitic. Following these initial deposits, thick HMC-deposits (layers 3 and 4) were precipitated. These layers merged from whitish cauliflower-like structure into a light brown layering. It would be plausible to explain the switch from aragonite to HMC as consequence of attack and damage of the conch. However, as outlined above, there is evidence that layers 3 and 4 were already present at the moment of the attack (see line of reasoning above). In contrast, the abrupt switch back to aragonitic deposits (layer 6) can be explained as a reaction to the bite. After equilibrium of the cameral fluid in the chamber was restored, deposition of the HMC-deposits (layer 7) occurred again. Because of the HMC-aragonite-alternation, we suggest that the studied specimen (BSPG 2011 0002) was physiologically disturbed after the attack and that alternation of aragonite/HMC-precipitation in the cameral deposits does not represent the normal state. A critical point, however, is the presence of primary HMC, which has not been reported from other cephalopods previously. Possible causes for this unusual mineralogy for molluscs could be an indisposition prior or even a change in the mineralogy of the cameral deposits during growth. A disease would probably be more plausible. This could have caused precipitation of the unusual HMC-deposits and at the same time would also have constrained the specimen which would make it more likely to be prey. The question about the HMC finds no unambiguous answer here.

What was the function of cameral deposits? Blind (1991) argued that the shell became too heavy to swim and that the animal dragged the heavy shell over the sea-floor. On the one hand this might be true, because the massive cameral deposits

seem too heavy to achieve buoyancy. On the other hand this might be wrong, because even a shell with such heavy deposits did have some buoyancy as long as not all open space was filled. Conclusive proof of a benthic life mode remains elusive. Blind's (1991) hypothesis of pseudorthoceratids dragging their shells behind lacks evidence, since traces documenting such "dragging behaviour" have never been reported. Nevertheless, it should be obvious, that if the animal would keep on growing during lifetime a counterweight to the body will be necessary. This counterweight can be achieved by the deposits. Otherwise it is possible that a heavy nautiloid would be headfirst with the conch upside. This orientation is certainly not suitable for active swimmers.

Was there gas at any time in some of the phragmocone chambers? Blind (1991) disagreed with Fischer and Teichert (1969), who suggested that the chambers were partially filled with gas. Blind (1991: 45) argued that complete chamber filling with fluid is likely, whereas Fischer (in Fischer and Teichert 1969) states that part of the chambers were also filled with gas to achieve balance and manoeuvrability. The predominantly ventral carbonate deposits of the chambers documents not only the horizontal syn vivo shell orientation but offers the possibility that there was a partial gas-filling with a dorsally positioned bubble in the chambers. Such an assumption is not parsimonious because it implies a repeated shift in siphuncle function as opposed to a single function as suggested by Blind (1991) who concluded that there was no gas in the chambers of these phragmocones at all. Support for the hypothesis that the phragmocone contributed to reduce the animal's buoyancy (Fischer and Teichert 1969) is provided by the fact that the predation marks are on the dorsal and ventral sides of the phragmocone suggesting it was not laying in the mud in a benthic life mode. That the nautiloid was not lying on the ground is also strongly supported by the facies in which the specimen was found. The facies is a typically offshore deposit lacking typical benthos but containing various cephalopods. It is very unlikely that the nautiloid would be the only benthic species. Thus, it is possible that at least some gas might have accumulated in the phragmocone chambers, increasing buoyancy of the shell and supporting swimming movements. Swimming is supported by the fact that many orthoconic nautiloids with massive cameral deposits are found in hypoxic to anoxic sediments lacking benthos, which is an unlikely habitat for animals that are unable to swim. This is strong support for our hypothesis, but the presence of such complexly-built phragmocones cannot be explained otherwise. It is also not a parsimonious assumption that the phragmocone functioned as a buoyancy device in some cephalopods and in some it did not. Nevertheless, further information is needed to answer this question.

## Conclusions

We studied well preserved cameral deposits with largely original mineralogy of orthocerid cephalopods from the Buckhorn



Asphalt deposit. The symmetrical arrangement of these predominantly aragonitic deposits supports a *syn vivo*-formation.

One of the new specimens, here tentatively assigned to the Pseudorthoceratidae gen. et sp. indet. shows a dorsal and a ventral hole in the phragmocone, a ruptured siphuncle, and unusually shaped cameral deposits, which partially consist of HMC. The specimen obviously is an individual which survived a predator's attack. It is only the second case of a survived puncture of a phragmocone and siphuncle. Earlier Kröger and Keupp (2004) studied a specimen of *Trocholites depressus* (Eichwald, 1840) and found that the specimen showed a healed injury of phragmocone and siphuncle. They accordingly concluded that the specimen had survived this normally lethal damage.

The event affecting the Buckhorn specimen occurred, when the first layers of cameral and siphuncular deposits had already been deposited. The initial cameral deposits were not completely destroyed but the bite visibly caused cracks and a hole into one chamber that allowed seawater to seep into the damaged chamber, thus altering the chemical composition of the chamber fluid. Initial post-predation deposits are abnormal in form and chemistry. The distribution of cameral and siphuncular deposits is a strong indication for the importance of a functional connecting ring involved in the precipitation of carbonate deposits. Blind (1991) hypothesised that the orthocerid shells were too heavy for swimming. By contrast, we suggest, in accordance with Fischer and Teichert (1969) that some younger chambers might have contained some gas, which might have enabled these cephalopods to swim.

Our conclusions, however, are based mainly on a single injured specimen with only two chambers preserved. Thus, we do not know if other chambers were also affected by the sublethal injuries. We think that it is likely that younger chambers showed similar effects (undamaged chambers should not contain layer 6, the dark brown deposits). Therefore, more specimens with same type of damage are needed to corroborate our hypothesis. The HMC-cameral deposits have not been reported from cephalopods before. We do have evidence that these are primary (Seuss et al. 2012). Therefore, either the specimen precipitated exceptional cameral deposits or this is an unknown taxon of orthocone nautiloids whose cameral deposits had not been examined before.

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## References

- Barrande, J. 1859. Dépôt organique dans le loges aériennes des Orthocères. *Bulletin Géologie France* 16: 828–856.
- Blake, J.F. 1882. *A Monograph of the British Fossil Cephalopods. Part 1.* 248 pp. Paleontological Society, London.
- Blind, W. 1987. Vergleichend morphologische und schalenstrukturelle Untersuchungen an Gehäusen von *Nautilus pompilius*, *Orthoceras* sp., *Pseudorthoceras* sp. und *Kionoceras* sp. *Palaeontographica, Abteilung A* 198: 101–128.
- Blind, W. 1991. Über Anlage und Funktion von Kammerablagerungen in Orthoceren-Gehäusen. *Palaeontographica, Abteilung A* 218: 35–47.
- Bond, P.N. and Saunders, W.B. 1989. Sublethal injury and shell repair in Upper Mississippian ammonoids. *Paleobiology* 15: 414–428.
- Brand, U. 1982. The oxygen and carbon isotope composition of Carboniferous fossil components: sea-water effects. *Sedimentology* 29: 139–147.
- Brand, U. 1987. Biogeochemistry of nautiloids and palaeoenvironmental aspects of Buckhorn Seawater (Pennsylvanian), Southern Oklahoma. *Palaeogeography, Palaeoclimatology, Palaeoecology* 61: 255–264.
- Brand, U. 1989a. Aragonite-calcite transformation based on Pennsylvanian molluscs. *Geological Society of America, Bulletin* 101: 377–390.
- Brand, U. 1989b. Biogeochemistry of Late Paleozoic North American brachiopods and secular variation of seawater. *Biogeochemistry* 7: 159–193.
- Cree, S.B. 1984. *A Biostratigraphic Study of the Asphalt-bearing Limestones of Pennsylvanian Age in the Arbuckle Mountains, Oklahoma.* 82pp. Unpublished Master Thesis, Graduate School, University of Texas, Arlington.
- Durham, J.W. 1967. The incompleteness of our knowledge of the fossil record. *Journal of Paleontology* 41: 559–565.
- Ebbestad, J.O.R. and Stott, C.A. 2008. Failed predation in Late Ordovician gastropods (Mollusca) from Manitoulin Island, Ontario, Canada. *Canadian Journal of Earth Sciences* 45: 231–241.
- Fischer, A.G. and Teichert, C. 1969. Cameral deposits in cephalopod shells. *The University of Kansas Paleontological Contributions* 37: 1–37.
- Flower, R.H. 1955. Cameral deposits in orthoconic nautiloids. *Geological Magazine* 92: 89–103.
- Foote, M. 1996. On the probability of *Ancestros* in the fossil record. *Paleobiology* 22: 141–151.
- Grégoire, C. 1962. On the submicroscopic structure of the *Nautilus* shell. *International Royal des Sciences Naturelles Belgique, Bulletin* 38: 1–71.
- Grégoire, C. 1988. Organic remnants in shells of Cambrian nautiloids and in cameral deposits of Pennsylvanian nautiloids. *Senckenbergiana lethaea* 69: 73–86.
- Ham, W.E. 1969. Regional geology of the Arbuckle Mountains Oklahoma Part 1. Regional geology. Geology of the Arbuckle Mountains. *Oklahoma Geological Survey, Guide Book* 17: 5–50.
- Hutchinson, L.L. 1911. Preliminary report on the rock asphalt, asphaltite, petroleum and natural gas in Oklahoma. *Oklahoma Geological Survey, Bulletin* 2: 1–256.
- Kase, T., Johnston, P.A., Seilacher, A., and Boyce, J.B. 1998. Alleged mosasaur bite marks on Late Cretaceous ammonites are limpet (patello-gastropod) home scars. *Geology* 26: 947–950.
- Kauffman, E.G. 2004. Mosasaur predation on upper Cretaceous nautiloids and ammonites from the United States Pacific Coast. *Palaios* 19: 96–100.
- Kauffman, E.G. and Kesling, R.V. 1960. An upper Cretaceous ammonite

- bitten by a Mosasaur. *Contributions to the Museum of Paleontology of the University of Michigan* 15: 193–248.
- Kelley, P.H., Hansen, T.A., and Kowalewski, M. (eds.) 2003. *Predator-Prey Interactions in the Fossil Record (Topics in Geobiology)*. 472 pp. Kluwer/Plenum Publishers, New York.
- Keupp, H. and Riedel, F. 1995. *Nautilus pompilius* in captivity: a case study of abnormal shell growth. *Berliner geowissenschaftliche Abhandlungen E* 16: 663–681.
- Klug, C. 2004. Mature modifications, the black band, the black aperture, the black stripe, and the periostracum in cephalopods from the Upper Muschelkalk (Middle Triassic, Germany). *Mitteilungen aus dem Geologisch-Paläontologischen Institut der Universität Hamburg* 88: 63–78.
- Klug, C. 2007. Sublethal injuries in Early Devonian cephalopod shells from Morocco. *Acta Palaeontologica Polonica* 52: 749–759.
- Klug, C., Brühwiler, T., Korn, D., Schweigert, G., Brayard, A., and Tilsley, J. 2007. Ammonoid shell structures of primary organic composition. *Palaeontology* 50: 1463–1478.
- Klug, C., Kröger, B., Kiessling, W., Mullins, G.L., Servais, T., Frýda, J., Korn, D., and Turner, S. 2010. The Devonian nekton revolution. *Lethaia* 43: 465–477.
- Kröger, B. 2002a. Antipredatory traits of the ammonoid shell—Indications from Jurassic ammonoids with sublethal injuries. *Paläontologische Zeitschrift* 76: 223–234.
- Kröger, B. 2002b. On the ability of withdrawing of some Jurassic ammonoids. *Abhandlungen der Geologischen Bundesanstalt* 57: 199–204.
- Kröger, B. 2002c. On the efficiency of the buoyancy apparatus in ammonoids. Evidences from sublethal shell injuries. *Lethaia* 35: 31–40.
- Kröger, B. 2004. Large size sublethal injuries in Middle Ordovician orthocerids. *Geologiska Föreningens i Stockholm Förhandlingar* 126: 311–316.
- Kröger, B. and Keupp, H. 2004. A paradox survival-report of a repaired *syn vivo* perforation in a nautiloid phragmocone. *Lethaia* 37: 439–444.
- Kröger, B. and Mapes, R.H. 2005. Revision of some common Carboniferous genera of North American orthocerid nautiloids. *Journal of Paleontology* 79: 954–963.
- Koch, C.F. 1978. Bias in the published fossil record. *Paleobiology* 4: 367–372.
- Kulicki, C., Landman, N.H., Heaney, M.J., Mapes, R.H., and Tanabe, K. 2002. Morphology and microstructure of the early whorls of goniatites from the Carboniferous Buckhorn Asphalt (Oklahoma) with aragonitic preservation. *Abhandlungen der Geologischen Bundesanstalt* 57: 205–224.
- Mapes, R.H. 1979. Carboniferous and Permian Bactritoidea (Cephalopoda) in North America. *University of Kansas Paleontological Contribution* 64: 1–75.
- Mapes, R.H. and Chaffin, D.T. 2003. Predation on cephalopods: a general overview with a case study from the Upper Carboniferous of Texas. In: P.H. Kelley, M. Kowalewski, and T.A. Hansen (eds.), *Predator-Prey Interactions in the Fossil Record*, 177–213. Kluwer/Plenum Publishers, New York.
- Mapes, R.H. and Hansen, M.C. 1984. Pennsylvanian shark-cephalopod predation. *Lethaia* 17: 175–183.
- Mapes, R.H., Sims, M.S., and Boardman, D.R. 1995. Predation on the Pennsylvanian ammonoid *Gonioloboceras* and its implications for allochthonous vs. autochthonous accumulations of goniatites and other ammonoids. *Journal of Paleontology* 69: 441–446.
- Mutvei, H. 1964. Remarks on the anatomy of recent and fossil Cephalopoda with description of the minute shell structure of belemnoids. *Stockholm Contributions to Geology (Acta Universitatis Stockholmiensis)* 11: 79–102.
- Mutvei, H. 2002. Connecting ring structure and its significance for classification of the orthoceratid cephalopods. *Acta Geologica Polonica* 47: 157–168.
- Newell, N.D. 1959. The Nature of the Fossil Record. *Proceedings of the American Philosophical Society* 103: 264–285.
- Nützel, A. and Frýda, J. 2003. Paleozoic plankton revolution: Evidence from early gastropod ontogeny. *Geology* 31: 829–831.
- Ristedt, H. 1971. Zum Bau der orthoceriden Cephalopoden. *Palaeontographica, Abteilung A* 137: 155–195.
- Sadd, J.L. 1991. Tectonic influences on carbonate deposition and diagenesis, Buckhorn Asphalt, Deese Group (Desmoinesian), Arbuckle Mountains, Oklahoma. *Journal of Sedimentary Petrology* 61: 28–42.
- Sandberger, G. and Sandberger, F. 1852. *Die Versteinerungen des rheinischen Schichtensystems in Nassau. Vol. 2*. 565 pp. Kreidel and Niedner, Wiesbaden.
- Schindewolf, O.H. 1967. Analyse eines Ammoniten-Gehäuses. *Akademie für Wissenschaft und Literatur (Mainz); Mathematisch-Naturwissenschaftliche Klasse, Abhandlungen* 8: 137–188.
- Seuss, B., Nützel, A., Mapes, R.H., and Yancey, T.E. 2009. Facies and fauna of the Pennsylvanian Buckhorn Asphalt Quarry deposit: a review and new data on an important Palaeozoic fossil Lagerstätte with aragonite preservation. *Facies* 55: 609–645.
- Seuss, B., Titschack, J., Seifert, S., Neubauer, J., and Nützel, A. 2012. Oxygen and stable carbon isotopes from a nautiloid from the Middle Pennsylvanian (Late Carboniferous) impregnation Lagerstätte 'Buckhorn Asphalt Quarry'—Primary paleo-environmental signals versus diagenesis. *Paleogeography, Paleoclimatology, Paleoecology* 319–320: 1–15.
- Slotta, F., Korn, D., Klug, C., and Keupp, H. 2011. Sublethal shell injuries in Late Devonian ammonoids (Cephalopoda) from Kattensiepen (Rhenish Mountains). *Neues Jahrbuch für Geologie und Paläontologie, Abhandlungen* 261: 321–336.
- Smith, H.J. 1938. *Fauna of the Buckhorn Asphalt*. 40 pp. Chicago University Library, Chicago.
- Squires, R.L. 1973. *Burial Environment, Diagenesis, Mineralogy, and Mg & Sr Contents of Skeletal Carbonates in the Buckhorn Asphalt of Middle Pennsylvanian Age, Arbuckle Mountains, Oklahoma*. 184 pp. Unpublished Ph.D. thesis, California Institute of Technology, Pasadena.
- Stehli, G.G. 1956. Shell mineralogy in Paleozoic Invertebrates. *Science* 123: 1031–1032.
- Teichert, C. 1964. Morphology of hard parts. In: R.C. Moore (ed.), *Treatise on Invertebrate Paleontology, Vol. K, Mollusca* 3, K13–K59. The Geological Society of America and The University of Kansas Press, Boulder.
- Unklesbay, A.G. 1962. Pennsylvanian cephalopods of Oklahoma. *Oklahoma Geological Survey Bulletin* 96: 1–150.
- Valentine, J.W. and Grubb, P.J. 1990. The fossil record: A sampler of life's diversity [and discussion]. *Philosophical Transactions: Biological Sciences* 330: 261–268.
- Vermeij, G.J. 1977. The Mesozoic Marine Revolution: Evidence from Snails, Predators and Grazers. *Paleobiology* 3: 245–258.
- Vermeij, G.J. 1987. *Evolution and Escalation*. 527 pp. Princeton University Press, Princeton.
- Ward, p.d. 1987. *The Natural History of Nautilus*. 267 pp. Allen and Unwin, Boston.
- Wisshak, M., Seuss, B., and Nützel A. 2008. Evolutionary implications of an exceptionally preserved Carboniferous microboring assemblage in the Buckhorn Asphalt Lagerstätte (Oklahoma, USA). In: M. Wisshak and L. Tapanila (eds.), *Current Developments in Bioerosion*, 21–54. Springer, Berlin.
- Woodward, S.P. 1851. *Manual of the Mollusca*. 542 pp. Virtue Brothers & Co, London.