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### Evidence for a composite organic–inorganic fabric of belemnite rostra

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Title: Evidence for a composite organic-inorganic fabric of belemnite rostra: Implications for palaeoceanography and palaeoecology

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Abstract: Carbonate skeletons of fossil marine organisms are widely used to reconstruct palaeoceanographic parameters. Specifically, the geochemistry of Jurassic and Cretaceous belemnite rostra is traditionally interpreted to represent near sea-surface seawater properties. More recently, an increasing number of workers, have reported significant scatter in geochemical data (e.g.,  $\delta^{18}O$ ,  $\delta^{13}C$ , element/Ca ratio) when comparing rostra from the same stratigraphic level or within a single belemnite rostrum. This scatter is not explained by differential diagenetic overprint alone. Here we report petrographic evidence on the primary ultrastructure of rostra of *Megateuthis* (Middle Jurassic) and *Belemnitella* and *Goniot euthis* (Late Cretaceous). The biogenic ultrastructure consists of a filigree framework of triaxial branches and tetrahedrons of variable size forming a honeycomb-like network. Data presented here suggest that these rostra yielded as much as 50 to 90% primary pore space. On the level of a working hypothesis - and in analogy with modern cephalopods - we propose that the pore space was formerly filled with body fluid and/or organic compounds during the life time of these organisms. Intra-rostral porosity was post mortem occluded by earliest diagenetic isopachous calcite cements of a non-biogenic origin. These may have been precipitated due to increased alkalinity related to the decay of organic matter. If this holds true, then the resulting fabric represents a composite biogenic/abiogenic structure. In order to optically separate the two calcite phases forming a single calcite fibre, we employed a wide range of state-of-the-art analytical tools to thin sections and ultra-thin sections of well-preserved specimens. Pending a verification of these well-supported ultrastructural data by means of high-resolution geochemical analyses from biogenic and abiogenic phases, we suggest that these findings have significance for those using belemnite rostra as archives of their palaeoenvironment.

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Bochum 2016-05-30

Dear Editor,

We greatly appreciate the input from two expert reviewers and have implemented the (minor) comments (see revision notes) in nearly all cases. Where we decided to not follow the reviewer's advice, we argue why we do so.

Thank you for your professional work!

Kind regards,

R. Hoffmann on behalf of the authors

Revision Notes

Dear Editor,

We greatly appreciate the input from two expert reviewers and have implemented the (minor) comments in nearly all cases. Where we decided to not follow the reviewer's advice, we argue why we do so.

General: We have included line numbering. Changed text passages are given in italics.

Reviewer SEDGEO5702\_revDF – Reviewer 1

Comments made directly in the manuscript:

Line 94:

Belemnite rostra are traditionally considered to secrete their endoskeleton in oxygen isotope equilibrium with ambient seawater...

*Belemnites are traditionally considered to secrete their endoskeleton in oxygen isotope equilibrium with ambient seawater...*

Comment: We agree with the reviewer, not the belemnite rostra secrete their endoskeleton but the belemnite animal.

Line 127:

Thin sections (30  $\mu\text{m}$ ) and ultra thin sections (< 10  $\mu\text{m}$ ) of two well-preserved specimens of *Megateuthis gigantea*...

Thin sections (30  $\mu\text{m}$ ) and ultra thin sections (< 10  $\mu\text{m}$ ) of two well-preserved orthorostra of *Megateuthis gigantea*...

Comment: We agree with the reviewer that it is useful to distinguish between the orthorostrum and the epirostrum, both are present in *Megateuthis*.

Line 317-318:

Referring to the high porosity observed in both belemnite rostra and sepiid cuttlebone it is important to note that these structures are not homologous (Fuchs 2012).

Comment: We agree with the reviewer and added one sentence pointing out that the belemnite orthorostrum and the sepiid cuttlebone are not homologue structures. See below.

Line 334:

Apical region

*Apical line region*

Comment: We agree with the reviewer that it is better to refer to the apical line region connecting all apical regions during ontogeny instead of the apical region.

Line 359:

...outside of (i.e., the belemnite animal itself)...

... outside of the orthorostrum (i.e., the belemnite animal itself)...

Line 424:

shell

*cuttlebone*

Comment: To avoid further confusion between the belemnite rostrum and the tiny rostrum or apical spine at the posterior end of the sepiid cuttlebone, we used the general term cuttlebone for the latter which includes the highly porous phragmocone (see below).

Line 425:

...belemnite skeleton...

...*belemnite orthorostrum*...

Comment: As pointed out earlier by the reviewer it is more precise to refer to the orthorostrum instead of the whole belemnite skeleton which would include the phragmocone as well – which has a different mineralogy and ultrastructure and was not analysed in this study.

Line 428:

...living belemnites...

...living belemnite rostra

Comment: Changes accordingly to the comment by the reviewer.

Line 434:

...ommastrephid...

...*onychoteuthid*...

Comment: We changed the text accordingly to the comment by the reviewer.

Line 495:

Reviewer question: Does this concentration refers to the entire cuttlebone or only the sepiid spine ("rostrum" )?

Comment: All cited references refer to the *Sepia* cuttlebone and do not specify a particular region, e.g., the spine.

Lines 518-521:

This tentative interpretation presented here with regard to belemnite rostra is arguably consistent with observations of 10-40% organic matrix in the *Sepia* cuttlebone (Birchall and Thomas, 1983; Florek et al., 2009). This is relevant as we suggest that the belemnite rostrum is structurally similar to the *Sepia* cuttlebone with regard to the primary intra-skeletal porosity.

*This tentative interpretation presented here with regard to belemnite rostra is arguably consistent with observations of 10-40% organic matrix in the Sepia cuttlebone (Birchall and Thomas, 1983; Florek et al., 2009). This is relevant as we suggest that the belemnite rostrum is structurally similar but not homologous (Fuchs 2012) to the Sepia cuttlebone with regard to the primary intra-skeletal porosity.*

Comment: The reviewer suggested to highlight here that the rostrum and sepiid cuttlebone are structurally similar, but not homologous. Accordingly, we added "but not homologous" to the text citing the work of Fuchs (2012). However, a discussion about the similarities and differences of the sepiid and belemnite rostrum is far beyond the scope of this paper.

Comments to the authors:

Reviewer #1: Dear authors, in some places, you compare the belemnite rostrum with sepiid cuttlebones. I recommend to provide a short explanation about the homologous shell parts of belemnites & sepiids. A clear differentiation between rostrum & phragmocone is essential to correctly interpret/comprehend observed porosities. In this context, it would be less confusing to compare the belemnite rostrum with the "rostrum" of sepiids and belosepiids (rather than their phragmocone).

*Comment: We agree with the reviewer that the comparison of a belemnite rostrum with the Sepia cuttlebone might be misleading when it comes to the phylogenetic reconstruction of coleoid evolution. However, the reconstruction of coleoid phylogeny is far beyond the scope of our paper. Further, it should be noted that there is an open discussion about the homologous shell parts in fossil and modern coleoids and that authors cited in our manuscript did not distinguish between the different shell parts, e.g., Florek et al. 2009 reported on the amount of organic matter for the whole cuttlebone and did not distinguish between phragmocone, dorsal shield, and rostrum. In order to avoid additional confusion we decide to keep the comparison between the belemnite orthorostrum and the Sepia cuttlebone (which refers to the complete internal shell). We do so specifically because earlier authors, when describing porosity observed in belemnite rostra, compared it with the porous structure of the Sepia cuttlebone not distinguished between the phragmocone and other shell parts. For the "rostrum-problem" the reader is referred to Fuchs (2012). As far as we know no detailed description of the sepiid rostrum is available.*

Apart from this, I would avoid the term "skeleton"; if then only in terms of the entire shell; not only shell parts, e.g. the rostrum.

*We agree with the reviewer and delete whenever it seemed adequate the term skeleton.*

I'm missing a paragraph discussing and verifying earlier observations/ ideas: who postulated a low porosity and what was wrong in the line argumentation?

*We provide information about earlier observations of pore space or the varying amount of organic matter in belemnite orthorostra in the introduction part (lines 84-92) and in chapter 4.3 citing the most important articles by Müller-Stoll, Spaeth, and Saelen. Müller-Stoll (1936) argues for varying amounts of organic matter in the observed lighter/darker concentric rings, while Spaeth (1971, 1973, 1975) was the first who described a higher amount of porosity (up to 20%). In his extensive review Saelen (1989) comes to the conclusion that it is most likely that the belemnite rostrum was a dense structure already during life time of the belemnite animal. The latter statement (Saelen 1989) agrees with the majority of contemporaneous and all subsequent researchers (e.g., Veizer 1974, Podlaha et al. 1998) largely neglecting the porosity in belemnite rostra. Maybe this was due to the fact that Spaeth could only present data for a single belemnite rostrum (Neohibolites). To keep the focus on our description of the new ultrastructure and to avoid duplication we do not provide an additional paragraph discussing and verifying earlier observations dealing with the belemnite porosity.*

Reviewer SEDGEO5702 Review 27 April 2016 IJ comments – Reviewer 2

All minor corrections were implemented in the revised version of the manuscript.

Line 275:

Reviewer question: Why specifically choose these elements for mapping? Common substitutions in the calcite lattice such as Sr, Ba, Fe, Mn, Zn are not mentioned. Do these not show any variation?

Comment: Fe, Mn content was quantitatively assessed using the cathodoluminescence microscope. Both show slight variation between the biogenic precipitates and secondary cement phases. We

specifically choose Mg, P, and S to collect arguments for the distribution of primary organic matter as we discussed in our manuscript.

Line 355:

... the dense fabrics observed in the case of most rostra collected in Mesozoic sedimentary successions...

*... the dense fabrics observed in rostra collected in Mesozoic sedimentary successions...*

*Comment: We agree with the reviewer that it is surprising that no examples of preserved pore space exist as far as we know. However, fossil echinoderm remains, with a primary comparable porous endoskeleton, are also preserved as massive fossil structures with nearly no pore space left. Some belemnite rostra are preserved as hollow tubes thanks to strong diagenetic alteration processes. In some cases the outer margin of belemnite orthorostra show increasing porosity. This porosity is taken as sign of diagenetic alteration and does not resemble the described ultrastructure.*

Line 384:

Reviewer statement: Yet echinoderm calcite commonly retains its intraparticle porosity in geological samples, despite being Mg-calcite!

*Comment. We do not agree with the reviewers statement. Based on our own observations the majority of the primary pore space in echinoderm skeletons is occluded by secondary calcite (see also Dickson 2001, 2002, 2004). However, due to staining it is possible to reveal the original skeletal structure and distinguish it from the secondary cement phase.*

Line 510:

Reviewer question: Are there any examples of cuttlebone being preserved in the way that you propose for belemnites?

*Comment. As far as we know the ultrastructure of fossil sepiid cuttlebones is not described in comparable details. Further, no taphonomic framework for fossil cuttlebones is available.*

Comments to the authors:

Reviewer #2: (1) The authors state (p14) that "The presence of a highly porous primary rostrum architecture during the life time of the belemnite organism as proposed here, is contrasted by the dense fabrics observed in the case of most rostra collected in Mesozoic sedimentary successions (Fig. 1A-B)."

They state "most", implying that not all belemnites have dense fabrics? I find it rather surprising that if their hypothesis is correct, why no examples of preserved porous calcite guards have ever been found. Is there any evidence of the existence of these, perhaps having been dismissed as 'altered' or 'leached' specimens? Such material would lend strong support to your hypothesis.



*Comment. We agree with the reviewer that it is surprising that no examples of preserved pore space exist as far as we know. We have collected belemnite rostra from many different localities (Russia, Japan) while the primary intention was to collect hollow ammonites. Hollow ammonite preservation is very rare and requires special conditions. It can be assumed that belemnites collected from the same beds share a similar unique taphonomy. However, also those belemnite rostra collected together with hollow ammonites show a massive structure. Some belemnite rostra are preserved as hollow tubes thanks to strong diagenetic alteration processes. In some cases the outer margin of belemnite orthorostra show increasing porosity. This porosity is taken as a sign of diagenetic alteration and does not resemble the described ultrastructure. By the observation of darker and lighter concentric rings earlier researchers speculated about varying amounts of organic within these rings. Recently, Ullmann et al. (2015), based on geochemical analyses, postulated a 40% porosity for the apical line region. It was assumed by Ullmann et al. (2015) that the porosity decreases towards the rostral margin. Concluding, as far as we know no pore space had been described so far the fits with the herein described ultrastructure.*

(2) The authors refer to the microstructure of echinoderm calcite (p16). They do not mention that echinoderm skeletons are also porous and subject to diagenetic infill. Yet echinoderm calcite may sometimes retain its intraparticle porosity even in Palaeozoic samples, despite originally being Mg-calcite! Why should belemnites be so uniform in their preservation style? A consequence of their unique crystallography?

*Comment. We do not agree with the reviewers statement. Based on our own observations the majority of the primary pore space in echinoderm skeletons is occluded by secondary calcite (see also Dickson 2001, 2002, 2004). However, due to staining it is possible to reveal the original skeletal structure and distinguish it from the secondary cement phase.*

(3) Cuttlebone is presented as the closest modern analogue to belemnite guards (e.g. p20). This seems to be perfectly logical. However, again, are there any examples recorded of cuttlebone being preserved in a similar manner to that proposed for belemnites? If the mechanism is valid, it seems rather surprising that no similar processes have been observed / described, even if only in a more superficial way. The different taphonomy a consequence of their aragonite mineralogy perhaps?

*Comment. Sepiid cuttlebones are rather rare compared to the globally distributed and highly abundant belemnite rostra. We assume the different preservation originally lies in their different primary mineralogy (low Mg calcite for belemnites and aragonite for sepiids).*

Thank you for your professional work!

Kind regards,

R. Hoffmann on behalf of the authors

1 **Evidence for a composite organic-inorganic fabric of belemnite rostra:**

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2 **Implications for palaeoceanography and palaeoecology**

3

4 Hoffmann, R.<sup>1</sup>, Richter, D.K.<sup>1</sup>, Neuser, R.D.<sup>1</sup>, Jöns, N.<sup>1</sup>, Linzmeier, B.J.<sup>2</sup>, Lemanis, R.E.<sup>1</sup>, Füsseis, F.<sup>3</sup>,  
5 Xiao, X.<sup>4</sup> and Immenhauser A<sup>1</sup>

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27 **Abstract**

28

29 Carbonate skeletons of fossil marine organisms are widely used to reconstruct palaeoceanographic  
30 parameters. Specifically, the geochemistry of Jurassic and Cretaceous belemnite rostra is traditionally

31 interpreted to represent near sea-surface ~~palaeoenvironmental parameters~~seawater properties.

32 More recently, an increasing number of workers, ~~however, report a~~have reported significant scatter

33 in geochemical data (e.g.  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , element/Ca ratio) when comparing rostra from the same

34 stratigraphic level or within a single belemnite rostrum. This scatter is not explained by differential

35 diagenetic overprint alone. Here we report petrographic evidence on the primary ultrastructure of

36 rostra of *Megateuthis* (Middle Jurassic) and *Belemnitella* and *Goniotoothis* (Late Cretaceous). The

37 biogenic ultrastructure consists of a filigree framework of triaxial branches and tetrahedrons of

38 variable size forming a honeycomb-like network. Data presented here suggest that these rostra

39 yielded as much as 50 to 90% primary pore space. On the level of a working hypothesis - and in

40 analogy with Recent-modern cephalopods - we propose that the pore space was formerly filled with

41 body fluid and/or organic compounds during the life time of these organisms. Intra-~~skeleton~~rostral

42 porosity was post mortem occluded by earliest diagenetic isopachous calcite cements of a non-

43 biogenic origin. These may have been precipitated due to increased alkalinity related to the decay of

44 organic matter. If this holds true, then the resulting fabric represents a composite biogenic/abiogenic

45 structure. In order to optically separate the two calcite phases forming a single calcite fibre, we

46 employed a wide range of state-of-the-art analytical tools to thin sections and ultra-thin sections of

47 well-preserved specimens. Pending a verification of these well-supported ultrastructural data by

48 means of high-resolution geochemical analyses from biogenic and abiogenic phases, we suggest that

49 these findings have significance for those using belemnite rostra as archives of their

50 palaeoenvironment.

51

52 **Keywords:** belemnite, ultrastructure, carbonate archive, diagenesis, Jurassic-Cretaceous

53

## 54 1. Introduction

55 The ultrastructure of recent biogenic carbonates is of great interest for those concerned with  
56 biomineralization research in general (Weiner and Addadi, 2011; Goetz et al., 2011), those studying  
57 the primary biogenic skeletal structures of fossil skeletal hardparts (e.g., Coronado et al., 2013), and  
58 for palaeoceanographers exploring these materials for their bearing on past climate dynamics  
59 (Saelen, 1989; Cochran et al., 2003; Parkinson et al., 2005; [Jarvis et al., 2015](#); Immenhauser et al.,  
60 2016). Whereas the tests of planktonic and benthic foraminifera (and coccoliths ~~etc.~~) are important  
61 archives of open marine environments throughout the Cenozoic and beyond (e.g., Zachos et al.,  
62 2001), much of what is known about Cretaceous and Jurassic palaeoceanography has been deduced  
63 from the geochemical archive of the calcareous rostra of extinct cephalopods, specifically belemnites  
64 (Dutton et al., 2007). Reasons for the wide use of these archive materials include their abundance in  
65 the fossil record, the diagenetically stable low-Mg calcite mineralogy of rostra (Veizer, 1974; Saelen,  
66 1989), and the broad palaeobiogeographic distribution of belemnites in the marine Boreal and  
67 Tethyan realms, (e.g., [Urey-Urey et al., 1951](#); Voigt et al., 2003; Wierzbowski, 2004; McArthur et al.,  
68 2007; Dutton, 2007; Price and Page, 2008; Wierzbowski and Joachimski, 2009; Price et al., 2009 2011;  
69 Li et al., 2012, 2013). As [with](#) all biogenic carbonates, however, these archives undergo post-mortem  
70 diagenetic alteration, representing a major obstacle in carbonate research (Swart, 2015).

71 Characteristic geochemical patterns and fabrics in biogenic carbonate hardparts have been used  
72 to test for example molluscks (e.g., Cochran et al., 2003, Sessa et al., 2015, Immenhauser et al.,  
73 2016), brachiopods (Parkinson et al., 2005), or foraminifera (e.g., Huber and Hodell, 1996; Kozdon et  
74 al., 2011) for evidence of diagenetic alteration. In the case of ammonites, the degree of preservation  
75 of nacre tablets provides evidence with regard to the preservation of these exoskeletons, to name  
76 one example (e.g., Cochran et al., 2010). With regard to belemnite rostra, the observation of ~~well-~~  
77 ~~preserved~~ [an intact](#) fibrous microfabrics in thin sections and polished rock surfaces in combination  
78 with cathodoluminescence is commonly used to identify ~~well-~~preserved belemnite rostra (Rosales et

79 al., 2001). In contrast, cloudy areas, exfoliation, fractures, stylolites, or boring traces are interpreted  
80 as evidence for post-mortem alteration (Saelen, 1989; Li, 2011; Benito and Reolid, 2012). A rigorous  
81 discussion of screening techniques, including trace-element concentrations, [and](#) isotopic ratios  
82 applied to biogenic low-Mg calcite macrofossils, [is has been](#) provided by Ullmann and Korte (2015).  
83 Similarly, a “best practice” approach for the interpretation of mollusc and brachiopod carbonate  
84 archives was presented [in by](#) Immenhauser et al. (2016).

85 The ultrastructure of belemnite rostra was first studied by Müller-Stoll (1936). This author  
86 described organic-rich (laminae obscura) and carbonate-rich (laminae pellucidae) concentric growth  
87 rings. Both of these were later shown to be calcitic but differ due to variable [degrees of amounts of](#)  
88 [occluded](#) organic matter (Saelen, 1989). Growth rings are made up by fibrous calcite crystals  
89 radiating from a central zone called apical line (Richter et al., 2011) forming what seems to be a low-  
90 porosity fabric (Saelen, 1989 and references therein; Fig. 1A-C). Single fibres (= radial structures of  
91 Saelen, 1989) can be arranged in bundles traversing the concentric growth layers. Each fibre thickens  
92 outwards and shows a sub-fibrous framework potentially first proposed - but not further explored -  
93 by Saelen (1989, Fig. 15a).

94 Belemnites ~~rostra~~ are traditionally considered to secrete their endoskeleton in oxygen isotope  
95 equilibrium with ambient seawater (e.g., Anderson et al., 1994; Price and Sellwood, 1997; Voigt et  
96 al., 2003; Price et al., 2009; Wierzbowski and Joachimski, 2007, 2009). The main argument brought  
97 forward is commonly the presence of what are considered cyclical oxygen isotope patterns  
98 interpreted as seasonal seawater temperature variations (Urey et al., 1951). The PeeDee belemnite  
99 used in Urey’s study was considered as well-preserved based on the compact fabric and the optical  
100 features of the calcite crystals (but see Li, 2011 [for discussion](#)). The assumption of equilibrium  
101 precipitation was further supported by data sets from recent cephalopods including *Nautilus*, *Sepia*,  
102 and *Spirula* precipitating their skeletal hardparts in near-equilibrium with  $\delta^{18}\text{O}_{\text{seawater}}$  (Lukeneder et  
103 al., 2010). In contrast to this traditional view, there is an increasing amount of evidence suggesting  
104 that belemnite rostra are problematic archives of their palaeoenvironment (see Immenhauser et al.,

105 2016 for detailed discussion). For example, Price et al. (2015) reported an offset of about 5°C  
106 between the aragonitic phragmocone and the calcitic rostrum of a single specimen of  
107 *Cylindroteuthis*. This offset was regarded as vital effect but it remains unclear whether the  
108 temperatures derived from the aragonite are too warm or from the calcite too cool. Similarly, high  
109 intra-rostral variability of elemental (Ca, Mn, Mg, Fe, Sr) and isotopic ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) composition, the  
110 latter with a scatter of up to 2‰, has been reported from belemnite rostra lacking evidence for  
111 diagenetic alteration (Podlaha et al., 1998).

112 The significant discrepancy of these data sets forms a strong motivation for a reconsideration of  
113 belemnite rostra as archives of their palaeoenvironment. Here, we report data from a wide set of  
114 state-of-the-art analytical infrastructure applied to thin- and ultra-thin sections of exceptionally well-  
115 preserved Jurassic and Cretaceous belemnite rostra. The following aims guided this paper: First, to  
116 present well-constrained petrographic evidence for the complex primary biogenic framework of  
117 these rostra; second, to document evidence that points to the highly porous nature of this biogenic  
118 framework; third, to assess the relative proportion between primary skeleton and porosity; fourth, to  
119 discuss the timing and nature of the pore-filling calcites phase. Evidence reported here has  
120 significance for the interpretation of proxy data from ancient belemnite rostra and forms the  
121 foundation of a detailed, high-resolution geochemical study that will be in the focus of forthcoming  
122 work.

123

## 124 2. Materials and Methods

### 125 2.1. Belemnites

126

127 Thin sections (30  $\mu\text{m}$ ) and ultra-thin sections (< 10  $\mu\text{m}$ ) of two well-preserved specimens  
128 ortho-rostra of *Megateuthis gigantea* (Schlotheim, 1820) from the Middle Jurassic and one specimen  
129 of *Belemnitella mucronata* (Schlotheim, 1813) and *Goniotteuthis quadrata* (Blainville, 1827) from the  
130 Upper Cretaceous were studied. Specimens of *Megateuthis* were collected in Bajocian marly

131 limestone deposits from southern Germany. *Belemnitella* rostra are from the late early Campanian  
132 (*mucronata* Zone), and *Goniatites* from the early Campanian *lingua/quadrata* –  
133 *gracilis/mucronata* Zone from northwestern Germany. *Goniatites* and *Belemnitella* rostra were  
134 embedded in calcareous (65-90%) epicontinental shelf deposits of the Misburg Formation (Niebuhr,  
135 1995; Niebuhr et al., 2007). Specimens did not display evidence for exfoliation nor did they show  
136 boring traces of the surfaces of rostra. Specimens were sectioned along their long axis in a marginal  
137 position and perpendicular to the c-axis of their calcite fibres. One section cuts the rostrum of  
138 *Megateuthis* perpendicular to the long axis.

139

## 140 2.2. Methods

141

142 Surfaces of thin sections were chemo-mechanically etched using colloidal silica (OP-S) for 5-15  
143 minutes to reduce surface irregularities on an atomic scale (Massonne and Neuser, 2005) and coated  
144 by a thin carbon layer. All coated thin sections have been studied under a high-resolution field  
145 emission scanning electron microscope (HR-FESEM) type LEO/ZEISS 1530 Gemini using a backscatter  
146 detector (BSD) at the Ruhr-Universität Bochum, Germany (Figs. 1-3).

147 Crystallographic orientation of belemnite calcite fibres was determined by electron  
148 backscattered diffraction (EBSD; Nordlys, OXFORD Instruments). The data acquisition and analysis  
149 was performed using the software packages AZtec and Channel 5 by Oxford Instruments (Fig. 4). The  
150 scanning electron microscope (SEM) was operated at beam energy of 20 kV, an aperture of 60 µm, a  
151 working distance of 25 mm and a tilt angle of 70°. Thin sections were mapped at Bochum University  
152 in the high-resolution mode using a grid matrix (1149x748 points) at a step rate-width of 2.017 µm  
153 (Fig. 4A) and (543x266 points) at a step rate-width of 1.652 µm (Fig. 4D) and for the single calcite  
154 fibre 50 µm to reduce artefacts and increase the reliability of the data. The orientations of the  
155 crystals of-in the individual maps were visualized using a rainbow colour coding ranging from blue  
156 over green and yellow to orange and red, where identical colours indicate identical crystal axis

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157 orientations. For visualizing the weak angular deviations in the crystal lattice in a single calcite fibre,  
158 we applied an angular resolution of 2 degrees for the complete rainbow colour range. In addition,  
159 orientations of the measured crystallographic axes [were](#) plotted into the lower hemisphere of a  
160 Schmidt net (Fig. 4E).

161 Rostra were further investigated under a cathodoluminescence microscope type HC1-LM by  
162 Lumic equipped with a hot cathode (Neuser et al., 1996) and a digital camera system (DP73 by  
163 Olympus) for recording digital images at Bochum. Beam energy of 14kV and a beam current density  
164 between 5 and 10  $\mu\text{A}/\text{mm}^2$  were generally used for the CL-measurements. Integration times for CL-  
165 spectra were commonly between 10 and 60 seconds (Fig. 5).

166 X-ray element distribution maps were acquired using a Cameca SX5FE field emission electron  
167 microprobe at Bochum. The acceleration voltage was 15 keV with a probe current of about 80 nA and  
168 a fully focused beam. The intensity of S K $\alpha$ 1 was recorded simultaneously on two wavelength  
169 dispersive spectrometers equipped with LPET and PET analyzing crystals. The Mg K $\alpha$ 1 line was also  
170 measured on two spectrometers (LTAP and TAP crystals), whereas P K $\alpha$ 1 was measured on a single  
171 spectrometer equipped with a LPET crystal. The images were acquired in continuous stage scan  
172 mode. They have a resolution of 2048 x 1536 pixel, and the dwell time was 17 ms per pixel (Fig. 6).

173 To test for the distribution of organic matter within the belemnite rostra, thin sections were  
174 studied under [thea](#) fluorescence microscope (Leica DM4500P) equipped with a mercury short-arc  
175 reflector lamp coupled with a Leica EL6000 compact light source. We used the blue light filter set  
176 producing bright green fluorescence images (filter set I3 for blue light excitation: excitation 450-490  
177 nm, emission 515 nm, voltage 100-240 VAC and 50-60 Hz frequency; Fig. 7). Fluorescence microscopy  
178 in the manner applied here is an optical tool to qualitatively document the spatial distribution of  
179 organic matter in shells. Fluorescence reflects organic matter and less commonly crystal lattice  
180 defects and solid inclusions in crystals. [Further more](#) details of this methods [have been presented](#)  
181 [please refer to](#) Wanamaker et al. (2009) and Ritter et al. (subm.).



182 Confocal laser fluorescence microscopy (CLFM) images on an uncoated *Megateuthis* mount  
183 were made using a Bio-Rad MRC-1024 scanning confocal microscope at the W. M. Keck Laboratory  
184 for Biological Imaging at UW-Madison (Fig. 8). The microscope was operated with a 40 mW laser at  
185 wavelengths of 488 nm, 568 nm, and 647 nm. All three wavelengths were simultaneously rastered  
186 across the sample. Naturally occurring compounds within the sample caused fluorescence at multiple  
187 wavelengths. Images were collected through the following three emission filters: visible green light ( $\lambda$   
188 = 505 to 539 nm); visible red light ( $\lambda$  = 589 to 621 nm); and far-red light ( $\lambda$  = 664 to 696 nm).

189 In order to analyze the three dimensional filigree framework, synchrotron radiation based  
190 micro-computed tomography was applied (Fig. 9). Data were collected at the bending magnet beam  
191 line 2-BM at the Advanced Photon Source, Argonne National Laboratory, USA. A double multilayer  
192 monochromator of 1.5% band-width provided 27.2 KeV X-rays. Images were collected in transmission  
193 mode by a CCD camera behind the sample in the hutch configuration. The sample-detector distance  
194 was set to 300 mm to collect quantitative phase contrast data. 1440 projections were acquired while  
195 the sample was rotated over 180° in steps of 0.125°. A microtomographic data set with a size of 2048  
196 x 2048 x 1948 voxels was reconstructed using a phase retrieval algorithm (Mokso et al., 2013).

197

198

### 199 3. Results

#### 200 3.1 Optical-, cathodoluminescence-, fluorescence-, and confocal laser fluorescence microscopy (TL, CL, 201 FL, CFLM)

202 Under transmitted light (TL), thin sections of rostra cut perpendicular to the c-axis of calcite  
203 fibres reveal a banded distribution of calcite fibres containing brownish triangular elements of  
204 variable size (Fig. 5A, D). Some of the larger fibres contain a triangular, organic-rich centre, with its  
205 innermost domains occluded by translucent calcite. Bundling of neighbouring calcite fibres is  
206 indicated by their subparallel orientation of their a-axis (Fig. 5D). A uniform extinction (orientation)

207 pattern of adjacent fibres under crossed polarizers is observed (Fig. 5B, E) and is in agreement with  
208 EBSD data (Fig. 4A). Individual fibres display an undulatory extinction (converging or diverging c-axes)  
209 under crossed polarizers. Calcite occluding space between organic-rich elements and fibre  
210 reinforcement is translucent and contains little or no organic matter (Fig. 5D). Brownish, triangular  
211 elements have a relatively low optical relief, compared to the surrounding translucent calcite with a  
212 relatively higher optical relief (supplement Fig. 1A-B).

213 Three different luminescence patterns are observed under the cathodoluminescence  
214 microscope (CL): (i) A light blue luminescence of the brownish, triangular elements (Fig. 5C, F); (ii)  
215 dark blue, intrinsic luminescence of the translucent phase; (iii) locally, orange to red luminescent  
216 fractures and microstylolites are observed. In rare cases, fractures retrace the triangular outline of a  
217 fibre (Fig. 5C, F, supplement figure 1D).

218 Brownish triangular areas under transmitted light display light green fluorescence while the  
219 translucent areas show a dark green fluorescence under the fluorescence microscope (FL).  
220 Microfractures are darker under transmitted light compared to the triangular elements and show a  
221 light green fluorescence (Fig. 7A-B).

222 Different fluorescence patterns under the CLFM reveals calcite domains visible in BSE (and  
223 other) imaging techniques (Figs. 3, 5-7). Filled cracks fluoresce brightly in green and red wavelengths  
224 (Fig. 8B-C). Domains that are dark in BSE do not fluoresce in CLFM (Fig. 8A-D). Bright domains in BSE  
225 fluoresce brightly in CLFM at all wavelengths observed (Fig. 8A-D). Higher magnification reveals  
226 brighter fluorescence between adjacent domains that appear bright in BSE (Fig. 8D).

227

### 228 *3.2 Scanning-electron microscopy equipped with a backscatter detector (SEM BSD)*

229 Images collected with the scanning electron microscope equipped with a backscatter detector  
230 present important evidence for the presence of two calcite phases (dark and bright) of different

231 chemical compositions building the rostra studied. The brownish triangular areas under transmitted  
232 light are dark in BSE. Thin sections cut perpendicular to the c-axis of the radiaxial fibrous calcite (Fig.  
233 1D I-IV) reveal a complex framework, dark in BSE, surrounded by relatively brighter calcite (Figs. 1-3).  
234 Cross sections of the majority of fibres are polygonal or, less often, honeycomb shaped with a tri-  
235 radial (120°) symmetry representing an ultrastructure that has not ~~yet~~ been described in previous  
236 studies (Figs. 1C-G, Fig. 3A-E). Individual fibre diameters vary between 10-80 µm. Calcite fibres  
237 terminate at individual concentric growth layers that also form the nucleation site for the overlying,  
238 next fibre generation, displaying increasing thicknesses and occurring in increasing numbers towards  
239 the outer portions of the rostrum (Fig. 1A-D). Brighter area in BSE are more likely to be composed of  
240 near-stoichiometric CaCO<sub>3</sub> with higher average atomic masses (mainly Ca), whereas excess C, P, Mg,  
241 or S will lower the average atomic mass. Accordingly, areas with decreasing amount of Ca and  
242 increasing amounts of C, P, Mg or S are darker.

243 Four section planes are presented to describe the intricate bio-composite mineral present  
244 within a single fibre. The following description distinguishes between the darker framework (i), i.e.,  
245 micro~~metre~~-thick branches terminating in wall-like reinforcements and (ii) tri-radial central  
246 portions; and brighter fabric (iii) consisting of calcite crystals forming isopachous cement layers with  
247 individual crystallites coated by submicro~~metre~~ thick layers of matter darker in BSE (Fig. 1G). In all  
248 sections, we observed isopachous calcite crystals oriented perpendicular to the inner dark walls (Fig.  
249 3A-E). Section plane I consists of three simple, dark in BSE branches of variable lengths. Often, these  
250 branches exhibit reinforcements of variable lengths and thicknesses (about 1 micro~~metre~~) and  
251 increasing widths towards neighbouring branches (Figs. 1D-I, 3A). Conversely, reinforcements being  
252 connected to neighboring triangles are rarely observed. Section type II is characterized by an  
253 enlarged, dark in BSE central element of variable diameter (2-30 µm, Figs. 1D-II, 3C). Some of the  
254 larger central elements display an inner zone with additional tri-radial structures comprising of  
255 smaller, isopachous, brighter in BSE area calcite crystals rotated by 60° relative to outer branches  
256 (Figs. 1D-III, 3D; section type III). Section type IV represents the most complex fabric. Here, the inner

257 portions of larger central elements display alternating darker and brighter in BSE areas (Figs. 1D-IV,  
258 3E). Generally, enlarged central elements correlate with a shortening of corresponding, darker  
259 branches.

260 Thin sections cut parallel to the c-axis of the radial fibrous calcite reveal an framework dark in  
261 BSE of triangular shaped elements with their tips pointing towards the outer margin of the rostrum  
262 (Fig. 1C-D, supplement Fig. 2). Lighter and darker areas within a single calcite fibre show their  
263 composite nature. Lighter and darker areas within concentric growth rings, as visible in transmitted  
264 light, depend on the number and size of these elements. Higher magnification reveals a homogenous  
265 central portion (“trunk” – white line) of pyramidal morphology dark in BSE surrounded by inclined  
266 isopachous calcite crystals coated by material dark in BSE. This overall pattern results in a “~~x-~~  
267 [Christmas tree like](#)” structure (Fig. 3F). The dark framework forms the substratum upon which an  
268 isopachous, translucent calcite phase nucleated (Fig. 1D, G 2-3). The boundary surface between the  
269 framework dark in BSE and the surrounding carbonates brighter in BSE is, in places, corroded and  
270 uneven (Fig. 2).

271

### 272 3.3 Electron microprobe analysis (EMPA)

273 The contrasting chemical composition of the two different calcite phases building these rostra is  
274 also revealed by EMP data. [Detailed WDS scans show that the strongest variability is displayed by](#)  
275 [Mg, P, and S, whereas other elements are almost constant or ~~contained~~present in amounts close to](#)  
276 [the detection limit \(e.g., SrO = 0.1-0.2 wt.%; FeO = <0.1 wt.%; MnO < 0.5 wt.%. X-ray element](#)  
277 [distribution ~~counts-maps~~ show a generally low concentration of the elements Mg \(MgO = 0.3-0.4](#)  
278 [wt.%\), P \(P<sub>2</sub>O<sub>5</sub> = 0.1-0.2 wt.%\), and S \(SO<sub>3</sub> = 0.20-0.50 wt.%\). The Mg- and P-content is slightly](#)  
279 [elevated in the darker, triangular areas in BSE images \(MgO up to 0.6 wt.%; P<sub>2</sub>O<sub>5</sub> up to 0.25 wt.%\)](#)  
280 [compared to the relatively brighter areas in BSE images in the centre of larger tetrahedrons and their](#)  
281 [surroundings vicinity. Lowest Mg ~~values-concentrations~~ were ~~collected-found~~ along microfractures](#)

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282 that ~~show a display~~ bright luminescence ~~in Cl colours~~ (MgO < 0.2 wt.%; Fig. 6B). Sulfur has a higher  
283 concentration in the brighter ~~in BSE areas~~ ~~in BSE images~~ (SO<sub>3</sub> up to 0.65 wt.%) and lower  
284 concentrations in the darker ~~areas~~ ~~in BSE area images~~ (SO<sub>3</sub> = 0.20-0.50 wt.%; Fig. 6D). For better  
285 comparison with BSE images from other samples and with the element distribution, ~~we collect~~ BSE  
286 data ~~were obtained~~ for the same field of view (Fig. 6A).

287

### 288 3.4 Electron Backscattered Diffraction imaging (EBSD)

289 Electron backscattered diffraction was used to document the biological controlled (sensu  
290 Lowenstam and Weiner, 1989; Dupraz et al., 2009; Weiner and Addadi, 2011) formation of what is  
291 here assumed to represent the primary biogenic skeletal carbonate. EBSD reveals a very low  
292 variation of c-axes orientation of calcite fibres (Fig. 4A). The sub-parallel orientation of the c-axes  
293 {001} is documented by their close fitting in the lower hemisphere of a Schmidt net (Fig. 4E, left plot).  
294 A different characteristic is found for the crystallographic orientation of the a-axes {010} of calcite  
295 fibres (Fig. 4E, right plot). All a-axes are aligned along a great circle whilst the colour code of the  
296 according fibres is indicative of an arrangement in bundles. Adjacent fibres (10 to 100 fibres) share a  
297 similar - if not identical - orientation (Fig. 4A-B). The majority of fibre bundles are characterized by  
298 blue, green and red colour coding. Specifically, the spatial orientation of individual a-axes within a  
299 single fibre bundle deviates by 20° or less from the bundle mean value. Variation in the orientation of  
300 the c-axis of a single calcite fibre in the range of 1-3° was observed (Fig. 4D). As the angular  
301 resolution from blue to red rainbow colour shown in EBSD maps (Fig. 4A-B) has a resolution of 50°,  
302 minor angular deviations (<1°) are not visible in ~~our image~~ Fig. 4A-B.

303

### 304 3.5 Synchrotron radiation based micro-computed tomography (SRμCT)

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305 Tetrahedral structures are visible in three dimensions in the tomographic dataset despite the  
306 high signal to noise ratio and artefacts. There is a distinct difference in X-ray attenuation between the  
307 inner tri-radial elements and the surrounding calcite.

308

#### 309 **4. Interpretation and Discussion**

##### 310 *4.1 Reconstruction of the primary belemnite rostrum ultrastructure*

311

312 Data presented here document a repeated pattern of triangular elements that seem to be  
313 originally connected, building a concentric layered, highly complex, and porous framework. The  
314 space between the former skeletal elements is interpreted as pore space probably filled by body  
315 fluids or organic material during the life time of these organisms. The latter assumption is based on  
316 analogous observations in the porous endoskeletons of recent *Sepia* (Sherrard, 2000; Guerra, 2006).  
317 [Referring to the high porosity observed in both, the belemnite rostrum and the sepiid cuttlebone, it](#)  
318 [is important to note that these structures are not homologous \(Fuchs 2012\).](#)

319     Accordingly, the belemnite rostra originally consisted of an organic-rich biogenic framework of  
320 calcitic tri-radial tetrahedrons (triangular pyramids arranged perpendicular to the concentric layers  
321 during lifetime). Tetrahedrons are elongated along their c-axis with the tip of the pyramid pointing  
322 towards the precipitation site i.e., in growth direction towards the outer margin of the rostrum (Fig.  
323 1C-D). Individual branches protruding from the edges of the tetrahedrons possess outer  
324 reinforcements acting as stabilizers. The central portion of the tetrahedrons may yield a channel-like  
325 cavity (Fig. 1D III-IV). Organic membranes at which nucleation of the tetrahedrons may have started  
326 and stopped are not preserved. However, it seems likely that such membranes were present because  
327 the bases of the tetrahedrons follow a concentric layer. Structurally, the bundling of the tri-radial  
328 elements forms a simple honeycomb-like framework in which the terminations of branches of

329 adjacent elements are connected. The mechanical stability of the honeycomb structure is enhanced  
330 by reinforcement walls (Figs. 1D, G, 3C).

331 Based on the variable dimensions of skeletal elements seen in thin sections, intra-rostral pore  
332 space was visually estimated to range between 50-90% of the total rostrum (Fig. 3A: 90% pore space  
333 and 10% skeletal elements; Fig. 3B; 50% pore space and 50% skeletal elements). In this context, the  
334 observation that pore space is not limited to the apical [line](#) region but is present across the bulk  
335 rostrum is important. The secretion of a porous, but mechanically stable [endoskeleton-orthorostrum](#)  
336 is probably best seen in the context of a considerable reduction of energy and building material  
337 required to form this structure compared to a massive ~~structure-endoskeleton~~ (Sherrard, 2000).  
338 Strict biological control, i.e. in the presence of organic templates (Chateigner et al., 2000; Richter et  
339 al., 2011), over the precipitation of primary skeletal elements is demonstrated by a systematic  
340 arrangement of adjacent elements into bundles of similar or identical orientation of their  
341 crystallographic a-axes. This configuration results in a much higher mechanical load capacity and  
342 torsion stiffness of the framework of the rostrum.

343 Alternating concentric Ca-rich (brighter; laminae obscurae) and C-rich layers (darker; laminae  
344 pellucidae) of Müller-Stoll (1936) are related with the banded distribution of larger and smaller  
345 organic-rich triangular elements of the primary skeletal ~~structure~~ [structure](#) of the belemnite [ortho](#)rostrum  
346 (Fig. 1D, supplement Fig. 2). These layers potentially indicate differences in calcite precipitation rates.  
347 Based on petrographic and ultrastructural evidence, the Mg and Ca elemental concentrations of the  
348 rostrum, the lack of secondary micro-dolomite, and the absence of blotchy luminescence, the widely  
349 held assumption of a primary low-Mg calcite mineralogy for the studied belemnite rostra is  
350 confirmed (see discussion in Richter et al., 2003).

351

352 *4.2 Early and late diagenetic processes*

353

354 The presence of a highly porous primary rostrum architecture during the life time of the  
355 belemnite organism as proposed here, is ~~in contrasted by~~ to the dense fabrics observed in ~~the case of~~  
356 ~~most~~ rostra collected in Mesozoic sedimentary successions (Fig. 1A-B). Hence, the diagenetic  
357 pathway from porous to dense fabrics deserves attention. The marine diagenetic alteration of  
358 biominerals is initiated directly after the death of a carbonate-secreting marine organism when  
359 metabolic processes come to a halt. At this early stage, organic matter outside of the orthostrum  
360 (i.e., the belemnite animal itself) and in the pore space of rostra and between biominerals  
361 decomposes (Saalen, 1989), triggering a series of complex bio-chemical processes. Essentially,  
362 decomposition of organic matter is mediated by microbial activity, and given the abundance of  
363 marine microbial life, there is no reason to assume that this would have been different in the case  
364 examples studied here.

365 Microbial metabolic products, the presence of microbial “mucus” (extracellular polymeric  
366 substance) and charged surfaces represented by microbial bodies influence the micro-environment  
367 in intra-rostrum pore space by altering the balance between more reduced and more oxidized forms  
368 of carbon as previously summarized under the term “alkalinity engine” (Dupraz et al., 2009).  
369 Specifically, Visscher and Stolz (2005) subdivided microbial species into 5-7 groups (“guilds”) having a  
370 similar metabolism. Some of these promote carbonate precipitation (e.g., cyanobacteria, sulphate  
371 reducers), whilst others favour dissolution (e.g., aerobic heterotrophs, fermenters). Dupraz et al.  
372 (2009) documented that the balance of microbial metabolic activities directly influences carbonate  
373 precipitation or, vice versa, dissolution. Initial microbial decomposition of organic matter may result  
374 in the production of organic acids lowering the pH-values in the pore space (Berner et al., 1978),  
375 enhancing intra-~~skeleton~~ orthostrum dissolution of biominerals (Fig. 2).

376 As soon as the bulk of organic matter is decomposed, alkalinity is increased due to microbial  
377 metabolic products enhancing the precipitation of carbonate minerals (intrinsic  
378 organomineralization) leading – in the view of the authors - to the formation of the translucent,  
379 isopachous calcite crystals that occlude primary pore space in rostra (Fig. 2). Obviously, any



380 assumption regarding microbial processes in these ancient carbonates must remain speculative.  
381 Nevertheless, following the basic concepts laid out in Dupraz et al. (2009), we tentatively assume  
382 that a first phase of decomposition was dominated by aerobic heterotrophy, sulphide oxidation, and  
383 fermentation decreasing the saturation index and resulting in the corrosion of skeletal elements in  
384 the belemnite rostrum. Evidence for this comes from micro-corrosion features at the outer surfaces  
385 of the primary skeletal framework forming the substratum upon which the pore-filling, secondary  
386 calcite phase nucleates (Fig. 2).

387 The nucleation and precipitation of the secondary calcite phase (Fig. 1D, G, 2-3) was possibly  
388 dominated by sulphate reduction increasing the saturation index and hence favoring precipitation of  
389 CaCO<sub>3</sub>. During crystals growth, remnants of belemnite organic matter combined with microbial  
390 mucus were likely trapped between single crystals or at the growth front of crystals and delineate  
391 crystal boundaries. Specifically, the growth of fibrous calcitic crystals will proceed as long as growth  
392 rate, fluid supersaturation, and temperature are low enough to discourage spontaneous nucleation  
393 (Oti et al., 1989). Similar processes have been described from extant echinoderm [endoskeletons](#)  
394 ~~skeletal remains~~[that share a comparable amount of primary porosity like the herein with the](#)  
395 [described belemnite orthorostra](#) (Richter et al., 2003).

396 During this early stage of diagenetic evolution, the rostra most likely preserved their original  
397 morphology due to the biogenic calcite framework and abiogenic calcite progressively occluding  
398 former pore space preventing, in combination, a collapse of the [endoskeletonsrostra](#). The directly  
399 comparable, dark blue intrinsic luminescence of the translucent secondary outer calcite layer and the  
400 calcite infill of central pore space of many of the larger triangles (Figs. 3D-E, 5A, D, 6) suggest that  
401 both phases precipitated from one fluid, or different fluids with near-identical geochemistry. This is,  
402 of course, within the limitations of the geochemical resolution of the ~~CL~~[cathodoluminescence](#)  
403 method and with reference to elements that affect luminescence patterns (e.g., Mn<sup>2+</sup>, Fe<sup>2+</sup> and REE;  
404 see discussion in Barbin 1991, 1993; Ritter et al., 2015). Conversely, the organic matter-rich triangles  
405 display a moderately brighter blue luminescence pattern (Fig. 5C, F). This feature is best explained by

406 calcite lattice deformation due to the incorporation of organic matter into the crystal lattice  
407 (intracrystalline) [and is](#) not necessarily indicative of a different geochemical composition. This  
408 [concept](#) is supported by x-ray diffractometry (Richter et al., 2011) documenting that the fibrous  
409 fabric of the belemnite rostra, lacking late diagenetic Mn-rich cements, is composed of  
410 stoichiometric or near-stoichiometric calcites ( $d(104) = 3.030$  to  $3.035 \text{ \AA}$ ).

411 A late diagenetic (burial) stage of rostra is documented by dissolution and compaction features  
412 as indicated by microfractures and microstylolites (Figs. 2, 5C, F; Rosales et al., 2004a, [b](#)). The  
413 circulation of  $\text{Mn}^{2+}$ -rich fluids caused the precipitation of a late calcite phase that occludes fractures  
414 and fissures. In some cases this late phase yields a bright luminescence and is zigzag or triangular  
415 shaped, tracing the morphology of the triangular biominerals (Fig. 5C).

416

#### 417 *4.3 Implications for the function of the rostrum*

418

419 It is generally accepted that the belemnite rostrum acts as a counterweight to the soft body.  
420 Based on the observation of a high primary porosity (see also Spaeth, 1971, 1973, 1975; Ullmann et  
421 al., 2015), this interpretation requires renewed consideration. Rostra are commonly considered to  
422 have the same density as inorganic calcite crystals, ranging from  $2.5$ - $2.7 \text{ g/cm}^3$ .

423 *Sepia*, the closest living relative of the extinct belemnites, incorporates a total of 10-40% organic  
424 matter in its [cuttlebone shell](#)—and comparably high amounts of intracrystalline organics were  
425 observed for the biogenic belemnite [skeleton/rostrum](#). Accordingly, ignoring open pore space, a  
426 reduced density of the biogenic belemnite calcite of about  $2.4 \text{ g/cm}^3$  (10% organic) –  $2.0 \text{ g/cm}^3$  (40%  
427 organic) results. Assuming that liquid or extracrystalline organic matter ( $1.03 \text{ g/cm}^3$ ) - with density  
428 comparable to that of seawater ( $1.026 \text{ g/cm}^3$ ) - filled up the pore space of living belemnite [rostra](#), an  
429 overall density of the rostrum ranging between roughly  $1.7$ - $1.1 \text{ g/cm}^3$  (mean  $1.4 \text{ g/cm}^3$ ) is tentatively  
430 assumed on the level of a working hypothesis. If these assumptions hold true, then the belemnite

431 rostrum had a cumulative density that is significantly lower than that of stoichiometric calcite.  
432 Therefore, questions regarding the locomotion of belemnites result.

433 A possible analogue may come from a structure reported from a modern  
434 ~~onychoteuthid~~ ~~mastrephid~~ squid (*Onykia*) that has remarkable morphological similarity to the  
435 *Megateuthis* rostrum. *Onykia* has a purely organic rostrum that due to its very low density does not  
436 act as a counterweight for the soft body. It is assumed that it supports the posterior part of the  
437 mantle and fins (= axial stability in Bizikov and Arkhipkin, 1997 and Arkhipkin et al., 2015). A function  
438 as a muscle attachment structure for belemnite rostra ~~has been~~ first put forward by Stevens  
439 (1965). Direct evidence for the presence of fins in belemnites has recently reported by Klug et al.  
440 (2015), favouring a squid-like high speed swimming ~~mode of life for~~ Jurassic belemnites.  
441 Noteworthy to report here, is the case of belemnites (*Chitinoteuthis*) with a non-calcified rostrum  
442 (Müller-Stoll, 1936).

443

## 444 5 Open questions and suggestions for future research

### 445 5.1. Paragenesis of porosity-occluding calcite phase

446 Within individual belemnite rostra, data presented here differentiate: (i) ~~the~~ biogenic, highly  
447 porous skeletal framework secreted during the life time of the ~~belemnite~~ ~~organism~~; (ii) ~~the an~~  
448 inorganic or organomineralic – arguably early diagenetic - calcite phase occluding the pore space of  
449 the biogenic framework; and (iii) a late diagenetic, burial, Mn-rich carbonate phase filling fissures and  
450 larger cracks within the rostra. Assuming that the above-discussed paragenetic succession is valid, a  
451 series of open questions result. In the view of the authors, it is at least conceivable that portions of  
452 the rostral pore space were occluded during the life time of the belemnites (remote  
453 biomineralization sensu Hücker and Hemleben, 1976; Chinzei and Seilacher, 1993; Seilacher and  
454 Chinzei, 1993). If this holds true, then the paragenetic sequence of primary framework and  
455 secondary infill calcite is even more complicated than presented here and gradual in nature.  
456 Moreover, individual growth increments within rostra are then not representative of specific

457 correlative time intervals. Specifically, each growth increment then represents a complex composite  
458 structure of paragenetic phases representing temporally different stages in the belemnite  
459 ontogenetic cycle. Obviously, this would render the interpretation of time series belemnite  
460 geochemical data difficult. Evidence against a biogenic infill of the skeletal pore space by remote  
461 biomineralization sensu Seilacher and Chinzei (1993), however, may or may not come from the  
462 presence of a corroded outer surface of what is considered the primary skeletal ultrastructure of  
463 these rostra (Fig. 2). It seems difficult to argue that intra-rostrum body fluids became corrosive at  
464 some stage during the life time of the belemnite animal. Clearly, these questions require further  
465 detailed work.

466

## 467 *5.2 Primary skeletal ultrastructure and preservation of organic matter*

468

469 The authors acknowledge the fact that despite the very detailed information regarding the  
470 belemnite ultrastructure shown here, our study lacks direct evidence for a primary biogenic origin of  
471 the complex, highly porous framework and the subsequent cementation by an early diagenetic  
472 calcite phase. Open questions, however, remain. Specifically, the significance of preserved organic  
473 matter in the biogenic belemnite calcite deserves attention. In the following, we present several lines  
474 (petrographic, optical, and geochemical data) of circumstantial evidence suggesting the presence of  
475 preserved organic matter.

476 The sector-wise systematic arrangement of triangular elements - with their a-axis being  
477 oriented subparallel to parallel (Figs. 3A-C, 4A-B, 5A, D) - in bundles, indicate a biologically controlled  
478 origin (Lowenstam and Weiner, 1989) of these fabrics. The primary belemnite rostrum ultrastructure  
479 is brownish (Figs. 5A, 7A) in thin sections under transmitted light and has a relatively low optical  
480 relief. According to Ullmann et al. (2014), brownish areas in thin sections of biogenic carbonates are  
481 indicative of remnant organic matter ( $C_{org}$ ). Under the cathodoluminescence- and fluorescence  
482 microscope, the primary filigree belemnite framework shows a light blue luminescence (CL) and light

483 green fluorescence (FL). According to Wanamaker et al. (2009) and Pérez-Huerta et al. (2008),  
484 fluorescence in biominerals is triggered by organic macromolecules associated with chitin  
485 polysaccharides and proteins. Dark fluorescence patterns commonly refer to portions of the skeletal  
486 hardparts that are relatively depleted in organic matter. Bright green fluorescence patterns typify  
487 areas with increased amount of organic matter (Wanamaker et al., 2009).

488 | Primary skeletal structures display darker colours in SEM-BSE images. Electron microprobe  
489 | analyses revealed that the biogenic skeletal calcites contain more P and Mg but less S compared to  
490 | what is here considered an early diagenetic, pore-filling calcite phase. Higher concentrations of P (Fig.  
491 | 6C) may be related to [the](#) presence of organic matter. Arguments for this have been presented by  
492 | Longinelli et al. (2002, 2003) and Gröcke et al. (2003) who found phosphate ( $\text{PO}_4^{3-}$ ) of presumed  
493 | biogenic origin being preferentially enriched along concentric growth rings. Generally, the phosphate  
494 | concentration of ancient belemnite rostra is variable but very low (less than 0.3%) comparable to  
495 | that in [Recent-modern Sepia](#).

496 | The primary filigree belemnite framework does not fluoresce under the CLFM. The factors  
497 | that cause fluorescence in samples studied under the CLFM are poorly constrained (Fig. 8). Naturally-  
498 | occurring organic compounds such as proteins or polysaccharides can cause fluorescence in other  
499 | biogenic carbonates, including brachiopods (Pérez-Huerta et al., 2008), gastropods (Guzman et al.,  
500 | 2007), or cephalopods (Linzmeier et al., 2016). In modern brachiopods and *Nautilus*, portions of the  
501 | exoskeletons with higher amounts of intracrystalline organic matter (Clark, 1999) appear dark under  
502 | CLFM ([Pérez-Huerta et al., 2008](#); Linzmeier et al., 2016; ~~[Pérez-Huerta et al., 2008](#)~~). This pattern lends  
503 | support to the argument that dark triangular areas in BSE images represent the primary biogenic  
504 | skeleton and contain remnants of organic matter. Marine sediments may contain abundant humic  
505 | substances resulting from the degradation of marine organic matter (Nissenbaum and Kaplan, 1972)  
506 | and evidence has been presented that the [sulphur](#) content of the humic substances increases with  
507 | degradation (Francois 1987). Concluding, it is here proposed that humic substances caused elevated  
508 | S concentrations in the diagenetic calcite phase that occludes the skeletal pore space (Fig. 6D) and

509 | causes the CLFM fluorescence in all three wavelengths (Blyth et al., 2008; Orland et al., 2009, 2012;  
510 | Fig. 8).

511 | Similarly, microtomographic data indicate the former presence of organic matter in dark  
512 | triangular areas of rostra (Fig. 9) as observed in BSE images. The brightness of a carbonate observed  
513 | in CT image indicates the degree of attenuation of an X-ray passing through this material (Mobilio et  
514 | al., 2015). As the inner tri-radial structures of rostra appear darker in colour relative to the calcite  
515 | phase fringing these structures, we suggest that the fringing phase is made of a denser calcite phase  
516 | compared to the inner structure. That observation is in line with the observation of a low optical  
517 | relief of these features (supplement Fig. 1A-B).

518 | This ~~tentative~~ interpretation presented here with regard to belemnite rostra is arguably  
519 | consistent with observations of 10-40% organic matrix in the *Sepia* cuttlebone (Birchall and Thomas,  
520 | 1983; Florek et al., 2009). This is relevant as we suggest that the belemnite rostrum is structurally  
521 | similar but not homologous (Fuchs 2012) to the *Sepia* cuttlebone with regard to the primary intra-  
522 | skeletal porosity. Having said this, the presence of preserved organic matter in ancient biogenic  
523 | carbonates particularly, intra-crystalline organic matter is not uncommon (Clark, 1999, 2005). Excess  
524 | carbon observed for *Megateuthis* has been interpreted as evidence for a former organic matrix  
525 | within these low-Mg calcite biominerals (Dunca et al., 2006). Similarly, Florek (2004) argued for an  
526 | excess of carbon in the rostra of *Belemnopsis* and *Hibolites*. Summing up: Different lines of  
527 | circumstantial evidence point to the presence of remnant organic matter within biominerals. These  
528 | data require verification or rejection via the application of spatially highly resolved geochemical data.  
529 | This work is presently under progress.

530

## 531 | 5. **Conclusions**

532 | Ultrastructural data documented here suggest that the calcitic rostra of Mesozoic belemnites  
533 | yielded 50-90% primary porosity probably filled with body fluids and/or organic matter during the life  
534 | time of the animal. Porosity was distributed throughout the rostrum as opposed to being limited to

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535 the central apical area. The primary biogenic rostrum framework consists of triaxial branches and  
536 tetrahedrons of variable size forming a honeycomb-like network. This structure arguably combined  
537 mechanical stability with an energy-efficient biomineralization strategy.

538 The recognition of belemnite rostra as a highly porous structure requires a re-interpretation of  
539 the function of the rostrum as counterweight to the soft body and has implications for the swimming  
540 mode of belemnites. On the level of a working hypothesis, we argue that the low-porosity fabric  
541 found in fossil rostra collected in outcrops worldwide is the result of a syntaxial, early diagenetic  
542 cement phase that nucleated upon the surface of the biogenic framework and subsequently  
543 occluded the pore space. The possibility of gradual occlusion of skeletal porosity by remote  
544 biomineralization during later ontogenetic stages during the life of the animal is possible but seems  
545 unlikely at present.

546 If the here-presented concepts hold true, then these new findings have significant implications  
547 with regard to geochemical proxy data collected from fossil belemnite rostra. Specifically, the fact  
548 that rostra may consist of biogenic and abiogenic calcite phases formed at different times may  
549 explain the controversially low reconstructed seawater temperatures and the uncommonly high  
550 scatter of proxy data even from well-preserved rostra collected in the same stratigraphic interval.  
551 This is because seawater properties of surficial water masses, the habitat of nekto-benthic  
552 belemnites, are recorded in the biogenic portions of the rostrum whereas the early diagenetic phase  
553 reflects cooler basinal bottom or marine pore water signatures. Findings presented here form a solid  
554 and well-constrained petrographic data set but one that must be verified by high-resolution  
555 geochemical data of all paragenetic calcite phases observed.

556

557

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811 **Figure captions**

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813 **Fig. 1A-B) Structural and ultrastructural composition of belemnite rostra.** *Belemnitella mucronata*,  
814 thin sections photographed under crossed polarizers. A) Cross section with pseudo-uniaxial cross  
815 indicating radially arranged calcite fibres, red box refers to C. B) Longitudinal section with central  
816 apical line and radiating fibres from the centre to the margin, stippled line refers to the position of  
817 cross section shown in A. C) Idealized bundle of calcite fibres, each fibre contains a stack of  
818 tetrahedral elements. D) SEM BSD image of the tetrahedral ultrastructure of *Megateuthis gigantea*,  
819 dashed lines (I-IV) indicate section planes and corresponding reconstructions. Primary skeletal  
820 framework is shown in blue, yellow and green whilst early diagenetic phase is shown in white and  
821 red for the crystal boundaries. The basis of tetrahedrons points toward the centre of the belemnite  
822 rostrum and its tip towards the rostrum margin i.e. the growth direction. E) Three dimensional  
823 reconstruction of a single tetrahedron of the belemnite endoskeleton. F) Reconstruction of the  
824 complex spatial arrangement of biogenic and early diagenetic phases. Colour code in lower right. G)  
825 SEM image of a single complex tetrahedron (black line) with indication of structural elements.  
826 Primary skeletal components: br = branch, trc = triradial centre, rf = reinforcement, ic = isopachous  
827 crystallites. **(full page width; bw in print, colour in pdf)**

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837 **Fig. 2A-B) SEM BSD images of *Megateuthis gigantea*.** A-B) Section perpendicular to the c-axes of  
838 calcite fibres (section plane II in Fig. 1D-II). White stippled line indicate dissolution features (early  
839 diagenetic), black stippled line indicate microstylolites ~~(late diagenetic)~~. **(full page width; bw in print,**  
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842 **Fig. 2A-B) SEM BSD images of *Megateuthis gigantea*.** A-B) Section perpendicular to the c-axes of  
843 calcite fibres (section plane II in Fig. 1D-II). Blue stippled line indicate dissolution features (early  
844 diagenetic), red stippled line indicate microstylolites ~~(late diagenetic)~~. **(full page width; bw in print,**  
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863 **Fig. 3A-F) SEM BSD images of *Megateuthis gigantea*.** A-E) Section perpendicular to the c-axes of  
864 calcite fibres. A) Triangular structures with a relatively thick outer, light grey margin of abiogenic  
865 early diagenetic cement and a small darker centre with branches giving rise to reinforcement  
866 structures representing the primary biogenic skeletal framework. B) Larger dark grey, organic rich  
867 triangular elements belonging to the biogenic skeletal framework, partly with light grey central  
868 abiogenic calcite filling of variable sizes. Branches are often short and cut off at variable distances  
869 from the centre. C) Some smaller and a few larger biogenic skeletal elements with cut off branches  
870 (lower arrow) and reinforcement structures (upper arrow). Note the variable expression of early  
871 diagenetic crystallites with sheaths of remnant organic matter. D) Close up of larger, biogenic skeletal  
872 elements and abiogenic isopachous calcites coated by remnants of organic matter within the brighter  
873 outer margin. Central portion of the biogenic skeletal elements shows abiogenic crystal; arrows point  
874 to dissolved branches. E) Centre of biogenic skeletal element completely filled with abiogenic bright  
875 calcite leaving only a thin dark inner margin. F) Same specimen, section subparallel to the c-axes  
876 showing a homogenous central portion (“trunk” – white line) of pyramidal morphology rich in  
877 intracrystalline organic matter surrounded by inclined isopachous calcite crystals coated by remnants  
878 of organic matter. This overall pattern results in a ~~an~~ “~~Christmas-mas~~ tree like” structure (compare  
879 with Fig. 1D). **(full page width; bw in print and pdf)**

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888 **Fig. 4A-E)** *Megateuthis gigantea*, EBSD map with colour code in sections perpendicular to the c-axes  
889 of the fiber bundles. Same colours represent same crystallographic orientations. In A and B angular  
890 deviation from blue to red is up to 40°, in D angular deviation is 2°. A) Overview map showing the  
891 bundling of fibres with identical orientation of a-axes, black frame indicates area for close up in B;  
892 blue frame refers to Fig. 5A-C. B) Close up map, within one bundle blue tinted fibres are mainly  
893 neighboured by other blue fibres, red tinted fibres are surrounded by red fibres. C) Close up ~~to~~  
894 ~~demonstrate slight~~ documenting minor angular deviation within one fibre (compare with D). D) Map  
895 of a single fibre with an angular deviation of 2° from blue to red, showing a slight systematic shift of  
896 axes orientation. E) Pole-plots of c-axes {001} and a-axes {010} from all fibres shown in A, all c-axes  
897 show nearly the same orientation while the a-axes demonstrate the bundled structure of the rostral  
898 fabric which may have improved the stability of the skeletal structure. **(full page width; bw in print,**  
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913 **Fig. 5A-F) Transmitted light, polarized light and cathodoluminescence.** Thin section of *Megateuthis*  
914 *gigantea*, A-C refer to the blue frame in Fig. 4A, D-F are close ups (black frame in A) A and D) TL  
915 image perpendicular to the c-axes of calcite fibres, filigree biogenic skeletal framework is indicated  
916 by the dark tinted structures, primary porosity is represented by the abiogenic translucent calcites.  
917 Note banded distribution of calcite fibre domains relating to larger and smaller organic-rich biogenic  
918 skeletal elements, single fibres may contain a central portion of transparent calcite of varying size,  
919 bundling of adjacent calcite fibres is indicated by the same orientation of the triangles. B and E)  
920 Uniform extinction (orientation) of adjacent fibres under crossed polarizers. C and F) CL of abiogenic  
921 calcite portions show a dark blue, intrinsic luminescence (pure stoichiometric calcite), CL of the  
922 biogenic skeletal framework show light blue luminescence. **(full page width; bw in print, colour in**  
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938 **Fig. 6) Electron microprobe data for *Megateuthis gigantea*.** A) Overview BSE map B) Shows higher  
939 Mg concentrations within the triangular areas dark in BSE images and a lower Mg concentration in  
940 the surrounding area bright in BSE images. C) Shows higher P concentrations within the triangular  
941 areas dark in BSE images and a lower P concentration in the surrounding area bright in BSE images.  
942 D) Shows lower S concentrations within the triangular areas dark in BSE images and higher S  
943 concentrations in the surrounding region bright in BSE images. **(full page width; bw in print, colour**  
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964 **Fig. 7) Fluorescence microscope images for *Megateuthis gigantea*.** A) Transmitted light shows  
965 brownish triangular structures, rich in organic matter and dark in BSE images, partly with central  
966 translucent areas (compare with Fig. 1D section plane IV, Fig. 3D, E, 5A, D). B) Shows brighter  
967 fluorescent triangular area compared to the in transmitted light translucent calcite. **(full page width;**  
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990 **Fig. 8) Confocal laser fluorescence microscopy images of *Megateuthis gigantea*. A)** CLFM images  
991 showing fluorescence in far-red light ( $\lambda = 664$  to  $696$  nm). B) CLFM images showing fluorescence in  
992 visible green light ( $\lambda = 505$  to  $539$  nm). C and D) CLFM images showing fluorescence in visible red light  
993 ( $\lambda = 589$  to  $621$  nm). Triangular structures visible in other imaging techniques (Fig. 3, 5-7) do not  
994 fluoresce as brightly as cracks (B) or early diagenetic calcite (Fig. 3) separating the triangles (A, B, C,  
995 D). D) Higher magnification shows some brighter fluorescing calcite between the triangular elements  
996 dark in BSE images (Fig. 1, 3). Brightly fluorescent early diagenetic calcite separating triangles ~~also~~  
997 ~~containsis enriched in-elevated S (Fig. 6), which may support inclusion of S-rich humic substances as~~  
998 ~~the cause of fluorescence.~~ **(full page width; bw in print, colour in pdf)**

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1016 | **Fig. 9) Three-dimensional visualization of the filigree biogenic framework.** Synchrotron radiation  
1017 | based tomographic visualization of a sub-volume of the rostrum of *Megateuthis gigantea*. Specimen  
1018 | was scanned with an isotropic voxel size of 0.74µm. A) Multi-planar image of a sub-domain of the  
1019 | original dataset with dimensions of 447x592x663 voxels, triangular elements dark in BSE images  
1020 | appear here as dark elements due to reduced densities. B-D) Volumetric renderings of the same sub-  
1021 | domain with variable rendering settings. **(full page width; bw in print, colour in pdf)**

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1042 **Supplementary Figures**

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1061 | **Fig. 1) Examples of the filigree framework from other belemnite species.** A-B) *Goniot euthis*  
1062 | *quadrata*, A) shows the Becke line outside of the triangular area with a relatively larger distance  
1063 | between the sample and objective. B) ~~Shows-Image shows~~ the Becke line within the triangular area  
1064 | while the distance between the sample and the objective was reduced, accordingly the triangular  
1065 | area (dark in BSE; ~~(Fig. 3)~~) has a lower optical relief. C-D) *Belemnitella mucronata*, C) thin section  
1066 | under polarized light, D) same area under CL showing microfractures filled with Mn-rich calcite  
1067 | tracing the outline of triangular elements (encircled). **(full page width; bw in print, colour in pdf)**

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1081 **Fig. 2) SEM BSD images of *Megateuthis gigantea*.** A-F) Section plane parallel to the c-axes of calcite  
1082 fibres. A-C) stepwise enlargement of a particular area. D-F) stepwise enlargement of a particular  
1083 area. A and D give the impression of a concentric arrangement of distinct darker and brighter layers  
1084 (black frames enlarged in B and E), arrow in D point to an organic rich layer (laminae obscura sensu  
1085 Müller-Stoll, (1936)). B and E) Allow the recognition of single darker structures of tetrahedral  
1086 morphology with their tips pointing towards the outer margin of the belemnite rostrum, i.e. the  
1087 growth direction (black frames enlarged in C and F). C and F) show the intricate framework of  
1088 biogenic (dark) and abiogenic (light) carbonate phase within the rostrum, larger dark grey, triangular  
1089 elements belonging to the biogenic skeletal framework, partly with light grey central abiogenic  
1090 calcite filling of variable size. **(full page width; bw in print, colour in pdf)**

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1 **Evidence for a composite organic-inorganic fabric of belemnite rostra:**

2 **Implications for palaeoceanography and palaeoecology**

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27 **Abstract**

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29 Carbonate skeletons of fossil marine organisms are widely used to reconstruct palaeoceanographic  
30 parameters. Specifically, the geochemistry of Jurassic and Cretaceous belemnite rostra is traditionally  
31 interpreted to represent near sea-surface seawater properties. More recently, an increasing number  
32 of workers, have reported significant scatter in geochemical data (e.g.,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , element/Ca ratio)  
33 when comparing rostra from the same stratigraphic level or within a single belemnite rostrum. This  
34 scatter is not explained by differential diagenetic overprint alone. Here we report petrographic  
35 evidence on the primary ultrastructure of rostra of *Megateuthis* (Middle Jurassic) and *Belemnitella*  
36 and *Goniotoothis* (Late Cretaceous). The biogenic ultrastructure consists of a filigree framework of  
37 triaxial branches and tetrahedrons of variable size forming a honeycomb-like network. Data  
38 presented here suggest that these rostra yielded as much as 50 to 90% primary pore space. On the  
39 level of a working hypothesis - and in analogy with modern cephalopods - we propose that the pore  
40 space was formerly filled with body fluid and/or organic compounds during the life time of these  
41 organisms. Intra-rostral porosity was post mortem occluded by earliest diagenetic isopachous calcite  
42 cements of a non-biogenic origin. These may have been precipitated due to increased alkalinity  
43 related to the decay of organic matter. If this holds true, then the resulting fabric represents a  
44 composite biogenic/abiogenic structure. In order to optically separate the two calcite phases forming  
45 a single calcite fibre, we employed a wide range of state-of-the-art analytical tools to thin sections  
46 and ultra-thin sections of well-preserved specimens. Pending a verification of these well-supported  
47 ultrastructural data by means of high-resolution geochemical analyses from biogenic and abiogenic  
48 phases, we suggest that these findings have significance for those using belemnite rostra as archives  
49 of their palaeoenvironment.

50

51 **Keywords:** belemnite, ultrastructure, carbonate archive, diagenesis, Jurassic-Cretaceous

52

53 **1. Introduction**

54 The ultrastructure of recent biogenic carbonates is of great interest for those concerned with  
55 biomineralization research in general (Weiner and Addadi, 2011; Goetz et al., 2011), those studying  
56 the primary biogenic skeletal structures of fossil skeletal hardparts (e.g., Coronado et al., 2013), and  
57 for palaeoceanographers exploring these materials for their bearing on past climate dynamics  
58 (Saalen, 1989; Cochran et al., 2003; Parkinson et al., 2005; Jarvis et al., 2015; Immenhauser et al.,  
59 2016). Whereas the tests of planktonic and benthic foraminifera and coccoliths are important  
60 archives of open marine environments throughout the Cenozoic and beyond (e.g., Zachos et al.,  
61 2001), much of what is known about Cretaceous and Jurassic palaeoceanography has been deduced  
62 from the geochemical archive of the calcareous rostra of extinct cephalopods, specifically belemnites  
63 (Dutton et al., 2007). Reasons for the wide use of these archive materials include their abundance in  
64 the fossil record, the diagenetically stable low-Mg calcite mineralogy of rostra (Veizer, 1974; Saalen,  
65 1989), and the broad palaeobiogeographic distribution of belemnites in the marine Boreal and  
66 Tethyan realms, (e.g., Urey et al., 1951; Voigt et al., 2003; Wierzbowski, 2004; McArthur et al., 2007;  
67 Dutton, 2007; Price and Page, 2008; Wierzbowski and Joachimski, 2009; Price et al., 2009 2011; Li et  
68 al., 2012, 2013). As with all biogenic carbonates, however, these archives undergo post mortem  
69 diagenetic alteration, representing a major obstacle in carbonate research (Swart, 2015).

70 Characteristic geochemical patterns and fabrics in biogenic carbonate hardparts have been used  
71 to test for example molluscs (e.g., Cochran et al., 2003, Sessa et al., 2015, Immenhauser et al., 2016),  
72 brachiopods (Parkinson et al., 2005), or foraminifera (e.g., Huber and Hodell, 1996; Kozdon et al.,  
73 2011) for evidence of diagenetic alteration. In the case of ammonites, the degree of preservation of  
74 nacre tablets provides evidence with regard to the preservation of these exoskeletons, to name one  
75 example (e.g., Cochran et al., 2010). With regard to belemnite rostra, the observation of an intact  
76 fibrous microfabrics in thin sections and polished rock surfaces in combination with  
77 cathodoluminescence is commonly used to identify well-preserved belemnite rostra (Rosales et al.,  
78 2001). In contrast, cloudy areas, exfoliation, fractures, stylolites, or boring traces are interpreted as



79 evidence for post mortem alteration (Saelen, 1989; Li, 2011; Benito and Reolid, 2012). A rigorous  
80 discussion of screening techniques, including trace-element concentrations, and isotopic ratios  
81 applied to biogenic low-Mg calcite macrofossils, has been provided by Ullmann and Korte (2015).  
82 Similarly, a “best practice” approach for the interpretation of mollusc and brachiopod carbonate  
83 archives was presented by Immenhauser et al. (2016).

84 The ultrastructure of belemnite rostra was first studied by Müller-Stoll (1936). This author  
85 described organic-rich (laminae obscura) and carbonate-rich (laminae pellucidae) concentric growth  
86 rings. Both of these were later shown to be calcitic but differ due to variable amounts of occluded  
87 organic matter (Saelen, 1989). Growth rings are made up by fibrous calcite crystals radiating from a  
88 central zone called apical line (Richter et al., 2011) forming what seems to be a low-porosity fabric  
89 (Saelen, 1989 and references therein; Fig. 1A-C). Single fibres (= radial structures of Saelen, 1989) can  
90 be arranged in bundles traversing the concentric growth layers. Each fibre thickens outwards and  
91 shows a sub-fibrous framework potentially first proposed - but not further explored - by Saelen  
92 (1989, Fig. 15a).

93 Belemnites are traditionally considered to secrete their endoskeleton in oxygen isotope  
94 equilibrium with ambient seawater (e.g., Anderson et al., 1994; Price and Sellwood, 1997; Voigt et  
95 al., 2003; Price et al., 2009; Wierzbowski and Joachimski, 2007, 2009). The main argument brought  
96 forward is commonly the presence of what are considered cyclical oxygen isotope patterns  
97 interpreted as seasonal seawater temperature variations (Urey et al., 1951). The PeeDee belemnite  
98 used in Urey’s study was considered as well-preserved based on the compact fabric and the optical  
99 features of the calcite crystals (but see Li, 2011 for discussion). The assumption of equilibrium  
100 precipitation was further supported by data sets from recent cephalopods including *Nautilus*, *Sepia*,  
101 and *Spirula* precipitating their skeletal hardparts in near-equilibrium with  $\delta^{18}\text{O}_{\text{seawater}}$  (Lukeneder et  
102 al., 2010). In contrast to this traditional view, there is an increasing amount of evidence suggesting  
103 that belemnite rostra are problematic archives of their palaeoenvironment (see Immenhauser et al.,  
104 2016 for detailed discussion). For example, Price et al. (2015) reported an offset of about 5°C

105 between the aragonitic phragmocone and the calcitic rostrum of a single specimen of  
106 *Cylindroteuthis*. This offset was regarded as vital effect but it remains unclear whether the  
107 temperatures derived from the aragonite are too warm or from the calcite too cool. Similarly, high  
108 intra-rostral variability of elemental (Ca, Mn, Mg, Fe, Sr) and isotopic ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) composition, the  
109 latter with a scatter of up to 2‰, has been reported from belemnite rostra lacking evidence for  
110 diagenetic alteration (Podlaha et al., 1998).

111 The significant discrepancy of these data sets forms a strong motivation for a reconsideration of  
112 belemnite rostra as archives of their palaeoenvironment. Here, we report data from a wide set of  
113 state-of-the-art analytical infrastructure applied to thin- and ultra-thin sections of exceptionally well-  
114 preserved Jurassic and Cretaceous belemnite rostra. The following aims guided this paper: First, to  
115 present well-constrained petrographic evidence for the complex primary biogenic framework of  
116 these rostra; second, to document evidence that points to the highly porous nature of this biogenic  
117 framework; third, to assess the relative proportion between primary skeleton and porosity; fourth, to  
118 discuss the timing and nature of the pore-filling calcites phase. Evidence reported here has  
119 significance for the interpretation of proxy data from ancient belemnite rostra and forms the  
120 foundation of a detailed, high-resolution geochemical study that will be in the focus of forthcoming  
121 work.

122

## 123 **2. Materials and Methods**

### 124 *2.1. Belemnites*

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126 Thin sections (30  $\mu\text{m}$ ) and ultra-thin sections (< 10  $\mu\text{m}$ ) of two well-preserved orthorostra of  
127 *Megateuthis gigantea* (Schlotheim, 1820) from the Middle Jurassic and one specimen of *Belemnitella*  
128 *mucronata* (Schlotheim, 1813) and *Goniotteuthis quadrata* (Blainville, 1827) from the Upper  
129 Cretaceous were studied. Specimens of *Megateuthis* were collected in Bajocian marly limestone  
130 deposits from southern Germany. *Belemnitella* rostra are from the late early Campanian (*mucronata*

131 Zone), and *Goniatiteuthis* from the early Campanian *lingua/quadrata* – *gracilis/mucronata* Zone from  
132 northwestern Germany. *Goniatiteuthis* and *Belemnitella* rostra were embedded in calcareous (65-90%)  
133 epicontinental shelf deposits of the Misburg Formation (Niebuhr, 1995; Niebuhr et al., 2007).  
134 Specimens did not display evidence for exfoliation nor did they show boring traces of the surfaces of  
135 rostra. Specimens were sectioned along their long axis in a marginal position and perpendicular to  
136 the c-axis of their calcite fibres. One section cuts the rostrum of *Megateuthis* perpendicular to the  
137 long axis.

138

## 139 2.2. Methods

140

141 Surfaces of thin sections were chemo-mechanically etched using colloidal silica (OP-S) for 5-15  
142 minutes to reduce surface irregularities on an atomic scale (Massonne and Neuser, 2005) and coated  
143 by a thin carbon layer. All coated thin sections have been studied under a high-resolution field  
144 emission scanning electron microscope (HR-FESEM) type LEO/ZEISS 1530 Gemini using a backscatter  
145 detector (BSD) at the Ruhr-Universität Bochum, Germany (Figs. 1-3).

146 Crystallographic orientation of belemnite calcite fibres was determined by electron  
147 backscattered diffraction (EBSD; Nordlys, OXFORD Instruments). The data acquisition and analysis  
148 was performed using the software packages AZtec and Channel 5 by Oxford Instruments (Fig. 4). The  
149 scanning electron microscope (SEM) was operated at beam energy of 20 kV, an aperture of 60  $\mu\text{m}$ , a  
150 working distance of 25 mm and a tilt angle of 70°. Thin sections were mapped at Bochum University  
151 in the high-resolution mode using a grid matrix (1149x748 points) at a step width of 2.017  $\mu\text{m}$  (Fig.  
152 4A) and (543x266 points) at a step width of 1.652  $\mu\text{m}$  (Fig. 4D) and for the single calcite fibre 50  $\mu\text{m}$   
153 to reduce artefacts and increase the reliability of the data. The orientations of the crystals in the  
154 individual maps were visualized using a rainbow colour coding ranging from blue over green and  
155 yellow to orange and red, where identical colours indicate identical crystal axis orientations. For  
156 visualizing the weak angular deviations in the crystal lattice in a single calcite fibre, we applied an

157 angular resolution of 2 degrees for the complete rainbow colour range. In addition, orientations of  
158 the measured crystallographic axes were plotted into the lower hemisphere of a Schmidt net (Fig.  
159 4E).

160 Rostra were further investigated under a cathodoluminescence microscope type HC1-LM by  
161 Lumic equipped with a hot cathode (Neuser et al., 1996) and a digital camera system (DP73 by  
162 Olympus) for recording digital images at Bochum. Beam energy of 14kV and a beam current density  
163 between 5 and 10  $\mu\text{A}/\text{mm}^2$  were generally used for the CL-measurements. Integration times for CL-  
164 spectra were commonly between 10 and 60 seconds (Fig. 5).

165 X-ray element distribution maps were acquired using a Cameca SX5FE field emission electron  
166 microprobe at Bochum. The acceleration voltage was 15 keV with a probe current of about 80 nA and  
167 a fully focused beam. The intensity of S K $\alpha$ 1 was recorded simultaneously on two wavelength  
168 dispersive spectrometers equipped with LPET and PET analyzing crystals. The Mg K $\alpha$ 1 line was also  
169 measured on two spectrometers (LTAP and TAP crystals), whereas P K $\alpha$ 1 was measured on a single  
170 spectrometer equipped with a LPET crystal. The images were acquired in continuous stage scan  
171 mode. They have a resolution of 2048 x 1536 pixel, and the dwell time was 17 ms per pixel (Fig. 6).

172 To test for the distribution of organic matter within the belemnite rostra, thin sections were  
173 studied under a fluorescence microscope (Leica DM4500P) equipped with a mercury short-arc  
174 reflector lamp coupled with a Leica EL6000 compact light source. We used the blue light filter set  
175 producing bright green fluorescence images (filter set I3 for blue light excitation: excitation 450-490  
176 nm, emission 515 nm, voltage 100-240 VAC and 50-60 Hz frequency; Fig. 7). Fluorescence microscopy  
177 in the manner applied here is an optical tool to qualitatively document the spatial distribution of  
178 organic matter in shells. Fluorescence reflects organic matter and less commonly crystal lattice  
179 defects and solid inclusions in crystals. Further details of this method have been presented by  
180 Wanamaker et al. (2009) and Ritter et al. (subm.).

181 Confocal laser fluorescence microscopy (CLFM) images on an uncoated *Megateuthis* mount  
182 were made using a Bio-Rad MRC-1024 scanning confocal microscope at the W. M. Keck Laboratory

183 for Biological Imaging at UW-Madison (Fig. 8). The microscope was operated with a 40 mW laser at  
184 wavelengths of 488 nm, 568 nm, and 647 nm. All three wavelengths were simultaneously rastered  
185 across the sample. Naturally occurring compounds within the sample caused fluorescence at multiple  
186 wavelengths. Images were collected through the following three emission filters: visible green light ( $\lambda$   
187 = 505 to 539 nm); visible red light ( $\lambda$  = 589 to 621 nm); and far-red light ( $\lambda$  = 664 to 696 nm).

188 In order to analyze the three dimensional filigree framework, synchrotron radiation based  
189 micro-computed tomography was applied (Fig. 9). Data were collected at the bending magnet beam  
190 line 2-BM at the Advanced Photon Source, Argonne National Laboratory, USA. A double multilayer  
191 monochromator of 1.5% band-width provided 27.2 KeV X-rays. Images were collected in transmission  
192 mode by a CCD camera behind the sample in the hutch configuration. The sample-detector distance  
193 was set to 300 mm to collect quantitative phase contrast data. 1440 projections were acquired while  
194 the sample was rotated over 180° in steps of 0.125°. A microtomographic data set with a size of 2048  
195 x 2048 x 1948 voxels was reconstructed using a phase retrieval algorithm (Mokso et al., 2013).

196

197

### 198 **3. Results**

#### 199 *3.1 Optical-, cathodoluminescence-, fluorescence-, and confocal laser fluorescence microscopy (TL, CL,* 200 *FL, CFLM)*

201 Under transmitted light (TL), thin sections of rostra cut perpendicular to the c-axis of calcite  
202 fibres reveal a banded distribution of calcite fibres containing brownish triangular elements of  
203 variable size (Fig. 5A, D). Some of the larger fibres contain a triangular, organic-rich centre, with its  
204 innermost domains occluded by translucent calcite. Bundling of neighbouring calcite fibres is  
205 indicated by their subparallel orientation of their a-axis (Fig. 5D). A uniform extinction (orientation)  
206 pattern of adjacent fibres under crossed polarizers is observed (Fig. 5B, E) and is in agreement with  
207 EBSD data (Fig. 4A). Individual fibres display an undulatory extinction (converging or diverging c-axes)

208 under crossed polarizers. Calcite occluding space between organic-rich elements and fibre  
209 reinforcement is translucent and contains little or no organic matter (Fig. 5D). Brownish, triangular  
210 elements have a relatively low optical relief, compared to the surrounding translucent calcite with a  
211 relatively higher optical relief (supplement Fig. 1A-B).

212 Three different luminescence patterns are observed under the cathodoluminescence  
213 microscope (CL): (i) A light blue luminescence of the brownish, triangular elements (Fig. 5C, F); (ii)  
214 dark blue, intrinsic luminescence of the translucent phase; (iii) locally, orange to red luminescent  
215 fractures and microstylolites are observed. In rare cases, fractures retrace the triangular outline of a  
216 fibre (Fig. 5C, F, supplement figure 1D).

217 Brownish triangular areas under transmitted light display light green fluorescence while the  
218 translucent areas show a dark green fluorescence under the fluorescence microscope (FL).  
219 Microfractures are darker under transmitted light compared to the triangular elements and show a  
220 light green fluorescence (Fig. 7A-B).

221 Different fluorescence patterns under the CLFM reveals calcite domains visible in BSE (and  
222 other) imaging techniques (Figs. 3, 5-7). Filled cracks fluoresce brightly in green and red wavelengths  
223 (Fig. 8B-C). Domains that are dark in BSE do not fluoresce in CLFM (Fig. 8A-D). Bright domains in BSE  
224 fluoresce brightly in CLFM at all wavelengths observed (Fig. 8A-D). Higher magnification reveals  
225 brighter fluorescence between adjacent domains that appear bright in BSE (Fig. 8D).

226

### 227 *3.2 Scanning-electron microscopy equipped with a backscatter detector (SEM BSD)*

228 Images collected with the scanning electron microscope equipped with a backscatter detector  
229 present important evidence for the presence of two calcite phases (dark and bright) of different  
230 chemical compositions building the rostra studied. The brownish triangular areas under transmitted  
231 light are dark in BSE. Thin sections cut perpendicular to the c-axis of the radiaxial fibrous calcite (Fig.

232 1D I-IV) reveal a complex framework, dark in BSE, surrounded by relatively brighter calcite (Figs. 1-3).  
233 Cross sections of the majority of fibres are polygonal or, less often, honeycomb shaped with a tri-  
234 radial (120°) symmetry representing an ultrastructure that has not been described in previous studies  
235 (Figs. 1C-G, 3A-E). Individual fibre diameters vary between 10-80 µm. Calcite fibres terminate at  
236 individual concentric growth layers that also form the nucleation site for the overlying, next fibre  
237 generation, displaying increasing thicknesses and occurring in increasing numbers towards the outer  
238 portions of the rostrum (Fig. 1A-D). Brighter area in BSE are more likely to be composed of near-  
239 stoichiometric CaCO<sub>3</sub> with higher average atomic masses (mainly Ca), whereas excess C, P, Mg, or S  
240 will lower the average atomic mass. Accordingly, areas with decreasing amount of Ca and increasing  
241 amounts of C, P, Mg or S are darker.

242 Four section planes are presented to describe the intricate bio-composite mineral present  
243 within a single fibre. The following description distinguishes between the darker framework (i), i.e.,  
244 micrometre-thick branches terminating in wall-like reinforcements and (ii) tri-radial central portions;  
245 and brighter fabric (iii) consisting of calcite crystals forming isopachous cement layers with individual  
246 crystallites coated by submicrometre thick layers of matter darker in BSE (Fig. 1G). In all sections, we  
247 observed isopachous calcite crystals oriented perpendicular to the inner dark walls (Fig. 3A-E).  
248 Section plane I consists of three simple, dark in BSE branches of variable lengths. Often, these  
249 branches exhibit reinforcements of variable lengths and thicknesses (about 1 micrometre) and  
250 increasing widths towards neighbouring branches (Figs. 1D-I, 3A). Conversely, reinforcements being  
251 connected to neighboring triangles are rarely observed. Section type II is characterized by an  
252 enlarged, dark in BSE central element of variable diameter (2-30 µm, Figs. 1D-II, 3C). Some of the  
253 larger central elements display an inner zone with additional tri-radial structures comprising of  
254 smaller, isopachous, brighter in BSE area calcite crystals rotated by 60° relative to outer branches  
255 (Figs. 1D-III, 3D; section type III). Section type IV represents the most complex fabric. Here, the inner  
256 portions of larger central elements display alternating darker and brighter in BSE areas (Figs. 1D-IV,

257 3E). Generally, enlarged central elements correlate with a shortening of corresponding, darker  
258 branches.

259 Thin sections cut parallel to the c-axis of the radiaxial fibrous calcite reveal an framework dark in  
260 BSE of triangular shaped elements with their tips pointing towards the outer margin of the rostrum  
261 (Fig. 1C-D, supplement Fig. 2). Lighter and darker areas within a single calcite fibre show their  
262 composite nature. Lighter and darker areas within concentric growth rings, as visible in transmitted  
263 light, depend on the number and size of these elements. Higher magnification reveals a homogenous  
264 central portion (“trunk” – white line) of pyramidal morphology dark in BSE surrounded by inclined  
265 isopachous calcite crystals coated by material dark in BSE. This overall pattern results in a “Christmas  
266 tree like” structure (Fig. 3F). The dark framework forms the substratum upon which an isopachous,  
267 translucent calcite phase nucleated (Fig. 1D, G 2-3). The boundary surface between the framework  
268 dark in BSE and the surrounding carbonates brighter in BSE is, in places, corroded and uneven (Fig.  
269 2).

270

### 271 3.3 *Electron microprobe analysis (EMPA)*

272 The contrasting chemical composition of the two different calcite phases building these rostra is  
273 also revealed by EMP data. Detailed WDS scans show that the strongest variability is displayed by  
274 Mg, P, and S, whereas other elements are almost constant or present in amounts close to the  
275 detection limit (e.g., SrO = 0.1-0.2 wt.%; FeO = <0.1 wt.%; MnO < 0.5 wt.%. X-ray element distribution  
276 maps show a generally low concentration of the elements Mg (MgO = 0.3-0.4 wt.%), P (P<sub>2</sub>O<sub>5</sub> = 0.1-0.2  
277 wt.%), and S (SO<sub>3</sub> = 0.20-0.50 wt.%). The Mg- and P-content is slightly elevated in the darker,  
278 triangular areas in BSE images (MgO up to 0.6 wt.%; P<sub>2</sub>O<sub>5</sub> up to 0.25 wt.%) compared to the relatively  
279 brighter areas in BSE images in the centre of larger tetrahedrons and their vicinity. Lowest Mg  
280 concentrations were found along microfractures that display bright luminescence colours (MgO < 0.2  
281 wt.%; Fig. 6B). Sulfur has a higher concentration in the brighter areas in BSE images (SO<sub>3</sub> up to 0.65



282 wt.%) and lower concentrations in the darker areas in BSE images ( $\text{SO}_3 = 0.20\text{-}0.50$  wt.%; Fig. 6D). For  
283 better comparison with BSE images from other samples and with the element distribution, BSE data  
284 were obtained for the same field of view (Fig. 6A).

285

### 286 *3.4 Electron Backscattered Diffraction imaging (EBSD)*

287 Electron backscattered diffraction was used to document the biological controlled (*sensu*  
288 Lowenstam and Weiner, 1989; Dupraz et al., 2009; Weiner and Addadi, 2011) formation of what is  
289 here assumed to represent the primary biogenic skeletal carbonate. EBSD reveals a very low  
290 variation of c-axes orientation of calcite fibres (Fig. 4A). The sub-parallel orientation of the c-axes  
291 {001} is documented by their close fitting in the lower hemisphere of a Schmidt net (Fig. 4E, left plot).  
292 A different characteristic is found for the crystallographic orientation of the a-axes {010} of calcite  
293 fibres (Fig. 4E, right plot). All a-axes are aligned along a great circle whilst the colour code of the  
294 according fibres is indicative of an arrangement in bundles. Adjacent fibres (10 to 100 fibres) share a  
295 similar - if not identical - orientation (Fig. 4A-B). The majority of fibre bundles are characterized by  
296 blue, green and red colour coding. Specifically, the spatial orientation of individual a-axes within a  
297 single fibre bundle deviates by  $20^\circ$  or less from the bundle mean value. Variation in the orientation of  
298 the c-axis of a single calcite fibre in the range of  $1\text{-}3^\circ$  was observed (Fig. 4D). As the angular  
299 resolution from blue to red rainbow colour shown in EBSD maps (Fig. 4A-B) has a resolution of  $50^\circ$ ,  
300 minor angular deviations ( $<1^\circ$ ) are not visible in Fig. 4A-B.

301

### 302 *3.5 Synchrotron radiation based micro-computed tomography (SR $\mu$ CT)*

303 Tetrahedral structures are visible in three dimensions in the tomographic dataset despite the  
304 high signal to noise ratio and artefacts. There is a distinct difference in X-ray attenuation between the  
305 inner tri-radial elements and the surrounding calcite.

306

## 307 **4. Interpretation and Discussion**

### 308 *4.1 Reconstruction of the primary belemnite rostrum ultrastructure*

309

310 Data presented here document a repeated pattern of triangular elements that seem to be  
311 originally connected, building a concentric layered, highly complex, and porous framework. The  
312 space between the former skeletal elements is interpreted as pore space probably filled by body  
313 fluids or organic material during the life time of these organisms. The latter assumption is based on  
314 analogous observations in the porous endoskeletons of recent *Sepia* (Sherrard, 2000; Guerra, 2006).  
315 Referring to the high porosity observed in both, the belemnite rostrum and the sepiid cuttlebone, it  
316 is important to note that these structures are not homologous (Fuchs 2012).

317 Accordingly, the belemnite rostra originally consisted of an organic-rich biogenic framework of  
318 calcitic tri-radial tetrahedrons (triangular pyramids arranged perpendicular to the concentric layers  
319 during lifetime). Tetrahedrons are elongated along their c-axis with the tip of the pyramid pointing  
320 towards the precipitation site i.e., in growth direction towards the outer margin of the rostrum (Fig.  
321 1C-D). Individual branches protruding from the edges of the tetrahedrons possess outer  
322 reinforcements acting as stabilizers. The central portion of the tetrahedrons may yield a channel-like  
323 cavity (Fig. 1D III-IV). Organic membranes at which nucleation of the tetrahedrons may have started  
324 and stopped are not preserved. However, it seems likely that such membranes were present because  
325 the bases of the tetrahedrons follow a concentric layer. Structurally, the bundling of the tri-radial  
326 elements forms a simple honeycomb-like framework in which the terminations of branches of  
327 adjacent elements are connected. The mechanical stability of the honeycomb structure is enhanced  
328 by reinforcement walls (Figs. 1D, G, 3C).

329 Based on the variable dimensions of skeletal elements seen in thin sections, intra-rostral pore  
330 space was visually estimated to range between 50-90% of the total rostrum (Fig. 3A: 90% pore space  
331 and 10% skeletal elements; Fig. 3B; 50% pore space and 50% skeletal elements). In this context, the

332 observation that pore space is not limited to the apical line region but is present across the bulk  
333 rostrum is important. The secretion of a porous, but mechanically stable orthorostrum is probably  
334 best seen in the context of a considerable reduction of energy and building material required to form  
335 this structure compared to a massive endoskeleton (Sherrard, 2000). Strict biological control, i.e. in  
336 the presence of organic templates (Chateigner et al., 2000; Richter et al., 2011), over the  
337 precipitation of primary skeletal elements is demonstrated by a systematic arrangement of adjacent  
338 elements into bundles of similar or identical orientation of their crystallographic a-axes. This  
339 configuration results in a much higher mechanical load capacity and torsion stiffness of the  
340 framework of the rostrum.

341 Alternating concentric Ca-rich (brighter; laminae obscurae) and C-rich layers (darker; laminae  
342 pellucidae) of Müller-Stoll (1936) are related with the banded distribution of larger and smaller  
343 organic-rich triangular elements of the primary skeletal structure of the belemnite orthorostrum (Fig.  
344 1D, supplement Fig. 2). These layers potentially indicate differences in calcite precipitation rates.  
345 Based on petrographic and ultrastructural evidence, the Mg and Ca elemental concentrations of the  
346 rostrum, the lack of secondary micro-dolomite, and the absence of blotchy luminescence, the widely  
347 held assumption of a primary low-Mg calcite mineralogy for the studied belemnite rostra is  
348 confirmed (see discussion in Richter et al., 2003).

349

#### 350 *4.2 Early and late diagenetic processes*

351

352 The presence of a highly porous primary rostrum architecture during the life time of the  
353 belemnite organism as proposed here, is in contrast to the dense fabrics observed in rostra collected  
354 in Mesozoic sedimentary successions (Fig. 1A-B). Hence, the diagenetic pathway from porous to  
355 dense fabrics deserves attention. The marine diagenetic alteration of biominerals is initiated directly  
356 after the death of a carbonate-secreting marine organism when metabolic processes come to a halt.  
357 At this early stage, organic matter outside of the orthorostrum (i.e., the belemnite animal itself) and

358 in the pore space of rostra and between biominerals decomposes (Saalen, 1989), triggering a series  
359 of complex bio-chemical processes. Essentially, decomposition of organic matter is mediated by  
360 microbial activity, and given the abundance of marine microbial life, there is no reason to assume  
361 that this would have been different in the case examples studied here.

362 Microbial metabolic products, the presence of microbial “mucus” (extracellular polymeric  
363 substance) and charged surfaces represented by microbial bodies influence the micro-environment  
364 in intra-rostrum pore space by altering the balance between more reduced and more oxidized forms  
365 of carbon as previously summarized under the term “alkalinity engine” (Dupraz et al., 2009).  
366 Specifically, Visscher and Stolz (2005) subdivided microbial species into 5-7 groups (“guilds”) having a  
367 similar metabolism. Some of these promote carbonate precipitation (e.g., cyanobacteria, sulphate  
368 reducers), whilst others favour dissolution (e.g., aerobic heterotrophs, fermenters). Dupraz et al.  
369 (2009) documented that the balance of microbial metabolic activities directly influences carbonate  
370 precipitation or, vice versa, dissolution. Initial microbial decomposition of organic matter may result  
371 in the production of organic acids lowering the pH-values in the pore space (Berner et al., 1978),  
372 enhancing intra-orthorostrum dissolution of biominerals (Fig. 2).

373 As soon as the bulk of organic matter is decomposed, alkalinity is increased due to microbial  
374 metabolic products enhancing the precipitation of carbonate minerals (intrinsic  
375 organomineralization) leading – in the view of the authors - to the formation of the translucent,  
376 isopachous calcite crystals that occlude primary pore space in rostra (Fig. 2). Obviously, any  
377 assumption regarding microbial processes in these ancient carbonates must remain speculative.  
378 Nevertheless, following the basic concepts laid out in Dupraz et al. (2009), we tentatively assume  
379 that a first phase of decomposition was dominated by aerobic heterotrophy, sulphide oxidation, and  
380 fermentation decreasing the saturation index and resulting in the corrosion of skeletal elements in  
381 the belemnite rostrum. Evidence for this comes from micro-corrosion features at the outer surfaces  
382 of the primary skeletal framework forming the substratum upon which the pore-filling, secondary  
383 calcite phase nucleates (Fig. 2).

384 The nucleation and precipitation of the secondary calcite phase (Fig. 1D, G, 2-3) was possibly  
385 dominated by sulphate reduction increasing the saturation index and hence favoring precipitation of  
386 CaCO<sub>3</sub>. During crystals growth, remnants of belemnite organic matter combined with microbial  
387 mucus were likely trapped between single crystals or at the growth front of crystals and delineate  
388 crystal boundaries. Specifically, the growth of fibrous calcitic crystals will proceed as long as growth  
389 rate, fluid supersaturation, and temperature are low enough to discourage spontaneous nucleation  
390 (Oti et al., 1989). Similar processes have been described from extant echinoderm endoskeletons that  
391 share a comparable amount of primary porosity with the described belemnite ortho-rostra (Richter et  
392 al., 2003).

393 During this early stage of diagenetic evolution, the rostra most likely preserved their original  
394 morphology due to the biogenic calcite framework and abiogenic calcite progressively occluding  
395 former pore space preventing, in combination, a collapse of the rostra. The directly comparable, dark  
396 blue intrinsic luminescence of the translucent secondary outer calcite layer and the calcite infill of  
397 central pore space of many of the larger triangles (Figs. 3D-E, 5A, D, 6) suggest that both phases  
398 precipitated from one fluid, or different fluids with near-identical geochemistry. This is, of course,  
399 within the limitations of the geochemical resolution of the cathodoluminescence method and with  
400 reference to elements that affect luminescence patterns (e.g., Mn<sup>2+</sup>, Fe<sup>2+</sup> and REE; see discussion in  
401 Barbin 1991, 1993; Ritter et al., 2015). Conversely, the organic matter-rich triangles display a  
402 moderately brighter blue luminescence pattern (Fig. 5C, F). This feature is best explained by calcite  
403 lattice deformation due to the incorporation of organic matter into the crystal lattice  
404 (intracrystalline) and is not necessarily indicative of a different geochemical composition. This  
405 concept is supported by x-ray diffractometry (Richter et al., 2011) documenting that the fibrous  
406 fabric of the belemnite rostra, lacking late diagenetic Mn-rich cements, is composed of  
407 stoichiometric or near-stoichiometric calcites ( $d(104) = 3.030$  to  $3.035$  Å).

408 A late diagenetic (burial) stage of rostra is documented by dissolution and compaction features  
409 as indicated by microfractures and microstylolites (Figs. 2, 5C, F; Rosales et al., 2004a, b). The

410 circulation of  $Mn^{2+}$ -rich fluids caused the precipitation of a late calcite phase that occludes fractures  
411 and fissures. In some cases this late phase yields a bright luminescence and is zigzag or triangular  
412 shaped, tracing the morphology of the triangular biominerals (Fig. 5C).

413

#### 414 *4.3 Implications for the function of the rostrum*

415

416 It is generally accepted that the belemnite rostrum acts as a counterweight to the soft body.  
417 Based on the observation of a high primary porosity (see also Spaeth, 1971, 1973, 1975; Ullmann et  
418 al., 2015), this interpretation requires renewed consideration. Rostra are commonly considered to  
419 have the same density as inorganic calcite crystals, ranging from 2.5-2.7 g/cm<sup>3</sup>.

420 *Sepia*, the closest living relative of the extinct belemnites, incorporates a total of 10-40% organic  
421 matter in its cuttlebone and comparably high amounts of intracrystalline organics were observed for  
422 the biogenic belemnite orthorostrum. Accordingly, ignoring open pore space, a reduced density of  
423 the biogenic belemnite calcite of about 2.4 g/cm<sup>3</sup> (10% organic) – 2.0 g/cm<sup>3</sup> (40% organic) results.  
424 Assuming that liquid or extracrystalline organic matter (1.03 g/cm<sup>3</sup>) - with density comparable to that  
425 of seawater (1.026 g/cm<sup>3</sup>) - filled up the pore space of living belemnite rostra, an overall density of  
426 the rostrum ranging between roughly 1.7-1.1 g/cm<sup>3</sup> (mean 1.4 g/cm<sup>3</sup>) is tentatively assumed on the  
427 level of a working hypothesis. If these assumptions hold true, then the belemnite rostrum had a  
428 cumulative density that is significantly lower than that of stoichiometric calcite. Therefore, questions  
429 regarding the locomotion of belemnites result.

430 A possible analogue may come from a structure reported from a modern onychoteuthid squid  
431 (*Onykia*) that has remarkable morphological similarity to the *Megateuthis* rostrum. *Onykia* has a  
432 purely organic rostrum that due to its very low density does not act as a counterweight for the soft  
433 body. It is assumed that it supports the posterior part of the mantle and fins (= axial stability in  
434 Bizikov and Arkhipkin, 1997 and Arkhipkin et al., 2015). A function as a muscle attachment structure  
435 for belemnite rostra was first put forward by Stevens (1965). Direct evidence for the presence of fins

436 in belemnites has recently reported by Klug et al. (2015), favouring a squid-like high speed swimming  
437 mode of life for Jurassic belemnites. Noteworthy to report here, is the case of belemnites  
438 (*Chitinoeuthis*) with a non-calcified rostrum (Müller-Stoll, 1936).

439

## 440 **5 Open questions and suggestions for future research**

### 441 5.1. Paragenesis of porosity-occluding calcite phase

442 Within individual belemnite rostra, data presented here differentiate: (i) a biogenic, highly  
443 porous skeletal framework secreted during the life time of the organism; (ii) an inorganic or  
444 organomineralic – arguably early diagenetic - calcite phase occluding the pore space of the biogenic  
445 framework; and (iii) a late diagenetic, burial, Mn-rich carbonate phase filling fissures and larger  
446 cracks within the rostra. Assuming that the above-discussed paragenetic succession is valid, a series  
447 of open questions result. In the view of the authors, it is at least conceivable that portions of the  
448 rostral pore space were occluded during the life time of the belemnites (remote biomineralization  
449 sensu Hücker and Hemleben, 1976; Chinzei and Seilacher, 1993; Seilacher and Chinzei, 1993). If this  
450 holds true, then the paragenetic sequence of primary framework and secondary infill calcite is even  
451 more complicated than presented here and gradual in nature. Moreover, individual growth  
452 increments within rostra are then not representative of specific correlative time intervals.  
453 Specifically, each growth increment then represents a complex composite structure of paragenetic  
454 phases representing temporally different stages in the belemnite ontogenetic cycle. Obviously, this  
455 would render the interpretation of time series belemnite geochemical data difficult. Evidence against  
456 a biogenic infill of the skeletal pore space by remote biomineralization sensu Seilacher and Chinzei  
457 (1993), however, may or may not come from the presence of a corroded outer surface of what is  
458 considered the primary skeletal ultrastructure of these rostra (Fig. 2). It seems difficult to argue that  
459 intra-rostrum body fluids became corrosive at some stage during the life time of the belemnite  
460 animal. Clearly, these questions require further detailed work.

461

462 *5.2 Primary skeletal ultrastructure and preservation of organic matter*

463

464         The authors acknowledge the fact that despite the very detailed information regarding the  
465 belemnite ultrastructure shown here, our study lacks direct evidence for a primary biogenic origin of  
466 the complex, highly porous framework and the subsequent cementation by an early diagenetic  
467 calcite phase. Open questions, however, remain. Specifically, the significance of preserved organic  
468 matter in the biogenic belemnite calcite deserves attention. In the following, we present several lines  
469 (petrographic, optical, and geochemical data) of circumstantial evidence suggesting the presence of  
470 preserved organic matter.

471         The sector-wise systematic arrangement of triangular elements - with their a-axis being  
472 oriented subparallel to parallel (Figs. 3A-C, 4A-B, 5A, D) - in bundles, indicate a biologically controlled  
473 origin (Lowenstam and Weiner, 1989) of these fabrics. The primary belemnite rostrum ultrastructure  
474 is brownish (Figs. 5A, 7A) in thin sections under transmitted light and has a relatively low optical  
475 relief. According to Ullmann et al. (2014), brownish areas in thin sections of biogenic carbonates are  
476 indicative of remnant organic matter ( $C_{org}$ ). Under the cathodoluminescence- and fluorescence  
477 microscope, the primary filigree belemnite framework shows a light blue luminescence (CL) and light  
478 green fluorescence (FL). According to Wanamaker et al. (2009) and Pérez-Huerta et al. (2008),  
479 fluorescence in biominerals is triggered by organic macromolecules associated with chitin  
480 polysaccharides and proteins. Dark fluorescence patterns commonly refer to portions of the skeletal  
481 hardparts that are relatively depleted in organic matter. Bright green fluorescence patterns typify  
482 areas with increased amount of organic matter (Wanamaker et al., 2009).

483         Primary skeletal structures display darker colours in SEM-BSE images. Electron microprobe  
484 analyses revealed that the biogenic skeletal calcites contain more P and Mg but less S compared to  
485 what is here considered an early diagenetic, pore-filling calcite phase. Higher concentrations of P (Fig.  
486 6C) may be related to the presence of organic matter. Arguments for this have been presented by



487 Longinelli et al. (2002, 2003) and Gröcke et al. (2003) who found phosphate ( $\text{PO}_4^{3-}$ ) of presumed  
488 biogenic origin being preferentially enriched along concentric growth rings. Generally, the phosphate  
489 concentration of ancient belemnite rostra is variable but very low (less than 0.3%) comparable to  
490 that in modern *Sepia*.

491 The primary filigree belemnite framework does not fluoresce under the CLFM. The factors  
492 that cause fluorescence in samples studied under the CLFM are poorly constrained (Fig. 8). Naturally-  
493 occurring organic compounds such as proteins or polysaccharides can cause fluorescence in other  
494 biogenic carbonates, including brachiopods (Pérez-Huerta et al., 2008), gastropods (Guzman et al.,  
495 2007), or cephalopods (Linzmeier et al., 2016). In modern brachiopods and *Nautilus*, portions of the  
496 exoskeletons with higher amounts of intracrystalline organic matter (Clark, 1999) appear dark under  
497 CLFM (Pérez-Huerta et al., 2008; Linzmeier et al., 2016). This pattern lends support to the argument  
498 that dark triangular areas in BSE images represent the primary biogenic skeleton and contain  
499 remnants of organic matter. Marine sediments may contain abundant humic substances resulting  
500 from the degradation of marine organic matter (Nissenbaum and Kaplan, 1972) and evidence has  
501 been presented that the sulphur content of the humic substances increases with degradation  
502 (Francois 1987). Concluding, it is here proposed that humic substances caused elevated S  
503 concentrations in the diagenetic calcite phase that occludes the skeletal pore space (Fig. 6D) and  
504 causes the CLFM fluorescence in all three wavelengths (Blyth et al., 2008; Orland et al., 2009, 2012;  
505 Fig. 8).

506 Similarly, microtomographic data indicate the former presence of organic matter in dark  
507 triangular areas of rostra (Fig. 9) as observed in BSE images. The brightness of a carbonate observed  
508 in CT image indicates the degree of attenuation of an X-ray passing through this material (Mobilio et  
509 al., 2015). As the inner tri-radial structures of rostra appear darker in colour relative to the calcite  
510 phase fringing these structures, we suggest that the fringing phase is made of a denser calcite phase  
511 compared to the inner structure. That observation is in line with the observation of a low optical  
512 relief of these features (supplement Fig. 1A-B).

513 The interpretation presented here with regard to belemnite rostra is arguably consistent with  
514 observations of 10-40% organic matrix in the *Sepia* cuttlebone (Birchall and Thomas, 1983; Florek et  
515 al., 2009). This is relevant as we suggest that the belemnite rostrum is structurally similar but not  
516 homologous (Fuchs 2012) to the *Sepia* cuttlebone with regard to the primary intra-skeletal porosity.  
517 Having said this, the presence of preserved organic matter in ancient biogenic carbonates  
518 particularly, intra-crystalline organic matter is not uncommon (Clark, 1999, 2005). Excess carbon  
519 observed for *Megateuthis* has been interpreted as evidence for a former organic matrix within these  
520 low-Mg calcite biominerals (Dunca et al., 2006). Similarly, Florek (2004) argued for an excess of  
521 carbon in the rostra of *Belemnopsis* and *Hibolites*. Summing up: Different lines of circumstantial  
522 evidence point to the presence of remnant organic matter within biominerals. These data require  
523 verification or rejection via the application of spatially highly resolved geochemical data. This work is  
524 presently in progress.

525

## 526 **5. Conclusions**

527 Ultrastructural data documented here suggest that the calcitic rostra of Mesozoic belemnites  
528 yielded 50-90% primary porosity probably filled with body fluids and/or organic matter during the life  
529 time of the animal. Porosity was distributed throughout the rostrum as opposed to being limited to  
530 the central apical area. The primary biogenic rostrum framework consists of triaxial branches and  
531 tetrahedrons of variable size forming a honeycomb-like network. This structure arguably combined  
532 mechanical stability with an energy-efficient biomineralization strategy.

533 The recognition of belemnite rostra as a highly porous structure requires a re-interpretation of  
534 the function of the rostrum as counterweight to the soft body and has implications for the swimming  
535 mode of belemnites. On the level of a working hypothesis, we argue that the low-porosity fabric  
536 found in fossil rostra collected in outcrops worldwide is the result of a syntaxial, early diagenetic  
537 cement phase that nucleated upon the surface of the biogenic framework and subsequently  
538 occluded the pore space. The possibility of gradual occlusion of skeletal porosity by remote

539 biomineralization during later ontogenetic stages during the life of the animal is possible but seems  
540 unlikely at present.

541 If the here-presented concepts hold true, then these new findings have significant implications  
542 with regard to geochemical proxy data collected from fossil belemnite rostra. Specifically, the fact  
543 that rostra may consist of biogenic and abiogenic calcite phases formed at different times may  
544 explain the controversially low reconstructed seawater temperatures and the uncommonly high  
545 scatter of proxy data even from well-preserved rostra collected in the same stratigraphic interval.  
546 This is because seawater properties of surficial water masses, the habitat of nektonic  
547 belemnites, are recorded in the biogenic portions of the rostrum whereas the early diagenetic phase  
548 reflects cooler basinal bottom or marine pore water signatures. Findings presented here form a solid  
549 and well-constrained petrographic data set but one that must be verified by high-resolution  
550 geochemical data of all paragenetic calcite phases observed.

551

552

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559

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803 **Figure captions**

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805 **Fig. 1A-B) Structural and ultrastructural composition of belemnite rostra.** *Belemnitella mucronata*,  
806 thin sections photographed under crossed polarizers. A) Cross section with pseudo-uniaxial cross  
807 indicating radially arranged calcite fibres, red box refers to C. B) Longitudinal section with central  
808 apical line and radiating fibres from the centre to the margin, stippled line refers to the position of  
809 cross section shown in A. C) Idealized bundle of calcite fibres, each fibre contains a stack of  
810 tetrahedral elements. D) SEM BSD image of the tetrahedral ultrastructure of *Megateuthis gigantea*,  
811 dashed lines (I-IV) indicate section planes and corresponding reconstructions. Primary skeletal  
812 framework is shown in blue, yellow and green whilst early diagenetic phase is shown in white and  
813 red for the crystal boundaries. The basis of tetrahedrons points toward the centre of the belemnite  
814 rostrum and its tip towards the rostrum margin i.e. the growth direction. E) Three dimensional

815 reconstruction of a single tetrahedron of the belemnite endoskeleton. F) Reconstruction of the  
816 complex spatial arrangement of biogenic and early diagenetic phases. Colour code in lower right. G)  
817 SEM image of a single complex tetrahedron (black line) with indication of structural elements.  
818 Primary skeletal components: br = branch, trc = triradial centre, rf = reinforcement, ic = isopachous  
819 crystallites. **(full page width; bw in print, colour in pdf)**

820

821 **Fig. 2A-B) SEM BSD images of *Megateuthis gigantea*.** A-B) Section perpendicular to the c-axes of  
822 calcite fibres (section plane II in Fig. 1D-II). White stippled line indicate dissolution features (early  
823 diagenetic), black stippled line indicate microstylolites. **(full page width; bw in print, colour in pdf)**

824

825 **Fig. 2A-B) SEM BSD images of *Megateuthis gigantea*.** A-B) Section perpendicular to the c-axes of  
826 calcite fibres (section plane II in Fig. 1D-II). Blue stippled line indicate dissolution features (early  
827 diagenetic), red stippled line indicate microstylolites. **(full page width; bw in print, colour in pdf)**

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830 **Fig. 3A-F) SEM BSD images of *Megateuthis gigantea*.** A-E) Section perpendicular to the c-axes of  
831 calcite fibres. A) Triangular structures with a relatively thick outer, light grey margin of abiogenic  
832 early diagenetic cement and a small darker centre with branches giving rise to reinforcement  
833 structures representing the primary biogenic skeletal framework. B) Larger dark grey, organic rich  
834 triangular elements belonging to the biogenic skeletal framework, partly with light grey central  
835 abiogenic calcite filling of variable sizes. Branches are often short and cut off at variable distances  
836 from the centre. C) Some smaller and a few larger biogenic skeletal elements with cut off branches  
837 (lower arrow) and reinforcement structures (upper arrow). Note the variable expression of early  
838 diagenetic crystallites with sheaths of remnant organic matter. D) Close up of larger, biogenic skeletal  
839 elements and abiogenic isopachous calcites coated by remnants of organic matter within the brighter  
840 outer margin. Central portion of the biogenic skeletal elements shows abiogenic crystal; arrows point

841 to dissolved branches. E) Centre of biogenic skeletal element completely filled with abiogenic bright  
842 calcite leaving only a thin dark inner margin. F) Same specimen, section subparallel to the c-axes  
843 showing a homogenous central portion (“trunk” – white line) of pyramidal morphology rich in  
844 intracrystalline organic matter surrounded by inclined isopachous calcite crystals coated by remnants  
845 of organic matter. This overall pattern results in a “Christmas tree like” structure (compare with Fig.  
846 1D). **(full page width; bw in print and pdf)**

847

848 **Fig. 4A-E)** *Megateuthis gigantea*, EBSD map with colour code in sections perpendicular to the c-axes  
849 of the fiber bundles. Same colours represent same crystallographic orientations. In A and B angular  
850 deviation from blue to red is up to 40°, in D angular deviation is 2°. A) Overview map showing the  
851 bundling of fibres with identical orientation of a-axes, black frame indicates area for close up in B;  
852 blue frame refers to Fig. 5A-C. B) Close up map, within one bundle blue tinted fibres are mainly  
853 neighboured by other blue fibres, red tinted fibres are surrounded by red fibres. C) Close up  
854 documenting minor angular deviation within one fibre (compare with D). D) Map of a single fibre  
855 with an angular deviation of 2° from blue to red, showing a slight systematic shift of axes orientation.  
856 E) Pole-plots of c-axes {001} and a-axes {010} from all fibres shown in A, all c-axes show nearly the  
857 same orientation while the a-axes demonstrate the bundled structure of the rostral fabric which may  
858 have improved the stability of the skeletal structure. **(full page width; bw in print, colour in pdf)**

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**Fig. 5A-F) Transmitted light, polarized light and cathodoluminescence.** Thin section of *Megateuthis gigantea*, A-C refer to the blue frame in Fig. 4A, D-F are close ups (black frame in A) A and D) TL image perpendicular to the c-axes of calcite fibres, filigree biogenic skeletal framework is indicated by the dark tinted structures, primary porosity is represented by the abiogenic translucent calcites. Note banded distribution of calcite fibre domains relating to larger and smaller organic-rich biogenic skeletal elements, single fibres may contain a central portion of transparent calcite of varying size, bundling of adjacent calcite fibres is indicated by the same orientation of the triangles. B and E) Uniform extinction (orientation) of adjacent fibres under crossed polarizers. C and F) CL of abiogenic calcite portions show a dark blue, intrinsic luminescence (pure stoichiometric calcite), CL of the biogenic skeletal framework show light blue luminescence. **(full page width; bw in print, colour in pdf)**

**Fig. 6) Electron microprobe data for *Megateuthis gigantea*.** A) Overview BSE map B) Shows higher Mg concentrations within the triangular areas dark in BSE images and a lower Mg concentration in the surrounding area bright in BSE images. C) Shows higher P concentrations within the triangular areas dark in BSE images and a lower P concentration in the surrounding area bright in BSE images. D) Shows lower S concentrations within the triangular areas dark in BSE images and higher S concentrations in the surrounding region bright in BSE images. **(full page width; bw in print, colour in pdf)**



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**Fig. 7) Fluorescence microscope images for *Megateuthis gigantea*.** A) Transmitted light shows brownish triangular structures, rich in organic matter and dark in BSE images, partly with central translucent areas (compare with Fig. 1D section plane IV, Fig. 3D, E, 5A, D). B) Shows brighter fluorescent triangular area compared to the in transmitted light translucent calcite. **(full page width; bw in print, colour in pdf)**

**Fig. 8) Confocal laser fluorescence microscopy images of *Megateuthis gigantea*.** A) CLFM images showing fluorescence in far-red light ( $\lambda = 664$  to  $696$  nm). B) CLFM images showing fluorescence in visible green light ( $\lambda = 505$  to  $539$  nm). C and D) CLFM images showing fluorescence in visible red light ( $\lambda = 589$  to  $621$  nm). Triangular structures visible in other imaging techniques (Fig. 3, 5-7) do not fluoresce as brightly as cracks (B) or early diagenetic calcite (Fig. 3) separating the triangles (A, B, C, D). D) Higher magnification shows some brighter fluorescing calcite between the triangular elements dark in BSE images (Fig. 1, 3). Brightly fluorescent early diagenetic calcite separating triangles is enriched in S (Fig. 6). **(full page width; bw in print, colour in pdf)**

**Fig. 9) Three-dimensional visualization of the filigree biogenic framework.** Synchrotron radiation based tomographic visualization of a sub-volume of the rostrum of *Megateuthis gigantea*. Specimen was scanned with an isotropic voxel size of  $0.74\mu\text{m}$ . A) Multi-planar image of a sub-domain of the original dataset with dimensions of  $447 \times 592 \times 663$  voxels, triangular elements dark in BSE images appear here as dark elements due to reduced densities. B-D) Volumetric renderings of the same sub-domain with variable rendering settings. **(full page width; bw in print, colour in pdf)**

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920 **Supplementary Figures**

921 **Fig. 1) Examples of the filigree framework from other belemnite species.** A-B) *Goniot euthis*  
922 *quadrata*, A) shows the Becke line outside of the triangular area with a relatively larger distance  
923 between the sample and objective. B) Image shows the Becke line within the triangular area while  
924 the distance between the sample and the objective was reduced, accordingly the triangular area  
925 (dark in BSE; Fig. 3) has a lower optical relief. C-D) *Belemnitella mucronata*, C) thin section under  
926 polarized light, D) same area under CL showing microfractures filled with Mn-rich calcite tracing the  
927 outline of triangular elements (encircled). **(full page width; bw in print, colour in pdf)**

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930 **Fig. 2) SEM BSD images of *Megateuthis gigantea*.** A-F) Section plane parallel to the c-axes of calcite  
931 fibres. A-C) stepwise enlargement of a particular area. D-F) stepwise enlargement of a particular  
932 area. A and D give the impression of a concentric arrangement of distinct darker and brighter layers  
933 (black frames enlarged in B and E), arrow in D point to an organic rich layer (*laminae obscura sensu*  
934 *Müller-Stoll, 1936*). B and E) Allow the recognition of single darker structures of tetrahedral  
935 morphology with their tips pointing towards the outer margin of the belemnite rostrum, i.e. the  
936 growth direction (black frames enlarged in C and F). C and F) show the intricate framework of  
937 biogenic (dark) and abiogenic (light) carbonate phase within the rostrum, larger dark grey, triangular  
938 elements belonging to the biogenic skeletal framework, partly with light grey central abiogenic  
939 calcite filling of variable size. **(full page width; bw in print, colour in pdf)**

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## Highlights

We present well-constrained petrographic evidence for the complex primary biogenic framework of belemnite rostra.

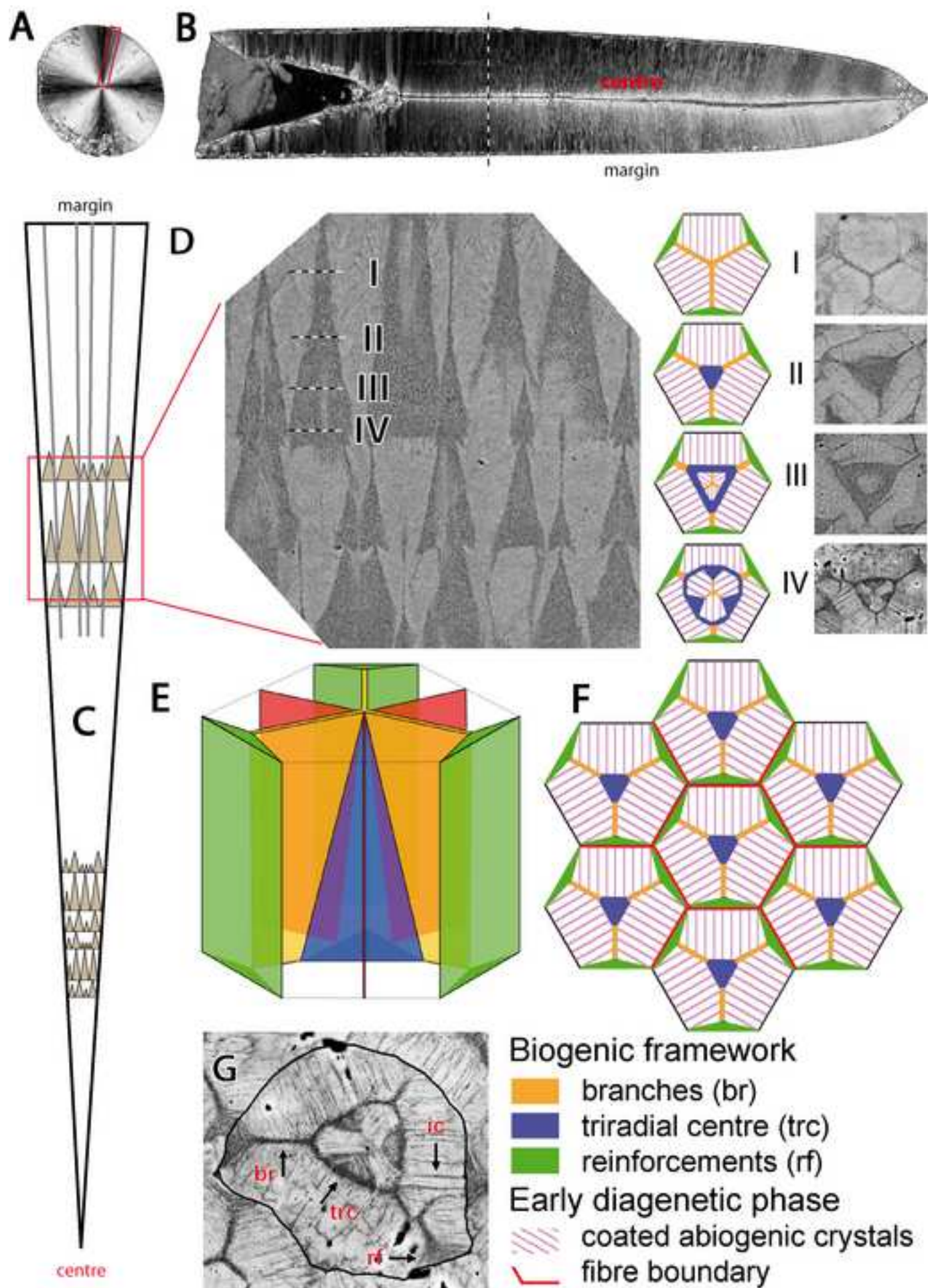
Petrographic evidence demonstrates a high (50-90%) primary porosity for the bulk of the belemnite rostrum.

The relative proportion of biogenic skeletal framework versus abiogenic, earliest diagenetic calcite occluding the former pore space in rostra is assessed.

We discuss the timing and formation modes of pore-filling calcites.

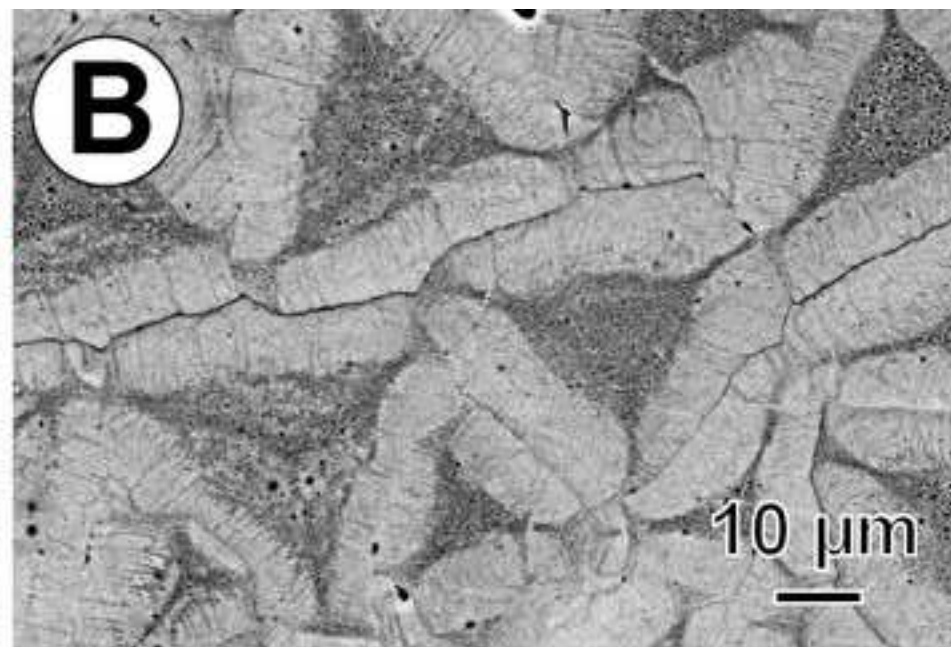
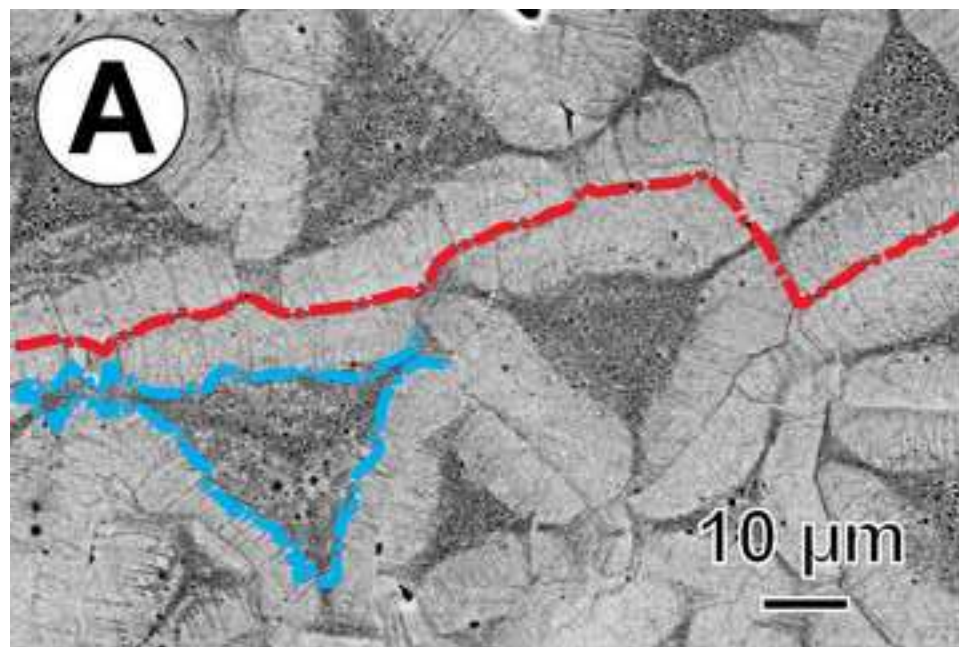
The significance of these findings for reconstructions of marine palaeo-environments and the function of the rostrum is discussed.

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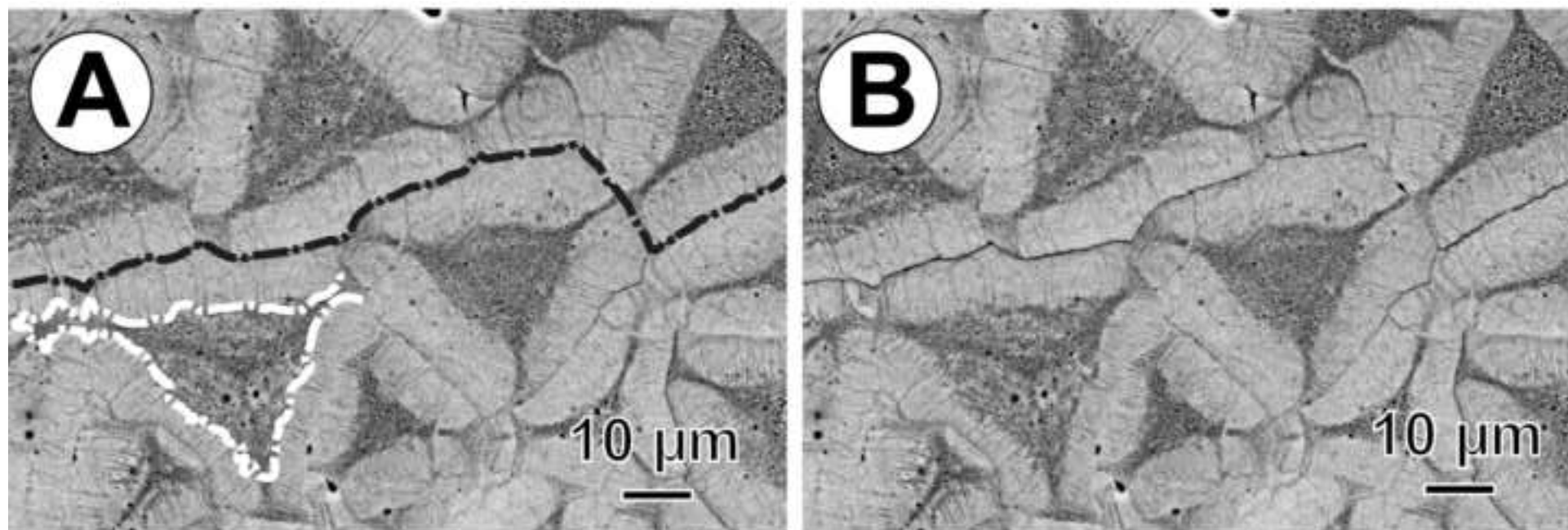


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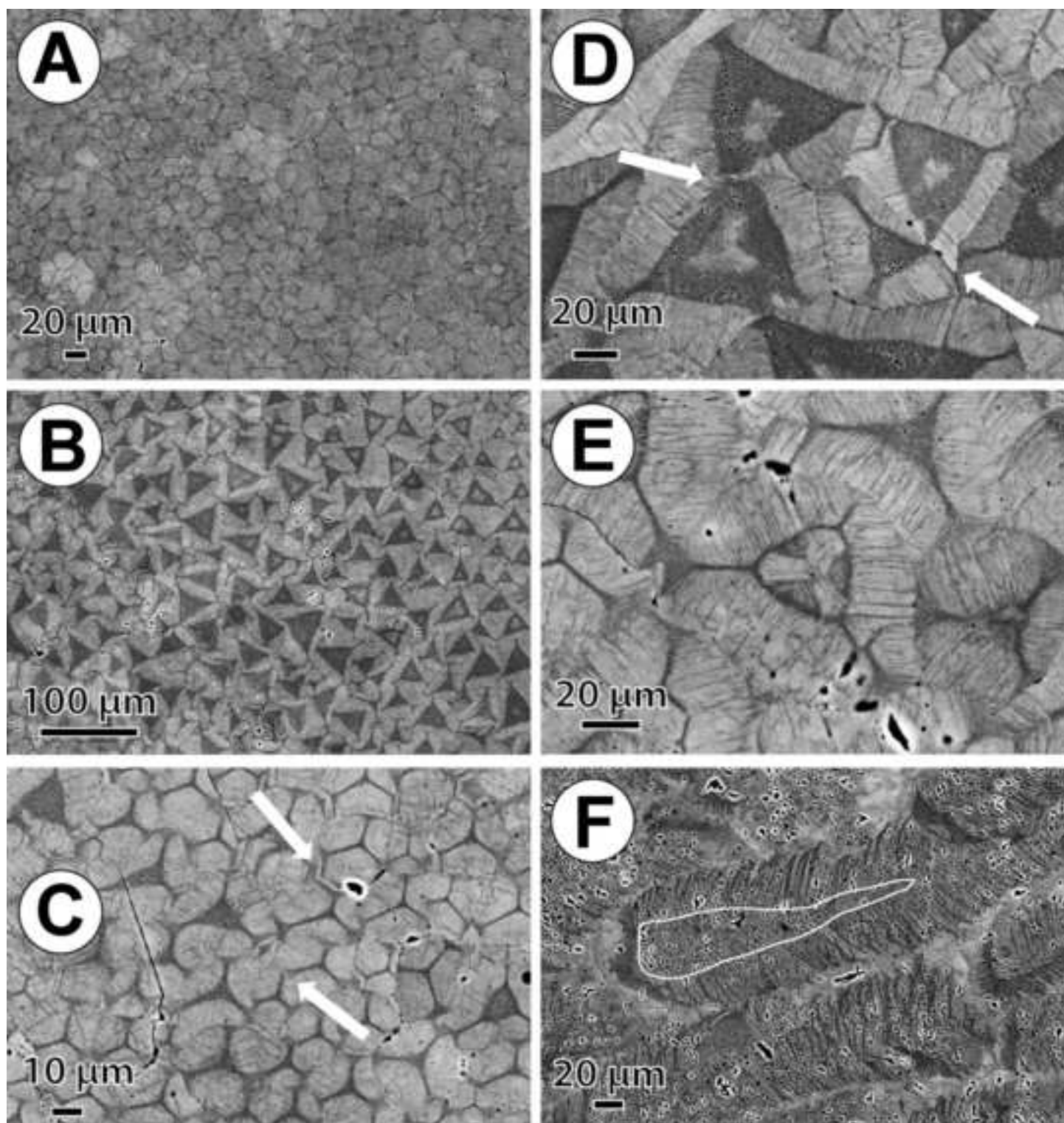


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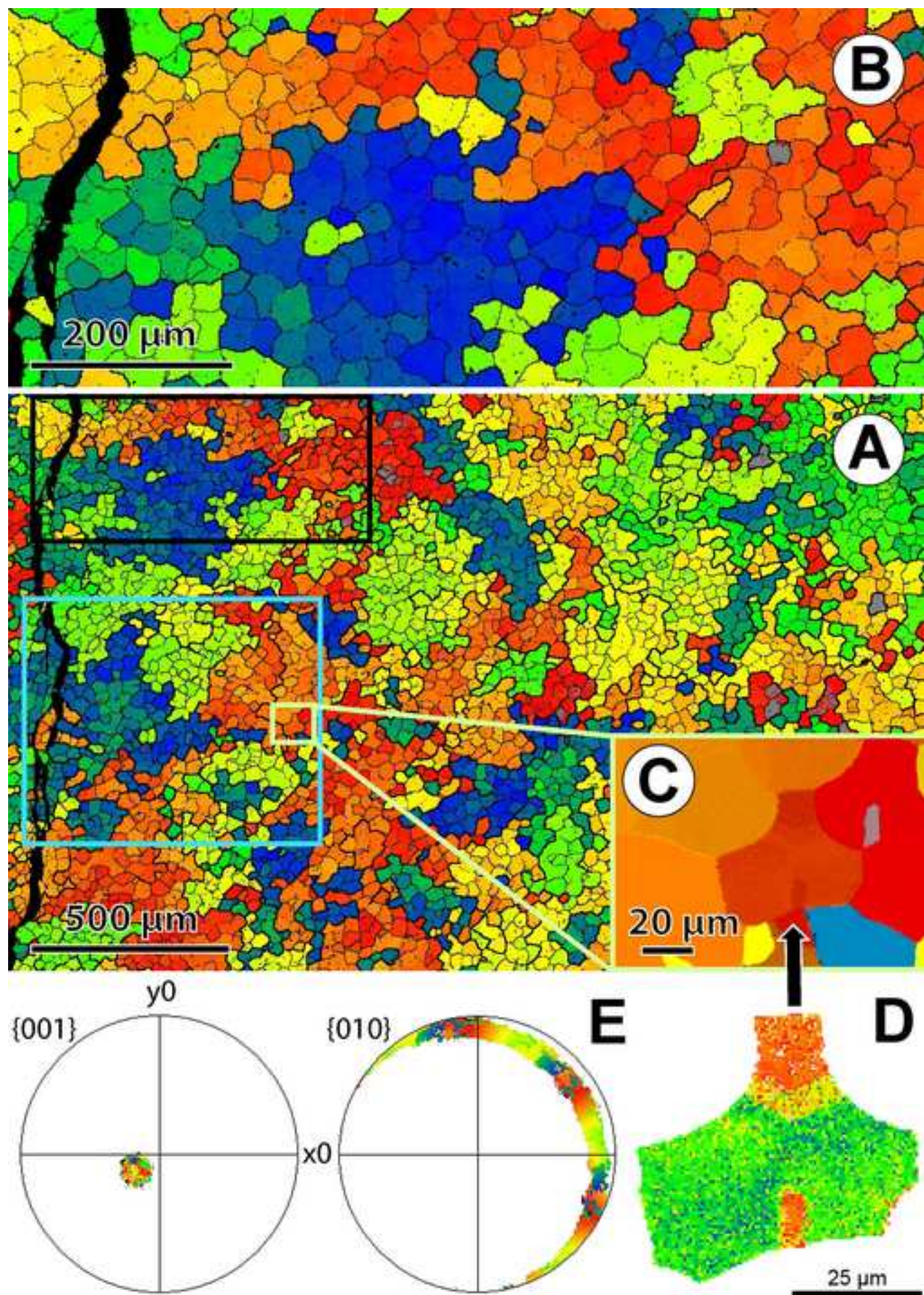




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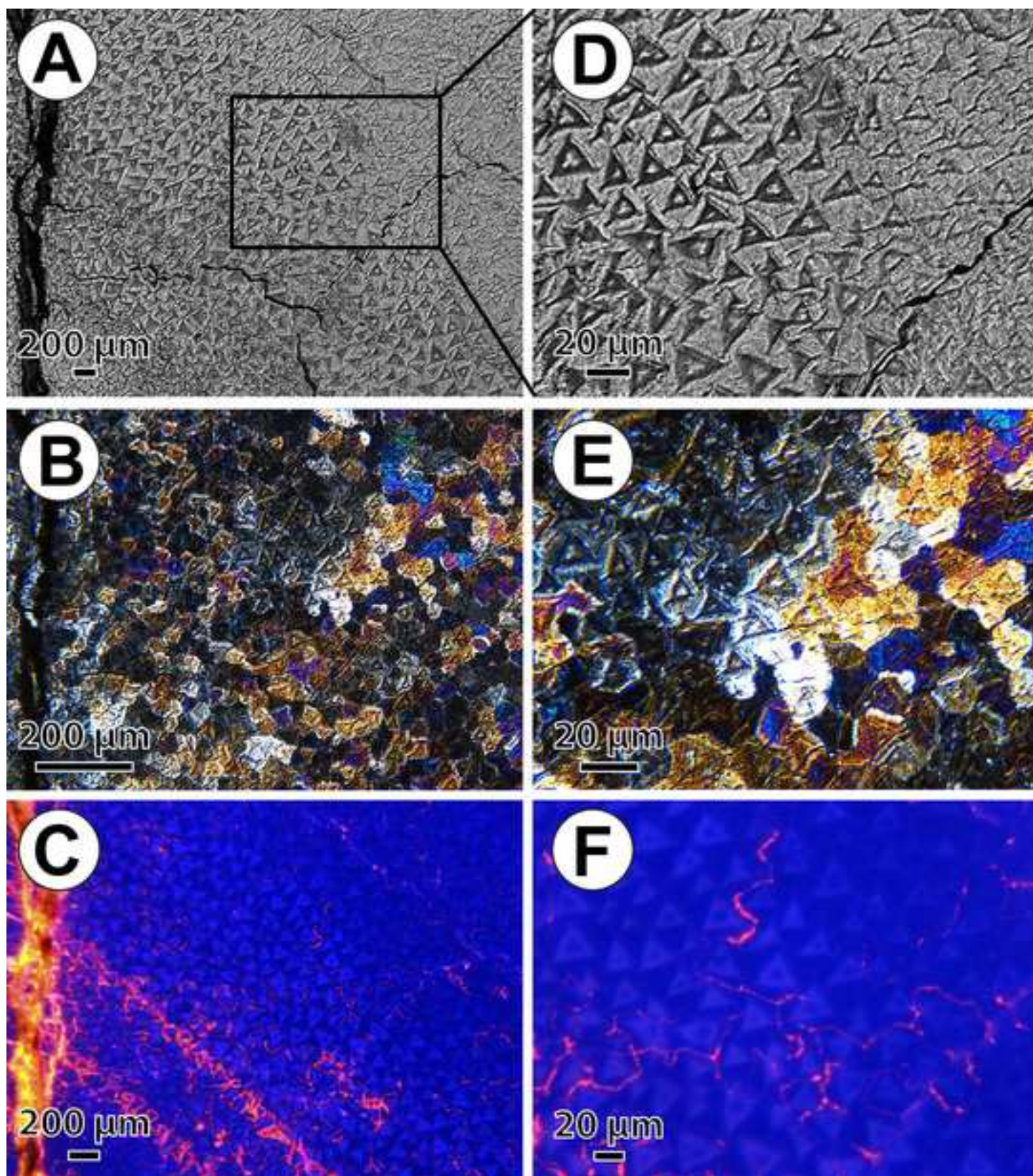
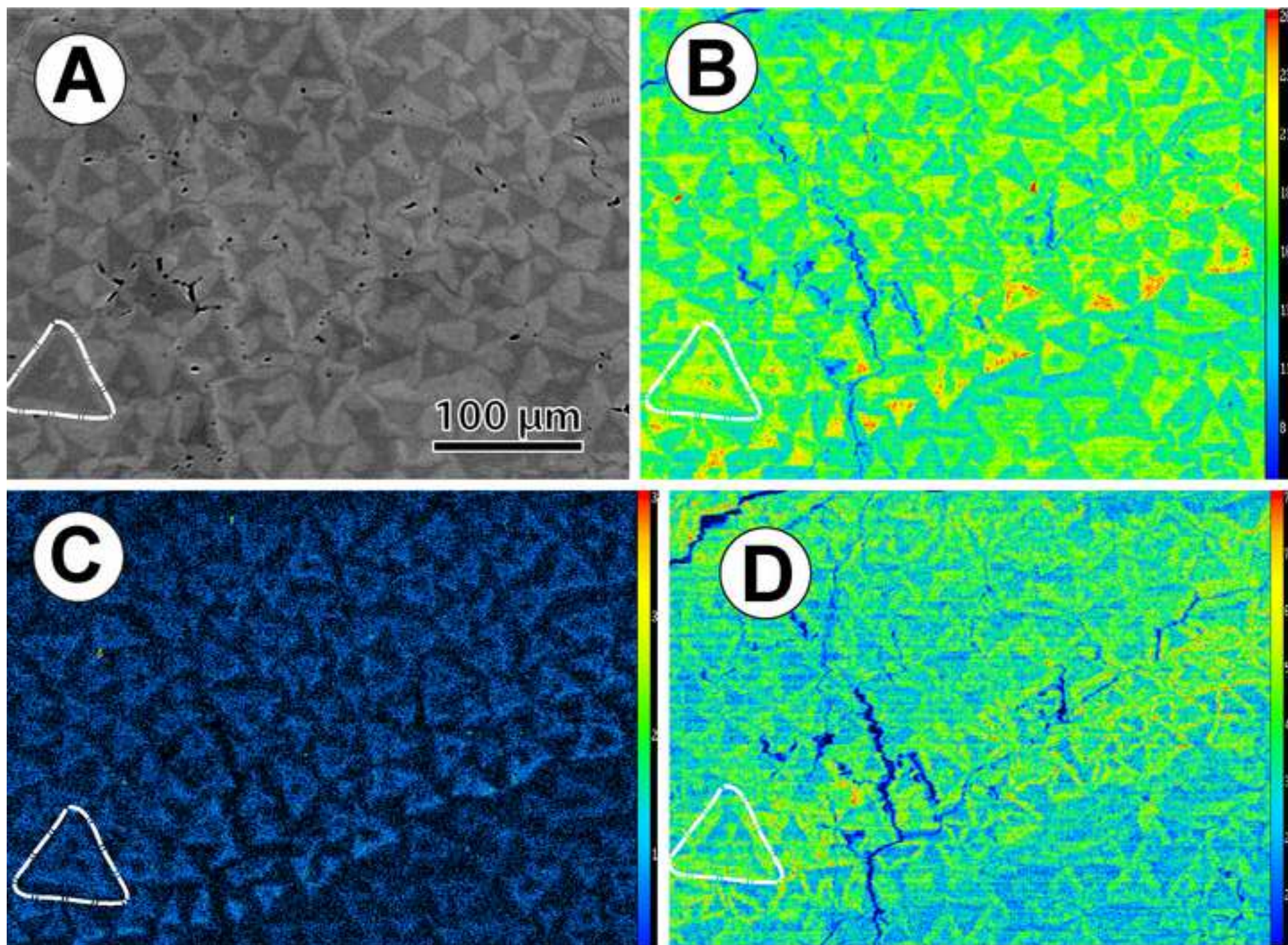


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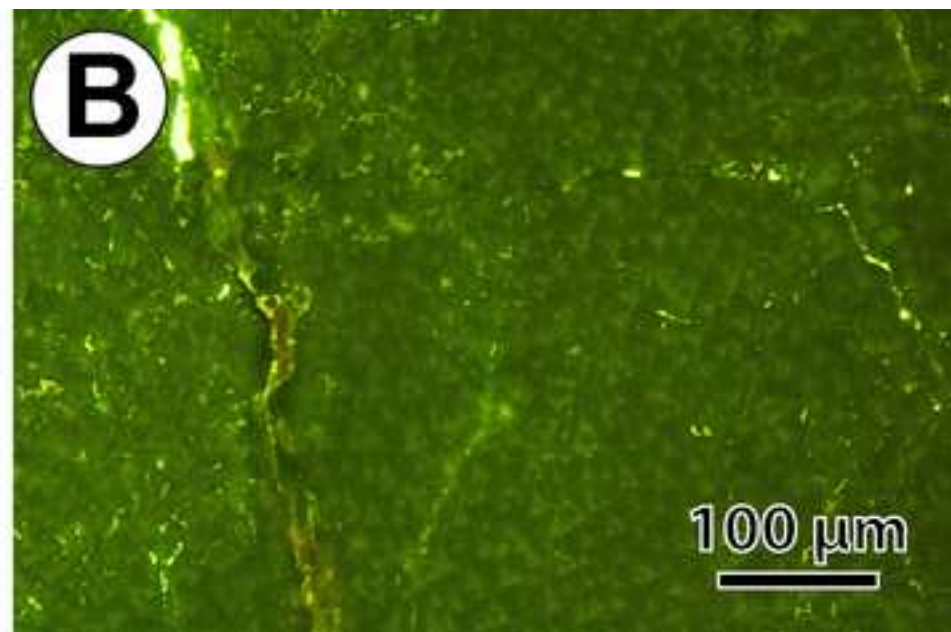
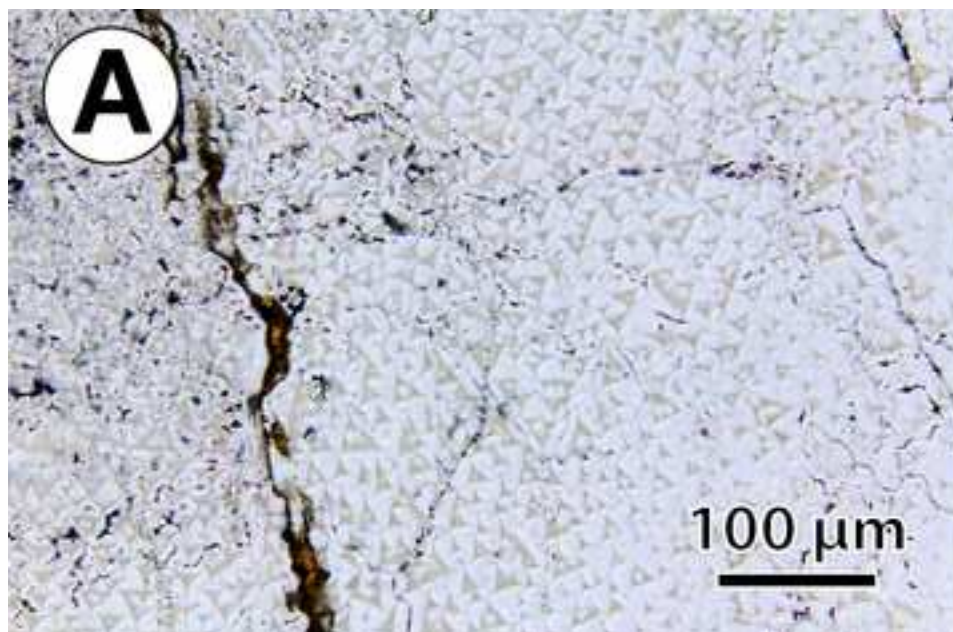


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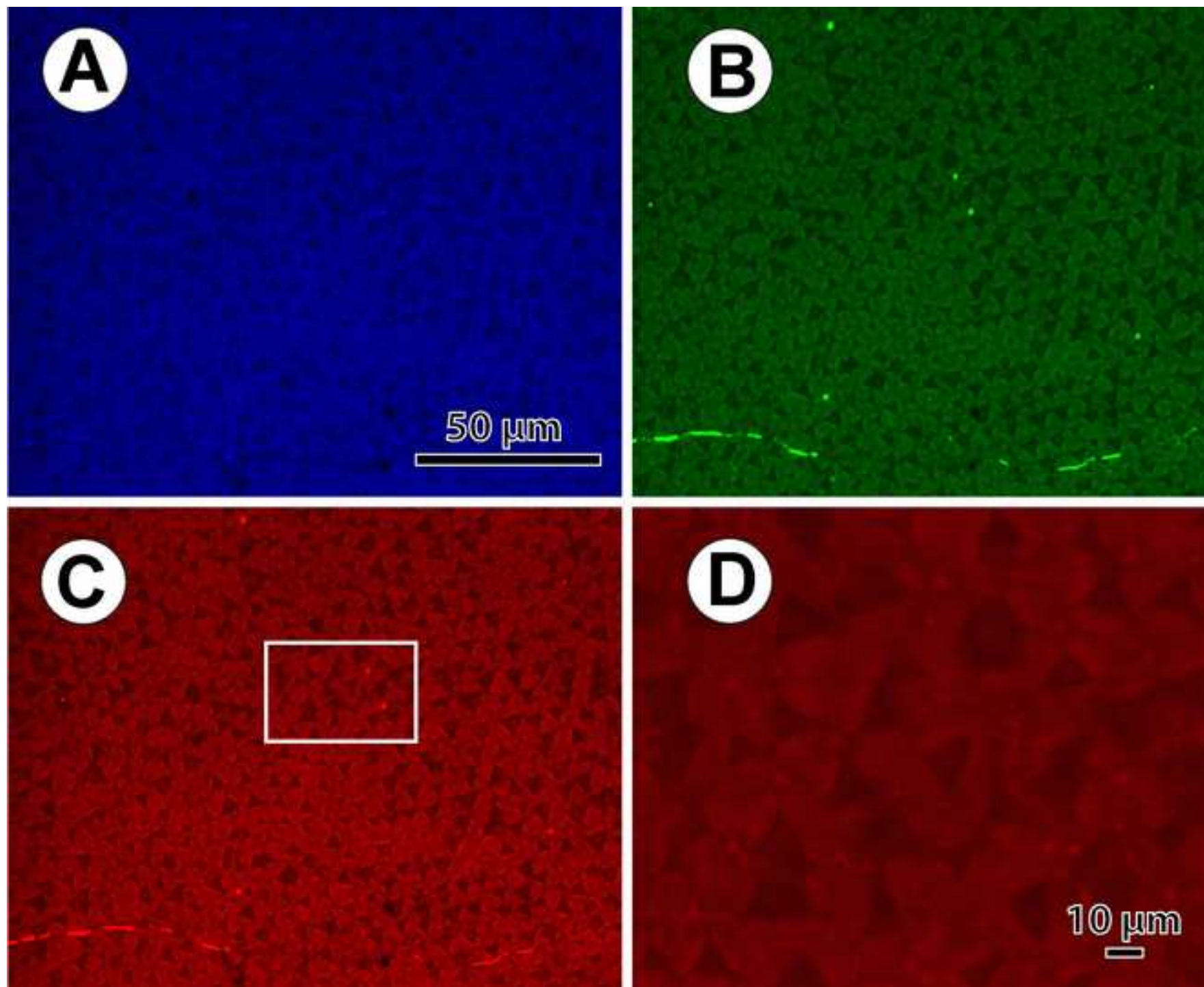
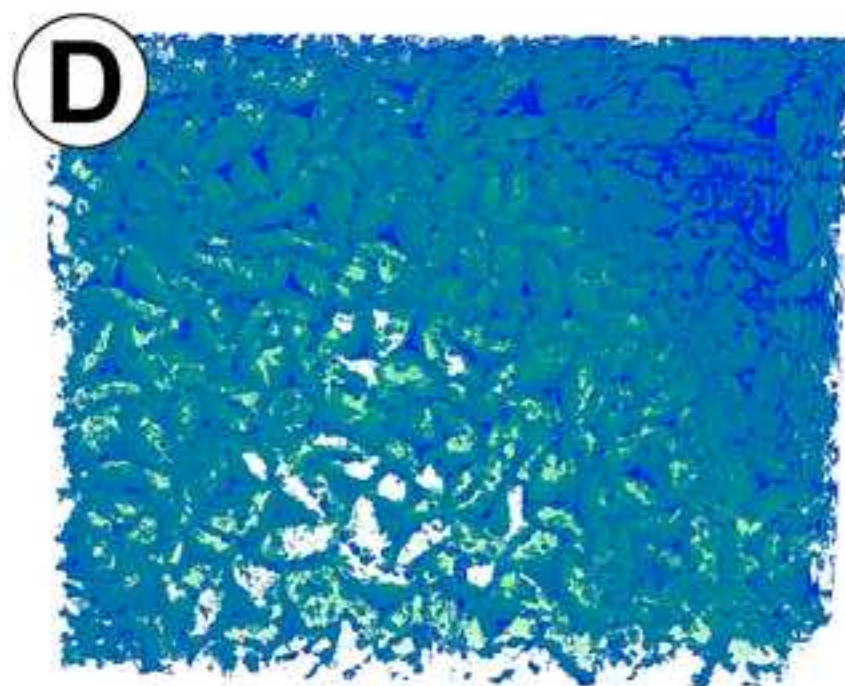
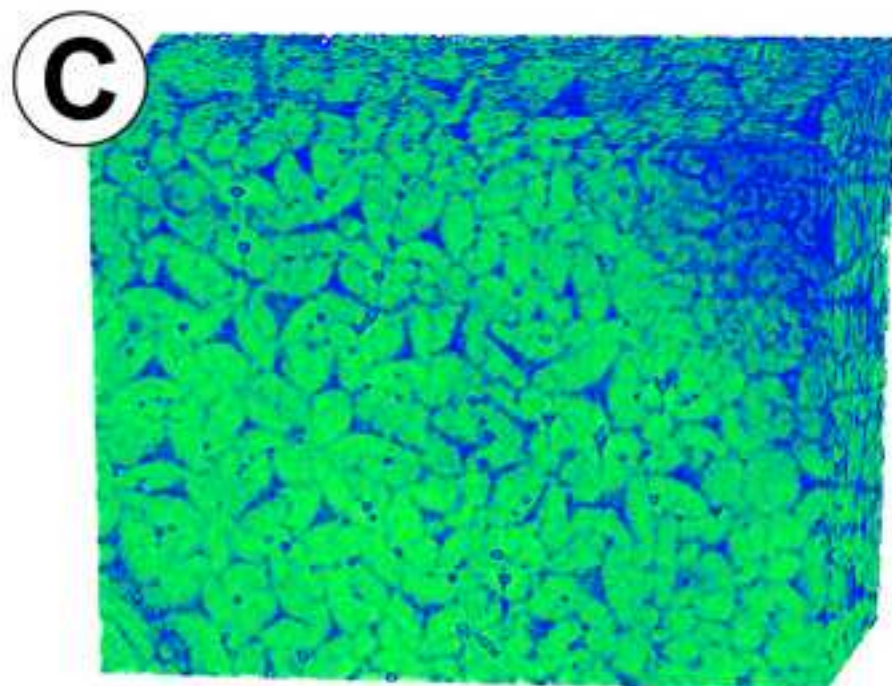
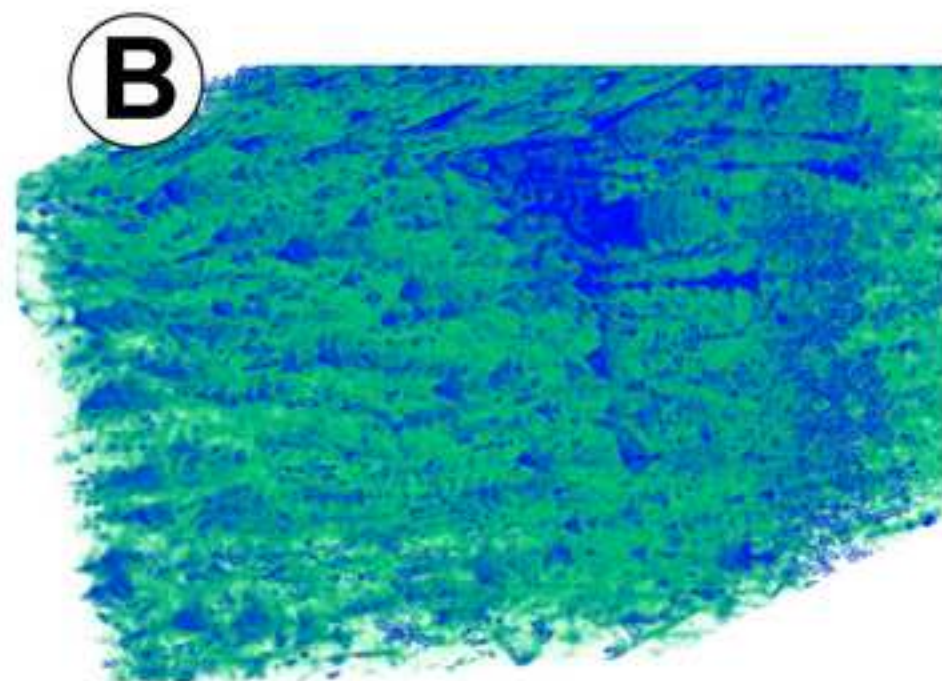
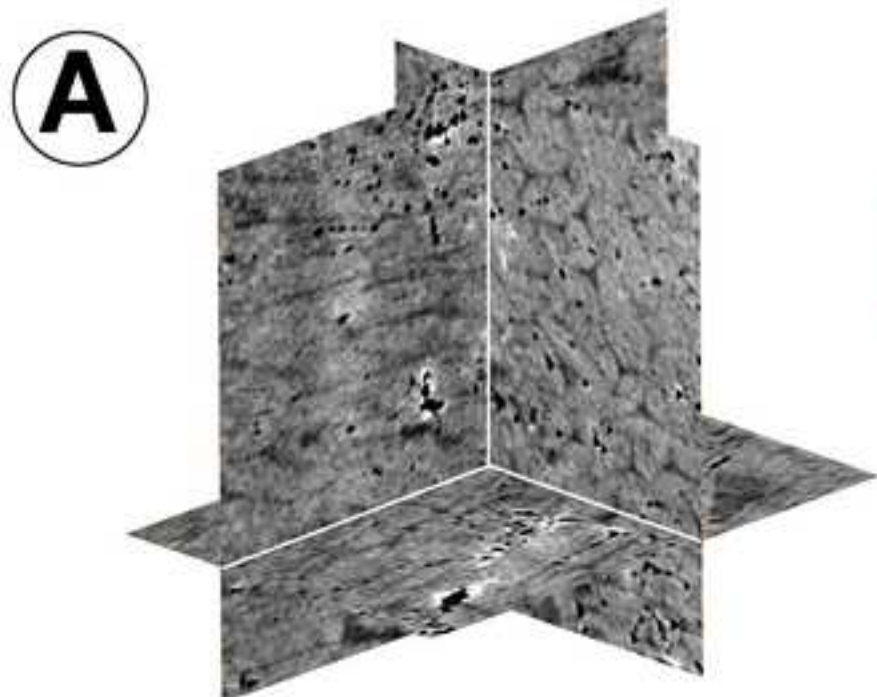


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