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## **Catshark Egg Capsules from a Late Eocene Deep-Water Methane-Seep Deposit in Western Washington State, USA**

Authors: Kiel, Steffen, Peckmann, Jörn, and Simon, Klaus

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# Catshark egg capsules from a Late Eocene deep-water methane-seep deposit in western Washington State, USA

STEFFEN KIEL, JÖRN PECKMANN, and KLAUS SIMON



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Fossil catshark egg capsules, *Scyliorhinotheca goederti* gen. et sp. nov., are reported from a Late Eocene deep-water methane-seep calcareous deposit in western Washington State, USA. The capsules are preserved three-dimensionally and some show mineralized remnants of the ribbed capsule wall consisting of small globular crystals that are embedded in a microsparitic matrix. The globules are calcitic, but a strontium content of 2400–3000 ppm suggests that they were originally aragonitic. The carbonate enclosing the egg capsules, and the capsule wall itself, show  $\delta^{13}\text{C}$  values as low as -36.5‰, suggesting that formation was induced by the anaerobic oxidation of methane and hence in an anoxic environment. We put forward the following scenario for the mineralization of the capsule wall: (i) the collagenous capsules experienced a sudden change from oxic to anoxic conditions favouring an increase of alkalinity; (ii) this led to the precipitation of aragonitic globules within the collagenous capsule wall; (iii) subsequently the remaining capsule wall was mineralized by calcite or aragonite; (iv) finally the aragonitic parts of the wall recrystallized to calcite. The unusual globular habit of the early carbonate precipitates apparently represents a taphonomic feature, resulting from mineralization mediated by an organic matrix. Taphonomic processes, however, are at best contributed to an increase of alkalinity, which was mostly driven by methane oxidation at the ancient seep site.

**Key words:** Elasmobranchia, Scyliorhinidae, taphonomy, exceptional preservation, collagen, Late Eocene, Washington State, USA.

Steffen Kiel [skiel@uni-goettingen.de], Georg-August Universität Göttingen, Geowissenschaftliches Zentrum, Abteilung Geobiologie and Courant Research Center Geobiology, Goldschmidtstr. 3, 37077 Göttingen, Germany;

Jörn Peckmann [joern.peckmann@univie.ac.at], Universität Wien, Erdwissenschaftliches Zentrum, Department für Geodynamik und Sedimentologie, Althanstr. 14, 1090 Wien, Austria;

Klaus Simon [ksimon@gwdg.de], Georg-August Universität Göttingen, Geowissenschaftliches Zentrum, Abteilung Geochemie, Goldschmidtstr. 1, 37077 Göttingen, Germany.

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## Introduction

Methane seeps in the deep sea are sites on the seafloor where methane-rich fluids are expelled. Such sites are often colonized by lush faunal communities dominated by animals living in symbiosis with chemotrophic bacteria, which take advantage of the abundance of methane and hydrogen sulfide at these sites. This high biomass on the otherwise nutrient-poor deep-sea floor attracts various fishes that appear to have the ability to cope with the elevated levels of hydrogen sulfide at these sites. The most common fishes at methane seeps are zoarcids, macrourids, and occasionally hagfish, eels, morids, and a few other groups (Ohta and Laubier 1987; Hashimoto et al. 1989; MacAvoy et al. 2002; Turnipseed et al. 2004; Sellanes et al. 2008). Reports of sharks from modern methane seeps are restricted, to the best of our knowledge, to the two species *Centroscyllium granulatum* (Dalatiidae) and

*Halaelurus canescens* (Scyliorhinidae) at seep sites in 740–870 m water depth northwest of Concepción Bay, Chile (Sellanes et al. 2008). In situ observations and stable isotope and fatty acid studies indicate that most of these fishes feed, at least to some extent, on chemosymbiotic animals, although this is unclear in case of the sharks (MacAvoy et al. 2002, 2003; Sellanes et al. 2008).

Living catsharks often attach their egg capsules to erect structures in the water column, such as gorgonians, octocorals, hydroids, and even derelict fishing gear (Able and Flescher 1991; Etnoyer and Warrenchuk 2007). Recently, catshark egg capsules were found associated with worm tubes and carbonates at a deep-water methane seep site in the eastern Mediterranean where the worm tube thickets might provide a substrate for protection and ventilation (Treude et al. 2011). At a Late Eocene methane-seep deposit in western Washington, USA, large numbers of similar egg capsules were found associated

with worm tubes, as well as hexactinellid sponges (Treude et al. 2011), showing that catsharks have been using such environments as nurseries for at least 35 million years. Predators have a significant role in ecosystem functioning and maintaining diversity. By serving as nurseries for predatory deep-marine catsharks and other elasmobranch taxa, methane seeps are important components of deep-sea ecosystems and should not be considered as only extreme and exceptional habitats; their presence or absence is likely to influence faunal diversity along continental slopes (Treude et al. 2011: 179).

Elasmobranch egg capsules are rare in the fossil record. Perhaps most common among them are the Paleozoic and Mesozoic spirally coiled capsules of the *Palaeoxyris* group found mainly in freshwater deposits (Fischer and Kogan 2008). There are occasional occurrences of chimaeroid egg capsules (*Chimaerotheca*) ranging back to the Triassic (Brown 1946; Bock 1949). Skate egg capsules are rare, with a few specimens from the Oligocene of central Europe, named *Rajitheca* (Steininger 1966). All these records represent internal or external molds, many are flattened, and a capsule wall has, to the best of our knowledge, never been reported. The scope of the present contribution is to (i) name the fossil egg capsules found in the Bear River methane-seep deposit, (ii) provide a detailed description of the capsule and its mineralized wall, and (iii) discuss the fossilization process.

*Institutional abbreviations.*—GMUG, Geowissenschaftliches Museum der Universität Göttingen, Germany; SMF, Senckenberg Museum, Frankfurt, Germany; USNM, United States National Museum of Natural History, Washington DC, USA; UWBM, University of Washington, Burke Museum, Seattle, USA.

*Other abbreviations.*—EDX, energy-dispersive X-ray spectroscopy; LA-ICPMS, laser ablation-inductively coupled plasma mass spectroscopy.

## Geological setting

The Bear River limestone is an isolated carbonate body found within uplifted deep-water siltstone beds mapped as “Siltstone of Cliff Point” (Wells 1989). It has long been interpreted as an ancient seep deposit based on its geological setting and the macrofaunal association (Goedert and Squires 1990; Goedert and Benham 2003; Kiel 2010a). The low  $\delta^{13}\text{C}$  values of the carbonate reported here provide unequivocal evidence for its origin at a methane-seep site. The host sediments were deposited in the Cascadia accretionary wedge during the Eocene when subduction of the Juan de Fuca plate under the North American continent started, and their exhumation started in the Miocene (Brandon and Vance 1992; Stewart and Brandon 2004). Foraminiferal associations indicate that the Bear River seep deposit formed in water depths of 500–2000 m (Goedert and Squires 1990; Kiel 2010b). The macrofaunal association is dominated by the mussel *Bathymodiolus willapaensis*, worm tubes are common, large sole-

myid, lucinid, and vesicomid bivalves occur throughout the deposit, as well as numerous small gastropods (Goedert and Squires 1990; Squires and Goedert 1991; Squires 1995; Goedert and Benham 2003; Kiel 2006, 2010a). A peculiar feature of this seep deposit is the abundance of uncrushed specimens of the hexactinellid sponge *Aphrocallistes polytretos* (Rigby and Jenkins 1983) that are intermingled with mussels, worm tubes, and the egg capsules reported here.

## Material and methods

Thin sections of 60  $\mu\text{m}$  thickness were prepared from cross sections of a specimen with the ribbed capsule wall preserved. They were studied using a Zeiss Axioplan optical stereomicroscope (lamb: VisiTron HBO 50; filter: BP 365, FT 395, LP 397), and a Zeiss 510 Meta confocal laser scanning microscope (LSM). The LSM was run with an excitation of 488 nm, emissions in the range of 490–704 nm were measured with spectral detection using a Lambda detector.

Samples for scanning electron microscope (SEM) imaging and EDX analysis were mechanically removed from the capsule wall, etched for ca. 10 seconds in 10% acetic acid, mounted on an aluminium sample holder, and coated with 14 nm of platinum. Images were taken with a LEO 1530 SEM at 3.8 KV, EDX analysis were done with an attached INCAX-act analyzer at 15.7 KV.

Samples for stable carbon and oxygen isotope analysis were extracted from the polished surfaces of the same rock samples from which thin sections were prepared, using a hand-held microdrill. Samples from outside the capsule wall were drilled from in between and up to a few millimeters away from the ribs; those from inside the capsule were drilled only from the micrite, not from any of the microsparitic or cement phases. Carbonate powders were reacted with 100% phosphoric acid at 75°C using a Kiel III online carbonate preparation line connected to a ThermoFinnigan 252 mass spectrometer. All values are reported in per mil relative to V-PDB by assigning a  $\delta^{13}\text{C}$  value of +1.95‰ and a  $\delta^{18}\text{O}$  value of -2.20‰ to NBS19. Reproducibility was checked by replicate analysis of laboratory standards and is better than  $\pm 0.05\%$ .

The mineralogy of the capsule wall was investigated by Raman spectroscopy. Spectra were recorded using a Horiba Jobin Yvon LabRam-HR 800 UV micro-Raman spectrometer with a focal length of 800 mm. As excitation wavelength the 488 nm line of an Argon Ion Laser (Melles Griot IMA 106020B0S) with a laser power of 20 mW was used. The laser beam was dispersed by a 600 l/mm grating on a CCD detector with 1024×256 pixels, yielding a spectral dispersion of 0.43  $\text{cm}^{-1}$ . An Olympus BX41 microscope equipped with an Olympus MPlane 100× objective with a numerical aperture of 0.9 focused the laser light onto the sample. With these settings, the focal point of the laser on the sample had a diameter of ca. 1  $\mu\text{m}$ . The confocal hole diameter was set to 100  $\mu\text{m}$ . The acquisition time was 15 seconds for wave numbers in the range of 100–2000  $\text{cm}^{-1}$ . For calibration of the spectrometer



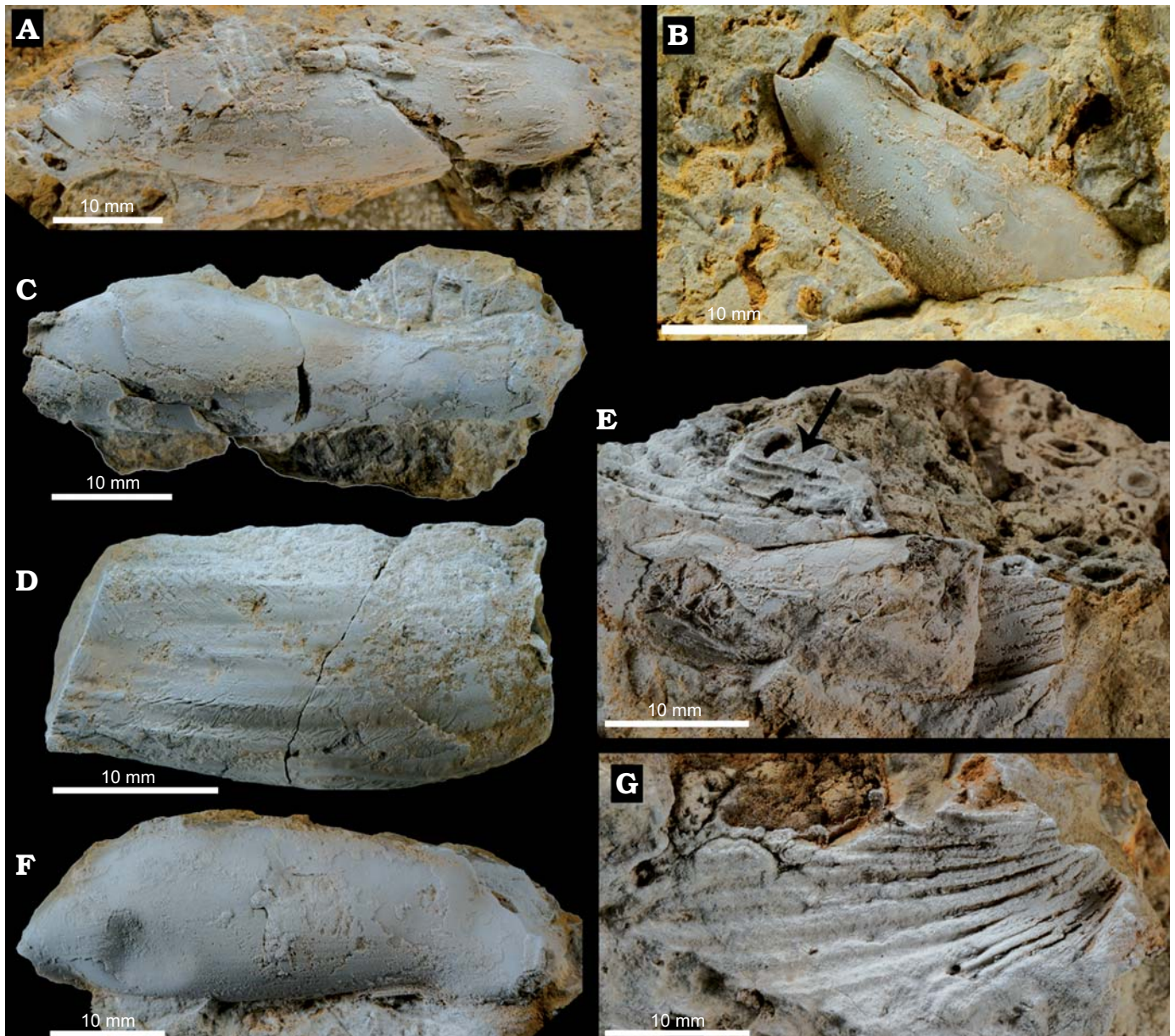


Fig. 1. The Late Eocene Bear River egg capsule *Scyliorhinotheca goederti* gen. et sp. nov. in different states of preservation. **A.** Steinkern showing the anterior and posterior ends (USNM 544321). **B.** Posterior half of a steinkern, showing the tapering end with a horn (USNM 544322). **C.** Deformed steinkern with spindle-like shape (USNM 544323). **D.** Steinkern with faint wrinkles on the surface, perhaps due to shrinkage (USNM 544324). **E.** Two specimens: the lower, main specimen shows the anterior constriction and the flattened anterior end (left) and remnants of the ribbed capsule wall (right); the upper specimen (arrow) is just a cast of a ribbed capsule surface; note relics of worm tubes on the right side of the block (USNM 544325) (image from Treude et al. 2011). **F.** Steinkern showing indentation on lower left (USNM 544326). **G.** Cast (external mold) showing ribbing on capsule surface (USNM 544327).

a silicon standard with a major peak at  $520.4\text{ cm}^{-1}$  was used. All spectra were recorded and processed using LabSpec™ version 5.19.17 (Jobin-Yvon, Villeneuve d'Ascq, France).

Trace element analysis of the capsule wall was done by laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS), using a PerkinElmer SCIEX ELAN DCR II mass spectrometer coupled to a Lambda Physik Compex 110 Argon-Fluoride-laser with a wavelength of 193 nm. Samples were placed in a low-volume sample chamber with a size of  $5\times 3\times 0.5\text{ cm}$  (L×W×H) that was flushed with argon gas. Each spot was measured for 10 seconds with a spot size of  $10\text{ }\mu\text{m}$ .

## Systematic palentology

The terminology follows Ebert et al. (2006).

### Genus *Scyliorhinotheca* nov.

*Type species:* *Scyliorhinotheca goederti* gen. et sp. nov. described below.

*Etymology:* From Scyliorhinidae, the catshark family that presumably produced those egg capsules; and from Latin *theca*, envelope, capsule.

*Diagnosis.*—Egg capsules generally having the elongated,



inflated fusiform shape of those of living catsharks (Scyliorhinidae), with or without longitudinal ribs.

*Scyliorhinotheca goederti* gen. et sp. nov.

Figs. 1–3.

*Etymology*: For James L. Goedert, who discovered these fossils.

*Holotype*: Almost complete internal mold USNM 544321 (Fig. 1A).

*Paratypes*: Internal and external molds; all figured specimens are deposited in the USNM (numbers 544322 to 544328); additional specimens are deposited at SMF (P9796 to P9798), UWBM (95285 to 95287) and at GMUG (GZG.IF.11020).

*Type locality*: The Bear River seep deposit, southwestern Washington State, USA (46°19.943 N, 123°55.964 W). This is LACM locality number 5802 and UWBM locality number C1459.

*Type horizon*: Siltstone of Cliff Point, latest Eocene (nannofossil zone CP15b of Okada and Bukry 1980), based on the presence of *Isthmolithus recurvus*.

*Diagnosis*.—The egg capsules have an inflated fusiform shape and a slightly constricted waist; the maximum dimensions are: length = 50 mm, width = 15 mm, thickness = 11 mm. The surface shows at least 12 rough ridges and two thin secondary ridges. The lateral edges extend to narrow lateral flanges along the entire length of the egg case. The anterior border is slightly concave, with two well-developed respiratory fissures but apparently no horns; the posterior end is tapering after a slight constriction, and the horns are short and pointing at, or twisting around, each other.

*Discussion*.—We have seen no tendrils on either end of the egg capsules, but this may be a preservational artefact. The most similar egg capsules produced by modern catsharks are those of the scylorhinid genus *Apristurus*: many have a similarly tapering posterior end, and some show coarse ribs on the surface (Sato et al. 1999; Iglésias et al. 2002, 2004; Flammang et al. 2007). Fossil teeth attributed to the genus *Apristurus* are known from the Late Eocene of European Tethys (Adnet et al. 2008), which agrees with the stratigraphic age of the egg capsules reported here. The only other extant scylorhinid with a fossil record ranging into the Eocene, including the Pacific Northwest of the United States, is *Scyliorhinus* (Welton 1972; Adnet et al. 2008); although the egg capsules of this genus resemble those of *Apristurus* in general shape (Rusaouën et al. 1976; Ebert et al. 2006), they are apparently smooth (cf. Treude et al. 2011). Similar in outline are the egg capsules of two species of the genus *Schroederichthys* (*S. tenuis* and *S. maculatus*), but on their surfaces the egg capsules show only tortuous longitudinal striations (Springer 1966; Gomes and de Carvalho 1995) instead of strong ribs as in the Bear River specimens.

## The capsule wall

In cross section, the capsule wall is approximately 100  $\mu\text{m}$  thick; individual ribs are up to 700  $\mu\text{m}$  high and between 100 and 150  $\mu\text{m}$  wide at their narrowest point; they are often bent sideways (Fig. 3A, B). The capsule wall consists of a micro-

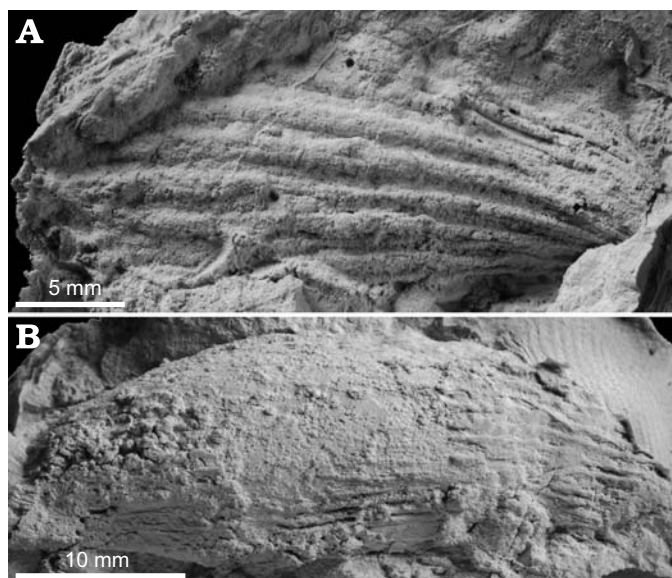


Fig. 2. Silicon rubber casts of external molds of the Late Eocene Bear River egg capsule *Scyliorhinotheca goederti* gen. et sp. nov. A. USNM 544327 (the same specimen as in Fig. 1). B. USNM 544328.

sparitic matrix enclosing abundant and roughly evenly distributed globules having a diameter of 15–20  $\mu\text{m}$  (Fig. 3C, D). The matrix and the globules are both made of calcite, indicated by peaks at the Raman bands at 280, 710, and 1084  $\text{m}^{-1}$  (Fig. 4; Urmos et al. 1991). The tips of the ribs are often made of sparry calcite (Fig. 3C, D). Under crossed nicols, the matrix shows extinction in patches, some of the globules also show extinction, some do not (Fig. 3F). Confocal laser scanning microscopy shows that the globules have a much stronger autofluorescence than the matrix (Fig. 3E). LA-ICPMS analysis of the globules ( $N = 3$ ) showed a Sr content of 2400–3000 ppm, measurements on the background matrix ( $N = 2$ ) showed a Sr content of 1300–2700 ppm. The small size of the globules and their close proximity to each other within the wall matrix meant that LA-ICPMS measurements of the globules were compromised by certain amounts of wall matrix material, and vice versa (Fig. 5). It is thus likely that the actual Sr contents of both globules and wall matrix are more distinct from each other than we were able to document. Small pyrite framboids

Table 1. Stable carbon and oxygen isotope values of the capsule wall and the carbonate associated with it; all values are relative to V-PDB.

	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Outside capsule	-35.1	-6.6
	-35.2	-6.0
	-36.3	-5.8
Capsule wall	-36.0	-4.4
	-36.5	-6.3
Inside capsule	-34.9	-5.0
	-35.1	-5.0
	-35.1	-4.9



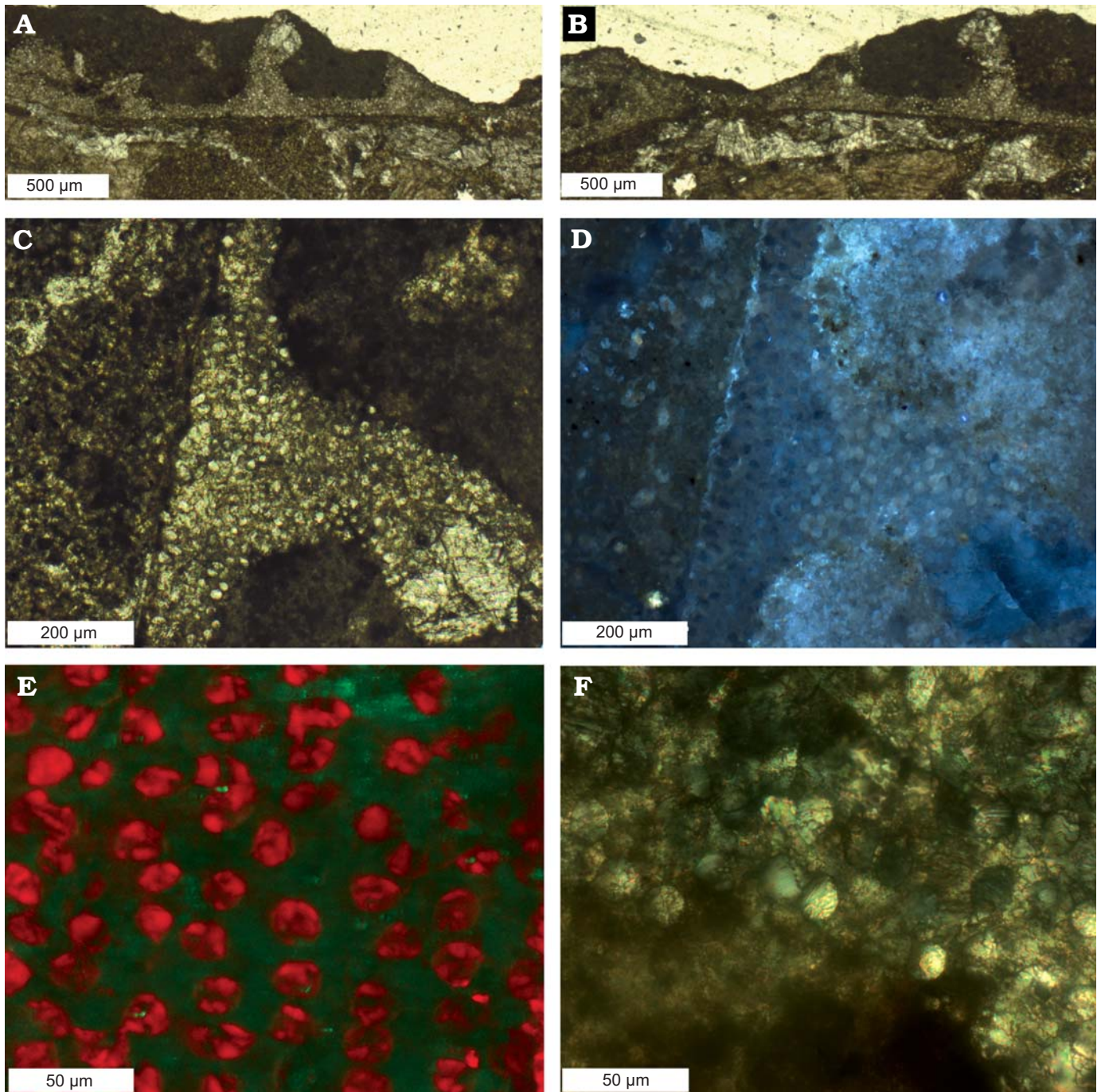


Fig. 3. Thin section micrographs of the capsule wall of the Late Eocene Bear River egg capsule *Scyliorhinotheca goederti goederti* gen. et sp. nov. **A, B.** Two sections of a capsule wall with several ribs, dark, micritic seep carbonate on the outside, and several diagenetic carbonate phases in the interior; plane-polarized light. **C, D.** Close-up on the middle rib in A, rotated ca. 90° clockwise. Note that the capsule wall consists of microsparite, enclosing globular calcite crystals; plane-polarized light (**C**) and UV light (**D**). **E.** Detail of the capsule wall; laser scanning microscope image generated by linear unmixing using the spectra of the globules versus that of the wall matrix. **F.** Detail of capsule wall, showing extinction of some of the globules; crossed-polarized light.

no larger than 5 μm diameter (most are < 1 μm diameter) are dispersed throughout the wall matrix (Fig. 6), as revealed by SEM imaging and EDX analysis of etched surfaces of the capsule wall. The Raman spectra (Fig. 4) of the wall matrix show a small peak at 375  $\text{m}^{-1}$ , which also indicates pyrite (Mernagh and Trudu 1993). This peak was not seen in the spectra of the globules (Fig. 4).

## Preservation and occurrence

All specimens are preserved in three dimensions, and several show indentations that most likely originated after hatching of the young shark (Fig. 1F). Many capsules are only preserved as internal molds (steinkerns; Fig. 1), some are external molds

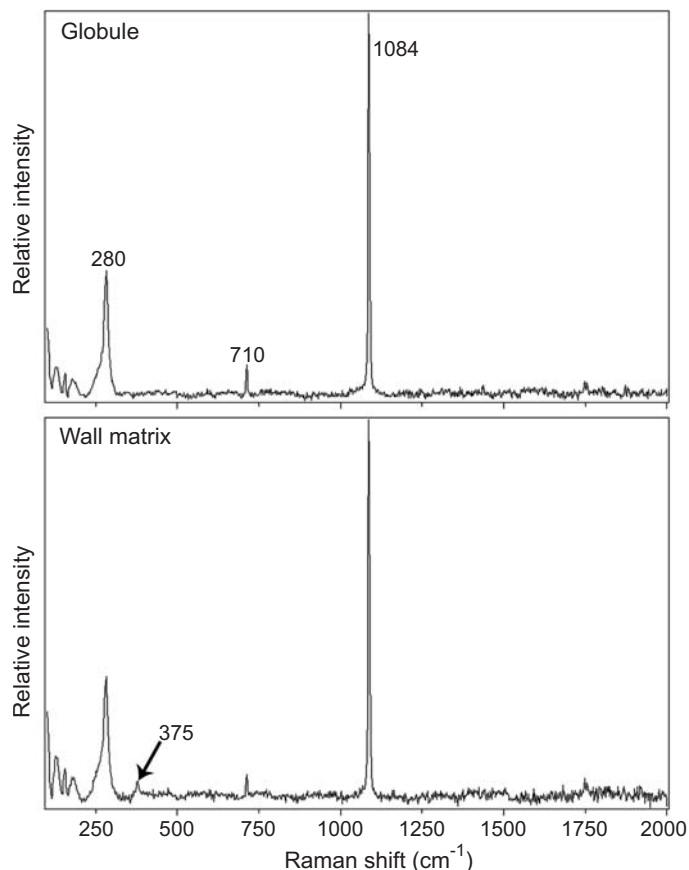


Fig. 4. Raman spectra of globules and microsparitic matrix of the capsule wall.

showing the ribbing of the capsule wall (Figs. 1, 2), and only in a few specimens is the capsules wall preserved in the mineralized form described herein. The egg capsules are enclosed in, and filled with, micritic, microsparitic, and peloidal carbonate as well as carbonate cement that show  $\delta^{13}\text{C}$  values as low as  $-36.3\text{‰}$ , the wall itself revealed values of  $-36.5$  and  $-36.0\text{‰}$  (Table 1). The capsules are always associated with worm tubes (Fig. 1E) and three dimensionally preserved specimens of the hexactinellid sponge *Aphrocallistes polytretos*, and often also with the mussel *Bathymodiolus willapaensis* (cf. Squires and Goedert 1991; Kiel 2006).

## Discussion

Shark egg capsules are virtually unknown from the marine fossil record (Fischer and Kogan 2008). Freshly laid catshark egg capsules are made of collagen (Rusaouën et al. 1976), a substance that is quickly hydrolyzed when exposed to water. Thus, the calcification of the capsule walls requires special conditions. We suggest the following scenario for the genesis of the calcitic capsule wall: (i) the egg capsules experienced a sudden change from an oxic to an anoxic environment; (ii) aragonitic globules precipitated within the collagenous capsule wall, likely favoured by the activity of bacteria degrading the organic wall; (iii) subsequently the remaining wall matrix

was mineralized by aragonite or calcite; (iv) finally the aragonitic parts of the wall recrystallized to calcite. This scenario is based on the following lines of evidence:

**Environment.**—When catshark egg capsules at modern methane-seep sites are laid into tubeworm thickets they develop in a fully oxic environment (Treude et al. 2011). At the Bear River site, the very low  $\delta^{13}\text{C}$  values of the capsule wall and the carbonate surrounding it, as well as the finely dispersed pyrite framboids show that at least part of the carbonate formed due to the anaerobic oxidation of methane (cf. Peckmann and Thiel 2004) and thus in an anoxic environment. Because collagen is quickly hydrolyzed in marine environments, we assume that a sudden change from an oxic to an anoxic environment facilitated the three dimensional preservation of the egg capsules and their walls.

**Shape and mineralogy of the globules.**—The growth of calcium carbonate globules like those documented here is commonly related to bacterial activity and the bacterial decay of organic matter (e.g., Buczynski and Chafetz 1991; Briggs and Kear 1993), but crystal habit is clearly not an unequivocal criterion for this kind of mineralization (e.g., Fernández-Díaz et al. 1996). The low  $\delta^{13}\text{C}$  values of the capsule wall including globules suggest that wall fossilization (i.e., replacement of collagen by carbonate minerals) was fostered by an increase of alkalinity induced by anaerobic oxidation of methane (cf. Peckmann and Thiel 2004). Although the globular crystal habit—a habit untypical for methane-derived carbonate minerals of seep limestone—most likely reflects the taphonomical alteration of the organic wall, the decay of the wall was apparently not responsible for the generation of an oversaturation with respect to carbonate minerals. Even so carbonate precipitation was probably mediated by an organic matrix provided by the decomposing wall, the decay of the collagenous wall did not contribute significantly to alkalinity increase based on the very similar carbon isotopic compositions of the wall and the adjacent methane-derived carbonate phases; shark collagen typically reveals higher  $\delta^{13}\text{C}$  values of approximately  $-15\text{‰}$  to

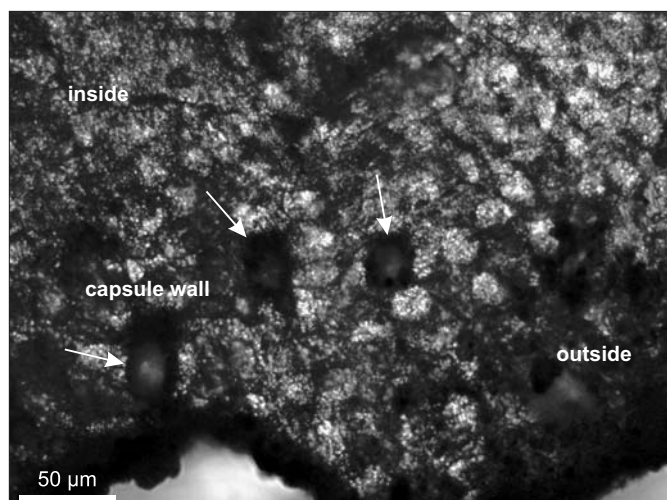


Fig. 5. Thin section micrograph of the capsules wall showing three of the craters produced during laser ablation (arrows).



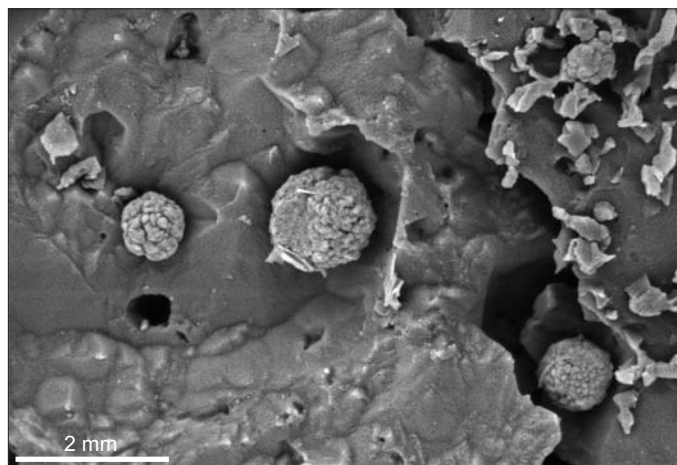


Fig. 6. Pyrite framboids in the egg capsule wall. SEM image of an etched fracture surface.

-13‰ (MacNeil et al. 2005). An originally aragonitic mineralogy of the globules is suggested by their high Sr content (2400–3000 ppm); such values are common for aragonite, but calcite or dolomite precipitated in marine environments typically have lower Sr contents (Tucker and Wright 1990; Compton 1992). Aragonite cement formed at methane seeps in the Black Sea exhibits Sr contents as high as 9500 ppm, the associated high-Mg-calcite revealed values of approximately 1200 ppm (Peckmann et al. 2001). Similarly, aragonite cement of seep carbonates from the Niger Delta showed Sr contents of up to 12 000 ppm, much higher than the contents of 100 ppm to 1000 ppm found for other carbonate mineralogies including calcite and dolomite (Bayon et al. 2007). Savard et al. (1996) reported as much as 11 000 ppm Sr in aragonite cement of Cretaceous seep limestone rocks. In many ancient seep deposits, aragonite is recrystallized to calcite (Buggisch and Krumm 2005; Peckmann et al. 2007). Fibrous calcite cements with an inferred aragonite precursor of Paleozoic seep limestone rocks revealed Sr contents as high as approximately 20 000 ppm (Iberg deposit; Buggisch and Krumm 2005), 13 000 ppm (Tentes Mound; Buggisch and Krumm 2005), and 13 000 ppm (*Dzieduszyckia* deposit; Peckmann et al. 2007), whereas the micrite (i.e., microcrystalline calcite) of ancient seep deposits typically exhibits contents in the range of a few hundred ppm to little more than 1000 ppm (e.g., Campbell et al. 2002).

**Wall matrix.**—Mineralization of the wall matrix subsequent to the precipitation of the globules is suggested by the regular shape of the globules. The growth of such globules within an already existing calcium carbonate wall seems impossible. Based on the Sr content of the wall matrix, ranging from 1300–2700 ppm, it is difficult to decide whether this carbonate was primarily aragonite or a mixture of aragonite and calcite. The very negative  $\delta^{13}\text{C}$  values of the capsule wall (globules plus matrix) and the pyrite framboids finely dispersed throughout the wall indicate that fossilization occurred under anoxic conditions. The Bear River capsule walls share a common fossilization mechanism with the tubes of seep-dwelling vestimentiferan worms (Haas et al. 2009) in that

fossilization was driven by carbonate precipitation induced by the anaerobic oxidation of methane. Unlike the fossilization of the organic-walled tubes of vestimentiferans, however, where individual layers of the organic wall function as templates for carbonate cement growth, the egg capsule walls were permineralized by authigenic carbonate, resulting in three-dimensional preservation.

## Conclusions

To the best of our knowledge, the catshark egg capsules reported here are the first fossil shark egg capsules from a fully marine environment. The shape of the fossil egg capsules closely resembles that of egg capsules produced by modern catsharks (family Scyliorhinidae), therefore we erect the new genus and species, *Scyliorhinotheca goederti*. Fossilization of the capsule wall was favoured by anaerobic oxidation of methane—the biogeochemical key process at seeps—inducing replacement of the organic wall by carbonate minerals. The crystal habit of the first replacive carbonate phase, however, reflects taphonomical processes within the decaying wall.

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