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Palaeozoic 'conodont pearls' and other phosphatic micro-spherules

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Sub-millimetre-sized phosphatic spherules are often found in acetic acid-insoluble residues produced for microfossil extraction. As they are typically associated with conodont elements and have a similar chemical composition, they are informally known as 'conodont pearls'. Still, the origin of these micro-spherules has been controversial, and authors have disagreed regarding their mode of formation, or if they are biogenic or not. In this study, an assortment of micro-spherules from several localities and stratigraphic levels were analysed using multiple methods, in an effort to shed light on the origin of these enigmatic objects: ocular investigation with a stereomicroscope; chemical analyses employing energy-dispersive mass spectrometry; imaging through scanning electron microscope; and synchrotron radiation x-ray microtomography. Collectively, the techniques employed allow for near-complete characterization and description of the study specimens. At least five different groups, or morphotypes, of spherules can be discerned, which differ both in morphological and chemical details. Most pearls are notably spherical and display concentric layers of growth. Several of the pearls have a central nucleus, sometimes with one or more objects located closely together. Internal details and chemistry suggest that the phosphatic spherules likely are of different origin. Thus, the term 'conodont pearl' encompasses confusingly similar objects deriving from different organisms and/or processes, and only careful analysis can reveal their individual origin. The only organisms unequivocally associated with (*in situ*) phosphatic micro-spherules are ceramoporid bryozoans, and the conodonts *Cordylodus* and *Westergaardodina*, but the possible function and significance of these objects remain enigmatic.

Keywords: Phosphatic micro-spherules, conodont pearls, affinity, chemistry, morphology

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Sub-millimetre-sized phosphatic spherules are sometimes found in residues following the digestion of rock samples in weak acids for microfossil extraction (e.g., Stauffer 1935, 1940). Close inspection has shown that the interior of many of these micro-spherules displays concentric layers, i.e., laminae of growth, with details indicating a biogenic origin (e.g., Youngquist & Miller 1948; Glenister *et al.* 1976; Wang & Chatterton 1993; but see Leuteritz *et al.* 1972). Whereas Stauffer (1935, 1940) hesitantly referred to such spherules as 'egg cases?' (see also Lindström 1954), Youngquist & Miller (1948) considered the possibility that the objects may be otoliths (calcareous inner-ear structures found in vertebrates). However, based on overall characteristics and morphology Glenister *et al.* (1976) argued that these micro-spherules are in essence pearls, presumably secreted by conodont animals in response to irritants, i.e., closely similar to the formation of mollusc pearls. Hence, these enigmatic objects have come to be informally known as 'conodont pearls'.

The association of these spherules with conodonts was primarily inferred from the observation that the latter are the only fossils that are invariably found in the same rock samples as the spherules, often so in somewhat proportional amounts, and that the conodonts and spherules are composed of closely similar francolite apatite (e.g., Glenister *et al.* 1976, and references therein). Moreover, 'conodont pearls' have never been found beyond the stratigraphic range of conodonts (Cambrian–Triassic). Direct and unambiguous association between phosphatic micro-spherules, or pellets, and the paraconodont *Westergaardodina* has been documented by Müller (1959, pl. 15.7a), Olgun (1987, tafeln 1–4) and Müller & Hinz (1991, pl. 31, fig. 10, pl. 32, figs. 13, 14), and recently mentioned by, among others, Nielsen *et al.* (2013, p. 253). In several instances, the spherules are attached to (or, rather, cradled within the posterior curvature of) elements belonging to this puzzling conodont genus. Still, the affinity of 'conodont pearls' is ambiguous, particularly because the pearls are usually found isolated in euconodont samples and have not been observed *in situ* or in direct association with euconodont elements (other than *Cordylodus*, as shown for the first time herein).

Giles *et al.* (2002) analysed late Devonian phosphatic micro-spherules fitting the description of 'conodont pearls' *sensu* Glenister *et al.* (1976), and compared their chemistry with that of coeval conodonts and fish teeth. Their results indicated that the overall chemistry of the tentative pearls was more similar to that of fish teeth than to that of conodont elements. Consequently, the authors concluded that the micro-spherules were fish otoliths, produced during brief times of significant phosphate excess in the shelf environment (cf. Youngquist & Miller 1948). Normally, otoliths consist almost entirely of calcium carbonate, mainly in the form of aragonite (Carlström 1963). In a study of various small phosphatic spherules, including forms similar to purported conodont pearls, Leuteritz *et al.* (1972) simply concluded that all their specimens were inorganically produced.

Oakley (1934; see also Oakley 1966) described numerous phosphatic micro-spherules (or 'spheruliths' of ~30–600 µm size), closely similar to 'conodont pearls' *sensu* Glenister *et al.* (1976), which were found *in situ* in middle Silurian (Wenlockian) bryozoan specimens from several localities in the UK. The observation of spherules within zooecia sealed by diaphragms, together with detailed study of their relation to the surrounding sediments and host fossils, led Oakley (1934) to exclude the possibility of an allochthonous origin. He argued that the spherules represent concretions (calculi) that grew within the coelomic fluid of the living bryozoans, comparable to the gall and bladder stones of higher organisms. Oakley (1934) noted that the studied spherules were only present in *Favositella* species and closely related genera of the Family Ceramoporidae, and ascribed this exclusivity to organism characteristics rather than to unusual environmental events (cf. Giles *et al.* 2002). Eisenack (1964) subsequently described a range of phosphatic microfossils from the Silurian of Gotland, Sweden, including spherules identical to those of Oakley (1934). The latter were referred to as 'Oakleyite'. Calcitic objects that are similar to the spherules described by Oakley (1934) have been found in different types of bryozoans, in various stratigraphic levels throughout the world, and include cyst-like bodies growing on internal walls of zooecia (e.g., Boardman 1960, 1991; Wass 1974). Alongside the phosphatic spherules in bryozoans, so-called phosphatic linings have been recorded in the skeletons of different Palaeozoic stenolaemate groups, the origin and function of which remains controversial (e.g., Martinsson 1965; Ma *et al.* 2014, and references therein).

In summary, it is safe to say that there is controversy as to what 'conodont pearls' really are, and what organism – if any at all – produced them. Herein, we examine phosphatic micro-spherules of different age and from different localities. Multiple techniques are used for chemical and

morphological analysis, with the aim of characterizing, describing and assessing the affinity of these objects.

Materials and methods

For this study, we have collected numerous sub-millimetre-sized phosphatic spherules from several stratigraphic levels, spanning the Cambrian through Devonian, from localities in Sweden and the USA (Table 1). A range of different depositional environments, including both carbonate platform and siliciclastic settings, are represented in the sample set. We investigated the chemical characteristics of these micro-spherules and associated conodont elements in an effort to reveal any possible relation(s) between the two. Additionally, we compared the external and internal physical characteristics of our specimens to the bryozoan-hosted spherules described by Oakley (1934, 1966). The interior details of 'conodont pearls' and similar objects have traditionally been investigated through more or less destructive methods, mainly splitting, grinding, polishing and etching of the specimens. In addition to such methods of analysis, we also employed synchrotron radiation x-ray tomographic microscopy (SRXTM) as a non-destructive method for revealing the exterior and interior details of the micro-spherules.

Treatment of rock samples and picking of specimens

The rock samples were digested in acetic acid following normal conodont extraction techniques (Jeppsson *et al.* 1999; Jeppsson 2005). Note that because the processing was done at different laboratories in Sweden and the USA, the methodology, e.g., buffering techniques and pH monitoring, differs in minor details (cf. Jeppsson 2005). After digestion, the residues were rinsed through a 63 µm or 125 µm sieve, dried and electrostatically hand-picked for conodont elements and micro-spherules under a binocular light microscope. All figured specimens are stored in the type collection of the Department of Geology, Lund University, Lund, Sweden, with repository number LO (for Lund Original).

Chemical analyses

In total, 27 micro-spherules and 22 associated conodont elements, and two conodont basal bodies/fillings, from a total of ten samples, were cast in epoxy and carefully ground down to reveal their interiors (see Table 1). The exposed interior surfaces were polished with the aid of diamond slurry and coated with a nanometre-thick carbon film. Semi-quantitative chemical analyses were then performed using an energy-dispersive mass spectrometer (EDS; Inca X-sight, Oxford instruments with a Si-detector) mounted in a Hitachi S-3400N scanning electron microscope (SEM), at the Department of Geology, Lund University, Sweden. At least three points per specimen, in spherules spanning from core to rim, were targeted and analysed for 60 s, and an average composition was then calculated for each specimen. Analyses were performed at 15 kV and 65 nA probe current. Cobalt was used as a standard for calibration and monitoring of drift throughout the process.

Synchrotron radiation X-ray tomographic microscopy

Nine micro-spherules of different stratigraphic age and morphotype (see below) were analysed using synchrotron radiation X-ray tomographic microscopy (SRXTM). SRXTM offers an effective and non-destructive method for detailed study of small objects such as micro-spherules. The technique allows for detailed characterization and documentation of intact spherules in three dimensions, and the voxel resolution in resulting images allows for discrimination of very fine details. The ability to manipulate the three-dimensional renderings in real time is of special importance, as it allows for detailed studies of small and potentially fragile objects, such as many microfossils, that are otherwise very difficult to handle when studied by means of traditional microscopy techniques. Moreover, the technique enables thorough documentation of specimens that may be destroyed in later stages of investigation.

Our analyses were performed at the TOMCAT beamline of the Swiss Light Source, Paul Scherrer Institute, Switzerland (Stampanoni *et al.* 2006). The technical setup for this analysis largely follows that of Eriksson *et al.* (2012, 2015). Two specimens were stacked vertically in thin-walled, low X-ray scattering, capillary glass tubes (see Eriksson *et al.* 2012), whereas the remainder were attached to a

low light refractive fishing line (0.3 mm in diameter) in accordance with the technique described by Eriksson *et al.* (2015).

In order to optimize the contrast, the beam energy was set to 12 keV. The X-ray radiation transmitted by the sample was converted into visible light by a 20 µm thick Ce-doped LuAG scintillator screen (Crytur, Turnov, Czech Republic). Projection images were magnified by microscope optics and digitized by a high-resolution CCD camera with a 2048 × 2048 pixel chip and a pitch of 7.4 µm (PCO2000; PCO GmbH, Kelheim, Germany) for the two specimens in glass capillaries, and a sCMOS camera called PCO.edge 5.5 with a 2560 × 2160 pixel chip with a 6.5 µm pitch and a 16 bit dynamic range, for the remaining specimens. The optical magnification was set to 20×, resulting in cubic voxels with sides of 0.37 µm (PCO2000) and 0.325 µm (PCO.edge) in the reconstructed data sets. The tomographic reconstructions were performed on a 60-node Linux PC cluster using a highly optimized routine based on the Fourier transform method and a gridding procedure (Marone & Stampanoni 2012). The resulting tiff microtomograms, or slices, were imported and rendered into 3D images, using the *Voxler 2* and *3* software packages.

Results

Characteristics of the micro-spherules

An overview of the sample and spherule characteristics is presented in Table 1. The retrieved spherules range in size from c. 0.1 to 0.5 mm in diameter. Their colours range from near hyaline through various grades of white, yellow, red, grey or brown tints, into opaque and glossy black. Some specimens have iridescent properties. Wetting of specimens, and also embedment in epoxy, generally increased transparency.

Several spherules contain a distinct nucleus in or near the centre. Nuclei vary in shape from near-perfect spheres to advanced polygonal (organic?) forms (Fig. 1). Some specimens contain a number of larger and smaller nuclei, which are sometimes intergrown. The innermost laminae of cortices generally mimic the shape of the nucleus, but the laminae become increasingly even and round in shape distally, ultimately reaching a near-perfect sphericity in many specimens. Several specimens appear to record cessation and repeated growth of cortices, marked by sharp transitions between laminae (e.g., Fig. 1W).

There is no consistent correspondence in colour between conodont elements and spherules within samples (cf. Glenister *et al.* 1976; Giles *et al.* 2002). Thus, the perceived colour alteration index (CAI) values would differ, given the use of the same colour scale. Some specimens host silt-sized 'grains' between laminae, but this is a rare feature (Fig. 1J).

Close inspection indicates that the collection at hand contains micro-spherules with significantly different external and internal characteristics. The spherules can be subdivided into at least five different categories or morphotypes, each with a set of unique characteristics:

Type 1 spherules

These are characterized by a high degree of sphericity and a smooth exterior (Figs. 1A–J). Internal lamination is generally evenly spaced, and invariably conformable and continuous. Individual laminae have exceptionally smooth outlines. A single depression ('dimple') is most often (always?) present on the exterior of the spherule. Some specimens contain nuclei that are visibly different from the host spherule in both colour and composition. Most nuclei are tinted bright orange-reddish and many appear to have flocculent properties. The type 1 spherules are closely similar to 'conodont pearls' as originally described by Glenister *et al.* (1976). All spherules from the samples 'Independence' and MGSM are assigned to this category (see Table 1).

Type 2 spherules

The overall characteristics are similar to those of the type 1 spherules, but cortical laminae are separated by spaces that are filled with fine-grained matter rich in Si, Al and Fe (siliciclastic clay and/or iron oxide; Figs. 1K, L). Only one specimen, MK2-4 Sph1 (Table 1), has been assigned to this category. This specimen has an indistinct nucleus.

Type 3 spherules

These are characterized by variably developed sphericity and distinctly asymmetrical outline, often with notable polygonal, or angular, properties (Figs. 1M–S). The exterior is often pitted and 'wrinkled'. Cortical lamination is uneven but mainly continuous, and crenulated laminae are common. Some specimens contain nuclei that are visibly different from cortices in both colour and composition, but characteristics vary. Multi-nucleic and composite (intergrown?) specimens occur. Overall characteristics are closely similar to those of the spherules found in bryozoans by Oakley (1934, 1966). The Bjärge and Follingbo (Table 1) specimens are assigned to this category.

Type 4 spherules

These are superficially similar to type 3 spherules, but typically lack polygonal properties (Figs. 1T–W, Z–AD). Composite specimens (i.e., intergrown spherules) are common. Internal lamination is often discontinuous, conspicuously uneven in outline, and laminae vary widely in thickness. Unconformable contacts between laminae occur. Contacts between laminae are often ragged, with crystal-like growth patterns. Specimens typically contain one or more dense 'nuclei' that do not differ significantly from laminae in chemical composition. The BOD-CON and Kakeled specimens (Table 1) are assigned to this category.

Type 5 spherules

These are characterized by variably developed sphericity and a general lack of cortical lamination (Figs. 1X, Y, 2C, D, G, H, K). The exterior surface is often pitted and uneven, with corrosion/abrasion sometimes apparent. Porosity is common. The Downing Creek and Mary's Mountain specimens are assigned to this category, as are the Stora Backor specimens (Table 1). Among the latter, specimens directly associated with *Westergaardodina* and *Cordylodus* elements are often clearly shaped according to their position relative to the conodont element, indicating that they grew in their present position.

Chemical composition of micro-spherules and associated conodont elements

Chemical analyses show that all micro-spherules are mainly composed of calcium phosphate (CaPO_4), as are the associated conodont elements (Tables 2, 3; Fig. 3). Fluorine (F) and sodium (Na) form the most common minor elements. Silica (Si) and sulphur (S) also occur in many spherules, but were only rarely detected in the conodont elements. Notable iron (Fe) enrichment is typically found in and around the centre of nucleus-bearing specimens, and as far as can be determined through EDS, all nuclei are essentially composed of iron-rich compounds, most likely (hydroxy-)oxides. Excluding nuclei of differing properties, most of the studied spherules show no significant change in chemical composition from core to rim. Some of the spherules associated with *Westergaardodina* and *Cordylodus* elements differ in this respect, in having a well-defined rim consisting of denser, 'cleaner' apatite than the main spherule body (Fig. 2). This is also seen in some *Westergaardodina* elements; in an optical microscope it appears as if they are enveloped by a shiny, fragile coating. Despite their distinctly deviating optical properties, these coatings are closely similar in chemical composition to the main cluster of conodont elements. The spherules of *Westergaardodina* and *Cordylodus* consistently lack nuclei.

The overall chemistry varies only a few per cent in major elements between most samples, and significant trends in the two-element data plots (Figs. 3A, B) are largely attributed to variations in analysis totals. Low analysis totals (see Tables 2, 3), which are associated with larger error bars (i.e., lower-quality results), are likely related to significant CO_3 or OH content, or dispersion of organic matter within the spherule or conodont structure (cf. Glenister *et al.* 1976; Giles *et al.* 2002). There is no clear pattern of co-variation between external and internal characteristics and analysis totals, but there is a tendency for lower analysis totals (i.e., sum of detected elements) in darker (heated?) specimens. This probably reflects a larger proportion of low-density organic components. The *Westergaardodina* elements stand out with exceptionally low analysis totals, together with some associated spherules. Basal bodies/fillings of euconodont elements from the Silurian of Gotland also produce unusually low analysis totals, probably in large part due to natural contamination (see Wenzel *et al.* 2000). A few conodont elements (notably *Cordylodus*) and the above mentioned *Westergaardodina* coatings stand out in the other direction, with curiously high analysis totals well

past 100%. This is likely due to an exaggeration of the concentrations of volatile elements (most notably F), and associated statistical corrections introduced by the analytical software.

Micro-spherules from the same samples most often cluster closely together in the analysis plots, as do conodont elements. However, spherules and conodont elements in the main cluster show a consistent separation with regards to P content, which is typically higher in the conodonts (Fig. 3A). This separation persists even in experimental (100%-)normalized analyses. For minor elements, there is a larger overlap in composition, but there is still a tendency for separation between conodonts and spherules (Fig. 3B). In order to facilitate comparisons between datasets with different analysis totals (proportion of 'clean' apatite?), a two-quota scatter plot was created using the most consistently detected elements (Fig. 3C). In this case, the majority of the analysed conodont elements cluster within a narrow area, whereas spherules scatter widely. Still, spherules from the same sample tend to cluster and several spherules cluster within the main 'conodont area'. Within error, the Bjärge and Follingbo spherules are essentially identical chemically to their euconodont element counterparts. It can be noted also that the basal fillings in some of the conodont elements recovered were strikingly similar in colour and appearance to that of the co-occurring spherules. Notably, the spherules with the most 'conodont pearl'-like characteristics *sensu* Glenister *et al.* (1976; morphotype 1, the 'Independence' and MGSM samples) are among those that plot farthest from the main conodont cluster. *Westergaardodina* elements are still distinctly separated from the main conodont cluster. The *Westergaardodina*- and *Cordylodus*-hosted spherules form a rather well defined cluster together with *Westergaardodina* elements, exhibiting lower P/Ca and Na/F values than most other specimens. The coatings surrounding the *Westergaardodina* elements and spherules (Fig. 2) collectively plot close to this cluster. In contrast, the *Cordylodus* elements plot with the highest P/Ca values in the entire diagram.

Discussion

Today, pearls in the true sense – aragonitic, nacreous and iridescent gemstones – are exclusively produced by molluscs, but other organisms may also produce similar objects. Direct fossil analogues to modern pearls, i.e., shell structures secreted in response to irritants, have been observed in, for example, ammonoids (de Baets *et al.* 2011), brachiopods (Chatterton 1975), conulariids (Babcock 1990), gastropods (Schäffer *et al.* 1997) and inoceramids (Brown 1940). A number of chiefly inorganic processes can also result in pearl-like objects (e.g., Leuteritz *et al.* 1972). Collectively referred to in the medical sciences as calculi (sing. calculus), mineralizations of vastly different sizes, shapes and compositions can form within various organs and parts of organisms, and are produced by animals and plants alike. Examples include enteroliths, which are formed in the digestive system as a protective reaction to irritants (e.g., around ingested mineral particles), and bladder and kidney stones, which result from accretion of unexpelled renal waste products. As commercial stones and gemstones, these objects are often referred to as bezoar stones, and are by some considered to have medicinal and mystical properties (see Milton & Axelrod 1951, and references therein). Lithopedia, deceased foetuses 'petrified' in utero, may be considered an extreme form of calculi (cf. Júnior *et al.* 2000). In regards to origin and mode of production, how can we characterize the phosphatic micro-spherules studied herein?

The general lack of compositional variation within individual specimens (i.e., between centre/nucleus, main and outer part) indicates that the spherules are in rather pristine condition, and thus that diagenetic alteration appears to be negligible. If biologically produced, this chemical homogeneity indicates that no significant change in constructional chemistry occurred during the aging of the host organism, and possibly that no migration through significantly different environments among organisms occurred (see Campana 1999 and references therein). However, the detection of such (often subtle) differences in chemistry is likely beyond the resolution of the EDS technique used herein. Also, due to the small size of the specimens complete diagenetic alteration cannot be excluded. The typical lack of cortical contaminants indicates that the main growth occurred inside a protective cavity or tissue. Complete isolation from influx of foreign matter was perhaps not always attained, as some spherule cortices contain silt-sized 'grains' between laminae. Yet many of these 'grains' may be diagenetic artefacts. Assuming a biological mode of production, the overall characteristics of many of the spherules would point to a pearl- or enterolith-like origin. Given the

excellent definition of some nuclei, they appear to have been coated by calcium phosphate relatively quickly. Whatever the nature of the nuclei, the enclosure in the spherules may entail objects of pristine shape, perhaps even retaining remnants of soft tissues (cf. Oakley 1934). Some of the nuclei of our micro-spherules (type 3) are closely similar to so-called bryozoan brown bodies, which consist of waste products (e.g., Boardman 1971, plates 1–11; Morrison & Anstey 1979, text-fig. 1).

Spherules with significant contamination between laminae, as seen in sample 11MK-4, are believed to be chiefly inorganic in origin, and produced in a fashion similar to ooids (cf. Glenister *et al.* 1976). Specimens with distinct crystalline properties in cortices (most notably type 4 spherules) are also likely to be inorganically produced, or significantly altered diagenetically. For example, together with crystalline features in the cortices, the distinct separation between the BOD-CON spherules in the scatter plots likely reflects that these spherules are inorganically formed, resulting from local supersaturation of CaPO_4 in the paleoenvironment or during subsequent diagenesis.

Literature dealing with 'conodont pearls' is overall scarce, and even scarcer is literature dealing with their chemistry. This, combined with differences in methodology, analytical standards and techniques used, hampers detailed comparisons between publications with regards to chemistry. Nonetheless, the micro-spherules analysed by Wang & Chatterton (1993) are closely similar in chemical composition to ours (Fig. 3). A comparison also shows that the conodont average of Giles *et al.* (2002) plots close to our conodont points in Fig. 3. The spherules and fish teeth of Giles *et al.* (2002) appear to have an apatite chemistry quite different from most of our sample specimens, however. This is especially evident in the P/Ca diagram, where their averages plot well outside all of our samples. Another difference is that, unlike Giles *et al.* (2002), we found that visible cores in spherules are typically distinguished by differing chemistry. Still, both externally and internally, the specimens documented by Giles *et al.* (2002) are morphologically closely similar to 'conodont pearls' *sensu* Glenister *et al.* (1976), as well as to our type 1 spherules.

The bryozoan calculi described by Oakley (1934) clearly show that phosphatic micro-spherules are not necessarily related to conodonts, despite the fact that micro-spherules and conodonts may co-occur in large numbers and show striking similarities in, for example, colour, texture and lustre. Moreover, the varying properties of bryozoan-hosted spherules show that significant morphological variation may exist within objects of demonstrably identical origin. When studied in detail, Oakley's bryozoan spherules conform to the type 3 spherules of this study. With regards to the external shape and the characteristics of the internal laminae, there are extraordinary similarities between Oakley's spherules and the specimens from the Bjärjes and Follingbo samples from the Silurian of Gotland, Sweden (Fig. 4; Table 1). Most significantly, the polygonal exterior shape of many of these spherules suggest that they grew in a confined space, bounded outwards by flat surfaces – much like the interior of bryozoan zooecia. Moreover, the geological ages of the samples are similar, and Oakley (1934, p. 303) indeed reported that, in addition to a number of localities throughout Great Britain, phosphatic spherules were found in bryozoans (putative *Favositella* sp.) from the 'Mülde-margelsten' (= Mulde Brick-clay Member of the Wenlockian Halla Formation) at Mulde, Gotland. This suggests that the Bjärjes and Follingbo micro-spherules derive from bryozoans, even though we have not been able to obtain specimens *in situ* (see below). Assuming that this is correct, these samples show that chemical similarity does not necessarily indicate a producer-product relationship. That is, although the Bjärjes and Follingbo micro-spherules have a distinctly similar chemistry to that of the co-occurring conodont elements (also the optical properties of the conodont basal fillings and the micro-spherules are similar) they were not formed by conodonts. The close similarity in chemical composition instead suggests that both were formed in chemical balance with the ambient environment. The Wenlock age of the Bjärjes and Follingbo samples, as those of Oakley (1934), may indicate that bryozoan spherules (or, calculi) constitute a feature that is relatively time-specific. None of the other samples, from different stratigraphic ages, hosted spherules with such resemblance to those found in bryozoans (type 3 spherules herein), but Oakley (1934, 1966) reported loose specimens from samples of Ludlow age. Given the variety of micro-spherules documented herein, it is possible that those Ludlowian specimens are not bryozoan spherules. A search for bryozoans with spherules *in situ* in the remaining Follingbo and Bjärjes sample materials was unsuccessful. In addition, two *Favositella* specimens were kindly supplied by the Natural History Museum, London, but these did not yield any spherules either (based on micro-CT scanning as well as vertical sectioning and subsequent light microscope and SEM studies).

The presence of nucleus-forming foreign objects, together with the distinctly deviant chemistry of nuclei, rule out that host spherules are otoliths. The interpretation by Giles *et al.* (2002) of fish as the producers of Devonian spherules may be correct, but it should be noted that the scarcity of phosphatic otoliths among modern fishes make this interpretation unlikely – the vast majority of otoliths are composed of calcium carbonate, and phosphate is typically only present in minor/trace amounts (see Carlström 1963; Campana 1999). Intriguingly, however, otoliths (otoconia/statoconia, statoliths) composed mainly of apatite are today found in cyclostomes (lampreys and hagfish, Agnatha; Carlström 1963; Fermin *et al.* 1998). The primitiveness of this (paraphyletic?) group of fishes and the similarities, and inferred phylogenetic relationship, between the modern representatives and the (eu-)conodont animal (see Aldridge & Donoghue 1998) may indeed indicate that some micro-spherules can be assigned to conodonts. But, instead of being 'pearls', they are rather otoliths, as suggested already by Youngquist & Miller (1948). Putative otoliths have actually been recognized *in situ* in fossil conodont animals, and these are phosphatic in composition (see Aldridge & Donoghue 1998 and references therein). Phosphatic spherules with concentric layers of growth are also found in the so-called rocker bone of some extant fish (see Parmentier *et al.* 2008), but they are of much smaller size than the spherules studied herein. It would certainly be of interest to search specifically for candidate otoliths in conodont-rich deposits and compare such specimens to the otoliths of (ancient and modern) cyclostomes, but this is beyond the scope of this paper. The lamprey otoliths figured by Carlström (1963, fig. 1a) are characterized by a high degree of sphericity and dense internal lamination. Their non-crystalline to poorly crystallized structure (Carlström 1963) result in poor fossilisation potential, however. Pristine otoliths can potentially record environmental information down to a resolution of days, and not only reveal information about the host conodont animal itself but also its living environment (see Campana 1999, and references therein). Regardless of potential chemical (dis-)similarities to different organisms, the lack of consistent findings of 'conodont pearls' in sample residues speaks against the otolith hypothesis. If the 'conodont pearls' were related to conodonts, they should be found in more or less all sample residues yielding conodont elements. Still, the same argument would be valid for the basal bodies/fillings of conodont elements, and these are undoubtedly part of the element construction but rarely present in sample materials. Also, it is possible that the majority of putative conodont otoliths have been lost during the sieving of sample residues, as many otoliths (otoconia/statoconia) are substantially smaller than 50 µm (see Carlström 1963) and the lower sieve limit for conodont processing is usually 63 or even 125 µm. However, many conodont workers have tried smaller sieve sizes and have not found (or reported) spherules. Should they be pathological, the reason for not finding 'conodont pearls' in all conodont-bearing samples could be due to the fact that the 'pearls' were relatively uncommon body structures and indeed analogous to modern gemstone pearls.

In the case of *Westergaardodina* and *Cordylodus*, there is an unambiguous relationship between the conodont elements and micro-spherules, as the latter were found attached to conodont elements (*in situ*). The examples in the scientific literature, of an association between *Westergaardodina* and micro-spherules (or, pellets), suggest that this is not just a coincidence (e.g., Müller 1959; Olgun 1987; Müller & Hinz 1991; Nielsen *et al.* 2013). The function, if any, and significance of the unevenly shaped spherules attached to the *Westergaardodina* elements are, however, not clear. The spherules may have been used as some kind of balance/ballast material, or they are simply pathogenic in origin. The relatively clean apatitic coating seen on many *Westergaardodina* elements and associated spherules is mysterious. The consistent coating and homogeneous appearance of the visible rims in sliced specimens suggest that they are of primary origin. With regards to *Cordylodus* this is, to our knowledge, the first recorded specimens of euconodont elements with 'pearls' attached. Both the *Cordylodus* and *Westergaardodina* spherules (herein assigned to type 5) deviate dramatically from the typical 'conodont pearls' *sensu* Glenister *et al.* (1976) and our corresponding type 1 spherules.

The differences in both appearance and chemistry between the many spherule specimens studied herein may simply reflect that sub-millimetre-sized, layered, phosphatic spherules in the fossil record come from disparate sources. In view of the number of inorganic processes (e.g., Leuteritz *et al.* 1972) and the variety of extant organisms that are able to produce pearl-like objects (e.g., Milton & Axelrod 1951, and references therein), this is a reasonable assumption. Hence, one cannot assign pearl-like microscopic objects to any one process or producer without detailed analysis and careful interpretation

of the results. Of course, the finding of spherules *in situ*, as is the case for bryozoans, *Westergaardodina* and *Cordylodus* specimens, is most valuable and informative.

Conclusions

Internal and chemical characteristics revealed that several types of phosphatic micro-spherules could be discerned in our collection of superficially similar specimens. Thus, the different conclusions of earlier studies regarding the zoological affinity of conodont pearl-like objects likely reflect that phosphatic spherules of different origin have been investigated.

The only organisms that are unequivocal producers of phosphatic spherules in our sample materials are bryozoans, and the conodonts *Westergaardodina* and *Cordylodus*. The function, if any, of the spherules in both these groups remains unclear, but a pathogenic origin is possible, or even likely. None of the isolated spherules could be tied to other euconodonts with certainty. By contrast, several of the micro-spherules found in euconodont sample residues most likely have a bryozoan origin.

A lack of records of 'conodont pearls' beyond the stratigraphic range of conodonts could be an artefact resulting from a lack of recognition of these bodies. However, in view of the many studies of fish teeth and other phosphatic structures this seems unlikely. The presence of phosphatic otoliths in today's hagfish and lampreys suggests that it may be possible to find conodont otoliths in finer fractions of acid-insoluble residues (cf. Youngquist & Miller 1948).

The main result from this study is that micro-spherules found in acid-insoluble residues represent a range of different objects, of both inorganic and organic origin (cf. Leuteritz *et al.* 1972; Wang & Chatterton 1993). An essential conclusion is that, as in many other cases in nature, similarity does not necessarily indicate identity.

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References

- Aldridge, R.J. & Donoghue, P.C.J. 1998: Conodonts: A sister group to hagfishes? In Jørgensen, J.M., Lomholt, J.P., Weber, R.E. & Malte, H. (eds): *The biology of hagfishes*, 15–31. Chapman & Hall, London. xxx pp.
- Babcock, L. 1990: Conulariid pearls. In A.J. Boucot (ed.): *Evolutionary paleobiology of behavior and coevolution*, 68–71. Elsevier, Amsterdam. 725 pp.
- Bergström, S.M., Calner, M., Lehnert, O. & Noor, A. 2011: A new upper Middle Ordovician–Lower Silurian drillcore standard succession from Borenshult in Östergötland, southern Sweden: 1. Stratigraphical review with regional comparisons. *GFF* 133, 149–171.
- Boardman, R.S. 1960: Trepostomatous Bryozoa of the Hamilton Group of New York State. *United States Geological Survey Professional Paper* 340, 1–87.
- Boardman, R.S. 1971: Mode of growth and functional morphology of autozooids in some Recent and Paleozoic tubular Bryozoa. *Smithsonian Contributions to Paleobiology* 8, 1–51.
- Boardman, R.S. 1991: Peculiar structures different from typical skeletal material in Devonian bryozoa: possible relations to the polypide life cycle. In Bigey, F.P. (ed.): *Bryozoa living and fossil. Bulletin de la Société des Sciences Naturelle de l'Ouest de la France, Mémoire H.S. 1*, 25–38. Nantes.

- Brown, R.W. 1940: Fossil pearls from the Colorado group of western Kansas. *Washington Academy Science* 30, 365–374.
- Campana, S.E. 1999: Chemistry and composition of fish otoliths: pathways, mechanisms and applications. *Marine Ecology Progress Series* 188, 263–297.
- Carlström, D. 1963: A crystallographic study of vertebrate otoliths. *Biological Bulletin* 125, 441–463.
- Chatterton, B.D.E. 1975: A commensal relationship between a small filter feeding organism and Australian Devonian spiriferid brachiopods. *Paleobiology* 1, 371–378.
- De Baets K., Klug C. & Korn D. 2011: Devonian pearls ammonoid-endoparasite co-evolution. *Acta Palaeontologica Polonica* 56, 159–180.
- Eisenack, A. 1964: Mikrofossilien aus dem Silur Gotlands Phosphatische Reste. *Paläontologische Zeitschrift* 38, 170–179.
- Eriksson, M.E., Terfelt, F., Elofsson, R. & Marone, F. 2012: Internal soft-tissue anatomy of Cambrian 'Orsten' arthropods as revealed by synchrotron x-ray tomographic microscopy. *PLoS ONE* 7(8), e42582. doi:10.1371/journal.pone.0042582
- Eriksson, M.E., Terfelt, F., Elofsson, R., Maas, A., Marone, F., Lindskog, A., Waloszek, D., Schmitz, B. & Stamparoni, M. 2015: Baring it all: undressing Cambrian 'Orsten' phosphatocopine crustaceans using synchrotron radiation X-ray tomographic microscopy. *Lethaia (in press)*. DOI: 10.1111/let.12149
- Giles, K.A., McMillan, N.J. & McCarron, B.L. 2002: Geochemical analysis and paleoecological implications of phosphatic microspherules (otoliths?) from Frasnian-Famennian boundary strata in the Great Basin, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology* 181, 111–125.
- Glenister B.F., Klapper, G., Chauff, K.M. 1976: Conodont pearls? *Science* 193, 571–573.
- Jeppsson, L., Anehus, R. & Fredholm, D. 1999: The optimal acetate buffered acetic acid technique for extracting phosphatic fossils. *Journal of Paleontology* 73, 957–965.
- Jeppsson, L. 2005. Biases in the recovery and interpretation of micropalaeontological data. In Purnell, M.A. & Donoghue, P.C.J. (eds): Conodont biology and phylogeny – interpreting the fossil record. *Special Papers in Palaeontology* 73, 57–71.
- Júnior, R.P., Knobel, R., Parpellini, M.Â., Pereira, B.G., Amaral, E., Surita, F.G.deC., Lett, C.R.deA., 2000: Calcified abdominal pregnancy with eighteen years of evolution: case report. *Sao Paulo Medical Journal, Revista Paulista de Medicina* 118, 192–194.
- Leuteritz, K., Pietzner, H., Vahl, J. & Ziegler, W. 1972: Aufbau, Zusammensetzung und Entstehung von Calciumphosphat-Sphären in paläozoischen Kalken. *Geologica et Palaeontologica* 6, 111–137.
- Lindström, M. 1954: Conodonts from the lowermost Ordovician strata of south-central Sweden. *Geologiska Föreningens i Stockholm Förhandlingar* 76, 517–604.
- Marone, F. & Stamparoni, M. 2012: Regridding reconstruction algorithm for real time tomographic imaging. *Journal of Synchrotron Radiation* 19, 1029–1037.
- Ma, J.-Y., Taylor, P.D. & Xia, F.-S. 2014: New observations on the skeletons of the earliest bryozoans from the Fenshiang Formation (Tremadocian, Lower Ordovician), Yichang, China. *Palaeoworld* 23, 25–30.
- Martinsson, A. 1965: Phosphatic linings in bryozoan zooecia. *Geologiska Föreningens i Stockholm Förhandlingar* 86, 404–408.
- Milton, C. & Axelrod, J.M. 1951. Calculi and other stones found in mammals. *Journal of Mammalogy* 32, 139–154.
- Morrison, S.J. & Anstey, R.L. 1979: Ultrastructure and composition of brown bodies in some Ordovician trepostome bryozoans. *Journal of Paleontology* 53, 943–949.
- Müller, K.J. 1959: Kambrische Conodonten. *Zeitschrift der Deutschen Geologischen Gesellschaft* 111, 434–485.
- Müller, K.J. & Hintz, I. 1991: Upper Cambrian conodonts from Sweden. *Fossils and Strata* 28, 1–153.
- Nielsen, A.T., Weidner, T., Stouge, S. & Bagnoli, G. 2013: The uppermost Furongian on Kinnekulle, Västergötland, Sweden: New trilobite and conodont data. In Lindskog, A. & Mehlqvist, K. (eds): *Proceedings of the 3rd IGCP 591 Annual Meeting – Lund, Sweden, 9-19 June 2013*, 252–254. Lund University.
- Oakley, K.P. 1934: Phosphatic calculi in Silurian polyzoa. *Proceedings of the Royal Society of London* 116, 296–314.

- Oakley, K.P. 1966: Some pearl-bearing Ceramoporidae (Polyzoa). *Bulletin of the British Museum (Natural History), Geology* 14, 1–20.
- Olgun, O. 1987: Komponenten-Analyse und Conodonten-Stratigraphie der Orthoceratenkalksteine im Gebiet Falbygden, Västergötland, Mittelschweden. *Sveriges Geologiska Undersökning Ca* 70, 1–79.
- Parmentier, E., Compère, P., Casadevall, M., Fontenelle, N., Cloots, R. & Henrist, C. 2008: The rocker bone: a new kind of mineralized tissue? *Cell and Tissue Research* 334, 67–79.
- Schäffer, T.E., Ionescu-Zanetti, C., Proksch, R., Fritz, M., Walters, D.A., Almqvist, N., Zaremba, C.M., Belcher, A.M., Smith, B.L., Stucky, G.D., Morse, D.E. & Hansma, P.K. 1997. Does abalone nacre form by heteroepitaxial nucleation or by growth through mineral bridges? *Chemistry of Materials* 9, 1731–1740.
- Stampanoni, M., Groso, A., Isenegger, A., Mikuljan, G., Chen Q, Bertrand, A., Henein, S., Betemps, R., Frommherz, U., Böhler, P., Meister, D., Lange, M. & Abela, R. 2006: Trends in synchrotronbased tomographic imaging: the SLS experience. *SPIE Proceedings "Developments in X-ray Tomography V"* 6318: 63180M. DOI:10.1117/12.679497
- Stauffer, C.R. 1935: The conodont fauna of the Decorah Shale (Ordovician). *Journal of Paleontology* 9, 596–620.
- Stauffer, C.R. 1940. Conodonts from the Devonian and associated clays of Minnesota. *Journal of Paleontology* 14, 417–435.
- Terfelt, F. 2003: Upper Cambrian trilobite biostratigraphy and taphonomy at Kakeled on Kinnekulle, Västergötland, Sweden. *Acta Palaeontologica Polonica* 48, 409–416.
- Youngquist, W. & Miller, A.K. 1948: Additional conodonts from the Sheetland Creek shale of Iowa. *Journal of Paleontology* 22, 440–450.
- Wang, K. & Chatterton, B.D.E 1993: Microspherules in Devonian sediments: origins, geological significance, and contamination problems. *Canadian Journal of Earth Sciences* 30, 1660–1667.
- Wass, R.E., 1974: Cyst-like bodies in Permian Bryozoa from Australia. In Pouyet, S. (ed.): *Bryozoa 1974. Documents des Laboratoires de Géologie de la Faculté des Sciences de Lyon, H.S.* 3, 155–159.
- Wenzel, B., Lécuyer, C. & Joachimski, M.M. 2000: Comparing oxygen isotope records of Silurian calcite and phosphate— $\delta^{18}\text{O}$ compositions of brachiopods and conodonts. *Geochimica et Cosmochimica Acta* 64, 1859–1872.

FIGURES AND TABLES

Fig. 1. Examples of micro-spherules. All scale bars 50 μm (individual specimens to same scale throughout). A. Type 1, characterized by high degree of sphericity and distinct, thin cortical laminae (sample 'Independence', LO 12278t). Reflected light. B–D. Three-dimensional reconstruction of specimen in A, from various angles, rendered from SRXTM data. A plane cut in D reveals a nucleus at the centre of the spherule. E. SRXTM virtual slice of specimen figured in A–D. Note the high degree of sphericity. F. Cut and polished type 1 spherule ('Independence', LO 12279t), as seen in backscattered electron (Backscattered Electron, BSE) imaging. G. Fractured type 1 spherule split ('Independence', LO 12280t). SEM (BSE). H. Type 1 (MGSM, LO 12281t). Reflected light. I. Same specimen as in H, rendered from SRXTM data. J. SRXTM virtual slice of specimen in H and I. K. Type 2, characterized by high degree of sphericity and mass-filled (clay-filled?) volumes between relatively well-spaced, thin cortical laminae (11MK2-4, LO 12282t). Reflected light. L. Same specimen as in K, cut and polished. SEM (BSE). Laminae are separated by spaces filled with siliciclastic matter. M. Type 3, characterized by outlines with one or more polygonal surface, and uneven cortical laminae (Follingbo, LO 12283t). Reflected light. N, O. SRXTM renderings of specimen in M. P. Type 3 (Bjärge, LO 12284t). Reflected light. Q–S. SRXTM virtual slices of specimen in P. T. Type 4, characterized by uneven outline and variably thick laminae, with crystal shapes at some contacts between laminae (BOD-CON, LO 12285t). Reflected light. U. Specimen in T, cut and polished. SEM (BSE). V. Type 4 (BOD-CON, LO 12286t). W. Specimen in V, cut and polished. SEM (BSE). Cortical laminae show angular/crystalline features. X. Type 5, characterized by uneven outline and lacking cortical lamination (Mary's Mountain, LO 12287t). Reflected light. Y. Specimen in X, cut and polished. SEM (BSE). Z–AD. Three-dimensional reconstruction of two specimens rendered from SRXTM data. Z. External view of a 'double' micro-spherule (BOD-CON, LO 12288t). AA. Specimen in Z, showing several, partly intergrown, internal nuclei. AB. Specimen in Z showing the cortical lamination outside from the nuclei and outwards. AC. External view of specimen (BOD-CON, LO 12289t). AD. Specimen in AC, showing several, partly intergrown, internal nuclei.

Fig. 2. Westergaardodina and Cordylodus elements, and directly associated micro-spherules (or, pellets). Scale bars 100 μ m. A. Westergaardodina element hosting two micro-spherules of different shape (arrows; Stora Backor, LO 12290t). Reflected light. B. Same as in A, cut and polished. SEM (BSE). C. Close-up of upper spherule (type 5) in A, B. The bright material around much of the spherule is pyrite. SEM (BSE). D. Specimen in C, as seen in reflected light. E. Westergaardodina element hosting a micro-spherule (arrows; Stora Backor, LO 12291t). A shiny outer coating is often seen on Westergaardodina elements. An opening in the left part reveals an interior of different composition and structure. Reflected light. F. Same as in E, cut and polished. In this SEM (BSE) image, the shiny coating seen in E forms a brighter, denser rim on both the conodont element and the associated spherule. G. Close-up of spherule (type 5) in E, F. SEM (BSE). H. Specimen in G, as seen in reflected light. I. Cordylodus element hosting a micro-spherule (arrow; Stora Backor, LO 12292t). Reflected light. J. Same as in I, cut and polished. SEM (BSE). Cutting of the conodont element revealed a second spherule, hidden from view in I. K. Close-up of spherule (type 5) in I, J. SEM (BSE). H. Specimen in K, as seen in reflected light.

Fig. 3. Results from chemical analyses of micro-spherules and conodont elements. A. Plot of calcium (CaO) and phosphorous (P_2O_5) content of specimens. Main clusters of different categories are indicated by shaded areas. The spherule from the Kakeled sample (see Tables 1 and 2) is omitted, as it plots well outside the concentration ranges in the diagram. A. Plot of fluorine (F) and sodium (Na_2O) content of specimens. A. Plot of quotas between P_2O_5/CaO and Na_2O/F of specimens.

Fig. 4. Thin-section images of micro-spherules *in situ* in bryozoans (*Favositella* sp., Silurian) and closely similar loose specimens from the Silurian of Gotland, Sweden. All scale bars 50 μm . A–D. Bryozoan-hosted specimens from Oakley (1934; A–C, sample D. 33729; D, sample D. 33685). E–H. Micro-spherules from the Bjärges (E, G; LO 12293t, 12294t) and Follingbo (F, H; LO 12295t, LO 12296t) samples.

Table 1. Sample characteristics.

Sample	Location and stratigraphy	No. of pearls	Size range ^a	Shape	Colour	Opacity	Morphotype ^b
'Independence'	Close to Hillcrest Dormitory (excavation for new dining hall in the mid 1950s), Iowa City, Iowa, USA; Independence Shale, Late Devonian	35	0.16–0.39	Spherical, sub-spherical	Light yellow to light reddish	Transparent to semi-transparent	1
MGSM #593	Missouri, USA; Devonian(?)	43	0.15–0.47	Spherical, sub-spherical	Dark, metallic brown	Opaque	1
11MK2-4	US 20 section near Cherry Valley, New York, USA; New Scotland Fm., 0.55–0.65 m below Bal Hill bentonite A, Lochkovian (Devonian)	1	0.22	Spherical	Brownish-golden-grey (glossy)	Opaque	2
Bjärges (G05-613L)	Bjärges (37), Gotland, Sweden; Halla Fm.(?), upper Wenlock (Silurian)	Thousands	0.10–0.48	Sub-spherical	Yellowish, brownish, pearly	Opaque to semi-transparent	3
Follingbo (G03-353L)	Follingbo (57), Gotland, Sweden; Slite Group, upper Wenlock (Silurian)	Hundreds	0.10–0.34	Sub-spherical	Light orange (amber-like) to glassy	Semi-transparent	3
BOD-CON 12	Borenshtult-1 core, Östergötland, Sweden; Freberga Fm., Sandbian/Katian (Upper Ordovician); see Bergström <i>et al.</i> (2011)	5	0.12–0.16	Spherical, sub-spherical	Two light yellow-white, three light grey	Opaque	4
Kakeled	Kakeled, Kinnekulle, Sweden; middle Cambrian/Furongian (upper Cambrian); see Terfelt (2003)	1	0.30	Sub-spherical	Black	Opaque	4
Downing Creek	Kentucky, USA; Lulbegrud Shale, Nolan Fm., middle Llandovery (Silurian)	1	0.20	Spherical	Light orange (amber-like)	Semi-transparent	5
Mary's Mountain	Near Carlin, Nevada, USA; Devil's Gate Limestone, Late Devonian(?)	3	0.20–0.23	Spherical	Light brownish-orange	Opaque to semi-transparent	5
Stora Backor	Stora Backor, Mösseberg, Sweden; 'Ånga, Bed 51', Cambrian/Ordovician; see Lindström (1955)	12 ^c	0.10–0.25	Sub-spherical, sub-angular	Greyish-brownish-black and bone white	Opaque	

^a Measured in mm at maximum diameter.

^b See section 'Characteristics of the micro-spherules'.

^c Including specimens associated with *Westergaardodina* and *Cordylodus* elements.

Table 2. Results from EDS analyses of phosphatic micro-spherules.

<i>Morphotype Specimen</i>	F	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	Cl	K ₂ O	CaO	FeO	Total
<i>1</i>												
'Independence' Sph1	4.21 ± 0.25	0.85 ± 0.11	n.d. ^a	n.d.	n.d.	39.14 ± 0.49	1.03 ± 0.07	0.12 ± 0.04	n.d.	52.06 ± 0.48	n.d.	97.41 ± 0.89
'Independence' Sph2	3.71 ± 0.12	0.92 ± 0.04	n.d.	n.d.	n.d.	38.94 ± 0.32	1.03 ± 0.11	0.16 ± 0.02	n.d.	51.63 ± 0.37	n.d.	96.38 ± 0.68
MGSM Sph1	4.07 ± 0.40	0.57 ± 0.09	n.d.	n.d.	n.d.	39.29 ± 0.23	1.05 ± 0.21	n.d.	n.d.	54.11 ± 0.31	0.00 ± 0.07	99.09 ± 0.86
MGSM Sph2	3.68 ± 0.17	0.72 ± 0.08	n.d.	n.d.	n.d.	39.00 ± 1.08	2.45 ± 1.09	n.d.	n.d.	52.28 ± 1.36	1.03 ± 1.04	99.16 ± 1.00
MGSM Sph3	4.00 ± 0.48	0.63 ± 0.13	n.d.	n.d.	n.d.	40.16 ± 0.75	1.02 ± 0.42	n.d.	n.d.	54.01 ± 0.60	n.d.	99.49 ± 0.97
<i>2</i>												
11MK2-4 Sph1	3.66 ± 0.31	0.79 ± 0.08	n.d.	n.d.	1.61 ± 0.25	38.00 ± 0.60	1.12 ± 0.04	n.d.	n.d.	47.70 ± 1.97	2.31 ± 0.64	95.18 ± 2.49
<i>3</i>												
Bjärages Sph1	3.78 ± 0.18	0.56 ± 0.14	n.d.	n.d.	0.39 ± 0.10	39.77 ± 0.56	0.81 ± 0.06	0.12 ± 0.09	n.d.	51.18 ± 0.20	1.58 ± 0.19	98.18 ± 0.84
Bjärages Sph2	3.84 ± 0.27	0.55 ± 0.06	0.19 ± 0.10	n.d.	0.56 ± 0.07	39.61 ± 0.11	0.76 ± 0.06	0.18 ± 0.07	n.d.	50.91 ± 0.32	1.16 ± 0.19	97.76 ± 0.17
Bjärages Sph3	3.87 ± 0.16	0.61 ± 0.04	n.d.	0.27 ± 0.08	0.31 ± 0.31	40.09 ± 0.36	0.92 ± 0.11	n.d.	n.d.	51.49 ± 0.26	0.98 ± 0.16	98.55 ± 0.47
Follingbo Sph1	3.21 ± 0.27	0.63 ± 0.11	n.d.	0.41 ± 0.08	2.54 ± 0.56	37.37 ± 0.85	0.95 ± 0.15	n.d.	n.d.	47.66 ± 0.82	1.38 ± 0.26	94.15 ± 1.27
Follingbo Sph2	3.40 ± 0.42	0.64 ± 0.08	0.23 ± 0.08	0.42 ± 0.09	1.56 ± 0.68	38.18 ± 0.44	0.90 ± 0.16	0.15 ± 0.09	n.d.	48.72 ± 0.24	1.53 ± 0.42	95.73 ± 0.95
Follingbo Sph3	3.48 ± 0.11	0.59 ± 0.13	0.25 ± 0.05	0.50 ± 0.11	0.68 ± 0.20	38.73 ± 0.24	1.03 ± 0.15	n.d.	n.d.	48.90 ± 0.22	1.00 ± 0.13	95.15 ± 0.42
<i>4</i>												
BOD-CON12 Sph1	3.47 ± 0.18	0.76 ± 0.08	n.d.	n.d.	1.78 ± 0.67	38.10 ± 0.68	0.71 ± 0.14	n.d.	n.d.	47.28 ± 0.95	2.37 ± 0.39	94.47 ± 1.31
BOD-CON12 Sph2	4.74 ± 0.00	0.66 ± 0.18	n.d.	n.d.	1.10 ± 1.20	38.37 ± 1.09	0.59 ± 0.15	n.d.	n.d.	51.73 ± 1.77	0.68 ± 0.91	97.87 ± 0.22
Kakeled Sph1	1.53 ± 0.11	n.d.	n.d.	n.d.	1.12 ± 0.54	12.45 ± 0.38	5.05 ± 0.27	n.d.	n.d.	15.67 ± 0.16	0.54 ± 0.16	36.36 ± 1.04
<i>5</i>												
Downing Creek Sph1	3.48 ± 0.43	0.79 ± 0.12	0.59 ± 0.14	n.d.	n.d.	43.99 ± 1.03	0.37 ± 0.19	0.14 ± 0.06	n.d.	54.01 ± 0.81	n.d.	103.37 ± 1.46
Mary's Mtn Sph1	4.57 ± 0.12	0.33 ± 0.16	n.d.	n.d.	n.d.	39.95 ± 0.10	n.d.	n.d.	n.d.	53.79 ± 0.16	n.d.	98.63 ± 0.29
Mary's Mtn Sph2	4.90 ± 0.07	n.d.	n.d.	n.d.	0.14 ± 0.20	41.45 ± 0.55	n.d.	n.d.	n.d.	54.60 ± 0.31	n.d.	101.08 ± 0.45
Stora Backor W1-Sph	4.43 ± 0.07	0.71 ± 0.07	n.d.	n.d.	n.d.	35.88 ± 0.32	1.07 ± 0.06	n.d.	n.d.	47.75 ± 0.64	n.d.	89.84 ± 0.99
Stora Backor W2-Sph	4.82 ± 0.27	0.58 ± 0.12	n.d.	n.d.	n.d.	40.39 ± 0.55	1.12 ± 0.21	n.d.	n.d.	52.20 ± 0.57	n.d.	99.11 ± 0.66
Stora Backor W3-Sph1	3.63 ± 0.26	n.d.	n.d.	n.d.	n.d.	35.97 ± 0.97	1.98 ± 0.52	n.d.	n.d.	48.37 ± 1.19	n.d.	89.95 ± 1.64
Stora Backor W3-Sph2	3.76 ± 0.60	0.51 ± 0.21	n.d.	n.d.	n.d.	30.15 ± 0.47	2.66 ± 0.40	n.d.	n.d.	39.75 ± 0.75	n.d.	76.83 ± 0.68
Stora Backor Cord1-Sph	3.87 ± 0.27	0.38 ± 0.03	n.d.	n.d.	n.d.	32.38 ± 1.01	1.98 ± 0.14	n.d.	n.d.	41.94 ± 0.67	n.d.	80.55 ± 1.58
Stora Backor Cord2-Sph	3.48 ± 0.27	n.d.	n.d.	n.d.	n.d.	29.49 ± 1.13	2.50 ± 0.21	n.d.	n.d.	38.71 ± 1.00	n.d.	74.18 ± 1.91
Stora Backor W4-Sph	1.96 ± 0.21	0.30 ± 0.12	n.d.	n.d.	n.d.	23.87 ± 0.94	3.46 ± 0.23	n.d.	n.d.	31.87 ± 0.35	n.d.	61.46 ± 1.01
Stora Backor W5-Sph1	2.55 ± 0.99	0.39 ± 0.06	n.d.	n.d.	n.d.	28.94 ± 1.02	2.52 ± 0.45	n.d.	n.d.	38.80 ± 1.88	n.d.	73.20 ± 2.28
Stora Backor W5-Sph2	4.45 ± 0.41	0.54 ± 0.11	n.d.	n.d.	n.d.	37.48 ± 0.31	1.19 ± 0.14	n.d.	n.d.	48.95 ± 0.47	n.d.	92.61 ± 0.47

^a Not detected.

Table 3. Results from EDS analyses of conodont elements, basal bodies/fillings, and apatitic coatings/rims.

Type of specimen Specimen	F	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	Cl	K ₂ O	CaO	FeO	Total
<i>Euconodont elements</i>												
'Independence' Con1	4.03 ± 0.31	1.01 ± 0.12	n.d. ^a	n.d.	n.d.	42.63 ± 0.20	n.d.	n.d.	n.d.	53.28 ± 0.39	n.d.	100.94 ± 0.46
'Independence' Con2	4.14 ± 0.30	0.92 ± 0.13	n.d.	n.d.	n.d.	42.09 ± 0.09	n.d.	n.d.	n.d.	53.56 ± 0.30	n.d.	100.70 ± 0.43
11MK2-4 Con1	4.20 ± 0.04	0.49 ± 0.04	n.d.	n.d.	n.d.	41.85 ± 0.11	n.d.	0.33 ± 0.06	n.d.	53.58 ± 0.50	n.d.	100.45 ± 0.40
Bjärages Con1	4.32 ± 0.19	0.67 ± 0.06	n.d.	n.d.	n.d.	43.00 ± 0.37	n.d.	0.21 ± 0.02	n.d.	54.25 ± 0.23	n.d.	102.45 ± 0.62
Bjärages Con2	3.85 ± 0.26	0.84 ± 0.11	n.d.	n.d.	n.d.	41.31 ± 0.33	0.31 ± 0.17	n.d.	n.d.	52.91 ± 0.54	n.d.	99.22 ± 0.57
Follingbo Con1	4.10 ± 0.35	0.81 ± 0.11	n.d.	n.d.	n.d.	42.49 ± 0.50	n.d.	0.15 ± 0.06	n.d.	52.96 ± 0.46	n.d.	100.52 ± 0.67
Follingbo Con2	4.16 ± 0.28	0.78 ± 0.09	n.d.	n.d.	n.d.	42.46 ± 0.67	n.d.	0.17 ± 0.06	n.d.	53.55 ± 0.37	n.d.	101.12 ± 0.91
BOD-CON 12 Con1	3.93 ± 0.11	0.78 ± 0.16	n.d.	n.d.	0.18 ± 0.13	41.18 ± 0.21	n.d.	n.d.	n.d.	50.94 ± 0.52	n.d.	97.01 ± 0.66
BOD-CON 12 Con2	3.76 ± 0.13	0.65 ± 0.07	n.d.	n.d.	n.d.	41.54 ± 0.45	n.d.	0.15 ± 0.07	n.d.	51.58 ± 0.37	n.d.	97.68 ± 0.50
BOD-CON 12 Con3	4.29 ± 0.11	0.66 ± 0.09	n.d.	n.d.	n.d.	41.32 ± 0.41	n.d.	n.d.	n.d.	50.90 ± 0.25	n.d.	97.16 ± 0.53
BOD-CON 12 Con4	4.09 ± 0.21	0.62 ± 0.07	n.d.	n.d.	n.d.	41.83 ± 0.61	n.d.	n.d.	n.d.	52.54 ± 0.52	n.d.	99.07 ± 1.17
Downing Creek Con1	5.08 ± 0.24	0.80 ± 0.14	n.d.	n.d.	n.d.	42.05 ± 0.70	n.d.	n.d.	n.d.	52.34 ± 0.44	n.d.	100.27 ± 1.01
Mary's Mtn Con1	3.91 ± 0.12	0.66 ± 0.19	n.d.	n.d.	0.03 ± 0.21	42.11 ± 0.33	n.d.	n.d.	n.d.	52.47 ± 0.74	n.d.	99.18 ± 0.91
Mary's Mtn Con2	3.68 ± 0.18	0.67 ± 0.03	n.d.	n.d.	1.78 ± 0.35	39.80 ± 0.16	n.d.	n.d.	n.d.	50.45 ± 0.24	n.d.	96.39 ± 0.13
Mary's Mtn Con3	3.78 ± 0.23	0.38 ± 0.07	n.d.	n.d.	n.d.	42.43 ± 0.32	n.d.	n.d.	n.d.	53.38 ± 0.18	n.d.	99.96 ± 0.43
Stora Backor Cord1	5.53 ± 1.25	0.49 ± 0.02	n.d.	n.d.	n.d.	44.50 ± 0.70	n.d.	0.21 ± 0.13	n.d.	53.88 ± 0.29	n.d.	104.61 ± 0.86

Type of specimen Specimen	F	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	Cl	K ₂ O	CaO	FeO	Total
Stora Backor Cord2	4.47 ± 0.69	0.58 ± 0.08	n.d.	n.d.	n.d.	44.97 ± 1.29	n.d.	0.22 ± 0.17	n.d.	54.60 ± 0.28	n.d.	104.84 ± 1.36
<i>Paraconodont elements</i>												
Stora Backor W1	1.35 ± 0.07	n.d.	n.d.	n.d.	n.d.	21.88 ± 0.45	2.54 ± 0.50	n.d.	n.d.	28.04 ± 0.70	n.d.	53.81 ± 1.52
Stora Backor W2	1.74 ± 0.50	0.21 ± 0.19	n.d.	n.d.	n.d.	24.66 ± 1.39	3.38 ± 0.90	n.d.	n.d.	31.53 ± 1.94	n.d.	61.52 ± 2.66
Stora Backor W3	6.01 ± 0.29	0.62 ± 0.10	n.d.	n.d.	n.d.	45.97 ± 0.74	n.d.	n.d.	n.d.	54.84 ± 0.39	n.d.	107.44 ± 0.98
Stora Backor W4	n.d.	43.06 ± 0.45	n.d.	n.d.	n.d.	n.d.	84.92 ± 0.87	n.d.	n.d.	0.42 ± 0.53	1.57 ± 0.12	129.97 ± 1.16 ^b
Stora Backor W5	2.33 ± 0.16	n.d.	n.d.	n.d.	n.d.	27.17 ± 0.74	2.82 ± 0.12	n.d.	n.d.	34.86 ± 0.76	n.d.	67.18 ± 1.43
<i>Basal bodies/fillings</i>												
Follingbo Bas1	4.12 ± 0.21	0.82 ± 0.09	n.d.	0.49 ± 0.10	n.d.	36.82 ± 0.62	1.00 ± 0.14	n.d.	0.15 ± 0.08	47.83 ± 0.66	2.30 ± 0.72	93.53 ± 0.65
Follingbo Bas2	3.69 ± 0.11	0.95 ± 0.16	n.d.	0.35 ± 0.05	n.d.	33.23 ± 1.16	1.30 ± 0.11	0.12 ± 0.03	0.17 ± 0.01	44.29 ± 1.22	2.04 ± 0.23	86.12 ± 2.46
<i>Coatings/rims</i>												
Stora Backor Cord1-Rim	6.21 ± 0.81	0.34 ± 0.18	n.d.	n.d.	n.d.	42.22 ± 1.66	0.60 ± 0.19	n.d.	n.d.	55.15 ± 0.14	n.d.	104.52 ± 1.51
Stora Backor W1-Rim	5.61 ± 0.72	0.38 ± 0.09	n.d.	n.d.	n.d.	42.37 ± 1.27	0.53 ± 0.16	n.d.	n.d.	54.50 ± 1.53	n.d.	103.39 ± 2.70
Stora Backor W3-Rim	6.05 ± 1.14	0.37 ± 0.16	n.d.	0.33 ± 0.26	0.69 ± 0.54	41.46 ± 0.74	0.62 ± 0.16	n.d.	n.d.	54.41 ± 0.63	n.d.	103.93 ± 0.72
Stora Backor W5-Rim	6.46 ± 0.81	0.38 ± 0.27	n.d.	n.d.	n.d.	42.85 ± 1.36	n.d.	n.d.	n.d.	54.11 ± 0.54	n.d.	103.80 ± 1.23

^a Not detected.

^b Original aragonitic composition completely substituted.