Reports

Conodont Pearls?

Abstract. *Conodonts are zoologically enigmatic, toothlike phosphatic microfossils occurring in marine sedimentary rocks ranging in age from Cambrian to Triassic. Dimpled spheres of less than 1 millimeter in diameter are sporadic associates of conodonts and have identical chemical composition and microstructure. Mineralogy, morphology, and occurrence of these spheres suggest that they are pearls secreted by the conodont-bearing animal.*

Conodonts are toothlike, blade- and platform-like phosphatic microfossils (Fig. 1, H and I), characterized by lamellar microstructure. They occur in sporadic abundance in marine sedimentary rocks and range in age throughout the Paleozoic era to apparent extinction at the end of the early Mesozoic Triassic period (*1*). Free specimens may be obtained by dissolution of carbonate rocks or by disaggregation of clastics; specimens are visible on shale bedding planes. Samples that yield conodonts generally contain approximately equal numbers of specimens that are mirror-image right and left pairs. Consistent association of disparate morphologic types suggests that as many as six or seven pairs of different conodont elements were arranged in a bilaterally symmetrical skeletal apparatus within the conodont-bearing animal (*2*). Biological affinities of the conodont-bearing animal remain enigmatic; however, conodonts may have functioned as an internal supporting structure for a food-gathering organ, such as a lophophore (*3*), or as an internal device for filtering plankton (*4*).

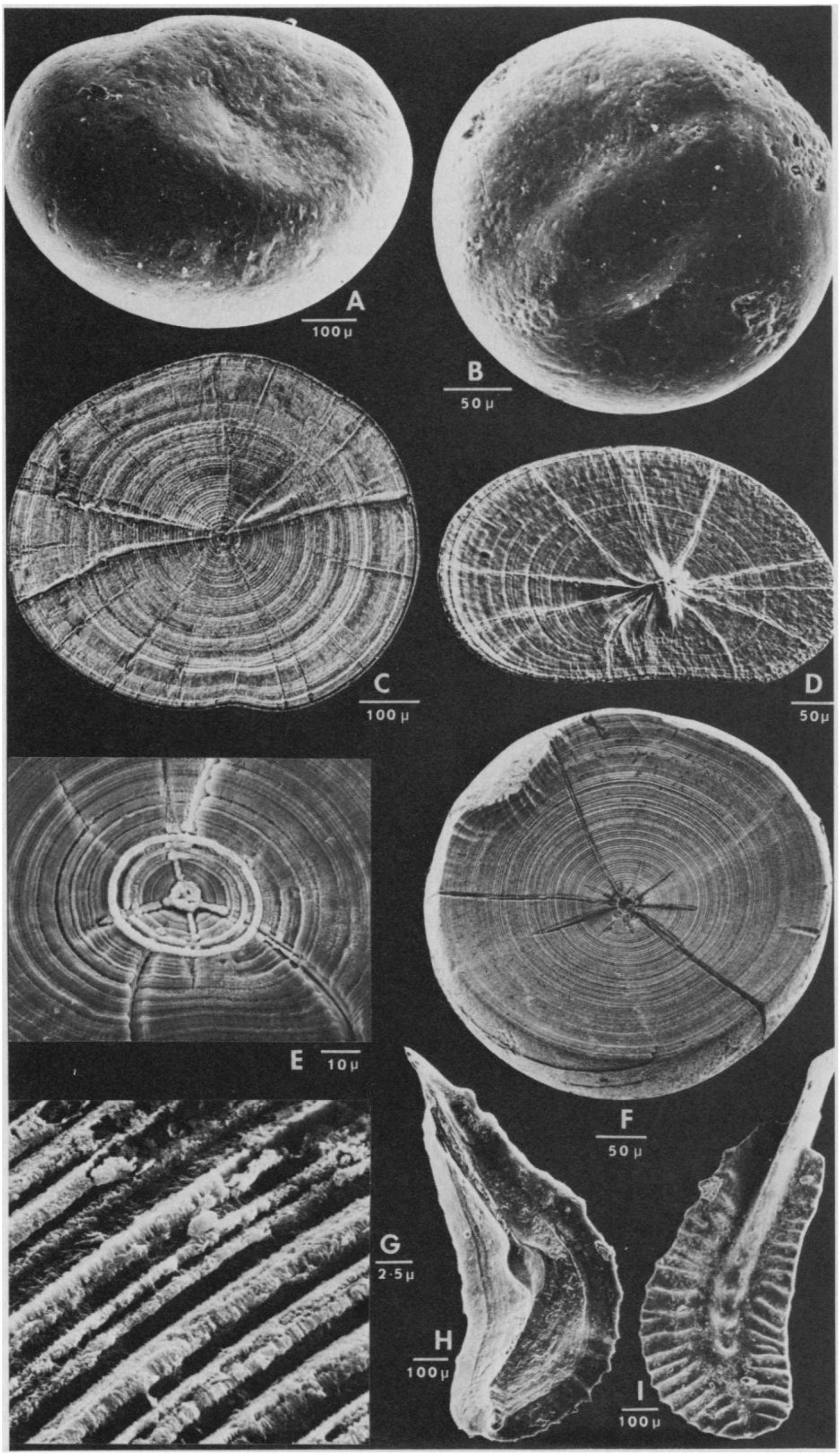
Stauffer (*5*) was the first to describe the occurrence, in Ordovician and Devonian samples, of microscopic spheres similar in color and mineralogy to the associated conodonts. Since these early descriptions, conodont workers have noted the sporadic occurrence of these phosphatic spheres in strata ranging in age from Cambrian through Carboniferous. Published references vary from casual notation to exhaustive description (*6*). Stauffer hesitantly interpreted the structures as "egg cases?" and later speculated that they belonged to the conodont animal (*5*). Youngquist and Miller (*7*) noted that the abundance of spheres is approximately proportional to that of the conodonts in some strata, and they raised the possibility that the spheres are otoliths. Leuteritz *et al*. (*6*) interpreted the spheres as inorganic precipitates. We present evidence to support our conclusion that the phosphatic spheres are pearls secreted by the conodont-bearing animal around a particulate or organic irritant.

The following description is based primarily on approximately 2000 specimens now in our collections; most are from the Devonian of Iowa and Missouri (Independence and numerous other Upper Devonian shales), Nevada (Woodpecker Limestone), and the Canning Basin of Western Australia (Virgin Hills Formation). Maximum dimensions of individual spheres in our collections range from 0.1 to 0.7 mm; specimens smaller than these presumably are lost through the 63-μm sieve mesh during sample preparation. Phosphatic "egg cases" up to 6 mm in diameter have been recorded from the Devonian of England, but neither we nor the authors of the report are able to verify the identity of these objects (*8*). We found that the smallest individuals in any given sample are almost spherical, although a shallow concave zone or "dimple" is present on the surface referred to herein as the base. Larger specimens from the same sample exhibit a broader dimple and, when resting on the base, are ovate in both plan and lateral views (Fig. 1D). They also display a shallow sinus in the outer layers adjacent to the dimple (Fig. 1A, upper left; Fig. 1C, bottom center). In rare instances a pair of dimples separated by an intervening low ridge is developed (Fig. 1B). The color of the spheres is a function of the diagenesis or metamorphism to which they have been subjected, and is matched by that of the associated conodonts. Under stable cratonic conditions, such as those in Iowa, specimens are transparent to honey-colored. However, both the conodonts and spheres from the Upper Devonian of the Rhenish Slate Mountains of Germany are dark gray to black when viewed in air, although they are translucent if immersed in oils. Slight color differences reveal that the spheres grew by centrifugal accretion of regular, complete shells around a darker-colored nucleus. The size of the nucleus varies widely and may be as large as 0.1 mm. One or two of the shells that surround the nucleus may appear conspicuously darker than surrounding lamellae when viewed in transmitted light [(*6*), plate 2, figures 1, 2, 8, and 9]. These same features are lighter in scanning electron microscope images of etched broken surfaces (Fig. 1E). Processes radiating from the nucleus have been interpreted (*6*) as the spines of "hystrichospheres" (*9*). However, electron microscopy and demineralization of specimens under the light microscope have failed to confirm this interpretation, and at least most of the radial structures are secondary cracks that were partially or completely filled during diagenesis. More than 50 alternately light and darker shells may be visible; the darker intervals are appreciably thinner (Fig. 1E). Successive lamellae and interlamellar spaces thicken away from the dimple (Fig. 1D). When the spheres are demineralized in dilute acid (HCl), the darker shells, nucleus, and radial crack fillings maintain their identity for several minutes before collapsing into a featureless mass. A significant aspect of the spheres is that the dimple is replicated by successive layers and invariably maintains a basal position (Fig. 1D). Each lamella covers its predecessor without apparent break. Surfaces of the best-preserved specimens are smooth, although pitting produces a frosted appearance in specimens subjected to weathering or metamorphism. Microscopic burrows present in some spheres [for example (*6*), plate 1, figures 2 and 3] and conodonts are secondary and are attributable to fungi (*10*). Müller and co-workers (*10, 11*) interpreted the presence of borings in the spheres as evidence of probable organic origin.

Occasionally, spheres are compound as a result of fusion of two to five spherules through envelopment by outer shells. In these cases the ultimate form is asymmetric.

The ultrastructure and chemical composition of spheres from Germany and Western Australia have been documented fully (*6*). Crystallites are aligned radially and are distributed in concentric bands, leaving a series of mineral-free interlamellar zones a few micrometers in thickness (Fig. 1G). Calcium and phosphorus are the only elements revealed by microprobe analysis of unmetamorphosed spheres. X-ray analysis of the spheres shows a *d*-spacing that is closest to the carbonate-apatite mineral species francolite. The x-ray diffraction pattern of the apatite composing the spheres is identical with that of the associated conodonts (*12*).

Most of the spheres that we have examined are from Silurian and Devonian strata, although comparable forms have been reported from the Ordovician (*5*, *13*) and the Lower Carboniferous (*6*). The phosphatic ball associated with the enigmatic *Westergaardodina* (*14*) may be related to our middle Paleozoic spheres. All known occurrences of spheres are from samples that contain conodonts. The reverse relation does not hold, since most residues that contain conodonts lack spheres. We have observed a general size increase from the Silurian to the Devonian, but spheres of the same size occur with widely varying sizes of Devonian conodonts. To our knowledge, there is no invariable association between the spheres and any group of organisms other than conodonts. Like conodonts, the spheres occur in virtually every marine lithofacies from shale to limestone.



Several lines of evidence lead us to conclude that the spheres were secreted by organisms. (i) Regular replication of the dimple in basal position would occur only if the spheres were lodged in a stable position as growth proceeded. Inorganic accretions, such as ooids, must be free to move often during formation in order to develop their roughly spherical form (*15*). (ii) The absence of any impurities, such as the clay rinds commonly incorporated in ooids (*16*), also suggests that the spheres were protected from the environment by some structure, such as organic tissue, during their growth. (iii) The progressive color darkening of the spheres in response to increasing diagenetic and metamorphic grades presum-

Fig. 1. Scanning electron photomicrographs of conodont pearls(?) (A to G) and conodonts (H and I). Specimens A to E and G are from an unnamed Upper Devonian shale at Pevely, Missouri [Chauff and Dombrowski (*21*)]; F is from the Middle Devonian Woodpecker Limestone at Oxyoke Canyon, Nevada [U.S. National Museum location 17456, Johnson (*22*)]; H and I are from the Lower Devonian McColley Canyon Formation at Lone Mountain, Nevada [sample LM 29, Klapper and Johnson (*23*)]. (A) Exterior view of SUI (State University of Iowa) specimen 42117 (×75) shows small sinus in upper left and characteristic single dimple; (B) exterior view of SUI specimen 42118 (×190) shows rare double dimple separated by ridge; (C) ground and etched surface cuts the sphere center parallel to the dimple [SUI specimen 42119 (×85)] shows concentric lamellae, small sinus at base, and radiating cracks; (D) ground and etched surface perpendicular to dimple [SUI specimen 42120 (×120)]; successive concentric lamellae replicate dimple and characteristic elliptical cracks are shown; (E) broken and etched surface displays nucleus, radiating and partly filled cracks, and concentric lamellae [SUI specimen 42125 (×530)]; (F) broken and etched surface through nucleus, radiating cracks, and crack fillings [SUI specimen 42121 (×140)]. Cracks in C to F were all visible with light microscopy prior to grinding and etching, but were accentuated by these processes; (G) enlargement of concentric lamellae (light) and interlamellar spaces (dark) on ground and etched surface of SUI specimen 42122 (×2000); (H and I) lower and upper surface views of the platform conodont species, *Polygnathus laticostatus* [Klapper and Johnson, SUI specimens 42123 and 42124 (×40 and ×50, respectively)]. All magnifications are approximate.

ably is a function of the carbon fixing by trace amounts of organic matter, as in conodonts (*17*). Demineralization of the spheres confirms the evidence provided by color banding; the dark color of the nucleus and the thin growth shells that surround it is due to the high concentration of organic matrix in these areas. Further arguments against the hypothesis that the spheres are inorganic precipitates are that they occur in a wide variety of lithofacies and that they are unknown after the Lower Carboniferous.

The only fossils invariably associated with the spheres are conodonts. Consequently, it can reasonably be assumed that the spheres belonged either to the conodont-bearing animal or to a group of organisms that possessed no other fossilizable hard parts. The identical chemical composition of conodonts and spheres tends to support the hypothesis that these two groups of structures were secreted by the same animal.

Despite evidence that the spheres belonged to the conodont-bearing animal, they cannot have represented a structure vital to that organism because of their sporadic association with the conodonts. Consequently, the speculation that they are conodont otoliths (*7*) or cnidarian statoliths (*18*) is untenable. Neither can they have been egg cases, because they are not hollow (*19*). An alternative explanation that appears compatible with all known facts is that the spheres are pearls secreted within the tissue of the conodont-bearing animal as a response to an organic or particulate irritant that formed the nucleus. Parasites provide the most common stimulus for pearl formation in bivalves growing under natural conditions (*20*), and the variability in the nuclei of our spheres may reflect the variety of infesting organisms. The dimple can be explained as the result of draping around a resistant area beneath the tissue that secreted the pearl. The depressed form of the largest conodont pearls may indicate that the height of the structure was close to the thickness of the tissue in which it was secreted.

Spherules within the basal plate of some Cambrian, Ordovician, and Silurian conodonts [for example (*10*), plate 16, figure 6] achieve diameters of only 20 μm before overgrowth by basal material but may have had a genesis similar to the conodont pearls described by us. Irrespective of this possible correlation, the spherules of the basal plate confirm the ability of the conodont-bearing animal to secrete concentric shells of apatite around a nucleus. Additional evidence that the conodont-bearing animal could respond to an irritant is the plugging of galleries burrowed into the conodont basal plate (*10*).

In conclusion, the mineralogy, structure, faunal associations, and geological occurrence of the spheres described by us suggest that they are pearls secreted by the conodont-bearing animal as a response to an organic or particulate irritant.

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Man-Made Carbon Tetrachloride in the Atmosphere

Abstract. *The emissions of man-made carbon tetrachloride and the rates of its removal from the atmosphere by natural sinks are evaluated. A large fraction, perhaps all of the carbon tetrachloride observed in the atmosphere, could be man-made, and carbon tetrachloride is a global atmospheric pollutant.*

In recent years, various halocarbon compounds including CCl_4 have been detected in the atmosphere (*1, 2*). The concentrations of CCl_4 in the stratosphere and troposphere are comparable to those of Fluorocarbon-11 ($CFCl_3$) and Fluorocarbon-12 (CF_2Cl_2). These three halocarbon compounds are photodissociated by ultraviolet (UV) radiation in the stratosphere. The resulting chlorine atoms can catalytically destroy O_3 (*3*). At present, CCl_4 is probably the major man-made source of chlorine in the stratosphere; CCl_4 provides perhaps three times as much chlorine in the stratosphere as the combined products from $CFCl_3$ and CF_2Cl_2 (*4, 5*).

There is an urgent need to identify the sources of halocarbons in the atmosphere and their natural loss mechanisms, as man-made halocarbon emissions may some day be sufficient to reduce the equilibrium O_3 concentration in the stratosphere and cause harmful biological effects as a result of the increased transmission of solar UV radiation (*6*). In earlier papers (*1, 3–7*), both man-made and natural sources of CCl_4 have been suggested. In this report I calculate the atmospheric concentration of CCl_4 due to man-made emissions.

Elevated CCl_4 concentrations of up to 1600 parts per 10^{12} (volume/volume) have been found in Los Angeles as compared with 50 to 200 parts per 10^{12} in clean background air over oceans (*1, 2*). Fluorocarbon-11, a known, man-made, atmospheric pollutant, and CCl_4 exhibit similar seasonal variations in concentration at Bowerchalke, United Kingdom, and Adrigole, Ireland (*8*). These results suggest that CCl_4, as well as Fluorocarbon-11, may be a man-made pollutant. The similar concentrations of CCl_4 found