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Microstructure and chemical compositon of duckbilled dinosaur eggshell

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Abstract: Dinosaur eggshell with preserved embryonic bones has provides a clear record of microstructure, mineralogy and chemistry of eggshell. Six fragments of duckbilled dinosaur eggshell collected from Alberta, Canada, were analyzed using X-ray powder diffraction, a scanning electron microscope, an energy dispersive analyzer, transmission electron microscope, and heavy-ion probe Rutherford scattering. Radial and tangential thin section of two shell specimens showed two layers which were mainly composed of calcite with traces of apatite and aragonite. Silicate and iron oxides were also precipitated on outer surfaces, whereas apatite was precipitated between the two layers by diagenesis. The presence of Fe, Cu and Zn, detected by energy dispersive analysis, suggest the presence of hematite, goethite, pyrite and Cu-Zn oxides which were a result of fossilization. Under the SEM, structural eggshell morphotype shows characteristic features of hadrosaurs, including irregular pore canals, columns, and crescent-shaped mammillary layers and cones. The outer surfaces of the shells show the typical columnar structure with pore openings. Organic material on the inner surface of the eggshell showing a mesh-like structure is interpreted as a fossilized membrane (chorion) of the eggshell. This would be the first record of such a delicate fine structure. Mosaic and lamellar deformation features of calcite show 3.85 Å (102) lattice images, apparent from high-resolution TEM. Rutherford scattering analysis reveals that the eggshell contains C, O, Si, Ca, Fe and some heavy elements, together with a trace of iridium. The presence of iridium and the pathological repetition of layers of Hadrosauria's eggshell may suggest that gradual environmental changes adversely affected the reproductive process.

Key words : dinosaur eggshell, microstructure, chemical composition, minerals, membrane, iridium.

1. Introduction

Dinosaur eggshell fragments have been reported and described worldwide, such as in Kazakhstan, Mongolia, China, India, France, Spain and Peru (Sahni, 1972, Hirsch, 1989, Mikhailov, 1991). Biomineralization and diagenesis of dinosaur eggshells from the Upper Jurassic / Lower Cretaceous boundary of Porto Pinheiro (Portugal) and Hadrosauria at the Upper Cretaceous sandstone of Bastus (Spain) were discussed by Kohring (1989, 1993). Abundant eggshell fragments with embryos were found in the Two Medicine Formation, Montana, USA (Horner and Makela, 1979; Horner, 1982, 1984, Horner and Gorman, 1988; Horner and Weishampel, 1988; Hirsch and Quinn, 1990).

On the other hand, nests of dinosaur eggs with embryos were found in the Two Medicine Formation of southern Alberta, Canada (Currie, 1987). Two of the nests included the remains of articulated hadrosaur embryos within the eggs, and bones found in an eroded nest may represent either embryos or hatchlings. A field crew from the Museum of the Rockies has recovered a skull of Hypacrosaurus from equivalent beds 50 km southwest of Devil's Coulee at Landslide Butte, Montana, USA (Currie, 1988a; Horner and Currie, 1994). The discoveries of dinosaur eggs, nests, eggs with embryos, and hatchlings in Montana have been reported by Currie (1988b), Horner and Weishampel (1988) and Horner and Currie (1994). Otherwise, embryonic dinosaur remains are extremely rare. These discoveries have had a great impact on the study of dinosaurs, providing new data concerning dinosaur behavior, ecology and habitats. Zhao et al., (1993) had been analyzed amino acids and proteins of dinosaur eggshells nearby the K-T boundary in Nanxiong, Guangdong Province, China. Their results indicate that amino acid composition of the eggshells varies greatly from specimen to specimen, and might reflect the different states of the original matrix protein when fossilization began. However, there is still little known about the microstructure and chemical composition of these eggshells.

This paper is a study of the microstructure, mineralogy and chemistry of six dinosaur eggshells offered to us by the Royal Tyrrell Museum of Palaeontology in Drumheller, Alberta, Canada, using electron microtechniques. Most dinosaur eggshells have a remarkably well preserved inorganic structure. In this case, the organic elements, such as membranes or fibrous matter, are also preserved.

2. Materials and methods

Six fragments of dinosaur eggshell from different locations in southern Alberta, Canada, were examined using an optical microscope, X-ray powder diffraction (XRD), a scanning electron microscope (SEM) equipped with energy dispersive X-ray analyzer (EDX), a transmission electron microscope (TEM), and heavy-ion probe Rutherford scattering (HIRS). The Devil's Coulee and Milk River site eggshells are from the same horizon in the upper part of the Oldman Formation in southern Alberta (Currie, 1987). They belong to species of the duckbilled dinosaur Hypacrosaurus, whereas the eggshell from Dinosaur Provincial Park can only be identified as hadrosaur, based on comparative histology. The following four eggshells were analyzed. Repetition of layer of the egg-shell was found in samples 2 and 4.

Sample 1 ; RTMP 86.49.15 (Dinosaur Prov. Park, Alberta)———— one layer
Sample 2 ; RTMP 87.79.85 (Devil's Coulee) ———— two layers
Sample 3 ; RTMP 88.121.2 (Milk River site — restricted) ———— one layer
Sample 4 ; RTMP 89.79.53 (new site near Onefour)———— two layers.

A JEOL JSM-T220A and HITACHI S-2100 with EMXA3000 scanning electron microscopes were used at an accelerating voltage of 20 kV and a JEOL-JEM 2000EX transmission electron microscopy was used at a voltage of 160 kV. The eggshells were examined by methods of heavy-ion probe Ruthurford scattering a RIKEN heavy-ion linear accelerator (RILAC) (Aratani, 1988). A 51 MeV Ar^{4+} beam or 62 MeV Cu^{4+} beam of 50 - 70 nA was used as incident particles. Beam size was about 1.5 mm × 3 mm on target (Yuyatani et al., 1989).

3. Results

Observation of duckbilled dinosaur eggshell have revealed 1) shape, size, and shell thickness of the egg, 2) structure of crystalline layer in radial and tangential views, 3) type of aeration system, and 4) microstructure of the outer and inner surface.

The matrix between the eggshells consists of quartz, K-feldspar, partly carbonate-replaced plagioclase, carbonate and microcrystalline altered volcanic glass. Alteration products of the glass consist of sericite and/or chlorite. The main organic consistituent is collophane. There is also a minor detrital constituent which could be volcanic tuff (Hirsch and Quinn, 1990). The matrix between two eggshell fragments from Devil's Coulee (RTMP 87.79.161) was analyzed by Karl Hirsch (pers. comm.) with the following results:

Matrix —— 56% carbonate
40% collophane + carbonate
tr. hematite
Mineral fragments 4%.

3.1 X-ray powder diffraction

Dinosaur eggshells of sample 2 (Fig. 1A) and sample 3 (Fig. 1B) bulk powder are mainly composed of calcite. These eggshells showed presence of apatite (Fig. 1). Only sample 3 contains a small amount of aragonite (B). Clay minerals were not found in the bulk sample. For comparison, modern chicken eggshell was also analyzed by XRD, similar to microstructure of the dinosaurs based on the evolution in Vertebrata, and showed pure calcite.

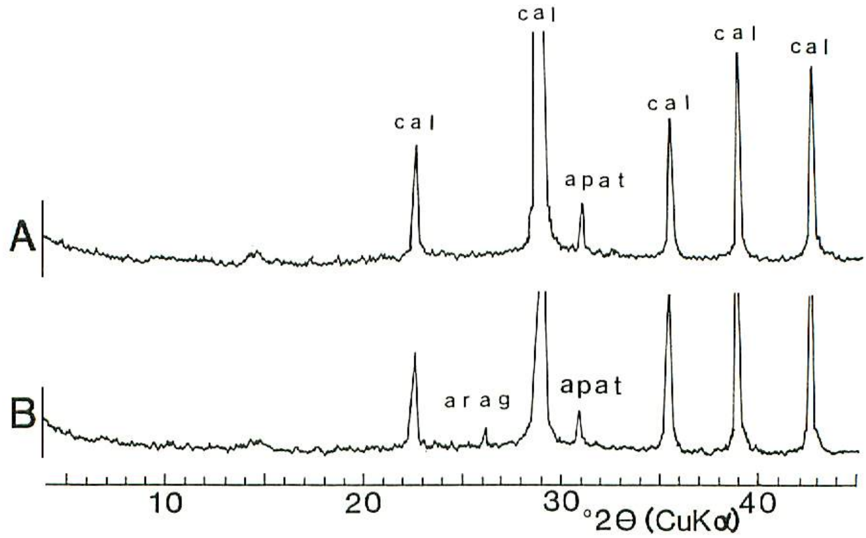

Fig. 1. X-ray powder diffraction patterns of dinosaur eggshells from sample 2; RTMP 87.79.85 (A) and sample 3; RTMP 88.121.2 (B).
cal; calcite, apat; apatite, arag; aragonite.

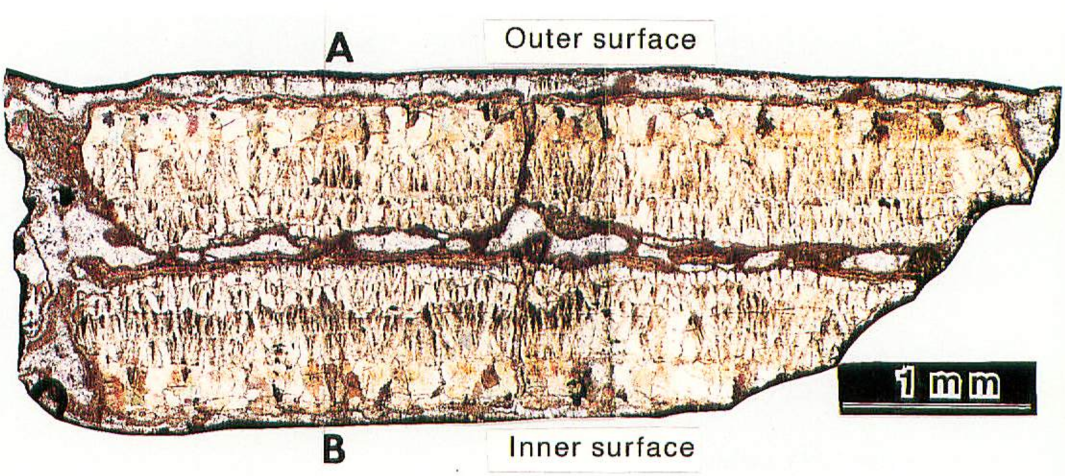

Fig. 2. Radial cross-thin-section of the dinosaur eggshell sample 2; RTMP 87.79.85 showing two layers. Outer surface of eggshell is up. A and B; points for line scanning analysis by EDX.

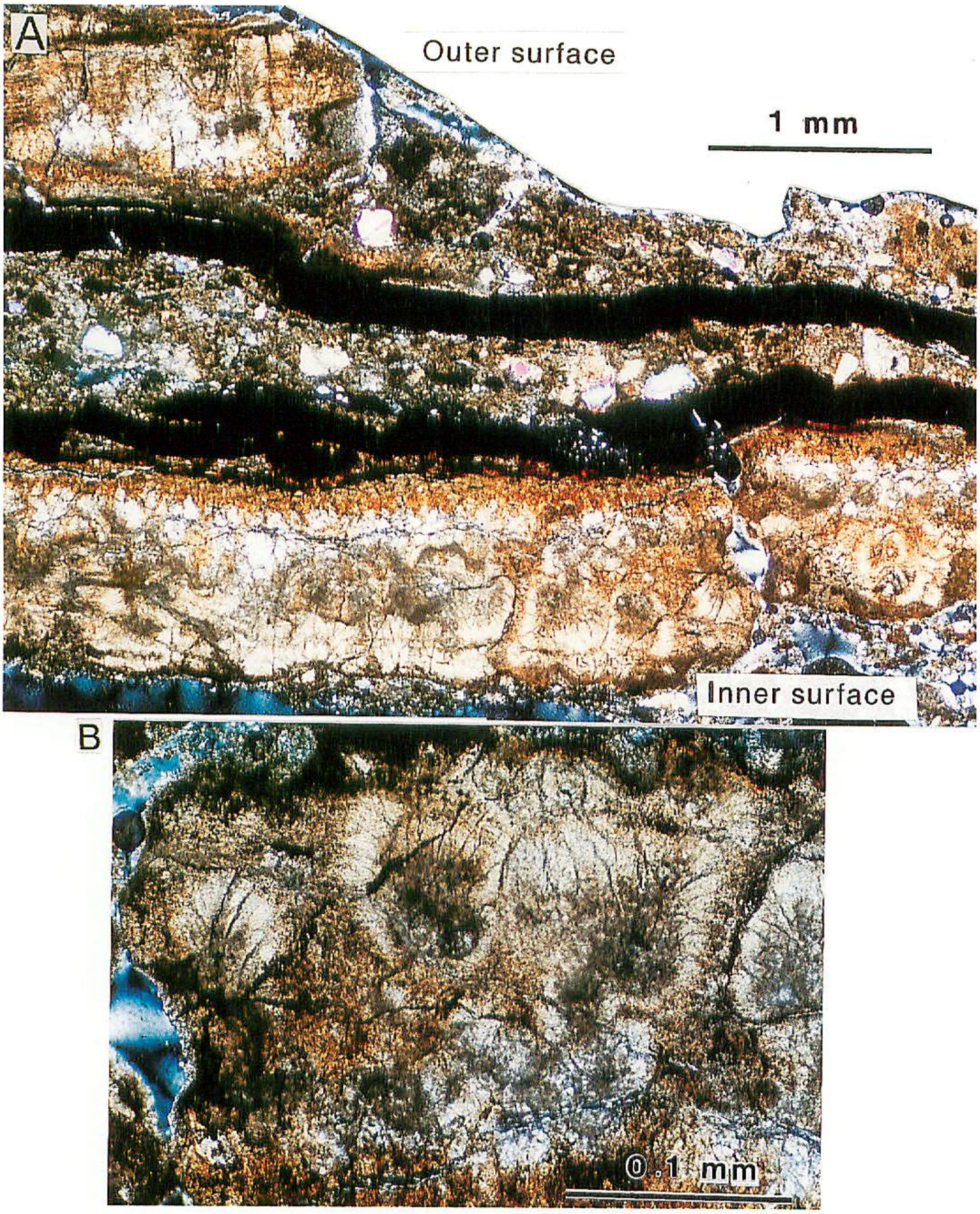

Fig. 3. Radial cross-thin-section of the dinosaur eggshell, sample 4; RTMP 89.79.53 showing two layers (A). Outer surface of eggshell is up. Close-up microphotograph shows mammillary layer and cone (B).

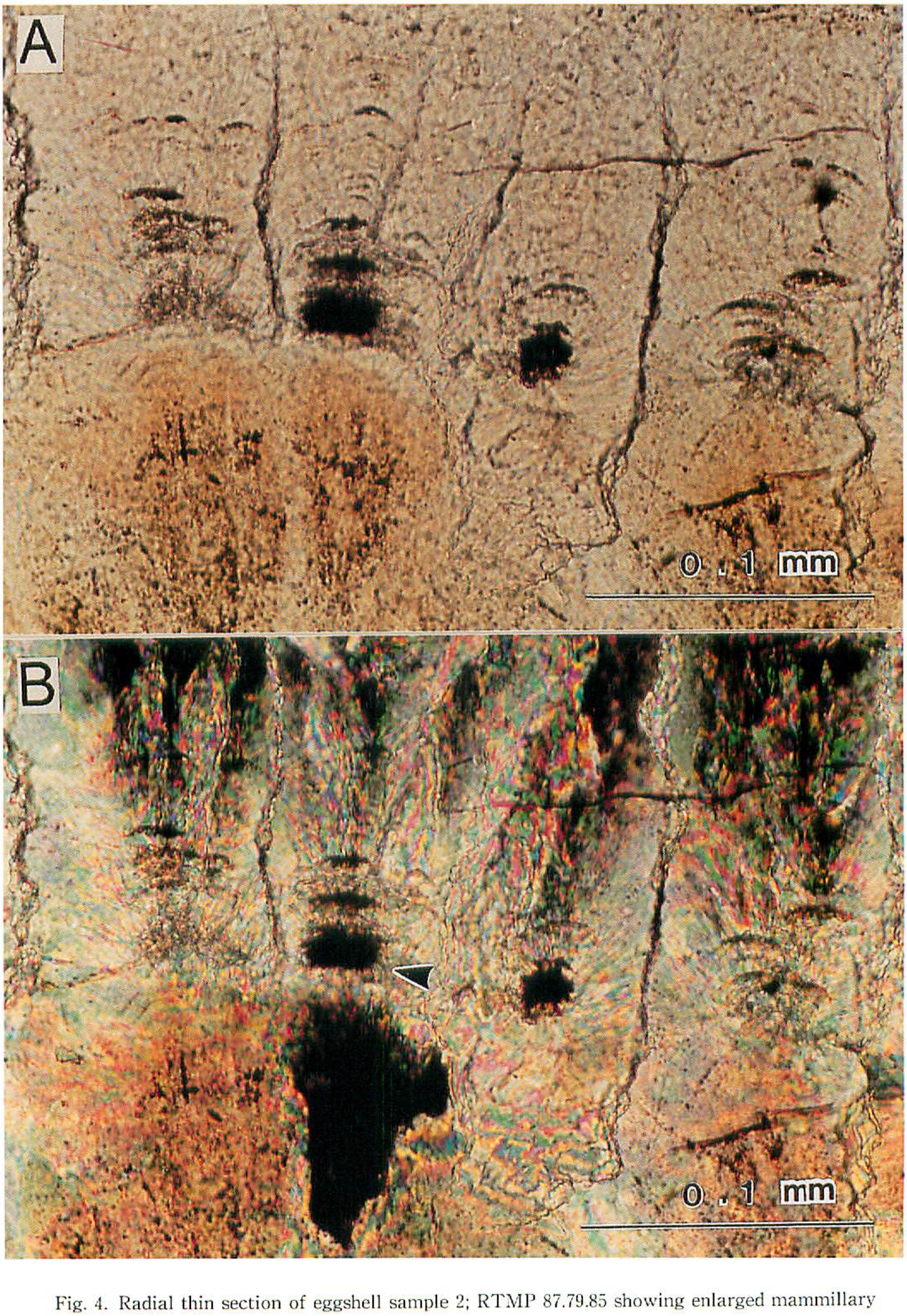

Fig. 4. Radial thin section of eggshell sample 2; RTMP 87.79.85 showing enlarged mammillary layer and cone (arrow). B as A, polarized.

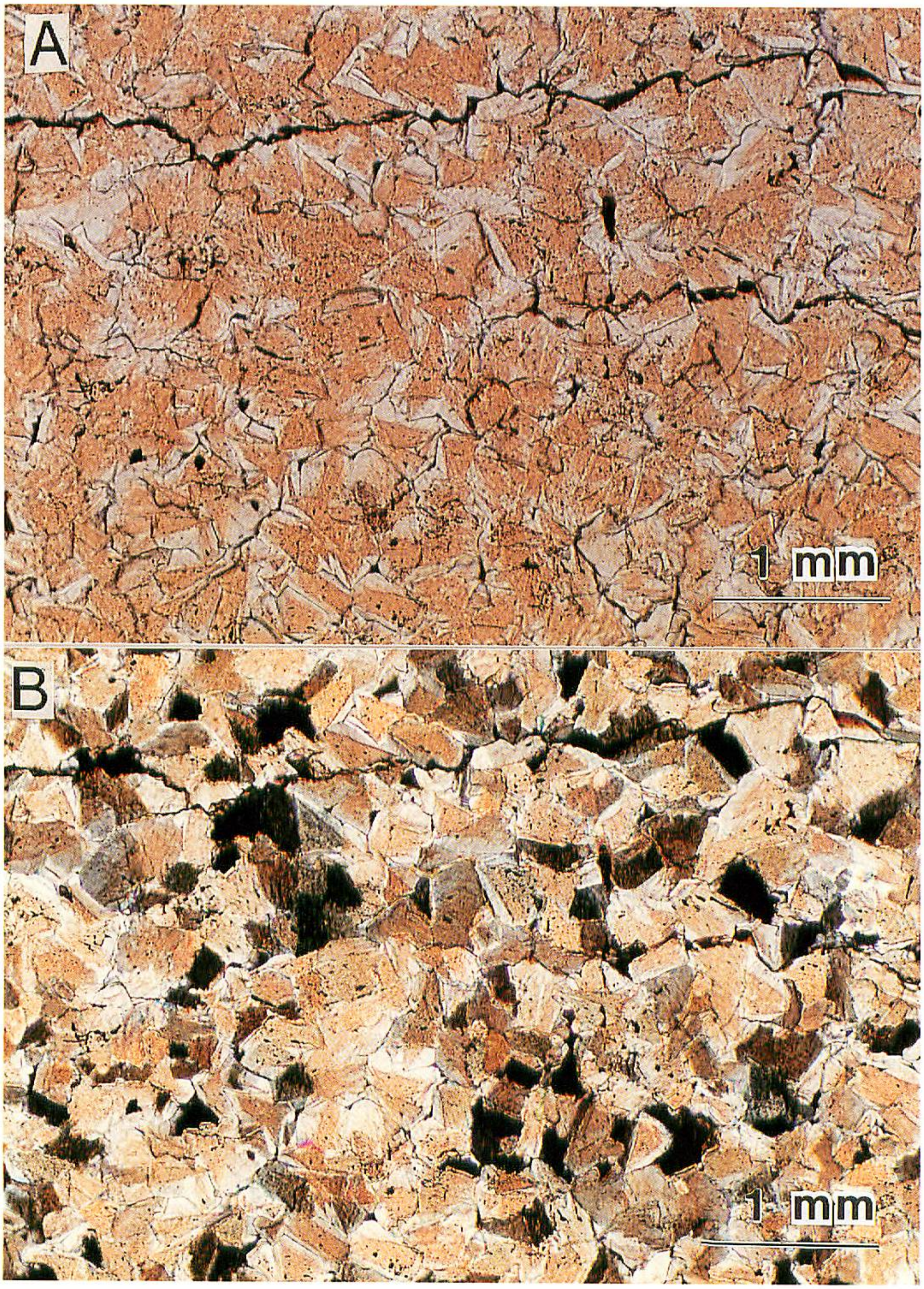

Fig. 5. Tangential thin section of eggshell sample 3; RTMP 88.121.2 showing calcitic smooth mosaic surface. B as A, polarized.

3.2 Thin-sections

Eggshell specimens were studied in radial and tangential thin sections by using optical microscopy and SEM-EDX. The total thickness of eggshell ranges 1.8 - 3 mm. Both eggshells of sample 2 (Fig. 2) and sample 4 (Fig. 3A) show two layers, whereas sample 3 shows one layer. Brown iron oxides were precipitated on the surface and between the two layers. In the thin sections the characteristic columnar structure of dinosaur eggshell with irregular pore canal and mammillary layers is clearly seen on the tangential surface (Fig.

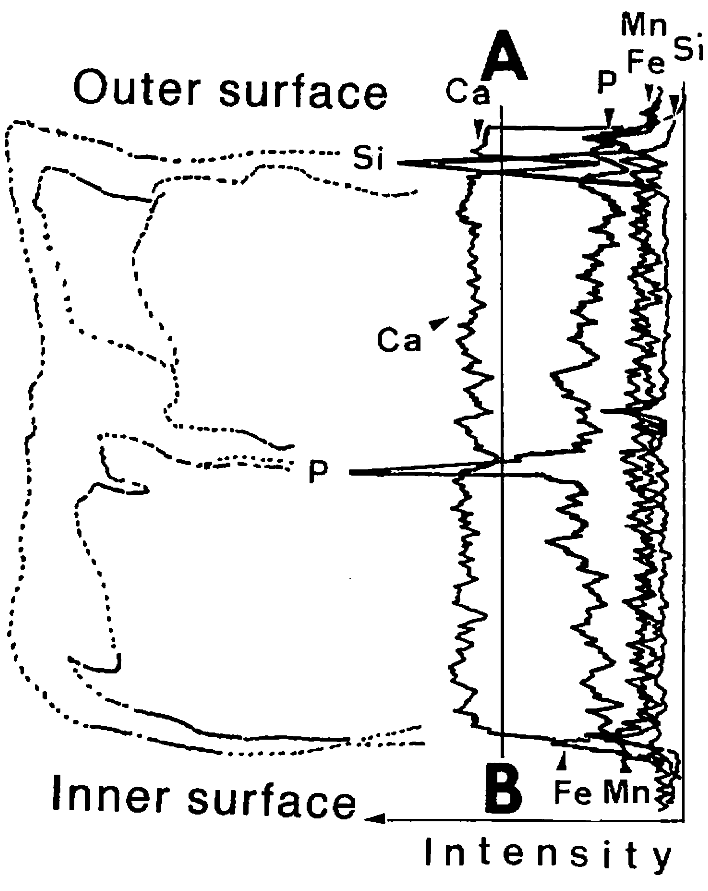

Fig. 6. EDX line scanning analyses of the dinosaur eggshell sample 2; RTMP 87.79.85 at line A - B in Fig. 2. High Si with Fe elements concentrated on outer surface, whereas high P with Ca elements concentrated between two layers.

3B and Fig. 4). Mammillary cones show extinction patterns of wedges. Note fine crystals radiating from nucleation points. The enlarged mammillary layer of sample 2 shows crescent-shaped layering in the mammillary cone (Fig. 4B, arrow). The outer surface of the eggshell (A in Fig. 2) is thicker than that of the inner surface (B in Fig. 2) because of coating materials. The radial thin section shows smooth mosaic structure of calcite on outer surface of sample 3. The sizes of the single calcite crystals in the eggshell are uniform (Fig. 5).

Line scanning analysis of sample 2 from the outer surface to the inner surface by EDX shows compositional variations of Si, Mn, Fe, P, and Ca (Fig. 6). The high Ca content is uniform in the whole cross section. Mn, Fe, and Si were precipitated on the outer surface. Mn and Fe were precipitated on the inner surface. The high P and Ca concentrated between two layers suggests that apatite has crystallized at the boundary of layers.

3.3 SEM observations

Eggshell were studied under the SEM-EDX, without any chemical treatment (Fig. 7). The pore openings are 7—10 μm in diameter and are located in round or elongated depressions. The outer surface of sample 4 shows prominent ridges, pore openings in deep valleys (Fig. 7B and C arrows), whereas weathered eggshell shows shallow ridges. A few strings of membrane with granules were preserved over the pore openings (Fig. 7C). The bare outer surface shows calcite crystalline assembly (Fig. 7D). The inner surface of sample 4 has widely spaced mammillae and many large interstices (Fig. 8). A microstructure of mammillary cones weave through the membrane (Fig. 8A and B). The abundance of membrane showing short sticks preserved on the inner surface suggests chorion components (Fig. 8C and D). Cratered mammillae indicate withdrawal of calcium. In sample 2, outer surface shows bundles of uniform-sized palisade crystallites (Fig. 9A and B). A gently crushed sample from sample 3 shows oval flaky particles suggesting hematite or goethite (Fig. 9C and D). Grains with straight outlines are interpreted as calcite. Rounded particles in sample 2 were identified as pyrite because of high S and Fe contents associated with Si, K, Ca, Cu and Zn (Fig. 10A). Strong Au peaks are due to ion -spattered coating material for electrical conductivity. The matrix of the particles exhibits very high Cu and Zn contents (Fig. 10B). Organic material showing no characteristic peak was found on the inner surface of sample 2 and is interpreted as membrane (Fig. 11) i. e. soft tissue preservation. A small bright grain of calcite on the organic material (Fig. 11) is responsible for the small Ca peak in the EDX pattern.

For comparison, modern chicken eggshell structure with chorion was observed by SEM. A cross section of the chicken eggshell (Fig. 12) shows pore openings similar to those of the dinosaurs (Fig. 7), but the size of openings of chicken eggshell are quite small, 0.1 - 0.4 μm in diameter (Fig. 12B). The membrane of modern chicken is attached to inner surface (Fig. 12A arrow). Development of pore openings on both outer (Fig. 12C) and inner

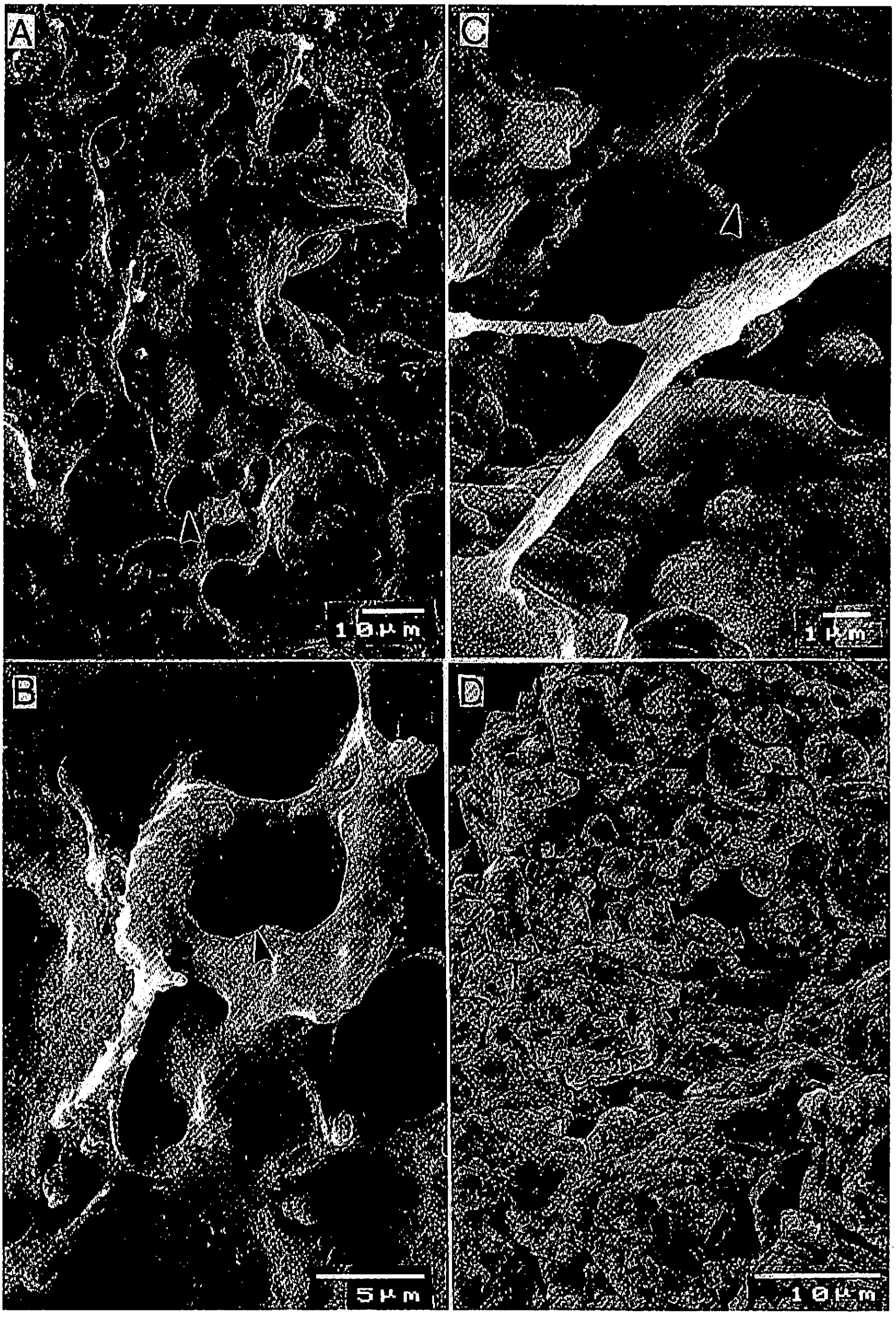

Fig. 7. Scanning electron micrographs of outer surface of dinosaur eggshell sample 4; RTMP 89.79.53 showing pore openings (arrows) in deep valleys (A and B), strings of membrane remain (C) and calcite mosaic structure (D).

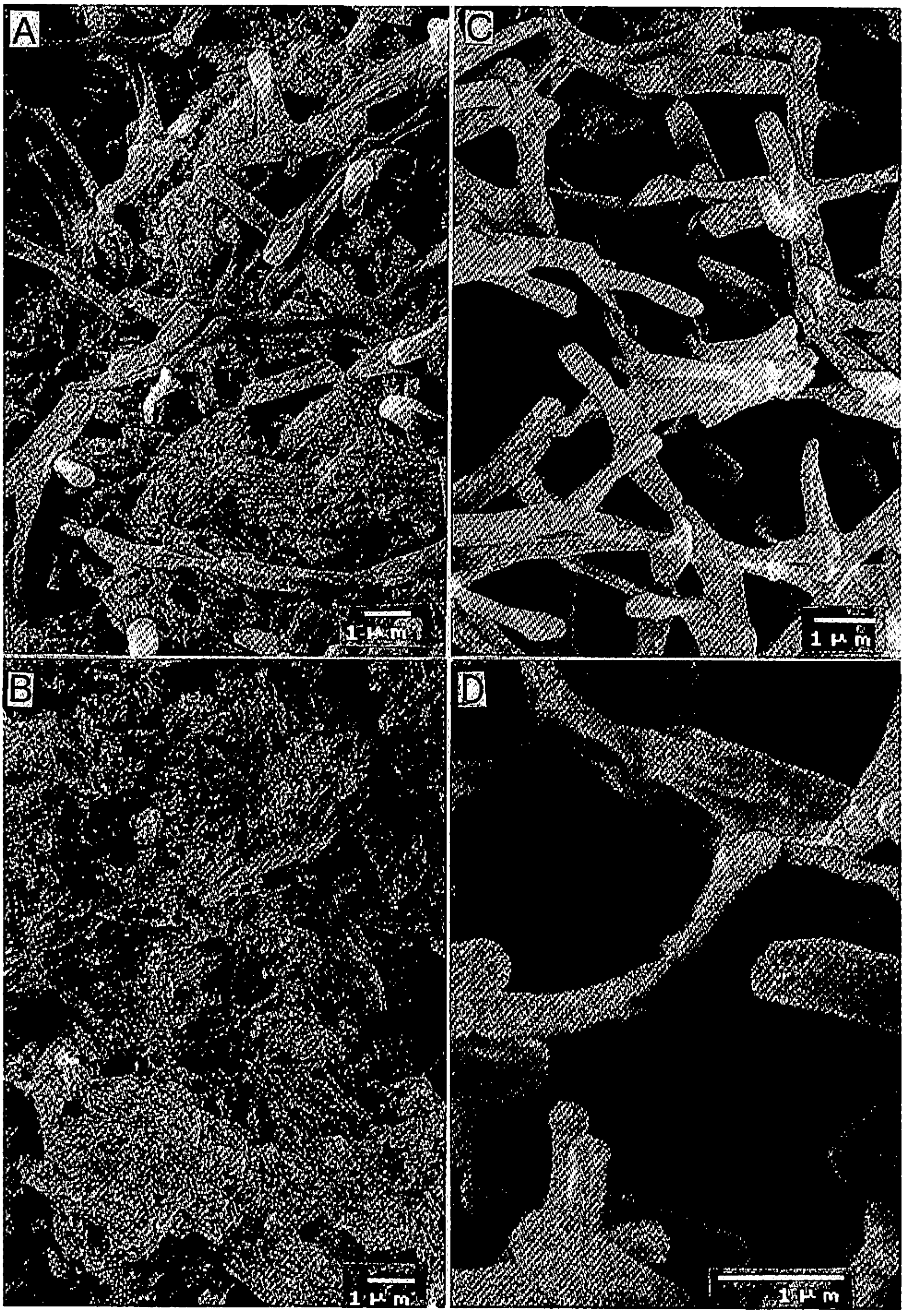

Fig. 8. Scanning electron micrographs of inner surface of dinosaur eggshell sample 4; RTMP 89.79.53 showing mesh structure with short-stick of membrane (A and C) on / in mosaic structure of calcite (A and B). D as C, enlarged.

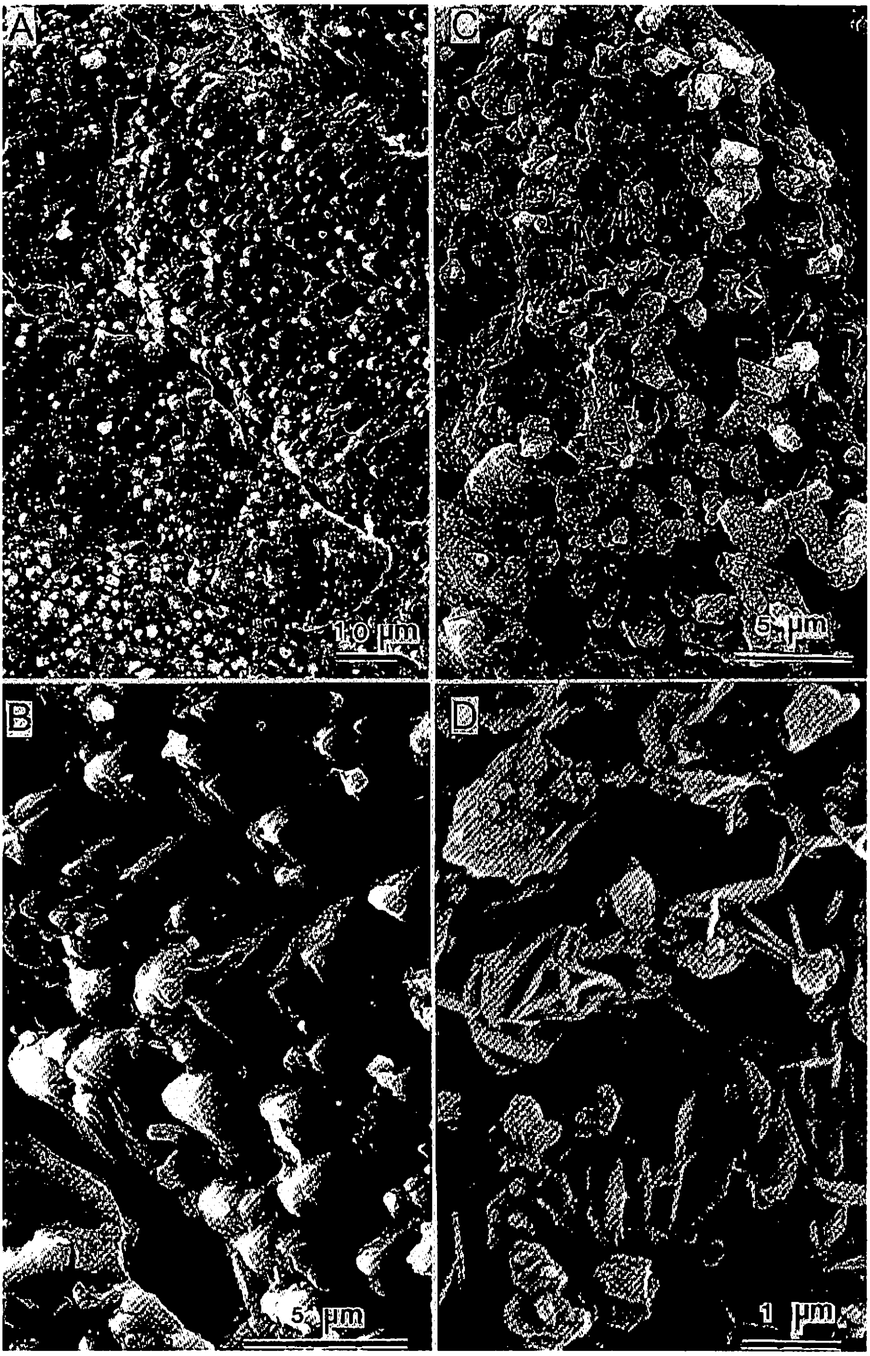

Fig. 9. Scanning electron micrographs of outer surface of dinosaur eggshell sample 2; RTMP 87.79.85 showing bundle palisade structure of small compact mammillae (A and B), and aggregate of calcite and iron oxides from sample 3; RTMP 88.121.2 (C) and the higher magnification of oval flaky particles of hematite or goethite (D).

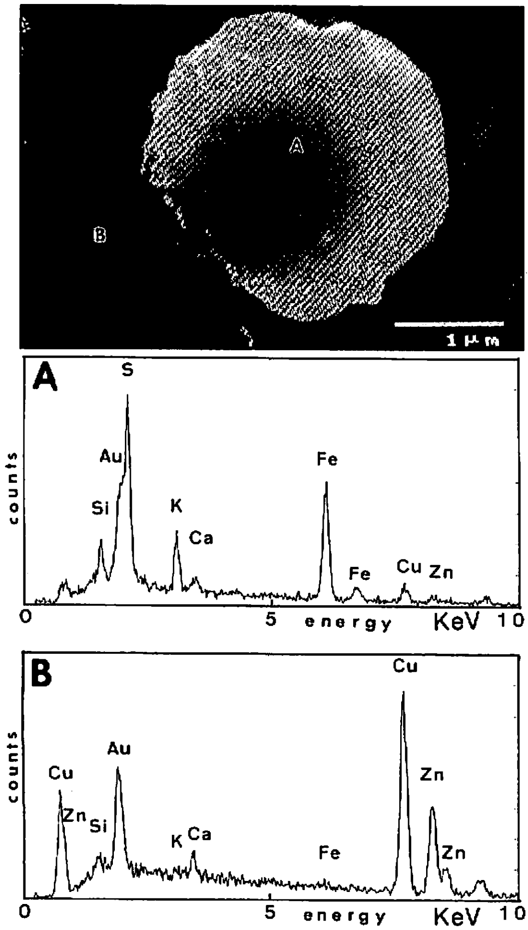

Fig. 10. Scanning electron micrograph of pyrite and its EDX from the powdered sample 2; RTMP 87.79.85. A; pyrite grain and its EDX, B; the matrix and its EDX showing concentration of heavy elements of Cu and Zn.

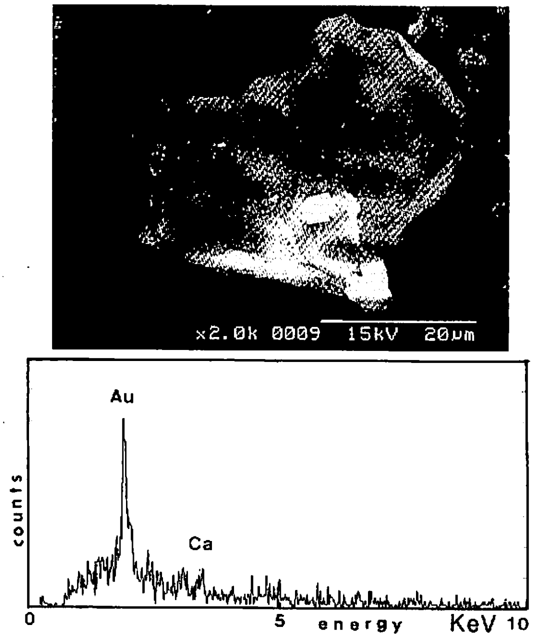

Fig. 11. Scanning electron micrograph of organic materials of membrane and its EDX from the powdered sample 2; RTMP 87.79.85. Strong peak of Au is due to ion -spattered coating material whereas small Ca peak is due to calcite grain on the surface.

(Fig. 12D) surfaces of the chicken eggshell can be seen. Small spheres attach to net strings of chorion in modern chicken eggs, whereas dinosaur eggshell has no spheres. The enlarged membrane of chorion in Fig. 12D shows closely packed network microstructure.

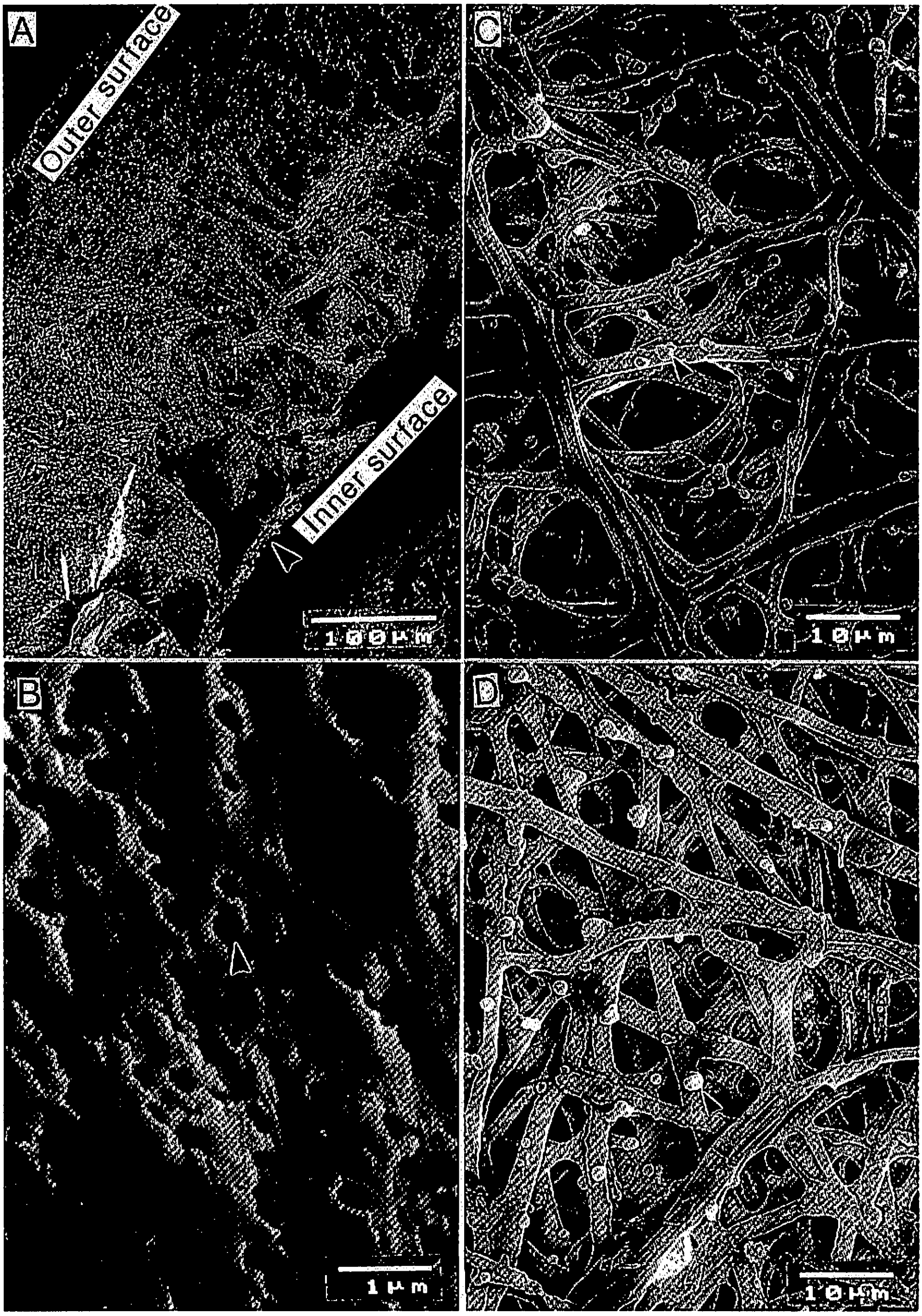

Fig. 12. Scanning electron micrographs of modern chicken eggshell showing radial cross-thin -section with membrane (A, arrow), small pore openings (B, arrow), membrane of chorion on outer surface (C) and inner surface (D). Note small spherules attached to network structure.

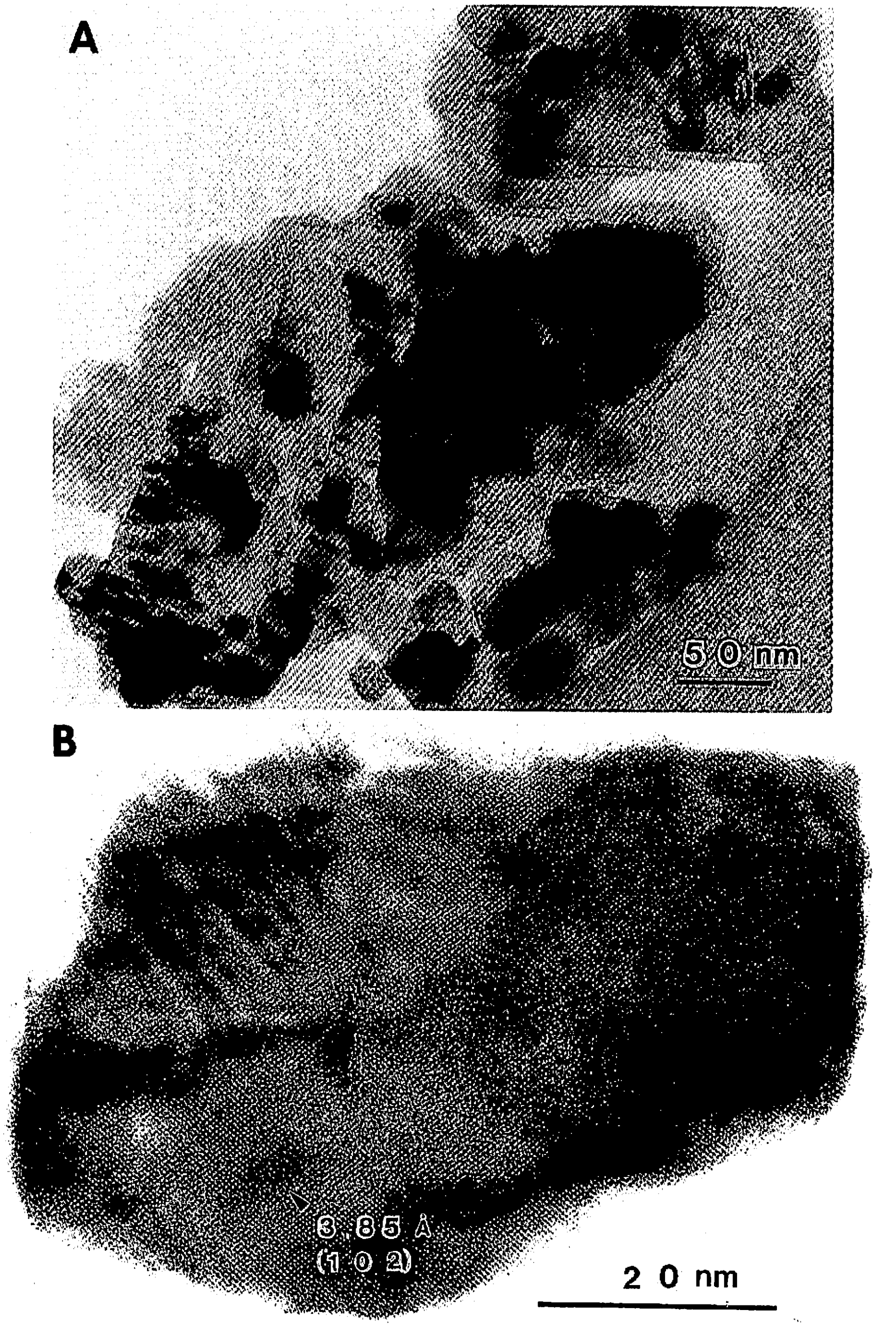

Fig. 13. Transmission electron micrographs of the dinosaur eggshell sample 2; RTMP 87.79.85. A; mosaic structure of calcite, B; higher magnification of A showing lattice images of calcite 3.85 Å (102) d-spacing with lamellar deformation features.

3.4 TEM observations

Most research on dinosaur eggshells is performed with thin sections, but no investigations of their ultrastructure exist. A suspension of a ground sample 2 clearly showed the mosaic structure of calcite in the eggshell by TEM. Each calcite crystal seems to be composed of a great number of small crystals with uniform orientation (Fig. 13A). High-resolution TEM revealed a crystal structure having 3.85 Å lattice images due to (102) d-spacing of calcite (Fig. 13B). The crystals appear to be irregular in thickness. The upper left side of Fig. 13B shows lamellar deformation features of calcite.

3.5 Heavy-ion probe Rutherford scattering

Heavy ion probe Rutherford scattering is useful for depth profiling of element distribution near the surface. The main constituents of sample 1 are C, O, Si, Ca, Fe and some heavy elements (Fig. 14). Several standard samples of C, O, Ca, and Ir were used for comparison with the eggshells. The inner surface of the eggshell contains high carbon content with oxygen, whereas the outer surface has O, Si and Ca with heavy elements. The analysis showed not only a high Fe content but also a significant iridium content on the outer surface. For comparison, heavy ion probe analysis of modern chicken eggshell did not detect any iridium concentration.

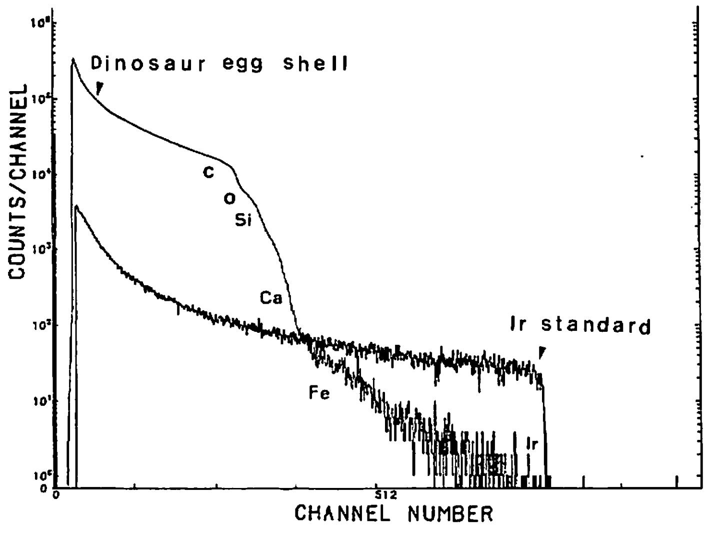

Fig. 14. Energy spectra by heavy ion probe Rutherford scattering for the dinosaur eggshell sample 1; RTMP 86.49.15 in comparison with iridium standard sample. The eggshell mainly composed of C, O, Si, Ca, Fe and a trace of Ir.

4. Discussion

Observation of microstructure and chemical compositon of duckbilled dinosaur eggshell give us information on palaeoenvironment, palaeobiology, and fossilization of the eggshells.

Eggshell microstructure

Even though embryological fossil data are very rare, Erben (1969) reported that the microstructure of dinosaur eggshells had a typical palisade structure which was quite different from bird, turtle and alligator eggs (Halstead, 1974; Schleich and Kastle, 1988). Accepting Sochava (1969, 1971), Erben et al., (1979) and Mikhailov (1991)'s divisions, which emphasized the air canal types, the dinosaur eggs from Montana and Alberta samples can be classified as *Prolatocanaliculate* and *Tubocanaliculate.* The paleobiological studies of dinosaur eggshells from Portugal, Spain and China show that a large number of eggshells reveal abnormalities (Erben, 1969; Kohring, 1989; Zhao, et al., 1993), suggest that severe environmental changes limited the reproductive process and contributed to the extinction of the dinosaurs. In the present study, samples 2 and 4 showed two layers with apatite where the shell collapsed during preservation. It is interesting that aeration system on the inner and outer surfaces of dinosaur and modern chicken eggshells show similar microstructure with difference in pore canal size. The fossilized membrane of the eggshell would be the first record of such a delicate fine structure show in Fig. 8.

Calcification

Although the overall mechanism of eggshell formation is not fully understood on the molecular level, it is clear that the organic matrix plays a key role during eggshell calcification (Ijiri and Kodera, 1994). Mucopolysaccharides play an important role in biological calcification in bone, dentine and cartilage, and the mucous layer mainly consisting of mucine, sometimes has calcite granules (Schmidt, 1957; Mano, 1985). The shell of a hen's egg contains 89-97 % calcium carbonate, 0-2 % magnesium carbonate, 0.5-5 % calcium and magnesium phosphate and 2-5 % organic compounds (Schmidt, 1929). Crocodilia, aves and theropoda have no aragonite. Calcareous shell in turtles, crocodiles, birds and dinosaurs contains aggregates of crystallite (Krampitz et al., 1972, Mikhailov, 1991). Most turtles and the Lacertilia have a very thin elastic eggshell in about 0.2 mm thickness, whereas the dinosaur has a thick hard calcareous eggshell in 2-3 mm thickness. The biosynthesis of eggshell protein can be affected by genetic as well as exogenic factors, and that the formation of both abnormal eggshells and the thick hard calcareous eggshells can be correlated with changed protein profiles of the biocrystalline layer. The relative amounts of different amino acids are specific for different taxa, and high amounts of neutral amino acids favour calcification (Krampitz et al., 1974; Zhao, et al., 1993).

The radial surface (edge) in freshly fractured eggshells is not affected by weathering and erosion and is thus reliable for identification of organics and minerals (Hirsch and Quinn, 1990). But, in this study, precipitates of Fe and Si were observed on the outer surface suggesting that primary $CaCO_3$ was replaced by Fe and Si during fossilization of the eggshells. The iron oxides were recrystallized to hematite or goethite during fossilization. Pyrite crystals around areas of Cu-Zn precipitation was also observed in the eggshells. A full-scale pathological study coupled with EDX and electron microscope methods applied to formation minerals would be very important for a better understanding of the possible role of organics in the primary calcification process, in the mineralogy and elemental oxidation states, and in processes such as Eh-controlled iron migration and redeposition.

Iridium

The cause of dinosaur extinction at the K-T baundary is still unknown and has become an interesting problem, since the publication of Alvarez et al. (1980). They showed that a major extinction episode on Earth, the K-T event some 65 million years ago, appeared to coincide with the hypothesized time of impact of a large comet or asteroid. While this event is most often linked to the extinction of the dinosaurs, fully 75 % of all the species and 90 % of all the biomass on Earth died out at the same time (Weissman, 1990). The key evidence for an extraterrestrial cause is a 160-fold enrichment of iridium in sediments at the K-T boundary (Orth et al., 1982; Tschudy et al.,1984; Weissman, 1990). More evidence has been found at the K-T boundary in the form of shocked quartz crystals and microtektites, both of which are by-products of giant impacts (Alexopoulos et al., 1988; Wolfe, 1990). Appearance and orientation of lamellar deformation in shocked quartz are clearly distinguishable from deformation features observed in explosive eruptions (Alexopoulos et al., 1988; Yagishita and Taira, 1990).

In this study, enrichment of iridium in the eggshells of dinosaur was determined by heavy ion probe Rutherford scattering. The enrichment is estimated to be several hundred times as large as natural abundance (atomic percentage of Ir to Ca from Clark Numbers). The presence of iridium suggest that the source of iridum in Upper Cretaceous sediments may be volcanic, since the eggs were found close to a layer of volcanic ash. We have analyzed the volcanic soils upper and lower sediments, but the iridum concentration in those layers was not clear. Radioactive elements and heavy metals are easily concentrated in organics and cells. Those elements are known to be toxic to some cellular systems and have been commonly used as microscopical stain method. It is also possible that iridium was being concentrated biologically in the eggshell, the same way that modern birds concentrare pesticides in their eggs (Currie, 1991). The presence of iridum in the dinosaur eggshell may suggest that gradual environmental changes adversely affected the reproductive process.

Acknowledgements

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