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Crystallographic and Chemical Analyses of Eggshell of Dinosaur (Sauropod Titanosaurids sp.)

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Abstract

Cretaceous dinosaurs eggshell was analyzed by means of X-ray diffraction, Fourier transform infrared absorption, energy dispersive spectroscopic techniques together with scanning electron microscopy. The results showed that the inorganic component of the eggshell was pure calcite and that these crystals arranged radiate from crystalization center and made knotty surface. This surface morphology was identified with the internal mammillary surface of eggshell.

Introduction

Eggshells are generally grouped into three main types; i) membrane-like, ii) pliable and iii) rigid type. Among them the rigid type has the best chance of fossilizing; e.g., in the case of dinosaurs eggshells. Structural studies on dinosaurs eggshell have been carried out extensively for the past three decades (see ref. in Sahni et al., 1994). Hirsch and Packard (1987) reviewed the fossil eggshell structure and presented the scanning electron microscopic observations about some dinosaur eggshells. Mohabey (1990) distinguished several types of dinosaurs eggshell from the Western part and Central part of India. Mikhailov (1991) classified the four basic types of dinosaurs eggshell based on microscopic structure; testudoid, crocodiloid, dinosauroid and ornithoid. The dinosauroid type includes two main groups, spherulitic and prismatic. They can be further subdivided into several morphotypes based on the nature of shell limits and the structure of pore canals. Sahni (1993) and Sahni et al. (1994) classified the five morphotypes of dinosaurs eggshell based on the microstructure; i) (?) Titanosaurid Type I, ii) (?) Titanosaurid Type II, iii) (?) Titanosaurid Type III, iv) Ornithoid type, and v) an intermediate dinosaurian type (see Fig. 13.5 in Shani et al., 1994). Compared with the plenty amount of morphological studies on dinosaurs eggshell structure (Zhao, 1993), there is a limited number of chemical and crystallographic studies on the inorganic components of dinosaur eggshells. It has been shown that eggshells of turtles are composed of aragonite and those of crocodiles, geckos and all aves are of calcite (Lowenstam and Weiner, 1989). Fukuda and Obata (1991) showed that fossil Cretaceous chelonian eggshell was composed of calcite using scanning electron microscopic, energy dispersive spectroscopic and X-ray diffraction techniques.

The aim of this study was to present crystallographic and chemical analyses data together with scanning microscopic observations on the dinosaur eggshell specimen from the Upper Cretaceous Formation of India.

Materials and Methods

The dinosaur (Sauropod Titanosaurids sp.) eggshell materials used in this study, composed of several polygonal fragments about 15×15mm in size and 2mm in thickness cemented in the matrix rock, were found from the Upper Cretaceous (Maastrichtian) sedimentary rocks, at Pat Bara

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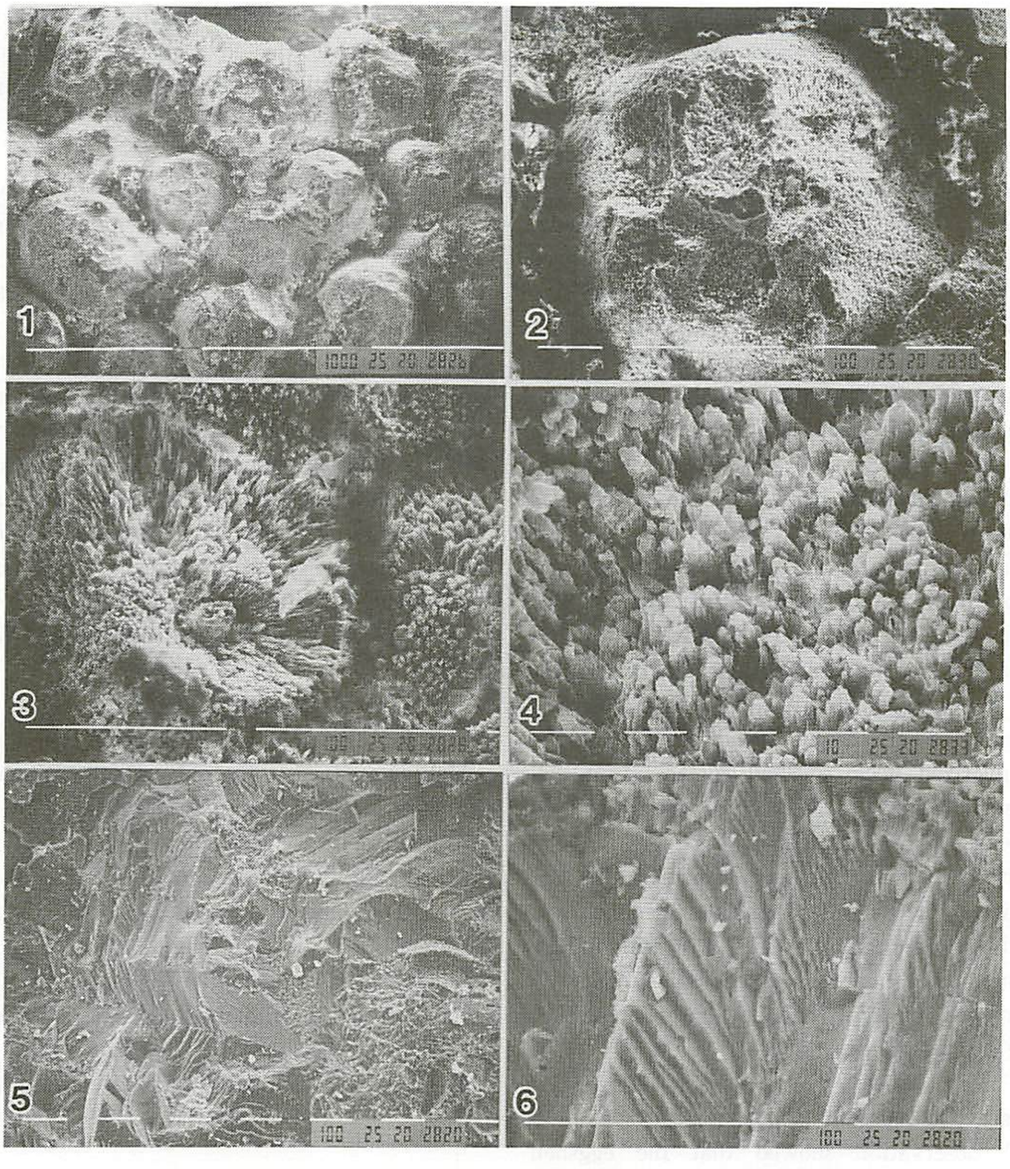

Fig. 1 SEM photographs of the dinosaurs eggshell. 1) "Mammillary" surface of the eggshell (bar=1μm). 2) High power view of the mammillary surface showing the surface being composed of needle-like crystals (bar=100μm). 3) Radiate aggregation of needle-like crystals composing "mammilla" (bar=100μm). 4) Enlargement of the needle-like crystals showing angular prism-like form (bar=10μm). 5) Fractured surface of the middle part of the eggshell showing compactly packed platy crystals (bar=100μm). 6) Enlarged view of a part shown in 5) (bar=100μm).

Mandir, Bara Sinela Hill, Jabalpur, India. The occurrence of the dinosaurs egg nesting was reported already (Srivastava et al., 1986). The details of geology about this bed was discussed in the papers published in the I.G.C.P. workshop volume (Sahni and Jolly, 1990).

For scanning electron microscopic (SEM) study, fragments of the well dried eggshell specimen were placed on aluminum place-holder using a adhesive carbon tape. They were coated with carbon using an Emscope carbon-coater. SEM images of the specimen were observed using a Jeol T-200 with the accelerating voltage of 25kV. Energy dispersive spectroscopic (EDS) analysis was simultaneously carried out using a Jeol JED-2000 which was attached to the T-200.

X-ray crystallographic study was carried out using a Rigaku X-ray powder diffractometer. The dinosaurs eggshell specimen was pulverized with a care of free from contamination with the matrix rocks. The X-ray diffraction (XRD) patterns were obtained from both the pulverized specimen and the non-pulverized bock eggshell surface. Unit cell dimensions of the crystal structure were calculated by a least squares method.

Fourier transform infrared absorption (FT-IR) analysis for the pulverized eggshell specimen was carried out using a Horiba FT-210 with a KBr pellet method to show carbonate ions and to identify polymorphic type of calcium carbonates; i.e., calcite and aragonite.

Results and Discussions

SEM observation showed that the eggshell fragments were composed of radiate needle-like crystals. These crystals may have the sizes of over 50micron meters in length and a few micron meters in width (Fig. 1. 1-1. 4). The surface knots were clearly composed of these radiate aggregations. This indicated that the observed surface was the internal surface of eggshell and that these knots were those known as "mammilla". Inside of the eggshell there was a rather massive platy appearance and needle-like crystals were not observed (Fig. 1. 5-1. 6).

Several points of EDS analyses revealed that the only detectable element was calcium (Fig. 2). Magnesium was carefully surveyed, but not detected. This did not indicate that the eggshell in this study was not affected from the environments, whereas generally fossil specimen contaminated from the circumstances (Parker and Toots, 1980; Fukuda and Obata, 1991).

The XRD pattern of the eggshell block surface was essentially identical to that of the pulverized specimen (Fig. 3A and 3B). The diffraction peaks in both patterns were identified with the peaks of calcite (JCPDS card no. 24-27). The pattern of the block surface specimen clearly showed the crystal orientation effect; the extensively increased intense peaks at 31.5 and 47.7 degree/2θ for 006 and 018 Miller's indecies, respectively, and the weakened peak at 29.5 degree/2θ for 104 Miller's index (Fig. 3A). This result was in harmony with the previous reports that the eggshell surface was composed of well oriented crystallites of calcite, of which the c-axes projected to the surface (Simkiss and Wilbur, 1989).

The other crystalline component was not observed in Fig. 3B, excluding the peaks of chemical KCl which was mixed in the pulverized specimen as a standard material. The unit cell dimensions of the eggshell calcite were calculated by a least squares method after the angle correction using the KCl peaks. The dimensions were a=4.9886(3) Å and c=17.060(3) Å, where figure in parenthesis is the estimated standard deviation. These values were in good accordance with the reported values of a=4.990 and c=17.002 Å (JCPDS card no. 24-27). The differences were negligible and suggested that there

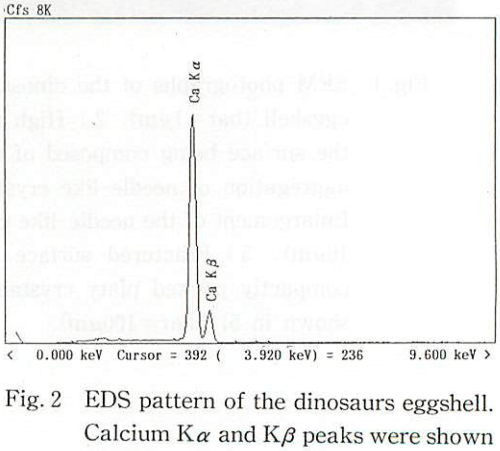

Fig. 2 EDS pattern of the dinosaurs eggshell. Calcium $K\alpha$ and $K\beta$ peaks were shown here, but the other elements such as magnesium ions were not detected.

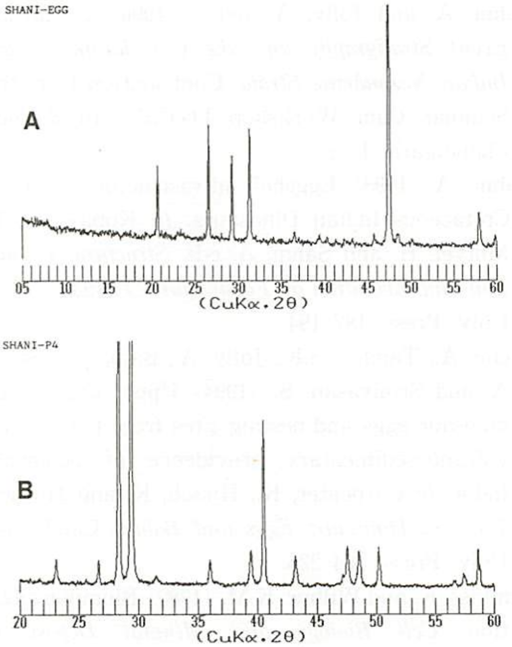

Fig. 3 XRD patterns of the dinosaurs eggshell specimen indicating that the crystal is calcite. A) Diffraction pattern from the bulk surface of the eggshell showing the orientaion effect. B) Diffraction pattern from the pulverized eggshell specimen. Abscissa axis scale is diffraction angle (2θ) and ordinate axis scale is diffraction intensity.

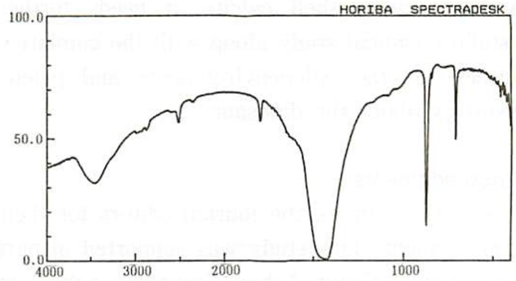

Fig. 4 FT-IR pattern of the dinosaurs eggshell showing absorption bands due to carbonate ions in calcite crystal. Abscissa axis scale is wavenumber (cm^{-1}) and ordinate axis scale is percentage transmission (% T).

was no essential ionic substitution occurred in the calcite crystal. Pure calcite in the dinosaurs eggshell is a matter of debate about the so-called "calcite-aragonite problem".

Of the FT-IR pattern of the dinosaurs eggshell (Fig. 4), the absorption bands appeared at about 870 cm^{-1} and 710cm^{-1} could be assigned to carbonate ions of calcite. Although both calcite and aragonite shows the strong and broad band at about 1400-1500 cm^{-1}, as appeared in Fig. 3, aragonite shows the bands at 851cm^{-1} and a doublet of 707cm^{-1} and 692 cm^{-1} together with the specific band at 1077cm^{-1} (White, 1974). It was notable that there was no appreciable bands due to other than carbonate ions.

Silyn-Roberts and Sharp (1986) had used an X-ray diffraction technique to show that the crystal growth in the eggshell of ostrich started as sperulitic with a crystallization center and at the latter stage the surviving crystals elongated their c-axes perpendicular to the outer surface. In this study, the XRD pattern from the eggshell block surface showed the apparent crystal orientation; the c-axes oriented perpendicular to the surface. The SEM observation of the fragments showed the surface knots composed of radiate aggregations of needle-like crystals. These knots were known as "mammilla" at the internal mammillary surface of eggshell. These results confirmed that the dinosaurs eggshell in this study had the structure proposed earlier (Sahni et al., 1994).

The EDS and FT-IR analyses showed the presence of calcium and carbonate ions. The XRD and FT-IR analyses strongly indicated that the crystals which composed the eggshell were pure calcite. However, this study did not deal with the problem that when the calcite crystals were formed; whether at the eggshell formation stage or fossilization. Some recent and fossil eggshells, especially those of turtles, are composed of aragonite (Lowenstam and Weiner, 1989) which is geologically unstable and may change to calcite on diagenesis. Calcite is a constituent of many eggshells and usually remains unaffected through geological time. However, sometimes recrystallization of calcite takes place as a result of diagenetic processes. In such cases, the recrystallized calcite can be easily made out as it cuts across the known internal structure of eggshell. This study did not aim to reveal such a change of the internal structure of the dinosaurs eggshell. To clarify the origin of the dinosaurs eggshell calcite, it needs further crystallo-chemical study along with the cumlative evidence for the paleoenvironments and paleophysiology about the dinosaur.

Acknowledgments

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