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Analysis of dinosaur samples by nuclear microscopy

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Abstract

Several dinosaur bone and eggshell fossil samples unearthed at different sites in China were analyzed by means of nuclear microscopy. Concentrations and distributions of elements such as Na, Mg, Al, P, S, Ca, Cr, Mn, Fe, Cu, Zn, As, Br, Sr, Y, Ce, Pb and U, etc. were obtained for each sample. The results of quantitative PIXE and RBS analyses show unusually high concentrations of U and Ce in several samples obtained from a period near the K–T boundary (between Cretaceous and Tertiary periods, 65 million years ago), suggesting that some form of environmental pollution could be the cause of dinosaur extinction. © 1997 Elsevier Science B.V.

1. Introduction

The dinosaur extinction that occurred 65 million years ago seems to be a never-dried spring of ideas for modern paleontologists. These monstrous creatures indeed disappeared from the Earth's stage around the Cretaceous–Tertiary (commonly abbreviated K–T) boundary. Since the discovery of the iridium anomaly in K–T clay by Alvarez in 1979 [1], the research on dinosaur extinction has entered into a new golden era. Up to now, about 40 different hypotheses of dinosaur extinction have been proposed [2]. One of the most popular hypothesis is that a huge asteroid hit the Earth [1]. Another competing hypothesis is a volcanic catastrophe [3]. In recent years, a new idea that environmental pollution may be the reason of the dinosaur extinction was proposed by Chinese paleontologists [4,5].

There are abundant deposits of dinosaur fossils in China. The study of Chinese dinosaurs began as early as 1920 and there have been a lot of discoveries and achievements up to now. The recent discovery of more than 10000 pieces of dinosaur eggs in Xixia Basin, Henan Province, further promoted the investigations of dinosaur extinction. However, most of the studies are mainly done by paleontologists and geologists. The results obtained in recent years indicate that it would be useful to study the microstructure, distributions of trace elements and their anomalies of dinosaur fossils for determining the real cause of dinosaur extinction [4,5]. The use of modern analytical techniques such as SEM (Scanning Electron Microscopy), nuclear techniques (XRF, PIXE, micro-PIXE, etc.) and so on, should consequently promote the study of dinosaur extinction but only a few reports are found up to now [5–8].

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In this paper some preliminary results of micro-PIXE and micro-RBS analysis of Chinese dinosaur bones and eggshells are presented. All measurements were carried out in the Nuclear Microscopy Laboratory, National University of Singapore. Specimens were unearthed at the Redbeds of Late Cretaceous in Xixia Basin, Henan Province and Tianzhen, Shanxi Province. Elemental distributions in a number of dinosaur bones and eggshells were obtained and quantitative analyses of different parts on these samples were performed. Our preliminary results show that uranium and cerium are present in unusually high concentrations in some of the bone and eggshell samples. For example, uranium was found in concentration higher than 100 ppm and Ce in concentration higher than 2000 ppm in a dinosaur bone sample. High concentration of Sr was found in the eggshells. These results indicate that environmental pollution could have influenced the health of dinosaurs and the hatchability of their eggs, and hence support the new hypothesis proposed by Zhao et al. [4,5] that elemental pollution finally lead to the dinosaur extinction.

2. Sample preparation

2.1. Samples

All of the dinosaur fossil samples analyzed were unearthed in China in recent years, and prepared by the geologists from Institute of Rock and Mineral Analysis, Chinese Academy of Geological Sciences, Beijing, China.

The dinosaur samples analyzed in this work are:

(a) Dinosaur eggshell sample **XL-01**: unearthed from Redbeds near K–T in Xixia Basin, Henan Province; type *Spheroolithidae.*

(b) Rib bone sample **KY9400**: unearthed from Redbeds near K–T in Xixia Basin; type *Spheroolithidae.*

(c) Leg bone sample **H-05A**: unearthed from Redbeds of Late Cretaceous in Tianzhen, Shanxi Province; type *Ornithischia, Ankyloosauria, Nodosauridae.*

(d) Leg bone sample **$10H_1$**: unearthed from Redbeds of Late Cretaceous in Tianzhen; type *Ornithischia, Ankyloosauria, Nodosauridae*, same as H-05A.

(e) Thighbone sample **${}^{6}_{1}H_2$**: unearthed from from Redbeds of Late Cretaceous in Tianzhen; type *Saurischia, Tibanosauridae, Amphicoclicaudiagen.nov., Aiallocategen.et.sp.nov.*

2.2. Sample preparation

Each sample was covered and fixed by a complex gum consisting of Epon618 and polyamide mixed in a ratio of 3:1. The fixed samples were cut into slices of sub-samples of 1–2 cm thick each. The surface of one side of each sub-sample was polished and then stuck to a 1.4 mm thick glass slide with a special glue. The other surface was then ground until its thickness reached approximately 100 microns. After polishing, the sub-samples were cleaned, dried and finally coated with a thin carbon film to avoid charging during irradiation.

3. Experimental

All dinosaur samples were analyzed by using the NUS nuclear microscopy facility built around a 2.5 MV Van de Graaff accelerator. A 2 MeV proton beam was focused to approximately 2–5 microns and scanned over the samples. Details of the experimental setup can be found elsewhere [9]. Elemental distributions in dinosaur samples were obtained by using micro-PIXE. Micro-RBS was used to detect low-Z elements such as C and O, and to obtain their distributions for the subsequent quantitative PIXE analysis with the program GUPIX [10]. To guarantee the reliability of PIXE analysis, each spot of interest on a sample was usually analyzed two times. The major matrix elements found in dinosaur fossils are Ca, C and O. To reduce the intensity of Ca K lines a 60 μm aluminum filter was used. No filter was used for the analysis of light elements such as Na, Mg, Al and P.

4. Results and discussion

4.1. Dinosaur eggshell

Dinosaur eggshell consists of many structural units. The components of a basic structural unit

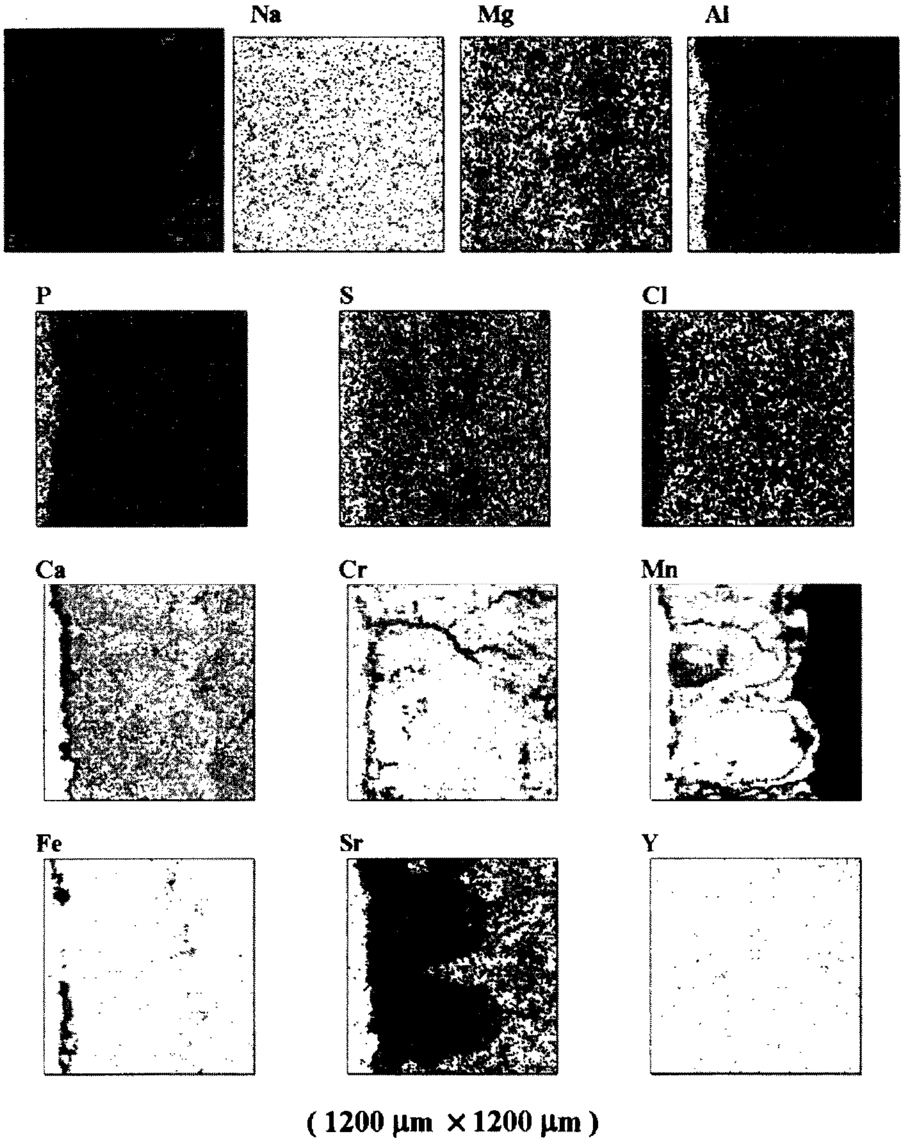

Fig. 1. Optical images and elemental distributions obtained from the dinosaur eggshell sample **XL-01** by nuclear microscopy. Scan size 1200 × 1200 μm^2.

include cuticle, surface crystal layer, columna, cone mammilla and the shell membrane [5]. The eggshell fossils are often surrounded by country rock. Fig. 1 shows the optical images and elemental maps of the dinosaur eggshell sample XL-01. There are two complete structural units and a part of the country rock within an area of 1200 × 1200 μm^2. The thickness of the eggshell is about 0.8 mm, much thinner than the normal value of a few mm [5]. The elemental concentrations in an eggshell unit and the country rock near the shell membrane are shown in Table 1. It can be seen in Fig. 1 and Table 1 that a high concentration of about 1600 ppm of Sr is present in the columna and the cone areas of the eggshell unit. The Mn concentration in the country rock is much higher than those in the mammillae and the edge of the unit. In the cone and the mammlilla areas, the elements such as Mg, S, Mn and Fe are more

Table 1
Elemental concentrations in dinosaur eggshell XL-01 and in the nearby country rock (in ppm; nd: nondetectable)

Element	Eggshell	Country rock
Na	742	453
Mg	1162	1517
Al	238	391
Si	nd	230
P	544	nd
S	386	89
Cl	nd	32
Ca	399439	396474
Cr	121	114
Mn	81	8434
Fe	5	nd
Zn	3	2
As	nd	nd
Br	5	21
Sr	1665	230
Y	nd	14
Ag	nd	15
Ba	32	nd
Ce	nd	57
Pb	nd	3

concentrated. The elements Mg, Cr, Mn and Fe also exist in the gaps of the unit. To summarize, the major component of eggshell is calcium carbonate while other elements are present only in trace concentrations. The two anomalies observed in eggshell units are the very high concentration of Sr and the very low concentration of Fe.

According to the above-mentioned results, it can be stated that there are less elemental replacements between the eggshell and the environment after the fossilization of the former because the country rock (calcite) has cut off the influence from the environment. For instance, the most common pollutant, iron, is only found on the edges of the eggshells and not within the unit bodies. It seems that Sr in the units is an original component of the eggshell and does not come from the country rock and the environment. There were replacements of Na, Mg, Al, S and Cr between the eggshell and the environment when the eggshells were being transformed to fossils. However, the observation of high concentration of Sr supports the results given by Zhao in 1991 [4].

4.2. Dinosaur bone

Table 2 shows the elemental concentrations of the four dinosaur bone samples obtained by PIXE analysis. During the fossilization of dinosaur bone, cells and other organic matter decomposed almost completely. Many gaps, like marrow cavities and tubes, were filled by minerals (mainly calcite, $CaCO_3$). For some elements, replacements between the bone and the country rock occurred. If the distribution of an element in the bone matrix is homogeneous, this element can be taken generally as the original component of the bone. Conversely, the replaced elements often concentrated in cavities, tubes and near the edges of bone fossils.

4.2.1. Bone sample KY9400 from Xixia

The type of KY9400 is Spheroolithdae. It can be seen in Table 2 that there are some unexpected elements present in high concentrations in the bone matrix of KY9400. There are about 2850 ppm of cerium and 124 ppm of uranium in the bone matrix. The concentrations of As, Sr and Y are also abnormally high. The PIXE spectra of the bone matrix and the tube are shown in Fig. 2a. The X-ray lines of Ce (L series) are very obvious in the spectrum of the bone matrix. The $L\alpha$ peak of U is also clear, and it is certainly not the $K\alpha$ peak of Rb due to the energy difference of about 0.34 keV between U $L\alpha$ and Rb $K\alpha$. The U$L\beta_1$ and U$L\beta_2$ lines overlap with the tails of the $K\beta$ peaks of strontium and yttrium respectively, and hence are not very obvious. The small $L\gamma_1$ peak of U can be seen in the spectrum. In order to make certain that these U peaks are correctly identified by GUPIX, another software AXIL [11] commonly used in PIXE analysis was also used to analyze this spectrum. The results given by AXIL agreed with those given by GUPIX. In the spectrum of the bone tube, a high concentration of Mn is found in the bone tubes and cavities, as well as in the country rock near the eggshell as mentioned above. There are no obvious peaks of U and Ce found in the spectrum of the bone tube. Fig. 2b shows the optical image and the elemental maps of this sample within a scanning area of $2 \times 2\ \mathrm{mm}^2$. The dark pattern in the optical image represents the bone matrix and the round white areas are the bone tube or marrow cavity. Ce and U are both present only in the bone

Table 2
Elemental concentrations in several dinosaur bone samples (all concentrations in ppm unless otherwise stated)

Sample	Rib (KY9400)		Leg bone (H-05A)		Leg bone end ($10H_1$)			Thighbone ($^{\circ}_{1}H_2$)	
Site	Xixia Basin, Henan Province		Tianzhen, Shanxi Province		Tianzhen, Shanxi Province			Tianzhen, Shanxi Province	
Type	Spheroolithidae		Nodosauridae		Nodosauridae			Aiallocategen.et.sp.nov.	
Region analysed	Bone matrix	Tube	High density	Low density	Low density	High density	Tube	Bone matrix	Tube
Element									
Na	2152	–	1430	1779	–	–	–	2778	–
Mg	955	–	1975	1464	–	–	–	1223	2955
Al	1302	–	2300	661	–	77270	–	835	989
Si	–	–	1917	322	–	–	–	–	2125
P	8.97%	–	8.12%	9.22%	–	–	–	9.23%	547
S	2036	–	1659	1787	–	–	–	1937	80
Cl	1060	–	339	415	–	–	–	599	–
K	127	–	–	–	–	23074	–	153	–
Ca	29.94%	39.55%	27.48%	29.77%	30.01%	23.77%	39.92%	29.98%	39.78%
Ti	–	–	48	–	–	5183	–	133	–
V	–	–	72	35	–	353	–	–	–
Cr	–	–	104	72	123	546	48	107	24
Mn	–	13172	154	–	104	2022	1549	207	3223
Fe	89	311	45805	9401	600	78503	36	326	1541
Cu	4	2	26	24	5	91	–	33	3
Zn	47	6	50	39	52	172	6	43	4
As	182	2	145	36	6	52	–	–	–
Br	11	14	10	15	12	–	–	–	–
Sr	1329	314	2076	2659	1956	384	209	4046	354
Y	1011	5	–	55	1456	47	–	88	–
Ce	2856	–	–	–	270	–	–	–	–
Pb	11	–	35	87	55	–	–	18	–
U	124	–	131	75	23	–	–	43	–

matrix whose composition is given in Table 2. The concentrations of As, Sr and Y in the bone tube are much lower than those in the bone matrix. It is hard to imagine that dinosaurs could live normally with such high concentrations of these toxic elements in their bodies.

This bone sample and the above-mentioned eggshell sample came from the same type of dinosaur and from the same site in Xixia Basin. That no Ce and U exist in the eggshell sample and the country rock indicates that these elements must be present in the dinosaur bone before fossilization. The low concentration of iron in the bone matrix and in the bone tube indicate that there was no serious elemental migration between the bone and the environment after the former was fossilized. Only some replacements of Mg, Al, Si, Fe and Br might have occurred during the fossilization, judging from their distributions in the sample shown in Fig. 2b. The fact that no Mn is found in the bone matrix supports this conclusion.

4.2.2. Bone samples from Tianzhen

The results obtained from the three bone samples from Tianzhen, Shanxi Province are listed in Table 2. High concentration of Sr is found in the bone matrices. The concentrations of U in the bone matrices are 20–130 ppm. Higher concentrations of Pb are also found in the same places. About 1500 ppm of Y and 270 ppm of Ce are found in the leg bone sample $10H_1$. The elemental distributions in the low density matrix region (near the center) and the high

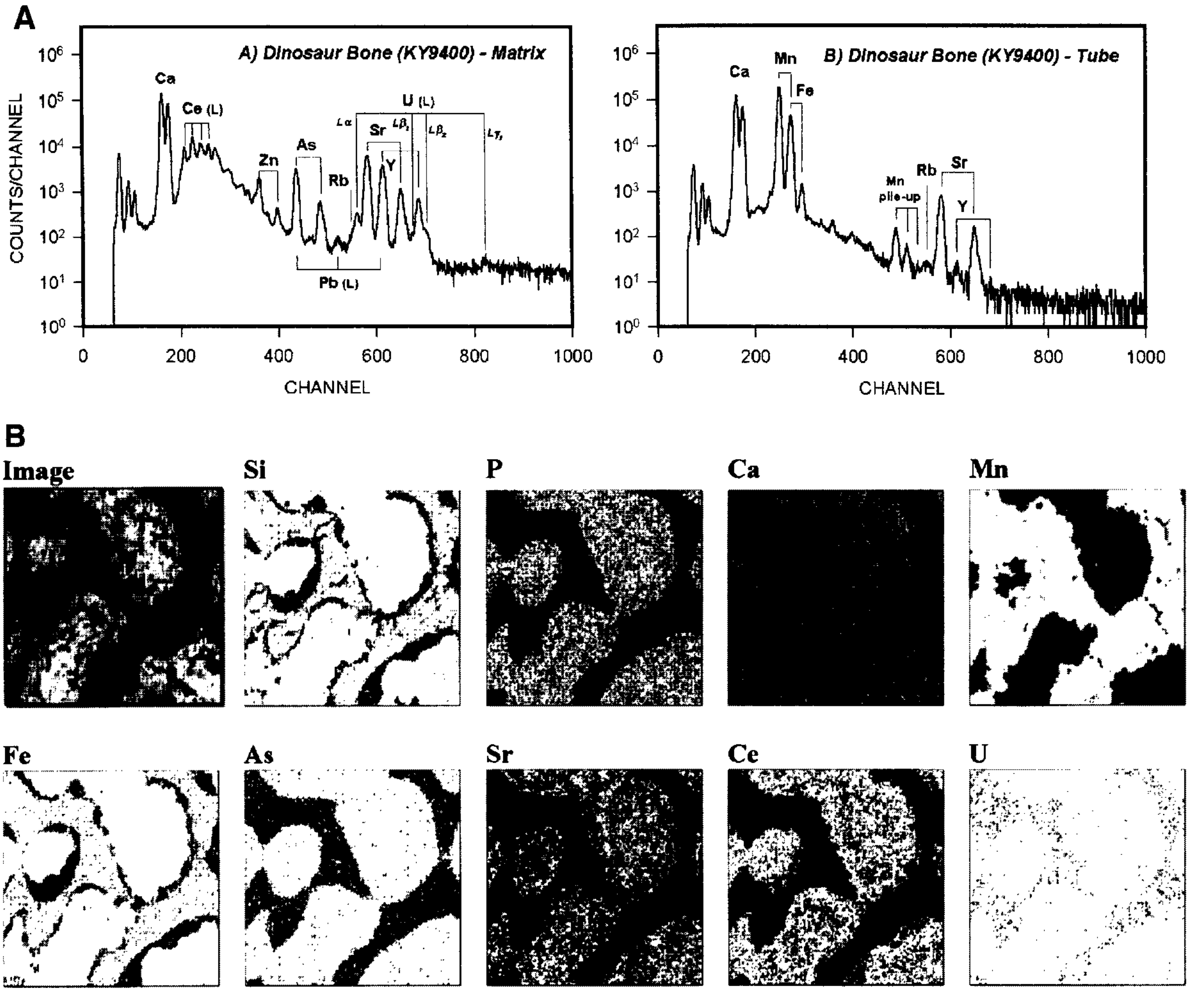

Fig. 2. (a) PIXE spectra of dinosaur bone matrix and tube (KY9400). (b) optical image and elemental distributions obtained from the dinosaur bone sample **KY9400** (2000 μm × 2000 μm).

density matrix region (near the edge) of $10H_1$ were compared. In the high density matrix region, the contents of toxic elements Sr, Y, Ce, Pb and U are below their minimum detection limit or much less than those in the low density matrix region. But the concentrations of other trace elements, such as Al, K, Ti, V, Cr, Mn Fe, Cu, Zn and As, in the high density area are much higher than those in the low density area. These results indicate that there were extensive elemental replacements in the edge area during fossilization and almost all of the toxic elements and a part of Ca were lost and replaced by other trace elements. It can be seen in the elemental maps obtained that there are many small holes in the bone matrix due to element loss and these holes were filled by trace elements such as K, Ti, Cr and Mn. Conversely, all elements in the central area of the bone section basically retained their original concentrations and little elemental migration occurred. The fact that very low concentrations of only a few trace elements are found in the bone tube also supports this deduction.

The results obtained from another bone sample H-05A are similar to that obtained from $10H_1$ but the replacements of elements in the former sample are not so extensive. The difference is that the uranium concentration in the high density area is higher than that in the low density area. The reason is probably that the original concentration of U in the edge area of the bone was much higher than that in the central area due to the density difference. Thighbone of the sample ${}_{1}^{6}H_2$, was found to have approximately 4000 ppm of Sr and 43 ppm of U. The elemental distributions in this sample are similar to those in other bone samples.

5. Conclusions

The micro-PIXE analysis we performed on a dinosaur eggshell sample unearthed in Redbeds of Late Cretaceous discloses the existence of an abnormally high concentration of Sr in it. It is reasonable to assume that Sr interfered with the formation of eggshells and impaired the hatchability of dinosaur eggs [5].

Our studies of four dinosaur bone samples from the Late Cretaceous reveal that there are anomalous amounts of As, Sr, Y, Ce, Pb and U present in their bone matrices. The results of micro-PIXE analysis indicate that these toxic elements existed in the dinosaurian bodies prior to their fossilization. These elements could have concentrated in the dinosaur body through the food chain when the environmental pollution had become serious around the K-T boundary, or migrated into the bone matrix from the surrounding soil during fossilization. If the former process was operative, these elements could have impaired the health of dinosaurs and increased the concentration of Sr in their eggs. Further investigations of more dinosaur eggshell and bone samples will be performed in a near future. To summarize, our results support the hypothesis that environmental pollution was the final lethal cause for the dinosaur extinction regardless of whether the environmental pollution was caused by an asteroid impact or a volcanic catastrophe.

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