Element Geochemical Characteristics of the Cretaceous Dinosaur Eggshell Fossils and Their Implications for Palaeoenvironment*

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Abstract: Dinosaur eggshells from the Cretaceous red beds of southern China were selected for element geochemical study. The concentrations of the major elements indicates that the eggshells did not change much in their chemical composition after they were formed. Variations in the contents of trace elements and REEs imply that a palaeoclimatic anomaly might occur during Late Cretaceous.

Key words: dinosaur eggshell; elemental geochemistry; palaeoclimatic anomaly

Geological Setting and Sample Analysis

The area studied, named the Nanxiong Basin, located in Nanxiong County and Shixing County, northern Guangdong Province, China, is a small fault basin formed on a pre-Cretaceous crystalline basement and it dominantly received red terrestrial clastic sediments during Late Cretaceous and Early Tertiary.

The Upper Cretaceous, the so-called Nanxiong Group, is divided into two formations: the Yuanpu Formation and the Pingling Formation. The Yuanpu Formation consists mainly of purple sandy conglomerates, sandstones and siltstones of alluvial or lacustrine facies. There exist eruptive basaltic interbeds in the upper part of the formation. The Pingling Formation is built up by a suite of purple sandstones, siltstones and silty claystones of shallow or nearshore lacustrine facies. It is the Pingling Formation that contains dinosaur eggshell fossils.

As shown in Fig. 1, all the samples examined were taken from the middle and upper parts of the Pingling Formation. Eight samples of dinosaur eggshell fossils were collected from four localities along the upper part of the formation. Locality one (including samples N92-09-1 and N92-09-2) is about 180 m under the K/T boundary, locality two (including samples N92-09-3 and N92-09-4) about 80 m, locality three (including samples N92-09-5 and N92-09-6) about 45 m and locality four (including samples N92-09-7 and N92-09-8) about 8 m under the boundary. Two samples of modern hen eggshells were collected and analyzed for the purpose of comparison.

All the samples were elaborately selected and cleaned with distilled water in a supersonic container. The major elements were analyzed by an ordinary chemical analytical procedure, the trace elements and rare-earth elements (REEs) by INAA (instrumental neutron activity analysis), some trace metals by ICP-MS (inductively coupled plasma mass spectrometry) and AAS (atomic absorption spectrometry).

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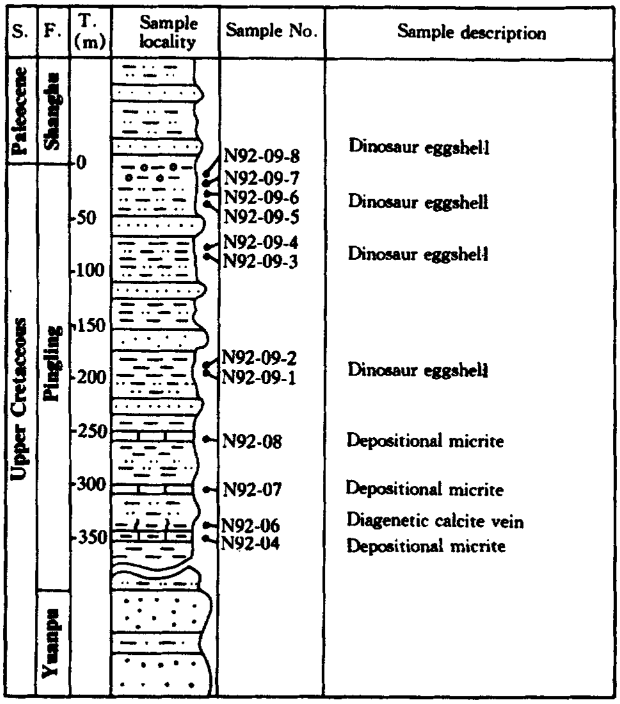

Fig. 1. The stratigraphic sites and the description of the samples studied.
S.—Series; F.—formation; T.—thickness.

Results

Major elements

The major element contents of dinosaur eggshells and modern hen eggshells are listed in Table 1.

It is clearly seen from Table 1 that the dominant chemical composition of dinosaur eggshells is $CaCO_3$, which accounts for 92.82% – 94.52% of the total. The other elements are low, generally less than 5% in weight with the exception of organic matter (which will be discussed later).

The modern hen eggshells, containing 92.77% $CaCO_3$, show almost no difference in main chemical composition from the dinosaur eggshells. This result implies that the dinosaur eggshells remained almost unchanged in chemical composition after they were formed.

Organic matter

The total organic matter (TOM) is estimated on the basis of the loss on ignition, and the total kjeldahl nitrogen (TKN) and total phosphorus (TP), mainly occurring in the form of organic matter, were analyzed by colorimetry. For comparison, the samples representing the host rocks were selected for those analyses. Listed in Table 2 are the analytical results.

The TOM in dinosaur eggshells varies from 2.6% to 4.36% with an average of 3.63%; the TOM in the host rocks ranges from 0.79% to 2.04% with an average of 1.30%, which is much lower than that of dinosaurs. The TOM of the modern hen eggshells is 5.63%, higher than that of dinosaurs.

Table 1. The major element contents of the dinosaur eggshells (%)

Composition	N92-09-2	N92-09-4	N92-09-5	N92-09-6	N92-09-8	N92-R2
SiO_2	1.24	1.11	1.89	1.02	1.16	0.030
TiO_2	0.014	0.01	0.01	0.01	0.015	0.005
Al_2O_3	0.29	0.25	0.20	0.28	0.16	0.001
TFeO	0.12	0.11	0.23	0.12	0.10	0.070
MnO	0.086	0.089	0.092	0.083	0.128	0.005
MgO	0.16	0.18	0.24	0.16	0.14	0.63
CaO	52.27	52.19	51.87	52.19	51.98	51.88
Na_2O	0.16	0.22	0.18	0.18	0.17	0.17
K_2O	0.091	0.085	0.108	0.075	0.077	0.32
P_2O_5	0.27	0.32	0.42	0.27	0.31	0.32
CO_2	41.17	42.33	40.95	41.12	41.11	40.89
OH	0.39	0.50	0.52	0.32	0.38	1.01
TOM	3.70	2.63	3.25	4.15	4.22	5.63
Total	99.96	100.02	99.96	99.98	99.95	100.70

Table 2. The contents of TOM, TKN and TP in the dinosaur eggshells and host rocks

Sample No.	TOM(%)	TKN($\times 10^{-6}$)	TP($\times 10^{-6}$)	Remark
N92-09-1	4.36	1722.31	1722.31	
N92-09-2	3.70			
N92-09-3	3.77	2119.8	2027.03	
N92-09-4	2.63			
N92-09-5	3.25	1887.29	2845.67	
N92-09-6	4.15			
N92-09-7	2.95	1991.96	2792.60	
N92-09-8	4.22			
N92-04	0.79	224.51	571.74	Clay micrite
N92-07	1.28	149.52	696.77	Micrite
N92-08	1.09	159.89	663.25	Micrite
N92-09-3b	1.31	345.69	775.55	Muddy sandstone
N92-09-5b	2.04	493.67	1533.59	Silty mudstone

The dinosaur eggshells contain TKN ranging from 1722.31×10^{-6} to 2119.83×10^{-6} with an average of 1930.35×10^{-6}; TP from 1722.31×10^{-6} to 2845.67×10^{-6} with an average of 2346.90×10^{-6}. The host rocks contain TKN ranging from 149.52×10^{-6} to 493.67×10^{-6} with an average of 274.66×10^{-6}, and TP from 571.74×10^{-6} to 1533.59×10^{-6} with an average of 848.18×10^{-6}. Significant differences in TKN and TP between the dinosaur eggshells and the host rocks also indicate that the former had not been greatly altered since they were produced.

Trace elements and REEs

Eight dinosaur eggshell samples and two modern hen eggshell samples were selected for trace element and REE analysis by INAA. Table 3 lists the analytical results.

Compared with the modern hen eggshells, the dinosaur eggshells are much higher in the concentrations of trace elements and REEs, which might indicate the differences in food type and surviving environment.

Table 3. The concentrations of trace elements and REEs in the dinosaur eggshell samples

Element	1 *	2	3	4	5	6	7	8	R1	R2
Rb * *	1.80	2.30	2.50	3.30	1.20	0.95	1.60	1.60	0.60	0.60
Cs	0.22	0.26	0.31	0.40	0.24	0.27	0.31	0.33	0.03	0.05
Sr	3304	3640	3937	4220	2111	1853	2035	1960	338	361
Ba	159	152	235	236	155	118	139	129	94	98
Sc	0.63	0.69	1.20	1.28	0.81	0.74	1.10	1.04	0.05	0.07
Co	1.10	1.10	2.00	2.30	0.38	0.36	3.70	3.70	0.02	0.03
Sb	0.21	0.22	0.21	0.19	0.13	0.13	0.29	0.31	0.10	0.10
As	4.60	4.60	17.10	20.40	1.30	1.20	0.70	0.73	0.06	0.23
Ag	1.60	1.60	1.90	1.90	1.10	0.97	1.60	1.60	0.70	0.13
Au	14.2	15.2	57.3	64.2	49.2	40.0	3.7	5.2	0.95	0.73
Th	0.36	0.40	0.58	0.67	0.20	0.33	0.50	0.39	0.05	0.01
U	0.93	0.92	1.40	1.70	0.70	0.64	0.30	0.30	0.01	0.003
La	2.30	2.30	3.10	3.60	1.40	1.40	2.10	2.10	0.05	0.04
Ce	4.40	4.80	6.60	7.30	2.50	2.30	4.70	4.70	-	0.05
Nd	2.80	2.50	3.60	3.90	1.50	1.06	2.40	2.40	-	0.09
Sm	0.72	0.71	0.94	1.04	0.34	0.29	0.65	0.65	-	0.01
Eu	0.15	0.17	0.21	0.23	0.08	0.08	0.14	0.15	0.01	0.02
Tb	0.09	0.10	0.13	0.16	0.04	0.04	0.06	0.08	0.01	0.01
Yb	0.23	0.28	0.40	0.43	0.16	0.13	0.26	0.25	0.03	0.03
Lu	0.04	0.04	0.06	0.07	0.03	0.02	0.05	0.04	-	-

* 1 - 8 represent N92-09-1—N92-09-8 and R2 represent N92-R1 and N92-R2 (two modern hen eggshell samples).
* * The unit for all the elements is 10^{-6} with the exception of Au ($\times 10^{-9}$).

Fig. 2 shows the vertical variation of each element in the dinosaur eggshells present in the strata from the lower to the upper. It is clearly seen that the concentrations of most of the trace elements and all the REEs are of positive anomaly in sample locality two (samples N92-09-3 and N92-09-4). This phenomenon coincides with their anomalous microtextures to be discussed below.

Discussion

The major element and organic matter data from the dinosaur eggshells not only provide us with the information about their chemical constituents, but also indicate no obvious alteration of these dinosaur eggshells after they were produced, as confirmed by their microtextures (Zhao Zikui et al., 1991) and their isotopic data (Yang Weidong, 1993). This conclusion is very important because it makes it possible for us to use dinosaur eggshell as a recorder for palaeoenvironment information.

It has been confirmed that the concentrations of trace elements in reptiles' and birds' eggshells depend on the food types taken by the animals (Folinsbee et al., 1970). However, trace elements in natural food are mainly derived from local environments so that those in reptiles' and birds' eggshells could serve as an indicator of their inhabitant environments.

The significant difference in the concentrations of trace elements and REEs between dinosaur eggshells and modern hen ones would be attributed to the difference in food type and surviving environment.

Trace element and REE anomalies of dinosaur eggshells from sample locality two (samples N92-09-3 and N92-09-4) are of profound interest, because of the coincidence with the anomalous microtextures and the disappearance of most types of dinosaur eggshells described by Zhao Zikui et

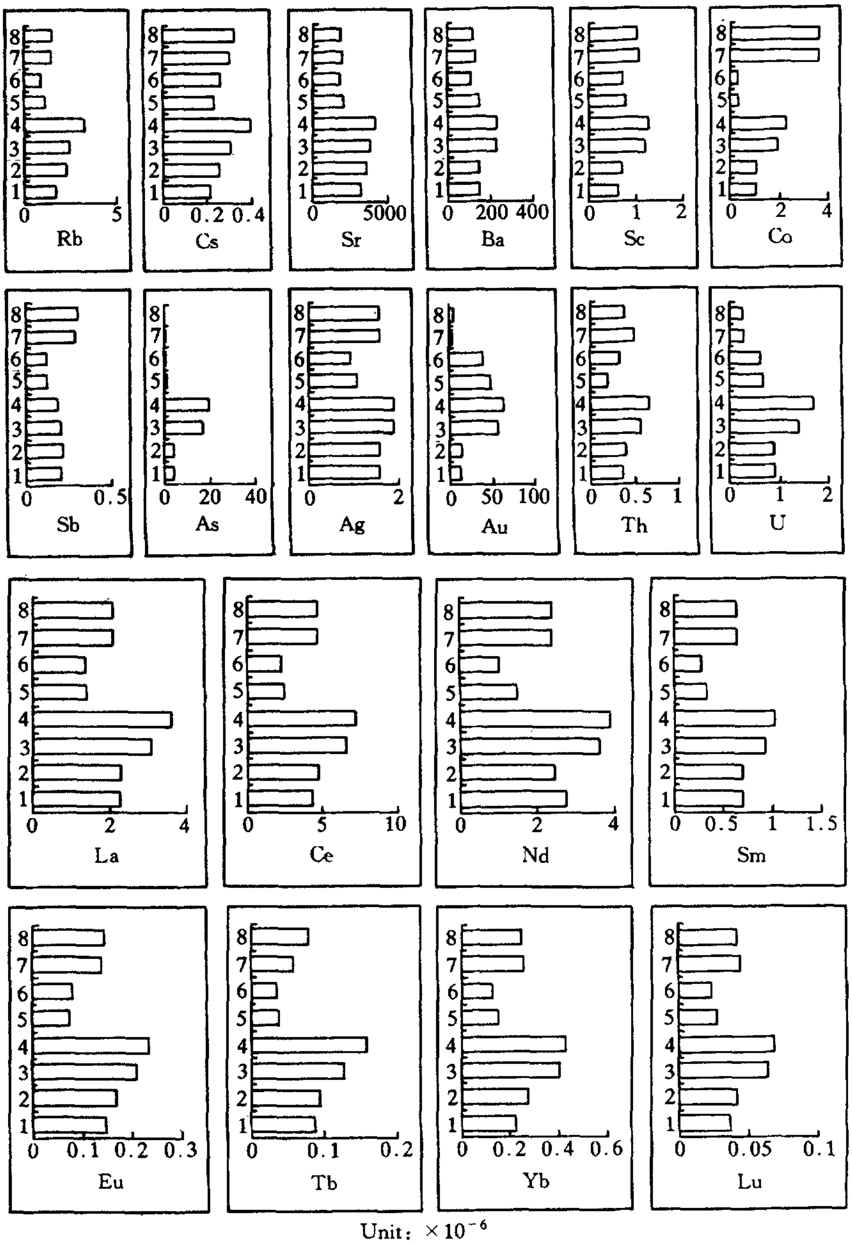

Fig. 2. The vertical variation of trace elements and REEs in the dinosaur eggshells.

al. (1991). The coincidence means that there had taken place some unusual event at that time.

According to the geological history, the unusual event might be one of the following: 1) extensive volcanic eruption; and 2) regional or global changes in palaeoclimate.

Generally speaking, the volcanic eruption was very active during the Late Cretaceous, but in the Nanxiong Basin there was no volcanic activity when the anomaly of dinosaur eggshells occurred. Hence, it seems impossible that the anomalies of dinosaur eggshells would be caused by volcanic activities.

It has been known that the palaeoclimate was quite warm during Cretaceous (O' Keefe et al., 1989; Frakes, 1979). On the basis of the oxygen isotope data for syndepositional micrites collected from the lower part of the Pingling Formation, the average temperature at the earth's surface was 3 – 9℃, higher than that at present (Yang Weidong, 1993). In this case, if the temperature went up further, it would cause a drastic change in both the inorganic and organic worlds. Although no temperature data are available, it is believed that the higher concentrations of trace elements and REEs in the dinosaur eggshells would reflect the changes of the palaeoenvironment where the dinosaurs were survived.

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