Stable isotopic studies of dinosaur eggshells from the Nanxiong Basin, South China

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Received February 26, 1999

Abstract Stable carbon and oxygen isotopes have been observed in dinosaur eggshell samples, identified as *Macroolithus yaotunensis*, collected in two sections of the Nanxiong Basin, Guangdong Province, South China. Multiple positive $\delta^{18}O$ perturbations that occurred during the K/T transition of about 150 ka suggest that there may have been at least three periods of the extreme dry climate with a mean annual air temperature over 27℃. $\delta^{13}C$ ranges from −8.37‰ to −11.60‰ of the dinosaur eggshells, added to the metabolic enrichment of 16‰, may indicate that the dinosaurs represented by this type of eggshells probably consumed the plant species of C_3 type with the $\delta^{13}C$ values of −24.3‰— −27.6‰. Moreover, the trend toward more negative $\delta^{13}C$ values of the eggshells during the K/T transition could be an indirect consequence of a lasting increase in atmospheric CO_2 concentration.

Keywords: K/T boundary, dinosaur eggshell, isotopic composition, paleoenvironment.

Recently, Zhao et al.[1] reported that three iridium anomalies have been identified by radiochemical neutron activation analysis (RNAA) in three dinosaur eggshell samples collected at and near the palynological K/T boundary interval[2] in the CGY-CGD Section of the Pingling Formation in the Nanxiong Basin, Guangdong Province, indicating that the geochemical environmental changes marked by these three Ir-bearing horizons lasted for at least 150 ka.

Well-preserved clutches of eggshell fragments lying about in heaps have been discovered in the Pingling Formation of the basin[1,3,4], indicating an original dinosaur nesting site. Excellent preservation of the clutch geometry indicates that the egg laying and sediment formation were nearly synchronous. Therefore, a knowledge of the associated paleoecological condition of the dinosaur habitats would help to explain the existence of such a large colony during the K/T transition. So far the published stable isotope data of the Nanxiong Basin[2,5,6] have not produced a clear picture because they are fragmentary and give only limited information. We have carried out carbon and oxygen isotope analyses of the dinosaur eggshells from the stratigraphic sequences of the Pingling Formation to obtain information on the sequence of environmental changes and food habits of these dinosaurs.

The available data[1,2,5] indicate that the CGY-CGD Section has relatively continuous deposits from the Late Cretaceous to the Early Tertiary and has been exposed very well. The section has been studied in detail by biostratigraphy and magnetostratigraphy, sedimentology and geochemistry, and presently serves as an informal type of section for the K/T boundary. Therefore, this section can be used as a scale of reference for the interpretation and comparison of data from other K/T boundary sections. In this study, the stable-isotope results for the CGY-CGD and CGT-CGF sections in the Nanxiong Basin are presented.

1 Materials and methods

The CGY-CGD Section is located south of Datang Village in the northeastern part of the Nanxiong County, and the CGT-CGF Section lies south of Feng-Men-Ao Village to the southwest of the county seat. The distance between the two studied sections is less than 40 km. A total of 56 eggshell samples, identified as *Macroolithus yaotunensis*, (36 from the CGY-CGD Section and 20 from the CGT-CGF Section) were used for the stable isotopic analysis. We chose this species because it is common and widely distributed in the Nanxiong Basin. The original eggshell structure is well preserved[7,8].

The eggshell samples used in this study were selected by micromorphological method. Outer and inner layers of these selected eggshell samples were scraped off to remove extraneous carbonates, cleaned ultrasonically in distilled water, dried, and powdered. Then, the powdered samples were reacted with 103% H_3PO_4 under vacuum at 75℃. The reactant CO_2 was purified and the isotopes were measured in a MAT 251 mass-spectrometer. All samples were analyzed in duplicate with an analytical precision of 0.1‰. The results are expressed in per mil (‰) deviations from the PDB isotopic standard using the δ -notation.

2 Results and discussion

The analytical results of carbon and oxygen isotopes are listed in tables 1 and 2 and plotted on figs. 1 and 2. It can be seen that the carbon- and oxygen-isotope composition from the two studied sections shows a similar systematic variation. The $\delta^{13}C$ values from the CGY-CGD Section vary from −8.74‰ to −11.60‰, and those from the CGT-CGF Section, from −8.37‰ to −11.09‰. They oscillate within a narrow range of about 3‰. The $\delta^{18}O$ values, by contrast, vary widely from +11.43 to −7.97‰ in the CGY-CGD Section, and from +6.90‰ to −6.68‰ in the CGT-CGF Section. Both have a range of nearly 19‰ and 13‰, respectively.

Before the isotopic data are discussed, it is important to examine whether the original composition has been seriously affected by any diagenetic effects. The eggshell samples analyzed here were selected by the micromorphological method mentioned above, and have well preserved microstructures with primary calcitic growth and little or no recrystallization.

According to Yang et al.[6], samples of the carbonate rocks collected in the middle and upper part of the Pingling Formation have $\delta^{13}C$ ranges from −8.14‰ to −10.31‰ (PDB) with an average of −9.18‰, $\delta^{18}O$ ranges from −7.36‰ to −10.94‰ (PDB) with an average of −8.91‰. It can be seen that the $\delta^{18}O$ values differ from those of the eggshells in this study. This is unlikely in any significant alteration of diagenesis because such effects tend to homogenize the oxygen and carbon isotopic composition.

On the other hand, within a single egg clutch, the $\delta^{18}O$ values of eggshell samples (tables 1 and 2) are fairly constant (within ±0.5‰), indicating that the eggs were laid by a single individual. This observation also lends support to our assumption that diagenesis did not play a significant role in changing the isotopic values. On the basis of these evidences, we believe that the variation of isotopic composition of the eggshells (*Macroolithus yaotunensis*) in this investigation represents environmental change in the Nanxiong Basin where the dinosaurs lived during the K/T transition.

Table 1 Carbon and oxygen isotope composition of eggshell samples, *Macroolithus yaotunensis*, from CGY-CGD Section

Sample No.	Sampling interval/m	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O$ PDB (‰)
CGD124	158—161	−9.95	−4.80
CGD123	146—152	−10.19	−0.18
CGD122	134—142	−10.29	−7.97
CGD121	122—133	−10.57	−3.77
CGD120[a)]	110—116	−11.58±0.32	−2.97±0.21
CGD119	104—110	−11.60	+4.10
CGD118	97—104	−11.19	+0.87
CGD117	88—97	−10.22	−1.76
CGD116	82—87	−10.07	−4.61
CGD115	76—81	−10.03	+11.43
CGD114	68—76	−9.24	+6.37
CGD113	65—68	−10.17	+0.27
CGD112[a)]	63—65	−10.36±0.31	−3.07±0.31
CGD111	60—63	−10.10	−2.83
CGD110	55—60	−10.58	+4.70
CGD109[a)]	52—55	−10.46±0.34	−2.06±0.14
CGD108	45—52	−10.12	−4.85
CGD107	34—42	−9.53	−2.15
CGD105	24—34	−9.72	−3.06
CGD104	21—24	−10.65	−6.14
CGD103	10—12	−11.37	−5.37
CGD102	3—6	−9.80	−1.33
CGY210	182—186	−8.74	−3.09
CGY209	177—182	−9.88	−2.52
CGY208	171—177	−9.15	−3.18
CGY207[a)]	168—171	−8.86±0.05	−3.11±0.11
CGY206	162—168	−9.44	+2.12
CGY204	150—154	−8.89	−3.48
CGY202	144—150	−8.76	−3.11
CGY201[a)]	141—144	−9.04±0.03	−1.76±0.51

a) Mean $\delta^{13}C$ and $\delta^{18}O$ values of 2—3 eggshell samples taken from a single egg clutch, respectively.

2.1 Oxygen-isotope stratigraphy

The oxygen-isotope stratigraphy of the CGY-CGD Section (table 1 and fig. 1) shows that the Late Cretaceous values, except $\delta^{18}O$=+2.12‰ of the sample (CGY 206) from 162 to 168 m, range from −1.33‰ to −6.41‰ and average $\delta^{18}O$=−3.22‰ from 141 m of the CGY Section below and up to 60 m of the CGD Section (the base of the palynological K/T boundary interval). However, a series of positive $\delta^{18}O$ values, or sharp spike-like perturbations suddenly appears at and above the K/T boundary interval. The values are characterized by three sharp positive $\delta^{18}O$ shifts separated by two negative $\delta^{18}O$. The eggshell sample (CGD 110) from 50—60 m has a value of $\delta^{18}O$=+4.70‰. The three samples (CGD 113, CGD 114 and CGD 115) from 65—81 m have $\delta^{18}O$=+0.27‰, +6.37‰ and +11.43‰, respectively; the two samples (CGD 118 and CGD 119) from 100—110 m, $\delta^{18}O$=+0.87‰ and +4.10‰, respectively. Afterwards, the trend reverses, from 110 to 161 m that marks the contact between the Pingling Formation and the Shanghu Formation the $\delta^{18}O$ values of the eggshell samples range from −0.18‰ to −7.97‰, average $\delta^{18}O$= −3.97‰, and are very similar to the average value measured in below the K/T boundary interval.

Table 2 Carbon and oxygen isotope composition of eggshell samples, *Macroolithus yaotunensis*, from CGT-CGF Section

Sample No.	Sampling interval/m	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)
CGF415	150—153	−10.75	−5.16
CGF414	126—129	−10.97	+6.05
CGF413[a)]	99—100	−10.93±0.45	+3.47±0.10
CGF410	87—91	−11.09	−2.08
CGF407	84—87	−10.34	+5.76
CGF404	81—84	−10.42	−3.50
CGF403	71—81	−10.85	+6.90
CGF402	66—68	−10.35	−0.87
CGF401	63—66	−11.08	+3.88
CGT312	372—390	−9.83	−6.18
CGT311	349—350	−10.16	−1.89
CGT310	332—333	−9.33	−3.20
CGT309	330—310	−8.83	−1.02
CGT308	288—291	−10.14	−2.96
CGT307	273—276	−8.37	−6.68
CGT306	250—258	−9.34	−2.38
CGT305	226—234	−8.75	−2.66
CGT304	135—154	−9.82	+2.10
CGT303	111—135	−9.04	−2.55

a) Mean $\delta^{13}C$ and $\delta^{18}O$ values of 2 eggshell samples taken from a single egg clutch.

The oxygen isotope record in the CGT-CGF Section (table 2 and fig. 2) is quite similar to that of the CGY-CGD Section mentioned above. The oxygen-isotope compositions of the sequential samples below the K/T boundary interval (CGT Section) range from −1.02‰ to −6.18‰, excepting the $\delta^{18}O$=+2.10‰ of the sample (CGT 304) from 135—154 m. In the CGF Section, however, the oxygen isotopic compositions are also characterized by multiple positive $\delta^{18}O$ perturbations from 63—129 m (at and above the K/T boundary interval).

It is interesting that the erratic behaviour of $\delta^{18}O$ values at and near the K/T boundary interval seems to have coincided with the anomalous concentrations of iridium enriched in the dinosaur eggshells. Zhao et al.[1] reported that three iridium spikes have occurred in 52—110 m of

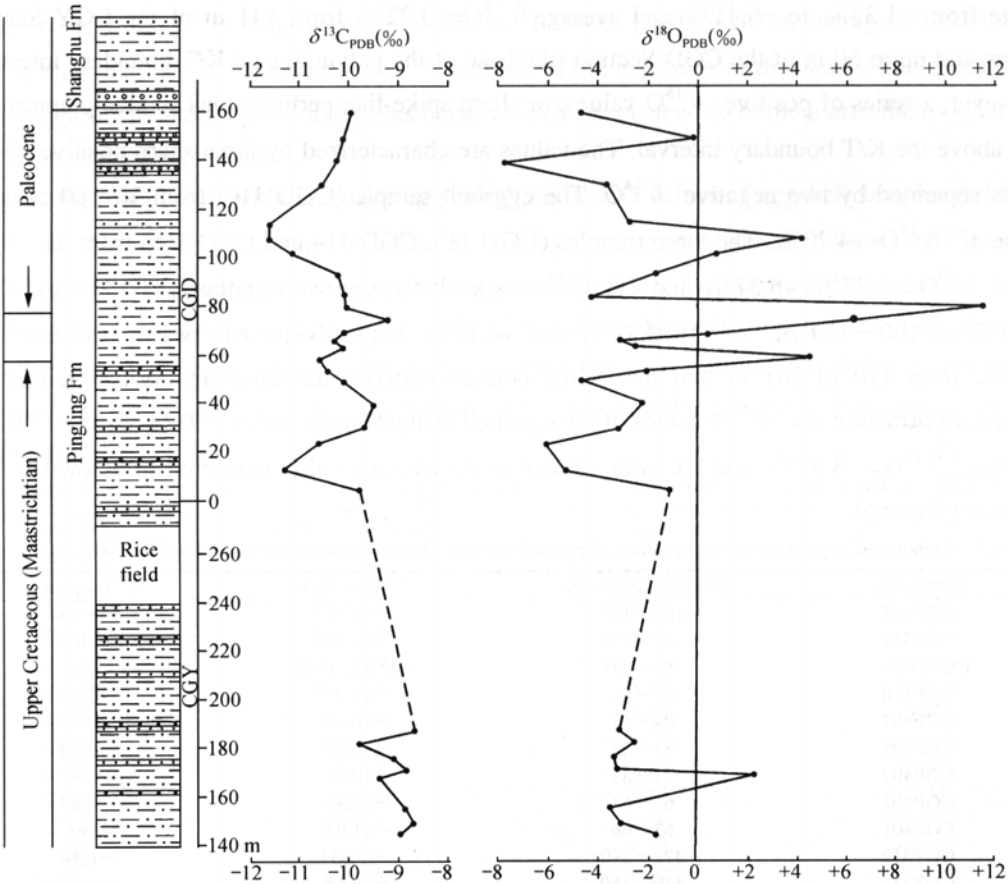

Fig. 1. Range of carbon- and oxygen-isotope of eggshells in CGY-CGD Section of the Pingling Formation in Nanxiong Basin.

the CGD Section. This coincidence indicates that drastic environmental changes occurred in the Nanxiong Basin during the K/T transition.

Folinsbee et al.[9] established first in a controlled feeding experiment an almost linear correlation between the $\delta^{18}O$ of water ingested by the species and that of corresponding eggshell carbonates. Erben et al.[10] subsequently verified this correlation by more measurements on modern eggshells from different parts of the world and tried to see the effect of mean annual air temperature on the $\delta^{18}O$ of the eggshells. Recently, in studying the carbon- and oxygen-isotope compositions of dinosaur eggshells discovered in the Kheda district, India, Sarkar et al.[11] further refined the correlation between the $\delta^{18}O$ of eggshells and mean annual air temperature, as shown in fig. 3. The $\delta^{18}O$ values of the eggshells in this study display a wide range. From a projection of these plots onto the temperature scale of fig. 3 most of them can be located in a range of mean annual air temperature about 22 to 27.6℃ except those higher positive values. This range is slightly lower or close to the temperature range of 26.66—33.95℃ calculated by Yang et al.[6] based on

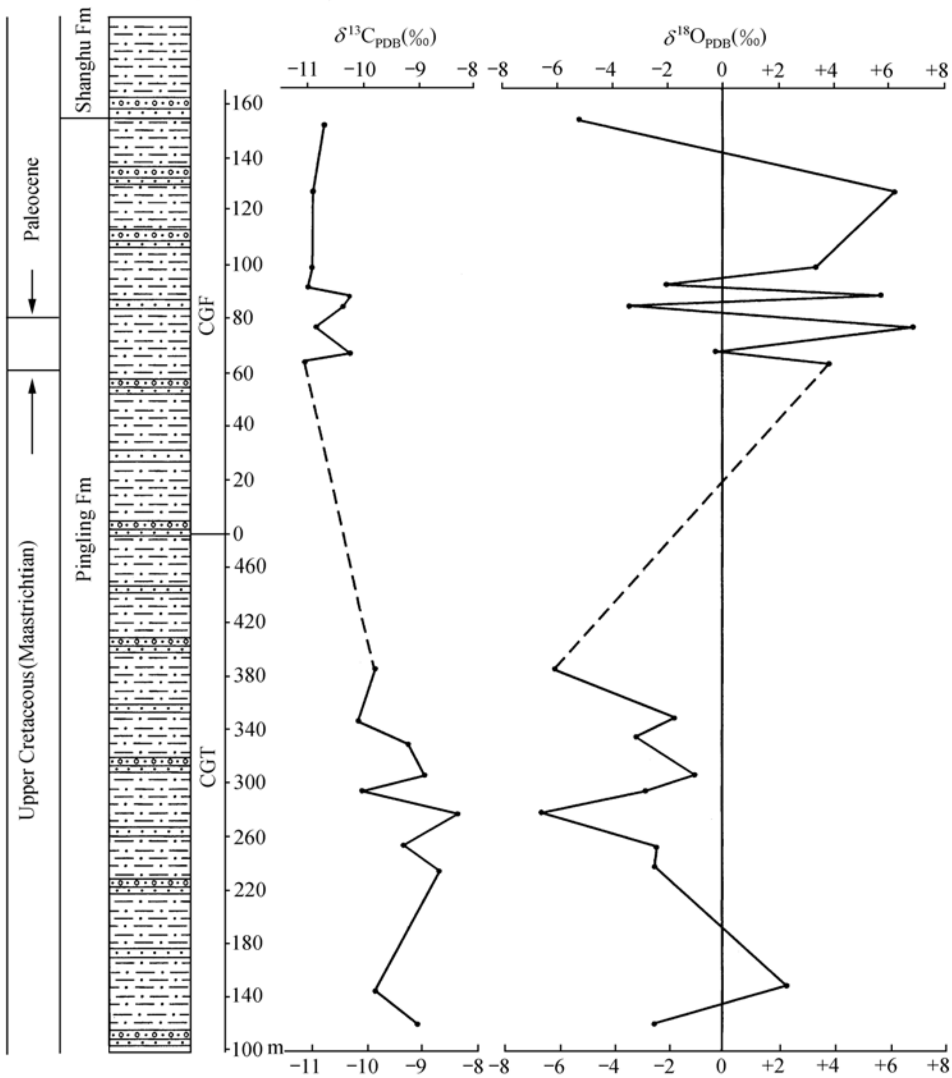

Fig. 2. Range of carbon- and oxygen-isotope of eggshells in CGT-CGF Section of the Pingling Formation in Nanxiong Basin.

the $\delta^{18}O$ of the carbonate rocks from the middle and upper part of the Pingling Formation.

It is notable, however, that the $\delta^{18}O$ values of the eggshells at and above the K/T boundary interval show a sudden increase and go beyond the given temperature range of fig. 3. This would imply an abnormally large change of temperature during the K/T transition time in the Nanxiong Basin. But the $\delta^{18}O$ values of the eggshells are directly related to the $\delta^{18}O$ values of water supply to the animals, as mentioned above. It is well known that the $\delta^{18}O$ of precipitation at a given place is not only controlled by the ambient temperature but by other factors, such as dynamically isotopic fractionation of local evaporation processes. According to Erben et al.[10], extant ostrich from a very dry natural environment in Africa must live on highly evaporated water at low latitudes. Their eggshell has a value of $\delta^{18}O$=+7.1‰ and the local mean annual air temperature is estimated

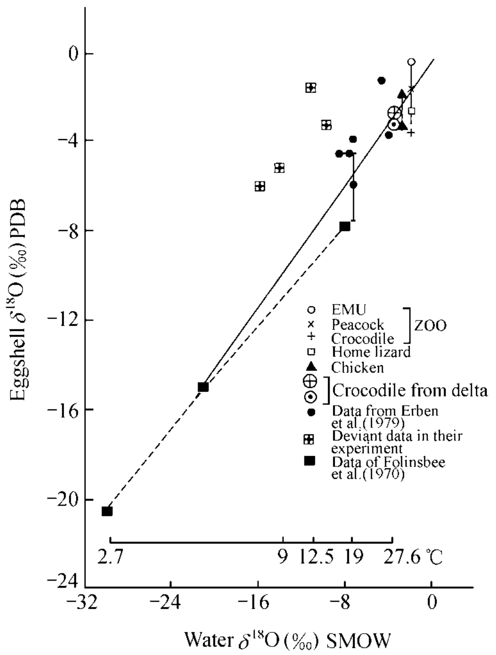

Fig. 3. Plot of δ^{18}O values of eggshell samples from modern birds and reptiles vs. δ^{18}O of local water and the mean annual air temperature (after Sarkar, A., Bhattacharya, S. K., Mohabey, D. M., 1991).

at above 30℃. The crocodile from the Nile River has δ^{18}O=+2.5‰, indicating evaporated water at an average air temperature above 25 ℃. The heavier oxygen in the eggshell also indicates a drier environment with a higher rate of evaporation besides the effect of temperature. Therefore, it seems reasonable to consider that unusual increases of δ^{18}O in the eggshells at the K/T transition time could be associated with the dinosaurs who consumed highly evaporated water, and to estimate that there may have been at least three periods of very dry climate with a mean annual air temperature of above 27℃.

The sedimentation rate of the red beds in the Nanxiong Basin is estimated at about 40 cm/ka[2] so the time span of the multiple positive δ^{18}O perturbations, spanning the interval of 55—110 m in the CGD Section and of 63—129 m in the CGF Section respectively, represents about 150 ka.

2.2 Carbon-isotope stratigraphy

Before making final conclusion on the basis of the carbon isotopic compositions, the origin of carbon in eggshell has to be explained. The available data [10,11] indicate that the δ^{13}C of the eggshell carbonate is primarily determined by the ^{13}C / ^{12}C ratio of the diet of the egg-laying animal modified by physicochemical fractionation due to metabolism. It is well known that most modern plants can be classified into three categories[12,13]: C_3 plants (δ^{13}C values vary between −20‰— −35‰, average −26‰), C_4 plants (δ^{13}C values, between −7‰— −15‰, average −12‰), and CAM plants (δ^{13}C values between −10‰—−22‰, average −16‰) on the basis of their different photosynthetic pathways, which yields characteristic carbon isotope signatures. Recent studies [11,14,15] have shown that the ^{13}C / ^{12}C ratios in the eggshell carbonate are enriched by about 16‰ relative to that of the food material. Therefore, the δ^{13}C of the food can be deduced from that of the eggshell and can be used to infer the predominance of one plant type over the other in the food of the dinosaurs.

The δ^{13}C values of the eggshells from CGY-CGD Section range between −8.74‰ and −11.60‰, with a spread of about 3‰ (table 1). Eggshells from CGT-CGF Section have similar

$\delta^{13}C$ values (between −8.37‰ and −11.09‰) (table 2). Such uniformity in $\delta^{13}C$ of the two studied sections reflects a preference for similar types of vegetation as diet for the dinosaurs represented by this type of eggshells. Considering a metabolic enrichment of 16‰ as mentioned above, the $\delta^{13}C$ values of −8.37‰—−11.60‰ of the dinosaur eggshells would indicate plant species of C_3 type having $\delta^{13}C$ of −24.3‰—27.6‰ as the main diet source.

It is notable, however, that there is a trend toward relative depletion of $\delta^{13}C$ from lower to upper horizons. The $\delta^{13}C$ values of the eggshells sampled from 141 m of the CGY Section below and up to 6 m of the CGD Section vary between −8.74‰ to −9.88‰, with an average of −9.17‰, whereas $\delta^{13}C$ values from 10 m below and up through the K/T boundary interval to 161 m of the CGD Section have the range of −9.24—−11.60‰ with an average of —10.38‰. This indicates a relative depletion in an average of 1.2‰. In the CGT-CGF Section, the $\delta^{13}C$ values of eggshells from the sequence of CGT Section have an average of −9.36‰, and those from the sequence of the CGF Section have an average of −10.75‰, indicating a relative depletion in $\delta^{13}C$ value of 1.4‰. The trend from heavier to lighter carbon in eggshells sampled from Upper Cretaceous to Lower Paleocene horizons could indicate the change in the ^{13}C / ^{12}C ratio in the plant species of C_3 type as main diet source for the dinosaurs.

The $\delta^{13}C$ in plants may represent CO_2 concentration in air and change in δ_a[16−18]. For example, $\delta^{13}C$ in the plant species of C_3 type growing in a condition of high CO_2 concentration is over −27‰[19]. Recently, Penuelas and Azcon-Bieto[20] measured $\delta^{13}C$ of herbarium specimens of 12 C_3 plants collected during the last 3 centuries in Catalonia, an area with a Mediterranean climate, and found an overall decrease of average $\delta^{13}C$ in the 12 C_3 plants from −25.8‰ in 1750 to −26.4‰ in 1988, and in the same periods the $\delta^{13}C$ value, δ_a, in the atmosphere has decreased from −6.4‰ to −7.9‰, indicating a significant correlation between the changes in $\delta^{18}C$ of the 12 C_3 plants and increase in the atmospheric CO_2 concentration. A study on the carbon isotope ratios in the tree rings of *Pinus massoniana* growing in the Dinghuashan, Guangdong Province, a Subtropical Nature Biosphere Reserve by Lin et al.[21] has also shown that the yearly variation rate of $\delta^{13}C$ value in the growth rings of the tree is modified with an increasing component of ^{13}C-depleted CO_2, released into the atmosphere by increasing fossil fuel combustion. Therefore, it seems logical to reason that the trend toward more negative $\delta^{13}C$ values of the eggshells in the two studied sections could be an indirect consequence of a lasting increase in CO_2 concentration in air during the K/T transition. This seems to agree with the model developed by McLean[22−24] who proposed that CO_2-induced greenhouse warming was caused by the Deccan Traps volcanism in India during the K/T transition.

Acknowledgements The authors would like to thank Prof. Lin Zhifang of South China Institute of Botany, Chinese

Academy of Sciences for her discussions and suggestions.

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