Determination of arsenic in dinosaur skeleton fossils by hydride generation atomic fluorescence spectrometry

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Abstract

Hydride generation atomic fluorescence spectrometry was for the first time utilized to determine trace toxic element arsenic in the skeleton fossils of four dinosaurs unearthed in Sichuan Province of China. The instrumental limit of detection (LOD) for arsenic was 0.03 μg/L under optimal experimental conditions, which compared favorably to that by ICP-AES and ETAAS. The samples were digested with aqua regia in boiling water bath. The recoveries of standard addition were found to be from 97 to 109%, and the analytical results were found in good agreement with those by ICP-AES. It is a simple, reliable, sensitive yet relatively inexpensive analytical method, compared to ICP-AES, ICP-MS or ETAAS. Interesting analytical results were found that the arsenic concentrations were all abnormally high in the skeleton fossils. The established analytical method and the analytical results may be helpful in revealing the mystery of the mass extinction of the dinosaur fauna. The analytical results, together with other data available to date, supported the argument that the arsenic toxicosis could be a contributing factor for the mass extinction of the dinosaur fauna in Sichuan Province of China.

1. Introduction

Besides eleven major elements, hydrogen, carbon, nitrogen, oxygen, phosphorus, sulfur, calcium, potassium, magnesium, sodium and chlorine, there are more than 50 trace elements in organisms [1]. Albeit low concentration levels, these trace elements are especially important for the growth, health and death of organisms. Trace elements in living organisms are frequently determined by various sensitive atomic spectroscopic methods. In recent years, some scientists have also studied the chemical composition of animal fossil samples, for example, dinosaur skeleton fossils, by different means in order to obtain the information of the ancient living environment and to trace the story behind the extinction of the dinosaur fauna. The content of trace elements in the skeleton fossil of a dinosaur could represent or correlate to that of the dinosaur when it was alive. Therefore, the investigation of the composition of trace elements in the skeleton fossil of a dinosaur and the adjoining rock would provide important evidence to elucidate the reasons for the mass extinction of dinosaurs. In 1980, Alvarez et al. [2] determined the trace elements of the layer of clay between Cretaceous and Tertiary by instrumental neutron activation analysis (INAA) and found out that the concentrations of iridium, cobalt, nickel, arsenic and antimony were much higher than those in the adjoining deposit rock. In 1993, Zhang et al. [3] measured trace elements, also by INAA, in the Jurassic dinosaur bones found in Dashanpu, Sichuan Province of China, and found extraordinarily high concentration of uranium in the fossil. In 1994, inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) were used for the determination of 31 elements in the fossils of dinosaur eggs, and the concentrations of iridium as high as the 10^{-6} level were found in the shells of the eggs [4]. The ICP-based

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techniques have the advantages of high sensitivity and multi-element capability, but their instruments and running cost are expensive. In 1998, INAA was applied by Li et al. [5] to study the composition and content of the trace elements in the skeleton fossil of a dinosaur and the adjoining rocks found in Guangyuan, Sichuan Province. They concluded that the toxicosis was caused by the abnormally high content of arsenic and barium and the abnormally low content of the antidotal element zinc in the dinosaur, and this could have led to the mass death of the dinosaur fauna. In the same year, they also determined the trace elements in the skeleton fossil of a dinosaur and the adjoining rocks from another spot, Kaijiang, Sichuan Province with the same INAA technique [6]. The analytical results showed that the abnormally high concentration of arsenic, cadmium and rubidium and the abnormally low concentration of zinc could have endangered the life of the dinosaur. When INAA is used, however, it is a prerequisite that the samples be radiated in a nuclear reactor with a high flux of neutron radiation, and it could take a long time to cool down the samples. In addition, it should be noted that the analytical results mentioned above are not compared with those obtained by other analytical methods, nor is the accuracy validated by the analysis of standard reference materials of dinosaur fossils since they are not available in the market.

In the determination of trace arsenic in real samples, various atomic emission spectrometric and atomic absorption spectrometric techniques are used frequently. Among these real samples, bone samples have similar matrix to a skeleton fossil. X-Ray fluorescence spectrometry (XRF) is a promising non-invasive method for the analysis of bone for lead, although some problems still remain [7,8]. Electrothermal atomic absorption spectrometry (ETAAS) is a good choice for this purpose. For example, Zong et al. [9] successfully measured the content of lead in various bone samples. The bone sample was digested in concentrated nitric acid by microwave or in room temperature, and then measured by an ETAAS instrument equipped with Zeeman-effect background correction. The method was accurate, fast, simple and convenient for bone-lead studies. In the course of determination, ammonium dihydrogenphosphate ($NH_4H_2PO_4$) was used as a chemical modifier, which also made the determination matrix matched for reliable analytical results. However, XRF and ETAAS are relatively expensive, or may not be sensitive enough for the determination of arsenic elements in these samples due to the complex matrix.

Hydride generation atomic fluorescence spectrometry (HG-AFS) has many advantages, compared to methods such as ETAAS [10], ICP-AES [11], ICP-MS [12] and XRF [13], when used for the single element determination of arsenic. Firstly, the analyte element is separated from mass matrix and enriched; secondly, this method is fast and easy to operate; thirdly, it is convenient and relatively inexpensive; and fourthly, it is more sensitive compared to ETAAS, ICP-AES and XRF. Therefore, HG-AFS has been widely used for the determination of arsenic in many fields, such as geochemistry [14–16], environmental science [17], food science [18], biology [19], and the like. The mechanism involved and the interferences occurring during the formation and the atomization of the hydride species have been well documented in the literature [20–22]. As early as 1968, the atomic fluorescence spectrometry for arsenic determination was thoroughly studied by Dagnall et al. [23], with an electrodeless discharge lamp as the excitation source. In 1969, Holak [24] first used hydride generation for sample introduction to atomic absorption spectrometry for the determination of arsenic, and later in the 1970s hydride generation was combined to atomic fluorescence spectrometry [25–28]. Nowadays, HG-AFS is successfully commercialized, and the sensitivity is greatly improved. For example, it offers an alternative sensitive way for arsenic determination at trace and ultratrace levels with a LOD of 0.05 ng/ml for As [29] in water samples. Shi et al. [30] reported an analytical procedure for determination of As (III) and As (V) in soils using sequential extraction combined with flow injection-HG-AFS. The detection limit (3σ) for As(III) and As(V) were 0.11 μg/L and 0.07 μg/L, respectively. A commercially designed automatic flow injection automatic vapor accessory hydride generator together with a commercial AFS system for mercury has been modified and used for arsenic and selenium measurements [31]. More than 200-time enhancement of sensitivity was achieved with a new flow injection-HG-AFS system, and the detection levels of a few parts per trillion for selenium and arsenic were achieved without a preconcentration stage [32]. Feng and Fu [33] proposed a simple and rapid method for the determination of arsenic, antimony, selenium, tellurium and bismuth in nickel metal by HG-AFS. The five elements were coprecipitated simultaneously with lanthanum hydroxide and separated quantitatively from a nickel matrix and other interfering elements prior to the determination. The LOD for arsenic in samples was 0.10 μg/g. Curtius et al. [34] determined arsenic in sediments, coal, and fly ash slurries after ultrasonic treatment by HG-AAS and trapping in an iridium-treated graphite tube. After grinding the samples to a particle size of ≤50 μm, the sample powder was mixed with aqua regia and hydrofluoric acid in an ultrasonic both for 30 min. The LODs for arsenic in the samples were 0.5 and 0.7 mg/g for the coal and sediment samples, respectively. Hydride generation and atomic fluorescence have also been used in arsenic speciation [35], for example, HG-AFS was employed in arsenic speciation in contaminated soils after liquid chromatographic separation [36] distillation separation [37]. With a multisyringe flow injection
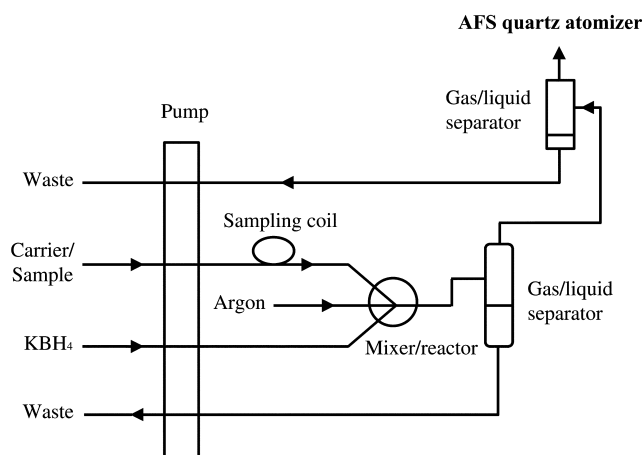
Fig. 1. A schematic diagram of the intermittent hydride generator.

system, a sample throughput of 36 samples/h was achieved by Semenova et al. [38].

In this paper, we report the determination of trace arsenic in the skeleton fossils of four dinosaurs found in Sichuan Province of China, in an attempt to establish a new, simple, reliable, sensitive and yet relatively inexpensive method for the determination of arsenic in fossil samples and to accumulate more data which may be helpful in revealing the mystery of the mass extinction of dinosaurs.

2. Experimental

2.1. Instrumentation

A commercial atomic fluorescence spectrometer (Model AFS-2202, Beijing Haiguang Instrument Co., Beijing, PR China) was used for the whole experiment described in this paper. The instrument can work in a simultaneous two-channel mode or one channel mode. The light source is coded hollow cathode lamps (HCLs), i.e. two HCLs are pulse-powered alternatively, providing narrow line, pulsed, and strong atomic emission radiation of analyte elements for the excitation of the respected atomic fluorescence. A hydride-generator is used to generate the hydrides of analyte elements, and the hydrides are introduced to a quartz atomizer with an argon flow. The argon together with the hydrogen produced from the hydride-generation reaction is ignited with an electrically heated wire to form an argon–hydrogen flame in the quartz atomizer for the atomization of the hydrides. The light beams from the HCLs were focused on to the quartz atomizer for the excitation. The resultant atomic fluorescence is focused on to a photomultiplier tube (PMT), via a non-dispersion optical system, followed by the amplification of electric signal and data processing with a personal computer. This commercial HG-AFS instrument is good for the routine measurement of 11 elements, i.e. arsenic, antimony, bismuth, mercury, selenium, tellurium, tin, germanium, lead, zinc and cadmium. Usually, $NaBH_4$ or KBH_4 is used as a reducing reagent to produce the hydrides of analyte elements. However, a special reducing reagent is required for the measurement of zinc and cadmium. The hydride generation system is a manufacturer-designed, computer-programmable, intermittent hydride generation reactor, as shown in Fig. 1. The optimized instrumental conditions for the measurements were listed in Table 1. Standard series (50 μg/L, 100 μg/L, 150 μg/L, 200 μg/L, 300 μg/L and 400 μg/L, respectively), in the medium of 5% aqua regia, were prepared by step-dilution of a stock arsenic standard solution of high concentration. All the chemicals were of analytical grade or better. KBH_4 solution was prepared daily prior to use. Sub-boiled de-ionized water was used for cleaning and dilution.

An ICP-AES instrument (Iris Advantage, Thermo Jarrell Ash Corporation, Massachusetts, USA) was used for the determination of arsenic in these samples for the comparison with the analytical results obtained by HG-AFS. The major instrumental parameters are: power

Table 1
The optimized major experimental conditions for the instrumental measurements

Element	Medium	KHB_4 (g/L)	Negative voltage (V)	Lamp current (mA)	Gas carrier (ml/min)	Observation height (mm)
As	5% aqua regia	20	300	30	400	10

Working conditions for the auto-sampler and hydride generator

Procedure	Rotate speed (rev./min)	Time (s)	Repetition time	Reading
0	70	7	1	N
1	0	5	1	N
2	110	14	1	Y
3	0	5	0	N

Table 2
The major elemental composition of the samples obtained by EDAX

Sample	Element (%)					
	O	Si	Ca	P	Mn	Fe
Adjoining rock	69	19	8	0.18	0.7	2.5
Skeleton fossil	53	3	27	16	–	–

1150 W; sampling rate 2.0 ml/min; nebulizer pressure 27 PSI; integration time 20 s; analytical lines 189.0 nm and 197.2 nm; and the two-line scheme was used for the background correction.

2.2. Sample digestion

The four samples are from the skeleton fossils of four dinosaurs dug from Anyue, Kaijiang, Guangyuan, and Jianyang counties of Sichuan Province of China. The samples were carefully taken and grounded into fine powder. The samples were digested in the following procedures: approximately 0.5 g of the samples were accurately weighed into 25 ml test tubes, and digested with 10 ml of aqua regia. The test tubes were heated in boiling water for 2 h. During the course of heating, the test tubes were shaken for two to three times. When cooled, the solutions were then quantitatively transferred to 25 ml volumetric flasks and diluted to the scale. While the skeleton fossils were almost completely dissolved, silicate residue was observed in the sample solutions of the adjoining rock. Before the instrumental measurements, the media of sample solutions were converted to approximately 5% aqua regia. The same sample digestion procedure was used for both the HG-AFS and ICP-AES measurements.

3. Results and discussion

3.1. Identification of the sample matrix composition and the choice of sample digestion method

EDAX spectra were used for the identification of the major matrix composition of the fossil samples. The fossil sample from Anyue was chosen for the test. The major composition of the skeleton fossil was found very different from the adjoining rock. As it was shown in Table 2, the major composition of the fossil was calcium phosphate (approx. 80%) as expected, while the adjoining rock was mostly silicate/silica (more than 80%). Fig. 2 shows the EDAX photos of the powder samples. Fig. 2a is the adjoining rock sample showing the silicate/silica particles, and Fig. 2b is the fossil sample showing the fine loosen calcium phosphate matrix.

For the determination of arsenic in solid samples, the sample treatment often involves wet-oxidation [39],

solvent extraction [40] or dry-ashing [41,42]. Aqua regia system is widely used for the measurement of arsenic in solid samples. Hot aqua regia totally decomposes sulfides, trioctahedral micos, clay minerals and amorphous compounds [43]. Aqua regia has also been used for the digestion of injectable drugs prior to arsenic determination by HG-AAS [44]. In order to simplify the sample preparation procedure, only a partial extraction with acids, such as aqua regia, is frequently preferred, which, however, does not assure a quantitative recovery of the analyte [45]. However, in spite of the fact that aqua regia does not extract the total metal content, the obtained results are very close to those reported as certified values, except for one Certified Reference Material (BCR320). In our experiments, considering the high silica/silicate content in the adjoining rock, HF–HNO_3–$HClO_4$ system was also tested for decomposing the samples. However, this system was found no significant difference from the aqua regia system in terms of analytical results (i.e. accuracy and precision). This means that arsenic is probably not part of the silicate or silica crystal lattice. To avoid the use of hydrofluoric
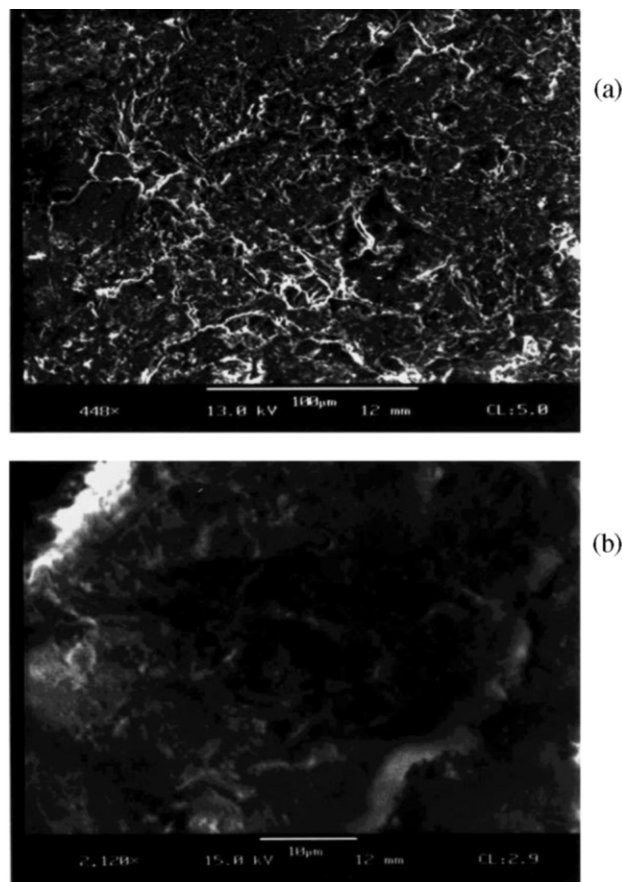

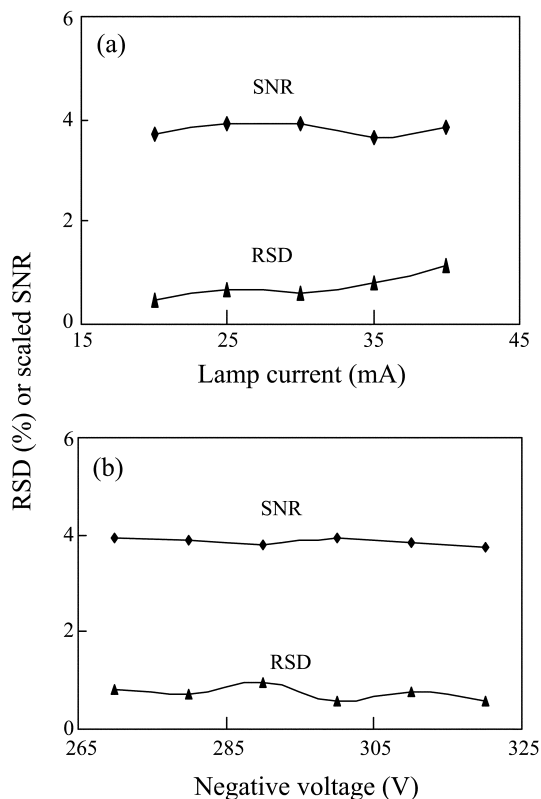Fig. 2. EDAX Photos of the adjoining rock and the fossil unearthed from Anyue County of Sichuan Province.

Fig. 3. The effect of the lamp current and the negative voltage for the photomultiplier tube on the SNR and R.S.D. of the measurements of the arsenic fluorescence signal.

Fig. 4. The effect of the concentration of aqua regia on the SNR and R.S.D. of the measurements of arsenic fluorescence intensity (*FI*).

acid, aqua regia system was chosen for the digestion of the samples throughout the rest of the experiments.

3.2. Optimization of experimental conditions

The optimized negative voltage and the lamp current were obtained by observing the change in atomic fluorescence intensity, the signal-to-noise ratio (SNR) and relative standard deviation (R.S.D.) as the negative voltage or the lamp current increased. As expected, the atomic fluorescence intensity increased as either the negative voltage or the lamp current increased. However, the noise level also increased at the same time. The results indicated that the negative voltage and lamp current of 300 V and 30 mA, respectively, would ensure the best SNR and R.S.D., as shown in Fig. 3. The flux of carrier gas affects the concentration of the free atoms generated in the atomizer. The flux of the carrier gas within the range of 400–600 ml/min was acceptable in terms of the R.S.D. and SNR, with an optimal flow rate at 400 ml/min. The optimal height of observation, 10 mm, was also determined for the best SNR and R.S.D.

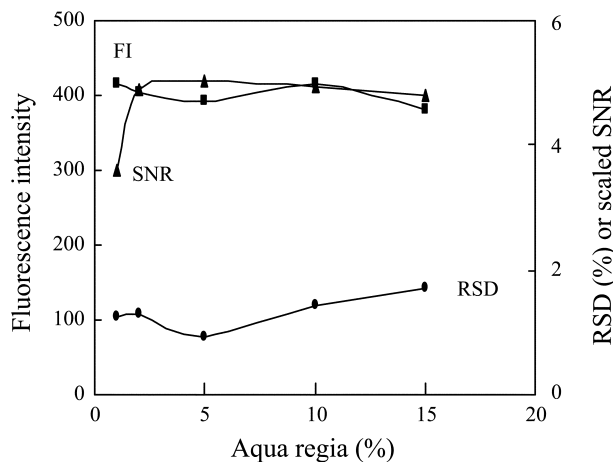To optimize the amount of reducing reagent, experiments were carried out using different concentrations of KBH_4. Both the fluorescence signal and SNR were steady in the range of 10–25 KBH_4 g/L, and 20 KBH_4 g/L was chosen for use. Finally, the effect of the concentration of aqua regia on the arsenic determination was also investigated, as shown in Fig. 4. It can be seen from Fig. 4 that the fluorescence signal was steady in the concentration range of 1–15% aqua regia. When the concentration of aqua regia was higher than 2%, the SNR would not change significantly. Therefore, 5% of aqua regia was chosen as the media of analyte solutions for ease and safety of operation.

3.3. Calibration curves and instrumental limits of detection (LODs)

The calibration curves (at least five points) were routinely constructed for arsenic (50–400 μg/L) with a correlation coefficient of at least 0.998. The LOD (3-σ) was obtained by 16 measurements of a blank solution. As shown in Table 3, the LOD for arsenic was 0.03 μg/L. This compared favorably to those by ICP-AES and ETAAS, and it was inferior to but within five times of the LOD for arsenic by ICP-MS. It should be noted that the LOD was obtained by using a much simpler and inexpensive HG-AFS instrument, compared to any of the commercial ICP-AES, ICP-MS or ETAAS instruments. However, the absolute LOD is 15 pg, considering the sampling volume of approximately 0.5

Table 3
Instrumental LOD for arsenic by HG-AFS in comparison with those by ICP-AES, ETAAS and ICP-MS (unit: μg/L)

HG-AFS	ICP-AES	ETAAS[*]	ICP-MS
0.03	50	0.5	0.006

[*] Assuming 20 μL sample volume; The LODs for comparison are taken from The Guide to Techniques and Applications of Atomic Spectroscopy, Perkin Elmer, 1997, p5.

Table 4
The analytical results of the samples for arsenic by HG-AFS in comparison with those by ICP-AES* (unit: μg/g)

Sample origin	Sample	$A \pm 3$ S.D. (n)* By HG-AFS	$A \pm 3$ S.D. (n)* By ICP-AES
Anyue	Adjoining rock	13±3 (3)	12±4 (3)
	Fossil	40±3 (6)	39±9 (6)
Kaijiang	Fossil	73±7 (6)	77±18 (6)
Guangyuan	Fossil	26±5 (6)	23±7 (6)
Jianyang	Fossil	85±5 (6)	92±10 (6)

* $A \pm 3$ S.D. (n) = Average $\pm 3 \times$ S.D. (number of measurements).

mL. This absolute LOD is equivalent to that by ETAAS, but HG-AAS obviously consumes a larger sampling volume.

3.4. Accuracy of the proposed analytical method

The accuracy of the proposed method was first validated by use of two geological reference samples (i.e. Chinese National Standard Reference Materials, GBW07310 and GBW07108) of similar matrices since no exact fossil reference samples were available. The arsenic concentrations for the two samples were 25 μg/g and 4.7 μg/g, respectively. The analytical errors were within 10%. In addition, recoveries of standard addition were found in the range of 97–109% for the fossil samples (for example, 103%, 109%, 101%, and 102% for Anyue, Kaijiang, Guangyuan, and Jianyang fossils, respectively). The accuracy of analytical results of the fossil samples was furthered confirmed by ICP-AES (Table 4).

3.5. Analytical results of arsenic in fossil samples and their implication

The analytical results for arsenic for the four fossil samples and one adjoining rock were listed in Table 4. The analytical results were in good agreement with those by ICP-AES. In the adjoining rock sample, the concentration of arsenic was found at a normal level. However, the content of arsenic in the fossil was abnormally high, three times as high as that in the adjoining rock, for the Anyue dinosaur fossil. This means that the arsenic toxicosis could be a factor for the mass extinction of the dinosaur fauna. This finding was consistent with the arsenic concentration in the other three dinosaur fossils, although the respected adjoining rock samples were not available. This reasoning is based on the fact that the common concentration of arsenic in sedimental rocks is only approximately 1.0 μg/g. These analytical results are also consistent with those by other analytical techniques: the concentration ranges of arsenic in the dinosaur fossils found in Guangyuan, Zigong and Kaijiang have been reported

for 10.1–28.7, 13.5–41.7 and mostly approximately 100 μg/g, respectively [46]. By comparison with the arsenic concentration of 4632 μg/g in the siliceous wood fossil found in Zigong [46], it might be reasonable to speculate that the arsenic in the dinosaur fossils was accumulated from some plants dinosaurs took in as food when they were alive.

4. Conclusion

A simple, sensitive yet relatively inexpensive method was proposed for the determination of arsenic in dinosaur skeleton fossils. The concentrations of arsenic in the fossils were abnormally high (25–86 times higher than the normal arsenic concentration in sedimental rocks). In summary, the presently available data show that the arsenic concentrations in dinosaur fossils are 10–100 times higher than the common concentration of arsenic in sedimental rocks. Therefore, the arsenic toxicosis could be an important contributing factor for the mass extinction of the dinosaur fauna in Sichuan, PR China. However, it is too early to make such a general conclusion for the worldwide dinosaur fauna because it remains unsolved whether the arsenic concentrations are also abnormally high or not in other dinosaur fossils found in other areas worldwide. Although it would take one's enormous efforts to collect the relevant samples worldwide and carefully analyze them, it may be helpful to provide such data in revealing the mystery of the mass extinction of the dinosaur fauna.

Acknowledgments

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