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# Concentrations of "elemental carbon" in samples from the Peking Man Site at Zhoukoudian and the possibility of their application in the development of evidence for the use of fire by humans

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Abstract "Elemental carbon" (EC) is a C-rich, O-H-S-Ndepleted substance that is necessarily produced in the process of combustion. Due to the long-term use of fire by cave-inhabiting ape-men, considerable amounts of "elemental carbon" would be necessarily left behind in the corresponding strata inside the cave. The separation of EC was effected by the chemical method and the contents of carbon were determined on an element analyzer and a self-made measuring system. The concentrations of EC in the hearth, the exhibited ash samples collected from near the hearth unearthed in the 1930s, and the three samples of accumulated material collected from the tenth bed are 43.74%, 1.77%, 3.88%, 1.87% and 1.11%, respectively; those of the equivalent samples from the tenth bed outside the cave and samples from the fourth and seventh beds are at least one order of magnitude lower than the former's. The above results show that the sampling location of the tenth bed may be close to the hearth. Sampling over a wider range may lead to the finding of a location where the concentrations of EC are corresponding to the maximum values of EC in the hearth. The determination and study of EC may provide new evidence for the use of fire by Peking Man.

Keywords: Zhoukoudian, Peking Man, fire, element carbon.

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Since the 1920s, a number of paleoanthropologists

and archaeologists have discovered, in succession, apeman fossils and large quantities of stone artifacts in the Longgushan Cave at Zhoukoudian in the southwestern suburbs of Beijing. Since the 1930s, considerable abundant traces of fire use by ape-men have also been discovered in the same region. In 1931 D. Black wrote an article on the basis of his experimental results, indicating that the cave deposits found in the tenth bed in the first location of Zhoukoudian did contain free carbon<sup>[1]</sup>. On this basis the history of use of fire by humans can be shifted forwards to about 500000 a BP. In the last few years Israelite scholars Steve Weinter et al.<sup>[2-4]</sup> have published research papers, launching challenges against the evidence for the in-situ use of fire by Peking Man. They found stone artifacts and fire-burnt bones in the tenth and fourth beds of the first location at Zhoukoudian, and the proportion of burnt bones of big and small animals is just like what was encountered in the affirmed young caves where fire had been used by humans. However, they emphasized that neither ash or residual wood charcoal nor sufficient amounts of siliceous aggregates that must be produced in the process of combustion had been found, and they had also observed the depositional characteristics of low-energy water environment. It is thus concluded from the above discussion that the aforementioned burnt bones and stone artifacts are hard to confirm as the *in-situ* remains. Only indirect, but no direct, evidence for the *in-situ* use of fire by Peking Man has been found at Zhoukoudian. The paper of Weiner et al. aroused great response and Chinese specialists and scholars held a special symposium on this issue<sup>[5]</sup>. In his paper<sup>[6]</sup> Wu Xinzhi pointed out that it is not wise to ignore previous findings and achievements in their discussion (Weiner et al.) on the problem of *in-situ* use of fire by Peking Man and they have not acquired sufficient evidence for their conclusion that the burnt bones and stone artifacts were transported by moving water to the cave. It is hard to make people believe their conclusion drawn merely on the basis of the analytical results for the limited cave deposits by the research group led by Weiner. The problem of in-situ use of fire by Peking Man at Zhoukoudian has again become a focus of debate in the global academic circles.

The authors of this work consider that other "clues" would be left behind in the history of fire. With the continuous progress and development in science and technology, more light will be shed on these "clues". The so-called "Elemental carbon" (EC) is considered as one of the clues to the *in-situ* use of fire by humans. "Elemental carbon" is an abbreviated name for a kind of C-rich, O-H-S-N-depleted substance produced in the process of combustion, and it usually embraces charcoal, soot, fusain, microcrystalline graphite, carbon black, etc. Charcoal is the product of incomplete combustion of plant tissues, belonging to amorphous inorganic compounds and it can be well preserved in sediments. Charcoal can be generally

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picked out directly by naked eyes or with the help of a microscope. The "elemental carbon", which is an indicator of the occurrence of historical fire, can not only be acquired from marine sediments, but also from terrestrial-facies accumulated materials. In most cases the "elemental carbon" is present in the dispersed form and is hard to observe under a microscope, but it can be separated and enriched by physical and chemical approaches. In case that various kinds of fire (including natural fire, artificial fire) can lead to the serious destruction of plant patterns, bring about a great influence on regional or even global climatic changes, scientific workers started earlier to study how to reconstruct the history of fire using "elemental carbon" as an indicator of fire<sup>[7]</sup>. The authors once conducted research on the relations between the history of big fire and palaeo-climate in the arid and semi-arid regions of China<sup>[8]</sup>. The method of separating "elemental carbon" has been further perfected with the deepening of the study of fire history<sup>[7,8]</sup>. The long-term use of fire by</sup> cave-inhabiting Peking Man would have left considerable amounts of "elemental carbon" in the cave deposits in the corresponding strata within the cave. Taking the cave deposit samples collected from the fourth, seventh and tenth beds of the first location at Zhoukoudian, samples from the outside of the cave and the ash samples unearthed in the 1930s, now on exhibition at the Peking Man Site Museum as the objects of study, the authors of this paper determined the abundance of "elemental carbon" and carried out a comparative study so as to explore the distribution characteristics of "elemental element" and their possible application prospects in developing evidence for the use of fire by ape-men.

### **1** Sample collection

Three cave deposit samples were collected in succession from the tenth bed on the western wall of the first location at the Zhoukoudian Peking Man Site: ZKD1, ZKD2 and ZKD3. For comparative study, one sample (ZKD4) was collected from the corresponding stratigraphic position outside the cave. Three cave deposit samples (ZKD5, ZKD6 and ZKD7) were also collected at the intervals of 50 cm from the upper, middle and lower parts of the ash bed on the western side of Gezitang on the eastern wall (the fourth bed). In addition, one sample (ZKD8) was collected from the seventh bed. For the purpose of direct correlation with the confirmed ash material, the following two samples were taken from the specimens on exhibition at the Museum: cemented earthy ash sample (ZKD9) and ash-bearing earth sample (ZKD10). For a comparative study of the record of natural fire and that of artificial fire, we also selected two loess samples (WN80 and WN81) from the Weinan loess section in western Shaanxi, and one sediment sample (B30) from the Lake Tern on the George King Island of the Antarctica, with the latter being the duplicate sample for <sup>14</sup>C dating provided

by Prof. Chen Xiaobai.

#### 2 Experimental

All the samples were baked till dryness and ground to 200 mesh in an agate mortar. Then, about 3 g of the sample was weighed and taken for chemical pretreatment. First, carbonate and silicate impurities were eliminated from the samples with 20% HCl and 1 : 1 HF-HCl solution, followed by the thorough elimination of organic carbon and residue (i.e. "elemental carbon") from the samples with  $K_2Cr_2O_7$  (1 mol/L) +  $H_2SO_4$  (2 mol/L) solution<sup>[8]</sup>. Fig. 1 shows a schematic chemical procedure for the separation and extraction of "elemental carbon".

The carbon content of the residue mentioned above was directly determined with the help of an element analyzer, or the content of "elemental carbon" was determined by using the self-developed "trace  $CO_2$  gas purifying and measuring (vacuum) system", i.e. under 800°C temperature condition the aforementioned residue was heated and oxidized to  $CO_2$  and the resultant  $CO_2$  gas was let to pass in order through a multi-stage (liquid nitrogen + dry ice + acetone) cold trap and a liquid nitrogen cold trap system for purification, and finally through a microbarometer for the determination of  $CO_2$  amount so as to work out the content of "elemental carbon".

#### 3 Results and discussion

The results of the determination of "elemental carbon" in all the samples are listed in Table 1.

As previously described, in order to acquire the information about paleo-climate and paleo-vegetation changes through the study of the intensity and frequency of paleo-fire disasters, the authors conducted research on the record of "elemental carbon" in the Weinan loess section and the results have shown that in the past 21 ka the average concentrations of "elemental carbon" in the Weinan loess section are about 0.2%; the peak concentration values of "elemental carbon" always appeared during the periods of rapid climatic change, generally less than 0.6%, in sensitive response to the frequent occurrence of fire disasters during these periods of time.<sup>[8]</sup>. Listed in Table 1 are the concentrations of "elemental carbon" in the samples WN80 and WN81 collected from the Weinan loess section, which are within the range of 0.11% and 0.20%, respectively. The record of "elemental carbon" in the loess section reflects the concentrations of "elemental carbon" produced by natural fire and then atmospherically settled down in the loess strata. Since the Antarctica is far away from the other continents, fire disasters on the other continents have little influence on it. For the convenience of correlation, Table 1 also lists the concentrations of "elemental carbon" (less than 0.095%), determined in this work, in the sediment sample B30 from the Lake Tern on the George King Island of Antarctica, which can be correlated with those of Antarctic marine sediments, as deter-

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Fig. 1. The sketch showing the chemical procedure for the separation and extraction of "elemental carbon".

mined by Bird<sup>[9]</sup>. Their concentrations of "elemental carbon" are obviously less than those of other types of samples and, therefore, can be regarded as the natural background for "elemental carbon" measurement. The Lake Tern sediments contain abundant terrestrial moss, belonging to the samples that are poor in "elemental carbon" but rich in organic matter. The fact that the concentrations of "elemental carbon" in the sediment sample B30 from the Antarctica are slightly lower indicates from another aspect that in the analysis procedure of this work no "elemental carbon" was produced by way of oxidation of organic matter.

Sample ZKD9 was taken from a large, very hard,

baked earth block on exhibition at the Zhoukoudian Peking Man Site Museum, and the earth block on exhibition is measured at 50 cm  $\times$  30 cm  $\times$  15 cm in size. Its surface is coated with black earth and underlying is the red cemented earth. The sample belongs to the surface black earth. This exhibit has been commonly accepted as a part of the "hearth". Sample ZKD10 was taken from a pile of brownish-red earth blocks on exhibition, which have also been commonly accepted as earth fragments dug out from the surroundings of the "hearth". It can be seen from Table 1 that the concentrations of "elemental carbon" in sample ZKD9 (black cemented earth) are 43.73% and those of ZKD10 (brownish-red earth) are 1.75%, both of them be-

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Table 1 The concentrations of "elemental carbon" in the samples from the Zhoukoudian Peking-man site and those from other locations						
Sample No.	Source and description	Initial amount/g	Remaining amount/g	Carbon content of remains(%)	Total carbon/g	Carbon concen- tration (%)
ZKD1	Brownish-red soil, sediment of the tenth bed (10-6)	2.8633	0.0424	26.19	0.0111	3.88
ZKD2	Brownish-red sandy clay, sediment of the tenth bed (10-4)	1.0238	-	_	0.00191	1.87
ZKD3	Brownish-red sandy clay, sediment of the tenth bed (10-4)	0.7967	-	_	0.00088	1.11
ZKD4	Brownish-red sandy clay, sediment of the corresponding tenth bed outside the cave mouth	2.7912	_	_	0.00033	0.12
ZKD5	Clayey silt, at the top of the fourth bed	3.9165	0.0565	89	0.0005	0.12
ZKD6	Clayey silt, at the middle of the fourth bed	2.9675	0.333	1.20	0.0004	0.13
ZKD7	Clayey silt, at the bottom of the fourth bed	3.0152	0.0313	1.60	0.0005	0.15
ZKD8	Fine silty bed at the 20—80 cm of the seventh bed	2.8201	-	-	0.00048	0.17
ZKD9	Black cemented earth, ash bed on exhibition (No.6),	2.3761	0.2473	42.03	0.1039	43.74
ZKD10	Brownish-red earth, ash bed on exhibition (No.5),	2.7367	0.0562	8.60	0.0048	1.77
WN80	Weinan loess	2.6490	_	_	0.00048	0.18
WN81	Weinan loess	3.0000	0.0131	4.65	0.0006	0.20
B30	Lake Tern sediment, Feldes Peninsula, Antarctica	3.1453	-	_	0.00048	0.095

ing one order of magnitude higher than the concentrations of "atmospheric "elemental carbon" from natural fire, and the former's "elemental carbon" concentrations are 25 times the latter's. This provides strong evidence for the fact that the concentrations of "elemental carbon" in the cave deposits in the locus of the "hearth " are precisely higher.

Sample ZKD1 was taken from the lower part of the tenth bed (10-6) on the western wall of the cave and is designated to blackish-brown earth interbedded with thin-bedded brownish-red earth. Its "elemental carbon" concentrations are 3.88%, intermediate between the "elemental carbon" concentrations of sample ZKD9 from the "hearth" and those of sample ZKD10 from the earth fragments, but more than one order of magnitude higher than the concentrations of "atmospheric "elemental carbon" from natural fire. Samples ZKD2 and ZKD3 were both taken from the fourth sub-bed (10-4) of the tenth bed on the western wall of the cave and they are designated to brownish-red sandy clays. Their "elemental carbon" concentrations are measured to be 1.87% and 1.11%, respectively, lower than those of sample ZKD1, but on the same order of magnitude. Sample ZKD4 was taken from the corresponding stratigraphic position of the tenth bed outside the cave and its "elemental carbon" concentrations only reach 0.12%. Sample ZKD8 was taken from the seventh bed on the western wall of the cave and its "elemental carbon" concentrations are measured to be 0.17%. The seventh bed is composed of gray, mica fragment-bearing fine siltstones with the characteristics of streamline sedimentation and no sign of human inhabitation<sup>[10]</sup>. The "elemental carbon" concentrations of samples ZKD4 and ZKD8 are one order of magnitude lower than those of the three samples collected from the tenth bed within the cave as described above, but are approximate to the concentrations of "atmospheric "elemental carbon" from natural fire. The above analysis has revealed that the fact that the "elemental carbon" concentrations of ash exhibits from the hearth and the cave deposits in the tenth bed are precisely higher has indicated that the position of the tenth bed where samples were collected is close to the hearth . If samples were collected over a wider range, the "elemental carbon" concentration-high location corresponding to the hearth could be defined accurately.

Samples ZKD5, ZKD6 and ZKD7 were taken from the "ash bed" on the northern side of Gezitang on the eastern wall of the cave (i.e. 4-3). The ash bed is composed of brownish-red earth interbedded with clayey silt. Their "elemental carbon" concentrations are 0.12%, 0.13% and 0.15%, respectively, on the same order of magnitude as those of atmospheric "elemental carbon" from natural fire. It seems that there is no evidence for the *in-situ* combustion in the localities of these three samples. Whether there is any evidence for the *in-situ* combustion in other locations is awaiting further work on the determination of "elemental carbon" concentrations.

As viewed from the lithologic character of the strata, the first location of Zhoukoudian is composed chiefly of breccia (or breccia-bearing sediments) inbedded with

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ashes and sandy conglomerates with the characteristics of moving-water sedimentation. Both the rocks occur alternatively. The cave deposits were derived predominantly from cliff debris from the surroundings outside the cave and alluvial and fluvial deposits<sup>[10]</sup>. Previous studies showed that the tenth bed belongs to reddish earth ash beds, which contains burnt bones and stone artifacts with cracks due to burning, and the black ash bed contains charcoal<sup>[10]</sup>. The higher "elemental carbon" concentrations of the three cave deposit samples taken from the tenth bed may be ascribed to the following two reasons: (1) the samples were collected from the surroundings of the "hearth" within the cave, or they are the fallen materials from the top and wall of the cave because of the long-time smoke suffocation; and (2) the samples are the EC-high sediments carried by moving water from outside into the cave. On account of the fact that the outside-the-cave samples are obviously low in EC concentration, the second possibility could almost be neglected. If the objectives of study are expanded to a wider scope and the locations of obviously high EC concentrations are found, the hypotheses of low-energy moving-water transport could be harder to hold water.

Jia Lanpo once pointed out that the black ash bed usually contains carbon fines and hackberry seed (C. sinensis) charcoal was also found in the black material from the second quartz bed at Gezitang<sup>[11]</sup>. He also pointed out that it is no doubt that the location is the locus where the "hearth" is located<sup>[12]</sup>. In the 1970s—1980s Guo Shilun et al. had conducted fission track dating of the samples collected from the tenth bed, and acquired a fission track age of  $0.462 \pm 0.045$  Ma, which is approximately consistent with the ages obtained by other dating methods<sup>[13,14]</sup>, indicating that the analyzed samples had been burnt in the ape-man period. Otherwise, the fission track age should be much older. At present, the burnt bones, ashes cemented together with earth, ash-bearing cave deposits, and burnt tree seeds are still shown as the exhibits at the Zhoukoudian Peking Man Site Museum. However, the face of the site is quite different from what was before the site was not unearthed in the 1930s. For this reason, the "elemental carbon" concentrations of the various types of samples revealed by this work do provide the basis for developing new evidence for the use of fire by Peking Man.

It is well known that fire usually includes natural fire and artificial fire. Generally the sediments contain two types of "elemental carbon" produced by natural fire. One is the atmospheric "elemental carbon" and the other is the outcome of *in-situ* spontaneous combustion of bird's droppings. Relative to the use of fire by human beings, the former's contributions are much less than the latter's. The former's EC concentrations can be discounted through the determination of "elemental carbon" concentrations of other kinds of atmospheric materials such as clays while the latter's "elemental carbon" concentrations can be distinguished in the light of the information about burning materials developed from the  $\delta^{13}$ C data of "elemental carbon"<sup>[15]</sup>. As stated previously, if samples are collected over a wider range, the "elemental carbon" concentration-high locations corresponding to the "hearth" can be substantially defined and the direct evidence for the *in-situ* use of fire by ape men can be acquired. Of course, it is quite necessary to distinguish artificial fire from natural fire, especially from *in-situ* spontaneous combustion fire. For this, the authors have begun to carry out systematic determination of the "elemental carbon" and detailed study of the distribution characteristics of its  $\delta^{13}$ C values in the relevant strata.

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