CPC(HEP & NP), 2010, **34**(3): 417–420 Chinese Physics C Vol. 34, No. 3, Mar., 2010

Study of the circumstance influence on the elemental distribution in ancient animal bone using μ-XRF*

YAN Ling-Tong(闫灵通)[1,2;1)] FENG Song-Lin(冯松林)[1,2;2)] FENG Xiang-Qian(冯向前)[1]
XIE Guo-Xi(谢国喜)[1,3] LI Li(李丽)[1,2] XU Wei(徐伟)[1,2]

[1] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
[2] Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[3] Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China

Abstract Elemental analysis of archaeological bone plays an important role in the study of the dietary habits of ancient animals. The elemental characteristic of diagenetic skeletons depends on the surrounding circumstance. The study of environmental influence on the elemental concentration of ancient bone is significant. In this paper, the diagenetic influence on archaeological skeletons is analyzed by microbeam X-ray fluorescence (μ-XRF). The results show that the enamel is an excellent barrier to the diagenesis and the element Sr in bone isn't susceptible to contamination from the buried environment.

Key words ancient animal bone, elemental distribution, μ-XRF

PACS 32.30.Rj, 87.85.gj

1 Introduction

Elemental analysis of archaeological bone plays an important role in the study of the dietary habits of ancient animals, but it still faces a number of problems now. The scientists, who put criticism on the study of trace elements in skeletons, took the contamination and nutrition into account [1, 2]. In any case, the elemental investigation in teeth is still going on. In fact, the tooth is an important object for osteoarchaeological science because it is of an apatite structure which is more steady and compact than a normal bone [3, 4]. The relationship between the buried teeth and the surrounding environment should be further investigated [5, 6].

In recent years, the study of Sr stable isotope in archaeological skeleton tissue has been booming. Strontium isotopes serve as a signature that can be used to "source" a prehistoric skeleton to its geologic area, depending on how the individual migrated during its life. The contamination intake of Sr from the surrounding buried environment is a barrier for the bone analysis [5]. Some authors had found that the empirical data showed distinguishable levels of Zn in bones of carnivorous and herbivorous animals. So it has been used as a discriminator of meat [7].

Based on the mentioned situation, the measurement of the elemental purity in the buried tooth was carried out by many researchers. Elemental distribution in archaeological bone has been analyzed by AAS [8], PIXE [1, 9, 10] and XRF for quantitative determination [11–14]. We collected tooth samples, two pieces of long bone from the Jiangxi Province and a piece of right thighbone from the Henan Province. In order to compare the differences in contamination between tooth and compact bone, the elemental distribution in ancient bone has been detected using microbeam X-ray fluorescence (μ-XRF).

2 Samples and experiments

2.1 Samples

Three pieces of teeth and two long bones were collected from the site of 100000 years ago which

Received 18 March 2009, Revised 29 June 2009
* Supported by Knowledge Innovative Program of Chinese Academy of Sciences (KJCX3.SYW.N12), National Natural Science Foundation of China (50432010, 10675143) and Young Scientist Innovative Foundation of IHEP, CAS (542007 IHEPZZBS546100)
1) E-mail: yanlt@ihep.ac.cn
2) E-mail: fengsl@ihep.ac.cn

is located at Jiangxi Province in South China. The exact species of these samples were not identified. A piece of the right thighbone of cattle was collected from the site of the Shang Dynasty (B.C. 16–11). This site is located at Henan Province in North China. Small slices of 2 mm in thickness were cut down from each bone sample. Three slice samples were cut down from the crown and the cross section with tooth enamel appeared. One tooth sample was surrounded by the soil which was from the buried environment. The slice samples were washed in ultrasonic cleaner with deionized water and then dried naturally. We document the condition of samples in Table 1.

Table 1. Initial condition of samples.

sample	species	origin	age	type
T1-1/T1-2/T1-3	pig	Jiangxi	100000	tooth
T2	unknown	Jiangxi	100000	tooth
T3	unknown	Jiangxi	100000	tooth
B1	unknown	Jiangxi	100000	bone
B2	cattle	Henan	3000-4000	bone
B3	unknown	Jiangxi	100000	bone

2.2 Experiments

The μ-XRF analytical experiments were carried out by a PV8880/00 Eagle 3 XXL μ-Probe Elemental Analyzer System produced by the EDAX Company. The working voltage of X-ray tube was 40 kV and current was 800 μA. The X-ray beam was focused to ϕ100 μm by optic capillary focusing lens. The angle of the incident μ-X-ray beam was 65° with respect to the sample plane and Si(Li) Detector for eagle XXL was set to gain the spectrum. The energy resolution is 154 eV. The selection of the experimental points on samples was performed manually. About 0.6 mm distance between two measuring points was adopted. Each point was irradiated up to 1000 s. The samples were measured in the air. All the obtained spectra of μ-XRF were analyzed with the VISION32 computer software which has all the basic EDX functions.

One piece of the tooth was analyzed along three different directions of radius. And we named them as T1-1, T1-2 and T1-3. The other samples were entitled T2, T3(tooth) and B1, B2, B3(bone).

3 Results and discussion

Net intensity in the μ-XRF experiment is mainly determined by the elemental concentration in the same matrix. In this paper, we use Net intensity to express the degree of elemental concentration. In our experiment, some elements like Mn, Cu and Pb couldn't be measured by μ-XRF because their concentration is too low to be detected. Both elements of Zn and Sr, which are important elements in the study of osteoarchaeological science, can be measured by the μ-XRF and will be the emphasis in our discussion.

As some research presented [1, 3], the compact bone is susceptible to Fe accumulation. The element Fe serves as a reference of contamination. The strong enrichment of Fe at the external surface was caused by the exchange mechanism between the archaeological bone and its neighborhood. Otherwise, the inner surface had a little enrichment because the inner part was exposed to the soil after marrow dissolving. The elemental distribution curves from the inner to the external surface, which are shown in Fig. 1, indicate that the decline is obvious.

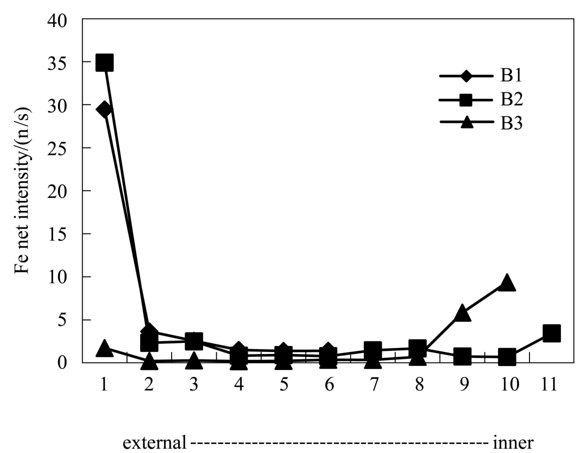

Fig. 1. Fe concentration for bone.

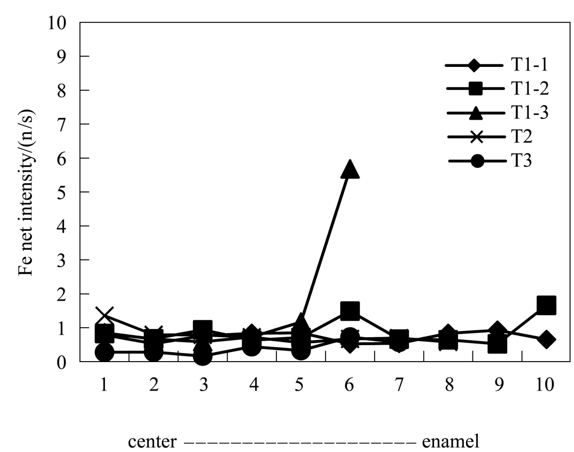

Fig. 2. Fe concentration for tooth.

The sample T1-3 whose enamel had worn off has a little Fe enrichment in the external surface as shown in Fig. 2. The element like Fe in the soil could easily penetrate the buried tissue, but their concentration was much lower in the dentine surrounded by the enamel which was emerged in the burial soil for a long time. So the enamel was the barrier to the Fe penetration and it protected the dentine against diagenesis.

Figure 3 is about the zinc distribution profiles in different teeth. It displays similar patterns. We can see obviously that the Zn concentration decreased from the central dentine and then reached a lower level in enamel as observed in the contemporary tooth before [12]. Further attention should be paid to this concentration distribution when we make the research regarding Zn element content [7], because the sampling area may affect the measuring result regarding elemental concentration. The concentration of Zn exhibited a steady level in the bone from the external surface to the inner part as shown in Fig. 4. It indicated that Zn was hardly contaminated.

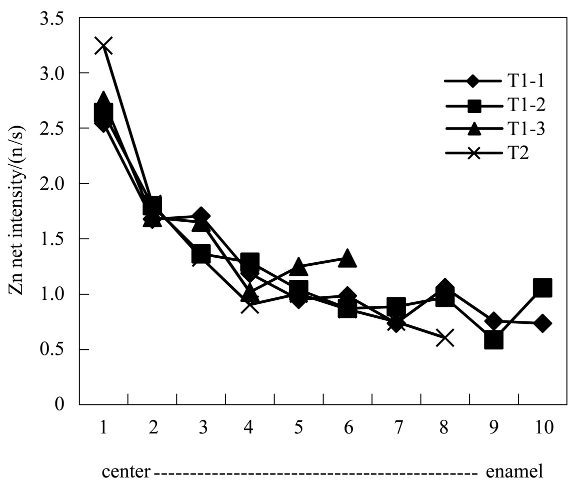

Fig. 3. Zn concentration for tooth.

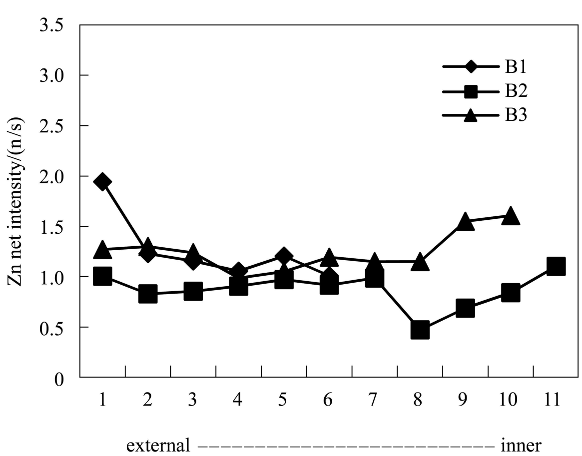

Fig. 4. Zn concentration for bone.

An important phenomenon is shown in Fig. 5 and Fig. 6. Although the samples were excavated on different sites, the concentration of Sr kept the corresponding level steady in both the tooth and bone samples. It didn't show the high concentration level of Sr at the bone external like Fe. It makes it clear that Sr is a comparatively credible element in osteoarchaeological science. The concentration of Sr in teeth was steadier than that in the bone.

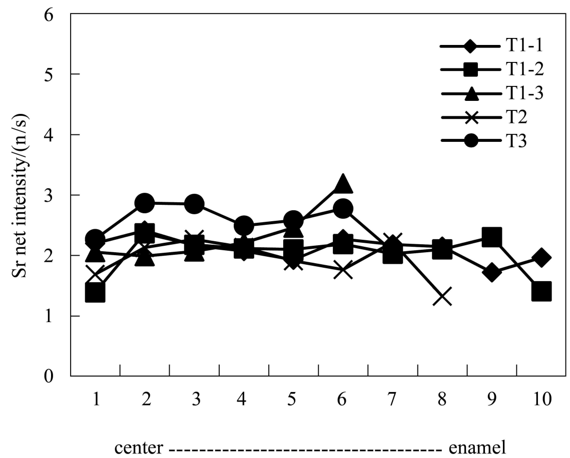

Fig. 5. Sr concentration for tooth.

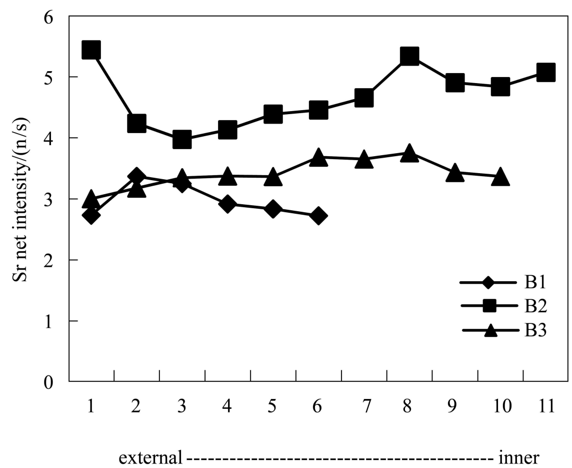

Fig. 6. Sr concentration for bone.

In Fig. 5, if we observe carefully, we could have an impression that the Sr contents in the central dentine and enamel were a little lower than the middle dentine. The distribution of Sr reminds us that its fluctuation may reflect the accumulation condition of this element during the growth of the tooth. It suggests that the isotope fractionation may present different values in different points of the tooth. It should be an important factor in the Sr isotope application study in osteoarchaeological science.

The concentrations of Zn and Sr showed some resemblance. They presented stabilization in the tooth and small fluctuation in the bone. The fluctuation in bone should owe to the individual diversity but not the environmental contamination, because their distribution profiles differ from those of Fe which is a typical element that is susceptible to contamination from the buried environment. We may conclude that they are not susceptible to ion penetration from the surrounding circumstance.

4 Conclusions

Although the concentration of element cannot be quantified, the results show that μ-XRF is a good technique for studying the elemental distribution profile. The quantification of this technique is necessary to be solved.

The results indicate that Fe could easily penetrate from the soil into the bone, but the penetration is difficult in the tooth because of the enamel's protection. The dentine surrounded by the enamel can be investigated without the consideration of contamination. Compared with Fe, they are able to be used in the following osteoarchaeological study. The curves of Zn and Sr vary in different teeth and bone samples. We consider that this phenomenon is mostly due to individual diversity, rather than the environmental contamination.

The authors greatly appreciate professor Yuan Jing who provided the ancient bone samples from Henan Province.

References

1 Ezzo J A. Journal of Anthropological Archaeology, 1994, **13**: 1–34

2 Burton J H, Price T D. The Use and Abuse of Trace Elements for Paleodietary Research. Biogeochemical Approaches to Paleodietary Analysis. New York: Kluwer Academic/Plenum Publishers, 2000. 159–167

3 Preoteasa E A, Preoteasa E, Kuczumow A et al. X-Ray Spectrom, 2008, **37**: 517–535

4 Hallin K A. Paleoclimate during Neandertal and Early Modern Human Occupation in Israel Tooth Enamel Stable Isotope Evidence, PhD Thesis. University of Wisconsin

5 Bertly R A. Journal of Archaeological Method and Theory, 2006, **13**(3): 135–187

6 Molleson T. Chemical Analysis of Human Dental Enamel from Archaeological Sites. In: Grupe G, Hermann B ed. Trace Elements in Environmental History. Berlin: Springer-Verlag, 1988. 67–82

7 Safont S. International Journal of Osteoarchaeology, 1998, **8**: 23–27

8 Gonzalez-Reimers E, Arnary-de-la.rosa M, Velasco-Vasquez J et al. Am. J. Human Biol., 1999, **11**: 405–410

9 Brenn R, Haug Ch, Klar U et al. Nuclear Instruments and Methods in Physics Section B: Beam Interactions with Materials and Atoms, 1999, **158**: 270–274

10 Tapper U, Vuorinen H, Mussalo-Rauhamaa H. Nuclear Instruments and Methods in Physics Section B: Beam Interactions with Materials and Atoms, 1990, **49**: 245–249

11 Carvalho M L, Brito J, Barreiros M A. X-ray Spectrom, 1998, **27**: 198–204

12 Carvalho M L, Marques J P, Marques A F et al. X-ray Spectrom, 2004, **33**: 55–60

13 Carvalho M L, Marques A F, Lima M T et al. Spectrochemica Acta Part B, 2004, **59**: 1251–1257

14 Zeoger N, Wobrauschek P, Streli C et al. X-Ray Spectrom, 2005, **34**: 140–143