THE PROGRESS OF ACCELERATOR MASS SPECTROMETRY AND THEIR APPLICATIONS IN CHINA

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Abstract

The facilities and technologies developed for AMS at Peking University, China Institute of Atomic Energy and Xi'an AMS Centre are presented. Interesting results about Chronology frame of Xia-Shang-Zhou dynasties based on radiocarbon dating with PKU-AMS on serial samples from various sites like Tianma-Qucun, Xinzha sites etc and oracle bones from Yinxu site, are given as examples of the AMS application in the field of Archaeology. Applications in the fields of earth sciences, biomedical sciences are introduced as well.

INTRODUCTION

As a result of substantial development for more than a quarter of a century, the accelerator mass spectrometry (AMS) has become a leading technique for the detection of long-lived radio nuclides such as ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl and ^{129}I at isotopic ratios between 10^{-10} and 10^{-15} and has been applied extensively in the fields of archaeology, earth sciences, environmental sciences, biomedical sciences, nuclear safeguards, nuclear physics and astrophysics.

Comparing with the conventional mass spectrometers and radio decay measurement, the AMS has following merits:

- Ultra high sensitivity. For a number of radioactive nuclides, the measuring background of isotopic ratios could be reduced down to 10^{-15} or even less, which is much lower than traditional mass spectrometer.
- Small sample size. The sample amount of AMS measurement is usually in the order of mg elements, which are three orders lower than that needed for decay counting method. In the case of meteorite measurement even 10 μg carbon sample is still workable.
- High throughput. The time of direct atom counting is much shorter than that of decay counting for the same precision.

However, to carry out a precise abundance measurement of rare nuclides is really a challenging issue. Careful precautions have to be made to eliminate various interferences in the whole process starting from sample collection and preparation, beam generation, beam handling and acceleration, gas stripping and finally to the data acquisition and processing. Precautions have to be made to ensure AMS facilities operating under conditions with extremely low machine background, low isotopic fractionation, high beam transmission efficiency, and high resolution beam analysis as well as with high performance stability.

There are about 60 AMS facilities around the world and more new facilities are to be developed or constructed. In China, AMS technology has been developed at the China Institute of Atomic Energy and Peking University since 1980's. There are now 5 AMS facilities working. In the following paragraphs, only tandem based AMS facilities in China and their features will be presented followed by some discussion on typical applications.

AMS FACILITIES IN CHINA

The HI-13 Tandem at China Institute of Atomic Energy (CIAE) was the first facility in China that used for AMS measurements of mid or heavy nuclei like ^{10}Be, ^{26}Al, ^{36}Cl, ^{41}Ca and ^{129}I etc.[1] and the applications has been concentrated on geosciences, biomedical sciences, nuclear physics and astrophysics. The layout of the facility is shown on fig. 1.

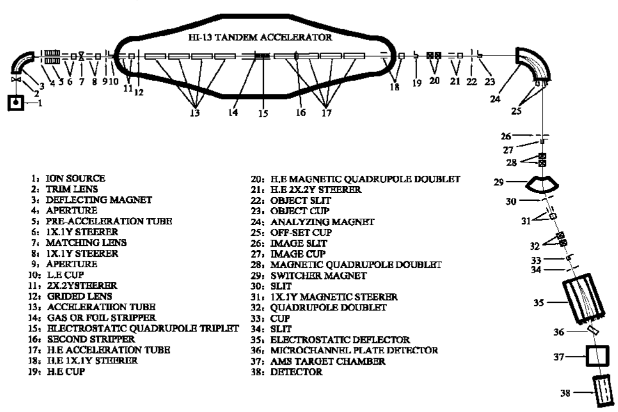

Figure 1: The layout of CIAE's HI-13 AMS system.

It consists of mainly a HI-13 Tandem accelerator, sputtering ion source, injection section with low energy beam analysis, post acceleration beam analyzing magnet and electrostatic deflector, as well as AMS target chamber and micro-channel plate detector. Typical parameters of the CIAE AMS used for measurements of ^{10}Be, ^{26}Al, ^{36}Cl, ^{41}Ca nuclides are listed in Table 1.

Various methods have been developed along with ΔE-E ionization chamber for the detection of rare nuclides and the elimination of their isotope and isobar interferences, as indicated in the Table 1. For instance to measure ^{10}Be, an absorber of 15.3mg/cm^2 Ni is added in front of the ΔE-E ionization chamber, and for the measurement of ^{129}I, TOF technique is adopted for isotope identification while for

Table 1: Main Parameters of CIAE AMS

Radio-isotopes	Negative ions	Terminal voltage	Detection method	Sensitivity
^{10}Be	BeO^-	8.4MV	Absorber +ionization chamber	11×0^{-14}
^{26}Al	Al^-,AlO^-	7.6MV	ionization chamber	$11\times0^{-14-15}$
^{36}Cl	Cl^-	8.0MV	ionization chamber	2×10^{-15}
^{41}Ca	CaF_3^-,CaH_2^-	8.2MV	ionization chamber	3×10^{-14}
^{79}Se	Se^-	8.2MV	Projectile X-ray	2×10^{-11}
^{129}I	I^-	8.0MV	TOF	11×0^{-13}

^{79}Se, projectile X-ray method was developed for the isobar identification. Typical spectra of AMS measurements are shown in fig.2-3.

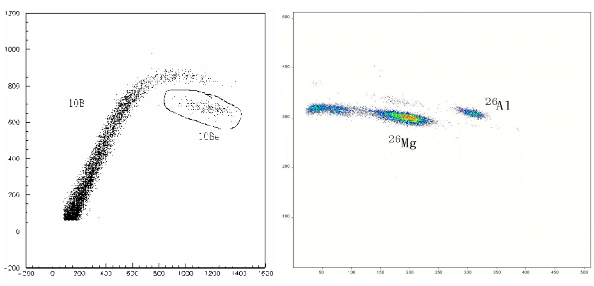

Figure 2: Two-dimensional spectra of standard sample ^{10}Be (10^{-11}), and standard sample of fully stripped ^{26}Al.

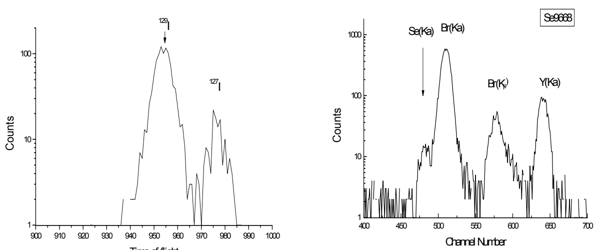

Figure 3: TOF spectrum of ^{129}I & projectile K_{α} ray of ^{79}Se.

The AMS facility at Peking University (PKU-AMS) is a user's facility mainly for ^{14}C, ^{10}Be and ^{26}Al measurements [2]. It is based on an EN tandem accelerator and the layout is shown in fig.4. It has been upgraded to a precision of 0.4%-0.5% for ^{14}C measurements, with a background corresponding to ^{14}C age of 50ka, since 1996, to meet the requirements of the Xia-Shang-Zhou Chronology Project. [3] The low energy injection part mainly consists of a NEC MC-SNICS ion source with 40 target positions, an Einzel lens and a 20kV pre-acceleration section. The power supplies for injection system, bending magnets as well as HV power supplies were replaced with high precision products. The charging belt and voltage-dividing resistors

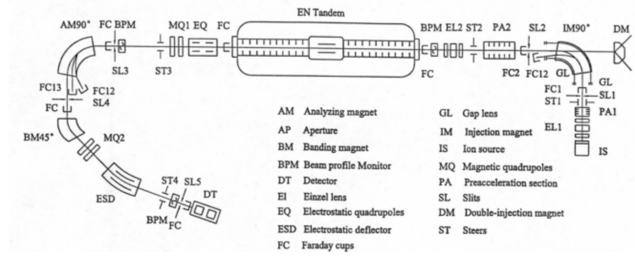

Figure 4: The layout of PKU-AMS.

in the EN tandem accelerator were upgraded too. Some instruments have installed to stabilize the humidity, temperature and AC voltage in the accelerator hall. Finally, a new control system for beam line was constructed, which is a distributing system contained 6 local control stations and one PC via a fibber-optical loop. The software for the system was developed on the LabVIEW platform. It has fine user interface and is easy to operate. The system is reliable and stable, with a control precision of 0.05% and a long-term stability of 0.1% for 8 hours [4]. A master PC is used to read the ^{14}C counts, the stable isotope beam current and to control the target changing in ion source as well as the sequential injection of isotopes.

To reach high accuracy, the measuring procedure has been designed carefully. One sample was distributed into multiple targets, which were measured individually and then the results were combined to see if they could pass the so called t or F test. The off-line data manipulation program (OLDMAP) has been developed, which can manipulate, analyze measured data and finally give ^{14}C age and its error. The measured ^{14}C age has to be converted into calendar date by using calibration curve and in order to minimize the error during the conversion, calibration of serial ^{14}C samples with Bayesian method has been studied and developed. [5].

A compact AMS system manufactured by NEC has been installed in 2004 at Peking University which is dedicated for ^{14}C measurements [6]. The system is based on Pelletron accelerator with a maximum terminal voltage of 0.6MV. The system has been strictly tested by using standard samples and the results clearly indicate that the precision and reproducibility of the system are better than 0.3% for modern samples and the machine background is 4×10-16, corresponding to ^{14}C age of 65ka. The system utilizes a NEC 40 sample Multi-Cathode SNICS ion source. The fast switching injection system injects the carbon ions ^{12}C-, ^{13}C-, ^{14}C- for 0.3, 1 and 100 ms sequentially with a repetition rate of 10 Hz. The terminal voltage is set to 0.46MV during routing operation. The high energy analyzing system includes a 90° double focusing magnet and a 90° electrostatic deflector. The final ion detector is a simple silicon surface barrier detector. A computer is used for data acquisition and control of the system while another one is used for off-line data analysis. At the terminal voltage of 0.46MV, the ion beam transmission of typically 43% (HE/LE ^{12}C particle current) has been reached at a range of stripper gas pressure from 14-16μτ. Since this machine is capable to measure 3000

^{14}C samples per year, EN tandem based AMS facility is now mainly used for measurements of ^{10}Be and heavier nuclides.

The Xi'an Center of Accelerator Mass Spectrometry (Xi'an AMS Center) was jointly established by the Institute of Earth Environment of the Chinese Academy of Sciences and the Xi'an Jiaotong University recently. The major equipment at this center is a 3 MV tandem-based accelerator mass spectrometer imported from High Voltage Engineering, Netherland. The equipments of sample preparation and set-up systems have been developed locally [7]. This spectrometer, in its present capability, is already able to make high quality measurement of nuclides such as, ^{10}Be, ^{14}C, ^{26}Al and ^{129}I. Its functionality can be further expanded to include several other nuclides such as ^{41}Ca, which also have important applications. It has the capacity of making routine high quality ^{14}C analyses with a precision better than 0.3% and a significant annual throughput. At the same time, it allows for a number of applications to be explored with ^{10}Be, ^{26}Al and ^{129}I, as well as the potential of the multi-element analysis offered by the facility. Its detection limit for ^{10}Be and ^{129}I is at the level of 10-15 and 10-14 respectively.

TYPICAL APPLICATIONS

A number of AMS applications have been carried out in China since 1990. Only some interesting examples are presented in this paper.

Archaeological Studies

The Chinese civilization has been lasting for several thousand years and has never been interrupted. The most authoritative book which gives a reliable chronicle of ancient Chinese history is Shi Ji, written by Sima Qian, an official historian of Han Dynasty in about 100 BC, which started from 841 BC in the later period of Western Zhou and is generally recognized. Shi Ji also gives all the King's names and their genealogy since Xia. However, the ancient Chinese chronology has not been well established so far. An important example is for the date of the conquest of Shang by King Wu of Zhou, there have been at least 44 different solutions offered spreading over a span of 112 years. Radiocarbon dating played an important role in Xia-Shang-Zhou Chronology Project. Nine series of samples were studied for this purpose [8], including 7 sites, one tomb series and a special series of oracle bone samples (Fig. 6). Most of the bones are from the final capital of the Shang Dynasty, they are important for establishing a chronology of late Shang Dynasty, since the inscriptions on oracle bones recorded the King's name, activities, war, sacrificial offerings and important astronomical phenomena. However, the ages of sites and cultural phases may have an offset compared with the ages of kings and dynasties. Furthermore, radiocarbon dating always has an error and sometimes it might be too large to be accepted by chronologists. For this reason, calibration of all the samples as a series with Bayesian method results much narrower confident intervals than that of the single sample calibration. Fig. 5 is an example, where boundaries were set at beginning and end corresponding to the beginning time of the Tianma-Qucun site and the end of Western Zhou. The results show that the end of Western Zhou is in 796–754 BC, which is consistent well with the historical record of 770 BC.

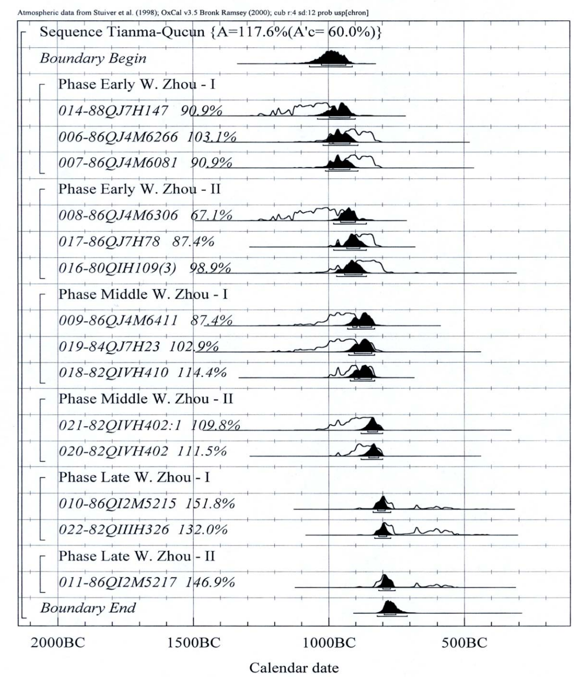

Figure 5: Calibration of sample series with Bayesian method.

Figure 6: Oracle bones with inscriptions.

Precise measurements of ^{14}C in oracle bones have been carried out on the compact NEC machine. The results obtained with OxCal 3.9 shows that the calendar ages of these oracle bones are from 1260 BC to 1050 BC. This indicates that the end of Shang Dynasty should be around 1050 BC. It is consistent with the ^{14}C dating result of serial bone samples from the Yinxu site and the result from the eclipse calculations according to the records in oracle bone inscriptions. So far, more than 100 oracle bone samples have been dated, among them more than 60 bone samples were measured with the new machine, and the results are consistent with the rest of the samples measured with EN based AMS system. The final results through the synthesis of various ways are listed in the Table 2.

Table 2

Dynasties	Dates
Xia	ca. 2070 BC – ca. 1600 BC
Shang	ca. 1600 BC – 1046 BC
Western Zhou	1046 BC – 771 BC

Another interesting example with ^{14}C dating is study on the chronology of Xia dynasty with serial samples from the cultures of Longshan, Xinzai and Er-li-tou. The cultural remains in Xinzhai site contain late Longshan, Xinzhai and early Er-li-tou. Bayesian method is used again for the calibration of the serial samples to reduce the calibrated ranges. Oxcal 3.9 Program was used for the calibration of ^{14}C ages of serial samples from Xinzhai. Samples were organized into three phases according to the layer sequence with an upper boundary and a lower boundary; boundaries are also added between the phases. To check the reliability, many samples were measured twice. The results show that the transition time from Longshan to Xinzhai was about 1840BC – 1820BC, Xinzhai culture lasted about 120a. The end age of Xinzhai (around 1720BC) is approximately the same with the beginning age of Er-li-tou [9]. Most archaeologists in China believe Xinzhai culture belongs to Xia, therefore the beginning of Xia dynasty was at least before 1820BC.

Recently Donghulin site which is located to the west of Donghuli village near Beijing city was discovered and excavated [10]. Tombs, ash-pits, fireplaces and other vestiges were found along with abundant objects including chipped stone implements, microliths, polished stone tools and potteries. More than 20 charcoal and bone samples were collected from this site and then dated with the AMS at Peking University. The results show that the Donghulin Man lived from 9000BC to 7000BC, the early Neolithic period. This is another very important archaeological discovery in Beijing area following the famous Peking Man site and Upper Cave Man site. Donghulin site has great significance to study the living style of the early Neolithic Man and the evolution of early Neolithic cultures in North China and the relationships between them.

Earth Science

^{10}Be produced in the atmosphere is soon attached to mineral aerosols and deposited on the earth surface by precipitation. It is a useful isotopic tracer for investigating the formation of Aeolian deposits and Quaternary climate evolution. The Matuyama-Brunhes polarity reversal which happened 0.78 Ma ago was recorded in loess L8 in Chinese loess sequence. This corresponds to a glacial period and is obviously different from the marine record where the same reversal boundary has been found in the sediments of Oxygen Isotope Stage 19, an interglacial period. One explanation is that the loess record of the Matuyama-Brunhes boundary (MBB) is displaced downwards by over 100 cm [11]. In order to determine the true position of the MBB in loess, ^{10}Be concentration in loess from Louchuan, Shanxi Province is investigating by AMS ^{10}Be measurements at Peking University based on the assumption that the increase of the ^{10}Be production rate due to the reduction of geomagnetic field intensity during the polarity reversal is significant and can be recorded in the loess sequence.

Bio-science

AMS is a powerful tool to study the adduction effect between the toxic material such as Nicotine, nitrobenzene, Methyl tart-butyl ether (MTBE) and acryl amide (AA) at environmental low dose levels and bio-macromolecules such as DNA and Hemoglobin (Hb). Recently this kind of research is extended to the study of the inhibition effects of adductions by dietary constituents [12].

Nicotine is a major alkaloid in tobacco products and has proven to be a potential geno-toxic compound. Many natural dietary products can suppress the DNA adduction, and hence act as inhibitors of cancer. The inhibitory effects of curcumin, garlic squeeze, grape-seed extract, tea polyphenols, vitamin C and vitamin E on nicotine-DNA adduction have been investigated using AMS. The results demonstrated that all these dietary constituents induced marked dose-dependent decrease in nicotine-DNA adducts as compared with the control. The reduction rate reached about 50% for all agents, except garlic squeeze (40%), even at its highest dose level. Amongst the six agents, grape-seed extract exhibited the strongest inhibition to the DNA adduct formation.

CONCLUSIONS

AMS technology has been well developed in China. Two of the AMS facilities are based on early developed HI-13 and EN tandem, while the other two are modern dedicated systems. Each of them performed successfully to meet their needs in the fields of archaeology, earth science, environmental sciences and biomedical sciences and etc. Meanwhile, all of them will be further upgraded according to the requirements of new applications.

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