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ACCELERATOR MASS SPECTROMETRY AND ITS APPLICATIONS IN ARCHAEOLOGY, GEOLOGY AND ENVIRONMENTAL RESEARCH*

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Accelerator Mass Spectrometry (AMS) is an ultra sensitive method for the measurement of isotope ratios in the range of 10^{-12} to 10^{-15}. Most frequently the ^{14}C/^{12}C ratio from biogenic samples is determined which gives information on the age of the sample of up to 40 ka with a precision of typically 40–80 years. In this paper the radiocarbon method is discussed and various applications to interdisciplinary research are presented. A main application at the Erlangen AMS facility is the ^{14}C dating of sediment samples which together with simultaneous pollen analyses can establish a better chronology of climate and vegetation during Holocene in Germany. For an enhanced reliability of sediment dating different fractions like bulk sediments, pollen grains, macrofossiles and humic acids have been measured. For environmental research the ^{14}C content of volatile chlorinated hydrocarbons can be used to disentangle the anthropogenic or biogenic origin of these compounds. Finally an interesting archaeological sample is discussed.

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1. Introduction

The radionuclide ^{14}C is produced in the atmosphere via the interaction of cosmic radiation with nitrogen with a nearly constant rate and decays weakly with a half life of 5730 years. Due to this interplay of production and decay an equilibrium concentration of ^{14}C in the atmosphere is established with an isotope ratio ^{14}C/^{12}C of about 10^{-12}. Radiocarbon forms CO_2 molecules and participates on the carbon bio-cycle similar to the stable carbon isotopes with the result that, except for some minor corrections, it

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is present in all living creatures and plants in equilibrium concentration. If the ^{14}C intake is discontinued *e.g.* by death of the organism, its concentration decreases with the half life mentioned above. This fact can be used for an absolute dating of carbon containing samples by measuring either the specific activity, introduced by Libby in 1946 [1] or by direct counting accomplished in accelerator mass spectrometry [2]. Since the production rate of radiocarbon is not exactly constant, a calibration of the time scale has to be performed by dendrochronology, where the ^{14}C content of single tree rings is determined and the calendar age is deduced from tree ring counting.

2. The methodology of accelerator mass spectrometry

The big advantage of AMS compared to decay counting is that the same precision can be obtained in a much shorter time with much smaller samples containing carbon of less than a milligram. This can be illustrated by the fact that a typical modern carbon sample of 1 g contains $6{\cdot}10^{10}$ atoms of ^{14}C resulting in only 14 decays per minute. Therefore with decay counting a measurement time of about 50 h is necessary to achieve a statistical accuracy of 0.5 %, whereas the same precision can be reached in 10 minutes with a modern AMS facility. However, the measurement of an isotope ratio ^{14}C/^{12}C of about 10^{-12} is an experimental challenge since it corresponds to the detection of one slightly heavier grain of sand in a living room filled with sand. Conventional mass spectrometry is not suitable for the measurement of such small isotope ratios since the separation of ^{14}C ions from intense fluxes of ions of the ^{14}N isobar and mass 14 molecular ions such as ^{13}CH and ^{12}CH$_2$ is not possible simultaneously with a high transmission of the ion beam. The use of a tandem accelerator with a high voltage of several MeV combines an excellent reduction of interfering background by many orders of magnitude with high beam transmission and hence a high count rate.

2.1. Typical AMS set-up

A typical AMS facility consists of a negative ion source, an injection spectrometer, a tandem accelerator, an analyzing spectrometer and a heavy ion detector. These different parts serve as efficient filters for the separation of ^{14}C from the abundant background. As an example the Erlangen AMS facility [3] is shown schematically in figure 1. Negative ions are generated from the sample in a high current sputter ion source, pre-accelerated to 50 keV and injected into the tanden accelerator by a combination of a 90° electrostatic deflector and a 90° magnet with fast isotope switching for the sequential injection of ^{14}C, ^{13}C and ^{12}C ions. The use of negative ions eliminates isobaric interference since ^{14}N do not form negative ions. The mass analyzed ions are first accelerated to the positive high voltage terminal

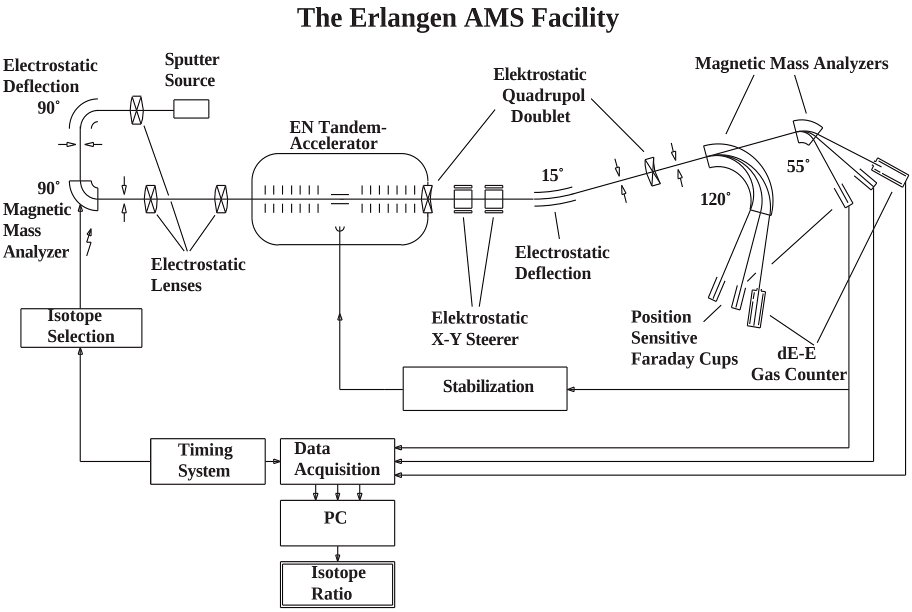

Fig. 1. Schematic view of the Erlangen AMS facility.

(5 MeV) of the EN tandem accelerator where several electrons are stripped off during a passage through a thin carbon foil. Molecular background is eliminated in this stripping process since molecular ions are dissociated and the corresponding positive fragments have a different energy compared to carbon ions emerging from negative atomic ions. In the second stage of the tandem accelerator the now positively charged ions are accelerated further back to ground potential. They are analyzed due to charge state, energy and mass in a spectrometer consisting of a 15° electrostatic deflector, a 55° analyzing magnet (for ^{14}C) and a 120° magnetic split pole spectrometer (for heavier ions). Finally the stable ions ^{13}C and ^{12}C are measured in Faraday Cups and ^{14}C is detected in a ΔE–E gas detector which serves as a last filter for the elimination of remaining background. Figure 2 shows ΔE–E spectra for a modern sample and for graphite demonstrating the success of background elimination: the spectrum for modern carbon shows a huge peak of ^{14}C, whereas the graphite spectrum only shows a few events. The beam transport between injection- and analyzing-magnet is completely performed by electrostatic devices, which ensures identical ion-optics for the different carbon isotopes. The particle transmission through the facility amounts up to 80% taking into account the charge distribution in the high voltage terminal. Thus even with conservative ion source conditions of 25 μA ^{12}C$^-$ current, a ^{14}C count rate of 100 Hz can be obtained for an ANU sucrose

calibration sample. Machine background determined with graphite samples is measured at 0.07 % modern carbon (pMC) corresponding to an apparent age of 58,000 years. The measurements are made in turns of one-minute-runs which allows statistical analysis of the data and an on-line control of the system via the particle transmission and the isotope ratios. In the routine sequence of AMS measurements the quality of the whole facility is first checked with calibrated samples of known ^{14}C content. Then two to three unknown samples are measured before another calibrated sample is used. In this way an accuracy in the range of 0.5-1% has been established.

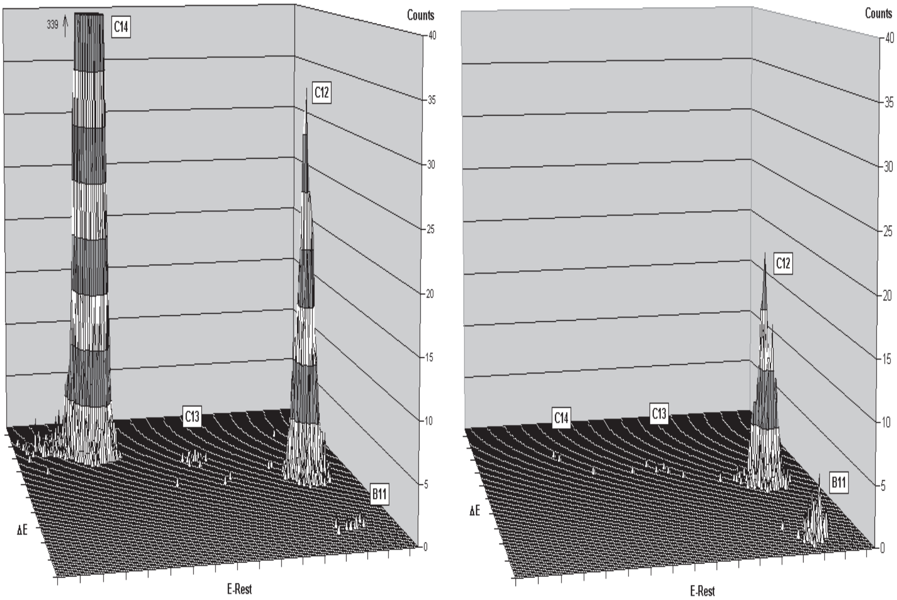

Fig. 2. ΔE–E-spectra for a modern sucrose sample (left) and a graphite sample (right).

2.2. Determination of calendar age

The isotope ratio ^{14}C/^{12}C is obtained from the integrated ^{14}C events shown in figure 2 and the ^{12}C current measured in the Faraday Cup behind the analyzing magnet. This ratio has to be corrected for an isotopic fractionation depending on the specific assimilation process for the intake of CO$_2$ by the plants. This fractionation, caused by mass dependent diffusion processes, can be deduced from the ratio of the stable carbon isotopes ^{13}C/^{12}C measured independently. The correction for ^{14}C/^{12}C is obtained under the assumption that its fractionation is twice as much as for ^{13}C/^{12}C. After a further correction for the machine background obtained from graphite measurements, the $^{14}C/^{12}C$ ratio from the unknown sample is compared to that of a calibration sample from 1950. Assuming a constant formation rate and the exponential decay with known half life, the so called "radiocarbon age" in years before present (BP), *i.e.* before 1950, is derived. Since the assumption of constant formation rate is only approximate, the radiocarbon age of single tree rings is compared to the calendar age deduced from tree ring counting. The result of numerous dendrochronological studies is that the true age deviates up to 10 % from the radiocarbon age, where the gross structure of this deviation can be related to variations of the earth magnetic field and fine structure may be due to solar activity. Thus for a determination of the calendar age the use of calibration curves is essential.

2.3. Sample preparation

In this section the conversion from the raw sample (soil, bones etc.) to a sputter target suitable for an efficient formation of negative carbon ions is described. In a first step the sample has to be chemically pretreated to remove carbon compounds, which are not representative for the age of the sample. Then the remaining material is oxidized to CO_2 which is finally reduced catalytically to carbon.

2.3.1. Pretreatment of sediment samples

Two major components may obscure the ^{14}C results: carbonates arising from the erosion of limestone could be considerably older than the investigated layer and humic acids could be younger due to their high mobility. A fast and efficient mechanical separation of the sample material in organic and inorganic components is possible due to their different density. The sediment material is dissolved in a zinc chloride solution of density $\rho = 2$ g/cm^3 and after ultra-cetrifugation with 3000 cycles per minute the material is divided into the light organic fraction with $\rho = 1.3$–1.5 g/cm^3 and the heavy inorganic fraction with $\rho = 2.65$ g/cm^3. Subsequently the organic fraction is treated by the usual acid-alkali-acid (AAA) method, where HCl is used to remove still remaining carbonates and NaOH to remove humic acids. Finally the pretreatment is finished by heating in HCl, washing in deionized water and drying the remaining material in an oven. The organic residue is called bulk sediment, since up to now no separation due to the size of the objects has been performed and since it represents a mixture of the remains of water plants, algae, pollen and different macrofossils. Since it is the aim of our project to deduce the vegetation history from the pollen distribution in the sediment core, a direct dating of the pollen is highly desirable. The extraction of pollen material is mainly accomplished by additional sieving with 100 μm and 20 μm nylon meshes, since the average size of pollen ranges from 20 to 100 μm. The cellulose is removed with H_2SO_4 and finally for the deflocculation of amorphous organic material a treatment with NaOCl is performed. Details of the sample pretreatment are discussed in [4] and [5].

2.3.2. Pretreatment of bones

For the dating of bones we modified the procedure proposed by Longin [6], which is based on the removal of the inorganic fraction and the extraction of collagen. In an ultrasonic treatment the bone is cleaned with deionized water. Then the carbonates can be removed in two alternative ways: either the dried and ground bone or the complete bone is treated with 0.5–1 N HCl. The grinding accelerates the procedure, but if the bone contains only a small amount of collagen it may be lost. In a next step humic acids are dissolved with 0.25–1 N NaOH and finally the collagen is extracted by dissolving the residues in acidic water ($\mathrm{pH} = 1$–3) at 58° C for 16 hours. Remaining insoluble residues are separated by centrifugation and can be dated for a comparison. By drying the solution at 80° C all collagen can be obtained in form of gelatine. There is also the possibility to get rid of some remaining contamination by an additional ultra-spin-macrofiltration. In this way the gelatine fraction with molecule masses > 30 kD can be extracted and then dried as described above. After each step the residues are washed with deionized water.

2.3.3. Combustion to CO_2 and reduction to carbon

For a higher sample throughput both the combustion to CO_2 and the reduction to carbon have been simplified, similar to the Groningen target preparation [7]. Therefore we developed a new sample preparation system consisting of an newly installed element analyzer (EA) in combination with a stable mass spectrometer (MS) and a suitable multi-sample reduction facility described in detail by Morgenroth [8]. The element analyzer produces purified CO_2 in a fast flash combustion, a small part (10%) of the CO_2 is transferred to the stable isotope magnetic mass spectrometer for a high precision measurement of $\delta\,^{13}$C and $\delta\,^{15}$N and 90% to the liquid nitrogen cryo trap, where CO_2 is collected for further treatment.

For a conversion to sputter targets the cryo traps are now coupled to a newly built multi-sample reduction facility, where graphitization takes place by heating an appropriate mixture of hydrogen and carbon dioxide at 625° C with iron powder of 10 μm as a catalyst. Details of the reduction procedure are described elsewhere [4]. Except for the fittings, the new reduction apparatus is made of glass, the vertical cooling traps are cooled by liquid nitrogen for the collection of the CO_2. During the reduction process they are cooled by Peltier elements for the trapping of water produced during reduction. The gas pressures are monitored by pressure sensors and are recorded in a computer. The heating for the horizontal reduction vessel and the electric power supply for the Peltier elements are automatically switched off in case of interruption of the water cooling for the Peltier elements. In this way up to ten reductions can be performed simultaneously without any supervision.

3. Applications of radiocarbon measurements to interdisciplinary research

3.1. Sediment dating

Due to a worldwide discussion about possible global climate change there is an increasing interest to predict the future development by climatic models. The key for verifying these models is situated in the different climatic archives of the earth, which supplies us with information about the climatic development of the past. Terrestrial sediments and peat profiles are one of these archives representing the main material to investigate the climate change in Central Europe. The current research program in Erlangen is concentrated on ^{14}C measurements with special focus to the investigation of sediment profiles [4]. Since the last glacial period the temperature in Germany has increased by about 10°C and vegetation has developed from only few species to a huge variety. In that time period of increased warming both animals and men have influenced the vegetation considerably. To establish a better chronology of climate and vegetation since the last glacial period in Germany the research program “change of geo-biosphere during the last 15.000 years” has been started in Germany. Sediment cores of several meters length from different locations have been taken mainly from bog sites. Radiocarbon dating of these profiles together with corresponding pollen analyses allows the deduction of vegetation history in Holocene. To obtain more reliable results, the dating of pollen grains and macrofossils is performed in addition to that of the bulk sediments. In this paper we discuss the results of two sediment cores from bog sites close to Klein Oelsa and Altliebel, in the Upper Lausitz northeast of Dresden, where also prehistoric settlements have been found. The results of other sediment cores from Southern Bavaria are discussed in Ref. [4] and [5].

The results of ^{14}C AMS dating for both cores is shown in figures 3 and 4: the calibrated age is displayed as a function of core depth. For the Klein Oelsa core the complete age profiles for three different fractions of the sediment, for pollen, humic acids and bulk and in addition from three layers small pieces of wood have been determined. For a depth below 2.5 m the amount of pollen is decreasing, resulting in a very small amount of extracted carbon and therefore increasing error bars. As demonstrated

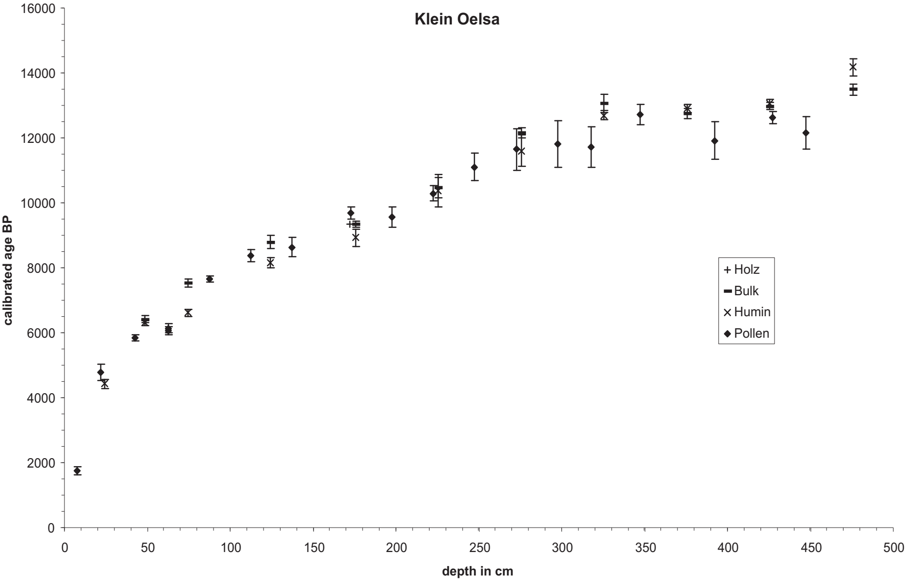

Fig. 3. Age profile for the sediment core of Klein Oelsa (NE of Dresden) using different fractions of the sediment (2σ errors).

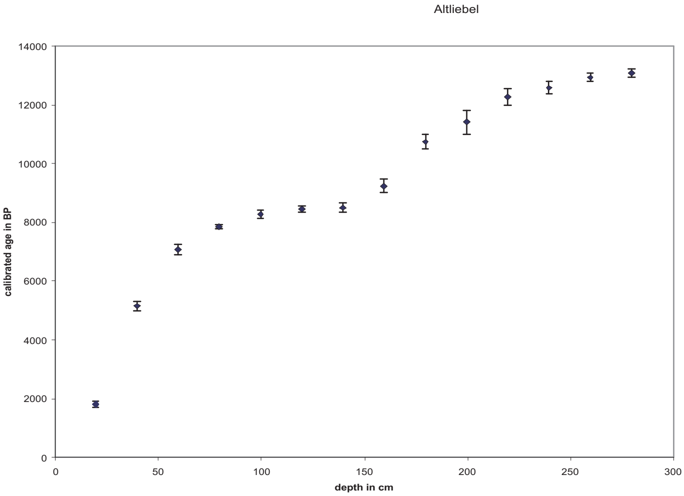

Fig. 4. Age profile for the sediment core of Altliebel (NE of Dresden) for bulk sediment (2σ errors).

in figure 3 the agreement of the different age profiles with each other is perfect within the errors. The results for the Altliebel core shown in figure 4 indicate a pronounced change in sedimentation rate at a depth of 1.50 m corresponding to an age of 8,200 BP. Both cores cover the time range of the last 14,000 years and together with the simultaneously performed pollen analysis (about 40 different pollen species) a reliable absolute chronology of vegetation history for the Upper Lausitz can be deduced.

3.2. Archaeological samples

Part of our samples are of archaeological interest ranging from Roman and Keltic re-mains to samples from Yucatan. As an example a Chinese banknote is shown in Fig. 5 which has been dated to be from Ming dynasty: the ^{14}C AMS measurement yields a radiocarbon age of 619 ± 22 BP and after calibration a calendar age of 1.350 ± 48 AD (2σ probability).

Fig. 5. Chinese banknote from Ming dynasty: calendar age of 1,350 ± 48 AD.

3.3. Environmental studies

The sources of chloroacetates in the environment are partly known. Photodegradation of volatile chlorinated hydrocarbons have been suggested as anthropogenic sources [9]. In the last few years, natural production of chloroacetates has also been proposed [10]. In a collaboration with Prof. Frank, University Bayreuth, we intend to provide an experimental approach to differentiate between the anthropogenic and biogenic contributions based on radiocarbon determinations ($^{14}C/^{12}C$ ratio) of haloacetates isolated from environmental samples. This can be achieved with accelerator mass spectrometry which has been used to determine the biogenic contribution of *e.g.* atmospheric methane [11] and carbonyl compounds [12].

The main assumption behind the method is that materials, derived from assimilation of atmospheric carbon dioxide, *i.e.* plant materials of all kinds, contain the equilibrium concentration of ^{14}C typical for modern carbon. On the other hand, fossil materials do not contain ^{14}C due to the relatively short half life ^{14}C, as compared to diagenetic processes of several hundred million years. One problem with this method is that the concentration of haloacetic acids in natural samples is very low: *e.g.* monochloroacetic acid (MCA) as the most abundant one in rain water has a concentration of about 0.2 μg/l. Thus an amount of about 500 litre rain water has to be collected to extract 50 μg carbon used for AMS measurements, assuming 100 % efficiency for GC separation and conversion to sputter target. With this tiny amount of carbon the problem of possible contamination with modern carbon during each step of sample preparation is very important. Since sediment samples also contain mostly small amount of pollen, the Erlangen sample preparation has already been optimized for sub-mg samples [5]. First tests were performed with haloacetic acids MCA and DCA produced in Bayreuth using modern carbon (equilibrium content of ^{14}C) or using carbon from petrochemical products (no ^{14}C). In this way we simulated samples produced either by biogenic and anthropogenic sources. The results showed the expected $^{14}C/^{12}C$ ratio even for samples with a carbon content of only 50 μg.

4. Concluding remarks

Since the first demonstration in 1977 that ^{14}C could be detected at natural level using a tandem accelerator as part of a mass spectrometer, the field of AMS has expanded into many areas of science. As shown in this contribution, radiocarbon measurements with AMS can be used in archaeology, geology and environmental research even for samples containing carbon in the 50 μg range which makes AMS superior to decay counting. Whereas the time range of ^{14}C measurements is limited to about 40 ka due to its relatively short half life, other long-lived isotopes such as ^{10}Be,^{26}Al, ^{36}Cl and ^{129}I can be used by AMS with emerging applications [13].

It is a pleasure to acknowledge the contributions made by my colleagues for the development of the Erlangen AMS facility, in particular by Prof. E. Finckh, H. Kerscher, Dr. M. Klein and Dr. G. Morgenroth. Special thanks to Prof. H. Küster for providing us with sediment cores and for valuable discussion. Finally, I thank Karin Kritzler, our technical assistant, for the help in target preparation and the Deutsche Forschungsgemeinschaft (contract Kr 549/18) for financial support.

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