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C-14 DATING BY MEANS OF ACCELERATOR MASS SPECTROMETRY: APPLICATION TO THE PALEOLITHIC CHRONOLOGY

by

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Until recently, $^{14}C/^{12}C$ ratios were only measured by the beta radioactivity counting method, this technique has allowed archeological dating with an upper limit of roughly 35-45,000 years B.P. The classical mass spectrometry was not applicable to the measurements of $^{14}C/^{12}C$ ratios for two main reasons: firstly this ratio is very small ($< 10^{-12}$ in natural samples) and secondly the isobars of ^{14}C (^{14}N, $^{12}CH_2$, ^{13}CH) could not be separated.

The recent development of mass spectrometers coupled with small electrostatic accelerators, makes it possible to measure directly the $^{14}C/^{12}C$ ratio and to remove totally the isobar particles. At the present time the Gif Tandetron can create positive ion beams with energies of up to several MeV (Figure 1). It is thus possible to use nuclear physics detectors able to identify the ions as a function of their mass, energy and atomic number (1, 2, 3).

In addition, the use of a Tandem accelerator allows for the destruction of the isobar molecular species which render inapplicable the classical mass spectrometry of carbon. In fact the "tandem" system implies a charge exchange near the central high voltage of the accelerator and monoatomic ions such as $^{14}C^-$ are simply stripped of their outer electrons in the argon cloud of the "stripping" canal. On the other hand, the interfering molecular ions dissociate because they are unstable as positive ions. It is then easy to use sophisticated spectrometric apparatus in order to distinguish the ^{14}C ions from the background of secondary ions formed by molecular dissociation.

The main advantages of this new method of carbon isotope measurements are:
- appreciable reduction of the amount of carbon needed for a ^{14}C measurement. We are currently dating samples containing only one milligram of carbon;
- possibility of ^{14}C measurements on specimens exhibiting down to a few per-mil of the ^{14}C activity of modern carbon.

The sample preparation at Gif can be divided into three steps:
- sample pretreatment. For charcoal and carbonate this step is similar to that used in the beta counting method. The extraction of collagen from bone followed by a chromatographic separation of specific amino-acids is still under study at Gif-sur-Yvette.

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- production of CO_2. Organic matter in sealed ampules is oxidised by copper oxide at roughly 850°C. Carbonate is hydrolised under vacuum with anhydrous phosphoric acid.
- reduction of CO_2. The carbon dioxide is reduced catalytically by hydrogen gas at 650°C over iron powder. The resulting graphite-iron mixture is compressed into a solid target ready for AMS use (4).

Figure 2 shows the results of a comparison between the two ^{14}C dating methods. Each sample has been dated first by the beta counting method and then by using the AMS. It is evident that the two age-sets are in good agreement (classical ^{14}C dating obtained by G. Delibrias, CFR Gif-sur-Yvette).

The actual limits of accelerator ^{14}C dating are expressed as percent of modern carbon activity which is equivalent to a so-called "background" age.

We estimate our machine background to be equal or lower than the ^{14}C activity of a very pure geological graphite from Alibert Mine, Siberia (obtained from the Ecole des Mines of Paris). The activity of an untreated sample of this graphite was 0.089 ± 0.017 %, which corresponds to an age of $56{,}500 \pm 1600$ years B.P.

In order to simulate the contamination produced during the preparation of targets from archeological charcoal, we have measured the activities of four samples obtained by the catalytic reduction of CO_2, which was generated by the combustion of the geological graphite from Siberia. The mean activity was 0.34 %, corresponding to an age of 45,600 years B.P. which represents our practical limit of archeological dating of organic material (charcoal, wood ...).

The total contamination expected in the treatment of carbonates has been measured in two samples of a calcite concretion whose age as measured by U/Th is greater than 100,000 years B.P. We obtained a mean value of 0.40 %; which is equivalent to an age of about 44,400 years B.P.

Therefore, it is evident that the main obstacle to the dating of samples aged 45-50,000 years is contamination in the course of target preparation which exceeds by at least a factor of four the background levels in the machine. Moreover, there are two other sources of contamination:
- "natural" contaminants, such as humic acids which can be absorbed on charcoal but can be totally removed by basic pretreatment in the laboratory;
- "artificial" contamination, which can occur during the recovery and the storage of the samples.

Preliminary results indicate that great care must be taken at the excavation site when one tries to understand the stratigraphic significance of very small fragments of charcoal. In fact vertical displacements of samples of about ten milligrams are not uncommon in coarse sediments.

In spite of all these methodological difficulties, the new method of ^{14}C accelerator mass spectrometry should help establish a better chronology for the transition from middle to upper Paleolithic and lead to a better understanding of the replacement of Neandertal man by *Homo sapiens sapiens*.

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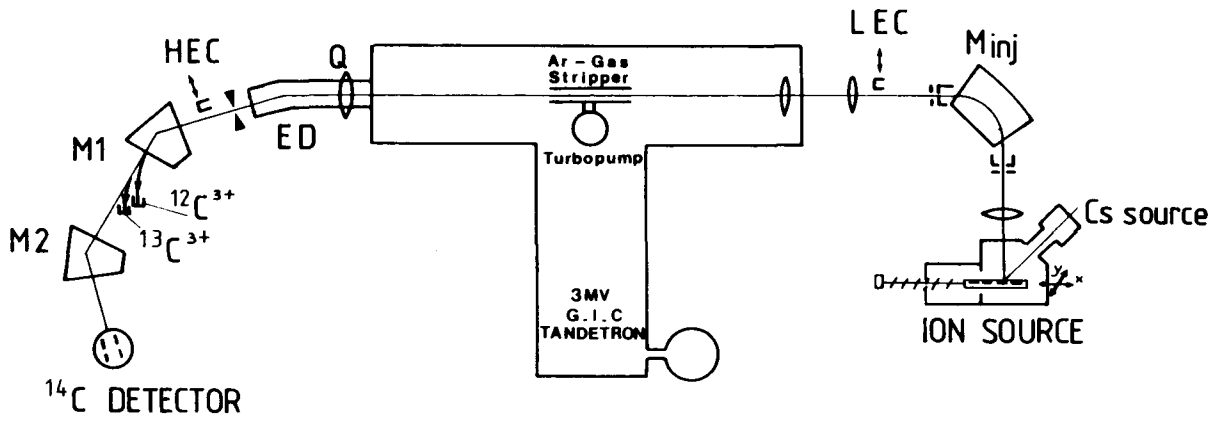

FIGURE 1

Schematic diagram of the Gif-sur-Yvette AMS facility

M_{inj} :	*injection magnet*	ED :	*electrostatic deflector*
LEC :	*low-energy Faraday cup*	HEC :	*high-energy Faraday cup*
Q :	*electrostatic deflector*	M_1, M_2 :	*strong focusing magnets*

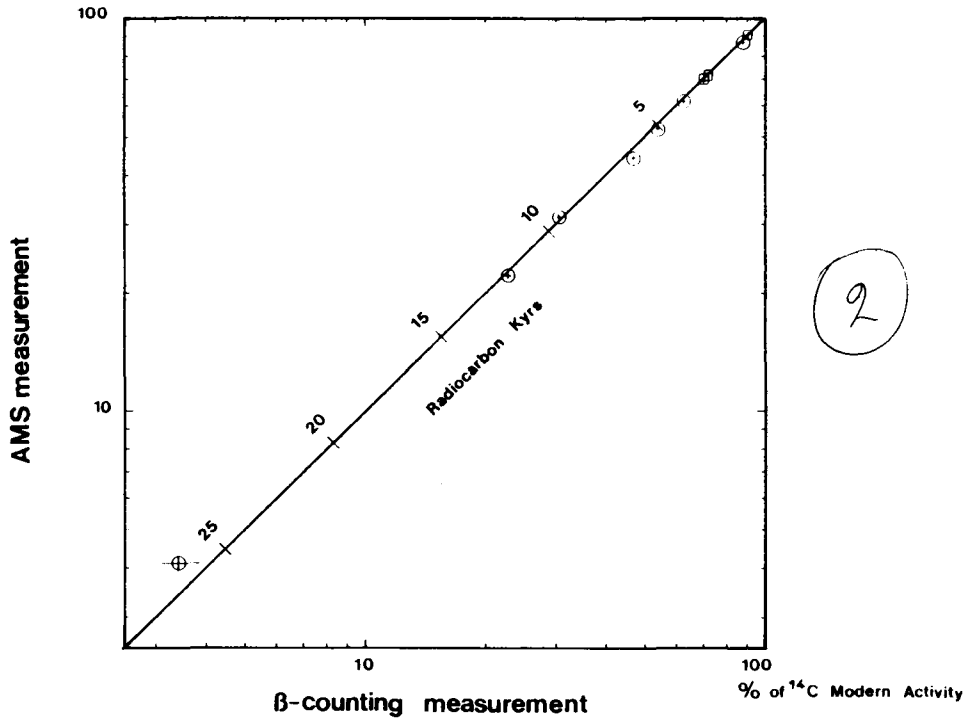

FIGURE 2

Comparison of ^{14}C ages obtained by AMS and β^- counting.
(O measurements on the same CO_2 samples, ❐ comparisons which include also the combustion)