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Article abstract

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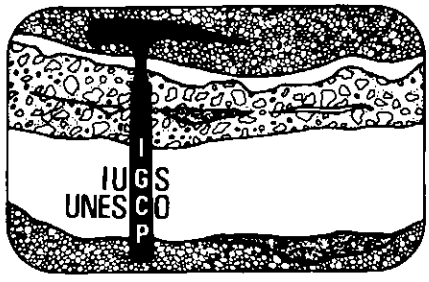

Dating Methods of Pleistocene Deposits and Their Problems: The Promise of Atom Counting

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Summary
Recent developments in mass spectrometry, using some of the apparatus and techniques of nuclear physics, have made possible the detection of the cosmic ray created ^{14}C, ^{10}Be and ^{36}Cl nuclei at natural concentrations by atom counting. The small sample size, a few milligrams, promises to revolutionize ^{14}C dating and to introduce new dating methods for the Pleistocene

Introduction
A great increase in sensitivity of the ^{14}C dating method, by counting the ^{14}C atoms in a few milligram sample rather than the beta rays emitted from a gram sample, has been demonstrated recently (Purser *et al.*, 1977; Litherland, 1978; Nelson *et al.*, 1977; Bennett *et al.*, 1977; Muller *et al.*, 1978 and Doucas *et al.*, 1978). The atom counting method has also been demonstrated for ^{10}Be (Raisbeck *et al.*, 1978a) and ^{36}Cl (Elmore *et al.*, 1978) in natural samples and as these isotopes have half lives ranging from 5730 years for ^{14}C, 1,600,000 years for ^{10}Be and 308,000 years for ^{36}Cl the possible significance of the atom counting method for dating of Pleistocene deposits is clear.

The work to be described has been done mainly by nuclear physicists using techniques derived from nuclear physics and consequently the discussion here will centre mainly on the recent advances in the atom counting. The full significance of the developments for the dating of Pleistocene deposits must await the active involvement of geologists in the exploitation of atom counting. The method is clearly very promising and it is hoped that this article will stimulate further discussion and experimental work

A Brief History of The Atom Counting of ^{14}C
The idea of the atom counting of ^{14}C has been discussed informally for many years but it was not until 1970 that Oeschger *et al.* (1970), put the challenge in print. This was followed by a determined attempt by Schnitzer *et al.* (1974) that nearly succeeded. Success was not in fact achieved until 1977 when several groups (Purser *et al.*, 1977, Nelson *et al.*, 1977, Bennett *et al.*, 1977, and Muller *et al.*, 1978) succeeded in detecting ^{14}C at natural concentrations. This was followed by an explosion of activity and two specialized atom counting devices have already been funded: one at the University of Arizona, U.S.A., and the other at Oxford University, U.K.

The full history and prehistory of this development is still being sorted out but two significant events were the realization that the destruction of interfering molecules with the help of a tandem accelerator could revolutionize mass spectrometry (Purser, 1976) and the realization that the acceleration to high energies in a cyclotron could be followed by range separation of the ^{14}C and ^{14}N atoms (Muller, 1977). The suggestion for using the negative ion $^{14}C^-$, which is stable, to discriminate against $^{14}N^-$, which is unstable, was made by Litherland in 1974. The full impact of this suggestion, which is as discussed below, basic to the devices being constructed, was only realized sometime after the development of the sputter negative ion source (Middleton *et al.*, 1974). This is because of the very small solid sample needed for these ion sources and because of the negligible memory effect of this type of ion source which made efficient rapid sequential counting of different samples possible. Ion sources using gases are notorious for remembering, often for several days, the gases previously used and are more prolific in their use of material.

All these developments are now being exploited vigorously and the users of the data generated by atom counting can look forward to a large increase in the quantity and quality of the data

Atom Counting of Radio Nuclei
Atoms are routinely counted in conventional mass spectrometry where they have energies of a few kilovolts. At these energies however molecules are hard to destroy and they cause ambiguities in element identification unless very great care is taken in sample purity or unless very high resolution is used (Lovering, 1975). Examples familiar to geologists are the molecules Ca_2^+, $CaAlO^+$, $CaSiO^+$ and $Al_2O_3^+$ which have masses very close to that of $^{86}Sr^+$. However these molecules can be destroyed quite easily if they are accelerated to about 2 MeV and then passed through a gas at low pressure. The removal of three electrons from a molecule by atomic collisions then ensures its spontaneous fragmentation in a short time, which is probably less then 10^{-9} seconds. The selection of charge +3 atoms after acceleration, by an electrostatic analyser, results in the elimination of all molecules and only atoms can be counted. This idea (Purser, 1976) is the basis for the recent proposal by a geologically oriented group in Southern Ontario to use higher energies in connection with secondary ion mass spectrometry (Strangway, 1978)

Molecular interference is even more serious for the detection of such radioisotopes as ^{10}Be, ^{14}C, ^{26}Al and many others because they are present at such low abundances. For example, ^{14}C is present at levels below one part in 10^{12} in natural samples. Also, as the radioisotopes decay to stable elements which have masses which differ by only one part in nearly a million, conventional mass spectrometry is completely out of contention for the separation of radionuclei and their isobars. However as discussed below the separation of isobars can be facilitated by the use of negative ions and the elimination of molecules achieved by the use of higher energies.

The acceleration to higher energies, higher than that achieved in conventional mass spectrometry, confers another advantage to atom counting besides molecular elimination. At the higher

energies it is possible to identify each particle, at the same time as it is counted, by using the fact that the rate of energy loss dE/dx in matter is proportional to the square of the average charge on the atom which in turn is related to the charge on the nucleus. This advantage of higher energy ion beams has been used to separate very cleanly ^{14}C and ^{14}N ions and even ^{36}Cl and ^{36}S of the same energy (Bennett *et al.*, 1977 and Elmore *et al.*, 1978). The separation can sometimes be obtained by using range measurement techniques and this has been done for ^{14}C by Muller *et al.*, (1978) and for ^{10}Be by Raisbeck *et al.* (1978a). The ^{14}C ions have, at high energies, a 30 per cent longer range in matter than the interfering ^{14}N ions and this method has been used to discriminate against a very high ratio (10^{10}:1) of ^{14}N to ^{14}C (Muller *et al.*, 1978). This demonstrates very well the power of the method of using high energies. Actually high energies are not needed to discriminate between the ^{14}N and ^{14}C as the $^{14}N^-$ negative ion is unstable with a very short half life whereas $^{14}C^-$ is stable. Consequently the use of negative ions alone is adequate to discriminate against ^{14}N when counting ^{14}C atoms. However the need to count the rare ^{14}C atoms efficiently without molecular interference implies, at present, that a minimum energy of about 2 MeV for the negative ions must be reached to eliminate completely the accompanying $^{12}CH_2^-$, $^{13}CH_2^-$ and $^{13}CH^-$ molecules and to count the $^{14}C^{-3}$ as efficiently as possible.

The system used at Rochester has been described by Bennett *et al.*, 1977 and 1978 and is illustrated schematically in Figure 1. It comprises a sputter ion source followed by an inflection magnet which is capable of resolving masses 25 and 26. This is followed by a 150 kV acceleration and then injection into the large, 8 MV tandem accelerator at Rochester. The total length of the pressure vessel of this accelerator is about 80 feet in contrast to the much smaller (less than 15 feet long) tandem accelerators being built specifically for ^{14}C dating. In the central electrode the negative ions and molecules encounter argon gas and several electrons are removed. The subsequent acceleration of the positive ions to ground potential produces 40 MeV $^{14}C^{+4}$ ions. These are analysed at present by a combination of electric and magnetic fields which eliminates all but $^{14}C^{+4}$ and a very few $^{14}N^{+4}$ ions from the acceleration of molecules of $^{14}NH_2^-$ or $^{14}NH^-$ followed by rare charge exchange processes. The few remaining $^{14}N^{+4}$ and $^{14}C^{+4}$ are completely separated and counted by the heavy ion detector (Shapira *et al.*, 1975)

The Results of Some Recent Measurements

The counting of ^{14}C atoms was used recently (Bennett *et al.*, 1978) to measure the ages of some geological samples which had been dated previously by the conventional beta ray counting method. The oldest sample dated was 40,000 years old. The results were in good agreement but the most striking feature was that less than 15 milligrams of carbon were used for each date. It can be estimated that it will be possible in future to use less than one milligram to obtain such dates. The clear separation by the apparatus between the ^{14}C atoms and ^{14}N, ^{12}C and ^{13}C atoms, from the fragmentation of molecules, followed by very rare charge exchanges in the accelerator, can be seen in Figure 2. The recent addition of an electrostatic analyser to the system used for these measurements at Rochester shown in Figure 1 has resulted in the elimination of the ^{12}C and ^{13}C atoms from the final detection apparatus.

The same apparatus has also been used recently for the detection of ^{36}Cl in natural samples (Elmore *et al.*, 1978) such as Lake Ontario water where the ratio $^{36}Cl/Cl$ was found to be 2×10^{-13}. This work, which reached a sensitivity of 3×10^{-15}, was a preliminary feasibility study which has considerable implications for the study of the age of ground waters and possibly for an alternative chronology of the Pleistocene.

The radionucleus ^{10}Be has been detected recently in Antarctic ice (Raisbeck *et al.*, 1978b) by atom counting. In this case the cyclotron at Grenoble was used together with range separation from the large flux of ^{10}B atoms. Recently the tandem accelerator at Rochester (Kilius *et al.*, 1978) has been used to detect ^{10}Be in ^{9}Be generated by the ^{9}Be (n,γ) ^{10}Be reaction down to levels of $^{10}Be/^{9}Be$ of 5×10^{-15}. In this case the BeO^- ion was used for the first stage of acceleration because of the metastability of the Be^- ion. The detailed study of ^{10}Be in ice caps and in lake and ocean sediments will be possible with either the cyclotron or the tandem accelerator systems although there are indications that quite small tandems will be useable and that they will be more efficient at detecting the ^{10}Be.

Conclusions

The recent application of nuclear physics techniques to the detection of radionuclei at natural concentrations promises to provide a new and powerful tool for their study in very small samples In fact only very small samples can be used for the new method because of the efficient and low rate of sample use in

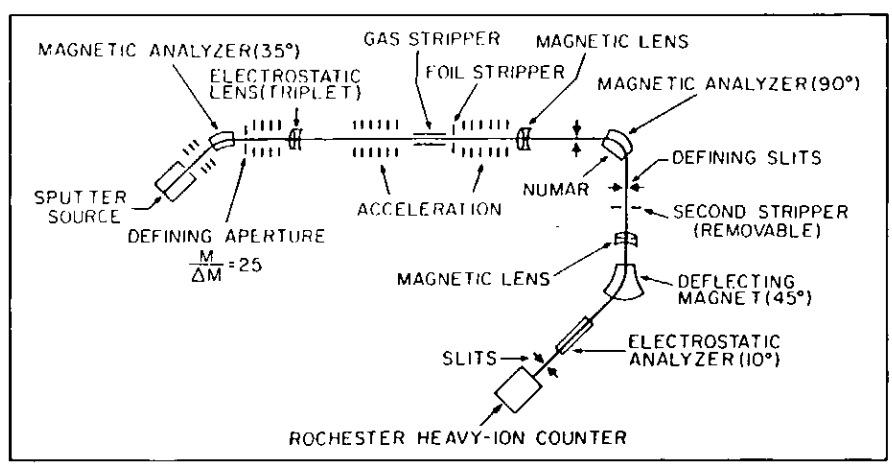

Figure 1

The apparatus used for ultra-sensitive measurements of ^{14}C, ^{10}Be and ^{36}Cl is shown schematically. 20 Kev Cs^+ ions were used to produce the sputtered negative ions which were then mass selected by the 35° inflection magnet.

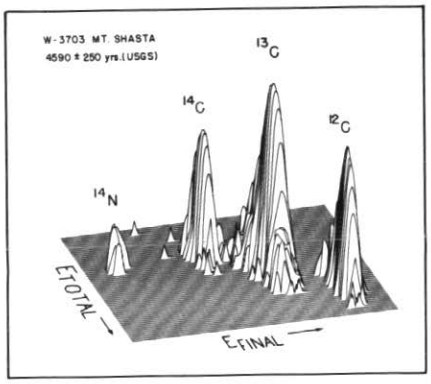

Figure 2
Logarithmic (three decades) plot showing the separation between ^{14}C and the ^{14}N, ^{13}C and ^{12}C backgrounds without the use of the 10° electrostatic analyser shown in Figure 1. The ^{13}C and ^{12}C backgrounds are eliminated by the electrostatic analyser.

the sputter ion source. The estimated overall efficiency, derived from data published by (Brand, 1977), is about five per cent for converting carbon atoms in the ion source to carbon atoms counted in the final detector. This efficiency for the negative ion tandem accelerator system, when fully realized, implies that ultimately a ^{14}C date accurate to plus or minus one per cent will be obtainable with only about three μg of carbon in a few minutes. The beta rays from such a small quantity of carbon would have to be counted for 500 years with a 100 per cent efficiency to equal this accuracy. These numbers illustrate very well the promise of atom counting (Stuiver, 1978).

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