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^{14}C Dating by Accelerator Mass Spectrometry of Carbonized Plant Remains from a Middle Paleolithic Hearth at Douara Cave, Syria*

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A number of radiocarbon dates, obtained by using a conventional β-counting method, have been reported concerning samples from Middle Paleolithic horizons in Douara Cave, Syria. Two dates on ostrich eggshells were $46,700+2,200/-1,700$ BP and $>53,800$ BP (GrN-8638, GrN-8058 respectively). Two dates on hearth ash materials were scaled out at $>43,200$ BP and $>52,000$ BP but another sample gave the result, $38,900\pm1,700$ BP. In addition, a date of 75,000 BP was obtained by a different method (fission track dating) on a barite pebble taken from the same hearth deposit as the ash samples noted above.

In order to examine this discrepancy in the chronological results we have turned to a third method, accelerator mass spectrometry, and used samples of carbonized seeds. Many pieces of these, which have been identified as *Celtis* spp., were also collected from the same hearth deposit as the ash and barite pebble. At present, there are no *Celtis* trees around Douara Cave or elsewhere in Palmyra Basin, but they can be found near the Mediterranean coast several hundred km away.

The accelerator mass spectrometry (AMS) technique which we used was recently developed using the tandem Van de Graaff accelerator in the Research Center for Nuclear Science and Technology at the University of Tokyo. Since the expected age was so old that natural contamination of the sample by recent carbon, and contamination by modern carbon in the process of sample preparation, were anticipated, chemical treatments to attempt to eliminate these were necessary.

Archaeological samples for dating may be contaminated by ^{14}C in several stages. In

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the site there will have been absorption of CO_2 gas and carbonate, and of organic materials, and similar contamination occurs during preparation for AMS. It seems easy to remove CO_2 and carbonate by adding diluted HCl solution and, in any case, it is difficult to produce C^- and CH^- ions from $CaCO_3$. Organic contaminants are more complicated. Alkali and acid soluble components are easily eliminated, but cellulose tissue, for instance, cannot be removed by this treatment, and the problem is accentuated by the small size of samples for AMS.

For our purposes, all chemical processing of samples is done in a box made of lucite. The glass-ware we use is made of fused quartz and other laboratory-wares are made of Teflon or polyethylene.

In the Douara Cave samples we analyzed there are apparently two types of material.

A) carbonized black seeds ; charcoal. (Sample No. 905-15, Sample No. 907-14, 15)

B) fragments of testae. (Sample No. 907-7)

The charcoal samples were prepared in several ways. Firstly, some material was left untreated. Secondly, a sample of a few mg was boiled in a 1N-HCl solution for one hour, and then washed with distilled water and dried at 100℃. Thirdly, a 10—20 mg sample was boiled in a 1, 2N-NaOH solution several times until the alkaline solution no longer took on a strong colour. After rinsing with distilled water, the sample was treated with 1N-HCl. In this case, only 30—40% of the sample was recovered. After the processing, all samples were baked *in vacuo* at about 1000℃, and mixed thoroughly with silver powder (10 μm) in a quartz mortar, using a pestle. The amount of silver was about twice the weight of the charcoal sample. This mixture was pressed by hand into a hole, 1, 5 mm in diameter, at the center of a sample holder.

The test samples were either directly pyrolized, or pyrolized after alkali treatment, but no useful products were obtained.

Laboratory contamination in processing was evaluated by applying the same treatment process to dead carbon samples which had been obtained as soot by burning toluene in open air and subsequently baking it in a sterile vacuum.

As described above the background level changes with every measurement and it is very difficult to estimate whether the source of the contamination is modern carbon arising from the sample preparation process, a machine background level caused by a memory effect in the ion source, a vacuum contaminated by oil vapour or some other cause.

By measuring the dead carbon samples we estimated our best background level to be $^{14}C/^{12}C < 3 \times 10^{-16}$ which corresponds to more than 67, 000 years. However, since the level is usually in the range 55, 000 to 60, 000 years it is very difficult to determine the age of samples which produce results close to the background level.

As a preliminary result, and neglecting the background counts, we calculate the age of the *Celtis* spp. seeds to be 52, 000 (+5, 000/−3, 000) BP. The calculated ages are based on Libby's half life of ^{14}C, i.e. 5, 570 years. Indicated errors are the years corresponding

to the standard deviation (1 σ) of ^{14}C counting statistic errors. Since other data from which younger ages were derived are assumed to be influenced considerably by modern carbon contamination, the oldest age seems the most reliable and it probably lies near the lower limit of the real age.