RECENT ADVANCES IN MODERN ARCHAEOLOGICAL DATING (AMS, ESR, $^{234}U - ^{230}Th$): FIRST OXFORD AMS DATES FOR MITOC – MALU GALBEN

BY

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Impressive recent advances have been made by physicists concerned with dating of archaeological materials too small or too old to be accurately dated by application of the conventional radiocarbon method. The lower limit of the latter is about 60,000—50,000 BP. At the same time, however, the lower limit of the new AMS, ESR and $^{234}U - ^{230}Th$ series dating methods has now been pushed back to at least 100,000 years BP. This will, of course, be of interest for Palaeolithic specialists, but also for those specializing in the post-Palaeolithic period, e.g. the Neolithic. These three innovative technically sophisticated, and costly, methods are now in use in Romania on projects developed by this author.

Accelerator Mass Spectrometry (AMS) [1]. In the first technique, samples containing only a few milligrams of carbon can be securely dated. However, Parkes [2] has noted that "The possibility of using very small samples for dating does, however, increase the risk of producing misleading dates unless the archaeologist is extremely careful to ensure that the samples dated do belong in the (archaeological) context in which they are found". In other words, the sample must be in a primary *in situ* position and not be intrusive due to soliflectional, cryoturbational or anthropogenic disturbances.

Theoretically, the AMS method could produce dates of 100,000 years BP. For the present, the Oxford Accelerator Unit has a lower capacity of 35,000 BP (R. Housley, 1988 personal communication). The ages determined are with an error of ± 1 per cent only and are quoted at one (68%) standard deviation (SD).

It is based on measuring the proportions of ^{14}C and ^{12}C in graphite prepared from sample carbon [3]. The meticulous chemical pretreatment of samples is needed to remove extraneous contaminants. It is carried out in the receiving laboratory [4].

In the Oxford facility, 200 mg or more of *pure* wood charcoal or 5—10 grams of either unburnt or charred compact long bone are needed for analysis. Other materials suitable for AMS dating are, in a closed stratigraphic context, masses of *in situ* burned seeds, food residues or soot on pottery, charcoal used as a fuel in iron or copper furnaces, charcoal in slag, molluscs (marine only), sediments and more. Samples are collected in aluminum foil or PV plastic bags. Labelling should be separately attached using permanent ink.

Ten AMS samples were collected by V. Chirica and this author in Upper Palaeolithic cultural levels at Mitoc-Malu Galben. Their interpretation is later presented.

Electron Spin Resonance (ESR) [5]. ESR spectroscopy is currently being used to solve a variety of archaeological problems but it is not widely available. This new method is the only one for dating such materials which are too old or too small to be dated by the ^{14}C technique [6]. Also, it can be carried out non-destructively and only small samples of teeth, long bones or calcite are required (1 gram).

[1] Parkes, P. A., *Current Scientific Techniques in Archaeology*, 1986, London, Croom Helm, pp. 27—34; Mook, W. G. and H. T. Waterbolk, *Radiocarbon Dating, Handbooks for Archaeologists*, N. 3, 1985, Strasbourg, European Science Foundation, pp. 15—17, 55; Taylor, R. E., *Radiocarbon Dating: An Archaeological Perspective*, 1987, Orlando, Academic Press, pp. 61—64, 90—95; Gillespie, R., *Radiocarbon Users Handbook*, Committee for Archaeology, 1986, Oxford, Oxford University, p. 3.

[2] Parkes, P. A., *op. cit.*, p. 29.

[3] Mook and Waterbolk, *op. cit.*, p. 15—16.

[4] Wand, J. O., R. Gillespie and R.E.M. Hedges, *Sample preparation for accelerator-based radiocarbon dating, Journal of Archaeological Sciences*, 1984, 11, pp. 159—163.

[5] Parkes, *op. cit.*, pp. 54, 57—58.

[6] Parkes, *op. cit.*, p. 58.

Arheologia Moldovei, XIII, 1990, p. 9—12.

"Whenver possible electrons combine to form pairs. For example, when atoms combine to form molecules they normally do so in such a way that a molecule has an even number of electrons and hence no unpaired electrons. Occasionally, however, atoms occur in which there are unpaired electrons" [7].

This method is a means of detecting these electrons. This is done by establishing whether there are any electrons present capable of absorbing energy of a particular wavelength when a sample is placed in a magnetic field of known strength. The amount of energy and the wavelengths over which this absorption occurs makes it possible to draw conclusions about some of the electrons present and their surroundings.

Technically, "...the ESR method is based on the measurement of unpaired electrons produced by environmental and internal radiation and trapped in a crystal at some charge defect site. The number of trapped electrons increases with age and, if the radiation dose rate remains constant (measured in years) is given by $Age = \frac{accumulated\ dose\ (AD)}{dose\ rate\ (DR)}$ when the accumulated dose (AD)... is the total radiation dose received by the sample since its formation, and the dose rate (DR).... is generated by the radioactive elements of the sample and its surroundings as well as by cosmic rays" [8].

The "crystal" in question is hydroxyapatite in either teeth or bone. A very large tooth, or about six individual teeth from a mandible or maxilla (which is to saved for future species identification) and 250 grams of soil surrounding the sample are collected. The latter is used for analysis of uranium (U), thorium (Th) and potassium (K) content. Calcite is also be dated by this method.

The upper limit of this method is about 30,000 years BP and the lower, more than 100,000 years (1–2 Ma).

ESR will be used at Mitoc-Malu Galben in 1989 and 1990 in dating the lower Aurignacian and Mousterian levels, below 10.50 m. Samples will be processed in Canada.

Uranium-Thorium Series [9]. This final new dating method is devoted to the ageing of various forms of calcite (calcium carbonate) as in bones, shell, certain calcareous concretions and travertine. It's range is from about 5,000 to 500,000 years BP. About 100–200 grams of calcite are needed for analysis.

When calcite is formed, it normally contains uranium from the surrounding soil matrix, but *no* thorium. As time passes, uranium undergoes radioactive decay producing thorium (^{234}U, ^{230}Th). "Thus, if one knows the concentration of uranium in the newly formed calcite, one can work out how old the calcite is by measuring the amount of thorium present today" states Parkes [10]. Their ratio, then, of the one to the other is the critical factor.

The calcite dissolved in a particular acid, chemically separating the thorium from the uranium. "The alpha particles emitted by both elements are then studied and used to determine the ratio $^{230}Th/^{234}U$. The ratio $^{238}U/^{234}U$ is determined at the same time because ^{234}U is produced by the decay of ^{238}U and so the concentration of ^{238}U in the sample will effect the $^{230}Th/^{234}U$ ration of the sample. The age of the sample can then be calculated from these measurements" [11].

The theoretical accuracy of uranium-thorium series dating method is better than ± 10 per cent at one sigma standard deviation (68%).

A series of samples, at least three should be collected in each material to be dated in a particular geoarchaeological level. In practice, the Groningen laboratory usually prefers to compare the ratios of $^{234}U/^{230}Th$ samples collected in an uppermost level with those in a lower level.

Several uranium-thorium date determinations will soon be available for Peştera Cioarei de la Boroşteni (Gorj County) where a Middle Palaeolithic level is correlated with one of the Upper Palaeolithic period.

This method will be used for the first time at Mitoc-Malu Galben in 1989 and 1990 in cross-dating Aurignacian and Mousterian levels.

Comparison of Methods. The AMS method operates with milligram quantities of samples carbon derived from wood charcoal, burnt seeds, soot, food particles, organic collagen in bone and marine molluscs.

ESR is used mainly to provide dates beyond those unattainble by conventional and AMS radiocarbon methods. Teeth, bone and calcite are the principal agents used in dating.

U-Th series dating method is used in the dating of calcite, bone, calcareous concretions, shells and travertine.

[7] Parkes, *op. cit.*, p. 57.

[8] Symela, S., H. P. Schwarcz and R. Gruen. *ESR dating of Pleistocene fossil teeth from Alberta and Saskatchewan, Contribution 147 from the McMaster Isotopic, Nuclear and Geochemical Group* (Canada), p. 235.

[9] Parkes, *op. cit.*, pp. 100–105; Schwarcz, H. P. and A. G. Latham, *Uranium Series age determinations of travertines from the site of Vertesszöllős, Hungary, Journal of Archaeological Science*, col. II, 1984, pp. 327–336.

[10] Parkes, *op. cit.*, p. 100.

[11] Parkes, *op. cit.*, pp. 101–102.

Mitoc-Malu Galben (Botoşani County): Ten critical Upper Palaeolithic radiocarbon samples were selected for AMS dating at the Oxford Radiocarbon Unit in England. They were shipped there in May 1987 and results were received in late 1988 and early 1989.

Due to the expected milligram carbon content of individual samples, all were meticulously *chemically pretreated* to remove contaminants [12].

Seven unburnt bone samples were used to produce analyses of collagen carbon with the aim of measuring aminoacid concentration in them. "This is needed since previous dating experience has shown us that low collagen bones give unreliable dates due to introduction of contaminants into the structure of the bone. The general cut-off point use (below which bones are not dated) is approximately 12—15 mg/g". (R. Housley, Senior Oxford Archaeologist, letter dated 5th August 1988).

The Mitoc bone samples analyses give the following results :

MMG 43 (Square A2, 8.15 m)—10 mg/g
MMG 44 (Square A2, 8.15 m)— 7 mg/g
MMG 46 (Square A3, 8.15 m)— 4 mg/g
MMG 63 (Square G8, 4.80 m)— nil
MMG 64 (Square G8, 5.05 m)—10 mg/g
MMG 67 (Square J8, 5.40 m)—21 mg/g
MMG 90 (Square C1, 9.75 m)— 3 mg/g

Samples 43, 64 and 67 only were dated in February 1989.

The three wood charcoal samples sent gave the following results of their respective carbon contents:

MMG 86 A (Square D5, 10.65 m)—20 mg/g
MMG 87 (Square B5, 10.65 m)—sparce (not dateable)
MMG 88 (Square B5, 10,65 m)—sparce (not dateable)

The Oxford results, expressed in years BP at one sigma standard deviation at 68% certainy, are

OxA—1 779	23,650 ± 400	24,050—23,250	Gravettian	G8,	5.05 m
OxA—1 780	24,650 ± 480	25,100—24,200	Gravettian	J8,	5.40 m
OxA—1 778	27,500 ± 600	28,100—26,900	Gravettian	A2,	8.15 m
OxA—1 646	31,100 ± 900	32,000—30,200	Aurignacian	D5,	10.65 m.

These samples can only be viewed in the context of the other 34 Upper Palaeolithic conventional radiocarbon dates, most of which were produced at Groningen (GrN) (23 samples). Eleven others were analyzed at Geochron (GX), Cambridge, Massachusetts, U.S.A.

The Oxford dates have greatly aided in resolving some particularly vexing temporal questions at Mitoc. Foremost of these are questions on geoarchaeological relationships and relic periglacial features there.

The above four samples are referenced to the field surface datum in square J8 (0.00 m). The lettered squares in the west profile are, from N to S : J, G, F, E, D, C, B, A, H and I. Their coordinates in the north profile are, from W to E, 8 to 1. The inclination (dip) of geoarchaeological levels in the north profile, from W to E, is about 15 degrees. That in the west, from N to S, is about 5 degrees.

Traces of ancient relic solifluctional disturbances are apparant throughout the levels in the A-I/8—1 transect in the southern and eastern peripheral sections. The latter phenomena will enter into the below discussion.

Discussion. Aurignacian Technocomplex. The AMS charcoal sample date of 31,100 ± 900 (OxA-1646), is matched by another conventionally processed one, 31,850 ± 800 BP (GrN-12 637 ; square B4, 8.70 m, charcoal). They seem to pertain to *different* archaeological events. Their technical ages are 750 years and the error is 100 years apart. According to Taylor, the affinity, should be only about 200—300 years [13]. The former was retrieved in square D5 at a depth of 10.65 m. The latter, however, was taken at distance of 6.50 m further south at a depth of 8.70 m. The differences in depth, then, is 1.95 m between the two measured from the square J8 datum (0.00 m). Since the geoarchaeological levels at the site are inclined to the south margin it can be argued cultural levels are also.

At the same time the OxA-1646 sample was collected, an another sparcer one was taken in the same square and depth. It produced an anomalous date of 24,400 + 2 200/1 700 BP (GrN-15 457) in reflection of its scanty carbon content.

Two additional radiocarbon (charcoal) samples, from square B-5 (10.65 m) further south, are now being processed at Oxford. Results are expected in 1990.

The other Aurignacian wood charcoal samples should be discussed at this point : 28,910 ± 480 (GrN-12636 ; D4, 7.85 m) and 29,410 ± 310 BP (GrN—15 454 ; H3, 9.45 m). Although the mean of the two is 29,160±395 BP, it seems the occupational levels appear to be different archaeological events. Their ages are 500 years and the error is 170 years apart.

[12] Taylor, *op. cit.*, pp. 41—61.

[13] Taylor, *op. cit.*, p. 141.

Thus, four distinctive occupation levels at Mitoc belong to the Aurignacian Technocomplex. However, confirming radiocarbon samples are still needed.

East Gravettian Technocomplex. The Oxford collagen date of 27,500 ± 600 (OxA—1778) marks the inception of the Gravettian occupation at Mitoc. However, the sample appears to have been slightly soliflucted. It was collected in square A2 at a depth of 8.15 m fairly close to the southern margin of the excavation area. The difference between this date and the uppermost Aurignacian one (28,910 ± 480 BP, GrN—12 636; D4, 7.85 m) is 1,400 years with a margin of error of 120 years.

Another Gravettian date that can be used in evaluation of this early period is 27,410 ± 430 BP (GrN—14 914; B4, 8.70 m, carbon). The difference of this date and the above Oxford one is only 90 ± 170 years. Essentially, the same point in archaeological time in radiocarbon years BP has been reached so that both can be seen as mutually equivalent. In this context, they appear to belong in the same geoarchaeological and cultural level (mean 27,450 ± 510 BP).

The second Oxford collagen date, at 24,650 ± 450 (OxA—1780; J8, 5.40 m), is also matched by the two closely allied ones of: 24,820 ± 850 (GX-9425; G7, 5.50 m, carbon) and 24,620 ± 810 BP (GX-9422; B7, 5.00 m, carbon). The latter two are 200 ± 40 years apart. They all seem to pertain to the same cultural level with a mean of 24,695 ± 700 BP.

The final Oxford assay of bone collagen, 23,650 ± 400 BP (OxA-1779; G8, 5.05 m) also has two counterparts. They are: 23,830 ± 330 (GrN-14034; J5, 5.75, charcoal) and 23,490 ± 280 BP (GrN-15805; J3-4, 6.15 m, bone collagen). Differences between the latter are 340±50 BP. The mean of all three is 23,655 ± 335 BP. Again, all point to a single archaeological event and habitation level.

Comparison of Aurignacian-Early Gravettian. Occupation Intervals at Mitoc.

A.	GrN-12637	31,850 ± 800 BP
	A—B	(750 ± 100 years)
B.	OxA-1646	31,100 ± 900 BP
	B—C	(1.690 ± 590 years)
C.	GrN-15454	29,410 ± 310 BP
	C—D	(500 ± 170 years)
D.	GrN-12636	28,910 ± 480 BP
	D—E	(1,400 ± 120 years)
E.	OxA-1778	27,500 ± 600 BP

The basic calculation presented above by Taylor regarding the close affinities of radiocarbon dates belonging together is about 200—300 years [14]. By extrapolation of the database at hand, it can be argued that ages between individual cultural levels follows the same pattern when a *series* of dates are presented.

A glance of the above list indicates several different things. The time interval between A—B/C—D is the smallest but those between B—C and D—E are about three times as great. The latter instances could point to occupational hiatuses or not.

CONCLUSIONS. In the context of the entire thirtyeight radiocarbon dates of Upper Palaeolithic levels already obtained at Mitoc, the above mentioned interval of 200—300 years will be utilized in defining specific stratigraphic archaeological events. It is possible, and is here suggested, that a particular cultural level may produce evidence of re-use of that same level over a period of more than 200—300 years [15].

In the core area of Malu Galben, between the transects squares of B—J in the west profile and coordinates 9—3 in the north profile, the geoarchaeological levels are about 30—40 cm in depth. They are separated by sterile sedimentary units about 50 cm deep. In some cases, though, shallower or deeper intrusive refuse or storage pits may have been dug into the below sterile deposits or lower cultural levels from an overlaying level. To complicate matters relic periglacial features must also be eventually dealt with.

The use of the very sensitive AMS and conventional radiocarbon methods have done much in resolving certain problems connected with the stratigraphy at the site. The auxilliary use of the ERS and U-Th techniques should greatly enhance the chancer of recovery of samples connected with the early Aurignacian and late Mousterian technocomplexes transitions. This should take place in the next five years digging at Mitoc with Vasile Chirica.

[14] *Ibidem.*
[15] Honea, K., *Tranziţii culturale în paleoliticul superior timpuriu şi cronostratigrafia de la Mitoc—Malu Galben (jud. Botoşani)* (in press).