L'HOMME DE NEANDERTAL

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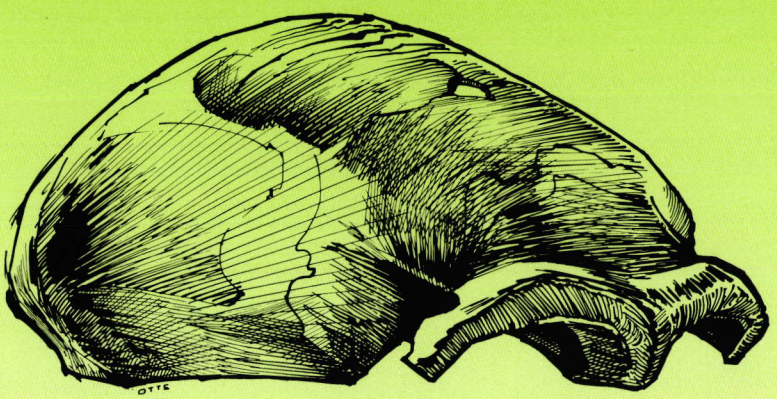

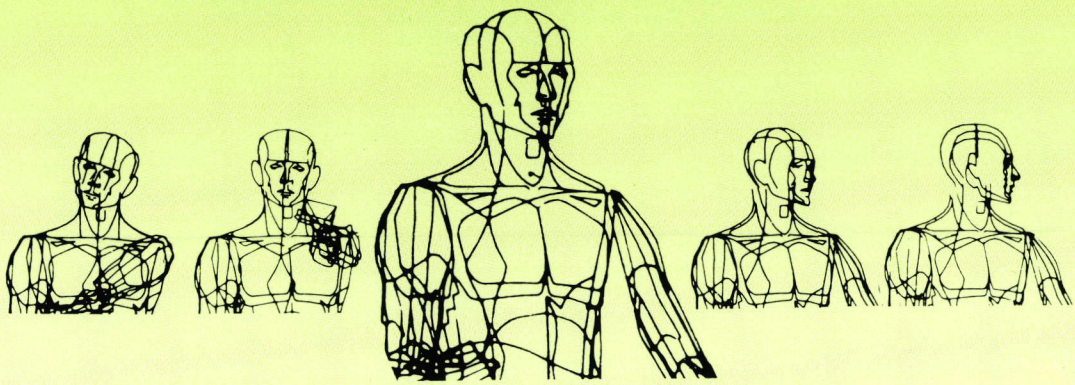

LA CHRONOLOGIE

LIEGE 1988

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En 1886, la découverte des sépultures néandertaliennes à Spy (Namur/Belgique) démontrait l'association de la culture préhistorique moustérienne à cette race fossile et l'existence, dès cette haute époque, de considérations de nature symbolique complémentaires aux activités techniques et économiques.

Cent ans plus tard, il nous a paru opportun de dresser le bilan des connaissances acquises depuis lors sur le mode de vie et les aptitudes culturelles de l'Homme du Néandertal considéré dans l'optique la plus large, à l'échelle de l'Ancien Monde.

Les meilleurs spécialistes mondiaux ont ainsi été sollicités afin de présenter le dernier état des connaissances et de confronter leurs théories quant aux relations entre les caractéristiques anatomiques et les aptitudes culturelles dans cette phase cruciale de l'évolution humaine.

Marcel OTTE

CONCEPTION GENERALE

Le bilan des connaissances et des théories récentes relatives au Paléolithique moyen a été divisé en huit thèmes généraux, soit en huit sessions d'une demi-journée chacune.

Devant l'abondance des données et le foisonnement des interprétations, il a été demandé à huit spécialistes internationaux d'en assurer la coordination.

Ces "coordinateurs", responsables de chaque thème, ont été invités à dresser une synthèse à partir de leur propre expérience et de leurs connaissances personnelles, mais également avec l'aide des orateurs qui leur ont fait parvenir les résumés de leurs récents travaux.

Les premières synthèses seront présentées au début de chaque session par ces personnalités responsables afin d'amorcer les débats thématiques auxquels chaque participant est convié.

En séance, il ne peut donc en aucun cas s'agir d'accumuler des exposés documentaires classiques mais bien de présenter des contributions critiques visant à forger une nouvelle intelligence des phénomènes culturels et biologiques considérés dans leur processus évolutif. Très souvent une démarche théorique préalable doit s'imposer afin d'assurer la cohérence du raisonnement archéologique.

Dans un troisième temps — la rencontre constituant le point fort — nous avons entrepris de publier dans les délais les plus courts l'ensemble des acquis et des opinions cohérentes qui en furent issus.

Marcel OTTE
Professeur
Université de Liège

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L'HOMME DE NEANDERTAL

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H.P. SCHWARCZ
Coordinateur

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TABLE DES MATIERES

L'Homme de Néandertal, vol. 1, LA CHRONOLOGIE, Liège, 1988, pp. 11 à 16

URANIUM-SERIES DATING OF CONTAMINATED CALCITE DEPOSITS

by

Henry P. SCHWARCZ * and N. CESAR *

The use of uranium-series (henceforth, U-S) dating in archaeology has allowed archaeometrists to extend the time scale of human cultural and biological evolution beyond the limits of ^{14}C dating. Using the U-S method it is possible to date certain types of deposits ranging in age up to a maximum limit of 350,000 years. The datable materials include (ranked approximately in order of their suitability for dating): coral, stalagmitic calcite, travertine, molluscan carbonate, tooth enamel, bone, marl, calcrete, and organic matter (peat, wood). The best materials that are commonly found in an archaeological context generally consist of relatively pure, chemically precipitated calcite. "Pure" in this instance principally refers to the amount of matter that was incorporated in the deposit in the form of detritus. The presence of this extraneous detrital component interferes with the dating process in two ways: 1) it may contain organic matter or clay minerals which interfere with the chemical extraction of uranium (U) and thorium (Th) from the sample, and thereby decreses the precision of the date; 2) the detritus may contribute to the sample, at the time of its deposition, a component of ^{230}Th that imparts an apparent finite age to the sample. While that "unsupported" ^{230}Th decays away in time, it will continue to make the apparent age of the sample greater than its true age, up to the age limit of the dating method. This problem has been discussed in various papers on U-S dating, e.g., SCHWARCZ (1980).

This second problem is particularly serious in archaeological sites where the calcite deposit has formed as a stratum in a sequence of detrital deposits, for example in the filling of a cave. Fortunately it is always possible to recognize the presence of the detrital contaminant because the ^{230}Th is accompanied by ^{232}Th, a long-lived isotope of Th that is ultimately derived from the weathering of crustal rocks, and is commonly associated with clay minerals. During the U-S dating of a calcite sample, both Th isotopes will be detectible by alpha spectrometry, if present. The abundance of ^{232}Th can be used as a measure of the *initial* concentration of ^{230}Th in the sample (most of which may have, by now, decayed away due to the 75,000 y half life of this isotope).

Various methods have been devised to "correct" for this detrital contaminant, making use of the ^{232}Th activity. The most widely used method in use at present is a graphical technique in which a plot of the ratios of isotope activities is used to obtain the parameters necessary for the age equation: $^{230}Th/^{232}Th$ vs $^{234}U/^{232}Th$ and $^{238}U/^{232}Th$ vs $^{234}U/^{232}Th$. If the data form linear arrays on these diagrams then the slopes of the lines are

* Dept. of Geology, McMaster University, Hamilton, Ontario, Canada, L85 4MI.

equal, respectively, to $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios. The samples whose analyses are plotted must satisfy the following criteria: a) they must be mixtures of a uniform, pure, chemically precipitated calcite mixed in varying proportions with a uniform, homogeneous detrital "phase" (e.g., mud, silt, clay); we shall henceforth call this mixture "dirty calcite"; b) there must be no isotopic or chemical fractionation of Th or U during the analysis procedure, so that the isotope activity ratios of the minor amounts of detrital Th and U that are taken into solution should be the same in each of the analysed aliquots. The fact that the samples lie on a single line is a *de facto* proof of (a); there is no easy way to demonstrate (b). If these two conditions are satisfied, then the respective slopes give the isotope ratios for the chemically precipitated calcite component of the mixture. These ratios, in turn, are used to determine the age of the sample as described in SCHWARCZ (1980).

There have been two different approaches in using this method: 1) in the method of KU and LIANG (1984) only two points are used to determine the slope, namely, a point for the insoluble residue (R) and a point for the soluble "leachate" (L) (Figure 1 a; 2) in the method used by SZABO and STERR (1978) and this author (e.g., SCHWARCZ and SKOFLEK, 1982) the plotted points consist of analyses of a number of replicate leachate solutions, obtained by the analysis of several aliquots of the same calcite deposit. It is understood that the all these aliquots were deposited at the same time (coeval), and that there is some natural variation in the proportions of detritus to calcite, which results in a variation in the isotope ratios of the leachates (Figure 1 b).

While both methods (a) and (b) seem to give satisfactory age data, it would be desirable to have some independent confirmation that the methods are both theoretically and experimentally valid. The present paper is intended to partially satisfy that need; a more complete version of this discussion is in preparation (SCHWARCZ and PRZYBYLOWICZ, 1988).

The theoretical proof was in effect presented by KU and LIANG (1984) who derived an equation for the slope of a line through the leachate (L) and residue (R) points as described above. It can be easily shown that their equation also applies to the case of an array of leachate points from several aliquots of dirty calcite. The equations are as follows:

$$\left(\frac{^{230}Th}{^{232}Th}\right)_L = \left(\frac{^{230}Th}{^{234}U}\right)_C \left(\frac{^{234}U}{^{232}Th}\right)_L + \left[\left(\frac{^{230}Th}{^{232}Th}\right)_R - \left(\frac{^{230}Th}{^{234}U}\right)_C \left(\frac{^{234}U}{^{232}Th}\right)_R\right] \quad (1)$$

$$\left(\frac{^{234}U}{^{232}Th}\right)_L = \left(\frac{^{234}U}{^{238}U}\right)_C \left(\frac{^{238}U}{^{232}Th}\right)_L + \left[\left(\frac{^{234}U}{^{232}Th}\right)_R - \left(\frac{^{234}U}{^{238}U}\right)_C \left(\frac{^{238}U}{^{232}Th}\right)_R\right]\right] \quad (2)$$

where L refers to leachate and C refers to the chemically precipitated calcite component of the mixture. These equations confirm that the graphs as defined above (and shown in Figure 1) yield lines with slopes as stated above. The age of deposition of the dirty calcite can then be obtained from these slopes.

In order to test experimentally whether this method does in fact provide a good estimate of the age of the calcite, we have analysed artificial mixtures of detritus and calcite, where the age of the calcite was independently known. The calcite component consisted of a homogenized sample of a pure calcitic stalagmite from a cave in West Virginia (Lew's Last Climb). The detritus consisted of a homogenized sample of the mud that surrounded the base of the stalagmite and which had been deposited during one or more floodings of the cave by

a stream, during the time that the stalagmite was growing. In spite of the presence of large amounts of mud in the cave, the stalagmite itself was extremely pure, and the amount of initial ^{230}Th present in it was negligible (as judged from the very high $^{230}Th/^{232}Th$ in the stalagmite at present). The age of the stalagmite was found to be 13 ± 1 ka, by $^{230}Th/^{234}U$ dating.

We prepared mixtures consisting of the following weight fractions of mud: 0.1 (2), 0.3; and 0.5. The mixtures dissolved in 2N nitric acid, filtered, and the leachates were then analysed following the procedures described by GASCOYNE *et al.* (1978). The analyses were then plotted and a linear regression was used to determine the $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios. From these the age was determined: 12 ± 2 ka, indistinguishable from the age of the pure calcite (Figure 2; only the graph for $^{230}Th/^{234}U$ determination is presented; the $^{234}U/^{238}U$ ratio generally does not vary appreciably as a function of detrital contamination and the graph for the determination of this ratio is not shown). As expected, the ^{232}Th activity in the leachates increased with increasing proportion of detritus, although there was not a good linear relation between these variables. In a continuation of this study we are also analysing the residues to test the method of Ku and Liang.

It thus appears, on the basis of this test (and as confirmed by other data which will be reported later) that the leachates alone provide a satisfactory sample for age determination. The main advantage of this method is that it avoids the necessity of completely dissolving the silicate residue, which commonly contains small traces of U-rich detrital minerals (zircon, sphene, etc.) that can only be dissolved completely in strong acid, with great difficulty. Incomplete dissolution of these minerals might lead to fractionation of the U or Th isotopes. The attack with mild acid (2N nitric) used in the leachate method probably does not remove a significant part of the U or Th from these resistant minerals, and therefore the incompleteness of the dissolution may be less problematic. In any case, we cannot claim to understand in great detail the chemical basis for the present method, but it appears to work.

As a further demonstration of the utility of this method, we shall present some new results on the dating of dirty calcite from a cave in Italy. A complete report on this study is in preparation (SCHWARCZ, BIETTI and GRÜN, 1987). The samples come from the cave Grotta Guattari located at the base of Monte Circeo, 100 km SE of Rome. The cranium of a "classical" Neandertal hominid was discovered there in 1950. The skull lays on the upper surface of a sequence of detrital deposits. Also present on the same surface were many bones of large mammals (horse, etc.) as well as large, rounded cobbles of rock. The skull, bones and cobbles were all encrusted with a coating of calcite. On cutting through a sample of this crust, we found that it consisted of several layers; we have carefully removed the outer layers and peeled off the innermost calcite layer which was partly contaminated with detritus. Four aliquots of this layer were analysed by uranium-series. The data are shown in Figure 3. The individual analyses of each aliquot of dirty calcite can, of course, also be used to obtain an age. These estimates are shown in Table 1, compared with the age as obtained from the slopes of the lines in Figure 3, determined by linear regression. Based on the latter technique, the age of the innermost calcite crust appears to be 51 ± 3 ka (where the error is based on the error in the slope). Note that the ages based on individual analyses are all *younger* than the slope-based estimate.

Other applications of the leachate method have been presented earlier by us (e.g. SCHWARCZ and SKOFLEK, 1982; SCHWARCZ and LATHAM, 1986; BLACKWELL and SCHWARCZ, 1986). It appears that this method can also be applied to samples in which the calcite component makes up only a small fraction of the total rock, such as a calcrete zone in a soil, or a calcite cemented sandstone. One should, however, note that the method assumes that the only acid-leachable carbonate component present in the rock is the chemically precipitated calcite whose age is sought. The detrital contaminant (sand, silt, etc.) may however also contain particles of limestone which also would dissolve during analysis.

This limestone component would generally have an apparently infinite age and would therefore give the leachate an anomalously great age. Furthermore, limestone typically does not contain any ^{232}Th and the presence of this material would therefore not be revealed by the analyses of isotope activity, themselves.

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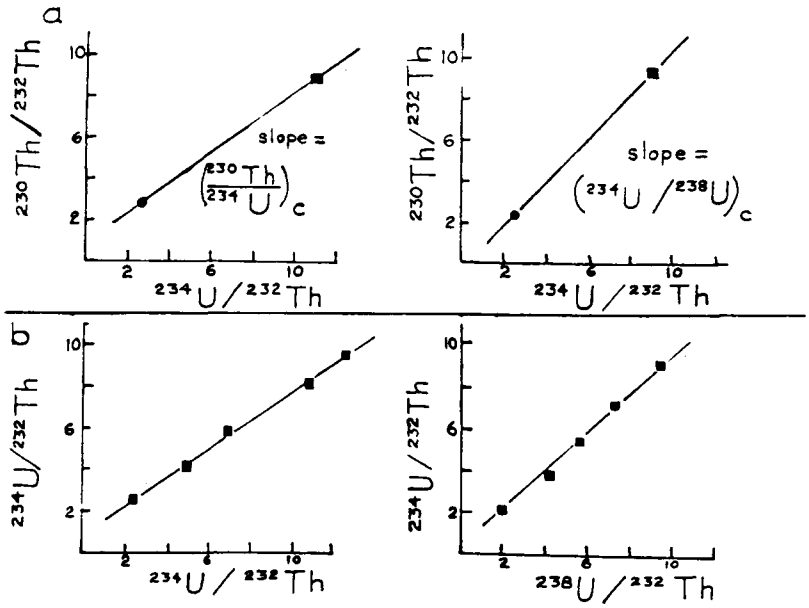

FIGURE 1

Isochron plots for determination of isotope ratios of the chemically precipitated (leachable) carbonate component in dirty calcite: a) Method of KU and LIANG (1984); (■) = leachate; (●) = residue; b) Leachate-only isochron (this paper); all points represent leachates from coeval samples with varying proportions of detritus.

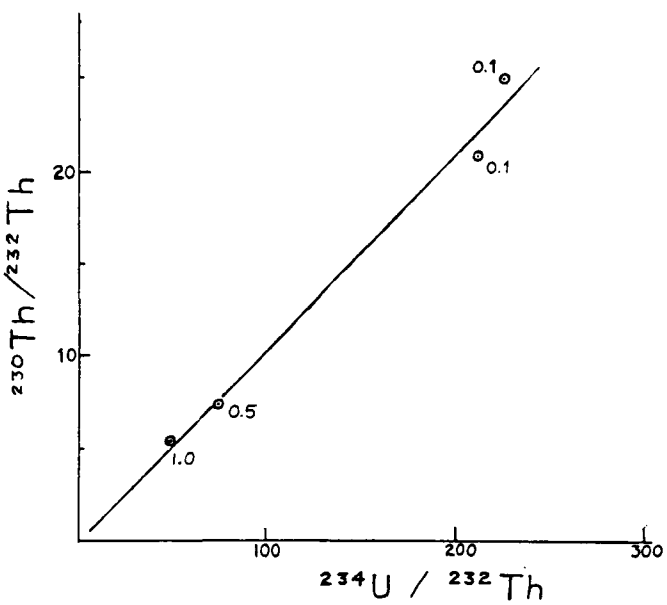

FIGURE 2

Isochron plot (Th-U only) for artificial mixtures of pure calcite (Age = 13 ± 1 ka) and associated detritus, from cave in West Virginia, USA. "0.1" = weight fraction of detritus in mixture. Slope corresponds to age of 12 ± 1 ka.

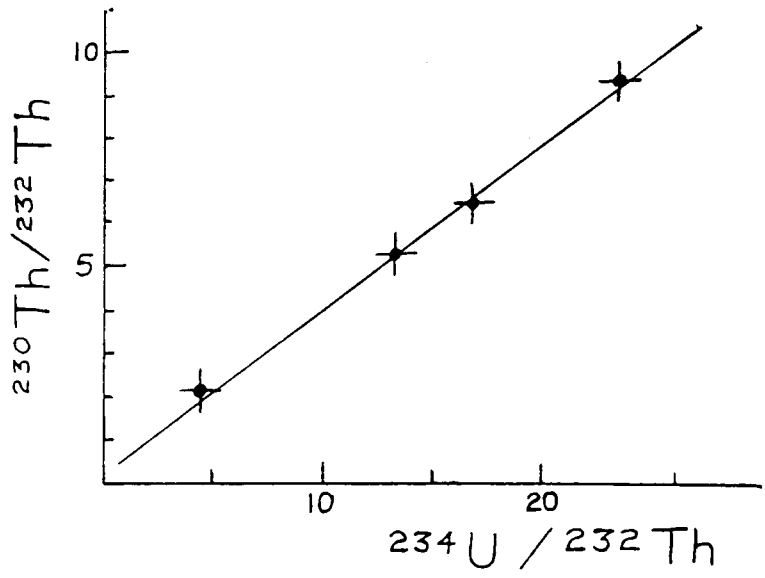

FIGURE 3

Isochron plot (Th-U only) for calcite layers covering bones at Monte Circeo, Italy. Slope corresponds to age of 51 ± 3 ka.

L'Homme de Néandertal, vol. 1, LA CHRONOLOGIE, Liège, 1988, pp. 17 à 19

LUMINESCENCE DATING: ITS CONTRIBUTION TO THE CHRONOLOGY OF NEANDERTHAL EVOLUTION AND EXTINCTION

by

M.J. AITKEN *

Of the two techniques concerned thermoluminescence (TL) is now well-established but optically-stimulated luminescence (OSL) is still at the research stage, though with high potential for making an important contribution; alternatively the OSL technique is called Optical Dating following the terminology of its originators (HUNTLEY, GODFREY-SMITH and THEWALT, 1985).

The principal contribution so far made by TL in the palaeolithic has been through the dating of burnt flint. This has been the work of Joan Huxtable at Oxford, Hélène Valladas at Gif-sur-Yvette, and Sheridan Browman at the British Museum. The work of Valladas has been particularly important in the present context since she has concentrated on the Mousterian of SW France; in particular she has dated the various levels of Le Moustier obtaining ages ranging from 56 to 40 ka (VALLADAS *et al.*, 1986). At another site, Vigne Brun, she was able to make comparative dating of burnt flint and burnt quartz (VALLADAS and VALLADAS, 1987); since the latter is well-established as a reliable TL dating material the satisfactory agreement found is confirmation of the validity of flint dates, already predicted from that material's intrinsic properties. Bowman has reported dates for the Lower and Middle Palaeolithic levels of Combe Grenal (BOWMAN and SIEVEKING, 1983). The youngest is 44 ka and the oldest 113 ka. Huxtable has produced upward of a dozen dates spanning the range 10-300 ka as reported in AITKEN, HUXTABLE and DEBENHAM (1986).

These published dates represent only the beginning of a new era in the dating of the period concerned and many more are already in process. Along with electron spin resonance (ESR) and uranium-series dating they represent a new dimension because they are essentially a 'physicist's view' of palaeolithic chronology and quite independent of other interpretations of the sites. Hence the generally good agreement with expectations from chrono-stratigraphic studies enhances the confidence to be placed on either system.

Of course there are limitations. The principal one is the need to make a reliable evaluation of the gamma dose-rate from the burial soil. This requires that the burnt flint must have been surrounded by soil to a distance of 30 cm for the major part of the burial period; this is liable to rule out open air sites. Another serious limitation is that the flint must be well burnt; it must also be large enough – at least 10 mm thick and 30 mm across.

* Research Laboratory for Archaeology and History of Art, 6 Keble Road, Oxford OX13QJ, England.

There is the same dependence on gamma contribution in the case of stalagmitic calcite and in general the stratigraphic complexity in which stalagmitic material is found makes calcite dating rather difficult. An exception is calcite fragments which have fallen off the ceiling of a cave and become buried in a thick layer of occupation sediment (as at Abri Vaufrey – see AITKEN and BUSSELL, 1982). At the Oxford Laboratory we have also applied calcite dating to the cave sites of Pontnewydd and Tautavel, as reported by DEBENHAM and AITKEN (1984).

SEDIMENT DATING

The application by DEBENHAM (1985) of the fine-grain TL technique to loess deposits from NW Europe indicates a limitation to 100 ka, with growing uncertainty once 50 ka is exceeded (DEBENHAM, 1985). However there are growing indications from other workers that use of coarse grain feldspar and possibly also quartz, will relieve these limitations; hence it is to be expected that sediment dating whether by TL or OSL will be making a strong contribution to the chronology of the period in question. The advantage of OSL over TL is that the OSL signal is primarily from light-sensitive traps and hence the setting to zero of the signal at the time of sediment deposition requires less exposure to sunlight. Thus it is to be expected that other types of sediment besides loess (e.g. riverborne) will be datable. In the first place quartz grains are being used.

ZIRCON DATING

With all the dating materials so far discussed the accuracy attainable is limited (to around ± 5 %) by uncertainty about the average humidity of the surrounding soil during the burial period; this is because of attenuation of the gamma contribution by the amount of water present, which of course depends on the climate. However within most sediment there are grains of zircon. Because of the high internal radioactivity of this mineral the gamma contribution to the annual dose is comparatively unimportant; hence the date is largely independent of climatic uncertainty (and also of geochemical disturbances too). This mineral is easily bleached and therefore it is to be expected that it will have an important role in sediment dating. Technical problems of measurement, due to zoning and anomalous fading, have now been largely solved (TEMPLER, 1986) and the prospects for its utilization, whether for TL or OSL are good.

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L'Homme de Néandertal, vol. 1, LA CHRONOLOGIE, Liège, 1988, pp. 21 à 24

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

by

E. BARD, M. ARNOLD, H. VALLADAS and J.C. DUPLESSY *

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.

* Centre des Faible Radioactivités, Laboratoire Mixte CNRS-CEA, Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex (France).

- 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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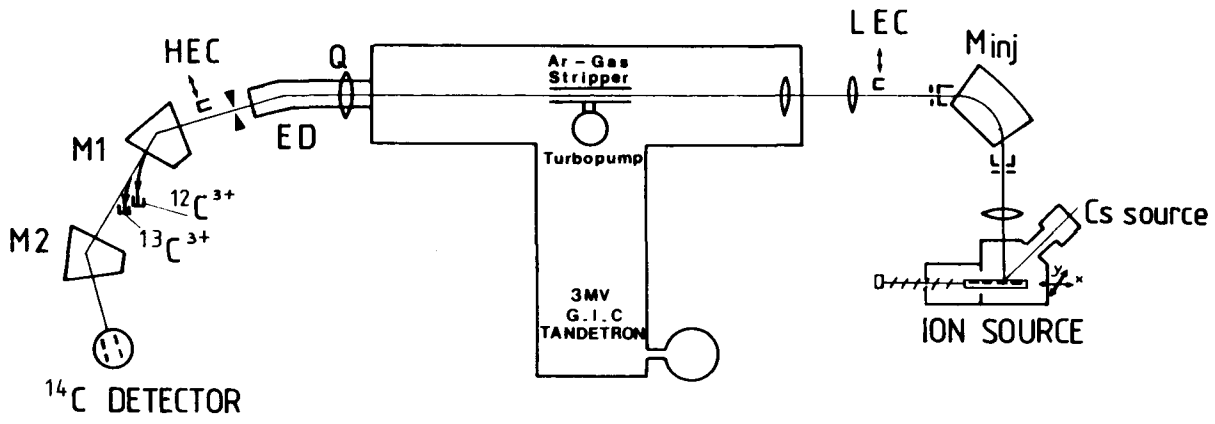

FIGURE 1

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*

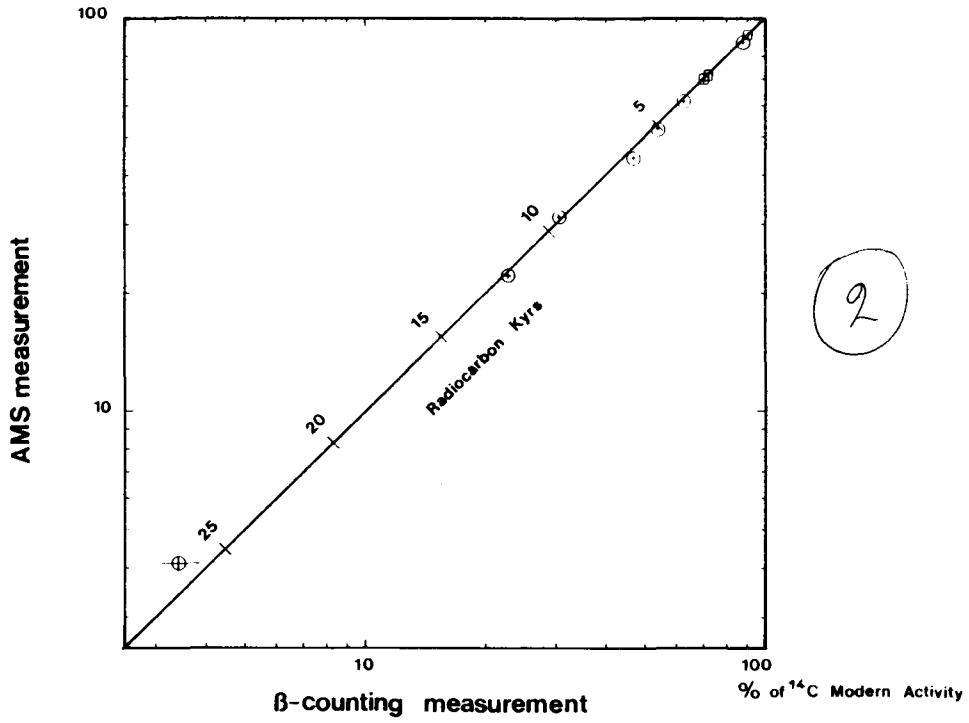

FIGURE 2

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)

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THE APPLICATION OF THERMOLUMINESCENCE DATING TO THE PALAEOLITHIC

by

S.G.E. BOWMAN and N.C. DEBENHAM *

ABSTRACT

The aim of this paper is to provide a brief introduction to the thermoluminescence (TL) mechanism and its application to dating of the Palaeolithic. The relevance of the TL signal measured in the laboratory to the archaeological event to be dated is discussed, together in general terms with the types of material that are datable. The stability and saturation of the signal and the bearing of these factors on the upper age limit of the method are also considered. The necessity for *in situ* measurement of radiation levels on any site to be dated is emphasised.

The development, limitations and some examples of the application of TL dating to three materials is then discussed in more detail. These materials are burnt flint, stalagmitic calcite and sediment and are those most commonly used for TL dating the Palaeolithic.

THE MECHANISM

Thermoluminescence (TL) is the light emitted by a crystalline material when it is heated after previously being exposed to radiation. This light is additional to the incandescence produced by heat alone.

In nature, the radiation is alpha, beta and gamma from the decay of uranium, thorium and potassium (^{40}K isotope) both in the sample itself and in the burial environment. In addition there is a small contribution from cosmic rays. When these ionizing radiations pass through matter, some of the free electrons they produce will be trapped at lattice defects if the material is crystalline. Depending on the nature of the defect (trap) the electrons can remain trapped at ambient temperature for long periods of time (millions of years in some cases). When heat is applied the electrons can be given sufficient energy to be released and, if recombination at a luminescence centre occurs, the light known as thermoluminescence is emitted.

"ZEROING THE TIME CLOCK"

The light emitted on first heating an archaeological sample in the laboratory is known as the natural TL. Taking for example pottery, this natural TL in simple terms is proportional

* British Museum Research Laboratory, London WC1B 3DG, England.

to three factors: the annual amount of radiation received by the pottery, the effective TL sensitivity of the mineral inclusions to radiation and the time that has elapsed since the pottery was last heated i.e. was fired. In principle therefore the age of the pottery can be determined if the other two factors and the natural TL can be determined. This is equivalent to the age equation:

$$\text{age} = \frac{\text{natural TL}}{(\text{TL per unit of radiation}) \times (\text{annual number of radiation units})}$$

or

$$\text{age} = \frac{\text{archaeological (or palaeo) dose}}{\text{annual radiation dose}}$$

where the archaeological dose (or palaeodose) is a measure of the total radiation received in antiquity, and is derived from the ratio of the natural TL to the effective TL sensitivity to radiation.

For pottery, firing acts as a "zeroing mechanism" that can be thought of as removing the geological TL so that the natural TL measured in the laboratory relates to a specific archaeological event. Temperatures in excess of about 400°C are required and such temperatures are readily reached in a fire. Hence hearth material is datable as demonstrated by HUXTABLE and AITKEN (1977) for baked clay from a fireplace at Lake Mungo. Similarly burnt flint or stone are potential candidates for TL dating. Lava flows should also be datable, but as discussed below stability of the TL signal can be a problem.

Apart from heat, there are two other main zeroing mechanisms: crystal formation and exposure to sunlight. Without a crystal structure, there can be no TL ; hence, the formation of a crystal such as calcite acts as a "zeroing mechanism" for TL dating. It is important that stalagmites or flow stones rather than stalactites are dated since the formation of the latter is not readily relatable to any archaeological event. With *in situ* stalagmitic calcite, the relative stratigraphic position of the calcite to the archaeological levels will provide at least a *terminus* result, and in some cases the archaeology may fortuitously be sandwiched between two datable calcite layers.

In some of the early work on TL dating of ocean sediments it was thought that the TL observed was from foraminifera or radiolaria and that the zeroing mechanism was the formation of the shells of these organisms (BOTHNER and JOHNSON, 1969; HUNTLEY and JOHNSON, 1976). In fact sediment particles attached to the shells were producing the TL and these were most likely to have been "zeroed" by the action of sunlight prior to deposition: the extent of zeroing is discussed further below. In recent years the application of TL to the dating of terrestial sediments has greatly expanded, especially in geology. Loess, in particular, is an obvious sediment for TL dating since it is fine-grained and through aeolian transport will have been exposed to sunlight for a considerable time prior to deposition.

SIGNAL STABILITY AND SATURATION

A zeroing mechanism and association of the TL material with the event to be dated are essential prerequisites of the technique. In addition it is necessary that the TL signals measured in the laboratory have certain characteristics: stability at ambient temperature for time periods well in excess of that to be determined and continuing growth with addition of further radiation dose.

Stability of both the trapped electrons and the activated luminescence centres is required, and two forms of instability exist. One is a function of the properties of the defects themselves and of the storage temperature of the sample, whereas the other, referred to as anomalous fading, is a less predictable phenomenon.

In the laboratory it is possible to determine the characteristics of a trap and predict the mean lifetime of an electron at ambient temperature in that trap. For example, the trap giving rise to the TL signal at about 370°C in figure 1 has a lifetime of approximately 600 Ma (1 Ma = one million years) at ambient temperature (BOWMAN, 1982). Hence the flint, which gave rise to this signal and which was burnt in the Palaeolithic, should be datable. In general terms traps giving rise to TL signals that require laboratory temperatures in excess of about 250°C for their measurement have lifetimes more than adequate for dating the Palaeolithic (see AITKEN, 1985, Table E.1, p. 272). It is less easy to determine the stability of the luminescence centres. If one such centre is dominant in a particular type of material, its lifetime can only be assessed by TL dating known age examples of that material as discussed below for sediments.

More problematic is the phenomenon of anomalous fading, so called because, despite the defect characteristics predicting long-term stability of the TL signal at ambient temperature, extremely rapid loss is observed. WINTLE (1973) found this to be a particular feature of volcanic feldspars and obtained TL ages an order of magnitude lower than expected. Quartz, however, does not seem to be subject to anomalous fading and lava flows have been successfully dated using quartz pebbles found within the lava (GILLOT *et al.*, 1978) or quartz extracted from sediment underlying a lava flow, the heat from which "zeroed" the sediment (HUXTABLE *et al.*, 1978). Similarly BERGER and HUNTLEY (1983) have dated Holocene volcanic ash falls using the fine-grained glass fraction.

Recent work (TEMPLER, 1985) has indicated that it might be possible to circumvent the effects of anomalous fading by storing samples at elevated temperature (*c* 120°C) prior to measurement of the TL signal. This method, however, is yet to be applied to TL dating of volcanic feldspars.

Saturation refers to the stage at which the TL signal no longer increases significantly with the addition of further radiation. This is due to the filling of the traps with time; when most or all of the traps are filled, little or no further growth of the signal can occur. The total radiation dose corresponding to this is a function of the concentration of defects in the crystal. However, the time at which this level of radiation dose is reached depends on the rate at which radiation dose is received; if this is low, saturation will be reached after a longer period of time.

The upper age limit of TL dating is therefore dependent on the stability of the signal, on the characteristics of the TL material and on the annual radiation dose. In consequence it is not possible to attach a single number to this limit, rather it is specific to each application. Nevertheless a few generalisations can be made and these are discussed below in the sections specific to materials.

ANNUAL RADIATION DOSE

Alpha, beta and gamma radiations have very different ranges in matter: approximately 0.03, 3 and 300 mm respectively in typical TL materials. If a fragment of flint weighing a few tens of grammes is considered, these ranges mean that the vast majority of the gamma contribution comes from the burial environment, not from the flint itself. If the outer 2-3 mm of the flint is removed, the alpha and beta contributions will then only be from the flint. Assessment of these is referred to as the internal dosimetry and the gamma plus cosmic contribution is the external, or environmental dosimetry.

Two further considerations are the effect of water and of radon emanation. Water absorbs radiation more than air does, hence the wetter the environment and sample are, the lower is the annual radiation dose received by the TL producing minerals. Radon emanation refers to the escape of the radioactive gas, radon, which is one of the members of the uranium series. Its loss makes the evaluation of the annual radiation dose, in particular the environmental contribution, difficult (see e.g. BOWMAN, 1985).

These and other factors mean that laboratory measurements to assess environmental dosimetry on samples isolated from the bulk of the burial environment may not be representative. It is better to make *in situ* measurements using either a portable gamma ray spectrometer or capsules containing a sensitive TL phosphor (see e.g. AITKEN, 1985). In the latter case the capsules must remain in the levels to be dated for a period of about a year. Without the burial environment information a site cannot be dated by TL, and without *in situ* measurements, errors may be introduced.

Consultation between TL laboratories and archaeologists are therefore essential before samples are submitted for dating so that the best samples are collected, the correct collection methods are employed and *in situ* measurements are arranged.

BURNT FLINT

Dating of other heated stones has received rather less attention than flint, perhaps due to factors such as inhomogeneity and higher levels of internal radioactivity that would restrict the upper age achievable (see below). This section will concentrate on flint, however, examples of TL dating of other stones include sandstone (HUXTABLE *et al.*, 1976; VALLADAS, 1981) and a biotite microgranite (SCHVOERER *et al.*, 1977).

For flint, crazing of the surface is a clear sign of burning, however, the absence of crazing does not necessarily mean the flint has not been adequately heated, since laboratory experiments have shown that the temperatures needed to produce crazing and other very obvious visual changes are in excess of those required to zero the geological TL. Laboratory tests however can readily determine if adequate heating was achieved in antiquity.

The initial work on burnt flint was hampered by non-radiation induced signals (GÖKSU and FREMLIN, 1972) that resulted from crushing in the preparation of samples for TL. These effects were overcome using a slice technique (GÖKSU *et al.*, 1972). This technique has the disadvantage that the optical attenuation characteristics of the flint must be measured to evaluate the effective TL sensitivity to radiation (AITKEN and WINTLE, 1977). It was, however, used to obtain two dates averaging to 230 ± 40 ka for the Lower Palaeolithic site of Terra Amata (WINTLE and AITKEN, 1977; 1 ka = one thousand years). Further disadvantages are the sample size required to facilitate preparation of slices and that the TL properties of a series of slices can be variable (BOWMAN and SEELEY, 1978).

VALLADAS (1978) showed that not all crushed flint exhibited the interfering signals observed in the early work, particularly if acid treatment was used in the sample preparation. This presumably removes unconverted calcium carbonate that can comprise up to 3% of the sample (COWELL and BOWMAN, 1985). Valladas used 100 μm grains for her TL measurements, and other workers (e.g. DANON *et al.*, 1982) have also had success with similar grain sizes. Crushing and deposition of the 1-8 μm grains as frequently used for pottery dating (ZIMMERMAN, 1971) greatly simplifies evaluation of the radiation contribution from alpha particles, and dating programmes employing this sample preparation technique are now being reported (e.g. HUXTABLE, 1982).

The stability of the signal in flint appears in general to provide no problems in dating

back as far as the Lower Palaeolithic at least. However substantial underestimates have been reported (BOWMAN *et al.*, 1982) and investigated (BOWMAN, 1982). Though no clear indication of instability of the signal could be found, equally no other unequivocal cause was identified.

It is interesting to note that where flint and other burnt stones are available on a site, the latter are more likely to be in saturation (e.g. the site of Sclayn reported by AITKEN *et al.*, 1986). Although the typical radiation dose needed to saturate the traps in flint is not high, the internal radioactivity is very low and hence the age limit determined by saturation depends on the level of external (gamma) radiation. For many environments, such as limestone caves, this will also be low, and the samples that are datable will be correspondingly older.

Other difficulties do, however, exist. When a flint is heated it tends to shatter into pieces that are often too small to be dated since the outer 2 mm is removed to simplify the evaluation of the annual dose (see above). Equally, insufficient heating will be a problem. Also low TL sensitivity to radiation can render the natural signal too low to be measurable. Large numbers of datable flints from a single site are consequently rare; the exception being the thirty four dates reported by VALLADAS *et al.* (1986) for Le Moustier. In contrast, only six of the fifty samples investigated from Combe Grenal were datable (BOWMAN and SIEVEKING, 1983). Despite being small in number these remain the only sequence of dates for a site covering a long time span: the interpretation of these dates in relation to the regional chronology is not straightforward as discussed by the authors (see also ASHTON and COOK, 1986, and MELLARS 1986 a,b). Such discussions emphasise that currently there are too few absolute dates for much of the Palaeolithic.

STALAGMITIC CALCITE

The first attempts at TL dating of stalagmitic calcite revealed the problem of interference from spurious luminescences, which were chemically rather than radiation induced. To overcome this problem, samples must be heated in an atmosphere of low oxygen and water vapour concentrations. WINTLE (1975) also showed the importance of careful preparation of samples, recommending a slight acid etch of the calcite grains following crushing of the stalagmite. In further studies (WINTLE, 1977) she examined the stability of the dominant TL glow curve peak, at a temperature of 275°C, and deduced that this signal was adequately stable for dating stalagmites throughout the Quaternary. Stalagmitic calcite suffers, however, from having a low TL intensity relative to other minerals, and BANGERT and HENNIG (1978) emphasised the difficulty of measuring samples with a high level of detrital contamination.

In a study of six stalagmites, WINTLE (1978) compared TL measurements of the archaeological doses with those calculated from uranium series disequilibrium data. Agreement was not encouraging, and several possible explanations were put forward to account for the discrepancies. One suggestion was that TL sensitivity variations within the stalagmites may be spatially correlated with concentrations of the radionuclides emitting short-ranged alpha particles. This possibility was investigated by WALTON and DEBENHAM (1982) who found evidence for anti-correlation in a small number of samples, but the effect was not thought to have major consequences. Meanwhile, spectral studies of calcite TL (DEBENHAM *et al.*, 1982) suggested an alternative explanation for the discrepancies by showing that rejection of an unwanted TL signal, present in newly formed samples, could be achieved by selecting emissions at blue wavelengths. The unwanted signal was thought to originate from limestone detritus embedded in the stalagmites.

This work was followed by a study of twenty seven stalagmites from Pontnewydd Cave, Wales, and Caune de l'Arago, France (DEBENHAM and AITKEN, 1984), in which TL age measurements were compared with uranium disequilibrium dates. Generally good

agreement was found between the two methods, suggesting that TL does provide a useful basis for dating stalagmites. However, the limitations of the method are at present not well defined. In particular, it is not yet clear how serious a limitation is imposed by the requirement for samples to have low levels of clay and limestone detritus. There may also be difficulties at some sites caused by geochemical action on the stalagmites during their burial. Only the application of the method to a wider range of sites can answer these questions.

Additionally, doubt still surrounds the time range over which TL dating can yield reliable dates for stalagmites. Because saturation of the TL does not occur until very high radiation doses, and because annual radiation doses to stalagmites are generally low, the upper age limit is almost certainly set by the lifetime of the signal. The oldest samples dated by DEBENHAM and AITKEN (1984) were 350 ka old, and independent testing of these pieces (DEBENHAM, 1983) has suggested that, at most, 15% of the TL signal may have been lost due to instability over this time. Further testing of older stalagmites is required before the upper age limit of the method can be established. The lower limit is set by the reliability of the assumption that the measured TL signal was at zero in the newly formed stalagmite. This in turn will depend on the level of detrital contamination. At present, dates younger than 30 ka should perhaps not be regarded as accurate to better than about ± 50%.

Despite these uncertainties, it would appear that TL has the potential for usefully supplementing the uranium series disequilibrium dating technique in the age range 50-300 ka, and possibly for extending the range considerably further.

SEDIMENT

The first attempts to date sediments by TL were carried out in the Soviet Union and in East Europe, and this early work has been reviewed by HÜTT and SMIRNOV (1982) and by WINTLE and HUNTLEY (1982). Interest in the technique in the West was aroused by studies on ocean sediments by WINTLE and HUNTLEY (1980), who found that TL measured palaeodoses increased with depth and suggested that sunlight exposure before deposition had caused a significant reduction (bleaching) of the TL signal. An example of the effect of sunlight on a TL signal from sediment is shown in figure 2. The method was next applied to Devensian loess (WINTLE, 1981), to sand dunes (SINGHVI *et al.*, 1982) and to glacial deposits (HÜTT and SMIRNOV, 1982a). WINTLE (1982) distinguished between a quartz TL peak at 320°C and a feldspar component at lower temperatures. While the first was found to saturate at too low a radiation dose to allow dating of sediments older than 30 ka, the feldspar signal was suspected to be unstable. DEBENHAM and WALTON (1983) studied the spectra of these two components, and showed that a much purer feldspar signal could be obtained by recording the TL at ultra-violet wavelengths. This signal, peaking at 260°C, was found to be removed much more rapidly by sunlight than was the quartz signal. Later investigation (DEBENHAM, 1985) showed that the 260°C signal did not suffer from saturation, but that a long-term instability apparently limited its application to sediments younger than 100 ka. This was revealed by TL dating a series of deposits whose ages, estimated on other evidence, ranged over the past 700 ka. Figure 3, in which the measured TL ages are plotted against their stratigraphic dates, shows severe underestimation of the TL results for older sediments. It was thought that this effect was due to instability of the luminescence centres since no loss of trapped electrons was apparent.

On the basis of these results, therefore, it seemed that neither the quartz nor the feldspar TL components could be used for dating sediments over 100 ka old; the former because of saturation of the TL, and the latter due to inadequate stability. If no other signals are present in TL from sediments, this implied that no dating of the older deposits was possible by TL. Many workers, however, disagree with this conclusion, believing either that the two signals do not invariably suffer these limitations, or that additional signals are available which are free of such problems. Thus, for instance, BRIDGLAND *et al.* (1985) and HUNTLEY *et al.*

(1985) both observe non-saturation of the quartz signal, with the former using it to date loams at Swanscombe to around 220 ka. Alternative signals are proposed by BERGER (1984) and MEJDAHL (1985 a,b) who employ different sample preparation techniques to separate mineral components, and Mejdahl obtains a date of 1.07 Ma for a sample of marine sediment. Similarly, WINTLE (1985) suggests a heat pretreatment in order to separate a more stable feldspar signal; however, the validity of this approach has been questioned (DEBENHAM, 1987).

Thus, there exists at present no consensus of opinion on the age range of sediments that are datable by TL, although it appears that valid ages back to 100 ka are obtainable. There is also some uncertainty about the range of sediment types that may be expected to have received sufficient sunlight exposure at deposition to adequately bleach the TL signal, but indications gained from many investigations (e.g. HUNTLEY, 1985; KRONBERG, 1983; GEMMEL, 1985) are that aeolian and slowly deposited fluvial or lacustrine sediments at least should be datable. For other types of sediment, which may have undergone only partial bleaching at deposition, techniques have been described (MEJDAHL, 1985c) to overcome this problem. Active research continues in all areas of uncertainty.

SUMMARY

The non-pottery materials datable by TL and the limitations of the method have been briefly discussed. Stability and saturation problems should present no problems at least back to, and including, the Middle Palaeolithic. However, consultation between TL laboratories and archaeologists are essential before samples are submitted for dating so that the best samples are collected, the correct collection methods are employed and *in situ* measurements are arranged.

A better absolute chronology is required for the Palaeolithic and by collaboration between archaeologists actively involved in excavations and TL laboratories, this should be achievable.

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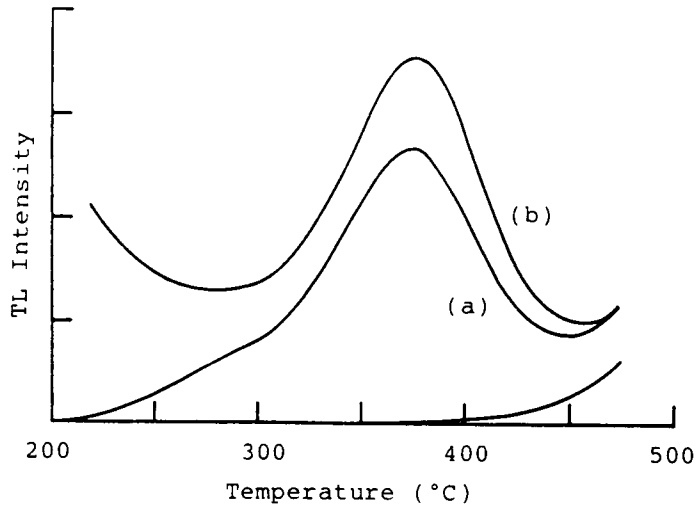

FIGURE 1

Typical TL signals from burnt flint, (a) is the natural TL and (b) is the signal in response to a known laboratory radiation dose (The TL in the blue part of the spectrum has been recorded).

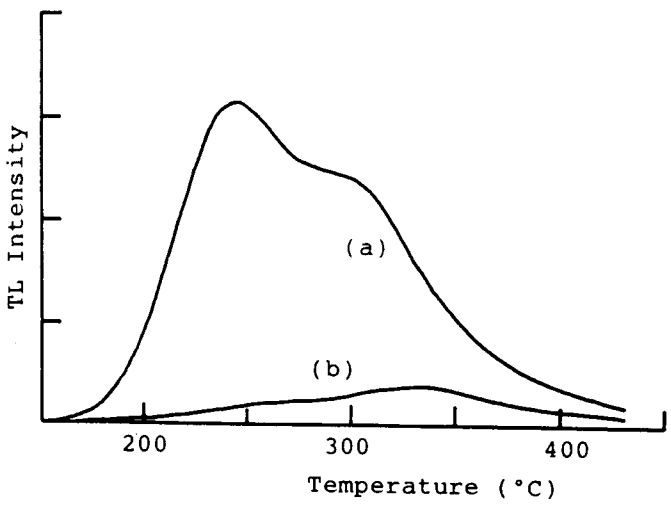

FIGURE 2

TL signals from fine-grains of a sediment from Susterseel, W. Germany, (a) is the natural TL of grains not exposed to light since the time of their deposition and (b) is the signal from grains exposed to sunlight for 16 hours (Only the TL emitted in the near ultra-violet part of the spectrum has been recorded).

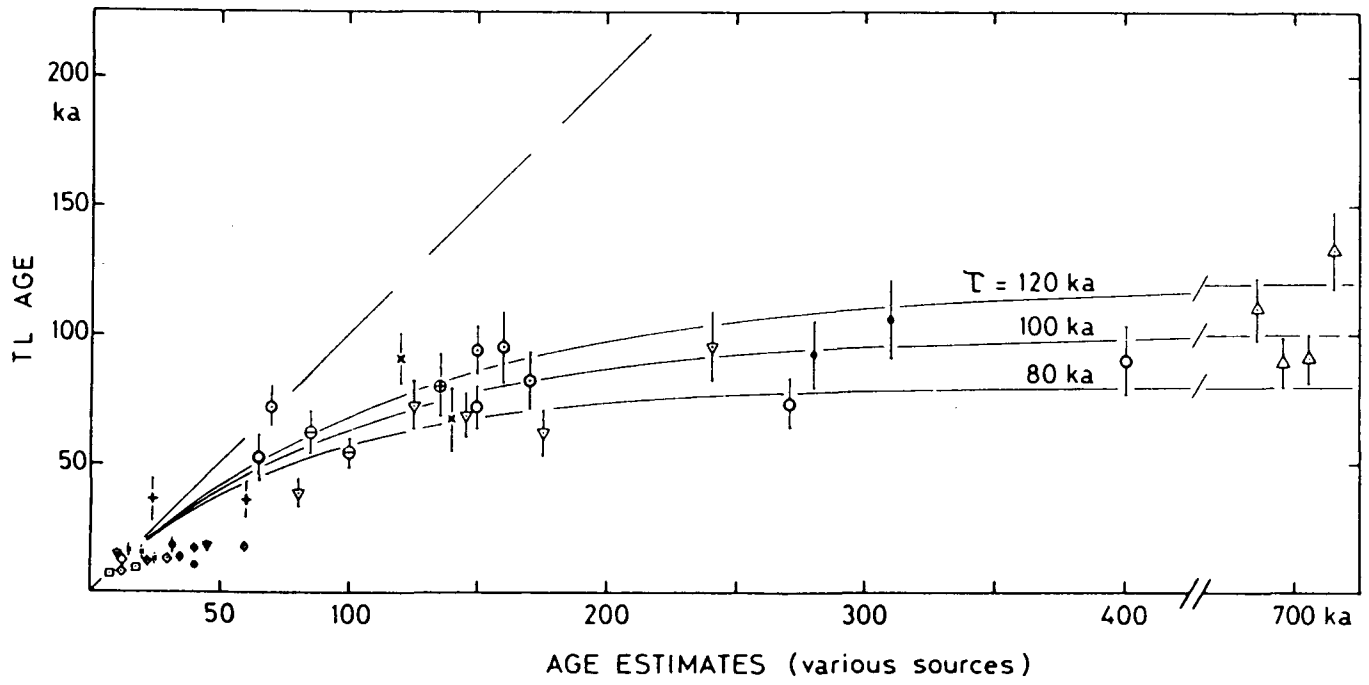

FIGURE 3

TL ages of a series of sediments from N.W. Europe plottet against their estimated ages based on geological evidence. The TL ages of the older sediments are seriously underestimated and appear to aproach a limit of around 100 ka.

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THE POTENTIAL OF ESR DATING OF TOOTH ENAMEL

by

Rainer GRÜN *

ABSTRACT

A problem often occurring in the attempt to date archaeological sites is a lack of material suited for the various dating methods, especially, when the site is assumed to be beyond the radiocarbon dating range.

Recent progress in ESR dating of tooth enamel opens the possibility to evaluate age assignments for many sites. The dating range of this new technique is between a few thousand to at least 1-2 million years, which covers approximately the entire Pleistocene epoch. However, this method, which is still under research, contains some problems, especially the still unknown process of uranium accumulation in teeth. Nevertheless, comparative studies with other dating methods, e.g., at Bilzingsleben gave very promising results.

INTRODUCTION

Electron spin resonance (ESR) spectroscopy allows the detection of free electrons or free radicals. After the discovery of the basic principles in 1945 by ZAVOISKY this method has been widely applied in mineraolgy, solid state physics, and biochemistry (see e.g. MARFUNIN, 1979; LOW, 1968; SYMONS, 1978).

ZELLER *et al.* (1967) were the first who suggested to use this technique for dating purposes, but it took until 1975 that Ikeya applied ESR for the dating of speleothems. From that time on, ESR dating was applied in many fields in geology and archaeology and review papers were published by IKEYA (1978), HENNIG and GRÜN (1983), and NAMBI (1985). Figure 1 summarizes the materials and minerals on which ESR dating has been applied so far (the brackets indicate that those materials still face some unsolved problems).

ESR DATING

In a mineral which is an insulator electrons can occur at two different energy states, the valence band and the conduction band (see Figure 2). Normally, all electrons are in the ground state, but they can be excited to the conduction band by interaction with radioactive particles (α-, β-, γ- , and cosmic rays). After a short time of diffusion these

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* Dept. of Geology, McMaster University, Hamilton - Ontario L8S 4M1 Canada.
Now at: Subdept. of Quaternary Research, Cambridge University, UK.

electrons recombine with the holes which were left behind near the conduction band. However, a few electrons are captured in the energy zone between those two bands by charge deficit sites (traps, which might be lattice defects or e.g., Y^{3+} substituting Ca^{2+}) and there they can be detected by ESR-spectroscopy. The number of trapped electrons is proportional to strength of the radioactivity and the irradiation time since these traps were emptied (zeroed) for the last time. Such a zeroing process can be the precipitation of the mineral (e.g., speleothems or, in this case, the growth of a tooth), heat (e.g., firing or contact-metamorphism), or stress (in fault zones).

Each of those defects shows a characteristic ESR-signal (see e.g., Figure 3) and the signal height is proportional to the number of trapped electrons and, hence, to the age of the sample. An ESR age is derived from the formula:

$$\text{AGE [a]} = \text{accumulated dose (AD) [Gy]} / \text{dose rate (D) [Gy/a]}$$

where the accumulated dose is the radioactive dose the sample has received since the time of its last zeroing and the dose rate is principally derived from the radioactive elements in the sample and its surroundings. In the attempt to date tooth enamel, several peculiarities have to be considered (a detailed description of this special application was given by GRÜN *et al.*, 1987).

DETERMINATION OF ACCUMULATED DOSE (AD)

The AD of the sample is determined by ESR spectroscopy. Several aliquots of the sample are irradiated with successively increasing artificial γ-doses and the extrapolation against zero-ESR intensity allows the determination of AD (Figure 4). However, several problems have to be considered: enamel (hydroxyapatite) shows an ESR signal at $g = 2.0018$ (see Figure 3, top) which is due to the CO^{3-}-radical. This peak is often interfered with organic radicals (see Figure 3, lower spectrum) which make it difficult to determine the height of the apatite signals. GRÜN *et al.* (1987) show that this effect can be eliminated by measuring the signal with a large modulation amplitude (5 G_{pp}), which actually "smears out" these interfering signals.

Another problem is the saturation behaviour of the signal upon radiation. It was shown (GRÜN *et al.*, 1987) that geological samples with AD's of $\geq$ 10 Grays do not show a linear growth of the ESR signal. Therefore, a logarithmic evaluation of AD as suggested by APERS *et al.* (1981) has to be performed. Figure 5 shows the effect of the logarithmic AD-extrapolation compared to a linear evaluation: although the linear curve-fitting shows a correlation coefficient of $r = .9993$, the logarithmic AD is about 20 % lower with $r = .9999$.

DETERMINATION OF DOSE RATE (D)

An enamel layer can principally be found in three different environments (see Figure 6) and the trapped electrons are possibly generated from four different radioactive sources:

(i) cosmic rays
(ii) the radioactive elements of the surrounding matrix
(iii) uranium and its daughter products in the dentine or cement attached to the enamel layer
(iv) uranium and daughters in the enamel layer itself.

Alpha-, beta-, and gamma-particles have very different ranges; in a material with a density of 2.95 g cm^{-3} (hydroxyapatite) they are about 20 µm, 2 mm, and 30 cm, respectively.

Cosmic rays can be determined with a calibrated, portable gamma-spectrometer at the site where the tooth was found or from attenuation curves as published by PRESCOTT and STEPHAN (1982).

The effect of α-rays from the surroundings can be eliminated by removing at least the outer 20 μm from enamel sample. The concentrations of the radioactive elements of the surrounding matrix can be determined by a portable gamma-spectrometer in the field or by chemical analysis (neutron activation analysis, fission track, atomic absorption-, mass-, or γ-spectroscopy) in the lab.

Since the attached dentine or cement layers are relative thin, only beta irradiation from this source has to considered. Generally, Th and K concentrations in these layers are negligible.

Enamel irradiates itself with α- and ß- rays from the U-decay chains (internal dose rate). Since alpha-particles do not produce as much ESR-intensity as an equivalent ß- or γ-dose, the so called "α-efficiency" has to be determined. Since this evaluation is relative expensive (see GRÜN, 1985), a value of .15 (determined independently by ^{210}Po-doping (DeCANNIERE *et al.*, 1986) and external alpha-irradiation of fine grain samples (GRÜN, 1985)) is normally assumed.

After determining the concentrations of the radioactive elements in the various sources, the dose rate can then be calculated by using published tables (e.g., BELL, 1979 or NAMBI and AITKEN, 1986).

These dose rate calculations are complicated by the following factors:

- water content in the sediment and dentine/cement;
- a complex history of the water content in sediment;
- a complex history of the sedimentation-rate (influencing the cosmic- and gamma dose rate);
- beta-ray attenuation in thin layers (see GRÜN, 1986);
- radioactive disequilibria in the U-series decay chains (between ^{234}U and ^{238}U; ^{230}Th and ^{234}U; ^{231}Pa and ^{235}U);
- ^{226}Ra and ^{222}Rn escape from the tooth or the sediment.

A detailed discussion and mathematical treatment of these processes are given by GRÜN *et al.* (1987).

However, the still unsolved problem of uranium uptake by teeth introduces the largest uncertainty in this particular application of ESR-dating. Recent teeth contain uranium in the range of a few 100 ppb. Fossil teeth, however, display U-concentrations up to about 1000 ppm.

Two different U-uptake models for teeth are discussed in the litarature (see e.g., IKEYA, 1982):

- **early U-uptake**: concordant Th/U and Pa/U ratios within U-series dating of bones (see e.g., BISCHOFF and ROSENBAUER, 1981a and b) imply an uranium uptake of the bone within a few thousand years after the bone was buried.

- **continuous, linear U-uptake**: even very old bones from Pliocene (TUREKIAN *et al.*, 1970) show disequilibria in the U-decay chains. Investigations by BADONE and FARQUHAR (1982) and GRÜN and INVERNATI (1985) show, that uranium is accumulated by bones and teeth up to a saturation level (which may be in the range of 500

to 1000 ppm) and that a saturation front migrated into the bone or tooth.

Figure 7 shows the effect of U-accumulation on the resulting age: as long as the U-concentration in dentine is low (< 5 ppm) the resulting age is mainly controlled by the radioactivity of the surrounding matrix. With increasing U-content the beta-dose rate from the dentine as well as the internal alpha- and beta- dose from the enamel gets more and more dominant and with it the discrepancy between the age calculated according an early and a continuous U-uptake (see Figure 7 below). The mathematical formulas for these models are given by GRÜN *et al.* (1987).

There are two possibilities to minimize the effect of U-uptake to some extent:

(i) samples are cut out of the center of a large tooth (e.g., mammoth), here, the outside accumulates nearly all the uranium and acts as a buffer for the center (see e.g., GRÜN and INVERNATI, 1985). Many such samples still show U-concentrations typical of recent teeth (see example from Saskatchewan).

(ii) small enamel pieces with no organic matter attached are collected, since the migration rate into enamel is much slower than into dentine or cement (by at least an order of magnitude) (see example from Bilzingsleben).

Although most of our results show a good agreement with other independent dating methods, when the model of linear U-uptake was applied, sometimes the early uptake model seems to give the "right" age (see e.g. ZYMELA, 1986). Therefore, it can only be stated, that the true age is normally somewhere between the "early" and the "linear" age.

LIMITS OF THE METHOD

The method is principally limited by two factors:

1. the sample is saturated, i.e. all traps available are filled with electrons and no signal increase can be induced by additional radiation. However, even after an artificial irradiation of 20 kGy no enamel sample which we have studied has been saturated. Considering dose rates in the range of 5000 mGy/ka complete saturation should not occur before 4 Ma.

2. thermal instability of the trapped electrons. All electrons have only a limited probability of being trapped. After the so-called mean life has passed about 69 % of the trapped electrons have left the trap (by recombination). This value can only roughly be determined (see DEBENHAM, 1983) and for tooth enamel, is supposed to be in the range of 10^7 to 10^8a (at 25°C). An age determination in the range of 20 % of this value (at least 2 Ma) would cause an underestimate of age of about 10 %.

APPLICATION

1. A mammoth tooth from the Saskatchewan Sands near Edmonton

The first example presented here is a mammoth tooth found in the Villeneuve Pit in Saskatchewan (see GRÜN *et al.*, 1987). Geological evidence shows only that the sediments are preglacial. Although the thirteen dates determined for this tooth scatter to such an extent (see Figure 8), that a very accurate age determination is not possible, the results combined with the geological setting (preglacial) allows a reliable assignment of these sediments into oxygen isotope stage 5.

2. Single enamel layers from Bilzingsleben archaeological site

The Bilzingsleben (E-Germany) archaeological site is famous for its *Homo erectus* remains. The remains from the so called "Steinrinne" are embedded in a spring deposited travertine, which today forms the top of a hill. Subsequent to the deposition of this travertine a valley lowering took place and at least three river terraces with gravel deposition were developed (for a profile see MANIA, 1983). Two previous U-series investigations on the travertine by HARMON *et al.* (1980) and BRUNNACKER *et al.* (1983) suggested an assignment of this deposit into stage 7 (about 190 to 250 ka, see Figure 9). This is in contradiction to the geological setting (at least stage 9) and the anthropological findings. Later, this profile was remeasured by the McMaster dating group headed by H.P. SCHWARCZ (for details and analytical data see SCHWARCZ *et al.*, 1988). All U-series results gave infinite ages. ESR-investigations on the travertine samples were complicated by interferences caused by organics (see GRÜN and DeCANNIERE, 1984); however, two samples yielded ages in the range of stage 11 to 13.

ESR studies on 4 enamel pieces (with dentine attached on one side) show, that even the age results determined according the early U-uptake are older than the previous U-series data by HARMON *et al.* (1980) and BRUNNACKER *et al.* (1983). The ages of the continuous linear U-accumulation suggest an assignment into stage 13. However, when we consider all results (U-series and ESR on the travertine and ESR on the teeth) this site can be correlated to stage 11 or 13; the resolution of the method is not good enough to distinguish between these two stages.

CONCLUSION

In my opinion, ESR dating of tooth enamel is at the present time a method which can support or contradict independent age determinations of other methods. The problem of U-uptake causes an uncertainty which often does not allow us to determine particular stage-assignments. However, as the two examples show, it can be a useful tool to get better stratigraphic evidence. It is hoped that comaprative U-series and ESR studies will solve the problem of U-uptake (GRÜN *et al.*, 1988).

ACKNOWLEDGMENTS

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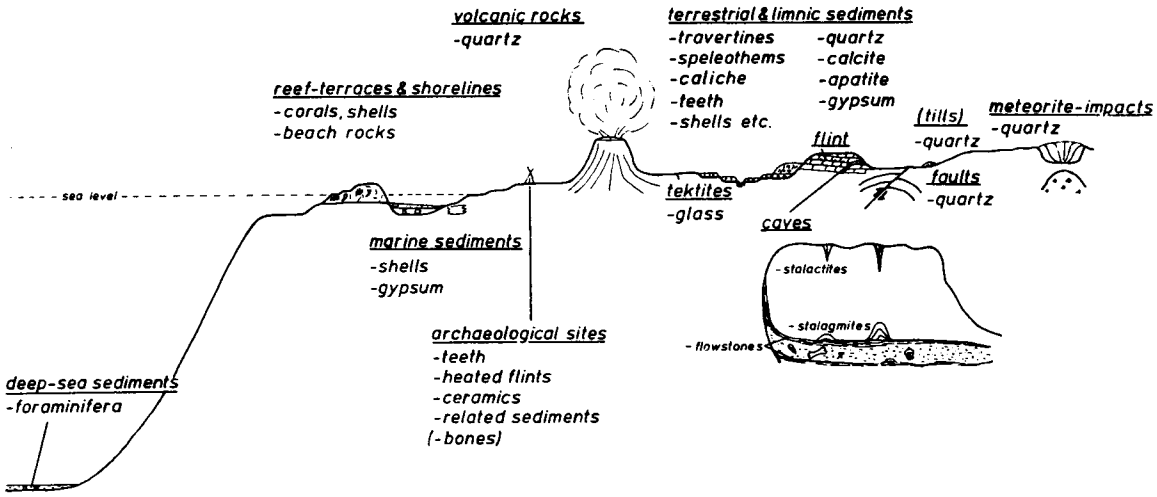

FIGURE 1

Fields and minerals on which ESR dating can be applied
(in brackets: many problems are not yet solved)

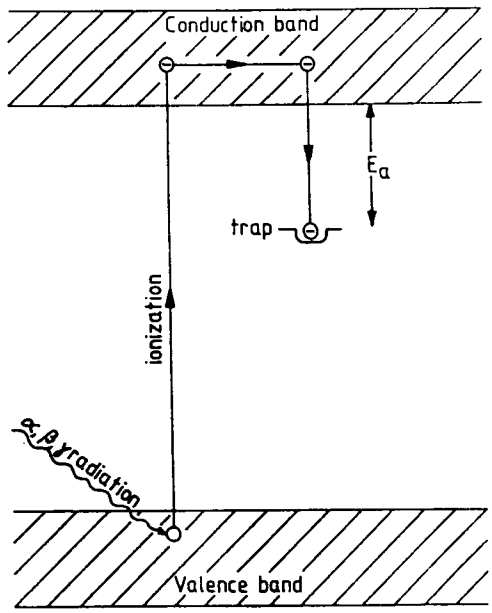

FIGURE 2

Trapping scheme of electrons in minerals

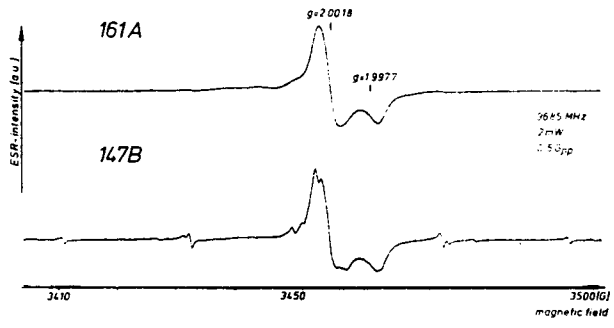

FIGURE 3

ESR spectra of tooth enamel
(hydroxyapatite)

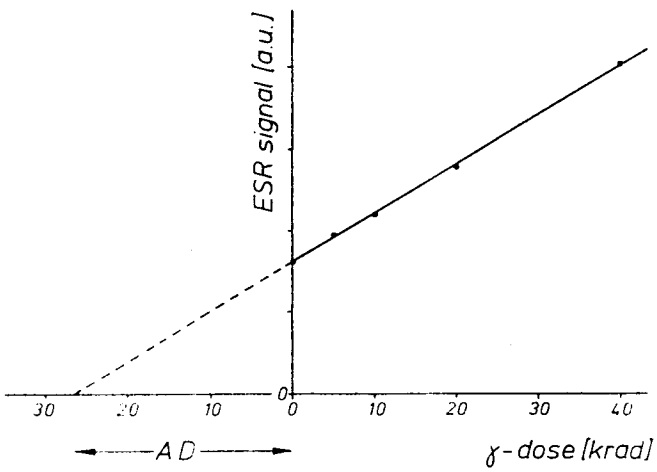

FIGURE 4

Determination of AD by artificial gamma-irradiation

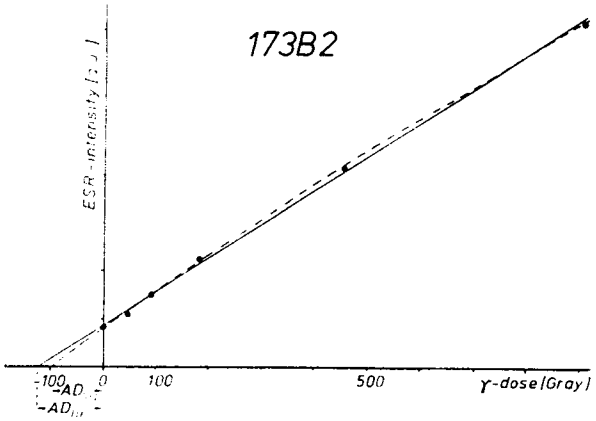

FIGURE 5

Determination of AD using linear extrapolation (ADlin: solid line) and logarithmic extrapolation (ADlog: dashed line)

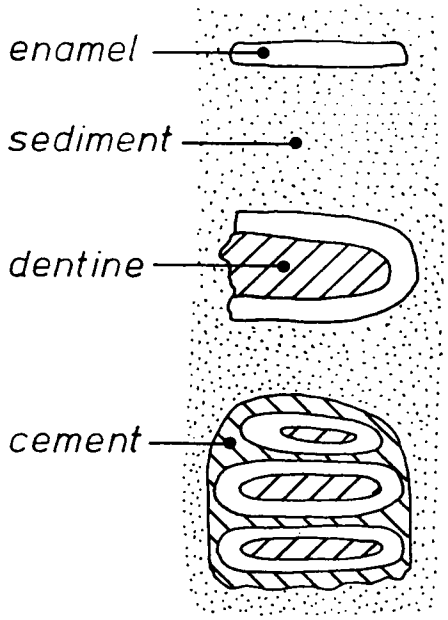

FIGURE 6

Possible environments of an enamel layer

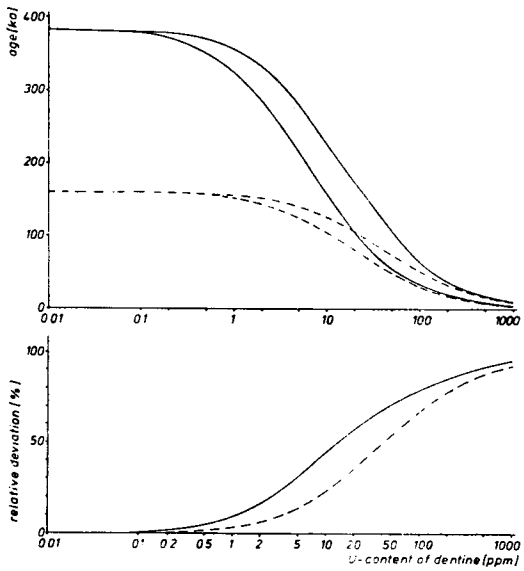

FIGURE 7

Dependence of the calculated age on the U-concentration in dentine (assuming U(enamel- = 1/10 U(dentine)). Solid line: average values for clay; dashed line: average values for sand. The line-splitting is cause by U-accumulation and each upper curve corresponds to continuous, linear U-uptake, the lower early U-accumulation. Below: relative deviation of the calculated ages due to the applied U-uptake models.

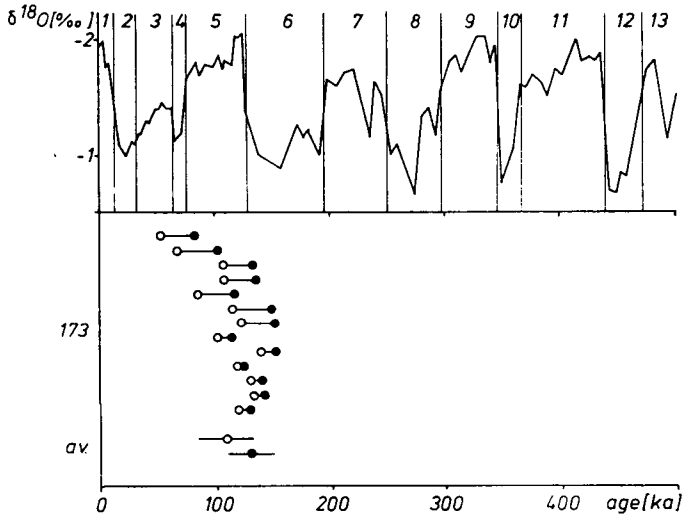

FIGURE 8

Repeated ESR ages of a single mammoth tooth from the Saskatchewan Sands near Edmonton. Open circles: ages according early U-uptake; black circles: ages according continuous U-accumulation. av: average ages with standard-deviation.

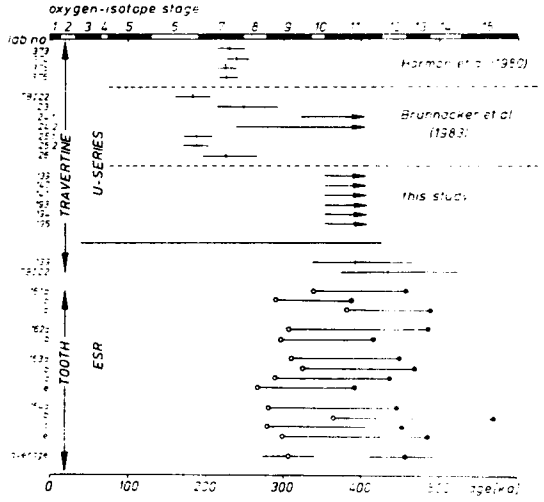

FIGURE 9

U-series and ESR results on travertines and tooth enamel from the archaeological site at Bilzingsleben. U-series results: meanvalues with 1-σ-uncertainty; arrows = infinite ages. ESR : travertine: mean values with estimated error; teeth: open circle = ages according early U-uptake; black circles = ages according continuous U-accumulation. Averages are given with standard-deviation.

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U-SERIES DATING OF MIDDLE EUROPEAN TRAVERTINES

by

Ruth HAUSMANN * and Karl BRUNNACKER *

Nearly all accessible travertines from Middle Europe have been dated by means of the Th/U method, in order to answer a temporal and regional orientated paleoclimatical questioning. These travertines are of warm climatic origin as proved by flora and fauna. Corresponding speleothems in Europe (about 600 samples) and correlative beach terraces are not mentioned here. The discussed Th/U results were produced by G.J. Hennig, R. Grün and R. Hausmann.

There seems to be a bipartition of the last interglacial according to the deep sea record into 5e ("Eemian") and 5c (R/W interglacial) with corresponding U-series ages of about 125 ka and 105 ka, respectively. An intercalated, eventually more cooler period has yet not been found.

The penultimate interglacial (stage 7) shows Th/U ages around 220 ka. These data were among others confirmed by ESR results of a tooth of *Paleoloxodon Antiquus* of the Bad Cannstatt region (R. Grün). Unfortunately diagenetical processes led to a broad scattering of the Th/U data of samples of the penultimate interglacial. The previous interglacial (stage 9) is determined tentatively around 350 ka.

The Th/U dating method has been applied to travertine complexes from A: Germany (Stuttgart Bad Cannstatt), B: Thüringen, C: Czechoslovakia, and D: Hungary.

A. TRAVERTINES FROM STUTTGART BAD CANNSTATT

Two periods of travertine growth can be distinguished:
1) about 100 ka and older (R/W interglacial), and
2) about 200 ka and older for the penultimate interglacial (Holsteinian?).

The older travertines show a relatively large scattering in the age results which disturbances mentioned above might be responsible for.

B. TRAVERTINES FROM THÜRINGEN

The travertine profile of Bad Langensalza is of Holocene age. Travertines of Eemian age (stage 5) are located in Burgtonna, Taubach, Weimar-Ehringsdorf Parktravertin, as well as in a part of Weimar Ehringsdorf (Upper Travertine). They show Th/U ages of about 100 to 130 ka.

* Universität zu Köln, Geologisches Institut, D-5000 Köln 1, Zülpicherstrasse, 49. R.F.A.

The penultimate interglacial has been determined with ages at about 200 ka (180-220 ka) in the travertine profiles of Weimar-Ehringsdorf and Bilzingsleben. In Weimar-Ehringsdorf the so-called Lower Travertine has been determined around 200 ka. The hominid finding in Bilzingsleben is older than the "Decktravertin" (around > 260 ka).

C. TRAVERTINES FROM CZECHOSLOVAKIA

Beside Holocene data travertines had been dated at about 100 ka (R/W interglacial). The penultimate interglacial seems to be represented especially in the profile of Vysne Ruzbachy (around 200 ka). Furthermore, there seems to be another warmer period at about 260 ka according to the Th/U data. The age of the hominid bearing layer in the profile of Ganovce is in the range of 80-120 ka.

D. TRAVERTINES FROM HUNGARY

The Th/U age results of the travertines under investigation seem to establish three periods of travertine deposition:
1) ages of about 100 ka (R/W interglacial),
2) ages of about 200 ka and older (Holsteinian II?), and
3) ages of more than 300 ka (Holsteinian I?).

In the profile of Vertesszöllös it was possible to date the hominid bearing layer with the help of the U-series method on more than 350 ka.

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TRAVERTINE-PROFILES

A. Stuttgart Bad Cannstatt

1 = Steinbruch Lauster
2 = Steinbruch Haas
3 = Kursaal
4 = Katzensteigle
5 = Naturdenkmal, Heinrich Ebner Str.
6 = Steinbruch Biedermann

Daten: GRÜN *et al.* (1982)

B. Thüringen

1 = Bilzingsleben
2 = Weimar Ehringsdorf, Bruch Fischer
3 = Weimar Ehringsdorf
4 = Weimar, Parktravertin
5 = Taubach
6 = Burgtonna
7 = Bad Langensalza

Daten: BRUNNACKER *et al.* (1983)

C. Czechoslovakia

1 = Hradisté pod Vrátnam
2 = Bejnice-Jaskyna
3 = Bejnice Hrad
4 = Besenova Drienok
5 = Hranovnica
6 = Gánovce
7 = Sobotisteo
8 = Siva Bracia
9 = Vysne Ruzbachy

Daten: HAUSMANN (unpublished)

D. Hungary

1 = Kalvaria
2 = Varpalota
3 = Buda
4 = Dunaalmás
5 = Vertesszöllös
6 = Tata

Daten: HAUSMANN and ASSMANN (unpublished)

Daten: HENNIG *et al.* (1983)

Altersdaten von Travertinen mittels Th/U-Datierung

Probe	Th230 / U234	U234 / U238	Th230 / Th232	U-Gehalt ppm	Alter ka	Alter korr. ka
TRD1	0.78±0.06	2.191±0.21	218.6±14.08		137 + 22 - 19	133 + 21 - 17
TRD2	0.865±0.02	1.773±0.05	504.4±52.90		107 + 6 - 5	106 + 6 - 6
TRD3	0.667±0.03	1.792±0.08	328.9±23.52		107 + 9 - 8	105 + 9 - 7
TRD4	0.662±0.02	1.871±0.04	699.7±89.19		106 + 4 - 4	105 + 4 - 4
THE1	0.655±0.02	2.124±0.05	430.6±42.99		103 + 4 - 5	101 + 5 - 4
THE2	0.635±0.02	1.909±0.08	178.8±10-36		99 + 6 - 6	95 + 6 - 5
TKN1	0.957±0.03	1.567±0.05	83.60±2.590		227 + 25 - 21	197 + 20 - 17
TKN2	1.003±0.06	1.487±0.09	90.10±4.930		269 + 93 - 41	255 + 82 - 46
TKU1	0.548±0.01	1.303±0.02	1.100±0.010		83 + 3 - 3	41 + 1 - 2
THA1	0.841±0.06	1.215±0.06	11.50±1.160		181 + 40 - 29	174 + 36 - 29
THA2	0.973±0.05	1.5990.06	852o ± ----		235 + 45 - 31	235 + 45 - 31
THA4	0.729±0.13	1.138±0.23	46.00±6.62o		136 + 99 - 42	134 + 96 - 41
THA5	1.009±0.03	1.467±0.04	74.10±10.37		286 + 50 - 34	285 + 50 - 34
THA6A	0.958±0.03	1.331±0.03	19.00±1.40o		247 + 35 - 27	243 + 34 - 27
THA6B ~	1,208±0.33	1.612±0.57	9.oo ±o.38o		>35o	>35o
THA7	0.842±0.11	1.428±0.05	15.70±0.82o		171 + 67 - 42	166 + 62 - 4o
THA8A	0.917±0.05	1.394±0.04	27.30±4,82o		212 + 42 - 31	2o9 + 41 - 31
THA8B	1-001±0.03	1.496±0.02	11.60±0.37o		199 + 65 - 38	192 + 59 - 35
TLA1	0.893±0.07	1.363±0.13	11.30±0.39o		199 + 65 - -8	192 + 59 - 35
TLA2	0.975±0.06	1.485±0.09	32H.9±2o.32		245 + 68 - 41	245 + 68 - 41
TLA3	0.861±0.06	1.574±0.1o	7o.6o±14.95		174 + 34 - 25	171 + 31 - 24
TLA4	0.935±0.05	1.219±0.07	4.80o±o.19o		241 + 73 - 41	225 + 58 - 36
TLA5	0.975±0.05	1.29o±o.06	37.4o±9.21o		268 +1o1 - 51	266 + 98 - 5o
TLA6	0.887±0.08	1.521±0.07	1o.8o±2.9oo		189 + 56 - 38	182 + 52 - 36
TLA7	1.oo2±o.o3	1.458±o.o1	16.9o±1.68o		272 + 35 - 27	267 + 35 - 27
TLA8	0.958±o.o8	1.559±o.o8	4.5oo±o.46o		228 + 76 - 45	212 + 64 - 41
TLA9	0.977±o.o3	1.487±o.o4	1o8.2±3.97o		247 + 31 - 25	227 + 26 - 21
TLA1o	0.955±o.o5	1.212±o.o4	7.5oo±o.68o		168 + 36 - 24	178 + 32 - 35
TLA11	0.477±o.o3	1.446±o.o4	61.7o±2o1o		68 + 6 - 7	67 + 7 - 7
TLA12	1.o74±o.o8	1.47oo±.o6	127.9±11.83		37o + ∞ - 86	37o + ∞ - 86
TLA13	0.934±o.o4	1.4o4±o.o4	66.4o±9.21o		222 + 34 - 25	221 + 33 - 24
TRLS1	o.138	1.533	6.57	o.356	15.9 +1.8 -1.7	13.7 +1.6 -1.5
TRLS2	o.13o	1.787	8.89	o.384	13.8 +1.6 -1.7	13.8 +1.6 -1.7
TRLS3.1	o.o83	1.949	68.o8	o.478	9.4 +o.7 -o.9	9.2 +o.7 -o.7
TRLS3.2	o.o86	1.95o	69.9o	o.477	9.6 +o.7 -o.7	9.5 +o.7 -o.7
TRUR5	o.648	1.599	252.o6	o.482	1o4 +8.o -7.6	1o4 +8.o -7.6
TRUR6	o.651	1.49o	12.27	o.383	1o6 +1o.o -9.1	1o1 +9.o -8.7
TRUR7	o.674	1.512	65.11	o.531	112 +7.o -7.o	111 +7.o -7.o
TTAU8	o.678	1.698	82.68	o.331	111 +13.o -11.7	111 +13.o -11.7
TTAU9	o.695	1.527	84.o4	o.426	117 +19.o -16.o	116 +19.o -15.o
TWE1o.1	o.69o	1.314	15.92	o.437	119 +22.o -18.o	115 +2o.o -18.o
TWE1o.2	o.723	2.137	31.95	o.166	12o +12.o -12.o	118 +12.o -12.o
TWE11	o.944	1.437	3.53	o.431	172 +22.o -19.o	151 +16.o -14.o
SWE14	o.749	1.166	1.29	o.441	142 + 17 - 16	121 + 13 - 11
SWE13	o.738	1.2o5	14.4o	o.536	137 + 18 - 15	132 + 17 - 15
SWE12	o.461	1.169	1.17	o.397	66.1+6.o -5.7	3o.7 +2.o -2.9
SWE11	o.626	1.122	1.72	o.386	1o4 + 11 -9.4	71.3 +6.8 -6.3
SWE1	1.o7o	1.159	622.65	o.424	>4oo	>4oo
SWE2	o.534	1.281	319.83	o.337	8o.o +13.3 -11.7	79.8 +13.2 -11.7
SWE3	o.652	1.227	12.73	o.573	11o + 16 -15.4	1o5 +16.o -13.1
SWE4 ~	o.888	1.132	19.64	o.5xo	216 +148 - 57	212 +135 - 55
SWE5	o.636	1.117	25.22	o.495	1o5 + 24 -19.5	1o3 + 24 -18.5
SWE6	o.83o	1.613	78.34	o.256	161 + 25 - 21	159 + 26 - 2o
SWE7	1.o83	1.253	113.77	o.282	>4oo	>4oo
SWE8	1.249	1.569	88.o2	o.226	>4oo	>4oo
SWE9	o.76o	1.189	2o6.42	o.299	14o + 17 - 15	145 + 17 - 14
SWE1o	o.83o	1.142	35.4o	o.516	179 + 2o - 16	177 + 19 - 16
TWE12	o.9oo	1.212	23.2o	o.649	215 + 32 - 24	212 + 3o - 24
TWE13	o.814	1.22o	8o.64	o.413	167 + 27 - 21	167 + 27 - 21
TWE14	o.946	1.257	54.36	o.475	24o + 51 - 33	244 + 5o - 34
TWE15	o.9oo	1.236	14o.7o	o.o42	16o + 16 - 14	156 + 16 - 14
TBI21.1	o.596	2.o88	8.63	o.356	89.5 +6.o -4.7	83.1 +5.5 -4.1
TBI21.1	o.568	1.3o5	4.61	o.299	87.4 +4.4 -4.2	8o.8 +4.1 -3.8
TBI22	o.873	1.522	32.11	o.368	182 + 22 - 18	179 + 22 - 17
TBI23	o.961	1.373	152.6o	o.543	245 + 34 - 36	244 + 54 - 35
TBI24.1	1.115	1.465	2o7.5o	o.o83	>32o	>32o
TBI24.2	1.o11	1.33o	3o.42	o.1o1	3o3 + ∞ - 57	3o1 + ∞ - 56
TBI25.1	o.88o	1.516	174.1o	o.38o	186 + 2o - 18	185 + 2o - 17
TBI25.2	o.878	1.465	195.6o	o.113	186 + 14 - 11	186 + 14 - 11
TBI26	o.935	1.4o6	1o2.33	o.1o9	223 + 4o - 3o	222 + 4o - 29
TBRU4	1.o44	1.184	13.56	o.729	4o2 + ∞ - 88	4oo + ∞ - 9o
VRo1	o.827±o.o27	1.o56±o.o15	13.89±1.371	o.662±o.o11	184.5+18.1 -15.3	178.1 +16.9 -14.5
VRo2	o.865±o.o32	1.o6o±o.o36	6.33o±o.252	o.678±o.o23	194.8+27.6 -21.o	179.9 +23.3 -18.4
VRo3	o.899±o.o21	1.o51±o.o16	13.85±1.o9o	o.862±o.o11	238.1+25.7 -2o.3	231.1 +23.9 -19.1
VRo4	1.o41±o.o62	o.972±o.o52	4.511+_o.316	o.543±o.o26	>2o4.9	>2o4.9
VRo6	o.649±o.o58	1.294±o.o52	7.3o±3.254	o.422±o.o15	1o7.8+18.1 -15.3	98.5 +16.4 -14.2
VRo7	o.11o±o.oo1	1.1o3±o.o13	79.o6±139.8	1.151±o.o18	12.8+o.6 -o.5	12.5 + o.5 - o.6
sVoo	o.196±o.o53	o.9o1±o.o91	1.238±o.389	o.o75±o.oo4	23.7+7.8 -7.o	5.o + 6.3 - 5.o
SOBu1	o.968±o.o72	1.177±o.o97	7.o76±1.419	o.o98±o.oo6	>2o6.9	>2o6.9
GHo1	o.576±o.o15	2.127±o.o19	12.91±1.357	3.3454o.o66	85.2+ 3.3 - 3.2	83.5 + 3.3 - 3.1
GHo2	o.761±o.o13	1.997±o.o24	63.o2±2.36o	1.468±o.o27	131.8+ 4.1 - 3.9	13o.8 + 4.o - 3.9
GHo3 ~	o.673±o.o39	1.836±o.o44	15.62±7.85o	o.332±o.oo8	1o8.6+1o.5 - 9.7	1o4.5 +1o.6 - 9.4
HAHo1	1.oo5±o.o26	1.542±o.o18	78.93±9.o44	1.341±o.o21	265.7+28.o -22.8	264.7 +27.7 -22.6
HAHo2	o.827±o.o21	1.7o3±o.o13	2o.56±o.6o4	1.835±o.o33	157.5+ 8.6 - 8.o	153.8 + 8.3 - 7.7
BDo1	o.634±o.o66	2,15o±o.299	2.3o3±o.268	o.o87±o.oo8	97.7+17.8 -14.8	67.7 +13.4 -11.8
BDo2	o.759±o.o63	3.o97±o.323	6.15o±1.426	o.o64±o.oo4	125.6+19.6 -16.7	114.5 +17.8 -15.4
bHo1	o.646±o.o38	1.443±o.o64	5.295±o.674	o.134±o.oo5	1o5.1+11.1 - 9.9	92.4 + 9.7 - 8.9
BHJo1	o.627±o.o69	1.265±o.o58	1.319±o.185	o.2o8±o.o11	1o2.1+2o.6 -17.1	36.3 +11.2 -1o.2
HVo2	1.8o2±o.o78	1.349±o.o5o	3.743±o.184	o.189±o.oo6	>234.4	>234.4
HVo3	1.o5z±o.o54	1.288±o.o63	1.o89±o.121	o.164±o.oo7	>265.7	>265.7
HVo4	o.781±o.174	1.561±o.o87	1.3o5±o.4o7	o.ouz±o.oo1	141.8+87.8 -49.8	59.8 +37.8 -2o.5
TATAo1	o.59o±o.o31	o.824±o.o21		o.6o1±o.o15	1o1 ± 1o	
TATA13	o.575±o.o26	o.79o±o.o17		o.651±o.o14	98 ± 8	
VERTo2	o.717±o.o53	1.276±o.o51		o.111±o.oo4	128 + 2o - 17	
VERTo3	o.893±o.o37	1.151±o.o52		o.143±o.oo6	217 + 4o - 2o	
VERTo4	1.ooo±o.o38	1.19o±o.o31		o.135±o.oo4	325 + ∞ - 6o	
VERTo5	1.134±o.o77	1.169±o.o44		o.128±o.oo4	>35o	
VERTo6a	o.85z±o.o74	1.oo7±o.o89		o.185±o.o13	21o +151 - 51	
VERTo6b	o.921±o.o5o	1.25o±o.o57		o.169±o.oo8	227 + 56 - 37	
VERTo7	o.9o1±o.o92	1.o12±o.o89		o.13o±o.oo9	248 + ∞ - 67	
VERTo8	o.694±o.o25	o.875±o.o19		o.591±o.oo4	135 - 12 - 11	
DUN09	1.oo2±o.o91	1.13o±o.o57		o.o98±o.oo3	291 + ∞ - 32	
DUN1o	1.oo2±o.o67	1.449±o.o62		o.o94±o.oo3	354 + ∞ - 94	
BUD11	1.o31±o.o13	1.262±o.o23		o.968±o.o22	358 + ∞ - 6o	
BUD12	o.917±o.o69	1.431±o.o95		o.1o4±o.oo6	16o + 38 - 27	
3o3	o.987±o.o5o	1.138±o.o23	24.86±5.214	1.184±o.o28	>249.3	
3o4	1.o34±o.o33	1.157±o.o31	8.854±o.395	o.745±o.o2o	>3o6.5	
3o5	1.o25±3.899	1.241±o.o37	o.863±1.133	o.526±o.o15	>35o	
3o6	o.819±o.o74	1.o46±o.o27	17.48±8.75o	o.882±o.o22	181.3+57.9 -36.7	176.2 +54.3 -35.3

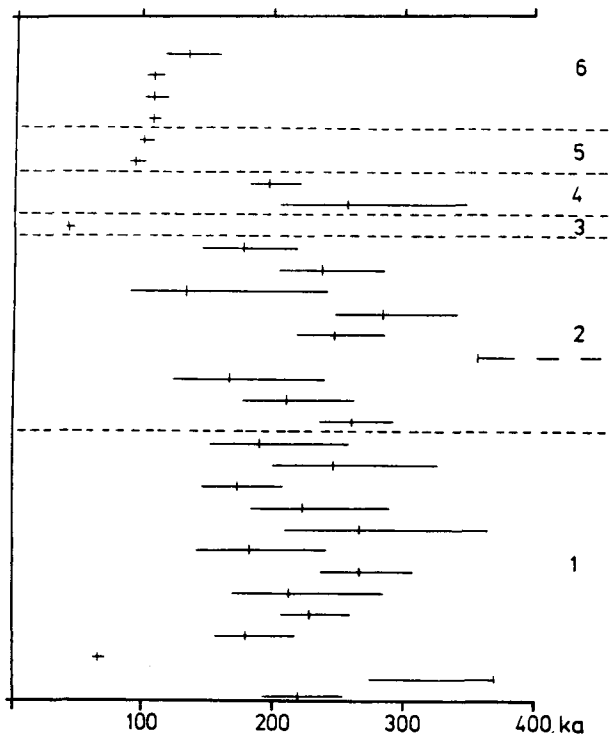
A: Germany, Stuttgart

B: DDR, Thüringen

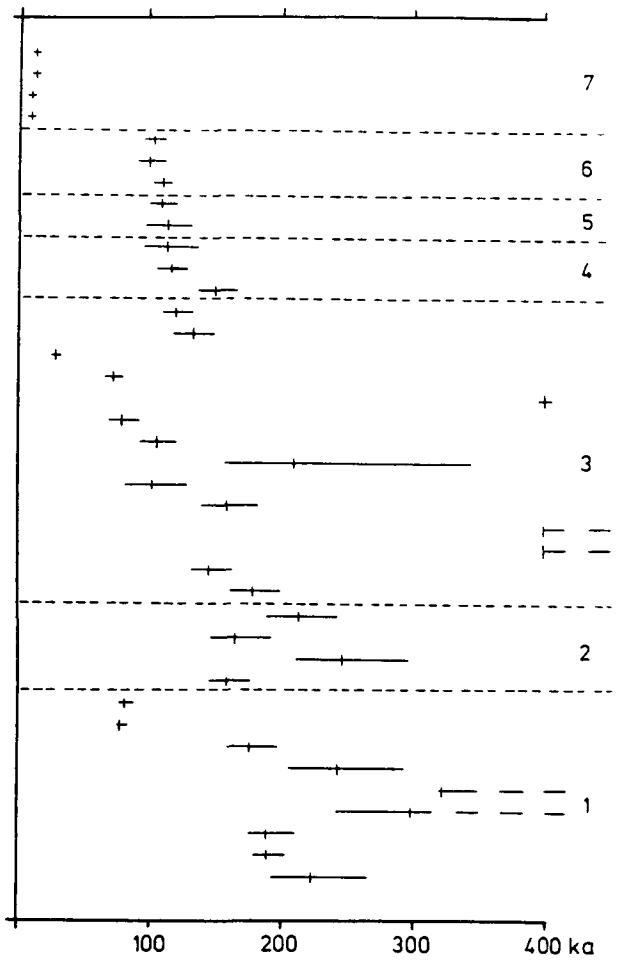
C: Czechoslavakia

D: Hungary

A
BRD, Stuttgart

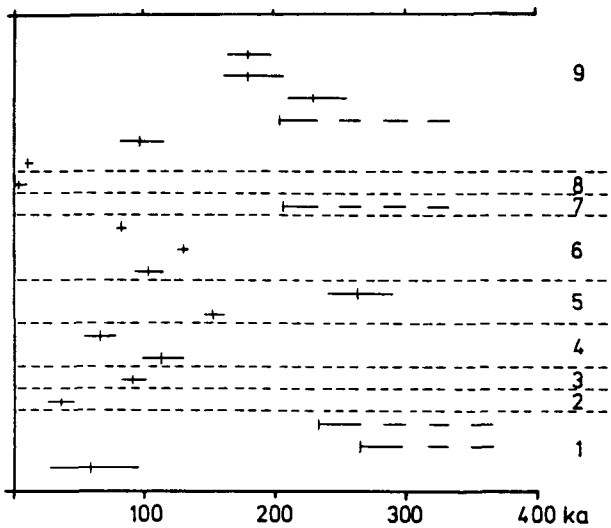


B
DDR, Thüringen

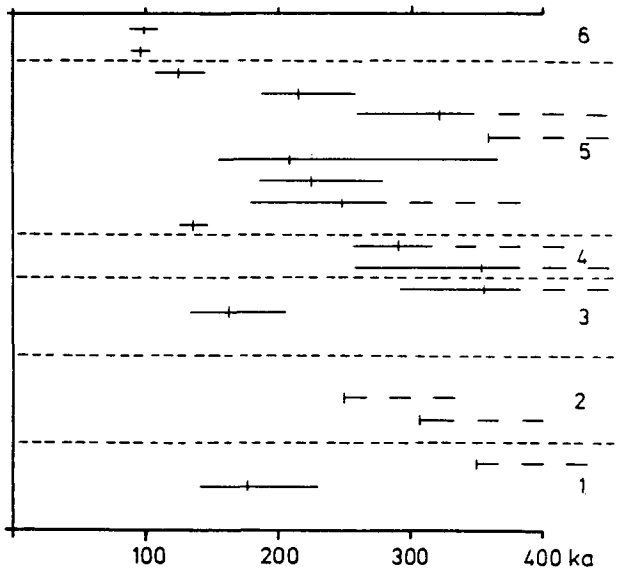


Thorium/Uran - Altersdaten
von
mitteleuropäischen Travertinen

C
ČSSR, Slowakei



D
UNGARN, Nordwesten



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CHRONOSTRATIGRAPHY OF "ABRIC ROMANI"

by

MORA R., MURO I., CARBONELL E., CEBRIA A., MARTINEZ J. *

I. HISTORY

The River Anoia passing through Capellades is the axis of a prehistoric ensemble called "Cingles del Capello". The places of known occupation are the "Abric Romani" and the "Abric Agut". The investigations were begun at the beginning of the century.

In this way in this initial period archaeological, geological and paleontological strata were documented, including in the last few all those that did not present a clear antropic activity.

In the initial period, that lasted about twenty years (1911-1932), the sedimentary potential was lowered about 4 metres from the total covering; also, two wells were excavated (wells 1 & 2), the second of which has a depth of 12,40 metres and its sequence will be analysed in this discussion.

From 1956-1962 work was started again under the direction of Eduard Ripoll. This corresponded to the time of the first synthesis of the Middle Paleolithic in Catalonia (RIPOLL, LUMLEY, 1965).

In this phase the stratigraphic documentation runs parallel to the archaeological documentation, including for the first time the stratigraphic sequences of all the places of occupation known of in Catalonia.

Twenty years passed before work was started again on these places of occupation. The results obtained after four years by the present team are presented in this paper.

II. GEOMORPHOLOGICAL CHARACTER OF THE AREA

The Anoia river, near Capellades, crosses three very different tectonic structures, the Prelitoral mountain range, the Ebro Basin and that of Penedes graben. Because of these factors the area of the Cingles of Capello has a very interesting geological history.

* CENTRE DE RECERQUES PALEO-ECO-SOCIALS, Museu d'història de la ciutat de Girona. E-17004 GIRONA (Espagne)

During the Quaternary the area presents different morphologies, among which three types are recognized:

a) Travertine formations occupy a wide area in the form of a triangle, limited by the localities of Capellades, Pobla de Claramunt and the Torre de Claramunt. The paleontological remains that have appeared allow us to date this formation as belonging to the Pleistocene age.

b) GARCIA RODRIGO (1957) has identified a Quaternary terrace on the River Anoia in the area we are analysing. It is about twenty metres above the river.

c) Recent alluvium composed of paleozoic and miocene clasts.

III. GENERAL TECTONICS

The prelitoral mountain range presents a "transversal dislocation" in a NNW-SSE direction, which is the one that the River Anoia takes advantage of for its course. The zone is divided into two areas:

1) The East with paleozoic materials (slates);
2) The West with triassic materials.

The zone of Capellades had residual movements during the Quaternary along a satelite fault which broke the consolidated travertine provoking its collapse and originating a depression which was later filled in. From this moment and from the stabilizing of the area the travertine began to form which provided the shelters and caves in this area.

IV. PROCESS OF TRAVERTINIZATION

A data that surprises us is the altimetric regularity of the great travertine platform of this zone, oscillating about 300 metres above sea-level. Interpreting this as an old lake terrace, the satellite fault would produce its emptyng and the process of the formation of the "Cingles del Capello" would begin.

The process of travertinization requires water rich in calcium carbonate and a great accumulation of vegetal remains, elements that are found not only in the paleolacustrian formation but also today in the springs of Capellades.

The travertine, with a spongy appearance, is formed through an increasing calcareous deposit, giving the morphological characeristic of the Capello in the form of a hat.

Three very strong pulsations have been documented, giving rise to three fossil cornices, as seen in Fig. 2.

The cornices I and II are now fossil, while III is now forming.

Man used these natural structures (shelters and caves): between cornice I and II is the Romani shelter, between II and III is the Shelter of the Consagració and Agut.

While the sedimentary filling in of the places of occupation is closely related to spring activity it is evident that the structure of the cornices I, II and III was already practically formed by the beginning of the Quaternary, varying only its morphology with the process of time.

V. STRATIGRAPHIC UNITS IN THE "ABRIC ROMANI"

This place of occupation is characterized by a dynamic alternation of autochthonous and allochthonous fillings. We shall take as a base for the analysis the work of RIPOLL and LUMLEY (1965) in which three important units are distinguished corresponding to:

1. Surface red muddy sand: deposited by sedimentation in small depressions (Wurm III).

2. Level of tufa or tobas: with a thickness of 4 metres consisting of interstratification of travertines with grains of sand (Wurm II-III).

3. Cryoclastic fragments: unkown lower contact, attribued to Wurm II.

It is interpreted as an alternation of a very cold climate and a cold and humid climate. In the work carried out between 1956-1962, they were unaware of the existence of a well that reaches 12,40 metres, and for this reason only the upper part of the sedimentary potential of the shelter was described, that is situated on top of point 0 (see Figure 3) and which corresponds with the ensemble II, III of the graph. On carrying out the classic sedimentology work, we were faced with the invalidity of the results, as on eliminating the organic material of these they disappeared in their entirety; its high percentage of carbonate makes the sedimentary parcel a homogeneous whole without any possibility of discerning the fluctuations or changes undergone in this period.

We had to resort to micro-morphological analysis, creating a nomenclature in order to distinguish the different facies that the travertines present, like the rest of the stuctures of the sequence.

Along all its potential, we distinguished important units that we name and that are numbered from II to X. Its individualization has been carried out based on ruptures or changes in the sedimentation, understanding by this important blocks looking for observable ruptures along the sequence.

Contrastable in extension, along all the surface of the shelter, in these moments, they have only been carried out in ensemble III, in which it has been possible to study in the sections that are shown in the ground plan of the shelter (Figures 3, 4).

The chronological control we have limit this unit , on the top at 1,40 metres at 48,5 (+ 3,1; -2,1) ka U/Th (J. BISCHOFF) and its inferior part at 56 (+3, -2,7) ka at about 4 metres.

The palinological analysis is being brought to an end at the moment and we do not have the results.

In this ensemble we have distinguished the following rules that are repeated systematically in all the sections.

1. Displaced levels of sand and fragments of the walls of the shelter and the travertine; its thickness varies in function of the zone of the shelter.

2. The platform of the travertine that presents three facies and systematically appears in all the sections of the figure.
   a) Travertine of filiform structure with ramifications.
   b) Travertine of longitudinal structure.
   c) Travertine of filiform structure with ramifications.

It is situated at 2,20-3,40 of the stratigraphic sequence.

Its lower limit limits a big parcel of fragments the walls of the shelter that correspond to the parcel of clasts of the sequences of RIPOLL-LUMLEY (1965), which we have proved correspond to erosive processes and not climatic alternatives as they expounded.

Synchronically with the formation of the second platform, a fall of blocks can be documented, the superior in our sequence and not documented in the column that is localized at 4 metres of depth, approximately.

A larger amount of data, as well as the results of the palinological analysis, will help us to interpret the sequence that we possess of the Upper Pleistocene in Catalonia.

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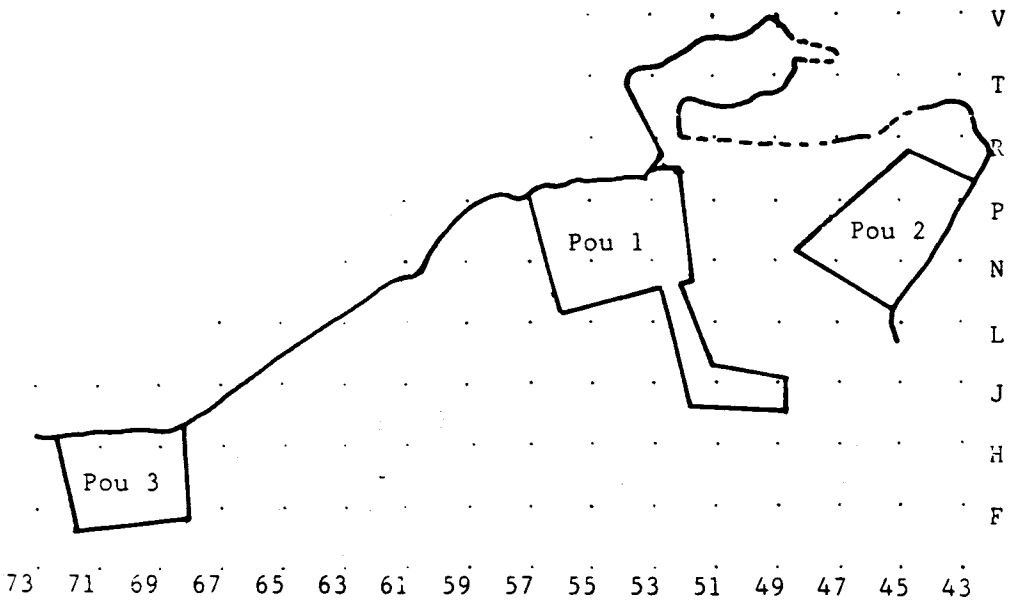

FIGURE 1

Excavation of Abric Romani (Capellades, Anoia)

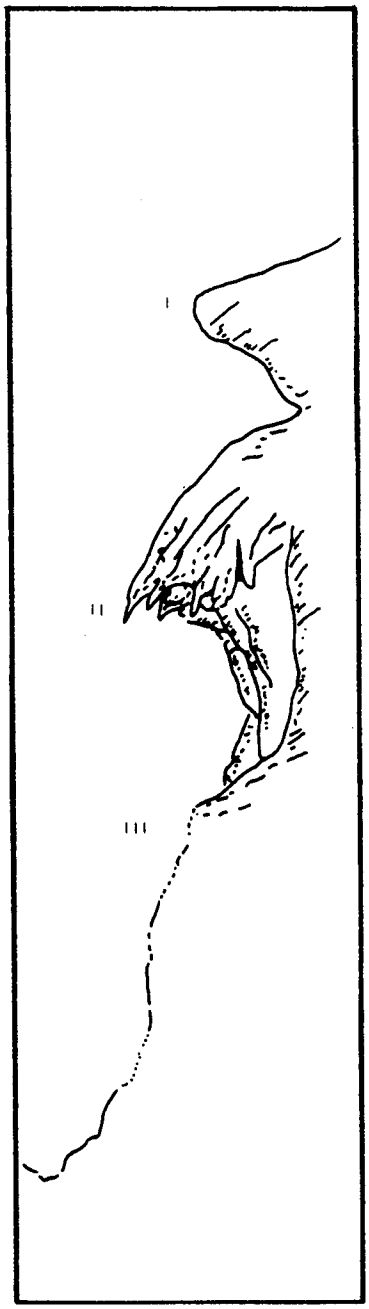

FIGURE 2

Evoluiive dynamic Cingles del Capelló

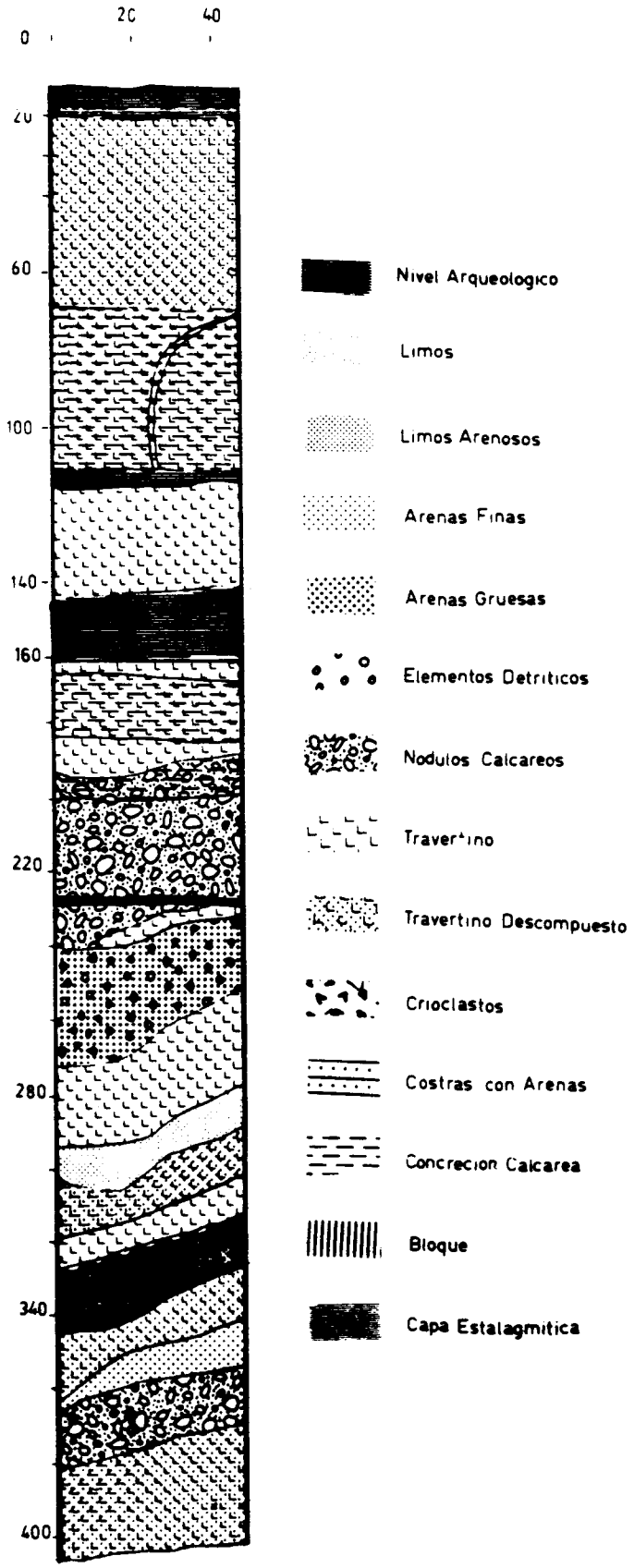

FIGURE 3

Stratigraphic sequence, Abric Romani

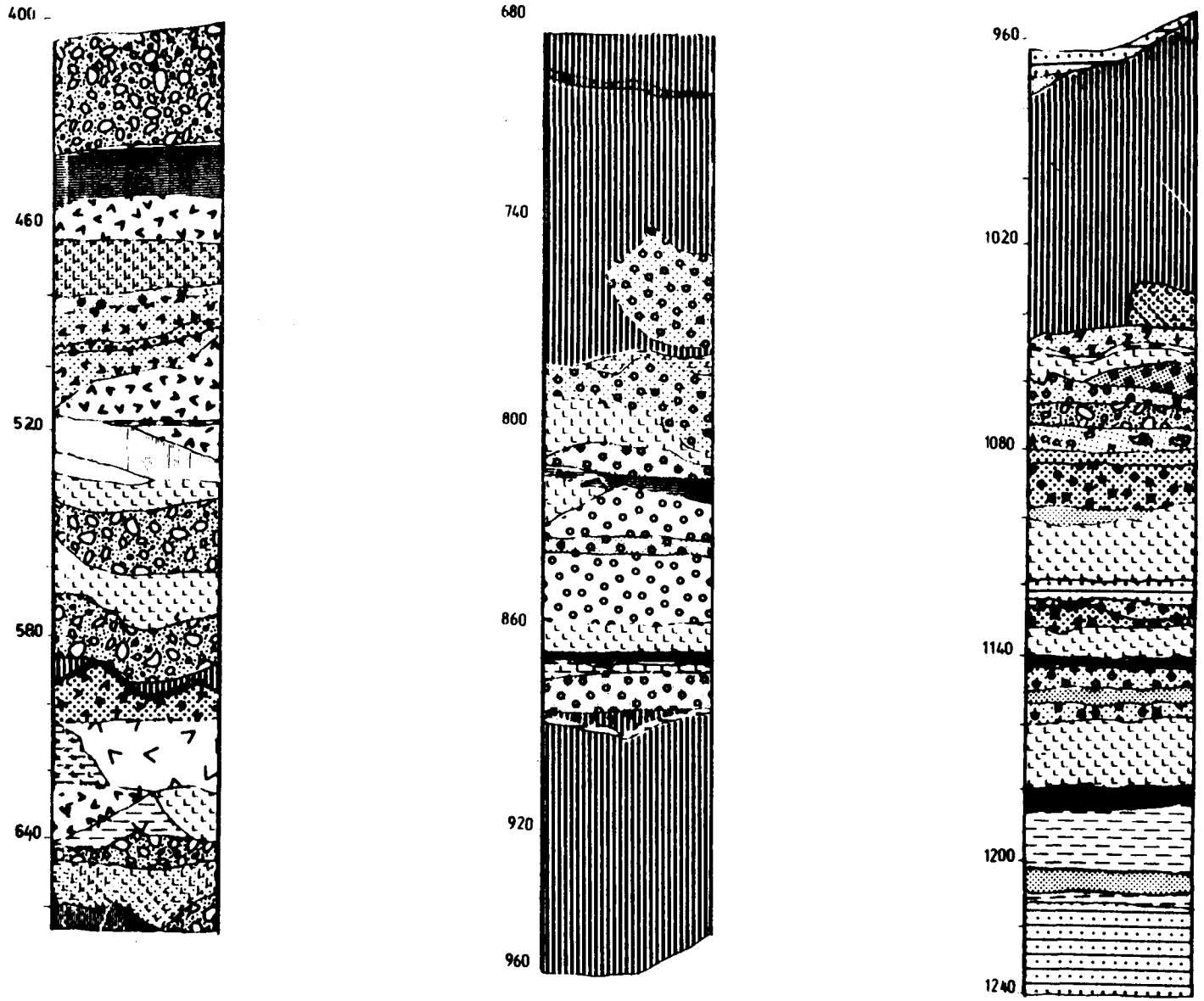

FIGURE 4

Stratigraphic sequence, Abric Romani

L'Homme de Néandertal, vol. 1, LA CHRONOLOGIE, Liège, 1988, pp. 61 à 71

EL PALEOLITICO MEDIO EN CATALUNYA

par

MORA R., CARBONELL E., MARTINEZ J., TERRADAS X. *

I. HISTORIA

Cuando en 1905 el Dr. Amador Romani inicia prospecciones en los "Cingles del Capelló", no podia imaginar que marcaba un hito estructural en la investigación del Pleistoceno Superior en Catalunya.

Quatro años más tarde dan comienzo las excavaciones en el Abric Romani, bajo la dirección de N. Font i Sagué y posteriormente, tras su muerte, por L1. Maria Vidal. Fruto de estos trabajos es la publicación en los "Annuaris del Institut d'Estudis Catalans" de una primera sintesis en 1911-1912.

En la década de los años cuarenta, pesonalidades como J.M. Corominas y el Dr. Vilaseca, trabajan en lugares geograficamente diferenciados, pero sobre una misma etapa de la humanidad, el primero de ellos lleva a cabo sus investigaciones en la zona del Reclau Viver (Banyoles, Girona) y el segundo en la zona de Tarragona y más concretamente en el lugar de ocupación de la Bóvila Sugranyes.

La celebración de 1957 del V Congreso del INQUA, en España, lleva consigo una enfebrecida actividad arqueológica en éste periodo, llevándose a termino trabajos en la cueva del Toll(Moianès, Barcelona) a cargo de J.M. Thomas Casajuana y F. de Rovira, asi como en un lugar muy próximo a este, la cueva de Teixoneres.

En estas mismas fechas se inicia una segunda fase de trabajo en el Abrix Romani, esta vez a cargo del Dr. E. Ripoll, que contarà con las colaboraciones de G. Laplace en 1959 y el Dr. H. de Lumley en 1961. Consecuencia de todo ello aparece el Paleolitico Medio en Catalunya publicado en 1965 en la revista Ampurias y en Anthropologie.

Nuevamente durante una decada quedan silenciados los trabajos sistemáticos en este campo, y si bien se efectuan intervenciones puntuales en toda Catalunya, serán las comarcas del noreste (Girona) las que llevaran a término una actividad continuada, se excavará els Ermitons (Garrotxa, Girona), Tut de Fustanyá (Ripollès, Girona) y en 1973 se inician los trabajos de excavación en la cueva de L'Arbreda (Banyoles, Girona). El resultado de todo ello es la publicación del Paleolitic a les Comarques Gironines en 1976.

* CENTRE DE RECERQUES PALEO-ECO-SOCIALS, Museu d'història de la ciutat de Girona. E-17004 Girona (Espagne).

En 1982 el equipo del cual formamos parte, inicia un proyecto de investigación sobre el Pleistoceno Medio y Superior en Catalunya, del cual expondremos los resultados preliminares obtenidos.

II. CONTEXTO GEOMORFOLOGICO

El relive de nuesto pais queda enmarcado por la personalidad que le imprimen las unidades estructurales que lo conforman. Axialmente discurren la Cordillera Litoral y Prelitoral, ambas paralelas al Mar Mediterráneo; transversalmente el sistema Pirenaico y Prepirenaico se ordenan a lo largo de la zone norte, entre ambas formaciones se situa la Depresión Central (Fig. 1).

La diversidad geomorfológica, es el marco natural en que se encuadran los lugares de ocupación del Pleistoceno Superior: En el litoral o actual linea de costa se localizan la Cova del Gegant (1), del Muscle (2) y Fumada (3). En la Despresión Prelitoral se encuentran la Bovila Sugrañes (4), Diable Coix (5) y Avetllaners (6). En la Depresión Central estan el Complejo de la Femosa: con Secanet (7) y Fonts (8), los Cingles del Capelló: con Abric Agut (9) y Abric Romani (10), la Cueva del Toll (11) y Teixoneres (12).

Al norte de la Cordillera Prelitoral y en contcto con la "Serralada Transversal" se localiza el Tut de Fustanya (13), Ermitons (14) y el Complejo de Reclau Viver con Mollet I (15) y la Cueva de L'Arbreda (16).

De los diecisiete lugares de ocupación que hemos citado, unicamente un reducido grupo formaran parte de la sintesis que llevamos a cabo, entre los cuales se encuentran:

- El conjunto de La Seval: – Diable Coix
  – Avetllaners
- El conjunto de la Femosa: – El Secanet
  – Fonts
- Abric Romani: capa 9 y 4
- L'Arbreda: (H30 - H43)

El resto de yacimientos presentan una problemática muy diversa, que va desde los que unicamente podemos constatar su existencia (Cova Fumada, Muscle, Gegant) por haber sido destruidos prácticamente en su totalidad, por agentes naturales o antrópicos, a los que por su problemática especifica (Ermitons, Toll, Agut, Fustanyà) no permite un conocimiento exhaustivo, sino una atribución cronológica o "cultural" en base a conocimientos empiricos. Otros estan en proceso de estudio y no se ha podido presentar los resultados en est trabajo.

Asi pues, únicamente seis lugares de ocupación son la referencia arueológica para interpretar este largo periodo, de ellos unicamente Abric Romani y niveles inferiores de l'Arbreda (H-30, H-44) quedan englobados dentro de un marco estratigráfico, el resto corresponden a tecno-complejos al aire libre.

III. INTERPRETACION PALEO-ECOLOGICA

Del escaso grupo de lugares de ocupación que analizamos únicamente los registros arqueólogicos en cueva o abrigo sumistran este tipo de información.

Durante todo el Wurm la vegetación de la Arbreda es abierta y prácticamente de estepa (LOUBLIER, 1978); si contrastamos este análisis con la fauna que se obtiene de los niveles H-30 al H-44, cuya secuencia jerarquizada es: ciervo, asno, bovido y caballo (ESTEVEZ, 1979).

La contradicción que se observa entre el tipo de paisaje y la fauna que se reseña, se interpreta dentro de la dinámica de espacios abiertos, donde debian existir zonas de bosque que permitirian la existencia de ciervos.

El Abrigo Romani suministra una fauna con dominancia de caballo y ciervo (ESTEVEZ, 1979), el paisaje era descubierto y las laderas de la montaña abundaban los pinos (METER, 1978).

Els Ermitons con una fauna de montaña esta representado por l*a Capra Pyrenaica, Ursus Spelaeus, Felix Lynx Pardina, Crocuta Spelaea, Ursus Arctos, Cervus Elaphus,* etc.

Es de destacar la grand variedad de fauna y la importancia de la *Capra Pyrenaica* y de los carnivoros. No se han efectuado estudios palinológicos de la secuencia estratigráfica, sin embargo se ha estudiado la microfauna dando *Apodemus Silvaticus, Eliomys Quercinus* (ALCALDE, 1986), esta asociación parece repetirse en otros lugares de Catalunya (Gegant) y es interpretada como caracteristica de nichos ecológicos forestales.

Como hemos podido ver son escasos los trabajos puntuales sobre el registro paleontológico, a excepción de la tesis de licenciatura de A. MIR (1973), M. CASTELLVI (1979), J. MAROTO (1986), solo se dispone de la sintesis llevada a cabo por el Dr. J. ESTEVEZ (1979).

IV. ANALISIS DE MATERIAS PRIMAS

La búsqueda, selección y aportación de materias primas es uno de los primeros pasos del proceso productivo de cualquier comunidad, en Catalunya se observa la siguiente distribución (Fig. 2).

Lo primero que se observa es una bipolarización en la utilización de materias primas, por un lado el cuarzo con una dominancia absoluta en el conjunto de La Selva y L'Arbreda, y por otro lado el silex en los conjunto de la Femosa y el Abric Romani.

En Catalunya todavia no existe una cartografia sistemática sobre los afloramientos de silex o cuarzo, pero un conocimiento exhaustivo del terreno nos permite plantearnos que se efectua un aprovechamiento sistemático de los materiales que hay en el entorno del Centro de Intervención (AA.VV.1985).

Asi el Noreste de Catalunya es una zona donde abundan los afloramientos de cuarzo filoniano localizandose en este contexto los lugares de ocupación de Diable Coix, Avetllaners y L'Arbreda.

En la zona sur los afloramientos de silex en forma de vetas, o terrazas con gran cantidad de nódulos, permite un aprovechamiento de esta materia prima con su desplazamiento por parte de la comunidad inferior a 15 Kms., tomanos dicha distancia como punto de referencia para los grupos humanos que analizamos (TAVOSO, 1984).

V. ESTRUCTURA TECNICA

Como ya hemos visto las materias primas no poseen una categoria estructural, las comunidades prehistóricas aprovechan los recursos más próximos a la ocupación.

En el proceso de talla las bases negativas de primera generación (BNIG) que presentan los yacimientos apenas poseen técnicas de debastamiento diferenciadoras, se trata de una explotación bifacial: en una de las caras se crean plataformas de percusión, centripetas y marginales, mientras que en la otra se desarrolla una talla centripeta total.

El aprovechamiento de las materias primas o grado de explotación de las bases negativas es variable, siendo mucho más marcado en los lugares de ocupación de Abric Romani y cueva de L'Arbreda, proceso lógico ya que estos lugares de ocupacón requieren un transporte de las mismas hasta la cueva o abrigo (espacio cerrado); todo lo contrario de lo que ocurre en los tecnocomplejos al aire libre, que al estar situados en zonas próximas a las fuentes de aprovisionamento no requieren un aprovechamiento tan sistemático de la misma.

Mediante los análisis clásicos de los productos de talla o bases positivas (BP), apenas podemos establecer diferencias entre las variables cualitativas que normalmente se analizan en estos objetos (talón, tipo de talón, bulbo, etc.) debido a que presentan una unifomidad generalizada, concretada en talones lisos y bulbos marcados.

La corticalidad o no corticalidad de la plataforma de percusión, es una variable que nos indica procesos de debastamiento "in situ" o en su defecto aportación de materiales elaborados. Se observa que los tecnocomplejos al aire libre presentan un porcentaje de plataformas corticales de .27 a .39, excepcionalmente alto al compararlo con los lugares de ocupación en espacios cerrados (Abric Romani, L'Arbreda).

Los estudios tipométricos en base al coeficiente de correlación múltiple (CARBONELL, GUILBAUD, MORA, 1984), sobre los productos de talla, en los que distinguimos las categorias de:

Bases Positivas (BP): todo aquel material que presenta morfologia de lasca y no ha sufrido transformación posterior por la técnica del retoque.

Bases Negativas de Segunda Generación (BN2G): todo aquel material que teniendo una morfologia de lasca, ha sido posteriormente transformado mediante el retoque.

Bases Negativas de Segunda Generación Fragmentos (BP2G F): todo aquel material que no teniendo morfologia de lasca ha sido transformado mediante retoque.

Anilizando la Fig. 3 observamos como a nivel de Bases positivas (1), los valores del coeficiente de correlación varian entre .57 a .71, presentando un alto valor, indicativo de una sistemática en el proceso de talla, tal como ya habiamos observado en el análisis de las Bases Negativas.

En la categotia de las BN2G (2), se produce una bipolarización que atribuimos al espacio geográfico en que se encuadran los lugares de ocupación, espacios cerrados (ocupaciones en cuevas o abrigos en nuestro estudio Abric Romani y L'Arbreda) o espacios abiertos (tecnocomplejos al aire libre, que corresponden al conjunto de la Femosa y de la Selva).

Los yacimientos encuadrados en espacios cerrados, se caracterizan por una correlación multiple baja que oscila alrededor de .30, mientras los tecnocomplejos en espacios abiertos les corresponden unas correlaciones que oscilan entre .61 y .90, que son altamente significativas.

La categoria de BN2G F presenta una buena correlación, desmarcándose el tecnocomplejo del Diable Coix por tener una correlación altamente significativa al igual que sucedia con las BN2G.

El tecnocomplejo del Diable Coix, con unos indices de correlación muy elevados en las categorias de BN2G y BN2G F, nos indica una selección tipométrica en el proceso de transformción de las bases positivas (BP), lo que interpretamos como una functionalidad diferenciada para este lugar de ocupación.

VI. ESTRUCTURA MORFOLOGICA

Para el análisis de las BN2G y BN2G F, de las industrias el Pleistoceno Superior en Catalunya, hemos utilizado el sistema analitico de G. LAPLACE (1972), introduciendo algunas modificaciones a fin de adaptarlo a las industrias de este periodo.

A partir de los tipos primarios creamos una tabla de contingencia, que tratamos estadisticamente mediante el test del Lien (VOLLE, 1981), del que representamos graficamente los resultados (ver Fig. 4).

La dicotomia queda muy marcada entre los lugares de ocupación en cueva o abrigo (espacios cerrados) y tecnocomplejos al aire libre (espacios abiertos), el primer grupo se caracteriza por presentar una secuencia donde domina el segmento de los denticulados (D), raederas (R), muescas (M) y abruptos (A), mientras que en el segundo grupo son las raederas (R) la categoria dominante que lo conforma, respecto al resto.

Esta diferenciación podemos visualizarla en las representaciones de los espectros de las categorias de denticulados y raederas, y se interpreta como una funcionalidad diferencial de las diversas ocupaciones en un marco de estacionalidad.

Los buriles (B), con una sensibilidad media significantiva vuelve a reafirmarnos la hipótesis inicial, y presenta un caracter positivo en las ocupaciones al aire libre, mientras que en las cuevas o abrigos tiene un caracter negativo, fenómeno inverso al observado en las categorias de denticulados (D) y raederas (R). Nos planeamos una especialización funcional cuya máxima expresión estaria en el tecnocomplejo del Diable Coix (D).

El resto de categorias si bien estan representadad no poseen una sensibilidad positiva y por lo tanto no nos caracterizan el complejo industrial.

CONCLUSION

El estrecho marco referencial con el que analizamos este largo periodo es uno de los primeros problemas con el que nos enfrentamos; las escasas referencias bioestratigráficas que poseemos, y los pocos estudios que se han hecho de ellas, nos obliga a mantenernos en un plano hipotético en todas nuestras conclusiones.

Respecto a la macrofauna las especies dominantes son euritermas, lo cual se interpreta como un indicador de que los cambios climáticos que parecen constatarse a lo largo del Pleistoceno Superior no tienen, ni el rigor ni la intensidad, en Catalunya que en el resto de Europa Occidental (tónica que, por otra parte, parece repetirse en toda la Peninsula Iberica a excepcion de la cornisa cantabrica).

Las especies mas representadas en el registro fosil parecen seguir la siguiente dinamica:

- Predominancia de equidos y/o cervidos, siendo ambos grupos los mas representados, excepto en la Cova dels Ermitons en que aparece fauna de montaña.

- Tambien tiene un peso especifico importante, aunque siempre de forma secundaria bovidos y suidos.

- Otro de los elementos jerarquizantes es la persistencia de grandes herviboros a lo largo del Paleolitico Medio: tanto *Rhinoceros* como *Elephas*.

Pero si quizás la dinámina paleobiológica queda mas o menos reflejada en el anterior esquema, otro problema muy importante, bajo nuestro punto de vista, aunque correlacionado de forma directa con el anterior, estriba en diferenciar cuando la aportacion de estos restos es producto de actuacion carnivora o antropica.

Asi surge el problema de que en algunos niveles de determinados lugares de ocupacion, abundan trazas que interpretamos como producto de la acción de carnivoros: huesos mordidos o roidos, bajo indice de fracturación y elevado grado de conexion anatómica.

Las especies mas abundantes son los ursidos en las zonas de montaña (Toll, Teixoneres, Ermitons), mientras la *Crocuta* (Gegant, Muscle, Romani) predomina en zonas planas. Tampoco hemos de olvidar la presencia en todos los yacimientos de pequeños felinos (*Linx* o *Felis silvestris*) que quiza puede ser un importante elemento aportador de lagomorfos (especies tambien muy abundantes en todos los yacimientos de este periodo).

A nivel tecnomorfologico podemos remarcar que tradicionalmente se han atribuido a diversos lugares de ocupación, cronologias o facies culturales de maneras muy poco consistente, asi vemos como los materiales de la Cova dels Ermitons son atribuidos al Musteriense tipo Quina (FULLOLA, PERICOT, 1975), la Cova de l'Arbreda se atribuye al Musteriense tipico (SOLER, 1983), Cova de Mollet I varia entre el Musteriense tipico y el Charentiense (SOLER, 1983), el Abrigo Romani se asigna al Musteriense de denticulados (RIPOLL, de LUMLEY, 1965).

Reestudiados un gran número de estos yacimentos, hemos visto como es la presencia de algun "fósil directo" lo que lleva a atribuirse a una u otra facies de los complejos musterienses. En otros casos se ha comprobado una selección muy marcada de materiales hasta conseguir los indices a gráficos acumulativos adecuados.

Por ello creemos que el enfoque de estos periodos ha de iniciarse desde una nueva perspectiva que permita caracterizar en conjunto cada lugar de ocupación asi como los diversos niveles que cada uno posee.

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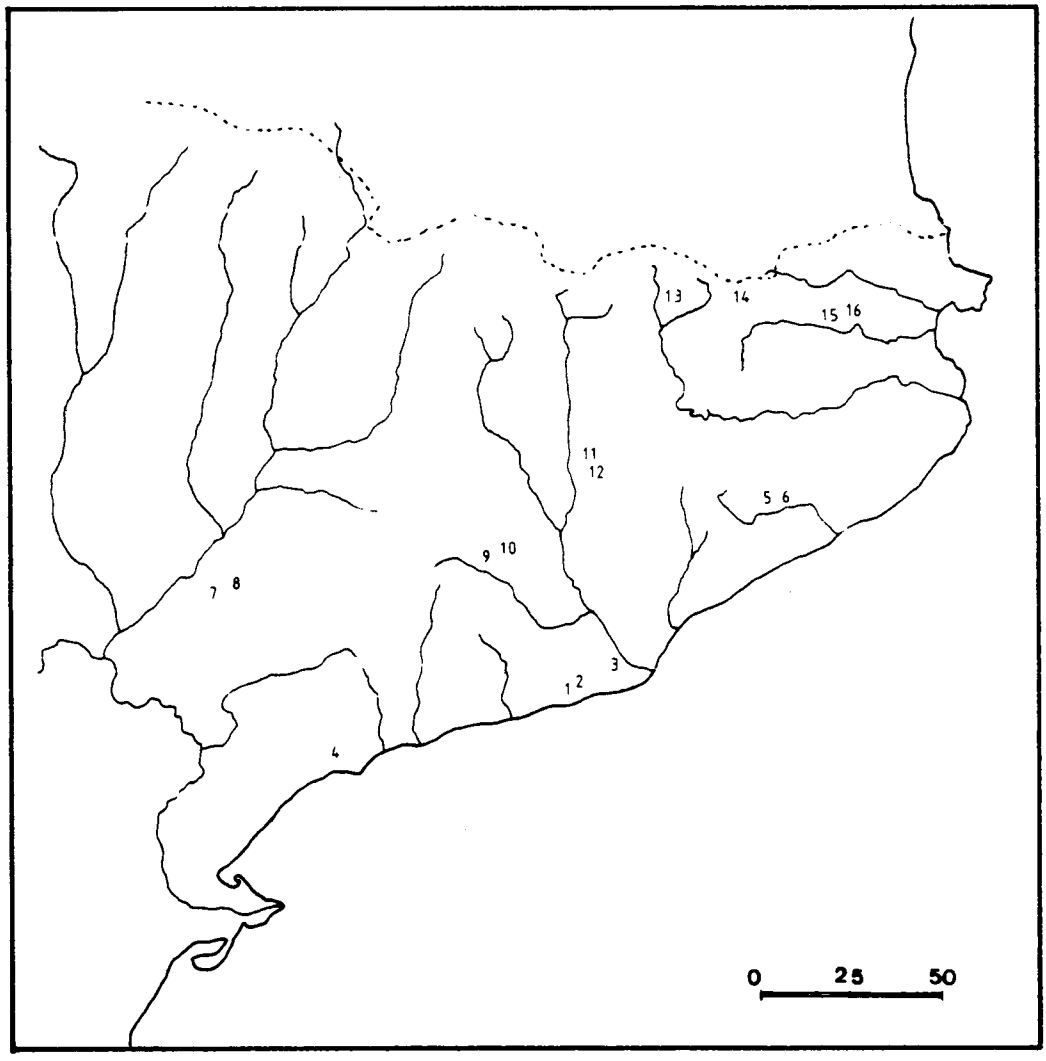

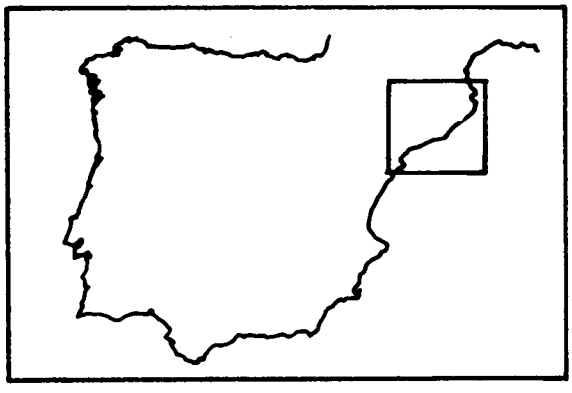

FIGURE 1

Localización de los diferentes Lugares de Ocupación

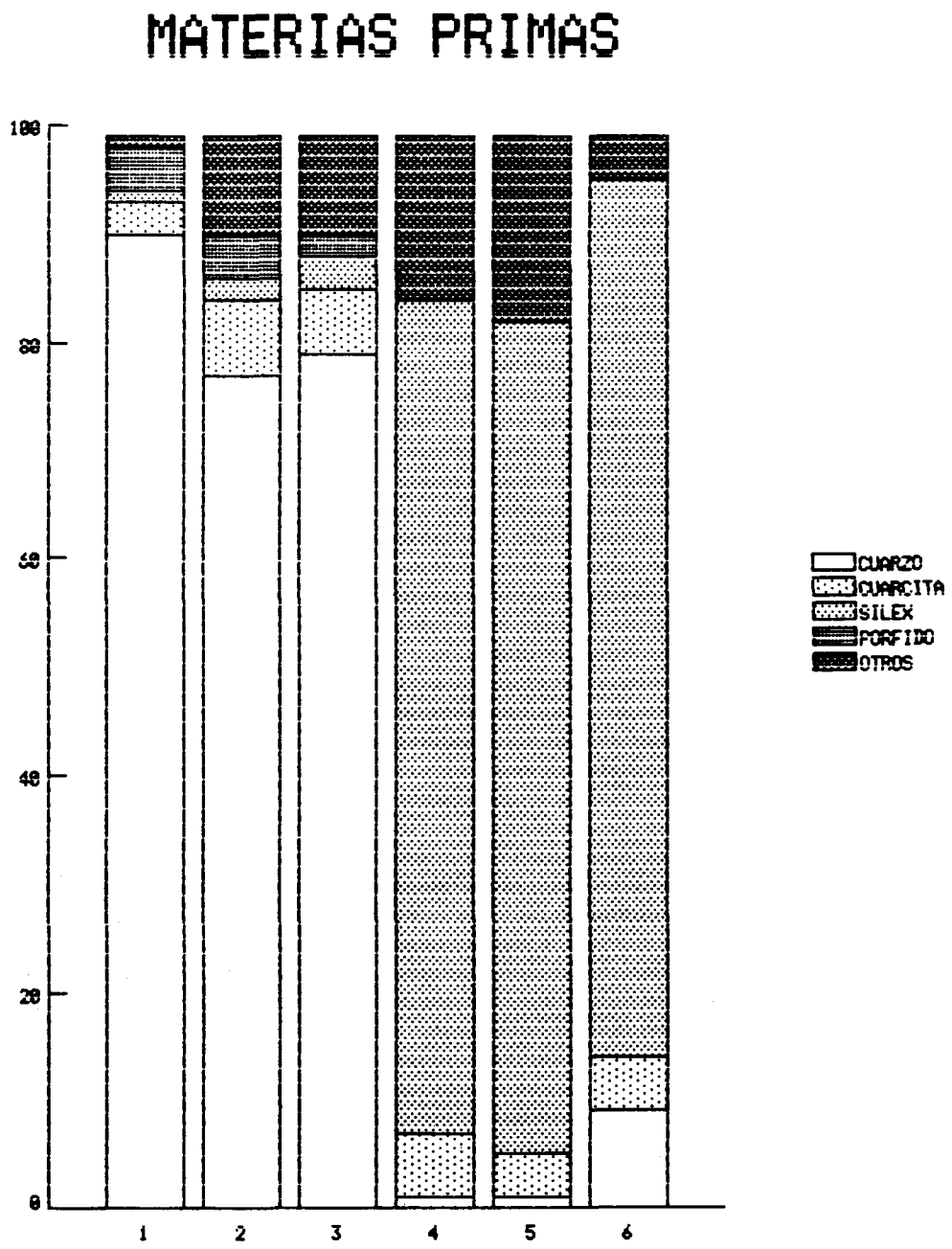

FIGURE 2

Distribución de materias primas en los lugares de ocupación de: 1.– Diable Coix, 2.– Avetllaners, 3.– Cova de L'Arbreda (H-30, H-43), 4.– Secanet, 5.- Fonts, 6.– Abrigo Romani capa 9 y 4

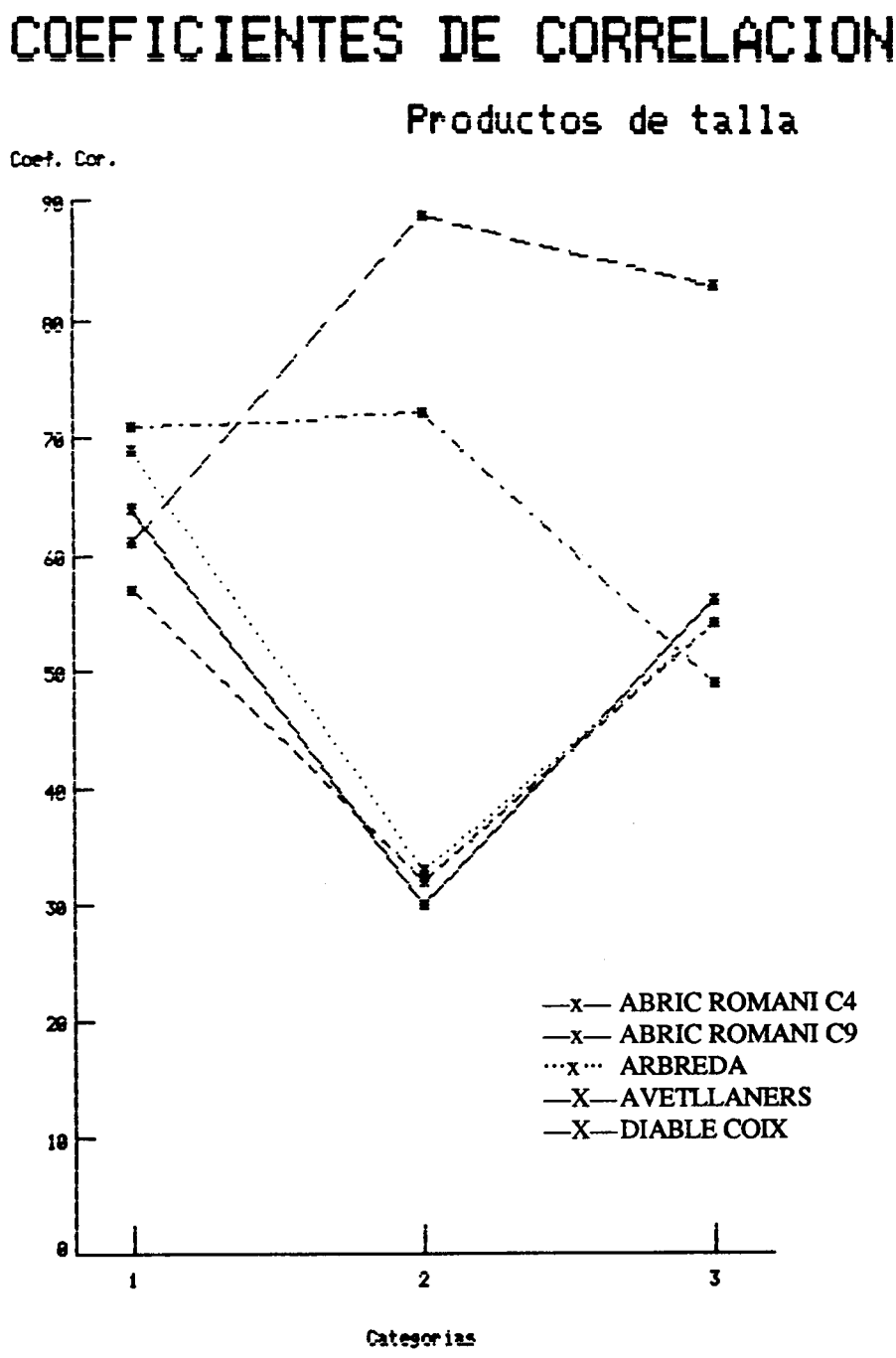

FIGURE 3

Representación de los Coeficientes de Correlación de las categorias 1.– Bases Positivas (BP), 2.– Bases Negativas de Segunda Generación (BN2G), 3.– Bases Negativas de Segunda Generación Fragmentos (BN2G F)

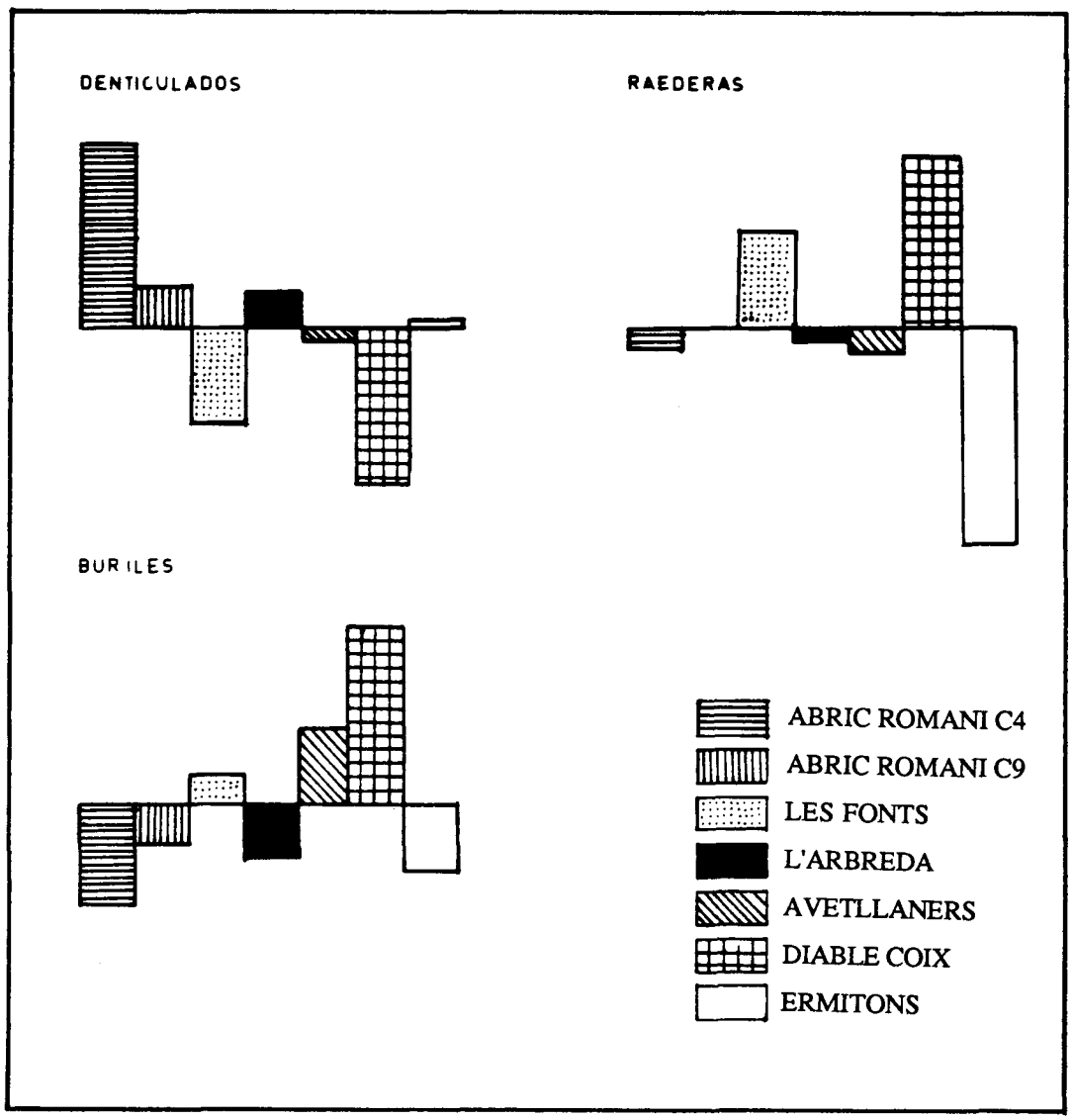

FIGURE 4

Dinámica de los tipos primarios en los jacimientos de Paleolítico Medio Catalán

L'Homme de Néandertal, vol. 1, LA CHRONOLOGIE, Liège, 1988, pp. 73 à 80

CHRONOLOGIE DU PALEOLITHIQUE MOYEN EN ROUMANIE DANS LE CONTEXTE DE CELUI DE L'EUROPE CENTRE-ORIENTALE ET MERIDIONALE

par

Alexandru PÀUNESCU *

Les recherches des trois dernières décennies – surtout – ont conduit à la découverte de près de 100 établissements attribués au Paléolithique moyen, dont une quarantaine ont été fouillés plus ou moins.

Certaines stations de grotte ou de terrrasse, à la stratigraphie assez complexe, avec des niveaux de foyers riches en charbon et os, nous ont offert la possibilité de prélever de nombreux échantillons, en vue des analyses de radiocarbone.

Pour le moment, nous disposons de 20 bulletins d'analyse, exécutés par le prestigieux laboratoire de Groningen, conduit par l'éminent Professeur Dr. W.G. Mook, auquel nous adressons nos plus vifs remerciements.

Même si certains de ces bulletins ne seront pas pris en considération ici, en raison des âges imprécis ou discutables qu'ils fournissent, nous chercherons toutefois, sur la base des données existantes, à esquisser le cadre chronologique du Paléolithique moyen de la zone carpato-danubiano-pontique[1].

Il ne semble pas exclu que le Paléolithique moyen en Roumanie, caractérisé par l'individualisation de plusieurs faciès moustériens – à la formation desquels les industries

* Institutul de Arheologie, str.I.C.Frimu, 11 – 71119, Bucureşti – Roumanie.

1 Al. PÀUNESCU, *Studii si cercetàri de istorie Veche si Arheologie (= SCIVA)*, Bucureşti, 35, 1984, 3, p. 235-247; idem, *SCIVA*, 34, 1983, 3, p. 187-195; Kenneth HONEA, *American Journal of Archaeology*, Princeton, 85, 1981, 4, p. 483-484; idem, *SCIVA*, 33, 1982, 2, p. 216-219; idem, *Revista muzeelor şi monumentelor*, Bucureşti, 3, 1984, p. 51-65; idem, *Dacia (Revue d'Archéologie et d'Histoire ancienne)*, Nouvelle Série, 28, 1-2, 1984, p. 23-37.

prémoustériennes ont joué un rôle important –, ait commencé vers la fin de l'Interglaciaire Riss-Würm, sinon même avec les débuts du Würm inférieur. Il s'est prolongé, selon nous, dans la zone en question, par ce que l'on appelle le Moustérien tardif, jusqu'au Würm moyen, approximativement vers 30.000 B.P., comme en témoigne l'habitat moustérien du niveau II b de la grotte de Gura Cheii - Rîşnov.

Les recherches effectuées jusqu'à ce jour ont montré que dans certaines régions géographiques de Roumanie ont pu être identifiés sur des bases technico-typologiques et stratigraphiques, plusieurs faciès moustériens qui se sont succédés (comme en Moldavie) ou ont persisté ailleurs plus longtemps. Un tel faciès est celui du Moustérien dit *typique*, de débitage Levallois, identifié tant dans les établissements en grotte que dans ceux de plein air.

Dans l'établissement bien connu de Ripiceni-Izvor (nord-est de la Moldavie), on a pu déterminer six niveaux moustériens: les trois premiers (I-III) ont été attribués au faciès moustérien dit *typique*, à débitage Levallois: les deux suivants (IV-V) appartiennent au faciès moustérien de tradition acheuléenne de débitage Levallois; le dernier (VI) est pauvre en matériel lithique et sans formes bifaciales (à l'exception d'un seul fragment). Pour les niveaux III et IV de cet établissement, nous disposons à l'heure actuelle de sept dates de radiocarbone.

Ainsi, pour l'habitat de la partie supérieure du niveau III moustérien dit *typique*, on connaît trois dates (une imprécise, deux exactes):

GrN - 12973 > 41000 BP

GrN - 11230 : $46400\,^{+4700}_{-2900}$ BP

GrN - 11571 : $45000\,^{+1400}_{-1200}$ BP

A noter que la seconde date (46.400 +4700/–2900 BP) représente jusqu'à présent l'âge le plus ancien que nous connaissions pour ce faciès moustérien identifié pour le moment dans la zone comprise entre les Carpates et le Prut.

Le faciès moustérien de tradition acheuléenne de débitage Levallois (avec d'assez nombreuses formes bifaciales) est représenté par les deux établissements de terrasse du Prut moyen: Ripiceni-Izvor (niveaux IV et V) et Mitoc-Valea Izvorului (niveau I). Pour le niveau IV de la première station mentionnée, nous disposons de quatre datations au radiocarbone:

GrN - 9208 : $44800\,^{+1300}_{-1100}$ BP;

GrN - 9209 : $42500\,^{+1300}_{-1100}$ BP ;

GrN - 9207 : $43800\,^{+1100}_{-1000}$ BP ;

GrN - 9210 : $40200\,^{+1100}_{-1000}$ BP , (date obtenue sur un échantillon prélevé dans un foyer situé dans la partie supérieure du niveau).

Ces dates nous permettent de constater que le niveau IV d'habitat moustérien de Ripiceni-Izvor a évolué sur une période d'environ 4500 ans, comprise entre 44.800 +1300/–1100 et 40.200 +1100/–1100 BP.

Un autre faciès est celui du Moustérien des grottes carpatiques, qui serait une variante régionale du *Charentien*, documenté par les habitats en grotte de Nandru (Peştera Curată et Peştera Spurcată), Baia de Fier (Peştera Muierilor), Boroşteni (Peştera Cioarei), Ohaba Ponor (Peştera Bordu Mare), Rîşnov (Peştera Gura Cheii), etc.

L'inventaire lithique de ces habitats consiste essentiellement en pièces de quartzite et autres roches (gréseuses, etc.) et se caractérise par la technique de taille des galets, dite "pontinienne".

Pour certains habitats moustériens des grottes de Boroşteni, Ohaba-Ponor et Rîsnov, nous disposons à l'heure actuelle de plusieurs dates de radiocarbone. Ainsi, pour la station de Pestera Cioarei, à Boroşteni (dép. de Gorj), au nord de l'Olténie, nous possédons pour le moment six dates: trois imprécises et trois exactes.[2]

A partir des observations stratigraphiques et typologiques de Maria Bitiri- Ciortescu et Marin Cârciumaru (les auteurs des fouilles récentes effectuées dans cette grotte), ont pu être identifiés six niveaux d'habitat paléolithique, dont cinq moustériens, et un aurignacien, séparés par des dépôts stériles.[3]

Les âges les plus anciens du Moustérien d'ici (nous nous référons aux niveaux inférieurs I-II) nous sont inconnus: ils dépassent l'intervalle présent de la méthode de datation par le carbone radioactif conventionnel (50000 BP). Ainsi, nous sont indiqués, pour le niveau II, les âges de: > 45.000 BP (GrN - 13004)
et > 50.000 BP (GrN - 13003).

Par contre, pour le niveau III, nous disposons de la date: 49.500 +3200/–1100 BP (GrN - 13002), et, pour le niveau stérile entre les niveaux III et IV: 43.000 +1300/–1100 BP (GrN - 13001).

Si cette dernière date est correcte, alors l'âge de > 46.000 BP (GrN - 13.000) pour le niveau V moustérien est inexact. La date la plus récente provient d'un échantillon prélevé dans le niveau stérile entre les niveaux V (moustérien) et VI (aurignacien): 37.750 ± 950 (GrN - 13005).

Pour le gisement de Peştera Bordu Mare, à Ohaba Ponor (dép. de Hunedoara), dans le sud-ouest de la Transylvanie, nous ne disposons que de trois dates. Elles se réfèrent à l'âge des deux niveaux de foyers (IIIa et IIIb) du niveau III moustérien.

Ainsi, pour le foyer du niveau IIIb qui, stratigraphiquement, se superpose (par près de 15 cm) au foyer du niveau IIIa, nous avons deux dates: l'une assez imprécise, > 41.000 BP (GrN - 11617), l'autre, de 43.600 +2800/–2100 BP (GrN - 12676). Par contre, pour le foyer du niveau IIIa, l'âge de 39.200 +4500/–2900 BP (GrN - 11618) est plus récent,

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2 Keneth HONEA, *SCIVA*, 37, 1986, 4, p. 326-332.

3 Nous remercions à cette occasion les chercheurs Maria Bitiri-Ciortescu et Marin Cârciumaru pour avoir bien voulu nous renseigner sur la stratigraphie de l'établissement de Peştera Cioarei, à Boroşteni, et nous avoir montré le matériel lithique qui y a été découvert.

comme on le constate, que celui du niveau IIIb. Il est probable que l'une de ces dates – la dernière plutôt – soit incorrecte.

Pour Peştera Gura Cheii-Rîşnov (dép. de Braşov), dans le sud-est de la Transylvanie, nous disposons également de cinq dates de radiocarbone. Deux niveaux d'habitat moustérien y ont été identifiés: l'un, inférieur, très mince et pauvre en matériel lithique et faunique; l'autre, supérieur, riche en restes de culture matérielle, et dans lequel ont été dégagés deux niveaux de foyers.

Le niveau I est situé stratigraphiquement par-dessus un dépôt archéologique stérile, dépôt qui recouvrait directement le lit de roche de la grotte. Un échantillon (d'os) prélevé dans ce dépôt stérile a donné comme âge: 44.900 +1800/–1500 BP (GrN - 13010).

Pour le niveau II moustérien, nous disposons de quatre dates. L'une se réfère au foyer de la base du niveau d'habitat (IIa): 33.300 ± 900 BP (GrN - 13009). Les deux autres dates correspondent au foyer situé à la limite supérieure du niveau (IIb): 29.700 +1700/–1400 BP (GrN - 11619) et 28.900 +2400/-1800 BP (GrN - 14620). Quant à la quatrième, elle a été obtenue à partir d'un échantillon prélevé dans le sol d'entre les deux foyers: 30.450 ± 300 BP (GrN - 13008).

Sur la base de ces dates, nous pouvons tirer deux conclusions. La première concerne l'âge du niveau I, qui pourrait se situer entre env. 40.000 et 35.000 BP (donc *post* 44.900 et *ante* 33.300 BP), et la seconde l'âge du niveau IIb, qui nous permet d'attribuer cet habitat à un Moustérien tardif.

Il semblerait donc, si ces dernières dates sont correctes, que le Paléolithique moyen du territoire de Roumanie ait pris fin vers 30.000 BP.

Des données exprimées plus haut, il résulte, semble-t-il, que, du moins pour une période de temps, le faciès moustérien des grottes carpathiques se soit développé en parallèle avec le faciès dit *typique* et avec celui de tradition acheuléenne découvert dans le nord-est de la Moldavie.

Un autre faciès moustérien identifié sur le territoire de la Roumanie est celui dit *denticulé* (avec quelques formes bifaciales). Il est connu par les établissements de Dobroudja situés soit à proximité du littoral de la Mer Noire (Mamaia-Sat, Peninsula, etc.), soit dans la zone centrale de cette province (Saligny-Faclia, Peştera, etc.). Bien que nous n'ayons aucune date de radiocarbone pour ces stations, nous n'excluons pas la possibilité que ce faciès ait évolué, du moins partiellement, en même temps que les autres faciès mentionnés d'Olténie, de Transylvanie et Moldavie.

Si la fin du Paléolithique moyen en territoire roumain semble se situer autour de 30.000 BP, par contre ses débuts sont difficiles à fixer. Il n'est pas exclu que ce moment se situe dans une période comprise entre environ 100.000 et 50.000 BP. Par exemple, le premier niveau moustérien de Ripiceni-Izvor pourrait dater de 60.000-65.000 ans ou même plus. Malheureusement, pour cet intervalle, comme on le sait, la méthode de datation par le carbone radioactif ne peut pas – ou pas encore – nous aider.

Dans ce qui suit, nous présenterons la chronologie du Paléolithique moyen du territoire carpato-danubiano-pontique dans le contexte plus large du Paléolithique moyen de la zone centre-orientale et méridionale.

Les dates de radiocarbone dont nous disposons pour le faciès du Moustérien *typique*

de débitage Levallois découvert dans les établissements du Dniestr Moyen (U.R.S.S.)[4], comme ceux de Cormani IV (niveau 11)[5], Molodova I (niveau 4)[6] et Molodova V (niveau 11)[7], nous permettent de considérer ce faciès comme en bonne partie contemporain de celui identifié dans les niveaux II-III moustériens de Ripiceni-Izvor.

En ce qui concerne le Moustérien d'Érd (Hongrie)[8], qui, aux dires de V. Gabori-Csánk, représente un faciès *charentien* de l'Europe du sud-est, pris dans un sens large, et dont l'inventaire lithique – en majorité de quartzite – a un débitage et un faciès non Levallois, il présente d'assez nombreuses similitudes technico-typologiques avec celui découvert dans certains niveaux moustériens des grottes carpatiques de Transylvanie et d'Olténie. Les âges absolus nous ont permis certaines observations intéressantes.

Ainsi, les dates attribuées au nivau "d" moustérien d'Érd[9] situe cet habitat dans une étape postérieure à l'habitat de l'horizon III de Peştera Bordu Mare, à Ohaba Ponor.

Par contre, l'âge du niveau "e" d'Érd [10] pourrait être mis en parallèle avec celui de l'horizon II de cette même grotte, pour laquelle nous ne disposons malheureusement d'aucune date de radiocarbone.

L'habitat moustérien de Tata (Hongrie)[11] donne une date [12] qui semble indiquer ici un Moustérien relativement tardif, une étape contemporaine en quelque sorte du niveau IIa de la station de Pestera Gura Cheii-Rîşnov.

En Moravie [13], l'horizon 7a de la grotte de Kulna [14] – attribué par K. Valoch au

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4 A.P. CERNIŞ, *Ranii i srednii paleolit Pridnestrovija*. Moscva, 1965, p. 28-70; idem, *Paleolit i mezolit Pridnestrovija*. Moscva, 1973, p. 18-23; A.P. CERNIŞ et I.K. IVANOVA, *Mnogosloinaja paleoliticeskaya stoianka Kormani IV na Srednem Dnestre*. Moscva, 1977, p. 7-74, 168-180; idem, *Molodova I. Unikalnoe musterskoe poselenie na Srednem Dnestre*. Moscva, 1982, p. 188-235, fig. 13, 15.

5 Cormani IV – niveau 11 moustérien: GrN - 6807: 44.400 +2050/–1630 BP.

6 Molodova I – niveau 4 moustérien: GrN - 3659: > 44.000 BP.

7 Molodova V – niveau 11 moustérien: GrN - 4017: > 40.300 BP; LG - 15: > 45.000 BP; LG - 17: > 45.600 BP.

8 V. GABORI-CSÁNK, *La station du paléolithique moyen d'Érd-Hongrie*. Budapest, 1968, p. 105-110.

9 Érd – couche supérieure, niveau "d": GrN - 4443: 35.300 ± 900 BP; GXO – 200: > 38.100 BP.

10 Érd – couche supérieure – niveau "e": GrN - 4444: 44.300 ± 1400 BP.

11 V. GABORI-CSÁNK, *Acta Archaeologica Academiae Scientiarum Hungaricae*. Budapest, 22, 1970, p. 4-5, 10.

12 Tata – couche moustérienne: GrN - 3023: 33.600 ± 1100 BP.

13 K. VALOCH, *Problemy paleolita Vostočnoi i Centralnoi Evropy*. Léningrad, 1977, p. 15-28.

14 La grotte Kulna – couche 7 a-Micoquien: GrN - 6060: 45.660 +2850/–2200 BP.

faciès micoquien – pourrait être synchronisé avec celui du Moustérien *typique* (niveau III) de Ripiceni-Izvor.

En Bulgarie, le faciès moustérien *typique* à débitage Levallois identifié dans l'horizon 13 de l'établissement en grotte de Bacho Kiro [15] peut être considéré à l'heure actuelle comme le faciès le plus ancien [16] de la zone en question.

D'autres habitats moustériens mis au jour en Yougoslavie [17] (la grotte Veternica[18]) et en Grèce [19] (l'abri Asprochaliko[20]) nous ont fourni des chiffres imprécis, qui les situent au-delà de 40.000 BP (Fig. 1).

Quant au passage du Paléolithique moyen au Paléolithique supérieur, comme cela a déjà été relevé, il ne s'est pas produit simultanément dans toute l'Europe.[21] Le processus s'est déroulé probablement sur une période d'environ 10.000 ans, peut-être même plus, en grandes lignes entre approximativement 40.000 et 30.000 BP, si nous prenons en considération les dates de radiocarbone concernant le plus ancien horizon attribué au Paléolithique supérieur. Toutefois, quelques dates C_{14} situent certains habitats du début du Paléolithique supérieur un peu avant 40.000 BP. Par exemple, l'âge de l'horizon 11 (niveau le plus récent) aurignacien de la grotte Bacho Kiro [22] indique un chiffre imprécis supérieur à 43.000 BP, tandis que l'habitat de Brno-Bohunice [23] nous a offert trois dates, comprises entre approximativement 43.000 et 40.000 BP.

Si les observations stratigraphiques, technico-typologiques et les dates C_{14} des deux stations mentionnées sont correctes, il nous faut prendre en considération une période qui serait comprise entre env. 45.000-44.000 et 40.000 BP.

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15 W.G. MOOK, *Excavation in the Bacho Kiro Cave (Bulgaria). Final Raport*, Varsovie, 1982, p. 168; J.K. KOZLOWSKI, *Prace Archeologiczne*, 28, 1979, p. 77-79.

16 La grotte Bacho Kiro – couche 13 – moustérienne: GrN – 7570: > 47.500 BP.

17 M. MALEZ, *Praistorija Yugoslavenskih Zemalja*, I, Sarajevo, 1979, p. 218-219.

18 La grotte Veternica – couche I – moustérienne: GrN – 4984: > 43.200 BP.

19 E.S. HIGGS, C. VITA-FINZI, *Proceedings of the Prehistoric Society*, Cambridge, 32, 1966, p. 1-25.

20 L'abri Asprochaliko – niveau 19 – Moustérien: I - 1957: > 39.900 BP.

21 J.K. KOZLOWSKI, L'Aurignacien et le Gravettien (Périgordien) dans leur cadre écologique. *Colloque International, Nitra*, 1980, p. 123-137.

22 J.K. KOZLOWSKI, *IXe Congrès UISPP-Colloque XVI*, Nice, 1976, p. 124-142; idem, *Prace Archeologiczne*, 28, 1979, p. 77-99; Boleslav GINTER, J.J. KOZLOWSKI, *Excavation in the Bacho Kiro ...*, p. 169-172; W.G. MOOK, op. cit., p. 168; Bacho Kiro – couche 11 – niveau I – Bachokirien: GrN – 7545: > 43.000 BP.

23 K. VALOCH, *L'Aurignacien et le Gravettien ...*, p. 286-287; idem, *IXe Congrès UISPP – Colloque XVI ...*, p. 112-123; idem, *Časopis Brno*, 67, 1982, p. 31-48; M. OLIVA, *L'Aurignacien et le Gravettien ...* p. 163-171; Brno-Bohunice: couche aurignacienne (Bohunicien): GrN – 6165: 42.900 +1700/–1400 BP; GrN - 6802: 41.400 +1400/–1200 BP; Q – 1044: 40.173 ± 1200 BP.

En ce qui concerne le territoire de la Roumanie ou du moins la zone comprise entre les Carpates et le Prut, les débuts du Paléolithique supérieur semblent se situer plus tard.

Dans la station de Mitoc-Malul Galben (situé dans le secteur épigénétique du Prut), un foyer aurignacien situé à 8,70 m de profondeur a été récemment daté de 31.850 ± 800 BP (GrN - 12637); un autre, à 7,85 m de profondeur, a reçu comme âge: 28.910 ± 480 BP (GrN – 12.636)[24].

Il est très possible que les âges de ces foyers soient équivalents à ceux des habitats aurignaciens (étape ancienne: Ia et Ib) de Ripiceni-Izvor (établissement situé à env. 25 km au sud de Mitoc). D'ailleurs le foyer trouvé dans la partie supérieure du niveau aurignacien Ib de Ripiceni nous donne comme chiffre 28.420 ± 400 BP (Bln – 809)[25]. Si cette date est correcte, alors l'habitat sous-jacent (niveau Ia) – habitat considéré actuellement comme représentant l'étape la plus ancienne de l'Aurignacien de la zone – pourrait être situé deux-trois mille ans plus tôt, étant probablement synchrone avec le niveau de foyer trouvé à 8,70 m de profondeur dans l'établissement de Mitoc-Malul Galben. Si la toute dernière découverte effectuée dans cette même station de Mitoc – les deux foyers et l'atelier de taille trouvés à 10,65 m de profondeur – représente une étape plus ancienne que celle du niveau Ia de Ripiceni-Izvor, il nous faut alors placer les débuts de l'Aurignacien de Roumanie vers 35.000 BP, ou peut-être même un peu plus tôt.

Sur la base de ces données actuelles, nous croyons que le passage du Paléolithique moyen au Paléolithique supérieur dans la zone carpato-danubiano-pontique s'est produit probablement entre 35.000 et 30.000 BP.

Nous avons essayé ici d'esquisser, sur la base des dates de radiocarbone connues dans le stade actuel des recherches, le cadre chronologique de la dernière étape d'évolution du Paléolithique moyen de la zone prise en considération.

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24 Kenneth HONEA, *op. cit.*, p. 326-332.

25 Al. PÀUNESCU, *SCIVA*, 35, 1984, 3, p. 247-248, 257-258.

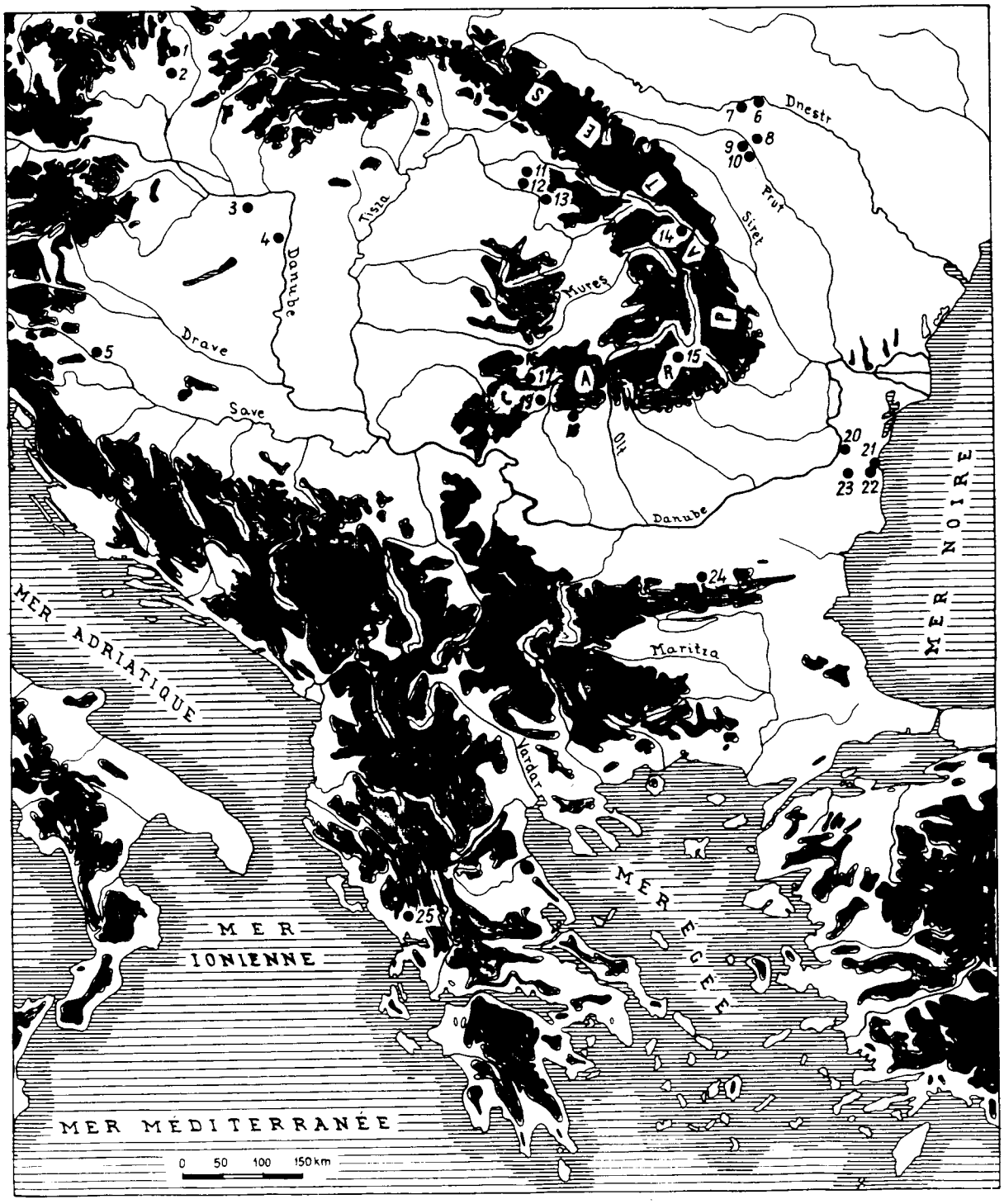

FIGURE 1

Carte des sites paléolithiques cités dans nos textes qui ont livré ou non des données C_{14}

1 Kulna; 2 Brno-Bohunice; 3 Tata; 4 Érd; 5 Veternica; 6 Cormani IV; 7 Molodova I et V; 8 Corpaci; 9 Mitoc-Malul Galben et Mitoc–Valea Izvorului; 10 Ripiceni-Izvor; 11 Boineşti; 12 Remetea-Somoş; 13 Buşag; 14 Cetàtica I-Ceahlàu; 15 Rîsnov (la grotte Gura Cheii); 16 Nandru (la grotte Curatà et la grotte Spurcatà); 17 Ohaba-Ponor (la grotte Bordu Mare); 18 Baia de Fier (la grotte Muierilor); 19 Boroşteni (la grotte Cioarei); 20 Saligny-Faclia; 21 Mamaia-sat; 22 Peninsula; 23 Peştera; 24 Bacho Kiro; 25 Asprochaliko.

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ABSOLUTE DATING BY RADIOCARBON- AND AMINO-ACID-DATING OF LATEST *HOMO SAPIENS NEANDERTHALENSIS* AND EARLIEST *HOMO SAPIENS SAPIENS* IN EUROPE

by

R.R.R. PROTSCH von ZIETEN *

INTRODUCTION

The chronological range in which Neanderthal (*Homo sapiens neanderthalensis*) existed in Europe is up until now solely based on relative age estimation, supported by archaeological and geological research. Dates are given for earliest Neanderthals at 70,000 years B.P., a time which coincides nicely with the beginning of the Würm glaciation. This date is probably due to the prevalent thinking of most archaeologists who see in Neanderthal a cold-adapted creature restricted in its geographical range only to Europe. Since there is little doubt as to the predecessor of the Neanderthal, *Homo erectus*, who disappeared on most continents and Europe around 200,000 years B.P., the chronological hiatus between 200,000 and 70,000 seems to be, according to many specialists, void of any hominid group. Much evidence seems to place now the beginning of the Neanderthal-phase back to 200,000 years B.P., in direct succession to *Homo erectus*. It would essentially mean that the Neanderthal was not purely a fossil hominid group restricted to a cold environment of the last 70,000 years, but a group that started its existence during the second last glaciation, the Riss, and lasted through the last interglacial (R-W Interglacial or Eemian) to the end of the Würm III stage, or the beginning of the Paudorf Interstadial about 30,000 years ago.

Relative age estimates place fossil hominids like Fontéchevade (150,000 – 200,000 years B.P.), Ehringsdorf (120,000 years B.P.), Petralona (ca. 200,000 years B.P.), Neanderthal (70,000 years B.P.), Steinheim (ca. 150,000 – 200,000 years B.P.), Montmaurin (ca. 150,000 years B.P.), Saccopastore (90,000 – 100,000 years B.P.), La Chaise (ca. 85,000 – 90,000 years B.P.), Bañolas (ca. 95,000 years B.P.), Biache-Saint Vaast le Prince (ca. 110,000 – 130,000 years B.P.) and possibly also Swanscombe (ca. 180,000 – 200,000 years B.P.) beyond the 70,000 year stage.

* Johann Wolfgang Goethe-Universität, Frankfurt am Main, Institut der Anthropologie und Humangenetik für Biologen, Siesmayerstraße 70 – Postfach 111932 – D–6000 Frankfurt am Main I. R.F.A.

None of these can be classified as *Homo erectus*, even though some seem to present morphologically a nice transition from *Homo erectus* into earliest Neanderthal, as for example Petralona. Most of these can be classified as Neanderthal, or at least as Neanderthal-like, and fill the gaps between latest *Homo erectus* and that time period at 70,000 years B.P. which is often quoted as the beginning of the Neanderthal phase. There is little doubt that most wellknown Neanderthal specimens can be placed within 30,000 to 70,000 years ago, but again based solely on relative age estimation. These are Chancelade, Staroselje, La Chapelle-aux-Saints, La Ferrassie, Monte Circeo, Krapina, Gibraltar, Saccopastore, La Quina, and Spy, just to mention some of the most important Neanderthals in Europe. Yet it is even more amazing that with the possibility of dating most of these finds absolutely, by either Radiocarbon– or Amino-Acid-Dating, none of the above were dated absolutely yet.

Especially with the advent of Radiocarbon-Accelerator Dating direct dates between 30,000 and 100,000 years can be obtained by sacrificing only a few grams of osteological material. Reliable dates of cave deposit materials above 100,000 to 200,000 years can also be obtained by the amino acid method, as will be explained later.

This paper will explain the methods of radiocarbon dating and amino acid dating, new advances of these techniques and the application of combination-dates of these techniques. It will then use as examples of the above the dating of the Cro-Magnon from Kelsterbach (Germany) (*Homo sapiens sapiens*) and the Neanderthals from Vindija and Velika Pecina (Jugoslavia).

Bones and teeth are often the only material adequately preserved in archaeological sites. Direct dating of these can solve important anthropological questions in that it can pinpoint the precise period of time to which a fossil hominid belongs. Designating a hominid as an early or very late representative of any one hominid group coul be crucial in solving an evolutionary controversy.

Similarly, problems related to more recently dated materials from Mesolithic, Neolithic (PROTSCH and BERGER, 1973), Bronze, Age, Iron Age or even historic times can be answered. Indeed, precise dating is often the only means by which an archaeologic interpretation is made possible, especially when archaeological materials are either unassociated with the burials or totally absent.

In time periods older than 10,000 years B.P., amino acid dating provides, under controlled conditions, a reliable tool to crosscheck C^{14} dating. Amino acid dating is the only direct dating technique available for use on bones older than 70 000 years (see below). However, amino acid dating cannot be used to solve dating questions below 10,000 years B.P.; radiocarbon dating presents the only physicochemical means of absolute time placement within this crucial period.

It is important to note that C^{14} dating should not be used simply to supply dates at random. It is often its application to specific anthropologic and archaeologic problems that provides the sole means of answering anthropologic questions. Unfortunately, absolute dating is occasionally viewed simply as additional information. If radiocarbon dates do not coincide with relative, purely archaeologic estimations, then absolute dates are often viewed with scepticism by archaeologists and anthropologists.

Under unfavourable environmental conditions bones may provide the only material capable of being dated. Such was the case in several large scale dating projects which sought to solve the question of the earliest appearence of "anatomically modern man" in Europe and his presence in Africa over 30,000 years B.P. (BEAUMONT, de VILLIERS and VOGEL, 1978; GLOWATZKI and PROTSCH, 1973; HENKE and PROTSCH, 1978; LEAKEY, HAY, THURBER *et al.*, 1972; LEAKEY, PROTSCH and BERGER, 1968; PROTSCH,

1974a,b,c, 1975, 1976a,b; PROTSCH, 1978a,b,c,d,e; PROTSCH, 1981; PROTSCH and de VILLIERS, 1974; PROTSCH and GLOWATZKI, 1974; PROTSCH and OBERHOLZER, 1975; PROTSCH and SEMMEL, 1978; VOGEL and BEAUMONT, 1972), early man in the Americas (BERGER *et al.*, 1971; and in references Mc NEISH, BERGER and PROTSCH, 1970; PROTSCH, 1978c; BADA and PROTSCH, 1980), and questions of the domestication of certain faunal species in the Near East and south-eastern Europe (BERGER and PROTSCH, 1973; PROTSCH and BERGER, 1973).

Bone can be dated by using both the organic and inorganic portions, but it has been found that the organic portion most often supplies more accurate dates. With very few exceptions, dates on the collagen portion of bone are accurate in historical time periods, in studies including late Middle Age dates (around the fourteenth and fifteenth centuries AD), early Middle Age dates (fourth to seventh centuries AD), and dates from Roman, Bronze Age and dynastic Egyptian times. When, however, other organics such as wood and charcoal are found in association with osteological materials, comparative dates are run on both. One is often confronted with the argument that absolute radiocarbon dates going beyond historical time, i.e. older than 5,000 years B.P., could be wrong, but why should contamination exist only in older materials? Here, relative geologic, palaeontologic, or archaeologic association correlating with absolute radiocarbon dates can be used to support accuracy of an absolute dating technique. If one compares dates on all organic materials commonly used for raiocarbon dating up to now, collagen-radio-carbon-dating proves to be as exact as dates obtained from wood, charcoal or other non-osteological organics.

There is a severe shortcoming in the radiocarbon dating of collagen, however. In about half of the samples processed an adequate amount of osteological material is not available for dating. On the other hand, only very little osteological material is needed in many cases. This distinction depends upon the conditions of preservation. Samples from extremely dry and hot environments are usually well preserved and only a few grams of bone are needed for dating. The same is true for preservation under extremely cold conditions, such as permafrost. In a number of cases from Arctic locations a few grams of bone are adequate for a radiocarbon date. The La Brea Tar Pits in California are an example of a third situation providing excellent preservation of bone collagen. In all three cases, the amount of organic material in the bone, the collagen, is comparable to that in fresh bone, i.e. 23 per cent to 27 per cent.

On the other hand, the inorganic portion may often be leached out of samples *in situ*. For example, in the Egyptian samples, a total of 20 g of bone contained as much as 16 g of collagen, the inorganic portion being virtually absent; only one quarter of the sample was sufficient for radiocarbon dating at the Frankfurt radiocarbon facility. The organic components of other osteologic materials, found in and completely covered by calcareous deposits such as loess and travertine, are often exceptionally well preserved. Here again, relatively little material is needed for collagen radiocarbon dating.

For these reasons, it is necessary for the dating specialist to collect detailed geologic and geomorphologic information on the site before accepting osteologic material for dating. If possible, one should collect the material personally if a large series of dates is planned.

In an environment that quickly dissolves either organic or inorganic portions of bones, such as jungle or other hot and humid areas, the bones are poorly preserved, if at all. An alkaline environment generally preserves only the inorganic portion of the bone, rapidly dissolving the collagen. In such a case, only a minimal portion of the organic matter is still preserved, and a date can be obtained only by processing large quantities of bones. A skull or postcranial bones preserved under such conditions might yield a date, but the total skull would have to be sacrified just to obtain the date. As explained below, the dating specialist can estimate with fair accuracy the amount of osteologic material needed for radiocarbon collagen dating.

Just as there are contaminating factors in the dating of organic materials such as wood and charcoal (rootlets etc.), bone samples present the same and many additional problems. When a date does not comply with the "relative" estimation of the archaeologist or anthropologist who submitted the sample for dating, the laboratory date is often cast into doubt. Careful re-examination of a large series of samples yielding such "questionable" dates often reveals that errors occur during selection, excavation, and handling before submission to the laboratory. False results may be caused by sloppy marking and collection procedures, including the handling of bone with fatty or oily hands, packing with other organic materials such as cotton or paper, or marking a stratigraphic position and origin incorrectly.

Whenever possible, samples should be collected by the dating specialist, who should also keep his own collection notes and a detailed record of the stratigraphic and geomorphologic peculiarities of the stratigraphic horizon. Bones should be packed in cellophane, aluminium foil or similar nonorganic materials. It is not meant to suggest that the archaeologist has insufficient knowledge of the dating procedures to be followed. These precautions simply serve to eliminate any errors that can occur before the material is even submitted to the radiocarbon specialist.

On occasion, a sufficient amount of soft tissue is preserved in mummified remains so that radiocarbon dating is possible; the tissue is lylophilised and the collagen extracted for dating – subject, of course, to the same principles and cautions as noted for bone.

Having outlined the above principles, this chapter now concentrates solely on the dating of bone samples. It is divided into the following sections:
- Principles of radiocarbon dating;
- Principles and application of microanalysis;
- Dating the inorganic portion of bone (apatite);
- Dating bone by accelerators;
- Dating the organic content of bone (collagen);
- Kelsterbach – a case study in C^{14} collagen and amino acid dating;
- Velika Pecina and Vindija – case studies in C^{14} collagen and amino acid dating.

The section dealing with collagen dating also includes the processing and dating by conventional means, using a gas proportional CO_2 counting system (Fra and UCLA).

PRINCIPLES OF RADIOCARBON DATING

Radiocarbon measurements have been used for a wide variety of purposes, only a small fraction of which involve age determinations useful in palaeoanthropology and archaeology. Familiar materials used for dating are wood, charcoal, peat, leather, paper and other organic materials. Some inorganic materials like shell and mortar have been used, but the organic and inorganic portion of teeth and bones are most often used. Of these, one should preferentially date the organic portion, as will be explained later. Before going into detail relating to dating the organic portion of bones and teeth, it is necessary to comment upon some of the basic principles of radiocarbon dating.

The same theoretical principles involved in the dating of the materials listed above apply to the dating of the organic portions of teeth and bones. These principles were orginally described by LIBBY (1952, 1955) and were covered thoroughly in the literature. A few corrections were added concerning the exact half-life computations and conversion of the absolute C^{14} age to a range of ages, for example, those of historic times. Only a brief review will follow here.

Three isotopes of carbon are contained in the total carbon reservoir of the earth (atmosphere, biosphere and oceans): C^{12} and C^{13}, the two stable isotopes, and the radioactive isotope, C^{14}. There is, however, a difference in the relationship of these three isotopes to one another, depending on whether they occur in the biosphere, the atmosphere, or the oceans, which mostly contain inorganic carbon. Regardless of these differences, the mean ratio among C^{12}, C^{13} and C^{14} is approximately 100:1:0,01.

Of the three isotopes, the stable isotopes C^{12} and C^{13} are not subject to physical changes, while C^{14} undergoes radioactive decay at a constant rate of about 1 per cent per 80 years. At the same time, the supply of C^{14} is continually replenished in the upper atmosphere by nuclear reactions associated with cosmic radiation. Highly energetic cosmic rays infuse into the upper atmosphere and interact with atmospheric nuclei to produce free secondary neutrons. These collide again with nitrogen atoms, specifically those of the isotope N^{14}, to form C^{14}:

$$N_7{}^{14} + n_0{}^{1} = C_6{}^{14} + H_1{}^{1}$$

The C^{14} produced in this reaction has a half-life of 5,730 ± 30 years (MAN, MARLOW and HUGHES, 1961), by the most recent calculation. However, in the radiocarbon date list reports, the "Libby half-life" value of 5,568 ± 30 years is still used. The chemical properties of C^{14} do not differ from those of the stable isotopes. The C^{14} atoms are oxidised by atmospheric oxygen and form radioactive carbon monoxide molecules. They are again oxidised, mostly by direct action with atmospheric oxygen or, to a lesser extent, through the action of bacteria in the biosphere (PANDOW, MacKAY and WOLFGANG, 1960; MacKAY, PANDOW and WOLFGANG, 1963). Thus, there is a continuous supply of radioactive carbon entering the total carbon reservoir of the earth.

The three individual reservoirs obtain radioactive carbon dioxide through its formation in the atmosphere, where it becomes a radioactive part of all atmospheric carbon dioxide. C^{14} then enters the oceans, mainly by interaction with surface water, which dissolves the C^{14} and eventually transports it to the deeper waters. It is then absorbed into the carbonate- and bicarbonate-containing portions of mollusc shells.

C^{14} also enters the organic portion of the biosphere, but by a somewhat different process. Carbon dioxide, including the C^{14} isotope, is incorporated into plants by photosynthesis. Herbivorous fauna accumulate the same amount of C^{14} when they eat plants. The same applies to carnivorous fauna, which prey upon the herbivores. Omnivorous animals, like man, ingest both sources and subsequently show the same activity of radiocarbon in all soft and skeletal components as do plants, herbivores, and carnivores.

The mean life of a C^{14} atom is about 8,000 years. When it disintegrates, the products of decay are, once again, a nitrogen atom and an electron, in this case a beta particle. The equation is as follows:

$$C_6{}^{14} = N_7{}^{14} + \beta_{-1}$$

It is estimated that the production of C^{14} in the atmosphere is in a state of equilibrium with its radioactive decay in the total carbon reservoir of the earth. LIBBY (1955, p. 5) calculated the equilibrium and its stabilisation in the reservoir at about 81 metric tons. Just as the equilibrium is maintained in the total reservoir, it is also maintained in every living organism. A living organism exchanges carbon with the atmosphere so that its specific

radiocarbon activity is identical to that of the atmosphere. At death, an organism – be it plant or animal – is no longer able to obtain additional C^{14} : at that moment its C^{14} activity begins to decrease through radioactive decay. The measurement of the C^{14} activity of the organism at any one time allows the calculation of that moment in time at which the organism ceased to exchange carbon with the total carbon reservoir. The rate of decay is known and one is thus able to calculate the total period lapsed since the death of the organism. Averaging the present activity and comparing it to a sample of modern activity (oxalic acid derived from Hawaiian sugar cane) gives the equation:

$$t = -\lambda \log_e \frac{I}{I_0}$$

It is now possible to calculate the age of the sample, t being the time of death, I the actual activity of the test sample, I_0 a modern sample's activity, and λ the decay constant of C^{14} . For λ there are presently two half-life values: 5,568 ± 30 with a 8,033-year lifespan, and another of 5,730 ± 30 with a 8,267-year lifespan.

It was originally assumed that the radiocarbon activity in the carbon reservoir was constant over time and the half-life of C^{14} was accurate. Although adjustments were found necessary, they did not have a noticeable effect on the relative accuracy of the radiocarbon dating method, as such. New corrections made it possible to use this technique with a high degree of accuracy when compared to other techniques presently available. A number of specialists supplied these corrections (de VRIES and BARENSEN, 1953; SUESS, 1965; DAMON, LONG and GREY, 1966). As the technique becomes increasingly more refined, one can expect more corrections.

The following assumptions are crucial for accurate age calculations using radiocarbon dating (Detailed explanations are mentioned elsewhere and are not the point of concentration of this particular chapter). It is crucial to observe the assumption of: first, an accurate half-life calculation (LIBBY, 1955, p. 36) (convert the old Libby half-life of 5,568 ± 30 to the new half-life of 5,730 ± 30 by multiplying the former by 1.03); second, the knowledge and detection of all forces causing variations in the production of C^{14} and making a detection possible (de VRIES, 1958; WILLIS, TAUBER and MÜNNICH, 1960; RALPH and STUCKENRATH, 1960; STUIVER, 1961, 1965; ELSASSER, NEY and WINKLER, 1956; KIGOSHI and HASEGAWA, 1965); third, the carbon reservoir exchange rates (SUESS, 1965); and, forth, the interference of C^{14} distribution and activity caused by man. Small variations in atmospheric C^{14} concentration, which can deviate up to 2 per cent over a few thousand years, were adequately corrected by the research of STUIVER (1961, 1965), SUESS (1965), and STUIVER and SUESS (1966).

PRINCIPLES AND APPLICATION OF MICROANALYSIS

If one assumes that the organic portion of bone is the only material that can be dated with acceptable accuracy using radiocarbon (unless extenuating circumstances, such as unusual contamination, are present), one must first deal with the question of the amount needed for dating. This question can easily be solved. Microanalysis, or FUN-dating (a relative dating technique, actually one part of R-dating) can be used for such computation (OAKLEY, 1968).

FUN-dating (fluorine, uranium and nitrogen) was used in the last century (MIDDLETON, 1844) and in the 1950's by Oakley to obtain some idea of the relative time periods involved in the burial of osteologic materials. Fluorine can be found in the mineral portion of bone-fluorapatite, the result of conversion from hydroxyapatite (calcium

hydroxyphosphate), to some extent in living bone material, and to a large extent in buried osteologic materials. The amount of fluorine found in adult human individuals is about 20 g. Of that, over 95 per cent is contained in the skeletal system as fluorapatite. Of this, the dentition contains 10-70 mg F/100 g dry substance. A healthy organism ingesting a daily minimum of fluorine will achieve a protective effect in his teeth against caries by drinking water containing 1 mg F^-/litre. The fluorine balance is at equilibrium up to a daily intake of about 10 g (6 mg F^-/litre water). Larger amounts are normally eliminated through the kidney.

Deviations in the accumulation of fluoride do occur, however. In such cases, just as extreme accumulation during dental development (eight to ten years) obstructs the development of enamel (dental fluorosis), an extreme uptake in bones can lead to certain pathologic changes. A probable example is seen in the femur of *Homo erectus (Pithecanthropus erectus)*, found in 1891 by Dubois in Java. It was suggested that in this locality, *Homo erectus* drank water with an unusually high content of fluorine, resulting in a large bony tumor mass (SORIANO, 1970). Bones, displaying such unusual antemortem histories, can, of course, hardly be used as relative dating tool.

Under normal circumstances, it is the irreversible substitution of fluorine, as well as uranium, in bones that makes them suitable as a relative dating tool. With the passing of time, both elements accumulate in greater amounts. When bones are buried in different levels at the same location, older bones positioned in lower levels show greater amounts of fluorine and uranium than do those positioned above them. The accumulation of both elements is dependent on time and water action present at that location.

On the other hand, the presence of uranium in bones immediately after combustion of a sample for radiocarbon dating, could interfere somewhat with the count-rate of the sample itself. This interference is due to the fact that combustion converts uranium to radon (Rn^{222}). One could theoretically calculate the total original amount of uranium present in the bone immediately after combustion. In fact, in order to avoid counting interference in C^{14}, it is necessary to store the CO_2 for a few weeks to allow Rn^{222} to decay to sufficient low amounts so that only the C^{14} activity is present (Rn^{222} half-life is 3,825 days).

In addition to fluorine and uranium, nitrogen can also be a useful tool for dating purposes. The concentration of nitrogen decreases with time and is directly related to the amount of total collagen present in bones, and thus also to the total carbon content of the organic portion. Nitrogen decreases with increasing bone age as protein is removed from the bones. All amino-acids containing the element are removed with the protein as well. In order to compute the total amount of a sample needed for radiocarbon dating, one simply performs a microanalysis of the N-content.

Studies on modern bones have shown that the amount of collagen, and therefore of nitrogen, differs only insignificantly in bones of the same individual, of individuals of different species, and of individuals of different ages of the same species. Comparative readings on bones in the same and in different strata of the same location supply a fairly accurate estimation of their time association relative to each other. Since collagen constitutes 20-25 per cent of modern bone, which contains about 50 per cent carbon, one can easily calculate the total amount of bone needed for radiocarbon dating. Nitrogen estimates in modern bone have ranged from 4.7 per cent (BERGER, HORNEY and LIBBY, 1964), to 5.36 per cent (EASTOE and COURTS, 1963), and 4.63 to 5.41 per cent in a series of own experiments using young to very old sheep bones.

A 30 mg sample of bone, from whatever locality or environmental condition, submitted for radiocarbon dating, and no matter what the collagenous carbon content, is simply subjected to nitrogen microanalysis. The result of the latter is multiplied by 3.0 ± 0.5. Bones can usually be dated unless they stem from a very old geological and unfavourable

environmental location in which nitrogen has decreased to unusually low amounts. This will indicate that practically no collagen, and therefore no carbon, is present. Total samples used for radiocarbon collagen dating have been as small as 8 g and as large as 6 kg.

The nitrogen content of bones can be determined by two different methods – Dumas or Kjerdahl. The Dumas method is based on the fact that organic compounds containing nitrogen yield nitrogen and oxides of nitrogen when decomposed at red heat (925° C) with copper oxide. A section of copper causes the oxides of nitrogen to be reduced to nitrogen. The procedure is accomplished in an atmosphere of pure carbon dioxide. Liberated nitrogen is carried through the decomposition chamber by the carbon dioxide and then absorbed in potassium hydroxide. The weight of the remaining nitrogen is then calculated at atmospheric pressure according to volume and temperature.

Even with counters having a volume of less than 1 litre, which need little collagenous material (a small 200 ml counter is, for example, used by Berger at the University of California, Los Angeles) it is not feasible to date and process bone samples with microanalytical readings below 0.10 per cent. Theoretically, a counter could still be filled to capacity using several hundred grams of bone with an extremely low nitrogen content but, during the process of hydrochloric acid treatment, and no matter how weak that solution, most of the extremely small collagen portion in the form of tropocollagen and free amico acids would be hydrolysed. Decalcification, with the sole purpose of saving the organic materials, can no longer be controlled. In the last 10 years about one-third of all samples submitted to the Frankfurt Radiocarbon Laboratory, dating relatively to between 20,000 and 50,000 years, have had readings below 0.10 per cent, particularly in samples from temperate environments, which were therefore unsuitable for radiocarbon dating. Such samples could only be used for amino acid dating, providing the temperature (palaeo)history is known.

A number of such samples from well-known archaeologic sites, and with great significance for palaeoanthropology, stem from Africa: for example, the Klaasies River, Otjiseva, Cave of Hearth, Tuinplaas, and Cape Flats. All are samples belonging to a geographicl subspecies of *Homo sapiens*, "anatomically modern man", as distinguished from other hominids such as Neanderthal man, *Homo erectus*, and so on. However, such small samples can now be dated by radiocarbon accelerator dating, which can be used effectively to date extremely small bone samples.

Even in the case of decisively low nitrogen readings, the chances are still good that a radiocarbon date on a hominid may be obtained by conventional dating. In such a case, one might be forced to use all of the osteologic material present. This is obviously unacceptable. Accelerator C^{14} dating now provides a solution in these cases. Direct association of hominid remains and abundant faunal remains, with the same or very similar microanalytical readings, would prove both to be contemporaneous. If that is the case, then the more abundant faunal material could be used for radiocarbon dating. That absolute date could, in turn, be applied to the hominid material. Such a procedure is called A_2–dating by OAKLEY (1968). Examples are absolute dating methods such as protactinium/thorium dating or all of the uranium series dating techniques applied to materials associated with australopithecines in East Africa.

It makes no difference whether the "associated" materials are vulcanics or other associated bones. In osteologic association there is at least the assurance that no intrusion from other levels has occurred. Substantiated by the additional support of relative microanalytical dating, it becomes a reliable dating tool. It might then be proper to term bone/bone association A_1–A_2 dating, since it is neither direct absolute dating (A_1) nor purely associated (A_2) dating. Examples of such A_1–A_2 dating application have been in Africa hominids and fauna from sites like Florisbad, Saldanha, Naivasha, Lukenya Hill

(Grm-22), Fish Hoek, Border Cave, and Bushman Rock Shelter.

Several of these hominids and their associated fauna could be dated directly by radiocarbon, yielding in all cases nearly the same or at least comparable results on both materials. This type of dating procedure was used at Florisbad ($A_1 - A_2$ date 38,680 ± 2,000, UCLA 1745B, on fauna; A_2 date on charcoal/wood 38,550 ± 3,800, UCLA 1745C). They are, undoubtedly, quite accurate. Unfortunately, even in more recent articles (RIGHTMIRE, 1979), older, contaminated C^{14} dates on the peat are still referred to as "accurate" dates. It is particularly odd that these peat dates are accepted as being accurate, since the peat itself has been proven to yield highly erroneous dates, as has been pointed out repeatedly over the years in all radiocarbon articles dealing with such plant materials.

This error is due to humic acid concentration, which cannot be completely eliminated. There is also serious doubt at Florisbad as to the direct association of the peat with the hominid finds. Florisbad is a typical example of a site where only bone dating, be it by radiocarbon or amino acid, can be applied. In this site, other organic materials are contaminated beyond control. The associated fauna at Florisbad, mainly *Hippopotamus amphibius*, illustrate that a C^{14} date can be obtained on associated materials. In this case it was necessary to use, unfortunately, large amounts of bone (764 g) due to low collagen content.

DATING THE INORGANIC PORTION OF BONE (APATITE)

Until a few years ago, most radiocarbon specialists and archaeologists claimed that radiocarbon dating of bone materials, both organic and inorganic, was in most cases unreliable. This caused specialists to run a series of dates on identical samples, using both the inorganic apatite portion and the organic collagen portion, and then compare the results.

HAYNES (1968) obtained different results using both portions of osteologic materials recovered from exactly the same horizon at the Lehner Site. The archaeologic age of the bone was estimated relatively to be of Clovis age. Using the apatite from mammoth bone he obtained an age of 9,980 ± 220 years BP (A–874 C), whereas the organic portion yielded a much more recent date of 5,610 ± 350 years BP (A–806 A). The apatite of the mammoth dental material yielded yet another age, 7,780 ± 150 years BP (A–876 C). The dates, estimated relatively to be the same, in fact showed a discrepancy among bone collagen, and tooth and bone apatite of as much as 2,000 years.

The various inorganic fractions had obviously suffered from different external exchange phenomena under changing geochemical and hydrological conditions at the site. It was not taken into account at the time that the fractions were essentially of different materials. Exchange of CO_2 in the two inorganic portions cannot be compared to organic materials under any circumstances. There is also a great microanalytical difference in the makeup of bone apatite and of teeth. Even though they are chemically essentially the same, their crystal packing differs substantially. That of compact bone being much less condensed than the enamelic structure of teeth.

Collagen, the main organic component of bone, undergoes a completely different exchange phenomenon, and this will be dealt with below. Collagen can never yield dates older than its true age if treated correctly in the laboratory: contamination can only result in younger dates. However, apatite can be contaminated either way, resulting in an age either too old or too young.

The two-phase system of bone consists of a bone mineral, plus minor components of other elements, surrounding the organic structure (McLEAN and URIST, 1968). The ultramicroscopic crystals are composed of hydroxyapatite with additional components of citrate and carbonate. VAUGHAN (1970) suggested, and it is now generally accepted by most specialists, that the hydroxyapatite is built up by surface exchange, internal defects and substitutions. If one converts these impurety percentages to molar ratios, the composition of bone (apatite) mineral is as follows, as determined by NEUMAN and NEUMAN (1958):

$$[Ca_g^{++} (H_3O^+)_2 (PO_4^{\equiv})_6 (OH)_2^-] \; [Ca^{++} . Mg_{0.3}^{++} . Na_{0.3}^{+} . CO_3^{\equiv} . Cit_{0.3}^{\equiv}]$$

The two major phases are calcium carbonate and calcium phosphate, the latter being amorphous and probably a second major phase of the apatite. The crystalline structure decreases with the age of the individual (TERMINE and POSNER, 1967).

NEUMAN and NEUMAN (1958) also suggested three zones in the crystals – the crystal interior, the crystal surface and the hydration shell – and that the superficial surface ions of the crystal lattice of hydroxyapatite are hydrated. In turn, surface ions absorb ions from extracellular fluid and the latter bind another layer of water, which is called the hydration shell. As can logically be assumed, under normal conditions the exchange in the hydration shell on the surface is rapid, while that of the interior of the crystal structure can be slow.

The substitution mechanisms in the hydroxyapatite of bone are important for relative dating (F, U, N). The mechanisms are, first, an intercrystalline exchange, similar to that of surface ions but occurring at a lower rate and, second, a recrystallisation due to dissolution and reformation of crystals, with the addition of new ions into the crystal structure. Third, thermal diffusion, analogous to the movement within the structure of other solids, plays an important part.

A common substitution in fossil bone is that which turns hydroxyapatite into fluorapatite. The amount of ground water available at any particular site is responsible for this substitution. The fluorine occupies the vacant oxygen site in order to maintain the electroneutrality of the crystal (McCLELLAN and LEHR, 1969). Two faces of the phosphate tetrahedron are parallel to the C-axis in the apatite structure. Whereas the two other faces are mutually inclined to the C-axis, the substitution carbonate takes up one of the planes inclined to the C-axis. Another substitution in the apatite structure is carbonate for phosphate.

Theoretically, primarily deposited bone apatite (in vivo) could be dated, if found in a geological environment free of secondary contaminants such as limestone or other calcium carbonate- and calcium phosphate-rich deposits (loess and travertine). Such secondary deposits in fossil bones could lead to a date either too recent or too old. Specifically, the formation of secondary apatite, replacing the calcium carbonate originally present in the primary markeup of the osteologic material, is responsible for this phenomenon. Exchange studies on $^{14}C_2$ in synthetic apatite show that 60 per cent of the CO_2 possibly in the form of CO_3, is contained within the crystal lattice, and that a possible 40 per cent of HCO_3 remains in the hydration shell. The latter portion can be substantially reduced (by half) by drying for 24 hours at 100°C.

Such treatment should be recommended if dating of the inorganic portion of bone is absolutely necessary. A major portion of exchangeable CO_2 must be eliminated from the bone. However, this approach may have serious side-effects, in that it causes artificial racemisation of some of the amino-acids in the organic portion, rendering the sample useless for other dating techniques.

POLACH and GOLSON (1966) showed that a difference in assimilation of the three major isotopes of carbon exists in living organisms. The sequence of the C^{13} concentration from lowest to highest in carbon compounds is: CO, CH_4, C_D, CO_2, CO_3. There are complications in the isotopic fractionation of fossil bone used for radiocarbon dating. In the case of sedimentary phosphorates, it was found that the oxygen and carbon in apatite CO_2 are enriched in the light isotopes of each element, as compared to the coexisting calcite. Another complication might be an isotopic exchange of the carbon present from another carbon of different energy.

Diagenetic processes may also be involved in fossil bone. AMES (1959) hinted that alkali-phosphate solution might replace calcite with a carbonate-apatite of variable composition. The relative replacement rate was dependent on the solution pH, the PO^{-3}_4 content relative to HCO_3, and the calcite grain size. Other experiments simulated the conditions under which calcite can be converted into hydroxyapatite. Calcite can be easily converted into apatite. A fossil's environment could have been exposed to numerous processes that introduce CO_2 into the osteologic material. These are all possible sources of error when the inorganic portion is being dated and include secondary apatite from alkali-phosphate solutions, carbonate substitution in bone apatite, and carbon isotopic exchange.

In order to determine possible contaminants and their origins, investigators have analysed the carbon isotopic composition of fresh and fossil bone. They have found their various fractions to be practically identical to present-day carbon isotopic composition. There are also no significant variations in the isotopic carbon composition of animals of different age, sex, species, or of different parts of the same animal. The isotopic carbon composition of these did show some slight differences from those of the atmosphere, but it was usually less than 1,5 per cent where fractionation or preferential assimilation occurred.

However, a series of fossil bones of mammoth (*Mammuthus primigenius*) and cave bear (*Ursus spelaeus*) has been analysed to show a great variation in chemical composition, particularly in CO_3, PO_4, and F^-, a good indication of carbonate substitution for phosphate. Here it is interesting to note that the finds originated from different environments, i.e. an openair site as opposed to a cave. Even bones in the same location but from different layers (either above or below each other) manifested a great variation in chemical makeup. This is precisely why microanalytical studies on different layers in the same location are of such great value. They can be used as relative age indicators, unless the site is greatly disturbed. Even bones of different species but in close proximity to one another in the same layer show, in most cases, quite similar results. Electron microscopic and thin-section studies using different crystals make it possible to distinguish variations in porosity, crystallinity, formation of secondary apatite, as well as fossil algae and fungi in the osteonic and osteocytic structure throughout the compacta (PROTSCH, in preparation).

Since there is carbonate substitution in the apatite structure, researchers have tried to remove the substituted carbonate by fractional hydrolysis. Using a method for collagen-apatite residue hydrolysis, they analysed the CO_2 for C^{13}/C^{14}, and then measured the C^{14} of the CO_2. McCONNELL (1962) employed a method of pyrolysis and hydrolysis. The heat separation of collagen-apatite from samples was undertaken at different temperatures (200, 400, 600 and 800° C) in a CO_2 purification system. The CO_2 was collected and analysed for C^{13}/C^{12}. The weight differences of the analysed sample were measured after pyrolysis, and the X-ray pattern of every fraction examined. After that, the sample was hydrolysed and the C^{14} of the CO_2 of every fraction was measured. The radiocarbon dates were then obtained through hydrolysis and compared to radiocarbon ages on collagen and known ages.

The latter procedures probably cause a side-effect of carbon isotope fractionation due to heating and hydrolysis (GREY, DAMON and HAYNES, 1969). Fractional hydrolysis and pyrolysis does not make possible the elimination of substituted carbonate and C^{14} can neither be separated nor detected in the carbonate in the interior of apatite crystals. All results using these techniques are thus unreliable when compared to known historical or, as shown later, radiocarbon collagen ages.

One of the major problems is that although secondary formation is known and can be detected by electron microscopy and luminescence studies, it cannot be removed from the primary apatite by any technique, including fractional hydrolysis. Radiocarbon dating of the apatite in fossil bone thus yields unreliable dates; only the organic portion seems to provide valid dates.

DATING OF BONE BY ACCELERATORS

Conventional radiocarbon dating measures the ß-decay of radiocarbon. Sample sizes vary quite drastically depending on the size of the gas counters used. In laboratories using very large counters, and based on the gas proportional CO_2 or on liquid scintillation equipment, some samples can never be processed. This problem led to a continuous improvement of the equipment, electronics as well as counters, with a specific tendency towards a reduction of the volume. Today, some conventional CO_2 laboratories use counters as small as 200 ml; ten years ago their research was dependent on counters as large as 7,5 litres. Regardless of how small a conventional counter is, it usually requires a relatively large sample to start with, and many grams of osteologic material may have to be sacrificed to obtain a date.

A second shortcoming of the concentional method of dating is the time required to obtain a date. This is because a long time period is required to achieve a statistically adequate number of atomic disintegrations or counts for dating, at least 10,000 or more for older dates. Usually, the smaller the counter, the longer the time needed to obtain a fairly accurate date. The time range may vary from an overnight count, to several days or even weeks. Large counters mean larger samples but shorter counting times, while small counters use small samples but require longer counting periods. Most laboratories use several counters, showing some extreme size ranges. For example, UCLA uses a 7,5 litre and a 200 ml counter. After combustion of the sample, an even greater time period is required to remove the radioactive radon gas. If not properly recognised, this can severely hamper an accurate measurement. There is a technique for the immediate removal of radon (Rn^{222}), but this is also time-consuming and requires special equipment.

Depending on the equipment (electronics, counters, and so on), most conventional dating laboratories can provide dates of up to 40,000 and possibly 50,000 years. Only with very special equipment is an extension of up to 75,000 years possible (BERGER, 1979; GROOTES, 1978; STUIVER, HEUSSER and YANG, 1978). The total cost of a conventional radiocarbon laboratory, depending on the country, is anywhere from US $ 70,000 to 200,000.

A new method – accelerator or cyclotron radiocarbon dating – was announced in 1977 (MULLER, 1977) with the aim of dating a minimal amount of material (much less than that needed in conventional radiocarbon dating), to give a longer time range, and a shorter counting time. Muller reported on an analytical method of dating using an 88-inch cyclotron. Soon after, another approach using a Van de Graaf accelerator was reported by NELSON, KORTELING and SCOTT (1977). Nuclear accelerators seem to be effective spectrometers and potentially useful for the dating of extremely small samples by radiocarbon (PAVLISH

and BANNING, 1980). Attempts of dating by conventional mass spectrometers have failed in recent years, but accelerator dating provides a possible solution for small-sample dating. Accelerator analysis completely eleminates N^{14}, which usually interferes with the minute signals of C^{14} (these occur in only one atom in 10^{11}–10^{14} in nature; the atmosphere is composed of 78 per cent nitrogen of identical mass 14).

For accelerator dating purposes, a sample is converted into carbon dioxide, which goes into the cyclotron in the ionised state. Positively charged ions are subsequently accelerated to 30–40 meV until they emerge from the accelerator as a beam. Since nitrogen has an equal mass, it is also mixed in the beam and has to be separated. This is accomplished by passing the beam through a cell containing xenon gas. Full separation of carbon and nitrogen is allowed by the fact that the atomic number of carbon (6) and nitrogen (7) differ and thus their travelling speeds through xenon also differ, with C^{14} travelling about 30 per cent faster than N^{14}. Since C^{14} is detected completely separately, an age calculation is possible for it. A sample of known age, dated by conventional radiocarbon method by BERGER (1979), was used to calibrate one of the first accelerator dates (MULLER, STEVENSON and MAST, 1978).

As is usually the case with any new method, there are some shortcomings to accelerator dating. First, the equipment costs 10 to 20 times as much as conventional equipment. Refinement has to proceed in such a way that statistical errors of cyclotron measurements better those presently achieved by conventional radiocarbon counters by at least one order of magnitude. BERGER (1979, p. 102) points out that large high-energy cyclotrons probably contain some contaminant radiocarbon that might inadvertently be produced by physical experiments. He also points out other shortcomings of accelerators.

There is also, of course, the question of mixture of radiocarbon from the inorganic portion of the bone, which might be secondary and thus either too recent or too old, as well as mixture of the inorganic with the organic portion. A clear separation of these is hard to achieve. These contamination and procedural factors might render cyclotron dating useless and favour conventional dating. It is suggested, therefore, that conventional radiocarbon counters are still more accurate and more suitable, whenever enough osteologic material is available from an estimated time frame of up to 50,000 years BP, and if nitrogen microanalysis suggests a fairly high carbon/collagen content in the sample.

The following factors favour accelerator dating: first, a low sample weight of a few (15) milligrams; second, a greater time range; and, third, a shorter counting time. Each of these are true providing that the shortcomings of the method can be eliminated in the future.

Using either a cyclotron or a Van de Graaf accelerator (BERGER, 1979; BENNETT *et al.*, 1977; NELSON *et al.*, 1977), the new technique extends conventional dates from 50,000 to 70,000 or even up to 100,000 years, doubling the present age range reached by conventional counters. It would also provide a means to date rare samples of fossil hominids, for example, *Homo sapiens neanderthalensis, H. sapiens rhodesiensis* and *H. sapiens soloensis*, which existed sympatrically and allopatrically with "anatomically modern man" during a crucial time period in human evolution. Most of these hominids cannot be dated by A_2 techniques such as K/Ar, fission track or uranium series dating, since most of them lack either associated materials suitable for such dating methods or associated faunal material. The only other method available for relative/absolute dates would be amino acid dating. The shortcomings of that technique could, however, be cross-checked by accelerator dating. Both require only minimal amounts of material, and the shortcomings and contamination of each method could be controlled, or at least limited, by their application to the same sample material.

BERGER (1979) pointed out that accelerator dating is subject to sample contamination and a 100,000-year-old sample, contaminated by as little as 10 ppm of modern carbon, will be wrong by as much as 10 per cent, thus dating to only 90,000 years. In a strict sense, accelerator radiocarbon dating of bones is, at present, only a "relative" dating technique. "Absolute" dating applies to those methods that show a deviation of ± 5 per cent. Those over 5 per cent are considered relative techniques. Many famous hominid samples presently available for accelerator dating have undergone not only natural contamination, but also subject to contamination caused by preservatives applied by an archaeologist, anthropologist, or museum specialist. This contamination makes impossible the accelerator or amino acid dating of well-known samples in palaeoanthropology, excavated several years ago, unless improvements are made in the future. Keeping this in mind, the next section will describe in detail the chemical preparation, combustion and dating of the organic components of bone by the conventional radiocarbon-collagen method.

DATING THE ORGANIC PORTION OF BONE (COLLAGEN)

It is obvious that apatite, the inorganic portion of bones, can only be used for radiocarbon dating when circumstances prevail during the entire duration of the burial of the bones to prevent the infiltration of secondary calcium carbonate and calcium phosphate.

The organic portion of bone, collagen, does not suffer under exchange phenomena. Only duner very rare circumstances does one observe an occurrance on non-osteological organics in the bone other then the collagen itself. These organics usually originate from algae, fungi, and saprophytes, most of which also feed on the organic portion of fresh bone. Even if they have intruded the bone itself, they also become "fossilised" organics. Just as the collagen itself, they present an age which, if not identical, is fairly close to that of the original burial date of the bone.

The only possible source of contamination could result from the entry of excessive humic acids from the surrounding environments at a later date. This is usually due to the excessive presence of plants, or even a bog deposit, in the immediate area of its location. However, this source of contamination is easily eliminated through laboratory procedures (LONGIN, 1971).

A second contaminant, though quite rare, could result from deposits such as tar. BERGER, HORNEY and LIBBY (1964) have shown that these can quite easily be eliminated through liquid chromatography, a procedure described below and probably standard in most laboratories dating osteological material.

Bone is composed of an interstitial substance that has a fibrillar structure similar to that of connective tissue. These fibres consist mainly of collagen and some reticular fibres. Collagen, the basic substance of bone, is characterised by its content of mucopolysaccarides. Within the organic matrix of collagen, a complex mineral substance is deposited, consisting chiefly of calcium, phosphate, carbonate, and citrate. Depending on the age of the individual, there are also some minor percentage differences among species. Anywhere from 25 per cent to as much as 35 per cent of the dry, fat-free weight of all bone is made up of collagen (McLEAN and BUDY, 1964; McLEAN and URIST, 1968). Because younger individuals are still in a developmental state, in which chondral ossification is in progress, they show a greater organic portion percentage. However, in older individuals, and under physiological conditions, differences also occur as a result of pathologic conditions. These deviations may occur in either direction, but the trained dating specialist can easily distinguish differences among bones of very young individuals, of different species, and also of pathologic conditions, using thin-section microscopy and other techniques. Most dating specialists are not experienced in this particular technique and may not consider it as a preliminary step in

bone processing. In spite of this, it is certainly an important aid in calculating the total bone material needed for radiocarbon dating.

Of the interstitial substances, collagen, the organic matrix, has two chief components: collagenous fibres and the ground substance. Bone collagen, which yields glue or gelatine when boiled, constitutes as much as 90-96 per cent of the dry, fatfree weight of the total organic fraction of bone. When intact, collagen is present in fibrils with a double-cross banding at intervals averaging 640 A^{o} and it produces a characteristic X-ray diffraction pattern. It is characterised chemically by a high content of pyrolidine amino acids and a low content of aromatic amino acids. Hydroxyproline is, for example, an index for a quantitative estimation of mature collagen, as is hexosamine for the ground substance. Individual collagen fibrils in fresh bone and in fossil bone found in locations protected from environmental influences, are typically 0.3–0.5 μ in diameter and are often found in small bundles 3–5 μ in thickness. Quite a large amount of collagen, tropocollagen, or amino-acids must be present in fossils bone to allow extraction of organic substances for radiocarbon dating, in contrast to the small amounts of amino-acids necessary for amino acid dating.

To allow sufficient extraction of the organic portion of bone, one would typically select compacta of long bones and, in some cases, the lamina externa or interna of the neurocranium. Less useful for maximum extraction of collagen are the spongiosa and diploë, since they are quite often intruded upon by rootlets and other foreign organic materials. In addition, they are frequently the first areas to be attracked by water, algae, fungi, and saprophytes due to their fragile and spongy nature. Compact bone, on the other hand, is ideal for the extraction of collagen. The dense mineral structure shields the inner organic portion from infiltration by both foreign substances and water, which would drastically diminish the organic portion. Studies on organics in one and the same bone have shown that the organic portion of compacta, as compared to the organic portion of the spongiosa, can differ by a magnitude of three.

Cement and dentine are preferentially selected over enamel when dating teeth of macrofauna. The total organic portion of enamel is much smaller than that of the compacta of bone; that of cement and dentine is somewhat less than that of spongiosa in living animals. Preservation of organics in enamel, cement, and dentine is enhanced over long periods by their denser mineralogic structure. A fully developed crown enamel consists of only 3 per cent organic substance, containing a glucoprotein; the rest consists entirely of calcium salts in the form of apatite crystals.

However, dentine, by volume the largest portion of a tooth (depending again on type of tooth and species), is a fibrillar, calcified collagenous matrix traversed by ondontoblastic processes composed of a specialised protein called elastin. Dentine is still much harder than compacta, but resembles bone in its structure, chemical nature, and development. As in bone, the organic portion of dentine consists of about 25–28 percent organic, with 70–72 percent inorganic fractions. Throughout the life of an individual, dentine is formed with a somewhat greater activity in old age, when the pulp cavity becomes reduced in size. Large teeth, for example, those of mammoth, hippopotamus, and other macrofauna, are quite suitable for radiocarbon collagen dating. First, the extremely dense inorganic structure of the enamel and cement overlying the dentine provide an excellent shield against deleterious environmental influences which could diminish the organic content of the dentine itself. Second, the enamel is thick enough in some animals to provide this shielding effect, yet it most often constitutes only 6–8 per cent of the total dental weight. It is erroneous to assume that the low organic content of teeth makes them unsuitable for dating. This is based on the misconception that enamel is the material to be dated. In fact, it is the dentine that provides the greater mass of dateable material. The organics in the cement, the layer of the tooth that continues to cover the dentine below the alveolar level, are much higher than in enamel and somewhat lower than in compacta.

Bone processing procedures, starting with a thin-section analysis and ending with the sample count, can be seen in Figure 1.

Processing of bone and dental material usually starts with the elimination of possible contaminants. If careful and tedious examination and treatment of materials in practically sterile laboratory conditions is undertaken, dates should ultimately be as correct as those obtained from other organic materials. The first step should be a thin-section analysis of the bones in order to determine whether contaminants such as algae, fungi, and others are present. With this method, man-made substances such as shellac or other preservatives, or tar, can also be recognised. Recent additions of saprophytes (algae and fungi) and bacteria can also be detected easily. This is important because their photo– or chemosynthesis could cause faulty radiocarbon results.

Contamination by these substances is equally possible in charcoal, wood, or other organic materials normally considered more suitable for radiocarbon dating (SELLSTEDT, ENGSTRAND and GEJVALL, 1966). Naturally occurring substances are thus a serious contamination problem in all organic substances. In fact, due to the dense nature of bone, it is actually less prone to contamination than all other materials.

The second step in analysis before bone dating is an estimation of total bone material needed. Nitrogen microanalysis of a few milligrams of compacta, specifically for nitrogen, makes it possible to calculate the total bone material needed. Only dentine should be used for analysis in the case of dental material.

In about half the samples processed for radiocarbon dating, extraneous recent materials such as rootlets are present. Hasty processing after failure to inspect the samples with a microscope is probably responsible for the fact that a large number of dates differ from the relative etimation of a sample. This type of visual inspection and removal by hand often constitutes the greater part of the total processing time of a sample. Part of this removal includes the estimation of sandy deposits within the spongiosa, often necessitating the latter's total removal. Sand and rootlets often infiltrate the Haversian canals and trabeculae which, unless the spongiosa is scraped totally clean, these cannot be detected and subsequently removed.

Insects of a more recent time period are quite often mixed in with the sand and are again a cause for contamiantion. The removal of sandy materials at this final stage should be carried out using doubly distilled water. The bones should then be dried and again inspected visually. Thereafter, about 1 mm of the compacta should be removed by scraping off the periosteal surface. This removes any remaining adherent extraneous natural contaminants that may have infiltrated the more porous periosteal surface of the compacta.

Also removed are man-made contaminants such as shellac, which may have been applied by the excavators. In the Frankfurt Radiocarbon Laboratory, preservatives have been found in every third sample of bone supplied by the excavator, even when it was indicated that the bones had not been treated. A contaminated bone would certainly falsify the date by a large margin. Bones should therefore be broken up into smaller pieces and treated on a reflux in a solution of acetone and 2-ethoxyethanol for several days to be absolutely certain that no contaminants remain. Bones treated several times over the years in museum collections will often require a much longer reflux treatment. In some cases this could last for weeks. After the bones have been dried, a mild hydrochloric acid treatment might be necessary. Usually, preservatives like shellac are easily recognised after the acetone reflux treatment, emerging as easily peeled-off, hardened, whitish deposits. In cases where several coats have been applied, a brief immersion in a 4 percent HCl solution for 20 minutes creates a space between the periosteal-compacta surface and the hardened preservatives. Persistent preservatives can

Thin section analysis
FUN-analysis
Visual contaminant removal
Sand removal by doubly distilled H_2O
1 mm compacta (shellac, etc) removal
Acetone/2-ethoxyethanol reflux
4 % HCl-20 min-periosteal/shellac border treatment
Hydrolysis by HCl

Collagen strands

Renewal of solution
NaOH humic acid treatment
Repeated doubly distilled H_2O washing
Neutralisation with HCl
Washing in H_2O
Collagen strand drying
Combustion of collagen

Tropocollagen

H_2O solution – weak HCl
Humic acid removal by NaOH
Repeated doubly distilled H_2O washing
HCl treatment – slight acidity
Gelatine conversion
6N HCl–24hr treatment
Liquid chromatography
Amino acid collection
Amino acid drying
(Collagen/gelatine/amino acid)
Sample combustion CO_2
CO_2 analysis for C
$\sigma C^{12}/\sigma C^{13}$ analysis
CO_2 cleaning by hot CuO
$KMnO_4$ and $AgNO_3$ treatment
CO_2 thermal circulation (CuO/Ag)
Sample count in 2 litre proportional counter (2,600 min. minimum)

FIGURE 1

Bone Processing Procedures

ultimately be peeled-off by this procedure. After repeated washing in doubly distilled water, the sample should again be dried.

Frequently, another type of contamination may be present which would ultimately affect samples used for amino acid dating. The author (PROTSCH, 1976b), as well as SIDLE (1967) and WOLMAN and MILLER (1971), conducted a number of experiments and found considerable amino acid contamination in commercially available analytical grade HCl (37 per cent). Such contamination could also be present in ammonium hydroxide used during the liquid chromatography stage. HCl may contain up to 8,300 nmol contamination, and ammonium hydroxide could have five to ten times as much. This can result in serious errors in very old samples. HCl used for processing bone samples should thus be doubly distilled; ammonium hydroxide should be made from distilled ammonia gas on a vacuum line if contamination is suspected.

Depending upon preference of the investigator, the total bone pieces are treated in an HCl solution until only the collagen strands show up. As an alternative, the bones could be pulverised and then treated with a weaker HCl solution and doubly distilled water. In the first case, the investigator is able to see how well the collagen is preserved but has to renew the solution constantly, possibly up to seven days. The concentration of the solution is always dependent on the reaction of the inorganic portion of the bone. A solution that is too concentrated could easily hydrolyse a large amount of the collagen itself and thus a sample must be watched constantly over several days. The second method, pulverising the bone, is certainly more expedient and might take only a few hours but the strength of the solution is more difficult to control.

After the inorganic portion is totally dissolved, the insoluble portion is separated with a Buechner funnel. Only glass filter paper is suitable for this purpose. The remaining organic portion is then washed several times with doubly distilled water and treated with a 1 per cent solution of sodium hydroxide to remove humic acids. It is washed again repeatedly in distilled water, neutralised with HCl, and washed again repeatedly until neutral. It is usually at this stage that smaller rootlets, which might still be present in the sample, can easily be detected on the filter paper.

The collagen, or tropocollagen, is then converted to gelatine by heating in doubly distilled water (pH = 3) at about 90°C, using a heater with a stirring magnet (IKA Combimag RCT) for four to six hours. Usually, some gelatine can be detected by two or three hours and nongelatinous preservative substances, if still present, would harden and show up in the solution. These can be removed by hand. Other remaining impurities are removed by centrifugation. Finally, only organic materials will be present in the gelatine formed.

The gelatine is then placed in a flask containing 6 N HCl, refluxed for 24 hours, and filtered. The clear solution is then concentrated to a volume of about 100 ml. At this point, two different processes for further analysis can be followed:

1. If no petroleum (tar) products are suspected in the sample, it can be neutralised, dried, and combusted in a pure oxygen atmosphere.

2. If contamination is still suspected, the following procedure should be applied. A volume (5 cm diameters) containing Dowex 50–WX8 resin charged with 4 N HCl is used to collect pure amino acids by liquid chromatography. The filtered hydrolysate is passed through the column at a rate of 30 ml/h (HO, MARCUS, BERGER, 1969). The resin is then washed repeatedly with distilled water to remove all contaminants. The column is eluted with an excess of 5 N ammonium hydroxide at a flow rate of 30 – 60 ml/h in order

to liberate the amino acids. One litre of yellow-brown affluent is collected per sample run. This affluent, containing the amino acids, is then evaporated to dryness, becoming dark brown with a distinctive odour.

In both cases the procedures by which the collagen or dried amino acids are converted to carbon dioxide in a stream of oxygen are identical at the Radiocarbon Laboratory in Frankfurt. A two-step combustion procedure involves the burning of the sample in an inner tube and passing of nitrogen through that tube while oxygen is passed through the outer tube. Complete combustion is achieved by a second process whereby the oxygen is again passed through the inner tube, thus burning the sample in a pure oxygen atmosphere.

The nitrogen gas simply operates as a pushing device in the first burning step. Further purification on the processing line is achieved by passing CO_2, the product of the combusted carbon of the organic sample, and the oxygen gas through five traps containing 0,1 N silver nitrate, chromic acid, potassium permanganate, hot copper oxide (500°C), hot copper/silver at 450°C, and dry ice/acetone water traps. Final purification is by thermal circulation over hot copper (600°C) and silver in a 5 litre glass container with an external quartz convection tube. Before this, and at each counter filling, the CO_2 is routinely passed over hot Cu/Ag (450°C) at least six times in a separate system and vacuum-distilled at -78°C. The gas quality after this procedure is excellent.

Counter plateaus are 500 V long with slopes of 0,6 per cent/100 V for muons and less than 1 per cent/100 V für C^{14} + background. The standard working point is 4,300 V. The absence of electronegative impurities is verified before and after each run by measuring the count rate at the steep part of the muon characteristic curve. An experimental linear correlation between guard gross and sample muon rates, valid within counting statistics, gives a post-measurement check on working point and a long-term check on instrument stability. Background is nominally 7.9 ± 0.08 cpm with slow seasonal variations in the maximum range of ± 0.2 cpm (95 per cent confidence level). No dependence on atmospheric pressure was found on the basis of 90 background measurements, each of 2,000 minutes. Four months of continuous monitoring of the laboratory aerosol radioactivity with a NaI detector and multichannel analyser (Camberra Series 30, 1,024 channels) showed an exchange background in the range covering 200 – 3,000 keV.

The modern standard CO_2 is prepared by wet oxidation of NBS oxalic acid. The AD 1950 C^{14} count rate is 12.10 ± 0.08 cpm at 20°C with normalisation of the σ–C^{14} value of – 19.75 ‰. Counting periods are two days for background, sample and standard. The samples are measured at least twice and the background at least a week. Routine χ^2 -analysis is applied to 100 minute print-outs. Age errors correspond to measured ± σ variations of sample, background and standard. Calculated errors smaller than 100 years are increased to this figure as a minimum. C^{13}/C^{12} measurements are done only for selected samples. Thus, 80 years have been added to all bone measurements to give a theoretical correlation for C^{13} fractionation, with an addition ± 60 years squared added to the variance (LERMAN, 1972). All dates are expressed in C^{14} years relative to AD 1950, using the half-life of 5,568 years. Calendar estimated and archaeologic comments are based on calibrated dates (PEARSON and BAILLIE, 1983; PEARSON, PILCHER and BAILLIE, 1983).

To calculate the uranium present, the CO_2 sample is passed into the counter after repeated passing over hot copper and elimination of free oxygen. Radon (Rn^{222}), the byproduct of uranium decay, allows this computation with fairly good accuracy. The radon count makes it possible to estimate the exact time at which the interference in the count due to Rn^{222} has decreased to less than one count per minute.

The 2 litre copper proportional counter is then filled to 1.013 mbar with the purified CO_2 sample. The counter is protected against cosmic and surrounding radiation by a 3.5 ton

lead shield and a copper multiwire anticoincidence ring-counter flushed constantly with purified 90 Ar/10 CH_4. Electronics are of the commercial NIM type.

KELSTERBACH – A CASE STUDY IN C^{14} COLLAGEN AND AMINO ACID DATING

In spring 1952 during bulldozing operations in the north-west corner of the Willersinn gravel pit, which is south-west of Frankfurt between Kelsterbach and Raunheim, a fossilised hominid calotte was discovered.

The original site of discovery has remained undisturbed until today because further digging was continued solely in northerly and easterly directions. These circumstances made it possible, 20 years later, for geologists to examine the precise stratigraphic relationship of the different finds in the location and stratigraphic levels. On the basis of the still undisturbed stratigraphic sequence and the graphs and drawings made at the time of discovery of the calotte, it was possible to make a relatively reliable and accurate estimation of the geological situation of the hominid and faunal remains in question (PROTSCH and SEMMEL, 1978; PROTSCH, 1987).

Accordingly, the calotte can be attributed to a layer at a depth of 4.60 m. The analysis of some sandy remains extracted from the left auditory meatus supported the accuracy of the observation that all materials originated from the stratigraphic layers as originally reported. The stratigraphic layer that yielded the hominid find belongs to the lower part of a 5 m thick gravel bed and is formed by intermittent sand gravel layers located at the "Obere Niederterrasse", the so-called $t_{(6)}$ terrace (BECKER, 1965, 1967; SEMMEL, 1969, 1972, 1974). It was deposited by the River Main in the location during the Upper Pleistocene period. It consists of clay flood-plain deposits and quicksand and is covered by remains of sediments of the "Laacher pumice-tuff" (Figure 2).

This gravel bed in which the fossils were found is the second youngest terrace of the River Main. Its chronological origin has been a point of frequent discussions (BECKER, 1965, 1967; SEMMEL, 1969, 1972, 1974; PROTSCH and SEMMEL, 1978). Other faunal remains were also discovered within the terrace, but in a much higher level. One of these, a mammoth molar, was dated by radiocarbon at the radiocarbon laboratory of the Niedersächsische Landesamt für Bodenforschung in 1960 and yielded a date of 15,810 ± 410 years BP (Hv-1961). Since the mammoth fragments were recovered from a level substantially above those of the hominid, it is reasonable to believe that the hominid is substantially older. However, because this date is based on the inorganic portion of the bone (apatite) and not the organic (collagen) components there is a probability that the apatite was contaminated with recent or old radiocarbon. However, the mineralogical makeup of the bed in the terrace makes such contamination improbable, since it was void of any calcitic material and leakage through the layers was practically nonexistent. Percolating waters with high solutions of calcium carbonate and calcium phosphate could cause secondary apatite accumulation into the bone, thus yielding C^{14} dates either too old or too recent. Another method had to be found to date the River Main terrace, and therefore the calotte, more accurately. Geormorphological analysis of the stratigraphy of the upper layer, and the results of pollen analysis of its clays, assign the terrace "relatively" reliably within the late phase of the Würm-Glacial.

To obtain a more accurate date for the calotte, a small bone sample was removed from it in the radiocarbon Laboratory of the Anthropological Institute of the University of Frankfurt. A sufficient amount of organic material could be extracted allowing both radiocarbon collagen dating as well as amino acid dating. The process of extraction and absolute dating

for Kelsterbach is described in detail by PROTSCH and SEMMEL (1978) as well as in this section. According to the radiocarbon results the calotte dates absolutely to 31,230 ± 1,580 years (Fra-5). By means of amino acid dating of the same sample an age of approximately 32,000 years BP could be estimated (PROTSCH and SEMMEL, 1978). The latter date should be judged as relative and should be viewed with caution due to the difficulty of reconstruction of the palaeotemperature necessary in making an accurate amino acid dating age calculation. However, the radiocarbon results can be considered quite accurate and therefore as absolute. In this case the results of both dating methods coincide and thus also supply a good palaeotemperature reconstruction. Because both dates coincide quite well, one can assume that a date of at least 31,000 years BP is acceptable for the calotte.Blind dates on the mammoth, positioned somewhat above the hominid and on the hominid itself, were also processed at UCLA and yielded somewhat younger dates: 23,675 ± 860 (YCLA-2359), and 29,000 ± 1,525 (UCLA-2361). These mammoth fragments were positioned below in a stratum substantially older than those dated by the Hannover Laboratory to 15,810 ± 410 years (Hv-1961).

The results of nitrogen analysis are unusually high for bones of such age (Table 1.1). This is easily understandable given the ecological circumstances in an early bog-type deposit. The same can be said for the increase of uranium and fluorine over time. Fluorine is unusually high but, here again, this is in keeping with expectations in a water-rich environment. The uranium is considered average and shows a continuous increase, from the higher stratrigraphic levels to the lowest hominid-bearing horizon. Overall, the microanalytical results show a clear relative age succession and placement, which support the absolute dates.

TABLE 1.1

FUN Analysis of *Mammuthus primigenius* and Hominid from Kelsterbach

Species	Material	Location	F(%)	U(ppm)	N(%)
M. Primigenius	Bone	420 m	2.80	109	2.00
M. primigenius	Bone	450 m	2.93	130	1.55
H.s. sapiens	Bone, os occipitale	460 m	2.98	138	1.20

RADIOCARBON COLLAGEN DATING OF THE KELSTERBACH HOMINID AND MAMMOTH

Sample pretreatment and collagen extraction as outlined in the previous section was identical in both the hominid and the mammoth. This treatment was basically the same as that described in 1964 (BERGER, HORNEY and LIBBY), with a few additional pretreatment techniques as described by PROTSCH (1972). It was preceded by examination of the microstructure of the bone by a thin-section technique using polarized light. The organic content of bone samples was identical and provides additional proof to substantiate the assumption that the samples were nearly or very closely associated in a similar environment.

The nitrogen content of the Kelsterbach hominid was 1,2 per cent N; 70 g of bone yielded about 6 g of collagen and 2,60 g of pure carbon, which yielded about 4,5 litres CO_2.

This was more than enough for a total counter filling at the Frankfurt Laboratory. Actually, only 30 to 35 g of bone would have been enough for C^{14} dating purposes. This sample was processed in 1978, before the samples of the stratigraphically associated mammoth material, but several years after radiocarbon measurements on mammoth teeth and shells were processed at the Hannover Laboratory. The yield of CO_2 from the collagen sample in the case of the Kelsterbach hominid was between 90 and 95 per cent. The hominid sample was counted for 36 hours (2,160 minutes) three times (two sigma-standard deviations), and yielded an age of 31,200 ± 1,600 years (PROTSCH and SEMMEL, 1978).

It was obvious from the similar microstructure of the bone that little material was needed for radiocarbon dating of the *Mammuthus primigenius* stratigraphically positioned slightly above the hominid. Microanalysis of the faunal material showed 1.55 per cent N, a slightly higher content than in the stratigraphically older hominid. A 150 g sample of bone yielded 13.4 g of collagen, of which about half (about 6.8 g) was carbon. This amount was more then enough for two counter fillings. The sample processing was continued until 4.6 litres of CO_2 was collected for sample counting. The results are shown in Table 1.2.

TABLE 1.2

Hominid (Fra-5) – Radiocarbon Collagen Dating Results

Counting period	Date
1.	31,600 ± 1,800 years BP
2.	31,000 ± 1,500 years BP
3.	31,000 ± 1,450 years BP
Final age (Fra-5)	31,200 ± 1,600 years BP
Final age (UCLA-2361)	29,000 ± 1,525 years BP

The sample was run for three counting periods, each of 2,160 minutes. Individual measurements show good reproducibility and give an average value of 31,200 years BP.

The sample was then run again for three counting periods, each of 2,000 minutes: the results are shown in Table 1.3.

The individual measurements in Table 1.3 show good reproducibility and give an average of 30,000 ± 2,500 years BP for the Kelsterbach mammoth.

The final age of *M. primigenius* (UCLA-2359) at 4.30 m is 23,675 ± 860 years BP.

It should be remembered that all radiocarbon dates are essentially asymmetric in accuracy and that the averaging of individual measurements should be preferred on the count rates, and not on the derived radiocarbon dates. This is because the radiocarbon date is a logarithmic function of the count rates of sample, background, and modern standard. However, the asymmetry is of importance only for very old samples, in which there is weak signal direction in the presence of noise caused by a counter background (CURRIE, 1968).

In the special case of the "very old" Kelsterbach mammoth, sample measurements were performed at different times during a time period of six weeks. It was stored for three months before the first measurement to allow for complete decay of Rn^{222} in the sample CO_2. The sample count rates were compared with 20 background measurements (each of 2,000

TABLE 1.3

Faunal Sample (Part of Humerus) – *Mammuthus primigenius* (Fra-5a) at 4.60 m

Counting period	Date	Average
1.	$29{,}650\ ^{+2{,}300}_{-1{,}800}$ year BP	
2.	$29{,}940\ ^{+2{,}400}_{-1{,}850}$ years BP	$30{,}300\ ^{+2{,}500}_{-1{,}900}$ years BP
3.	$31{,}350\ ^{+2{,}950}_{-2{,}200}$ years BP	

2,000 minutes) performed during a time period of four months bracketing the sample repetitions. In the age calculations, the fluctuations of background, sample, and modern standard are accounted for on a 95 per cent confidence level (chi-squared test). The error margins thus calculated are more rigorous than the usual ± 1 standard deviation error margins used for young radiocarbon samples.

It can be noted that each of the individual sample measurements gave count rates at a sigma level above background. The rigorous statistical test is necessary because the dating is not too far from the systems limits of resolution (age limit about 44,000 years BP). The procedure used in error calculation is in accordance with the recommendations of STUIVER, MINZE, and POLACH (1977), and WALANUS and PAZDUR (1980) for age reporting on very old radiocarbon dated samples.

COMPARATIVE AMINO ACID DATING FOR THE KELSTERBACH HOMINID AND MAMMOTH

BADA, PROTSCH and SCHROEDER (1973) showed that comparative dating by C^{14} and amino acid dating can supply absolute dates on hominids at sites that could not be archaeometrically determined by other methods. The site of Kelsterbach provides different samples in several stratigraphic levels (bone, teeth and molluscs) which can also be dated by different methods.

Cranial hominid and postcranial faunal material of *Mammuthus primigenius* was processed by the isoleucine epimerisation method. For each sample, 5 g of compact bone was used. Small pieces of bone were removed from the calotte of the hominid, specifically on the os occipitale close to the lambdoid suture, and part of a femur of *M. primigenius* was sampled. The outer surface was mechanically abraded and cleaned with a dental abrading machine and thus about 1 mm of the surface removed.

Samples were subsequently treated in doubly-distilled water, ultrasonification twice (each for five minutes), and 0.2 N HCl_{aq} (five minutes). The pretreated bone material was then submerged in 2 N HCl_{aq} and nearly totally preserved collagen strands removed and immediately neutralised. Hominid as well as faunal sample showed nearly completely preserved collagen strands.

The collagen samples were subjected to hydrolysis with 6 N HCl_{aq} at a temperature of 105°C for 24 hours in order to dissolve the peptide bonds. The resulting clear fluid was evaporated at a temperature of 55°C; the residue was dissolved in double-distilled water and desalted on Dowex 5 W-X8 resin. The amino acids were eluted with 1.5 N NH_4OH. The solution was reduced again with the help of a rotary evaporator at 55°C and the remainder resolved with buffer pH 2.28.

The actual analysis was done using a Multichrome B 4255 automatic amino acid analyser, by Beckman. Its column was filled with the ionic exchanger M 82. The time for analysis took 210 minutes with a total sample of four.

Excellent preservation on the organic substance could be observed on the chromatograms. Qualitatively, even those amino acids that normally disintegrate rapidly (threonine, serine, and hydroxyproline) were present. Even the diastereomere type of L-hydroxyproline could be shown. Unfortunately, no constants of this amino acid are available yet which presently makes dating by this amino acid impossible.

The isomeres of isoleucine (L- and D-allo-Ile) used for dating displayed the D/L-ratios for the samples as shown in Table 1.4.

TABLE 1.4

D/L Ratios of Isoleucine Isomeres

Sample	Laboratory n°	D/L-ratio
1	FRA-A-10a-(3b)	0.02548
2	FRA-A-10a-(3c)	0.02693
3	FRA-A-10a-(3d)	0.02593
4	FRA-A-10a-(4)	0.02548

The equation for the age computation is as follows:

$$1. \qquad \text{Age (yr)} = \frac{\ln \frac{1 + (D/L)}{1 - (D/L)\,K'} - C}{(1 + k')\,k}$$

For the equilibrium constant $K' = K^{-1}$ the value 0.725 was taken; for the reaction rate constant k the value $10^{19.41 - 7.304.O/T}$; and the value of 0.028 was taken for the integration constant C (BADA, 1972).

The following is then applicable:

$$2. \qquad \text{Age (yr)} = \frac{\ln \frac{1 + (D/L) - 0.028}{1 - 0.725\,(D/L)}}{1.725 \times 10^{19.41 - 7.304.O/T}}$$

The temperature during burial of the fossils (hominid and mammoth) was taken as 8.8°C (PROTSCH and SEMMEL, 1978). The ages of the samples are then as follows:

Mammuthus primigenius

Sample 1	28,650 years BP
Sample 2	33,170 years BP
Sample 3	30,060 years BP
Sample 4	28,650 years BP

The average computed for *Mammuthus primigenius* on the basis of four sample runs was 30,100 ± 2,100 years BP. The isomeres of isoleucine used for dating the hominid show the following D/L rtios for the samples:

Sample 1	Laboratory no.	D/L Ratio
1	Fra-10-(1)	0.02655
2	Fra-10-(2)	0.02653

TABLE 1.5

Absolute Dates and Stratigraphic Depth of Samples

Depth (m)	Method	Material	Species	Age (years BP)	Laboratory
0.50	C^{14}	Charcoal		510 ± 400	Fra-52
3.30 to 3.50	C^{14}	Molars	*Mammuthus primigenius*	15,810 ± 410	(Hv–1961)
4.00	C^{14}	Molluscs	–	18,500 ± 950	(Hv–1296)
4.20	C^{14}	Bone	*M. primigenius*	21,000 ± 1,400	(Hv–1297)
4.30	C^{14}	Bone	*M. primigenius*	23,675 ± 860	(UCLA–2359)
4.30 to 4.50	C^{14}	Bone	*M. primigenius*	30,300 ± 2,000	(Fra-5a)
	A-a (isoleucine)		*M. primigenius*	30,100 ± 2,100	(FRA-A-10a)
4.60	C^{14} (collagen)	Bone	*H.s. sapiens*	29,000 ± 1,525	(UCLA–2361)
	C^{14} (collagen)	Bone	*H.s. sapiens*	31,230 ± 1,580	(Fra-5)
	A–a (isoleucine)	Bone	*H.s. sapiens*	32,000	(FRA-A-10)

Notes:
Hv – Radiocarbon Laboratory, Hannover;
Fra – Radiocarbon Laboratory, Frankfurt; UCLA – Radiocarbon Laboratory, Los Angeles.

Using the same equation (2) as above on the *M. primigenius* samples, the ages for the hominid are as follows:

Sample 1	32,000 years BP
Sample 2	32,900 years BP

The average age of the hominid on the basis of two sample runs is 32,000 years BP.

Since the mammoth was positioned stratigraphically slightly above the hominid (see Figure 1.3), its follows that these ages should be expected to be younger than the hominid positioned below. This is indeed the case.

All radiocarbon and amino acid dates from the different laboratories in their respective stratigraphic position are shown in Table 1.5.

As can be easily seen in the case of Kelsterbach, a series of radiocarbon collagen dates can be supported or verified by amino acid dates. If, in addition to this, relative chronological evaluation by means of microanalysis, faunal analysis, and geomorphological/stratigraphic analysis is undertaken one can be assured of a reasonably sound chronological placement for any fossil hominid.

VELIKA PECINA

The Hrvatzko Zagorje region in Croatia, northwestern Yugoslavia, yielded recently a number of hominid fragments from several sites, the most important being the caves Velika Pecina and Vindija (MALEZ, 1978; SMITH, 1982, 1984). None of the osteological finds represents a complete skull, but the fragments are sufficiently large enough to assure a more detailed morphological analysis and thus assignment to a particular fossil hominid group. Some of the larger frgments of the Os frontale, mandibulae, and Ossa parietalia show some morphological characteristics, like evenly curved contours on a right parietal fragment (Vi 302 and Vi 204), somewhat typical for Neanderthals. The presence of a large suprainiac fossa on some occipital fragments (Vi 299) is also considered by some (STRINGER *et al.*, 1984) as a characteristic Neanderthal feature and also present to the same degree in the regionally closely located Neanderthals from Krapina. Some of the frontal fragments reach a robusticity that can only be seen again in frontals of Neanderthals. All above mentioned fragments come from level G_3, a stratum assigned to the lower Würm stadial containing Mousterian lithic elements. The abundant faunal remains present and directly associated with each level and most hominid fragments, made it possible for us to undertake an intensive investigation as to the relative and absolute dating of the hominids from level G_3 assigned to *Homo sapiens neanderthalensis*. Besides the dating of hominids and fauna from Vindija and Velika Pecina, all fossil hominid specimens, fifty one, belonging to *Homo sapiens neanderthalensis* and upper level *Homo sapiens sapiens,* were casted in our laboratories.

Relative age indicators at Vindija are based on the stratigraphic faunal and archaeological analysis, as well as their comparison to other nearby sites; like the dating of level 7 at Kulna Cane in Czechoslovakia which is also correlated to a Lower Würm Stadial (VALOCH, 1967, 1977; JELINEK, 1880). The ages are there between 45,600 and 38,600 years BP. The above dates are those which correlate to level G_3, which contains the Neanderthal fragments.

THE DATING OF THE VINDIJA HOMINIDS AND FAUNA

Samples of fauna were collected by us in 1982 at the locality and from that level in which hominid fragments Vi 306, Vi 206, Vi 231, Vi 305, and others were found. The fauna collected belongs to *Ursus spelaeus*. Microanalytical dating with the same results (based on F, U, N) clearly indicates that the hominids and fauna are from the same level and are of fairly similar relative time. The hominid itself could only be dated by amino acid dating (Isoleucine) whereas the fauna was dated by both amino acid and radiocarbon. Detailed description of dating procedures of both techniques will appear elsewhere (PROTSCH and ZÄNGL-KUMPF, in prep.).

The basic form of the mandibular symphysis of specimen Vi 306, a well developed supraorbital torus and a rather complex frontal sinus (Vi 305), strongly suggest Neanderthal features (see also SMITH, BOYD and MALEZ, 1985). The socalled "progressive tendencies" in these hominids as WOLPOFF (1980) and SMITH (1982) see them are not clearly present. The latter interpretation could be wishful thinking placing these "Neanderthal" individuals into a transitional population between typical Neanderthals and *Homo sapiens sapiens*, "anatomically modern man" in Europe. As most authors point out, and our own morphological research indicates, those Neanderthal features present place the population clearly into the "typical" Neanderthal group.

The F-Complex, which is situated directly above G_3, contains Upper Palaeolithic elements and a hominid specimen which clearly distinguishes itself from those of the Neanderthals below. It can be assigned to early anatomically modern man, *H. sapiens sapiens*, in southcentral Europe.

The absolute dating of these levels and assignment of dates would give a possible chronological fix-point to the time-transition of arriving "anatomically modern man" and the disappearence of Neanderthal in this area. Those who see some "progressive" features, and a possible morphological transition from Neanderthal to *Homo sapiens sapiens*, would also get a chronological fix-point for that transition.

A comparison of dates by radiocarbon and amino acid dating of Kelsterbach and Vindija was undertaken, since Kelsterbach represents a very early date of "anatomically modern man" in Europe and the level between G_3 (Neanderthal level), and G_1 (or i), and F at Vindija which is that stratum which contains for the first time *Homo sapiens sapiens* in that location. Prior C^{14} dates on level F yielded dates of 26,970 ± 630 BP (MALEZ and ULLRICH, 1982) and for the transitional zone between G_3 and level G_1 or i 33,850 ± 520 BP (MALEZ and VOGEL, 1970; MALEZ and RUKAVINA, 1979). The latter dates on the first "anatomically modern man" level at Vindija coincide nicely with those at Kelsterbach. A date based on amino acid dating (Isoleucine) at the Frankfurt Laboratory came to 42,400 years BP (SMITH, BOYD and MALEZ, 1985). The osteological material used was that of *Ursus spelaeus* collected personally by Protsch at the Cave in 1982. Since one date by itself, based on a dating technique which is considered by many still as more relative than absolute, does not supply a good absolute indicator (BADA and HELFMAN, 1975; PROTSCH, 1976; SMITH, 1977) further dating by different techniques and the same technique of different associated samples was necessary. Therefore, additional dates were processed by amino acid dating using one of the hominids (Vi 299) (right occipital fragment) and a radiocarbon date on the fauna *(U. spelaeus)*.

The resulting hominid date, based on Isoleucine, came to 33,200 years and the associated radiocarbon faunal date to 32,900 ± 800 years. Both dates seem to be in nice agreement with each other and also support those earlier dates of level G_1 and G_3 above.

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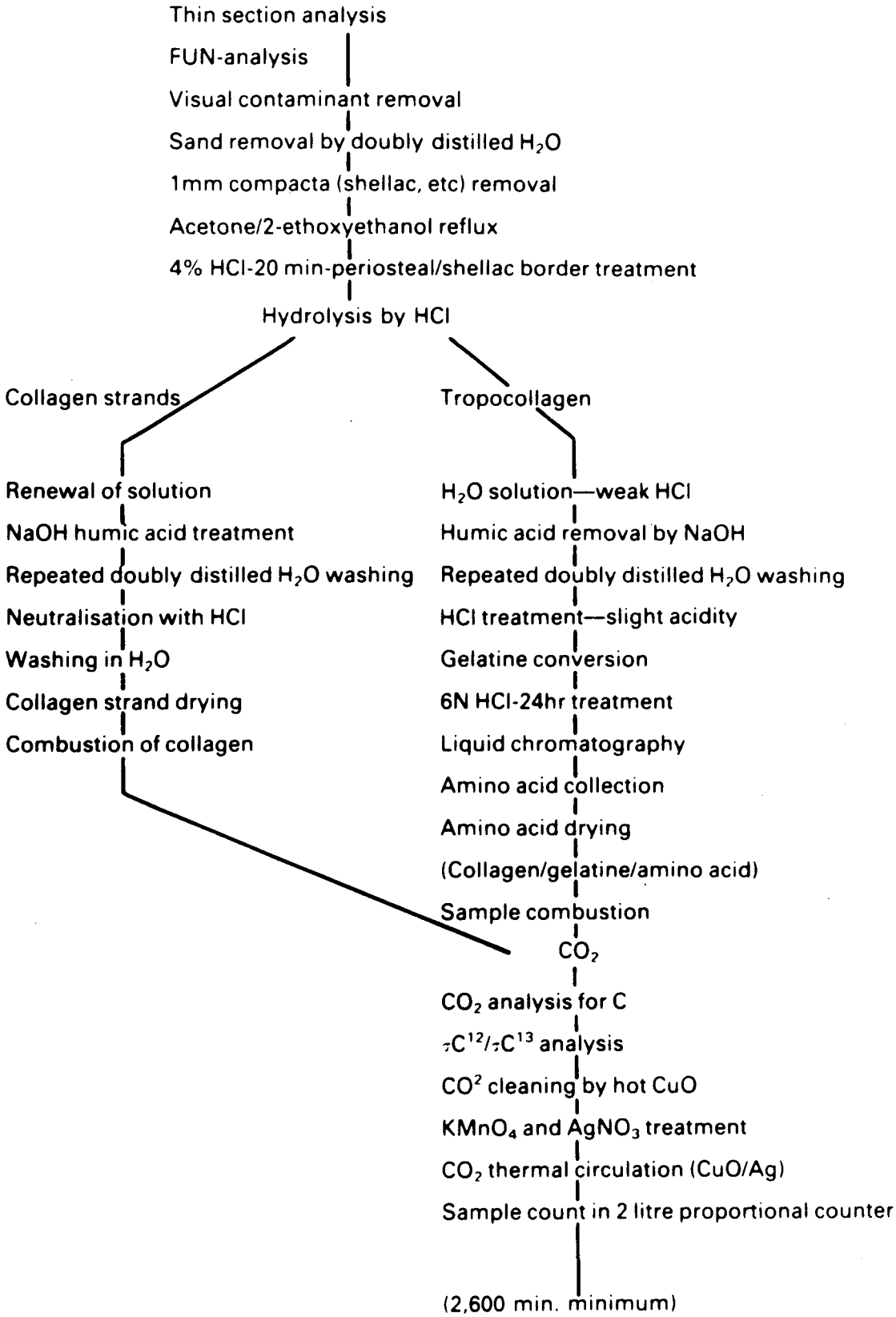
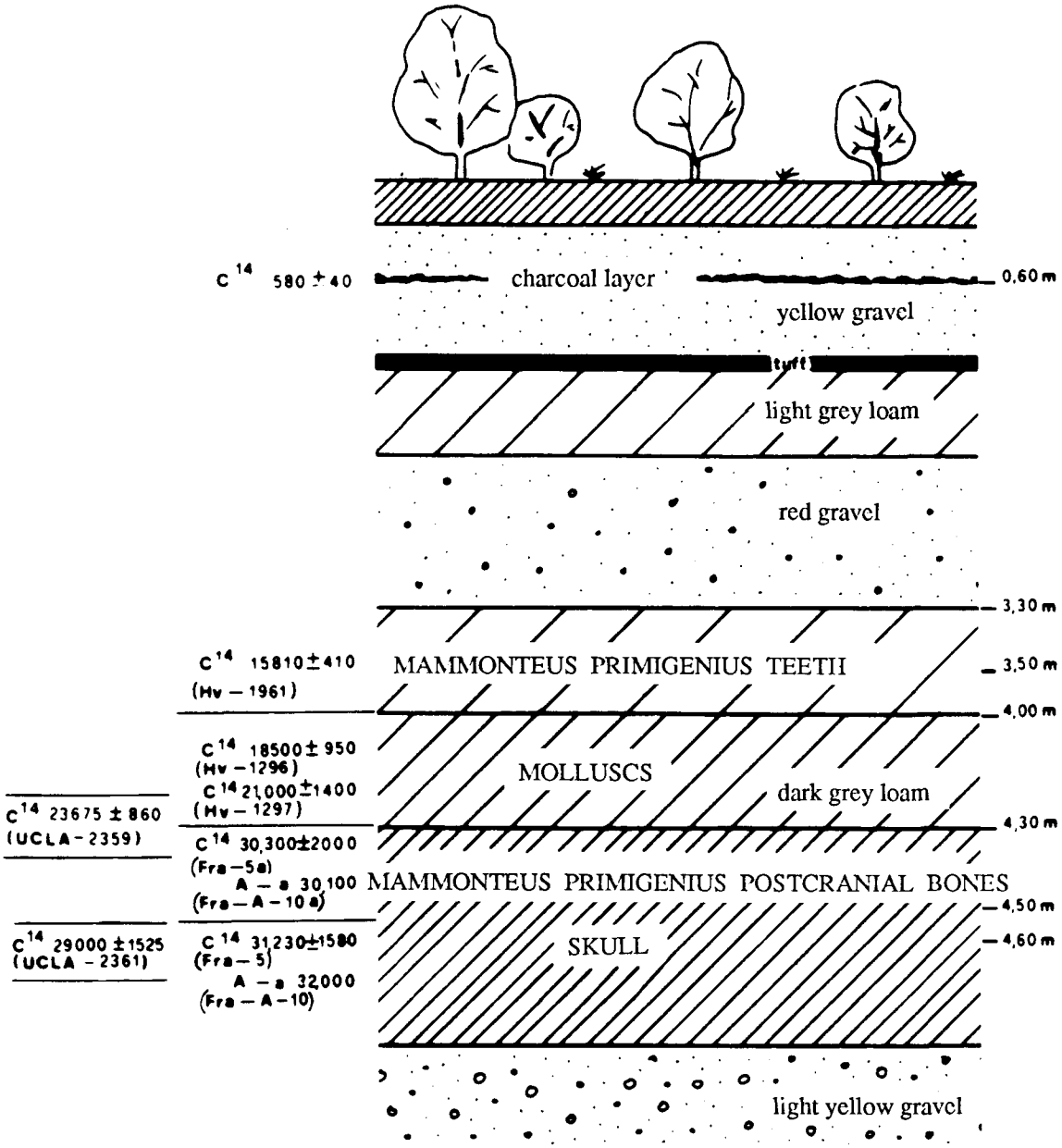


FIGURE 1

Bone Processing Procedures



Hv = Radiocarbon Laboratory Hannover
Fra = Radiocarbon Laboratory Frankfurt/Main
UCLA = Radiocarbon Laboratory Los Angeles

FIGURE 2

L'Homme de Néandertal, vol. 1, LA CHRONOLOGIE, Liège, 1988, pp. 117 à 120

OPTICAL DATING OF ARCHAEOLOGICAL SEDIMENT

by

E.J. RHODES * and M.J. AITKEN *

ABSTRACT

The new technique of Optical Dating, primarily applicable to unburnt sediment which has been exposed to sunlight during transportation by wind or water, is briefly described. The technique is compared to TL (Thermoluminescence) dating of sediments, to which it is closely related. The particular advantage of using zircon grains is indicated as well as the likely age range for the techniques in general, and expected archaeological applications.

INTRODUCTION

Luminescence Dating comprises the well-established technique of Thermoluminescence (TL) Dating together with the new technique of Optical Dating recently demonstrated by HUNTLEY, GODFREY-SMITH and THEWALT (1985), the latter being based on Optically Stimulated Luminescence (OSL) and seen as being primarily advantageous in application to unburnt sediment. For TL dating of burnt material the event being dated is the last heating in excess of about 400°C and for calcite it is the time of crystal formation. For sediment TL it is the last time at which there was substantial exposure to sunlight, eg during transportation by the wind before deposition. If OSL is used the necessary duration of exposure is at least an order of magnitude less than if TL is used; this gives the possibility of dating sediment that has had relatively brief exposure such as during transportation by flood water or while lying on the surface prior to burial by succeeding layers.

THE BASIC TECHNIQUE

Both types of luminescence represent the release of energy that has been stored in the crystal lattice of the mineral concerned (eg quartz, feldspar, zircon, calcite). This storage is in the form of electrons that are trapped at defects in the crystal lattice and when released (by heat in the case of TL; by light in the case of OSL) some of the de-trapped electrons find *luminescence centres* thereby causing light to be emitted (these centres are usually formed by impurity atoms present in the crystal lattice).

* Research Laboratory for Archaeology and History of Art, 6 Keble Road, Oxford OX1 3QJ, England.

The amount of light emitted is proportional to the number of trapped electrons (to a good approximation). These latter are the result of exposure to nuclear radiation and there is a weak flux of this from the radioelements (potassium-40, thorium and uranium) naturally present in all sediment. The trapped electrons build up to an equilibrium level during geological times and an essential requirement for dating is that the number of trapped electrons is reduced to near zero at the time of the event being dated; by sunlight in the case of sediment dating.

The important difference betwen OSL and TL, and the real advantage of OSL over TL is that in OSL, light from a laser source is used to release electrons from only those traps which are sensitive to light. Hence, the signal measured is produced by electrons from the most easily light-bleachable traps. These are the traps which are emptied first on exposure to sunlight during deposition. For sunlight to reduce the signal in quartz to a few percent of its original value, it takes only a few hundred seconds in the case of OSL, while it takes tens of hours in the case of TL. It is this rapid bleaching which ensures the zeroing of the OSL of sediments, allowing dating of sediments which have had only a brief exposure to sunlight during deposition. For further details see HUNTLEY *et al.* (1985) and AITKEN *et al.* (1986).

The basic equations for both TL and OSL are

$$\text{Age} = \frac{\text{Palaeodose}}{\text{Annual Radiation dose}} \qquad (1)$$

and

$$\text{Palaeodose} = \frac{\text{Accrued luminescence}}{\text{Luminescence per unit dose of radiation}} \qquad (2)$$

The ACCRUED LUMINESCENCE, more usually referred to as the 'NATURAL', is the luminescence observed, by means of a photomultiplier, when the sample is heated (for TL) or exposed to a laser beam (for OSL). The LUMINESCENCE PER UNIT DOSE, or SENSITIVITY, is evaluated by measurement of the 'ARTIFICIAL' signal (TL or OSL) observed after exposure of the sample to radiation from a calibrated radioisotope source. Thus the PALAEODOSE represents the total dose that the sample must have received since the traps were last emptied; alternative terminology is EQUIVALENT DOSE, ARCHAEOLOGICAL DOSE, ACCRUED DOSE, etc.

The ANNUAL DOSE, or DOSE-RATE, is determined by both laboratory and on-site measurements. For on-site measurements we use (i) TL capsules and (ii) a portable gamma spectrometer. A TL capsule, usually of copper, contains a highly-sensitive TL powder and is buried in the soil in a situation that represents that of the sample as closely as possible; it is about 8 mm diameter and 40 mm long. Minimum burial time is a few months, a year being preferred. The portable gamma spectrometer measurement time is only an hour (per level).

The annual dose is influenced by the water content of the sediment during antiquity. Though an upper limit to the effect is obtained by measuring the saturation water content and the present day value can be measured, there is a degree of uncertainty about the situation in the past and at some sites this may significantly limit the accuracy attainable.

Laboratory measurements by thick-source alpha counting combined with gamma spectrometer determination of relative proportions of radioisotopes (allowing for identification of disequilibrium) are made.

For further information refer to AITKEN (1985), WINTLE and HUNTLEY (1982), MEJDAHL (1986) and BERGER (1986).

AGE RANGE

For quartz, the age range is dependent on the luminescence characteristics of the sample and the radioactivity of the environment. The upper limit is not yet firmly established but certainly it reaches to 100,000 years. The lower limit for sediment dating is set by the effectiveness of the zero setting and the sensitivity of the sample. This is expected to be around 1,000 years.

ZIRCON DATING (SUTTON and ZIMMERMAN, 1976; TEMPLER, 1986)

The levels of thorium and uranium in zircon are several hundred parts per million and consequently the annual dose for a grain of 0.1 mm or more is dominated by the internal contribution. This means that uncertainty about water content and other environmental factors (eg geochemical leaching and radioactive disequilibrium effects) are relatively unimportant. This removes an important source of systematic error. However the technique is a much more difficult one than dating by conventional TL or OSL, and so far its success has been demonstrated only for zircon grains extracted from pottery, bricks and lava. Nevertheless there is good prospect that it will shortly become available for sediment. The technique involves the manipulation of single grains and so it is to be expected that it will not be applicable to very fine grained sediments. About 100 grains are required; these have to be extracted and identified using only a dim red light (to avoid bleaching of the 'natural') and it is only worth attempting to use this technique for sediments known to be fairly rich in zircon.

ACCURACY AND APPLICATION

The accuracy attainable, as for TL dating of sediments, is currently in the range 5-10% of the age (and in adverse conditions it is worse), though zircon dating may prove to be more accurate. Obviously, because of this accuracy limitation the technique is not necessarily the best one to use. However for sites beyond the range of radiocarbon, the technique will hopefully prove to be an important new dating tool.

Because of the necessity to sample the sediment without exposure to light and to make on-site radioactivity measurements, samples are usually collected by laboratory staff. Depending on the number of levels sampled the time taken is usually less than one day. About two kilograms of sediment are removed, an auger hole of 0.3 metres depth and 65 mm diameter being made. If possible, a dosimeter capsule (as mentioned above) is left buried.

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DATATIONS PAR LA THERMOLUMINESCENCE DE GISEMENTS MOUSTERIENS DU SUD DE LA FRANCE

par

H. VALLADAS [1], J.M. GENESTE [2], L. MEIGNEN [3], P.J. TEXIER [4]

La datation par la thermoluminescence (Réf. 1) a été appliquée à des silex chauffés provenant de sept gisements moustériens du sud de la France, attribués au Würm ancien (Réf. 2): l'abri inférieur du Moustier, le gisement de plein air de Fonseigner (Dordogne), l'abri du Brugas, le gisement de plein air de loton, la grotte de la Roquette II (Gard), l'abri des Canelettes (Aveyron) et celui de Pié-Lombard (Alpes Maritimes). Au total, une soixantaine d'échantillons ont été datés, dont 34 ont été récoltés, au cours d'un sondage récent, dans la partie supérieure de la séquence stratigraphique du Moustier attribuée à la fin du Würm ancien: 3 silex proviennent de la couche K (outillage du Périgordien inférieur mélangé à des pièces moustériennes altérées par la gélifraction, qui pourraient avoir pour origine les niveaux moustériens sous-jacents), 4 des niveaux J5 à J1 (Moustérien typique), 1 du niveau I3 (Moustérien à denticulés), 24 des niveaux H9 à H1 (Moustérien de tradition acheuléenne, type B), et 2 seulement des niveaux G4 à G1 (Moustérien de tradition acheuléenne, type A), pour lesquels de nouvelles datations sont en cours. Jusqu'à présent, les couches inférieures (A à F) n'ont pas livré de silex chauffés.

Un seul niveau des autres gisements a été daté, sauf dans le cas de Fonseigner et de la Roquette.

Les résultats obtenus et leur discussion sont présentés en détail par ailleurs (Réf. 3, 4 et 5). Les âges moyens et leur erreur (statistique plus systématique) obtenus pour chaque site sont portés dans le tableau 1.

Au Moustier, les couches G à K sont datées entre environ 55.000 et 40.000 ans BP. En raison du nombre insuffisant de datations pour la couche G, il n'est pas possible de savoir si l'occupation de l'abri a été continue pendant les ≈10.000 ans séparant le dépôt des couches G1 et H1. Les résultats obtenus pour les couches H à K suggèrent qu'elles se sont déposées

1 Centre des Faibles Radioactivités, Laboratoire mixte CNRS-CEA, Avenue de la Terrasse, 91198-Gif-sur-Yvette Cedex, France.

2 U.A. 133 du CNRS, Direction des Antiquités préhistoriques d'Aquitaine, 26-28, place Gambetta, 33074 Bordeaux Cedex, France.

3 CRA du CNRS, Sophia Antipolis, 06565-Valbonne Cedex, France.

4 CRA du CNRS, Sophia Antipolis, 06565-Valbonne Cedex, France.

en un temps relativement court, 6.000 ± 3.000 ans. Compte tenu des erreurs, l'inversion des âges pour les couches K (42.600 ± 3.200) et J (40.300 ± 2.600) n'est pas significative. Comme la couche K contient des vestiges moustériens et chatelperroniens, l'âge obtenu peut être attribué à l'une ou l'autre de ces industries.

Les autres gisements sont placés entre 70.000 et 48.000 ans BP.

Le faciès lithique découvert dans les différentes couches est indiqué dans le même tableau. On constate qu'il n'y a pas de corrélation marquée entre l'âge des gisements et les faciès lithiques qu'ils ont livrés. Selon nos résultats le Moustérien typique et le Moustérien charentien ont pu coexister dans le sud de la France entre 65.000 et 40.000 ans BP. Pour les deux gisements de Dordogne (Le Moustier et Fonseigner) les âges obtenus sont compris entre 55.000 et 40.000 ans BP. Durant cette période le Moustérien de tradition acheuléenne, le Moustérien typique et le Moustérien à denticulés ont pu être contemporains. Dans ces deux gisements, la succession des faciès a été relativement rapide. Le fait que les différents faciès aient pu être contemporains est en accord avec les résultats de l'étude des gisements moustériens du sud de la France (Réf. 16 et 17).

La datation d'autres gisements moustériens est nécessaire à une meilleure connaissance de l'histoire des différents faciès lithiques.

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TABLEAU 1

Ages moyens des gisements moustériens

Gisement	Couche	Faciès moustériens	Nombre échant.	Age moyen [1] 10^3 ans
Le Moustier (réf.6,7,8)	K		3	42,6±3,2
	J5 à J1	Moustérien typique	4	40,3±2,6
	I3	Moustérien à denticulés	1	40,9±5,0
	H9 à H2	MTA [2] type B	20	42,5±2,0
	H1	"	4	46,3±3,0
	G4	MTA (type A)	1	50,3±5,5
	G1	"	1	55,8±5,0
Fonseigner (réf. 9)	D Sup.	MTA (type A)	1	50,2±5,3
	D moyen	Moustérien typique	1	52,8±5,5
	E	Moustérien typique	1	56,4±6,8
Brugas (réf.10)	4	Moustérien charentien (type Quina)	3	63,0±5,8
Ioton (réf. 11)	Ag	Moustérien charentien (type Quina)	7	48,0±3,0
La Roquette II (réf. 12)	2 et 3	Moustérien charentien (type Quina)	6	57,2±4,3
Les Canalettes (réf. 13)	2	Moustérien typique	3	73,5±6,0
Pié-Lombard (réf. 14)	4	Moustérien typique	2	70,0±7,7

(1) L'erreur est calculée selon AITKEN (1976)

(2) Moustérien de tradition acheuléenne.

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THE IMPLICATIONS FOR MIDDLE PALAEOLITHIC CULTURE HISTORY OF RECENT ATTEMPTS AT RADIOMETRIC DATING

by

R. Esmée WEBB *

ABSTRACT

A considerable number of attempts have been made to apply various radiometric techniques, in particular U-series and TL, to that part of the later Middle and early Upper Pleistocene beyond the reach of 14-C dating. Many of the ages obtained relate to Middle Palaeolithic industries or the hominids we assume made them. While undoubtedly many of these datings will come to be revised in future as our understanding of the technical problems involved in these dating techniques evolve, nonetheless enough dates now exist for us to re-examine the chronological pattern of cultural change they suggest. An attempt will be made to present an overview of the corpus of dates already published and their implications for the thorny, if ancient, question of the meaning of the patterned technological variation found in Middle Palaeolithic assemblages, particularly from deeply-stratified sites.

INTRODUCTION

In the late 1960s the Middle Palaeolithic was a vibrant research topic. Excavations had just finished at Combe Grenal, were still continuing at Pech de l'Azé, both in the Dordogne, and the debate over Mousterian variation had just broken over a bemused world (BINFORD and BINFORD, 1969). However, in retrospect it seems that since the early 1970s, specifically since the Sheffield conference published in 1973 as *The Explanation of Culture Change* (BINFORD, 1973; BORDES, 1973), Middle Palaeolithic research has lost its impetus. It is true that excavations have continued at major sites such as the Abri Vaufrey, Dordogne (RIGAUD, 1982), but few really major research papers have been published on the archaeology of the early Upper Pleistocene, papers that really set the archaeological world talking in the way it is *still* discussing the Bordes-Binford debate (BORDES, 1981; DENNEL, 1983a; COLLINS, 1986; GAMBLE, 1986), and the period has become somewhat the Cinderella of Prehistory. Of course archaeology is as prone to fashions as any other subject. In the 1970s attention was caught by finds of early hominids in Africa, that

* University of London, Department of Extra-Mural Studies, 26 Russell Square, London WC1B 5DQ, England.
Present address: Centre for Prehistory, University of Western Australia, Nedlands WA 6009, Australia.

research has now slowed down for good reasons not unconnected with political instabilities in eastern and southern Africa. Now the climate is changing again. This is the second major meeting to be organised on the Middle Palaeolithic and Neandertals in 1986, the first was a workshop held at Albuquerque in April. In 1987 Paul Mellars is organising in Cambridge a colloqium on the origins of modern man. Both the apparent desuetude into which the Middle Palaeolithic fell in the later 1970s and the present revival of interest in the period are due to the same factors. As the impact of deep sea oxygen isotope research began to make itself felt a decade ago (SHACKLETON, 1977), it was realised that the geological framework we had worked within for so long was simply inaccurate due to the inadequacies of the fragmentary terrestrial record, but we had no other framework with which to replace it. However, the 1980s are seeing a determined effort to try to fit the scraps of terrestrial record to the wiggles in either the ocean ooze (DUCHADEAU-KERVAZO and KERVAZO, 1983) or long pollen cores (WOILLARD, 1978), or both (WOILLARD and MOOK, 1982), and to provide the new complicated Pleistocene with a reliably dated timescale. The aim here is to draw some preliminary conclusions from how this new timescale affects our ideas on Middle Palaeolithic culture process.

Through a reasonably systematic literature search, those radiometric age determinations which purport to relate to archaeological assemblages which are either definitely considered to be Middle Palaeolithic, or which can be attributed on geological or vegetational grounds to either the penultimate or the last glaciation, or the intervening interglacial have been assembled. However, no claim is made that the information shown graphically in Figure 1 is anywhere near comprehensive, leaving aside any new ages announced at this meeting, but it is sufficient to suggest some major revisions of Middle Palaeolithic culture history may be called for. The dating techniques used include thermoluminescence (TL), Uranium-series and Electron Spin Resonance (ESR). Radiocarbon as is well-known is only relevant to dating the timing of the Middle to Upper Palaeolithic transition (LEROI-GOURHAN, 1984). Plenty of radiocarbon dates exist on Middle Palaeolithic material, the radiocarbon database I update annually now has nearly 150 such dates, but most of them are not worth the paper they were printed on, let alone the time and money they cost to produce. The application of newer techniques to sites already dated by radiocarbon has shown this clearly (SCHWARCZ and SKÖFLEK, 1982).

Perhaps this is the place to suggest that some means of publishing at least the bare essentials of ALL archaeologically relevant dates, with a bibliographic reference, in some journal which most archaeologists at least glance at would be very useful. *Archaeometry* would be a suitable place for such a check list. At the moment far too many dates made using techniques other than radiocarbon sink without trace because they appear in non-archaeological specialist journals.

MIDDLE PALAEOLITHIC CHRONOLOGY

Despite the considerable problems inherent in the terrestrial record it does appear to be possible to correlate, more or less, the familiar Riss/Würm sequence to both the ocean and the pollen record (LEROI-GOURHAN, 1983; HAESAERTS, 1985). The picture that is emerging is as follows. Riss III at least can be assumed to date to stage 6, about 200-130,000 BP. It is generally accepted now that the last (Riss-Würm or Eem) interglacial is represented by stage 5e, 130-120,000 BP. Würm I, therefore, probably comprises stages 5d-5a, possibly also 4, about 120-70,000 BP, while Würm II comprises stages 4 and the early part of 3, 80-35,000 BP; the Würm II/III interstadial, which appears to coincide with the Middle to Upper Palaeolithic transition in Western Europe, would correlate with pollen stage les Cottés or Hengelo 37,000 BP (LAVILLE, RAYNAL and TEXIER, 1984, 1986). This schema fits the known terrestrial record quite will given our present limitations of knowledge but will no doubt be subject to further revision in the light of future research (DENNELL, 1983b). It suggests that BORDES' (1961) timescale for the Mousterian is

relevant only to the latter half of the Middle Palaeolithic. Actually, it is now apparent that such a correlation has been implicit since before the deep sea data became available. The warm oscillations which probably correlated with stages 5c and 5a show up clearly at Combe Grenal (LAVILLE, 1973), while it has long been recognised that Würm I faunas represented milder more forested conditions than Würm II ones (BORDES, 1972). It seems we must accept RUDDIMAN's view (1977) that it was not until stage 4, Würm II times, that terrestrial glaciation made its presence felt in Europe.

These correlations have considerable culture-historic implications. BORDES originally defined five major distinctive variations on the Mousterian theme (1961). Many attempts to clarify and explain these variants have been made by BORDES himself (1977, 1981) and others (MELLARS, 1969; BINFORD, 1973; ROLLAND, 1977; CALLOW and WEBB, 1980) without great success. However, certain tentative conclusions can be drawn from this work. The most distinctive variants are the Quina and Denticulate Mousterian and the evolved Mousterian of Acheulean Tradition (MTA), while the so-called Typical Mousterian is the lest discrete and may even be a catch-all category for assemblages which cannot be assigned to other variants (CALLOW and WEBB, 1980; BORDES, 1981). Bordes preferred a sociocultural explanation for the difference between the variants. However, MELLARS (1969) attempted to demonstrate the presence of chronological patterning in southwestern France with Charentian (Quina or Ferrassie) assemblages overlain by MTA material in certain Périgordian cave sites which preserve complicated and lengthy sequences. Recent debate in *Nature* has revived the question of contemporaneity or sequentiality in the later Würmian Mousterian (ASHTON and COOK, 1986; MELLARS, 1986a and b). While it is true that considered individually those Périgordian sites which contain both Charentian and MTA assemblages do exhibit the sequence Mellars proposed 20 years ago, his argument has always ignored the geological evidence (LAVILLE, 1973, 1975; LAVILLE, RIGAUD and SACKETT, 1980; LAVILLE, RIGAUD and TEXIER, 1986). It is beyond doubt that caves and rock shelters in this region with long sequences of deposits exhibit discontinuities which are associated with pedogenic phenomena, whether these soils relate to non-glacial conditions, how much erosion has taken place and how long the discontinuities in the different sequences lasted are slightly different questions.

The crux of Mellars' reformulation of his argument (1986a) is that the correlations proposed between these soils at different sites are unproven and irrelevant. A similar argument has been put forward by REYNOLDS (1985). While there are considerable problems with LAVILLE's scheme (1973, 1975), some of the correlations he proposed do seem to be supported by pollen analytical and faunal information at the individual sites. The techniques of deriving pseudoclimatic information from sedimentological data have been demonstrated by other sedimentologists working in both adjacent caves (FARRAND, 1975) and adjoining areas (BUTZER, 1981) to produce patterns they consider analogous to those outlined by Laville. It may well be that his scheme is due for serious revision, but his general correlation of pedogenic phenomena may well survive the test of scepticism. It is after all possible to correlate his synthetic paraclimatic sequence with the oxygen isotope record. The fit between the two data sets is not perfect (LAVILLE, RAYNAL and TEXIER, 1984), has already been revised (LAVILLE, RAYNAL and TEXIER, 1986) and no doubt will be again, but it is sufficiently good to suggest that more credance must be placed in the geological record than Mellars is prepared to admit.

Rather than sterile arguments based on a comparison of one or two specific sites which may well not be representative, a wider view needs to be taken. Sites are now being reported which suggest that the Middle Palaeolithic has its roots in the cultural traditions of the late penultimate glaciation, 200-150,000 BP, and that even then more than one technical variation existed. For northern France TUFFREAU (1979) would include the artefacts from Biache-Saint Vaast (Pas de Calais) within the Typical tradition, but the site is Saalian and possibly 200-150,000 years old, on the basis of a single Uranium date. Other sites in this area are less well dated but there is evidence for a Ferrassie facies at Champroisy

(TRUFFREAU *et al.*, 1981) at about the same time. There is plentiful evidence for the MTA at sites like Epouville and Goderville (Seine Maritime) traditionally assigned to Würm I but probably dating to the beginning of stage 4, 80-70,000 BP (FOSSE, 1982). This is relatively late but considerably earlier than both the traditional and recently produced TL dates (see below) for the 'cave' MTA of the Dordogne.

In the Dordogne both the Quina and MTA traditions appear to have been present by 150,000 BP. At Les Tares (RIGAUD and TEXIER, 1981), an open air site attributed on geological grounds to the late Riss or stage 6, since it was found under a well-developed palaeosol, an industry was recovered having both MTA and Quina affinities, while at the Abri Vaufrey (RIGAUD, 1982) a long cave sequence terminates with a Quina assemblage attributed to early Würm I, possibly stage 5d. These ages are concordant with the age of 100,000 BP announced for Tata (SCHWARCZ and SKÖFLEK, 1982), associated with another Quina industry. Beneath the Quina level at Vaufrey at least 6 archaeological horizons were found comparable to the Typical Mousterian but considered to be of Rissian age. This material is presumably of approximately the same age as the southern Acheulean in the lowest complex at Combe Grenal (BORDES, 1972). Dates for these levels at the Abri Vaufrey fall in the range 200-100,000 BP. Samples were dated by Uranium and TL and, as at so many other sites, the ages produced by the two techniques are not entirely in agreement with each other (RIGAUD, 1982). However, they do indicate the extreme antiquity of the Quina variant at this site. There is also a series of concordant dates for la Chaise-de-Vouthon (Charente) suggesting that the Abri Suard was in use at least during the period 200-100,000 BP, while the Grotte Bourgeois-Delauney was occupied about 150-100,000 BP (SCHWARCZ and DEBENATH, 1979; RAE and IVANOVICH, 1986; RAE, IVANOVICH and SCHWARCZ, 1987). When the site was thought to be of Würmian age the associated industry was considered to be MTA but it has now been reassigned to the terminal Acheulean (DEBENATH, 1974). RENAULT-MISKOVSKY (1986) has recently attempted to correlate the well-known palynological record of the Mediterranean region to the oxygen isotope record. One can infer from her work that in Provence variants of the Typical and possibly the Denticulate Mousterian survived late into stage 3 at sites like Hortus (Hérault) (de LUMLEY, 1972), la Calmette (Gard) and les Ramandils (Aude) (de LUMLEY, 1969), all possibly dating to about 60-40,000 BP.

These data would suggest that not only the TL dates from Combe Grenal (BOWMAN and SIEVEKING, 1983) and Pech IV (BOWMAN *et al.*, 1982) but also the recently reported dates from le Moustier (VALLADAS *et al.*, 1986) are all rather younger than might have been expected, particularly since the breccia in Pech I, thought by BORDES (1972) to correlate to the deposits in Pech II, has been dated to 140-110,000 BP (SCHWARCZ and BLACKWELL, 1983). However, it seems premature to reject any of them categorically on those grounds alone. Considerable difficulties have been noted in obtaining reliable TL dates from burnt flint (BOWMAN, 1982). Those obtained often differ markedly from dates based on other isotopic decay sequences (SCHWARCZ, 1980; DEBENHAM and AITKEN, 1984; DEBENHAM, 1985; AITKEN, HUXTABLE and DEBENHAM, 1986). It may well be that, as with radiocarbon dating, it will take archaeology at least a decade to assess the validity of the ages these new techniques produce.

The only good evidence for MTA in Britain is the so-called bout-coupé bifaces found within a +7 m beach (SHACKLEY, 1977) thought to correlate with the Eemian high sea level. They are likely to be a little older than the raised beach deposits in which they are found, possibly 150,000 BP. A flake assemblage of clear Middle Palaeolithic affinity has recently been excavated from Pontnewydd, Dyfed (GREEN, 1984, 1986), which may date to 220-170,000 BP, but both the material dated and the artefacts have been redeposited. Many age estimations have been made for this site using the Uranium and TL techniques (DEBENHAM and AITKEN, 1984; RAE, DEBENHAM and IVANOVICH, n.d.). Considerable discrepancies were noted between the ages produced by different techniques when applied to samples supposedly of the same age. The problems encountered here

illustrate the difficulties inherent in interpreting radiometric age determinations. At la Cotte de Saint Brelade in Jersey (Isles Normandes) an industry dominated by notches and denticulates but lacking bifaces was found below a palaeosol dated by TL to 250-200,000 BP (CALLOW, 1986). This might be compared with the Tayacian and High Lodge type of assemblages, if only the latter were published and its approximate age known! Higher up the la Cotte sequence in Weichselian deposits is a Typical Mousterian rich in racloirs, which may date back to stage 4.

Elsewhere in Europe few sites have yet been radiometrically dated apart from Tata (Hungary) where U-series dates on travertine deposits overlying the archaeological layer suggest that the artefacts, which are considered to be similar to the Charentian Mousterian, were deposited about 100,000 BP (SCHWARCZ and SKÖFLEK, 1982). Carefully planned programmes of radiometric dating are urgently needed in central and eastern Europe if we are to begin to understand the systematics of culture process rather than merely describing as a series of discrete phenomena the material recovered. The stratigraphy at many of the key sites is still available for study, its re-examination and dating should be given top research priority.

CONCLUSIONS

On the basis of the dates briefly referred to above it seems reasonable to suggest that the cultural systematics of the early Upper Pleistocene are far more complicated than has been generally appreciated. They seem to indicate that by the end of the penultimate glaciation, approximately stage 6 time, the Middle Palaeolithic was well-developed, particularly in France, and that all the most discretely characteristic variants of the Mousterian were present in fairly developed form. Although, if the Uranium dates from the Grotte du Prince can be accepted (SHEN, 1986), the earliest Middle Palaeolithic was contemporary with the latest Acheulean, which is not at all surprising. Figure 1 would suggest that Mellars' argument for a unidirectional chronological sequence in the Würmian Mousterian is, even if correct, only applicable to a very limited geographical area which may be untypical of Europe as a whole. Both the MTA and Quina variants appear to have been present in France by at least 150,000 years ago. Even if they have not been found in the caves of the Périgord. Many of the French Middle Palaeolithic sites now tentatively dated to oxygen isotope stages 6 and 5 were open air occupations which present a simpler technological picture than do the later Mousterian cave sites, since the tools recovered appear to belong to a single tradition. It may even be that the Mousterian complex as defined by twentieth century archaeologists represents a unique aspect of the Middle Palaeolithic which relates more to the preservation of late assemblages in caves rather than to human behavioural or cultural differences. Moreover, the evidence on which BORDES based his formulation of the Mousterian complex hypothesis (1961, 1981) may also be specific to the mid Würm in Aquitaine, since Würm II sequences from cave sites in the Midi for example (de LUMLEY, 1969) present a simpler picture of multiple layers of a single variant in any given site.

The recently produced radiometric datings are beginning to help us build a new chronological framework for the Middle Palaeolithic, but at the moment they are not assisting in the clarification of culture-historic problems nor in the explanation of 'Mousterian variation'. If anything they have made matters worse since the picture appears to be becoming more complicated, with each Bordian tradition lasting for ever longer periods of time, which makes them even more difficult to explain in cultural or behavioural terms. Mellars is probably correct in his fundamental assumption that there was evolution within the Mousterian. LE TENSORER (1978) has demonstrated convincingly that the Quina variant evolved over time. However, the argument MELLARS has developed (1969) and reiterated (1986a and b) is insufficient to prove his case. Before we can tackle intelligently the problem of Middle Palaeolithic cultural variation we need to accumulate more data. Every effort needs to be made to build up a corpus of credible radiometric ages determined on multiple reliable

samples from unquestioned stratigraphic contexts. When such information has accumulated we may be able to tackle this thorny problem afresh.

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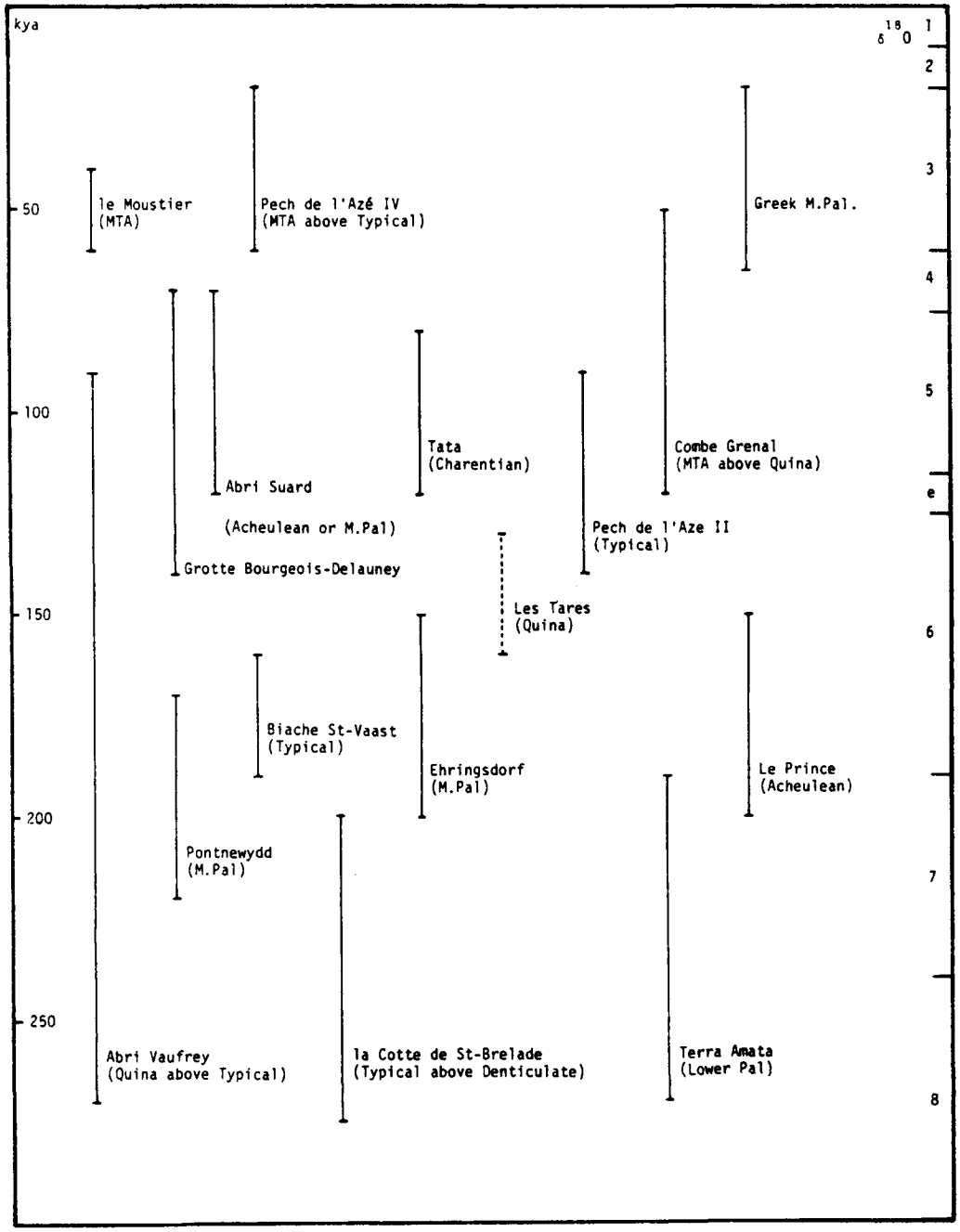

FIGURE 1

Chronological patterning in Middle Palaeolithic industries based on sites dated radiometrically

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DIRECT DATING OF NEANDERTHALIAN REMAINS AND ANIMAL BONES BY THE NON-DESTRUCTIVE GAMMA-RAY SPECTROMETRY: COMPARISON WITH OTHER METHODS

by

Yuji YOKOYAMA *, Christophe FALGUERES ** and Roland BIBRON *

ABSTRACT

A non-destructive gamma-ray spectrometry is used for the direct dating of fossil human bones and animal bones taken from several Neanderthalian and Mousterian sites in France, Italy and Spain.

1. For the Neanderthal child and adult remains from Fate cave (Finale Ligure, Italy), we obtained a U-Th age of 83 +35/–24 Kiloyears (ky) and a U-Pa age of 76 +18/–13 ky. These ages are in good agreement with the ESR ages of the two lower stalagmitic layers of this cave: 78 ± 9 ky and 78 ± 13 ky.

2. Animal bones from Tournal cave, Genay Breccia site (France) and Arbreda cave (Spain) are also dated. U-Th and U-Pa ages of these sites are respectively, 33 ± 8 ky and 33 ± 4 ky for Tournal cave, 82 +20/–16 ky and 75 ± 6 ky for Genay Breccia site, 85 +38/–28 ky and 83 +11/–9 ky for Arbreda cave.

1. INTRODUCTION

Recent developments of the gamma-ray spectrometry have made possible the determination of long-lived natural radionuclides such as U-238, U-234, Th-230 and Pa-231 (YOKOYAMA and NGUYEN, 1980, 1981a). This new technique does not need any chemical treatment and hence it is non-destructive. It is therefore particularly useful for the U-Th (and U-Pa) datings of very precious samples such as human fossil bones and was used to date the skull of Tautavel Man (YOKOYAMA and NGUYEN, 1981a,b).

Using this technique, we have dated the Neanderthalian remains from Fate cave in Northern Italy (GIACOBINI *et al.*, 1984). Animal bones of some mousterian sites are also dated with this method. In the present paper, the results of these datings are presented and compared with the results obtained with other methods.

* Centre des Faibles Radioactivités, UG/CFR, CEN de Saclay, 91190 Gif-sur-Yvette, France.

** Laboratoire de Préhistoire, UA 184 du CNRS, Institut de Paléontologie Humaine, 1 rue René-Panhard, 75013 Paris, France.

2. EXPERIMENTAL

A high purity germanium detector, ORTEC Gamma-X detector, is used with a micro-computor controled pulse height analyser, ENERTEC PC7182. The detector has a 9% relative efficiency and a resolution of 0.7 KeV at 63 KeV. The sample is counted for 1-5 weeks. Counting efficiencies are measured with mouldings made of a mixture of plaster and pitchblende. Activities of U-234 and Th-230 are determined from the gamma-rays emitted directly by these nuclides: 53.3 KeV and 67.7 KeV respectively. U-238 is determined from the gamma-rays of its short lived decay product Th-234: 63.3 KeV and 92.3+92.8 KeV. For the determination of Pa-231, gamma-rays of Th-227, Ra-223 and Ra-219 are used. Their energies are 269.4 KeV, 271.0 KeV and others (YOKOYAMA and NGUYEN, 1980, 1981b).

Figure 1 shows an example of gamma-ray spectra. The gamma-ray peaks used to the determination of U-238, U-234, Th-230 and Pa-231 are visible in this figure.

3. RESULT AND DISCUSSIONS

We dated Neanderthal child and adult bones from Fate cave (Final Ligure, Italy) and some animal bones from french and spanish Mousterian sites. Table 1 summarizes results.

3.1. Fate cave

G. Giacobini has identified human remains during a recent revision of the bone assemblage collected by G.B. Amerano in 1887-1888 from the Mousterian layers of the Caverna delle Fate (Cave of the Fairies), near Finale Ligure, Italy (GIACOBINI and LUMLEY de, 1983; GIACOBINI *et al.*, 1984). These human remains are a child frontal bone (Fate I), a child half mandible (Fate II) and an adult mandible fragment (Fate III).

A rapid preliminary gamma-ray measurement of each sample showed similar Ra-226/U-238 ratios: 0.51±0.14, 0.52±0.12 and 0.60±0.12 for Fate I, II and II respectively. This similarity suggests that their ages are virtually the same. Since the each sample alone was not sufficiently active, we decided to count them together. We obtained a U-Th age of 82 +35/–24 ky and a U-Pa age of 76 +18/–13 ky (the ages given in the text are rounded from the values given in Table 1). The good agreement between the U-Th age and the U-Pa age indicates that these samples were relatively well conserved and therefore we can place some degree of confidence in these ages.

Since these human remains are discovered from the old collection of the last century, it is impossible to know exactly their stratigraphic position in the cave deposit. These remains were taken in the corridor No. 3, where the deposits are inter-stratified by several stalagmitic layers. We have dated three principal stalagmitic layers by the ESR method. The details will be published elsewhere. We obtained an age of 40±12 ky for an upper layer (layer 2) and ages of 78±9 ky and 78±13 ky for two lower layers (layers 9 and 18) respectively.

The ESR ages of the layers 9 and 10 are in good agreement with the age of the human remains. This agreement permits to postulate that these human remains come from the lower part of the deposit in the corridor No. 3.

According to the morphological studies of these remains (GIACOBINI *et al.*, 1984), Fate I (child frontal bone) has the appearance of an archaic Neanderthal with a marked postorbital narrowing. Fate III displays also classical Neanderthalian characteristics with minor archaic features. The morphology of these two remains is in close agreement with our dating. The child half mandible, however, having several modern features, for example its

small permanent canine, resembles the Hortus Neanderthals. These "modern" features may be attributed to the proper characteristics of a Mediterranean Neanderthal population. This interpretation may be supported by our preliminaly gamma-ray dating of Hortus IV mandible, which suggests a similar age as that of Fate samples.

3.2. Arbreda cave

This cave is situated near Serinya (Gerona) in the North-East of Spain. Discovered in 1947 by M.A. Corominas, the cave is actualluy excavated by N. Soler. A deposit of 9 m thick successively contains from the top to the bottom: a Neolithic layer, an Epipaleolithic one, two Solutrean ones, two Gravetian ones, Aurignacian ones and Mousterian ones. Some charcoal samples from the Upper Paleolithic layers are dated by G. Delibrias. Their ages are ranged between 17 320 y BP and 25 838 y BP. Some animal bones from these layers are also dated by the gamma-ray spectrometry and the ESR method (YOKOYAMA *et al.*, 1987).

The Mousterian layers of this cave are remarkable by the abundance of lithic tools and fauna. We dated an animal bone from the bottom of these layers. The results (Table 1) show a U-Th age of 85 +38/–25 ky and a U-Pa age of 83 +11/–9 ky. Again, we found a good agreement between the U-Th age and U-Pa age.

3.3. Tournal cave

Tournal cave at Bize is situated at 20 km North-West of Narbonne. The excavations carried out under the direction of A. Tavoso permit to understand its extremely complex stratigraphy comprising wells and drains. The deposit of this cave contains a succession of Magdalenian layers, Aurignacian layers and Mousterian layers. According to the C-14 datings made by J. Evin, the Magdalenian layers have an age between 12 550±210 y BP at the top and 14 250±450 y BP at its bottom. A Mousterian layer is dated to be 33 650±1 258 y BP.

We report here the results of the dating of a Cervides bone (Table 1). We obtained a U-Th age of 33 000±8 000 y and a U-Pa age of 33 000±4 000 y. These ages are in good agreement with the C-14 age and also with the ESR age of the same bone: 38 000±10 000 y.

3.4. Genay Breccia site

This open air site is situated at 30 km North of Avallon (Côte-d'Or). It was discovered in 1834. The excavations carried out by J. Joly and J.J. Puiségur between 1953 and 1960 yielded Neanderthalian remains (JOLY, 1955). Its deposit successively contains from the top to the bottom: a Neolithic layer, a series of light yellow layers (layers 8-11), a series of brown layes (layers 5-7), a series of red layers (layers 3-4) and a series of fairly red layers (layers 1-2). The last two series are consolideted in a breccia. Most of archaeological materials, animal bones and the Neanderthalian remains come from the layers 3-4. These human remains are fragments of a skull and 25 teeth, belonging to the same individual.

We dated two fragments of animal bone, M1-25 and 12-4. The samples are taken from the layer of the human remains. Two samples are measured together. We obtained a U-Th age of 82 +20/–16 ky and a U-Pa age of 75±6 ky.

These ages correspond to the beginning of Würm in good agreement with the estimation of Father Joly, based on the malacofauna (PUISSEGUR, 1962) and microfauna (CHALINE, 1972). The archaic characters of the Neanderthalian remains of Genay (LUMLEY de, 1976, 1987) and the characteristic of Genay's industry (PAUTRAT, 1987) are consistent with these ages. The macrofauna (PATOU, 1987) and the flora (RENAULT-MISKOVSKY and HAKIM, 1987), however, suggest a cold climate, which is

in manifest conflict with a warm climate estimated from the malacofauna and microfauna. It seems therefore that the Neanderthal of Genay lived in a climatically fluctuated phase of the beginning of Würm.

4. CONCLUSION

The non-destructive gamma-ray spectrometry being capable to date with the two independent methods, U-Th one and U-Pa one, is a good tool for the dating of Neanderthalian sites.

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TABLE 1

Direct dating of human and animal bones by the non destructive gamma-ray spectrometry

	Fate Italy Man Mandibles	Arbreda Spain Animal Radius ?	Tournal France Cervidas Tibia	Genay France Animal n.d.
U(ppm)	3.68	17.3	23.3	8.37
U-234/U-238	1.189±0.223	1.096±0.207	1.007±0.118	1.068±0.121
Th-230/U-234	0.542±0.117	0.549±0.117	0.261±0.048	0.534±0.070
Th-230/Th-232	29	> 390	110	51
Pa-231/U-235	0.797±0.865	0.827±0.035	0.503±0.043	0.795±0.025
U-Th age (y)	82600^{+35300}_{-24300}	85100^{+38200}_{-25300}	32800^{+7600}_{-6900}	82000^{+19700}_{-15600}
U-Pa age (y)	75500^{+18300}_{-13100}	83000^{+10700}_{-8700}	33100^{+4300}_{-3900}	75000^{+6200}_{-5400}
Age (y) by other methods				
C-14	n.d.	n.d.	33650±1250	n.d.
ESR calcite	78000±9000	n.d.	n.d.	n.d.
ESR bone	n.d.	n.d.	38000±10000	n.d.

n.d.: not determined

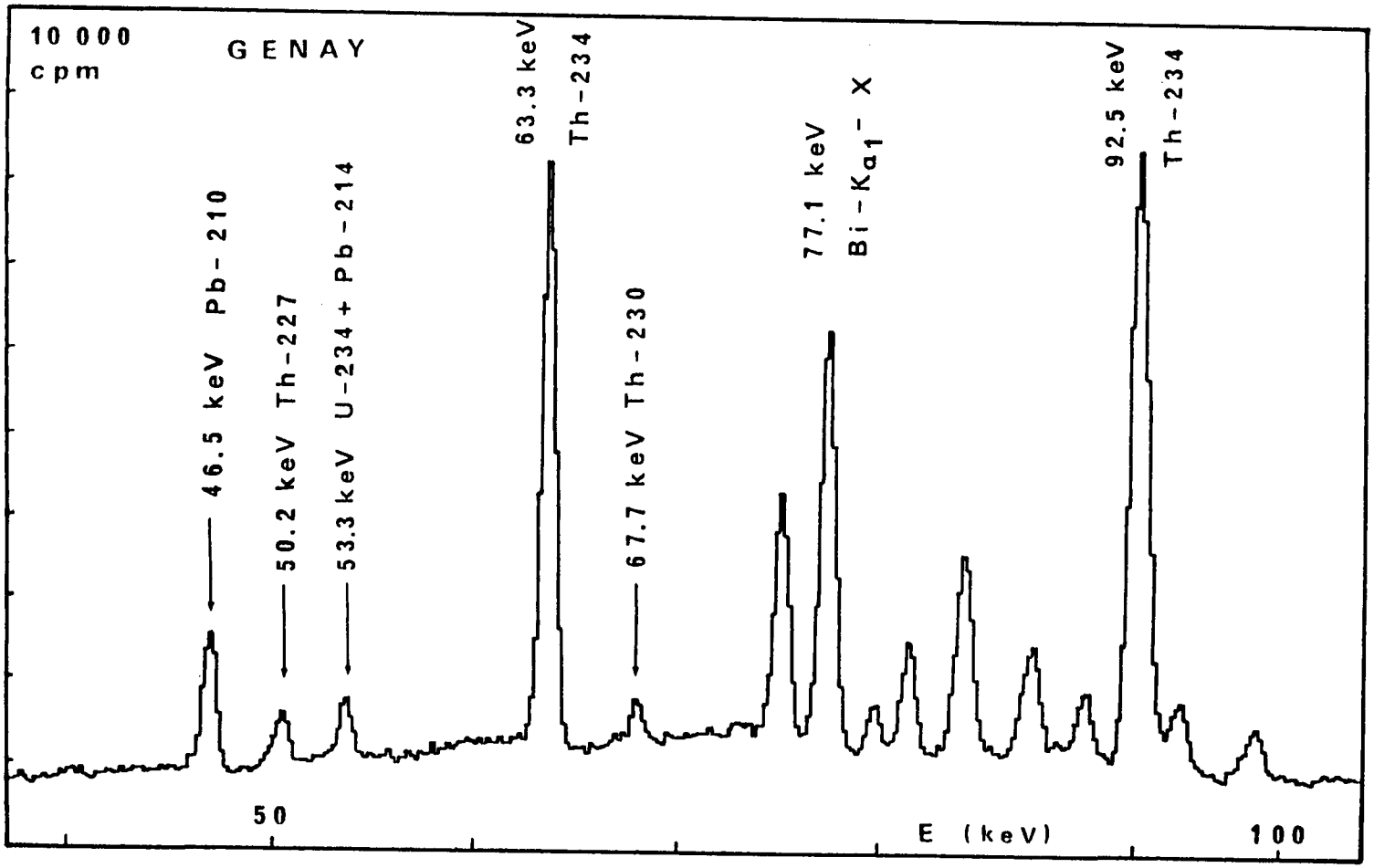

FIGURE 1

Gamma-ray spectrum of an animal bone sample taken from the Neanderthalian skull layer of the Brèche de Genay, Bourgogne, France (counting time: 19856 min.). In this figure, the gamma-rays emitted from Th-230, U-234, Th-234 (descendant of U-238) and Th-227 (descendant of Pa-231) are visible. For the determination of Pa-231, gamma-ray of higher energies are also used.

Dessin de Christian OTTE
Maquette : Ed. RUSINOWSKI