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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

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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.

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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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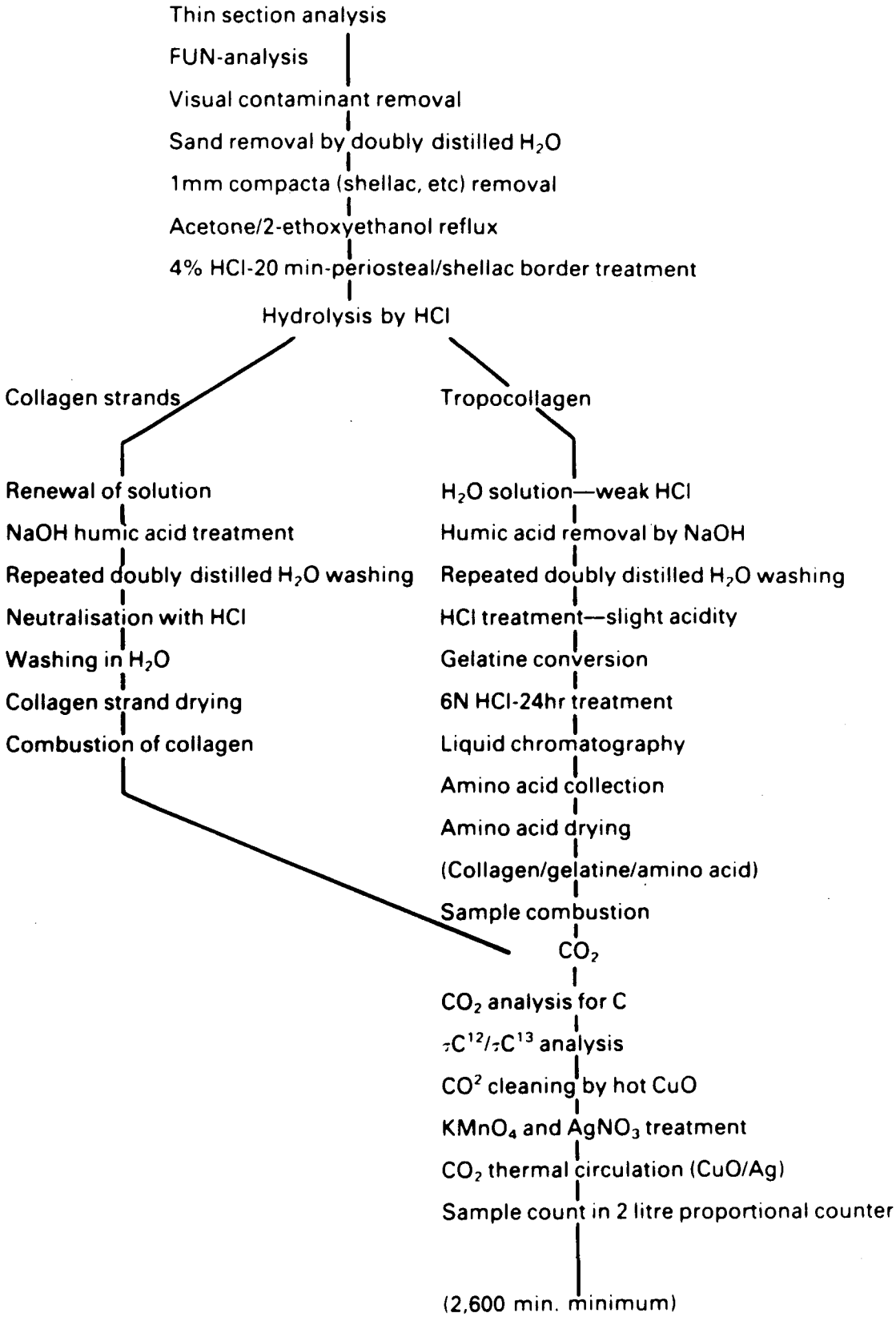
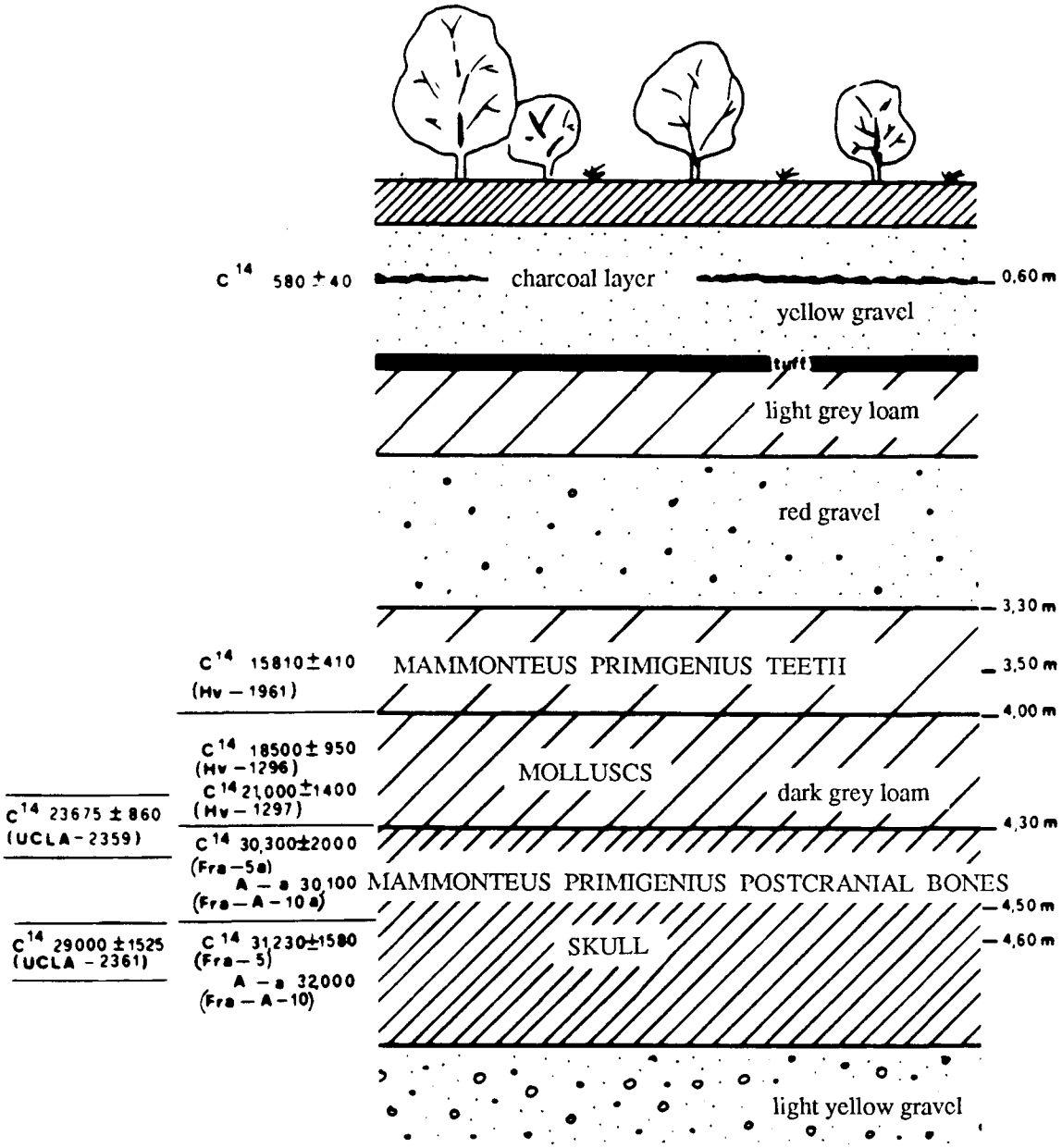


FIGURE 1

Bone Processing Procedures



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

FIGURE 2