

Improving the Accuracy of Radiocarbon Dates Using Annually Laminated Sediments

Abstract

Much like tree-rings, annual laminations (non-glacial varves) may be used to calibrate radiocarbon dates in terms of calendar years. The classic study of this type is that of Stuiver (1971) at Lake of the Clouds, Minnesota. Varve chronologies may also be used to resolve problems of interpreting radiocarbon dates from lake sediment profiles affected by influx of « old » carbon washed in from the catchment, a process which has been in operation in many areas since at least Neolithic times.

Most « conventional » radiocarbon dating of lake sediments is performed on whole samples, or on those from which only carbonates have been removed. The material dated thus still contains a mixture of carbon fractions derived from a variety of sources, each of which may possess different radiocarbon ages. The dates obtained therefore represent some kind of composite value, depending on the ages and relative contribution of each of the respective fractions.

The main approach adopted in order to try to overcome this problem is to date separate fractions of the sediments. On a simple (and therefore more economical) basis, these may be defined as the alkali soluble and alkali insoluble fractions, a practise which separates the sediment into the « humic » component, and the rest, both of which may still be mixtures.

A more exhaustive (but therefore *less* economical) approach is to define further fractions, and to distinguish rather more critically between, on the one hand, « conventional » dates, and those obtained from (a) any recognisable and sufficiently abundant macrofossils present in the sediment, (b) the purified humic fraction, (c) the undifferentiated organic residue of the sediment remaining after all other extraction, and (d) the lipids. Even this last fraction, however, contains a wide range of compounds which may have been produced in many different parts of the lake-watershed system, and which therefore may yield a date which has been performed on a mixture of carbon atoms of widely differing ages.

Modern techniques of organic geochemistry may then be used to address this aspect of the problem, and to divide the lipid fraction even further, first on the basis of what is known about the respective compounds synthesised

by terrestrial and aquatic higher and lower organisms, and second, of the $\delta^{13}\text{C}$ departure of various lipids, with lower values being associated with terrestrial materials, and high departures with carbon synthesized by bacteria at the sediment-water interface. Such fractions and sub-fractions might conceivably then be radiocarbon dated separately, using AMS dating, in order to address the question « Which (carbon) fraction (of the sediment) gives the radiocarbon date closest to the « true » (i.e. varve, calendar) age ? »

Results of previous investigations relevant to the above themes are reviewed, and a proposed framework for increasing the accuracy of radiocarbon dating of lake sediments is provided. Some preliminary results from studies of sediments in the Shropshire-Cheshire meres, a group of eutrophicated, lowland lakes in the UK, are also discussed.

Introduction

From a chronological point of view, the most important attribute of annually-laminated sediments is that they contain a record of the passage of calendar (ie sidereal) years. By definition, such laminations (or *varves*, Renberg, 1982) are composed of at least two laminae, each of which is produced by changing sediment quality, and perhaps also quantity, over the course of the seasons (O'Sullivan, 1983; Saarnisto, 1986, 1992; Simola, 1992).

If they can be accurately counted (and sometimes this is not so easy as would first appear – see below), the presence of varves therefore offers the investigator the prospect of a chronology which is both independent of the earth's magnetic field (or connected to it on only a very remote basis), and which is not dependent upon the determination of the rate of decay of radioactive isotopes. It is in fact a detailed archive of the history of processes in the lake itself, and in its catchment, so that using varve chronologies, such records may be both very accurately, and very precisely, dated. Indeed, to those of us initially trained in « pre-lamination » times, such dates sometimes appear almost too precise to be true (but are, in fact, extremely accurate – see Fig. 1).

Varved lake sediments, and the physical, chemical and biological information they include, are, by now, of course, very extensively used in palaeoecological studies (Renberg, 1982; Saarnisto, 1986, 1992; O'Sullivan, 1983). Again from the point of view of chronology, their main use has been in the calibration of other dating techniques, notably, in very recent sediments, ^{210}Pb dating (Appleby *et al.*, 1979; Oldfield, this volume), Holocene palaeomagnetism (Sprowl and Bannerjee, 1985; Zolitschka, 1991), and radiocarbon dating (Stuiver, 1971).

Previous work

One of the earliest modern studies of varved sediments was that based on Lake of the Clouds, Minnesota (Anthony, 1977; Craig, 1972; Swain,

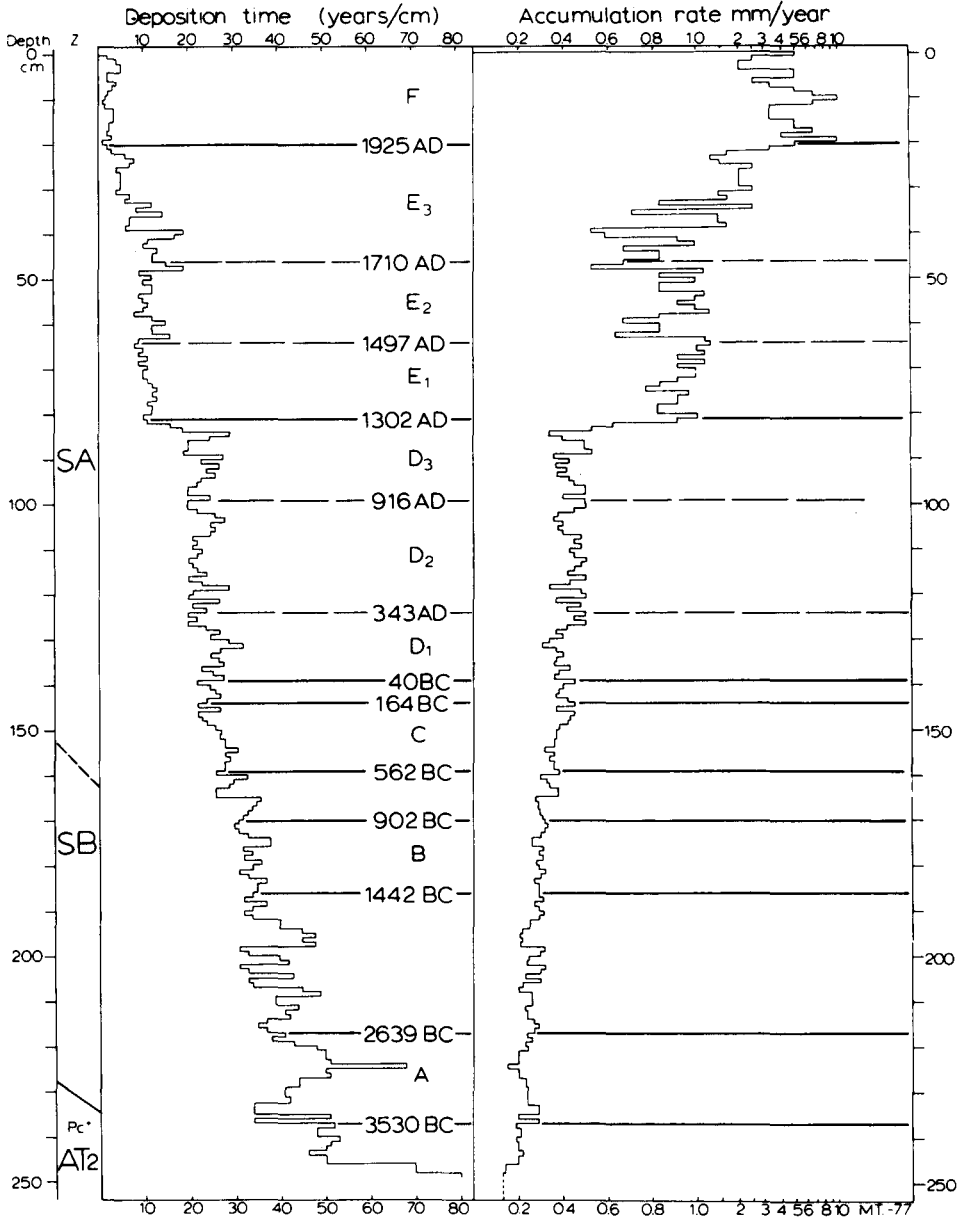


Fig. 1. Deposition time ($a\ cm^{-1}$) and accumulation rate ($mm\ a^{-1}$) from a core from Ahvenainen, South Finland (M. Tolonen, 1978b). Note the sharp increase in accumulation rate associated with the intensification of slash/burn in the catchment of the lake, dated by varve counting to A.D. 1302 precisely!

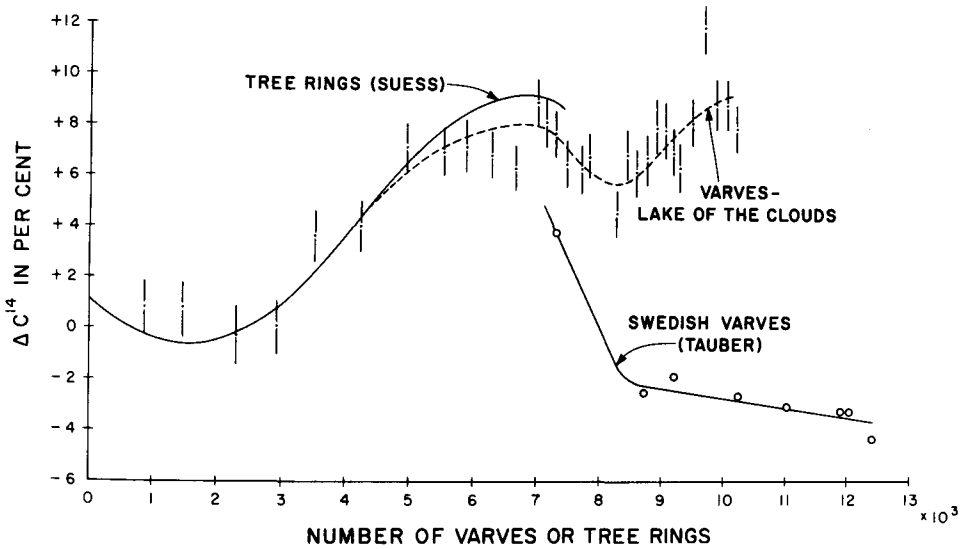


Fig. 2. Correlation between radiocarbon age and lamination counts for Lake of the Clouds, Minnesota (Stuiver, 1971).

1973). Here, Stuiver (1971) used lamination counts to calibrate the radiocarbon chronology for the last ten millennia (Fig. 2). For the first four, there is good agreement with the Bristlecone Pine calibration of Suess (1970), but beyond 4000 B.P., the dates obtained from the varves are significantly younger than the tree-ring based data (by as much as ca. 15%). Stuiver's results were also very different from those obtained by Tauber (1970) by dating material from Swedish *glacial* varves deposited in the 8th to 13th millennia B.P.

The tree ring calibration of radiocarbon dating has since, of course, been extended well beyond 10,000 B.P. (Stuiver *et al.*, 1986), and given high precision for more recent millennia (Pearson and Stuiver, 1986; Stuiver and Pearson, 1986). Calibration of the radiocarbon timescale using varved sediments has not developed at the same pace, and this may be the result of the kind of discrepancies just described. They may be explained by the observations that unlike tree-rings, lake sediments are composed of a mixture of materials, all of which may possess widely differing radiocarbon ages (Olsson, 1986), and that their radiocarbon activity is also much lower (Olsson, 1991). This makes the calibration of radiocarbon dating and other chronological techniques using varves a much more difficult proposition than using tree-rings, and the exercise by Stuiver referred to above has not often been repeated. An exception, for the early and middle Holocene, is, of course, the classic study by Geyh, Merkt and Müller (1971) of the sediments of the Schleinsee, southern Germany.

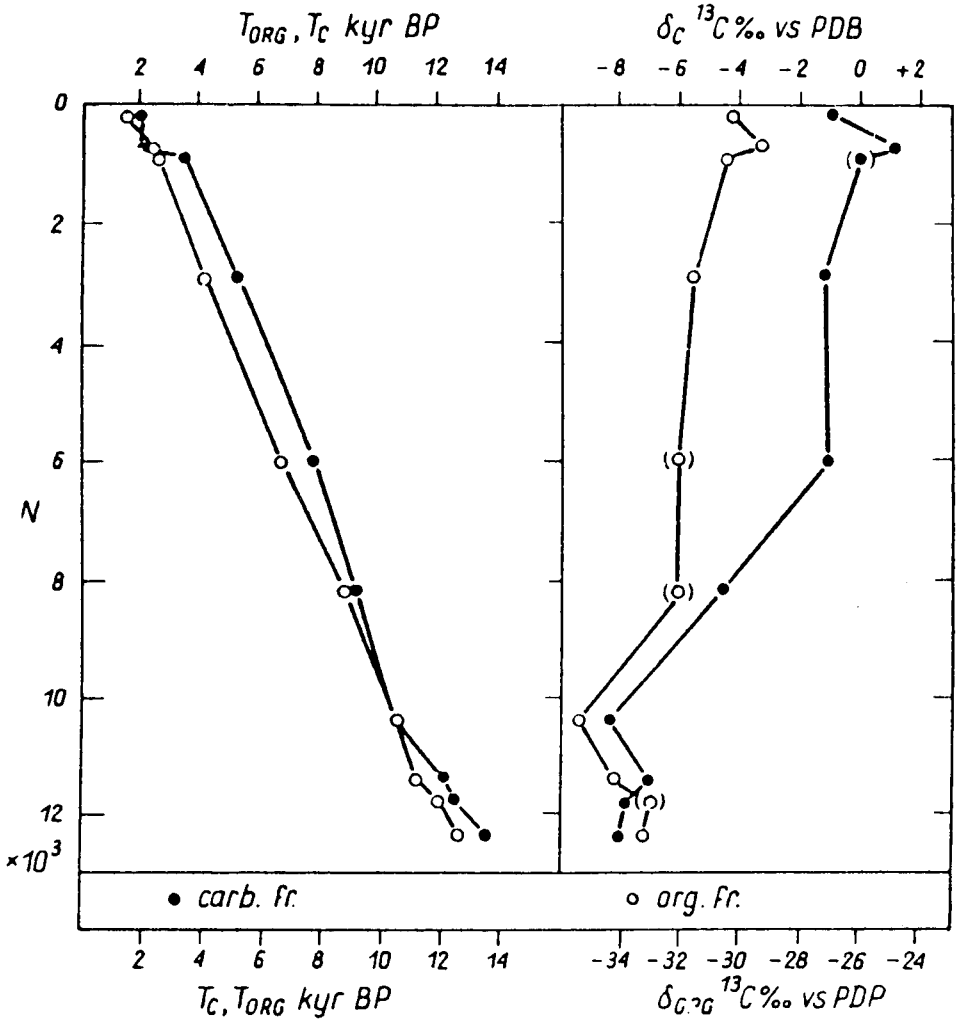


Fig. 3. Radiocarbon dates and ^{13}C values from core G85 from the lake Gościąg, Central Poland (Pazdur et al., 1985).

At the lake known as Gościąg, in the Gostynin lake district of central Poland (Ralska-Jasiewiczowa, Wicik & Wicowski, 1987; Goslar, Pazdur & Pazdur, 1992), Pazdur *et al.* (1987) found that the relationship between varve age and radiocarbon dating of a 16 m core showed that in the basal part (Fig. 3), there was a discrepancy between the two chronologies (here called the apparent age, T_{app}) of ca. 600 years. In the uppermost sections, this increased to ca. 1700 years. The difference was present even when the effect of carbonates was removed. However, when the dates were corrected for apparent age, and then calibrated in terms of calendar years, there was

excellent agreement between calibrated dates and lamination numbers (Table 1).

TABLE 1. — COMPARISON OF CORRECTED AND CALIBRATED ^{14}C DATES FROM CORE G85 FROM THE LAKE GOŚCIAŻ, CENTRAL POLAND (FROM PAZDUR *et al.*, 1987)

Sample	N	T _{corr}	T _{cal}	Δ
G85/10	150	130	0-300	0
G85/9	700	740	660	- 40
G85/8	900	1130	1030	+130
G85/7	2900	2630	2810	- 90
G85/6	6000	5240	6040	+ 40
G85/5	8200	7360	8000	-200

Key N = lamination number

T_{corr} = Corrected date (= age of organic fraction (T_{org}) - apparent age (T_{app}))

T_{app} = T_{org} - varve age

T_{cal} = calibrated age

Δ = T_{cal} - N

So we can find varved sediment sequences in which there is, given careful treatment of the data, good agreement between radiocarbon dating, and calendar age. However, at Gościąg, radiocarbon dates were used, as in many other investigations (O'Sullivan, 1983) to test the theory that the laminations found were indeed varves. It was not a case of using the varves to calibrate the radiocarbon time scale.

One investigation in which such a calibration is being carried out is that by Zolitschka (1991, 1992), in the sediments of the Maar lakes of the Eifel region of SW Germany. Results show that there is a good correspondence between the varve chronology from Holzmaar and the geomagnetic record from Paris for the last 1000 years. The next step is to produce a radiocarbon calibration curve for the past 12,800 years.

One area in which the presence of annually laminated sediments can certainly help in improving the interpretation of radiocarbon dates is in the all too common case where human impact upon sources of sedimentary material has liberated a significant quantity of radiometrically « old » carbon from the catchment (Olsson, 1986). This process normally begins to operate in lake-watershed systems with the arrival of peoples practising agriculture, and generally involves the erosion into the lake of mineral, humic, and other organic matter originating in soils, vegetation, or even in peat deposits (O'Sullivan, Oldfield and Battarbee, 1973; Pennington *et al.*, 1976).

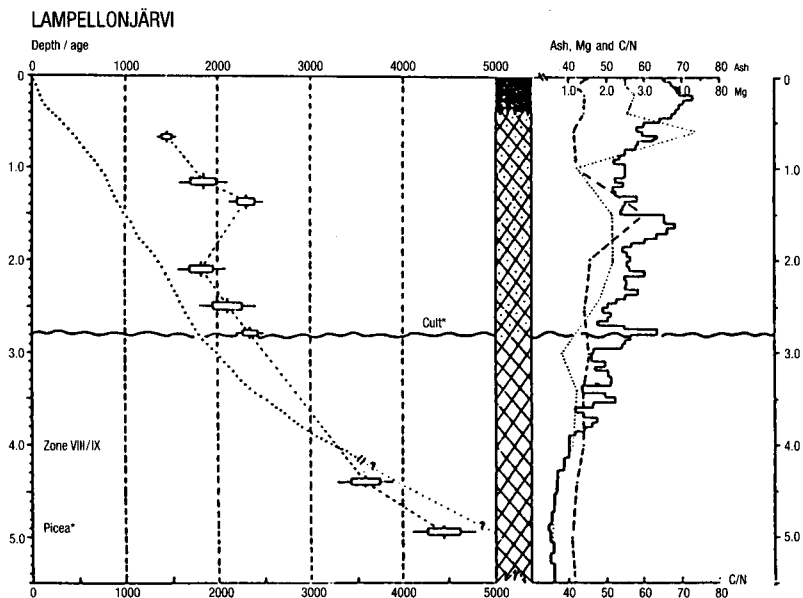
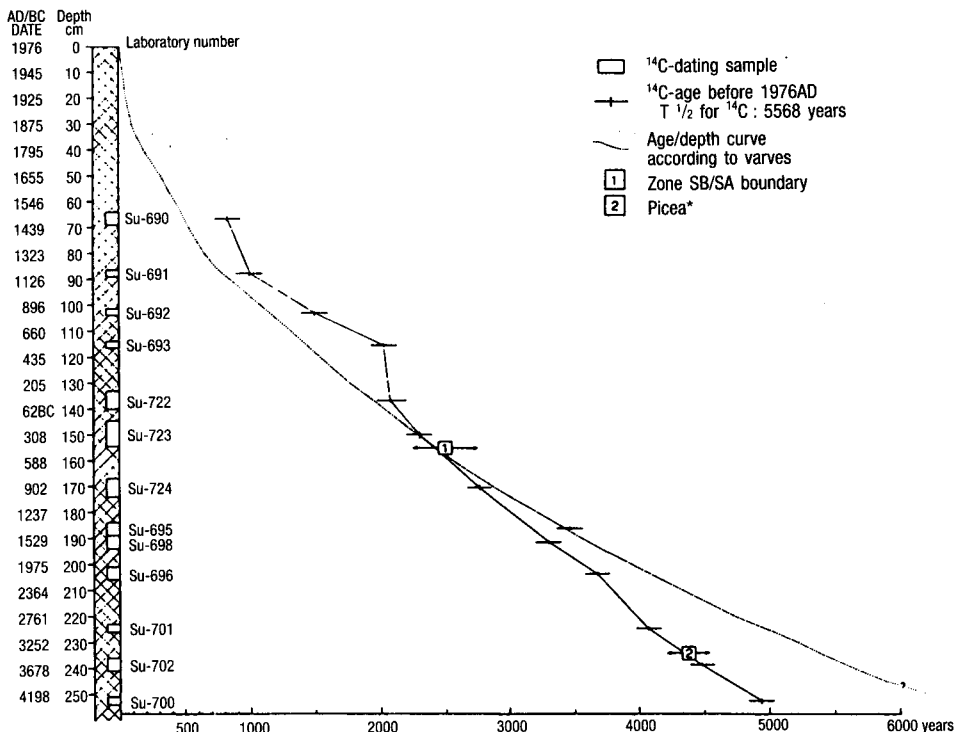


Fig. 4. Comparison between lamination counts, radiocarbon age and sediment depth in (a) Ahvenainen (M. Tolonen, 1978b), and (b) Lampellonjärvi (K. Tolonen, 1980), South Finland.

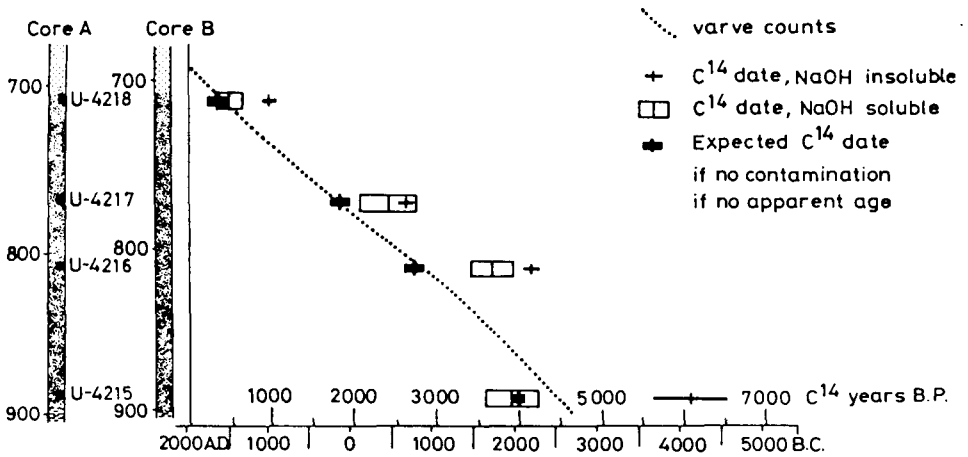


Fig. 5. Comparison of radiocarbon dates from alkali soluble and insoluble fractions with varve chronology from the sediments of Rudetjärn, Northern Sweden (Olsson, 1979).

So long as there is no serious disruption of the process of formation, deposition of varves will persist, and a chronology independent of the now modified terrestrial nutrient cycles will remain available. Examples can be found in the sediments of two lakes in South Finland (Ahvenainen, M. Tolonen, 1978; Lampellonjärvi, K. Tolonen, 1980), where the varve chronology was used to identify parts of the sediment sequence where «old» carbon had been washed in (Fig. 4). However, both studies also show that varve counts themselves may contain systematic errors, in that during the early Holocene, sedimentation rates in some lakes may be so slow ($0.2\text{--}0.3\text{ mm a}^{-1}$) as to make accurate counting of the varves themselves fairly difficult, even for experienced operators like the Tolonens.

The effect of «dilution» by «old» carbon was also investigated in the varved sediments of Rudetjärn, Northern Sweden (Renberg, 1976) by Olsson (1979). She found (Fig. 5) that dates performed on the alkali soluble (ie «humic») fraction of the sediment yielded results closer to the varve count than those obtained from the insoluble carbon, which at this site contained a substantial amount of graphite.

Unfortunately, it seems that the arrival of farming cultures in a catchment, and in particular, the deforestation of an area, sometimes results in disruption of varve formation, either by means of (a) mild eutrophication, or (b) increased rate of sedimentation, or (c) enhanced mixing and/or circulation of lake waters and/or the superficial sediments, by more powerful water movements and/or (d) the increased activity of benthic biota (Fritz, 1989; Merkt, this volume; Peglar, this volume; Peglar, Fritz & Birks, 1989; Peglar *et al.*, 1984; Simola, this volume; Simola *et al.*, 1981). Therefore, in

some cases, perhaps the best means of independently assessing the effect of dilution tantalisingly disappears at the precise moment at which it is most needed.

Improving the accuracy of radiocarbon dates

These latter points leave us with a series of questions regarding the applications of studies of varved lake sediments to the improvement of the dating of palaeoecological and other similar changes. Some of those have been implicitly and explicitly addressed already, and some are new to this discussion. The questions are :

1. Where annual laminations/varves *are* present, what is the relationship between varve age and radiocarbon age? Is there a relationship which is consistent, and which can be used as the basis of calibration?
2. In particular, where radiocarbon age deviates significantly from calendar age, is there some fraction of the sediment to which we can refer which will give us a radiocarbon date which is closest to the true (ie varve, sidereal) age and which will thus fit best to the varve chronology? Can we isolate this fraction in sufficient quantity that it can be dated separately from the rest of the sediment?
3. Using varve sediments, can we attempt to address that most insidious of problems of radiocarbon dating of lake sediments, the « hard water » or « reservoir » effect (Donner, Jungner and Vasari, 1971 ; Geyh, Merkt and Muller, 1971 ; Olsson, 1979, 1986, 1991 ; Olsson, El-Daoushy & Vasari, 1983) ?
4. Where varves have disappeared owing to the kinds of disruption described above, can we still use this approach of dating particular fractions to give us radiocarbon dates from the unlaminated sediments which are closer to the « true » age ?
5. Can we use this approach in sediment sequences which are entirely unlaminated ?

The first question has already been addressed here and in many investigations. Radiocarbon dating of varved sequences sometimes gives us a set of dates whose apparent age (T_{app}), as at Gościąg, can be shown to deviate from the « true », calendar age by a standard amount. We can quantify this amount and use it as the basis of improving the precision of chronologies.

Similarly, we can begin to answer question two, if, again as at Gościąg, and at Rudetjärn, and in the Schleinsee, the sediment is fractionated so that carbonates, and the residual alkali-insoluble carbon, both of which may include much older material than the rest of the organic matter present (but not necessarily as we shall shortly see), are removed or dated separately.

The results from these several sites show a much better fit between the varve counts and the calibrated radiocarbon dates, when this procedure is adopted.

The development of radiocarbon dating using accelerator mass spectrometers (AMS, Hedges, 1981, 1987, 1991) however, has, because of its potential for accurately dating much smaller amounts of material than hitherto, allowed the differentiation of further fractions (Batten *et al.*, 1986 ; Fowler, 1986 ; Fowler, Gillespie & Hedges, 1986 ; Hedges, 1991 ; Hedges *et al.*, 1989). Basically these consist of (a) the « conventional » date, which as explained earlier, is performed after removal of carbonates, (b) any remaining macrofossils – recognisable plant or animal remains (eg seeds, fruits, leaves of higher plants, exoskeletal parts of insects), (c) the total crude lipid fraction, extracted from the sediment using some common solvent such as dichloromethane, (d) the « humic » fraction, extracted with dilute alkali, and (e) the remaining undifferentiated « insoluble » carbonaceous material (insoluble in common organic or inorganic solvents), which in some cases may consist largely of polysaccharides such as (in a lake sediment) cellulose, but which (again, in a lake sediment) may also contain many other much more resistant biomacromolecules (such as cutans, suberans, algenans, lignin, tannins, sporopollenins and bacterial lipopolysaccharides), and other carbonaceous substances such as graphite (Fowler *et al.*, 1986 ; Hedges, 1991 ; de Leeuw & Largeau, 1993 ; Olsson, 1979 ; Tegelaar *et al.*, 1989). This fraction is referred to by operators of radiocarbon dating facilities, and some organic geochemists, as « humins » (Hedges, 1991), and by other organic geochemists (eg de Leeuw & Largeau, 1993 ; Meyers & Ishitawari, 1993) as « protokerogens », or the « residual undifferentiated complex mixture » (Lewis & Rowland, 1993 ; Parkes *et al.*, 1993).

Generally it has been found (Olsson, 1986 ; 1991) that the « oldest » dates are given by this last fraction, which, as it consists of a large range of compounds, and is not strictly extracted from the sediment, but obtained by solution of the residue of preparation, is the one most likely to be an eclectic mixture. As its chemical composition is difficult to determine, (Tegelaar *et al.*, 1989) it is also the fraction most open to contamination (Hedges, 1981).

« Younger » dates are given by the « humic » fraction, and by the total crude lipids (Fowler *et al.*, 1986 ; Olsson, 1991). In the first case, it must be ascertained that all contamination with other macromolecules such as, on the one hand, cellulose and lignin, and on the other, humins, to which this fraction is susceptible, has been removed (Hedges *et al.*, 1989). Where this is not carried out, dates may consequently be too « old ». In the second, it can often be determined (eg by GC analysis of the length of the carbon

chain) whether the compounds extracted are of terrestrial or aquatic, higher or lower plant origin (Cranwell, Eglinton & Robinson, 1987; Fowler *et al.*, 1986; Robinson *et al.*, 1984), a significant factor when also attempting to answer question 3.

Finally, it has also been found (eg. Andrée *et al.*, 1986; Brown, Farwell and Grootes, 1995; Hajdas *et al.*, 1993, 1994; Jones *et al.*, 1993; Long, Davis and de Lanois, 1992; Wohlfarth *et al.*, 1993; Zbinden *et al.*, 1989) that dating of macrofossil remains, in this case mainly the seeds or catkins of birch (*Betula pubescens* L.) or terrestrial pollen, may give results which are closer to the « expected » date than that obtained from other fractions. Crucial here, however, is the selection for dating of the remains of terrestrial organisms, as aquatic plants (which obtain carbon dioxide from the water column, or in some cases from the sediments) and therefore aquatic biota, are again subject to the « hard-water » or « reservoir » effect. Similarly, pace Regnéll (1992), one must be aware that the pollen present in a lake sediment is also a very eclectic mixture, even when size separations can be successfully achieved.

Using this approach, then, it does indeed seem that we can obtain radiocarbon dates from certain fractions of the sediment which may be inherently « older » or « younger », and which may therefore give us results which are closer to, or further from, the « expected age ». Furthermore, by carefully removing the influence of carbon contributed by aquatic sources, it may eventually be possible to circumvent the « reservoir » effect. This would be an important methodological advance, and one in which the use of annually laminated sediments would be crucial.

I would like to propose a means of taking the above approach one or two more stages further, based, first of all on (a) more sophisticated organic geochemical extraction of the various components of part of the organic (free lipid) fraction of the sediment, and (b) identification of the *source* of the groups of compounds thus obtained, by means of measurement of their $\delta^{13}\text{C}$ departures. For much of this work I am indebted to my colleagues Dr Martin Jones of the University of Newcastle, and Professor Geoffrey Eglinton of the University of Bristol. I have recently described some of these results at greater length (O'Sullivan, 1992), but not the work on $\delta^{13}\text{C}$ departures.

In Fig. 6 are shown gas chromatograms of silylated (BSTFA) total extractable organic matter from a 1 m core from the sediments of Ellesmere Mere, a small, deep, eutrophicated lake ($A = 46$ ha, $Z_{\text{max}} = 18.8$ m) in the English Midlands (Farr *et al.*, 1991; O'Sullivan 1992; O'Sullivan *et al.*, 1989; Reynolds, 1979). The uppermost layers (0.5 cm, Fig. 6a) are rich in

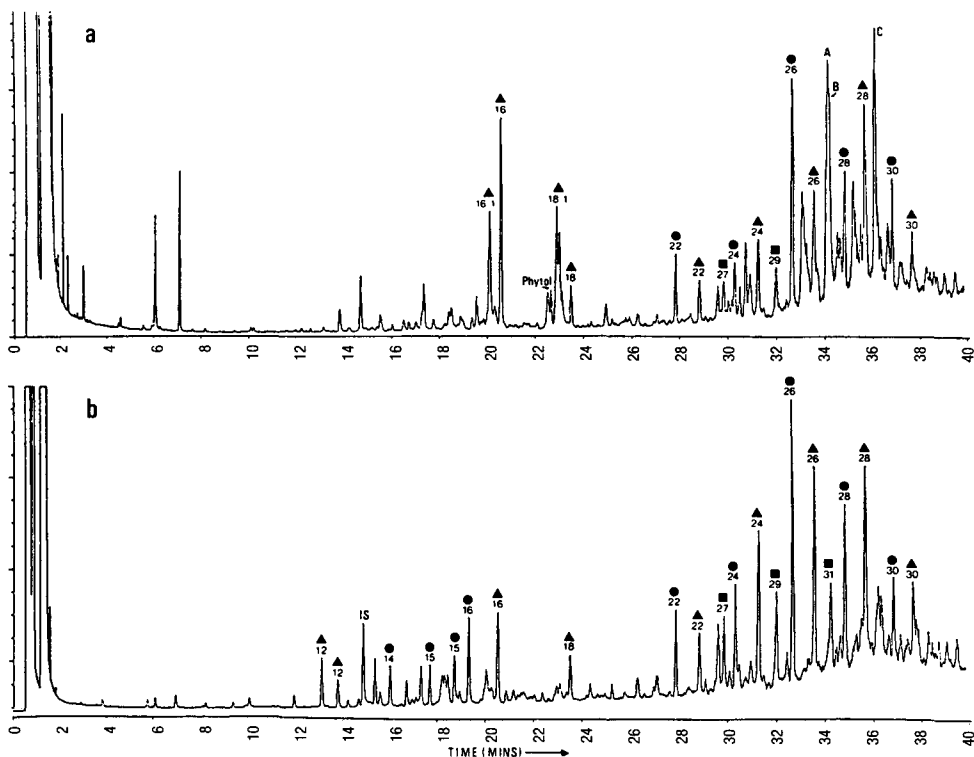


Fig. 6. Gas chromatograms of silvated (BSTFA) total extractable organic matter from the sediments of Ellesmere Mere (English Midlands). Fig. 6a. 0-5 cm depth, Fig. 6b 10-40 cm. Circles, triangles and squares represent, respectively, alcohols, fatty acids and *n*-alkanes, with their carbon numbers indicated. IS = internal standard. Compounds containing a double-bond are indicated by Peak A = cholest-5-en-3B-ol, B = cholestan-3B-ol, C = ethylcholest-5-en-3B-ol.

compounds such as phytol, cholest-5-en-3B-ol (peak A), and 24-ethylcholest-5-en-3B-ol (peak C), and phytol, which are derived mainly from higher plants (but also, unfortunately, to a certain extent, from algae). Other components present represent inputs from aquatic microorganisms such as bacteria and algae.

In contrast, the deeper sediments (10-40 cm, Fig. 6b) are rich in long chain *n*-alcohols, carboxylic acids and *n*-alkanes derived from higher plants, with a substantial secondary component of C_{12} - C_{16} *n*-alcohols and carboxylic acids, probably produced by bacteria. Reference to a comparison between the distribution of sterols in the surface sediments (peaks A and C, Fig. 6a) with that of deeper sections (Fig. 7) indicates that the ratio of $C_{27}\Delta^5$ cholesterol (peak A) to $C_{29}\Delta^5$ 24-ethylcholesterol (peak C) is much lower in the deeper layers. Both sets of changes (preference for longer chain

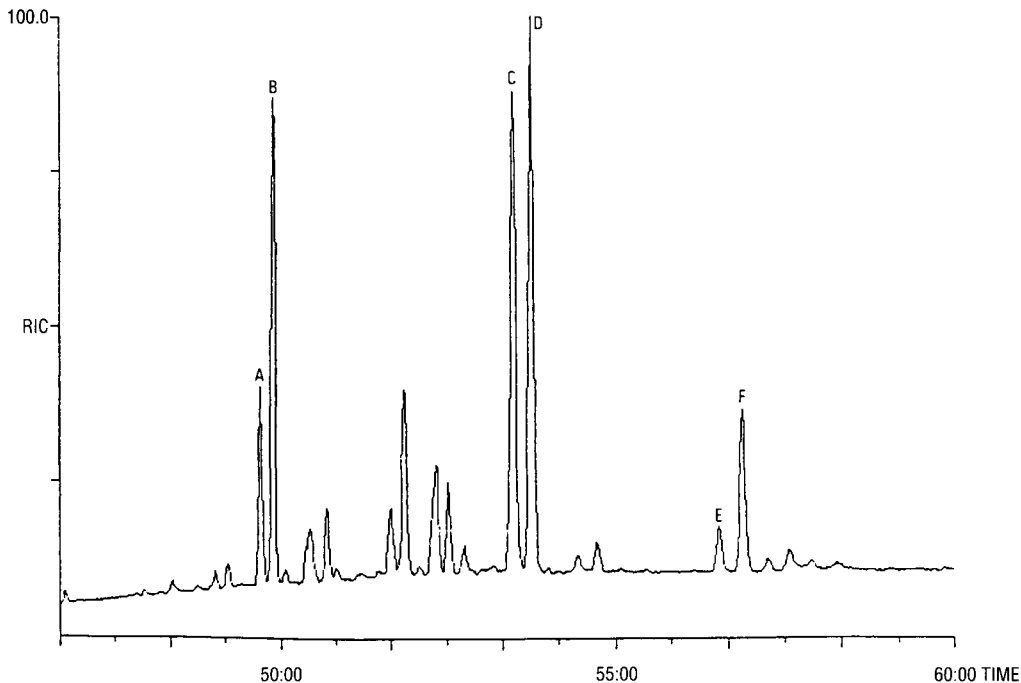
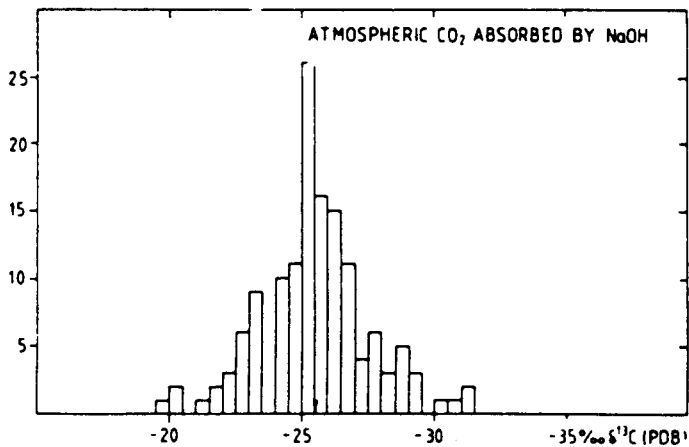
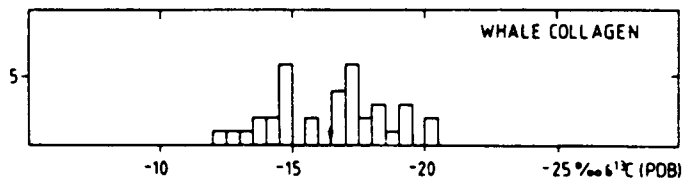
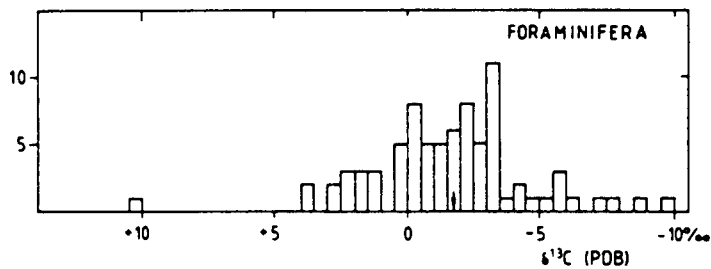
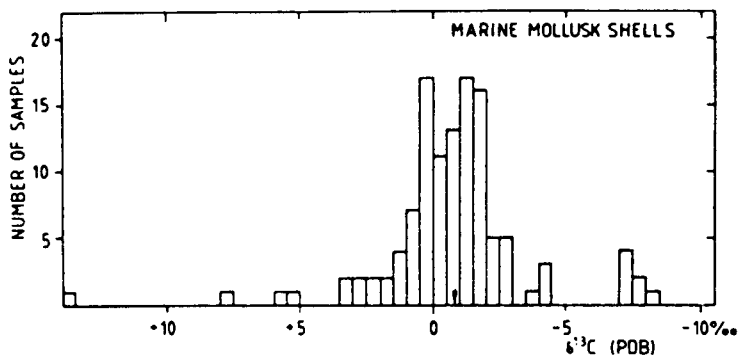


Fig. 7. Partial reconstructed ion chromatogram (RIC) of silylated (BSTFA) sterol fraction from the sediments of Ellesmere Mere (10-40 cm). Peaks A, B, and C as for Fig. 5. Peak D = ethylcholest-3B-ol, E = gorgosterol, F = gorgostanol.

compounds in deeper sediments, change in the ratio of shorter to longer chain sterols and their derivatives) are typical of early diagenesis of organic compounds in lake environments (Meyers & Ishiwatari, 1993).

Therefore we can see that by careful isolation, we can identify some of the major groups of organic compounds in lake sediments, and their likely origin, in terms of terrestrial or lacustrine or other organic matter. Calculations by Dr Jones show that the most abundant groups of compounds are present in these sediments in sufficient concentration to be isolated and dated by Accelerator Mass Spectrometry (AMS, Hedges, 1981, 1991).

Work on the origin of the organic compounds contained in the Ellesmere Mere sediments and their likely source has been further extended by studies of their $\delta^{13}\text{C}$ departures (Rieley *et al.*, 1991). It should be noted (Fig. 8) that of the results presented by Olsson (1986), those given for lake sediments cover the widest range of values (16.5 to 35 ‰, where ‰ = per mill). This underlines the point made earlier, that lake sediments are a *mixture*, and for the purposes of radiocarbon dating may (and indeed *should*) be treated as such.



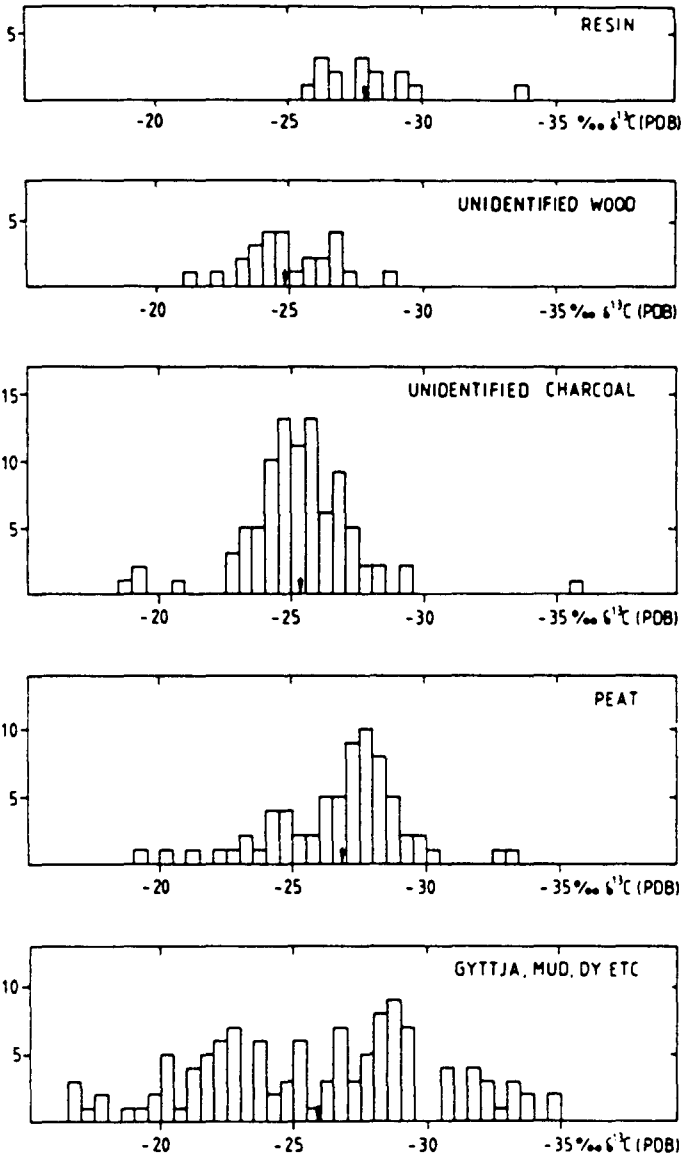


Fig. 8. Variation in ^{13}C in a range of environmental materials as presented by Olsson (1986). Note that, of the materials examined, the lake sediments contain the widest range of values.

TABLE 2. $-\delta^{13}\text{C}$ VALUES OF FREE LIPIDS FROM THE SEDIMENTS OF ELLESMERE MERE, ENGLISH MIDLANDS (BASED ON DATA IN JONES *et al.*, 1991, AND RIELEY *et al.*, 1991)

Compound	$\delta^{13}\text{C}$ ‰ (mean)
C ₁₄ n-alcohol	-22.72
C ₁₆ n-alcohol	-23.57
C ₂₉ 24-ethylcholestanol	-27.81
C ₂₅ -C ₃₃ n-alkanes	-31.8
C ₃₂ alcohol	-33.15

In Table 2 is shown data by colleagues based at the Organic Geochemistry Unit, University of Bristol (Jones *et al.*, 1991; Rieley *et al.*, 1991) which records $\delta^{13}\text{C}$ departures of n-alkanes and sterols from the sediments of Ellesmere Mere. The main groups of compounds present are C₁₄ and C₁₆ n-alcohols (which are thought to be derived from autochthonous algal and bacterial production), C₂₉ 24-ethylcholestanol (which is of terrestrial higher plant origin), a C₃₂ hopanoid alcohol (probably synthesized at the sediment-water-interface by bacteria), and a wide range of C₂₅ to C₃₃ terrestrially derived n-alkanes with a maximum at C₂₇ to C₂₉. As shown in Table 2, $\delta^{13}\text{C}$ departures of these compounds, determined by GC-IRMS (Jones *et al.*, 1991) vary from 22.7 and -23.57 ‰ for the C₁₄ and C₁₆ alcohols, to -30.1 to -33.5 ‰ for the C₂₅ to C₃₃ n-alkanes, with the stanols (also terrestrial in origin) intermediate in position, at -27.81 ‰. However, the separation between compounds of terrestrial and lacustrine origin is not simple, as is shown by the hopanoid alcohols, whose $\delta^{13}\text{C}$ value (-33.15 ‰) is greater than that of the terrestrial material.

It is thought that the reason for this is that the hopanoids are synthesized at the mud water interface (MWI) by bacteria, which use organic matter already produced elsewhere, so that what we have here is a group of compounds whose $\delta^{13}\text{C}$ departure has been *enhanced* by diagenesis at the MWI. In other words, what we may be able to achieve, with this approach, is discrimination between authigenic organic carbon, synthesized in the water column by algae and bacteria ($\delta^{13}\text{C}$ ca. -25 ‰), terrestrial organic carbon which is allogenic in a lacustrine context ($\delta^{13}\text{C}$ -27 ‰ to -33 ‰), and endogenic organic carbon, produced diagenetically at the MWI ($\delta^{13}\text{C}$ > -33 ‰).

This may be an important step in improving the accuracy of radiocarbon dates (Fig. 9). Whereas the authigenic (aquatic) input to sediments refers

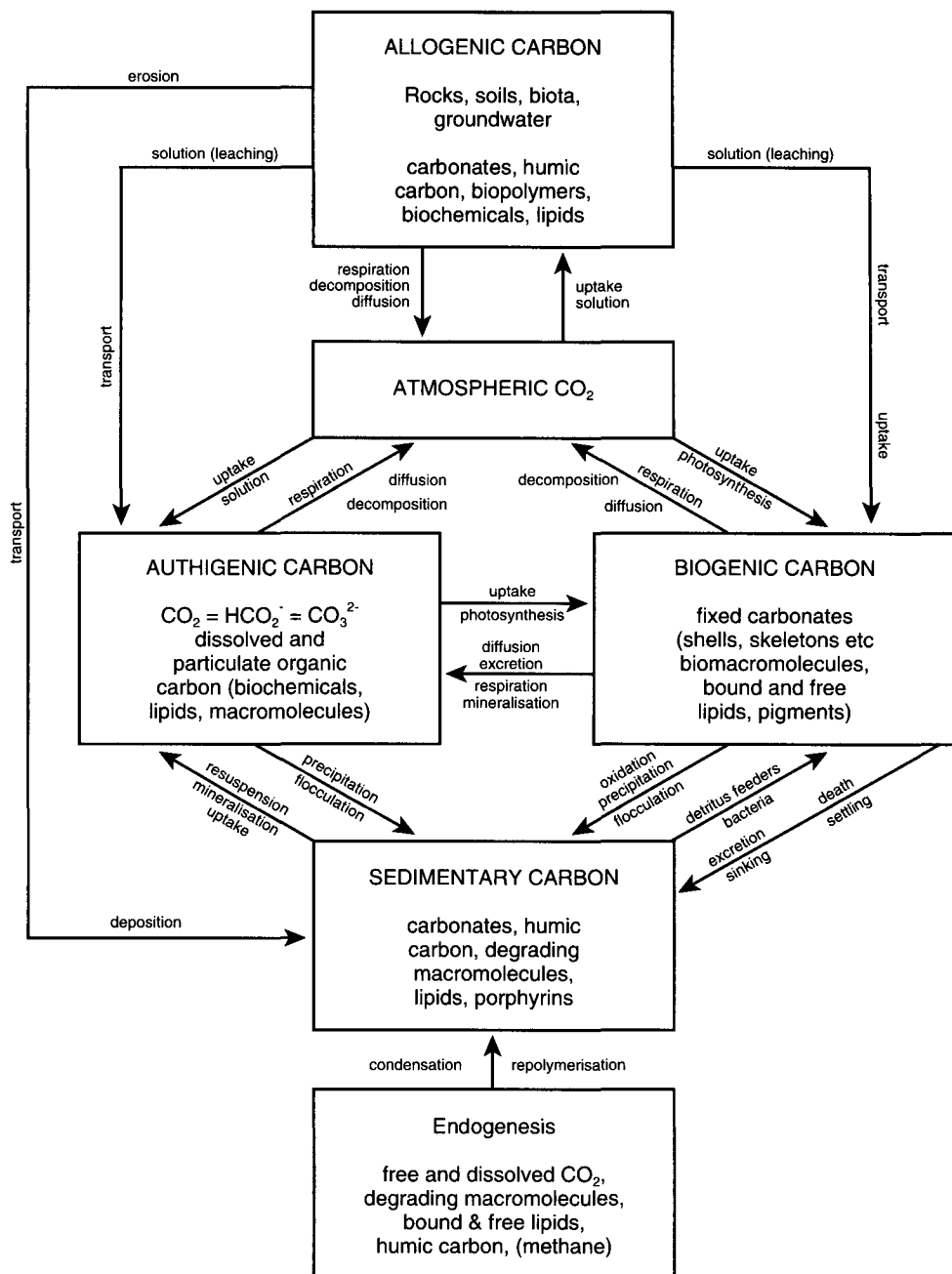


Fig. 9. Schematic representation of the likely sources of carbon present in lake sediments. Note that the fractions defined may overlap somewhat, and that the inputs (allogenic, authigenic, biogenic and endogenic) may not apply in every case.

to carbon dissolved in the water column (which is therefore susceptible to the « hard water effect »), the components of terrestrial origin present are produced by the fixing of contemporary, *atmospheric* carbon source. In theory then, lipids synthesised in the latter environment should possess a different, younger radiocarbon age than that of their aquatic counterparts, as they are not subject to the hard water effect.

Protocol

The theory and methodology of this part of the discussion is not yet fully developed. In particular, some organic geochemists possess strong reservations as to whether the kind of separation I have just described is possible on such a straightforward manner (but see Druffel & Williams, 1992; and Hayes, 1993). However, on the basis of the above work, what I would propose is that annually-laminated sediments may be used to improve the accuracy of radiocarbon dates from lake sediments in the following way. The procedure would operate in a number of stages (Fig. 10), based very much on those already put forward by Fowler *et al.* (1986), Hedges *et al.* (1989), and Hedges (1991).

The sediment must clearly be fractionated into its major constituent parts, and radiocarbon dating of each fraction conducted. Fig. 9 attempts to show that, in any lake sediment, four principal carbon fractions – carbonate, « insoluble », humic and lipid may be present. Clearly, there is some degree of overlap between these (especially, as listed, the second and the third), but they probably do represent the main categories of carbon present which may contribute to variations between radiocarbon, and « true » and calendar age. The free fraction contains the kind of compounds isolated from the sediments of Ellesmere Mere described above. Any protocol therefore needs strongly to take into account the means by which these various fractions arrive in the sediment, and indeed, as pointed out by Fowler *et al.* (1986) the dating of fractions is in some ways as much an investigation of sediment *history* as of sediment age.

Carbonates may of course be removed by treatment with dilute acid (Olsson, 1986), but in the case of lake sediments are traditionally seldom dated (Fowler *et al.*, 1986). I would like to propose that in a palaeolimnological context, it might sometimes be useful to date the CO₂ produced by dissolution of carbonates, especially as it seems that they too can be differentiated as to their terrestrial or aquatic origin by means of their $\delta^{13}\text{C}$ departures (terrestrial carbonates from rocks possessing a $-\delta^{13}\text{C}$ of zero, and authigenic lacustrine carbonates one of ca. -8 to -9 ‰, Srodoč *et al.*, 1986). Slight etching with weak, dilute acid in order first to remove surface contamination, may be desirable (Hedges *et al.*, 1989).

Macrofossils must then be picked out by hand. As stated above, they are really part of the biomacromolecular component, but if they retain their physical structure, they may be both taxonomically identifiable, and sufficiently abundant to date separately (Andrée *et al.*, 1989; Jones *et al.*, 1993; Zbinden *et al.*, 1989). In respect of the lipids, the kind of extraction procedures developed by organic geochemists such as my colleagues could then be used to differentiate further between the major components of this fraction. Determination of the $\delta^{13}\text{C}$ of each component may then be used to identify its source.

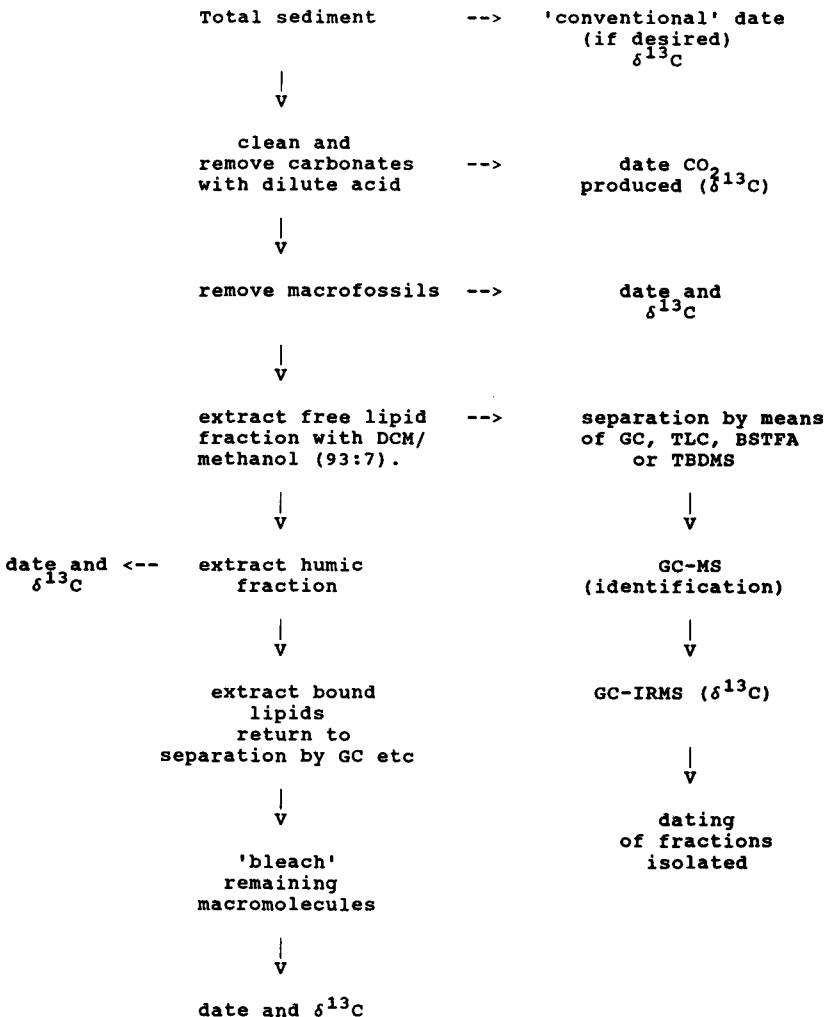


Fig. 10. Proposed protocol for fractional radiocarbon dating of lake sediments based on GC-IRMS and AMS dating of free lipid organic fraction. Key – BSTFA = bis (trimethylsilyl) trifluoroacetamide, TBMS = tertbutyldimethylchlorosilane.

Humic acids are extracted with sodium hydroxide, and then purified by reprecipitation in hydrochloric acid. Finally, the residue of « insoluble » bio- and geomacromolecules (« humins ») is broken down by bleaching with sodium hypochlorite (Hedges *et al.*, 1989 ; Hedges, 1991). This mixture could conceivably be separated further, eg into cellulose, lignin, and even other groups of macromolecules, but the complexity of some aspects of the chemistry involved, and the difficulty of identifying the provenance of the compounds isolated, has so far deterred most investigators (Hedges, 1991).

One further way of approaching this problem might be to extract from the « insoluble » fraction (by means of hydrolysis) the « bound » lipids – those which despite the decomposition process, are still bound into the cellular matrix of the decaying organic matter (Meyers & Ishiwatari, 1993). These could then be separated by GC-MS and identified and quantified in the same manner as described for the « free » lipid fraction above.

Determination of $\delta^{13}\text{C}$ is routinely applied to radiocarbon dating by AMS, so that differentiation as to source of the carbon being dated may be applied to all fractions. In that parts of all four major components of the sedimentary carbon (carbonate, lipid, humic and insoluble macromolecular) may be allogenic, authigenic, biogenic or even endogenic in origin (Fig. 9), this may also be deemed an advantage. As in the case of their observed relative ages, one would expect the biogeomacromolecular fraction, as the least differentiated, to possess the widest range of values of $\delta^{13}\text{C}$ and the other components to be more easily referred to ranges of values characteristic of a terrestrial, aquatic or endogenetic origin.

The results of dating of each fraction, and especially of the major groups of lipids present, may then be compared with the varve chronology, and the fraction (or fractions) producing dates closest to that chronology based on lamination counts, identified. In theory one would expect the macromolecules (which are a mixture, and which are most open to contamination), and the carbonates (which may consist of very « old » allochthonous carbon, as well as that precipitated from solution in the lake waters), to provide the oldest dates (as at Gościąg), and the macrofossil and lipid components, to yield the youngest, although there is evidence to suggest that sometimes humic matter may be radiometrically younger than this prediction would suggest (Fowler *et al.*, 1986). Once again, it is probably important here to state that using $\delta^{13}\text{C}$ and GC-IRMS it may be possible to discriminate between lipids of autochthonous origin, which are therefore susceptible to the « hard water effect », and allogenic lipids which, in theory anyway, are not, especially as « bound » lipids also often show a preference for terrestrial origin (Meyers & Ishiwatari, 1993).

Concluding - Remarks

Consideration of the composition of the respective types of varved sediments defined by O'Sullivan (1983) suggests that all four of the main categories could be analysed using the above approach, but with the proviso that again, it must be remembered that lake sediments are a mixture of materials, and that treatment protocols would therefore need to be adjusted accordingly.

Thus, calcareous laminations of the kind found e.g. in the Zürichsee (Kelts and Hsü, 1978) would clearly be rich in authigenic carbonate-based material, but also other mineral matter, humic material, other macromolecules, and lipids. Biogenic laminations of the type present in Lovojärvi, Southern Finland (Saarnisto, Huttunen and Tolonen, 1977) contain a similar they are the product of a soft-water lake-watershed system, little calcareous material. The ferrogenic laminations of other soft water lakes found in N.Europe and North America (Anthony, 1977; Renberg, 1981) may well be similar.

The size of the lake and its drainage basin may however be important as well, as the materials present in the sediments of a large lake such as the Zürichsee may well be very different from those found in small lakes such as Fayetteville Green (Ludlam, 1969) or Gościąg. This point may therefore apply to the sediments of lakes in which clastic varves (Sturm, 1979) have been deposited, with the proviso that dating material low in organic matter is a hazardous procedure (Olsson, 1979).

From the point of view of cost, what I have suggested, involving the increase in number of fractions dated from two (Olsson, 1991), or five (Fowler *et al.*, 1986), to maybe eight or nine, is clearly not advantageous. However, as we learn more about such procedures, and in particular the origin of the compounds present in the lipid component, it may be possible to reduce the number of fractions dated. It should also, eventually, be possible to extend the procedure to the dating of unlaminated sediment sequences, given good control on the kinds of lipids present, and their site or sites of synthesis. And now I would like nothing better than to be able to show you some results of radiocarbon dating of a long series of annually laminated sediments. However, I am afraid that I do not yet have any, and so, in conclusion, all I can say is that I have yet to test my main hypothesis.

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