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CONDITIONS INVOLVED IN DATING TERRESTRIAL SHELLS

JACQUES EVIN, JOËLLE MARECHAL, CHRISTIANE PACHIAUDI,

Centre de Datations et d'Analyses Isotopiques, Université Claude-Bernard, Lyon, France

and J J PUISSEGUR

Département de Géologie, Université de Dijon, France

ABSTRACT. Mollusks living only on ground surface can be expected to give the most reliable results in ^{14}C dating from carbonates of continental origin. One may assume they have a homogeneous biotope and are not affected by any hard-water effect. In order to verify these assumptions and to test shells as routine dating material, results from terrestrial gastropods are compared with other ^{14}C dates from classic biologic material, such as peat, charcoal, or bone, collected in the same archaeologic or geologic levels in miscellaneous places. Two sites were selected for which other chronologic data, such as prehistoric industries or malacologic diagrams were available.

All results indicate older values for ^{14}C shell dates. The discrepancy between "normal" and snail dates amounts to 300 to 1200 ^{14}C years and remains the same whatever the absolute age of the sample. All ^{13}C values of perfectly cleaned shells are between −5 to −10‰ versus PDB. The initial ^{14}C content of shells that is too low may be different according to species, as suggested by ^{13}C variations.

Although fairly constant, this deviation of ^{14}C ages generally makes such samples unreliable for most archaeologic studies, which often need more precise results. However, some measurements were performed on microfauna shells from several Würmian loess to show that dating of shells may be useful in fairly ancient geologic sediments for lack of better carbonaceous samples. Good agreement of some snail dates with expected sediment ages point to the importance of proper sample selection and pretreatment that might be checked by ^{13}C measurements.

INTRODUCTION

Although radiocarbon dating, may in principle, be applied to any type of carbonaceous sample, many Quaternary geologists and archaeologists submit unusual materials for lack of classical samples, such as charcoal, peat, or bone. The laboratory bears the responsibility for selecting suitable samples, thereby avoiding questionable results. Experience shows that reservations about the accuracy of dating are, unfortunately, often ignored, so that it is most important to carry out thorough investigations on any new type of material proposed for age determinations.

Terrestrial shells as dating materials

It is generally known that dating groundwater, speleothems, or organic matter from open soils poses certain problems. The suitability of carbonate samples, however, is still an open question. Despite the uncertainty about initial isotopic composition, marine carbonates (shells or precipitated carbonates) are widely used, whereas continental carbonates (shells or tufa) are generally discarded.

Due to the mobility of calcium bicarbonate, continental sediments are often rich in carbonates of biologic or chemical origin, and these often constitute the only carbonaceous material present. Some tests have previously been performed on tufa (Vita-Finzi, 1974), speleothems (Labeyrie and others, 1967), and on the calcitic crust around bones

(Srdoc and others, 1977) but the lack of precise knowledge about the chemical and isotopic processes involved in their formation renders them unreliable for ^{14}C dating.

Mollusk shells seem to offer several advantages as useful dating material. They are frequently well distributed in geologic formations. Many different species exist, and ecologically oriented malacologic studies have recently provided a good definition of the biotope of many individual species. Single, very large shells may suffice for a ^{14}C analysis, but often a number of smaller shells is needed to make up adequate samples. These shells have a very strong structure, and even the oldest may remain unaltered under a carbonate crust, so that the elimination of secondary carbonate is to some extent, facilitated.

Most of these advantages have already been indicated in studies on chiefly aquatic species (Broecker and Walton, 1959; Keith and Anderson, 1963). However in both cases, the authors met with the same difficulties as with dating groundwater, tufa, and speleothems, because of the complexity of the isotopic environment of aquatic animals.

It would appear, however, that terrestrial species of gastropods which are supposed to live out of contact with the bicarbonate of fresh water and which feed on plants growing in the open air should have less uncertainty in the origin of their shell carbonates. They might, therefore, be suitable for dating continental carbonates, given the greater isotopic homogeneity of their biotope.

Only a few studies dating terrestrial snail shells have been reported. Shells from American sites were measured by Tamers (1970) and those from British sites by Burleigh (ms). Snails were also used in a general chronologic study of North Africa (Camps, Delibrias, and Thommeret, 1973), but the exact correlation between the snail dates and those derived from other materials was not well established. Apart from these studies, it is noteworthy that snails have practically never been used as the only dating material in geologic or archaeologic research.

Experimental studies on mollusk shells

One approach for estimating the validity of dates obtained from snail shells is precise knowledge of the isotopic composition of the shells formed under controlled conditions. The first results of the incorporation of labelled components were published by Rubin, Likens, and Berry (1963). It appears, however, that there are technical difficulties in providing laboratory conditions for feeding and breeding snails, closely resembling their natural environment. It is, for example, difficult to estimate the possible influence of soil carbon dioxide.

An alternative apprach is to measure shells from modern gastropods sampled from various natural environments. Some preliminary measurements are presented in table 1. These show a wide range in ^{14}C content and may indicate that bomb-derived ^{14}C exerts a strong influence. It might be possible to extend these observations by selecting species from unusual and restricted environments.

A third approach has been used for the major part of this study. We compared snail shells with other datable materials in samples submitted to our laboratory for geologic or archaeologic studies. We selected samples in which snail shells were numerous and associated with presumably reliable materials, such as charcoal, peat, or bones. In addition, other chronologic data suggested that certain sites had not been disturbed, either during deposition or thereafter. These conditions are not easily fulfilled, and certain promising sites turned out to be unsuitable. For example, Layer 5 from the Pégourie site, Quercy, France, had previously been attributed to the Boreal or Mesolithic period by snail shell dating (Gif-2668: 8450 ± 250 BP) but the associated industry (Séronie-Vivien, 1973) and ^{14}C dating of bone samples (Ly-1391: 11,680 ± 330 or Ly-1832: 11,870 ± 290) later indicated that the layer belonged to the Alleröd or Azilian period. It had presumably been contaminated by the downward intrusion of younger snail shells, whose ^{14}C activity has been confirmed by two recent measurements (Ly-1838: 8310 ± 220 and Ly-1837: 8450 ± 310).

Technical procedure

Specimens from only one species of gastropod were selected, even if this reduced the size of the available sample. Before preparing CO_2 by dissolution in acid, the specimens were treated as follows:

— Careful hand scraping to eliminate most of the gangue

— Leaching with hydrogen peroxide (200vols): if necessary, the apex of the shells was pierced to ensure penetration into the deeper parts

— Washing by ultrasonic agitation to remove adherent dust

— Selection of the most nacreous shells

— If possible, a brief leaching with dilute acid to remove the outer layer of the shells

Measurements were then made by liquid scintillation counting of 3ml of benzene, using about 20 to 40g of sample.

Archaeologic correlation: Poeymaü site

This site is perhaps the finest snail heap in France. It is situated in a fissure about 10m wide at the foot of a calcareous cliff at Poeymaü, near Arudy, Bearn, France (43° 7′ N, 0° 29′ W) in the northwestern Pyrénées. This site was formerly excavated for a five-year period by

TABLE 1

^{14}C activities of modern gastropod shells

Gastropod species	Colln date of living animals	Lab no.	^{14}C activities % modern
Helix pomatia	1930	Ly-1005	93.3 ± 2.4
Lymnea sp	1966	Ly-1007	164.4 ± 3.9
Xerotrichia sp	1971	Ly-1003	109.8 ± 1.5
Unio sp	1971	Ly-1008	106.4 ± 1.4
Helix nemoralis	1971	Ly-1009	131.2 ± 3.4
Helix pomatia	1972	Ly-1006	151.7 ± 3.8

Laplace (1953), and the samples were sent to our laboratory (Ly-1379-1389). At present, a new study is being made by M Livache, who provided us with the other samples. The layers consist of a mound of hearths interstratified into levels merely consisting of shells of *Helix nemoralis* without other sediments. With all layers, industries are associated that demonstrate a human occupation of the site over at least ten millennia from the Azilian period up to Roman times (fig 1). ^{14}C measurements were made on various materials from most of these layers (table 2).

The ^{14}C dates from the shells from the upper three layers studied are very similar, but do not correlate with corresponding charcoal ages. This is probably due to the presumed peculiarities of deposition during the Neolithic and later periods. The surface of the latest Mesolithic shell accumulation appears to have been deeply hollowed out before the subsequent Neolithic deposition. Late artifacts are, thus, found associated with earlier snail shells. In the lower layers, the ages obtained from the shells or from other materials agree with the stratigraphic order; the shell dates, however, are consistently about 1000 years too old.

Geologic correlation: Molesme and Clenay sites

These are two neighboring sections at Molesme (47° 47′ N, 4° 21′ E) and at Clenay (47° 24′ N, 5° 07′ E) in the Burgundy region of France. They are composed of alternations of tufa, peat, and clayey layers deposited at the bottom of shallow valleys. Samples from upper layers were taken from outcropped sections whereas the lower layers were sampled by borings. These sites were selected and studied by J J Puissegur (1976);

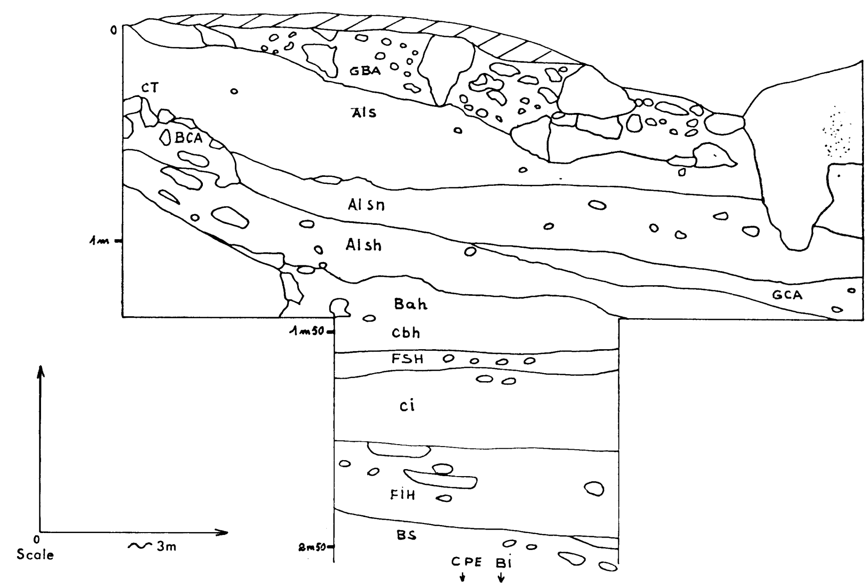

Fig 1. Simplified section of Poyemaü site, according to G Laplace and M Livache.

the pollen diagram was prepared by M Denèfle (figs 2, 3). The ^{14}C dates obtained from samples of peat, organic detritus, and snail shells are shown in table 3.

The peat ages agree with the malacologic data, showing continuous sedimentation at both sites during the Pre-Boreal (Molesme) and Boreal (Clenay) periods, with a presumed short hiatus during the climatic optimum of the Atlantic period. The shell dates are in the same stratigraphic order, but, once again, show a tendency to be about 1000 ^{14}C years older.

^{13}C measurements

For technical reasons we were unable to perform ^{13}C measurements on all ^{14}C samples analyzed. For ^{13}C analysis CO_2 was separately prepared

TABLE 2

^{14}C ages of different layers of the Poeymaü site using various dating materials

		^{14}C dating materials (lab nos)		
Layer	Associated industry	Charcoal	Bones	Snails
Als sup	Iron age or later	1610 ± 140 (Ly-1839)	—	—
C T	Eneolithic	3970 ± 270 (Ly-1383)	—	—
Alsn	Neolithic	4680 ± 300 (Ly-1841)	—	7940 ± 310 (Ly-1785)
G C A	Neolithic	5170 ± 320 (Ly-1842)	—	—
B C A	Early Neolithic	5830 ± 330 (Ly-1840)	—	7830 ± 200 (Ly-1784)
Alsh	Late Mesolithic	6830 ± 320 (Ly-1843)	—	7690 ± 310 (Ly-1786)
B A H	Late Mesolithic	7940 ± 150 (Ly-1891)	—	—
C B H	Late Mesolithic	7960 ± 160 (Ly-1892)	—	—
F S H	Mesolithic	8300 ± 300 (Ly-1382)	8490 ± 400 (Ly-1389)	—
FSH Inf	Mesolithic	—	—	9240 ± 220 (Ly-1787)
C I	Mesolithic	8620 ± 250 (Ly-1381)	9400 ± 420* (Ly-1388)	—
FIH Sup	Early Mesolithic	9470 ± 220 (Ly-1380)	—	10,300 ± 250 (Ly-1788)
FIH Moy	Early Mesolithic	—	9430 ± 210 (Ly-1387)	10,700 ± 290 (Ly-1789)
FIH Inf	Early Mesolithic	—	—	10,250 ± 240 (Ly-1790)
FIH Base	Early Mesolithic	9960 ± 210 (Ly-1379)	—	—
B S	Late Azilian	—	10,420 ± 230 (Ly-1386)	—
C P E	Azilian	—	11,540 ± 220 (Ly-1385)	—
B I	Late Magdalenian	—	12,000 ± 250 (Ly-1384)	—

* Uncertain attribution.

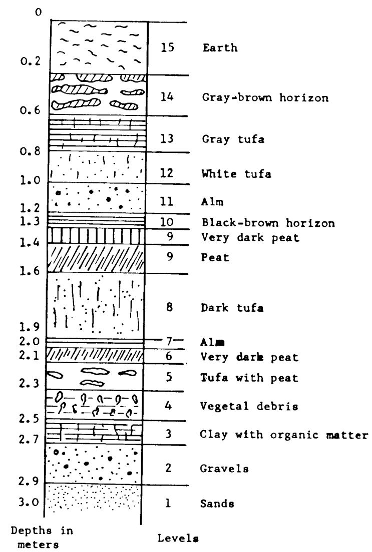

Fig 2. Profile of Molesme site.

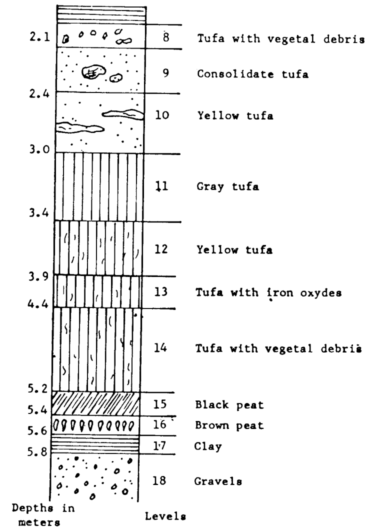

Fig 3. Profile of Clenay site.

TABLE 3
^{14}C ages from different materials at the Molesme (Mol) and Clenay (Cle) sites

Layer	Sediments	Climatic period	^{14}C dating materials (lab nos) Peat	Organic matter	Snails
Mol 10	Brown horizon	End of Atlantic	—	5130 ± 120 (Ly-840)	5250 ± 140 (Ly-835)
Mol 9	Peat	End of Atlantic	5230 ± 130 (Ly-839)	—	6270 ± 170 (Ly-834)
Mol 7	Clay	Boreal	—	—	9510 ± 210 (Ly-833)
Mol 6	Peat	Boreal	8720 ± 150 (Ly-838)	—	—
Mol 4	Clay	Pre-Boreal	—	9280 ± 170 (Ly-837)	—
Mol 3	Clay	Late Dryas	—	9900 ± 290 (Ly-836)	11,670 ± 340 (Ly-832)
Cle 15	Peat	Boreal	7900 ± 170 (Ly-841)	—	—
Cle 15	Peat	Boreal	8210 ± 300 (Ly-1881)	—	—
Cle 16	Peat	Boreal	—	—	9630 ± 240 (Ly-1844)
Cle 16a	Peat	Boreal	8010 ± 130 (Ly-842)	—	—
Cle 16ab	Peat	Boreal	8870 ± 200 (Ly-1882)	—	—
Cle 16b	Peat	Boreal	8540 ± 170 (Ly-843)	—	—
Cle 17a	Clay	Pre-Boreal*	—	8410 ± 180 (Ly-844)	9440 ± 250 (Ly-831)

* Uncertain attribution.

from a few milligrams of the ^{14}C samples by the usual method using phosphoric acid. The samples from the Poeymaü site were analyzed on an AEI isotopic mass spectrometer (M S 20), and the other samples were measured using a CAMECA mass spectrometer (215 M I). The values presented in table 4 are given as ‰ (per mil) relative to the PDB standard.

Despite the rather small number of measurements available, the dated materials appear to be isotopically fairly homogeneous. From this, we conclude that no significant isotopic exchange has occurred during the fossilization of the shells or their preservation in the soil. All measured $\delta^{13}C$ values lie between −5 and −11‰, and thereby agree with previously obtained values for the same type of material. The lack of correlation between the age discrepancies and the $\delta^{13}C$ values means that they cannot be used as a correction to obtain more accurate ^{14}C dates.

The small number of observations presently available are consistent with the hypothesis that the variations of the $\delta^{13}C$ values relate to metabolic differences between the different species studied. All values for a single species *(Helix nemoralis)* from the Poeymaü site are very similar despite the considerable time range involved. Many more measurements

TABLE 4

$\delta^{13}C$ value (vs PDB) from miscellaneous terrestrials gastropod shells

Site	Gastropod species	Period	Lab nos	$\delta^{13}C$ ‰	^{14}C ages
Poeymaü	*Helix nemoralis*	Atlantic	Ly-1785	− 7.9‰	7940 ± 310
"	" "	"	Ly-1786	− 8.9‰	7690 ± 310
"	" "	Boreal	Ly-1787	− 8.0‰	9240 ± 220
"	" "	Pre-Boreal	Ly-1788	− 9.0‰	10,300 ± 250
"	" "	" "	Ly-1789	− 8.9‰	10,700 ± 290
"	" "	" "	Ly-1790	− 9.0‰	10,250 ± 240
Clenay	*Helix* sp	Boreal	Ly-1844	− 7.9‰	9630 ± 240
Pompertuzat	*Pupilla muscorum*	Würmian III	Ly-1883	− 6.7‰	$22{,}020^{+1700}_{-1400}$
"	" "	" "	Ly-1913	− 6.8‰	$20{,}700^{+900}_{-800}$
Trebous	*Bulimus tentaculatus*	" "	Ly-1884	− 5.6‰	$29{,}200^{+2800}_{-2000}$
Achenheim	*Columella columella*	Würmian	Ly-1888	− 5.3‰	$35{,}200^{+2200}_{-1800}$
Baume	*Trichia hispida*	Holocene	—	− 7.6‰	—
Saint-Apollinaire	*Succina oblonga*	Atlantic	—	− 5.4‰	—
Val Suzon	*Cepaea hortensis*	Holocene	—	− 7.5‰	—
"	*Succina oblonga*	Actual	—	− 9.6‰	—
Saint-Martin	*Pupilla muscorum*	"	—	− 9.5‰	—
La Combaz	*Cepaea* sp	Atlantic	—	−10.9‰	—
Flavigny	*Trichia hispida*	Actual	—	− 6.1‰	—
Marsannay	*Vallonia costata*	"	—	− 5.3‰	—
Flavigny	*Discus rotundatus*	"	—	− 6.4‰	—
Dampierre	*Cepaea* sp	Atlantic	—	−10.4‰	—
Chenove	*Helicella striata*	Würmian	—	− 6.6‰	—

on samples of different species will be needed to establish this point, beyond doubt.

Possible origin of the age discrepancy of snail dates

The deviations of 300 to 1300 ^{14}C years in our samples (fig 4) indicate a mean depletion of about 4 to 15 percent of the initial ^{14}C content of the snail shells. The ^{13}C measurements suggest metabolic differences between different species. Rubin, Likens, and Berry (1963) suggested that some carbon incorporated in the shell is derived from digested ancient solid carbonates. Such an origin of a part of the shell carbon would explain the observed discrepancy, and should not provoke a detectable alteration in the natural ^{13}C content. This mechanism might easily be tested by labelled feeding experiments.

Applicability of terrestrial mollusk shells for chronologic studies

Although the deviation of snail shell dates from those derived from more classical materials is rather constant, the absence of a suitable correction makes these dates generally unreliable for most archaeologic studies which often require more precise results. They may, in some cases, provide useful information about disturbances in deposits, as was the case for the Pégourié site or the upper layers at Poeymaü.

The observed difference of about 1000 ^{14}C years is less troublesome in the context of geologic studies on relatively old sediments of the Late Glacial period. Frequently the sediments contain no other carbonaceous material (*ie,* loess), and shells may then be the most reliable material available. The uncertainty in the snail dates does not exceed the usual statistical margins for such ancient samples, and they may give interesting chronologic data.

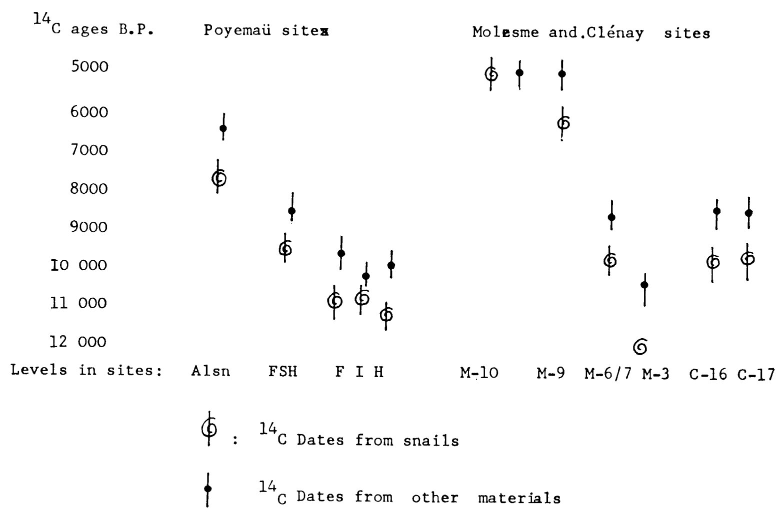

Fig 4. Comparison between snail ^{14}C dates and ^{14}C dates from other material from the same strata.

We have measured samples from various loess sites in France and find satisfactory agreement with the ages established from palaeographic, faunal, and sedimentologic evidence (table 5). A stratigraphic series containing enough snail shells at different levels was found at Achenheim, near Strasbourg, Alsace, France (48° 34′ N, 7° 37′ E). This site is a former loess quarry in which sediments from the Early Quaternary to the Holocene periods outcrop between a very complex system of faults. The overall stratigraphy of the site was studied first by Wernert (1957), and later by Thevenin and Marnot-Houdayer (1978) who provided us with samples. A black horizon, attributed to the Early Würmian (Ly-1276: ⩾ 43,500 BP), underlies the most recent series of the site which is composed of four layers of loess (fig 5). ^{14}C measurements were made on snail shells and on calcareous worm secretion (table 5). The worm secretions are found in considerable amounts, scattered over all levels. They are small, about 2mm long, ovoid pellets composed of well-crystallized carbonates showing radial orientation: similar structures are produced by modern worms. The concordance between the ^{14}C dates obtained from secretions and from snail shells, and their agreement with the attribution of the loess to the Würmian II and Würmian III periods indicate that the secretion might also be a suitable carbonate material for ^{14}C dating.

CONCLUSION

This study on the use of terrestrial mollusk shells for ^{14}C dating should be completed by measurements on stable isotopes, and by laboratory experiments on living snails. It would also be useful to extend the range of ages examined. At present, we can only consider these samples

TABLE 5

^{14}C dates of gastropod shells and worm secretions from Würmian sediments

Site	Presumed geologic period	Dating material	Lab nos	^{14}C ages BP
Sathonay	Würmian III or IV	Snails	Ly-1004	12,300 ± 380
Pompertuzat	Würmian III	Snails	Ly-1883	$22{,}020^{+1700}_{-1400}$
″	″ ″	″	Ly-1913	$20{,}700^{+900}_{-800}$
″	″ ″	″	Gif-2512	20,900 ± 570
Trebous	Würmian II or III	″	Ly-1884	$29{,}200^{+2800}_{-2000}$
Achenheim 1	Würmian II or III	Snails	Ly-1885	$30{,}700^{+1200}_{-1000}$
″ 1	″ ″	Worms	Ly-1886	$24{,}900^{+2200}_{-1800}$
″ 2	″ ″	Snails	Ly-1887	$33{,}200^{+3200}_{-2300}$
″ 2	″ ″	Worms	Ly-1888	$35{,}200^{+2200}_{-1800}$
″ 3	Würmian II	Snails	Ly-1889	⩾35,000
″ 3	″	Worms	Ly-1890	⩾35,000

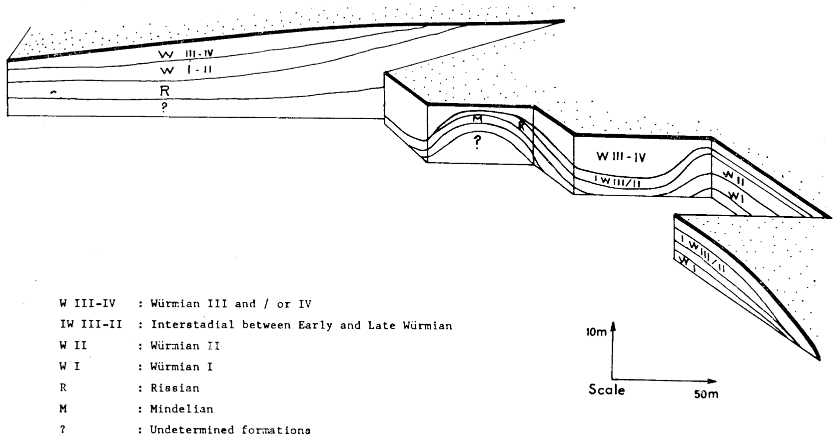

Fig 5. Simplified section of the Würmian layers of Achenheim site, according to G Thevenin.

reliable to within 1000 ^{14}C years, but a selection of particular species, or of other carbonaceous material, may improve this. These terrestrial species only living in the open air and away from waterborne carbonates can already be very useful in the absence of more suitable organic carbonaceous material, particulary in studies of the Late Glacial period. In any case, the dates present valuable *termini post quem*.

The selection of a single species, a careful cleaning procedure and check of the homogeneity of the sample by numerous stable isotope determinations may allow the estimation of reasonably accurate dates from the natural radiocarbon activities of these fossil shells.

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DISCUSSION

Srdoc: Did you clean the shell surface by acid treatment? If yes, did you measure the activity of the evolved CO_2 to check for any contamination of the original sample?

Evin: Yes, we sometimes dissolved the upper layer of the shell by dilute acid but we never measured the CO_2 obtained.

Fritz: Experimental work in the USA done ~15 years ago shows that terrestrial snails can digest significant amounts of carbonate carbon which, at least in part, is then found in the shell. Therefore, could one expect that snails living on carbonate terrain show larger "old carbon" contaminations than snails from carbonate-free environments?

Evin: Rubin, Likens, and Berry (1963) suggested that digestion of ancient carbon would give a depletion of about 10 percent of the initial ^{14}C content of shells. We do agree with this hypothesis which involves apparent ages about 1000 years too old, quite in agreement with the present results on fossil snails. We have no indications of a greater age discrepancy in calcareous areas.