THE SELECTION OF NON-MARINE MOLLUSCAN SHELLS FOR RADIOCARBON DATING

by

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The use of shells from terrestrial and freshwater molluscs for radiocarbon dating has in the past been viewed with scepticism or even dismissed entirely because the results are prone to distortion from post-depositional diagenesis, or the incorporation of material with a low $^{14}C/^{12}C$ ratio whilst the mollusc was alive, or both. The thesis attempts to discuss how the relative importance of the two factors can be assessed and the corresponding ages corrected accordingly.

Diagenesis was studied by comparing the structure and chemical composition of 39 species of British molluscs from modern specimens with those of fossil samples. Three main effects of diagenesis were studied using light and scanning electron microscopy, mass spectrometry and atomic absorption spectroscopy: the transformation of aragonite to calcite, a reduction in the standard deviation associated with the distribution of major ion concentrations within a shell population, and an enrichment in the lighter isotopes of carbon and oxygen. Only the transformation of mineralogy proved to be sufficiently sensitive to detect diagenetic material present at levels of 1-2%. The effects of diet and ambient carbon dioxide were studied by chemical analysis and mass spectrometry. Differences in stable isotope ratio values between micro-environments were found to be significantly greater than those between and within species. The established relationship between ^{13}C, ^{14}C and the environment can be used to identify shells in which the apparent age effect will be at a minimum.

Comparison of ^{14}C dates for charcoal and untreated shell samples showed that the above sources of error led to discrepancies of as much as 1500 years in the shell dates. Seven samples selected and pretreated in accordance with the procedures proposed in this thesis gave ages within two standard deviations of the values accepted for the deposit in question, and four samples gave ages which were being statistically identical with the accepted values. In addition, the screening tests permitted samples destined to give erroneous ages to be identified from the outset.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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NOTES ON ISOTOPE CONVENTIONS

All stable isotope results were determined relative to the PDB standard using a secondary standard MCS-8 or MCS-9.

All ^{14}C dates are given as bp and are, therefore, uncalibrated before 1950 dates. Each ^{14}C date is followed by the laboratory measurement number. A few numbers are incomplete as the full reference was not available at the time of writing. The laboratory codes are as follows:

OxA	Accelerator Unit, Oxford Laboratory for Archaeology and the History of Art.
Q	Godwin Laboratory, Cambridge.
HAR	Low-Level Measurements, AERE Harwell.
BM	British Museum, London.

"Uncontaminated dern Wood is equivalent to the Primary D ng Standard 95% NBS Ox li cid S dar)

CHAPTER 1. INTRODUCTION

1.1 SHELLS IN ^{14}C DATING

During the first half of this century the chronological framework for studies of past environments was provided by stratigraphy, environmental indicators and, where available, human artefacts. In general these were capable of supplying only relative or implied ages. As the resolution of environmental chronologies improved their interpretation increasingly required quantitative dating. This was generally provided by radiometric dating, in the case of the Late Quaternary by means of ^{14}C assay. Charcoal, plant and other organic materials (including bone collagen) came to be considered as the most suitable for ^{14}C dating, with soil nodules, tufa, marine and non-marine shells and other carbonates as a last resort because of their alleged unreliability. Yet this standpoint is hardly valid if carbonates provide the only usable material available at the site or section under review (e.g. Young and Renaut 1979; Clark *et al.* 1972).

Carbonates can be divided into two groups; those deposited from groundwaters (tufa, nodules, travertine) and shells. The former are likely to be less reliable because of their naturally low ^{14}C content. Shells can also be subject to this defect but as they also incorporate atmospheric and plant-derived ^{14}C it is potentially less severe, particularly in marine shells where the ^{14}C is largely from the oceanic reservoir. Shells are often the only datable material in tufas, buried soils, alluvium from fluvial or lacustrine environments, dunes and beach deposits. The information gained from accurate dating of these deposits can be applied to areas such as environmental history, neotectonics, and isostatic and eustatic changes on coasts. The present study focuses on non-marine species, which are considered the least reliable and which have received less attention than marine species.

1.2 SOURCES OF AGE ERROR IN ^{14}C DATES ON NON-MARINE SHELLS.

Four main sources of error in the dating of shells can be identified:

(i) Misattribution by the collector.

(ii) Displacement of the shell from one depositional horizon to another.

(iii) Post-depositional alteration of the shell leading to exchange of ^{14}C with the environment.

(iv) Incorporation, at the time of shell formation, of material depleted in ^{14}C (the "apparent age effect").

The first item (i) is human error and can be overcome by good fieldwork techniques and careful recording. The second source of error can, at least in part, be overcome by careful examination of the context and shells. Evidence for reworking may be seen in the type of deposit (e.g. hillwash), or in the state of preservation of the shells (e.g. evidence of wear on the external surfaces). The movement of shells through sediments is unlikely to have occurred if complete large shells are collected.

Post-depositional alterations to the shell may cause exchange of shell ^{14}C with the surrounding environment. In general this will lead to the shell's having an age less than that of the context. When the shells of non-marine molluscs are altered there will be detectable changes, particularly in mineralogy and crystal structure.

Comparison of modern and fossil shells allows the nature and type of alteration to be investigated.

The "apparent age effect" leads to dates greater than that is the context. The source of error is the incorporation of CO_3^{2-} ions from the environment, particularly chalk, limestone and tufa. The magnitude of the error will depend on the degree of ^{14}C depletion and the amount of material that becomes incorporated. Selection of shells in which this effect is at a minimum will be possible if the depletion in ^{14}C is accompanied by other measurable changes (e.g. in ^{13}C content, the relative proportions of different cations, etc.).

Detection of such errors will be at its best when the sample to be dated is screened in its entirety, and this in practice is only possible where dating is by Accelerator Mass Spectrometry (AMS) since this uses a few milligrams of material. Otherwise only a small percentage of the sample can be studied and in any case time will generally permit only a few of the shells in a sample destined for conventional ^{14}C dating to be subsampled.

1.3 RADIOCARBON DATING OF SHELLS

1.31 Origins of Radiocarbon

Radiocarbon is produced in the upper atmosphere by the interaction of nitrogen atoms and thermal neutrons:

$$^{14}N + n \longrightarrow {}^{14}C + H \qquad \text{(eq. 1.1)}$$

The neutrons concerned are secondary particles produced by the incidence of primary cosmic ray flux on the atmosphere. The global production of ^{14}C is estimated at 7.5kg per year.

The ^{14}C atoms become incorporated in living plants and animals and in the dissolved carbonate of the ocean; the concentration is about 10^{-12} relative to natural carbon (^{12}C). The level is effectively uniform owing to the comparatively rapid mixing throughout the carbon exchange reservoir (atmosphere, biosphere and oceans) (Aitken 1978). Variations arise from the residence time of ^{14}C in ocean waters, fractionation between different carbon states and variations in production; these are discussed in the substantial literature that has developed (e.g. Stuiver et al. 1981).

In living material the ^{14}C remains in equilibrium with the environment until that material is removed from the system by growth (tree rings) or death. The carbonate of shells is effectively isolated from the environment after death. The potential sources of ^{14}C for shells are the atmosphere (CO_2), plant material, groundwaters (including dissolved carbonates and CO_2) and $CaCO_3$ materials (e.g. limestone, chalk, tufa and calcareous sands).

After the ^{14}C is removed from exchange with the environment it decays by emmission of low-energy beta particles (max.160 keV) according to:

$$^{14}C \longrightarrow {}^{14}N + e^- \quad \text{(eq. 1.2)}$$

The presently accepted half-life for ^{14}C is 5730 years but the older value of 5570 years is used for the sake of uniformity.

1.32 Conventional Measurement of ^{14}C Activity

(i) Gas-proportional counting

Gas-proportional counting was favoured during the early work on ^{14}C, and in recent years again it has come into use for counting very old samples under heavily shielded conditions (Stuiver et al. 1979) and particularly in miniture gas counters for small samples (Otlet et al. 1983).

The carbonate is converted to CO_2 and the gas used to fill a counter several litres in volume to a pressure of 1-2 atmospheres. In a traditional counter the gas will contain 1-2g of carbon giving a count rate of 10-20 counts per minute. The counter requires substantial shielding from external radiation.

(ii) Liquid scintillation counting

Liquid scintillation counting requires the sample to be converted to a liquid, usually benzene. The liquid is used as a solvent for a scintillator and the "cocktail" placed so as to be viewed by two photomultipliers in coincidence. The concentration of carbon atoms in benzene allows a high count rate to be obtained. The use of vials and a liquid scintillation counter allows standards and samples to be measured alternately and the effects of drift in detection, sensitivity or background to be eliminated. This method is used by the Godwin Laboratory at the University of Cambridge where some measurements for this thesis were undertaken.

At Cambridge the carbonate samples were reacted with hydrochloric acid (HCl) under low-vacuum. The resultant CO_2 was dried in dry ice/methanol traps and collected in a vessel cooled by liquid nitrogen. The cleaned gas was transferred to a synthesis line and converted first to acetylene and then to benzene to which the scintillant was added.

The benzene was left for several weeks to allow any radon that might be present to decay; it was then measured until 10,000 counts had been recorded, statistically giving counting errors of 1%. Correction for ^{13}C fractionation from the standard value of -25°/oo was made by measuring a sub-sample taken at the beginning of the synthesis line.

1.33 Accelerator Mass Spectrometry (AMS)

Measurement of ^{14}C by AMS allows the direct counting of atoms and does not rely on their decay for detection. Direct detection reduces the necessary sample size to 1-5mg of carbon and reduces the preparation and measurement time to a few hours (depending on age). AMS dates were obtained on shell samples for this thesis at the Research Laboratory for Archaeology and the History of Art at Oxford.

Carbon dioxide was derived from the shell samples (10-100mg) and converted to acetylene and finally graphite coated onto a tantalum wire. Duplicate wires of samples were prepared and placed along with standards and background samples in the source of a tandem accelerator (figure 1.1). The caesium ion source converts the graphite to C^- ions and these were then accelerated towards a positive electrode and any ^{14}N that might have been present was lost due to its short path length prior to decay. The carbon atoms were converted to C^{3+} ions and accelerated through mass/charge selectors to remove any contaminating ions (e.g. $^{12}CH_2$). The ^{14}C and ^{13}C ions were then measured alternately at the collector. The mean age determined for the duplicate sample wires was obtained and then corrected for ^{13}C fractionation.

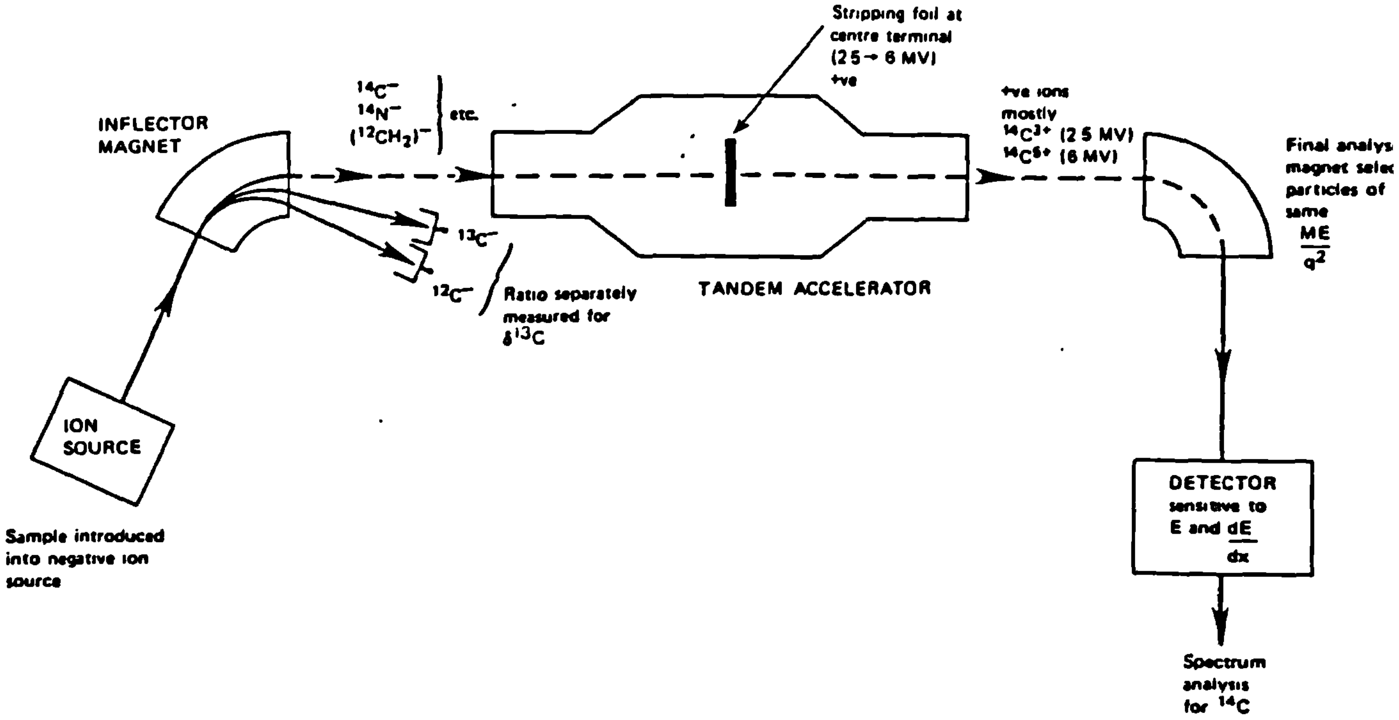


Figure 1.1. Principles of AMS ^{14}C dating (After Otlet 1979).

1.4 Struture of the Thesis - Aims and Methods

1.41 Aims of the thesis

The aims of the thesis are:

(i) To investigate the sources of age error associated with non-marine mollusc shells.

(ii) To identify methods for detecting shells in which age errors are likely to be present.

(iii) To identify methods for selecting material in which age errors are at a minimum.

(iv) To study the possibility of correcting for errors when they are present.

(v) To establish the magnitude of the age errors present in samples subjected to different levels of pretreatment.

1.42 Methods and approaches

(i) Approach

The overall approach was to make a comparative study of the structure and composition of modern molluscs and the ecology of the sites where they were collected, apply the findings to fossil samples, and validate the conclusions using samples from independently dated contexts. Comparative studies were undertaken for the post-depositional changes in shells and the "apparent age effect".

(ii) Methods

(a) Shells - formation, ecology, and environment.

It will be shown later that the ecology of a species, the availability of $CaCO_3$ and its ^{14}C content are important factors in controlling age errors. These features were studied by combining field observations, previous studies, and laboratory analyses (e.g. particle size, $CaCO_3$ content). The materials required for the formation of shell carbonate and their sources are considered, as is the effect these will have on shell chemistry. The resultant effect of environment and ecology on the ^{14}C content is also discussed.

(b) Comparative studies of shell structure, mineralogy and chemistry in modern shells.

Previously little work had taken place on the structure and chemistry of non-marine shells, largely because they were considered to have little or no variation. Shells of the commoner large species of Mollusca found in north-west Europe were collected or obtained from the British Museum (Natural History). The structures of the shells were studied using Scanning Electron Microscopy (SEM) and optical microscopy, and the mineralogy using X-ray Diffraction analysis (XRD). The detection and feasibility limits of each technique were studied and where possible quantified.

The chemistry and stable isotope composition were analysed by Atomic Absorption Spectroscopy (AAS) and Mass Spectrometry respectively. The results were applied to both the problem of post-depositional alteration, by examining changes between modern and sub-fossil populations, and to the "apparent age effect" by relating environment, ecology and composition of the carbonate source of modern samples to the shell composition.

(c) Study of structure, mineralogy and chemistry in fossil shells.

Having established a "baseline" by the study of modern shells it was possible to observe and analyse sub-fossil samples for post-depositional changes to structure and chemistry, and to examine variations in the chemistry between modern and sub-fossil populations. The implications of the observed changes for ^{14}C dating could then be considered and levels of suitability for dating established for individual shells or populations.

(d) Selection and validation

The conclusions from the three above sections were then combined to give an integrated approach for the selection of shells with minimal or quantifiable age errors. The integrated approach was then applied to sub-fossil shells from contexts which were independently dated, usually by ^{14}C dating of charcoal. The ^{14}C ages obtained from the shell samples were then considered in the light of the selection criteria and unexpected errors discussed.

1.43 Limiting constraints associated with the methods applied

As it is intended that the procedures should be applicable by other researchers and ^{14}C laboratories three constraints had to be considered: availability of equipment, time, and sample material. The final integrated procedure is ideally suited to a laboratory which has access to a mass spectrometer, and AAS, XRD, and SEM equipment, and which can obtain AMS ^{14}C dates. The total sample size required for all these is a minimum population of 10 shells (ideally 20), each with a minimum weight of 200mg. The total time for pretreatment and selection would be approximately 16 hours (2 working days). The procedure can be shortened, but each step removed will increase the possibility that age error will increase. If conventional ^{14}C dating is to be used the sample size will need to be much greater (minimum 12g of shell after pretreatment and selection, probably 25g before). The sample dated will necessarily be more mixed and the material analysed a smaller sub-sample of that submitted for dating. These factors will again increase the likely age errors.

The equipment required for full pretreatment and selection will generally be available in a radiocarbon laboratory, but the time required may not be. The submitter would be more likely to have time but is unlikely to have the full range of equipment without the co-operation of other researchers.

1.5 RADIOCARBON DATING OF NON-MARINE MOLLUSCA - PREVIOUS STUDIES AND ANSWERS

The chapters dealing with each of the four methods of research outlined above contains a review of the most important work in that field. The present section outlines seven key works which deal specifically with the subject of the thesis.

Tamers (1970) dated shells and charcoal taken from the same contexts in cave deposits in Texas and Venezuela. The results for the Texan sites showed the shells to have apparent ages of 235 to 2785 years. The shells from Venezuela generally gave dates that, owing to the large standard deviations of each pair, were not significantly different from the charcoal dates but five shell dates were younger than the corresponding charcoal age. Tamers concluded that under some conditions the shell dates could be considered reliable or the errors of acceptable magnitude, in this case a mean error of 450 years. He considered the possibility of improving the accuracy of the shell dates by correction with the $\delta^{13}C$ value and concluded that too many factors influenced the $\delta^{13}C$ value to allow its use.

Evin <u>et</u> <u>al</u>. (1980) applied a fairly rigorous approach to shells from calcareous deposits including tufa. The contexts were dated by associated ^{14}C dates on peat and charcoal, or by environmental evidence. Samples of shells were from single species and each shell was thoroughly cleaned. The pairs of dated samples showed the shells to be older by 300-1300 years. One pair of samples gave an error of 2280 years which was attributed to admixture of later charcoal and artefacts, an example of the potential range of human error.

Evin _et_ _al_. (1980) comment that age errors of this magnitude make shells unsuitable for dating archaeological contexts but of some value for dating geological deposits, particularly of the Late Pleistocene. They also suggested that the $\delta^{13}C$ variations observed in shells were due to metabolic differences between species and not to digested ancient solid carbonates. However, they also suggested that the $\delta^{13}C$ values of a shell population could be used as a measure of sample homogeneity.

Evin _et_ _al_. conclude that ^{14}C dates on terrestrial shells can only be considered reliable to within 1000 years although the dates provide valuable maximum limits.

Two papers (Goodfriend & Hood 1983; Goodfriend & Stipp 1983) suggest that the ^{13}C value of a terrestrial snail shell will reflect the contribution to the shell made by limestone, plants and the atmosphere. Formulae for estimating the proportion of each of the components are described and then applied to shells of species from limestone and non-limestone areas. Radiocarbon dates on shells from non-limestone areas showed no apparent age effect, whilst shells from limestone areas had up to 33% of their shell derived from the limestone. When the $\delta^{13}C$ and age error of the samples were plotted a weak relationship was observed. Goodfriend considers exchange due to shell volume to be more important than the limestone contribution in determining the δ^{13}C value.

The four papers described above consider the age errors and apparent age problems associated with non-marine shells. A possible correction method for these problems was studied by Burleigh and Kerney (1982) and Burleigh (pers. comm. in Preece 1980). The method relies on the similar ^{14}C depletions being displayed by modern and fossil samples from the same area. The first paper compares the age error associated with fossil shells with that of pre-bomb shells. The former was found to be 510 years and the later 1350 years, which suggests that the method is not valid under normal conditions. The second paper (Burleigh 1980) applies a "blank" of some 2500 years, based on the ^{14}C content of a modern (post-bomb) sample. The "corrected" fossil date of 500 ad was acceptable but the unquantifiable errors in determining the "blank" for a modern sample make the corrected date very approximate. Preece (1980) comments on the less equivocal results from analysis of other samples (e.g. those in Burleigh and Kerney 1982) and suggests that an extensive series of ^{14}C determinations of charcoal and shell carbonates from identical contexts is required.

One futher paper is of great relevance to this thesis: that by Chappell and Polach (1972). It discusses the detection of recrystallised carbonate in marine shells by SEM and thin-sectioning. Their work included measuring the effect of different types of recrystallisation on the ^{14}C date and was the first paper to recognise that ^{14}C dates on shell carbonates could be reliable if proper attention was paid to their pretreatment. This work was followed up by Walker (1979) and Vita-Finzi and Roberts (1983) at

University College London.

The seven papers discussed in this section represent the approaches others have taken to the dating of shells and also the limits that each considered accompanied shell ^{14}C dates. Other workers have been less optimistic and consider all shells to be inaccurate and non-marine shells to be completely unreliable, though few committed their views in print. The attitude of the "pessimists" was summed up by the sponsors of the present research:

> "It is universally accepted by radiocarbon chronologists that the carbonate laid down by freshwater and terrestrial molluscs is totally unreliable for objective ^{14}C dating"
> (NERC, pers.comm. 1984)

A critical look will be taken at the sources of error associated with ^{14}C dating of non-marine shells and some of the previous research outlined above will be reassessed. By these means it is hoped to quantify the level of unreliability to avoid blanket condemnation of a potentially valuable technique.

CHAPTER 2 ENVIRONMENT AND ECOLOGY

2.1 THE IMPORTANCE OF ENVIRONMENT AND ECOLOGY

The origins of the "apparent age effect" and post-depositional alteration of shells lie in the ecology and environment of the mollusc. The ecology of a particular species and the materials available for shell construction will control the composition of the shell at the time of deposition. The environment of the shell after deposition will exert a considerable amount of control over any post-depositional alterations and contamination that occurs.

Six aspects of ecology and environment are considered to be particularly important to the present study:

(i) Type of site (e.g. slopewash, alluvium, tufa)
(ii) History of the site
(iii) Habits of the species (e.g. burrowing, diet)
(iv) Homogeneity of the shell population (e.g. inclusion of reworked shells, shells from a number of micro-environments)
(v) Type and ^{14}C content of solid $CaCO_3$ (e.g. chalk, tufa)
(vi) Drainage and groundwater (e.g. potential movement of material for ion exchange, contamination, or structural alteration)

These aspects were combined to give a description of each species and site studied, both modern and fossil. The chapter also discusses the use of molluscs as environmental indicators and concludes with a discussion of the effect of the environment on post-depositional alteration, and the potential effect of environment and ecology on the ^{14}C activity of shells.

The ways in which the environmental shell components are utilised and their effect on shell composition are discussed in chapters 3 and 5.

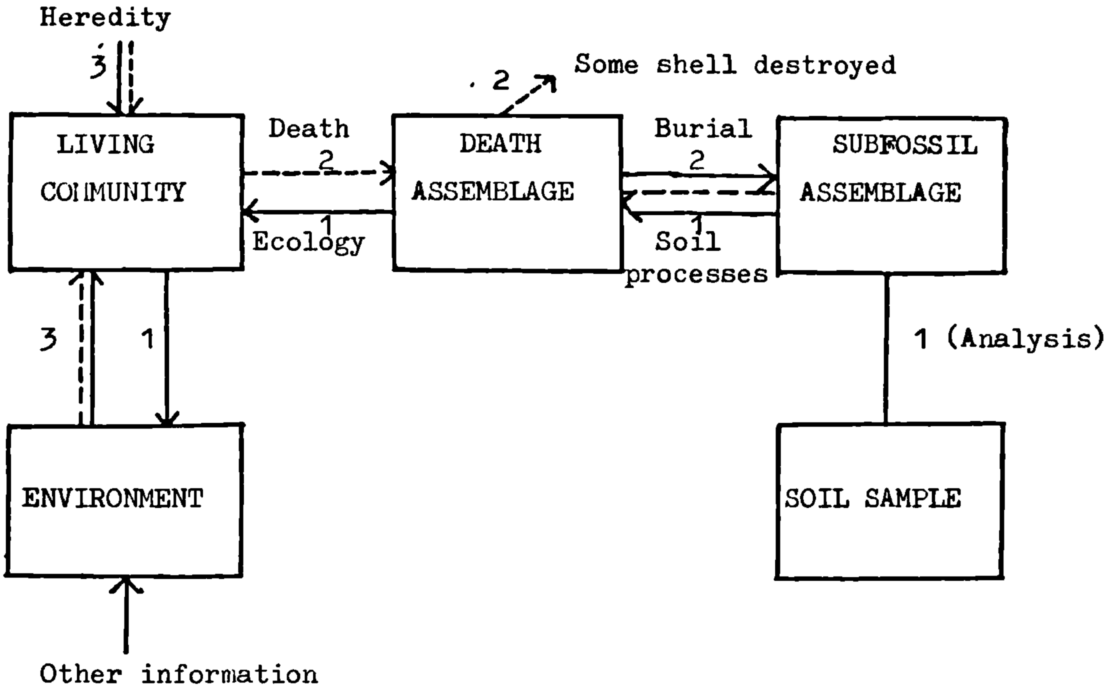
2.2 HABITATS AND ECOLOGY OF MODERN SPECIES

2.21 The Use of Terrestrial Mollusca as Environmental Indicators

The use of molluscs as environmental indicators relies on the same narrow niche being occupied by a species at a range of sites. A narrow environmental niche will benefit ^{14}C dating because any observed variation must reflect changes within the niche (diet or metabolic) rather than a change in the environment. The importance of this will be shown in chapter 5.

The basis for the interpretation of assemblages of mollusc shells from fossil sites is the ecology of their present-day counterparts (Evans 1972). Two main categories of difficulties occur in this basic assumption, and can be generalised as stratigraphical and ecological. The former includes the changes that the composition of the assemblages undergoes in the course of soil formation and sediment deposition. The latter includes the factors that control the composition of modern faunas and the way in which the influence of these factors has changed with time (figure 2.1).

The use of snails as environmental indicators in fossil contexts dates back to the work of Pitt-Rivers in Sussex over a century ago (Lane-Fox 1869; 1876). In Britain much of the early work on land and freshwater Mollusca was done by A.S. Kennard, in conjunction with others such as Woodward and Cunningham. This work took place between the end of the nineteenth century and the 1940's. In more recent times many reports have been published on faunal assemblages from



1 = Stages in the formation of a subfossil assemblage
2 = Stages in analysis and interpretation
3 = Factors controlling composition of snail communities

Figure 2.1. Stages in the formation of a subfossil landsnail assemblage (After Evans 1972)

geological and archaeological sites (Sparks 1964; Sparks & West 1964; 1968; 1970; Kerney 1963; 1968; Kerney <u>et</u> <u>al</u>. 1980; Preece 1980; Preece & Robinson 1984).

Snails offer certain advantages as environmental indicators: they are small; they are plentiful in calcareous soils; and there is a limited number of species covering a wide range of habitats. Snails are particularly sensitive to changes in land use and are good indicators of open ground, shade and moisture. Environments that appear different to humans may seem identical to the snail. The environments need to be considered at a micro-level and consideration given to the factors important to the snails such as availability of calcium carbonate and lack of disturbance. The converse is also true: apparently identical habitats will contain different faunas because of small specific differences.

Evans (1972) describes most snail species as occupying a general ecological niche in which they act as small herbivores, scavengers and carnivore feeders. Most species favour moister and less disturbed habitats and they live on low vegetation or the ground surface or burrow in the loose topsoil. It will be shown in the chapter 5 that the exact niche and its micro-environment are critical in creating the final chemical and isotopic composition of the shell. Species are not restricted to living on or in association with particular plant species and are capable of eating a wide range of plant species (Grime <u>et</u> <u>al</u>. 1968), though some are preferred. The structure of the vegetation is important as some species prefer decaying to living plant material. The species of plant eaten will not affect the stable isotope values in temperate European climates but in arid and Mediterranean areas the different $\delta^{13}C$ value for groups of plants will be reflected in the $\delta^{13}C$ of the organic and inorganic components of the shells (Goodfriend pers.comm. 1985).

The ability of snail species to live in an apparently wide range of environments and adapt to a new macro-environment by locating a suitable micro-environment must be considered when assuming that shells from fossil sites reflect the same environments as modern snails. In order to obtain the most accurate picture of a past environment the structure and species diversity as well as the particular species present should be examined.

Evans (1972, 207ff) discusses the mechanisms by which snail shells become incorporated into soils and deposits. Shells will only be preserved in calcareous environments and Evans divides calcareous soils and sediments into three groups: soils formed by *in situ* weathering of the parent material, colluvial deposits or sediments formed by accumulation (e.g. hill wash, water lain sediments and wind lain sediments), and colluvial soils (weathered as they accumulate). The formation of the deposit has an important bearing on the population of shells found within it. An extreme case of this is a hill wash deposit which could contain shells that were originally some distance from the place of deposition and possibly are not contemporaneous if reworked material is involved. Soils formed by weathering could also contain reworked material if the parent material were a colluvial deposit formed appreciably earlier than the weathering episode. These problems are discussed further in chapter 2.4.

2.22 Ecology of species in this study.

Six species were collected for study and analysis: *Cepaea* nemoralis, C.hortensis, Arianta arbustorum, Helix pomatia, Pomatias elegans and Xeropicta vestalis.

Cepaea nemoralis

This species is found over much of the British Isles but is absent from the north of Scotland and the Outer Isles. Its distribution is controlled by its preference for lime and calcium carbonate (Boycott 1934). It occupies a variety of habitats: woods, hedges, marsh, grassland and dunes. It is generally found in drier and warmer habitats than C.hortensis. C.nemoralis is found in Hoxnian and Eemian Interglacial deposits and appears in the early Post-glacial (Boreal or Pre-boreal). Its present distribution is smaller than when it attained its maximum distribution about 4000 bp, probably due to the clearance of forest by prehistoric agriculturalists (Cain & Currey 1963). The diet of C.nemoralis consists predominantly of senescent or dead plant material (e.g. Taraxacum officinale and Ononis repens) (Richardson 1975) with green material from Urtica dioica (Wolda et al. 1971). It is also recorded as eating algae, animal remains and fungi (Wolda et al. 1971). They feed and rest on the lower vegetation at ground level and up to 0.5m above depending on the plants that are present.

Cepaea hortensis.

Cepaea hortensis is more widespread than C.nemoralis but rarer. As with C.nemoralis it lives in woods, grassland, hedges and dunes, but commonly in wetter or colder places. Mixed communities of the two species are uncommon though the change from one species to the other may occur over a short distance. In areas with adjacent colonies of the two species C.hortensis is often found in valleys with C.nemoralis on more exposed uplands. In mixed colonies C.hortensis is found in the vicinity of trees and shaded areas. Cain & Currey (1963) suggest this is because competition between the species is less important in these micro-environments. In areas beyond the range of *C.nemoralis* the habitats that it would occupy in more southerly areas are taken over by *C.hortensis*.

Since the prehistoric period the distribution of *C.hortensis* has become reduced. Studies of the fossil dunes at Northton (Evans 1971) showed it to be common in the pre-Iron Age levels but to have declined at the time when *Cochlicella acuta* and *Helicella itala* were introduced. The modern fauna in the study area at Hayle Towans shows a similar composition with *C.nemoralis*, *C.acuta* and *H.itala* common whilst *C.hortensis* rare. The decline of *C.hortensis* was also evident in Co.Mayo, Eire; 39% of the *Cepaea* shells from a fossil deposits at Carrowmore were *C.hortensis*, whereas in the modern sample from the nearby site of Graffy there was no evidence of living *C.hortensis*.

Arianta arbustorum

This species is widespread in Britain but is rare in Ireland where it is restricted to the north. It is found in a range of habitats such as meadows, herbage, woods and hedgerows, but is always restricted to damp places. The preference for damp areas is due to its low degree of resistance to drought. *Arianta* can be found in colder places than *Cepaea* and, therefore, can be found in thick vegetation, valley bottoms and north facing slopes.

Helix pomatia

Helix pomatia was introduced to England, probably during the Roman period. It is a calcicole and has a limited southern distribution in Britain; it is not recorded from Ireland. It was included in this study because of its large shell size which allowed detailed analyses of within shell variations to be undertaken (section 5.3). The large size of *H.pomatia* has also led to its being widely used as a laboratory animal in education and research; its morphology and ecology are, therefore, well studied.

Pollard (1975b) showed that *H.pomatia* feeds on live plant material in fresh condition, particularly *Centaurea* species, often above the ground surface. Juveniles and young adults were seen less frequently and tended to occupy a habitat with more cover, particularly by concealing themselves under leaf litter and vegetation at ground level.

Pomatias elegans

This species is restricted to areas with highly calcareous soils and is the most characteristic calciphile found in Britain. It is found in open woods, hedgebanks, and screes. It is also recorded from sand hills and arable land but in Britain it favours shaded and moist habitats. It also requires broken ground and loose soil into which it can burrow. Its presence generally indicates some form of disturbance of the soil surface. Comparison of modern and fossil occurrences of *P.elegans* indicates a contraction of the distribution from the south and west (Kerney 1968), perhaps linked to a reduction in winter temperatures since the Sub-boreal period. *P.elegans* is recorded in Britain from about 8000 bp but does not occur in Ireland, probably because it is slow to establish and spread itself. It is known to live for four to five years but the time to reach maturity is not known (Fretter & Graham 1978). Because it feeds at or below the ground surface in areas of broken ground a significant calcium carbonate component is included in its diet.

Xeropicta vestalis

One species of snail not found in Britain was used in part of the study of fossil shells, namely X.vestalis. This species is common throughout the Mediterranean region of Israel, both in the hills and in the Coastal Plain (Heller & Tchernov 1978). It is frequently observed on low vegetation and grass and is found in groups on stems and branches particularly during warm weather. It exhibits banding morphs similar to those found in Cepaea; the number of bands varies from nought to six.

Xeropicta vestalis is the commonest snail found in fossil assemblages in the eastern Mediterranean and shifts occur in its morph frequencies from the Palaeolithic to recent layers, particularly a rise and fall in the numbers of the unbanded morph (Heller & Tchernov 1978).

2.3 ENVIRONMENT AND ECOLOGY OF MODERN SAMPLE SITES

2.31 Introduction

The samples used for the comparative part of the study of chemical and stable isotope composition were collected at three sites in the British Isles selected to cover a range of geologies and the types of site that are most frequently encountered in fossil deposits. The sites were open woodland on chalk at Oldlands Wood, Surrey, calcareous sand dunes at Hayle, Cornwall, and an open site on tufa at Graffy, Co.Mayo (figure 2.2).

2.32 Oldlands Wood, Surrey

Oldlands Wood is a Forestry Commission plantation between Effingham

Figure 2.2. Location of modern and fossil sample site in the British Isles.

and East Horsley, Surrey (G.R. TQ 106517). The site is on the dip slope of the chalk escarpment of the North Downs, on gently sloping north facing ground 105-180m above O.D.

Geology

The geology of most of the wood, including the collection site, is Upper Chalk (H5'''). Tertiary Beds (Reading and Thanet) overlie the chalk about 400m north of the wood on the southern edge of the London Basin. To the south the dip slope is capped by Pleistocene deposits. South-west of the wood and including a small area of the wood are Netley Heath Deposits consisting of sand and very coarse gravels containing blocks of Greensand, Red Crag and flint. To the south-east are deposits of Clay-with-flints which extend over much of the adjacent Ranmore Common. The boundary between the Netley Heath Deposit and the Clay-with-flints is a dry valley which is incised to expose the Upper Chalk and is partly filled with valley gravel. All the lithologies except the chalk yield acid soils and no molluscs were found from any natural habitats on them. Exposures of chalk were observed within the wood and to the north; samples were taken from both of these sites (sample numbers Ch.S3, Ch.S4).

Soils

Two soil pits were dug at the collection site; descriptions of the horizons are given below. The soils are classified as rendzinas.

Soil Description: Site 1

0-2cm Litter L

Consists of slightly decayed material, all derived from leaves. Collected prior to 1984 leaf fall therefore no recent leaves found.

2-3cm Litter F

Partly decomposed material, some original plant material visible.

3-12cm AH1

Dark brown (10YR 4/3) silty loam, roots common, angular fragments of flint (maximum dimension (max.dim.) 2cm)

12-40cm AH2

Dark yellowish brown (10YR 4/4) silty clay loam, angular fragments of flint (max.dim. 2cm) and rounded chalk fragments (max.dim. 0.5cm).

40+cm BH

Yellowish brown (10YR 4/4-5/4) silty clay loam, inclusions as 12-40cm.

Soil Description: Site 2

0-2cm Litter L

Consists of slightly decayed plant material, largely pine needles but some beach leaves. Collected prior to 1984 leaf fall therefore no recent leaves found.

2-3cm Litter F

Partly decomposed material, some original plant material visible.

3-10cm AH1

Light greyish brown (10YR 5/2-6/2) silty loam, many roots, rounded chalk frag. (max.dim. 1cm), some finer particles of chalk influencing the colour.

10-15cm AH2

Greyish brown (10YR 5/2) silty clay loam, roots, rounded fragments chalk (max.dim. 1cm), some finer particles influencing colour.

15-20cm Cr

Weakly consolidated, little altered Chalk, many angular fragments.

20+cm R

Chalk bedrock.

Site 1 appeared to be disturbed and is probably not representative of the area.

Particle size analysis, and organic and calcium carbonate contents were measured (tables 2.1 to 2.4).

Particle size and loss on ignition

Site 1

			(1)	(2)	(3)		
Sample	Type	Depth	LOI (%)	$CaCO_3$	Sand (%)	Silt (%)	Clay (%)
1	AH1	3-12	13.7	3.0	67.9	25.1	6.9
2	AH2	12-40	10.0	0.0	69.7	22.5	7.8
3	BH	40+	7.5	0.0	84.1	14.5	1.5

(1) Loss on ignition (2) Percentage of whole sample (3) All fractions

Table 2.1 Particle size and LOI for samples from Oldlands Wood Site 1

Site 1 Sand Fractions (%)

Sample	Type	Depth	>1mm	1.000-0.500mm	0.500-0.250mm	0.250-0.125mm	0.125-0.063mm
1	AH1	3-12	5.7	7.1	20.2	25.0	9.9
2	AH2	12-40	5.2	4.6	15.4	30.4	14.1
3	BH	40+	3.5	3.9	13.7	39.1	23.9

Table 2.2 Sand fractions for samples from Oldlands Wood Site 1.

Site 2

			(1)	(2)	(3)		
Sample	Type	Depth	LOI (%)	$CaCO_3$	Sand (%)	Silt (%)	Clay (%)
4	AH1	3-10	14.4	28.0	32.3	55.3	12.7
5	AH2	10-15	9.3	45.0	63.1	21.8	15.0
6	Cr	15-20	7.3	71.0	60.6	5.3	34.6

(1) Loss on ignition (2) Percentage of whole sample (3) All fractions

Table 2.3 Particle size and LOI for samples from Oldlands Wood Site 2.

Site 2 Sand Fractions (%)

Sample	Type	Depth	>1mm	1.000- 0.500mm	0.500- 0.250mm	0.250- 0.125mm	0.125- 0.063mm
4	AH1	3-10	5.5	3.3	5.4	11.1	7.0
5	AH2	10-15	14.4	6.1	9.2	19.6	13.8
6	Cr	15-20	20.8	10.0	7.5	14.7	7.6

Table 2.4 Sand fractions for samples from Oldlands Wood Site 2.

Site 2 is considered to be representative of the wooded area. It shows increasing $CaCO_3$ content down the profile but access to the calcium carbonate is restricted by the litter layers. Site 1 shows very low levels of $CaCO_3$ and must represent a dump or artificial deposit.

The only source of $CaCO_3$ will be the chalk present as exposures or particles in the soil; it all has a zero ^{14}C content.

Drainage

The wood and surrounding area are well drained through the rendzina and the permeable chalk. No standing water was observed and although small incised valleys occur on the south side all are dry at present. The Clay-with-flints at the south-east end of the wood is less freely drained, but any overland flow is rapidly drained at the clay/chalk boundary.

History of the Wood

The area was used in the nineteenth century for lime burning. Two areas at the south end of the wood are called Kiln Field Coppice and Pump Pond Wood; a number of disused pits are located near Kiln Field Coppice. Two embanked track ways run roughly north-south through the wood. This evidence suggests chalk pits, kilns and slaking ponds, and a mineral line running north to the main railway at East Horsley. The area is shown as woodland on late 19th century maps and the presence of kilns also suggests a traditional area of woodland. The fields surrounding the wood on the north and south sides are arable, whilst to the east and west are further areas of woodland and grassland.

Vegetation

The wood is a mixture of pine, ash and beech; the trees are not fully grown and include saplings. The density of the trees combined with the litter layer inhibits the growth of ground cover and other plants below the canopy. The wood is divided by a number of open areas that act as fire-breaks; these contain a wider diversity of plant species.

Sampling Sites

The location of the sampling sites within the wood is shown in figure 2.3. The area covered woodland and a fire-break and snails were mainly collected from Site 2. Site 1 produced few shells probably because of the low levels of $CaCO_3$ present in the soil. Snails were found on the edges of the open area but few were seen in the centre of it. The snails were collected live where possible; if only shells were available those on which the periostracum was intact were collected. All snails were collected on or within the litter layer;

very few were seen higher in the vegetation at the edge of the wood and fire-break.

Molluscan Fauna

Pomatias elegans and C.hortensis were common and large numbers were available for collection, C.nemoralis was much rarer and only recently dead shells were collected. The large shells of H.pomatia were also rare and had to be collected over a wide area, but they were all from within 50m of the sample area. Study of the distribution of species within the environment showed that each of the four collected species occupied a distinct niche.

Pomatias elegans was found within the litter layer and in the top 5cm of the soil horizon; it was not observed on living plants and only rarely on or above the litter surface. C.nemoralis and C.hortensis were found on the litter surface or occasionally just below it. They were also observed on living plant material but never far above the ground. H.pomatia appeared to spend its active periods at the edge of the wooded area, generally at ground level. It is known to bury itself in the litter layer during inactive periods and hibernation.

2.33 Hayle Towans, Cornwall

Hayle Towans is an area of about 720ha of wind-blown sand on the north coast of Cornwall; it faces onto St.Ives Bay and the location is shown in figure 2.4 (centred on G.R. SW 560390). This type of deposit is found on the western seaboard of Britain from Cornwall to the Western Isles, and also on the northern and western shores of Ireland. The deposits consist largely of fragments of marine shell

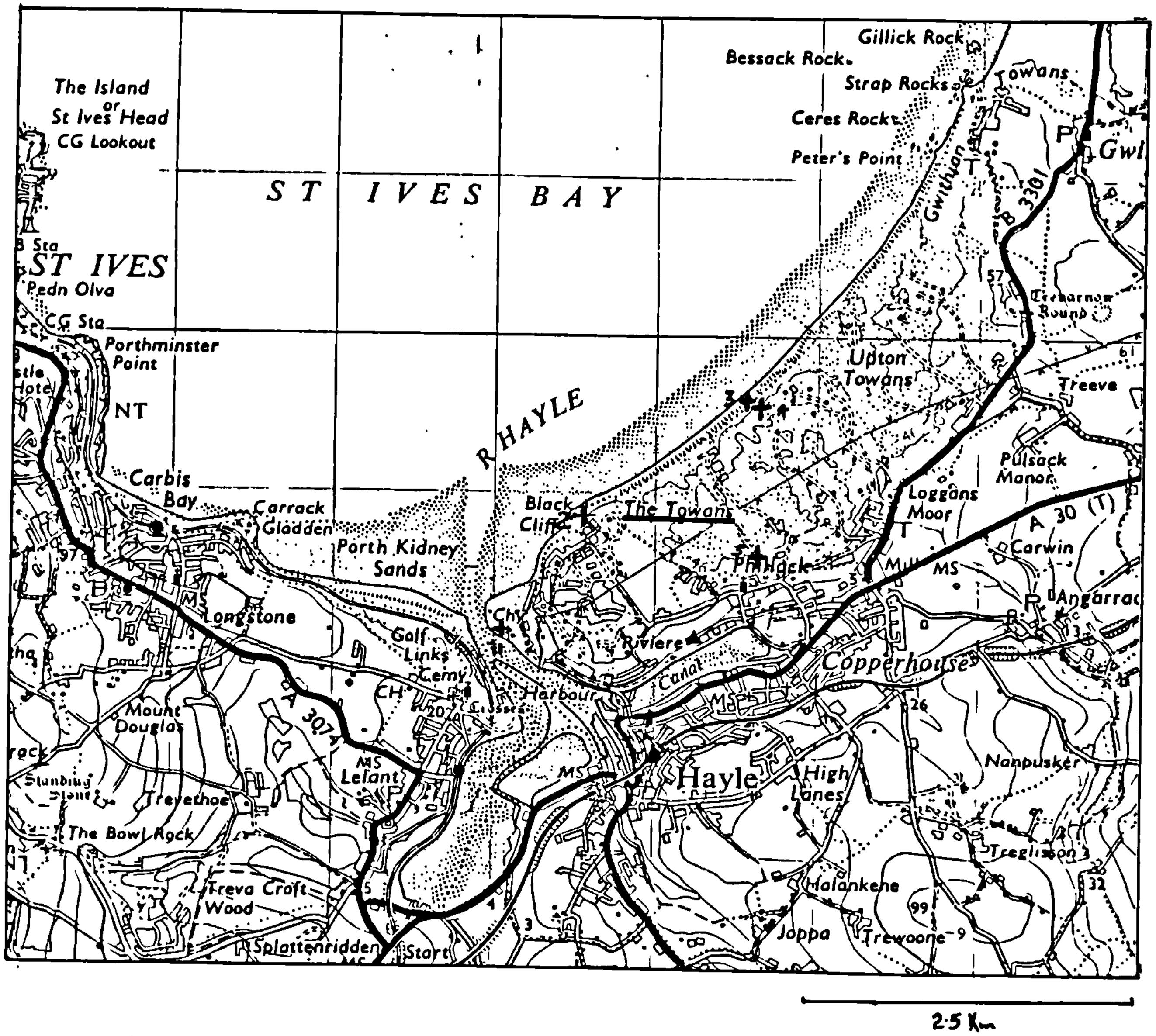


Figure 2.4. Location of the modern sample sites at Hayle Towans.

and quartz sand, and there is an appreciable organic component in soils that have formed on stable surfaces. The dunes are undulating and rise from sea-level to 57m above O.D. at their highest point.

Sample Sites

Five sites were studied and detailed chemical and particle size analysis was undertaken on samples from sites 2,4 and 5. Figure 2.4 shows the location of the sites.

Site 1 Grid Ref.: SW 552382 +5m O.D.

Location: Near a series of old quays on the western edge of the main area of dunes. The area was open-ground with some low scrub nearby.

Site 2 Grid Ref.: SW 557388 +25m O.D.

Location: On the cliff edge above Black Cliff, on the western side of a stone and bank wall. This site was in the area where the slate bedrock rises as a ridge at right-angles to the coast. The sand cover is much thinner with a more even surface.

Site 3 Grid Ref.: SW 565396 +20-25m O.D.

Location: On the top of the dunes immediately above high water mark. The area is open dune, stablised by vegetation in most places but with some exposed sand.

Site 4 Grid Ref.: SW 566395 +30-35m O.D.

Location: Inland from Site 3, an area of unstable dunes. Samples were taken from the present surface (PS) and a buried stable soil horizon (BS).

Site 5 Grid ref.: SW 566386 +40-45m O.D.

Location: On the south side (land side) of the dunes, about 200m from their edge. An area of open, but stable, dunes with small trees and low scrub.

Geology

The sand dunes overlie fine grained slates and sandstones that form the metamorphic contact aureole around the granite to the south and west. A band of alluvium has developed on the south side, between the dunes and the slate, there is also valley gravel and head deposits at this point. Two smaller areas of blown sand are found nearby. One lies west of the River Hayle and the other east of the main area and separated from it by a ridge in the slate bedrock. The alluvium to the south may be due to the flooding of the area behind the sand-dunes by tidal waters coming up the River Hayle; the alluvium is only 5-10m above O.D. As the surrounding rocks are all acidic the dunes represent an isolated area of calcareous deposits and have developed a rich molluscan fauna.

Soils

Soil pits were dug at Sites 1,2 and 5; descriptions of the horizons are given below.

Soil Description: Site 1

0-3cm Turf L

Closey knit coarse grass.

3-13cm

Loamy sand, contains many roots.

13-23cm

Slightly loamy sand.

23+cm

Clean sand.

Soil Description: Site 2

0-2cm Turf

Closely knit coarse grass.

2-8cm

Dark yellowish brown (10YR 4/4) loamy sand, some roots and angular stone fragments (max.dim. 2cm).

8-28+cm

Dark greyish brown (10YR 4/2) loamy sand, some angular stone fragments (max.dim. 1cm).

Soil Description: Site 4

Present surface: Greyish brown (10YR 5/2) sand, occasional grass plant and roots.

Buried surface: Light yellowish brown / yellow (10YR 6/4-7/6) sand.

Soil Description: Site 5

0-5cm

Dark yellowish brown (10YR 4/4) sand.

5-20+cm

Yellowish brown (10YR 5/4) sand.

Particle size and loss on ignition

Site No.	Sample	Depth	(1) LOI (%)	(2) CaCO$_3$	(3) Sand (%)	Silt (%)	Clay (%)
Site 2	7	2-8	12.8	44.8	86.4	7.3	6.3
	8	8-25+	6.6	49.1	86.5	7.7	5.8
Site 4	9	PS	2.1	77.3	99.1	0.9	
	10	BS	4.8	71.7	97.1	0.8	2.1
Site 5	11	0-5	6.6	69.2	96.7	3.3	0.0
	12	5-20+	1.9	69.6	98.9	1.1	0.0

(1) Loss on ignition (2) Percentage of whole sample (3) All fractions

Table 2.5 Particle size and LOI for smples from Hayle Towans Sites 2,4 and 5.

Sand Fractions (%)

Site	Sample	Depth	>1mm	1.000- 0.500	0.500- 0.250	0.250- 0.180	0.180- 0.125	0.125- 0.090	0.090- 0.063
2	7	2-8	0.1	2.8	45.6	20.8	9.5	3.0	4.5
	8	8-25+	1.3	3.7	47.1	21.5	8.0	2.1	2.7
4	9	PS	0.1	5.1	69.1	20.6	3.9	0.2	0.1
	10	BS	0.4	4.0	53.8	29.4	8.0	0.9	0.5
5	11	0-5	0.4	6.5	64.1	20.7	4.3	0.6	
	12	5-20+	0.1	2.7	64.7	26.0	5.0	0.3	1.2

Table 2.6 Particle size analysis of sand fraction for samples from Hayle Towans Sites 2,4 and 5.

Distribution of $CaCO_3$ by grain size

Site	Sample	Depth	>1mm	1.000- 0.500	0.500- 0.250	0.250- 0.180	0.180- 0.125	0.125- 0.090	0.090- 0.063
2	7	2-8	34.1	63.2	46.2	45.7	30.7	25.6	28.0
	8	8-25+	27.1	64.2	61.9	51.6	26.4	27.5	24.7
4	9	PS	77.7	86.2	81.3	69.1	58.8	48.6	55.6
	10	BS	97.3	90.2	78.6	66.8	60.4	63.2	60.4
5	11	0-5	93.3	82.4	74.5	64.1	56.0	47.5	
	12	5-20+	100.0	84.6	74.1	63.1	54.3	61.2	60.7

Table 2.7 Distribution of $CaCO_3$ content by particle size for samples from Hayle Towans Sites 2,4 and 5 (expressed as % of that fraction).

<u>Analysis of particle size data</u>

Site	Depth	Median (Md)	Graphic Mean (M_z)	Std Dev. (θ_I)	Skewness (SK_I)	Skewness	Sorting
2	2-8	2.55	3.20	1.68	0.82	Strong-fine	Poor
	8-25+	2.45	2.87	1.54	0.76	Strong-fine	Poor
4	PS	2.35	2.37	0.30	0.14	Fine	V.well
	BS	2.45	2.52	0.39	0.32	Strong-fine	Well
5	0-5	2.35	2.40	0.37	0.29	Fine	Well
	5-20+	2.40	2.45	0.29	0.34	Strong-fine	V.well

Calculated using methods in Folk (1974)

Table 2.8 Analysis of the particle size data for samples from Hayle Towans Sites 2,4 and 5

The particle size analysis of the soils shows there are three different types of sediment defined by different degrees of soil development. The least developed are represented by Site 4 PS (present surface) and Site 5 5-20+; the former is an erosion surface, the latter the layer below a humic level. The second group are stable surfaces but with minimal soil development; Site 4 BS (buried surface) and Site 5 0-5 are of this type. The final group are well developed loamy sands; Site 2 2-8 and Site 2 8-25 are of this type. Site 2 was an area where the sand was thinner and a more permenant surface had become established; the degree of soil development suggests that this is a long established surface and that its level and exposed position keep it free from further inundation by sand. This development of Site 2 is reflected in the high organic content and the lower level of $CaCO_3$ (45-49%) compared to the other sites (69-77%).

Microscopic examination of the sediments shows the $CaCO_3$ component to be largely formed from fragments of marine shell but also to include some terrestrial shell fragments and spines of echinoderms. The samples from Site 4 PS had fragments of shell in which the pigments were still fresh. This suggests that the dunes are not only active if exposed but that fresh material is still being blown from the wide area of the beach present at lowtide (210ha).

The ^{14}C age of a sample of calcareous sand from site 5 was 6320±20 bp (Q-2???), this corresponds to 46% of the activity of uncontaminated modern wood.

Drainage

The highly permeable sand dunes are freely drained and except in areas closely associated with the metamorphic slates the waters will be alkali or neutral. The reduced level of $CaCO_3$ at Site 2 may be associated with the underlying slates which produce acidic groundwaters. The Towans area is cut by the River Hayle and the Red River which drain the surrounding countryside. The slates underlying the Towans must act as an impermeable horizon allowing water that percolates through the dunes to flow along the bedrock surface on the dipping strata towards the sea or the two main rivers. If the base of the dunes is below present high water level saline water may also be present below the sand dunes forming a marine phreatic zone.

The free movement of waters should preclude any post-depositional changes occuring, but as will be shown for the site at Netanya these can still occur under certain conditions.

History of the Area

The chronology of the development of the Towans in Hayle is poorly documented, but one can combine data obtained by excavations and analyses of molluscan assemblages at Gwithian (eastern end of the Towans) (Megaw et al. 1961; Spencer 1975), Newquay (Kennard & Warren 1903; Woodward 1908) and elsewhere (Evans 1971; Simpson 1966) to reconstruct their evolution.

During the last interglacial period a raised beach developed; in some areas this is covered by wind-blown sand that is completely decalcified in places (Reid & Flett 1907). The sand, which is partly lithified, is overlain by head and solifluxion deposits of clay and angular stones. The top of the head deposit is a band of clayey sand, possibly a post-glacial ground surface; this is covered with wind-blown sand. Mesolithic occupation is recorded by the frequent artefacts found in the Towans area (Spencer 1975).

The evidence from Towan Head, Newquay shows a distinctly woodland snail fauna below the blown-sand. A similar fauna was seen at Northton (Evans 1971) where the deposition that is said to be no earlier than 5000 bp. Evidence from other areas in north Cornwall (Arkell 1943) also suggests that sand deposition does not pre-date the Neolithic period. The analyses by Spencer (1975) show the Gwithian site to have been open when dune formation began. Spencer suggests that this fact, taken with the archaeological evidence for early man in the area, suggests human interference with the forest. Evans (1972) suggests that the decline of woodland was due to the dune formation, and that these were formed because of a change in the prevailing winds creating storm banks that were easily eroded. However, the area of beach exposed at present (210ha) and the presence of fresh and coloured shell fragments suggest a steady and continuing process of dune formation. The well sorted nature of the dune sands indicates that particles of shell and sand are scoured from the beach at lowtide and that the wind strength is critical in controlling the size of particle that is moved. Destruction of shells to this size is by wave action. The inundation of stable soil surfaces shows that large scale movement of new and reworked material is continuing.

The use of the area in the Medieval period for arable fields (Fowler & Thomas 1962) and the presence of churches at Gwithian and Phillack suggest that extensive use was made of the area. The Towans have remained open spaces and are now largely used for recreation. This has helped to stablise some areas but has led to the rapid erosion of access areas. In the nineteenth century the central area was occupied by an explosives factory and it may be that the large unvegetated area left by this, combined with present use, has led to much of the destablisation and inundation of the old land surfaces.

Vegetation

The stable areas of the dunes are covered with halophytes such as Maram grass. Sites 1 and 5 had small shrubs and trees, whilst at Site 2 the long period of stability has produced a more diverse flora in the thick turf.

Molluscan Fauna

Table 2.9 lists the species of terrestrial mollusc found on Hayle Towans. One example of A.arbustorum was found; this was not previously recorded from the area. C.acuta was present in large numbers but as with Helix aspersa and H.itala it is not found in the early fossil deposits.

Candidula intersecta
Cernuella virgata
Helicella itala
Cochlicella acuta
Ashfordia granulata
Trichia hispida
Cepaea nemoralis
Cepaea hortensis
Helix aspersa
Arianta arbustorum

Table 2.9 Terrestrial mollusc species observed on Hayle Towans.

Cepaea nemoralis was active at ground-level on both the turf and the dune surfaces but rarely on open sand. It was found sheltering in vegetation and under walls and stones.

2.34 Graffy, Co.Mayo, Eire

Graffy is an extensive area of calcareous tufa 6.6km north-west of Swinford, Co.Mayo (Grid Ref. G 346047, Lat.53° 59'N,Long. 8° 59'W) (figure 2.5). The site is on the lower slopes on the southern side of the Ox Mountains, about 75m above O.D. The total area of tufa is c.2ha and its maximum observed depth was 4.30m. There is a small lake (Marl Lough) on the north-west side of the area and this has at times produced marl and sedge peat deposits which interdigitate with the tufa at the lake margin.

Geology

The tufa deposit overlies Lower Carboniferous Limestone; immediately

to the north are the Ox Mountains, an area of intrusive rocks that are surrounded by metamorphic schist and gneiss. During the last glacial period ponds of water that had formed behind ridges of drift (associated with the "Young Ice" and including large quantities of limestone) drained through the drift and became calcareous as they did so (Frank Mitchell, unpub.notes). The change in external conditions as the water emerged at the spring head led to the precipitation of tufa; as this occurred atmospheric carbon dioxide becames incorporated and the final isotopic values depend on the relative contribution of dissolved carbonate and carbon dioxide. The area around the tufa has extensive areas of peat growth which is exploited for fuel in places.

The lake was formed by a drift ridge which blocked the natural outflow of the stream. The tufa contains some till which slumped into it.

Soils

The modern samples were collected from the base of a shallow quarry from which tufa and marl had been extracted for spreading on the surrounding acid farm soils. Many of the molluscs were on exposed tufa or areas where only a thin soil had developed. The ground between the quarries had a more developed soil some 10-15cm thick with a peaty texture. The thin soil is dominated by tufa and contains 85-90% calcium carbonate; much of the remainder is organic material. Tufa in exposed areas is 97-98% calcium carbonate with the remainder formed by a mineral component.

The tufa is the source of calcium for the shells and is probably depleted in ^{14}C by at least 50% relative to uncontaminated modern wood. Part of the depletion is due to the snails occupying an exposed surface of fossil tufa. Fossil samples are less subject to problems from tufa depleted in ^{14}C. Provided the tufa is occupied soon after deposition it will only be depleted by the disssolved carbonates present in the groundwater.

Drainage

The high rainfall for the area (120-140cm per year) has led to leached soils; the vegetation and peaty soil indicate an acid environment despite the alkali tufaceous subsoil. The water table is immediately below the quarried area and 2-3m below ground level; a small stream drains down the slope above the tufa and into the lake. The presence of the high water table and the lake suggest movement of groundwaters bringing carbonate from lower levels of the tufa or limestone.

History of the Area

During the period of tufa growth conditions varied to allow the development of soils (no tufa growth and some erosion), peats (expansion of marshy conditions at the lake margin) and lake marl (expansion of the lake water). The formation of tufa is no longer occurring, or only at a very slow rate by reworking of older material; it has probably been at this level since c.3000 bp. Since then some erosion and dissolution of the upper layers will have taken place. The good land in the surrounding area is farmed and the tufa and marl have been quarried, at least in recent times, for neutralising the acid soils.

Molluscan Fauna

The most prominent living snails were C.nemoralis; no modern C.hortensis were seen although present as fossil shells. P.elegans and H.pomatia are unknown from Ireland.

Cepaea nemoralis is assumed to live on the tufa surface and in the low vegetation; hibernation is probably in the vegetation as burrowing is difficult in the tufa surface.

2.4 FOSSIL SITES

2.41 Introduction

The samples used for the study of sub-fossil shells were collected from six sites in Britain and Ireland (figure 2.2). They were chosen because they were independently dated and because of the amount of palaeoenvironmental data that was already available. Fieldwork was undertaken at three sites (Carrowmore, Caerwys and Newlands Cross) and material from the other sites (Castlethorpe, Binnel Point and Inchrory) was made available by Dr Richard Preece of the Godwin Laboratory, Cambridge.

2.42 Carrowmore, Co.Mayo, Eire.

Carrowmore is an extensive area of calcareous tufa on the lower slopes of the southern side of the Ox mountains (G 361064; lat.54° 00'N, long.8° 58'W); it lies about 3.3km east of the site at Graffy and about 120m above O.D. The tufa is exposed in two quarries and also where it is incised by a stream. The samples for analysis were collected at the upper site (Carrowmore B; CB) where the stratigraphy consisted of a series of 12 thin (1-5cm thick) organic horizons separated by clean tufa. Samples were taken from three layers which contained large numbers of shells and charcoal for conventional ^{14}C dating.

Geology

The geology of the area is described under Graffy in the preceding section.

Drainage

The site is cut by a small stream which has deeply incised the tufa in places. At the bottom of the slope the stream flows less freely and much of the area is marshy and waterlogged. The lower levels of the tufa at Site A were also waterlogged and the water welled out where the tufa had been cored. These factors, combined with the heavy rainfall in the area, suggest that there will be leaching and movement of ions within tufa and any associated shells.

Description of stratigraphy

The maximum observed thickness of tufa was at Site A where 7.15m of deposits formed from channels and flowng water were observed.

Site B was 3.30m thick and probably underlain by clay (found by augering). It contained eleven organic rich horizons in the main section; an additional one was observed at a second section. The tufa between these horizons was generally soft but was nodular and hard in two horizons. The position of the organic horizons and the nodular tufa is shown in figure 2.6).

History of the site

The organic horizons at Site B represent periods when the springs were not depositing tufa in that area and dry ground surfaces

developed. However, it is likely that tufa was still being deposited in adjacent areas of the site. The deposits appears to have accumulated over a short period of time, probably about 6000 bp to 4500 bp (Preece pers.comm.1986). The snail shells in the clean tufa suggest the area contained some standing water and trickling streams. Only the top 20cm showed any marked change in the snail assemblage and this is interpreted as being somewhat later than the main deposit but there was no evidence of a hiatus between the two.

2.43 Newlands Cross, Dublin, Eire

Newlands Cross is a shallow (1.20m thick) deposit of tufa on the western edge of Dublin (O 078 297; lat.53° 18'N, long.6° 23'W) and about 80m above O.D. The tufa was originally exposed during road construction work but can now only be sampled by excavation. The basic stratigraphy is tufa overlying a buried soil; there is then a second layer of tufa and finallly a diamicton of clay and angular limestone fragments. The shell samples came from the buried soil and were collected by excavating a 0.7m x 0.7m section through the deposit.

Geology

The tufa overlies diamicton that forms part of the Cloughran Till of the Devensian Dublin Formation (Hoare 1975). This in turn overlies Lower and Middle Carboniferous Limestone of the Belgard Formation ("Calp"). Limestone from this formation is also found in the diamicton. The tufa is about 1.20m thick and spans the early post-glacial period; if the sequence was originally longer the upper part has since been eroded though it may be present elsewhere in the deposit.

The tufa formed where the carbonate rich water left the local limestone and shale and flowed onto the relatively impervious till. The tufa covers a ridge that slopes between 7° and 1.5°.

Drainage

The area has some standing water but no streams were observed; nor is there likely to be a large volume of runoff as the ground is flat or gently sloping.

Description of the stratigraphy

The excavated section showed 25cm of soil and then 90cm of soft tufa; this was interrupted by a soil horizon at 85-87cm (see figure 2.7). At the base of the tufa was diamicton deposit (figure 2.7).

History of the site (After Preece *et al.* 1986)

The tufa began to form soon after 10,000 bp; a date of 9720±300 bp (OxA-569) was obtained on a charcoal sample from the interface between the tufa and diamicton. The tufa below the buried soil contains shells that show the early post-glacial change from alpine conditions. The presence of freshwater species indicates stagnant pools. About 8000 bp a soil horizon developed and a number of species died out. Seeds extracted from the tufa above the soil are dated to 7600±500 bp (OxA-568). The tufa included in the soil horizon was dated and gave an age of 9250±195 bp (Q-2...) and therefore shows a depletion of 14% relative to the suggested date for the soil. The shells that were analysed in the present study were from the soil horizon.

The molluscan fauna indicates a clearance of the woodland about 7500

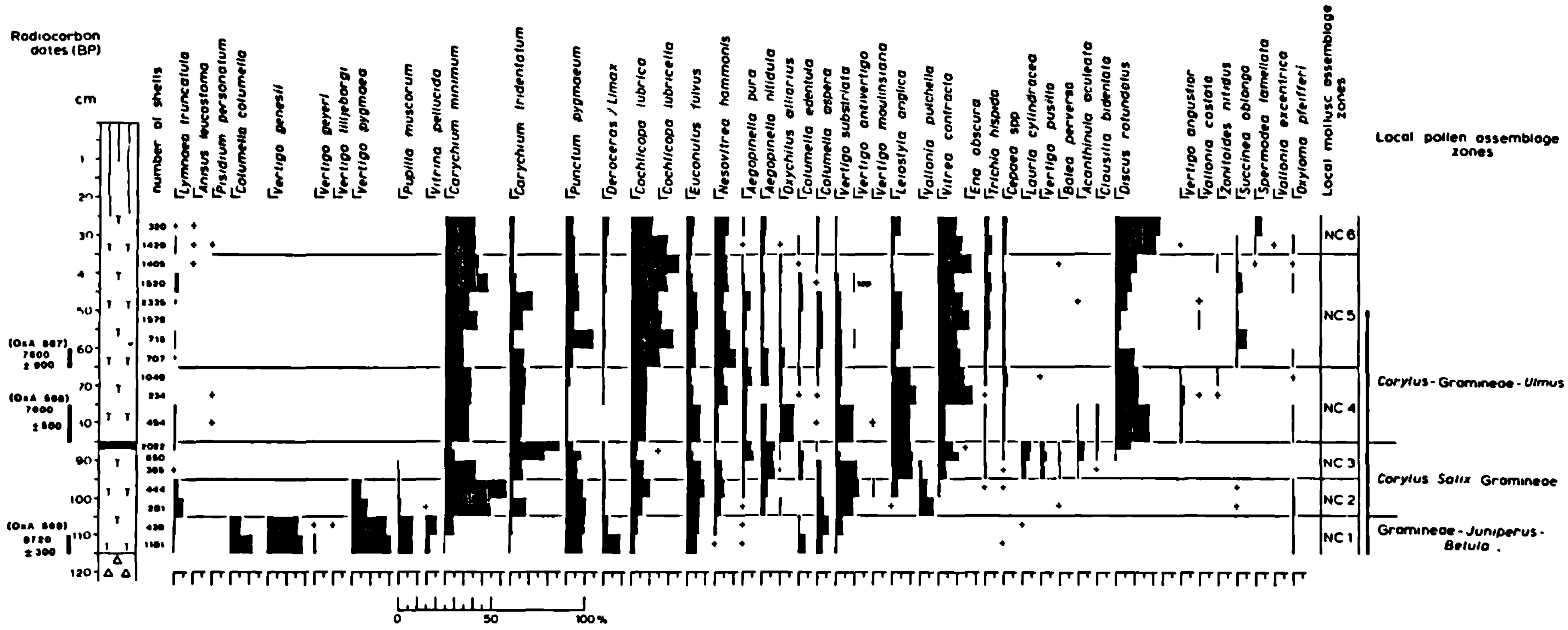


Figure 2.7. The stratigraphy and molluscan fauna from Newlands Cross, Dublin. (After Preece et al. 1986)

bp; this is confirmed by the presence of high levels of microscopic charcoal in the tufa. The fauna recovers gradually and the clearance is probably short lived. The presence of a flint flake and the burning suggests that Mesolithic man was present in the area.

The top of the section probably dates from around 7000 bp.

2.44 Caerwys, Clwyd, Wales

The tufa at Caerwys (G.R. SJ 128138) and the nearby site of Ddol (G.R. SJ 142713) form large deposits covering an area of about 81ha. It has a maximum observed thickness of 10m on the northern face of the quarry at Caerwys. The tufa has been quarried for more than 100 years and evidence of lime-burning was observed. The sample site is at Caerwys on the north side of the valley of the River Wheeler and is between 90 and 135m above O.D. The stratigraphy covers the late glacial and early Post-glacial periods. The samples were taken from a soil horizon that marks a major change in the tufa lithologies.

Geology

The Carboniferous Limestone bedrock has fluvio-glacial sand and gravel overlying it. The tufa appears to have its source at a springline on the upper slopes and to have begun covering the sand and gravel deposits towards the end of the last glacial period.

Drainage

The tufa is incised by two small streams which join the River Wheeler to the south of the site. The stream at Caerwys becomes sub-surface drainage at the edge of the tufa and consequently streams have formed where the tufa has been quarried. The original base level of the water table must have been much higher than at present.

The sample horizon appeared to be above the level at which groundwater occurred and is probably only subject to drainage from the ground surface above.

Description of the stratigraphy (After Preece 1978)

The stratigraphy of the whole site is very complicated, that in the immediate area of the sample site is shown in figure 2.8. The basic stratigraphy starts with a fluvio-glacial sand, probably formed by outwash. The first tufa formed in late glacial times and produced a ^{14}C date of 11,725±120 bp (Q-2376) for the organic material in two horizons within it. Also during the late glacial period sedge peat formed, indicating the former presence of standing water.

Between the late glacial and the main Flandrian tufas is a further deposit of fluvio-glacial sand; this is not formed by slumping as it contains evidence for channels. The Flandrian tufa is varied in form (see below) and reaches 10m in thickness.

History of the site

The types of tufa present range from marl to nodular tufa. The fauna and tufa types are largely controlled by the hydrological regime. Deposition in freshwater pools produces marl, running water produces a nodular type, and marginal swamps give organic layers that show the area had occasionally drained to give a stable terrestrial surface. The presence of petrified reeds and sedges shows that marshy areas with standing water also existed. The horizon (375-393cm) from which the snail shells (*C.nemoralis*, *C.hortensis*, *A.arbustorum*) for the present study were collected is of this later type and produced a ^{14}C date of 7880±150 bp (BM-1736). The tufa from immediately below this layer gave a ^{14}C date of 10040±120 bp (HAR-4738), a depletion of

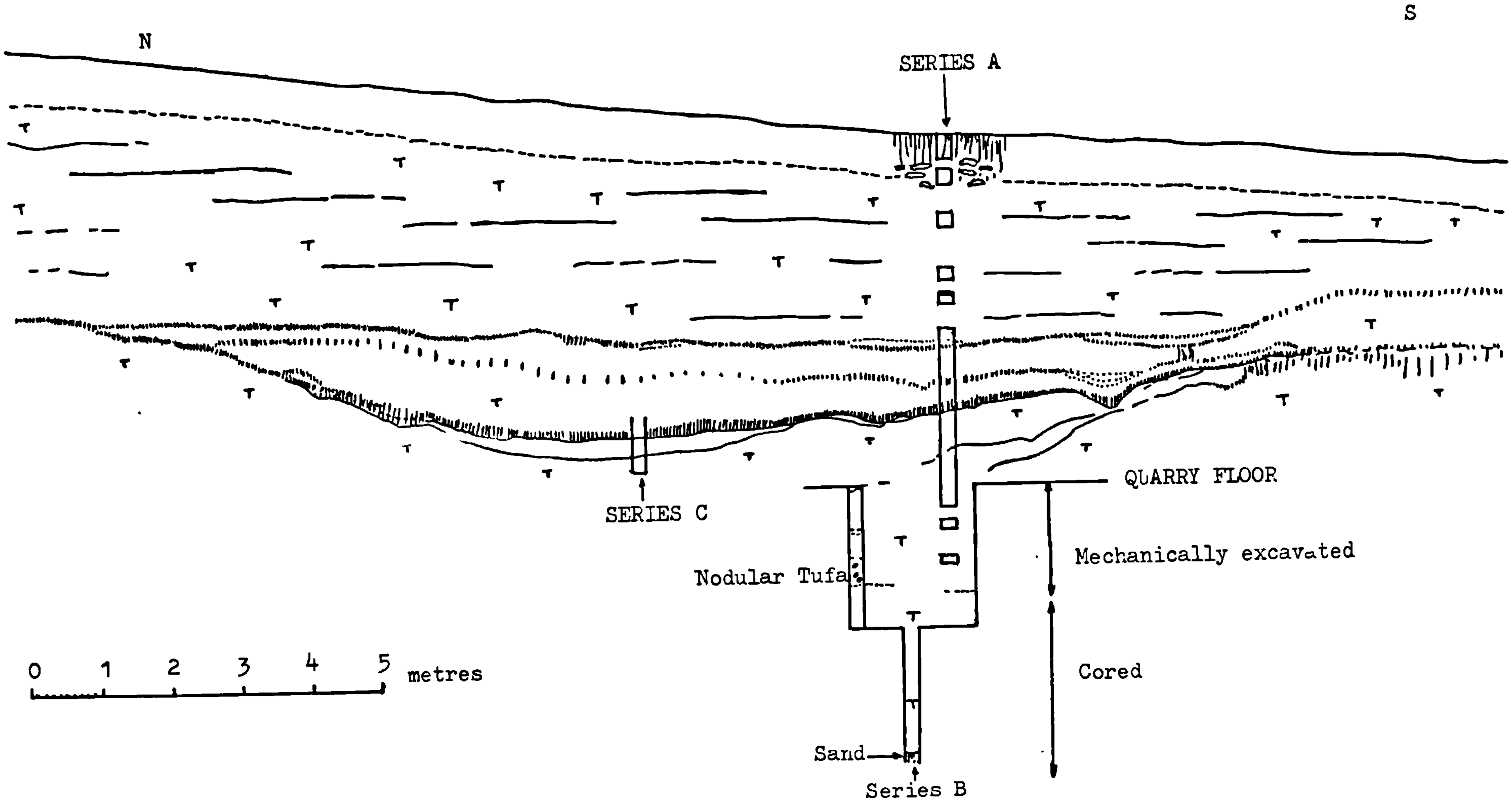


Figure 2.8. Quarry section at Caerwys, Clwyd (after Preece 1978)

23% relative to the ^{14}C content of the charcoal in the soil layer. The soil represents a compressed time period, probably 200-400 years; its merging with a higher soil level at one end of the section indicates that tufa deposition was continuing in some areas. The whole area was probably a series of channels, pools and small streams that moved around as tufa deposition altered the water courses. The preceeding deposits were nodular tufa containing freshwater and swamp species of snail; these are abruptly replaced by a tufaceous silt that was rich in land mollusca.

2.45 Inchrory, Glen Avon, Banffshire

Inchrory is a six metre thick deposit of tufa of early Flandrian age. The site was studied in detail by Preece *et al.* (1984) and this is used as the basis for the present description. The tufa contains six buried soils separated by units of relatively hard tufa and layers with a more powdery lithology. The site is located 11km south of Tomintoul (G.R. NJ 175086) and is approximately 400m above O.D. Similar isolated tufa deposits also occur to the north of Inchrory. Samples were collected by Dr Preece from an exposure caused by improvement to the road leading to Inchrory.

Geology

The tufa overlies a bed of gravel composed of local schist, probably a fluvio-glacial deposit. The underlying geology is composed of rocks of the Upper Dalradian Supergroup and the source of carbonate is probably a band of limestone which runs parallel with the valley axis.

Drainage

The site is on the north side of Glen Avon, near the point where the

Marl Burn enters the valley and joins the main river. The nature of the deposit suggests that the tufa formed in an area of damp ground fed by springs. The steepness and free drainage prohibited, and probably still prohibits, the formation of standing bodies of water.

Stratigraphy (After Preece et al. 1984)

The stratigraphy of the site at Inchrory is given in table 2.10 and figure 2.9. All depths are measured from the top of the section.

Depth	Brief description
0-150cm	Soft granular tufa
150-155	Tufaceous silt
155-230	Soft granular tufa
230-240	Tufaceous silt, some charcoal fragments
240-310	Soft granular tufa
310-325	Angular clasts of local schist, some coated in tufa
325-345	Tufaceous silt
345-350	Tufaceous silt, abundant charcoal
350-385	Soft lightly cemented tufa
385-395	Tufaceous silt
395-535	Soft granular tufa with many harder layers
535-540	Tufaceous silt
540-550	Soft tufa
550-555	Soft tufaceous silt
555-590	Soft tufa
590cm+	Fluvio-glacial gravel

Table 2.10 Stratigraphy of the site at Inchrory, Banffshire.

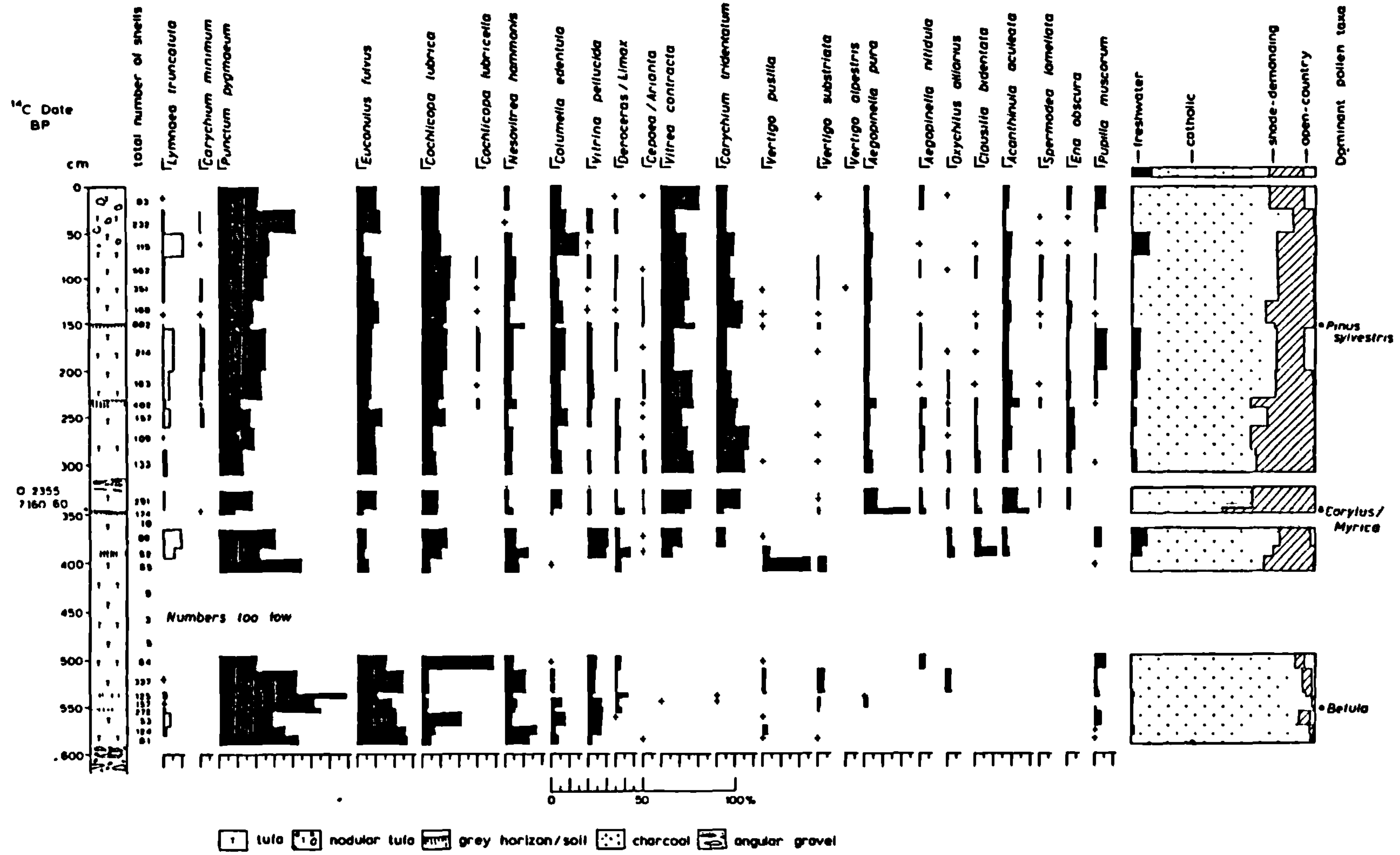


Figure 2.9. The stratigraphy and molluscan fauna from Inchrory, Banffshire. (After Preece et al. 1984)

History of the site

The six soil horizons are interpreted as brief pauses in tufa deposition caused by the springs drying up. The presence of fragments of local bedrock and scattered charcoal in the deposit indicates a contribution from the valley side by slope processes. The horizon at 310-325cm is formed from clastic material some of which is coated with tufa. Fifteen centimetres below this is a band of soil rich in charcoal, which provided shells and charcoal for dating.

Four shells of C.hortensis were collected from a context dated by ^{14}C to 7360±60 bp (Q-2355). The tufa immediately below the soil was dated by ^{14}C to 8565±100 bp (Q-2xxx), a depletion of 14%. (345-350cm). The soil horizon appears to represent a short period as it is thin and because there is tufa separating the charcoal from the clastic material, both are interpreted as being the result of slope instability and a local forest fire. The shells and charcoal should be contemporary though the possibility that the shells were eroded from higher up the slope cannot be completely discounted. However, the condition of the shells suggests they are in situ and that the age will be representative of the age of the context.

The snail fauna of the entire sequence is dominated by terrestrial species though a change from open to shaded-loving species is apparent. The ostracod evidence confirms that deposition was from calcareous springs and is only unusual in its low species diversity, a feature also observed in the molluscan fauna. Pollen analysis suggests that deposition began 9700-8600 bp in an area of open woodland. This gave way to hazel scrub before 7360±60 bp (Q-2355), and finally to pine forest. However, pine was present by 7360±60 bp as traces of it were found in the charcoal which provided this ^{14}C date.

2.46 Castlethorpe, Lincolnshire

The site at Castlethorpe (Castlethorpe 3) is one of four studied by Preece & Robinson (1984) in the Ancholme Valley. In turn these sites are part of a larger group of tufa deposits that occur in most of the dip slope valleys of the Middle Jurassic escarpment that form the western margin of the Ancholme Valley. The Castlethorpe site was exposed in the ditches of a new motorway west of Brigg (G.R. SE 988075) and was 1.90m thick and situated 10m above O.D.

Geology

The tufa overlies diamicton (clay with angular limestone fragments). The calcium carbonate source is the Middle Jurassic Limestone higher up the valleys in which the tufa formed. Alluvium is present and glacial lake deposits are also found in the vicinity of the site.

Drainage

The Castlethorpe sites are close to a small stream (site 1 was cut by it) that drains into the River Ancholme to the east. During the deposition of the tufa the valley contained swamps and marshes and also pools of standing water.

Stratigraphy of the site (After Preece & Robinson 1984)

The stratigraphy of Castlethorpe site 3 is given in table 2.11 and figure 2.10. All depths are below the surface.

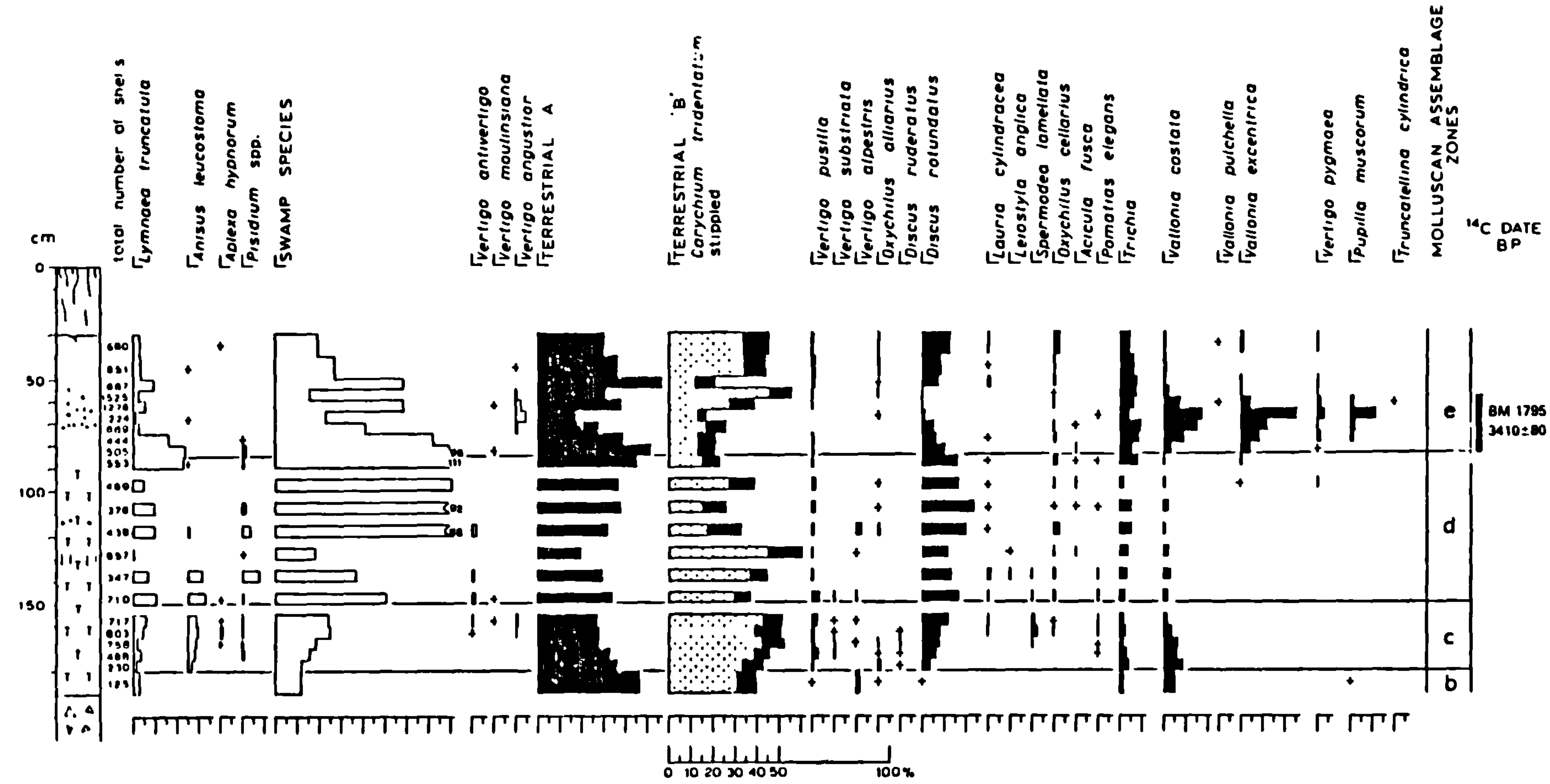


Figure 2.10. The stratigraphy and roll scan fauna from Castlethorpe Site 3, Lincolnshire. (After Preece and Robinson 1984)

Depth	Brief description
0-30cm	Modern soil (disturbed)
30-85	Clayey silt, small charcoal fragments concentrated between 60-85cm
85-190	Tufa
190cm+	Clay with angular limestone fragments

Table 2.11 Stratigraphy of Castlethorpe site 3, Lincolnshire.

History of the site

Tufa formation in the Castlethorpe area began during the very early Flandrian (c.10,000 bp). At Castlethorpe Site 1 the evidence suggests that the site was initially an open calcareous marsh fed by springs; shallow pools that periodically dried up were also present. The earliest deposit at Site 3 pre-dates the extinction of Discus ruderatus (c.8000 bp). Marshy conditions were present throughout the sequence at all three sites but there is evidence for a progressive increase in woodland. At Site 3 there was a sudden change to an open environment in the upper layers. This occurs at the point where the tufa gives way to slopewash tufaceous silt (a change in lithology rather than $CaCO_3$); charcoal from the base of the slope-wash (69-85cm) gave a ^{14}C date of 3410±80 bp (BM-1795). The shells analysed for the present study were collected from this layer; they consisted of 23 shells of C.nemoralis. The molluscan evidence in the slopewash revealed that the forest clearance was not followed by a prolonged period of agricultural activity because woodland species reappear towards the top of the stratigraphy. There is no major hiatus between the tufa and the slopewash.

Since the shells for analysis from Site 3 were part of the slopewash, and were associated with clearance, there is a strong possibility that they are not all contemporary with the wash or the charcoal. However, the fineness of the slopewash material, and the low-angle slopes involved, suggests the shells may not have moved this way. The short period before the woodland returned to the area suggests that the shells should represent a period in the order of 200 years but may be derived from a number of micro-environments. The source of $CaCO_3$ for the shells will also be difficult to establish as it may be a mixture of limestone, reworked tufa and in situ tufa. The faunal evidence indicates that little reworking of shells took place.

2.47 Binnel Point, Isle of Wight

The samples from Binnel Point were collected from a buried soil exposed on the Undercliff. This is a narrow band of landslipped terraces that stretches for about 11Km along the south coast of the Isle of Wight. The site is located on the coast (G.R. SZ 52537579) 4-8m above O.D. The site is fully described in Preece (1986) which also includes the nearby site at St.Catherine's Point. The environmental histories of the two sites are very similar.

Geology

The deposit at Binnel Point is composed of blocks and fragments of Upper Greensand and Lower Chalk. These form disturbed and mixed deposits, usually the result of landslips, rockfalls and debris flows.

Drainage

There are no streams or rivers associated with the Binnel Point deposits. The site is also at present above high water mark but earlier deposits may have been eroded by the rise in sea levels during the early Flandrian period.

Stratigraphy of the site (Preece 1986)

The stratigraphy of the site at Binnel Point is shown in figure 2.11.

Key to figure 2.11.

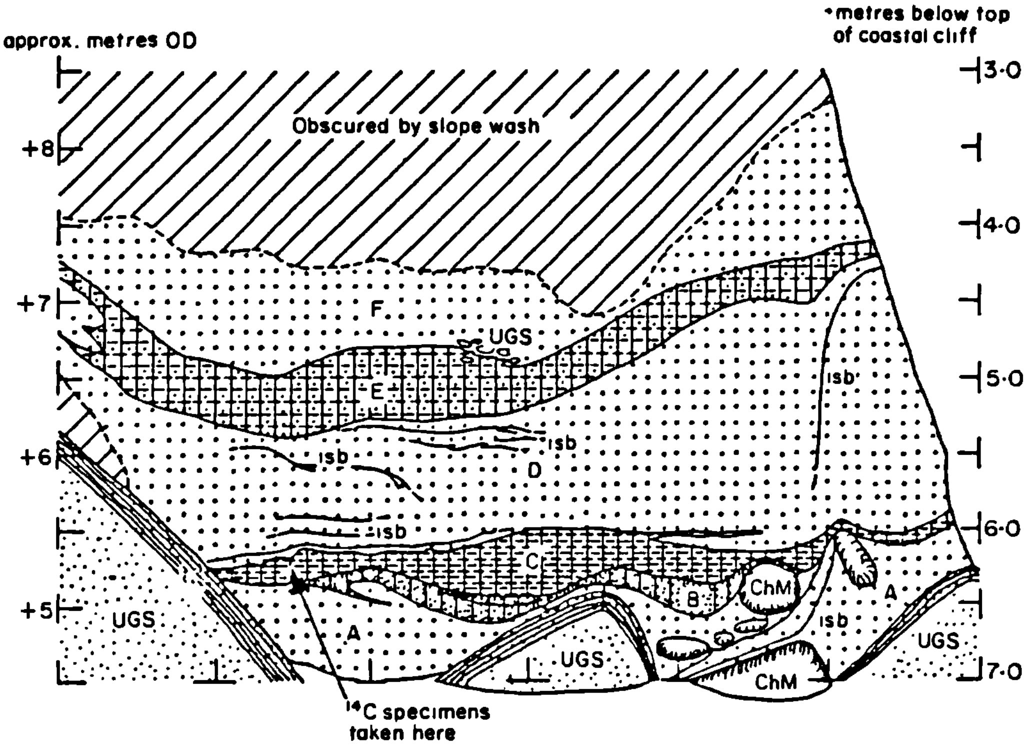
F	Landship debris composed of chalk and Greensand clasts
E	Clayey silt, contains marine and terrestrial shells
D	Landslip debris largely composed of chalk clasts
C	Clayey silt, contains terrestrial shells and vertebrates
B	Sandy silt, contains abundant terrestrial shells
A	Landslip debris composed of chalk and Greensand clasts

Environmental history of the sites

The two soil horizons contained virtually identical molluscan faunas, composed of species favouring shaded environments. The presence of large numbers of P.elegans suggests a loose broken ground surface suitable for burrowing. Remains of vertebrates were also recovered and these were also indicative of woodland. The present environment is open ground but most of the fossil species are found in the nearby woods of the Undercliff (on old landslip deposits). Charcoal from the lower buried soil gave a ^{14}C date of 4480±100 bp (BM-1737). Marine shells and large animal bones are interpreted as midden material, and the charcoal may be due to forest burning.

Tufas and marls were found at the nearby site of St.Catherine's Point indicating the presence of pools and springs amongst the rock debris.

The shells for analysis were P.elegans from the lower buried soil;



Key to layers in text.

Figure 2.11. The stratigraphy at Binnel Point, Isle of Wight. (After Preece 1986 and Chandler 1984).

a modern sample was collected from hedge banks above the section. The fossil soil must have taken some time to develop unless it was partially formed by mass movement of soil at the time of forest burning. If the former is true then the shells may cover a period in the order of 200-300 years; if the later is true then reworked material may also be included. However, the consistency of the fauna along the Undercliff indicates that reworking is not involved. Access to $CaCO_3$ will have been similar for the modern and fossil samples but may have varied within the population if a mixture of chalk, tufa and marl were available.

2.48 Netanya, Israel

The samples from Netanya are from sand dunes on the Mediterranean coast of Israel. The four horizons (OL20-23) represent two cycles of an organic rich horizon and clean sand. The exposure was visible due to disturbances of the sand dunes and are located at Lat.34° 53'N, Long.32° 26'E; the site was 0-30m above sea-level. The stratigraphic sequence can be extended by refernce to other nearby sites.

Geology

The coastal plain of Israel has three "Kurkar" sandstone ridges parallel to the present coast. These are interpreted as fossilised and cemented dunes associated with earlier coast lines. Deposits of blown sand (Kurkar) are separated by a red sandy loam (Hamra). Exposures on the present coast at Netanya show a sequence of horizons rich in organic material and sand dunes; the latter are becoming cemented in the lower layers. The underlying geology is Tertiary marine sandstone, but this is under at least 30m of alluvial and marine deposits.

Drainage

The dunes and coastal deposits drain freely. The dissolution of shells confirms this. The apparent redeposition of the carbonate lower in the sequence is probably due to a cooling of the water as it permeates the lower sand deposits.

Stratigraphy of the site

A composite sequence based on two exposures at Netanya is shown in table 2.12.

Horizon	Depth (m)	Description	Number	Date(bp)
(1)	0.0-0.0	Blown sand, present surface	(OL22)	0
(2)	0.4-0.8	Organic rich horizon	(OL21)	-
(3)	0.8-2.0	Partly cemented sand dune	(OL20)	-
(4)	2.0-2.4	Organic rich sandy loam	(OL23)	c.3000
(5)*	2.4+	Cemented sand dune (Kurkar)	-	7000-10000
(6)	-	Red sandy loam (Hamra)	-	c.13000
(7)	-	Cemented sand dune (Kurkar)	-	-

* Top of (5) seen at Site 1, lower part in cliff section (Site 2)

Table 2.12 Stratigraphy at Netanya, Israel (Sites 1 and 2).

Inland from the present coast similar sequences from much earlier periods are exposed. These deposits include "Hamra" and "Kurkar", and also grey clays interpreted as being deposited in swampy conditions. The inland deposits are often separated by periods of non-deposition, for instance at one site the 'Hamra" was thought to be 300,000 bp but the overlying clay probably dates from 17000 bp.

Environmental history of the site

The lowest "Kurkar" represents a sand dune deposit associated with a period of lower sea-level, probably from the last glacial period. The "Hamra" developed during "continental" conditions at the beginning of the Flandrian. The red loam was then inundated by blown sand and dunes developed over the area. These general conditions have continued until the present day. The two horizons rich in organic material represent periods when an increase in moisture or rainfall allowed a more substantial vegetation and soil to develop.

2.5 DIAGENETIC ENVIRONMENTS

The environments in which diagenetic changes take place must have a substantial effect on the type of change and the apparent "date" of any redeposited material. The effect of the environment is not confined to the time of deposition but continues throughout the post-depositional history of the shell and site.

For changes to occur, within the time span of Quaternary history, water must be present. It may act as a solvent during dissolution and as the source of new carbonate material in the periods of redeposition. In general dissolution requires the water to be undersaturated with respect to Ca^{2+} and CO_3^{2-} ions, whilst deposition requires these ions to be at or above saturation, either naturally or because of some change in the external conditions (e.g. a sudden temperature drop at a spring head).

Redeposition may take place immediately after dissolution within a closed system, leading to no change in ^{14}C activity; or it may occur over a time span that allows the incorporation of external material. Sources of external material are ions derived from the atmosphere, biogenic decay, the leaching of carbonates higher in the stratigraphy, or material drawn from the lower stratigraphy by evaporation (figure 2.12). Although dissolution and redeposition may occur concurrently there can be a net gain of redeposited material only if the rate of deposition exceeds the rate of dissolution.

The probability of diagenetic changes taking place will depend on the hydrological regime; therefore, periods of increased susceptability to change will occur during the depositional history of the samples.

Four basic environmental zones in which diagenetic changes could occur can be defined (figure 2.13). Zone 1 may occur at anytime after deposition; it represents an area or deposit near the surface. Therefore, it contains atmospheric CO_2 and biogenic CO_2 and the groundwater that comes into contact with this zone may contain dissolved CO_2 from these sources as well as CO_3^{2-} ions derived from carbonate rocks. The slight acidity of rainfall and runoff will aid dissolution of carbonate deposits. Any material that forms by recrystallisation can contain CO_3^{2-} derived from the atmosphere (no apparent age), biogenic sources (apparent age 0-5000 bp), and carbonate rocks (infinite apparent age). Therefore, it is possible for the recrystallised material to have a date older or younger than the true age of deposition.

The diagenetic changes may take place immediately after deposition, whilst the shell is surface material, or whilst it is only shallowly

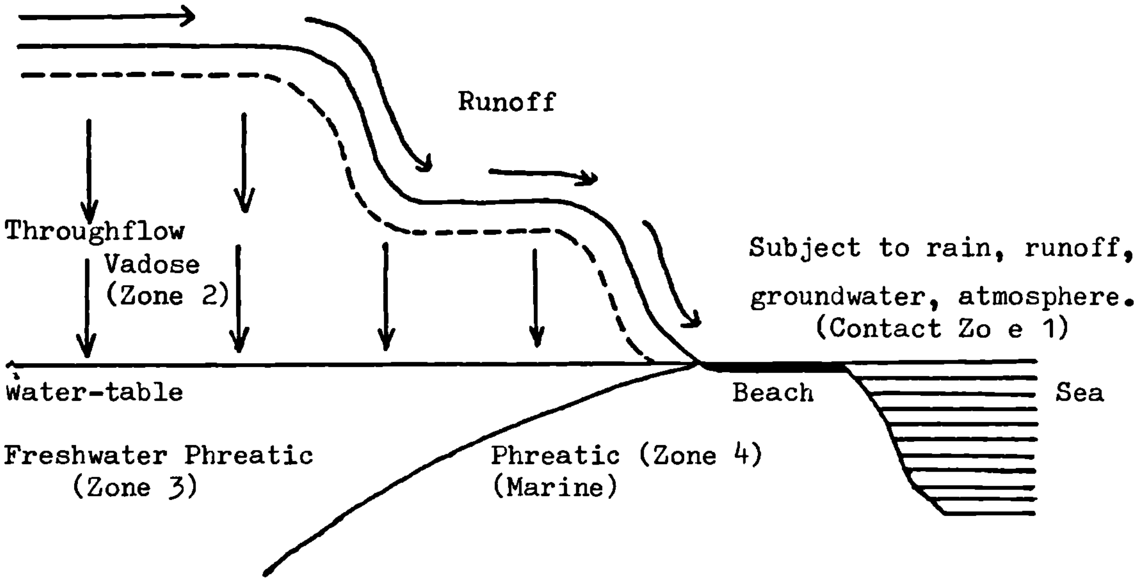


Figure 2.13. Basis diagenetic environments (Zones 1 -4)

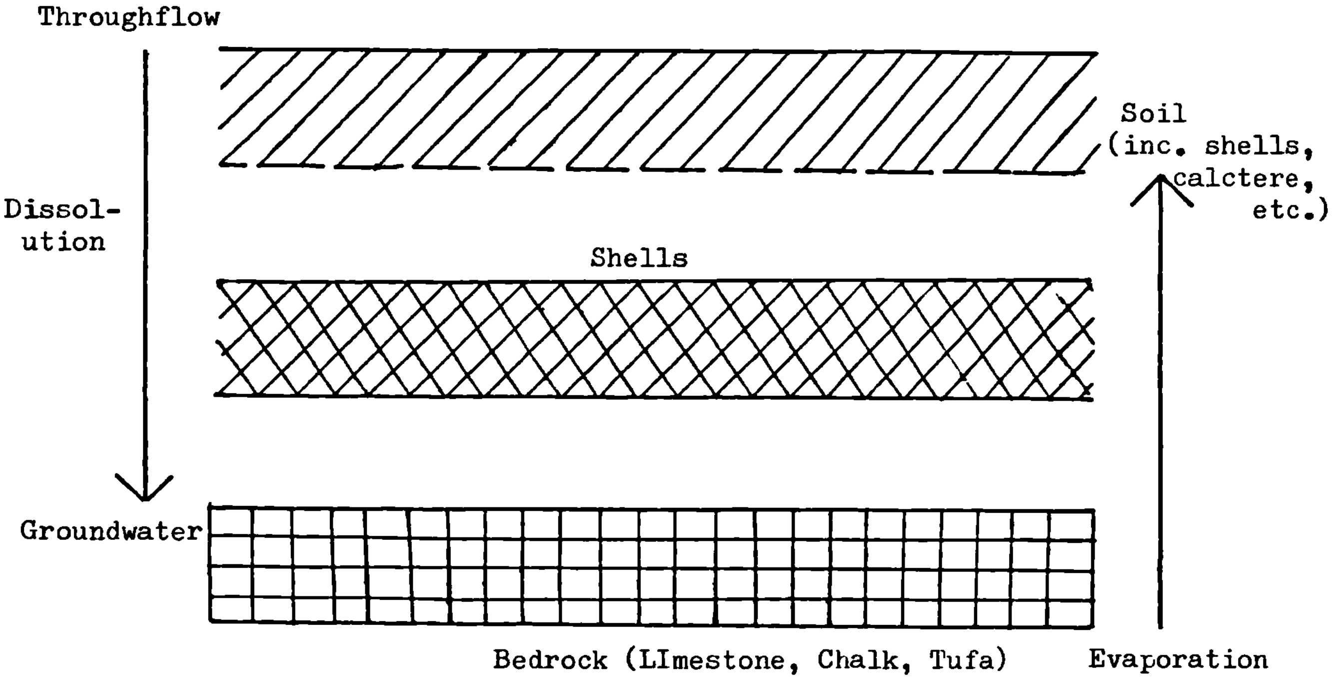


Figure 2.12. Sources of external calcium carbonate available for redeposition.

buried. If the new CO_3^{2-} ions are derived from the atmosphere or biogenic material with a rapid turnover no age error will occur. However, problems will occur if the CO_3^{2-} is derived from carbonate rock or biogenic material with a slow turnover (>500 years). This simple model suggests that the greater the burial depth at which the changes take place the greater the "infinite age" component, and nearer to the surface a greater "modern" component with be incorporated.

At greater burial depths the conditions change to the second environmental zone (2). In substantial deposits (e.g. the inner part of a raised beach) shells will be little influenced by atmospheric CO_2 or biogenic CO_2 (which will also decrease with time). However, they will come under increased influence from groundwater, particularly if seasonal or periodic variations occur in the water table. During periods of lowered water-table dissolution by throughflow may occur. As the water-table rises the shells may suffer recrystallisation and secondary deposition from by the Ca^{2+} and CO_3^{2-} ions dissolved in the groundwaters.

Zone 3 represents freshwater phreatic conditions, here diagenetic changes will occur only if the groundwater throughflow changes the degree of saturation, with respect to Ca^{2+} and CO_3^{2-} ions, of the phreatic zone. Pingitore's (1976; 1978) models suggest that all recrystallisation occurs with aquifer or groundwater flow. Since most groundwater has an apparent age (0-20,000 years bp depending on geology) the recrystallised material will be older than the true age if the diagenetic change takes place at or soon after the shell was buried. However, if a shell of "infinite" ^{14}C age (e.g. >50,000 years bp) is subjected to recrystallisation by groundwater at a more recent time (i.e. 10,000 bp) then the final ^{14}C value will suggest an age from 10,000 bp to infinity depending on the degree of recrystallisation.

In a Zone 4 environment (marine phreatic) the same controlling factors as described for zone 3 will in general apply. Exceptions are the high levels of magnesium and strontium which may inhibit the initial dissolution of the shells (Srivastava 1975; Folk 1974); and the consistent values for Ca^{2+} and CO_3^{2-} ion concentrations in marine waters will lead to steady dissolution or no dissolution. Redeposition is unlikely to occur.

A deposit may begin life in a zone in which conditions are unfavourable to diagenetic change, it may then bcome lifted or eroded in such a way that it becomes open to change. A common example of this is the erosion of a raised beach deposit that exposes shell material to a vadose environment. In this position dissolution and redeposition from adjacent material, combined with atmospheric CO_2, may occur (a Zone 1 change). Re-exposure of deposits suggests a long period of time passing prior to diagenetic alteration; giving recrystallised material which will be considerably younger than the true age.

The shells for this study were collected from three calcareous environments: tufa, calcareous sands and chalk.

Tufa deposits represent a zone 2 environment but the nature of its conditions set it apart. Although the shells may be deeply buried and subjected to a high throughflow diagenetic change may still be excluded. The most common deposit of this type are the substantial tufa deposits. The shells in these are unlikely to suffer dissolution because of the large amounts of Ca^{2+} and CO_3^{2-} ions that are available. Contamination may occur due to the secondary depositon of carbonate as a surface deposit on the shell during or after the formation of the surrounding tufa. Secondary redeposition may occur whilst the shell is in a zone 1 environment prior to burial, with tufa as the underlying material. If the shell remains exposed for a length of time (>10 years) it is possible that dissolution or etching of the crystals may take place. When the shell does become inundated by the tufas the voids will fill with tufa, the age of which will depend on the apparent age of the groundwater that it is deposited from.

Calcareous sands are found in coastal areas; in Britain they are generally restricted to the Atlantic coast. They are liable to be subjected to zones 1, 2 and 4 depending on their exact position. The sands consist of a series of soil horizons indicating stable periods; these are periodically inundated by further blown sand. The calcium carbonate is in the form of fragments of marine shell that are distributed evenly through the sand. Terrestrial shells deeply buried in the soil horizons would under normal circumstances be subject to diagenetic alteration (zone 2). However, the high permeability of the sand gives free drainage and little time for dissolution of the marine fragments or secondary deposition in the terrestrial shells. The exception would be be substantial soil horizon that inhibited drainage. Shells in zone 1 environment are likely to suffer abrasive destruction due to the blown sand; but free drainage will again favour retention of the original shell structure.

However, certain conditions do lead to dissolution of shells in sand dunes. Observations on the Mediterranean coast of Israel showed that the dunes are cemented to form "Kurkar" sandstone. The only source of calcium carbonate for this are the terrestrial shells in the soil horizons. It is suggested that the elevated temperatures may account for this (see chapter 6.35).

Shells from areas with chalk bedrock will be subjected to zone 1 and zone 2 environments. This type of deposit will generally conform to the conditions discussed above, but the free drainage on chalk will reduce the effect of the groundwater dissolved carbonate.

2.6 EFFECT OF ECOLOGY AND ENVIRONMENT ON ^{14}C ACTIVITY

The descriptions of the modern sample sites show three important factors that will effect the ^{14}C values of the shells: variation in micro-environment between species, access to $CaCO_3$, and the ^{14}C activity of the carbonate.

At Oldlands Wood all four species occupied a limited area and should have had equal access to the particulate chalk in the sub-soil. However, the niche occupied by P.elegans brings the snails into much greater contact with the chalk particles. The snail can take in $CaCO_3$ particles with no ^{14}C activity by ingestion, by incorporation into the shell as it forms at the mantle edge, and through groundwater containing dissolved $CaCO_3$. Cepaea species in the same area will have less direct contact with particulate chalk both in their diet and in their shell formation. The groundwaters will still be available but will contain more dissolved CO_2, increased by exchange with the atmosphere (see chapter 3.2).

At Hayle Towans the carbonate occurs as shell fragments that have a

^{14}C activity equivalent to 6320±60 bp (Q-2xxx), 46% of uncontaminated modern wood. Access to the $CaCO_3$ is easy at sites 4 and 5 where the vegetation is sparse and the soil thin; site 2 is more difficult because of the turf. The distribution of the $CaCO_3$ by particle size (table 2.7) shows that 0.180-0.500 mm fragments are dominant. They are too coarse to be included in the diet or incorporated into the shell at the growing edge. Dissolution of shell fragments will lead to their incorporation by the snail but the high activity of the $CaCO_3$, relative to chalk, will reduce the errors in the final snail ^{14}C activity. This activity was measured on modern shells of C.nemoralis from Site 5 and was found to be 12% below the calculated value (see chapter 3.3).

The tufa at Graffy is also readily available and its fine particles can easily be removed from the open ground surfaces. It is easily eroded and can become suspended in water and then deposited onto plant material. These factors suggest it will be incorporated into the shells by ingestion and at the growing edge. However, the tufa has some ^{14}C activity, 33% to 50% of uncontaminated modern wood, in the samples analysed from other tufa sites, and the apparent age effect that it causes will be reduced compared to the incorporation of chalk. The reduced activity of the tufa will be an increasingly important factor if the surface becomes exposed and re-occupied by snails as was the case at Graffy. It is possible for the tufa to be "dead" if the period between deposition and occcupation is great enough. However, at sites such as Carrowmore, Newlands Cross or Caerwys (fossil tufa sites) the snails occupied the surface immediately after tufa deposition when depletion was only 10-20% relative to contemporary wood.

The development of the soil will also affect the shell composition. A poorly developed soil, such as at Hayle Towans sites 4 and 5, or Graffy, will be less productive in terms of humus activity than a highly organic soil, as at Oldlands Wood. The contribution of soil CO_2 should be lower at the sites with a poorer soil and seasonal fluctuations should also be reduced (see chapter 6.6).

When the fossil sites are considered four features standout. The first is the probability of a high apparent age effect at Binnel Point due to the solid $CaCO_3$ source being chalk; and also the species analysed (P.elegans) is known to burrow through sub-soil and incorporate particles of chalk in its diet.

The second is the dissolution and redepositon of shell material at Netanya. The permeable sand should allow free drainage but the change in external conditions (particularly temperature) leads to cementing of the shells and dune.

Thirdly the high water table and flow of groundwaters through the tufa at Caerwys. These conditions could lead to the deposition of secondary material on shells; and, if the presence of water is periodic, dissolution and recrystallation could occur in the buried shells.

Lastly the high ^{14}C content in tufa at Newlands Cross and Inchrory suggest that the shells from these sites will give ^{14}C ages in complete agreement with the expected dates.

One further factor that was not observed at the sites in this study, though considered at Inchrory and Castlethorpe, was reworking of material. Some types of context such as slope derived deposits, must be prone to including reworked material that is not contemporary with the deposit.

These features are all very important in selecting sites and samples; and they demonstrate the amount of information that can be gained by study of the potential material and by fieldwork prior to laboratory analysis beginning.

CHAPTER 3. SHELL FORMATION AND GROWTH

3.1 THE FORMATION OF MOLLUSCAN SHELLS

3.11 Introduction

The shells of molluscs are composed of organic and inorganic components. A range of nomenclature has been used for the inorganic shell layers of bivalves, the most simple and least ambiguous being that of Taylor *et al.* (1969; 1973) who refer to the inner, middle and outer layers. These seem to have gained general acceptance and the terms used by Oberling (1964), namely Ectostracum, Mesostracum and Endostracum, are only mentioned if reference is made to that study. Oberling (1955; 1964) uses the term myostracum for calcareous deposits secreted beneath muscle attachment areas, including both the layer below the pallial line and that beneath the adductor muscle scars. This is now in common use for both bivalves (Taylor *et al.* 1969; 1973; Petit *et al.* 1980) and gastropods (MacClintock 1967).

The inorganic shell layers of gastropods have also been the subject of different nomenclatures. Although the number of shell layers varies from one to four the commonest is two, this allows the terms inner and outer to be used in most cases. MacClintock (1967) considered these two layers to be different and described them as concentric and radial. Philippon (1974) also considered them distinct and called them Type B and Type C. However, they are identical structures with different alignments and here are referred to as inner and outer (see chapter 4.35 for further discussion).

The organic component consists of the periostracum, interlamellar structures, intercrystalline structures and intracrystalline structures, the last three being known collectively as the matrix.

All these terms are in common usage and are defined in the following section. There is also the soft body and ligament of the mollusc, but they are rarely, if ever, preserved in fossil specimens and are mentioned only in connection with the calcification process. In this context the mantle is particularly important.

3.12 The Organic Components

(i) The Mantle

In pelecypods the mantle edge is divided into three folds, each of which has a different function (figure 3.1). The inner is muscular, the middle sensory and the outer secretory. The cells responsible for shell secretion are the epithelial cells. Those on the inner surface of the outer fold secrete the periostracum; the first calcareous material is laid down by the epithelial cells on the outer part of the outer fold. The rest of the shell is laid down by the cells of the general outer surface of the mantle.

As would be expected, the cells secreting these various parts of the shell are different, but all are formed alike. The generative zone is thought to be at the inner part of the periostracal groove. The cells produced there migrate around the mantle edge, changing their shape, chemistry and function as they do so. Each cell in turn secretes periostracal material, outer shell layer and middle shell layer and then becomes an attachment area at the pallial line in bivalves. The cells then secrete the inner shell layer and may eventually becomes part of the muscle attachment.

(ii) The Periostracum

The periostracum is continuous from below the mantle edge and over the outer inorganic layer. It consists of a thin layer of quinone

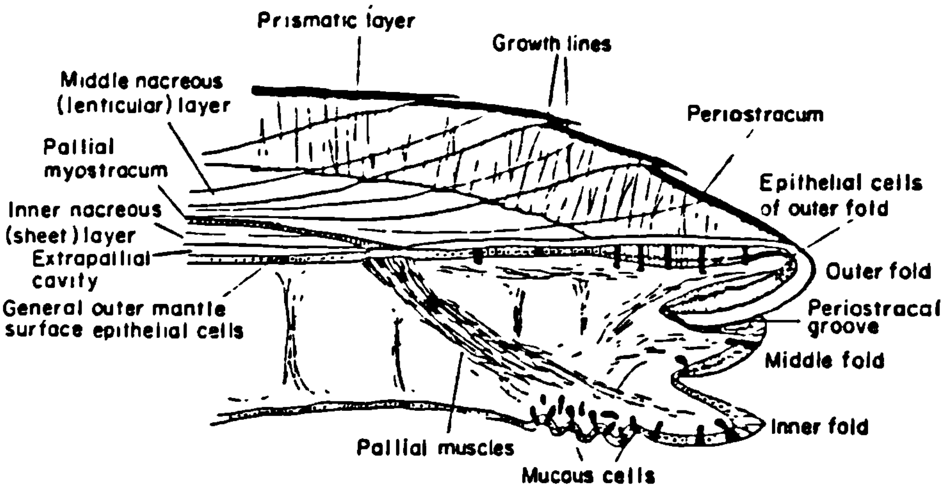


Figure 3.1. Diagram of the relationship between shell and mantle in a freshwater clam. (After Taylor et al. 1969).

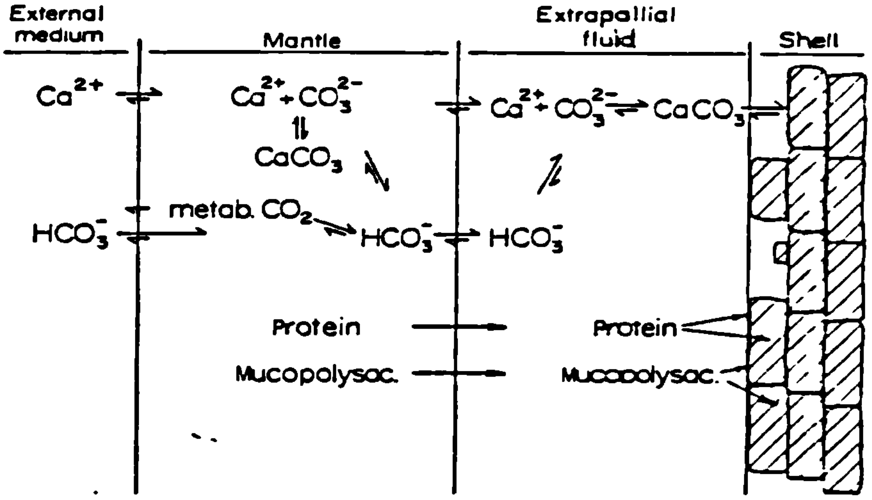


Figure 3.2. Diagram of compartments in molluscs. (After Wilbur 1972).

tanned protein, usually termed conchiolin. The amino-acids found in the periostracum are also found in the rest of the shell but the ratio of acidic to basic amino-acids is lower (Hare 1963). A summary of the results of studies on conchiolin composition is given by Gregoire (1972). His survey shows that the periostracum consists of a number of layers, more being found in freshwater gastropods than marine species. The conchiolin protein contains 15-17 amino-acids (Wilbur & Simkiss 1968; Meenakshi et al. 1969); lipids and polysaccharides are also present. Acid mucopolysaccharides, commonly associated with calcification, are absent. The composition of the periostracum is influenced by a number of factors, including the degree of protein tanning, environment and taxonomy. It can act as a protective layer and is prominent in species which are subject to attack by "boring" species, in species that themselves produce acid for boring and in freshwater species that live in acidic waters.

The organic matrix within and around the calcium carbonate structure is also proteinaceous. Its relationship to the crystal structure is dealt with in chapter 3.13. Amino-acid determinations on the organic matrices have been made by a number of researchers including Stegemann (1961; 1963) and Degens et al. (1967). The general conclusions are that the matrix closely resemble the keratin - myosin - epidermin - fibrin group of proteins.

3.13 The Inorganic Components

The nomenclature of shell layers was briefly discussed earlier in the chapter. A similar diversity of terms has arisen for the ultrastructural types that compose those layers. Oberling (1964) distinguishes nine types of structure, Kobayashi (1969) eleven types (five of which were dealt with by Wise 1969). MacClintock (1967) based his work on Bøggild (1930), modifying it where it lacked critical detail or new work had come to light. In the process he created eleven types from Bøgglid's eight.

The nomenclature and types followed here are those of Taylor et al. (1969; 1973).

Calcification

The calcification process was touched on in dealing with the organic components as the shell is secreted from these. Wilbur (1972) suggests it is convenient to consider the shell-forming system as consisting of four compartments in a linear arrangement (figure 3.2). The first compartment represents the medium or environment in which the mollusc lives, that is seawater, freshwater or soil/atmosphere; the relationship of the last two to the shell composition will be discussed in later chapters (3.2, 5.3, 5.4). The other compartments, in order, are the mantle, the extrapallial fluid, and the shell.

The secretory epithelial cells are not in direct contact with the shell except at muscle attachment areas and in the periostracal groove. The shell is separated from the mantle by the extrapallial cavity, which contains the extrapallial fluid. It is within this fluid that the calcium carbonate and the organic matrix are formed.

There are interconnections between the compartments going towards the shell and from the shell back to the extrapallial fluid and mantle. Movement of ions can occasionally take place from the tissues to the medium, but only if the external medium is sufficiently low in ions of that particular type. In the case of calcium ions, loss of these from the tissue is compensated for by loss of shell material

(Greenaway 1971).

The sources and pathways by which calcium, carbonate and bicarbonate ions reach the extrapallial fluid will be dealt with in detail in the next section (3.2). Here a summary will suffice. The calcium normally comes from the environment, but may also be supplied from solubilized solid calcium carbonate in the tissue or from spherites of calcium carbonate and organic shell matrix found in the mantle (Wilbur 1972). The shell bicarbonate derives from three sources: the environment, metabolic carbon dioxide, and tissue carbonate. The organic matrix of the shell consists mainly of protein and mucopolysaccharide and is secreted from the mantle via the epithelial cells. The calcium is also largely secreted via the epithelial cells to the extrapallial fluid but may also come from dissolution of the inner shell surface.

The ionic calcium passes through the epithelium largely by diffusion. It is also possible that the environment may directly contribute to shell deposition by inclusion of particles of solid calcium carbonate.

Calcium is known also to bind to mucoproteins, some of which form the organic matrix. The bound calcium that they transport may contribute to the crystal nucleation on the shell surface (Wilbur 1972). However, the bulk of the calcium in the mantle of bivalves (c 87%) is in the form of spherites, which are presumed to be deposited from ionic calcium when conditions are suitable. Istin & Girard (1971) showed that the spherites could easily be converted back to ionic calcium if conditions in the mantle became acidic owing to metabolism.

The thin layer of extrapallial fluid contains calcium carbonate in solution as well as proteins, mucopolysaccharides, glycoprotein, organic acids and several inorganic ions (sodium, potassium, magnesium, manganese, chloride, sulphate, phosphate). Wilbur (1964) suggests that it is the physico-chemical properties and composition of the fluid that define the nature of the organic matrix and the calcium carbonate polymorph form. This view finds some confirmation in S.Kobyashi's (1964) study of the protein and mucopolysaccharide content of extrapallial fluid in eleven species of bivalve. This showed that in a shell that was almost wholly calcitic the extrapallial fluid contained only one protein and one or two muccopolysaccharide fractions, whilst one containing aragonite produced three fractions of each in the fluid.

The extrapallial fluid of both terrestrial (Helix aspersa) and freshwater (Anodonta sp.) species are saturated or supersaturated with respect to aragonite or calcite. Although this could be taken to indicate that the crystal structure may be precipitated in vivo through a change in carbon dioxide concentration or pH, crystals generally develop from nuclei on the growing shell surface and edge.

The mechanisms by which calcium carbonate is precipitated from the pallial fluid are discussed by Wilbur (1972).

The formation of individual crystal layers and highly ordered growth in a variety of arrangements are probably controlled by the organic matrix. The shell matrix protein can be divided into water-soluble and water-insoluble fractions. The soluble fraction is intracrystalline and has been observed by Watabe (1965), though Towe & Hamilton (1968) dispute this interpretation of the observed structures. The insoluble fraction is primarily intercrystalline, but may occasionally occur in an intracrystalline form.

The mechanisms by which the organic matrix is deposited are not clearly understood. Wilbur (1972) suggests the evidence indicates at least three possibilites:

(i) That the matrix is secreted by the mantle directly onto the inner shell. This is supported by the presence in bivalves of different mineralogy and structures either side of the pallial line. However, if the epithelial cells do change function and type as they move across the shell there is no reason why they should not secrete different material to the extrapallial fluids either side of the pallial line.

(ii) Polymerisation or hardening of proteins may take place after secretion.

(iii) Soluble organic material is secreted into the extrapallial fluid and incorporated into the matrix as a soluble fraction. This is indicated by the presence of a soluble calcium-binding glycoprotein both in the extrapallial fluid and within the shell crystals.

It has been suggested that the organic matrix plays an important role in the concentration and nucleation prior to crystallisation. Hare (1963) considered that the carboxyl side chains of aspartic and glutamic acids attract Ca^{2+} ions, whilst the amino groups of lysine or glucosamine attract bicarbonate ions. Calcium ions and oxygen could form co-ordination polyhedra and provide the basic crystallographic structure for calcite (CaO_6) or aragonite (CaO_9). The polyhedra could serve as the nucleation centres of calcium carbonate crystals.

An alternative mechanism is advocated by Crenshaw (1972). In this case Ca^{2+} would be selectively bound to a highly sulphated glycoprotein, and could then be chelated by ester sulphates located on adjacent polysaccharide chains. A change in the conformation of the glycoproteins could release calcium, which would cause a local increase in calcium and the initiation of crystal structures.

The crystals for shell growth are deposited in two distict types: one for the thickening of the shell, the other for extending the shell margin. The first of these occurs where the extrapallial fluid meets the existing shell. The shell acts as a stable substrate, the existing structure and organic matrix serving as a template for the new crystals (Clark 1973). The organic matrix provides orientation for the new crystals and therefore must itself be orientated. The substrate has a relatively flat surface, offering a more satisfactory source of orientation than the mantle surface.

The extension of the shell margin occurs by the formation of new crystals on the mantle immediately beneath the periostracum. Initially the crystals are not integrated into the margin but become so after only a few hours as they grow and coalesce (Clark 1973).

The mineralogy of the crystals is predominantly calcite and aragonite. Many shells are wholly aragonitic, some contain both aragonite and calcite, but none is known that is wholly calcitic. Freshwater and terrestrial species are almost entirely aragonitic, calcite being a reliable indicator of shell regeneration or structural diagenesis. Vaterite has also been observed in some samples, such as the regenerated shell of Helix sp.

Three principal factors appear to be influential in controlling the mineralogy: the organic matrix, the environmental temperature during growth and the salinity of the environmental water.

The influence of the organic matrix has already been discussed above, particularly the different numbers of proteins and polysaccharides found in the extrapallial fluid. Further evidence comes from Hare (1963) who recognised differences in the amino-acid contents between aragonitic and calcitic shell layers.

The effect of temperature on the aragonite-calcite ratio in species forming both minerals is less important to this thesis since it is only noticeable between tropical and temperate conditions. Even at these extremes of temperature the differences can be masked by differences due to species size (Taylor et al. 1969).

The extent to which salinity affects mineral composition is unclear. It may be a combination of temperature and species size effects, but in any case it is of little importance in the study of non-marine species.

The shell will contain small amounts of trace elements, as mentioned above with respect to the pallial fluid. These will be considered in more detail in chapter 5.4. They are known to vary with temperature and salinity, but in non-marine environments any variations will be dominated by the water, soil or atmosphere encountered by the molluscs.

3.2 INPUT SOURCES FOR SHELL COMPONENTS

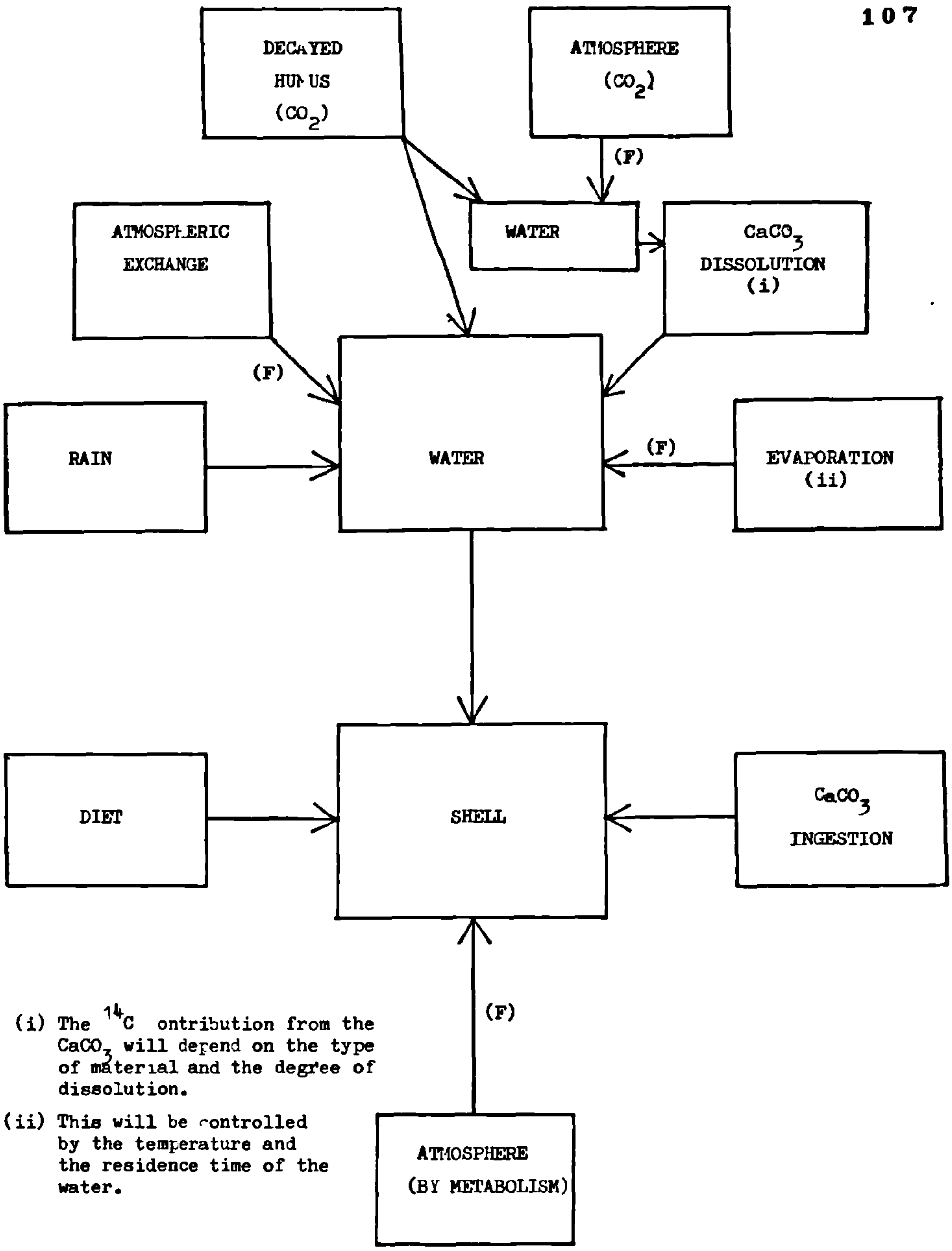
3.21 Introduction and Previous Studies

In recent years there has been an increase in the use of marine shells as a source of $\delta^{13}C$ and $\delta^{18}O$ values for reconstructing palaeoenvironments. This work has been extented to include the shells of freshwater and terrestrial species (Lécolle 1985; Magaritz & Heller 1980; Magaritz et al. 1981). The use of any shell material relies on the assumption that the $\delta^{13}C$ and $\delta^{18}O$ values of the calcium carbonate are representative of the environment in which the shell was formed. The difference in stable isotope values between the environment and the shell will depend on the fractionation that occurs during uptake of the shell components and their exact sources. Figure 3.3 illustrates some of the possible sources of carbonate that may contribute to the final shell composition. Figure 3.4 (based on Goodfriend & Hood 1983) is a more complex diagram which includes details of the biochemical processes that the components can undergo within the mollusc prior to deposition.

(i) Diet

DeNiro & Epstein (1978) studied the influence of diet on the distribution of carbon isotopes. Terrestrial snails (Helix aspersa) were fed on Romaine lettuce leaves and $CaCO_3$ or $Ca_3(PO_4)_2$. The results are given below:

Diet	-26.6	Organic fraction ($Ca_3(PO_4)_2$	-25.1
$CaCO_3$ (Diet)	-13.4	Organic fraction ($CaCO_3$)	-25.0
$CaCO_3$	-12.5 to -13.0		



(i) The ^{14}C contribution from the $CaCO_3$ will depend on the type of material and the degree of dissolution.

(ii) This will be controlled by the temperature and the residence time of the water.

Figure 3.3. Sources of carbon that can contribute to the shells of terrestrial molluscs.

(Shell, fed $Ca_3(PO_4)_2$)

(All values are in per mill. relative to PDB).

The snails used had been kept on the same diet for several generations and the enrichment in the ^{13}C value of their shells must therefore be an atmospheric contribution rather than a reworking of enriched shell material. The $\delta^{13}C$ shows that there was a considerable plant/dietary contribution. Assuming the atmospheric $\delta^{13}C$ to be $+1^{o}/_{oo}$ after dissolution in water (or body fluids), and the dietary material to be fractionated by $-2^{o}/_{oo}$ between the extrapallial fluid and the shell (Emrich et al. 1970) then the relative contributions are 49-51% for both diet and atmosphere. Similar values were obtained by Tanaka et al. (1986) in their studies of marine molluscs.

(ii) Atmosphere

The atmospheric CO_2 contribution enters the extra-pallial fluid through respiration during metabolism or by gas exchange at the mantle edge as the shell forms. The absence of atmospheric CO_2 in the organic fraction suggests that the gas exchange may be the more important route. The isotopic values of the acid insoluble organic fraction show this to be formed from the diet only. The ^{14}C value for the diet (plant) is about $-50^{o}/_{oo}$, a 5% depletion relative to an uncontaminated modern standard, whilst the ^{14}C in atmospheric CO_2 undergoes no apparent fractionation during dissolution of the CO_2.

Under controlled laboratory conditions (DeNiro & Epstein 1978) the $\delta^{13}C$ of the CO_2 can be assumed to be that for the general atmosphere. However, in a natural environment the $\delta^{13}C$ of the CO_2 at ground level is influenced by soil CO_2 from decayed organic material which has a

$\delta^{13}C$ value of -20 to $-25^{o}/_{oo}$. The $\delta^{13}C$ of the CO_2 at ground level can range from -7 to $-25^{o}/_{oo}$; its exact value will depend on the bacterial activity of the soil, the density of vegetation (respiration) and the temperature and humidity that control the movement of CO_2 in the soil.

Dörr and Münnich (1980) showed that the concentration of CO_2 increases with temperature (i.e. bacterial activity) and with increasing soil depth. The $\delta^{13}C$ showed no changes with depth and remained steady at -22 to $-24^{o}/_{oo}$. The $\delta^{13}C$ and $\delta^{14}C$ values varied through the year and, by implication, with the temperature. The range of $\delta^{13}C$ was from $-25^{o}/_{oo}$ in the spring to $-22^{o}/_{oo}$ in the autumn. The ^{14}C level from soil respiration was similar to the atmospheric value but showed a lag of 2-3 years. O'Brien (1986) suggests that there are two types of carbon present in the soil: one has a rapid turnover but the other represents "old" carbon and remains within the soil for 400-500 years. The presence of "old" carbon can also be due to the slow decay of humus that has been in the soil for a long time; times prior to decay of up to 3000 years have been suggested by Likens _et al._ (1977). Overall the addition of CO_2 from the soil will contribute CO_2 naturally depleted in ^{14}C by $50^{o}/_{oo}$ and if the humus has a long soil residence time the CO_2 will become increasingly depleted in ^{14}C as the humus age increases.

(iii) Limestone ingestion

The effect of limestone ingestion on the $\delta^{13}C$ and $\delta^{14}C$ values of shells was studied by Goodfriend and Stipp (1983). They analysed shells of species from limestone and non-limestone areas, and within the limestone species that feed on leaf-litter and those that feed by scraping limestone. Their results show that (_Pleurodonte_ *carmelita*), a species which feeds on leaf litter in a non-limestone area, had no age anomaly. Those species that feed by scraping rock surfaces (*Urocoptis ambigua* and *Eutrochatella pulchella*) had ^{14}C values that were depleted by 21-27% relative to pre-bomb wood. The δ^{13}C values are less depleted than for the other samples, again an indication of a high limestone derived carbon level. The two species from limestone areas that fed on leaf litter (*Poteria jamaicensis* and *Pleurodonte sublucerna*) gave very different results. One was slightly depleted (6-7%) in ^{14}C, the expected result, the other was very depleted (33%). A replication gave a depletion of 27%. This severe depletion is a real effect but cannot easily be explained since the species is considered to feed exclusively on dead plant material.

Goodfriend & Stipp (1983) suggest a second possible means of limestone carbonate uptake; namely absorption of dissolved carbonate through the foot. The carbonate is dissolved by acidic snail foot secretions and as *P.sublucerna* is found attached by its foot to overhanging rocks the uptake of limestone carbonate may occur at this time. However, enriched ^{13}C values would be expected as a result and this was not found in the analyses.

Rubin *et al.* (1961) also studied the uptake of calcium carbonate by ingestion. ^{14}C-labelled $CaCO_3$ was fed to snails as fine powder. The shells of the snails were broken and the ^{14}C activity of the regenerated and original shell measured; the new shell contained 10-12% labelled $CaCO_3$ whilst the old shell contained 1%. The 10-12% $CaCO_3$ taken up by ingestion in the new shell is considerd a maximum as the conditions for ingestion were very favourable. The ^{14}C-labelled $CaCO_3$ found in the old shell is attributed to mechanical occlusion of particles within the surface grooves, though in the aquatic species it is partly attributed to exchange between the aqueous environment and the shell.

(iv) Water

The last main source of material for shells is the water; figure 3.3 shows that the water component can be the result of a large number of individual sub-components.

The direct effect of atmospheric exchange and evaporation on the $\delta^{13}C$, $\delta^{14}C$ and $\delta^{18}O$ composition of water will be small in terrestrial species as these effects are generally confined to bodies of standing water. However, they could be important if the groundwater is derived from standing water. In the case of aquatic species evaporation and exchange of CO_2 with the atmosphere, combined with CO_2 from the decay of humus and dissolution of limestone, control the $\delta^{13}C$ and $\delta^{18}O$ values of the dissolved inorganic carbonate (DIC). These aqueous carbonate species are the primary controllers of the $\delta^{13}C$ and $\delta^{18}O$ values of the mollusc shells whilst vital effects and food appear to have only minor importance (Fritz & Poplawski 1974). Laboratory experiments in which $\delta^{13}C$ values were controlled confirmed that the mollusc shell and dissolved carbon were in equilibrium (Fritz & Poplawski 1974).

If aquatic species are in equilibrium with the DIC of the available water it is logical to presume that the same is true for terrestrial species. The environmental water available to terrestrial species is more limited and therefore more susceptible to changes around it (Yapp 1979). Two sources of water are available to the mollusc: one is rain and the other condensed air moisture (dew). Assuming air moisture to be free from CO_2 or other carbonate species when it forms it can be seen as passing through a number of situations during which it can gain soluble carbon species. These situations are summarised in figure 3.5.

The absorption of atmospheric CO_2 during rainfall is considered to be a minor effect in areas that are vegetated and have active breakdown of organic material (Magaritz & Heller 1980). At ground level the rain or dew comes into contact with soil CO_2 which is present at concentrations that are many that of CO_2 in the higher atmosphere. The possible absorption of soil CO_2 continues during percolation when contributions from standing water and dissolution of $CaCO_3$ in the soil or underlying strata can also be made. The water may re-surface if external conditions (e.g. temperature and humidity) draw soil moisture to the surface. The soil moisture may contain calcium, magnesium and other cations that have been taken into solution.

Heller & Magaritz (1983) demonstrated that the $CaCO_3$ of snail shells records seasonal changes in the carbon and oxygen isotope composition of the environment. By calculating the isotopic composition of the water and carbon dioxide from which these $\delta^{13}C$ and $\delta^{18}O$ values should have been derived they were able to show that the source of the carbon, oxygen and probably the calcium was the water at the air-soil interface (dew) and the soil CO_2 (or dissolved carbonate) in these waters. They suggest that the seasonal variations are due to the upward movement of water, increased evaporation rates for dew, and seasonal changes in the activity of perennial versus annual vegetation. They do not consider this source to be the only one (the intake of $CaCO_3$ by ingestion of soil is mentioned), but they do see it as the major source. The values quoted

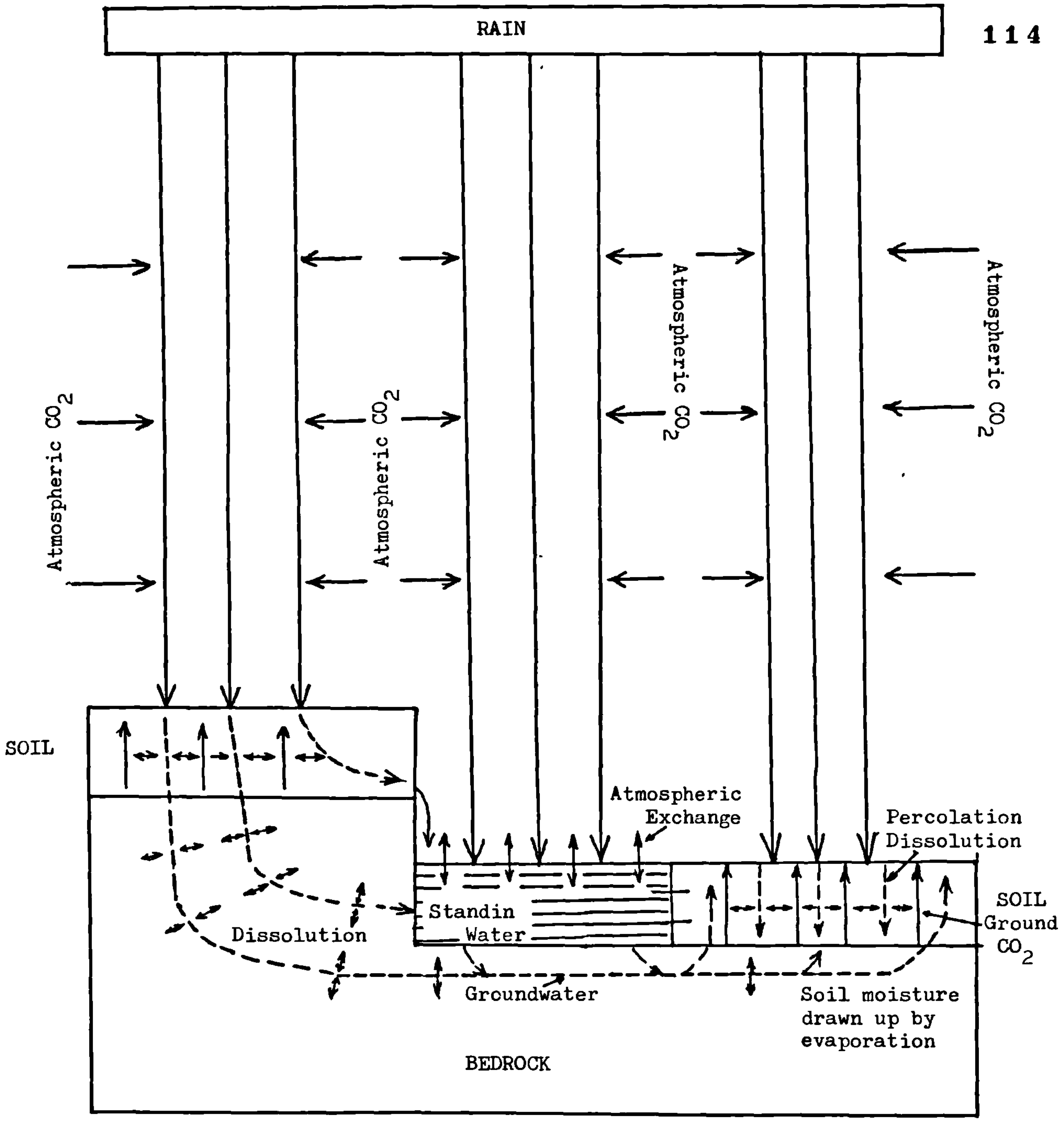


Figure 3.5. Pathways for the incorporation of carbonate and CO_2 in water.

for $\delta^{13}C$ soil CO_2 are enriched compared to those of Dörr & Münnich (1980); this could be due to the presence of a higher atmospheric CO_2 or dissolved carbonate component.

Yapp (1979) calculated the $\delta^{18}O$ values for waters that would have been in equilibrium with the shells. The results indicated that the water was of meteoric origin although the $\delta^{18}O$ values had been changed by steady-state evaporation; which is related to the relative humidity. The study also included $\delta^{13}C$ measurements but no interpretation was given. However, the results suggest a correlation between ^{13}C depletion and increased levels of vegetation, which in turn implies greater plant respiration and humic decay.

Lécolle (1983; 1984) measured the $\delta^{13}C$ composition of terrestrial snails and concluded that the $\delta^{13}C$ value was controlled by metabolism rather than climate or feeding habits. Lécolle (1983; 1984; 1985) agrees with other workers that there is a strong correlation between $\delta^{18}O$ values of the shell carbonate and the annual mean $\delta^{18}O$ value of percipitation, at least for altitudes of less than 1200m above sea-level.

The general conclusions to be drawn from the studies outlined above are that the four main sources of calcium, carbon and oxygen are all capable of contributing to the $CaCO_3$ of the shell. If one source is removed or reduced the mollusc is able to compensate by increasing the contribution of the others. The availability of calcium is more limited than carbon or oxygen since it is not present in the atmosphere or in plant material in sufficient quantities. The primary source of calcium must in general be $CaCO_3$ and therefore this must also represent a source of carbon and potentially a depletion in the

^{14}C content. Section 5.4 will discuss the levels of cations in shell carbonate and the relationship of these to the environment. The measurement of cations which can substitute for calcium in the aragonite or calcite crystal lattice could give an indication of the presence of soil $CaCO_3$ particles that have become incorporated into a shell at the time of formation.

3.22 Estimates of the Relative Contributions of the Different Sources of Shell Material.

Goodfriend & Hood (1983) estimated values for the relative contributions of each of the main sources of shell material. They assumed that all carbon is ultimately derived from plants, air, or limestone; soil CO_2 is considered to be a combination of air and plant-derived carbon. Limestone is not the sole source of mineral derived carbon, but for each different material (e.g. chalk, tufa or limestone) the equations must be recalculated with appropriate $\delta^{13}C$ values.

Goodfriend and Hood (1983) assume the $\delta^{13}C$ values to be:

$C_p = -27‰$

$C_l = 0$ "

$C_a = +1$ " (effective value after dissolution)

p = plant derived carbon
l = limestone derived carbon
a = atmospheric derived carbon
P = proportion from that source

cw = contemporary wood
s = shell

After correcting for ^{14}C fractionation between the different sources they obtained equations for the shell activity:

$$A_s = A_{cw}(0.996P_p + 1.054P_a) \quad \text{(eq.3.1)}$$

$$P_a = 27P_p + \delta^{13}C \quad \text{(eq.3.2)}$$

$$P_p = (0.03395 \times A_s/A_{cw}) - 0.03578\,\delta^{13}C \quad \text{(eq.3.3)}$$

By applying these equations to samples of known age Goodfriend & Hood concluded that plant-derived carbon made up c.25-40% of the shell, atmospheric derived carbon 30-60% and limestone derived carbon 0-33%. The level of carbon derived from atmospheric CO_2 is higher than would be expected if soil CO_2 were the major source of CO_2, even if part of the atmospheric level includes CO_2 that has its origin in the soil. However, if the plant derived carbon is also considered to be in a gas phase (as CO_2 from decayed humus) then the $\delta^{13}C$ values could be $-19^{o}/_{oo}$ rather than $-27^{o}/_{oo}$ The equations then become:

$$A_s = A_{cw}(1.012P_p + 1.054P_a) \quad \text{(eq.3.4)}$$

$$P_a = 19P_p + \delta^{13}C \quad \text{(eq.3.5)}$$

$$P_p = (0.0475 \times A_s/A_{cw}) - 0.0501\delta^{13}C \quad \text{(eq.3.6)}$$

If these revised equations are used the influence of the plant/soil CO_2 component becomes much greater; the ranges are 36-53% plant derived carbon, 14-46% atmospheric carbon and0-33% limestone derived carbon.

The values assumed by Goodfriend & Hood (1983) were for their research area in Jamaica. The appropriate values for this study are different owing to the types of plants, sources of calcium carbonate and values for soil CO_2 dissolved in water. The $\delta^{13}C$ for plant carbon in northern Europe is generally assumed to be $-25^{o}/_{oo}$. Burleigh _et_ al. (1984) list the $\delta^{13}C$ values of plant material other than wood as -25 ± 3.3‰ , and wood as -25.7 ± 1.9‰. The $\delta^{13}C$ values of soil CO_2 have already been discussed (see above) and in this section a value of -23‰ prior to fractionation by $+8$‰ on dissolution is used.

The $\delta^{13}C$ values for the carbonate sources are given in table 5.13. The analysed chalk samples were taken from unweathered outcrops (Ch.S3 and Ch.S4) and the calcium carbonate present in the soil. The unweathered bedrock is assumed to be free of ^{14}C and the mean $\delta^{13}C$ value is $+1.88$‰. The calcium carbonate in the soil, the material that will be available to the snail by ingestion, has a mean $\delta^{13}C$ value of $+0.78$‰; the value does not appear to vary with depth. When the calcium carbonate (solid) is dissolved there is a fractionation of $+1.27$‰ (Emrich et al. 1970); however, this does not affect the final ^{13}C value of the shell carbonate as there should be no fractionation in the system $CaCO_3$(solid) – HCO_3^- – $CaCO_3$(solid). This fractionation is included so that a value for the pallial fluid can be obtained and a single fractionation factor then applied to the solution to solid change. The $\delta^{13}C$ values that are appropriate for calculation of the plant, atmospheric and $CaCO_3$ contribution to shells living on a chalky subsoil are:

$^{13}C_p = -25$‰ (−17‰ if as soil CO_2 in solution
$^{13}C_a = -7$ " (+1 " if as CO_2 in solution)
$^{13}C_{CaCO_3} = +0.75$ " (+2 " if in solution)

The final shell ^{13}C value should be depleted by $+1.5-2.0$‰ relative to the hemolymph and pallial fluids. Based on these values the equations of Goodfriend and Hood (1983) are:

$$P_p = (-0.05544 \times \delta^{13}C) - 0.0526A_a/A_{cw} \quad \text{(eq.3.7)}$$

$$P_a = -\delta^{13}C - 19P_p \quad \text{(eq.3.8)}$$

$$P_{CaCO_3} = 1 - (P_p + P_a) \quad \text{(eq.3.9)}$$

Three sets of data for shells from deposits overlying chalk were available and the values calulated for P_p, P_a and P_{CaCO_3} for these are given in table 3.1.

Species	Site	Ref.	$\delta^{13}C$	Age Shell	Age Wood	P_p	P_a	P_{ch}
P.eleg	Binnel	(1)	-6.52	5540	4480	0.32	0.44	0.24
P.eleg	Kent	(2)	-6.61	5050	4540	0.31	0.53	0.15
C.nem	Kent	(2)	-9.90	4930	4540	0.50	0.43	0.07

P.eleg = Pomatias elegans (1) = This study
C.nem = Cepaea nemoralis (2) = Burleigh and Kerney (1982)
All dates are years bp (1950 AD)
$\delta^{13}C$ in per mill.

Table 3.1. Sources of shell $CaCO_3$ for samples from a chalk area.

The values for P_{ch} (proportion derived from chalk) are within those obtained by Goodfriend & Hood (1983). The data also confirm their finding that atmospheric CO_2 is a major contributor to the shell carbon and that it is consequently more important than Heller & Magaritz (1983) suggest.

If the equations are applied to carbonate sands or tufa the activity of the calcium carbonate source can no longer be assumed to be zero.

The age and activity of the carbonate must be determined and included in the equations. The activity of a sample from Hayle Towans (HT5/5+) and tufa from Inchrory were determined. The new equations for Hayle are:

$$P_a = 1.852(A_s/A_{cw}) - 0.852 + 0.0411\delta^{13}C \quad \text{(eq.3.10)}$$

$$P_{caco_3} = 0.9174 - 0.9541P_a + 0.0367\delta^{13}C \quad \text{(eq.3.11)}$$

$$P_p = 1 - (P_a + P_{caco_3}) \quad \text{(eq.3.12)}$$

When applied to the modern shell sample (C.nemoralis) from Hayle that was submitted for ^{14}C dating (Q-2???) the results are:

$$P_a = 0.414$$

$$P_{caco_3} = 0.159$$

$$P_p = 0.427$$

This shows that 16% of the shell carbon is derived from the shell fragments in the sand.

The equations for the fossil tufa site at Inchrory are:

$$P_a = 5.196(A_s/A_{cw}) - 4.129 + 0.0463\delta^{13}C \quad \text{(eq.3.13)}$$

$$P_{caco_3} = 1.4204 - 1.4773P_a + 0.0568\delta^{13}C \quad \text{(eq.3.14)}$$

$$P_p = 1 - (P_a + P_{caco_3}) \quad \text{(eq.3.15)}$$

When applied to the shell of Cepaea hortensis that was submitted for AMS ^{14}C dating (OxA-711) the results are:

$$P_a = 0.673$$

$$P_{caco_3} = 0.000$$

$P_m = 0.327$

As expected the shell contains no measureable tufa-derived carbon (see chapter 8.5 for further discussion).

Goodfriend & Hood (1983) found the relationship bewteen P_{CaCO_3} and $\delta^{13}C$ to be relatively weak, with variation in the proportion of $CaCO_3$-derived carbon accounting for only about 0.25 of the variation in the shell $\delta^{13}C$. Goodfriend & Hood (1983) attributed the rest of the variation to an increased surface area/volume ratio with decreasing shell size. They demonstrated this by plotting the proportion of atmospheric CO_2 as a fraction of the non-limestone CO_2 against the estimated shell volume. Lécolle (1985) also attributed ^{13}C variations to metabolism rather than feeding or climate, but Magaritz et al. (1981) propose that the micro-environment of the snail is important. Evin et al. (1980) and Tamers (1970) investigated the relationship between age error and ^{13}C values and concluded there was no relationship. All of these studies, with the exception of that by Magaritz et al. (1981), were conducted on a range of species and sites and the combined results used in the interpretation. If $\delta^{13}C$ and $\delta^{18}O$ values are related to the environment then the combining of data from different species and sites will distort and conceal any variations that are present. Therefore, for this thesis detailed study of intra-shell, inter-shell and inter-species variations were undertaken; the results are given in chapter 5.3.

3.23 Conclusions

The range of potential sources for the organic and inorganic fractions of shells is very great. The way in which they are combined and their relative contributions are controlled among other things by the availability of the input sources at the time of shell construction. The different inputs form an interrelated dynamic process which can only be defined in exceptional circumstances such as controlled laboratory conditions.

The chemical and isotopic value of the shell must be a combination of signals or fingerprints from each of the sources; only in cases where one or two are dominant will individual ones stand out. Chapter 5 examines the chemical and isotopic composition of modern and fossil shells and links the observed values to the macro- and micro-environments from which they were collected and which were described in chapter 2. It attempts to demonstrate that the signal from the environment can be distinguished from the others and then these findings are used as part of a selection procedure for shells in which the apparent age problem will be at a minimum.

3.3 SHELL GROWTH AND MOLLUSC POPULATIONS

Chapter 3.1 described how shells form and the previous section (3.2) the sources for the organic and inorganic components that make up the shell. This section describes the age distribution of populations and the growth of shells.

3.31 Age Structure and Radiocarbon Activity

Study of the age structure within terrestrial mollusc populations is important to this work because it allows an estimate of the ^{14}C content of a sample containing a number (>20) of individuals to be established. The calculated value assumes that no solid $CaCO_3$ is incorporated. The difference between the measured and the calculated values gives an estimate of the apparent age effect in a particular sample. The present day atmospheric ^{14}C value is a combination of natural ^{14}C production in the upper atmosphere, the fossil fuel effect and contamination from nuclear weapons testing. The effect of nuclear weapons testing reached a peak in the early 1960's and has declined since then owing to mixing with oceanic CO_2. Values for atmospheric ^{14}C values over the period 1970-84 are given in table 3.2

Year	^{14}C Vermunt(1)	^{14}C Schauinsland
1970	530	-
1971	499	-
1972	465	-
1973	429	-
1974	401	-
1975	368	-
1976	352	-
1977	334	333
1978	325	324
1979	291	295
1980	261	267
1981	257	-
1982	238	239
1983	225	225
1984	220(2)	-

Table 3.2. ^{14}C values for the period 1970-84

(1) Based on Levin et al. (1985), in ‰ above pre-bomb wood

(2) Estimated by extrapolation of preceeding values.

The values in table 3.2 are not corrected for fossil fuel effects as it is the actual level of ^{14}C available to the snail that is required.

The age structure for C.nemoralis and C.hortensis can be established using the work of Williamson et al. (1976; 1977). They give the period for Cepaea to reach maturity, defined as the period from hatching to lip-formation, as three years. Field studies established the survival rates for adult *Cepaea* as 73% for the first five years of adult life. Senility is thought to lead to a higher mortality rate and a value of 50% survival is used for ages greater than eight years (three as juvenile and five as adult). The age structure for an adult population based on these figures is:

	Juvenile										
AGE	0	1	2	3	4	5	6	7	8	9	10
Proportion in each age category	-	-	-	0.29	0.21	0.16	0.12	0.09	0.06	0.03	0.02

Age 3-8 73% survival. Age 9-10 50% survival

Williamson (1979, table 1) allows the weight increase in the adult shell to be calculated:

Age since lip formation	Shell diameter (mm)	Shell weight (mg)
0	18.1±0.7	253
1	18.1±0.7	467
2	18.1±0.8	543
3	18.2±0.8	551
4	18.3±1.0	540
5+	18.0±1.0	512

Maximum weight and shell thickness are reached in the third year after lip-formation; if this is taken as 100% of shell weight then the weight percentage for earlier years can be calculated:

Age since lip formation	Shell weight (mg)	% Shell weight
0	253	45.9
1	467	84.8
2	543	98.5
3	551	100.0

The shell is 45.9% of final weight when adult size is reached and the increases in weight during the juvenile period can also be calculated. Williamson (1979, figure 1) allow the mean diameter for each of the juveniles to be estimated for three age groups based on time since hatching. However, in order to have a realistic estimate of the relative shell sizes a volume or weight is required. No data on weight were available and an estimate of volume based on diameter had to be made assuming a shell to be equivalent to a flattened cone over a cylinder. Measurement of shells gave the height-diameter(d) values 0.5d for the cone and 0.25d for the cylinder. The volume of the two bodies is:

$$V = 3.14 \times 5d^3/48 \qquad \text{(eq.3.16)}$$

The volume of juveniles and adults at the time of lip-formation were obtained, as were the percentages of maximum shell weight that each juvenile shell age group represents:

Year since hatching	Diameter (mm)	Volume (mm^3)	% max. shell weight	% change that year
0	3.8	18	0.4	0.4
1	8.1	170	4.0	3.6
2	13.1	730	17.3	13.3
3	18.1	1940	45.9	28.6

Combining the data set out above allows estimates of the activity in shells that hatched in a specific year to be made. Shells from snails that hatched in 1979-81 will not have had time to reach maturity and the percentage shell formed in each year is corrected for this. The activities for each hatching can then be combined using the age structure data to give an estimate of the activity for a shell population. The results are given in table 3.3.

Year of hatching	Proportion surviving from that year	^{14}C enrichment	Sample ^{14}C enrichment contribution
1983	-	-	-
1982	-	-	-
1981	0.30	223.2	66.96
1980	0.22	226.3	49.78
1979	0.16	233.8	37.40
1978	0.12	246.7	29.60
1977	0.09	262.4	23.61
1976	0.06	280.2	16.81
1975	0.03	304.3	9.13
1974	0.02	327.4	6.55

Total sample activity = +239.84$^{o}/_{oo}$ (24% above pre-bomb wood).

Table 3.3. Sample activity for a population of shells collected in 1984 if they were uneffected by the apparent age effect.

The values in table 3.3 assume that the number of snails reaching adult life is the same for each year; this is not necessarily valid (Cameron pers.comm.) but cannot easily be quantified. A more accurate value for the sample activity would have been obtained if shells that were just reaching the stage of lip-formation had been used. These could then have been assumed to be of a single year of hatching. However, the estimate of 240‰ is probably accurate to ±7‰, estimated by removing the largest contribution (1981) and by doubling it.

The work of Pollard (1975b) shows that H.pomatia has a similar life history and development to that of Cepaea and it should be valid to assume the same activity for that species. The age structure and growth of P.elegans maybe such that it requires a different estimate. However, the shortage of published information on the development of P.elegans precludes this and the δ^{14}C value calulated for Cepaea is assumed.

3.4 Banding Polymorphism

Cepaea nemoralis and C.hortensis are found in a wide range of banding polymorphs which have been extensively studied for their implications for genetic changes and development within a population. The predominance of a polymorph in one colony is attributed to the action of predators (visual selection of distinct colours: Cain 1968) and differential climatic selection (an increased ability of some morphs to survive high or low-temperatures because of the shell colour: Richardson 1974). The main morphs found are unbanded (00000), mid-banded (00300) and five-banded (12345), the last of these has a number of sub-groups defined by the spreading (S) and fusing (F) of the bands. The background colour is also variable and may be pink (P), white (W), yellow (Y) or brown (B).

Currey & Cain (1968) and Cain (1971) studied the alteration in the proportions of polymorphs through the Flandrian period: these changes were considered consistent with climatic variations. The general trend that they put forward is for a decline in the occurence of unbanded forms during the period preceeding 2500 bp and little change since then. The present study provided data on four dated fossil sites and three modern sites. The details are given in table 3.4.

The modern samples from the two sites at Hayle Towans show that the micro-environment is an important influence. The sites are only 2Km apart and both are on the dunes, site 2 is dominated by mid-banded and five-banded forms whilst at site 5 the predominant morph is unbanded. The main difference in the environments is that site 2 has more vegetation and less open sand, site 5 has large open dune areas. Therefore, the unbanded yellow shells blend much more easily in to the open dune than do banded-morphs, the converse is true on site 2. The background colour of the shells is predominantly yellow at both sites which argues against climatic selection (Richardson 1974) and indicates that the differences are due to camouflage against predators.

Currey & Cain (1968) suggest that unbanded morphs were more common before 2500 bp. The sites at Newlands Cross, Co.Dublin, Eire and Caerwys, Clywyd are nearly contemporary but the morphs present are very different. At Caerwys no examples of banded C.nemoralis were found (in line with Currey & Cain) but at Newlands Cross 75% of the C.nemoralis were banded. At the later site of Carrowmore 95% of the C.nemoralis were banded. The data on C.hortensis are quite different; Caerwys has banded morphs and Newlands Cross unbanded forms, though the numbers of shell present are much smaller. At Carrowmore the C.hortensis shells were also unbanded and were present in large numbers. No examples of living C.hortensis were found at any of the Irish sites. The site at Castlethorpe, Lincs also had no C.hortensis

Site	Species	Date	00000	00300	12345	12345S	12345F	Others
Oldlands	nemoralis	Modern	5	8	0	0	0	0
Wood	hortensis	Modern	9	0	2	15	3	0
Graffy	nemoralis	Modern	0	17	17	7	9	11
	hortensis	Modern	0	0	0	0	0	0
Hayle	nemoralis	Modern	8	8	7	14	1	2
Site 2	hortensis	Modern	0	0	0	0	0	0
Hayle	nemoralis	Modern	19	0	6	2	0	8
Site 5	hortensis	modern	0	0	0	0	0	0
Newlands	nemoralis	7600±	5	0	3	0	12	0
Cross	hortensis	500	4	0	0	0	0	0
Caerwys	nemoralis	7880±	24	0	0	0	0	0
	hortensis	150	0	0	3	0	2	0
Carrow-	nemoralis	5410±	3	0	32	5	16	4
-more	hortensis	50	38	0	0	0	0	0
Castle-	nemoralis	3410±	0	1	4	5	14	1
-thorpe	hortensis	80	0	0	0	0	0	0

(1) Others consists of 3 and 4 banded shells.

Table 3.4. Banding polymorphs from dated contexts.

present and the C.nemoralis were all banded morphs, mostly five-banded. The trends observed in these data suggest that neither climate nor predator selection can explain the results completely. Evidence that different morphs within a single population occupy different micro-environments is put forward and discussed in chapter 5.31.

CHAPTER 4. THE STRUCTURE OF NON-MARINE MOLLUSCAN SHELLS

4.1 THE MINERALOGY OF SHELL MATERIAL

Shells are formed almost exclusively from calcium carbonate; minor levels of magnesium, strontium and iron are found, and trace levels of other elements, but these rarely total more than 2% of the shell.

Shell calcium carbonate is found in three mineral forms: aragonite, calcite, and vaterite. Calcite is found with high (>7%) and low (<7%) magnesium. Low magnesium calcite is the stable form; all other forms tend to change by recrystallisation or leaching from their metastable states to this form. The decay of metastable forms and the mechanisms by which this occurs are discussed in chapter 6.

Calcite belongs to the hexagonal-trigonal (ditrigonal - scalenohedral) crystal systems. The Ca-ions are situated at the corners of a rhombohedron and the CO_3-ions are arranged with their centres midway along the rhombohedral edge and lie in horizontal planes (figure 4.1).

When calcite forms as a primary crystal (not as a recystallisation product) three main habits occur:

(i) nail-head, combination of flat rhombohedron and prism
(ii) dog-tooth, combination of scalenohedron and prism
(iii) prismatic

Other forms are fibrous, lamellar, stalactitic, nodular, granular, compact and earthy.

When occurring as a recystallisation product the main forms are sparry calcite, drusy calcite, micrite and cryptocrystalline forms.

Aragonite belongs to the orthorhombic system. The structure differs from that of calcite in that the CO_3-ions are not midway between the calcium layers and the co-ordinations are different; the symmetry is lowered to orthorhombic.

The commonly found forms of aragonite are prismatic crystals (often terminated by acute domes), acicular, globular, stalactitic, coralloidal, and encrusting.

Vaterite belongs to the hexagonal system, and is a spherulitic form of u-$CaCO_3$. Vaterite was first discovered as an artificial product but has now been located in shell material, particularly gastropods. It is less stable than either aragonite or calcite, and rapidly decays to one of these forms.

Table 4.1 gives more details of the three forms of calcium carbonate.

PROPERTY	CALCITE	ARAGONITE	VATERITE
Colour	Colourless/ white	White,grey,yellowish	-
Streak	White	Colourless	-
Lustre	Vitreous or earthy	Vitreous	-
Fracture	Conchoidal	Subconch.,britle	-
Hardness	3.00	3.5-4.0	-
S.G.	2.71	2.94	2.65

Table 4.1. Properties of calcium carbonate mineral forms.

4.2 THE BACKGROUND TO ULTRASTRUCTURAL ANALYSIS

The study of shell form and structure has a long history that is closely associated with both palaeontology and zoology. The study has developed from the macroscopic study of shell form (Reaumur 1709; Hatchett 1799), through early microscopic works (Carpenter 1844; 1847; Bowerbank 1844), and reached a pre-war pinnacle in the studies of Schmidt (1921-25) and Bøggild (1930). The studies of Schmidt, based on observations made with a light microscope, were of such high quality that they were not superseded until forty years later.

Bøggild's research concentrated on the mineralogy of shell structure types and their distribution in bivalves and other molluscs. Despite changes in the identification of the palaeontological material on which Bøggild based his study, it forms the basis of later work such as that by Oberling (1964) and MacClintock (1967).

Since the mid-1950's light microscopy has been supplemented by electron microscopy, at first in transmission mode, later in scanning mode as well. Numerous studies have been undertaken by electron microscopy, with research by Gregoire, Wada, Watabe and Kobayashi prominent amongst them. These workers concentrated on pelecypods, particularly species of importance to the pearl industries.

The high magnification possible with electron microscopy allows observation of crystal form such as third-order lamellae, the presence of which had previously been known only by postulation or implication. Scanning electron microscopy also gives a much greater depth of field than optical microscopy, the image appears to be three-dimensional and its structural interpretation is thereby facilitated.

MacClintock (1967) and Oberling (1964) surveyed the distribution of microstructures within Mollusca but only using optical microscopy and in the case of Oberling using a somewhat controversial nomenclature for the division of shell structures (see chapter 4.31). MacClintock's (1967) work concentrated on patelloid and bellerophontoid gastropods and was aimed at integrating ultrastuctural observations into the formal systematic description and classification of these groups. Similar work had already been completed by Newell (1937; 1942) on pectiniod and mytiloid pelecypods. Oberling (1964) also concentrated on pelecypods but compared their structures to those of other molluscs.

The most comprehensive surveys of shell structures are those by Taylor et al. (1969; 1973); Kobayashi (1969), Wise (1969), Bathurst (1975) and Grégoire (1972), and are based on evidence from optical and electron microscopy, X-ray diffraction and morphology. Carter & Tevesz (1978) also cover a wide range of fossil material using the structures defined by Taylor et al.(1969; 1973). It is the studies of Taylor et al. (1969; 1973) that have gained the widest acceptance and have been cited in many recent works. They are used as the basis of the present research on structure.

Taylor et al., like MacClintock (1967), have linked the shell ultrastructure to the classification and evolution of fossil forms. Taylor (1973) postulates "trends" for the development of shell structures. Although these are clearly related to phylogeny there is also a strong correlation between structure and the mode of life of the animal concerned. Taylor (1973) links phylogeny and mode of life by suggesting that in various phylogenetic lineages combinations of shell structures evolve at different rates in response to specialization to diverse modes of life.

4.3 THE STRUCTURE OF MOLLUSCAN SHELLS

4.31 The Nomenclature of Shells

The complete differences in the form of bivalve and gastropod shells has led to distinct sets of terms being used for the description of shells and their features.

Bivalves

The two saucer-like valves are joined together at the top by an elastic ligament (figure 4.2). The valves are marked on the exterior by growth lines that form a series of concentric lines parallel to the margin or free edge of the shell.

The first part of the shell to form is the umbo; this is the thickest part of the shell and may be deeply incised by growth lines (known in the region of the umbo as umbonal rugae).

The main interior features of bivalves are a hinge plate and hinge teeth. The size and position of these teeth are important diagnostic features of the shells of different species of freshwater bivalves. They are found in three groups in each valve of the shell and are termed anterior laterals, posterior laterals, and cardinals.

The muscles which open and close the valves, and those used in locomotion, are marked by impressions or muscle scars on the inner shell surface. The anterior and posterior adductor scars are connected by the pallial line, which indicates the position of the

muscular margin of the mantle (figure 4.2).

Gastropods

The first part of the shell to form is the protoconch, which is formed inside the egg. This will form the apex of the shell of the adult. During the growth period the rate at which shell material is formed will vary with conditions (such as cold weather or drought). This often leaves irregular radial growth lines (figure 4.3). In adult life the pattern of growth changes. The shell does not get larger, but the area round the aperture may be strengthened with a lip or rib and with various other thickenings.

The growth of the shell in a spiral form creates an internal columella which may be hollow or solid (figure 4.3B). Each successive coil of the spiral is a whorl; all the whorls except the last or body whorl form the spire, the tip of which is the apex. The line of contact between whorls is the suture. On the underside the last whorl circles the umbilicus, which may be closed in some species.

Within the mouth the thickening of the lip may develop into teeth, the location of which is given relative to the parietal, columellar and palatal regions.

4.32 Nacreous Structures

The nacreous structure is well known and widely studied, particularly in bivalves. There are three types of nacreous structure, one of which appears to be confined to gastropods. Nacreous structures are present in a wide range of bivalve sub-orders of which the Unionacea and Trigonacea are the most relevant to this thesis. The presence of nacreous structures in freshwater and

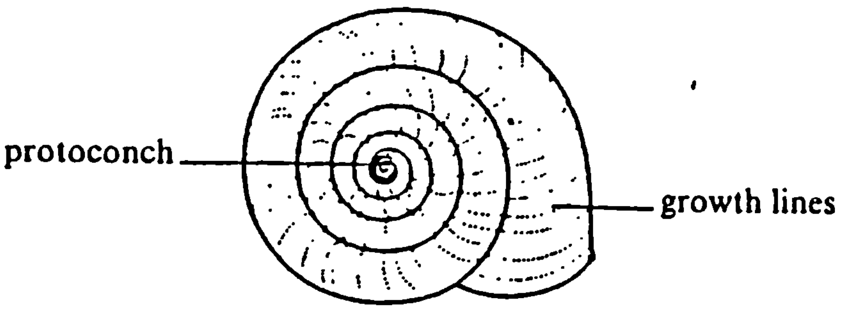


Figure 4.3A. External features of a terrestrial snail shell.

terrestrial gastropods is less well attested, but it is known from marine gastropods such as _Turbo castanea_ and _Haliotis rufescens_ (Wise 1970). Taylor _et al._ (1969) state that nacreous structures in bivalves are invariably aragonitic, and no example of calcitic structures is recorded from gastropods.

(i) Introduction

The three forms of nacreous structure are sheet, lenticular and 'stacked', the last being the gastropod form. In all of them the calcium carbonate is present as round or euhedral (ideally hexagonal) tablets, which in turn are formed from crystal individuals and laths. Mutvei (1979) described the internal structures of nacreous tablets. Those of bivalves are composed of two layers. The outer layer consists of four, radially arranged, crystal individuals, one pair of which is described as more soluble (Mutvei 1977) and may therefore be more susceptible to diagenesis. Mutvei (1977) had earlier thought these individual crystals went through the full depth of the tablet; his later work showed them to be confined to a thin outer layer. The surface of this outer layer exhibits concentric growth lamellae. The inner layer apppears to be formed from numerous parallel crystalline laths which are probably associated with the intracrystalline organic matrix.

In gastropods only a single layer has been distinguished. It consists of a varying number of radially arranged individual crystals. The surface shows a series of parallel laths similar to those found on the inner layer of pelecypod tablets (Mutvei 1979).

Each tablet is surrounded by an intercrystalline matrix, 0.03-0.1 microns thick. The layers of tablets are separated by the interlamellar matrix, which is 0.02-0.3 microns thick. It consists of lace-like networks of trabeculae defining a fenestration or pore pattern. Grégoire (1972) showed that the pattern of structures was related to taxonomic groups (nautiloid, gastropod and pelecypod), and suggested that it might be possible to define family characteristics that would allow shell fragments to be identified from their protein structures.

(ii) Sheet Nacre

Sheet nacre is distinguished by the regular arrangement of layers parallel to the shell interior. The overall effect is that of the bricks of a wall, with the interlamellar and intercrystalline matrices as mortar. The size and shape of the tablets varies with the rate of deposition. They vary from small rounded tablets when deposition is rapid to larger euhedral forms when growth is slower. Cyclic changes in the thickness of the layers was observed in this study in a *Unio* sp.; similar observations were made by Taylor *et al.* (1969) in a section of *Quadrula metanerva*. The section of the *Unio* sp. had a cyclic period of approximately 50 microns, the tablets varied in thickness from 0.7 microns to 1.5 microns. The thinner tablets were also narrower, 3-4 microns compared to 4-6 microns.

Once the tablets have reached their maximum size the next layer begins to form. Mutvei (1977) suggests that nucleation of the new nacreous tablets invariably takes place on the top surface of the less soluble crystal individuals. Therefore growth of new crystals is offset from the old crystal centre and the "brickwall" like structure forms.

The inner surface of sheet nacreous layers show the rounded or euhedral tablets, often with the layer below showing where growth is incomplete. The growth margins may be visible as smooth curves. However, if they are broken or uneven it may indicate natural dissolution, probably due to changes in the pH of the extrapallial fluid.

(iii) Lenticular nacre

This type of nacreous structure is distinguished by the euhedral or rounded tablets being formed from piles of thin layers, up to five high. Each layer shows a similar form to those below it. In general the surfaces are distorted which leads to the horizontal layers being less regular than in sheet nacre. The growth surface of the gastropod nacre appears granular when viewed at low magnification owing to the presence of the crystal stacks all across the surface.

The different form of the crystal individual in gastropods must contribute to the growth of the stacks, with central nucleation taking place rather than offset nucleation as in pelecypods. This type of structure is well attested in marine gastropods (Cittarium pica (L), Wise and Hay 1968b), but is not recorded in freshwater or terrestrial species.

4.33 Foliated Structures

This structure is always calcitic and is only recorded in marine genera, particularly the Ostreacea, Pectinacea, Anomiacea and Limacea. It is composed of more or less regularly arranged tablets which are joined side by side to make "fine sheets grouped in larger lenticular folia in turn forming larger units" (Taylor et al. 1969). The tablets are completely surrounded by intracrystalline organic matrix. This also surrounds the individual smaller laths which agglomerate to create the tablets.

Bøggild (1930) described the foliated structure as being similar to a nacreous structure, the main difference being its mineralogy. However, it is now clear that the unit carbonate particle is not a euhedral tablet but an elongated lath. MacClintock (1967) shows that it is possible to confuse nacreous and foliated structures in vertical section, provided that the foliated section is parallel to the outcrop pattern. In section at right angles to the outcrop pattern the sloping tablet formation is quite distinct. The surface of the foliated tablet is also distinct, showing the overlapping laths with their obtusely angled ends.

4.34 Prismatic Structure

The intensity with which prismatic structures have been studied is comparable with that for nacreous structures. Early work on prismatic structures included Carpenter (1844; 1847), Schmidt (1922; 1924; 1925) and Bøggild (1930). Prismatic layers usually form the outer layers of shells and two distinct forms have been recognised: simple and composite. Simple prisms can be calcitic or aragonitic; composite prisms are always aragonitic.

(i) Simple Prismatic Structure

This is the more common of the two prismatic structures, and the aragonitic and calcitic forms differ only in minor details. Both forms are recorded as having transverse striations, but in the aragonitic form the striations are less prominent and totally absent in some specimens. The aragonitic form has longitudinal striations; these may be present in the calcitic form but do not diverge as they do in the aragonitic form.

In radial and transverse section the prisms are columnar and more or less regular; they are separated from each other by vertical walls of organic matrix. The prisms are narrower (c.10 microns, compared to c.50 microns towards the centre of the cell) where they contact the periostracum, which leads to a larger number of smaller prisms. Taylor et al. (1969) suggest two reasons for this effect: the simultaneous growth of spherulites on an uneven surface, or the growth of prisms from spherulites on an even surface, but with individuals growing at different rates. Under either of these conditions some of the small growing prisms will be eliminated for lack of space in which to grow; this is termed geometric selection.

Grégoire (1961) showed that the prisms were constructed of disc-shaped calcium carbonate lamellae (0.7-7.0 microns thick). Each lamella was separated from adjacent ones by thin (0.04-0.5 microns) conchiolin sheets. Taylor et al. (1969) found a different structure present in Margaritifera margaritifera. They found that each prism was divided longitudinally into blocks (2-3 microns wide), and adjacent blocks were separated by a thin organic matrix. The longitudinal blocks intersected the conchiolin of the prism wall obliquely, giving the divergent striation effect. The two different structures are probably associated with calcitic and aragonitic prisms.

The surface of the prismatic layers has a honeycomb-like appearance. The prism cells are usually pentagonal, but may also be four-sided or hexagonal. The cells are divided by thick conchiolin walls. The prisms are made up of very small irregualr scale-like crystals

(0.2-2.0 microns), and lack any obvious orientation.

(ii) Composite Prismatic Structure

This prismatic structure is not found in non-marine species. The structure is formed from prisms of square cross-section which radiate from the umbo region. They become wider towards the shell margin and are separated by thin conchiolin walls. The first-order prisms are constructed from second-order prisms or needles, which are responsible for the characteristic "feathering" appearance of the first-order prisms. The needles are curved and become larger toward the outer faces of the first-order prisms.

Growth lines can also be seen on the faces of first-order prisms. They are strongly convex ventrally, producing a concentric appearance.

4.35 Crossed-Lamellar Structure

The crossed-lamellar structure is always aragonitic, the calcitic form being called a crossed-foliated structure. The crossed-lamellar structure occurs in both gastropods and bivalves. In freshwater bivalves the structure is only occasionally recorded, such as the example in *Corbicula fluminea* found by Taylor *et al.* (1973). However, if Mackie (1978) mistook crossed-lamellar for complex crossed-lamellar then the former is much more common, being found in all Sphaeriacea. It is the only structure recorded in terrestrial and freshwater gastropods, though its exact form shows wide variation.

The structure is formed from a three-fold hierarchy consisting of first-, second-, and third-order lamellae (figure 4.4). The first-order are clearly visible with conventional light microscopy.

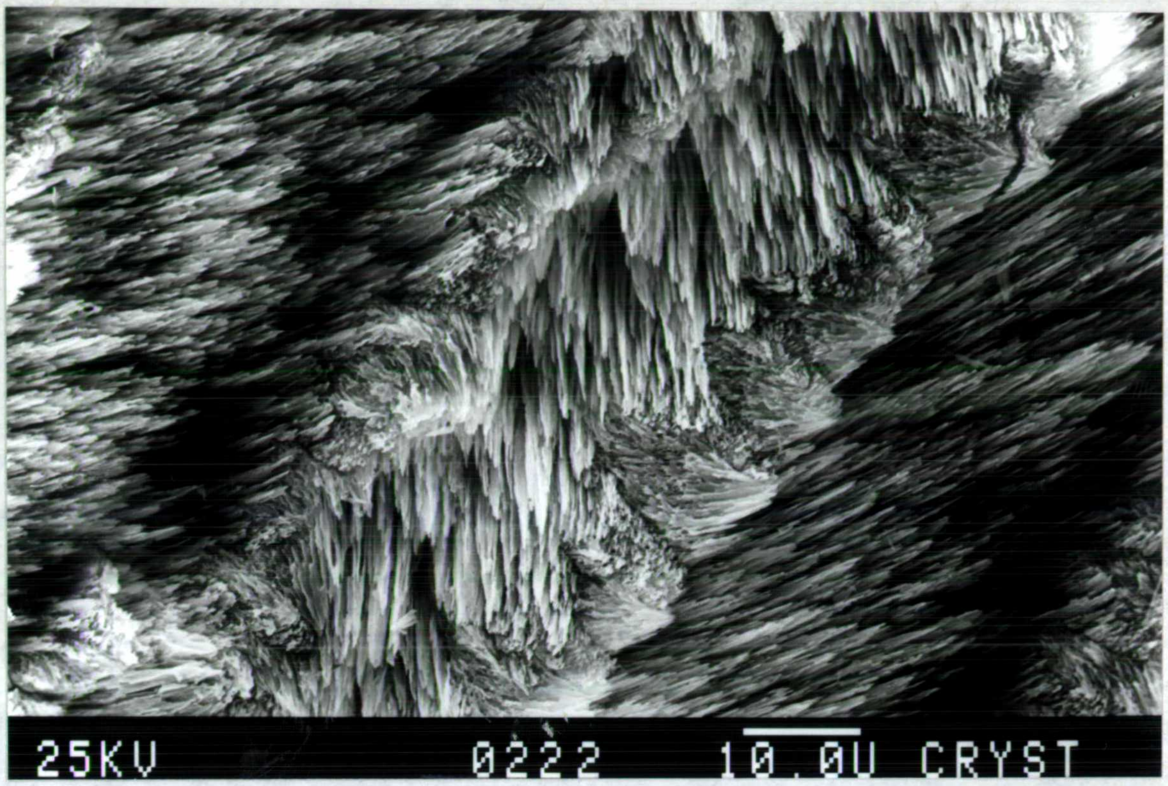


Figure 4.4. Crossed-lamellar structure in a shell of <u>Theodoxus fluviatilis</u>.

On the inner shell surface they appear as a series of elongated, branching and interdigitating lenses. These outcrops occur in a wide-range of shapes and sizes. Lengths of up to several millimetres and widths of 0.5 mm are recorded (Taylor <u>et al.</u> 1969), though it is more common to find widths of 10-20 microns in freshwater bivalves (MacClintock 1967; Uozumi <u>et al.</u> 1972), and 2-10 microns in gastropods.

In transverse and radial section the first-order lamellae show up as differently coloured areas, being distinct bands in radial section due to the arrangement of the lamellae concentrically and parallel to the shell margin. The situation is more complex in gastropods and is discussed below.

The first-order lamellae are in direct contact along their boundaries, no conchiolin being present between them.

The presence of second- and third-order lamellae was known from light microscopy (I. Kobayashi 1964; MacClintock 1967; Taylor <u>et al.</u> 1969), but detailed description was not possible until electron microscopy became available. The second-order lamellae are parallel sheets running the width of the first-order lamellae; they are separated by a layer of organic matrix. Second-order lamellae of adjacent first-order lamellae are inclined in opposite directions, which intersect at angles of 82° and 98° (Bøggild 1930). This arrangement gives both the name of the structure and the characteristic banding effect. First-order lamellae cut approximately along the second-order lamellae are lighter in colour than those cut transversely which exposes a greater area of organic matrix.

In the present study of freshwater and terrestrial species four distinct forms of second-order lamellae were observed; these are described as block, irregular block, sheet and pointed sheet.

The block type is defined as having a width to length ratio of 3 to 1 or less.

The irregular block type is similar to the block type but the unit are non-rectangular (e.g. trapezoid or paralleloid).

The sheet type is defined as having a width to length ratio of 3 to 1 or greater.

The pointed sheet type is similar to the sheet type but the units have pointed ends.

The second-order lamellae are constructed of fine laths or rods some 0.1-2.0 microns wide, 0.1-1.0 microns thick and up to 8 microns long. The rods are rather irregular in section, though usually rounded or rectangular; they can have a sharp appearance and these are termed "needle-like". They are parallel sided and joined together in side-to-side contact. Each lath seems to be surrounded by a thin envelope of organic matrix, though less prominent than that between second-order lamellae.

Two distinct types of crossed-lamellar structure were recognised by both MacClintock (1967) and Philippon (1974). MacClintock describes these as concentric and radial, which are equivalent to Philippon's type B and type C respectively. As the names imply, the structures have different arrangements relative to the shell margins. In vertical section the radial structure has the first-order lamellae radiating from a theoretical point, the section cutting nearly parallel to the first-order boundaries. The concentric structure has the first-order lamellae parallel to the outer shell surface; they are cut normally to the boundaries between adjacent first-order lamellae.

4.36 Complex-Crossed-Lamellar

This structure is not recorded from freshwater or terrestrial species found in Britain and therefore is dealt with only briefly. It is found in *Corbicula fluminea* (Taylor *et al.* 1973) a species closely related to the British Quaternary fossil *Corbicula fluminalis*.

Mackie (1978) describes all Sphaeriacea as having a layer, often the only layer, of complex-crossed-lamellar structure. However, it seems likely that he confused this structure with the crossed-lamellar structure (see chapter 4.41).

The structure is built up of the same structural units as the crossed-lamellar structure but with four orientations of crystallites instead of two. This results from the intergrowth of two crossed-lamellar structures in alignments at right-angles to each other (Taylor 1973).

The third-order lamellae are joined in side-to-side contact to form second-order lamellae. However, these do not build up to become first-order lamellae but form large blocks that are much less regular and more variable in form. This gives the shell layers the appearance of being formed from a few large blocks of interpenetrant second-order lamellae. This arrangement gives transverse and radial sections that are very similar whilst the surface shows the laths dipping into the shell surface. Each third-order lamella is surrounded by a thin organic membrane, but no organic matrix is found between the second or first-order lamellae.

The exact form and arrangement of the blocks of second-order lamellae varies widely with species; the major forms are discussed by Taylor et al. (1969).

4.37 Homogeneous Structure

This structure is restricted to aragonitic species. It is very finely crystalline, a term usually taken to mean composed of laths less than 5 microns in width (Carter 1980b). In conventional light microscopy this form appears structureless and therefore difficult to decipher in peels or sections. In the electron microscope minute carbonate granules with similar crystallographic orientation can be observed. They appear as elongate, lenticular, or irregular blocks of carbonate. The granules seen by Taylor et al. (1969) measured approximately 1 x 3 x 0.5 microns and were enclosed in organic envelopes.

In shell sections containing this structure banding of greys and browns can often be seen inside the pallial line. These bands are composed of finer "sheets" parallel to the shell interior which may reflect repeated, perhaps diurnal, deposition of carbonate.

Examination of the interior surface shows a complicated pattern which lacks the regularity seen in many other types of shell structures. The granules vary in size and have highly irregular contacts with their neighbours; their surfaces are generally rounded, though less so outside the pallial line.

4.38 Myostracal Layers

Myostracum is the general term for the shell substance laid down below the areas of muscle attachment. It is partly equivalent to the "helle Schicht" of Schmidt (1923; 1924), and the hypostracum and "pellucid layer" of S.Kobayashi (1964) and other authors. The two most important forms of myostracal layer found in bivalves are the pallial myostracum and the adductor myostracum. The shell below the muscle attachments in gastropods appears affected less than in bivalves (see below).

Taylor *et al.* (1969) describe two forms of bivalve myostracum, extremes of a range for which all intermediates exist. At one extreme the myostracum is represented by a thick sheet which is invariably aragonitic, and composed of a characteristic prismatic structure. The other extreme is where the myostracum is so thin as to appear only as a line or dislocation in the shell structure.

The thicker myostracal layers have a distinct appearance when seen in thin section or as peels. They are colourless or light grey in contrast to the translucent or opaque aspect of the surrounding shell layers. The prisms that compose the layer are distinct in form from those of the prismatic structure. They are very varied in size and shape, not only between species but also within a single myostracal layer. As with the prismatic structure the prisms are orientated normal to the shell surface but they lack a regular outline and a thick conchiolin wall.

In general the pallial myostracum lies between different structural layers, and in cases where a structural change occurs but no myostracum is apparent a thin layer of prisms may be seen if viewed at high magnification. In the nomenclature of MacClintock (1967) the structures above and below the myostracal layer are given positive and negative prefixes respectively. Nevertheless the structures can remain unchanged across myostracal layers. For instance where the structures are crossed-lamellar there is often a correspondence of first-order lamellae on either side of the pallial myostracum.

The surface of the adductor myostracum varies between species but is always composed of irregular polygonal "cells" which correspond to the surface outcrops of individual prisms building up the myostracum. There is evidence also of an organic matrix between the prisms though it can become discontinuous in places and larger "cells" may form.

The pallial myostracum also shows evidence of an inter-prismatic organic matrix both in section and on the surface. Organic material may also be present within the "cells" (Taylor _et al._ 1969).

Myostracal prisms can occur as columns or "pillars" within another shell layer, the "pillar" bases being in the pallial myostracum. The "pillars" are visible in thin section and peels as distinct units with an elongated oval cross-section. They are very prominent in Chamidae and Carditidae, but are not recorded in freshwater species. The prisms are also found as thin sheets alternating with layers of nacre (as in some mytilids) or crossed lamellar structures.

A different myostracal structure was observed by Petit _et al._ (1980) in the freshwater mussel _Amblema_. The interior adductor muscle scar was deeply embedded in the nacreous material. Anterior to this slope was a series of ridges and grooves forming the muscle insertion system. Within the grooves were identified large cylindrical pores, 50-100 microns in diameter. The surface of the pores was bordered by nacreous tablets which were fused in places. Inside, the pores were walled by inward facing pyramidal nacreous tablets. The other muscle scars show similar pyramidal nacreous tablets but in the case of the posterior adductor and retractor scars the ridges, grooves and pores were missing leaving a flat area of pyramidal nacre. The pallial line was in the form of a groove bordered by fusing nacreous tablets, but no pyramidal nacre was observed.

Tompa and Watabe (1976) discuss the mechanism of muscle attachment in terrestrial and freshwater gastropods. They observed an extensive network of extracellular organic fibres linking the shell to the muscle but do not record any structural changes in the shell.

4.4 THE STRUCTURE OF BRITISH FRESHWATER AND TERRESTRIAL MOLLUSC SHELLS.

This section gives the results of the examination of species of non-marine mollusc found in Britain. The results in section 4.41 are largely based on Mackie (1978), and Taylor et al. (1969; 1973). All the results in sections 4.42 and 4.43 are based on Scanning Electron Microscopy and thin sections prepared by the acetate film method for this study. Experimental details of these methods are given in chapter 7.3 and 7.4. The shell sections were parallel to the columella, through the spire and aperture, unless otherwise stated. If it was not possible to examine an entire section, observations were made at as many points as possible.

The tables of results for this section show the main features that were observed for each species. In the last four columns the abbreviations n.o. and n.d. are used: n.o. stands for not observed, and n.d. for not determined. The former indicates that the SEM photographs and thin sections were detailed enough to have allowed these features to be seen but none was observed. "Not determined" indicates that the photographs and images did not allow these details to be observed.

4.41 The Structure of Freshwater Bivalves

The structures of freshwater bivalves have in the past received much attention. Many of the species found in Britain have been previously studied by other reseachers (Taylor et al. 1969; 1973; Mackie 1978) and it is their results that form the basis of this section.

Subclass HETERODONTA, Order CYRENODONTA, Suborder SPHAERIACEA

Families: CORBICULIDAE, SPHAERIIDAE, PISIDIIDAE

Taylor *et al.* (1973) found two layers to be present in all species of these families. The outer is a crossed-lamellar structure that also forms the hinge and teeth. The inner is bounded by the pallial line and is a complex crossed-lamellar structure. In most forms no pallial myostracum is recorded.

Mackie (1978) records three different structural arrangements, none of which are identical to that described by Taylor *et al.* (1973). Mackie found complex crossed-lamellar structures in all shells, and a prismatic pallial myostracum underlying this in many cases. Mackie's third stuctural arrangement is two layers of complex crossed-lamellar structure separated by a prismatic pallial myostracum. Mackie (1978) also claimed that different structural arrangements could be observed within a single species.

The different results obtained by Mackie and Taylor *et al.* may be due to the observation of different species; only one species, *Corbicula fluminea*, was examined by both groups. This species is closely related to *C.fluminalis*; a species found in British Quaternary deposits. Taylor *et al.* (1973) describe *C.fluminea* as containing a finely crossed-lamellar outer layer, a complex crossed-lamellar inner layer, and an indistinct pallial myostracum. The complex crossed-lamellar layer shows laths arranged in very regular columns.

Mackie (1978, figure 1a) shows *C.fluminea* to be entirely of a complex crossed-lamellar structure.

These two interpretations can both be accepted if the outer crossed-lamellar structure is thin and was not observed by Mackie (1978). More difficult to accept is the presence of an entire layer of prismatic pallial myostracum. This implies that no shell material is laid down inside the extra-pallial cavity after the mantle has moved with the growth margin of the shell.

The confusion over whether crossed-lamellar or complex crossed-lamellar structures are present can only be resolved by further work. The description of complex crossed-lamellar in Mackie (1978) as a structure where "crystals in adjoining cross-lamellae are inclined in opposite directions" is more applicable to crossed-lamellar than complex crossed-lamellar. It is possible that Mackie misinterpreted the structure that he observed or misnamed it.

Mackie's (1978) record of the presence of intra-species variation is also difficult to understand; it may reflect the sampling position within the shell. Samples taken inside the pallial line will give two layers whilst those outside will give only one.

Table 4.2 gives details of the layers found in the studied species. Those marked with an asterix are based on Mackie (1978) and therefore may not be reliable.

Suborder DREISSENACEA Family: DREISSENIDAE

Only a single living species of this suborder is known from Britain: Dreissena polymorpha. The shell is formed from two aragonitic layers: an outer crossed-lamellar layer, which also forms most of the hinge; and an inner complex crossed-lamellar layer. The layers are separated by a thin pallial myostracum. (See table 4.2)

Subclass PALEOHETERODONTA, Order UNIONOIDA, Suborder UNIONACEA Families:MARGARITIFERIDAE, UNIONIDAE

Nacreous and prismatic structures form the layers that are present in Unionids. The prismatic structure is a complex prismatic form and is the outer layer of the shell. It is present is most Unionids, the recorded exceptions being the genus Etheria. The prismatic layer may also be absent in the umbonal region of other species due to abrasion and dissolution.

The nacreous structure is present in both the lenticular and sheet form. Sheet nacre is present as the inner layer of all Unionid species (figure 4.5), whilst lenticular nacre forms the middle layer of most species.

A very thin prismatic pallial myostracum is found in most species. The adductor muscle scars are also formed of thin prismatic myostracal layers.

Table 4.2 gives details of the layers found in studied British species.

4.42 The Structure of Freshwater Gastropods

The crystal structures of freshwater gastropods appear to be an area of study that has been dismissed because of its apparent simplicity. Only the crossed-lamellar structure is found; and the absence of variation allows no possibility for evolutionary studies. However,

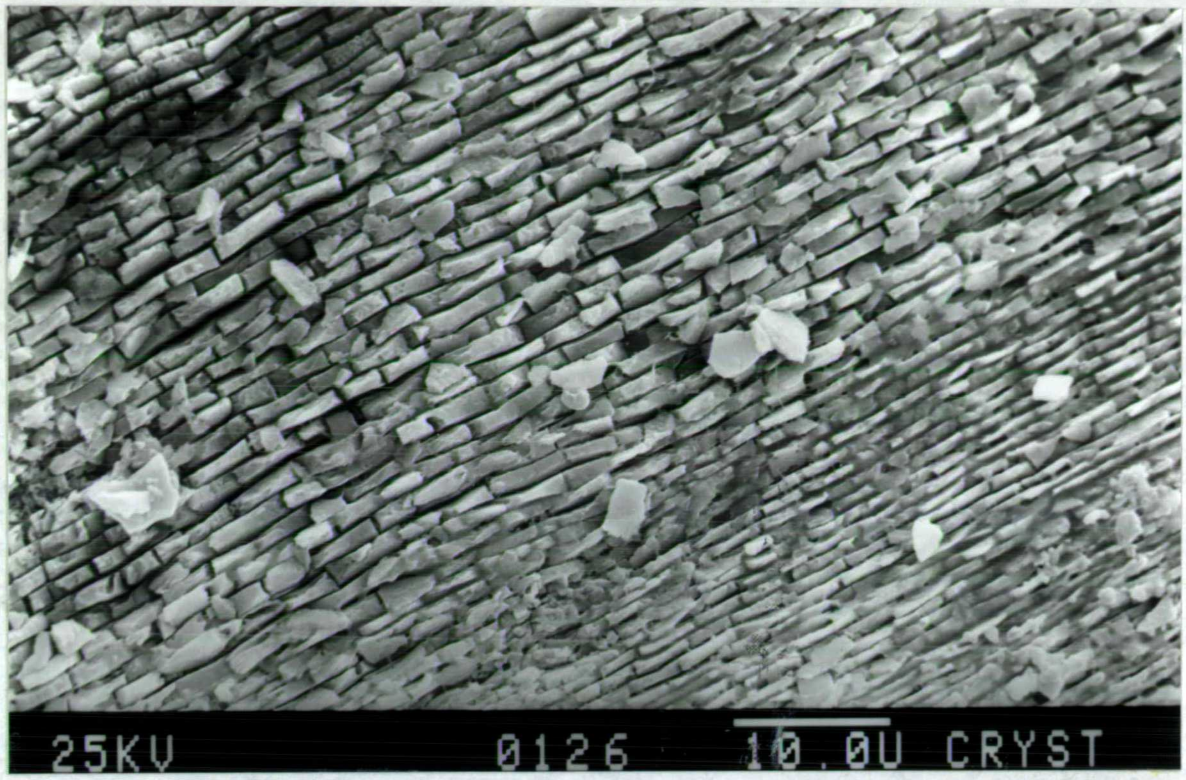


Figure 4.5A. Nacreous structure in a shell of *Unio* sp.

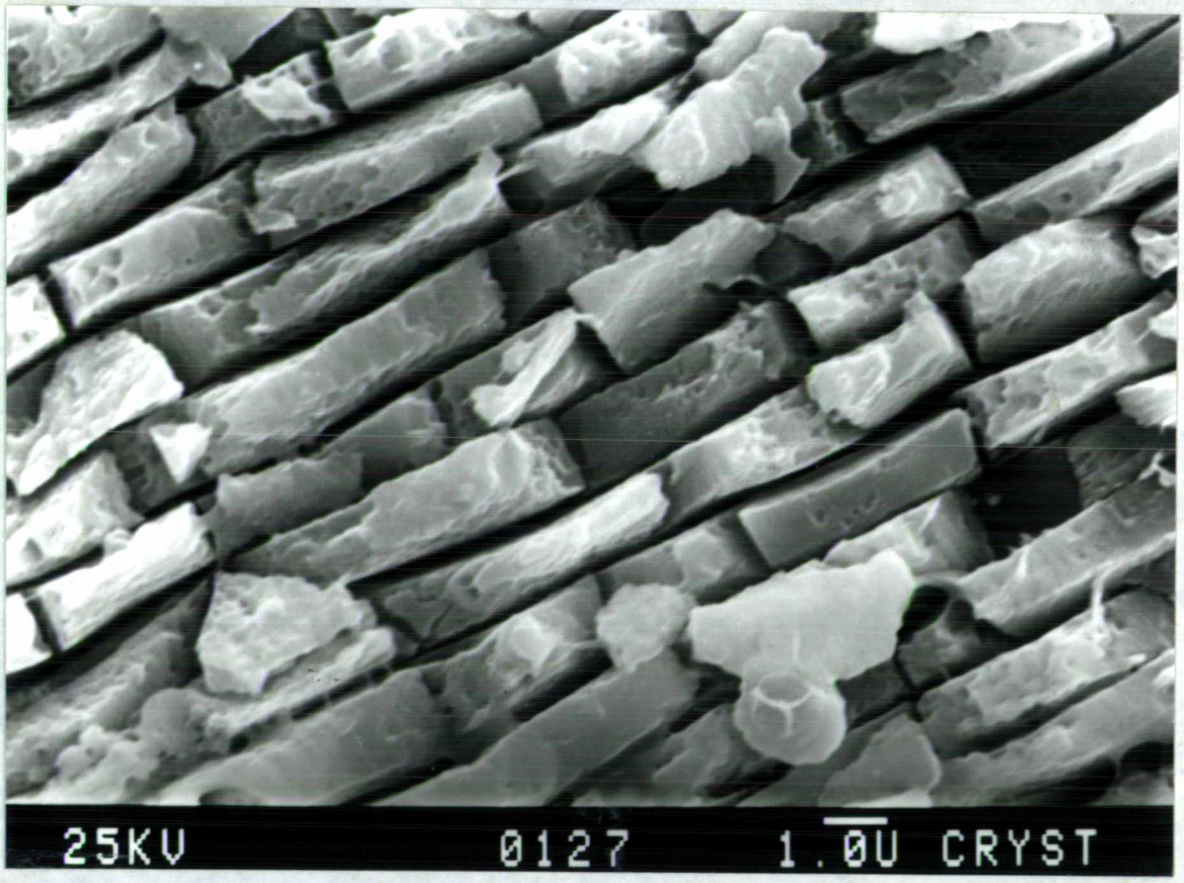


Figure 4.5B. Detail of figure 4.5A.

for the purposes of this study it is essential that the exact nature and form of unaltered structures be known and therefore seven of the common larger species of British freshwater gastropods have been examined using electron and optical microscopy, and X-ray diffraction analysis.

Table 4.3 gives details of the structures observed in the studied species.

Subclass PROSOBRANCHIA, Order ARCHEOGASTROPODA

Family NERITIDAE

The only species of this family found in Britain, Theodoxus fluviatilis, was examined. The shell consists of a single layer of aragonitic crossed-lamelllar structure, within which were observed a number of variations. The variations are not considered to be different layers, merely variations in growth. This conclusion is based on the fact that the orientations of the first-order lamellae do not change across the variation boundaries; three types of structural variation are discussed below.

The first-order lamellae are 5-15 microns wide and composed of "needle-like" third-order lamellae c. 0.8 microns wide. Second-order lamellae are not clearly visible.

The three vartiatons on this structure are probably due to interuptions in the growth of the shell. Figure 4.6 shows the first-order lamellae to be offset across a break, this is suggestive of a natural break in growth, possibly due to a dormant season.

The second type of variation is, also seen in figure 4.6, an apparent

SPECIES	LOCALITY	MINERALOGY	NO. OF LAYERS	2nd ORDER LAMEL.	3rd ORDER LAMEL.	GROWTH BANDS
Theodoxus fluviatilis	Sussex, England	Aragonite	1	n.o.	Needle like	Prismatic bands Structural thickening
Theodoxus fluviatilis	Greece	"	1	n.d.	"	n.o.
Viviparus contectus	Norfolk,England	"	2	Block like	Fine	Structural thickening
Viviparus viviparus	Devon, England	"	2	"	"	"
Lymnaea peregra	Norfolk,England	"	2	Sheet like	n.d.	n.d.
Lymnaea auricularia	Leics.,England	"	2	Pointed sheets	n.d.	n.o.
Lymnaea stagnalis	Herts.,England	"	2	n.d.	n.d.	n.d.
Lymnaea palustris	Sussex, England	"	2	Block like	Needle like?	n.o.
Planorbarius	Suffolk,England	"	2	"	n.d.	n.d.

Table 4.3. Structure of freshwater gastropods. All data from the present study.

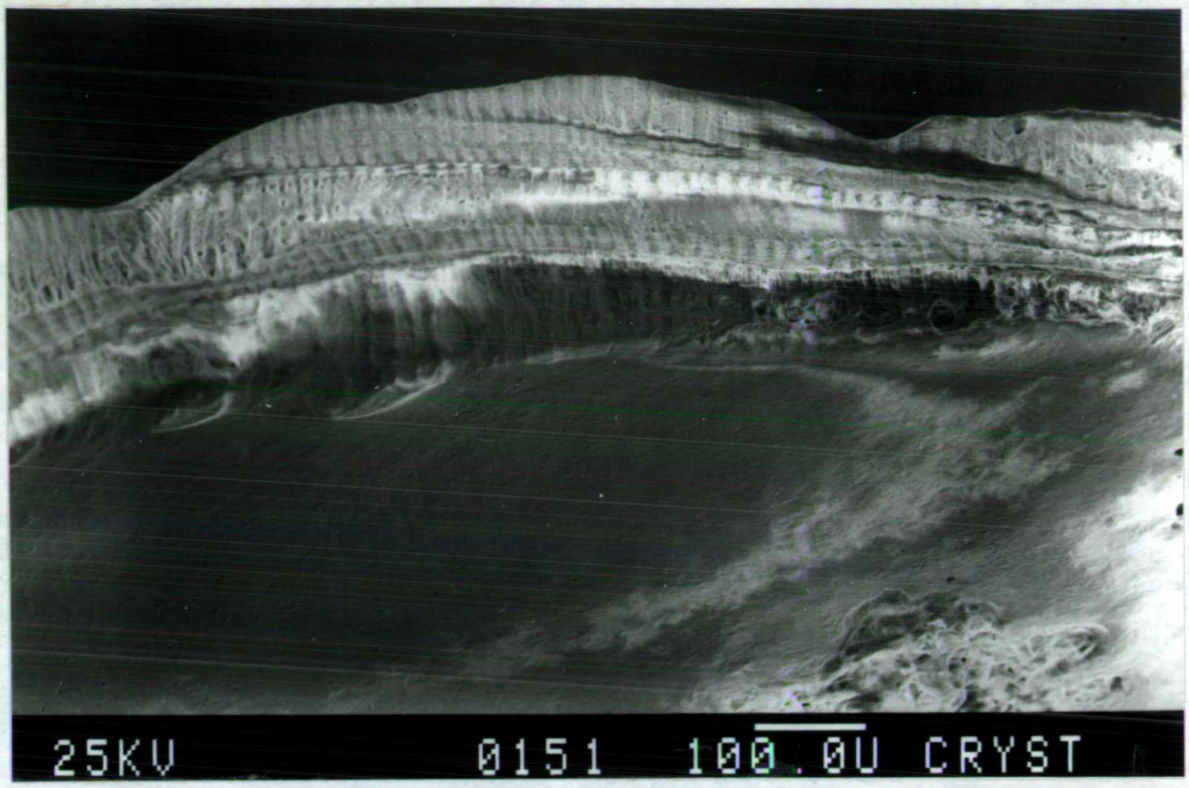


Figure 4.6. Breaks in the growth of a shell of Theodoxus fluviatilis. Both offsetting of first-order lamellae and structural thickening is present.

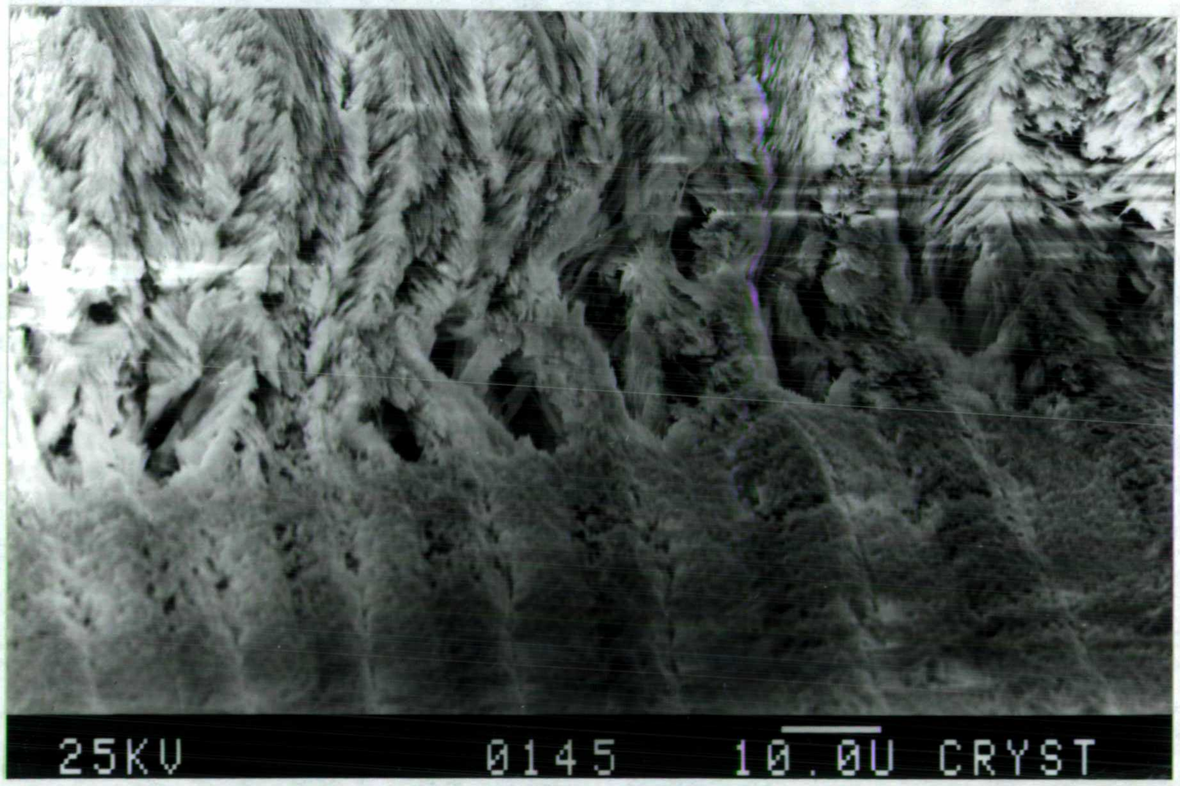


Figure 4.7. Pitting and fine crystals in a shell of Theodoxus fluviatilis. These features are probably caused by damage and shell regeneration.

thickening of the structure, detailed observation shows it to be an area where the third-order lamellae are much finer (0.3 microns wide) whilst the first-order lamellae remain the same width. Immediately above this band are a series of "pits" surrrounded by even finer "needle-like" crystals (0.1 microns); these fine "needle-like" crystals are also visible between the first-order lamellae (figure 4.7). These variations and "pits" are interpreted as the point where damage occurred to the shell and rapid shell growth was necessary to repair it. The fine crystals around the pits are the initial growth, the band below the later covering of the damaged area.

The possibility of regeneration in shell material must be taken into account when interpreting SEM photographs and acetate peels since the new shell material can be calcitic (Saleuddin 1971). If XRD were used alone as a criterion for selection the presence of calcite would be interpreted as due to diagenetic recrystallisation. In fact the shell is unaltered from its state at the time of death.

The third type of variation is a narrow band of crystals similar in appearance to the myostracal prisms observed in bivalves. However, the physiology of gastropods is such that the prisms cannot be due to muscle attachment. Therefore, they are interpreted as short interruptions in the growth of the shell. The bands are 2-5 microns thick. Also visible in figure 4.8 are areas of thickening in the structure which are again interpreted as variations in the growth rate.

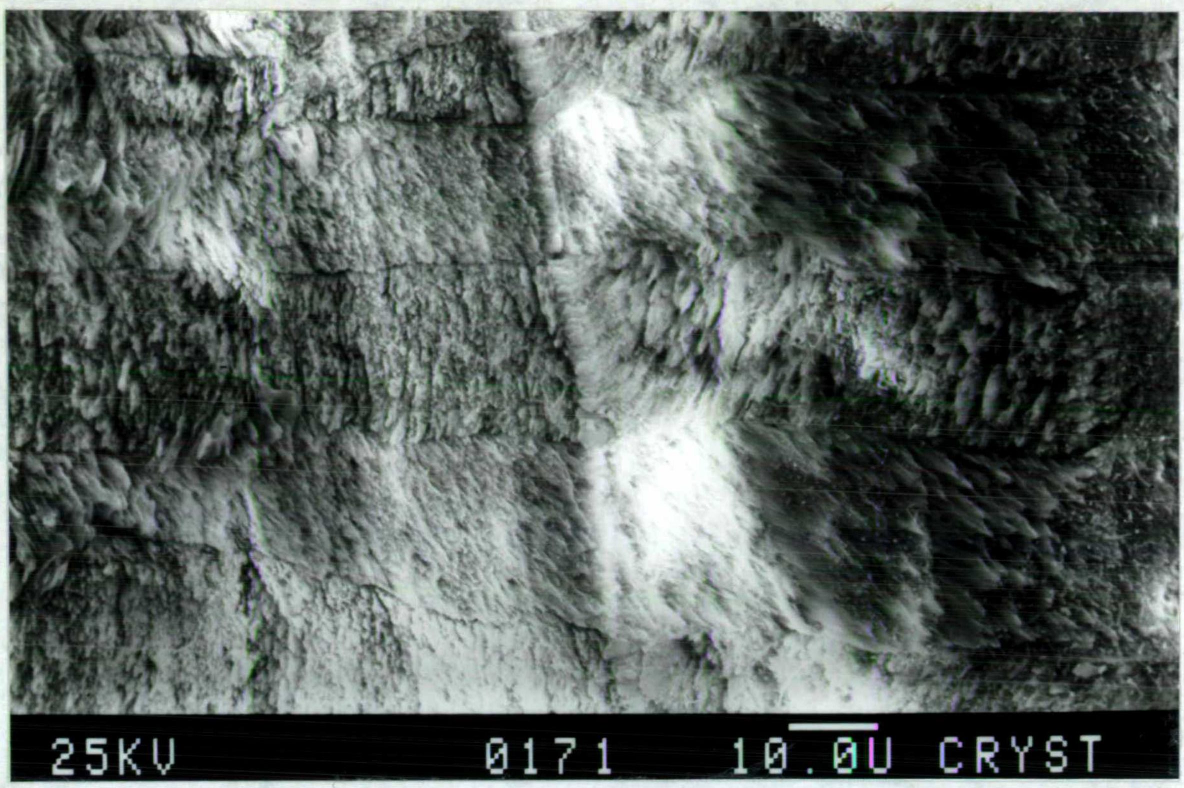


Figure 4.8. Pseudo-prismatic crystals in a shell of <u>Theodoxus fluviatilis</u>, probably caused by interruptions in growth.

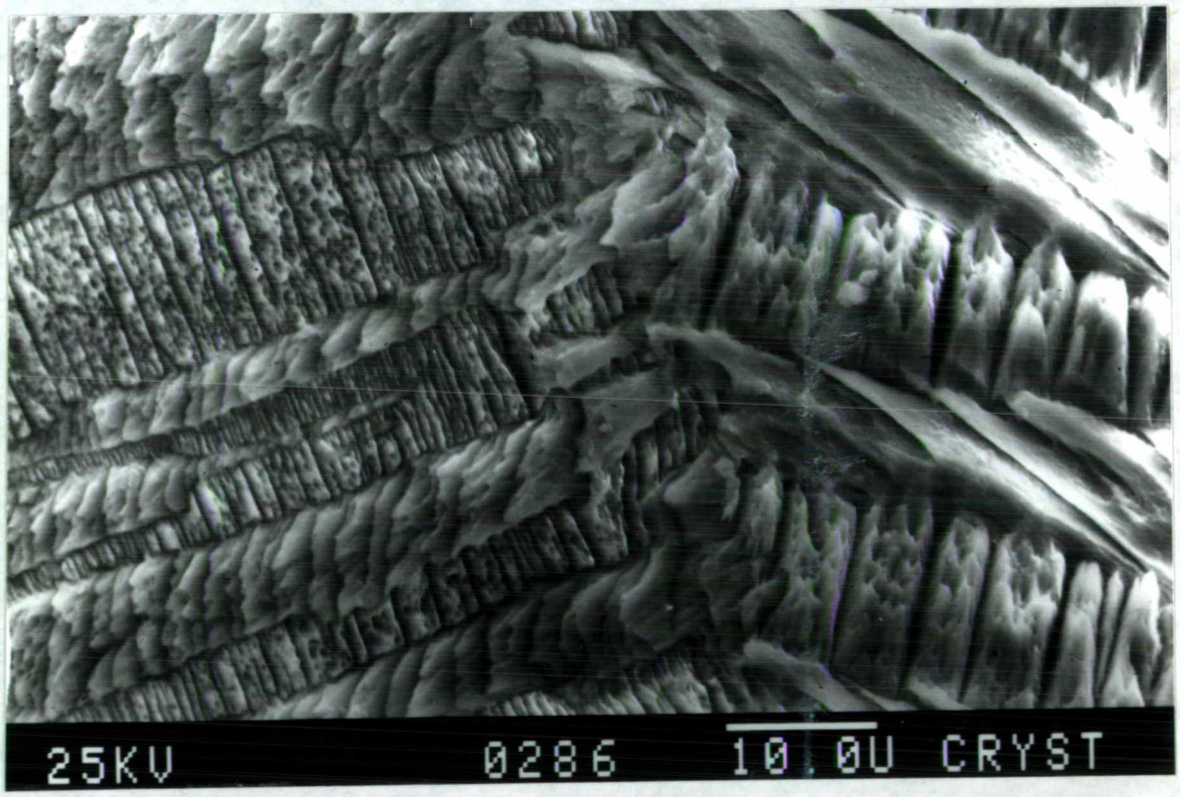


Figure 4.9 Crossed-lamallar structure in <u>Viviparus</u> <u>viviparus</u>.

Order MESOGASTROPODA

Family VIVIPARIDAE

Two species of this family are found in Britain, Viviparus contectus (fasciatus) and Viviparus viviparus; both were examined. The shells are composed of two layers of aragonitic crossed-lamellar structure. In the observed sections the outer layer was thinner than the inner (10-30% of the total thickness). The first-order lamellae are 5-12 microns wide; second-order lamellae, 2-4 microns thick in V.viviparus and 1-2 microns in V.contectus, can clearly be seen (figure 4.9). The second-order lamellae are composed of fine third-order lamellae.

The SEM examination of V.contectus showed only one layer; two were observed in the acetate peels, though the outer was very thin.

Growth bands were observed in V.viviparus as thickenings in the crossed-lamellar structure.

Sub-class PULMONATA, Order BASOMMATOPHORA

Family LYMNAEIDAE

Seven species of this family are found in Britain, six in the genus Lymnaea, four of which were examined; and one in the genus Myxas, which was not examined. All the species examined were composed of two layers of crossed-lamellar structure, the outer represents 5-40% of the total thickness.

In L.peregra the first-order lamellae are 3-4 microns wide and are composed of extremely fine second-order lamellae (0.05-0.1 microns thick). These features are shown clearly in figure 4.10. The first-order lamellae in the other species vary in size being 1 micron wide in L.auricularia and up to 10 micron in L.palustris.

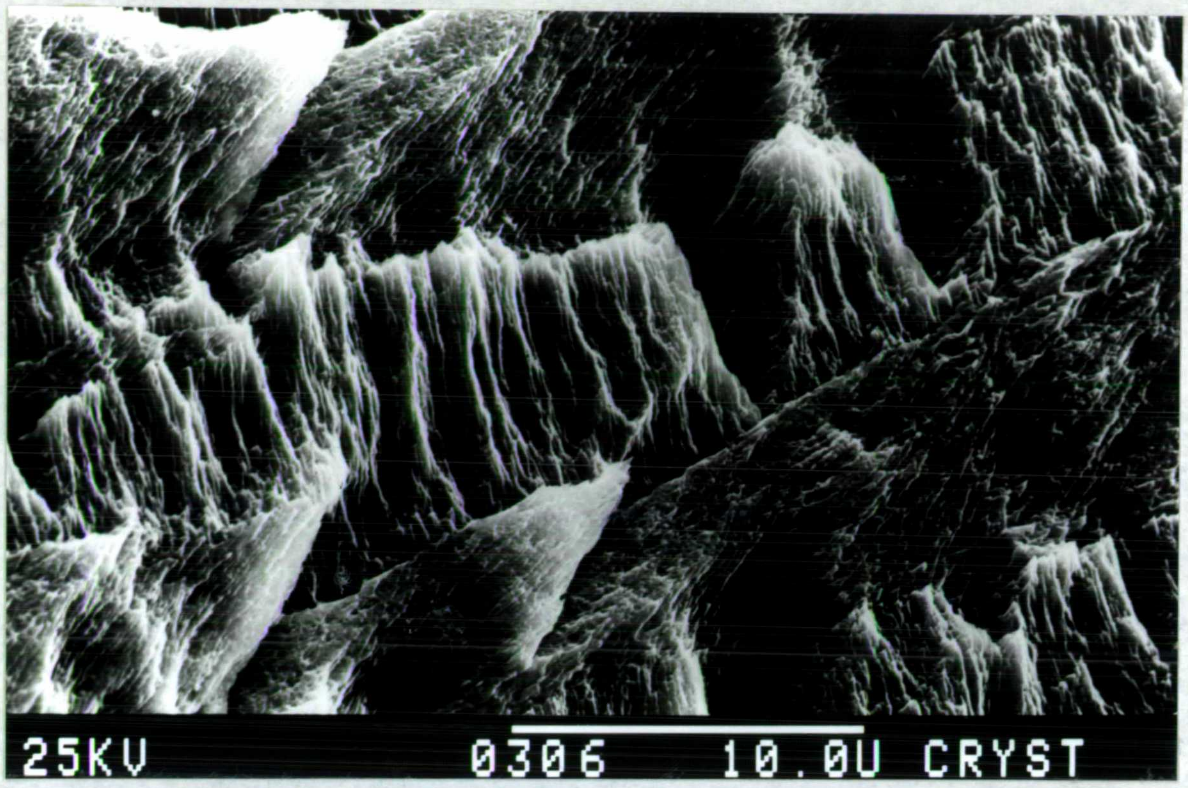


Figure 4.10. Crossed-lamellar structure of *Lymnaea peregra*. Note the fine second order lamellae.

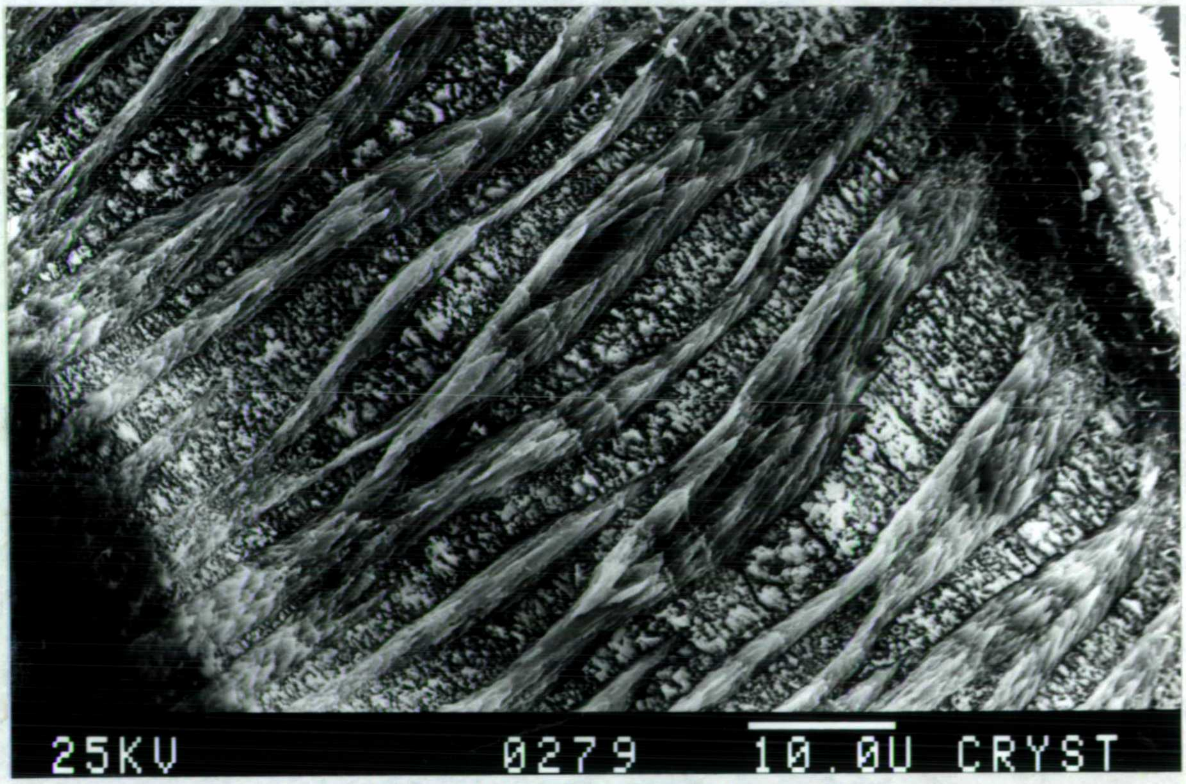


Figure 4.11. Crossed-lamellar structure of *Pomatias elegans*, only a single layer is present.

Order BASOMMATOPHORA

Family PLANORBIDAE

Only one member of this family was examined, Planorbarius corneus. The shell is composed of two layers of aragonitic crossed-lamellar structure. The outer layer is the thinner and forms 25-35% of the total shell thickness. The first-order lamellae are approximately 2 microns wide and composed of second-order lamellae 0.5-1.0 microns thick.

4.43 The Structure of Terrestrial Gastropods

The intensity of study of terrestrial gastropod shells is intermediate between that for freshwater bivalves and freshwater gastropods. One species, Helix pomatia, has received much attention (Saleuddin 1971, Pollard et al. 1977), but no record of the study of other species has been found.

As was the case for freshwater gastropods it is important for this study that the nature and form of unaltered specimens be known. Sixteen species were selected; they represent the larger species at present found in Britain; also included are one or two small species that are important in the fosil record (e.g. Discus ruderatus). Five of these species are considered aliens because they do not appear in the fossil record until after the land bridge to mainland Europe was flooded. However, they are included as they are frequently found in European Quaternary contexts, and also in deposits of the last 2000 years in Britain. All species were examined by SEM and X-ray diffraction; a number of the larger ones were also studied using acetate peels.

Table 4.4 gives details of the structures observed in the studied species.

Subclass PROSOBRANCHIA, Order MESOGASTROPODA

Family POMATIIDAE

Pomatias elegans is the only member of this family found in North-West Europe. The shell is a single layer of aragonitic crossed-lamellar structure (figure 4.11); the operculum is calcitic.

The first-order lamellae vary in width from 1.5 to 5.0 microns; this range can be partially explained by the tendency for the first-order lamellae to diverge toward the outer shell margin. The divergence can be interpreted as being similar to the geometric selection found in bivalves (chapter 4.34 (i)); it is more exaggerated in *P.elegans* than other gastropod species because of the tight coil formed by the shell.

Within the first-order lamellae both second-order lamellae (c.0.5 microns thick) and "rod-like" third-order lamellae are visible.

The outer whorls show evidence of growth bands (figure 4.12); these are a thickening of the lamellae and run diagonally across the section. They are similar to the bands found in *T.fluviatilis* and can also be compared to the "growth breaks" found in *Helix pomatia* (Pollard *et al.* 1977).

A different structure was observed in a fossil shell of *P.elegans* (figure 4.13). This consisted of sheets of crystal showing no evidence of second- or third-order lamellae. They are generally

SPECIES	LOCALITY	MINERALOGY	NO. OF LAYERS	2rd ORDER LAMEL.	3rd ORDER LAMEL.	GROWTH BANDS
Pomatias elegans	Sussex, England	Aragonite	1	Sheet like	Rod like	Structural thickening
Clausilia bidenta	Hants., England	"	2	"	n.d.	n.d.
Discus rotundatus	Surrey, England	"	1	"	"	Structural thickening
Discus ruderatus	England	"	1	n.d.	"	"
Retinella nitidula	Devon, England	"	2	Sheet like	Rod like	n.o.
Arianta arbustorum	England	"	4	"	n.d.	n.o.
Helix pomatia	Surrey, England	"	4	Irregular blocks	Rod like	n.o.
Helix aspersa	Leics.,England	"	4	n.o.	Needle like	n.o.
Cepaea nemoralis	Surrey, England	"	4	Sheet like	"	Structural thickening
Cepaea hort nsis	Surrey, England	"	4	"	Rod like	n.o.
Monacha cantiana	Kent, England	"	2	n.o.	Needle like	Structural thickening
helicella itala	Kent, England	"	2	Block like	Rod like	n.o.

Table 4.4. Structure of terrestrial gastopods. All data from the present study.

SPECIES	LOCALITY	MINERALOGY	NO. OF LAYERS	2nd ORDER LAMEL.	3rd ORDER LAMEL.	GROWTH BANDS
Cernuella virgata	Wilts.,England	Aragonite	2	n.o.	Needle like?	Structural thickening
Candidula gigaxii	Wilts.,England	"	2	Pointed sheets	n.o.	n.o.
Candidula intersecta	England	"	2	n.o.	Needle like	n.o.

Table 4.4. Structure of terrestrial gastropods. All data from the present study.

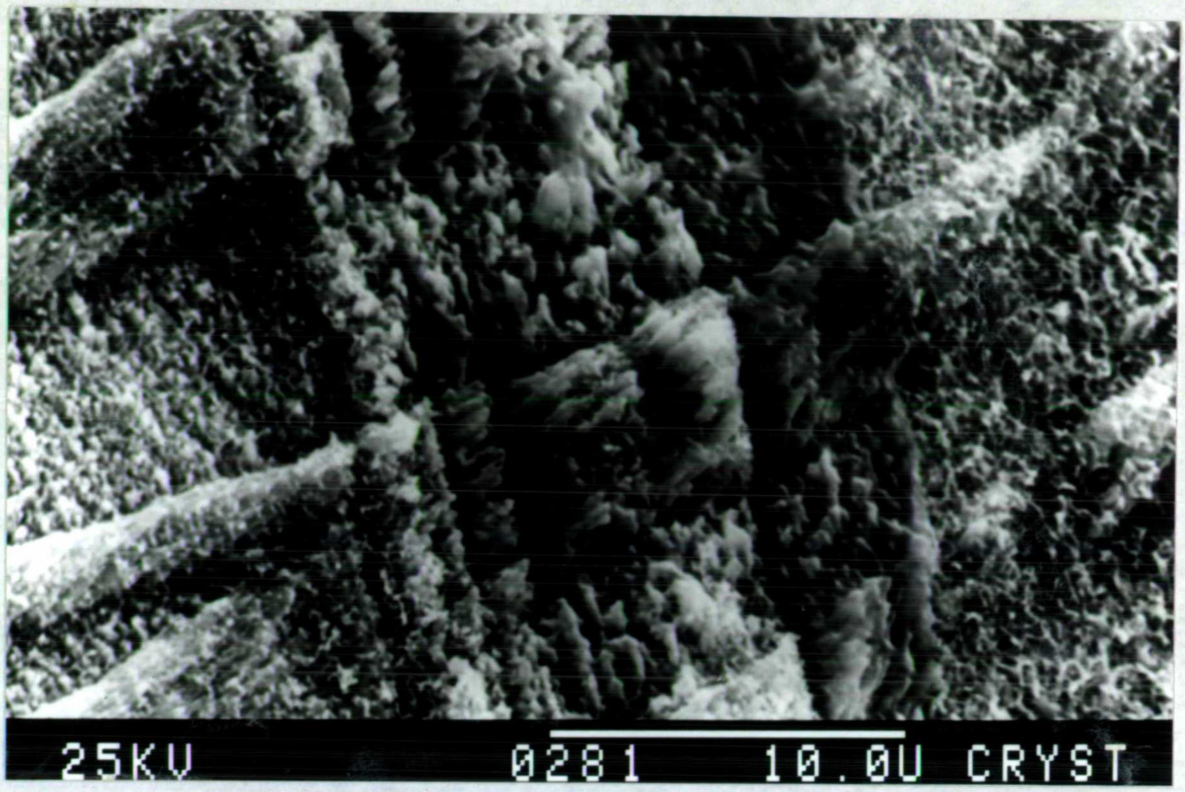


Figure 4.12. Growth bands in the form of structural thickening. (Pomatias elegans).

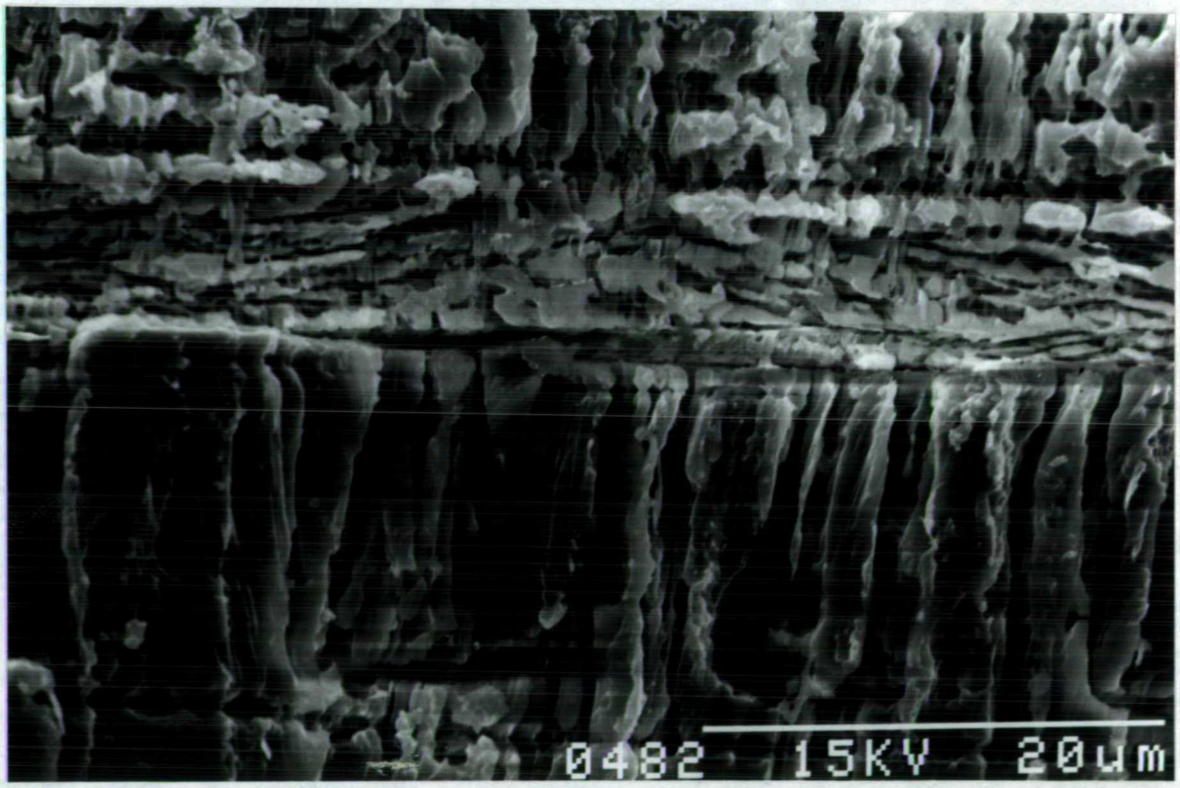


Figure 4.13. Unusual structure observed in a fossil shell of Pomatias elegans.

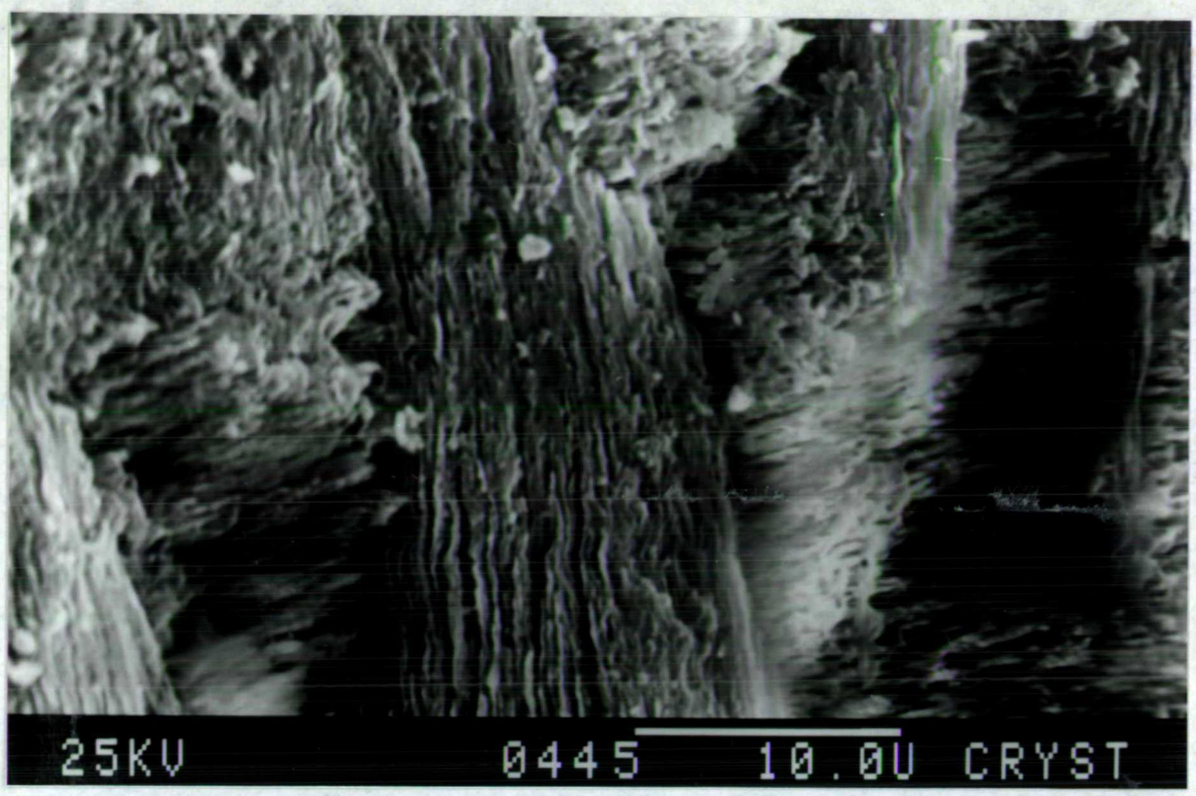


Figure 4.14. Detail of the unusual structure observed in Pomatias elegans.

radial to the shell margin but are interrupted by horizontal bands that more closely resemble a crossed-lamellar structure. In appearance the radial crystals resemble a prismatic structure but their thin sheet-like appearance is inconsistent with this. The possibility that the structure is diagenetic is discounted as it does not resemble other diagenetic forms encountered. The crystals in figure 4.14 could be interpreted as lamellae, but they are not the usual form. On the basis of these observations this structure is interpreted as a form of crossed-lamellar structure that grew unusually due to external conditions.

Subclass PULMONATA, Order STYLOMMATOPHORA

Family CLAUSILIIDAE

One species, *Clausilia bidenta*, of this family was examined. The shell is composed of two equally thick layers of aragonitic crossed-lamellar structure. The first-order lamellae are 1-2 microns wide and are composed of fine "sheet" like second-order lamellae which are 0.05-0.1 microns thick.

The inner layer appears to have a number of variations in the orientation of the first-order lamellae which can lead to confusion as to the true number of layers.

Order STYLOMMATOPHORA

Family ENDODONTIDAE

Two species of this family are commonly found living in Britain, *Punctum pygmaeum* and *Discus rotundatus*. Also relevant to fossil assemblages is *Discus ruderatus* which is now extinct in Britain. The two species of *Discus* were examined for this study.

The shell of *D.rotundatus* is composed of a single layer of aragonitic crossed-lamellar structure. The first-order lamellae are 2-8 microns wide and are composed of sheets of second-order lamellae. Growth bands are visible running diagonally across the structure in the form of structural thickening.

Discus ruderatus also has a single layer of crossed-lamellar structure. The second-order lamellae were difficult to observe because of the angle at which they were sectioned. Structural growth bands were again visible.

Order STYLOMMATOPHORA

Family ZONITIDAE

One member of this family was examined, *Aegopinella nitidula*. The shell is composed of two layers of aragonitic crossed-lamellar structure; the layers are approximately equal in thickness. The first-order lamellae are 3-4 microns wide and are composed of "sheets" of second-order lamellae (c.0.1 microns thick) (figure 4.15. The third-order lamellae are not clearly visible but appear to be "rod-like" in the inner layer (figure 4.15).

Order STYLOMMATOPHORA

Family HELICIDAE, Sub-family ARIANTINAE

Two members of this sub-family are found in Britain, and of these *Arianta arbustorum* was examined. The shell is formed of four layers of aragonitic crossed-lamellar structure which are clearly seen in figure 4.16. Sheets of second-order lamellae are clearly visible, but third-order lamellae were not observed. The outer layer is less clearly identifiable as crossed-lamellar structure, a problem

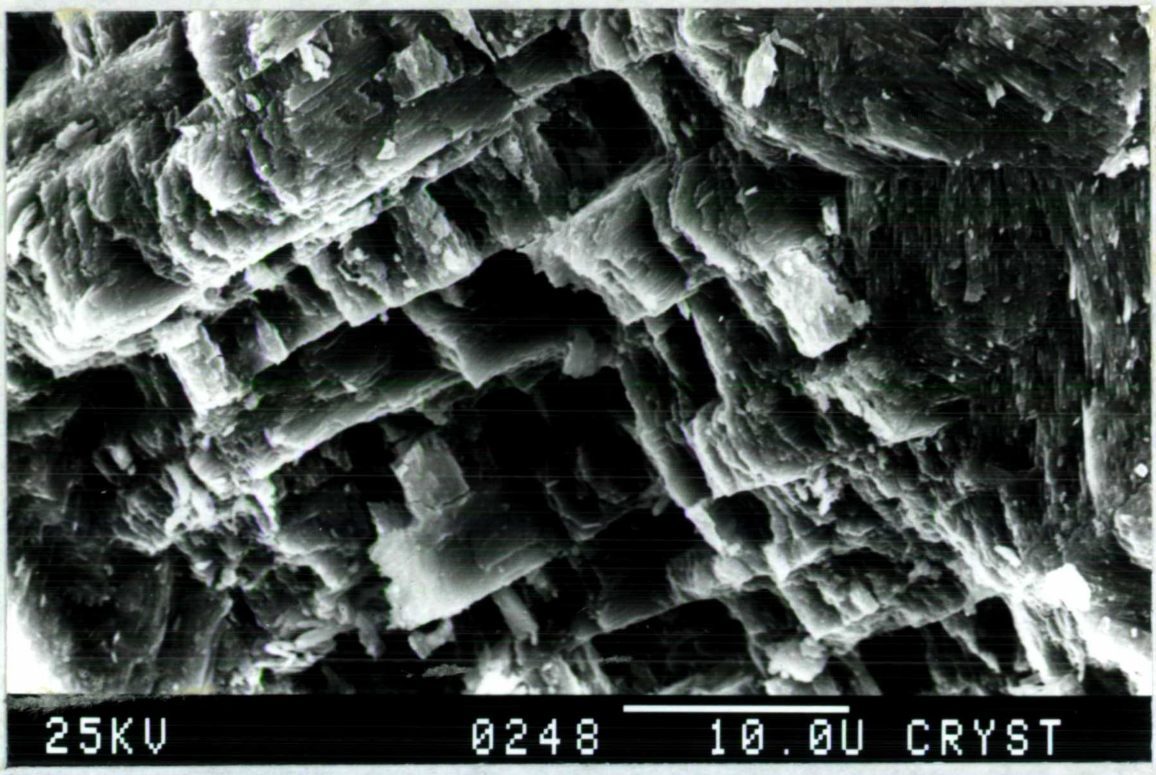


Figure 4.15. Crossed-lamellar structure of Aegopinella nitidula.

Figure 4.16. Four layers of crossed-lamellar structure in a shell of Arianta arbustorum.

encountered by Pollard *et al.* (1977) when studying *Helix pomatia*.

Family HELICIDAE, Sub-family HELICINAE

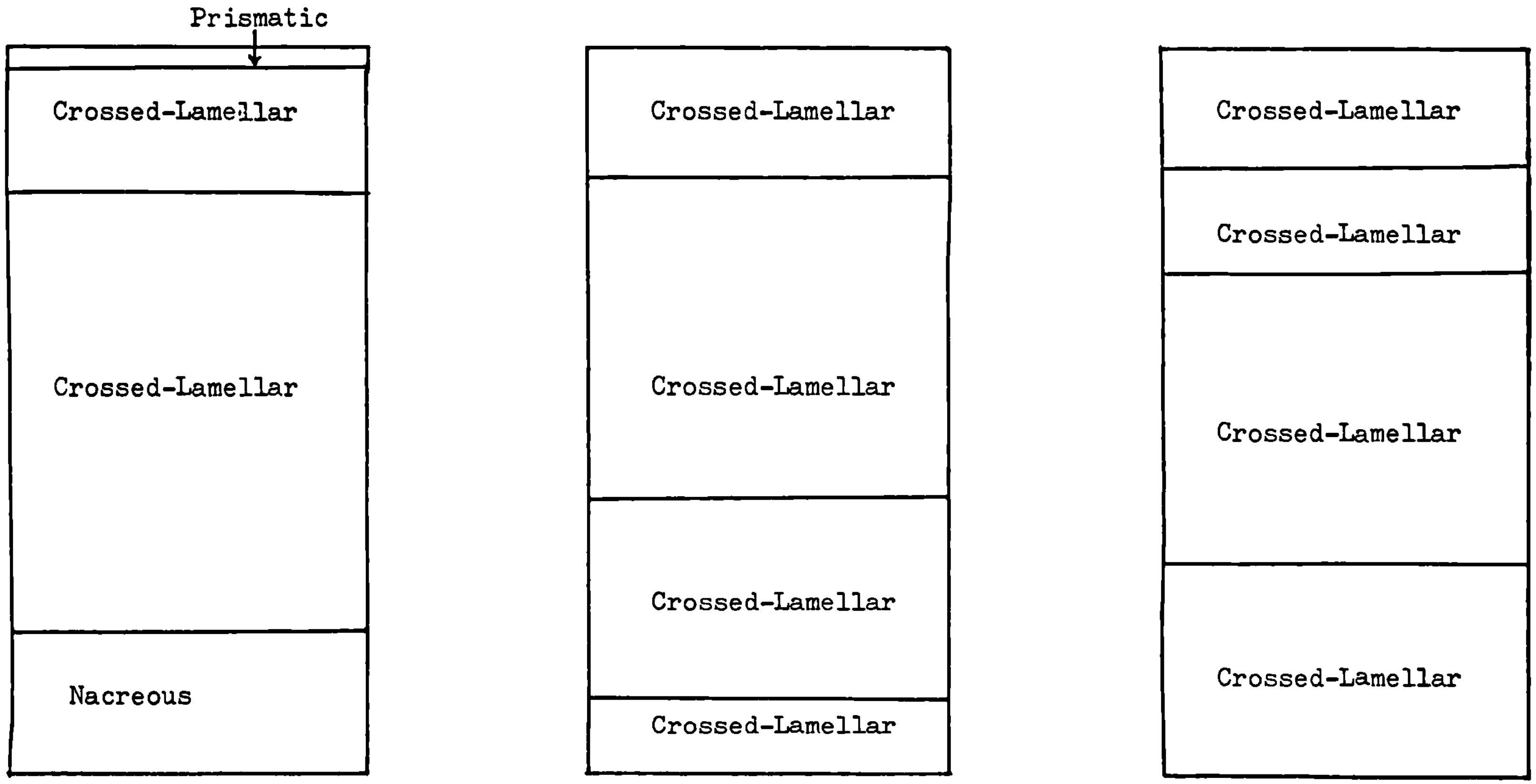
Five members of this sub-family are found in Britain and four of these were examined (*Helix pomatia*, *Helix aspersa*, *Cepaea nemoralis*, *Cepaea hortensis*). All have four layers of aragonitic crossed-lamellar structure.

H.pomatia has previously been studied by Saleuddin (1971) and Pollard *et al.* (1977). Both studies identified four layers, but did not described them, nor did they name them in the same manner. Saleuddin (1971) took a vertical section of normal shell parallel to the growing edge (therefore nearly parallel to the columella). Figure 4.17 illustrates his results.

Pollard *et al.*(1977) examined a square section taken from the last whorl. The results showed two clear crossed-lamellar layers and two probable layers of crossed-lamellar structure on the inner and outer surfaces. The probable layers were described as more complex in appearance and orientation, in the case of the outer layer this may be due to its being the place where shell growth initiates.

Examination of the shells of *H.pomatia* for this study clearly showed four layers of aragonitic crossed-lamellar. These layers were seen on acetate peels (figure 4.18) and using a SEM (figure 4.19).

The first-order lamellae are 2-8 microns wide, and are generally thinner in the outer layer. Second-order lamellae are clearly visible (e.g. figure 4.19); and "rod-like" third-order lamellae are visible



(Saleuddin 1971)

(Pollard *et al.* 1977)

(Present Study, see also figure 4.9)

Figure 4.17. Comparison of the structures observed in shells of *Helix pomatia*.

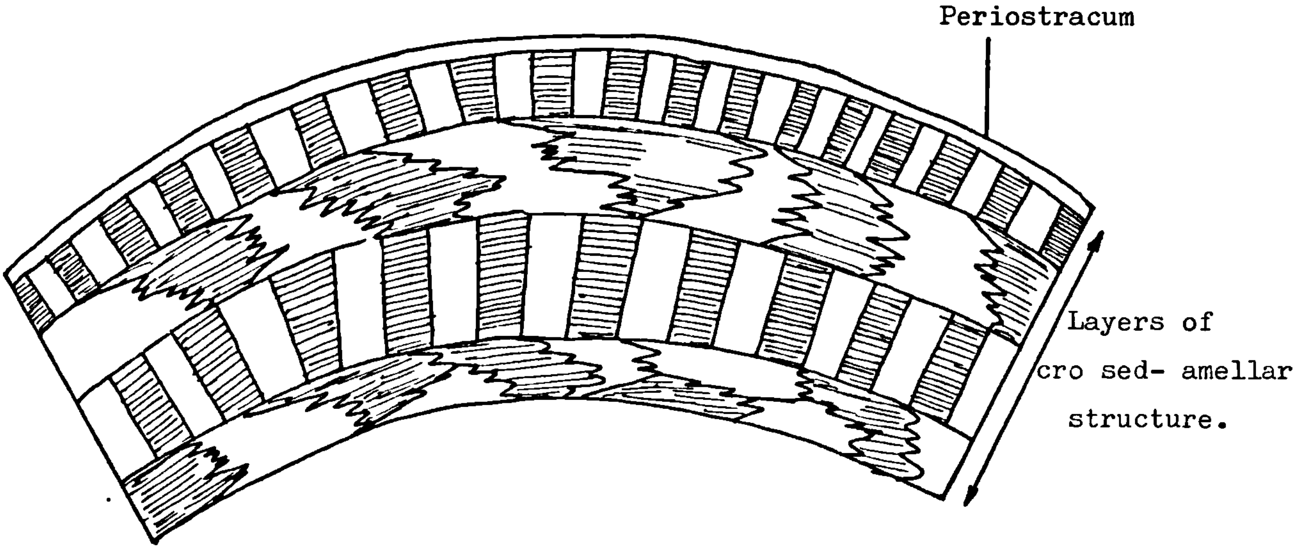


Figure 4.18. Sketch diagram of the structure of a shell of <u>Helix pomatia</u> based on observations of an acetate peel thin section.

Figure 4.19. Composite diagram of a cross section of a shell of Helix pomatia based on SEM photographs. Shell thickness is 240 microns.

(figure 4.20).

Helix aspersa is distinguished from H. pomatia by having the third-order lamellae "needle-shaped" and sharply pointed; the second-order lamellae are not clearly visible. The overall effect of these differences are best seen on sections that are cut nearly parallel to the third-order lamellae; the first-order lamellae are then seen to have a "comb-like" appearance (figure 4.21).

Growth bands are also present in the form of structural thickening.

Cepaea nemoralis has first-order lamellae that are c.1.0 micron wide and therefore narrower than those of H. pomatia or H. aspersa. Sheets of second-order lamellae were seen and fine third-order lamellae were clearly visible. Growth bands in the form of structural thickening were observed running parallel to the layer boundaries (figure 4.22).

In Cepaea hortensis the outer and inner layers vary in size and form between 15 and 25% of the total width. The inner middle layers were of approximately equal thickness and occupy 25 to 35% of the width. The second-order lamellae were visible in the form of sheets, these in turn were composed of very fine "rod-like" third-order lamellae.

Family HELICIDAE, Sub-family MONACHINAE

One species (Monacha cantiana) of the three found in Britain was examined. The shell was composed of two aragonitic crossed-lamellar structures. The first-order lamellae are 10-12 microns wide, with third-order lamellae (0.15-0.4 microns wide) clearly visible (figure 4.23). The third-order lamellae are arranged differently to that seen in other shells. They appear to slope across the width of the

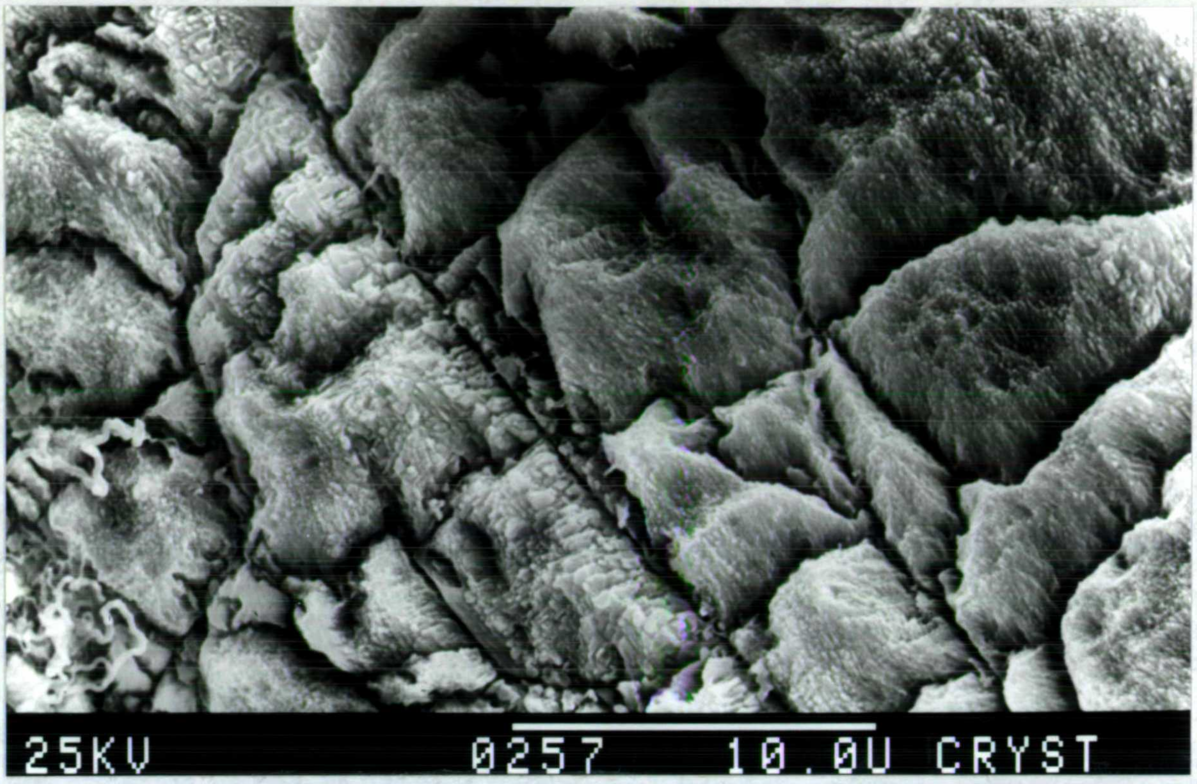


Figure 4.20. Third-order lamellae in a shell of Helix pomatia.

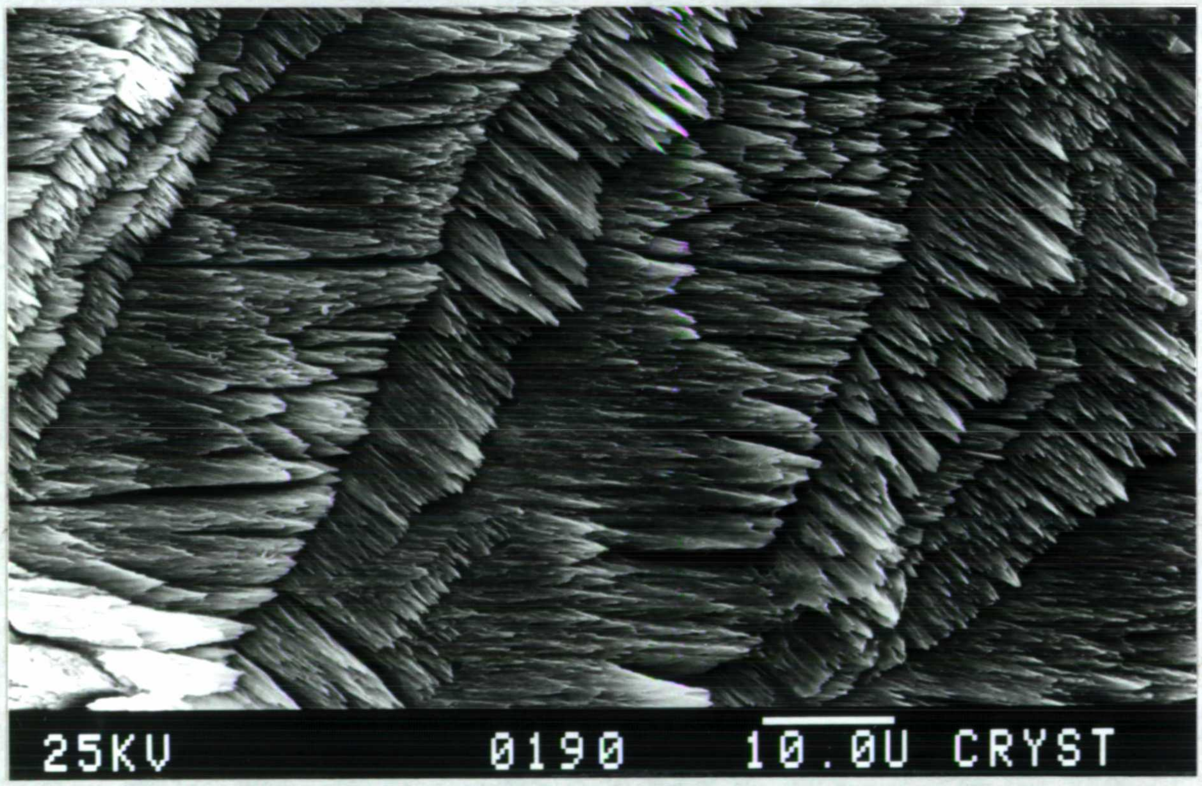


Figure 4.21. Detail of the crossed-lamellar structure of Helix aspersa.

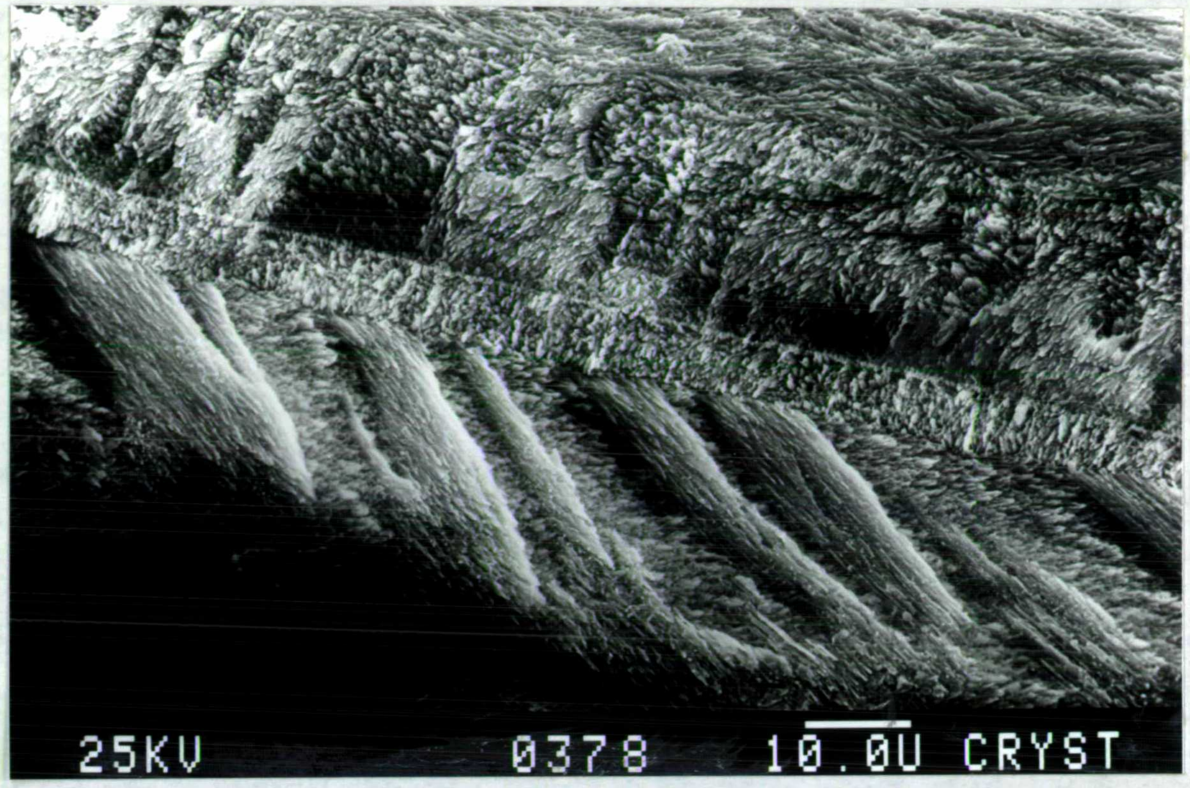


Figure 4.22. Growth bands in the form of structural thickening in a shell of Cepaea nemoralis.

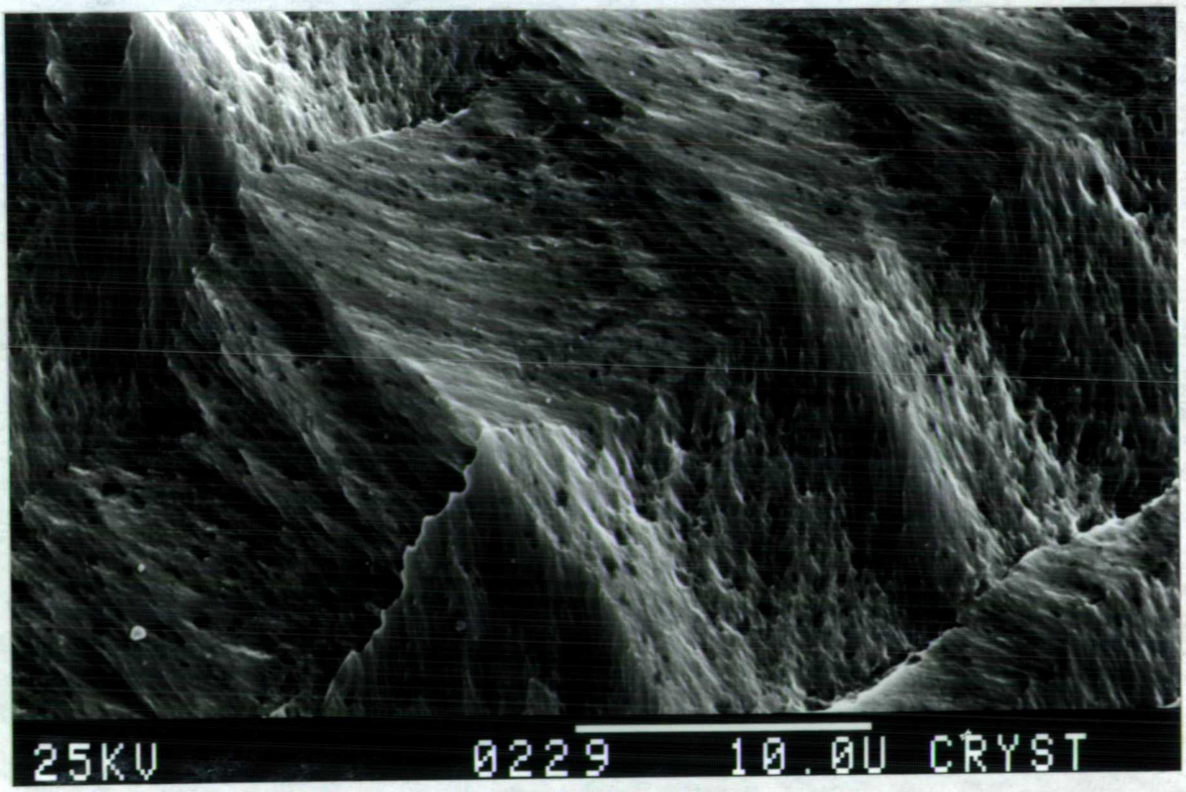


Figure 4.23. The structure of Monacha cantiana.

first-order lamellae, rather than down their length.

Figure 4.24 shows "bands" running parallel to the shell face which are interpreted as breaks in growth; the first-order lamellae are continuous across the "bands".

Figure 4.23 shows many small holes in the structure; these are interpreted as tubules; their cleanness indicates that no diagenesis has taken place (Walker 1979).

Family HELICIDAE, Sub-family HELICELLINAE

Shells of four species from this sub-family were examined, all of which are composed of two layers of aragonitic crossed-lamellar structure.

In the shell of Helicella itala the first-order lamellae of the outer layer (which is 70-80% of the total thickness) are arranged in a similar manner to those in the shell of M.cantiana. One first-order lamella has the third-order lamellae parallel to the orientation of the first-order lamellae, the adjacent first-order lamellae have the third-order lamellae arranged nearly at right-angles to the first-order lamellae orientation (figure 4.25).

The first-order lamellae are 3-5 microns wide; the second-order lamellae are block type, and are composed of rod type third-order lamellae that are 0.1-0.3 microns wide. The first- and third-order lamellae of the inner layer appear to be slightly larger (5-8 microns and 0.25-0.5 microns respectively).

The crossed-lamellar structure of Cernuella virgata is very similar

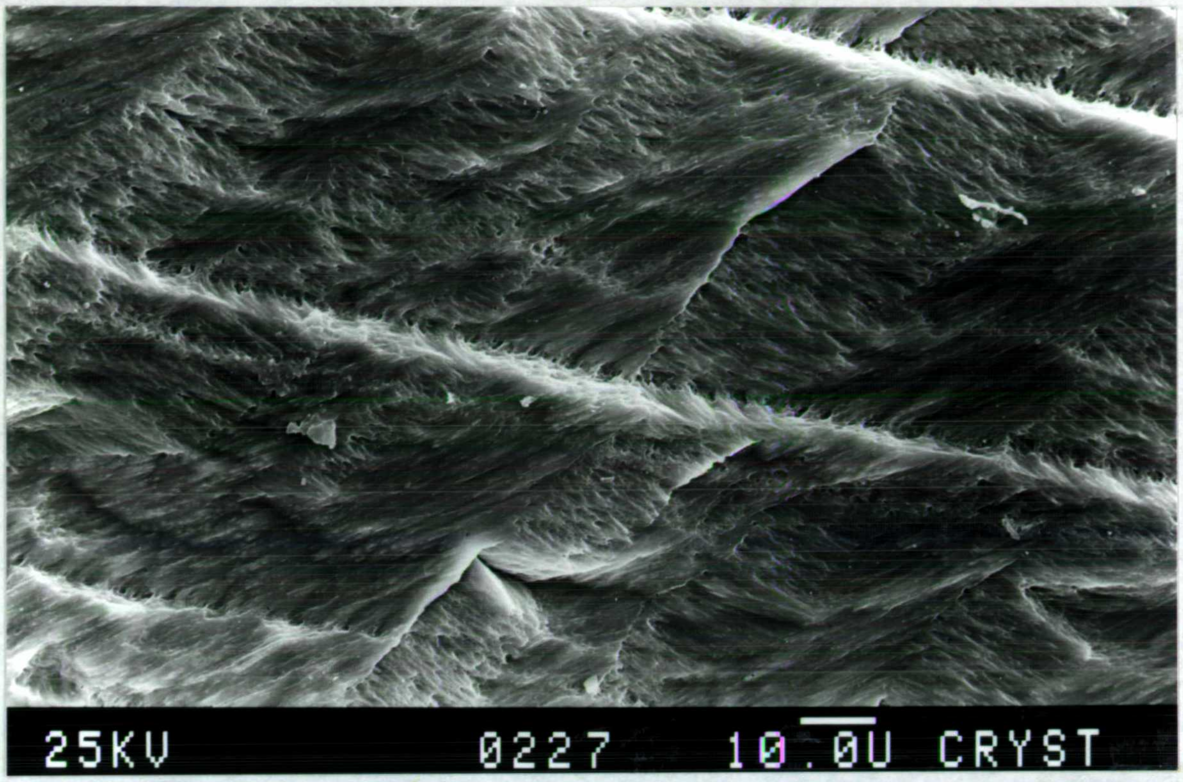


Figure 4.24. Breaks in growth in a shell of <u>Monacha cantiana</u>. Note that the first-order lamellae are continuous across the breaks.

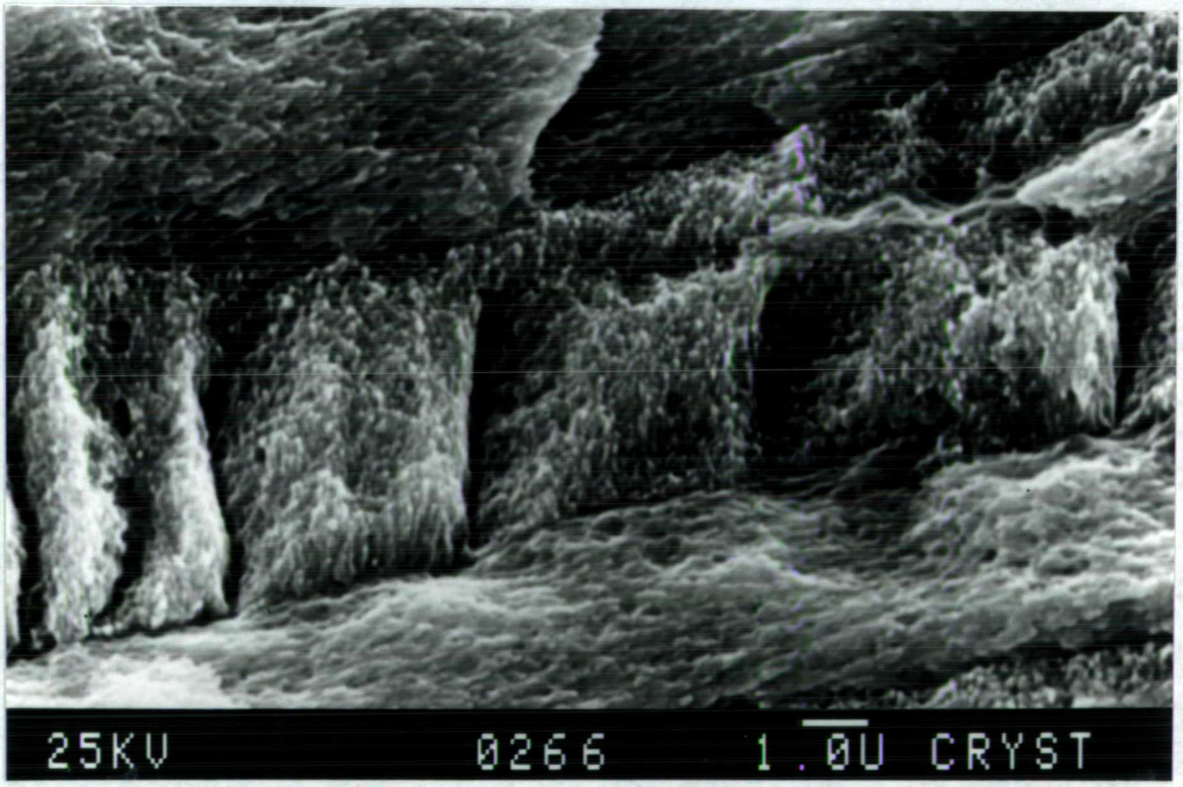


Figure 4.25. The structure of <u>Helicella itala</u>.

to that of H.itala, the exception being that the third-order lamellae are arranged conventionally.

Growth bands are visible in the form of structural thickening.

In the structure of Candidula gigaxii the first-order lamellae appear to be built up of point "sheets" (probably second-order lamellae) rather than "needles" or "rods" of third-order lamellae. These pointed "sheets" lead to a ridged appearance (figure 4.26).

Candidula intersecta has two layers of aragonitic crossed-lamellar structure. The outer is the thicker and forms a minimum of 65% of the total shell thickness. The inner layer thins in places and disappears totally at some points. The first-order lamellae are 1.5-8.0 microns wide and are composed of "needle-like" third-order lamellae. Second-order lamellae could not be distinguished.

4.44 Conclusions

The results from the examination of shell structures that are presented in chapter 4.4 allow a number of general conclusions to be made.

The Unionacea and Dreissenacea are a distinct group; they are the only freshwater genera that have nacreous and prismatic structures . The Sphaeriacea have simple structures consisting of one or two layers of crossed-lamellar structure.

The freshwater and terrestrial gastropods form three main groups, depending on the maximum number of layers of crossed-lamellar structure present in the shell. Most genera have two layers which are

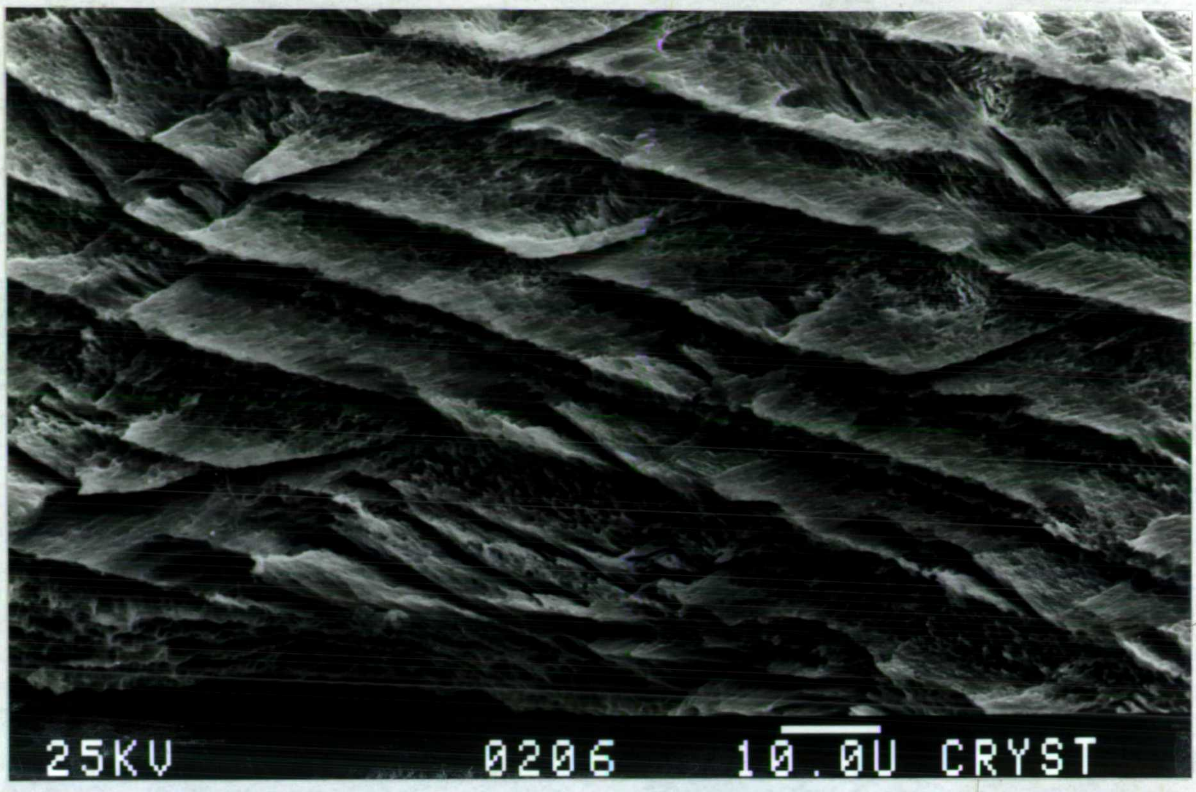


Figure 4.26. The structure of Candidula gigaxii. Note the pointed sheets of lamellae and the ridged appearance.

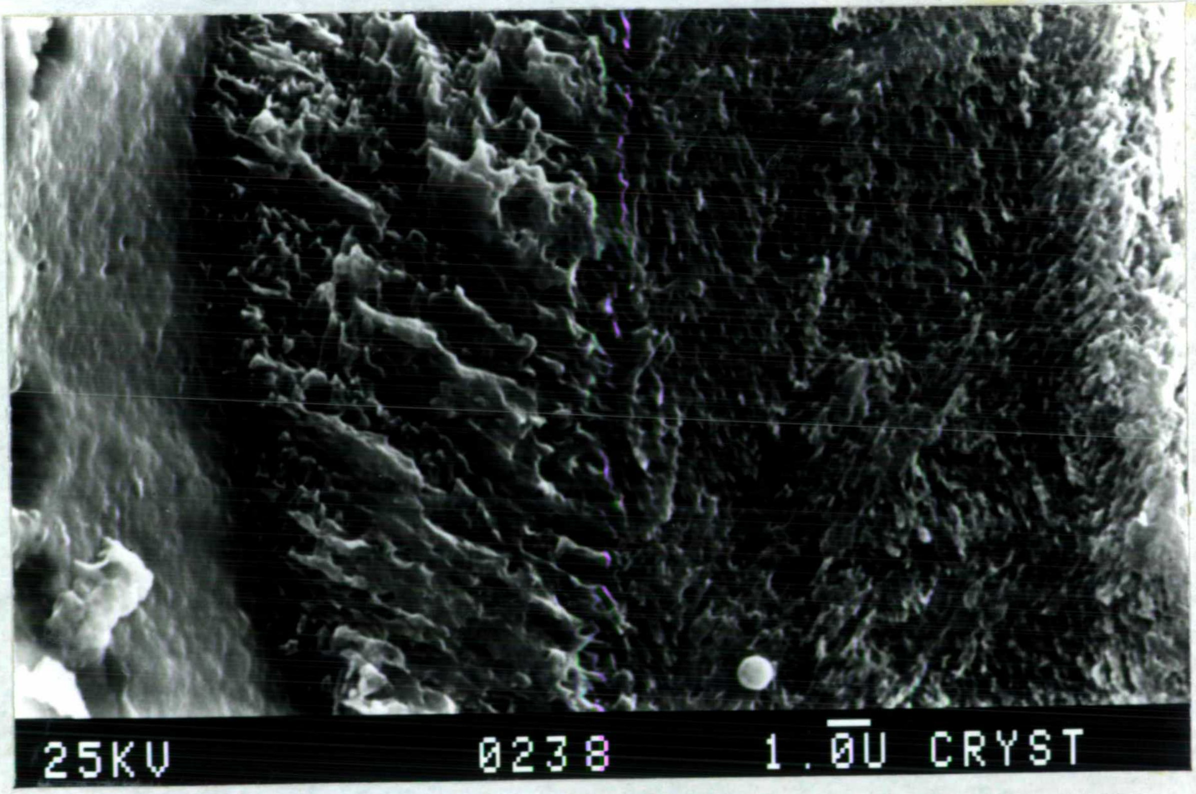


Figure 4.27. The periostracum preserved between two layers of crossed-lamellar structure in the early whorls of a shell of Cernuella virgata.

consistent throughout the shell and are found in all the whorls but may be worn away or very thin in the protoconch region. Figure 4.27 shows the overlap of the second and third whorls of *C.virgata*; the periostracum is still visible between the two layers, indicating that the section is complete. Two layers are clearly visible even though the total shell thickness is only 30 microns at this point.

Four species were found to have a single layer of crossed-lamellar structure: *P.elegans*, *T.fluviatilis*, *D.rotundatus* and *D.ruderatus*. The first two are both prosobranchs, but the other two species of this sub-order, *V.contectus* and *V.viviparus*, appear to have two layers.

Four species were found to have four layers (*H.pomatia*, *H.aspersa*, *C.nemoralis*, and *C.hortensis*); all of the sub-family Helicinae. Since they are also the largest species examined it was important to examine *A.arbustorum*. This is also a large species but of the sub-family Ariantinae. Four layers of aragonitic crossed-lamellar structure were clearly visible which suggests that the larger number of layers is asociated with age or shell size. Four layers with varying orientation will be stronger than one or two layers; this allows a large strong shell to be formed whilst minimising the weight and amount of calcium carbonate required.

The shells having four layers seem only to do so in the outer whorls. Examination of the inner whorls of *H.aspersa* and *H.pomatia* show only two layers. The development of two extra layers is thought to be associated with the thickening of the shell that takes place in species that live for a number of years. The relationships between age, shell size and shell thickness are discussed in chapter 3.3.

Establishing the structures of unaltered shells allows accurate determination of the presence of diagenetic material. The mechanisms by which diagenetic alteration occurs and the forms the altered material takes are discussed in chapter 6.

CHAPTER 5. CHEMICAL AND ISOTOPIC COMPOSITION OF TERRESTRIAL SHELLS

5.1 GENERAL INTRODUCTION

Chapter 3 showed that the chemical and isotopic composition of terrestrial snail shells is controlled by the environment in which they formed and the metabolic processes to which the components are subjected. After death the inputs and metabolism cease, so that the shell may be out of equilibrium with its burial environment and become subject to chemical and isotopic changes required to achieve a new equilibrium.

In this chapter the relationships between environment, habit and composition of the species on which the analyses were undertaken are thus used to qualify data derived from sub-fossil shells. In addition, the implications of using the chemical and isotopic composition as criteria for selection of shells in which depletion of ^{14}C is at a minimum are discussed.

5.2 METHODS OF ANALYSIS

5.21 Stable Isotopes

Measurement of stable isotope ratios for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ was undertaken at the British Geological Survey, London and The Weizmann Institute of Science, Israel. Samples from four modern sites and seven sub-fossil sites were available. The modern sites are described in chapter 2.3, the sub-fossil sites in chapter 2.4. The analyses were confined to five species (Cepaea nemoralis, C.hortensis, Pomatias elegans, Helix pomatia and Xeropicta vestalis) whose ecology was outlined in chapter 2.2. Modern samples for analysis were selected to cover intra-shell, intra-species, and inter-species variation of stable isotope values. The analyses were duplicated to cover different environmental niches, which allowed site specific and species specific variations to be determined. Comparable data were obtained for fossil specimens. Where possible fossil and modern populations from the same site were analysed.

(a) British Geological Survey

(i) Acid soluble carbonate fraction

Samples of cleaned shell (for method see chapter 8.2) were ground using a Microne Mill or, if small, an agate pestle and mortar; the particle size was 10-100 microns.

Many of the modern samples contained 2-3% of acid insoluble organic matrix. Duplicate samples of ground shells were prepared and one set treated in an oxygen plasma furnace for 16 hours to remove the organic material prior to extraction and analysis.

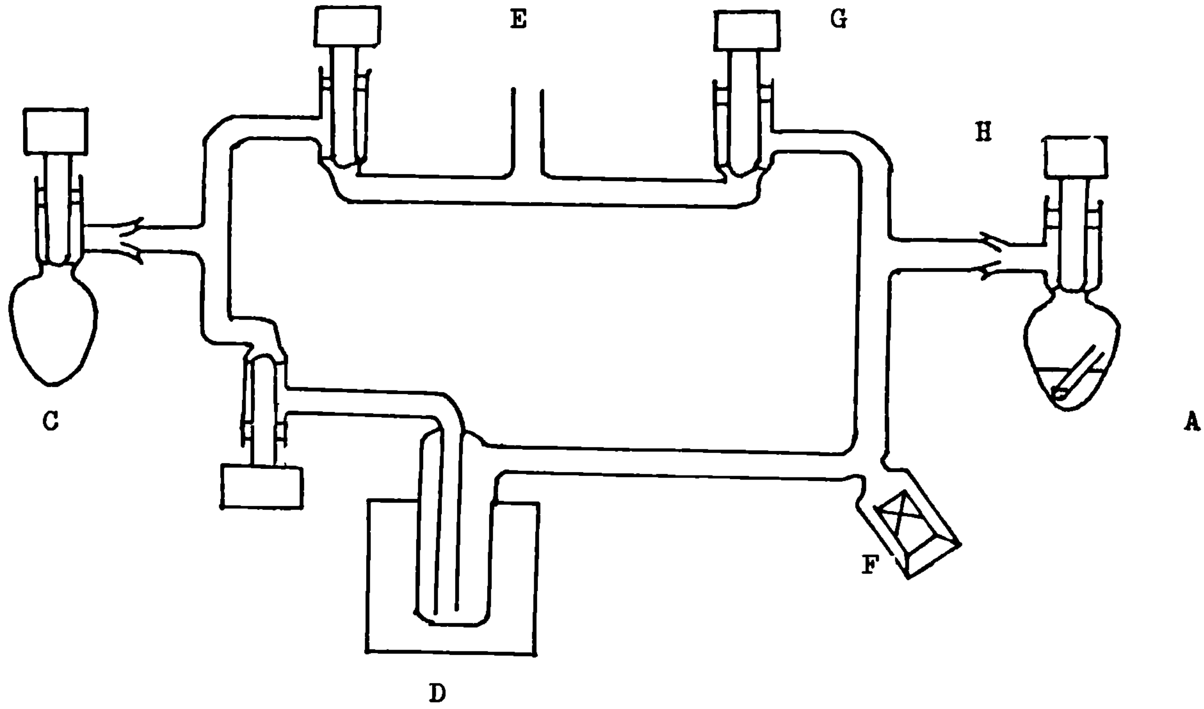
Sample Code	Untreated		Treated	
	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
OPE 2	-7.141	-1.522	-7.213	-1.975
HCN 1	-10.425	-0.486	-10.615	-1.007
HCN 2	-9.350	-0.520	-9.426	-0.764
OHP 6A	-9.429	-1.644	-9.643	-1.946

Mean difference: $\delta^{13}C$ = -0.138 $\delta^{18}O$ = -0.380

Table 5.1. $\delta^{13}C$ and $\delta^{18}O$ analyses of samples with and without acid insoluble matrix present.

The results (table 5.1) show an enrichment in the untreated samples that was greater than the expected reproducibility between duplicate samples (±0.030‰ $\delta^{13}C$, ±0.062‰ $\delta^{18}O$). As the main source of organic material in terrestrial shells is the outer periostracum, it was removed by immersion in 30 vol. H_2O_2 and mechanical cleaning. The remaining organic material forms the intra- and inter-lamellae matrix. Its finely divided nature would require the shell to be ground to sub-micron sized particles prior to treatment. The increased possibility of contamination involved in grinding to this level outweighs the possible increased accuracy that removal of the fine organics might give.

Sub-samples (c.10mg) of the ground shells were transferred to glass reaction tubes. Four millitres of 100% orthophosphoric acid (P_2O_5 in H_3PO_4) were dispensed into reaction vessels with side-arms, the reaction tube placed in the vessel and the vessel sealed at the top but not at the side-arm. The vessels were then placed on a vacuum line and evacuated to 5×10^{-5} torr, which allowed the acid to outgas, and sealed completely. The vessel was left in a water bath (25.18°C) for one hour to reach equilibrium and then reacted in three stages to avoid excessively rapid gas formation. The reaction was left overnight to ensure completion. The CO_2 was extracted under high vacuum (min.10^{-4} torr) through a refrigerated acetone trap (-89°C) to remove water vapour and was collected in vessels cooled by liquid nitrogen. The line is shown in figure 5.1. The sealed collection vessels were transferred to a V.G. Isotopes Micromass 903 "triple collector isotope ratio mass spectrometer" linked to a Hewlett Packard microcomputer control system. Each batch of samples contained two or three in-house standards (MCS-8 or MCS-9) and all were analysed relative to a reference gas (also MCS-8 or MCS-9). The raw data were corrected for instrumental effects (Craig 1957; Deines 1970).



A) Reaction vessel containing 100% phosporic acid and sample tube.
C) Collection vessel.
D) Solid CO_2 / acetone trap.
E) To rotary and diffusion pumps.
F) Thermocouple gauge.
G) High vacuum stopcock in closed position.
H) B14 joint fitted with Vitron 'O' ring.

Figure 5.1. Carbonate extraction line used at the British Geological Survey.

(ii) Acid insoluble organic shell matrix

The acid insoluble shell matrix was extracted by dissolving complete shells in 100% glacial acetic acid. The residue was centrifuged and washed in distilled water three times, then dried at 50°C. The reaction method was based on Cox _et al._ (1981). The organic residues were weighed (2.0-3.5mg) and placed with 500mg of finely milled cupric oxide in quartz glass tubes that had previously been heated to 900°C for two hours to remove contaminants. The tubes had a constriction 50mm from the open end and this had to be kept free from the sample and the cupric oxide. The tubes were labelled with a heat-proof marker and attached via a Cajon "Ultratorr Union" to a vacuum line and evacuated to 10^{-2} torr. The constriction was sealed with an oxy-gas flame whist pumping continued. The sealed tubes were heated for one hour at 850°C. The cooled tubes were cracked in a Cajon flexible bellows under vacuum and the CO_2 extracted by the same method as for carbonate CO_2. Graphite standard samples were reacted with each batch of organic samples and MCS carbonate standards extracted with the organic derived CO_2 samples.

(iii) Reproducibilty

Duplicate analyses of carbonate samples for measurement of reproducibility were undertaken at the British Geological Survey, with repeats within runs and in different runs. The results are given in table 5.2.

Sample Code	$\delta^{13}C$	$\delta^{18}O$
NC 12	-9.441	-0.789
	-9.383	-0.821
Difference:	0.058	0.032
CW 4	-10.698	-1.139
	-10.500	-0.892
Difference:	0.198	0.247
CW 31	-9.889	-1.976
	-9.836	-1.927
Difference:	0.053	0.049
CBM 7	-9.197	-1.102
	-9.213	-1.067
Difference:	0.016	0.035
INCH 4	-3.449	-2.078
	-3.440	-2.197
Difference:	0.009	0.119
BPM 5	-7.621	-0.497
	-7.635	-0.423
Difference:	0.014	0.074
MEAN DIFFERENCE: (all samples)	0.058	0.093
Mean Difference: (excluding CW 4)	0.030	0.062
Precision: (all samples)	0.062	0.084
Precision: (excluding CW 4)	0.026	0.049

Table 5.2. Replication analyses on carbonate samples.

b) Weizmann Institute of Science

i) Acid soluble carbonate fraction

Ground samples of shell were heated to 75°C for 24 hours in 10ml of 30 vol. H_2O_2, dried at 75°C for 24 hours. Sub-samples of 20-50mg were placed in a reaction vessel and 10ml of orthophosphoric acid dispensed into a glass tube. The vessel was pumped down for 2-3 minutes and sealed. The sample was reacted and placed in a cabinet at 28°C. The CO_2 was extracted through an acetone/dry ice trap (-89°C) and collected in an evacuated vessel. The vessel was then transferred to a Varian M250 mass spectrometer. Standards were added at the beginning and end of each run from a large volume of standard CO_2. Reproducibility was given as ±0.15‰ for both $\delta^{13}C$ and $\delta^{18}O$.

5.22 Atomic Absorption Spectrophotometry (AAS)

(i) Method

The measurement of ions (magnesium, strontium, iron and manganese) which can substitute for calcium in a $CaCO_3$ crystal was undertaken at the Department of Geography, University College London. Sub-samples from the material prepared for stable isotope analysis were used. Four species (*C.nemoralis*, *C.hortensis*, *P.elegans* and *H.pomatia*) from four modern and six sub-fossil sites were analysed. No study of intra-shell variations was possible owing to the limited amount of shell material available.

A weighed quantity of powdered shell (c.100mg) that had previously been cleaned and ground (chapter 8.2 and above) was placed in a labelled 50ml beaker. Ten millilitres of 100% glacial acetic acid and 10ml of distilled water were added and the reaction left for 24 hours to reach completion. The solution was then transferred to a volumetric flask and further distilled water added to make the volume up to 25ml.

Standards were prepared using Stan-Ion solutions and dilution was made with a solution of Analar pure $CaCO_3$ in acetic acid in which the concentration of calcium ions was equal to that in the sample solutions. Three standards and a "blank" (Analar $CaCO_3$ in acetic acid and distilled water) were prepared for each element.

Samples and standards were analysed using a Pye Unicam SP912 AAS using an air/acetylene flame under the conditions defined in the operating manual. When analysing for magnesium, iron and manganese linear relationships between absorption and concentration were obtained for the standards, which allowed direct measurement of concentration for the samples. The relationship was non-linear for strontium and a calibration curve was produced. Concentrations of the ions in solution were converted to ppm for the sample by standard methods using the formula:

$$ppm_1 = \frac{ppm_2 \times 2.5 \times 10^4}{\text{wt of sample in mg}}$$

(1) = sample (2) = solution

(ii) Reproducibility

Reproducibility was tested using chalk samples from Oldlands Woods (Ch.S3, Ch.S4). The results are given in table 5.3.

Sample	Mg (ppm)	Sr (ppm)
Ch.S3	1665	453
	1630	471
	1731	480
	1828	427
	1663	458
Mean	1703.4	457.8
Std.Dev	78.7	20.2
2 x Std.Dev as % of mean	9.25	8.8
Ch.S4	1864	586
	1934	521
	1843	523
	1923	557
	2032	565
Mean	1919.2	550.4
Std.Dev	73.8	28.0
2 x Std.Dev as % of mean	7.7	10.2

Table 5.3. Reproducibility of AAS results.

The variation in results for some soil samples (e.g. Hayle Towans) were greater than these due to the coarse particles and shell fragments causing inhomogeneity. The mean of these results is still considered valid.

5.3 RESULTS OF STABLE ISOTOPE ANALYSES

5.31 Modern samples

(i) Variations within a single shell

The analysis of 41 shells of the species Helix pomatia and three shells of Cepaea nemoralis was undertaken to assess whether variations in $\delta^{13}C$ and $\delta^{18}O$ values were present within single shells, and, if so, whether these variations were random or controlled by one or more of the external factors. Thirty-nine of the H.pomatia were from Oldlands Wood, Surrey (HP1-39) and two were from Woldingham, Surrey (HP41-42). The C.nemoralis shells came from Hayle Towans, Cornwall (HCN33,37) and Graffy, Co.Mayo, Eire (GCN36).

Thirty-two shells (HP1-32) were sampled at the apex (protoconch and early juvenile whorls) (A) and in the last part of the ultimate whorl (B). The remaining nine H.pomatia (HP33-39, HP41-42) were sampled at 5-10 points chosen to represent different periods of growth and development between hatching and becoming adult.

The results from the analysis of the pairs of samples from shells HP1-32 showed that the $\delta^{13}C$ values were significantly different (see table 5.4 and figure 5.2) when the means were compared using a two sample "t" test (95% c.l.). The $\delta^{18}O$ values were not significantly different at the 95% level. The apices were enriched in ^{13}C relative to the ultimate whorls, which could be explained by a decrease in exchange of CO_2 through the snail's body with the decrease in the surface area to volume ratio. If this theory were correct then detailed analysis of the $\delta^{13}C$ values should have conformed to the general model (shown in figure 5.3). This was constructed by plotting surface area / volume (SA/V) against radius for a sphere (S) and a cylinder (c). The curves are very similar with a generally

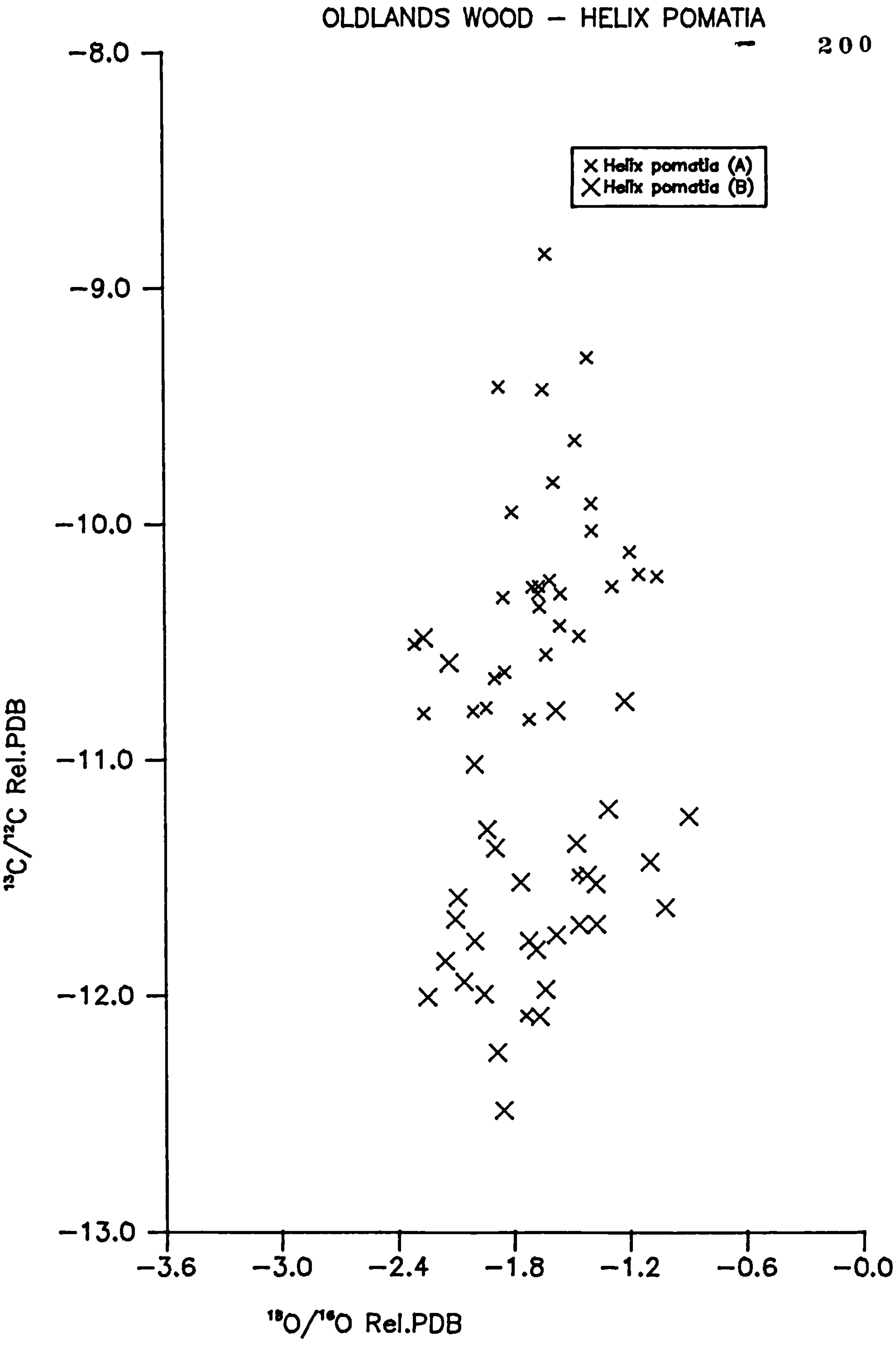


Figure 5.2. Isotopic differences between the apex (A) and the last whorl (B) in shells of *Helix pomatia*.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
HPA 1	-10.118	-1.197	50	260	*	*
2	-9.912	-1.395	244	239	*	*
3	-10.264	-1.701	66	250	*	*
4	-10.213	-1.149	70	204	*	*
5	-12.083	-1.738	493	204	*	*
6	-9.429	-1.644	121	218	*	*
7	-10.264	-1.288	245	241	*	*
8	-10.793	-2.012	64	234	*	*
9	-9.823	-1.590	246	266	*	*
10	-8.854	-1.627	244	285	*	*
11	-9.294	-1.414	155	256	*	*
12	-10.803	-2.266	134	238	*	*
13	-10.431	-1.559	113	231	*	*
14	-10.028	-1.392	*	*	*	*
15	-10.309	-1.852	*	*	*	*
16	-10.553	-1.631	*	*	*	*
17	-10.294	-1.671	*	*	*	*
18	-9.645	-1.477	*	*	*	*
19	-10.262	-1.668	*	*	*	*
20	-10.653	-1.897	*	*	*	*
21	-10.627	-1.844	*	*	*	*
22	-10.222	-1.056	*	*	*	*
23	-10.349	-1.664	*	*	*	*
24	-10.293	-1.556	*	*	*	*
25	-9.948	-1.805	*	*	*	*
26	-10.474	-1.461	*	*	*	*
27	-10.508	-2.314	*	*	*	*
28	-10.238	-1.611	*	*	*	*
29	-10.828	-1.718	*	*	*	*
30	-10.779	-1.942	*	*	*	*
31	-9.418	-1.870	*	*	*	*
32	-11.487	-1.470	*	*	*	*

* = Not measured

Table 5.4A. Results from the chemical and isotopic analyses of shells of *Helix pomatia* from Oldands Wood, Surrey.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
HPB 1	-10.752	-1.223	26	266	*	*
2	-11.973	-1.638	32	176	*	*
3	-11.805	-1.686	199	267	*	*
4	-11.354	-1.475	63	199	*	*
5	*	*	69	218	*	*
6	-9.454	-1.572	*	*	*	*
7	-10.482	-2.266	*	*	*	*
8	-11.941	-2.063	123	230	*	*
9	-11.700	-1.463	131	271	*	*
10	-10.588	-2.136	79	201	*	*
11	-11.527	-1.375	*	*	*	*
12	-11.697	-1.373	70	215	*	*
13	-12.005	-2.251	138	216	*	*
14	-11.296	-1.938	*	*	*	*
15	-11.768	-1.723	*	*	*	*
16	-11.769	-2.006	*	*	*	*
17	-12.484	-1.854	*	*	*	*
18	-11.018	-2.004	*	*	*	*
19	-12.239	-1.887	*	*	*	*
20	-11.584	-2.095	*	*	*	*
21	-11.994	-1.956	*	*	*	*
22	-11.434	-1.095	*	*	*	*
23	-11.675	-2.108	*	*	*	*
24	-11.627	-1.017	*	*	*	*
25	-11.488	-1.419	*	*	*	*
26	-11.241	-0.894	*	*	*	*
27	-11.374	-1.895	*	*	*	*
28	-10.791	-1.580	*	*	*	*
29	-11.853	-2.160	*	*	*	*
30	-11.520	-1.764	*	*	*	*
31	-11.743	-1.581	*	*	*	*
32	-12.087	-1.668	*	*	*	*

Table 5.4B. Results from the chemical and isotopic analyses of shells of Helix pomatia from Oldlands Wood, Surrey.

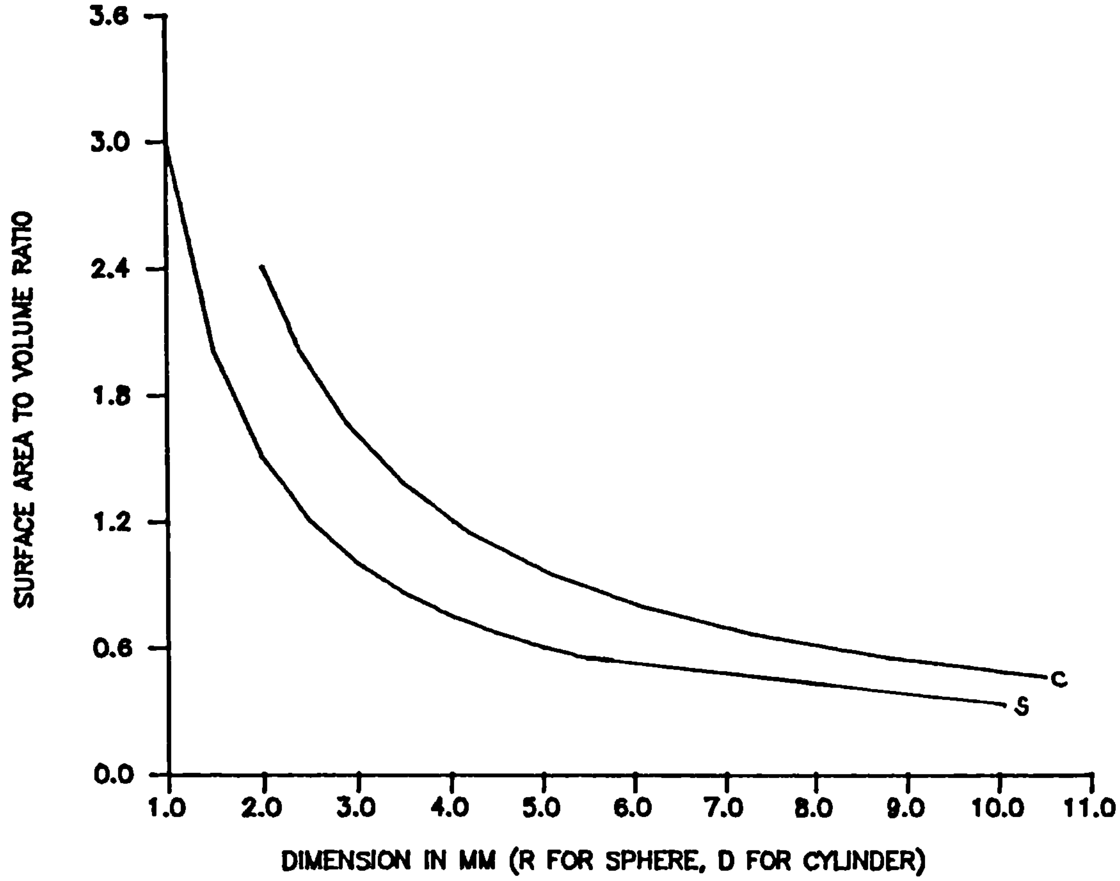


Figure 5.3. Model of relationship between surface area, volume and radius

exponential form. Figure 5.3 assumes that the radius increases linearly. If the rate of increase in the radius is related to the size of the shell then the gradient will be steeper as the rate increases but the general form will still be exponential.

If it is assumed that the SA/V ratio controls the exchange of CO_2 between the snail and the atmosphere and that the rate of change per unit area remains constant a curve for $\delta^{13}C$ against time since hatching can be constructed (figure 5.4). If there are other factors influencing the $\delta^{13}C$ values then significant variations from this model should be observable.

Alternatives for the x-axis are the thickness, weight and radius of the shell. Figure 5.5 shows a graph of $\delta^{13}C$ against radius. The trend is very similar to those for "age" against $\delta^{13}C$.

Seven shells from Oldlands Wood (HP33-39) were sampled at representative points between growth bands. The bands are not thought to be annual but probably represent two periods of growth in each year. They were numbered consecutively from the apex and were termed age of growth. The results of these analyses are given in table 5.5 and are shown graphically in figure 5.6. All seven samples had the apex enriched in ^{13}C relative to the ultimate whorl but do not show an exponential curve between the two extremes. The curves are generally convex rather then concave. The general trend is for the maximum gradient to occur when the shell is nearing maximum (adult) size, after a period when the gradient was positive or very shallow. The effect is more clearly seen when a composite diagram from HP33-39 is examined (figure 5.6). The results do not fit with the proposed model and the idea that variations are primarily due to SA/V changes

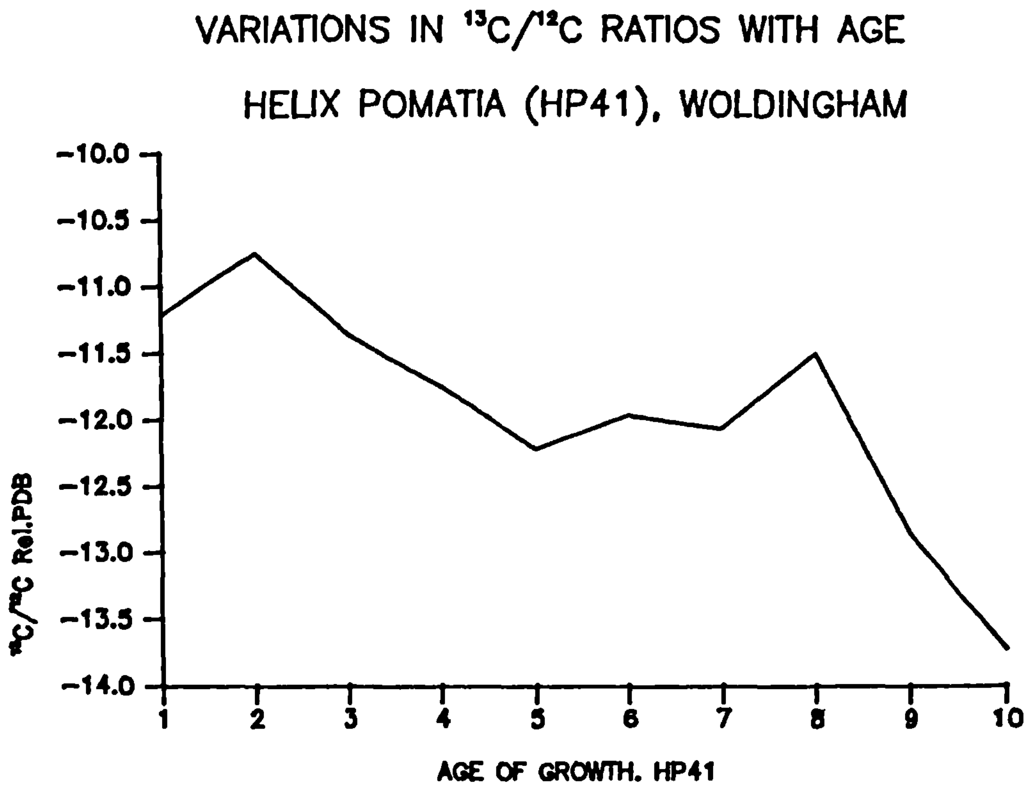


Figure 5.4. Variations in stable isotope values with age

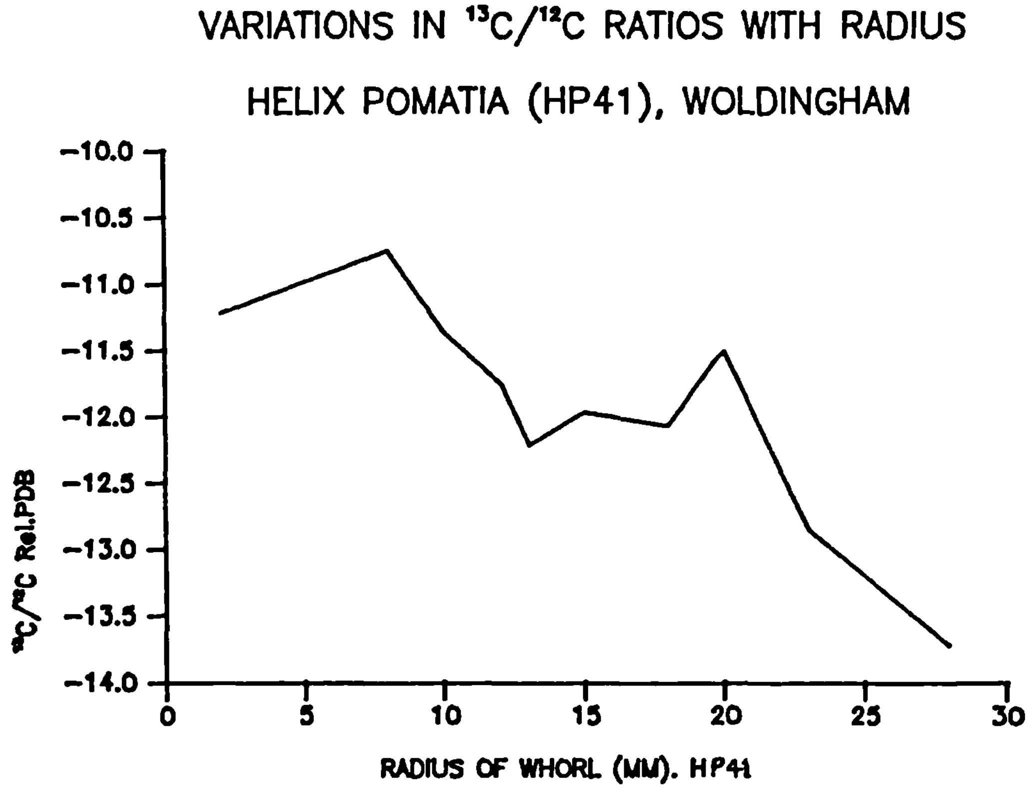


Figure 5.5. Variations in stable isotope values with radius

VARIATIONS IN $^{13}C/^{12}C$ RATIOS WITH AGE

HELIX POMATIA, OLDLANDS WOOD

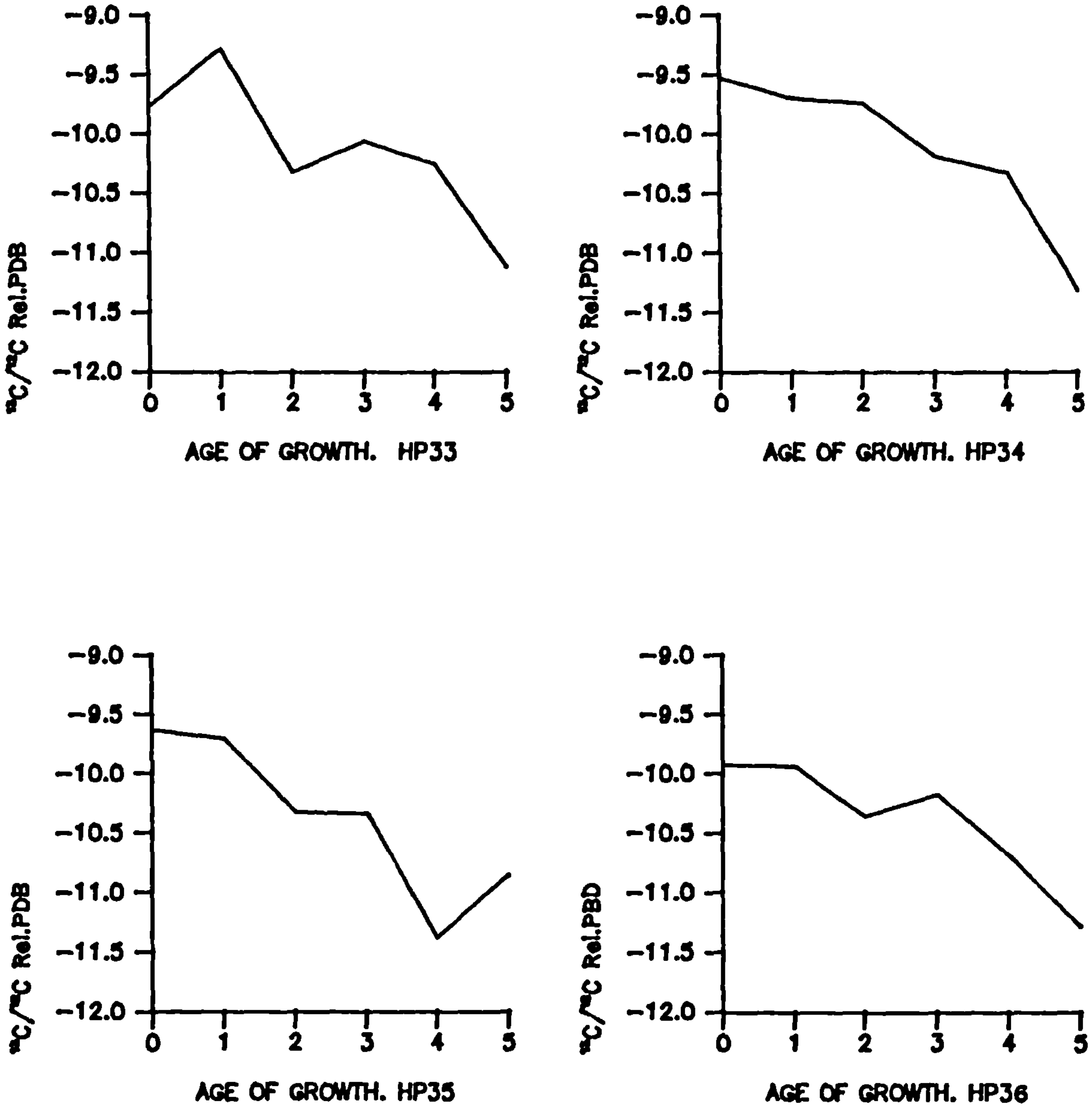


Figure 5.6A. Within shell variations in stable isotope values.

VARIATIONS IN $^{13}C/^{12}C$ RATIOS WITH AGE

HELIX POMATIA, OLDLANDS WOOD

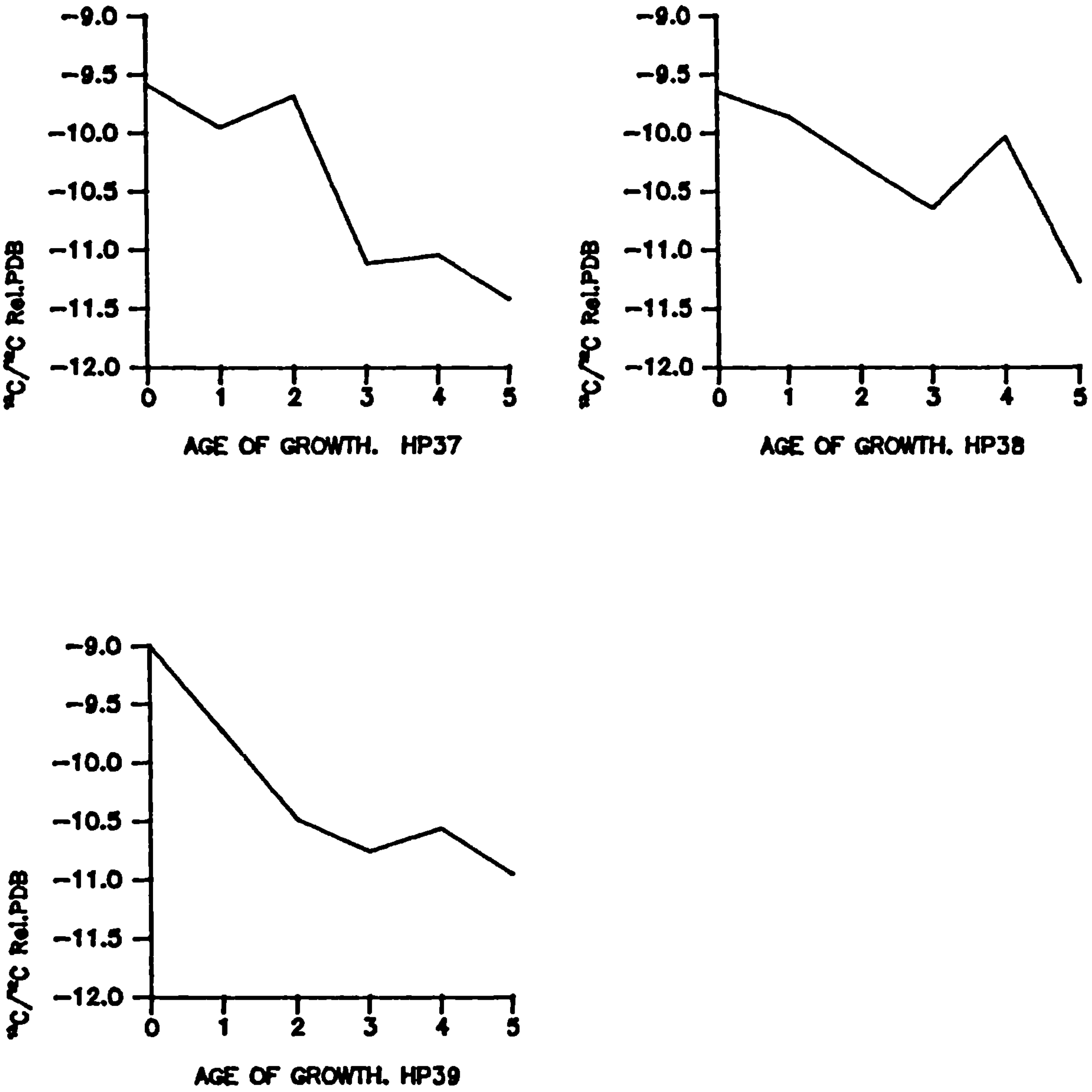


Figure 5.6B. Within shell variations in stable isotope values.

GROWTH	HP33	HP34	HP35	HP36	HP37	HP38	HP39
			$^{13}C/^{12}C$ Rel PDB				
5	-11.12	-11.31	-10.86	-11.28	-11.42	-11.27	-10.95
4	-10.25	-10.32	-11.38	-10.68	-11.04	-10.03	-10.56
3	-10.06	-10.18	-10.33	-10.17	-11.11	-10.64	-10.75
2	-10.32	-9.73	-10.32	-10.35	-9.68	-10.26	-10.48
1	-9.28	-9.69	-9.70	-9.93	-9.95	-9.85	-9.74
0	-9.77	-9.52	-9.63	-9.92	-9.58	-9.64	-9.00
			$^{18}O/^{16}O$ Rel PDB.				
5	-1.20	-1.13	-1.45	-1.94	-1.77	-1.55	-1.88
4	-2.83	-0.13	-1.83	-0.97	-1.78	-1.67	-1.71
3	-1.75	-1.57	-2.52	-1.98	-1.97	-1.33	-1.17
2	-1.12	-1.12	-2.73	-1.95	-2.08	-1.06	-0.55
1	-1.28	-1.13	-2.19	-1.91	-0.81	-1.52	-0.87
0	-0.96	-1.29	-2.02	-1.97	-1.74	-1.56	-1.19

Table 5.5A. Isotopic variations within shells of Helix pomatia from Oldlands Wood, Surrey.

GROWTH	HP41	GROWTH	HP42	GROWTH	HCN33	GROWTH	HCN37
			$^{13}C/^{12}C$ Rel PDB				
10	-13.721	8	-11.433	7	-10.798	7	-8.818
9	-12.847	7	-10.805	6	-9.873	6	-9.162
8	-11.500	6	-10.519	5	-10.108	5	-8.518
7	-12.061	5	-10.645	4	-10.072	4	-8.607
6	-11.960	4	-11.124	3	-9.904	3	*
5	-12.214	3	-10.898	2	-9.297	2	-8.253
4	-11.745	2	-10.728	1	-9.584	1	-7.622
3	-11.351	1	-10.543				
2	-10.742						
1	-11.215						
			$^{18}O/^{16}O$ Rel PDB				
10	-1.933	8	-0.516	7	-0.382	7	-0.627
9	-1.246	7	-0.544	6	-0.287	6	-0.592
8	-1.361	6	-1.606	5	-0.322	5	-0.342
7	-1.358	5	-0.512	4	-0.225	4	-0.242
6	-2.174	4	-1.005	3	-0.175	3	*
5	-1.725	3	-0.751	2	+0.033	2	-0.435
4	-1.743	2	-0.693	1	-0.258	1	-0.457
3	-1.213	1	-1.151				
2	-1.128						
1	-1.925						

Table 5.5B. Isotopic variations within shells of *Helix pomatia* (Oldlands Wood, Surrey; HP) and *Cepaea nemoralis* (Hayle Towans; HCN).

GROWTH	GCN36 ^{13}C/^{12}C Rel PDB	GROWTH	GCN36 ^{18}O/^{16}O Rel PDB
7	-11.353	7	-1.954
6	-11.252	6	-1.503
5	-10.899	5	-1.233
4	-10.714	4	-1.112
3	-10.730	3	-1.233
2	-10.687	2	-1.366
1	-10.640	1	-1.453

Table 5.5C. Isotopic variations within shells of *Cepaea nemoralis* from Graffy, Co.Mayo, Eire.

can be rejected.

A possible explanation for the similarity of the variations in $\delta^{13}C$ values in the shells is that they represent a change in the habitat, such as clearance of vegetation. The hypothesis was tested by analysing two shells of the same species from a different site (HP41-42). The results are given in table 5.5 and figure 5.7. The pattern is clearly repeated in these shells. The changes in $\delta^{13}C$ are therefore unlikely to be due to a change in habitat.

An alternative interpretation of the results is that the changes are associated with the ecology or habits of the species. The ecology of H.pomatia was studied by Pollard (1973; 1975a; 1975b). He observed that juveniles spent most of their time concealed under vegetation and in litter; only when the thicker adult shells developed did the snail spend time in the open. Boycott (1934) also observed these differences and suggested that because juveniles were more vulnerable to bird predation they were mainly nocturnal. The $\delta^{13}C$ values from the present study can be equated with the change from nocturnal activity in litter to daytime activity in open areas. Nocturnal activity will occur when air moisture (dew) levels are high, reducing the soil-CO_2 component in the surface water. Activity under vegetation and litter will increase ingestion or incorporation of particles of $CaCO_3$. Both of the factors will lead to enrichment in the ^{13}C levels. Adult activity will occur when temperatures and humidity favour increased levels of soil-CO_2 and occupation of open sites will reduce particulate $CaCO_3$ uptake.

The internal reservoir from which the shell is deposited will also be affected as the snail changes from a juvenile to an adult. As the

VARIATIONS IN $^{13}C/^{12}C$ RATIOS WITH AGE

HELIX POMATIA, WOLDINGHAM

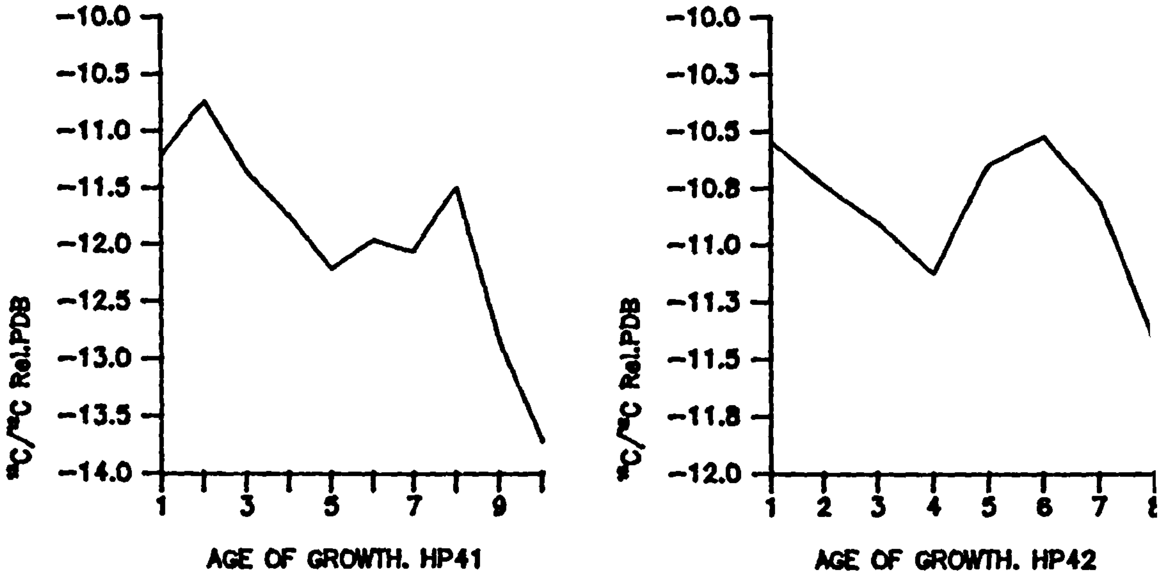


Figure 5.7. Within shell variations in stable isotope values.

VARIATIONS IN $^{13}C/^{12}C$ RATIOS WITH AGE

CEPAEA NEMORALIS, HAYLE CEPAEA NEMORALIS, GRAFI

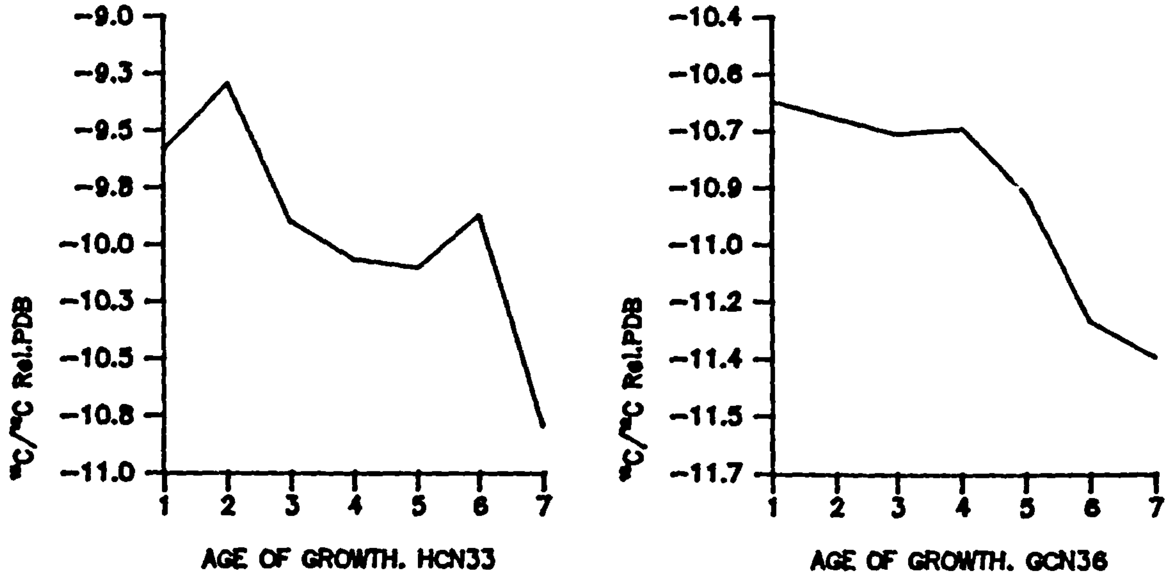


Figure 5.8. Within shell variations in stable isotope values.

volume of the reservoir increases and the rate of deposition of $CaCO_3$ decreases the rate of turnover within the reservoir will decrease. This will allow the reservoir to come closer to equilibrium with the environment and apparently increasingly depleted in ^{13}C.

Three further shells were analysed in detail to establish whether the variations observed in H.pomatia were restricted to that species or could be observed in other species. The shells were C. nemoralis from Hayle Towans (HCN33,37) and Graffy (GCN36). The results are given in table 5.5 and figure 5.8. The data from Hayle have similar characteristics to those of H.pomatia but the range of $\delta^{13}C$ values is much reduced (1.2-1.5$^{\circ}/_{\circ\circ}$) compared with HP41 (4$^{\circ}/_{\circ\circ}$) but similar to the other H.pomatia shells. Although no further evidence is available it is reasonable to assume that the data also represent a change in activity pattern between adults and juveniles. Samples from GCN36 showed a less clear pattern and a narrow range of $\delta^{13}C$ values (0.7$^{\circ}/_{\circ\circ}$) and suggest that changes in activity at this site were less pronounced.

Analysis of the C.nemoralis shells also involved measurement of $\delta^{13}C$ values of the inner and outer surfaces at the lip of HCN37 and immediately either side of a growth break on GCN36. The former have values of -9.162$^{\circ}/_{\circ\circ}$ for the outer layer and -8.818$^{\circ}/_{\circ\circ}$ for the inner. It is thought that the inner layer is formed during shell thickening after maturity has been reached. The results suggest that deposition occurs under conditions slightly different from those that prevailed at the initial deposition of the shell. Similar conclusions can be drawn from the change across the growth break on GCN36, the respective values being -10.899$^{\circ}/_{\circ\circ}$ and -11.253$^{\circ}/_{\circ\circ}$ When considered with the figures on either side of these, within the same growth bands, a significant change in external conditions across the banding is apparent whilst conditions are more stable within growth bands. This is not always the case; HP42 had three points (2-4) within a single growth band and a steady increase in ^{13}C depletion was observed.

The variations in $\delta^{18}O$ values within shells were less consistent (table 5.5, figure 5.9 - 5.11). There was no significant correlation between ^{18}O and ^{13}C except in the case of HCN33 and no general trends common to the shells were observed. The general pattern for HP33-38 was of $\delta^{18}O$ values remaining nearly constant but with one or two exceptional periods. The "constant" levels are not all identical with two groups centred on -1.5 and $-2^{o}/_{oo}$ being apparent. This can be interpreted as two environments with different microclimates with occasional significant changes in external conditions causing sudden variations in the microclimates.

The $\delta^{18}O$ tends in HP41-42 suggest a less stable environment or more variation in the habits of the snails. Confirmation of less stable conditions can perhaps be seen in the $\delta^{13}C$ values which have much greater ranges at this site than the other one. The two shells from Hayle show an increase in $\delta^{18}O$ depletion in the adult shell but the preceding trends are different. The similarity between GCN36 and HCN33 can only be coincidental. The three analyses within a single growth band (HP42) show an increase in depletion, consistent with a decline in temperature during the growing season (e.g. summer to autumn). A seasonal effect can be identified in the change across the growth boundary in GCN36 from -1.233 to $-1.503^{o}/_{oo}$, but there is no significant change between the inner and outer layers layers of HCN37.

VARIATIONS IN $^{18}O/^{16}O$ RATIOS WITH AGE

HELIX POMATIA, OLDLANDS WOOD

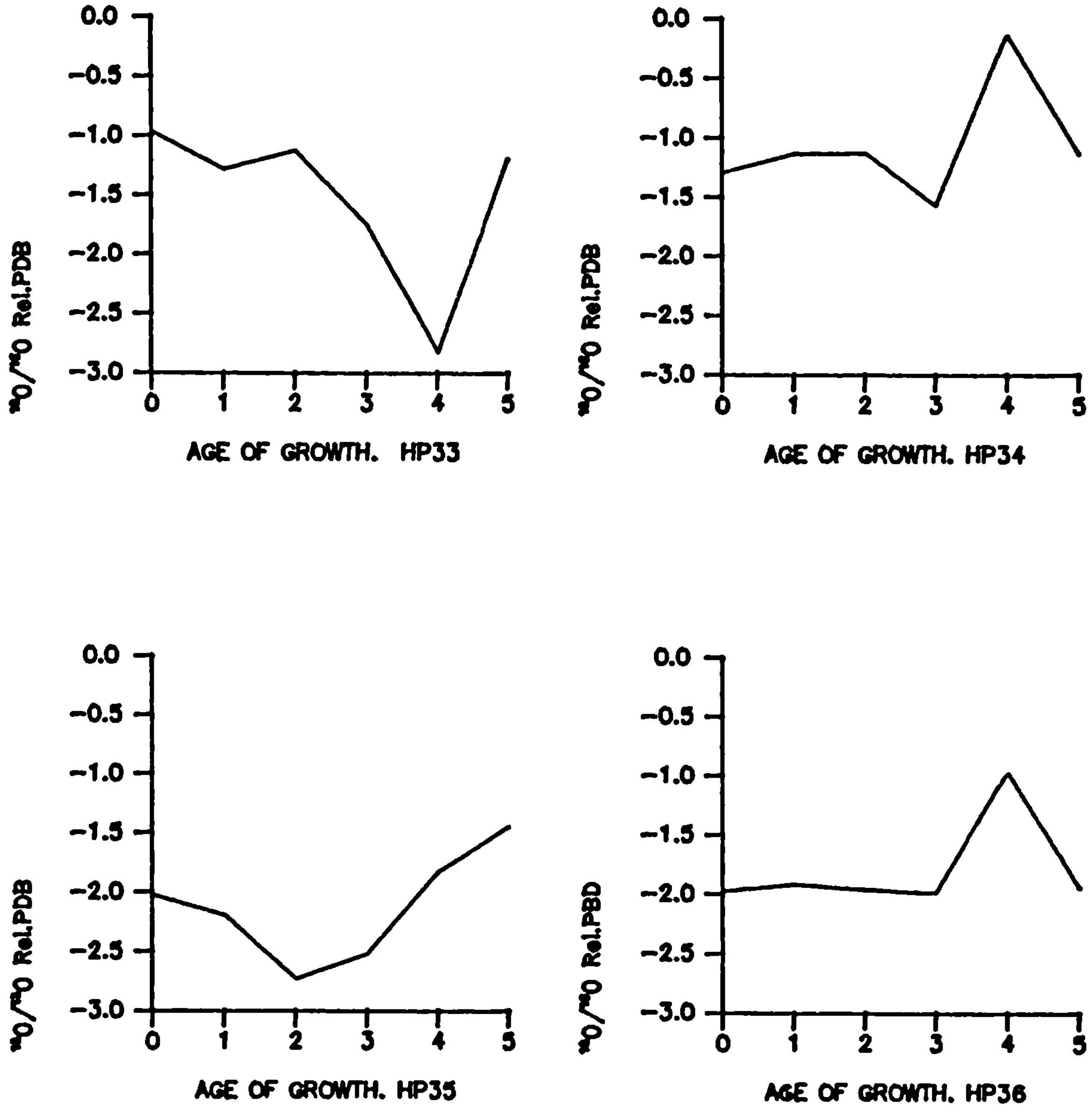


Figure 5.9A. Within shell variations in stable isotope values.

VARIATIONS IN $^{18}O/^{16}O$ RATIOS WITH AGE

HELIX POMATIA, OLDLANDS WOOD

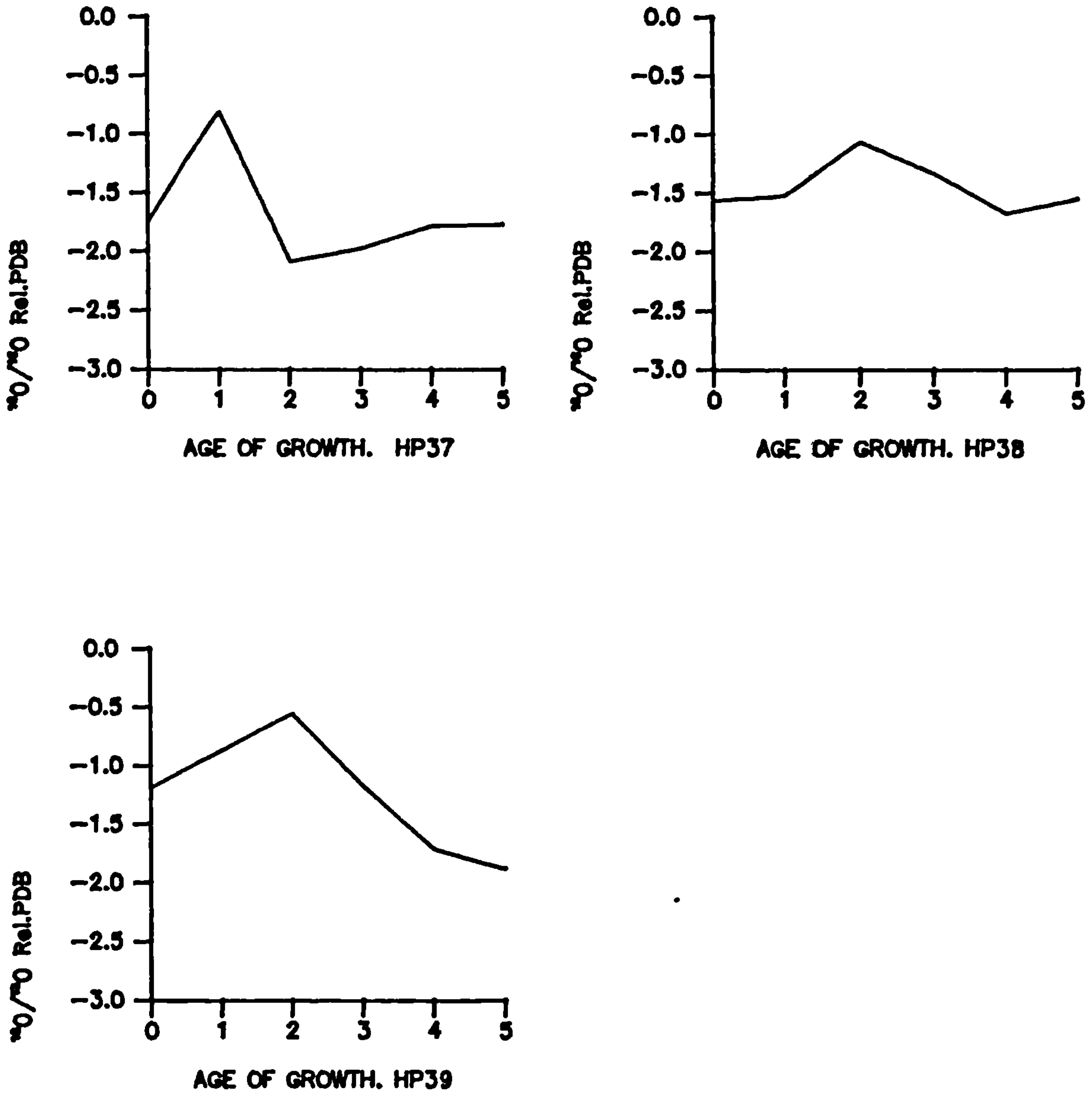


Figure 5.9B. Within shell variations in stable isotope values.

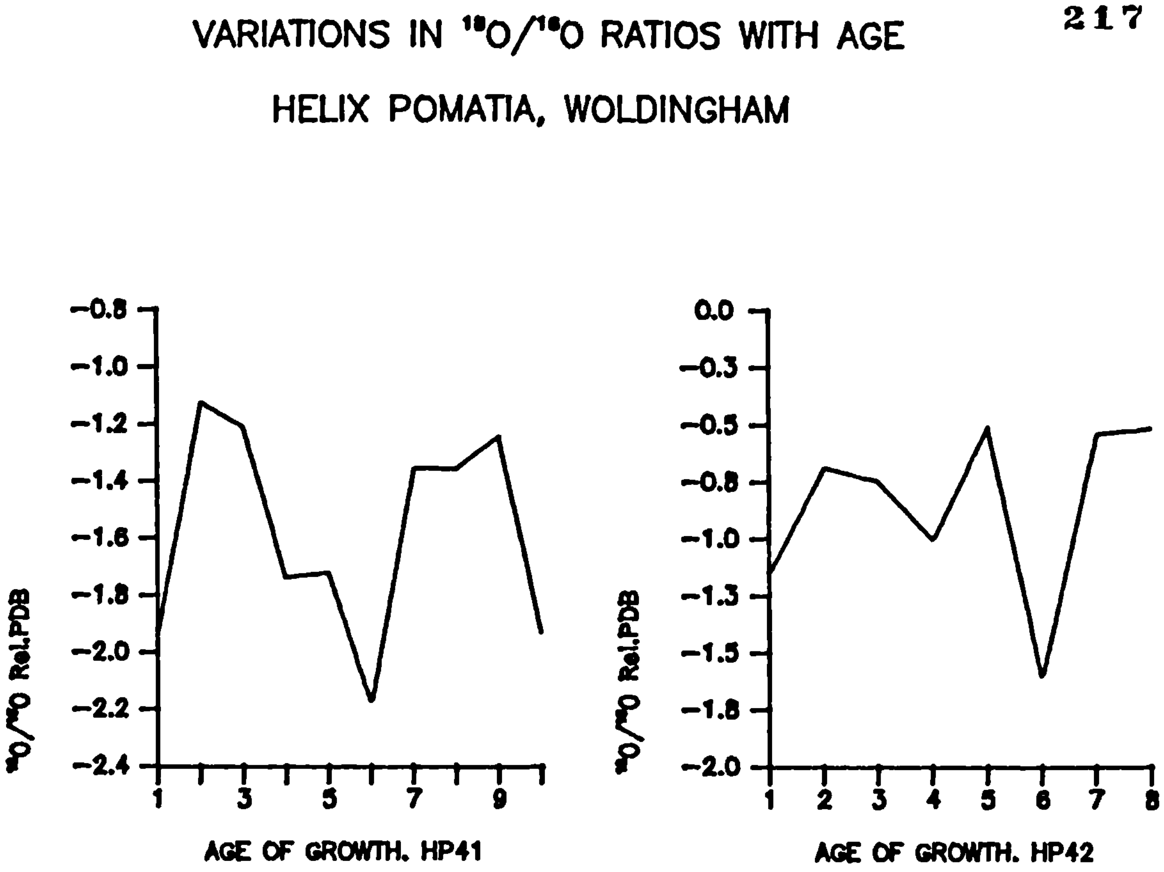


Figure 5.10. Within shell variations in stable isotope values.

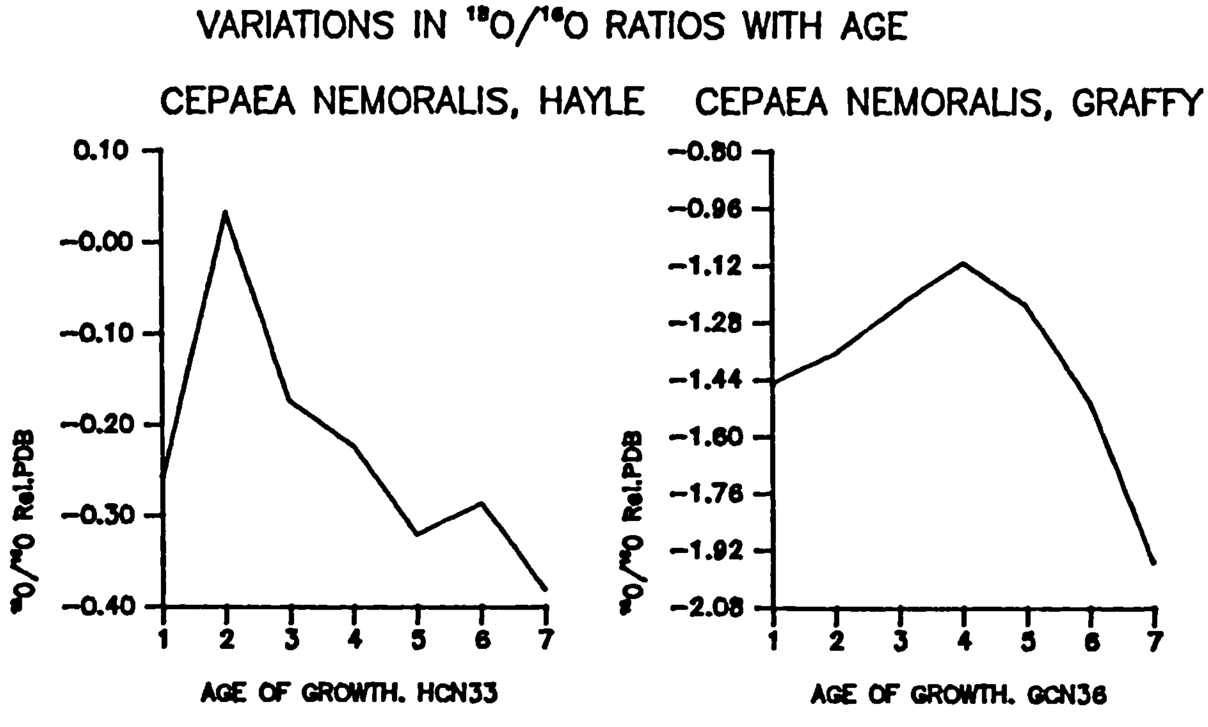


Figure 5.11. Within shell variations in stable isotope values.

The general conclusions from analysis of $\delta^{13}C$ intra-shell variations are that an increase in depletion due to metabolic exchange may occur but it is frequently obscured by stronger influences from changes in habitat or microenvironment. The changes can be particularly prominent across growth boundaries which are taken as indicators of lengthy breaks in growth so that new growth occurred under different external conditions.

The $\delta^{18}O$ variations are controlled by the microclimate which the snail inhabits and also by the exact temperature (e.g. season) during which growth occurred. The results are also subject to changes in site location, with the oceanic effects at Hayle giving distinctly enriched values. Sampling of the shells must have some effect on the results if the sample represents a particular part of the growing season rather than the whole growth period. Variations of 0.35‰ within a growth band of HP42 are nearly equal in magnitude to those observed in HCN33, HCN37 and GCN36.

(ii) Variations between species within one sample site.

The results from the analysis of 32 shells of H.pomatia (HPA, HPB) were supplemented by analysis of three other species from the Oldlands Wood site: Cepaea nemoralis (OCN, 20 shells), Cepaea hortensis (OCH, 20 shells) and Pomatias elegans (OPE, 25 shells). The samples analysed were obtained by sectioning each shell vertically through the columella and were, therefore, representative of the whole shell. The results are given in table 5.4, 5.6 - 5.8 and as a scattergram ($\delta^{13}C$ vs $\delta^{18}O$) in figure 5.12.

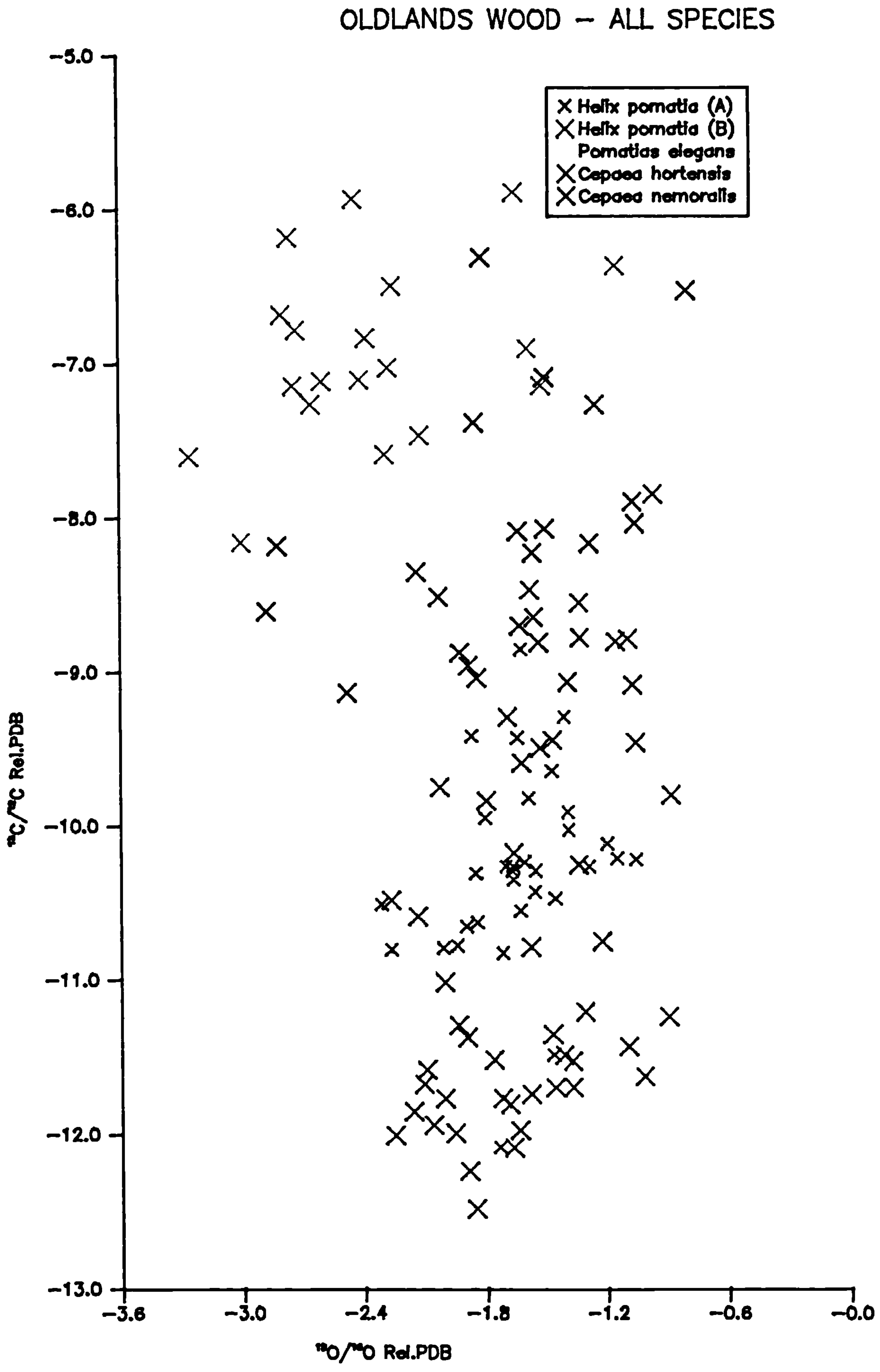


Figure 5.12. Isotopic differences between shells of different species from Oldlands Wood, Surrey.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
OCN 1	-8.183	-2.821	77	248	*	*
2	-8.811	-1.539	77	265	46	*
3	-8.166	-1.282	59	265	43	*
4	-7.897	-1.068	63	268	48	*
5	-8.069	-1.508	84	251	52	*
6	-9.066	-1.398	119	308	43	*
7	-8.699	-1.633	58	272	45	*
8	-9.132	-2.481	87	238	68	*
9	-8.037	-1.057	63	311	42	*
10	-6.525	-0.796	119	302	50	*
11	-8.604	-2.876	67	285	*	*
12	-8.875	-1.928	71	285	42	*
13	-8.511	-2.033	61	287	*	*
14	-6.309	-1.816	70	247	*	*
15	-7.382	-1.854	71	288	*	*
16	-8.087	-1.640	125	172	*	*
17	-8.227	-1.569	65	246	*	*
18	-7.090	-1.506	85	335	*	*
19	-10.254	-1.342	40	192	*	*
20	-8.644	-1.564	69	292	*	*

Table 5.6. Results of chemical and isotopic analyses of shells of *Cepaea nemoralis* from Oldlands Wood, Surrey.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
OCH 1	-7.266	-1.250	100	251	30	*
2	-8.958	-1.887	93	224	65	*
3	-9.460	-1.057	46	207	30	*
4	-9.590	-1.627	61	171	35	*
5	-9.837	-1.801	84	237	55	*
6	-8.787	-1.095	63	211	39	*
7	-9.293	-1.695	49	233	30	*
8	-7.847	-0.965	59	265	31	*
9	*	*	*	*	*	*
10	-10.175	-1.665	65	215	39	*
11	-9.494	-1.534	82	200	59	*
12	-9.444	-1.474	79	230	*	*
13	-8.349	-2.139	162	272	*	*
14	*	*	*	*	*	*
15	-8.468	-1.582	96	208	*	*
16	*	*	*	*	*	*
17	-9.039	-1.846	115	179	*	*
18	-9.748	-2.029	77	197	*	*
19	*	*	*	*	*	*
20	*	*	*	*	*	*
21	-9.086	-1.072	115	179	*	*
22	-8.551	-1.336	96	234	*	*
23	-8.777	-1.334	82	245	*	*
24	-8.804	-1.155	76	245	*	*
25	-9.800	-0.882	87	209	*	*

Table 5.7. Results of chemical and isotopic analyses of shells of *Cepaea hortensis* from Oldlands Wood, Surrey.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
OPE 1	-6.832	-1.902	253	400	65	*
2	-7.141	-1.522	230	426	97	*
3	-6.698	-1.348	169	282	45	*
4	-7.585	-2.291	159	270	54	*
5	-6.900	-1.589	356	244	65	*
6	-7.462	-2.120	158	234	55	*
7	-7.461	-2.581	128	236	41	*
8	-5.887	-1.651	165	244	68	*
9	-7.601	-3.256	240	218	42	*
10	-5.930	-2.439	214	223	45	*
11	-6.482	-1.989	296	174	*	*
12	-6.779	-2.725	202	184	*	*
13	-7.102	-2.412	172	225	*	*
14	-8.156	-2.999	164	174	*	*
15	-6.495	-2.252	147	240	*	*
16	-7.111	-2.599	*	*	*	*
17	-6.780	-2.567	*	*	*	*
18	-6.679	-2.796	*	*	*	*
19	-7.666	-2.531	*	*	*	*
20	-7.143	-2.741	*	*	*	*
21	-6.832	-2.381	156	185	*	*
22	*	*	153	185	*	*
23	-6.178	-2.762	246	167	*	*
24	-6.363	-1.148	159	182	*	*
25	-7.262	-2.652	167	212	*	*
26	-7.024	-2.273	*	*	*	*

Table 5.8. Results of chemical and isotopic analyses of shells of *Pomatias elegans* from Oldlands Wood, Surrey.

The five different groups (HPB, HPA, OCH, OCN, OPE) show some degree of overlap but can be seen to form discrete groups, the greatest degree of overlap being between the two species of Cepaea. The means of the $\delta^{13}C$ and $\delta^{18}O$ values show a progressive enrichment in ^{13}C values from HPB through HPA, OCH, OCN to OPE, the $\delta^{18}O$ values are more homogenous. The fact that the OPE and HPB groups are the extremes of the $\delta^{13}C$ means could be interpreted as evidence for a size (SA/V)/CO_2 exchange effect. However, the data in the preceding section show that the protoconch of the H.pomatia shells is still depleted relative to the P.elegans shells. Further evidence against a size effect is found in the enrichment of the $\delta^{13}C$ values for C.nemoralis relative to the smaller H.pomatia apices. The evidence in the preceding section on intra-shell variations and the next section on variations within one species from different locations confirms the view that $\delta^{13}C$ value is not primarily controlled by metabolism and CO_2 exchange.

Table 5.9 represents a probability matrix based on a two-sample "t" test (95% c.l.). It shows that the $\delta^{13}C$ values for each of the five samples are significantly different. The matrix for $\delta^{18}O$ values shows that only OPE is distinct. The other values are not significantly different from each other. Since all the sample shells come from a limited area the factors controlling $\delta^{18}O$, primarily temperature, should be equal across the area. The depletion of the ^{18}O values associated with P.elegans can be interpreted by reference to its habit of burrowing through friable sub-soil. The time spent in contact with the ground, where temperatures will generally be lower than those of the atmosphere, will give an ^{18}O value depleted relative to the air above ground-level. A significant difference would be expected between HPA and HPB $\delta^{18}O$ values if they represented

	OHPA	OHPB	OFE	OCN	OCH
OHPA	1.000	0.000	0.000	0.000	0.000
OHPB	0.000	1.000	0.000	0.000	0.000
OPE	0.000	0.000	1.000	0.000	0.000
OCN	0.000	0.000	0.000	1.000	0.004
OCH	0.000	0.000	0.000	0.004	1.000

^{13}C

	OHPA	OHPB	OPE	OCN	OCH
OHPA	1.000	0.430	0.000	0.730	0.089
OHPB	0.430	1.000	0.000	0.880	0.032
OPE	0.000	0.000	1.000	0.005	0.000
OCN	0.730	0.880	0.005	1.000	0.150
OCH	0.089	0.032	0.000	0.150	1.000

^{18}O

Table 5.9. For description see third sheet of this table.

	OHPA	OHPB	OPE	OCN	OCH
OHPA	1.000	0.064	0.480	0.016	0.023
OHPB	0.064	1.000	0.000	0.350	0.530
OPE	0.480	0.000	1.000	0.000	0.000
OCN	0.016	0.350	0.000	1.000	0.390
OCH	0.023	0.530	0.000	0.390	1.000

Magnesium

	OHPA	OHPB	OPE	OCN	OCH
OHPA	1.000	0.320	0.880	0.017	0.110
OHPB	0.320	1.000	0.580	0.011	0.910
OPE	0.880	0.580	1.000	0.110	0.470
OCN	0.017	0.011	0.110	1.000	0.000
OCH	0.110	0.910	0.470	0.000	1.000

Strontium

Table 5.9. For description see next sheet.

	OHPA	OHPB	OPE	OCN	OCH
OHPA	1.000	-	-	-	-
OHPB	-	1.000	-	-	-
OPE	-	-	1.000	0.130	0.024
OCN	-	-	0.130	1.000	0.200
OCH	-	-	0.024	0.200	1.000

Iron

Table 5.9. Probability matrix for species from Oldlands Wood, Surrey. OHPA = Helix pomatia (apices); OHPB = H.pomatia (aperture); OPE = Pomatias elegans; OCN = Cepaea nemoralis; OCH = C.hortensis. The samples all have normal distributions, probabilities are based on a two sample "t" test and are considered significantly different when <0.050.

occupation of different habitats. Its absence may be due to the coarse sampling two samples represent or the temperature ranges within the habitats of the two groups obscuring the differences that are seen in the $\delta^{13}C$ values.

The differences between the two Cepaea species may reflect the tendency for C.hortensis to occcupy colder and more shaded niches (see chapter 2.2). The $\delta^{13}C$ and $\delta^{18}O$ values for C.hortensis can be interpreted as cooler conditions with a greater soil-CO_2 component relative to C.nemoralis.

The variations between shell populations within a site show that the microenvironment and habits of the snails are reflected in the $\delta^{13}C$ and $\delta^{18}O$ values. These values represent a combination of the external and internal variables that form the microenvironment and metabolism of the snail. Therefore, stable isotope values, combined with a knowledge of the ecology of different species, allows selection of individuals where the ^{14}C will be least depleted.

(iii) Variations within species from different sites.

Two species were studied in this section: C.nemoralis from three sites (Oldlands Wood (OCN) 20 shells, Graffy (GCN) 24 shells, Hayle Towans (HCN) 35 shells) and P.elegans from two sites (Oldlands Wood, OPE 25 shells, Binnel Point, BPM 10 shells). Shells were sectioned vertically through the columella and half of each shell was used to give a representative sample. All the shells used were from full adult-sized shells and of approximately the same size. The Hayle Towans sample had thicker heavier shells owing to the high levels of $CaCO_3$ available and presumably also the need for extra protection in the abrasive dune environment.

The three samples of Cepaea form discrete groups with little overlap between them, only one point from each sample falling in another group's domain (tables 5.6, 5.10, 5.11, figure 5.13). The $\delta^{18}O$ values reflect the contrasting areas the samples are taken from, particularly the oceanic $\delta^{18}O$ values of HCN. The groups have greater overlap if only the $\delta^{13}C$ values are considered as HCN then overlaps with the other two groups. Table 5.12 shows a probability matrix for the samples and confirms that each is significantly different for both $\delta^{13}C$ and $\delta^{18}O$ values.

The range of depletion from -6.3 to -11.8‰ (3.5‰) is similar to that for the four different species from Oldlands Wood (see above), namely -5.8 to -12.4‰ (6.6‰). This adds further weight to the idea that the environmental niche of each species at each site is important in determining the $\delta^{13}C$ and $\delta^{18}O$ values.

The $\delta^{13}C$ and $\delta^{18}O$ values for the $CaCO_3$ material on which these samples lived were also measured. The results are given in table 5.13. The results from Oldlands site 2 (OLD2), the sample collection site, show the $CaCO_3$ to be depleted relative to the chalk from nearby outcrops. This indicates that the $CaCO_3$ undergoes fractionation or diagenetic alteration during the weathering process.

It has been argued that if the shells contain a significant $CaCO_3$-derived carbon component it should be reflected in the stable isotope values of the shells. The shells from Graffy ($CaCO_3$ $\delta^{13}C$ = -10.649‰) should then have $\delta^{13}C$ values that show a greater depletion than do those from Hayle (c.+1.1‰) or Oldlands (c.+0.7‰). The mean $\delta^{13}C$ value for the Graffy samples is depleted

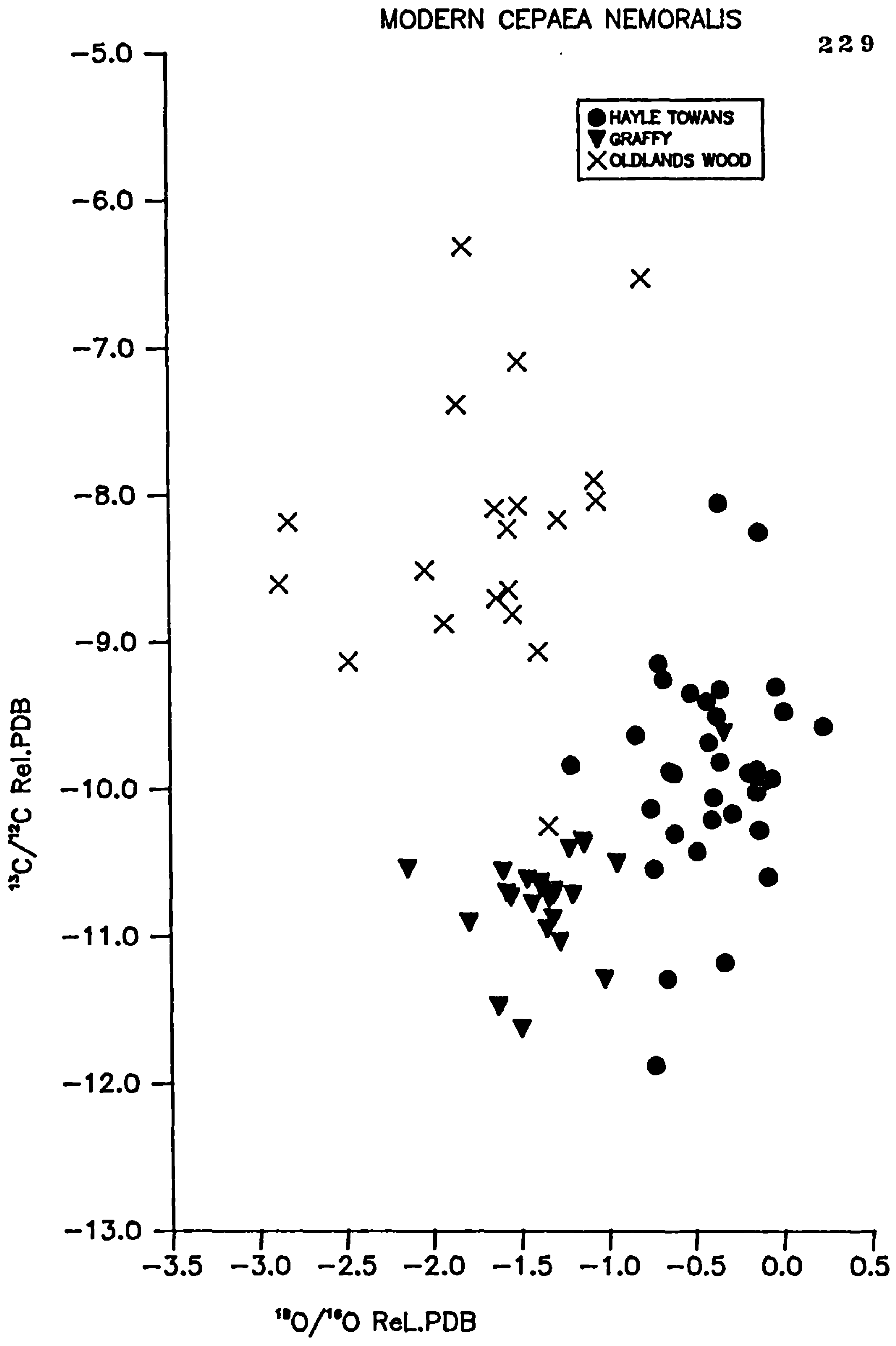


Figure 5.13. Variations in stable isotope values between shells of Cepaea nemoralis from different modern sites.

Sample Code		$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
HCN	1	-10.425	-0.486	62	1626	38	*
	2	-9.350	-0.520	78	1582	55	*
	3	-10.134	-0.754	69	2113	59	*
	4	-8.253	-0.132	65	1563	54	*
	5	-9.507	-0.370	88	1767	62	*
	6	-9.405	-0.427	77	1575	45	*
	7	-9.894	-0.623	105	1762	52	*
	8	-10.280	-0.133	79	1534	46	*
	9	-9.255	-0.679	121	2081	49	*
	10	-9.327	-0.350	74	2040	41	*
	11	-10.169	-0.283	67	1539	*	*
	12	-9.947	-0.098	87	2021	*	*
	13	-9.578	0.230	*	*	*	*
	14	-10.596	-0.087	65	1767	*	*
	15	-10.303	-0.616	77	1912	*	*
	16	-9.882	-0.646	*	*	*	*
	17	-9.839	-1.213	*	*	*	*
	18	-9.893	-0.191	77	2113	*	*
	19	-9.684	-0.415	68	1931	*	*
	20	-9.149	-0.709	73	1761	*	*
	21	-8.054	-0.357	*	*	*	*
	22	-9.871	-0.147	81	1501	*	*
	23	-9.308	-0.037	81	1869	*	*
	24	-9.816	-0.353	90	1999	*	*
	25	-10.059	-0.389	*	*	*	*
	26	-9.476	0.007	*	*	*	*
	27	-11.289	-0.664	*	*	*	*
	28	-11.178	-0.331	*	*	*	*
	29	-9.635	-0.839	*	*	*	*
	30	-11.878	-0.735	*	*	*	*
	31	-10.022	-0.147	*	*	*	*
	32	-10.543	-0.740	*	*	*	*
	33	-9.930	-0.065	*	*	*	*
	34	-9.903	-0.171	*	*	*	*
	35	-10.207	-0.399	*	*	*	*

Table 5.10. Results of chemical and isotopic analyses of shells of *Cepaea nemoralis* from Hayle Towans, Cornwall.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
GCN 1	-10.351	-1.148	409	146	41	*
2	-11.035	-1.280	784	128	40	*
3	-10.405	-1.225	579	113	28	*
4	-10.633	-1.390	491	123	29	*
5	-10.949	-1.354	799	103	27	*
6	-10.541	-2.139	146	120	41	*
7	-10.879	-1.319	177	103	28	*
8	-10.778	-1.435	67	105	31	*
9	-10.690	-1.313	141	104	33	*
10	-10.734	-1.558	78	122	36	*
11	-11.473	-1.634	*	*	*	*
12	-10.504	-0.950	70	114	*	*
13	-9.616	-0.331	*	*	*	*
14	-10.746	-1.341	*	*	*	*
15	-10.372	-1.140	190	98	*	*
16	-10.716	-1.206	227	110	*	*
17	-11.626	-1.500	*	*	*	*
18	-10.559	-1.604	480	73	*	*
19	-10.904	-1.796	937	90	*	*
20	-10.721	-1.317	166	91	*	*
21	-11.289	-1.024	177	98	*	*
22	-10.652	-1.397	213	98	*	*
23	-10.614	-1.465	629	83	*	*
24	-10.704	-1.583	381	86	*	*

Table 5.11. Results of chemical and isotopic analyses of shells of <u>Cepaea nemoralis</u> from Graffy, Co.Mayo, Eire.

	OCN	HCN	GCN
OCN	1.000	0.000	0.000
HCN	0.000	1.000	0.000
GCN	0.000	0.000	1.000

^{13}C

	OCN	HCN	GCN
OCN	1.000	0.000	0.023
HCN	0.000	1.000	0.000
GCN	0.023	0.000	1.000

^{18}O

	OCN	HCN	GCN
OCN	1.000	0.650	0.000
HCN	0.650	1.000	0.000
GCN	0.000	0.000	1.000

Magnesium

	OCN	HCN	GCN
OCN	1.000	0.000	0.000
HCN	0.000	1.000	0.000
GCN	0.000	0.000	1.000

Strontium

	OCN	HCN	GCN
OCN	1.000	0.540	0.000
HCN	0.540	1.000	0.000
GCN	0.000	0.000	1.000

Iron

Table 5.12A. Probability matrix for *Cepaea nemoralis* from different modern sites in the British Isles. OCN = Oldlands Wood, Surrey; HCN = Hayle Towans, Cornwall; GCN = Graffy, Co.Mayo, Eire. The samples all have normal distributions, probabilities are based on a two sample "t" test and are considered significantly different when <0.050.

	E	M	B F
O	1)	.910	0.130
B M	0.910	.0	0.51
B F	0.13	0.⁼1	1 0 0

¹ C

	E	B M	F
O	0)	0.)0	0
PM	(	1.0 0	0 ⁼
F	0	0 15	1

¹ O

	OPE	B M	B F
OPE	1.000	0.001	0.710
BPM	0.001	1.000	0.000
BPF	0.7 0	0.000	1.000

Magnesium

	PE	PM	BFF
OFE	1.000	0.001	0 CC
BPM	0.001	1.)00	0.025
BPF	0.000	0.0 5	1. 0

Strontiu

	OPE	BPM	BF
OPE	1.0 0	0. 00	0.001
BPM	0.0C0	1 0	0.014
B F	0.001	0.014	.000

Ir n

	OPE	BPM	PF
OPE	1.000	-	-
BPM	-	1. 0	
F	-	0.6	.

Ma ga e

T le 5.12B. P b bility ma r x for Po atia <u>e ga s</u> from d f ites in t e Br ti I s. OPE 01 W Surre ; M = n el nt, I ern F Po t Io (Fos)· T e p es a l av a uti , r a l t e e a a re c r f t f w 0 0.

Type	Sample	Site	$\delta^{13}C$	$\delta^{18}O$	$^{14}C^{(1)}$
Chalk	Ch.S3	Oldlands	1.676	-1.819	0.000
"	Ch.S4	"	2.087	-1.752	0.000
"	OL2/3-10	"	0.777	-2.113	"
"	OL2/3-10	"	0.838	-1.992	"
"	OL2/10-15	"	0.522	-2.168	"
"	OL2/10-15	"	0.992	-2.055	"
Calc.	HT5/0-5	Hayle Towans	1.136	1.999	-
Sand	HT5/0-5	"	1.262	2.091	-
"	HT5/0-5	"	1.154	2.073	-
"	HT5/5+	"	1.119	2.065	0.460
"	HT5/5+	"	1.176	2.079	-
"	HT2/0-8	"	0.639	1.883	-
"	HT2/0-8	"	0.368	1.833	-
"	HT2/8-20+	"	0.934	1.995	-
"	HT2/8-20+	"	0.769	1.988	-
Tufa	TCW	Caerwys	-9.681	-5.776	0.770
"	TG	Graffy	-10.649	-5.116	-
"	NCT	Newlands Cross	-8.377	-5.307	0.820
"	INCHT	Inchrory	-8.590	-7.282	0.860
"	CASTT	Castlethorpe	-9.317	-5.741	-
"	CBTT1	Carrowmore	-9.653	-5.030	-
"	CBTT2	"	-9.570	-5.026	-
"	CBMT1	"	-9.597	-4.986	-
"	CBMT2	"	-9.596	-4.926	-
"	CBBT1	"	-9.761	-4.926	-
					-

(1) Relative to contemporary wood, or pre-bomb wood (HT5/5+).

Table 5.13. ^{13}C, ^{14}C and ^{18}O values of calcium carbonate source materials analysed for this study.

by 0.842°/₀₀ relative to the Hayle value, but the difference between Hayle and Oldlands is 1.659°/₀₀ although the $CaCO_3$ sources have very similar $\delta^{13}C$ values. Assuming a 10-20% $CaCO_3$ bedrock component in the shell the 10°/₀₀ difference between the Graffy and Hayle $CaCO_3$ sources should give a difference of 1-2°/₀₀ in the final shell $\delta^{13}C$ values. The difference between Oldlands and Hayle shells, based on the same assumptions, should be less than 0.1°/₀₀. These results point to an extra factor. A large increase in the bedrock component of the Oldlands shell would not produce the necessary difference. Therefore a change in the balance between the plant derived and atmospheric/soil-CO_2 derived carbon must also be involved.

The intake of gaseous CO_2 will increase whist the snail is active. If the availability of, or access to, the bedrock $CaCO_3$ is limited then the snail would require greater activity to obtain the required amount of calcium. The snails from Hayle and Graffy were all collected from areas in which there were large areas of open sub-soil. At Hayle 70% of the sub-soil was composed of shell fragments, whilst at Graffy the subsoil included areas of exposed tufa (>97% $CaCO_3$). The Oldlands Wood site had a layer of leaf and plant litter over the soil which isolated the larger species from direct access to particulate chalk. The increased activity necessary at Oldlands could explain the enrichment in the $\delta^{13}C$ values observed in the shells. The thick litter layer is due to the Oldands site being open woodland. Therefore, it is possible that $\delta^{13}C$ values can be used as indicators of woddland and open environments (see below). The increased activity levels cannot explain all the enrichment, P.elegans has the highest values at Oldlands (and also at Binnel Point) but has direct access to chalk material because of its burrowing in loose soil.

Comparison of the results from the analysis of P.elegans gave less clear results (table 5.8, 5.9, 5.12, 5.14). Although the $\delta^{13}C$ values were not significantly different the two samples groups were rather diffuse. In the case of the Binnel Point sample it was possible to produce two sub-groups that were significantly different (-6.242 and -7.905 $^{o}/_{oo}$). The $\delta^{18}O$ values for the same sub-goups were also significantly different, as were the magnesium and strontium contents (see below). The results suggest that the apparently homogeneous living population was in fact occupying two different microenvironmental niches.

Pomatias elegans is of the sub-class Prosobranchia and consequently the shell is sealed by an operculum. The operculum is the only part of a terrestrial shell that is naturally calcitic. Stable isotope analysis of fossil and modern shell opercula from Binnel Point gave values that are similar to those for the associated shells (table 5.14). The analyses represent 5-6 opercula because of their low weight. The modern sample had $\delta^{13}C$ and $\delta^{18}O$ values in the upper quartile of the shell population values, whilst the fossil samples were enriched relative to any of the fossil shell population. The differences can be explained by the fractionation that occurs betwen aragonite and calcite. Rubinson & Clayton (1969) measured a fractionation of +1.8$^{o}/_{oo}$ for ^{13}C and report values (Tarutani et al. 1969) of +0.6$^{o}/_{oo}$ for ^{18}O. The difference between the values of the opercula and shells are within these fractionation values.

Similar subdivisions based on microenvironmental changes were observed within the Hayle Towans site 5 C.nemoralis population. The 35 shells were divided into three groups on the basis of their

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
BPF 1	-6.804	-1.590	254	443	208	25
3	-7.069	-0.610	147	391	98	9
4	-6.508	-0.924	130	283	74	11
6	-6.137	-1.042	173	469	104	13
7	-6.589	-1.096	228	465	160	11
9	-6.986	-1.277	185	434	134	16
11	-6.436	-0.719	171	466	154	13
12	-6.587	-1.120	198	472	214	16
14	-7.315	-2.024	222	422	120	9
16	-6.524	-1.030	215	361	212	15
BPFop 1	-5.863	-0.500	1367	342	101	25
2	-5.886	-0.489	*	*	*	*
BPMop 1	-6.019	-0.356	2402	444	56	25

Table 5.14A. Results of chemical and isotopic analyses of fossil shells and opercula of Pomatias elegans from Binnel Point, Isle of Wight.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
BPM 1	-6.098	-0.389	306	408	130	17
2	-6.295	-0.462	344	242	119	12
3	-5.914	-1.375	271	362	97	14
4	-5.744	-0.808	347	239	93	16
5	-7.621	-0.497	171	427	64	12
6	-7.989	-0.491	296	429	81	14
7	-6.621	-1.180	422	284	114	23
8	-7.791	-0.051	312	335	125	18
9	-6.783	-0.659	256	374	61	8
10	-8.219	-0.705	278	378	86	12

Table 5.14B. Results of chemical and isotopic analyses of modern shells of *Pomatias elegans* from Binnel Point, Isle of Wight.

banding morphs. The groups were unbanded (19 shells; 17 yellow, 2 pink), three- or four-banded (8 shells; pink or white) and five-banded (8 shells; 6 yellow, 2 pink). The $\delta^{13}C$ and $\delta^{18}O$ values for each group were then compared. The five-banded morph group were significantly different from the other two groups. The unbanded and five-banded groups were almost entirely yellow suggesting that banding rather than background colour are important. The $\delta^{18}O$ values are not significantly different, the expected result in the limited collection area. The selection and adaptation to different environmental conditions (discussed in chapter 3.4) that are associated with the different morphs are also reflected in the $\delta^{13}C$ values.

(iv) Analysis of the organic shell matrix.

Six samples of acid insoluble organic matrix were analysed for $\delta^{13}C$ values. The results are given in table 5.15.

Sample Code	$\delta^{13}C$ (‰)
HCN 25	-22.044
GCN 37	-22.883
OCN 21	-22.951
HCN 36	-22.362
OCH 36	-22.192
OPE$_{(1)}$	-22.781

(1) Sample containing five shells

Table 5.15. $\delta^{13}C$ results of the analysis of acid insoluble organic matrix.

The range of values was very narrow (0.907$^{o}/_{oo}$) for samples from three sites and three different species. Neither environmental variation nor the $\delta^{13}C$ of the $CaCO_3$ source appears to have any measurable effect. The values are similar to those obtained by Burleigh & Kerney (1982) of -23.98$^{o}/_{oo}$ for P.elegans and -23.30$^{o}/_{oo}$ for C.nemoralis organic matrices.

5.32 Fossil Samples

(i) Variations within shells

Variations in fossil shells were studied by analysis of shells from Netanya on the Mediterranean coast of Israel. Chapter 3.2 discussed the input sources for shells and considered the work of Magaritz *et al.* (1981) on the seasonal variations in shells of X.vestalis. Shells of this species were collected from four horizons at Gevat Olga, Netanya (OL20-23). Since the snails are annuals the inner and outer whorls should represent the winter and summer growths respectively. Magaritz *et al.* (1981) found a change in the $\delta^{13}C$ values from -7$^{o}/_{oo}$ in the winter months to -9.5$^{o}/_{oo}$ in the summer. The $\delta^{18}O$ values ranged from +0.2 to -0.55$^{o}/_{oo}$ during the winter and +0.3 to +2.0 $^{o}/_{oo}$ in the summer. Analysis of modern samples from Ashquelon in southern Israel gave a mean $\delta^{13}C$ value of -8.83$^{o}/_{oo}$ and $\delta^{18}O$ values of +1.59 to 3.36$^{o}/_{oo}$ for summer growth. The winter values were -6.39$^{o}/_{oo}$ and +1.48 to -0.70$^{o}/_{oo}$ respectively (Heller & Magaritz 1983; Magaritz *pers. comm.* 1985).

Four or five samples from each horizon were cleaned and the apex and inner whorls removed to former the "winter" sample. The last half of the ultimate whorl was removed to form the "summer" sample. The results are given in table 5.16.

Sample	Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
OL20	1A	-6.03	+1.24	*	*	*	*
	1B	-7.09	+1.16	*	*	*	*
	2A	-4.36	+0.82	*	*	*	*
	2B	-5.97	+1.07	*	*	*	*
	3A	-5.96	+0.26	*	*	*	*
	3B	-7.42	-0.32	*	*	*	*
	4A	-5.33	+0.71	*	*	*	*
	4B	-6.27	+0.69	*	*	*	*
OL21	1A	-5.42	-1.68	*	*	*	*
	1B	-7.03	-0.17	*	*	*	*
	2A	-5.21	-0.17	*	*	*	*
	2B	-6.63	-0.29	*	*	*	*
	3A	-5.28	-2.09	*	*	*	*
	3B	-6.04	-2.51	*	*	*	*
	4A	-5.24	-1.52	*	*	*	*
	4B	-6.47	-1.38	*	*	*	*
OL22	1A	-8.02	+2.15	*	*	*	*
	1B	-7.12	+0.95	*	*	*	*
	2A	-7.55	+1.60	*	*	*	*
	2B	-8.06	+1.40	*	*	*	*
	3A	-6.41	+2.40	*	*	*	*
	3B	-8.26	+1.09	*	*	*	*
	4A	-3.68	+1.41	*	*	*	*
	4B	-3.68	+0.22	*	*	*	*
OL23	1A	-5.87	+0.41	*	*	*	*
	1B	-6.42	+0.05	*	*	*	*
	2A	-5.32	+0.05	*	*	*	*
	2B	-6.35	-0.84	*	*	*	*
	3A	-4.47	+0.79	*	*	*	*
	3B	-5.10	+0.56	*	*	*	*
	4A	-4.67	+1.35	*	*	*	*
	4B	-5.28	+0.28	*	*	*	*
	5A	-5.42	+0.60	*	*	*	*
	5B	-6.19	-0.04	*	*	*	*

Table 5.16. Results of isotopic analysis of shells of _Xeropicta vestalis_ from four contexts at Netanya, Israel.

A = winter
B = summer

The $\delta^{13}C$ values are enriched in the inner whorls relative to the outer one, as was observed by Magaritz (Magaritz et al. 1981; Heller & Magaritz 1983). However, the $\delta^{18}O$ values do not vary as expected from the earlier studies with the exception of the shells from sample OL21 which showed evidence of dissolution and was cemented to sand grains. Depletion of ^{13}C is expected in the summer whorls if soil CO_2 is important, as more CO_2 will be drawn throught the soil with moisture in the hotter weather. The $\delta^{18}O$ values should increase in the summer with the higher temperatures.

The four horizons represent two cycles of organic-rich and sand layers which are taken as evidence of fluctuations in the moisture or rainfall that was available. The suggested climatic variations should be reflected in the $\delta^{13}C$ and $\delta^{18}O$ values because of the less extreme summer conditions. Samples OL21 and OL23 show less depleted $\delta^{13}C$ and $\delta^{18}O$ values but the differences are not large enough to be significantly different when the within-sample variation is considered. The variation between the organic and sand horizons may be masked by OL21, the sample that had been subjected to dissolution and cementation.

The results of the analysis of these snail samples suggests that yearly climatic variations within a shell and differences between shells deposited in different climates can be detected in the $\delta^{13}C$ and $\delta^{18}O$ values of shells.

(ii) Variations between species within one sample site.

Study of the variations between species from one site was undertaken on shells from three sites: Caerwys (CW, three species), Newlands

Cross (NC, two species) and Carrowmore (CB, two species from each of three horizons within a sequence). These sites are described in detail in chapter 2.4.

Caerwys

The 13 shells that were analysed consisted of eight C.nemoralis (CWCN), three C.hortensis (CWCH) and two Arianta arbustorum (CWAA). The results are given in table 5.17 and figure 5.14. The small sample sizes for CWCH and CWAA allowed only tentative conclusions to be drawn. The $\delta^{13}C$ and $\delta^{18}O$ values for the three species are not significantly different, and the results are quite closely grouped. Visual examination of figure 5.14 suggests that the CWAA results are confined to the depleted ^{13}C and enriched ^{18}O side of the centroid of CWCN and would probably be a distinct group if further data were available.

Newlands Cross

Ten shells were analysed (eight C.nemoralis (NCCN) and two C.hortensis (NCCH)). The results are given in table 5.18 and figure 5.15. The small sample size of NCCH again reduces the significance of the conclusions. The $\delta^{13}C$ and $\delta^{18}O$ values of the two species are not significantly different. The sample was taken from a small area (0.7m x 0.7m) and the shells were on a buried land-surface and apparently in their original positions (i.e. undisturbed by soil development or slope soil movement). The results are probably representative of larger samples and imply that the same stable environment was occupied by the two species.

Carrowmore

Samples were collected and analysed from three organic rich horizons

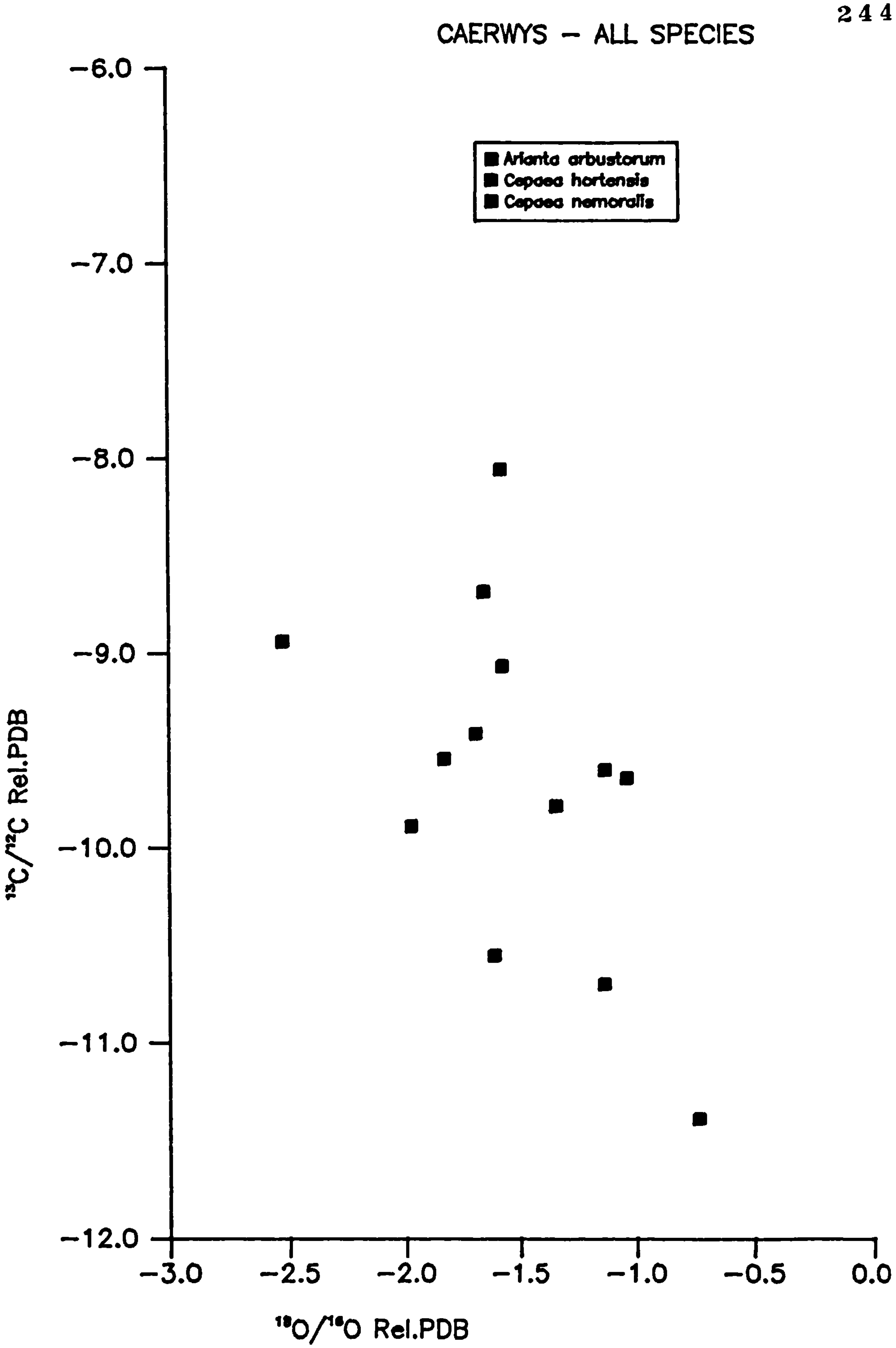


Figure 5.14. Variations in stable isotope values between shells of different species from the fossil site at Caerwys, Clwyd.

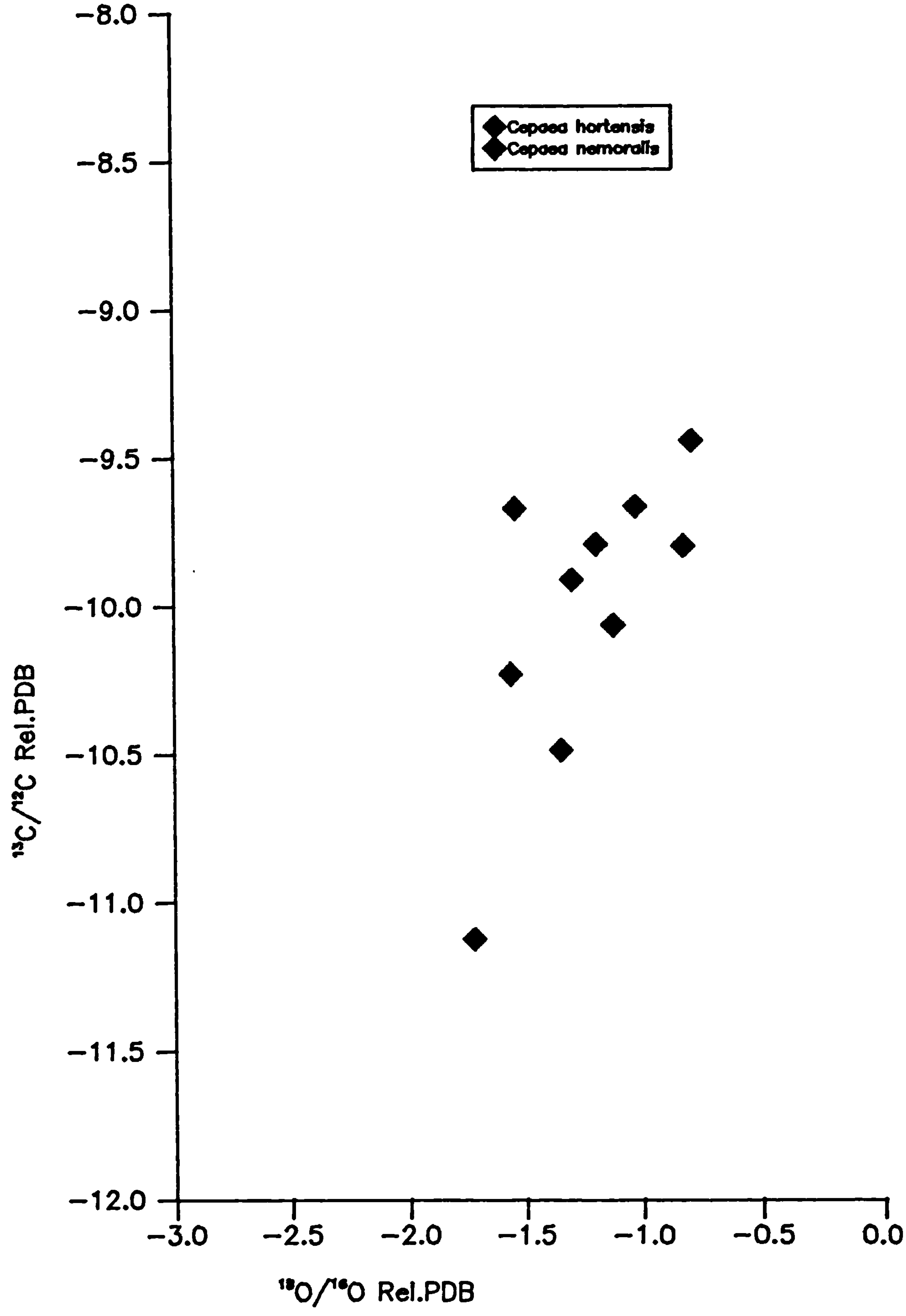


Figure 5.15. Variations in stable isotope values between shells of different species from the fossil site at Newlands Cross, Dublin.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
		Cepaea nemoralis				
CW 3	-9.601	-1.132	53	21	45	16
7	-9.542	-1.833	40	47	72	18
14	-8.684	-1.658	50	70	89	22
23	-9.643	-1.039	66	5	138	22
26	-10.552	-1.617	42	56	102	21
31	-9.889	-1.976	49	118	54	17
35	-8.939	-2.526	71	53	84	17
37	-9.068	-1.579	39	25	81	24
		Cepaea hortensis				
CW 9	-9.414	-1.693	46	56	72	21
30	-8.057	-1.584	78	5	136	36
		Arianta arbustorum				
CW 2	-9.782	-1.343	73	39	96	19
4	-10.698	-1.139	60	49	138	22
8	-11.385	-0.736	55	83	90	19

Table 5.17. Results of chemical and isotopic analyses of shells from Caerwys, Clwyd.

Sample Code		δ^{13}C	δ^{18}O	Mg	Sr	Fe	Mn
			Cepaea nemoralis				
NC	2	-11.124	-1.723	87	373	89	17
	4	-10.486	-1.344	94	375	93	20
	7	-9.910	-1.295	96	364	91	20
	12	-9.441	-0.789	115	195	156	31
	13	-9.669	-1.544	88	417	106	17
	14	-9.796	-0.826	90	441	135	19
	19	-10.063	-1.121	97	485	104	22
	22	-9.790	-1.192	85	490	96	20
			Cepaea hortensis				
NC	1	-9.663	-1.026	255	227	169	16
	25	-10.229	-1.565	100	446	130	19

Table 5.18. Results of chemical and isotopic analyses of shells from Newlands Cross, Dublin, Eire.

separated by clean tufa. These horizons were 141-143cm (CBT_1), 164-170cm (CBM_1) and 182-186cm (CBB_1) below the present ground surface. C.nemoralis and C.hortensis were present in all three horizons. Horizons CBT_2 and CBM_2 were the tufa between the organic horizon and these produced no shells of Cepaea. The results are given in table 5.19 and figure 5.16.

Ten shells from CBT_1 were analysed, six C.nemoralis and four C.hortensis, including analysis of the apex and ultimate whorl of one C.nemoralis shell. The $\delta^{13}C$ and $\delta^{18}O$ values are generally confined within a narrow range, the exception being $\delta^{13}C$ values for C.hortensis. There is no significant difference between the stable isotope values for the two species. The analysis of the apex and ultimate whorl from CBT22 showed a difference of 0.300 and 0.450°/₀₀ for $\delta^{13}C$ and $\delta^{18}O$ respectively. These are similar to the other analyses on intra-shell variation for C.nemoralis (see above).

Analysis of ten shells from CBM_1 (five C.nemoralis, five C.hortensis) showed a similar pattern with the distribution of both isotope ratios being very narrow for both species. Despite the narrow ranges the values for the two species show no significant difference.

Twenty shells (ten of each species) were analysed from CBB_1. The ranges of values were greater than for CBM_1, but the similarity of the standard deviations suggests this is only due to the larger sample size. The range of $\delta^{13}C$ values for C.hortensis is greater than that for C.nemoralis but probably not significantly so. As with the other samples there is no significant difference between the values for the two species.

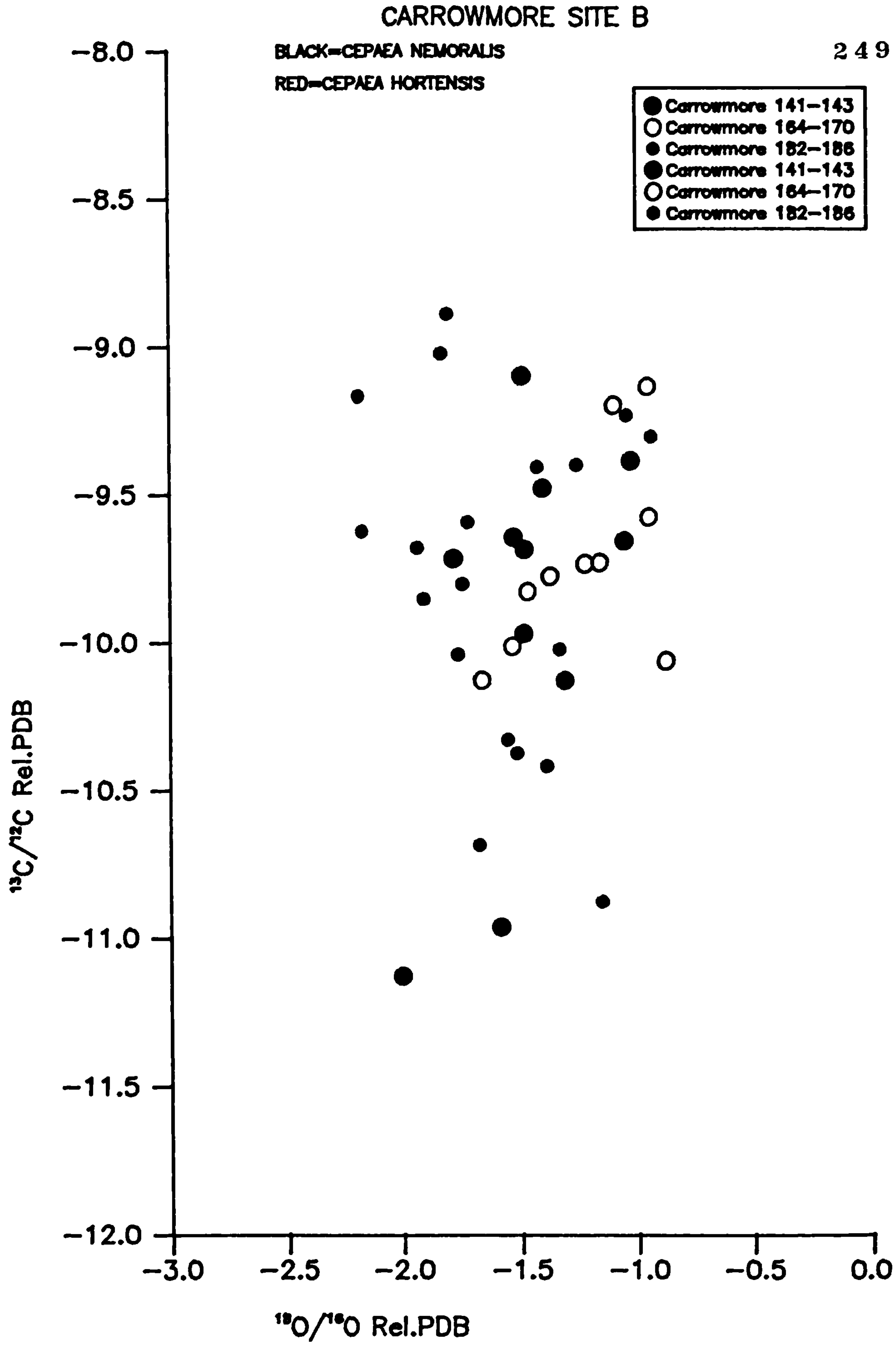


Figure 5.16. Variations in stable isotope values between shells of species and from three contexts, Carrowmore, Co.Mayo.

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
		Cepaea nemoralis				
CBT 1	-9.969	-1.488	47	72	*	*
4	-9.477	-1.405	26	159	*	*
11	-9.656	-1.058	38	169	*	*
20	-9.642	-1.531	36	136	*	*
23A	-9.385	-1.029	*	*	*	*
23B	-9.683	-1.485	*	*	*	*
28	-9.714	-1.785	129	214	*	*
		Cepaea hortensis				
CBT 2	-9.097	-1.492	42	46	*	*
12	-10.128	-1.312	28	69	*	*
19	-11.128	-2.003	41	42	*	*
21	-10.963	-1.587	*	*	*	*
		Cepaea nemoralis				
CBM 7	-9.197	-1.102	290	52	*	*
8	-10.062	-0.881	40	70	*	*
9	-9.728	-1.164	34	89	*	*
42	-9.732	-1.227	34	66	*	*
43	-9.774	-1.376	30	67	*	*
		Cepaea hortensis				
CBM 11	-10.126	-1.666	49	69	*	*
12	-9.575	-0.951	39	46	*	*
14	-10.011	-1.537	45	126	*	*
24	-9.133	-0.956	55	72	*	*
32	-9.825	-1.471	40	75	*	*

Table 5.19A. Results of chemical and isotopic analyses of shells from Carrowmore, Site B, Co.Mayo, Eire. (From three contexts.)

Sample Code	$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
		Cepaea nemoralis				
CBB 3	-9.166	-2.196	48	143	33	*
10	-9.622	-2.181	35	46	55	*
12	-9.406	-1.428	65	97	64	*
15	-10.039	-1.768	52	151	45	*
16	-9.231	-1.047	69	215	40	*
19	-10.328	-1.558	75	63	*	*
20	-10.373	-1.519	103	115	*	*
31	-9.800	-1.748	81	113	*	*
37	-9.399	-1.260	66	96	*	*
38	-9.021	-1.834	74	184	*	*
		Cepaea hortensis				
CBB 1	-10.417	-1.391	69	140	49	*
2	-9.662	-1.509	72	123	39	*
4	-9.678	-1.936	65	67	30	*
14	-9.851	-1.910	70	130	44	*
18	-9.303	-0.940	85	164	58	*
23	-8.887	-1.807	93	93	*	*
24	-10.877	-1.156	74	128	*	*
30	-9.591	-1.724	88	152	*	*
32	-10.022	-1.335	68	69	*	*
35	-10.684	-1.679	80	134	*	*

Table 5.19B. Results from chemical and isotopic analyses of shells from Carrowmore Site B, Co.Mayo, Eire. (From three contexts.)

When the samples of each species from the different horizons are compared the $\delta^{13}C$ values are seen to be very similar. The probabilities for C.hortensis are lower than for C.nemoralis but there is still no significant difference between the samples from the three horizons. The values for $\delta^{18}O$ are more difficult to interpret, C.hortensis samples show no significant differences between the horizons but C.nemoralis has only a low probability of the samples being the same.

If the results for each species from the three horizons are combined there is no significant difference between the $\delta^{18}O$ values but only a low probability that the $\delta^{13}C$ values are the same.

The overall interpretation of these results suggests that despite the destruction of environments by the development of tufa over the ground surface the new environment that developed after deposition ceased was very similar to its predecesor. This suggests that the period between the horizons may have been short, perhaps only a few years. If inundation by tufa is quite localised then the surrounding environment that remains unaffected can quickly recolonise the tufa with a virtually unaltered vegetation. The similarity of the results for the two species suggests that they are occupying almost identical niches within the environment. The apparent difference in the $\delta^{18}O$ values for C.nemoralis, when no change is observed for C.hortensis, indicates that these results may be an artefact of the statistical analysis.

The similarity of the stable isotope values for the different species is interesting when considered with the ecological differences discussed in chapter 2.23. At Caerwys C.nemoralis, C.hortensis and

A.arbustorum were found together within the 25m long horizon. Either there were a number of microenvironments within this area or the species were more adaptable than their modern counterparts appear to be. The mixing of two species is seen within a very small area at Newlands Cross where the sample was collected from 0.50m^2 of a buried land-surface. There could have been no environmental changes within this area and assuming that the shells had not been transported (which seems unlikely in view of their condition) the two species must have existed in a mixed colony.

(iii) Variations within species from different sites

Samples of fossil C.nemoralis from four sites (Caerwys, Newlands Cross, Carrowmore, Castlethorpe) were analysed. The results are presented in tables 5.17 - 5.20 and figure 5.17. The sample sizes ranged fom 8 to 10 shells. Table 5.21 shows a probability matrix from two sample "t" test (95% c.l.). There is no significant difference between the $\delta^{13}C$ values and only three pairs where the $\delta^{18}O$ values are significantly different.

The similarity of the samples from a wide spatial and temporal range can be interpreted in two ways. The first is that the sites are not sufficiently different to significantly affect the isotopic composition. All four sample sites were on tufa with a limited range of $\delta^{13}C$ (0.444°/oo) and $\delta^{18}O$ values (0.850°/oo); access to $CaCO_3$ would be similar but the differences in time and space should produce significant difference in composition unless the $CaCO_3$ source is one of the dominant factors. Two other sets of data are relevant to this point, the modern and fossil samples of P.elegans from Binnel Point (figure 5.18). These were collected at the same site from a buried horizon and the modern surface. The present environment is similar to

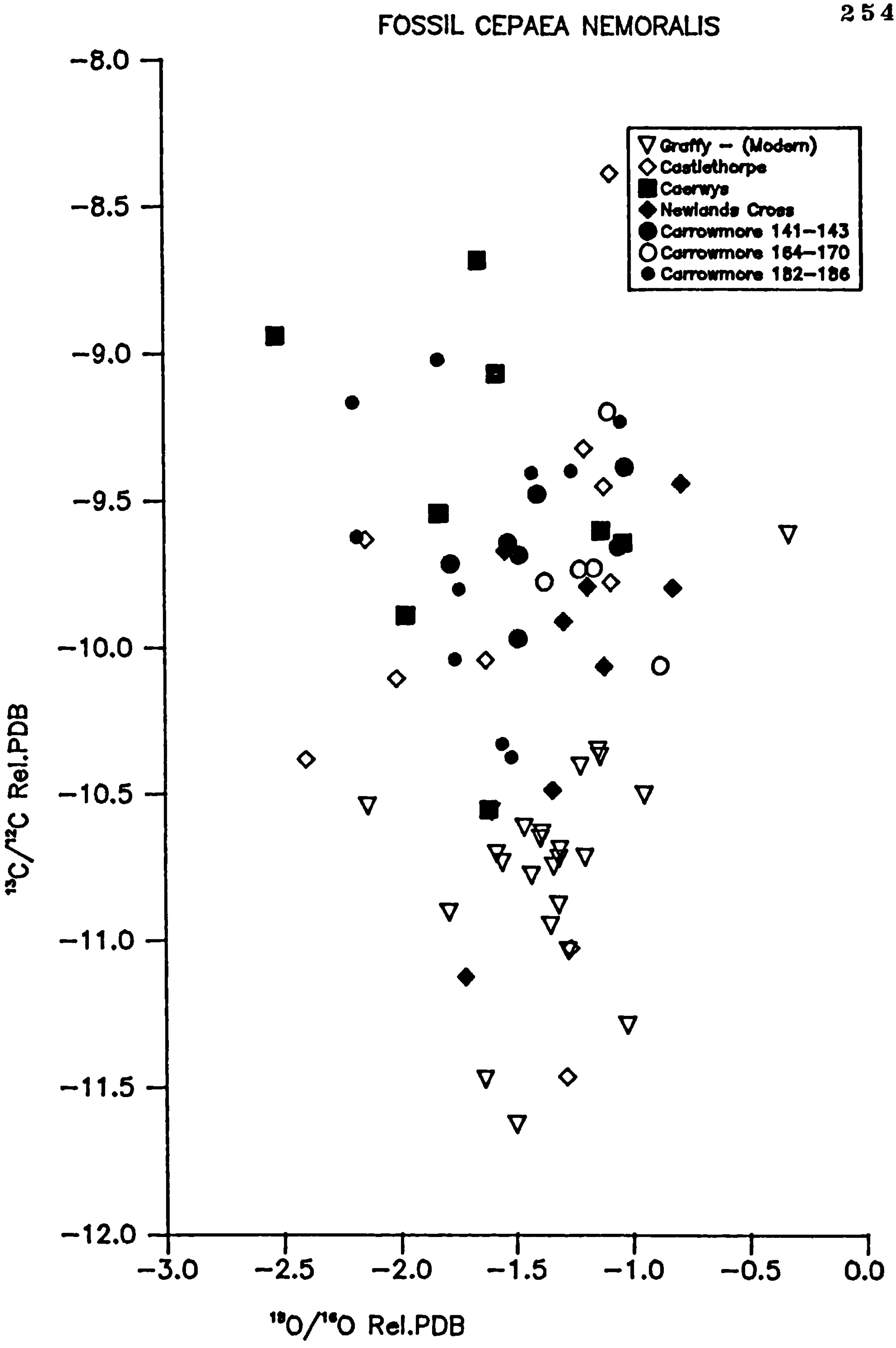


Figure 5.17. Variations in stable isotope values between shells of *Cepaea nemoralis* from different fossil sites.

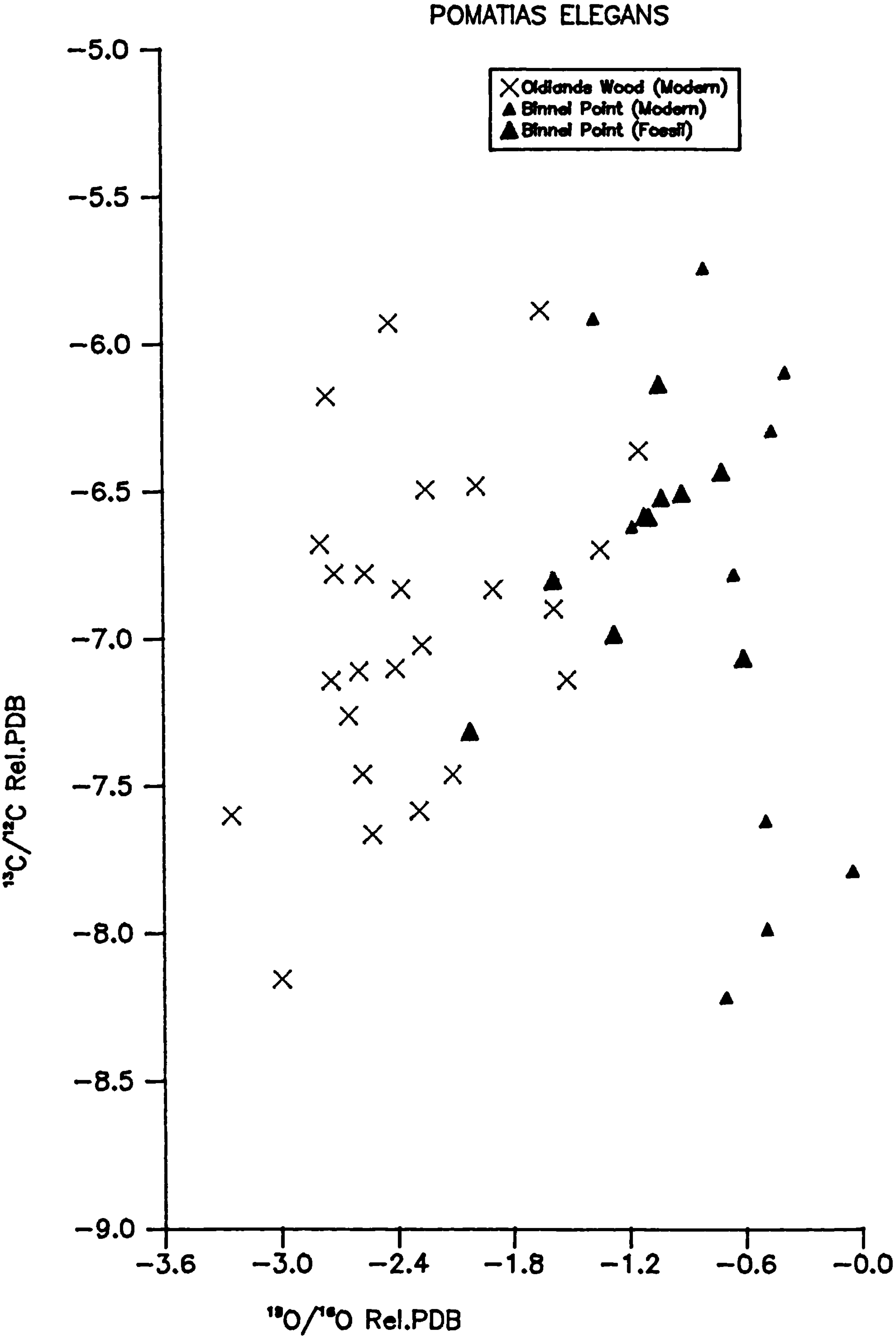


Figure 5.18. Variations in stable isotope values between fossil and modern shells of Pomatias elegans.

Sample Code		$\delta^{13}C$	$\delta^{18}O$	Mg	Sr	Fe	Mn
CAST	1	-8.387	-1.088	64	145	110	23
	2	-11.025	-1.269	68	189	104	22
	3	-10.041	-1.629	65	135	145	15
	4	-9.630	-2.147	72	135	253	17
	5	-10.105	-2.016	71	152	184	14
	6	-11.463	-1.286	139	162	82	15
	7	-9.777	-1.091	53	146	161	14
	8	-10.380	-2.402	57	165	120	19
	9	-9.451	-1.120	58	201	126	15
	11	-9.322	-1.205	67	212	101	16
INCH	1	-7.734	-2.359	29	517	99	32
	2	-9.462	-2.641	15	229	83	30
	3	-8.666	-2.622	23	391	72	30
	4	-3.440	-2.197	40	749	79	51

Table 5.20. Results of chemical and isotopic analyses of shells from Castlethorpe, Lincolnshire (CAST; *Cepaea nemoralis*) and Inchrory, Banffshire (INCH; *Cepaea hortensis*).

	NC	CW	CBB	CBM	CBT	CAST
NC	1.000	0.076	0.130	0.180	0.091	0.820
CW	0.076	1.000	0.580	0.430	0.500	0.200
CBB	0.130	0.580	1.000	0.780	0.960	0.330
CBM	0.180	0.430	0.780	1.000	0.750	0.420
CBT	0.091	0.500	0.960	0.750	1.000	0.300
CAST	0.820	0.200	0.330	0.420	0.300	1.000

^{13}C

	NC	CW	CBB	CBM	CBT	CAST
NC	1.000	0.050	0.020	0.580	0.290	0.150
CW	0.050	1.000	0.940	0.020	0.019	0.530
CBB	0.020	0.940	1.000	0.004	0.120	0.520
CBM	0.580	0.020	0.004	1.000	0.090	0.054
CBT	0.290	0.019	0.120	0.090	1.000	0.500
CAST	0.150	0.530	0.520	0.054	0.500	1.000

^{18}O

Table 5.21. For description see next sheet.

	NC	CW	CBB	CBM	CBT	CAST
NC	1.000	0.000	0.002	0.000	0.000	0.020
CW	0.000	1.000	0.050	0.006	0.042	0.040
CBB	0.002	0.050	1.000	0.000	0.018	0.650
CBM	0.000	0.006	0.000	1.000	0.660	0.000
CBT	0.000	0.042	0.018	0.660	1.000	0.003
CAST	0.020	0.040	0.650	0.000	0.003	1.000

Magnesium

	NC	CW	CBB	CBM	CBT	CAST
NC	1.000	0.000	0.000	0.000	0.000	0.000
CW	0.000	1.000	0.003	0.190	0.009	0.000
CBB	0.000	0.003	1.000	0.017	0.680	0.043
CBM	0.000	0.190	0.017	1.000	0.073	0.000
CBT	0.000	0.009	0.680	0.073	1.000	0.590
CAST	0.000	0.000	0.043	0.000	0.590	1.000

Strontium

Table 5.21. Probability matrix for Cepaea nemoralis from different fossil sites in the British Isles. NC = Newlands Cross, Dublin, Eire; CW = Caerwys, Clwyd; CB = Carrowmore Site B, Co.Mayo, Eire (three contexts); CAST = Castlethorpe, Lincolnshire.The samples all have normal distributions, probabilities are based on a two sample "t" test and are considered significantly different when <0.050.

the fossil one since the availability of components should have remained broadly the same. The $\delta^{13}C$ and $\delta^{18}O$ values are different by 0.212 and 0.481$^{\circ}/_{\circ\circ}$ respectively. The difference in $\delta^{18}O$ values may reflect the more wooded environment (e.g. cooler) of the fossil site relative to the modern site (see chapter 2.47). These are similar to the data for fossil <u>C.nemoralis</u> but in the case of Binnel Point there has been a temporal but not spatial change.

The alternative interpretation is that the compositions at the time of deposition were different and post-depositional changes have occurred and produced a movement of values towards a new equilibrium with their environment. This will be considered further in chapter 6.5. It is also possible that the similarity is due to a combination of both of these mechanisms.

5.33 Conclusions

The analysis of variations in the stable isotope values allows a number of conclusions to be drawn from the interpretation of the results.

The analysis of the intra-shell variations clearly shows that the exchange of CO_2 across the body of the snail during active periods does not play a dominant role in the final composition. Its influence is obscured by the effects of the microenvironment, habit and climatic variations between the growth periods.

Two other important factors are the availability and the isotopic composition of the $CaCO_3$ source. An area in which the $CaCO_3$ is covered will require more effort and a greater input of CO_2 through metabolism than one where access is simple. The habits of different species also affects the access to $CaCO_3$. P.elegans burrows into loose soil giving easy access to $CaCO_3$ and also leading to the inclusion of particles of the $CaCO_3$ in the shell at the time of formation. The $\delta^{18}O$ values for P.elegans also indicate its burrowing habit by showing a cooler temperature of shell deposition. These effects were observed in the present study.

The importance of environment is also seen in the data for the banding morphs at Hayle Towans. Factors such as availability of $CaCO_3$, metabolism and climate must have been constant but the adaptation to different microenvironments seen in the banding morphs is also reflected in the stable isotope composition.

Fossil samples were more difficult to interpret particularly those from tufa sites. The similarity of the results both between sites and between species has been ascribed to the similarity of the environment or a post-depositional affect.

The study of modern C.nemoralis suggested that $\delta^{13}C$ values may reflect the degree of cover (woodland) at a site. When the environmental data available for the fossil sites is compared to the $\delta^{13}C$ values a trend of increasing woodland with enrichment of $\delta^{13}C$ is again observed. Table 5.22 gives details of ^{13}C and "openness" for the fossil sites that were studied.

Site	"Openness"	Mean $\delta^{13}C$ (Pop^n)
Oldlands Wood	Wooded	-8.828
Caerwys, Clwyd	Partially Wooded	-9.490
Carrowmore B	"	-9.685
Hayle Towans	Scrub	-9.887
Castlethorpe	Clearing	-9.956
Newlands Cross	"	-10.035
Graffy	Open	-10.729

Table 5.22. Relationship between "openness" of site and $\delta^{13}C$ of shells of *Cepaea nemoralis* from the site.

5.4 RESULTS OF CHEMICAL ANALYSES

5.41 Modern samples

(i) Variations between species within one sample site

Samples from five groups of shells (C.nemoralis (OCN), 20 shells; C.hortensis (OCH), 20; P.elegans (OPE), 20; H.pomatia (HPA), 13; H.pomatia (HPB), 20) from Oldlands Wood were analysed for magnesium (Mg) and strontium (Sr). The results are given in table 5.4, 5.6 - 5.8 and figure 5.19.

The results show less distinct species groups than were obtained by stable isotope analysis. However, general trends can still be observed particularly the higher Mg contents of OPE and HPA. When the results were statistically tested the observed trends of Mg were shown to be two distinct groups. One contains HPA and OPE; the other OCN, OCH and HPB. The Mg values for HPA can be sub-divided into three significantly different sub-groups based on the Mg content. The same sub-groups produced no significant differences in $\delta^{13}C$, $\delta^{18}O$ and Sr values. The "low" Mg sub-group is similar to the results for OCN, OCH and HPB. The strontium results are less clear but with the exception of OCN are not significantly different (n.s.d.) from each other. OCN has slightly higher values and is similar only to OPE.

The results are interpreted as indicating a "background" level of magnesium which is increased by the inclusion of high Mg material. The "background" level is defined by the mean values of groups OCN, OCH and HPB at 75-95 ppm. The "low" sub-group of HPA can also be considered as "background" (63 ppm). The remaining groups (OPE, HPA "medium", HPA "high") have mean values of 199, 131 and 294 ppm respectively. The Sr values are stable and may also represent a

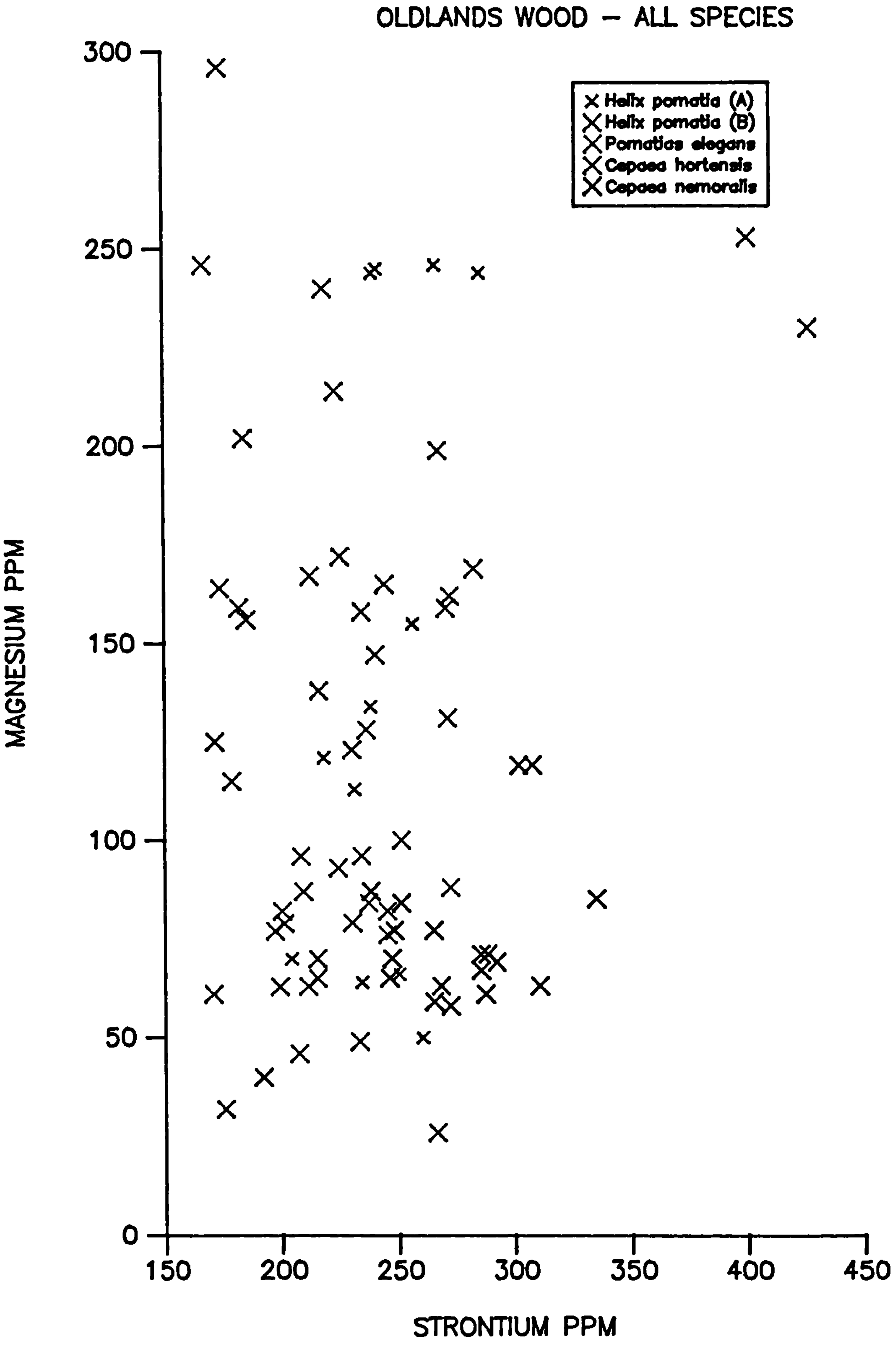


Figure 5.19. Variations in the magnesium and strontium contents between shells of different species from Oldlands Wood, Surrey.

"background" level. In order to interpret the Mg and Sr values more fully the cation contents for the environments (table 5.23) and variations between sites must be considered.

(ii) Variations within species from different sites.

The results from the analysis of OCN were compared to those from Hayle Towans (HCN, 20 shells) and Graffy (GCN, 20 shells). The results are given in tables 5.6, 5.10, 5.11.

The Mg contents from HCN have a mean value of 79 ppm (75 ppm if two high values are excluded) which is close to the "background" observed at Oldlands. Sample GCN contained considerably higher and more varied Mg levels. Three sub-groups were defined with mean values of 71, 180 and 610 ppm ("low", "medium" and "high"). The "low" sub-group is again consistent with the "background" level from the other two sites. The Sr levels (mean 1803 ppm) for samples from Hayle are much higher than those from Oldlands; at Graffy the levels are lower with a mean value of 120 ppm.

The data from the analysis of modern <u>P.elegans</u> from Binnel Point (BPM) is also relevant to the interpretation of the Mg and Sr levels. The samples studied included aragonite shells and calcite opercula deposited by the same population of snails. The results for the aragonite shells show mean Mg levels of 300 ppm and mean Sr levels of 348 ppm. The calcite opercula gave values of 2402 ppm and 444 ppm for Mg and Sr respectively.

(iii) Interpretation

The only source of Mg and Sr (also calcium (Ca)) available to the snail for construction of its shell is the inorganic material on which it lives. Within the inorganic material the principal source of Mg and Sr will be the $CaCO_3$ that is present. A contribution from clay or silt particles included in the diet may also occur. The organic material of the diet contains only very low levels of cations and these cannot represent a significant component in the shell. The chemical compositions of the $CaCO_3$ in solution and as a solid will be different owing to selective or incongruent dissolution.

Magnesium, strontium and other 2+ ions (e.g Fe, Mn, Ba) are able to substitute for calcium in the aragonite or calcite lattice. If a direct substitution of ions with no restriction other than ionic charge were possible then the composition of the shell should be identical to the source (particulate or dissolved $CaCO_3$). Table 5.23 summarises the data for shell and $CaCO_3$ for the four modern sites at Oldlands, Hayle Towans, Graffy and Binnel Point.

The results clearly show that the Mg content of the shells is not controlled by the Mg content of the source material. The Sr content appears to be more closely related to the environment and represents a much greater proportion of the Sr that was available than do the Mg contents. The Mg "background" level appears to be limited by the ability to include ions in the lattice rather than their availability. This is confirmed by the results for the Binnel Point samples. The availability of the Sr and Mg must have been the same for the shells and opercula , and since the mechanisms of deposition are identical the only explanation for the different Mg contents is the differing mineralogies. The change in the Sr content (5-10%) is not a statistically significant amount. This similarity is suprising in view of the different distribution coefficients (K) of Sr in aragonite and calcite. The distribution coefficient is defined as:

Site	Sample	Mg	R	Sr	R	Fe	R	Mn	R
Oldlands	Chalk (Ch.S3)	1743		458		183		208	
	Chalk (Ch.S4)	1919		550		243		311	
	HPA "low"	63	0.036	240	0.524	-		-	
	HPA "medium"	131	0.075	"	"	-		-	
	HPA "high"	294	0.169	"	"	-		-	
	HPB	93	0.053	226	0.493	-		-	
	OCN	77	0.044	268	0.585	48	0.262	-	
	OCH	83	0.048	225	0.491	41	0.224	-	
	OPE	199	0.114	238	0.520	58	0.317	-	
Hayle	HT5 0-5	8742		2121		-		-	
	HT5 5-20+	10611		2217		-		-	
	HCN	75	0.0086	1803	0.850	50		-	
		113	0.0129	"	"	-		-	
Graffy	Tufa (TG)	564		120		127		59	
	GCN "low"	71	0.126	105	0.875	33		-	
	GCN "medium"	180	0.319	"	"	-		-	
	GCN "high"	610	1.082	"	"	-		-	
Binnel	Chalk	-		-		-		-	
	BPM (shell)	300		349		97		15	
	BPM (opercula)	2402		444		56		25	

R = ratio of shell content/ source content

All values are mean content in ppm

Table 5.23. Magnesium, strontium, iron and manganese contents of shells and CaCO3 sources analysed in this study.

$$K_{Sr} = \frac{(mSr^{2+} / mCa^{2+})_{solid}}{(mSr^{2+} / mCa^{2+})_{solution}} \quad \text{(eq. 5.2)}$$

m = molecular ratio Solid = aragonite or calcite

$(K_{Sr})_{arag.}$ = 1.12 +/-0.04 $(K_{Sr})_{calc.}$ = 0.14 +/-0.02

(After Kinsman & Holland 1969; Bathurst 1975 - see below for discussion of variation of values).

If calcite and aragonite are precipitated from the same solution (e.g. the pallial fluid of P.elegans at Binnel Point) there should be a Sr ratio of 8:1 (aragonite : calcite). The measured ratio can be considered as 1:1 indicating that other important factors are operating. The Sr contents from Oldlands, Hayle and Graffy suggest that a depletion of the Sr occurs prior to the Sr reaching the pallial fluid. The values also suggest that this depletion is more prominent on the chalk sites than on the other two.

Bathurst (1975) warns that the uncertainty of the distribution co-efficients means that they cannot be considered reliable. Treese et al. (1981) observed that the values of K_{Sr} for biogenetically precipitated carbonates are significantly lower than the corresponding values for inorganically precipitated forms. This difference is attributed to the ability of some organisms to regulate the amount of certain trace elements in the body fluids such that their shell material is derived from a solution of composition different from the environment in which they live. The data in this study are derived from a limited range of organisms and should not be affected by these variations. The only significant difference could be that the species are from two different sub-classes (Prosobranchia and Pulmonata).

The magnesium content of the Binnel Point opercula is 6-8 times that for the shells. Availability of Mg in the pallial fluid is obviously not the limiting factor; therefore, the large difference indicates that a distribution coefficient exists for Mg. The ratio of Mg contents for aragonite and calcite is 0.18; this is in agreement with Treese et al. (1981) who found K_{Mg} values 5-10 times larger in calcite than aragonite.

The limited Mg contents that form the "background" observed throughout the samples must represent the limit of Mg that can easily be included within the aragonite lattice. A number of authors (e.g. Friedman 1968) defined "high" and "low" Mg contents in marine aragonites, the "low" being confined to molluscs and the "high" to corals. The terrestrial molluscs analysed in this study were of "low" Mg content, lower than that defined for marine molluscs. The presence of "high" (8000 ppm) Mg aragonite indicates that it is not only the mineralogy but also the structure and the mode of deposition that are important in determining the Mg content.

However, it is clear from the preceding discussion that Sr contents are not limited in the same way in aragonite, but Sr values are more limited in calcite. The Sr content is probably controlled by the co-ordination values for calcite and aragonite (Goldschmidt 1954). Aragonite has a nine-fold co-ordination and can accept ions of radii that area greater than its own (1.06Å). $SrCO_3$ has a nine fold co-ordination and a radius of 1.12-1.27Å (Roseler & Lange 1972); this allows the Sr to be directly substituted for Ca in the lattice.

Calcite has a six-fold co-ordination and can only be stable for ions whose radius is equal to or less than that of Ca^{2+}. The ionic radius of Sr^{2+} is greater than that of Ca^{2+} which does not allow it to be substituted. The converse is true for magnesium. Its co-ordination and small ionic radius (0.65-0.78Å) restrict its presence in aragonite.

Schroeder (1969) defines three ways in which ions (e.g. Ca^{2+}, Sr^{2+}, Mg^{2+}) can be accommodated in a lattice: lattice site (substitution), lattice interstices, and as inclusions (small areas of different mineralogy). The Mg "background" level can be seen as the limit of substitution, a limit that appears to be restricted to certain crystal structures if not to the crossed-lamellar structure alone.

The presence of inclusions is possible but would require a change in the mechanism of deposition to allow any different mineralogy to occur or the incorporation of particles from the surrounding environment. Chapter 3.1 discussed the role of the organic matrix in determining the mineralogy; if these theories are correct then it would be feasible for a particular formation in the matrix to deposit $MgCO_3$ under certain conditions. However, the presence of higher Mg contents in a limited number of species, and often only part of a sample population, argues against the presence of inclusions but is not conclusive proof.

The most feasible explanation of the higher magnesium contents in samples OPE, BPM and parts of HPA and GCN is the presence of Mg ions at interstices. Walls et al. (1977) defined the interstitial ions as loosely bound and expanded the category to include mineral or fluid inclusions, and organic components of the conchiolin matrix as well as the adsorbed ions on crystallite surfaces. Experiments by Amiel et al. (1973) and Walls et al. (1977) suggest that 10-12 times as much Mg as Sr is present at adsorbed positions. Amiel et al. (1973) determined that up to 25% of the magnesium content could be at adsorption sites; as their study was on aragonite corals (Mg content c.8000 ppm) it is quite possible for the extra 100-500 ppm of Mg present in some terrestrial snails to be due to this process. The suitability of Sr ions to substitute for Ca suggests that they are generally present at lattice sites.

The association of the species that have "high" Mg levels and their higher levels of contact with $CaCO_3$ in the soil suggests that the increase in Mg content may be derived from the soil. Berner (1966) found that aragonite grains were capable of exchanging both Ca^{2+} and Mg^{2+} ions with the surrounding aqueous environment. The environment surrounding terrestrial snails will almost certainly contain a higher Mg content that the shell. If exchange occurs towards an equilibrium value an increase in Mg ions, particularly in interstices, may occur.

Two other mechanisms could lead to the higher Mg levels: increased deposition from the pallial fluid owing to some physio-chemical change, and the inclusion of particles of the $CaCO_3$ source at the mantle edge or into the shell grooves. The inclusion of particles is unlikely to occur if they are coarse, and no higher Mg contents were observed from Hayle Towans samples where the average $CaCO_3$ particle size was 0.125mm. If the increased Mg content in sample OPE were due to particles of chalk the percentage present can be calculated. The chalk (Ch.S3) contains 1740 ppm Mg; therefore, an increase of Mg in the shells of 100 ppm would require 5-6% chalk. A chalk content of this size would be detected as calcite unless a mechanism exists that allows the particles to be absorbed by the existing structure and become aragonite.

It is clear that if the increased Mg content is due to the inclusion of particles of the $CaCO_3$ source material there will be a significant increase in depleted ^{14}C carbonate. It the increased Mg content is due to the adsorption of Mg^{2+} ions from the environment then it is possible that other ions including CO_3^{2-} will have also been exchanged and again a depletion in the ^{14}C content of the carbonate taken place.

5.42 Fossil samples

(i) Variations between species within one sample site.

Variations between species within one sample site were studied by the analysis of samples from Carrowmore (40 shells), Caerwys (13) and Newlands Cross (10 shells). The smaller sample sizes for samples of C.hortensis from Newlands Cross and Caerwys, and A.arbustorum from Caerwys, does not allow significant conclusions to be drawn between these samples and C.nemoralis. However, it is worth nothing that there was no significant difference between these samples or between them and the C.nemoralis from the same contexts.

The Carrowmore samples were collected from three horizons (CBT_1, CBM_1 and CBB_1); these are described in chapter 5.32 and chapter 2.4. C.nemoralis and C.hortensis were present in all three contexts. The results are given in table 5.19.

There is no significant difference between the species in any of the horizons for Mg or Sr with the exception of Sr in layer 141-143cm. When the results from the different horizons are compared the Mg contents are found to be not significantly different for C.nemoralis but only layer 141-143cm and 164-170cm are statistically similar for C.hortensis samples. Analysis of Sr values for C.nemoralis shows only CBB$_1$ and CBT$_1$ as being similar; only CBM$_1$ and CBT$_1$ are similar for C.hortensis.

The similarities between C.nemoralis samples are different if two unusually high Mg results from CBT$_1$ and CBM$_1$ are not included. The recalculated probabilities show only one pair (CBT$_1$ and CBM$_1$) are not significantly different. The Mg results for the two species from CBM$_1$ show that they are now also significantly different.

	Tufa		C.nemoralis		C.hortensis	
Sample	Mg	Sr	Mg	Sr	Mg	Sr
CBT$_1$	506	46	36.75	134	37.00	52.30
CBM$_1$	519	65	34.50	74	45.60	77.60
CBB$_1$	563	37	66.80	122	76.40	120.00

Table 5.24. Comparison of source with shell Mg and Sr contents. Samples from Carrowmore, Co.Mayo.

Table 5.24 shows a comparison of the Mg and Sr contents for the shells and source materials. The Mg content of samples CBT$_1$ and CBM$_1$ are below the "background" level defined in the modern results and CBB$_1$ is also rather low. Less variation is seen in the tufa analyses and since the species and mineralogy are identical for the three horizons post-depositional changes may have occurred in the shell. The Sr contents also suggest post-depositional changes by their being above the Sr content of the source material.

(ii) Variations within species from different sites.

The results from the analysis of C.nemoralis from Carrowmore were supplemented by analyses from Castlethorpe (CAST), Caerwys (CW) and Newlands Cross (NC); the results are given in tables 5.17 - 5.20.

There is a significant difference between each of the sites for both Mg and Sr with the exception of CBB_1 and CAST for Mg and CBT_1 and CAST for Sr. The similarities must be coincidental as the sites are widely separated both spatially and temporally.

	Tufa		C.nemoralis		C.hortensis	
Sample	Mg	Sr	Mg	Sr	Mg	Sr
NC	3014	209	94	392	178	336
CW	755	28	51	49	62	32
CAST	461	119	71	164	-	-
INCH	226	267	-	-	27	472

Table 5.25. Comparison of source and shell Mg and Sr contents, different tufa sites.

Comparison of the Mg and Sr contents of the $CaCO_3$ sources and shells show a similar pattern to that observed in the Carrowmore samples (table 5.25). The Sr contents are enriched relative to the tufa source material. Shell Mg contents are generally lower than the "background", but the NC values are higher. The NC Mg contents were expected to be higher because of the very high Mg content of the tufa.

The apparent depletion of Mg and enrichment of Sr contents, relative to the modern shells and the source materials, observed for all sites strengthens the view that post-depositional changes must have taken place (see chapter 6.5).

5.5 THE RELATIONSHIP BETWEEN SHELL COMPOSITION AND ^{14}C CONTENT

The results presented in this chapter clearly demonstrate that the environment occupied by terrestrial mollusca affects their shell composition. Others factors, particularly metabolism, also affect the composition but the environmental "signal" is rarely completely obscured by these. The composition may undergo post-depositional alteration which could distort the environmental record, particularly that recorded in the cation content; these changes are discussed in chapter 6.5.

The results also clearly show that any selection procedures that rely on composition must be based on variations within a single site and within a single genus. The variations between microenvironments occupied by a single species at different sites and by different species at a single site all affect the composition of the shells by sufficient to obscure the environmental "signal".

However if the crystal structure and composition of a shell indicate that little or no post-depositional alteration has occurred then the stable isotope and cation contents can be used as selection criteria. This should allow selection of samples in which the incorporation of solid $CaCO_3$, and hence a depletion in ^{14}C content, is at a minimum.

The two critical values for these selection procedures are the $\delta^{13}C$ value and the Mg content. The $\delta^{13}C$ value can be linked to the solid $CaCO_3$ component (chalk, limestone, calcareous sands) incorporated in the shell from the environment. The $\delta^{13}C$ values for these solid $CaCO_3$ sources and atmospheric CO_2 in solution are very similar at about -1 to +1°/oo. It is possible to select reliable samples by concentrating on those in which the $\delta^{13}C$ is depleted relative to the population mean. These must be associated with a low solid $CaCO_3$ content. Enrichment relative to the population mean could be due to a high level of atmospheric CO_2 or a high level of solid $CaCO_3$ and is therefore unreliable. The inverse is true for Mg contents. A high level of Mg implies contamination or a high solid $CaCO_3$ component; a low level could be attributed to a small initial solid $CaCO_3$ component or post-depositional alteration.

If the solid $CaCO_3$ source is naturally depleted in $\delta^{13}C$ (e.g. tufa) the maximum range variations of $\delta^{13}C$ value in shells that incorporate it must be smaller than for enriched sources. However it will be shown later that there is still a relationship between $\delta^{13}C$ and ^{14}C contents (chapter 8.5).

CHAPTER 6 POST-DEPOSITIONAL CHANGES IN SHELL STRUCTURE AND CHEMISTRY

6.1 INTRODUCTION

From the moment of death the shell of a mollusc will be subjected to alteration and decay; after deposition the rates of change will increase in all but the most stable environment. The first changes will be in the organic component, the decay of which will allow ground waters access to the crystal structure.

This chapter considers the effect of diagenetic alteration on inorganic shell structures: the general types of alteration and the mechanisms by which they occur; diagenetic alteration observed in the present study; and the limits of detection of diagenetically altered material. The last part of the chapter considers the effect of post-depositional changes on the isotopic and chemical compositions of shells.

6.2 POST-DEPOSITIONAL CHANGES IN MINERALOGY AND STRUCTURE

6.21 Introduction

In chapter 2.5 the environments in which diagenesis takes place were discussed. This section examines the changes that occur in crystal structures, particularly in the mineralogy and crystal size when shells are subjected to diagenetic environments. Also covered is the effect of certain external conditions (the presence of magnesium and the organic matrix) on the mineralogy.

The exact mechanisms by which the crystal lattice of a material, such as aragonite or calcite, undergoes structural rearrangement during diagenesis are not known. However, a number of general theories that are compatible with the available data have been put forward.

According to Land (1967) the change from aragonite to calcite can take place by three distinct routes:

(i) recrystallisation: the aragonite dissolves but is almost instantly recrystallised as calcite.

(ii) dissolution and reprecipitation: the aragonite is dissolved and the cast or void that is formed is filled at a later date, probably by material from beyond the immediate environs of the diagenetic site.

(iii) phase transformation: usually whilst the minerals remain in the solid state.

It is obvious that there is a difference in the degree of contamination of the shells involved in these modes of change: in the last the shells are uncontaminated, in the second the shells are probably completely contaminated. The extent of contamination in the first will be controlled by the openness of the system.

6.22 The Mechanisms of Diagenetic Change

(i) Dissolution with rapid recrystallisation.

Pingitore (1976) suggests two modes of transformation to account for different forms of products from diagenetic processes (figure 6.1); he associates these modes with vadose and phreatic environments. Those samples that were exposed in a vadose environment were said to have undergone "thin-film transformation". The aragonite and calcite phases are separated by a narrow water-filled crack (c.1 micron); aragonite dissolves on one side; the calcium and carbonate ions diffuse leaving a diffusion gradient across the crack. The recrystallisation front slowly migrates in the direction of

relatively soluble aragonite . The insoluble organic tissue is not destroyed by this delicate process and the texture and crystal unit boundaries (e.g. lamellae or nacreous tablets) are preserved to a scale similar to the crack width. Strands of organic tissue presumably bridge the film, extending from the aragonite across the crack, and become incorporated in the calcite.

The second mode of transformation put forward by Pingitore (1976) is described as "chalkification" and is considered to occur in phreatic zones. As the name implies this mode takes place within a zone of chalk between the aragonite and calcite. (This mode was originally noted by Schlanger (1963).) The chalk zone is extensive, though short lived; it has a friable consistency because of its secondary porosity.. Under phreatic conditions a zone of chalk several millimetres or more in width separates the fresh aragonite from the calcite. The calcium and carbonate ions diffuse from the dissolution sites in the chalk area to precipitation sites at the calcite mosaic. Precipitation is controlled by the presence of a nucleation surface on the calcite edge of the chalk zone. The secondary porosity and large voids between the aragonite and the calcite give the calcite mosaic an inferior textural preservation compared to the "thin-film" mode of transformation.

Pingitore (1976) suggests that the availability of water in the vadose and phreatic environments causes the difference in the transformation modes. The intermittent character of vadose water cannot easily create and maintain a broad zone of chalk, however, both modes could be maintained under phreatic conditions. Pingitore (1976) reasons that the "thin-film" mode does not occur in phreatic conditions because of the large quantities of water present. The water initiates the development of secondary porosity by dissolution and transport of some calcium out of the structure before much calcite is present within the structure. However, in his later paper (discussed below) he suggests that both modes can occur under phreatic conditions. Once calcite nucleation and crystal growth occur the zone of secondary porosity (chalky zone) is maintained by continued dissolution of fresh aragonite. A steady state is reached in which the rates of dissolution and precipitation are equal and the chalk zone is maintained.

Sandberg and Hudson (1983) dispute that a correlation exists between diagenetic type and environment. Their study of Neomiodon shells indicated that they had undergone burial diagenesis (i.e. phreatic); but the textural properties of the replacement calcite mosaics, combined with the nature and extent of the aragonite relic preservation, suggest alteration in a shallow meteoric environment (i.e. vadose). They conclude that the nature of the intraskeletal alteration front is of greater importance than the general diagenetic environment.

In a later paper Pingitore (1982) expands on the two modes of transformation and links them to the pore sizes involved. These are termed macropore and micropore, and are in turn linked to the openess of the system to external water.

"Thin-film" transformation occurs in intragranular pores (c.1 micron) and is associated with vadose environments where the rate of flow of water is low. If a rapid aquifer flow does occur the pore size (<10 microns) in which the "thin-film" transformation is taking place is small enough to make significant flow through pores of this geometry impossible.

In this later paper Pingitore (1982) considers it possible that under phreatic conditions carbonates can be subjected to both forms of transformation taking place as a range of degrees of isolation from the aquifer and diagenetic solutions are possible. Diagenetic sites along the path of the aquifer flows will act as open systems and be subject to broad zone chalkification. Sites in more isolated positions, pores which form cul-de-sacs off the flow path, will be subject only to "thin-film" transformation.

Pingitore (1976; 1978; 1982) based his theories on the study of corals; it is believed that the diagenesis of shells occurs by similar mechanisms but that they will differ on a number of points. The intragranular porosity found in corals is not present in shell structures or not on the same scale, any openings usually being considerably less than 1 micron. Wardlaw et al. (1978) studied the aragonite-calcite interface in diagenetically altered shells of Strombus gigas and were unable to observe any "cracks" even as small as 15nm (0.015 microns) between the altered and unaltered areas. The extensive nature of the diagenesis in the Strombus gigas shells suggests that "chalkification" was taking place; this would require an open system with considerable aquifer flow. However, Wardlaw et al. (1978) were unable to find any significant loss of strontium between the aragonite and calcite phases; this is not in agreement with Pingitore's (1978) observations of 60% loss of strontium during "broad band" diagenesis.

Wardlaw et al. (1978) observed some evidence for textural preservation (figure 6, p1865) which by Pingitore's criteria should indicate "thin-film" transformation. The overall conclusions are that a "thin-film" transformation does take place but with an extremely narrow "crack" across which diffusion takes place. The necessary expansion in volume (8%) as the aragonite changes to calcite is accounted for by the loss of the organic matrix in the original aragonite structure (7% of the total volume).

The areas in which the shells are prone to diagenesis are the boundaries between the lamellae, particularly the first-order lamellae which have no organic matrix between them. Walker (1979) observed dissolution taking place along the first-order lamellae boundaries; it is possible that widening of the boundaries can occur, allowing "chalkification" or more conventional "thin-film" transformations to take place. Omori (1976), in their work involving deliberate recystallisation, also observed that the first evidence of diagenetic change occurred along first-order lamellae boundaries, and also the boundaries between different shell layers.

If "chalkification" should take place in terrestrial shells then the weak structure produced, prior to the calcite, will make the shell very susceptible to disintegration. The will lead to reduced preservation unless the sediment surrounding the shell is compacted and able to support the weakened structure.

(ii) Total dissolution prior to recrystallisation.

This mode of transformation is associated with the formation of micrite envelopes and drusy calcite (see below). It may be found in Pleistocene deposits but is more generally found in far older beds. It requires the system to be open and for material to be dissolved at a rate many times greater than that for any deposition that is taking place.

The total dissolution of the original shell before a significant amount of neomorphic calcite has been formed leaves a void. Therefore, if a cast of the original shell is to form the sediment must be sufficiently lithified to stop the void filling with the surrounding matrix.

Bathurst (1964; 1975) gives details of the changes that occur in this mode of transformation, the main details of which are given below (6.33 (iii) c).

(iii) Solid state transformation.

Taft (1967b) considered that the recystallisation from aragonite to calcite could occur by either solution and reprecipitation or by solid-state recrystallisation. Taft (1967b) comments that solution of aragonite and subsequent reprecipitation as calcite obliterates the original texture (equivalent to Pingitore's "chalkification mode"), whilst textures may be preserved by solid-state recrystallisation. Taft continues by suggesting that the perfect textural preservation in many ancient limestones indicates that in those instances, if the original sedimentary particles were metastable carbonates, solid-state recrystallisation must have taken place.

Bathurst (1964) dismisses solid-state recrystallisation as being very unlikely to occur in normal burial conditions. He argues that a buried sediment is subjected to increased pressure, the aragonite becoming more stable, and that changes cannot be due to temperature as altered and unaltered shells occur in adjacent beds.

If solid-state recrystallisation is equivalent to the self-diffusion of Anderson (1969) then the time-scale involved (100 million to 1000 million years) means that this type of transformation will not be of any interest to Quaternary studies. However, Taft's (1967b) observations can be interpreted in at least two other ways. The textural transformation may be due to the "thin-film" mode or the structures could originally have been calcite and therefore have been preserved in preference to any aragonite features.

6.23 Structures of Diagenetic Change

The literature concerning previous studies on this subject suggests the structures formed in material that is, or has been, subject to diagenetic effects can be divided into four types:

(i) Etching of the crystal surfaces
(ii) Formation of neomorphic aragonite
(iii) Formation of neomorphic calcite
(iv) Preservation of aragonite relics

(i) The etching of the crystal surfaces

Alexandersson (1978) described the earliest stages of dissolution using scanning electron microscopy. The method depends on the condition that etch patterns develop on the surfaces of skeletal grains when they are exposed to dissolution. The patterns then remain as a microscopic topographic record as long as the grains stay intact. If conditions remain favourable to dissolution attack then the process may proceed several hundred microns into the grain fabric. The progress of attack is probably governed by the microarchitecture of the skeletons. The dissolution process leads to a large increase in the reactive surfaces of the dissolving grains. The etched topographies that the skeletal grains develop reflect the biogenic organisation of the calcified tissue, rather than simple crystallographic patterns.

Walker (1979) observed similar etching of crystals in marine shells. Third-order lamellae 200-300 microns from the surface of the shell of the bivalve _Anadara uropigmelana_ show etching on what were originally planar surfaces. The resulting structure has a more pitted appearance (Walker 1979, fig 2.3). More severe corrosion was observed in the shell of the gastropod _Purpura rudolphi_. Walker (1979) suggests that there are two distinct zones for possible solution: fissures along the boundary between first-order lamellae, and those across first-order lamellae (second-order lamellae boundaries). Each of these zones allows access to the crystal surfaces of the third-order laths which become heavily corroded. This in turn leads to a greater internal surface area and an increased susceptibility to diagenetic attack.

The etching of crystal surfaces is destructive diagenesis; no material is deposited in its place. This can only occur in an open system where the dissolved material is removed. The absence of deposition requires other closely defined conditions, particularly volumes of water low in bicarbonate and calcium ions. This condition is most likely to be met in a meteoric environment where shell material is at a shallow depth. The other types of structure involve some form of constructive as well as destructive diagenesis.

(ii) The formation of neomorphic aragonite

Bathurst (1975) records a number of workers (P.R. Brown (1961); Tebbutt (1967); Shinn (1969)) as having found examples of aragonite skeletal structures that had been replaced by "sparry" aragonite. The samples in which this diagenetic change was observed included Jurassic bivalves, and Pleistocene corals and bivalves. Tebbutt (1967) observed disturbance of the primary aragonite structure by the neomorphic aragonite, and also noted that where ghosts of the primary structure occurred in the neomorphic spar they had frquently been displaced or rotated from their original position. The coarse neomorphic crystals were not always confined within the boundaries of the primary structure and commonly extended beyond the original surface. Bathurst (1975) comments that this process appears to be complete by itself and there is no reason to believe that it is an essential step towards calcitization.

Purdy (1968) also discusses the possibility that neomorphic aragonite can be formed during diagenesis. He suggests that the aragonite skeletons of some of the smaller carbonate organisms (e.g. algae) can recrystallise to cryptocrystalline carbonate with no perceptible change in mineralogy, and that voids in the structure are also filled with aragonite. Purdy (1968) also suggests that it may be possible for low Mg-calcite to recrystallise to cryptocrystalline aragonite, but this is considered unlikely as it requires a change from a stable to a metastable mineralogical state.

The formation of neomorphic aragonite during diagenesis may be linked to the presence of high concentrations of magnesium which can act as an inhibitor to the formation of low Mg-calcite. If this is the case then the formation of neomorphic aragonite is probably confined to subsea environments. The effect of high magnesium concentrations is discussed in more detail below.

The preservation of primary structure suggests that the aragonite was being replaced very soon after dissolution, which conforms to Pingitore's "thin-film" model. However, Pingitore envisaged calcite rather than aragonite replacement.

(iii) The formation of neomorphic calcite

The literature on the development of neomorphic calcite records five main types of growth:

(a) aragonite to calcite, retaining fine-scale primary structure.

(b) aragonite to calcite, retaining coarse-scale primary structure.

(c) aragonite to micrite by recrystallisation or replacement with the formation of drusy calcite.

(d) aragonite to fine crystalline calcite, and then to sparite or cryptocrystalline structure by crystal growth or replacement.

Micrite is defined as micro-crystalline calcite, the grain size being less than 10 microns. If the grain size is greater than 10 microns it is termed sparite or "sparry" if a limestone matrix is being described, or cryptocrystalline if a shell structure is being described. The other term that is commonly encountered is druse or drusy which is defined as a cavity in a rock (e.g. a shell cast after dissolution) into which euhedral crystals of a mineral project.

(a) The formation of neomorphic calcite in which the primary fine structure of the aragonite is preserved is described by Chappell and Polach (1972). In their studies of Tridacna they observed a subtle coarsening of the highly regular structure of parallel fine aragonite fibres which appeared to represent gradual replacement by calcite. They describe the resultant structure as highly similar to the original with the fine growth lines of the skeleton apparently unaffected. Their ^{14}C determinations on samples that had undergone this type of diagenetic change showed no evidence of recrystallisation although the presence of up to 5% calcite (as shown by XRD) should give a considerable error on a sample that is older than 45,000 years. These results suggest that this mode of recrystallisation occurs within a closed system and that the sample thus affected will yield reliable results.

An alternative interpretation of these results is that the samples may have undergone diagenetic changes in an open system but that these changes took place more than 45,000 years ago, and that the sample has not been in conditions that encourage diagenetic change in the period that would leave a trace in the ^{14}C record. This possibility could be checked by examination and ^{14}C dating of samples that have undergone this mode of transformation but are known to be less than 45,000 years old.

Sandberg and Hudson (1983) dispute the existence of a transformation to calcite in which fine details are preserved. They use the examples of Wardlaw et al. (1978) which show no fine texture but have some evidence for transformation across a narrow front. However, Wardlaw et al. explain the transformation as occurring in a nearly closed system with the expansion of the calcite relative to the aragonite being taken up by the removal of organic material. If this is correct then preservation of the fine texture could not occur, at least on the model proposed by Pingitore (1976), since this requires preservation of the organic matrix across the diagenetic front.

Further confirmation of the need for an organic structure to be present if fine detail is to be preserved is given by Bathurst (1975). He observed that where sparry calcite had replaced in situ the radial fibrous calcite of cave ooids which lacked organic matrix, there was no relic of the radial-fibrous fabric in the spar.

(b) The formation of neomorphic calcite with the retention of the coarser parts of the primary structure is recorded by a number of authors. Bathurst (1964; 1975) describes a linear pattern of inclusions cutting across the calcite crystal mosaic and continuing with no deviation across the intercrystalline boundaries. The patterns are said to be similar to those seen in sections through the lamellar structure of unaltered molluscan shell walls and they are assumed, therefore, to be relics of the original structure.

A similar structure is recorded by Chappell and Polach (1972) in partly recrystallised corals. They observed bundles of spherically radiating aragonite needles of the original structure becoming replaced by coarser laths of calcite, up to 15 microns in width and arranged in a similar radial pattern.

Sandberg and Hudson (1983) also show evidence of retention of the coarse structure based on the earlier work of Hudson (1966). In this earlier study gastropods from the Jurassic that are unknown as aragonite shells were studied. The former presence of crossed-lamellar structure can be inferred from the organic relics preserved in the replacement calcite. Sandberg and Hudson (1983) also discuss the possibility that calcite crystal growth can be constrained by the presence of organic boundaries (particular growth boundaries) from the primary structure. The greater the preservation of the organic layers, the more regular the calcite mosaic becomes.

(c) The formation of micrite is generally considered to be associated with the total replacement of shells by dissolution and later recrystallisation; it is also generally associated with the formation of drusy calcite. Bathurst (1964) discusses in detail the transformations which lead to the formation of micrite and drusy calcite.

The micrite initially forms as a thin coating (10-50 microns thick) forming an envelope around the original shell; however, it is not an encrustation but a replacement of the original fabric. In cases where the envelope is incomplete the micrite may be concentrated in the tubes formed by boring algae. In extreme cases the whole skeleton or shell may be replaced in this way by grey-looking micrite.

The development of micrite may stop after the formation of the envelope and the filling of the borings, the rest of the shell or skeleton remaining unaltered. If diagenesis continues the most common course appears to be the total dissolution of the skeleton leaving a void within the micrite envelope. At this point the envelope may rupture, particularly if compression of the sediments takes place, and the fragments collapse into the void. If cementation of the sediment has begun the void will remain open and at some point later become filled with drusy calcite. If cementation has not occurred the surrounding sediments will collapse into the void as disssolution occurs, leaving the micrite fragments as the only evidence that the shell had existed.

(d) The growth of neomorphic calcite is described by Bathurst (1975) as a two-stage process in some cases. The aragonite skeleton or shell first suffers wet polymorphic transformation to finely crystalline calcite (micrite); this structure then undergoes a wet recrystallisation wherein large calcite crystals (sparite) grow at the expense of smaller crystals. It is possible that this happens to the calcites that retain the fine primary structure of aragonite, leading to the formation of cryptocrystalline mosaics with the retention of the coarse primary structure or the total absence of any primary structure.

The problem with a two-stage process is that it requires dissolution of the stable calcite in the wet recrystallisation stage. The idea that the formation of neomorphic calcite is a multi-stage process is a popular theory but has recently been challenged by Sandberg and Hudson (1983). They suggest that the dissolution of the stable polymorph calcite is unlikely and suggest that the presence of aragonite relics (see below) is indicative of a single phase of dissolution and recrystallisation.

Bathurst (1975) suggests that the micron sized crystals are less stable because of their increased surface area relative to larger crystals. Preferential dissolution of the smaller crystals allows a small number of crystals to grow at the expense of others and so dominate the structure. This process can be seen as similar to the geometric selection found in the growth of the prismatic structure during the lifetime of the mollusc. If the growth of the large crystals during diagenesis is comparable it is likely that a large number of small crystals will develop on the initial diagenetic front, and then as the front progresses a small number will begin to dominate. This is not secondary recrystallisation of micron sized crystals but rather the selective growth of some crystals leaving a mixture of large and small crystals.

Chappell and Polach (1972) describe a similar development from small to large crystals; they describe an initial development of fine aragonite laths. When this type of recrystallisation is well advanced a coarsening of the calcite to much larger spar takes place.

(iv) The preservation of aragonite relics

Relic aragonite is attested by a large number of researchers (including Walker 1979; Sandberg & Hudson 1983; Schneidermann et al. 1972) and usually takes the form of individual third-order lamellae surrounded by neomorphic calcite. Sandberg and Hudson (1983) discuss in detail the reasons behind this selective preservation; they conclude that the aragonite is initially protected by its organic envelope, the formation of neomorphic calcite then takes place around the aragonite crystals. Once the aragonite is sealed within the calcite it is isolated from further diagenetic attack. Walker (1979) found the aragonite relics present near the front, but the work of Sandberg and Hudson (1983) shows that the relics remain when the diagenetic front moves on.

Sandberg and Hudson (1983) also record the presence of "islands" of crossed-lamellar structure surrounded by replacement calcite that is nearly free from aragonite relics. Similar "islands" were observed in this study in the shells of Patella vulgata; in this case the primary structure is of fine cross-foliated calcite.

Therefore, it appears that preservation of the organic matrix is required for aragonite relics to occur; organic preservation indicates that the formation of calcite took place early in the history of the sediment or that the initial conditions were conducive to the preservation of organic material.

Bathurst (1975) also discuses the inhibiting effect organic coatings can have on the formation of neomorphic calcite. He gives evidence from laboratory experiments (Chave & Suess 1967) that marine carbonate particles would not react with sea-water unless they were first treated with an oxidising agent.

The other factor that has been suspected of inhibiting the formation of neomorphic calcite is the presence of high-levels of magnesium ions. Srivastava (1975) states that published results show that the transformation of aragonite to calcite does not take place in the presence of "surface protective or nucleation- inhibiting layers of adsorbed magnesium". The level of magnesium necessary for this effect to take place is suggested as >0.0002 mol. Mg ions (2.4ppm). Folk (1974) suggested that Mg^{2+} ions inhibit growth of calcite crystals because of the accumulated lattice strain caused by incorporated Mg^{2+} ions, and that the changes in the morphology of the calcite grains (e.g. a predominance of "needle" crystals) are caused by selective poisoning of crystal growth perpendicular to the calcite c-axis.

Therefore, it is apparent that if a high Mg-calcite or aragonite is to be diagenetically altered to low Mg-calcite then the Mg^{2+} level must be reduced. The level of Mg^{2+} ions in a marine phreatic environment will inhibit growth of calcite but in a vadose environment the meteoric water will be low in Mg^{2+} ions, as will the ground water in a non-marine phreatic environment. The ground water will initially selectively dissolve Mg^{2+} ions from the crystal lattices, this in turn will allow later waters to initiate diagenesis in the shells or skeletons. The changes in the levels of Mg and other ions will be discussed later in this chapter (6.5).

6.24 Conclusions

Chapter 6.2 has summarised the mechanisms and products of diagenetic change that occur in shell calcium carbonate. The effect of the different types of change on the ^{14}C date of a sample will largely depend on the "openess" of the system in which the diagenesis takes place. The exact form of change will affect the selection of samples for dating as some types of recrystallisation will be far easier to remove than others. This is considered below in 6.61 and in chapter 8.2.

6.3 STRUCTURAL CHANGES OBSERVED IN THE SHELLS OF TERRESTRIAL MOLLUSCS

6.31 Introduction

The present study of fossil shells (3000 bp - 9000 bp) revealed four forms of post-depositional change. The shells from the British Isles had suffered surface etching, formation of surface crusts, and recrystallisation. Associated with these is the exfoliation of shell layers. The fourth form of change was observed in shells from Israel, this is the dissolution of the shell carbonate and its redeposition as cement.

From the time of death the shells of molluscs will undergo changes; the rate at which these take place will depend on the environment of deposition. The length of time the shell remains unburied will be related to its environment, particularly the rate of litter build up. Small shells will also be affected by the activity of soil invertebrates, particularly earthworms.

The first change the shell will suffer is the loss of the periostracum; only in exceptional circumstances will this survive for more than 1-2 years. The removal of the protective surface of organic matrix allows water to penetrate the crystal structure. Initially this will be meteoric water but as burial proceeds an increasing amount of ground water will be present. Access to the crystal structure becomes easier when exfoliation of the crystal layers occurs. The terestrial gastropods studied, with the exception of Pomatias elegans, are formed from 2 or 4 layers of crossed-lamellar structure. These layers begin to part after a short time, possibly before burial is complete (figure 6.2). Exfoliation probably occurs because the differently orientated crystals suffer differential expansion when subjected to changes in temperature and moisture. The extremes of these fluctuations will be reduced as the shells become buried. Exfoliation was also observed between aragonite and replacement calcite layers. In these cases burial is usually complete but the formation of calcite leads to a volume change in the crystals and therefore stress along the diagenetic front. The exfoliation that occurs prior to, or early in burial, accounts for the "flakey" texture frequently found on non-marine gastropod shells. The gaps caused by exfoliation are susceptible to both contamination and the growth of secondary calcite.

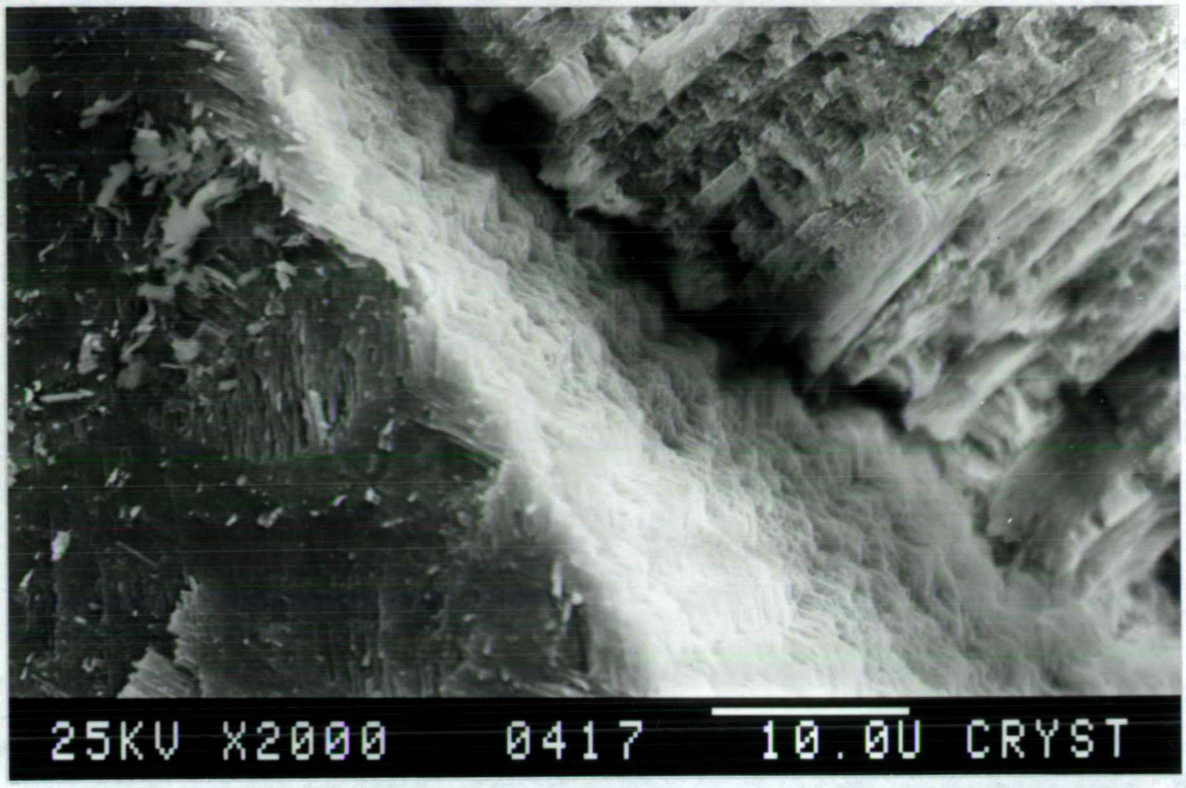


Figure 6.2. Exfoliation occurring between layers of crossed-lamellar structure in a fossil shell of <u>Arianta arbustorum</u> (Caerwys, Clwyd).

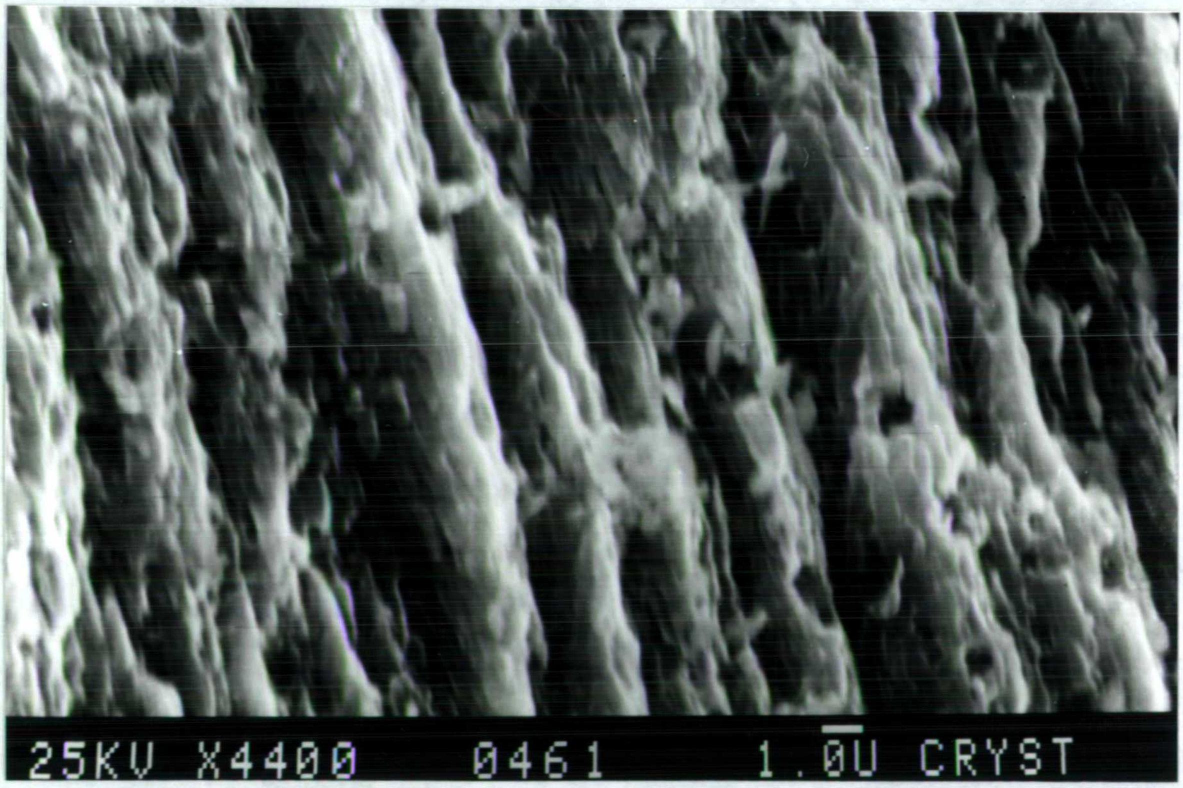


Figure 6.3. Surface of third-order lamellae showing etching and pitting (<u>Cepaea nemoralis</u>, Newlands Cross, Dublin).

6.32 Etching

This appears to represent the earliest stages of dissolution. Alexandersson (1978) and Walker (1979) observed this effect up to 300 microns from the surface. However, in the terrestrial gastopods examined the attack was confined to accessible surfaces and had penetrated only a few microns, perhaps because each of the third-order lamellae in the structure was protected by an organic matrix. The accessible surfaces are the inner and outer shell surfaces and the interfaces between shell layers. The interfaces between first-order lamellae are also prone to dissolution as they are not protected by organic matrices.

The commonest observed form of etching was the pitting of crystals; this suggests preferential attack of certain areas of the crystal structure (figure 6.3).

Surface etching will cause no error in the ^{14}C date as it is the removal of material. However, it can be taken as evidence of an environment in which dissolution is taking place and in which recrystallisation may also occur.

6.33 Surface Crusts

This form of diagenetic change was observed on many shells. A similar structure was recorded by Evans (1972), who suggested it was a secondary deposit on the original shell surface. The present study suggests that it can also be formed by recrystallization of original shell material, comparable with the formation of micrite envelopes (Bathurst 1964). It was observed on both inner and outer surfaces, but only occasionally exceeded 10 microns in thickness (figures 6.4 - 6.6). The thickness is limited by the crust breaking away from the

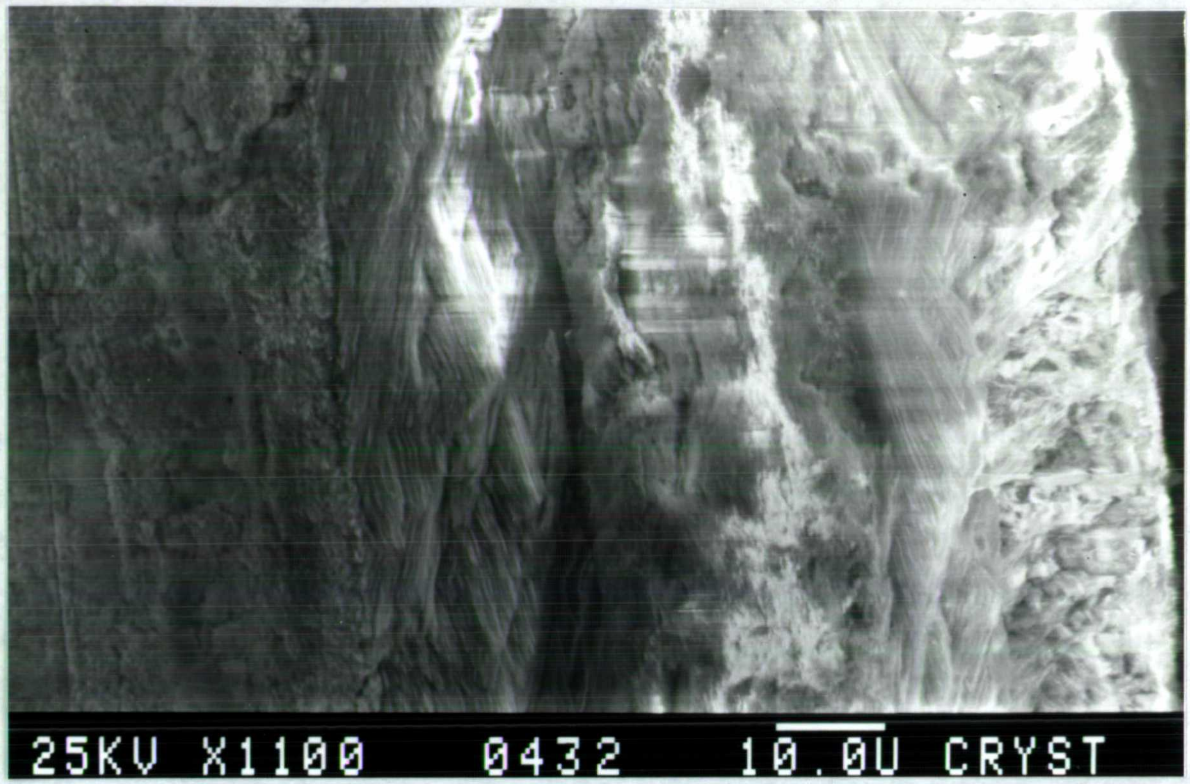


Figure 6.4. Thick crust of secondary carbonate on the inner surface (left) of a fossil shell of Cepaea hortensis (Caerwys, Clwyd).

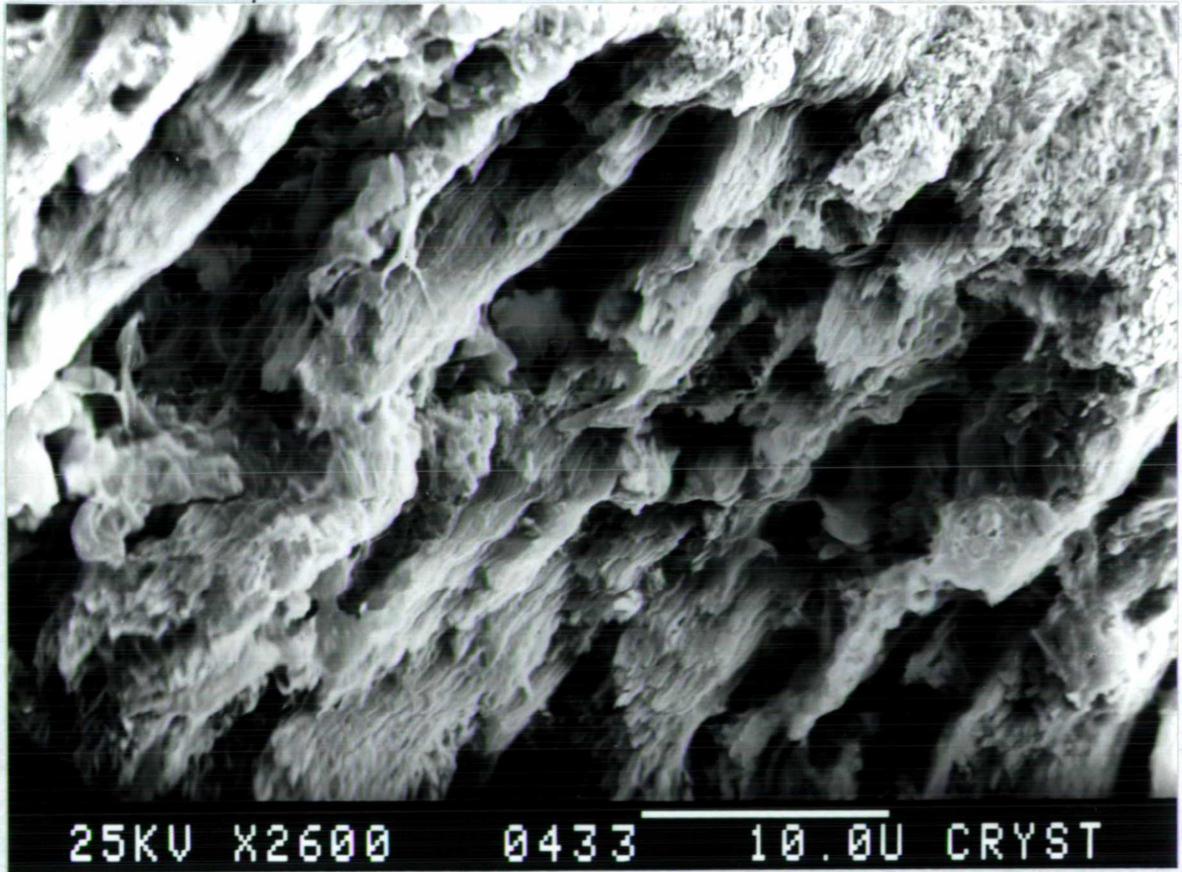


Figure 6.5. Thin crust of secondary carbonate on the outer surface (top right) of a shell of Cepaea hortensis (Caerwys, Clwyd). Note how it fills areas between the lamellae.

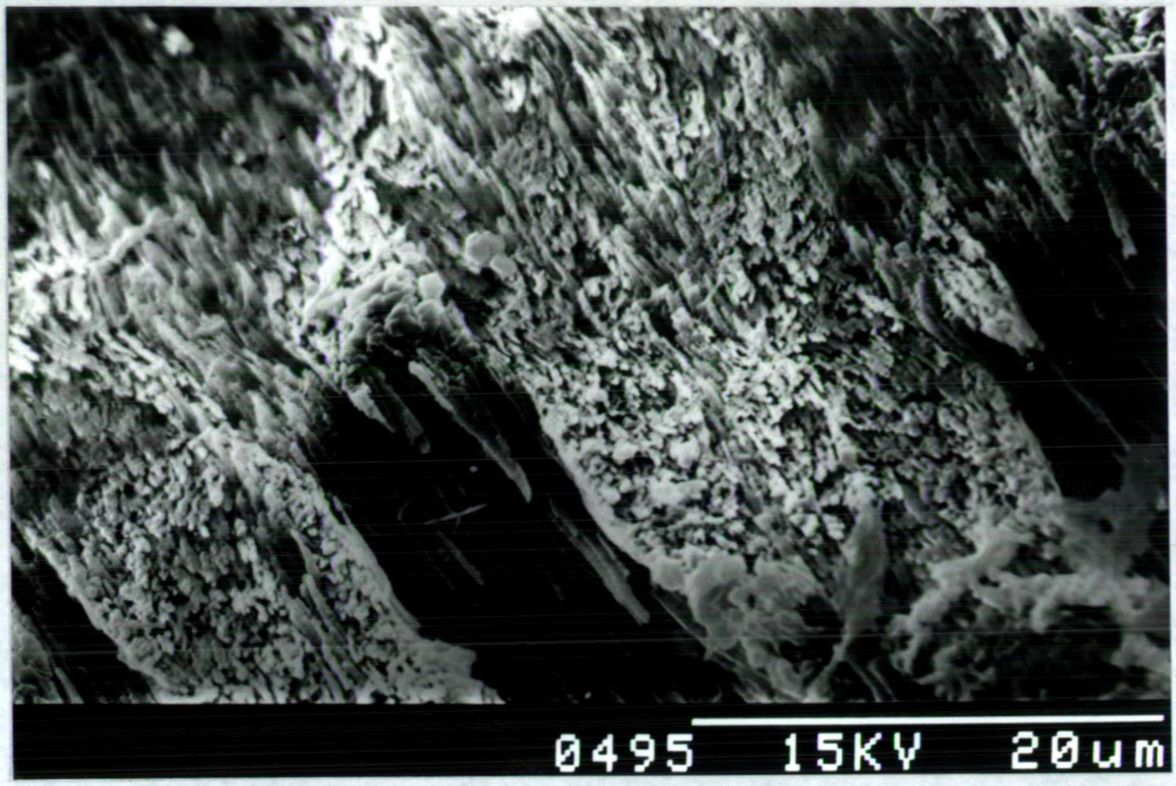


Figure 6.6. Thin crust of secondary carbonate coating individual lamellae of a shell of Cepaea hortensis (Carrowmore, Co.Mayo).

shell surface, as was clearly seen in a number of specimens. This is also seen as exfoliation and is comparable with the loss of the hydration layers observed on obsidian. The exfoliation of crusts may owe something to differential expansion of the shell aragonite relative to the calcite crust, as well as the stress from the increased calcite volume.

In the studied example the origin of the material for the crust was almost certainly ground water since the material was found to be depleted in ^{14}C relative to the shell (see chapter 8.5 for further discussion).

The crusts are of an homogeneous or grainy appearance, with no clear crystal structure visible. This is interpreted as being due to gradual deposition allowing sub-micron crystals to form a loosely bound porous structure. Many of the shells examined had thick crusts (2-3mm) of tufa but this was distinct from the surface crusts which appeared to be bound into the surface of the crossed-lamellar structure.

6.34 The replacement of aragonite by calcite

Where the surface crusts have not exfoliated, or where the recrystallisation had taken place from an inner layer surface, larger areas of replacement calcite where found. In the shells studied this did not form a major part of the shell, the highest level being about 5% of the volume of the specimen. However, this would still represent an unacceptably high level of contamination in samples >20,000 years old.

The mineralogy of the replacement material was confirmed as calcite by XRD and its post-depositional origin is confirmed by its enrichment in ^{14}C relative to the unaltered shell material (see chapter 8.5). In the most extensive area studied the replacement calcite was 15-25 microns thick and extended for 4-5mm. The calcite had formed by progressive diagenesis from the inner shell surface. Figure 6.7 shows the boundary between the altered and unaltered material. A gap is clearly visible near the boundary, but the replacement calcite remaining with the aragonite structure suggests the gap is due to exfoliation rather than its being a diagenetic front. The presence of previous boundaries preserved in the calcite indicates phases of diagenesis alternating with stable periods.

The recrystallisation process appears to conform to the "thin-film" model proposed by Pingitore (1976; 1982); however, the apparent absence of a "gap" at the diagenetic front and the poor textural preservation in the calcite are closer to the observations of Wardlaw et al. (1978). The replacement calcite shows no definite crystal structure but is composed of rounded or elongated grains 0.1-0.5 microns across. This can be described as a form of micrite.

Replacement or neomorphic calcite was also observed developing at the boundary of the layers of shell structure (figure 6.8) where exfoliation had given ground water access to the unprotected crystal layers.

Examination at higher magnification (15,000-60,000 times) revealed the presence of material between individual third-order lamellae. The homogeneous appearance of the material between the lamellae suggests it is of secondary origin. The distance between the third-order lamellae is 0.1-0.2 microns and in the area observed this was filled

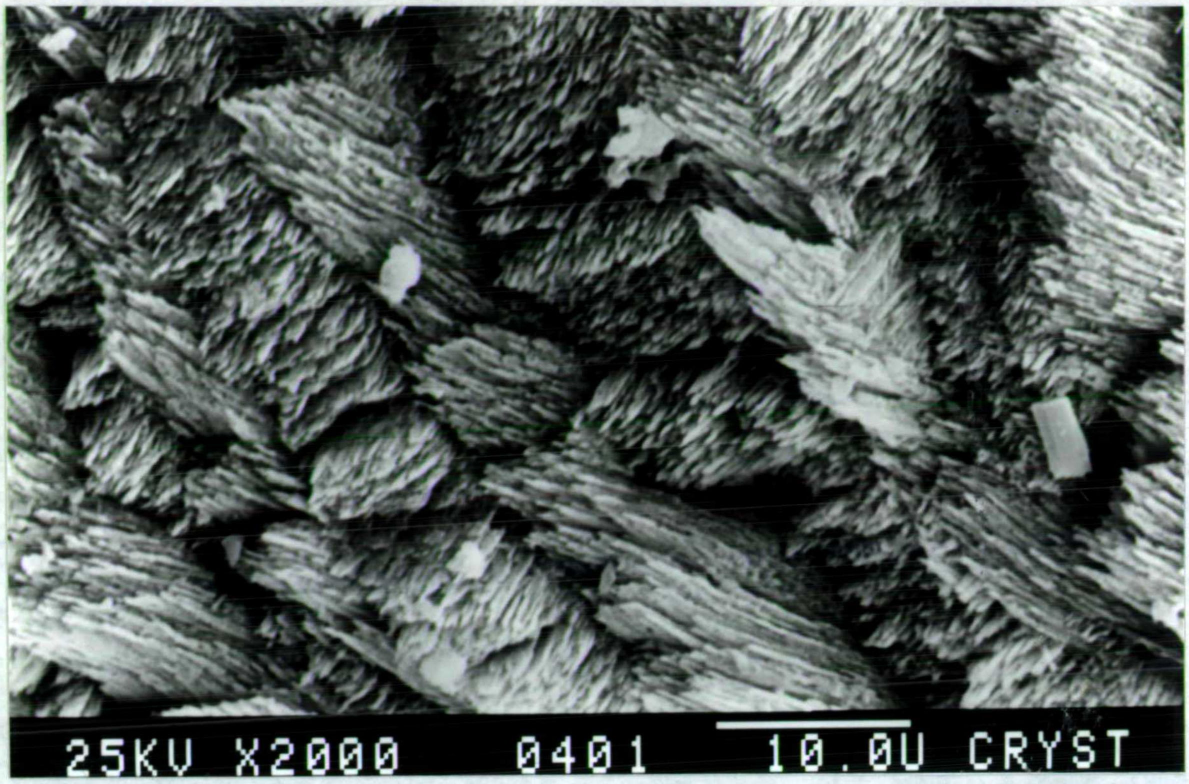


Figure 6.7A. Unaltered crossed-lamellae structure in a shell of *Cepaea nemoralis* from Caerwys, Clwyd.

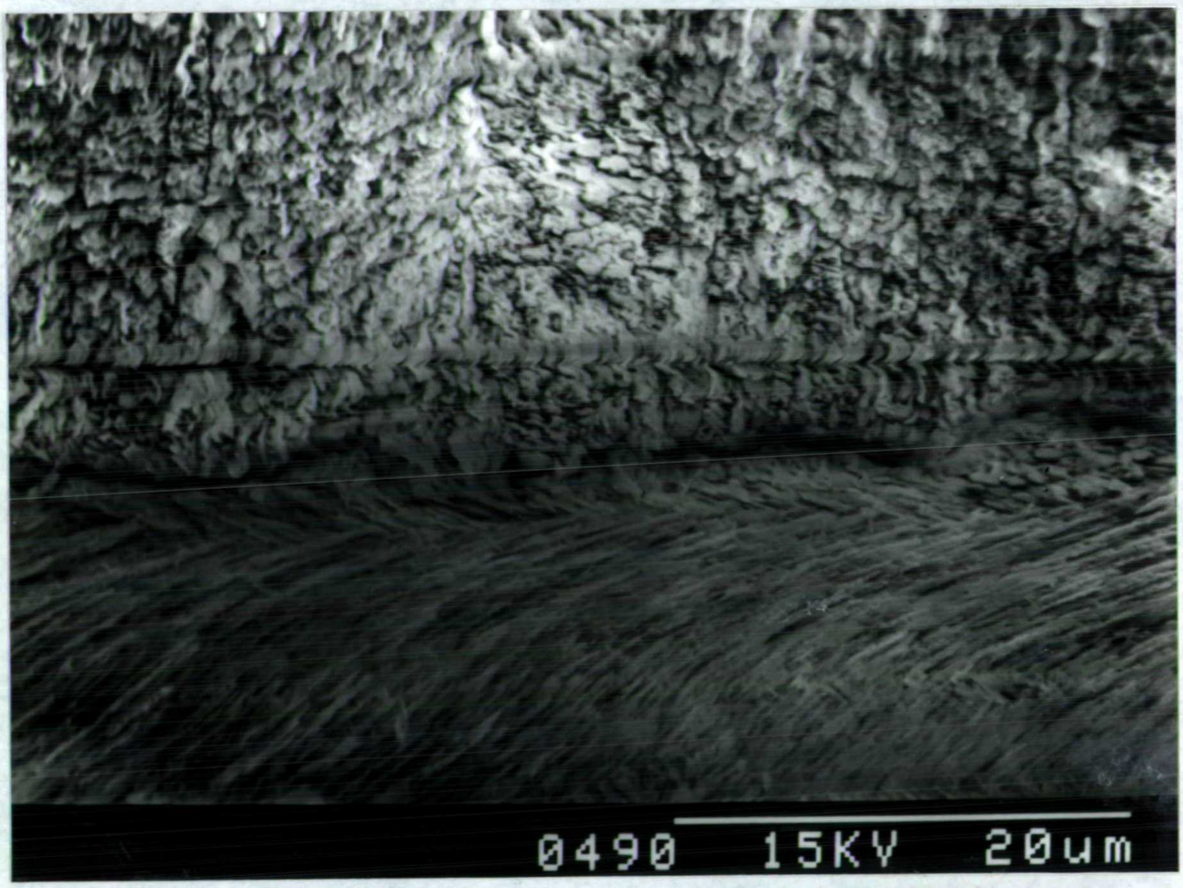
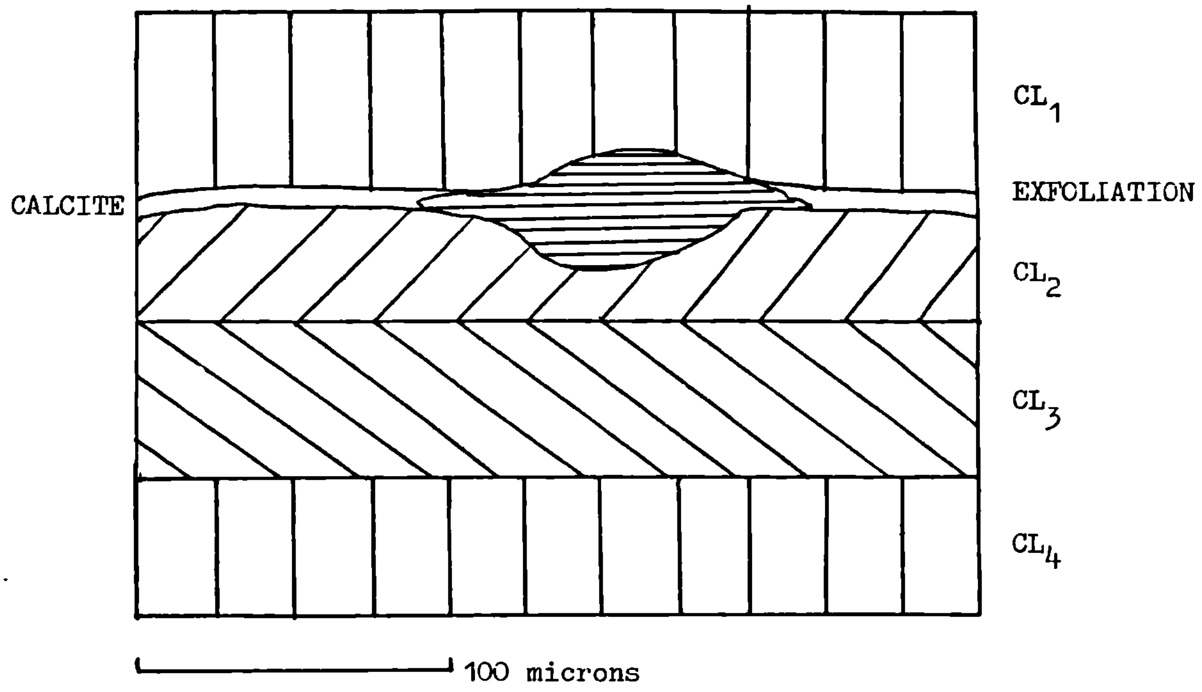


Figure 6.7B. Calcite (C) formed by recrystallisation of aragonite (A). A series of former (F) diagenetic fronts and the present one (A) are clearly visible. (*Cepaea nemoralis*, Caerwys, Clwyd)>



CL = Crossed-lamellar structure.

CALCITE = Area of secondary calcite developing between the layers of crossed-lamellar structure.

EXFOLIATION = Post-depositional opening of the layers of crossed-lamellar structure.

Figure 6.8. Diagram based on SEM photographs showing secondary calcite forming between layers which have parted due to exfoliation.

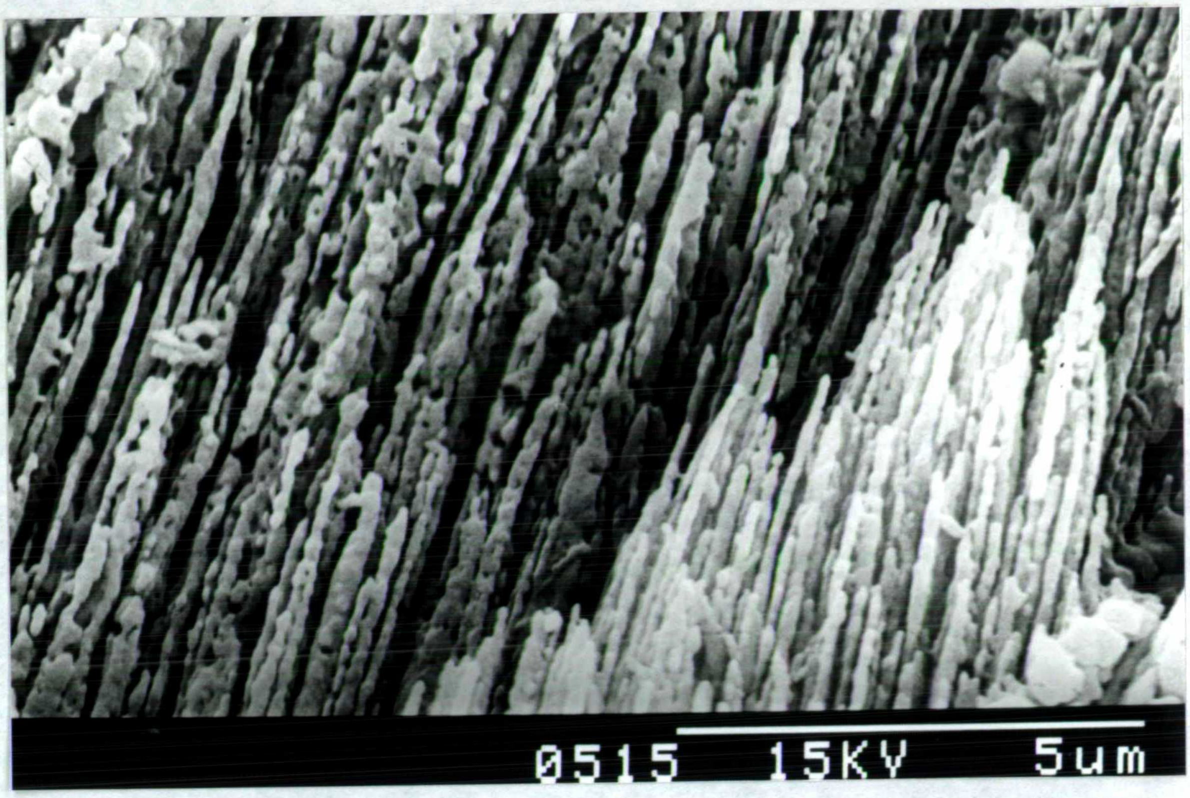


Figure 6.9. Secondary carbonate between individual third-order lamellae in a shell of Cepaea nemoralis from Castlethorpe, Lincolnshire.

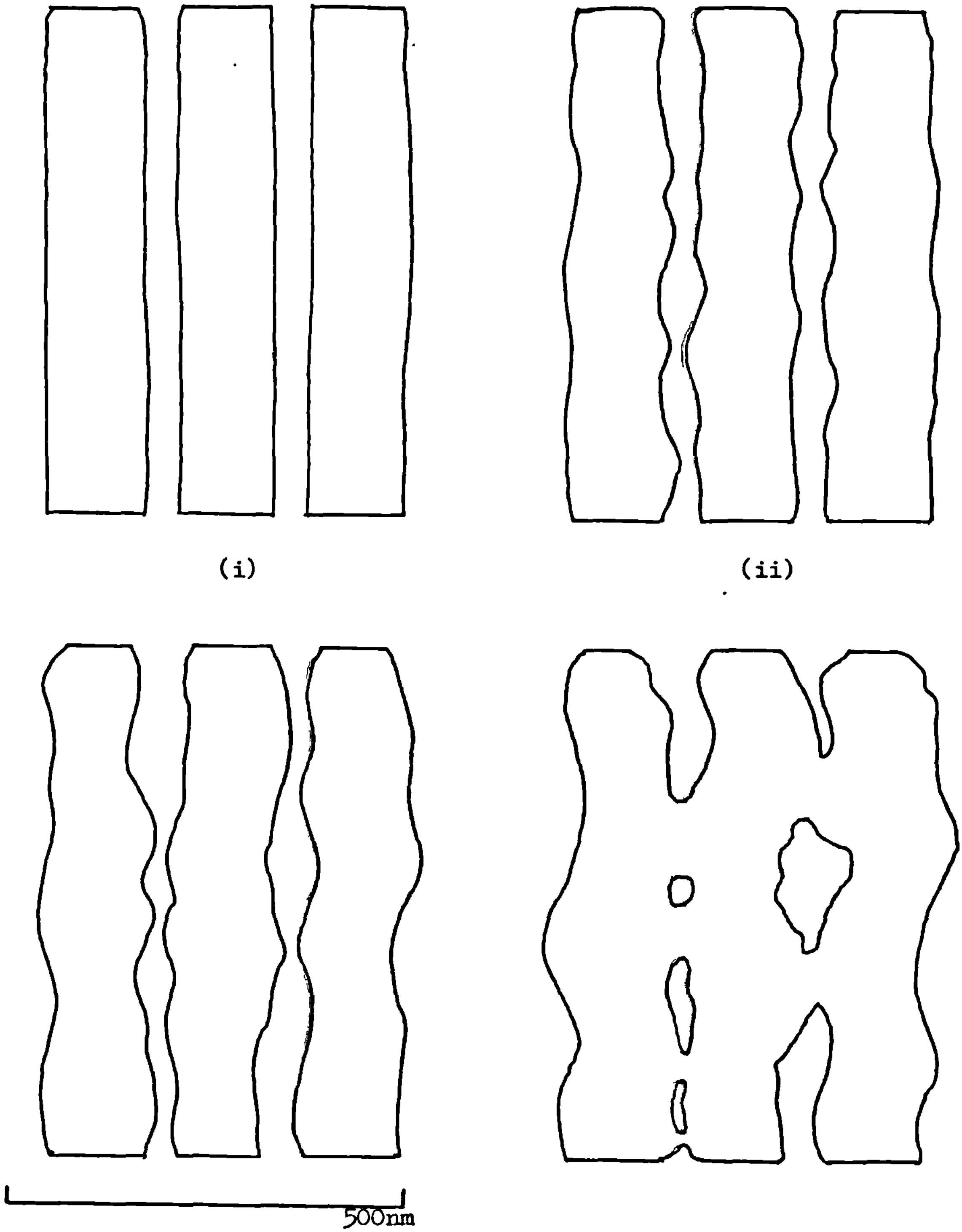
with material (figure 6.9). The enhanced ^{14}C value recorded in a shell of this type, relative to the expected value for this site, indicates that this material entered in an open-system. This type of deposit did not occur throughout the shell section but was asociated with a small area of replacement calcite between exfoliating layers of shell.

Recrystallisation of third-order lamellae was also observed. The initial appearance was of an etched and pitted surface but closer observation suggested that there was a progressive development from individual lamellae to a pitted structure combining two or three lamellae. The proposed development is shown in figure 6.10.

To achieve the progressive diagenesis outlined above the lamellae would have to have undergo dissolution and redeposition. This requires periodic variations in the external conditions such as the availability of ground waters. It also suggests that there is selective dissolution on the individual lamellae, i.e. some parts of the crystal structure are more susceptible to dissolution. Confirmation of this progressive diagenesis and that it is linked to an open-system requires experimental weathering of shells and ^{14}C analysis of samples exhibiting this type of diagenesis.

6.35 Dissolution of shell material and cementation of sediments

Sand dunes on the Mediterranean coast of Israel show evidence for climatic variation in the form of organic rich horizons. These horizons are rich in the shells of terestrial molluscs and the sand contains a scatter of shells. The upper sand horizons are loosely cemented, whilst the lower ones and those further inland have become Kurkar sandstone. The only available source of carbonate cement is



(i) (ii)

(iii) (iv)

(i) Unaltered individual lamellae.

(ii) Etching of surfaces (dissolution) combined with redeposition. This leads to an uneven surface on the crystals.

(iii) Dissolution and redeposition continues leading to the fusion of the lamellae in places.

(iv) The crystals lose their individuality with only the "pitting" left of the original gaps between them.

Figure 6.10. Diagram based on SEM photographs showing the recrystallisation of third order lamellae.

the shell material within the deposits. Examination of the shells showed that dissolution was taking place, and redeposition was occurring in the immediate environs of the shell, leading to the cementation of sand grains (figure 6.11). The lower sand deposits are cemented and contain no shells, the implication being that the shells have completely disssolved.

The sand in which this process is taking place is highly permeable and would not normally be considered suitable for secondary deposition to occur. However, dunes are recorded as containing water in the cores, the outer layers of sand acting as insulation. It is suggested that dissolution occurs in the warm surface environment and deposition takes place as the water cools in the lower sands.

6.4 THEORETICAL LIMITS OF DETECTION FOR CONTAMINATION AND DIAGENETICALLY ALTERED MATERIAL.

The previous section described the diagenetic structures recognised during this study. In connection with this it is important to consider the limits of detection using SEM and XRD. Two particular problems are considered to be important; the uptake of modern CO_2, and the formation of a thin layer of contaminated material on individual laths.

The possibility of post-excavation changes due to absorption of modern CO_2 was suggested by Olsson et al. (1968), who found that Tertiary shell material became of finite age after storage in a moist atmosphere. If post-excavation, these changes must be due to the alteration of external conditions after excavation, the shell and its voids coming to equilibrium with their new surroundings. If the contamination has occurred during burial then it most probably

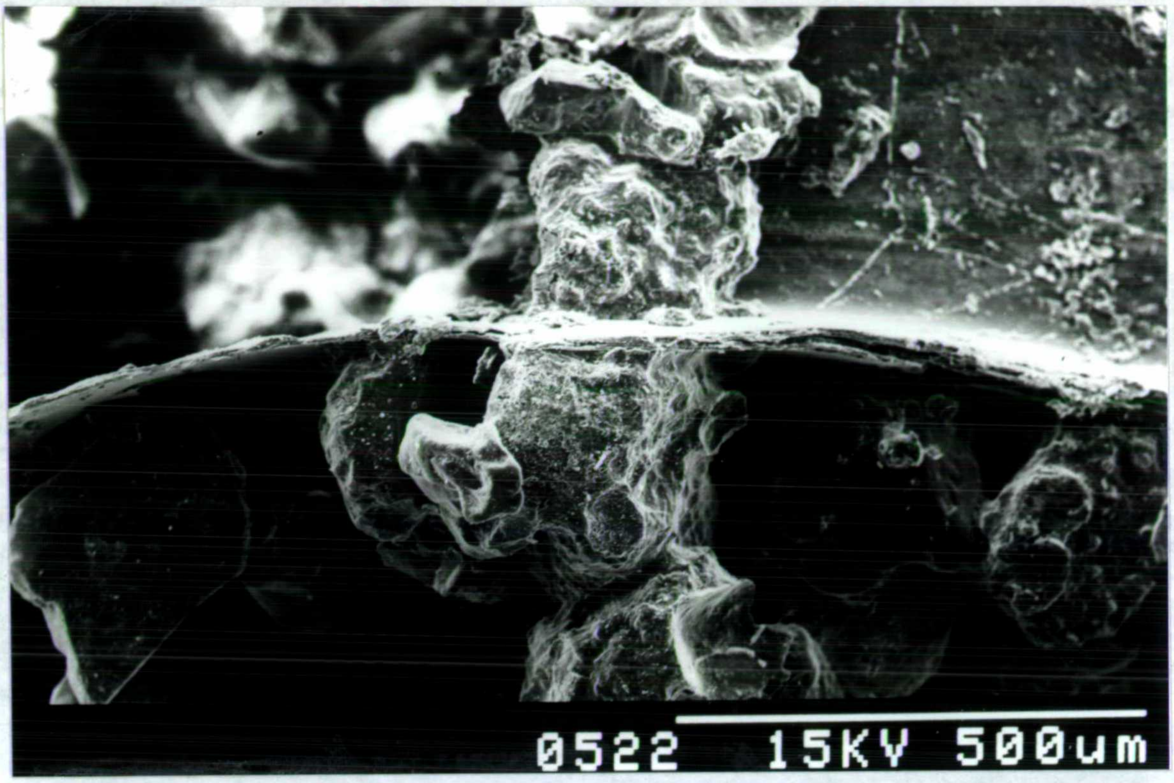


Figure 6.11A. Sand grains cemented to a shell of *Xeropicta vestalis* from Netanya, Israel.

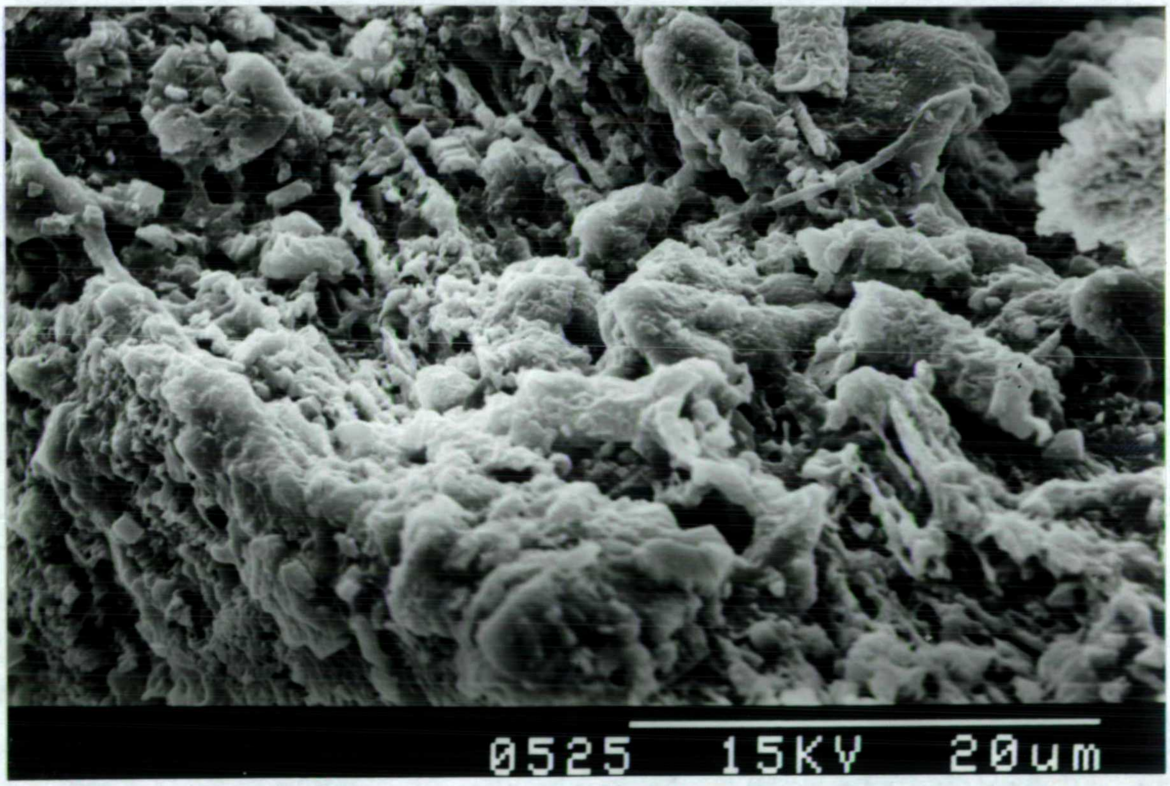


Figure 6.11B. Detail of the shell in figure 6.11A showing recrystallisation in the shell.

occurred in a period when the shell was subject to weathering in a vadose and meteoric environment. These two types of condition are similar in that they are produced by rapidly changing conditions. In constantly wet conditions the voids will be filled with water; this will not be circulating with the external aquifer but will remain within the shell. In dry conditions the voids will fill with the local atmosphere; this should diffuse through the pores and remain in equilibrium with the surroundings. In conditions of varying moisture the pore water may be replaced by the atmosphere if dry periods are of sufficient length and intensity. A meteoric environment is such a case.

Once the samples are removed from their burial environment they come to equilibrium with their new surroundings. The pores will become filled with the local atmosphere and if sufficient moisture is present some recrystallisation of the surface layers may take place. Variations in burial conditions will produce a similar change on the crystal surfaces. It is suggested that this type of recrystallisation is partially responsible for the occurrence of dates of 30,000 - 40,000 bp in "infinite" age samples. The presence of a crust formed by ion-exchange is considered to be more probable than contamination by gaseous CO_2. The example below shows why:

Sample 20 grams	Density 2.93
Pore space 50%	Volume of pore space 6.8cm^3

If all CO_2 (preferentially retained) % contamination

= 0.14%

If filled with atmosphere (0.03% CO_2)% contamination

= 4.2×10^{-5}%

However, if it is assumed that each crystal unit (lamella, prism, nacreous block) exchanges CO_2 at its surface then it is theoretically possible to get ion exchange of CO_3^{2-} ions from the atmosphere into the crystal lattice. If this takes place without disruption of the lattice (on individual ions) then replacement could occur without any mineralogical or optical change.

The depth of exchange required to produce a fixed level of contamination will depend on the size and shape of the unit that is being affected. An example is given in table 6.1 using first-, second-, and third-order lamellae from a typical crossed-lamelar structure. (All units are in microns).

UNIT	LENGTH	WIDTH	DEPTH	VOLUME	SURFACE	THICK.1%	THICK.10%
1st	2500	10	100	2000000	442000	0.0450	0.450
2nd	4	10	10	400	160	0.0250	0.250
3rd	10	1	1	10	42	0.0024	0.024

Table 6.1. The effect of lamellae size and shape on recrystallisation thickness. (All units are in microns).

x	y	z	p	th
1	1	1	0.1	0.017
100	100	100	0.1	1.667
1000	1	1	0.1	0.025
1000	1000	1	0.1	0.250
1000	1000	1000	0.1	16.670

If only the external surfaces of a shell are affected then:

th = 0.5 x p x shell thickness

e.g. shell thickness = 200 microns

th = 0.5 x 0.1 x 200 = 10 microns

x = length

y = width

z = depth

P = proportion

th= crust thickness

Table 6.2. The effect of size and shape on contamination.

These results (tables 6.1, 6.2) show that size and shape are important. Small grains (cubic) and needle crystals only need exchange to occur to a shallow depth, sheets and large cubic units will develop much thicker crusts for the same percentage alteration.

These findings can be linked to work described by Bathurst (1975). This discusses the enhanced solubility of very small crystals, compared with that of large masses of stable lattice. The work of Fyfe and Bischoff (1965) and Schmalz (1963) showed that significant increases in solubility can only arise when the size of the grain or crystal unit is less than 0.1 - 1 micron. Chave and Schmalz (1966) concluded that calcite is unstable in water if grains are less than 0.1 micron and that an enormous increase in solubility is to be expected for particles between 0.1 and 0.01 micron. Dimensions of 0.1 to 1.0 micron are similar to those for third-order lamellae and strengthens the case for an "ionic crust".

The separation of CO_3^{2-} units in aragonite is in the order of 0.2-0.5 nm, therefore the recrystallisation depth would represent only 5 to 12 lattice layers. The detection of such an exchange "crust" by direct means is nearly impossible since it is below the resolution of an SEM, and there need be no mineralogical change to be detected by XRD. Stable isotope ($^{13}C/^{12}C$, $^{18}O/^{16}O$) and major ion values (Mg, Sr) are also unlikely to reveal such a layer since the variations of their initial values will be greater than changes due to "crust" formation. The recrystallisation of third-order lamellae discussed in the previous section may be an extension of an "ionic crust" over a longer time and greater area.

The precautions necessary to avoid post-excavational exchange and contamination are discussed in chapter 8.2, but those problems due to the formation of "ionic crusts" during burial will be very difficult to overcome.

6.5 POST-DEPOSITIONAL ALTERATION OF THE CHEMICAL AND ISOTOPIC COMPOSITION OF SHELLS

The post-depositional alteration of the composition can occur in two forms; one is associated with the recrystallisation of the shell structure from aragonite whilst the other is a compositional change only. Compositional changes associated with recrystallisation have been extensively studied but generally on a time scale of millions of years. Previous studies of marine shells have indicated that four measurable effects may occur: depletion of ^{13}C content, depletion of Mg content, enrichment of Sr content, and a reduction in the distribution range (e.g a reduction in the isotopic or cation content variance).

The depletion of ^{13}C content is associated with a change in mineralogy (Buchardt & Weiner 1981; Gavish & Friedman 1969); and there is a positive correlation between $\delta^{13}C$ and percentage aragonite. Gavish and Friedman (1969) studied a stratigraphic sequence covering the Quaternary and late Tertiary periods. The sequence showed progressive diagenesis over a period of 200,000 years and a depletion in ^{13}C from +3 to $-6^{o}/_{oo}$. The ^{18}O values were also depleted but only from -1 to $-4^{o}/_{oo}$. Analysis of the mineralogy showed the depletion was associated with a complete change in mineralogy from 100% aragonite to 100% calcite. Buchardt and Wiener (1981) studied Cretaceous ammonites. The samples were divided by visual examination into four groups according to the degree of preservation and the presence of secondary concretions. Samples with secondary concretions were depleted in ^{13}C but the $\delta^{18}O$ values were more stable.

It is clear from these studies of diagenesis that recrystallisation can involve isotopic changes. The magnitude of the changes must be linked to the source of the ions that replace original material. If recrystallisation occurs within a closed system there need be no change in the isotopic composition and there will be no contamination from external sources. An open system will allow exchange of Ca^{2+} and CO_3^{2-} ions with the immediate environment and if this material is influenced by soil- or plant-derived CO_2 the new material will assume a $\delta^{13}C$ value in equilibrium with this source. In marine deposits, such as those used by Gavish and Friedman (1969), the initial $\delta^{13}C$ value of the unaltered material is $0-4^{o}/_{oo}$, the exact value depending on location. The incorporation of soil- or plant-derived CO_2 will lead to depletion and theoretically a value in the order of $-17^{o}/_{oo}$ could be achieved. A more likely value would be $6-8^{o}/_{oo}$, calculated on the basis of 50% soil-/plant-derived CO_2 and 50% original material. In an exposed meteoric environment the exchange may include atmospheric CO_2 in solution ($\delta^{13}C$ $+1^{\circ}/_{\circ\circ}$) which would produce little change in the $\delta^{13}C$ value of the recrystallised material relative to an original marine shell.

The isotopic changes in terrestrial shells will be different because their initial values are in the range -6 to $-12^{\circ}/_{\circ\circ}$. Isotopic changes will only be visible in the shells that are depleted (-10 to $-12^{\circ}/_{\circ\circ}$ prior to recrystallisation and only then if a substantial percentage is altered. Shells with an initial $\delta^{13}C$ value of $-8^{\circ}/_{\circ\circ}$ will still have values in the normal range unless the population of shells had a narrow range; even then the evidence would not be conclusive.

Goslar and Pazdur (1985) carried out contamination experiments, under laboratory conditions, on shell in alkali and acid depositional environments. Samples of ground shells (*Helix pomatia*) were mixed with ^{14}C-free chalk, peat and water. After 133 days at 50-60°C no significant isotopic changes were observed. A similar experiment using aragonitic marine shells (*Mya truncata*) in an acid environment (recent active soil with plant fragments and water). After exposure in the same conditions (133 days at 50-60°C) a small shift in ^{14}C age and $\delta^{13}C$ value were found but no measurable calcite was present. The $\delta^{13}C$ change was probably only detected because of the enriched initial value ($1.81^{\circ}/_{\circ\circ}$).

Changes in $\delta^{18}O$ values will generally be controlled by the temperature at the time of initial formation and recrystallisation. Unless there is a substantial change between the two temperatures the old and new $\delta^{18}O$ values will be indistinguishable.

The results from the present study recorded only small changes in mineralogy (>5%), and no measurable changes in $\delta^{13}C$ and $\delta^{18}O$ would be expected from this level. If recrystallised material could have been isolated and analysed differences from the unaltered shell could possibly have been observed but the quantities of recrystallised material were too small for this.

Any changes in the ^{13}C content will be accompanied by changes in the ^{14}C content. If the exchange took place a significant time after deposition then the shell will appear to be younger than its depositional age. An exception to formation of "younger" material would occur if the replacement CO_3^{2-} ions contained a component from ground water sources which themselves had an apparent age; exchange could then produce an age greater than the apparent or true age.

The alteration of magnesium levels is recorded from recrystallised material and shells that have retained their original mineralogy though the effects can occur in opposite directions. Buchardt and Wiener (1981) observed an increase in the Mg/Ca ratio from unaltered well preserved ammonites to the poorly preserved ones. Further analysis showed the Mg increase was correlated with an increase in the percentage of calcite. Buchardt and Wiener use the increase in Mg and calcite contents as a criterion to form a diagenetic classification. Turekian and Armstrong (1961) also observed a correlation between percentage calcite and Mg content.

Gavish and Friedman (1969) found the opposite trend: the concentration of Mg decreased through time and with increasing calcite content. Over a 100,000 year period a depletion to 18.5% of the initial value was observed. The depletion was most rapid in the period immediately after deposition (0-10,000 years) during which 85%

of the total depletion occurred. In contrast the $\delta^{13}C$ changes were slower with only 33% of the total occuring in the same period. The different rates of change suggest that Mg can be lost without any mineralogical change occurring.

Enrichment of Mg contents was also recorded by Polifka _et al._ (1972) in their study of sub-sea diagenetic effects on aragonite bivalves. The shells had unaltered mineralogies and only in one case had either ^{18}O or ^{13}C significantly changed. Polifka _et al._ (1972) suggest five mechanisms that could give the observed changes but considered that selective dissolution of $CaCO_3$ leading to an enrichment of Mg and Sr was the most likely. They suggested that the selective dissolution of $CaCO_3$ would be accompanied by preferential loss of the lighter ^{12}C atoms giving an enrichment in the $\delta^{13}C$ value. However, the overall picture suggests that a more probable explanation is the adsorption of Mg and Sr on the crystallite faces in an environment richer in these ions than the shells.

Depletion of Mg contents in fossil shells with unaltered mineralogies relative to modern samples is recorded by a number of workers (Pilkey & Goodwell 1964; Walls _et al._ 1977). The magnitude of the depletion varies but is generally 20-35% in the research mentioned above. Similar depletions were observed in the present study in most of the fossil samples. The clearest evidence came from Binnel Point where fossil shells and opercula of _P.elegans_ were depleted in Mg relative to the modern samples from the same location (table 6.3).

Sample	Mg (ppm)	Sr (ppm)	Fe (ppm)	Mn (ppm)
Fossil shell	192.3+38.5	420.6+60.6	147.8+50.7	13.8+4.7
Opercula	1367	342	101	25
Modern shell	300.3+65.9	347.8+71.1	97.0+24.5	14.6+4.1
Opercula	2402	444	56	25
% change shell	-36%[1]	+21%[1]	+52%[1]	+6%[1]
Opercula	-43%	-23%	+80%	0%

(1) = significantly different at p=0.05. Based on ratio of modern/fossil.

Table 6.3. Comparison of chemical composition of fossil and modern shells from Binnel Point, Isle of Wight.

Evidence of magnesium depletion was also seen in the Mg content in the other fossil sample. The observed levels were generally below the "background" observed in the modern samples. Comparison of fossil samples from Carrowmore with those from the nearby site of Graffy show the Mg content of the fossils to be below the modern "background" if two anomalous results are not included (table 6.4). Two factors suggest that this is due to diagenetic alteration; the first is the small number of "high" Mg from Carrowmore compared to Graffy, the second is the enrichment of Sr contents (see below).

	Tufa		Shell	
Sample	Mg	Sr	Mg	Sr
Graffy	564	120	71	105
			180	
			610	
Carrowmore (CBB$_1$)	563	37	67	122
Carrowmore (CBM$_1$)	519	65	35	73
Carrowmore (CBT$_1$)	506	46	37	134

Table 6.4. Composition of modern and fossil shells, and tufas from Graffy and Carrowmore, Co.Mayo.

Turekian and Armstrong (1961) suggested that the change in magnesium, and other impurity, contents was connected to the location of these ions at interstices. Chapter 5.4 showed that the Mg^{2+} ions are present in the lattice structure and in large numbers at interstices. It is the loosely bound interstice ions that are removed during the early stages of deposition; and the main agent of removal must be meteoric and ground waters. This type of mechanism allows rapid depletion of some ions followed by a stable concentration of lattice ions that are more difficult to remove without some disruption of the lattice. The interstices ions are more stable whilst the mollusc is alive because the organic matrix and periostracum reduce the rate of water movement thought the shell.

Manze and Richter (1979) observed a depletion of Mg in high

Mg-calcite; this was associated with a depletion in ^{13}C but no alteration to the crystalline structure was observed. They attributed this to a micro-scale process of dissolution and reprecipitation rather than a compositional change without any structural effects.

The depletion of Mg ions is generally accompanied by an enrichment in the concentration of Sr ions. Enrichment of Iron (Fe) and Barium (Ba) concentrations has also been observed. Turekian and Armstrong (1961) suggested that the Sr enrichment was due to adsorption of ions at interstices made vacant by the decay of organic matter, which caused new areas of exposed crystal surfaces. Further vacancies are created by the loss of Mg ions. Turekian and Armstrong comment that the incorporation of large ions (e.g. Sr) is more likely to occur by adsorption than by inclusion in the lattice because of the size of the ion. However, the Sr must be more tightly bound to the structure than the Mg ions or an increase could not occur. Walls *et al.* (1977) attribute the increase in Sr to the replacement of Ca ions in lattice sites. Schroeder (1969) shows that Ca is more easily dissolved than Sr and this could create lattice vacancies for the more stable Sr to fill. The relative location of Sr and Mg at interstices and lattice sites is demonstrated by the increased exchange capacity of Mg relative to Sr (Treese *et al.* 1981).

Treese *et al.* (1981) suggest that the rate of depletion or enrichment of ions is related to the surface area of the material, and that there was an increase in adsorbed ions in fine grained materials relative to sands.

In the present study modern shells contained Sr levels below those of the surrounding environment; fossil shells all contained levels above their environments and above their modern counterparts (see tables 6.3, 6.4). At Binnel Point the Sr concentration increased by 21% in the aragonite shells but decreased by 23% in the calcitic opercula. This suggests that the Sr ions are mainly located at interstices in calcite but within the aragonite lattice.

The alternative mechanisms for the enrichment of Sr have important implications for ^{14}C dating. The adsorption of Sr ions requires no disruption of the lattice but replacement of Ca by Sr does. The latter may also be accompanied by substitution or exchange of CO_3^{2-} ions.

The final effect observed in the compositional alteration of shells is a reduction in the variance associated with the means for each sample. This effect can be seen as a result of the depletion or enrichment of impurities; it must also be related to the environment. Curtis and Krinsley (1965) suggested that the chemical composition of a population moves towards equilibrium with its environment after deposition. This is accompanied by a reduction in the variance of the sample. The variance for the modern and fossil samples form Binnel Point were calculated and compared (table 6.5) either as per mill. ($\delta^{13}C$, $\delta^{18}O$) or as a percentage of mean values (Mg, Sr, Fe, Mn). The results show a decrease in the variance of $\delta^{13}C$, Mg and Sr but an increase in $\delta^{18}O$, Fe and Mn. Examination of the mean variance for all fossil Cepaea nemoralis (6 samples) and modern C.nemoralis (3 samples) shows a reduction in $\delta^{13}C$, $\delta^{18}O$ and Mg variance but not Sr variance.

Sample	δ^{13}C	δ^{18}O	Mg(ppm)	Sr(ppm)	Fe(ppm)	Mn(ppm)
Fossil shell	0.120	0.171	7.71	8.73	17.39	1.61
Modern shell	0.851	0.149	14.46	14.53	6.19	1.17

Variances of ^{13}C and ^{18}O are expresssed as per mill., those of Mg, Sr, Fe and Mn as the variance/population mean expressed as a percentage.

Table 6.5. Comparison of the variances of the isotopic and chemical composition of fossil and modern shells from Binnel Point, Isle of Wight.

The results of the present study seem to confirm the earlier results of Curtis and Krinsley (1965). When considered with the mechanisms that lead to alteration in composition, discussed above, a movement towards equilibrium with the environment seems evident. Cases where the variance increases can be interpreted as indicating chemical alteration under two or more different conditions (such as a change in ground water source or exposure to a meteoric environment). However, if increases and decreases are observed in one sample then the results are more difficult to interpret.

Reductions in the variance of the δ^{13}C and δ^{18}O values suggest that dislocation and exchange are taking place within the aragonite lattice. If ^{13}C atoms are being exchanged there must also be a movement of ^{14}C atoms and a consequent contamination. The direction of the error (older or younger age) will depend on the source of the new ^{14}C atoms.

6.6 IMPLICATIONS OF STRUCTURAL CHEMICAL AND ISOTOPIC CHANGES FOR ^{14}C DATING.

6.61 Effect of structural and mineralogical changes

The present chapter has described the structural and mineralogical changes observed in this study; the descriptions included some comments on their effect on the ^{14}C content. It is clear from these comments that the critical factors are the "openness" of the system in which the changes occur; the time at which the changes occur (relative to the time of deposition); and the source of any new material that enters if the system is open. Table 6.6 gives details of the combined effect of the three factors and the four types of diagenetic alteration (etching, crusts, replacement calcite and cementation) on the ^{14}C content of shells. The shells are assumed to have a true age equivalent to one half-life for ^{14}C (5730 years). The values assumed for the date of alteration and the sources of external carbon are chosen to be the extremes that could be encountered.

Chapter 8.5 contains details of AMS ^{14}C ages obtained on diagenetically altered shell material.

6.62 Effect of chemical and isotopic exchange

Chapters 5.3, 5.4 and 6.5 have shown that the original and post-depositional chemical and isotopic compositions of shells contain important information on the ^{14}C level that is present. The isotopic analysis of modern samples showed that the environment contributes a significant amount to the shell composition and that

System	Closed	Open			
Time of alteration	No effect	Recent		5730 bp	
Source of new carbon	Not applicable	CO_2 (0bp)	$CaCO_3$ (inf[7])	CO_2 (0bp)	$CaCO_3$ (inf[7])
Etching	No dep. (5)	No dep.	No dep.	No dep.	No dep.
	5730 bp (6)	5730 bp	5730 bp	5730 bp	5730 bp
Crust[1]	Unlikely to occur	0 bp	Infinite	5730 bp	Infinite
(Surface)	5730 bp	2380 bp	11460 bp	5730 bp	8100 bp
Crust[2]	Unlikely to occur	2380 bp	11460 bp	5730 bp	11460 bp
(Recryst.)	5730 bp	3880 bp	8100 bp	5730 bp	8100 bp
Replacement	May occur within	2380 bp	11460 bp	5730 bp	11460 bp
Calcite[3]	crystal structure				
	5730 bp	3880 bp	8100 bp	5730 bp	5730 bp
Cementation	Unlikely to occur	2380 bp	Unlikely	5730 bp	Unlikely
[4]		3880 bp	to occur	5730 bp	to occur

(1) Material deposited on the shell surface.
(2) Crust formed by recrystallisation of original shell.
(3) Recrystallisation of aragonite to calcite proceeding through the shell.
(4) Dissolution and redeposition of carbonate, including external matrix (e.g. sand).
(5) ^{14}C age of altered or new material.
(6) ^{14}C age of whole shell assuming 50% is affected.
(7) Infinite ^{14}C age (e.g. chalk).

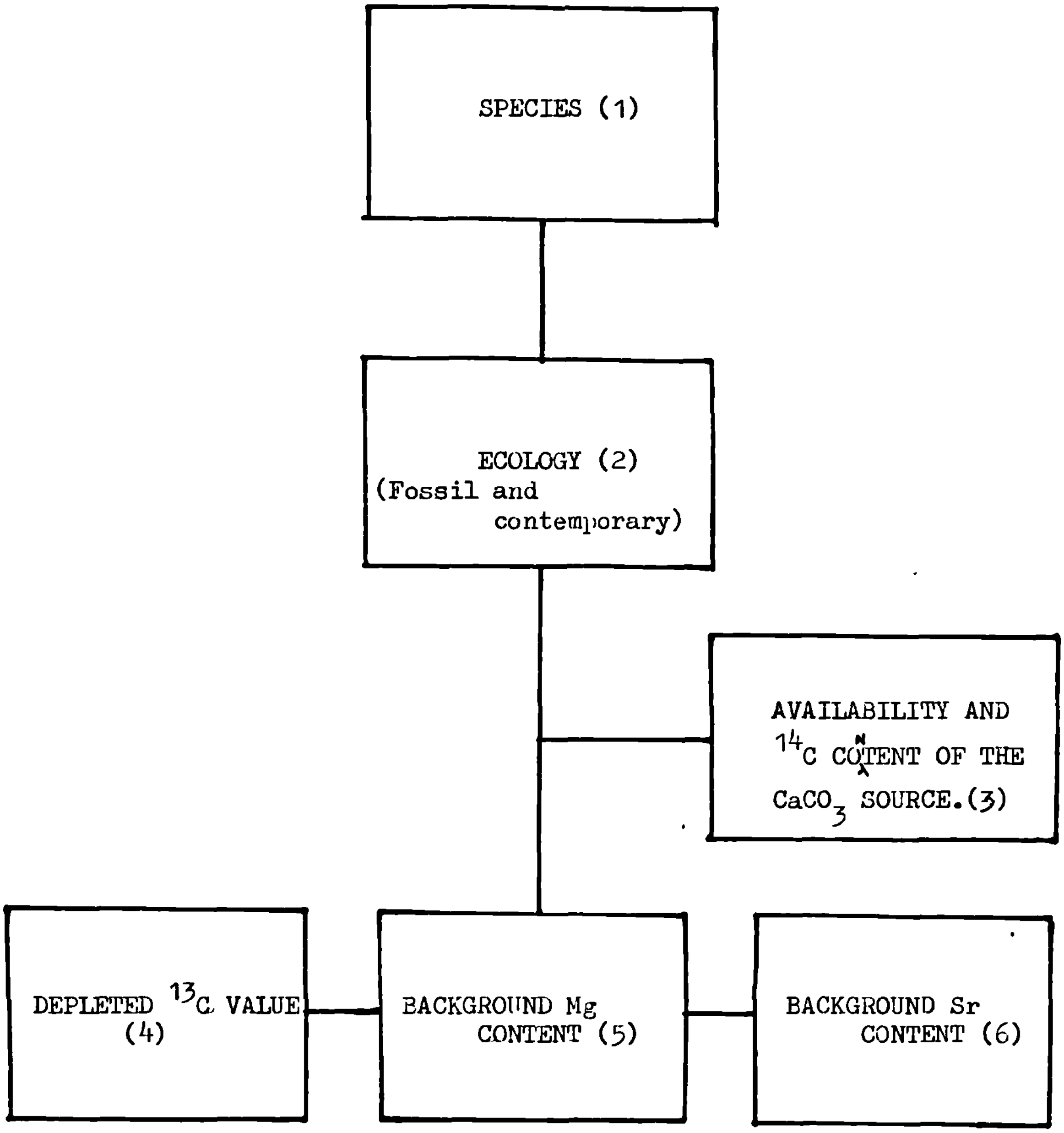
Table 6.6. The effect of different external conditions and types of diagenetic alteration on the ^{14}C age of shells.

metabolism and atmospheric CO_2 are not dominant. The nature of the $CaCO_3$ source (e.g particle size) and availability are important in determining the amount of depleted material that a snail can take up. The apparent age of the material is also important as it will affect the final ^{14}C values of the shell. Other important factors are the ecology of the snail and its changing habitats during its life (e.g. the different niches occupied by adults and juveniles). Analysis of the organic matrix suggested that it is not influenced by variations and changes in environment nor the different sources of $CaCO_3$.

The chemical analyses showed that strontium concentrations were primarily controlled by metabolism and the availabilty of Sr. Magnesium concentrations were controlled by mineralogy and a "background" level was defined. Some shells had Mg concentrations well above the "background" and are interpreted as having adsorbed extra ions into the lattice or interstices sites from the external environment. The "high" Mg levels are associated with species that have high levels of contact with particulate $CaCO_3$ sources. It is probable that an increase in Mg is accompanied by CO_3^{2-} ions and hence ^{14}C contamination.

Post-depositional depletion of Mg occurs by loss of loosely bound ions. Their loss is indicative of water moving through the shell and depletion of ^{13}C is recorded, as are reduced variances. Alteration to ^{13}C levels must be accompanied by some change in the original ^{14}C both by incorporation of inclusions at interstices and at lattice locations.

The changes in ^{14}C levels described above can be combined to give a selection procedure (figure 6.12); not all the criteria can be



(1) Select species that are common, large and live above ground.

(2) Select sites that are not subject to diagenetic environments, that show no evidence of reworking and where the shell population is homogenous.

(3) Determine the ^{14}C content of the $CaCO_3$ source material and its availability (e.g. was there a thick litter layer).

(4) Select sample in which the ^{13}C value is depleted.

(5) Select samples in which the Mg content is near "background".

(6) Select samples in which the Sr content is near "background".

Figure 6.12. Selection procedure for samples, based on the isotopic and chemical analyses. The complete selection procedures are discussed in chapter .

achieved but by choosing shells and species that closely fit these there must be a reduction in the apparent age effect.

The integration of this selection procedure with the study of diagenetic changes in structure is discussed in chapter 8.2, and these methods are then validated by application to fossil samples in chapter 8.5.

CHAPTER 7. METHODS OF DETECTION OF STRUCTURAL CHANGES IN SHELLS

7.1 INTRODUCTION

Two of the previous chapters discussed the structures of shells and the diagenetic alterations that were observed during this study. The samples on which these observations were based were studied under good conditions, with sufficient material and time to allow detailed examination of those samples that would produce the clearest results. However, when studying samples that are of limited size, and where time is also limited, it is important that the range of techniques applied should be efficient and give clear results that are representative of the material being studied. The order in which they are applied is discussed in chapter 8; this chapter gives details of the methods which were applied.

The four methods that were used to assess changes were:

(i) Observations of shells using a low-powered binocular microscope.

(ii) Acetate film peels.

(iii) Scanning electron microscopy.

(iv) X-Ray diffraction analysis.

These methods cover a range of detection sensitivities and are able to cover varying percentages of the shell material. The observed limitations of each method are considered and where appropriate a theoretical discussion of the limits is included.

7.2 LOW-POWERED BINOCULAR MICROSCOPY

The appearance of the shell and its relationship to the matrix can give important information on the diagenetic alterations that the shell may have undergone. It may be studied by eye or using a low-powered binocular microscope. It was the first method applied to each sample as it allowed a general appraisal of the condition of the material. It can be applied to the sample prior to the removal of the surrounding matrix, but cannot at this stage reveal information on the inner shell surface or the internal structure.

7.21 Matrix

The context from which the material was collected should be recorded and sampled in the field. However, it is important to assess the degree of cementation between matrix components, and the matrix and the shell in the laboratory. Since the cement will usually be calcium carbonate a high degree of cementation is evidence that dissolution has taken place in the surrounding environment. The source of cement may be adjacent shells or if the hydrology is suitable from groundwaters. Reprecipitation of carbonate as cement suggests that the shells may also have suffered deposition of secondary carbonate within the crystal structure. The cementation of sand grains to each other and the shell is clearly seen in material from the coastal zone of Israel (figure 6.11). The extent to which the matrix is adhering to the shells will also indicate the most appropriate cleaning methods.

7.22 Shell

When the shell had been removed from the matrix, and if possible the outer surface cleaned, it was studied further. The typical appearances ranged from surfaces with much of their original sculpture (e.g. on Pomatias elegans) and decoration visible (e.g. banding on Cepaea nemoralis) to heavily pitted surfaces. The pitted surfaces were generally associated with exfoliation of the shell which gave the surface a "flaky" texture. The surfaces also felt "chalky" with loose particles of shell; this may be due to diagenetic crusts or the final stages of exfoliation where the "flakes" have weathered to a powder.

After the shells had been sectioned visual examination of the interior frequently showed large deposits of matrix and secondary carbonate. If the shell had been cleaned internally by flushing with distilled water through the aperture or apex, contamination was still observed on sectioning. Many shells were fragmentary and only needed to be pulled apart with tweezers to reveal the interior contamination. Examination of the shells after initial cleaning frequently revealed adhering matrix particles which were removed by mechanical cleaning under a low-powered binocular microscope. In extreme cases of recrystallisation, cryptocrystalline calcite crystals were visible in the fracture surfaces.

7.3 ACETATE FILM PEELS

7.31 Introduction

The preparation of peels by the acetate film method is widely used in petrology and has been an accepted technique for more than fifty years. Among the researchers who developed the technique were Appel (1933), Butler (1935) and Darrah (1936). These early studies used collodion or cellulose dissolved in a suitable solvent (e.g. butyl acetate or xylene). The solution was applied to the polished section in a number of coats and allowed to dry completely before removal. More recently cellulose acetate sheets have been used in conjuction with acetone or another suitable solvent. The present study used 0.1mm acetate film with both sides polished and acetone as the solvent.

Acetate peels are generally equivalent to thin sections as they take a thin layer of crystals from softer materials. They also contain a record of the topography of the section surface, and, in the case of hard materials, they are only an impression with no material being transferred.

7.32 Method

The more solid samples, generally with shell wall thicknesses greater than 2mm, were sectioned using a water-lubricated petrological diamond saw. Samples that were thinner or more delicate were sectioned using a Black and Decker "Minicraft" drill mounted on a retort stand and fitted with a 1mm thick cutting disc. None of the studied samples required embedding but if necessary a hard clear plastic can be used or the sample consolidated with araldite.

The cut shell edge was then ground using a series of grades of corundum powder (3F, F600, F800) on a glass plate. The samples were carefully washed with distilled water between each grade of corundum and a separate glass plate was used for the finest grade. The finished sections had a smooth flat surface with a satin sheen and no grinding scratches from the coarser grades of corundum. After the final polish the samples were cleaned in an ultrasonic cleaner and distilled water, then the surface was etched.

Etching of the surface increases the micro-topography, and a number of different effects can be achieved. If the surface is etched in an oxidising agent (e.g. hydrogen peroxide) the organic matrix is removed leaving the crystal structure more prominent. If acid (usually hydrochloric acid) is used the crystal strucure is etched, but not evenly, as parts of the structure are more easily dissolved.

In a shell containing aragonite and secondary calcite, the aragonite is preferentially attacked (Vita-Finzi & Roberts 1984) leaving the calcite as raised areas. If the shell is only aragonite some prefential dissolution will still occur because some areas will be more protected by organic matrix, an example being the first-order lamellae of the crossed-lamellar structure when they are sectioned transversely rather than radially.

The etching is critical in producing a peel in which the structure is clearly defined and experimentation is required for each type of material used to achieve optimum results. In this study the most successful etching was achieved using 10 vol. hydrogen peroxide for 10 seconds, rinsing in distilled water and then etching in 2% hydrochloric acid for 5 seconds. Whilst etching is taking place it is important to hold the sample at an angle, this allows the gas bubbles to escape and ensures even etching.

After the samples had been etched they were rinsed in distilled water and placed in a clean drying oven for one hour at 50°C. The dried shell sections were placed in acetone and then immediately onto a piece of acetate film and held firmly in place with the polished section flat on the film. When the acetone had evaporated the acetate film was peeled back.

An alternative method is to place the sample, with the polished section horizontal and facing upwards, in a sand box. The surface of the section is flooded with acetone and the piece of acetate film, bent into a "U" shape, placed on one end of the section. It is then carefully allowed to unroll across the section and float on the layer of acetone. The film comes into full contact with the section as the acetone evaporates. This method helps to reduce air bubbles forming between the film and the shell.

The film pulls away a thin, semi-transparent, layer of calcium carbonate crystals and an impression of the micro-topography. Those areas of the section that were more prominent after etching transfer more material to the acetate film and, therefore, produce a more opaque layer. Some of the larger crystals may fail to be removed from the shell section as they cannot be pulled from the crystal structure. The acetate peel that is produced is not a true thin section but rather a record of topography and the size and shape of the crystal units that are present. If the shell section is contained in a hard cement matrix (e.g. beachrock) the whole any be sectioned and polished and grains from the matrix will be transferred to the peel. This will give details of the relationship betwen matrix, cement and shell structure.

The excess film was trimmed off with scissors and the peel mounted betwen two glass slides (usually standard microscope slides); the ends of the slides were bound with tape and the slides labelled.

The peels were viewed under normal or polarised light and when the stage was rotated some extinctions were apparent in the peels that contained shell material. The structural details observed in the acetate peels included structural variations in a thick marine shell

and layers of crossed-lamellar structure in the feather-like bands of crystals parallel to the margin of shells of Helix pomatia. Magnification is limited by the depth of field of the peel; the most successful magnifications were found to be between 30 and 70 times.

Diagenetic recrystallisation could only be observed on a coarse scale. Areas of secondary calcite, particularly cryptocrystalline and micrite forms, stood out clearly against the ordered aragonite nacreous and crossed-lamellar structures. Secondary crusts and finer inter-lamellar deposits could not be resolved. Extinctions were visible under polarised light but the variable orientations of the recrystallised and original material made them indistinct.

The thickness of section that could be used to produce a peel appeared to be limited to greater than 1mm; samples with thinner shell walls were used but the results were poor. This is considered to be due to a narrow band being lost at the edge of the peel, in the order of 0.2mm. This is unimportant on a shell that is >5mm thick but becomesunacceptable on the thin shells when it represents 40 or 50% of the total thickness. The alternative method for producing peels, with the polished surface facing upwards, may be better for thin walled shells since it does not allow the acetone to run down the shell walls onto the film. However, it would be difficult to flood a 0.1-1.0mm thick section and float a piece of acetate film on it without any movement. The only other method considered is to embed the shell in resin and thereby increase the apparent shell wall thickness.

The detection of calcite in non-marine shells (i.e. ones that are aragonitic) can be enhanced by the staining of the polished and etched section prior to producing the peel. Bissell (1957), and Davies and Till (1967) discuss the techniques and applications of combined staining and peels. The ease with which peels can be produced allows separate sections to be stained for different minerals, in this study aragonite and calcite. After staining the peel is produced by the usual method and the impression contains details of the colours from the preferential staining. The stained peel allows the relationship and identity of the different minerals to be clearly seen under the microscope. Preferential staining can also be applied to complete shell fragments if there is no more accurate method of testing for calcite deposits.

Allman and Lawrence (1972) give details of the preparation of the stains; the two relevant ones are Rodger's Method for calcite and Feigl's solution for aragonite. Staining calcite with the solutions in Rodger's method leaves the calcite blue or green, Feigl's solution stains aragonite black, both tests leave the other mineral unaffected. High and low magnesium calcites can also be distinguished by using a solution of Alizain red and 30% sodium hydroxide. Two general methods for distinguishing carbonate minerals by preferential staining are described by Friedman (1959).

7.33 Conclusions

Acetate peels give a general impression of the structures and any large areas of recrystallisation in shell sections but are unable to resolve fine diagenetic alterations. They allow a complete section of a shell (in all but the largest species) to be studied at one time and the relationships of the shell layers to be clearly seen. The total percentage of a shell that can be sampled is limited by the number of sections that can be cut in a shell without becoming excessively destructive or, if staining is used, the risk of contamination becoming to high. The method is best suited to thick-walled bivalve shells or the largest of the terrestrial gastropod species; the thinner and smaller shells can best be studied using scanning electron microscopy and this is discussed in the next section.

7.4 SCANNING ELECTRON MICROSCOPY

7.41 Introduction

The development of scanning electron microscopy (SEM) in the 1950's greatly improved the resolution of detail in crystal structures. As mentioned in chapter 4.2, it allowed the first clear observations to be made of third-order lamellae in the crossed-lamellar structure, and has enabled researchers to study the components of nacreous tablets (Mutevi 1979). The highest magnification requires the electron microscope to be used in transmission mode, but the scanning mode allows magnification of 150,000 times to be obtained with modern instruments. These modern instruments have a theoretical resolution of 5nm, but this is only possible when using a fine planar grating under near perfect conditions. In this study the maximum resolution was found to be the finest third-order lamellae, in the order of 50nm. The limiting factor was probably the fact that no crystal units smaller than these were observed; there was no evidence of smaller crystal units within the third-order lamellae.

The other main advantages of the SEM are the depth of field that can be obtained, even at magnification ranges of conventional light microscopy, and the three-dimensional quality of the images particualrly when produced as stero pairs.

The previous chapters show the wide use that this study made of the SEM. In total some 130 stubs were examined and over 400 photographs taken; anotated diagrams were also extensively used during the study of samples. Two other techniques were used with the electron microscope: energy dispersive X-ray analysis (EDAX) and backscattering of primary electrons. They are discussed later in this section.

7.42 Preparation of Stubs

Standard 15mm Cambridge type stubs were used for this study, and samples were fixed to the stubs using a fast-setting acrylate adhesive. Completed stubs were coated with gold-palladium in a low vacuum argon atmosphere using a sputter coater. Coating times were 40 seconds and 2 minutes depending on the coater being used (an EM Scope Sputter Coater at Birkbeck College London, or an Edwards S150B Cool Sputter Coater at the Institute of Archaeology, London).

Three different types of shell sample were studied: unetched fracture surfaces, unetched cut surfaces, and polished, etched cut surfaces. The shells were sectioned parallel to the columella, though the apex, in the case of gastropods, and radially from the umbo to the margin in bivalves. Sections were cut on a diamond petrological saw or a Black and Decker "Minicraft" drill depending on shell thickness. The speed at which the "Minicraft" drill was operated was critical in avoiding the samples flaking whilst being cut.

TYPE	THICKNESS	SPEED
HARD	THICK	FAST
	THIN	MEDIUM
SOFT	THICK	MEDIUM
	THIN	SLOW

Table 7.1 Cutting speeds for different shell types

Table 7.1 shows that the critical speeds are related to thickness and hardness (how flaky or chalky the sample has become). When used at the correct speed the "Minicraft" drill allows shell sections of thickness 0.1mm to be accurately sectioned.

The sectioned shell was then polished using the methods described for the production of peels. The samples for mounting were then cut from the polished section; first a cut was made parallel to, and 2-3mm from, the polished edge for 5-10mm. Then this segment was cut or broken free. The segments were cut from places that were considered to be representative of the whole shell, such as the aperture, last whorl or apex. Segments were also cut directly from some larger shells, without prior sectioning. Small shells, less than 15mm at their largest dimension, could be sectioned, polished on both sides and then mounted complete. The smallest shells (e.g. Discus rotundus) were not sectioned but ground and polished to produce the section. When using shells that were fragmentary it was found better to break representative fragments to produce fracture sections and mount these directly onto the stub.

Modern shell sections were etched twice prior to mounting. The samples were placed in 10 vol. hydrogen peroxide to remove the organic matrix from between the crystals, rinsed and then placed in 2% hydrochloric acid for 5-10 seconds. This combination produced good results but was not considered suitable for fossil shells as it etched individual crystal units and obscured diagenetic crystal etching. The best results for fossil samples were achieved by lightly polishing the section to remove any loose material from cutting, but leaving it unetched. The polishing also removes any material that may have undergone mineralogical or crystallographic changes due to heating in the cutting process.

When the samples were ready for mounting precautions were taken to keep them free from contamination from the air. Some of the first stubs that were made were found to have attracted dust between polishing and coating. It is believed that this was due to electro-static charges on the stub boxes and possibly the stubs as well. To lessen this problem the sections were mounted in a clean room and the boxes sprayed with anti-static fluid. After mounting the samples were allowed to dry for 24 hours. This was to avoid out gassing from the adhesive when under vacuum during coating. Each stub had a number engraved into the underside and a record of the location of each section within the shell was kept.

7.43 Equipment

Two different SEMs were used in this project: a JEOL 35CF in the Department of Crystallography, Birkbeck College London, and a HITACHI S-530 in the Department of Geography, University College London. The JEOL system was operated at 25 Kv and produced images that were clearly resolved in the range of 30 to 15,000 times magnification. The HITACHI system was operated at 15-20 KV with coated samples and produced good images in the range of 40 to 80,000 magnification. Experiments were conducted using uncoated samples in the HITACHI S-530; when it was operated at 2-4 KV images could be obtained at low magnification (40 to 400 times). These were not as clear as when coated samples were used but allowed a rapid general view of the samples to be obtained.

Poor contact between the stub and sample led to charging under some conditions; this was avoided by reducing the voltage or by increasing the sample-to-stub contact with a metallic silver paint.

All photographs were taken using a Mamiya 6x7 roll film camera. The angular nature of some of the crystal structures led to harsh contrasts from some samples on the screen and photographs. A combination of tilting and rotation of the stage was used to reduce this. The HITACHI allowed the extremes of contrast to be removed by reducing the secondary gamma-ray signal.

7.44 Stero-Pair Photographs

Although images produced by SEM have an increased depth of field relative to conventional microscopy they still have limitations in this area. Improved resolution and an increase in the details of the structures can be obtained by producing stero-pair photographs.

On the JEOL 35CF the pair of photographs was created by first taking an ordinary picture of the required area. The stage was then tilted by 6° whilst the x and y positions were adjusted to keep the original image centred and a second image was then taken. The HITACHI system had provision for taking two half-frame photographs in one full frame. Using this provision, and taking two pictures of the same area, a stero-pair was obtained without tilting the stage. When viewed with a steroscope the pair of images produce a three-dimensional image; the vertical axis stands out from the photographs with an exaggerated scale.

7.45 Energy Dispersive X-Ray Analysis (EDAX)

The JEOL 35CF system was fitted with an EDAX attachment to detect and analyse the X-rays produced by electron bombardment of the sample. The energies of the X-rays are characteristic of the elemental composition of the sample. The spectrum received by the multi-channel analyser can also contain an interference signal from the sample coating and holder. This interference can be reduced by coating the sample with carbon rather than gold/palladium, and by reducing the diameter of the electron beam and concentrating it on the sample.

The X-ray spectrum will give information on the composition of a shell if it contains reasonable levels of elements such as strontium, iron, manganese or magnesium. Table 7.2 shows the minimum detectable levels for these elements; the values are generally above those found in non-marine shells. Any contamination or matrix adhering to a sample can also be analysed. This technique is particulary useful for identifying quartz grains within a deposit of secondary carbonate. The output from an EDAX analyser can be in the form of a spectrum or as a distribution map. The former is a plot of X-ray energy against intensity for the area under the electron beam. The latter is a distribution map for a nominated element; the map covers the area visible on the SEM screen and has a point for each occurrence of the nominated element. If the distribution of silica is mapped the extent and nature of any surrrounding matrix or contamination between exfoliated layers can be defined.

In theory it is possible to detect X-ray diffraction peaks (see below) using an EDAX system, and this technique has been applied to metallic samples. When it was applied to aragonite and calcite samples no signals other than those of those characteristic X-rays were detected. This may have been due to the geometrical relationship of the source, sample and detector. If so the technique may still be

Element	Minimum detectable limit
Magnesium	0.5% (5000ppm)
Strontium	0.1% (1000ppm)
Manganese	0.1% (1000ppm)
Iron	0.1% (1000ppm)

Table 7.2. Minimum detectable limits for selected elements on an EDAX system.

viable but its sensitivity will be below that of conventional XRD analysis.

7.46 Backscattered Electron Images

A recent paper by Dilks and Graham (1985) used backscattered electron images (BSE) as a method to characterise sandstone mineralogy. This technique uses backscattered primary electrons to create an image and requires a separate detector system. Different mineral phases are distinguished largely by their grey-levels (intensities) which on a flat specimen are due to atomic number contrast rather than micro-topographical variations. Dilks and Graham (1985) processed the grey-levels by computer and were able to produce areas for each mineral phase. BSE imagery could be applied to carbonates, but only if the sample contains minerals other than calcite or aragonite. It will not be possible to distinguish polymorphs of calcium carbonate as the grey-intensity variations are due to elemental not mineralogical variations.

Although genuine BSE analysis could not be applied to calcium carbonate shell samples useful information was obtained using a conventional SEM to detect backscattered primary electrons. To achieve this the post HV was switched off, the condenser lens closed and the sample tilted (c.45°) until an image appeared on the screen. The resultant picture gave an enhanced image of the surface micro-topography which had been produced by differential etching.

It is considered possible to enhance the topographic images and true BSE images further by linking the SEM to a computer and image intensification system. It should be possible to attribute colours to the grey levels and then intensify these and calculate the areas of mineralogical phases.

7.47 The Limits of Scanning Electron Microscopy

The SEM is a versatile instrument and can be applied very widely, but it still has limitations when being used to detect diagenetically altered material. The main problem, with regard to sample selection, is the limited area of each shell that can be studied. It is possible to select shell sections in areas that appear to have been subjected to alteration, as defined by visual examination or staining, but there can be no guarantee that all areas of altered material will be detected. Detection will be particularly difficult if small areas of recrystallisation have formed between shell layers. The SEM is most useful when used with XRD analysis as this allows a more representative sample of the shell to be analysed for calcite and to determine whether it will be possible to eliminate that type of contamination.

7.5 X-RAY DIFFRACTION ANALYSIS

7.51 Introduction

X-ray diffraction analysis is a well established technique that allows identification of the minerals present in mixed samples. It is very sensitive to the presence of calcite and, therefore, is ideally suited for use with shell samples that are pure aragonite in their unaltered state. If the shell originally contained high-magnesium calcite diagenetic alteration can be detected by the presence of low-magnesium calcite. Shell samples that originally contained both aragonite and low-magnesium calcite can only be studied if the original percentage of calcite can be reliably established by comparative work on modern samples.

The instrument used in this study allowed quantitative results to be obtained by using standards for calibration and peak intensity ratios rather than absolute values. Reproducibility of results was tested by repeat analyses of sub-samples of one standard.

7.52 Theory of X-Ray Diffraction Analysis

Figure 7.1 shows two consecutive planes in a crystal lattice; their separation is d and the angle of incidence of the X-rays is θ. Part of the X-ray beam is diffracted by the top crystal plane and follows the path AD. A further part is diffracted by the second plane and follows path BC. The diffracted beams are parallel and will interfere at a distance from the crystal; the result will depend on the difference in their path lengths. The second beam travels further than the first by ABC-AD. It can be shown geometrically that:

$ABC=EBC$

that $EBC-AD=EF$

and $EF=2d \sin\theta$ (eq.7.1)

Constructive interference takes place and a peak forms when the path difference is equal to an integral number of wavelengths of the incident radiation, i.e.

$n = 2d \sin\theta$ (eq.7.2)

As the combination of lattice plane spacings is distinct for each mineral a beam of monochromatic radiation will produce different values for θ ; the angle is usually expressed as 2θ. Tables allowing identification of minerals by the values of d or 2θ are available. The values for pure aragonite and pure calcite are:

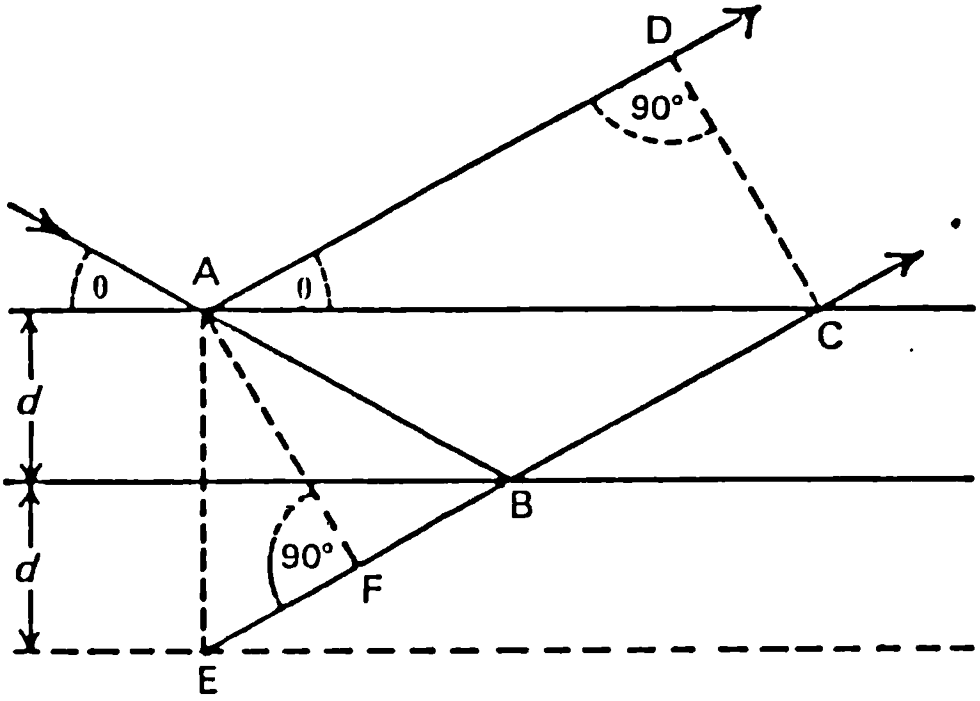


Figure 7.1. Interference between X-rays diffracted at successive crystal planes.

	Aragonite	Calcite
d	3.40Å	3.03Å
2θ	26.21°	29.43°

7.53 Sample Preparation

Standards were prepared that contained between 0.1 and 30% calcite. These were made by mixing weighed quantities of pure aragonite and pure calcite. These were homogenised and ground using a McCrone Micronising Mill. Samples for grinding were placed in a container with 48 cylindrical corundum grinding elements, and 10ml of methanol was added. The sample was ground for three minutes and the resulting slurry poured into a 25ml beaker. The container and elements were then rinsed with 5ml of methanol and this slurry added to the beaker. The suspended sample was then evaporated to dryness at 50°C and the dry powder transferred to a plastic container which was then sealed. The grinding elements and container were then rinsed again with methanol and the liquid discarded. The recovery rate for the ground sample was 70-80% of the original weight.

Modern samples were prepared by sectioning and cleaning the shell (as for acetate peels and SEM stubs, see chapter 7.3 and 7.4); one half of the shell was ground to <400 microns in a percussion mortar and then transferred to the grinding container. The sample was then treated in an identical way to the standard preparation.

Fossil samples were treated slightly differently because of the limited amount of material that was available. A Black and Decker "Minicraft" drill fitted with a diamond tipped drill bit was used to remove 5-10 samples, each of c.10mg, from different areas of a clean shell. The powder was then ground in an agate mortar to the same particle size as the standards. If the shells were larger, sections were cut from these shells and then ground as for the standards. Calcite samples with mixed high and low magnesium polymorphs had sodium chloride added (1% of sample weight) prior to grinding. This acted as a "spike" and allowed the position of the calcite peak to be accurately determined.

The resulting powder had an average particle size of c.10 microns and should have contained no particles over 30 microns. These values are within the critical range (3-30 microns) that give the technique maximum sensitivity. Pure aragonite samples were subjected to identical procedures to check for conversion of aragonite to calcite during milling and evaporation.

Immediately prior to analysis approximately 50mg of the sample was mixed with acetone in an agate mortar to produce a slurry; this was then poured onto a clear glass slide to give an even layer. The slide was then allowed to dry for a minimum of 10 minutes.

7.54 Analysis

The instrument on which the analyses were undertaken was a Philips PW1010 diffractometer with a Cu K_α source fitted with a nickel filter. The operating voltage was 40Kv at 20 milliamps, the scan speed was 1° per minute. The sample slide was placed in the diffractometer with the goniometer set to scan from 25° to 30° 2θ for aragonite-calcite samples and 22° to 30° 2θ for high-low magnesium calcite samples. The results were produced as a spectrum of the diffraction peaks on a pen plotter.

7.55 Calibration and Reproducibility

The results from the analysis of the standards were used to produce an aragonite:calcite calibration curve. The peaks were normalised using the formula:

$$R_v = \frac{A + B}{C} \qquad \text{(eq.7.3)}$$

where A = area under the main aragonite peak

B = area under secondary aragonite peak

C = area under calcite peak

The calibration curve is shown in figure 7.2.

The minimum detectable limit of calcite was 0.6%, but, for standards in which there was less than 1% calcite present, accurate percentages cannot be calculated. Replicate analyses of a 10% calcite standard showed a reproducibility of ±1% calcite. The calibration curve gives a linear relationship for the range 0 to 15% calcite.

Analysis of 8 freshwater and 15 terrestrial species of gastropod showed all of them to have no detectable calcite present.

The analysis of samples containing high and low magnesium calcite relies on the shift of calcite peak due to the presence of high magnesium calcite. The calibration curve for this is shown in figure 7.3.

7.56 Limitations of the Method

X-ray diffraction analysis has two main problems that limit its application to the detection of diagenetic calcite. The first is the

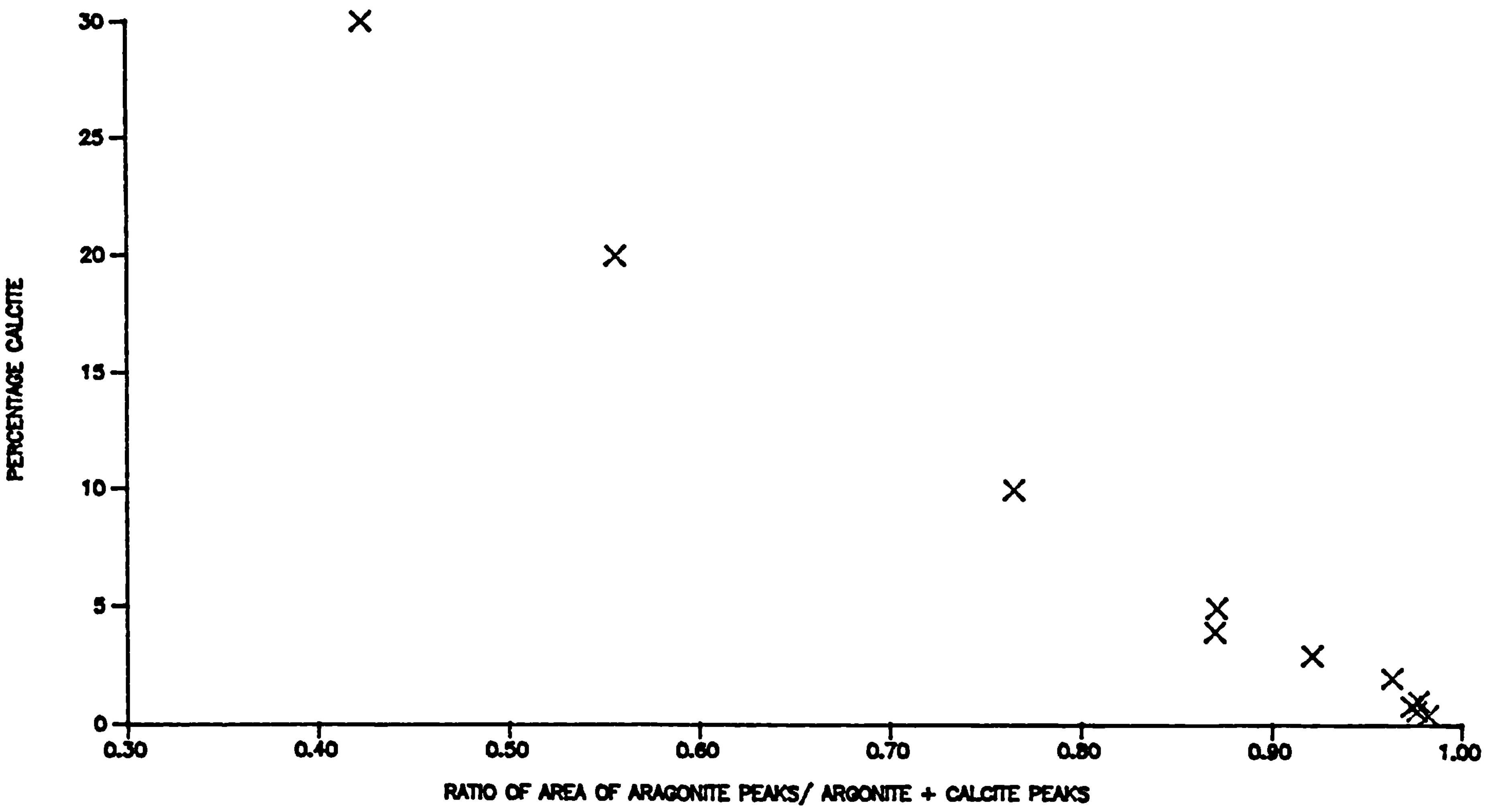


Figure 7.2. Calibration curve for determination of percentage calcite by X–ray diffraction analysis.

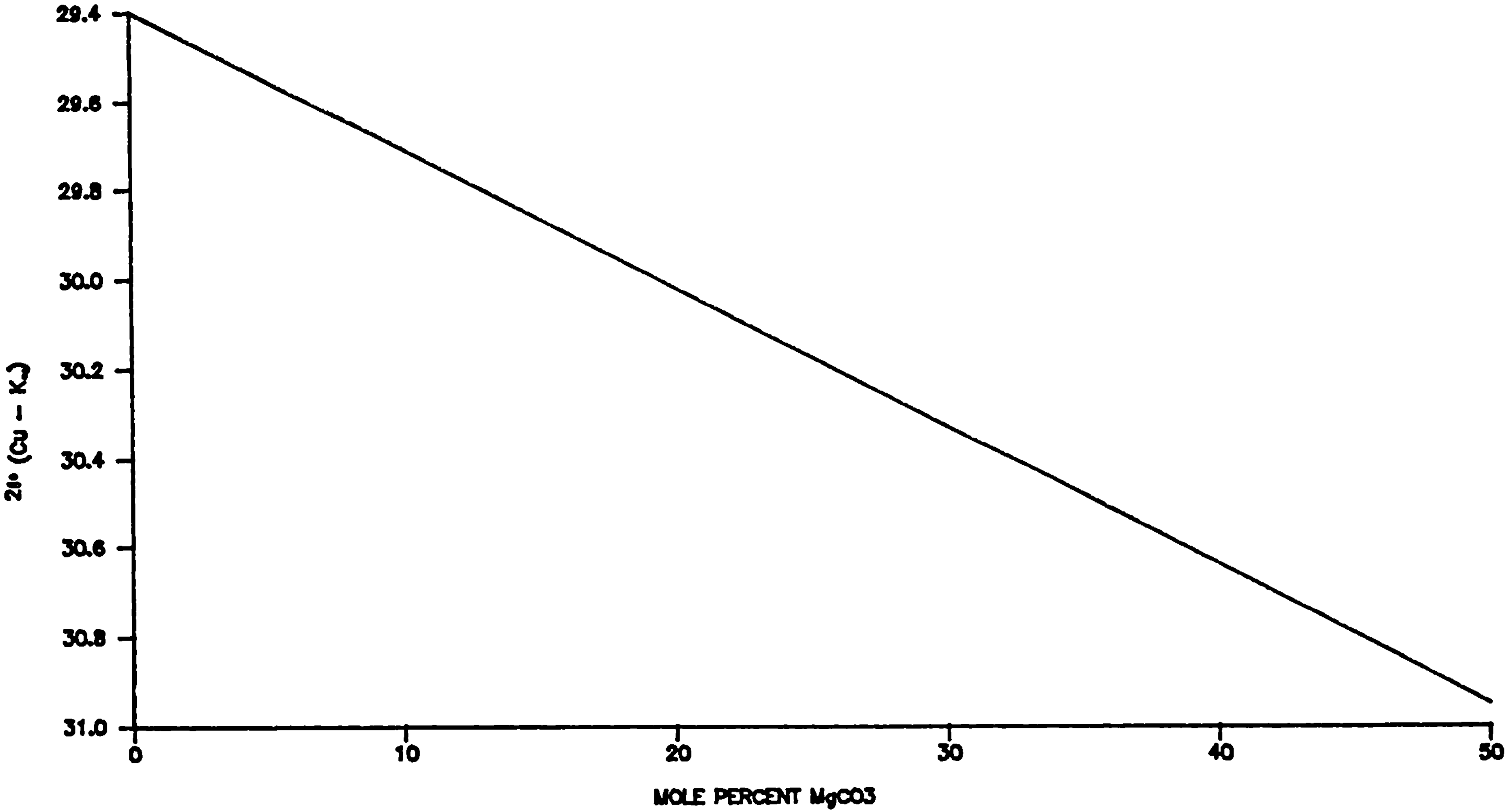


Figure 7.3. Calibration curve for determination of percentage Mg–calcite by X–ray diffraction analysis.

problem of sampling shells: taking 5-10 samples from a shell should give a representative sample of the material present but it cannot be assumed that all areas of calcite will be detected. The problems associated with sampling can be reduced by analysing a second sample of the shell. This is taken after the shell has undergone the complete pretreatment and has been powdered prior to submission; it should then be representative of any diagenetic material that was present.

The second problem is the sensitivity of the technique and the minimum detectable limit of 0.6% in this study. This level of calcite is not a serious problem in Flandrian age samples, but in any shell >25,000 years old the possibility that 0.6% modern carbon could be present leaves serious doubts concerning the validity of any dates obtained on the material. (For further discussion see chapter 6.6, 8.5.)

CHAPTER 8. SELECTION AND VALIDATION OF SAMPLES

8.1 INTRODUCTION

To validate the observations and theories on the problems of post-depositional changes and the apparent age effect they must be applied to a range of fossil samples. This required the techniques and selection criteria to be integrated to give a consistent and reliable method. The method (summarised in figure 8.1) covers the period from the observation of the samples and their context to assessment of the final ^{14}C date. It includes pretreatments, selection and in some cases tentative corrections based on measured values. The first part of the chapter discusses the methods, the second their application to fossil samples from six sites in the British Isles covering the period 3000-9000 bp.

8.2 SELECTION METHODS

8.21 Site Collection

During collection of samples four main factors need to be taken into account: the ecology of the available species, the ecology of the area at the time of deposition, the nature of the deposit (e.g. land-surface, slope-wash), and the type and availablity of the $CaCO_3$ at the time of deposition.

It has been shown that Pomatias elegans is likely to have a greater apparent age because of its contact with the soil whilst burrowing. It is natural to assume that other species that occupy similar niches will also be affected in a similar way. The small size of burrowing species also makes them difficult to use. They cannot easily be cleaned (see below), individual shells cannot be fully screened by analytical techniques, and large numbers of shells are required to

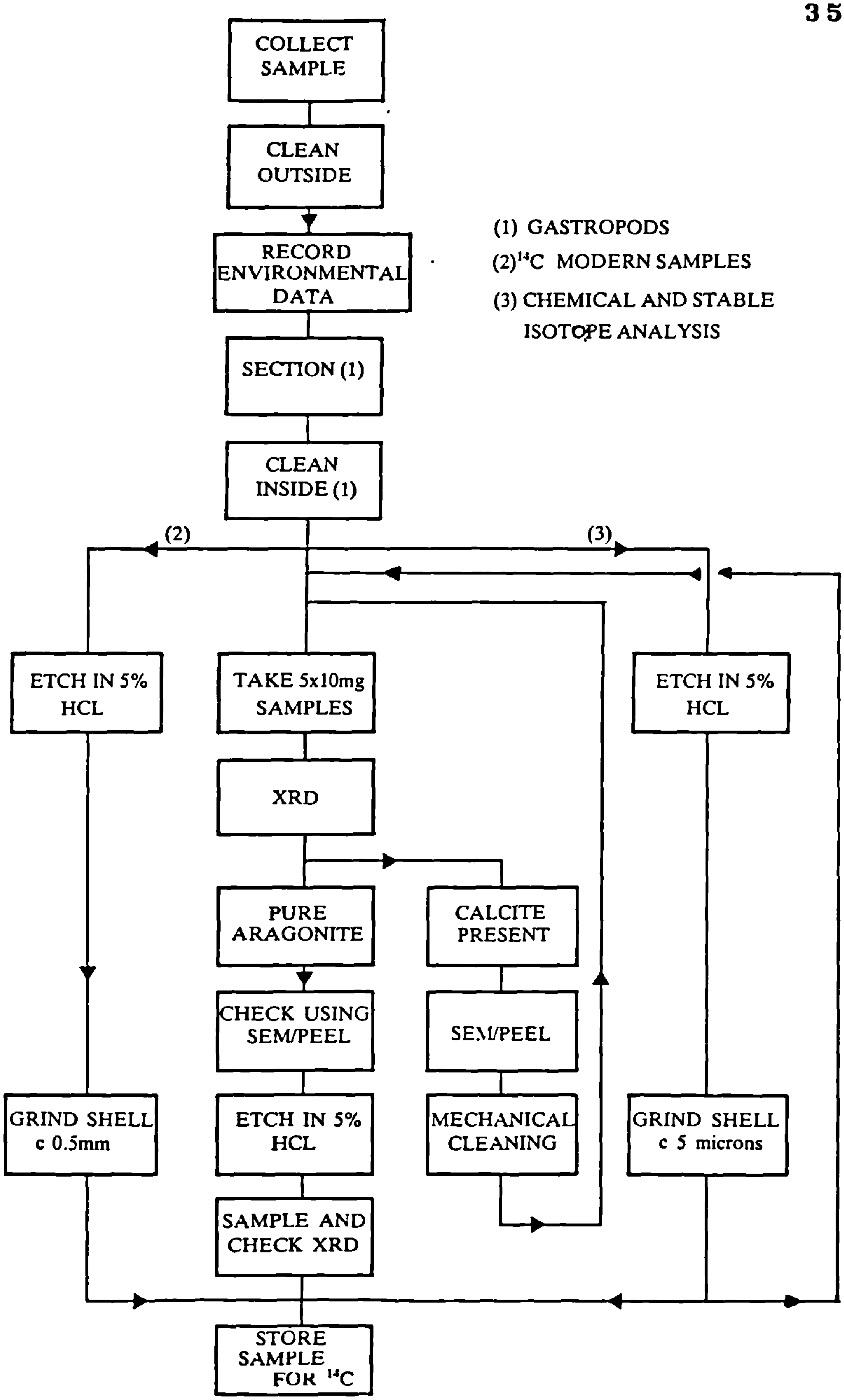


Figure 8.1. Selection procedure for non-marine shells for ^{14}C dating.

provide a ^{14}C sample.

Some details of the palaeoecology of the area can be obtained in the field but most evidence will require laboratory analysis. In many cases it will be clear whether the deposits contain land surfaces and how long they were stable (by the degree of soil development). Evidence for lacustrine or fluvial inundation should also be visible in sections or exposures.

Under favourable conditions the stratigraphy will preserve more detailed evidence of the palaeoenvironment. Samples should be collected from the sequence for pollen analysis though the alkali conditions associated with shell preservation often give poor preservation of pollen. Organic horizons should be sampled for possible charred organic material and evidence of human occupation. The other major source of environmental evidence is the shell assemblage. Therefore, it is important to sample the stratigraphic sequence fully as well as collecting shells for dating. This will allow the study of the composition of the snail fauna and consequent environmental interpretation.

The development and formation of the deposits is of great importance as it controls the availability and type of $CaCO_3$ source material. It also has important implications for the origin of the shells. If the deposit is derived from slope-wash or is covered by this type of deposit there must be a possibility of reworked material being included. Reworked or secondary shells may also occur if shells have become concentrated in hollows or middens by natural, human, or animal agencies. Natural movement includes the washing of shells into caves or crevices. A similar phenomenon was observed by Evin *et al*.

(1980): artefacts were washed into a hollow and became associated with earlier shell material. Movement of shells by animals, particularly rodents, is recorded (Goodfriend pers. comm. 1985) and can lead to the movement of shells through the stratigraphy. In a developed soil shells are also moved through the soil by earthworms (Evans 1972; Carter 1985) but this usually involves small shells and only fragments of larger ones.

The best type of deposit is a thin (c.5cm thick) buried soil with the shells of large species in situ on a soil surface that was rapidly buried after the death of the snails. Possible evidence for rapid burial includes the shells being intact or crushed, presence of pigments, and unweathered shell surfaces.

The formation of the deposit will also be important in controlling the availability of $CaCO_3$ at the time of shell formation. Earlier chapters have discussed the increased probability of incorporation of $CaCO_3$ from exposed tufa deposits and chalk, the reduced level of incorporation of coarse shell fragments, and isolation of $CaCO_3$ by thick soils or litter layers. The type and formation of the $CaCO_3$ will also control the depletion of ^{14}C in the shell source material. The range will be from chalk which will be totally depleted to tufa with only a 10-15% depletion. Therefore, the $CaCO_3$ source should be sampled in the contexts from which shell samples are being collected. It is also advisable to sample the layer immediately below and if necessary the bedrock $CaCO_3$ (only usually necessary if chalk derived soils are involved).

The collection of samples for analysis should include only complete or nearly complete individual shells. Shells which have been exposed for sometime on a surface or section should be avoided if possible as they are likely to have suffered post-depositional alteration. Each should be numbered and stored separately in a closely sealed polythene bag. The work of Olsson et al. (1968) has demonstrated the danger of contamination of fossil shells by contact with atmospheric CO_2. The samples should come from the minimum area necessary to obtain the required number of shells, and ideally the location of each shell relative to a fixed point should be recorded. Details of location are especially important if the collection area is large or varied.

8.22 Cleaning and Pretreatment

When collected the shells are usually filled with the matrix that had surrounded them and often have material adhering to the outer surfaces. The outer material consists of matrix and in many cases a "crust" of $CaCO_3$; this was particularly common on the shells from tufa sites.

All external surfaces were cleaned in distilled water using a soft paint- or tooth-brush. Each shell was kept separate and even if crushed all fragments were kept together. After drying in a cabinet at 50°C the shells were examined and details of species, banding morphs and general shell condition were recorded. At all times between examination the shells were kept in sealed bags.

Each sample population was also assessed for its suitability for ^{14}C dating; this was based on the formation of the deposit, species ecology, and the source of $CaCO_3$. Each population was graded on a scale 1 to D, from the potentially best to worst (table 8.1).

Site and Ecology

Species:

Lives below ground	Lives above ground
1	5
Large shell	Small shell
3	1

Type of deposit:

In situ soil	Reworked deposit
5	1

^{14}C content of

$CaCO_3$ source:

(Relative to contemporary wood)

0-0.05	0.05-0.3	0.3-0.6	0.6-0.8	0.8-1.0
1	2	3	7	10

Each population is scored and the total expressed as a fraction of the maximum.

Chemical and Isotopic Composition

$\delta^{13}C$ ($^{o}/_{oo}$):

Relative to the population:

$<\bar{x}-2\sigma$	$\bar{x}-2\sigma - \bar{x}-\sigma$	$\bar{x}-\sigma - \bar{x}$	$\bar{x} - x+\sigma$	$\bar{x}+\sigma - \bar{x}+2\sigma$	$>\bar{x}+2\sigma$
5	4	3	3	2	1

Relative to the "optimum" value:

<-11.0	-11.0 - -10.0	-10.0 - -9.0	-9.0 - -8.0	-8.0 - -7.0	>-7.0
7	5	3	2	1	0

Table 8.1A. Criteria for the selection of shell samples for ^{14}C dating.

Magnesium content (ppm):

Relative to the population:

$<\bar{x}-2\sigma$	$\bar{x}-2\sigma$ – $\bar{x}-\sigma$	$\bar{x}-\sigma$ – $\bar{x}$	$\bar{x}$ – $\bar{x}+\sigma$	$\bar{x}+\sigma$ – $\bar{x}+2\sigma$	$>\bar{x}+2\sigma$
2	4	5	4	2	1

Relative to "background":

<30	30-40	40-50	50-60	60-70	70-90	90-100	100-110	110-120	>120
1	2	4	4	5	7	5	3	2	1

Strontium content (ppm):

Relative to the population:

$<\bar{x}-2\sigma$	$\bar{x}-2\sigma$ – $\bar{x}-\sigma$	$\bar{x}-\sigma$ – $\bar{x}$	$\bar{x}$ – $\bar{x}+\sigma$	$\bar{x}+\sigma$ – $\bar{x}+2\sigma$	$>\bar{x}+2\sigma$
0	1	3	3	1	0

^{18}O, iron, manganese:

Score 1 if values are not unusual; 0 if they are.

Each shell is scored and the total expressed as a fraction of the maximum. The final grading is obtained by averaging the two scores.

Table 8.1B. Criteria for the selection of shell samples for for ^{14}C dating.

The shells were then sectioned parallel to the columella using a Black and Decker "Minicraft" drill fitted with a cutting disc 1mm thick. The columella was discarded as its narrow cylindrical form is difficult to clean. The samples were then placed in an ultrasonic cleaner, filled with distilled water, for 10 minutes and then examined under a low-power binocular microscope for any adhering particles. If after further brushing the particles remained cemented to the shell mechanical cleaning using diamond drills and grinding wheels was undertaken before further ultrasonic cleaning.

Some of the samples (those studied in Israel) were treated slightly differently in that the shells were sectioned by crushing in a vice prior to internal cleaning.

Samples for further analysis were then removed from the shells as 5-10 10mg samples or half of a sectioned shell. Both types of sample were assumed to be representative of the whole shell. These samples were then subjected to stable isotope analysis and X-ray diffraction analysis (XRD); the methods are described in chapter 5.2 and 7.5. Ideally 10-20 shells of each species from each sample were analysed, but this was not always possible owing to the availability of shells and equipment.

Samples of the $CaCO_3$ source material were analysed for loss on ignition (LOI), particle size distribution, and $CaCO_3$. Sub-samples were treated with hydrogen peroxide (H_2O_2) to remove organic material, and then ground prior to stable isotope analysis and atomic absorption spectroscopy.

On the basis of the results of the analysis of shells and $CaCO_3$

source material each of the shells was graded on a scale of 1-5; the numbers representing the relative importance of apparent age effects. The criteria for grading are shown in table 8.1. Shells that were graded as "suitable" and "unsuitable" were then analysed using XRD analysis (for method see chapter 7.5) and all of those containing calcite and most of the pure aragonite shells were then examined using a SEM (see chapter 7.4 for method). The type and location of the calcite was recorded and any evidence of dissolution or internal recrystallisation (structural change without a change of mineralogy) looked for in all samples.

If calcite was present as an external crust then this could be removed by further mechanical cleaning. However, if the calcite was present in the form of areas of recrystallisation then the shell was considered unsuitable for ^{14}C dating. If internal recrystallisation was observed its presence was noted but did not immediately lead to the shell being rejected.

The remaining shells were etched in 5% HCl to remove any contamination that remained. They were then ground and stored in sealed tubes. If the remaining material permitted, a further XRD sample was taken to check that the initial sample was representative of the whole shell. Pure aragonite shells with optimum δ^{13}C, Mg and Sr values were submitted for ^{14}C dating by AMS. Also submitted were samples that were considered unsuitable because of their composition and also samples of calcite from "crusts" and recrystallised areas. Submission of unsuitable samples was designed to show that the selection procedures were valid.

Two other selection criteria were considered: measurement of amino-acid racemization (isoleucine to alloisoleucine), and first-order ^{14}C dating.

8.3 Amino-Acid Racemization

8.31 Introduction

Measurement of the racemization of isoleucine to alloisoleucine was used to determine if all the shells in a sample were a single population or whether intrusive material (modern or reworked) was present. Amino-acid dating has been applied by Goodfriend (*pers. comm.* 1985) to late Quaternary shell samples in the Negev desert, Israel. It has also been applied by Bowen *et al.* (*pers.comm.*) to isolate reworked material from raised beaches on the British coast.

The principle of the application is that since the degree of racemization is dependant on temperature and time a sample population containing shells from two periods can be divided by the different ratios present. The minimum age differences that are resolvable is controlled by the temperature of burial and will be shorter in warmer areas.

8.32 Method

Shell samples were cleaned by the standard method with extra care taken during the final etching when any surface amino-acid contamination due to handling is removed. About 100mg of shell was accurately weighed and placed in a labelled boro-silicate glass tube. The volume of 30% HCl required to produce a 6M solution after complete reaction with the shell was then calculated.

$$\text{Vol.HCl in microlitres} = 2.4 \times \text{wt of shell in mg} \quad \text{(eq.8.1)}$$

The acid was then slowly added and the samples left to react; it is important to keep the reaction near the bottom of the tube in order to avoid loss of organic material.

The necks of the tubes were then drawn down to 2-5mm in an oxy-gas flame, flushed with CO_2, sealed under vacuum, and placed in a hotblock at 145°C for 45 minutes. After cooling the tops of the tubes were removed and the hydrolysed sample transferred to a micro-fuge tube. Hydrofluoric acid was then added to precipitate the calcium as calcium fluoride; the volume required was calculated as:

$$\text{Vol.HF in microlitres} = 1.25 \times \text{wt of shell in mg} \quad \text{(eq.8.2)}$$

The samples were then centrifuged for five minutes and the liquid decanted to new tubes. These were then evaporated to dryness under a constant flow of nitrogen. The sample tubes were placed in a high vacuum for 1 hour to remove any ammonium chloride that might have formed. Finally 100 microlitres of buffer solution were added and the liquid transferred to new plastic tubes; the samples were then ready for analysis. The peak areas for isoleucine and alloisoleucine were then measured on an automatic amino-acid analyser and the ratio calculated.

8.33 Results

Amino-acid ratios were measured for nine samples from Netanya, Israel; three each from horizons OL22, OL20 and OL23. The results are given in table 8.2.

Sample	Ratio	Sample	Ratio	Sample	Ratio
OL22 (1)	0.388	OL20 (1)	0.414	OL23 (1)	0.506
(2)	0.000	(2)	0.544	(2)	0.432
(3)	0.133	(3)	0.413	(3)	0.560

Table 8.2. Alloisoleucine/Isoleucine ratios for samples from Netanya, Israel.

The limited number of results allows only the principle of the selection method to be shown. OL22 is an organic-rich horizon near the surface of the deposit and should produce low ratios; sample OL22 (1) stands out as being "older" and probably reworked. The samples from OL220 and OL23 are more consistent though the ratios suggest a considerably older date than that of >10,000 bp that is assigned to those contexts. The range of values within each context is partly due to the increased racemization that takes place prior to burial if the shells are in direct sunlight. Therefore differences in the length of exposure to the sun are reflected in the different ratios.

8.4 First-Order dating

Occasionally samples from contexts whose approximate date is not known (e.g. Flandrian or last inter-glacial) will require analysis. It is convenient to be able to determine whether it is worth while proceeding with high precision dating by "first-order" dating. The technique is also suited to making broad correlations between deposits.

In this method cleaned shell samples are treated with HCl, the CO_2

dried in dry-ice traps, and collected in an organic base. The CO_2 can be collected in the counting vials and these transferred to a scintillation counter. Modern standards and background samples are counted with the unknown shell samples. Twenty millilitres of the organic base is capable of absorbing 0.7g of carbon, therefore, the minimum amount of shell required is 6.0g to allow saturation. In terms of study and dating of non-marine shells 6.0g can be difficult to obtain and more are usually required as absorption is not 100% efficient. If further conventional dating were to be undertaken considerably more material would be required. The method would be suitable if a limited number of shells were available and further dating was to be by AMS.

8.5 VALIDATION OF THE SELECTION PROCEDURES

8.51 Introduction

The validity of the selection procedures can only be assessed by ^{14}C dating of shells from contexts for which independent dating exists. Samples were collected from six sub-fossil sites from which ^{14}C dates on charcoal or other organic material already existed or could be obtained. The selection procedures were applied to a total of 89 fossil shells from a complete sample of 223 shells. The results of the analyses are given in tables 5.14, 5.17 - 5.20. From these samples 14 were selected and submitted for ^{14}C dating by AMS at the Research Laboratory for Archaeology and the History of Art, Oxford. The samples were selected to be representative of those that were considered good and reliable and also some that were considered liable to give erroneous results.

8.52 Details of the Samples

The data for each sample including discussion of their suitability for ^{14}C dating are given in tables 8.3 - 8.16. These tables include consideration of the suitability of each sample and the possible age errors thought likely to be present in them. All stable isotope values are in per mill. and AAS values in ppm.

8.53 Discussion of results

Samples OX1 and OX2 are from a single shell (CBT 23) and were taken from the apex (A) and aperture (B) respectively. The ^{13}C depletion observed in the apex of modern shells, relative to the aperture, is seen again in this fossil shell. The ^{14}C content of the apex is also depleted, though not by a significant amount.

Sample OX3 is from the same site but of a different species (CBT 21; C.hortensis). The depleted ^{13}C value (relative to the population and CBT 23) suggested less age error and this was confirmed by the ^{14}C analysis. The Mg and Sr contents of OX1-3 were not determined owing to the limited sample size.

Samples OX4, OX5 and OX6 are from the same horizon. They represent three different species all occupying the similar habitat. OX4 and OX6 are in good agreement with the ^{14}C date for charcoal from that layer. Shell CW 30 (OX5) showed evidence of recrystallisation; this was not detected as calcite. However, the structural alterations combined the with the unusual chemical composition (very low Sr, high Mg) suggest post-depositional changes in the shell. The ^{14}C result showed the shell to be too young, which is in agreement with a post-depositional alteration.

Sample No. CBT 23A Radiocarbon No. OX 1 Site: Carrowmore, Co.Mayo

Species: Cepaea nemoralis Banding: 12345 Condition of shell: Clean, some pitting, flaking????

Environment: Soil horizon (141-3cm) in Flandrian tufa. Context also contained burnt material including hazelnut shells suggesting an open environment but with some scrub, perhaps cleared by burning.

δ^{13}C Shell: -9.385 δ^{18}O Shell: -1.029 Mg Shell:

Pop^{n}: -9.647 Pop^{n}: -1.397 Pop^{n}: 55.2

S.D.: 0.186 S.D.: 0.269 S.D.: 41.9

Sr Shell: Fe Shell: Mn Shell:

Pop^{n}: 150.0 Pop^{n}: - Pop^{n}: -

S.D.: 52.0 S.D.: - S.D.: -

Grading: 0.64

XRD:? calcite,<0.5% Stub No. 101 Photo No. -

SEM: No recryst.seen but some areas of crust (>2μ). Lamellae are tightly packed and very fine.

Comments: Stucture suggests that only very slight contamination has occurred and no recrystallisation.

Overall suitability for dating: This sample is from an apex and the ^{13}C value is enriched relative to pop^{n}. The environment would have allowed contact with the tufa. Some apparent age effect expected.

^{14}C Age of context (Years bp): 5410±50 (Q-2601)

^{14}C Age of shell (Years bp): 6250±100 (OxA-701)

Comments: The apparent age effect (840 yrs) is greater than expected.

Table 8.3. Details of sample CBT23A submitted for ^{14}C dating by AMS

Sample No. CBT 23B	Radiocarbon No. OX 2	Site: Carrowmore,Co.Mayo
Species: Cepaea nemoralis	Banding: 12345	Condition of shell:Clean, some pitting, flaking????

Environment: Soil horizon (141-3cm) in Flandrian tufa. Context also contained burnt material including hazelnut shells suggesting an open environment but with some scrub, perhaps cleared by burning.

$\delta^{13}C$ Shell: -9.683	$\delta^{18}O$ Shell: -1.485	Mg Shell: -
Pop^n: -9.647	Pop^n: -1.397	Pop^n: 55.2
S.D.: 0.186	S.D.: -0.269	S.D.: 41.9
Sr Shell: -	Fe Shell: -	Mn Shell: -
Pop^n: 150.0	Pop^n: -	Pop^n: -
S.D.: 52.0	S.D.: -	S.D.: -

Grading: 0.67

XRD: ?calcite,<0.5% Stub No. 101 Photo No. -

SEM: No recryst.seen but some areas of crust (2μ). Lamellae are tightly packed and very fine.

Comments: Structure suggests that only very slight contamination and no recrystallisation has taken place.

Overall suitability for dating: This sample is from the last whorl, the ^{13}C value is similar to the pop^n. The environment would have allowed contact with the tufa. Some apparent age effect expected.

^{14}C Age of context (Years bp): 5410±50 (Q-2601)

^{14}C Age of shell (Years bp): 6170±90 (OxA-702)

Comments: The apparent age effect (760 yrs) is greater than expected.

Table 8.4. Details of sample CBT23B submitted for ^{14}C dating by AMS

Sample No. CBT 21	Radiocarbon No. OX 3	Site: Carrowmore,Co.Mayo
Species: Cepaea hortensis	Banding: 00000	Condition of shell:Clean, some surface pitting.

Environment: Soil horizon (141-3cm) in Flandrian tufa. Context also contains burnt material including hazlenut shells, suggesting an open environment but with some scrub, perhaps cleared by burning.

δ^{13}C Shell: -10.963	δ^{18}O Shell: -1.587	Mg Shell: -
Pop^n: -10.329	Pop^n: -1.599	Pop^n: 37.0
S.D.: 0.931	S.D.: 0.293	S.D.: 7.8
Sr Shell:	Fe Shell:	Mn Shell:
Pop^n: 52.3	Pop^n: -	Pop^n: -
S.D.: 14.6	S.D.: -	S.D.: -

Grading: 0.67

XRD: No calcite	Stub No. 100	Photo No. 495-8

SEM: No recryst.seen, "fusing" on surface may be natural

Comments: Structure suggests that shell is free from contamination and recrystallisation.

Overall suitability for dating: This sample is representative of the whole shell. The δ^{13}C value is depleted rel. to pop^n and rel. to CBT 23A and B. Error less than CBT 23 expected.

^{14}C Age of context (Years bp): 5410±50 (Q-2601)

^{14}C Age of shell (Years bp): 5960±90 (OxA-703)

Comments: As expected the error is less than for CBT 23A or B.

Table 8.5. Details of sample CBT21 submitted for ^{14}C dating by AMS

Sample No. CW 35	Radiocarbon No. OX 4	Site: Caerwys, Clwyd
Species: Cepaea nemoralis	Banding: 00000	Condition of shell: Clean, thin, chalky.

Environment: Soil horizon (393-400cm) in Flandrian tufa. Context marks the transition from swamp to dry conditions, probably open ground.

δ^{13}C Shell: -8.939	δ^{18}O Shell: -2.526	Mg Shell: 71
Pop^{n}: -9.490	Pop^{n}: -1.670	Pop^{n}: 51.3
S.D.: 0.592	S.D.: 0.471	S.D.: 11.8
Sr Shell: 53	Fe Shell: 84	Mn Shell: 17
Pop^{n}: 49.4	Pop^{n}: 83.1	Pop^{n}: 19.6
S.D.: 35.0	S.D.: 28.9	S.D.: 3.0

Grading: 0.75

XRD: ?calcite,>0.5%	Stub No. 89	Photo No. 436,480

SEM: Exfoliation seen on steep curves (5μ gaps). Small areas of recrystallised material between unaltered structure.

Comments: Exfoliation could allow contamination. Recryst. very limited if present at all.

Overall suitability for dating: Mg content suggests some leaching. ^{13}C slightly enriched rel. to pop^{n}. Access to tufa in soil thin, but tufa only depleted by 23%. Small error expected.

^{14}C Age of context (Years bp): 7880±150 (BM-1736)

^{14}C Age of shell (Years bp): 7950±95 (OxA-704)

Comments: No significant difference between context and shell.

Table 8.6. Details of sample CW35 submitted for ^{14}C dating by AMS

Sample No. CW 30	Radiocarbon No. OX5	Site: Caerwys, Clwyd
Species: Cepaea hortensis	Banding: 12345	Condition of shell: -

Environment: Soil horizon (393-400cm) in Flandrian tufa. Context marks the transition from swamp to dry conditions, probably open ground.

δ^{13}C Shell: -8.057	δ^{18}O Shell: -1.584	Mg Shell: 78
Pop^n: -8.736	Pop^n: -1.638	Pop^n: 62.0
S.D.: 0.960	S.D.: 0.309	S.D.: 22.6
Sr Shell: 5	Fe Shell: 136	Mn Shell: 36
Pop^n: 30.5	Pop^n: 104.0	Pop^n: 28.5
S.D.: 36.1	S.D.: 45.3	S.D.: 10.6

Grading: 0.77

XRD: No calcite. Stub No. 93 Photo No. 433-5, 467-479

SEM: Exfoliation of crust on inner surface. Recryst.material seen between layers of c.l. and between individual 3rd-order lamellae.

Comments: Despite absence of calcite the exfoliation, crusts, and secondary material all suggest the inclusion of post-dep. material.

Overall suitability for dating: High Mg and enriched ^{13}C indicate presence of CaCO$_3$ source material or secondary material. Structure suggests cause is post-depositional. Age younger than context.

^{14}C Age of context (Years bp): 7880±150 (BM-1736)

^{14}C Age of shell (Years bp): 7530±110 (OxA-705)

Comments: The shell sample is too young by 350 years.

Table 8.7. Details of sample CW30 submitted for ^{14}C dating by AMS

Sample No. CW 8 Radiocarbon No. OX 6 Site: Caerwys, Clwyd

Species: Arianta arbustorum Banding: - Condition of shell: -

Environment: Soil horizon (393-400cm) in Flandrian tufa. Context marks the transition from swamp to dry conditions, probably open ground.

$\delta^{13}C$ Shell: -11.385	$\delta^{18}O$ Shell: -0.736	Mg Shell: 55
Pop^{n}: -10.622	Pop^{n}: -1.073	Pop^{n}: 62.7
S.D.: 0.840	S.D.: 0.077	S.D.: 9.3
Sr Shell: 83	Fe Shell: 90	Mn Shell: 19
Pop^{n}: 57.0	Pop^{n}: 108.0	Pop^{n}: 20.0
S.D.: 23.1	S.D.: 26.2	S.D.: 1.7

Grading: 0.82

XRD: No calcite Stub No. 92 Photo No. 417-422

SEM: No recryst.seen. The main layers are parting by exfoliation and etching of individual lamellae was observed.

Comments: Contamination may have occured but the etching suggests an open system with loss of material.

Overall suitability for dating: The structure suggests leaching may have occurred, but the chemistry indicates this is not severe. The depleted ^{13}C value indicates reduced error from $CaCO_3$ source.

^{14}C Age of context (Years bp): 7880±150 (BM-1736)

^{14}C Age of shell (Years bp): 7860±100 (OxA-706)

Comments: Age error of 20 years. The two dates are not significantly different.

Table 8.8. Details of sample CW8 submitted for ^{14}C dating by AMS

Sample No. NC 4 Radiocarbon No. OX 7 Site: Newlands Cross,Eire

Species: Cepaea nemoralis Banding: (123)(45) Condition of shell: -

Environment: Soil horizon (87-90cm) in Flandrian tufa.

δ^{13}C Shell: -10.486	δ^{18}O Shell: -1.344	Mg Shell: 94
Pop^{n}: -10.035	Pop^{n}: -1.229	Pop^{n}: 94
S.D.: 0.536	S.D.: 0.323	S.D.: 9.5
Sr Shell: 375	Fe Shell: 93	Mn Shell: 20
Pop^{n}: 392.5	Pop^{n}: 108.8	Pop^{n}: 20.8
S.D.: 93.7	S.D.: 24.1	S.D.: 4.5

Grading: 0.90

XRD: No calcite Stub No. 103 Photo No. 455-8,499-507

SEM: Crust on inner surface, and some surface pitting. Exfoliation of a number of layers seen on outer surface.

Comments: No evidence for recrystallisation, high mag. showed no secondary material between the individual lamellae.

Overall suitability for dating: Absence of structural alteration and chemical analysis suggests the shell should produce a good date. Only the high Mg (rel. to background) is indicative of any problem.

^{14}C Age of context (Years bp): 7600±500 (OxA-568) (above context)

^{14}C Age of shell (Years bp): 8300±90 (OxA-707)

Comments: The age error is a maximum of 700 years, the true context date is probably c.8000 bp. Therefore the error is c.300 yrs, but may be less.

Table 8.9. Details of sample NC4 submitted for ^{14}C dating by AMS

Sample No. NC 1 Radiocarbon No. OX 8 Site: Newlands Cross, Eire

Species: Cepaea hortensis Banding: 00000 Condition of shell: -

Environment: Soil horizon (85-7cm) in Flandrian tufa.

$\delta^{13}C$ Shell:	-9.663	$\delta^{18}O$ Shell:	-1.026	Mg Shell:	255
Pop^{n}:	-10.229	Pop^{n}:	-1.565	Pop^{n}:	100
S.D.:	-	S.D.:	-	S.D.:	-
Sr Shell:	227	Fe Shell:	169	Mn Shell:	16
Pop^{n}:	446	Pop^{n}:	130	Pop^{n}:	19
S.D.:	-	S.D.:	-	S.D.:	-

Grading: 0.69

XRD: No calcite Stub No. 104 Photo No. 459-460,508

SEM: No recrystallisation observed. Thin (1μ) crust on inner surface.

Comments: No evidence for post-depositional structural changes. Surface crust would be removed by final etching.

Overall suitability for dating: The structure and chemistry suggest no post-dep. changes but the high Mg, low Sr and depleted ^{13}C suggest a large contribution of $CaCO_3$ source material.

^{14}C Age of context (Years bp): 7600±500 (OxA-568)

^{14}C Age of shell (years bp): 8930±150 (OxA-708)

Comments: The age error is a maximum of 1330 years. The true date of the context is c.8000 bp and the age error is probably less than 930 yrs (see text for further discussion).

Table 8.10. Details of sample NC1 submitted for ^{14}C dating by AMS

Sample No. BP 16	Radiocarbon No. OX 10	Site: Binnel Point, IoW
Species: Pomatias elegans	Banding: -	Condition of shell: Clean, some ? iron staining.

Environment: Soil horizon in landslip deposits. Loose broken ground in a shaded environment.

δ^{13}C Shell: -6.524	δ^{18}O Shell: -1.030	Mg Shell: 215
Pop^{n}: -6.695	Pop^{n}: -1.143	Pop^{n}: 192.3
S.D.: 0.347	S.D.: 0.413	S.D.: 38.5
Sr Shell: 361	Fe Shell: 212	Mn Shell: 15
Pop^{n}: 420.6	Pop^{n}: 147.8	Pop^{n}: 13.8
S.D.: 60.6	S.D.: 50.7	S.D.: 4.71

Grading: 0.36

XRD: No calcite	Stub No. 95,96	Photo No. 440-7,480-8

SEM: Unusual crystal structure seen, but no recrystallisation. Pitting of surfaces and exfoliation of crusts observed.

Comments: No evidence of secondary material except crusts. Pitting suggests destructive diagenesis taking place.

Overall suitability for dating: Structure unaltered but the species and the chemistry (high Mg, enriched ^{13}C) suggest there will be a substantial age error.

^{14}C Age of context (Years bp): 4480±100 (BM-1737)

^{14}C Age of shell (Years bp): 5590±80 (OxA-710)

Comments: As predicted the age error is large (1110 years).

Table 8.11. Details of sample BP16 submitted for ^{14}C dating by AMS

Sample No. ICH 1 Radiocarbon No. OX 11 Site: Inchrory, Banffshire

Species: Cepaea hortensis Banding: 00000 Condition of shell: Clean, thin, some pitting.

Environment: Soil horizon (345-350cm) in Flandrian tufa. Shaded ground (pine, etc.), evidence of burning and some soil erosion.

δ^{13}C Shell: -7.734 δ^{18}O Shell: -2.359 Mg Shell: 29
Pop^{n}: -8.621 Pop^{n}: -2.455 Pop^{n}: 23.3
S.D.: S.D.: S.D.: 7.0
Sr Shell: 517 Fe Shell: 99 Mn Shell: 32
Pop^{n}: 379.0 Pop^{n}: 84.7 Pop^{n}: 30.7
S.D.: 144.4 S.D.: 13.6 S.D.: 1.2
Grading: 0.79

XRD: No calcite Stub No. 98 Photo No. -
SEM: No evidence of crusts or recrystallisation.

Comments: Structure appears to be unaltered.

Overall suitability for dating: High Sr levels (above that of the tufa) suggests exchange via open system, but the other chemistry and structure suggest the shell is suitable for dating.

^{14}C Age of context (Years bp): 7360±60 (Q-2355)
^{14}C Age of shell (Years bp): 7420±100 (OxA-711)
Comments: There is no significant difference between the shell and the context dates.

Table 8.12. Details of sample ICH1 submitted for ^{14}C dating by AMS

. Sample No. D1(CW 31) Radiocarbon No. OX 13 Site: Caerwys, Clwyd

Species: Cepaea nemoralis   Banding: 00000   Condition of shell: -

Environment: Soil horizon (393-400cm) in Flandrian tufa. Context marks the transition from swamp to dry conditions, probably open ground.

$\delta^{13}C$ Shell: -9.889 $\delta^{18}O$ Shell: -1.976   Mg Shell: 49
Pop^n: -9.490   Pop^n: -1.670   Pop^n: 51.3
S.D.: 0.592   S.D.: 0.471   S.D.: 11.8
Sr Shell: 118   Fe Shell: 54   Mn Shell: 17
Pop^n: 49.4   Pop^n: 83.1   Pop^n: 19.6
S.D.: 35.0   S.D.: 28.9   S.D.: 3.0

Grading: -

XRD: 2% calcite   Stub No. 99   Photo No. 451-4,489-494

SEM: Areas of recrystallised material with "diagenetic fronts" observed. Some exfoliation of diagenetic and unaltered material.

Comments: Material that was suspected to be recrystallised structure was isolated from the shell, some unaltered material must also have been present. This was submitted for dating.

Overall suitability for dating: The chemistry suggests that the shell is suitable, but the structure is altered. The submitted sample should exaggerate the overall error this would cause.

^{14}C Age of context (Years bp): 7880±150 (BM-1736)

^{14}C Age of sample (Years bp): 6360±600 (OxA-713)

Comments: The age is too young by 1520 years. This is the expected result because of the presence of recrystallised material.

Table 8.13. Details of sample D1 submitted for ^{14}C dating by AMS

Sample No. D2(CW 9) Radiocarbon No. OX 14 Site: Caerwys, Clwyd

Species: Cepaea hortensis Banding: 12345 Condition of shell: -

Environment: Soil horizon (393-400cm) in Flandrian tufa. Context marks the transition from swamp to dry conditions, probably open ground.

δ^{13}C Shell: -9.414	δ^{18}O Shell: -1.693	Mg Shell: 46
Pop^{n}: -8.736	Pop^{n}: -1.638	Pop^{n}: 62.0
S.D.: 0.960	S.D.: 0.309	S.D.: 22.6
Sr Shell: 56	Fe Shell: 72	Mn Shell: 21
Pop^{n}: 30.5	Pop^{n}: 104.0	Pop^{n}: 28.5
S.D.: 36.1	S.D.: 45.3	S.D.: 10.6

Grading: -

XRD: No calcite Stub No. 91 Photo No. 423-432,464-466

SEM: Exfoliation occurring between the main shell layers. Crust seen on inner surface and ?between layers. No evidence of recryst.

Comments: Crust is interpreted as secondary material deposited from groundwaters. This was isolated and submitted for dating.

Overall suitability for dating: The chemistry and mineralogy suggest that the sample is suitable but the presence of the crust should give an apparent age effect.

^{14}C Age of context (Years bp): 7880±150 (BM-1736)

^{14}C Age of shell (Years bp): 8990±650 (OxA-714)

Comments: The age error (1110 years) demonstrates that the presence of a crust will give a substantial age error.

Table 8.14. Details of sample D2 submitted for ^{14}C dating by AMS

Sample No. CAST 1 Radiocarbon No. OX 15 Site: Castlethorpe,Lincs.

Species: Cepaea nemoralis Banding: 123(45) Condition of shell: Good

Environment: Horizon at the boundary of tufa and slopewash tufaceous silt (69-85cm). Contained charcoal and appeared to be a short-lived clearance.

$\delta^{13}C$ Shell: -8.387	$\delta^{18}O$ Shell: -1.088	Mg Shell: 64
Pop^{n}: -9.958	Pop^{n}: -1.525	Pop^{n}: 71.4
S.D.: 0.874	S.D.: 0.492	S.D.: 24.5
Sr Shell: 145	Fe Shell: 110	Mn Shell: 23
Pop^{n}: 164.2	Pop^{n}: 138.6	Pop^{n}: 17.0
S.D.: 27.5	S.D.: 50.4	S.D.: 3.3

Grading: 0.72

XRD: No calcite Stub No. 133 Photo No. 509

SEM: No signs of recrystallisation or surface crusts.

Comments: No evidence of structural contamination.

Overall suitability for dating: Selected because of the enriched ^{13}C value. A greater apparent age effect is expected in CAST 1 than CAST 6.

^{14}C Age of context (Years bp): 3410±80 (BM-1795)

^{14}C Age of shell (Years bp): 3560±80 (OxA-924)

Comments: The age error is smaller than expected, suggesting that the tufa is not very depleted in ^{14}C.

Table 8.15. Details of sample CAST1 submitted for ^{14}C dating by AMS

Sample No. CAST 6 Radiocarbon No. OX 16 Site: Castlethorpe,Lincs.

Species: Cepaea nemoralis Banding: (123)(45) Condition of shell: Good

Environment: Horizon at the boundary of tufa and slopewash tufaceous silt (69-85cm). Contained charcoal and appeared to be a short-lived clearance.

δ^{13}C Shell:	-11.463	δ^{18}O Shell:	-1.286	Mg Shell:	139
Pop^{n}:	-9.958	Pop^{n}:	-1.525	Pop^{n}:	71.4
S.D.:	0.874	S.D.:	0.492	S.D.:	24.5
Sr Shell:	162	Fe Shell:	82	Mn Shell:	15
Pop^{n}:	164.2	Pop^{n}:	138.6	Pop^{n}:	17.0
S.D.:	27.5	S.D.:	50.4	S.D.:	3.3

Grading: 0.71

XRD: No calcite Stub No. 134 Photo No. 510-518

SEM: No surface crusts observed, some evidence of etching. High magnification showed some recrystallisation but it appeared to be internal.

Comments: No evidence of external contamination or external recrystallisation.

Overall suitability for dating: Structure good, ^{13}C value is depleted relative to the population but the Mg level is high. No age error expected.

^{14}C Age of context (Years bp): 3410±80 (BM-1795)

^{14}C Age of shell (Years bp): 3350±80 (OxA-925)

Comments: No significant difference between the context and the shell.

Table 8.16. Details of sample CAST6 submitted for ^{14}C dating by AMS

The good agreement between OX4, OX6 and the charcoal from layer 393-400cm at Caerwys is partly due to the the tufa which in this layer has an activity which is only 23% depleted relative to contemporary wood (HAR-4378). A similar depletion (<33%) was observed for a lower layer of tufa, below the upper fluvioglacial sand. (HAR-3903, Q-2376). If shells from layer 393-400cm had obtained 40% of their carbon from the tufa, Goodfriend and Hood (1983) suggest a maximum of 33%, the effect on the ^{14}C age would be 800 years. If a more normal value of 12% of the carbon is assumed to be derived from the tufa the maximum error is 220 years which is not significantly different from the charcoal date. It will be shown below that this is also within the length of time that a similar soil horizon was active.

OX7 and OX8 were samples of two different species from the same context. The ^{14}C age of the context is based on AMS dating of seeds extracted from the tufa layer at 75-85cm. The shells were from the soil horizon at 87-90cm. The errors associated with the context dates are large because of the small sample size. The ^{14}C date for the context and OX7 are not significantly different, but only because of the large standard deviations on the context date. The ages of OX7 and OX8 are significantly different but the composition of OX8 suggested that it could have a considerable age error. The soil horizon must be earlier than the dated tufa immediately above and the palaeoecological evidence suggests it should be about 8000 bp (Richard Preece pers.comm.) Sample OX7 is close to this date and the two dates can be considered not significantly different.

The tufa from the Newlands Cross soil horizon produced a ^{14}C date of 9250±195 bp (Q-2xxx) which is equivalent to a maximum depletion of

18% (assuming the context to be dated to 7600 bp). If the true date of the context is 8000 bp then the depletion is only 14%. Therefore a shell that derived 40% of its carbon from the tufa will produce an age error of 475 years. If 12% of the shell carbon is from the tufa the error would be 140 years which is not significantly different from the context date. Sample OX8 produced a ^{14}C date of 8930±150 bp which is 930 years older than the context date. To obtain an error of 930 years by incorporation of tufa-derived carbon would require 70% of the shell to be from this source. This is far higher than any other evidence suggests occurs naturally and suggests that the soil horizon was open for a minimum of 400 years. The time is determined by assuming OX7 contains no tufa-derived carbon (i.e. to be the correct date) and that OX8 has 40% of its shell carbon from the tufa. A duration of 400 years for a 3cm soil horizon has important implications for dating as it is far greater than analytical error and as great as the age differences that are attributed to the "apparent age" effect.

Sample OX10 has a ^{14}C age that is older than that of the context by 1060 years. The composition of the shell suggested there would be a large error. Two previous analyses on *P.elegans* (Burleigh and Kerney 1982) produced errors that are of the same order and direction. The primary reason for the error is thought to be the environmental niche that *P.elegans* occupies (burrowing in chalky matrix). *Cernuella virgata* occupies a similar niche; ^{14}C dates on this species gave results that were about 2500 years too old (Burleigh *pers.comm.* in Preece 1980).

Sample OX11 (shell INCH 1) showed evidence of chemical alteration in an open system, but there was no apparent structural change. The chemical changes do not seem to have affected the ^{14}C content and the date of the context and shell sample are not significantly different. It is possible that the success of the shell date is only by chance. If the original shell had an apparent age and then suffered open system alteration of the chemical composition then the final ^{14}C content could be near to that of the context. However, the tufa from Inchrory was depleted in ^{14}C by only 14% (^{14}C age 8565±100 bp, Q-2xxx). The age error of sample OX11 was 60 years which corresponds to 6% of the shell carbon being derived from the tufa. These facts suggest that the measured shell age is a genuine one.

OX13 was a sample of diagenetic material from shell CW31. Areas of calcite formed by recrystallisation were detected by XRD and SEM. Their presence could not be identified by reference to the composition. The ^{14}C age of this sample was younger than the context by 1580 years; the direction is as expected if the recrystallisation included post-depositional material. The material submitted must also have contained some unaltered aragonite so that the "age" of recrystallisation was probably <6360 bp. That the recrystallisation occurred over a period of time is suggested by the series of "diagenetic fronts" observed in the recrystallised material (figure 6.7).

OX14 was isolated from shell CW9 and was largely composed of material from the crust on the external surface; this was identified by SEM. It was thought that this "crust" was formed by groundwater deposition. The ^{14}C date for this "crust" was 1110 years older than the context, though the standard deviation is large at 650 years. The implication is that the "crust" was deposited soon after the shell itself; if it had occurred considerably later the ^{14}C date would probably be more recent than the shell date unless the groundwaters were severely depleted in ^{14}C. As was the case for OX13, the chemical composition and mineralogy did not indicate the presence of the contamination.

Samples OX15 and OX16 were from Castlethorpe, Lincolnshire and the context was dated at 3410±80 bp (BM-1795). Sample OX16 was selected to be a reliable sample; OX15 was considered to be less so. The results show OX16 to be not significantly different from the context date whilst OX15 has an apparent age of 150 years which is also not significantly different. It was thought that the high Mg level in OX16 might indicate a high level of tufa-derived carbon. This is not reflected in its ^{14}C age which suggests that the tufa is only slightly depleted in ^{14}C.

Nine of the 14 shell samples were expected to give ^{14}C ages that were not significantly different from that of the context or only give small errors (<300 yrs); in fact six samples did so (table 8.17). Those that had greater errors were from Carrowmore. The other five samples were expected to give greater errors; three because of structural alteration or contamination, one because of its ecology and the other because of its composition.

These results show that the presence of errors and their direction can be successfully estimated; and shells that will not be subject to significant errors selected. However, it would be desirable to be able to "correct" erroneous dates and thereby increase the number of suitable samples. Corrections can only be applied to "apparent age" errors as the effect of post-depositional changes will vary with the source of the new carbonate and the period of time between deposition and exchange. In chapter 5 it was shown that two variables, Mg content and δ^{13}C value, were closely related to the environment of

Sample no.	Exp.diff[1]	Obs.diff[2]	Prob.sig.diff.[3]
1	Age > context	+840	High
2	Age > context	+760	High
3	Error less than OX1,2	+550	High
4	Small error (n.s.d.)	70	n.s.d.
5	Age < context	-350	Probably
6	Small error (n.s.d.)	-20	n.s.d.
7	Small error (n.s.d.)	+300[4]	n.s.d.
8	Age < context[5]	+930[4]	n.s.d.
10	Large error[6]	+1110	High
11	Small error (n.s.d.)	60	n.s.d.
13	Age < context	-1520	High
14	Age > context	+1110	Probably
15	Age > context[5]	+150	n.s.d.
16	Small error (n.s.d.)	-60	n.s.d.

(1) Expected difference between the dates of context and shell.

(2) Observed difference between the dates of context and shell.

(3) Probability that the dates of shell and context are significantly different.

(4) Difference relative to assumed date for soil (8000 bp).

(5) Error expected because chemical composition.

(6) Error expected because of species ecology and $\delta^{13}C$ value.

Table 8.17. Summary of the results of the ^{14}C analysis of the validation samples.

deposition.

Tamers (1970) and Evin et al. (1980) examined the possibility of using the $\delta^{13}C$ value as a correction factor for the depletion in ^{14}C; neither found any significant correlation between the age error and $\delta^{13}C$. Figure 8.2 shows a graph of age error versus $\delta^{13}C$ for samples in the present study and from Evin et al. (1980); no significant correlation is present. However, if the data are examined more closely trends for individual sites can be seen. Each of the four sites from which more than a single sample was dated show an increase in age error associated with an enrichment of the $\delta^{13}C$ value. This is the relationship expected if an increased $CaCO_3$ source component leads to an enrichment of the ^{13}C value. The most enriched shells from Caerwys and Carrowmore have $\delta^{13}C$ values higher than the tufa (assumed to be the source of calcium and therefore part of the carbonate). This is because the atmospheric contribution also enriches the final shell $\delta^{13}C$ value.

The small number of data points for each site limits the conclusions that can be drawn. The apparently site specific nature of the correlations precludes the construction of a general "correction" or "calibration" curve. However the data available does suggest that an "optimum" $\delta^{13}C$ value may exist. Lines drawn between the two Castlethorpe points and between the two Caerwys points (CW30 is not included because it contained recrystallised material) intercept at $-10.75^{\circ}/_{\circ\circ}$ which is the zero age error point. Extrapolation of the Newlands Cross points also leads to a zero age error at between -10.75 and $-11.25^{\circ}/_{\circ\circ}$. If NC1 has a reduced age error because the soil existed for 400 years (see above) then the extrapolation leads to $-11.50^{\circ}/_{\circ\circ}$. When the same theory is applied to the Carrowmore

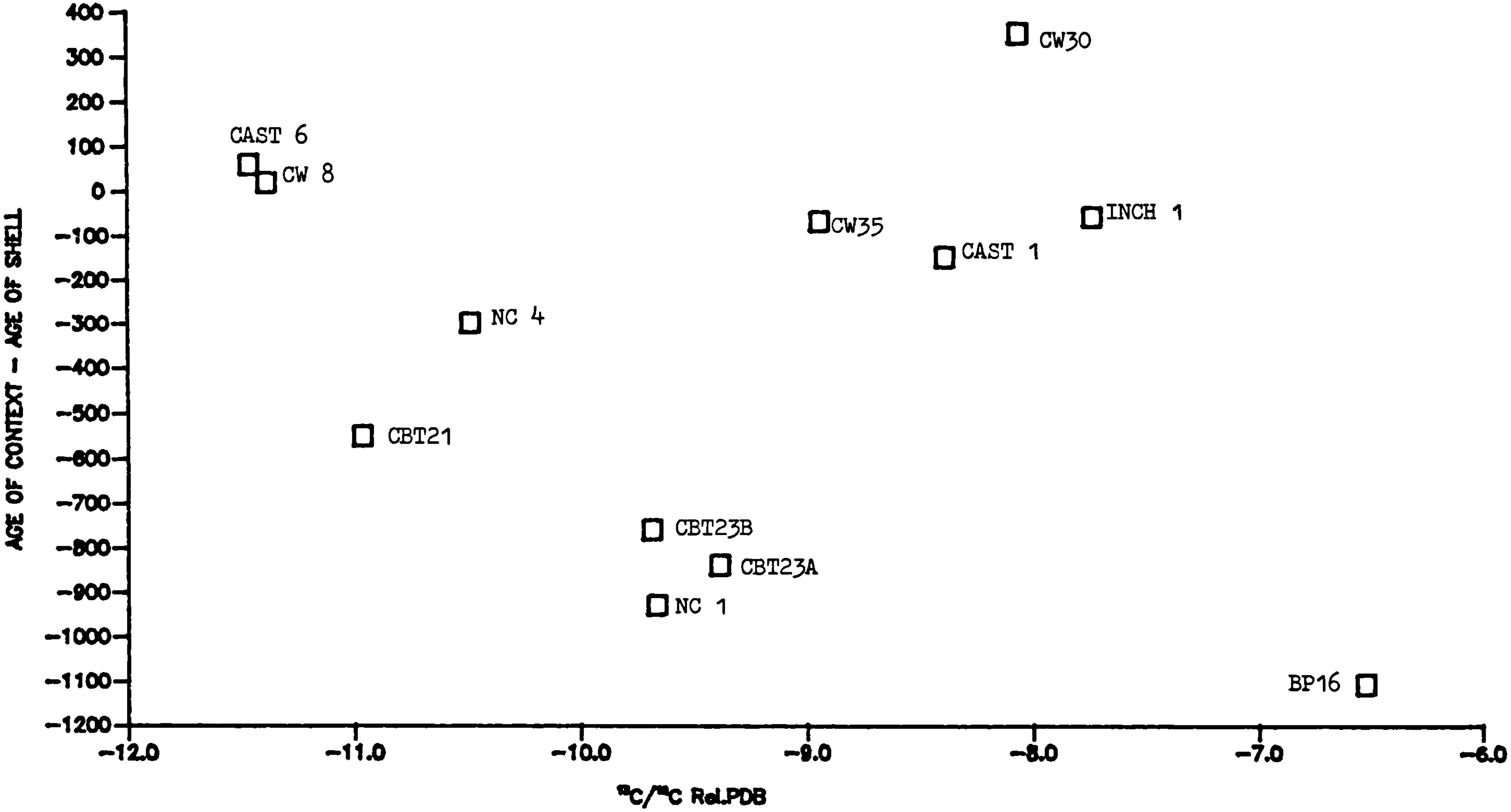


Figure 8.2. Relationship of age error and $^{13}C/^{12}C$ ratio in fossil shells.
Age error = context age − shell age. $^{13}C/^{12}C$ Rel.PDB.

samples the extrapolated line intercepts the zero age error line at -13.80°/oo. However, if CBT21 is not included the lines intercept at -11.50°/oo. In view of the discussion above, that the Newlands Cross soil lasted for 400 years, it is possible that the same occurred at Carrowmore and CBT21 was 250 years older than CBT23. It is not possible for each of the 12 soils observed at Carrowmore to have lasted for 250 years but those from which the shells were collected were selected as being the thickest and most developed.

The possibility of using the Mg content of the shells as a selection procedure does not appear to have received the attention of previous workers. The "background" level defined in chapter 5.4 was used to produce a normalised ratio of Mg contents for each shell (ppm/bkgd). Figure 8.3 shows a plot of age error against ratio. A significant correlation ($R^2 = 0.73$) exists between the two variables with a regression line equation of:

$$\text{Age Error} = 227 - 355\ (\text{Mg ratio}) \qquad (\text{eq.}8.3)$$

The Mg ratio assumes the Mg content of the shell to be independent of the Mg content of the $CaCO_3$ source material; this seems likely as the ratio of shell ppm / source ppm is <0.13 (chapter 5.4).

The x-axis intercept (no age error) occurs at 48ppm, slightly below the "background". Using the equation the age error associated with the "background" would then be about -130 years. The data points for which the ratio is <0.64 (48ppm) should have positive age errors. These points are less clearly correlated which would be expected as positive age errors require post-depositional changes which in turn will produce variable Mg contents. Post-depositional loss of Mg could

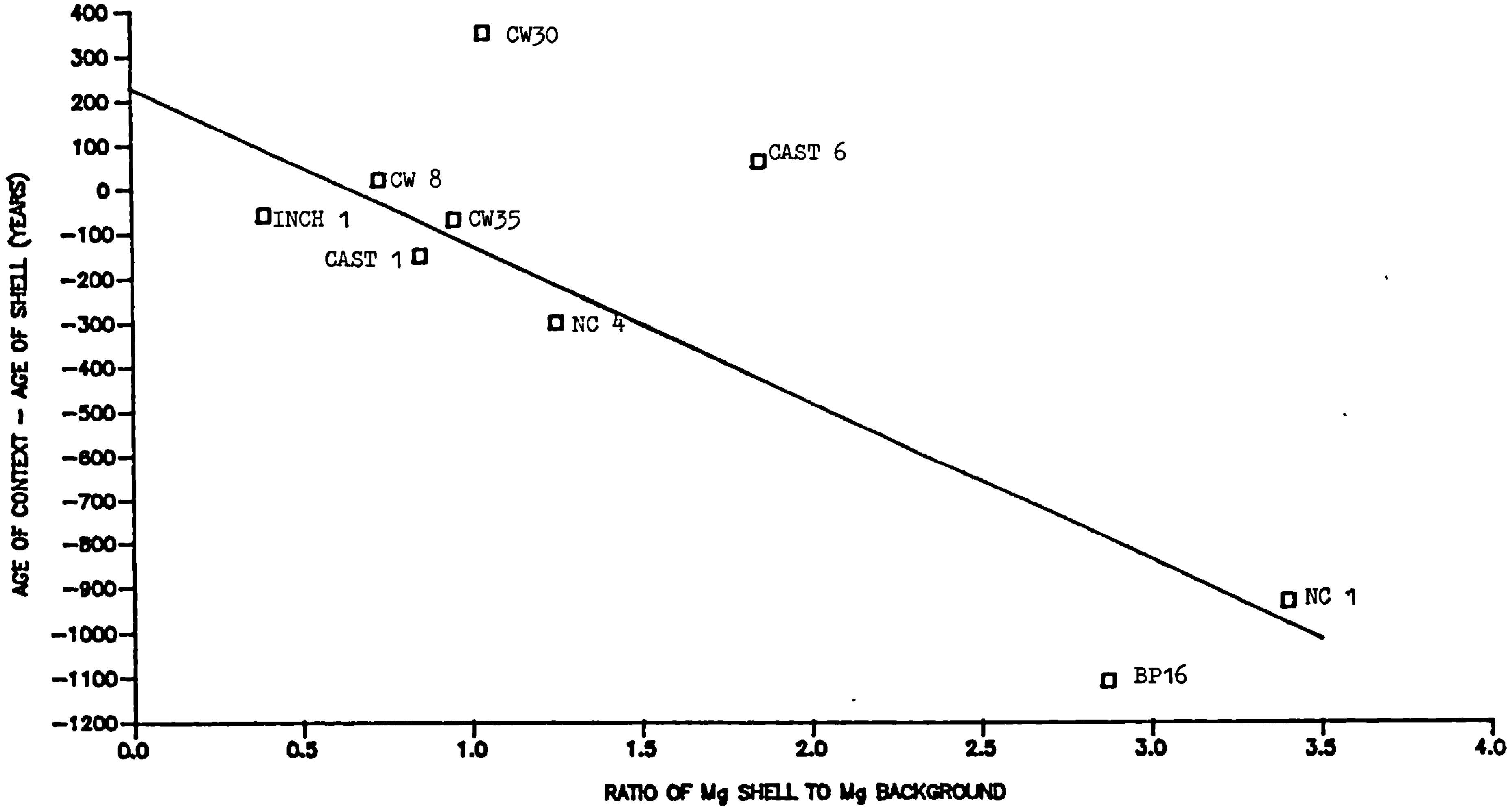


Figure 8.3. Relationship of age error and magnesium content in fossil shells.
Age error = context age − shell age. Magnesium content = shell/background

also affect those shells with a negative age error and give apparent age errors lower than the true values. This does not seem to have occurred in the samples plotted in figure 8.5, unless each of the shells was leached by a similar amount, but would need to be considered if the shells had other indications of leaching such as etched crystals or a high Sr level. It is reasonable to assume that if the shell appears to have suffered little leaching then the samples with Mg contents in the 50-75 ppm range should produce the lowest apparent age effects.

8.6 Conclusions

The validity of the selection procedures has been demonstrated by the results of analyses presented in this chapter. It has been shown that a careful and rigorous approach is required both in the field and in the laboratory. The procedures are ideally suited to samples for AMS ^{14}C dating as the smaller quantity required allows each shell to be subjected to extensive analysis which reduces errors due to sampling only a small part of the material prior to submission. A minimum shell size of 200mg is necessary to allow the full range of analyses to take place.

The exact order in which the laboratory procedures are applied will be different for marine shells. The thickness of marine shells allows acetate peels to be widely applied and this can be used as an initial screening procedure. The thin shells of terrestrial and freshwater mollusc species make acetate peels unsuitable, therefore it is easier to select by composition prior to analysis for diagenetic changes.

However, in all types of shells four factors are considered critical:

1) The type, availability and ^{14}C content of the environmental $CaCO_3$.
2) The species of mollusc and its ecology.
3) The chemical and isotopic composition of the shell, both as absolute values and relative to the population from which it is drawn, particularly the Mg content and the $\delta^{13}C$ value.
4) The presence of post-depositional changes in the shell structure.

If all of these factors are optimised then the shell will produce a ^{14}C date in which the errors are at a minimum, and the date can then be considered as reliable as a ^{14}C date on other more conventional materials.

CHAPTER 9. CONCLUSIONS

9.1 THE QUESTION

The thesis set out to examine the sources of error associated with ^{14}C dating of non-marine shells; the detection of potential errors in shells; and finally selection of material that will give reliable results. The unreliability caused by human error, such as misattribution of shells to a context or misinterpretation of a context, are dealt with only briefly as they are within the control of the researcher or collector.

9.2 GENERAL CONCLUSIONS

The study has shown that, given suitable samples, equipment and time, reliable ^{14}C dates can be obtained on terrestrial shells. The definition of a "suitable sample" is based on the ecology of the species, the sources of $CaCO_3$ and their availability, and the composition and structure of the shell. If all of these factors are optimised then ^{14}C dates that are not significantly different from those obtained on other materials from the same context will be obtained. If some of the criteria are not met the age errors of that sample will be quantifiable but reliability and accuracy will be much reduced. The same applies to samples for which a reduced pretreatment and selection procedure are undertaken. Useful information can still be obtained from a sample that appears to be unreliable provided any post-depositional structural or chemical changes are eliminated. In this case a maximum limiting date can be established with some confidence.

9.3 SPECIFIC CONCLUSIONS

The thesis describes selection and pretreatment procedures for non-marine mollusc shells; though parts are also applicable to marine shells. The reliability of ^{14}C ages is shown to be controlled by optimisation of six selection and pretreatment criteria. Combined together the pretreatment and selection criteria allow both the errors due to the incorporation of material depleted in ^{14}C ("apparent age") and post-depositional diagenetic changes to be overcome.

9.31 Type of context and availability of samples

Observation at the collection site can provide important information on the suitability of shells for ^{14}C dating. The thesis describes the types of environment in which diagenetic changes could be expected to occur. The most important are surface or near surface deposits which are subjected to a meteoric environment; and deposits which are subjected to groundwater movement or a variable water-table. These conditions are likely to lead to structural or chemical alterations to the shells and, therefore, potentially to changes to the original ^{14}C content.

Other deposits which are likely to be unsuitable are those containing slope-washed material or evidence for reworking. The condition of shells from this type of deposit gives a good indication of the probability that they originated outside the deposit. The location and availability of samples are also important. Samples that are in exposed sections or surfaces, will be subject to a meteoric environment. The number and condition of the shells will affect the types of pretreatment that can be applied and the type of ^{14}C dating for which they can be submitted.

It is also important to consider the size and type of shell. Large shells will be more easily cleaned and fewer are required; they also generally have thicker walls and will be less prone to diagenetic alteration throughout the shell.

At the time of sample collection precautions are also required to stop changes and contamination occurring to the shell after removal from the depositional environment. Samples should be stored in sealed bags and where possible dried to reduce contamination by recrystallisation occurring at this time.

9.32 The availability of $CaCO_3$ sources and their ^{14}C content

The "apparent age" effect is due to the incorporation in the shell of material that, at the time of shell formation, is depleted in ^{14}C. Although "old" organic material as plant material or CO_2 may be responsible for part of this the main source will be $CaCO_3$ from the substrate. In the present study three contrasting types of $CaCO_3$ were considered: chalk, containing no ^{14}C; calcareous sand, approximately 50% depleted in ^{14}C; and tufa, 10-30% depleted in ^{14}C. It is clear that if all other factors are equal then shells from tufa sites will be much less subject to "apparent age" problems. The availability of the $CaCO_3$ is also very important. The shell fragments in calcareous sand are easily available in the open dune surfaces but are not likely to be included in the snail's diet because of their coarseness. The fine particles of tufa are both easily available in exposed areas and are often found attached to plant material which will lead to their inclusion in the diet. Chalk particles in the soil will behave in a similar manner to tufa but the soil is often isolated from the snails that live above ground by a thick layer of vegetation or litter.

These theories were confirmed by observation of modern snail species. It is important to establish the environment associated with fossil deposits as accurately as possible.

9.33 Ecology and habits of snail species

Field observation and studies by other researchers suggested that certain species would be prone to "apparent age" effects because of the environmental niche which they occupy. These observations are partly linked to the availability of $CaCO_3$ discussed above. However they show that in an area where availability of $CaCO_3$ is constant species that burrow through the soil (e.g. Pomatias elegans and Cernuella virgata) will be more likely to become contaminated and have a greater "apparent age" effect. Other species, such as Cepaea nemoralis or C.hortensis, can under some circumstances be found in contact with soil $CaCO_3$ sources but P.elegans can only live in areas where the soil is chalky and friable.

Changing habits during a snail's life can also affect the uptake of material depleted in ^{14}C. It was shown that Helix pomatia spends its juvenile years in leaf litter and in ground contact. When it matures, and the shell is thicker, it moves into open grassland areas. It is clear that the time spent in contact with leaf-litter and soil will be more likely to lead to an age error in the shell.

9.34 Isotopic and chemical composition of shells.

Shells from the environments and species described above were analysed to determine how these factors affected the chemical, stable isotope and ^{14}C composition. Modern shells were selected to allow study of variations within shells, within a species both from the same site and different sites, and between species from a single site. The intra-shell variation showed that the shell formed during the later juvenile and adult period was depleted in ^{13}C relative to the earlier shell. This is due to a change in habitat and the fact that the reservoir from which the shell is deposited is nearer to equilibrium with the environment. Both will lead to a reduction in the $CaCO_3$ from the environment and a shell less depleted in ^{14}C.

The micro-environment occupied by different species within a single site and by the same species at different sites are recorded in the $\delta^{13}C$ and $\delta^{18}O$ values of the snail shells. This effect is most clearly seen in the stable isotope values for *P.elegans* which reflect its burrowing (incorporation of particles of chalk) and its contact with the cooler ground. Micro-environmental changes were also detected within a population of *C.nemoralis* from Hayle Towans where the two dominant banding morphs had significantly different $\delta^{13}C$ values. More general isotopic differences were found in *C.nemoralis* from different sites, both modern and fossil, and are interpreted as being caused by the degree of cover at the sites, enriched ^{13}C values being associated with woodland sites.

The magnesium, strontium, iron and manganese contents of modern shells are interpreted as being controlled by mineralogy and environment. The strontium content is related to its environmental availability in aragonitic shells but by mineral structure in calcitic opercula. Magnesium behaves in the opposite way and in the aragonitic shells its level is controlled by the crystal structure. The shells of species which are in contact with high magnesium $CaCO_3$ sources show higher levels of magnesium, which is interpreted as being due to the adsorption of magnesium at interstices in the crystal lattice. The high levels are associated with the species that are in ground contact or burrow. The level of magnesium without adsorbed ions is termed "background" and defined as 75-95ppm.

Fossil shells showed depletion in magnesium and enrichment in strontium relative to modern counterparts; these are interpreted as post-depositional changes (see below).

9.35 Post-depositional structural and chemical changes

The results from the chemical and isotopic analyses were combined with details of the mineralogy and structure of modern shells. The structures were studied using scanning electron microscopy, acetate peels and X-ray diffraction. Freshwater bivalves were found to contain five structures but gastropods (terrestrial and freshwater) only one; all structures were aragonitic. Similar studies were undertaken to determine the types of diagenetic or post-depositional changes that occurred in the fossil shell structures. Four basic types of post-depositional change were found: etching, "crusts", recrystallisation, and exfoliation. The theoretical effect of the diagenetic changes on ^{14}C are discussed and samples of altered material were ^{14}C dated by AMS.

Chemical and isotopic changes were also observed. Particularly important amongst them were the enrichment of strontium, the depletion of magnesium, and a reduction in the statistical variance of the isotopic and chemical compositions associated with fossil shells relative to their modern counterparts. No direct evidence for the exchange of ^{14}C, without mineralogical or structural change, was observed but the implications of the movement of other ions are obvious.

9.36 Availability of time and equipment

The availability of time and equipment can have an important bearing on the reliability of ^{14}C dates obtained on shells. The complete pretreatment and selection procedure takes about two working days per sample and requires a wide range of equipment. If any parts of the procedure are cut out or reduced then it must be assumed that greater age errors will occur. Errors must also increase if the percentage of the submitted sample that is studied is reduced. The methods are more suited to AMS dating than conventional ^{14}C dating where a larger number of shells are required.

9.37 Validation

The selection and pretreatment criteria were applied to a total of 89 shells from a complete sample of 223 fossil shells; 14 samples were selected and submitted for AMS ^{14}C dating. The previous chapter shows that nine of the 14 samples were expected to give dates that were not significantly different from that of the context or only have small errors (<300 years); in fact seven did so. All the five that gave greater errors were expected to do so and the direction of the error was also predicted.

Further analysis of the results suggested that an optimum $\delta^{13}C$ value ($-11.00^{o}/_{oo}$ to $-11.50^{o}/_{oo}$) existed and that shells enriched in ,^{13}C relative to this produced increasingly large age errors. The rate of age error increase was site dependant. A significant relationship was also observed between magnesium content and age error. In a shell that shows no evidence of leaching this could be used to correct for the age error.

9.4 FUTURE WORK

The present study has been undertaken within a limited time period (three years) and with limited access to equipment, particularly ^{14}C dating. The thesis deals mainly with terrestrial molluscs; the same techniques are applicable to freshwater species but more work on the relationship between shell composition, environment, and age errors would be required. However the studies of unaltered and diagenetic structures are applicable to freshwater and marine mollusc species.

The optimum $\delta^{13}C$ values are based on limited data and require further AMS ^{14}C dates on samples from the present sites and additional sites. In particular analysis of more than five samples from a single context and covering a minimum range of $3^{o}/_{oo}$ is needed. The relationship between magnesium content and age error also requires further data to confirm it. The evidence from Newlands Cross that the soil horizon may be active for 400-500 years also requires study as it has great implications for ^{14}C dating of any context and for palaeoenvironmental studies. Finally, further studies on the AMS ^{14}C dating of diagenetically altered shell material and secondary deposits would give valuable information on which types of deposit must be removed, which can be left, and when a shell is worthy of further study.

The results obtained so far are not seen as the final answer to the problem of age errors associated with ^{14}C dates on shells but they do go along way towards dispelling the view that "they are totally unreliable for objective ^{14}C dating".

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