

STABLE ISOTOPE AND TRACE ELEMENT STUDIES

IN CARBONATE DIAGENESIS

by

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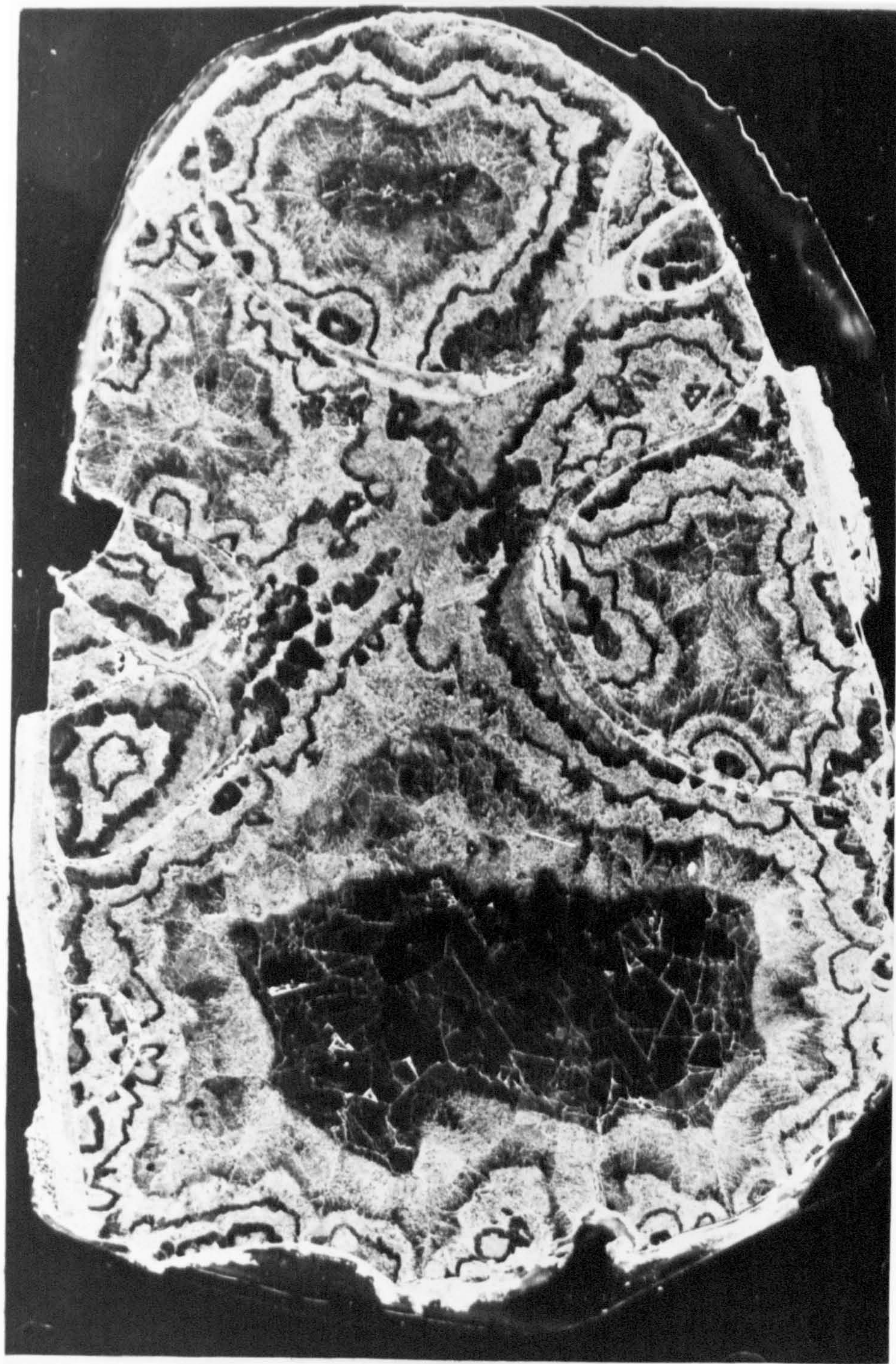
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(CHAPTER III)



STABLE ISOTOPE AND TRACE ELEMENT STUDIES IN CARBONATE DIAGENESIS

by J.D. MARSHALL

ABSTRACT

The thesis is presented as a series of papers.

1. Middle Jurassic hardgrounds from the Lincolnshire Limestone demonstrate synsedimentary submarine cementation. Intensity of early cementation reflects sea-water turbulence. Composite fringing cements have isotopic and magnesium content ($\delta^{13}\text{C} = 3$, $\delta^{18}\text{O} = 0$ and $\approx 2\text{wt}\%\text{MgCO}_3$) interpreted as relics of high-magnesium calcite cements which stabilised in early diagenesis. Marine isotopic values are preserved despite subsequent precipitation of ferroan calcite ($\delta^{18}\text{O} = -9$).

2. The isotopic composition of Mesozoic, Tethyan limestones is related to their lithologies. Micritic, pelagic limestones have $\delta^{18}\text{O}$ from -0.9 to 0.38 , they were cemented on the sea-floor. Heavy $\delta^{18}\text{O}$ in widespread nodular limestones reflects their former (high-magnesium calcite) mineralogy. Shelf carbonates ($\delta^{18}\text{O}$ from -2.5 to -6.5) were fully cemented, after burial and modification of pore-water isotopic composition.

3. Sequences of zones in calcites filling phragmacone chambers of three Jurassic ammonites result from neomorphism and cementation of acicular carbonates during burial. Isotopic trends ($\delta^{18}\text{O}$ from 0 to -20% , $\delta^{13}\text{C}$ from -26 to 0%) demonstrate: shallow-burial cementation with input of organogenic carbon followed by cementation and neomorphism after temperature increase, $\delta^{18}\text{O}$ depletion and introduction of marine bicarbonate. Isotopic, trace element and inclusion density variation between zones reflects neomorphic rate and degree of exchange with burial pore-waters.

4. Fibrous calcite veins in shales grew by successive antitaxial addition at the vein-margins. Isotopic data suggest a late diagenetic origin. Discontinuities are reflected in reversals in isotopic and trace element composition trends. Changes reflect renewed ground-water flow tapping different sources of bicarbonate.

5. The isotopic composition of 'normal' epicontinental marine limestones reflects the modal proportions of allochems and cements. Allochems retain marine isotopic composition ($\delta^{18}\text{O} = 0$, $\delta^{13}\text{C} = +1$ to $+3$) by mineralogical stabilisation with minimal external pore-water exchange. Late cements (with $\delta^{18}\text{O} -5$ to $+13$ and marine $\delta^{13}\text{C}$) precipitated during normal sediment burial but, depth of burial and cause of the ubiquitous $\delta^{18}\text{O}$ depletion remain problematical.

Limestones and diagenetic calcites are clearly inhomogenous; individual components preserve isotopic and trace element compositions, which reflect the environment of precipitation or stabilisation, throughout later phases of diagenesis.

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INTRODUCTION

An ability to determine the time, mechanism and chemical environment of carbonate precipitation and stabilisation is of increasing academic and industrial importance. Carbonate diagenesis often commences on the sea floor and can continue throughout burial. Each stage can leave traces in the chemical composition or fabric of the resultant calcites, this thesis is concerned with unravelling those traces to determine the diagenetic history of ancient sediments.

Pioneer studies in carbonate diagenesis centred on the petrographic description of calcite fabrics and by attempts to determine their genetic significance (see Bathurst, 1958, 1959, 1975). Recent carbonate sediments and cements are largely composed of metastable aragonite and high magnesium calcite, enriched in strontium and magnesium respectively. Chemical studies have concentrated on the behaviour of these two elements (and that of iron which is commonly introduced in reducing burial environments) during diagenesis and the production of the 'normal' mineralogically stable limestones of the stratigraphic column. (Folk 1974, Bathurst 1975, Veizer, 1977). Isotopic analysis was initially employed to determine 'palaeotemperatures' and the 'fresh' or 'marine' origin of limestones (Epstein et al, 1953, Keith and Weber, 1964). In many of the early studies the effects of diagenesis were largely ignored or regarded as an unwanted 'extra', producing a chemical overprint which was hard to separate from the primary environmental data. The differences in isotopic composition of diagenetic carbonates formed under different environments was recognised in the mid 1960's in the original work on the effects of subaerial exposure and diagenesis under the influence of decaying organic matter. (Gross, 1964, Hodgson, 1966, respectively)

These studies and many subsequent reports have concentrated on large numbers of bulk samples where the effects of minor diagenetic events are obscured. In the early 1970's it became apparent that much useful information could be gleaned by taking sampling profiles across concretions (e.g. Hoefs, 1970) and by analysing phases of obviously different diagenetic origin. (e.g. Tan and Hudson, 1974). The majority of the papers continued to rely on 'whole-rock' data and in 1977, Hudson suggested that "Most obviously we must take our limestones to pieces" - This thesis is an attempt to do just that.

By integrating detailed isotopic, trace-element and petrographic data is possible to unravel, often very complicated, sequences of diagenetic events. Important recent advances in this field have been the recognition of relics after original sea-floor cements in ancient sediments (Davies, 1977) and the observation of intra-crystalline as well as within-specimen variation in the isotopic composition of limestone cements. (Dickson and Coleman, in press).

This thesis is presented as a series of self-contained papers each with an introduction and a summary of conclusions in the form of an abstract. The case histories presented here cover the spectrum of carbonate diagenesis from examples of sea-floor cementation (Chapters 1, 2, 3 and 5), the effects of secondary neomorphism (Chapters 3) to those of carbonate precipitation during burial (Chapters 4 and 5). Each example provides further evidence for the complexity of diagenetic history of superficially simple "normal" sedimentary rocks.

Note of Co-Authorship

Chapter one of this thesis was written jointly by the author and by Dr. M.Ashton. I am responsible for the isotopic, trace element and petrographic data, and their interpretation, Dr.Ashton carried out the field work and was responsible for the interpretation of the stratigraphy and depositional environment of the limestones.

The manuscript was written jointly.

All the other chapters are the work of the author. The thesis is the result of work undertaken between September 1976 and September 1979.

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Isotope analysis was carried out at the I.G.S. Isotope Laboratory in London. I am most grateful for the friendly and patient technical assistance rendered by Max Coleman, John Rouse and John Durham. Thanks are also due to Rob Wilson for help with the 'probe', XRD and computing.

Geological samples were obtained by myself and from the collections of many people. The following are to be thanked for lending specimens, many of which are now marred by the scratch of my dental drill :-

Dr. R.G. Clements (Leicester) for some of the Lincolnshire Limestone hardgrounds (Chapter I)

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Production of this volume has been made a pleasure by the willing help given by a great many people. I would like to thank Carolyn Paterson, Maureen Podesta and Norma Corby who between them spent many evenings, typing from my often illegible manuscripts. Sue Button drafted many of the figures and provided immeasurably useful, friendly advice on presentation of the line-drawings. Particular thanks must be expressed to Lesley Richardson, who untiringly and uncomplainingly shared the work of producing the thesis. Without her friendship and help this thesis would have been several months overdue and far less tidily presented.

My debt to my parents and the rest of my family for their support and encouragement throughout my education is immeasurable.

CHAPTER 1

ISOTOPIC AND TRACE ELEMENT EVIDENCE FOR SUBMARINE LITHIFICATION
OF HARDGROUNDS IN THE JURASSIC OF EASTERN ENGLAND.

ABSTRACT

Geochemical and petrographic data suggest early submarine cementation of hardgrounds from the Lincolnshire Limestone Formation, Middle Jurassic, England. The three hardgrounds, from Cowthick, Castle Bytham and Leadenham quarries, developed in tidal-inlet, on-barrier and lagoonal subenvironments of a carbonate barrier-island complex.

At Cowthick early composite (acicular-bladed) radial-fibrous cements, which pre-date aragonite dissolution, completely fill intergranular pore-space at the hardground surface; away from it isopachous fringing cements decrease in thickness. Microprobe analyses demonstrate zoning within the fringes with magnesium concentrations ($> 2 \text{ wt.}\% \text{Mg.CO}_3$) higher than those in allochems or later, ferroan cement ($\approx 0.5 \text{ wt.}\% \text{MgCO}_3$, $1.7 \text{ wt.}\% \text{FeCO}_3$). At Castle Bytham early granular isopachous cements, which post-date aragonite dissolution, occur within 5 cm of the surface. At Leadenham early lithification is superficial and represented by ferruginous crusts and micritic internal sediment. Late blocky cement fills residual pore-space in all three examples.

Carbon and oxygen isotopic composition of whole-rock samples taken at intervals away from each hardground surface demonstrate the increasing proportion of late ^{18}O depleted cements ($\delta^{18}\text{O} -8$ to -10). Early cements must have a marine isotopic composition; different $\delta^{18}\text{O}$ values from each hardground reflect the intensity of early lithification and exclusion of late cements at the hardened surface. There is no isotopic evidence for subaerial cement precipitation during possible emergence at Castle Bytham. Oyster samples (with $\delta^{18}\text{O}$; -2.9 and $\delta^{13}\text{C}$, 2.4) give estimated palaeotemperatures of $22\text{--}25^\circ\text{C}$. Early cements from Cowthick are enriched in ^{18}O and ^{13}C ($\delta^{18}\text{O} = 0$ $\delta^{13}\text{C} \approx 3\%$) compared to the oyster values.

In conjunction with trace element data this is interpreted as evidence for high-magnesium calcite precursor cements which underwent replacement in a system with a low water-rock ratio.

The intensity of early lithification is related to depositional environment: maximum circulation of sea-water producing the most lithified hardground (Cowthick). This is directly analogous to the formation of Recent hardgrounds

INTRODUCTION

Synsedimentary submarine cementation has been widely recognised in Recent and Ancient sediments (Bathurst, 1974), where it is of critical importance in the study of porosity distribution in reservoir rocks (Purser, 1978). The pioneer work on the recognition of submarine cementation centred on the use of petrographic fabrics but isotopic and trace element studies have become increasingly important in the identification of cements and in unravelling diagenetic histories (Davies, 1977; Hudson & Coleman, 1978).

Hardgrounds are surfaces of synsedimentary lithification (Bathurst, 1975; Bromley, 1978) which are identified, in the field, by their encrusting and boring faunas (Goldring & Kazmierczak, 1974; Baird & Fursich, 1975; Bromley, 1975; Palmer & Palmer, 1977). Detailed faunal analysis (e.g. Palmer & Fursich, 1974) and petrographic interpretation (e.g. Purser, 1969) have been used to indicate the environment of early cementation in hardgrounds, while isotopic analyses show that some hardgrounds retain evidence of submarine cementation (Scholle & Kennedy, 1974).

In this paper we integrate geochemical and petrographic information to determine the range and style of early cementation in three hardgrounds from the Lincolnshire Limestone Formation, Middle Jurassic, England. The results are related to the depositional environments of the hardgrounds.

STRATIGRAPHY AND ENVIRONMENTAL SETTING

The Lincolnshire Limestone is the major marine carbonate formation within the Middle Jurassic of eastern England, extending from the Humber estuary southwards to Northamptonshire (Fig. 1). The principal ammonite faunal boundaries appear to coincide with major lithostratigraphical divides, producing a broad tripartite subdivision of the formation in Lincolnshire (Fig. 2; Ashton and Parsons, in press). Further south, in Northamptonshire, the middle Lincolnshire Limestone is usually missing, partly as a result of downcutting by the upper Lincolnshire Limestone, which channels into the Grantham Formation in some localities (Fig. 3). Figures 1 and 2 show the stratigraphical and geographical setting of the hardgrounds discussed in this paper.

The carbonate succession of the Lincolnshire Limestone Formation reflects the landward migration of an off-shore barrier complex across protected lagoonal and tidal-flat deposits; the barrier sediments are represented by the upper Lincolnshire Limestone while the lower and middle Lincolnshire Limestone contain the back-barrier facies (Ashton, 1977). Hardgrounds occur throughout the formation, reflecting development within several palaeo-environments, as illustrated by the three examples discussed below.

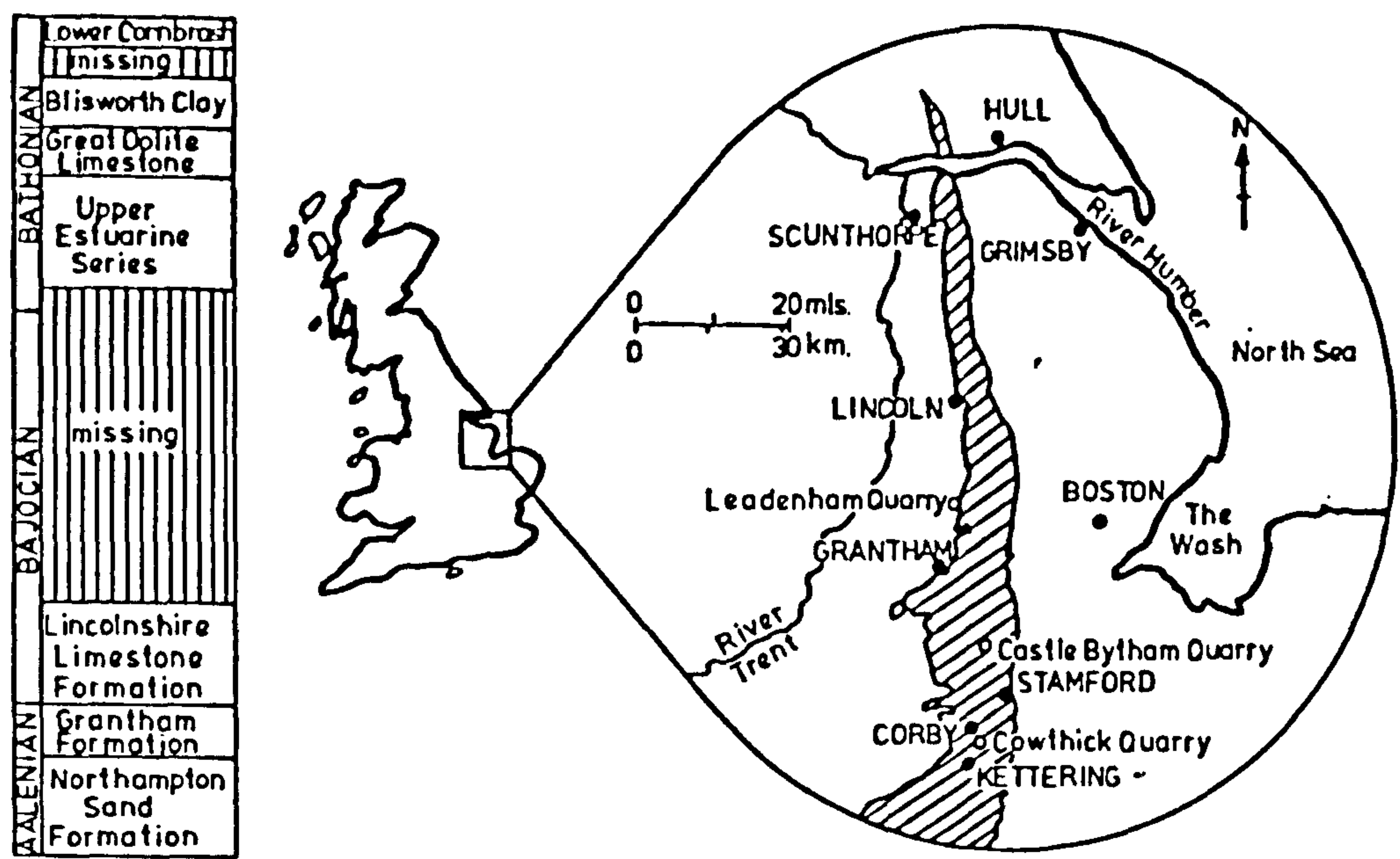


Figure 1 Location map and major stratigraphical divisions of the Middle Jurassic in eastern England .

Figure 3A An Upper Lincolnshire Limestone channel downcutting into the Grantham Formation at Cowthick quarry, near Corby.

Figure 3B Same, showing channel margin.

3A



3B



HARDGROUNDS

LEADENHAM HARDGROUND

The Leadenham hardground, which caps a sequence of strongly-bioturbated oolites, is encrusted by thin-shelled, flat oysters and serpulid worms; multiple phases of biological reworking can be determined. The hardground surface and walls of the last extensive phase of burrow formation have a ferruginous coating (Fig. 4). Serpulids encrust the roof of a large burrow implying a degree of syndepositional lithification. There are no clearly defined syndepositional cements and the matrix of the limestone is largely microspar-sized calcite with ferroan spar occasionally filling voids.

Environment

A consideration of field, petrographic and faunal evidence suggests that the oolites (wackestones and packstones) underlying the hardground accumulated in a shallow subtidal environment of varying but generally low levels of turbulence, leeward of the main oolith-generating zone. Above the hardground thinly-bedded, bioturbated biomicrites (mudstones and wackestones) with a prolific molluscan-dominated marine fauna, reflect deposition in a quiet-water lagoon (Ashton, 1977). In terms of modern carbonate facies the oolites can be compared with the Stable Sand Habitat of the Great Bahama Bank (Newell et al., 1959) or the Callianassa Sand Sheets of Aldabra (Farrow, 1971) while the biomicrites might equate with the Mud Facies of the Great Bahama Bank (Purdy, 1963). In both instances, however, the gross palaeogeographical setting of the deposits is much more in keeping with the lagoons of the Trucial Coast (Purser and Evans, 1973).

Despite the differences in the facies above and below the hardground it is evident that early lithification took place in a marine lagoon situated leeward of a protective off-shore barrier.

CASTLE BYTHAM HARDGROUND

The Castle Bytham hardground caps a burrowed peloidal limestone in a predominantly oolite sequence; the hardground is encrusted by thick-shelled oysters and bored by bivalve molluscs. Early lithification is patchily developed within 5 cm of the encrusted surface and is represented by $> 20 \mu\text{m}$, isopachous, non-ferroan, equidimensional calcite crystals; there is no micritic internal sediment. Non-ferroan granular cements are found inside micrite envelopes as well as in the pore space, indicating precipitation after aragonite dissolution. The residual pore space is filled with large poikilotopic calcite spar with variable Fe^{II} content: non-ferroan, inclusion-rich spar at the hardened surface gives way to inclusion-free ferroan spar approximately 3 cm from the surface. The lack of iron in near surface late spar is possibly due to the incorporation of early micrite internal sediment during its precipitation.

Environment

The Castle Bytham hardground occurs within the barrier complex of the upper Lincolnshire Limestone. Although detailed interpretation of every bed within the barrier complex is not possible, the Castle Bytham hardground appears to cap a sequence of semi-protected oolitic facies and to be overlain by spillover lobe sediments (sensu Ball, 1967), which are represented by massive, tabular cross-bedded oosparites of upwardly-decreasing set size; both seaward and lagoonward 'spilling' is evident from the contrasting bipolar cross-bedding directions

(Ashton, 1977). Thus the hardground probably developed at the interface between the semi-protected, leeward side of the barrier and the highly turbulent spillover-lobe zone to seaward.

COWTHICK HARDGROUND

Hardgrounds occur in channels within the Upper Lincolnshire Limestone of Cowthick quarry, Corby. The sediment filling the channels are medium-grained, well-sorted pure oosparites and coarse-grained, relatively poorly-sorted shelly oolites; cross-bedding is common in both lithologies. The hardgrounds have two principal modes of occurrence: 1) as near-vertical hardened surfaces within the channel fill, which represent either temporary channel margins during a phase of re-exhumation or fissures within the channel fill (these surfaces are hereafter referred to as channel wall), and 2) the margins of rafted blocks within the channels. In both cases the lithified surfaces are encrusted by oysters and serpulids, and very densely bored by bivalve molluscs and, to a lesser extent, worms; multiple generations of bores can be demonstrated (Fig.6).

Synsedimentary cements are represented by composite isopachous fringes which line the intergranular pore space; mollusc borings cut both allochems and fringing cements. Early cements occupy the entire pore-space at the hardened surface but decrease in thickness (and volume) to $< 20 \mu\text{m}$ at 20 cm from the base of the mollusc bores (Figs. 10, 11, 12, 13). Micritic internal sediment geopetally fills open mollusc-bores and similar micrite occurs within and coating the fringing cements near the bore walls.

Grain contacts are generally short and compaction has had minimal effect. Late blocky ferroan spar fills the remaining pore

Figure 4 Leadenham hardground. A large crustacean () burrow is filled with micrite and coral debris. The burrow margins have a ferruginous coating and the roof is encrusted by serpulids (arrowed). Scale in cms.

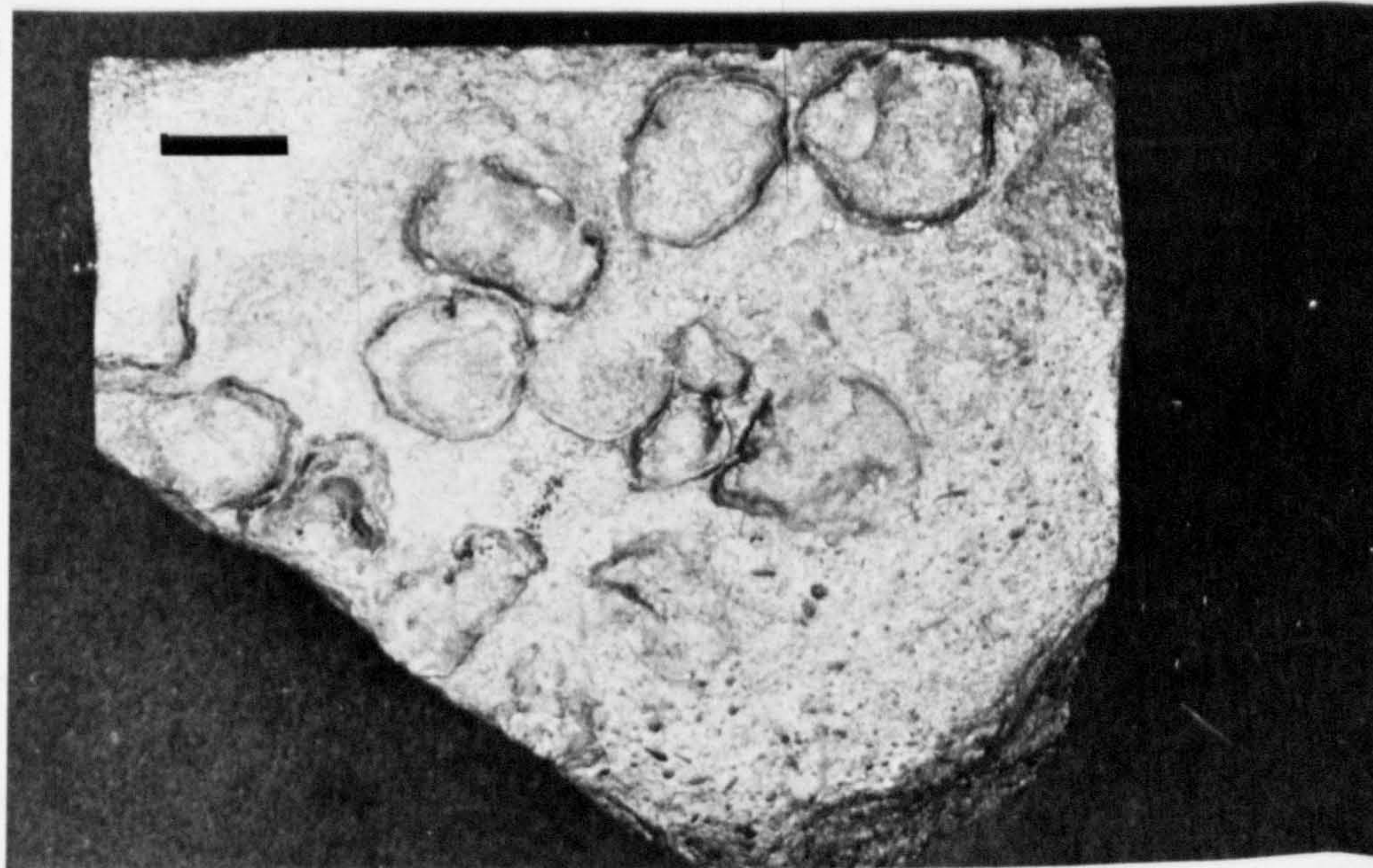
Figure 5 Oysters encrusting the Castle Bytham hardground. (Bar = 1 cm.).

Figure 6 Cowthick hardground (channel wall). The surface has been bored by gastrochaenid molluscs and 'worms', (Bar = 2 cm.).

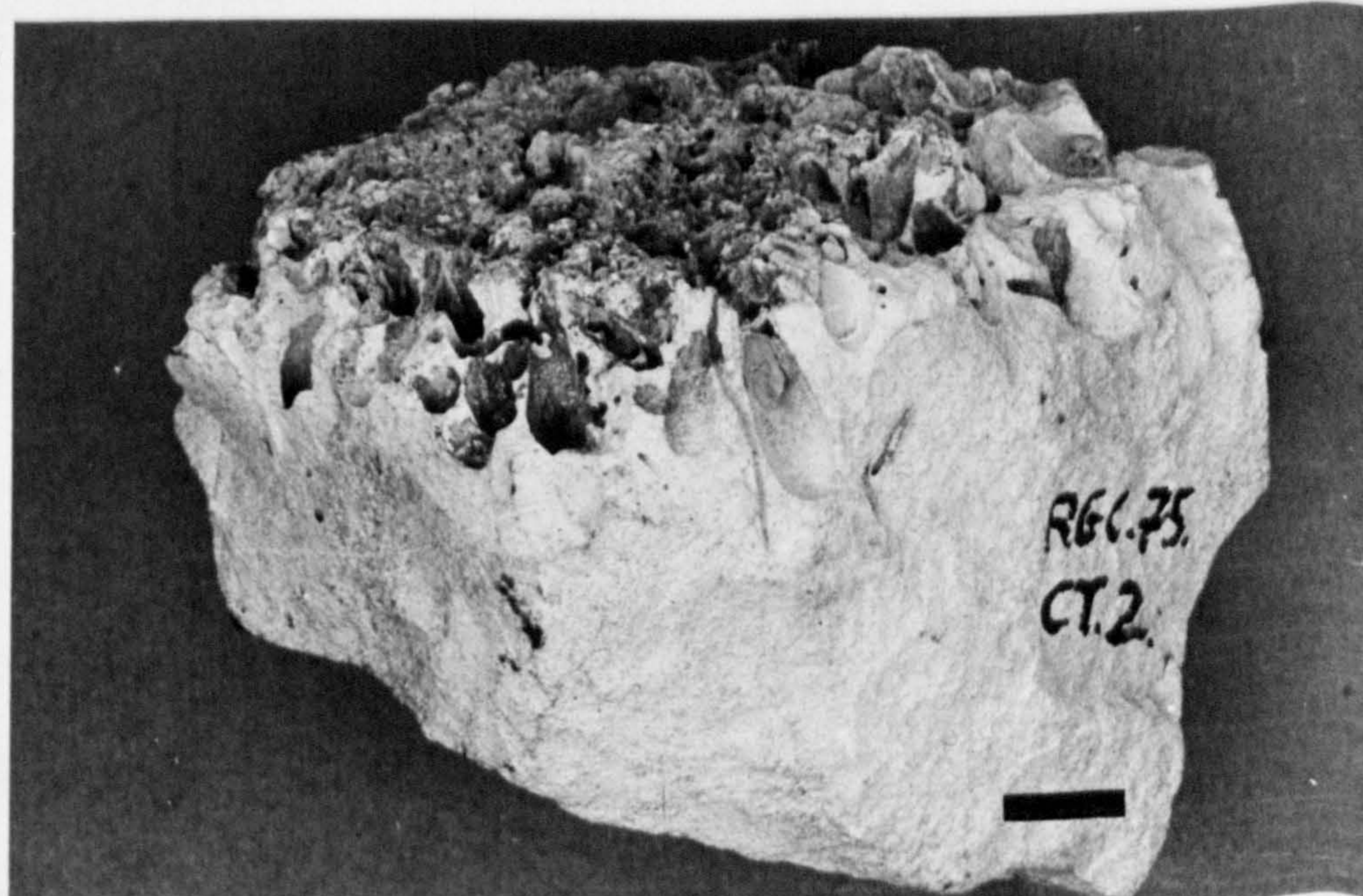
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5



6



space and the solution voids of formerly aragonitic shell fragments, which are outlined by micrite envelopes. The cements from these hardgrounds will be discussed in detail in conjunction with chemical data in a later section.

Environment

Taylor (1946) interpreted the Lincolnshire Limestone channels of the Northamptonshire area as discontinuous, elongated basins resulting from tidal or current activity within the Lincolnshire Limestone sea. It now seems more likely that they are analogous to the barrier-inlets seen further north in the Lincolnshire Limestone (Ashton, 1977); the smaller size and strikingly channelised form of the Northamptonshire scours (Fig. 3) is probably a function of the migration of the barrier across its former hinterland (represented by the Grantham Formation).

METHODS

ISOTOPES

Small, whole-rock samples were taken at the hardground surface and at intervals from it. Separate samples were taken from the surface fauna, the sediment filling bores and burrows and from the late spar concentrated in former voids. Samples were extracted with a dental drill.

All samples were treated with 15 mls of a 1% solution of sodium hypochlorite ("clorox") solution to remove organic matter and washed with deionised water (Forester et al., 1973). Samples that continued to show organic contamination, after pretreatment and further purification during CO₂ extraction, were disregarded and an additional sample prepared (for rejection criteria see Weber et al., 1976). Analysis of pure carbonate standards has

shown this treatment to have negligible effect on their isotopic composition.

Carbon dioxide for analysis was liberated by reaction of around 10mg of carbonate with 100% phosphoric acid at 25°C (McCrea, 1950). Isotopic ratios were determined on a 'Micromass 602' mass spectrometer at the Institute of Geological Sciences, London, and corrected using standard procedures (Craig, 1957). Analytical errors of less than 0.05 ‰ are associated with individual isotopic determinations.

ELECTRON MICROPROBE

A Cambridge Instruments - Microscan 5 microprobe was used for quantitative and semi-quantitative determination of trace-element composition. Experimental detail will be reported in some detail to facilitate comparison with published data (e.g. MacQueen and Ghent, 1970; Benson and Matthews, 1971; Wardlaw et al., 1978).

Quantitative 'point' analysis

Moderate operating conditions were chosen to obtain maximum accuracy with minimal decomposition of the specimen surface. Beam conditions of 15 KV accelerating voltage and 20 μ A specimen current, on a pure copper standard, were used throughout. A defocussed, $\approx 20 \mu$ m beam minimised surface burning effects. These conditions allowed 30 second count integration times and a correspondingly high precision. Count rates on carbon-coated polished samples were compared with those on silicate, metal and metal oxide standard materials. Results were corrected for background, drift and interference effects using the MAGIC IV computer program. Minimum detection limits and sensitivities are given in the caption of table 3.

Qualitative 'scan' analysis

Trace element variation within a cement generation was monitored using a fully focussed ($\approx 2\mu\text{m}$) beam with a continuous sample scan velocity of $3\mu\text{m}/\text{min}$. The harsher conditions gave a noticeable increase in surface deterioration but quantitative results calculated from continuous output (Fig. 14) give good agreement with point analyses of the coarser grained material (Table 3). Repeated scans across grain boundaries and fringing cements give a consistent pattern of variation (Fig. 14).

STABLE ISOTOPES

The relative isotopic concentration in a carbonate grain or cement is indicative of the physical conditions of precipitation and the composition of ambient pore water. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ express the parts-per-thousand difference in $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios from those in the P.D.B. standard.

The isotopic composition of the components of 'normal' marine limestones are illustrated by Hudson (1977, Fig. 1). Precipitates from sea water generally have an equilibrium isotopic composition, with low positive $\delta^{13}\text{C}$ and low negative values for $\delta^{18}\text{O}$. Non-marine carbonates are enriched in ^{12}C due to isotopically 'light' soil CO_2 and have negative $\delta^{18}\text{O}$ due to ^{16}O enriched rainwater. 'Late' blocky ferroan spar filling residual pore spaces also has negative $\delta^{18}\text{O}$ (Irwin *et al.*, 1977; Hudson, 1978) but generally retains 'marine' values of $\delta^{13}\text{C}$ (Hudson, 1975).

Once a carbonate phase has attained mineralogical stability it can retain its isotopic composition without exchange with later, often isotopically-modified pore-water (e.g. Hudson & Friedman, 1976). Whole-rock isotope values

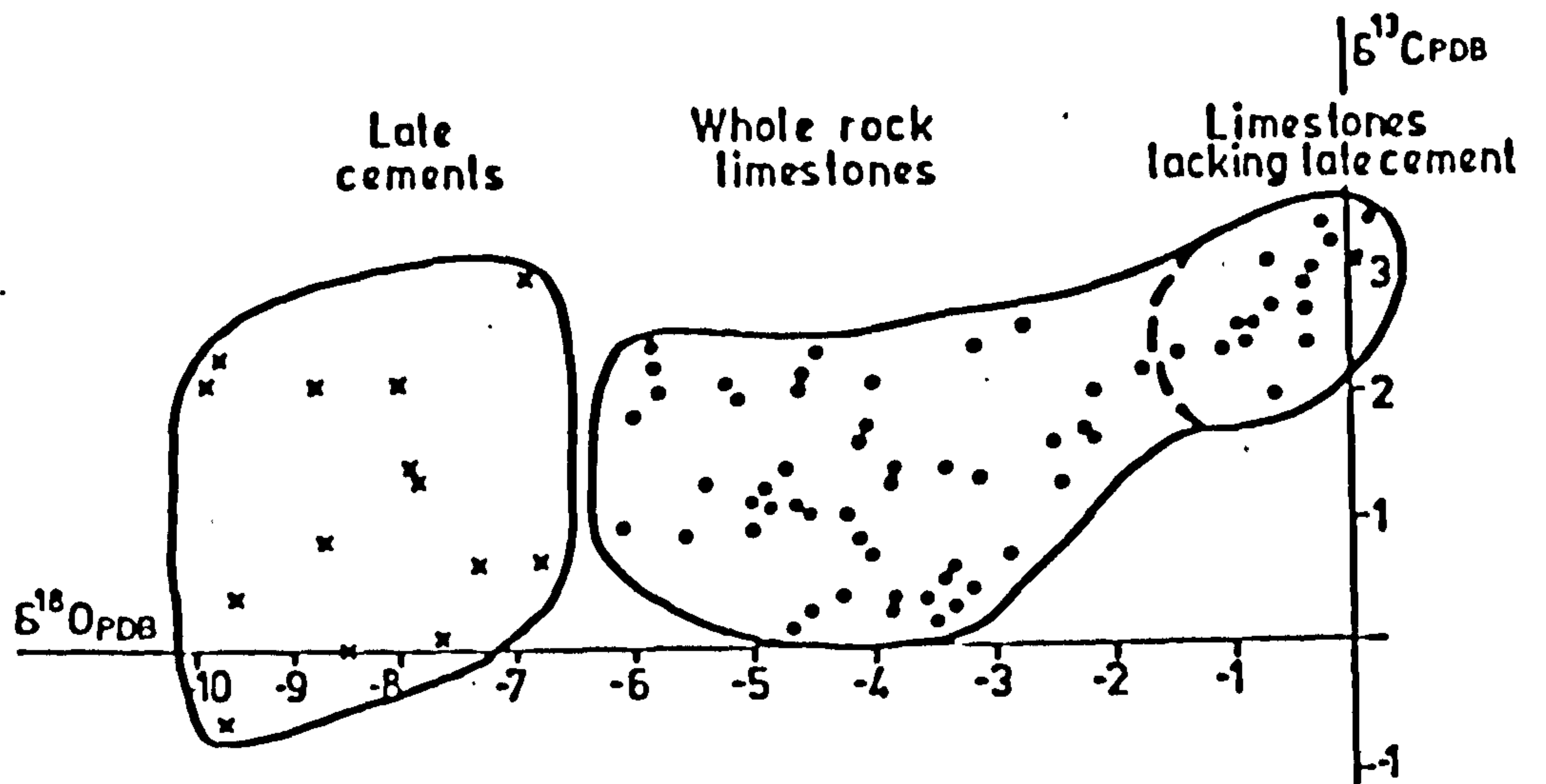


Figure 7 Isotopic composition of samples from the Lincolnshire Limestone including hardground and other material. 'Whole-rock' values (dots) are dependent on the varying proportions of allochems, 'early' and 'late' cements' (crosses). All values lie within the normal range of marine limestones.

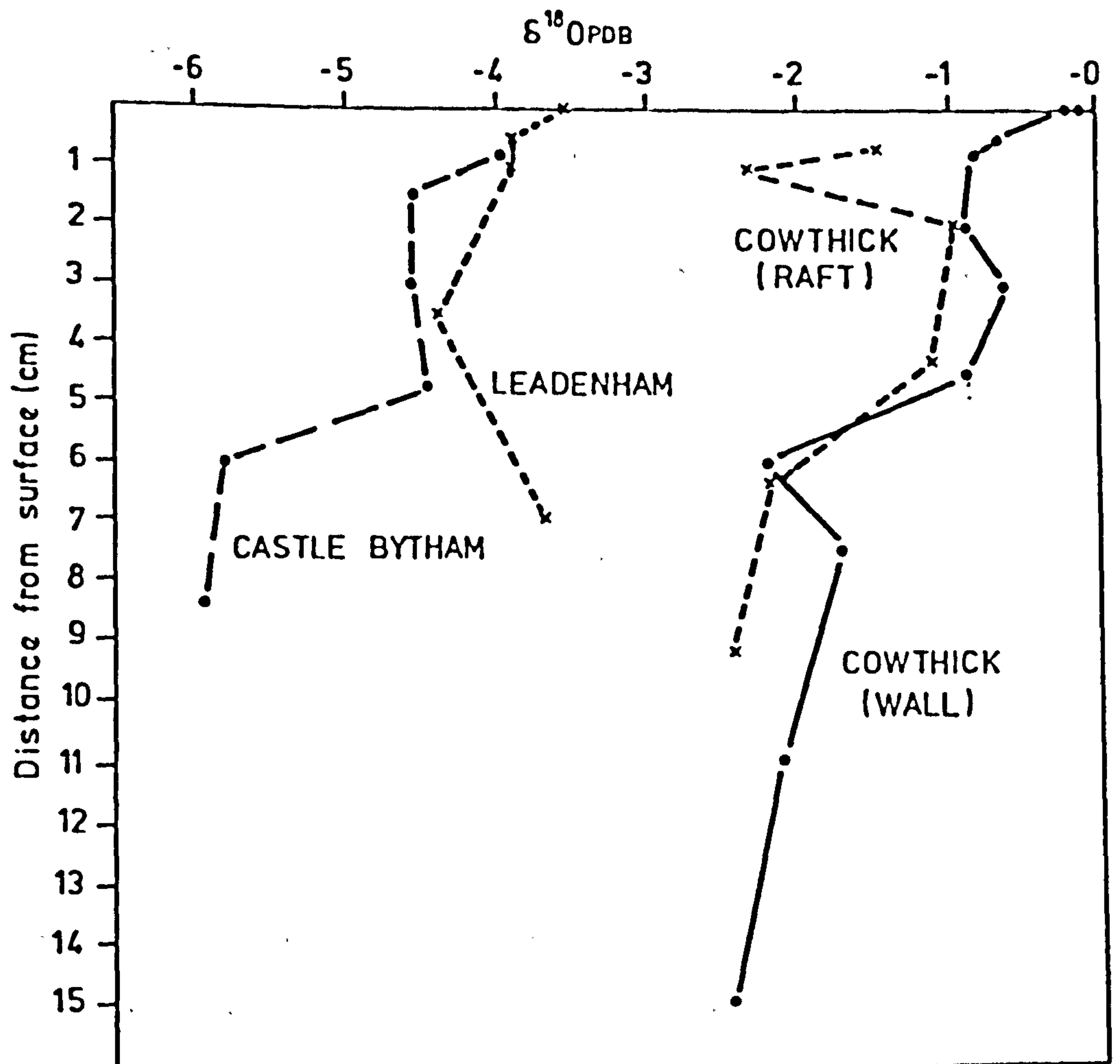


Figure 8 Oxygen isotopic variation with distance from the hardground surface.

demonstrate the proportions of allochems and different generations of cement (Fig. 7). The distribution of samples from the Lincolnshire Limestone Formation (Fig. 7) is due to the cementation of marine allochems and cements by late blocky calcite. The 'limestone lacking late cement' include unconsolidated oolite sands and samples from the surfaces of the fully-lithified Cowthick hardgrounds.

ISOTOPES IN LINCOLNSHIRE LIMESTONE HARDGROUNDS

Initial lithification of a hardground is produced by inter- and intra-granular cements, which are impossible to separate mechanically for isotopic analysis. However, as these early cements are generally concentrated within a few centimetres of the hardground surface, samples taken at intervals away from the hardened surface demonstrate the range and isotopic composition of the early cements.

In all three Lincolnshire Limestone hardgrounds, samples from near the surface have 'heavier' $\delta^{18}\text{O}$ than those from further away (Tables 1 & 2, Fig. 8). In the case of the Cowthick hardground these values approach $\delta^{18}\text{O}$ of 0‰ whilst at Leadenham and Castle Bytham values of less than -3‰ are obtained. This is consistent with early cements precipitated from waters relatively enriched in ^{18}O and suggests a submarine rather than fresh-water influence (Scholle & Kennedy, 1974; Schlager & James, 1978). The difference in $\delta^{18}\text{O}$ in near-surface samples reflects the greater intensity of early cementation: at Cowthick early cements fill all the intergranular pore space whilst at Castle Bytham and Leadenham there is a significant contribution from late cements in all the whole-rock samples.

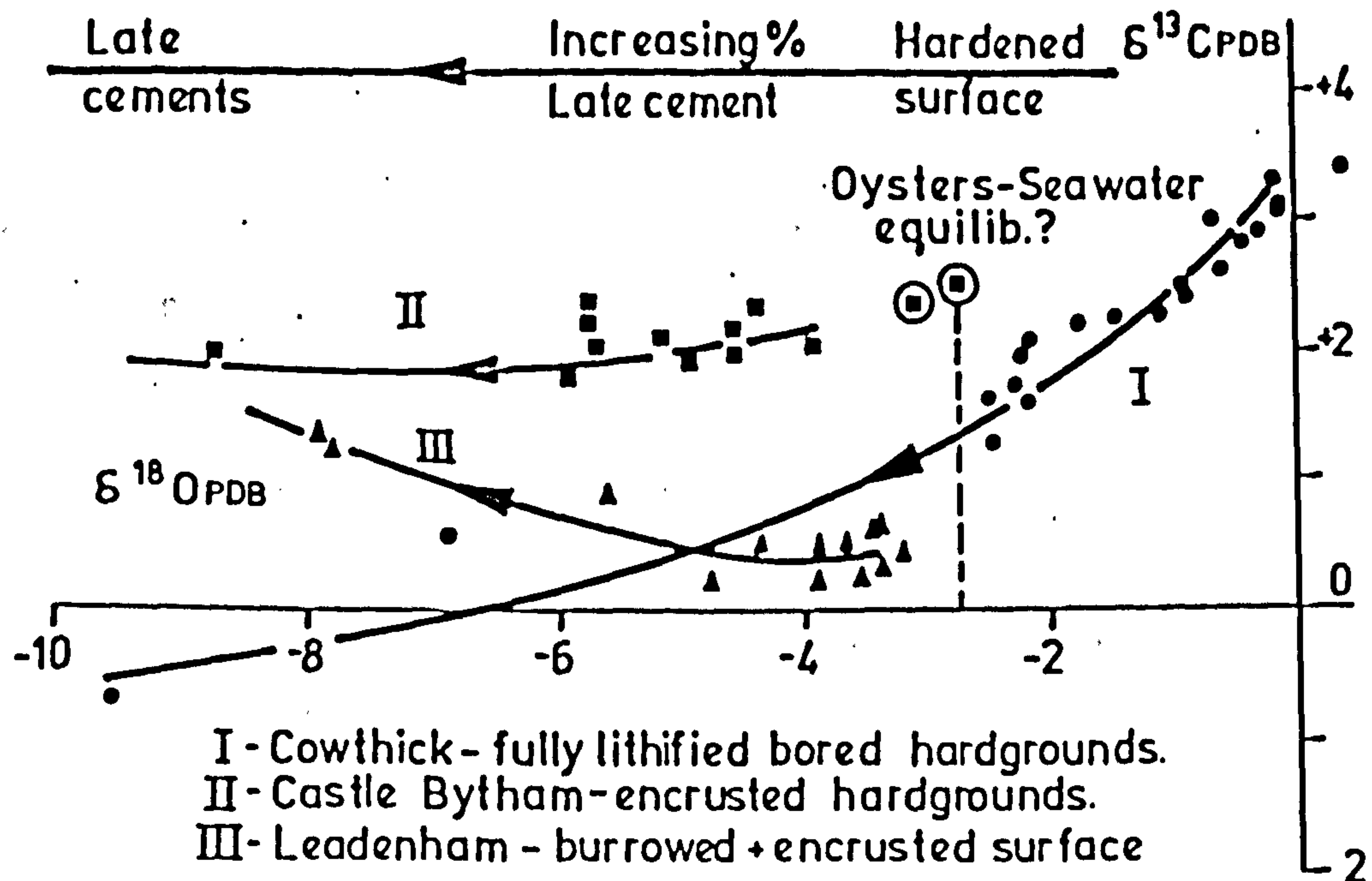


Figure 9 Carbon and oxygen isotopic composition of the Lincolnshire Limestone hardgrounds. Samples from Cowthick are notably enriched in δ^{18} .

Stage	Fabric	Description	Distance from surface	% Early fringing cement 0 50	'Whole rock isotope comp.'	
					$\delta^{18}\text{OPDB}$	$\delta^{13}\text{CPDB}$
A		Hardground surface: Borings cut allochems & fringing cements.	0 to 4 cm			
B		Two zones of early fringing cement fill interstitial voids	~5cm			
C		Early cement dominates voids. Late ferroan spar fills residual cavities.	~7cm			
D		Late ferroan spar dominates voids (Two zones still apparent in fringe)	~10cm			
E		No early cement voids filled with blocky ferroan spar.	>20cm			

Figure 10 Schematic representation of the fabric and isotopic composition away from the bored surfaces of the Cowthick hardgrounds. The percentage of early and late cement have been determined by point counting; the proportions of early and late calcites are inversely related and therefore inter-granular pore space remains virtually constant.

Table 1 Carbon and oxygen isotopic analyses from the Cowthick hardgrounds.
 ('Depth' is measured from base of mollusc borings.)

Table 1(a) - Cowthick Hardground - channel wall

<u>SAMPLE</u>	<u>DEPTH (CM)</u>	<u>DESCRIPTION</u>	<u>δC^{13} PDB</u>	<u>δO^{18} PDB</u>
L1	-	Unconsolidated geopetal sediment	3.41	0.38
L2	0	Hardground surface	3.14	-0.16
L3	0	Wall of mollusc boring	3.27	-0.18
L4	0.5	'Whole-rock' oosparite	3.02	-0.68
L5	0.7	" "	2.94	-0.83
L5-1	2.0	" "	2.45	-0.90
L5-2	3.0	" "	2.62	-0.64
L5-3	4.5	" "	2.50	-0.91
L5-4	6.0	" " shelly layer	1.73	-2.22
L5-5	7.5	" "	2.23	-1.73
L5-6	11.0	" "	2.04	-2.13
L5-7	15.0		1.60	-2.45

Table 1(b) - Cowthick Hardground - rafted block

L30	-	Poorly consolidated bore-fill	3.04	-0.10
L31	-	Fine-grained early-lithified internal	2.33	-0.37
L32	-	" " " " sediment	2.81	-0.49
L33	-	Late spar vein (contaminated with 1st)	0.58	-6.85
L34	0.7	Whole-rock' oosparite	2.27	-1.48
L35	1.0	" " " - shelly layer	2.00	-2.34
L35-1	2.0	" " "	2.45	-0.91
L35-2	4.3	" " "	2.30	-1.12
L35-3	6.3	" " "	1.63	-2.17
L35-4	9.2	" " "	1.79	-2.46
L35-5	-	Late blocky ferroan spar	-0.66	-9.51

Table 2 Carbon and oxygen isotopic analyses from the Castle Bytham and Leadenham hardgrounds. ('Depths' measured from encrusted surface and base of large crustacean burrow, (Fig. 4), respectively.)

Table 2(a) - Castle Bytham Hardground

<u>Sample</u>	<u>Depth</u>	<u>Description</u>	<u>δC^{13} PDB</u>	<u>δO^{18} PDB</u>
L20	-	Oyster - encrusting hardground surface	2.47	-2.76
L20-1	-	Oyster " " "	2.30	-3.12
L22-1	0.8	'Whole-rock' pelsparite	2.02	-3.96
L22	1.5	" "	1.99	-4.57
L22-2	3.0	" "	2.04	-4.57
L22-3	4.7	" "	2.22	-4.45
L23	6.0	" "	2.31	-5.80
L23-1	8.5	" "	1.75	-5.94
L24	-	Spar supported burrow fill	1.87	-5.09
L25	-	" " " "	2.13	-5.80
L26	-	" " " "	1.98	-5.75
L27	-	Overlying oosparite	1.94	-5.21
L28	-	Late spar	1.83	-8.28

Table 2(b) - Leadenham Hardground

L17	0	Hardground surface	0.32	-3.55
L16	0	Ferruginous burrow wall	0.33	-3.41
L7	0.5	'Whole-rock' oopelmicrite	0.29	-3.89
L8	0.5	" " "	0.19	-4.79
L18	1.0	" " "	0.42	-3.91
L9	3.5	" " "	0.45	-4.40
L10	7.0	" " "	0.49	-3.66
L6	-	Burrow fill-spar rich	-0.35	-5.81
L12	-	" " - fine-grained	0.59	-3.48
L13	-	" " " "	0.64	-3.41
L19	-	" " " "	0.41	-3.27
L11	-	Ferroan calcite - coral replacement	1.23	-7.82
L15	-	" " - inside serpulid tubes	1.33	-7.89
L14	-	" " " " "	0.89	-5.63

(1st cont?)

Samples from below the surface have progressively lighter $\delta^{18}\text{O}$ at Cowthick and Castle Bytham but at Leadenham there is no clear trend. Reversals in the pattern (Fig. 8) are due to lithological variation in the substrate limestone; shelly horizons generally have a higher proportion of late, ^{16}O enriched, blocky cements which fill the solution voids of formerly aragonitic skeletal material.

The combined $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ diagram (Fig. 9) shows that all samples lie within the 'marine limestones' field. Late spar taken from open mollusc borings, serpulid colonies and replacing coral debris have $\delta^{18}\text{O}$ from -7 to -9.5. There is an almost linear distribution of samples from each locality; the different values represent mixing of end-member components (allochems and early cement, and late cement, Fig. 9) in their modal proportions. Point counts from the Cowthick hardground show that the percentage of late cement increases as the volume of early cements decreases away from the surface (Fig. 10).

The more positive $\delta^{18}\text{O}$ values obtained from the micritic sediment filling mollusc bores and crustacean burrows indicates early stabilisation of the micrite and a low percentage of late cement in such calcilutite samples.

Thick-shelled oysters encrusting the Castle Bytham hardground have oxygen isotopic compositions of -2.76 and -3.12‰. Such restricted data are not sufficient for true palaeotemperature determination but may be used for a "working estimate". Shackleton and Kennett (1975) have produced a modified version of the palaeotemperature equation (Epstein et al., 1953):-

$$T^{\circ}\text{C} = 16.9 - 4.38 (\delta\text{c} - \delta\text{w}) + 0.10 (\delta\text{c} - \delta\text{w})^2$$

(δ_c being the isotopic composition of CO_2 produced from the carbonate at 25°C and δ_w the isotopic composition of CO_2 in equilibrium with formation water).

A value of $\delta_w = -1.2$ for the sea water composition prior to the establishment of polar ice caps (Shackleton & Kennett, 1975) gives palaeotemperatures of 24.0°C and 25.7°C for the Castle Bytham oysters. The possibility of sample contamination by late, ^{16}O enriched cement must be taken into consideration, (10% late spar contamination will give a temperature of 23.0°C) but a palaeotemperature of $22-25^\circ\text{C}$ is clearly indicated. This is consistent with some other estimates of palaeotemperatures for the British Jurassic (Tan et al., 1971; Irwin et al., 1977).

Assuming vital effects to be negligible (Mook & Vogel, 1968), the isotopic results from the oysters give an indication of $\delta^{18}\text{O}$ for calcite precipitated in equilibrium with Middle Jurassic sea water: whole-rock samples from Cowthick are enriched in ^{18}O relative to this value (Fig. 9; see discussion of Cowthick cements below).

ENVIRONMENT OF EARLY LITHIFICATION

Syn depositional cements have heavier $\delta^{18}\text{O}$ than later precipitates; in modern sediments at the present latitude of the hardgrounds this would almost certainly imply early submarine lithification. To ascertain the environment of hardground cementation it is necessary to consider the likely composition of alternative pore waters.

Freshwater cements in Recent limestones are depleted in ^{18}O and ^{13}C in comparison to marine carbonates; would similar depletion characterise the cements of the Jurassic hardgrounds if they had been emergent?

The $\delta^{18}\text{O}$ of modern rainwater is latitude dependent (Dansgaard, 1964). Assuming a palaeolatitude for Bajocian Britain of around 35°N (Smith & Briden, 1977) and climatic zones similar to those prevailing today, Jurassic rainfall would have had $\delta^{18}\text{O}$ of about -7 in comparison to oceanic water. However, global conditions in the Mesozoic were probably very different from today (Hallam, 1975) and rainwater $\delta^{18}\text{O}$ cannot be assumed. Evidence from British Jurassic and Lower Cretaceous freshwater limestones is not conclusive (Allen & Keith, 1965, Allen *et al.*, 1973, Tan & Hudson, 1974) but in general well-preserved freshwater fossils are a few per-mil lighter than their marine equivalents (e.g. Tan & Hudson, 1974, Fig.1) so fresh water $\delta^{18}\text{O}$ was probably significantly lighter than seawater. If the Lincolnshire Limestone hardground cements had been precipitated from such water, samples from the hardground surfaces would almost certainly be depleted by more than 1‰ from sea-water equilibrium (Leadenham and Castle Bytham) and could not attain the 2‰ $\delta^{18}\text{O}$ enrichment which is observed at Cowthick. Under conditions of local emergence and with considerable evaporative loss of ^{16}O , it would be possible to produce a small reservoir of fresh water with heavy, virtually marine isotopic composition, but there is no petrographic or faunal evidence to suggest that such extreme conditions occurred.

By similar arguments the absence of negative $\delta^{13}\text{C}$ does not necessarily rule out exposure to fresh water. Enrichment in ^{12}C in non-marine limestones is due to the contribution of light, plant derived, soil CO_2 . During temporary emergence plant life would not become established and any subaerial precipitates would not have negative $\delta^{13}\text{C}$.

Early aragonite dissolution at Castle Bytham may suggest emergence but the isopachous cements there and at Cowthick indicate early precipitation in fluid-filled pores. Without substantial faunal or petrographic evidence for extreme conditions like those suggested above, the isotopic data from all three hardgrounds most readily demonstrate submarine lithification.

COWTHICK HARDGROUNDS : CEMENTS

Hardgrounds in the channels at Cowthick provided a rocky substrate which was repeatedly bored by bivalve molluscs.

Similarities in cement fabric, trace element and isotopic composition of the two hardgrounds, suggests that they formed in similar environments and that the rafted block subsequently underwent transportation. Detailed petrographic and geochemical analysis suggests that the early cements are analogous to Recent submarine cements:

FABRIC

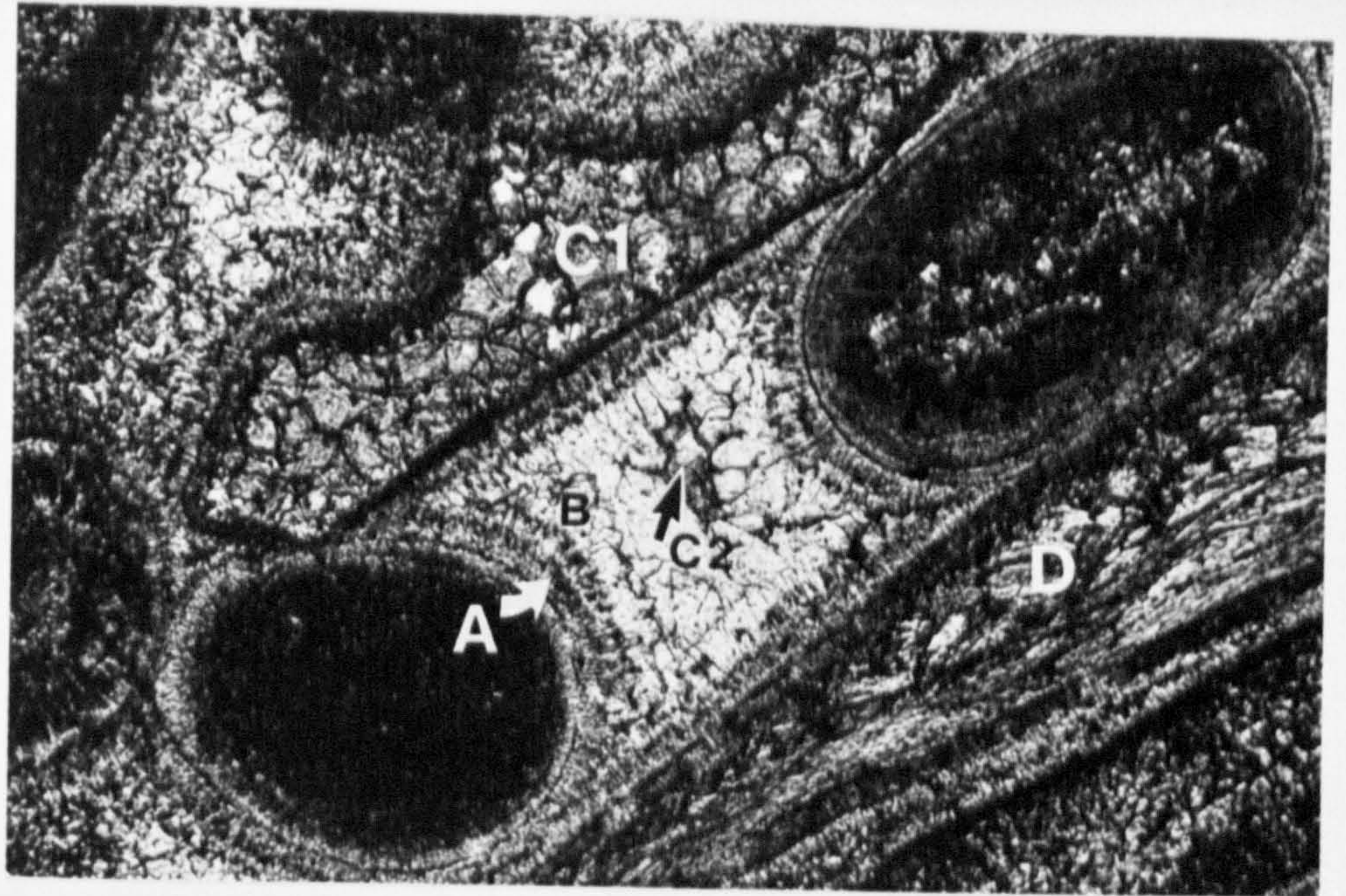
The fringing cements are composite. An initial, apparently 'acicular' division, characterised by close-packed radial linear inclusions is succeeded in optical continuity by apparently 'bladed' calcite, which has fewer inclusions and common euhedral terminations (Fig. 12). The 'bladed' calcite and adjacent 'acicular' division may either extinguish as a single crystal or, more commonly, combine as a series of radial crystallites within a larger strained crystal unit. There is no apparent increase in crystal size away from the substrate and curved cleavage planes are rare. Both divisions are maintained as the overall thickness of the fringe decreases away from the hardground surface (Fig. 10).

Figure 11 Cowthick hardground. Photomicrograph of stained thin section approximately equivalent to stage C of Fig. 10. Early cement dominates the inter-granular pore space. Acicular (A) and bladed (B) divisions can be recognised. Late cement 'replaces' an aragonitic shell (C1) and fills the residual pore space (C2). A calcitic shell (D) has not suffered alteration. (Field of view = 3.2 mm.).

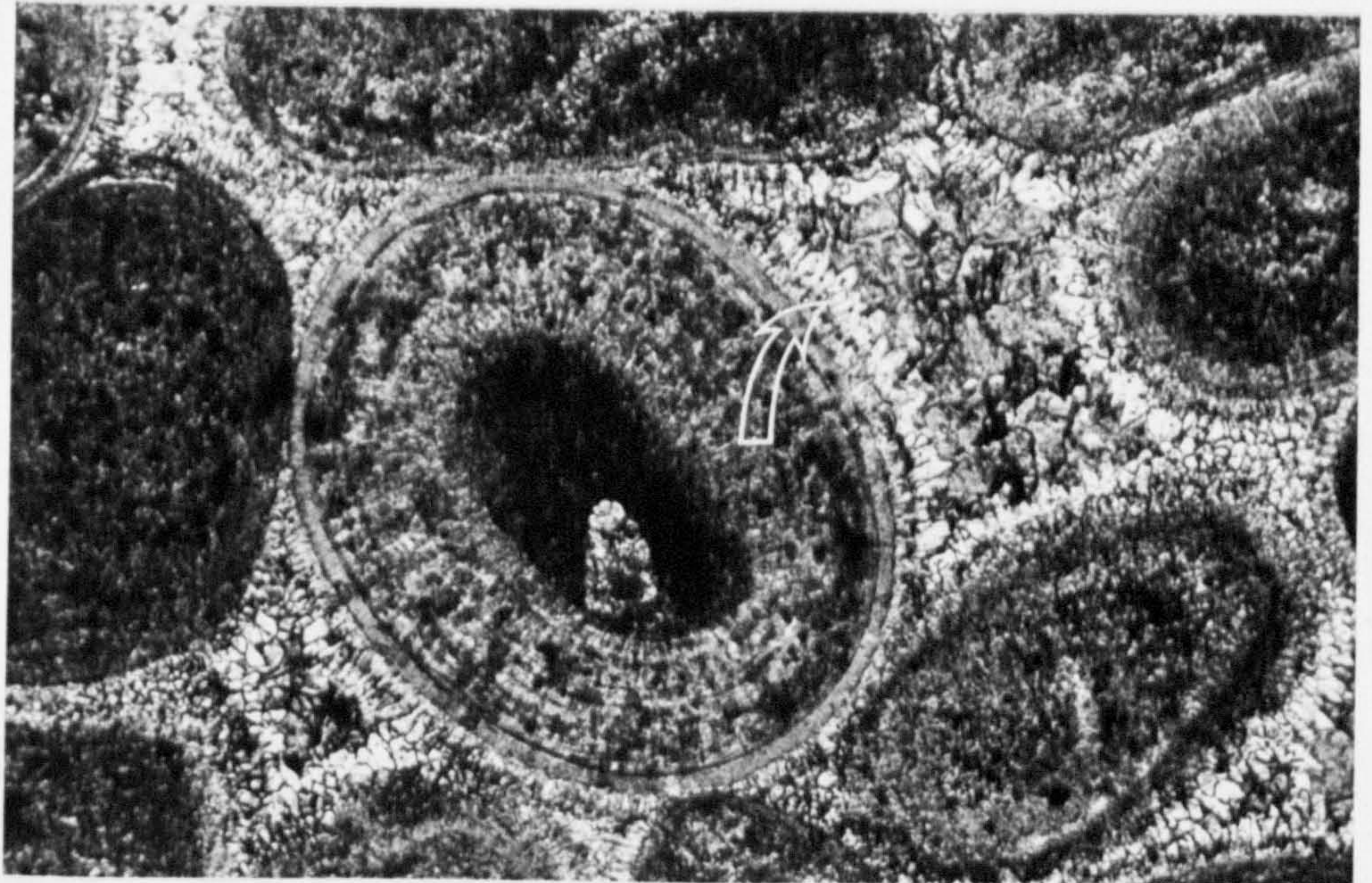
Figure 12 Cowthick hardground. Photomicrograph of stained thin section approximately equivalent to Stage D of Fig. 10. Early cements (arrowed) form an isopachous pore lining. The acicular division is surrounded by bladed calcite commonly with euhedral terminations. Late ferroan spar fills the centre of the void. (Field of view = 3.2. mm.).

Figure 13 Cowthick hardground. Photomicrograph of stained thin section approximately equivalent to Stage A of Fig. 10. Pore space is filled with early cement. The acicular division (A) has two diffuse ferroan zones; the bladed non-ferroan calcite part of the fringe (B) fills the residual void. (Field of view = 1.6 mm.).

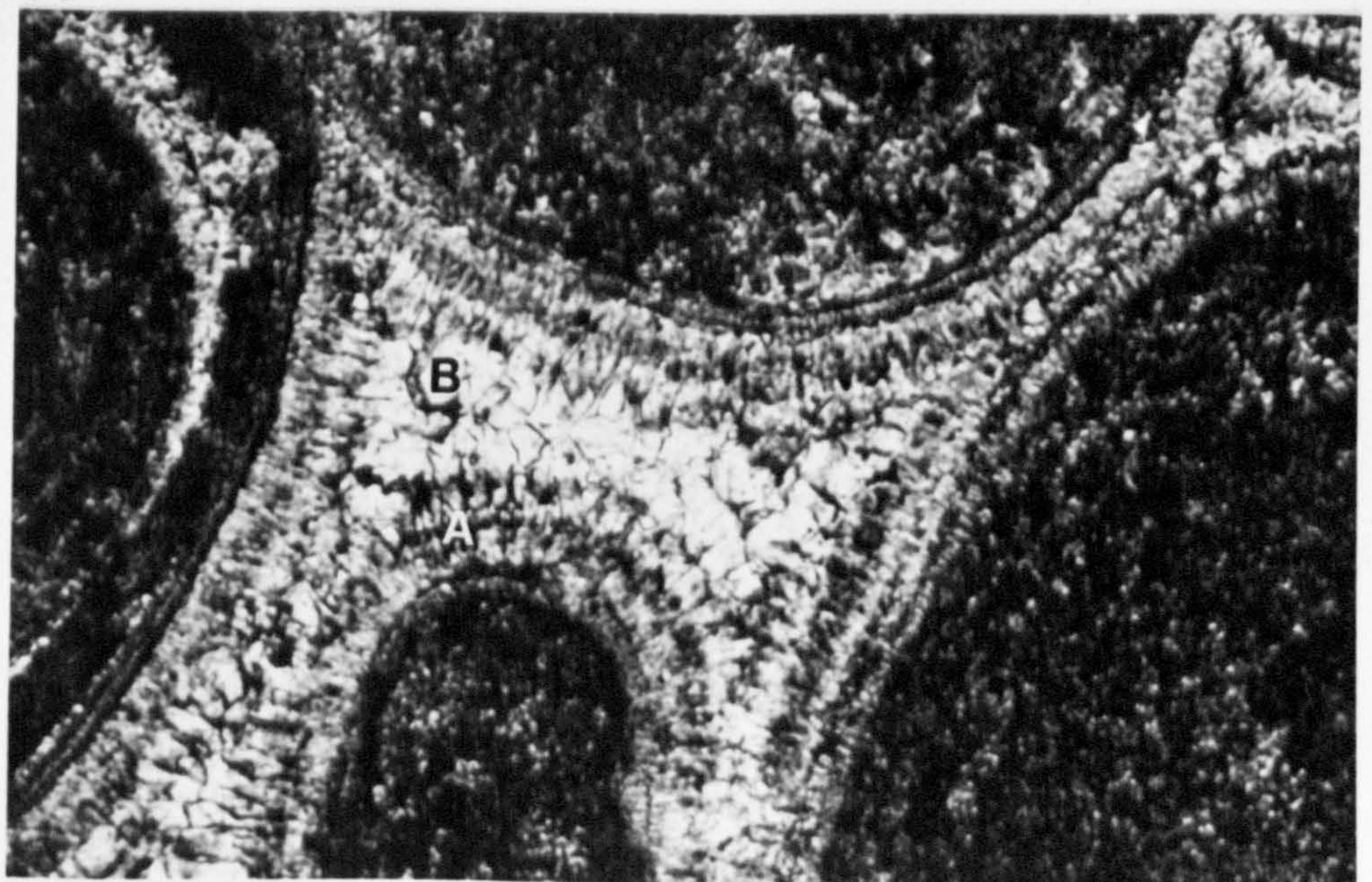
11



12



13



The fabric is not identical to true radiaxial-fibrous calcite (Bathurst, 1959; Kendall & Tucker, 1973) or fascicular-optic calcite (Kendall, 1977) but the distinct morphological similarity suggests that they share a common origin as the replacement of an acicular or bladed submarine cement. Kendall & Broughton (1978) argue that both radiaxial-fibrous and fascicular-optic fabrics may be explained by the primary coalescence of crystallites in the vadose environment without resort to a precursor cement. Vadose precipitation is most unlikely for the Cowthick hardground cements; the fringes form an isopachous pore lining, indicating phreatic conditions, and there is no evidence for syngedimentary emergence.

MINERALOGY AND TRACE ELEMENTS

Cements and allochems are all low-magnesium calcite, there are no traces of dolomite, aragonite or high-magnesium calcite that could be detected by X-ray diffraction analysis or electron microprobe scans.

Staining (Dickson, 1965) reveals variation in iron content within carbonate cements (Figs. 11, 12, 13). Late, blocky spar is uniformly ferroan but the early, fringing cements are zoned. The 'acicular' division is generally slightly iron enriched (mauve stain) and has diffuse ferroan zones which parallel the substrate; the 'bladed' calcite is invariably non-ferroan.

Electron microprobe point analyses (Table 3) demonstrate the main features of the trace element content. The fringing cements are enriched in magnesium (≈ 2.0 wt.% MgCO_3) in comparison to the allochems and late cement (≈ 0.5 wt.% MgCO_3), which is, predictably, ferroan (≈ 1.7 wt.% FeCO_3). Strontium values are uniformly low in all cases (< 400 ppm SrCO_3).

Table 3

Electron microprobe 'point' analyses from the Cowthick hardground.

Sensitivities (wt. % carbonate) Ca: 0.25, Mg: 0.06, Fe: 0.04, Sr: 0.02.

Minimum detection limit (wt. % carbonate) Ca: 0.01, Mg: 0.02, Fe: 0.02, .

Sr: 0.01.

Description	Wt.% Carbonate				Total Carbonates
	CaCO ₃	MgCO ₃	FeCO ₃	SrCO ₃	
Early fringing cement	97.83	2.22	1.08	0.05	101.18
Early fringing cement	98.59	2.46	0.68	0.03	101.76
Early fringing cement	97.71	1.84	0.27	0.03	99.85
Early fringing cement	95.96	1.49	0.54	0.05	98.04
Early fringing cement	<u>95.71</u>	<u>2.05</u>	<u>0.27</u>	<u>0.03</u>	<u>98.06</u>
MEAN	<u><u>97.15</u></u>	<u><u>2.01</u></u>	<u><u>0.57</u></u>	<u><u>0.04</u></u>	<u><u>99.78</u></u>
Mol.% Carbonate	97.12	2.39	0.49	0.03	
Oolith	<u><u>95.34</u></u>	<u><u>1.49</u></u>	<u><u>0.40</u></u>	<u><u>0.03</u></u>	<u><u>97.26</u></u>
Mol.% Carbonate	97.80	1.82	0.35	0.02	
Late spar-void	94.76	0.62	1.78	0.03	97.17
Late spar-void	<u>95.19</u>	<u>0.59</u>	<u>1.99</u>	<u>0.05</u>	<u>97.75</u>
MEAN	<u><u>94.94</u></u>	<u><u>0.61</u></u>	<u><u>1.89</u></u>	<u><u>0.04</u></u>	<u><u>97.46</u></u>
Mol.% Carbonate	97.56	0.74	1.68	0.03	
Late spar-shell replacement	97.78	0.66	1.37	0.05	99.91
Late spar-shell replacement	98.55	0.28	1.64	0.02	100.47
Late spar-shell replacement	<u>98.68</u>	<u>0.45</u>	<u>1.66</u>	<u>0.05</u>	<u>100.79</u>
MEAN	<u><u>98.34</u></u>	<u><u>0.46</u></u>	<u><u>1.56</u></u>	<u><u>0.40</u></u>	<u><u>100.39</u></u>
Mol.% Carbonate	98.09	0.55	1.34	0.03	

Detailed variation is monitored by microprobe scans across allochems and the two cement generations (Fig. 14). Iron distribution confirms the stain evidence and is inversely related to the magnesium distribution in the early cements. At about 12 cm from the hardground surface the isopachous fringe contains two iron-rich zones, corresponding to the base and top of the acicular division. (Fig. 15). Similar scans for calcium and strontium show no significant variation.

INTERPRETATION

The characteristics of the early cements of the Cowthick hardgrounds can be summarised:-

1. Cements ~~from~~^{form} an isopachous pore-lining which is truncated by molluscan bores, indicating synsedimentary precipitation in submarine phreatic conditions.
2. They have a two stage fabric with a similar morphology to calcites which are believed to be a replacement of acicular or bladed submarine cements.
3. Magnesium concentration is much greater than in adjacent allochems or later cements. Strontium content is low in common with the other phases.
4. Ferroan zones occur within the acicular subdivision.
5. Whole-rock isotopic values indicate that early cements have $\delta^{18}\text{O}$ which is heavier than local surface sea water equilibrium.

Fabric and trace elements

The cement morphology and relic fabric indicate an initial submarine cement. Magnesium enrichment relative to allochems and later cements may suggest a high-magnesium calcite precursor

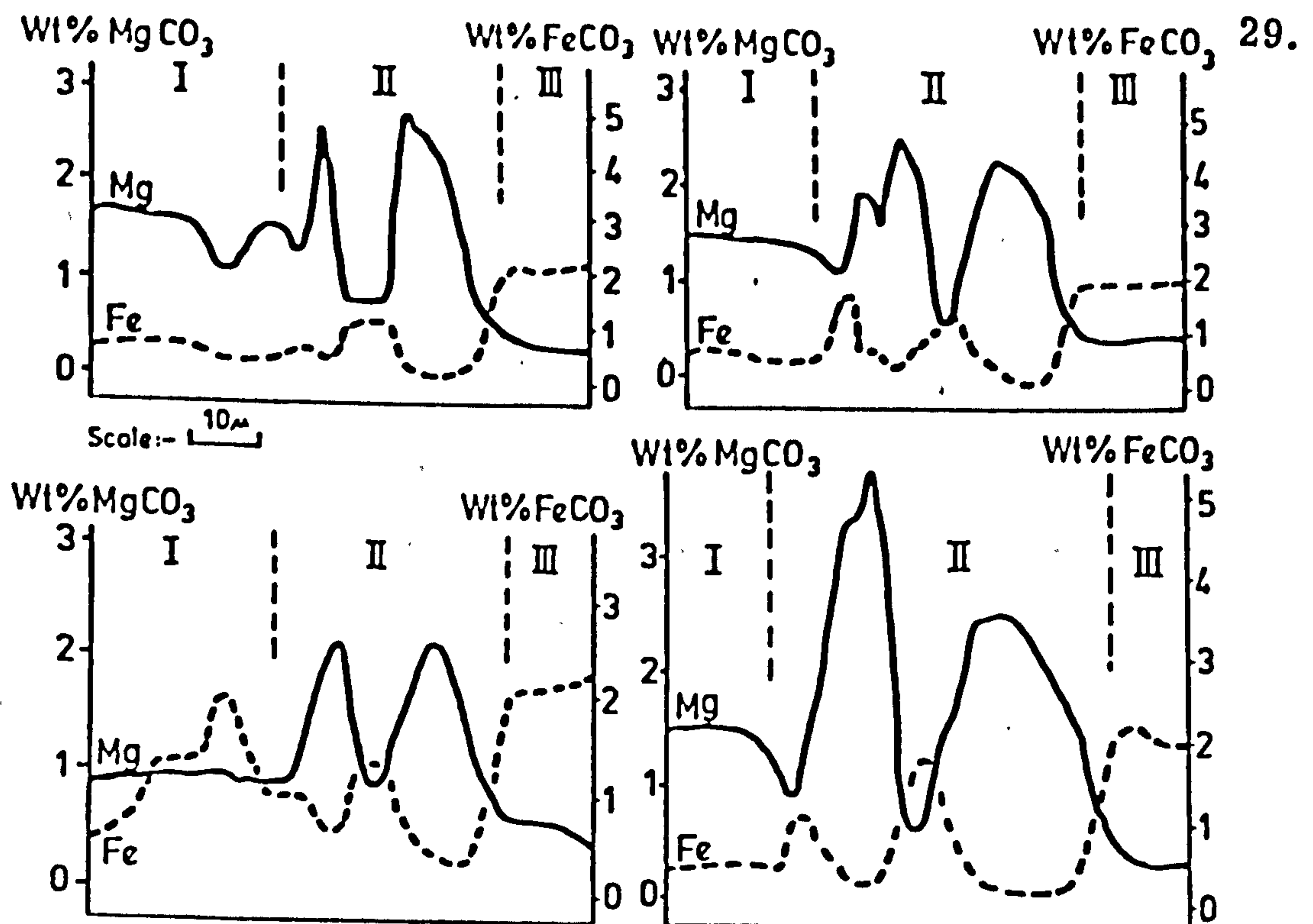


Figure 14 Cowthick hardground. Examples of simultaneous microprobe scans for iron and magnesium (calibrations determined independently). In each case I = allochems; II = early isopachous cement; III = late blocky cement. The early cement is always found to be enriched in magnesium.

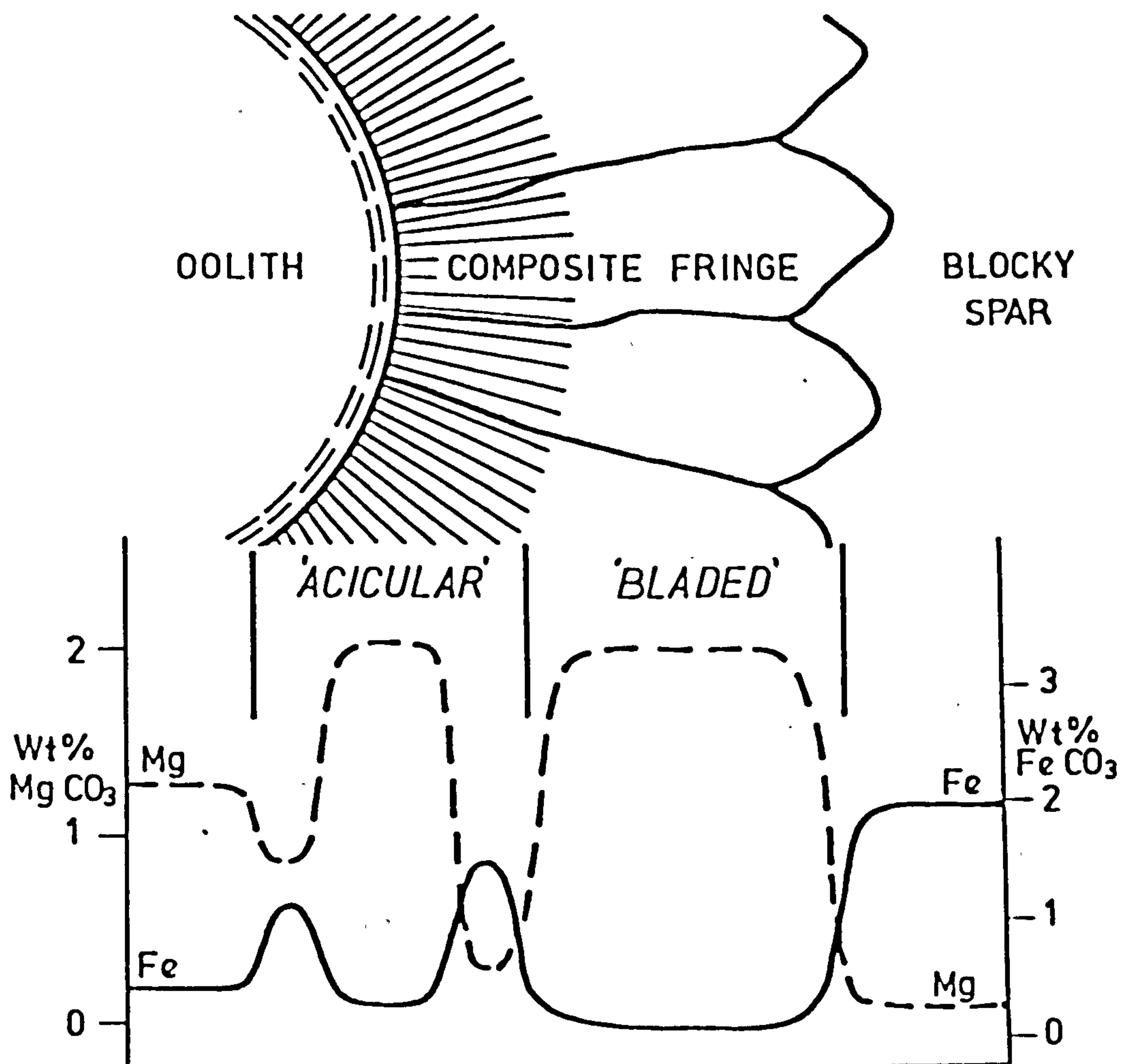


Figure 15 Schematic representation of the microprobe results from the Cowthick hardground. The narrow ferroan zones occur within the acicular cement.

(Davies, 1977) and the concentration values are near the calculated solution minimum for that mineral (Schlager & James, 1978). There are no microscopic dolomite inclusions in these cements (cf. MacQueen & Ghent, 1970; Davies, 1977; Lohmann & Meyers, 1977) so the neomorphic environment, in which recrystallisation and mineralogical stabilisation took place, cannot have been 'closed' with respect to magnesium (cf. Lohmann, 1978). Low strontium content makes an aragonitic precursor unlikely, although this is not strictly diagnostic (Davies, 1977). Recent submarine cements exhibit successive growth stages with textures which are strikingly similar to the Cowthick hardground cements (e.g. Shinn, 1969; Bricker, 1971; Schroeder, 1973; James et al., 1976). By analogy the bladed subdivision at Cowthick represents an epitaxial overgrowth of bladed high-magnesium calcite cement seeded on a more fibrous initial cement.

The diffuse ferroan zones within the 'acicular' division (Figs. 11 & 13) are more problematic. They are unlikely to be a primary feature for although temporary burial of the hardground surface may give sufficient Eh reduction for Fe^{II} formation, bacterial sulphate reduction would, almost certainly, result in the formation of pyrite rather than a ferrous carbonate (Curtis & Spears, 1968; Raiswell, 1976; Richter & Fuchtbauer, 1978).

Chemical and mineralogical variation is common within Recent submarine cements. Primary aragonitic microcrystalline rinds (cf. Shinn, 1969, Fig. 19) would suffer the same fate as aragonite shell material; dissolution and replacement by ferroan calcite in later diagenesis. A separate dissolution event would, however, probably leave textural relics for which there is no evidence in the Cowthick cements; the ferroan zones are only apparent

after staining.

The stability of high-magnesium calcite is inversely related to its magnesium content (Richter & Fuchtbauer, 1978). Zones within the initial acicular cement with excess magnesium content, perhaps caused by temperature fluctuations (Fuchtbauer & Hardie, 1976), would be particularly susceptible to replacement by ferroan calcite cement. It is tentatively suggested that this is a likely cause of the ferroan zones within the fringing cements.

Isotopes

Heavy $\delta^{18}\text{O}$ values have been recorded from Recent and Chalk hardgrounds where, as here, they provide evidence of submarine diagenesis (Scholle & Kennedy, 1974; Scholle, 1977; Schlager & James, 1978). Additional enrichment above surface sea water equilibrium composition has been attributed to equilibration with cold water on the ~~deep~~^{deep} sea floor or under shallow burial (Irwin et al., 1977; Schlager & James, 1978) and to precipitation from sea water of unusual isotopic composition (Hudson & Coleman, 1978). These mechanisms are unlikely in the setting of the shallow submarine channels at Cowthick. The observed $\delta^{18}\text{O}$ values at the hardground surface would imply a temperature of 12°C which is at least 10°C below that calculated for the oysters at Castle Bytham. A temperature difference of this magnitude is unlikely to have arisen during cement precipitation while the pores were in contact with circulating channel waters. $\delta^{18}\text{O}$ enrichment of the channel waters above normal seawater composition is conceivable if the water was derived from an evaporative back-barrier lagoon (e.g. Lloyd, 1964) but there is no evidence for such an enrichment in the lagoonal sediments at Leadenham. The Cowthick channels were probably tidal and the water in constant

exchange with the open sea.

At Cowthick samples of unconsolidated geopetal sediment with no discernable cements have an almost identical isotopic composition to those taken from the fully-lithified hardground surface (Table 1, Figs. 8 & 9). The early cements and allochems must both have a non-equilibrium isotopic composition ($\delta^{18}\text{O} = 0$, $\delta^{13}\text{C} = +3$). Similar enrichment in Recent ooids has been attributed to the influence of algae in precipitation (Milliman & Muller, 1977). A slight $\delta^{18}\text{O}$ enrichment is inherent in the precipitation of magnesium-rich calcite (Tarutani *et al.*, 1969), but Recent submarine cements often have heavier values than those predicted by the experimental data (Shinn, 1969; Land & Goreau, 1970).

The Cowthick hardground samples have apparently retained their initial isotopic composition but trace element data indicates substantial loss of magnesium. Alternative interpretations of this apparently conflicting evidence can be suggested.

1. Open-system replacement. The substantial loss of magnesium during mineralogical stabilisation must have involved a fluid phase (Bathurst, 1975, p.50). The retention of essentially marine isotopic composition suggests that transformation took place while the pores were still filled with sea water (Hudson, 1978): anomalously high $\delta^{18}\text{O}$ values may reflect re-equilibration with shallow burial marine pore waters which were colder than ambient surface waters (e.g. Irwin *et al.*, 1977).

2. Closed-system replacement. Initial stabilisation again took place in sea water filled pores. The low rate of pore-water flow enabled the allochems to inherit their original isotopic composition while losing the majority of the original magnesium content.

CEMENTATION AND DEPOSITIONAL ENVIRONMENT

The hardgrounds have suffered different intensity of early cementation, confirmed by petrographic and isotopic evidence. It is suggested that the variation can be related to differences in depositional environment.

In Recent sediments intensive early cementation accompanies the most turbulent conditions (e.g. Alexandersson, 1972; Macintyre, 1977), since a continued supply of pore water supersaturated with calcium carbonate is always necessary for cement precipitation (Bathurst, 1974). High magnesium calcite and aragonite intergranular cements are found where there is already a degree of sediment coherence (Bathurst, 1974; James et al., 1976). In quieter regimes hardened layers are associated with non-deposition; the early cementation takes place beneath a shallow cover of unconsolidated sediment (Shinn, 1969). Mineralised crusts, geopetal internal sediment and micritic cements indicate prolonged non-deposition in the least turbulent conditions (Shinn, 1969).

The hardgrounds from the Lincolnshire Limestone mirror the Recent almost exactly.

At Cowthick the hardgrounds formed during the re-excavation of submarine channels, mollusc borings are found on vertical and overhanging surfaces and on large blocks of early lithified limestone which form part of the channel fill; evidence that suggests prolonged exposure in a highly turbulent environment. Early fringing cements fill the entire intergranular pore space producing an almost fully cemented rock at the exposed surface. Although decreasing progressively in volume away from this surface, such cements penetrate at least 20 cm of substrate sediment. Lithification and repeated colonisation by boring

and encrusting molluscs proceeded together.

The Castle Bytham hardground was exposed to only periodic turbulence as it probably formed in a semi-protected environment. Hardground formation coincided with non-deposition on the barrier complex. Early aragonite dissolution points to temporary subaerial exposure but this was followed by submergence and submarine cementation. Thick-shelled oyster colonies testify to the hardening of the surface and periodic turbulence. Restriction of early cementation to the immediately subjacent sediment ($\approx 3 - 5$ cm) gives an indication of the shallow penetration of bottom currents.

The Leadenham hardground probably developed during reduced sedimentation in a lagoon. More agitated conditions gave way to quiet water deposition and the sediments were subjected to intense biological reworking. Early lithification is superficial; oxide crusts (Krumbein, 1942) and micritic internal sediments introduced by the burrowing fauna enable hardground surface colonisation by thin-shelled oysters and serpulid encrustation of the open crustacean burrows (Fig. 4, cf. Palmer & Fursich, 1974). No crystalline syndepositional cements have been recognised.

SUMMARY AND CONCLUSIONS

1. The three Lincolnshire Limestone hardgrounds (Cowthick, Castle Bytham and Leadenham) have all undergone synsedimentary submarine lithification.
2. At Cowthick the early isopachous cements are composite, with proximal acicular and distal bladed divisions; they penetrate at least 20 cm. of substrate oolites. At Castle Bytham early granular isopachous cements are restricted to within 5 cm of the oyster encrusted surface. At Leadenham

early lithification is superficial and represented by ferruginous crusts and micritic internal sediment.

3. Whole-rock samples from the hardground surfaces have more positive $\delta^{18}\text{O}$ than those from the immediately underlying limestone. Early cements must have a 'marine' isotopic composition; those from Cowthick are enriched in ^{18}O when compared to oysters that are presumed to have been precipitated in equilibrium with seawater.
4. Serial whole-rock carbon and oxygen isotopic values demonstrate increasing percentage of late ^{18}O depleted cement away from the hardened surface.
5. The trace element and isotopic composition of early cements at Cowthick are interpreted as evidence for a high-magnesium calcite precursor cement which underwent replacement in a restricted chemical environment (low effective water:rock ratio).
6. The intensity of early cementation is related to the depositional environment of the hardgrounds. The most intense syndepositional cementation occurred in the tidal-inlet deposits at Cowthick where the hardgrounds were exposed to considerable volumes of circulating pore-water; the least well-developed early cementation occurred in the lagoonal sediments at Leadenham, where the degree of pore-water circulation was probably small even though the hardground may have been exposed for a considerable period.

After the original submission of this paper Dravis (1979) published environmental and petrographic data on oolitic hardgrounds from the Bahamas which provide further Recent analogues for our Jurassic examples.

CHAPTER 2

STABLE ISOTOPE EVIDENCE FOR THE ENVIRONMENT OF LITHIFICATION
OF SOME TETHYAN LIMESTONES

ABSTRACT

Carbon and oxygen isotopic analysis of some Tethyan limestones (Lower Jurassic to Cretaceous) from Sicily and Northern Italy show that the different lithologies have been cemented at different stages of burial. Pelagic chalks and limestone nodules have a narrow range of $\delta^{13}\text{C}$ (0.5 to 2.75) and $\delta^{18}\text{O}$ (-0.9 to 0.38); values which imply that all the cementation took place at, or immediately below, the sea-floor. It is suggested that the heavy oxygen values were inherited from former high-magnesium calcite cements and do not, as previously suggested, necessarily indicate abnormal sea-water composition. The shelf limestones and their component cements have similar $\delta^{13}\text{C}$ values but exhibit a wider range of $\delta^{18}\text{O}$ (-2.5 to -6.5); the high initial pore space has been reduced by the later precipitation of cements whose composition reflects temperature increase and modification of pore-water composition during burial. Similar late diagenetic processes have affected the composition of marly sediments and sparry calcite veins in the pelagic limestones.

INTRODUCTION

Differences in the isotopic composition of pelagic sediments have been variously attributed to changes in depositional or diagenetic environment. Analyses of unaltered and uncemented samples of a particular genus or class of fossil will yield useful information about changes in palaeotemperatures, (e.g. Shackleton, 1974; Shackleton and Kennett, 1975) but bulk sediment sampling is more likely to contribute to knowledge of the diagenetic environment (e.g. Hudson and Coleman, 1978; McKenzie et al., 1978) rather than produce a strict palaeoclimatic determination.

In this paper bulk samples of different lithologies demonstrate some of the ways in which isotopic analysis can aid sedimentological and diagenetic interpretation. Mesozoic sediments from Sicily and Northern Italy have a range of lithologies which are directly analogous to Recent shelf and pelagic sediments. The contrasting isotopic content reveals the importance of diagenetic and lithological control on chemical composition.

SICILIAN SUCCESSION AND TECTONIC SETTING

The Mesozoic succession in western Sicily (Wendt, 1964) has been interpreted in terms of deposition on and between fault-controlled seamounts within the Tethyan ocean (Fig. 2.1, after Jenkyns and Torrens, 1971). Samples for isotopic analysis have been taken from each of the main lithological units:

Triassic and Liassic shallow water sedimentation (e.g. Dolomia Principale, Fig. 2.1, Table 2.1) gave way to progressively

GROUP	LITHOLOGY	AGE	ENERGY REGIME	INFERRED DEPTH	SUBMARINE TOPOGRAPHY
Lattimusa etc.	Pelagic Chalks	Cretaceous	Low	Shallow Bathyal (~ 200m?)	Uniform Basin
Ammonitico Rosso	Red nodular marly Limestones	Upper Jurassic	↑ Decreasing ↑	↑ Deepening ↑	↑ Transitional Relief ↑
Condensed Beds	Red & Yellow Micrites	Middle Jurassic	High	Some Subtidal Influence (< 150 m)	Isolated Sea Mounts
Crinoidal Calcarenites	Red Biosparites	Upper Lias	High	Shallow Subtidal	Embryo Sea Mounts
Dolomia Principale	Shelf Pelsparites	Lower Lias and Trias	High (Variable)	Supratidal to shallow Subtidal	Subsiding Platform

Figure 2.1 Stratigraphy and environmental interpretation of the Western Sicillian lithological groups (after Jenkyns and Torrens, 1971).

more pelagic conditions with the onset of tectonic activity in the lower Jurassic. Disintegration of the carbonate shelf, with the isolation of differentially subsiding fault-controlled blocks gave rise to a series of locally variable condensed deposits (e.g. Crinoidal calcarenites, Condensed beds, Fig. 2.1). In the Upper Jurassic and Cretaceous there was a general decrease in tectonism; continued sedimentation reduced the submarine topography and quiet water pelagic sediments accumulated over the entire area (Ammonitico Rosso, Lattimusa, Fig. 2.1).

LITHOLOGIES

The platform deposits are typical Bahamian-type shallow-water carbonates. Fenestral fabrics testify to periodic emergence and solution (Jenkyns, 1970) and give a high initial porosity. They are commonly succeeded (Fig. 2.1) by crinoidal calcarenites which represent localised deposition on the current swept crests of isolated seamounts (Jenkyns, 1971). Crinoidal debris is cemented by blocky syntaxial overgrowth cements (Jenkyns, 1971, Fig. 4). The crinoidal biosparites are locally capped by 'karstic' solution surfaces (Jenkyns, 1971, Fig. 3) which are in turn encrusted by ferromanganese nodules. Isolation of individual seamounts had reached its maximum extent and sedimentation was reduced to locally variable extremely condensed micritic facies (Fig. 2.1). Deposition was restricted to fissures and neptunian dykes on the crests of the seamounts (Wendt, 1971, Jenkyns & Torrens, 1971). These micritic sediments are succeeded by red argillaceous limestones (Knollenkalk, Ammonitico Rosso) which progressively develop a nodular texture. Stratigraphically condensed red pelagic nodular limestones of late Jurassic age can be found on land throughout the Mediterranean

area and in cores in the central Atlantic. (Bernoulli, 1972; Bernoulli and Jenkyns, 1974). In this paper results from North Italian Ammonitico Rosso are presented for comparison with the Sicilian data and with published data from similar red nodular deposits of Liassic age from Austria (Hudson and Coleman, 1978).

In Sicily facies differentiation between pure calcareous deposits on palaeohighs and the more marly limestones accumulating between them, waned as the sea-floor topography decreased. Nodular limestones are succeeded by nannofossil chalks which have uniform lithology throughout the area.

ISOTOPIC ANALYSIS

Analysis was predominantly of bulk limestone samples extracted with a small dental drill. It was possible to analyse late cements from shell cavities and fissure-fills and to separate material from the Ammonitico Rosso nodules and internodule matrix. All samples were treated with dilute sodium hypochlorite solution, to remove possible contaminants. (Forester et al., 1973) Carbon dioxide for analysis was prepared by reaction of around 10 mg of calcite with 100% phosphoric acid at 25°C (McCrea, 1950).

Carbon and oxygen stable isotopic measurements were determined on a Micromass 602 C mass-spectrometer at the Institute of Geological Sciences, London. Standard correction procedures for mass and background effects were employed (Craig, 1957; Deines, 1970). Values are expressed in 'per-mil' difference in isotopic ratio from the PDB international standard (Tables 2.-1, 2). Analytical errors of less than 0.05‰ are associated ^{with} individual isotopic analyses but replicate whole-rock samples can differ by up to 0.5‰ suggesting real small-scale inhomogeneity in the limestones.

The isotopic composition of a calcite depends on the temperature of precipitation and the isotopic composition of the water from which it precipitated. Values from Recent marine sediments are reviewed by Milliman and Muller (1977) and those of cements by Hudson (1977).

Skeletal material and marine precipitates generally have a 'marine' isotopic composition; (low positive $\delta^{13}\text{C}$ and low positive or negative values for $\delta^{18}\text{O}$ - see Milliman and Muller, 1977); calcites precipitated during burial usually have negative $\delta^{18}\text{O}$ values which reflect temperature increase and/or pore-water modification during burial. Marine isotopic values can be preserved in ancient limestones without re-equilibration with burial pore-waters (Hudson and Coleman, 1978; Marshall and Ashton, in press)

ISOTOPIC RESULTS

All the limestones and their components have isotopic compositions which lie within the range of 'common marine limestones' (Hudson, 1977). The composition of each lithological type will be presented and the results will then be discussed with reference to proposed depositional and diagenetic environments.

SHELF LIMESTONES

The name 'Dolomia Principale' (Fig. 2.1) is somewhat misleading as dolomite is almost completely absent from the upper part of the succession; only calcite samples were chosen for analysis. Whole-rock and late cement samples produce an almost linear distribution on the isotopic scatter diagram (Fig. 2.2).

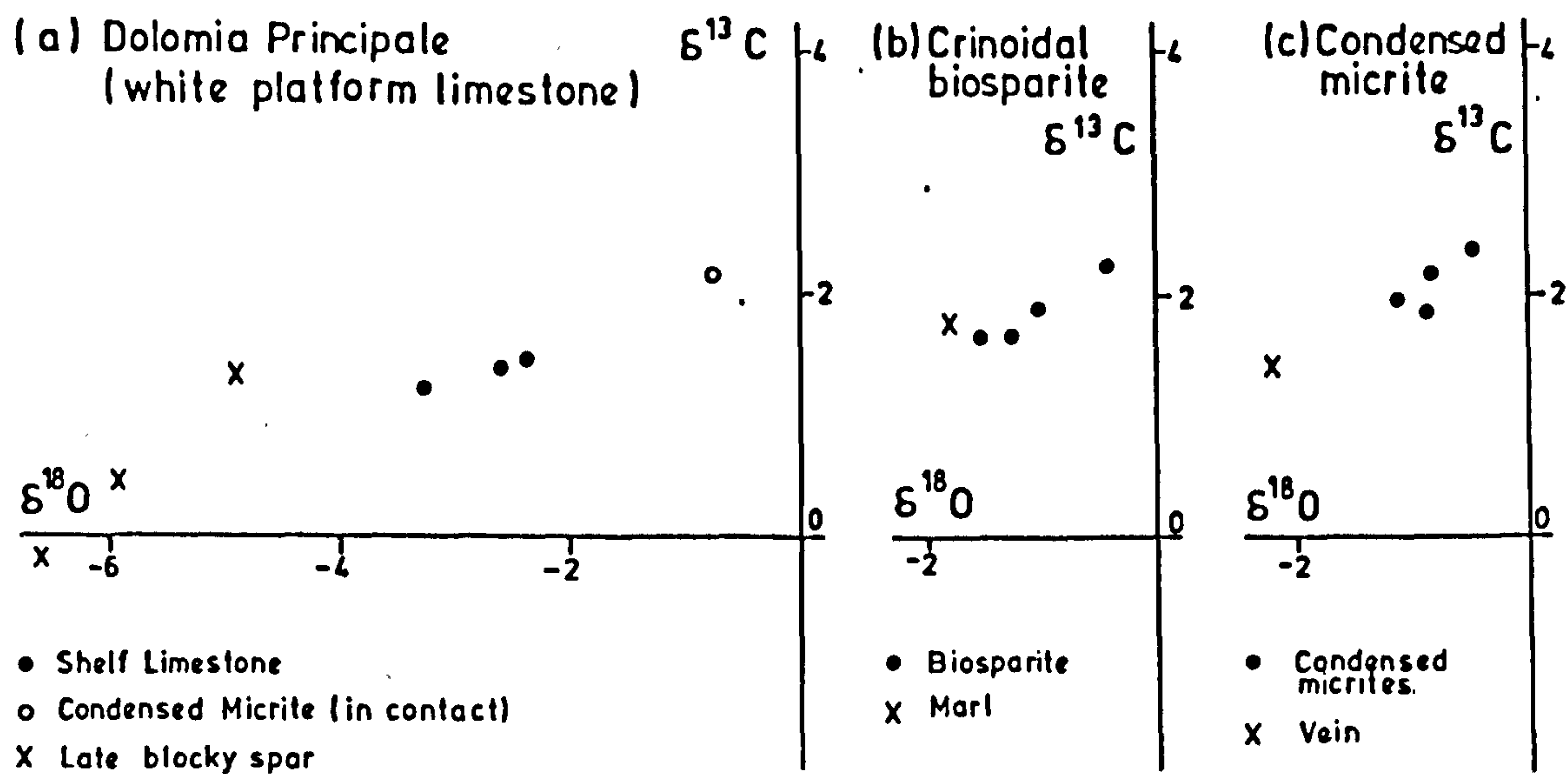


Figure 2.2 Carbon and oxygen isotopic composition of middle and lower Jurassic limestones from Western Sicily.

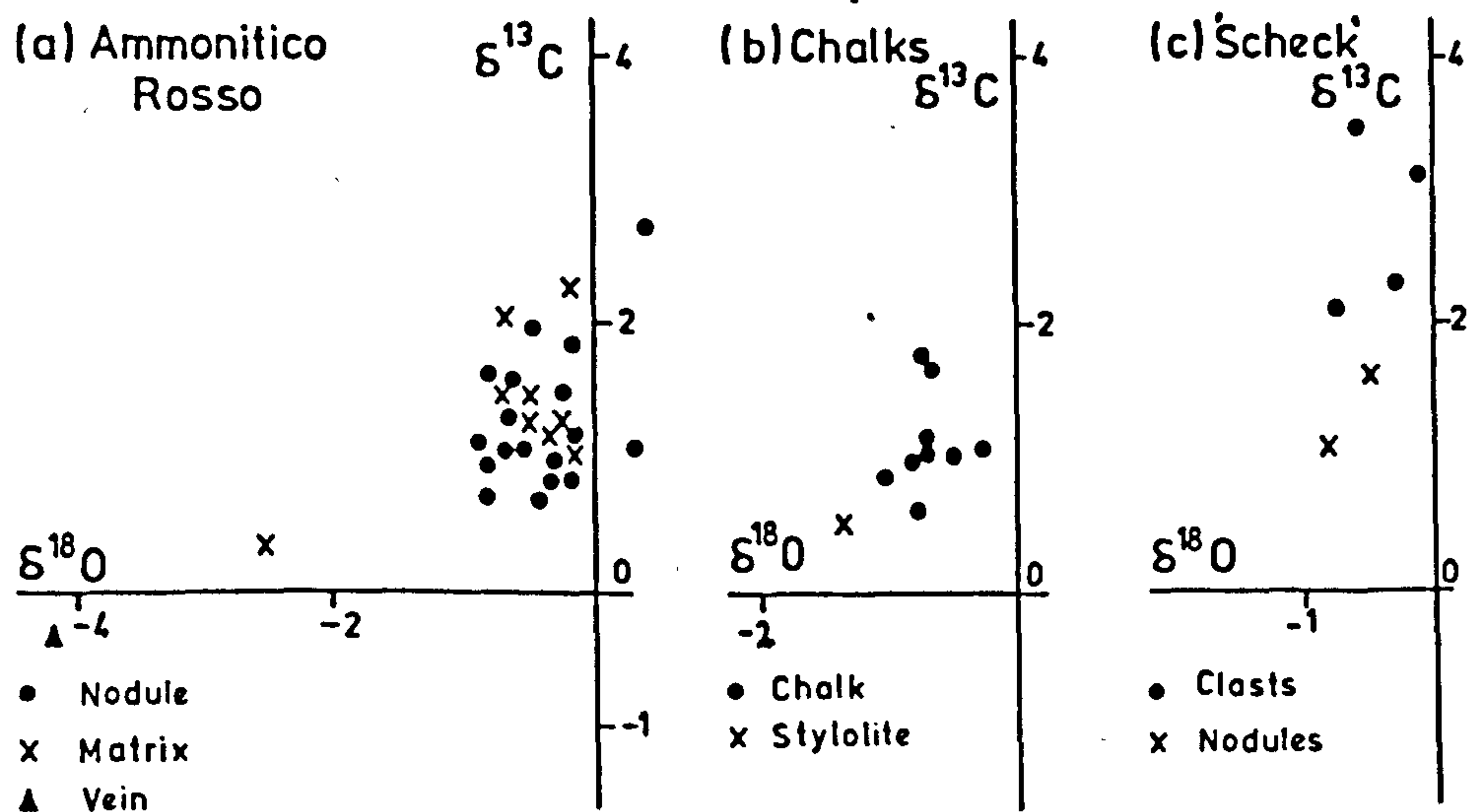


Figure 2.3 Carbon and oxygen isotopic composition of some Tethyan pelagic limestones ('Scheck' data from Hudson and Coleman, 1978).

TABLE 2.1 Isotopic composition of the shelf limestones and immediately overlying deposits.

(a) SHELF LIMESTONES

		$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$
<u>White Limestone (Dolomia Principale) Rocca Marafusa, Sicily</u>			
P.19	'Whole-Rock' pelsparite	1.39	-2.58
P.16	" " "	1.23	-3.26
P.17	Birds-eye calcites	0.44	-5.93
P.18	Late spar in shell cavity	1.34	-4.91
<u>Transition to condensed facies, Rocca Marafusa</u>			
P.49	Whole-rock shelf limestone	1.47	-2.37
P.50	Late spar	-0.20	-6.65
P.51	Condensed facies limestone	2.22	-0.81

(b) CRINOIDAL LIMESTONES

Crinoidal limestones, Monte Kumeta, Sicily - capped by 'karstic' surface with ferro-manganese crust. (with distance from karst surface)

P.20	Crinoidal biosparite (10 cm.)	2.27	-0.42
P.21	Marly Lens within crinoidal biosparites (4 cm.)	1.80	-1.81
P.22	Crinoidal biosparite (1 cm.)	1.69	-1.25
P.23	Crinoidal biosp. (0.5 cm.)	1.68	-1.53
P.24	" " "	1.91	-1.02

(c) CONDENSED MICRITES

Associated with ferromanganese deposits; Monte Kumeta, Sicily.

P. 25	Red and yellow micritic limestone	1.89	-0.85
P.27	Grey to pink micritic limestone	2.41	-0.43
P.28	Deep red micritic limestone	2.00	-1.09
P. 26	Secondary, milky calcite, vein	1.47	-2.20

Late cements have negative oxygen isotopic compositions which are typical of burial conditions (e.g. Lawrence, 1973; Hudson, 1978); combination of such cements in different proportions with allochems, precipitated in near equilibrium with sea water produces the observed linear distribution (Marshall and Ashton, in press). A limestone sample from a ^{hand specimen} surface area of obvious spar concentration has more negative $\delta^{18}\text{O}$ than that from an area dominated by pellets.

CRINOIDAL CALCARENITES

Bulk samples (Fig. 2.2(b)) have a narrow range of isotopic composition $\delta^{18}\text{O}$ -0.4 to -1.8, $\delta^{13}\text{C}$ +1.7 to +2.3) which is comparable to Recent marine sediments (Milliman and Muller, 1977). The blocky syntaxial cements, accounting for at least 30% of the limestone, (e.g. Jenkyns 1971, Fig. 4) must have similar isotopic composition to the original crinoidal debris. Virtually all cement precipitation took place while the pore-space was still filled with sea-water and at sea floor temperatures.

Karstification of the upper surface of the sampled specimen has not affected the substrate composition; corrosion may have been purely submarine or if subaerial it did not involve carbonate precipitation in the underlying limestone.

A marly lens (0.5 cm thick) within the calcarenite has a marginally lower $\delta^{18}\text{O}$ (Table 1) suggesting that some precipitation of 'lighter' carbonate took place in more porous horizons. The cement is likely to have been precipitated during burial rather than emergence.

CONDENSED BEDS

Micritic limestones are found in association with ferromanganese crusts. The extremely condensed deposits commonly represent

deposition within fissures on the crests of wave swept seamounts (Jenkyns and Torrens, 1971). They have a very narrow range of isotopic composition ($\delta^{18}\text{O}$ from -0.4 to -1.1, $\delta^{13}\text{C}$ from 1.9 to 2.4) which is within the range of values from marine precipitates. A secondary calcite vein has $\delta^{18}\text{O}$ of -2.2 ; precipitation most likely took place at slightly elevated temperatures but from water which was still essentially marine. Minor contamination of the micritic sediment with late calcite produces the observed isotopic distribution (Fig. 2.2).

AMMONITICO ROSSO (Nodular Limestones)

Examples of nodular limestones from Sicily and North Italy have very similar isotopic compositions (Table 2.2, Fig. 2.3(a)). The majority of samples have $\delta^{18}\text{O}$ between -1‰ and +0.4‰ and $\delta^{13}\text{C}$ between +0.6 and +2.8‰. The nodule sample which lies outside this range (P.2, Table 2) can be seen to be contaminated by joint-filling calcites which clearly are not related to the depositional or early diagenetic environments.

The oxygen isotopic compositions of the nodules are comparable with those obtained from similar facies in Austria (Hudson & Coleman, 1978; and Fig. 2.3). The values will be discussed in the light of recent models for the origin of nodular limestones (Jenkyns, 1974).

Marly sediment surrounding the nodules generally has a similar isotopic composition (Table 2.2, Fig. 2.3); a slight decrease in $\delta^{18}\text{O}$ in some of the samples can be attributed to post-burial cement precipitation but it is clear that nodule formation and most of the marl cementation took place in contact with sea water at depositional temperatures.

TABLE 2.2 Isotopic composition of the pelagic limestones

(a) AMMONITICO ROSSO (nodular limestones)

		$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$
<u>Montagna Granda, Sicily</u>			
P.10	Core of nodule - pink micrite	2.75	+0.38
P.11	Outer zone of nodule - pale green micrite	1.97	-0.50
P.12	Matrix between nodules - dark red marl	2.05	-0.69
P.34	Core of nodule	1.16	-0.19
P.35	Outer zone of nodule	0.95	-0.85
P.36	Matrix between nodules	1.23	-0.26
P.37	Matrix between nodules	1.27	-0.51
<u>Monte Bonifato, Sicily</u>			
P.38	Nodule core - pale pink micrite	1.30	-0.68
P.41	" " " " "	1.06	-0.61
P.39	Matrix between nodules	1.45	-0.50
P.40	" " "	1.46	-0.71
<u>Balata di Baida, Sicily</u>			
P.13	Core of nodule-pink micrite	1.51	-0.27
P.15.1	" " " "	1.63	-0.83
P.15.2	" " " "	1.54	-0.67
P.14	Outer zone of nodule-pale green nodule	1.85	-0.18
P.15	Matrix - dark red micrite	2.28	-0.21
<u>La Stua, Italian Dolomites</u>			
P.1	Core of nodule - pink micrite	0.84	-0.24
P.2	" " " "	-0.51	-2.70
P.021	" " " "		
	(duplicate of P.2)	0.70	-0.89
P.062	" " " "	0.83	-0.31
P.3	Outer zone of nodule - pink micrite	1.05	-0.71

TABLE 2.2 (cont.)

La Stua, Italian Dolomites

		$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$
P.4	Outer zone of nodule - pink micrite	1.02	-0.30
P.063	" " " "	0.72	-0.45
P.5	Matrix - deep red marl	1.15	-0.33
P.6	" " " "	1.05	-0.18
P.061	" " " "	-0.34	-4.20

Madonne della Corona, Lake Garda, Italy

P.7	Core of nodule - pink micrite	1.09	+0.29
P.8	Outer zone of nodule - pale green micrite	1.11	-0.92
P.9	Matrix - pink marl	0.36	-2.57

(b) PELAGIC CHALKS

P.29	Lattimusa. Balata di Baida, Sicily	0.65	-0.83
P.30	Scaglia Rosso. Montagna Granda, Sicily	1.05	-0.55
P.31	Pelagic Chalk. Monte Pispisa, Sicily	1.12	-0.73
P.42	Pelagic Chalk. Balata di Baida, Sicily	1.07	-0.31
P.43	" " " " "	0.90	-1.07
P.44	Pelagic Chalk Montagna Granda, Sicily	1.72	-0.71
P.45	" " " "	1.78	-0.74
P.48	Siliceous (cherty) grey limestone, Balata di Baida, Sicily	1.03	-0.82

Transitional facies Ammonitico Rosso/Pelagic Chalks

P.46	Pink micritic limestone, Montagna Granda, Sicily	1.14	-0.73
* P.47	" " " "	0.52	-1.41

* Sample from stylolitised surface.

PELAGIC CHALKS

Micritic nanno-fossil chalks have a narrow, marine, range of isotopic composition ($\delta^{18}\text{O}$ -1.1 to -0.3, $\delta^{13}\text{C}$ +0.5‰ to +1.8‰, Fig. 2.3, Table 2.2). The sample from a stylolite ~~vein~~ (Table 2.2) has the lightest $\delta^{18}\text{O}$ (-1.42) which is a reflection of increased temperature during ^{burial and} pressure solution and reprecipitation. Values all lie within the ranges determined for Recent chalks and samples of nanno-fossil ooze from Deep Sea Drilling Project cores (e.g. Matter et al. 1975). Most of the Tethyan samples are well-cemented so the isotopic values preserve evidence of submarine lithification as well as skeletal precipitation (c.f. Scholle 1974, 1977)

DISCUSSION

'Heavy' Oxygen Values

Most of the limestones have retained relatively heavy $\delta^{18}\text{O}$ values and therefore a 'marine' isotopic composition. Unlike many pelagic limestones they have neither 'recrystallised' at depth (Brenneke 1977, Letolle et al. 1978) nor have they been subjected to a substantial degree of burial cementation (Anderson and Schneiderman 1973; Matter et al. 1975; McKenzie et al. 1978). The porous 'shelf' and marly sediments, together with zones of obvious late precipitation (fissure fills and stylolite veins), have more negative $\delta^{18}\text{O}$ composition, some precipitation did take place during burial (see below). The pelagic sediments had very low rates of deposition (Jenkyns 1978); early cementation at or just below the sea-floor has prevented later precipitation in all but the most porous lithologies.

The oxygen isotopic composition of the Ammonitico Rosso nodules from Sicily and Italy are very close to values from similar

facies in the Austrian Alps (Adnet Limestone and Scheck conglomerate, Fig. 3); the results confirm the conclusions of Jenkyns (1974) and Hudson and Coleman (1978) that the nodular limestones formed by early diagenetic precipitation in 'the uppermost few centimetres of sediment' on the sea floor. Hudson and Coleman (1978) further suggest that their clast with the heaviest isotopic composition should be the least diagenetically altered and should be in near equilibrium with sea water. The low palaeotemperatures (12.2°C) that they calculate from this is taken as evidence that the local sea water in semi-restricted small oceanic basins was isotopically enriched ($\delta_{\text{w}} = 0$ or 1.5) in comparison to the contemporary world ocean ($\delta^{18}\text{O} = -1.2$).

The heaviest nodule from the Sicilian ammonitico rosso with $\delta^{18}\text{O} = +0.38$ would give a 'temperature of' 10.2°C (using the equation of Shackleton 1974 and assuming a world ocean $\delta_{\text{w}} = -1.2$ after Shackleton and Kennett 1975). This is probably too low for the likely depth of formation of nodular limestones in a relatively shallow tropical sea (Jenkyns 1974). The temperature calculation assumes equilibrium inorganic precipitation of pure calcite, but there is some evidence that this may prove to be an oversimplification.

The Ammonitico Rosso nodules have been compared to Recent and Quaternary high magnesium calcite nodules on the East Mediterranean ridge (Jenkyns 1974, Muller and Fabricus 1974, Hudson and Coleman 1978). The nodules have heavy $\delta^{18}\text{O}$ values (Milliman and Muller, 1977) which are not 'in equilibrium' with present East Mediterranean sea water ($\delta^{18}\text{O} = +1.5$, temperature of 13 to 16°C , Milliman and Muller, 1973; Muller and Fabricus, 1974; Cita et al. 1977). Laboratory experiment have shown that the precipitation of Mg-rich calcite involves a greater incorporation of the heavy oxygen isotope (0.06% per mol.% MgCO_3) than the precipitation of pure calcite (Tarutani et al. 1969).

This will cause an apparent temperature difference of 3 to 4°C for most naturally occurring Mg-calcites. The East Mediterranean nodules have between 12 and 16 mol.% MgCO_3 (Muller and Fabricus 1974) so the application of this correction does not totally account for the extremely heavy values. They probably reflect conditions during the complicated Quaternary evolution of the present Mediterranean (Milliman and Muller, 1973; Hudson & Coleman 1978). This mineralogical difference however, may account for the smaller enrichment in the Ammonitico Rosso nodules.

Sea floor cementation is associated commonly with a positive 'shift' in oxygen isotopic composition (Schlager and James, 1978) and Mg-calcite cemented layers on Recent seamounts have heavy δO^{18} values (Milliman 1971). Enrichment in O^{18} is often greater than the experimental data suggest (Land and Goreau 1970).

X-ray diffraction of the Ammonitico Rosso nodules shows them to consist solely of low magnesium calcite; if, as seems likely they originally precipitated as unstable magnesium-rich calcite they must have retained their isotopic composition during mineralogical stabilisation. Recent work (Marshall and Ashton, in press) has shown that ^{18}O enrichment in former magnesian calcites can be retained through stabilisation and later cementation. It is suggested therefore that the Ammonitico Rosso nodules were precipitated as high magnesium calcite nodules at a minimum temperature of 14°C and in equilibrium with sea water of similar if not identical composition to the contemporary 'world ocean'. This makes them analogous to Recent seamount deposits and oceanic sea floor hardgrounds; (Milliman 1971; Milliman and Muller, 1977, Schlager and James 1978). Heavy isotopic values may be explained therefore in terms of ubiquitous mineralogy of nodules throughout the Tethyan Mediterranean; they do not necessarily imply modified oceanic conditions as suggested by Hudson and Coleman (1978).

Carbon Isotope Composition

All the carbon isotopic values lie between -0.5‰ and +2.3‰; they are consistent with marine precipitation and imply that the late cements derived the majority of their carbon by dissolution and reprecipitation of marine carbonate (Hudson 1975). Data are too restricted to make definite statements about the variation in carbon content which is probably controlled by local and climatic factors (c.f. Kroopnick et al. 1977). Linear distribution of values from the Dolomia Principale, crinoidal calcarenites and condensed micrites (Fig. 2) suggests that they share a common source of marine carbon and were cemented by similar late calcites. The trend toward slightly lighter $\delta^{13}\text{C}$ in late cements is a common factor of burial cementation (Dickson and Coleman, in press; Own unpublished data)

Burial Cements

Porous lithologies and zones of obvious late cement precipitation (veins and vugs) have lighter $\delta^{18}\text{O}$ values. Negative oxygen isotopic composition characterises late cements from all sedimentary environments and mechanisms to explain the depletion are numerous; increase in temperature during burial (e.g. Anderson and Schneiderman 1973; McKenzie et al. 1978), pore-water evolution by diagenetic reactions (e.g. Lawrence et al. 1975; Irwin et al. 1977) and pore-water mixing with meteoric-derived water (e.g. Hitchon and Friedman, 1969; Hudson 1978) are commonly proposed.

Cements in the Dolomia Principale could argueably have been influenced by fresh water karstification of the overlying crinoidal calcarenites. There is, however, no evidence for freshwater precipitation in the crinoidal limestones themselves and the condensed micrites above the 'karst' surface apparently share a common late cement with the deposits below them. Further exposure to fresh water

under burial is unlikely during the known palaeotectonic evolution (c.f. Hudson, 1978) although fresh water cementation in conjunction with the present cycle of erosion cannot necessarily be discounted. Temperature increase during burial cannot explain the total observed depletion in the cements from the Dolomia principale; calcite with $\delta^{18}\text{O} = -6.65$ would be in equilibrium with sea water ($\delta^{18}\text{O} = -1.2$) at a temperature of almost 44°C : equivalent to burial to around 1 km under normal geothermal gradients (Lawrence, 1973; McKenzie et al. 1978). It is however, more likely that diagenetic modification of the pore water has taken place (e.g. Anderson et al. 1976). Slight decrease in $\delta^{18}\text{O}$ in the late veins in the pelagic sediments can be attributed to temperature increase during the early stages of burial.

CONCLUSIONS

The isotopic composition of Tethyan limestones from Sicily and Northern Italy can be related to ~~the lithology of the sediment and hence~~ the environment in which cementation took place. Low rates of deposition enabled submarine cementation to be the dominant lithifying process in all but the most porous sediments. Heavy $\delta^{18}\text{O}$ values in Ammonitico Rosso and other limestone nodules are probably relics of former high magnesium calcite cements. Only the highly porous peloidal shelf limestones and a few late diagenetic veins exhibit the normal diagenetic trend toward lighter $\delta^{18}\text{O}$ found in both Mesozoic epicontinental limestones (e.g. Gokdag, 1974; Hudson, 1977; Marshall and Ashton, in press and own unpublished data); and in pelagic limestones encountered in Deep Sea Drilling cores (e.g. Anderson and Schneiderman, 1973; Matter et al., 1975).

The majority of the Tethyan limestones have a narrow range of both carbon and oxygen isotopic composition which must indicate that lithification took place at or just below the sea-floor.

CHAPTER 3

ZONED CALCITES IN JURASSIC AMMONITE CHAMBERS: TRACE ELEMENTS,
ISOTOPES AND NEOMORPHIC ORIGIN

ABSTRACT

Zoned calcites were found in the phragmacone chambers of three Sonniniid ammonites from marine Middle Jurassic sandstones (Isle of Skye, U.K.). Each ammonite has a characteristic sequence of up to nine calcite zones, determined by inclusion density banding and variation in trace-element composition, which is developed in each of its former voids. ^{Proximal} ~~Outer~~ (early) calcites ^{have undulose extinction} ~~are strained~~ and exhibit radial-fibrous, fascicular-optic and radiaxial fibrous mosaics, microdolomite inclusions are found in one specimen. The early calcites, interpreted as replacements after a single isopachous fringe of acicular submarine cement (probably high magnesium calcite), are succeeded by unstrained ferroan calcite cement. In one specimen there are two distinct generations of calcite in the others there is a continuous, transitional mosaic from the early calcites into the late cement.

Isotopic composition of the separated calcites demonstrates the early importance of organic derived carbon ($\delta^{13}\text{C} = -26\text{‰}$, $\delta^{18}\text{O} \approx 0$). Later precipitation and mineralogical stabilisation took place at increased temperatures and after modification of the pore water isotopic composition (Calcites with $\delta^{13}\text{C} \approx 0\text{‰}$, $\delta^{18}\text{O} \approx -10\text{‰}$). The distinctive fabrics and zonal pattern developed during the replacement of the precursor cement and are not primary growth features. Zonal differences are related to the rate of neomorphic growth and hence the degree of exchange with external pore waters. Finally, increased temperature during Tertiary igneous activity gave rise to additional $\delta^{18}\text{O}$ depletion in calcites filling residual void space ($\delta^{13}\text{C} \approx 0$, $\delta^{18}\text{O} \approx -20\text{‰}$).

INTRODUCTION

Diagenetic calcites which exhibit undulose extinction are common void-filling features of sedimentary rocks of all geological ages. Specific morphological criteria have been used to suggest that some of these calcites are neomorphic replacements after original, bundled, acicular carbonate which was analogous to Recent submarine cements. (Kendall and Tucker, 1973, Kendall, 1977, Davies, 1977). Integration of detailed petrographic and geochemical (trace element and isotopic) analysis of complex sequences of diagenetic precipitates provides evidence for the nature of precursor cements and for the chemical environment during subsequent processes of cement precipitation and recrystallisation (e.g. Dickson and Barber, 1976, Davies, 1977, Scherer, 1977).

In this paper strained calcites from the septal chambers of three Middle Jurassic ammonites which exhibit distinctive patterns of internal zonation have been analysed to determine the nature of the original cements and to investigate the process of neomorphism. By analysing calcite from successive zones of strained and later unstrained calcites it has been possible to unravel a complex diagenetic history spanning at least 100 M.years and to suggest that the distinctive zonal patterns developed in response to local conditions of neomorphism rather than those of primary precipitation.

GEOLOGICAL SETTING

The Bearreraig Sandstone Formation (Bajocian) outcrops, in its type-section, in sea cliffs at Bearreraig Bay, Isle of Skye (fig.3.1). The Formation is represented by 180 m of massively bedded shaly sandstones and interbedded shales; interpreted as relatively near-shor^e open-marine deposits (Morton, 1965).

Tertiary igneous activity has had little metamorphic effect on the sediments in this part of Skye and they are undeformed except for a gentle regional dip of around 12° to the West. Small dolerite dykes cut the sandstones in several places and dolerite sills up to 200 m in total thickness preferentially intrude the shales in the overlying sediments of the Great Estuarine Group (280 m Bathonian). The Jurassic succession in Northern Skye is unconformably overlain by around 1 km of Tertiary basalt lavas.

Uncrushed Sonniniid ammonites (Morton, 1975) are preserved, at Bearreraig, in lenticular, calcite cemented, concretions or "doggers" within the friable and generally poorly fossiliferous fine to medium grained pale grey sandstones. Specimens for the present study were collected by Dr. N. Morton from nodules about 65 m below the top of the Formation at Bearreraig burn. (Holm Sandstone Member of Morton, 1976). Dr. N. Morton (Birkbeck College, London) kindly lent the specimens to the author for the present study.

METHODS

Trace elements and mineralogy

Variation in Fe^{II} content was monitored by the use of standard Alizarin Red S and potassium ferricyanide mixed stain technique (Dickson, 1965). The electron microprobe was used for quantitative point analyses and for more qualitative scan analysis of polished thin sections (method outlined in Marshall and Ashton, in press). Qualitative identification of different carbonate phases was achieved by X-ray diffraction using a fluorite internal standard to determine peak position.

Isotopes

Samples of host sediment and blocky calcite spar were extracted from stained slices cut normal to the plane of symmetry of the ammonite, using a dental drill; those from the early zoned calcites and shell wall were extracted using a gramophone needle attached to an electric engraving tool. Repeated surface polishing and staining during sampling was necessary to obtain sufficient material by the latter method. Around 10 mg of calcite (2 to 10 mg for needle extractions) was reacted with 100% phosphoric acid at 25°C to release carbon dioxide for isotopic analysis.

Isotopic ratios were determined on Micromass 602 and 903 mass-spectrometers at the Institute of Geological Sciences, London. Standard correction procedures were employed (Craig, 1957). Measurements are expressed in the usual ' δ ' notation in 'per mil' (‰) difference from the P.D.B. international standard for both $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios. Analytical uncertainties of less than 0.06‰ are associated with individual determinations; repeat samples of the same calcite zone differ by up to 2‰ suggesting real

isotopic variation on a minute scale.

The isotopic composition of a calcite is mainly dependent on the temperature of precipitation and the isotopic composition of the ambient pore water. Factors which can affect pore water composition during burial are summarised by Hudson (1977) and Curtis (1978). Marine carbonate has $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ near 0‰. During early burial, reactions involving organic matter can modify the $\delta^{13}\text{C}$ of the local bicarbonate and give rise to carbonates with extreme (light or heavy) $\delta^{13}\text{C}$ values. Oxygen isotopic composition is strongly temperature dependent, negative values accompany temperature increase in the diagenetic environment. Excess depletion in ^{18}O may reflect modification of pore water composition by diagenetic reactions (e.g. Irwin et al., 1977) or mixing of formation waters with a supply of ^{18}O depleted meteoric water (Hitchon and Friedman, 1969, Hudson, 1978).

AMMONITE PRESERVATION

INTRODUCTION

Virtually all the ammonites in the Bearreraig concretions have been broken before deposition and the septal chambers are now filled with calcite-cemented sediment. The three specimens on which this discussion is based are exceptional in that, although sediment fills the last chambers of the outer whorl and in some instances penetrates nuclear chambers where the shell wall was broken before deposition, the majority of the chambers remained open for successive diagenetic precipitation.

Each ammonite has a characteristic succession of calcites which is found in each of the formerly open chambers. Two of the specimens (I and II) have a single outer isopachous fringe of turbid calcite (Figs. 3.2, 3.8), the third has a complex outer pattern of zones with different inclusion density (Fig. 3.11); all three have clear blocky ferroan calcite in the centre of each void.

SHELL PRESERVATION

Skeletal aragonite has been replaced by clear pale-brown commonly pseudopleochroic calcite; relic shell microstructure is preserved by inclusions within the granular calcite mosaic. Calcitization must have taken place in-situ and have involved the gradual microscopic replacement of the aragonite (Hudson, 1962, Bathurst, 1975, p.347).

Shell walls and septa are generally uniformly ferroan (Table 3.2); in Specimen III they exhibit internal zonation which mirrors the changes in chemistry of the void filling calcites (Fig. 3.12). The isotopic composition of shell and septal calcites is very variable (Table 3.2, and Fig. 3.14), all have negative $\delta^{13}\text{C}$

(-13 to -2) and light $\delta^{18}\text{O}$ (-3 to -10%). Values fall within the range for the 'early' void filling calcites (see below) and reflect the temperatures and porewater chemistry during burial rather than primary precipitation. Isotopic evidence therefore points to open re-equilibration with a fluid phase during the calcitization of the aragonite (c.f. Tan and Hudson, 1974, fig. 7).

PYRITE

Aggregates of iron sulphide are the earliest diagenetic precipitates now preserved in the septal voids. Small stalactites (up to 0.25 mm in length) hang from the lateral shell wall in one specimen (Fig. 3.3) and a fine, crystalline, geopetal layer of pyrite is found in several of the ammonite chambers.

Early diagenetic pyrite is a common feature of ammonite preservation (e.g. Hudson and Palframan, 1969, Seilacher et al., 1976); the anaerobic bacterial reduction of seawater sulphate under shallow burial is the most likely mechanism of precipitation (e.g. Hudson, 1978(b)). Involvement of organic matter releases ^{12}C enriched bicarbonate which is available for precipitation as calcite (e.g. Raiswell, 1976, Curtis, 1977, Hudson, 1978(a)).

VOID-FILLING CALCITES; TERMINOLOGY

Sparry calcite fills or partially fills the ammonite septal chambers. Outer, and therefore early, crystals generally exhibit a radial-fibrous fabric with individual crystals (specimen III only) showing the specific internal structure of radiaxial fibrous and fascicular optic mosaics as originally defined. (Bathurst, 1959 and Kendall, 1977 respectively). Central, blocky, ferroan calcites are unstrained.

Intuitively all the calcites are cements, that is, they were precipitated as space-filling crystals attached to the free surface of the septal voids (Bathurst, 1975, p.416). Strained extinction and inclusion patterns suggest that the outer zones in each void are the replacement of precursor acicular cements (Kendall and Tucker, 1973) and are therefore strictly neomorphic calcites. The transition within a septal chamber from early replacement fabrics to later blocky cements is often gradational (Specimens II and III) and need bear no relationship to zonal (see below) or crystallographic boundaries (cf. Orme and Brown, 1963). The term "cement" will be used only for those unstrained calcites which most clearly fulfill Bathurst's (1975) rigorous definition.

"Generations" of precipitates are easily defined where there is a clear crystallographic break between early calcites terminated by well defined euhedral faces and a blocky late cement with different chemical composition: two generations are clearly displayed in specimen I (Fig. 3.2) where the early calcite forms an isopachous pore-lining and large late cement crystals only partially fill many of the cavities.

In voids where there is a single ^{spar}~~crystal~~ mosaic (specimens II and III), in which strained radial-fibrous calcite grades into equigranular cement no clear boundary between 'generations' can be defined. The calcites are arbitrarily referred to as early or late on the presence or absence of strained extinction rather than on a distinct crystallographic break.

Zones within the mosaics are determined in terms of bands of different inclusion density or chemical composition as deduced by staining. Zonal boundaries may mirror the position of early crystal faces of the present crystal mosaic or may reflect growth stages of

a former fabric; those determined by inclusion density banding do not always coincide with chemical or crystallographic breaks. There is no firm evidence to suggest that changes in isotopic composition coincide with changes in any of the above features; but as it was impossible to monitor continuous isotopic variation samples were chosen to coincide as nearly as possible with morphological and chemical zonation.

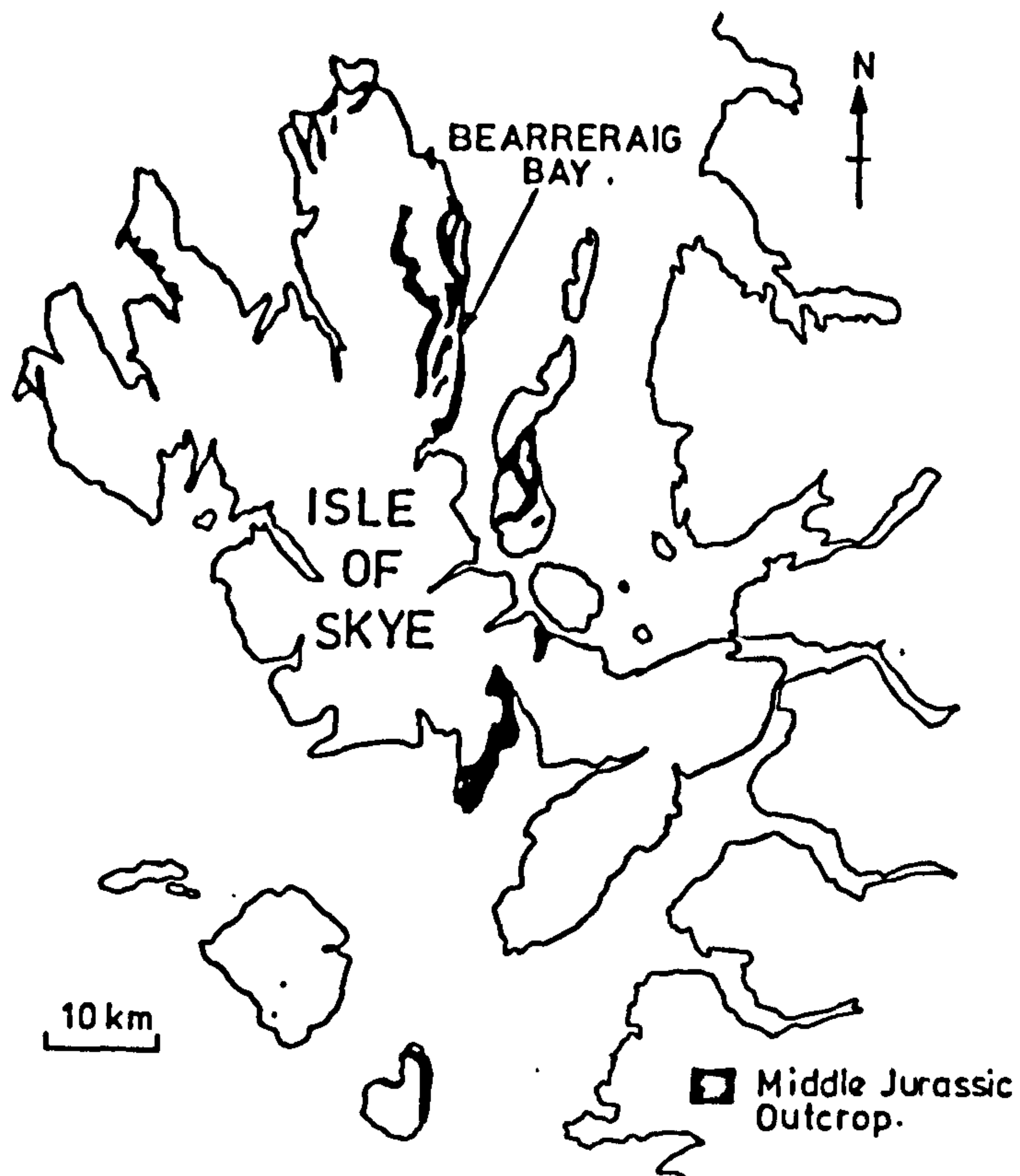


Figure 3.1. Locality Map

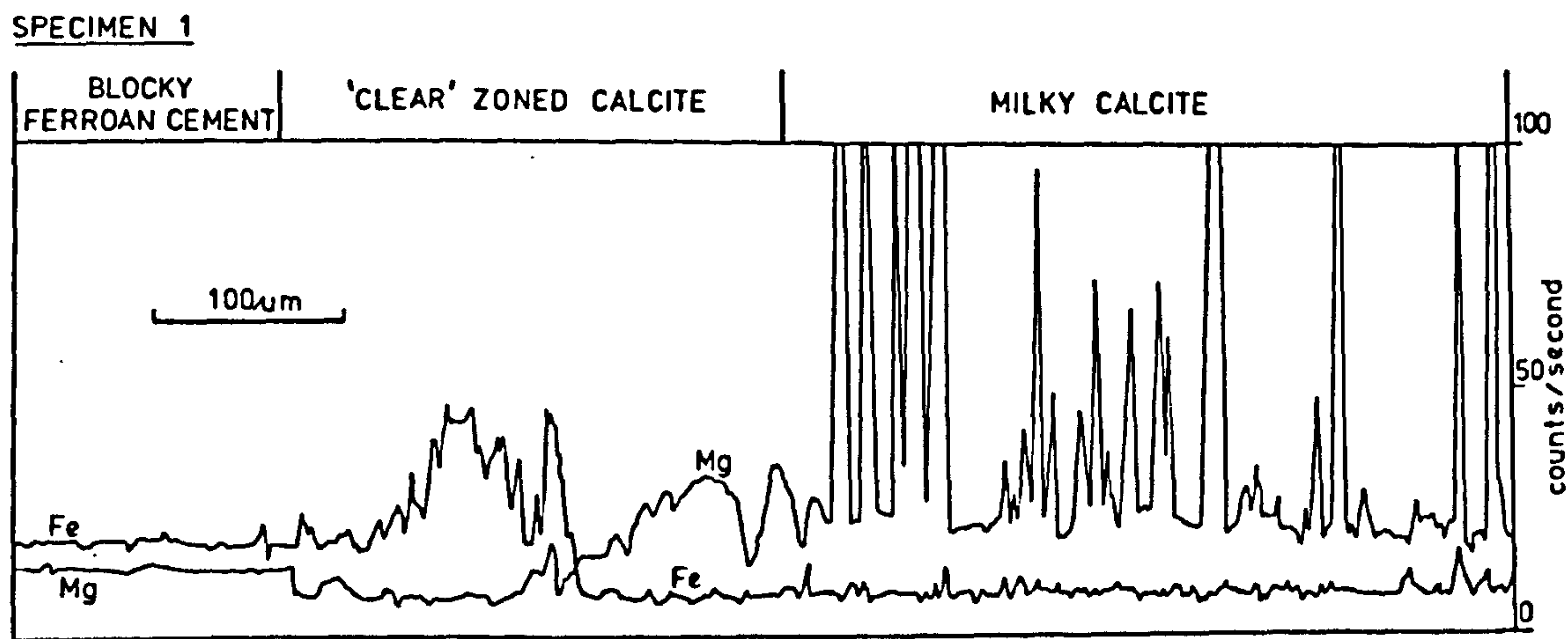


Figure 3.6. Specimen 1: Microprobe scan for Fe + Mg across the inner margin of the inclusion-rich fringe, clear overgrowth zone and contact with late ferroan cement. Note Mg peaks in the "milky" calcite.

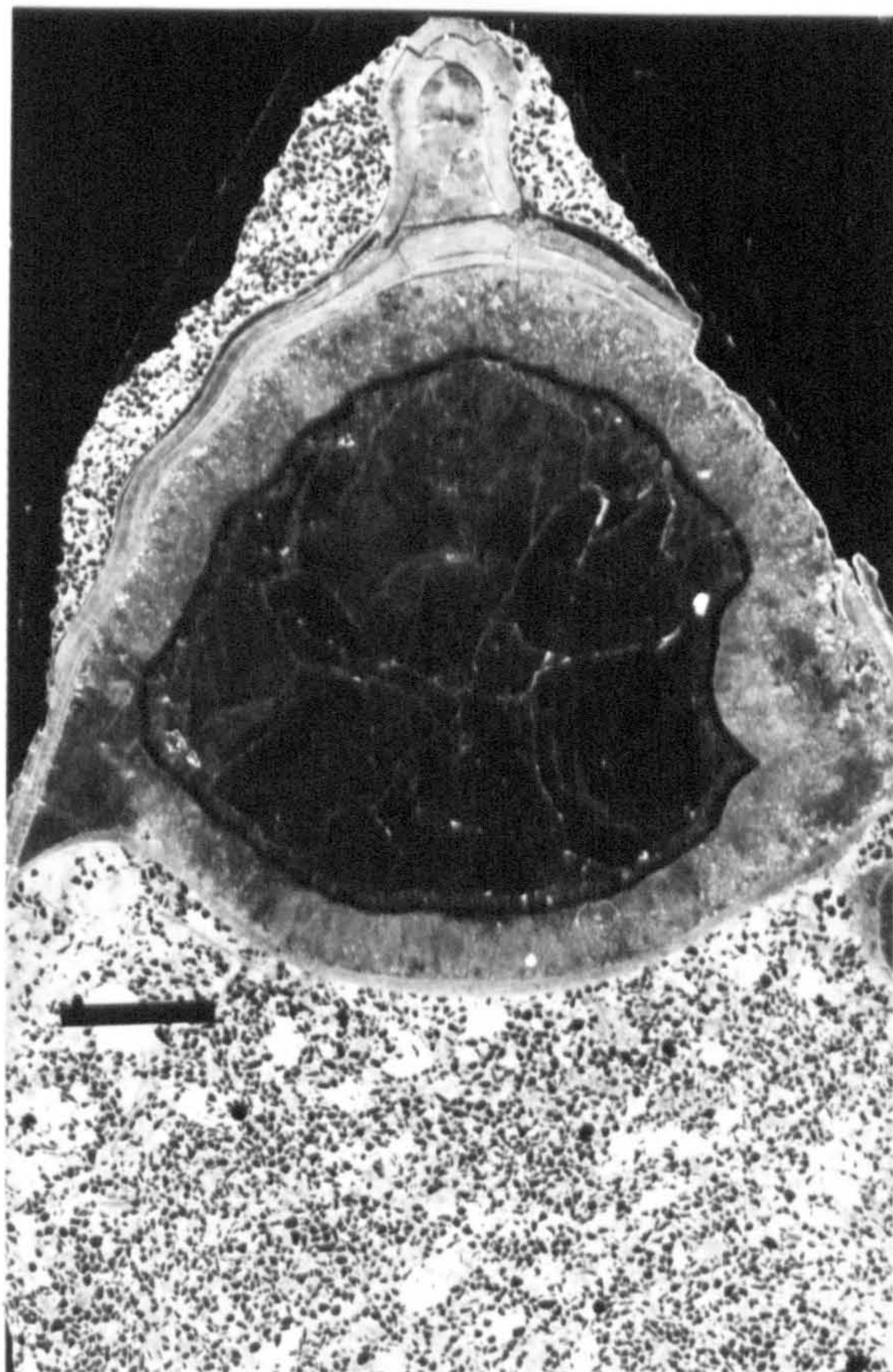
Figure 3.2 Outer whorl chamber Specimen I - direct from stained peel. Isopachous non-ferroan calcite fringe lines former cavity in septal fold. Blocky ferroan spar fills centre of former void space. (Bar = 2 mm).

Figure 3.3 Specimen I: Pyrite stalactites suspended from lateral shell wall (left margin, Fig. 3.2) within turbid calcite fringe. (Bar = 0.25 mm). Photo from polished thin section.

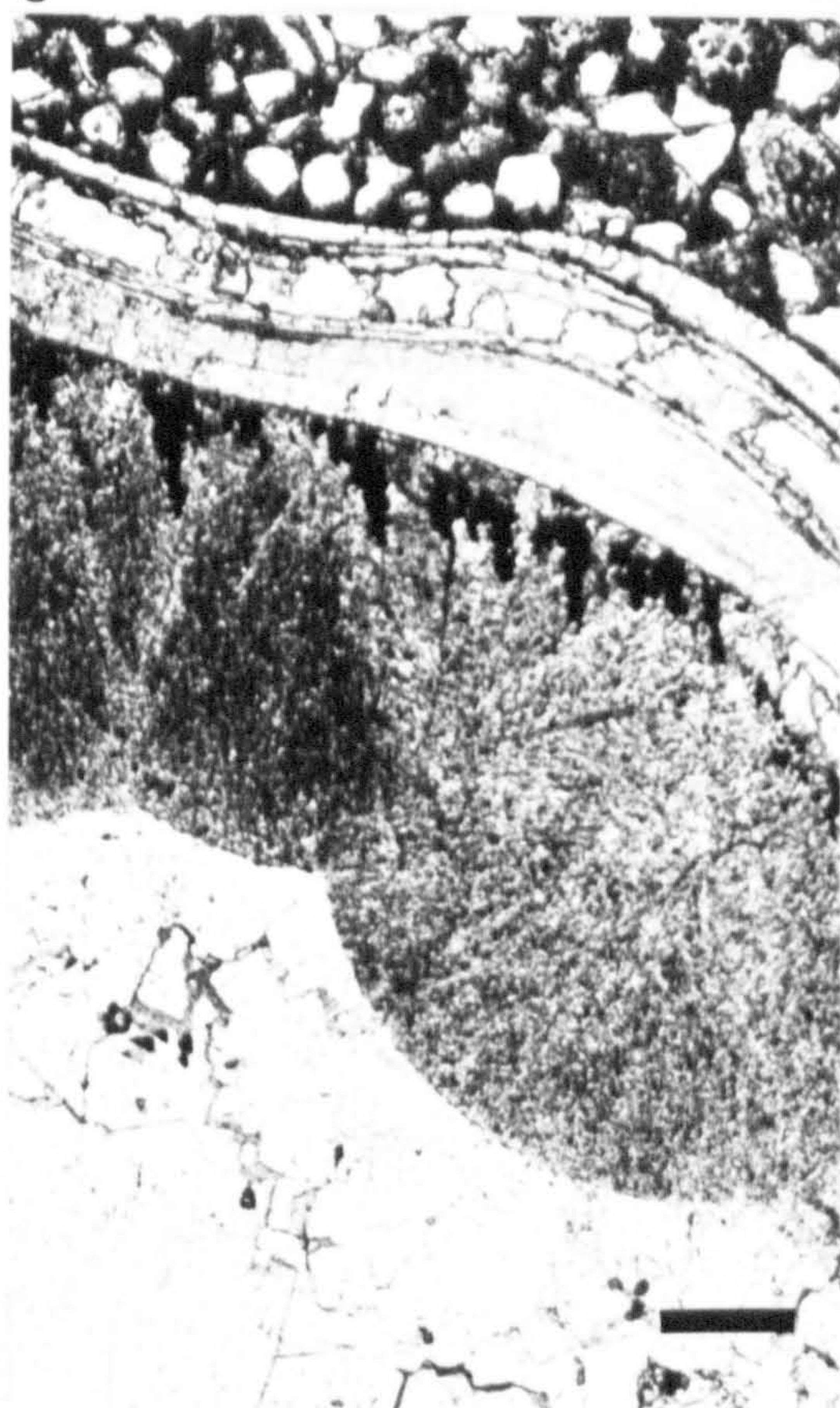
Figure 3.4 Specimen I: Radial-fibrous extinction and inclusion pattern define bundled fabric in turbid fringe. Strain is continued into clear overgrowth zone. Blocky ferroan spar top of photo. (Bar = 0.2 mm). Photograph from polished thin section.

Figure 3.5 Specimen I: Reflected X-ray image of the turbid fringe. Mg concentrated in discrete rhombic areas. (Bar = 20 μ m).

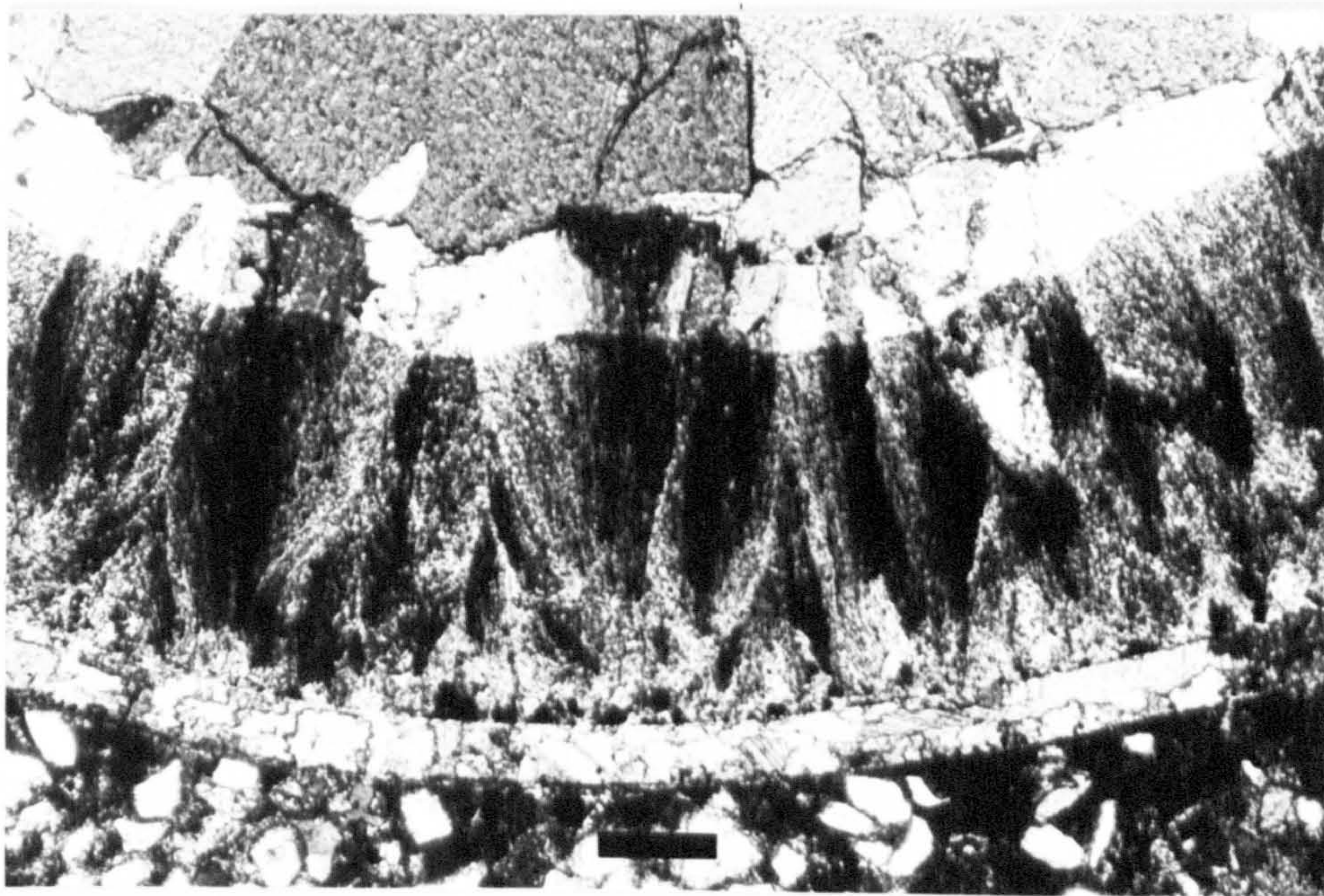
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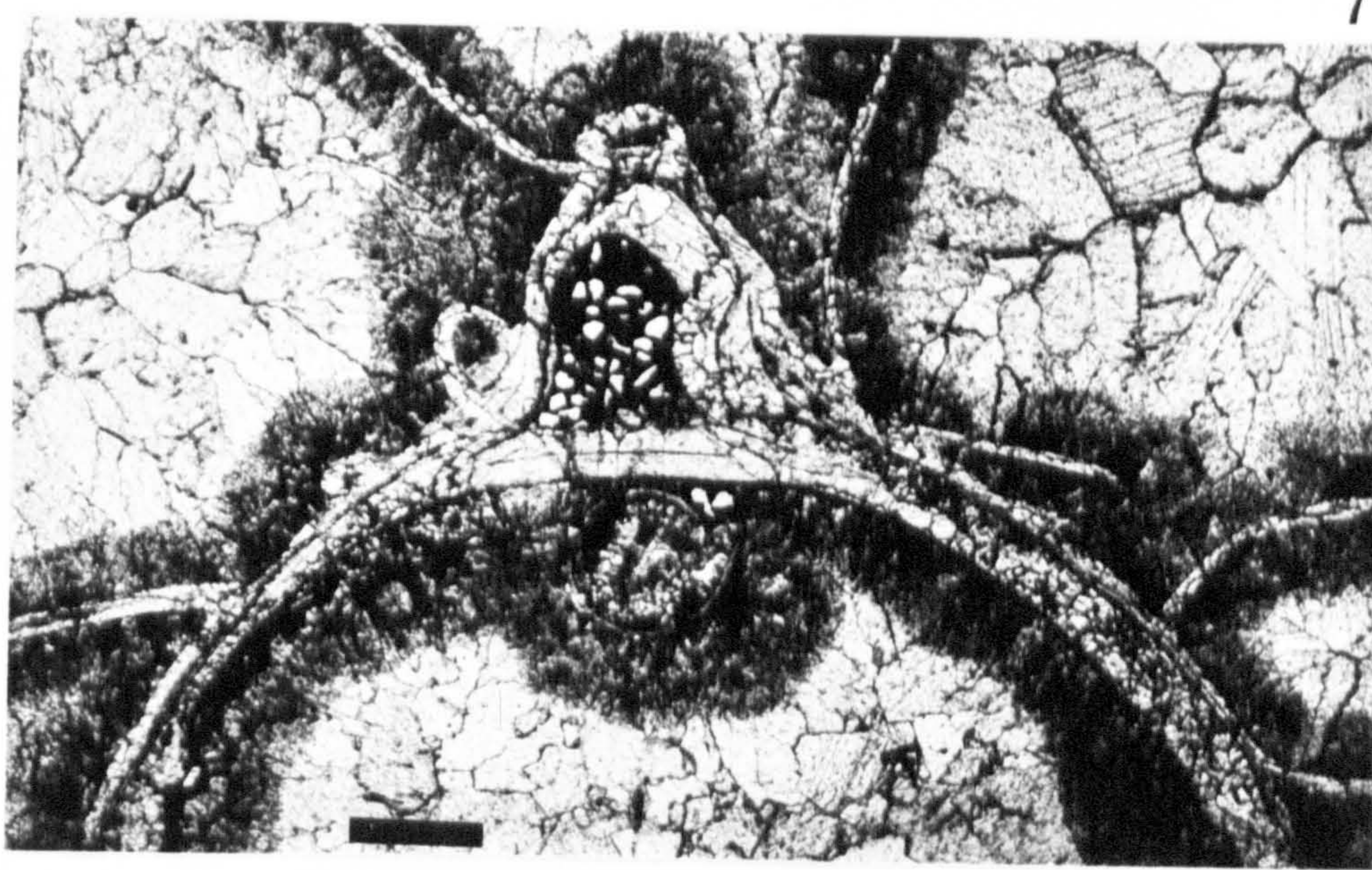
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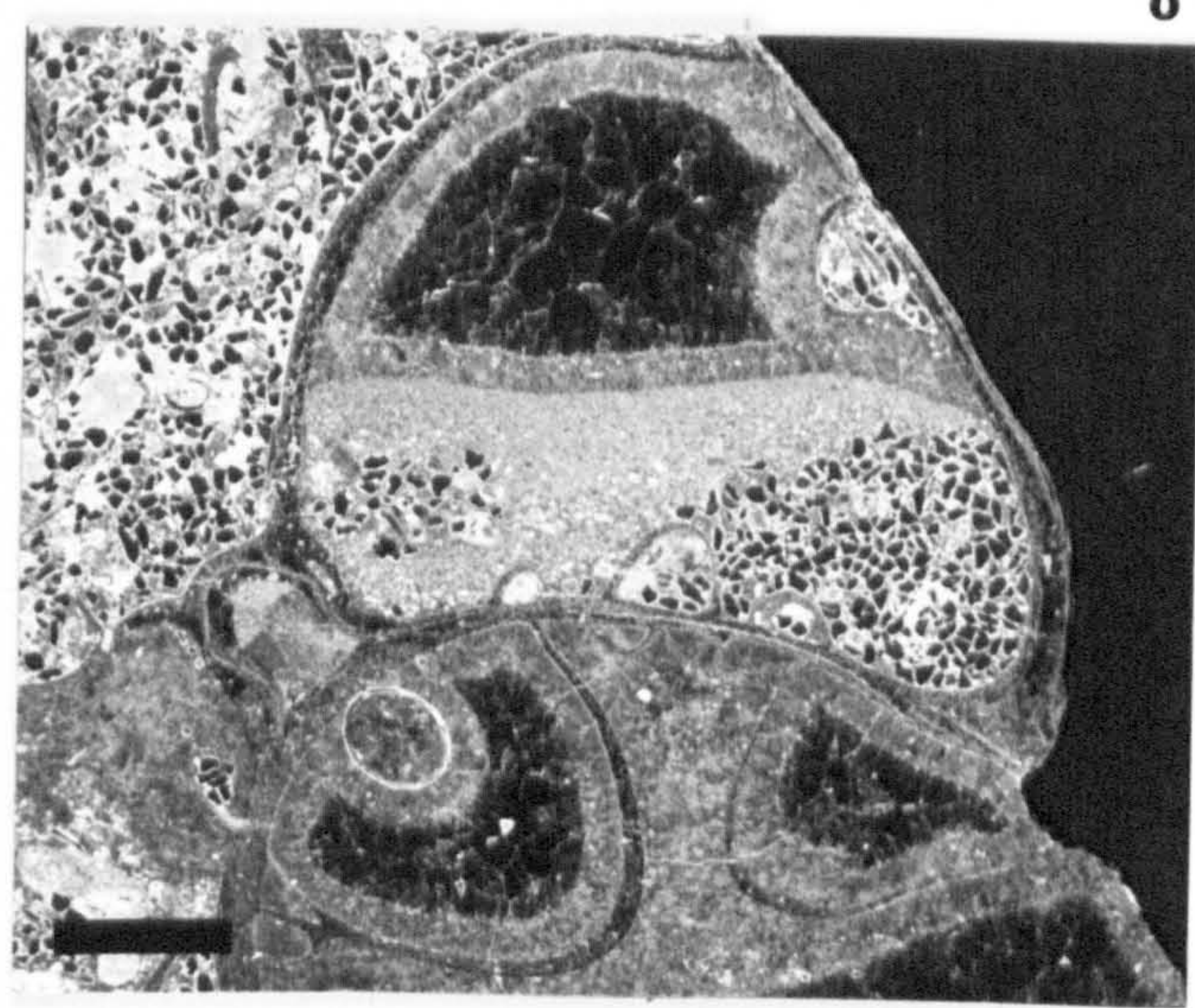
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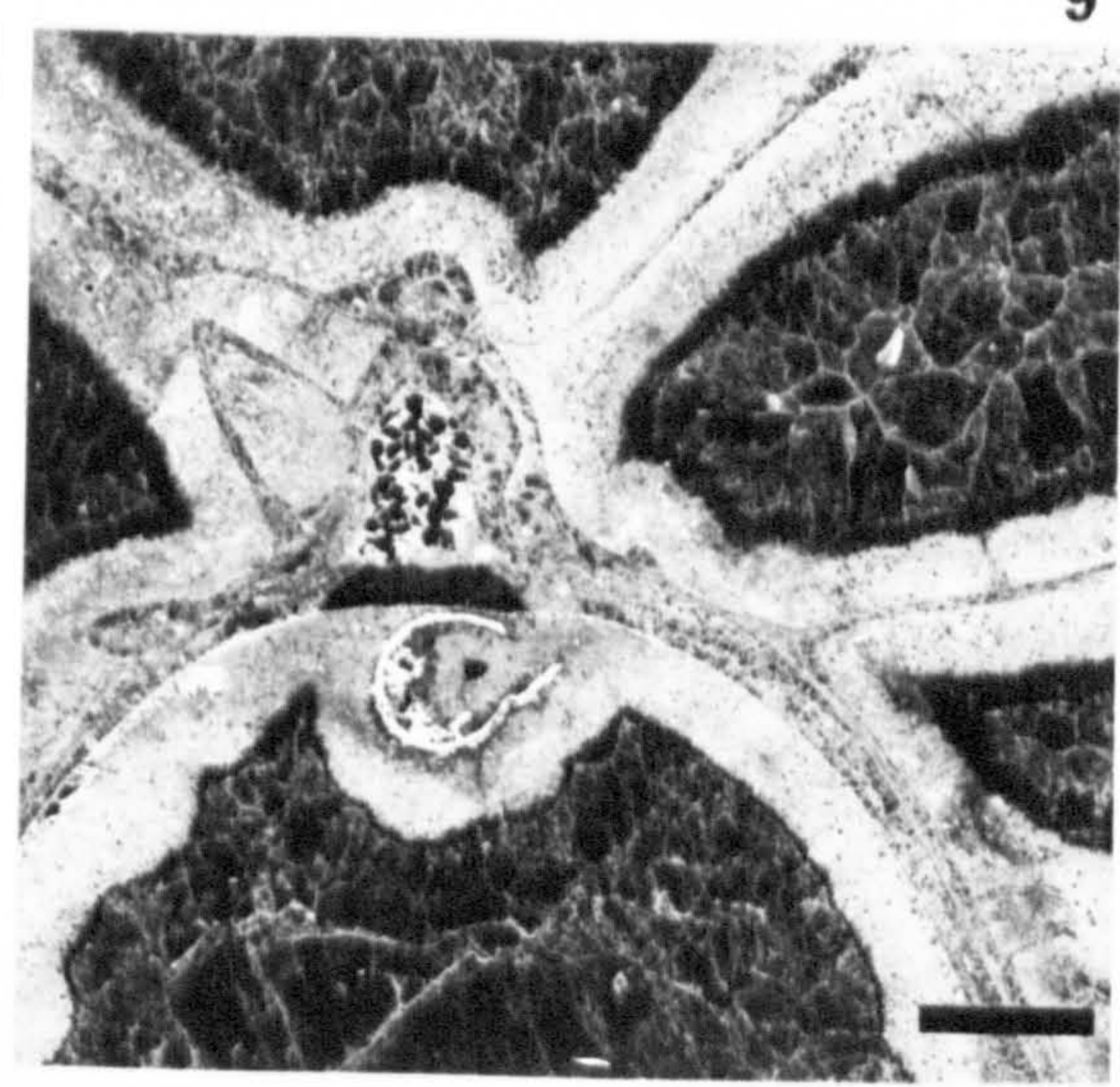
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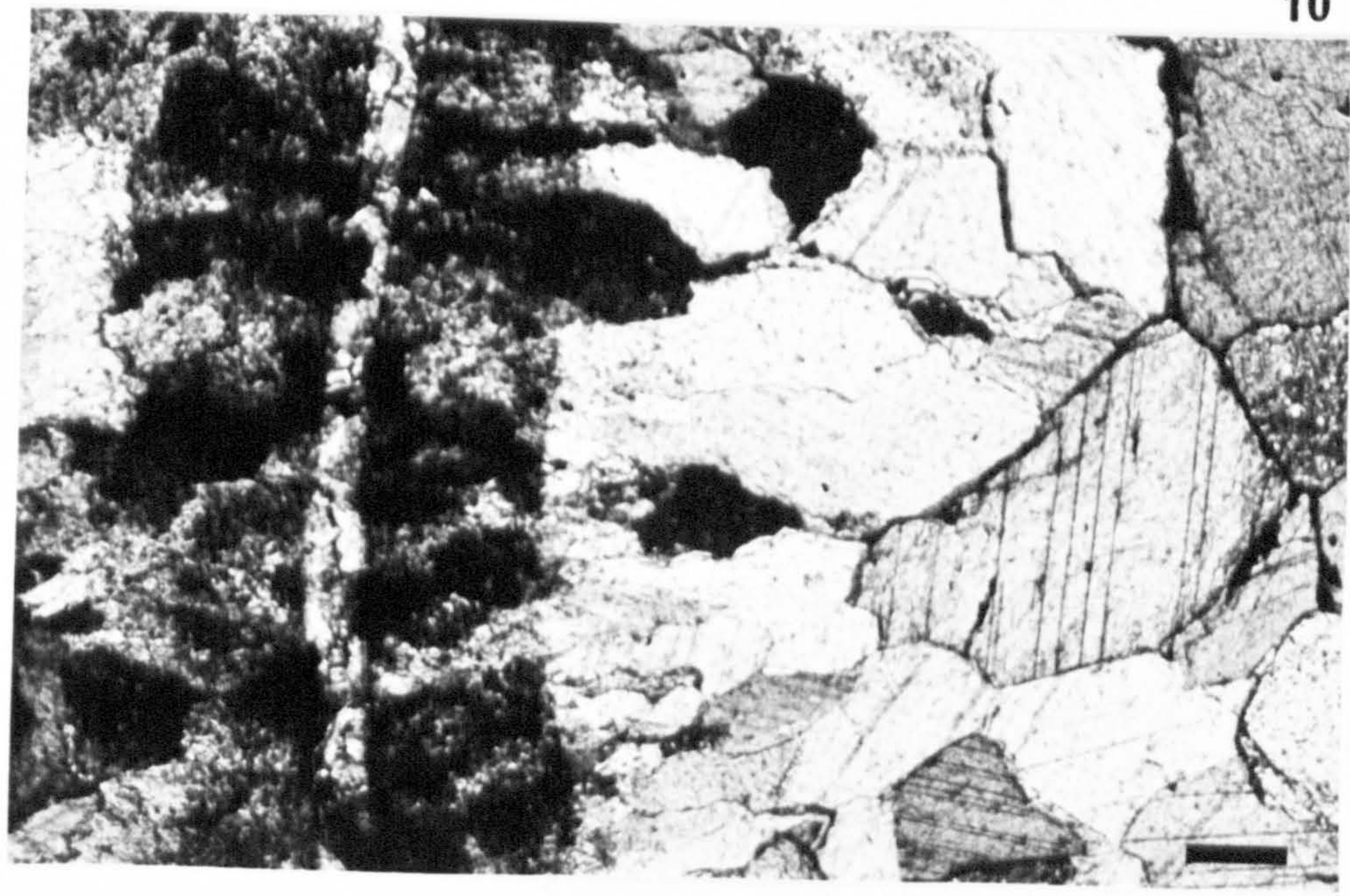
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9



10



- Figure 3.7 Specimen II: Photomicrograph of polished thin section. Keel of inner whorl filled with sand grains. Siphuncle preserved as organic sheath. Inclusion-rich fringe in drusy mosaic with ferroan cement (clear). (Bar = 0.25 mm).
- Figure 3.8 Specimen II: Septal fold in outer whorl partially filled by internal sediment, turbid fringe lines former void. Spar filled the residual cavity. Direct print, unstained acetate peel. (Bar = 1 mm).
- Figure 3.9 Specimen II: Stained peel - direct photograph. As Figure 3.8. Fringe is ferroan (pale grey on photo.) Non ferroan zone (dark grey/black). Late spar (medium grey). (Bar = 2 mm).
- Figure 3.10 Specimen II: Photomicrograph (crossed polars) of septal wall, turbid fringe and late cement, showing transitional, drusy mosaic. (Bar = 0.2 mm).

Figure 3.11 Specimen III: Direct prints from stained acetate peels. Multiple zoning in neomorphic calcites. Sections cuts normal to the ammonite plane of symmetry. Inclusion-rich zones are light grey, inclusion-poor are dark.

Figure 11.1

Outer whorl chamber - septal folds divide chamber into a series of 'voids'.
(Bar = 5 mm).

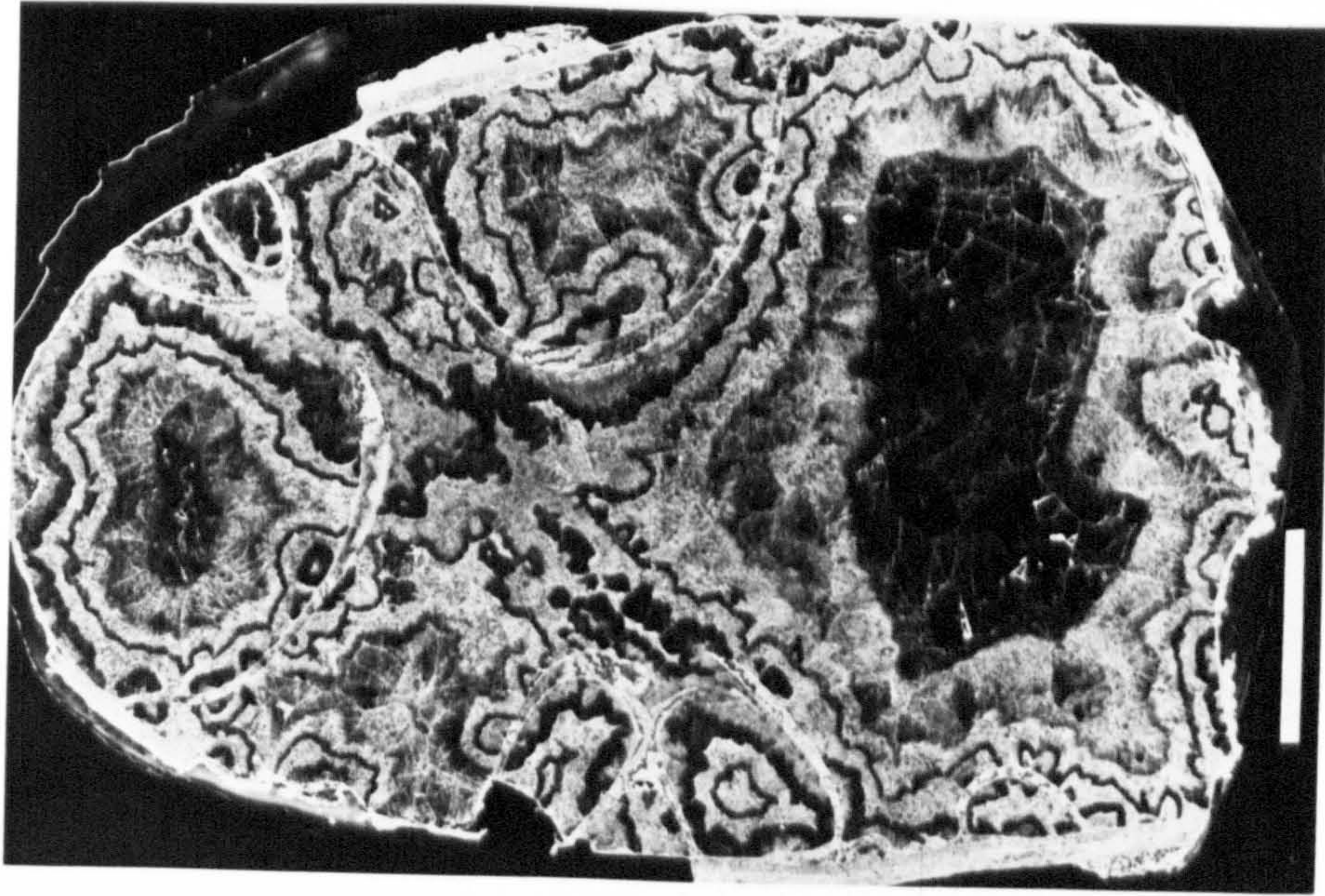
Figure 11.2

Top section of Fig. 11.1.
A-progressive zone coalescence toward centre of former void.
B-diagram to illustrate zones 1-8.

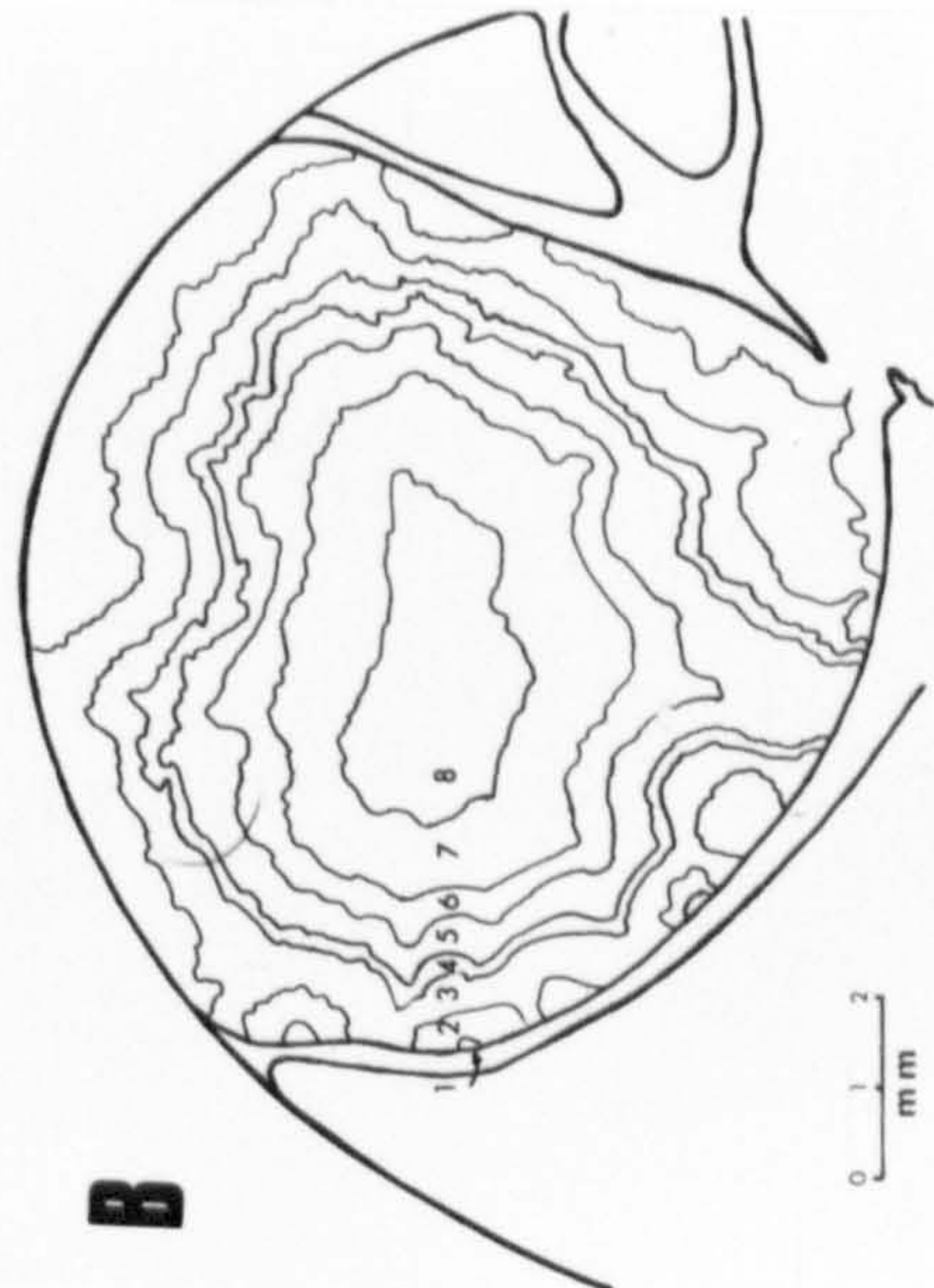
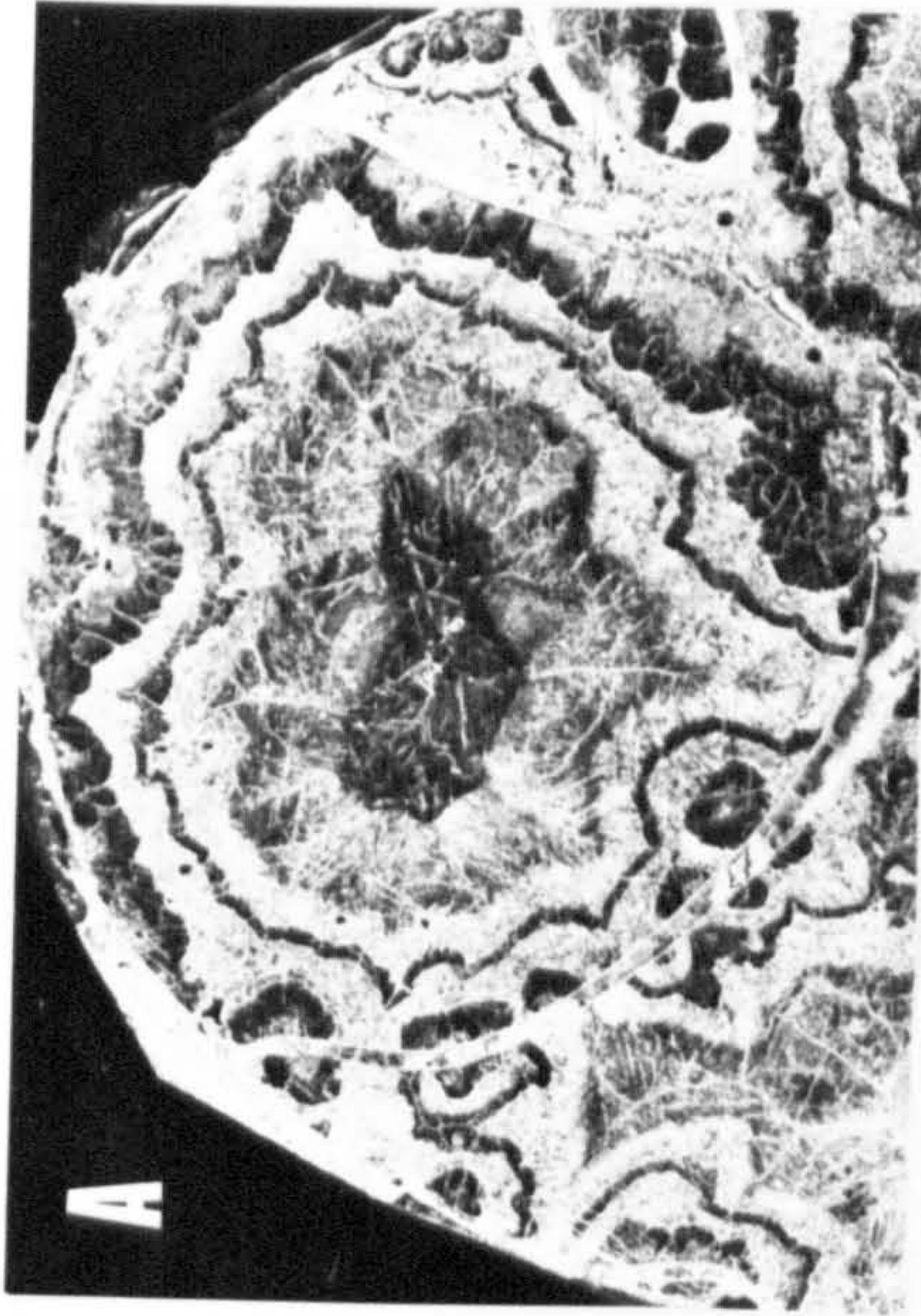
Figure 11.3

Section through centre of septal chamber. Triangular inclusion relics indicate former crystal faces in late cement.
(Bar = 5 mm).

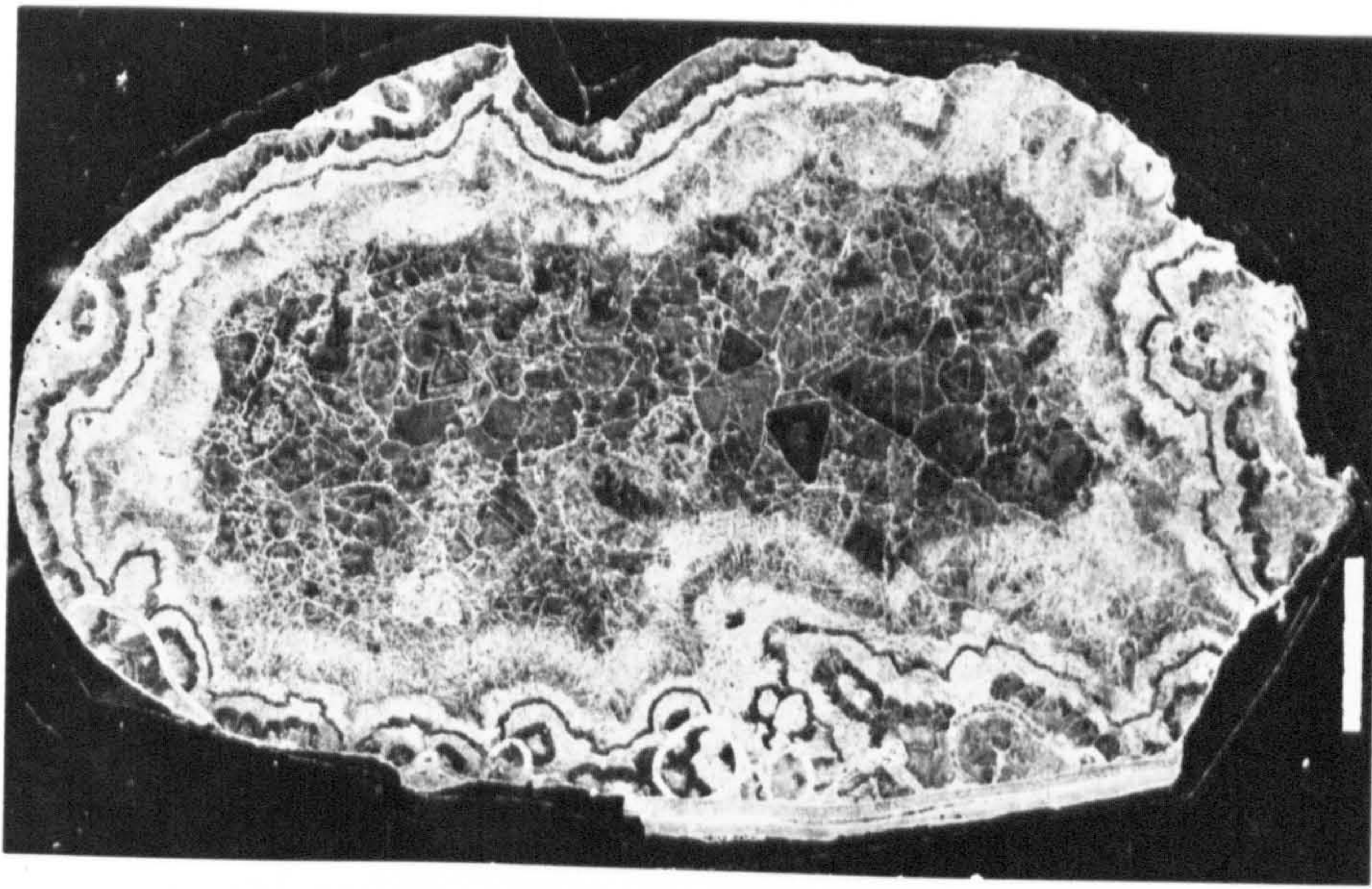
11.1



11.2



11.3



3.
 Figure 12.1[^] Specimen III: Photomicrograph of polished thin section showing relationship between inclusion zones and crystal morphology. (Bar = 0.5 mm).

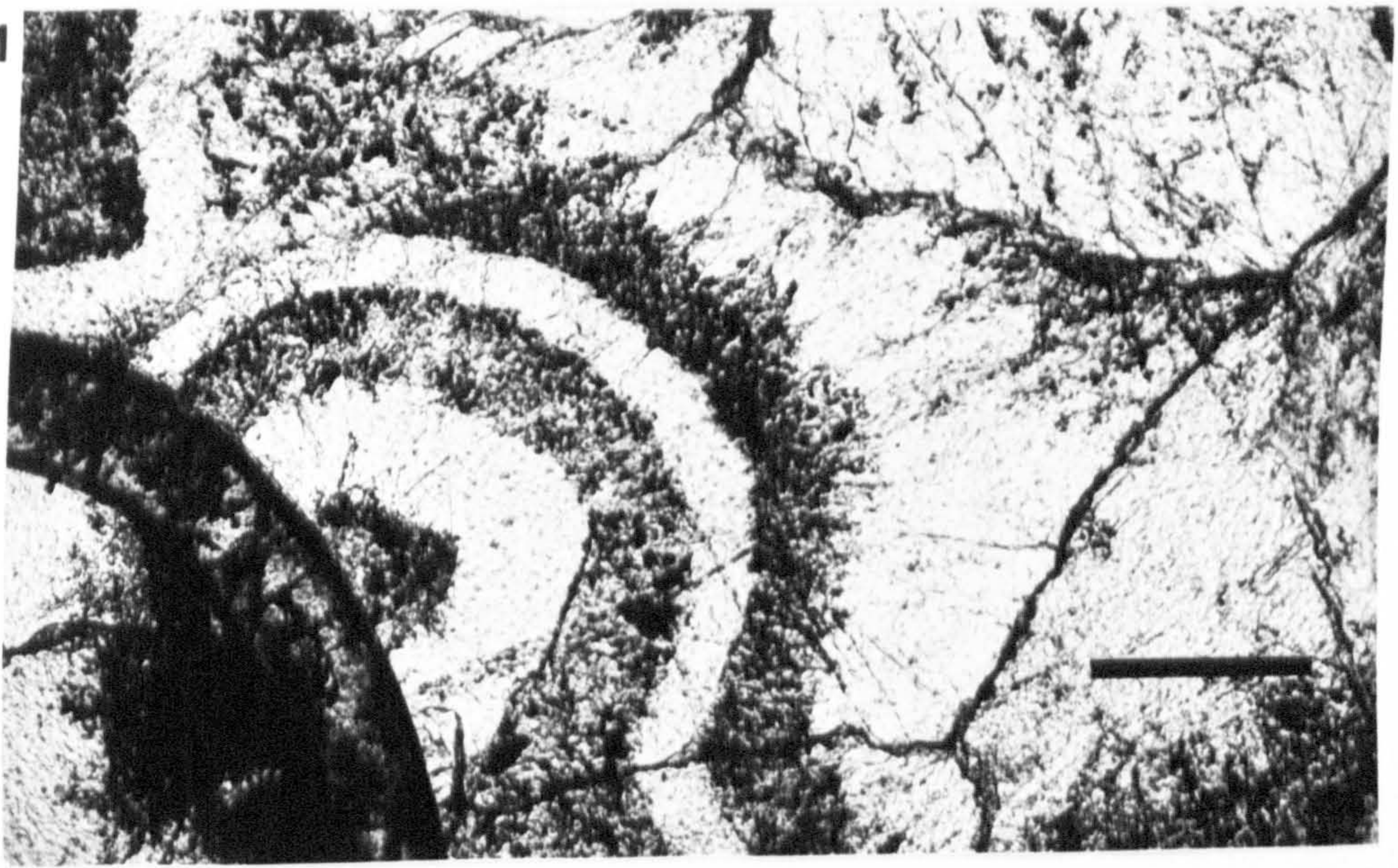
3.
 Figure 12.2[^] Specimen III: Direct print from acetate peel demonstrates relationship between zones and crystal boundaries. Zones can also be traced ~~through~~^{within} septal wall replacement. (Bar = 1 mm).

Figure 3.13 Specimen III: Photomicrograph of transitional mosaic from early, strained, (and zoned) calcites (LHS) to clear, unstrained late cement (RHS). Numbers refer to the zones of Fig. 11.2.

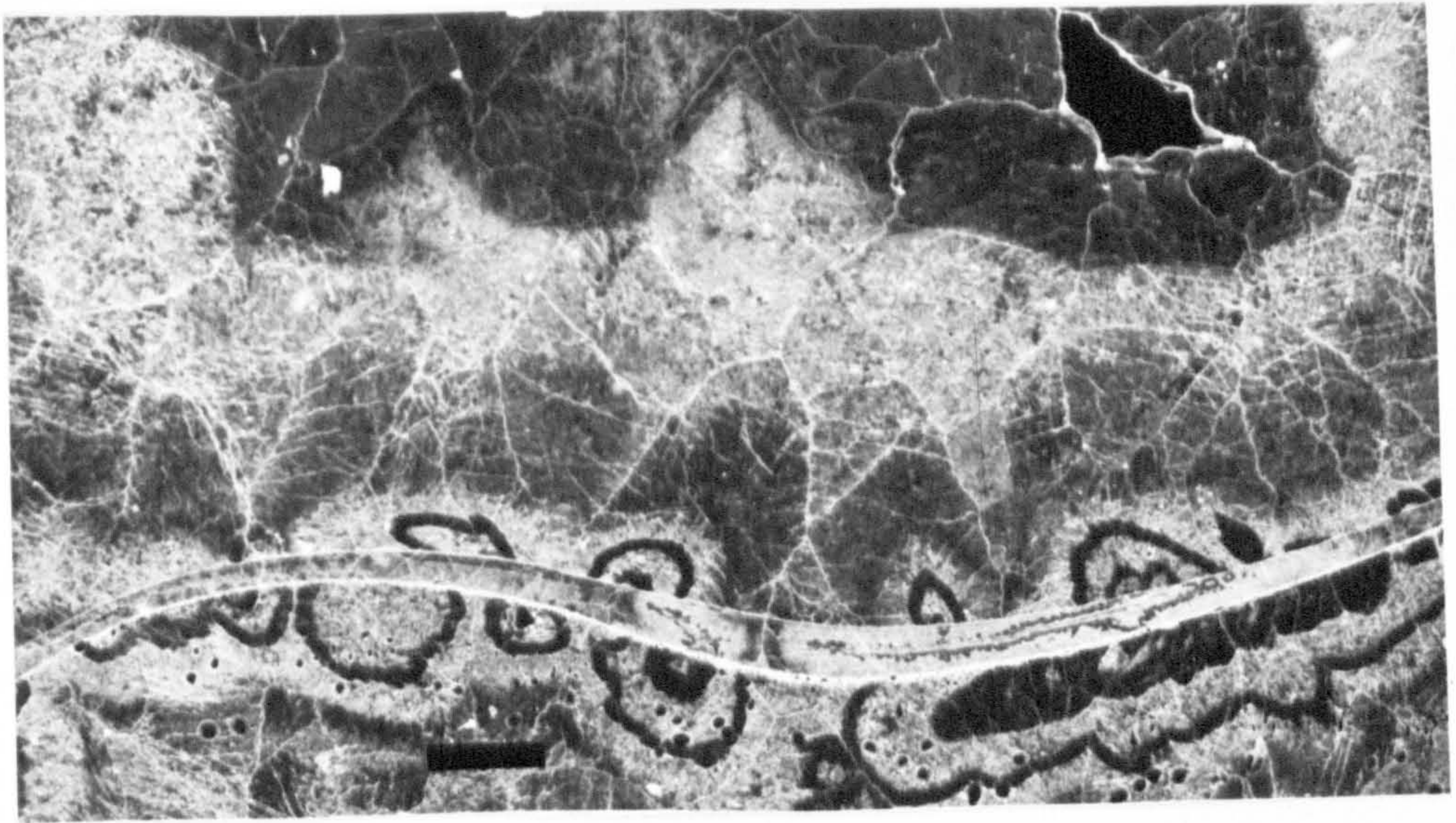
Fig. 13.1 Plane polarised light.

Fig. 13.2 Crossed polars. (Bar = 1 mm).

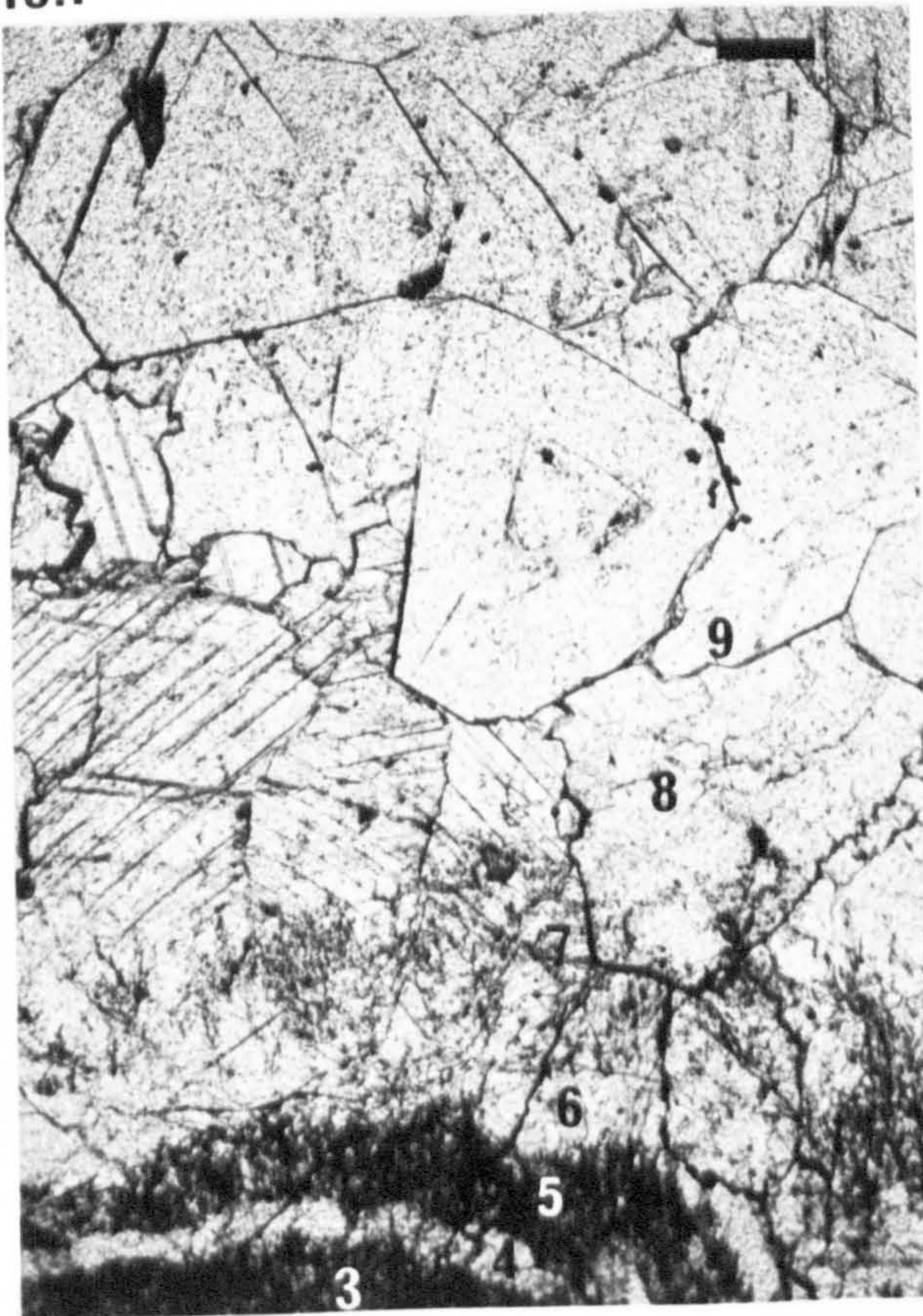
12.1



12.2



13.1



13.2



FABRICS AND TRACE ELEMENTS

EARLY CALCITES

Outer, strained, radial-fibrous calcites from each specimen have different morphologies and chemical compositions, the salient features of each succession of calcites are summarised in Table 3.1.

Specimens I and II

Both have a single isopachous fringe of turbid (inclusion rich) calcite which coats the internal sediment and chamber walls (Figs. 3.2, 3.7). Small opaque inclusions (≈ 5 mm) define a bundled acicular fabric which is further reflected in the pattern of divergent crystallite optic axes within the radial-fibrous mosaic (Fig. 3.4). The strained extinction of the inclusion rich fringe is continued into an optically continuous zone of clear pale brown calcite in both examples. The junction between inclusion rich and inclusion free calcite is sharp and defines a convex botryoidal surface toward the centre of the cavity (Fig. 3.4).

In specimen I the turbid fringe (1.5 mm thick) is generally non-ferroan while the clear strained calcite (0.25 mm) is zoned with minor Fe-rich bands parallel to euhedral crystal faces which terminate the first generation of calcite. Microscopic (5 to 10 μ m) dolomite inclusions are identified within the milky calcite: Mg-enrichment (to approximately 43% MgCO_3) is reflected in calcium depletion (while Fe, Sr, ^{and} ~~and Si~~ concentrations are virtually ^{and Si absent throughout} constant) in probe scans across the surface (Fig. 3.6). Further evidence for discrete (rhombic) Mg-enriched areas is provided by X-ray reflection images (Fig. 3.5) and the presence of a small amount ($\approx 5\%$) of dolomite is confirmed by XRD.

In specimen II Staining reveals an opposite relationship between iron content

I

II

III

Shell wall	Ferroan	Ferroan	Zoned
Pyrite	Stalactites + geopetal layer	Trace at shell margin	Trace at shell margin
Internal Sediment	Outer whorl chambers only	Geopetal layer in inner whorl	Outer whorl chambers only
Inclusions and Fe content	Single non-ferroan milky fringe + clear weakly zoned overgrowth. Microdolomite inclusions.	Single ferroan turbid fringe + non-ferroan overgrowth.	Multi-zoned with ferroan inclusion-rich zones and non-ferroan clear calcites.
Fabric	Radial-fibrous crystals. Bundles of radiating inclusions.	Radial-fibrous crystals. Bundles of radiating inclusions.	Complex, equant to ^{columnar} bladed radial and fascicular-optic crystals within radial-fibrous mosaic.
Continuity with late cement	Distinct early generation terminated by euhedral faces.	Irregular-gradational contact within drusy mosaic.	Irregular-gradational contact within drusy mosaic.
LATE CEMENTS	Partial void fill in some chambers. Early rhombs. Ferroan + Mg poor. $\delta^{18}O = -18\%$	Complete void fill. Ferroan + Mg poor. $\delta^{18}O = -7.5\%$	Complete void fill - inclusions define former faces of rhombohedra. Ferroan + Mg poor. $\delta^{18}O = -9\%$

Table 3.1 Summary of the diagenetic features of Specimens I, II and III

Table 3.2 Microprobe point analyses of calcites from the three specimens. Results are shown in weight % element. The range of values obtained are shown for calcites shown to be inhomogeneous by microprobe scans. Typical sensitivities are Ca 0.13, Mg 0.02, Fe 0.06, Sr. 0.03.

Description	Number of Analyses	Wt % Ca	Element (mean or range)		
			Mg	Fe	Sr
SPECIMEN I					
Shell replacement	15	38.53	0.21	0.56	0.08
Milky fringe	9	38.74	(0.16-2.82)	(0.01-0.38)	0.06
Clear, zoned, calcite	12	38.96	0.18	(0.0 -0.64)	0.01
Late cement	16	38.90	0.15	0.26	0.08
SPECIMEN II					
Shell replacement	6	40.05	0.10	0.49	0.06
Milky fringe	11	39.95	0.25	(0.42-1.06)	0.06
Non-ferroan spar	5	40.41	0.53	0.03	0.04
Late cement	15	39.34	0.11	0.43	0.07
SPECIMEN III					
Zone 2	4	38.59	0.48	0.01	0.05
Zone 3	5	38.31	0.13	0.61	0.08
Zone 4	4	37.45	0.50	0.03	0.04
Zone 5	4	38.90	0.17	0.52	0.05
Zone 6	3	38.48	0.47	0.16	0.03
Zone 7	4	38.90	0.17	0.53	0.05
Zone 8	4	38.35	(0.04-0.41)	(0.33-0.62)	0.04
Zone 9	6	39.07	0.05	0.24	0.03

and morphology in the early fringe ~~of specimen II~~ (Table 3.2).

Milky calcites are ferroan, with a decreasing iron content away from the shell wall culminating in a clear, non-ferroan calcite zone (Fig. 3.8, 3.9). There is no clear 'generation' boundary between early and late cement (Fig. 3.7, 3.10); trace element concentrations (other than Fe) are generally low in the early calcites (Table 3.3) with minor Mg enrichment in the non-ferroan zone.

Specimen III

Staining reveals nine zones of calcite which fill the chambers (Fig. 3.11). All nine zones occur within a single drusy spar mosaic, the separation of early, strained, calcites from the later, unstrained, cements approximately corresponds to the contact between zones 8 and 9 (Figs. 3.11, 3.13). There is a general increase in crystal size toward the centre of the void and a preferred orientation of long crystal axes normal to the substrate (Fig. 3.12).

The outer, strained, part of the crystal mosaic has irregular intercrystalline boundaries with individual crystal groups identified as radiaxial fibrous (*sensu* Bathurst, 1959) and fascicular optic (*sensu* Kendall, 1977) on the basis of internal structures (curved cleavage and crystallite optic axis orientation).

Zonal boundaries defined by variation in iron content correspond exactly to bands of different inclusion density. Iron content and the presence of inclusions together vary inversely with magnesium concentration (Fig. 3.16, Table 2); changes that are also reflected in the isotopic composition (see isotopic discussion below).

The outer zones of calcite (1 to 3, Fig. 3.16) only occur sporadically around the margins of each void; inner zones are successively more continuous. The pattern of growth and zone

coalescence is related to the present intercrystalline boundaries (Fig. 3.12); a feature which is of fundamental importance in the interpretation of the calcites and the origin of the zones.

LATE CEMENTS

Blocky ferroan calcites were the last diagenetic precipitates in all three specimens. Intuitively the unstrained calcites are cements; triangular inclusion ^{trails} ~~relies~~ indicate the presence of former crystal faces (specimen III, Fig. 3.13) but intercrystalline boundaries are extremely irregular and enfacial (180°) triple ^j functions are ~~very-rare~~ ^{by no means ubiquitous} (cf. Bathurst, 1975, p.417-9). Dickson (1977, 1978) has pointed out that many of the existing criteria for cement recognition (e.g. Bathurst, 1975) are based on simplistic growth models and that more complex fabrics including irregular intercrystalline boundaries can be produced by considering more realistic models for crystal propagation. The late ferroan spar is unzoned within the limits of detection of staining and microprobe scans.

In specimens II and III the late cement forms a single drusy mosaic with the early calcites and completely fills the septal voids. In I the late cement is recognised as a distinct second generation precipitate and it only partially fills some of the outer whorl chambers. In the incompletely filled chambers a few small (≈ 0.5 mm) yellow rhombic crystals (which may have undergone internal dissolution, Dr. A. Seager, Birkbeck College, personal communication) may represent an ~~intermediate~~ [?] stage of (dolomite) precipitation ^{between early and late calcites}. The small rhombic crystals were not found in sections cut for microprobe analysis and were too rare to be sampled for isotopic analysis.

NEOMORPHIC ORIGIN OF FABRICS AND ZONES

Early radial-fibrous calcites form isopachous linings to the septal chambers in specimens I and II where pattern of inclusions and botryoidal form (Figs. 3.2, 3.4) immediately suggest similarities with Recent acicular submarine cements (e.g. Schroeder, 1973, Ginsburg and James, 1976) and their ancient equivalents (e.g. Schlager, 1974, Davies, 1977, Scherer, 1977). Analysis of the crystal fabrics in specimen III has identified radiaxial-fibrous and fascicular-optic calcite mosaics which have been attributed to be the replacements of early acicular carbonates (Kendall and Tucker, 1973, Kendall, 1977). It is therefore suggested that all three ammonites originally contained syn-depositional isopachous acicular fringing cements. Strained extinction suggests that all the early calcites have undergone a degree of recrystallisation or secondary crystallite coalescence (primary, vadose coalescence proposed by Kendall and Broughton, 1977, is not applicable to these isopach^o_{us}, therefore probably phreatic calcites); their present morphological differences must therefore be attributed to the mode of replacement.

According to the mechanism of acicular carbonate replacement proposed by Kendall and Tucker (1973) and Kendall (1977) neomorphic crystals nucleate on the original substrate and the precursor fibres are recrystallised during the progressive advance of a replacement front. A similar model can be used to explain the morphological and chemical differences in the Bearreraig ammonite calcites.

In specimen I (Fig. 3.4) each original bundle of acicular ~~fibres~~ ^{fibres} has been replaced by an equivalent strained radial fibrous crystal. Divergent optic axes and inclusion trails (Fig. 3.4) indicate the position of the former acicular cement. Microdolomite inclusions and non-ferroan nature of the inclusion-rich fringe may indicate that

an original submarine high magnesium calcite cement has been replaced without a great deal of exchange with later pore-waters (cf. MacQueen and Ghent, 1970, Lohmann and Meyers, 1977, Lohmann, 1978) but see isotopic evidence below. The clear, zoned overgrowth (Fig. 3.4) may represent final stage replacement of the acicular fabric during which the neomorphic calcite was able to rid itself of inclusions. It more probably represents a later syntaxial overgrowth of clear calcite cement precipitated during, or immediately after, recrystallisation (cf. Kendall and Tucker, 1973, and Bathurst, 1975, p.427). A distinct generation boundary between early calcites and blocky cement implies that later precipitation took place as a separate event. There is no evidence of a biogenic layer which could have protected the fibrous cement during spar precipitation (cf. Orme and Brown, 1963).

Ammonite II's milky ferroan fringe has no microdolomite inclusions and both magnesium and strontium concentrations are low (Table 3.2, cf. Davies, 1977, Marshall and Ashton, in press), so there is no direct evidence for the nature of the precursor cements. The mechanism of replacement is similar to that observed in I. Low Mg + Sr concentrations together with high iron content (Table 3.2) indicates recrystallisation by open exchange with late reducing pore-waters. Fabric continuity with both the shell wall and late cement (Fig. 3.10) is further evidence for virtually synchronous replacement of the submarine fringe and shell wall, together with "late" cementation of the central void. The clear non-ferroan zone must represent local reduction in the availability of iron or changes in the local chemical environment (see below).

Specimen III: the close association of fascicular-optic and radiaxial fibrous calcites is common in voids formerly occupied by

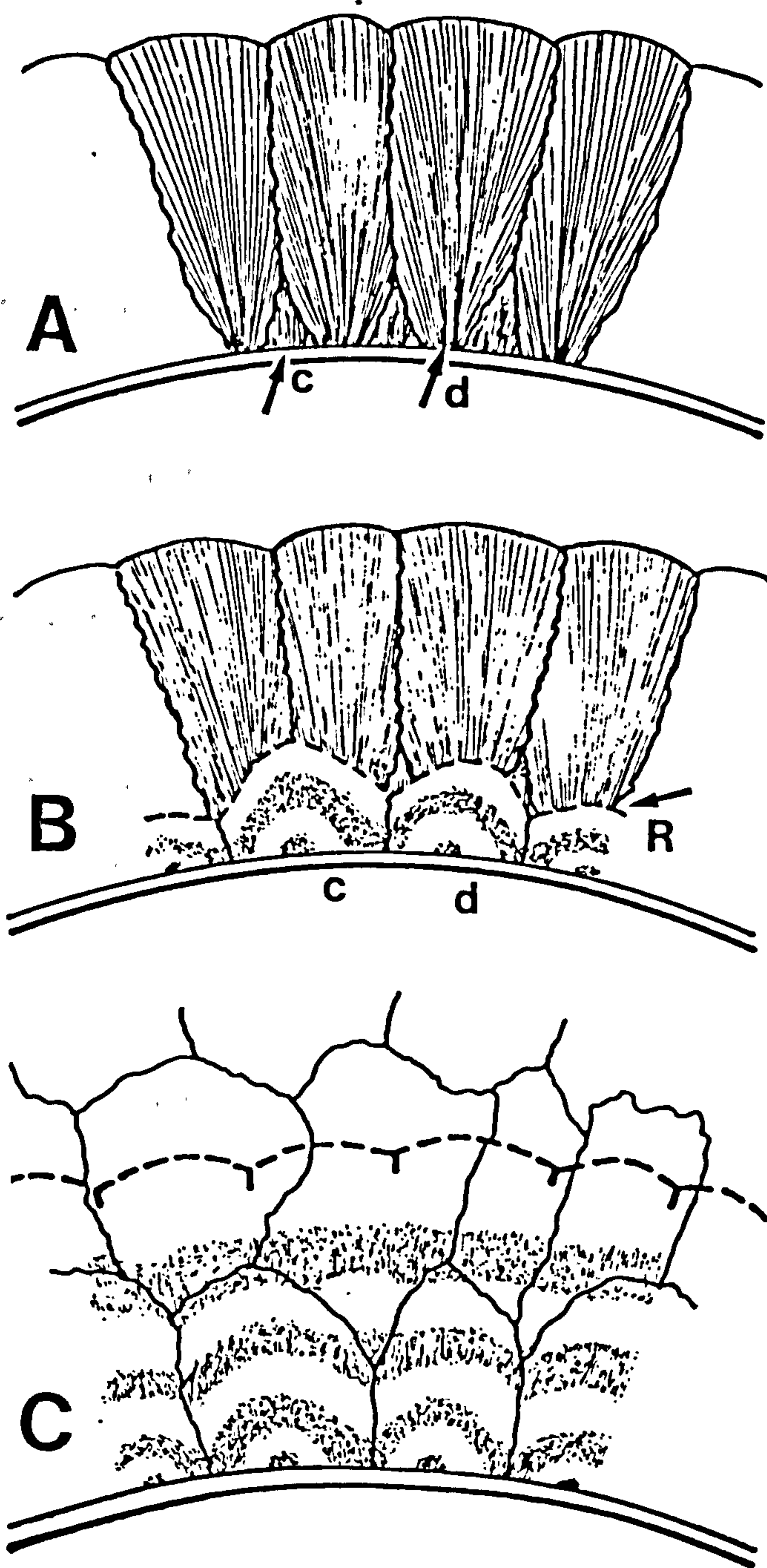


Figure 3.14. Development of the multiple zonation in ammonite III.

- A - initial fringe of bundled acicular cement (c and d mark the nucleation site of replacement crystals which will develop convergent and divergent internal optic axis orientations, respectively).
- B - Fabric during replacement. R marks the position of the 'replacement front'.
- C - Fabric after completion of replacement and cementation.

early submarine cements (e.g. Kendall, 1977, Chafetz, 1979). The differences in intracrystalline fabrics between the two crystal types is explained by differences in the choice of nucleation site of the neomorphic calcite. Replacive growth nucleated between bundles of acicular fibres will produce radiaxial-fibrous calcite with its characteristic convergent optic axes and convex twin lamellae (e.g. Kendall and Tucker, 1973) whereas neomorphic growth which coincides with the original fibre bundles will give rise to fascicular optic and radial fibrous calcites (Kendall, 1977). Zonal boundaries (stain and inclusion bands) in specimen III are apparently related to former growth ^{fronts} ~~faces~~ of the present, replacive, crystal fabric. Outer zones are discontinuous, and sporadically developed in contact with the shell wall (Figs. 3.11, 3.12); inner zones are progressively more continuous, reflecting coalescence to a single replacive front in later stages of alteration (Fig. 3.14). Interzonal differences in trace element and isotopic composition (Fig. 3.17) must represent changes during replacement environment rather than during original growth (see isotope discussion).

The continuous mosaic between early, strained calcites and later blocky cement again testifies to continuity between fringe replacement and late cementation. Zones developed within the shell walls demonstrate simultaneous replacement of shell aragonite and early cement. As in specimen II there is no direct trace element evidence for the nature of the precursor cement.

ISOTOPES

Separated calcites from the three ammonites exhibit a wide range of isotopic composition (ranges of almost 20‰ in $\delta^{18}\text{O}$ and more than 25‰ $\delta^{13}\text{C}$; Fig. 3.15, Tables 3.3, 3.4, 3.5). Scatter diagrams show a general trend from light carbon, heavy oxygen to heavy carbon, light oxygen values in the late cements (Figs. 3.15, 3.16). The overall pattern is common to sediments with availability of organic material limited to early diagenesis and later cementation at depth after considerable temperature increase and modification of the pore water composition (e.g. Hoefs, 1970, Tan and Hudson, 1974, Hudson and Friedman, 1976, Hudson, 1978(a)). The isotopic composition of each group of calcites will be discussed with reference to the scatter plots.

CARBON

The range of $\delta^{13}\text{C}$ values can be explained by changes in the relative contributions of light 'organic' carbon (average $\approx -25\%$, Garlick, 1969) and heavy, marine bicarbonate ($\delta^{13}\text{C} \approx 0\%$) during diagenesis.

The strained calcites have light $\delta^{13}\text{C}$ values which indicate an early source of organic carbon. Pyrite formation testifies to early bacterial activity which would release suitably light bicarbonate, but quantities of pyrite are too low for bacterial sulphate reduction to have been the sole source of organic carbon (cf. Raiswell, 1976, Hudson, 1978). Other processes of organic decay must have been active in early diagenesis (e.g. Hodgson, 1966). The most extreme $\delta^{13}\text{C}$ value in the outermost zone of specimen III (-26.5%) suggests formation from pure organic matter or equilibration with a source of extremely light carbon (cf. Recent, methane

Table 3.3 Isotopic composition of separated calcites from Specimen I

SPECIMEN I

Sonninia (Papilliceras) mesacantha (Waagen)

Sample	Description	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$
SHELL REPLACEMENT CALCITES			
A3	Pale brown, ferroan calcite, replacing outer shell wall	-7.40	-3.97
A8	Pale brown, ferroan calcite, replacing outer shell wall	-12.82	-3.22
A7	Pale brown, ferroan calcite, replacing septal wall	-7.24	-4.92
FIRST GENERATION CEMENT			
A2	Milky fibrous isopachous non-ferroan calcite	-13.27	-6.59
A4	Milky fibrous isopachous non-ferroan calcite	-10.70	-8.12
A6	Pale brown inclusion free overgrowth cement	-10.54	-8.09
SECOND GENERATION CEMENT			
A1	Blocky inclusion-free ferroan calcite	-1.71	-19.06
A5	Blocky inclusion-free ferroan calcite	-1.09	-17.65
CALCITE CEMENTED INTERNAL/EXTERNAL SEDIMENT			
A9	Internal sediment	-11.78	-11.25
A38	External sediment	-10.24	-8.67

Table 3.4 Isotopic composition of separated calcites from Specimen II

SPECIMEN II

Sonninia (Papilliceras) arenata (Quenstedt)

Sample	Description	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$
SHELL REPLACEMENT CALCITE			
A27	External shell wall	-3.58	-9.60
EARLY (STRAINED) CALCITES			
A21	Milky fibrous ferroan isopachous calcite	-11.58	-5.48
A22	Pale brown, inclusion-free, non-ferroan calcite	-18.46	-2.00
LATE (GRANULAR) CEMENTS			
A23	Granular ferroan spar - outer zone	-0.99	-6.31
A24	Granular ferroan spar - inner zone	-0.29	-7.63
A25	Blocky ferroan spar - in centre of cavity	0.03	-8.68
CALCITE CEMENTED INTERNAL/EXTERNAL SEDIMENT			
A26	Calcareous sandstone in outer whorl chamber	-5.25	-12.79
A36	Calcareous sandstone in outer whorl chamber	-3.20	-8.08
A37	External calcareous sandstone	-7.37	-7.99

Table 3.5 Isotopic composition of separated calcites from Specimen III

SPECIMEN III

Sonninia (Papilliceras) arenata (Quenstedt)

Sample	Description	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$
SHELL REPLACEMENT CALCITE			
A19	Outer shell wall - external lamination	-1.83	-8.24
A20	Outer shell wall - internal lamination	-1.85	-5.05
A18	Internal septal wall	-10.49	-2.44
EARLY (ZONED) CALCITES (Zones as in Figs. 3.11, 3.13)			
A11	Zones 1 + 2	-25.86	-0.65
A12	Zone 3	-9.47	-5.89
A13	Zone 4	-15.69	-3.12
A14	Zone 5	-10.14	-5.69
A15	Zone 6	-12.28	-2.31
A16	Zone 7	-7.23	-3.75
A16 R	Zone 7	-3.84	-6.54
BLOCKY FERROAN CALCITE			
A17	Blocky ferroan calcite - late cavity fill (Zone 9)	0.18	-7.70
A17 A	Blocky ferroan calcite - late cavity fill (Zone 9)	-0.67	-10.10
INTERNAL SEDIMENT			
A35	Calcareous sandstone in outer whorl	-13.83	-9.02

equilibrated aragonite and high magnesium calcite cements of Hathaway and Degens, 1969). Contribution of organic derived carbon decreases in the later precipitates and there is no evidence of the successive burial stages, each with distinctive $\delta^{13}\text{C}$ proposed by Curtis 1978, and Irwin et al., 1977. The late cements have $\delta^{13}\text{C} \pm 0\%$ suggesting that the dissolution of marine carbonates dominated the deep burial bicarbonate supply (Hudson, 1975).

OXYGEN

Void-filling calcites from each specimen define distinct diagenetic trends on the isotopic scatter diagram (Fig. 3.15; cf. Hudson, 1978). Early calcites in each ammonite have the heaviest $\delta^{18}\text{O}$ values but the majority even of these are too light to reflect equilibrium with normal sea water under shallow burial conditions; values must therefore indicate an early source of O^{18} depleted water or re-equilibration with light water or at increased temperature during recrystallisation (see discussion below).

Early Calcites

Sample All. from the outermost zone of early calcite in specimen III has the lightest $\delta^{13}\text{C}$ and the heaviest $\delta^{18}\text{O}$ values encountered in any of the samples (Fig. 3.15, Table 3.5). Diagenetic trends are toward depletion in O^{18} and C^{12} so this zone has apparently suffered least subsequent diagenetic alteration. The $\delta^{18}\text{O}$ value (-0.65) would indicate equilibrium precipitation in seawater of normal oceanic composition at a temperature of approximately 14.5°C (using the equation and assumption $\delta^{18}\text{O}_{\text{WATER}} = -1.2$ of Shackleton and Kennett, 1975) which is a reasonable estimate for shallow burial conditions in a sea with surface temperatures of around 20°C (Tan et

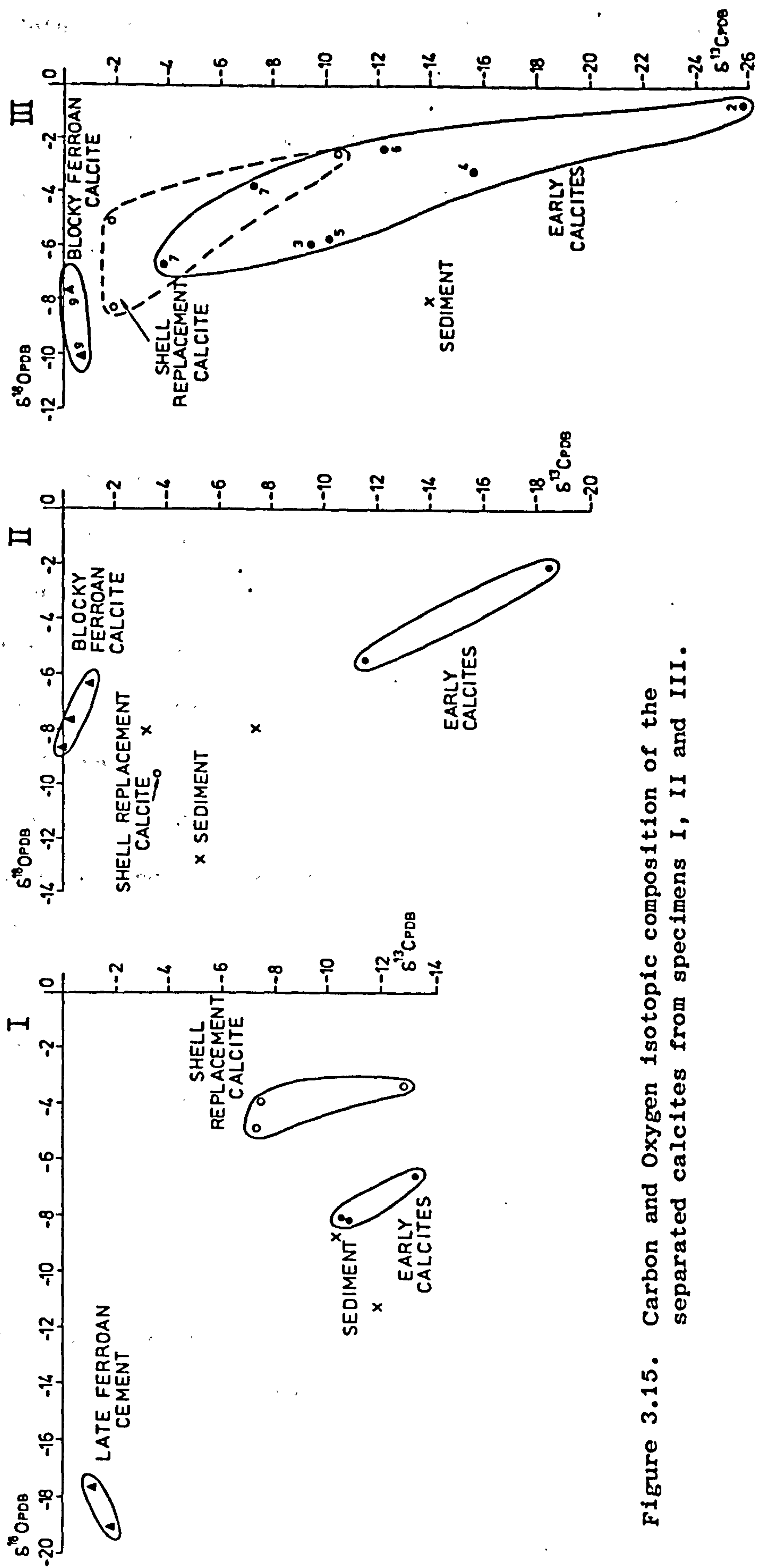


Figure 3.15. Carbon and Oxygen isotopic composition of the separated calcites from specimens I, II and III.

et., 1971, determination for the overlying Great Estuarine Group sediments in Skye). There is therefore no evidence of an early supply of $\delta^{18}\text{O}$ depleted bicarbonate in association with the maximum input of organic carbon and it is likely that the other "early" calcite values were modified during later re-equilibration (see discussion of zones).

Late Cements

Late cements are characterised by negative $\delta^{18}\text{O}$ values in each ammonite (Tables 3.3, 3.4, 3.5; Figs. 3.15, 3.16). The trend toward lighter $\delta^{18}\text{O}$ in later precipitates is a common feature in sediments from all geological environments. Temperature increase and corresponding changes in the isotopic fractionation factor cannot usually explain the magnitude of the depletion (cf. Scholle, 1974) and mechanisms for the diagenetic evolution or mixing of pore waters have been proposed (see discussion in Hudson, 1978, or Chapter 5 of this thesis). Isotopic data from the Bearreraig ammonites are not sufficient to determine the nature of the process which caused $\delta^{18}\text{O}$ depletion but it is obvious that the late diagenetic pore waters must have had a modified oxygen isotopic composition. Void-filling calcites from specimens II and III exhibit virtually coincident diagenetic trends (Fig. 3.15) toward late cements with $\delta^{18}\text{O} \approx -10\%$. The scatter of values along clearly defined trend lines (Fig. 3.16) may be an indication of gradual evolution of the pore water composition (cf. Dickson and Coleman, in press) or may reflect the degree of early calcite re-equilibration (see discussion of zones below).

The values from the shell calcites of specimen I fall on the same trend as the void and shell calcites from II and III rather than on the diagenetic trend defined by ammonite I's own calcites

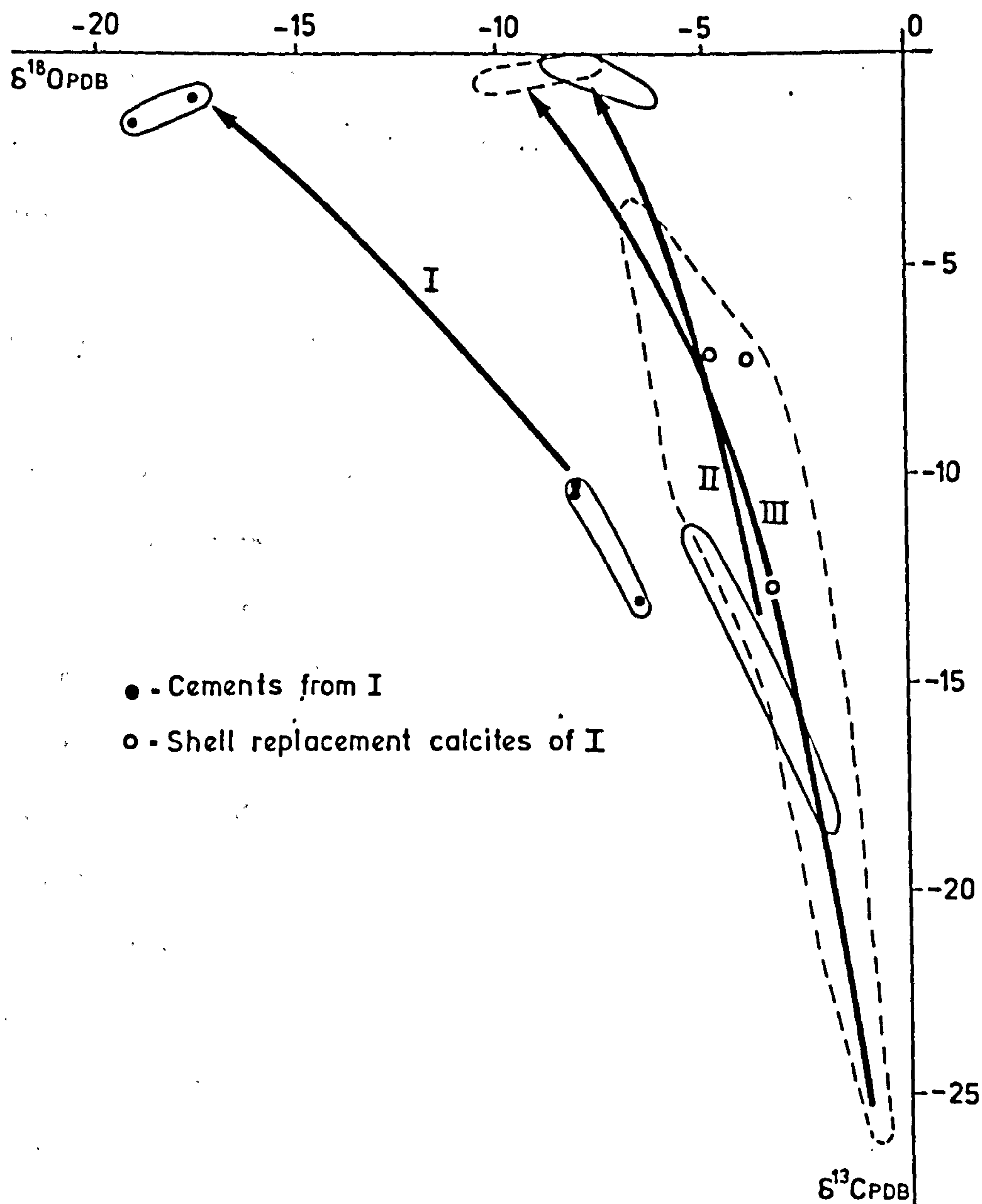


Figure 3.16. Carbon and oxygen isotopic trends for the 3 specimens. The shell replacement calcites from specimen I coincide with the evolutionary/mixing trend from II and III.

(Fig. 3.16). All the other calcites from specimen I, including the early cements which appear to have retained their original trace element composition, and the host sediment values from II and III are notably depleted in O^{18} (Fig. 3.15). The late cements are almost 10% lighter than their counterparts in specimens II and III.

From the distribution described above specimen I's shell re-equilibrated in the same burial pore-waters as did the calcites from II and III but the late cement (and to some extent the early calcite) was affected by pore waters of unusual temperature or isotopic composition. Ten 'per mil' additional fractionation by local diagenetic reactions is extremely unlikely so an external source of 'light' or 'hot' water must be sought. The extremely 'light' values in specimen I calcites probably therefore reflects increased temperature during Tertiary igneous activity. Trace element and carbon isotope compositions are virtually identical to those from the late cements in II and III the oxygen values probably reflect the input of already modified water which had been heated by about an additional $50^{\circ}C$.

DISCUSSION - ISOTOPES AND ZONES

Individual zones apparently preserve chemical compositions which differ from those of adjacent calcites: is it possible to relate the pattern of changes in isotopic and trace element concentrations to the process of zone formation?

In specimen III there are nine zones of ~~pore-filling~~ calcite which, it has been demonstrated, originated during the replacement of a single fringe of acicular cement. There is an apparent correlation between changes in trace element composition, inclusion density and isotopic values (Fig. 3.17). Changes in trace elements correspond

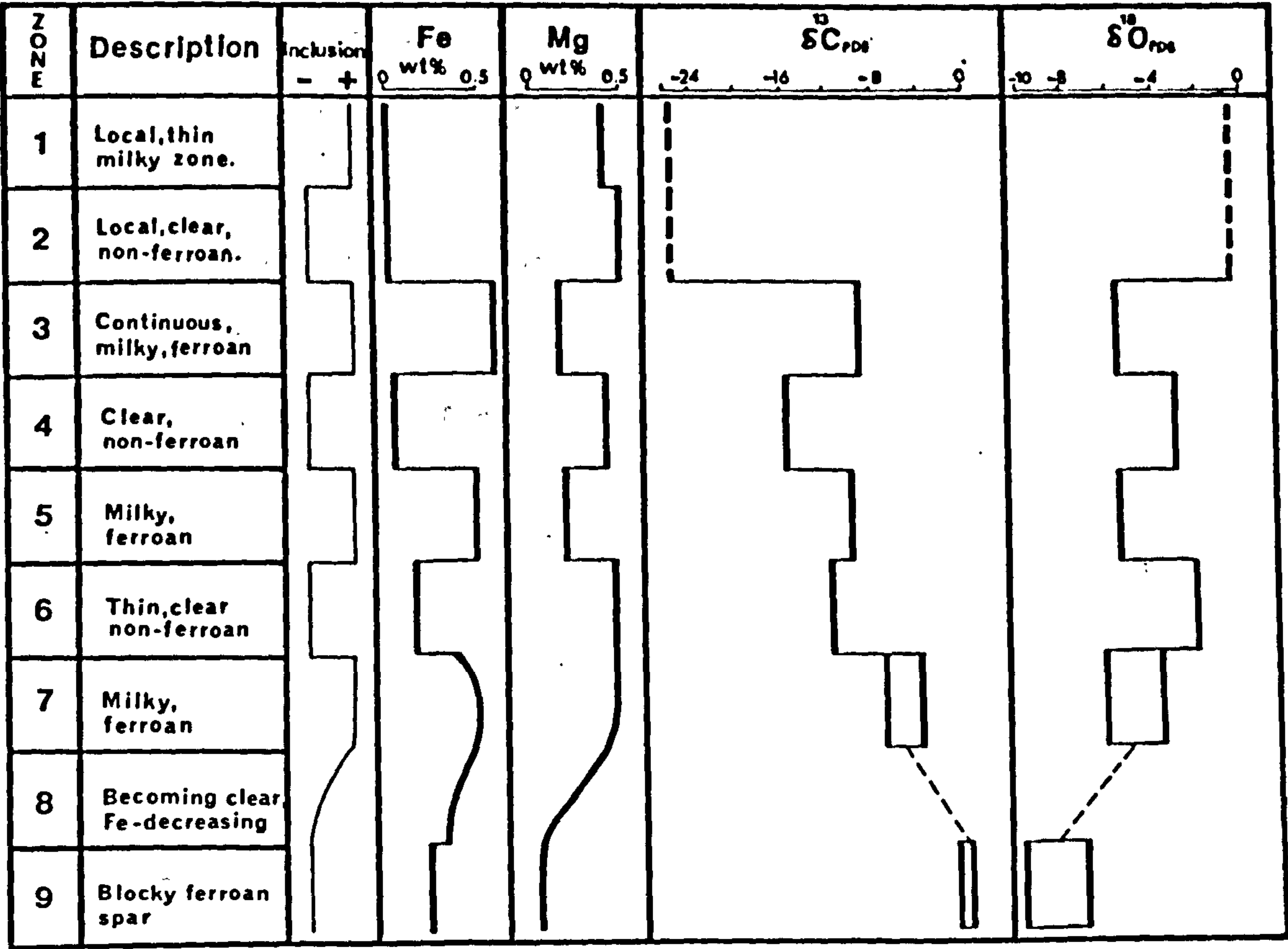


Figure 3.17. Specimen III: correlation of isotopes, trace elements and inclusion density. (Zones 1-9 as in Fig. 11.2).

exactly to the boundaries of inclusion rich zones; it was possible to cross-check this pattern by the use of staining, microprobe point analyses (Table 3.2) and repeated microprobe scans. There is no 'a priori' reason to assume that isotopic composition changes exactly in phase with either trace element or fabric variation, (Chapter 4 of this thesis), but samples taken from individual zones are commonly depleted or enriched with respect to both neighbours (Fig. 3.17) so, in view of sampling difficulties, the reversals probably reflect the minimum variation in isotopic composition that occurs. Further caution in accepting the pattern of isotopic variation (Fig. 3.17) is introduced by the differences in repeat analysis of the innermost zones ('boxes' in Fig. 3.17) which show intrazonal variability of similar order of magnitude to the steps in isotopic composition. However, for the reasons stated above and in view of the consistent correlation of isotopic and trace element variation within specimens II and III further interpretation will be based on the assumption that the pattern in Fig. 3.17 represents real changes in isotopic composition.

In the early calcites in II and III there is consistent correlation between inclusions, trace elements (Fe + Mg) and both carbon and oxygen isotopic variation; for ease of description it is possible to recognise two types of zone:

Type A. Inclusion free, non-ferroan, Mg rich, relatively light carbon and relatively heavy $\delta^{18}O$.

Type B. Inclusion rich, ferroan, Mg poor, relatively heavy carbon and relatively light $\delta^{18}O$.

The overall diagenetic trends in the three ammonites have been shown to be:

- (a) from light to heavy carbon
- (b) from heavy to light oxygen
- (c) from non-ferroan to ferroan calcites
- and (d) from magnesian to non magnesian (assuming precursor cements were high magnesium calcite as in specimen I).

This implies that Type A zones are more 'primitive' than Type B; they represent, earlier, less evolved, diagenetic conditions. A further clue to the origin of the zones is provided by the pattern of inclusion density, Type A zones are inclusion free and Type B zones inclusion rich. The presence or absence of inclusions in replacive crystals is probably related to the rate of neomorphic growth (e.g. Spry, 1969, p. 173); inclusion free calcites represent periods of slow growth during which the calcite was able to expel inter-acicular inclusions while the inclusion-rich calcites demonstrate periods of more rapid growth.

Zonal boundaries therefore represent changes in the growth rate of the neomorphic crystals and, from trace element and isotopic considerations, degree of exchange with the external evolving or, more probably, already evolved pore waters. Present isotopic values represent the relative contribution of original, metastable carbonate and bicarbonate introduced by the later burial pore waters. Changes in pore-water flow conditions and hence the effective water:rock ratio during neomorphism can account for the zonal differences. The more primitive non ferroan (Type A) zones in both II and III represent periods of lower pore water flow, marginal magnesium enrichment in comparison to the ferroan zones (Fig. 3.17), may indicate that the precursor cements were high magnesium calcite (cf. specimen I and Marshall and Ashton, in press), but the magnitude of the likely Mg depletion in all the zones implies considerable exchange with burial

pore waters.

Calcite zones therefore developed as a result of changes in the availability of external pore waters in later diagenesis. The ammonites were collected from within a few metres of each other yet have developed quite different zonal patterns. The changes in 'openness' of the diagenetic system must be related to conditions local to each specimen and therefore probably reflect the development of the calcite-cemented concretions in which the ammonites occur. Unfortunately, the ammonites were collected as palaeontological specimens and samples of the adjacent concretion were not collected at the same time. 'Sediment' isotopic values (Fig. 3.15, Tables 3.3, 3.4, 3.5) represent the immediately adjacent concretion but show no clear relationship to the void-filling calcites. $\delta^{13}\text{C}$ values are negative but variable and $\delta^{18}\text{O}$ values are within the range of late cements. In view of the complex diagenetic history of the ammonites the values are probably 'composite' and reflect cement addition at more than one stage. With the present data it is not possible to identify the mechanism which produced such localised changes in the availability of external pore water.

SUMMARY - DIAGENETIC HISTORY OF THE THREE AMMONITES

A complex pattern of events has led to the development of the present fabrics and chemical zones (Fig. 3.18); these can be summarised in the form of a brief diagenetic history.

1. Deposition and shallow burial. The three ammonites escaped early fracturing and provided suitably isolated 'microenvironments' for early bacterial activity and consequent pyrite precipitation. The semi-protected surroundings, still in contact with circulating seawater, provided a site for the precipitation of a fringe of acicular metastable carbonate (probably high magnesium calcite) in each of the three specimens.
2. During burial - temperature increased and early bacterial and other organic reactions ceased - to be replaced by a supply of marine bicarbonate. The pore-waters became additionally depleted in $\delta^{18}O$ due to either diagenetic reactions or mixing with a supply of meteoric water. At this stage the three ammonites developed their characteristic features.

I - was almost sealed; at least there was no free flow of pore water through the ammonite. The shell re-equilibrated with the evolved pore water and the fringe of early cement probably started to stabilise to low magnesium calcite with microscopic dolomite inclusions.

II - was relatively open to exchange with the ground waters. The fringe started to recrystallise under more or less open conditions but exchange gradually became more restricted (gradual decrease in Fe^{II}) and the rate of replacement slowed down (clear non-ferroan zone). Renewed supply of external pore-waters after the complete stabilisation of the fringe caused syntaxial growth of the late cement in the residual voids.

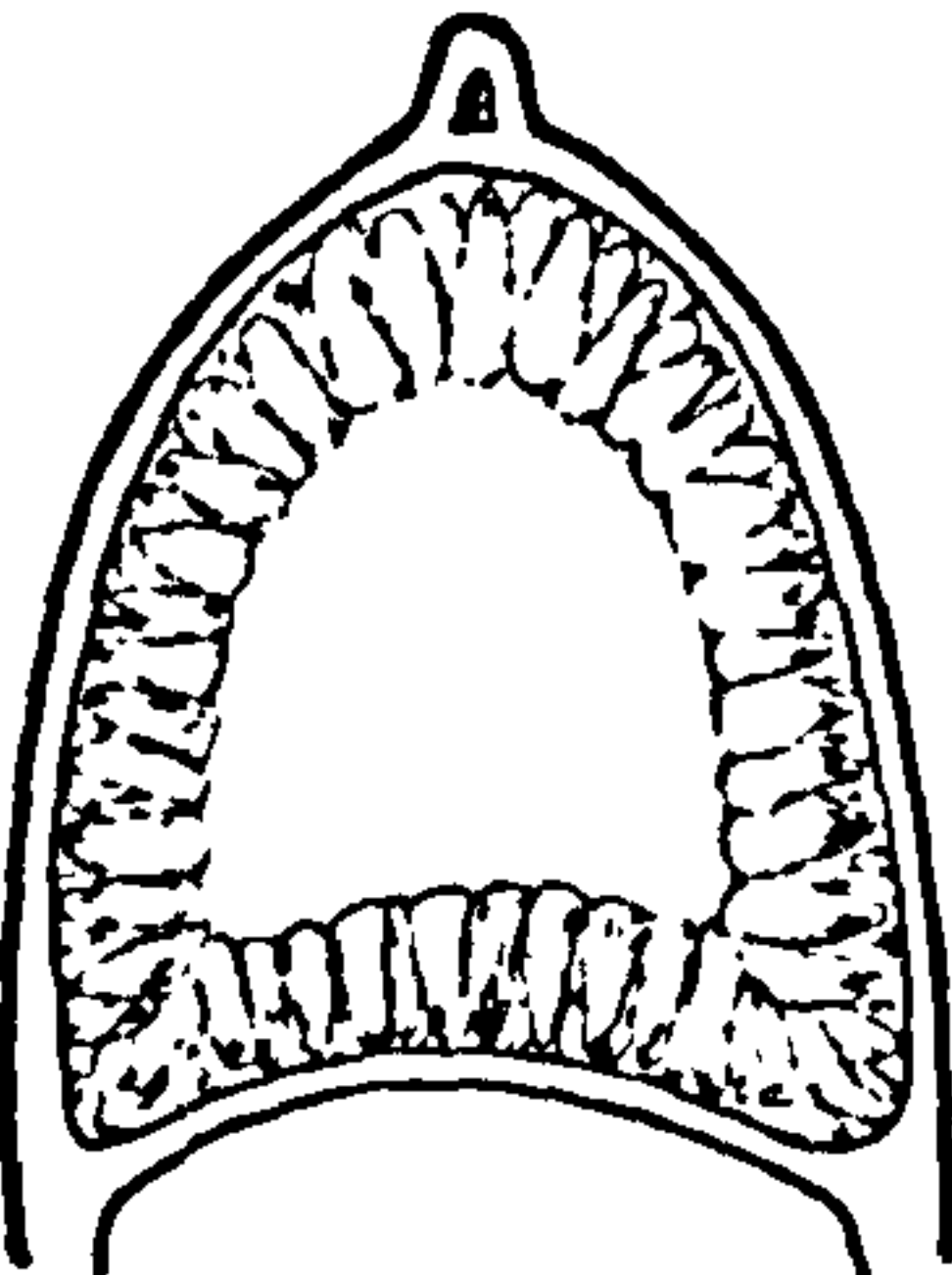
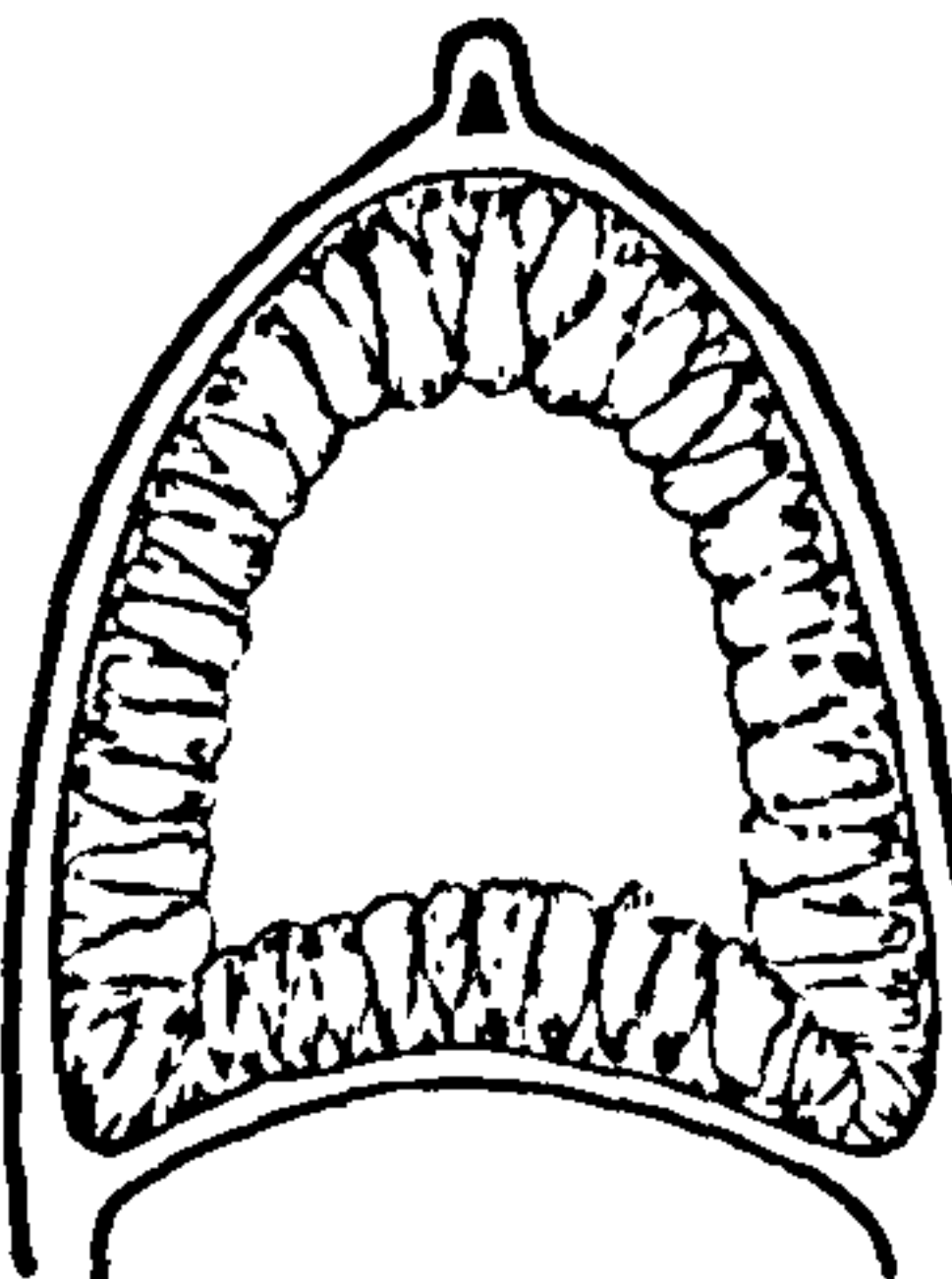
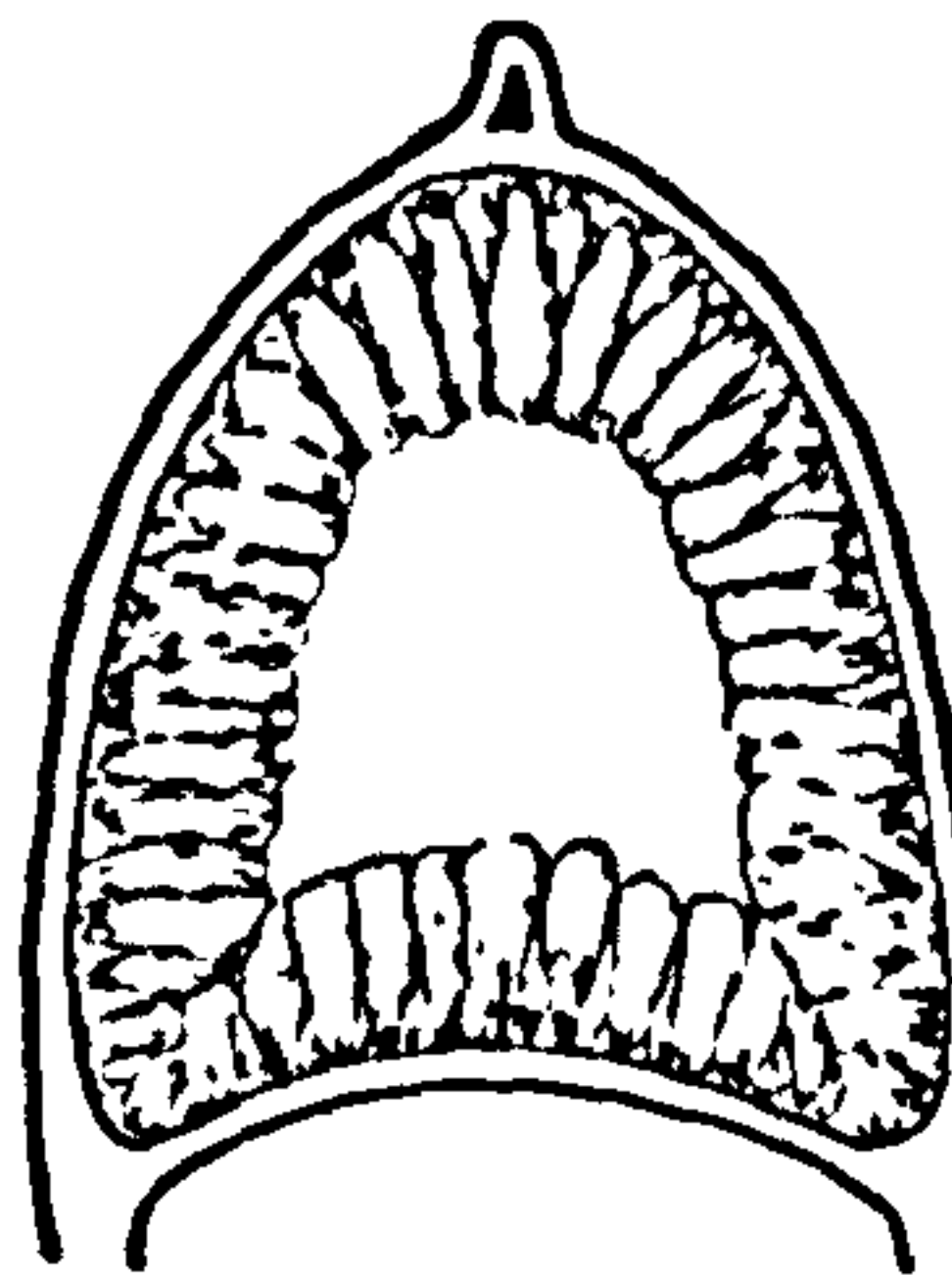
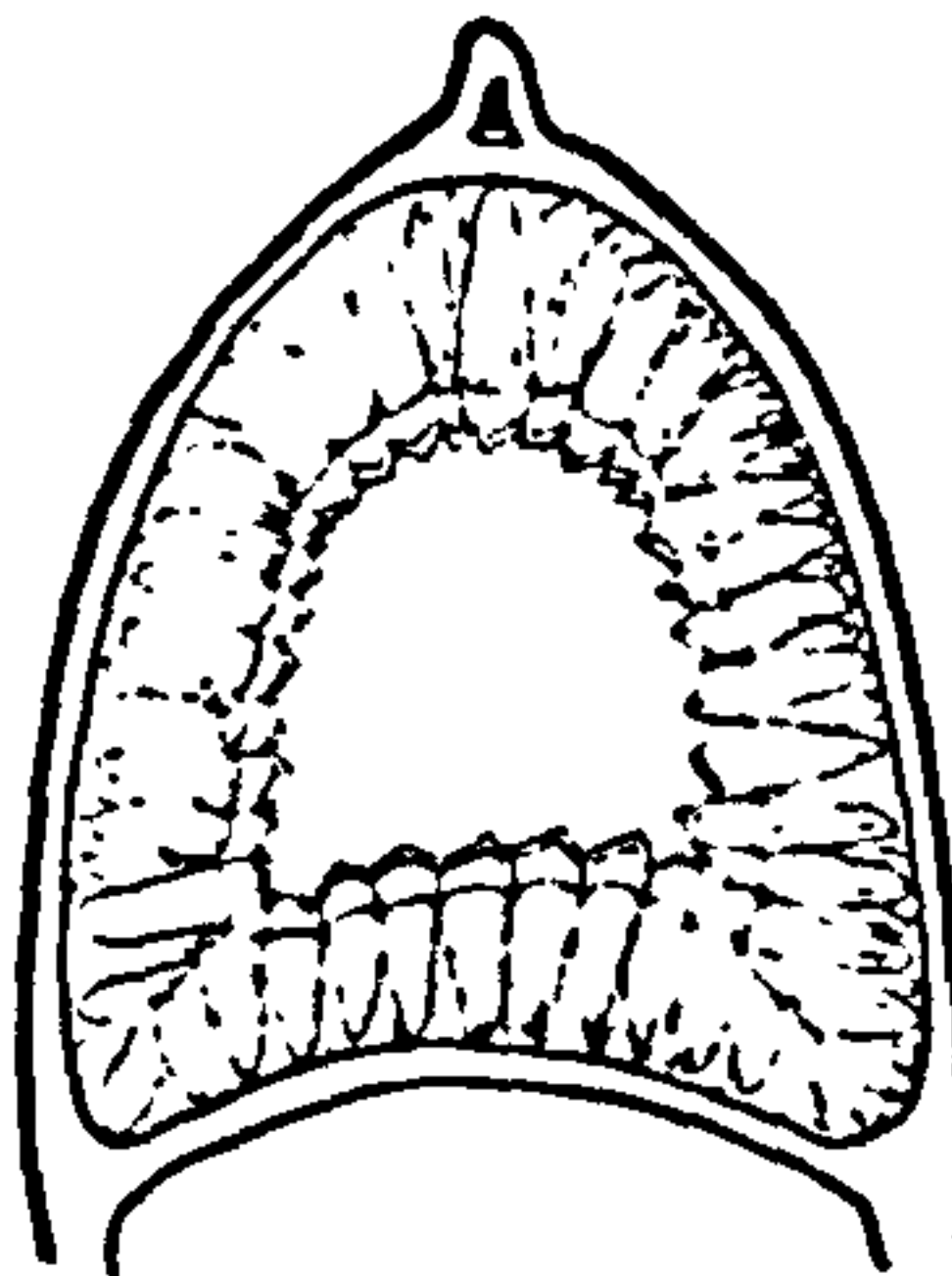
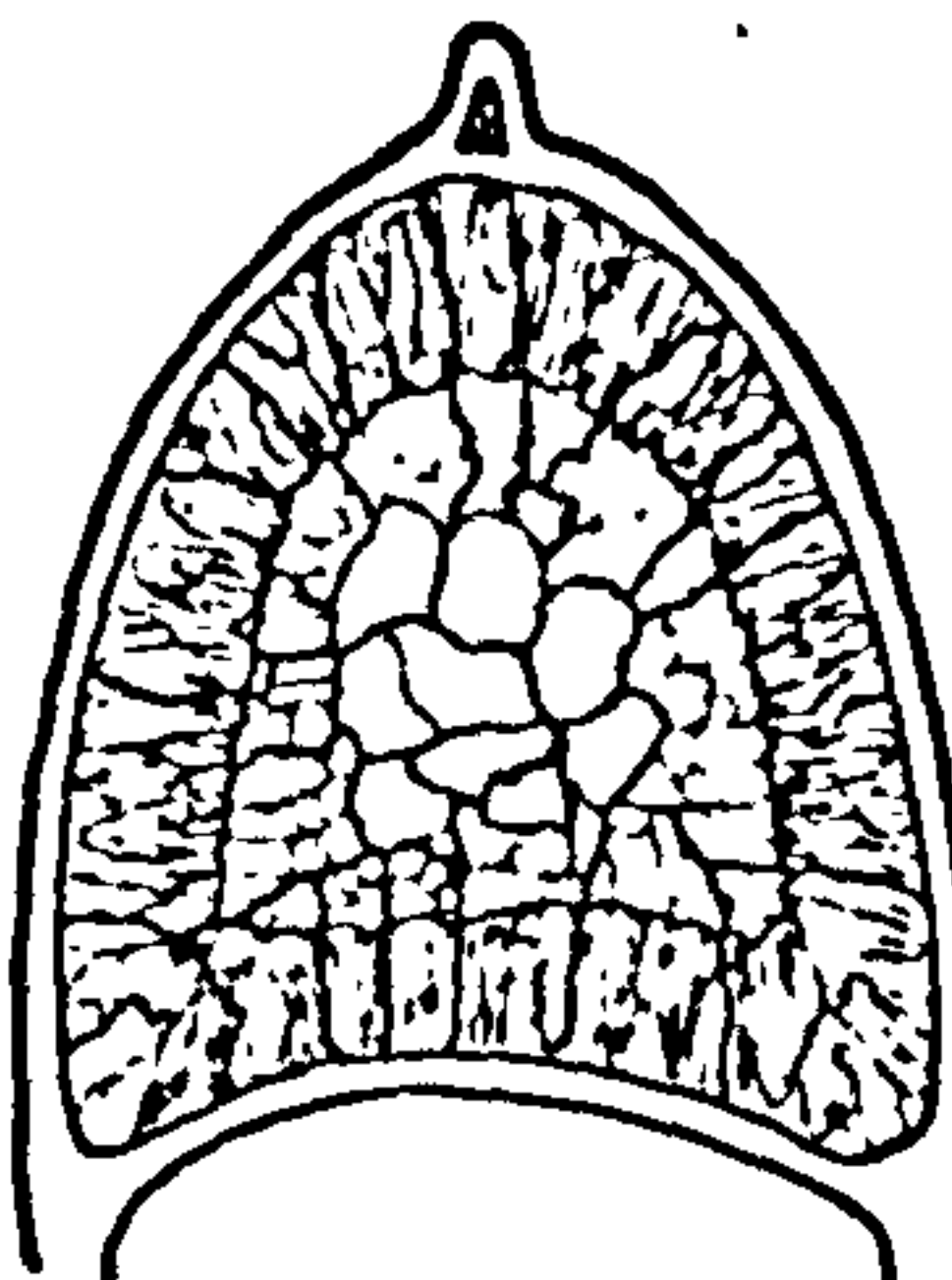
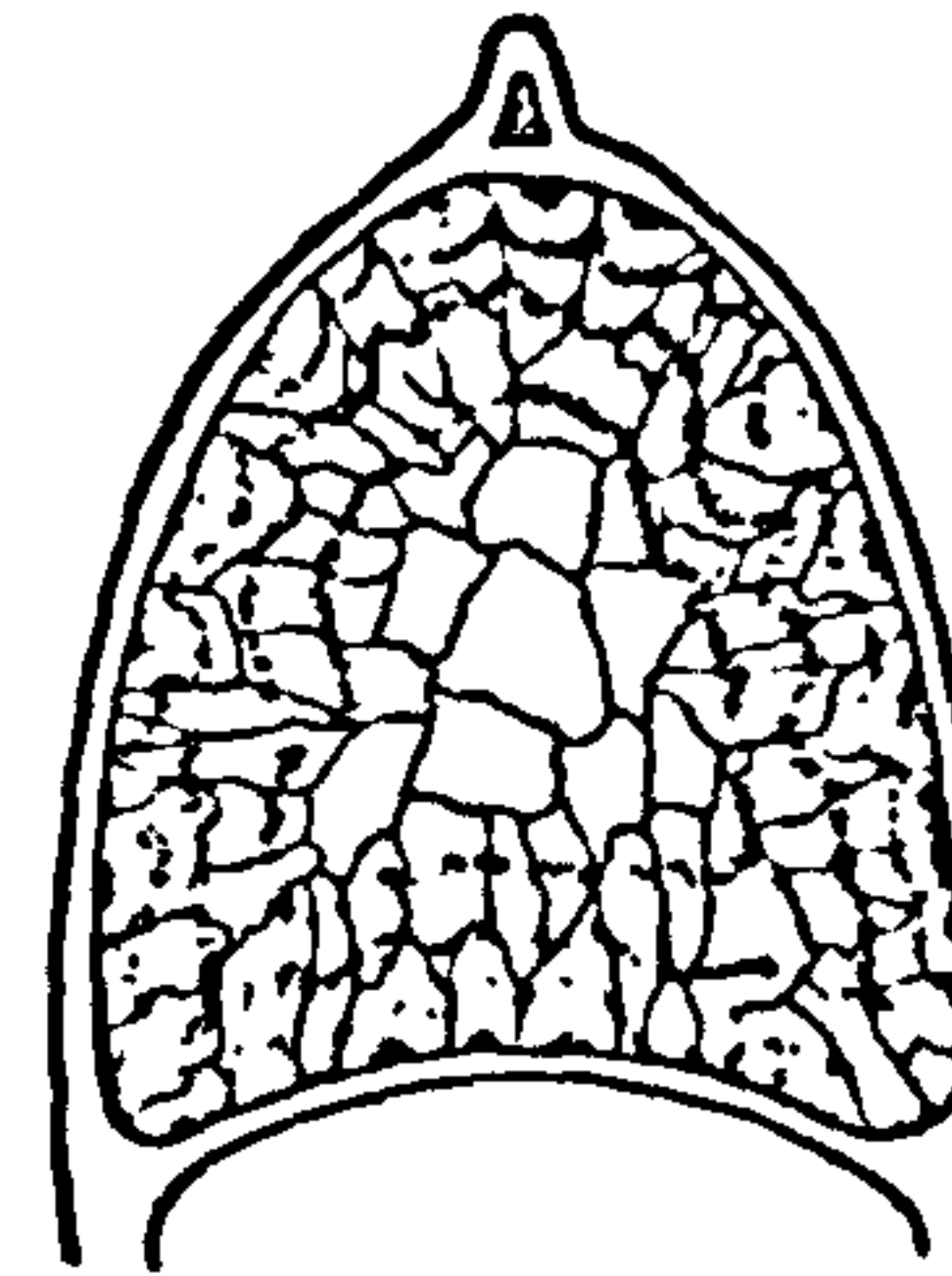
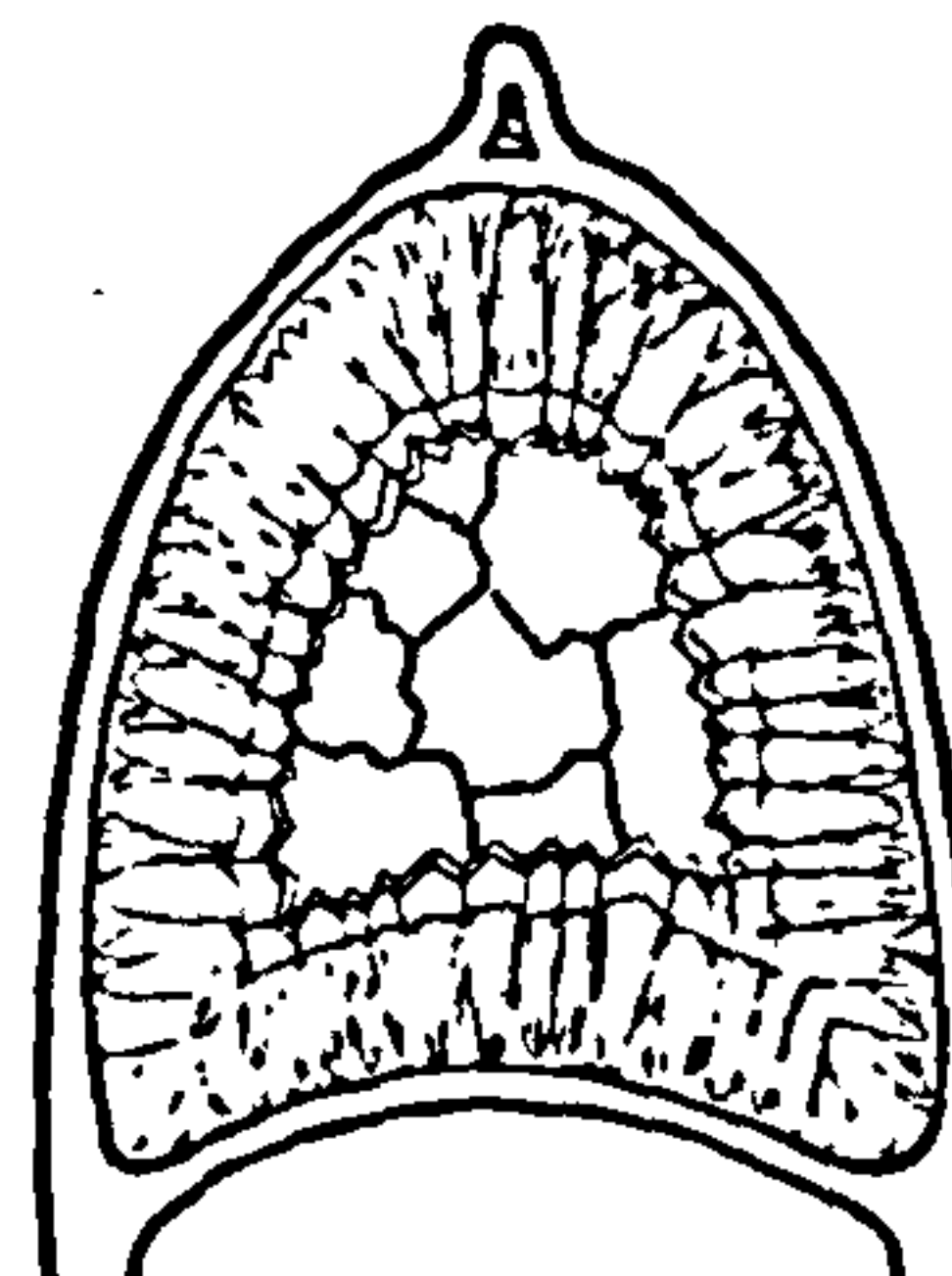
BURIAL STAGE	SPECIMEN		
	I	II	III
Shallow Burial :— less than 5m? (Middle— —Jurassic)			
PRECIPITATION OF A FRINGE OF BUNDLED ACICULAR CEMENT			
During Burial :— 450m,?, maximum (M.Jurassic to ?, Cretaceous)			
High-Mag. Calcite goes to Calcite + Microdolomite Clear, zoned Calcite precipitated. — Shell replaced			
Total Recrystallisation & Cementation			
Gradual Neomorphism & Cementation produces Multiple Zones			
+Warm Water (Tertiary igneous activity)		NO CHANGE	NO CHANGE
Final Cementation & Stabilisation			

Figure 3.18. Schematic summary of the diagenetic history of the three ammonites.

III - replacement started in a system with a low effective water:rock ratio enabling retention of the primary isotopic composition but loss of the magnesium from the precursor cement. The nucleation site of the replacement crystals with respect to the original bundles of fibres determined the nature of the internal structure of the neomorphic crystals (radial, fascicular or radial fibrous). Three separate episodes of renewed access of the external pore water together with intermediate periods of slow recrystallisation gave rise to zonation within the replacement fabric. Late ferroan cement again filled the residual void space.

3. Finally - during Tertiary igneous activity hot pore water was circulating through the sandstones, some found its way into the central cavity in specimen I. Final stabilisation of the fringe took place and late ferroan spar grew as a discrete second generation of cement.

CONCLUDING REMARKS

In concentrating a large number of analyses on a few specimens it has been possible to demonstrate the importance of intracrystalline variation in chemical composition and how the local (micro-) environment can determine the pattern of fabrics, trace element distribution and above all isotopic composition of diagenetic calcites. The story of these three ammonites is a further cautionary tale for those who attempt to interpret 'whole-rock' isotopic and geochemical data!

ISOTOPIC COMPOSITION OF DISPLACIVE FIBROUS CALCITE VEINS:
 REVERSALS IN PORE WATER COMPOSITION TRENDS DURING BURIAL
 DIAGENESIS

ABSTRACT

Stable isotope and petrographic analyses of diagenetic calcite (cone-in-cone and 'beef' veins) from British Jurassic and Lower Cretaceous shales are used to determine the environment of precipitation of fibrous calcites. Successive growth took place by antitaxial displacive addition at the vein margins, away from primary sedimentary laminations or early diagenetic concretions. Carbon and oxygen isotopic ratios ($\delta^{13}\text{C} \pm 0$ $\delta^{18}\text{O}$ -4 to -11) indicate a relatively late diagenetic origin (tens or probable hundreds of metres burial) for the veins; after cessation of bacterial activity and considerable modification of the oxygen isotopic composition of the pore water. Vein growth was discontinuous and took place in waters of changing isotopic and trace element composition. Changes are not unidirectional and are unlikely to result from the simple evolution of a single connate pore water; reversals in isotopic trends indicate that precipitation took place during periods of renewed (lateral?) groundwater flow, tapping different sources of bicarbonate.

INTRODUCTION

The suggestion that shales are potential donors of carbonates for porosity-^{re}producing cements in adjacent sandstones and limestones has added impetus to the study of the chemical composition of diagenetic carbonates in the shales themselves.

Diagenetic fibrous calcite ('cone-in-cone' and 'beef') veins are common features in shales and marls throughout the stratigraphic column, their morphology has been studied for more than 120 years but controversy remains over the time and mechanism of emplacement and the chemical environment in which precipitation took place.

A diagenetic origin for the veins was recognised by Sorby (1860) who noted formation of cone-in-cone structure by the "mutual interference" of radiating bundles of fibrous crystals. Vein growth is commonly shown to have been displacive; impressions of a fossil can be found on the upper and lower surfaces of the same vein (Brown, 1954, Woodland, 1964, and this study) and shale inclusions may be ruptured into crude conical form ('cone-cups' of Woodland, 1964). Association with organic matter (Hodgson, 1966, Franks, 1969; Tarney and Schreiber, 1976) or with aragonitic fossils (Usdowski, 1963, El Shahat, 1977) has led to the suggestion of alternative sources for the carbonate. The relationship between the apical angle of the conical structures and the likely plasticity of the surrounding sediments (acute angle = high plasticity and V.V.) has led to the conclusion that veins grew in early diagenesis under a cover of only a few metres of sediment (Franks, 1969). However many veins post date concretions whose curved internal laminae reveal syncompactional growth (e.g. Lang et al. 1923, and this study) and some veins have been shown to post date hydrocarbon emplacement (Füchtbauer, 1975).

This paper reports the results of petrographic, isotopic and trace element analysis of fibrous calcite veins from four localities in the British Mesozoic (Fig. 4 .1). By analysing successive growth stages within the fibrous calcite veins and material from the adjacent concretions and host sediment it has been possible to monitor changes in pore water composition during carbonate precipitation. The results from the fibrous calcite veins are interpreted to suggest the environment in which precipitation took place.

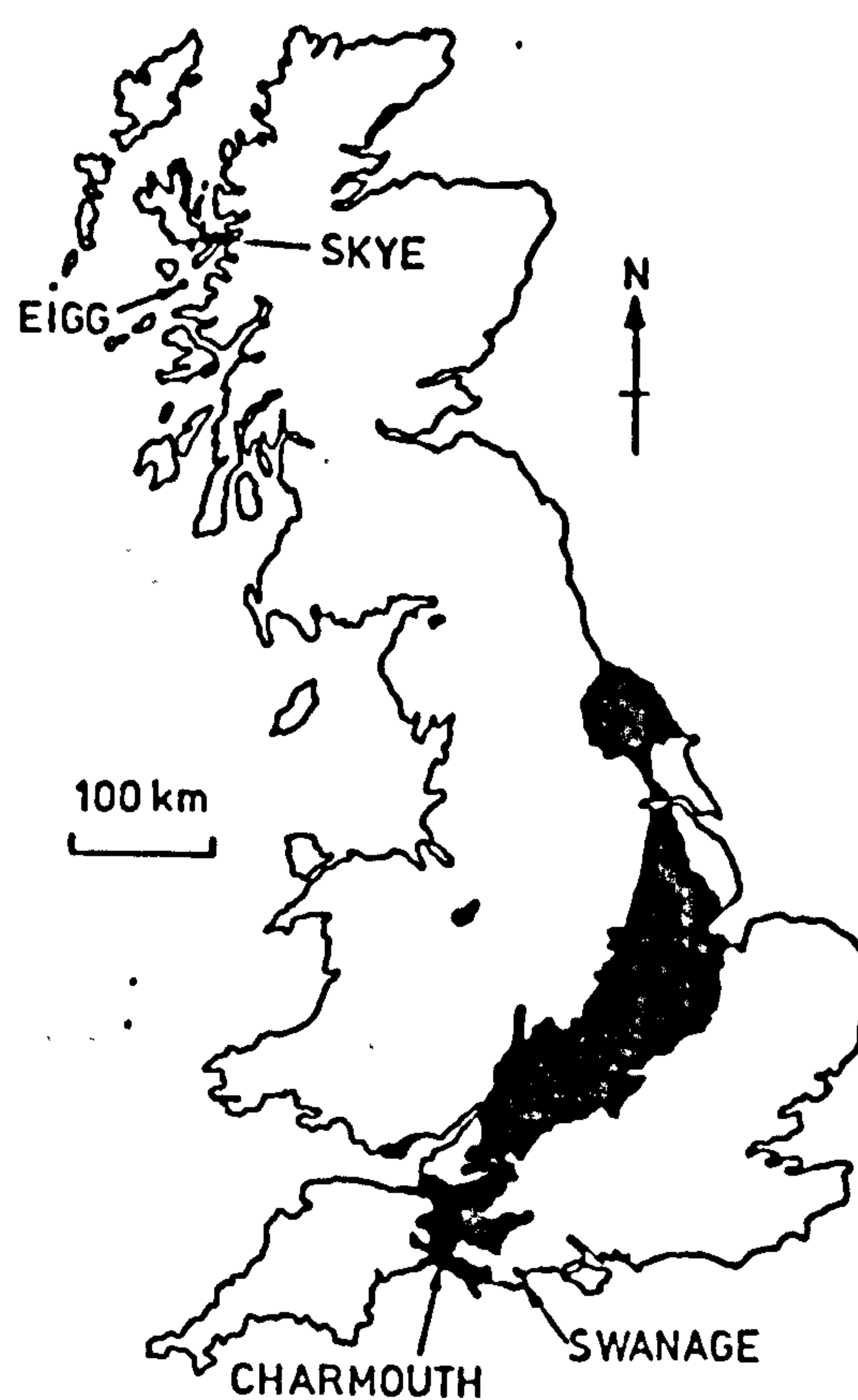


Figure 4.1 Locality map for the samples of fibrous calcite veins. (Jurassic outcrop shown in black.)

METHODS AND SAMPLING

Vein samples were sliced in a direction approximately parallel to the cone axes and fibre orientation: stained thin sections and peels were prepared in the usual way (Dickson, 1965, 1966). Staining reveals qualitative variation in Fe^{II} content and each of the veins studied proved to be zoned with marked iron banding ^{approximately parallel to the vein margins.} ~~in an approximately horizontal plane.~~ Zonal boundaries do not always correspond to discontinuities within the crystal structure but generally parallel the base of the cones (Figs. 7, 9, 14, 16). Samples for isotopic analysis were extracted from individual zones using a dental drill.

X-ray diffraction and insoluble residue analysis was carried out on representative material from each locality. Microprobe analysis on the fibrous vein from Eigg was carried out using a defocussed beam to minimise surface decomposition (method outlined in Marshall and Ashton; in press).

Samples for isotopic analysis were treated with 1% sodium hypochlorite solution to remove organic contaminants prior to analysis (Forester et al., 1973). Carbon dioxide was extracted with 100% phosphoric acid and analysed on 'V.G.'- 'Micromass' mass spectrometers at the Institute of Geological Sciences, London. Standard correction procedures were employed (Craig, 1957) and the results were expressed in 'per mil' difference from the PDB international standard. An analytical error of less than 0.06% is associated with individual determinations.

'Marine' carbonate has $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of approximately 0. Carbon supplied from an organic source (average $\delta^{13}\text{C}$ of -2.5) will modify the carbonate $\delta^{13}\text{C}$ value; ^{18}O depletion reflects temperature increase and pore-water modification during burial (review by

Hudson, 1977). Serial samples from each zone of fibrous calcite or adjacent concretion should demonstrate successive changes in diagenetic environment.

RESULTS

Occurrence morphology and isotopic composition

The sediments in which the cone-in-cone veins grew are all fine-grained; they represent a range of sedimentary environments from open marine to fresh water conditions. The field occurrence, morphology and isotopic composition of samples from each locality will now be described.

CHARMOUTH

Clues to the relative time of cone-in-cone formation are provided in the open-marine Lower Lias "Shales-with-beef" of the Dorset coast (Fig. 4.1) where the fibrous calcite veins demonstrably post-date concretion precipitation (e.g Lang, Spath and Richardson, 1923). Composite cone-in-cone (beef) veins, up to 10 cm. thick, fringe large (1 m horizontal diameter) early diagenetic concretions in the Birchi Nodular Bed (Bed 75(a); Lang et al. 1923) in the coastal exposure at Black Ven, Charmouth. (Figs. 4.1, 2, 3).

Concretion - morphology and staining

The concretions are elliptical in vertical section (Fig. 4.2) and approximately circular in a horizontal plane. The internal zonation is illustrated in Fig. 4.7(6). A non-ferroan calcite-cemented core preserves primary sedimentary lamination. It contains foraminifera; which are preserved in 3-D with a sparry calcite fill, within the microsparitic concretion matrix. Curved laminae in the outer part of the concretion testify to syncompactional growth (Raiswell, 1971). The lack of skeletal material in the coarser

Figure 4.2A . Concretion, in the shales-with-beef succession at Charmouth. Core zone is bordered by septarian calcites. (Fringing beef veins obscured by shale debris)

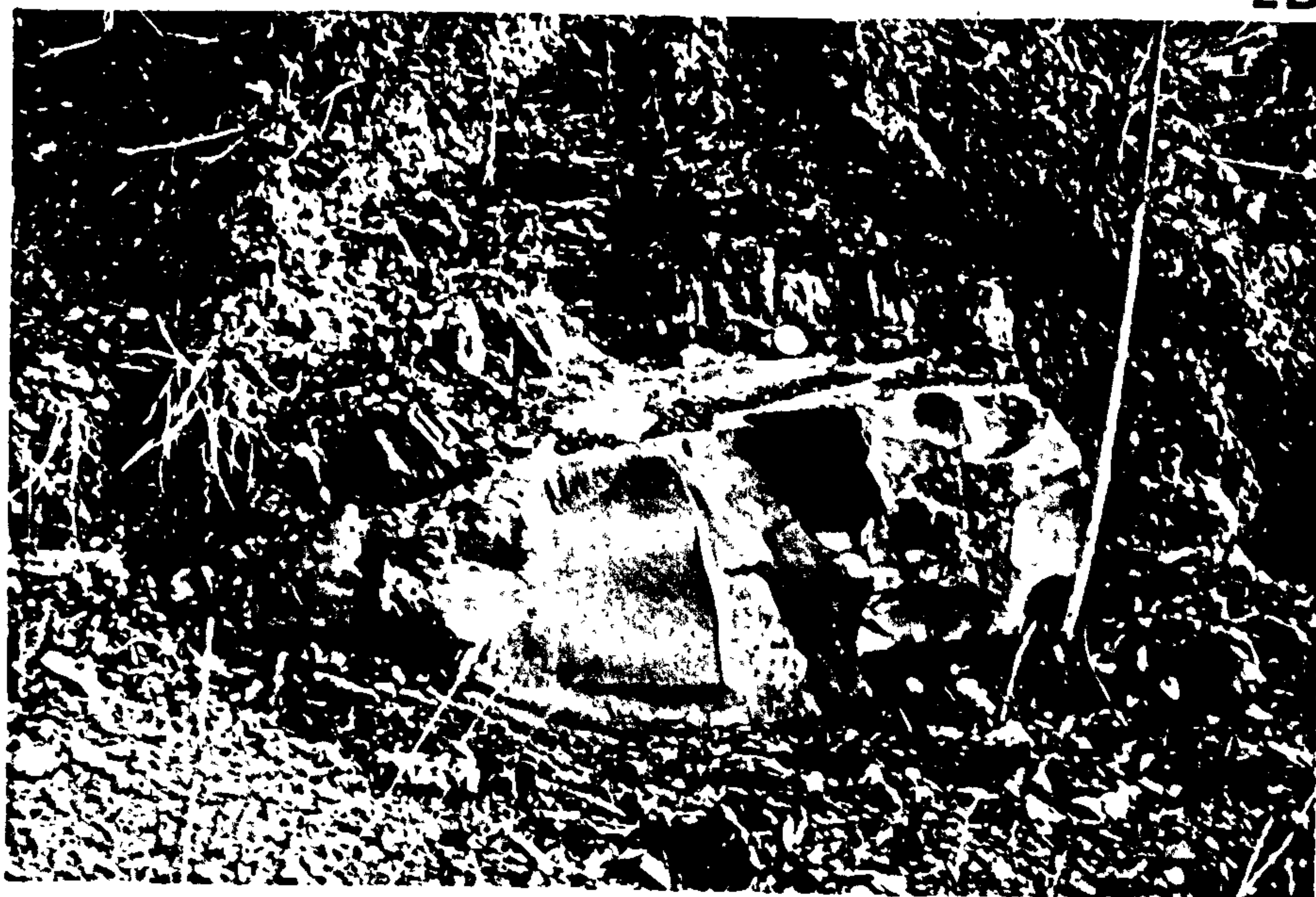
Figure 4.2B As Fig. 2A - layers of cone-in-cone calcite visible above the concretion.

Figure 4.3 Fibrous calcite vein from above a Charmouth concretion. Cone-in-cone layer is succeeded by two layers of fibrous calcite.

2A



2B



3

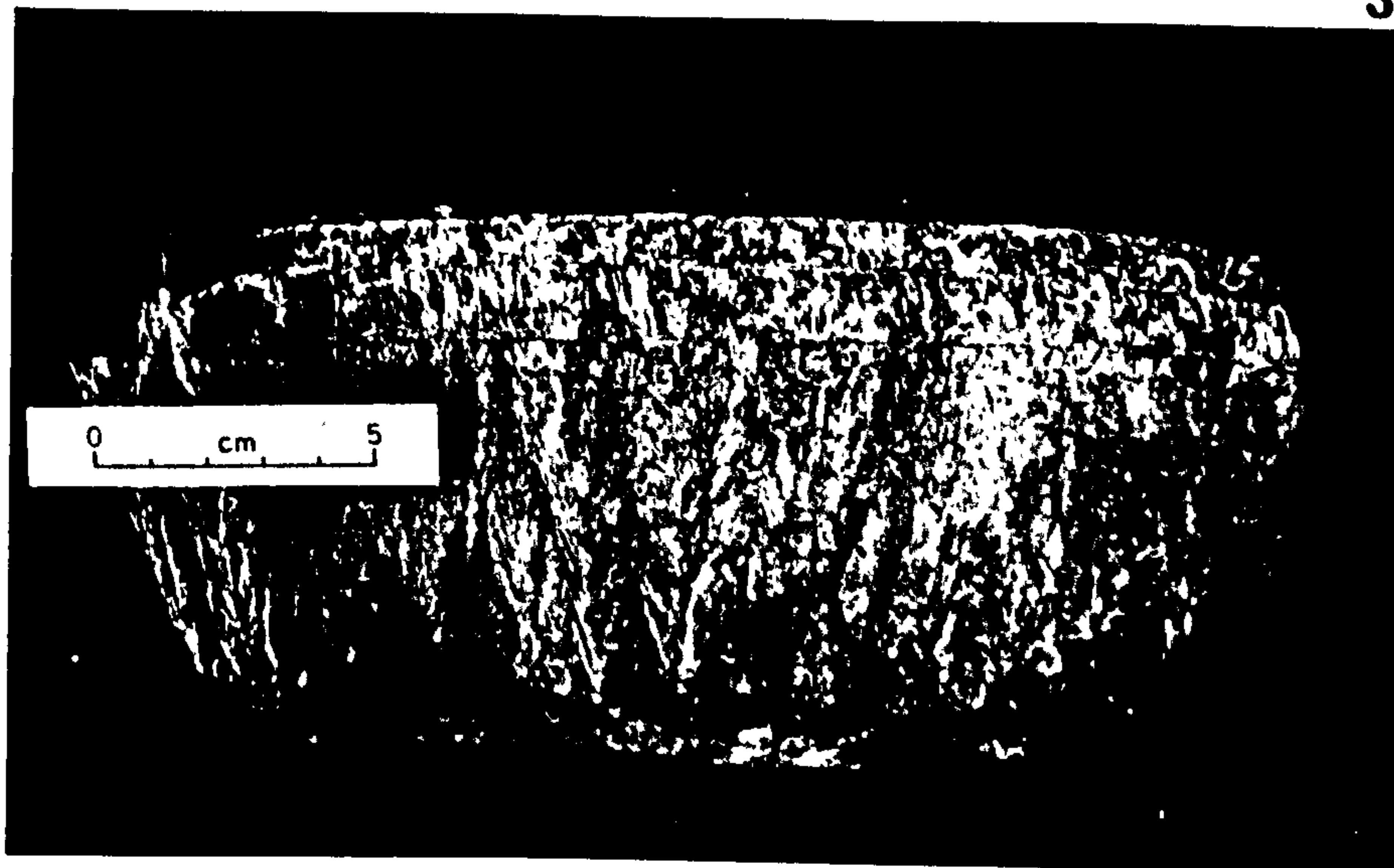


Figure 4.2A . Concretion, in the shales-with-beef succession at Charmouth. Core zone is bordered by septarian calcites. (Fringing beef veins obscured by shale debris)

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Figure 4.3 Fibrous calcite vein from above a Charmouth concretion. Cone-in-cone layer is succeeded by two layers of fibrous calcite.

2A



2B



3

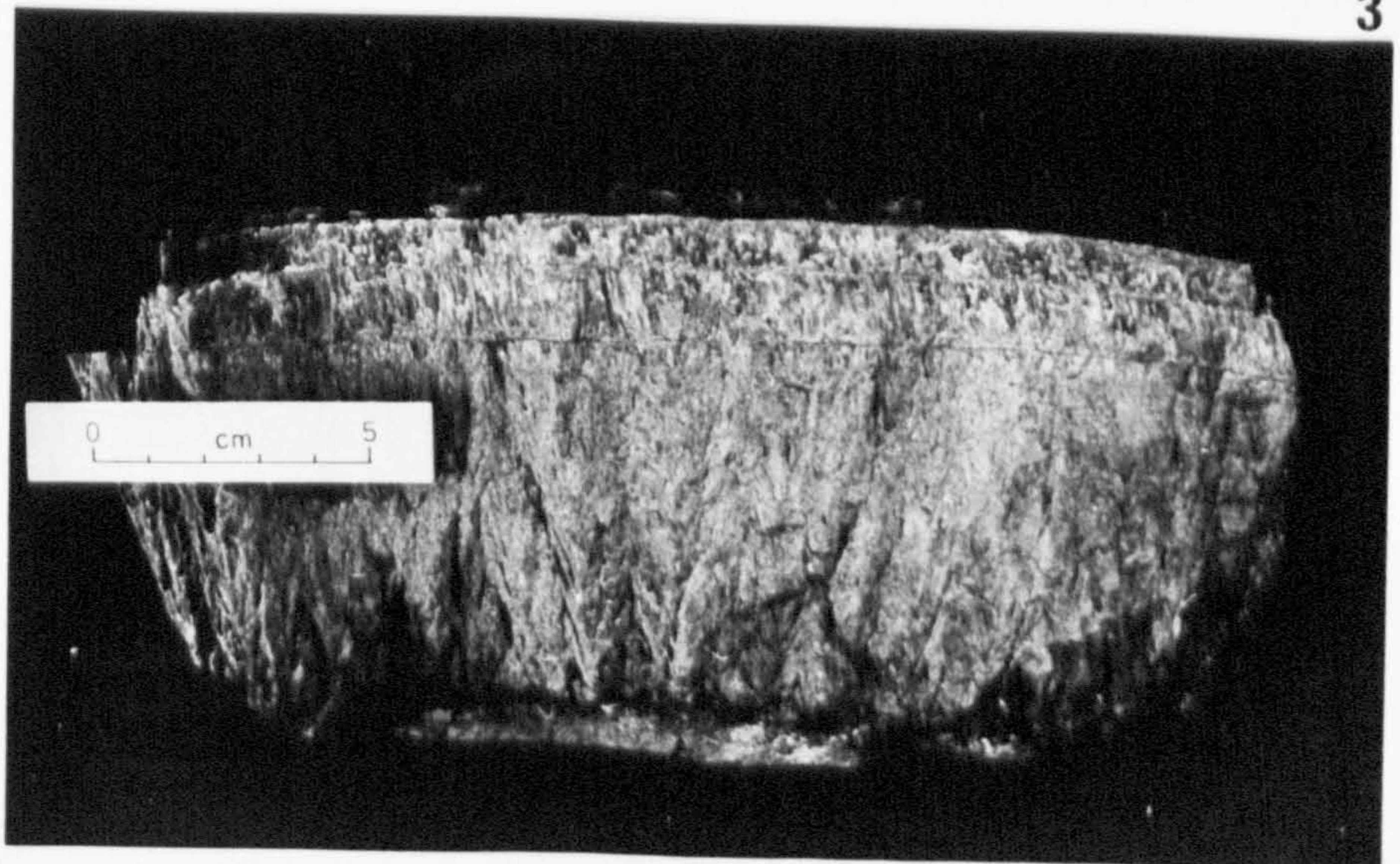


TABLE 4.1 RESULTS OF INSOLUBLE RESIDUE ANALYSIS BY ACETIC ACID DIGESTION. (VALUES ARE MEANS OF AT LEAST 3 DETERMINATIONS. VARIATION OF ± 2 % ENCOUNTERED)

Locality	Description	Mean % Acid Insoluble Residue	(Carbonate)
Charmouth	Host Shale	86%	14%
"	Core	13%	87%
"	Ferroan dolomite zone	20%	80%
"	Outer Rim	27%	73%
"	Cone-in-cone vein	5%	95%
Eigg	" " " "	4%	96%
Skye	" " " "	2%	98%
Swanage	" " " "	4%	96%

microsparite calcite outside the core can be attributed to recrystallization during the formation of the ferroan dolomite zone (Fig. 4.7, 6). Insoluble residue analysis (Table 4.1) demonstrates very high carbonate content. A gradual decrease from 87% carbonate in the core to 73% in the outer rim, suggests growth under shallow burial (5 m maximum?) in gradually compacting sediments with a very high initial porosity (Raiswell, 1971). Septarian cracks are filled with bladed calcite spar which is ferroan in early (outer) stages and non-ferroan in the centre of the vein.

Isotopes (Fig. 4.7, 8)

The concretion core and outer rim have similar isotopic composition: light $\delta^{13}\text{C}$ (-10 to -14) and $\delta^{18}\text{O}$ of -3.5 to -4.5. Ferroan dolomites have heavier $\delta^{13}\text{C}$ (-0.4 to +3.9) and $\delta^{18}\text{O}$ (-1.8 to -0.1). The later (non-ferroan) part of the septarian vein is characterised by lighter $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (-6.0 and -17.0) than the early ferroan zone (-3.9 and -12.6; respectively). The diagenetic trends will be discussed in a later section.

Fibrous calcites

Morphology. Fibrous 'beef' veins occur in thin lenticular beds throughout the shales (0.5 to 5 cm.) and reach their maximum development (\approx 10 cm.) around the early diagenetic concretions. Vein structure and internal zonation is commonly symmetrical about a shale or concretionary parting, with the apices of cone structures pointing toward but not crossing the parting (c.f. Lang et al., 1923). Growth of a thin symmetrical vein (0.5 cm.) has displaced the impression of a small ammonite which appears on both upper and lower surfaces (c.f. fish impression of Brown, 1954, or trilobite of Woodland, 1964). Veins developed above

Figure 4.4 Photomicrograph of cone-in-cone calcite layer from below the concretion at Charmouth. Conical growth gives way to sub-parallel fibres away from the concretion (downwards).

Scale bar = 1 mm

A. Plane polarised light

B. Under crossed polars

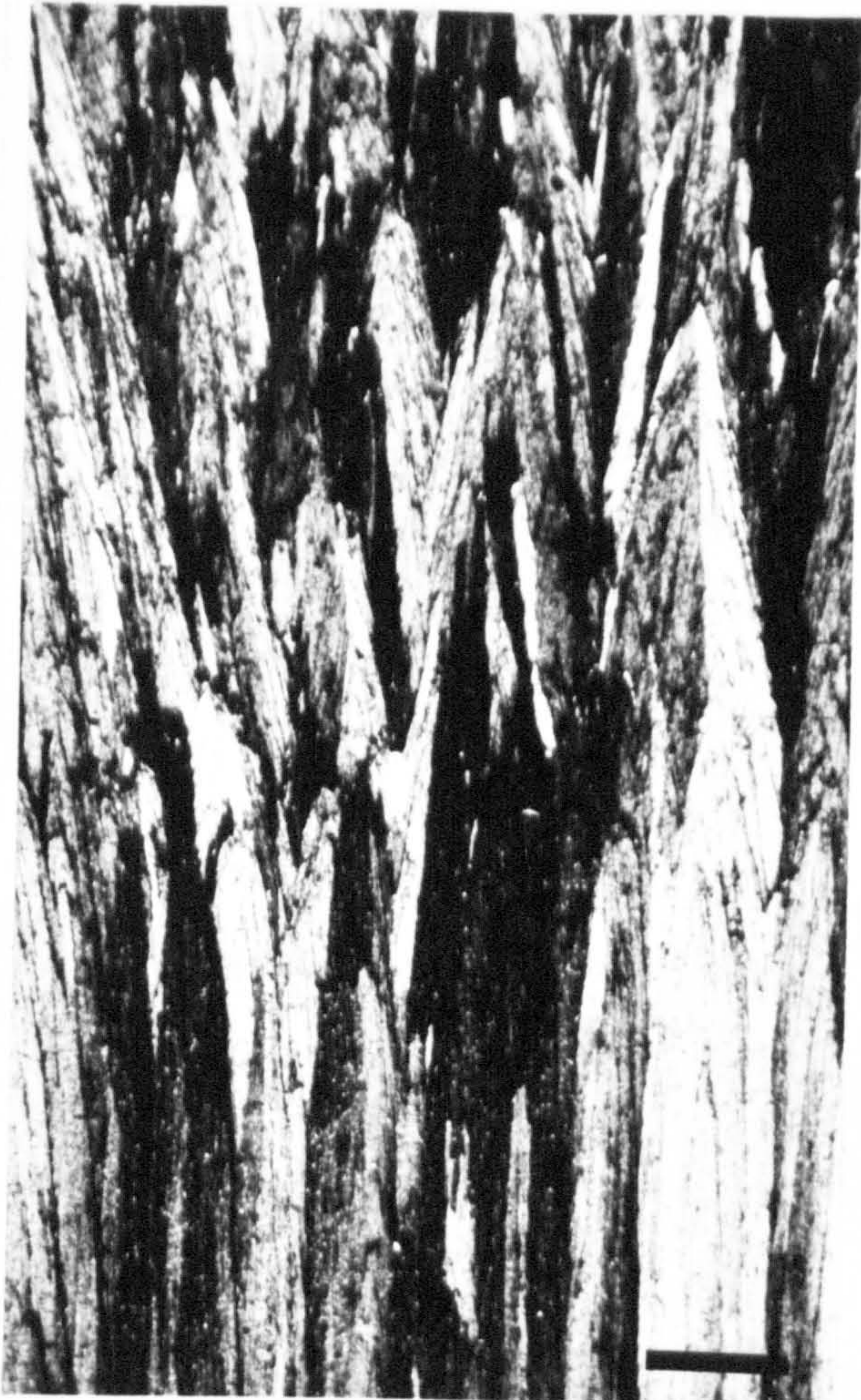
Figure 4.6 Photomicrograph of stained acetate peel showing 'streaked' zonation within a fibrous growth layer at Charmouth. Ferroan zones (dark areas on photo) represent incorporation of inter-fibre veinlets in the strained non-ferroan calcite.

Scale bar = 0.1 mm

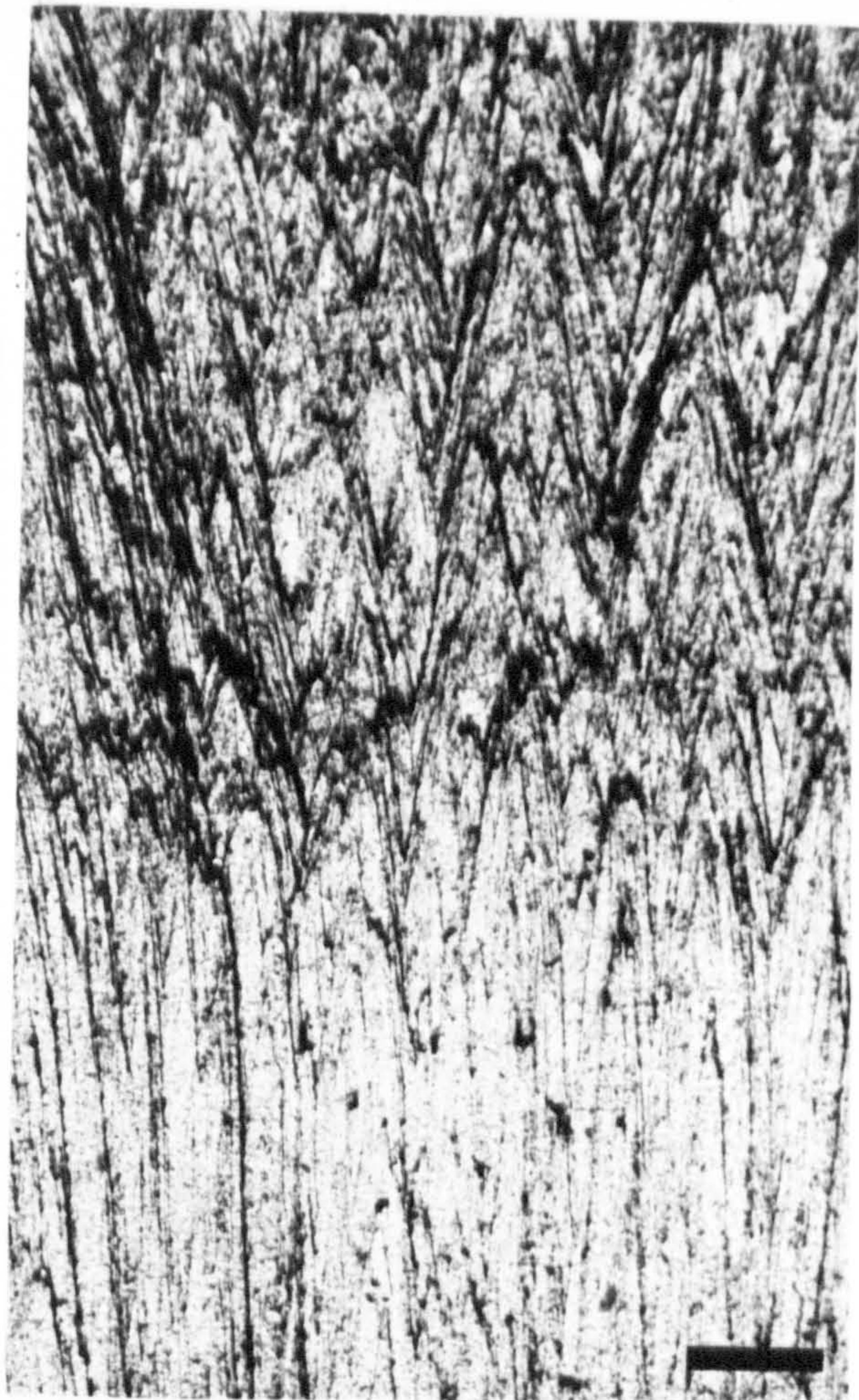
Figure 4.5 Photomicrograph of fabric discontinuity between the cone-in-cone layer (top of photo) and Fibrous Calcite I (lower part of photo). Conical growth form is restricted to the early growth stage of the fibrous calcite I layer.

Scale bar = 0.5 mm

4B



4A



6



5



concretions are commonly thicker than those below them with both veins thinning toward the perimeter. Cone structure is radially distributed around the concretion.

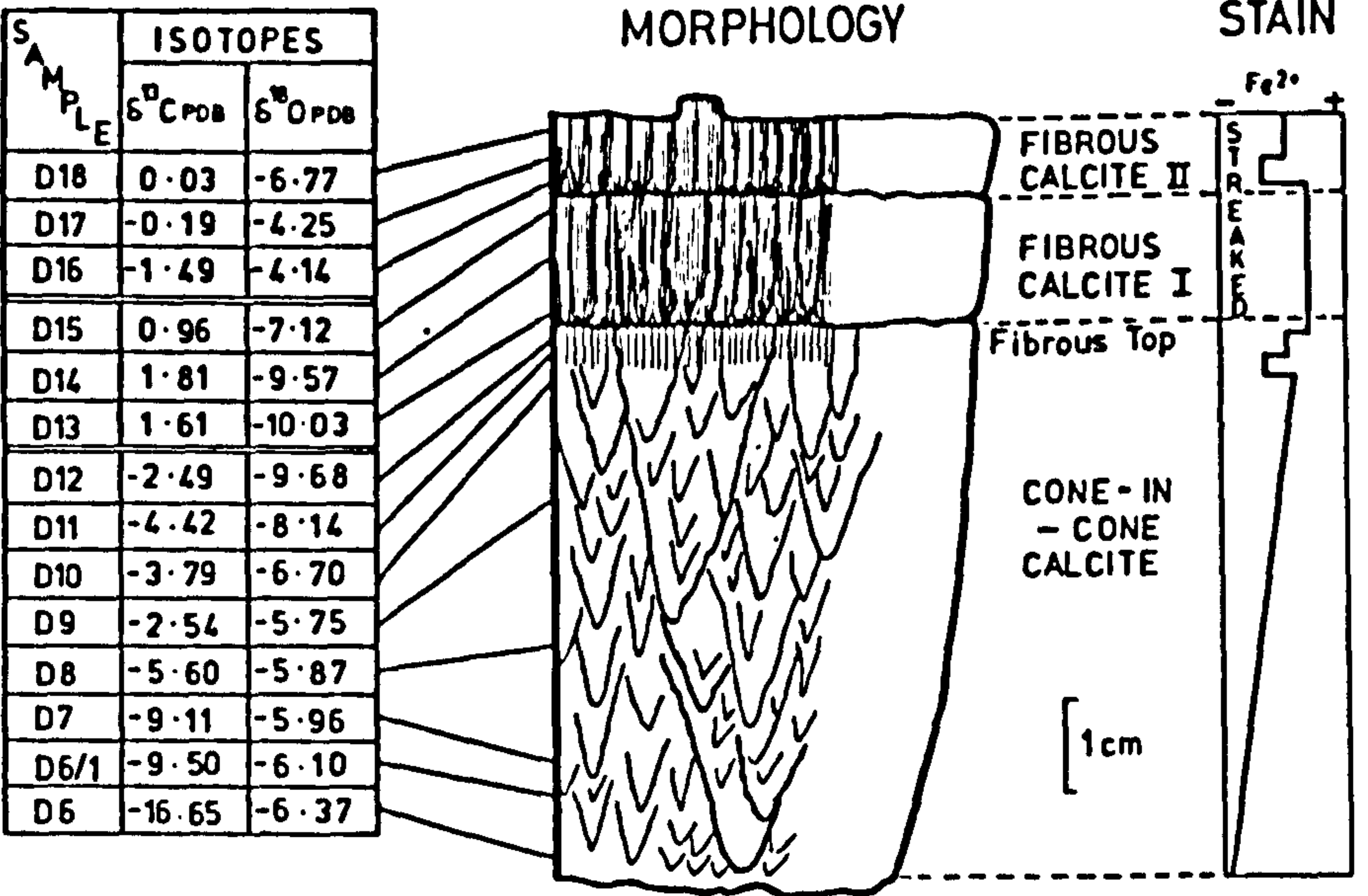
The veins analysed for this paper exhibit three well defined growth stages which are developed with different relative thicknesses above and below the concretion (Fig. 4.7). A massive (6.5 cm. maximum) vein with well defined cone-in-cone structure is succeeded with two distinct growth bands of fibrous calcite in which cone structure is restricted to early growth stages (Figs. 4. - 3,7). The outermost surface ^{has} ~~has~~ raised circular areas which demonstrate internal conical growth form (Woodland, 1964).

Petrography. Microscopic structure reflects the large scale morphological features. The well-defined cone-in-cone layer is formed by stacks of mutually interfering bundles of fibrous calcite crystals, which become progressively more coarsely crystalline away from the cone-apex (Fig. 4.4). Cone-structure and an intra-crystalline fibrous fabric are defined by microscopic inclusions. Fibres do not cross the growth discontinuity between the three growth layers (Fig. 5), the junctions are marked by dense layers of inclusions and renewed conical form in the outer growth layer (Fig. 5). Outer, ^{with fibrous appearance} ~~fibrous~~ layers are composed of bladed calcite whose radial -fibrous undulose extinction parallels the fibrous form defined by linear trails of intracrystalline inclusions.

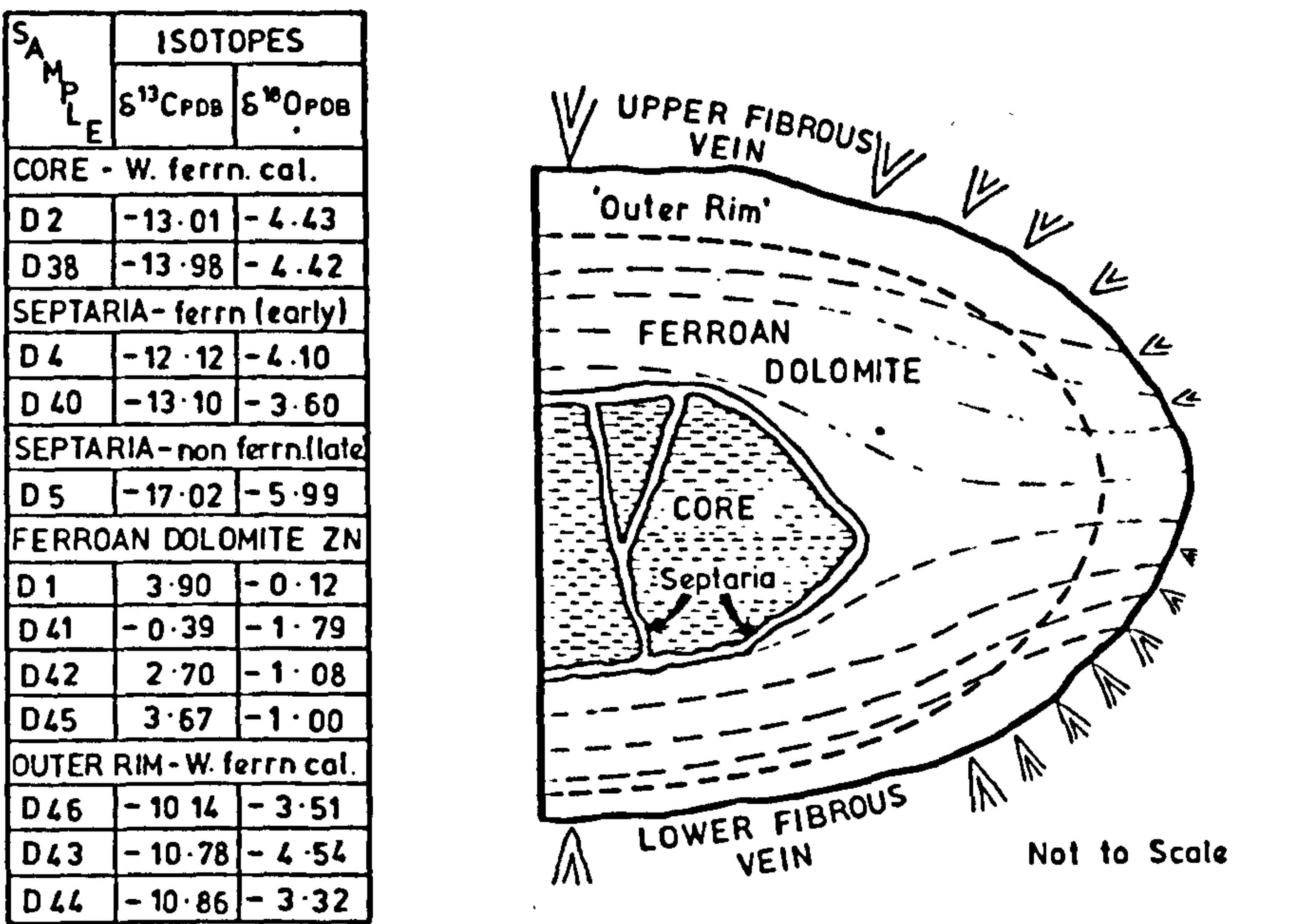
Staining

Staining reveals a pattern of zones with different Fe^{II} content which parallel the margins of the veins (Fig. 4.7). Zonal sequence is repeated almost exactly in the veins above and below the concretion. The zonal boundaries are planar but do

(a) Upper Fibrous Vein



(b) Concretion



(c) Lower Fibrous Vein

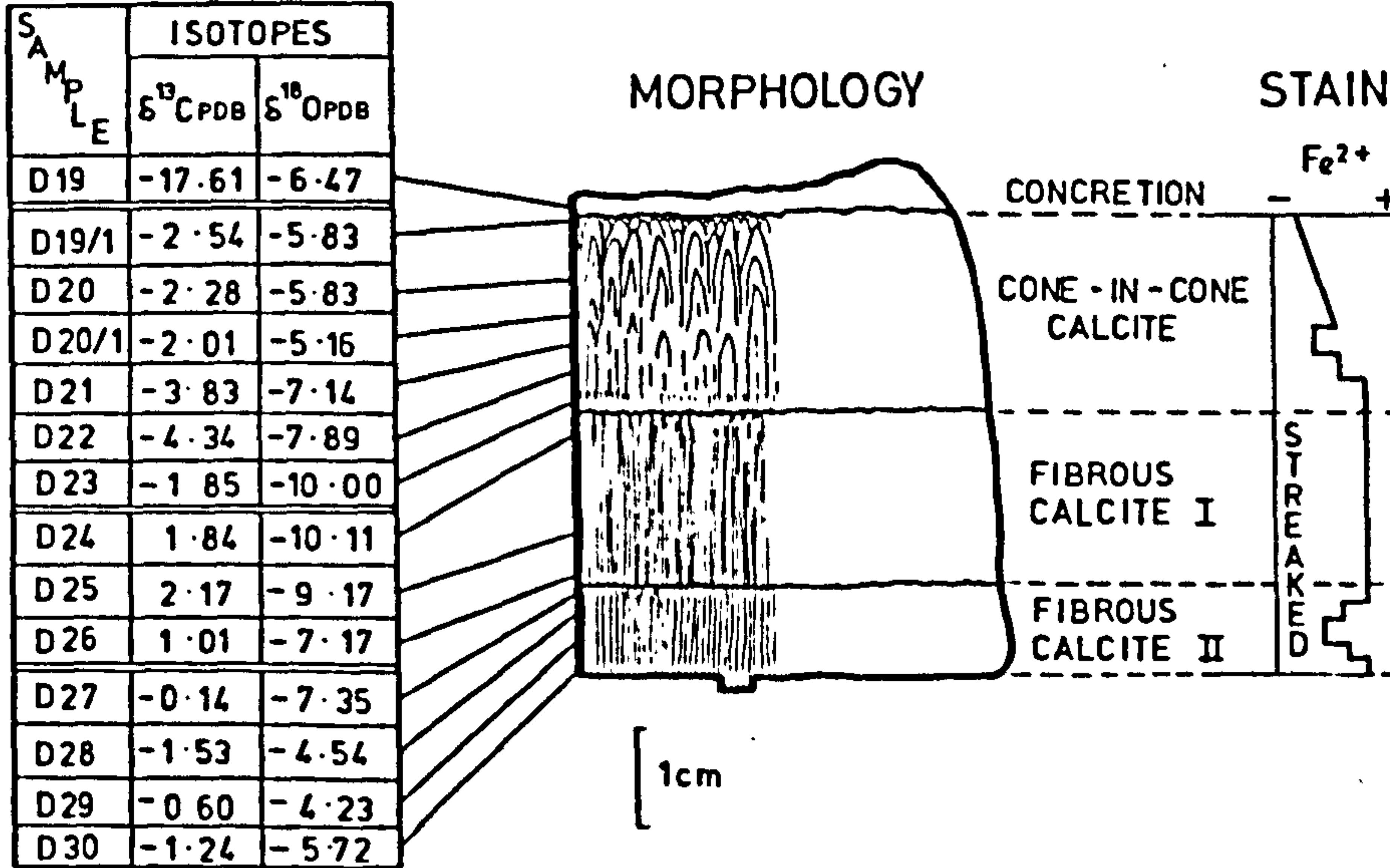


Figure 4.7 Isotopic composition, morphology and ~~relative~~ ^{II} ~~approximate~~ Fe content of samples from the Concretion and surrounding fibrous calcite veins at Charmouth.

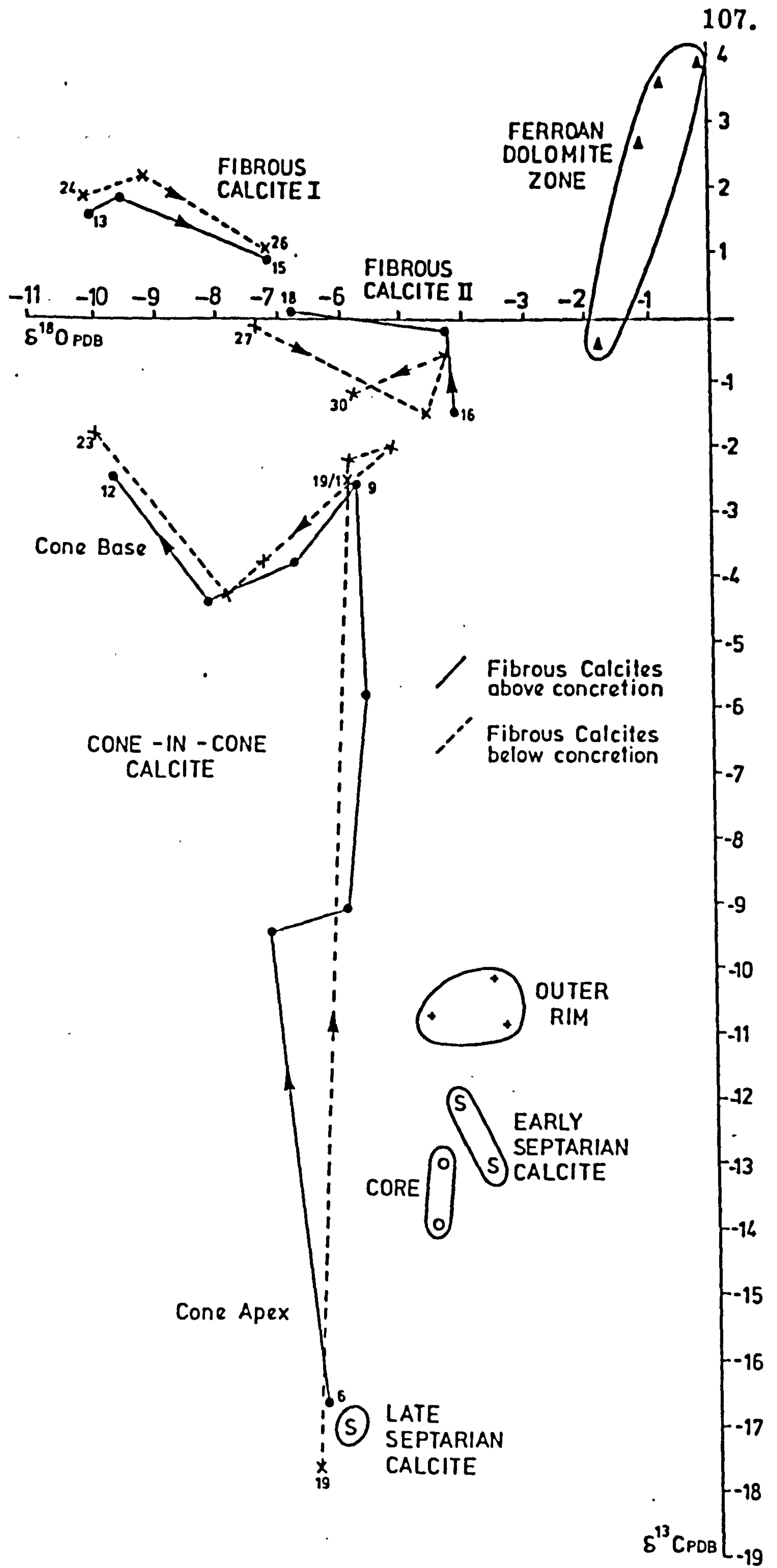


Figure 4.8 Carbon and oxygen isotopic scatter diagram for samples from Charmouth.

not correspond to the major growth discontinuities (Fig. 4.7) and are not deflected at intercrystalline boundaries. A clear, weakly ferroan veinlet (0.5 mm.) obliquely cuts the cone-in-cone and fibrous fabric of the coned growth stage; it is in optical continuity with the adjacent calcite. Similar veinlets can be traced into the fibrous layers where they are sub-parallel to the fabric and are incorporated within the radial-fibrous crystals (Fig. 4.6)

Isotopes

Early fibrous zones have similar isotopic composition to the calcitic parts of the concretion and the later zone of (non-ferroan) septarian calcites ($\delta^{18}\text{O}$, -5.9, $\delta^{13}\text{C}$ - 16.7). In early growth stages light, organogenic, carbon is replaced by heavier $\delta^{13}\text{C}$ while $\delta^{18}\text{O}$ remains almost constant (Fig. 4.8). Changes in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in successive zones are not unidirectional but reversals in trend generally correspond to the fabric discontinuities ($\delta^{18}\text{O}$ varies between -10 and -4 and $\delta^{13}\text{C}$ between -4.3 and +2.2 after the initial increase in value (Figs. 4.7, 8). Isotopic trends from calcites above and below the concretion are very similar except in the outer, fibrous calcite II, stage.

EIGG AND SKYE

Two morphologically different veins were collected from shale horizons within the fresh to brackish water, generally arenaceous, sediments of the concretionary Sandstones (Great Estuarine Group and Bathonian) of the Inner Hebrides (Fig. 1).

EIGG

An asymmetric^{al} coned vein 3 cm. thick was collected from

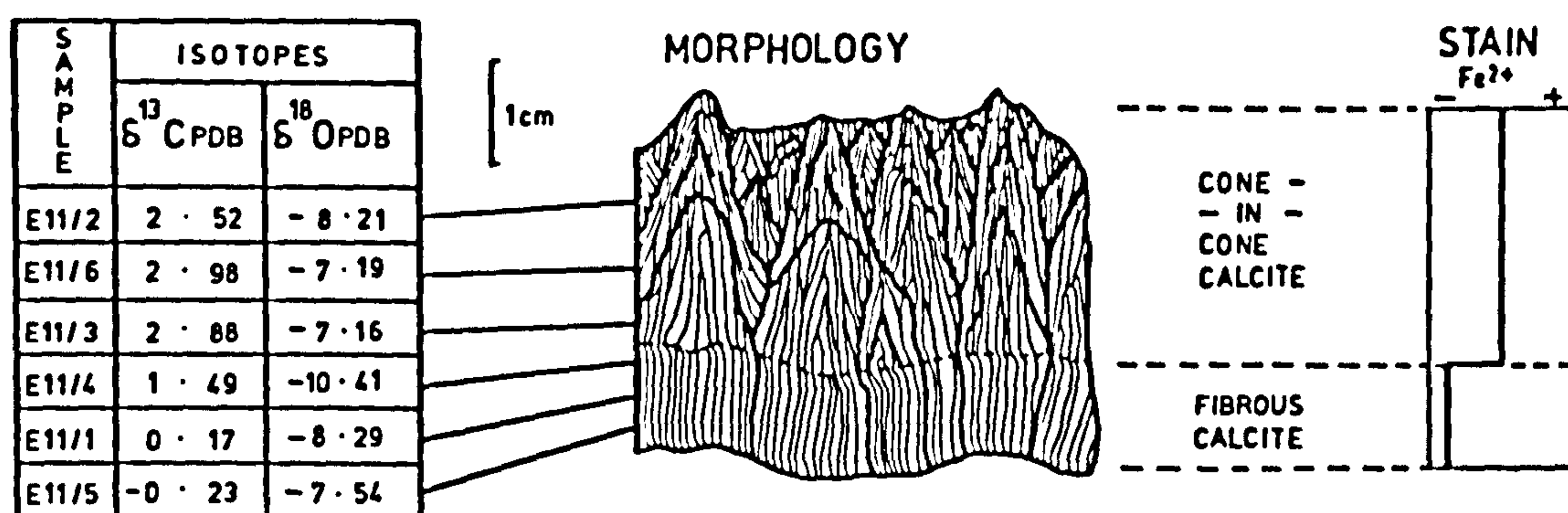


Figure 4.9 Isotopic composition morphology and stain zones within the fibrous calcite vein from Eigg.

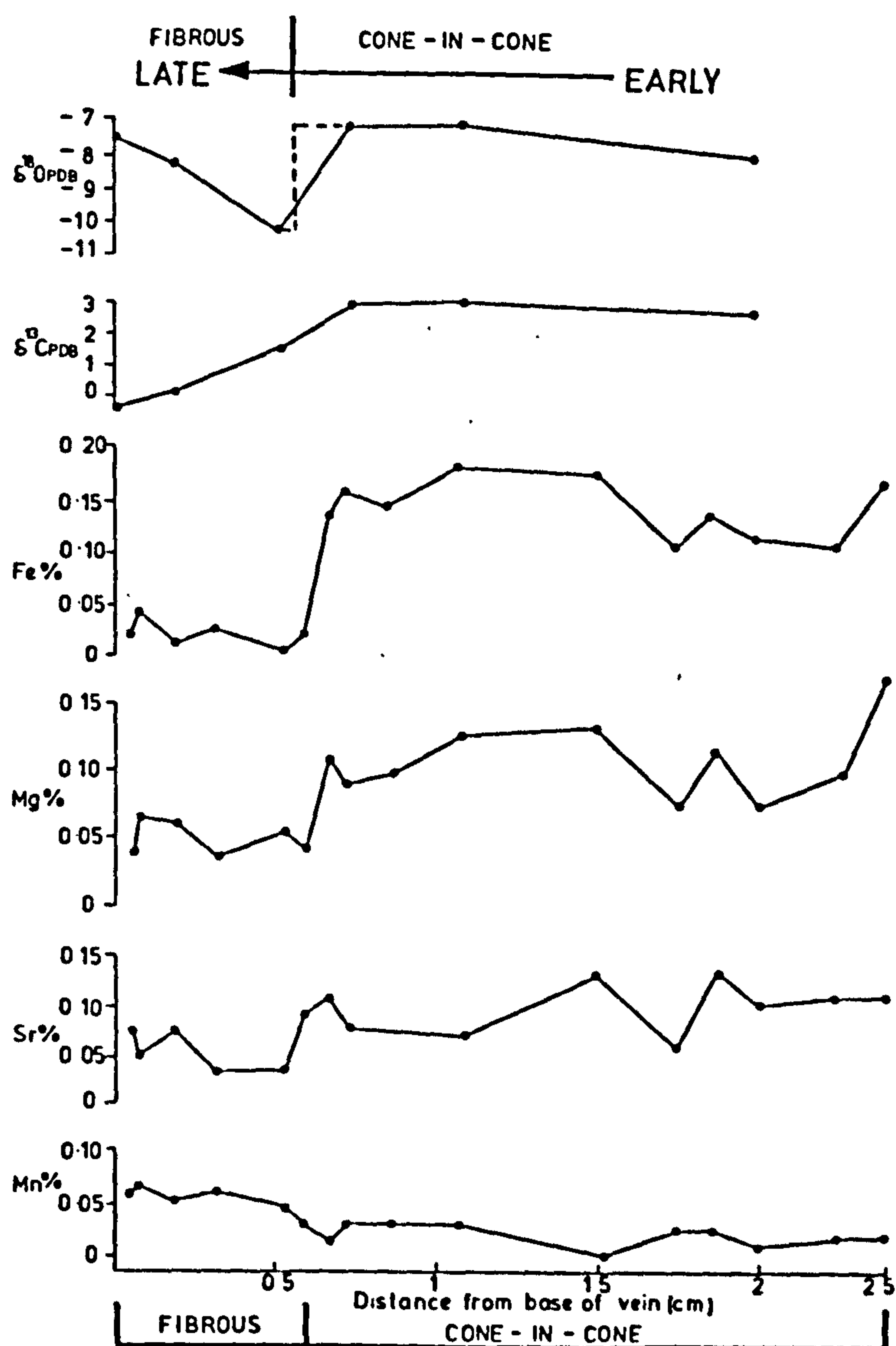


Figure 4.12 Variation in isotopic composition and trace element concentration across the fibrous calcite vein from Eigg. (Trace element point analyses by electron microprobe.)

Figure 4.10 Vein from Eigg. Photomicrographs of fabric discontinuity between ferroan (top of photo) and non-ferroan (lower part of photo) calcite stages. Note curvature of the fibrous crystals at the junction.

A. Plane polarised light

B. Same, under crossed polars

Scale bars = 1 mm

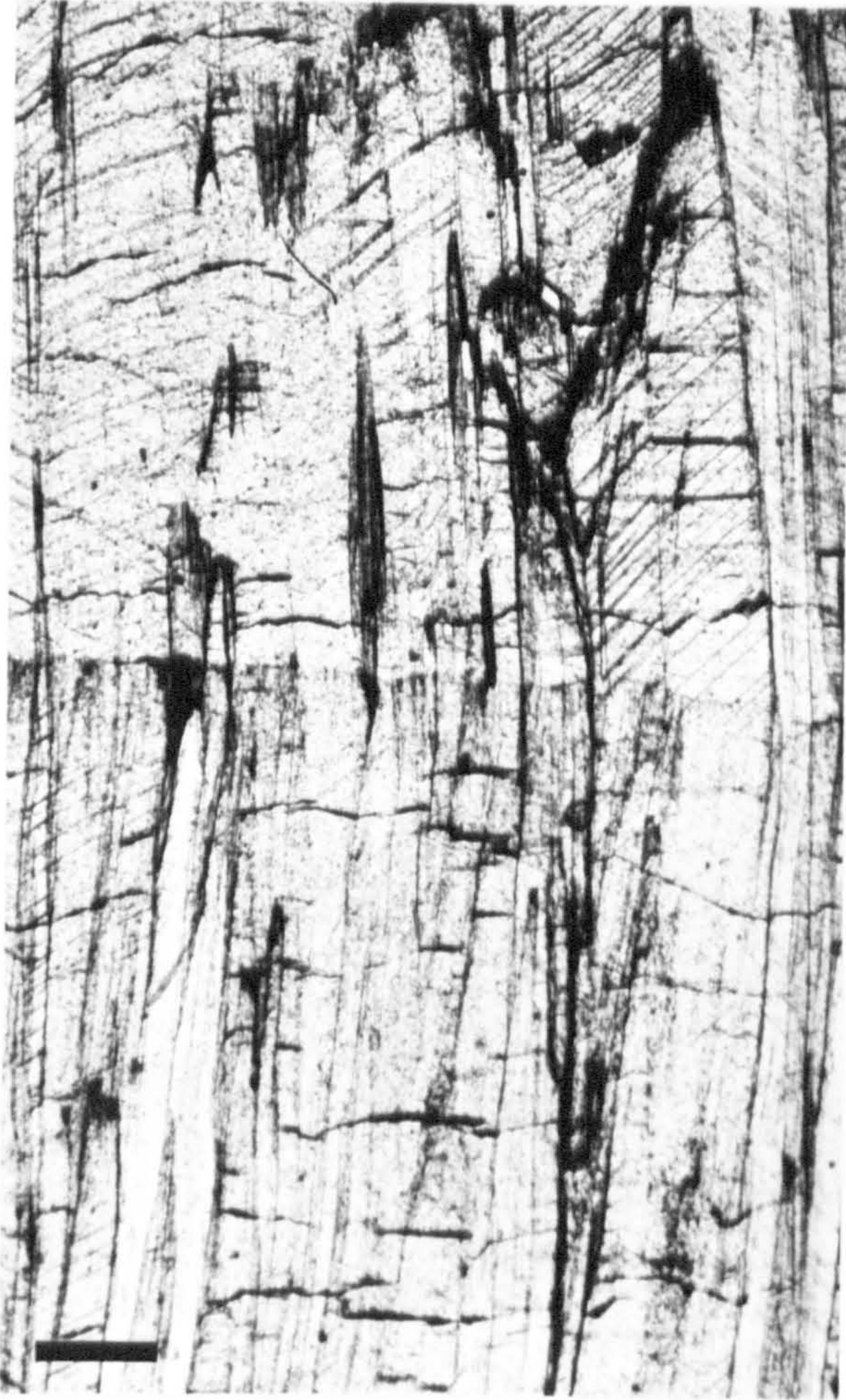
C. Detail of same; showing increase in inclusion density below the discontinuity. Inclusion trails ^{outline a} ~~define~~ divided fibrous fabric within the coarser crystal fabric.

Scale bar = 0.1 mm

Figure 4.11 Vein from Eigg. Photomicrograph of curved fibrous crystals near the base of the vein. Crossed polars.

Scale bar = 1 mm

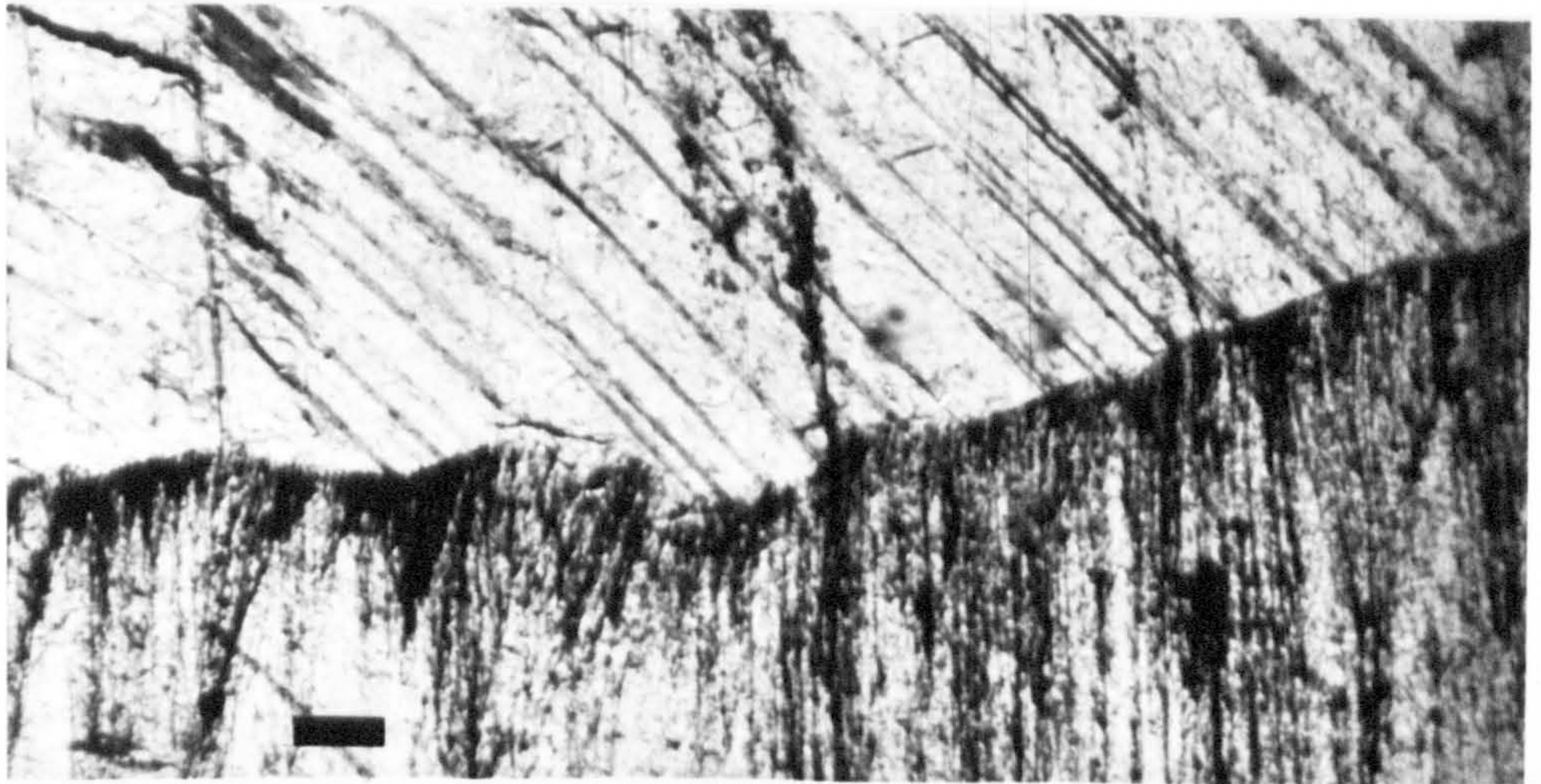
10A



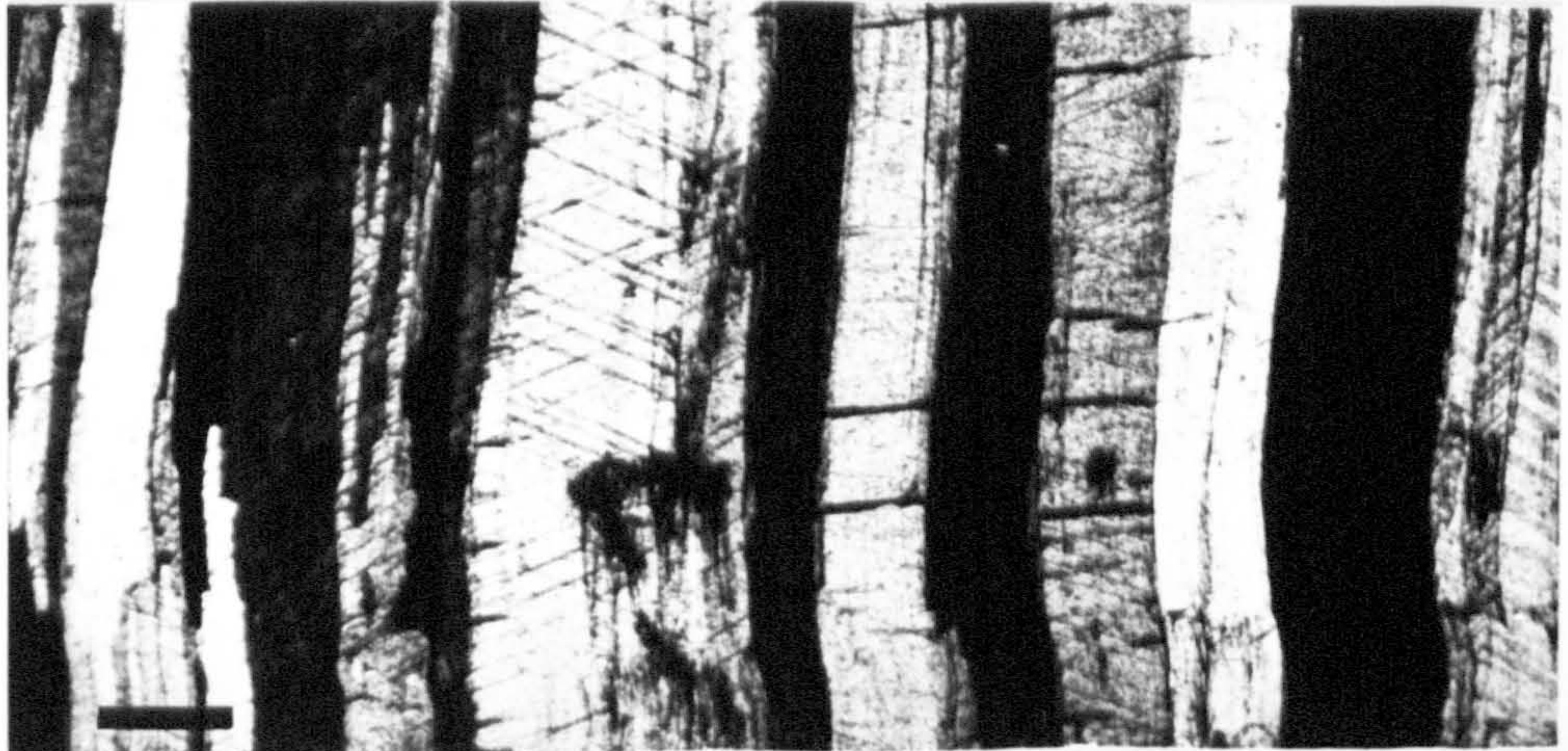
10B



10C



11



4.13.

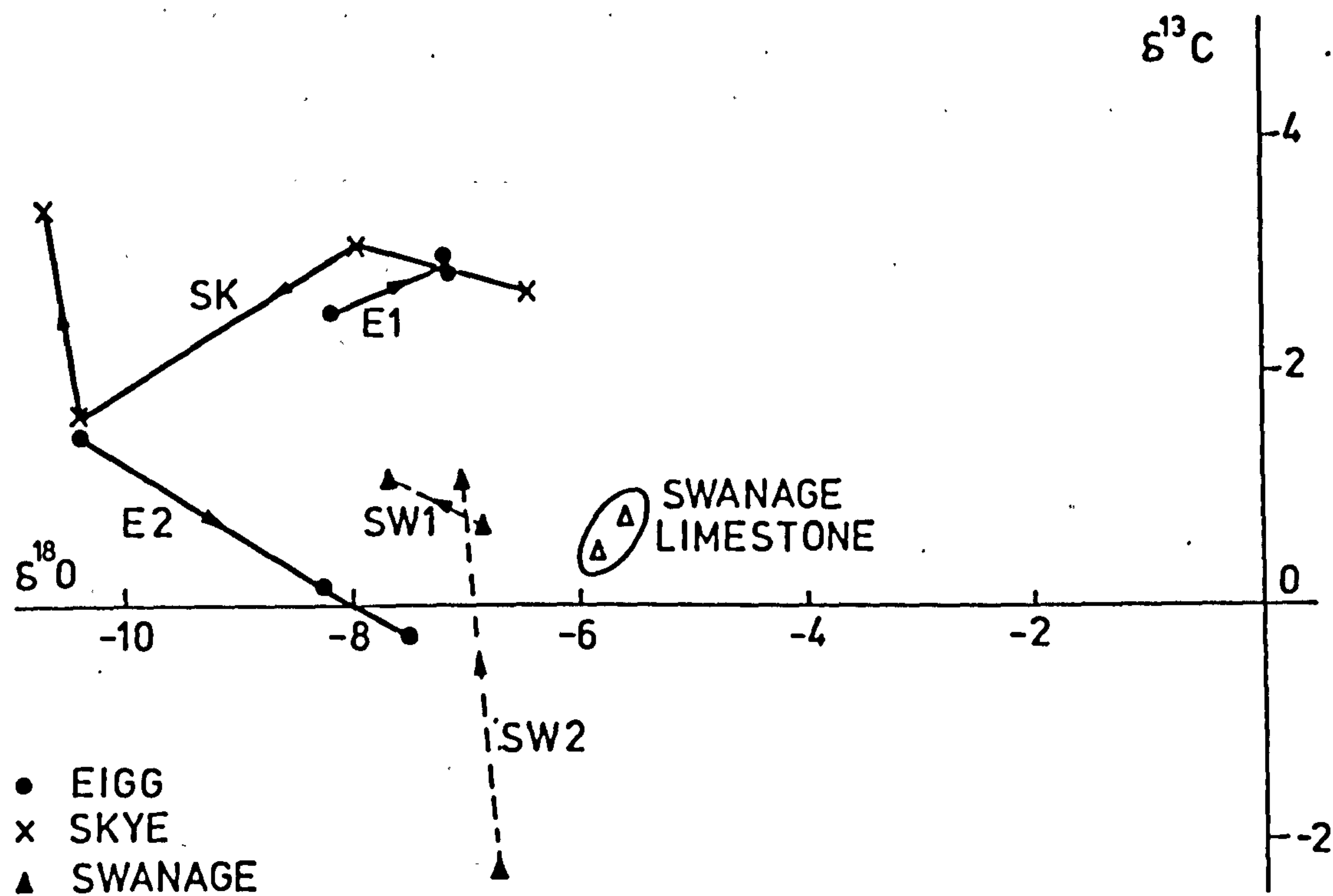


Figure 4.13 Carbon and oxygen isotopic scatter diagram for calcite samples from the veins from Eigg, Skye and Swanage.

shales beneath a prominent sandy biosparite in sea cliffs, Laig Bay, Isle of Eigg (Division F, Hudson and Harris, 1979).

cones nucleated against the base of the limestone and subsequent growth took place downward into the shale. Major cone structures initiated at the top of the vein may be traced throughout its entire thickness, but most of the ^{conical} ~~competitive~~ growth was restricted to the upper 2 cm.; simple fibrous calcite characterises the lower, later, precipitates (Fig.4.9). A change from ferroan to non-ferroan calcite coincides with the fabric discontinuity (Fig.4.9, 10) between coned and fibrous layers.

Cone structure in the ferroan calcite is defined by fine inclusions within and terminating the elongated, bladed crystal fabric (Fig.4.10), a few shale partings define larger "macrocones" (c.f Woodland, 1964). Radial lines of inclusions within the unstrained to radial-fibrous fabric indicate the former presence of more finely fibrous carbonate. At the fabric discontinuity (Figs.4.10, a + b) there is a marked angular change in crystal growth direction and sharp increase in inclusion density. Inclusions in the basal non-ferroan zone reveal small scale cone structures which are not reflected in the crystal fabric. Toward the base of the vein both crystal boundaries and inclusion 'fibres' are sinusoidally curved (Fig.4.11) but the calcite is unstrained; curvature is probably a response to growth induced stress (e.g Durney and Ramsey, 1972).

Trace elements

Microprobe analyses across the vein show very low trace element concentrations (Fig. 4.12). Iron concentration confirms the stain results. A decrease in magnesium concentration in the later calcites apparently coincides with the decrease in Fe^{II}

but the magnitude of the change is very low. Strontium and Manganese concentrations are low and variation is within limits of analytical error for these elements

Isotopes

Two distinct trends of increasing $\delta^{18}\text{O}$ (E1 and E2; Fig. 4.13) are defined by calcite samples from within each of the two growth stages. A sharp reversal ($\delta^{18}\text{O}$ from -7.2 to -10.4) corresponds to the fabric discontinuity and change from ferroan to non-ferroan calcite (Fig. 4.9). In view of the sharp change encountered in trace element variation (Fig. 4.9) it is most likely that the isotopic changes are also sharp and correspond to the fabric discontinuity (dotted line, Fig. 4.9).

STRATHAIRD, SKYE

Fibrous calcite veins follow the load-cast base of laminated shaly sandstones in the laminated Concretionary Sandstone outcrop on the shore south of Glen Scaladal, near Elgol, Isle of Skye (Hudson, 1962, Fig.2). Displacive growth into the underlying shale has parted the basal laminations of the load structure from the main sandstone bed (Fig.4.14). Further growth ruptured shale partings into crudely defined conical form (Fig.4.15, 16).

The analysed vein is approximately 6.5 cm. thick with a composite shale and sandstone parting about 2 cm. from the top (Fig.4.14); it was collected from the sloping base of the load structure. Fibrous calcite crystals are elongated normal to the parting and exhibit symmetrical sinusoidal curvature and increased fibre thickness away from it. There are no major fabric discontinuities but staining again reveals Fe^{II} banding which cuts the crystal fibres and whose boundaries mirror the base of the vein.

4.14

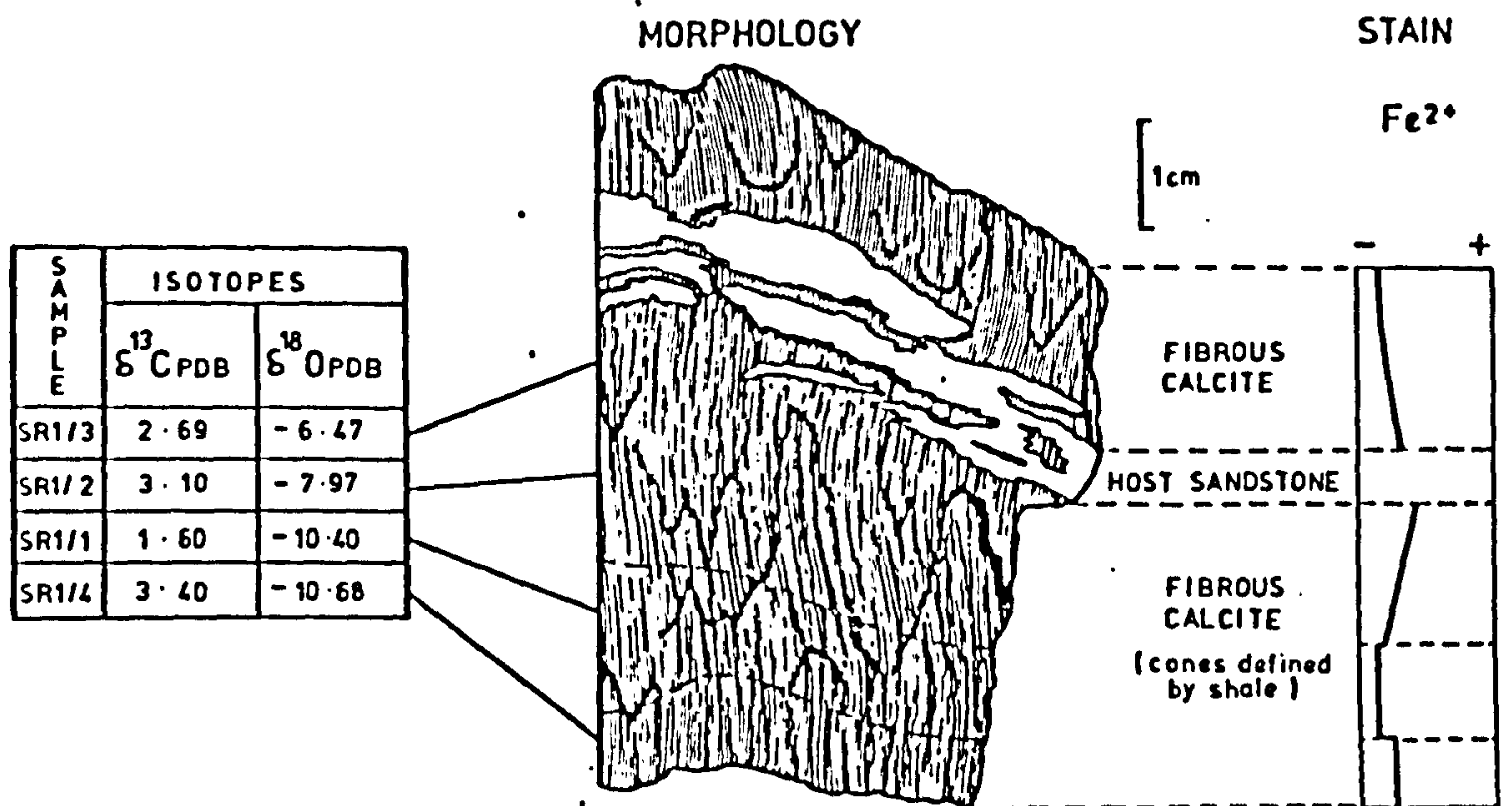


Figure 4.14 Isotopic composition morphology and approximate Fe^{II} distribution within the fibrous calcite vein from Skye.

Figure 4.15 Vein from Skye. Photomicrograph of shale inclusion within the fibrous calcite showing crude conical form. Crossed polars. Scale bar = 1 mm

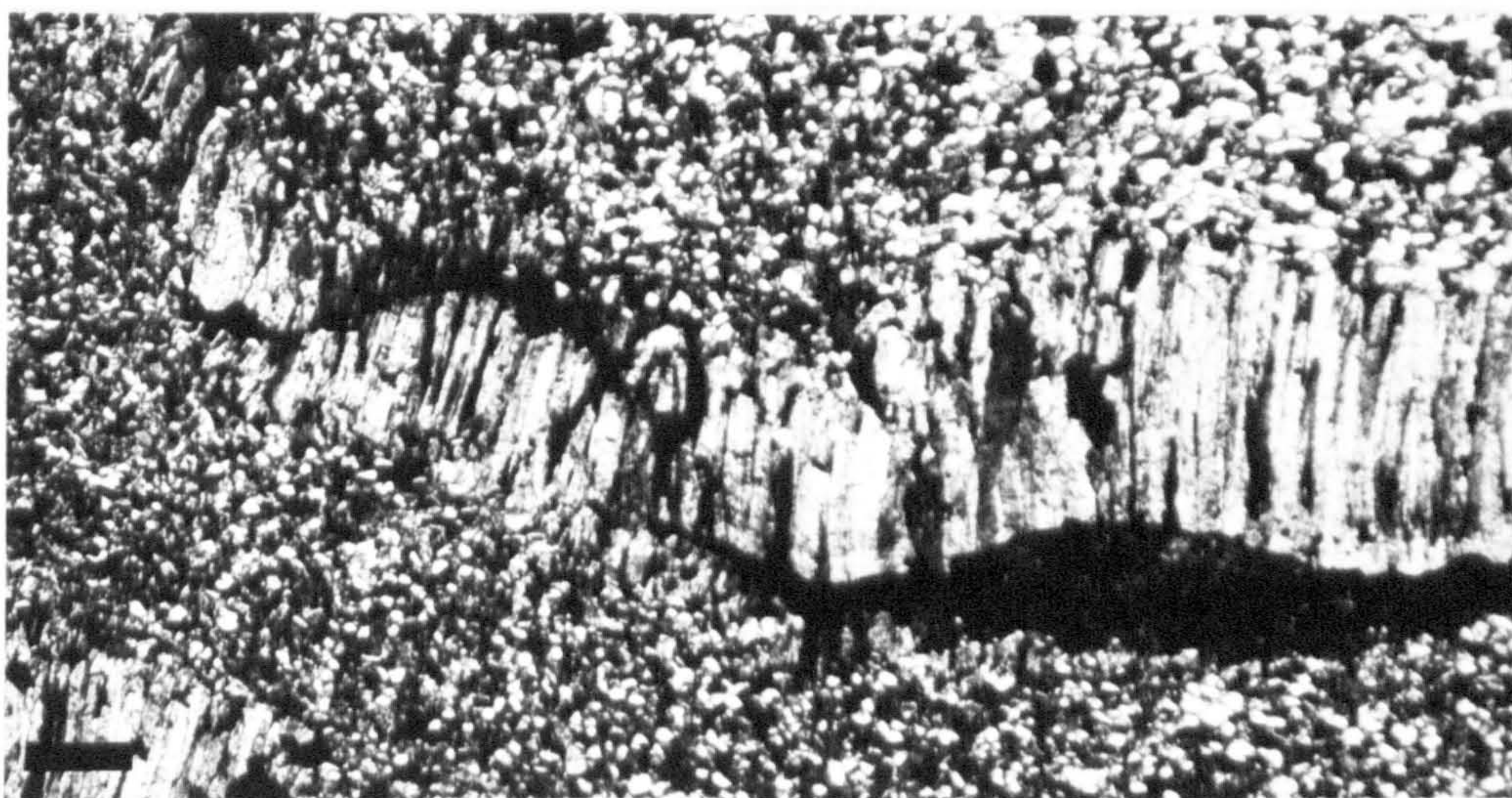
Figure 4.16 A and B. Vein from Skye. Displacive crystallization of calcite has parted shale laminae from fine sand matrix. Photomicrographs under cross-polarised light. Scale bar = 0.5 mm for both photos.

Figure 4.17 Vein from Swanage. Photomicrograph of fabric discontinuity between ferroan (upper part of photo) and non-ferroan (lower part of photo) growth stages. Discontinuity is marked by divergent growth at the base of the upper stage and transition to the more finely fibrous calcite of the lower (later) stage. Scale bar = 1 mm

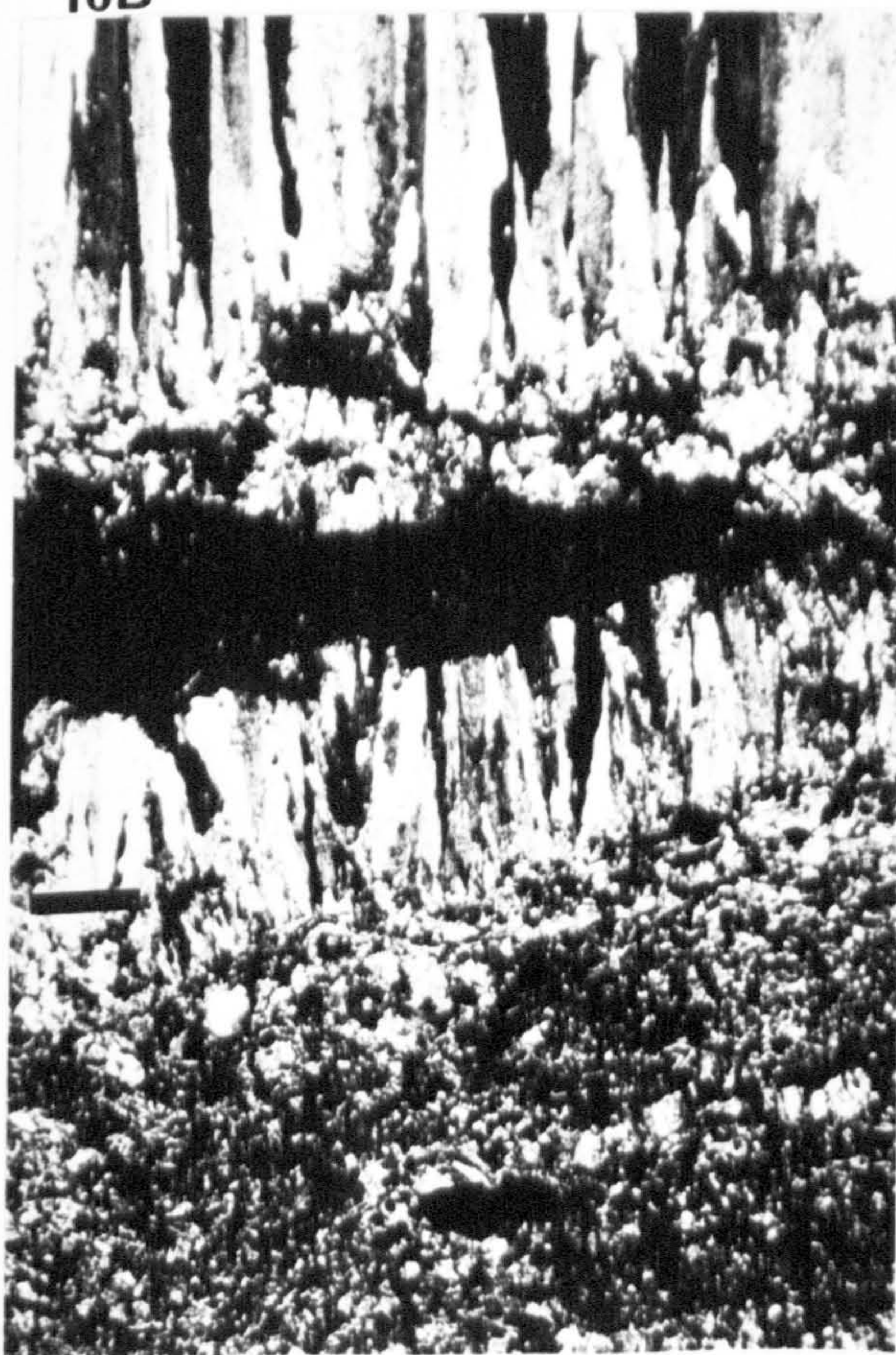
15



16A



16B



17



SWANAGE Chief Beef Beds

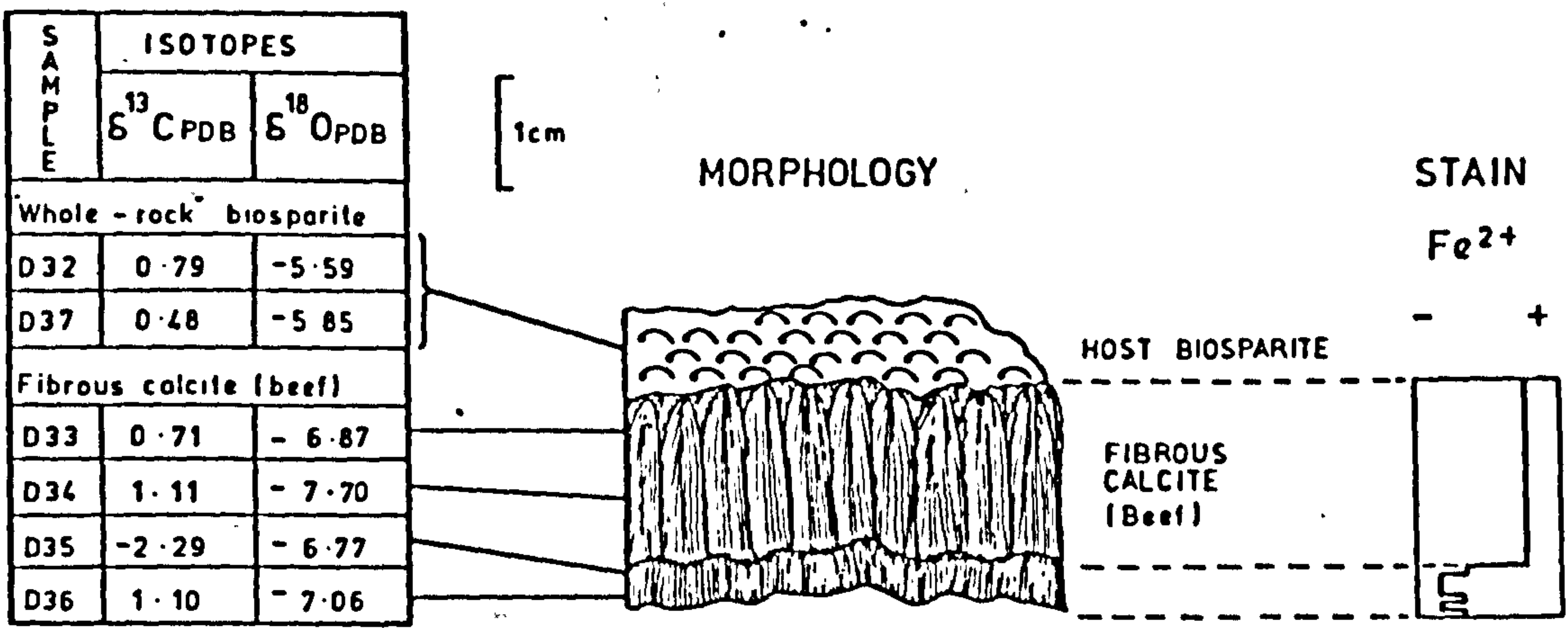


Figure 4.18 Isotopic composition, morphology and stain-defined zones within the fibrous calcite veins from Swanage.

Isotopes

Continuity of growth is further reflected in progressive decrease in $\delta^{18}\text{O}$ (from -6.5 to -10.7) in samples away from the sandstone parting. Carbon isotopic composition varies between 3.40 and 1.60, with decrease in $\delta^{13}\text{C}$ corresponding to a zone of low iron content (Fig. 4.1⁴).

SWANAGE

The upper section of the 'Chief-Beef-Beds' (basal Cretaceous) at Durl^ston Bay, Swanage (Fig. 4.1) contains a fauna of fresh water ostracod^es and gastropods (R.G. Clements, unpublished data). Thin symmetrical fibrous calcite veins (beef) occur throughout the shales but reach a maximum thickness (≈ 2 cm.) where asymmetric^d downward growth has taken place beneath an overlying molluscan biosparite. (Broken Shell Limestone; Bed 220, R.G. Clements in Torrens, 1969).

The veins are predominantly ferroan with a basal stage (0.4 mm.) of non-ferroan calcite with weak ferroan zones (Fig. 4.18). Aragonitic bivalve debris in the overlying limestone has been dissolved out and the voids filled by ferroan calcite cement (Brown, 1954).

Competitive conical growth is restricted to the upper part (0.3 cm) of the vein where bundles of fibrous calcite crystals nucleated against the irregular base of the limestone (Fig. 4.18). Distinct sub-parallel bundles of radial fibrous calcite can be traced through the entire thickness of the vein. These 'cone' boundaries are defined by intercrystalline inclusions; an inner delicate fibrous fabric is defined by linear trails of intracrystalline intrusions near the top of the vein. A distinct fabric discontinuity, 0.4 cm. above the base of the vein (Fig.

4.18), corresponds to the stain-defined ferroan to non-ferroan boundary, and occurs where the coarse, radial-fibrous, ferroan crystals splay outwards and are split into discrete radiating non-ferroan fibrous calcite (Fig. 4.17). Stain-defined zonal boundaries which parallel the base of the vein (Fig. 4.18) are not reflected in the crystal morphology.

Isotopes

Serial samples from the two growth stages apparently define two isotopic trends (Fig. 4.13). However, three of the samples have very similar compositions (range of 0.4%, $\delta^{13}\text{C}$ from 0.7 to 1.1 and 0.8%, $\delta^{18}\text{O}$ -6.87 to -7.70) and the third is significantly different only in $\delta^{13}\text{C}$ ($\delta^{13}\text{C}$ -2.29, $\delta^{18}\text{O}$ -6.77). The decrease in $\delta^{13}\text{C}$ corresponds to the decrease in Fe^{II} beneath the fabric break (Fig. 4.17). Limestone samples have positive $\delta^{13}\text{C}$, a detailed discussion of the values is not warranted on two analyses (see Allen and Keith, 1965, Allen et al. 1973) but it is likely that the late cements in the limestone have similar isotopic composition to the adjacent beef vein (Marshall and Ashton in press; own unpublished data).

DISCUSSION

RECRYSTALLISATION - POSSIBLE EFFECT ON

GEOCHEMICAL TRENDS

Each vein displays a pattern of intracrystalline inclusion trails which indicate the presence of a former, more finely divided, fabric; Charmouth veins have apparently incorporated secondary ferroan veinlets within the strained crystal mosaic. A degree of secondary calcite growth or 'recrystallisation' has, undoubtedly taken place, but several features suggest that any

such growth may have had minimal effect on the chemistry of the calcites.

1) Inclusion trails parallel crystal boundaries which in turn define the primary cone structure. The pattern of inclusions at the major fabric discontinuities bear a marked resemblance to growth-stage fabrics in speleothem calcites (e.g. Folk and Asseretto, 1976, Kendall and Broughton, 1977, 1978). By analogy it is likely that crystal growth and coalescence may have been virtually simultaneous and have taken place in pore-waters of similar composition.

2) Zonal boundaries are apparently primary: they parallel the vein margins and fabric breaks and at Charmouth they are related to similar growth stages above and below the concretion. A neomorphic origin for the zones would have to account for relative recrystallisation rates which varied in exactly the same way as those of primary growth.

3) The retention of primary zoning and ferroan 'streaks' where veinlets have been incorporated in the outer fibrous calcites from Charmouth suggests that wholesale recrystallisation and chemical re-equilibration cannot have taken place during coalescence. The isotopic values from these calcites must therefore be composite (primary fibre and veinlets) and the trends treated with caution.

4) With the very limited trace element data available there is no evidence for a metastable precursor carbonate (aragonite or high magnesium calcite; c.f. Davies, 1977). Calcite to calcite 'recrystallisation' or fabric stabilisation without major exchange with external waters is unlikely to

produce major changes in the isotopic composition of the calcites (Lawrence, Gieskes and Anderson, 1976).

ISOTOPES AND IRON-REVERSALS IN PORE WATER COMPOSITION

TRENDS DURING BURIAL.

The isotopic and trace element composition of successive carbonate precipitates can be used to indicate the changing composition of the pore waters during sediment burial. Fibrous veins from Eigg, Skye and Swanage have similar $\delta^{18}\text{O}$ range to the later fibrous calcites at Charmouth. The concretion from Charmouth is the earliest diagenetic precipitate described in this paper.

CHARMOUTH CONCRETION-SHALLOW BURIAL (0-10 m?)

Core and outer rim $\delta^{13}\text{C}$ values indicate mixed organic and marine carbon sources in early diagenesis. Bacterial reactions are commonly cited as a mechanism for the production of light bicarbonate carbon ($\delta^{13}\text{C} \approx -2.5$, Hodgson, 1966, Hoefs, 1970, Tan and Hudson, 1974, Hudson and Friedman, 1976, Irwin et al., 1977) under shallow burial conditions (10 m maximum). The pyritic preservation of uncrushed ammonites in the surrounding shales testifies to the early onset of bacterial activity (Hudson, 1978(6)). $\delta^{18}\text{O}$ values (Fig. 4.7) are too light (-4) to reflect inorganic equilibrium precipitation in seawater of normal isotopic composition at shallow burial temperatures; they must therefore reflect either an early source of ^{18}O depleted water or late re-equilibration at increased temperature or with water of modified isotopic composition (c.f. Hodgson, 1966, Irwin et al. 1977). Isotopic data are not sufficient to determine which is the more likely mechanism.

The carbon isotopic composition of the ferroan dolomite zone (average $\delta^{13}\text{C} = 2.5$, Fig. 4.7, 8) indicates a 'marine' source of bicarbonate carbon but the $\delta^{18}\text{O}$ (mean of -1.0) is less easy to interpret. The isotopic fractionation factor between co-existing calcite and dolomite has not been determined experimentally at sedimentary temperatures (Friedman and O'Neil, 1977, and discussion in Dickson and Coleman, in press). It is likely that dolomite is enriched by around 4% in $\delta^{18}\text{O}$ and 1% in $\delta^{13}\text{C}$ in comparison to the co-existing calcite. On application of this correction to the Charmouth data; the dolomites could have formed during original concretion growth from pore water with similar oxygen isotopic composition to that which precipitated the calcite zones.

Septarian calcites have similar isotopic composition to the calcite zones (light $\delta^{13}\text{C}$, and $\delta^{18}\text{O} \approx -4$) and probably precipitated soon after the main body of the concretion. The change from ferroan to non-ferroan calcite corresponds to a decrease in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Figs. 4.7, 8). Renewed bacterial decay probably reduced the availability of iron and released light carbon; the shift in $\delta^{18}\text{O}$ (from -4% to -6%) may suggest that reactions involving organic matter may also have released a source of light oxygen. (Organisms may preferentially incorporate ^{16}O , Garlick, 1969) but data are again too restricted for firm conclusions to be drawn.

The non-ferroan zone of septarian calcite has similar isotopic composition to the earliest stage of fibrous calcite (Fig. 4.8), an indication of continuity of precipitation between concretion and fibrous calcites.

FIBROUS CALCITES

PORE WATER COMPOSITION AND ORIGINS

The pore waters in which the fibrous veins were precipitated did not have constant chemical composition. Growth of all but the Skye vein must have been discontinuous. Although the isotopic trends do not preserve a continuous record of pore water composition changes during burial; they reflect the composition at times in the burial history when pore waters contained sufficient bicarbonate for carbonate precipitation and the physical state of the shales was such that displacive fibrous growth could take place. This discussion will centre on the chemical aspects of the origin of the bicarbonate and the subsequent model for growth (Environment - section below) will attempt to account for the resumption of suitable physical conditions.

The oxygen isotopic composition of the fibrous calcites are all too light to reflect equilibrium precipitation at realistic burial temperatures from water of normal marine isotopic composition (Hudson, 1978). The range of $\delta^{18}\text{O}$ values (-4 to -11) corresponds to those of common late diagenetic cements in limestones and sandstones (Tan and Hudson, 1974, Dickson and Coleman, in press) and the similarity in $\delta^{18}\text{O}$ in veins from sediments from such different depositional environments suggests that the veins grew in burial rather than in depositional waters (Franks, 1969, MacKenzie, 1972)

In many diagenetic systems there is a systematic ^{18}O depletion in successive precipitates which can be attributed to increasing temperature and gradual pore water evolution with burial (Lawrence 1973, Hudson, 1978, Dickson and Coleman in press).

Such a model could perhaps be proposed for the vein from Skye but successive fibrous calcites from the other veins show reversals in isotopic composition which would indicate substantial 'temperature' fluctuations which are extremely unlikely under normal sedimentary burial conditions. The reversals must therefore be due to changes in pore water composition. Most of the mechanisms proposed for the modification of the $\delta^{18}\text{O}$ during burial are unidirectional, gradual and depth related. Fractionations induced by temperature increase, diagenetic reactions with clay minerals or organic matter or through shale ultrafiltration have all been proposed to explain the almost ubiquitous lightening of pore water oxygen values (Anderson and Schneidermann, 1973, Coplen and Hanshaw, 1973, Lawrence, Gieskes and Anderson, 1976, Lawrence et al., 1979, Irwin et al., 1977). Mixing of connate and meteoric-derived groundwaters at depth will also give rise to waters with light $\delta^{18}\text{O}$ (Hitchon and Friedman, 1969, Hudson, 1978).

Possible mechanisms for the isotopic reversals and trends toward heavier oxygen in later stages can now be considered.

1) Local input of heavy marine bicarbonate. Dissolution of metastable (aragonite and high magnesium calcite) fossils and cements during burial would introduce marine bicarbonate with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ near to zero. The process would probably be sufficient to maintain marine carbon values but because of restricted solubility in each pore volume would be unlikely to affect the much greater reservoir of pore water oxygen.

2) Reversals in connate water evolution. Shales undergoing compaction act as ionic filters and semi-permeable membranes which induce isotopic and salinity variation in the

expelled pore waters (Coplan and Hanshaw, 1973, Magara, 1974). The ultrafiltration process produces residually O^{18} enriched waters which may be released under final stages of compaction. It is not known at what stage expulsion occurs or indeed the magnitude of the fractionation in natural pore water systems so it is difficult to assess whether the process may have been able to account for the observed isotopic reversals.

3) External supply of pore waters. Pore water mixing with external (meteoric?) supply is a common occurrence in the geological history of sedimentary basins (Hitchon and Friedman, 1969) and provides a possible source of isotopically different water. Isotopic data are not sufficient to determine the exact nature of the origin of such external pore waters.

Carbon

As suggested above the $\delta^{13}C$ variation can be attributed to minor input of organogenic carbon in waters dominated by a marine bicarbonate source. Dissolution of metastable fossil and cement carbonate together with production during stylolite^l formation are likely sources of marine carbonate (Hudson, 1975).

The earliest fibrous calcites at Charmouth mark the end of major contribution of light carbon from bacterial sources; it is likely (and consistent with the oxygen values) that the minor fluctuation in later stages at Charmouth and those in the other veins reflect a later diagenetic^{et} (10's or probably 100's of metres burial) input of light carbon. Alternative sources for such material are minor proportions of bicarbonate carbon from abiotic redox and decarboxylation reactions within the shales (Irwin et al. 1977, Curtis, 1978) or the introduction of marginally ^{13}C depleted meteoric-derived water during burial (Allan and Matthews, 1977, Wigley, 1978, Hudson, 1978).

ENVIRONMENT AND MECHANISM OF FIBROUS CALCITE PRECIPITATION

1. Direction of pore water flow.

At Charmouth the relative thickness of each growth stage and chemical zone is different above and below the concretion (Fig. 4.7). Early precipitation was concentrated above the concretion, demonstrating early vertical pore water movement (e.g. Lang et al., 1923) probably during expulsion of connate waters and cessation of bacterial activity. Chemical trends show that later precipitation of the two veins took place in pore water of similar isotopic composition and probably therefore the same stage of burial. In common with lenticular horizons in the surrounding shales, lateral groundwater flow may have been important in supplying new bicarbonate (Kendall and Simpson, 1974). The veins from the other three localities are best developed next to potentially permeable sand and limestone beds against suggesting the importance of laterally flowing waters. Growth discontinuities suggest that supply of bicarbonate was intermittent and ^{growth} probably took place during periods of maximum pore water flow.

2. Mechanism of emplacement.

Cone structure is ~~mirrored~~^{shown} by crystallographic boundaries and shale inclusions. The fibrous and conical form must have been primary growth features and not induced by later tectonic strain (Shearman et al. 1972, MacKenzie, 1972). Fibre curvature and ^{the} pattern of internal zones in symmetrical veins demonstrate growth by a process of antitaxial (outward) addition of carbonate at the vein margins (Durney and Ramsay, 1972, Watts, 1978) so a syntaxial ~~(void-filling)~~ mechanism (Shearman et al. 1972) is not applicable.

The fibrous calcites are displacive and presumably grew into relatively plastic sediments (Woodland 1964, Franks 1969), but the isotopic evidence suggests a later diagenetic origin after the cessation of bacterial activity and considerable modification of pore water oxygen composition. To explain this apparent contradiction it is necessary to invoke a mechanism whereby effective overburden pressures (and shale plasticity) could be temporarily and periodically reduced under several tens or more probably, hundreds of metres of burial. Shearman et al. (1972) encountered a similar problem in the origin of late diagenetic gypsum veins. They suggested that hydraulic jacking by the introduction of high pressure pore waters during re-exhumation of the sediment column had supported the overburden pressure and that gypsum had grown syntaxially into the water sheets. With the calcite veins it is not necessary to propose such extreme pore water pressures; development of hydrostatic pressures which approach lithostatic overburden pressure could cause the increased plasticity necessary to trigger displacive growth. Such over-pressured horizons are common features in shales undergoing relatively rapid burial where the hydraulic conductivity of the sediment cannot cope with the expulsion of the pore waters (Magara, 1968, Bredehoft and Hanshaw, 1968). Moreover during overpressuring migration of pore fluids in and adjacent to shale horizons reaches maximum intensity. Waters with differing chemical composition are expelled toward and along more permeable horizons (Magara, 1974). The mechanism may therefore explain both the density and distribution of the veins. Shale horizons containing the Skye and Eigg veins are probably too thin to have been overpressured to any great extent (Bishop, 1979) but it is

possible that the sandstone formations in which they occur may have been receptors of waters expelled from adjacent shales during times of increased burial rate. Reversals in isotopic composition may be due to variation in the degree of mixing of local and more distant bicarbonate supplies.

CHAPTER 5

The isotopic composition of epicontinental marine limestones, with emphasis on the Jurassic limestones of Britain.

ABSTRACT

Bulk limestone samples are composite and their carbon and oxygen isotopic values are mixtures of the compositions of their original marine components and those of late cements. The depositional components (Allochems, micrite and early cement) have retained a primary 'marine' isotopic composition ($\delta^{18}\text{O}$ 0.0 $\delta^{13}\text{C}$ +2 to +3) throughout diagenesis without re-equilibration with burial waters. Mineralogical stabilisation must have taken place in a system with a low effective water:rock ratio and before major cementation. Hardground isotopic data cannot be used to indicate the precise composition of ambient sea water but the preservation of heavy $\delta^{18}\text{O}$ values in some Palaeozoic examples ($\delta^{18}\text{O} > -2\%$) may indicate that sea water has not changed significantly since the Ordovician.

The spread of isotopic values at an individual locality may be attributed to the presence of variable proportions of late sparry calcite cement (with light $\delta^{18}\text{O}$ of -5 to -13‰ and variable but generally marine $\delta^{13}\text{C}$) in bulk limestone samples. Sparry cements are interpreted as having been generally precipitated after sediment burial (to an unknown depth) and modification of the pore water isotopic composition rather than shallow freshwater phreatic conditions. The origin of the almost ubiquitous decrease in $\delta^{18}\text{O}$ in late cements remains problematical.

INTRODUCTION

Shallow marine carbonates accumulating to-day have a narrow range of carbon and oxygen isotopic composition (Milliman and Muller, 1977, Hudson, 1977); their ancient counterparts are characterised by a similar range of carbon isotopic values but exhibit a much wider range of $\delta^{18}\text{O}$. (Keith and Weber, 1964, Hudson, 1975, 1977). The causes of the almost ubiquitous depletion in ^{18}O are the subject of this paper.

Results of isotopic analysis of 295 samples from Mesozoic and a few Palaeozoic epicontinental limestones are used to determine overall diagenetic trends. By relating the isotopic values to the modal proportions of primary 'depositional' components and sparry calcites at individual localities it has been possible to demonstrate that precipitation of ^{18}O depleted calcite cements was the dominant diagenetic process.

SAMPLING

This study has centred on diagenetic trends within the carbonates of the Middle Jurassic, Lincolnshire Limestone Formation of Eastern England and discussion of the results from this Formation will form a major part of this paper (Section I). Sampling of features of obviously different diagenetic history enables the pattern of cementation to be determined : oolitic sands with no discernable cements can be found at the same locality as can oosparites with a total intergranular fill of blocky ferroan cement. Hardgrounds, surfaces of syndepositional lithification, display the effect of both early and late cementation while blocky calcites filling the former solution-voids of coral colonies are ~~invaluable~~ concentrations of later diagenetic precipitates.

In Section II results are presented from samples of a number of other British Jurassic Limestones. Again sampling was directed toward obvious diagenetic features particularly hardground surfaces and late cement concentrations. The limestones at Dagham Downs which are thought to have been temporarily emergent were analysed for comparison with values from Recent and Pleistocene carbonates undergoing subaerial diageneses in the Bahamas (e.g. Gross, 1964, Allan and Matthews, 1977). Coral colonies at Shellingford Cross Roads Quarry exhibit a range of diagenetic features in sediments which were subjected to penecontemporaneous emergence erosion and smothering of coral growth by clays of volcanic origin,

Results presented in Section III are from hardground surfaces in French (Jurassic) and North American (Ordovician to Cretaceous) limestones. The latter extend the stratigraphic range to which the suggested diagenetic models can be applied and enable limited discussion of proposed time-trends in the isotopic composition of seawater.

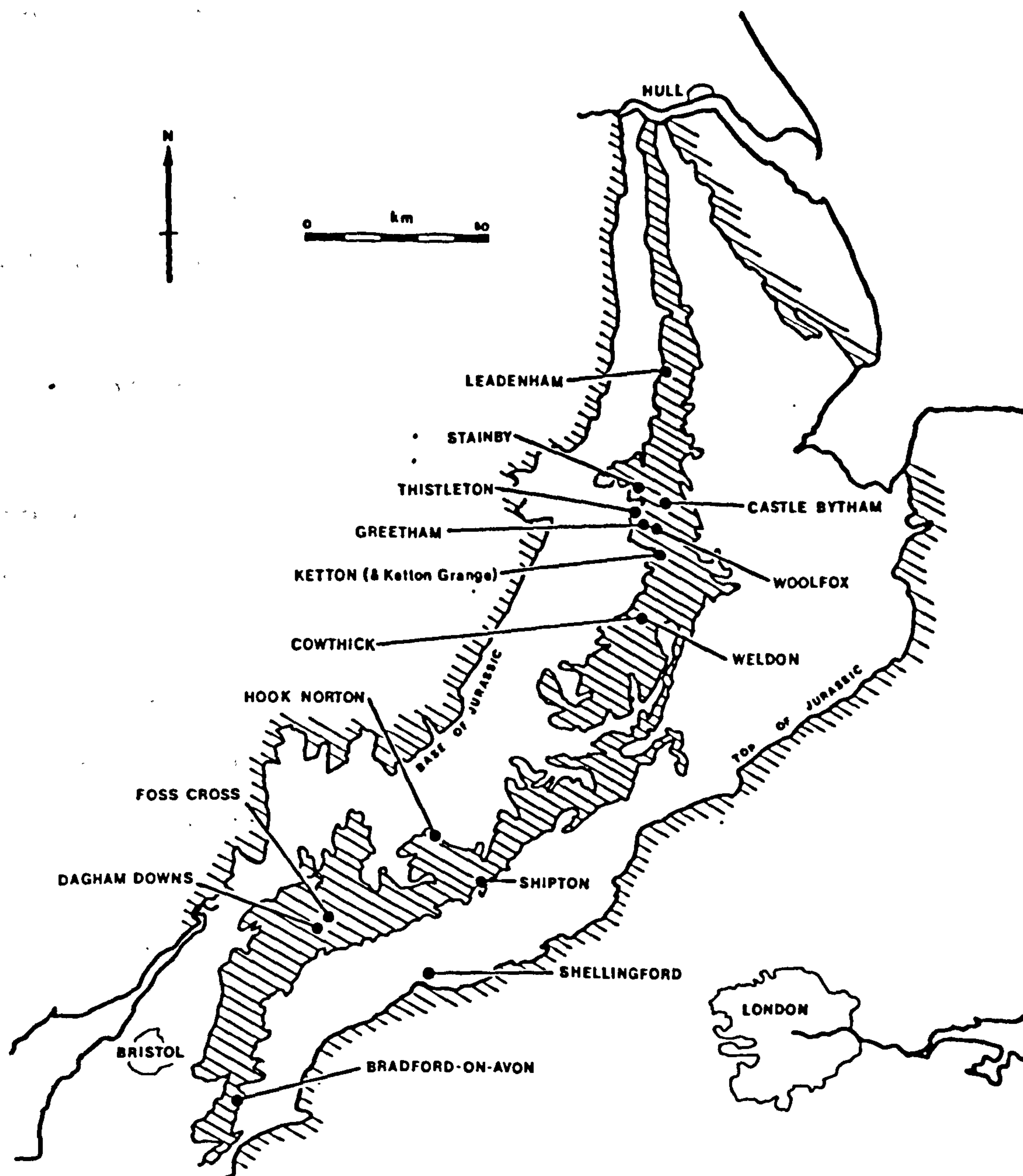


Fig. 5.1. Lincolnshire Limestone and other British Jurassic localities. (Results sections I and II). Middle Jurassic outcrop (Great Oolite and Inferior Oolite) shown by continuous hatching.

METHODS

ISOTOPES

Samples were extracted from ^h and specimens using a dental drill; 20-30mg of calcite was then treated with 15ml of 1% sodium hypochlorite solution to remove organic contaminants (Forester et al, 1973). Carbon dioxide was extracted by reaction of around 10mg of carbonate with 100% phosphoric acid at 25°C. (McCrae, 1950). Isotopic ratios were determined on 'VG-Micromass' mass-spectrometers at the Institute of Geological Sciences, London and results were corrected for mass and background effects using standard procedures. (Craig, 1957., Deines, 1970). ¹⁸O/¹⁶O and ¹³C/¹²C ratios are expressed in the usual way as 'per-mil' difference from the PDB international standard.

POINT COUNTING

Point counts were carried out on thin-sections of material from Lincolnshire Limestone and from Dagham Downs Quarry (Section II). A minimum of 200 points per thin section were counted. To determine the ratio of late sparry calcite to original components all allochems (ooliths, pellets, calcite shell fragments and intraclasts), early fringing cements and micrite were classed as primary marine (or depositional) components; all clear calcites other than fringing cement, whether inter or intragranular were counted as late cement ('spar' of figs. 5.9 and 5.10). Repeat counts on the same thin section generally agreed to within 2%.

RESULTS

Section I - Lincolnshire Limestone

The Lincolnshire Limestone (Bajocian) is the major marine carbonate Formation in the Middle Jurassic of Eastern England, (Arkell, 1933, Sylvester-Bradley in: Sylvester Bradley and Ford 1968), it outcrops over

a distance of around 200km from the Humber Estuary in the north to Northamptonshire in the south. It reaches a maximum thickness of 40m near Grantham but thins out to both north and south. The Limestone is an important aquifer (Downing and Monkhouse, 1969) and is bordered both stratigraphically and laterally by the shales of the Grantham Formation and Upper Estuarine Series. The carbonate succession has been interpreted as representing the landward migration of an offshore barrier complex (oolite of the Upper Lincolnshire Limestone) across back barrier lagoonal sediments (peloidal and micritic sediments of the lower and middle divisions; Ashton, 1977). Material for this study was collected from the ten localities shown in fig.5.1. Brief location and lithological details are given in Tables 5.1. and 5.2.

Lithologies and Diagenetic fabrics

The Lincolnshire Limestone encompasses a range of lithologies from oolitic bioclastic and peloidal calcarenites to micritic limestones. The degree and style of lithification varies from oolites with little or no recognisable intergranular cement or matrix, through calcarenites with a mixed spar/micrite matrix, to 'clean' oosparites with a total intergranular fill of poikilotopic ferroan spar. Distribution of blocky calcite cement is sporadic and not consistently related to lithology or particular beds (e.g. Ketton). Occasionally sparry cements are concentrated in horizons with a predominance of molluscan shell debris, in oolites which otherwise lack intergranular precipitates (e.g. mollusc biosparite 'rag' in the Building Stone Quarry at Weldon).

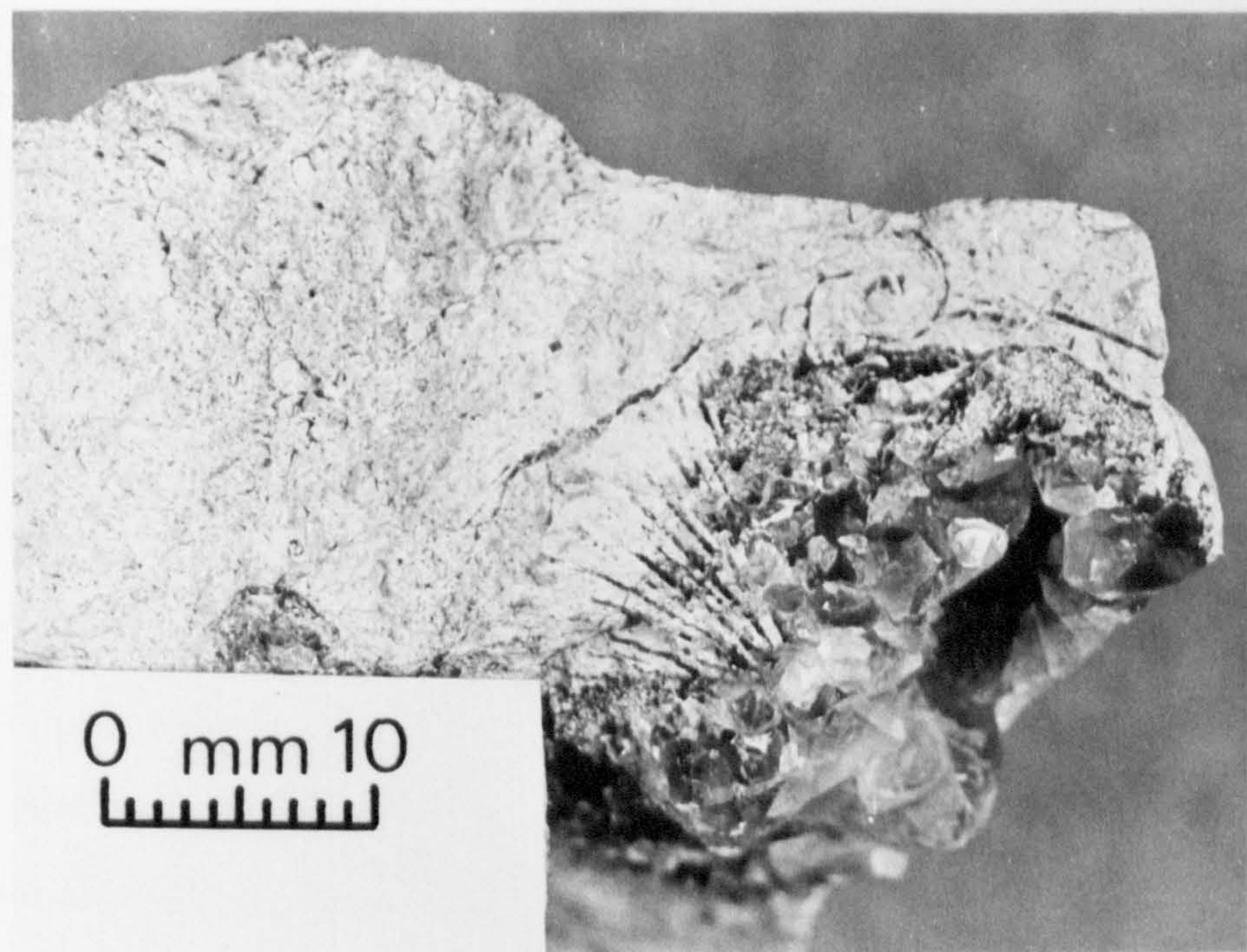
Uncemented horizons and poorly consolidated burrow-filling sediment have apparently never been cements, there are no relics of precipitates which have been dissolved in later diagenesis. Grain contacts in these sediments are generally short, though compressed concavo-convex grain boundaries can be found in some of the more massive uncemented units. (e.g. oolite 'freestones' of Weldon and Ketton). Lithification of these sediments must have been brought about by grain contact welding

Fig.5.3. A. 'Coral' from Woolfox Quarry (Results-section I) Interseptal sediment preserves the outline of the skeletal structure. Central solution void and individual septal voids have been filled with ferroan spar (dark areas)

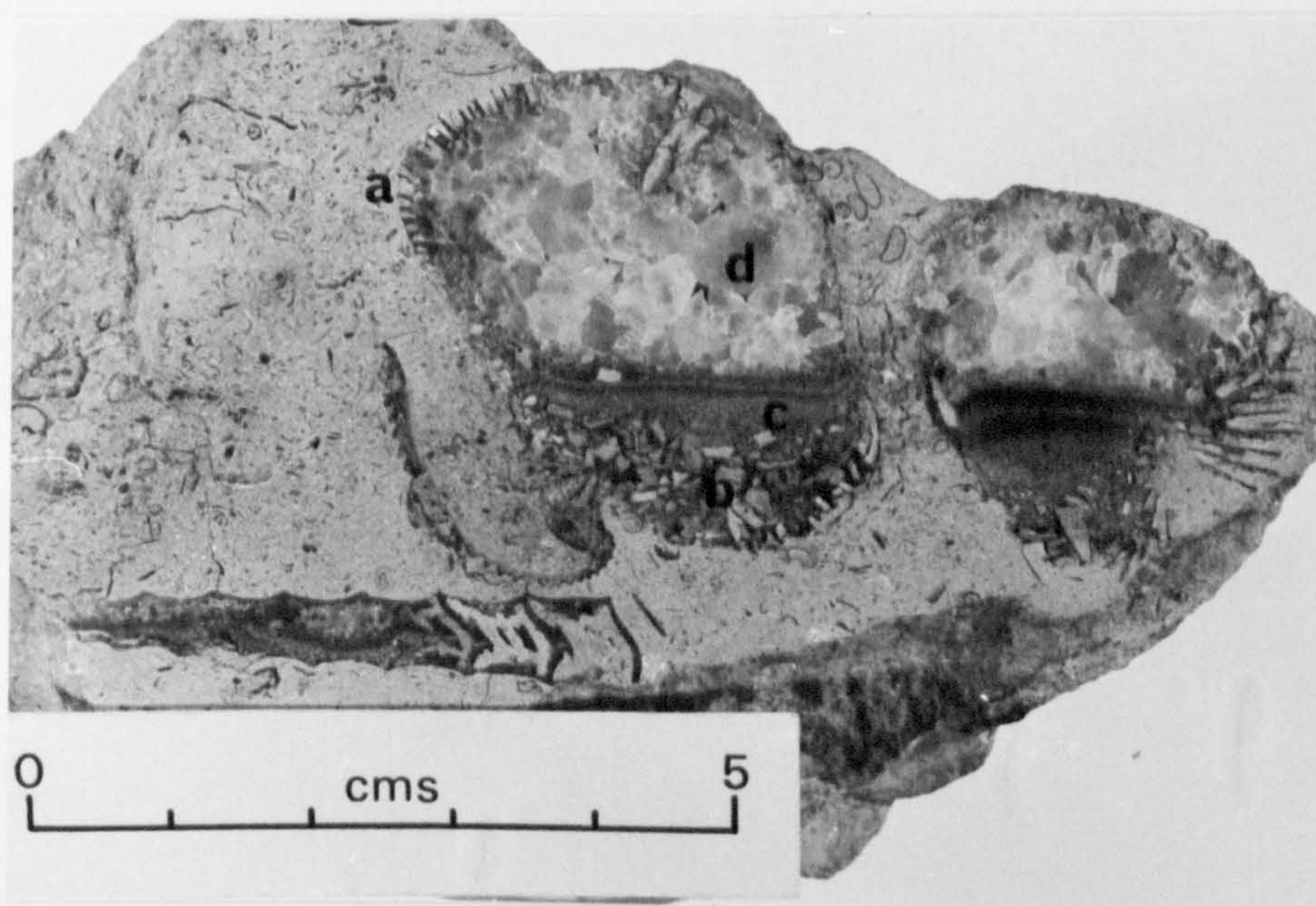
B. Coral from Woolfox Quarry (Results - Section I).

- a. early-lithified interseptal sediment forms projections into the spar-filled former solution void.
- b. fragments of (a) are incorporated in the geopetal sediment.
- c. laminated calcitute internal sediment.
- d. ferroan spar filling the centre of the former solution void.

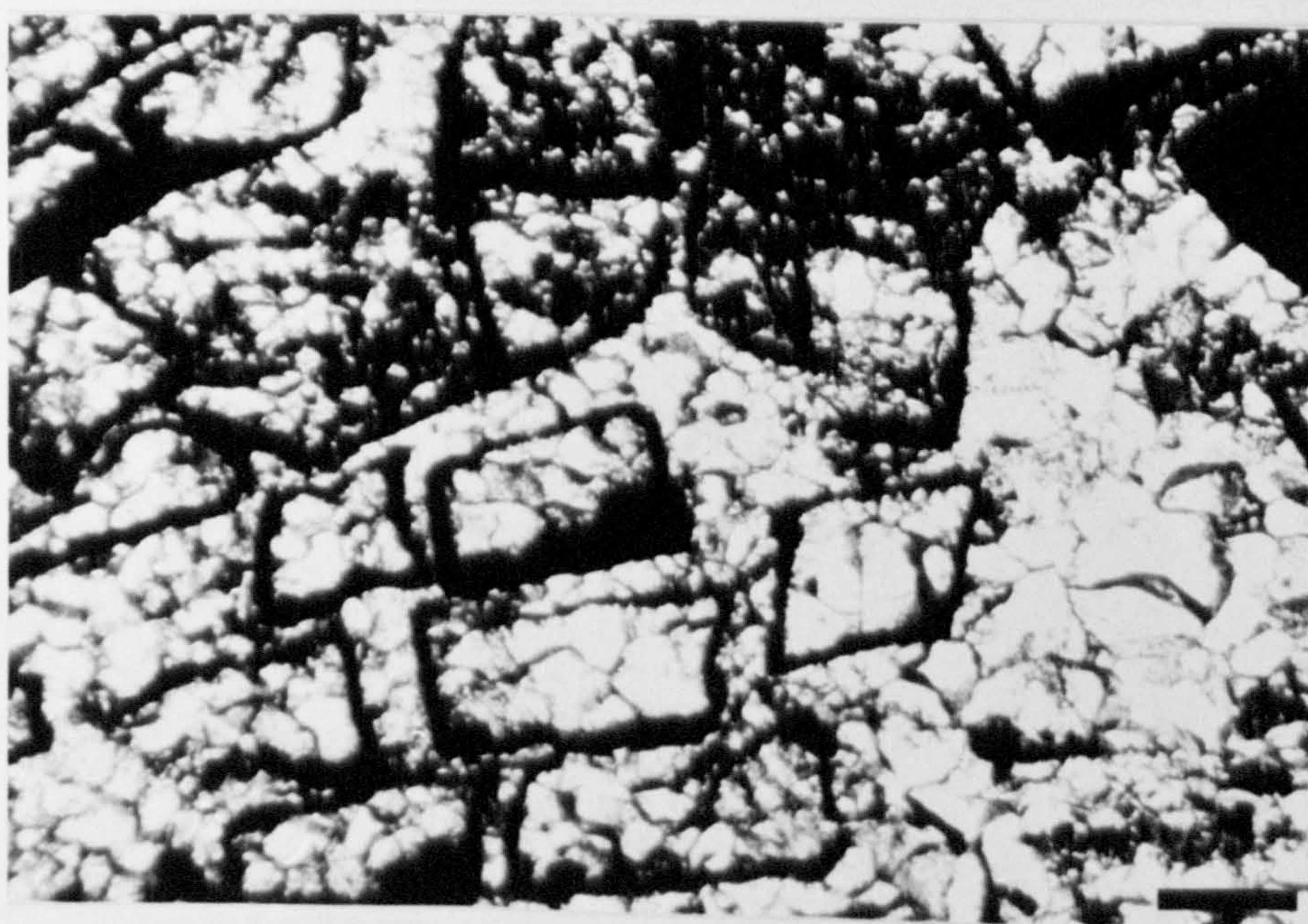
C. Micrite envelopes preserve the outline of interseptal areas in coral "replacement" from Stainby Quarry. Photomicrograph. Bar = 0.6mm.



A



B



C

or by minute amounts of early cement.

Syn depositional, fringing, cements are patchily developed throughout the limestones and are particularly abundant at some hardground surfaces (e.g. Cowthick and Kings Cliffe). Hardgrounds developed in each of the sub-environments within the barrier and back barrier complex: three of them (Cowthick, Castle Bytham and Leadenham) have been the subject of more detailed petrographic and geochemical analysis. (Marshall and Ashton; in press). The intensity of early submarine lithification is related to the turbulence of the depositional environment. $\delta^{18}\text{O}$ and Mg enrichment in the early cements provide evidence for former high-magnesium calcite submarine cements at the Cowthick hardgrounds.

All the limestones and cements sampled for the present study proved to be low magnesium calcite (by X-Ray Diffraction analysis); there are no traces of aragonite or dolomite. Former aragonite of mollusc and coral skeletal debris has been dissolved and the resultant voids filled or partially filled with blocky calcite cement. (Hereinafter loosely described as 'replaced' c.f. strict definition of Folk 1959). Micrite envelopes (Bathurst, 1966) are a common feature of preservation of both mollusc and coral skeletons.

The timing of the aragonite dissolution and blocky cement precipitation is problematic. At Cowthick and Kings Cliffe dissolution post-dates the precipitation of early fringing cements and probably therefore took place during subsequent burial. At Castle Bytham and Stainby however there are traces of fringing cements on both sides of micrite envelopes suggesting the early dissolution of aragonite.

Large colonies of corals (predominantly Thecosmilia.sp.) at Woolfox Quarry (fig. 5.5) are seen only in outline: the position of the former septa are preserved where early lithified interseptal

sediment forms projections into the former aragonite solution void. Broken fragments of interseptal sediment debris (non ferroan calcite) are incorporated in the laminated geopetal micrite (ferroan) which lines the floor of some of the former voids. There are no fringing cements in the adjacent pelmicrites but the sparitic areas of the matrix are variably ferroan. Aragonite dissolution must have post-dated a phase of early cementation but the laminated micrite internal sediments testify to the later resumption of turbulent pore water flow. Aragonite dissolution probably took place in early diagenesis before the sediment was buried to any extent. The central parts of the former solution voids are filled or, in some cases, partially filled, by blocky calcite spar. An outer(early) generation of pale green non-ferroan calcite lines some of the former cavities. The final calcite cement generation is in all cases uniformly ferroan. Euhedral, flat rhombohedral, crystals can be found in some of the partially filled voids.

At all the other localities the late blocky calcite is ferroan and unzoned. Depositional components are generally composed of non-ferroan calcite but in some of the fully cemented lithologies staining (Dickson, 1966) suggests that well preserved ooliths and micrites have an intermediate iron content and that a degree of intragranular cementation has taken place (see isotopic results).

Lincolnshire Limestone - isotopic results

The results of carbon and oxygen isotopic analysis of bulk and separated fossil or cement samples are presented in Table 5.2 and a 'scatter diagram' for each locality in Fig.5.4.(a) to (k). Details of the distribution of values and trends for each specimen are noted in the data table; only the general features will be presented here:-

1. All the samples lie in the marine limestones field on the C/O scatter diagram (Keith and Weber, 1964, Hudson, 1977).

There is no evidence for calcite precipitation during emergence

Fig.5.4. Carbon and oxygen isotopic scatter diagrams for the Lincolnshire Limestone data.







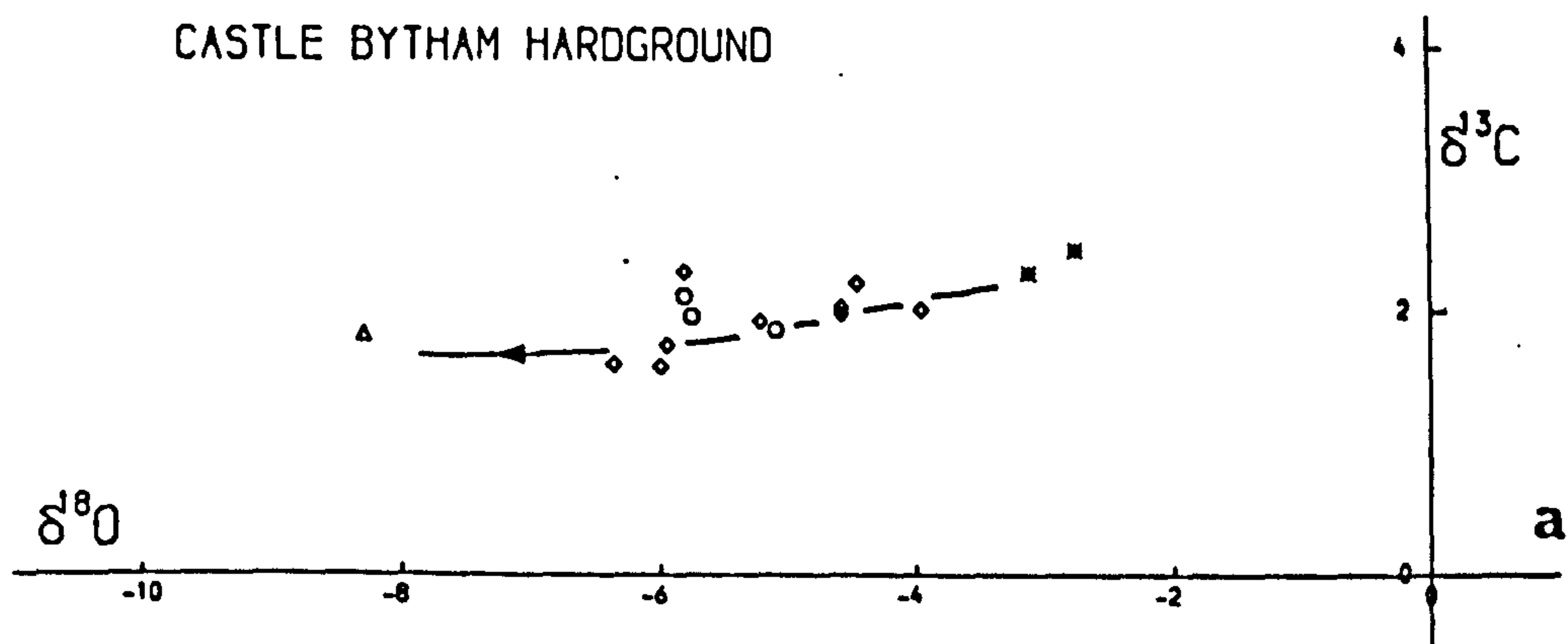
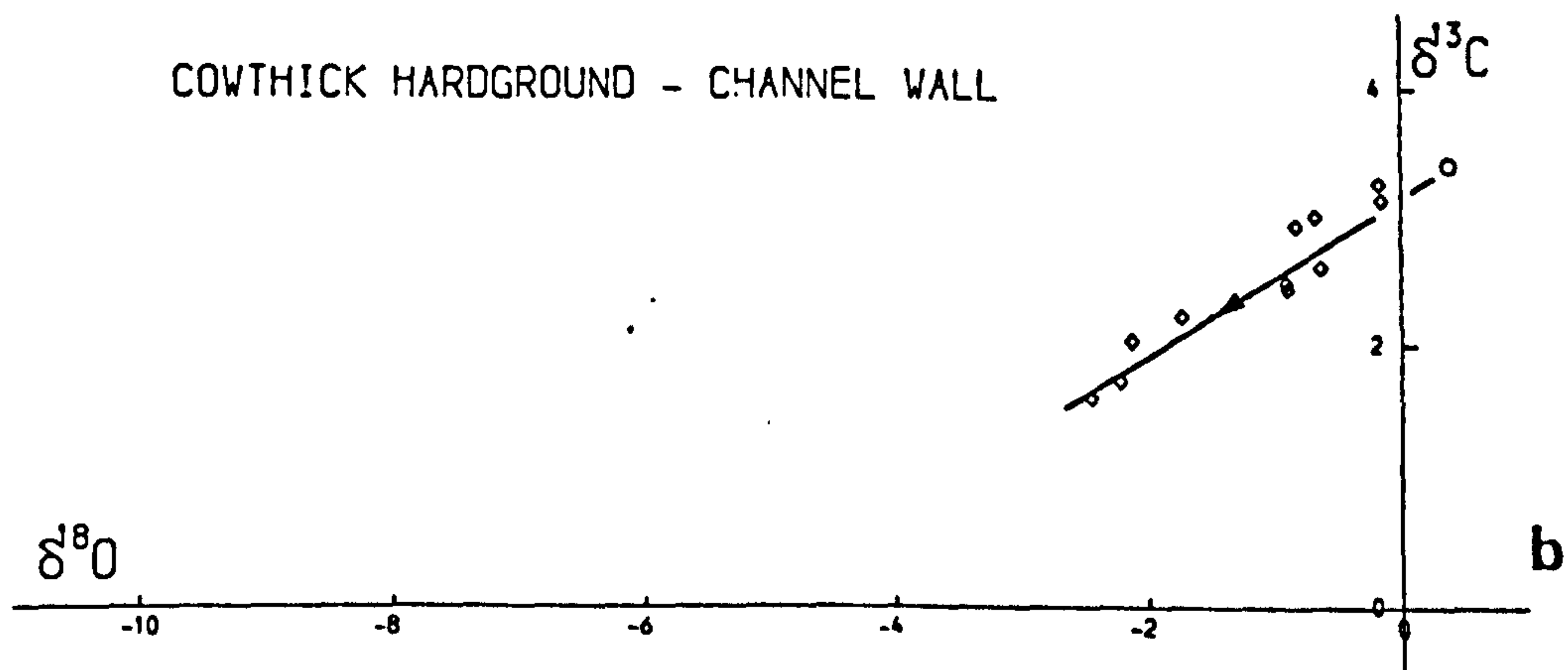
-  - Shell
-  - Whole-rock Limestone
-  - Burrow-fill or other geopetal sediment
-  - Sparry calcite - Non-ferroan or with well preserved skeletal inclusion relics
-  - Sparry calcite - ferroan (or only generation)
-  - Sparry calcite - in secondary veinlet

Fig.5.4

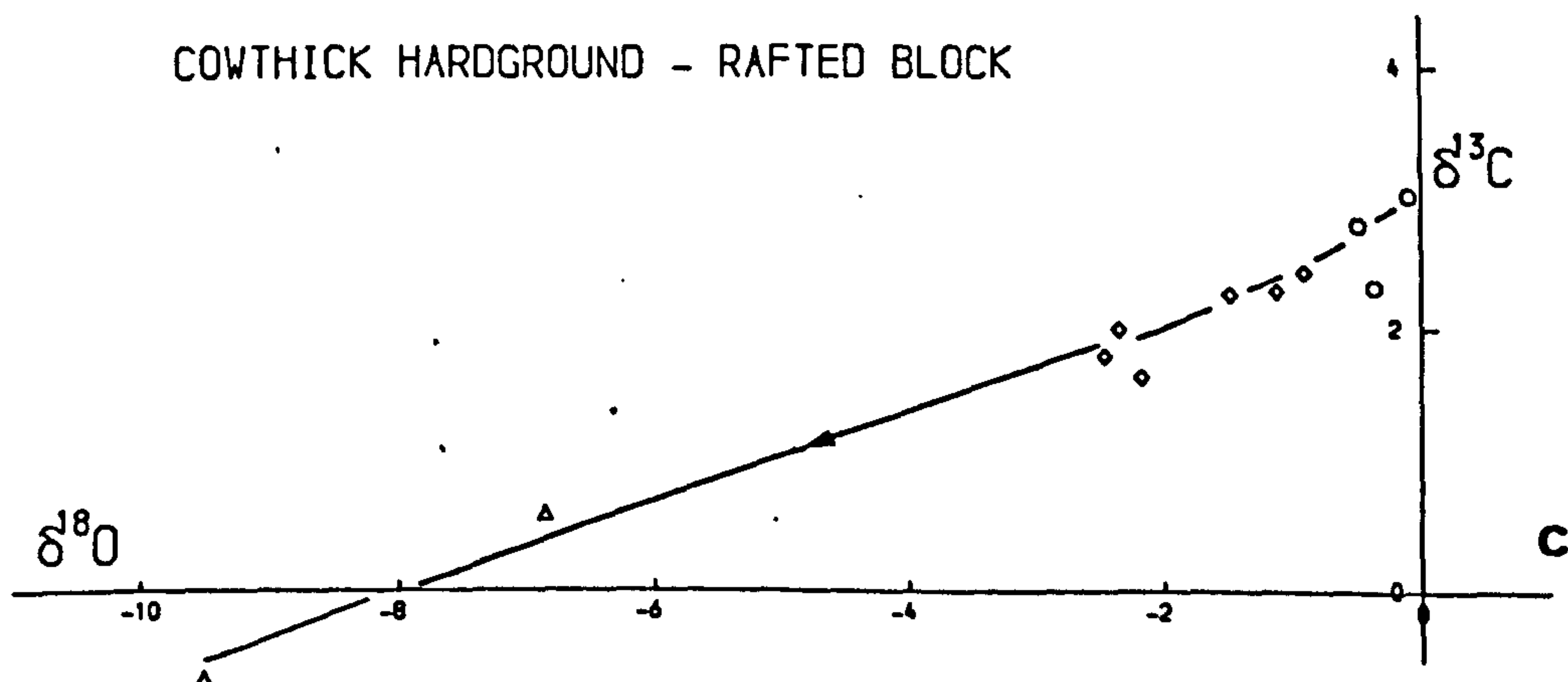
CASTLE BYTHAM HARDGROUND



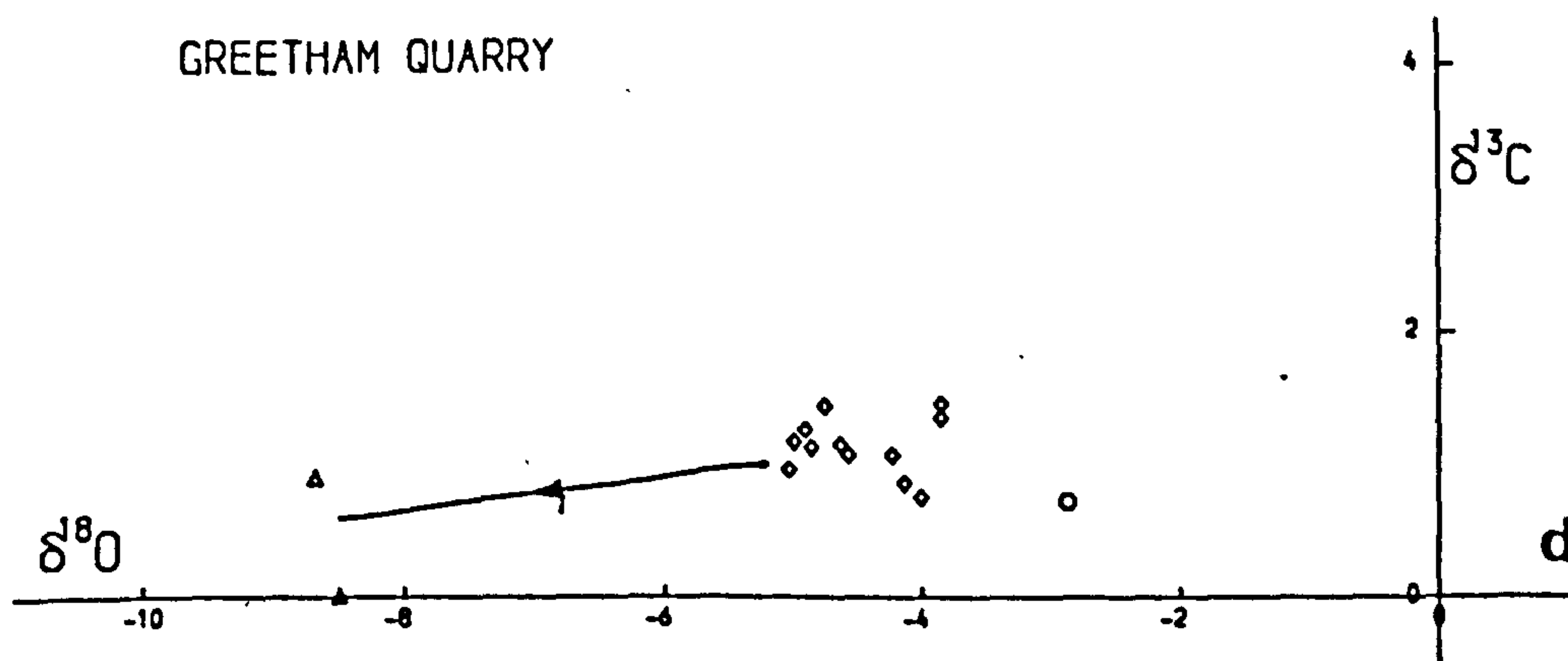
COWTHICK HARDGROUND - CHANNEL WALL



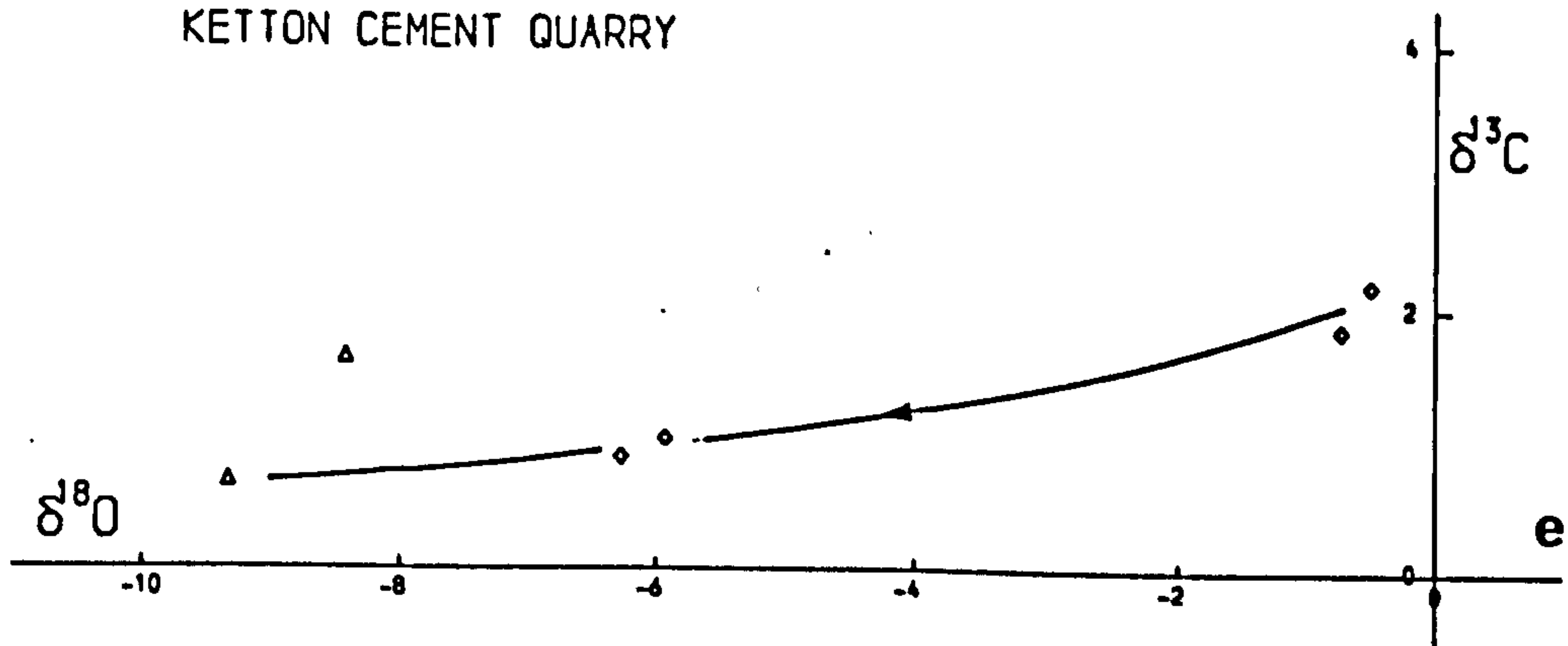
COWTHICK HARDGROUND - RAFTED BLOCK



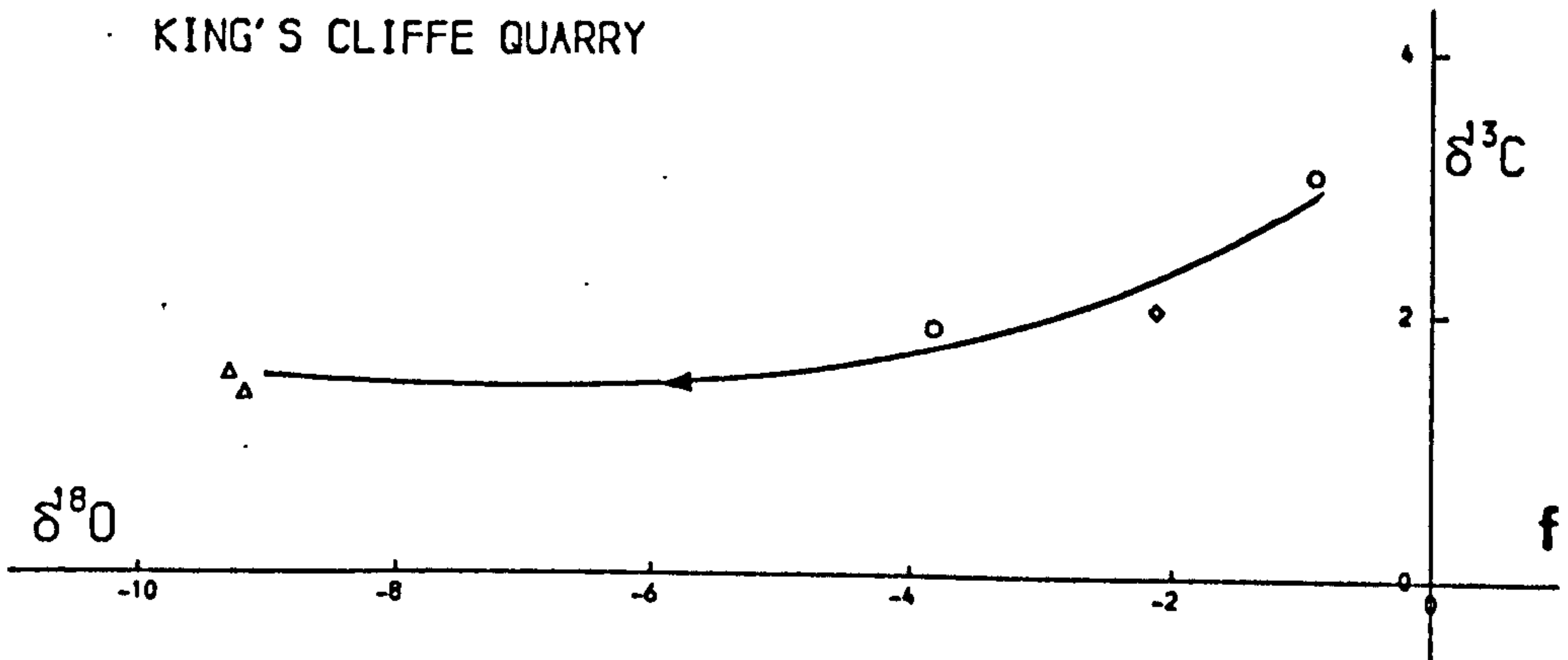
GREETHAM QUARRY



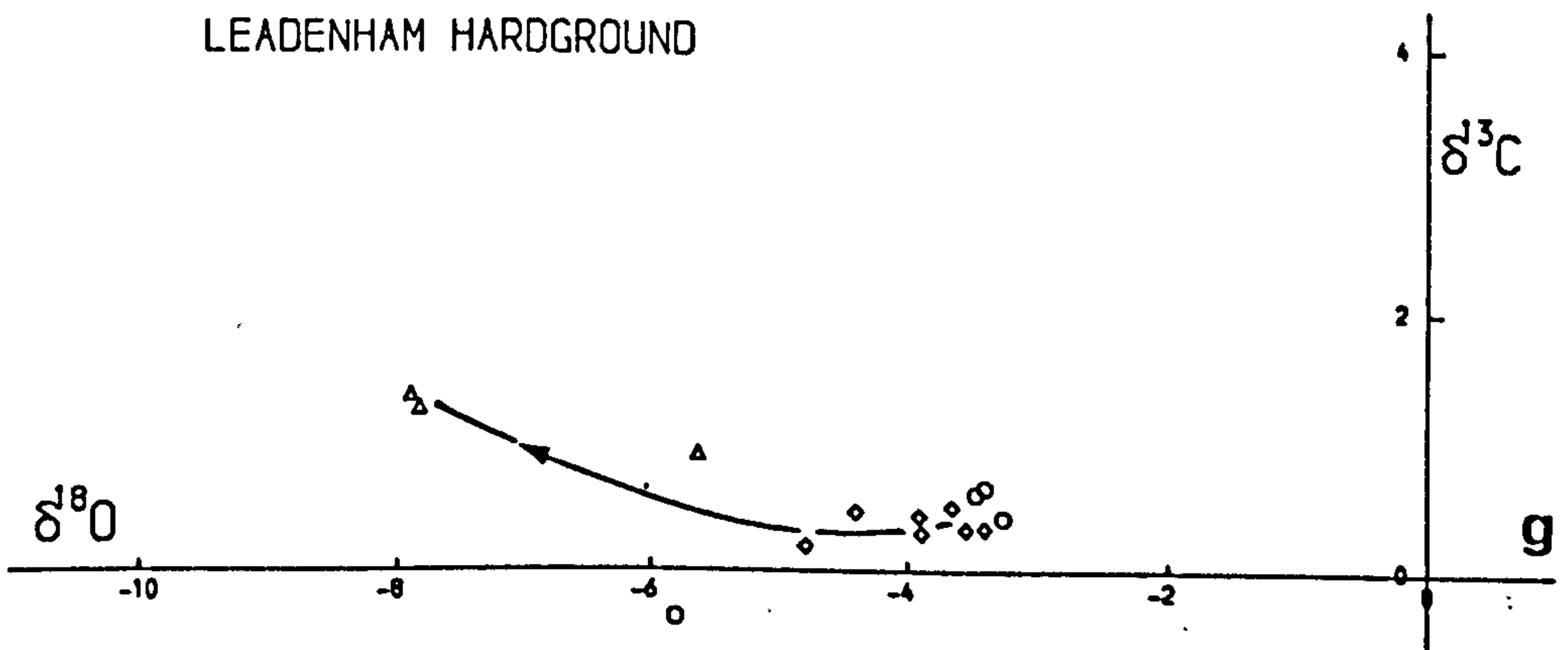
KETTON CEMENT QUARRY



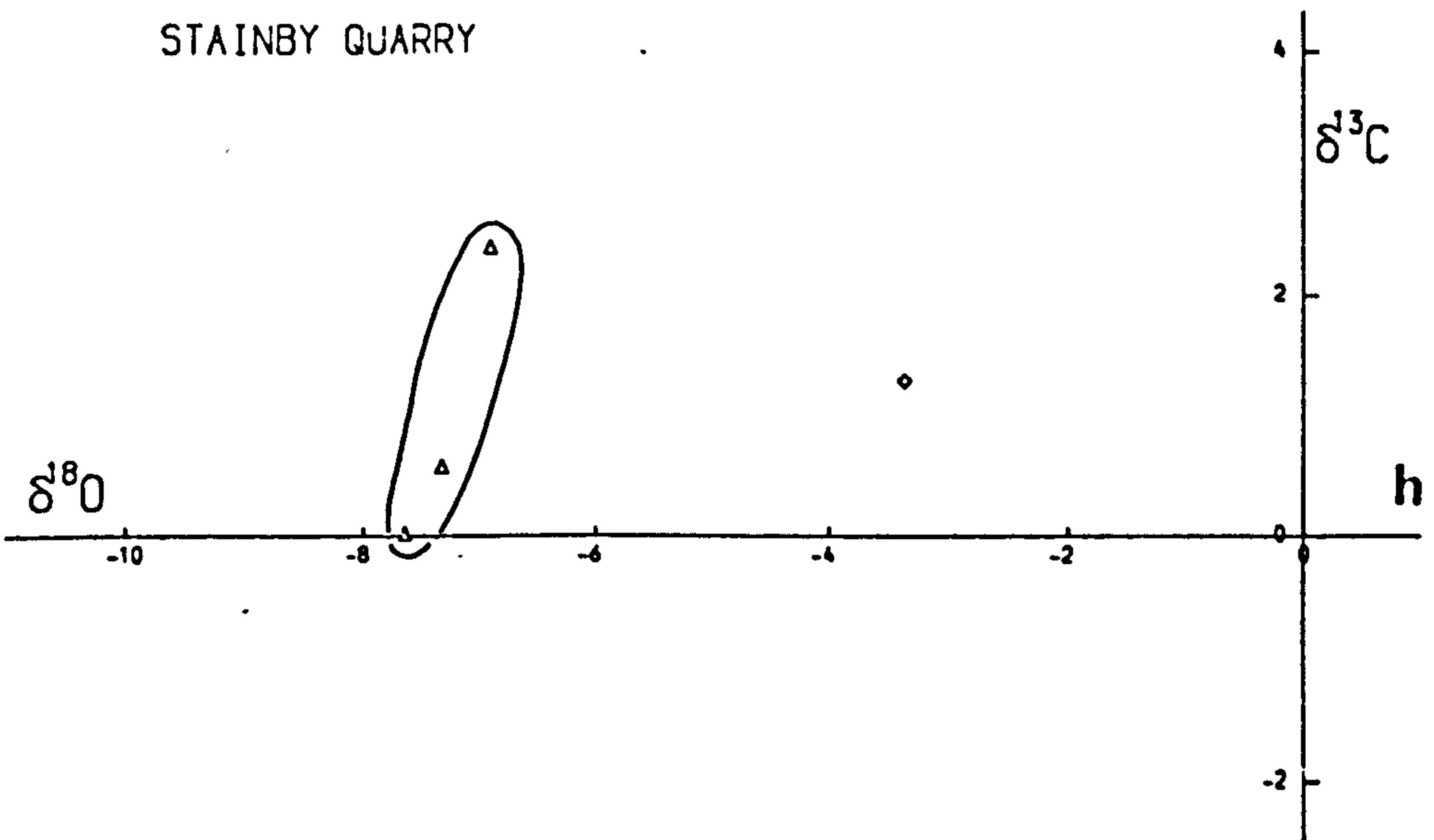
KING'S CLIFFE QUARRY

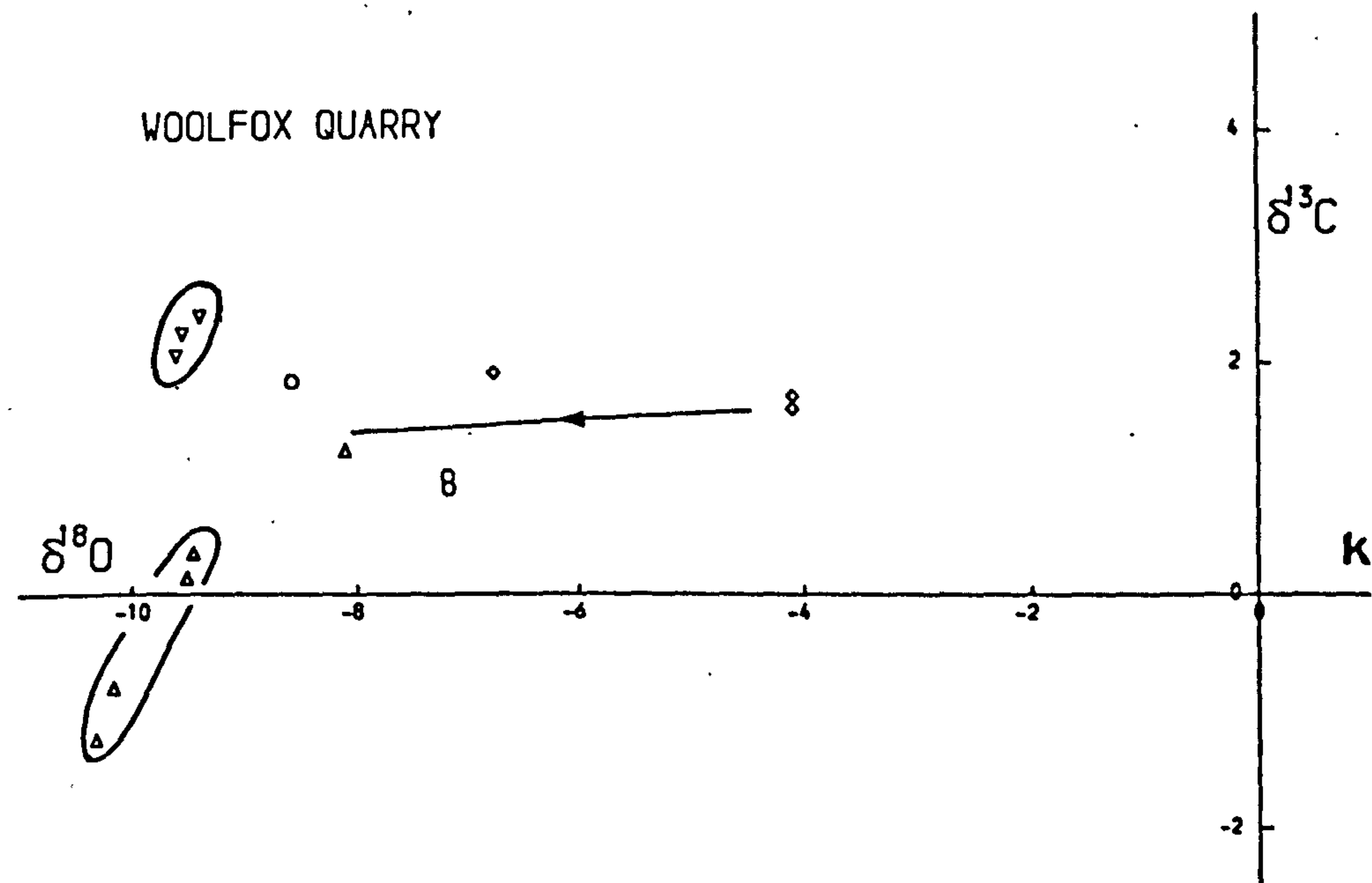
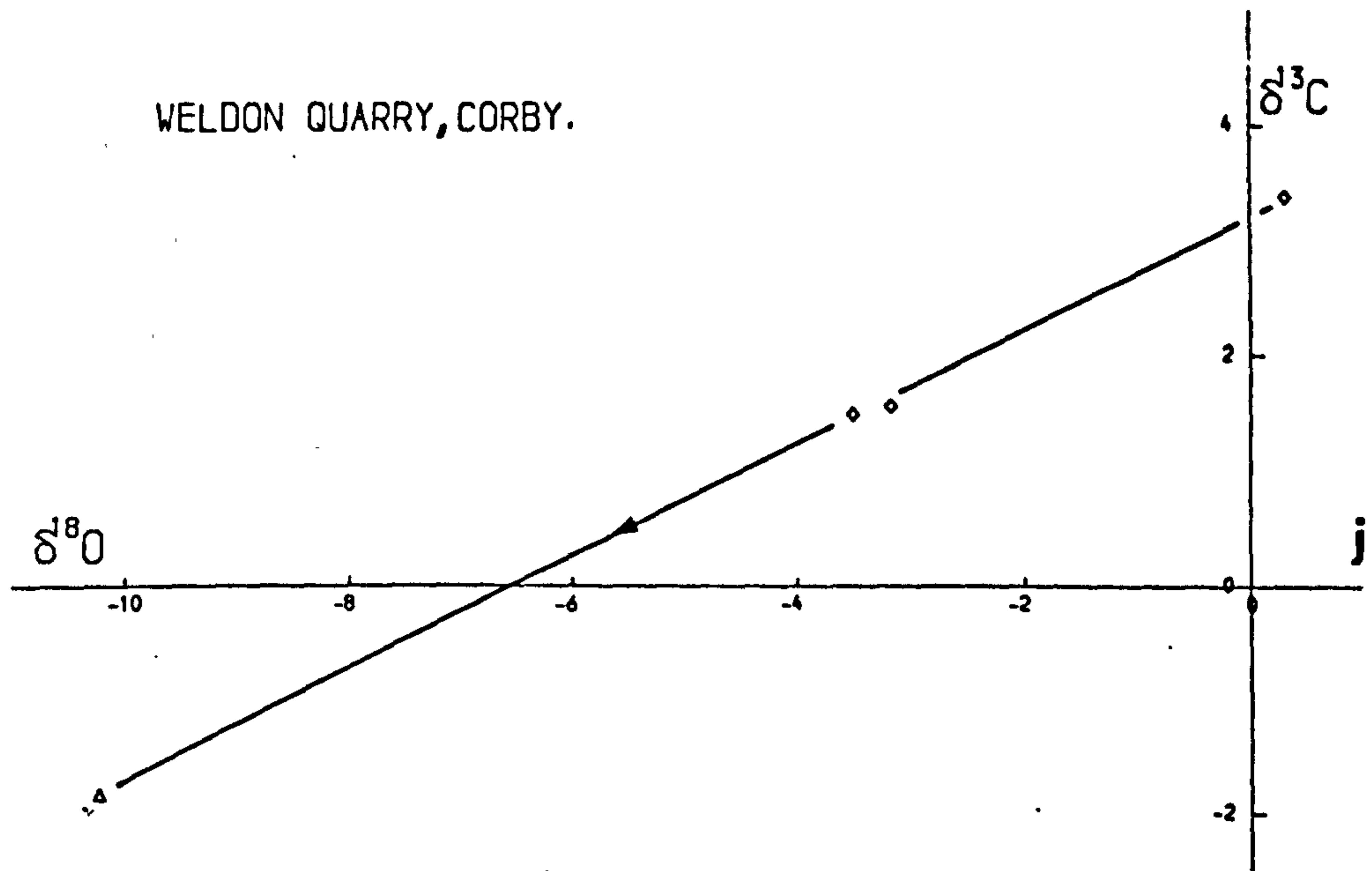
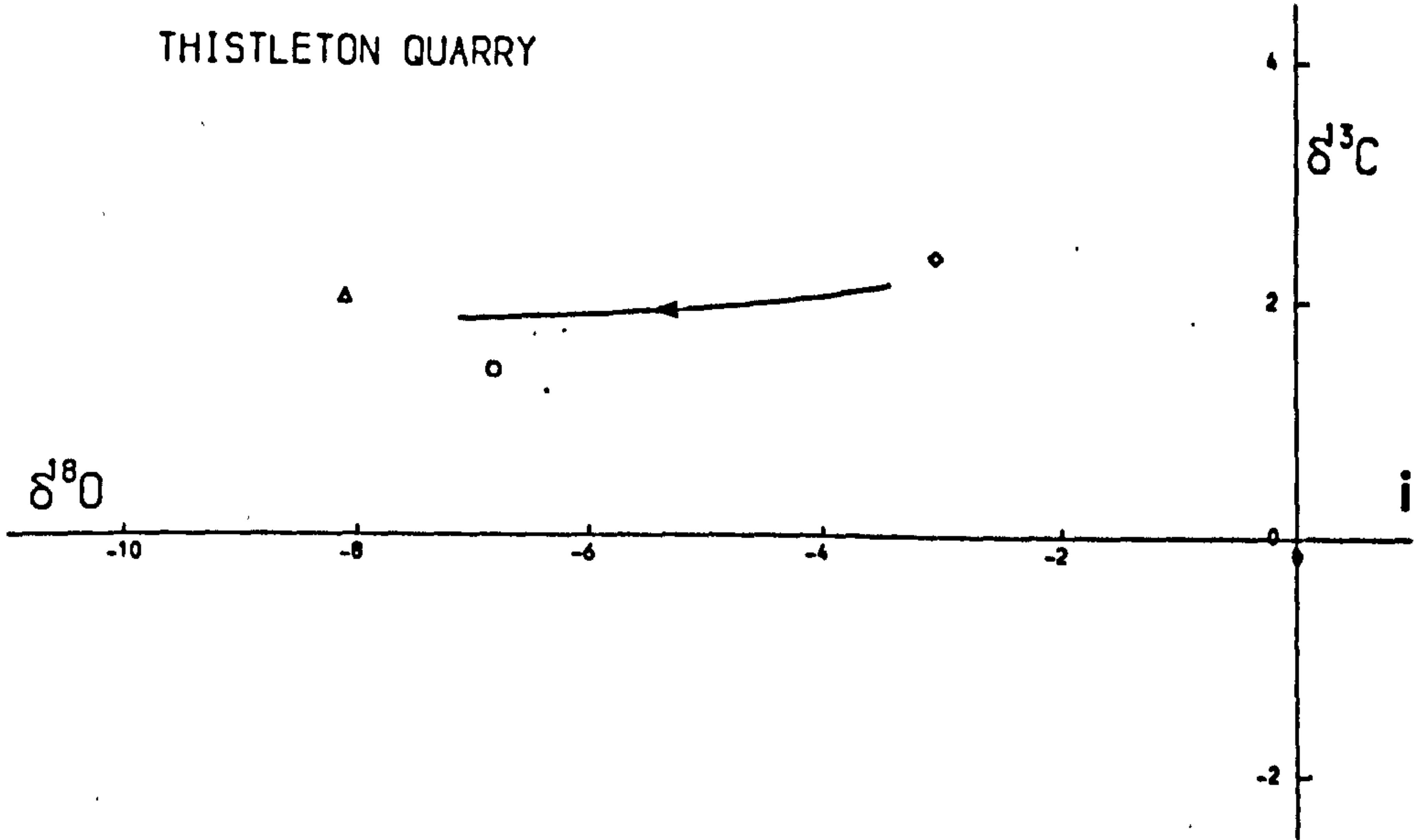


LEADENHAM HARDGROUND



STAINBY QUARRY





- and early aragonite dissolution. (See discussion in Marshall and Ashton; in press).
2. Samples from an individual locality generally plot along a single smooth (and often near-linear) trend line.
 3. Samples with no discernable intergranular cement and those with a complete intergranular fill of early cements have heavy $\delta^{18}\text{O}$ (-1.0 to +0.5) and $\delta^{13}\text{C}$ (+2.0 to +3.2); values which correspond to those from Recent oolites and marine-cemented limestones (Milliman and Muller, 1977).
 4. Blocky cements are depleted by between 6 and 10‰ $\delta^{18}\text{O}$ and by up to 4‰ $\delta^{13}\text{C}$; values which correspond to late diagenetic precipitates in other limestones (Dickson and Coleman, in press, Tan and Hudson, 1974), sandstones and shales (Tan and Hudson 1974, Hudson and Fieldman, 1976, and own unpublished data). Where more than one sample of late cement was taken at a single locality a greater spread of $\delta^{13}\text{C}$ than $\delta^{18}\text{O}$ values was observed (e.g. Woolfox, fig. 5.4.(k) and Stainby, fig. 5.4(h)).
 5. Whole-rock samples have intermediate isotopic composition, immediately suggesting that the spread of values is due to simple addition of late cement to depositional components which have retained their original composition. The process is identified more rigorously by considering the modal proportions of cement and depositional components in bulk samples (see below).

SECTION II - Results from British Jurassic Limestones from Formations other than the Lincolnshire Limestone .

A few samples have been analysed from each of the major carbonate formations in the Middle and Lower part of the Upper Jurassic of Central and eastern England. The limestones are predominantly oolitic, all contain marine fauna and all were deposited in a shallow epicontinental sea. (Hallam, 1975). The limestones are laterally discontinuous and

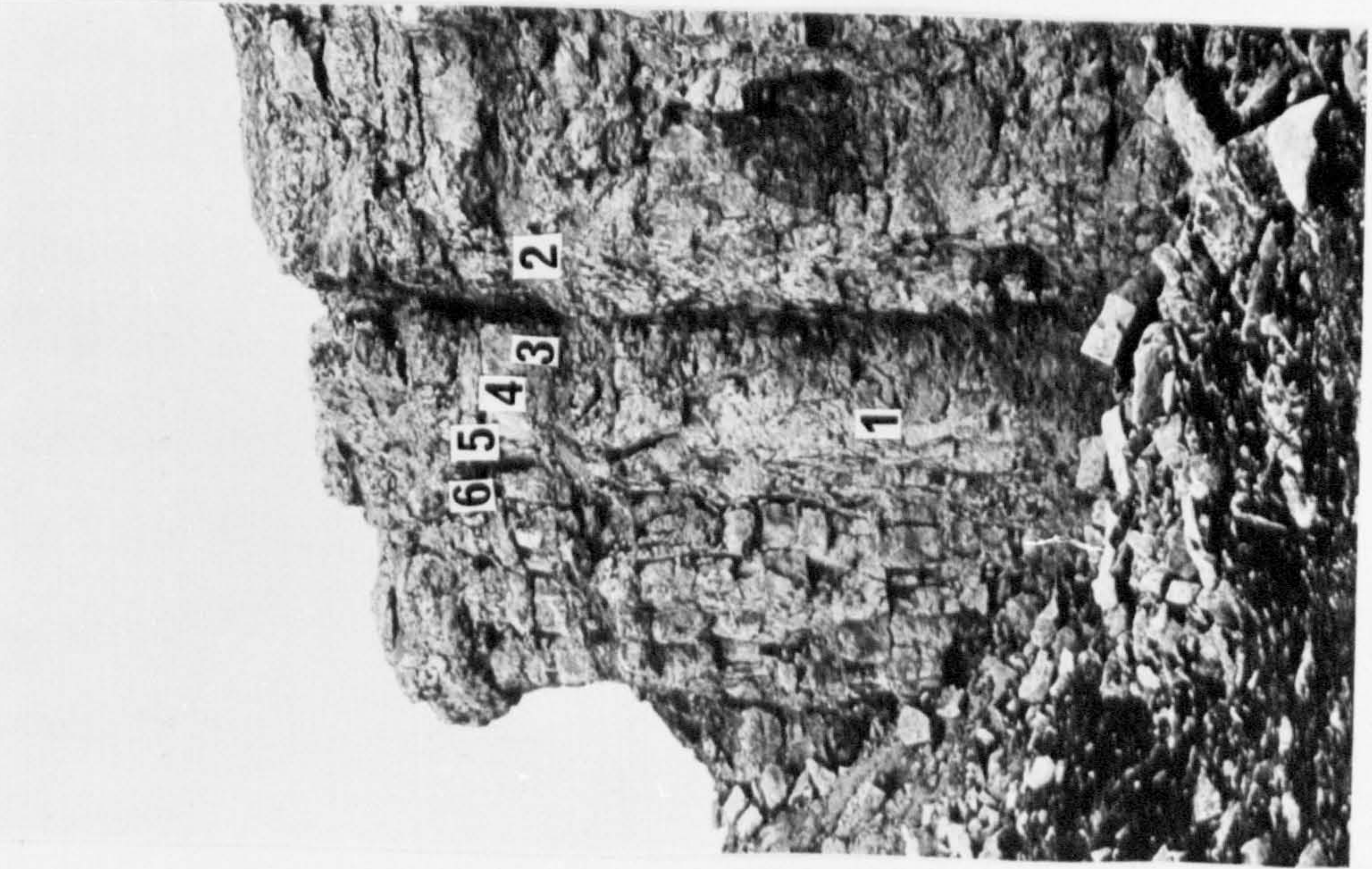
Fig.5.5. A1 and A2. Dagham Downs Quarry
(Results - Section II) Numbers
refer to block (DD) numbers,
Table 5.3.(b).

B. Direct print from stained acetate
peel of Thecosmilia coral,
Shellingford Cross Roads Quarry
(Results - Section II) - see
Talbot 1971.

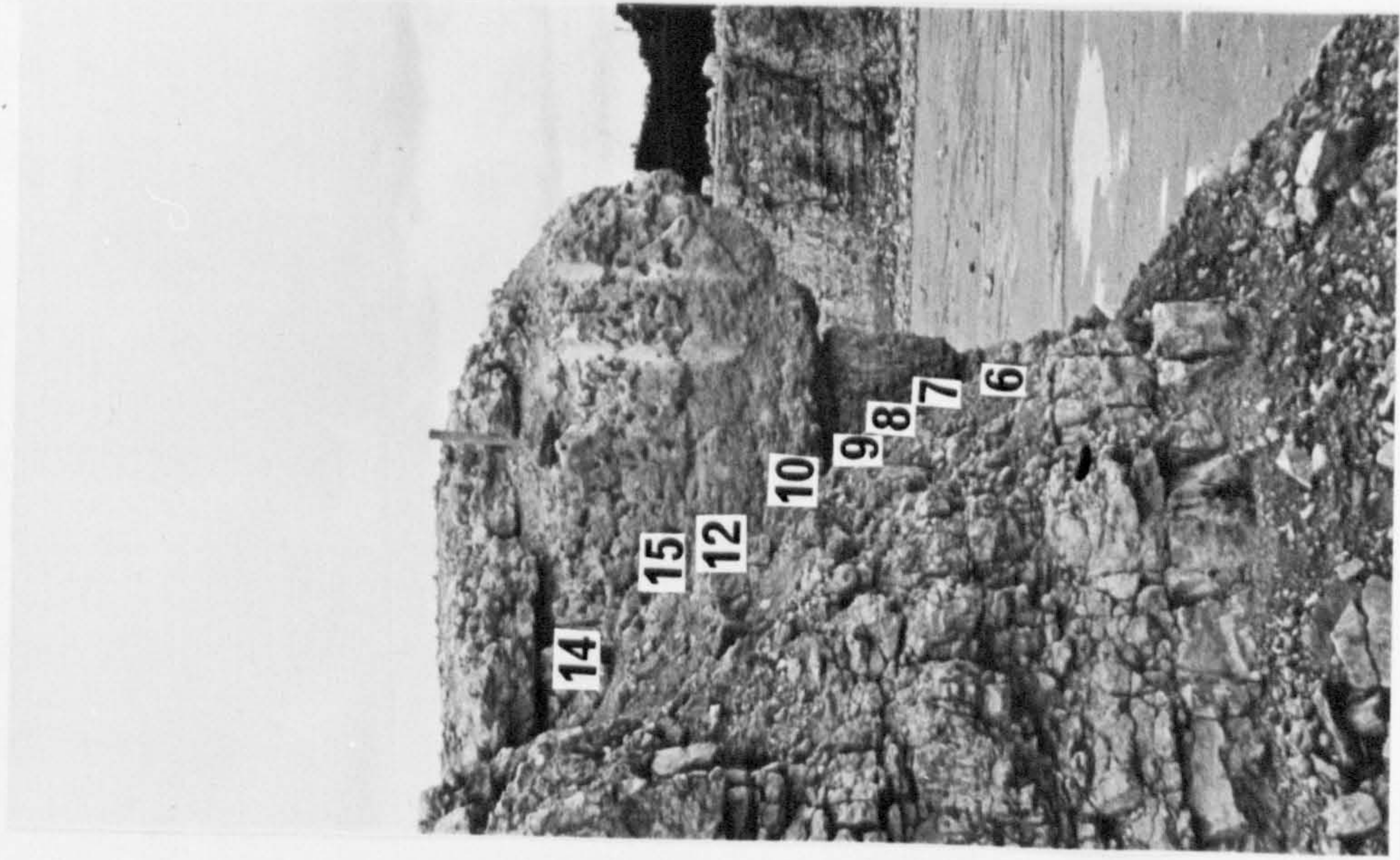
A - non-ferroan calcite (early
lithified) interseptal sediment

B - non-ferroan calcite early cement
fringe (also fills former
solution voids of septae)

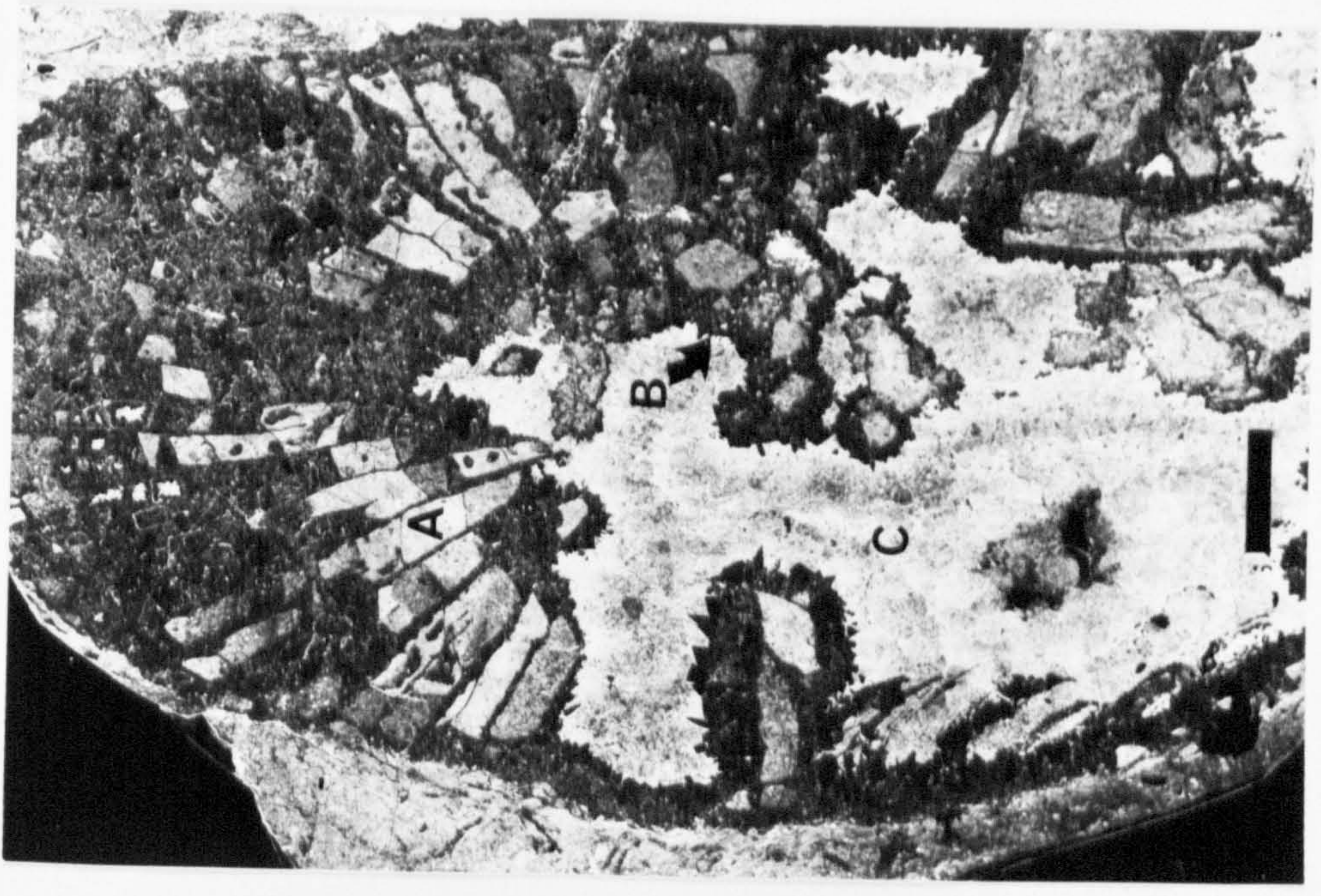
C - ferroan calcite cement fills
centre of former solution -
voids.



5A.1



5A.2



5B

contemporaneous brackish facies can be recognised in some instances (e.g. Palmer, 1979). The generalised stratigraphic column (fig.5.2) shows the relative ages of formations mentioned in the text and the distribution of the limestone units between much greater thicknesses of shales. Petrographic details, isotopic results and comment on individual distributions (Scatter diagrams fig. 5.6.(a)-(g)) are given in the data table; (Table 5.3.): Location details and previous descriptions of each locality in Fig 5.1 and Table 5.1 respectively.







Isotopes and Lithologies

The limestones do not show the same range of degree of cementation that is found in the Lincolnshire Limestone and have a correspondingly narrower range of $\delta^{18}\text{O}$. At six of the seven localities a general trend toward ^{18}O depletion with increased spar content can be determined (fig. 5.6). Results from the coral bed at Shellingford are apparently anomalous: $\delta^{13}\text{C}$ values are all negative and blocky ferroan calcites have $\delta^{18}\text{O}$ values which are heavier than some of the bulk rock samples (see below).

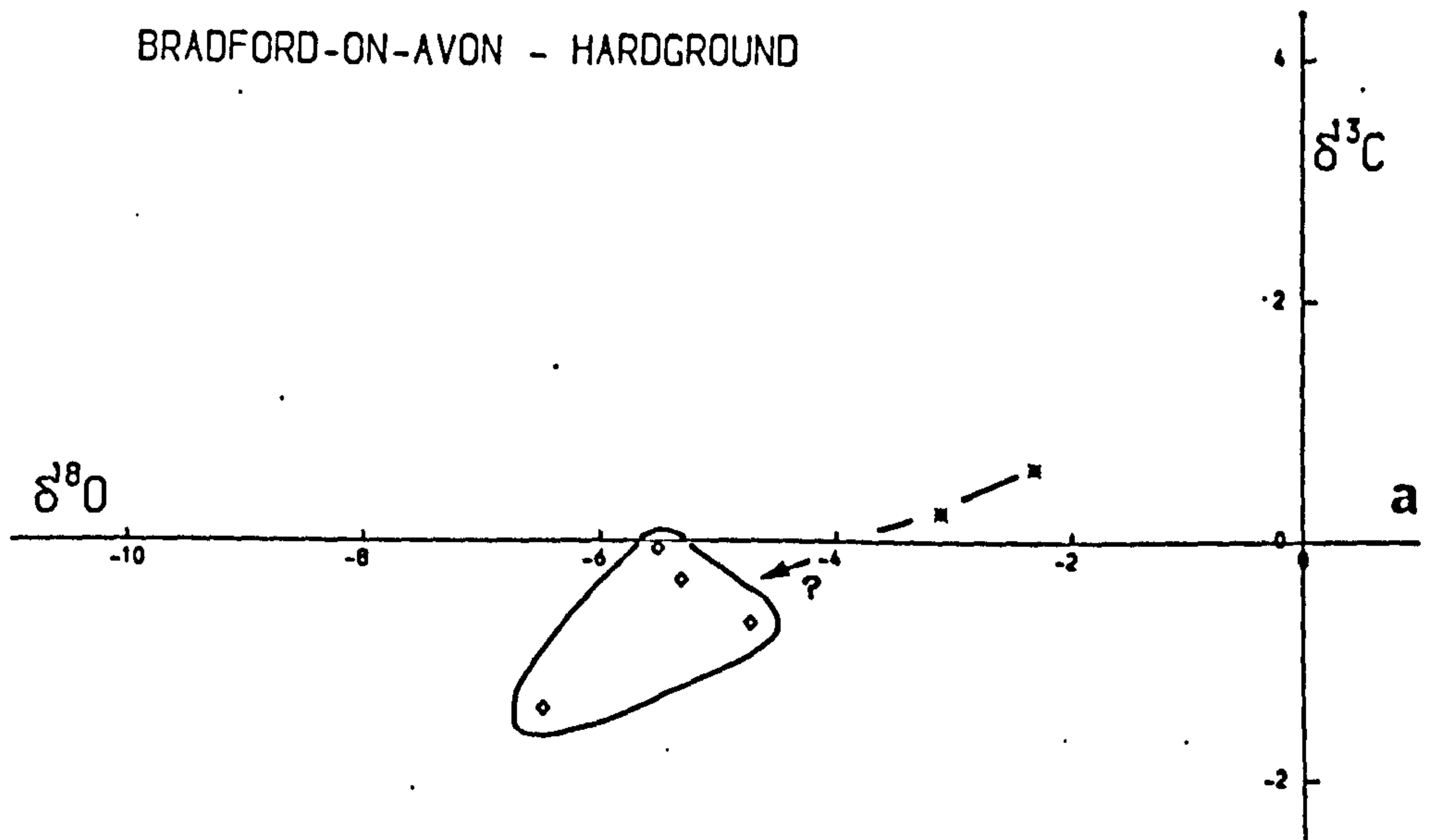
Hardgrounds

None of the hardground surfaces (Bradford-on-Avon, Dagham Downs, Foss Cross, and Hook Norton) have well developed early fringing cements and there is no clear trend in isotopic composition in samples taken at intervals away from the hardened surface. The range of $\delta^{18}\text{O}$ values (from -2 to -4.7‰) probably indicates the varying proportion of light cements at the surface (Marshall and Ashton; in press). Early aragonite dissolution at Dagham Downs has been used to suggest that the hardground was emergent (Fursich and Palmer, 1974) but there is no evidence of precipitation of light (w.r.t. both C and O) early diagenetic cements (see discussion in Marshall and Ashton; in press). Modal analysis has been used to identify the mechanism producing the scatter of isotopic values at this locality (see below).

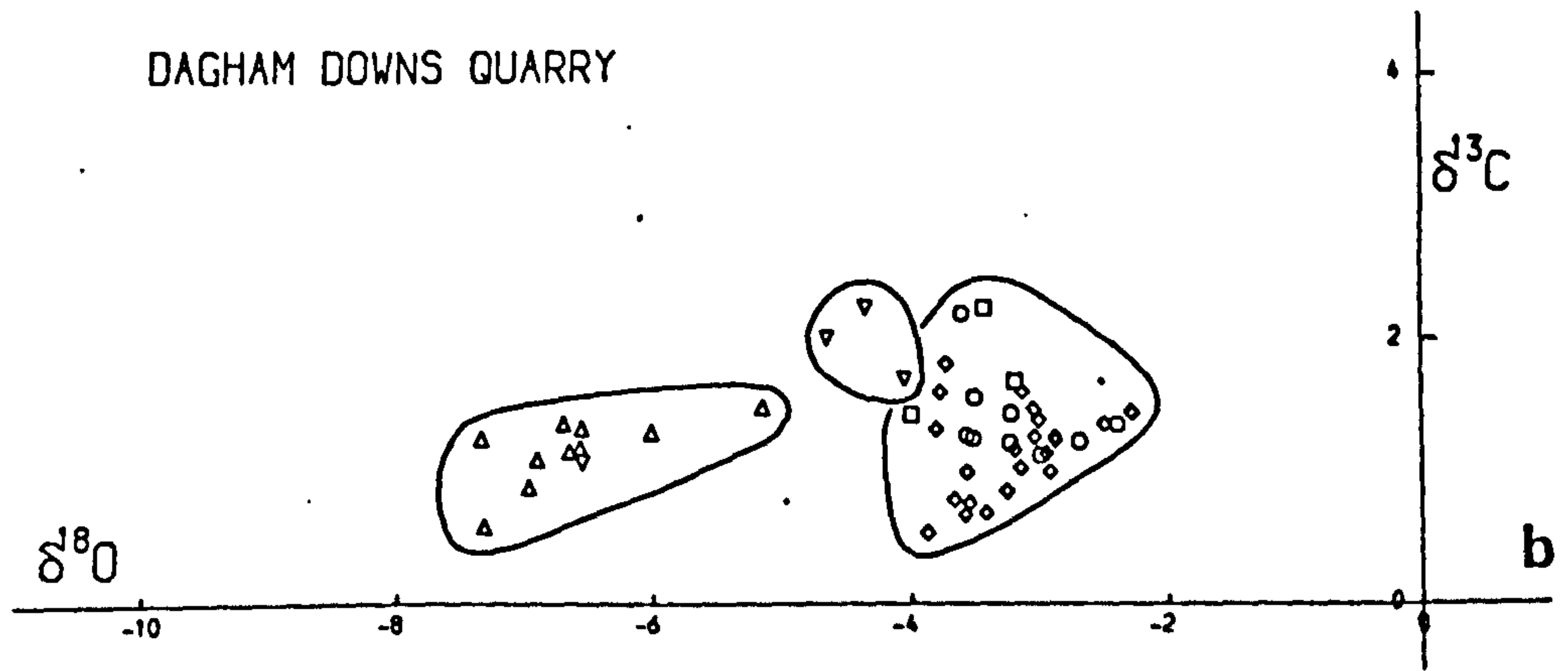
Fig.5.6. Carbon and oxygen isotopic scatter diagrams for data from individual localities in "British Jurassic Limestones other than the Lincolnshire Limestone". (Results Section II).

-  - Shell
-  - Whole-rock Limestone
-  - Burrow-fill or other geopetal sediment
-  - Sparry calcite - Non-ferroan or with well preserved skeletal inclusion relics
-  - Sparry calcite - ferroan (or only generation)
-  - Sparry calcite - in secondary veinlet

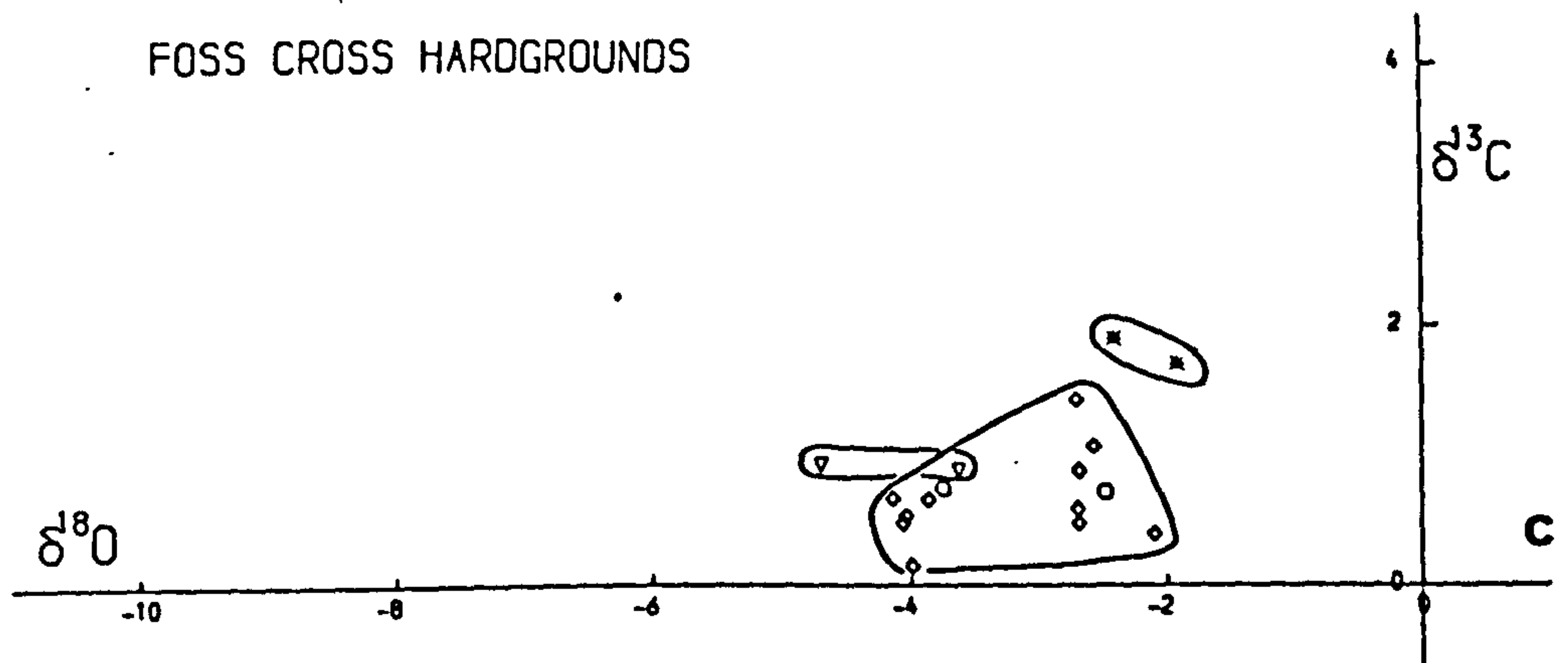
BRADFORD-ON-AVON - HARDGROUND



DAGHAM DOWNS QUARRY



FOSS CROSS HARDGROUNDS



HOOK NORTON - HARDGROUND

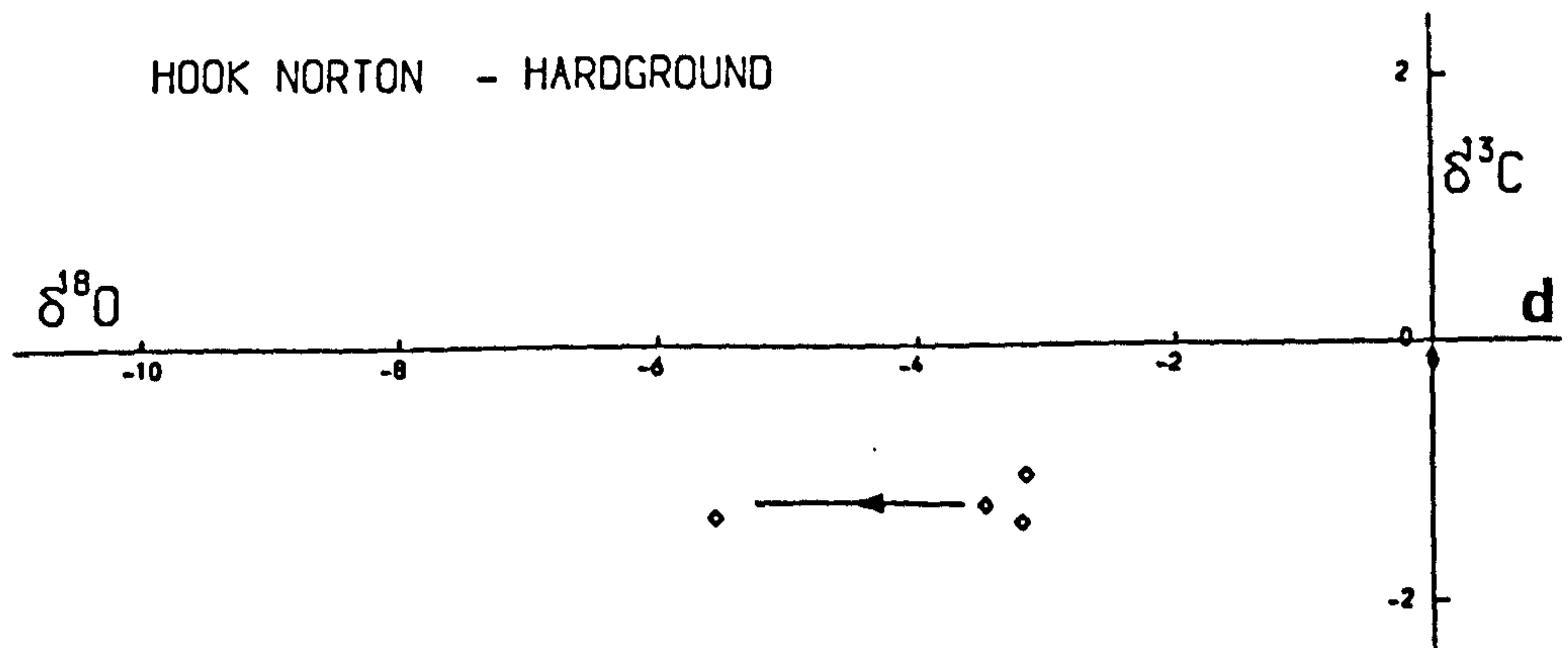
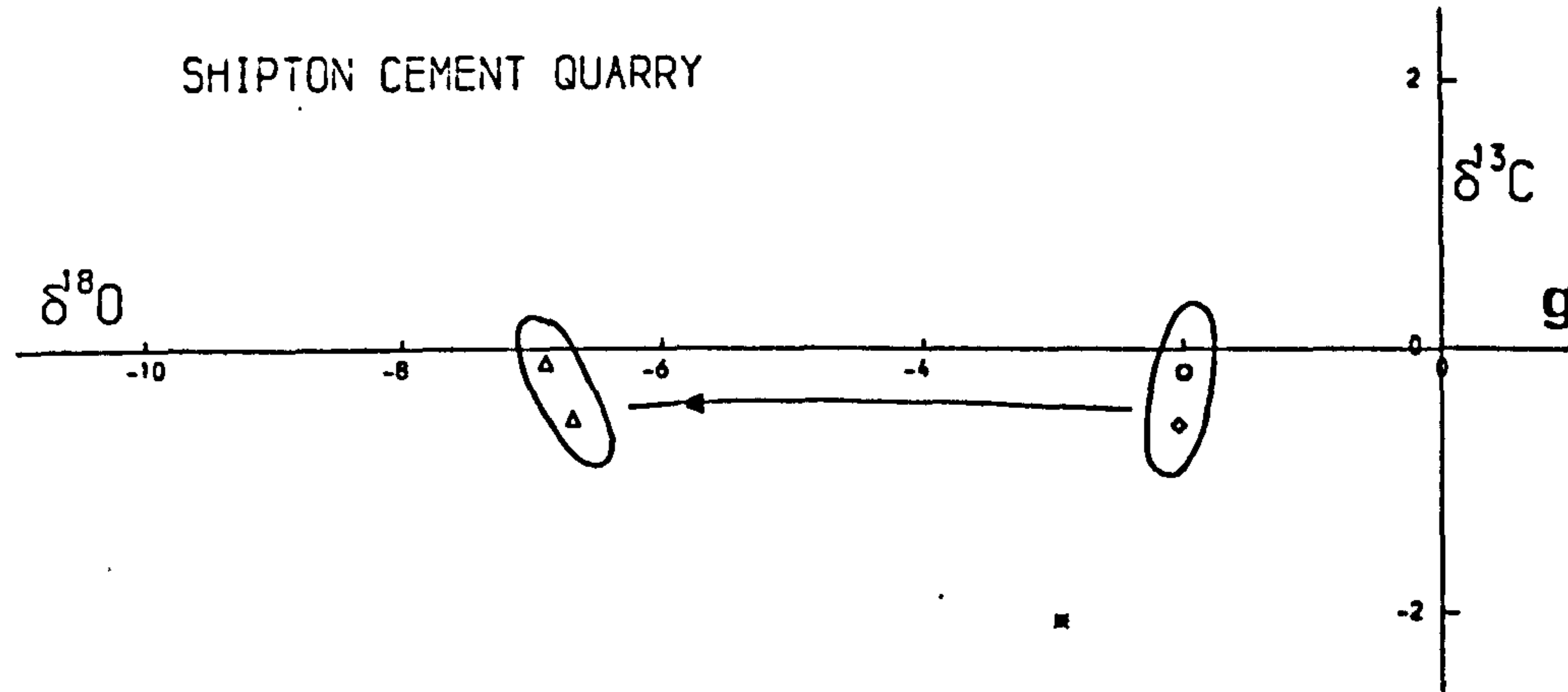
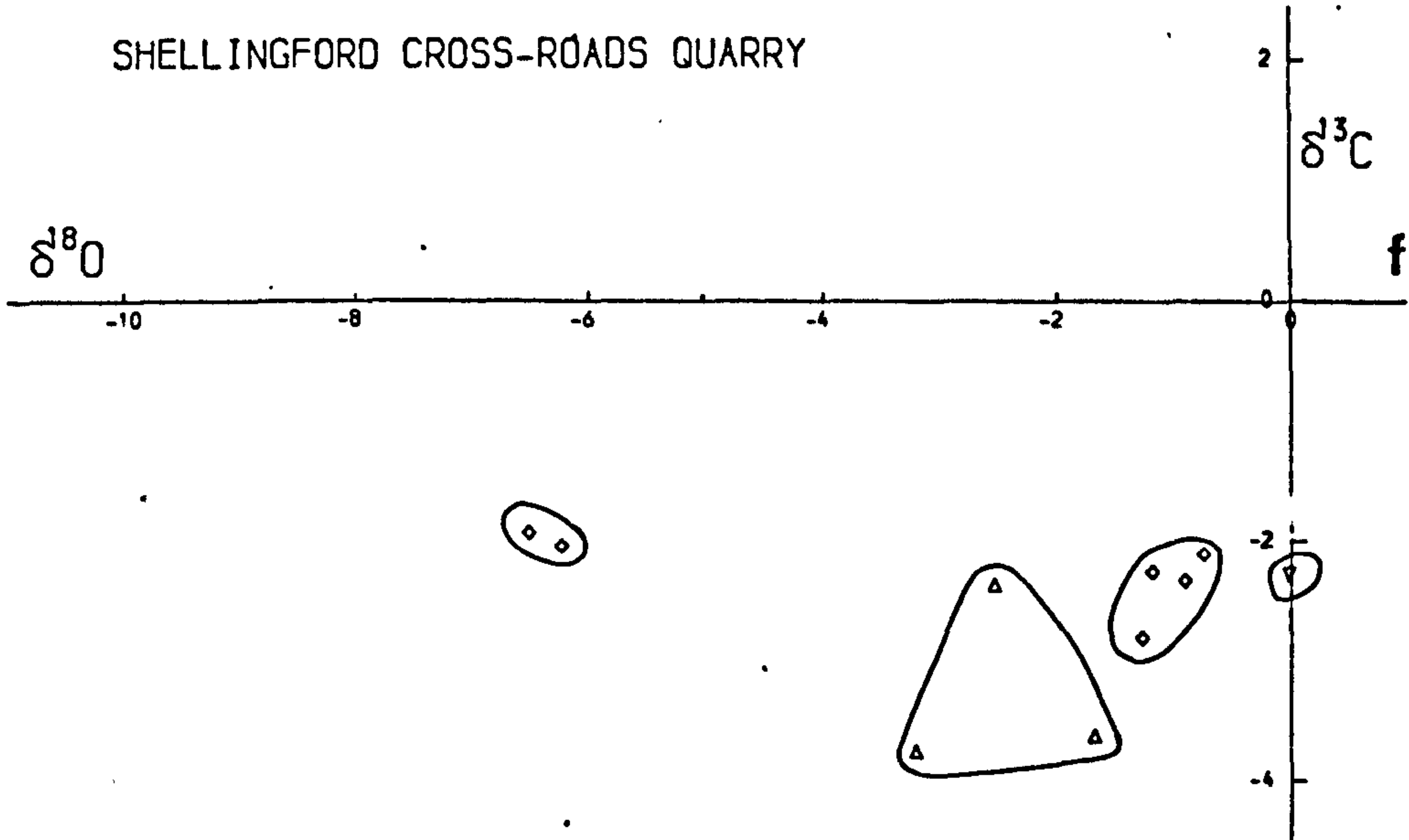
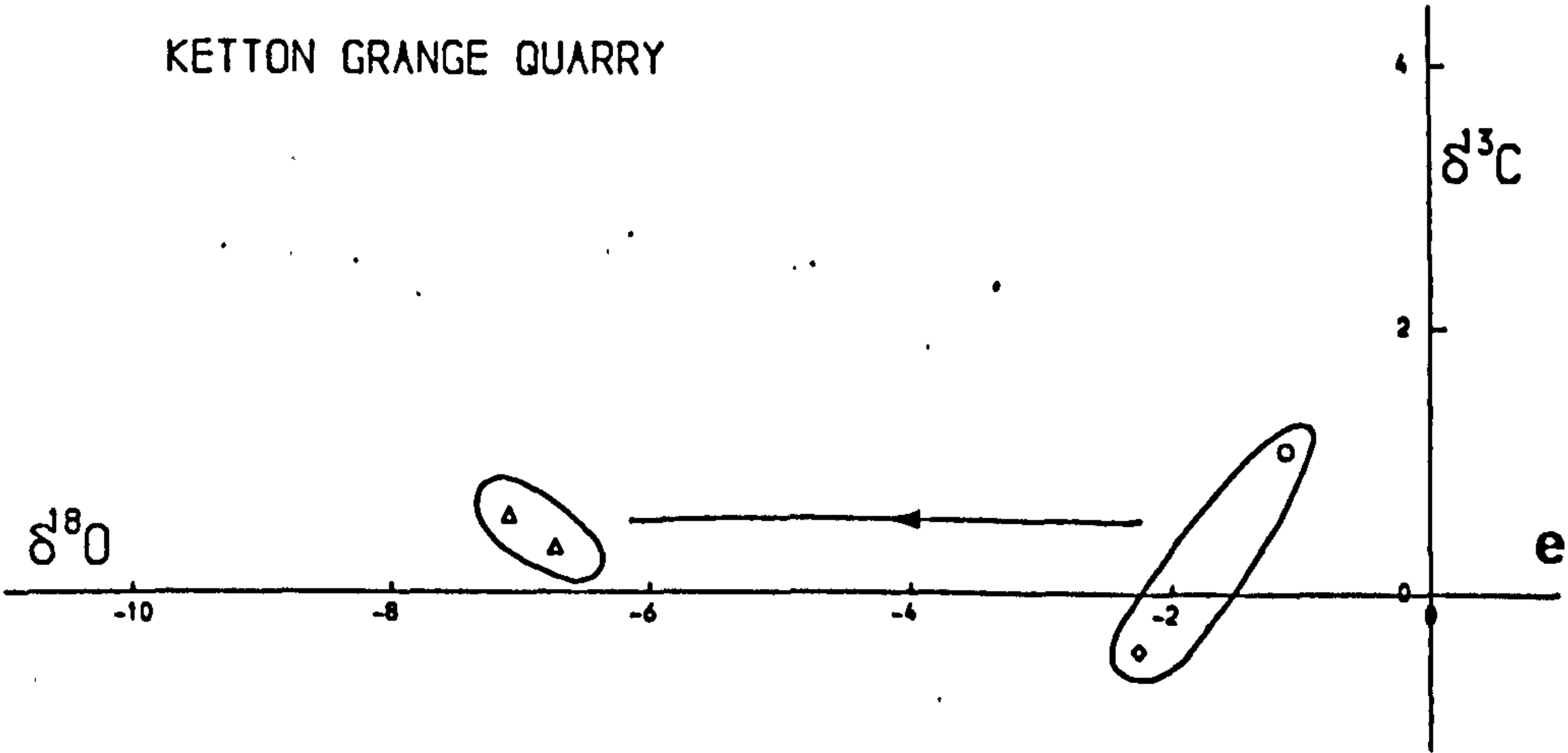


Fig.5.6



The Bradford-on-Avon and Hook Norton hardgrounds both contain pyrite; calcite samples from both surfaces have negative $\delta^{13}\text{C}$. It is possible that the $\delta^{13}\text{C}$ values reflect minor early diagenetic input of organogenic carbon produced during pyrite formation by bacterial activity.

Blocky Cements: in 'corals' and shell supported voids

The ferroan calcite from Dagham Downs, Ketton Grange and Shipton quarries (fig.5.6(b), (e) and (g)) are similar to those from the Lincolnshire Limestone with low (positive and negative) $\delta^{13}\text{C}$ and light $\delta^{18}\text{O}$ ($\approx -7\%$). Blocky calcites associated with coral colonies at Foss Cross (an early generation of spar^{at}) Dagham Downs and at Shellingford have a range of values which overlap with those from bulk limestone samples.

Foss Cross and Dagham Downs - The Septa and corallite walls of small colonial (Isastrea - type) corals at Foss Cross are preserved as inclusion relics in equidimensional calcite spar. The isotopic composition is related to the degree of preservation of the coral structure (Scherer, 1977) samples with well preserved septa have heavier $\delta^{18}\text{O}$. The non ferroan zone at Dagham Downs has an isotopic composition which is transitional between that of the bulk limestone and blocky ferroan cement. Formation of both non-ferroan zone and equidimensional spar with inclusion relics probably involved aragonite 'replacement' in situ such that the isotopic composition (and iron content?) represent a mixing of original skeletal and late cement component carbonate (c.f. modes of recrystallisation described by Sandberg et al, 1973, Scherer, 1974).

Shellingford Coral Beds.

Thecosmilia corals from the Corallian (Upper Jurassic) at Shellingford Cross Roads Quarry have been the subject of detailed petrographic (Talbot 1971, 1972) and ecological study (Fursich, 1977).

Coral growth was intermittent and throughout the 2m section there are numerous horizons where colonies are truncated by lenses of biosparite and clay sediment; features which have been attributed to subaerial erosion and swamping by volcanic ash respectively (Ali, 1977).

The internal structure of individual coral branches show diverse preservational features (Talbot, 1971, 2). Samples for isotopic analysis (Table 5.3(f)) have been taken from each of the cement-types recognised by Talbot (1971). Host (non-ferroan calcite) limestone well preserved 'coral' (with septa preserved as inclusion relics) and early non-ferroan fringing cement have similar heavy $\delta^{18}\text{O}$ (from -1.3 to +0.02‰) and negative $\delta^{13}\text{C}$ (-2.3‰). Petrographic analysis suggests a fresh-water subaerial origin for the non-ferroan cements (Talbot 1972). The late blocky and fibrous ferroan calcites also have negative $\delta^{13}\text{C}$ (from -3.8 to -2.4), but have only slightly lighter $\delta^{18}\text{O}$ than the non-ferroan components (-1.68 to -3.22‰).

Bulk samples from a biosparite lens have much lighter $\delta^{18}\text{O}$ (-6.4‰) so the ferroan spar similar to that in the corals cannot have been responsible for cementation of the biosparite lens.

A complete interpretation of the diagenetic history of these corals is beyond the scope of a summary paper, but it is interesting to note; that the calcites for which there is good petrographic evidence for subaerial precipitation are the only samples to have isotopic compositions in the range predicted from studies of Recent shallow cementation by freshwater in the Bahamas. (e.g. Gross, 1964, Allan and Matthews, 1977). The analysis of calcites within the corals suggest that both the non ferroan and ferroan cements may have precipitated under relatively shallow burial (a few metres) in fresh water conditions. External biosparite samples may have suffered secondary cementation by late calcites with normal late diagenetic composition (i.e. $\delta^{18}\text{O}$ -8 to -10‰ $\delta^{13}\text{C} \approx 0$).

SECTION III - Hardgrounds from France and North America.

Hardgrounds are surfaces which were lithified before the deposition of overlying sediment. Samples have been analysed from a large number of examples to try to determine the environment of lithification and isotopic composition of the ambient waters.

(a) Hardgrounds from the Middle and Upper Jurassic of France.

Hardgrounds cap sequences of coarse oolite and peloid calcarenites of Bajocian to Callovian age from Burgundy and Normandy. Cement fabrics in the Burgundy examples demonstrate hardground formation in a range of environments from subtidal to supratidal conditions. (Purser, 1969, 1977). The Ranville hardgrounds from Normandy have a mixed micrite + spar matrix and no syndepositional cements have been recognised. Blocky calcite cement is generally non-ferroan.

Samples for isotopic analysis were all taken from within a few centimetres of the bored or encrusted hardground surface. Many of the hardgrounds contain early cements to a depth of up to 50cm (Purser, 1977) so it is not unexpected that the samples show no clear isotopic trend in the few centimetres away from the surface (c.f. Lincolnshire Limestone examples where depth of cement penetration was much lower). The coarse peloidal sediments had a very irregular pattern of primary porosity; a feature which is now reflected in the distribution of late cement and the spread of isotopic composition of the samples. There is a qualitative correlation between spar content and decrease in $\delta^{18}\text{O}$ (Table 5.4 Figs. 5.7.(a) to (f)), and a single isotopic determination from blocky calcite cement at Ravieres confirms the late cement composition ($\delta^{13}\text{C}$, 0.53 $\delta^{18}\text{O}$, -12.4). There is no isotopic evidence for the precipitation of cements in the subaerial environment (with negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ - see discussion in Marshall and Ashton; in press) and the heaviest $\delta^{18}\text{O}$ value from Ranville hardground (-0.65‰) must demonstrate submarine cementation. The other hardgrounds with intermediate isotopic composition were initially cemented in sea water as demonstrated by Purser (1969, 1977) but the isotopic

Fig.5.7. Carbon and oxygen isotopic scatter diagrams for data from the hardgrounds of Burgundy and Normandy (Results - Section IIIa).



- Shell



- Whole-rock Limestone



- Burrow-fill or other geopetal sediment



- Sparry calcite - Non-ferroan or with well preserved skeletal inclusion relics

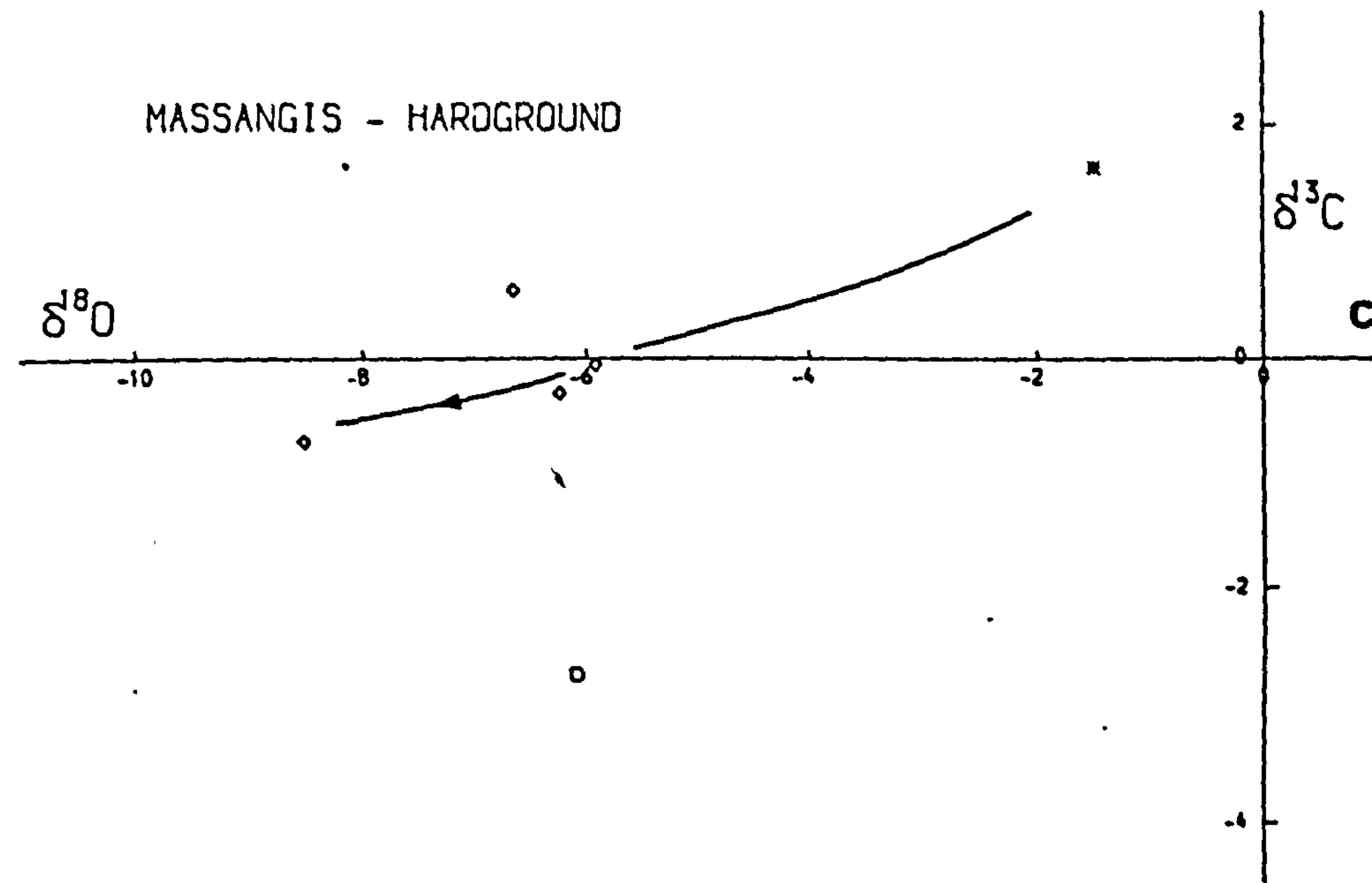
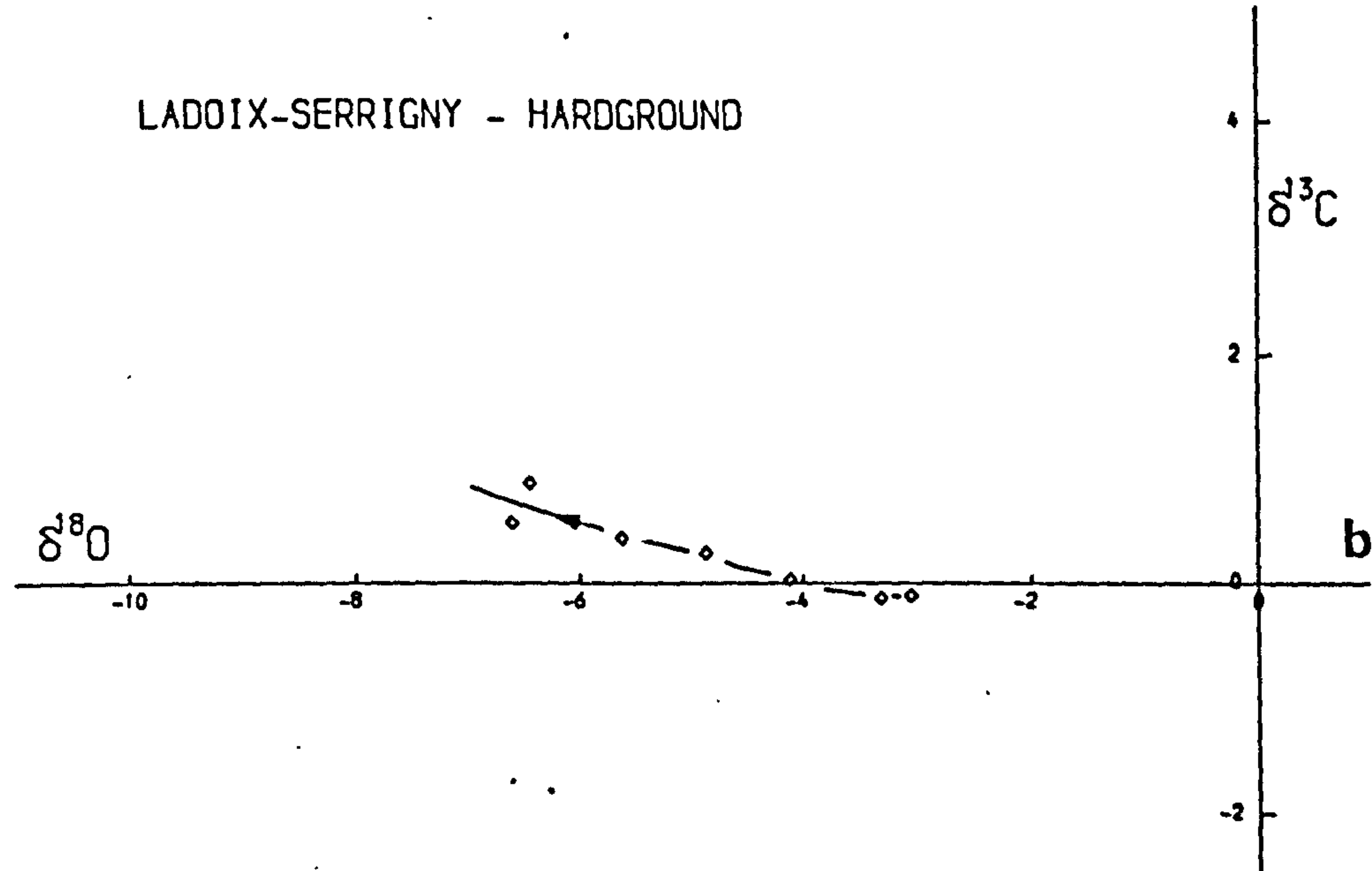
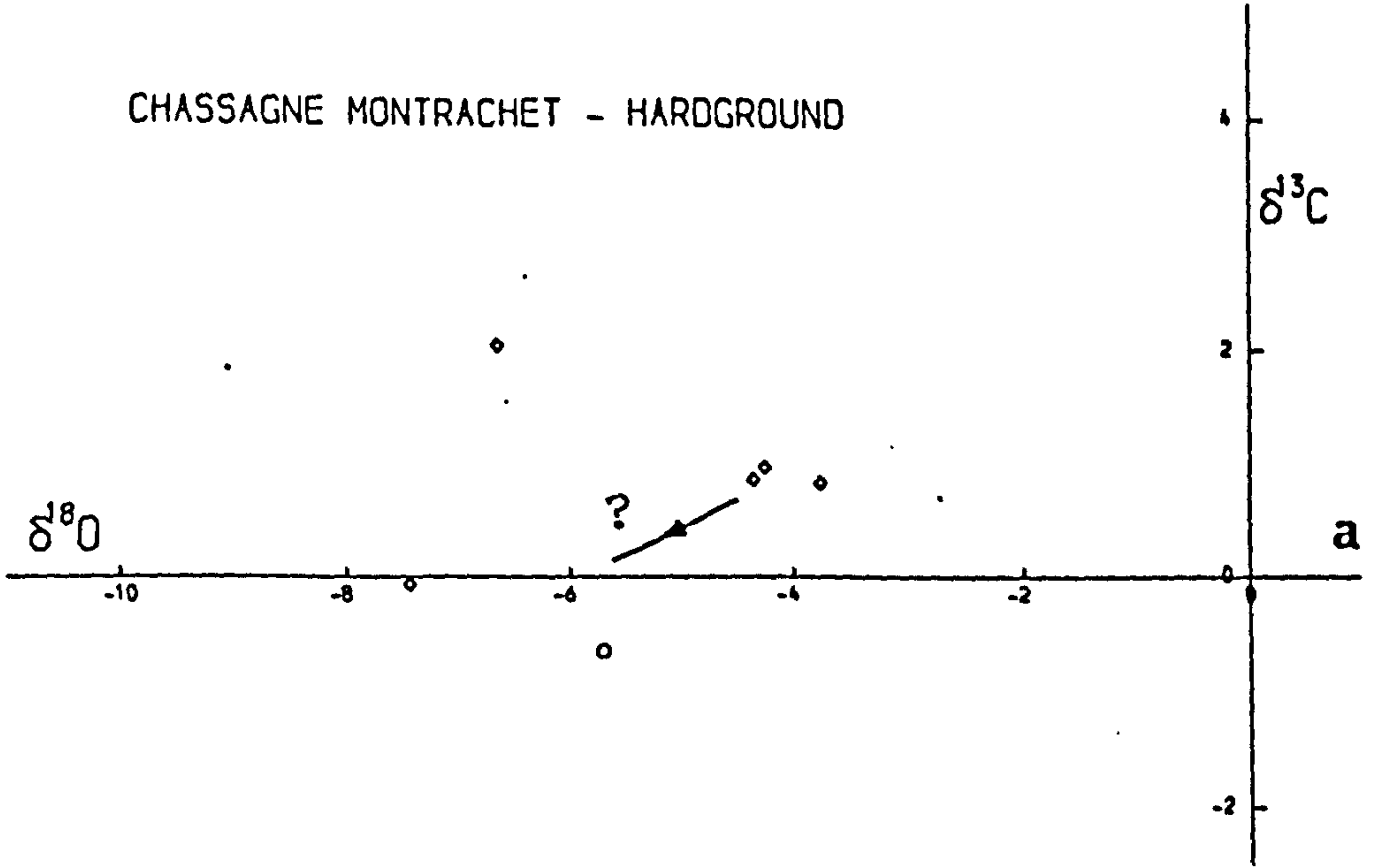


- Sparry calcite - ferroan (or only generation)

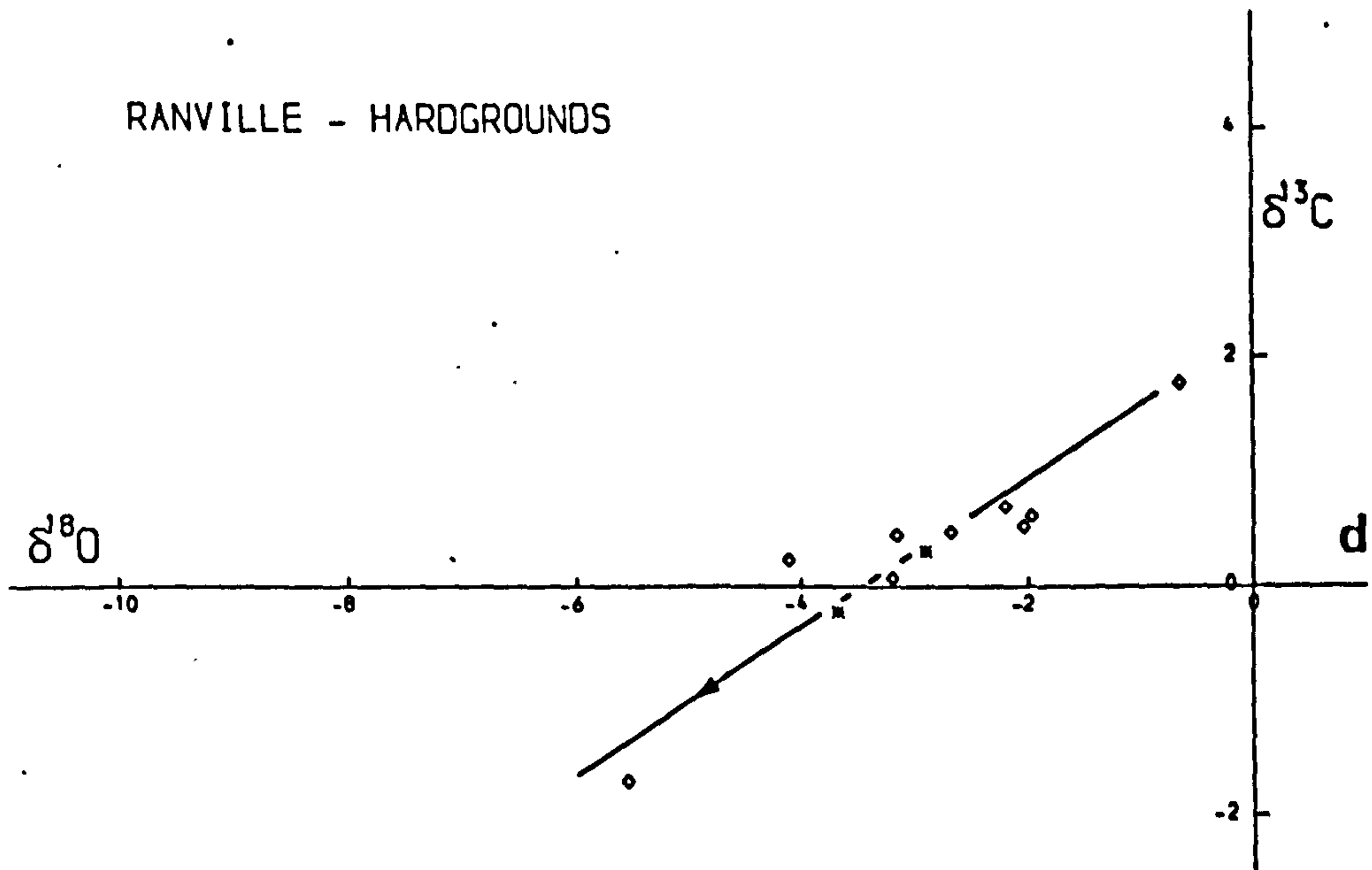


- Sparry calcite - in secondary veinlet

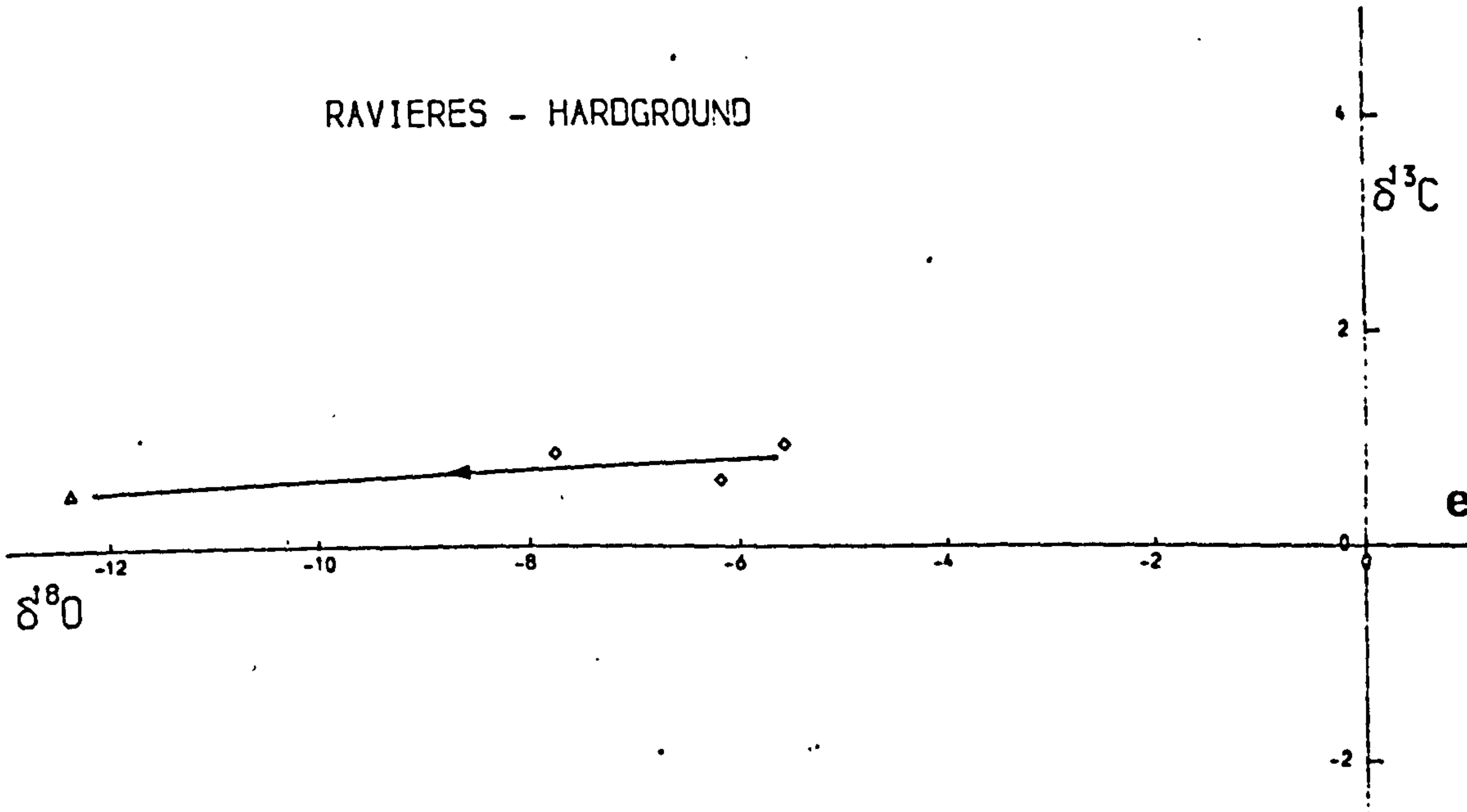
Fig.5.7



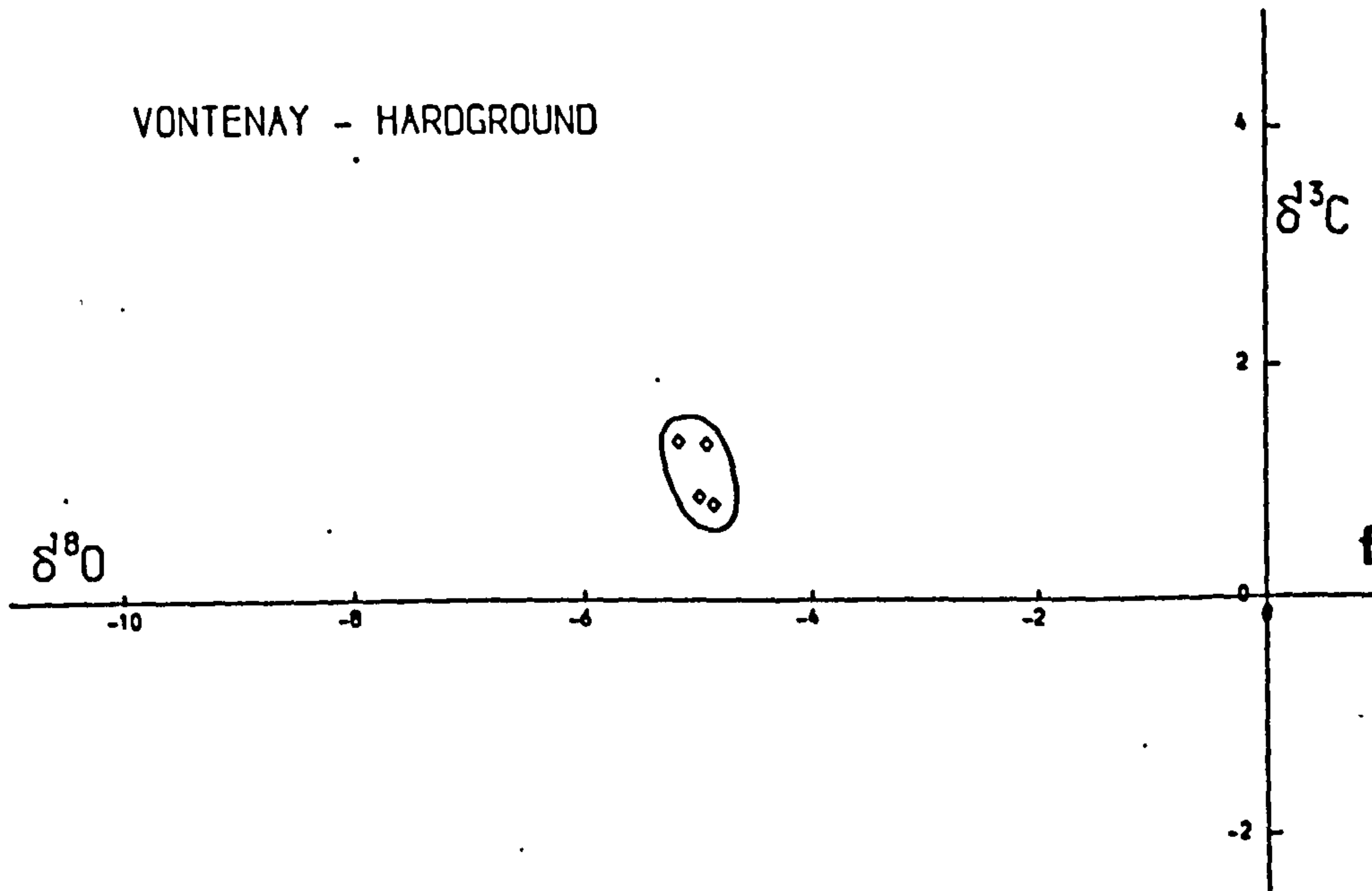
RANVILLE - HARDGROUNDS



RAVIERES - HARDGROUND



VONTENAY - HARDGROUND



evidence alone would not be conclusive (c.f. Leadenham hardground, Marshall and Ashton; in press).

(b) Palaeozoic and Mesozoic hardgrounds from North America.

Samples were analysed from hardground surfaces from Ordovician to Cretaceous limestones to determine whether the isotopic composition of early-lithified sediments showed any significant variation with age and hence if there were any evidence for the proposed increase in sea water $\delta^{18}\text{O}$ during the Phanerozoic. (Keith and Weber, 1964, Veizer and Hoefs, 1976). Descriptions of lithologies and individual isotopic trends are given in the data table (Table 5.5(a) to (h), scatter diagrams, fig. 5.8 (a) to (h).

Samples from each locality generally define a 'normal' near-linear trend on the scatter diagram. Whole-rock sample $\delta^{18}\text{O}$ from all localities corresponds to the range determined for the Lincolnshire Limestone hardgrounds (i.e. 0 - 6‰) where surface values are clearly related to the intensity of early cementation (Marshall and Ashton; in press). The North American data clearly cannot be interpreted wholly in terms of changing sea water composition. However the heaviest $\delta^{18}\text{O}$, from sediments where ^{18}O enrichment by evaporation can be discounted, may be significant as later diagenetic processes are likely to involve depletion rather than enrichment in $\delta^{18}\text{O}$ (Hudson, 1977). A sample from the Silurian, Laurel Limestone hardground which formed a lithified sea-floor (Halleck, 1973) has $\delta^{18}\text{O}$ of +0.32‰; a value which is comparable to Recent submarine cements (Milliman and Muller, 1977) and is clearly incompatible with formation in sea water with even slightly negative $\delta^{18}\text{O}$. Similarly a Mississippian brachiopod (fig. 5.8(f)) has $\delta^{18}\text{O}$ of -1.6‰ which again indicates equilibrium precipitation in sea water of normal Mesozoic composition (c.f. Dickson and Coleman, in press).

The existence of these few heavy values together with those from another example of submarine cementation in Palaeozoic sediments (Davies

Fig.5.8. Carbon and oxygen isotopic scatter diagrams for data from the North American Hardgrounds. (Results - Section III b.)



- Shell



- Whole-rock Limestone



- Burrow-fill or other geopetal sediment



- Sparry calcite - Non-ferroan or with
well preserved skeletal inclusion
relics

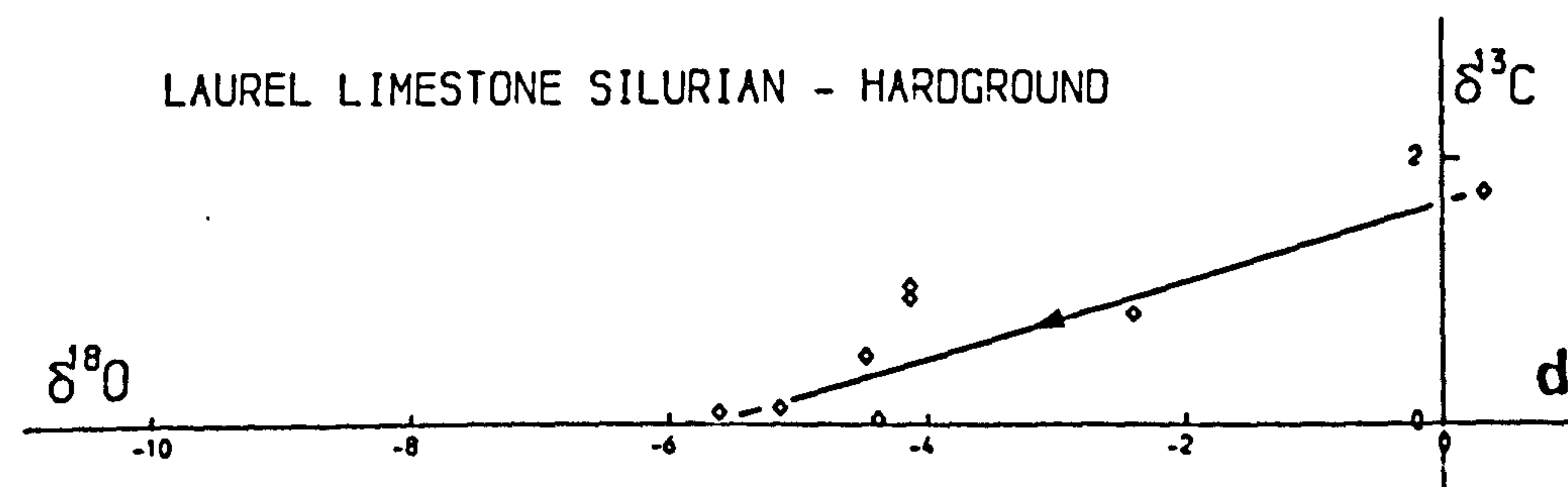
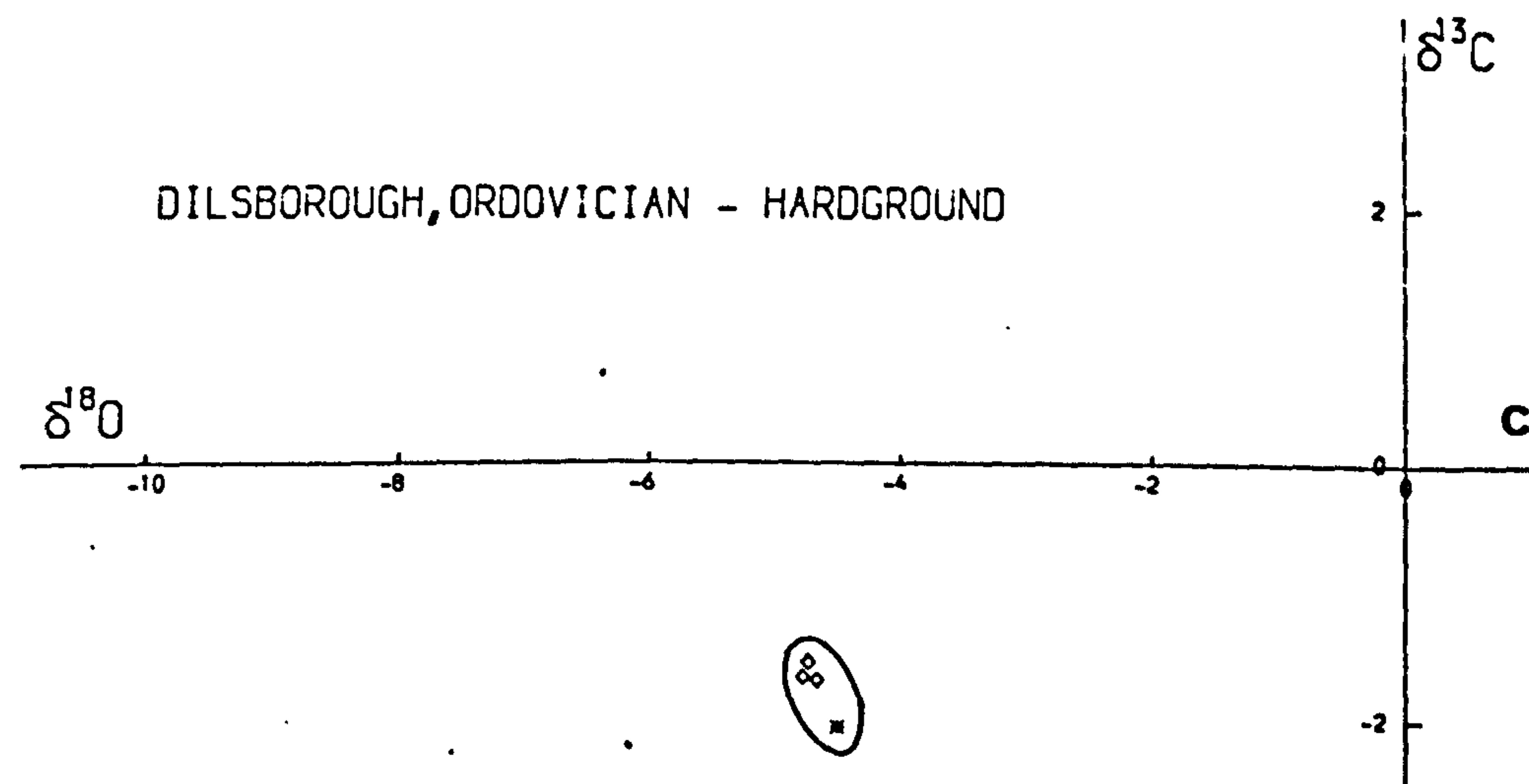
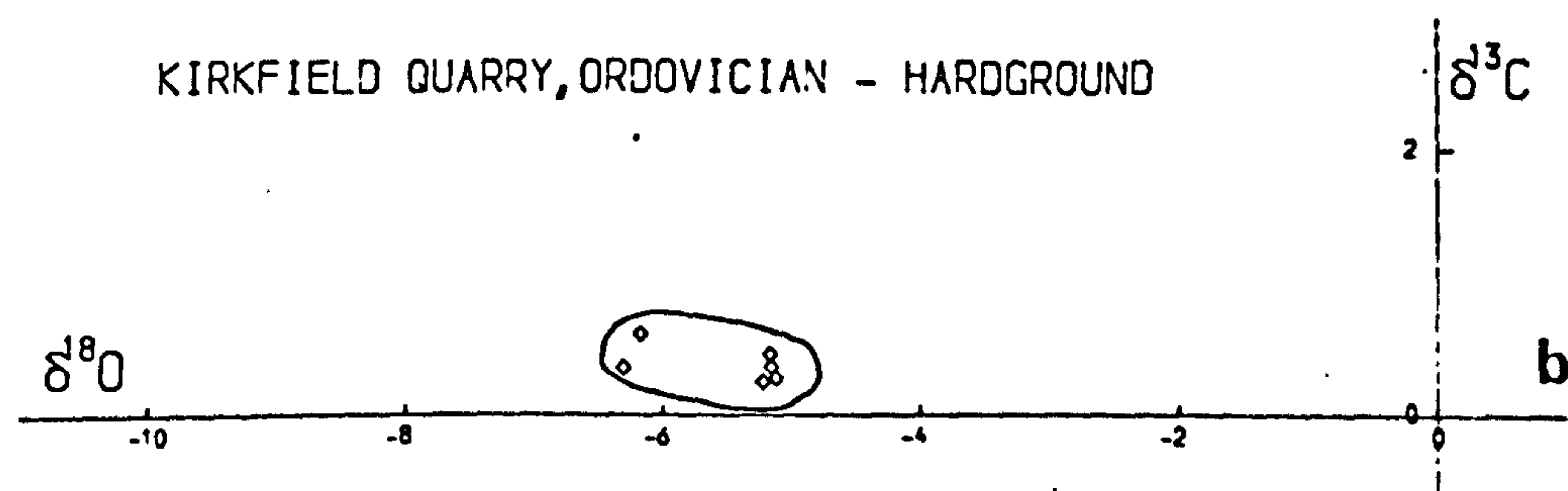
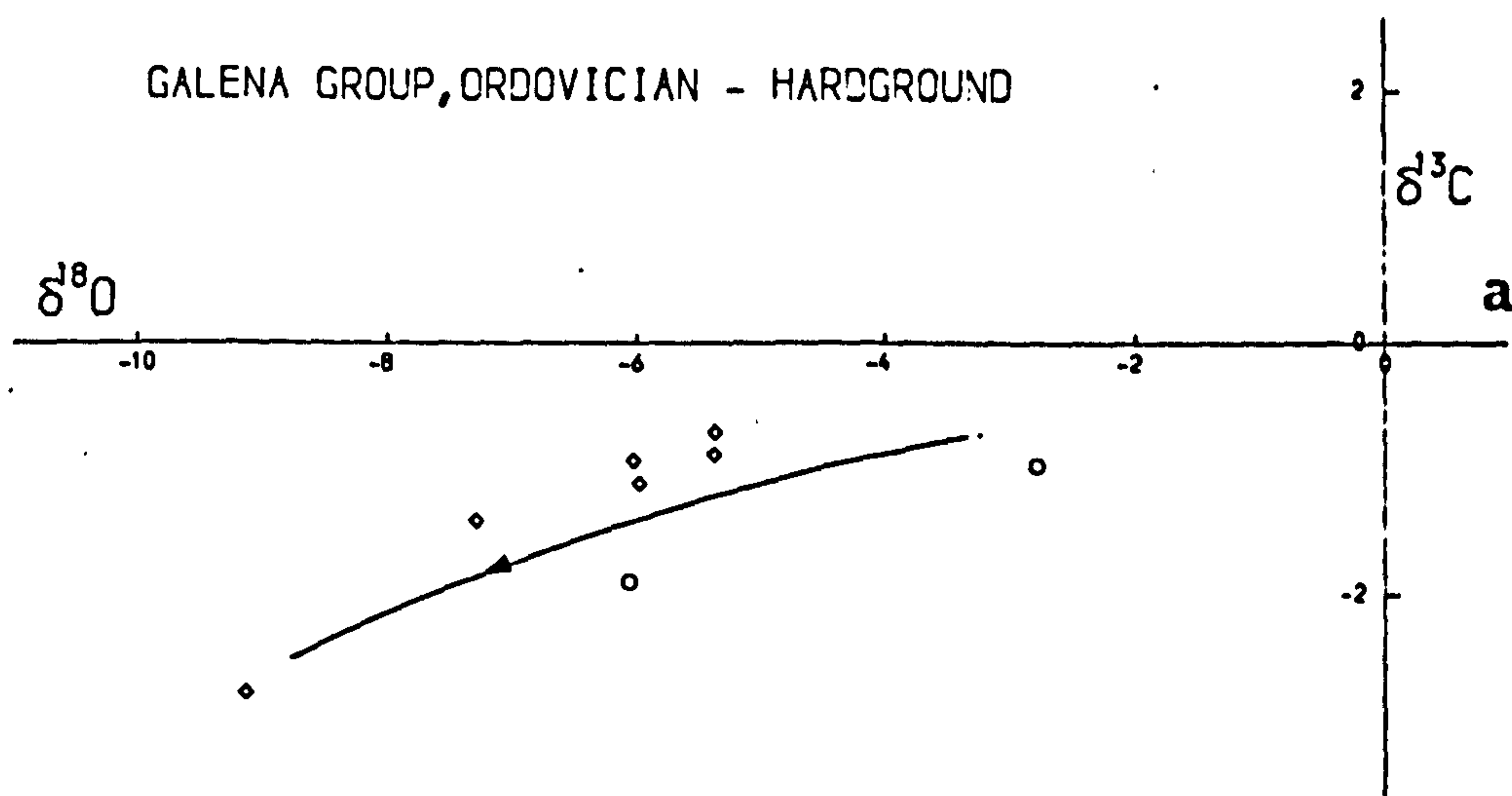


- Sparry calcite - ferroan (or only
generation)

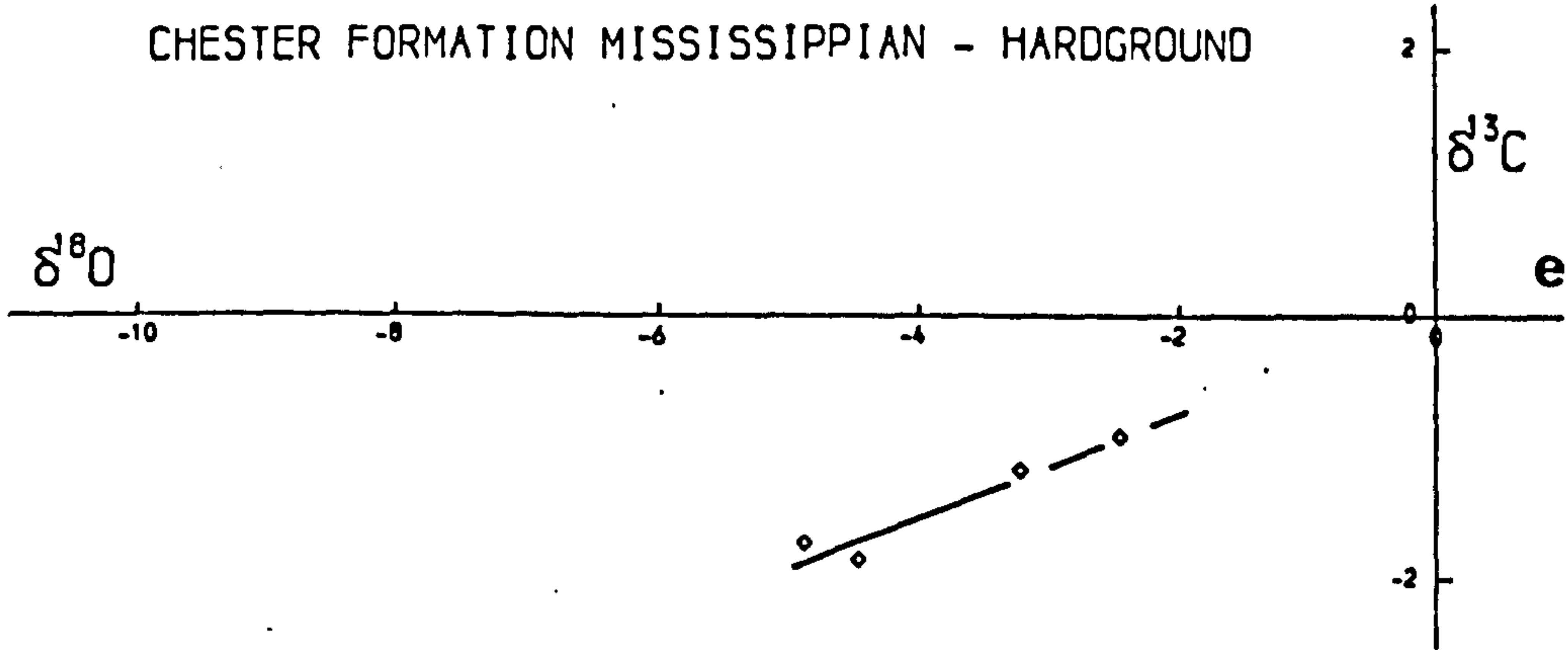


- Sparry calcite - in secondary veinlet

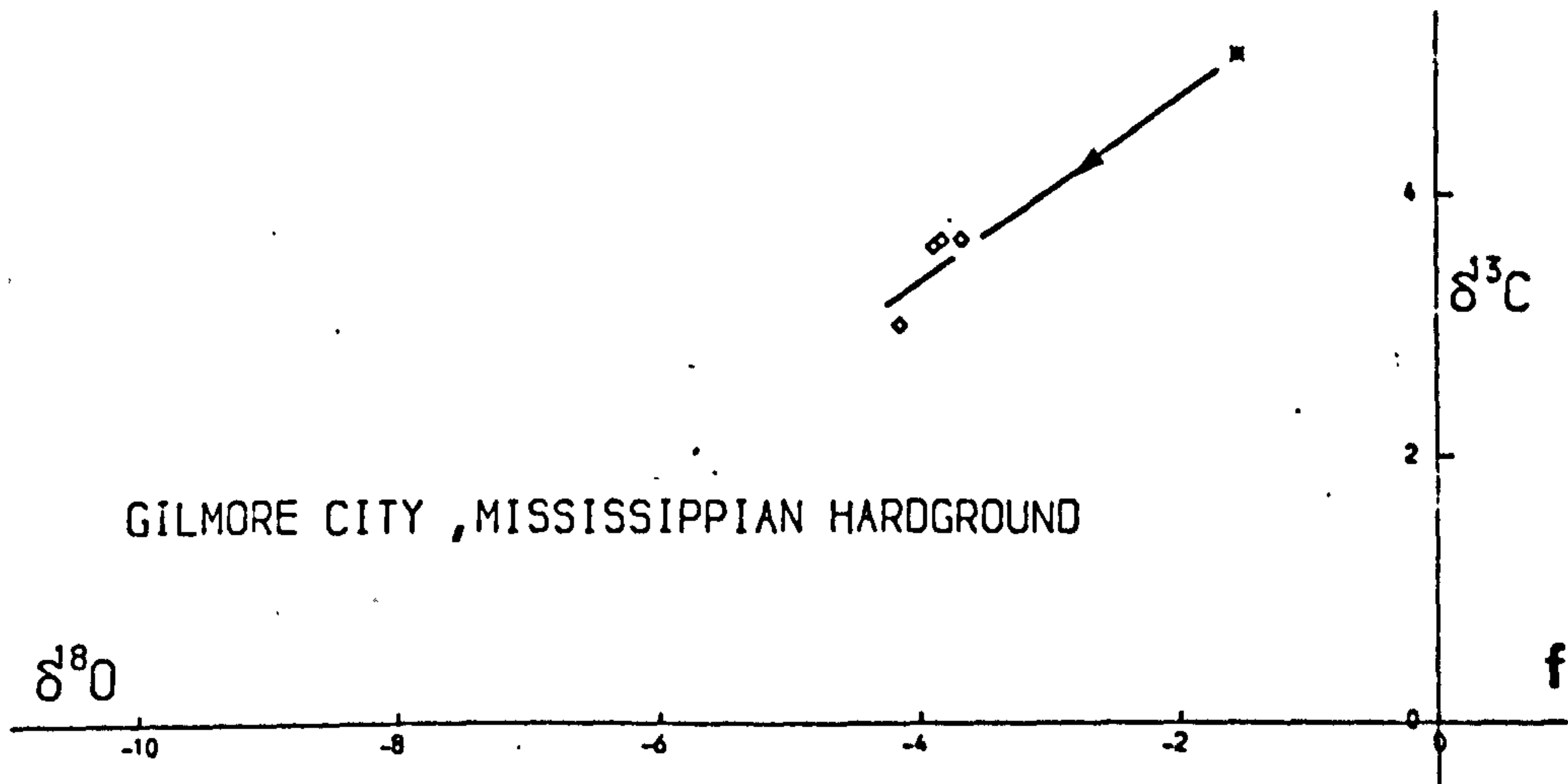
Fig.5.8



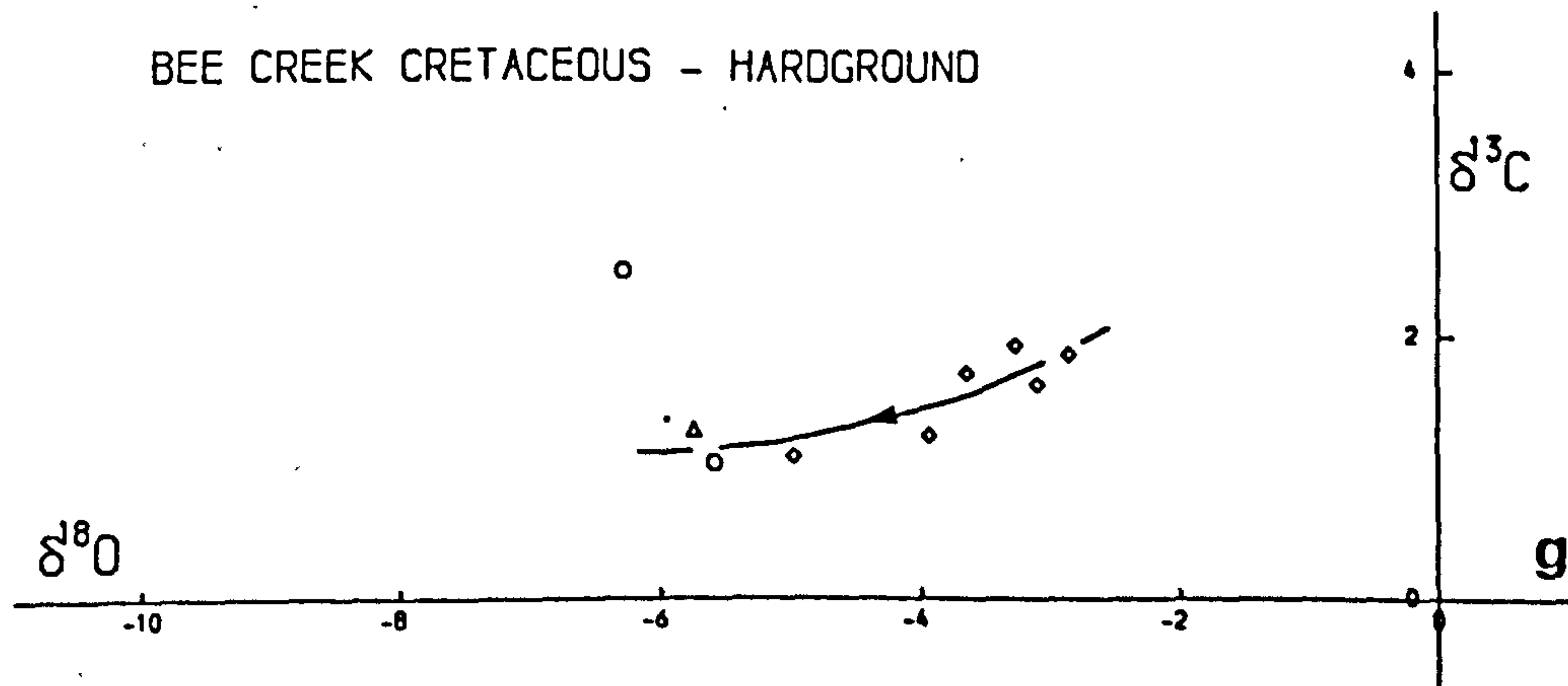
CHESTER FORMATION MISSISSIPPIAN - HARDGROUND



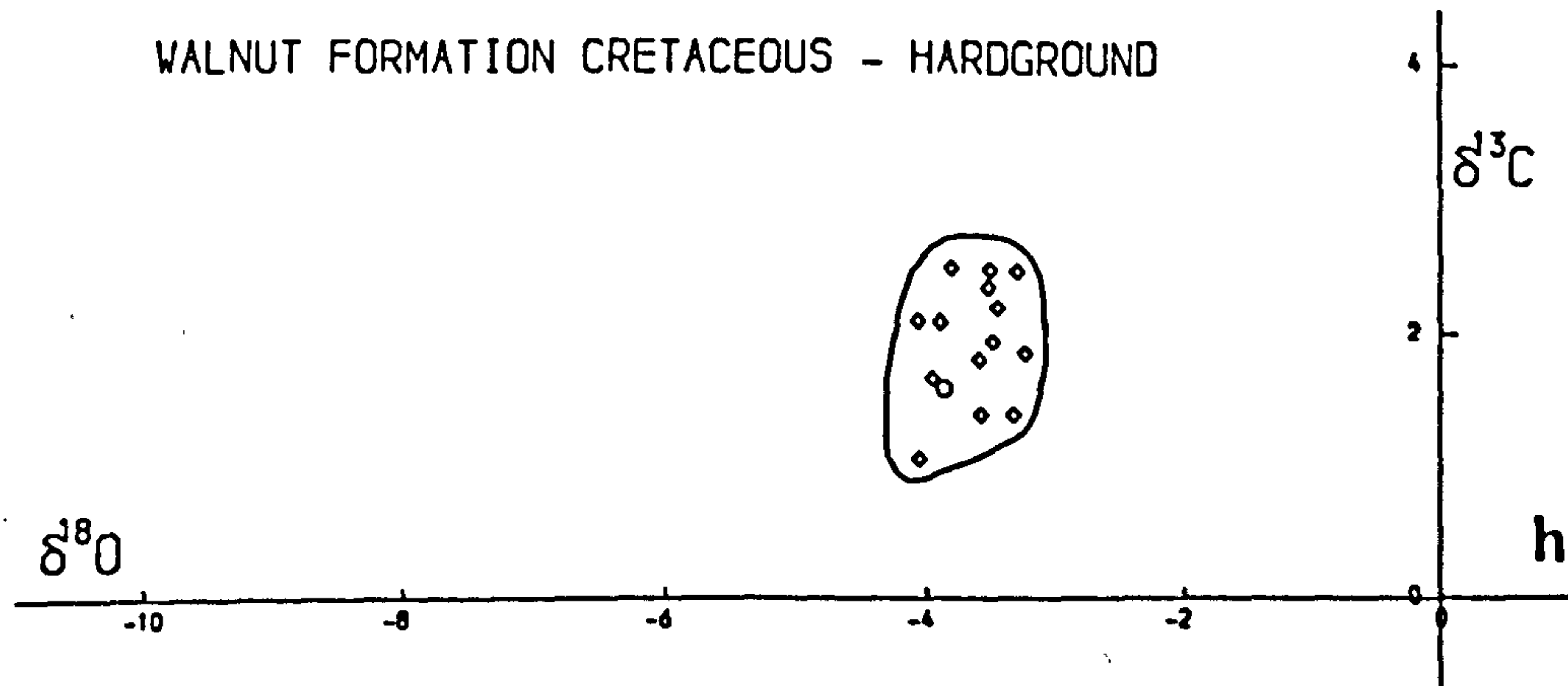
GILMORE CITY, MISSISSIPPIAN HARDGROUND



BEE CREEK CRETACEOUS - HARDGROUND



WALNUT FORMATION CRETACEOUS - HARDGROUND



and Krouse, 1975) cannot conclusively disprove the existence of an isotopically light ocean in Palaeozoic times. They do however, raise the possibility that the secular trends observed by other workers (Keith and Weber, 1964, Veizer and Hoefs, 1976) may require an alternative explanation.

DIAGENETIC TRENDS - cementation or whole-rock
re-equilibration?

Samples from an individual locality or hand specimen generally define a smooth and often near-linear trend on the isotopic scatter diagram. A marked depletion in ^{18}O and slight decrease in ^{13}C accompanies greater lithification of the sediment. Similar isotopic trends have been variously attributed to progressive cementation or re-equilibration during diagenesis (Keith and Weber, 1964, Scholle, 1974, Tan and Hudson, 1974). To determine whether any re-equilibration has taken place during the undoubted cementation of the majority of the limestones isotopic values have been compared with the modal proportion of allochems and late cements (fig.5.9., 5.10).

Proportions of primary depositional components (see above) and late sparry calcite were determined by point counting material from the Dagham Downs Quarry section and from the five localities in the Lincolnshire Limestone which showed the greatest range of degrees of cementation (and $\delta^{18}\text{O}$). Both sets of results demonstrate similar features:-

1. The graphs of $\delta^{18}\text{O}$ against spar content are nearly linear. A regression line determined for the whole rock samples from Dagham Downs fig.5.9 (with a correlation coefficient of 0.933 and significant to greater than 0.1%) predicts a spar $\delta^{18}\text{O}$ of -6.83. This is only 0.09% different from the mean of 10 analyses of separated spar samples ($\delta^{18}\text{O}$ of -6.74). Exceptions to the general trend for the Lincolnshire Limestone data (fig.5.10) are a whole-rock oosparite at Ketton and the micrite internal sediment at Greetham. Both have too light a $\delta^{18}\text{O}$ for their estimated spar content, and deviation from the general trend can be attributed to the

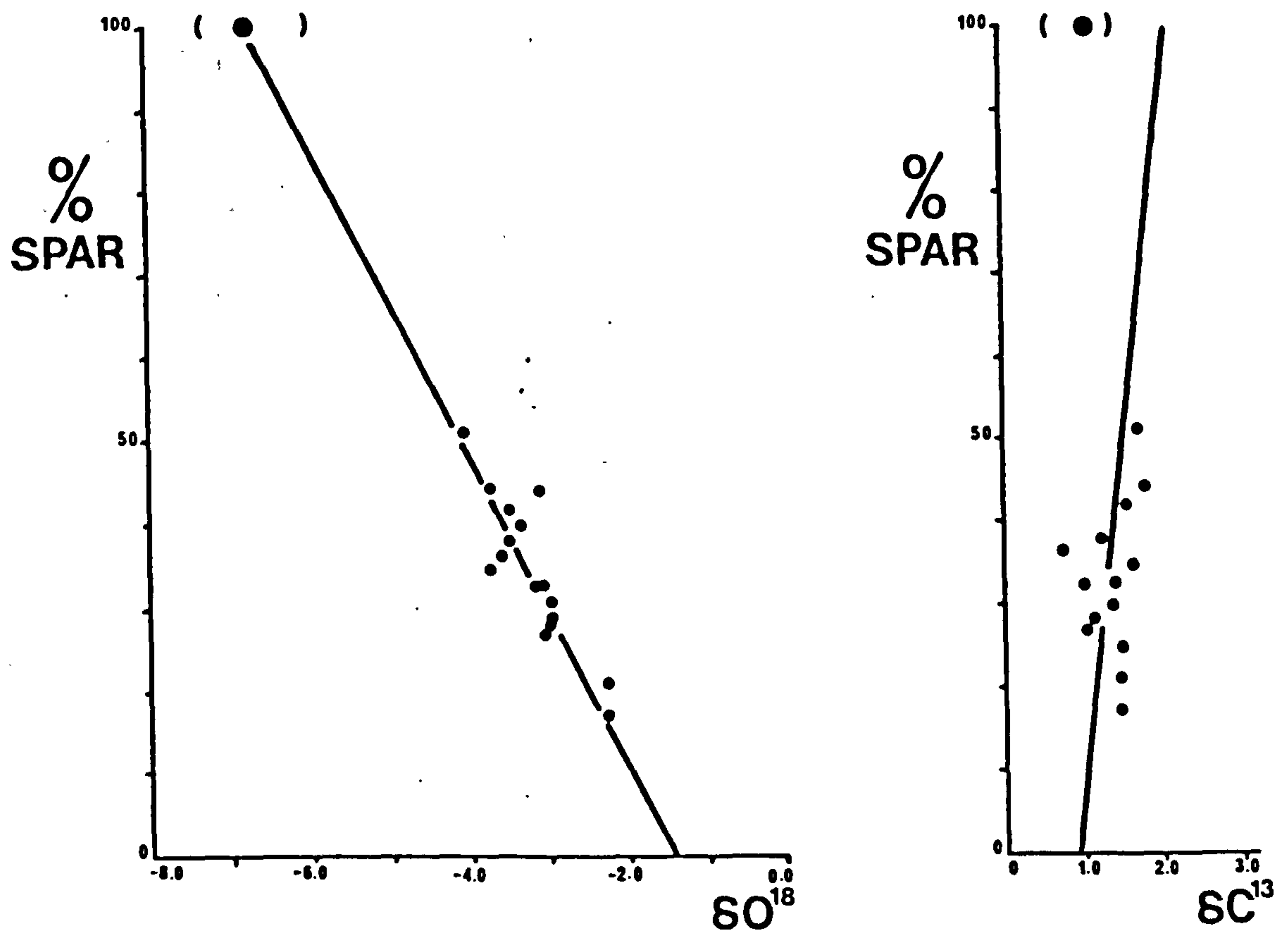


Fig.5.9. Dagham Downs. Plots of isotopic composition against spar content (as determined by point-counting). Small dots represent individual point count determinations. Large dot = mean of 10 spar analyses. (Brackets define range of values). Regression lines determined for point-count data only.

presence of fine grained (intragranular - in the case of Ketton), late cement which could not be detected by point counting. Late spar contamination is confirmed by the anomalous mauve stain which results when both the ooliths at Ketton and the micrite from Greetham are treated with standard stain solutions (see above).

2. Carbon isotopic ratios do not give a clear linear relationship when plotted against spar content. At Dagham Downs a regression line has a correlation coefficient of only 0.36 and clearly cannot be used to predict spar or allochem compositions (fig. 5.9). The trends from Lincolnshire Limestone localities (fig. 5.10) show an overall decrease in $\delta^{13}\text{C}$ with increase in spar but the lines are far from coincident.

The linear relationship between $\delta^{18}\text{O}$ and spar content demonstrates that simple cementation has been the prime mechanism of lithification (Scholle, 1977, Matter et al, 1975, Scherer 1977). Re-equilibration of marine components with pore waters during diagenesis or derivation of sparry calcite by neomorphism of an existing micrite would give data points removed to the left or right, respectively, of the observed regression line. Depositional components have retained a uniform isotopic composition throughout cementation. The value obtained by extrapolation of the Dagham Downs regression line to zero spar content ($\delta^{18}\text{O}$ of -1.41) and those samples without late cement from the Lincolnshire Limestone may be used to indicate a 'primary' marine isotopic composition (see below).

Trends of $\delta^{13}\text{C}$ against spar content are non-linear: can the distribution still be attributed to a simple process of cementation? The difference in carbon isotopic composition between uncemented allochems and late cement is of much smaller magnitude than the corresponding $\delta^{18}\text{O}$ variation and all the carbon values are still within the normal marine range. Moreover, where multiple samples of late cement have been taken at the same locality the spar commonly exhibits a

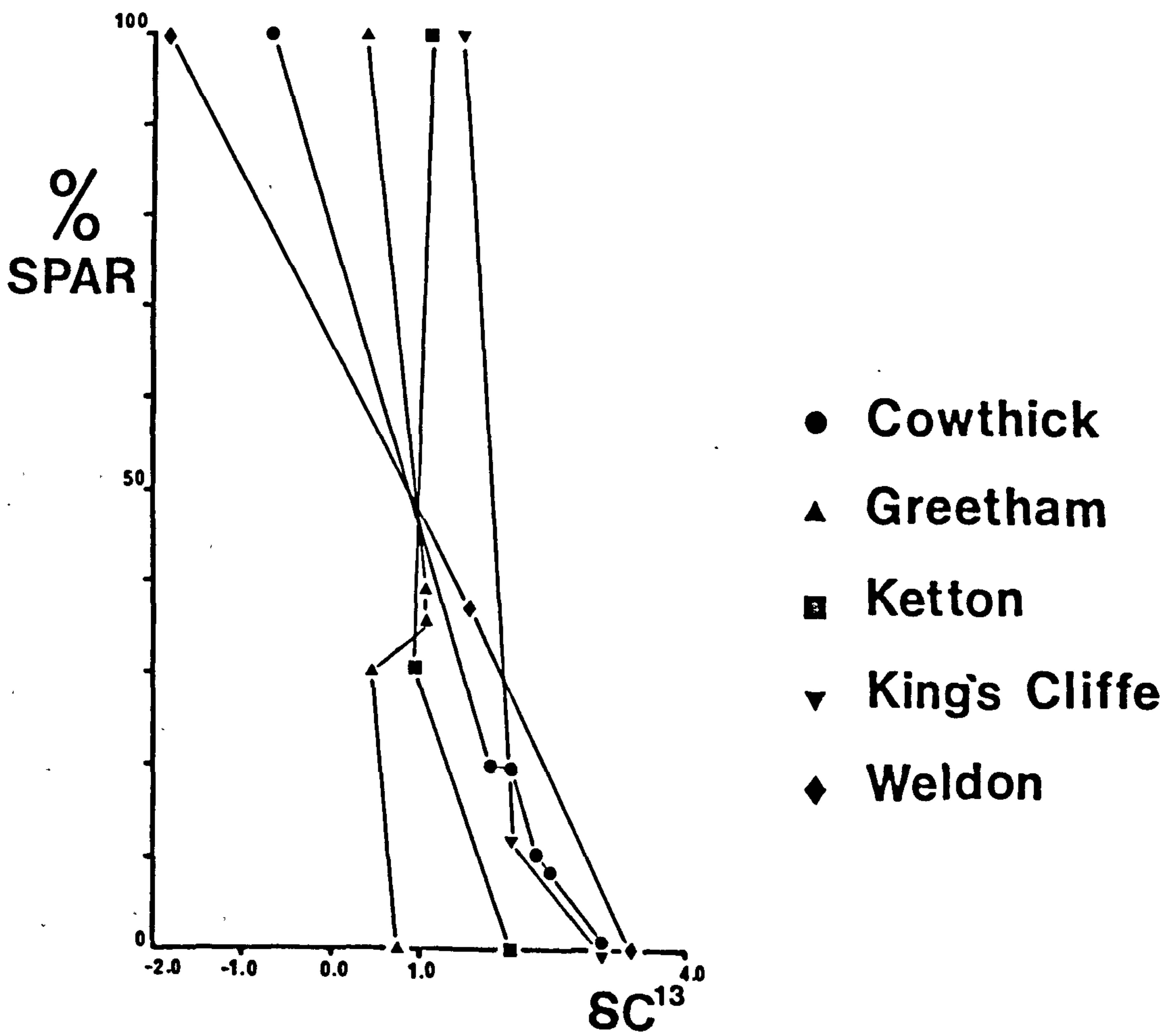
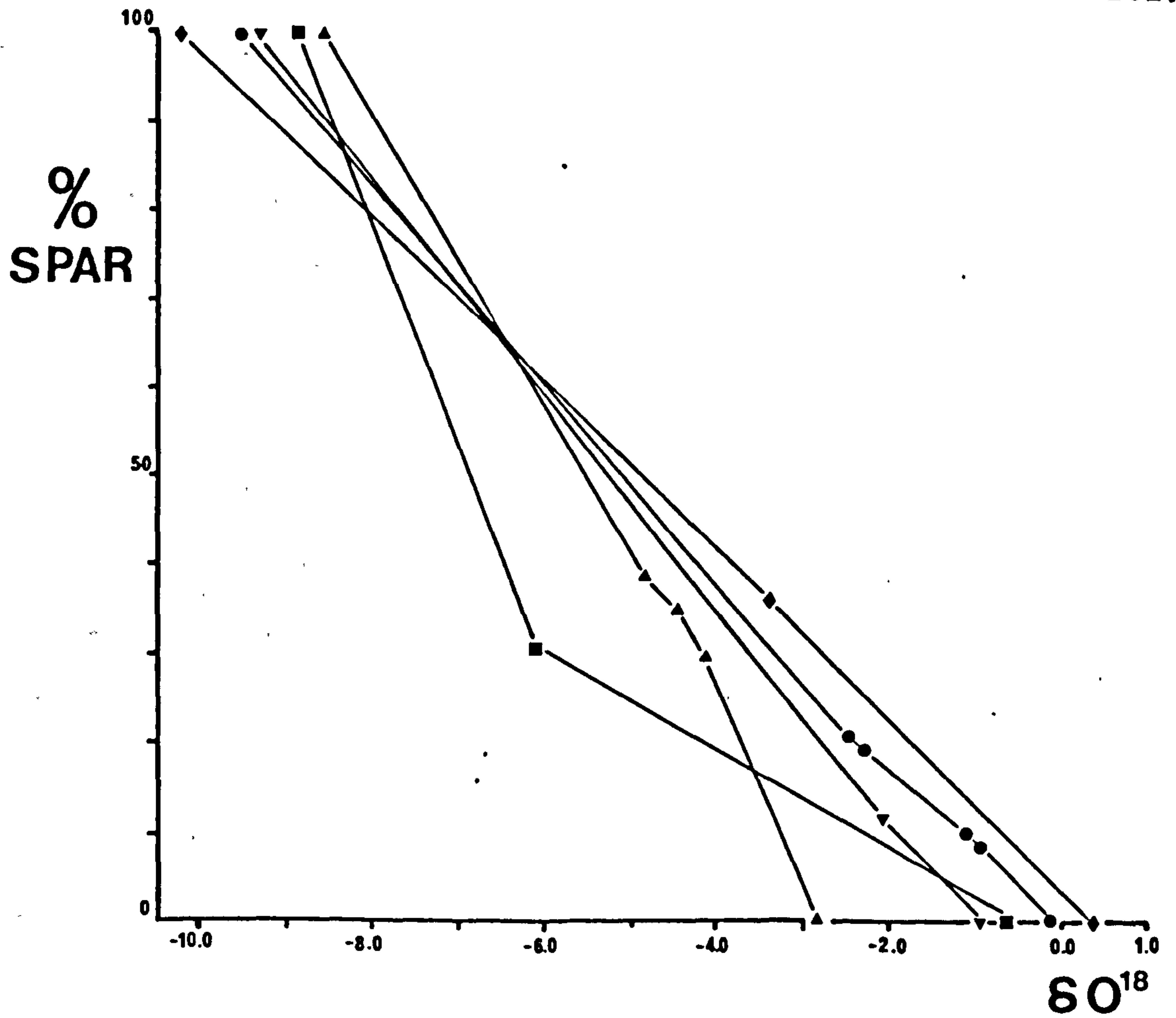


Fig.5.10, Lincolnshire Limestone, Plots of isotopic composition against spar content (as determined by point-counting).

much wider range of $\delta^{13}\text{C}$ than $\delta^{18}\text{O}$ (e.g. fig.5.4 (e), (h), (k)).

Although the regression line cannot be used to predict an end member composition, cementation of allochems with primary marine values by late cement of locally variable $\delta^{13}\text{C}$ could produce the observed trends.

OXYGEN ISOTOPIC COMPOSITION OF THE PRIMARY COMPONENTS

Recent shelf carbonates are largely composed of aragonite or high magnesium calcite (Milliman, 1975); all the limestones discussed here are composed solely of low magnesium calcite. Slight enrichment in magnesium (to up to 2wt.% Mg CO_3) in hardground cements from the Lincolnshire limestone has been used to suggest that precursor cements may have been more highly magnesian. (Marshall and Ashton; in press). Do the marine isotopic compositions of the Jurassic 'primary' components reflect the primary depositional environment or are they the product of the environment of secondary mineralogical stabilisation?

Allochems, micrites and early cements preserve heavy $\delta^{18}\text{O}$ values (from -1.4‰ to 0.1‰) which are compatible with inorganic equilibrium precipitation of calcite in normal pre-glacial oceanic water ($\delta^{18}\text{O}$ of -1.2, Shackleton and Kennett, 1975) at temperatures from 17.8°C to 11.4°C. Samples of apparently unaltered calcitic shell material from the British and French Jurassic hardgrounds have a range of $\delta^{18}\text{O}$ from -3.12 to -1.49‰ (neglecting a value of -3.68 from one of the Ranville hardgrounds oysters which has evidently been affected by secondary cementation, Fig.5.7(d)); equivalent to a temperature range from 25.7°C to 18.1°C respectively. The 'marine' components of the limestones (themselves averages that include calcitic shell fragments) are significantly enriched in ^{18}O in relation to the shell samples. This could be explained by one of several mechanisms.

1. That the shell material has all undergone a degree of secondary diagenetic alteration or cementation.

2. That the difference in isotopic composition was primary and that

the allochems were originally low magnesian calcite non-equilibrium precipitates, or

3. That the isotopic enrichment was inherited directly from a primary enrichment in a metastable precursor

4. That the allochems early cements and calcite mud became enriched in ^{18}O during mineralogical stabilisation by equilibration with shallow burial waters at cooler than depositional temperatures.

The $\delta^{18}\text{O}$ values of calcitic shell material does not give an infallible guide to palaeotemperature (Veizer 1974, Stevens and Clayton, 1971) but the estimated values give good agreement with estimates obtained from well-preserved Jurassic aragonite (Tan et al 1971, Hudson, 1978). It is unlikely that mechanism 1, could explain the difference in value. The calcite shell material came from bottom-dwelling creatures (oysters and attached brachiopods) and so it is likely that the temperatures reflect bottom-water conditions. In shallow shelf seas there would not be a major difference between surface and bottom waters but the temperature difference between allochems and shells could conceivably have arisen if shell calcite precipitation took place only during warm seasons.

The depositional components have $\delta^{18}\text{O}$ values which are consistently heavy and have a very similar range to samples of Jurassic nodular pelagic limestones (Hudson and Coleman, 1978, Chapter 2 of this thesis and own unpublished data). In view of tracer studies which have demonstrated that Palaeozoic and Mesozoic sediments had similar mineralogy to those of to-day (Davies, 1977, Veizer, 1977) it is most unlikely that the Jurassic allochems were primarily low magnesium calcite. The oxygen isotopic composition may therefore reflect equilibration with cool shallow burial waters (Irwin et al, 1977) but is most likely to be due to inheritance of primary enrichment from the metastable precursor (Milliman and Muller, 1977). The process of transformation from aragonite or high magnesium

calcite to calcite involves considerable decrease in Sr and Mg concentration respectively. Transformation must have involved a fluid phase but to preserve original fabrics and isotopic composition it must have taken place in a system with a low effective water:rock ratio (Veizer, 1977, Katz and Matthews, 1977) where pore water exchange was severely restricted.

PRIMARY COMPONENTS - Carbon isotopic composition.

Samples of oolites with no discernable cements together with those from a fully lithified hardground surface (Cowthick) have $\delta^{13}\text{C}$ values heavier than 3‰ (Table 5.2). The retention of heavy $\delta^{13}\text{C}$ may be further evidence for the inheritance of isotopic enrichment from metastable precursors, as Recent ooliths commonly have non-equilibration (heavy) $\delta^{13}\text{C}$ values (Milliman and Muller, 1977).

ORIGIN OF LATE CEMENTS

Samples from 28 of the 32 localities studied produce a near-linear distribution on the isotopic scatter diagrams. Modal analysis has demonstrated that the distribution can be explained by cementation of primary components with 'marine' isotopic composition by late cements depleted in ^{18}O and to some extent ^{13}C . At an individual locality late cements have a virtually constant $\delta^{18}\text{O}$ but exhibit a wider range of generally low positive $\delta^{13}\text{C}$. The uniformity of oxygen isotopic composition and the fact that they are unzoned (as far as the limits of detection of staining and microprobe scans) implies that the pore-waters in which they precipitated had attained a stable composition before cementation commenced; (c.f. changes within cements described by Dickson and Coleman, in press).

Blocky calcite cements with light $\delta^{18}\text{O}$ and slightly negative $\delta^{13}\text{C}$ can be the result of diagenesis under 1. shallow burial in freshwater vadose or phreatic conditions or 2. under deeper burial at increased temperature from waters with modified connate or mixed connate-meteoric origin (for 1. see Allan and Matthews, 1977, Wigley et al 1978, Meyers,

1978, Meyers and James, 1978, -for 2. see Hudson 1975, 1978, Dickson and Coleman in press). Subaerially exposed limestones would be expected to demonstrate a wider range of $\delta^{13}\text{C}$ than $\delta^{18}\text{O}$ (Gross, 1964, Allan and Matthews, 1977) although the characteristically light ($\delta^{13}\text{C}$ of -12) values associated with near surface cementation may not always occur. (Wigley et al, 1978). Only the coral bed at Shellingford for which there is petrographic and environmental evidence of emergence has secondary blocky calcites with substantially negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of 0 to -4 which correspond to values from recent subaerial diagenetic calcites (Allan and Matthews 1977). In addition there is no sedimentological evidence for widespread emergence on the scale of Recent Caribbean Islands or for the precipitation of cements with characteristic vadose fabrics. It is therefore likely that the blocky cements in the majority of the limestones were precipitated during subsequent burial history.

The isotopic composition of the sparry calcites is similar to that of burial cements in limestones, sandstones and shales throughout the stratigraphic column. (Tan and Hudson, 1974, Hudson and Fieldman 1976, Dickson and Coleman; in press). There is no evidence for cementation during the early diagenetic stages defined for organic-rich sediments by Irwin et al. (1977) and Curtis, (1978) each of which is characterised by different carbon isotopic composition. A predominance of 'marine' $\delta^{13}\text{C}$ values suggests that the dissolution of metastable fossils or cements or of limestones during stylolitisation may have been important sources of bicarbonate (Hudson, 1975, 1978, Purser, 1978). The general trend toward slightly lighter $\delta^{13}\text{C}$ in later cements cannot be a function of temperature increase (c.f. Enrich et al. 1970) and must be due to differences in the source of bicarbonate. $\delta^{13}\text{C}$ variability within a single generation of cement suggests that the addition of light bicarbonate was intermittent. It is possible that the comparatively minor fluctuation in $\delta^{13}\text{C}$ are related to minor input of very light bicarbonate

($\delta^{13}\text{C} = -24$) produced by abiotic reactions under burial (Irwin et al., 1977).

The magnitude of the decrease in $\delta^{18}\text{O}$ (from 0‰ in the allochems to -6 to -13‰ in the late cements) makes it unlikely that temperature increase alone could have produced the observed diagenetic shift. The waters from which the cements precipitated must themselves have been depleted in ^{18}O in comparison to sea water. A multitude of processes can and have been invoked to account for the diagenetic decrease in $\delta^{18}\text{O}$.

The majority of the late calcites are ferroan, an indication, according to Oldershaw and Scoffin (1967) and many subsequent workers, that shales, with readily available adsorbed Fe^{2+} and dispersed metastable fossil carbonate, could have provided bicarbonate for limestone cementation. Shales are abundant in the stratigraphic column in Central England (Fig. 5.2). During their compaction history they could have produced significant volumes of super-saturated (w.r.t. bicarbonate) connate water which in turn could, as a result of diagenetic reactions and ultrafiltration have had light $\delta^{18}\text{O}$ (Coplen and Hanshaw, 1973, Lawrence et al., 1976). The lack of iron in late cements in the Burgundian limestones may reflect the scarcity of local interbedded shales and a different source for the cement bicarbonate (Purser, 1978). Alternatively, as the partition coefficient for iron between calcite and pore-water is large (Richter and Fuchtbauer, 1978) minor concentrations of iron, perhaps released by redox reactions in the English limestones themselves would have been sufficient to produce at least slightly ferroan calcites.

Cements with similar oxygen isotopic composition (and trace-element concentrations?) to the Jurassic late cements are to-day being precipitated under burial in waters of diverse origins. The calcites are apparently in equilibrium with their surrounding waters (Fleischer et al 1977, Land and Dutton, 1979 and own calculations from the data of Hitchon & Friedman, 1969). Salinity and oxygen and hydrogen isotopic studies

on deep burial waters themselves show them to have originated by a range of processes from evolution of connate waters by ultrafiltration to connate water mixing with meteoric-derived waters (Hitchon and Friedman, 1969, Dowgialla and Tongiori, 1977, Flescher et al 1977). Pleistocene rainwater trapped at depth in the Lincolnshire Limestone to-day has $\delta^{18}\text{O}$ of -7.8‰ (Smith et al. 1975) which is only marginally too light for equilibrium with the lightest of the late cements analysed here ('cement' of -11‰ would be in equilibrium with such water at 30°C). It is however possible that at some stage during the 150 Myrs available between deposition of the limestone and their appearing at outcrop meteoric derived waters could have helped cement the limestones (Hudson, 1978). Carbon isotopic ratios cannot be used to help differentiate between meteoric or connate sources because the relatively small carbon reservoir in fresh pore waters come into virtual equilibrium with marine limestones at only a short distance from outcrop. (Allan and Matthews, 1977, Wigley, 1978, Smith et al. 1975, 1976).

Without additional temperature or salinity data, perhaps from studies of fluid inclusions in the calcite cements it would be unwise ~~to~~ ^{to} speculate further on the origin of the late cement isotopic composition.

CONCLUSIONS

1. The results of carbon and oxygen stable isotope analysis of samples taken from a single locality commonly have a near-linear distribution on the isotopic scatter diagram. There is a general correlation between decrease in $\delta^{18}\text{O}$ and to some extent $\delta^{13}\text{C}$ with increased content of sparry calcite cement.
2. The range of isotopic values can be attributed to cementation of depositional components which have retained a primary 'marine' isotopic composition ($\delta^{18}\text{O}$ -2.0 to 0.5‰, $\delta^{13}\text{C}$ 1.5 to 3.5‰) by late ^{18}O depleted cements. There is no evidence for re-equilibration of the marine components during later diagenesis. Mineralogical stabilisation must have taken place in shallow burial marine pore waters with restricted external exchange.

A difference in apparent temperature of formation between such components and fossil material is attributed to the inheritance of non-equilibrium ^{18}O enrichment from the metastable precursor of the allochems or possibly to equilibration with cold shallow burial waters during mineralogical stabilisation.
3. Bulk samples from hardgrounds cannot always be used to indicate the isotopic composition of ancient sea waters but the presence of a few isotopically heavy samples ($\delta^{18}\text{O}$ -1 to 1) from Palaeozoic hardgrounds may suggest that the sea water may not have been significantly different from that in Mesozoic or later times.
4. Cementation by sparry calcite probably took place during the normal burial history of the limestones as there is no evidence of widespread cementation in shallow freshwater phreatic environment. Constancy of $\delta^{18}\text{O}$ within late cements at an individual locality is an indication of cementation after pore-water evolution or mixing

(c.f. continuity of burial diagrams encountered by Land and Dutton, 1979, Dickson and Coleman; in press) and any temperature increase rather than during such processes and is most likely to be encountered under stable, burial conditions.

Cursory examination of the sporadic field occurrence of sparry calcites suggests that permeability and therefore lateral ground water flow may have been important during cementation. This would explain cement concentrations in bioclastic horizons while uncemented oolites would be the product of zones of low rates of groundwater flow (Purser, 1978). Further, more rigorous studies of cement distribution on both locality and regional basis are needed to confirm these observations.

The origin of the ubiquitous light $\delta^{18}\text{O}$ values in late cements remains problematical and on the basis of isotopic analyses alone could have resulted from the evolution of shale connate waters or from the introduction of meteoric-derived ground waters.

Table 5.1. Map reference, stratigraphic horizon and key references for the specimens of British middle and upper Jurassic Limestones.

<u>Locality</u>	<u>Map refernce</u>	<u>Stratigraphy</u>	<u>Succession Recorded or interpreted in:</u>
1. <u>LINCOLNSHIRE LIMESTONE</u> - Bajocian (Inferior Oolite)			
Castle Bytham	SK990180	Upper Lincs.Lst.	1.2.4.
Cowthick	SP921886	Upper Lincs.Lst.	4.
Greetham	SK933146	l + m Lincs.Lst.	2.3.
Ketton	SK973058	Upper Lincs.Lst.	1.
King's Cliffe	SP013961	Upper Lincs.Lst.	1.
Leadenham	SK962523	Lower Lincs.Lst.	2.4.
Stainby	SK910233	l + m Lincs.Lst.	3.
Thistleton	SK903180	Lower Lincs.Lst.	2.3.
Weldon	SP919887	Upper Lincs.Lst.	1.
Woolfox	SK951136	Middle Lincs.Lst.	2.

- 1. Sylvester-Bradley in: Ford and Sylvester-Bradley 1968
- 2. Ashton, 1976
- 3. Ashton, 1979
- 4. Marshall and Ashton: in press

II OTHER BRITISH JURASSIC LOCALITIES

Bradford-on-Avon	ST826600	Bathonian (Great Oolite Forest Marble Fm)	5.
Dagham Downs	SP003060	Bathonian (Great Oolite White Lst.Fm)	2.6.7.
Foss Cross	SP056091	Bathonian (Great Oolite White Lst.Fm)	3.6.7.
Hook Norton	SP360324	Bajocian (l.Inferior Oolite)	4.
Ketton Grange	SK970050	Bathonian (Great Oolite)	4.
Shellingford	SU325940	Oxfordian (Corallian-Osmington Oolite Series)	3/A
Shipton	SP470170	Bathonian (Great Oolite White Lst.Fm)	1.7.

- 1. Arkell, 1931
- 2. Torrens, 1967
- 3. Torrens, 1969 3/A J.H.Callomon in: Torrens 1969
- 4. Sylvester-Bradley in: Ford and Sylvester-Bradley 1968
- 5. Palmer and Fursich, 1974
- 6. Fursich and Palmer, 1975
- 7. Palmer, 1979

Table 5.2. Isotopic composition of samples from the Lincolnshire Limestone Formation (Bajocian) Eastern England. Each section of the table includes brief stratigraphic and petrographic description and comment on the isotopic results.

Localities shown on fig.5.1. map reference and reference to previous descriptions of each locality are given in Table 5.1. (Distances in cm. refer to depth below hardground surfaces).

Table 5.2(a).

Castle Bytham Quarry. Upper Lincolnshire Limestone.

Oolite and peloidal limestones. Oyster-encrusted hardground (LN8) caps pelsparite bed - fringing cements developed within 5cm of surface. Late cement ferroan. Joints filled with blocky non-ferroan spar (LN9).

<u>Sample</u>	<u>Block</u>	<u>Description</u>	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
L20	(LN8)	Oyster - encrusting hardground surface	2.47	-2.76
L20-1	(LN8)	Oyster " " " "	2.30	-3.12
L22-1	(LN8)	"Whole-rock" pelsparite (0.8cm from hardground)	2.02	-3.96
L22	(LN8)	" " (1.5cm)	1.99	-4.57
L22-2	(LN8)	" " (3.0cm)	2.04	-4.57
L22-3	(LN8)	" " (4.7cm)	2.22	-4.45
L23	(LN8)	" " (6.0cm)	2.31	-5.80
L23-1	(LN8)	" " (8.5cm)	1.75	-5.94
L24	(LN8)	Spar supported burrow fill	1.87	-5.09
L25	(LN8)	" " " "	2.13	-5.80
L26	(LN8)	" " " "	1.98	-5.75
L27	(LN10)	Overlying Oosparite	1.94	-5.21
L28	(LN10)	Late	1.83	-8.28
L53	(LN9)	Whole-rock oosparite (adj. to joint)	1.59	-5.99
L54	(LN9)	" " "	1.61	-6.35
L51	(LN9)	Non ferroan spar - joint fill.	-4.82	-3.99

Comment

(Scatter diagram Fig.5.4.a.). Samples show a near linear trend of decreasing $\delta^{18}\text{O}$ from Oyster samples to late ferroan cement. Hard-ground surface samples have heavier $\delta^{18}\text{O}$ than those below (see discussion in Marshall and Ashton, in press). Non ferroan joint calcite is not related to main diagenetic trend.

Table 5.2(b) + (c).

Cowthick Quarry, Corby. Upper Lincolnshire Limestone.

Upper Lincolnshire limestone channels cut underlying Grantham Formation shales - bored and encrusted hardgrounds developed in channel-fill sediments. (Marshall and Ashton= in press). Oosparites cemented by early fringing cements at the hardground surfaces. Ferroan spar fills the residual former intergranular and aragonite solution voids.

(b) Cowthick hardground- rafted block

<u>Sample</u>	<u>Depth (Cm)</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
L30	-	Poorly consolidated bore-fill	3.04	-0.10
L31	-	Fine-grained early-lithified internal sediment	2.33	-0.37
L32	-	" " " "	2.81	-0.49
L33	-	Late spar vein (1st contaminated?)	0.58	-6.85
L34	0.7	'Whole-rock' oosparite	2.27	-1.48
L35 ⁺	1.0	" " " - shelly layer	2.00	-2.34
L35-1	2.0	" " "	2.45	-0.91
L35-2	4.3	" " "	2.30	-1.12
L35-3	6.3	" " "	1.63	-2.17
L35-4	9.2	" " "	1.79	-2.46
L35-5	-	Late blocky ferroan spar	-0.66	-9.51

(c) Cowthick hardground - channel wall

<u>Sample</u>	<u>Depth (Cm)</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
L1	-	Unconsolidated geopetal sediment	3.41	0.38
L2	0	Hardground surface	3.14	-0.16
L3	0	Wall of mollusc boring	3.27	-0.18
L4	0.5	"Whole-rock' oosparite	3.02	-0.68
L5	0.7	" " "	2.94	-0.83
L5-1	2.0	" " "	2.45	-0.90
L5-2	3.0	" " "	2.62	-0.64
L5-3	4.5	" " "	2.50	-0.91
L5-4	6.0	" " " - shelly layer	1.73	-2.22
L5-5	7.5	" " "	2.23	-1.73
L5-6	11.0	" " "	2.04	-2.13
L5-7	15.0	" " "	1.60	-2.45

Comment

(Scatter diagrams figs.5.4.(b) and (c))

Both backgrounds give similar non-linear trend of isotopic values. Hardground surface samples and unconsolidated sediments have exceptionally heavy $\delta^{18}\text{O}$ (discussion in Marshall and Ashton; in press).

Table 5.2(d).

Grantham Quarry. Lower and middle Lincolnshire Limestone.

Oolitic limestones, with burrows. Solution voids of coral colours filled with ferroan spar

<u>Sample</u>	<u>Block</u>	<u>Description</u>	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
L61	GR1	Whole-rock oosparite	0.85	-4.13
L62	GR1	" " "	1.25	-4.90
L63	GR1	" " "	1.06	-4.23
L64	GR2	Micrite burrow fill	0.72	-2.86
L65	GR2	Whole-rock oosparite	1.16	-4.99
L67	GR3	" " "	1.14	-4.63
L69	GR4	" " "	1.12	-4.86
L70	GR4	" " "	0.95	-5.03
L71	GR4	" " "	1.07	-4.57
L72	GR5	" " "	1.43	-4.75
L73	GR5	" " "	1.44	-3.84
L74	GR5	" " "	1.34	-3.84
L75	GR6	" " " - adjacent to coral	0.75	-4.00
L76	GR6	Late ferroan spar in coral solution void	0.89	-8.68
L77	GR6	" " " "	0.01	-8.50

Comment

Scatter diagram, fig.5.4.(d). Limestone samples show cluster of values (at $\delta^{18}\text{O}$ -4.5 $\delta^{13}\text{C}$ + 1.2)

Trend toward ^{18}O depletion (and minor ^{13}C depletion) with increasing spar content.

Table 5.2(e).

Ketton Cement Quarry. Upper Lincolnshire Limestone

Lithologies range from oolite sand with no discernable intergranular cement to fully cemented oosparites with blocky ferroan cement. (Allochems are non-ferroan in uncemented varieties; weakly ferroan in the fully-cemented limestones).

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
Ki	Whole-rock oolite - no discernable spary cement	2.19	-0.51
K4	Whole-rock oolite - unconsolidated oolite sand	1.85	-0.74
K2	Whole-rock oosparite - poikilotopic ferroan spar	0.99	-5.93
K3	Whole-rock oosparite - poikilotopic ferroan spar	0.85	-6.27
K6	Late ferroan spar in coral solution void	1.60	-8.42
K7	Late ferroan spar in coral solution void	0.66	-9.33

Comment

(Scatter diagram fig.5.4(e)).

Correlation between spar content and $\delta^{18}\text{O}$ decrease combined with slight decrease in $\delta^{13}\text{C}$ produces smooth trend line on scatter diagram. Oolite sand (= pure allochem) has similar isotopic composition to Allochems + early cement at Cowthick hardground surface.

Table 5.2(f).

Kings Cliffe Quarry. Upper Lincolnshire Limestone, Bajocian.

Oosparite with early fringing cements cut by mollusc bores.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
L85	Whole-rock oosparite with early fringing cement	2.03	-2.13
L86	Micrite geopetal sediment in mollusc bore	1.87	-3.82
L84	Micrite internal sediment	3.06	-0.91
L82	Late ferroan spar in mollusc bores	1.36	-9.15
L83	" " " " "	1.51	-9.30

Comment

(Scatter diagram fig.5.4(f)).

"Horizontal" trend to negative $\delta^{18}\text{O}$ in scatter diagram corresponds to increasing spar content.

Table 5.2(g)

Leadenham Quarry. Lower Lincolnshire Limestone.

Intensely bioturbated oopelmicrites capped by encrusted hardground. Ferruginous crusts line burrow margins. No early cements. Late ferroan spar fills former intergranular voids.

<u>Sample</u>	<u>Depth (Cm)</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
L17	0	Hardground surface	0.32	-3.55
L16	0	Ferruginous burrow wall	0.33	-3.41
L7	0.5	'Whole-rock' oopelmicrite	0.29	-3.89
L8	0.5	" " "	0.19	-4.79
L18	1.0	" " "	0.42	-3.91
L9	3.5	" " "	0.45	-4.40
L10	7.0	" " "	0.49	-3.66
L6	-	Burrow fill-spar rich	-0.35	-5.81
L12	-	" " -fine-grained	0.59	-3.48
L13	-	" " " "	0.64	-3.41
L19	-	" " " "	0.41	-3.27
L11	-	Ferroan calcite - coral replacement	1.23	-7.82
L15	-	Ferroan calcite - inside serpulid tubes	1.33	-7.89
L14	-	Ferroan calcite - inside serpulid tubes (1st cont?)	0.89	-5.63

Comment

(Scatter diagram, fig.5.4(g).

Late cement is marginally heavier/ⁱⁿ $\delta^{13}\text{C}$ than whole-rock samples but $\delta^{18}\text{O}$ is 4% lighter. Sample with intermediate spar concentration confirms cementation trend.

Table 5.2(h).

Stainby Quarry. Lower to middle Lincolnshire Limestone.

Oosparites with solitary Montivaltia-type corals preserved as ferroan spar-filled former solution voids. Micrite envelopes define the septa .

<u>Sample</u>	<u>Description</u>	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
1.29	Whole-rock oosparite	1.29	-3.37
1.28	Blocky ferroan spar - in 'coral'	0.57	-7.32
1.27	" " " " "	2.38	-6.90
1.26	" " " " "	0.02	-7.64

Comment

(Scatter diagram. fig. 5.4(h)).

The three samples of spar from the same 'coral' replacement demonstrate the much greater variability of $\delta^{13}\text{C}$ (range of almost 2.4‰) than $\delta^{18}\text{O}$ (0.7‰) in a single generation of late cement.

Table 5.2(i).

Thistleton Quarry. Lower Lincolnshire Limestone.

Intensely burrowed oosparite.

<u>Sample</u>	<u>Description</u>	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
I25	Whole-rock oosparite	2.36	-3.05
I23	Bio-pelsparite burrow fill	1.40	-6.81
I24	Late ferroan spar (in gastropod chamber)	2.01	-8.09

Comment

(Scatter diagram. fig. 5.4(i)).

Increase in spar corresponds to decrease in $\delta^{18}\text{O}$.

Table 5.2.(j).

Weldon Quarry, Corby. Upper Lincolnshire Limestones.

Weldon building stone - oolite sand with no discernable cement and 'rag' - shelly limestone horizon with aragonite shell debris 'replaced' by late ferroan cement.

<u>Sample</u>	<u>Description</u>	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
L55	Whole-rock oolite - no discernable late cement	3.38	0.31
L57	Late ferroan cement within bivalve cavity	-1.82	-10.23
L59	Whole-rock - shelly bio-sparite ("rag")	1.56	-3.17
L60	" " " " "	1.49	-3.50

Comment

(Scatter diagram, fig. 5.4(j)).

The four samples define a clear linear trend. The late spar is 10.5‰ lighter in $\delta^{18}\text{O}$ and 5.2‰ lighter in $\delta^{13}\text{C}$ than the uncemented oolite.

Table 5.2(k).

Woolfox Quarry. Middle Lincolnshire Limestone

Oomicrites and oosparites with large colonial corals.

Corals are preserved as solution voids which have a layer of micritic internal sediment and up to two generations of late blocky spar (see main text).

<u>Sample</u>	<u>Block</u>	<u>Description</u>	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
L39	(W1)	Whole-rock oosparite	1.92	-6.76
L36	(W1)	First generation non-ferroan spar	2.41	-9.40
L37	(W1)	Central ferroan spar	-0.80	-10.16
L38	(W1)	" " "	0.14	-9.52
L43	(W1/1)	Whole-rock oomicrite	1.61	-4.10
L42	(W1/1)	'Septal debris' - geopetal sediment	1.85	-8.59
L40	(W1/1)	First generation (green-brown) non-ferroan spar	2.26	-9.56
L41	(W1/1)	Final generation ferroan spar	-1.23	-10.31
L46	(W2)	Geopetal sediment (early)	1.02	-7.19
L45	(W2)	Geopetal sediment (late)	0.92	-7.18
L44	(W2)	Late ferroan cement	1.25	-8.11
L49	(W3)	Whole-rock biomicrite	1.72	-4.10
L48	(W3)	First generation non-ferroan cement	2.07	-9.61
L47	(W3)	Late ferroan spar	0.36	-9.46

Comment

(Scatter diagram, fig. 5.4(k)).

The points define a general trend with decrease in $\delta^{18}\text{O}$ with increased spar. Seven of the eight late spar determinations of both generations have a range of $\delta^{18}\text{O}$ of only 0.9‰ (the eighth was probably contaminated by host sediment during sampling). The early generation (non-ferroan) spar is notably enriched in $\delta^{13}\text{C}$ compared to second generation calcite (by up to 3‰, $\delta^{13}\text{C}$).

Table 5.3. Results of carbon and oxygen isotopic analysis of samples of Jurassic limestones from Formations other than the Lincolnshire limestone. Localities are shown on figure 5.1. map references and reference to previous descriptions of each locality are given in Table 5.1.

Table 5.3(a).

Bradford-on-Avon Quarry, Bradford Clay, Bathonian.

Oobiosparite bed 10cm thide encrusted on top and basal surfaces (Hardground described by Palmer and Fursich, 1974). Local pyritisation.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
O.84	Oyster shell	0.24	-3.11
O.91	Rhynchonellid (?) brachiopod shell	0.61	-2.31
O.85	Whole-rock oobiosparite	-0.69	-4.72
O.88	" " "	-0.33	-5.31
O.89	" " "	-0.07	-5.51
O.87	" " "	-1.41	-6.48

Comment

(Scatter diagram, fig. 5.6(a)).

Whole-rock limestone samples show no clear trend but the points cluster around $-0.5\delta^{13}\text{C}$ and $-5.3\delta^{18}\text{O}$. Relatively low $\delta^{13}\text{C}$ values may be attributed to minor proportion organic involvement in carbonate and pyrite precipitation.

Table 5.3(b).

Dagham Downs Quarry. Great Oolite, Bathonian.

Succession of oolitic and peloidal limestones with varying sparitic/micritic matrix. Large crustacean burrows in upper part of sequence have remained open or only partially filled with poorly consolidated sediment. Coral and bryozoan colonies show a range of replacement/cementation fabrics. Late spar is weakly ferroan in the sparite limestones (and early non-ferroan zone is found in some of the corals)

(Block number refer to quarry section, Fig.5.

<u>Sample</u>	<u>Block</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
J1	(DD1)	Whole-rock-oobiosparite	1.81	-3.72
J2	(DD2)	" " -pelmicrite	1.44	-2.28
J3	(DD3)	" " -pelmicrite	1.43	-2.27
J7	(DD4/B)	" " -pelsparite-spar rich	1.31	-3.80
J8	(DD4/B)	" " " spar poor	1.38	-3.00
J5	(DD4/B)	" " -peloidal burrow-fill	1.24	-3.51
J4	(DD4/B)	Late ferroan spar	1.28	-6.00
J6	(DD4/B)	" " "	1.17	-6.55
J9	(DD4/B)	Joint calcite	1.68	-3.18
J12	(DD4/T)	'Whole-rock -pelsparite	1.46	-3.04
J13	(DD4/T)	" " -pelsparite	1.16	-3.18
J14	(DD4/T)	" " "	1.60	-3.12
J15	(DD4/T)	" " " burrow fill	1.55	-3.50
J16	(DD4/T)	Late spar - non-ferroan	1.06	-6.53
J17	(DD4/T)	" " - ferroan	1.08	-6.89
J10	(DD4/T)	" " "	0.58	-7.31
J11	(DD4/T)	" " "	0.88	-6.95
J18	(DD4/T)	Joint calcite	1.42	-3.99
J23	(DD5)	Whole-rock pelmicrite	1.25	-3.03
J24	(DD5)	" " "	1.00	-2.91
J22	(DD5)	Micritic internal sediment	1.12	-2.99
J19	(DD5)	Coral replacement calcite	2.23	-4.34
J20	(DD5)	" " "	2.00	-4.64
J21	(DD5)	Bryozoan " "	1.69	-4.04
J28	(DD6)	Whole-rock oosparite	1.02	-3.14
J26	(DD6)	" " " - burrow fill	1.35	-2.39
J27	(DD6)	" " " " "	1.21	-3.22
J25	(DD6)	Late ferroan spar	1.31	-6.54
J31	(DD7)	Whole-rock oosparite	1.59	-3.77
J29	(DD7)	" " " - burrow fill	1.26	-3.56
J30	(DD7)	" " " " "	1.43	-3.21
J32	(DD7)	Late ferroan veinlet	1.47	-5.14
J34	(DD8)	Whole-rock oopelsparite	0.99	-3.56
J35	(DD8)	" " " - burrow fill	2.19	-3.60
J33	(DD8)	Late ferroan spar	1.14	-6.63
J36	(DD9)	Whole-rock oopelmicrite	1.22	-2.87
J37	(DD9)	" " oosparite	0.69	-3.41

Dagham Down Quarry continued.

J38	(DD9)	Whole-rock oomicrite	0.85	-3.25
J40	(DD10)	" " pelsparite	1.13	-2.94
J39	(DD10)	Blocky non-ferroan spar-coral replacement	2.23	-3.42
J49	(DD12)	Whole-rock oopelsparite	1.25	-2.87
J47	(DD12)	Late ferroan spar	1.35	-6.68
J54	(DD15)	Whole-rock oopelsparite	1.35	-2.49
J55	(DD15)	" " "	0.76	-3.54
J60	(DD14)	" " oobiosparite	0.67	-3.57
J61	(DD14)	" " "	0.78	-3.66
J56	(DD14)	Poorly consolidated oolite burrow fill	1.22	-2.68
J59	(DD14)	Whole-rock oosparite burrow fill	0.53	-3.87
J57	(DD14)	Late ferroan spar	1.24	-7.32

Comment

(Scatter diagram fig.5.6(b)).

$\delta^{18}\text{O}$ decreases from whole-rock limestones to first generation cements and again to second generation spar. $\delta^{13}\text{C}$ show no clear trend and values vary between 0.5 and 2.2‰ with the early non-ferroan generation of sparry calcite marginally enriched in ^{13}C . Minor calcite veinlets have an isotopic composition which is with the range for whole-rock samples.

Table 5.3(c).

Foss Cross Quarry. White limestone, Bathonian.

Bored erosion surface at top of Lucina Bed. (Torrens, 1969 page A.13). Samples from hardened surfaces, coral colony and surrounding oolites.

Hardground

<u>Sample</u>	<u>Description</u>	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
J67	Oyster shell	1.89	-2.40
J68	Whole-rock sandy biomicrite (at hd.gd)	0.47	-2.68
J70	" " " " "	0.87	-2.69
J71	" " " " "	1.39	-2.09
J72	" " " " not related to hd.gd.	1.42	-2.70
J69	" " " " "	1.06	-2.56

Coral Colony

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
J66	Whole-rock biomicrite between corallites	0.58	-2.69
J64	Pelmicrite burrow fill	0.71	-2.47
J63	Corallite with 'septa' well preserved	0.87	-3.62
J64	" replaced by blocky ferroan spar	0.91	-4.69
<u>Hardground</u> - (different part of quarry - same horizon)			
J47	Oyster shell	1.70	-1.91
J45	Whole-rock oobiosparite at hardground	0.65	-3.85
J49	" " "	0.53	-4.03
J50	" " "	0.47	-4.05
J50/1	" " "	0.66	-4.13
J46	" " burrow fill	0.74	-3.74
J48	" " overlying bed	0.15	-3.99

Comment

(Scatter diagram, fig.5.6(c)).

Values produce a marine limestones cluster. Correlation between degree of preservation, of coral colony and $\delta^{18}\text{O}$ (Scherer, 1977). - See main text.

Table 5.3(d).

Hook Norton Railway Cutting, Lower Inferior Oolite.

Ferruginous biosparite with 'hardened' surface encrusted by serpulids. (Loose block collected by T.J.Palmer).

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
0.79	Surface - including spar-filled serpulids	-1.30	-5.56
0.80	Whole-rock 1cm below surface	-0.99	-3.17
0.81	" " 2cm " "	-1.22	-3.48
0.82	" " 3cm " "	-1.35	-3.20

Comment

(Scatter diagram, fig. 5.6.(d)).

Negative $\delta^{13}\text{C}$ may be due to minor input of organogenic carbon during pyrite precipitation. Spread of $\delta^{18}\text{O}$ (-3.2 to -5.6) suggests cementation by ^{18}O depleted spar.

Table 5.3(e).

KettonGrange Quarry. Great Oolite, Bathonian.

Biomicrite

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
L78	Whole-rock biomicrite	-0.43	2.25
L79	Internal sediment in brachropod void	1.08	-1.12
L80	Late ferroan cement (overlying L79)	0.34	-6.72
L81	" " " 'replacement' of thick shelled gastropod	0.58	-7.08

Comment

(Scatter diagram, fig.6 (e)).

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of micrites suggest retention of primary marine isotopic composition. Late cement and gastropod replacement have very similar values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and were probably syngenetic.

Table 5.3. (f).

Shellingford Cross Roads Quarry. Corallian, Oxfordian (SU327941)

Two metre thick coral bed. Thecosmilia corals with varying modes of replacement (- see main text).

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
J73	Whole-rock biomicrite - between corals	-2.81	-1.27
J79	" " " " "	-2.33	-0.91
J80	" " " " "	-2.26	-1.19
J78	Micrite pseudosepta	-2.11	-0.75
J77	Non-ferroan calcite cement	-2.27	-0.02
J75R	Central ferroan spar	-3.77	-3.22
J76	" " "	-3.63	-1.68
J74	" " "	-2.38	-2.54
J81	Whole-rock biosparite	-2.07	-6.24
J82	" " "	-1.96	-6.52

Comment

(Scatter diagram, fig.5.6.(f)).

Spread of values cannot be explained by normal trend. (See main text).

Table 5.3(g).

Shipton Cement Quarry, Bladon Member White Limestone Formation,
Bathonian.

Biomicrite; brachiopod 'voids' with internal sediment and
dog-tooth spar. Corals preserved as spar-filled solution voids.

Brachiopod

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
J86	Brachiopod shell	-2.04	-2.95
J84	Micrite, internal sediment	-0.17	-1.99
J85	Ferroan, dog-tooth, spar	-0.10	-6.89

Coral

J88	Whole-rock biomicrite	-0.57	-2.04
J87	Blocky ferroan spar	-0.53	-6.69

Cement

(Scatter diagram 5. 6(g)).

Whole-rock limestone to late cement trend shows $\delta^{18}\text{O}$ depletion
and no change in $\delta^{13}\text{C}$. Brachiopod shell has anomalous negative $\delta^{13}\text{C}$.

Table 5.4. Isotopic composition of samples from selected Middle and Upper Jurassic hardgrounds from Burgundy and Normandy. The Burgundy examples were collected by Dr.J.D.Hudson (University of Leicester) and are those described by Purser (1977), the examples from Normandy (Ranville-hardgrounds) were collected by Dr.T.J.Palmer (University of Oxford).

Table 5.4(a)

Chassagne Montrachet. Bathonian

Peloidal limestone capped by hardground. Isopachous fringing cements developed near hardground surface. Late spar - non-ferroan.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
B2	Hardground surface - whole rock pelsparite	0.82	-3.76
B3	Whole-rock pelsparite (1.5cm)	0.85	-4.35
B4	" " " (4cm)	0.96	-4.25
B5	" " " (7.5cm)	2.03	-6.64
B6	" " " - Burrow fill	-0.65	-5.70
B1	Whole-rock pelsparite (40cm) no fringing cement	-0.07	-7.43

Comment

(Scatter diagram fig.5.7(a)).

The separation of whole rock samples with and without fringing cements suggests that there is a diagenetic trend from allochems and early cements with marine composition to late cements depleted in $\delta^{18}\text{O}$ and (?) C^{13} .

Table 5.4(b).

Ladoix-serriguy, Upper Bathonian.

Complex minor sequences of pelsparites with early cements with submarine to vadose fabrics. Limestone are strongly stylolitised. Late spar: Non ferroan.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
B19	Whole-rock pelsparite (LS1) (with early stalactitic cement?)	0.39	-5.62
B20	" " " (LS1)	0.26	-4.86
B21	" " " (LS1)	0.52	-6.60
B22	" " " (LS2) porous - little late spar	0.03	-4.11
B23	Non ferroan (pel?) micrite (LS3)	-0.11	-3.05
B24	" " " (LS4)	-0.13	-3.31

B25	Whole-rock pelsparite (with beachrock cements?) (LS5).	0.87	-6.44
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Comment

(Scatter diagram, fig. 5.7(b)).

Linear trend of whole-rock samples. Sparites are ¹⁸O depleted compared to micrites.

Table 5.4(c).

Massangis. Bathonian

Oobiosparite capped by hardground.

Isopachous fringing cements, patchily developed internal sediment, blocky non ferroan late cement.

<u>Sample</u>	<u>Description</u>	<u>δ¹³C</u>	<u>δ¹⁸O</u>
B14	Oyster encrusting the hardground surface	1.62	-1.49
B8	Whole rock limestone (O)	(-0.71)	(-8.52)
B9	" " " (1cm)	-0.05	-5.92
B10	" " " (2cm)	-0.29	-6.24
B12	" " " Bore fill	-2.72	-6.09
B13	" " " underlying oolite	0.58	-6.65

Comment

(Scatter diagram, fig. 5.7(c)).

Oyster has retained marine composition. Whole rock samples have light δ¹⁸O due to high % spar. Bore-fill sediment has anomalously light δ¹³C (-2.72).

Table 5.4(d).

Ranville Member. Hardgrounds, Middle Jurassic, (Bathonian) Normandy (10km N. of Caens)

Shelly biomicrite, surface encrusted by oysters and bored by molluscs all limestone samples >4cms from surface.

Pegasus Bridge Quarry.

<u>Sample</u>	<u>Description</u>	<u>δ¹³C</u>	<u>δ¹⁸O</u>
0.19	Oyster on hardground surface	0.31	-2.91
0.20	Whole-rock shelly biomicrite - hardground surface	1.77	-0.65
0.21	Whole-rock shelly biomicrite - 0.5cm below surface	0.62	-1.97
0.22	Whole-rock shelly biomicrite - 1.0cm below surface	0.07	-3.20
0.23/3	Whole-rock shelly biomicrite - 1.6cm below surface	0.70	-2.20
0.23	Whole-rock shelly biomicrite - 2.4cm below surface	-1.71	15.55

O.23/1	Whole-rock shelly biomicrite - 3.0cm below surface	0.48	-2.69
O.23/2	Whole-rock shelly biomicrite - 3.6cm below surface	0.23	-4.11
Ranville cement works.			
O.32	Oyster on hardground surface	-0.22	-3.68
O.31	Whole-rock shelly biomicrite - hardground surface	0.45	-3.16
O. 33	Whole-rock shelly biomicrite - 1cm below surface	0.53	-2.04

Comment

(Scatter diagram.fig.5.7(d)).

All samples are from within 4cm of a hardground surface. The linear spread of values is probably a normal cementation trend (see main text) and demonstrates the patchy distribution of late cement near the hardground surface.

Table 5.4(e).

Ravieres-sur-Armancon. Upper Bathonian.

Bio-pel-sparite with early fibrous and late blocky spar in voids. All peloids and fibrous fringes non-ferroan, weak ferroan zoning in late spar. All samples taken with zone of submarine cementation Stylolites well developed.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
B26	Whole rock pelsparite	0.88	-7.75
B28	" " " (low spar content)	0.97	-5.78
B29	Whole rock pelsparite (high spar content)	0.63	-6.18
B27	Late blocky cement	0.53	-12.38

Comment

(Scatter diagram, fig. 5.7(e)).

Linear trend demonstrates mixing trend with exceptionally light late cement ($\delta^{18}\text{O} = -12.4$). Qualitative correlation between spar content and ^{18}O depletion.

Table 5.4(f).

Vontenay. Callovian

Oolites capped by hardground. Fringing cements (submarine) penetrate 50cm of limestone. All samples are from zone of submarine cementation.

<u>Sample</u>	<u>Description</u>	<u>13_C</u>	<u>18_O</u>
B15	Whole-rock oolites limestone	0.88	-4.99
B16	" " " "	0.81	-4.87
B17	" " " "	1.33	-4.92
B18	" " " "	1.35	-5.17

Comment

(Scatter diagram, fig.5.7(f)).

Cluster of values suggests uniform proportions of cements and
allo^hcems.
^

Table 5.5. Isotopic composition of calcites from hardground surfaces from North America (Cretaceous to Ordovician; in age). Specimens collected by Dr.T.J.Palmer (University of Oxford). Reference to previous descriptions are given in the table where possible. Localities are listed in decreasing geological age.

Table 5.5(a).

Galena Group. M.Ordovician, N.E. Iowa.

Dark grey micritic limestone, intensely bioturbated, capped by hardground. (Described by Palmer and Palmer, 1977).

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
0.16	Whole-rock micrite. Hardground surface (w.pyrite)	-0.93	-6.03
0.12	" " "	-2.77	-9.14
0.15	Whole-rock micrite Burrow margin	-1.11	-5.98
0.11	" " 2cm below surface	-1.41	-7.29
0.10	" " 5cm below surface	-0.88	-5.38
0.9	" " 7cm below surface	-0.70	-5.37
0.13	" " Burrow fill	-0.95	-2.79
0.14	" " " "	-1.90	-6.06

Comment

(Scatter diagram, fig. 5. 8(a)).

All samples have negative $\delta^{13}\text{C}$. There is no clear trend away from the hardground surface. Distribution field may represent a mixing trend (see main text). A range of almost 2‰ $\delta^{13}\text{C}$ and 3‰ $\delta^{18}\text{O}$ from adjacent samples at the pyritised surface suggests isotopic variation on a minute scale.

Table 5.5(b).

Kirkfield Quarry. M.Ordovician, Southern Ontario.

Dark grey micritic limestone capped by hardground. (Described by Brett and Liddell, 1978).

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
0.65	Whole-rock biomicrite - at hardground	0.28	-5.12
0.66	" " " 1cm below	0.36	-5.15
0.67	" " " 2cm "	0.25	-5.22
0.68	" " " 3.5cm "	0.45	-5.16
0.69	" " " 6cm "	0.35	-6.30
0.70	" " " 7.5cm "	0.50	-6.17

Comment

(Scatter diagram, fig.5.8(b)).

Values produce a cluster of points on the scatter diagram. Near hardground surface samples have marginally heavier $\delta^{18}\text{O}$ (-5.1 compared to -6.2) than those from below it - possibly indicating early ^{18}O -enriched surface cementation.

Table 5.5(c).

Dilsborough. Upper Ordovician, Dilsborough, Indiana.

(from Dam Spillway section, Dilsborough).

Dark grey pyritized biosparite, surface encrusted by bryozoa and (?) echinoderms. (Bed 2cm thick).

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
O.35	Calcite echinoderm (?) holdfast	-2.04	-4.52
O.34	Whole-rock biosparite - at hardground surface	-1.54	-4.74
O.36	Whole-rock biosparite - 1cm below surface	-1.67	-4.67
O.37	Whole-rock biosparite - 2cm below surface	-1.65	-4.78

Comment

(Scatter diagram, fig. 5.8(c)).

Values cluster at $\delta^{18}\text{O}$ of -4.7 and $\delta^{13}\text{C}$ of -1.6. Pyritisation is again accompanied by negative $\delta^{13}\text{C}$.

Table 5.5(d).

Laurel Limestone. Wenlock, Silurian. Indiana.

Dark grey strongly bioturbated micrites, surface (hardground) supports encrusting fauna (crinoid holdfasts etc). Surface (+below) is pyritized. (Hardground described by Halleck, 1973).

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
O.27	Whole-rock micritic limestone - Hardground surface	0.83	-2.40
O.28	Whole-rock micritic limestone - 0.3cm below surface	1.75	0.32
O.30/3	Whole-rock micritic limestone - 0.8cm below surface	0.04	-4.38
O.29	Whole-rock micritic limestone - 1.2cm below surface	0.95	-4.13
O.30/4	Whole-rock micritic limestone - 2.0cm below surface	0.13	-5.14
O.30	Whole-rock micritic limestone - 2.5cm below surface	1.04	-4.13

0.30/1	Whole-rock micritic limestone - 3.5cm below surface	0.52	-4.48
0.30/2	Whole-rock micritic limestone - 4.7cm below surface	0.09	-5.61

Comment

(Scatter diagram 5.8(d)).

Values from immediate vicinity of hardground surface exhibit linear trend (mixing trend?). Surface sample has a very heavy $\delta^{18}\text{O}$ (0.32) - see main text.

Table 5.5(e)).

Chester Formation. Mississippian, Kentucky.

All samples at hardground surface.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
0.24	Whole-rock biomicrite	-1.86	-4.47
0.25	" "	-1.17	-3.22
0.26	" "	-0.92	-2.46
0.26/1	" "	-1.73	-4.89

Comment

(Scatter diagram, fig. 5.8(e)).

Linear distribution of whole-rock samples may represent a mixing trend within the micrite limestone but as all the samples come from the hardened surface no further conclusions can be drawn. Heaviest $\delta^{18}\text{O} = -2.46$.

Table 5.5(f).

Gilmore City Formation. Mississippian, Gilmore City, Iowa.

Oosparite intraclast with isopachous fringing cements and late blocky spar.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
0.55	Brachiopod shell	5.07	-1.55
0.56	Whole-rock oosparite with early fringes	3.65	-3.67
0.57	" " " " " "	3.59	-3.88
0.58	" " " " " "	3.64	-3.82
0.59	" " " " " "	2.99	-4.14

Comment

(Scatter diagram, fig. 5.8(f)).

Values cluster at ^{13}C of +3.6 ^{18}O of -3.9. Heaviest $\delta^{18}\text{O}$ is a brachiopod with $\delta^{18}\text{O}$ of -1.55. All samples have anomalously (?) heavy $\delta^{13}\text{C}$.

Table 5.5(g).

Bee Creek. Upper Cretaceous, Austin, Texas.

5cm bed of buff/yellow biomicrites and biosparites -bored from above and below. All samples form hardground.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
0.71	Whole-rock limestone (surface)	1.08	-4.97
0.72	" "	1.63	-3.10
0.73	" "	1.86	-2.86
0.74	" " (Centre)	1.93	-3.27
0.75	" "	1.71	-3.64
0.76	" " (base)	1.23	-3.93
0.77	Spar cemented bore-fill	2.50	-6.28
0.78	Late spar (part fills bore)	1.28	-5.74
0.83	Micrite adhering to upper surface	1.03	-5.58

Comment

(Scatter diagram 5.8(g)).

Samples show a near linear mixing trend toward the late cement composition. There are no clear trends within the hardground surface.

Table 5.5(h).

Walnut Formation. Cretaceous, Travis County, South Texas.

18cm bed of buff/yellow micritic limestone, hardground surface has been bored by molluscs.

<u>Sample</u>	<u>Description</u>	<u>$\delta^{13}\text{C}$</u>	<u>$\delta^{18}\text{O}$</u>
0.8	Whole-rock limestone at hardground surface	1.79	-3.59
0.17	Whole-rock limestone at hardground surface	1.04	-4.05
0.60	Whole-rock limestone at hardground surface	1.65	-3.95
0.5	Whole-rock limestone 0.5cm below surface	1.84	-3.24
0.61	" " 1.5cm " "	1.38	-3.58
0.4	" " 2.5cm " "	1.38	-3.33
0.62	" " 3.2cm " "	2.07	-3.89
0.3	" " 5.5cm " "	2.19	-3.45
0.63	" " 5.5cm " "	2.08	-4.06
0.18	" " 5.5cm " "	2.48	-3.81
0.64	" " 10cm " "	2.46	-3.30
0.2	" " 12cm " "	2.34	-3.52
0.1	" " 16.5cm " "	2.47	-3.51
0.6	" " margin of mollusc bore	1.93	-3.49
0.7	" " in filling mollusc bore	1.58	-3.86

Comment

(Scatter diagram 5.8(h)).

Samples plot as a marine limestones cluster with no clear isotopic trend.

CONCLUDING REMARKS

Each chapter of this thesis contains a summary of conclusions in its abstract. This section is not intended to reiterate specific points made in each case-history, but rather to highlight some of the more general conclusions and identify areas for further research.

Whole-rock limestones and diagenetic calcites clearly have a composite chemical composition. Individual zones of calcite preserve isotopic and trace element values which indicate the environment in which precipitation or mineralogical stabilisation took place. In the case of metastable marine allochems and cements, the isotopic composition of the replacement calcite is dependant on the environment of stabilisation and the degree of exchange with isotopically modified pore waters. (Effective water:rock ratio of Chapters 1 and 3). Stabilisation commonly must have taken place in restricted or shallow-burial conditions as many 'primary components' retain 'marine' isotopic values (Chapters 1, 2 and 5). Detailed isotopic studies of well-documented examples of submarine cementation in Palaeozoic sediments are needed to determine the accuracy of time-trends in sea water composition proposed in the literature.

Late, burial, diagenetic calcites in virtually all ancient sediments have light $\delta^{18}\text{O}$ (from -5 to -20‰). Depletion in ^{18}O may be attributed to temperature increase or isotopic changes in the isotopic composition of ambient pore waters. The latter can be brought about by diagenetic reactions or by mixing of waters of different genetic history. To resolve the most common cause of the negative $\delta^{18}\text{O}$ values in ancient sediments it will be necessary to have additional temperature and/or salinity control.

Studies of fluid inclusions within cements or further analysis of pore waters and their adjacent carbonates at depth today may help to provide the answer to the problem. This study has shown that ^{18}O depletion in later carbonates is not always part of a gradual evolutionary process (Chapter 3). Trends can be discontinuous and reversals take place which may correspond to periods of renewed ground-water flow.

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