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Petrography and geochemistry of some Carboniferous and Precambrian dolomites

Kevin Hird, B.Sc.

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A thesis submitted to the University of Durham for the degree of Doctor of Philosophy.

Department of Geological Sciences

December 1985



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Petrography and geochemistry of some Carboniferous and Precambrian dolomites

Kevin Hird, B.Sc.

Abstract

Dolomite forms a significant proportion of many ancient (particularly shallow marine) carbonate sequences. It is interesting from a diagenetic point of view, representing the mineralogical transformation of originally calcium carbonate sediments or rocks, and from an economic point of view, forming important hydrocarbon reservoirs and hosts for lead-zinc mineralisation.

Petrographic study, supported by geochemical data and integrated with broader tectono-sedimentary information has provided the basis for investigation of some dolomites in the Dinantian of South Wales and the Upper Proterozoic of Arctic Norway. Three distinct types of dolomite are recognised in the Dinantian of South Wales, based on their stratigraphic and facies distribution, petrography and geochemistry (viz: stoichiometry, ordering, minor and trace element and stable isotope variations). Peritidal dolomicrites of syn-sedimentary origin were probably stabilised and augmented during shallow burial. Pervasive stratal dolomites formed during the progradation of ooid shoals within underlying subtidal bioclastic packstones and wackestones. Meteoric-marine mixing-zone flow and perhaps reflux of seawater with slightly elevated salinity are invoked to satisfy the requirement for allochthonous Mg^{2+}. Late diagenetic vein dolomites exhibit a structural control on their distribution and together with later phases in pervasive dolomites, probably formed during maximum burial at the end of the Carboniferous. The Porsanger Dolomite displays a range of essentially primary depositional and diagenetic fabrics, despite replacement by dolomite. An early diagenetic origin by stabilisation-replacement of high-magnesium calcite or perhaps calcian-dolomite marine precursors is suggested for much of this dolomite. Late diagenetic, post-burial compaction dolospars in the Porsanger appear to be direct precipitates.

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Intellectual and not-so-intellectual conversation was provided throughout by my 'lab.-mates', Roger, Adrain, Dave, Neville, Sally and Ian. Gastronomic advice from Dave Schofield is gratefully acknowledged.

The production of this thesis would not have been possible without the expert typing of Mrs. Carole Blair and the continuous help and support of

Anne Wright, who also helped to keep me sane. I would also like to thank my parents, to whose memory I dedicate this thesis, for their encouragement and support.

Declaration

The content of this thesis is the original work of the author and has not previously been submitted for a degree at this or any other university. Other people's work is acknowledged by reference.

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CHAPTER 1

Petrography and geochemistry of some Carboniferous and Precambrian dolomites: Introduction

1.1 Introduction

This introduction cannot hope to provide a comprehensive review or a true representation of the now broad field of research into dolomite, its chemistry and formation. Instead it presents some general background information and a discussion of what the author considers to be some of the more important developments in the study of dolomites and dolomitisation. This is attempted without needless repetition of information already provided by several excellent reviews, referred to in section 1.2. The subsequent chapters deal with the subject of this research project and the thesis may be divided into two parts. The first, (Chapters 2 to 5) deals with dolomites which occur in the Dinantian of South Wales, and the second (Chapters 6 to 9) deals with the late Proterozoic Porsanger Dolomite Formation of northern Norway. Whilst each part can be considered independently, and represents a petrographic-geochemical investigation into the origin of the dolomites, many of the techniques and the findings have wider application and although this may not be stressed, the integrated approach taken here is recommended for studies of other ancient dolomites. The final chapter provides a brief resumé and goes on to discuss the broader significance of some of the conclusions drawn from the previous chapters.

1.2 Why study dolomites?

There is now an immense research literature on dolomites and dolomitisation covering all aspects from the crystal structure and chemistry through theoretical and experimental insight into the chemistry of formation, to sedimentological and petrological studies of modern and ancient dolomites. The reader is referred to the following recent reviews which provide a general appreciation of the range of studies, Zenger (1972), Chilingar et al., (1979) and Morrow (1982a and b). Much of this research has been stimulated by the economic importance of dolomites, as reservoirs for liquid hydrocarbons and as hosts for lead-zinc mineralisation. A compilation of reservoir information from United States oil fields reveals a tendency for carbonate reservoirs to occur preferentially in dolomites, indicating that dolomitisation leads to an improvement in the reservoir properties of carbonate formations (Schmoker et al., 1985). The data of Schmoker et al., suggest that generally matrix porosities and permeabilities in dolomite reservoirs are less than in limestone reservoirs. Morrow (1982a) has argued in favour of volume for volume replacement and suggested (after N.C. Wardlaw) that an increase in permeability results from the idiomorphic shape and uniformity of crystal size that may accompany complete dolomitisation. Schmoker et al., (1985) concluded that open fracture systems are more likely to occur in dolomites than in limestones and this, combined with the fact that dolomite reservoirs are on average larger and deeper than those of limestones, leads to an improvement in the reservoir potential of carbonate rocks upon dolomitisation. From an explorationists' point of view the ultimate aim of research into dolomites and dolomitisation processes should be the formulation of a set of genetic characteristics which will enable the

recognition of different dolomite types and therefore aid the prediction of their reservoir potential and distribution. Examples of successful exploration for dolomite reservoirs include Bird and Jordan (1977), Sears and Lucia (1980), Longman et al. (1983). These studies generally combine structural, sedimentological, petrographic and geochemical data which allow the depositional and diagenetic setting of dolomitisation to be established. In this way the likely control on the dolomitisation process may be determined and hence the distribution of resulting dolomites predicted.

The following study of Dinantian and Late Precambrian examples follows this approach but with particular emphasis placed on petrographic and geochemical investigation with a view to determining the timing and diagenetic environment of dolomitisation. The pre- and post-dolomitisation histories of the sediments/rocks are also important and will be discussed. In addition, the broader significance of these dolomites to studies of secular variations in seawater chemistry and marine carbonate mineralogy are also considered.

Before this, it is necessary to discuss briefly the chemistry of dolomitisation and the likely environments in which dolomite may form. A brief review of the major dolomitisation models is also presented, together with a summary of some of the criteria used in recognising ancient dolomites of different origin.

1.3 The chemistry of dolomite and dolomitisation - application to natural examples

1.3.1 Structural considerations

Dolomite ($CaMg(CO_3)_2$) represents the intermediate stable phase in the

$CaCO_3$-$MgCO_3$ solid solution. Dolomite is the major mineral in the $R\bar{3}$ group, comprising 15 or more carbonates of which five may have the same structure as dolomite itself (Reeder, 1983). In common with the calcite group ($R\bar{3}c$) dolomite has a rhombohedron unit cell and a three-fold axis of symmetry (connecting the apices of the rhombohedron, this being the c-axis of the hexagonal unit cell). Calcite and dolomite also comprise alternating layers of cations and anions, which in the case of dolomite produces a slightly reduced symmetry because of the complete substitution of Mg^{2+} ions for Ca^{2+} ions in alternate cation layers (Lippman, 1973; see Reeder, 1983). This 'ordering' uniquely characterises the dolomite structure; however, natural and experimentally produced dolomites frequently depart from ideal composition and structure. A degree of interchange of Ca^{2+} and Mg^{2+} ions between alternating layers (disorder), Ca^{2+} excess and substitution of other cations (Fe^{2+}, Sr^{2+}, Mn^{2+} and Na^{+}) is common and may result in detectable changes in unit cell dimensions. Further discussion of these variations by reference to actual examples is given in Chapters 4 and 8.

The term 'protodolomite' (or pseudodolomite) has been applied to dolomites which are not ideal in structure or composition; however, Land (1980) argued that the name dolomite should be retained for all phases which approach ideal composition and which have recognisable superstructure reflections in X-ray diffraction patterns. Phases without these are not dolomite.

Carpenter (1980) has shown that the degree of ordering in a stoichiometric dolomite plays an important role in determining its stability relative to calcite. As will be discussed in subsequent chapters, variations in these parameters may well have a genetic significance.

1.3.2 Chemistry of dolomitisation

Attempts to determine the chemistry of dolomitisation by experimental precipitation at sedimentary temperatures and pressures have largely been unsuccessful, with calcian phases showing weak or absent superstructure reflections as the only product (see various reviews). However, the following general observations emerge from these attempts, from more successful high temperature dolomitisation experiments, from theoretical reasoning and from observations of supposed extant systems (see 1.3.4 below).

1) Dolomitisation can be regarded as a wet chemical (dissolution-precipitation) process.

2) It appears that in most natural waters (including seawater) there is a thermodynamic drive towards dolomitisation of $CaCO_3$ and that kinetic factors are responsible for inhibiting this reaction. These factors arise out of the need to form regularly alternating sheets of Ca^{2+}, CO_3^{2-}, Mg^{2+}, CO_3^{2-}, Ca^{2+} etc.

3) The three main solution parameters thought to affect the kinetics of dolomite growth are: salinity, Mg^{2+}/Ca^{2+} and CO_3^{2-}/Ca^{2+} ratios. Morrow (1982a) discusses the molecular mechanics of these parameters. Additionally, dissolved sulphate (see below), time available for dolomitisation (e.g. Mattes and Mountjoy, 1980; Zenger, 1983) and precursor reactivity (e.g. Sibley, 1980) may be significant and are discussed at appropriate points in the text.

1.3.3 The dolomitisation reaction

The dolomitisation reaction may be represented by the following generalised equations (see Chilingar et al., 1979; Morrow, 1982a, for

example):

1) $2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+}$

or

2) $Ca^{2+} + Mg^{2+} + 4HCO_3^- = CaMg(CO_3)_2 + 2CO_2 + 2H_2O$

or, as Morrow (1982a) discussed, the reaction may be written with a range of intermediate stoichiometries (see also Baker and Burns, 1985).

Which of these reactions actually occurs in nature is important because it determines the source of reactants and hence the likely controls on reaction rates. Baker and Burns (1985), in examining assumed extant dolomitising systems in DSDP sites, suggested that a reaction in which the rate of $CaCO_3$ dissolution is an important limiting step, viz:

$CaCO_3 + Mg^{2+} + 2HCO_3^- = CaMg(CO_3)_2 + CO_2 + H_2O$

but note that other reactions may occur in different dolomitisation sites, for example where $CaCO_3$ precursors are abundant. Such is the case in the following study of Dinantian and Precambrian examples of replaced shallow marine carbonates. It is assumed that Mg^{2+} is a more important rate limiting factor in these situations and much of the accompanying discussion is based on the need to determine a source and supply for Mg^{2+}.

1.3.4 Application to natural examples

Many modern natural occurrences of dolomite exist and attempts have been made to explain them in terms of the solution parameters described above (section 1.3.2). For example, increasing Mg/Ca ratios due to precipitation of calcium sulphate in sabkha and evaporite lagoon environments have been used to explain the formation of dolomite in marginal ponds of the Red Sea (Friedman, 1980) and in the Arabian Gulf Sabkhas (McKenzie, 1981, Patterson and Kinsman, 1982), although other

contributory factors may exist. Rapid precipitation in solutions of high salinity will tend to produce disordered Ca-Mg carbonates (Folk and Land, 1975). This may be overcome by dilution with meteoric waters as inferred from apparent modern examples of dolomitisation in the zone of marine-meteoric water mixing. For example, dolomites in the Floridan aquifer (Hanshaw et al., 1971), in the Mediterranean coastal aquifer of Israel (Magaritz et al., 1980) and by implication in Pleistocene limestones of Jamaica (Land, 1973a and b).

Alkaline solutions with high CO_3^{2-} (especially relative to Ca^{2+}) include continental groundwaters which have been involved in the weathering of silicates or dissolution of continental carbonate deposits and waters (including marine) in which anaerobic sulphate reduction has occurred. The best documented example of dolomites forming under the influence of continental groundwaters in a relatively humid climatic regime are those of the Coorong Lagoon, South Australia (see Muir et al., 1980). An example in which sulphate reduction and increased alkalinity is thought to have caused localised dolomitisation around burrows occurs in the temperate waters of Loch Sunart, west Scotland, (Brown and Farrow, 1978), but note that super-structure reflections are absent.

Baker and Kastner (1981) provided experimental evidence for dolomitisation of aragonite and calcite (at 200°C) from solutions of low sulphate concentration. They proposed that dolomitisation is not primarily controlled by the Mg^{2+}/Ca^{2+} ratio or the crystallisation rate but by the decrease in dissolved SO_4^{2-} resulting from calcium sulphate precipitation and concomitant bacterial sulphate reduction or through mixing of seawater or modified connate waters with meteoric water. They further noted that minor amounts of dissolved SO_4^{2-} appear to inhibit dolomitisation of

calcite but may still permit dolomitisation of aragonite, hence offering a possible explanation for selective dolomitisation on sabkhas.

This idea of dissolved sulphate control on dolomitisation receives further support from the increasing number of reports from the Deep Sea Drilling Project (D.S.D.P.) of dolomite in continental margin hemipelagic sediments. For example, Kelts and McKenzie (1982) report dolomites apparently forming in organic-rich, anoxic diatomaceous muds in the Gulf of California, where porewaters are characterised by high alkalinity and low dissolved sulphate concentrations. Similar dolomitic sediments occur off Baja California and along the continental margin of California (Kelts and McKenzie, 1982; Shimmield and Price, 1984) and in late Cenozoic mud lens facies of the accretionary wedge off Peru (Suess et al., 1982; Kulm et al., 1982). Baker and Burns (1985) discuss the importance of these and other discoveries of dolomite in continental margin sediments accumulating at rates less than 500 m/m.y. with organic carbon contents greater than 0.5 wt.%. they suggest that most dolomite forms within a few tens of meters of the seafloor in the zone of microbial sulphate reduction and where Mg^{2+} is derived from overlying seawater. The initial poorly-ordered calcian dolomite which forms has a high potential for subsequent ageing, or stabilisation, during later diagenesis to produce more ordered and near-stoichiometric dolomite, presumably by a solution-reprecipitation process (Baker and Burns, 1985). The authors extend their interpretation to suggest that previously interpreted mixing-zone dolomites replacing shallow marine carbonates may have formed initially as a poorly ordered calcian phase in sediments undergoing sulphate reduction and later transform to more ordered dolomite in fresh water or at elevated temperatures. This interpretation may be questioned on the following lines. If initial phases

were incomplete replacements of the precursor carbonate there remains a need to import large volumes of Mg^{2+}-bearing seawater in order to produce massive dolomites. This requires a nearsurface, seawater connected, diagenetic environment for 'ageing' and is therefore incompatible with the suggested involvement of fresh water or elevated temperatures. Alternatively, the Baker and Burns (1985) interpretation may suggest that these dolomites formed by early, massive replacement by poorly ordered calcian phases, which somehow became ordered and near-stoichiometric during burial. In this scenario, a major early diagenetic seawater (i.e. Mg^{2+}) flux into the sediments is required (see discussion in Chapter 5) and implies an open diagenetic system in which anoxic conditions are unlikely to have developed. Indeed, most examples of this kind of extensive platform dolomite occur in organic-poor grainstones, packstones and wackestones with no evidence for anoxic conditions during early diagenesis. In such an active depositional setting organic matter is far more likely to have been oxidised rapidly by aerobic processes. The mixing-zone model of dolomitisation is discussed more fully in Chapter 5.

With regard to the dissolved sulphate control on dolomitisation, Mullins et al. (1985) described calcium-rich dolomites forming in Pliocene-Upper Miocene carbonate slope deposits of the Little Bahama Bank under normal open-marine conditions without the aid of sulphate reduction or methanogenesis. The influence of hypersaline brines or mixing of marine and meteoric water was also discounted and stable isotope data (see field 16 on Fig. 1.2) are consistent with the proposed origin from cold, deep seawater via dissolution of aragonite and HMC-LMC transformation.

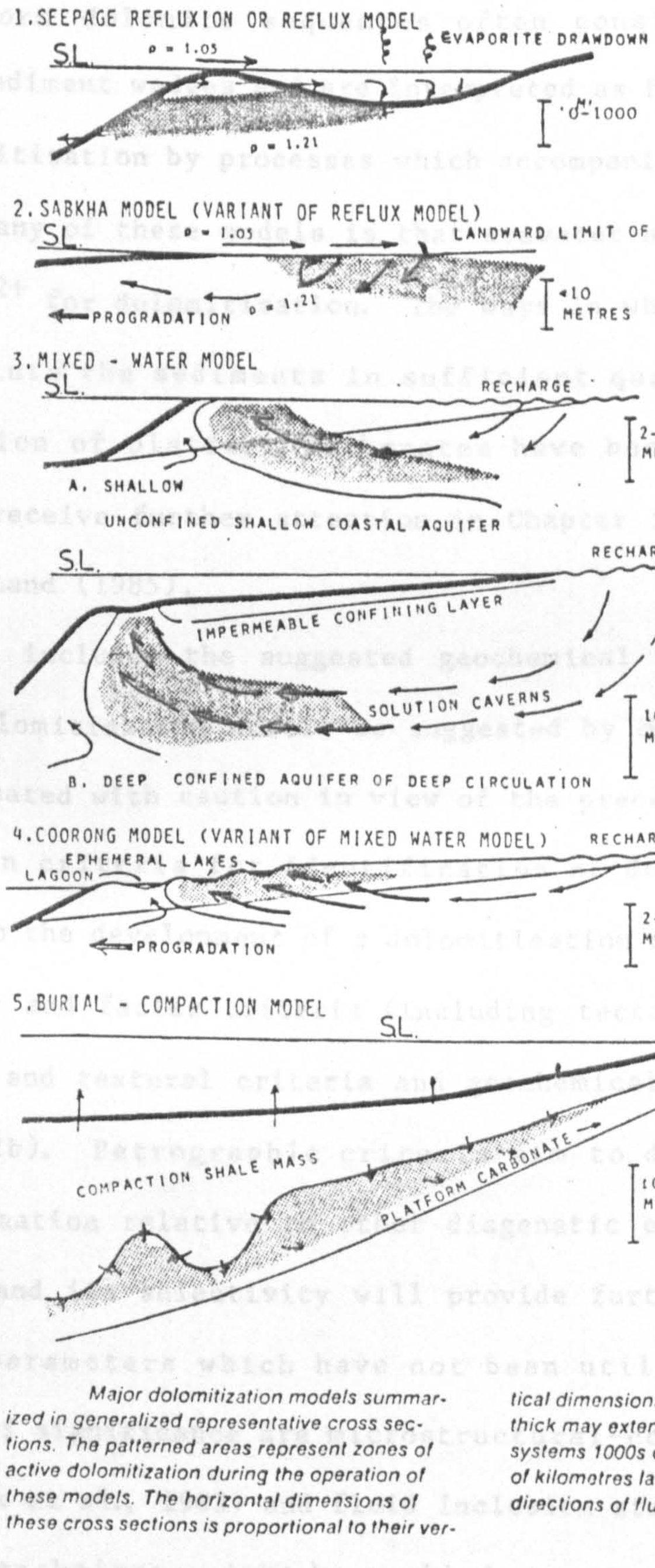
1.4 Dolomitisation models and the principal criteria for their recognition

Morrow (1982b) and Land (1985) provided annotated summaries of the major dolomitisation models currently being applied to ancient dolomites and the reader is referred to these reviews for further details and additional references. Discussion of some of these models is also given in the following chapters, in particular Chapters 5 and 9. It should be noted that what we are considering here are models for the massive dolomitisation of shallow marine carbonate sequences and that other, more localised occurrences are not included but may be mentioned briefly elsewhere in this text.

The tectono-sedimentary setting (viz: Platform vs. Ramp vs. Shelf) and the active depositional processes are of prime concern, providing insight into the geological distribution of dolomite. The key components of any dolomitisation model must be a source of Mg^{2+}, a supply mechanism and a suitable chemical environment for dolomitisation. With regard to chemical environment, the preceding discussion has shown that there is clearly some debate over the precise conditions under which dolomite may form. A valid approach therefore seems to be, to provide constraints on the likely chemical environment by careful definition of how the first two requirements might be met. Such definitions require integration of broad tectono-sedimentary, petrographic and geochemical criteria. This study incorporates two examples where this approach has been taken and more detailed discussion of its application is provided in the following chapters, for summary see Chapters 5 and 9.

Fig. 1.1 is reproduced from Morrow (1982b) and summarises the important aspects of the major models. One could add to this by suggesting that depositional processes, in particular depositional progradation and

DOLOMITIZATION MODELS



Major dolomitization models summarized in generalized representative cross sections. The patterned areas represent zones of active dolomitization during the operation of these models. The horizontal dimensions of these cross sections is proportional to their vertical dimensions so that systems 10s of metres thick may extend several kilometres whereas systems 1000s of metres deep may extend 100s of kilometres laterally. Arrows correspond to directions of fluid movement.

(after Morrow, 1982 b)

eustatic sea level are important components of the mixed-water model. As Morrow (1982b) discusses (see also discussion in Chapters 5, 9 and 10), thick platform dolomite sequences often consist of many individual regressive sediment wedges and are interpreted as forming by penecontemporaneous dolomitisation by processes which accompanied their progradation. A feature of many of these models is that seawater appears to be the primary source of Mg^{2+} for dolomitisation. The ways in which this seawater may be introduced into the sediments in sufficient quantity to cause massive dolomitisation of platform carbonates have been investigated by Simms (1984b) and receive further attention in Chapter 5 (section 5.5., Fig. 5.3) and also in Land (1985).

Fig. 1.1 includes the suggested geochemical conditions applicable to the major dolomitisation models as suggested by Morrow (1982b), but these should be treated with caution in view of the preceding discussion.

The main criteria for identification of dolomite types and hence ultimately to the development of a dolomitisation model may be divided into stratigraphic and facies criteria (including tectono-sedimentary setting), petrographic and textural criteria and geochemical criteria as reviewed by Morrow (1982b). Petrographic criteria aim to determine the timing of dolomite formation relative to other diagenetic events. The distribution of dolomite and its selectivity will provide further clues to its origin. Additional parameters which have not been utilised here but which are potentially of significance are microstructural-compositional studies by TEM (see Wenk et al., 1983) and fluid inclusion studies. Examples of areas where these techniques might be applied are given in the text. Once the paragenesis of a given dolomite body has been determined it may be useful to combine geochemical data. In this study the principal geochemical

Fig1_2

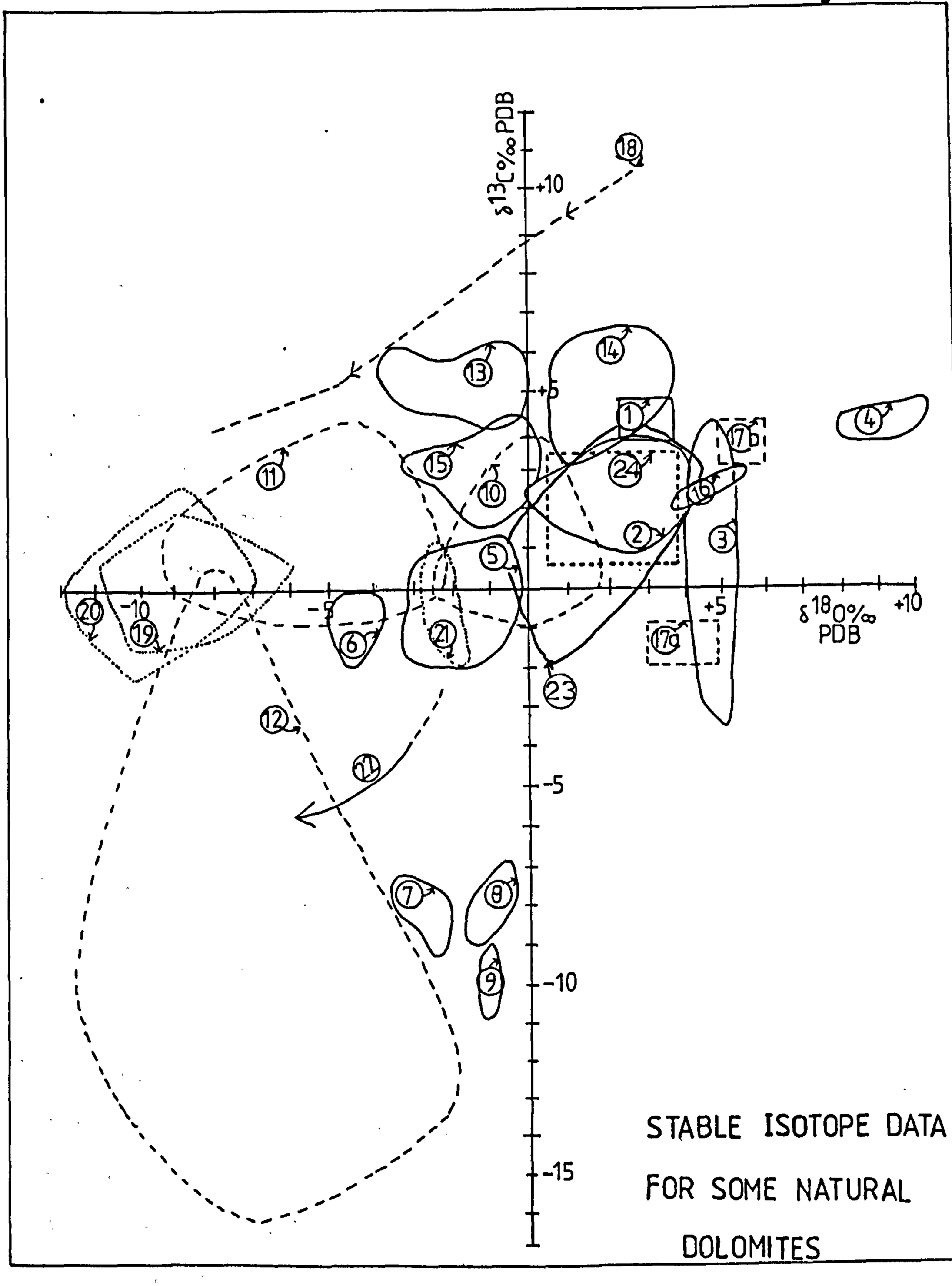

δ13C‰ PDB
+10
+5
-5
-10
-15
δ18O‰ PDB
+10
+5
-10
-8
-5
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
17a
17b
18
19
20
21
22
23
24
STABLE ISOTOPE DATA
FOR SOME NATURAL
DOLOMITES

Fig. 1.2 Caption

Stable isotope data for some natural dolomites

A. Modern "evaporative" dolomites

(1.) Kinsman and Paterson 1973 - Holocene sabkha dolomites

(2.) McKenzie 1981 - " " "

(3.) Behrens and Land 1972 - Baffin Bay, Texas

(4.) Aharon et al. 1977 - Gulf of Elat

B. Ancient analogues?

(14.) Vinet, 1984 - Uppermost Smackover and Buckner dolomites (Upper Jurassic)

(15.) Vinet, 1984 - Lower Smackover dolomites (Upper Jurassic)

C. Recent and Pleistocene "mixed-water" dolomite

(7.) Land and Epstein, 1970 - Pleistocene reefs, Jamaica

(8.) Land, 1973a - Holocene dolomitisation of Falmouth Formation, Jamaica

(9.) Magaritz et al., 1980 - coastal acquifer of Israel

(23.) Land, 1973b - Middle Pleistocene dolomitisation of Hope Gate reefs, North Jamaica

(24.) Choquette and Steinen, 1980; Supko, 1977 - subsurface, San Salvador, Plio-Pleistocene

(17a) + (17b). Botz and von der Borch, 1984 - Coorong sediments, South Australia

D. Ancient analogues?

(5.) Land et al. 1975 - El Naqb Formation, Eocene

(6.) Badiozamani, 1973 - Plattville Fm., Middle Ordovician

(13.) Vinet, 1984 - Upper Smackover

?Marine dolomite (continental margin sediments)

(16.) Mullins et al. 1985 - Bahaman periplatform oozes

(18.) Keltz and McKenzie, 1982 - Gulf of California

E. Miscellaneous examples

⑩. Mattes and Mountjoy, 1980 (compilation) - early diagenetic dolomite replacing marine limestone

⑪. " " " late diagenetic low temperature dolomite

⑫. " " " hydrothermal dolomite

⑲. Fritz, 1971 - mid-Devonian, hydrothermal dolomite

⑳. " " - late diagenetic dolomite

㉑. " " - supratidal - early diagenetic dolomite

㉒. Irwin et al., 1977 - trend in Kimmeridge (Upper Jurassic) burial dolomites (organic-rich sediments)

parameters utilised are: ordering and major element (Ca, Mg) stoichiometry; minor and trace element (Fe, Mn, Sr and Na) and stable isotope variations. The main sections dealing with the application and possible significance of these variations are presented in Chapters 4 and 8. Stable isotope variations in ancient dolomites are increasingly being used as a guide to the origin of dolomite and a compilation of data is included as Fig. 1.2. However as this study reveals (see also Land, 1980, 1983 for example) the stable isotopic composition of dolomites is best interpreted in combination with a range of other criteria.

CHAPTER 2

Dolomites in the Dinantian of south-east Wales : Introduction

2.1 Structure of the South Wales coalfield

Dinantian limestones and Namurian Millstone Grit form an approximately oval outline around the South Wales coalfield (Westphalian) synclinorium (see Fig. 2-1). The western portion of the coalfield, in Pembrokeshire, is separated from the eastern coalfield by Carmarthen Bay, and has extensive thrust faulting and tight folds (Owen, 1971). The eastern coalfield, of specific interest in the present study, has suffered minor flexuring and more important, faulting.

Three main fault directions are seen in the coalfield, east-west, NE-SW and NNW-SSE (see Fig. 2-1). The second group of structures are probably Caledonoid and have parallel folding axes. The first and third groups are mainly Variscan (Hercynian) structures (Owen, 1971). To the east of the coalfield, the Usk axis (anticline) brings Silurian rocks to the surface, and its NNE-SSW trend probably continues southwestwards as the Cardiff-Cowbridge axis (see Fig. 2-1). The Usk axis separates the South Wales and Forest of Dean Coalfields, and appears to have been an important influence on Carboniferous and Post-Carboniferous deposition and erosion (see below).

To the south of the Coalfield, the Cannington Park Thrust lies along the north coast of Devon (see Fig. 2-1). It separates the Dinantian shallow-marine carbonate rocks of South Wales from the Culm Facies (turbidites and shales) of Devon. The original depositional areas may have been a considerable distance apart (Owen, 1971) and the exact nature of the

Fig 2.1 LOCATION MAPS

a. showing palaeogeographic position of South Wales in the Dinantian.
(1 = Cannington Park thrust)

b. showing outcrop of Lower Carboniferous strata in South Wales (shaded) and the main structural elements (based on Owen, 1971 :

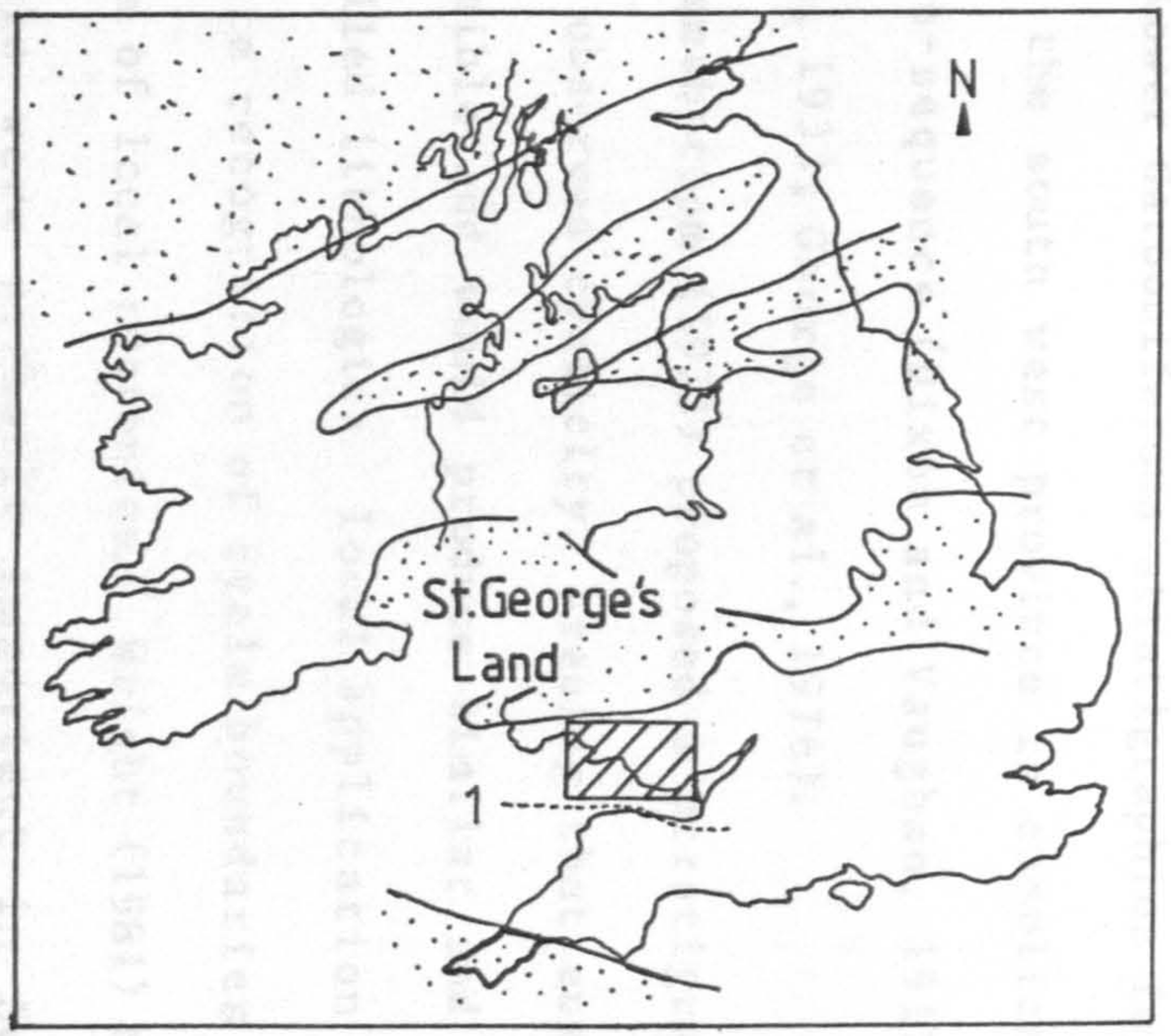
2 = Usk axis

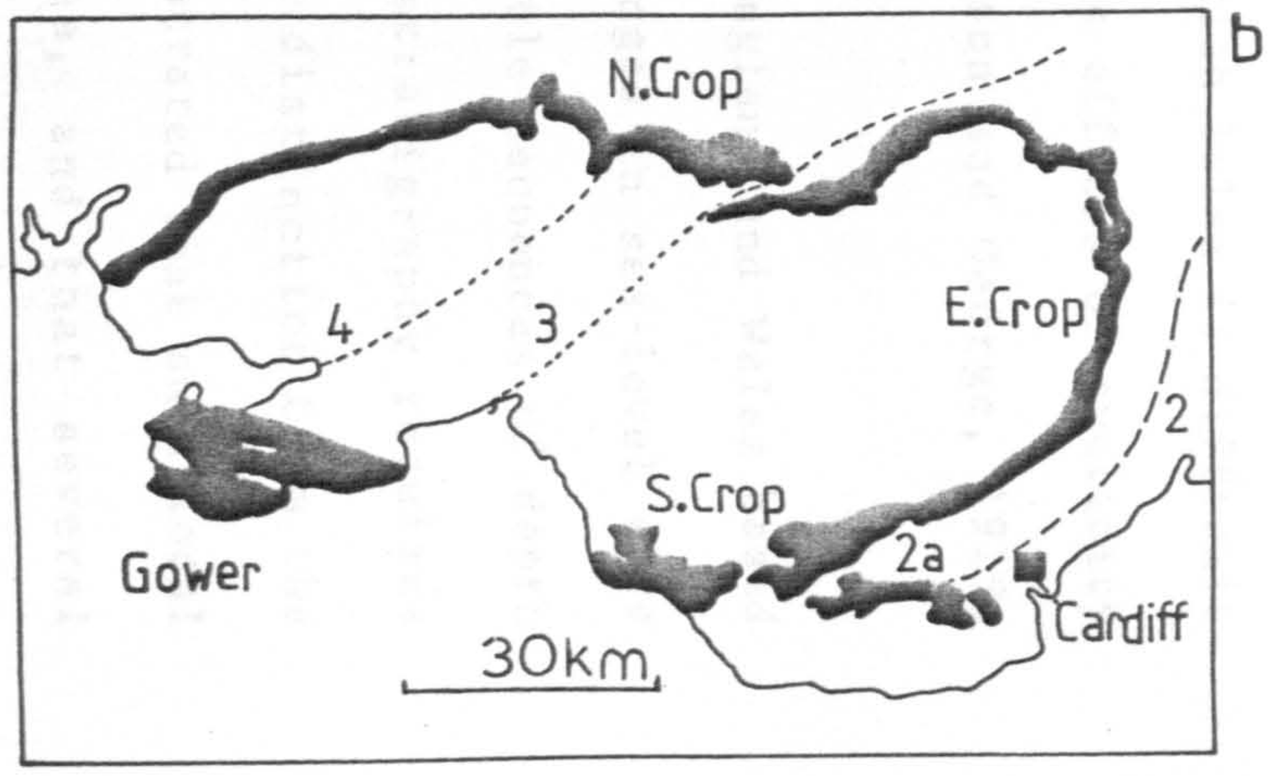
2a = Cardiff - Cowbridge anticline

3 = Neath distubance

4 = Tawe disturbance)

c. south-east area showing the main localities (see Fig 2.4 for details)


a
N
St.George's
Land
1


b
N.Crop
E.Crop
S.Crop
Gower
Cardiff
2a
2
3
4
30km

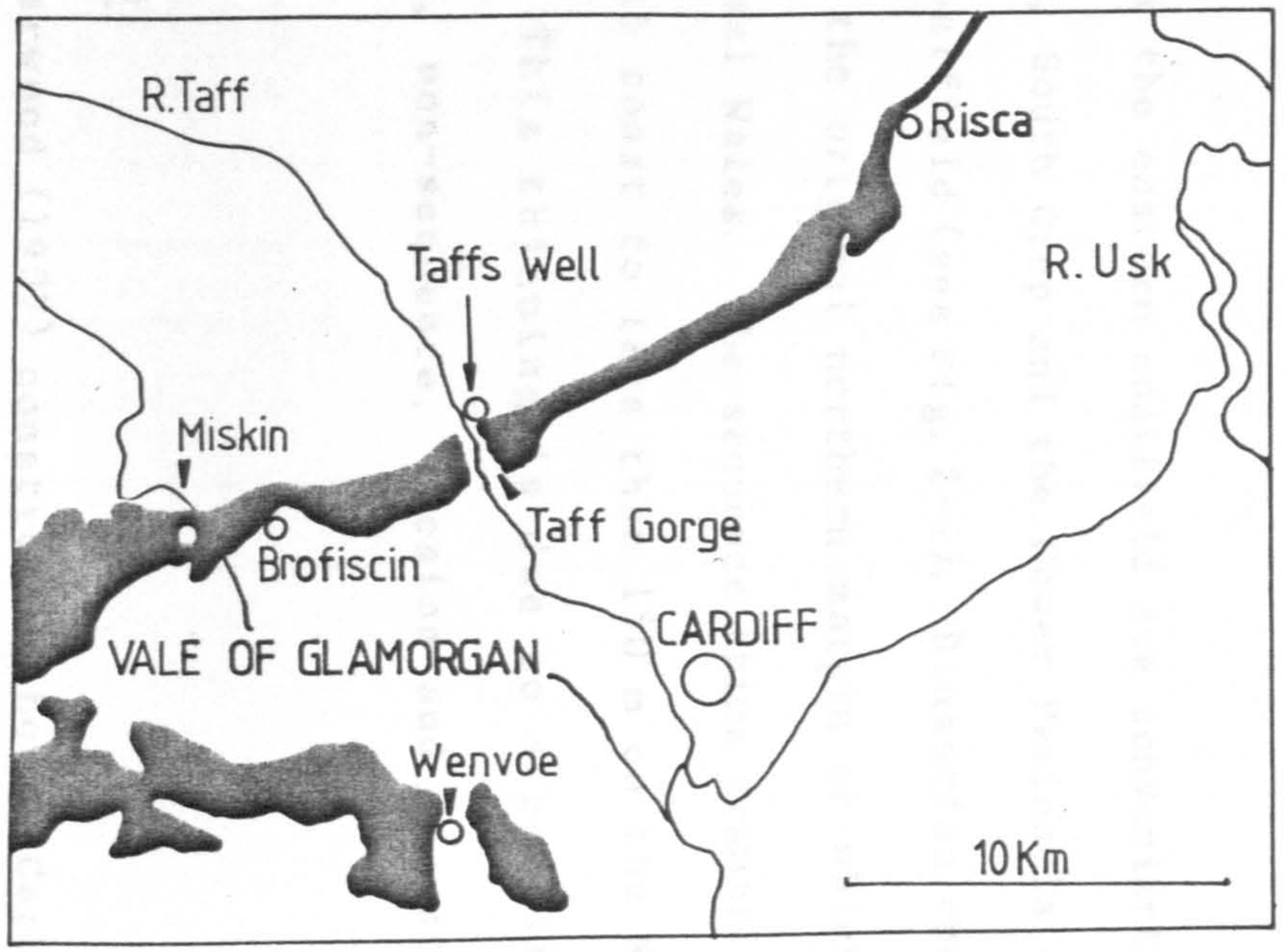

c
R.Taff
Risca
Taffs Well
R.Usk
Miskin
Brofiscin
Taff Gorge
CARDIFF
VALE OF GLAMORGAN
Wenvoe
10Km

Fig 2.1

north-south transition is a matter of debate (e.g. Wright 1984a and see below).

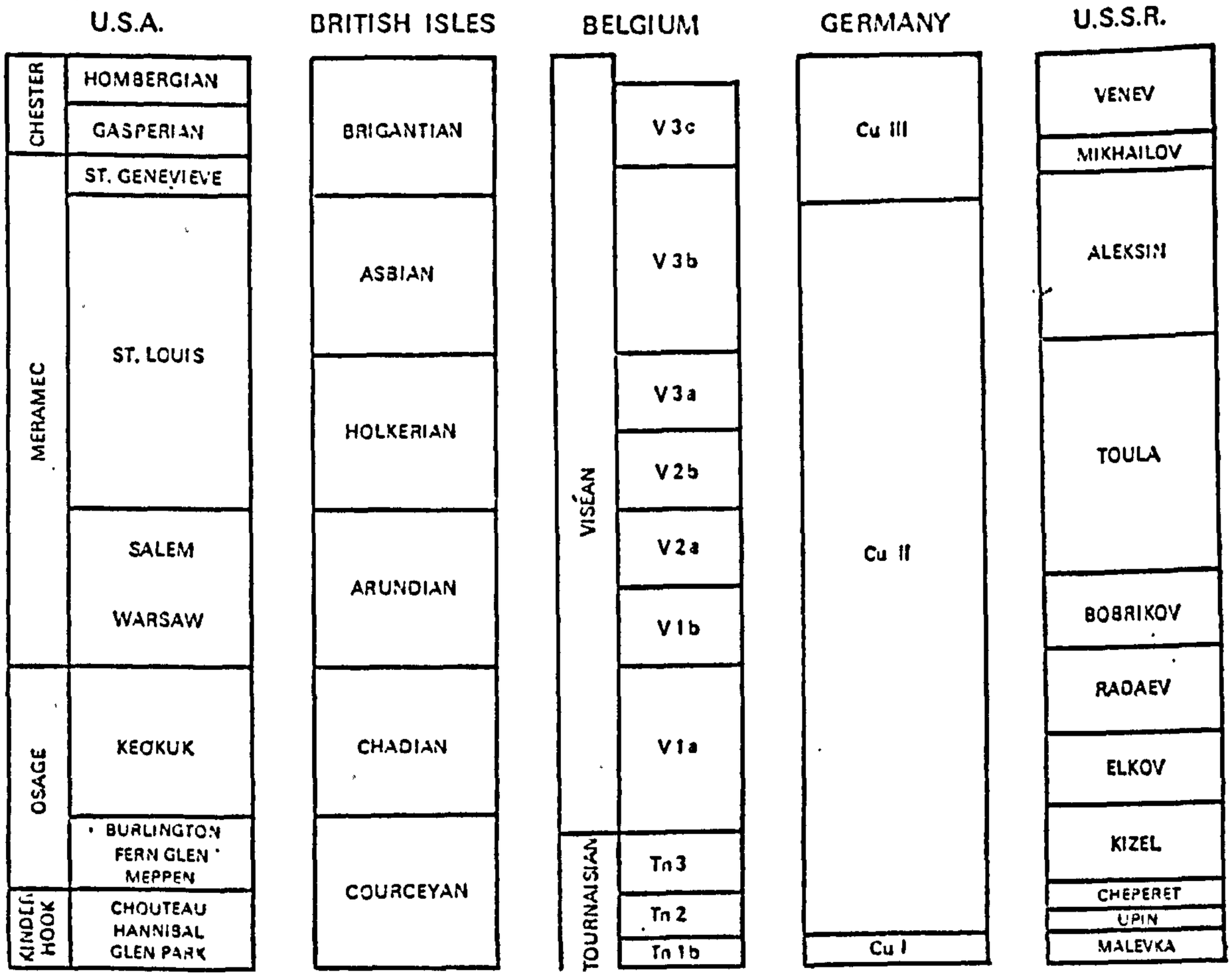
Dinantian exposures of the eastern coalfield are conveniently divided into North Crop, East Crop, South Crop and the Gower Peninsula and define the 'rim' of the eastern coalfield (see Fig. 2-1). Dinantian rocks form a northward tapering wedge, the original northern margin of which has been removed by erosion in central Wales. The sequence thins dramatically from around 1000 m on the south coast to less than 150 m on the North Crop (George et al., 1976). This thinning is due to a combination of depositional attenuation, non-sequence, erosion and overstepping by Namurian rocks.

2.2 Dinantian Stratigraphy

Vaughan (1905) and Garwood (1907) constructed Lower Carboniferous stratigraphies based on coral-brachiopod biozones for the Bristol and northern England regions respectively. However, correlation of these, and other Lower Carboniferous stratigraphies for the British Isles is difficult and in the south west province is complicated by the effects of cyclicity and non-sequence (Dixon and Vaughan, 1912; Robertson and George, 1929; George, 1933; George et al., 1976).

Ramsbottom (1973) proposed a stratigraphy for England and Wales based on the observed cyclicity, arguing that eustatic changes in sea-level were responsible and would produce similar and recognisable sequences of depth controlled lithologies. Local application of this stratigraphy requires accurate recognition of cycle boundaries and their distinction from the effects of local tectonics. Wright (1981) has demonstrated that such local controls were probably important in South Wales, and that several

Fig 2-2



Dinantian stratotype stages and overseas correlations

[reproduced from George etal. 1976]

significant exposure surfaces appear to have been overlooked by Ramsbottom.

George et al., (1976) proposed a new six-fold subdivision of the British Dinantian, based on precisely defined (stratotyped) stages (see Fig. 2-2). These stages approximately correspond to Ramsbottom's (1973) 'megacycles', showing that each 'major transgression' was accompanied by a change in the overall faunal assemblage. The stages of George et al. (1976) replace all earlier subdivisions and are used in the present study, following the British Geological Survey's survey maps of the area (e.g. 1:50,000 sheet 263, Cardiff (1985) and R.A. Waters, pers. comm.).

In some areas of the South Wales Dinantian extensive dolomitisation, faunal sparsity and marked facies change makes correlation difficult. This is particularly the case in the south-east and in North Crop-South Crop correlations. The stratigraphic position of the studied dolomites is based largely on the B.G.S. re-survey work (see below).

2.3 Depositional and tectonic history

(a) General

The broad tectono-palaeogeographical context of the south-west province Dinantian appears to have largely been inherited from the upper Old Red Sandstone (George, 1974a). St. George's Land to the north (see Fig. 2-1) was established during middle Devonian times, dividing the south-west province from the central province Dinantian.

Initial marine transgression northwards onto the ORS fluvial plain in South Wales is marked by the Lower Limestone Shales. These intertidal, lagoonal, barrier and shelf sediments record a diachronous, pulsed transgression with minor regressional (progradational) phases (e.g. Burchette, 1981, 1984). The final transgressive 'pulse' resulted in a

broad shelf-like (ramp) area reaching at least as far north as the present North Crop exposures and stretching west to southern Ireland and east into Somerset (Burchette, 1984; Wright, 1984a). A three-fold division of this area into a deepening basin (outer ramp), a subsiding shelf (mid ramp) and a stable shelf fringe (inner ramp) is recognised (Wright, 1984a,1985).

In north Devon, the Devonian-Dinantian transition is marked by a gradual deepening from a muddy-clastic shelf (Pilton Beds) to a turbidite basin by Chadian times. The deepening was probably due to a combination of eustatic sea-level rise and tectonic subsidence (Wright, 1984a) In Somerset, south Dyfed and southern Ireland, Waulsortian reef-mounds occur within the deeper subtidal (outer ramp) Black Rock Limestones.

In South Wales, George (1974a) differentiated shelly limestone, purer oolite and algal mudstone lithofacies and showed that the pure oolites of the North Crop merge southwards into thicker, less pure oolites. The attenuated North Crop sequence (George, 1954) comprises predominantly oolitic and peritidal limestones with a number of subaerial exposure surfaces marked by palaeokarsts and palaeosols (e.g. Raven, 1983, 1984; Wright, 1981, 1984a) The North Crop represents the inner ramp area, and the importance of high energy shoal deposits (i.e. oolites) suggests that a ramp or open-shelf regime had developed (Wright, 1984a, 1985).

To the south, in the subsiding mid-ramp area, oolitic limestones (e.g. the Brofiscin, Gully and Hunts Bay Oolites, see Fig. 2-3) within subtidal bioclastic packstones and wackestones (e.g. Black Rock and High Tor Limestone) represent the southward progradation of oolite shoals (Wright, 1984a, 1985). Oolites only occur within these regressive sequences, suggesting the development of restricted, barred shorelines during these phases (Wright, 1985). Progradation was probably a response to localised

Fig 2.3 NORTH-SOUTH LITHOSTRATIGRAPHIC CROSS-SECTION FOR SOUTH WALES DINANTIAN (COURCEYAN TO ARUNDIAN)

(based on Wright , 1984a, 1985)

A = Courceyan, B = Chadian, C = Arundian

Facies interpretation (see text for sources of information)

1 = Lower Limestone Shales

Pulsed transgression - barriers and lagoons

2 = Barry Harbour Limestone

2'= Friars Point Limestone

Subtidal, storm dominated bioclastics - in central subsiding part of ramp

6 = High Tor Limestone

3 = Brofiscin Oolite

4 = Gully Oolite

Regressive shoal facies - prograde southwards

7 = Cefnyrhendy Oolite (= Gilwern Oolite ?)

5 = Caswell Bay Mudstone

Peritidal transgressive facies

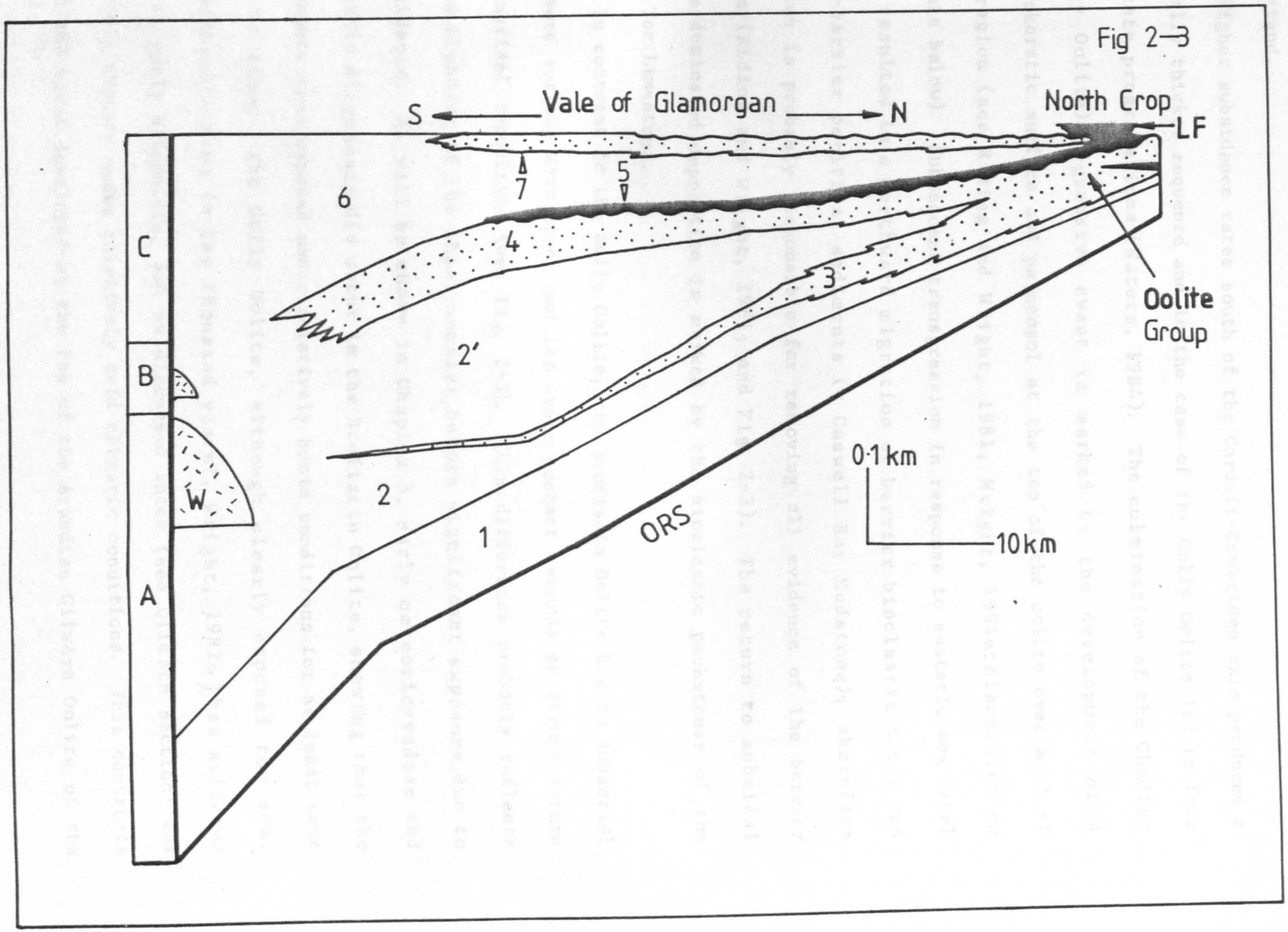
LF = Llanelly Formation

complex marginal marine

W = Waulsortian reef mounds

Deeper subtidal

Fig 2–3


S
Vale of Glamorgan
N
North Crop
LF
7
5
6
4
3
2'
2
1
W
ORS
C
B
A
Oolite
Group
0·1 km
10 km

tectonic base-level changes and/or to phases of reduced sea level rise or stillstand.

Higher subsidence rates south of the Cardiff-Cowbridge axis produced a generally thicker sequence and in the case of the Gully Oolite led to four separate progradations (Waters, 1984). The culmination of the Chadian (Gully Oolite) regressive event is marked by the development of a palaeokarstic surface and palaeosol at the top of the oolite over much of the region (see Riding and Wright, 1981; Wright, 1984a; discussion on climate below). Subsequent transgression in response to eustatic sea level rise resulted in a northward migration of barrier bioclastic sands and back-barrier peritidal sediments (= Caswell Bay Mudstone); shoreface erosion is probably responsible for removing all evidence of the barrier sands (Riding and Wright, 1981; and Fig. 2-3). The return to subtidal storm-dominated deposition is marked by the bioclastic packstones of the High Tor Limestone.

In contrast to the Gully Oolite, the Brofiscin Oolite has no subaerial exposure surface developed, and its upper contact records an abrupt return to subtidal deposition (see Fig. 2-3). This difference probably reflects rapid flooding of the shoal complex, before significant exposure, due to subsidence. As will be shown in Chapter 3, early meteoric-vadose and phreatic diagenesis did occur in the Brofiscin Oolite, showing that the sediments were exposed under relatively humid conditions for at least some of the time. The Gully Oolite, although clearly exposed for some considerable time (a few thousand years?, Wright, 1982a) has suffered little early diagenesis, and as discussed later (see Climate section) was probably exposed under relatively arid climatic conditions. This contrasts with the karst developed at the top of the Arundian Gilwern Oolite of the

North Crop, which records a relatively humid climate (see below).

The general facies distribution and depositional pattern suggests an open shelf or ramp-like structure for the Dinantian of South Wales. Because the transition to the deeper water (culm) facies to the south is now obscured by the Bristol Channel and Mesozoic cover in Devon and the exact position of north Devon relative to South Wales in the Dinantian is unknown, it is not possible to choose between a gently inclined ramp or a distally-steepened ramp model (Wright, 1984a, 1985). The tectonic setting is therefore not entirely clear, however, the general pattern of differential subsidence and the suggested movement along the Cardiff-Cowbridge axis may support the suggestion of early Carboniferous extension in the region (Leeder, 1982; Wright, 1984a). A horst structure (the Bristol Channel landmass) is known to have formed a positive feature in the Middle Devonian and Upper Carboniferous, separating north Devon and South Wales at these times and adds support to the general tectonic interpretation.

The Hercynian Orogeny appears to have had a pulsed development, with an early Bretonic (late Devonian) phase having most effect in south Cornwall. Successive phases in the late Dinantian (Sudetic) and late Carboniferous (Asturic) moved progressively northwards, ultimately producing the major synclinorium and related structural features of the coalfield (see Fig. 2-1). Post-Dinantian faulting in response to compressive stresses appears to be a late Carboniferous event (Roberts, 1966, 1979; Leeder, 1982).

(b) South-East Crop

The Dinantian strata in the study area (see Fig. 2-1) are characterised by a marked attenuation and a dramatic increase in the

proportion of dolomite to limestone in the sequence in a north-easterly direction (Dixey and Sibly, 1918). Dixey and Sibly (1918), George (1956, 1974) and Owen (1971) have shown that the NNE-SSW trending Usk Axis had a definite effect on Dinantian sedimentation in the East Crop. A north-north easterly shallowing of the carbonate shelf sea is suggested by the increased thickness of Modiola phase micritic (? marginal marine) carbonates in this direction (Dixey and Sibly, 1918; George, 1956). The Usk Axis also marks the approximate eastern limit of George's (1974) South Wales 'cuvette' and by Westphalian times it was an important positive feature, which probably extended south-westwards as far as Risca (Owen, 1971). The progressive positive growth of the Usk Axis from as early as late Arundian (mid-Seminulan) is suggested by the introduction of sand and gravel into fringes of the South Wales and Forest of Dean 'coalfields' from this time (Owen, 1971). Erosion of Dinantian and some Devonian strata from late Dinantian to the end of Namurian times is indicated by the overstepping by Namurian and younger rocks from a north-north easterly direction.

2.4 Dinantian climate in South Wales

The low palaeolatitude of the British Isles in the Dinantian (e.g. Windley, 1977; Habicht, 1979) and the extensive development of shallow marine carbonates suggests a tropical or sub-tropical climate for South Wales in the Dinantian.

Wright (1980) has shown that climatic fluctuations were significant in the Dinantian. Based on his studies of palaeokarsts and palaeosols in the South Wales Dinantian rocks, Wright (1984b, c) has recognised climatic fluctuations from humid (e.g. the karst at the top of the Gilwern Oolite,

Arundian, North Crop, Wright, 1982a) to arid or seasonally arid (e.g. palaeosols in the Llanelly Formation, Arundian, North Crop (Wright, 1982b) and small scale karst at the top of the Gully Oolite, Chadian, Gower).

The relationship between prevailing climate and early diagenetic style, especially when subaerial exposure occurs, appears to be strong (Longman, 1980). In the South Wales Dinantian, Wright (1982b, 1984b and c) and Raven (1983) have suggested the role of climate in early diagenesis. These ideas will be discussed further in Chapters 3 and 5.

2.5 Dolomites in the Dinantian of South Wales: (i) regional and stratigraphic distribution

Dolomites are variously developed in the Dinantian of South Wales and the adjacent Forest of Dean (George et al., 1976). The Langland (Laminosa) Dolomite (George et al., 1976), is a particularly extensive example which occurs in the Upper Courceyan limestones, stretching from Tenby in the west through Gower (type locality, Langland Bay) and Miskin to Risca on the East Crop (see George et al., 1976). The Langland Dolomite is a relatively coarse grained, pervasive stratal dolomite and is similar to dolomites in the Oolite Group of the North Crop (George, 1954) and to the dolomitised upper Courceyan (Black Rock Limestone) rocks of the Forest of Dean and Bristol districts (see George et al., 1976 fig. 4; Kellaway and Welch, 1948).

In south-east Wales a marked increase occurs in the proportion of dolomite to limestone in a north-easterly direction along the South and East Crops (Dixon, 1907; Dixey and Sibly, 1918; see also 'This Study' below). Between Bridgend (15 km west of Miskin) and Risca the Lower Limestone Shales maintain their lithological and faunal facies, whereas the

Main Limestone (post-LLS Dinantian rocks) changes from a sequence of limestones with subordinate dolomites to an almost unbroken succession of dolomites (Dixey and Sibly, 1918). East of the Taff Valley, the upper part becomes dolomicritic and is probably equivalent to the Modiola phase (Arundian?) carbonate mudstones (Dixey and Sibly, 1918). The South and East Crop dolomitised Main Limestone was re-named the Rudry Formation by George et al., 1976, and in the East Crop is probably equivalent to Courceyan and Arundian limestones. The Rudry Formation achieves its maximum development at Risca, and north of there the proportion of dolomite:limestone increases (George, 1956). In the north-east of the coalfield, dolomite comprises a large proportion of the Oolite Group below the Arundian (Coral Bed-Gilwern Oolite), but rapidly dies out westwards along the North Crop (George, 1954).

Dolomites in the Dinantian of South Wales: (ii) Previous research

Ideas about the origin of the dolomites were suggested in the earliest papers and reports. Dixon (1907) suggested 'contemporaneous' and 'subsequent' forms, with the former implying formation whilst under the influence of the Carboniferous sea and the latter by later metasomatic replacement along joints and faults. Dixey and Sibly (1918) also drew a distinction between 'contemporaneous' dolomites and 'vein' (subsequent) dolomites and went further by suggesting that 'contemporaneous' dolomites may be dolomitised further during 'subsequent' dolomitisation.

The recognition of dolomicrites replacing carbonate muds and algal laminites (the Modiola phase deposits) as a subdivision of the contemporaneous stratal dolomites was also an important development (Dixey and Sibly, 1918; George, 1956).

A more recent, petrographic-geochemical study was carried out by Bhatt (see Bhatt, 1976 and reference to his earlier works therein). Bhatt (1976 recognised six microfacies types in the Dinantian of the South, East and North-east Crops. He describes similar textures to those described in more detail in this study (Chapter 3) and concluded that dolomites of early, late and epigenetic origin occur. However, certain details of Bhatt's work are unclear and, as pointed out by Wright (1981), in some cases totally inaccurate. For example, Bhatt (1976) suggests that the bulk of dolomitisation occurred due to the refluxion of high Mg/Ca, hypersaline solutions derived from a supratidal sabkha area near Clydach on the North Crop (see fig. 8, Bhatt, 1976). However, there is little evidence for evaporites having formed in the peritidal Llanelly Formation of this region (Wright, 1981), and they are also rare in the peritidal dolomicrites at Danygraig near Risca on the East Crop (Chapter 3, this study). Indeed, Bhatt himself confesses (Bhatt, 1975) that the evidence for evaporite formation in the Main Limestone is not extensive, which may explain his rather confusing appeal to a 'biogenic' source of Mg^{2+} for dolomitisation, whilst proposing a 'reflux model' (p. 82, Bhatt, 1976). Wright (1981) dismissed Bhatt's (1976) suggestion of a back-reef supratidal sequence, because in addition to the absence of supratidal-sabkha deposits there is no evidence that a reef (essential to Bhatt's model) ever existed in the Taffs Well area, or anywhere else on the Dinantian carbonate shelf in South Wales (see Section 3 above).

Further criticisms of Bhatt's work include the rather simplified representation of 'microfacies' distribution (stratigraphic and regional) and the apparent predominance of dolobiomicrites, for example at Tongwynlais (Taff Gorge) which is clearly not the case (see sections 3 and

5(i) above, section 5(ii) below). Bhatt's (1976) geochemical data (Ca/Mg, Mole % Mg) are useful in providing an estimate of the proportion of dolomite in bulk limestone samples, or of the composition of dolomite in bulk dolomite samples, providing careful petrographic control is shown. The use of this data by Bhatt to support his conclusions regarding the formation of carbonates during (a) open marine and (b) restricted lagoonal conditions seems invalid considering the inaccuracy of his depositional model (see Chapter 4 of this study for further discussion on the usefulness of dolomite geochemical data).

A Triassic age for the vein dolomites has been suggested on the basis of hematite inclusions in the dolomite, supposedly resulting from the downward percolation of fluids from the Triassic land surface (e.g. Greensmith et al., 1971, p. 256). However, Eustance (1981) has shown from palaeomagnetic studies and from fabric relationships that iron-redistribution and vein dolomitisation accompanied late Carboniferous earth movements, tectonic fracturing and microbrecciation (see also this study, Chapter 3). Eustance (1981) suggested a Westphalian source for the iron in vein dolomites. Late Hercynian activity (? Upper Permian) may have been responsible for further disruption of the dolomites, but a Permo-Carboniferous magnetic remenance was retained (Eustance, 1981). Raven (1983) studied the diagenesis of the Oolite Group (Chadian-Arundian) of the North-East Crop (see Fig. 2-1), including the dolomitisation which affects an increasing proportion of the limestones in an easterly direction and represents the northern limit of the East Crop dolomites (see also George, 1954). Raven (1983) constructed a diagenetic history for the Oolite Group based on petrographic (including cathodoluminescence) and stable isotope studies, and identified two distinct diagenetic areas. Area 1 is fairly

restricted, occurring in the lower and middle part of the Oolite Group at the eastern end of the North Crop. Area 2 includes the upper part of the Oolite Group in the east and the entire formation west of Craig y Gaer (see Raven, 1983). Pervasive dolomites occur within area 1, rising to include all the Oolite Group at the eastern end of the area. In the oolite members, dolomite occurs as a replacement mosaic after allochems and cements as well as a sparry cement in voids. Finer grained beds have also been dolomitised and are often associated with concretionary horizons (e.g. Daren Ddu beds, Raven, 1983). Fault-related dolomites also occur.

The form of area 1 suggests that a lobe of porewaters distinct from those of area 2, extended up-dip under area 2 in the Clydach region and may indicate that these porewaters were denser than those in area 2. At their down-dip end the area 1 porewaters rested on the relatively impermeable Lower Limestone Shales (Raven, 1983). Petrographic evidence suggests that the pervasive dolomite formed after an early phase of meteoric/marine cementation and before the end of the Dinantian. The general absence of typical area 2 cement zones in area 1 precludes the timing of dolomite relative to the complex marine-meteoric diagenetic history established for area 2 (Raven, 1983).

Stable isotope data for area 1 cements and dolomite are rather inconclusive, being consistent with either a marine or meteoric origin. However, the typical negative $\delta^{13}C$ values of area 2, reflecting a light (soil-gas) CO_2 influence (see Chapter 4) are not seen in area 1 (Raven, 1983). The nature of dolomitising fluids is therefore problematic. 'Hypersaline brines' would be consistent with the inferred higher density of area 1 porewaters, however the evidence for meteoric diagenesis and negative $\delta^{18}O$ values, suggests that the fluids were not hypersaline all of

the time (Raven, 1983). Meteoric-marine mixing zone dolomitisation is consistent with the nature of diagenesis in area 2, however Raven (1983) concludes that the distribution of area 1 and the regional extent of dolomitisation suggests that this hypothesis is unlikely. Whatever the source of porewaters, the geometry of area 1 suggests that they were introduced laterally from the east and there is no evidence that they ever passed through area 2 (Raven, 1983).

Vein dolomites in Raven's(1983) study area have a late diagenetic origin, truncating late Dinantian cement zones. The vein dolomites themselves are succeeded by late calcite cement of probable post-Carboniferous age (Raven, 1983).

Dolomites in the Dinantian of South Wales: (iii) This Study

This study concentrates on the South and East Crop exposures, representing the transition from a predominantly limestone sequence to dolomites (the Rudry Formation).

Three major and distinct types of dolomite are recognised in the field and receive further consideration in Chapter 3, these are:

(i) Dolomicrites (peritidal facies)

(ii) Pervasive stratal dolomites (dolomitised grainstones, packstones and wackestones).

(iii) Vein dolomites.

Types (i) and (ii) are the 'contemporaneous' dolomites of earlier workers and have a marked stratigraphic and regional distribution (see Fig. 2-4). The pervasive stratal dolomites are volumetrically the most important type and occur as replacements of the Black Rock Limestone (Barry Harbour Limestone - Brofiscin Oolite - Friars Point Limestone) and the High

Fig 2.4

Lithostratigraphic section and regional-stratigraphic distribution of pervasive dolomite (not to scale). Figures are approximate thicknesses in metres , based on British Geological Survey data and measured sections.

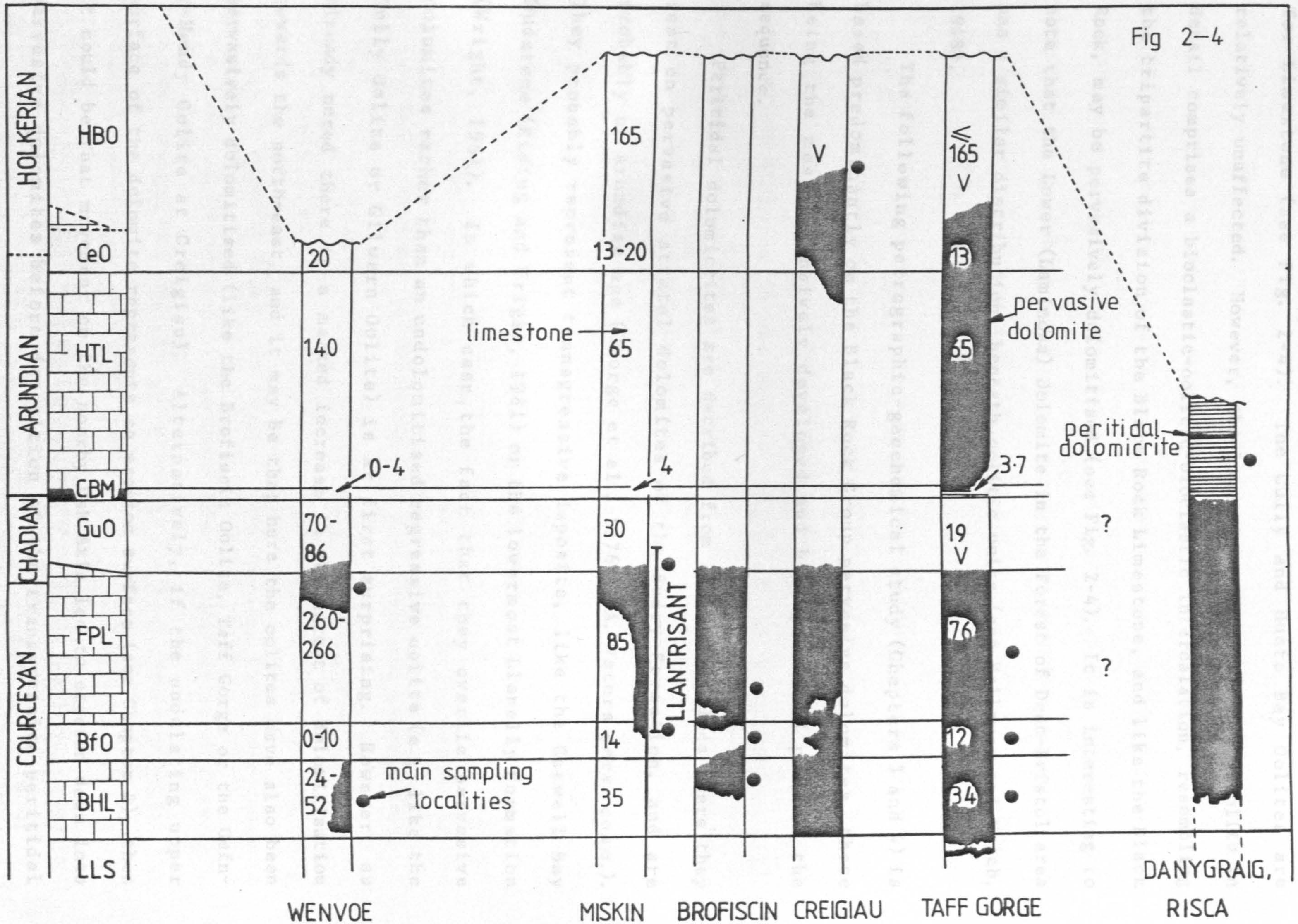
Filled circles = main sampling localities,
V = vein dolomite

Grid references for the principal sampling localities are as follows :

Wenvoe quarries		ST 118 735 to 115740
Llantrisant road section		ST 057 812
Brofiscin Oolite		ST 069 813
Creigiau quarries		ST 088 820
	Taff's Well quarry	ST 123 822
	Steetly old quarry	ST 125 826 - 122 829
Taff Gorge	Tynant quarry	ST 127822
	Tongwynlais	ST 128 828
Danygraig, Risca		ST 233 907

Sample numbers referred to in the geochemistry chapter (4) and in the appendices have prefix letters which identify the sampled unit as follows :
LLS = Lower Limestone Shales
CeO = Cefnyrhendy Oolite
R = dolomicrites, Danygraig, Risca.
CBM = Caswell Bay Mudstone , Taff Gorge
BO = (BfO) Brofiscin Oolite
BR = 'Black Rock Group' - refers to Friars Point Limestone (FPL) and Barry Harbour Limestone (BHL)
HBO= Hunts Bay Oolite
GuO= Gully Oolite
other units were also sampled for petrographic study only, as indicated on Fig 2.4

Fig 2–4


HOLKERIAN
ARUNDIAN
CHADIAN
COURCEYAN
HBO
CeO
HTL
CBM
GuO
FPL
BfO
BHL
LLS
20
140
0-4
70-86
260-266
0-10
24-52
main sampling localities
limestone
165
13-20
65
4
30
85
14
35
LLANTRISANT
V
≤165 V
13
65
3·7
19 V
76
12
34
pervasive dolomite
peritidal dolomicrite
?
?
WENVOE
MISKIN
BROFISCIN
CREIGIAU
TAFF GORGE
DANYGRAIG, RISCA

Tor Limestone (see Fig. 2-4). The Gully and Hunts Bay Oolites are relatively unaffected. However, the lower part of the Hunts Bay Oolite in detail comprises a bioclastic-oolitic-bioclastic intercalation, resembling the tripartite division of the Black Rock Limestone, and like the Black Rock, may be pervasively dolomitised (see Fig. 2-4). It is interesting to note that the Lower (Laminosa) Dolomite in the Forest of Dean-Bristol area has a similar distribution, beneath oolitic units (see Kellaway and Welch, 1948).

The following petrographic-geochemical study (Chapters 3 and 4) is based predominantly on the Black Rock Group pervasive dolomites, these being the most extensively developed and best preserved part of the sequence.

Peritidal dolomicrites are decribed from Danygraig, Risca where they rest on pervasive stratal dolomites of the Rudry Formation, and are probably of Arundian age (George et al., 1976; R.A. Waters pers. comm.). They probably represent transgressive deposits, like the Caswell Bay Mudstone (Riding and Wright, 1981) or the lowermost Llanelly Formation (Wright, 1981). In which case, the fact that they overlie pervasive dolomites rather than an undolomitised regressive oolite (e.g. like the Gully Oolite or Gilwern Oolite) is at first surprising. However, as already noted there is a marked increase in the extent of dolomitisation towards the north-east, and it may be that here the oolites have also been pervasively dolomitised (like the Brofiscin Oolite, Taff Gorge or the Cefn-y-Hendy Oolite at Creigiau). Alternatively, if the undulating upper surface of the dolomite represents an erosion surface (see Chapter 2), then it could be that movement on the nearby Usk Axis led to erosion down into pervasive dolomites before deposition of the transgressive peritidal

facies.

Vein dolomites in the study area are most obviously developed within otherwise undolomitised or partially dolomitised Gully Oolite and Hunts Bay Oolite, although they have also been seen within undolomitised Black Rock Limestones outside the study area on the South Crop (R.A. Waters, pers. comm.) and in the Oolite Group of the North Crop. A structural control on the distribution of vein dolomites is clear. A small number of vein orientations were measured and found to strike around 280°, 340° and 360°. These are similar to joint sets recorded by Roberts from the North Crop (Roberts, 1966) and South Gower (Roberts, 1979), and interpreted by him to be late Carboniferous structures, having formed in response to north-south compressive stresses in the Asturic phase of the Hercynian orogeny. Brittle fracture resulted, despite estimated overburdens of 1.5 km probably because of low confining pressures produced by the presence of pore-fluids or a porosity (Roberts, 1966).

2.6 Burial History of the Dinantian in south-east Wales

Dickson (1985) produced a time-depth reconstruction (burial curve) for the Dinantian limestones in the Gower (see Fig. 2-5a) and Swansea areas of south-central Wales. Both sequences suffered rapid burial (to approximately 7 km) and uplift, with the Gower limestones becoming subaerial by Triassic times. In contrast, the Swansea limestones remained buried under 3 km of post-Dinantian cover. Deposition of Mesozoic sediments resulted in a further 1.5 km burial for both sequences, until the subsequent erosion of Mesozoic rocks by the Oligocene. The Gower limestones were thus re-exhumed, whilst those under Swansea have remained

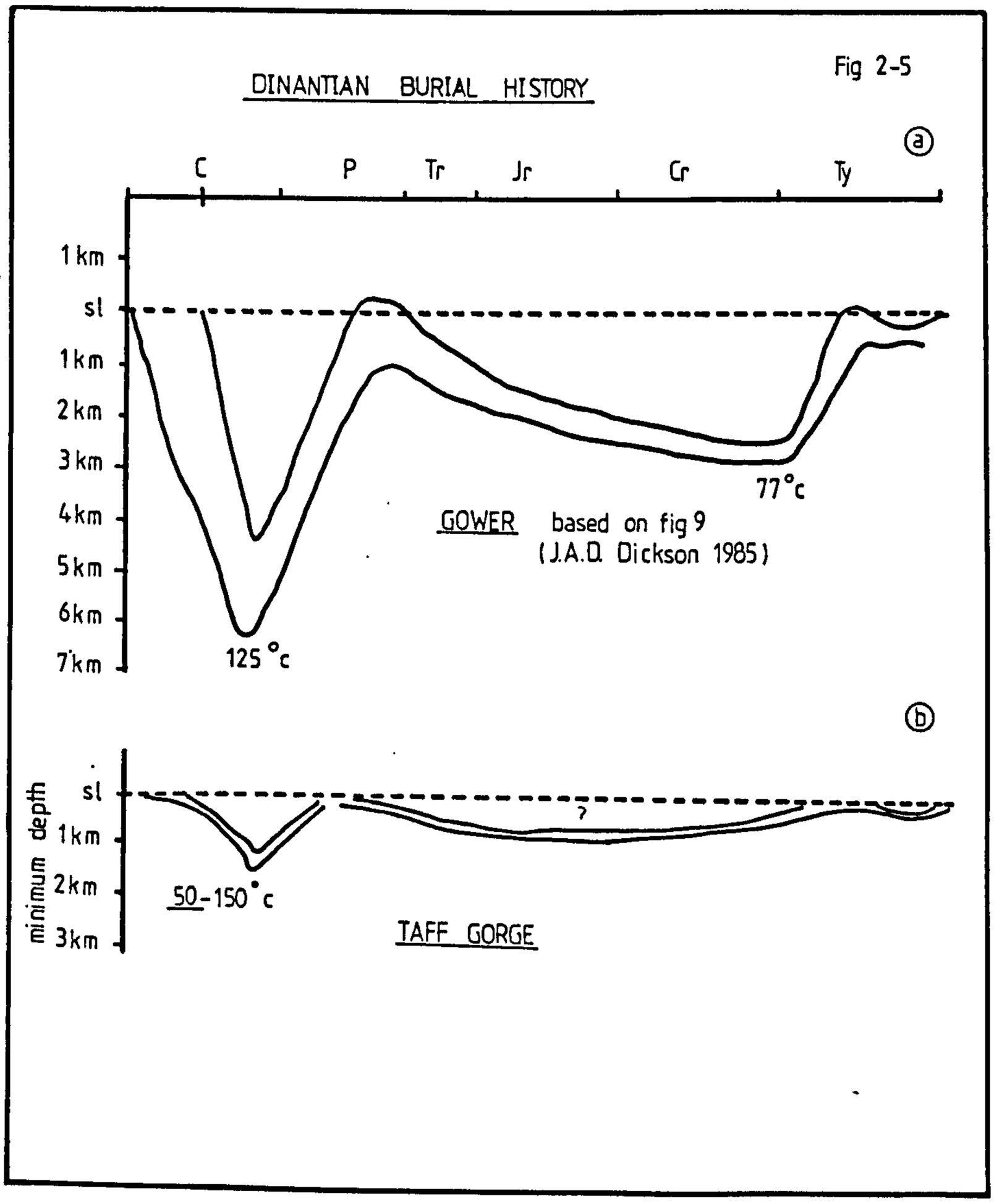


Fig 2.5

Burial curves for the Taff Gorge rocks are based on the Gully Oolite (lower curve) and the Hunts Bay Oolite (see text for explanation).

buried to the present day (see Dickson, 1985, fig. 9). Because of the relatively short residence time at maximum burial (during late Carboniferous), equilibrium-burial temperatures (c. 200°C) were probably never reached (Dickson, 1985). In the case of the Swansea limestones, which never re-emerged following initial burial, pressure-temperature conditions through their post-Carboniferous history are likely to have been very different from those in the Gower.

In the present study area, Dinantian limestones (and dolomites) are now at the surface. However, it is clear that they have been buried (see petrography, Chapter 3), and that their burial history is likely to be significant in any interpretation of their paragenesis.

As with the Swansea and Gower sequences, maximum burial was probably attained during the late Carboniferous. Hercynian uplift was followed by Permian and early Triassic erosion. Triassic cover in South Wales appears to have been rather insignificant and probably localised (Ivimey-Cook, 1974). In the Vale of Glamorgan, islands of Carboniferous limestone developed during the Rhaetian, as evidenced by the presence of fissures with Triassic sediments, and were followed by a short-lived period of more general uplift (Ivimey-Cook, 1974). Liassic sediments were deposited in Glamorgan, the Bristol Channel and Severn Valley areas (Ager, 1974), representing a return to marine conditions. Subsequent transgression produced a Jurassic cover over most of Wales, including the area of St. George's Land (Ager, 1974). There is little physical evidence of a Chalk cover in South Wales, although George (1974b)showed that a projection of the Wiltshire Downs escarpment suggests a Chalk blanket at least over south-east Wales. By geomorphological reasoning, the Chalk and earlier Mesozoic cover rocks appear to have been removed by the end of the

Palaeogene (Geroge, 1974b).

End-Carboniferous burial depths for the top of the Gully Oolite and Hunts Bay Oolite in the Taff Gorge are calculated at 1550 m and 1300 m repsectively (R.A. Waters, pers. comm.), but are only minimum depths because an unknown thickness of Pennant Sandstone has been removed by erosion.

Although grain-grain compaction and pressure solution, and through-going stylolite pressure solution were probably completed during Carboniferous burial (see Chapter 3), the presently observed thicknesses of limestones and dolomites may have been considerably reduced during the longer-lived post-Permian burial phase, due to other, less readily identifiable compaction - pressure solution effects (e.g. non-seam pressure solution, see Schofield (1983) and Vein dolomite discussion, Chapter 3).

Even considering that the estimated burial depths are probably minimum values, it is unlikely that the Taff Gorge rocks were buried to the same depths as their Gower-Swansea equivalents. On the basis of coal grade (high volatile bituminous) and clay mineralogy (illite crystallinity studies, Gill et. al., 1977). The Carboniferous rocks in the eastern part of the coalfield did not progress much beyond the diagenetic stage (Tissot and Welte, 1978). In contrast, the Gower and Swansea limestones, although they did not reach equilibrium (greenschist stage), did reach a considerably higher (metagenetic) stage than the Taff Gorge rocks.

The calculated equilibrium temperatures for the Taff Gorge rocks (see Fig. 2-5b) are based on minimum estimates of burial depth and are therefore probably under-estimates of the potential conditions during maximum burial. However, because burial and uplift was rapid, these (unknown) 'higher' temperatures were almost certainly not achieved (see above discussion). It

seems reasonable therefore, to take the calculated temperatures as a first approximation in any subsequent discussion (in particular, see Chapter 4).

Fig. 2-5b is a burial curve based on the information presented above for the Gully Oolite and Hunts Bay Oolite in the Taff Gorge. Differential subsidence across the Cardiff-Cowbridge axis (see above and Waters, 1984) means that the south Vale of Glamorgan rocks were probably buried deeper than shown on Fig. 2-5b (approximately 370 m for the Black Rock Limestone, 60 m for the Gully Oolite, Waters, 1984).

CHAPTER 3

Petrography of dolomites in the Dinantian of South Wales

3.1 Introduction

This chapter deals with the petrographic description and interpretation of the different dolomite types which occur within the Dinantian of South Wales. It follows on from Chapter 2, which serves as a general introduction providing a broad geologic background to the South Wales Dinantian and more specific stratigraphic and sedimentologic information.

The three major types of dolomite (see section 2.5 (iii)) are dealt with in turn. The general format is a 'petrographic description' section followed by an 'interpretation' section. However, variations include an extended discussion of the depositional-early diagenetic context of the Danygraig dolomicrites, as this is essentially new information. The other dolomites (pervasive and vein) are discussed within the more general context presented in Chapter 2.

The chapter is intended to provide a basis for the subsequent geochemistry in Chapter 4.

3.2.1 Peritidal dolomicrites, Danygraig, Risca

At Danygraig quarry, Risca, an approximately 20 m thick sequence of dolomitised 'peritidal' carbonates rests above an erosion surface at the top of massive crystalline dolomites of the pervasive stratal type (see section 3.3 below). The top of the 'peritidal' sequence is marked by an unconformity representing the overstep by Namurian sediments.

Fig 3.1

Section,with environmental interpretation, re-drawn from field log of the Danygraig sequence.

Fig 3.2

Polished cut surface of hand specimen from cryptalgal laminites,showing intraformational conglomerates,syndepositional fracturing and graded storm beds.
Danygraig,Risca.

Fig 3.1

Key

- laminoid fenestrae
- calcispheres
- gypsum pseuds.
- intraclasts
- bioturbation
- rootlets

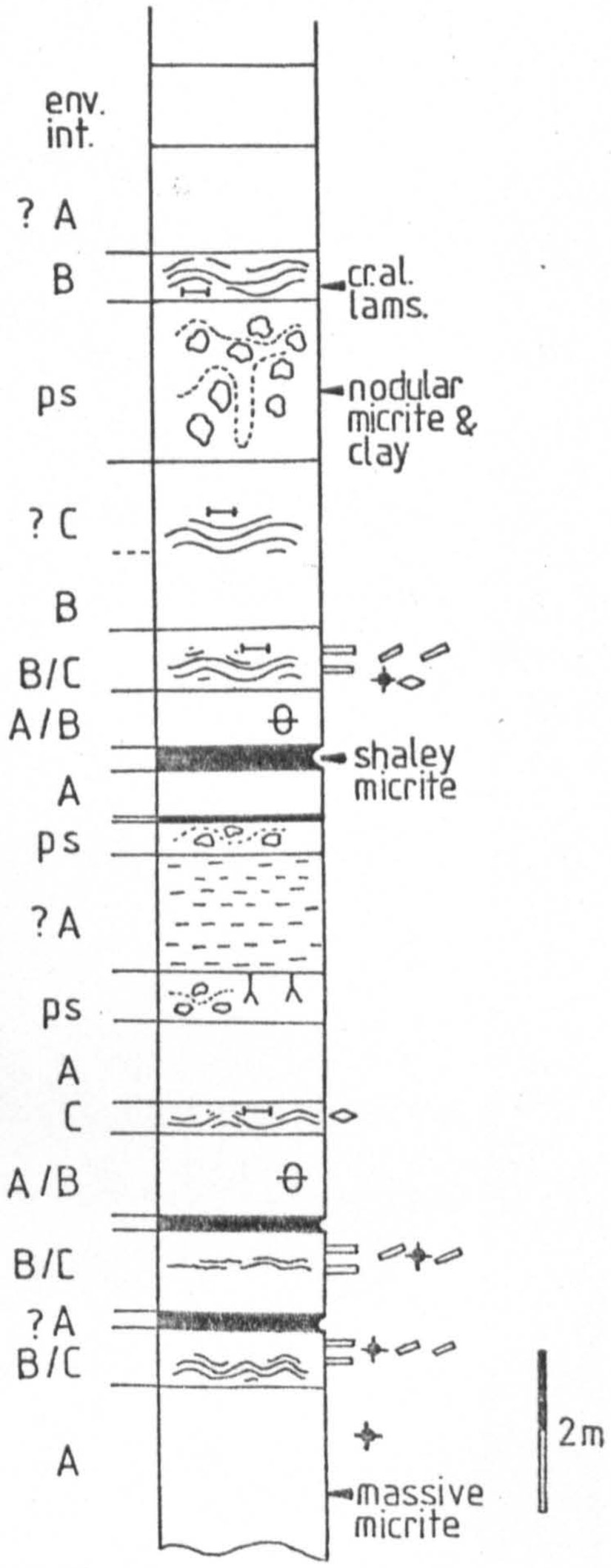
Environmental interpretation

A - subtidal/ lagoonal

B - intertidal

C - supratidal

ps - palaeosol



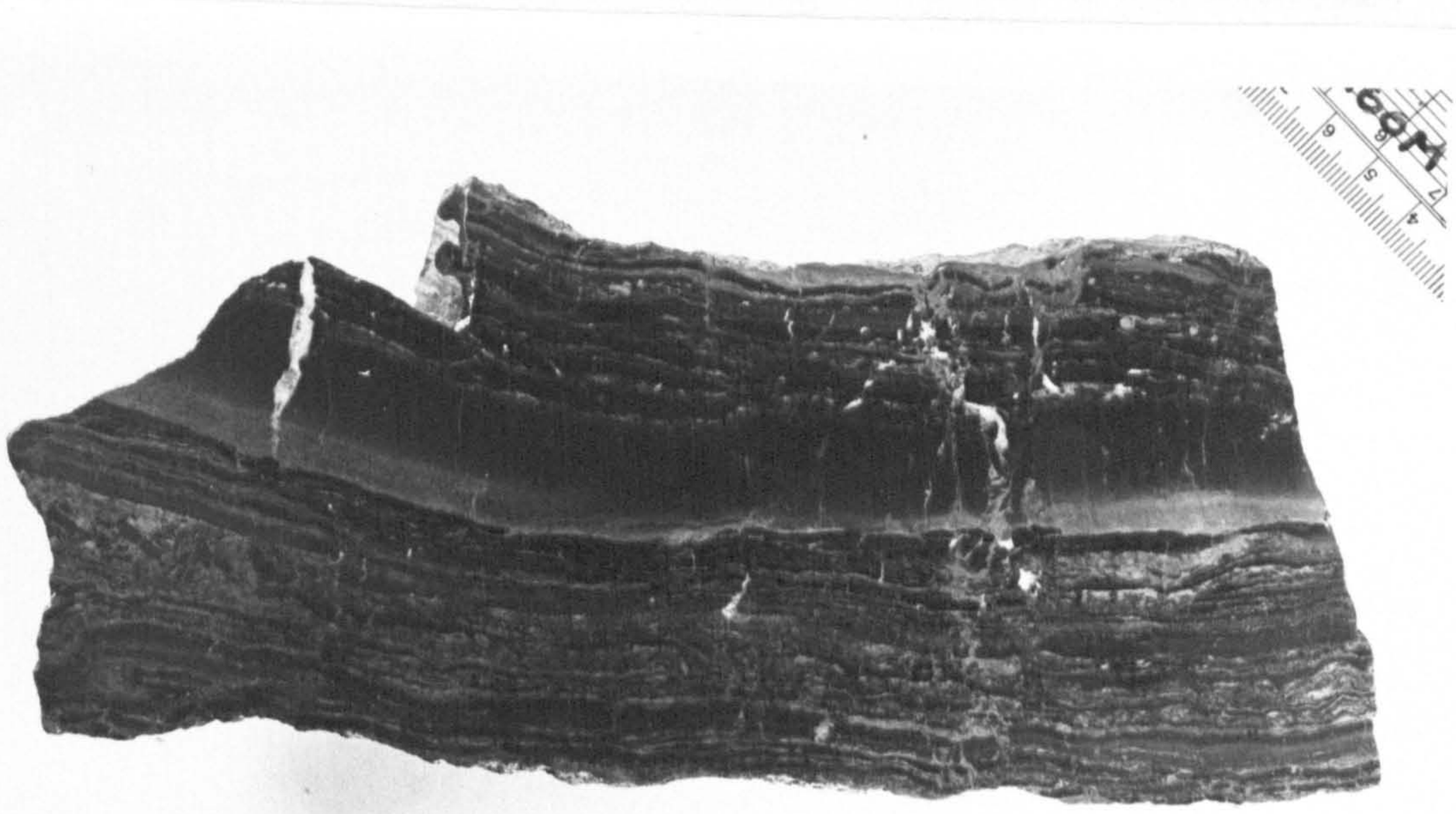


Fig 3.2

The sequence at Danygraig (see Fig. 2.1; 3.1) comprises massive and laminated micrites with coarser grained laminae and intraformational conglomerates Fig. 3.2). Nodular micrites, green clays, clay-dykes, thin shales and rootlet horizons also occur.

Dolomite occurs as a dense microcrystalline (<3 μm grain diameter) mosaic, the monomineralogy of which is identified by X-ray diffraction (see Appendix I). This mosaic forms both the massive micrite units and the laminae in laminated units. The latter laminae are typically 0.05 to 5.0 mm thick, planar to undulatory and domed, they are commonly fractured with minor displacement or may be brecciated giving rise to in-situ and transported clasts (intraformational conglomerates). Vertically oriented fractures usually cut through several laminae and are now filled with sediments from overlying layers (Fig. 3.2). The thicker laminae and massive micrites commonly display vertical to sub-horizontal tubular structures (0.05-0.2 mm wide, 0.1 to 4.0 mm long in plane of thin section) identifiable because of their slightly coarser or less dense fill (Fig. 3.3a).

The microcrystalline laminae in the laminites are often interbedded with slightly coarser dolomite (3 to 15 μm diameter anhedral crystals) or with layers of graded 'clastic' material comprising angular quartz (up to 120 μm maximum diameter) and generally unidentifiable carbonate grains in a fine dolomitic matrix, maximum 15 μm grain size. They also contain spherical structures, 40-80 μm diameter, resembling calcispheres, Bathurst (1975, p. 69-70), see Fig. 3.3b. They are common in many Palaeozoic limestones, particularly fine-grained micrites of back reef or lagoonal origin (Tucker, 1981, p. 109).

Irregular to laminoid cavity structures or fenestrae are common in the

Fig 3.3

a. Bioturbation in dolomicrites (T.S.,XPL) and

b.calcispheres in dolomicrites (T.S. PPL)

a,b 0.1mm

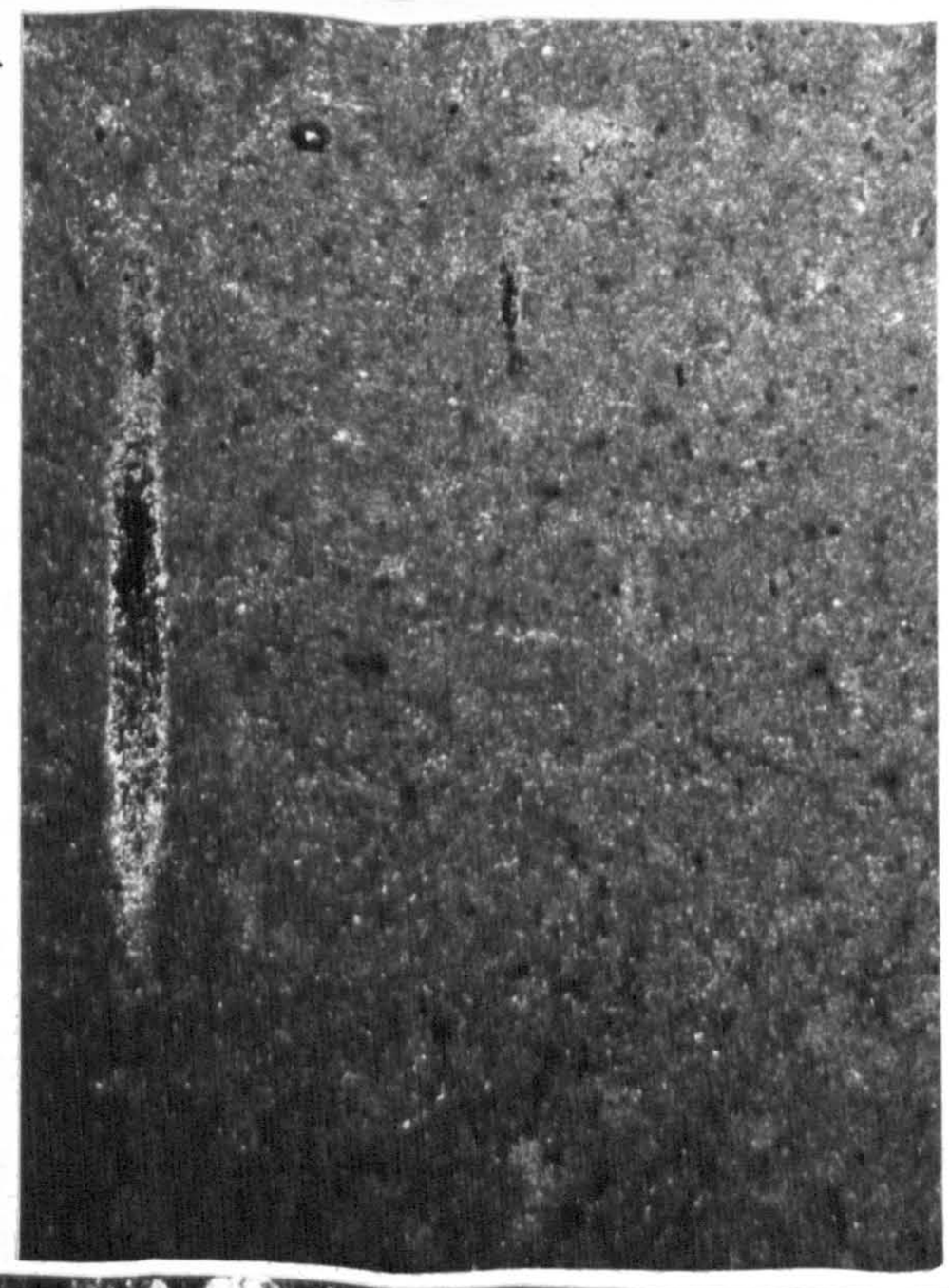
Fig 3.4

Gypsum pseudomorphs and internal sediments in cavity structures (PPL)

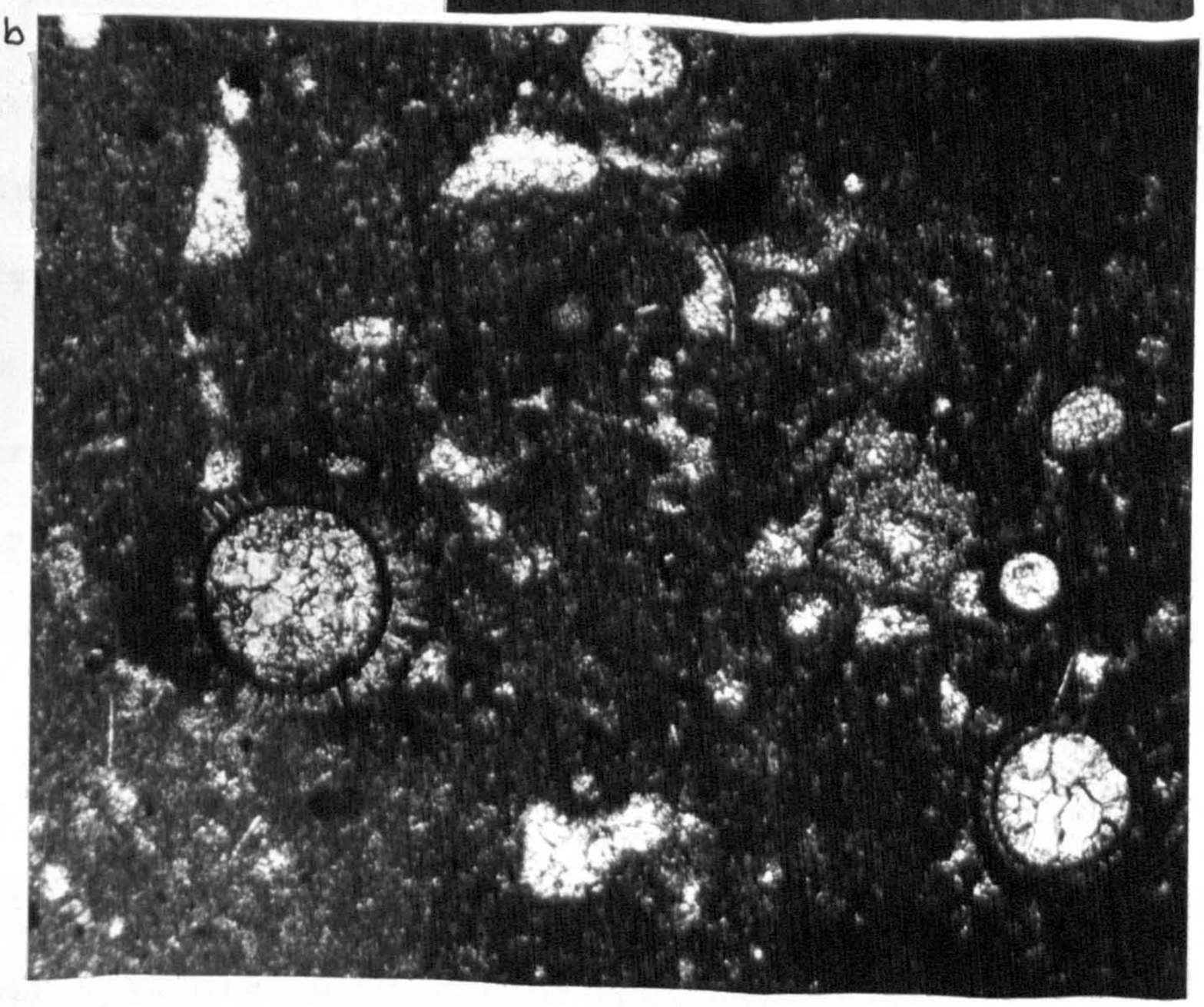
0.5mm

Danygraig,Risca.

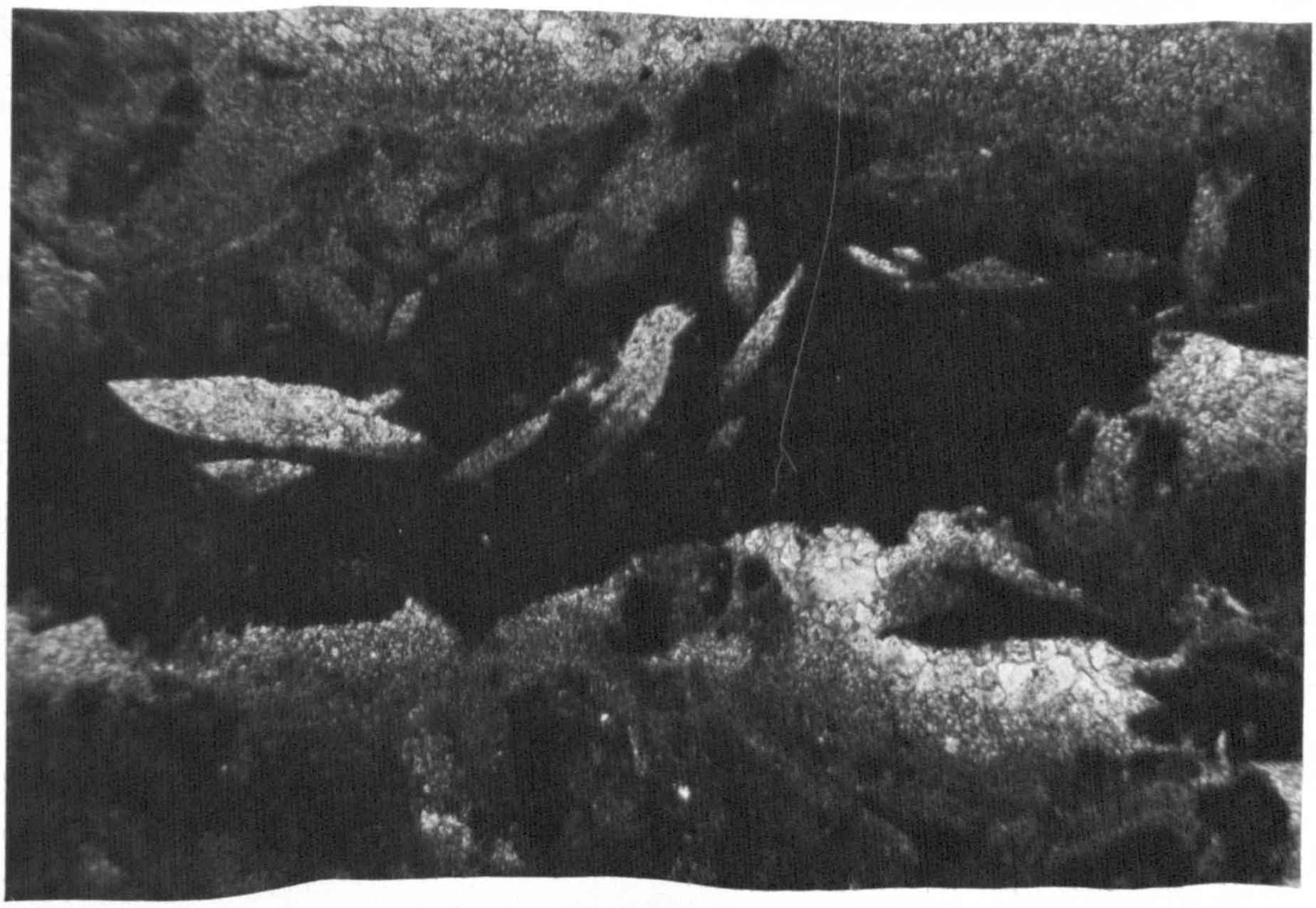
a



b



3.4



laminites. They commonly contain fine internal sediments showing geopetal distributions, with dolomite and/or calcite spar filling the remainder of the cavity (Fig. 3.4). Where dolomite is the filling material, it forms cloudy subhedral-euhedral crystals around the margins of the cavities, passing into clearer, coarser dolospar towards their centres. Commonly one large crystal occupies the entire central pore area. These crystals may show undulose extinction. Calcite is a less common cavity-fill and occurs pore-ward of the cloudy dolomite crystals.

Of limited importance are lozenge to irregular shaped structures, up to 500 μm long and filled with internal sediment and/or dolomite spar. They occur within dolomitic laminae or adjacent to cavity structures (Fig. 3.4), and are very similar in form to pseudomorphs after gypsum reported by several authors (e.g. West, 1964; Hudson, 1969; Tucker, 1976). The presence of internal sediment and preservation of form suggest early, near surface, pre-compactional dissolution and replacement of the gypsum.

Diagenetic pyrite occurs in the following forms, both within fine dolomicrite and coarser spars, (i) irregular masses (clusters) up to 750 μm maximum dimension; (ii) cubic crystals 6-150 μm side length; (iii) hexagonal crystals approx. 100 μm diameter and (iv) individual or clusters of lozenge shaped crystals up to 500 μm long dimension. The last form resembles the gypsum pseudomorphs described above, and has a similar distribution.

Raven (1983) has described similar diagenetic pyrite from the Oolite Group on the North Crop, including pyrite pseudomorphs after gypsum ('lenticular' forms), scattered cubes and clusters. She concluded that they formed during later diagenesis, but probably before the mid-Carboniferous (Raven, 1983).

To summarise the observations of transmitted light petrography, there are three or possibly four distinct phases of dolomite in the Danygraig sediments:

i) A fine, dense mosaic forming laminae or more massive micrites.

ii) A slightly coarser, less dense mosaic of generally anhedral crystals, commonly forming the matrix for coarse clasts of carbonate or non-carbonate material.

iii) Coarse subhedral to euhedral cloudy crystals, perhaps with clearer rims, occurring around the margins of cavities and as gypsum pseudomorphs.

iv) Dolospar forming the final fill of larger cavities (calcite may also occur in this form).

Cathodoluminescence reveals that (i) and (ii) have a uniform dull orange luminescence; (iii) has a blotchy luminescence; cloudy areas are dull orange and clear areas are an extremely dull orange or non-luminescent; the boundary between these areas is diffuse, giving the blotchy appearance; (iv) has an extremely dull luminescence or is non-luminescent; calcite has the same characteristics.

3.2.1 Interpretation of depositional environment of the Danygraig dolomicrites

Fig. 3.1 shows the sequence at Danygraig with the main sedimentary features and broad environmental interpretation, based on field and petrographic study and by comparison with modern and ancient analogues. Diagnostic features of tidal flat sediments have recently been reviewed by Shinn (1983a) and Wright (1984d), and these works provide the basis for the

present interpretation.

Supratidal sediments in the Danygraig sequence are identified by the following features. The presence of laminites, which are interpreted to be of cryptalgal origin due to their lateral continuity and undulose to domed geometry. The graded nature of some of the laminae and their clastic component suggest deposition of allochthonous material by storm processes.

Early cementation, or at least desiccation and the production of mudcracks and polygons, is suggested by the fractured and brecciated laminae and the presence of intraclasts and intraformational conglomerates. The common occurrence of laminoid and irregular fenestrae provides further evidence of a supratidal origin (e.g. Shinn, 1968, 1983b), being the products of shrinkage and expansion, gas bubble formation, air escape during flooding or wrinkles in algal mats (see Shinn, 1983a). The limited occurrence of pseudomorphed evaporites suggests that evaporite formation was not an important process. Petrography suggests that those gypsum crystals which did form were soon dissolved and replaced by internal sediment and/or dolomite spar. These observations suggest that the supratidal area suffered frequent flooding perhaps under a humid or seasonally arid climate. Similar conditions prevail today on the tidal flats around Andros Island in the Bahamas (Gebelein et al., 1980) and contrast with the arid tidal flats of the Arabian Gulf (see papers in Purser, 1973).

Further evidence for the prevailing climate and for the existence of a supratidal area comes from the occurrence of palaeosol horizons. They comprise nodular micrites (? calcretes) with clays and clay-dykes and include rootlet horizons. Wright has carried out much detailed work on the palaeosols of the Llanelly formation (e.g. Wright, 1982b, 1983; and in

Riding and Wright, 1981) and suggested, in broad terms, that they formed under a seasonally arid climate.

The tubular structures described earlier may also have an origin related to subaerial exposure, although they do not possess the characteristic features of root moulds (rhizocretions) or the burrows of soil dwelling animals described by Wright (1983). Similar tubular structures have been described from modern subtidal to supratidal sediments in Florida (included in the 'pseudo-bird's-eyes' of Shinn, 1983a) and in ancient supratidal storm layers (see Shinn, 1983a); their origin remains uncertain.

Intertidal and lagoonal sediments in the Danygraig sequence are characterised by the general lack of lamination, a typical feature of intertidal sediments due to the homogenisation by burrowing organisms (Shinn, 1983a). The upper intertidal zone is likely to be transitional with the supratidal and some preservation of lamination and fenestrae might be expected, however, the distinction between upper intertidal and supratidal sediments is subtle and has not been made. Units comprising massive micrite, clayey-micrite and thin shales, and which appear bioturbated, are tentatively interpreted as subtidal, representing deposition in a protected lagoonal environment. The lack of evidence for tidal channels in the studied section suggests deposition on Andros Island - type passive tidal flats (see Tucker, 1985a for review), which escaped the full force of storm winds and waves. Wright (1984d) has suggested that prograding tidal flats may be typified by the absence of tidal channels.

In summary, the Danygraig sediments appear to have formed in a fairly restricted depositional setting, in that there is an absence of the open-marine and shoal bioclastic and oolitic grainstone-packstone facies known

to exist elsewhere in the Dinantian of South Wales. The sediments comprise a series of shallowing-up units, with the development of soil horizons during emergence, and probably represent regressive or progradational events. Dolomite forms a major part of the sequence, as is discussed further below. The poor development of evaporites and the presence of plant rootlet horizons and soils suggest that the climate was relatively humid, perhaps seasonally arid.

3.2.3 Paragenesis of the Danygraig dolomicrites

The fine preservation of sedimentary structures such as fenestrae, algal laminae, gypsum pseudomorphs, graded-bedding, and tubular structures is characteristic of these sediments. It suggests that dolomitisation may have occurred during early diagenesis, perhaps by initially selective and partially mimetic replacement. The clear sparry dolomite which fills cavity structures and forms gypsum pseudomorphs may, by its association with geopetal internal sediments and lack of inclusions, be interpreted as a cement phase.

The distinct cathodoluminescent character of dolomicrites compared to the sparry cavity-filling dolomite, and the 'intermediate' character of cloudy marginal-cavity-filling crystals suggest a geochemical differentiation of dolomite types (see discussion of C.L. in Section 3.3.4.vi). This may or may not represent a genetic differentiation. The cloudy marginal-cavity-filling crystals are interpreted as representing cement overgrowths on dolomicritic internal sediment.

There are many modern and ancient examples of tidal flat dolomite (see Chapter 1, and Shinn, 1983a). Of these, the most appropriate modern

analogue to the Danygraig example appears to be the western Andros Island tidal flats.

Shallow, subsurface dolomites in the prograding, passive tidal flats (see Tucker, 1985a) of south-west Andros Island have been described by Gebelein et al. (1980). The sediments are aragonitic muds with minor magnesium calcite skeletal material. Dolomite occurs as calcium-rich, poorly ordered rhombs in subtidal, intertidal and supratidal sediments. The dolomite is most abundant beneath hammocks (beach ridges) where freshwater lenses and marine-groundwater/freshwater mixing-zones are developed, although the relationship between dolomite and mixing-zones is uncertain (Gebelein et al., 1980). Dolomite of probable evaporitic origin, occurs as crusts on algally laminated and mud-cracked supratidal sediments, and has been described from the active-type tidal flats of northwest Andros Island (see Shinn et al., 1965; Shinn et al., 1969; Tucker, 1985a).

The Andros Island tidal flat dolomites provide a good analogue for the Danygraig dolomicrites except that the former only form a minor (up to 50% in crusts) component of the sediments. However, with subsequent diagenesis it is possible that the Andros dolomites would become ordered and be augmented to produce a more complete dolomite replacement (see, for example, Morrow, 1982b; McKenzie et al., 1980; Gregg and Sibley, 1984). If the paragenesis of the Danygraig sediments involved an initial, incipient calcian-dolomite phase, there is no petrographic evidence to show this, at least at the light-microscope level. The original mineralogy of the fine-grained sediments can not be determined from petrographic study.

The presence of diagenetic pyrite indicates that reducing conditions occurred in the presence of organic material, dissolved marine sulphate and Fe^{2+} at some time during the diagenesis of these sediments (Berner, 1970,

1984). The exact timing of pyrite formation has not been established; however, its cross-cutting relationship with dolomicrite and dolospars suggests it formed after dolomitisation. The requirement for dissolved marine sulphate, organic material and Fe^{2+} suggests it formed during relatively shallow burial, whilst still in contact with marine porewaters and before complete oxidation of organic matter.

The apparently random distribution of pyrite, through subtidal, intertidal and supratidal units suggests that reducing conditions developed fairly uniformly. This contrasts with the tide-level control exhibited by Andros Island tidal flats (Shinn et al., 1969) where reducing conditions only develop in sediments permanently below the water table. Again, this supports the contention that pyrite formed essentially after deposition, during shallow burial.

3.3 Pervasive stratal dolomites

Petrographic description of pervasive dolomites and their host limestones

The stratigraphic and regional distribution of pervasive dolomites has been described in Chapter 2.

To the south and west of the Taff Gorge, pervasive dolomite bodies pass into partly dolomitised or undolomitised limestones and it is from this 'transitional area' that the following information is obtained:

(a) the diagenesis of limestones

(b) the relative timing of dolomitisation

and (c) the sequential development of dolomite mosaics

3.3.1 The Brofiscin Oolite

Of specific interest is the Brofiscin Oolite, within the Black Rock Group (see Fig. 2.4), which, because of its distinctive nature can be readily traced from the limestone sequence into pervasive dolomites.

3.3.1.i Depositional grains in the Brofiscin Oolite

(a) Ooids

The principal depositional grains in the Brofiscin Oolite are ooids. Spherical, non-spherical and superficial forms occur. Compound ooids and intraclasts are less important. Spherical ooid diameters are typically in the range 0.2 to 0.5 mm, but smaller (peloidal) grains also occur, usually defining vague, finer-grained laminae within the oolite. Many of the ooids have been micritised, though they may retain evidence of radial and concentric fabrics (see Fig. 3.5a-c). Ooid cortices are usually complete; however some ooids appear to have lost portions of their outer laminae (Fig. 3.5a) and occasionally large parts of the ooid are apparently missing (Fig. 3.5c). Deformed ooids (spastoliths) also occur and in places adjacent ooids appear to be linked together by portions of their mutually deformed cortices (see Fig. 3.5a-c). Some of these deformation features appear to have occurred before the precipitation of fringing cement (incidentally, almost always type 1, see below), whereas more obvious compaction features (the spalling of outer laminae and grain fracture) occur after the fringing cements developed.

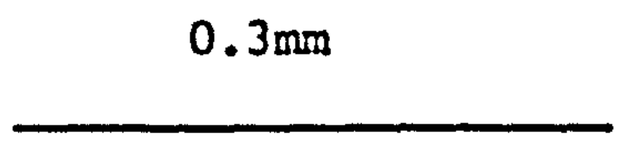
Similarly deformed ooids have been illustrated or described by many authors, for example Scholle (1978, figs. on pages 118 and 207), Kettenbrink and Manger (1971), Conley (1977), Heckel (1983), Wilkinson, Buczynski and Owen (1984) and have variously been interpreted as due to

Fig 3.5

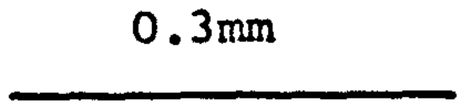
a. Brofiscin Oolite showing radial-concentric fabric in ooids, delicate compaction-dissolution structures and type 1 fringing cement (PPL)



b. detail of a. (PPL)

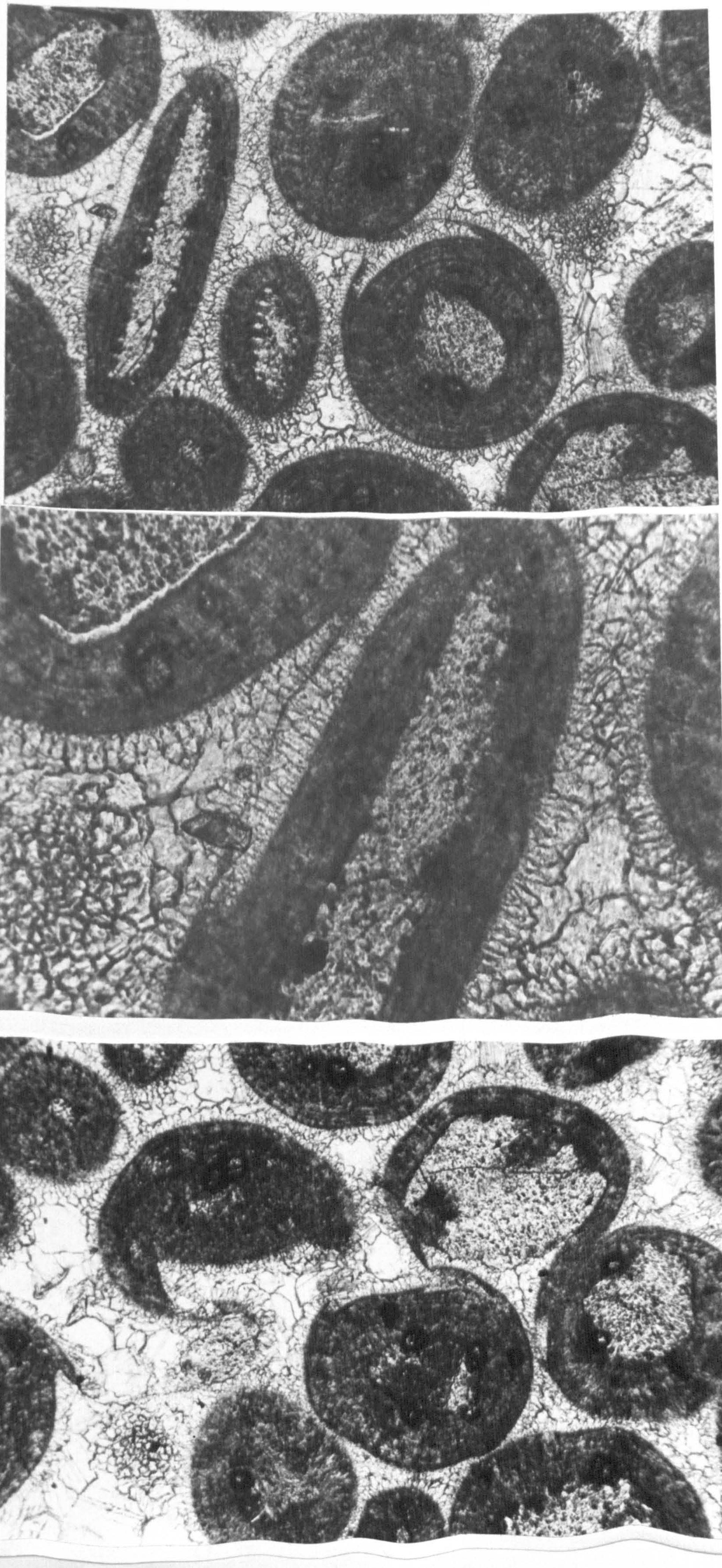


c. more intense compaction-deformation of ooids, note also scattered dolomite rhombs with dense rims (PPL)



Brofiscin Oolite, Brofiscin quarry.

a



b

c

compaction and selective dissolution.

An early dissolution origin is nevertheless preferred over a later compaction-shearing process. This is particularly the case for the more delicate features illustrated in Fig. 3.5b, which appear to have been overgrown by fringing cements. It is not difficult to envisage these features developing,during subsequent compaction, into the more deformed 'spastolithic' structures seen in Fig. 3.5c. See further discussion in "Type 1 fringing cements" below. Ooids have a uniform dull to medium cathodoluminescence, which is locally punctuated by small, brighter dolomite rhombs (see section v). A vague concentric lamination may be visible and nuclei are usually distinguishable.

(b) Bioclasts

Echinoderm fragments are an important component of the Brofiscin Oolite. Plates and spines occur both as individual grains and as the nuclei of ooids. Foliated pseudopunctate and prismatic brachiopod shell fragements also occur. Bivalves are less common and are usually preserved as delicate micrite envelopes, with calcite spar filling the main body of the shell. Fragments of fenestrate bryozoans commonly form the nuclei of ooids. Foraminifera are rare components.

Bioclasts typically have a dull to medium, uniform or patchy cathodoluminescence. In the case of echinoderm fragments, the micritic calcite which partially or completely fills the pore-system has a dull to medium luminescence, whereas the grain itself is non-luminescent.

(c) Intraclasts

Rare intraclasts within the Brofiscin Oolite comprise muddy, bioclastic wackestones. Such lithologies are typical of the subjacent

Barry Harbour Limestone, subtidal open-shelf facies. This would suggest that the Barry Harbour Limestone was at least partially lithified at the time of Brofiscin Oolite deposition.

3.3.1.ii Fringing cements

The morphology of cements which fringe depositional grains in the Brofiscin Oolite appears to be quite variable. The different types appear to have a patchy distribution, even within a single thin section. Most of the described material was collected from the Brofiscin Oolite at Brofiscin Quarry, but additional samples come from Wenvoe (see Chapter 2 for localities). The terminology used in describing the cements is after Folk (1965) and Kendall and Broughton (1978).

(a) Type 1 fringing cement

Isopachous rims up to 30 μm thick occur around depositional grains. They comprise crystals (3-10 μm wide, 15-30 μm long) which may be founded upon smaller equant crystals (< 3 μm diameter). The crystals may be parallel-sided or may thicken away from the substrate. Crystal terminations are triangular, rhombic or locally square- or slightly round-ended. They have unit extinction (mostly length fast), appear relatively inclusion-free and have uniform, very dull cathodoluminescence. The cement commonly occurs between grains, and has been fractured or spalled-off with the outer laminae of ooids during compaction.

Discussion, type 1 cement

The development from many small, equant crystals to fewer larger

columnar crystals with long axes normal to substrate and the isopachous geometry suggests formation around fluid-filled (phreatic) pores. The cement appears to have formed before significant burial-compaction, in a nearsurface diagenetic environment.

Although on a rather small scale comparatively, the cement does not show any of the features thought to be typical of replacement mosaics, for example Mazzullo (1980; replacement of acicular aragonite), Kendall and Tucker (1973) Kendall (1977) (replacement of acicular precursors and crystallite coalescence respectively, but c.f. Sandberg, 1985; Kendall, 1985); Braithwaite (1979); speleothem fabrics) and Lohmann and Meyers (1977; replacements of high-magnesium calcites). The optic-axis orientations (mostly length-fast) probably have no replacement significance (see Dickson, 1978). The present low-magnesium calcite composition and bladed to fibrous habit of the cement crystals may, therefore, be original. This contrasts with the generally accepted relationship between composition and morphology, e.g. Bricker (1971), Schroeder (1973), Lindholm (1974), Folk (1974), Lahann (1978), i.e. that low-magnesium calcite crystals are typically equant (and form from meteoric or dilute basinal fluids) and high-magnesium calcite and aragonite crystals are fibrous (and precipitate from seawater or hypersaline brines). Notable exceptions have been recorded. For example, fibrous low-magnesium calcite is recorded from some meteoric vadose environments (Longman , 1980; Wright, 1984c) where rapid degassing of CO_2 (e.g. Hanor, 1978) results in enhanced 'c-axis growth' of crystals because of increased CO_3^{2-} supply by dissociation of HCO_3^- (Given and Wilkinson, 1985). Conversely in deep-cold or cool-temperate marine environments dissolved CO_2 may be elevated, producing a low degree of supersaturation and lower crystal growth rates. The result

is a cement comprising equant crystals of high-magnesium calcite. Given and Wilkinson (1985) stressed the importance of crystal growth rate related to CO_3^{2-} availability (see also Lahann, 1978), in addition to the Mg^{2+}/Ca^{2+} ratio of precipitating fluid, in determining crystal compositon and morphology. They also showed that the distribution coefficient $D^{Mg}_{Calcite}$ may vary with CO_3^{2-} availability, so that the composition of crystals may or may not relate to the Mg^{2+}/Cg^{2+} ratio in the ambient fluid (see fig. 11 in Given and Wilkinson, 1985).

Type 1 cements clearly formed in an early, pre-compactional, phreatic diagenetic environment. The close association of type 1 cements with deformed ooids, and interpreted dissolution features suggests that the environment may have been influenced by non-marine (i.e. meteoric) waters. Perhaps introduced into the marine sediments at times of local emergence of the oolite shoals. The fibrous habit of the cement might be explained in terms of an enhanced supply of CO_3^{2-} (see Given and Wilkinson, 1985) due to the local dissolution of oolitic laminae. Halley and Harris (1979) have suggested a similar autochthonous origin for meteoric cements in the vadose and upper phreatic zones of Joulters Cays oolites in the Bahamas. Here, leaching of ooids is on a very fine, lamella scale comparable to the delicate features seen in the Brofiscin Oolite.

The development of type 1 cements preferentially around and in intimate association with less 'advanced' deformation features (see Fig. 3.5a, b) is intriguing. A possible explanation might be that local dissolution of ooids by meteoric waters led to rapid precipitation of fibrous cement around certain grains, choking-up the dissolution-deformation site. Elsewhere the process of deformation was able to continue relatively unhindered, perhaps developing into burial-compaction.

(b) Type 2 fringing cement

This cement forms isopachous rims, up to 100 μm thick, around grain margins or completely fills intergrain pore space. The cement around any single grain shows a marked thickening from points of contact with adjacent grains into pore spaces (see Fig. 3.6). This geometry results from the development of compromise boundaries where cements from adjacent grains meet. These boundaries extend as approximately straight lines, between grain-grain contacts into neighbouring pores, producing a polygonal pattern. In plane polarised light the cement has a fibrous appearance due to fine substrate normal inclusions. Etched thin sections reveal acicular to columnar forms, up to 12 μm wide and 100 μm long, and smaller acicular 'sub-crystals' (approx. 3 μm x 20 μm). Long axes are oriented normal to substrate and the crystals may have rhombic to triangular terminations but more commonly the outer (poreward) boundary of the cement is irregular and pitted.

Viewed under crossed polars, the crystals are seen to have unit extinction, with extinction positions parallel to crystal long-axes. Thus, cement rims on convex grain surfaces have a radial-fibrous appearance, with swinging extinction from one crystal to the next. Some of these cement crystals appear to be in optical continuity, with more equant crystals occupying the adjacent 'pore-space'.

Discussion of type 2 cements

The fibrous appearance of the cement and the occurrence of polygonal cement boundaries or sutures favour a marine-phreatic origin (Longman, 1980).

For the reasons discussed above (3.3.1.ii.a), marine cements are typically columnar or acicular and composed of high-magnesium calcite or

Fig 3.6

a. Brofiscin Oolite type 2 fringing cement,note polygonal boundaries (PPL)

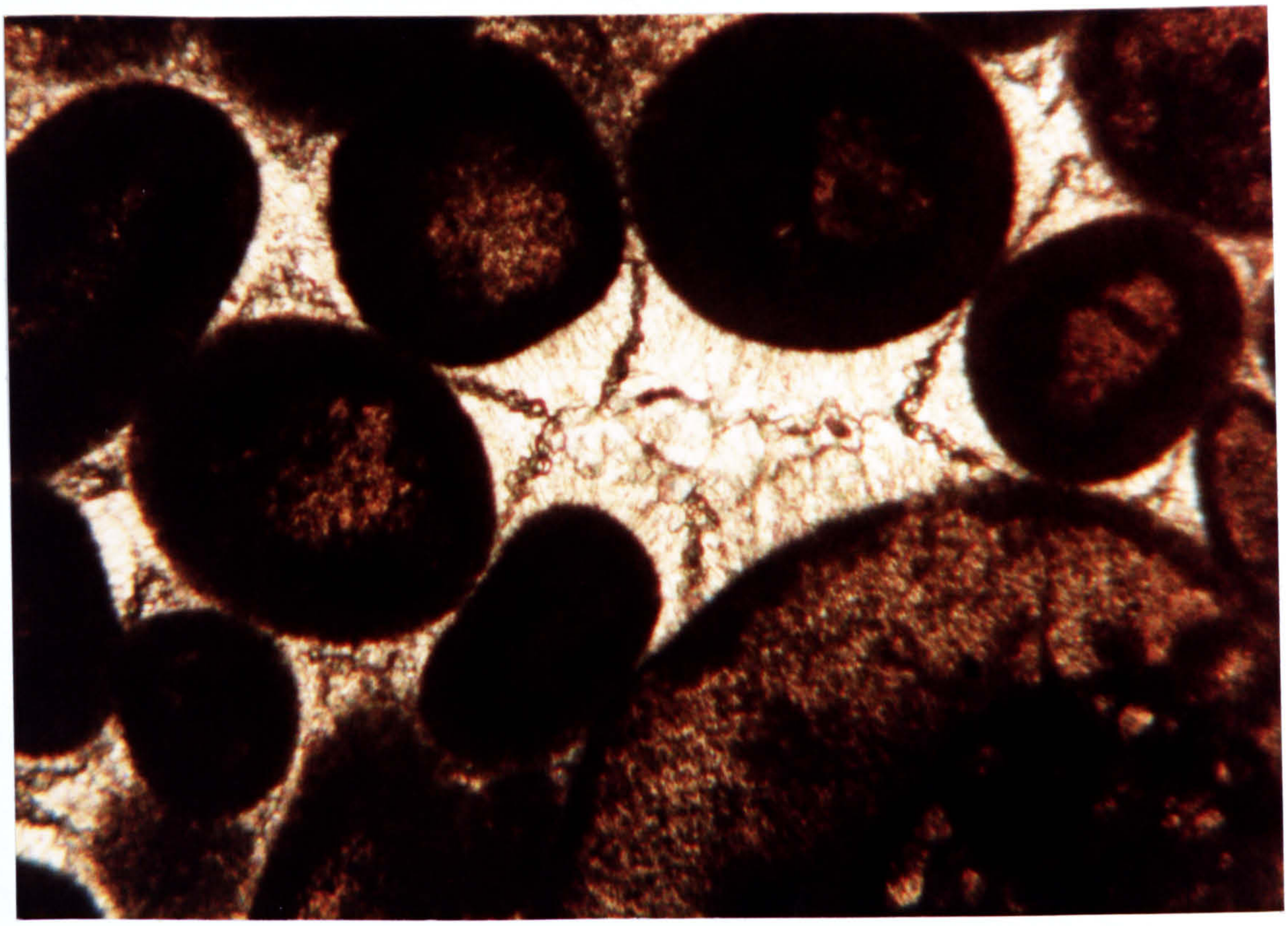
0.4mm

b. types 3 & 4 fringing cements, note equant calcite crystals and scattered type A & B dolomite rhombs, pore-filling poikilotopic calcite (XPL)

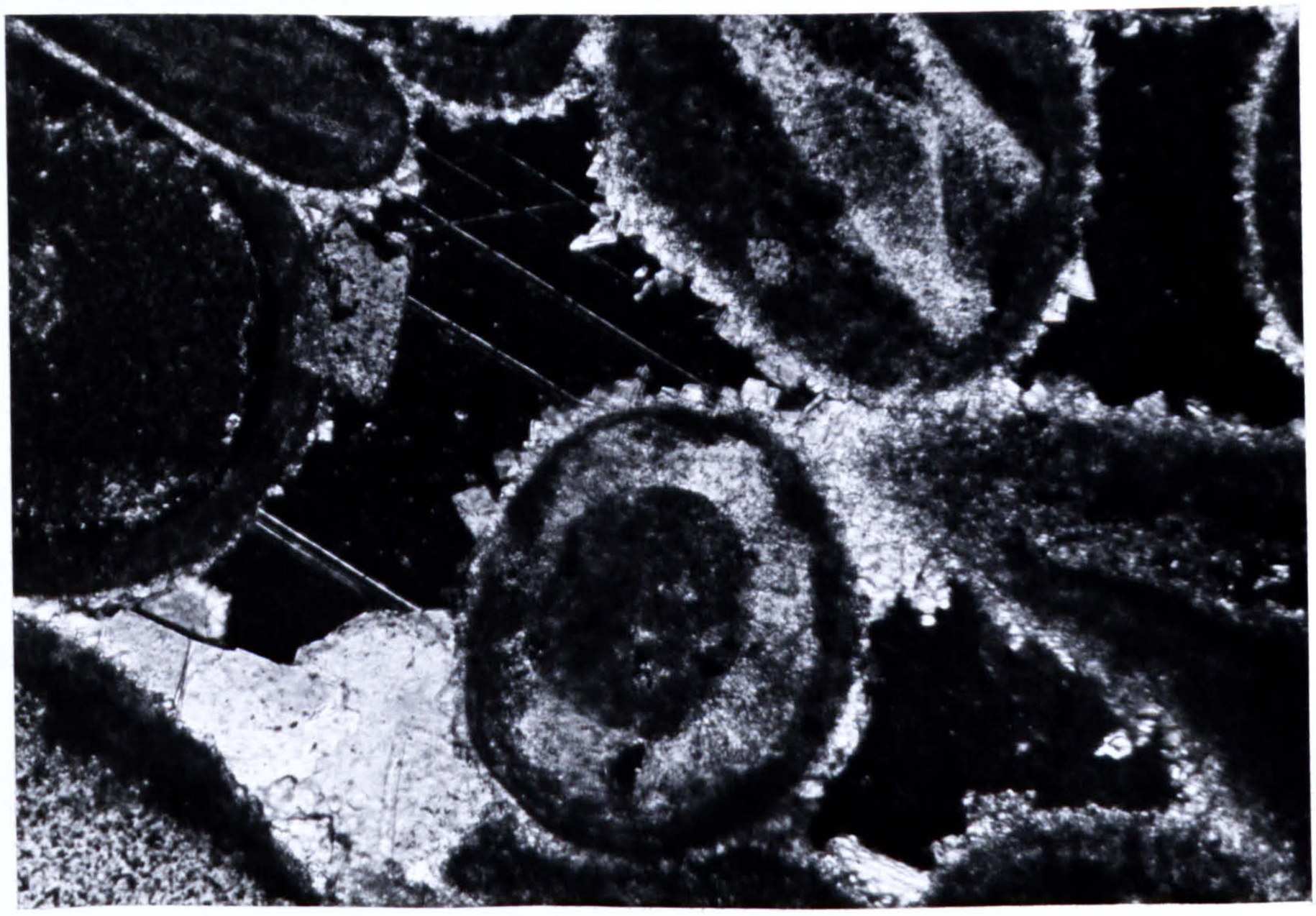
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Brofiscin Oolite, Brofiscin quarry.

a



b



aragonite. The often irregular outer boundaries of the fibrous cements suggests partial leaching prior to their replacement. Polygonal boundaries in cements of marine-phreatic origin have been described and/or illustrated by many authors. For example, Marlowe(1971), from high-magnesium calcite cements on Aves Swell seamount in the Caribbean. The features are very well developed in acicular aragonite cements around ooids from the Yellow Bank area of the Great Bahama Bank (see fig. 29 in Halley, Harris and Hine, 1983). Shinn (1975) compared Holocene sediments with the Cambrian of New York (see also Mazzullo, 1977), and Longman (1980) provided an example from the Jurassic Smackover Formation of Louisiana to show that the criterion is applicable to ancient as well as modern sediments. Polygonal sutures have also been described from meteoric-phreatic cements in the Joulters Cays Oolite, by Halley and Harris (1979), but are not as well defined as the marine examples.

(c) Type 3 fringing cement

Type 3 fringing cement forms a non-isopachous rim around depositional grains, comprising equant to rhombic calcite crystals typically 3.0 to 30 μm diameter (long axes in the case of rhombs) but locally up to 100 μm (Figs. 3.6b, 3.7a). Calcite crystals have unit extinction and are non-cathodoluminescent. Where these crystals rim larger pores (200 μm or more pore diameter) they are succeeded by coarse, poikilotopic calcite (Figs. 3.6b, 3.7a, b). Some of this coarse calcite has grown syntaxially on echinoderm fragments and is discussed further below. In smaller pores, type 3 cement coalesces and fills the entire pore space as a drusy or equigranular mosaic (Fig. 3.7a). It occurs between interpenetrating grain contacts indicating its pre-compaction origin (Fig. 3.7c).

Fig 3.7

a. type 3 & 4 fringing cements, note concentration of type 4 at grain contacts and echinoderm-syntaxial spar (E) (XPL)

0.5mm

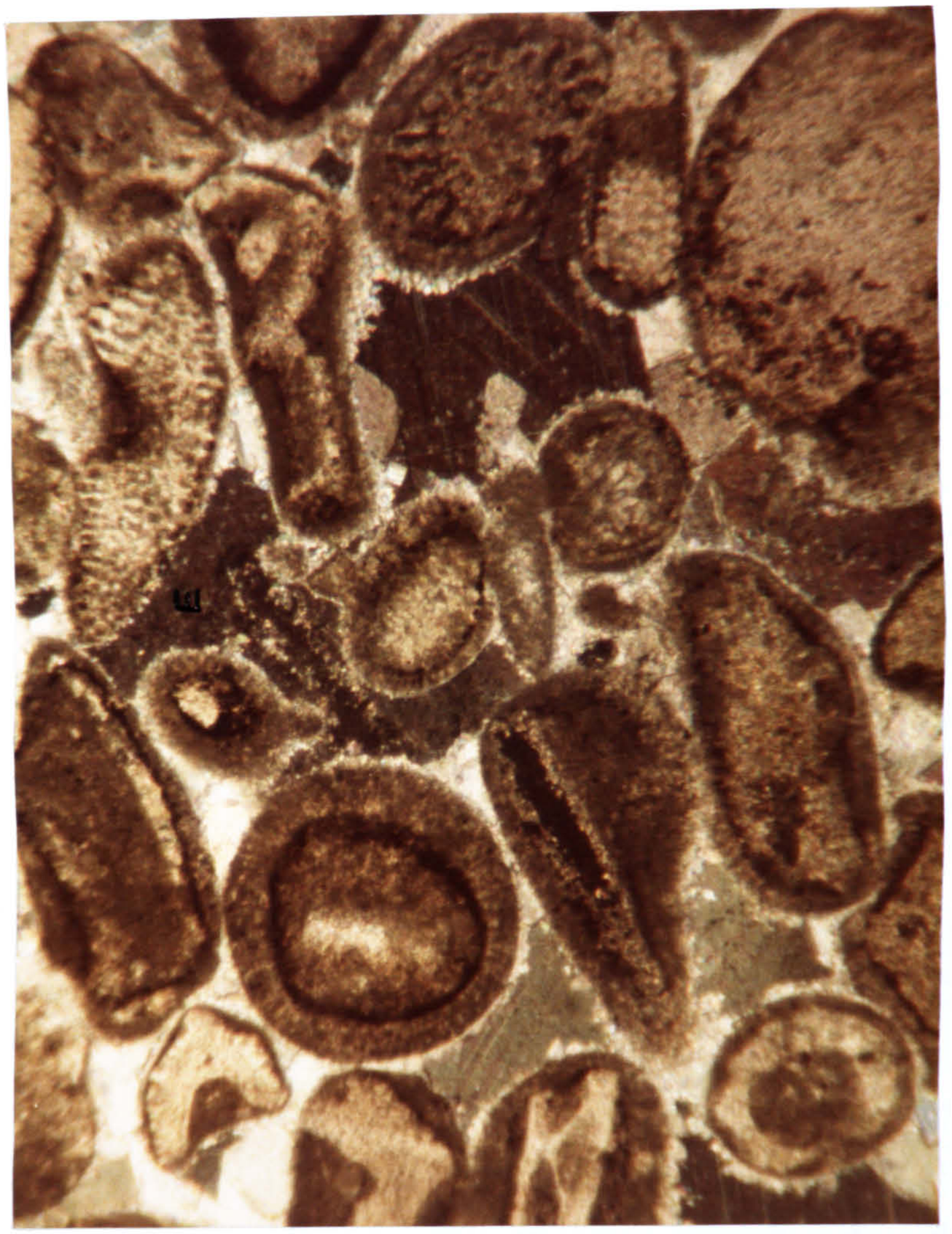
b. detail of a, showing meniscus geometry of type 4 cement (XPL)

0.2mm

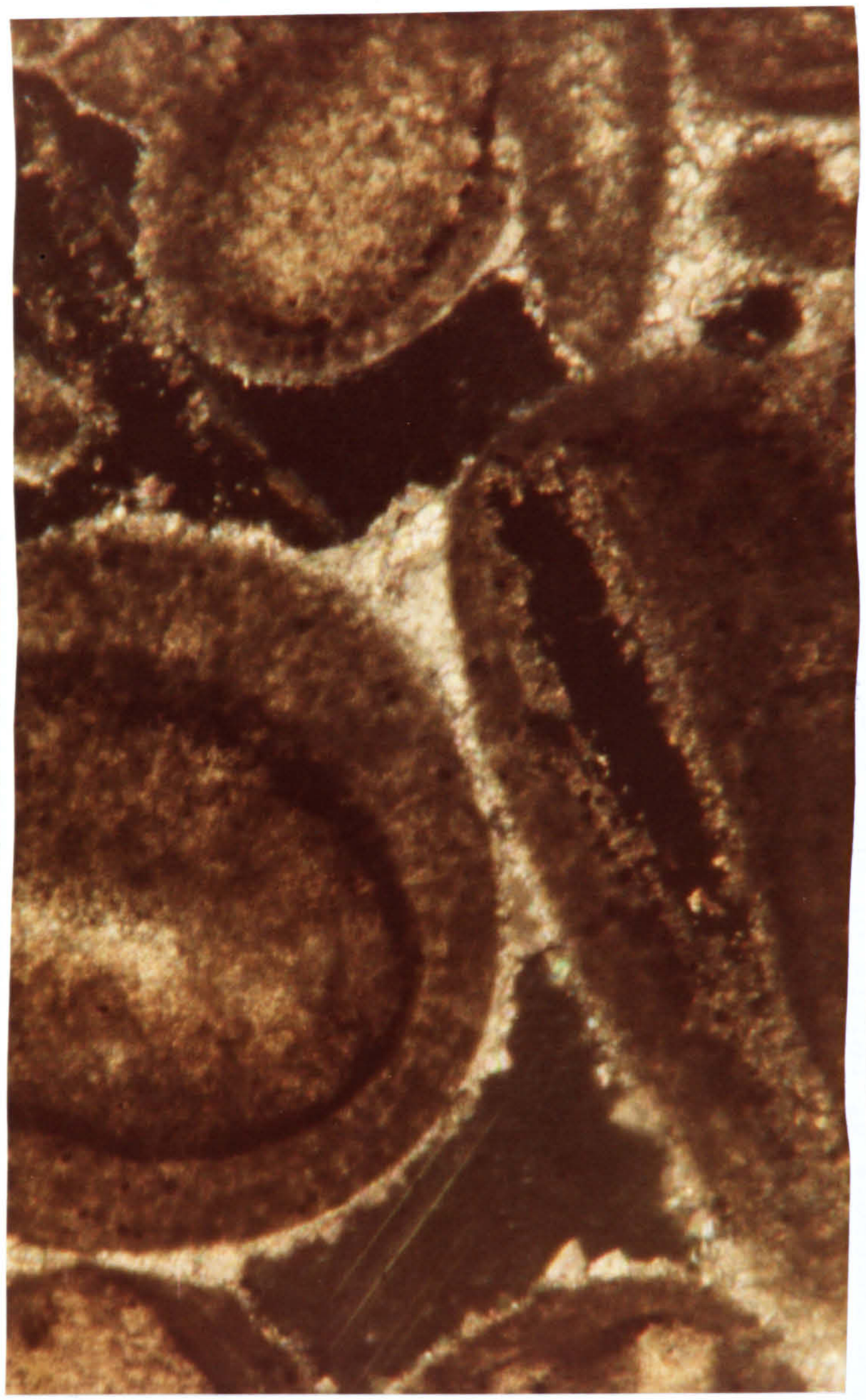
c. Brofiscin Oolite showing post-early cement grain fracture and pressure solution (compare to fig. 322 of Bathurst, 1975) (XPL)

0.5mm

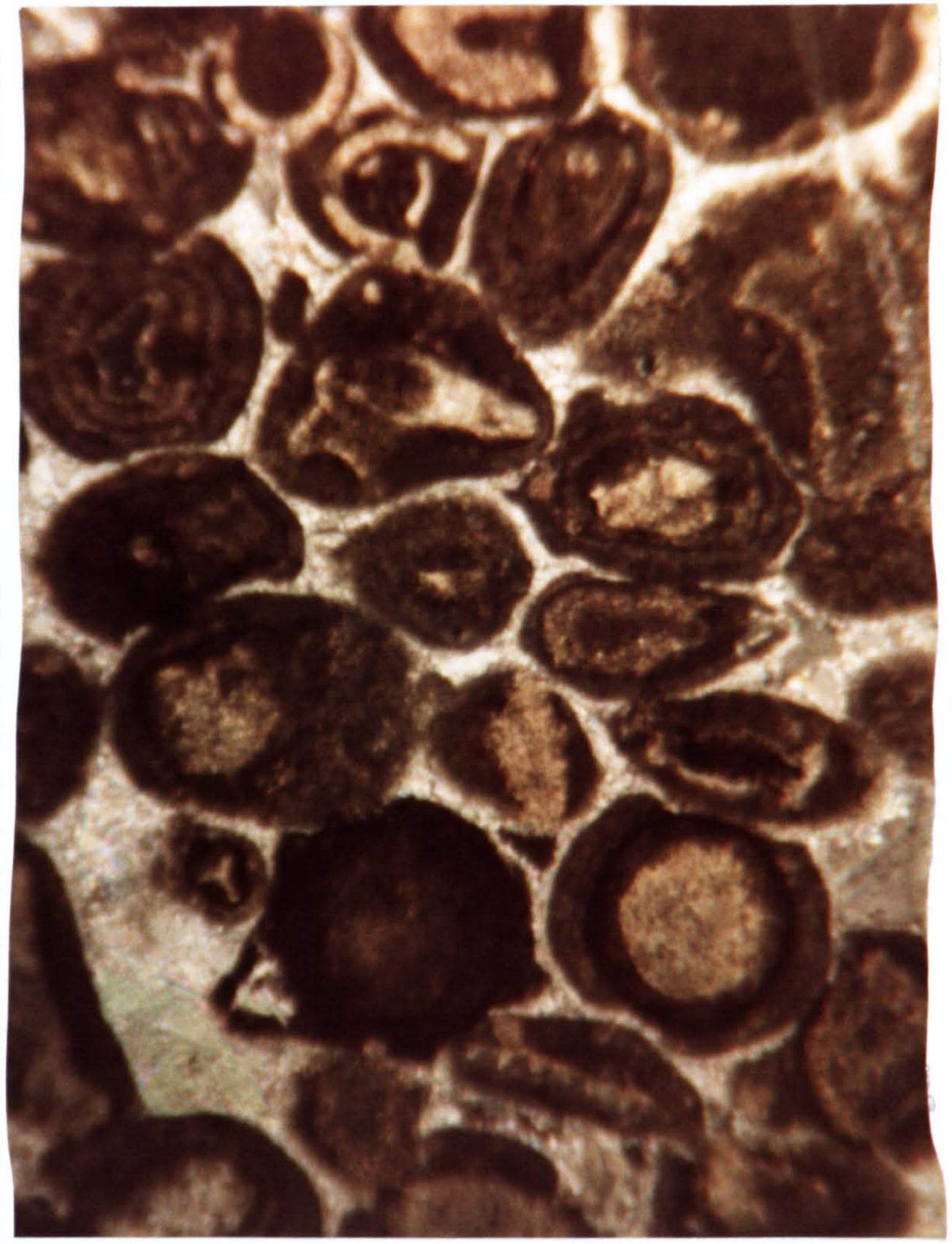
Brofiscin Oolite, Brofiscin quarry.



a



b



c

Discussion of type 3 cements

A nearsurface origin for this equant calcite cement is indicated by its pre-compactional, grain-fringing distribution. Similar early, equant low-magnesium calcite cements are typical products of the meteoric-phreatic diagenetic environment (see Halley and Harris, 1979; Longman, 1980) and the fluid-compositional control on their distinctive morphology has already been discussed (3.3.1.ii.a). The cements described here are very similar to those described by Halley and Harris (1979) from the oolitic sediments of Joulters Cays, Bahamas. They represent the 'even-style' of meteroic cementation (Dunham, 1971). Ancient examples of this cement typically have developed into drusy mosaics by continued cementation (e.g. Friedman and Kohesar, 1971; Muller, 1971; examples in Bathurst, 1975; and Longman, 1980) and are comparable to those in the smaller intergranular areas of the Brofiscin Oolite. Examples where only fringes developed, preserving much intergranular porosity are illustrated by Scholle (1978) from the Mississippian Ste. Genevieve Limestone (p. 163) and the Oligocene Suwannee Limestone (p. 165).

(d) Type 4 fringing cement

This cement has a limited distribution, occurring only at or close to grain contacts at points of pore restriction (see Fig. 3.7b). Although not strictly a 'fringing' cement it is a first generation, pre-compaction cement as defined by Bathurst (1971a).

The cement has an homogeneous appearance, comprising single or a small number of roughly equant crystals (see Fig. 3.6b). It commonly has a curved surface, concave towards 'pore' interiors, creating a meniscus effect (see Fig. 3.7b). Type 4 cement is often closely associated with type 3 cement, and the latter may overgrow the surface of the former,

modifying its meniscus appearance (see Fig. 3.6b). Clearly, where type 3 cement is very well developed, type 4 may be modified beyond recognition.

Discussion of type 4 cements

'Uneven-style' meteoric cements have been described by Dunham (1971) who showed that they form in vadose pores, mimicking the water-air meniscus which forms near grain contacts or in the corners of pores, where water is held by capillarity. Schroeder (1973) described examples which clearly succeed marine cements, indicating that the Pleistocene reef rocks in which they occur became exposed to meteoric water. Halley and Harris (1979) and Halley, Harris and Hine (1983, fig. 31) illustrated meniscus cements from the Recent oolites of Joulters Cays, Bahamas, where the processes of formation are still in progress. Holocene dune sands from New Mexico offer a further example of recent meniscus cements (see Scholle, 1978, p. 160).

As predicted by Dunham (1971), meniscus cements are uncommon in ancient rocks because they are easily masked by subsequent cementation. In the Brofiscin Oolite, this is seen where type 3 phreatic cements overgrow meniscus cements. The latter are best preserved where poikilotopic syntaxial overgrowths from echinoderm fragments occur. These overgrowths may have acted as an early cement competing with the meteoric-phreatic fringing forms, although they clearly post-date fringing cement in many cases (see below).

Gravitational cements, also characteristic of vadose zone cementation, as described by Muller (1971), have not been observed in the Brofiscin Oolite.

3.3.1.iii Other Features in the Brofiscin Oolite

(a) Syntaxial overgrowths on echinoderm fragments

Syntaxial overgrowths on echinoderm fragments are a common mode of cementation in the Brofiscin Oolite. The faintly ferroan calcite cements can readily be distinguished from their host fragments because the latter are typically cloudy due to the partial or complete filling of their pore-systems with fine micritic calcite. The clear overgrowths commonly abut type 3 and 4 cements and in places these cements appear to have partially grown on to the echinoderm fragments themselves (Fig. 3.8a).

Type 3 fringing cements often appear less well developed around those parts of grains bordering syntaxial-overgrowths suggesting competitive growth (see Fig. 3.8a). In many cases however, early cement rims and the outer parts of depositionnal grains (ooids in particular) have been fractured due to compaction before precipitation of syntaxial overgrowths. Dolomite crystals (of type B, see section 3.3.1.iv) which are in contact with syntaxial overgrowths often have etched or pitted surfaces, these irregularities have been filled with echinoderm-syntaxial cement (see Fig. 3.8b). That syntaxial overgrowths developed at different rates and at different times relative to compaction is demonstrated where smaller grains with their syntaxial overgrowths are enclosed within syntaxial overgrowths on larger grains.

Under cathodoluminescence, echinoderm fragments have a patchy dull luminescence within a generally non (or very dull) luminescent matrix. The luminescent areas correspond to areas of micritisation within the echinoderm fragments. Syntaxial overgrowths appear non-luminescent, as do the early fringing cements.

Discussion of syntaxial overgrowths on echinoderm fragments

The overgrowths described above are clearly of the passive cement fill type (e.g. Evamy and Shearman, 1965, 1969; Freeman, 1971; Bathurst, 1975 p.

Fig 3.8

a.type 3 & 4 fringing cements,note pore-bridging geometry (at left) and later syntaxial overgrowth cement on echinoderm fragment (XPL)

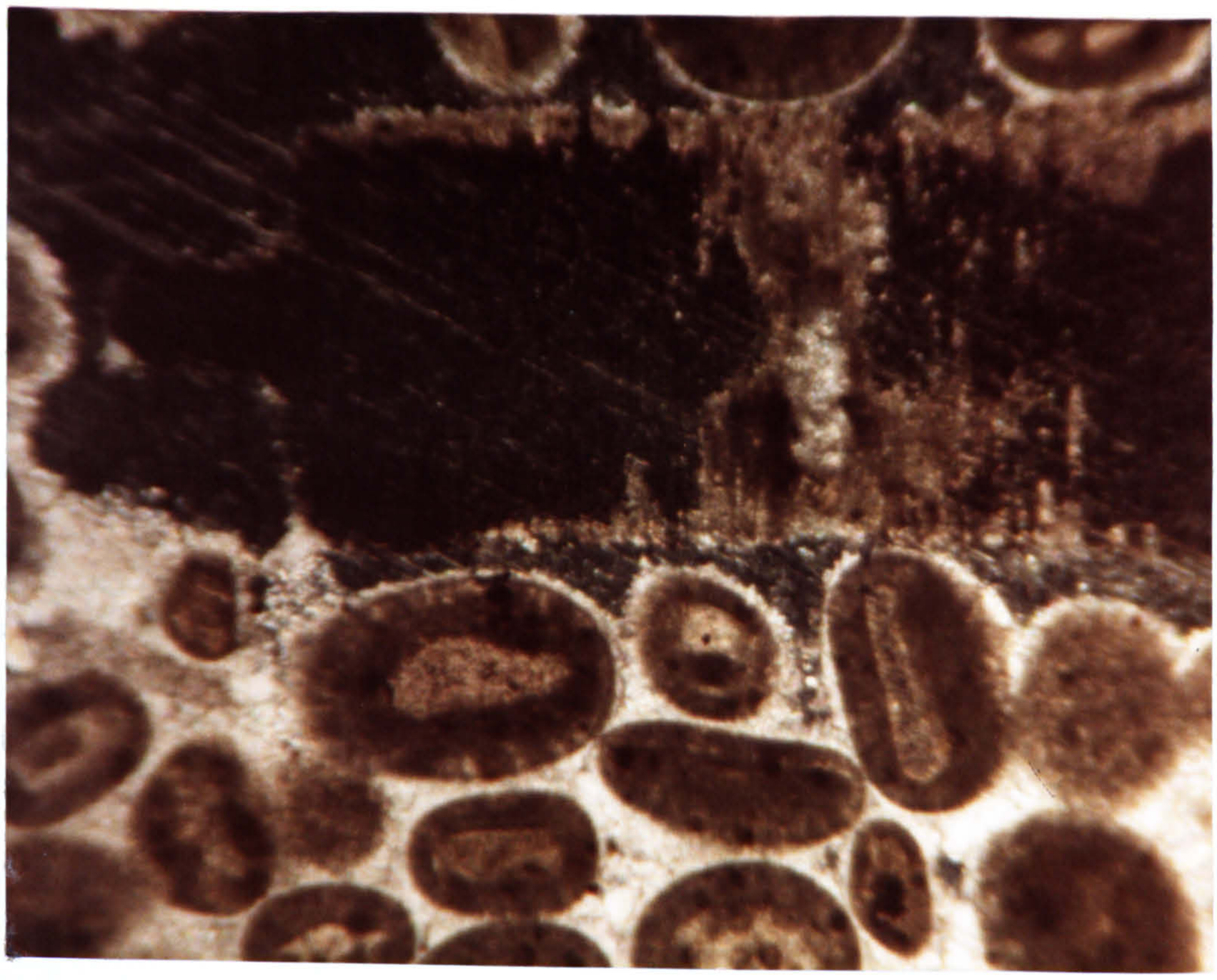
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b. type B dolomite rhombs with etched or pitted surfaces, indicating partial dissolution prior to precipitation of echinoderm-syntaxial cement, note also the scattered type A dolomite rhombs (PPL)

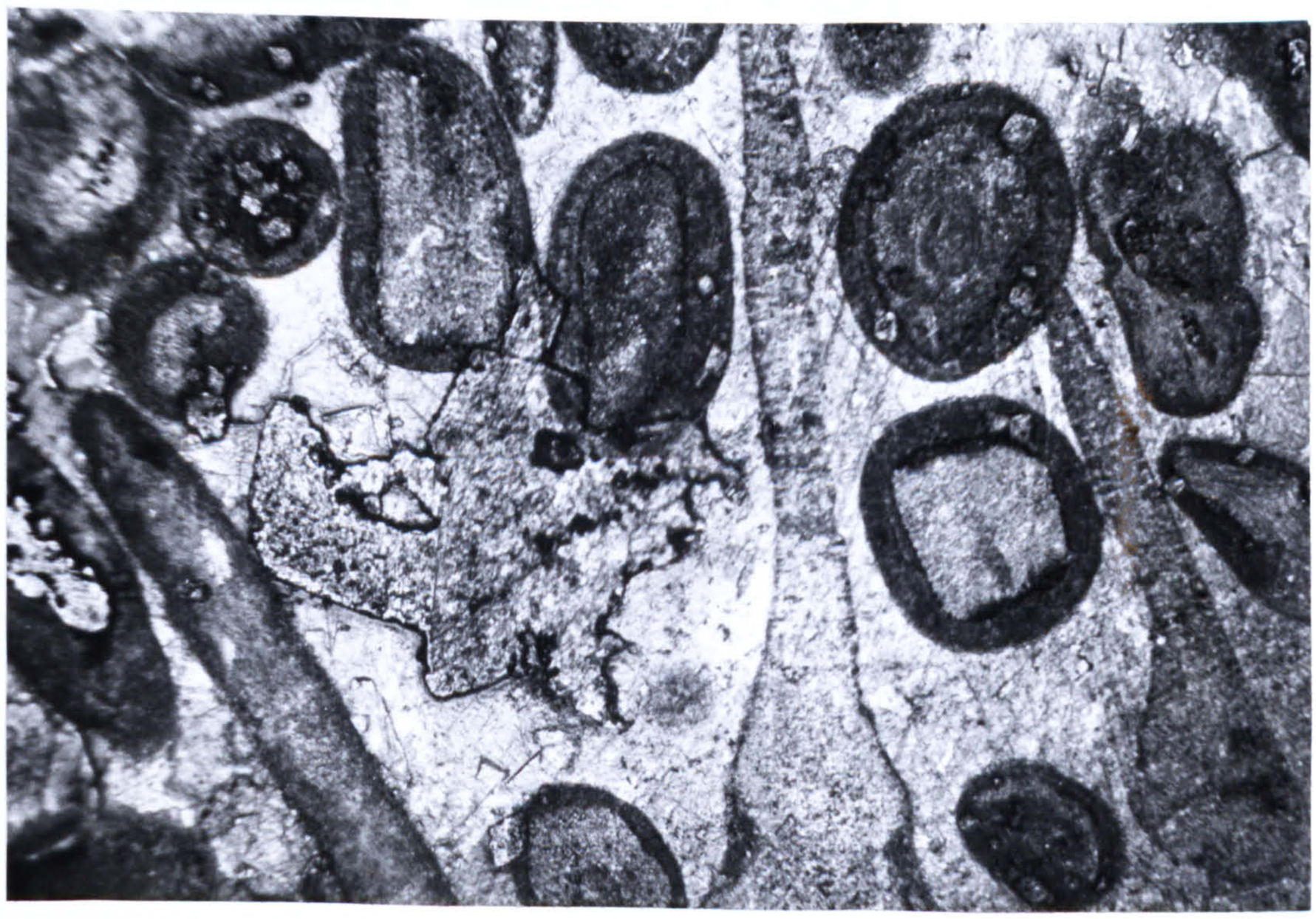
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Brofiscin Oolite, Brofiscin quarry

a



b



429-431), having grown within original or slightly compacted intergranular pores. They contrast with overgrowths in non-grainstone lithologies (i.e. wackestones and possibly packstones of Dunham) which have neomorphic (e.g. Bathurst, 1975, Chapt. 12) or complex micrite dissolution - void fill (Walkden and Berry, 1984) origins.

Syntaxial overgrowths on echinoderms are thought to form most rapidly from water of meteoric origin (see Longman, 1980) and are common products of meteoric-phreatic diagenesis. They are also known from meteoric vadose and burial environments (Longman, 1980). However, at a recent meeting of carbonate sedimentologists (Liverpool, 1984) it was apparent that many workers believe syntaxial overgrowths may also form in marine diagenetic environments. Clearly then, syntaxial overgrowths should be interpreted with caution.

The petrographic relationships of overgrowths in the Brofiscin Oolite suggest that they may have formed in competition with interpreted meteoric phreatic (type 3) cements, as the latter appear less well developed in the presence of syntaxial overgrowths. However, type 3 and 4 cements are also seen to have formed directly on the surface of echinoderm grains, and may be enclosed in syntaxial overgrowth cement. Together with the observation that fractured early cement rims are also often enclosed within overgrowths, this suggests a post-early meteoric cementation, post-compaction origin for many of the syntaxial overgrowths. Dolomite of types A and B also appear to pre-date syntaxial cementation, as they are frequently etched, and their pitted surfaces have been filled with the echinoderm-syntaxial or other coarse calcite cement.

It may be that syntaxial crystals were initiated in a near-surface meteoric environment and continued to grow during burial and compaction of

the sediments. Such a suggestion can only be tentative in the absence of more detailed petrographic information (e.g. Meyers, 1974, 1978). This would suggest that meteoric waters had access to, or were retained within the Brofiscin Oolite during shallow burial. As Meyers (1980) has shown, meteorically derived syntaxial overgrowths can form important 'post-compactional' cements, which may prevent or retard further grain-grain mechanical or chemical compaction.

The coarse calcite cements which are not obviously related to echinoderm fragments, nevertheless have very similar petrographic relationships to those of syntaxial overgrowths. On the basis of this, and their cathodoluminescent character (non or very dull luminescence), a similar origin is concluded.

(b) Fracture filling calcites in the Brofiscin Oolite

Several vein-types are seen in the Brofiscin Oolite, and can be grouped as follows:

1. irregular fractures, often with non-parallel sides and filled with granular to equant calcite (types I and III of Wilson, 1967) and may include dolomite.
2. more regular, parallel sided, locally anastomosing fractures, filled with coarse equant calcite (type III, Wilson 1967). They are usually oriented at high angles to bedding, and may contain fragments of the host rock. This type also occurs in the pervasive dolomites.

Group 1 includes irregular fractures of uncertain origin, which may be linked laterally to fossil-mouldic cavities (also calcite filled). Fractures may also be traced into through-going stylolites, suggesting they formed by opening of the latter. The dolomite in these structures predates the calcite filling cement (see type C dolomite below) as it is often

Fig 3.9

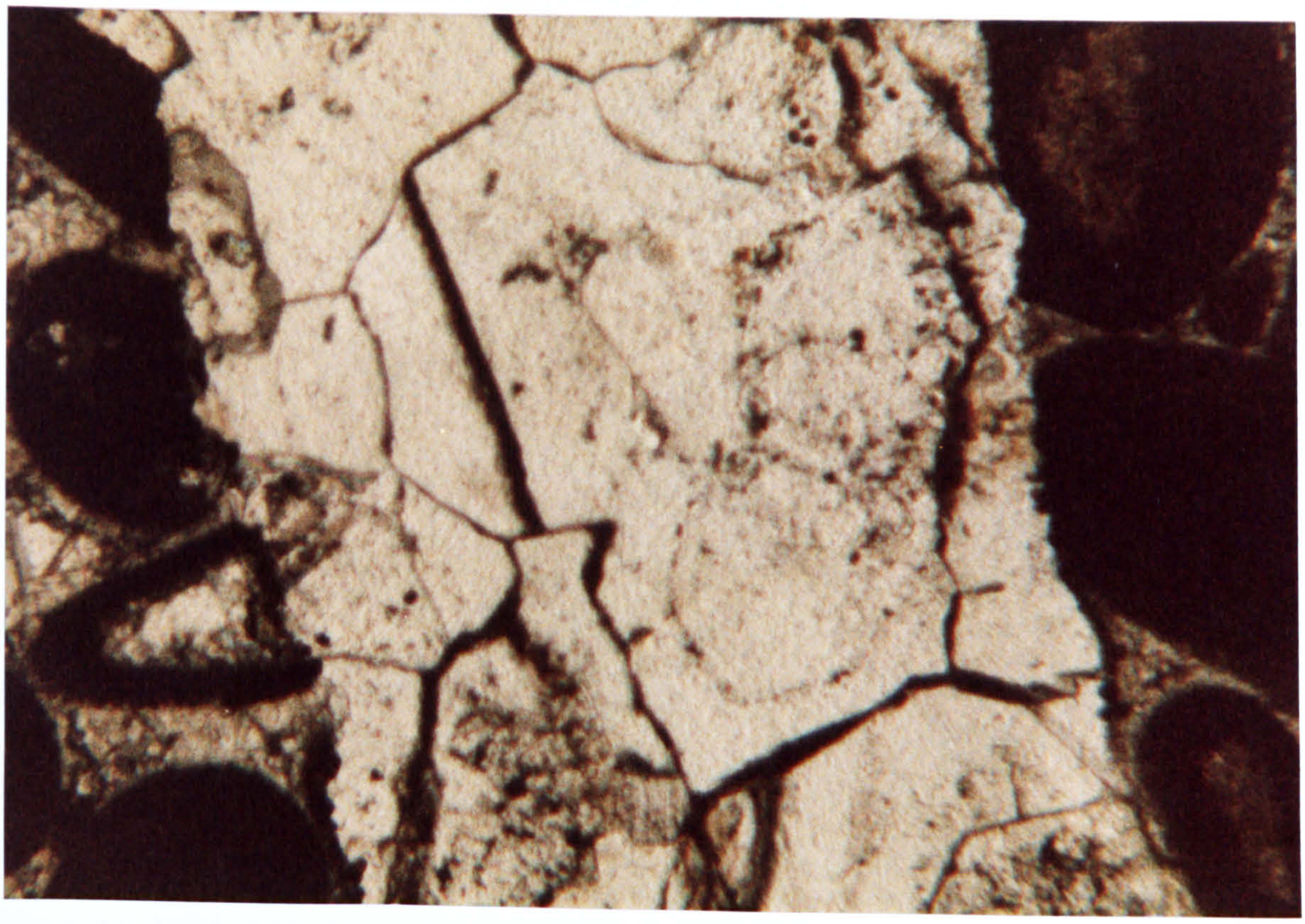
a. vein filling calcite in Brofiscin Oolite (PPL)

b. same field of view under cathodoluminescence showing multiple zonation (compare to Figs. 3.16 & 3.23)
note also bright rims around scattered type A dolomite rhombs in ooids

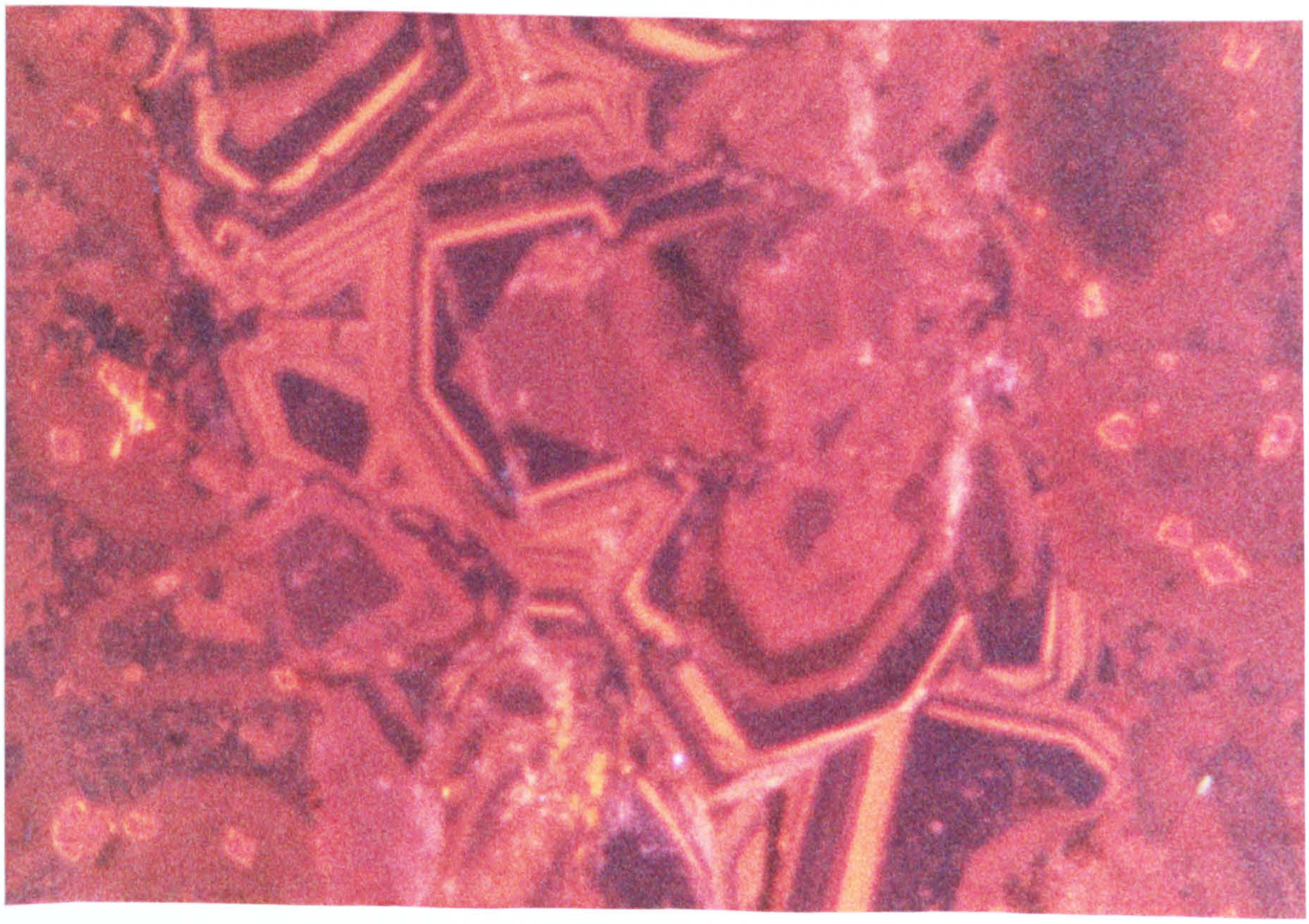
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Brofiscin Oolite, Brofiscin quarry

a



b



dedolomitised. The calcite is non-ferroan and is very dull to non-luminescent.

Group 2 veins have a distinctive parallel-sided cross-cutting morphology. The host rock was clearly fully cemented at the time of their formation as all cement generations and Group 1 veins have been truncated. The vein-filling cement comprises coarse, equant crystals of ferroan calcite with a similar fabric to type III of Wilson (1967). No dolomite has been observed in group 2 veins. The calcite has a zoned cathodoluminescence with an early patchily developed dull (to blotchy) zone correlating with slightly cloudy calcite crystals. Later zones include a dark zone with bright thin subzones and a multiple-zoned medium to bright luminescence (Fig. 3.9a, b). This C.L. pattern compares with those displayed by late calcites in pervasive dolomite mosaics (section 3.3.2) and vein dolomites (section 3.4). The presence of host rock fragments in the veins and the C.L. pattern of the calcite suggests that these were open structures into which the cement was precipitated passively rather than originating by displacive growth. This may indicate a nearsurface, telogenetic origin.

3.3.1.iv Dolomite in the Brofiscin Oolite

Dolomite occurs in several forms in the Brofiscin Oolite, showing the following broad petrographic relationships:

Type A scattered, inclusion-rich euhedral crystals (rhombs) in ooid cortices and other depositional grains.

Type B clusters and individual subhedral to euhedral crystals around grain margins.

Type C euhedral crystals, usually limpid, formed in 'fossil-mouldic'

cavities, fractures and opened stylolites.

Type D inclusion-rich rhombs or clusters of subhedral-anhedral dolomite crystals associated with through-going stylolites.

The first two types are volumetrically the most important and, as will be shown, are the principal constituents of pervasive dolomite mosaics. The distinction between types A and B is not as sharp as the above classification suggests and this point should emerge in the following descriptions.

Dolomite crystal dimensions will be given as follows:

Euhedral and subhedral crystals - measurement will be the rhomb long diagonal or a dimension approximating thereto.

Anhedral crystals (includes 'odd' sections through euhedral and subhedral forms) - the maximum dimension, being the approximate diameter of near equigranular grains.

(a) Type A dolomite

Type A dolomite occurs as scattered inclusion-rich euhedral crystals (10-20 μm). They are particularly well developed in ooid cortices although they also occur within other depositional grains. However, certain components, in particular echinoderm fragments, appear to have resisted dolomitisation more than others (see Section 3.3.4.iii).

The inclusions in type A dolomite have not been positively identified, however, they are probably relics of the host grains, because under S.E.M. of lightly etched surfaces the inclusions appear to have been partially or completely removed (they appear like those in Fig. 3.24b). Some of these dolomite crystals may exhibit a vague zonation of inclusions; however, most

have a uniform inclusion density and an irregular outer coat of dense (? non-carbonate) material (see for example, scattered rhombs in Fig. 3.5).

Type A dolomite typically has a medium cathodoluminescence with bright yellow euhedral rims (see Fig. 3.9b), the significance of these rims in terms of dolomite composition, however, is uncertain and their occurrence only at dolomite boundaries in contact with calcite suggests the luminescence may be related to the concentration of material at the replacement front. The host calcite typically has a uniform dull orange luminescence.

(b) Type B dolomite

Type B dolomite occurs as individual or clusters of subhedral to euhedral crystals (50-400 μm) around the margins of grains and in intergrain areas. Crystals which cross grain boundaries have inclusion rich areas which define 'ghosts' of the host grains (Fig. 3.10a, b). Larger crystals commonly incorporate more than one grain boundary together with the intergrain area. A common feature, although not an ubiquitous one, is for dolomite crystals which cross grain boundaries to have their rhomb long diagonals oriented at high angles to the grain boundary, giving a radial appearance. This is particularly the case where several crystals have grown competitively (note anhedral compromise boundaries) around an ooid margin (Fig. 3.10a). As with type A dolomite above, echinoderm fragments appear to have resisted replacement by type B dolomite.

In the intergrain areas type B dolomite crystals have planar to irregular intercrystalline boundaries which probably represent compromise boundaries developed between the growing crystals as they met and interrupted each others growth towards euhedral rhombs. Unfortunately the relatively uniform, poorly or un-zoned cathodoluminescence of these crystals does not provide additional information (see discussion, section

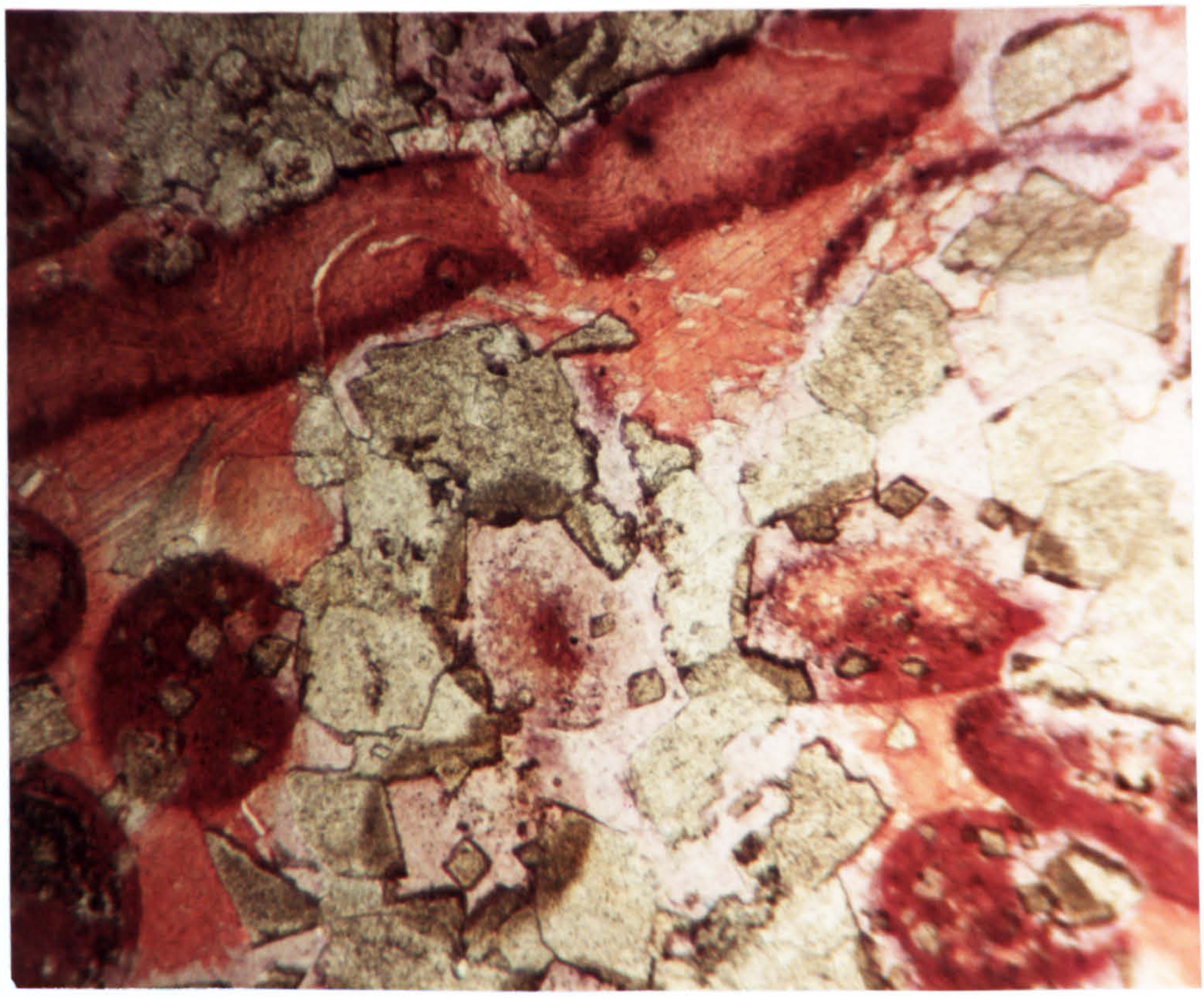
Fig 3.10

a,b incipient dolomite mosaics (type B) in Brofiscin Oolite, note: ghosts of depositional grains, radial arrangement of dolomite rhombs around grain margins, compactional fracturing and (?) pressure solution of some rhombs and enclosed grains (see text for further description) (PPL, alizarin red-S)

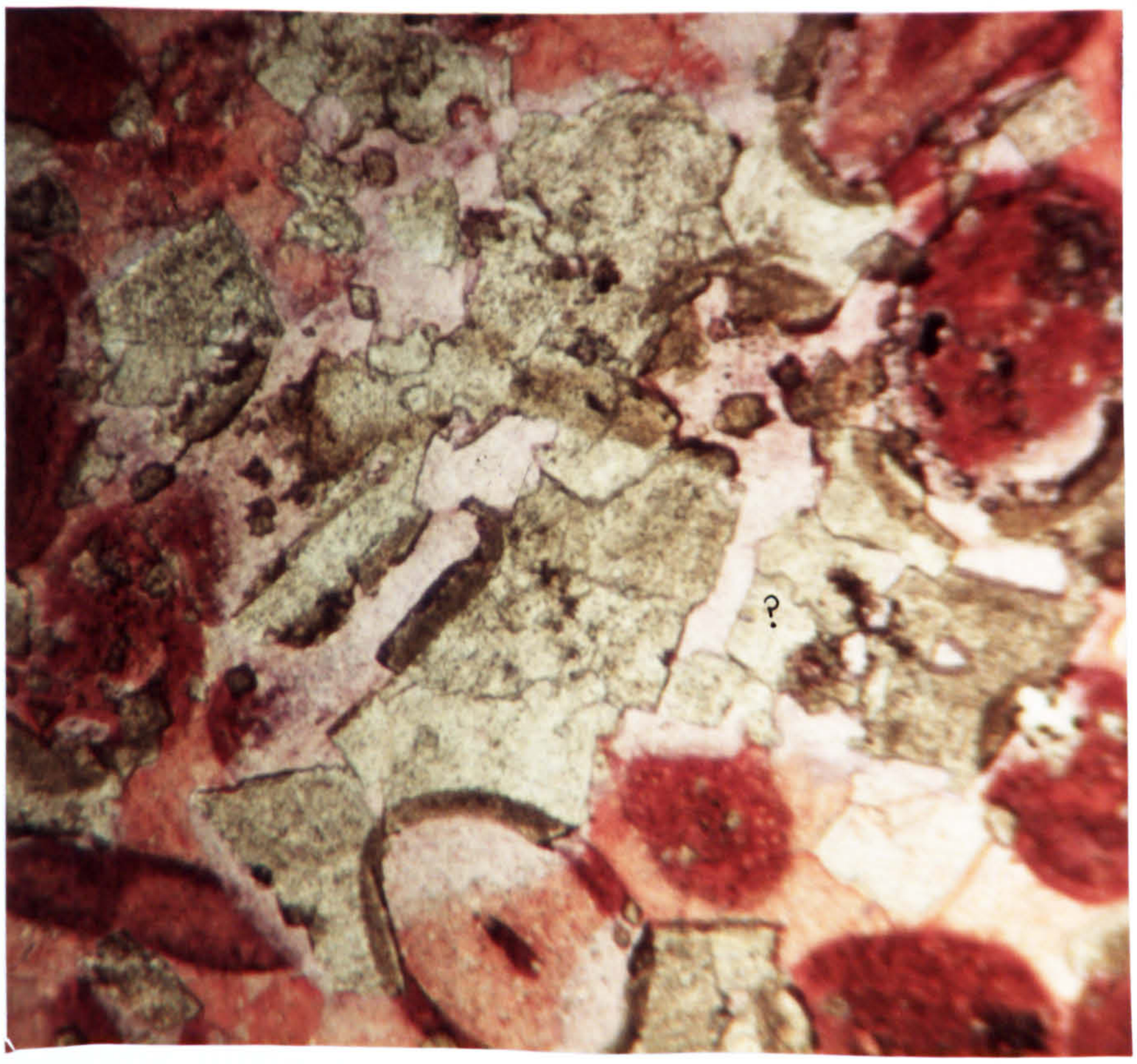
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Brofiscin Oolite, Brofiscin quarry.

a



b



3.3.4.iv). Some of these intercrystalline boundaries are very irregular, and in places have a sutured or microstylolitic appearance (see Fig. 3.10b).

Depositional grains, early fringing cements (where present) and type B dolomite appear to have been compacted and fractured prior to the formation of coarse calcite (see section iii above). The evidence for this comes from the following observations:

1. In places, dolomite which has partially replaced and overgrown grain boundaries (typical type B dolomite) appears to have broken away from the host grain, taking with it that portion of the grain which it replaces (see Fig. 3.10b).
2. Irregular fragments and shards of fractured dolomite are enclosed in calcite spar (Fig. 3.10a).
3. These fragments may constitute a part of the rather jumbled clusters of dolomite crystals (incipient mosaics) with which irregular (?microstylolitic) grain boundaries and mismatched inclusion patterns (ghosts) are common (see for example Fig. 3.10b).
4. Dolomite rhombs in contact with coarse calcite often have etched or pitted surfaces.

Similar features have also been observed in the Gully Oolite, at the upper transitional surface of the pervasive dolomite body (see section 3.3.3.iv). The schematic diagram, Fig. 3.20, used to illustrate the development of the Gully Oolite incipient dolomite mosaics is also applicable here.

Generally, however, early cements are well developed in the Brofiscin Oolite and compaction does not produce such obvious effects. The variation between compacted and non-compacted occurs on a small scale; the features

illustrated in Fig. 3.10 have been observed within the same thin section as the well developed early fringing cements (e.g. Fig. 3.7a).

On a larger scale, the 'incipient dolomite mosaics' described here are seen to be transitional with those of the pervasive dolomites which replace the Brofiscin Oolite and the other parts of the Black Rock Group. The component dolomite types (A and B) can be recognised within the pervasive mosaics and these will be described further in section vi.

(c) Type C dolomite

Euhedral, relatively limpid (inclusion-free) dolomite crystals (100-700μm) occur in irregular fractures, fossil mouldic cavities and opened-stylolites. These 'voids' are now filled with granular to equant calcite (similar to types I and III of Wilson, 1967). The host limestone may be undolomitised or may contain scattered crystals of type A and B dolomite.

The type C dolomite locally replaces host limestones at the margins of fractures. The replacement crystals tend to be smaller than those which occur in the fractures, and where they replace depositional grains do not preserve their form as 'ghosts' (contrast types A and B dolomite). See Fig. 3.11a.

Dolomite crystals which occur in the fractures are enclosed and partially replaced by the coarse calcite (see Fig. 3.11a).

Cathodoluminescence reveals that type C dolomite has a blotchy to uniform medium luminescence, both where it occurs as a replacement of the host limestone and in the fractures. The calcite has a vaguely zoned luminescence comprising a very dull zone and a non-luminescent zone (see Fig. 3.11b).

Fig 3.11

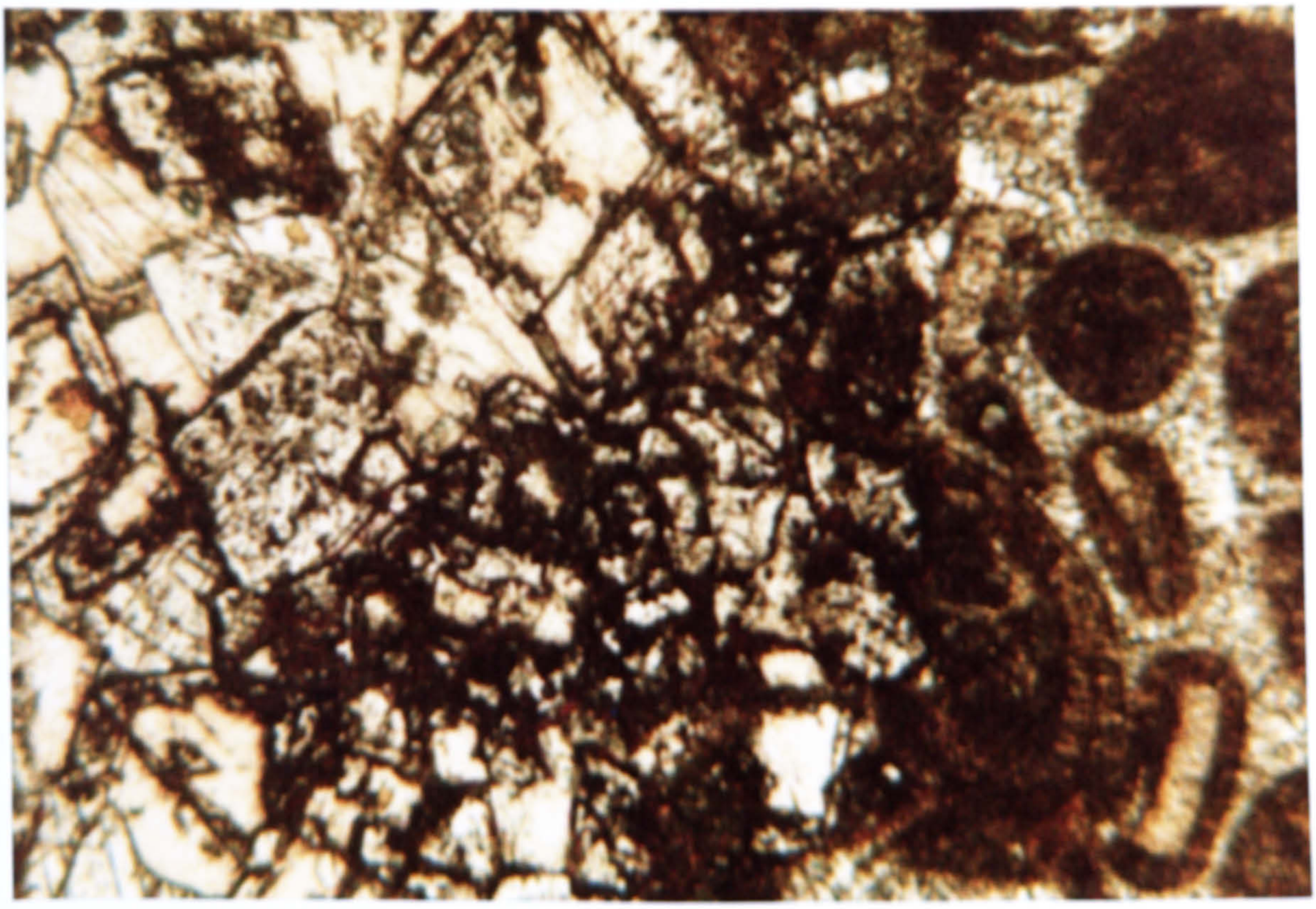
a. type C dolomite in fractures and locally replacing host limestone, some rhombs have been partially replaced by pink staining calcite (alizarin red S), which also fills the remainder of the fracture (PPL)

b. same view under C.L., note the uniform to blotchy luminescence of type C dolomite, scattered type A dolomite with bright luminescent rims and dull luminescence of vein filling calcite (? two zones)

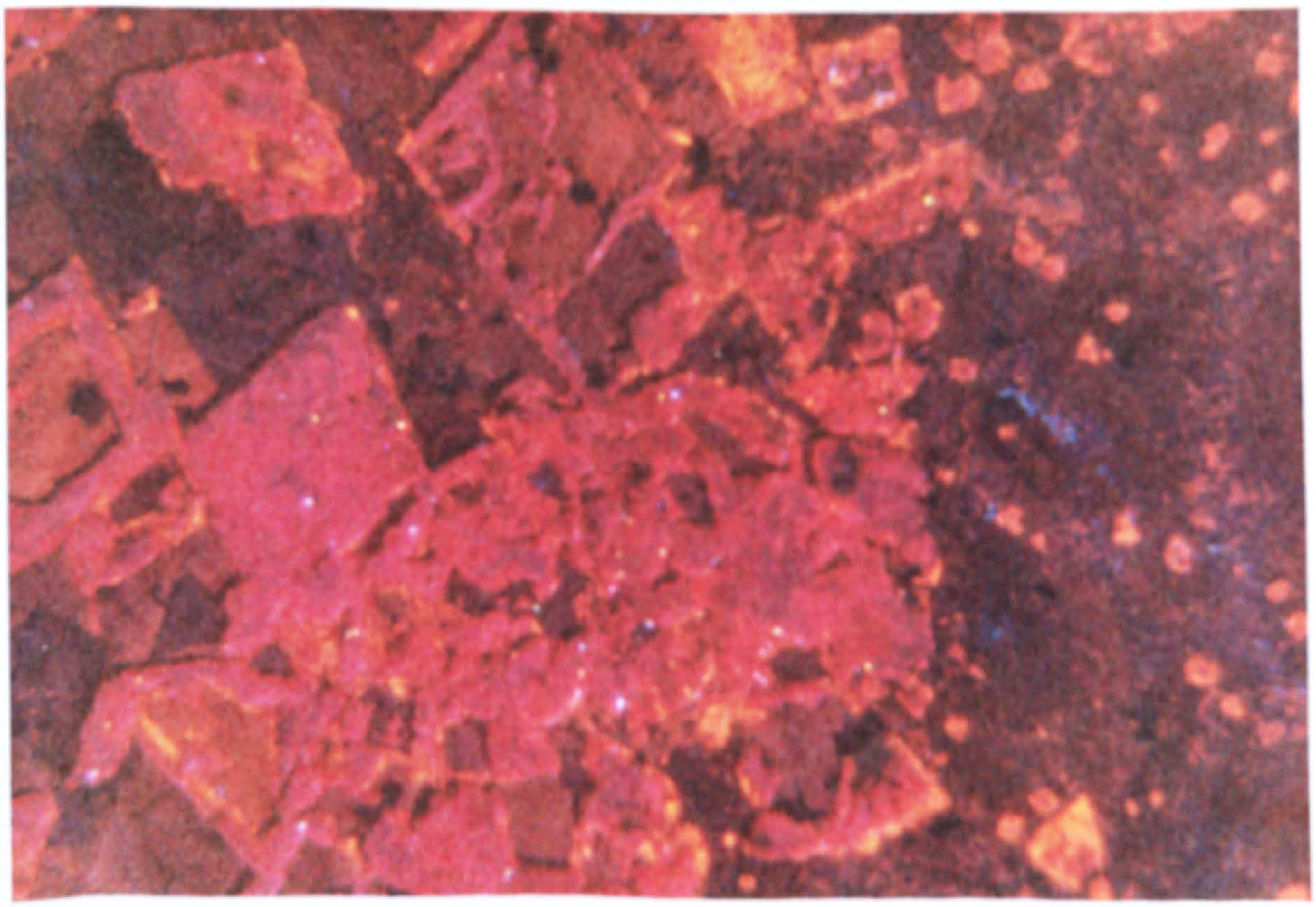
0.4mm

Brofiscin Oolite, Brofiscin quarry

a



b



(d) Type D dolomite

Type D dolomite has a limited distribution, occurring in association with through-going stylolites. The crystals tend to be small (10-400 μm), inclusion rich and often surrounded by dense insoluble material (see Fig. 3.12a). The largest of these crystals appear to have been partially replaced by calcite.

The precise petrographic relationship between dolomite crystals and stylolites is uncertain. There does appear to be an increase in the number of dolomite crystals towards stylolites suggesting a genetic relationship. However, cathodoluminescence reveals that many of these crystals have had their rhombic form truncated by the stylolite plane (compare to rhombs away from plane, see Fig. 3.12b) which would suggest that the dolomite pre-dates pressure solution.

It is suggested that much of this dolomite comprises type A and B crystals and that its 'association' with stylolites is the product of selective dissolution of calcium carbonate and accumulation of dolomite as an 'insoluble' residue (Wanless, 1982). The larger crystals, which are often partially dedolomitised, may be related to pressure solution, or may post-date this solution. Their similarity to locally-replacive type C dolomite supports the latter interpretation. Dedolomitisation may, similarly, be related to that seen in type C dolomites, as the replacive calcite has a similar non- or very dull luminescence. When traced laterally, stylolites may be seen to open into 'fracture-like' structures, now filled with the above discussed calcite, supporting the suggested relationship.

Fig 3.12

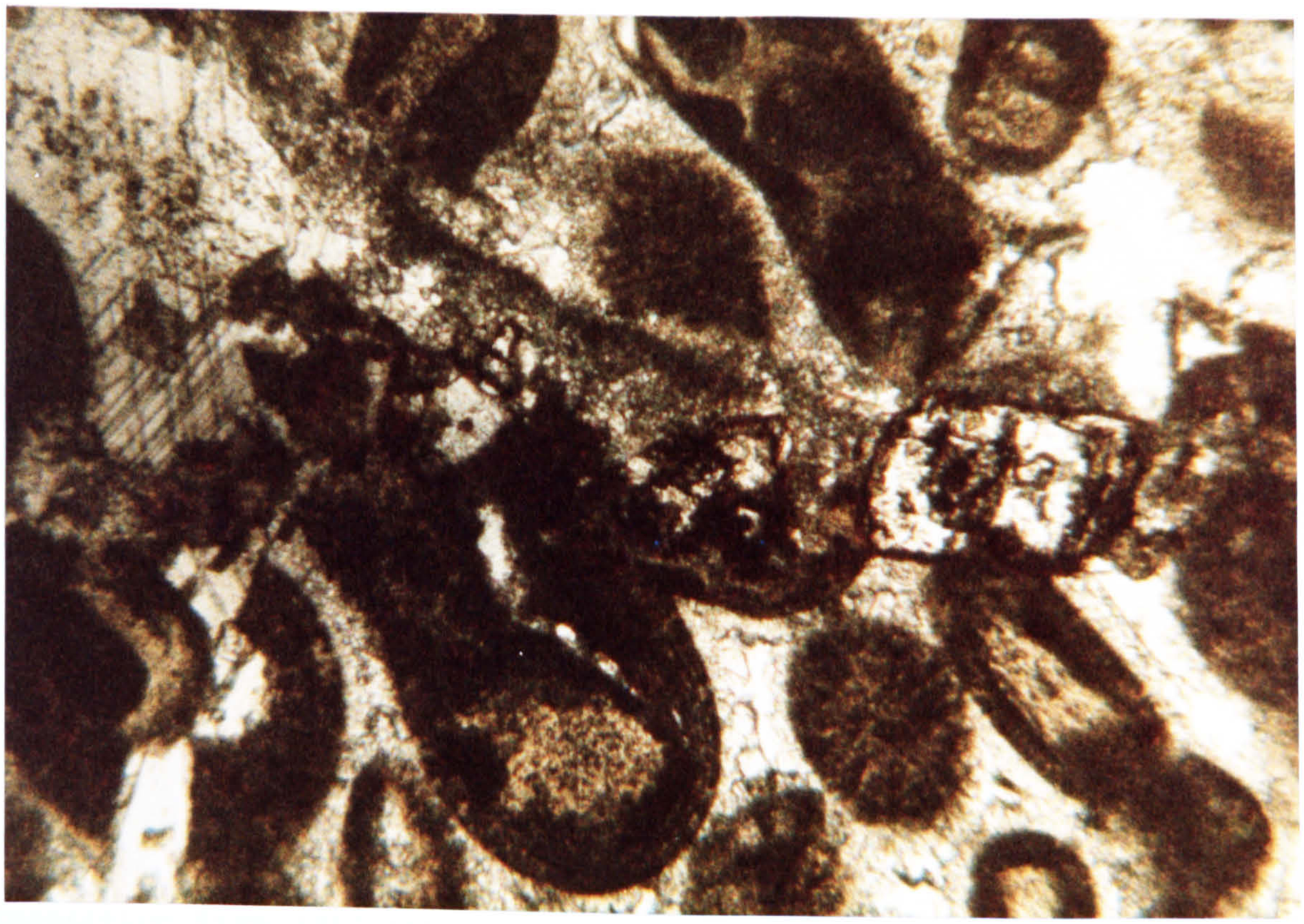
a. type D, stylolite related dolomite (PPL)

b. same view as a, under C.L. , note truncation of dolomite rhombs (type D), which have similar luminescence to type A seen away from stylolite. Note also two-zoned luminescence of pore-filling calcite (C)

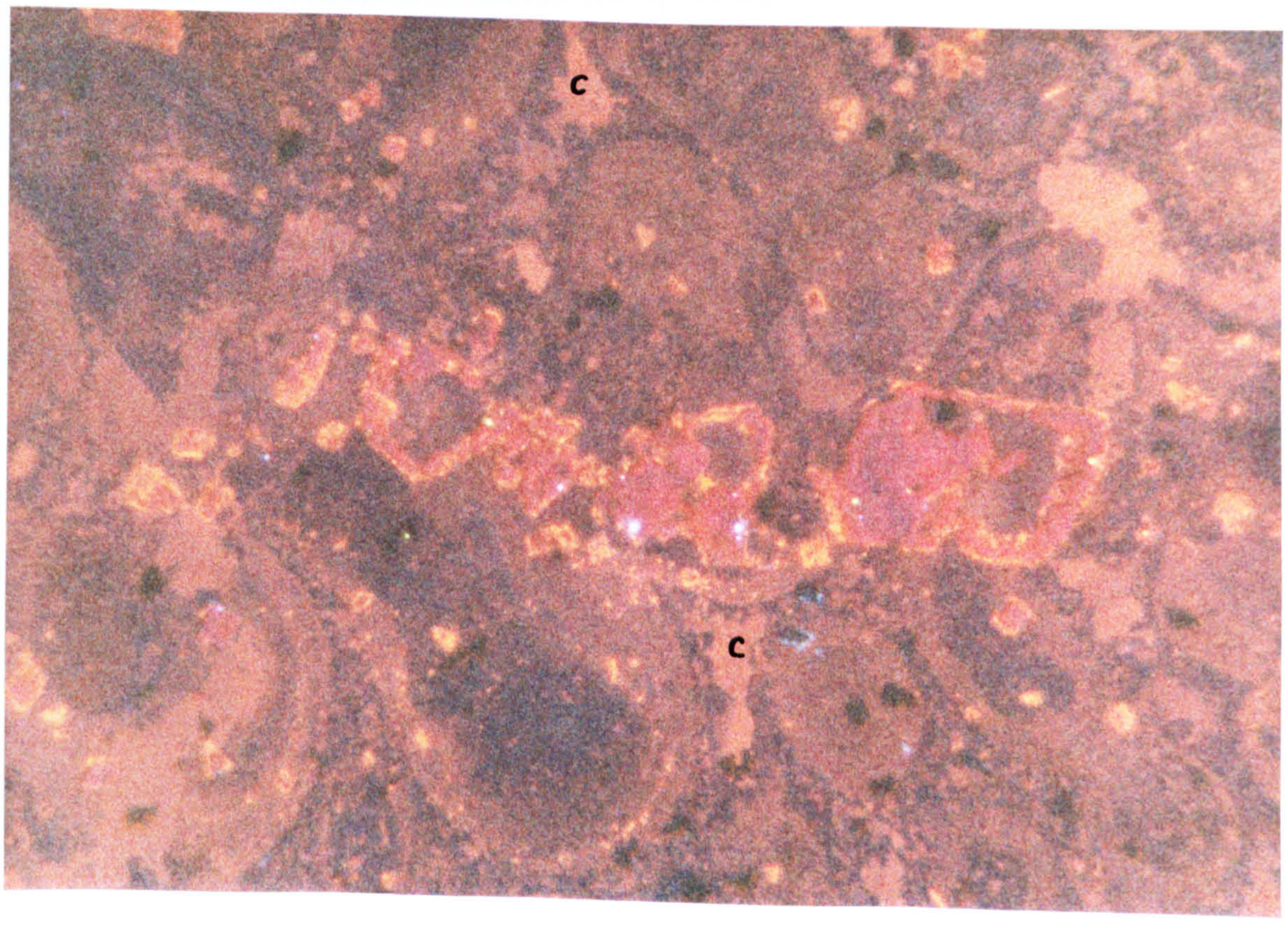
0.4mm

Brofiscin Oolite, Brofiscin quarry

a



b



3.3.2 Pervasive dolomites

3.3.2.i Dolomite mosaics

The 'incipient' dolomite mosaics described above can be traced petrographically into the pervasive dolomite mosaics which characterise the lower and upper Black Rock Group (the Barry Harbour and Friars Point Limestones respectively) at Brofiscin and the entire Black Rock Group to the east in the Taff Gorge. Pervasive mosaics from Wenvoe will also be described in this section, as they represent a more southerly equivalent of those in the Taff Gorge - Brofiscin area (Chapter 2).

The top of the Black Rock pervasive dolomite is similarly transitional where it passes into the Gully Oolite and will be described in section vi.

Mosaics with relic grains (e.g. Fig. 3.13a) represent the next stage in the transition from incipient mosaics. Relic ooids and bioclasts float in a mosaic of type B dolomite. The dolomite crystals impinge on the boundaries of these relic grains and well developed euhedral faces are common. Type B dolomite may coalesce with type A dolomite rhombs and the distinction becomes blurred.

Pervasive mosaics which replace predominantly oolitic sediments (i.e. essentially within the Brofiscin Oolite) appear to be simple progressions of this 'mosaic with relic grain' fabric (see Fig. 3.13b). These replaced oolites may have a minor intercrystalline secondary porosity which is best developed between relatively inclusion-free crystals. This may be in ("ghost" defined) inter- or intra-grain areas. The largest of these pores may contain calcite as a partial or complete fill (Fig. 3.14a).

Cathodoluminescence reveals that this mosaic dolomite has a medium to bright blotchy luminescence. The small amounts of calcite are non-luminescent. The bright luminescing areas of dolomite often have

Fig 3.13

a. dolomite mosaic (predominantly type B) with relic ooids and bioclasts (PPL)

0.3mm

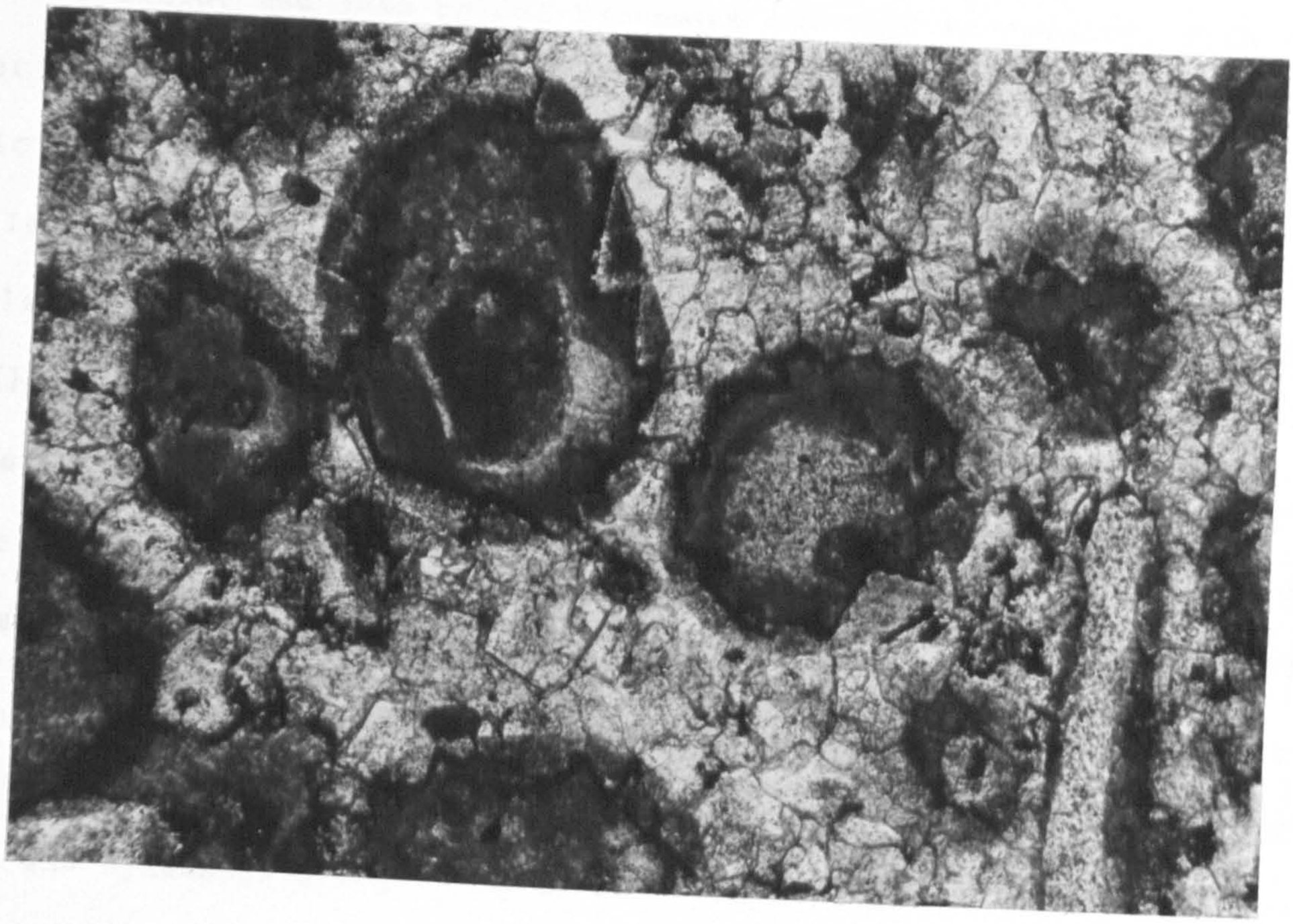
Brofiscin Oolite, Brofiscin quarry

b. pervasive dolomite mosaic with secondary intercrystalline porosity and ooid ghost fabric (PPL)

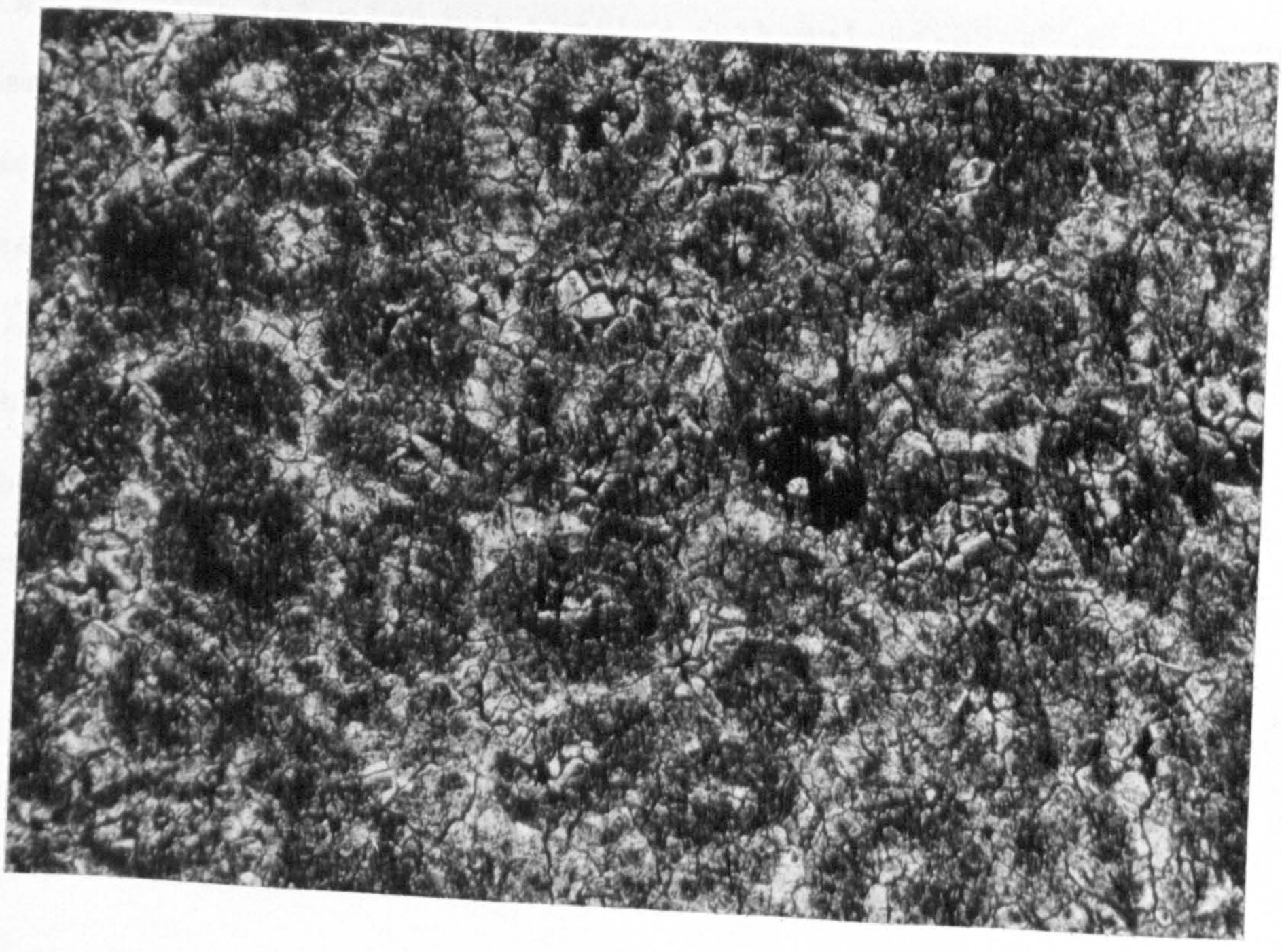
0.5mm

Brofiscin Oolite, Tynant quarry

a



b



alternating bright and less-bright sub-zones and tend to coincide with the coarser and less inclusion-rich areas of the mosaic. These zones define rhombic faces which approximately parallel the termination faces of the crystals in which they occur. The zones may be traced between adjacent crystals, and in places partially or completely around intercrystalline pores (Figs. 3.14b).

Coarser grains, including echinoderm fragments and larger ooids appear to have resisted replacement and are retained as relics in mosaics otherwise similar to those which replace oolites (just described), see Fig. 3.15a. Partial dolomitisation of echinoderm fragments is recorded where dolomite crystals impinge on their boundaries. The relationship between dolomite and syntaxial overgrowths is not always clear. However, dolomite crystal boundaries against syntaxial overgrowths may be irregular and pitted, suggesting partial dissolution of the former before precipitation of the latter.

A coarse secondary intercrystalline porosity occurs in mosaics similar to those with coarser relic grains, and may be due to selective dissolution of the latter. The dolomite has similar cathodoluminescence characteristics as previously described, including euhedral zones forming rims around secondary pores.

Some of these pores may be filled with coarse calcite (see Figs. 3.16a, b). This calcite has a distinctive cathodoluminescence comprising dark to bright zones with sub-zones. An initial dark zone is punctuated by one to three thin, bright sub-zones and resembles the pattern in group 2 calcite vein structures described above (section 3.3.1.iii.b).

Fig 3.14

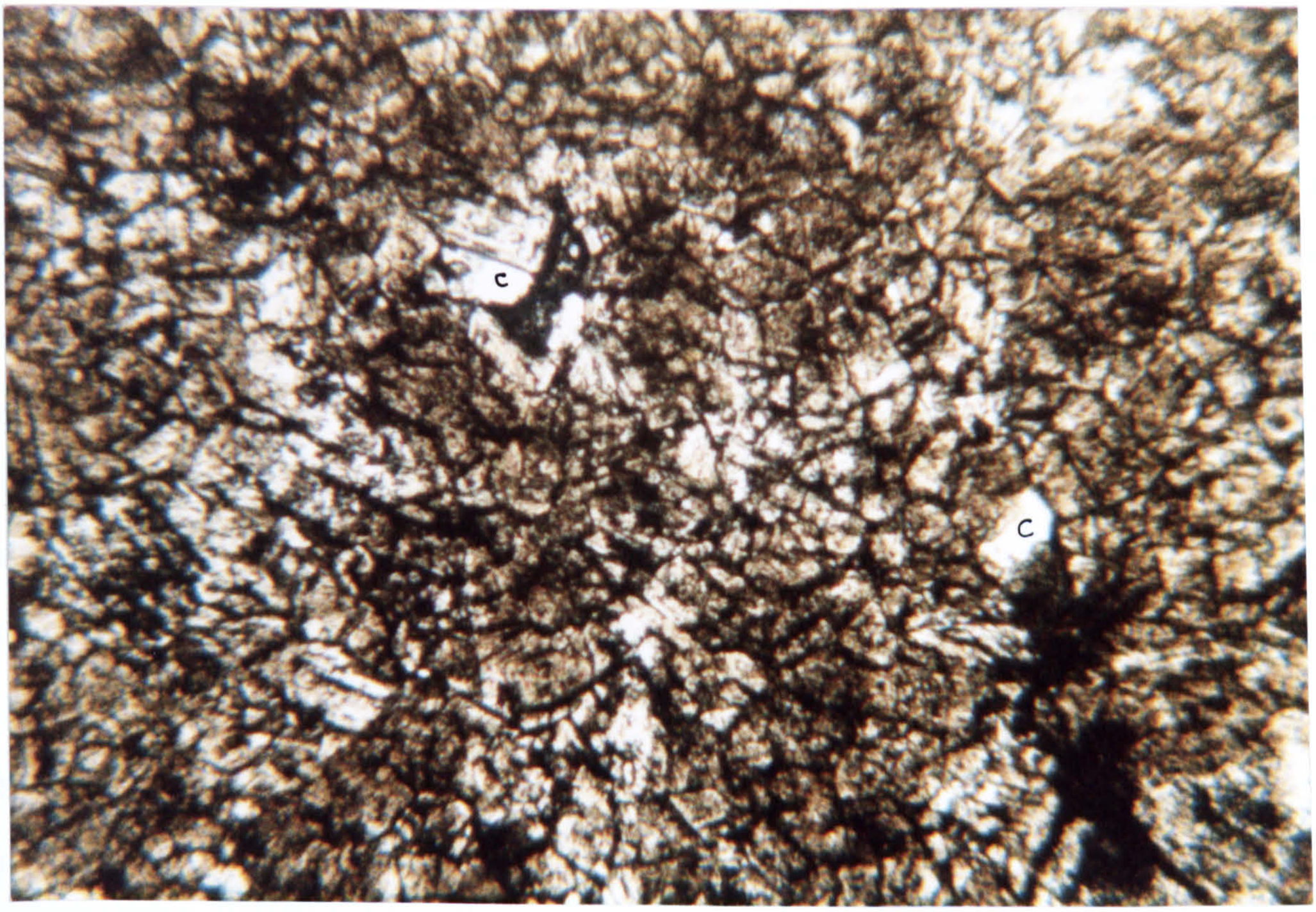
a. pervasive dolomite mosaics with secondary intercrystalline porosity , inclusion ghost fabric and minor calcite (C) (PPL)

0.4mm

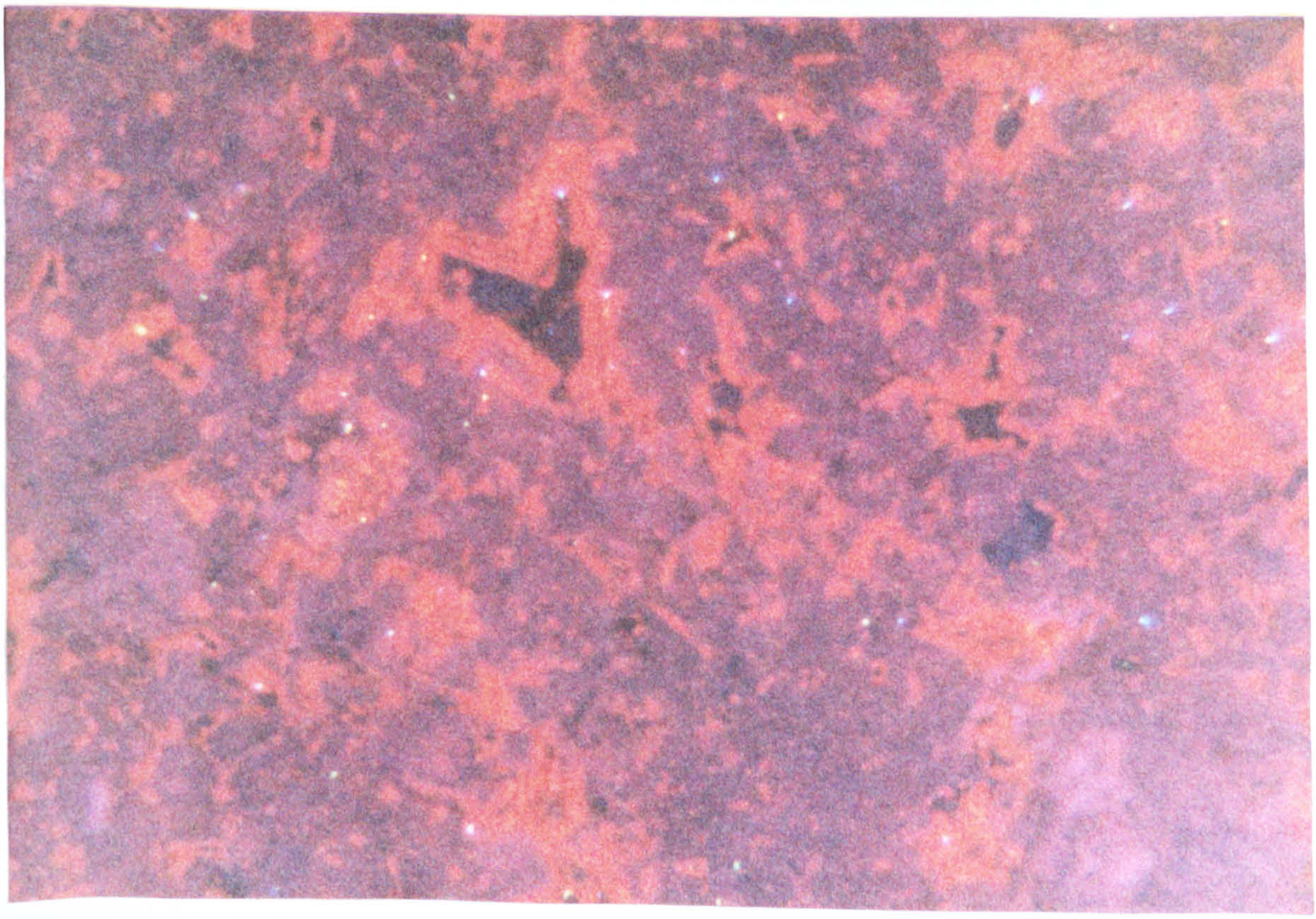
b. same view under C.L.,note zonation in dolomite around secondary pores

Brofiscin Oolite, Tynant quarry,

a



b



3.3.2.ii Baroque dolomite in pervasive mosaics

Baroque dolomite has a restricted distribution in pervasive mosaics. It occurs within structures similar to the 'secondary pores' described above, in inclusion rich pervasive mosaics of the Barry Harbour Limestone from the Taff Gorge (Fig. 3.15b). It also occupies less regular cavities (Fig. 3.15c) where crystals up to 700 μm (long dimension) occur. The baroque dolomite may be a replacement of relic grains, a pore filling cement or perhaps a neomorphic replacement of existing dolomite. Limpid, euhedral overgrowths of dolomite on mosaic dolomite crystals resemble the baroque dolomite, and occur in mosaics from the Taff Gorge and Brofiscin areas. These overgrowths become more important to the south at Wenvoe, where they may form the dominant component of anhedral (xenotopic) mosaics. Within these mosaics there is evidence for grain and early type B dolomite compaction prior to formation of limpid baroque overgrowths. This is much like the situation described in Section 3.3.1.iv.b except the dolomite crystals are generally smaller and probably formed a more complete mosaic at the time of compaction. Baroque dolomite is uniformly non-luminescent.

3.3.2.iii Silicification in pervasive mosaics

The bioclastic wackestones and packstones of the Barry Harbour Limestone are particularly affected by silicification. Microquartz, mega-quartz and chalcedonic quartz occur as replacements of bioclasts, as cements and as a general groundmass in pervasive mosaics. Dolomite rhombs are commonly enclosed within the silica and may have irregular boundaries where the silica impinges on the crystal.

Where silica replaces depositional grains within dolomite mosaics it

Fig 3.15

a. relic bioclasts (echinoderm fragments) in partial dolomite mosaic, note smaller grains (ooids) may be completely replaced (PPL)

0.4mm

Brofiscin Oolite, Brofiscin quarry

b. inclusion-rich pervasive dolomite mosaic with later limpid baroque (xenotopic) dolomite (X) (PPL)

0.7mm

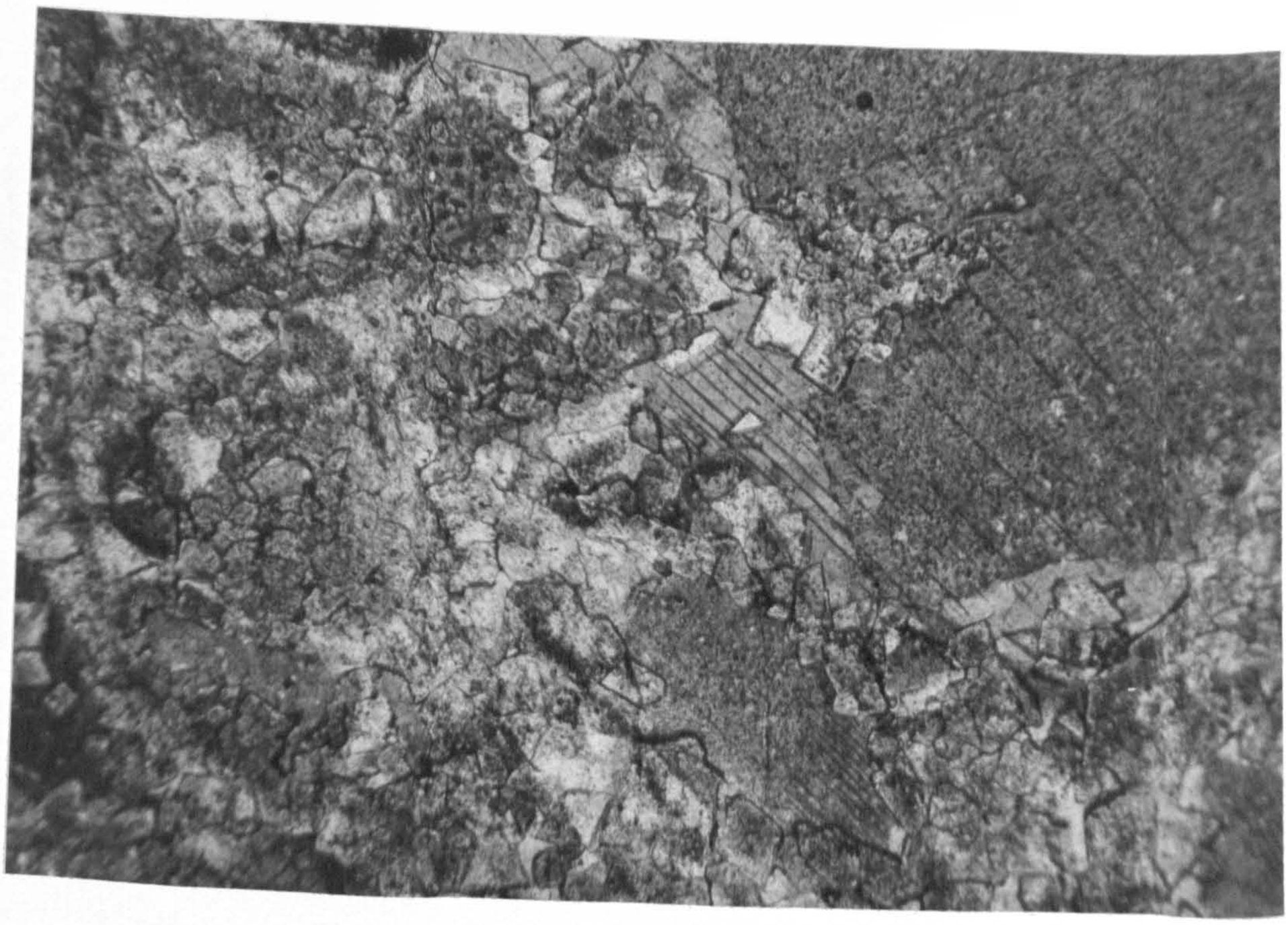
Barry Harbour Limestone, Brofiscin quarry

c. area of coarser xenotopic dolomite within pervasive idiotopic mosaic (XPL)

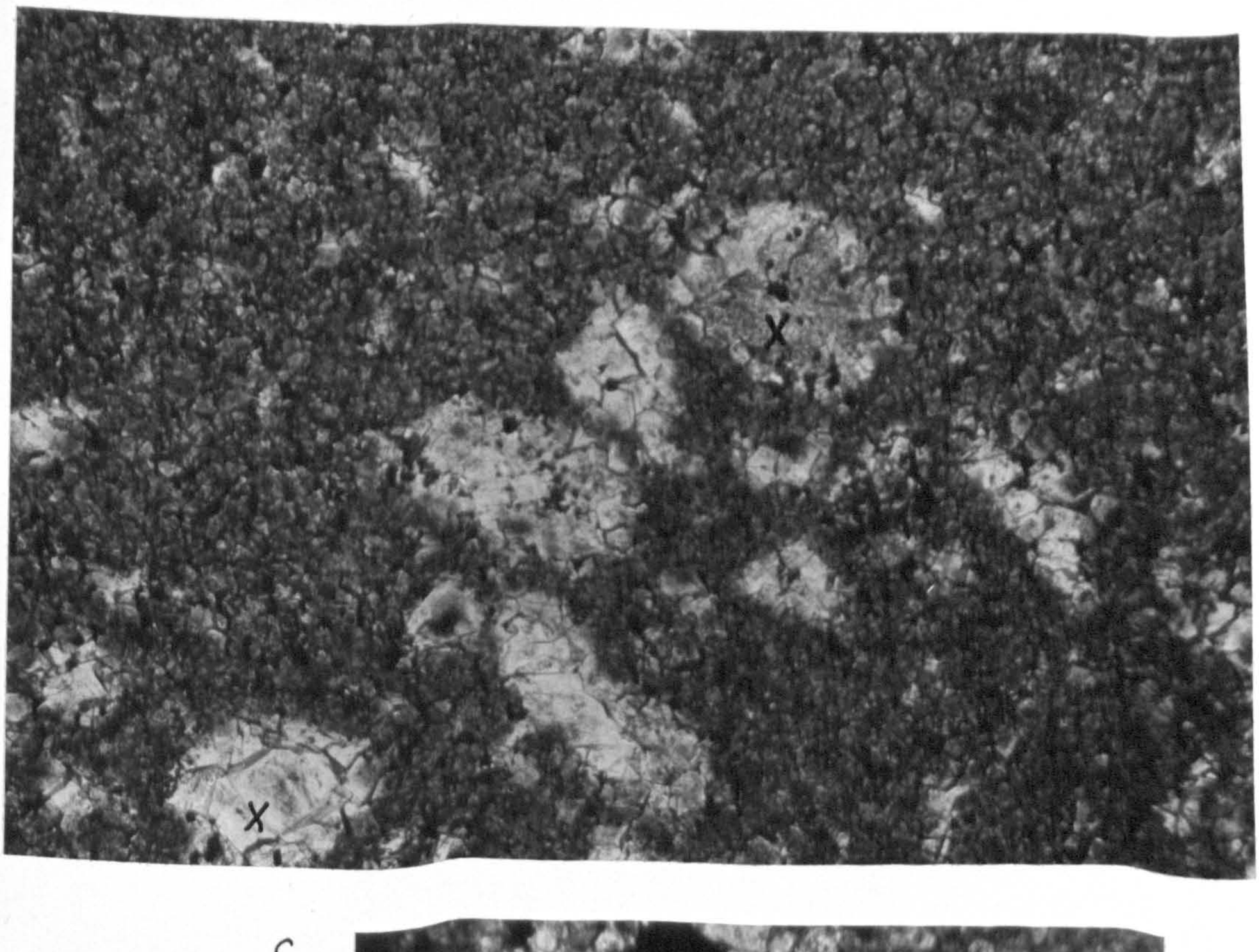
0.4mm

Barry Harbour Limestone, Brofiscin quarry.

a



b



c



Fig 3.16

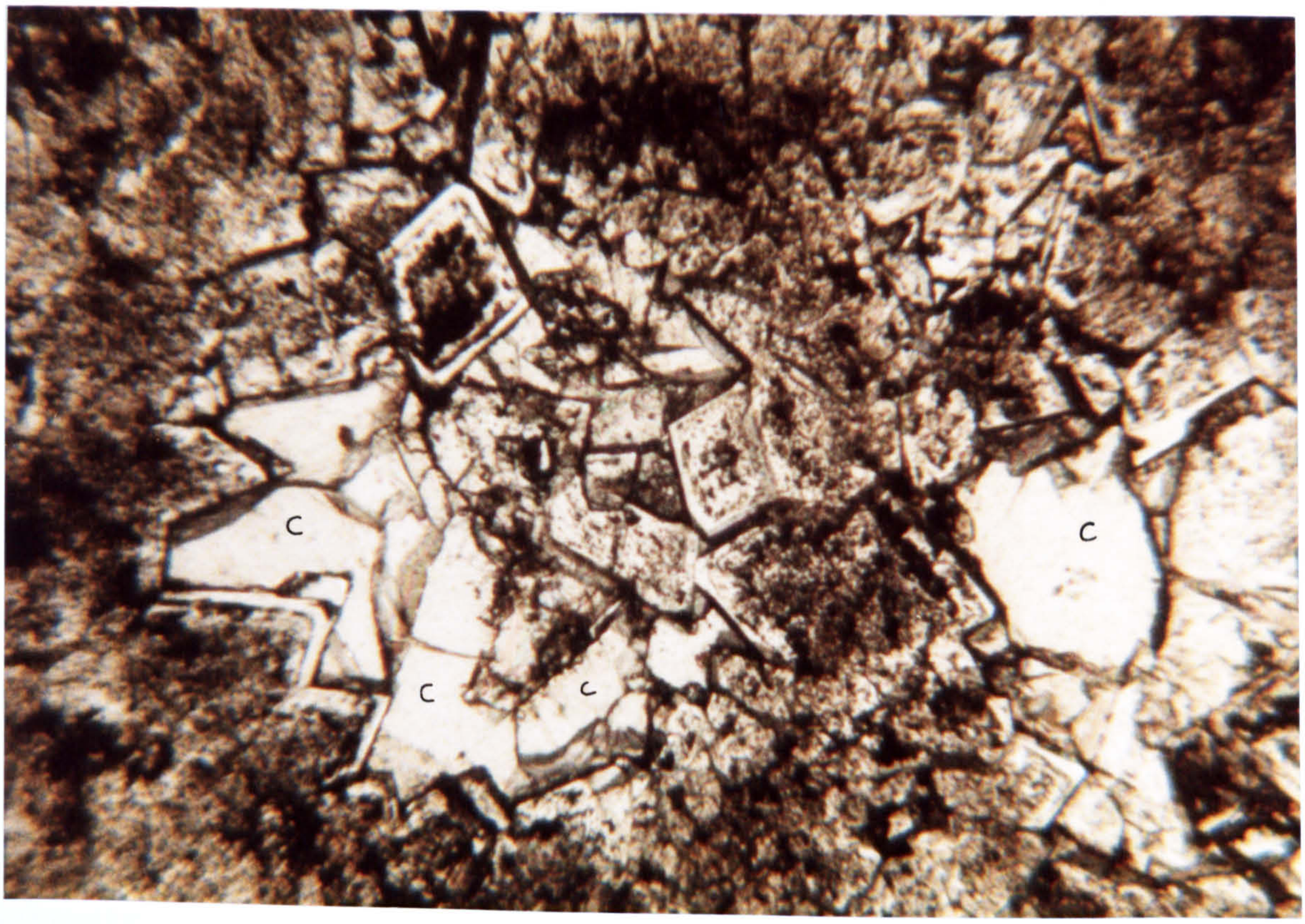
a. pervasive dolomite mosaic with late calcite spar (C), note limpid euhedral dolomite rims around pores (ppl)

b. same view under C.L., note blotchy luminescence of dolomite mosaic, vague zonation around pores (compare to Fig 3.14 b) and multiple-zoned calcite (compare to Figs 3.9 b & 3.23 b)

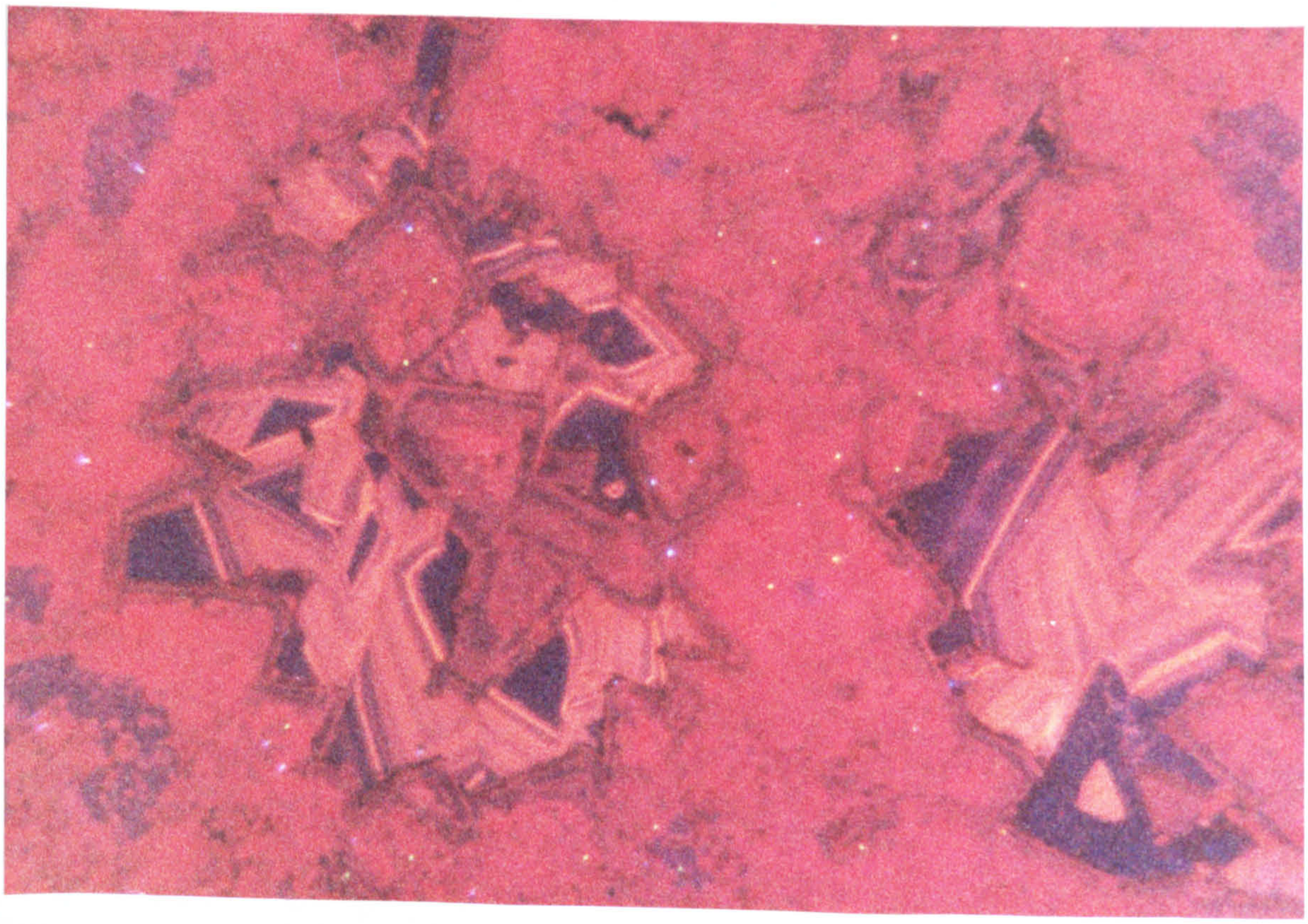
0.4mm

Friars Point Limestone, Llantrisant road section.

a



b



is not possible to identify the mineralogy of the precursor; however, the fabrics suggest silica has selectively replaced relic calcium carbonate grains (and cements?) in preference to dolomite. Drusy megaquartz occupies cavities, within bioclasts for example, and has the appearance of a cement.

3.3.2.iv The upper boundary of the pervasive dolomites

As already explained (Chapter 2), there are two important, and apparently distinct, pervasive dolomite formations in the South Wales Dinantian sequence. The upper boundary of these dolomites approximately conform with that of their limestone hosts; that is the 'Black Rock' and High Tor Limestones and can be seen at Llantrisant and Creigiau respectively.

The contact between 'dark' pervasive dolomite and 'pale' oolitic limestone appears distinct. However, in detail the lower 1 to 3 metres of limestone are also pervasively dolomitised and weather to a buff-grey colour. The actual contact between pervasive dolomite and limestone is quite subtle, but can be traced in the field and usually occurs as an undulating surface with an amplitude of a few tens of millimetres to a metre or so (see Fig. 3.17a). Petrography reveals that the limestones above these undulating surfaces in fact contain dolomite as scattered crystals or in clusters; these will be discussed further in the following section.

The tops of the pervasive dolomites are transitional and therefore are similar to their lateral margins. However, there are important diagenetic-textural differences between the limestones which occur above and those which are laterally adjacent to the dolomites. These differences are best illustrated by comparing the Brofiscin Oolite (described in section 3.3.1)

Fig 3.17

a. field photograph showing the upper boundary of pervasive dolomites within the lower part of the Gully Oolite, Llantrisant road section

hammer shaft is 0.4 metres

b. Gully Oolite showing radial-concentric fabric and radial fracture of ooids, also note drusy calcite spar (PPL)

0.4mm

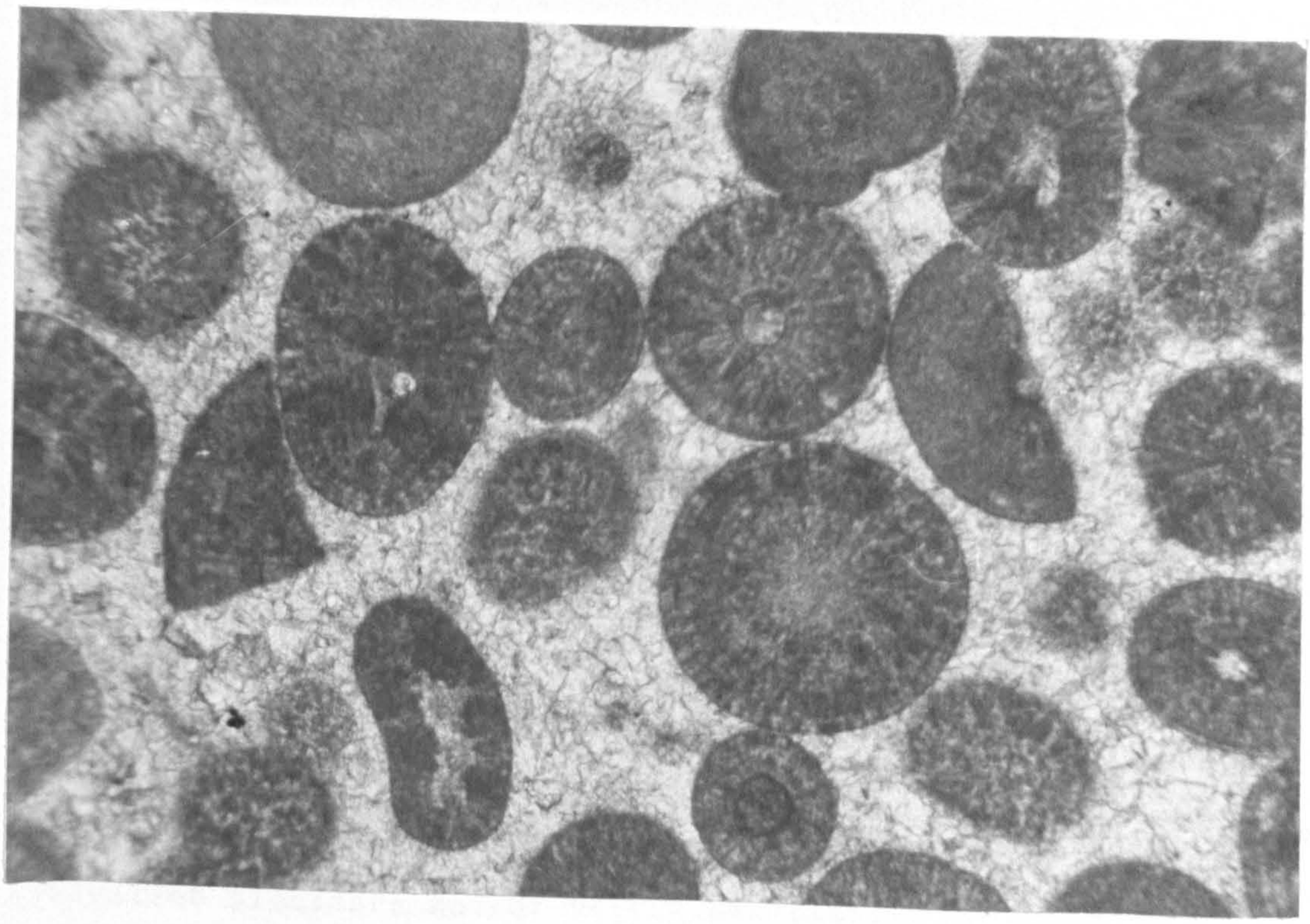
Gully Oolite, Taff's Well quarry.

UNIV DUNDEE

a



b



and the Gully Oolite (which will be described in section 3.3.3).

Summary of pervasive dolomite mosaic variations

It has been shown that the development of pervasive mosaics can be traced petrographically from incipiently dolomitised limestones. However, it is clear that a simple increase in the proportion of early dolomite phases (types A and B) cannot account for all the observed mosaic fabrics, as other phases are often involved. The most important types of pervasive dolomite mosaic are listed below.

1. Mosaics comprising predominantly subhedral type A and B dolomite crystals with no other phase or with very minor limpid dolomite or calcite overgrowths in intercrystalline pores. These are the idiotopic or hypidiotopic fabrics of Friedman (1965).

2. As 1, but with coarse relic depositional grains.

3. Mosaics as 1, with coarse intercrystalline porosity, which may be lined with limpid dolomite rims and/or filled with coarse calcite which has a distinctive zoned cathodoluminiscence.

4. Mosaics as 3 with subhedral to anhedral (hypidiotopic-xenotopic) baroque dolomite as the pore-filling phase.

5. This category grades into category 4, comprising idiotopic to hypidiotopic mosaic dolomite with irregular patches of xenotopic baroque dolomite, or with baroque dolomite crystals forming overgrowths on the earlier mosaic crystals producing a 'tight' xenotopic mosiac.

6. Idiotopic (type A and B) mosaics with partially or completely silicified bioclasts and/or matrix material.

3.3.3 Petrography of the Gully Oolite and the transition to pervasive dolomite

The following descriptions are based mainly on studies of material from the Llantrisant and Taff's Well localities (see Fig. 2-4, in Chapter 2).

3.3.3.i Depositional grains

(a) Ooids

Ooids are the predominant depositional grains in the Gully Oolite. They typically range from 300 μm to 1mm in diameter and are spherical with radial-concentric structure, which is often preserved despite micritisation (see Fig. 3.17b). Non-spherical, compound and superficial ooids also occur. In some samples ooids appear to have been broken before early cementation, suggesting that the radial fabric is primary (Halley, 1977; Wilkinson and Landing, 1978), and that the ooids were deposited in a high energy environment (Halley , 1977). Ooid nuclei include echinoderm fragments, bryozoans (fenestrate) and other unidentified carbonate material, and quartz grains.

Smaller ooids, together with peloids, and bioclastic debris (including calcispheres, peloids and foraminferas) (max. dimensions 40-400 μm) occur locally in thin laminae or flaser structures.

(b) Bioclasts

Bioclasts are generally subordinate in the Gully Oolite, although bioclastic packstones-grainstones are locally interbedded with purer oolitic grainstones. Debris of echinoderms, brachiopods, bivalves and foraminfera are the most important bioclasts. Fenestrate bryozoans also

occur.

(c) Intraclasts

Intraclasts approximately 20-50mm max. diameter comprise ooids, peloids, brachiopod and echinoderm debris. Brachiopods have commonly been bored and micritised around their margins. Compound ooids and smaller intraclasts cemented by micritic carbonate also occur. Between these grains is a finer sediment which may only partially fill an intergrain area comprising peloids and bioclastic debris (see Fig. 3.18a). The intraclasts are cemented by a fibrous, isopachous cement, micrite and calcite spar (see below), however, syntaxial overgrowths on echinoderm fragments are not developed. These intraclasts have a general lithological similarity to the sediments in which they occur (contrasting with those within the Brofiscin Oolite).

3.3.3.ii Fringing cements

Fringing cements of the types described from the Brofiscin Oolite (section 3.3.1.ii) are rare in the Gully Oolite. However, the following occurrences are recognised.

(a) Isopachous fibrous cement and associated features

A fibrous isopachous rim, up to 100 μm thick (normal to substrate) occurs around depositional grains and develops polygonal boundaries in the corners of pores. In the studied sections this cement only occurs within the intraclasts described above and contrasts with the style of cementation in the host sediment (see descriptions below). The cement comprises acicular crystals up to 100 μm long and 10 μm wide (Fig. 3.18b). They may be parallel sided columns or may increase in width away from the substrate. Where visible, crystal terminations appear triangular; however, the cement

Fig 3.18

a. detail of intraclast within Gully Oolite, note : micritised or partially micritised depositionl grains, isopachous fibrous first generation cement, internal sediment and late calcite spar (PPL)

0.4mm

b. detail of a, showing isopachous fibrous cement with micritic outer (poreward) coat (PPL)

0.2mm

c. margin of intraclast (as above), note poikilotopic spar beyond intraclast and pore-bridging micrite, together with features already descibed, within intraclast (PPL)

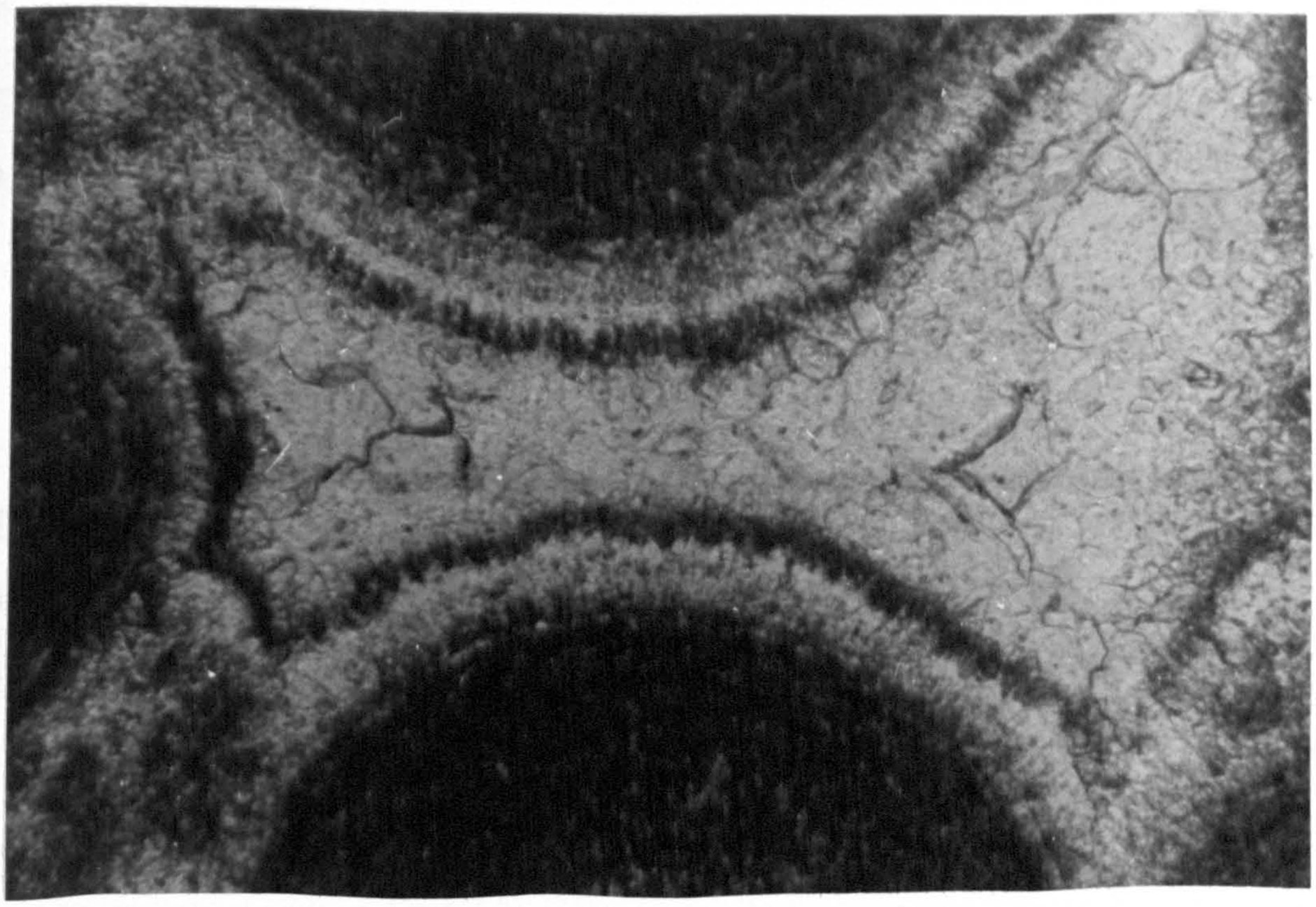
0.4mm

Gully Oolite, Llantrisant road section.

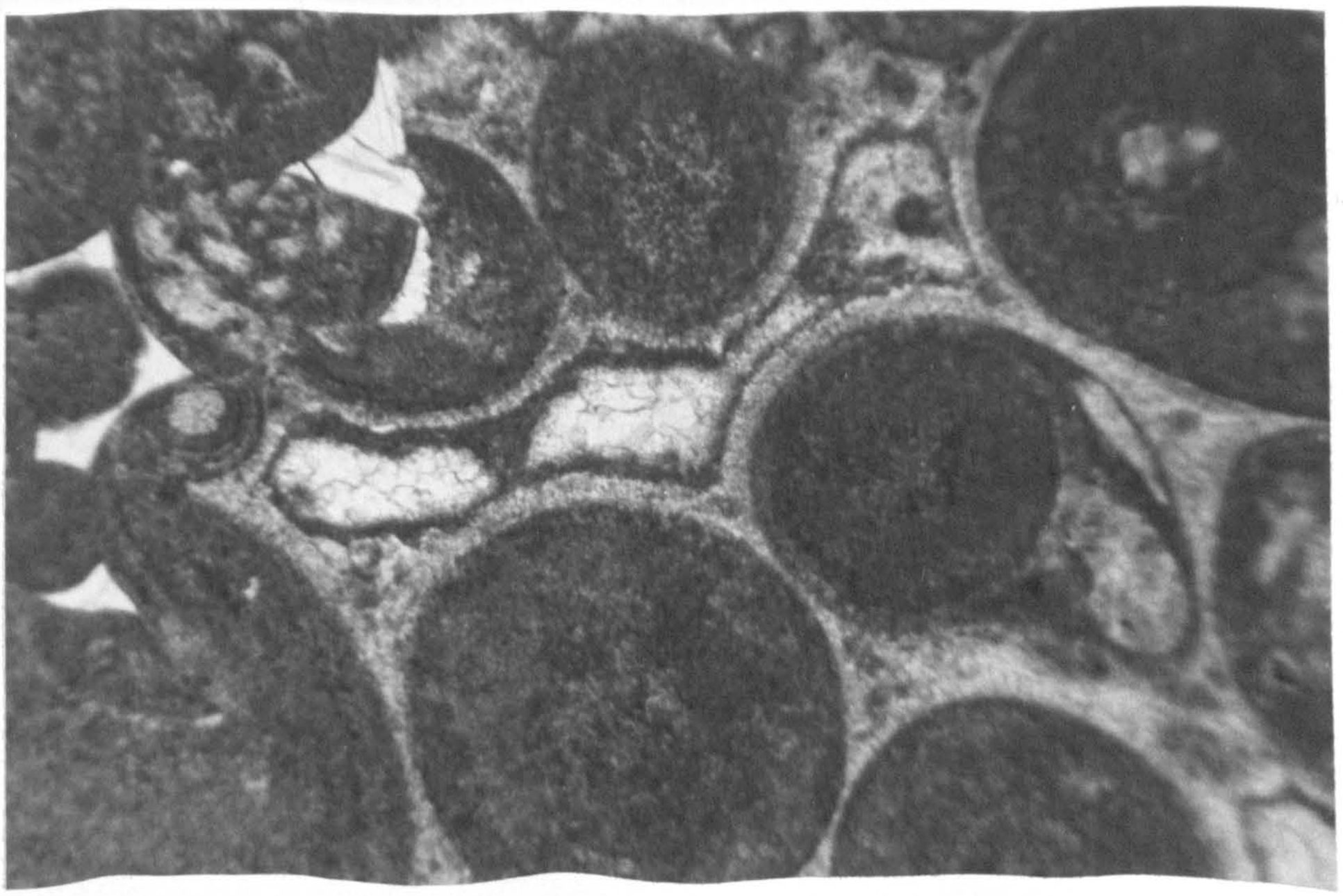
a



b



c



often has a micritic 'coat' at its poreward margin which partially masks its form. This micrite has a uniform distribution around pore structures, and may be a partial replacement of the fibrous cement. Alternatively, the micrite itself may be a cement; see for example Fig. 3.18c, where it forms a bridge across a pore.

The fine sediments which were described earlier (section c), occur poreward of the isopachous fibrous cement and where they form only partial pore-fills, the remainder of the pore is occupied by calcite spar (see Fig. 3.18a). Spar-sediment contacts appear as flat surfaces and these surfaces have approximately the same orientation in all pores where they occur. They are geopetal internal sediments, but because of their occurrence within intraclasts the original depositional orientation cannot be proved.

Discussion/interpretation of fibrous isopachous cement

The occurrence of these cements within intraclasts comprising marine sediments (ooids, echinoderms, brachiopods, etc.) of similar composition to the host sediments suggests a penecontemporaneous, marine origin. The following features also support a marine origin for this cement.

i) acicular nature of crystals.

ii) isopachous distribution and polygonal boundaries in combination with (i) (see Longman, 1980) suggesting a marine phreatic origin.

iii) association with micrite cement, a common feature of modern fibrous marine cements (see for example, Halley, Harris and Hine 1983, fig. 30) and/or micritisation perhaps due to boring algae.

iv) association with marine internal sediments. These are similar to type

1 of Aissaoui and Purser (1983), which occur directly below hardgrounds of marine origin in grainstones and produce a 'diagenetic packstone' texture.

These fibrous cements represent early submarine lithification in the Gully Oolite. Lithified sediments were subsequently eroded and incorporated into oolitic sediments as intraclasts.

(b) Uniform, non-isopachous cement

This cement also has a limited distribtuion, occurring within the finer grained laminae in the Gully Oolite at Llantrisant (see section 3.3.3.i (a)). It comprises equant crystals uniformly to patchily distributed around depositional grains and with the same general form as type 3 cements in the Brofiscin Oolite (see section 3.3.1.ii(c) for further description and discussion).

Interpretation

These cements are interpreted as meteoric-phreatic on the grounds of their close similarity to Brofiscin type 3 fringing cements. Of further interest here is their occurrence within fine-grained sediments whereas immediately adjacent coarser sediments have apparently escaped early cementation. This situation compares with that described by Dunham (1971).

(c) 'Drusy' to equigranular calcite spar

This cement also has a limited distribution within the studied sections of the Gully Oolite, occurring in the upper 3 to 5 metres. The description of this cement is included here because it forms the first generation, pre-compaction cement. It comprises bladed to equant crystals (15-200μm max. dimension) whose size may increase away from the substrate producing a drusy mosaic, or may be fairly uniform (see Fig 3.17b).

On a thin-section scale, this cement has a patchy distribution and

where it is absent grains have been compacted. Micro-stylolitic, sutured grain-grain contacts are common in these areas.

The cement has a blotchy, irregular, dull cathodoluminescence, which shows a vague zonation from dull luminescent at grain boundaries to non-luminescent in the centres of pores.

Discussion of drusy to equigranular cement

This cement clearly formed during early, pre-burial diagenesis. The dominantly equant crystal morphology and drusy to equigranular texture suggest a meteoric phreatic origin (see Longman, 1980). The karstic surface at the top of the oolite (see introduction and Riding and Wright, 1981) may have provided an access for meteoric waters. However, Riding and Wright (1981) suggested that the Caswell Bay Oolite (= Gully Oolite) near Miskin, on the South Crop, was unlithified at the time of exposure at the top of the unit. Early cementation occurred in the form of micritic coats (cutans) of pedogenic origin at the time of exposure. The prevailing climate appears to have been arid to semi-arid (see Wright, 1984 b and c) which would suggest meteoric water was not readily available for early diagenetic cementation.

3.3.3.iii Coarse calcite spar and syntaxial overgrowths

The predominant cement in the studied sections of the Gully Oolite is a coarse, non-ferroan or faintly ferroan calcite spar. The crystals are often poikilotopic, enclosing part or all of several grains (Fig. 3.19a). Crystal shape is largely determined by pore shape, as a single crystal may occupy one pore or several adjacent pores. Smaller crystals are typically equant. This calcite is non-cathodoluminescent (or has a uniform,

Fig 3.19

a. Gully Oolite with compacted and fractured grains predating poikilotopic calcite spar (PPL)

0.5mm

Gully Oolite, Taff's Well quarry.

b. fine echinoderm fragments and other bioclasts in anhedral mosaic of echinoderm-syntaxial overgrowth cement (PPL)

0.5mm

Gully Oolite, Llantrisant road section.

c. anomalous inclusion patterns within incipient dolomite mosaics (see text and Fig 3.20 for discussion) (PPL)

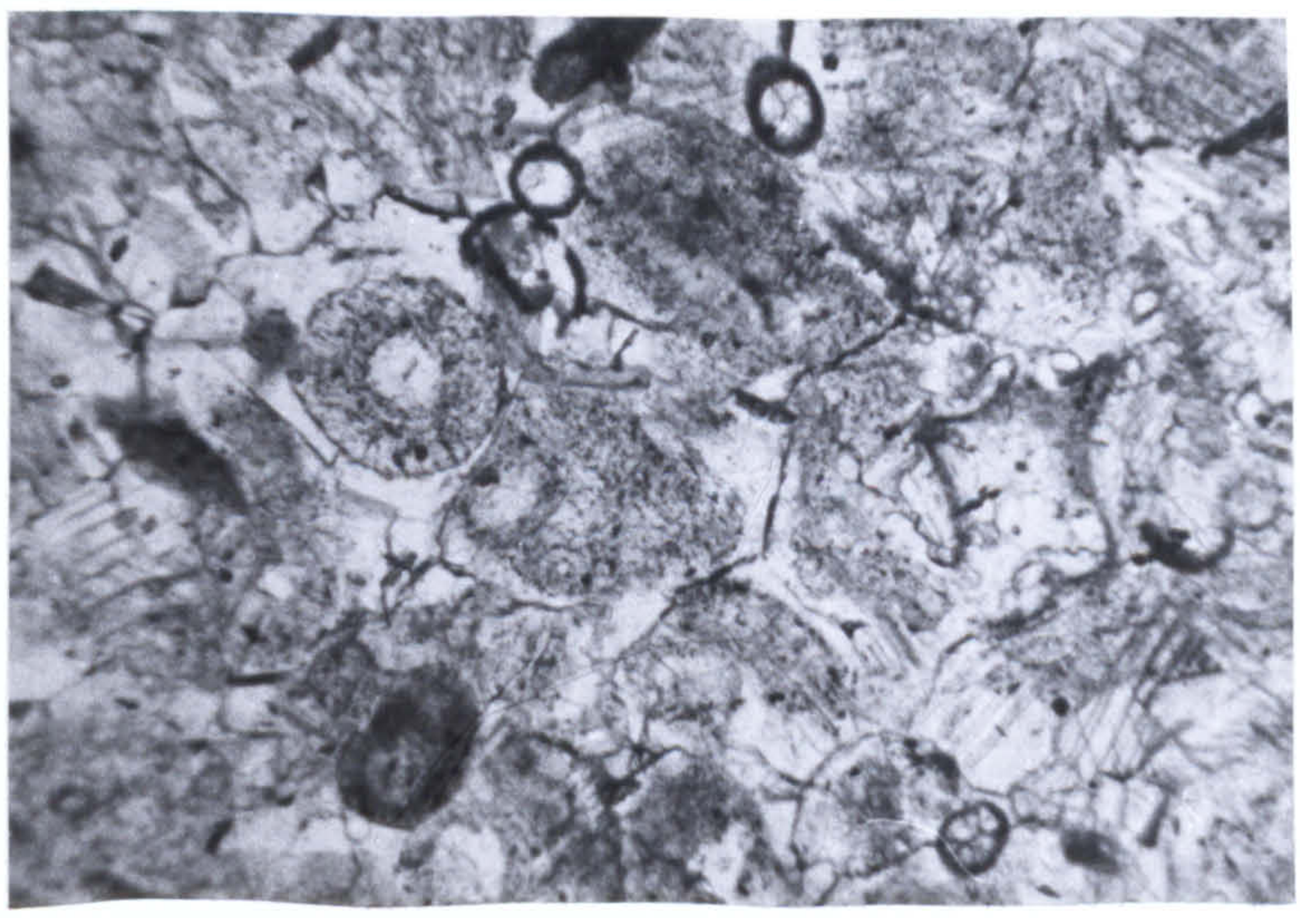
0.4mm

Gully Oolite Llantrisant road section.

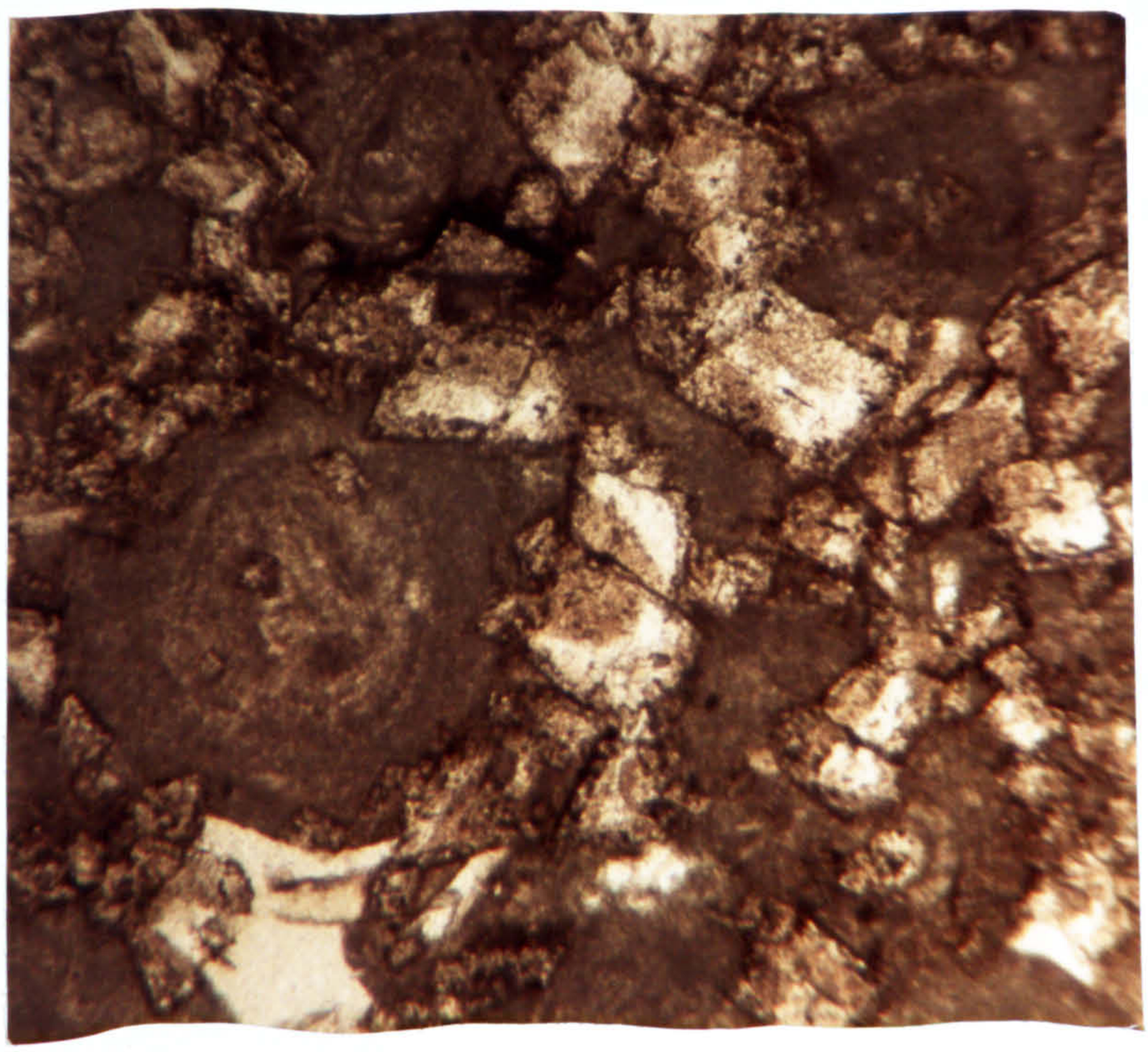
a



b



c



extremely dull luminescence) and is comparable with the coarse calcites in the Brofiscin Oolite.

Where echinoderm fragments are present, the cement has grown syntaxially upon them. In the basal Gully Oolite at Llantrisant, there occur thin laminae (0.5 to 5mm) of fine crinoidal debris (<500 μm max. dimension). Syntaxial overgrowths on these fragments form a tight anhedral cement mosaic (see Fig. 3.19b). The immediately adjacent coarse oolitic layers are cemented by coarser calcite spar. Syntaxial overgrowths are similarly dull- or non-luminescent.

In these coarsely cemented oolites grain-grain compaction is a typical feature. Longitudinal and microstylolitic contacts (see Figs. 3.19a) between ooids indicate that compaction resulted in pressure solution of these grains (see Bhattacharyya and Friedman, 1984). Bioclasts are often fractured. Dolomite, as individual or clusters of crystals also shows evidence of compaction (see section 3.3.3.iv) and where rhombs project beyond grain boundaries they often appear to have been etched before precipitation of the calcite spar.

Discussion

The coarse calcite spar is clearly a post-compaction cement, enclosing compacted and fractured depositional grains and dolomite. Syntaxial overgrowths on echinoderm fragments are equated with the cement on the basis of their close association, similar post-compaction grain relationships and identical C.L. characteristics. This equation might suggest that the cement formed from fluids derived from meteoric water, in a burial diagenetic environment. Etching of dolomite rhombs seems to have predated this cementation. The sparsity of early cements in a large part of the Gully Oolite suggests that nearsurface diagenesis was

restricted to micritisation of grains and local marine or meteoric cementation with perhaps some grain leaching and stabilisation of marine components. Pervasive dolomitisation appears to have been largely restricted to the base of the Gully Oolite and is discussed below.

3.3.3.iv Dolomite in the Gully Oolite

The most important dolomite occurrence in the Gully Oolite is related to faults or fractures which cut through the formation at high angles to bedding. These 'vein' dolomites are described and discussed further in section 3.4. The purpose here is to describe the limited occurrence of dolomite at the base of the Gully Oolite which, as explained in section 3.3.2.iv above, forms the transitional top of the pervasive Black Rock Group dolomite.

Dolomite occurs as scattered rhombs throughout most of the Gully Oolite in the study area. Some of these rhombs can be related to the vein dolomites (see section 3.4). However, at Llantrisant, where the base of the Gully Oolite is seen, rhomb density increases downwards (stratigraphically) into the pervasive dolomite body.

Dolomite crystals of types A and B (described in sections 3.3.1.v.a and b) are recognised and type B in particular are useful in determining the petrographic timing of dolomite formation. Type B crystals cross grain boundaries and record, as inclusion defined 'ghosts', the form of replaced grains. Superficially these dolomite crystals appear to have formed after grain compaction, apparently crossing grain-grain contacts of the longitudinal or microstalactitic type. However, when studied in detail the inclusion patterns within these crystals often do not match the surrounding textures. Specifically, inclusion defined grain boundaries within dolomite

crystals are not continuous with boundaries outside these crystals (Fig. 3.19c). Another common feature is for the inclusion-free 'extra-grain' portion of type B dolomite crystals to penetrate adjacent grains. Many of these dolomite crystals have irregular boundaries, often with dense inclusion-rich rims. This is particularly the case where they abut or appear to have penetrated depositional grains. Dolomite intercrystalline boundaries are also irregular and some appear sutured (see Fig. 3.19c).

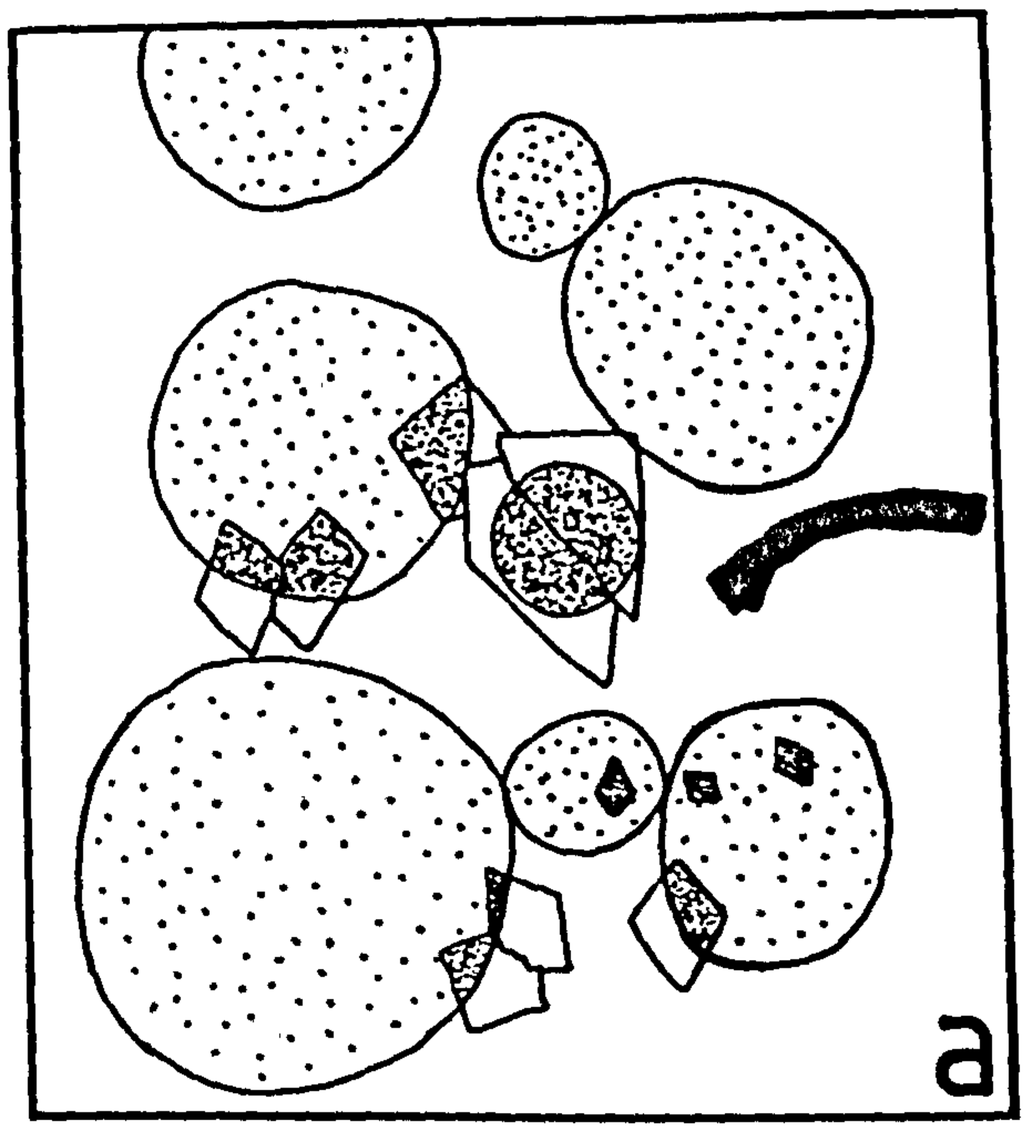
Discussion of anomalous inclusion patterns and dense rims

An explanation of the anomalous inclusion patterns in dolomite crystals is that the dolomite formed whilst the sediment was relatively uncompacted. Subsequent burial compaction, in the absence of a well cemented framework, would have led to fracturing and grain-grain or grain-crystal pressure solution.

The differential rate of dissolution, at pressure-solution surfaces, between less soluble dolomite crystals and more soluble calcite grains would lead to penetration of the latter by the former (see Bathurst, 1975). The inclusion-defined 'ghosts' of depositional grains or grain boundaries in dolomite crystals would thus become displaced. Fig. 3.20 is a schematic representation of how these features may have developed.

The dense rims around many of the dolomite crystals where they penetrate depositional grains, may similarly be interpreted as the products of pressure solution, representing accumulations of insoluble impurities (probably clay minerals). Similar rims have also been observed, however, around many dolomite crystals where there are no other indications of pressure solution (e.g. type A in the Brofiscin Oolite). In such cases they probably represent the accumulation of impurities at the growth surfaces of crystals (see section 3.3.4.iii), which may well be similar in

Fig 3.20



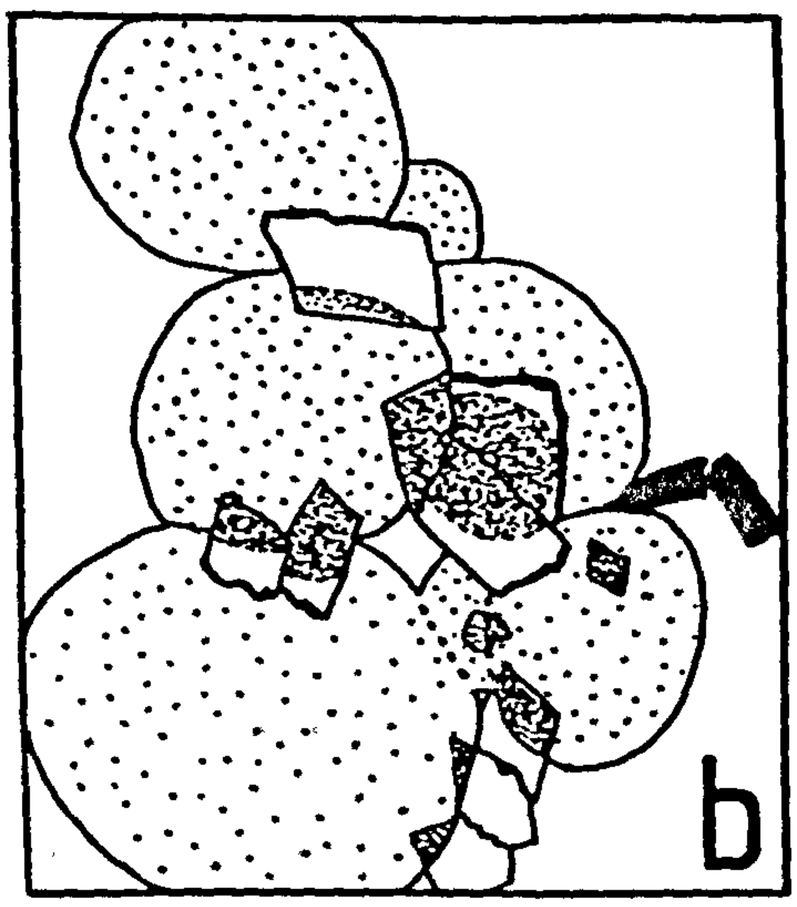


Fig 3.20 Development of anomalous inclusion patterns

a. incipient dolomitisation in uncompacted oolitic sediment - note inclusion ghosts of depositional grains
b. result of compaction : grain fracture, pressure solution and inter-penetration of grains and dolomite crystals

composition to the rims described here. However, the bright luminescence associated with the type A crystal rims is not seen, suggesting a compositional difference.

3.3.4 Paragenesis of incipient and pervasive dolomites

3.3.4.i Timing of Type A and B dolomite formation

Dolomite of types A and B is interpreted as having formed during early, near-surface diagenesis on the basis of the following observations.

(a) Where replacive, the dolomite is confined to depositional grains and only locally replaces fringing cements.

(b) Type B crystals occur in close association with fringing cements and locally themselves appear to form pre-compaction cement fringes.

(c) Depositional grains, early cements and dolomite in incipiently dolomitised limestones may all show evidence of compactional fracturing and/or pressure solution. Where early cements and/or dolomite are well developed the effects of compaction are less obvious. This variability is also observed in pervasive mosaics, despite overgrowth by later phases.

(d) Where type B crystals project into 'porespace', they may appear pitted or etched. These 'pitted' surfaces are filled by second generation cement.

(e) Second generation cements, usually echinoderm-syntaxial, clearly formed after the dolomite and during or after compaction.

The non-uniform leaching of dolomite crystals before precipitation of calcite spar cements suggests that a change in pore-water chemistry occurred, which was able to exploit compositional or structural weaknesses

in the dolomite (e.g. Al-Hashimi and Hemingway, 1973; Scherer, 1977). This change in porewater chemistry need only have been in Eh conditions, allowing the oxidation of Fe^{2+} in the dolomite lattice (Scherer, 1977) or it may have resulted in the thermodynamic instability and dissolution of the dolomite (e.g. Katz, 1971).

3.3.4.ii Early diagenesis

Fringing cements in the Brofiscin Oolite suggest a complex early diagenesis, involving marine and meteoric pore fluids in phreatic and locally vadose environments (see section 3.3.1.ii).

In addition to fringing calcite cements, type B dolomite (see section 3.3.1.v) appears to have provided a form of early cementation. The dolomite crystals partially replace depositional grains and extend beyond grain boundaries, often forming 'bridges' between adjacent grains. The form and distribution of these crystals does not suggest that they are replacements of fringing calcite cements, and in common with fringing cements they clearly pre-date compaction and precipitation of second generation cements. Where dolomite is well developed it appears to have provided a more rigid, compaction resistant framework. Type B dolomite occurs in close association with calcite fringing cements on a thin-section scale and locally may rim the same pore-space. Both fringing cement and dolomite are succeeded by echinoderm-syntaxial cements of possible meteoric phreatic origin. The most likely diagenetic environment for the formation of early dolomite would therefore seem to be the meteoric-marine mixing zone (e.g. Badiozamani, 1973, and Chapter 1).

Kaldi and Gidman (1982) described early dolomite cements and

replacements from the Permian and Pleistocene. In the Permian Lower Magnesian Limestone early selective replacement dolomitisation of micrite envelopes by mixed marine-meteoric waters was followed by precipitation of isopachous dolomite cement as the pore-waters became diluted by meteoric water introduced during marine regression (Kaldi and Gidman, 1982). Similar relationships were also observed in the Pleistocene Gt. Abaco carbonates, where dolomite occurs as a replacement of bioclasts and early fibrous cement and as an isopachous limpid rim cement around intergranular and intragranular pores. Dolomite cement is usually succeeded by coarse calcite spar. This diagenetic sequence is interpreted as representing progressive dilution of porewaters from originally marine (fibrous cements) through mixed marine-meteoric (replacement dolomite then dolomite cement) to meteoric (blocky calcite spar), reflecting a marine regression (Kaldi and Gidman, 1982). Ward and Halley (1985) described a similar sequence of replacement and cement dolomite from reefal carbonates of the Yucatan.

In the Brofiscin Oolite, the distinction between replacement and cement dolomite is not as clear as that described by Kaldi and Gidman (1982), and Ward and Halley (1985), and the isopachous geometry of the Permian and Pleistocene examples is not seen. However, the broad diagenetic associations and the timing of dolomitisation do appear comparable.

In contrast, the Gully Oolite which formed under similar depositional conditions (see Chapter 2), largely escaped early fringing cementation, with only localised occurrences of marine fibrous isopachous and meteoric cements (see section 3.3.3.ii). Dolomite of type A and B is developed in significant amounts only in the lowermost transitional beds of the Gully Oolite and in the underlying pervasive dolomites.

Climatic fluctuations may have influenced the contrasting early diagenetic histories of the Brofiscin and Gully Oolites via its effects on the development and activity of meteoric lenses and mixing-zones (see Longman, 1980 and Chapter 5). Fluctuations in the Dinantian climate of South Wales have been suggested by Wright (e.g. 1980, 1984b, 1984c) and these appear to have occurred on a scale which may explain the observed variations in early diagenetic style. That fluctuating meteoric-marine diagenetic conditions occurred in much of the Oolite Group of the North Crop (including equivalents of the Gully and Brofiscin Oolites) has been demonstrated by Raven (1983).

3.3.4.iii Selectivity of early dolomite

On a broad outcrop scale, the selectivity of dolomitisation can be seen at Brofiscin Quarry, where the incipiently dolomitised Brofiscin Oolite grainstone occurs between patchily to completely dolomitised wackestones and packstones of the Barry Harbour Limestone and Friars Point Limestone. This lithological selectivity is only apparent around the transitional margins of pervasive dolomite bodies.

On a petrographic scale, dolomite appears to replace selectively the muddy matrices of wackestone-packstone lithologies, leaving relic grains of ooids and bioclasts. Where these units are completely replaced by dolomite the evidence for selectivity becomes more subtle. However, in certain cases, where later phases of dolomite or calcite are present, it may be possible to infer initial selectivity. Preferential dolomitisation of micrite in packstones and wackestones is commonly observed in partially dolomitised limestones (e.g. Murray and Lucia, 1967; Choquette and Steinen, 1980; Mattes and Mountjoy, 1980) and more selectively in fine burrow

fillings (e.g. Morrow, 1978; Choquette and Steinen, 1980; McHargue and Price, 1982). Possible causes for the apparent greater dolomitisation potential of lime mud include differences in sediment porosity produced by burrowing (Morrow, 1978), the presence of marine clays from which Mg^{2+} could be released during burial diagenesis (McHargue and Price, 1982), grain surface area, solubility and permeability (Murray and Lucia, 1967).

In the Brofiscin Oolite grainstone, dolomite appears to have selectively replaced ooid cortices in preference to bioclasts. Echinoderm fragments, as individual grains or forming the nuclei of ooids appear to have offered the most resistance, although brachiopod and coral debris also forms relic grains in dolomite mosaics. In the transition to pervasive dolomite, dolomite rhombs are seen to impinge upon the margins of echinoderm fragments, and they also occur as replacements of material which occupied the axial canal. These impingement-replacement relationships are similar to those described by Lucia (1962). In addition, fine (less than 10 μm) rhombs occur within the matrix of the fragments. Complete dolomitisation of echinoderm fragments may render them unrecognisable within pervasive dolomite mosaics, or it may produce coarser dolomite crystals which define the vague shape of the original grains. More typically, however, echinoderm fragments are retained as relics. These relics may subsequently have been leached or replaced by later phases of dolomite, calcite and rarely, silica.

The apparent resistance of echinoderm fragments to dolomitisation in ancient rocks has been noted by many authors (e.g. Lucia, 1962; Murray, 1964; Murray and Lucia, 1967; Buchbinder, 1979; Schofield and Adams, 1985). However, selective early replacement of echinoderm fragments has also been observed (Sibley, 1982). Bullen and Sibley (1984) have reviewed the

subject of dolomite selectivity, and provided experimental evidence to show that an important control on the selectivity of dolomitisation is the availability of nucleation sites in the grain to be replaced. Cryptocrystalline grains, such as provided by echinoderms and coralline algae should be replaced more rapidly and with a greater retention of fabric (mimic replacement) than microcrystalline grains such as corals (Bullen and Sibley, 1984). This control appears to be independent of grain composition, as echinoderm fragments (usually high magnesium calcite) were rapidly dolomitised in Bullen and Sibley's experiments, even when artificially converted to low magnesium calcite before dolomitisation. However, under natural conditions of fresh-water diagenesis, this conversion may lead to crystal coarsening as well as formation of authigenic low-magnesium calcite, thereby reducing the number of nucleation sites and hence increasing resistance to dolomitisation.

In the Brofiscin Oolite, the main phase of syntaxial-overgrowth cementation clearly post-dates early dolomite formation and compaction. However, it has been shown that early pre-compaction meteoric diagenesis occurred in close proximity to echinoderm fragments, and it therefore seems unlikely that they would have completely escaped alteration. Their resistance to dolomitisation demonstrates that some crystal coarsening probably did occur.

Syndepositional micritisation of ooid cortices by boring algae (e.g. Bathurst, 1966) may have encouraged their early selective replacement by dolomite due to the production of a microporosity and an increase in surface area and hence availability of nucleation sites. The low magnesium calcite inclusions within the replacement dolomite suggest that the micrite was low-magnesium calcite (Sibley, 1982) at least at the time of

dolomitisation.

The effect of intragrain porosity or microporosity as a control on dolomite selectivity has been considered by Simms (1984a). As an external supply of reactants is necessary, the size and distribution of micropores within allochems will influence the diffusion flux to the dolomitisation site. The general effects of a diffusion constraint may be seen in the Brofiscin Oolite, where type A crystals entirely enclosed within ooid cortices, are typically much smaller than type B crystals at the free surfaces of ooids, suggesting that supply was the size-limiting step. In addition, the dark rims around type A dolomite crystals, which have been interpreted as accumulations of impurities derived from dissolution of the ooid, may also have affected the supply of material to the dolomitisation site.

3.3.4.iv Types C and D dolomite and dedolomitisation

Type C limpid dolomite occurs in irregular fractures which may be laterally linked to fossil mouldic cavities and to opened stylolites. The dolomite probably formed as a partial cavity-filling cement as well as a replacement of the adjacent host limestone. Type C dolomite clearly formed after cementation and stylolitisation of the host limestone.

Most type D dolomite crystals have been interpreted as insoluble (or less soluble) residues, which accumulated along stylolite planes during pressure solution. As such, they probably represent type A or B dolomite crystals. However, a small number of type D crystals may have an origin related to pressure solution (see Wanless, 1979) or, because of their general similarity to type C dolomite, may post-date stylolitisation.

Dedolomitisation (Shearman et al., 1961; Lucia, 1961) of types C and D dolomite crystals is common. The phenomenon has long been regarded as a

nearsurface weathering effect, whereby 'metastable' ferroan or calcian dolomite is preferentially replaced by calcite (e.g. Evamy, 1963; Katz, 1971; Al-Hashimi and Hemingway, 1973; Al-Hashimi, 1977). However, subsurface leaching of dolomite rhombs (e.g. Schofield and Adams, 1985) and burial dedolomitisation (Clark, 1980, Budai, Lohmann and Owen, 1984) appear to be viable alternative interpretations.

The dedolomites described here (after type C and D crystals) comprise coarse calcite which is optically continuous with and has the same (extremely dull) cathodoluminescence characteristics as the coarse fracture-filling calcite beyond the dolomite crystal boundaries. They are interpreted as 'burial' dedolomites on the following grounds:

i) They occur in fractures and cavities which clearly post-date cementation and stylolitisation of the host limestone.

ii) They comprise the same calcite which fills the fractures and which has been truncated by a later set of fractures (Group 2, section 3.3.1.iii).

iii) This calcite has distinctly different cathodoluminescent characteristics to that which fills the cross-cutting fractures and which may be of nearsurface origin.

3.3.4.v Paragenesis of pervasive dolomite mosaics

The variants of pervasive dolomite mosaics indicate a complex diagenetic history. In an attempt to unravel this history, it is often possible to draw direct analogy between features seen in pervasive dolomite mosaics and those in incipiently dolomitised limestones. For example the relationship between type B dolomite crystals and echinoderm-syntaxial

cements in which the dolomite has commonly been etched prior to the precipitation of calcite can be seen in limestones and pervasive dolomites with relic grains. The pre-compactional origin of type A and B dolomite, clearly demonstrated in limestones, can sometimes be seen in pervasive mosaics where it is suggested that a paucity of early cements and only minor type B dolomite development, perhaps followed by dissolution of relic grains, led to collapse of the carbonate matrix with compaction. Subsequent overgrowth by limpid baroque dolomite produced a xenotopic mosaic.

A tentative correlation has been made between the distinctively cathodoluminescent-zoned calcite which fills late fractures (group 2) in limestones and pervasive dolomites, and that which occurs as a late void-fill in pervasive mosaics (section 3.3.2.ii) and vein dolomites (section 3.4).

Other features appear to be confined to either limestones or pervasive dolomites. For example the fracture-filling limpid dolomite (type C) does not appear to have an equivalent in pervasive mosaics, although limpid rims around voids have a similar appearance and cathodoluminescent character.

Baroque dolomite occurs in pervasive dolomite mosaics and in vein dolomites. The following origins are suggested for baroque dolomite in pervasive mosaics.

i) passive cementation, where limpid, euhedral-anhedral crystals occupy well defined void-like structures within the mosaic.

ii) replacement of relic grains, where subhedral-anhedral cloudy crystals occur in similar structures to (i).

iii) neomorphic replacement of pre-existing dolomite, where subhedral to anhedral crystals occupy irregular areas within the mosaic.

The observation that baroque dolomite tends to form xenotopic mosaics and the more typical 'non baroque' dolomite forms idiotopic mosaics, with transitional hypidiotopic fabrics, has also been made by Gregg and Sibley (1984) for various pre-Cenozoic dolomites. Gregg and Sibley (1984) suggested that xenotopic dolomite texture results from the replacement of limestone or pre-existing dolomite (by neomorphic recrystallisation) at elevated temperatures (>50°C). Their conclusions were based on petrographic studies which established the timing and distribution of dolomite in the Ordovician Galena Group (Wisconsin) and Trenton Limestone (Michigan). Additional evidence comes from a contact metamorphic aureole and from laboratory experiments in which non-stoichiometric idiotopic Cenozoic dolomites were recrystallised, and aragonitic and calcitic skeletal fragments dolomitised at high temperature (250-300°C). Gregg and Sibley (1984) also showed that crystal growth theory predicts the development of anhedral crystal mosaics (e.g. xenotopic dolomite) above a 'critical roughening temperature' (CRT). They suggest that, for dolomite, this temperature is approximately 50°C, below which smooth crystal growth surfaces are energetically favoured and subhedral to euhedral crystal mosaics develop. The CRT for calcite is probably lower (around 25°C), so that neomorphic textures are more readily produced in limestones (Gregg and Sibley, 1984).

The suggestion that baroque dolomite may be used as a geothermometer has been made by Radke and Mathis (1980), on the basis of its close association with liquid hydrocarbons, and with yellow fluorite and calcite containing fluid inclusions suggesting temperatures of formation in the range 100-129°C. The 'replacement mode' of baroque (saddle) dolomite described by Radke and Mathis (1980) is analogous to the xenotopic-A

(anhedral) dolomite of Gregg and Sibley (1984) and to much of the baroque dolomite described here. Saddle-shaped crystals (xenotopic-C of Gregg and Sibley) are rarely developed in pervasive mosaics but occur around intercrystalline porosity in vein dolomites.

Authigenic silica also appears to be confined to pervasive dolomites, where it replaces bioclasts, forms a more diffuse matrix or occurs as a coarse void-filling cement. It only occurs in association with idiotopic dolomite mosaics, which it appears to post-date, so that its relationship to other phases cannot be determined. However, the petrographic distribution of silica is similar to that of baroque dolomite, suggesting either (i) it formed before baroque dolomite, by replacement of relic grains or as a void-fill, or (ii) it formed after baroque dolomite as a selective replacement. The latter case is less likely, as it is difficult to explain why idiotopic mosaic dolomite should have been more resistant to silicification. Whilst it might be possible to make a case for preferential silicification of baroque dolomite due to compositional differences, it is more likely that calcium carbonate has been preferentially replaced. This being the case, silicification appears to have 'interrupted' the process of dolomitisation, and probably occurred sometime after early diagenesis, but before later burial dolomitisation. Dolomitisation interrupted by silicification has been described by Dietrich, Hobbs and Lowry (1963), who concluded that silica formed under relatively near surface, oxidising conditions in the Cambro-Ordovician Knox Group dolomites. Meyers (1977) has shown that silica formed in a shallow burial, probably meteoric diagenetic environment in the Lake Valley Formation of New Mexico.

The following summarises the main pervasive mosaic variants

identified, and suggests their possible paragenetic relationships. A diagrammatic representation is presented in Fig. 3.21.

i) early selective dolomitisation, with coarse relic grains.

ii) early complete dolomitisation, with minor intercrystalline porosity.

iii) early selective dolomitisation followed by dissolution of relic grains.

iv) as (iii) with limpid dolomite rims around secondary pores and/or a later calcite fill.

v) as (iii) with limpid baroque dolomite filling dissolution voids.

and/or

(vi) as (i) with later replacement of relic grains by xenotopic baroque dolomite.

and/or

(vii) as (ii) or (iii) with isolated or pervasive neomorphism of dolomite to xenotopic baroque dolomite.

viii) as (i) or (iii) with later replacement of bioclasts or filling of voids by silica.

3.3.4.vi Cathodoluminescence petrography as an aid in the study of pervasive dolomites

Cathodoluminescence (C.L.) petrography of carbonates as a quantitative tool is complicated by uncertainties regarding the precise controls on luminescence (Pierson, 1981; Fairchild, 1983; Machel, 1983; ten Have and Heijnen, 1985). In general, variations in luminescence can be ascribed to variations in chemical composition of the carbonate. In particular, Mn^{2+} is considered to be the main activator and Fe^{2+} the main quencher of

Fig 3.21 FOLDOUT

Schematic representation of the paragenesis of pervasive dolomite mosaics and host limestones.

Left to right of the main part of the figure represents increasing proportion of early dolomite and illustrates dolomite selectivity. Top to bottom represents the possible development of pervasive dolomite mosaics and limestones, the variations are described more fully in the text.

INCREASING PROPORTION OF EARLY, PRE-COMPACTIONAL DOLOMITE.

OTHER EXAMPLES

NEARSURFACE

SHALLOW BURIAL

DEEPER BURIAL

? UPLIFT

Early selective dolomitisation of ooids (early cements omitted for clarity)

Mosaics with relic grains

Hypidiotopic to idiotopic mosaic with minor intercrystal porosity (ϕ)

Barry Harbour Limestone (wackestone/packstone) selective dolomitisation of mud matrix. (idiotopic dolomite)

Wenvoe oolite (part of BHL)

compaction and leaching of dolomite

mismatched inclusion patterns common in incipient mosaics

Echinoderm syntaxial and poikilotopic calcite spar cementation

Grain dissolution → 2° ϕ subtle compaction effects

Silicification of relic grains ± silica cement

Grain dissolution and compactional fracture due to poorly developed early cements; and incomplete dolomitisation

Vein dolomite

Stylolite formation

Irregular fractures; opening of stylolites ± fossil mouldic cavities. Limpid dolomite rhomb growth.

Limpid dolomite rims

?

Irregular cavity filling of neomorphic xenotopic dolomite

Minor limpid dolomite or calcite in intercrystal ϕ

Replacement of relic grains or cementation by xenotopic dolomite following grain dissolution.

Xenotopic mosaic overgrowth

Xenotopic and idiotopic dolomite with intercrystalline porosity and limpid dolomite rims locally

Dedolomitisation and calcite fracture fill.

Late fracturing; fracture filling coarse, C.L. zoned calcite

Porosity filling coarse, C.L. zoned calcite.

Coarse C.L. zoned calcite filling fractures in dolomite.

Porosity filling coarse C.L. zoned calcite

luminescence. Other elements may act as sensitisors, transmitting energy to the activators (Machel, 1983 for example). Variations in luminescence colour and intensity may then be taken, qualitatively to represent variations in the chemical environment of precipitation or recrystallisation of dolomite. The bulk chemistry of the diagenetic fluids would be governed by large-scale factors, but local microenvironmental conditions (e.g. Eh) and their effects on partitioning (see Chapter 4) would control the availability of ions to the precipitating carbonate phases. Experimental evidence suggests that the rate of crystal growth may also influence Mn^{2+} uptake, independant of the fluid concentration (ten Have and Heijnen, 1985).

Variations in luminescence of pervasive dolomite mosaics therefore has the potential to guide identification of different phases, by virtue of their formation in different or changing chemical environments.

The results of C.L. petrography of pervasive mosaics show that replacement type A and B dolomite forming idiotopic mosaics have a fairly uniform or slightly blotchy luminescence. Less inclusion-rich parts of type B crystals, occurring beyond grain boundaries, have a brighter luminescence which may show a vague zonation. Zones define euhedral shapes parallel to crystal faces where they abut intercrystal porosity. This texture may be interpreted as representing the 'pore-filling' phase of type B crystal growth as suggested by transmitted light petrographic study of incipient dolomite mosaics. However, the C.L. zonation is <u>not</u> observed in these crystals where a 'cementation' origin seems most likely. The interpretation of C.L. zonation is, therefore, difficult. As Fairchild (1980) and Gregg and Sibley (1984) have shown, replacive dolomite is quite cable of forming crystal faces (at least below the C.R.T., Gregg and

Sibley, 1984), and so it may prove impossible to distinguish between cement and replacement textures in pervasive dolomite mosaics on C.L. evidence alone.

Where limpid overgrowths on dolomite crystals only occur centripetally, around secondary pores, a cement origin may be more likely. These rims typically have a zoned luminescence, which distinguishes them from the uniform or blotchy luminescing host crystals. Zones can be traced around pores, showing the limpid dolomite to be continuous from one host crystal to the next.

Limpid dolomite rims are distinguished from limpid baroque dolomite by the uniform, extremely dull or locally blotchy luminescence of the latter. In terms of C.L. characteristics, limpid rims and xenotopic baroque dolomite appear to have different origins. However, petrographic-cathodoluminescence studies of vein dolomites (see section 3.4) show that non-luminescent or blotchy luminescent xenotopic baroque dolomite mosaics are closely associated with C.L. zoned euhedral limpid rims. A further point of interest to the paragenesis is that both vein dolomites and limpid rims in pervasive mosaics may be succeeded by distinctively C.L. zoned, coarse calcite cement.

Whilst C.L. is clearly of little quantitative value at present, it offers a tool for qualitative geochemical interpretation. In the pervasive mosaics it shows that the chemistry of the dolomitising environment and the conditions under which dolomite precipitated, varied during the formation of pervasive dolomites as a whole.

3.4 Vein dolomites

Background information (regional and stratigraphic distribution, etc)

for the vein dolomites is presented in Chapter 2.

Dolomite veins form distinctive irregular tongues to laterally persistent vertical or sub-vertical sheets ('dykes'). The latter are well exposed in the Taff Gorge where the host limestones (Hunts Bay Oolite) have been selectively quarried (see Fig. 3.22a). In detail these bodies comprise several dolomite 'veins' from a few tens of millimetres up to a metre wide and are approximately parallel-sided with limestone between. Strike orientations have been measured at approximately 280° and at 340° in the Taff Gorge. At Creigiau veins are oriented about 360°.

Smaller veins have been observed only in two-dimensional exposures, where they form upward-narrowing tongue-like bodies up to 0.5m wide. The relationship between these and the more continuous veins is uncertain.

Dolomite vein boundaries appear sharp in field exposures, but in thin section they appear transitional.

The central parts of veins comprise coarse mosaics (up to 1mm crystal long dimensions) of anhedral ferroan dolomite. Crystals have sweeping extinction (typically through angles of c. 60°), and contain numerous micron-sized inclusions (Fig. 3.22b). Euhedral crystal faces are rarely developed in these mosaics, but may occasionally be seen around intercrystalline pores where they appear curved. Very rarely, spear-shaped crystals are developed. All these features are typical of saddle (or baroque) dolomite as defined by Radke and Mathis (1980) (see also discussion by Zenger, 1981). The term 'baroque dolomite' is preferred here because the distinctive saddle-form is not observed in anhedral mosaics.

Locally within these baroque dolomite mosaics two generations of dolomite are recognised, with the second slightly coarser phase identified by its euhedral inclusion-defined intracrystalline zones (Fig. 3.22c).

Fig 3.22

a. field photograph showing residual vein dolomite bodies in Steetly old quarry, following selective quarrying of limestone (Hunt's Bay Oolite)

scale is c. 1.75 metres

b. anhedral mosaic in vein dolomite showing undulose extinction (xenotopic) and numerous micro-inclusions (XPL)

0.2mm

Gully Oolite, Taff's Well quarry.

c. vein dolomite mosaic showing two phases of development : 1, anhedral mosaic with local intercrystalline porosity (dark areas), 2, coarse mosaic,with inclusion defined euhedral zones, forming a veinlet in the anhedral mosaic.

Most crystals show undulose extinction and mosaics have intercrystalline porosity which may be partially filled with calcite (C, see also Fig 3.23) (PPL)

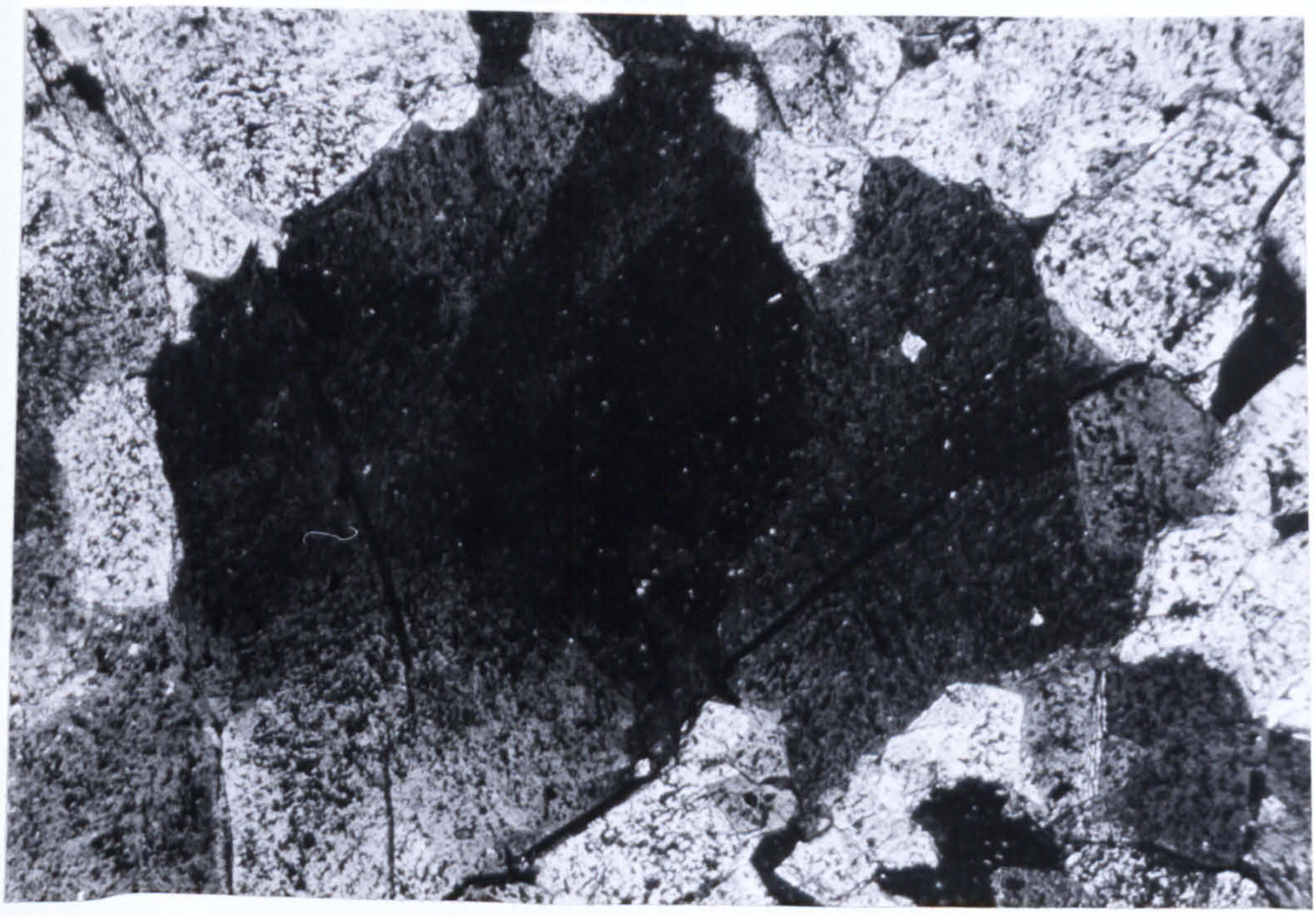
0.5mm

Hunt's Bay Oolite, Steetly old quarry, Taff Gorge.

a



b



c

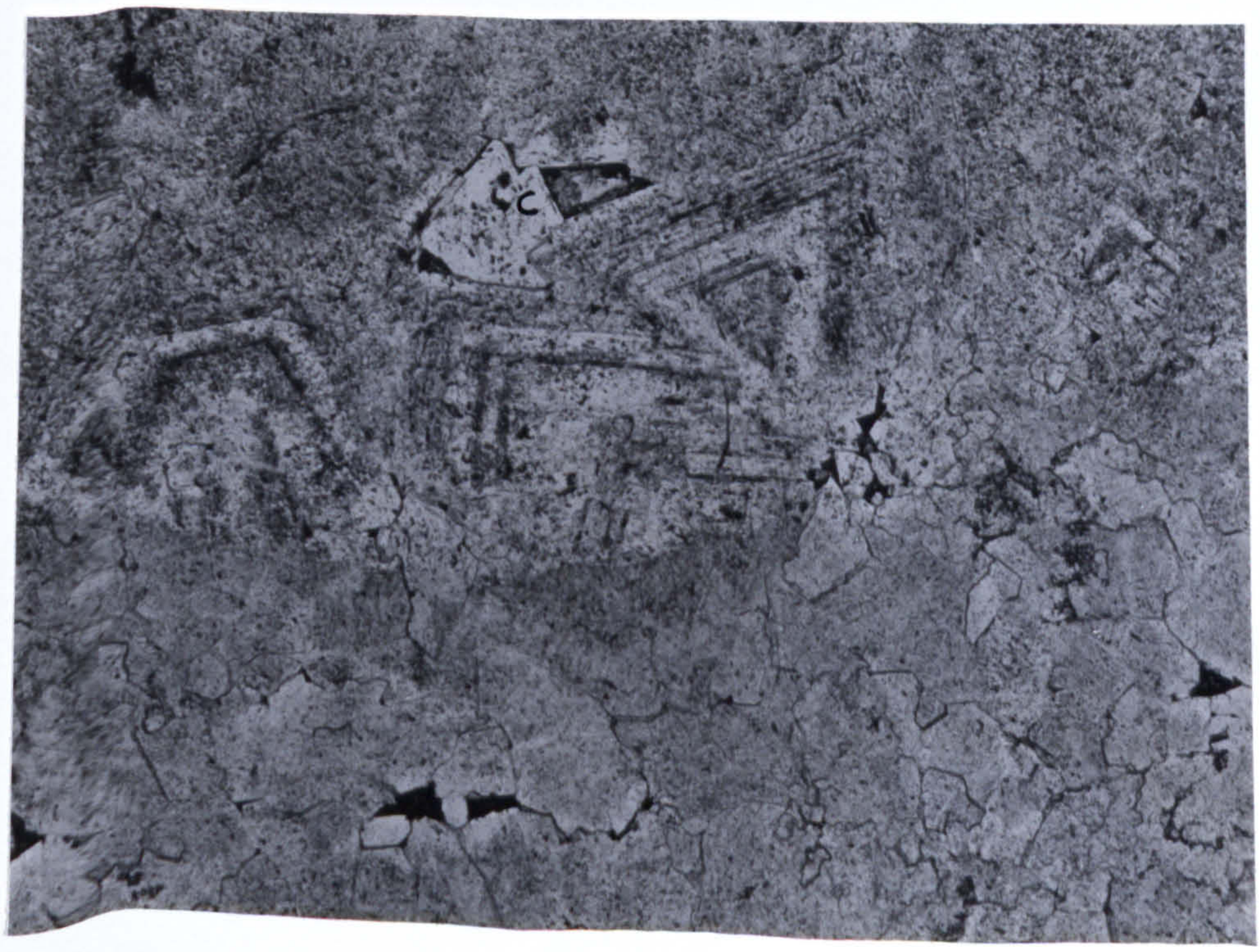


Fig 3.23

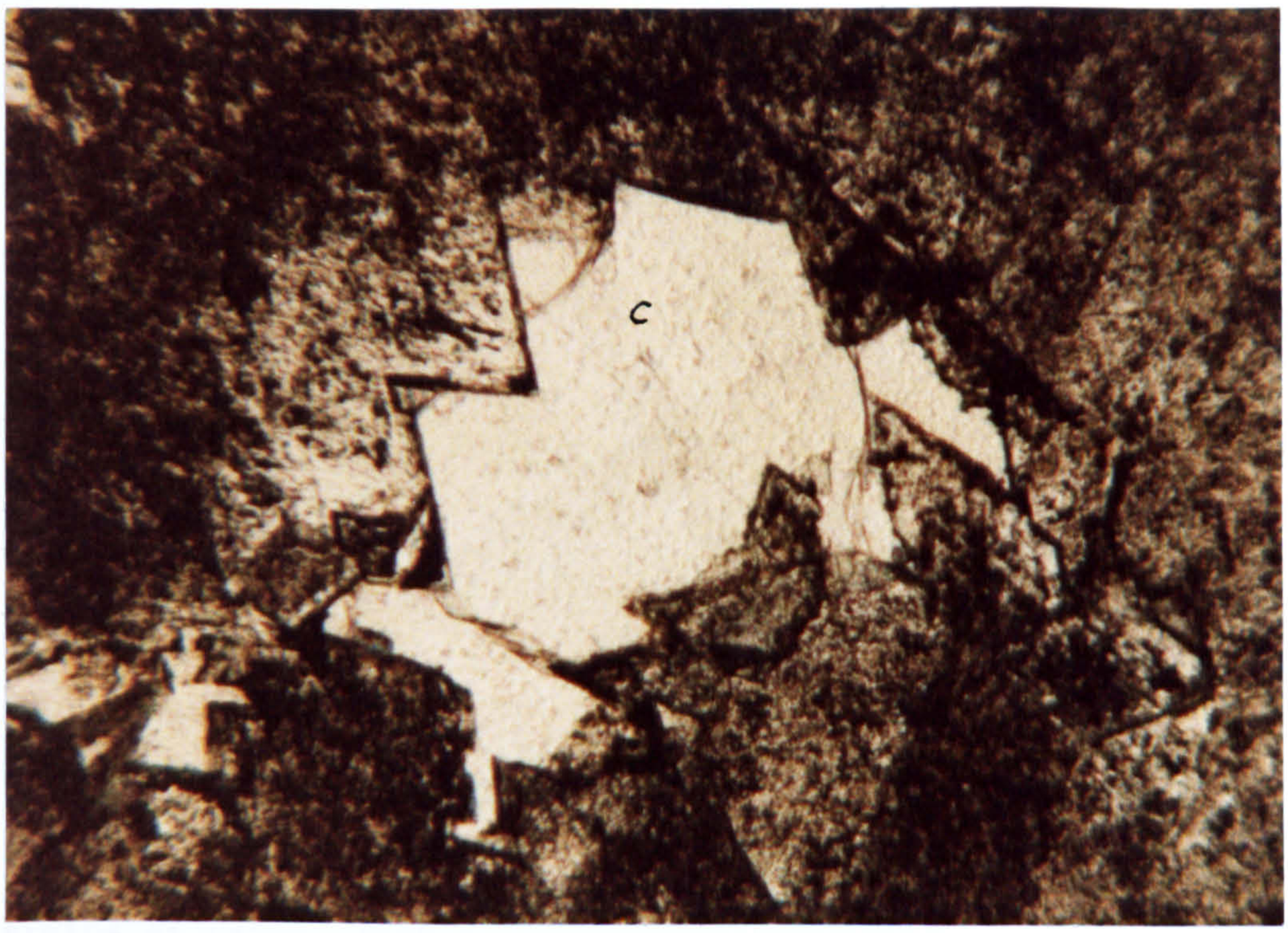
a. replacive vein dolomite mosaic with calcite (C) filling intercrystalline porosity

b. same view under C.L., showing dull blotchy luminescent dolomite and multiple zones in calcite (compare to Figs 3.9 & 3.16)

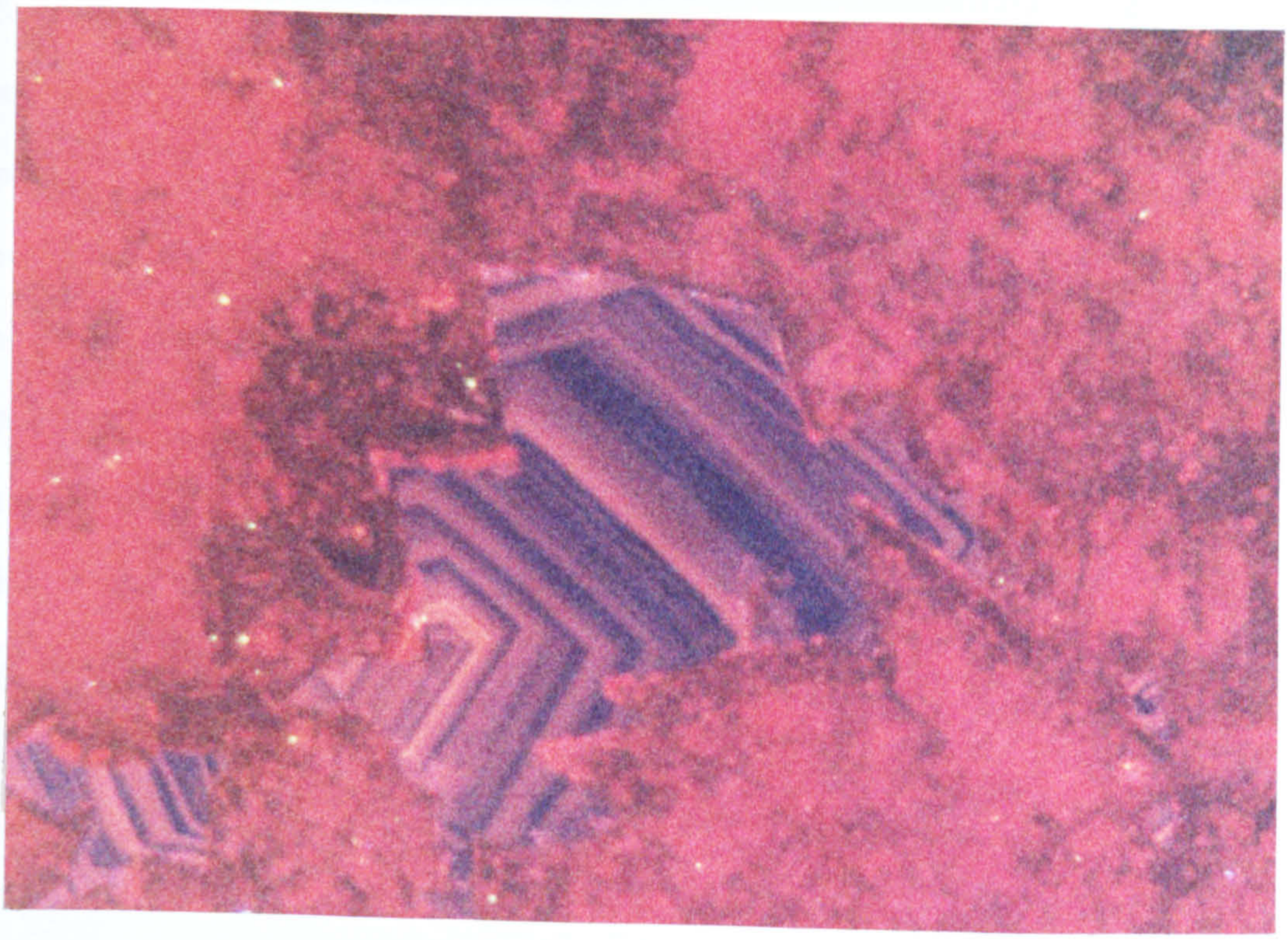
0.4mm

Hunt's Bay Oolite, Steetly old quarry.

a



b



This dolomite may occupy 'veinlets' within the baroque mosaics, but the boundary between the dolomite types is not sharp (Fig. 3.22c).

Intercrystalline porosity may be partially or completely filled with coarse ferroan calcite (Figs. 3.22c, 3.23a, b). Cathodoluminescence petrography reveals that the non-inclusion zoned dolomite has an extremely dull-luminescence, or is 'dead', whilst the inclusion-zoned dolomite has a dull to very dull blotchy luminescence. The ferroan calcite has a complex, multiple-zoned luminescence and is very similar to the calcite observed as a late phase in pervasive dolomite mosaics and as a fracture fill in the Brofiscin Oolite Limestone (see section 3.3.1.iii).

Towards the margins of veins, subhedral-euhedral non-baroque dolomite crystals become important within the baroque mosaics (Fig. 3.24a). They commonly have inclusion-rich cores and more limpid rims. The limpid rims have zoned medium to dull cathodoluminescence, comparable to the limpid rims on pervasive mosaic dolomite. Intercrystalline 'porosity' may be filled with the ferroan calcite already described. Subhedral to euhedral, non-baroque dolomite may form the only dolomite phase at the margins of veins and the rhombs of which it is comprised may also occur as scattered crystals in immediately adjacent limestones. Where type B dolomite crystals (described in section 3.3.1.v) are present, they may be confused with the scattered vein-related dolomite. However, the latter always have a cross-cutting relationship to depositional grains and cements in the host limestone, and their inclusions do not define 'ghosts' of depositional grains (Fig. 3.24b). At the margins of some veins in the Hunts Bay Oolite, dolomite rhombs or clusters of rhombs appear to float in a mosaic of neomorphic calcite spar, which has a bright, uniform to blotchy luminescence.

Fig 3.24

a. vein dolomite mosaic showing limpid euhedral rims on subhedral to euhedral dolomite crystals. Note coarse intercrystalline porosity, some calcite fill(C) and locally developed anhedral (xenotopic) dolomite mosaic (centre of field of view) (PPL)

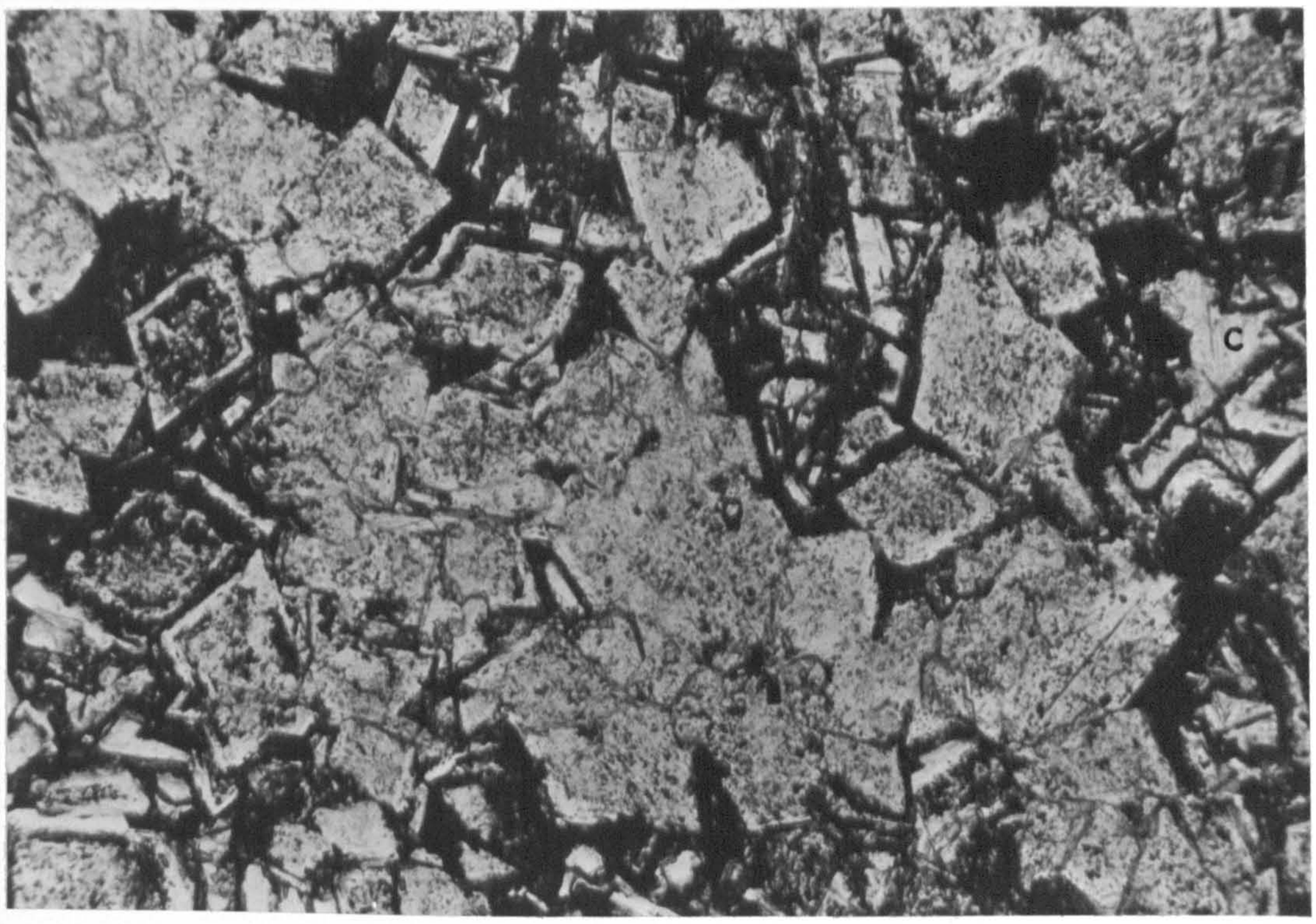
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Hunt's Bay Oolite, Steetly old quarry

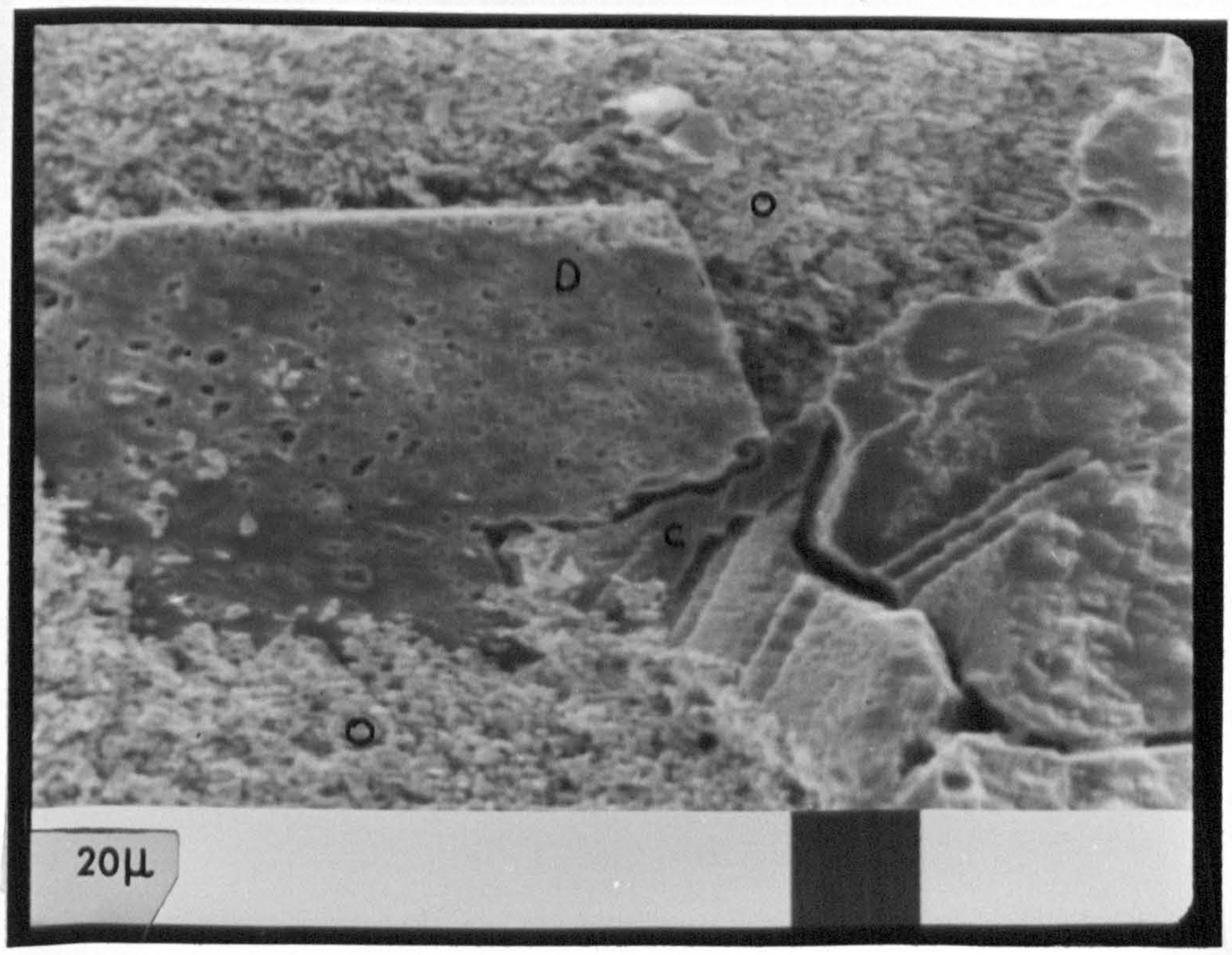
b. type B dolomite (D), here replacing part of two ooids (O) in Gully Oolite, note inclusions within dolomite rhomb, some of which have been etched during sample preparation. Later calcite spar (C) replaces part of dolomite rhomb (SEM photomicrograph , sample etched for 30 secs. witn 1% HCl)

Gully Oolite, Llantrisant road section.

a



b



Discussion

The marginal fabrics of dolomite veins suggest that they are replacements of their host limestones. However, their geometry suggests that their distribution is controlled by pre-existing structures (i.e. joints, faults or fractures) and they may therefore have formed partially as a void fill.

Locally developed 'porosity' (now largely calcite-filled) may represent relics of original (pre-dolomite) voids, and where spear-shaped crystals are developed, a void-filling origin is likely (Radke and Mathis, 1980), limpid overgrowths may also represent a void-filling phase. The majority of the baroque dolomite mosaics, however, have typical 'replacement-mode' characteristics (Radke and Mathis, 1980). The neomorphic calcite spars (pseudospars) seen in some limestones adjacent to vein dolomites are similar to those described by Schofield (1983) and Schofield and Adams (1985). Schofield (1983) suggested that enhanced neomorphism in dolomitic limestones in Woo Dale (Derbys.) could be due to stress anisotropy produced by the growth of dolomite in the rock, and related the neomorphic process (thin-film migration) to non-seam pressure solution.

That vein dolomitisation occurred in phases is suggested by the two generations of baroque dolomite, with slightly different inclusion patterns and cathodoluminescence character, and by the limpid overgrowths on inclusion-rich mosaic crystals. However the 'phases' are intimately associated with no suggestion of a break in the development of mosaics. Furthermore, they may all be succeeded by the same coarse ferroan calcite which forms an intercrystalline pore-fill. The cathodoluminescent zonation

of this calcite is similar to, and may be partly correlated with, that seen in the pervasive dolomite mosaics, and as a fracture-fill in the Brofiscin Oolite. Using the principle of cement stratigraphy (Meyers, 1974, 1978), a genetic relationship between these cements may be proposed. The post-fracture, post-limpid dolomite, post- baroque dolomite distribution of the cement in vein dolomites is supported, in combination, by the other two occurrences.

Although the actual fault or joint planes or fractures are no longer visible the distribution of vein dolomites is clearly structurally controlled (see Chapter 2 for further discussion of structure).

The timing of vein dolomitisation with respect to the development of the joint systems cannot be accurately determined. However, the baroque form of the dolomite suggests that it formed at temperatures in the range 60-150°C (Radke and Mathis, 1980). These temperatures are consistent with the estimated end-Carboniferous burial depths for the main vein bearing units (1550m and 1300m minimum for the Gully Oolite and Hunts Bay Oolite respectively - see Chapter 2). Vein dolomitisation may therefore be approximately coeval with joint formation, see further discussion in Chapter 5.

CHAPTER 4

Dinantian Dolomites - Geochemistry

4.1.1 Introduction

In the preceding chapters, the sedimentological and regional stratigraphic setting (Chapter 2) and petrographic relationships (Chapter 3) of dolomites in the Dinantian of South Wales were described and the probable timing and progression of dolomitisation discussed. The purpose of this chapter is to present some geochemical data which provide further constraints on the interpretation of these dolomites.

There are still many uncertainties regarding the chemistry of dolomitisation and the interpretation of chemical variations in dolomite. Important variations include Ca:Mg ratio, degree of crystal ordering and content of minor and trace elements, principally Fe, Sr, Na and Mn, and oxygen and carbon stable isotopic compositions (Morrow, 1982a, 1982b). The most useful studies combine some or all of these geochemical parameters with stratigraphic, sedimentological and petrographic data (see Morrow, 1982b, and papers in Zenger et al., 1980 for review). For example, studies of major element variations in numerous dolomites (mostly of pre-Cenozoic age) have revealed a tendency for dolomite to be either calcian or more nearly stoichiometric (around 55 mole % and 51 mole % Ca respectively). These variations occur between both dolomites of clearly different origins and between rocks comprising different proportions of dolomite; they also occur within stratigraphic sequences or single dolomite bodies (see for example, Lumsden and Chimahusky, 1980; Morrow, 1982b; Sperber et al., 1984).

In Holocene examples, it also appears that the degree of order

exhibited by dolomite crystals may vary independantly from their Ca:Mg composition (Land, 1980). Although the degree of order in ancient dolomites has not commonly been measured (Morrow, 1982b), order versus stoichiometry may provide a means of empirically grouping dolomites.

The interpretation of trace element and stable isotope compositions of dolomites is complicated by uncertainties regarding the distribution coefficients or fractionation factors which control the incorporation of trace elements or stable isotopes under sedimentary-nearsurface diagenetic conditions and by the unknown effects of compositional and ordering variations (Land, 1980, 1983; Viezer, 1983a). Largely by extrapolation from experimental results or from calcium carbonate systems, Na and Sr offer some potential for qualitative interpretation of dolomite geochemistry (e.g. Viezer et al., 1978; Land, 1980; Sass and Katz, 1982; Veizer, 1983a). The behaviour of Mn in carbonate diagenesis (e.g. Brand and Veizer, 1980; Veizer, 1983a) together with Fe provides a further possibility for qualitative interpretation.

Dolomite stable isotope (oxygen and carbon) compositions may reflect the temperature ($\delta^{18}O$) and composition ($\delta^{18}O$ and $\delta^{13}C$) of dolomitising fluids and therefore provide supporting evidence for interpretation. However, interpretation must be strongly constrained by petrographic and broader sedimentological criteria. For example, whilst 'open-system' diagenesis may be invoked for large scale dolomitisation because of the requirement for allochthonous Mg^{2+}, the source of dolomitising fluids will depend on the environmental setting and the timing of dolomitisation. The possibility that partially closed system dolomitisation or recrystallisation of pre-existing dolomite may occur during the formation of massive dolomites (dolostones) should be considered (e.g. Land, 1980,

1983), and will affect the interpretation of geochemical data. Recognition of neomorphic, replacement and cementing phases is therefore very important (e.g. Gregg and Sibley, 1984).

4.1.1.a Methods

This chapter is divided into three main sections: (1) Stoichiometry and order; (2) cation chemistry; (3) stable isotope chemistry. Each dealing with aspects of geochemical data obtained by the following methods: X-ray diffraction analysis (XRD, section 1), atomic absorption spectrometry (A.A.S.), inductive coupled plasma atomic emission spectrometry (I.C.P.S.), electron microprobe analysis (in support of AAS and ICPS) and stable isotope mass spectrometry.

4.1.1.b Sample selection

Field, stratigraphic-sedimentological (Chapter 2) and petrographic data (Chapter 3) provided the basis for sample selection. Emphasis was placed on sampling the different dolomite types by preparing whole-rock samples of as close to homogenous appearance as possible. Any clear inhomogeneity (e.g. more than one phase of dolomite) was identified, and where possible samples were separated. In the case of mixed-carbonate samples (identified by petrography and XRD) attempts were made to physically separate the usually minor calcite phase by heavy liquid techniques. Only where this appeared to be successful, were 'purified' dolomites analysed further. A small number of dolomites comprising clearly distinct phases were separated by scraping material from the surface of thin sections, and data from the analysis of these samples is presented together with those from single- and mixed-phase whole-rock analyses.

In addition a small number of whole-rock and dissected limestone

samples were prepared.

The following groups of dolomite samples were analysed.

1.	Dolomicrites	whole rock and separated dolomicrite and separated fenestral dolospar samples.
2.	Pervasive dolomites	whole-rock idiotopic and mixed idiotopic-xenotopic dolomite; separated pairs of idiotopic and xenotopic dolomite, from mixed samples.
3.	Vein dolomites	whole rock idiotopic, xenotopic and mixed idiotopic-xenotopic dolomite.

4.1.2 Stoichiometry and crystal order

X-ray diffractometry (see Appendix I) was carried out on whole-rock dolomite samples, pre-selected on the basis of petrographic study to (a) confirm their mineralogical composition, (b) identify compositional (Ca:Mg) variations, and (c) determine the degree of crystal order.

A few samples were found to contain small amounts of calcite, as predicted from petrographic identification. Where possible these samples were purified to a point where the calcite major peak [104] was reduced to background levels on X-ray diffractograms. Where this could not be achieved, samples were excluded from further analyses.

Except for quartz in a small number of samples (confirming petrographic identification), non-carbonate components were not detected above background levels on X-ray diffractograms. Although acid-insoluble residue data suggest that clay minerals or other fine non-carbonate phases may be present (0 to 7 wt. %), no quantitative XRD has been carried out on these.

Mole % $CaCO_3$ in dolomite was calculated from the d spacing of the

[104] peak measured relative to an internal standard (cerium oxide), using the relationship Mole % $CaCO_3$ = Md + B (Lumsden, 1979), where:

M = 333.33

d is the observed d spacing in Ångstroms

and B = -911.99

The accuracy of this method depends upon the relationship between lattice constant and composition; for example, using available calibrations for $MgCO_3$ in calcite Milliman (1974) showed that a range of values (up to several mole %) are possible for a single measured d spacing. The method used here is based on d spacings of 2.886 Å = 50 mole % $CaCO_3$ and 2.901 Å = 55 mole % $CaCO_3$ (Goldsmith and Graf, 1958a). The data are therefore comparable with those of several other workers (e.g. Lumsden, 1979; Lumsden and Chimahusky, 1980; Sperber, Wilkinson and Peacor, 1984). Emphasis should be placed on the relative and not the absolute values obtained by this method.

Results

The data for all groups fall within the compositional range 50 to 55 mole % $CaCO_3$ and there is considerable overlap between the groups (see fig. 4.1).

However, AAS analyses suggest Ca^{2+} up to 5 mole % ($\bar{x}$ = 1.7 mole %) in excess of XRD calculated compositions. This discrepancy may be due to one or a combination of factors, including the following:

1. Mechanical errors involved in the measurement of peak positions (see Appendix I), probably very small.
2. Errors due to the presence of more than one dolomite compositional phase, producing 'composite peaks'. As most of the measured peaks

Fig 4-1

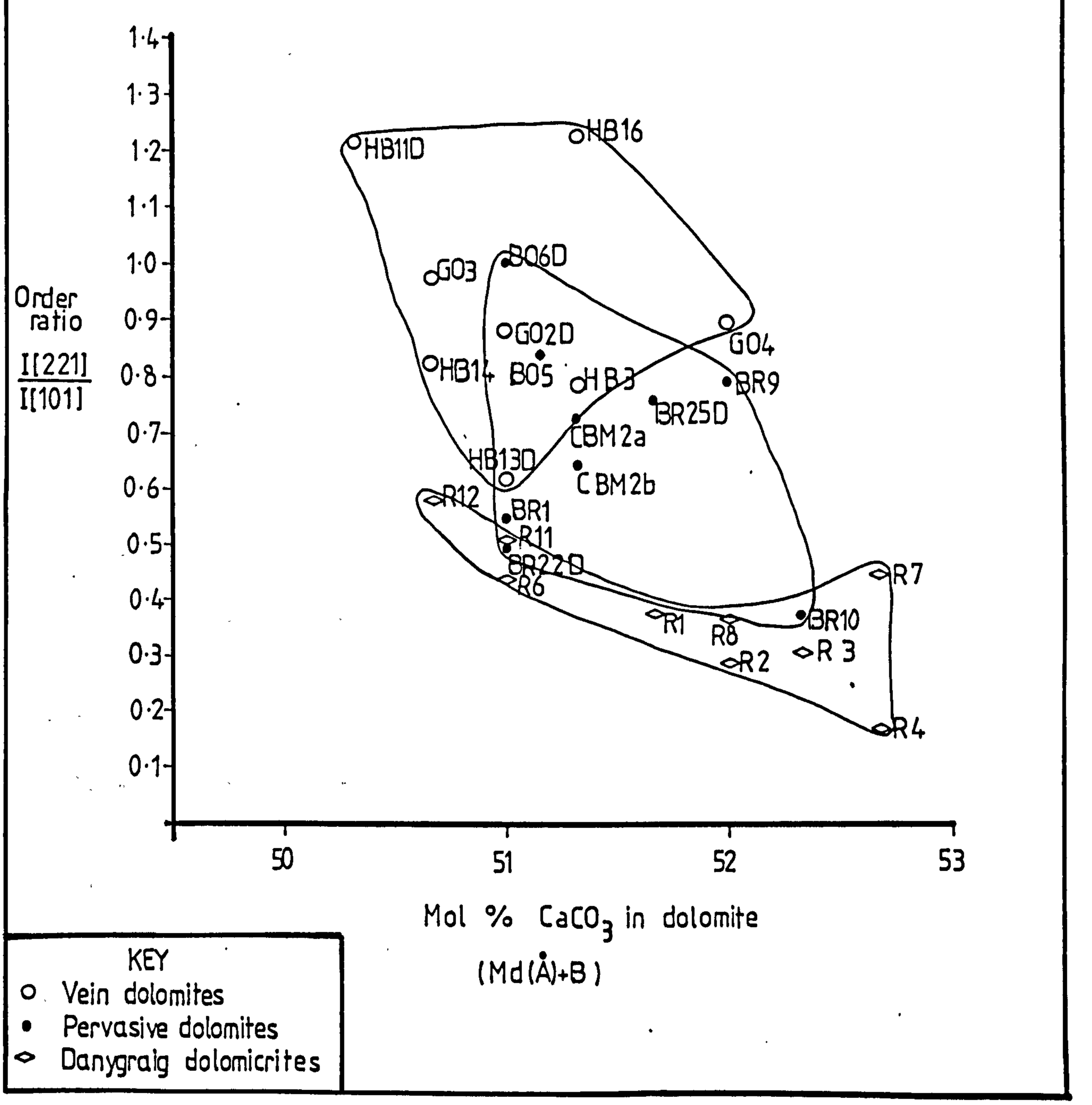


Fig 4.1 : XRD data showing stoichiometry of dolomite (as mol% $CaCo_3$) and ordering (see text and appendix 1 for explanation).

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enclose areas representing a range of compositions at least as wide as those possible in dolomite (e.g. 55 to 49 mole % $CaCO_3$), it is possible that strong peaks for more stoichiometric dolomite include minor peaks for calcian (and/or ferroan) phases.

3. The presence of minor amounts of calcite (less than c. 4 wt. % by XRD) or other calcian phase not detected by XRD or petrographic examination; but which on acid digestion contributed Ca^{2+} to the solution for AAS analysis.

4. Errors in AAS analysis ($\pm$0.8% at 30 wt. % Ca^{2+}).

Ordering data

The degree of order of dolomite, that is the extent to which the principal cations (Mg^{2+} and Ca^{2+}) are mixed in the c-axis direction, was calculated by dividing the intensity of the ordering line [221] by that of the diffraction peak [101] (Goldsmith and Graf, 1958b; McKenzie, 1981). The greater the ratio, the higher the degree of order.

The results are plotted against stoichiometry data on Fig. 4.1.

Discussion

Compilations of data on ancient (pre-Cenozoic) dolomites (e.g. Lumsden and Chimahusky, 1980; Morrow, 1982b; Sperber, Wilkinson and Peacor, 1984) reveal that most have compositions in the range 48-57 mole % $CaCO_3$, with means around 51 and 55 mole % (Sperber, Wilkinson and Peacor, 1984). Morrow (1982b) and others, have noted the following compositional groups of dolomite (see Morrow, 1982b, fig. 8).

1. ancient sucrosic and sparry dolomites (49-56 mole % $CaCO_3$)

2. finely crystalline modern and ancient dolomites <u>not</u> associated with

evaporites (50-62 mole % $CaCO_3$).

3. finely crystalline modern and ancient dolomites associated with evaporites (50-56 mole % $CaCO_3$).

Clearly the considerable overlap in compositions and the likely uncertainties in analysis, require that detailed petrographic and facies criteria support interpretation.

The dolomites reported in this study have compositions which fall within the range of overlap of the above groups, but on the basis of petrographic and facies criteria pervasive and vein dolomites fall into group 1 and the dolomicrites into group 2. The minor occurrence of evaporite pseudomorphs in the dolomicrites indicates at least localised increases in salinity and perhaps some of the initial dolomite in these sediments formed under these conditions. However, large scale evaporative dolomitisation (e.g. Friedman, 1980) seems unlikely (see Chapters 2 and 3).

Sass and Katz (1982) have related the Mg/Ca ratio of ancient dolomites to the degree of isolation of the dolomitising system from overlying seawater. They showed that dolomitisation under increasing isolation may cause a gradual decrease in the Mg/Ca ratio of the solution and hence in any dolomite forming from it. Sperber, Wilkinson and Peacor (1984) recognised two distinct populations of ancient dolomites: (i) dolomitic limestones (with around 20 wt. % dolomite) and (ii) dolostones (with a modal dolomite content of 97 wt. % dolomite). Although both populations include stoichiometric and calcian dolomite, a tendency for dolostones to comprise more stoichiometric dolomite and limestones to contain more calcian dolomite exists. This pattern may reflect the relative openness of the diagenetic systems in which dolomite forms. In particular, Sperber, Wilkinson and Peacor (1984) suggested that dolomitic limestones originate

in diagenetically closed systems (with high rock/water ratios, see section 2 below), deriving their Mg^{2+} from dissolution of Mg-calcite. The requirement for allochthonous Mg^{2+} in the formation of more massive dolostones implies relatively open diagenetic systems. However, Sperber et al., pointed out that the strongest bimodality of composition is shown by dolostones. They suggested that calcian dolostones may form in nearsurface settings and more stoichiometric dolostones may form at depth, either by replacement of precursor limestones or by recrystallisation of calcian dolomite. They further suggested that the strong bimodality indicates a single dissolution-precipitation event rather than multiple recrystallisations for the transformation of calcian dolomite to stoichiometric dolomite. Only in closed systems will the metastable calcian dolomite be preserved (e.g. Blake, Peacor and Wilkinson, 1982), and Sperber et al., interpreted this as being due to the absence of allochthonous Mg^{2+}.

The absence of distinctly calcian phases in the dolomites reported in this study suggests that, in general, they formed in relatively open diagenetic systems. On petrographic and facies criteria, the dolomicrites were interpreted as forming initially in a nearsurface environment. The possibility that they may have recrystallised or been augmented at some time after sedimentation was also suggested. Compositionally these dolomicrites range from poorly ordered dolomite with approximately 53 mole % $CaCO_3$ to better ordered, nearly stoichiometric dolomite (see Fig. 4.1). This trend towards increasing order and better stoichiometry (approaching ideal compositions) may be significant, perhaps suggesting that cation order (disorder) is principally controlled by Ca^{2+} substitution in these dolomites. High resolution electron microscope studies of dolomite (e.g.

Reeder and Wenk, 1979; Reeder, 1981; Wenk, Barber and Reeder, 1983) have revealed variations in the microstructure of dolomite crystals which may be related to their composition. It has been suggested (Land, 1980; Reeder, 1981; Blake et al., 1982) that unmodulated, poorly ordered, highly calcian phases may recrystallise with time, burial and increasing temperature to ordered calcian dolomites with modulated ("tweed") structure and then to ordered homogeneous stoichiometric dolomite. If these suggestions are correct, then the order-stoichiometry trend in the dolomicrites may represent an incomplete transformation of this type, perhaps under partially closed system (high rock/water ratio) conditions. This interpretation is consistent with petrographic evidence and it is suggested that the fine grain size of the sediments contributed to the rapid development of closed-system conditions.

Pervasive and vein dolomites show less pronounced trends and generally tend to be nearly stoichiometric and moderately to well ordered (see Fig. 4.1). This may indicate that they formed as more ordered, more nearly stoichiometric phases initially, or that they underwent more complete and uniform recrystallisation than the dolomicrites.

The pervasive dolomites have been interpreted (Chapter 3) as forming in nearsurface environments by partial to complete replacement of grainstones, packstones and wackestones. The diagenetic system for this replacement is likely to have been more open to allochthonous Mg^{2+} than that in the fine grained dolomicrites, so one might expect the initial dolomite to have been more stoichiometric (see Sperber et al., 1984). If stoichiometric, well ordered dolomites represent open-system conditions (Sperber et al., 1984), these are more likely to have been achieved, on a scale capable of producing the pervasive dolomites, in a nearsurface

environment. Here, connection with seawater (the principal source of Mg^{2+}) would be good compared to the burial environment where porosity and permeability reduction by compaction and cementation, and covering by later sediments would soon lead to isolation from the marine Mg^{2+} reservoir. Although much of the pervasive dolomite appears to be early diagenetic, later phases (xenotopic dolomite) also occur (Chapter 3), and these are consistent with formation at elevated temperatures at depth. Their low volumetric importance is consistent with formation in a relatively closed-system, with a limited Mg^{2+} supply.

Vein dolomites are generally well ordered and near stoichiometric. This suggests that they formed in a relatively open diagenetic system with a low rock/water ratio, or by effective and complete recrystallisation of metastable precursors. Field and petrographic data indicate that this dolomite formed by replacement of limestone and perhaps by direct precipitation along joint and fault systems during late diagenesis. The host limestones were almost certainly stabilised to diagenetic low-magnesium calcite at this time, necessitating an allochthonous supply of Mg^{2+} and hence by implication, open-system conditions. The extent of rock-water interaction probably varied, depending on the distance from the fault or joint planes along which dolomitising fluids gained access to the rocks and it may be responsible for the observed variability in composition and order.

Summary

In addition to the points already discussed, the data presented here offer further support to the following observations of Sperber et al.

(1984). (i) dolomite stoichiometry increases with crystal size - compare dolomicrites with vein dolomites (ii) dolomite stoichiometry increases with porosity, clearly original sediment porosity and grain size may well influence the crystal size of resulting dolomites. Compare for example dolomicrites with pervasive dolomites. High porosity in vein dolomites however was probably very localised (along joint planes), so that here it is perhaps the grain size of the precursor limestone which is influencing dolomite crystal size.

To summarize the main observations and conclusions from XRD analysis combined with petrographic and sedimentologic interpretation:

1. The petrographic groups of dolomite fall into broad groups on the basis of stoichiometry and ordering.
2. Dolomicrites formed by rapid early replacement of marine carbonate mud by poorly ordered, calcian dolomite. Their metastability encouraged recrystallisation and augmentation with time, burial and increased temperature, to produce better ordered and more stoichiometric dolomite. This stabilisation probably occurred in a partially closed (high rock/water ratio) system and was incomplete.
3. Pervasive dolomites formed principally in nearsurface diagenetic environments. A fairly open (low rock/water ratio) system is suggested by the nearly stoichiometric composition and moderate to well ordered structure of these dolomites. Subsequent burial led to further dolomitisation and/or recrystallisation, presumably in a less open system, producing xenotopic dolomite. The effect of these relatively minor phases on whole-rock XRD data is not known.
4. Vein dolomites formed during burial diagenesis probably under locally produced low rock/water ratio conditions. Their moderate to well

ordered, near stoichiometric compositions reflect this and are probably primary rather than the result of later recrystallisation.

Cation Chemistry

4.2.1 Introduction and background information

As pointed out by Veizer et al., 1978, "Carbonate rocks are polyphase and *polycompositional* assemblages, with each phase and component having variable chemical attributes". Dolomites are clearly no exception (e.g. Land, 1980). The most meaningful data can therefore only be acquired by point analysis or by physical separation of components. Therefore, the predominantly whole-rock treatment adopted in this study requires some justification.

Initial investigation of compositional variations using XRD and electron microprobe techniques provided useful data on major element (Ca and Mg) compositions. Electron microprobe analyses for minor and trace elements (Fe, Mn, Na, and Sr) however proved less helpful, as concentrations generally fell close to or below the detection limit of the instrument (see appendix 2). Spectrometric methods of analysis (AAS, ICPS) were therefore chosen.

Although physical separation of dolomite phases prior to analysis is desirable, in many of the studied rocks the fine distinction between phases is unclear. For example, the results of cathodoluminescence petrography (see Chapter 3) suggested compositional variations within pervasive dolomite mosaics. However, the intensity and colour of these 'zones' appeared quite variable and their boundaries diffuse. In general it was not considered possible to confidently separate sufficient quantities of

material of correlatable petrographic character to justify such an approach. However, two pairs of samples were separated for combined cation and stable isotope analysis.

Following the approach of Veizer et al., 1978, the study of bulk carbonate samples (acid soluble fraction) is considered valid on the grounds that samples within broad petrographic groups probably have similar depositional and diagenetic histories, and therefore similar bulk compositions. Careful petrographic characterisation identifies any inhomogeneties and the use of Me/Ca (cation/Ca) ratios allows for any minor mineralogical (mixed carbonate) or compositional (Ca:Mg in dolomite) variations (Veizer et al., 1978).

Veizer (1983 a and b) has outlined the potential of trace element and stable isotope studies in aiding the interpretation of carbonate rocks and their diagenesis. The utility of Veizer's 'tracer technique' relies on the fact that during the diagenesis of marine carbonate, stabilisation of metastable components (aragonite, high- and low-magnesium calcite bioclasts, cement etc.) involves <u>aqueous</u> dissolution-reprecipitation reactions. During these reactions, 'tracers' may be repartitioned, so that the resulting diagenetic phase(s) has a different composition from the precursor phase(s). The degree of repartitioning depends principally on the following factors (Veizer, 1983a):

a) the difference in chemical composition (m Me/m Ca; $^{13}C/^{12}C$; $^{18}O/^{16}O$) between seawater and the incoming diagenetic water (see Fig. 4.2a for variation of m Me/m Ca ratio in modern natural waters.

b) the deviation of distribution coefficients and isotope fractionation factors from unity (see below).

c) the proportion of solutes (elements or isotopes) derived from the

dissolving phase versus those contributed by the incoming water (i.e. the degree of openness, rock/water ratio or solute index of the system, see Veizer, 1983b).

At this point the use and significance of distribution coefficients requires some comment and the term 'effective D' will be introduced.

As reviewed by Veizer (1983a), minor and trace elements can be incorporated into carbonate minerals in the following ways:

1) substitution for major cations in carbonate lattice (variable).
2) be present interstitially between lattice planes
3) occupy lattice positions which are free due to defects in the structure
4) be adsorbed due to remanent ionic charges, and
5) be present in non-carbonate solid and liquid inclusions.

Thus, empirically derived estimates of D, as defined by the relationship:

$$(mMe/mCa)_{carbonate} = D \times (mMe/mCa)_{water}$$

represent the partitioning of Me (minor or trace elements) between water and all or any combination of the above sites in the solid carbonate. Although we have some understanding of factor 1, factors 2 to 5 are essentially random and beyond quantitative treatment at present (Veizer, 1983a). Therefore, D is best described as an effective distribution coefficient and should be regarded as a descriptive term allowing only qualitative interpretation and at best, order of magnitude estimates of fluid compositions.

Empirical and theoretical work on distribution coefficients for various elements (mostly Sr) and carbonates has been reviewed by Veizer (1983a) and Dickson (1985) and need not be repeated here (although see

Fig 4-2

a

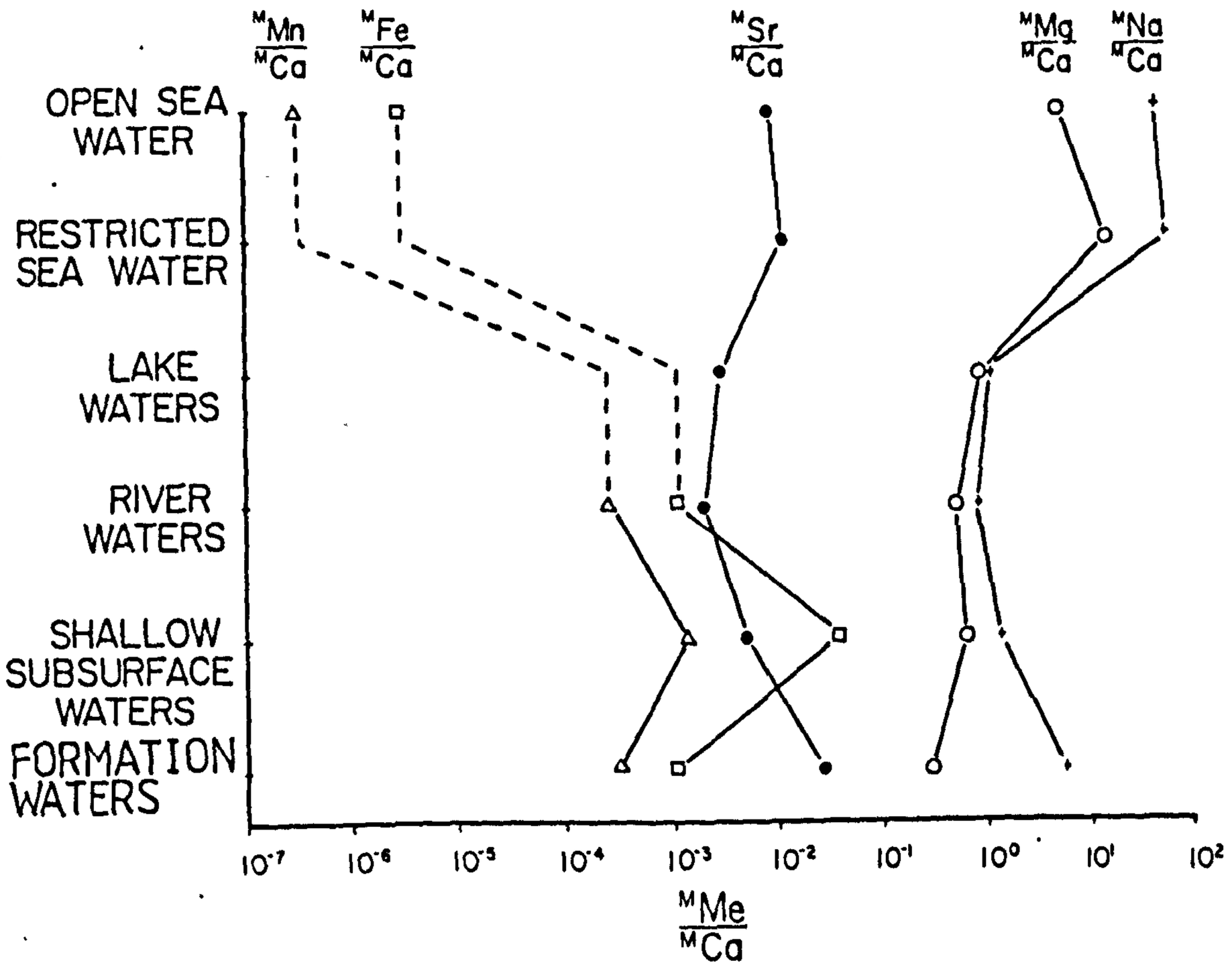


Fig 4.2 a. mMe/mCa variations in natural waters (from Veizer 1983a)

b

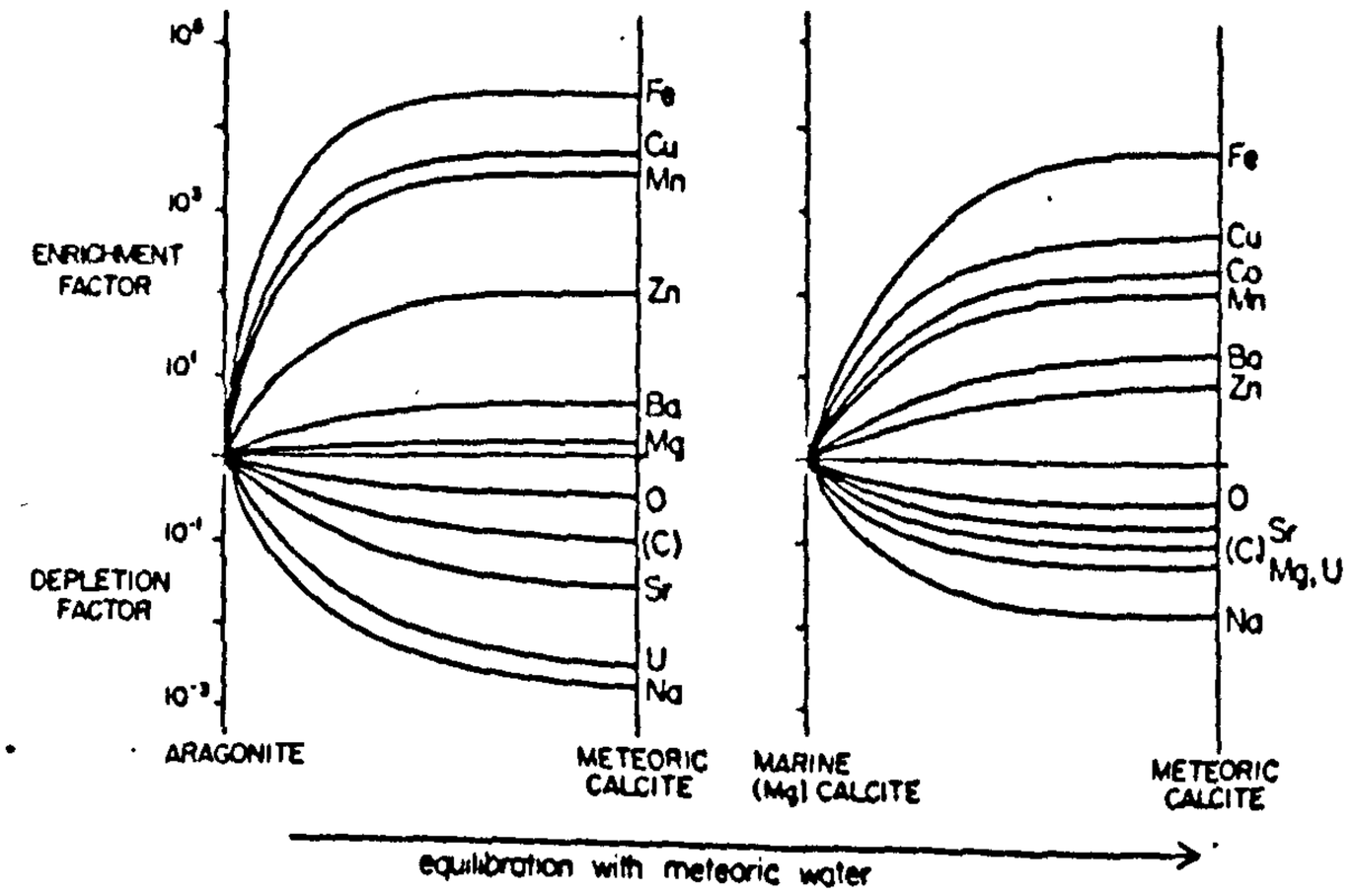


Fig 4.2 b. Repartitioning of tracers (trace elements, oxygen and carbon isotopes) during diagenesis of carbonates (from Veizer, 1983b)

section 4.2.2.c). Suffice it to say that most quoted distribution coefficients in the literature are best treated as effective D's and that these D's appear to show considerable variation with temperature, rate of precipitation, type of reaction and state of equilibrium.

Dickson (1985) advocated that, wherever possible local distribution coefficients should be determined by examination of extant systems or *through fluid inclusion work on ancient carbonates. In this way, the Me/Ca ratio of the solid carbonate is known and that of the precipitating fluid* may be reasonably estimated, thus allowing a local or effective D to be derived. Comparison of effective D's from different diagenetic environments may then provide information about the reactions themselves.

In the present study, data on the composition of dolomitising fluids are lacking; however, from petrographic study and general geological considerations the diagenetic environments of dolomitisation can be reasonably well constrained and therefore it should be possible to say something about the likely origin and composition of dolomitising fluids. This information is presented in Chapters 2 and 3 and discussed together with the data presented in this chapter, in Chapter 5. In section 4.2.2.c determination of approximate effective D's for the dolomites is attempted and the values derived are compared to theoretically derived values for $D^{Me}_{dolomite}$ as a simple function of empirical $D^{Me}_{calcite}$ for similar diagenetic environments.

Considering factor (c) above, the effect of system openness on repartitioning of tracers, Veizer (1983a and 1983b for corrected definition of S.I.) pointed out that the degree of openness in a given diagenetic environment will be different for each solute, depending upon its relative concentration in the diagenetic fluid (Pingitore, 1982). As an example,

Veizer (1983a) cited subsurface meteoric systems saturated with respect to calcite. Overall, the solute index is low (high rock/water ratios) and it is likely that dissolving phases will contribute the bulk of the diagenetic fluids' solute content, due to the low solute to water ratio of meteoric water (c. $1:10^4$). The total oxygen pool however is dominated by H_2O and will not be greatly affected by the dissolving phase. Resulting diagenetic phases (LMC or dolomite) will then have mMe/mCa and carbon isotope ratios modified only by effective distribution coefficients and the $^{13}C/^{12}C$ fractionation factor (assuming no authigenic source of carbon, see section 4.3.3.b). In the case of carbon isotopes the fractionation factor is close to unity and the $\delta^{13}C$ composition of the metastable (marine) precursor carbonate may be transferred almost intact to the diagenetic phase. Assuming that effective distribution coefficients differ from unity, then in a low solute index system their magnitude will be reduced (i.e. effective D's approach unity), thus original chemical gradients will be partially preserved whilst overall trace element compositions will be enriched or depleted (Veizer, 1983a). In contrast, the $\delta^{18}O$ composition of the diagenetic phase in a system will reflect that of the diagenetic fluid and the temperature dependant fractionation factor. Fig. 4.2b is reproduced from Veizer (1983b) and summarizes the effect of variable SI on the apparent repartitioning of tracers during meteoric stabilisation of marine components (refer also to Fig. 4.2a).

To summarize, in general terms the degree of repartitioning of tracers in diagenetic systems can be seen as a product of changes in the diagenetic environment - principally in the availability or mobilisation of tracers, related to the source and chemistry of diagenetic fluids and to the solute index of the system. Effective distribution coefficients, if they can be

determined, are an expression of this diagenetic environment. Clearly then, the list of empirical D's compiled from the literature by Veizer (1983a, table 1) should be applied with caution. In effect, they are simply descriptions of the observed behaviour of given cations during specified diagenetic reactions. For example, if a cation Me has a higher concentration relative to Ca, in the solid phase than in the fluid from which it precipitated, this enrichment is described by a D greater than unity. Conversely, the behaviour of cations which are concentrated preferentially in the fluid phase during precipitation is described by D less than unity.

The next section deals with the presentation and possible significance of cation chemical variation between the major groups of dolomite studied.

4.2.2 Dolomite cation chemistry

The above discussion, largely a review of Veizer (1983a) has introduced the concept of diagenetic repartitioning and indicated that at present, rigorous treatment of carbonates and in particular dolomite, may be premature. Clearly a wholly geochemical approach is inappropriate; however, provided petrographic and facies control is good, sufficient is known or can reasonably be inferred about dolomite geochemistry to enable at least a qualitative treatment.

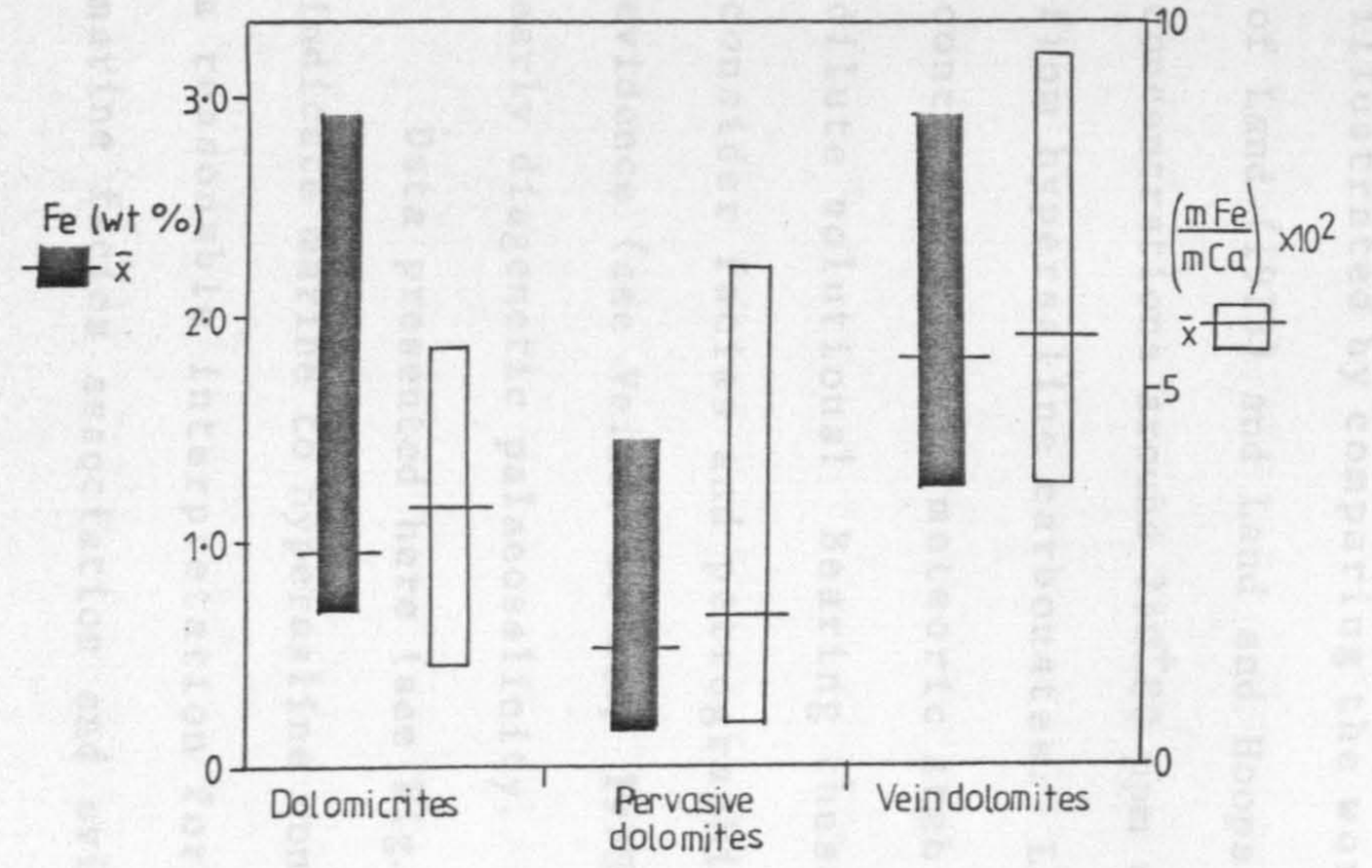
It is hoped that this will be shown in the following account, especially with reference to Mn and Sr, and that the value of geochemical analyses on dolomites will become apparent.

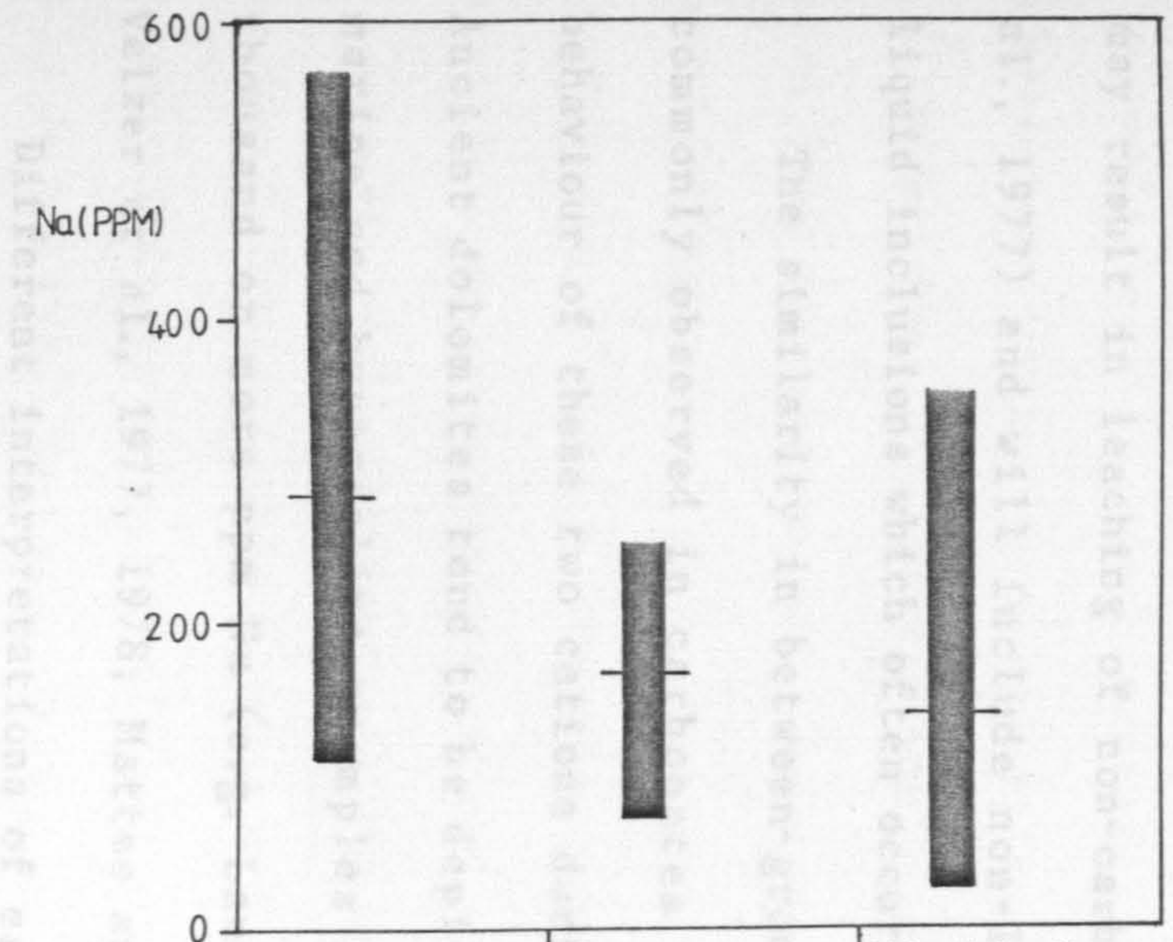
The following will deal with each element (Na, Fe, Sr, and Mn) in turn

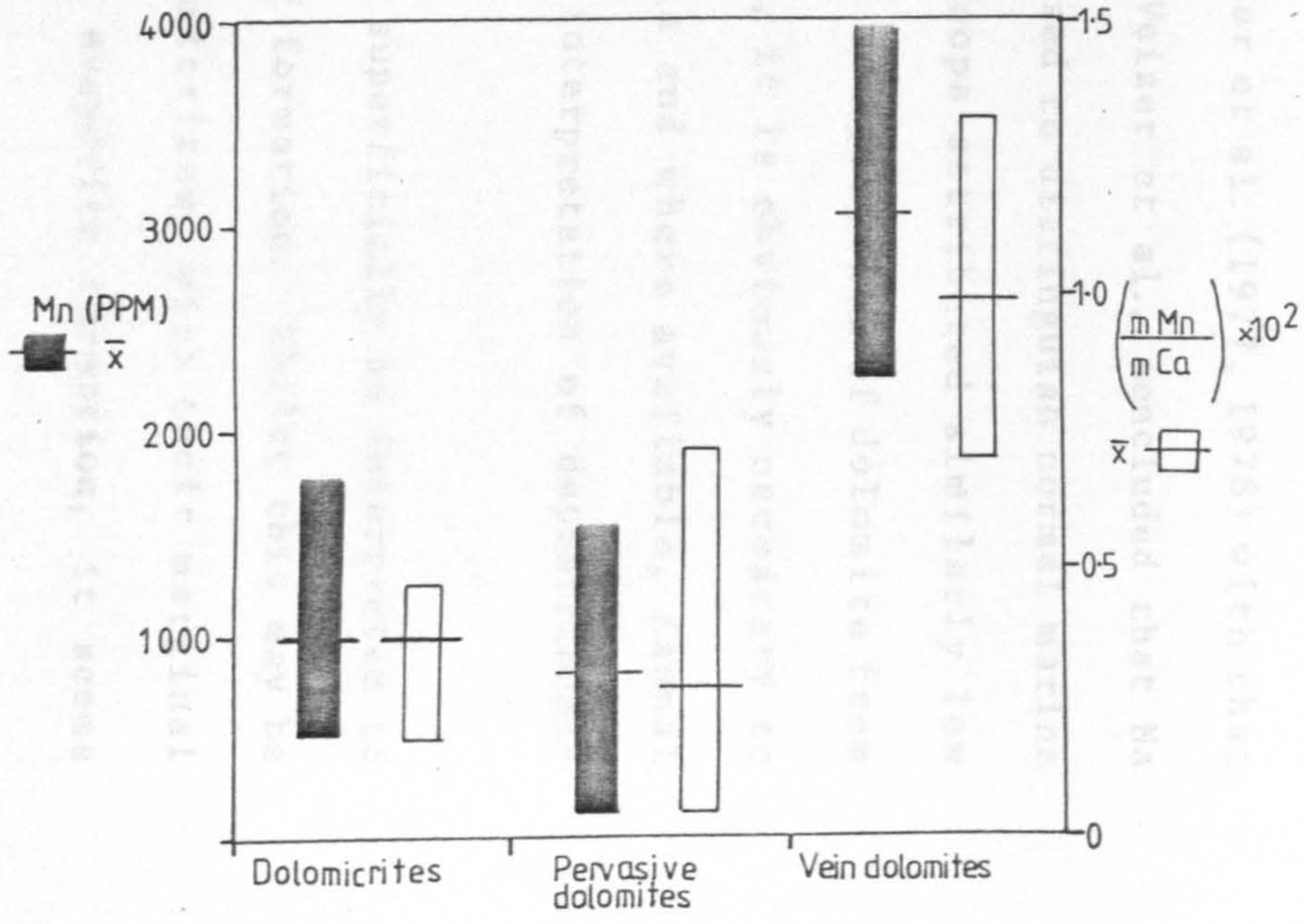
Fig 4.3

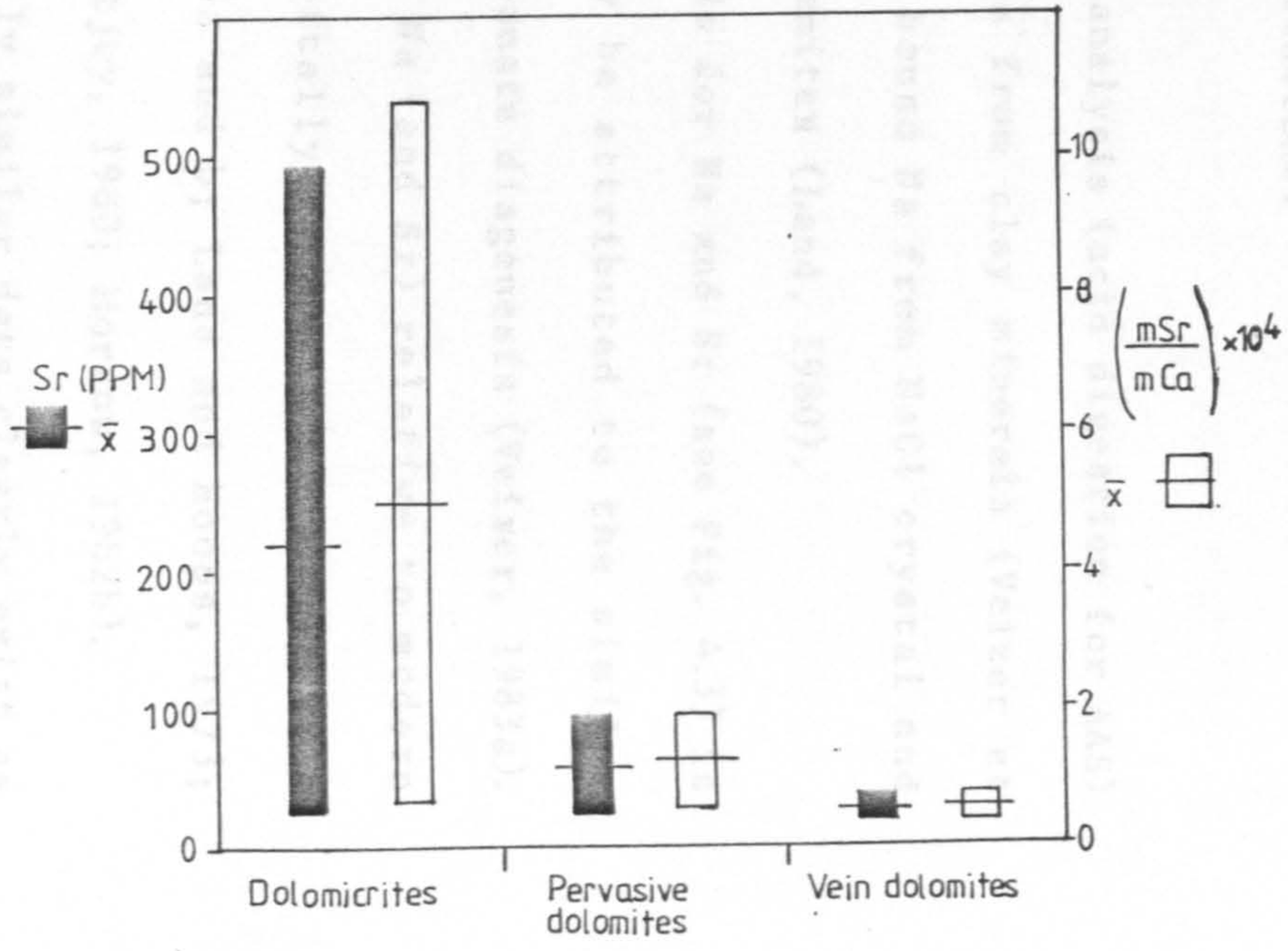
mMe/mCa and Me(ppm) variations in the studied dolomites (data in appendix 2, discussion in text).

Fig 4–3


Fe (wt %)
x̄
3·0
2·0
1·0
0
10
5
0
(mFe/mCa) x10²
x̄
Dolomicrites
Pervasive dolomites
Vein dolomites


Na (PPM)
600
400
200
0
Dolomicrites
Pervasive dolomites
Vein dolomites


Mn (PPM)
x̄
4000
3000
2000
1000
1·5
1·0
0·5
0
(mMn/mCa) x10²
x̄
Dolomicrites
Pervasive dolomites
Vein dolomites


Sr (PPM)
x̄
500
400
300
200
100
0
10
8
6
4
2
0
(mSr/mCa) x10⁴
x̄
Dolomicrites
Pervasive dolomites
Vein dolomites

and refers principally to between-group variations.

(a) Sodium

The method of sample preparation and analysis (acid digestion for AAS) may result in leaching of non-carbonate Na from clay minerals (Veizer et al., 1977) and will include non-lattice bound Na from NaCl crystal and liquid inclusions which often occur in dolomites (Land, 1980).

The similarity in between-group trends for Na and Sr (see Fig. 4.3) is commonly observed in carbonates and may be attributed to the similar behaviour of these two cations during carbonate diagenesis (Veizer, 1983a). Ancient dolomites tend to be depleted in Na (and Sr) relative to modern marine and hypersaline examples and typically have a few hundred to a thousand or more ppm Na (e.g. Land, 1973a and b; Land and Hoops, 1973; Veizer et al., 1977, 1978; Mattes and Mountjoy, 1980; Morrow, 1982b).

Different interpretations of essentially similar data clearly exist as illustrated by comparing the work of Veizer et al. (1977, 1978) with that of Land (1973) and Land and Hoops (1973). Veizer et al., concluded that Na concentrations around 230±80 ppm could be used to distinguish normal marine from hypersaline carbonates. Land and Hoops attributed similarly low concentrations to meteoric stabilisation or formation of dolomite from dilute solutions! Bearing these in mind, it is obviously necessary to consider facies and petrographic criteria and where available, faunal evidence (see Veizer et al., 1978) in the interpretation of depositional-early diagenetic palaeosalinity.

Data presented here (see Fig. 4.3) may superficially be interpreted to indicate marine to hypersaline conditions of formation. Whilst this may be a reasonable interpretation for the dolomicrites, with their marginal marine facies association and evidence for evaporite formation, it seems

less likely for the pervasive and vein dolomites. Even for the dolomicrites, petrography suggests early dissolution of evaporites probably by dilute, meteoric, solutions, before dolomitisation was complete. The relatively high Na concentrations (up to 560 ppm) would appear to be inconsistent with this suggestion, unless, as proposed earlier (section 4.1.2. above) final dolomitisation/stabilisation occurred in a relatively closed (low SI) system and therefore partially retained original high Na concentrations.

Turning now to a consideration of the pervasive dolomites. In nearsurface early diagenesis of shallow marine sediments the elevated Na/Ca of seawater (~46) will dominate the diagenetic fluid (Sass and Katz, 1982) even where considerable mixing with dilute (low ionic strength) waters occurs. This is true for all the major species in seawater (Wigley and Plummer, 1976; Veizer, 1983a). As proposed from petrographic interpretation, the pervasive dolomites formed initially in a nearsurface diagenetic environment. The requirement for allochthonous Mg^{2+} to dolomitise on such a large scale almost certainly implicates seawater, and suggests an open diagenetic system. The presence of meteoric water during early nearsurface and shallow subsurface diagenesis is also suggested on petrographic evidence (see Chapter 3). Mixing of marine and meteoric waters therefore seems likely to have occurred during early diagenesis and provides a plausible process for pervasive dolomite formation. Badiozamani (1973) in his application of the mixed-water model (Hanshaw, Back and Deike, 1971) indicated a mean Na concentration of 190 ppm for supposed ancient examples of "Dorag" dolomite. The pervasive dolomite data ($\bar{x}$ = 170 ppm Na) are consistent with this interpretation, although as petrography has shown, later phases also occur, so that bulk composition is probably a

reflection of more than one process, and may include the effects of variable SI recrystallisation.

The vein dolomites are interpreted as forming during late burial diagenesis (see Chapter 3) and the involvement of marine water is very unlikely. However, the range in Na data (see Fig. 4.3) suggests formation from solutions with a range of salinities. Dolomite forming from connate brines might be expected to contain high Na concentrations, perhaps as inclusions (Mattes and Mountjoy, 1980) and is a possible explanation for at least the higher Na concentrations (up to 350 ppm). The SI, with respect to Na, of the dolomitisation system was probably an important influence on the variation in resulting dolomite Na concentration. Host limestones have low Na concentrations (46-75 ppm) and dolomites forming under low SI (high rock/water ratio) conditions are likely to be more depleted than those forming under higher SI's (depending on the composition of dolomitising fluids and the degree of equilibrium reached).

Although the above is largely speculation, the idea of variable SI is consistent with the likely mode of formation of vein dolomites along highly localised permeability channels (fractures) and by replacement of well cemented, diagenetically stabilised limestones.

(b) Iron and Manganese

Fe and Mn show similar between-group variations (trends) and generally oppose trends in Sr and Na (Fig. 4.3). In broad terms this might be expected because of the considerable variation (to several orders of magnitude) of mFe/mCa and mMn/mCa ratios in natural waters and the opposing, though less pronounced trend of mSr/mCa and mNa/mCa ratios (Fig. 4.2a).

The relatively high Fe and Mn contents of dolomicrites are at first

surprising considering their interpreted syndepositional-early diagenetic origin. Do these values reflect a depositional or a diagenetic environment? If they are original depositional values they are inconsistent with a marine origin unless they represent a significant terrigenous input (feasible in the marginal marine depositional setting of these rocks). Alternatively, they may represent remobilised Fe^{2+} and Mn^{2+} (presumably also ultimately of terrigenous origin) during diagenesis and incorporation in diagenetic carbonates. A way to test which of these hypotheses is more likely, is to consider the mMn/mFe ratios of the dolomicrites ($\bar{x}$ = 0.12, range 0.08 to 0.17) and to compare them to those of terrigenous input. The latter may be approximated by average river water mMn/mFe ratios of 0.41 (range 0.02 to 0.51, Calculated from data in Veizer 1983a Fig. 4.2a). Based on average ratios one could suggest that significant remobilisation has occurred. Clearly this evidence is not conclusive. However, as already suggested, these dolomites probably formed by augmentation and recrystallisation of synsedimentary dolomite in a partially closed (low SI) system (see section 4.1.2). Under these conditions it is likely that oxidation of any included organic matter (probably abundant algal remains) would result in consumption of oxidants according to the order of decreasing energy production per mole of organic carbon oxidised (Froelich et al., 1979), i.e. O_2>Mn-oxides>nitrate>Fe-oxides>sulphate. In this way terrigenous Fe and Mn would be remobilised at different rates, for incorporation in precipitating dolomite. The liberation of isotopically light carbon (^{12}C enriched) is also an important outcome of oxidation of organic matter and will similarly be incorporated in diagenetic carbonate (Irwin et al., 1977). This relationship provides a possible method of checking the proposed model by stable carbon isotope analysis. Whilst ideally, serial

samples are required to allow the precise relationship between the chemical and isotopic composition to be determined, the whole-rock approach employed here ought at least to provide a qualitative appreciation. To summarize the results of stable isotope analysis to be presented later, the dolomicrites have relatively depleted $\delta^{13}C$ compositions (to -2.3$^{o}/_{oo}$ PDB), consistent with a significant biogenic contribution to the carbon reservoir (see section 4.3.3.b for further discussion).

The occurrence of authigenic pyrite of post-dolomitisation origin (Chapter 3) is consistent with the presence of marine sulphate, Fe^{2+} and organic matter for some time after deposition (Berner, 1970, 1984). Although the implied presence of marine sulphate during dolomitisation might be seen as a problem (i.e. because of its inhibiting effect, Baker and Kastner, 1981) it appears that dolomitisation of aragonite can occur at higher sulphate concentrations than calcite (Baker and Kastner, 1981; Jorgenson, 1983; Mullins et al., 1985). The presence of metastable aragonite and/or poorly ordered calcian dolomite, the suggested influence of dilute waters and syn-depositional gypsum precipitation (and hence removal of some sulphate) may then have encouraged further dolomitisation.

The pervasive and vein dolomites probably formed in more open diagenetic systems (see section 4.1.2). Higher Fe contents (Fig. 4.3) in vein dolomites perhaps suggest the involvement of different fluids and/or conditions (temperature, Eh, precipitation rate, etc.) of formation and are consistent with a later diagenetic, ? burial origin. The observed overlap in composition of pervasive and vein dolomites is similarly consistent with petrographic interpretation that pervasive mosaics include later diagenetic, xenotopic dolomite phases (see Chapter 3).

A small number of electron microprobe point analyses of Fe^{2+} and Mn^{2+}

Fig 4-4

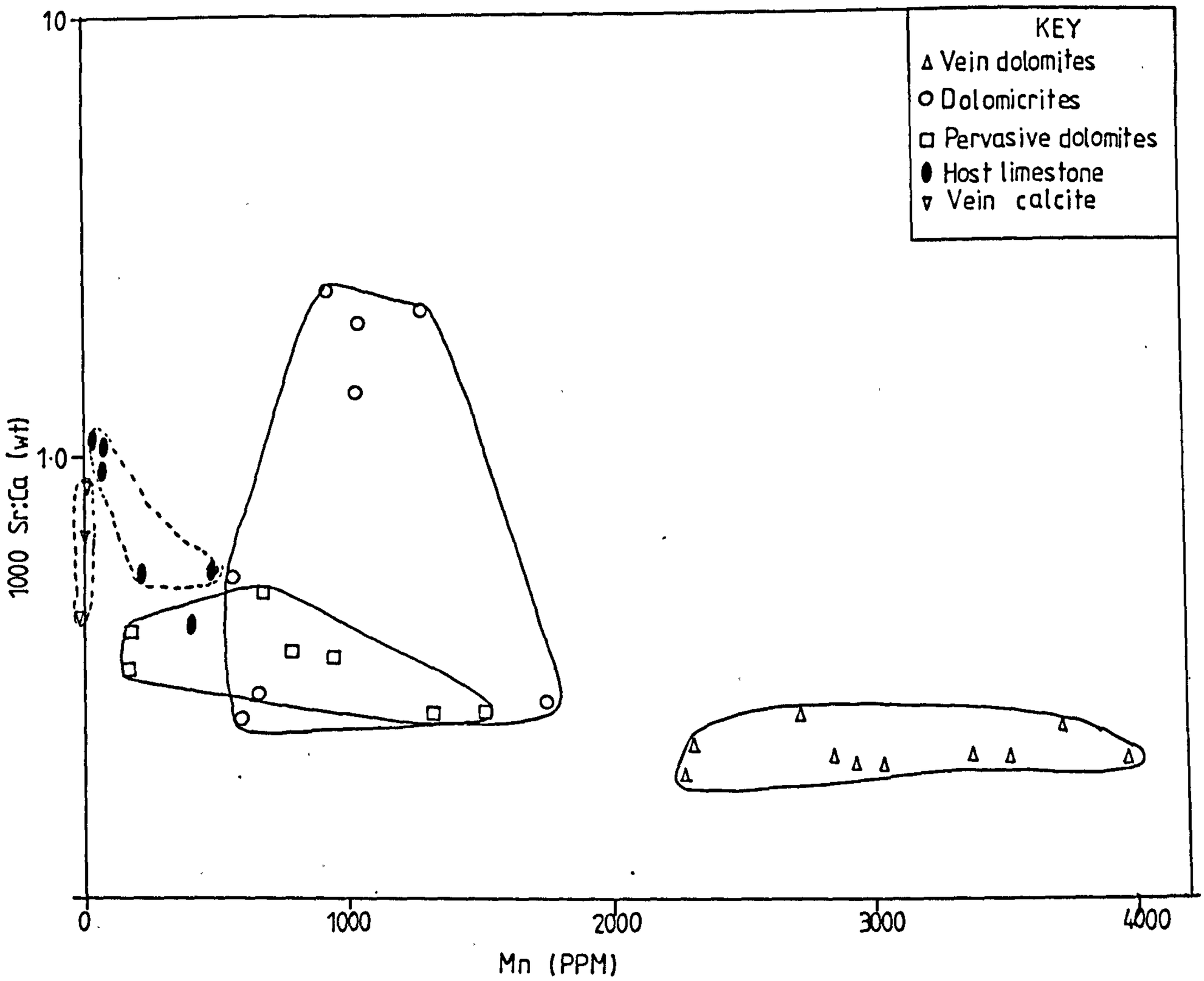


Fig 4.4 Sr:Ca versus Mn variation between groups , for the three dolomite types ,host limestones and vein calcites (data in appendix 2).

were carried out to determine the composition of individual crystals. Whilst averaged data are comparable to whole-rock analyses for the same samples (see Appendix 2), probe analyses reveal that considerable within-sample variation has been smoothed by whole-rock analysis. This observation emphasizes the need for realistic constraint on interpretation of whole-rock data. The constraint, as here, should be provided by careful petrographic characterisation of samples and interpretation limited to between-group variations.

(c) Strontium and manganese

Fig. 4.4 is a plot of Sr/Ca vs. Mn for the various dolomite types and for host limestones and vein calcites. The interpretive value of such a plot is limited because of the previously discussed constraints; however, it is interesting to note the negative correlation between Sr and Mn both within the whole-rock limestone samples and between the different dolomite groups. The limestone data fall within the range of meteoric stabilisation trends for component minerals defined by Brand and Veizer, 1980 (see their fig. 9), trending towards open-system equilibrium compositions. Dolomites generally have higher Mn and lower Sr than the limestones. The principal exception to this pattern is the Sr content of some of the dolomicrites. These values (up to 493 ppm Sr) may reflect partial retention of original (?) marine Sr values due to relatively closed-system replacement (see discussion of Na above). In this respect Sr data may be more informative than Na because they are less likely to include an extraneous component.

Effective $D^{Me}_{dolomite}$

The partitioning behaviour of Sr and Mn is probably the most studied of the numerous cations which can substitute into the carbonate lattice

Table 4-1a

Dolomite type	Composition	Type of reaction	Likely fluid and composition (from Fig 4-2)		Effective $D^{Me}_{dolomite}$
Dolomicrites	$X\frac{m_{Sr}}{m_{Ca}} = 5.0\times10^{-4}$ Range 7.1×10^{-5} to 1.1×10^{-3} $X\frac{m_{Mn}}{m_{Ca}} = 3.7\times10^{-3}$ Range 1.9×10^{-3} to 6.6×10^{-3}	Early stabilisation ± direct precipitation	Seawater end/or meteoric water	s/w $\frac{m_{Sr}}{m_{Ca}}$ 10^{-2} $\frac{m_{Mn}}{m_{Ca}}$ 10^{-6} m/w $\frac{m_{Sr}}{m_{Ca}}$ 10^{-2} $\frac{m_{Mn}}{m_{Ca}}$ 10^{-3}	Assuming s/w D^{Sr}_{dol} X=0.05 (range 0.007 to 0.11) D^{Mn}_{dol} X=3700 (range 1900 to 6600) Assuming m/w D^{Sr}_{dol} as s/w D^{Mn}_{dol} X=3.7 (range 1.9 to 6.6)
Pervasive dolomites	$X\frac{m_{Sr}}{m_{Ca}} = 1.29\times10^{-4}$ Range 6.1×10^{-5} to 1.9×10^{-4} $X\frac{m_{Mn}}{m_{Ca}} = 2.8\times10^{-3}$ Range 5×10^{-4} to 7.2×10^{-3}	Mixture of early stabilisation, replacement of stabilised carbonate and direct precipitation	Predominantly mixed Marine-Meteoric	Assume s/w and m/w as above.	Assuming s/w D^{Sr}_{dol} X=0.013 (range 0.006 to 0.019) D^{Mn}_{dol} X=2800 (range 500 to 7200) Assuming m/w D^{Sr}_{dol} as s/w D^{Mn}_{dol} X=2.8 (range 0.5 to 7.2)
Vein dolomites	$X\frac{m_{Sr}}{m_{Ca}} = 5.8\times10^{-5}$ Range 4.0×10^{-5} to 7.7×10^{-5} $X\frac{m_{Mn}}{m_{Ca}} = 9.9\times10^{-3}$ Range 7.0×10^{-3} to 1.3×10^{-2}	Replacement of stabilised limestone ± direct precipitation	Meteoric water and formation water.	m/w as above F/w $\frac{m_{Sr}}{m_{Ca}}$ 10^{-1} $\frac{m_{Mn}}{m_{Ca}}$ 10^{-3}	Assuming m/w D^{Sr}_{dol} X=0.006 (range 0.004 to 0.008) D^{Mn}_{dol} X=9.9 (range 7.0 to 13.3) Assuming F/w D^{Sr}_{dol} X=0.0006 (range 0.0004 to 0.0008) D^{Mn}_{dol} as m/w

Table 4-1b

Theoretical derivation of $D^{Me}_{dolomite}$

(See text for explanation)

Empirical $D^{Me}_{calcite}$ values ⟶ Theoretical $D^{Me}_{dolomite}$

(From Veizer, 1983a)

A. Direct precipitation of calcite

$D^{Sr}_{calcite} \sim 0.13 \longrightarrow D^{Sr}_{dolomite} \sim 0.06$ to 0.07

$D^{Mn}_{calcite} \sim 6.0 \longrightarrow D^{Mn}_{dolomite} \sim 7.08$ to 7.62

B. Early stabilisation (A, HMC → LMC)

$D^{Sr}_{calcite} \sim 0.05 \longrightarrow D^{Sr}_{dolomite} \sim 0.02$ to 0.03

$D^{Mn}_{calcite} \sim 15.00 \longrightarrow D^{Mn}_{dolomite} \sim 17.7$ to 19.05

C. Recrystallisation (LMC → LMC)

$D^{Sr}_{calcite} \sim 0.03 \longrightarrow D^{Sr}_{dolomite} \sim 0.01$ to 0.02

$D^{Mn}_{calcite} \sim 30.00 \longrightarrow D^{Mn}_{dolomite} \sim 35.4$ to 38.1

(Veizer, 1983a; Dickson, 1985). However, as already discussed (section 4.2.1) considerable uncertainty surrounds the interpretation of empirical data. In this section the likely diagenetic environment of the main dolomite types as constrained by petrographic and general geologic considerations will be used in an attempt to approximate the likely composition of diagenetic fluids. In this way effective D's with respect to Sr and Mn can be determined, assuming the simple relationship defined in section 4.2.1. Although of limited interpretive value, these D's may be compared to $D^{Me}_{dolomite}$ values derived theoretically from empirical $D^{Me}_{calcite}$ values compiled by Veizer (1983a). This derivation follows the reasoning of Kretz (1982), that cations with ionic radii larger than Ca^{2+} substitute proportionally more in calcium sites of dolomites, whereas small ions substitute more in magnesium sites (see also Behrens and Land, 1972, and Jacobson and Usdowski, 1976). In this way equilibrium molar concentrations of trace elements in dolomite relative to calcite are derived (see Veizer, 1983a, table 1 caption). For Sr the value ($mMe_{dolomite}/mMe_{calcite}$) is 0.43 to 0.50 and for Mn it is 1.18 to 1.27. This relationship may be used to derive theoretical $D^{Me}_{dolomite}$ values from empirical $D^{Me}_{calcite}$'s and these are given in Table 4.1b. The severe limitation of these derived $D^{Me}_{dolomite}$ values is that the empirical $D^{Me}_{calcite}$'s on which they are based are actually effective D's and therefore represent total cation contents (see section 4.2.1), whereas the reasoning employed above assumes that all cations are in lattice sites. However, it is worth noting that the measured effective $D^{Me}_{dolomite}$ (0.0231 to 0.0278) produced during the experimental dolomitisation of $CaCO_3$ by Katz and Matthews (1977) are very similar to those derived theoretically (i.e. approximately half the value of empirical $D^{Me}_{calcite}$).

PAGE

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i) Effective D's for dolomicrites

Within the depositional-early diagenetic setting of the dolomicrites (see Chapter 3) a range of early diagenetic fluid compositions from restricted marine (evaporative) to meteoric water are possible. Initial dolomite phases probably formed principally under the influence of seawater and together with aragonite and/or high magnesium calcite represent the metastable precursors to the dolomicrite. Complete dolomitisation occurred in the shallow subsurface, in a relatively closed (low SI) system. The influence of meteoric or mixed marine-meteoric waters is consistent with petrographic evidence (e.g. gypsum dissolution).

Thus, in determining effective distribution coefficients for dolomicrites it is necessary to assume both marine and meteoric water compositions. Taking the average mMe/mCa ratios of modern natural waters (Fig. 4.2a) as order of magnitude estimates, values for $D^{Sr}_{dolomite}$ and $D^{Mn}_{dolomite}$ are derived from dolomicrite mSr/mCa and mMn/mCa ratios. The data are summarized and the determined effective D's presented in Table 4.1a.

ii) Effective D's for pervasive dolomites

A nearsurface origin by replacement of marine and partially stabilised marine sediments is most likely. Petrography also suggests direct precipitation of dolomite may have occurred during initial dolomitisation and during later burial when recrystallisation (dolomite to dolomite) and replacement of relic calcite (LMC to dolomite) also occurred. A meteoric influence is strongly implied by petrography and is supported by geochemical data, including stable isotopic data to be presented in section 4 below. However, a seawater flux is considered essential as an early

diagenetic source of allochthonous Mg^{2+} necessary to produce the massive units of pervasive dolomite. Relatively minor late diagenetic phases are not considered in this discussion.

As with dolomicrites, marine to meteoric fluids are considered appropriate in determining effective distribution coefficients for the pervasive dolomites. Details are given in Table 4.1a.

iii) Effective D's for vein dolomites

A late diagenetic origin for vein dolomites by replacement of stabilised and cemented limestones and perhaps by direct precipitation along joint or fracture planes is considered most likely. The composition of dolomitising fluids is uncertain; however mixing of formation waters and surface derived meteoric waters along fracture zones is a possible mechanism for production of these burial dolomites, as will be discussed more fully in Chapter 5, section 5.8. Therefore, effective D's are determined using meteoric and formation water mMe/mCa ratios (see Table 4.1a).

For the data presented here a range of effective $D^{Me}_{dolomite}$ values emerge, dependent upon the suggested diagenetic fluid and the variability of dolomite composition. In the absence of more rigorous constraints on diagenetic fluid compositions, such as might be provided by fluid inclusion studies, the accuracy of these effective D's remains poor. However, effective $D^{Sr}_{dolomite}$ values for the early replacement dolomites (i.e. dolomicrites and pervasive dolomites) are broadly similar and are comparable to theoretically derived $D^{Sr}_{dolomites}$ based on early replacement/stabilisation $D^{Sr}_{calcite}$ values (see Table 4.1a and b).

Regarding effective $D^{Mn}_{dolomite}$ values, where mixing of meteoric and marine waters is suspected as with the pervasive dolomites and perhaps the

dolomicrites, it is likely that meteoric water mMn/mCa ratios will dominate. In this situation therefore, effective $D^{Mn}_{dolomite}$ values closer to meteoric equilibrium are probably more appropriate than marine equilibrium values. Thus, the somewhat elevated $D^{Mn}_{dolomite}$ values in Table 4.1a can probably be discounted.

4.2.3.
Summary of cation chemistry: main conclusions

Taken alone, cation compositions do not provide conclusive evidence for the origin of the studied dolomites. Interpretation is best supported by sedimentological and petrographic (paragenetic) interpretation. Rigorous quantitative interpretation of the data is not possible, however the following broad conclusions may be drawn from the above account.

1. The studied dolomites are depleted in Sr and Na relative to modern marine and hypersaline examples. This suggests that they formed under different conditions and/or have been modified during diagenesis.
2. Fe and Mn concentrations are relatively high and suggest the involvement of Fe and Mn enriched (i.e. non-marine) solutions.
3. Overall, dolomicrites have Sr and Na compositions consistent with a penecontemporaneous origin from marine (or restricted marine) waters followed by stabilisation in a shallow subsurface non-marine or mixed water diagenetic environment. Fe and Mn are consistent with this interpretation and suggest reducing conditions (created by oxidation of organic matter) during this stabilisation.
4. Pervasive dolomites have trace element compositions consistent with their interpreted shallow subsurface origin from non-marine or mixed waters, i.e. they are relatively depleted in Sr and Na and enriched in Fe and Mn. there is also a broad negative correlation between Mn and

Sr content.

5. Vein dolomites continue the trend toward lower Sr and higher Mn and Fe, consistent with their later diagenetic origin. Their variable to high Na content may reflect a variable SI system, involving Na depleted host limestones and Na rich formation waters.

6. From the observed $(mMe/mCa)_{dolomite}$ ratios and assuming approximate diagenetic fluid compositions, as constrained by petrographic and geological interpretation, a range of effective $D^{Me}_{dolomite}$ values are suggested.

4.3 Stable isotope chemistry

4.3.1 Introduction I : Systematics

Stable isotope data for the Dinantian dolomites and selected whole-rock limestones together with a small number of dissected components are presented with experimental details in the appendix(3). The data are summarised in Fig. 4.5. Before attempting to interpret this data, it is first necessary to summarize stable isotope systematics, particularly as regards dolomites. In this study solid carbonate $\delta^{18}O$ and $\delta^{13}C$ values are given on the PDB scale and water $\delta^{18}O$ values on the SMOW scale (see Friedman and O'Neil, 1977, for details of the two scales).

The temperature dependance of the fractionation of ^{18}O between water and dolomite is well known from experimental work at high temperatures (e.g. Northrup and Clayton, 1966; O'Neil and Epstein, 1966; Sheppard and Schwarcz, 1970) and from lower temperature precipitation of protodolomites (Fritz and Smith, 1970). The fractionation is typically expressed in the form $10^3 \ln \alpha$ (per mil fractionation) as defined by Friedman and O'Neil

Fig 4-5

KEY

- ● Dolospars } dolomicrites
- ○
- □ Idiotopic } pervasive
- ■ Xenotopic } dolomites
- ◇ Idio } vein
- ◆ Xeno } dolomites
- ⬭ Dolomite fields
- ✕ Brofiscin oolite whole rock
- ▽ Vein calcites (in Br.O)
- ⊗ Gully oolite poikilotopic calcite
- ⊠ Gully oolite dolomite rhombs
- ◊ Gully oolite brachiopods
- ⊙ Gully oolite ooids
- ● Gully oolite whole rock

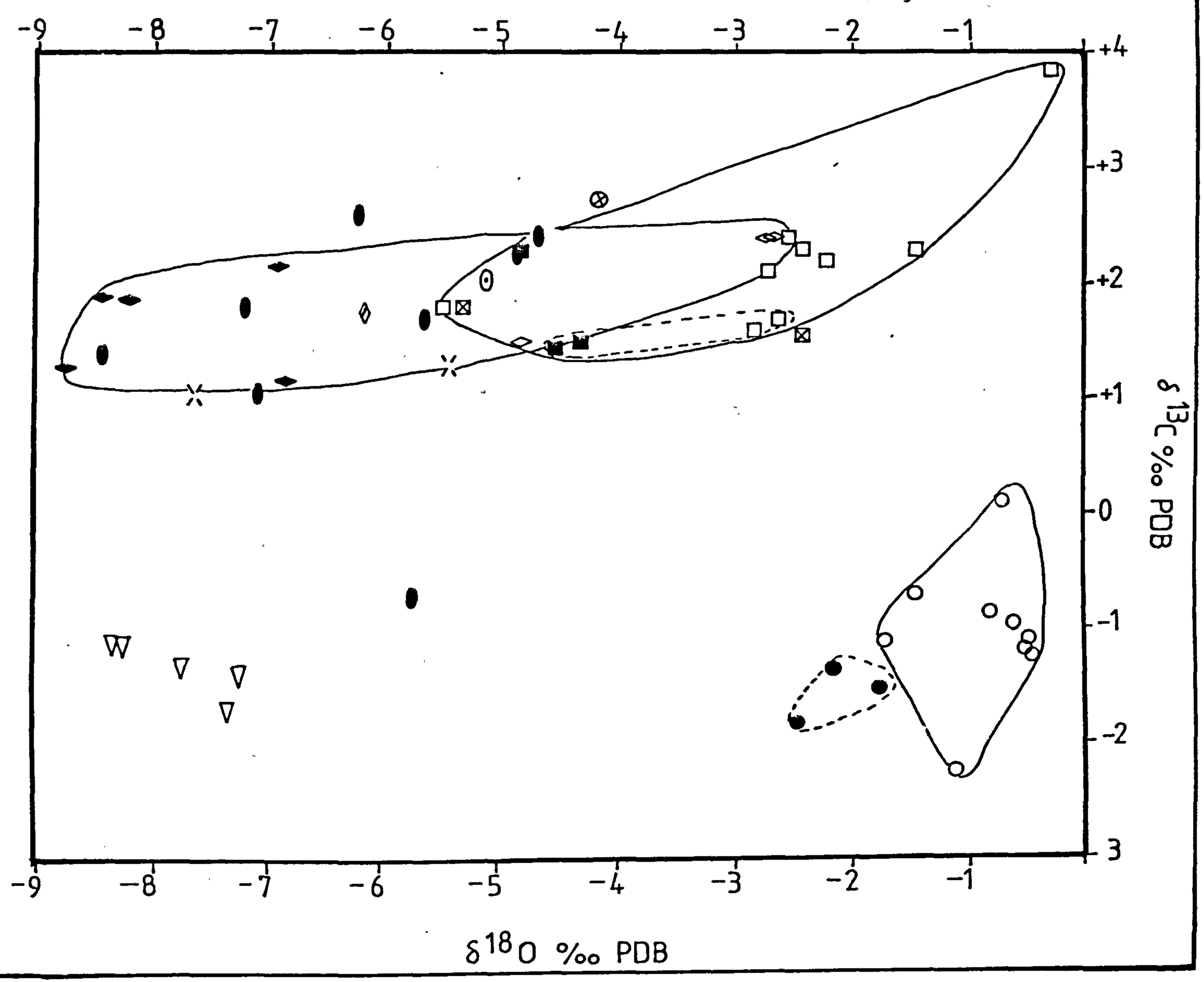


Fig 4.5 Stable isotope variations in dolomites and associated limestones, S.Wales Dinantian.

(1977) and for values of $\delta_A - \delta_B (= \Delta_{A-B}$, the fractionation between between substances A and B) and δ less than about 10, the following is true: $\delta_A - \delta_B \cong 10^3 \ln \alpha$.

Based on the above experimental work, the following empirical fractionation equations are available for the dolomite-water fractionation of oxygen isotopes (the experimental temperatures are given in parentheses after each equation).

1. $10^3 \ln \alpha_{\text{dolomite-water}} = 3.2 \times 10^6 T^{-2} - 2.0$ (300° to 510°C)
2. $= 3.34 \times 10^6 T^{-2} - 3.34$ (350° and 400°C)
3. $= 3.23 \times 10^6 T^{-2} - 3.29$ (100° to 650°C)
4. $= 2.78 \times 10^6 T^{-2} + 0.11$ (25° to 79°C)

T in °Kelvin

The data on which these equations are based are from (1) Northrup and Clayton, 1966; (2) O'Neil and Epstein, 1966; (3) Sheppard and Schwarcz, 1970 based on co-existing calcite and dolomite in marbles and (4) Fritz and Smith, 1970. A subset of Fritz and Smith's data was used by Irwin et al. (1977) to derive the following: $T°C = 31.9 - 5.55 (\delta_d - \delta_w) + 0.17 (\delta_d - \delta_w)^2$, where $\delta_d - \delta_w$ is the measured difference in $\delta^{18}O$ between dolomite and water.

Curves for each of the above equations (1-4) are plotted on Fig. 4.6 as temperature (°C) vs. dolomite-water fractionation for $\delta^{18}O_{\text{water}} = 0‰$ (after Land, 1983). A similar equation for calcite ($10^3 \ln \alpha_{\text{calcite-water}} = 2.78 \times 10^6 T^{-2} - 2.89$, Friedman and O'Neil, 1977) is also plotted. The curves illustrate the relative uncertainty in dolomite-water fractionation (up to 3 ‰) and suggest that at 25°C (for example) dolomite will be approximately 3 to 6‰ heavier than calcite co-existing at equilibrium.

As most of the studied Dinantian dolomites probably formed at

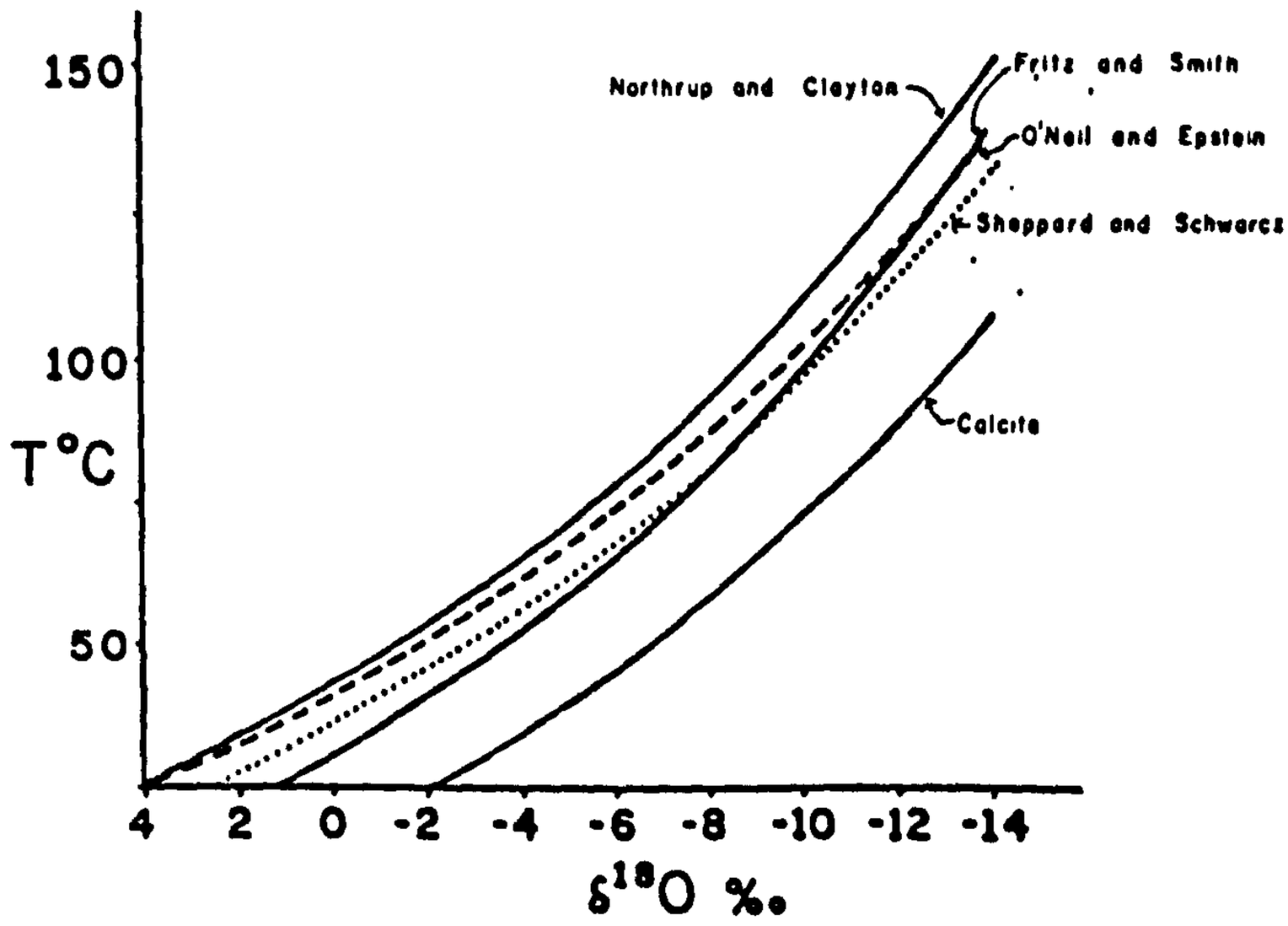


Fig 4.6

Plots of the four available dolomite-water fractionations, plus one for calcite, as a function of temperature.

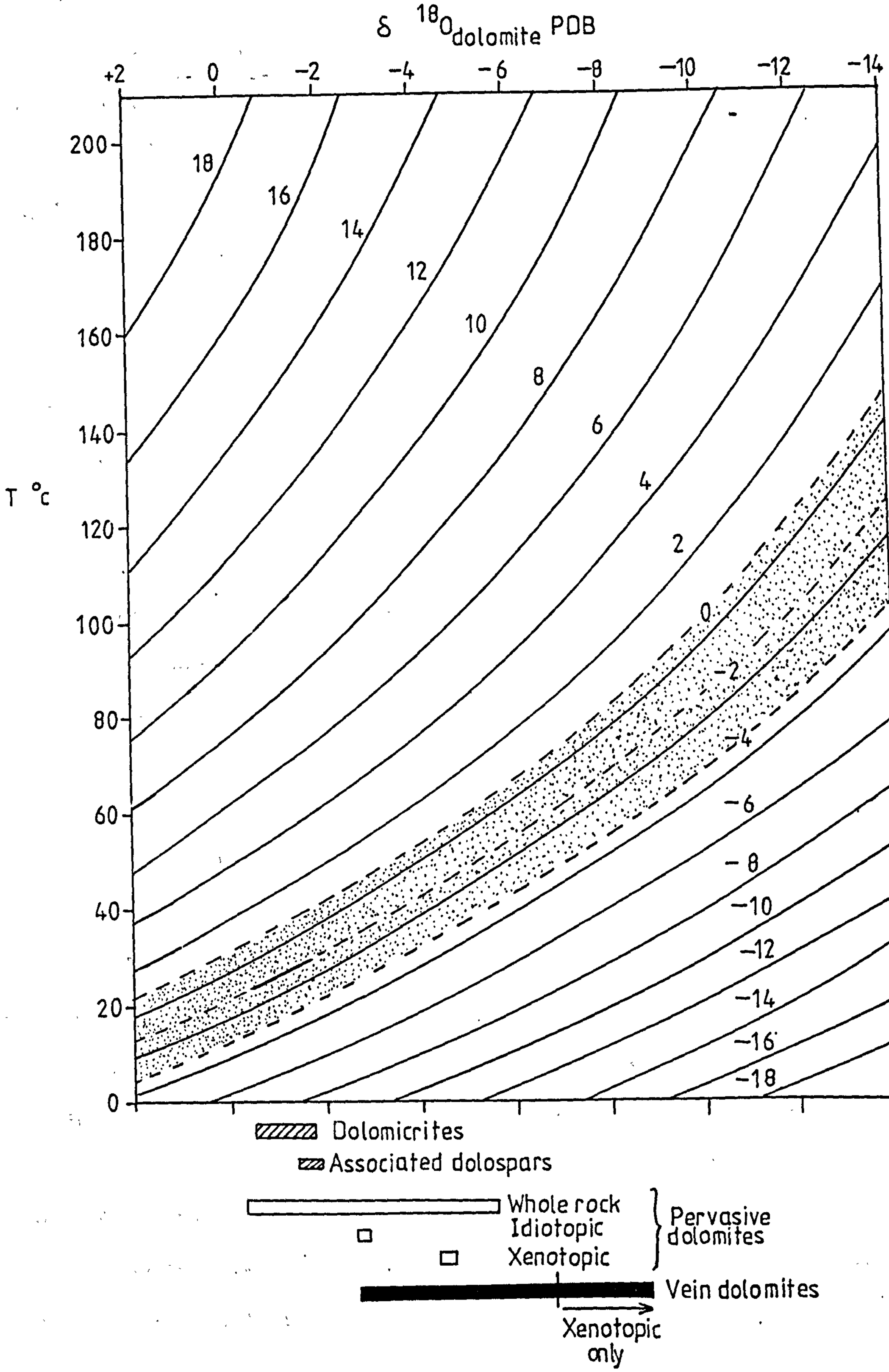
Plotted for $\delta^{18}O_{water}$ = 0 °/₀₀ (from Land, 1983)

Fig 4.7 Temperature vs. $\delta^{18}O_{dolomite}$ (PDB), water composition contoured in ‰ relative to SMOW, using the fractionation equation based on the data of Fritz and Smith (1970) :

$$10^3 \ln\alpha_{dolomite-\ water} = 2.78 \times 10^6\ T^{-2} + 0.11$$

A field showing Carboniferous seawater estimates is included (stippled area); however, this is strictly only appropriate at near-surface temperatures (as indicated by the short solid line). The oxygen isotopic composition of the studied dolomites is also shown (see text for explanation).

Fig 4—7


δ 18O dolomite PDB
+2
0
−2
−4
−6
−8
−10
−12
−14
T °C
200
180
160
140
120
100
80
60
40
20
0
18
16
14
12
10
8
6
4
2
0
−2
−4
−6
−8
−10
−12
−14
−16
−18
Dolomicrites
Associated dolospars
Whole rock
Idiotopic
Xenotopic
Pervasive dolomites
Vein dolomites
Xenotopic only

PAGE

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relatively low (sedimentary) temperatures, the fractionation equation of Fritz and Smith (1970) is considered to be the most appropriate, although the uncertainties should still be noted. Fig. 4.7 is then a plot of temperature ^{o}C vs. $\delta^{18}O_{dolomite}$ PDB with water compositions contoured in $^{o}/_{oo}$ SMOW, as calculated from the equation after Fritz and Smith (1970), and will be referred to further in the following discussion of the Dinantian dolomites.

4.3.2 Introduction II: Carboniferous carbonates and seawater

Before embarking on a discussion of the present stable isotope data, it is worth reviewing the literature relating to the isotopic composition of Carboniferous carbonates and seawater. Veizer and Hoefs (1976) provided a useful compilation, showing secular variations in $\delta^{18}O$ and $\delta^{13}C$ of ancient carbonates from the Archean to the Tertiary. Their data show Carboniferous limestones to have $\delta^{18}O$ from $0^{o}/_{oo}$ to $-13^{o}/_{oo}$ PDB and $\delta^{13}C$ from $+5^{o}/_{oo}$ to $-5^{o}/_{oo}$ PDB. Carboniferous dolomites have $\delta^{18}O$ $+4^{o}/_{oo}$ to $-11^{o}/_{oo}$ and $\delta^{13}C$ $+5^{o}/_{oo}$ to $-9^{o}/_{oo}$ PDB. However, these ranges represent an uncritical compilation of whole-rock data with no account taken of the variable proportion of depositional and diagenetic components. More rigorous attempts to define marine depositional carbonate and ultimately ancient seawater have been made, and for the Carboniferous include Dickson and Coleman (1980), Brand and Veizer (1981) and Brand (1981, 1982).

Brand (1982) provided data for Pennsylvanian aragonitic molluscs and lime muds (Buckhorn asphalt) and Mississippian low-magnesium calcite brachiopods (Lake Valley Formation), which he claimed precipitated in isotopic equilibrium with ambient seawater. Combining this data with that of Lowenstam (1961), Dickson and Coleman (1980), Brand and Veizer (1981)

and Brand (1981) he defined the oxygen and carbon isotopic field for Carboniferous marine carbonate as $\delta^{18}O$ = +0.5°/$_{oo}$ to -3.5°/$_{oo}$ PDB and $\delta^{13}C$ = +4.5 to 0°/$_{oo}$ PDB. The suggested Carboniferous seawater values are $\delta^{18}O$ = -1.5±2°/$_{oo}$ PDB and $\delta^{13}C$ = +2.6±2°/$_{oo}$ PDB (Brand, 1982). The range in $\delta^{18}O$ values is plotted on Fig. 4.7 for reference (note that <u>water</u> measured on the SMOW scale differs by approximately +0.2°/$_{oo}$ relative to water measured on the PDB scale, Craig, 1961; Friedman and O'Neil, 1977; Shackleton and Kennett, 1975).

4.3.3 Dolomicrites

The stratigraphic-sedimentological (Chapter 2) and petrographic (Chapter 3) background of the dolomicrites has already been discussed. In this chapter, the stoichiometry order and cation chemistry have been presented and they are generally consistent with an origin by early penecontemporaneous diagenetic replacement and augmentation (including dolospar cementation) of dolospar samples were separated from laminated fenestral dolomicrites for stable isotope analysis.

Relatively high rock/water ratios and the presence of organic matter during dolomitisation are suggested by ordering and cation chemistry data.

a) <u>Oxygen</u> ($\delta^{18}O$)

The possibility that dolomitisation occurred in a partially closed-system complicates quantitative interpretation of stable isotope data. However, as already discussed (section 2, introduction), the very high oxygen pool in water, and the necessity for water to be present during any diagenetic recrystallisation, means that the diagenetic phase will probably be dominated by the $\delta^{18}O$ of the diagenetic fluid (Veizer, 1983a). So, it

can be assumed that the oxygen isotopic composition of the dolomite reflects approximate equilibrium with diagenetic fluids, with the fractionation being essentially temperature controlled (Friedman and O'Neil, 1977 and Introduction I).

Assuming surface to shallow burial temperatures of formation (20-50°C) and a water dominated system (with respect to $^{18}O/^{16}O$), dolomicrite ($\delta^{18}O$ values ($\bar{x}$ = -0.87 range -0.46 to -1.72) suggest fluid compositions in the range $+4^{o}/_{oo}$ to $-3^{o}/_{oo}$ SMOW. This compares with the estimates of Carboniferous seawater composition, viz $-1.5\pm2^{o}/_{oo}$ PDB (Brand, 1982), equivalent to $-1.3\pm2^{o}/_{oo}$ SMOW, and suggests formation from slightly evaporated to normal seawater.

The small number of fenestral dolospars analysed have slightly depleted compositions ($\bar{x}\,\delta^{18}O$ = $-2.1^{o}/_{oo}$ range -1.9 to -2.8) relative to the dolomicrites. This shift may reflect formation from more depleted (? more dilute) waters and/or at elevated temperatures (see Fig. 4.7). In an open system, and assuming the relationship between $\delta^{18}O$ dolomite, $\delta^{18}O$ water and temperature used in Fig. 4.7 (see introduction) and a diagenetic solution composition $\delta^{18}O$ = $-1.3 \pm 2^{o}/_{oo}$ SMOW (best estimate for Carboniferous seawater), the temperature of formation of the dolospars is estimated at 35 ± 10^{o} and the dolomicrites at 25 ± 10^{o}C (see Fig. 4.7).

b) <u>Carbon</u> ($\delta^{13}C$)

In contrast to oxygen the principal source of carbon during carbonate diagenesis is the dissolving carbonate phase. Because of this, and the relatively insignificant temperature effect on the carbonate-bicarbonate fractionation ($\sim+0.035^{o}/_{oo}/^{o}C$, Emrich et al., 1970), dissolution-precipitation reactions involving marine carbonates results in diagenetic products with similar $\delta^{13}C$ compositions to the precursor phase (around

$0^{o}/_{oo}$, Hudson, 1977; see Veizer, 1983a also).

The estimated carbon isotopic composition of Carboniferous seawater is $+2.6\pm2^{o}/_{oo}$ PDB (Brand, 1982). Therefore dolomicrite compositions (+0.1 to $-2.3^{o}/_{oo}$) suggest a light-carbon contribution to precipitating dolomite. As already suggested (section 4.2.2.b), oxidation of organic matter in the low-permeability sediments during shallow burial resulted in the rapid consumption of molecular O_2 followed by suboxic/dysaerobic oxidation of organic carbon and concomitant release of Mn^{2+} and Fe^{2+}. Degradation of organic matter (average $\delta^{13}C \sim -24^{o}/_{oo}$, Hudson, 1977) would have liberated light-carbon CO_2, producing ^{13}C depleted bicarbonate in porewaters, and ultimately in diagenetic carbonates (Irwin et al., 1977). Dolomicrites, however, have much less depleted $\delta^{13}C$ compositions than would be expected from an entirely organic source (to $-25^{o}/_{oo}$, Irwin et al., 1977), and this may be due to the dominant effect of marine bicarbonate contributed by the dissolution of metastable precursors. This is consistent with the interpretation of a low-SI system, at least with respect to Na, Sr and the Mg:Ca ratio. The early diagenetic origin suggested by petrography and supported by geochemistry ($\delta^{18}O$, Sr, Na and ordering) implies rapid, nearsurface oxidation of organic matter in order to account for the observed Fe, Mn and $\delta^{13}C$ compositions and for early post-dolomitisation pyrite formation.

4.3.4 Pervasive dolomites

A shallow subsurface origin is suggested for the bulk of the pervasive dolomites on the basis of mass-balance considerations and petrographic evidence. High SI systematics have been invoked because of the requirement for allochthonous Mg^{2+} and the stoichiometry , ordering and cation

chemistry data are generally consistent with formation from dilute, shallow subsurface diagenetic fluids. However, it is clear from petrographic study that many pervasive mosaics comprise more than one phase of dolomite, and it has been shown that later recrystallisation, replacement and cementation by dolomite and in some cases calcite or silica has occurred.

The concept of Critical Roughening Temperature (CRT) as a control on crystal morphology (Gregg and Sibley, 1984) was introduced in Chapter 3 and will now be pursued further. Pervasive mosaics are predominantly idiotopic (idiotopic plus hypidiotopic of Friedman, 1965), which, it was suggested (Chapter 3, Gregg and Sibley, 1984) formed at temperatures below the CRT (estimated at 50°C), consistent with a relatively early diagenetic origin. Later dolomite phases are almost invariably xenotopic mosaics, and suggest temperatures of formation above 50°C (60°C to 150°C ?, Radke and Mathis, 1980).

This basic information may be used in an attempt to understand stable isotopic compositions of dolomite and perhaps place further constraints on the dolomitisation process.

a) Oxygen ($\delta^{18}O$)

Pervasive dolomites have a range of oxygen isotopic compositions from $\delta^{18}O$ -5.5 to -0.3$^{o}/_{oo}$ (see Fig. 4.5). Broadly the data may be separated into groups based on the petrographic character of the samples as follows:

i) relatively fine-grained idiotopic dolomite, with uniform inclusion density; $\delta^{18}O$ -1.5 to -0.3$^{o}/_{oo}$.

ii) coarser-grained idiotopic dolomite with inclusion-ghost fabric, showing replacement of grainstones through wackestones; $\delta^{18}O$ -2.8 to -2.2$^{o}/_{oo}$.

iii) idiotopic dolomite (as ii) with patchy xenotopic dolomite; $\delta^{18}O$ -5.5

to $-4.3^{o}/_{oo}$.

Within these data are two pairs of analyses representing xenotopic and idiotopic dolomite separated from mixed (type iii) samples (see Fig. 4.5). They indicate a $\delta^{18}O$ shift of $-1.7^{o}/_{oo}$ from idiotopic to xenotopic dolomite. In contrast, whole rock data suggests shifts up to $5.2^{o}/_{oo}$ between idiotopic and mixed dolomites. However, confining the study to 'separated samples', it is possible to <u>estimate</u> the composition of dolomitising fluids assuming equilibrium fractionation and the suggested formation temperatures for idiotopic and xenotopic dolomite.

Assuming that idiotopic dolomite formed at or below 50°C and xenotopic dolomite at or above 50°C and using the average (of two) $\delta^{18}O$ compositions of $-2.7^{o}/_{oo}$ for idiotopic and $-4.4^{o}/_{oo}$ for xenotopic, a range of equilibrium fraction$^{n.}$ $\delta^{18}O_{water}$ compositions may be derived from Fig. 4.7. For idiotopic dolomite forming at temperatures between 20°C and 50°C, equilibrium water compositions in the range -4 to $+1.5^{o}/_{oo}$ SMOW are possible. At low temperatures these are consistent with an origin from essentially unmodified sea water. Xenotopic dolomite indicates $\delta^{18}O_{water}$ compositions of c. -0.5 to $+11^{o}/_{oo}$ SMOW at temperatures in the range 50° to 150°C. This suggests fluids with elevated salinities or isotopically evolved formation waters, relative to seawater at surface temperatures (Clayton et al., 1966).

An alternative approach to the interpretation of these data is to assume an homogeneous fluid composition (e.g. $-1.3\pm2^{o}/_{oo}$ SMOW) and calculate expected equilibrium $\delta^{18}O$ dolomite compositions across the suggested range of formation temperatures (e.g. Gregg and Sibley, 1984). Around the (?) significant CRT, the following range of equilibrium dolomite

compositions are produced; noting that it is the shift and not absolute values that are important:

	Temp ^{o}C		
	35	50	65
Calculated $\delta^{18}O$ dolomite (PDB) assuming $\delta^{18}O$ water = $-1.3\pm2^{o}/_{oo}$ SMOW	-2.7	-5.3	-7.5

Clearly the observed shift in $\delta^{18}O$ dolomite composition between idiotopic and xenotopic dolomite of $1.7^{o}/_{oo}$ (see Fig. 4.5) represents a smaller temperature range across the CRT. This range is calculated using the equilibrium fractionation equation derived by Irwin et al., (1977) (see introduction) and a $\delta_{w} = -1.3^{o}/_{oo}$ (SMOW) is 39 to 49°C. This temperature gradient is inconsistent with petrographic data which suggests that idiotopic dolomite formed during early diagenesis, presumably at nearsurface temperatures, and xenotopic dolomite formed later, during deeper burial. The explanation by Gregg and Sibley (1984) that similarly small $\delta^{18}O$ shifts ($-1^{o}/_{oo}$) between idiotopic-xenotopic pairs across wide temperature gradients (up to 400°C) may result from closed-system (rock, dominated) recrystallisation of idiotopic dolomite is considered unlikely for the reasons discussed in section 4 (discussion of factor C, degree of openness of diagenetic systems with respect to different solutes). It is more likely that xenotopic dolomites formed from fluids with a similar isotopic composition to those from which idiotopic dolomites formed. These are unlikely to have been the same fluids because formation waters undergo

significant isotopic modification with time and burial (e.g. Clayton et al., 1966; Lawrence et al., 1975; Fleischer et al., 1977).

Although subsurface recrystallisation (presumably below the CRT) cannot be ruled out for the idiotopic dolomite, a nearsurface, open-system origin seems most likely on independant evidence (see previous sections and Chapter 3). Following from this, it seems likely that seawater was a significant influence on the composition of early idiotopic pervasive dolomites, in agreement with the oxygen stable isotopic data.

b) Carbon ($\delta^{13}C$)

As already discussed (Dolomicrites, above), solution-precipitation reactions during carbonate diagenesis will only produce changes of a few $^{o}/_{oo}$ in $\delta^{13}C$ in the absence of organic carbon derived bicarbonate in solution. The small range in $\delta^{13}C$ data for pervasive dolomites and their low positive value (+1.8 to $+3.9^{o}/_{oo}$ PDB) is consistent with a marine-carbonate precursor or formation at equilibrium with Carboniferous seawater ($\delta^{13}C$ $+2.6^{+}2^{o}/_{oo}$). The trend towards slightly depleted $\delta^{13}C$ with $\delta^{18}O$ depletion perhaps reflects some change in conditions of dolomitisation affecting the fractionation or degree of equilibrium and rock/water ratio, with burial and increasing temperature.

What is clear, is that there appears to be little organic influence on the bulk $\delta^{13}C$ composition of these dolomites. This is consistent with them having formed by replacement of open-marine grainstones and packstones, with low organic content and beyond the influence of soil processes (c.f. Hudson, 1977).

4.3.5. Vein Dolomites

Stratigraphic and petrographic data suggest that vein dolomites formed

during late burial diagenesis, probably around the time of maximum burial in the late Carboniferous. The presence of baroque dolomites is consistent with, although does not confirm, elevated temperatures of formation expected from the estimated end-Carboniferous burial depths. However, because burial and subsequent uplift were probably quite rapid equilibrium burial temperatures may not have been reached (Dickson, 1985).

Host limestones were well cemented and diagenetically stabilised at the time of fracturing and dolomitisation. Low rock/water ratios (SI ≈100) were probably important locally, but variable host-rock influence is suspected overall (see preceding sections). Vein dolomites probably do not represent a simple open-system equilibrium situation, therefore, any attempt at interpretation of stable isotope data should be constrained by this possibility.

a) Oxygen ($\delta^{18}O$)

Having drawn attention to the potential difficulties of interpretation, the first approach to $\delta^{18}O$ data is to assume that the dolomites formed under equilibrium conditions.

The vein dolomite data fall into two categories: (i) idiotopic dolomite with some xenotopic (baroque) crystals and/or limpid overgrowths; (ii) xenotopic or baroque dolomites comprising coarse anhedral, locally euhedral crystals. Group (ii) vein dolomites have the most negative $\delta^{18}O$ values (-6.8 to -8.7$^{o}/_{oo}$ PDB).

Discussion Assuming equilibrium fractionation according to the relationship given in Fig. 4.7 a range of possible $\delta^{18}O_{water}$ compositions are suggested, depending on the temperature of formation. As suggested in Chapter 2, section 2.6, the temperatures reached during burial of the

Dinantian sequence were probably at the lower end of the expected range (i.e. c. 50°C). Taking this as the temperature of formation for group (ii) xenotopic vein dolomites, the suggested range in water composition is c. -3°/$_{oo}$ to -5°/$_{oo}$ SMOW, these values are depleted relative to Carbóniferous seawater at surface temperatures.

The temperature of formation of the group (i) idiotopic-with-xenotopic vein dolomites is not likely to have been significantly different from the xenotopic dolomite, as these two types are petrographically intimately related. The range in $\delta^{18}O_{dolomite}$ therefore implies changes in fluid composition over very short distances or perhaps dolomite formation under non-equilibrium conditions. Sverjensky (1981) has argued in favour of the latter interpretation to explain $\delta^{18}O$ depletion in carbonates adjacent to Mississippi Valley lead-zinc ore bodies, where porosity appears to have a greater control than temperature on the $\delta^{18}O$ of carbonates. In the vein dolomites, it may be that the relatively more depleted xenotopic dolomite formed in localised areas of higher porosity. The problem remains unresolved.

b) <u>Carbon</u> ($\delta^{13}C$)

As with the pervasive dolomites, the $\delta^{13}C$ composition of vein dolomites (see Fig. 4.5) suggests marine carbonate as the principal source of bicarbonate in solution. Again a slight depletion with decreasing $\delta^{18}O$ is observed, but the exact significance of this is uncertain. However, there are a number of host limestone whole-rock analyses available for comparison (see Fig. 4.5).

By extrapolation from the high temperature (100-650°C) fractionation curve of Sheppard and Schwarcz (1970) (in Friedman and O'Neill, 1977) to

50°C dolomite should be heavier by approximately $2^{o}/_{oo}$ relative to 'coexisting' calcite ($1.5^{o}/_{oo}$ at 100°C).

Clearly host-limestone and dolomite are not 'coexisting' (= cogenetic) pairs; however, in a closed, rock-dominated system the suggested equilibrium fractionation may be approached. The measured difference between average vein dolomite and average limestone $\delta^{13}C$ compositions (δ_d-δ_c) is $0.3^{o}/_{oo}$ (maximum = $2.95^{o}/_{oo}$). This suggests that calcite-dolomite equilibrium may have been approached and thus argues for a rock-dominated system, at least with respect to carbon. Marine carbonate therefore seems to have been the only significant source of carbon for the vein dolomites.

4.3.6 Vein Calcites

These calcites occur as microfracture fills in the Brosficin oolite limestone and dolomite, and therefore apparently have no connection with vein dolomites. However, on the basis of their distinctive cathodoluminescence zonation and their paragenetic timing they may be equivalent to late calcites in both vein and pervasive dolomite mosaics (see Chapter 3). They are included here because insufficient material was available from the pervasive and vein dolomite examples.

The calcites have $\delta^{18}O$ compositions (see Fig. 4.5) suggesting formation at elevated temperatures and/or from depleted (dilute) waters, consistent with either a burial or a nearsurface, meteoric origin. Their $\delta^{13}C$ compositions, on average depleted by $3^{o}/_{oo}$ relative to vein dolomites. As the calcites clearly post-date vein dolomites equilibrium-fractionation cannot be readily invoked unless the calcites formed in a rock (dolomite) - dominated system. However as the analysed samples are <u>not</u> directly related to vein dolomites such a suggestion cannot be made. The vein calcites are

also depleted relative to their host limestones (by approximately $2^{o}/_{oo}$, see Fig. 4.5) which suggests that a light carbon source was available. This is probably more consistent with a nearsurface (soil gas CO_2 or rainwater bicarbonate influence) origin than late burial. Considering the burial-rapid uplift history of these rocks, a nearsurface connection may have been achieved quite soon after vein dolomite formation, perhaps by the end Carboniferous-early Permian.

4.3.7

Summary and main conclusions from stable isotope studies

The studied dolomites have stable isotope compositions within the range of Carboniferous dolomites compiled by Veizer and Hoefs (1976).

Many authors (e.g. Mattes and Mountjoy, 1980; Choquette and Steinen, 1980; Vinet, 1984) have compiled data for modern and ancient dolomites in attempts to categorise the stable isotopic (and trace element) composition of different dolomite types. Fig 1.2 (Chapter 1) is a similar compilation. Whilst this approach offers a qualitative means of comparison, it is restricted as an interpretative tool because:

(a) secular variations in $\delta^{18}O$ and $\delta^{13}C$ (Veizer and Hoefs , 1976) may affect comparison of dolomites of different geological age.

(b) differences in the experimental procedure between investigators are common (see Land, 1980).

(c) uncertainties about the precise origin of dolomites in many (if not all) cases makes grouping into 'genetic fields' a subjective judgement, depending on the emphasis placed on different genetic criteria. Examples exist where a single dolomite formation has been interpreted in entirely different ways by different workers.

(d) Post-dolomitisation alteration (neomorphism and further dolomitisation) may be a common phenomenon in the formation of ancient dolomites (Land, 1983), so that single, simple genetic interpretations are probably inappropriate (well illustrated by the present study).

In general terms, compilations of dolomite data (e.g. Fig. 1.2) show that penecontemporaneous dolomites of probable evaporative or marine origin have the least depleted $\delta^{13}C$ and $\delta^{18}O$ compositions. Depletion, to negative $\delta^{18}O$ and less positive $\delta^{13}C$, generally accompanies a trend towards mixed-water and later diagenetic, burial dolomites, where the most depleted $\delta^{18}O$, and possibly $\delta^{13}C$, values are typically observed. Significant departures in this pattern commonly involve $\delta^{13}C$, where organic-carbon sources are locally important (e.g. in soil-related meteoric systems, or burial of organic-rich marine sediments).

The studied dolomites have stable isotope trends consistent with the above generalisations. More specific interpretation is based on a combination of facies interpretations, petrographic study and geochemical analysis. The following main conclusions may be drawn.

1. Dolomicrite stable isotopic compositions are consistent with a penecontemporaneous-early diagenetic origin, including some modification by recrystallisation and augmentation in a shallow-subsurface, relatively closed-system diagenetic environment.

2. Slightly evaporated to normal marine waters may have been responsible, based on the interpretation of dolomicrite $\delta^{18}O$ data.

3. A light-carbon influence on $\delta^{13}C$ composition is consistent with cation chemistry (Fe and Mn) for dolomicrites, suggesting organic matter degradation; the volumetric importance of this to the overall carbon reservoir was probably small.

4. Pervasive dolomites have stable isotopic compositions consistent with early replacement of marine carbonates, perhaps within the influence of seawater. The data fall in the range of mixed marine-meteoric dolomites shown on Fig. 1.2 (Chapter 1).

5. Observed shifts in $\delta^{18}O$ of pervasive dolomite composition probably represent increased temperature effects and/or dilution (to lighter $\delta^{18}O$) of porewaters.

6. $\delta^{13}C$ data for pervasive dolomites are consistent with an origin by replacement of marine carbonate.

7. Vein dolomites have a late diagenetic, burial origin; probably having formed at elevated temperatures under variable rock/water ratio conditions.

8. Depending on the temperature of formation, burial dolomitising fluids may have had $\delta^{18}O$ compositions similar to, or heavier than Carboniferous seawater. Equilibration with host limestones is also suspected for some of the vein dolomites, and a porosity control may have been important.

9. A marine-carbonate influence on vein dolomite $\delta^{13}C$ is likely, and suggests rock dominated equilibrium isotope fractionation and/or fluids lacking organic-carbon derived bicarbonate.

CHAPTER 5

Summary and discussion: dolomites in the Dinantian of South Wales

5.1 Introduction

In Chapters 2 to 4 stratigraphic-sedimentologic, petrographic and geochemical data for the dolomites and associated limestones in the Dinantian sequence of South Wales were presented. The following conclusions may be drawn from these data.

1) Following a major eustatic sea-level rise in the early Dinantian an extensive carbonate ramp developed over South Wales.

2) Three distinct tectono-palaeogeographic zones are recognised: inner-ramp, mid-ramp and outer-ramp. The inner ramp sequence of the North Crop comprises oolitic and peritidal shoal and back shoal lithofacies with numerous subaerial exposure surfaces and some palaeokarstic horizons. Subtidal, storm dominated, bioclastic limestones with important oolitic shoal limestones characterise the mid-ramp sequences of the South Crop and Gower. They represent repeated transgressive and regressive (shoal progradational) events in response to sea level change, subsidence and sedimentation rate. The outer-ramp sequence, to the south of South Wales is represented by muddy bioclastic limestones which formed below storm wave base and in which Waulsortian reef mounds are developed.

3) In south-east and east Wales, representing the mid-ramp to inner-ramp transition much of the Dinantian sequence is dolomitised. Three main types of dolomite are recognised: dolomicrites, pervasive stratal dolomites and vein dolomites. These dolomite types have a marked stratigraphic and regional distribution, which is summarised on Fig. 5-1 (see Chapter 2 for

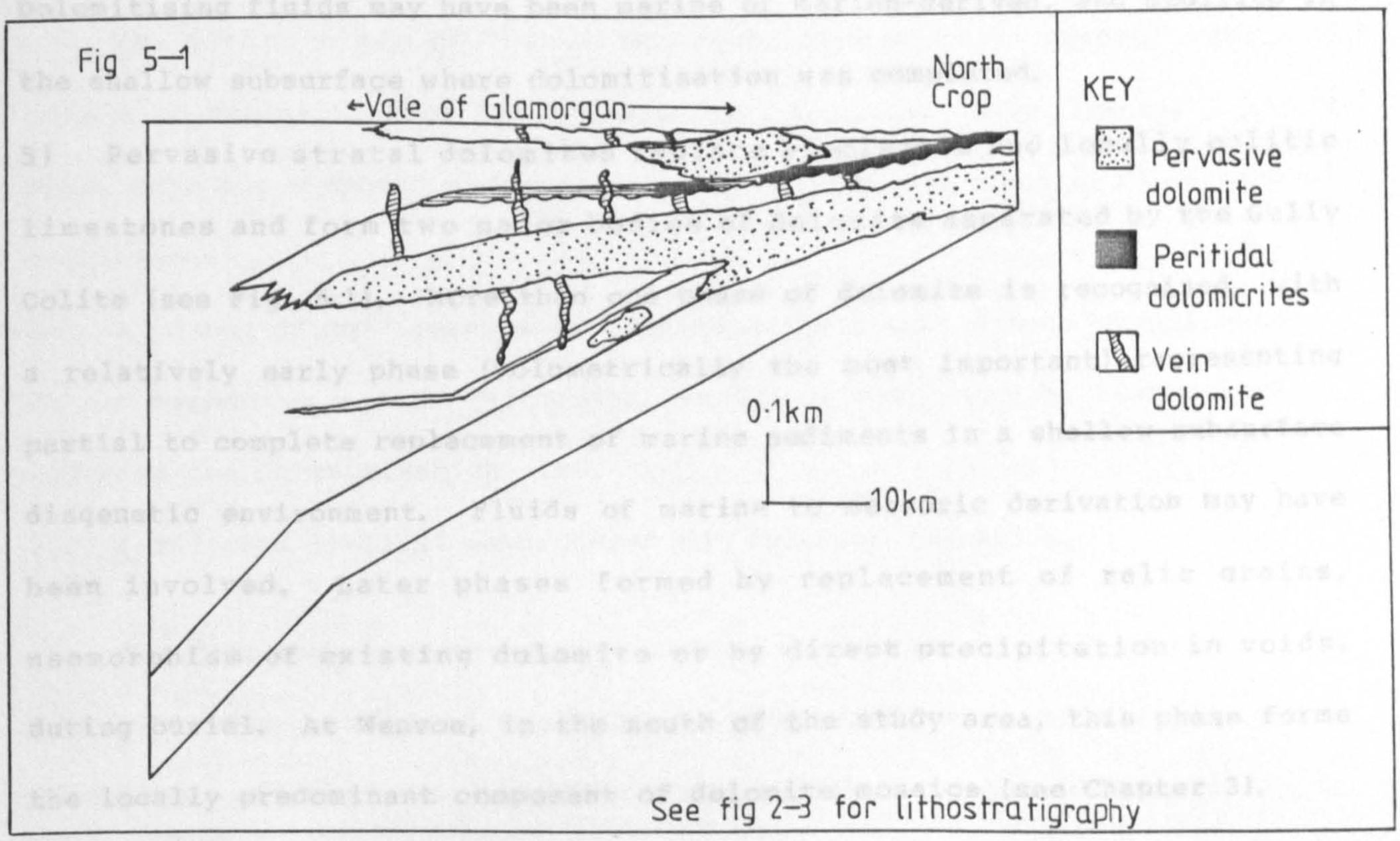


Fig 5.1 Lithostratigraphic cross section (as Fig 2.3), showing approximate distribution of dolomites

more details).

4) The dolomicrites form 'peritidal' carbonates representing shallow subtidal to supratidal environments. A penecontemporaneous origin for the dolomite is suggested by its petrographic and geochemical characteristics. Dolomitising fluids may have been marine or marine-derived, and modified in the shallow subsurface where dolomitisation was completed.

5) Pervasive stratal dolomites replace bioclastic and locally oolitic limestones and form two major bodies of dolomite separated by the Gully Oolite (see Fig. 5.1). More than one phase of dolomite is recognised, with a relatively early phase (volumetrically the most important) representing partial to complete replacement of marine sediments in a shallow subsurface diagenetic environment. Fluids of marine to meteoric derivation may have been involved. Later phases formed by replacement of relic grains, neomorphism of existing dolomite or by direct precipitation in voids, during burial. At Wenvoe, in the south of the study area, this phase forms the locally predominant component of dolomite mosaics (see Chapter 3).

6) Vein dolomites have a limited distribution, reflecting a structural control, and are most clearly developed in the otherwise undolomitised parts of the Gully and Hunts Bay Oolites. They formed during burial, probably around the time of maximum burial and joint development at the end of the Carboniferous. Dolomitising fluids may have been relatively dilute meteoric or marine derived formation waters or connate brines. The presence of baroque dolomite is consistent with, although does not necessarily confirm elevated temperatures of formation.

7) Vein dolomites and late-phase dolomites in pervasive dolomite mosaics have similar petrographic and geochemical characteristics, and are interpreted as being approximately coeval.

Of the three main types of dolomite, the pervasive stratal dolomites are volumetrically the most important and will receive the immediate attention of this discussion. Dolomicrites and vein dolomites will be discussed subsequently.

The ultimate aim of this discussion chapter is to suggest possible models of dolomitisation for the studied dolomites. From Chapter 1 it is clear that any proposed model must be able to satisfy the following general conditions:

1) A source of Mg^{2+} capable of supplying the observed mass of dolomite.

2) A mechanism whereby materials, including Mg^{2+}, may be transported to and from the dolomitisation site.

3) A suitable chemical environment for dolomite formation.

The following sections are intended to illustrate how these conditions may have been satisfied, principally with reference to the pervasive dolomites, and they draw on information and data presented more fully in preceding chapters and on the research literature reviewed in Chapter 1.

5.2 Mg^{2+} source for pervasive dolomites

The pervasive dolomites represent replaced marine sediments which, by comparison with laterally equivalent limestones comprised ooids and assorted bioclasts (see Chapter 3). Although these depositional grains (allochems) are all now composed of low-magnesium calcite it is probable that they represent a range of original mineralogies from low-magnesium- to high-magnesium-calcite and aragonite.

Maximum Mg^{2+} contents for individual grains in excess of 30-40 mole % are unlikely by comparison with modern high magnesium calcite grains

(Bathurst, 1975; Scholle, 1978) and bulk averages were probably considerably less. In the case of the Brofiscin Oolite petrographic study indicates that early meteoric diagenesis was important and would have resulted in Mg loss from high-magnesium calcite components, as well as introduction of low-magnesium calcite cement. How far meteoric diagenesis had affected the sediments at the time of dolomitisation is, however, uncertain (see Chapter 3) and it would be unwise to extrapolate observations from the Brofiscin Oolite to an interpretation of the Pervasive dolomites in general.

Whatever the state of diagenesis of the marine sediments at the time of dolomitisation it is highly unlikely that sufficient Mg^{2+} was present to produce the massively dolomitised rocks. As with other examples of massive dolomite, an allochthonous source of Mg^{2+} is necessary (e.g. Morrow, 1982b; Simms, 1984b; Land, 1985). However, minor, scattered dolomite rhombs may have formed due to solution cannibalisation (e.g. Goodell and Garmen, 1969) of metastable phases.

For the early, shallow-surface phase of pervasive dolomite, the most likely source for Mg^{2+} is seawater, which formed the depositional medium and presumably a major component of the sediment's porewaters, at least during shallow burial. Alternative sources of Mg^{2+} in different (deeper or closed) diagenetic systems are discussed in later sections relating to the dolomicrites and vein dolomites.

5.3 Regional and stratigraphic distribution of pervasive dolomites - clues to the source of dolomitising fluids and the process of dolomitisation

The pervasive dolomites have a marked regional and stratigraphic distribution (see Fig. 5.1), which indicates their increasing importance in a north-easterly direction, approaching the Usk Axis (see Chapter 2). A similar pattern is observed on the North Crop, where dolomite increases in thickness in an easterly direction (George, 1954; Raven, 1983). and in the Forest of Dean and Bristol areas, where dolomite becomes more important towards the Usk Axis in the north-west (see fig. 6 in Kellaway and Welch, 1948). Whilst no genetic connection between the dolomites in these different regions is implied, the apparent common influence of the Usk Axis on their distribution is intriguing.

The Usk Axis certainly acted as a sediment source region in Westphalian times and there is evidence that it formed a positive feature north of Risca as early as late Arundian times (Chapter 2). Although there is no evidence that the Usk Axis was emergent during deposition of the studied rocks (Courceyan-Arundian), it probably was active from the Devonian and provided a regional or local palaeoslope down to the west (on the North Crop), south-west (on the East Crop) and east (in Forest of Dean and Bristol areas) of the Usk Axis.

On the North Crop the effects of the Usk Axis appear to have been limited to the most easterly area, and following deposition of the Gilwern Oolite (mid-Arundian) a regional downward dip to the east developed in response to movements along the Neath Disturbance (Wright, 1981; Raven, 1983).

Thus it seems likely that dolomitising fluids were derived from an updip source area to the north-east of Risca. Much or all of the Dinantian

strata in this area has been removed by erosion so it is not possible to say whether or not it was emergent, however, the presence of important peritidal carbonates (Arundian?) at Danygraig, Risca suggests a proximal palaeogeographic position developed in the region by this time.

Raven (1983) in a study of the diagenesis of the Oolite Group (Chadian-Arundian) of the North Crop, identified two distinct diagenetic areas. Dolomites are essentially confined to Raven's diagenetic area 1, which occurs in the east and partially underlies area 2. Raven (1983) also postulated an easterly source for the dolomitising solutions, but presented conflicting evidence as to their nature. Hypersaline brines are consistent with the geometry and position of the dolomites, but not with their negative $\delta^{18}O$ signatures (-1.6 to -3.4 $^{o}/_{oo}$ PDB) or the abundant evidence for meteoric diagenesis (Raven, 1983). Extensive meteoric diagenesis occurred in diagenetic area 2 in association with the many exposure surfaces developed there. Negative $\delta^{13}C$ values for area 2 calcite cements support this association, indicating a significant soil-gas contribution (Raven, 1983). In contrast, no such influence is suggested by area 1 $\delta^{13}C$ (+1.87 to -0.97 for dolomite), and if meteoric waters were involved they probably represented the distal part of a phreatic system (e.g. Lohmann, 1982; Moldovanyi and Lohmann, 1984), consistent with the suggestion of a recharge area some distance to the east.

As already summarised (section 5.1), petrographic and geochemical data for pervasive dolomites in the present study area support a meteoric-marine mixing zone origin (see Chapter 1) for the early phases of dolomite. The preceding discussion suggests that a potential recharge area may have existed to the north-east, with the geometry of the dolomite bodies reflecting the migration of the mixing-zone in the shallow subsurface

through time (as Dunham and Olson, 1980). This hypothesis is strongly supported by the observed relationship between regressive oolite units and dolomite (see Fig. 5.1). The regressive/progradational phases were probably accompanied by an increase in recharge area and expansion of phreatic freshwater lenses in the shallow subsurface. Local exposure of ooid shoals during progradation (as in the Brofiscin Oolite) may have provided additional recharge or produced isolated meteoric lenses and mixing-zones.

Many similar examples of this relationship between regressives phases and dolomitisation exist. Choquette and Steinen (1980) showed that dolomites in the Ste. Génévième Limestone, Mississippian, Illinois Basin are essentially restricted to subtidal (lagoonal) mudstone and wackestone lithofacies which occur beneath lenses of ooid grainstone. Choquette and Steinen, (1980) suggested that dolomitisation began during deposition of the oolites, when shoals became temporarily emergent and mixing-Zones developed beneath associated meteoric lenses. With shallow burial, dolomitisation continued in mixing-zones produced by the introduction of phreatic meteoric waters via the porous oolitic grainstones connected to subaerial recharge areas updip.

Dolomites in the subtidal carbonates of the Ordovician-Silurian Hanson Creek Formation of Eureka County, Nevada, display a distinct palaeogeographic control on their distribution (Dunham and Olson, 1980). This has been related to the development of a subaerial exposure surface, due to regional offlap in the mid-Llandovery, which acted as a meteoric-water recharge area under the prevailing humid-tropical climate. Mixing-zones are thought to have developed in the shallow-buried, subtidal sediments offshore, producing dolomites with depleted trace-element (Sr 20-

100 ppm) and oxygen isotope ($\delta^{18}O$ -0.8 to -0.67$^{o}/_{oo}$ PDB) compositions.

The Hanson Creek Formation, in fact, is just one of several 'shoaling upward shelf cycles' (Wilson, 1975) which makes up the Cambrian through Devonian carbonate platform of central Nevada, and Dunham and Olson (1980) suggested that the mixing-zone process may have operated repeatedly in response to the regional onlap and offlap throughout this time. The suggestion that shallow subsurface dolomites of this type may provide valuable palaeogeographic information (Dunham and Olson, 1980; see also Badiozamani, 1973) appears to be true for the South Wales Dinantian rocks studied here. Another example from southern Britain in which a similar control would seem a suitable interpretation occurs in the Bathonian Great Oolite Group of the Humbly Grove oilfield (see Sellwood et al, 1985).

5.4 Climate significance to dolomitisation

Fig. 5.2 summarises data presented in Chapters 2 and 3, providing evidence for climatic fluctuations through the Dinantian in South Wales. These fluctuations appear to have had a pronounced effect on Karst style and on soil formation at exposure surfaces (Wright, 1984b, for example, see also Chapter 2).

In Chapters 2 and 3 attention was drawn to the contrast in early diagenetic style between the Brofiscin Oolite (mid-Courceyan) and Gully Oolite (upper Chadian) of the South Crop. Whilst early diagenetic, first generation, marine cements have been observed in both oolites, early meteoric vadose and phreatic cements appear to be largely confined to the Brofiscin Oolite, suggesting exposure of prograding ooid shoals under a relatively humid climate. Despite extensive exposure at the top of the Gully Oolite (as a strand plain) early cements are generally limited to

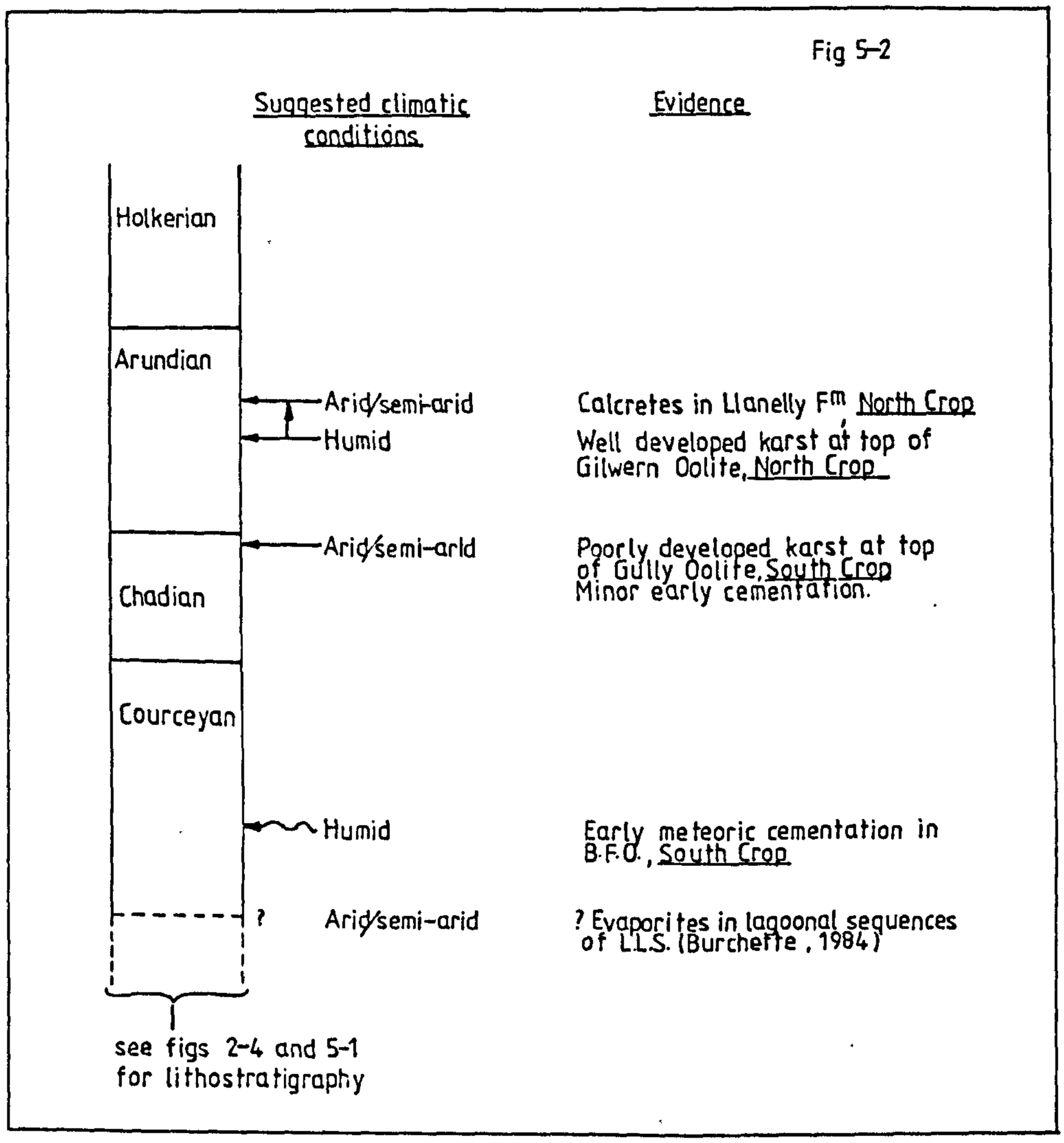


Fig 5.2 Suggested climatic fluctuations in the Dinantian of South Wales.

micritic coatings (cutans, see Riding and Wright, 1981) and minor Karst-related cements (see Chapter 3), indicating that an arid/semi-arid climate prevailed (supported by evidence from Karst style, see Wright, 1982a).

Intuitively, one would expect these climatic fluctuations to have influenced the position and size of meteoric lenses in the subsurfaces beneath islands and in coastal aquifers. As a result the position of marine-meteoric mixing-zones would also be expected to vary in response to climate, as well as to palaeogeography and sea-level.

High mixing-zone mobility, and hence the greatest potential for dolomitisation of large volumes of sediment, would be achieved under a seasonally humid climate (Longman, 1980). In contrast, periods of aridity would be marked by reduced or absent meteoric lenses and mixing zones and therefore insignificant dolomitisation. The development of mixing zones capable of extensive dolomitisation, however, also requires an active seawater circulation to provide the necessary Mg^{2+} (see 5.2 and 5.5), so the mixing-zone dolomitisation model is only applicable to marine-connected diagenetic environments in the shallow subsurface. This point was made by Dunham and Olson (1980) who demonstrated that the lack of extensive dolomite in part of the Hanson Creek Formation could be related to the late introduction of meteoric water, after the sediments were buried and direct communication between their porewaters and seawater reduced. A similar situation may have existed in the Gully Oolite, where early cements and dolomite are poorly developed in comparison with post-compaction blocky calcite cement (including syntaxial overgrowths on echinoderm fragments of probable meteoric-phreatic origin).

In the Brofiscin Oolite, early marine and meteoric cements and dolomite are succeeded by similar blocky calcite cements to those in the

Gully Oolite, suggesting that their post-dolomitisation diagenetic histories were similar and that meteoric water continued to be introduced during burial. Thus it is suggested that recharge areas continued to operate, periodically, through much of the Dinantian. From this it is apparent that the potential for mixing-zone dolomitisation in the nearsurface also may have existed at various times during the Dinantian. Whether or not dolomites actually formed would have been dependant upon the interaction of a number of factors, including climate.

Sibley (1980) suggested a climatic control on dolomitisatin in the Pliocene Seroe Domi Formation of Bonaire, Netherlands Antilles. Here the essential control appears to have been the pre-dolomitisation history of the metastable marine precursor sediments. Under arid conditions meteoric diagenesis was limited by low P_{CO_2} (little vegetation) and relatively brackish groundwaters, so that metastable aragonite and high-magnesium calcite remained available for dolomitisation in the mixing-zone. During more humid phases, which Sibley correlated with regression and increased orographic rainfall, aragonite and high-magnesium calcite were converted to low-magnesium calcite by diluted groundwaters with high P_{CO_2} (due to increased vegetation). As already discussed (see Chapter 3) LMC is more resistant to dolomitisation than its metastable precursors, so that sequences exposed to intense meteoric diagenesis <u>prior</u> to the passage of mixing-zones (i.e. before a transgression) are unlikely to be pervasively dolomitised.

Other workers have also suggested the importance of pre-dolomitisation history (e.g. Kaldi and Gidman, 1982); however, although Sibley's (1980) suggested close relationship between sea-level and climate may be demonstrable on Bonaire, and perhaps throughout the Caribbean area, it

seems unlikely to be generally applicable. It is certainly not the case in the South Wales Dinantian, where depositional and tectonic processes influenced sea level in addition to eustatic changes (contrast climates at peak of Brofiscin Oolite, Gully Oolite and Gilwern Oolite regressive events).

In South Wales Dinantian, difficulties in correlating North and South Crop sequences, in dating pervasive dolomitised units and in the precise timing of dolomite and cement formation relative to climatic events preclude the accurate definition of the climate-dolomitisation relationship. However, it is hoped that the preceding discussion has emphasised the potential importance of climate to dolomitisation, and some possible interpretations are presented in Fig. 5.3.

5.5 The need for an active hydrology: application to possible model of dolomitisation for the Pervasive dolomites

Proposed dolomitisation models must be able to satisfy the three criteria listed in section 5.1 (viz: (i) a source of Mg^{2+}; (ii) a supply-disposal system and (iii) a suitable chemical environment for dolomitisation). It was concluded above that seawater was the most likely source of Mg^{2+} for pervasive dolomitisation, and that the meteoric-marine mixing-zone was the probable environment of formation. Within this context the following discussion concludes that (a) an active hydrology is required for massive dolomitisation and (b) that possible groundwater flow mechanisms include mixing-zone flow and bankwater reflux, offering a variation on the traditional mixing-zone model of dolomitisation.

Assuming an average marine Mg^{2+} concentration (c. 1000 ppm) in pore

fluids, Choquette and Steinen (1980) calculated that of the order 7,500 pore volumes of seawater would be required to produce one pore volume of dolomite. Their calculations assumed that 10% of available Mg^{2+} would be incorporated in dolomite. This value seems a reasonable estimate of the compounded effects of (i) transport limitation in the porewaters, (ii) transport limitation in the allochems (diffusion) and (iii) the Kinetics of the dolomitisation reaction itself (see Simms, 1984a, 1984b). The above estimate of required pore-volumes increases by an order of magnitude if only 1% of available (seawater) Mg^{2+} is used or if porewaters are diluted (e.g. by meteoric mixing) to 100 ppm Mg^{2+}.

Clearly then, an active hydrology, as opposed to a stagnant pore fluid system, is required for the import of sufficient seawater-derived Mg^{2+} to produce the pervasive dolomites. Confining the discussion to seawater-connected, shallow subsurface systems on active carbonate platforms; possible flows include freshwater lens flow, reflux and thermal convection (Simms, 1984b and references therein, see also Land, 1985). In the depositional-tectonic context of the present study, the first two flow processes may be applicable. Thermal convection, however, is based on a specific example from the margin of the South Florida platform, where a density gradient occurs between the deep, cold ocean waters and geothermally heated porewaters in the adjacent platform (so-called Kohout Convection, see Simms, 1984b).

Considering the earlier interpretation, a mixing-zone origin for initial phases of the pervasive dolomites seems most likely, with meteoric phreatic lenses located (a) beneath emergent ooid shoals and (b) within shallow subsurface marine carbonates, with the freshwater being derived from a recharge area to the north-east. As reviewed by Simms (1984b),

seaward flow in the freshwater lens induces circulation of seawater, the highest velocities being reached in the zone of convergence and mixing of meteoric and marine water. The mixing zone thickens and velocities increase toward the recharge area (shoreline), thus dolomitising potential should also increase in this direction. An obvious result of this is the palaeogeographic control on dolomite distribution suggested by Dunham and Olson, 1980, for example (see section 5.3). On the Florida platform, low-lying islands and prograding tidal flats are the most likely sites of operation of this coastal groundwater system (Simms, 1984b). The apparent rarity of modern mixing-zone dolomite (see for example Land 1973, Magaritz et al, 1980) may be due in part to the relative paucity of data from areas where mixing-zones may be presently active - the Mediterranean coastal aquifer of Israel is a notable exception (Magaritz et al., 1980). Another factor may be the rapid post-glacial oscillations of sea-level compared to ancient more stable systems, which may have precluded the development of 'steady-state coastal hydrologic systems' (Land, 1985).

Variations of the 'mixing-zone model' include shallow, coastal aquifers and deeper (to c. 2 km), confined aquifers (see fig. 3 in Morrow, 1982b). Both may be applicable to the South Wales Dinantian, providing a free-circulation of seawater was available. However, the extensive, confined freshwater aquifers of the Florida Platform which extend up to 100 km offshore (Choquette and Steinen, 1980) may not be a good analogue for ancient systems. As Longman (1980) pointed out, the Floridan situation is a geologically unusual case resulting from repeated exposure and meteoric cementation of certain units, producing strong permeability contrasts and hence the potential for confined aquifers to develop in the shallow subsurface. During periods of more stable sea-level (outside the

last 1 million years), freshwater lenses are unlikely to have extended so far offshore, at least in the shallow subsurface, because of the inherent gravitational instability of less dense meteoric water beneath seawater. However, as Simms (1984b) has shown, such a situation provides further potential for seawater to enter into the deposited sediments, by reflux.

In a modification of the hypersaline reflux model (e.g. Adams and Rhodes, 1960, see Chapter 1), Simms (1984b) showed, theoretically, that reflux is not restricted to hypersaline settings and that it may also occur with seawater of only slightly elevated salinity. On the Bahama Banks, salinities greater than normal seawater (c. $35^{o}/_{oo}$) are typical and may range from $37^{o}/_{oo}$ to $45^{o}/_{oo}$ across the platform, and in restricted areas salinities up to $80^{o}/_{oo}$ have been reported (Simms, 1984b). These elevated salinities result from progressive evaporation (even in humid climates) across the platform and should be typical of any wide, shallow or rimmed carbonate platform, providing the waters have a relatively long residence time (e.g. c. 1 yr on Bahama Banks), over which salinity gradually increases until, in the case of the Bahama Banks, the heavy Autumn rainfall results in a rapid return to more normal salinities (Simms, 1984b).

Whether reflux of bankwaters will occur depends upon the relative density (proportional to the concentration of solutes, pressure and temperature^{-1}) of porewaters in the underlying platform sediments or rocks. In the case of the Bahama Banks, Simms (1984b) suggested that the porewaters are normal seawater introduced during Holocene sea level rise, and that the potential for massive reflux of bankwaters is high.

More general application of this new reflux model (i.e. non-hypersaline) to ancient carbonate platforms, such as the South Wales

Dinantian, may be valid where open, unrestricted environments evolve into progressively more restricted environments.

In the South Wales Dinantian, open-marine conditons are represented by the subtidal bioclastic facies (e.g. the Barry Harbour, Friars Point and High Tor Limestones) and more restricted conditions by regressive oolitic shoal facies (e.g. the Gully and Brofiscin Oolites, see Wright, 1985; and Chapter 2). Thus, in theory, reflux may have operated, at least during 'regressive' phases simply by the density contrast of restricted marine waters overlying more normal marine porewaters. If, as suggested, meteoric porewaters were introduced into the shallow-buried sediments, either as prograding phreatic lenses or by temporary exposure of ooid shoals, the density contrast and hence the potential for reflux, would be increased. Clearly, the suggestion of meteoric influx implies a humid climate which, as discussed above (section 5.4), was probably seasonal and therefore analogous to that of the Bahama Banks. During periods of more permanent aridity, as are thought to have existed at times throughout the Dinantian in South Wales, the potential for reflux during shoal progradation was probably much increased. However whether a suitable chemical environment existed would depend upon the nature of the porewaters with which the refluxing seawater mixed (see Table 5.1 for a summary of hypothetical situations which may have existed and Fig. 5.3 for a schematic representation).

The lower boundary of any refluxing system within the porous media of shallow sub-surface sediments or rocks will be defined by (a) a subsurface permeability contrast or (b) the depth at which porewaters achieve a density equivalent to or greater than that of the refluxing seawater. In the South Wales Dinantian, possible examples of (a) may include cemented

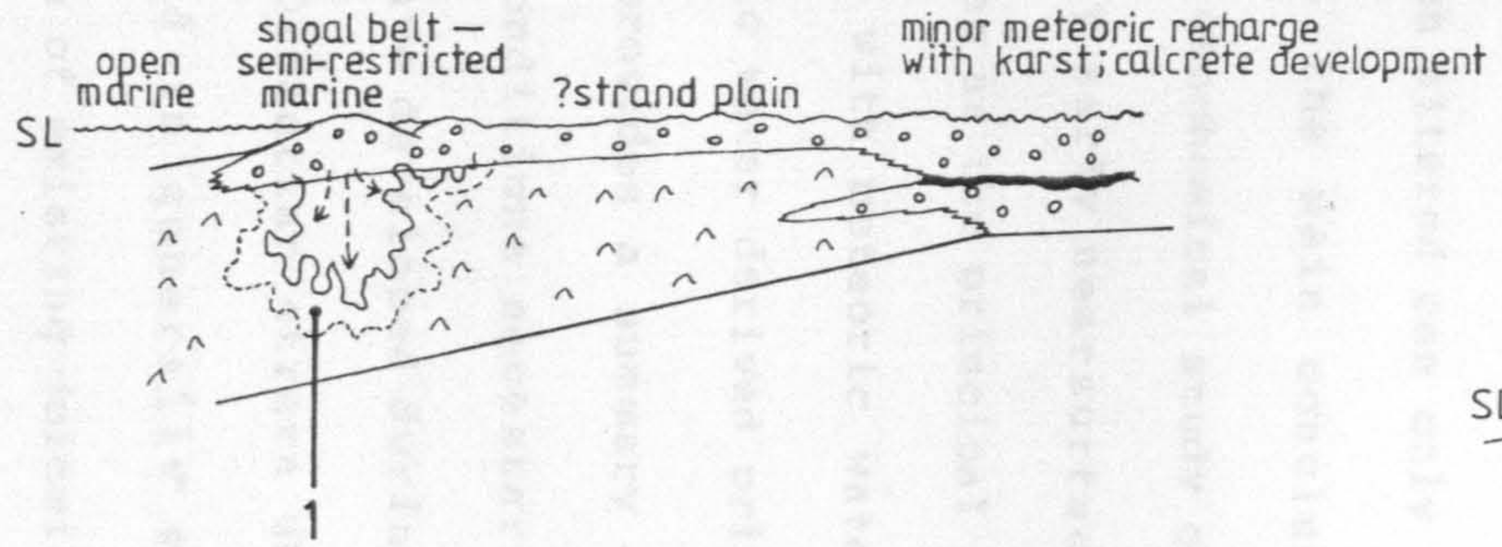
Table 5.1

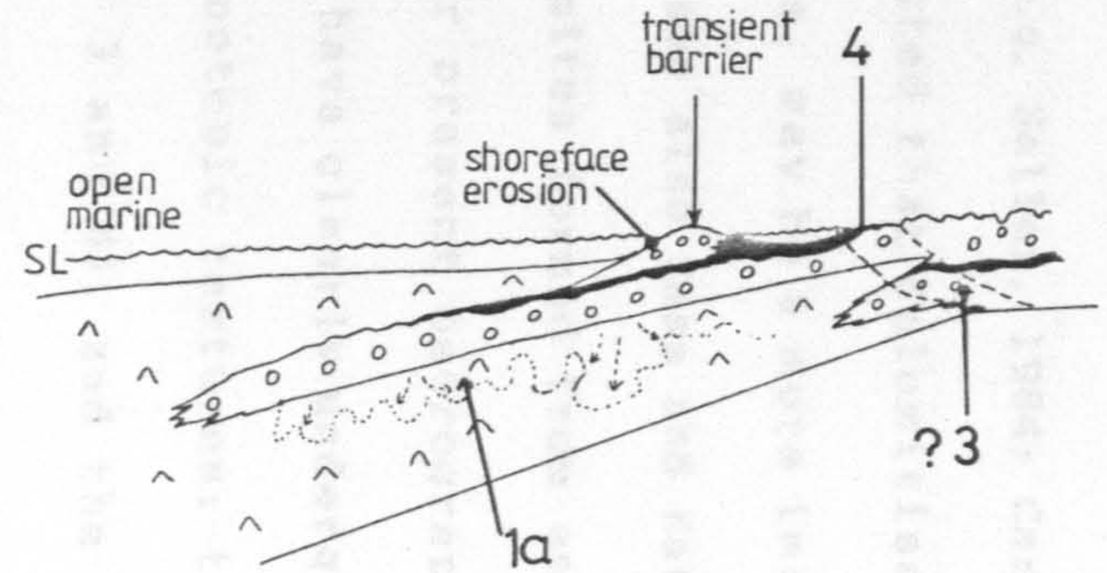
Depositional system	Climate	Mixing zones?	Reflux ?	Dolomitisation potential	Examples and comments.
Progradational (regressive)	Arid	Restricted	Beneath ooid shoals	May be high, reflux depends on porewater chemistry.	E.g dolomitisation in Black Rock Group beneath Gully Oolite especially if meteoric(phreatic) porewaters were introduced during deposition. Mg^{2+} from refluxing seawater(more humid?)
Transgressive		Restricted or absent	Probably not at sediment water interface but may continue in subsurface.	Reflux in subsurface plus localised evaporite dolomitisation in peritidal environments.	Reflux in subsurface depends on rapid burial and maintenance of porewater density contrast. E.g of evaporite: Danygraig dolomicrite precursors?
Progradational (regressive)	Humid-seasonal	Well developed and active beneath emergent shoals and in subsurface aquifers linked to recharge areas.	Dry-season increases in salinity may have encouraged temporary reflux.	Mixing-zone dolomitisation potential high; Seasonal climate favours seaward/landward migrations of M-Z for extensive dolomitisation. Seawater reflux provides additional Mg^{2+}?	E.g progradation of Brofiscin oolite and dolomitisation of Black Rock Group a subsurface dolomitisation of dolomicrites.
Transgressive		Restricted to proximal areas	?	Localised mixing-zone in subsurface and in peritidal sediments. Seasonal evaporative dolomitisation in peritidal environments.	E.g pervasive dolomites and dolomicrites. E.g Danygraig dolomicrites.

Fig 5-3

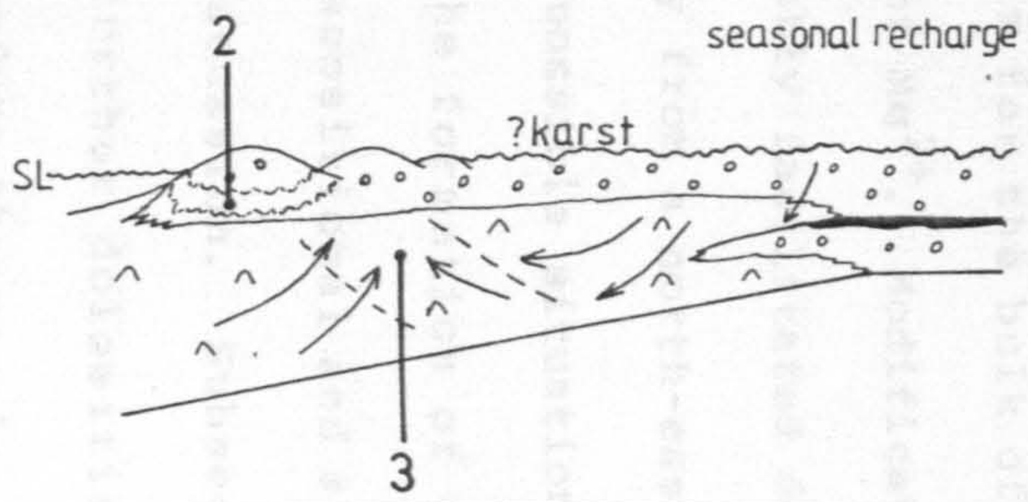
PROGRADATION (depositional regression) ⟵ TRANSGRESSION ⟶

a. Arid/Semi-arid climate





b. Humid climate



KEY

- Transgressive peritidal facies
- Oolites–shoal facies
- Bioclastics–subtidal, open marine facies

(dolomite omitted for clarity, see fig 5-1)

Dolomitisation sites (see text and table 5-1)

1 mixing of refluxed seawater with interstitial seawater ± meteoric water. Reflux may continue temporarily in subsurface (1a)

2 temporary mixing zones beneath emergent ooid shoals

3 meteoric phreatic-seawater mixing zone (progrades with ooid shoals)

4 local evaporative and/or shallow mixing zone dolomitisation plus augmentation in subsurface (?3)

Fig 5.3 Suggested dolomitisation model for the pervasive dolomites and dolomicrites (see Table 5.1).

limestones or dolomites and fine grained units (e.g. parts of the Lower Limestone Shales, or the various micritic units such as the Caswell Bay Mudstone).

Recent studies (e.g. Saller, 1984; Carballo and Land, 1984; Mullins et al., 1985) have suggested that dolomitisation by normal seawater, where active pumping occurs, may be a more important process than previously realised (Land, 1985; see also Sass and Katz, 1982). Whether any component of the pervasive dolomites formed from essentially unmodified seawater is questionable on their present petrographic and geochemical character. However, these rocks have clearly undergone some degree of modification (e.g. idiotopic to xenotopic textures; trend toward more negative $\delta^{18}O$ values, see Chapters 3 and 4), and the degree to which their original character has been altered can only be loosely assessed.

On balance, the main conclusions drawn from combined geologic, petrographic and geochemical study of the pervasive dolomites seem valid: viz: A relatively early nearsurface origin for the bulk of the dolomite with seawater as the principal source of Mg^{2+}. Modification by mixing of seawater with meteoric water probably facilitated dolomitisation, with meteoric water derived principally from a north-easterly source.

Figure 5.3 provides a summary of the possible situations under which the principal conditions necessary for the formation of the pervasive dolomites may have developed during the depositional and shallow burial history of the Dinantian strata under discussion. Subsequent, deeper burial resulted in generally minor further dolomitisation and/or recrystallisation of existing dolomite to produce the massive dolomites now observed. Possible controls on burial dolomitisation are discussed further in section 5.8, below.

5.6 Are the suggested processes capable of producing the observed mass of dolomite?

The period from Post Lower Limestone Shale deposition to the transgression following Gully Oolite deposition and exposure, was, very approximately, 10 million years (see Fig. 2.2) and represents the maximum time over which the flow systems hypothesised in Fig. 5.3 may have operated. Clearly they would not have operated continuously. The present maximum thickness of pervasive dolomite developed in sections of this age is 140m. From mass balance considerations and groundwater flow modelling, Simms (1984b) calculated thicknesses of dolomite along a flow path as a function of time and rate of dolomitisation for the main flow processes under consideration. Fig. 5.4 is reproduced from Simms (1984b) and shows that mixing-zone and/or reflux flow are capable of supplying sufficient Mg^{2+} to produce the observed thickness of dolomite (140m max.) in the time available (10 m.a. max). For details of the assumptions made in this modelling see Simms (1984b); as a first approximation the suggested models seem geologically and theoretically reasonable.

Within this context the likely modes of formation of the dolomicrites and vein dolomites will now be briefly discussed.

5.7 Dolomicrites: Danygraig, Risca

Interpretation of data presented in Chapters 3 and 4 suggests that dolomite in these peritidal deposits formed initially by rapid precipitation of poorly ordered calcian-dolomite phases under the influence of evaporation-concentrated seawater (e.g. Shinn et al., 1965) and/or mixed marine-meteoric water (e.g. Gebelein, 1977; Gebelein et al., 1980) by analogy with the modern tidal flats of Andros Island.

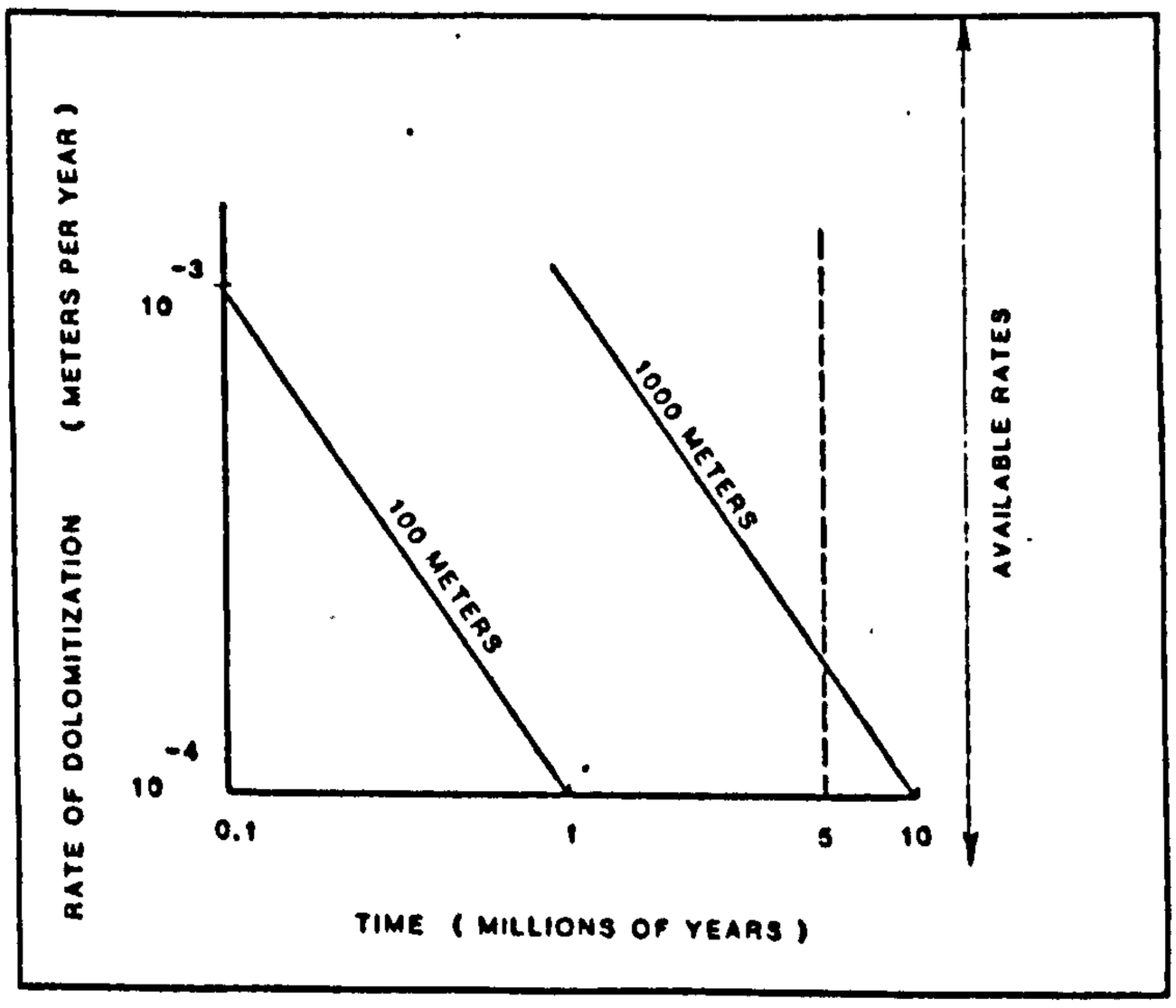


Fig 5.4 : Length of rock along a flow path dolomitised as a function of time and the rate of dolomitisation (from Simms, 1984b) ,see text for explanation.

This type of dolomite (fine grained, non-stoichiometric, poorly ordered) has a high potential for subsequent recrystallisation (Gregg and Sibley, 1984) and geochemical data (Chapter 4) support the suggestion from petrography that initial dolomite phases in the Danygraig sediments were rapidly augmented in shallow subsurface environment. This 'stabilisation' and porosity reduction probably precluded any further diagenesis (Bathurst, 1975, p. 502; Lasemi and Sandberg, 1984).

A source and supply mechanism for Mg^{2+}?

Clearly, seawater is the most likely source of Mg^{2+}, and during initial dolomitisation was probably introduced at times of periodic flooding or storm-recharge on the intertidal-supratidal flats (see Chapter 3).

Subsequent augmentation and stabilisation of early phases appears to have occurred in a relatively closed diagenetic system (low S.I.), in which reducing conditions developed, due to the oxidation of organic matter (see Chapter 4). An autochthonous source of Mg^{2+} is therefore likely for this second stage of dolomitisation; a combination of metastable phases (dolomite and Mg-calcite) and interstitial seawater may have been able to supply the necessary Mg^{2+} under the influence of compaction-driven flow. The suggested introduction of meteoric waters (e.g. gypsum dissolution) during early diagenesis, however, implies that the system was not entirely 'closed' (i.e. S.I.>0), and therefore the potential for more active pumping of dolomitising solutions probably existed. As pointed out by Land (1985) and discussed above (section 5.5) immersion of carbonate sediments in static fluids of whatever composition is unlikely to generate signficant amounts of dolomite, and therefore in order to produce a dominantly dolomitic rock an active pump is almost certainly required (see also

Patterson and Kinsman, 1982).

A model for dolomitisation?

It is plausible then, that during shallow burial, the incipiently dolomitised peritidal deposits were exposed to the same groundwater flow systems which produced the pervasive dolomite (see Fig. 5.3). Although flow rates through these micritic sediments were probably significantly lower, resulting in a less open diagenetic system and the development of reducing conditions (see Chapter 4). Their dolomitisation potential, however, probably remained high because of the presence of metastable phases.

In conclusion, the dolomicrites probably formed by initial penecontemporaneous evaporative and/or shallow mixing-zone dolomitisation. These incipient metastable dolomites, together with calcium carbonate phases were then subjected to larger scale processes, resulting in more complete replacement by dolomite in the shallow subsurface. The distribution of dolomicrites (c.f. calcite micrites of similar facies) supports a genetic relationship to the pervasive dolomites, being best developed in the north-east. Dolomicrites probably retained or attained their geochemical identity (see Chapter 4) by virtue of their fine grain size, allowing relatively closed system diagenesis compared to the intimately associated pervasive dolomites. Pervasive dolomites were then further modified during deeper burial (see Sections 5.5 and 5.8).

5.8 Vein dolomites - the problem of burial dolomitisation

It has been clearly demonstrated that vein dolomites in the south east Wales Dinantian formed during late diagenesis. Their distribution is controlled by a series of late Carboniferous joints and an end

Carboniferous age for the 'emplacement' of dolomite concluded on independant lines of evidence (see Chapters 2, 3 and 4), this is the time of maximum burial (see Chapter 2).

A correlation with the later phases in pervasive dolomite mosaics was made on the basis of petrographic similarity to vein dolomite, and on geochemical trends.

Within this context, and in a broader consideration of 'burial dolomites', it is necessary to define the following: (i) a source of Mg^{2+} (ii) a mechanism of supply and (iii) a suitable chemical environment for vein dolomitisation.

Mg^{2+} Source

Redistribution of Mg^{2+} during burial of pervasive dolomites has been suggested as a possible source for late dolomite phases. This may have been achieved by pressure solution or neomorphism of existing pervasive mosaics (see also Wanless, 1979; Gregg and Sibley, 1984; Land, 1983, 1985).

The idea of Mg^{2+} remobilisation during burial diagenesis of existing phases is attractive for at least some of the late phases in pervasive dolomites because of the interpretation that they may have formed during relatively closed system recrystallisation (see Chapters 3 and 4). However, it appears less appropriate for the volumetrically more important vein dolomites, and it is necessary to consider alternative Mg^{2+} sources. Three significant sources of Mg^{2+} may exist in the burial environment (following Land, 1985) (i) 'bittern' salts (ii) interstitial waters and (iii) clay mineral transformations. Of these, (ii) and (iii) may be applicable to the South Wales Dinantian because of the presence of a thick shale-turbidite sequence (Culm facies) to the south (see Chapter 2).

However, Morrow (1982b) and Land (1985) (for example), have questioned the ability of these mechanisms to account for more than local pore-filling cements and scattered dolomite rhombs, despite the supposed favourable conditions for dolomitisation at depth, due principally to the reduced kinetic constraints at elevated temperatures (Mattes and Mountjoy, 1980; Zenger, 1983). In the specific example under consideration here, further doubt is cast on the applicability of the 'burial compaction model' (Morrow, 1982b) because of the following:

1. The uncertain position of the Culm Basin and its structural relationship to the Dinantian carbonate sequence during the late Carboniferous (see Chapter 2).

2. The distribution of vein dolomites does not favour a southerly (basinal) source for dolomitising fluids.

A further possibility is that minor amounts of Mg^{2+} and additional porewaters were derived by diagenesis and compaction of argillaceous units within the ramp sequence itself (e.g. parts of the Lower Limestone Shales). However, the estimated burial depths, at least north of the Cowbridge Axis (generally less than 2km) and the evidence from illite crystallinity studies (see Chapter 2) suggest that clay mineral transformation was not important. South of the Cowbridge axis, greater burial depths may have been reached. This is supported by the apparent increase in importance of late diagenetic, xenotopic dolomite in some of the pervasive dolomites at Wenvoe (see Chapter 2), indicating dolomitisation and/or neomorphism of existing dolomite at elevated temperatures (see Chapter 3). Dolomitising fluids may have been derived from compacting sediments within the formation and possibly from the adjacent shale basin.

A 'supply' mechanism and suitable chemical environment for dolomitisation

As already discussed (section 5.5) regardless of the source of Mg^{2+}, an active flow system is required in order to produce significant volumes of dolomite. In burial environments this is a particular problem, because of the effects of cementation and solution-compaction. Whilst the details remain unclear (Zenger, 1983) the development of extensive fluid flows in deeply buried (>2km) overpressured, microfractured systems (Suchecki and Hubert, 1984) is potentially very signficant. However, it seems unlikely that these flows may be responsible for massive dolomitisation, because the problem of a Mg^{2+} source remains (Land, 1985).

In the studied rocks, burial depths much in excess of 2 km were probably not attained, and it is likely that subsurface flows were restricted to major permeability channels. Principal among these would have been the system of late Carboniferous joints and possibly a secondary intercrystalline porosity developed within the pervasive dolomites.

It was suggested in Chapter 2, from the work of Eustance (1981), that redistribution of iron and its incorporation in dolomite ocurred during the end Carboniferous earth-movements, and presumably involved the subsurface circulation of surface-derived, (?) meteoric waters. The interaction of these meteoric waters with circulating connate fluids along fracture zones may have created suitable chemical conditions and high enough fluid fluxes for dolomite formation. This suggestion is compatible with the interpretation of cation chemistry and stable isotope analyses of the vein dolomites (see Chapter 4). Variants of this 'mixing-model' for similar vein dolomites have been suggested by several other authors (e.g. Lovering, 1969; Mattes and Mountjoy, 1980; Woronick and Land, 1985).

In summary, the following conclusions regarding the origin of late-diagenetic, burial dolomite in the south-east Wales Dinantian seem appropriate.

1. Mg^{2+} for burial dolomitisation was probably derived from one or more of the following sources: existing dolomite, via pressure solution or neomorphism; interstitial, marine-derived fluids; clay mineral transformation (restricted to the south).

2. Active 'pumping' of dolomitising fluids, achieved by compaction-driven circulation, appears to have been confined to high permeability channels created by late Carboniferous fracturing. Intercrystalline porosity in pervasive dolomites may have provided an additional channel for circulation of dolomitising fluids.

3. A suitable chemical environment for dolomitisation may have resulted from mixing of connate fluids with surface-derived meteoric water, at least within the fracture systems, where the bulk of late dolomitisation occurred.

4. Whilst elevated temperatures (>50°C) clearly were attained during burial of the South Wales Dinantian (see Chapter 2), and probably did influence the formation of dolomite, the data presented and reasoning herein support Land's (1985) contention that burial processes are unlikely to account for large amounts of 'new' dolomite (c.f. Mattes and Mountjoy 1980; Zenger, 1983).

CHAPTER 6

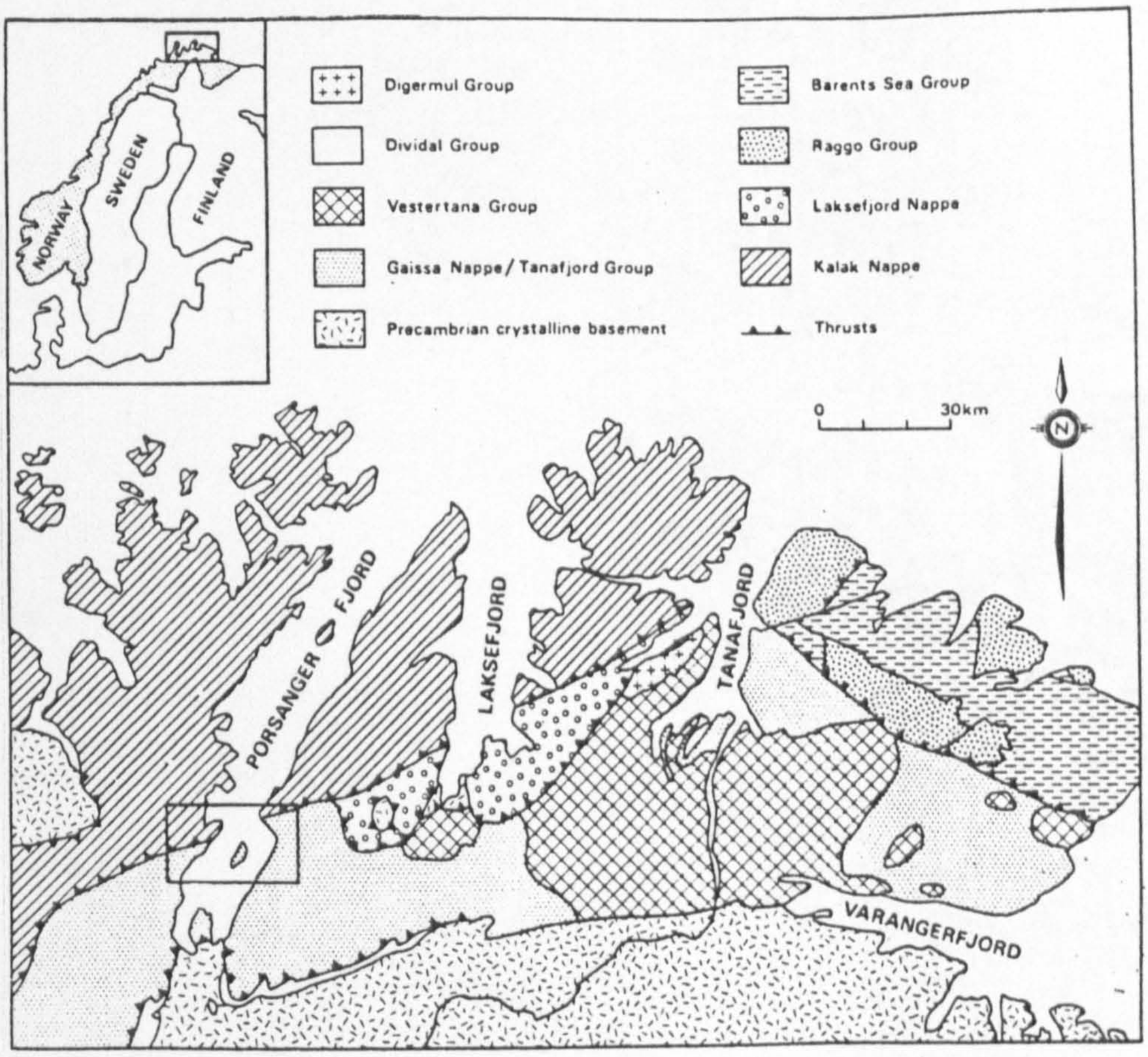
The Porsanger Dolomite, Late Precambrian, Norway: Introduction

6.1 The second part of this study concentrates on the late Precambrian (Riphean) Porsanger Dolomite of Finnmark, northern Norway. The Porsanger Dolomite Formation is one of several dolomites which occur at different locations world-wide, beneath Vendian tillites (Roberts, 1976; section 6.2.1 below). It is of interest here because it represents an example of pervasive dolomitisation in which depositional and diagenetic fabrics are well preserved. As will be shown in the following chapters, the Porsanger Dolomite preserves both a textural and a geochemical heterogeneity, comparable on a scale and pattern to that of ancient limestones. This style of dolomitisation is unusual on such a large scale and contrasts with pervasive dolomitisation in the Dinantian of South Wales, for example, where obliterative or semi-obliterative fabrics prevail and textural or chemical heterogeneity is largely a result of the replacement rather than a relic of the original character. Thus the Porsanger Dolomite deserves further study from a carbonate diagenetic point of view. Indeed, it has already been suggested that the Porsanger fabrics may represent direct precipitation of dolomite (Tucker, 1982) and this possibility is discussed further in Chapter 7, where an early diagenetic replacement origin is preferred for most of the dolomite (see also Tucker, 1983a). Additionally, as a 'chemical sediment' (Perry and Ahmad, 1983) the Porsanger Dolomite has potential for revealing information about the Proterozoic environment, in particular about the composition of seawater and early diagenetic fluids.

The following sections deal with the broad tectonic and stratigraphic background and more detailed sedimentological interpretation of the

Fig 6-1

a



b

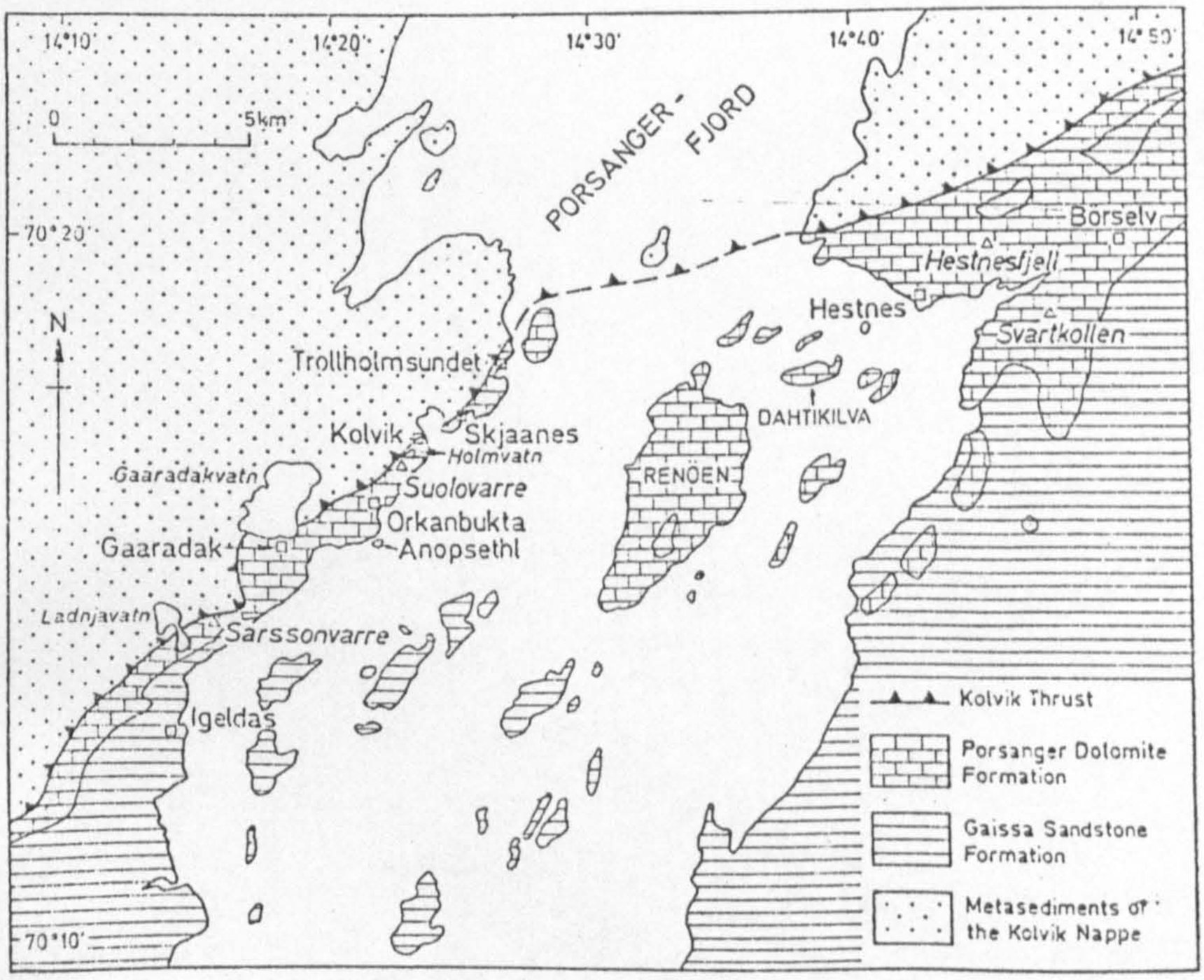


Fig 6.1 Geological location maps (from Tucker, 1977)

a. showing location of Porsangerfjord, Finnmark, Arctic Norway and the main geological Groups.

b. outcrop and locality map for the Porsanger Dolomite Formation.

Porsanger Dolomite, providing a framework for the subsequent chapters which present the petrographic and geochemical data and interpretation of this study.

6.2.1 Stratigraphic and tectonic setting: the northern Scandinavian Caledonides

The Porsanger Dolomite is the highest formation in the Porsangerfjord Group of the Gaissa nappe in Finnmark, north Norway, (Fig. 6.1a). The Gaissa nappe is one of a series of up to seven nappes in the northern Scandinavian Caledonides. The nappe pile comprises rocks of late-Precambrian to Silurian age which have undergone various degrees of deformation and metamorphism. Detailed nappe stratigraphy and correlation are complicated and differs between authors (e.g. Gayer and Roberts, 1973 and Binns, 1978). However, to summarize, nappe 1 comprises essentially unmetamorphosed or very low grade allochthonous and para-autochthonous associations of quartzite, shale and dolomite of probable late Precambrian to Cambrian age (Binns, 1978). Included in nappe 1 are the Riphean quartzites, turbidites and stromatolitic dolomite of the Porsangerfjord Group (i.e. the Gaissa nappe of Gayer and Roberts, 1973).

The Porsanger Dolomite reaches a thickness of 250 m, but its areal distribution is difficult to determine. In the Porsangerfjord area (see Fig. 6.1), it is truncated by the Kolvik thrust and metasediments of the Kalak nappe (= nappe 3 of Binns, 1978), whereas to the east in the Laksefjord area it is overlain by Vendian tillite (Roberts, 1974). Further east, in the Varangerfjord area, only the tillites are present, but they contain clasts of dolomite. How much of the original Porsanger Dolomite was stripped-off in the Varanger glaciation is not known, but it may have

covered an area 200 x 80 km (Roberts, 1976). Gayer and Roberts (1973) carried out a basin analysis for units comprising Riphean to Ordovician (Tremadocian) sedimentary rocks. They identified a land barrier (the Finnmark ridge) dividing basins to the north and south (see Fig. 6.2). The Finnmark ridge, a southwest-northeast trending anticline, existed in northernmost Finnmark (Gayer and Roberts, 1973) and provided the northern limit of the southern basin, with the Fennoscandian basement to the south. The Porsangerfjord Group (see Fig. 6.2) was deposited in this basin. Evidence presented by Tucker (1977) from the Porsanger Dolomite itself, supports the existence of a southwest-northeast oriented shoreline, and implies tectonic instability in the basin as a control on cyclic sedimentation (see section 6.3.2 below).

During its late Precambrian to Tremadocian history, the southern basin received at least 5000m of predominantly clastic fluviatile to marine sediments. These resulted mainly from the peneplanation of the surrounding land-masses. The Porsanger Dolomite rests above approximately 1000m of the Gaissa Sandstone Formation (see Fig. 6.2), suggesting a minimum burial depth for the Porsanger of 4000m. However, its basin-margin position probably means that it did not receive such a thick cover.

6.2.2 Nappe formation and deformation history

Two major and several minor phases of deformation and metamorphism characterize the northern Scandinavian Caledonian orogeny. The first event in the closure of Iapetus occurred during late Cambrian to middle Ordovician time and is marked by local breaks in sedimentation in basins marginal to the Baltoscandian and Greenlandian continents. Elsewhere it is characterised by widespread, diachronous polyphase deformation and

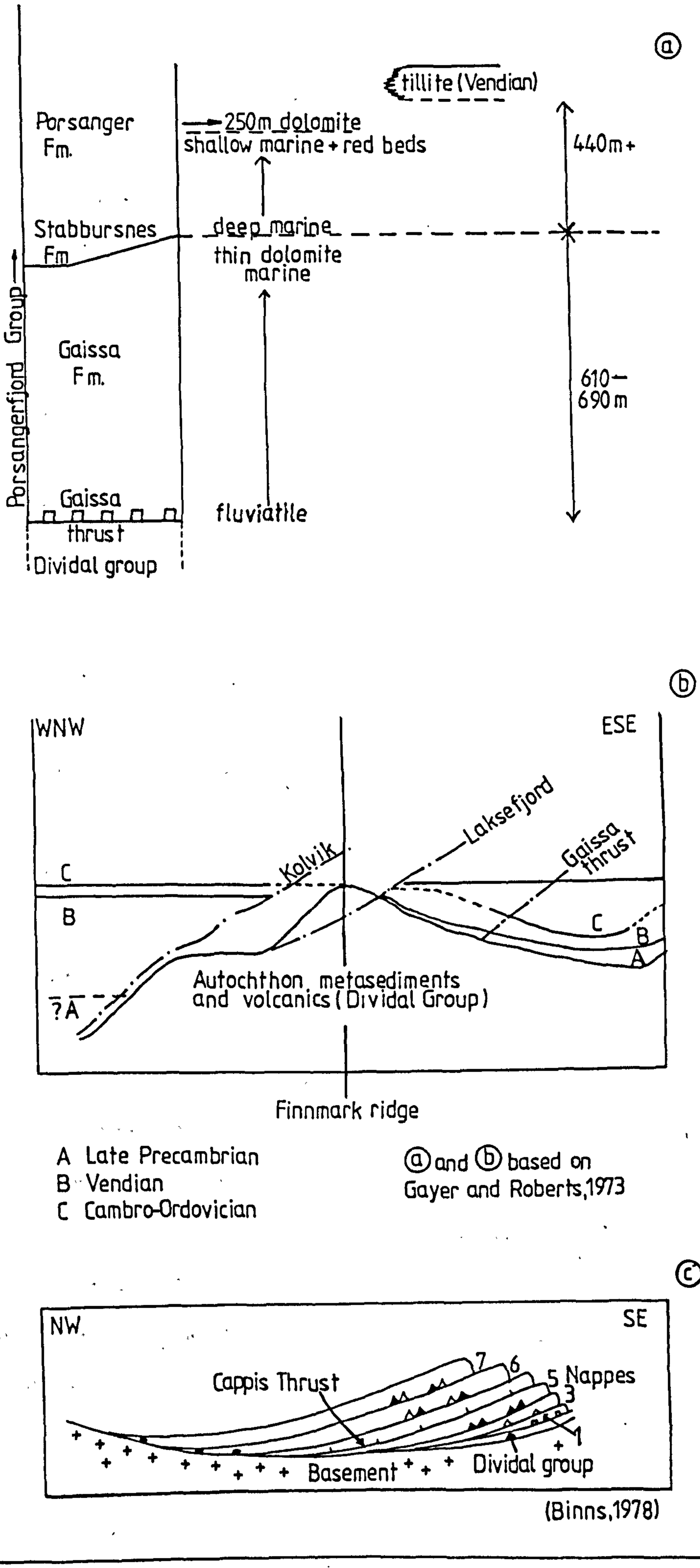
Fig 6.2 Stratigraphic and structural setting of the Porsanger Dolomite Formation.

a. showing the position of the Porsanger Dolomite within the Gaissa Nappe.

b. cross-section of the late Precambrian to Cambro-Ordovician depositional troughs and the Finnmark Ridge before deformation, as proposed by Gayer and Roberts (1973).

c. schematic section through the northern Scandinavian nappe pile (after Binns, 1978), note the position of the Gaissa thrust, as marked in a.

Fig 6-2


a
tillite (Vendian)
Porsanger Fm.
250m dolomite
shallow marine + red beds
440m+
Stabbursnes Fm
deep marine
thin dolomite
marine
Porsangerfjord Group
Gaissa Fm.
610–690 m
Gaissa thrust
fluviatile
Dividal group
b
WNW
ESE
Laksefjord
Kolvik
Gaissa thrust
C
B
A
?A
Autochthon metasediments and volcanics (Dividal Group)
Finnmark ridge
A Late Precambrian
B Vendian
C Cambro-Ordovician
a and b based on Gayer and Roberts, 1973
c
NW
SE
Cappis Thrust
7
6
5 Nappes
3
1
Basement
Dividal group
(Binns, 1978)

metamorphism, and igneous intrusion (see summary in Binns, 1978). Final closure of Iapetus and continental collision mark the second major orogenic event, occurring in mid-Silurian to mid-Devonian times. Formation of the northern Scandinavian nappes probably occurred during and after this event (Binns, 1978). The intimate association of metamorphosed and unmetamorphosed allochthonous and autochthonous strata from the entire length and breadth of the orogenic belt indicates that nappe emplacement must have occurred after cooling of metamorphic rocks and involved translation over considerable distances. Gayer and Roberts (1973) suggested translation of thrust units equivalent to nappes 1, 2, 3 and 5 of Binns (1978) of the order of 50km each. Binns (1978) claimed that nappes 1 and 3 may be derived from up to 200km to the north-west, and proposed similar or greater distances for the younger rocks.

6.3 Lithostratigraphy, sedimentology and palaeoenvironment of the Porsanger Dolomite

6.3.1 Lithostratigraphy

Early descriptions and mapping of the Porsanger Dolomite include the work of Holtedahl (1918) and more recent studies by White (1969) and Roberts, (1971a, 1971b and 1974). The last two authors worked on the west and east sides of Porsangerfjord respectively, where the most extensive and predominantly undeformed exposures occur. Their work was followed by Tucker (1977) who carried out a more detailed sedimentological and stratigraphic study. Tucker (1977) worked on both sides of the fjord and on the major islands, and recognised all eight of White's (1969) litho-stratigraphic units and was able to subdivide the upper unit (H) to give a total of nine distinct members (see Fig. 6.3). In this study the units of

a

White's unit West Porsanger	Roberts' unit East Porsanger	Informal Member Names	Facies Association	Formal Member Names
H	Σ	fourth biostrome	B C B	Hestnesfjell M.
		third biostrome	C	Suolovarre M.
G		upper quartz sand unit	B A/B B	Holmvatn M.
F	δ	second biostrome	C	Skjaanes M.
E			B A/B B	Orkanbukta M.
D	γ	lower quartz sand unit	A/B	Gaaradak M.
C	β		B A/B B	Ladnjavatn M.
B		first biostrome	C	Dahtikilva M.
A	α		B A	Svartkollen M.

b

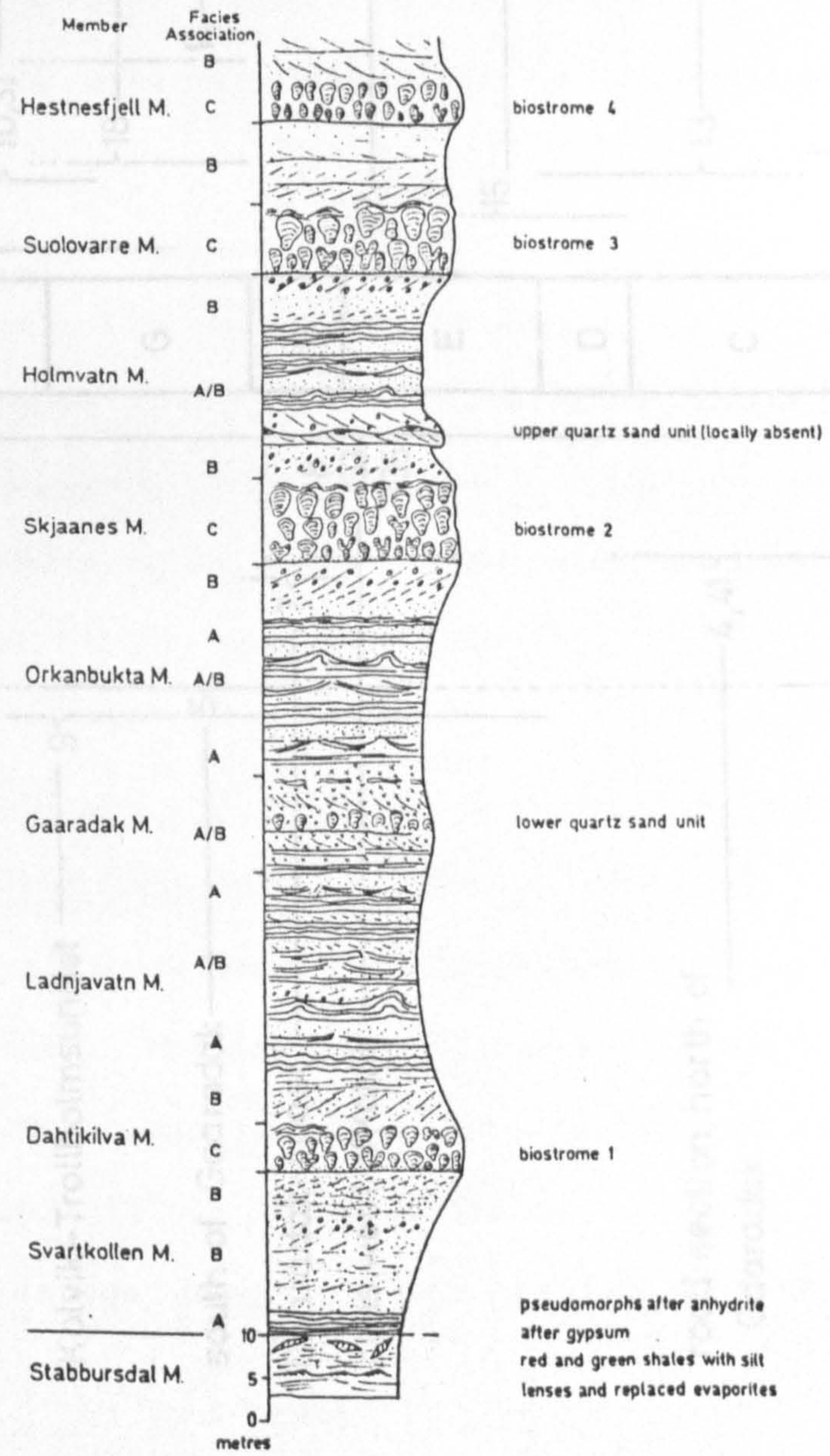
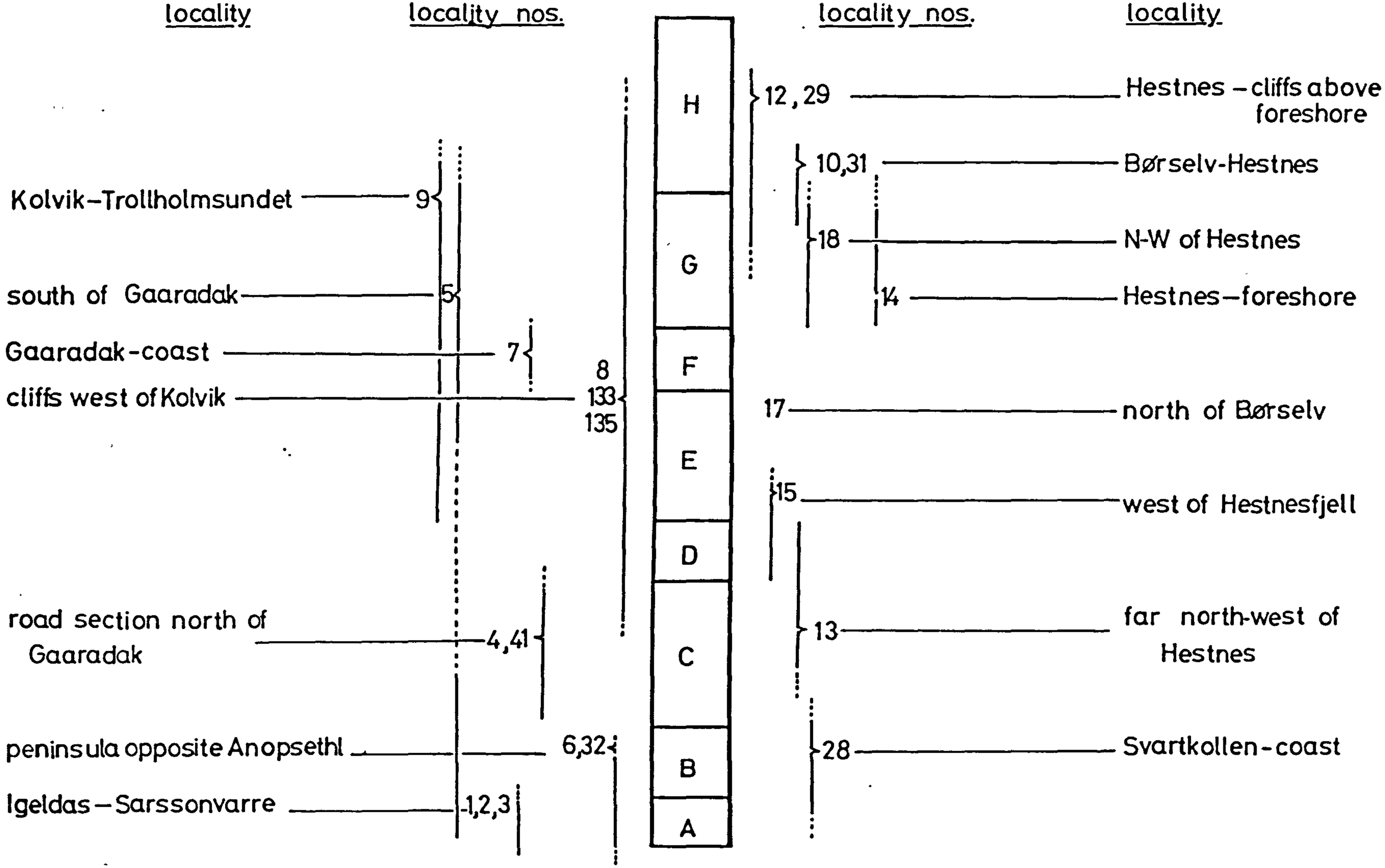


Fig 6.3 Lithostratigraphic units and formal member names for the Porsanger Dolomite as proposed by Tucker (1977). The facies associtions A, B, and C are identified in the text.

SAMPLED HORIZONS IN THE PORSANGER DOLOMITE

TABLE 6_1



White (1969) are used to identify sampled horizons and with minor exceptions correspond to Tucker's 'formal' members (see Fig. 6.3).

The Porsanger Dolomite is characterised by its lateral lithological uniformity and Tucker (1977) recognised indivudual beds as thin as 10cm over distances of 20km (the width of the fjord). The basis of Tucker's litho-stratigraphy is the presence of up to four stromatolite biostromes and two distinctive quartz sand units within the Formation (see Fig. 6.3).

The basal beds of the Porsanger Dolomite mark the transition from Igeldas Shale (= Stabbursdal Member of Williams, 1976) shallow marine argillites (mudflat facies) and include dolomitic silts and shales with local intraformational conglomerates. Tucker (1976) has recorded replaced evaporites from these beds, but otherwise evaporites are not developed in the Porsanger Dolomite.

The principal lithologies recognised in the Porsanger Dolomite above the basal beds are: (i) stromatolite biostromes, bioherms and cryptalgal laminites: (ii) flakestones; (iii) grainstones, (iv) oolites; (v) dolomicrites and (vi) quartz sands. They have been divided into various lihtofacies, based on bed thickness, sedimentary structures and grain size by Tucker (1977) and these are briefly described below.

6.3.2 Sedimentology: lithofacies associations and environmental interpretation

Detailed descriptions of individual lithofacies are given in Tucker (1977) and are not repeated here. The following discussion summarizes the main environmental interpretations for each lithofacies and briefly outlines the results of Tucker's (1977) facies analysis.

Stromatolite biostromes are interpreted as shallow subtidal (few

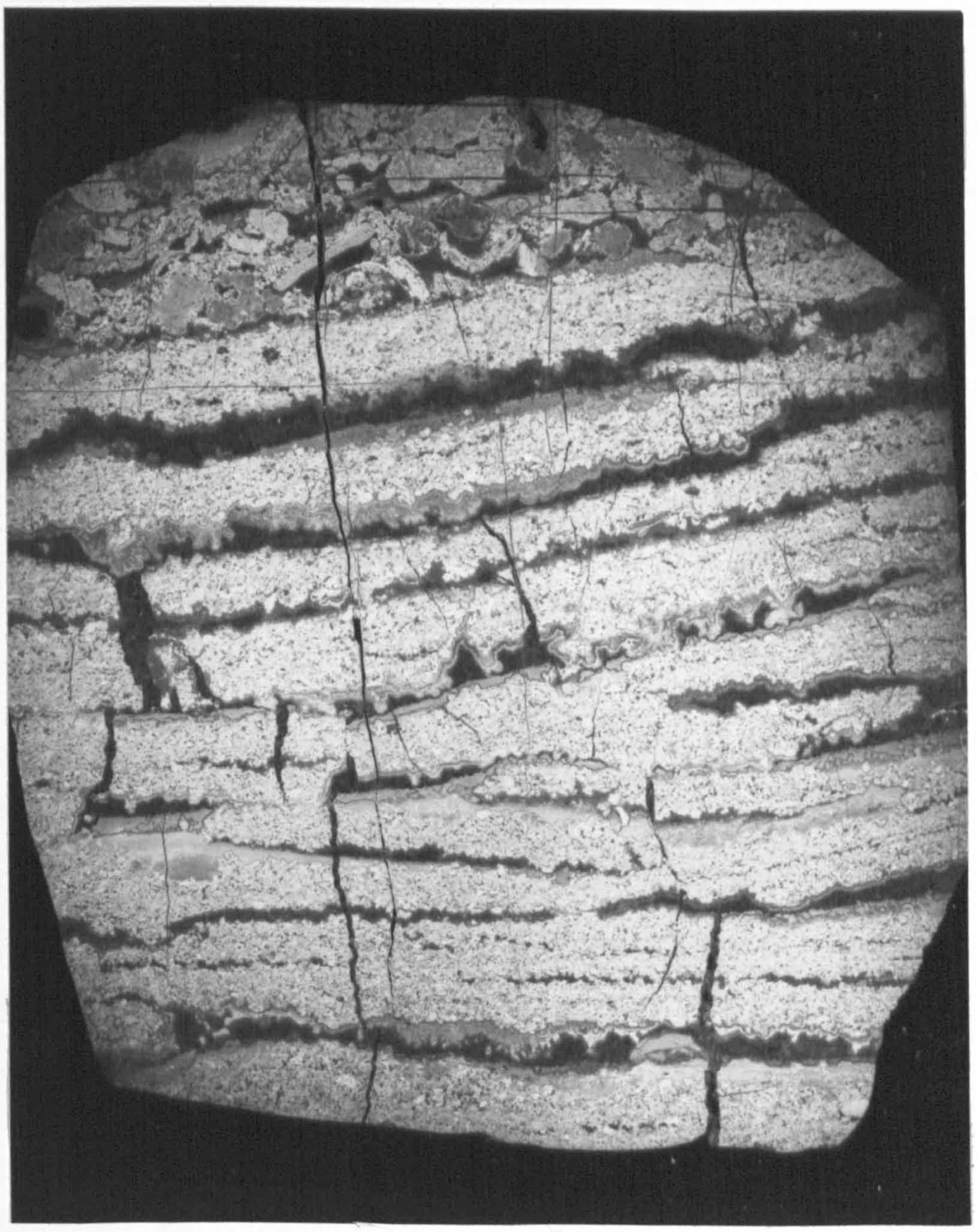


Fig 6.4

Negative print from large thin section of fenestral grainstone, showing intraformational conglomerate (top) and laminoid cavity sructures (fenestrae) with internal sediment, fibrous dolomite and dolospar.

8.0mm

Unit C, near Gaaradak, west Porsangerfjord.

metres water depth), despite the rarity of subtidal stromatolites in modern environments or Phanerozoic carbonate rocks. This interpretation is based on the lack of lateral facies variations or evidence for subaerial exposure, the occurrence of biostomes only above carbonate sands of shallow subtidal to low intertidal origin and the ubiquitous occurrence of high energy, low through to higher intertidal (beach) sediments on top of the biostromes. The delicate growth form of many of these stromatolites supports a relatively low energy environment of formation.

Algal bioherms also developed in the Porsanger Dolomite. They occur in cross-bedded flakestones and grainstones, indicating a more turbulent depositional environment and are thought to be analagous to modern patch reefs.

Cryptalgal laminites (Aitkin, 1967) are very common and occur at several horizons. They comprise laminated dolomicrite and thin clastic laminae of pellets, flakes and other depositional grains (e.g. ooids, catagraphs). Laminar cavity structures, now filled with fibrous dolomite, internal sediment and dolospar (see Chapter 7) also occur (see Fig. 6.4). There is also some evidence for desiccation and early lithification in the form of disrupted laminae, 'teepee' structures and polygonal cracks. Intra-formational conglomerates of flaked laminae are also common. Analogy is drawn with algal mats of intertidal and supratidal environments in the Bahamas, Arabian Gulf and Shark Bay as well as to permanently submerged tidal channel mats.

Flakestone comprising clasts of dolomicrite are very common in the Porsanger Dolomite. Two types were recognised by Tucker (1977). Type A, of storm origin, occur in relatively thin beds with scoured bases and may be graded or have 'edgewise' conglomerate fabrics. Type B flakestones

occur in thicker beds and are commonly cross-stratified and include herring-bone cross-stratification and bi-polar palaeocurrent directions, suggesting a tidal origin.

Grainstones comprise dolomicrite grains of sand and silt size, with up to 10% flakes. Although resembling pellets, the finer grains probably result from current and wave abrasion of flakes and micrite lumps derived from tidal flats. Tucker (1977) subdivided grainstones in a similar way to flakestones, with types A and B of storm and tidal origin respectively.

Dolomicrite occurs as massive and laminated beds up to 4 metres thick, although most are less than 10 cm. They are commonly associated with type A flakestones and cryptalgal laminites and occur as matrix in many stromatolite biostromes. Desiccation features are very common in the bedded and massive dolomicrites, indicating frequent subaerial exposure. Products of this were the abundant micrite flakes and clasts incorporated in flakestones and grainstones. Fine parallel laminations in the dolomicrites result from subtle grain size variations. Deposition from suspension or weak currents in protected shallow lagoons or on tidal flats is suggested.

Oolites typically include flakes and dolomicrite grains in addition to ooids, although occasionally pure oolites are developed. By comparison with modern oolite shoals, a very shallow, relatively high energy subtidal depositional environment is interpreted for this lithofacies.

Two quartz sand units are recognised in the Porsanger Dolomite, and Tucker (1977) uses these in his lithostratigraphic correlation. They comprise well rounded quartz, composite quartz and rarely chert grains. Horizontal lamination, planar cross-stratification and locally herring-bone cross-stratification are recognised, and may pass up into wavy and flaser

bedded sands with micrite drapes. The texture of the quartz grains indicates an aeolian origin; however, sedimentary structures show that they were deposited subaqueously on tidal flats by normal and storm currents or from much higher energy currents in the low intertidal or subtidal zones. Tucker (1977) drew analogy with the depositional system operating in the Qatar Peninsula at the present day, where aeolian dunes are migrating into the Arabian Gulf.

Facies analysis of the various lithofacies, described briefly above, reveals three main facies associations, which show a broad symmetrical cyclic pattern (Tucker, 1977). Facies association A comprises cryptalgal laminites, dolomicrites and thin-bedded type (A) grainstones and flakestones and is interpreted as indicating tidal flat (intertidal, locally supratidal) environments. Facies association B consists of cross-bedded carbonate sands and bioherms of shallow subtidal to low intertidal origin. Facies association C comprises the stromatolite biostromes with lenticular carbonate sands filling channels and is of shallow subtidal origin. These facies associations are marked on Fig. 6.3 which illustrates the symmetrical cyclicity (ABCBA) within the Porsanger Dolomite. Tucker (1977) interpreted this in terms of eustatic or more likely local tectonic controls on sea level, producing slow transgressive phases followed by depositional regression due to progradation of tidal flats.

6.3.3 Palaeolatitude and palaeoclimate of Porsanger Dolomite deposition

Palaeomagnetic data from Norwegian late-Precambrian (Vendian) tillites which overlie the Porsanger Dolomite, suggest that they were deposited close to the geomagnetic equator (Harland and Bidgood, 1959). This is in common with many other late-Precambrian tillites from Britain (Tarling,

1974), America and the Arctic (Greenland and Spitsbergen). Similar Vendian tillites are known from many locations globally, including China, U.S.S.R., Uganda, the Sahara, West Congo and Australia. These examples have associated dolomite sequences which may include sedimentary features similar to those in the Porsanger Dolomite (Roberts, 1976). The palaeo-environmental significance of dolomite-tillite association in the Precambrian of Scotland has been questioned by Eyles and Eyles (1983), who suggest a glaciomarine origin for the tillites and point out that palaeo-magnetic data may be misleading, since there is evidence for metamorphic remagnetisation in the early Ordovician.

The presence of evaporite pseudomorphs, dolomite after gypsum and quartz after anhydrite after gypsum, indicate a subtropical, arid or semi-arid climate at least during early Porsanger Dolomite deposition (Tucker, 1976).

6.4 Summary

To summarize, the Porsanger Dolomite represents a marginal marine, shallow subtidal to supratidal carbonate depositional environment. There is a general sparsity of terrigenous material, implying that adjacent landmasses were much reduced by peneplanation. The climate was probably subtropical and arid/semi-arid, consistent with the implied low palaeo-magnetic latitude. Relative sea level, determined by depositional progradation of tidal flats and the rate of subsidence (and perhaps eustatic sea level changes) appears to have been the principal control on the depositional cyclicity developed in the Porsanger Dolomite. Following deposition the Porsanger Dolomite suffered an uncertain amount of erosion prior to or during deposition of the overlying Vendian tillites. A total

late-Precambrian to Tremadocian sequence of between 5 and 10 km is suggested for the basin as a whole; however, the likely burial depths attained by the Porsanger Dolomite itself are uncertain. Considering its stratigraphic and palaeogeographic position, and the absence of metamorphism extreme burial depths are unlikely. The Porsanger Dolomite was probably emplaced in its present position during mid-Silurian to mid-Devonian nappe translation.

CHAPTER 7

Petrography of the Porsanger Dolomite

7.1 Introduction

This chapter deals with the petrographic description of the Porsanger Dolomite introduced in Chapter 6. It concentrates on identifying and describing depositional components and diagenetic phases. Other aspects, such as petrography of stromatolite biostromes are not included.

As will emerge, the Porsanger Dolomite displays a range of fabrics which are very similar to Phanerozoic Limestones, except that here they are developed entirely in dolomite. Tucker (1983a) described similar features from the late Precambrian Beck Spring Dolomite of California and provided inspiration for the present study (see also Tucker, 1982).

7.2 Depositional components in the Porsanger Dolomite

7.2.1 Dolomicrites and micritic grains

Micritic grains and micrites in the Porsanger Dolomite are composed entirely of dolomite except where local silicification has occurred. The micrite comprising peloids and flakes is texturally similar to that forming the massive and laminated dolomicrites, and laminae in cryptalgal laminites (see Chapter 6, section 6.3.2). The grains are therefore thought to have been derived from the dolomicrites, following exposure and desiccation or syndepositional cementation. Abundant evidence for this process is seen, particularly in the cryptalgal laminites, where micritic laminae may be brecciated to form intraformational conglomerates or flakestones. More rounded grains presumably resulted by abrasion of the angular flakes or micritic lumps (see Tucker, 1977).

Petrographically, the dolomicrites in the Porsanger Dolomite comprise 3-30μm anhedral crystals, typically forming dense, homogeneous mosaics. Locally, crystals up to 300μm diameter are developed, particularly in the micritic basal beds of the Porsanger Dolomite. Pelleted and more angular brecciated fabrics also occur, with pellets or clasts comprising dense mosaics (<15μm crystal diameter) in less dense micritic matrix (3-15μm diameter). Locally abundant small drusy dolospar filled spherical structures, resembling calcispheres and rare to locally abundant through-going stylolites occur in some micrites in the Porsanger Dolomite.

Under cathodoluminescence, dolomicrites have a dull, blotchy luminescence or are non-luminescent.

Discussion

The similarity of textures of dolomicrites within the Porsanger Dolomite (excluding the basal beds), suggests similar origins and diagenetic histories. The massive and laminated dolomicrites are interpreted as representing deposition of fine carbonate mud from suspension in protected areas of tidal flats or shallow lagoons developed behind barriers formed by algal biostromes or carbonate sand bars (Tucker, 1977). The origin of this mud is uncertain, however in modern Florida Bay examples, the principal source of carbonate mud is the disaggregation of calcareous algae with additional minor contributions from the mechanical breakdown of carbonate grains, bioerosion and chemical/biochemical precipitation (Neumann and Land, 1975; Loreau, 1982). However, Loreau (1982) concluded that in most other environments (in particular, Arabian Gulf lagoons and the Great Bahama Bank) aragonite muds are direct precipitates from seawater. Of these, bioerosion is unlikely in the

Precambrian, with no metazoans, the other factors may be significant but their relative importance is difficult to assess. The presence of calcisphere-like structures (see also catagraphs in section 7.2.3 below) suggests that there may have been an algal contribution (by analogy with Phanerozoic calcispheres, common in fine grained limestones, Tucker, 1981). Numerous carbonate grain types of various origins (see below) may also have provided abundant fine grained material on mechanical breakdown. The possibility of direct precipitation of an aragonite precursor should also be considered in view of Loreau's (1982) work.

The absence of obvious compaction features, especially noticeable in fenestral micrites, and the presence of abundant micritic clasts throughout the Porsanger Dolomite suggests that early cementation was an important process in these carbonate muds. The mineralogy of these cements and of the carbonate mud itself are not known, as all are now composed of dolomite. However, the fine preservation of detail and the similarity of fabrics between individual grains and massive micrite units suggest that if the dolomite is a replacement, the process of replacement was fabric retentive and replacement occurred during very early, syndepositional, diagenesis. Alternatively, dolomite may be the original mineralogy of these micrites.

Although the local importance of through-going stylolites shows that some modification of dolomicrites occurred during burial, textural evidence indicates that their present form was achieved essentially during early diagenesis. Recent work by Lasemi and Sandberg (1984) on aragonite-dominated lime muds from Florida and the Bahamas suggests that 'micrites' (crystal diameter up to 31μm) with much reduced porosities, resembling ancient fine-grained limestones formed during pervasive early diagenetic

Fig 7.1

a. grainstone showing a range of depositional grains,principally ooids and compound ooids, in a drusy dolospar matrix.The two grains in the lower middle field of view resemble microphytolites (see text) (PPL)

0.4mm

b. note radial-fibrous fabric of ooid cortices. Nucleus of ooid at centre of field of view is a catagraph (PPL)

0.4mm

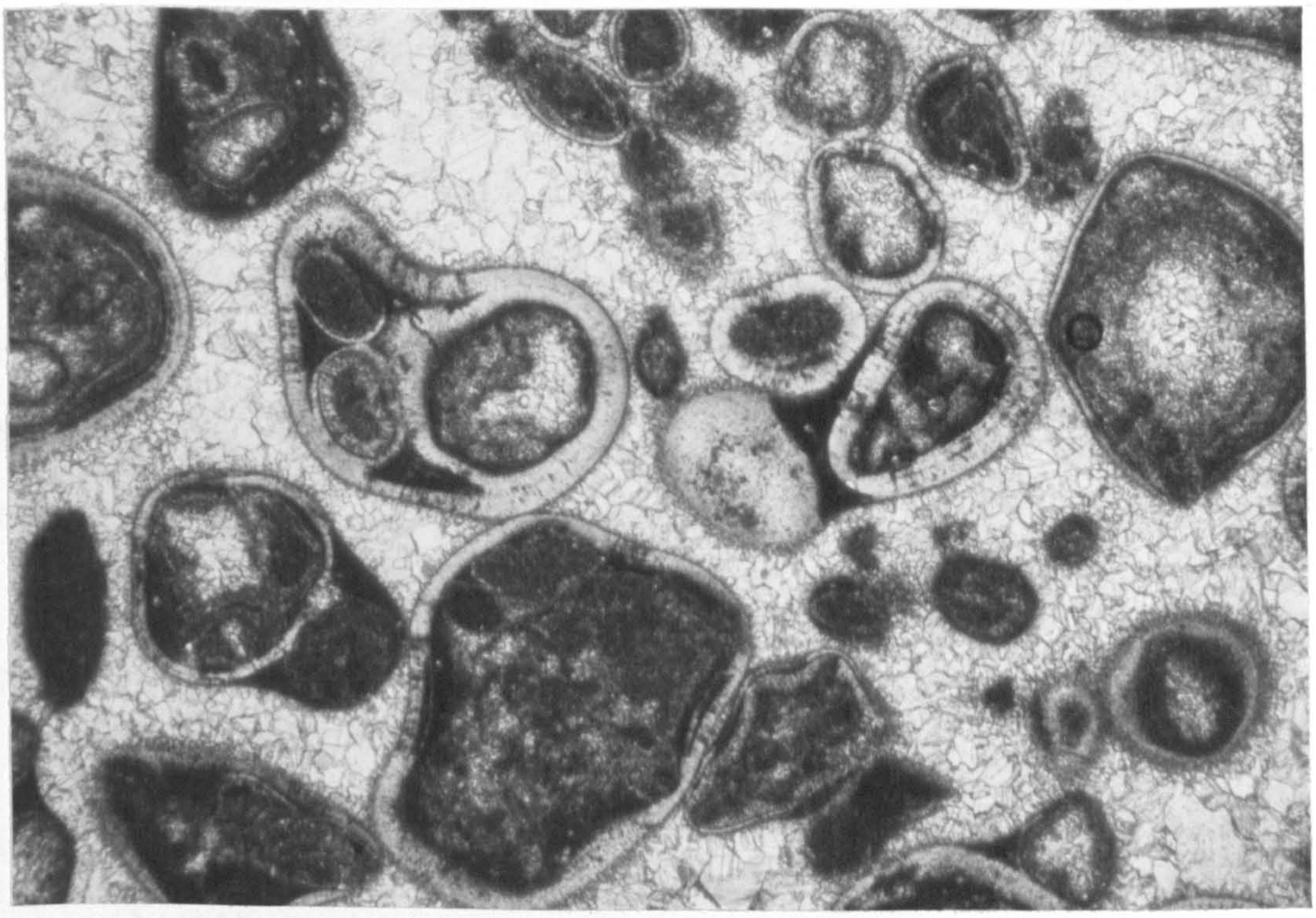
Unit C,Hestnes foreshore,east Porsangerfjord.

c. pseudouniaxial extinction crosses in ooids (XPL, section is c. 15um thick)

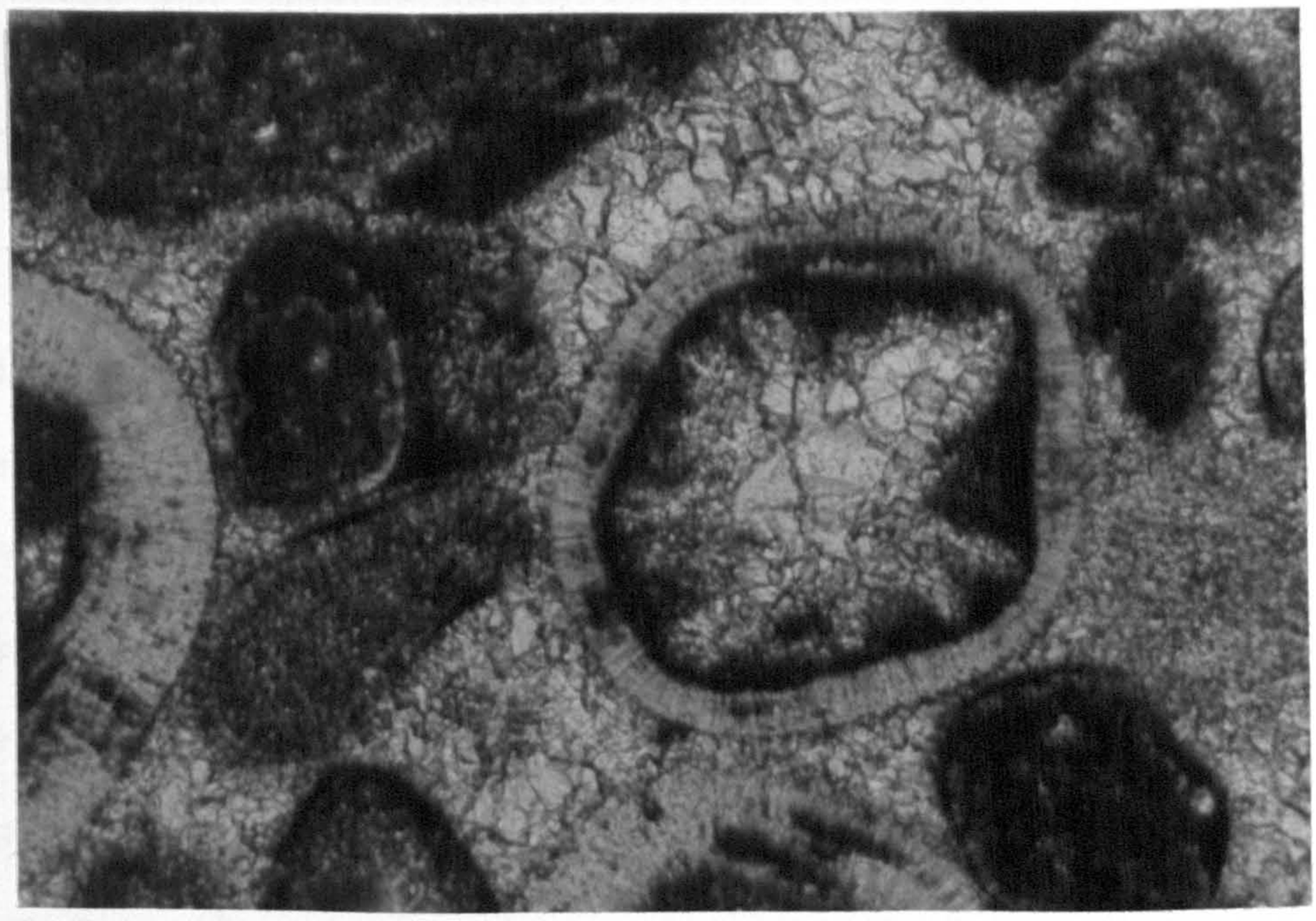
0.4mm

Unit F,Gaaradak coast,west Porsangerfjord.

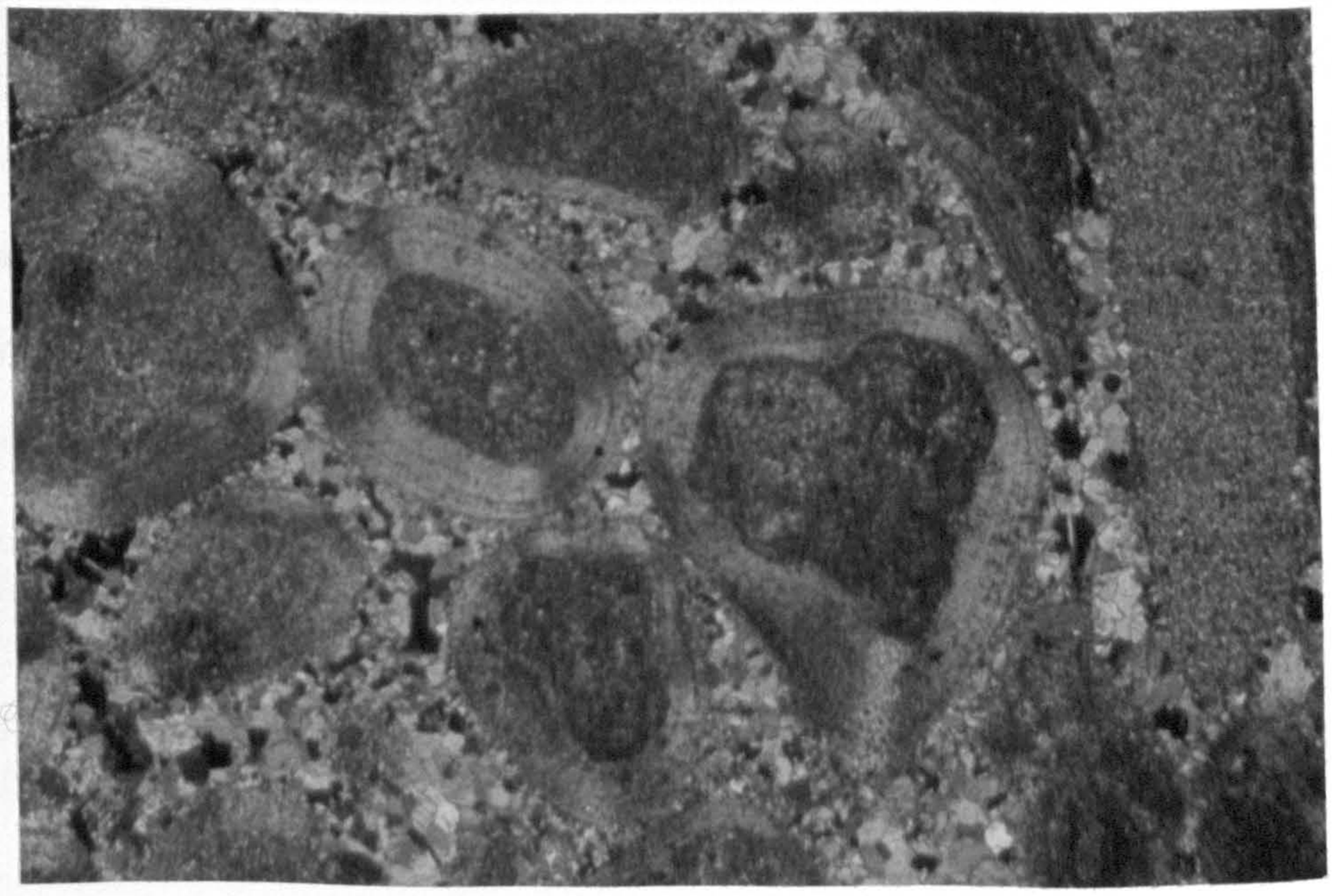
a



b



c



stabilisation of aragonite to calcite (calcitisation and meteoric cementation). Whilst clearly not directly applicable to the dolomicrites described here, the concept of early stabilisation of metastable phases may be significant, and will be discussed further in Chapter 8.

7.2.2 Oolitic grains

Oolitic grains are not ubiquitous in the Porsanger Dolomite, but are locally abundant and display a variety of morphologies. Simple, spherical ooids to compound ooids and complex oolitic-coated intraclasts are common (see Fig. 7.1).

Cortical fabrics are generally well preserved and typically are radial-concentric (see Heller, Komar, and Pevear, 1980; Tucker, 1984), consisting of radially arranged acicular crystals in concentric layers. The crystals are generally <6μm and between 10 and 30μm long, depending on layer thickness. They exhibit a radial fibrous extinction pattern, which because crystals in successive layers are syntaxial, produces a pseudouniaxial cross in sections which transect the nucleus (Fig. 7.1c).

Micritic areas of anhedral crystals (<3μm diameter) and unidentified material, range from irregular patches or vague concentric layers to better defined radially arranged ray-structures (Fig. 7.2a). These micritic areas typically have a brown colour (plane polarised light) in otherwise straw-yellow or colourless cortices.

The spalled outer-laminae and fractured cortices of some ooids demonstrate a phase of pre-spar compaction (Fig. 7.4). In places there is a suggestion of selective dissolution of thin laminae. In other examples, ooid cortices show little fabric preservation due to micritisation and/or partial replacement by clear dolospar (Fig. 7.2b).

Fig 7.2

a. ooid showing radial-fibrous fabric and intra-cortical micrite. Note also the compactional spalling of the outer coats of surrouding grains (right and top) (PPL)

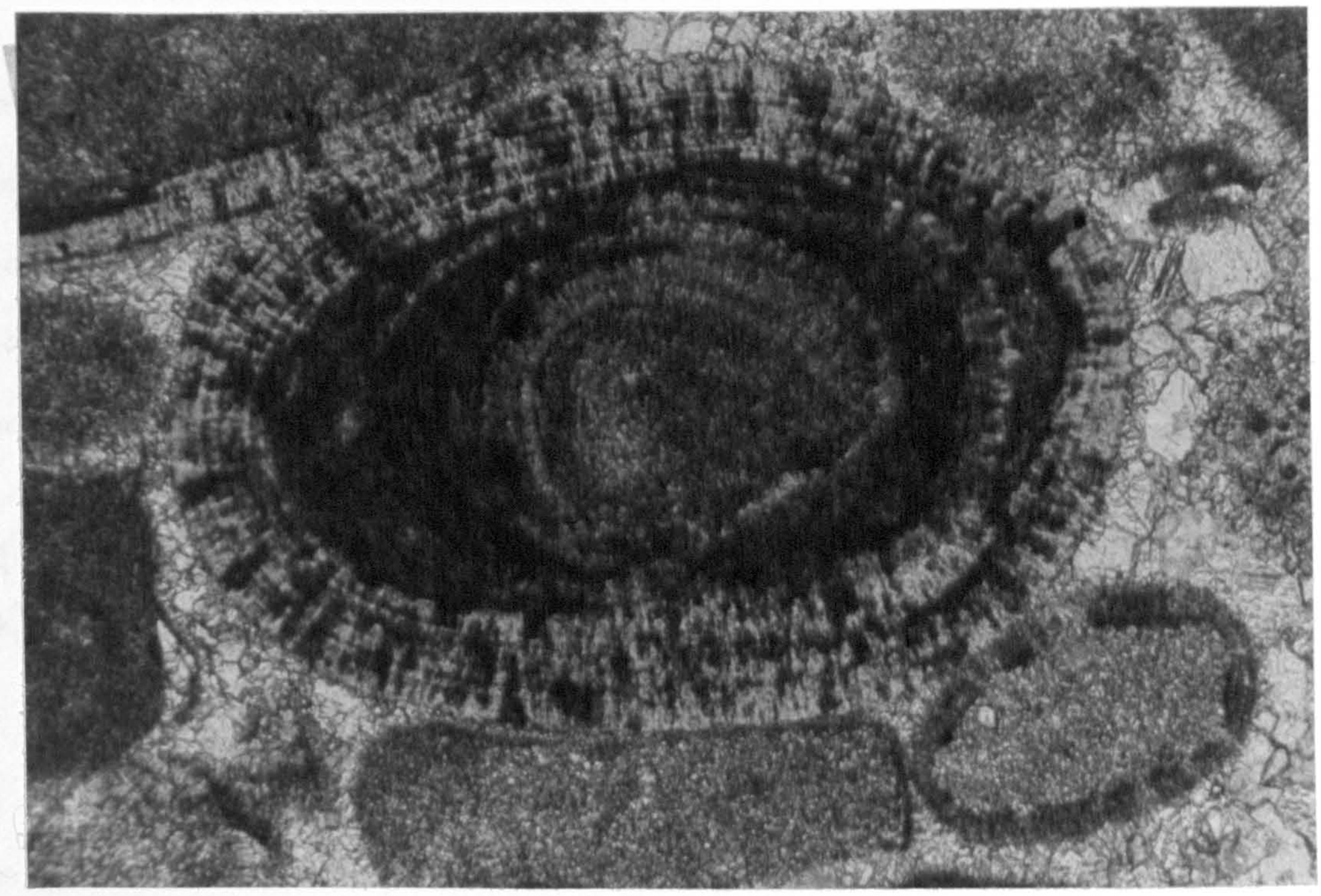
0.3mm

b. ooids with radial-fibrous fabric (left) and with micritised and spar replaced cortex (right) (PPL)

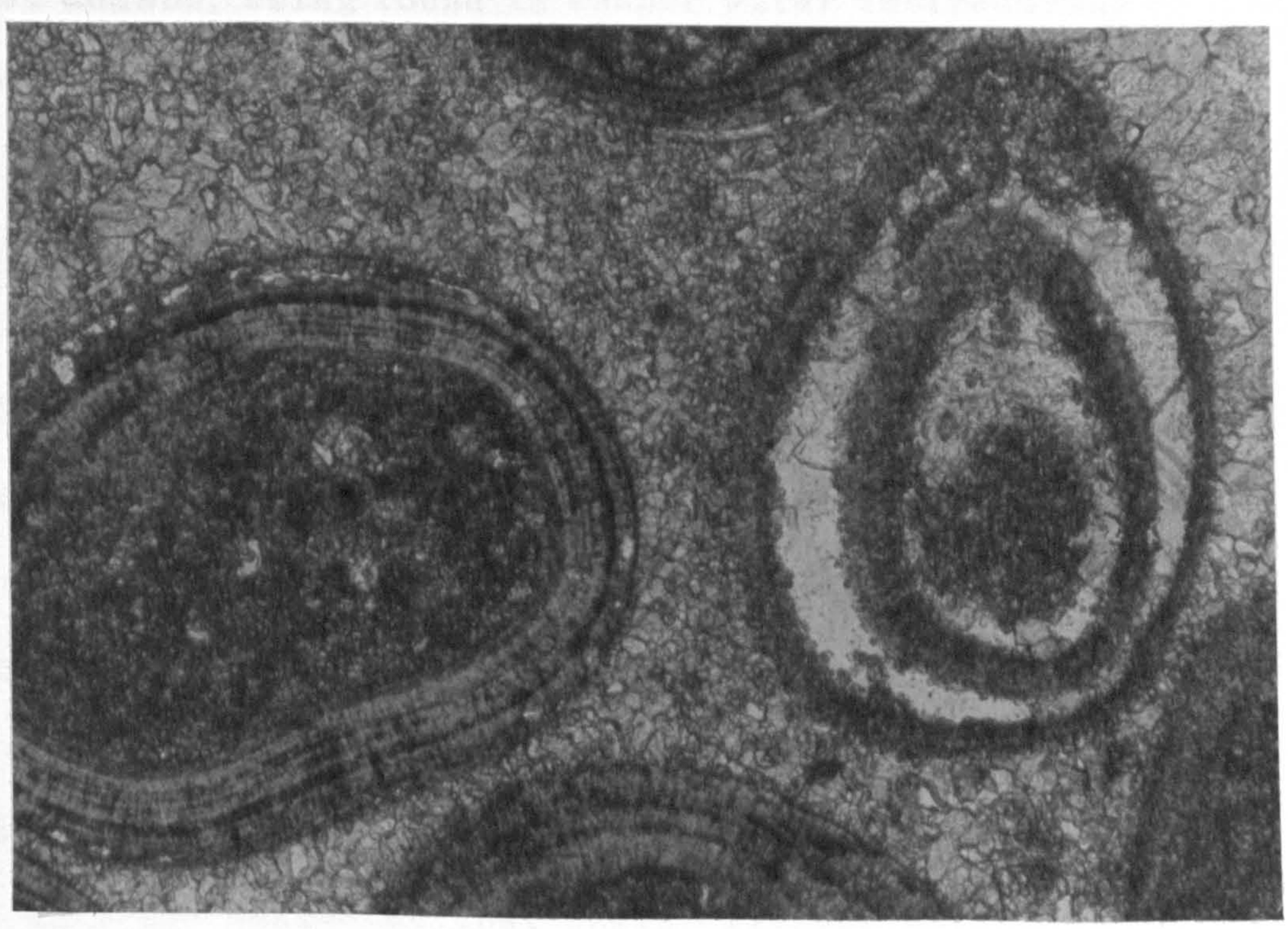
0.3mm

Unit F, cliffs west of Kolvik, west Porsangerfjord.

a



b



Cathodoluminescence petrography reveals little additional fabric information about the ooids themselves - they typically have a uniform or concentrically zoned dull luminescence. However, there is a clear distinction between pre-compaction first generation and post-compaction second generation dolospar (see section 7.3.1).

Discussion

Ooids with radial fabrics have been described from ancient carbonate sequences. Modern normal marine ooids are aragonitic and typically have tangential fabrics (e.g. Illing, 1954, from the Bahamas; Loreau and Purser, 1973, from the Arabian Gulf). However, aragonitic ooids with radial or mixed tangential-radial fabrics have also been reported (e.g. Davies and Martin, 1976, Great Barrier Reef; Loreau and Purser, 1973, Arabian Gulf; Kahle, 1974 and Sandberg, 1975, Great Salt Lake). High-magnesium calcite ooids are less common, being found in deeper water environments of the Great Barrier Reef (Marshall and Davies, 1975) and Amazon Shelf (Milliman and Barreto, 1975). They have radial fabrics but are not forming today, being early Holocene in age. Even rarer are mixed calcitic-aragonitic (two-phase) ooids, which today form in the schizohaline environment of Baffin Bay, Texas (Land, Behrens and Frischman, 1979).

Ooids in ancient limestones are typically composed of low-magnesium calcite and display a range of fabrics (e.g. Wilkinson, Owen and Carrol, 1985). Sorby (1879), Sandberg (1975), Wilkinson and Landing (1978) and others have suggested that radial-fibrous fabrics in ooids are primary. Sandberg (1975) used Great Salt Lake ooids (aragonitic, radial) to demonstrate this and suggested that radial-fibrous calcitic ooids in ancient limestones could also be primary. Sandberg (1975) derived support

for this interpretation from the observation that originally aragonitic grains (including Pleistocene ooids and older bioclasts) have typically been altered to coarse calcite spar, with or without relic structures, in ancient limestones. From this work came the recognition that originally aragonitic ooids have been similarly altered and form distinctive sparry structures contrasting with well preserved calcitic ooids (e.g. Wilkinson, Owen and Carroll, 1985). Whether the present low-magnesium calcite mineralogy of ancient radial-fibrous ooids represents their original composition or is a result of fabric-rententive replacement of a high-magnesium calcite radial fibrous structure is more difficult to assess (see Sandberg, 1975; Richter, 1983; Tucker, 1984; Wilkinson, Owen and Carroll, 1985).

The radial-fibrous structure of the dolomitic ooids described here may therefore be interpreted as a primary feature. Support is added to this interpretation by the presence of micritic ray-structures, which probably represent mud incorporated between fibrous crystals during growth of the ooids, as suggested for calcitic ooids by Sandberg (1975) and Tucker (1984). The behaviour of Porsanger radial-fibrous ooids during compaction (e.g. Fig.7.4a) also supports a primary fabric interpretation (e.g. Wilkinson and Landing, 1978). The question remains, however, were the ooids originally precipitated as dolomite or is their present mineralogy and structure the result of an early diagenetic, fabric retentive transformation?

It is not possible to answer this question on fabric evidence alone, and it is necessary to appeal to geochemical data (Chapter 8) and more general considerations for further interpretation.

The fine preservation of ooid fabrics in the Porsanger Dolomite is not

unusual for Precambrian carbonate formations (Tucker, 1982). For example, Radwanski and Birkenmajer (1977) described radial-fibrous dolomite ooids from the late Precambrian Hoferpynten Dolomite of south Spitsbergen. They interpreted the dolomite ooids to be primary. Richter (1983) considered the same ooids to be a burial-replacement of high-magnesium calcite radial-fibrous ooids on the basis of their ferroan character. A range of grain types, termed microphytolites (see below), which display a variety of radial-fibrous fabrics occur in dolomites of the Draken Conglomerate, Late Precambrian of east Spitsbergen (Swett and Knoll, 1985). Grotzinger and Read (1983) have described dolomitised ooids and pisoids from the Rocknest dolomite (lower Proterozoic, northwest Canada), which preserve fine radial-concentric structures and which they interpret as possible replacement of aragonitic grains (see discussion in section 7.3.2.f). Radial fibrous calcitic, spar-replaced originally aragonitic and two-phase ooids have been described from the mid-Proterozoic Belt Supergroup of Montana (Tucker, 1984). Aragonitic ooids also appear to have been important in the Late Precambrian Biri Formation of Southern Norway (Tucker, 1983b).

7.2.3 Miscellaneous grains

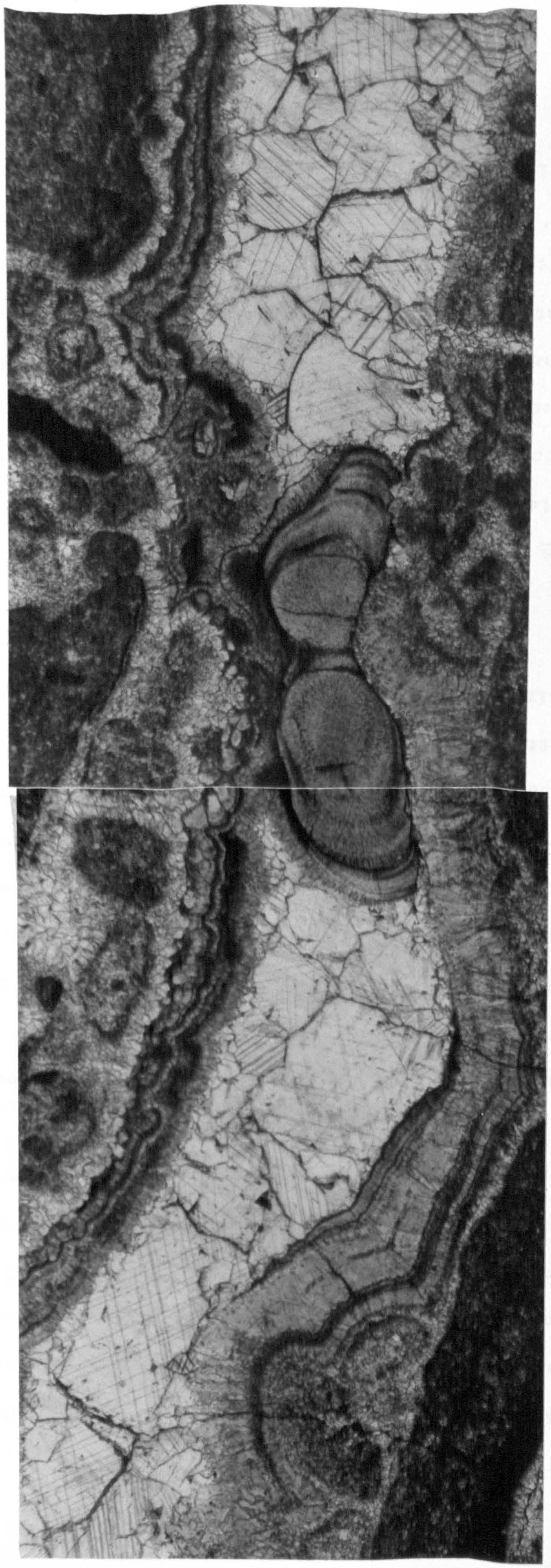
In this category are included a variety of depositional grains. The most important are intraclasts comprising ooids, micrite grains, micrite (?) cement and catagraphs (see below). They often have thin oolitic coats, displaying radial-concentric fabrics (Fig. 7.1a). Many are irregular aggregates and resemble the 'microphytolites' illustrated by Swett and Knoll (1985). These grains are interpreted as 'genetic composites' arising from bacterial or cyanobacterial growth and mineralisation, inorganic precipitation, periodic rip-up abrasional or erosive events and neomorphic

Fig 7.3

Cavity structure in peloid-intraclast grainstone, with fibrous dolomites and dolospar (see text and following figures for description) (PPL)

0.4mm

Unit G, Hestnes foreshore.



processes (Swett and Knoll, 1985). They appear to be particuarly abundant in Precambrian carbonates, producing microphytolitic grainstones and representing current conditions intermediate between low energy microbial mats and more turbulent oolitic or pisolitic sands. Swett and Knoll (1985) attributed the apparent absence of microphytolitic grains in Phanerozoic carbonates to the evolution of metazoans that graze microbial films and/or sessile invertebrates and seaweeds that stabilise carbonate sands.

Catagraphs occur as individual grains as well as components of intraclasts and as nuclei of ooids. They are recognised by their sparry interiors and micritic coats, the internal margins of which are irregular giving the central sparry area a stellate appearance (Fig. 7.1b). They most likely have an algal origin, representing calcified algal cells or cell clusters or micritised intraclasts and are a common component of Precambrian carbonates (Tucker, 1982). Their presence in the Porsanger Dolomite, together with microphytolites confirms the importance of algal activity during deposition as suggested by abundant cryptalgal laminites (see Chapter 6).

7.3 Diagenetic fabrics in the Porsanger Dolomite

The term cement is used in this section in a non-genetic sense, to include all intergranular crystal mosaics. An origin by direct precipitation is not necessarily implied, however as will emerge is quite likely for some of the mosaics on textural evidence. All mosaics now comprise dolomite crystals. Whether this is the original mineralogy or a replacement of some precursor is an important consideration, especially for the 'first generation' fibrous dolomites (see section 7.3.2). Fig. 7.3 shows a fenestral cavity in a grainstone-laminite in which a variety of

Fig 7.4 (on following two pages)

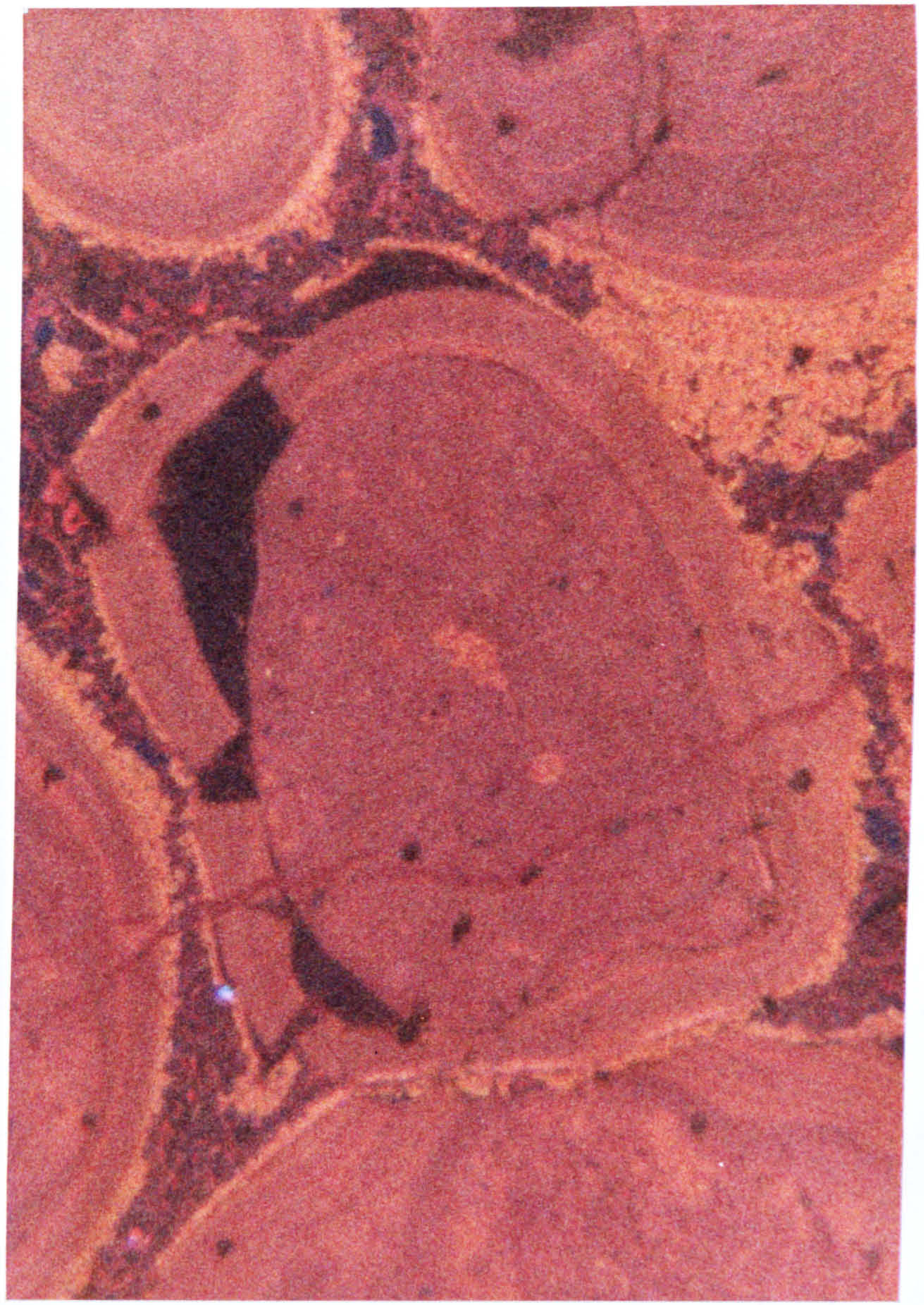
a. + b. and c. + d. are PPL - C.L. photomicrograph pairs showing first generation, pre-compaction fringing cement (dolomite) with bright luminescence and post-compaction dolospar with dull luminescence. C.L. also reveals the concentration of first generation cement at grain contacts (see section 7.3.1 for discussion).

scale: width of field of view
is 1.5mm

Unit F, Gaaradak.

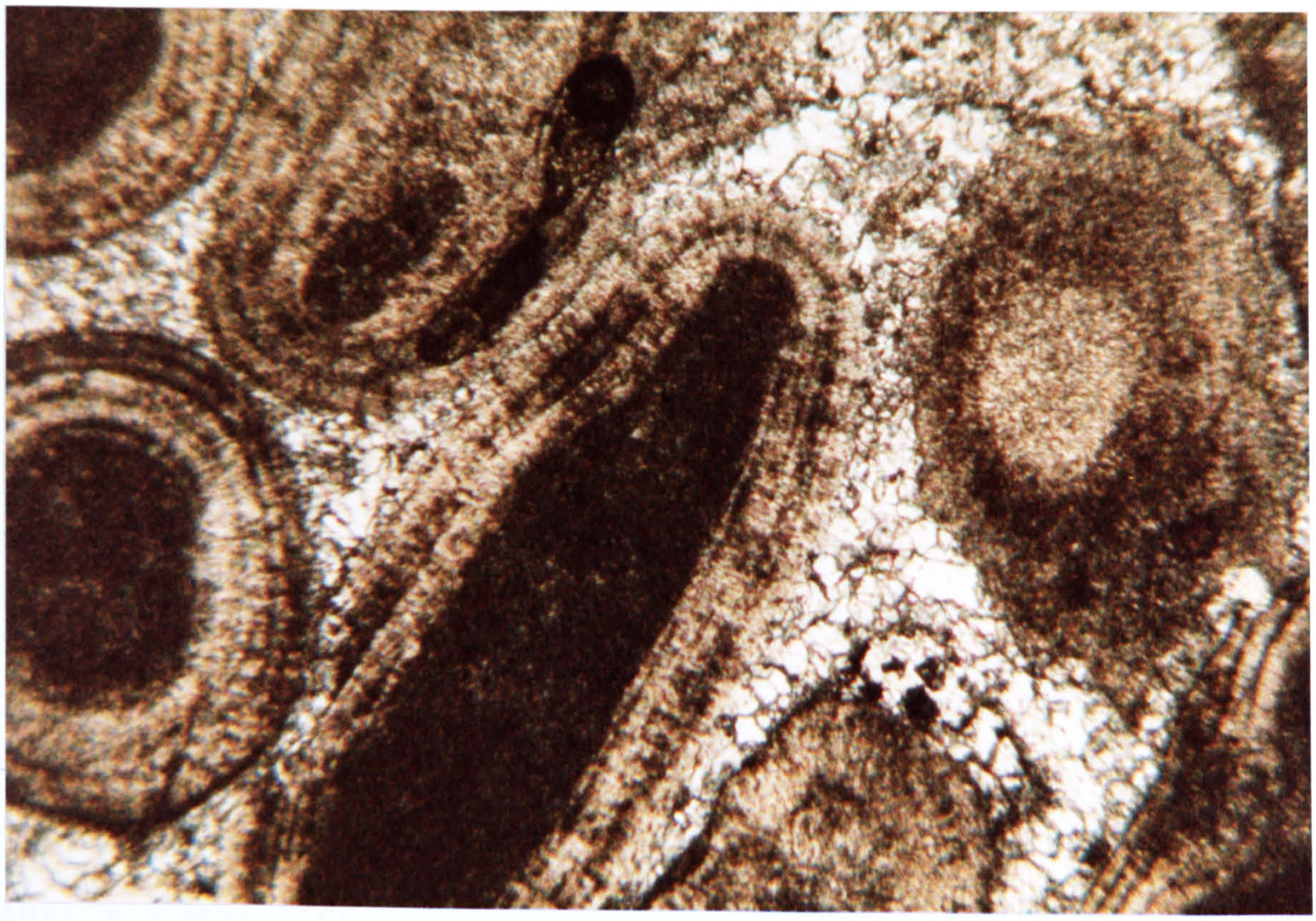


a

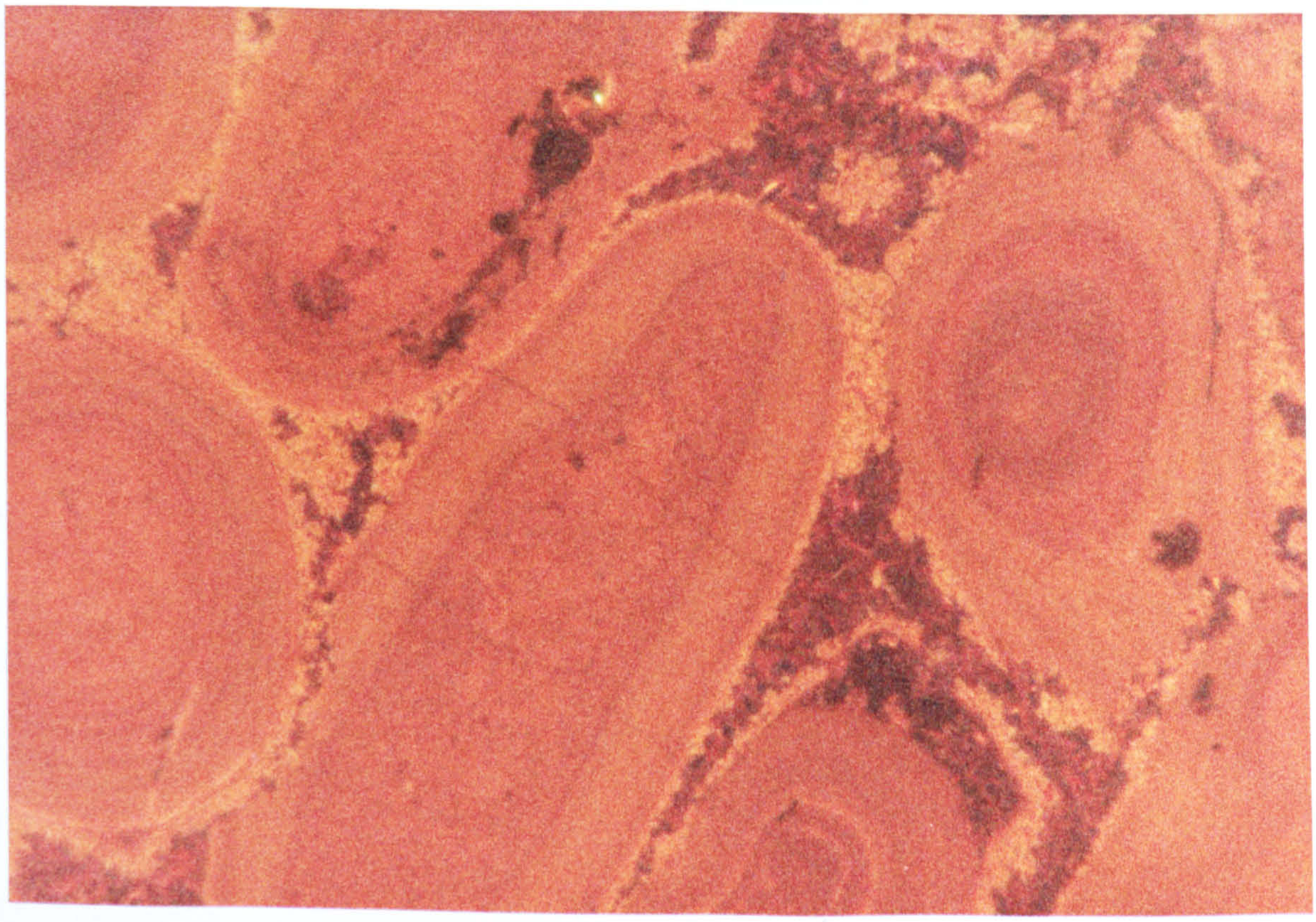


b

c



d



dolomite diagenetic fabrics are displayed.

7.3.1 Dolospars in oolitic grainstones

The predominant cement in the Porsanger Dolomite is a blocky anhedral mosaic of dolospar. It occurs as a pore fill in most lithofacies and can often be demonstrated to post-date compactional fracturing in grainstones, flakestones and fenestral laminites.

In oolitic grainstones associated with the unit F biostrome (see Chapter 6), two generations of dolospar are recognised. An early, precompaction and later post-compaction phase. The first generation comprises small (c. 3-16μm) equant crystals which fringe depositional grains, and have been fractured or spalled-off together with oolitic laminae during compaction (Fig. 7.4a, c). These features and the distribution of first generation dolospar are more clearly visible under cathodo-luminescence. Fig. 7.4b, d shows medium to bright luminescing first generation dolospar fringing grains and showing a tendency to thicken at grain contacts and across pore constrictions.

The second generation dolospar comprises relatively coarse crystals (10-200μm) and has a uniform, dull cathodoluminescence, clearly distinct from the first generation (Fig. 7.4). Second generation dolospar post-dates compactional fracture of earlier spar and depositional grains.

Discussion

The distribution of first generation, pre-compaction cements is typical of meteoric phreatic and vadose cements in ancient limestones and modern carbonate sediments (see Longman, 1980, and additional references and discussion in Chapter 3, section 3.3.1.ii). Similar cements, although composed of low magnesium calcite rather than dolomite, have already been

described from the Brofiscin Oolite in the Dinantian of South Wales (Chapter 3).

Perhaps, then, the first generation dolomite cements in the Porsanger grainstones represent an early diagenetic replacement (? pre-compaction) of a meteoric precursor (? low-magnesium calcite). An alternative interpretation is that these cements formed by direct precipitation, possibly from mixed marine-meteoric porewaters. Early diagenetic, mixing-zone dolomite cements have been reported (e.g. Land, 1973b; Kaldi and Gidman, 1982; Ward and Halley, 1985) and typically comprise equant, euhedral to subhedral crystals arranged in isopachous fringes and in close association with fabric rententive replacement dolomite.

The second generation dolospar is clearly post-compactional, suggesting that it formed during burial of the grainstones. Its presence through much of the Porsanger Dolomite Formation supports a 'burial-phreatic' origin (see Longman, 1980), in contrast to the localised, depositionally controlled distribution of early cements (e.g. first generation dolospars; fibrous dolomites). Dolospars are discussed further in section 7.3.3.

7.3.2 Fibrous dolomite in cryptalgal laminites

Fibrous dolomite in the Porsanger Dolomite occurs principally within cavity structures (fenestral cavities and birdseyes) in peloidal and micritic cryptalgal laminites of lithofacies association A or A/B, representing intertidal and locally supratidal flat depositional environments. Minor developments of fibrous dolomite also occur in peloidal grainstones associated with the cryptalgal laminites.

Fibrous dolomite typically forms continuous isopachous to

Fig 7.5 (on following two pages)

Illustrating type 1 fibrous dolomite:

a. botryoidal crust lining upper part of a fenestral cavity . Note wedge-shaped crystals in crust, botryoidal mass in lower part of cavity and drusy dolospar filling remainder of cavity (XPL)

0.6mm

Unit G, Hestnes foreshore.

b. detail of similar crust as in a.,note acicular crystallites (XPL)

0.3mm

c. isopachous fibrous dolomite crust with substrate parallel inclusion pattern lining upper part of cavity structure. Geopetal internal sediment is seen in bottom of cavity (PPL)

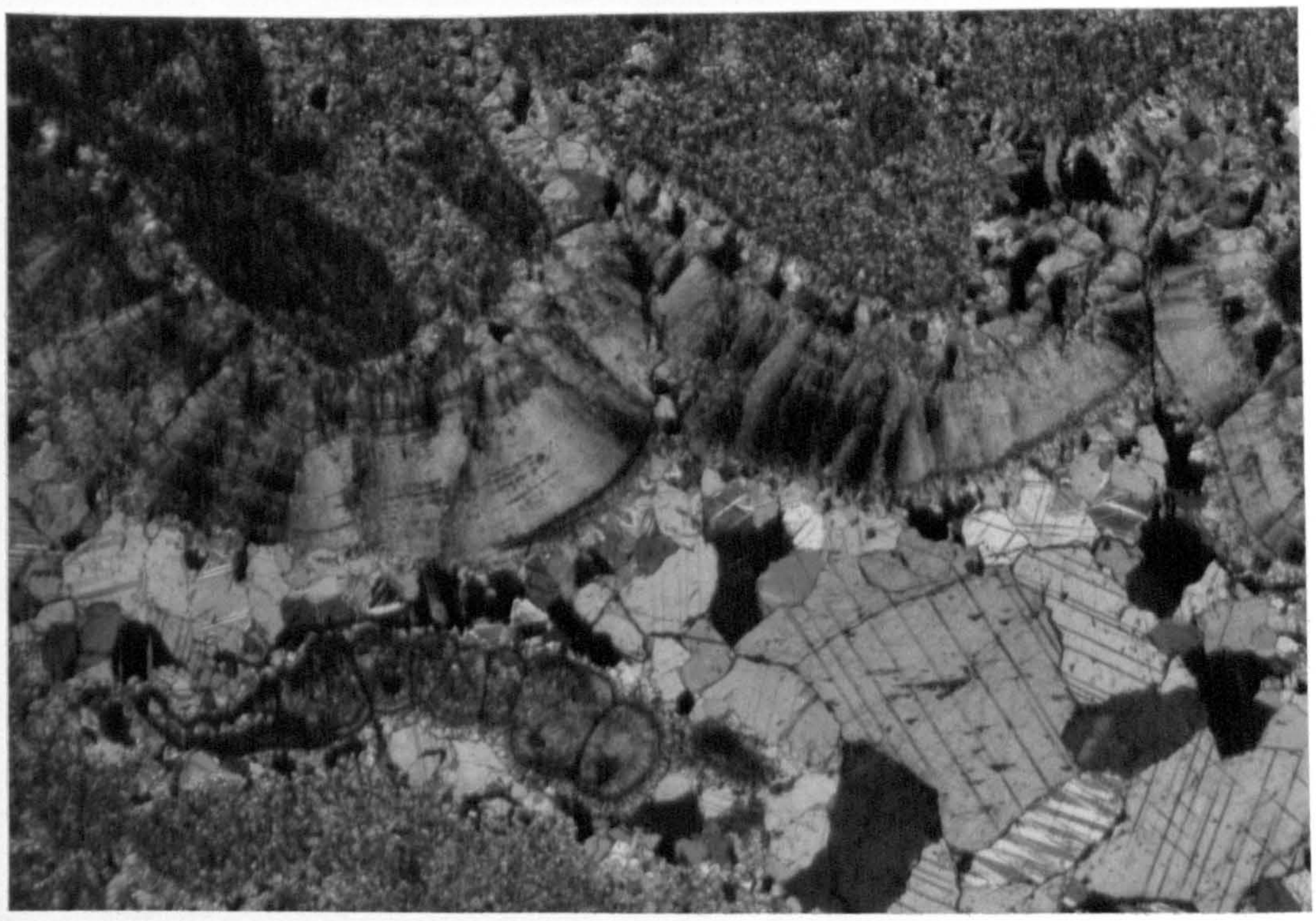
0.6mm

d. detail of c., note substrate-normal, inclusions defining acicular crystallites and the irregular growth surface of fibrous crust (PPL)

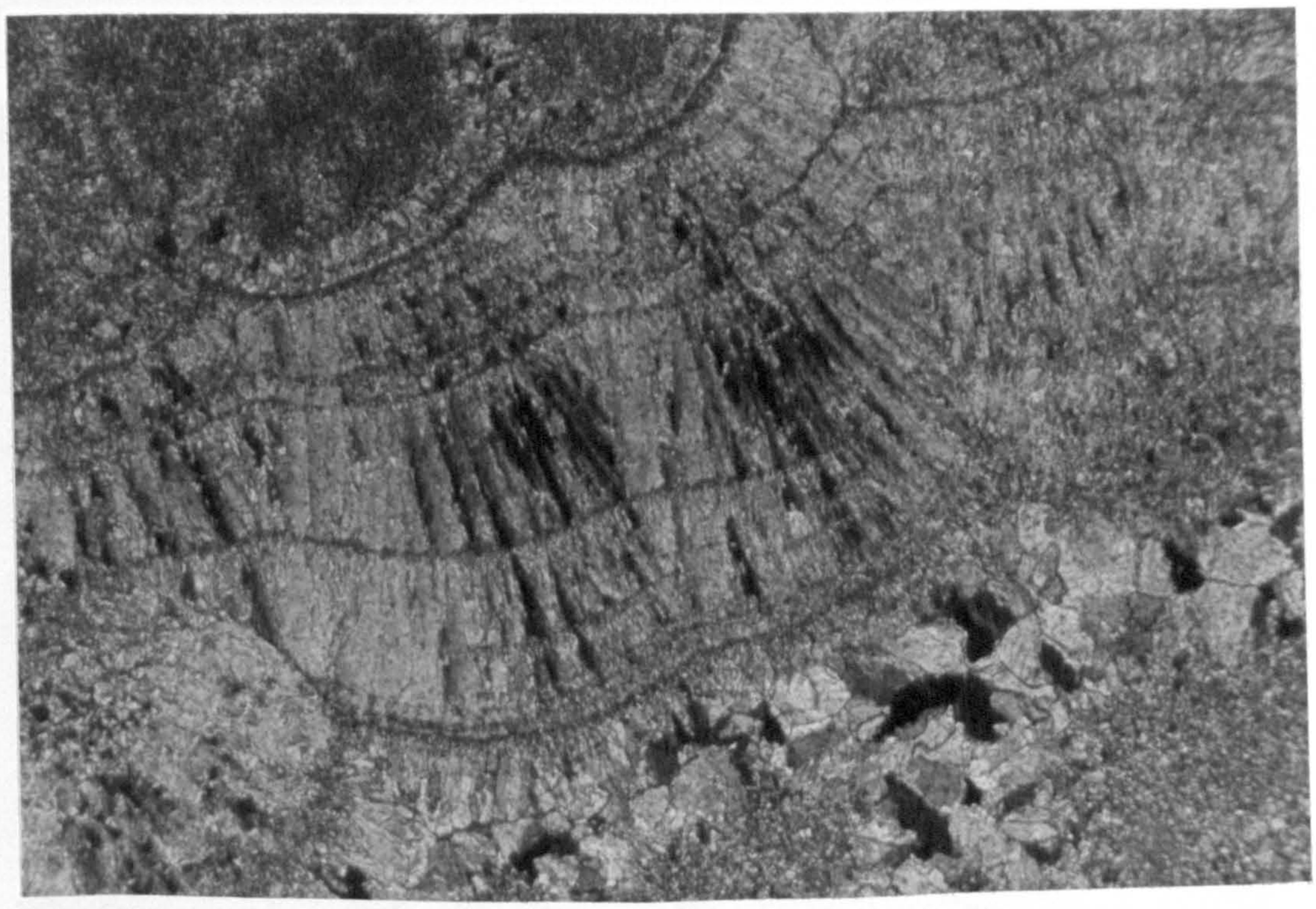
0.3mm

b.,c.,d. from unit C , north of Gaaradak, west Porsanger.

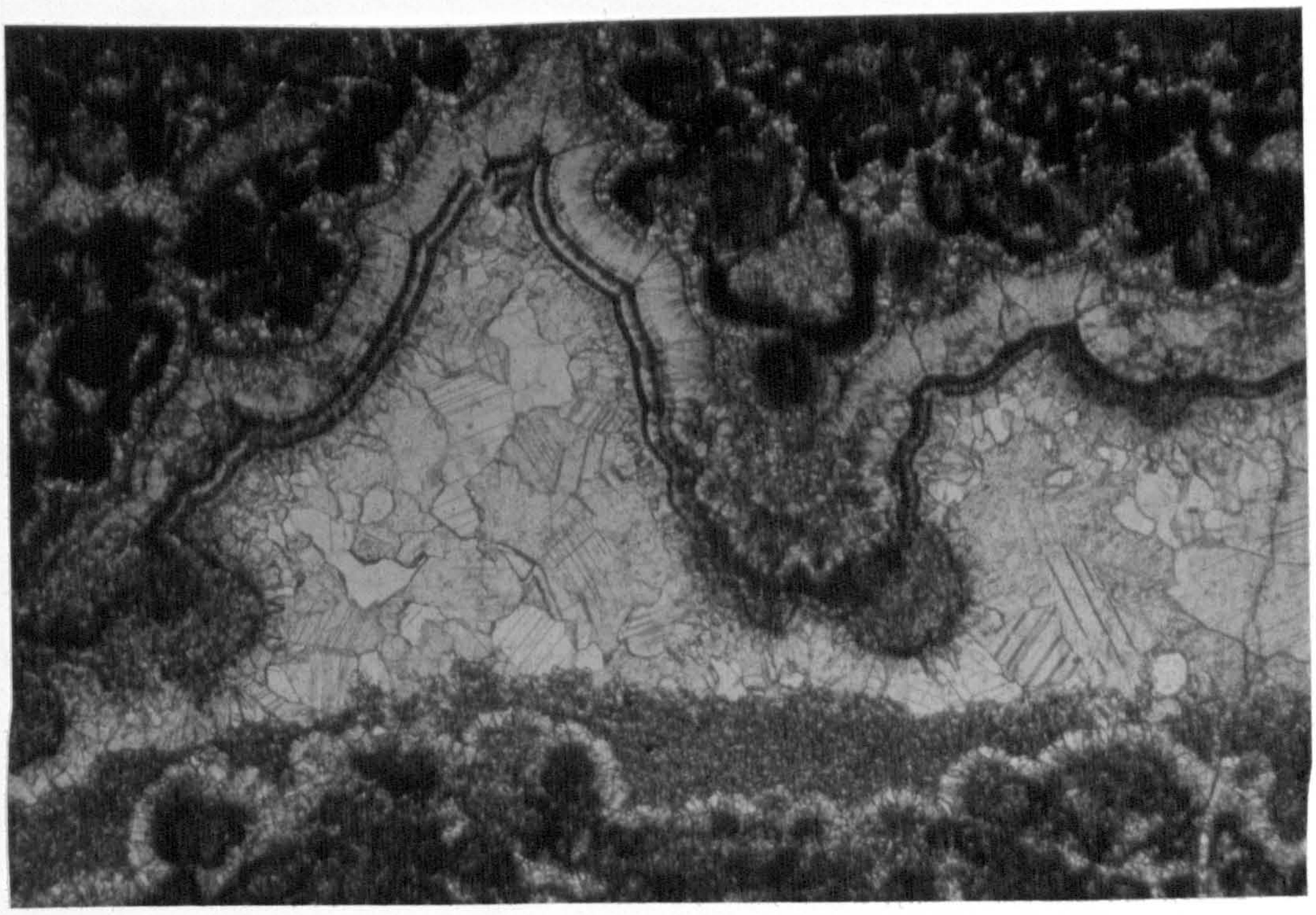
a



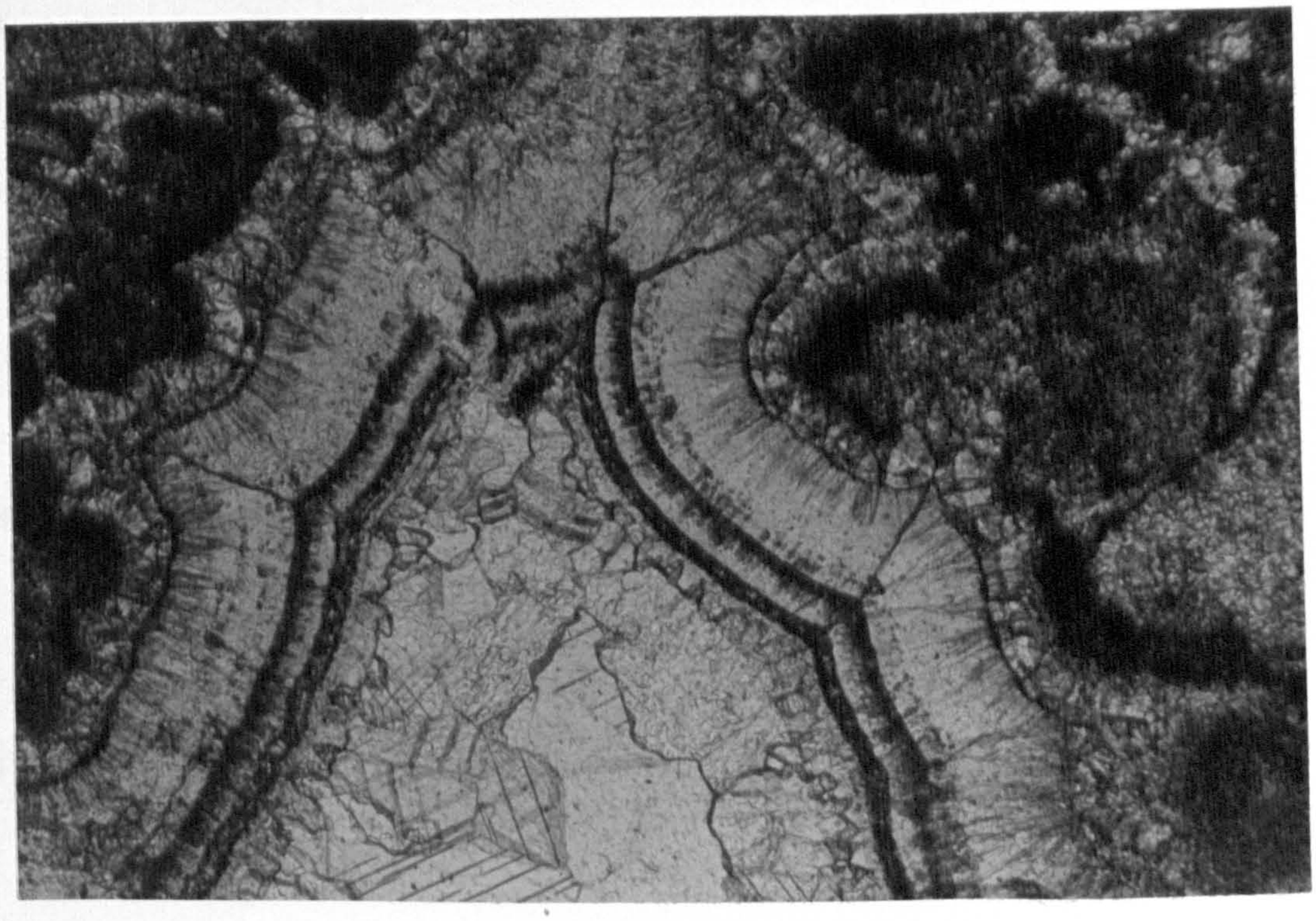
b



c



d



discontinuous, asymmetric centripetal fringes around laminoid to irregular cavities, the remaining volume being filled by coarse dolospar and/or internal sediments.

Several types of fibrous dolomite are recognised on the basis of their distribution and petrographic character and will be described below. 'Acicular' refers to crystals or crystallites <10μm wide and 'columnar' to crystals >10μm and length:width ratios >6:1 (Kendall and Broughton, 1978).

(a) Type 1 fibrous dolomite

This dolomite forms discontinuous isopachous to non-isopachous mammilated crusts and botryoids in the larger fenestral cavities (Fig. 7.3).

Thicknesses normal to substrate ranges from 0.4 to c. 1mm. Type 1 fibrous dolomite comprises wedge-shaped crystals which widen away from the substrate and are made up of acicular 'crystallites', typically < 3μm wide and 0.4 to 1 mm long (Fig. 7.5a,b). Fine, unidentified, substrate normal and substrate parallel inclusions define crystallites and smooth growth surfaces respectively (Fig. 7.5c,d). The outer boundary of these crusts may be irregular, suggesting pre-spar dissolution (Fig. 7.5d).

In plane polarised light these crusts and botryoids are pale brown or colourless. Under crossed-polars they exhibit a radial-fibrous extinction pattern where developed on substrate convexities. Individual wedge-shaped crystals have sweeping extinction, with optic axes diverging away from the substrate, resembling fascicular-optic calcite (Kendall, 1977).

Viewed under cathodoluminescence, type 1 fibrous dolomite is non-luminescent or has a very dull blotchy luminescence. Where crusts are fractured, the fractures are filled with brightly luminescent dolomite spar.

(b) Type 2a fibrous dolomite

Fibrous fringes (40-80μm thick normal to substrate) occur syntaxially on some of the botryoids and crusts of type 1 fibrous dolomite (Fig. 7.3, 7.7b). They comprise acicular crystals approximately 6-8μm wide and 40-80μm long, with triangular or square terminations. Where developed on substrate (i.e. type 1 dolomite) convexities the crystals tend to widen distally. They have uniform extinction under crossed polars and are non-cathodoluminescent.

Type 2a fibrous dolomite may be traced laterally into type 2b fibrous dolomite where type 1 crusts thin to zero.

(c) Type 2b fibrous dolomite

Type 2b fibrous dolomite comprises non-isopachous crusts which thicken (up to 0.3mm) into substrate embayments (Fig. 7.6a). In the figured example, type 2b dolomite occurs above a thin isopachous layer of type 1 fibrous dolomite. Between the two dolomite types is a dark layer of micritic dolomite.

Type 2b dolomite crystals are inclusion rich (dark brown in plane polarised light) and wedge shaped. They increase in width away from the substrate (up to 20μm wide x 60μm long). An overall banded appearance is produced by multiple stacked layers of crystals combined with substrate parallel variations in inclusion density. Inclusion patterns may define triangular shapes within the crystals. Layers of micrite between the crystal layers add to the banded appearance.

Type 2b dolomite crystals have uniform extinction and are non-luminescent or have a dull blotchy luminescence.

Fig 7.6

a. type 2b fibrous dolomite, note substrate parallel growth banding and thickening into substrate embayment (PPL)

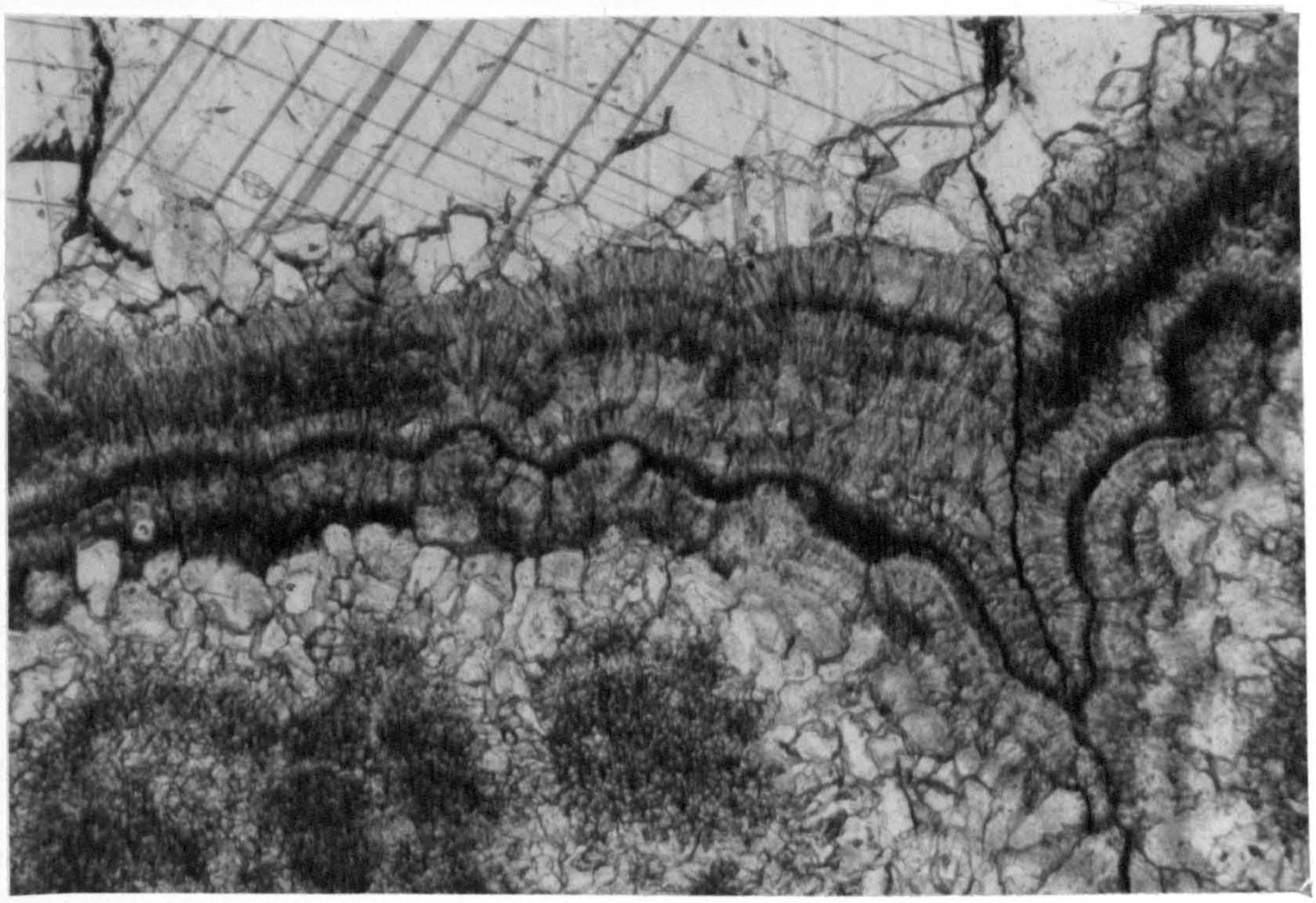
0.3mm

b. type 3 fibrous dolomite, note substrate parallel inclusion pattern , wedge-shaped columnar crystals and ? internal sediment (lower middle) (PPL)

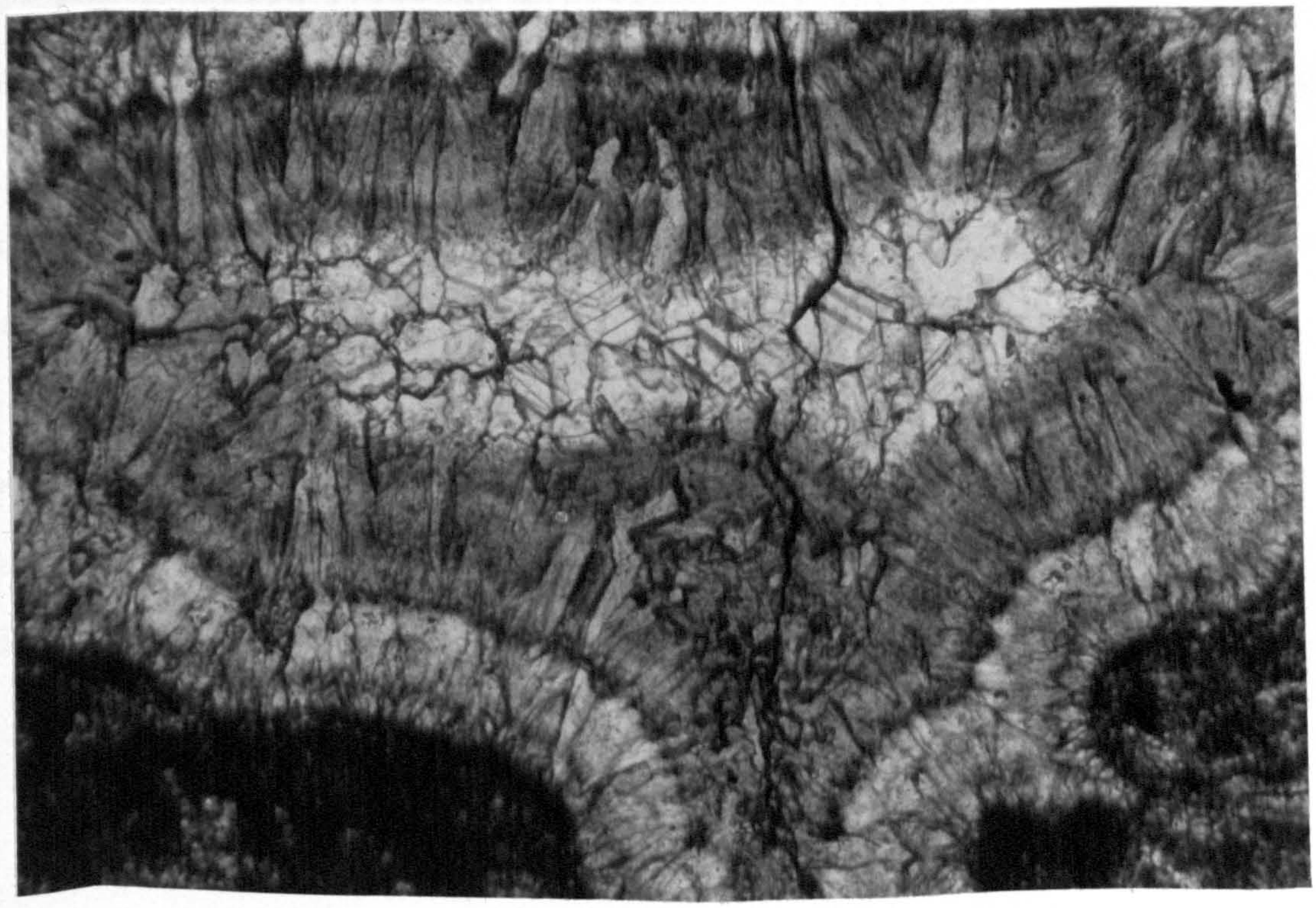
0.3mm

Unit G, Hestnes foreshore.

a



b



(d) Type 3 fibrous dolomite

This dolomite type tends to occupy the smaller, irregular cavity structures in peloidal grainstones. It comprises wedge-shaped columnar crystals, 6 to 30μm wide and 50-100μm long. They have triangular to irregular terminations and in places have been abraded to produce a 'crystal-silt' (Fig. 7.6b). Crystals are clear to inclusion rich with inclusions in substrate parallel arrangement and often defining triangular shapes. Under crossed-polars crystals have uniform, unit extinction and under cathodoluminescence are non-luminescent or blotchy where in contact with overlying dolospar. Layers or patches of crystal-silt or internal sediment also occur within the isopachous rims of type 3 dolomite.

(e) Scanning Electron Microscope study of fibrous dolomites

An SEM study of the Porsanger Dolomite fibrous dolomites (including radial fibrous ooids) was carried out using a Cambridge Instruments Stereoscan 600 scanning electron microscope and variously prepared gold coated samples (fractured surfaces, polished and etched surfaces). Little additional fabric information was revealed, except to confirm the form and dimensions of crystals already determined by light microscopy, and also to reveal that ooids may have a micritic structure.

There appears to be no evidence to suggest the presence of relic structures within the fibrous dolomite. However, because this study represents only a minor part of the research project it is possible that further detailed SEM investigtion may reveal more positive information.

(f) Discussion of fibrous dolomites

Description and much less interpretation of fibrous dolomite is rare in the research literature. Precambrian (late Proterozoic) examples have been described by Ruiji and Yaosong (1982) from the Sinian of China and Fairchild and Hambrey (1984) from north-east Spitsbergen. Betrand-Safarti and Moussine-Pouchkine (1985, figs. 6 and 9) illustrated isopachous fibrous dolomite lining fenestral-like cavity structures in the Atar Dolomite (upper Proterozoic) of Mauritania. Tucker (1982, 1983a) provided interpretation of fibrous dolomites in the Beck Spring Dolomite of California (see discussion below) and also drew attention to those in the Porsanger Dolomite described in more detail here. Columnar dolomite crystals replace isopachous high magnesium calcite cements in the Pleistocene of the Canary Islands and have been used as an analogue for a Precambrian (mid-Riphean) example from Brazil, (Muller, Scholl and Tietz, 1973).

Bona-fide first generation dolomite cements in Phanerozoic (usually Plio-Pleistocene) rocks usually consists of subhedral to euhedral rhombs arranged in isopachous rims, e.g. Land (1973b), Kaldi and Gidman (1982), Ward and Halley (1985). They are generally thought to form from mixed meteoric-marine water, although Ward and Halley (1985) suggest an almost marine origin for their dolomite cements from Yucatan.

Many of the features described here from fibrous dolomites in the Porsanger Dolomite are consistent with a primary origin for these fabrics. The original mineralogy, however cannot be so easily inferred.

The columnar nature of crystals (e.g. types 2 and 3 in the Porsanger) and fine substrate parallel layering have been used by Tucker (1983) to suggest a primary origin for fibrous dolomite fabrics in the Beck Spring

Dolomite, by comparison with fabrics in speleothems (Kendall and Broughton, 1978) and radial-fibrous ooids (Sandberg, 1975). Smooth growth surfaces (e.g. type 1), close association with internal sediments and planar boundaries between adjacent fibrous crusts, by analogy with modern marine cements provide supporting evidence for primary fabrics in the Beck Spring Dolomite (Tucker, 1983) and can equally be applied to the Porsanger Dolomite fibrous dolomites.

The fact that all the components in the Porsanger Dolomite are composed of dolomite, however raises the question is the mineralogy also a primary feature or does it represent a fabric- retentive replacement?

Sandberg (1975, 1985) has shown that there is no evidence for paramorphic replacement (that is, replacement in which fine crystal morphology is duplicated) of aragonite by calcite, so it seems unlikely that the Porsanger fibrous dolomites represent replaced aragonitic cements. For reasons already explained (Chapter 3, Section 3.3.1.ii) fibrous calcites in shallow marine settings are usually high magnesium calcite. 'Paramorphic' replacement of HMC, typically by low magnesium calcite, is a common and well documented phenomenon (see for example Bathurst, 1975; Wilkinson, Owen and Carroll, 1985). The result of these transformations is considered to be good fabric retention with distinctive extinction patterns e.g. radiaxial-fibrous calcite (Kendall and Tucker, 1973) and fascicular-optic calcite (Kendall, 1977). However, unaltered calcite cements displaying both these optical properties and other features previously thought to indicate a replacement origin and in close association with unaltered aragonite cement and skeletal grains, have recently been discovered in Pleistocene limestones from Japan (Sandberg, 1985). Thus, ancient RFC and FOC cements can no longer be unequivocally regarded as

products of replacement (Sandberg, 1985 and Kendall, 1985 for reappraisal of RFC). Sandberg (1985) further suggested that RFC-FC cements may form from non-marine (?meteoric) as well as normal marine water.

Tucker (1983) described fibrous dolomites in the Beck Spring Dolomite with fascicular-optic and less importantly radiaxial-fibrous fabrics and concluded, by analogy with FOC and RFC that they represented replacement of acicular (probably HMC) precursors. In view of the above discussion and new evidence, the most likely interpretation is that they formed by fabric-retentive replacement of FOC or RFC cements. This interpretation is strengthened in light of recent work which shows that Tucker's fibrous dolomites have calcitic equivalents in the Beck Spring Dolomite, Zempolich, Lohmann and Wilkinson (1985).

Similarly, fibrous dolomites in the Porsanger Dolomite have fabrics which may be interpreted as primary and are best explained as paramorphic replacements of calcium carbonate precursors. This interpretation is probably not restricted to fascicular-optic (or radiaxial-fibrous) fabrics and has already been suggested for radial-fibrous ooids (see section 7.2.2). Grotzinger and Read (1983) have described primary aragonite fabrics preserved in the lower Proterozoic Rocknest dolomite of northwest Canada. They draw analogy with calcitised aragonite botryoids and cement fans in younger rocks (Permian and Triassic) and suggest that dolomite may be a direct replacement of similar aragonitic structures in the Proterozoic. However an alternative interpretation, which they do not consider, is that the dolomite may be a replacement of calcitised aragonite (i.e. aragonite→calcite→dolomite). Aissaoui (1985) has described dolomite after calcite after aragonite botryoid fabrics which show gross fabric preservation, although fine detail (i.e. acicular habit of aragonite) is

not preserved. The interpretation of these fabrics is,however, the subject of some debate (see Kendal discussion of Aissaoui, 1985, in press) and it may be that dolomite directly replaces aragonite, with calcite representing a later porefilling phase. If this is the case, the replacement is nontheless obliterative of fine fabric and therefore differs from that described by Grotzinger and Read (1983). A further example of dolomitised aragonite cements comes from the Permian reef of north-east England (Tucker and Hollingworth, 1986). Here aragonite botryoids have also been calcitised and display a range of fabrics. Whether the dolomite replaces aragonite directly or is a replacement of previously calcitised aragonite is unclear. Taking the evidence from aragonitic ooids (see section 7.2.2) it appears that generally aragonite is not paramorphically replaced and combining this with the fabric evidence from Porsanger fibrous dolomites (e.g. fascicular optic dolomite) a high magnesium calcite seems most likely. However, an alternative interpretation, put forward by Tucker (1983a) for Beck Spring fibrous dolomites is that the original precipitate was a poorly ordered, calcian-dolomite. In the case of the Beck Spring examples this latter interpretation may now be ruled out in the light of the recent discovery of fibrous calcites (see above) but remains a possibility for the Porsanger Dolomite fibrous dolomites. However, even if rapid precipitation of a poorly ordered, non-stoichiometric dolomite is invoked to overcome the kinetic inhibitions of low temperature dolomite formation (c.f. Ricketts, 1982) the fact remains that Mg-bearing carbonates are unlikely to form aragonite-like crystal structures (Lippmann, 1973, p. 64).

7.3.3 Internal sediments and dolospars in cavity structures

In addition to fibrous dolomite, cavity structures are also occupied by internal sediment and dolospar. The latter usually forms the volumetrically most important phase in most cavities.

Internal sediments typically have a geopetal distribution and may succeed and/or be succeeded by fibrous dolomite. Some of the internal sediment may also have a centripetal distribution. Most or all is ultimately succeeded by dolospar (see Figs. 7.5c, 7.6b). Internal sediments comprise micritic (<30μm) dolomite, locally including coarser angular fragments, probably formed by fracturing and erosion of earlier fibrous dolomite and internal sediment can actually be demonstrated (see Fig. 7.6b).

Internal sediments are non-luminescent under C.L., so no further textural details are available, however this fact itself is consistent with an origin by erosion of fibrous dolomite, which is similarly non-luminescent.

Dolospars occur in cavity structures, post-dating fibrous dolomite and internal sediment where these are developed. These dolospars occupy larger pores and are coarser than those described in section 7.3.1. They comprise clear, equant crystals with irregular to straight intercrystalline boundaries, and may range from 20 to 1000μm in diameter. A drusy fabric is often displayed (see various Figs.).

This dolospar also has distinctive cathodoluminescence characteristics (Figs. 7.7a-f). These zones indicate that dolomite crystals developed initially at numerous nucleation sites around the margins of cavities on a substrate of depositional grains, fibrous dolomite or internal sediment. The earliest spar crystals, typified by a generally

Fig 7.7 a to f (on following pages)

Dolospars in cavity structures (PPL-C.L. photomic.pairs)

a + b note type 1 fibrous dolomite botryoid to left of field of view (as in Fig 7.3), which has a concentric fracture filled with bright luminescent dolospar.

0.5mm

c + d note bright luminescent patches within matrix, and dull luminescent substrate parallel zonation in fibrous dolomite (top left)

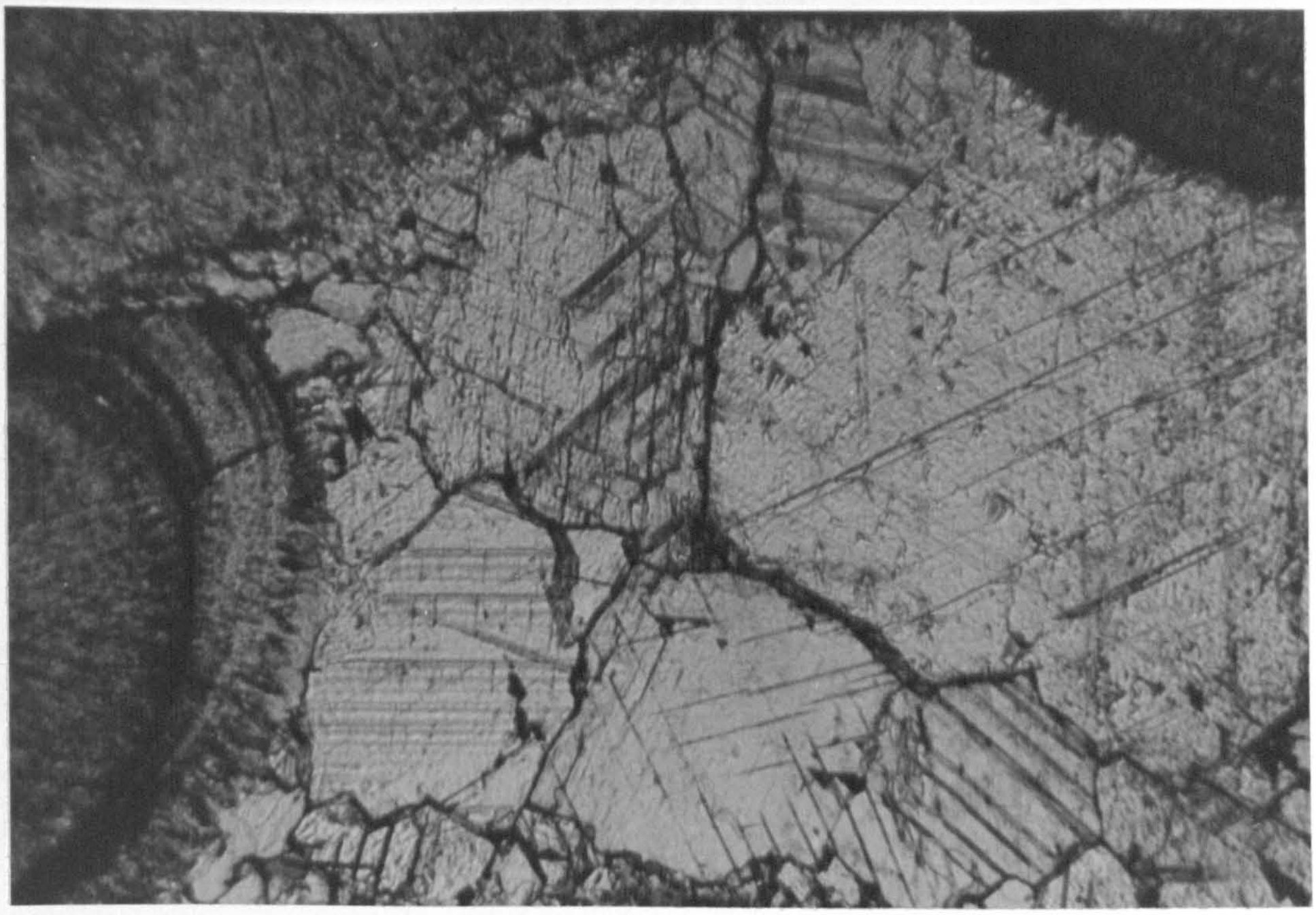
0.5mm

e + f note cloudy columnar marginal dolospar crystals (left and bottom) passing into equant dolomite mosaic

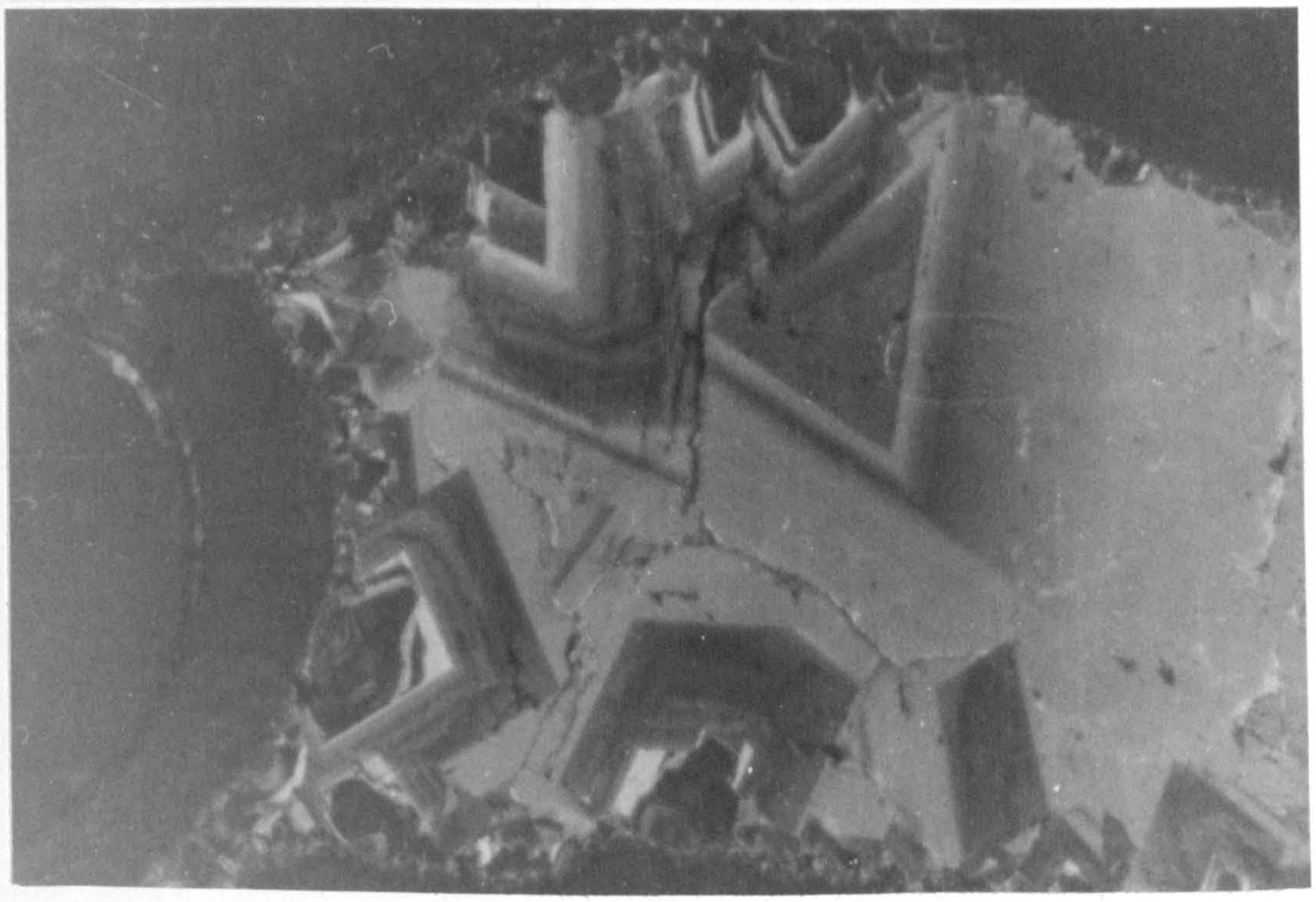
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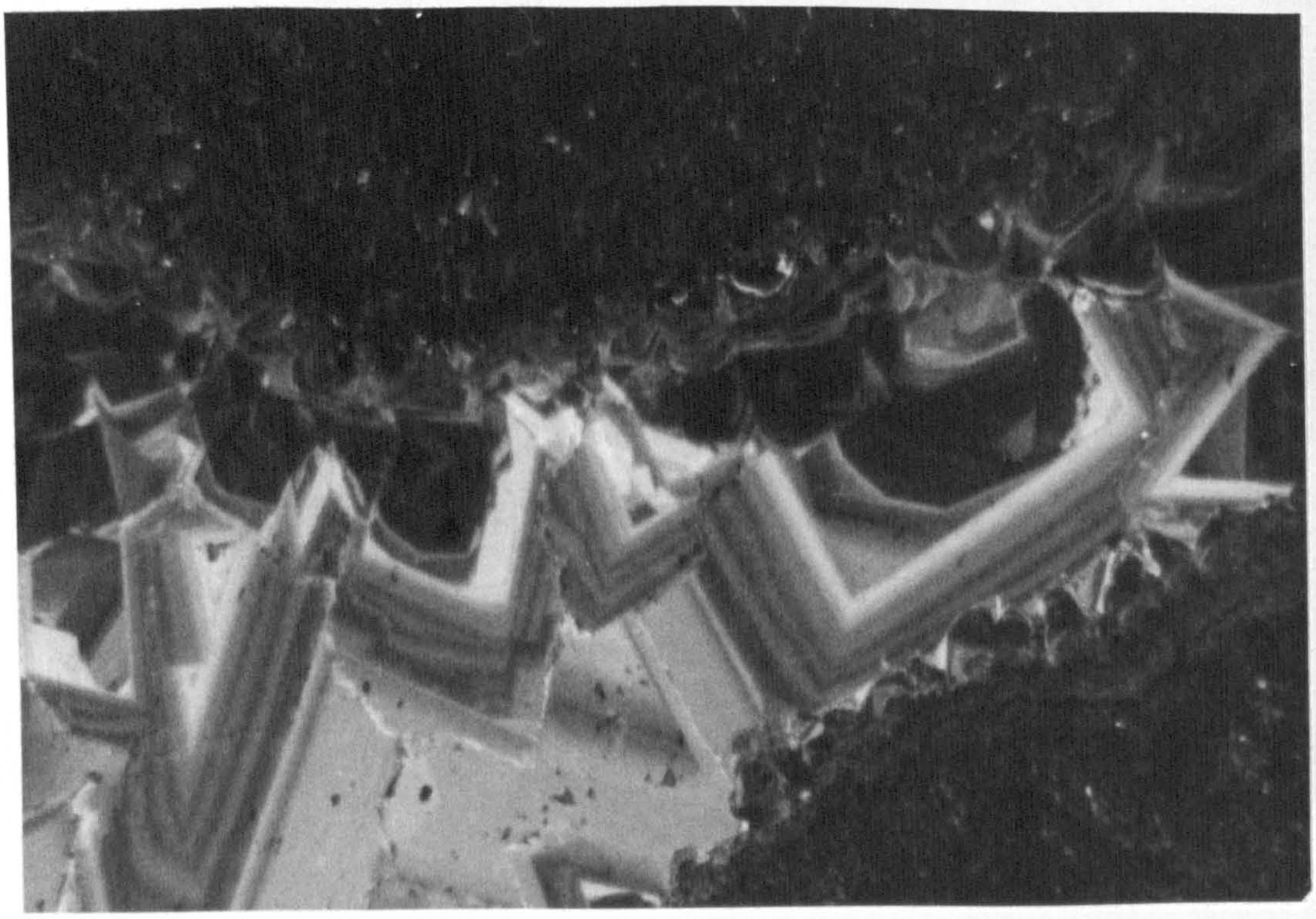
Unit G, Hestnes foreshore, east Porsanger.

a

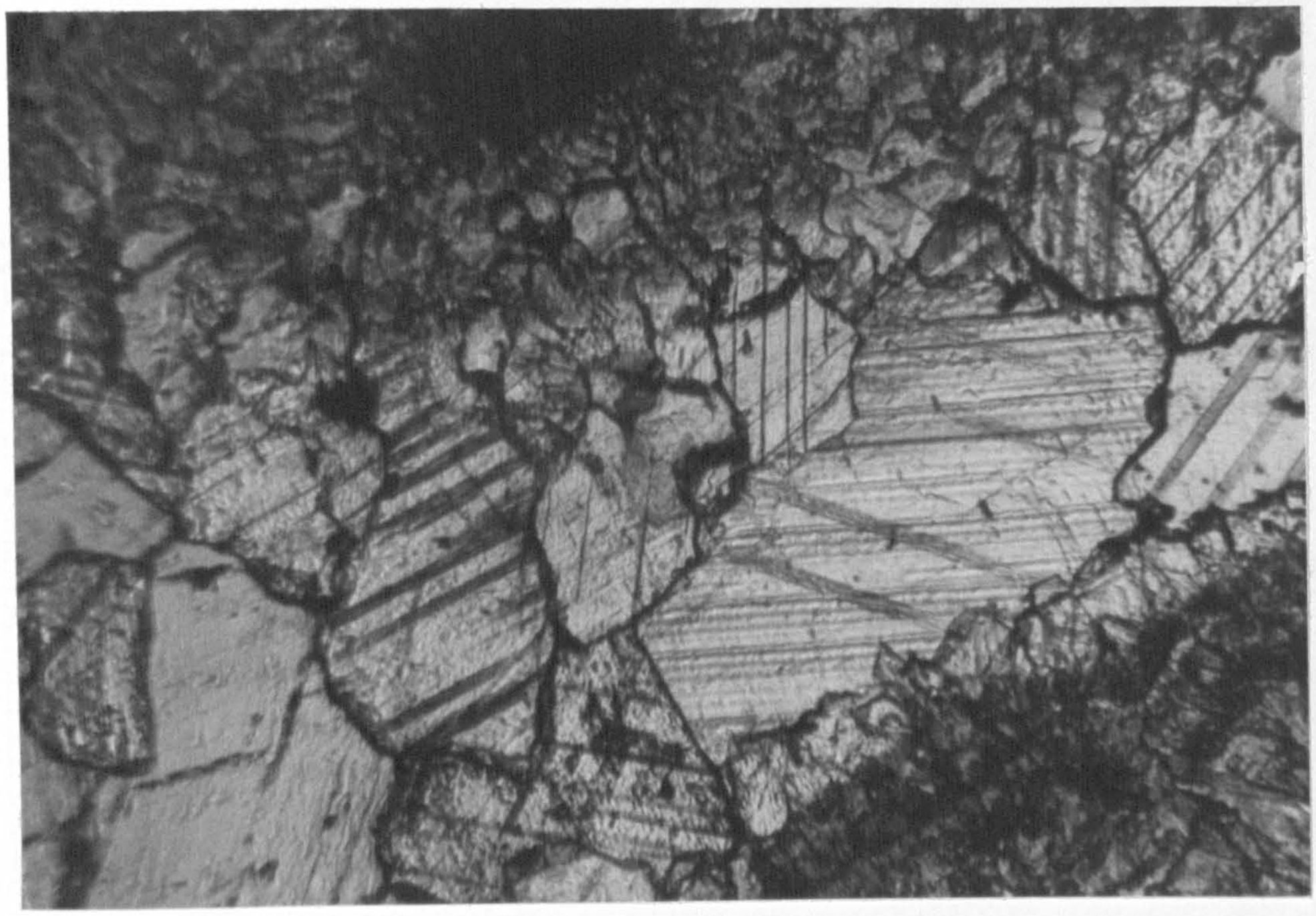


b



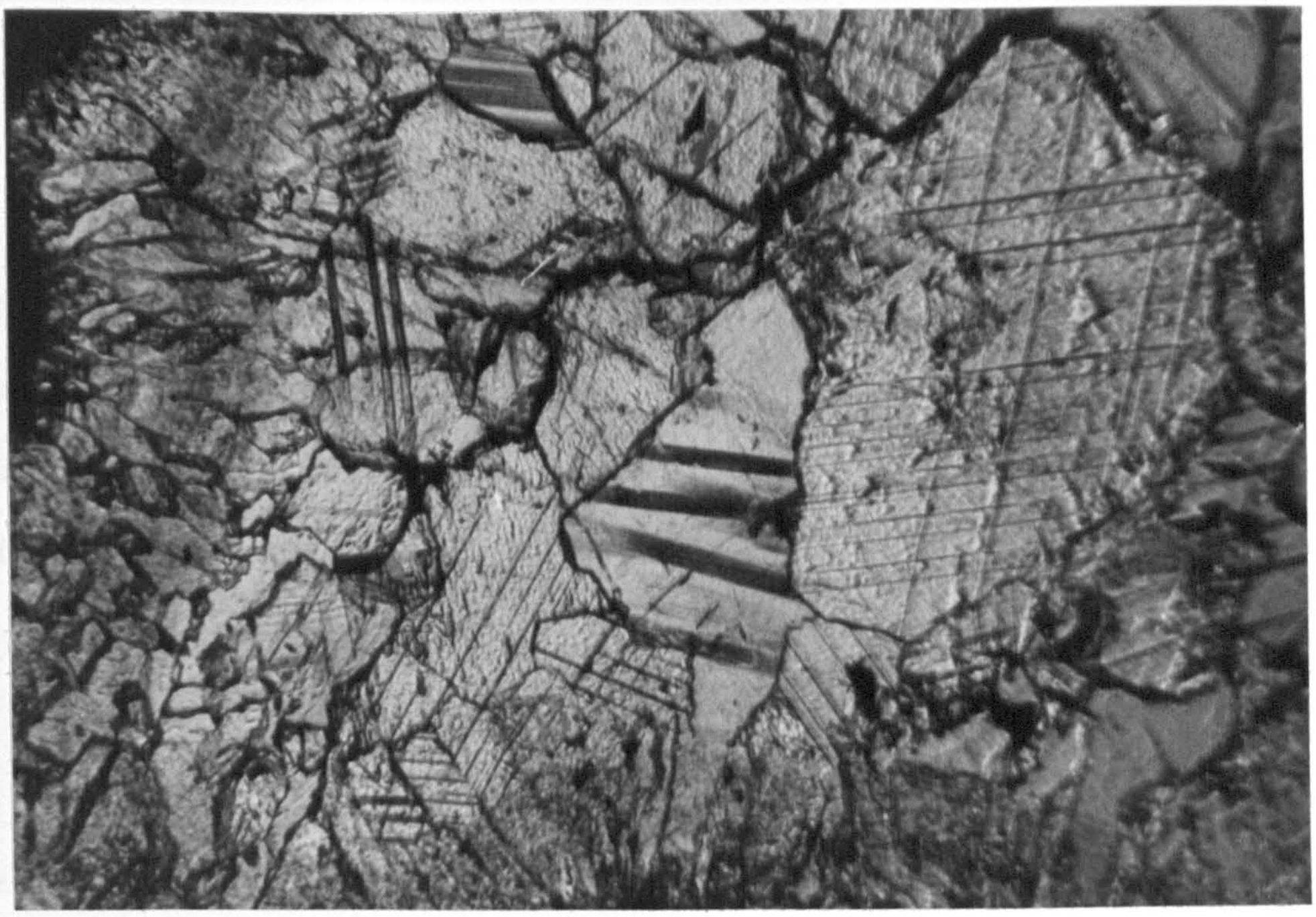


P



ɔ

e



f



dull luminescence have an equant (? rhombohedral) or more elongate form. The former resemble second generation dolospars in grainstones (section 7.3.1). A large number of early crystals give rise to a smaller number of later, coarser crystals with brighter, zoned luminescence. These growth zones predominantly define obtuse rhombohedra, although more acute forms also occur, and are characterised by truncation surfaces (Fairchild, 1980) and discontinuities (see Figs. 7.7b,d,f). Some of this brighter luminescing dolomite is also seen filling fractures in fibrous dolomite crusts and in the matrix material.

Discussion

Internal sediments, in association with fibrous dolomite, suggest a marine early diagenetic environment, perhaps characterised by periods of meteoric influence resulting in dissolution and erosion of cement crystals. This interpretation is consistent with an intertidal-supratidal flat depositional setting, as indicated by facies analysis (Tucker, 1977, and Chapter 6). Aissaoui and Purser (1983) have described a sequence of internal sediment types, including geopetal micrite, centripetal micrite and crystal silt, reflecting accretional or erosional tidal flat sequences in Jurassic carbonates from France and Algeria. Although the Porsanger internal sediments have not been studied in detail, they clearly are consistent with a marginal marine-meteoric early diagenetic origin.

The drusy fabric, lack of relic structures and C.L. character of cavity-filling dolospars is consistent with a cement rather than replacement origin. The various truncation surfaces and discontinuities indicate hiatuses and perhaps periods of dissolution and overgrowth during the cementation process (Meyers, 1978; Fairchild, 1980; Kendall, 1982; and

Fairchild, reply). The multiple zonation indicates variations in fluid chemistry during precipitation, probably principally in Fe/Mn ratio (see Pierson, 1981; Fairchild, 1983; and Chapter 3, section 3.3.4.vi). The dolospar cementation process occurred in a complex diagenetic environment, subject to frequent changes in fluid compositon and/or conditions of precipitation affecting the partitioning of cations. Dolospar precipitation clearly occurred after compaction and (? tectonic) fracture of fibrous dolomite crusts and therefore can be regarded as a second generation late diagenetic cement.

In contrast to late diagenetic dolomites in many Phanerozoic carbonates, saddle or baroque crystal forms are not developed in the Porsanger Dolomite. This may reflect the temperature of formation and/or chemical effects (Radke and Mathis, 1980). Saddle (baroque) dolomite is thought to result from lattice distortion produced by compositional variations (localised Ca enrichment) within individual growth laminae. Radke and Mathis (1980) suggested that selective ion adsorption due to surface charge effects during crystal growth is responsible for these variations. Surface charge variations may result from pyro-electric effects at elevated temperatures or the pH and ionic concentration characteristics of the parent fluid (Radke and Mathis, 1980).

Considering the likely thermal history of the Porsanger Dolomite (see Chapter 6) it is surprising that baroque dolomite did not develop (c.f. Gregg and Sibley, 1984). However, it is possible that chemical effects (see Radke and Mathis, 1980) were more important during precipitation of dolospars. The rarity of obvious neomorphic dolomite fabrics (Gregg and Sibley, 1984) in the Porsanger Dolomite may indicate that early dolomite phases were near ideal composition and structure and therefore had limited

potential for recrystallisation (c.f. Gregg and Sibley, 1984 and pervasive dolomites in the South Wales Dinantian, Chapter 3).

7.4 Conclusions

Petrographic study of the Porsanger Dolomite reveals a range of fabrics, from depositional grains through early and late diagenetic phases, which are very similar to many limestones.

Ooids and fibrous dolomites have fabrics which may be primary. They probably reflect fabric-retentive replacement of some precursor. The mineralogy of the original precipitates is not known, but metastable calcium carbonate phases (? HMC) seem most likely. An alternative interpretation is that poorly ordered, calcian-dolomite was precipitated and was subsequently stabilised to ordered, stoichiometric dolomite, with retention of primary fabrics (see also Tucker, 1983; and c.f. discussion in section 7.3.2.(f) above).

Whatever the original precipitate of ooids and fibrous cements, the fabric-retentive transformation to dolomite appears very similar to HMC LMC stabilisation in limestones. It is suggested, therefore, that early replacement dolomitisation in the Porsanger Dolomite can similarly be regarded as a stabilisation reaction. This idea will be discussed further in the following chapter.

A marginal marine to meteoric early diagenetic setting is suggested from general facies considerations and is supported by cement morphologies (including fibrous and equant isopachous and meniscus types) and internal sediment types.

Coarse dolospars in cavity structures and filling fractures in fibrous dolomites and substrate material have more obvious primary fabrics, especially under cathodoluminescence. An origin by direct precipitation in

a late diagenetic, burial (?) environment is likely.

CHAPTER 8

Geochemistry of the Porsanger Dolomite

8.1 Introduction and Sample selection

This chapter is organised in a similar way to Chapter 4, dealing with the geochemistry of Dinantian dolomites. Much of the background information is common to Chapter 4 and need not be repeated here.

The petrography of the Porsanger Dolomite is presented in Chapter 7 and from that work it was concluded that many of the fabrics in the Porsanger are consistent with a primary or fabric-retentive replacement origin for most of the dolomite. The present chapter attempts to provide additional information from which it may be possible to place further constraints on the origin of the dolomite.

Whole-rock samples were prepared only from dolomicrites of nearly homogeneous textural composition (see Chapter 7, section 7.2). Most samples were dissected, using scalpel and dental drill from uncovered thin sections (c. 60μm thick), mounted in Canada balsam or epoxy resin, under a binocular microscope. Careful sampling ensured that little or no mounting medium was included in samples. The dissected samples comprise depositional grains, fibrous dolomites (types 1 and 3 only), internal sediments and dolospars. Many of these components represent relatively small volumes of the whole-rock and sample sizes were therefore generally less than 10 mg and occasionally less than 1 mg. In order to obtain as much information as possible from these single samples a combined technique of cation chemical and stable isotopic analysis was employed (see Coleman, Walsh and Benmore, in prep.).

8.2 Stoichiometry and crystal order (XRD)

Powder X-ray diffraction analyses,to determine stoichiometry and crystal order,were carried out on whole-rock dolomicrite samples. Dolomite stoichiometry was calculated using Lumsdens' (1979) equation (mole % $CaCO_3$ = Md + B, see Chapter 4, section 4.1.2). The degree of order is expressed as the ratio of the intensities of the [221] and [101] diffraction peaks.

Results

A small number of samples were found to have minor amounts of quartz, most samples however, are composed only of dolomite confirming petrographic identification.

Dolomite comprising the dolomicrites is stoichiometric, falling in the range 49.3 to 51.0 mol% $CaCO_3$ and is moderately to well ordered (ratios 0.46 to 1.63), see Fig. 8.1 and Appendix I.

It should be noted that dolomite stoichiometry has also been determined from cation chemical analyses (see section 8.3) and that this data differs by up to 2.6 mol% from XRD determined compositions. This should not affect general interpretation of this data however, as all the dolomites analysed are essentially near stoichiometric (see Sperber, Wilkinson and Peacor, 1984).

Discussion

Porsanger dolomicrites occur in association with subtidal to supratidal facies. There is evidence for local subaerial exposure and desiccation but evaporites are only developed at the base of the Formation (Tucker, 1976) and not in association with the dolomicrites described here.

The stoichiometric nature of the dolomicrites suggests that they

Fig 8·1

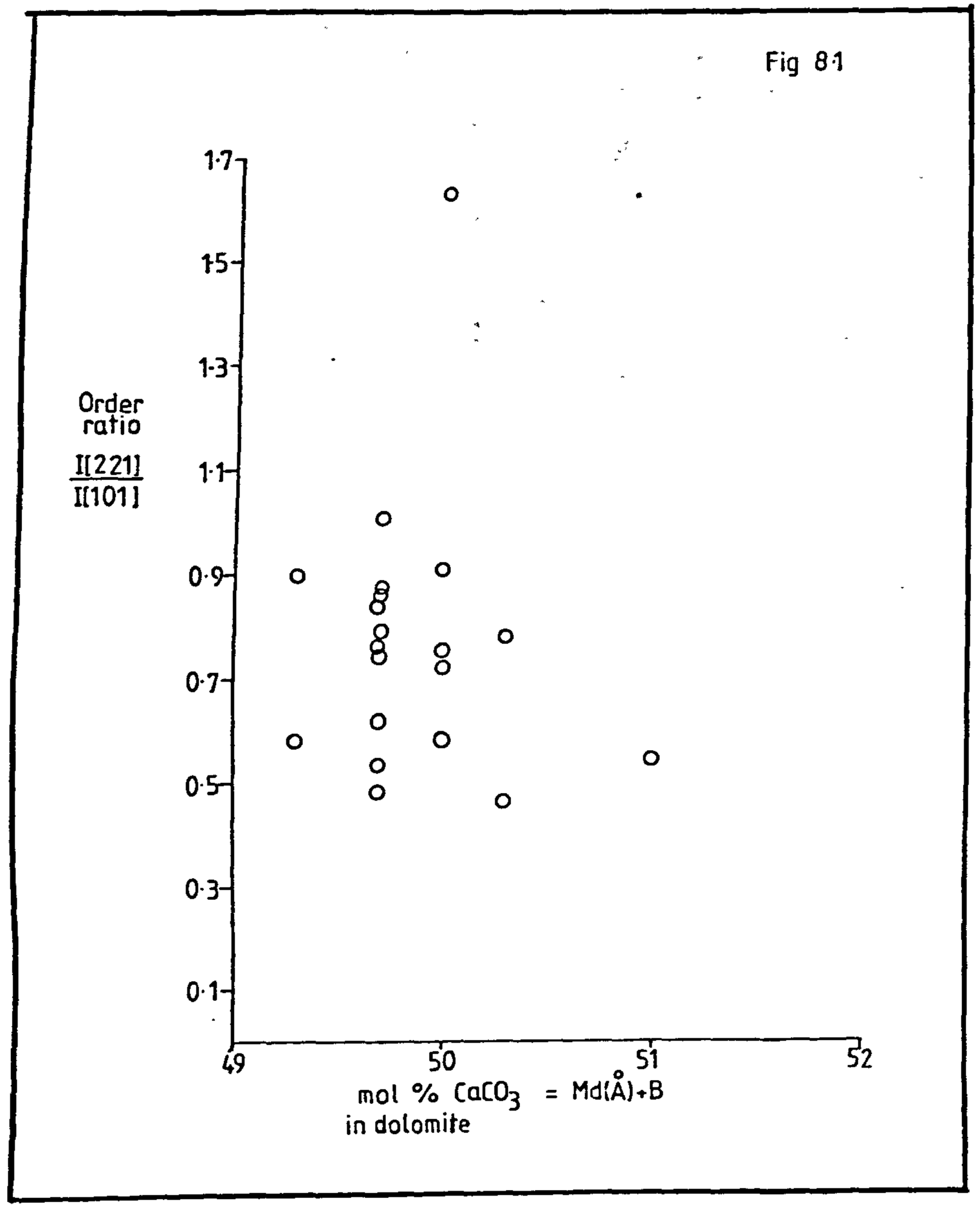


Fig 8.1 XRD data for Porsanger dolomicrites plotted as mol% $CaCO_3$ in dolomite vs. order ratio. Explanation in text.

Fig 8-2

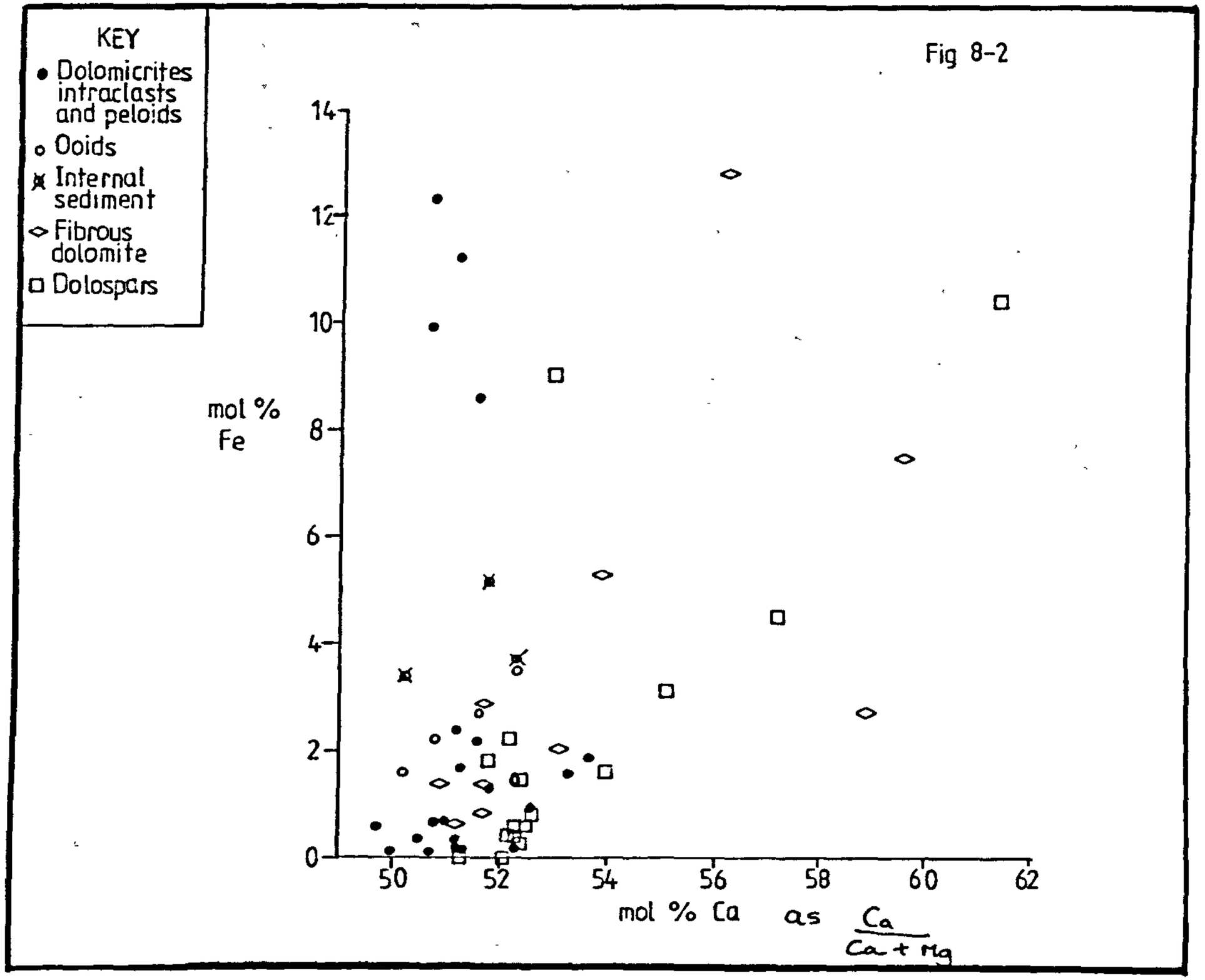


Fig 8.2 Fe^{2+} vs. Ca^{2+} (from ICP data given in appendix 2) showing covariation in non-dolomicrite samples with more than 3 mol% Fe, suggesting substitution of Fe^{2+} for Mg^{2+} in the dolomite lattice. High-Fe in dolomicrites is thought to be present in non-lattice sites. This data is discussed, together with XRD data in section 8.3.3.

formed in a relatively open diagenetic system (Sperber, Wilkinson and Peacor, 1984; see Chapter 4, section 4.1.2 for further discussion). This is more likely to have been achieved in a nearsurface diagenetic environment, before isolation from the marine Mg^{2+} reservoir, compaction and lithification with burial. Petrographic evidence suggests that the present textural form of the dolomicrites developed during syn-depositional diagenesis (see Chapter 7, section 7.2.1) and is therefore consistent with the data presented here.

The question remains, however, were the micrites originally composed of dolomite or a calcium carbonate mineral? If they were originally dolomite, this may have been a metastable poorly ordered, calcian-phase which subsequently altered (stabilised) to the present ordered, near stoichiometric form. Alternatively, a calcium carbonate precursor may have been replaced either by 'ideal' dolomite, or initially by poorly ordered calcian-dolomite which stabilised later (see discussions of Dinantian dolomites in preceding chapters). In a 'stabilisation' scenario, either of a directly precipitated or a replacement calcian-dolomite, one might expect little obvious textural evidence (c.f. TEM studies, e.g. Reeder and Wenk, 1979 and Chapter 4), so that further clues may only come from structural-stoichiometry studies.

The Porsanger dolomicrites show less pronounced stoichiometry vs. order trends than the Dinantian dolomites described in Chapter 4. This may be interpreted as reflecting more complete and uniform stabilisation, or that Porsanger dolomicrites formed initially as relatively more ordered and near-stoichiometric dolomite. The more complex, and to some extent less certain, burial history of the Porsanger Dolomite complicates further comparison with the Dinantian examples. Overall, however, the well ordered

and stoichiometric nature of Porsanger dolomicrites suggests a relatively more open diagenetic system during the formation and/or stabilisation of the dolomite. This is consistent with a near surface, penecontemporaneous origin as suggested by petrographic study. If there has been significant post-depositional modification of the micro-structure and composition of the dolomite (e.g. Land, 1980; Reeder, 1981; Blake, Peacor and Wilkinson, 1982), it is not apparent from the petrographic and geochemical studies carried out here (see Chapter 7 and remainder of present chapter).

8.3 Cation chemistry

8.3.1 Introduction

As with the Dinantian dolomites (see Chapter 4) concentrations of Fe, Mn, Na and Sr in the Porsanger Dolomite generally fell close to or below the detection limits of the electron microprobe (viz. Fe and Mn = 0.04 wt%; Na = 0.2 wt % and Sr = 0.03 wt %). Analysis of the principal cations (Ca, Mg, Fe, Mn and Sr) was therefore carried out by spectrometric methods.

Whole-rock (dolomicrite) and dissected samples from the Porsanger Dolomite were dissolved in phosphoric acid, as in the preparation of samples for stable isotope analysis, and after the evolved CO_2 was removed, the acid plus dissolved carbonate was prepared for I.C.P.S. analysis. The technique allows combined stable isotopic and cation chemical analysis of the same milligramme-size sample (Coleman, Walsh and Benmore, in prep.). Results are presented as normalised molar ratios, which allow semi-quantitative interpretation (see below) and eliminates the possibility of weighing errors in calculations of absolute weight concentrations.

8.3.2 Major element stoichiometry

Ca and Mg concentrations determined by I.C.P.S. are presented in Appendix 2 and summarised in Table 8.1.

TABLE 8.1

Stoichiometry by I.C.P.S.

(expressed as mol% Ca/Ca + Mg)

	Range	$\bar{X}$
Dolomicrites (whole rock)	49.7 to 52.3	51.1 n=14
Micritic intraclasts/ flakes	50.8 to 53.3	52.0 n=5
Ooid cortices	50.2 to 52.3	51.4 n=5
Peloids	51.6 to 53.7	52.4 n=3
Fibrous dolomite type 1	51.7 to 59.6	54.4 n=7
Fibrous dolomite type 3	50.9 to 56.2	52.8 n=3
Internal seds.	50.2 to 52.3	51.4 n=3
Dolospars	51.3 to 61.4	53.4 n=16
Overall:		$\bar{X}$ = 52.5 n=56

The Porsanger components show a range of compositions from 49.7 to 61.4 mol % Ca, with averages within each group ranging from 51.1 to 54.4 mol % Ca. The data for dolomicrites are in general agreement with those obtained by XRD (see section 8.2).

Except for dolomicrites with high iron (>3 mol % Fe, see Fig. 8.2), all dolomite samples with excess Ca relative to Mg (>c. 54 mol % Ca) are also enriched in Fe (see Fig. 8.2).

Discussion

Taken as a whole, the Porsanger Dolomite appears to comprise predominantly near-stoichiometric dolomite, in common with the Beck Spring Dolomite of California (Tucker, 1983). This may be interpreted as indicating a relatively open system, with an allochthonous supply of Mg^{2+} during initial dolomite formation and/or during subsequent stabilisation if initial phases were poorly ordered and calcian (Sperber, Wilkinson and Peacor, 1982). However, the relationship between Ca:Mg (as mol % Ca on Fig. 8.2) and Fe (mol % Fe) for non-dolomicrite samples suggests that the main cause of Ca-excess is preferential substitution of Fe^{2+} for Mg^{2+} in the dolomite lattice. This is in agreement with Kretzs' (1982) calculated distribution coefficient for Fe in the Mg and Ca sites of dolomite (Fe^{2+} in Mg^{2+} site $\div$ Fe^{2+} in Ca^{2+} site $\approx$1.54). Fe in Porsanger dolomites is discussed further in section 8.3.3 below.

Clearly then, any discussion about Ca:Mg stoichiometry in dolomite should also consider the possible effects of Fe^{2+} substitution, and caution should be applied to any attempt at genetic classification of dolomites using Ca:Mg data alone (see Morrow, 1982b, for example).

8.3.3 Minor and trace elements

As already discussed in Chapter 4, the interpretation of minor and trace element chemistry in carbonates is far from refined. It was shown in section 4.2.1 that in general terms the degree of repartitioning of tracers in diagenetic systems can be seen as a product of changes in the diagenetic environment. These are determined by the availability or mobilisation of tracers, related to the source and chemistry of diagenetic fluids and to the solute index of the system. An expression of these factors combined with those of classical partitioning are effective distribution coefficients, expressed simply as $(mMe/mCa)_{solid} = D_{solid} \times (mMe/mCa)_{fluid}$. In this form, D is essentially a descriptive term, however it may vary between diagenetic environments and types of reaction (see Veizer, 1983a) and therefore is usefully recorded. In this study empirical D's cannot be derived accurately as one ideally requires an extant system or some physical record of the precipitating fluid (e.g. fluid inclusions). However, paragenetic studies may provide constraints on the likely origin of diagenetic fluids and therefore allow approximate (i.e. order of magnitude) estimates of effective D's. For the purposes of this study it is assumed that the relative magnitudes of mMe/mCa in modern natural waters (as listed by Veizer, 1983a) are applicable to the late Precambrian (for further discussion, see Holland, 1978).

Minor and trace element data, expressed as mMe/mCa, for the various components of the Porsanger Dolomite are presented in Fig. 8.3, together with similar data obtained from the mid-Proterozoic Beck Spring Dolomite by Tucker (1983). In qualitative terms, the trend toward decreasing Sr and increasing Mn and Fe from early to late diagenetic phases is consistent with diagenetic stabilistion or recrystallisation of marine carbonate (e.g.

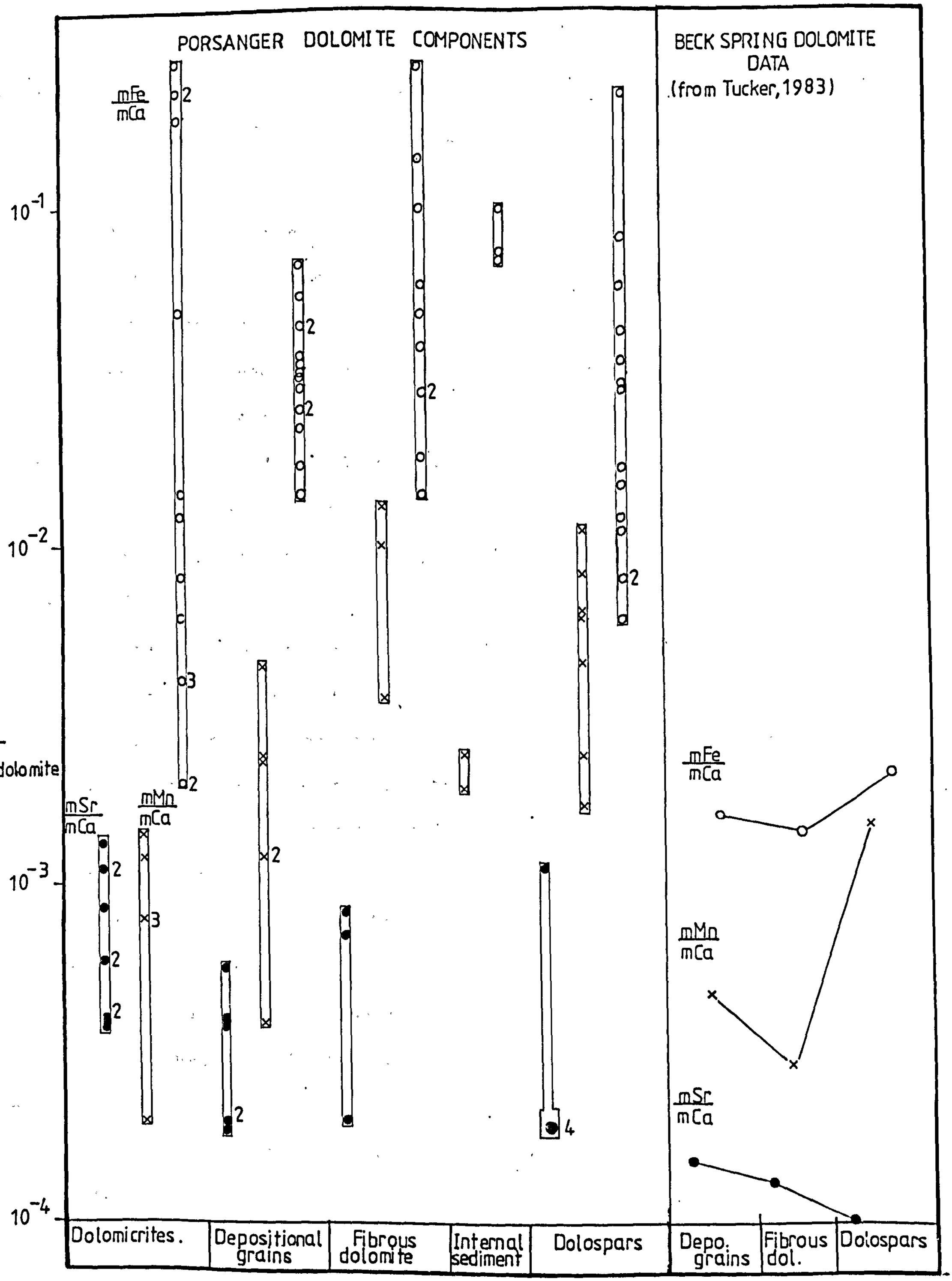


Fig 8.3 Cation chemistry variation (m Me/ m Ca) in Porsanger Dolomite components (data from ICP analysis, see appendix 2). Data for the Beck Spring Dolomite are included for comparison.

Brand and Veizer, 1980; Veizer, 1983a). An early diagenetic replacement origin has already been suggested for much of the dolomite comprising dolomicrite, depositional grains and fibrous dolomite (see Chapter 7). The interpretation is supported by ordering and major element data for the different components (sections 8.2 and 8.3.2) and is discussed further in the section on stable isotopes (section 8.4.2). Dolospars generally have the most depleted Sr and enriched Fe and Mn contents and represent late diagenetic addition under burial conditions. Some of the variations in minor and trace element data will now receive further explanation.

a) Iron in depositional grains

Depositional grains in the Porsanger dolomite have up to 3.5 mol % Fe (see Fig. 8.2), with the highest concentrations in ooid cortices. The variation between ooids and other depositional grains may reflect variations in the physico-chemical conditions of dolomite precipitation and/or may be due to incorporation of non-carbonate iron (detrital material) in ooid cortices. It has already been suggested (Chapter 7, section 7.2.2) that micritic-ray and concentric structures in ooid cortices may represent areas of detrital accretion and it is possible that iron is present as non-carbonate inclusions (e.g. oxides/hydroxides) in this material.

b) Iron in dolomicrites

Dolomicrites in the Porsanger were analysed as whole rock samples; they generally have low Fe concentrations (less than 3 mol %) and are comparable with dissected samples of micritic intraclasts. However, four samples have higher Fe (greater than 8 mol %, see Fig. 8.2) and the lack of correlation between Ca-excess (above c. 53 mol % Ca) and Fe in these samples suggests that the measured Fe includes a component not present in Mg^{2+} sites in the dolomite lattice (see section 8.3.2 for reasoning). This

interpretation is also consistent with XRD data (Fig. 8.1) which shows no apparent relationship between Fe content and mol % Ca as calculated from the d_{104} spacings (section 8.2). The significance of this observation lies in the fact that at concentrations greater than 3 mol % Fe substitution of Mg^{2+} (ionic radius c. 0.66 A) by Fe^{2+} (ionic radius 0.74 A) results in an increase in the d_{104} spacing of the dolomite lattice (Goldsmith and Graf, 1958b; Runnells, 1970; Al-Hashimi and Hemingway, 1974). This effect should therefore be seen in the calculated mol % Ca using Lumsden's (1979) equation (as Fig. 8.1). The lack of such an observation therefore implies a non-lattice bound origin for the excess Fe (i.e. at least greater than 3 mol %). Further support for this interpretation comes from the I.C.P.S. data (Fig. 8.2) which show that Fe enrichment in dolomicrites has little effect on their Ca:Mg stoichiometry. Thus, in the case of high-Fe dolomicrites the calculated mol % Fe contents of the dolomite are likely to be in error. By implication, the calculated normalised ratios of other cations in these four samples will also be in error (under estimates).

c) Iron in fibrous dolomites and dolospars

Fibrous dolomites and dolospars in the Porsanger Dolomite have variable to high Fe contents (Fig. 8.2 and 8.3). Although some of this Fe may be present as non-carbonate inclusions (note cloudy appearance of some fibrous dolomites) the correlation with mol % Ca (Fig. 8.2), at least for samples with excess Ca, supports Fe^{2+} substitution for Mg^{2+} in the dolomite lattice (see section 8.3.2 and (b) above).

d) Iron and manganese

Fe and Mn display similar overall trends (see Fig. 8.3) and are opposite to those of Sr, consistent with stabilisation and/or addition of later diagenetic phases from non-marine fluids. It has already been argued

that Fe is present predominantly in the dolomite lattice of fibrous dolomites, internal sediments, dolospars and perhaps low-Fe dolomicrites (section 8.3.2 and Fig. 8.2). Mn/Fe ratios in these components are generally less than the average terrigenous input (taken as river water Mn/Fe 0.4) suggesting that some geochemical process may be controlling the availability and incorporation of Mn and Fe. A plot of mMn/mFe versus $\delta^{13}C$ for these components shows a positive covariance (see Fig. 8.6) and suggests oxidation of organic carbon under suboxic conditions (see discussion in Chapter 4, section 4.2.2.b). Under these conditions Mn and Fe bound up in oxides (presumably of terrigenous origin) would be released for incorporation in precipitating carbonate. The observation that depositional grains (ooids and peloids) do not fall on the expected trend is consistent with their containing a relatively high detrital Fe component (see section 8.3.3.a). The significance of $\delta^{13}C$ variations in the Porsanger Dolomite is discussed further in section 8.4.2.c

e) Manganese and strontium: determination of effective D's

The possible significance of the trend towards lower Sr and higher Mn (viz. a change in diagenetic environment) has already been mentioned (8.3.3 introduction). In this section paragenetic interpretation will be used to constrain the likely diagenetic fluids and type of reaction in order that effective distribution coefficients may be suggested.

Overall, a marginal marine depositional setting (shallow subtidal to supratidal) is suggested. Early pre-compactional diagenesis therefore may have involved marine or meteoric fluids. The direct evidence for meteoric diagenesis is limited to sparry first generation non-isopachous and meniscus cements in some oolitic grainstones (see section 7.3.1), and perhaps to internal sediments (section 7.3.3). Primary marine fabrics are seen in

Table 8.2

Dolomite type	Composition (see Fig. 8.3)	Likely fluid (See Table 4.1 for composition)	Type of reaction	Effective D
Dolomicrites, depositional grains and fibrous dolomite.	$X\frac{mSr}{mCa} = 5.1\times10^{-4}$ range 1.9×10^{-4} to 1.3×10^{-3} $X\frac{mMn}{mCa} = 4.2\times10^{-3}$ range 2.0×10^{-4} to 1.3×10^{-2}	Seawater to meteoric water (Mixing?)	Early stabilisation of marine phases.	Assuming seawater D^{Sr}_{dol} X = 0.05, range 0.02 to 0.13 D^{Mn}_{dol} X = 4200, range 200 to 13000 Assuming meteoric water D^{Sr}_{dol} X = as s/w D^{Mn}_{dol} X = 4.2, range 0.2 to 13
Dolospars with early diagenetic meteoric fabrics.	(One sample only) $\frac{mMn}{mCa} = 1.1\times10^{-2}$	Meteoric	Direct precipitation? or replacement of meteoric cement.	$D^{Mn}_{dol} = 11.0$
Dolospars	$X\frac{mSr}{mCa} = 4.4\times10^{-4}$ range 1.9×10^{-4} to 1.1×10^{-3} $X\frac{mMn}{mCa} = 5.7\times10^{-3}$ range 1.7×10^{-3} to 1.1×10^{-2}	Meteoric to formation waters.	Direct precipitation	Assuming meteoric water D^{Sr}_{dol} X = 0.04, range 0.02 to 0.11 D^{Mn}_{dol} X = 5.7, range 1.7 to 11.0 Assuming formation water D^{Sr}_{dol} X = 0.004, range 0.002 to 0.011 D^{Mn}_{dol} X = as m/w

Determination of effective D for Porsanger Dolomite components

ooids and probably fibrous dolomites; however, it is likely that they represent fabric-retentive replacement and it is suggested that these were essentially stabilisation reactions (section 7.2.2, 7.3.2 and 7.4). The transformation to dolomite, regardless of the original precipitate (metastable calcium carbonate or calcian dolomite), appears to have been very similar to the HMC to LMC stabilisation reaction in limestones. Dolomitisation or recrystallisation of existing phases to the present ordered and near stoichiometric dolomite (section 8.2 and 8.3.2) requires an allochthonous source of Mg^{2+}. In an early diagenetic setting this almost certainly implicates seawater, so marine or marine derived diagenetic fluids are therefore strongly suggested. This is also true for the dolomicrites, where syndepositional lithification occurred. A meteoric influence cannot be ruled out, however because of the depositional setting and the evidence for meteoric diagenesis. Thus in deriving values for effective $D^{Me}_{dolomite}$ both marine and meteoric Me/Ca ratios are used (see Table 8.2).

Dolospars in the Porsanger Dolomite formed during later, burial diagenesis, after compaction. An origin by direct precipitation is suggested by their fabrics (section 7.3.3). A complex diagenetic environment subject to frequent changes in fluid composition and/or conditions of precipitation is indicated. Regarding the origin of diagenetic fluids and a source for Mg^{2+}, it was shown in Chapter 6 that the Porsanger Dolomite represents the shallow marginal facies of a deeper clastic basin, the predominantly shaley component of which may have provided dolomitising fluids on compaction. Alternatively or additionally, it is clear that dolomite of early diagenetic origin was present in abundance within the Porsanger Dolomite itself, so it is possible that Mg^{2+}

for late diagenetic dolospars was derived internally, i.e. was essentially autochthonous. The problem of burial dolomitisation has already been addressed and the reader is referred to Chapter 5 (section 5.8) for further discussion. As a first approximation to dolomitising fluid compositions it seems reasonable to take those of formation water and meteoric water (shallow subsurface) from Fig. 4.2a in order to estimate effective D's for dolospars (Table 8.2).

The range of values for effective D in different diagenetic (dolomitising) environments thus determined (Table 8.2) may be compared with theoretically derived D's in Table 4.1b. As with the Dinantian dolomites (Table 4.1a), values for effective $D^{Mn}_{dolomite}$ which assume seawater compositions are probably unrealistic if mixing with meteoric water is suspected, because meteoric Mn/Ca ratios are likely to dominate.

8.4 Stable isotope chemistry

8.4.1 Introduction

As with other sections in this chapter, much of the interpretative background information applicable to this section is common to the equivalent section in the chapter dealing with Dinantian dolomite geochemistry and need not be repeated here.

The purpose of this section is to provide additional information on which to base an interpretation of the diagenetic history of the Porsanger Dolomite. As will emerge, stable isotope data alone do not allow unequivocal interpretation, however in combination with petrographic and other geochemical data, they provide a powerful interpretative tool.

Sampling procedures are as described in the general introduction to this chapter (section 8.1) and samples of the major depositional and diagenetic components have been analysed.

8.4.2 Results and discussion

Full details of results obtained from stable isotope and combined stable isotope-cation chemical analyses, including experimental precision and reproducibility of samples, are given in the appendix. Fig. 8.4 shows the stable isotope variations for the depositional and diagenetic components in the Porsanger Dolomite (viz. dolomicrites and dolomicritic intraclasts, ooids, peloids, catagraphs, fibrous dolomites, internal sediments and dolospars).

Discussion of stable isotope data

The broad trend is for $\delta^{18}O$ to become more negative and $\delta^{13}C$ less positive (with a smaller range) from dolomicrites and depositional grains to dolospars (Fig. 8.4). This sort of general pattern is typical of

KEY
- ● Dolomicrite–whole rock
- × Dolomicrite–intraclasts
- ⊙ Ooids
- O Peloids
- c Catagraphs
- ◊ Fibrous dolomite
- IS Internal sediment
- □ Dolospar–columnar
- ◨ Dolospar–blocky proximal
- ■ Dolospar–blocky distal

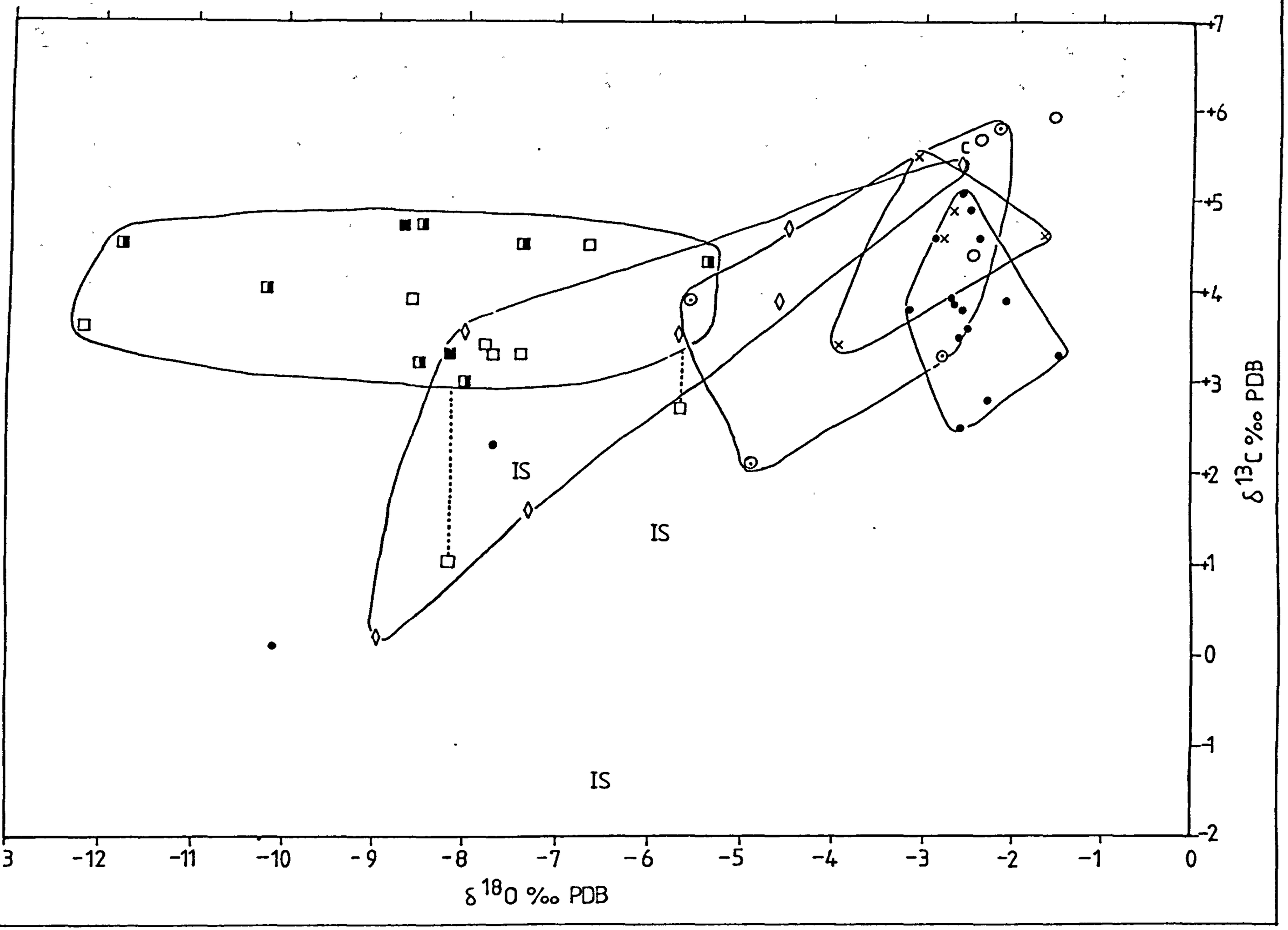


Fig 8.4 Stable isotope variation diagram for Porsanger Dolomite components (data in appendix 3).

ancient limestones (e.g. Hudson, 1977), where such heterogeneity results from the progressive addition of diagenetic phases at higher temperatures and/or from evolving porewaters and under variable degrees of rock-water interaction (e.g. Walls, Mountjoy and Fritz, 1979; Meyers and Lohmann, 1985). In ideal situations these variations may be detected within single cement generations, allowing identification of discrete isotope-chemical zones (e.g. Dickson and Coleman, 1980; Marshall, 1981).

Tucker (1983), and Zempolich, Lohmann and Wilkinson (1985) noted similar trends in the mid-Proterozoic Beck Spring Dolomite (see Fig. 8.5), where well preserved fabrics, similar to those described from the Porsanger Dolomite, are seen. The study by Zempolich, Lohmann and Wilkinson (1985) included analyses on some previously unreported limestone equivalents of the Beck Spring Dolomite (see Fig. 8.5). The most significant feature of this data is the c + $8^{o}/_{oo}$ shift in $\delta^{18}O$ of dolomitic ooids and acicular cements relative to their calcitic equivalents. Zempolich, Lohmann and Wilkinson (1985) interpreted this to indicate peritidal syndepositional dolomitisation of most of the formation, with localised meteoric stabilisation producing the limestones. In his study, Tucker (1983) argued that stable isotope data could be interpreted in terms of either a marine (direct precipitation or seafloor/sub-seafloor replacement) or an early diagenetic replacement origin. A meteoric-marine mixing zone model was considered most appropriate for the latter (Tucker, 1983).

The Porsanger Dolomite, although lacking limestone equivalents provides a further example of Precambrian dolomite in which depositional and diagenetic fabrics are well preserved. There is also a consistent isotopic, and to some extent chemical (see section 8.3) variation between the different component groups.

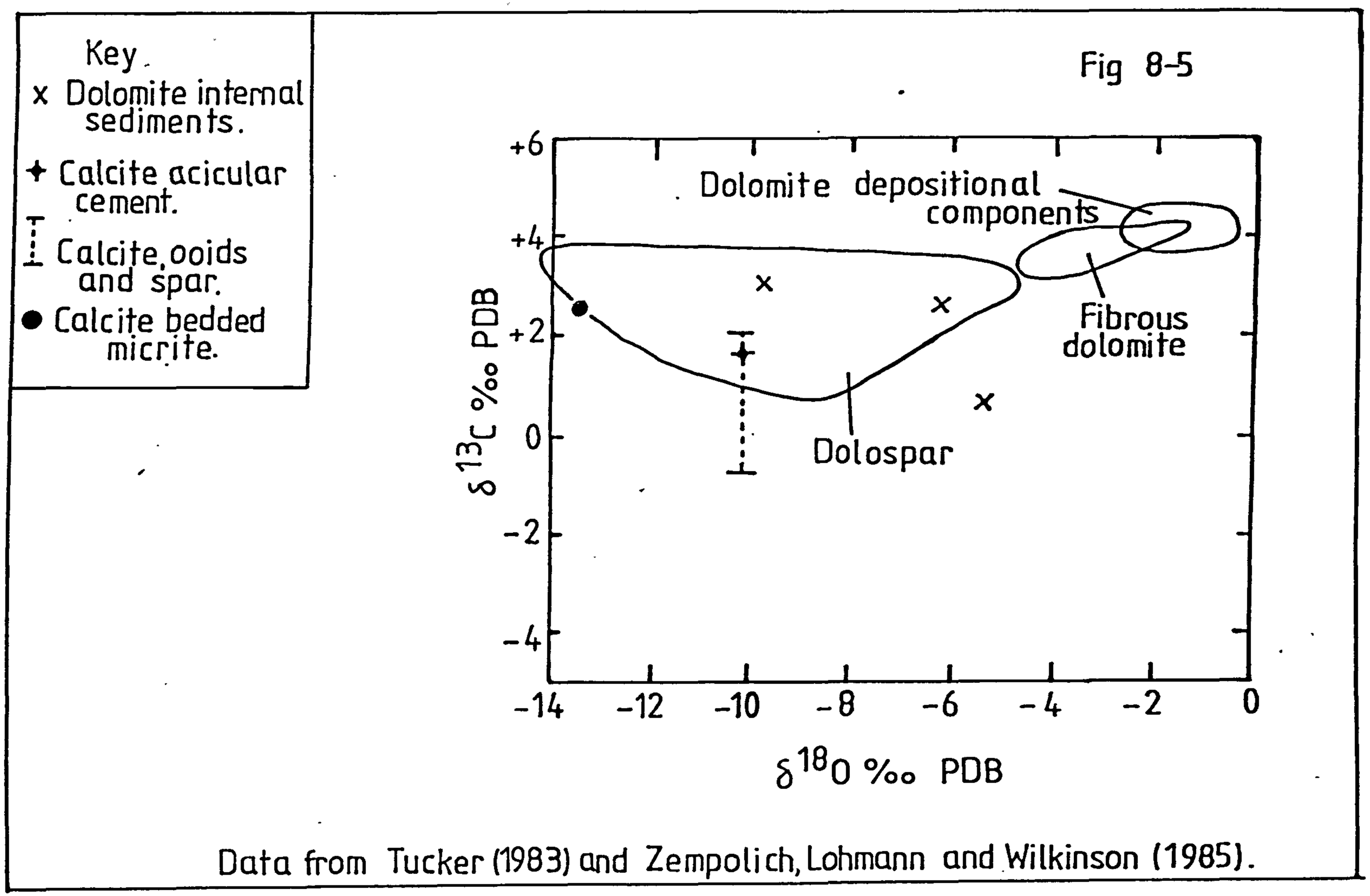


Fig 8.5 Stable isotope variation diagram for Beck Spring Dolomite and Limestone components

Ideally, to attempt a detailed interpretation of this data, it is necessary to know the starting composition of the original marine components. It is not advisable simply to assume modern marine carbonate isotope ratios because of the well documented secular variations in these values (e.g. Anderson and Arthur, 1983). To estimate the starting composition of marine carbonates, it is first necessary to identify marine components. From facies interpretation (Tucker, 1977), and petrographic study (Chapter 7) it is concluded that dolomicrites, ooids, peloids, catagraphs and fibrous dolomites represent the original marine components of the Porsanger Dolomite. Their present isotopic and cation chemical compositions are then the result of post-depositional alteration (i.e. dolomitisation and/or stabilisation). Variations in composition presumably result from variations in solute-index (rock-water interaction or system openness) and, depending on the time scale of the replacement and precursor reactivity, may also reflect a range of temperatures and porewater compositions. The closest approximation to the original composition of all these components, assuming a common (i.e. marine) origin, will therefore be represented by the area of overlapping compositional fields on Fig. 8.4. The best approximation to this value is considered to be $\delta^{18}O = -2.5\ ^{o}/_{oo}$ PDB and $\delta^{13}C = +5^{o}/_{oo}$ PDB, with a possible range of values $\delta^{18}O$ c.-1.5 to $-3.5^{o}/_{oo}$ and $\delta^{13}C$ c. +2 to $+6^{o}/_{oo}$. The actual numerical value of this overlap is not immediately important here; however, its possible significance will be discussed later (section 8.4.3). What has just been defined is, of course, not the isotopic composition of Precambrian marine carbonate, but the 'least altered' composition of replacement dolomite. This can be used as a starting point against which to discuss the various diverging trends of component groups.

In general terms, the trend towards lower $\delta^{18}O$, and less importantly, $\delta^{13}C$, from dolomicrites and depositional grains through fibrous dolomites to dolospars is paralled by decreasing Sr and increasing Mn and Fe (see Fig. 8.3). Within and between group variations and their possible significance are reviewed below.

a) Dolomicrites

Stable isotope ratios are fairly well clustered for all samples (whole-rock and dissected micritic intraclasts), suggesting that the dolomite formed under similar and uniform conditions (S.I., temperature, porewater composition).

Petrographic study indicates that dolomicrites were lithified during syndepositional diagenesis, perhaps by replacement of metastable carbonate muds or pore-fill cementation (see Chapter 7, section 7.2.1). Cation data support a relatively early diagenetic origin for the dolomicrites, being generally Sr enriched and Mn and Fe depleted relative to other components.

Two samples (1A, 2A) fall outside the field of dolomicrite stable isotope variation (see Fig. 8.4). These are from the clastic-dominated basal beds of the Porsanger Dolomite (see Chapter 6). Petrographically they comprise dolomicrite (< 31μm) and coarser, neomorphic microspar. Their stable isotopic compositions are therefore consistent with a later diagenetic, recrystallisation origin. Because of their relative unimportance these samples are not considered further here.

b) Depositional components

Of the depositional components analysed, ooids show the greatest composition variation (see Fig. 8.4). Preservation of primary fabrics is

typical of ooids; however, the trend in isotopic composition supports a secondary origin and it is suggested that fabric-retentive replacement occurred over a range of S.I.'s, porewater compositions or temperatures. The trend away from the 'least altered' field towards lower $\delta^{13}C$ and $\delta^{18}O$ may indicate a progressively more open diagenetic system, tending towards equilibrium with $\delta^{13}C$, $\delta^{18}O$ depleted diagenetic solutions (see discussion of fibrous dolomites below).

Cation chemistry data for ooids also supports a secondary origin, being depleted in Sr and enriched in Mn and Fe relative to dolomicrites (see Fig. 8.3).

c) Fibrous dolomite

The trend in fibrous dolomite stable isotopic compositions is similar to that of ooids, but extends to less positive $\delta^{13}C$ and more negative $\delta^{18}O$. As with ooids, primary fabrics in fibrous dolomite are well preserved. The most acceptable interpretation of these dolomites is that they represent a fabric-retentive replacement of fibrous calcite cements (see Chapter 7, section 7.3.2). The replacement probably occurred before burial compaction, in a nearsurface diagenetic environment. Therefore, the trend toward more negative $\delta^{18}O$ values cannot be explained in terms of increasing temperature effects on the dolomite-water isotopic fractionation (see discussion of Fig. 8.7b in section 8.4.2.f, below). A more likely explanation is that variations in the isotopic compositions of diagenetic waters and possibly in the openness of the diagenetic system (the degree of rock-water interaction) are responsible for the observed trends in $\delta^{18}O$ and $\delta^{13}C$.

The positive covariance between $\delta^{13}C$ and $\delta^{18}O$ within fibrous dolomites (see Fig. 8.4) may have further significance. Allan and Matthews (1982)

Fig 8-6

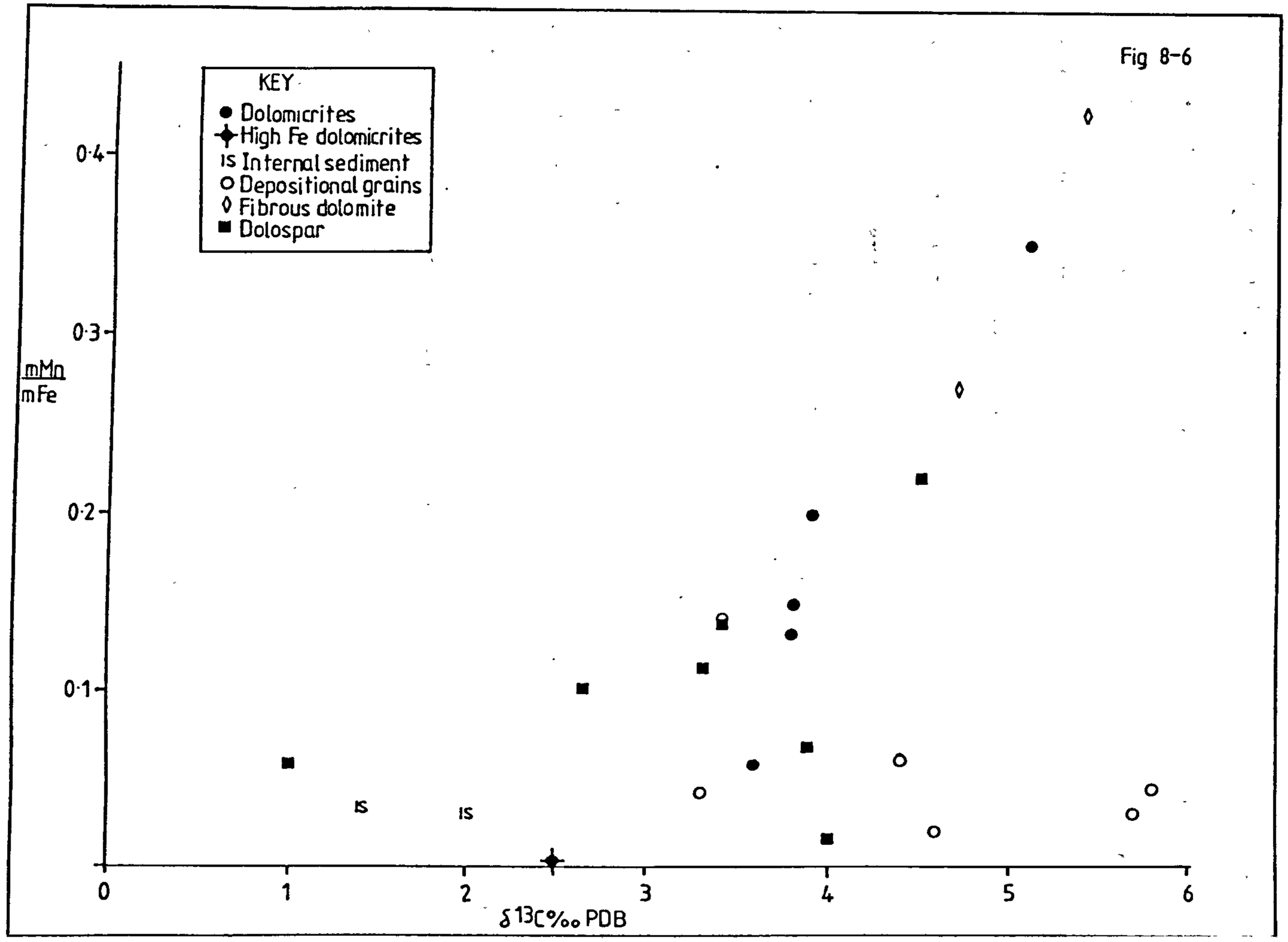


Fig 8.6 m Me/m Fe vs. $\delta^{13}C$ for Porsanger Dolomite components (see text section 8.3.3.d for discussion).

have shown that similar trends in single generations of cement beneath exposure surfaces may result from precipitation in meteoric-marine mixing zones. Although the data for fibrous dolomites come from two different units within the Porsanger Dolomite, there is sufficient data (samples 41L and 41E) from one of these (unit C) to confirm the trend. It is possible, therefore that the originally fibrous marine cements were replaced by dolomite in a shallow-subsurface meteoric-marine mixing zone. A remaining question is, did a suitable organic soil horizon, through which percolating meteoric waters could pass and inherit light $\delta^{13}C$ compositions, exist? In the absence of higher plants, it is possible that crude organic soils may have developed from accumulations of algal material (average $\delta^{13}C = -15^{o}/_{oo}$ for modern algae, Deines, 1980) along exposed tracts of the carbonate platform. Within unit C itself there is abundant evidence for subaerial exposure and desiccation of algally laminated sediments (see Chapter 6). An organic contribution to the carbon isotope reservoir by oxidation of organic carbon is also supported by Mn and Fe data, which suggest that suboxic conditions developed (see section 8.3.3.d).

Beeunas and Knauth (1985) have described distinctive stable isotope variations beneath a late Proterozoic (1.2 b.y.) subaerial exposure surface in dolomites of the Mescal Limestone, Arizona. They recognise two zones: (i) unaltered dolomites, retaining early meteoric diagenetic signatures of $\delta^{18}O = -10.7$ to $-5.1^{o}/_{oo}$ PDB (original data in SMOW, conversion after Coplen et al., 1983) and $\delta^{13}C = +3.7^{o}/_{oo}$ PDB. (ii) an altered zone, beneath the subaerial exposure surface, in which dolomite has $\delta^{18}O = -16.5$ to $-8.3^{o}/_{oo}$ PDB and $\delta^{13}C = 0^{o}/_{oo}$. They concluded that the observed variation in $\delta^{13}C$ indicates the development of a biologically active zone at the exposure surface. This in turn implies the existance of non-vascular plants within

the primitive soil. They suggest that disseminated algal colonies provide suitable candidates, and that these would have been responsible for the early production of oxygen on Precambrian continents (although unimportant compared to the marine photosynthetic contribution) and for the accumulation of significant amounts of organic carbon on the land surface.

Although distinctive soil horizons have not been seen in the Porsanger Dolomite, the suggestions of Beeunas and Knauth (1985), that subaerial exposure surfaces in the late Proterozoic may have been biologically active appears to be supported by the Porsanger data.

d) Dolospars

Dolospars are depleted in $\delta^{18}O$ relative to depostional grains and dolomicrites, and overlap with the field for fibrous dolomites. $\delta^{13}C$ ratios for dolospars fall generally between +3 and $+5^{o}/_{oo}$ PDB. By comparison with 'least altered' carbonate $\delta^{13}C$ values (c. $+ 5^{o}/_{oo}$), an essentially marine source for the bicarbonate in dolospar-precipitating solutions is suggested. This marine bicarbonate may have been derived directly from incorporated marine formation waters or may have been supplied by dissolution of marine components. Meyers and Lohmann (1985) have shown that low magnesium calcite meteoric-phreatic cements resulting from progressive rock-water interaction on a formation scale will have variable $\delta^{18}O$ and fairly constant $\delta^{13}C$. Carbon isotopic signatures are inherited from dissolving marine carbonates, whereas $\delta^{18}O$ of diagenetic phase is dominated by the oxygen reservoir of the diagenetic water and the effect of temperature on the fractionation of isotopes.

One dolospar sample with $\delta^{18}O = -8.2$ and $\delta^{13}C = +1.0$ (sample number 133.4) comes from the grainstones of unit F and differs petrographically as well as isotopically from the other dolospars. It comprises two

generations, identified by cathodoluminescence petrography and described in Chapter 7 (section 7.3.1). The first generation has a distinctive geometry suggesting a meteoric vadose to meteoric phreatic origin for the original cement. The second generation has a post-compactional origin. Both generations are included in the analysed sample and the shift away from least altered compositions supports a meteoric influence.

Cation chemistry and petrography of the majority of dolospars are consistent with an origin from late diagenetic solutions of probable meteoric or formation water composition, with elevated Fe and Mn and depleted Sr relative to marine waters (see section 8.3.3). Fluctuating fluid compositions and/or conditions of precipitation are suggested by the cathodoluminescent zonation (Chapter 7, section 7.3.3), and supported by variable chemistry and $\delta^{18}O$ values for dolospar samples.

e) Internal sediments

Internal sediments formed by partial dissolution and erosion of fibrous dolomites in a near surface marine-meteoric diagenetic environment (see Chapter 7, section 7.3.3). They may occur within fibrous dolomite sequences or may be directly overlain by dolospars.

The stable isotopic compositions of internal sediments lie on the general trend defined by ooids and fibrous dolomites and interpreted as reflecting re-equilibration of marine components with non-marine (? meteoric) waters under variable degrees of system openness.

The shift to lower $\delta^{13}C$ values suggests a relatively more open system for the formation of internal sediments compared to other components, and their overall chemistry (cation and isotopic) is consistent with a meteoric origin. Further support is added to this interpretation because of the similarity of internal sediment compositions to dolospar sample 133.4,

displaying distinctive meteoric vadose and phreatic fabrics (see d. above).

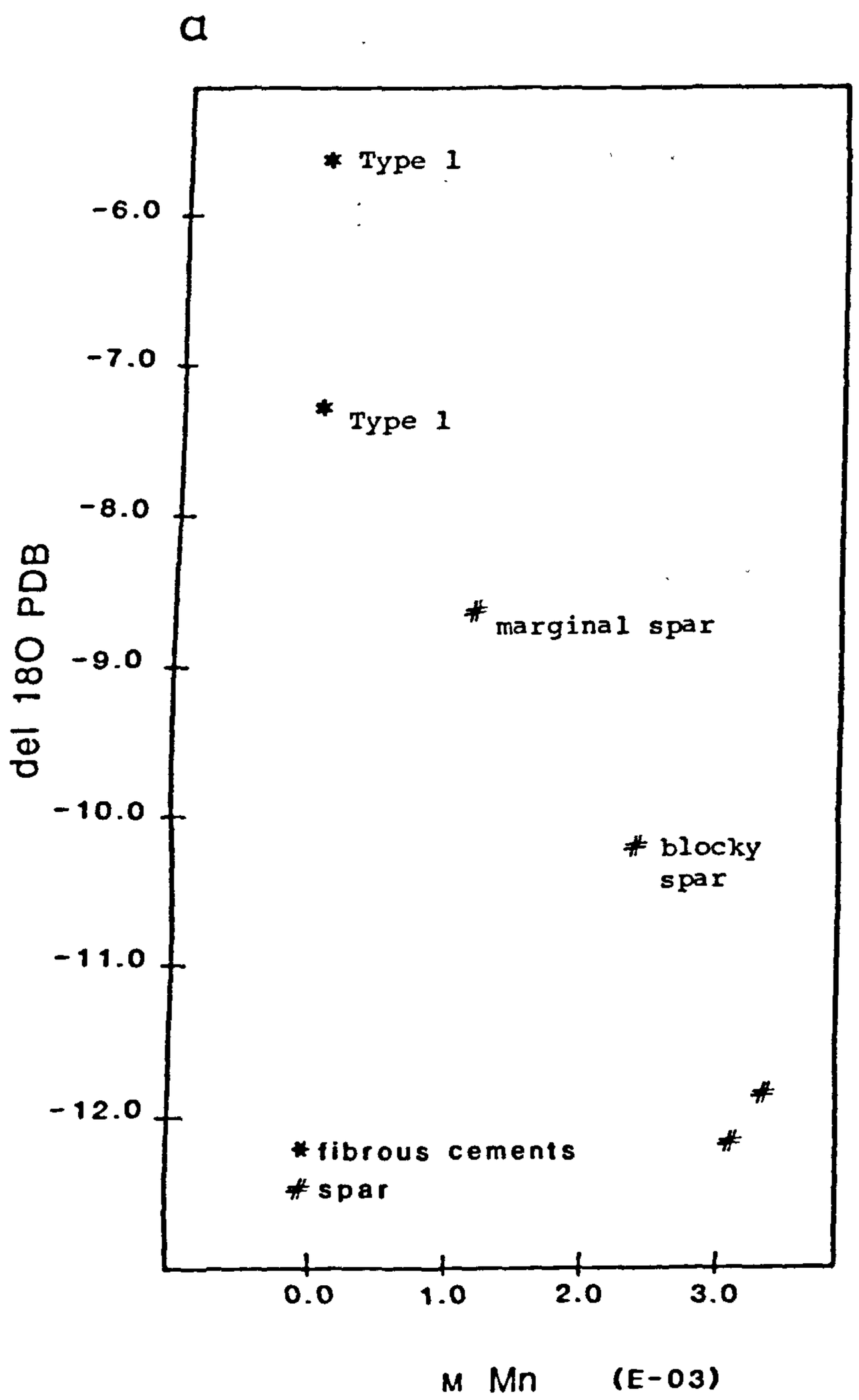
f) Individual diagenetic sequences

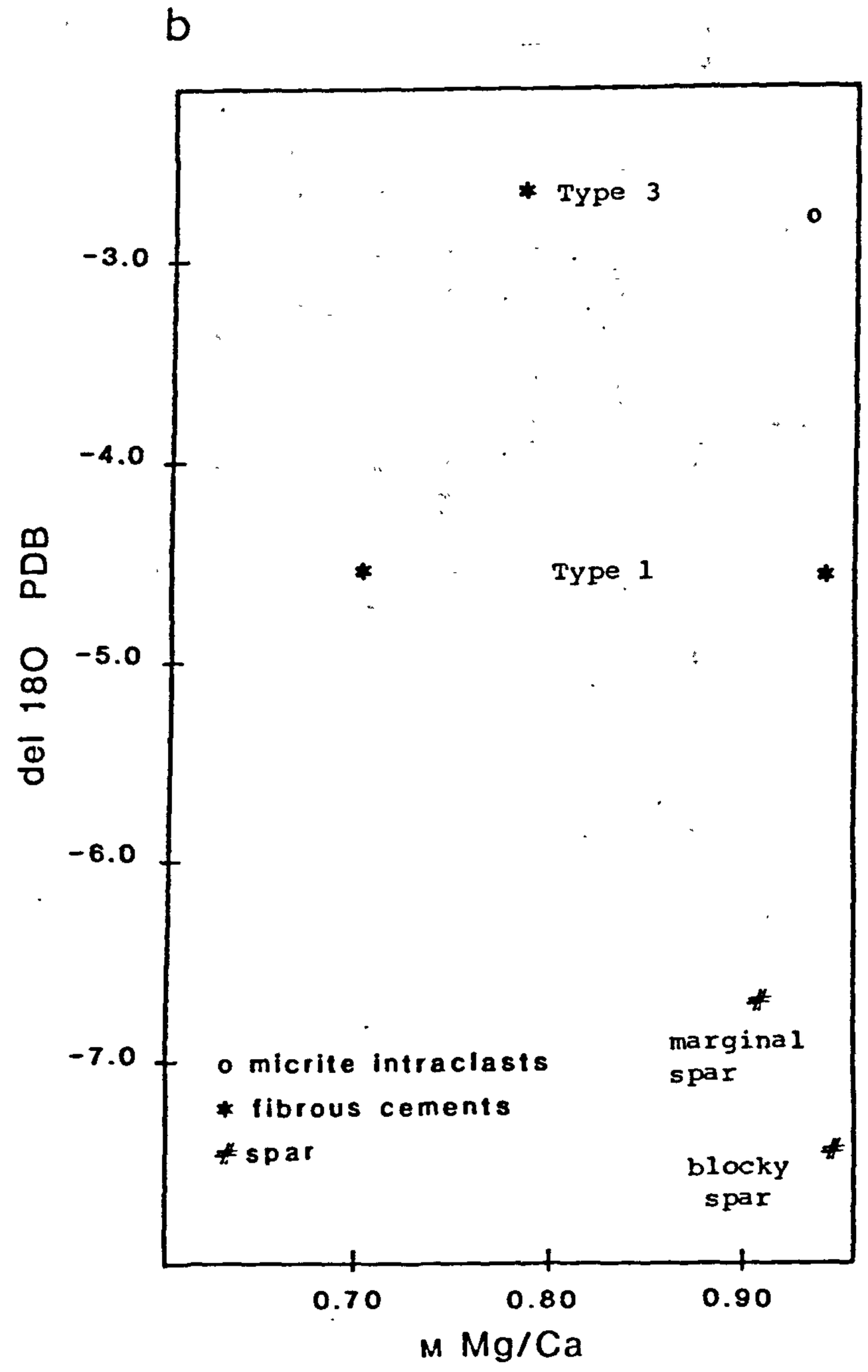
In the preceding sections (a to e), the broad between and within group variations were discussed. A trend towards more negative $\delta^{18}O$, and in some groups less positive $\delta^{13}C$, was identified and a number of suggestions as to their origin made. It was also suggested that cation chemical compositions could also be related to diagenetic setting and an attempt was made to integrate cation and stable isotopic data with petrographic interpretation. In this section a few specific examples are described, where the component samples come from single, petrographically identified diagenetic sequences, having been dissected from single or a small number of sections taken from the same hand specimen.

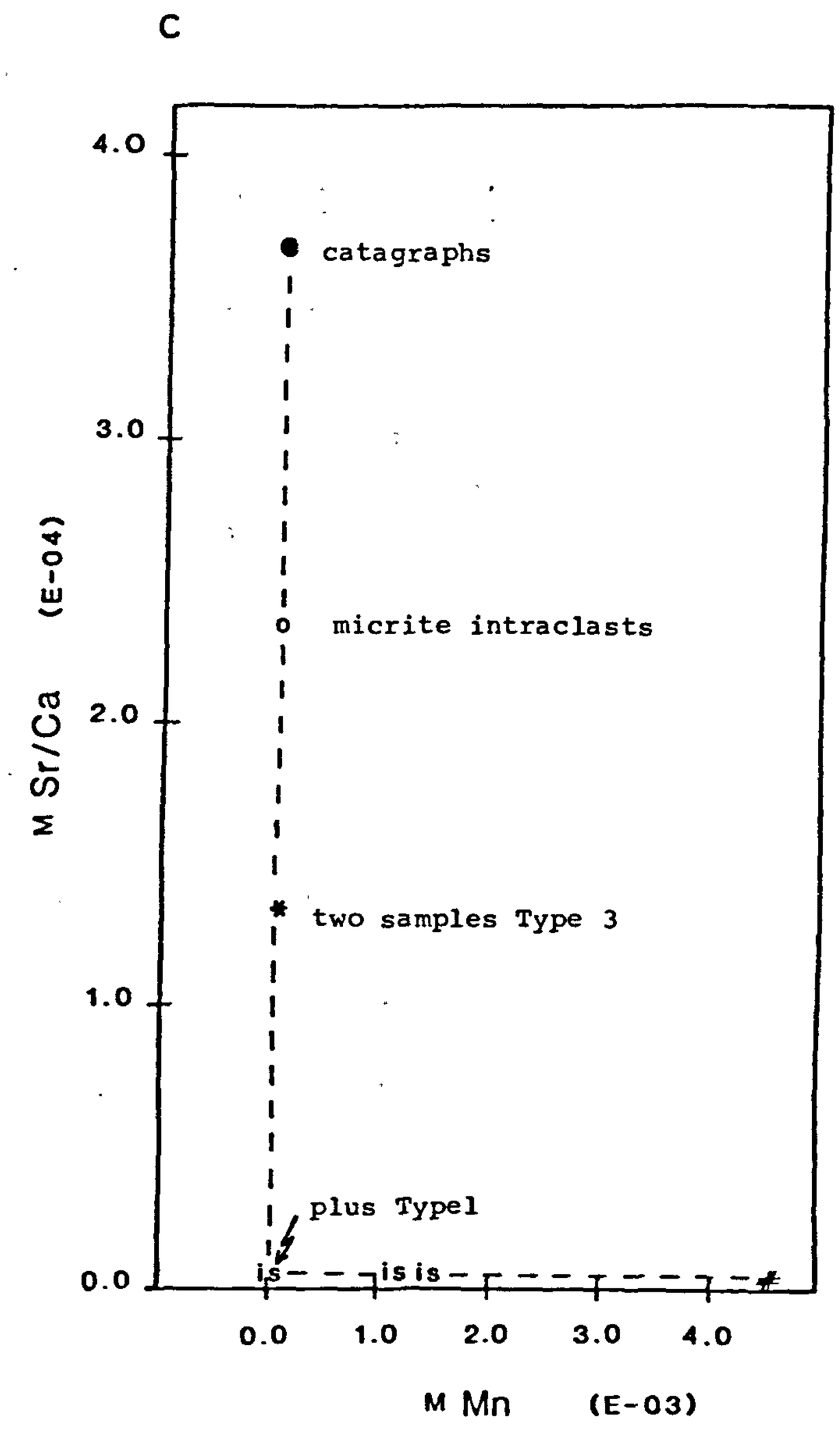
The combined stable isotope - cation chemistry data obtained from these samples confirms the general trends identified above. Some of these data are illustrated in Fig. 8.7. For example Fig. 8.7a shows increasing Mn (as mMn) with decreasing $\delta^{18}O$ from type 1 fibrous dolomites through marginal to distal dolospars in fenestral laminites from unit G. 0.0 mMn indicates Mn present below 0.01 μg/ml in solutions prepared for I.C.P.S. (see appendix2). The latest dolospars to form (confirmed by C.L. petrography) have the most negative $\delta^{18}O$ and enriched Mn compositions. The $\delta^{18}O$ trend is similarly illustrated by Fig. 8.7b (data from unit C fenestral laminites) where type 3 fibrous dolomite and micritic intraclasts have less negative $\delta^{18}O$ than type 1 fibrous dolomite, columnar (proximal) and blocky (distal) dolospars. The shift to slightly more negative $\delta^{18}O$ ratios from type 3 to type 1 fibrous dolomite may be interpreted as indicating formation of type 1 from more depleted fluids and/or at elevated temperatures relative to type 3 fibrous dolomite or micritic intraclasts.

Fig 8.7 Variations in $\delta^{18}O$ and cation chemistry for individual diagenetic sequences (see text section 8.4.2.f for discussion).

Fig 8-7


a
* Type 1
* Type 1
# marginal spar
# blocky spar
* fibrous cements
# spar
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
del 18O PDB
0.0
1.0
2.0
3.0
M Mn (E-03)


b
* Type 3
o
* Type 1
*
o micrite intraclasts
* fibrous cements
# spar
# marginal spar
blocky spar
-3.0
-4.0
-5.0
-6.0
-7.0
del 18O PDB
0.70
0.80
0.90
M Mg/Ca


c
catagraphs
o micrite intraclasts
* two samples Type 3
plus Typel
is is is
4.0
3.0
2.0
1.0
0.0
M Sr/Ca (E-04)
0.0
1.0
2.0
3.0
4.0
M Mn (E-03)

Assuming homogeneous fluid compositions and equilibrium fractionation, a temperature increase of c.13°C is implied by the $\delta^{18}O$ shift from type 3 to type 1 fibrous dolomite (using equation of Irwin, Curtis and Coleman, 1977; see Chapter 4, section 4.3.1). Such a large temperature change suggests formation of fibrous dolomites occurred progressively during burial. This is incompatible with the petrographic evidence for an early diagenetic, pre-burial-compaction origin, and a change in porewater $\delta^{18}O$ composition must be proposed.

Figure 8.7c shows the variation of Mn versus Sr (as mSr/mCa) in components of a fenestral laminite from unit C. 0.0 mSr/mCa and mMn indicates samples with <0.01 μg/ml Sr or Mn in solutions prepared for I.C.P.S. The samples range from catagraphs, micritic intraclasts and fibrous dolomites through internal sediments to dolospars, representing progressively later diagenetic phases. The trend in Sr vs. Mn is typical of the Porsanger Dolomite as a whole and the implications of these trends have already been discussed (see section 8.3.3 above). As with stable isotopic compositions, there is a shift to lower Sr from type 3 to type 1 fibrous dolomites. This is consistent with the stable isotope data of Fig. 8.7b and suggests more open system conditions (with respect to Sr) or equilibration with more dilute solutions during formation of type 3 fibrous dolomite.

<u>To summarize</u>: Stable isotopic data from the various Porsanger Dolomite components may be interpreted in conjunction with cation chemistry data, providing petrographic constraints are applied. The possible significance of individual variations has been discussed in the preceding sections; however, an overall interpretation of stable isotope data is given in Fig. 8.8 and the broader significance of this is discussed in the following

Fig 8-8

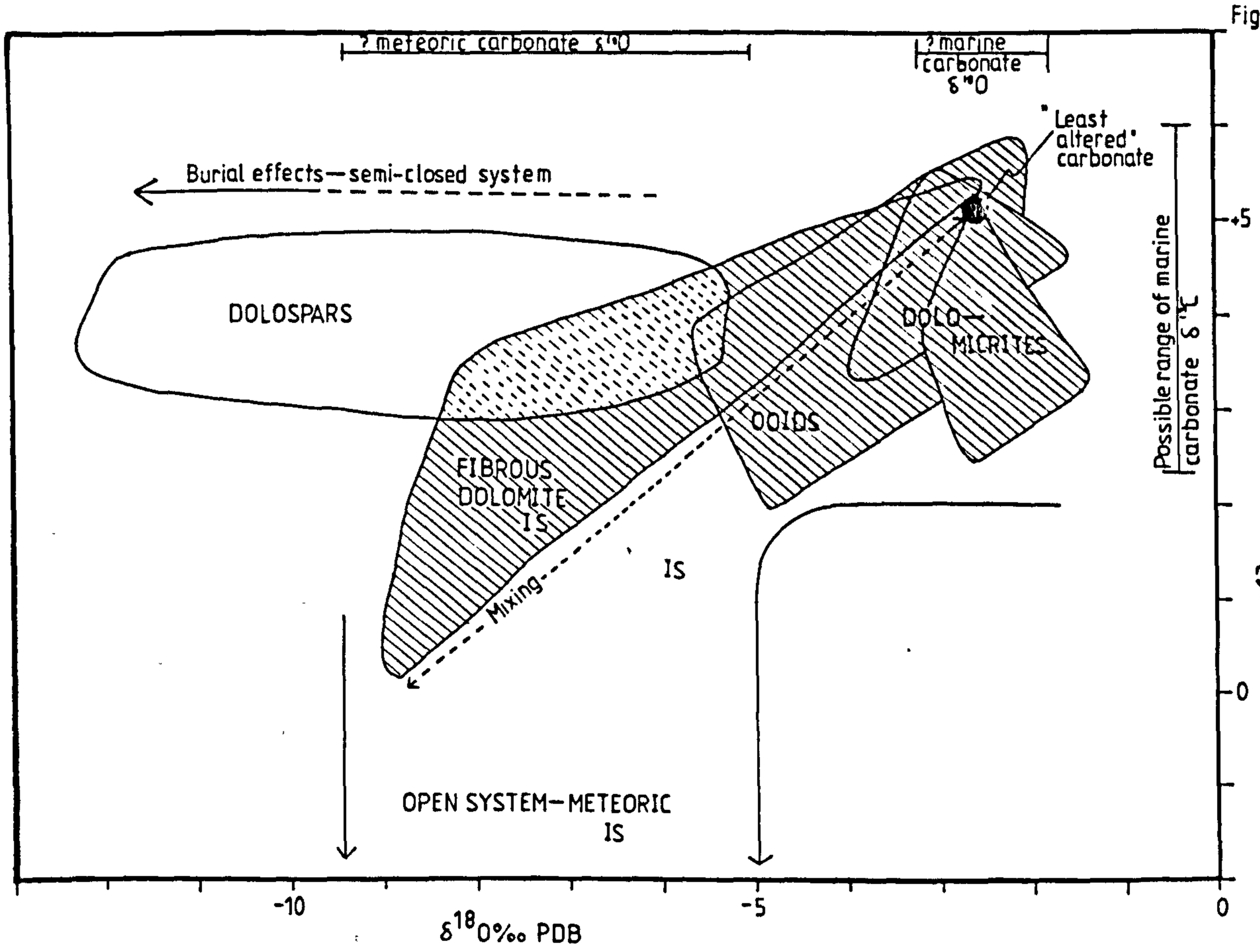


Fig 8.8 Interpretation of stable isotope variations in the Porsanger Dolomite, constrained by petrographic interpretation and cation chemistry data. Shaded area indicates depositional and early diagenetic component fields.

sections.

8.4.3.a Significance of Porsanger Dolomite $\delta^{18}O$ to secular variations in marine carbonate

The isotopic composition of ancient oceans and by implication all natural waters, is a matter of some debate (see discussion in Anderson and Arthur, 1983). The subject has received considerable attention since the publication of data compilations showing secular variations in the isotopic composition of ancient carbonates and cherts (e.g. Degens and Epstein, 1962; Keith and Weber, 1964; Veizer and Hoefs, 1976). In particular there is a tendancy for $\delta^{18}O$ of marine carbonate rocks and chert to decrease with increasing age. The Porsanger Dolomite data fall within the range of Proterozoic dolomites given by Veizer and Hoefs. Various explanations of these trends have been proposed, however and the following alternatives are based on the discussion by Anderson and Arthur (1983) with original references in parentheses. They will be evaluated both by reference to general data and to the Porsanger Dolomite.

Alternative 1

$\delta^{18}O$ depleted cherts and carbonates have been subjected to continuous post-depositional exchange with warm and/or isotopically light (meteoric) water. Thus their isotopic compositions represent conditions of burial diagenesis and not the temperature and isotopic composition of seawater from which they precipitated (Degans and Epstein, 1962; Keith and Weber, 1964).

Alternative 2

Cherts and carbonates have not been signficantly altered and the age trends represent precipitation at continuously decreasing temperatures

(higher in past) from an ocean of constant $\delta^{18}O$ (Knauth and Epstein, 1976; Knauth and Lowe, 1978). A consequence of this hypothesis is that the climate in Proterozoic times was significantly warmer than modern climate (Perry and Ahmad, 1983).

Alternative 3

Cherts and carbonates are unaltered, but the age trends represent precipitation at constant temperature from an ocean of continuously increasing $\delta^{18}O$ (lower in the past) (Perry, 1967; Perry and Tan, 1972).

Each of these interpretations suffers major drawbacks. The first requires that older rocks have suffered continuous post-depositional exchange, which presumably (although not necessarily, Hudson, 1977) was achieved via solution-precipitation reactions. These ought to produce marked textural changes. No such textural evolution (i.e. older carbonates more 'recrystallised' than younger) has been observed (Anderson and Arthur, 1983). In the Porsanger Dolomite primary depositional and diagenetic fabrics are well preserved and the rocks are characterised by their chemical heterogeneity. Whilst this could be interpreted as reflecting incomplete solid state isotopic exchange (Hudson, 1977), the trend towards lighter (most altered) values in coarser grained, and therefore less reactive, phases argues against this. Alternative 1 therefore seems unlikely as an explanation of the Porsanger Dolomite and perhaps all ancient carbonates (Anderson and Arthur, 1983).

Considering alternative 2 (hot Proterozoic oceans) 'least altered' marine components in the Porsanger and Beck Spring Dolomites ($\delta^{18}O$ = -2.5 and -2$^{o}/_{oo}$ respectively) suggest seawater temperatures between 30 and 40°C assuming a seawater composition equivalent to Pleistocene preglacial oceans (-1$^{o}/_{oo}$ SMOW; -1.2$^{o}/_{oo}$ PDB, Shackleton and Kennett, 1975) and assuming

equilibrium fractionation (see Fig. 4.7, Chapter 4). Perry and Ahmad (1983) carried out similar calculations (assuming post-glacial seawater, $0^{o}/_{oo}$ SMOW) on Lower Proterozoic cherts and derived a seawater temperature of c.60°C. However, they dismissed this interpretation because of the close association with glacial deposits and instead suggested that Proterozoic seawater may have been depleted by up to $20^{o}/_{oo}$ relative to modern seawater. This interpretation (alternative 3) requires no major differences between Proterozoic and modern climates (although does not discount them) and is based on changing chemical interaction of the crust, mantle and hydrosphere (see Veizer et al., 1982). Perry and Ahmad (1983) provided further indirect evidence against hot Proterozoic seawater in the form of interpreted brackish water iron formations in the late Archaean of Western Australia. This implies a hydrologic regime similar to today, with significant equator-to-pole temperature gradients allowing Raleigh fractionation of meteoric water and thus $\delta^{18}O$ depleted rain. Increased surface temperatures (alternative 2) would interfere with this system by increasing the water content of the atmosphere, thereby improving global atmospheric heat transfer and reducing thermal gradients. Further support for this interpretation may also come from the Beck Spring limestone data, where early meteoric diagenesis is interpreted to have produced $\delta^{18}O$ depleted marine depositional components (Zempolich, Lohmann and Wilkinson, 1985). The difference of c.$8^{o}/_{oo}$ between $\delta^{18}O$ of calcitic and dolomitic depositional components in the Beck Spring (Fig. 8.5) is greater than would be expected (0 to $6^{o}/_{oo}$, see Chapter 4) if the minerals had precipitated at equilibrium from the same fluid, and was interpreted by Zempolich, Lohmann and Wilkinson (1985) as suggesting a marine or restricted marine origin for the dolomite (c.f. meteoric for the calcite). The shift in $\delta^{18}O_{water}$

composition between marine and meteoric water thus implied (c.4$^{o}/_{oo}$) is consistent with modern values in mid- to low latitudes (see Anderson and Arthur, 1983, Fig. 1.12).

The situation in the Beck Spring Formation, whereby dolomitic components reflect more closely the original marine isotopic composition, is as predicted by Perry and Ahmad (1983) and may be generally applicable to mixed carbonate formations, providing independant petrographic and geochemical criteria confirm the origin of the different phases.

The similarity of 'least altered' components in the Porsanger and Beck Spring Dolomites adds support to a marine interpretation of the Porsanger data. Considering alternative 3, these data suggest Proterozoic seawater had a $\delta^{18}O$ of c.-2 to -4$^{o}/_{oo}$, assuming equilibrium fractionation at 25^{o}C (see Fig. 4.7). This value is somewhat heavier than the estimates of Perry and Ahmad (1983) and may indicate a different temperature of formation and/or formation from more restricted (evaporated) seawater.

Whilst a marine involvement is clearly implied, and certainly necessary from mass balance point of view (as supply for Mg^{2+}) a meteoric influence on early diagenesis is also strongly suggested by mixing-zone $\delta^{18}O$ vs. $\delta^{13}C$ trends in fibrous dolomites in the Porsanger and by trace element and petrographic data for various components (see above). Further evidence comes from the Beck Spring where meteorically stablised limestones are found. Taking $\delta^{18}O$ of <u>most</u>-altered fibrous dolomites from the Porsanger and low-magnesium calcite components from the Beck Spring (-8.9 $^{o}/_{oo}$ and -10.2 $^{o}/_{oo}$ respectively), meteoric water compositions of $\delta^{18}O$ -10$^{o}/_{oo}$ and -8$^{o}/_{oo}$ are suggested by the Porsanger dolomites and Beck Spring calcites respectively (assuming equilibrium fractionation at 25^{o}C according to the relationships shown in Figs. 4.6 and 4.7). Modern meteoric water

(precipitation) has $\delta^{18}O$ between +2 and $-24^{o}/_{oo}$ SMOW (average = $-4^{o}/_{oo}$), depending on latitude, altitude and temperature of evaporation/condensation (Anderson and Arthur, 1983). As already explained, the relative difference between marine and meteoric water (marine-meteoric) $\delta^{18}O$ compositions implied by the Beck Spring data are consistent with a mid- to low-latitude origin, by comparison with fig. 1.12 in Anderson and Arthur (1983). The Porsanger fibrous dolomite data, if they represent a marine-meteoric mixing trend as suggested, indicate a marine-meteoric difference of c. $8^{o}/_{oo}$ suggesting an unlikely mid- to high-latitude of formation. However, such an interpretation involves several gross assumptions, which include: (i) equilibrium fractionation of end-member phases with fluids of marine and meteoric (precipitation) ^{18}O composition respectively, at constant temperature and (ii) a hydrologic regime similar to the present. Whilst the latter may be justified (see preceding discussion), the former are probably not, and therefore place severe constraints on precise interpretation (see preceding sections and Chapter 4, section 3).

8.4.3.b Significance of $\delta^{13}C$ values

A range of $\delta^{13}C$ values from -1.4 to $+6^{o}/_{oo}$ PDB are seen in components from the Porsanger Dolomite. These fall within the range of Proterozoic dolomite values compiled by Veizer and Hoefs (1976). It is clear from the preceding discussions that some of the Porsanger data may reflect diagenetic alteration and the introduction of isotopically light organic-derived carbon (sections 8.3.3.d and 8.4.2.c). It is possible; however, to define a field of least altered compositions (viz. $\delta^{13}C$ + 2 to + $6^{o}/_{oo}$ PDB), which may represent approximate compositions of marine carbonate for the late Proterozoic. A similar approach to data from the mid-late

Proterozoic Beck Spring Dolomite yields a value around $+4^{o}/_{oo}$ (see Fig. 8.5).

Modern shallow marine carbonates have $\delta^{13}C$ values in the range 0 to $+4^{o}/_{oo}$ PDB (Hudson, 1977; Anderson and Arthur, 1983) and approximately reflect marine total dissolved inorganic carbon (TDC) $\delta^{13}C$ values (around $0^{o}/_{oo}$). Departures in the $\delta^{13}C$ of ancient shallow marine carbonate from modern values may therefore reflect changes in the $\delta^{13}C$ of TDC relative to modern seawater (Anderson and Arthur, 1983).

There are two major sedimentary reservoirs for carbon, one is TDC in seawater the other is organic carbon. Organic carbon has very negative $\delta^{13}C$ (range -20 to $-30^{o}/_{oo}$ PDB, Hudson, 1977) because of the preferential incorporation of ^{12}C during photosynthesis. Increases in the rate of burial of ^{12}C-enriched organic carbon, due to increased organic productivity or preservation potential of organic carbon, relative to the amount of carbonate being precipitated will therefore lead to a heavier isotopic composition (^{13}C enriched) of TDC (Mackenzie and Pigott, 1981; Anderson and Arthur, 1983), and therefore also in precipitating carbonates. Tucker (1985b) has suggested that two significant positive excursions in carbonates of the Precambrian-Cambrian boundary beds of Morocco can be interpreted in terms of increased levels of organic productivity. He relates a late Riphean excursion (to $+7^{o}/_{oo}$) to the radiation of eukaryotic plankton. The second excursion (to $+ 3^{o}/_{oo}$) may be related to a period of metazoan evolution and a further radiation of microplankton around the Tommotion-Atdabanian boundary (Tucker, 1985b). Background $\delta^{13}C$ values around $0^{o}/_{oo}$ for beds above the Precambrian-Cambrian boundary and between 0 and $-5^{o}/_{oo}$ for older beds suggest that the observed positive excursions represent departures from TDC $\delta^{13}C$ values equivalent to or lighter than

modern seawater TDC (see also Anderson and Arthur, 1983; Veizer, 1984).

The significance of the $\delta^{13}C$ data for the Porsanger and Beck Spring Dolomites cannot easily be assessed in terms of secular variation because they essentially represent single time intervals and show no apparent stratigraphic variation. However, added to an extrapolation (back in time) of Tucker's (1985b) curve, or plotted on Veizers' curve (fig. 4 in Veizer, 1984), showing $\delta^{13}C$ for late Precambrian carbonates around $-1^{o}/_{oo}$, they appear to indicate that mid-late Proterozoic seawater TDC was significantly more positive than in the latest Precambrian (Tucker, 1985b) or than suggested by compilations of carbonate whole-rock data (Veizer and Hoefs, 1976; Veizer, 1984).

CHAPTER 9

Summary and discussion: Late Precambrian Porsanger Dolomite

The purpose of this chapter is to review the main conclusions and observations from the three preceding chapters and to go on to briefly discuss how the principal conditions considered necessary for dolomitisation (viz. a source of Mg^{2+}, a supply mechanism and a suitable chemical environment) may have been achieved. In Chapter 10 the broader implications of the Porsanger Dolomite will be discussed by reference to the Dinantian dolomites of South Wales and the geological record of dolomites.

9.1 The main conclusions from the preceding chapters, dealing with the broad tectono-sedimentary, palaeoenvironmental background, and the petrography and geochemistry of the Porsanger Dolomite may be summarized as follows:

1) The Porsanger Dolomite was deposited on a shallow marine carbonate platform which became established at the north-west margin of a subsiding sedimentary basin (the Finnmark basin) situated between the Fennoscandian landmass or shield area and a basement high (the Finnmark ridge), bordering the Iapetus Ocean. Principal controls on the deposition of the Porsanger Dolomite were probably the prevailing climate (arid or semi-arid) and the lack of significant terrigenous detritus, due to successful peneplanation of surrounding landmasses. The carbonate platform was regionally extensive, covering an area of approximately 200 x 80km.

2) The principal lithofacies in the Porsanger Dolomite are (i) subtidal stromatolite biostromes, (ii) shallow subtidal to low intertidal cross

bedded carbonate sands: flakestones, grainstones and oolites and (iii) intertidal to supratidal cryptalgal laminites, dolomicrites and thin bedded grainstones and flakestones of storm origin. These facies exhibit a cyclicity (shallowing-upward cycles) which probably resulted from a combination of basin subsidence ($\pm$ eustatic effects) and tidal flat progradation and is characteristic of ancient platform carbonates (Tucker, 1985a).

3) The post-depositional burial history of the Porsanger Dolomite is difficult to assess. A minimum burial depth of 4km is possible; clearly the rocks did not reach the metagenetic stage of Tissot and Welte (1978) because mineral compositions and textures appear well preserved (see below).

4) Petrographic and geochemical study of the Porsanger Dolomite reveals a textural and chemical heterogeneity suggesting preservation of primary marine and early diagenetic features, despite being composed almost entirely of dolomite. The reader is referred to Chapters 7 and 8 for detailed discussion, however the following conclusions may be drawn.

5) Dolomicrites have fabrics suggesting early diagenetic-syndepositional-lithification, allowing incorporation of dolomicrite flakes and grains in carbonate sands. The well ordered and near-stoichiometric character of the dolomite composing the dolomicrites supports an early diagenetic origin, suggesting a relatively open (with respect to Mg^{2+}) system, and implicating seawater. Relatively high Sr and low Fe and Mn (although see Chapter 8, section 8 for discussion) are also consistent with an early diagenetic origin. Dolomicrites show the least variable stable isotopic compositions, which in combination with the above and, because of the common overlap with marine depositional grain compositions are interpreted as approximate

marine or least-altered marine carbonate values (see Fig. 8.8).

6) Depositional grains (ooids) and fibrous dolomites have fabrics which may be primary and probably reflect fabric retentive replacement of a marine precursor [HMC, A or Ca-dolomite]. It is suggested that early replacement dolomitisation in the Porsanger can be regarded as a stabilisation reaction, similar to the HMC-LMC (paramorphic) replacement in limestones. This hypothesis is supported by geochemical data, which in general terms suggest stabilisation with meteoric (i.e. Sr depleted, Fe and Mn enriched) water, producing distinctive stable isotopic trends, reflecting variable fluid composition and/or system openness (Fig. 8.8). The introduction of isotopically light (^{12}C enriched) carbon via a subaerial exposure surface is also suggested.

7) Internal sediments, representing dissolution or abrasion of fibrous dolomites and introduction of fine carbonate mud during tidal flat accretion and exposure, lie on a stable isotopic trend consistent with the above interpretation. The interpretation is strengthened by the occurrence on the same trend of a dolospar which displays distinctive first generation meteoric vadose and phreatic fabrics.

8) Dolospars are clearly second generation cements and show CL fabrics which suggest they formed by direct precipitation from fluids of fluctuating composition and/or under fluctuating conditions of precipitation. A late diagenetic origin is supported by relatively low Sr and high Fe and Mn contents, but their variability confirms C.L. interpretation. A marine-carbonate source of carbon isotopes (rock dominated system) is suggested by $\delta^{13}C$ data. $\delta^{18}O$ variations reflect a water dominated system and indicate fluctuating water compositions and/or temperatures of precipitation for the dolospars.

9) 'Least altered' isotopic compositions for the Porsanger Dolomite components offer a reasonable approximation to Proterozoic marine carbonate values. It is suggested that early diagenetic replacement dolomites, such as those in the Porsanger and Beck Spring Dolomites have a greater potential for retaining original or only slightly modified marine isotopic compositions than limestones which frequently show meteoric diagenetic alteration. The reason for this is the requirement for Mg^{2+} for dolomitisation, which in an early diagenetic setting is most likely to have been seawater. Thus marine carbonate (depositional grains and cements) will be dolomitised by fluids with a signficant if not dominant seawater component. Preservation of marine isotopic composition is even more likely if dolomitisation is the primary stabilisation reaction, as suggested here for the Porsanger and Beck Spring dolomites.

The discussion will now turn briefly to a consideration of the likely processes of dolomitisation in the Porsanger Dolomite.

9.2.1 Early diagenetic dolomite

If high magnesium calcite or poorly ordered Ca-dolomite was the precursor to early diagenetic dolomite in the Porsanger, then a partially autochthonous source of Mg^{2+} for dolomitisation may be proposed. However to produce the observed pervasive dolomite fabrics an allochthonous supply of Mg^{2+} is required. Seawater was the principal source of this Mg^{2+}, however an active supply mechanism and suitable chemical environment for dolomitisation are also required. The most likely hydrological flow processes to have operated on the Porsanger carbonate platform are reflux and fresh-water lens flow (see Chapter 5 section 5.5). Prograding tidal flats (as in the Porsanger) are potentially important locations for fresh-

water lens (mixing zone) flow (Simms, 1984b; Tucker, 1985a). However, the absence of evaporites from the main body of the Porsanger does not necessarily preclude the application of a reflux model either. As discussed in section 5.5, slightly elevated salinities developed across a wide platform due to progressive evaporation of seawater may permit the development of reflux systems and hence the potential for dolomitisation. This is particularly likely in a cyclical shallowing-upward depositional setting, such as that represented by the Porsanger Dolomite. Similar shallowing-upward cycles, probably due to local basin tectonics have been reported from the Middle Proterozoic Altyn Formation in the Belt Supergroup, Montana by White (1981). He suggested that 'cyclical' dolomitisation of intertidal-subtidal carbonates occurred during repeated progradation of evaporitic, high-intertidal to supratidal facies. In the Porsanger, the evidence for frequent subaerial exposure, the suggestion of a semi-arid climate and petrographic and geochemical data suggesting significant meteoric influence during early diagenesis favour a marine-meteoric mixing-zone interpretation as this would also provide a suitable chemical environment for dolomitisation. The proposed system, controlled essentially by depositional progradation and climate is therefore similar to that suggested for pervasive dolomite formation in the Dinantian of South Wales (see Chapter 5 section 5.5 and Fig. 5.3, Table 5.1), except in the Porsanger it operated on a smaller scale both in time and space. Four or five progradational (shallowing-up) cycles are recorded in the 150 metres of the Porsanger Dolomite represented by exposures around Porsangerfjord. Taking modern non-reef carbonate depositional rates (0.5-1m $10^3 yr^{-1}$) and rates of tidal flat progradation (several km yr^{-1}) (Tucker, 1985a), the existing Porsanger Dolomite may have accumulated in as little

as 150,000 years (not accounting for post-depositional compaction or periods of relative still-stand or emergence and non-deposition). By comparison with Fig. 5.4, this implies relatively high rates of early dolomitisation, even allowing for the proportion of later dolomite in the total mass, but is compatible with the suggestion that dolomitisation represents a stabilisation reaction.

9.2.2 Late diagenetic dolospars

Possible sources of Mg^{2+} for dolospars have already been considered (Chapter 8, section 8.3.3.e). To summarize,it is suggested that adjacent shales may have provided Mg^{2+} during burial compaction (via expelled interstital water and clay mineral transformation), an autochthonous source (i.e. within Porsanger Dolomite) may also be suggested (redistribution of Mg^{2+} from early dolomite?). The problem of burial dolomitisation has been discussed in Chapter 5 (section 5.8) and need not be repeated here; however, the ability of any of the suggested sources to supply sufficient Mg^{2+} for more than local pore-filling cements is questioned (Morrow, 1982b; Land, 1985). However, as late diagenetic dolomite in the Porsanger is essentially a cementing phase these sources may be viable.

The origin of dolomitising fluids is similarly problematic. Compaction driven flow of formation waters is one possible explanation. Alternatively, or perhaps additionally, meteoric (?) surface waters may have been introduced updip. The present allochthonous position of the Porsanger Dolomite precludes any serious attempt to model flow systems during burial, before nappe translation.

As will be discussed further in Chapter 10, study of the Porsanger Dolomite may be able to offer additional data to broader considerations,

such as the apparent secular trends in marine carbonate mineralogy. This discussion will be particularly concerned with the early diagenetic dolomite; however, the possible significance of ubiquitous dolospar cement deserves consideration and may also be a signal of some larger scale control.

CHAPTER 10

Dolomite petrography and geochemistry - summary and discussion

10.1 Introduction

This chapter presents a general discussion of the main conclusions of this study. The broad sedimentological and tectonic setting and petrographic and geochemical character of the two studied formations are discussed and their significance to studies of other ancient dolomites suggested. The principal concern in any study should be the determination of a suitable source of Mg^{2+}, a supply mechanism and a suitable chemical environment for dolomitisation. It has been shown that these requirements are more likely to be met in depositional-tectonic settings where Mg^{2+} bearing fluids are actively pumped through calcium carbonate sediments (see Chapter 5). Within marine carbonate depositional/early diagenetic environments seawater is the only significant Mg^{2+} source for massive dolomitisation. The additional requisite, for a suitable chemical environment, provides a further constraint on interpretation. Overall, massive pervasive stratal dolomites are likely to be the products of early diagenesis on shallow carbonate platforms, shelves or ramps. Later diagenetic addition of dolomite and/or alteration (?stabilisation) of existing phases is volumetrically less important but may be significant in terms of (i) interpretation of geochemical data and (ii) porosity characteristics of dolomites. The latter is a particularly important factor, governing the hydrocarbon reservoir potential of dolomites.

The significance of dolomites to larger scale, global studies of secular variations in seawater, and geotectonic implications are discussed in section 10.4.

10.2 Sedimentological-tectonic setting

The studied dolomite formations, from the Dinantian of South Wales and the Proterozoic of Norway, occur within shallow carbonate platform/ramp sequences, in common with the majority of ancient massive pervasive dolomites (see Chapter 1). Several phases of shallowing are evident in both the studied sequences, in the case of the Dinantian example more than one scale of cyclicity may be recognised. In both examples a depositional control on dolomitisation appears to have been important, at least for the demonstrably early diagenetic phases which generally form the most important component.

The broad geotectonic setting is of course that which controls carbonate sedimentation. Essentially, this requires a lack of siliciclastic sediments and is a product of geotectonic control on hinterland topography and drainage (Tucker, 1985a). The morphology of shallow-marine carbonate depositional environments (platform vs. shelf vs. ramp) is determined by geotectonics, which together with climate also controls depositional processes via effects on sea level, the position and orientation of shorelines, the energy level and direction of storm and tidal currents and larger scale circulation patterns. Rates of tectonic subsidence in combination with eustatic effects also control the state of transgression or regression. In the studied dolomites, the demonstrated link between depositional and dolomitisation processes implies a geotectonic-climatic control. Similarities with other ancient dolomites (see Chapters 5 and 9) suggests that these controls are broadly applicable, and attempts should be made to relate these factors in other studies.

10.3 Petrography and geochemistry

Petrography and geochemical data for dolomites should provide constraints on the timing and diagenetic environment of dolomitisation. In combination with sedimentological and tectonic information this should allow the formulation of dolomitisation models which incorporate a source and supply mechanism for Mg^{2+} and a suitable chemical environment for dolomitisation.

The relative timing of dolomite formation within a paragenetic scheme is of fundamental importance to an understanding of any dolomite body. In the case of pervasively dolomitised rocks, such as those studied here, this may be difficult unless dolomite bodies can be traced laterally into partially dolomitised limestones (e.g. pervasive dolomites in the Dinantian of South Wales) or where dolomite mosaics comprise distinct types of dolomite which can be related to other phases and/or diagenetic events (e.g. the Porsanger Dolomite and some mosaics in the Dinantian dolomites).

Dolomite selectivity and the degree of fabric-retention upon dolomitisation may give further clues to the timing of dolomite formation with relation to the pre-dolomitisation history. In the pervasive dolomites of the Dinantian, depositional mineralogy (predominantly calcite), grain size and pre-dolomitisation exposure to meteoric water have affected dolomitisation potential and influenced dolomite selectivity. The resulting mosaics are poorly fabric retentive, even though the dolomite may be regarded as an early diagenetic phase. In contrast, the late Proterozoic Porsanger Dolomite displays excellent fabric preservation of many depositional and early diagenetic components. This dolomite is interpreted as a stabilisation replacement of marine (and meteoric?) components and it is suggested that primary mineralogy (probably HMC) is a

significant control (see section 10.4 for further discussion). There is no apparent selectivity in the Porsanger because all components are now replaced by dolomite.

Geochemical data for dolomites should be treated largely in support of petrographic and broader sedimentological interpretation. They can provide useful constraints and may allow development of interpretation. For example, ordering and stoichiometry data may provide an indication of the openness of the dolomitising system (see Chapter 4, section 4.1.2 for example). There does appear to be a variability in the data for the studied dolomites, which together with petrographic and other geochemical data (viz: Fe, Mn, Sr and $\delta^{13}C$) can be related to system openness. Although overall, it should be stressed that a relatively open system (with respect to Mg^{2+}) is required in all cases of pervasive dolomitisation.

Cation chemistry variations in dolomites, principally in Sr, Mn, Fe and possibly Na, may provide supporting data to petrographic interpretation. In combination with trends in stable isotope data it may be possible to implicate specific geochemical processes in the formation of dolomite. For example, the oxidation of organic matter may produce distinctive trends in Mn, Fe and $\delta^{13}C$ data in diagenetic carbonates. Uncritical interpretation of minor and trace element concentrations in terms of dolomitising environments or fluids is cautioned against. The use of Na data from dolomites in this way, is particularly susceptible to ambiguous interpretation (see Chapter 4, section 4.2.2.a).

In conclusion, determination of the relative concentrations and trends for several cations is suggested as a suitable adjunct to petrographic and stable isotope studies. In this study, a series of effective distribution coefficients (termed D) have been determined for dolomite in different

diagenetic environments see Table 4.1 and 8.2, clearly these are of no quantitative value; however, it would be useful for comparative purposes if similar coefficients could be presented in other studies where the diagenetic fluid can be reasonably constrained. In the case of fluid inclusion studies or studies of extant dolomitising systems these fluids may be determined with more accuracy, in which case effective D may be more meaningful.

Stable isotope data for dolomites provide further constraints on interpretation of petrographic and other data. $\delta^{13}C$ values supply information about the source of the carbon. In the case of most platform dolomites, including those studied here, there appears to be relatively little variation in $\delta^{13}C$ values, indicating insignificant accumulation and oxidation or fermentation of organic matter in shallow marine carbonate sediments, most being oxidised rapidly in the depositional environment. In the studied dolomites, $\delta^{13}C$ variations can be related to system-openness and localised development of reducing conditions, indicating the presence of organic matter and allowing the incorporation of Fe^{2+} and Mn^{2+} in precipitating dolomite (see Chapter 4 section 4.2.2.b and Chapter 8 section 8.3.3.d).

$\delta^{18}O$ data for dolomites reflect both the temperature of precipitation and the $\delta^{18}O$ composition of dolomitising fluids. It may be possible to determine the controlling factors if the diagenetic environment can be constrained by other data. In particular, petrographic data, allowing the timing of dolomite formation in relation to other recognisable diagenetic phases and to the burial history of the rocks. More specific interpretation and discussion of stable isotope data are given in Chapters 4 and 8 (sections 4.3 and 8.4 respectively).

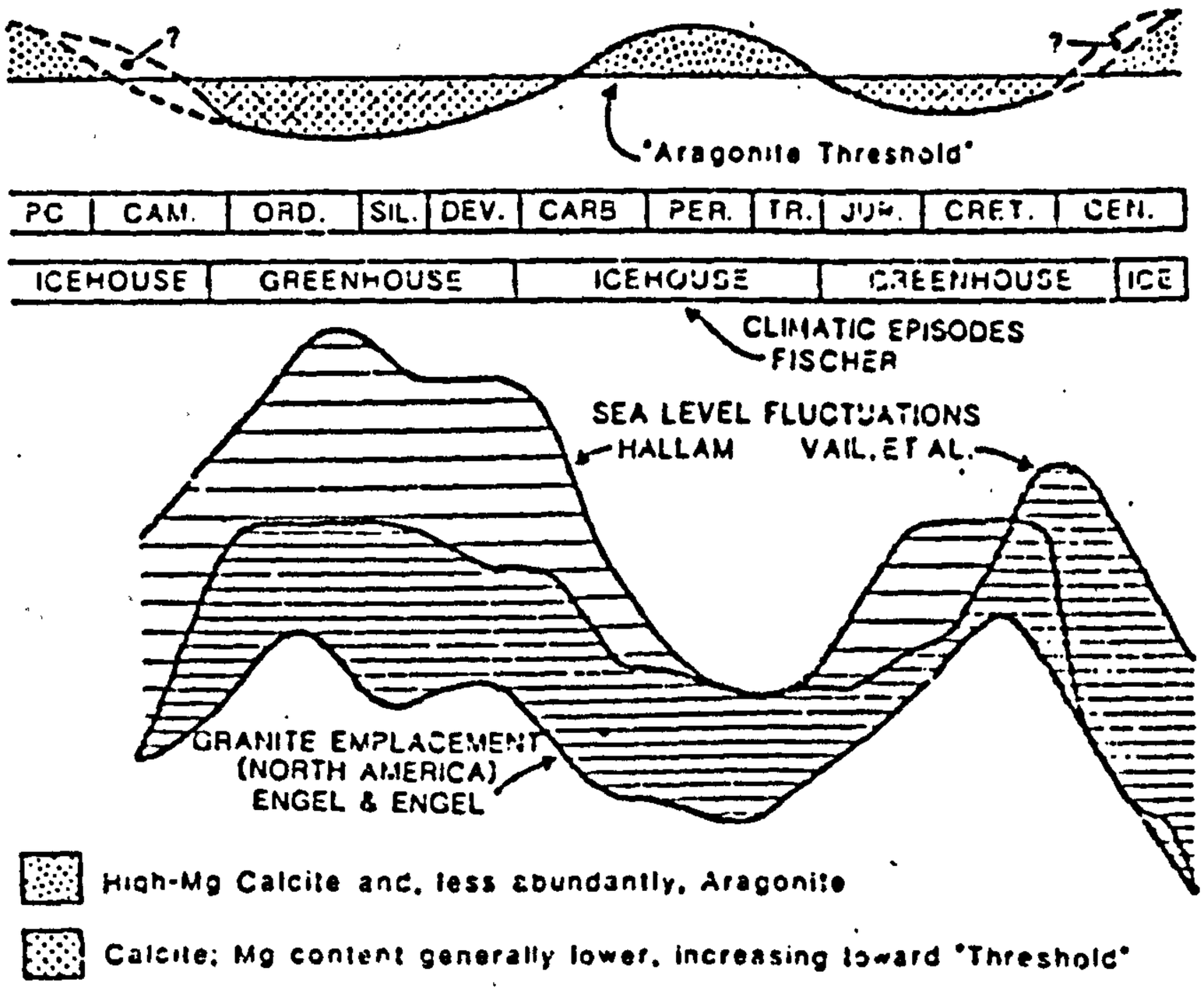
The following section deals with the broader significance of dolomites in the geological record and draws on information presented at various points throughout this thesis.

10.4 Dolomites in the geological record

There has been considerable discussion in the research literature regarding the significance of Precambrian dolomites. Much of this discussion has focussed on the apparent predominance of dolostones over limestones in the Precambrian, although Chilingar (1956) noted that the relative importance of dolomitic versus calcitic limestones shows a cyclical variation through the Phanerozoic. There are also many examples of Precambrian limestones (e.g. Gebelein and Hoffman, 1973; references in Roberts, 1976; Tucker 1983b, 1984; Zempolich et al., 1985). It has also been suggested that some Precambrian dolomites may have precipitated directly from seawater (Chilingar, 1956; Tucker, 1982).

Data from the Porsanger Dolomite and also from the Beck Spring Dolomite (Tucker, 1983a) suggest that, in these particular examples at least, dolomites with good preservation of primary depositional and early diagenetic fabrics may represent early diagenetic stabilisation to dolomite. In terms of large scale fluctuations in the mineralogy of inorganic marine precipitates (e.g. Sandberg, 1983; Wilkinson, et al., 1985) the data support the suggestion that high magnesium calcite and aragonite were the principal precipitates from seawater in the Proterozoic, since the dolomite probably represents a replacement of HMC. Similar conclusions may be drawn from petrographic study of Proterozoic limestones where there is evidence for original aragonite and high magnesium calcite ooids (e.g. Tucker, 1983b, 1984).

Fig 10-1



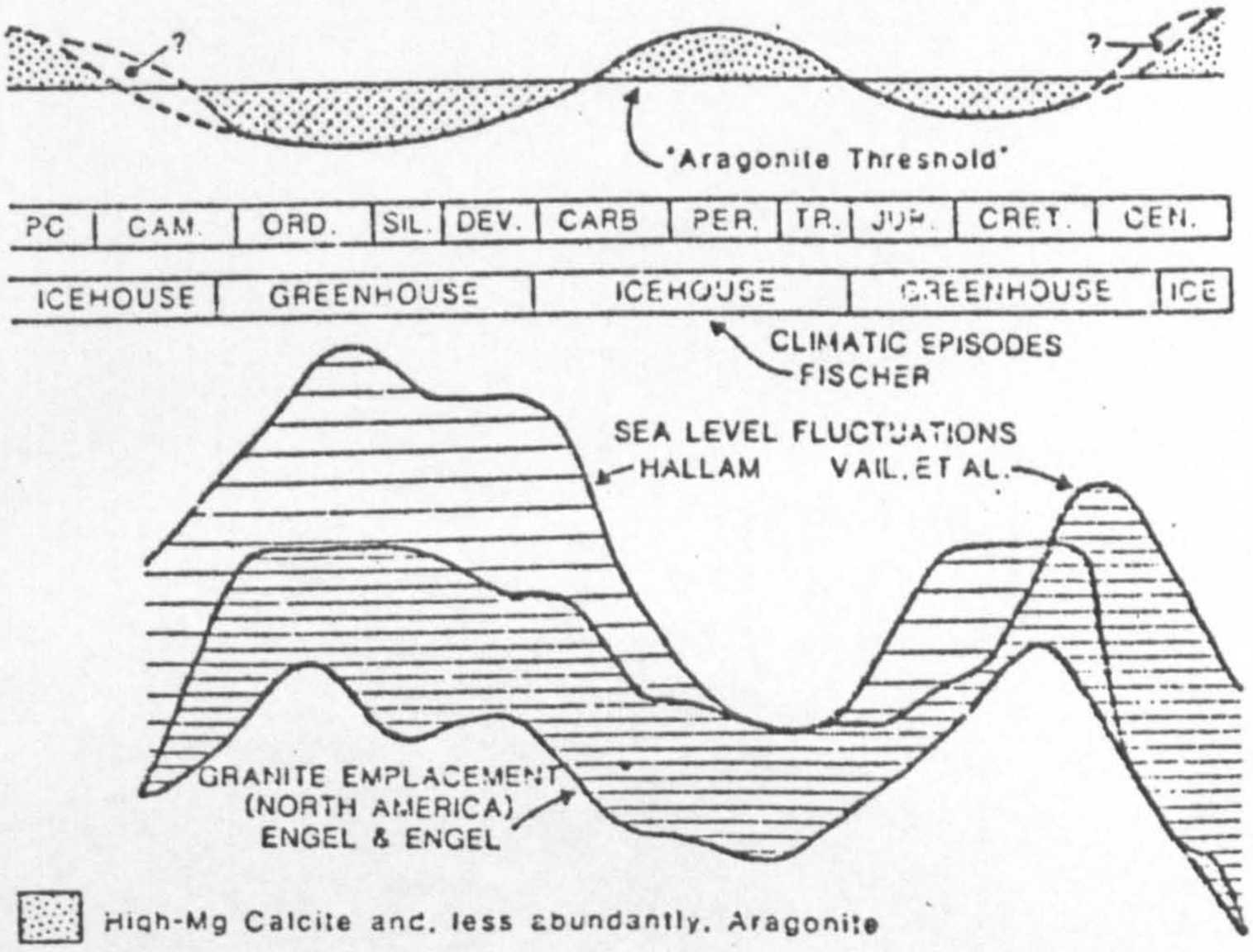
? Stabilisation dolomite (see text for discussion)

(modified after Sandberg,1983)

Fig 10.1 Secular variation in marine carbonate mineralogy

Periods when fabric retentive (stabilisation) dolomite may have been more likely to form are marked. These correspond to periods of high-Mg calcite dominance.

Fig 10-1



? Stabilisation dolomite (see text for discussion)

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Periods when fabric retentive (stabilisation) dolomite may have been more likely to form are marked. These correspond to periods of high-Mg calcite dominance.

MacKenzie and Pigott (1981), Sandberg (1975, 1983) and Wilkinson et al. (1985) have suggested underlying geotectonic controls on the mineralogy of marine carbonate, since the trend coincides with the global sea level curve (see Fig.10.1). MacKenzie and Pigott (1981) defined 'submergent modes' in which cratons were depressed below sea level, plate convergence and subduction of oceanic margins were active and higher ocean ridge volumes produced higher sea levels. The principal processes affecting sedimentary reservoir transfers and reactions were input of diagenetic and metamorphic CO_2 at subduction zones, erosion of sulphate and organic carbon and precipitation of carbonate and pyrite. A further feature was restriction of terrestrial biota and nutrient supply to oceans, leading to increased respiration (oxidation). In addition, Wilkinson et al. (1985) suggested that greenschist metamorphism at hydrothermal ridges would remove magnesium and add calcium and hydrogen to convecting seawater. During 'emergent modes' of low sea level, cratonic areas were far from continental margins and ocean ridge volumes were low (MacKenzie and Pigott, 1981). Increased emergence of terrestrial materials would increase the rate of sulphide oxidation (also aided by increased photosynthetic production of O_2). Erosion of previously deposited carbonates and metal silicates would further deplete CO_2 levels. Evaporite precipitation ($CaSO_4$) and reduced activity at hydrothermal ridges combined with weathering of silicates would serve to elevate the Mg/Ca ratio (MacKenzie and Piggot, 1981; Wilkinson et al., 1985).

Thus high pCO_2 and relatively low Mg/Ca ratios characterise submergent modes and favour the precipitation of calcite, whereas emergent modes with relatively low pCO_2 and higher Mg/Ca ratios are characterised by aragonite and high magnesium calcite precipitation.

The data from the Porsanger Dolomite presented here indicate that high magnesium calcite may have been the important marine precipitate. An alternative interpretation is that poorly ordered, Ca-dolomite may have precipitated. In either case stabilisation to relatively ordered and stoichiometric dolomite during early diagenesis is consistent with elevated Mg/Ca ratios in seawater and early diagenetic fluids (including meteoric water) and suggests that 'emergent mode' geotectonic and geochemical processes may characterise the Riphean.

If this relationship is real, then we would expect to see a pattern in the geological distribution of fabric retentive, early stabilisation dolomites. As already described there are many potential examples in the Precambrian (see references in Chapter 7, sections 7.2.2, 7.2.3 and 7.3.2). In the Phanerozoic, examples are reported from the Pliocene and Pleistocene mainly (e.g. Muller et al., 1973; Land, 1973b; Kaldi and Gidman, 1982; Sibley, 1982; Ward and Halley, 1985) and also possibly from the Permian (Kaldi and Gidman, 1982), consistent with the suggested trend (see Fig. 10.1). However, these examples and others should be examined in more detail before a firm conclusion can be drawn. This may be illustrated by reference to the Permian. The specific example described by Kaldi and Gidman (1982) is of early diagenetic fabric-retentive and cementing dolomite from the Lower Magnesian Limestone, Permian of eastern England. Although the fabrics are not as pristine as examples from the Precambrian or the Plio-Pleistocene they appear to represent similar early replacement (after HMC or aragonite), which probably occurred upon exposure to mixed marine-meteoric water during depositional regression. This dolomite may then be interpreted as a stabilisation product, resulting from a combination of precursor mineralogy, pre-dolomitisation history (i.e. no

previous exposure to meteoric water) and suitable conditions for dolomitisation. In general however, Permian dolomites show a range of dolomitisation fabrics. For example, the Permian (EZ1) reef of northeast England is extensively dolomitised and displays largely obliterative or only poorly preserved fabrics. This difference may reflect the predominance of aragonite precursors over high magnesium calcite or calcite, hence providing a relatively low potential for fabric-retentive dolomitisation. In support of this, evidence is emerging that early aragonite cements formed in the reef (Tucker and Hollingworth, 1986), but the interpretation remains speculative. The Permian reef complex of west Texas and New Mexico offers a contrast. Here the main reef facies (the Capitan) are largely undolomitised whereas the backreef facies are extensively dolomitised (Wilson, 1975, chapt. viii). Without going into details,it appears that the reef was periodically exposed to meteoric waters during early diagenesis, due to subaerial exposure of the Platform following tectonic subsidence. Perhaps then, dolomitisation potential was severely reduced because of stabilisation of HMC and aragonite to LMC before suitable conditions for dolomitisation developed.

Dolomites in the Dinantian of South Wales (this study) do not tend to preserve much detail of the original fabric of their marine precursors and this is interpreted as reflecting a predominantly calcite mineralogy for the components and/or their pre-dolomitisation history (Chapter 3). Again, this could be interpreted on a large scale, placing the Lower Carboniferous within an essentially 'submergent' regime (see Wilkinson et al., 1985 and curve on Fig. 10.1).

Zenger (1982) summarized the published compilations of limestone/dolomite trends through time and showed that the most radical

increase occurred during the Mesozoic and not across the Precambrian-Phanerozoic boundary. This increase approximately correlates with the marine carbonate mineralogy curve (Fig. 10.1) suggesting perhaps that dolomite forms preferentially at times of aragonite and high magnesium calcite dominance (i.e. 'emergent mode' geotectonics, MacKenzie and Pigott, 1981). However, as Zenger (1982) pointed out, there are many lower to middle Palaeozoic dolomites. If, as suggested by Sandberg's (1983) curve (Fig. 10.1), the dominant marine carbonate at this time was calcite, then we might expect to see a range of fabrics from obliterative to vaguely fabric-retentive in dolomites of this age: rather like those described from the Dinantian of South Wales. A review of papers referenced in this text and those in Zenger et al. (1980) tends to confirm this expectation. However, the problem remains, why is there such an abundance of dolomite in the lower to middle Palaeozoic. To answer this, perhaps we should consider the possible controls on flow systems necessary to produce massive dolomite (i.e. for import of Mg^{2+}), which presumably, operated within the broad depositional system. Is there a relationship between regression and massive dolomitisation, as in the South Wales Dinantian?

Clearly, more research is necessary; however, dolomite may be able to contribute to discussions about secular variations in seawater chemistry and geotectonics, providing that we identify carefully the types of dolomite involved and are able to constrain their environment and timing of formation. The concept of dolomitisation potential is stressed, and can be seen essentially as a product of diagenetic environment, which may ultimately be linked to global secular variations. It is apparent that local environmental controls on carbonate precipitation are superimposed on the proposed secular trends. For example aragonite and variable Mg-calcite

ooids and cement are known to coexist in Holocene environments (see Wilkinson et al., 1985). Similar situations are also known in ancient carbonates, for example, Strasser (1986) described Purbeckian (Jurassic) ooids of mixed original mineralogy from the French and Swiss Jura. He suggested that originally aragonite ooids formed in nearshore environments, whereas originally calcite ooids formed offshore. Despite these and other examples of local variations in the mineralogy of coeval inorganic carbonates and the relative uncertainty in the estimates of global sea level there is a significant correlation with eustatic indexes and mean ooid mineralogy variations throughout the Phanerozoic (Wilkinson et al., 1985), the mineralogy trends may be extended with less certainty into the Proterozoic (Sandberg, 1983; Tucker, 1984). In terms of dolomitisation potential, we must also consider skeletal grain mineralogy, which varies between carbonate secreting organisms (Milliman, 1974, Chapter 4, see also discussions in Chapter 3 of this thesis).

In conclusion, the concept of dolomitisation potential as a product of diagenetic environment seems valid; whether this can ultimately be linked to global secular variations deserves further consideration and the types of data presented in this study may contribute to this aim.

Appendices

Appendix 1: Stoichiometry and ordering of dolomite

Powder X-ray diffraction analysis was carried out to determine: (a) the approximate mol % $CaCO_3$ in dolomite as measured by the displacement of the d[104] spacing (Goldsmith and Graf, 1958a; Lumsden, 1979); (b) the degree of ordering as reflected in the ratio of intensities of the 01.05[221]/11.0[101] diffraction peaks. The latter is approximately a measure of the extent of mixing of the principal cations in the c-axis direction (Goldsmith and Graf, 1958b).

Samples of whole-rock were prepared by grinding,to pass through a 61μm mesh and were smear mounted on glass slides. Analyses were carried out on a Philips PW 1130 generator/diffractometer assembly using iron filtered Co-Kα or nickel filtered Cu-Kα radiation. Operating conditions were as follows (unless stated otherwise): 40 kV, 20 mA; range 2-4 x 10^2 cps; divergence and scatter slits 1, 1^o and receiving slit width 0.1mm; scan speeds $1/8^o$ 2θ min^{-1}.

Preliminary scans covered a range from 20 to $70^{oo}2\theta$ (cu-Kα) at $1^o2\theta$ min^{-1} for each sample to establish, qualitatively, its bulk mineralogy. The scans confirmed petrographic studies, which showed that most samples were essentially monomineralic (i.e. dolomite). One sample (BRI) contained appreciable amounts of quartz, other samples had minor amounts, confirming petrographic identification of detrital and authigenic quartz. Mixed carbonate (i.e. dolomite + calcite) samples were also identified and attempts were made to purify these using a heavy liquid separation technique (Di-iodomethane plus 'Anala R' acetone, see Hutchison, 1974). This was achieved by repeated separations on a small number of dominantly dolomitic samples, where it was possible to reduce calcite to a level

within the background of XRD traces (less than approximately 4 wt % $CaCO_3$). These samples are marked D on the accompanying tables.

More quantitative work was carried out on selected peaks, located relative to an internal standard (cerium oxide) at scan speeds of $1/8^{o}2\theta min^{-1}$ (Co-Kα). The 211[104] diffraction peak, used to determine mol % $CaCO_3$ in dolomite, was located in the d-space range 2.888 to 2.894 Ångstroms (calculated from 2θ values using the Bragg equation) and these are listed in column 2 of Table A1.1 and A1.2. Mol % Ca (column 3) was calculated using the equation of Lumsden (1979) based on Goldsmith and Graf (1958a), as described in Chapter 4 section 4.1.2. Samples are repeatable to $\pm$0.25 mol %; however, the accuracy of the technique is less certain and is susceptible to variations in Fe^{2+} substitution (see Chapter 4, discussion).

Order ratios (column 4) were calculated from the normalised (to internal standard) intensities of the 01.05[221] and 11.0[101] diffraction peaks. Intensity is represented by the peak area calculated by multiplying peak height by peak width at half peak height (see Milliman, 1974, chapter 2). Order ratios are repeatable to $\pm$0.13

TABLE A1.1

XRD data for Dinantian dolomites (see text for explanation)

1 Sample no.	2 d spacing	3 mol % Ca	4 $\frac{I[221]}{I[101]}$
a, Dolomicrites (Danygraig)			
R1	2.891	51.67	0.38
R2	2.892	52.00	0.29
R3	2.893	52.33	0.31
R4	2.84	52.67	0.17
R5	2.893	52.30	—
R6	2.889	51.00	0.44
R7	2.894	52.67	0.45
R8	2.892	52.00	0.37
R11	2.889	51.00	0.51
R12	2.888	50.67	0.58
b, Dolomicrites associated with Pervasive dolomites			
CBM2a	2.890	51.33	0.73
CBM2b	2.889	51.33	0.65
c, Pervasive dolomites			
BR25D	2.891	51.67	0.76
B05	2.889	51.00	0.88
B06D	2.889	51.00	1.03
BR10	2.893	52.33	0.38
BR22D	2.889	51.00	0.50
BR9	2.892	52.00	0.79
BR1	2.889	51.00	0.55
d, Vein dolomites			
G02D	2.889	51.00	0.88
G03	2.888	50.67	0.97
G04	2.892	52.00	0.89
HB14	2.888	50.67	0.82
HB11D	2.887	50.33	1.21
HB3	2.890	51.33	0.79
HB16	2.890	51.33	1.24
HB13D	2.889	51.00	0.62

TABLE A1-2

XRD data for Porsanger Dolomite dolomicrites.

1 Sample no.	2 d spacing	3 mol % Ca	4 $\frac{I[221]}{I[101]}$
1A*	2.891	51.67	
2A*	2.889	51.00	0.54
3A	2.887	50.33	0.46
3B	2.885	49.67	0.84
4D	2.887	50.33	0.78
5C/1	2.885	49.67	0.62
5C/2	2.884	49.33	0.58
6A/1	2.886	50.00	0.91
6A/2	2.885	49.67	1.05
6B	2.886	50.00	0.75
7C	2.886	50.00	0.72
8C	2.855	49.67	0.50
13C	2.884	49.33	0.90
14B/1	2.885	49.67	0.76
14B/2	2.885	49.67	0.86
14J	2.886	50.00	1.63
14L	2.886	50.00	0.58
14T	2.885	49.67	0.74
14X	2.885	49.67	0.79

*Samples 1A and 2A are from the basal Porsanger Dolomite and are best described as microdolospars, they are probably recrystallised.

Appendix 2: Cation chemistry of dolomites and associated limestones

1. Electron microprobe analysis

Electron microprobe investigation provided supporting data for major and minor element concentrations (principally Ca, Mg, Fe and some Mn). Carbon-coated polished mounts were prepared from selected samples and analyses were carried out on a Cambridge Instruments Geoscan electron probe microanalyser by Dr. A. Peckett at the University of Durham. The probe was operated at an accelerating voltage of 20 kV and probe current of 50nA. Data was processed on-line using a ZAF correction procedure. The following standards were used for frequent calibration during analysis: wollastonite (Ca), periclase (Mg), celestine (Sr) iron metal (Fe) and rhodonite (Mn). Analysis totals were generally low (95-98%) due to the decomposition of carbonate under the electron beam. The following detection limits and counting errors were recorded:

	LLD	counting error
Fe	200 ppm	$\pm$ 170
Mn	200 ppm	$\pm$ 90
Mg	300 ppm	$\pm$ 800
Sr	200 ppm	$\pm$ 80

Samples with detectable Fe are listed in Table A2.1 and A2.2 and are included for comparative purposes only. Sample numbers indicate the whole-rock A.A.S. analyses to which they should be compared. Data for Porsanger Dolomite samples have been converted to molar proportions to be comparable with I.C.P. data.

TABLE A2.1

Probe analyses for Dinantian dolomites

Sample number and description	Wt %			
	Mg	Ca	Fe	Mn
A, Pervasive dolomites				
BR22.1 cloudy mosaic dolomite	12.2	21.3	0.42	0.13
BR22.2 cloudy mosaic dolomite	11.9	19.2	0.15	0.04
BR25.1 cloudy mosaic dolomite	11.9	21.9	0.18	---
BR25.2 clear dolomite zone	12.2	22.2	---	---
BR25.3 clear void-fill	12.0	21.7	---	---
BR25.4* dedolomite in vein	0.5	37.9	0.08	---
BR25.5 mosaic dolomite	11.8	21.8	---	---
BR25.6 clear dolomite	11.9	22.1	---	---
B06.1 cloudy mosaic	11.9	21.6	0.29	---
B06.2 cloudy mosaic	11.8	21.6	0.13	---
B06.4 cloudy mosaic	11.8	21.1	0.47	---
B06.3 clear void-fill	11.8	21.6	0.08	---
B06.5 clear void-fill	11.8	21.1	0.91	0.16
B06.6 clear void-fill	11.8	21.3	0.47	0.05
B01.1 scattered dolomite rhomb in oolite	12.3	22.0	0.20	---
B01.3 scattered dolomite rhomb in oolite	11.9	22.5	0.11	---
B01.2 scattered dolomite rhomb in oolite (plus calcite contamination)	10.9	24.1	0.23	---
B, Vein dolomites				
G02.1 cloudy core, zoned dolomite rhomb	11.3	21.0	1.68	0.19
G02.2 clear rim zoned dolomite	11.4	21.0	2.50	0.43
G02.3 cloudy core etc.	11.0	20.6	2.32	0.27
G02.4 clear rim etc.	11.5	20.4	2.42	0.32
G02.5 cloudy core etc.	11.7	21.0	1.94	0.21
G02.6 clear rim etc.	11.7	21.0	1.48	0.31
G02.7 dense core etc.	11.0	20.0	3.84	0.37
G02.8 cloudy zone etc.	11.8	21.2	1.14	0.23

TABLE A2.1 continued

Probe analyses for Dinantian limestones

Sample number and description.	Wt %			
	Mg	Ca	Fe	Mn
B,Vein dolomites contin.				
G03.1 large baroque crystal	11.2	21.4	1.61	0.29
G03.2 outer part of above	11.0	22.2	1.44	0.29
G03.3 baroque crystal	11.5	21.9	1.81	0.32
G03.4 clear euhedral rhomb	11.5	21.7	2.08	0.27
G03.6 clear euhedral rhomb	11.4	21.7	1.78	0.34
G03.5*late calcite	0.3	40.3	0.06	0.06

TABLE A2.2

Probe analyses for Porsanger Dolomite

Sample number and description	Wt % and (normalised molar proportion)			
	Mg	Ca	Fe	Mn
140.4 dolospar	12.3	20.4	0.38	0.16
	(0.494)	(0.497)	(0.006)	(0.003)
140.16 "	12.4	21.2	0.55	0.18
	(0.485)	(0.503)	(0.009)	(0.003)
14A.3 "	12.0	20.8	0.71	0.30
	(0.479)	(0.504)	(0.012)	(0.005)
14A.7 "	12.6	21.1	0.10	0.04
	(0.496)	(0.501)	(0.002)	(0.001)
14A.2 inclusion rich dolomite	12.6	21.2	0.20	0.08
around peloids	(0.493)	(0.502)	(0.004)	(0.001)
14A.6 clear dolomite within	12.6	21.0	0.07	---
fibrous layer	(0.498)	(0.501)	(0.001)	---
14A.8 dolospar	12.6	20.9	0.12	0.03
	(0.496)	(0.501)	(0.002)	(0.001)
4Ab.1 marginal dolospar	12.6	21.0	0.03	---
	(0.496)	(0.503)	(0.001)	---
4Ab.3 micritic matrix	12.6	21.2	0.05	---
	(0.495)	(0.504)	(0.001)	---
4Ab.4 marginal dolospar	12.6	21.3	0.02	---
	(0.494)	(0.505)	(0.001)	---
4Ab.5 distal dolospar	12.7	21.1	0.12	---
	(0.497)	(0.501)	(0.002)	---
4A.1 distal dolospar	12.5	20.7	0.12	---
	(0.498)	(0.500)	(0.002)	---
4A.2 micritic matrix	12.8	21.1	0.03	---
	(0.500)	(0.499)	(0.001)	---
4A.3 marginal dolospar	12.7	20.9	0.06	---
	(0.499)	(0.500)	(0.001)	---

TABLE A2.2 continued

Probe analyses for Forsanger dolomite

	Mg	Ca	Fe	Mn
4A.4 marginal dolospar	12.7	20.8	0.05	---
	(0.501)	(0.498)	(0.001)	---
4A.6 marginal dolospar	12.9	21.0	0.07	---
	(0.503)	(0.496)	(0.001)	---
4A.7 beyond .6	12.6	20.3	0.08	---
	(0.504)	(0.495)	(0.001)	---
4A.10 beyond .7	12.7	20.8	0.05	---
	(0.502)	(0.497)	(0.001)	---
4A.11 distal dolospar	12.8	21.0	0.05	---
	(0.501)	(0.498)	(0.001)	---

2. A.A.S. analysis (method after Angino and Billings, 1972; Robinson, 1980)

Whole rock samples were prepared from dolomites and some calcites (limestones) from the South Wales Dinantian as follows: samples were ground to pass through a 61μm mesh, washed and oven dried to 100°C overnight. Dolomite samples were dissolved in 10% v/v (Aristar) hydrochloric acid (0.2g sample, 25ml acid) over four hours at 60°C. Calcite samples were dissolved in 3% v/v (Aristar) acetic acid overnight at room temperature. The HCl method for dolomites is preferred because (i) it produces relatively rapid digestion, (ii) low volumes of acid required and (iii) there is a comparatively low risk of contamination (see Robinson, 1980 for discussion). The problem of Fe contamination due to leaching from clay minerals is considered to be relatively unimportant because of the low insoluble residue content of most samples (less than 7 wt%). Microprobe analyses for Fe are also in general agreement with whole-rock A.S.S. determination.

A range of standard solutions were prepared by complete digestion of the following international rock standards, using nitric, hydrochloric, perchloric and hydrofluoric acids at 200°C. BCS 393 limestone and 368 dolomite, NBS 88a dolomite and 1C limestones; CCRMP SY-1 and SY-2 syenites; Zentrales Geologisches Institut (Berlin) TB shale, BM basalt and KH limestone. The choice of standard for a given sample analysis depended upon the approximate element concentration in that sample, thus ensuring the most accurate calibration (concentration vs. absorbance). For Sr analyses, a standard Sr solution (50μg/ml) was prepared and a La-base solution (100 mg/ml) added to samples.

Analyses were carried out on a Perkin-Elmer 2380 Atomic Absorption

TABLE A2.3

AAS data for Dinantian dolomites and limestones.

	Sample no.	Wt %			ppm		
		Mg	Ca	Fe	Mn	Sr	Na
Dolomicrites	R1	10.8	20.1	1.52	1300	423	204
	R2	9.8	18.6	1.44	1065	365	287
	R3	11.1	20.9	0.70	931	493	564
	R4	10.9	21.0	0.94	1040	294	533
	CBM2a	10.9	19.6	1.56	1778	34	192
	R5	9.9	18.6	0.66	563	81	230
	R6	11.2	19.5	0.39	668	37	139
	R12	11.3	19.4	0.42	595	30	114
Pervasive dolomites	BR25	11.4	22.6	0.20	173	70	170
	BR25	12.6	25.1	0.20	158	58	136
	B05	11.8	22.0	0.47	695	93	250
	B06D	15.4	28.5	0.57	972	70	174
	BR10	11.6	23.2	0.50	800	60	210
	BR22D	12.7	24.3	0.58	1332	39	75
	BR1	8.93	15.6	1.47	1545	25	156
Vein dolomites * baroque	G02	10.9	21.9	2.51	3719	31	183
	G02D	11.8	24.3	1.94	3386	27	184
	G03*	11.9	21.8	1.58	3522	25	157
	G04*	11.7	21.9	2.93	3976	25	133
	HB14*	12.1	21.8	1.77	2857	25	349
	HB11*	11.4	23.2	1.48	2719	37	125
	HB11D*	11.7	24.0	1.29	2309	29	63
	HB3*	12.8	23.3	1.42	2935	25	71
	HB16	12.5	21.8	1.64	2283	20	119
	HB13D*	11.9	21.9	1.54	3032	23	28
Limestones	G06	0.5	38.5	0.05	222	210	46
	G020	4.2	32.7	0.07	404	139	68
	HB9	0.2	39.2	0.03	493	216	49
	HB2	0.4	38.9	0.02	87	354	75
	B01	0.9	39.3	0.03	41	440	46
	B03	1.0	40.2	0.03	66	430	73

Spectrophotometer using air/acetylene (for Na, Fe and Mn) or nitrous oxide/acetylene (for Mg, Ca, Sr) oxidant/fuel mixtures. The following relative detection limits (μg/ml) were possible: Ca 0.005; Mg 0.003; Mn 0.01; Fe 0.02; Sr 0.02; Na 0.005. Recalculated sample concentrations are given in Table A2.3. Analytical precision was as follows: Ca ± 0.8 wt%; Mg ± 0.4 wt%; Mn, Fe, Sr and Na ± 10 ppm (at concentrations less than 200 ppm) or ± 5% of content. Within sample variation is likely to be greater than this because of the whole-rock sampling procedure (see Chapter 4 for discussion).

3. Inductively coupled plasma source spectrometry

Samples were prepared as for stable isotope analysis (viz: mg-sized samples dissolved in 100% phosphoric acid). Acid volumes were adjusted according to sample size (see Appendix 3) and, following extraction of CO_2 for mass spectrometric analysis, an aliquot of residual acid plus dissolved sample was diluted to approximately 7% v/v. Although the actual concentration of this solution (below 20% v/v) does not appear to be critical it is important that all samples and standards are approximately 'matrix-matched' (see Thompson and Walsh, 1983; and Coleman et al., in prep.). The samples were analysed for Mg, Ca, Fe, Mn and Sr on a Rank Hilgar E100 simultaneous I.C.P. spectrometer by analysts at The British Petroleum Co. Research Centre. Spec. pure or commercially available A.A.S. standards were prepared to a similar viscosity as the samples (i.e. 7% v/v). Simultaneous analysis and nebulisation of samples makes the technique useful for relatively small samples and is relatively free from interferences (Thompson and Walsh, 1983). Molar concentrations down to 0.1% for Ca, Mg and Fe and 0.01% for Mn and Sr can be detected. In the

studied samples, as in most ancient carbonates, Sr concentrations (and some Mn concentrations) fell close to this limit. Duplicate analyses could not be performed on many samples because of the relatively small quantities of material available (a few mg). However, sufficient material was available from the Dinantian samples and some Porsanger dolospars and whole-rock dolomicrites to permit the following reproducibilities to be determined (as mol %): Ca $\pm$ 0.3; Mg $\pm$ 0.5; Fe $\pm$ 0.18; Mn $\pm$ 0.01; Sr $\pm$ 0.01.

Data are presented in Table A2.4 and A2.5 (as normalised mol %) together with stable isotope compositions for the same samples.

Table A2.4 ICPS data and stable isotope composition for Dinantian dolomites and limestones.

Sample number and description		Mol% (* = below detection) Mg	Ca	Fe	Mn	Sr	°/₀₀ PDB $\delta^{13}C$	$\delta^{18}O$
A, Dolomites : Pervasive mosaics								
BO 13c	idiotopic	43.6	55.9	0.5	*	0.01	+1.7	-2.6
BO13d	"	43.6	55.5	0.9	*	0.01	+1.7	-2.8
BO13a	xenotopic	42.4	56.7	0.8	*	*	+1.5	-4.3
BO13b	"	43.7	55.9	0.4	*	*	+1.5	-4.5
Dolospars in fenestral dolomicrites								
RDS 1		40.5	55.2	4.3	*	*	-1.8	-2.5
RDS 2		37.1	60.6	2.3	*	0.03	-1.5	-1.8
RDS 3		33.9	61.0	4.2	0.9	0.05	-1.4	-2.1
B, Calcites								
GO PC	poikilotopic spar	8.2	91.5	0.3	0.05	*	+2.6	-4.2
BO1 CS	spar	4.0	95.5	0.5	*	*	-	-
BO2 V2	vein calcite	1.5	98.4	*	*	0.03	-1.1	-8.3
" V4	"	1.2	98.8	*	*	0.04	-1.2	-8.1
" V1	"	1.2	98.7	*	*	0.02	-1.3	-7.7
" V5	"	1.5	98.3	0.2	*	0.04	-1.4	-7.2
" V3	"	1.3	98.3	0.3	0.03	0.03	-1.7	-7.3

Table A2.5 ICPS data and stable isotope composition for Porsanger Dolomite components

Sample description and number		Mol% (* = below detection)					°/₀₀ PDB	
		Mg	Ca	Fe	Mn	Sr	$\delta^{13}C$	$\delta^{18}O$
A, whole rock dolomicrites	13C	44.2	47.1	8.6	0.01	0.04	+2.5	-2.6
	14T	49.2	50.2	0.4	0.06	0.02	+3.8	-3.2
	7C	44.4	45.7	9.9	*	0.06	+4.6	-2.4
	8C	42.3	45.3	12.3	*	0.05	+2.8	-2.3
	3B	43.3	45.4	11.2	*	0.05	+3.3	-1.5
	14X	50.0	49.4	0.6	*	*	+4.6	-2.9
	5C	47.6	52.2	0.2	*	0.02	+4.9	-2.5
	14L	48.7	51.1	0.2	0.04	0.02	+3.9	-2.7
	14J	48.7	51.0	0.2	0.07	0.03	+5.1	-2.6
	6A/2	48.7	50.6	0.7	0.04	0.03	+3.6	-2.5
	3A	49.3	50.6	0.1	*	*	+3.9	-2.7
	6B	47.6	50.0	2.4	*	0.02	+3.9	-2.1
	4D	48.6	51.0	0.3	0.04	*	+3.8	-2.6
	14B	49.9	50.0	0.1	*	*	+3.5	-2.6
	1A	-	-	-	-	-	+0.1	-10.1
	2A	-	-	-	-	-	+2.3	-7.7
B, depositional grains :								
micrite intraclasts and flakes	41L.8	48.8	50.4	0.7	*	0.01	+5.5	-3.1
	133.2	47.8	50.4	1.7	*	0.02	+4.9	-2.7
	133.3	47.0	52.1	0.9	*	0.02	+4.6	-1.7
	41E.3	47.6	51.1	1.3	0.02	0.01	+4.6	-2.8
	4A/m	45.9	52.3	1.6	0.23	0.03	+3.4	-3.9
ooids	7Ai.3	47.0	50.2	2.7	0.12	*	+3.3	-2.8
	7Ai.2	48.2	49.7	2.2	*	*	-	-3.5
	7A.1	46.9	51.5	1.5	0.06	*	+5.8	-2.2
	7Ai.1	46.0	50.5	3.5	*	*	+2.1	-4.9
	135.1	49.0	49.4	1.6	*	*	+3.9	-5.6
peloids	7A.2	47.5	51.1	1.3	0.06	*	+5.7	-2.4
	7Ai.3a	45.4	52.6	1.9	0.12	0.01	+4.4	-2.5
	133.1	47.3	50.5	2.2	*	*	+6.0	-1.6
catagraphs	41L.9	47.9	51.0	1.1	*	0.02	+5.6	-2.6
C, fibrous dolomite and internal sediments :								
type 1	41L.3	43.7	50.9	5.3	*	*	(-8.8)	(-16.6)
	41L.1	46.0	52.0	2.0	*	*	(-2.1)	(-10.9)
	FC1b	47.6	50.9	1.4	*	*	+3.5	-5.7
	FC2b	37.3	55.0	7.5	0.2	*	(-2.7)	(-11.5)
	FC2a	46.9	50.2	2.9	*	*	+1.6	-7.3
	41E.1	47.9	51.2	0.9	*	*	+3.9	-4.6
	41E.6	39.7	56.8	2.7	0.73	0.04	+4.7	-4.5
type 3	41L.7	48.5	50.8	0.7	*	0.01	+3.6	-8.0
	41L.4	48.4	50.2	1.4	*	*	+0.2	-9.0
	41E.2	37.9	48.7	12.8	0.51	0.04	+5.4	-2.6
internal sediments	41L.isa	45.7	49.2	5.1	*	*	-1.4	-6.5
	41L.isb	48.1	48.4	3.4	0.09	*	+2.0	-7.4
	41L.isc	45.8	50.3	3.7	0.12	*	+1.4	-5.9
D, dolospars								
marginal	41L.5	40.7	54.4	4.5	0.45	*	+2.7	- -5.7
distal	41L.6	46.6	52.5	0.9	*	0.01	+4.3	-5.4
marginal	SC3a	46.6	50.9	2.2	0.31	*	+3.6	-12.2
"	SC2	47.3	50.8	1.8	0.21	*	+3.9	-8.6
blocky distal	SC3b	46.7	51.5	1.5	0.33	*	+4.5	-11.8
" "	SC1	45.1	53.0	1.6	0.24	*	+4.0	-10.2
marginal	CF3	43.5	53.5	3.1	*	*	+3.4	-7.8
distal	CF124 x	47.6	52.0	0.4	*	*	+4.7	-8.5
"	CF567 x	47.6	52.0	0.4	*	*	+4.7	-8.7
	41E.5	48.7	51.3	*	*	*	+4.5	-7.4
	41E.4	47.2	52.2	0.6	*	0.06	+4.5	-6.7
with meteoric fabric	133.4	34.4	54.6	10.4	0.59	*	+1.0	-8.2
marginal	4AA x	47.4	52.0	0.6	*	*	+3.3	-7.4
distal	4AB x	47.5	52.2	0.3	*	0.01	+2.0	-8.0
marginal	4AC x	46.9	52.2	0.8	0.09	0.01	+3.3	-7.7
distal	4AD x	47.8	51.9	*	*	*	+3.2	-8.5
"	4AE	47.4	52.1	0.5	*	0.01	+3.3	-8.2

Appendix 3: Stable isotope analysis

The method of sample preparation and analysis of stable isotope (carbon and oxygen) composition of carbonates is standard and based on McCrea (1950) and Craig (1957). The technique involves extraction of CO_2 from carbonate samples and measurement of its isotopic composition by mass spectrometry.

Samples were pre-selected on the basis of petrographic study and in the case of whole-rock samples also from the results of XRD analysis. Component samples were dissected from thin sections. All the sampled material is described more fully in the main text and only brief descriptions are given in these appendices. Samples weighing less than 3 mg were reacted with 1ml of 100% phosphoric acid and samples weighing over 3 mg were reacted with 4mls of acid. 100% phosphoric acid was prepared by adding P_2O_5 (phosphorous pentoxide) to AnalaR orthophosphoric acid (80-85%). Following evacuation (under vacuum) of reaction vessels and equilibration to temperatures of $25^oC \pm 0.1$ (calcite and dolomite) or $60^oC \pm 0.1$ (dolomite) samples were reacted with the acid over periods of a few hours to several days, depending upon reaction temperature and sample mineralogy, until reaction was completed. Laboratory standards (calibrated to the international standards PDB and SMOW) were prepared in a similar way and included in each batch of samples to be analysed, allowing operation precision to be monitored and sample values to be calibrated to the PDB scale.

Following extraction, the evolved CO_2 was analysed on a V.G. isogas Sira 12 and V.G. micromass 903 triple collector mass spectrometer. Raw data (as $\delta 45$ and $\delta 46$ ratios) were corrected for mass and instrumental

effects (essentially after Craig, 1957; Deines, 1970) by on line computer and final results given in δ-notation relative to the PDB standard. viz:

$$\delta\,{}^{o}/_{oo} = (RX/RS - 1) \times 1000$$

where $R = {}^{13}C/{}^{12}C$ or ${}^{18}O/{}^{16}O$ for sample (X) and standard (S).

Additional corrections are necessary to take account of the temperature dependant fractionation of oxygen isotopes, which occurs between solid and evolved CO_2 (see Friedman and O'Neil, 1977). In the case of dolomites reacted at 60°C it was necessary to carry these corrections out manually using 'raw' data in the form $\delta^{18}O\ {}^{o}/_{oo}$ PDB for CO_2. A fractionation factor (α_{60}) was calculated by comparing the $\delta^{18}O$ composition of the laboratory standard dolomite (TDS, $\delta^{18}O = -10.797$) to the $\delta^{18}O$ of evolved CO_2 thus:

$$\alpha_{60} = R\ gas/R\ solid$$

where $R = (\delta^{18}O/1000) + 1$

A value of $\alpha_{60} = 1.00972$ repeatable to 0.0001 based on standards run with each batch of samples. Duplicate samples reacted at 25°C were corrected using $\alpha_{25} = 1.01109$ (Sharma and Clayton, 1965). However, these samples were found to be up to 0.7 ${}^{o}/_{oo}$ heavier than duplicates reacted at 60°C. This indicates that fractionation factors derived from standard dolomites can only be regarded as approximations and that the fractionation behaviour of dolomites probably varies. All data for dolomite presented in this thesis are from the high temperature reaction and have been corrected using the fractionation factor (α_{60}) given above.

Operation precision was monitored by duplicated analyses of the laboratory calcite standard (MCS) and the following data obtained (n = 25):

		σ	$2\sigma/\sqrt{n}$
$\delta^{13}C$ =	-0.697	$\pm$ 0.101	0.04
$\delta^{18}O$ =	-9.177	$\pm$ 0.048	0.019

Average sample reproducibility, based on 15% of the total sample, is $\delta^{18}O \pm 0.13$ $^{o}/_{oo}$ and $\delta^{13}C \pm 0.14$ $^{o}/_{oo}$. However, considerable variation exists and is probably due to sample heterogeneity, particularly in whole-rock samples.

Stable isotope data are presented in Tables A2.4, A2.5 and A3.1 in parts per thousand on the PDB scale.

TABLE A3-1

Stable isotope data for Dinantian limestone components and whole rock limestones and dolomites, (see also Table A2-4).

Sample description and number		$\delta^{13}C$‰ PDB	$\delta^{18}O$‰ PDB
A, Limestone components			
Gully Oolite ooids	G06.1	+1.8	-6.2
Gully Oolite brachiopods	G06.2	+2.1	-5.1
Gully Oolite dolomite rhombs	G05.1	+1.8	-5.3
Gully Oolite dolomite rhombs	G05.2	+1.7	-2.4
B, Limestone whole-rocks			
Gully Oolite	G06	-0.6	-5.7
Gully Oolite	G020	+2.3	-4.9
Gully Oolite	G021	+1.8	-5.6
Gully Oolite	TW1	+2.4	-4.7
Hunts Bay Oolite	HB9	+1.4	-8.4
Hunts Bay Oolite	HB2	+2.6	-2.2
Hunts Bay Oolite	HB1	+1.0	-7.1
Hunts Bay Oolite	HB10	+1.8	-7.2
Brofiscin Oolite	B01	+1.3	-5.4
Brofiscin Oolite	B03	+1.1	-7.6
C, Dolomite whole-rocks			
Dolomicrite	R1	-1.1	-1.7
Dolomicrite	R2	-0.7	-1.5
Dolomicrite	R3	-1.2	-0.5
Dolomicrite	R4	-1.2	-0.5
Dolomicrite	R5	-2.3	-1.1
Dolomicrite	R6	-1.1	-0.5
Dolomicrite	R12	-0.8	-0.8
Dolomicrite associated with	R11	-0.9	-0.6
Pervasive dolomite	CBM2a	+0.1	-0.7
Pervasive dolomite	BR25D	+2.3	-4.8
Pervasive dolomite	B05	+2.3	-2.4
Pervasive dolomite	B06	+2.4	-2.5
Pervasive dolomite	BR10	+2.1	-2.7
Pervasive dolomite	BR22D	+1.8	-5.5
Pervasive dolomite	BR7	+2.3	-1.5
Pervasive dolomite	BR9	+2.2	-2.2
Pervasive dolomite	BR1	+3.9	-0.3

TABLE A3-1 continued

Sample description and number		$\delta^{13}C‰$ PDB	$\delta^{18}O‰$ PDB
Vein dolomite	GO2D	+1.5	-4.8
Vein dolomite	GO3*	+1.2	-6.8
Vein dolomite	GO4*	+1.3	-8.7
Vein dolomite	HB14*	+2.4	-2.7
Vein dolomite	HB11D*	+1.9	-8.2
Vein dolomite	HB3*	+2.2	-6.9
Vein dolomite	HB16	+2.4	-2.7
Vein dolomite	HB13D*	+1.9	-8.4

*baroque dolomite

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