GEOCHEMICAL ANALYSIS AND ENVIRONMENTAL RECONSTRUCTION OF A DEVONIAN LAKE BASIN IN NORTHERN SCOTLAND

By

KELLEY ANN CLINTON RACE

Bachelor of Science in Geology

University of Oklahoma

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GEOCHEMICAL ANALYSIS AND ENVIRONMENTAL

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Thesis Approved:

R. Nowell Donovan

Thesis Adviser

John R. Groves

A. A. Hounslow

Norman N. Durham

Dean of the Graduate College

PREFACE

The author wishes to express her sincere appreciation to her major adviser, Dr. R. Nowell Donovan, for his assistance, guidance, suggestion of the thesis topic, and critical evaluation of this manuscript. Dr. Donovan's limitless knowledge of the Orcadian Basin proved to be invaluable throughout this study. I am also thankful to the other committee members, Dr. John Groves and Dr. Arthur Hounslow for their manuscript revisions and advice concerning the depositional environment and the geochemistry.

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Special appreciation to my parents, Jack and Sue Clinton, and to my sisters, Megan and Tracy, whose constant support, encouragement, and understanding helped me through the last few years. Deepest appreciation to my husband, Chuck, for his love and understanding.

This thesis is dedicated to my grandmother, Helen Lorey.

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CHAPTER I

INTRODUCTION

Statement of Purpose

This thesis describes the geochemical analysis and environmental reconstruction of a Devonian lake basin in Northeastern Scotland. Emphasis is on 1) petrologic studies of the provenance and diagenesis, and 2) geochemical analysis of lithologies contained within the lake basin.

Earlier work in the area has defined the environment of deposition and correlation of lithologies. However, a complete reconstruction through the use of a geochemical analysis, has not been included in previous investigations. Therefore, this thesis endeavors to expand on the role that chemical and mineralogical controls have played on the deposition and alteration of the lacustrine rocks under discussion.

Location of Study

The work for this study was conducted in Northeastern Scotland, in the area of Caithness (Figure 1). Caithness

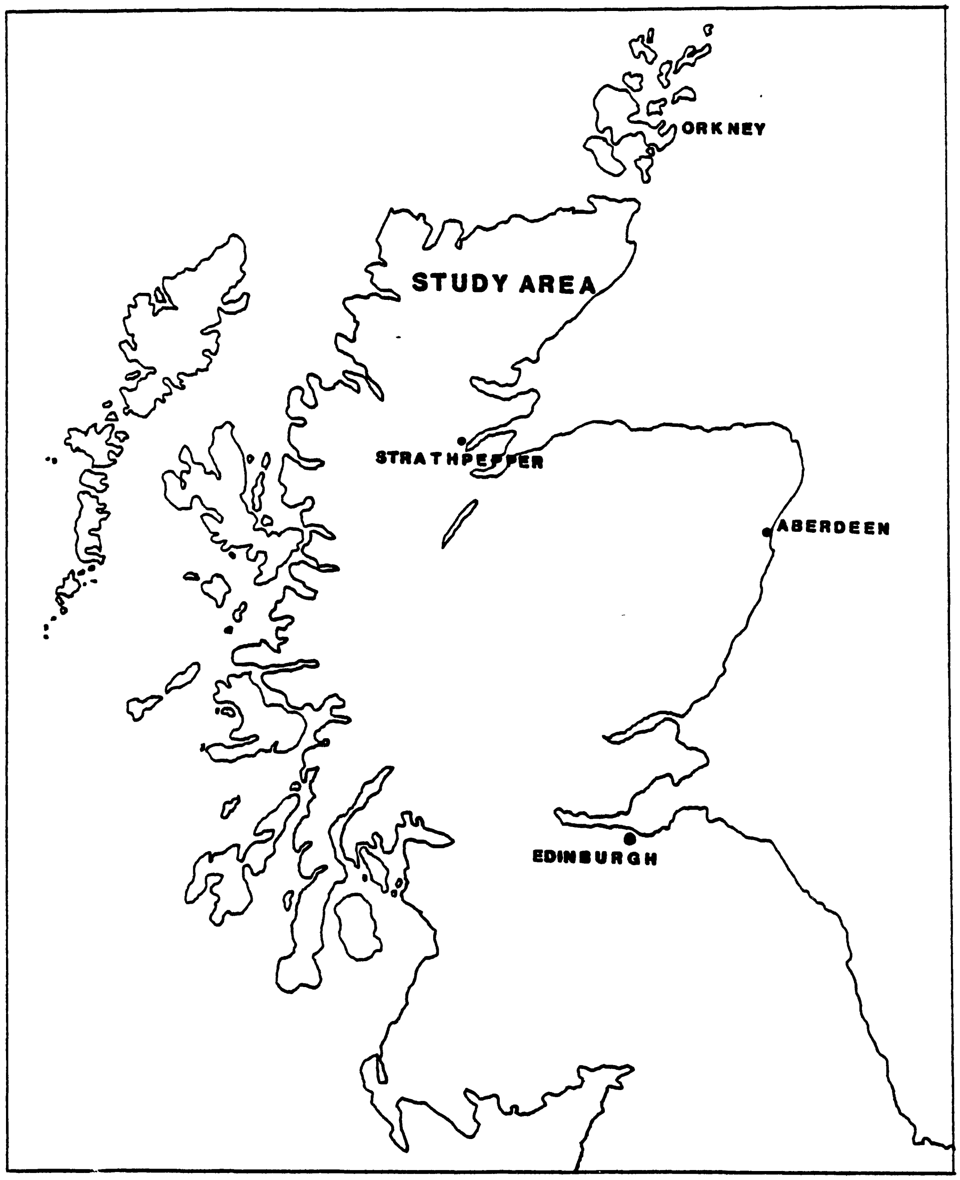


Figure 1. Location Map of Scotland
(After Donovan, 1984)

and Orkney contain the most extensive development of the Middle Old Red Sandstone (hereinafter abbreviated as O.R.S.) in Scotland. Southwest of Caithness and Orkney, the outcrop continues intermittently through east Sutherland into Easter Ross, where it forms most of the Black Isle and parts of the Tarbat Ness peninsula. Further to the south, the Middle O.R.S. forms a narrow outcrop east of the Great Glen Fault along the southern shore of Loch Ness and the inner Moray Firth between Foyers and Nairn. Further to the east in the Fochabers-Buckie area, south of Cullen, and in the Turriff Outlier, several Middle O.R.S. outliers occur.

In general, all these southerly outcrops illustrate a dramatic change in facies from a predominantly lacustrine (in Caithness) to a predominantly fluvial character (Figure 2). The Middle O.R.S. as exposed around the shores of the Inner Moray Firth was deposited on an alluvial plain which was periodically inundated by a large lake system. By contrast,in Orkney and Caithness the Middle O.R.S. is composed of predominantly lacustrine sediments which are characterized by well-developed sedimentary cycles resulting from long-term transgressive and regressive cycles within the closed lake basin (Donovan, 1984).

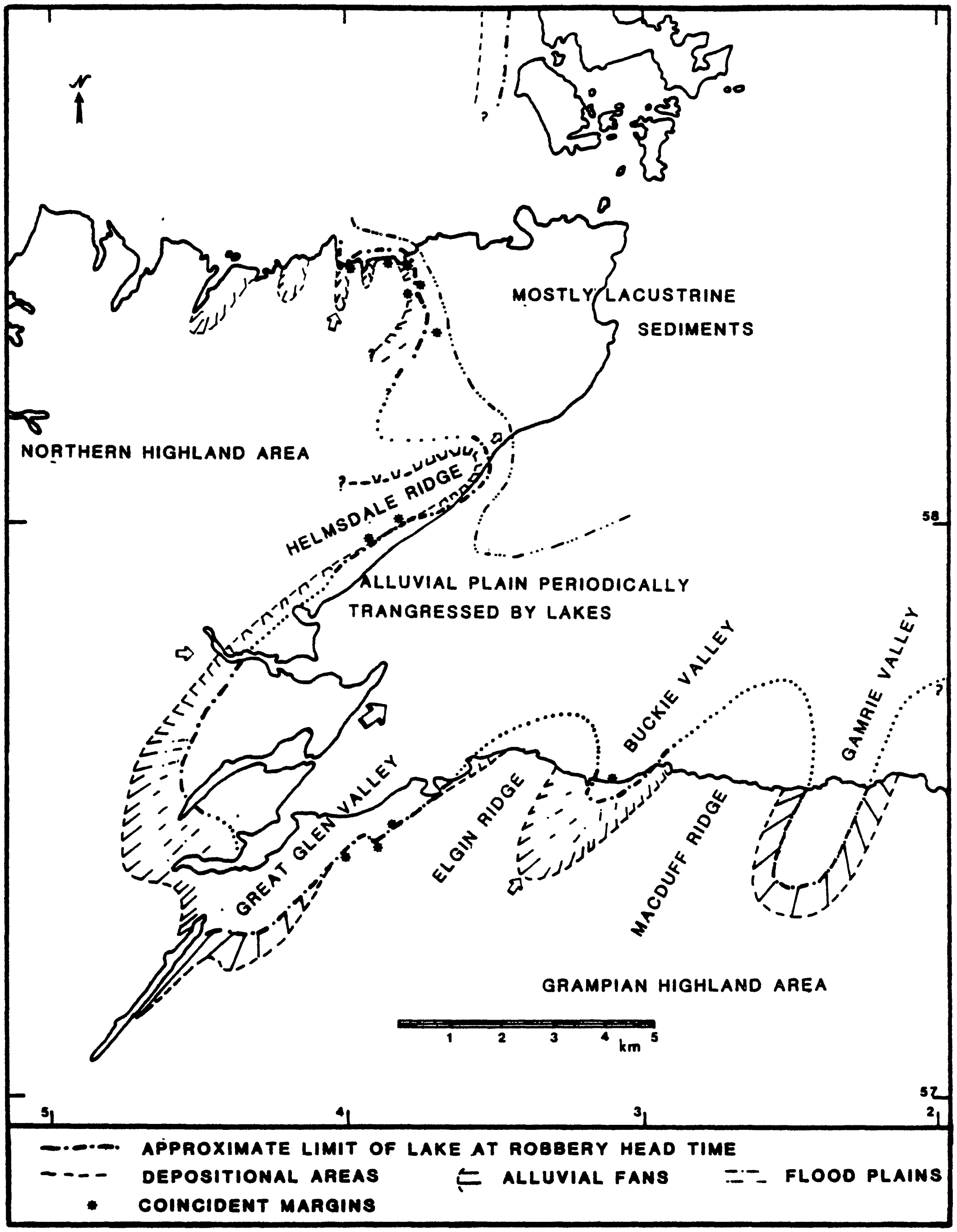


Figure 2. Devonian Environments of Northern Scotland and Caithness Area (From Donovan, 1984)

Procedure

The rock samples for this thesis were collected by R.N. Donovan during July and August of 1983. Five major and four minor sections were measured and sampled (Appendix A). Field work was conducted at the following localities: Robbery Head, Tarbat, Ackergill, Achvarsdal, Baligill, Buckie, Red Point, Dirlot and Loth (Figure 3). These samples were used for megascopic, petrographic, x-ray diffraction, isotope, geochemical and electron microscope analysis.

Megascopic descriptions undertaken include textural analysis and color classification according to the Rock Color Chart (Goddard et al., 1963). Petrographic analysis was conducted on fifty thin sections which yielded information concerning texture, detrital composition, authigenic constituents, based on the percentage of organic matter and paragenesis. Thin section slides were stained with alizarin red and potassium ferricyanide in order to differentiate between ferroan calcite, nonferroan calcite, and dolomite. Twenty-five samples were used in x-ray diffraction analysis. Samples were x-rayed through a 20-600 spectrum, to distinquish the main constituents. Results of x-ray diffraction analysis appear in Appendix B. Geochemical evaluations were based on total organic carbon (TOC) and percent of organic matter (POM) using the Soil Organic Method used by the Oklahoma State University

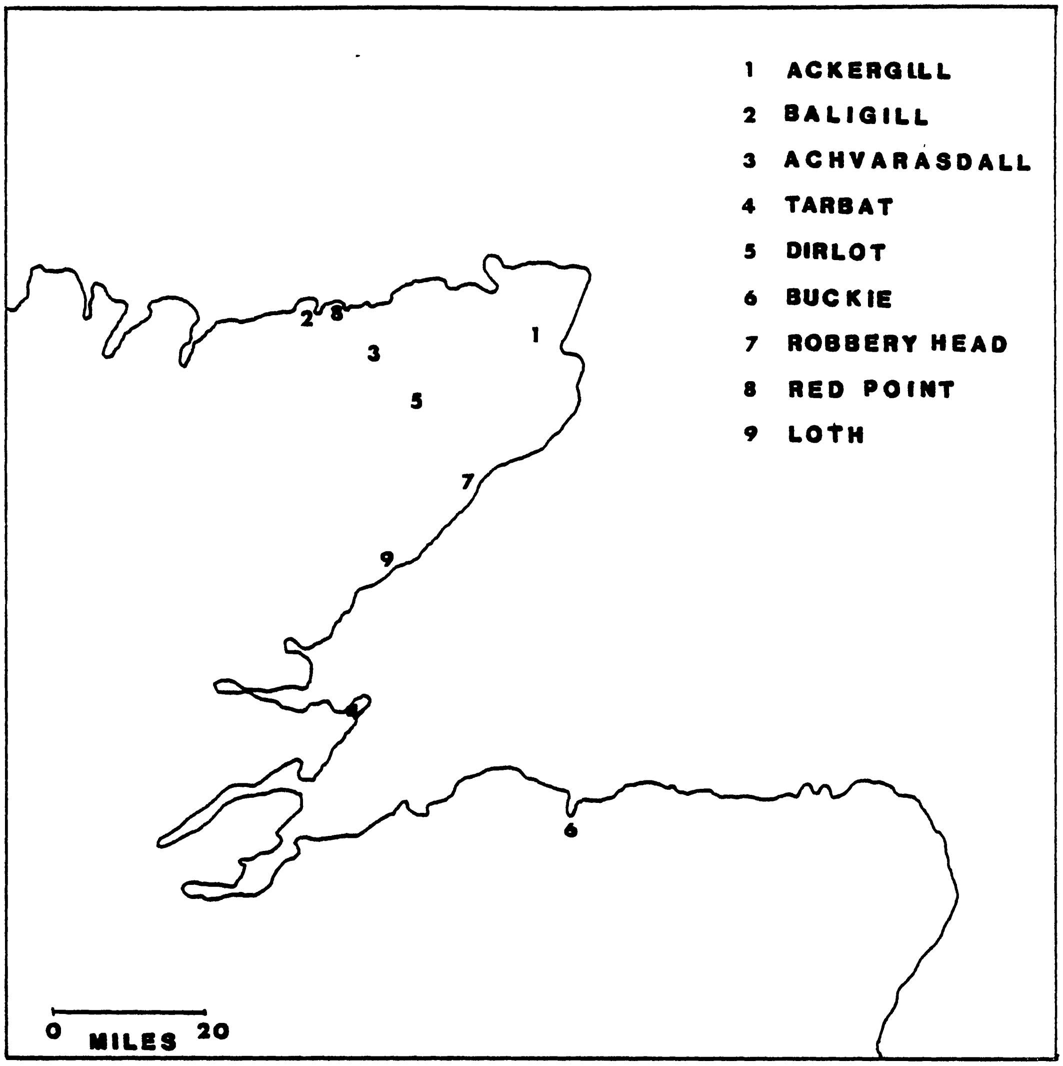


Figure 3. Location Map of Field Areas

Agronomy Department (Appendix C). Scanning Electron Microscopy was used on selected limestones to identify cements and delineate authigenic and detrital clays. Isotope analysis, completed at the Conoco Refinery in Ponca City was used to compare isotope values of other lacustrine environments with those found in Scotland.

CHAPTER II

GEOLOGIC HISTORY

Background

The Orcadian Basin of Northeastern Scotland was the site of thick sediment accumulation (6000m) during the Devonian period. The Sediments were deposited in a non-marine NE/SW trending basin within the Caledonian orogenic belt. During subsidence of the basin, enormous quantities of sediment were trapped and deposited over a span of 12 million years from late Devonian time until the end of Middle Devonian time. During late Devonian times, subsidence was sporadic and subsidence rates dropped off dramatically (Figure 4).

Paleomagnetic data indicates that during the Lower Devonian, Britain lay between 20° and 30° S. At the end of the Devonian period, Britain had slowly moved northward to between 10° and 20° S (Figure 5). The climate of Britain during this time was warm to hot, semi-arid to arid, with sporadic torrential downpours (Allen, 1979).

During Lower Devonian times, the topography of Scotland was greatly influenced by contemporaneous normal faults which gave rise to major fault scarps and rift

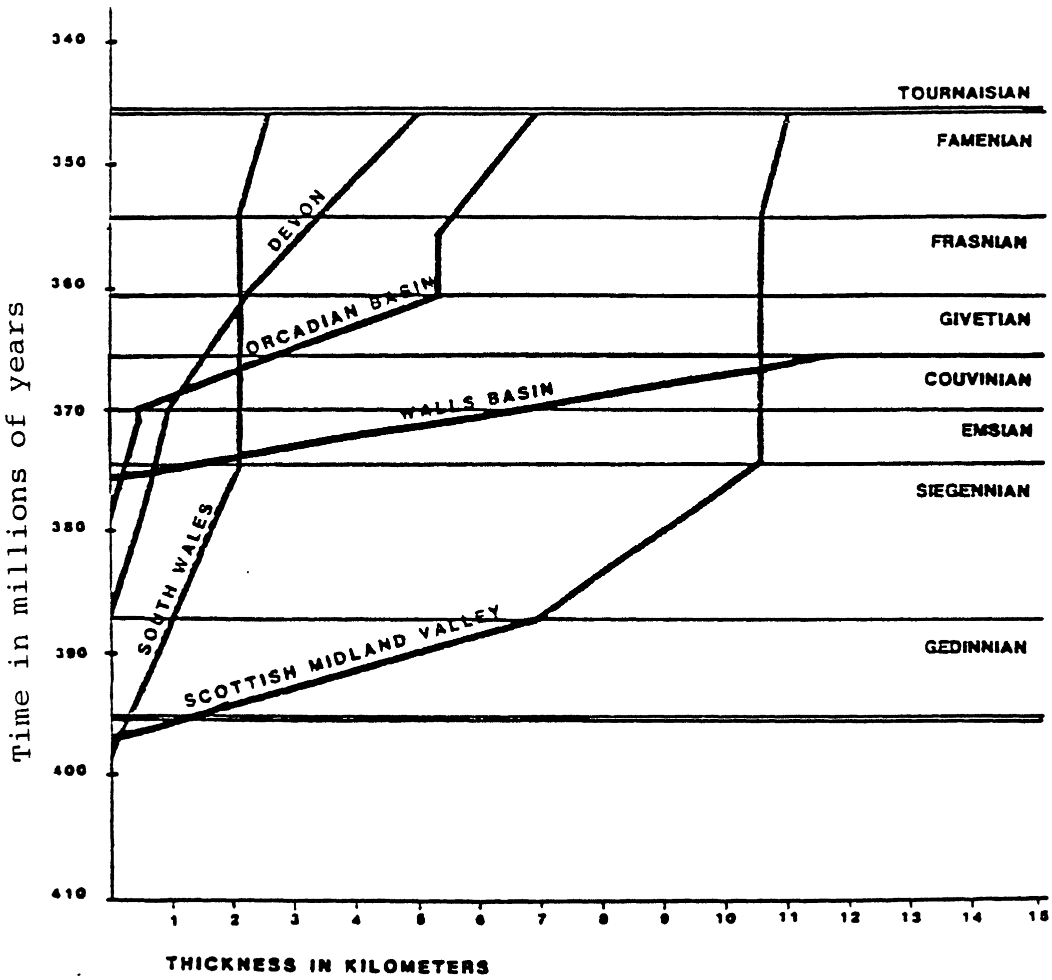


Figure 4. Orcadian Basin Sediment Rate and its Comparison to Other Major British Basin Settings During the Devonian (From Donovan, 1984)

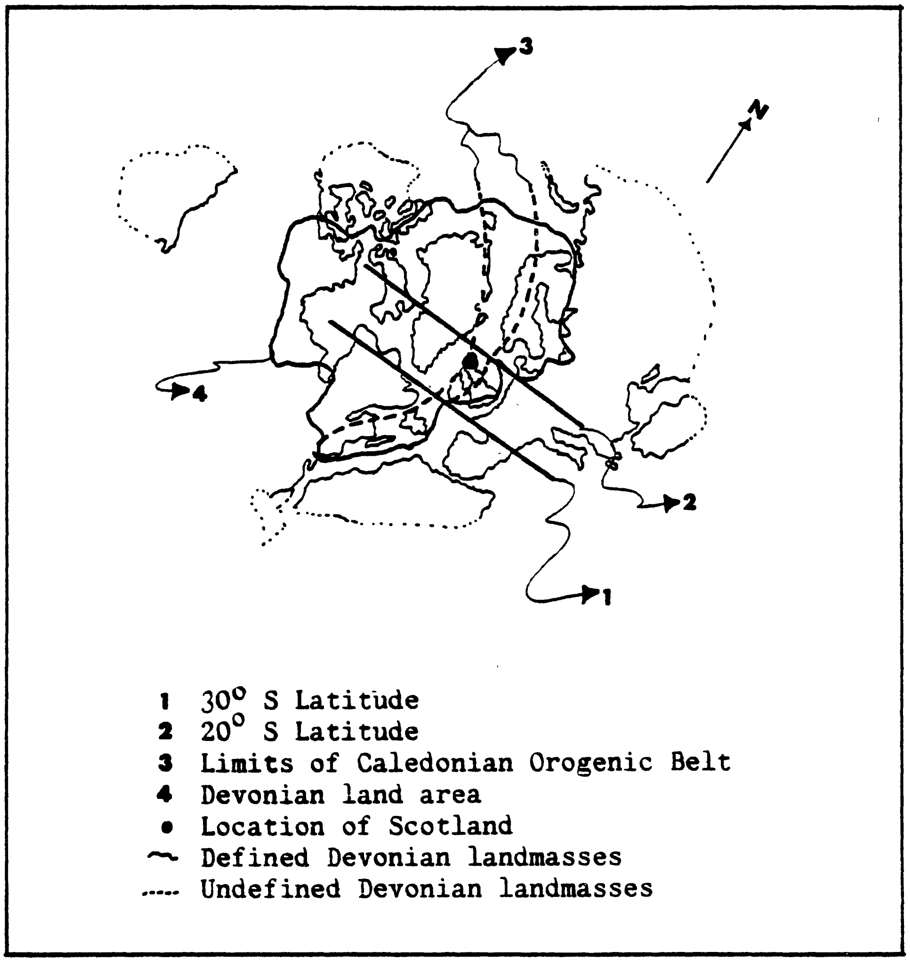


Figure 5. Paleolatitude of Scotland and the Old Red Sandstone During the Early Devonian (After Faller and Briden, 1978)

valleys (Mykura, 1984). The valleys were bounded by alluvial fans which resulted from the deposition of large quantities of sediment within the rift valleys. The most important of these valleys was the Scottish Midland Valley. Faulting during early Middle Devonian time produced gentle folding in the Midland Valley and intense localizing folding and thrusting in the valleys to the north. This tectonism led to reversals of drainage directions. Large incised rivers and streams flowed to the northeast on to alluvial flats around the Moray Firth area. North of the alluvial flats, lay a large basin in which accumulated fine grained sediment from the rivers which formed an extensive, shallow lake which deepened with age (Mykura, 1984). This area is known as Caithness and Orkney.

The depositional basins of the Old Red Sandstone can be classified as either open or closed in character. The open basins were bounded on one side by the Caledonian Orogenic Belt and on the other side by the sea. They are characterized by alluvial plain, fluvial, and shallow marine deposits. The closed basins (which include the Orcadian Basin) were self-contained entities within the orogenic belt. The closed nature of the basin allowed for the development of lacustrine and fluvial deposits.

Local Stratigraphy

Conybeare and Phillips (1822) were the first to use the term "Old Red Sandstone" to describe the Devonian fluvial, aeolian, lacustrine, and marine deposits found in Britain. The Old Red Sandstone of Scotland was divided into three subdivisions (Murchinson, 1859) based on its geographical location. Geikie (1878), later recognized similar facies within the Old Red Sandstone which were not unique to particular geographical areas, thus correlating beds in which Murchinson had separated. The units of the Old Red Sandstone include the Upper and Lower O.R.S. which are predominantly fluvial in origin and the Middle O.R.S. which is comprised of a lower part which is dominated by lacustrine sedimentation and an upper part dominated by fluvial deposition.

The Lower O.R.S. unconformably overlies a Caledonian basement of igneous and metamorphic rocks. It then is unconformably overlain by the Middle O.R.S. The succession of the Lower, Middle, and Upper O.R.S. is discontinuous throughout most of Scotland, but similar facies within the O.R.S. can be correlated and have been found to be equivalent in age (Mykura, 1984).

Regional Stratigraphy

The Orcadian basin of Northern Scotland contains all three divisions of the Old Red Sandstone (Table I). A

TABLE I

DEVONIAN STRATIGRAPHY IN NORTHERN SCOTLAND
(AFTER WESTOLL, 1977)

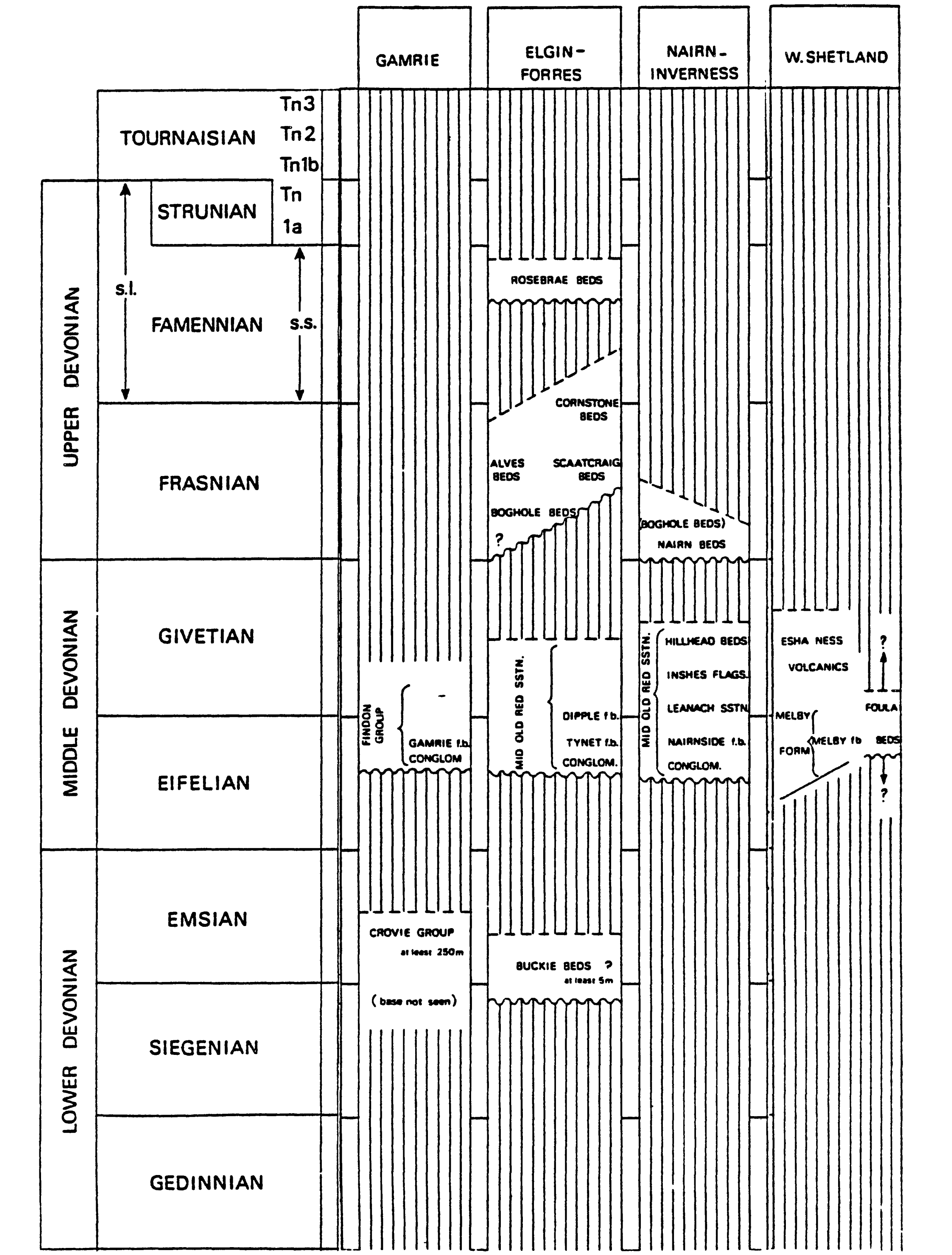
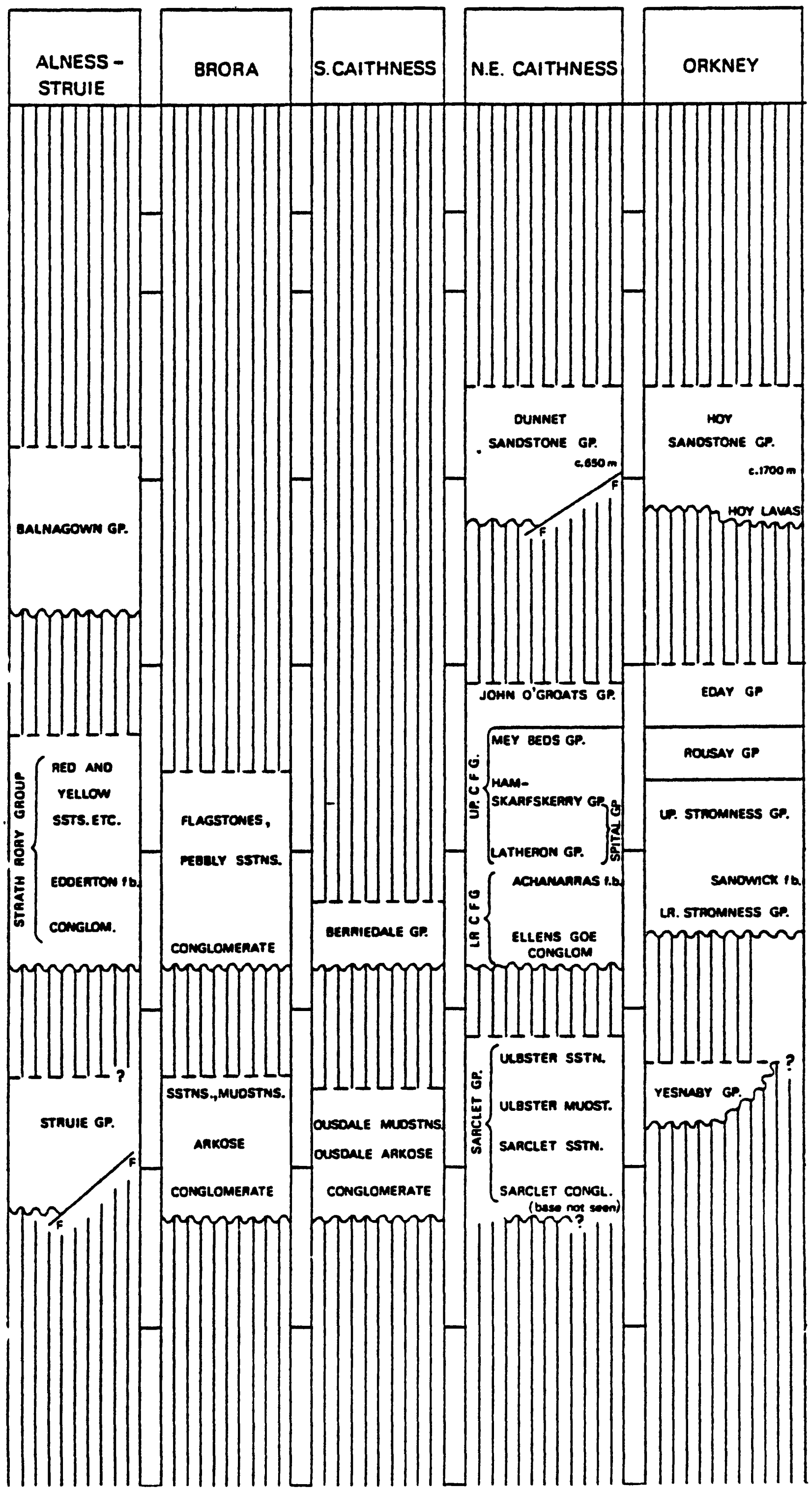


TABLE I (Continued)



brief introduction to the Lower, Middle, and Upper O.R.S. and its occurrence in and around the Caithness area will be discussed in the following pages.

The Lower O.R.S. sediments of the Orcadian Basin in Caithness are restricted in their areal distribution (Figure 6). The limited exposures at Sarclet and Ousdale suggest that the sediments were deposited in isolated, playa-filled basins, within the Caledonian Mountain Chain (Mykura, 1984). The Caithness Lower O.R.S. sequence is as follows (Donovan, 1974):

1. Sarclet Conglomerate Formation
2. Sarclet Sandstone Formation
3. Ulbster/Riera Geo Mudstone Formation
4. Ulbster/Ires Sandstone Formation

The Sarclet Conglomerate facies consists of lenses of conglomerate deposited as pebbly alluvium. Subsequently non-pebbly braided rivers and streams deposited the alluvium now known as the Sarclet Sandstone. The Ulbster/Riera Geo Mudstone is composed of a rhythmic sequence of green mudstones and marls. This facies appears to have been deposited in a shallow lake which underwent periodic wetting and drying (Mykura, 1984). The fluvial sandstones which cap the mudstone/marl cycles are known as the Ubster/Ires Geo Sandstones.

The Lower O.R.S. of Southern Caithness lies directly on the Helmsdale granite and consists of a basal member referred to as the Ousdale Arkose. Overlying the arkose is the Ousdale Mudstone which is comprised of purple,

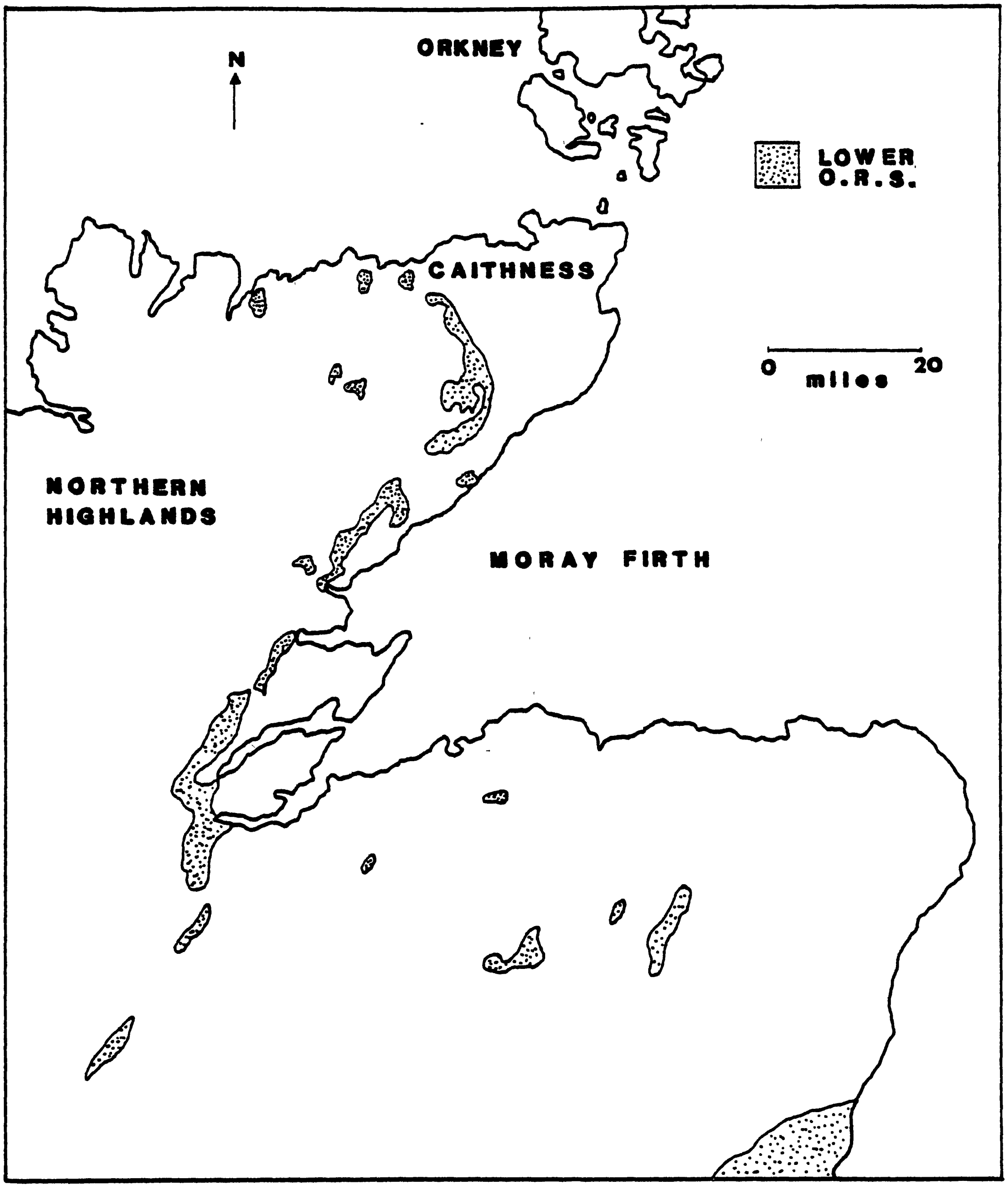


Figure 6. Outcrops of the Lower Old Red Sandstone

light green, and red siltstones and mudstones. The siltstones and mudstones locally alternate with pebbly sandstones.

The Middle O.R.S. of the Orcadian Basin, in the Caithness area is Eifelian-Givetian in age (Figure 7). The succession of Middle O.R.S. deposits contains numerous fossil fish-bearing beds. The most important of these beds (which form the basis for stratigraphic subdivision) is the Achanarras Limestone which is placed at the Givetian-Eifelian boundary. Many fish made their only appearance in the stratigraphic record during this time (eg. Paleospondylus gunni) (Donovan, 1984). The deposits of Caithness, known informally "flagstones", reach an estimated thickness of 4 km. The flagstone succession of Caithness consists of numerous well-defined rhythmic units or cycles. The cycles represent a sequence of events which were repeated in the shallow lake throughout most of its existence. The Middle O.R.S. is the most prevalent outcrop in the Orcadian Basin and will be covered in more detail in the succeeding chapters (Figure 8).

The Upper O.R.S. in Northern Scotland is extremely limited in outcrop (Figure 9). The only exposures in Caithness are located at Dunnet Head. The rocks are composed of pinkish, medium-grained, trough-cross-bedding sandstones (Mykura, 1984). Some of the sandstones are locally pebbly with convolute bedding and minor amounts of

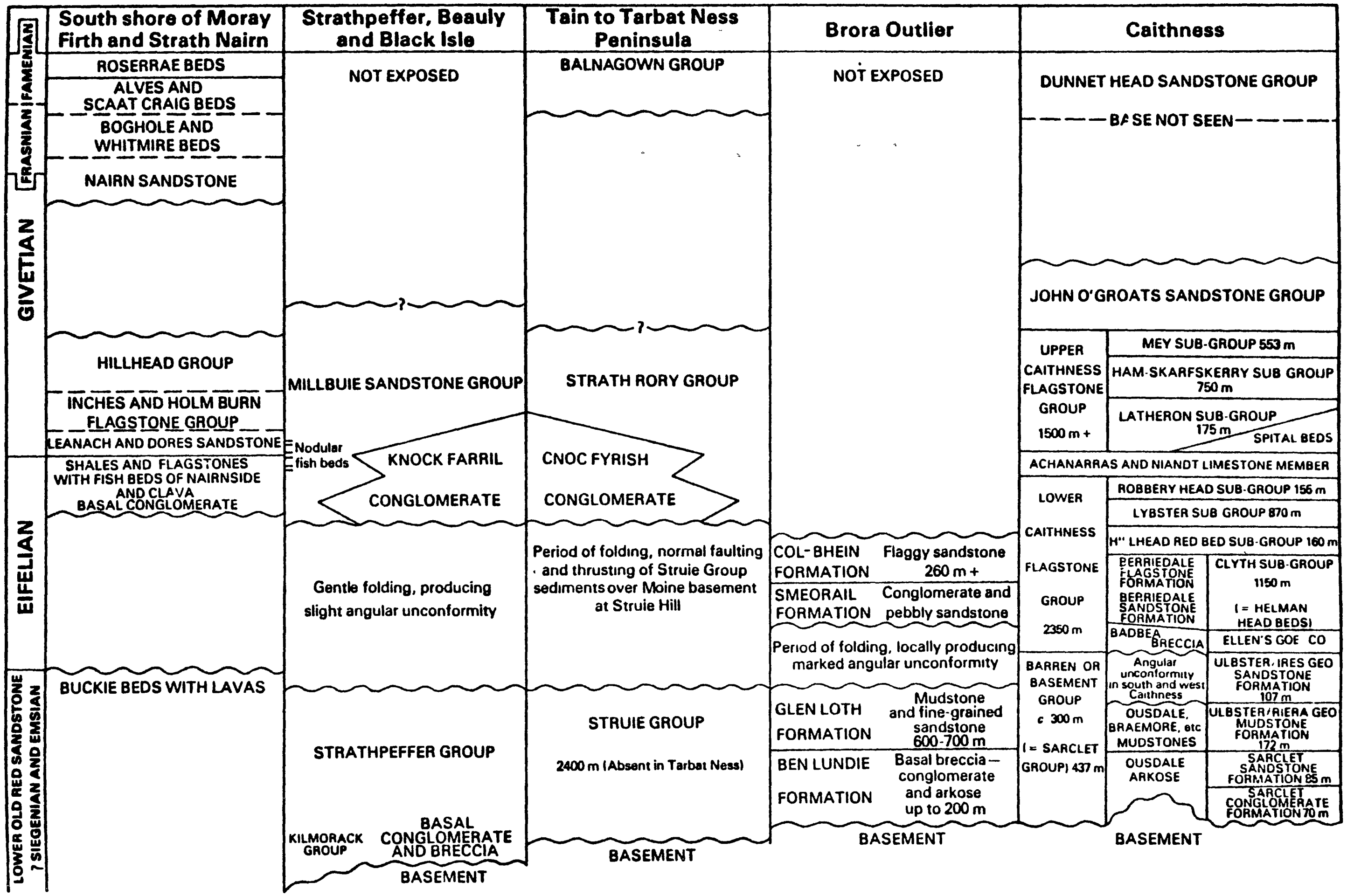


Figure 7. Stratigraphical Divisions of the Old Red Sandstone of Northern Scotland (From Mykura in PADS, 1978)

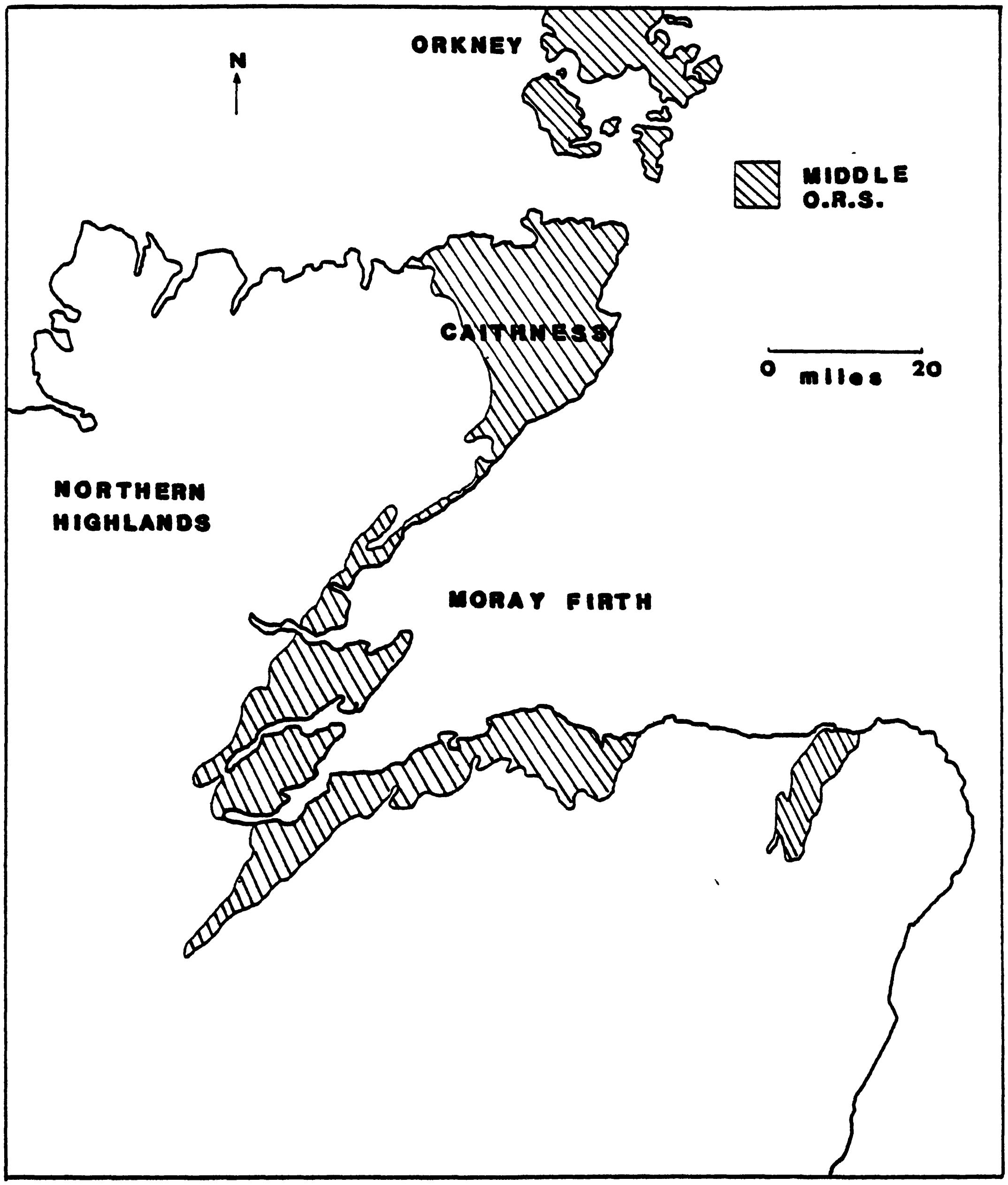


Figure 8. Basin Localities of Middle O.R.S.

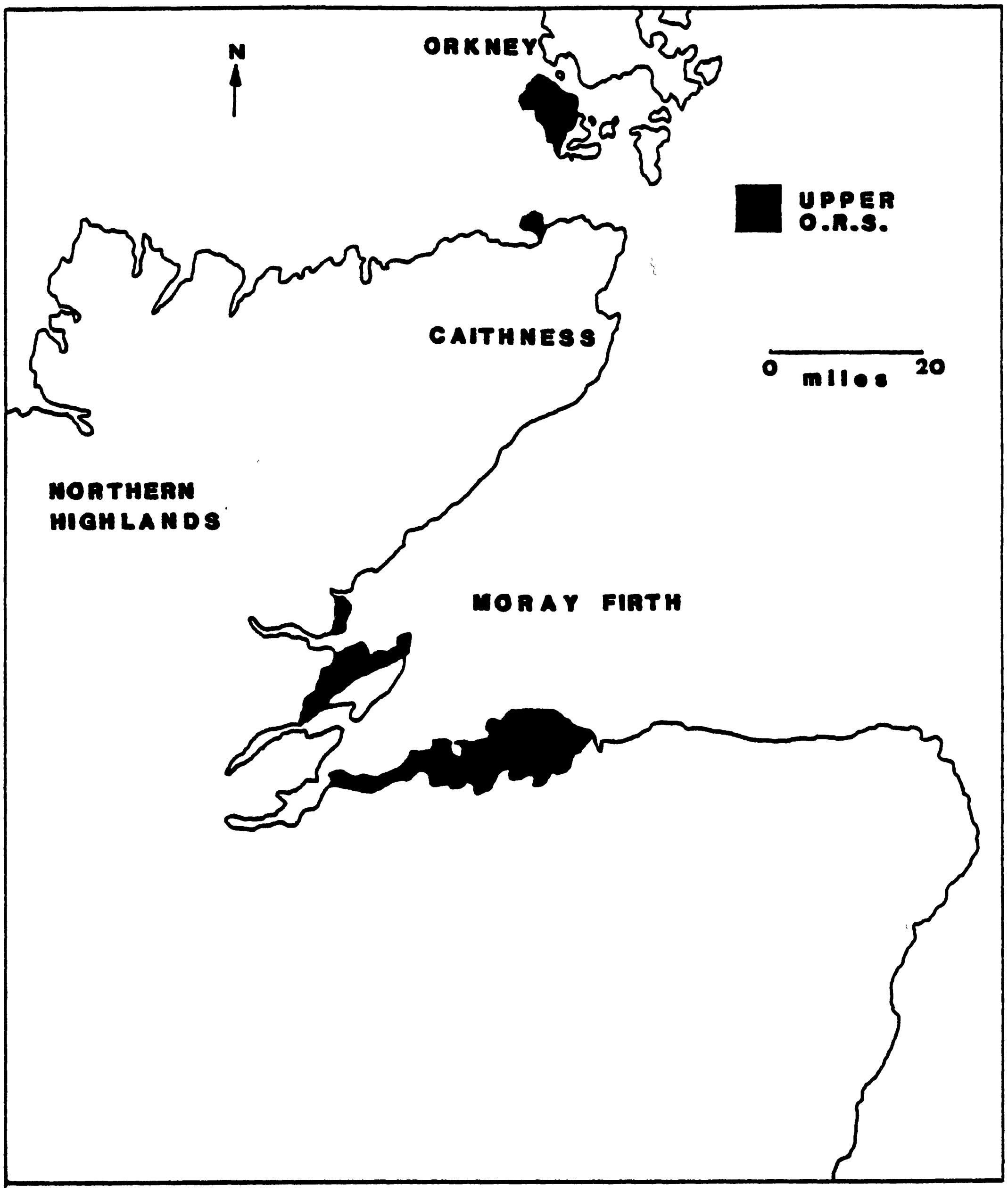


Figure 9. Location Map for Upper O.R.S. Deposits

intraformational red mudstone clasts. The deposit is believed to have been deposited by braided streams and rivers which originated from the southwest (Mykura, 1984). Other Upper O.R.S. deposits, further to the south around Moray Firth, are of similar character.

CHAPTER III

DEVELOPMENT OF THE MIDDLE OLD RED SANDSTONE

Paleogeography

The Middle Devonian rocks of northern Scotland are mostly lacustrine in origin (Conybeare and Phillips, 1822; Murchinson, 1859; and Crampton and Carruthers, 1914). Sedimentation in the basin began with streams and rivers which inundated a complex tectonic depression in Northern Scotland. Floodplains and small lake systems developed. Sediment supply was from major river systems which originated to the west, northwest, and the southwest. The positioning of the rivers was probably in part controlled by the eroded fault lines of the Helmsdale Great-Glen Fault system located to the south of the Orcadian Basin (Mykura, 1984). Initially, it is probable that a ridge to the south of Caithness which ran in a northwest to southeast direction limited the northward passage of coarse clastic sediments. Therefore the shallow lake forming in the Orcadian Basin recieved little to no fluvial material from the south and west during the early stages of its formation (Mykura, 1984).

The maximum extent of the lake formed in the Orcadian

Basin is believed to have covered an area of approximately 50,000 km (Donovan, 1984). At this time, the lake extended over most of the exposed part of the basin, from the southern part of Caithness to the northern islands of Orkney (Figure 10).

The period of greatest lake development is marked by the occurrence of a distinctive fish fauna (the so-called "Achanarras Fauna"). Deposits containing elements of this fauna can be found at sites all around the basin, both in its presumed center and around its periphery. The southern boundary was formed by the Moray Firth alluvial plain. The western limit of the present O.R.S. outcrop coincides with the gradually transgressing northwest-ward boundary of the lake's western margin. The alluvial plain of a river flowing from the west/northwest was probably the boundary for the northern margin of this lake (Mykura, 1984). An eastern boundary for the lake is undefined due to lack of exposure.

Lake Facies

The thickness and lithological components of the lake deposits are influenced by their stratigraphical and geographical position within the lake basin. The lake record reflects fluvial influences (and delta development) tufa formation, stromatolitic activity, and an oscillating shoreline (as evidenced by ripple marks and desiccation cracks). Deepening of the water and progression towards

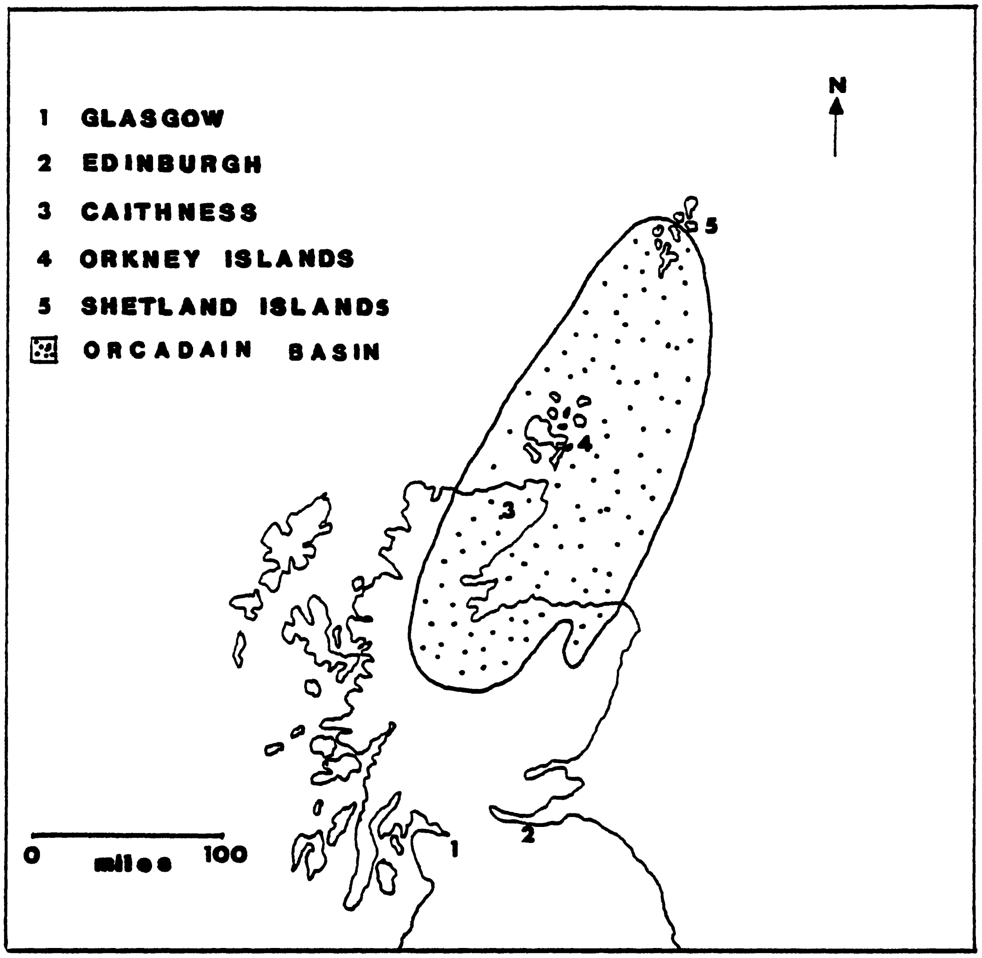


Figure 10. Orcadian Basin Development in Northern Scotland

the center of the lake is reflected by the occurrence of varves, deepwater laminites, and turbidity flows (Donovan, 1984).

Specific stratigraphical and geographical localities within the Orcadian Basin were chosen to illustrate the transformation from lake margin deposits to those of deepwater deposits (Figure 11). Lake margin localities include Red Point, Baligill, Dirlot, Loth, Tarbat Ness, Buckie, and Achvarasdal. Lake center localities include Robbery Head and Ackergill. Measured stratigraphical sections of these areas are located in Appendix A. A brief summary of each area and its field relationship as well as a lithologic description is included here. The summaries are based on field observations (Donovan 1973, 1975). A more detailed petrographic and geochemical analysis will be presented in the following chapters.

Red Point

At this location an exposure of Precambrian granite was eroded in Devonian time to an irregular unconformity. Complex facies exist in the overlying Devonian sediments. The basal rocks at Red Point consist of angular breccias in a closed-work fabric with a matrix of arkosic sandstone. In some areas an open-work texture cemented by nonferroan calcite has been observed (Donovan, 1975). Marginally, the breccias interdigitate with and pass

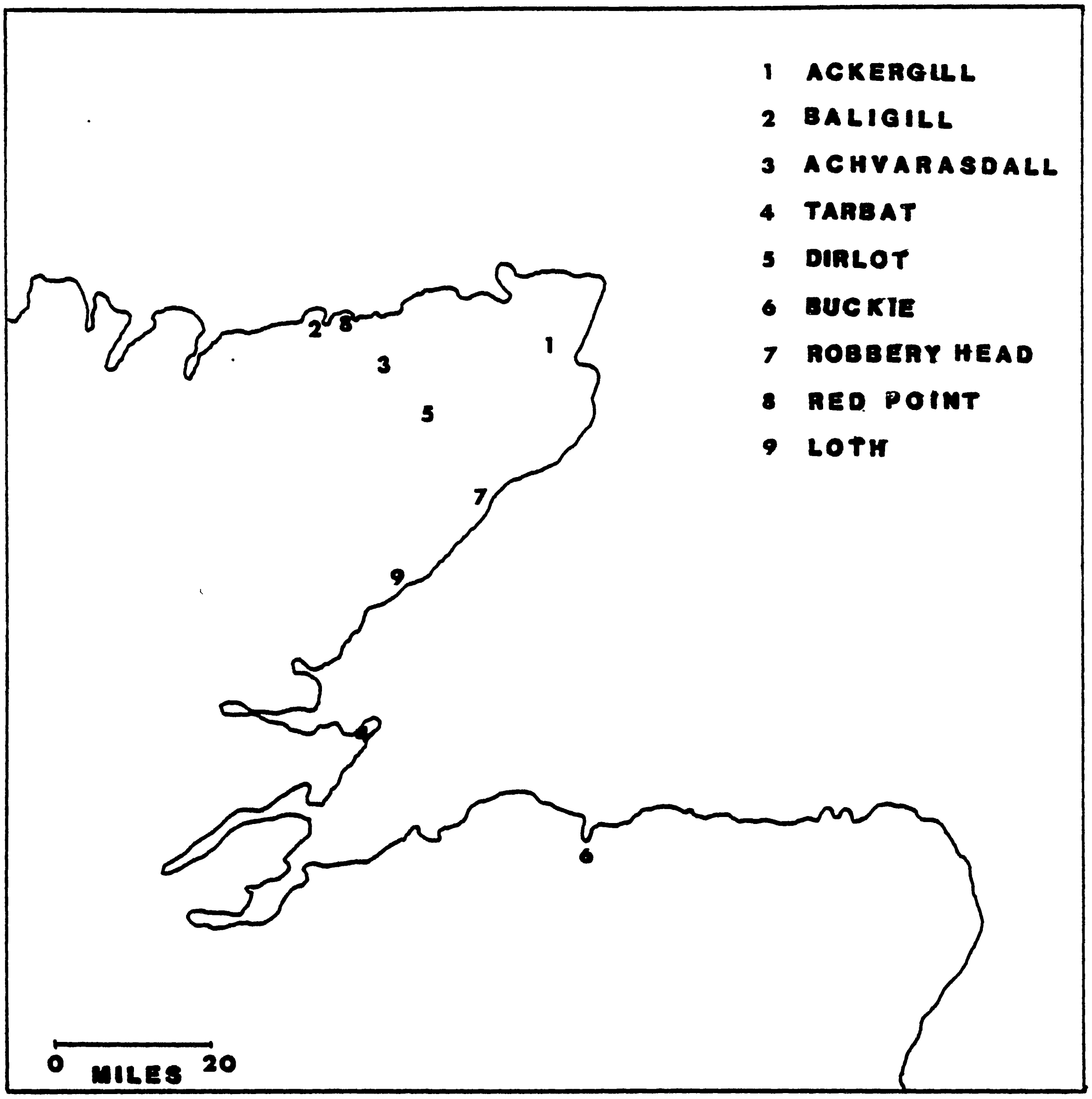


Figure 11. Basin Localities of Marginal and Basinal Lake Facies

laterally into laminated sandy limestones. Basinwards of the brecciated lithofacies, typical flagstones (offshore lacustrine facies) of grey/green mudstones and flaggy-bedded siltstones occur. These contain abundant symmetrical ripple marks and subaerial desiccation cracks (Figure 12). At the western end of the inlier it has been suggested that the granite surface was covered by a transgressing lake; as a result, a rapid variation in facies has been noted (Donovan, 1975). The lithologies present include marginal massive and platy-bedded limestones which pass basinward into a carbonate laminite (Figure 13). The carbonates appear to have been deposited rapidly at high original dip angles upon granodiorite knolls which have also acted as a generating slope for small turbidity flows (Donovan, 1975). Further west of Red Point the sequence continues but is inaccessible due to high cliff sections.

Baligill

At the Baligill locality, the relationship between basement rock and the Old Red Sandstone is similar to that at Red Point. Similar facies relationships to those described at Red Point also exist (Figure 14). The massive limestone at Baligill is overlain by a platy limestone. Unlike Red Point, a lateral passage from the platy limestone to a calcareous laminite cannot be detected due to lack of exposure. Mudstones and

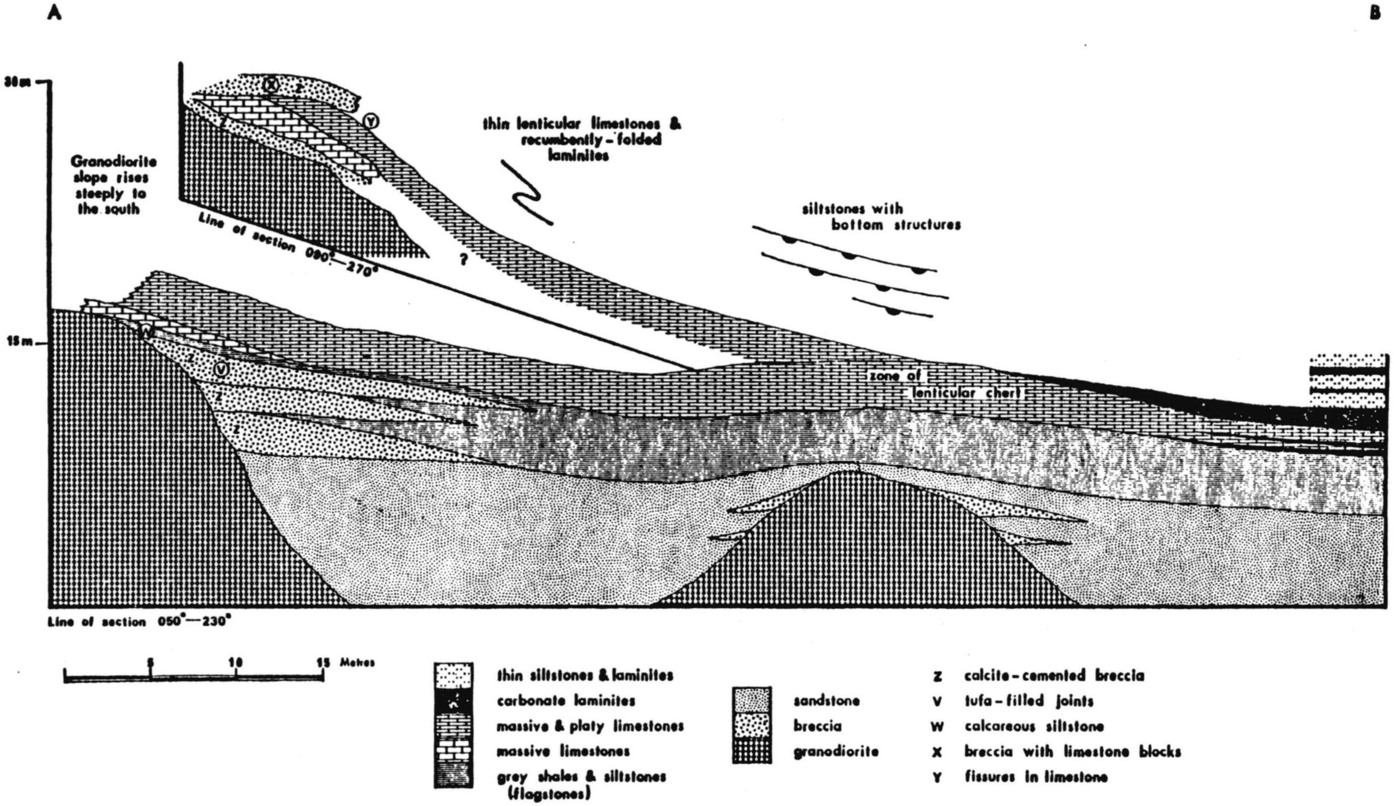


Figure 12. Relationship of Rocks at Red Point
(From Donovan, 1975)

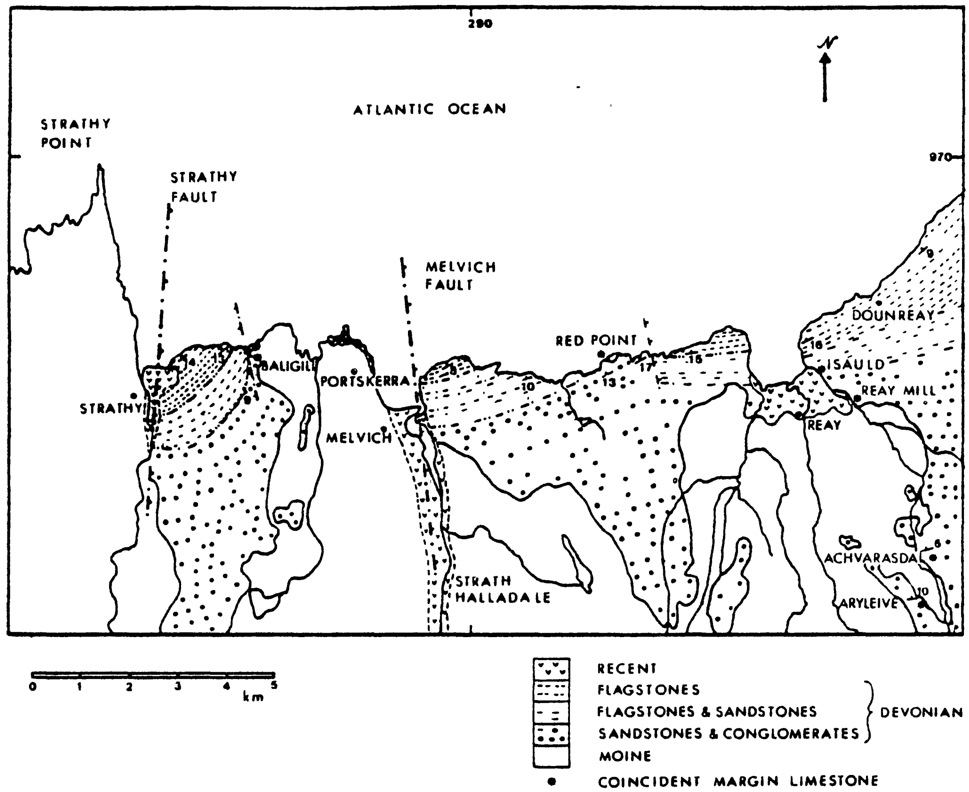


Figure 13. Lithologies of Deposits at Red Point

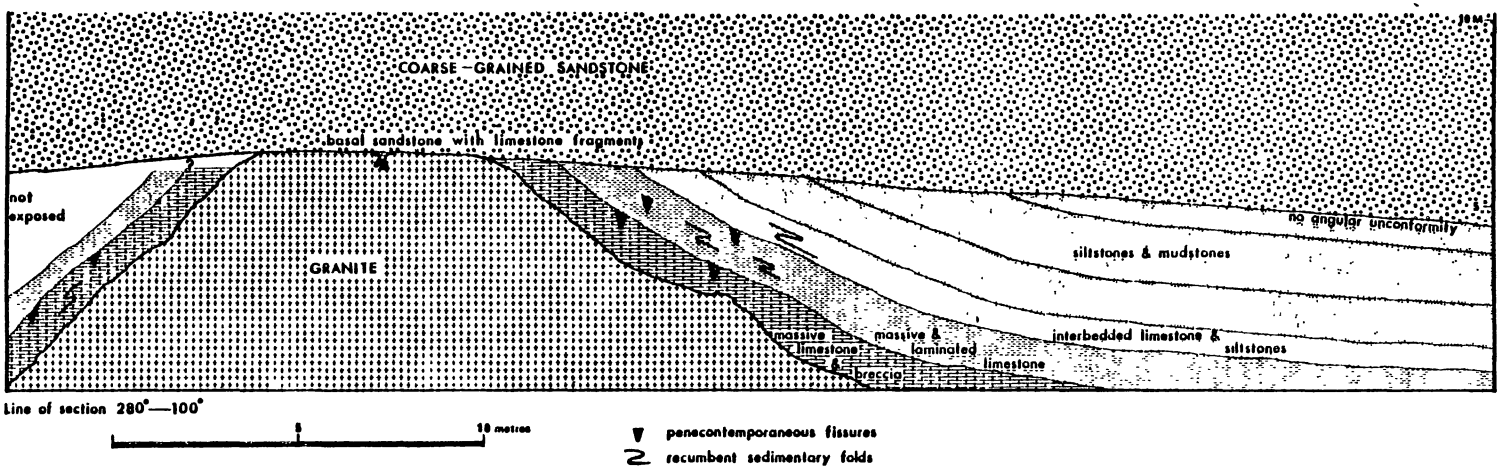


Figure 14. Relationship of Rocks at Baligill
(From Donovan, 1975)

siltstones overlie the platy limestone in the same fashion as seen at Red Point. A coarse-grained, buff weatered sandstone unconformably overlies the interbedded mudstones and siltstones. Due to the limited exposures at Baligill, a complete section description was unattainable (Figure 15).

Dirlot

The basal deposits of the O.R.S. at Dirlot consist of coarse pebbly sandstones which fine upward into medium-grained sandstones. The finer sandstones exhibit cross-stratification which indicates transport from the west (Donovan, 1973). Two distinct breccia deposits with stromatolitic coatings and interparticle tufas are found above the basal sandstones. The tufa deposits are confined to fissures and occur sporatically throughout the lower breccia. The stromatolites occur as coatings around well-rounded pebbles. The breccias are overlain disconformably by grey sandstones which exhibit low-angle, medium-scale, cross-stratification.

Buckie

The deposits of the Middle O.R.S. located in the Buckie area have been classified as uppermost, Lower O.R.S.by earlier workers, but the age of the sediments has been questioned. Some authors (Donovan, 1975; Westoll, et al., 1977; Mykura, 1984), believe that these beds may in

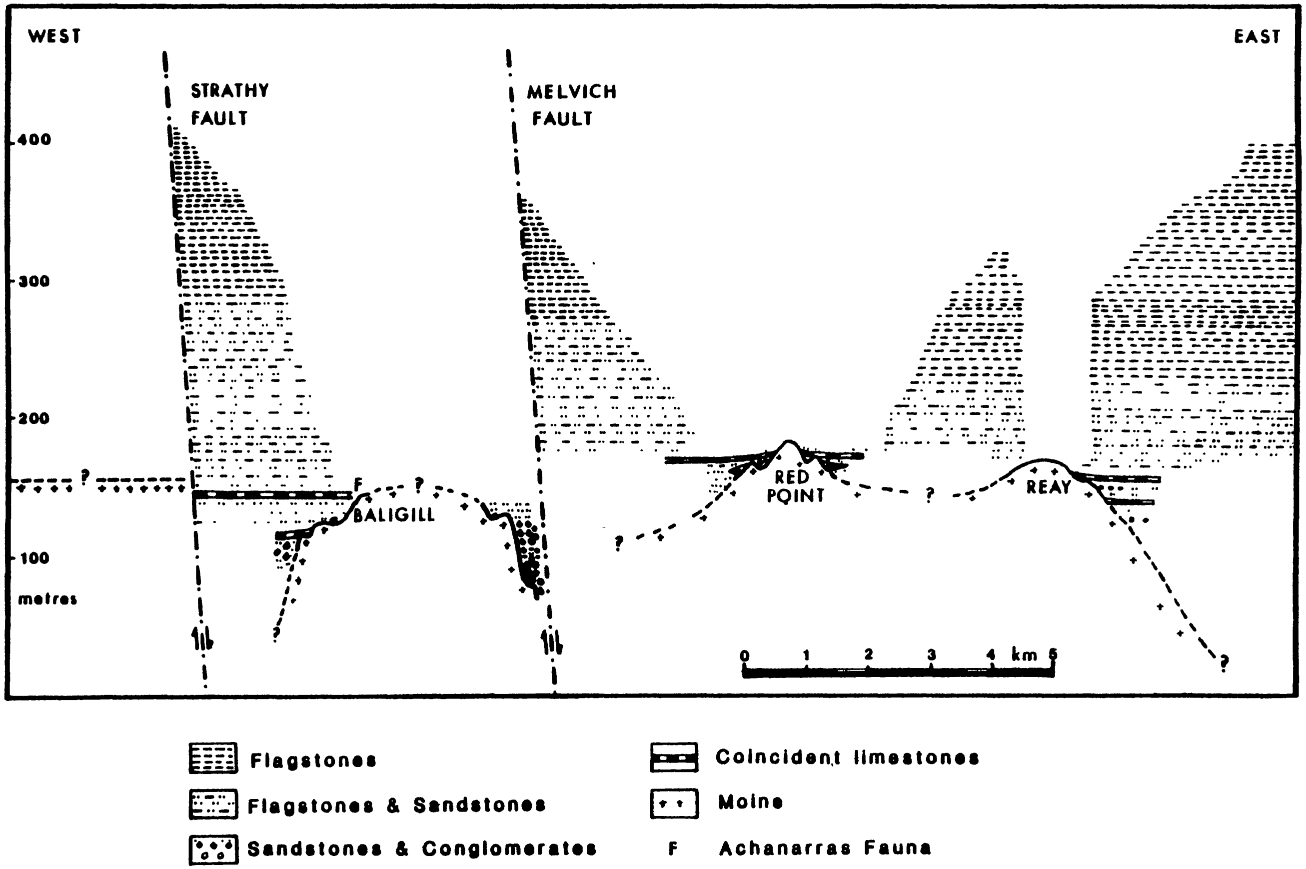


Figure 15. Similar Facies Relationships Between Red Point and Baligill

fact be lower Middle O.R.S.. Donovan (1975) has described sediments at Red Point similar to those at Buckie. The deposits may be lacustrine marginal deposits with an original dip which was truncated by "marginal" river-current action, therefore adding to the confusion surrounding the age of the Buckie deposits. Since the age of the sediments is questionable, they will be treated here as lower Middle O.R.S. because of their similarity to the sediments of Red Point. The sequence consists of a 3m thick sequence of limestones and carbonate-cemented breccias overlain by 2m of flaggy bedded sandstone. The beds rest unconformably on the Cullen Quartzite.

Tarbat Ness

The deposits located at Tarbat Ness belong to the Strath Roy Group (Armstrong, 1975). The lowest member of the Strath Roy Group is the Meikle Daan Conglomerate. The conglomerate also contains beds of yellow and red pebbly sandstones with intermittant horizons of siltstones and calcareous shales. Within the shale sequence is the Edderton Fish Bed. The overlying Cnoc Fyrish conglomerate is composed of thick breccias and conglomerates which interfinger with flaggy sandstones (Westoll, 1977).

Loth

The Middle O.R.S. basal conglomerates and arkoses in the area of Loth are here described for the first time.

The site at Loth shows a coincident marginal limestone resting on granodiorite which in its essentials is similar to that seen at Red Point. These sediments have undergone basinal folding, faulting, and erosion. These deposits are overlain by interfingering sandstones and mudstones. contain poorly preserved spores which have been dated as late, early Devonian (Westoll, 1977).

Achvarasdal

The Middle O.R.S. of Achvarasdal are poorly exposed, therefore the description is limited. The rocks are limestones and breccias with scant exposures of both dolomite and calcite-cemented breccias. Tufas similar to those at Dirlot are seen lining fissures among the limestones and breccias.

Robbery Head

The deposits at Robbery Head have been formally classified as the Robbery Head Subgroup (Donovan, et al., 1974). These subgroups consist of two formations: the Forse Castle Formation, and the Niandt Formation. The Forse Castle Formation is conposed of thinly bedded flagstones. The Niandt Limestone Formation conformably overlies the Forse Castle Formation. It is composed of laminites which are frequently dolomitic and weather to shades of orange. The Niandt Limestone is particularily fossiliferous and has yielded several species of fish including elements of the Achannaras Fauna especially, the diagnostic *Palaeospondylus gunni*.

Ackergill

The Ackergill Beds, once under the classification of the Survey's Thurso Flagstone Group (Crampton and Carruthers, 1912) are now recognized as part of the Mey Subgroup (Donovan, et al., 1974; Westoll, 1977). The Ackergill Beds can be divided into two distinct lithologies. The lower unit consists of red beds with an upper unit of coarse and massive sandstones up to a meter in thickness. The fossiliferous fish beds of Ackergill do not contain the orange weathering dolostones as seen in the Robbery Head Formation.

CHAPTER IV

MARGINAL DEPOSITS

The marginal limestones of the Orcadian Basin contain a variety of textural as well as numerous depositional patterns. The margin deposits are defined as those which compose the periphery of the basin. This chapter includes descriptions based on petrographic analysis and concentrates on major grain constituents, cement types, textures, and diagenetic features. Since some of the geographical localities are similar in description, they will not be treated as separate entities as they were in their field descriptions (Chapter III). The descriptions will be separated based on the petrographic features found within the deposits.

Carbonate Petrography

The marginal deposits vary from "sandy" (i.e. siliclastic-bearing) limestones to dolomitic limestones. The percentage of detrital constituents within the deposits is related to the relative positioning within the lake basin. Progression away from the extreme lake margins is related to a decrease of detrital sediment supply. This decrease causes the limestones to become less "sandy" and more micritic.

The petrologic analysis of the marginal limestones includes the mineralogy (quartz, feldspar, muscovite, tourmaline, pyrite, hematite, and organic material), the cements (calcite, dolomite, and hematite), the textures (varves, tufa, nodules, and pseudomorphs), and the diagenesis of the limestones.

Mineralogy

Quartz

Monocrystalline quartz is the most abundant detrital constituent found within the marginal limestones of the Orcadian Basin. It ranges from 3% up to 45% and averages to 26% of the deposits examined. The quartz grains are usually moderately sorted and subangular to subrounded. The size and spericity of the quartz is misleading because of the corrosion by calcite, therefore only the quartz grains which appear not to have undergone dissolution by calcite were examined for textural features. Although, some of the quartz was found to be slighty undulose and contain a few carbonate inclusions, most of the grains exhibited straight extinction. Polycrystalline quartz was rare throughout the marginal limestones. It was found only in trace amounts in a few of the samples examined.

The percentage of quartz found in the samples is related to its positioning along the margins of the basin.

Samples closer to the extreme margins of the lake basin contain upto 50% quartz. The large amount of quartz is due to the influence of streams and exposed rock surfaces close to the margins. Quartz was also found to be a major constituent in the marginal varves (Figure 16). Quartz and other detrital debris was probably brought into the system through the processes of wind and stream influence over the lake basin.

Feldspar

Feldspars are rare throughout the marginal limestones; they constitute approximately 1-2% of the thin-sections examined. Plagioclase feldspars, which are more abundant than microcline, show varying degrees of honeycomb dissolution. Microcline when present, generally is fresher and has developed fewer dissolution fabrics. Generally, the feldspars are scattered randomly throughout the grain population.

Muscovite

Muscovite is common throughout all of the marginal limestones. Percentages range from 3-6% of the grain population. Muscovite, unlike some of the other detrital grains, has not undergone partial or complete dissolution. The grains range in length from .25mm near the extreme lake margins to .15mm towards the basin. Where partial

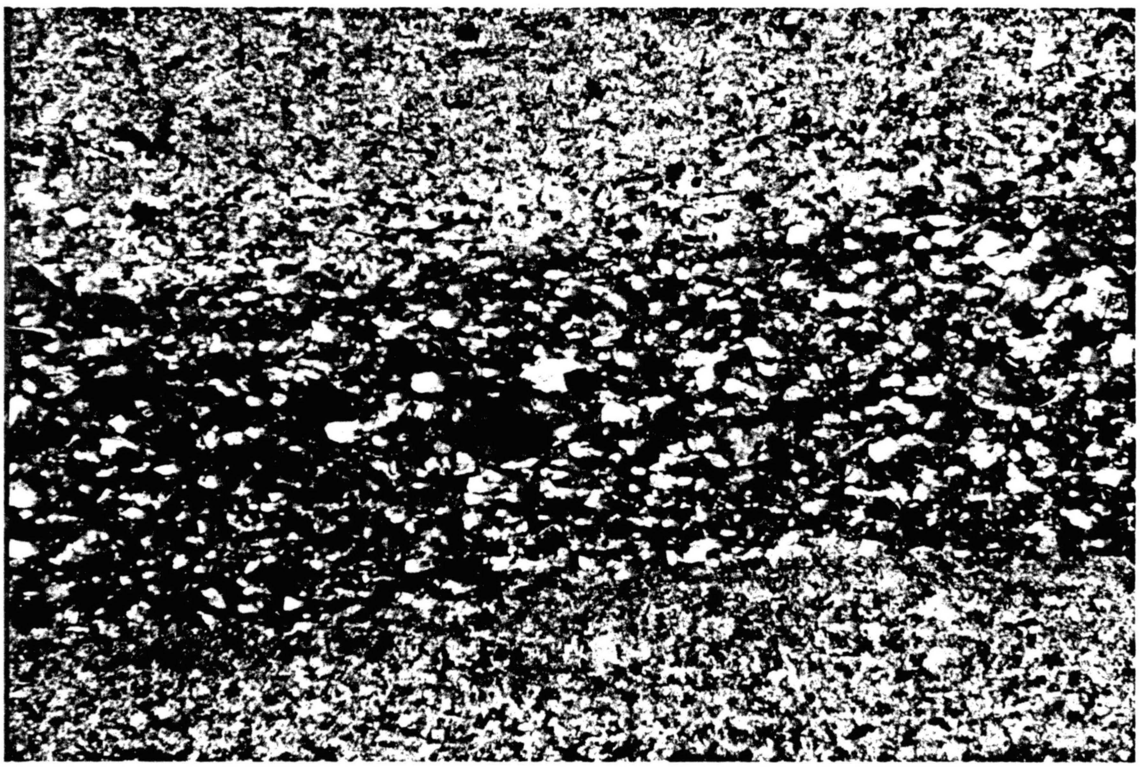


Figure 16. The Occurrence of Quartz in the Marginal Varves (X2-XN)

varves have formed near the margins, muscovite is aligned horizontally with the varve (Figure 17). The amount of muscovite is related to the relative amount of quartz seen in the deposit.

Tourmaline

Tourmaline is the only heavy mineral found in the marginal limestones of the Orcadian Basin. It is rare and only occurred in a few of the samples examined.

Pyrite

Authigenic pyrite was observed in varying amounts throughout the marginal limestones. The pyrite was recognized on the basis of its cubic crystal form (Figure 18) and characteristic yellowish, metallic appearance under reflected light. Most of the pyrite is believed to have formed as a replacement for organic matter. Pyrite was abundant (up to 5%) in areas where phosphatic varves had been produced. Otherwise only one or two crystals of pyrite were observed in the grain populations.

Organic Material

Opaque black constituents which did not exhibit any specific properties under reflected light are believed to be of organic origin. The organic material ranges from subrounded to angular stringers and clasts. The grains which exhibit some sphericity are approximately .13mm to

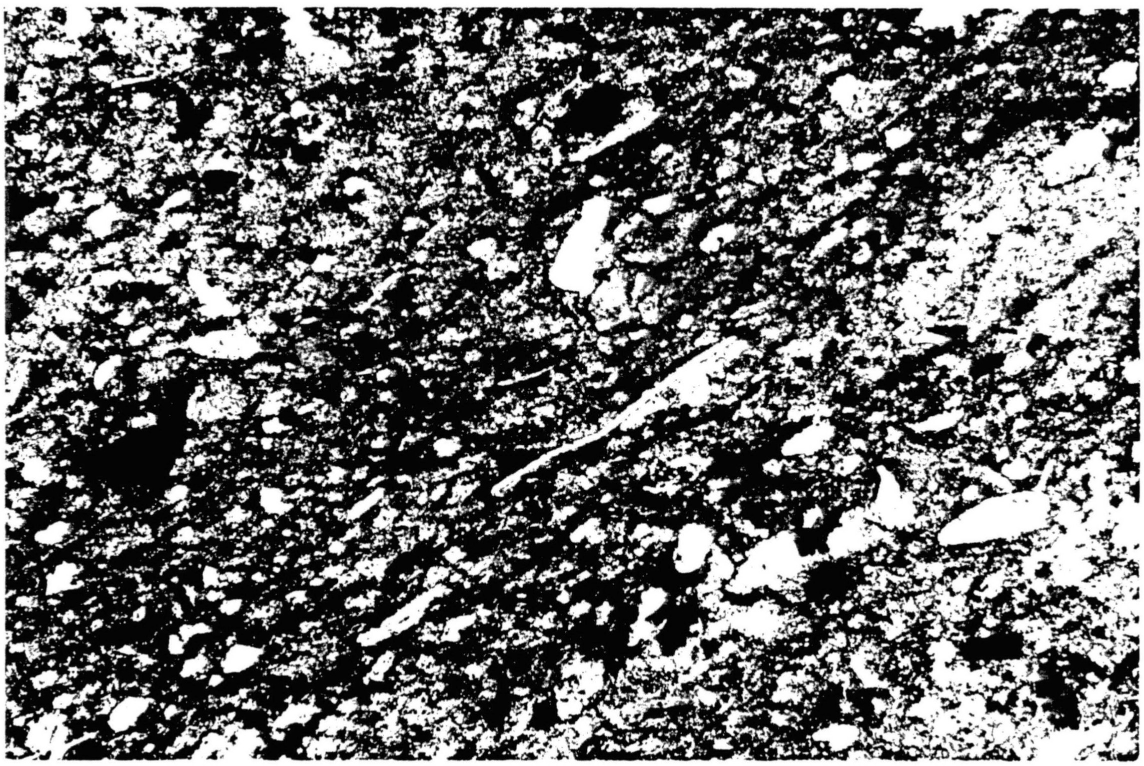


Figure 17. Muscovite Aligned Parallel Within Marginal Varves (X4-XN)

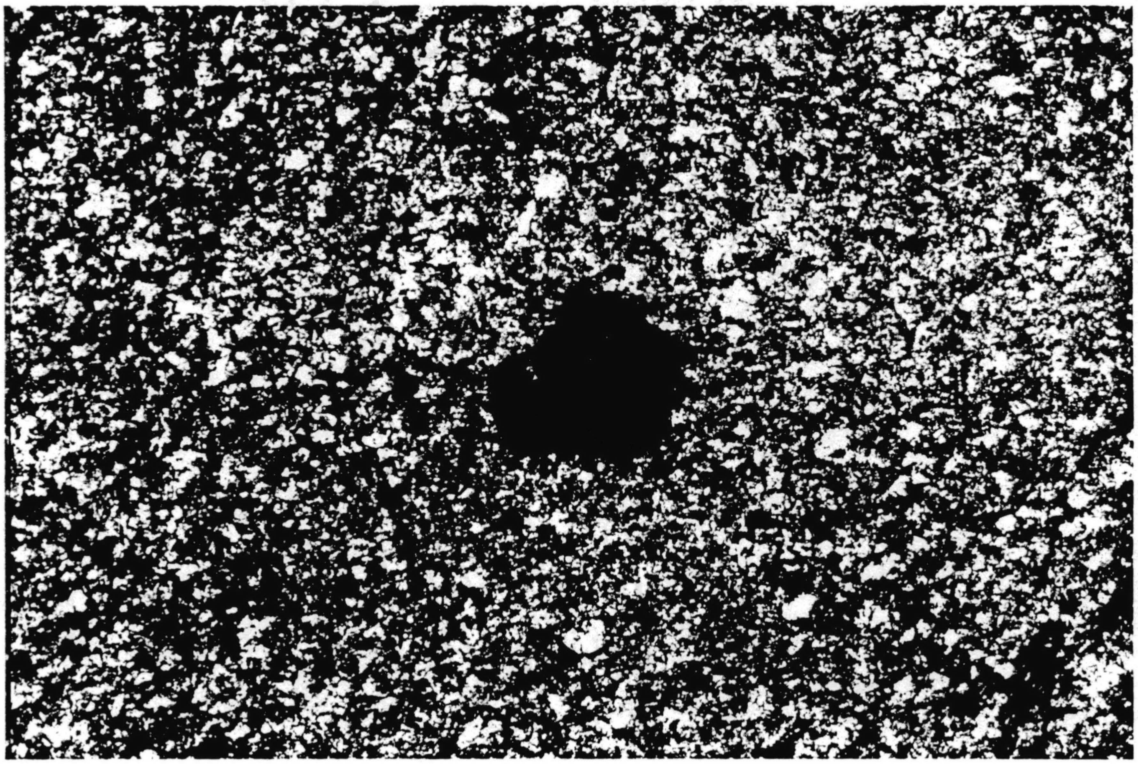


Figure 18. Authigenic Cubic Pyrite in the Marginal Limestone (X4-XN)

.18mm in size. The black stringers range in length from .16mm to .25mm (Figure 19).

Cements

Calcium Carbonate

Calcite cement is the most abundant cement in the marginal limestones. The calcite matrix occurs as dense lime mud and as a coarse sparry calcite cement. Although the rocks are classified as limestones, high percentages of detrital grains prohibit the use of a strict Folk (1962) classification. Since the rocks do contain an abundance of carbonate cements, they are classified as limestones and "sandy" limestones.

Calcium carbonate cement is seen replacing detrital constituents, infilling voids, and as a dense mud within the marginal varves (Figure 20). Sparite textures include equant anhedral spar and secondary, euhedral, vein-filling spar.

Dolomite

Dolomite cement was recognized on the basis of its euhedral rhombic crystal shape. Two forms of dolomite were recognized in the marginal deposits. Small interlocking crystals of dolomite formed part of the matrix, whereas large crystals infilled voids. Samples containing the large dolomite crystals were stained with

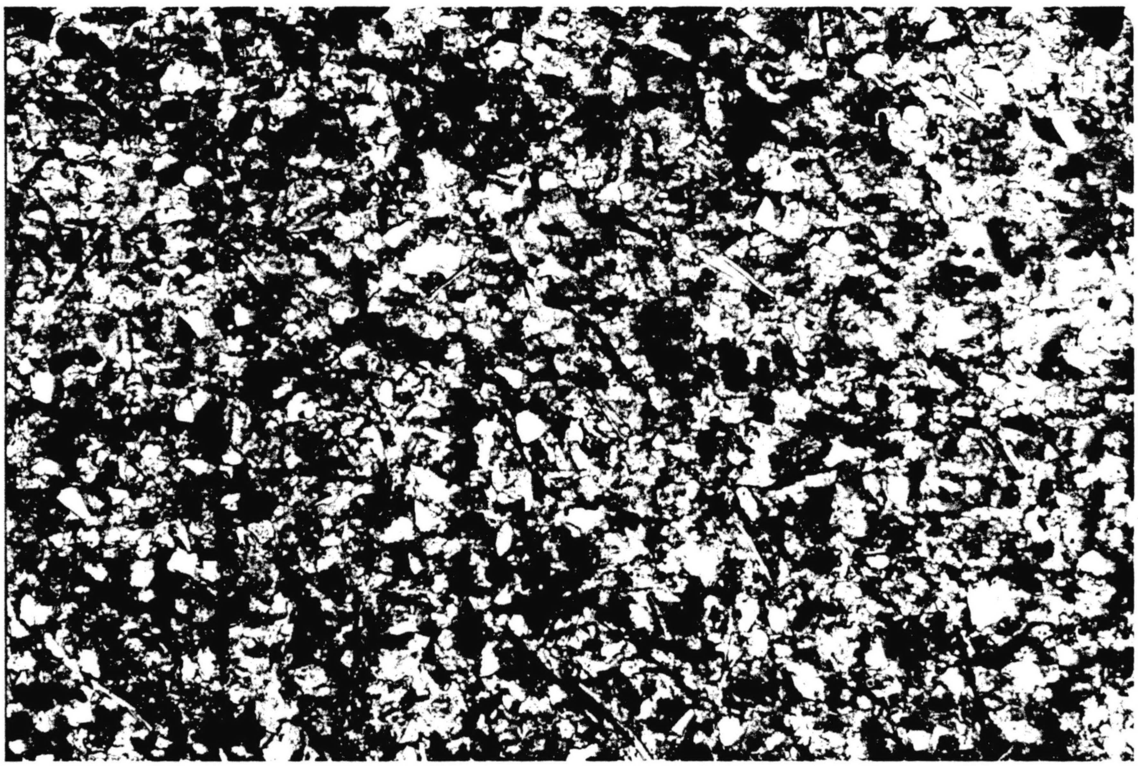


Figure 19. Black Stringers of Organic Material (X4-XN)

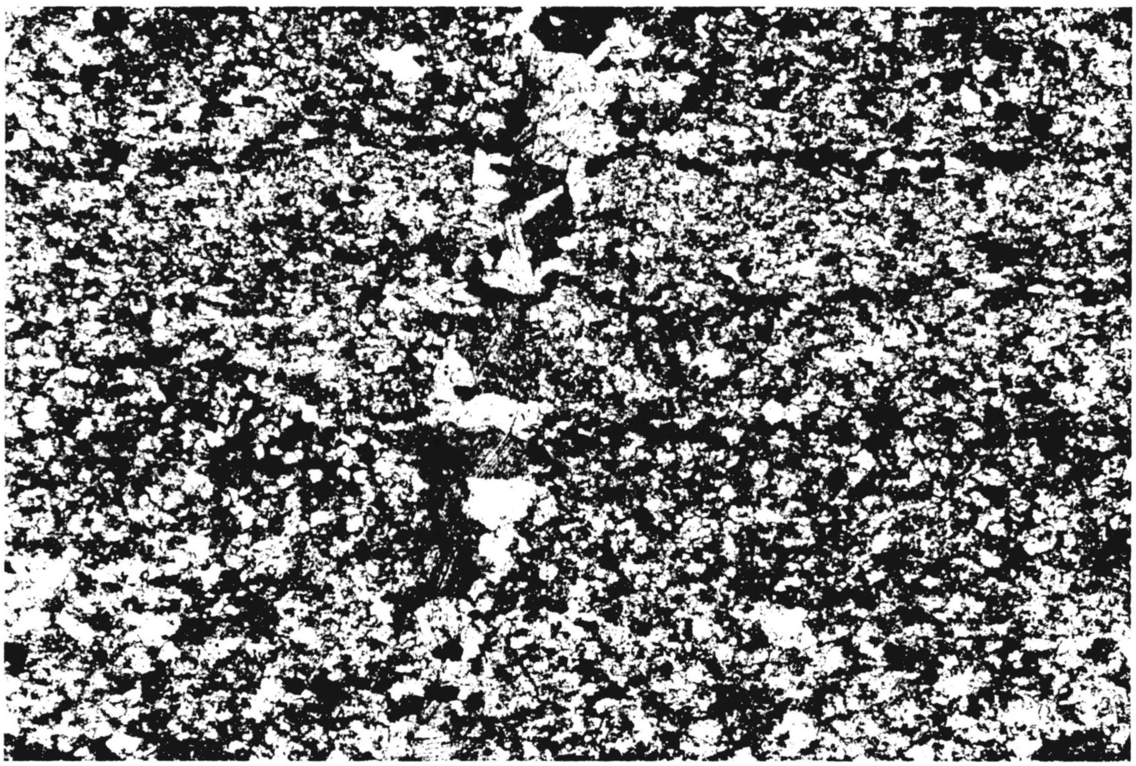


Figure 20. Calcium Carbonate as Vein-Filling and Occurring as a Dense Mud Matrix (X4-XN)

Alizarin Red. The dolomite all turned pink, thus indicating its calcitic nature and the dedolomitization of the samples. The small interlocking crystals, which were stained did not turn pink. Dolomite percentages ranged from trace amounts up to 8% of the population.

Hematite

Hematite cement is present as grain coatings and pore-fillings. Hematite was recognized on the basis its bright red color under reflected light.

Textures

Laminations (Varves-?)

Thin laminations along the marginal deposits have been termed marginal varves by previos authors (Geike, 1878; Donovan, 1975; and Faller and Briden, 1978). Laminations of this type will be termed marginal varves within this study. They are believed to be non-glacial varves. Varved sequences along the margins of the Orcadian Basin range from two types (type A and type B) of thinly laminated sequences (25um -35um) to micritic and detrital couplets (type C) (2mm). Compositionally, the varves are composed of several components. The first thinly laminated varved sequences (type A) are composed of organic laminae interdispersed with micrite (Figure 21). Detrital quartz and minor muscovite occur sporadically throughout such laminae. The thinly bedded laminae are

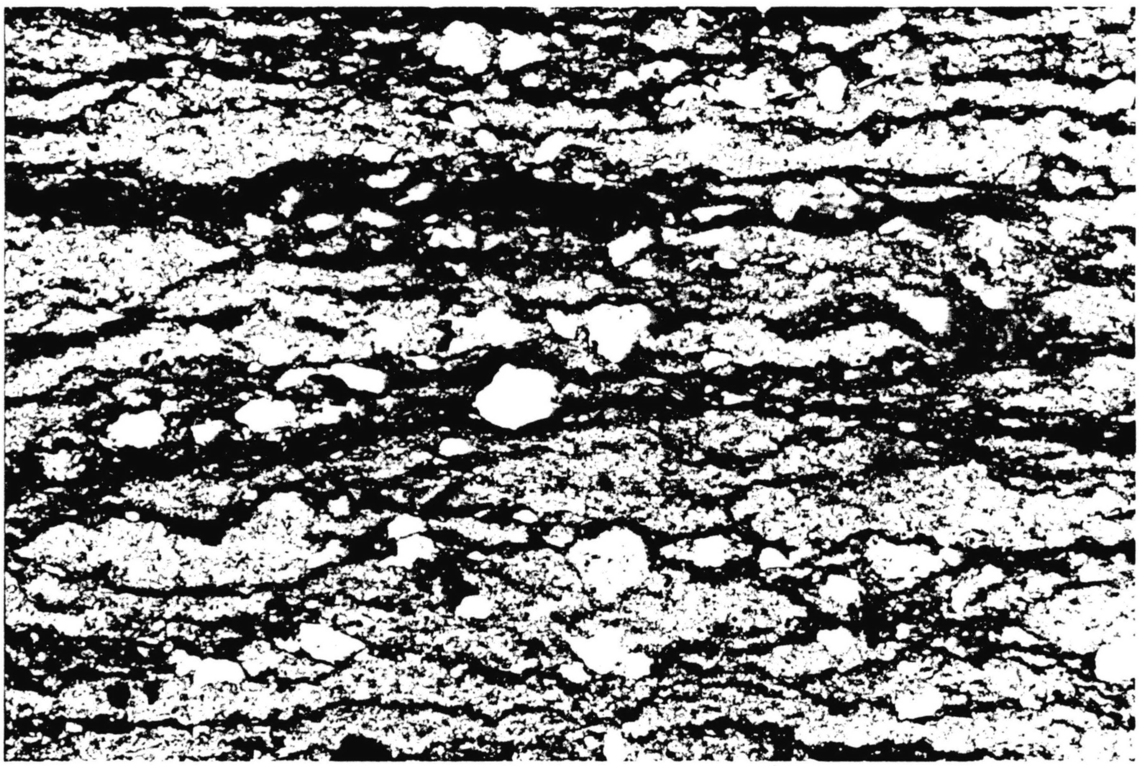


Figure 21. Marginal Varves of Organic Laminations Interdispersed With Lime Mud and Quartz (X4-XN)

quesi-horizontal although their primary layering may have been modified by stylotization. The thin marginal varves are discontinous and appear to have undergone several disruptions and breaks along their "horizontal" bedding surface during deposition.

The second type of thinly laminated varves (type B) are composed of phosphate and hematite alternating with micrite and detrital debris (Figure 22). The phosphate appears as orange brown in plane light and is isotropic. Consequently, it is interpreted to be collophanite. The phoshpatic varves are associated with the presence of trace amounts of authigenic pyrite. The varves associated with the phosphate can be divided into three units. The first unit of the triplet is composed of a dense micrite, c. 50um in thickness with 5-7% detrital debris. The second unit of the triplet is composed of a thin (25um) lamina of phosphate and organic material. The third unit is dominantly detrital debris consisting of quartz and muscovite.

The micrite and detrital varve (type C) couplet is composed of two units. The first unit is approximately 1mm in thickness and consists of dense micrite with minor (3-5%) amounts of quartz, muscovite and organic stringers. The second unit of the varve is composed of 80% quartz, 5% muscovite, 3% organic material, and is cemented by calcium carbonate. It also measures approximately 1mm in

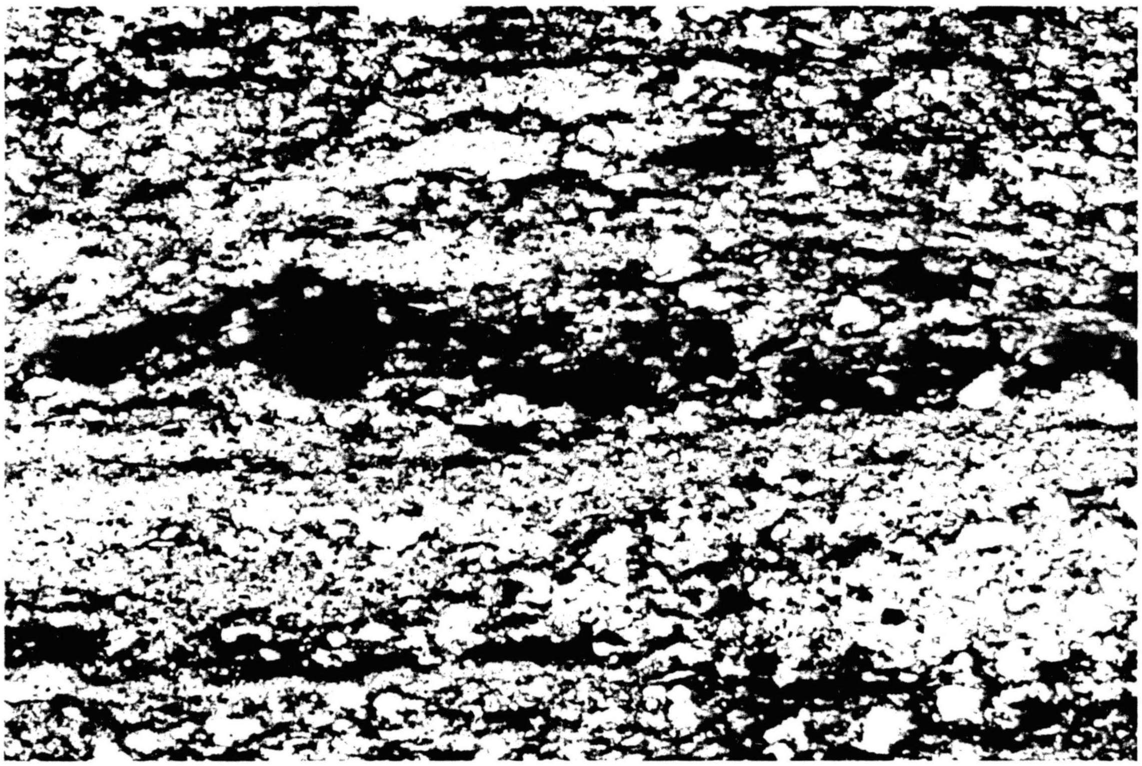


Figure 22. Phosphate and Hematite-Marginal Varved Sequences (X10-XN)

thickness.

Tufa

The tufa textures of the marginal limestones consist of laminae approximately 2-3mm thick. They are composed of tufts of fibrous (Figure 23) and bladed ferroan and nonferroan calcite. The blades are occaisionally separated by hematite rims. Late dolomitization of the tufas has partially destroyed the internal fabric of the sequence.

Nodules

Patches of phosphate surrounded by spar are believed to be poorly defined nodules (Figure 24). The phosphate is characteristically light yellow-brown rather than its typical orange-brown color. The "patches" range in size from 250um to 300um. They are elongate to spherical in shape and are surrounded by equant anhedral sparite. One layer of nonferroan sparite crystals surrounds the phosphate. The whole nodule (phosphate and spar) is in turn surrounded by a dense micritic cement. The pseudonodules are not associated with any of the marginally varved sequences. The host material for the nodules is a calcitic mud matrix with minor (<10%) amounts of dolomite. The overall rock type is classified as a dolomitic limestone.

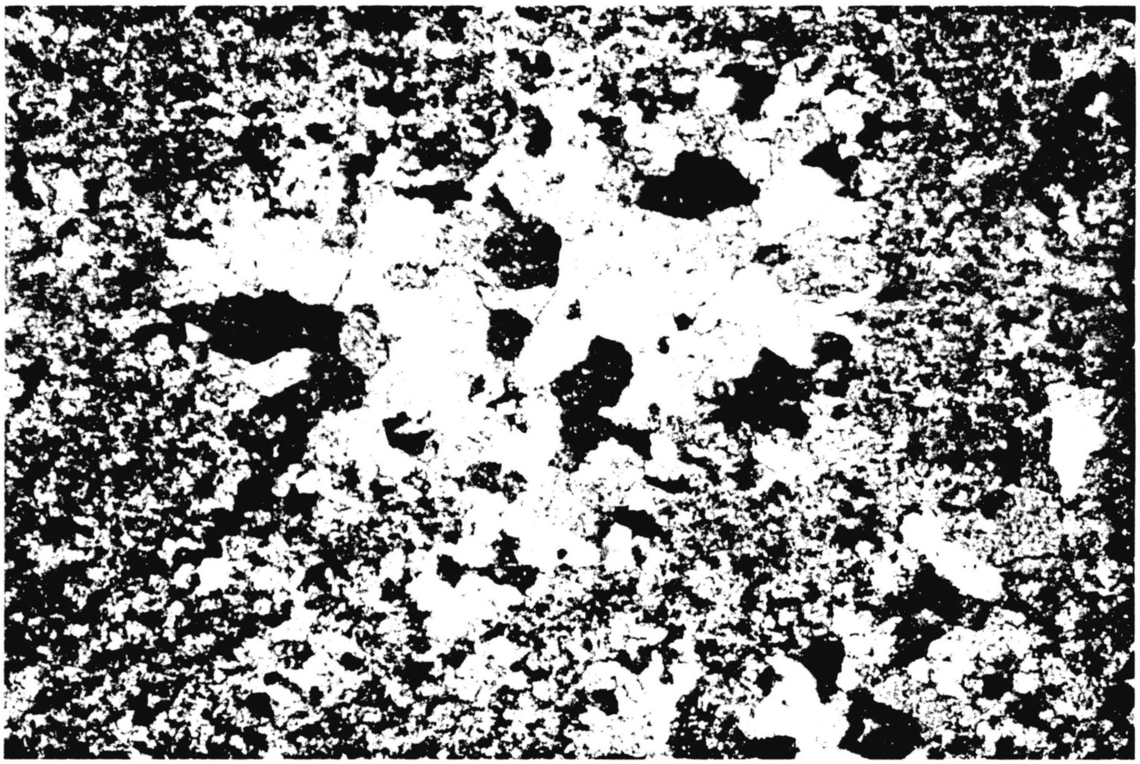


Figure 23. Tufa Textures Composed of Non-Ferroan Calcite Along the Basin Margins (X4-XN)

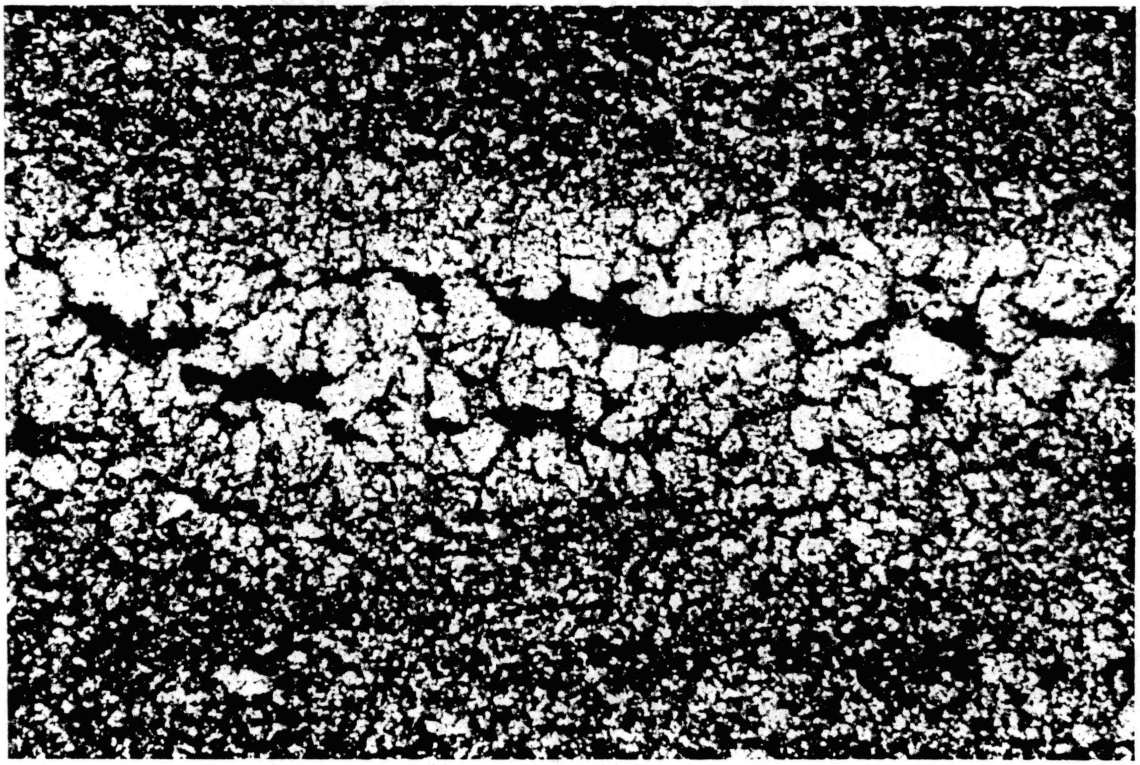


Figure 24. Phosphatic Nodules Surrounded by Sparry Calcite (X10-PP)

Diagenesis

Several diagenetic processes have altered and destroyed the fabrics and textures of the marginal limestones of the Orcadian Basin. Each of the events will be dealt with separately so that their complexity may be better understood. However, it is probable that single alterations cannot be considered as totally discrete events.

Dissolution

Dissolution of quartz, feldspar and matrix has affected the "sandy" limestones of the margins. Most of the quartz grains have corroded margins and some have undergone complete dissolution as evidenced by large pore spaces now filled with calcite. Similarily, feldspar grains have been highly altered and appear as remnants. Some grains show slight sericitization while others show faint honeycomb textures.

Replacement

Several detrital grains in the marginal limestones have undergone replacement by other minerals. The detrital grains include feldspar, quartz, muscovite, and biotite. Quartz, feldspar and muscovite have all undergone replacement by non-ferroan calcite. In some areas, muscovite has undergone partial pseudomorphing by calcite (Figure 25).

Physical Diagenesis

Physical diagenesis of the marginal limestones is evidenced by stylolitization, flowage, and compaction. These processes have altered the textures of the marginal varves. The "sandy" limestones of the margins do not appear to have been physically altered.

Stylolitization of the varved sequences has partially destroyed the horizontal stratification. The varves which have undergone stylolitization are wavy, disruptive and may not be continuous (Figure 26). Flowage is restricted to the phosphatic varves. The flowage of the phosphate is probably due to the overburden of seasonal clastic material.

Chemical Diagenesis

Chemical diagenetic alterations played a major role in the evolution of the marginal limestones. The primary carbonate fabric is a dense micrite which represents a well-cemented lime mud. Fenestral textures seen in the micrite and along varved sequences probably resulted from gas escape following from the partial decay of organic material. Fenestrae and voids were then infilled with drusy spar.

Dolomite is uncommon in the marginal limestones. The conversion of calcite to dolomite probably occurred during

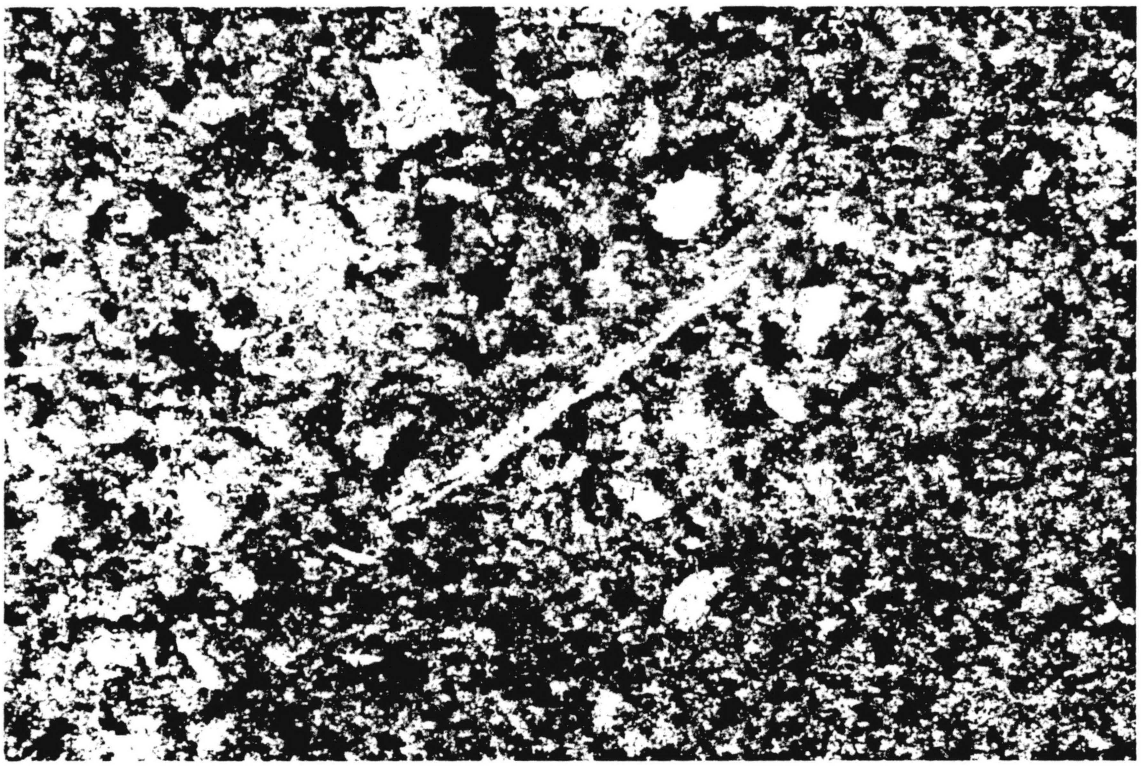


Figure 25. Pseudomorphing of Muscovite by Calcite (X10-XN)

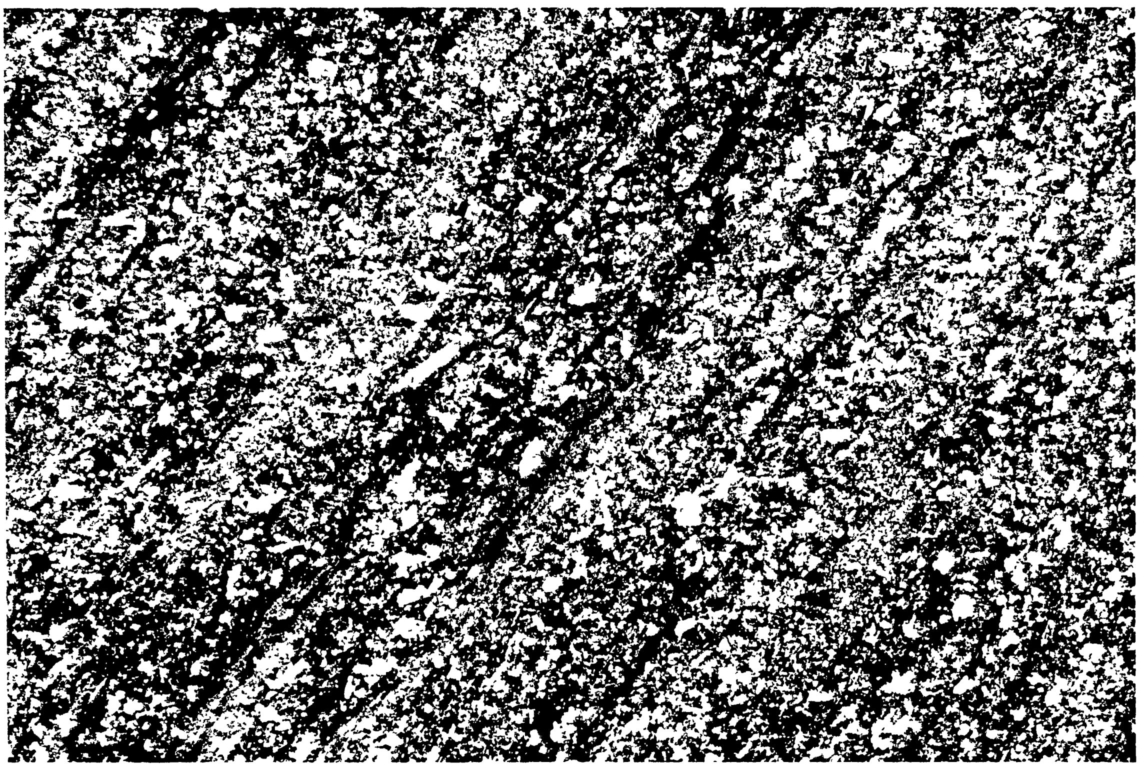


Figure 26. Styolitized Varves Along the Basin Margin (X4-XN)

two separate intervals within the diagenetic history of the sediments. The large dolomite crystals which have been dedolomitized are seen as a minor cement in cavities. These are believed to be a late diagenetic stage. Earlier in the diagenetic history, the dolomite was replaced by calcite (as noted above). This dedolimitization is evidenced by the rhombic shape of the previous dolomite and the staining for calcite by Alizarin Red.

Hematite cementation was one of the last stages in the diagenetic history of the marginal "sandy" limestones. Hematite cement is seen replacing calcite cement (Figure 27). The hematite may have been derived from the breakdown of unstable iron-bearing minerals.

Figure 28 illustrates a complete paragenetic sequence for the marginal limestones of the Orcadian Basin.

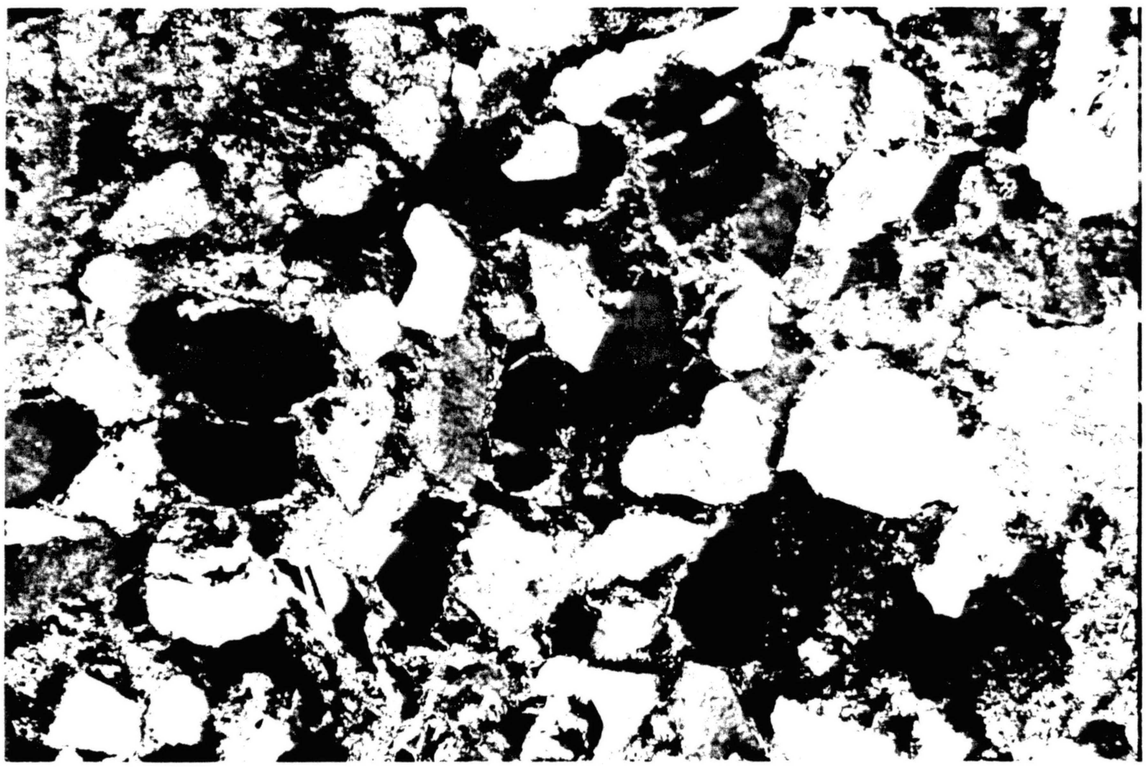


Figure 27. Hematite Cement Replacing Calcite (X10-XN)

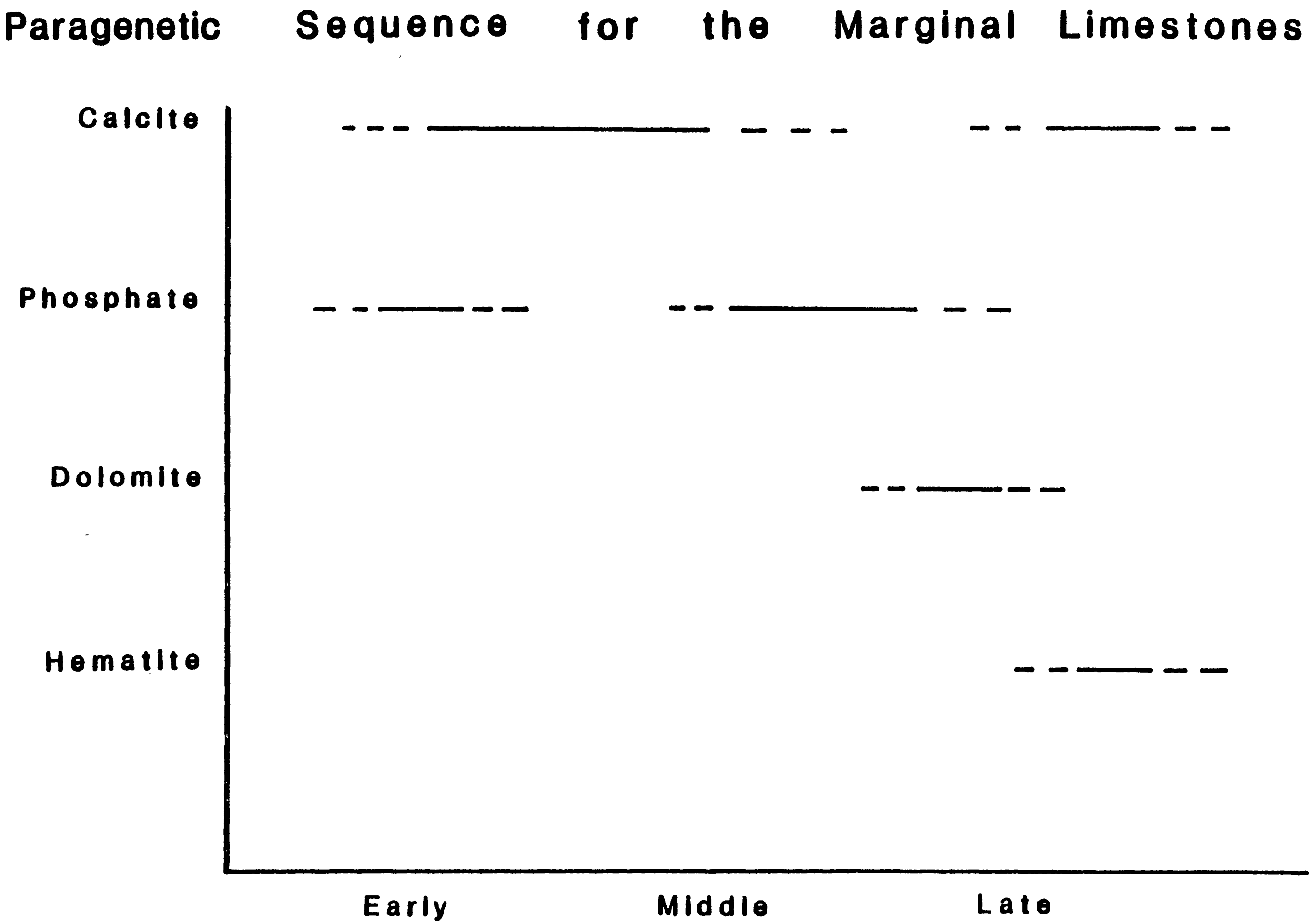


Figure 28. Paragenetic Sequence for the Marginal Deposits

CHAPTER V

BASINAL DEPOSITS

The basinal deposits of the Orcadian Basin are composed of a variety of constituents which record numerous depositional environments. The basin deposits are defined as those which record deposition within the center of the lake basin. The descriptions of the basin includes a detailed petrographic analysis which concentrate on major grain constituents, cement types, varied textures and diagenetic features and processes.

Lake Basin Classification

The basinal deposits vary from mudstones to wackestones (Dunham, 1962) (Figure 29). Compositionally, the rocks of the basin can be classified as dolostones, limestones, marlstones, and oil shales. Although the rocks are classified as carbonate in origin, a strict Folk (1962) classification cannot be applied to the basinal deposits of the Orcadian Basin. Folk's (1962) classification of carbonate rocks, disregards dolomite, clay, chert, and terrigenous sand. Folk (1962) has divided limestone constituents into three main families.

<table>
<tr><th colspan="5">DEPOSITIONAL TEXTURE RECOGNIZABLE</th><th rowspan="2">DEPOSITIONAL TEXTURE NOT RECOGNIZABLE</th></tr>
<tr><td colspan="4">Original Components Not Bound Together During Deposition</td><td rowspan="4">Original components were bound together during deposition... as shown by intergrown skeletal matter, lamination contrary to gravity, or sediment-floored cavities that are roofed over by organic or questionably organic matter and are too large to be interstices.</td></tr>
<tr><td colspan="3">Contains mud
(particles of clay and fine silt size)</td><td rowspan="3">Lacks mud and is grain-supported</td><td rowspan="4"><u>Crystalline Carbonate</u>

(Subdivide according to classifications designed to bear on physical texture or diagenesis.)</td></tr>
<tr><td colspan="2">Mud-supported</td><td rowspan="2">Grain-supported</td></tr>
<tr><td>Less than 10 percent grains</td><td>More than 10 percent grains</td></tr>
<tr><td><u>Mudstone</u></td><td><u>Wackestone</u></td><td><u>Packstone</u></td><td><u>Grainstone</u></td><td><u>Boundstone</u></td></tr>
</table>

Figure 29. Dunham Classification of Carbonate Rocks (After Dunham, 1962)

These are allochems, microcrystalline ooze, and sparry calcite (Figure 30). Since two of the three end members are present in small (up to 7%) amounts, a new classification scheme for the basinal rocks of the Orcadian Basin has been initiated by this author.

The classification is based on cement types and the presence of clay and carbonaceous material within the sample. The presence of detrital quartz, feldspar, biotite, and muscovite are disregarded. The petrographic carbonate textural classification appears in figure 31. The suffix micrite as used in this study as a carbonate rock with a very fine grained (less than 5 um) subcrystalline texture. The prefixes applied to the suffix, reflect the type of cement and presence of clay and carbonaceous material. The prefixes may be combined, so as to describe the different types of cement and matrix found within the population. An example of this classsification would be a varved dolomarlmicrite. Petrographically, the sample is a fine grained, dolomite cemented varved sequence with clay and carbonaceous material.

All classifications are incomplete and have limitations as does this one. This classification is presented so that a simpler description of the petrology of the basinal "limestones" may help the reader to better understand the compositional differences present in the rocks.

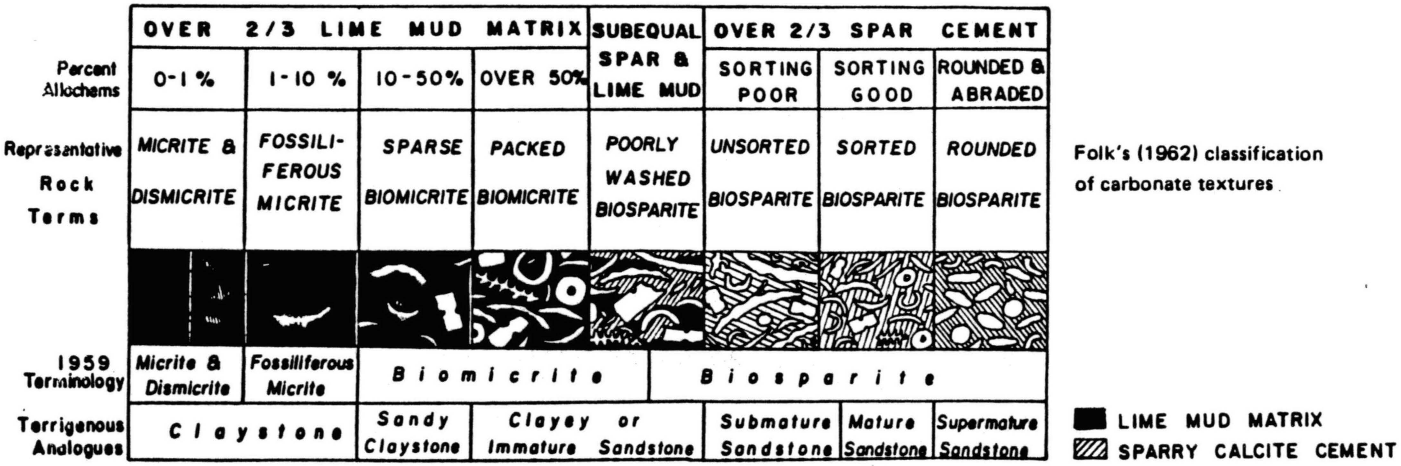


Figure 30. Folk Classification of Carbonate Petrology (After Folk, 1962)

Representative Petrographic Terms			
Dolomicrite	Limemicrite	Marlmicrite	
dolomite cement >15%	lime (calcite) cement >15%	clay and carbonaceous material >25%	
Dolostone	Limestone	Marlstone	Terrigenous Analogues
Wackestone - - - - - - - - Mudstone			Dunham
Clayey or Immature SS - - - - → Sandy - Claystone - - - - - → Claystone			Folk

Figure 31. Petrographic Carbonate Textural Classification for Basinal Deposits

Carbonate Petrography

The petrographic analysis of the basinal deposits includes a description of the grain constituents (quartz, feldspar, muscovite, biotite, pyrite, and tourmaline), the cements (dolomite, calcite, quartz, hematite), the clays (illite and chlorite), other minerals (aegirine, phosphate, and hydrocarbons), the textures (varves, psuedomorphs, micro-faults, styolites, turbidity currents and tectonic veins), and the diagenesis of the basinal deposits.

Mineralogy

Quartz

Monocrystalline quartz is the most abundant detrital constituent found within the basinal deposits. It ranges from 5% up to 30% and averages to 15% of the deposit. The quartz grains are very well sorted, (Pettijohn, Potter and Siever, 1972) silt to sand size grains and are concentrated along the varved and styolitized portions of the samples. The quartz grains are usually subangular, but this characterization is somewhat misleading because of corrosion by calcite. Some of the quartz associated with dolomite cements have several dolomite inclusions within the grain (Figure 32). This is due to the parital replacement of quartz by dolomite. No polycrystalline

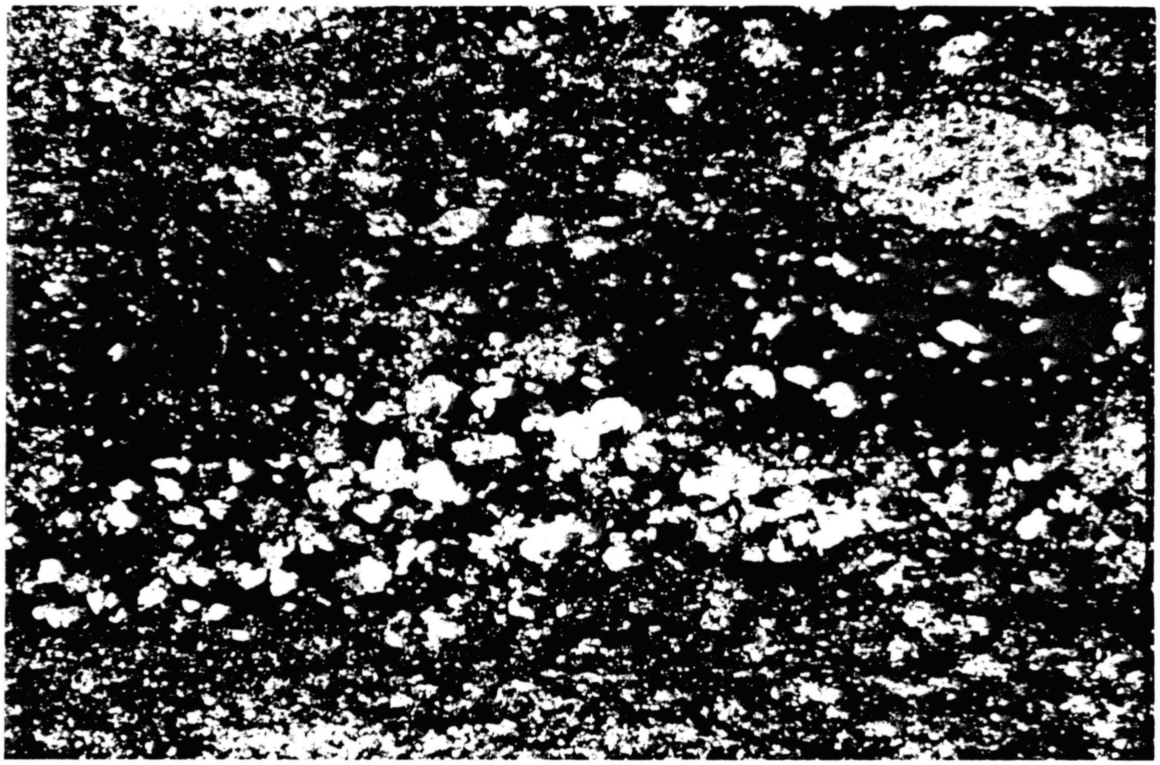


Figure 32. Dolomite Replacement of Detrital Quartz Grains in Hydrocarbon Pockets (X4-XN)

quartz was observed in the samples analyzed (probably because of the small size of the grains present).

Feldspar

Small amounts of feldspars are found throughout the basinal deposits. They constitute approximately 1% of the grain population. The types of feldspar present in the samples include plagioclase, potassium feldspar, and microcline. Of these, plagioclase is the most abundant. Plagioclase feldspars show varying degrees of dissolution. Some of the grains are almost completely replaced, while others show slight honeycomb dissolution. The feldspars are also concentrated along the varved and styolitized sequences.

Muscovite

Muscovite is common throughout all of the samples. Percentages range from 3% upto 10% of the grain population. Muscovite has not undergone any dissolution but it has undergone compaction. The compaction of muscovite is represented by broken and fragmented grains. Muscovite is commonly seen aligned parallel to and within the clastic laminae of the basinal deposits (Figure 33). Within the varves muscovite ranges from 7-10%; outside the varves within the micrite, muscovite is less common and constitutes approximately trace amounts up to 2 percent. Samples classified as limemicrites without any trace of

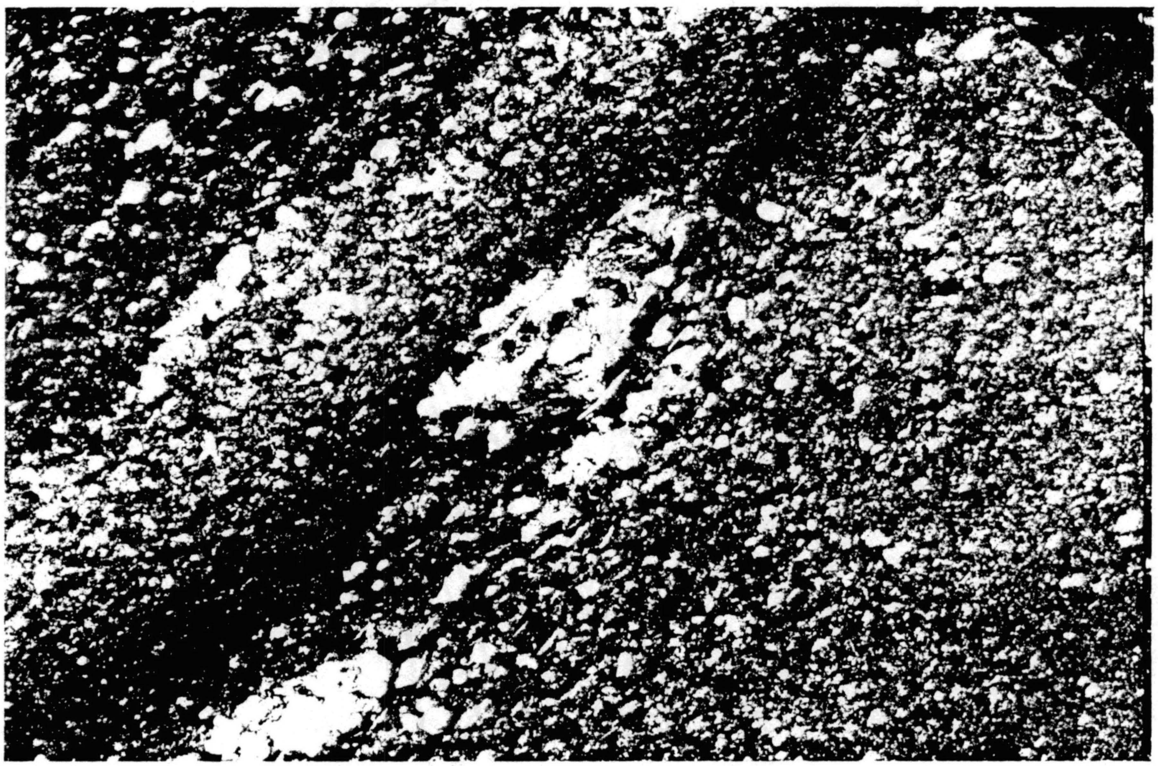


Figure 33. Parallel Alignment of Detrital Muscovite in the Basinal Limestones (X4-XN)

varves do not contain any muscovite.

Biotite

The biotite of the basinal deposits is all detrital in origin. The composition of the grains ranged from unaltered brown (PP) biotite, to green (PP) paritally chloritized biotite, to black (PP) totally altered biotite. The black "biotite" has been altered to hematite. The transformation of biotite to hematite was also noted by Turner and Archer (1977) in the red beds and sandstones of the Old Red Sandstone of Scotland. All three stages of biotite previously mentioned occur in amounts ranging from trace up to 2 percent of the grain population.

Pyrite

Authigenic pyrite was observed in varying amounts ranging from trace amounts up to 3% of the samples. Pyrite was recognized on the basis of its yellowish, metallic appearance under reflected light. The pyrite of the basinal deposits is believed to be a replacive mineral for organic material.

Tourmaline

Tourmaline is the major heavy mineral observed in the samples of the basinal deposits. The occurrence of tourmaline was rare and was only observed in a few of the grain populations.

Cements

Dolomite

Dolomite cement occurs in a variety of forms within the rocks of the basinal deposits. Dolomicrites contain finely crystalline (4 mm) dolomite which appears to have totally replaced the original limestone (Figure 34). The dolomite occurs as a mosaic of anhedral crystals. Dolomicrites were stained with alizarin red to determine if the replacement process was complete. None of the samples turned the characteristic pink needed to determine the presence of calcite.

Another type of dolomite cement observed contained zoning. The zoned dolomite ranged in size from .08 mm to .12 mm. The areas of zoned dolomite were rare and associated with hydrocarbons. When the dolomite did occur within the hydrocarbon pockets it ranged from 7 to 20 percent of the sample. The medium crystalline replacive dolomite showed considerable zoning (Figure 35). The rhombic shape of the dolomite crystals is clearly outlined by the presence of iron. The zoning found in the dolomite may be partly caused by chemical differences in the dolomite during precipitation. Another explanation for

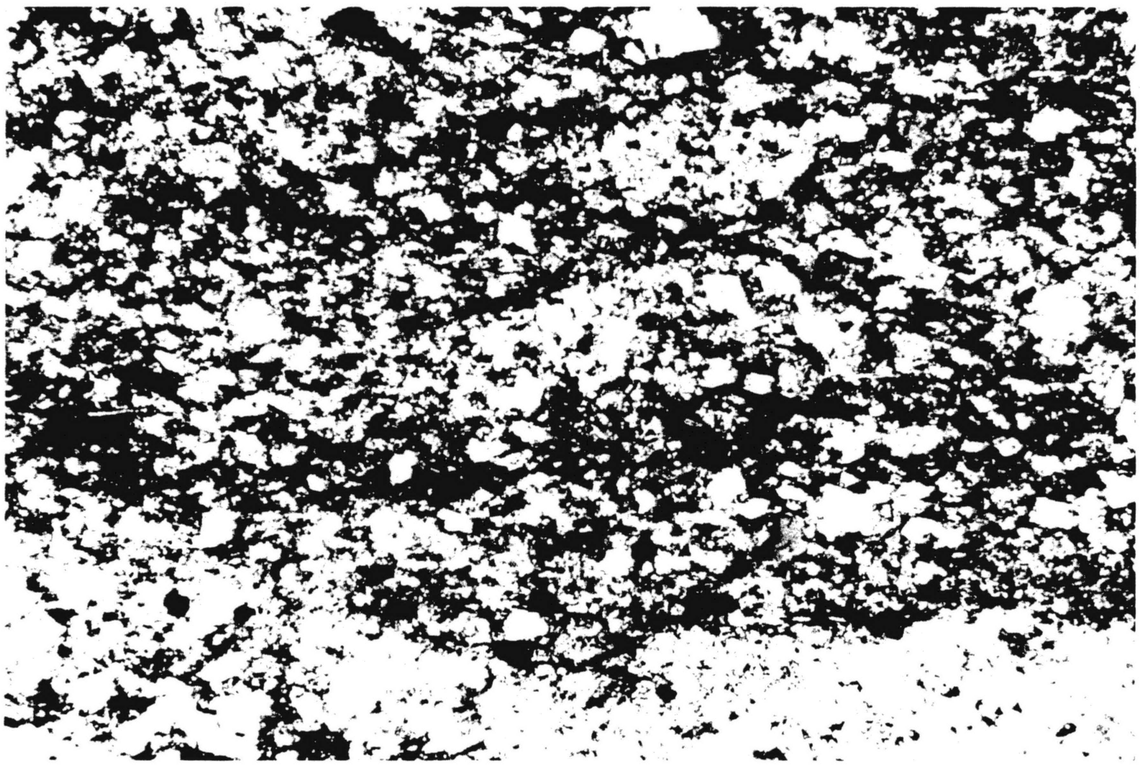


Figure 34. Dolomite (Dolomicrites) in Hydrocarbon Pockets (X10-XN)

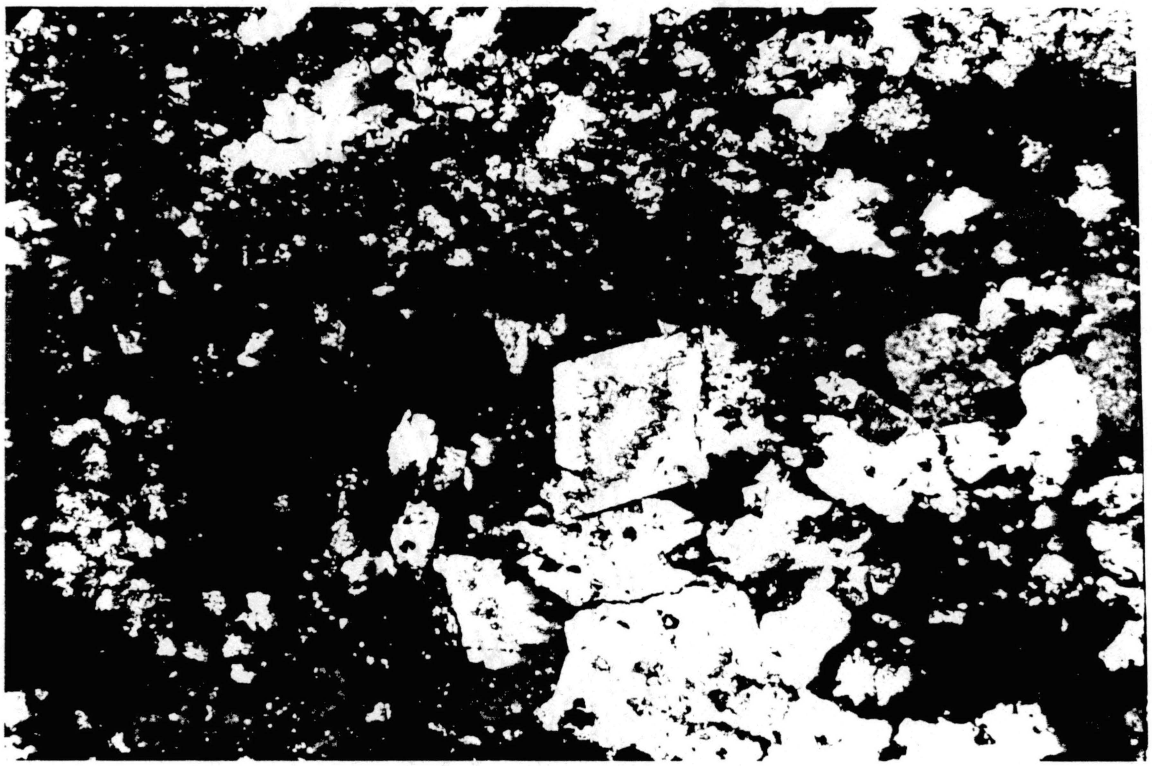


Figure 35. Compositional Zoning of Dolomite in Hydrocarbon Pockets (X10-XN)

the zoning may be the incorporation of varying amounts of foreign matter incorporated within the crystals as they grew. Some crystals show up to 4 periods of zoning but most show 2 periods. Consistency of the zonation from crystal to crystal may indicate simultaneous formation (Scholle, 1978). The zoned dolomite was stained with alizarin red to determine its true composition. The zoned dolomite associated with the hydrocarbons did not turn pink whereas dolomite outside of the hydrocarbon pockets did turn the characteristic pink indicating calcite. Thus the latter dolomites crystals have therefore undergone dedolomitization. The process of dolomite being replaced by calcite is probably the result of oxidizing meteoric waters infiltrating the system. The undedolomitized dolomite was probably "protected" by hydrocarbons.

The third type of dolomite seen in the samples is associated with fractures and voids. The dolomite is finely crystalline and ranges in size from .02 to .03 millimeters in size. There is no zoning associated with this third type of dolomite cement.

Calcium Carbonate

Calcite cement occurs in a variety of forms in the basinal deposits. Fine grained (.01-.02mm) calcite occurs as matrix and void fillings. The limemicrites contain calcite matrix ranging from 20 percent to 90 percent. Samples containing over 80 percent calcite are devoid of varves and other sedimentary features. There are no fossils present in the limemicrites. Calcium carbonate is also seen as a dense micrite within the basinal varves. Coarse grained sparry calcite occurs as void fillings. The calcite increases in size from the wall of the cavity to the center of the void. The coarse spar also in fills fractures and tectonic veins.

Quartz

Three varieties of quartz cement have been noted in the basinal deposits. Quartz cement occurs as void fillings, fracture fillings and as a syntaxial cement. The quartz in voids and fractures is predominantly chalcedony and chert. Of these, chalcedony is more abundant. Vein-filling chalcedony is associated with hydrocarbon voids (Figure 36). Chert is associated with tectonic fractures.

The last variety of quartz cement occurs as quartz overgrowths. This type of quartz cement can only be seen in trace amounts because of later corrosion by calcite. The authigenic overgrowths are outlined by a thin layer of iron oxides and clay material. Fully developed overgrowths exhibit euhedral crystal shapes.

Hematite

Hematite cement is associated with the varves of the basinal deposits. Percentages of cement range from 2-6%

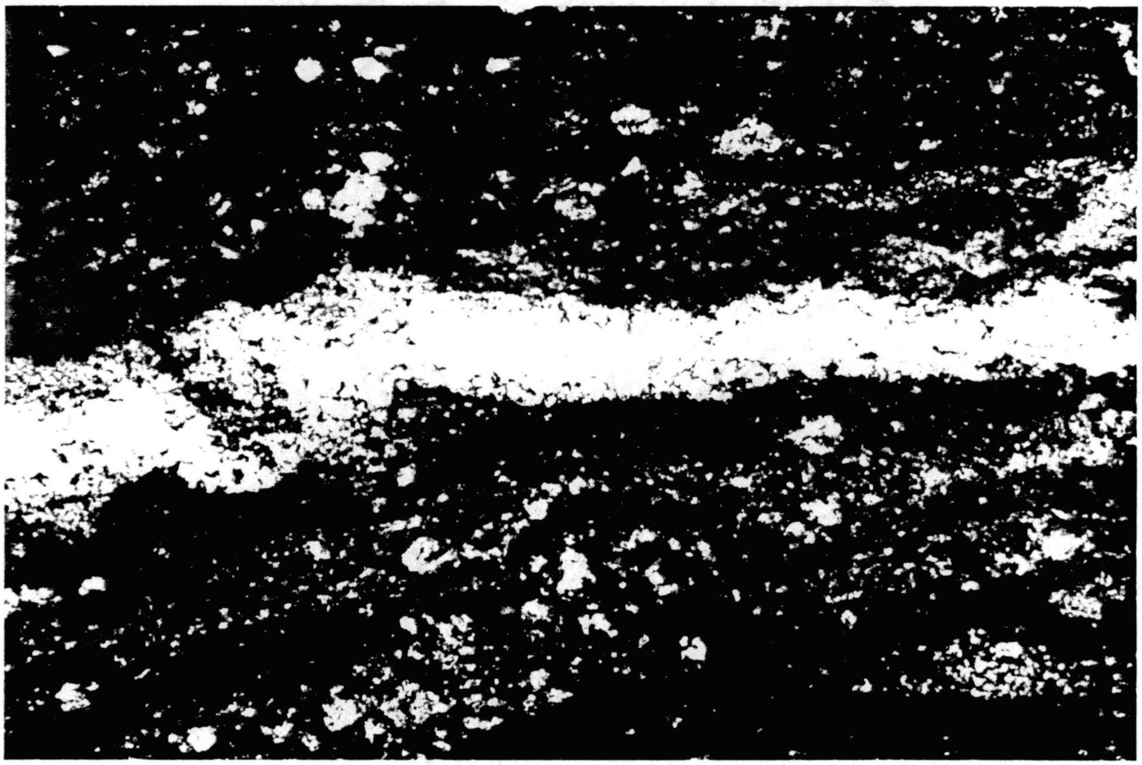


Figure 36. Vein-Filling Chalcedony in the Basinal Deposits (X10-XN)

of the varves and 1-3% of the total sample. The hematite cement appears as void and pore fillings along the varved sequences.

Clays

Illite

Clay minerals were difficult to distinguish in thin section analysis. Illite was the most abundant clay mineral seen in the samples of the basinal deposits. Illite occurs as inclusions within quartz grains (Figure 37), as grain coatings and as pore linings. Illite cement was recognized on the basis of its elongate needle-type form (Figure 38). Illite inclusions within quartz are iron stained and ranged from .01mm to .016 microns in length. Some of the clay minerals form thin coatings around the detrital grains within the varves and outside the varves. Clay minerals in basinal deposits are important cementing agents within the varved sequences.

Chlorite

Chlorite does not occur as a true cement in the basinal deposits. Chlorite produced during the alteration of biotite (Figure 39) is yellow-green in plane light and green-brown in crossed polars. Where compaction has occurred in the varves, chlorite acted as a psuedomatrix-cement. It appears to have been squeezed along the grain

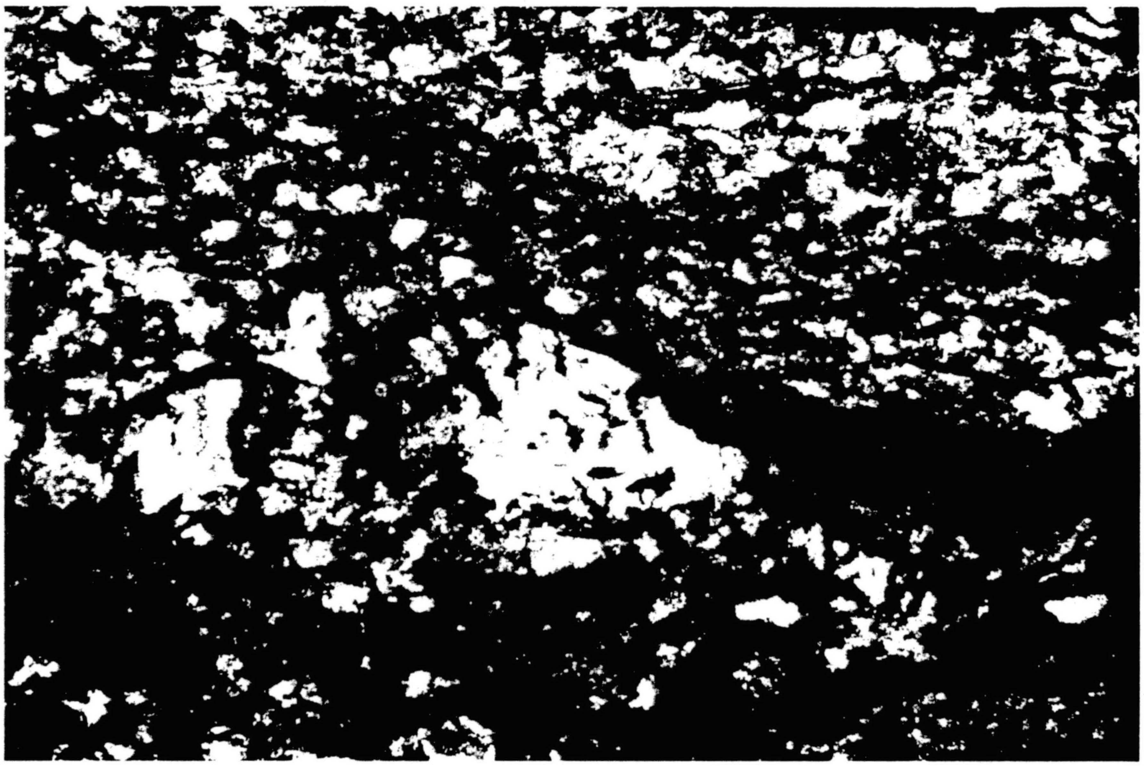


Figure 37. Illite Inclusions Within Quartz Grains (X10-XN)

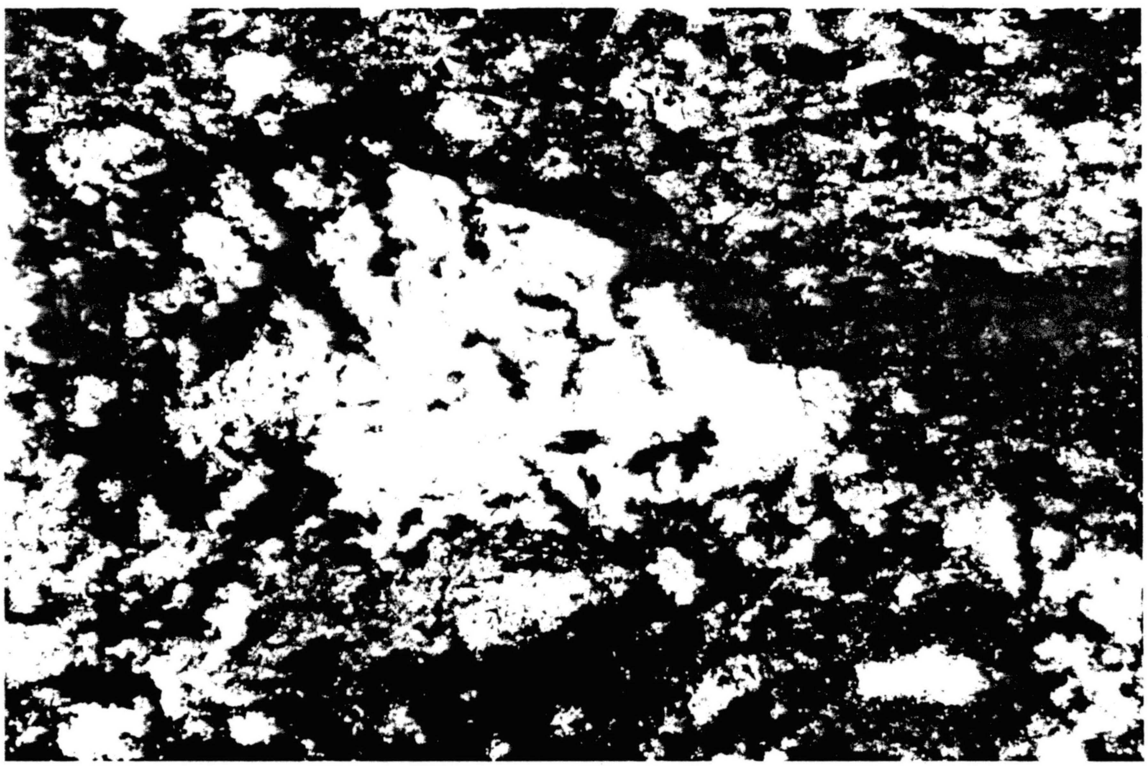


Figure 38. Elongate Illite Needles Within Quartz of the Basinal Deposits (X10-XN)

Figure 39. Chloritized Biotite (Yellow-Brown Mineral) (X10-XN)

boundaries. Chlorite ranges from trace amounts up to 1 percent of the sample analyzed.

Other Minerals

Aegirine

A high relief, subrounded to rounded mineral has been identified as aegirine (personal communication, Donovan, 1985). Aegirine, a soda pyroxine with the chemical formula of NaFeSi2O6 is observed within the lower section of the Robbery Head Formation within the basinal deposits (Figure 40). The crystals are found in fine grained laminated limemicrites (mudstones). The aegirine crystals have edges which appear to have been rounded during the reworking of the sediment during tectonic events. The crystals vary from pale yellow/green to colorless in plane light. In cross nicols the mineral exhibits high birefringence colors. The crystals are larger than the surrounding detrital material. They lie parallel to the bedding in small goups, or where the bedding has been tectonically disurbed they "flow" along with the laminae (Figure 41).

The occurrence of aegirine in the sediments of the Orcadian Basin has been reported by Fortey and Michie (1978) who described an occurrence very similar to those observed by this author. Fortey and Michie (1978) observed aegirine in a ditch section near Halkirk,

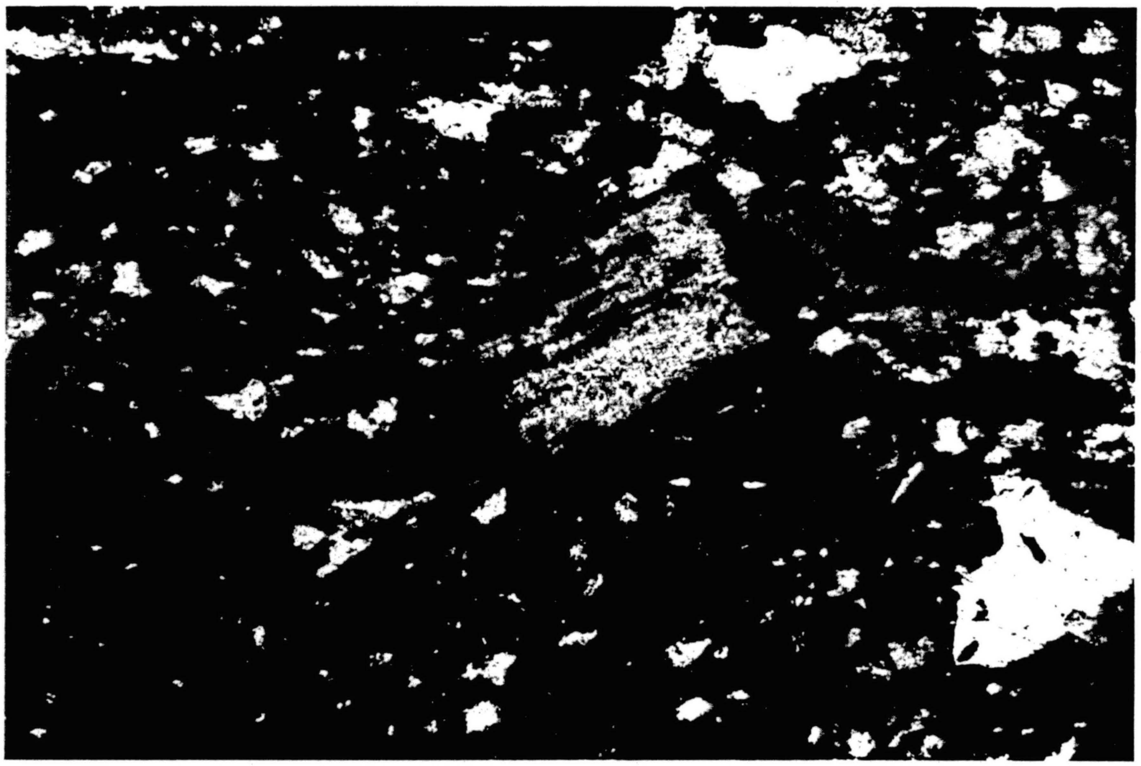


Figure 40. Authigenic Aegirine Produced Within the Basinal Varves (X10-XN)

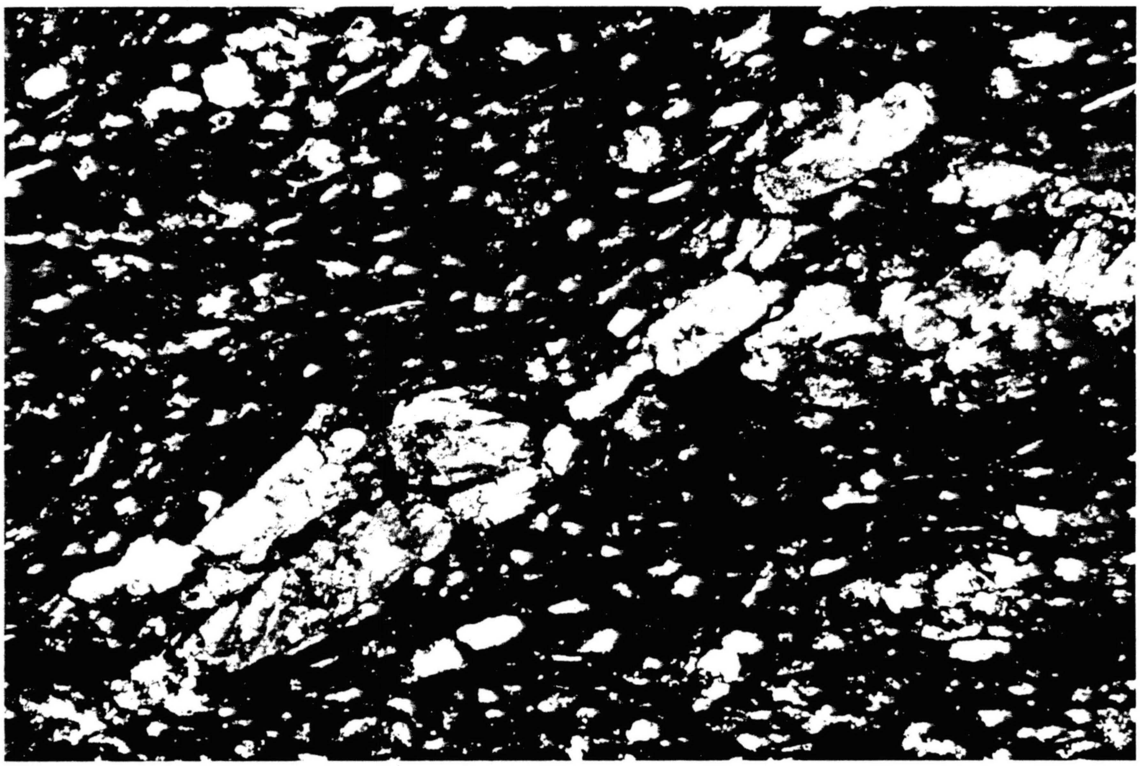


Figure 41. Aegirine Flowing Along With the Turbidity Currents of the Basinal Varves (X10-XN)

Caithness. They reported that the relative stratigraphic positioning of their occurrence within the lake is somewhat obscure. This author has been able to stratigraphically locate the exact position in the stratigraphic section where aegirine occurs.

The presence of aegirine in the lake sediments is unusual. It is believed by this author and by Fortey and Michie (1978) to be of authigenic origin. Sodic pryroxenes usually are characterized by an association with alkaline igneous and or metamorphic rocks (Fortey and Michie, 1978). The presence of sodic pyroxenes in association with sedimentary environments suggest an uncommon environment of formation. The Eocene Green River Formation is also another sedimentary site where aegrine occurrences have been reported (Mitten, et.al. 1960; Hay, 1963).

The genetic model favored by Milton et.al. (1960) for the formation of sodic mineral assemblages involves the presence of volcanic ash. The formtion of authigenic minerals in the Green River Formation involves the reactive phases of volcanogenic crystals, glasses and gels to produce such minerals as aegirine (Surdam and Eugster, 1976).

Volcanism within the Orcadian Basin during Middle Devonian was rare. However, in Orkney and Shetland Islands, alkaline volcanism has been noted (Fortney and Michie, 1978). This volcanism could have provided the necessary volcanic ash material for the formation of aegirine within the lake basin.

Phosphate

Phosphate in the basinal deposits occurs in a variety of forms. The phosphate appears as laminations (streaks), varves, and in pockets (small nodules). Phosphatic laminations are thin (.01-.03mm), light brown (PP), horizontal usually discontinous and are associated with organic matter. Pockets of phosphate are yellow brown in color, 250+microns in length and appear to have undergone flowage (Figure 42). The phosphate varves are one of the most striking textures seen in the basinal deposits. The phosphate in the varves ranges from bright orange to orange-brown in color (Figure 43). The color differences between the varves and pockets may be related both to the percent of phosphate present in the sample and the type of phosphate. Sedimentary apatite is a complex mineral in which substitutions by OH, Cl, F, and CO3 -2 are common. The phosphatic varves are not arranged in couplets or triplets as are the organic varves. The varves are wavy, horizontally bedded sediments (Figure 44). The amount of the detrital debris within these sequences is relatively low (2-3%) as compared to the clay and organic varves which contain up to 20% detrital debris.

Dolomicrite pockets associated with the phosphate

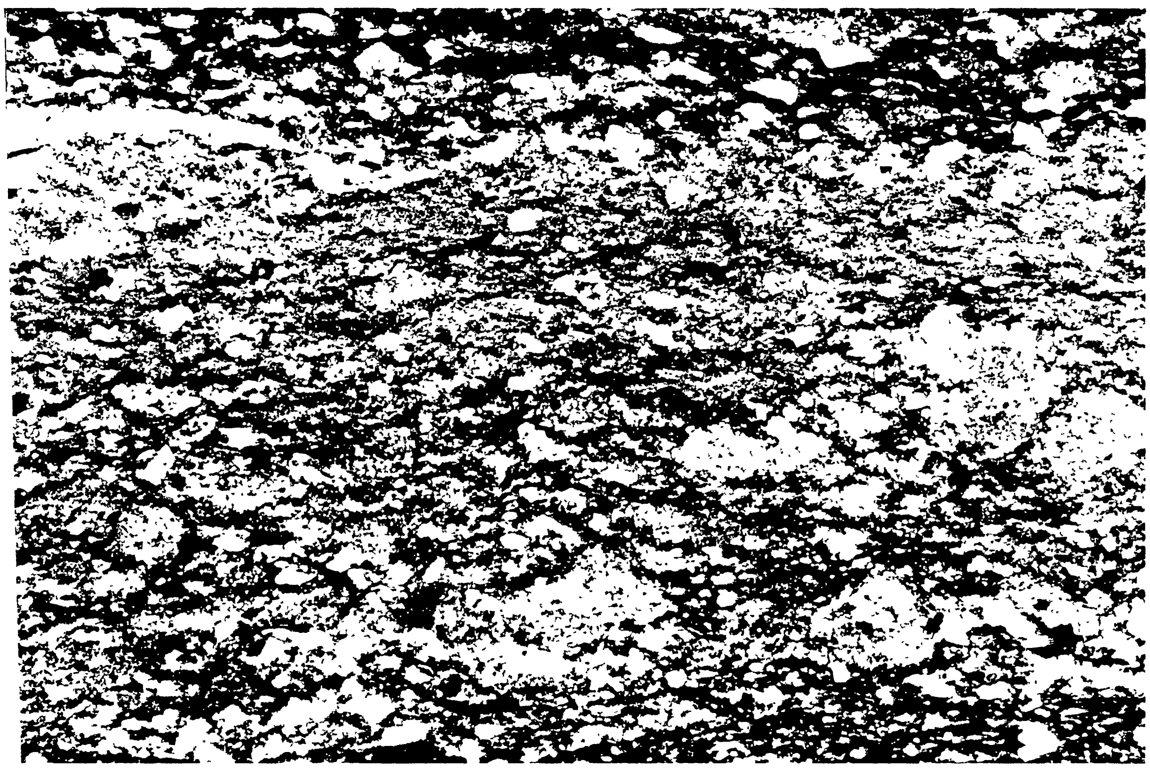


Figure 42. Discontinuous Phosphatic Pockets in the Basinal Deposits (X4-PP)

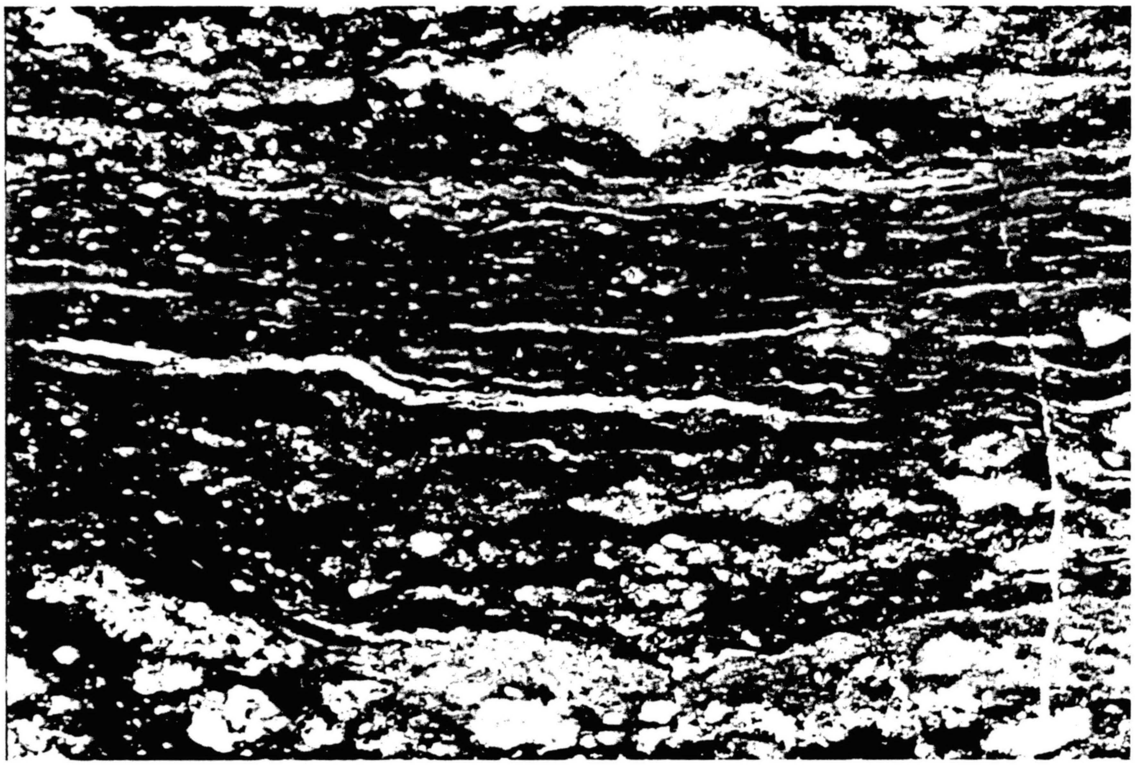


Figure 43. Phosphatic Varves of Cryptocrystalline Carbonate Fuorapatite (X4-PP)

Figure 44. Wavy Bedded Phosphatic Varves of the Basinal Deposits (X4-PP)

varves were stained with alizarin red and potassium ferrocyanide to determine if iron was present. The dolomicrite pockets stained light blue indicating the ferroan nature of the dolomite. Dolomite outside of the varves was not ferroan. Iron, dolomite, and organic material appear to be important constituents associated with the precipitation of phosphate. The origin and occurrence of phosphate in the freshwater deposits of the Orcadian Basin is problematic. It will therefore be dealt with as a separate chapter within this study.

Hydrocarbons

Hydrocarbon pockets occur sporadically throughout the samples of the basinal deposits (Figure 45). In hand-specimen some of the rocks smell of bitumen when freshly broken. In thin section, the kerogen rich material is black in plane polarized light and cross nicols and does not exhibit any particular characteristics under reflected light. The presence of hydrocarbons in the Orcadian Basin has been noted by earlier authors (Parnell, 1983; Donovan, 1978). The hydrocarbon minerals found in the lacustrine setting probably originated from the dark laminites, which contain up to 4% organic material (Donovan, 1978). Gas chromatography studies by Donovan (1978) were useful in suggesting an algal source for the organic matter in the rocks. The range of occurrences of hydrocarbon minerals in the Orcadian Basin has been well documented by Parnell

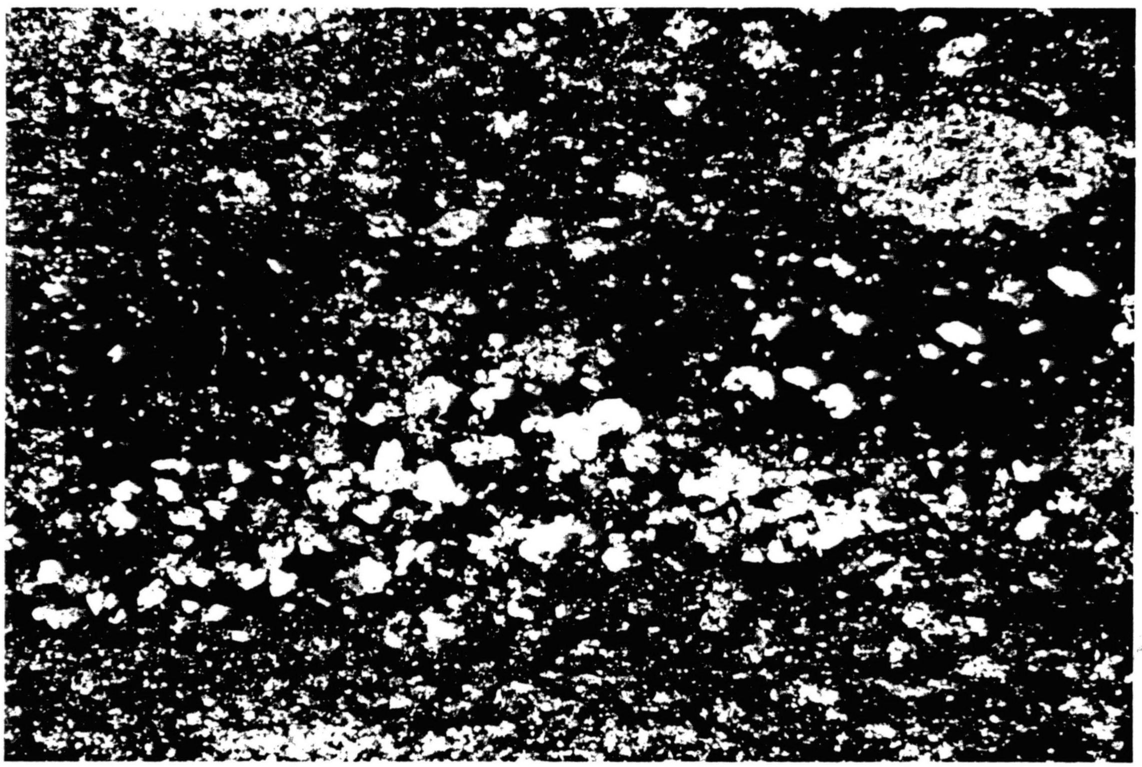


Figure 45. Pockets of Hydrocarbons in the Basinal Deposits (X10-PP)

(1983) (Table II).

Textures

Varves

Several of the samples from the basinal deposits exhibit laminations interpreted as varves. The composition and type of varves vary throughout the section. The types of varves found within the deposits include,

a) light and dark couplets

b) quartz-rich, light, and dark triplets

c) thin (.02mm) organic laminations

d) and tightly packed phosphatic varves.

Compositionally, the varves are composed of quartz, muscovite, biotite, chlorite, calcite, dolomite, feldspar, heavy minerals, hematite (after biotite), clays, carbonaceous material, hydrocarbons, phosphate, and pyrite. Each type of varve and its main constituents will be discussed separately.

The light and dark couplets (Figure 46) are predominantly composed of silt sized quartz and muscovite. The varves are composed of clay material, carbonaceous material and calcitic and dolomitic micrite. The size of the laminae ranges from .02mm-.15mm (light laminae) to .01mm-.05mm (dark laminae). The light laminae contain calcite, dolomite, and minor clastics, while the dark laminae contain organic material, calcite, and clastic

TABLE II

OCCURRENCE OF HYROCARBONS AND HOST ROCKS FROM THE ORCADIAN BASIN (AFTER PARNELL, 1983).

HOST ROCK	NATURE OF OCCURRENCE
Fossil Fish	Coatings and Replacement
Laminites	Masses on Bedding Planes
Laminites	Tension-Gash Fills
Laminites	Vein-Fills
Stromatolites	Inter-Head Fractures
Laminar Limestones	Masses up to 1 cm
Carbonate Nodules	Nodule-center Cavities
Carbonate Nodules	Oil Impregnations
Carbonate Nodules	Early Diagenetic Slickensides
Basin Margin Deposits	Masses up to 1mm
Cert Nodules	Vug Fills
Chert Nodules	Oil Impregnations
Chert Nodules	Tension-Gash Fills
Sandstones	Center of Reduction Spots

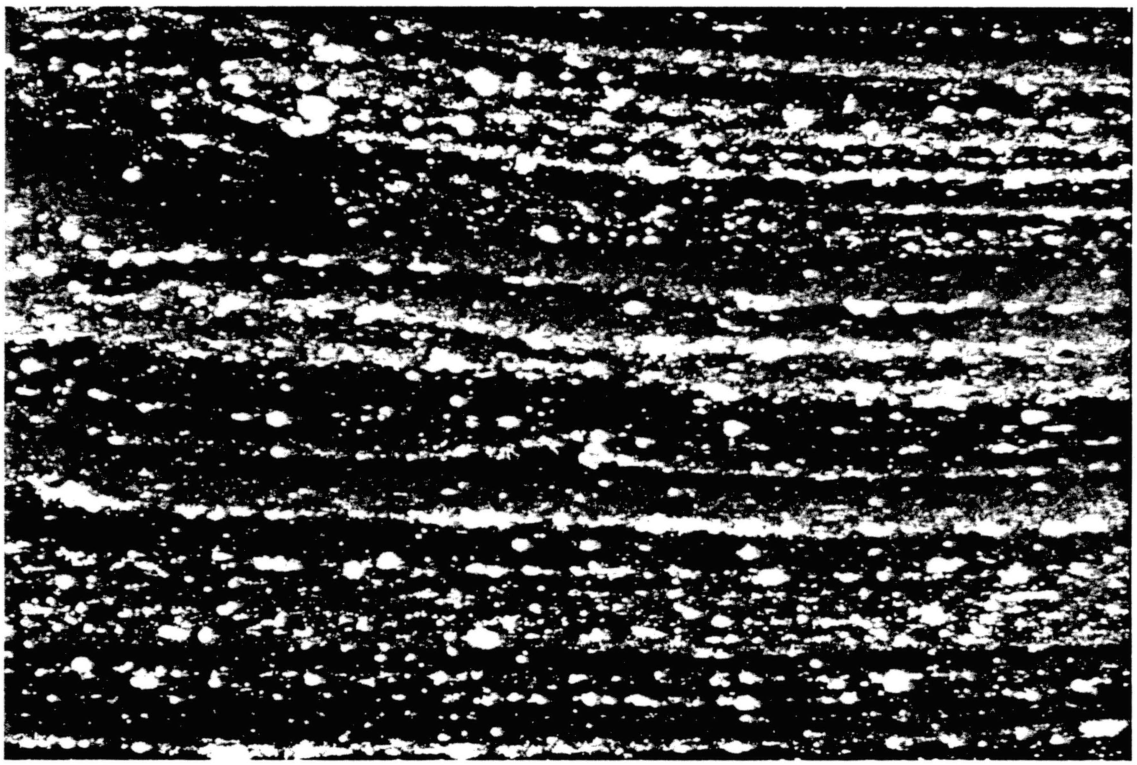


Figure 46. Varved Sequences-Light and Dark Couplets (X2-XN)

debris.

The quartz-rich, light and dark triplets are similar to the light and dark couplets but can be divided into three units (Figure 47). The first (quartz-rich) type is composed of detrital clastic debris (quartz, muscovite, heavy minerals (minor), organic stringers) cemented by calcite and minor amounts of dolomite. The second (light type) is composed of light brown clay and carbonaceous material, cemented with calcite. The third (dark layer) consists predominantly of dark brown carbonaeous material. The clastic units average 0.25mm thick. The light brown clay unit averages 0.18mm and the organic unit is 0.049 millimeters.

The third type of varve observed in the basinal deposits is similar to those described in the marginal limestones. The varves are composed of thinly laminated (.01-.02mm) organic material interdispersed with calcium carbonate cement (Figure 48). This type of varve contains very little (2-3%) clastic debris. These varves usually are styolitized, disruptive (not continuous) and semi-horizontal.

Phosphate varves are the fourth type of varve observed in the basinal deposits. Since they were covered in detail within the phosphate section, they will be discussed briefly. The phosphatic varves contain very little detrital debris (2-3%). They usually have a wavy

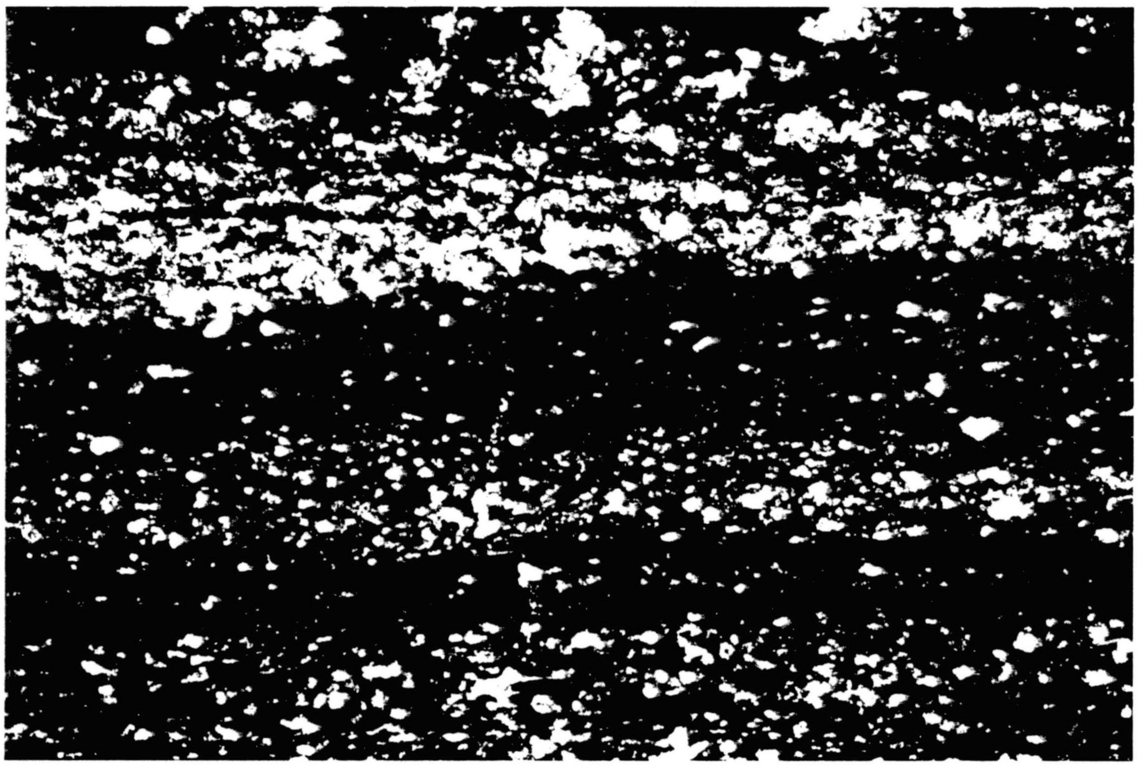


Figure 47. Varved Sequences-Light, Dark, and Clastic Triplets (X2-XN)

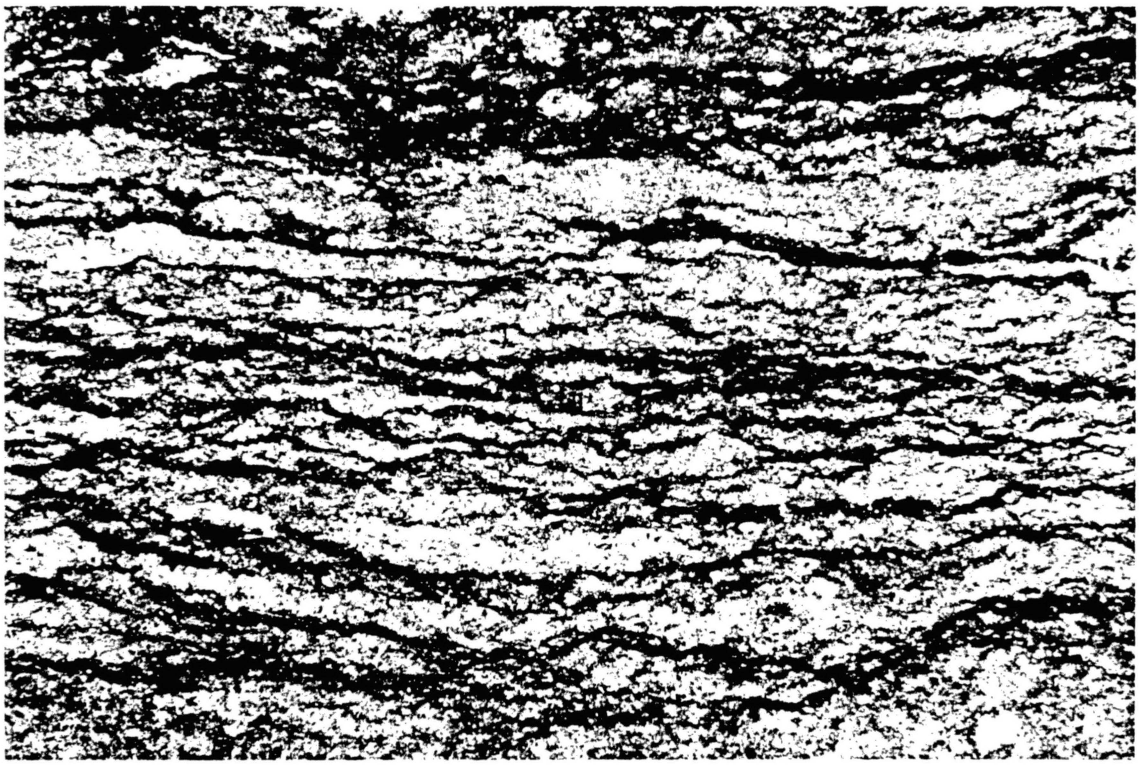


Figure 48. Thinly Laminated Varved Sequences of the Basinal Deposits (X2-XN)

texture and cannot be divided into couplets or triplets.

Pseudomorphs

Pseudomorphs after unknown evaporitic minerals are present within the basinal deposits. Some pseudomorphs have morphological outlines similar to gypsum crystals (Figure 49), and are assumed to have been gypsum. Gypsum crystals usually have a six-sided lath structure. However other pseudomorphs appear to have been deformed during compaction, therefore the original evaporitic mineral which produced the pseudomorphs cannot be interpreted with complete accuracy. The pseudomorphs have been replaced by ferroan calcite, and pyrite (Figure 50). Pseudomorphs are embedded within some of the varved sequences of the basinal deposits. For the most part they do not appear to be a disruptive feature within the varve.

Micro-faults, Tectonic Veins and Styolites

Microfaults and small scale tectonic events have affected some of the varved sequences of the basinal deposits. Figure 51 illustrates a typical microfault seen within the varved samples. Tectonic veins also occur within the varves. They are usually infilled with megaquartz or sparry calcite. The varved sediments have also been subjected to styolitization. Styolitized varves are wavy, disrupted and appear to have undergone

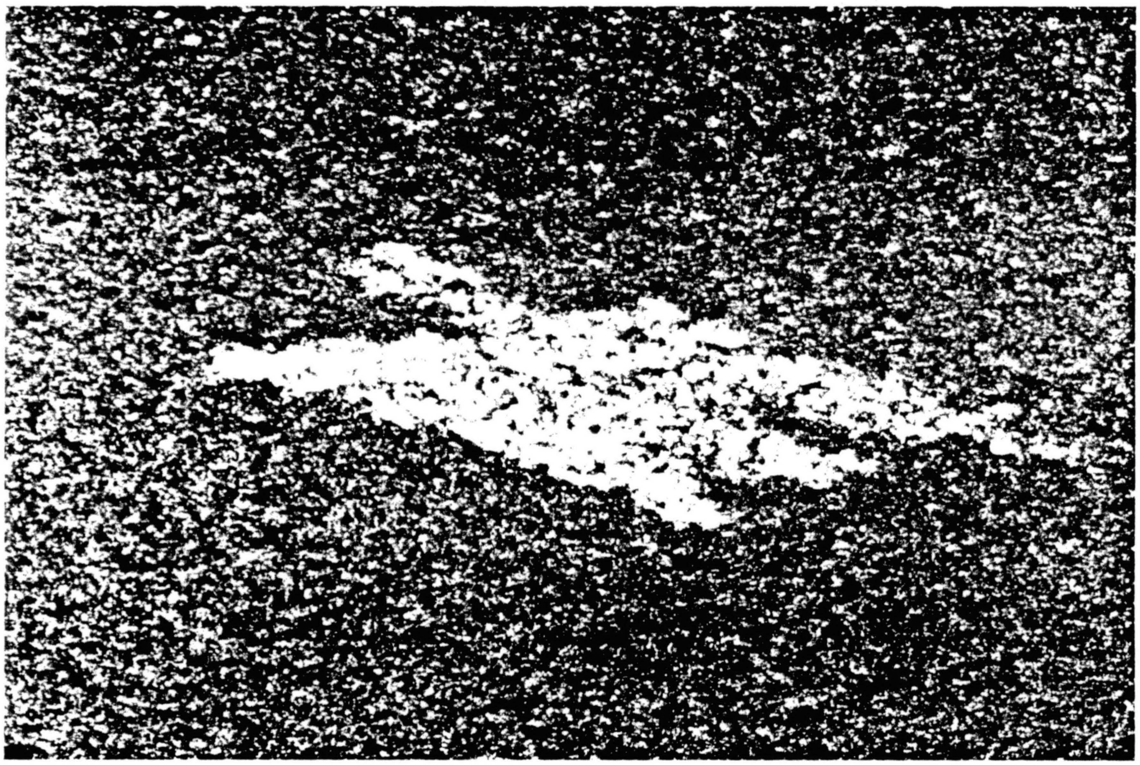


Figure 49. Pseudomorphs of an Evaporic Mineral-
Possibly Gypsum (X4-XN)

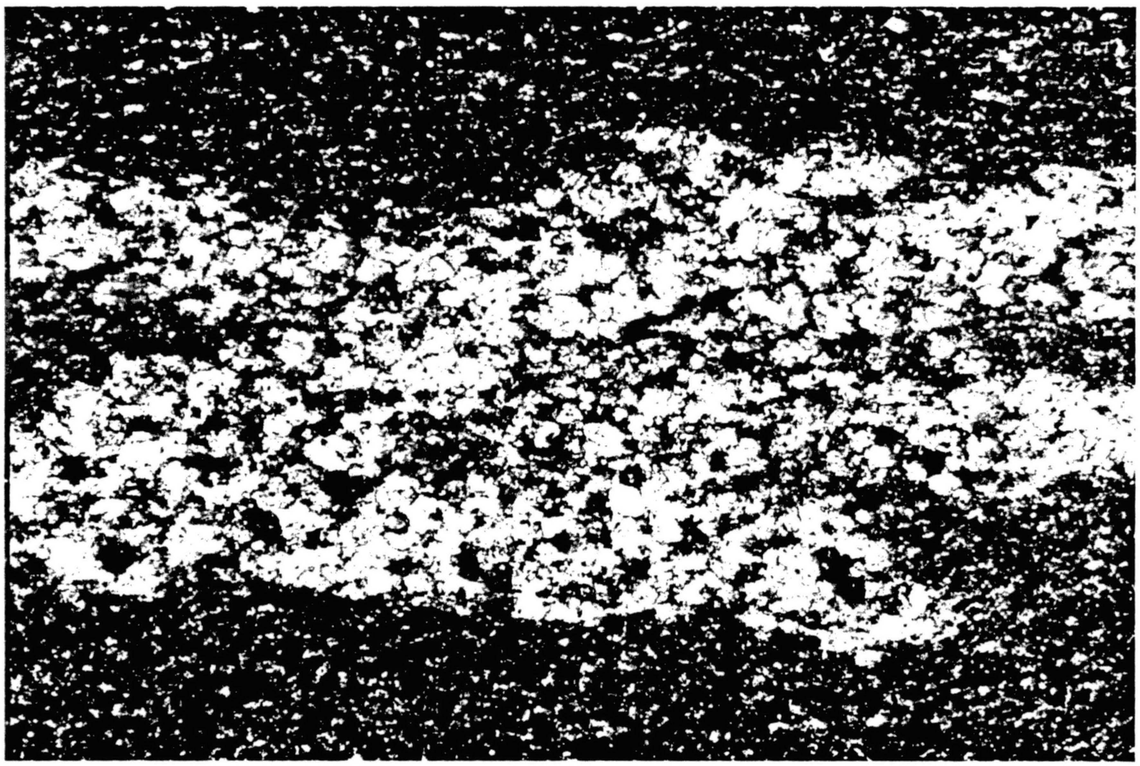


Figure 50. Pseudomorphs Containing Ferroan Calcite and Pyrite (X10-XN)

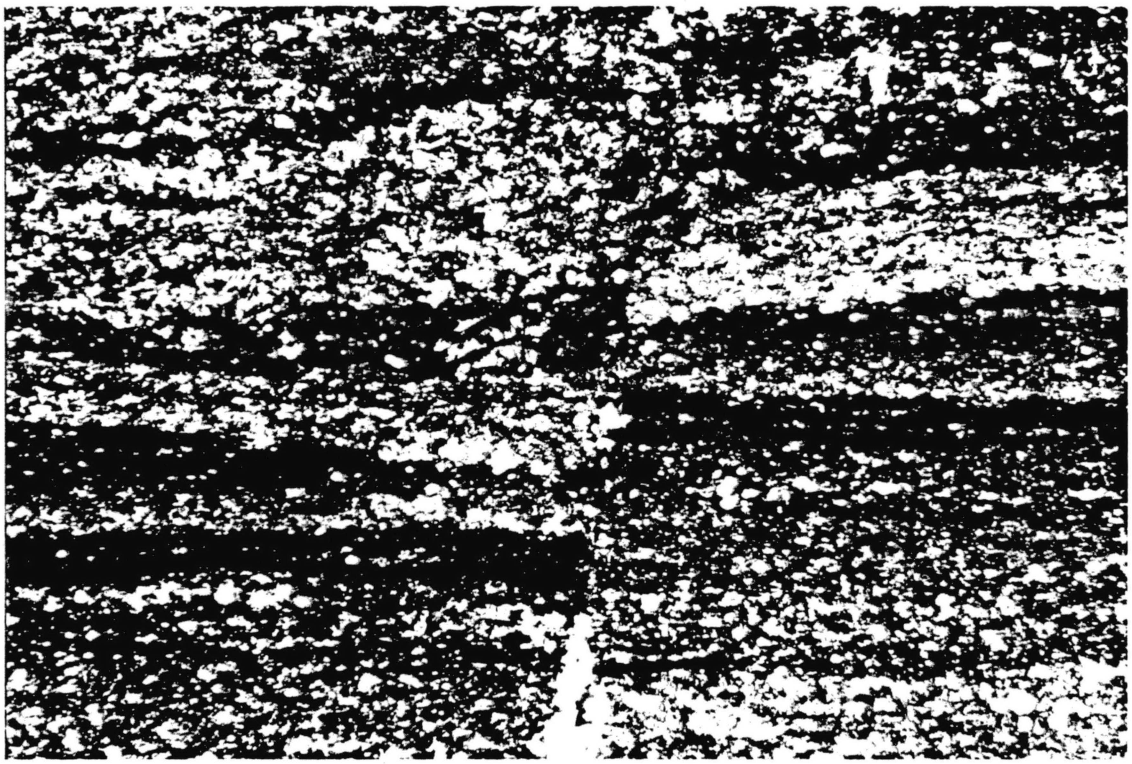


Figure 51. Microfaults Along the Varved Sequences of the Basinal Deposits (X2-XN)

compaction.

Turbidity Currents

Some of the varves of the basinal deposits appear to have undergone large scale flowage, resulting in the complete destruction of the horizontal laminae (Figure 52). Flowage patterns are illustrated by muscovite and detrital quartz which "flow" along the path in which the turbidity current moved. This type of destruction could have resulted from turbidity flows reworking laminae prior to their lithification.

Diagenesis

Both physical and chemical diagenesis has occurred in the basinal deposts of the Orcadian Basin. Physical diagenesis includes microfaults, styolites, and turbidity currents (flowage) (see above). Chemical diagenesis played an important role in the alteration, dissolution, replacement, and precipitation of minerals within the basin. This section will concentrate on the role of minerals associated with chemical diagenesis in the basinal deposits.

Dissolution

Dissolution of detrital debris played a minor role in the diagenesis of the basinal deposits. This is probably

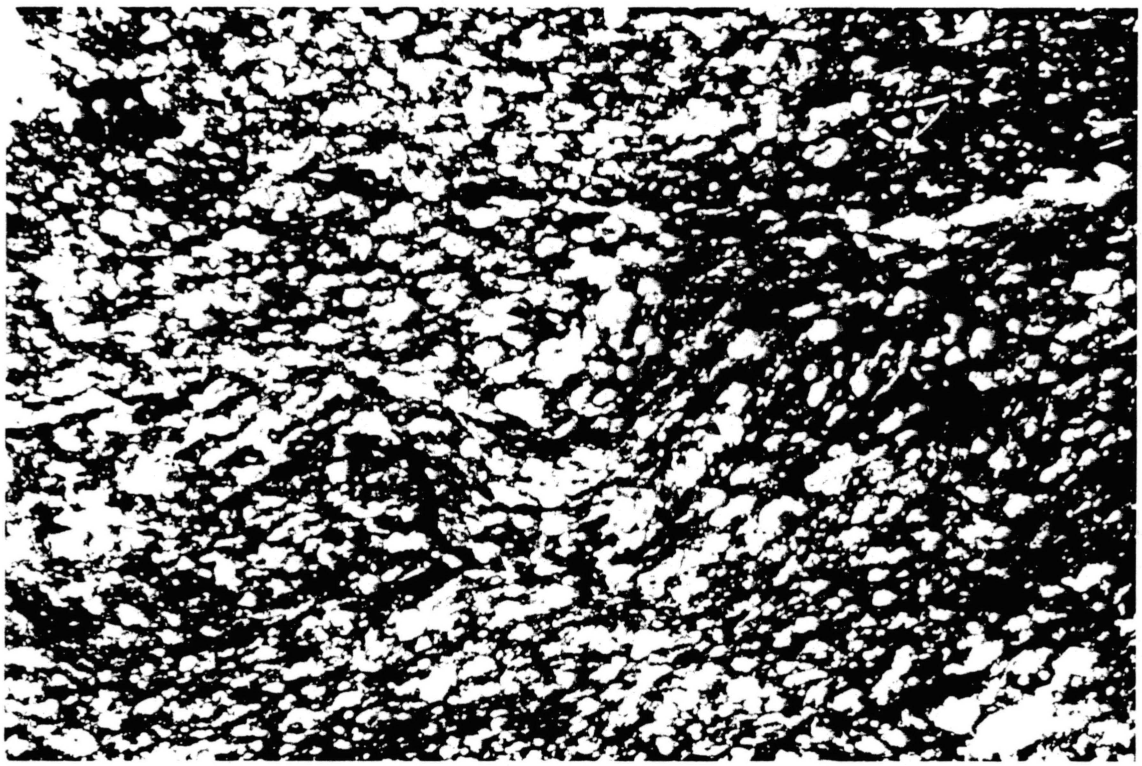


Figure 52. Destruction of Basinal Varves by Turbidity Currents (X2-XN)

due to the small size and small amount of clastic debris in the basinal deposts as compared to the marginal limestones. Quartz and feldspar are the only minerals which have undergone partial dissolution. Feldspars are generally rare within the varved sequences, but some of the grains present have undergone considerable dissolution. Quartz dissolution is evidenced by corrosion around the crystal edges.

Replacement and Alteration

Several detrital grains have undergone replacement and alteration by other minerals. The detrital grains include feldspar, quartz, and biotite. Feldspar and quartz have undergone dissolution and subsequent replacement by calcite. Bioite grains have undergone complete alteration to chlorite. The coarseness and the shape of the chlorite grains indicates that the grain was probably biotite.

Precipitation

The formation of inorganic primary carbonates is controlled by three major processes. The first process involves the loss or extraction of CO_2. The chemical equation which controls the precipitation of $CaCO_3$ is as follows:

$$CO_2 + H_2O + CaCO_3 \rightleftharpoons 2HCO_3^- + Ca^{+2}$$

A reduction in the amount of CO_2 in the system will drive the reaction to the left which will result in the precipitation of $CaCO_3$. The loss of CO_2 from the lacustrine environment occurs usually in areas with humid climates (Muller, et.al., 1972). The second process is related to the concentration of ions through evaporation. By increasing the concentration of Ca-Mg and CO_3 ions past their solubility will result in the precipitation of Ca - Mg carbonates. The third process involved in the formation of carbonates which involves the precipitation of Ca - Mg carbonates through the process of mixing of different water bodies.

The type of primary Ca - Mg carbonate precipitated depends upon the Mg/Ca ratio of the lake water. Muller (1972) showed that when the Ca/Mg ratio is less than 2, low-Mg calcite will precipitate. If the ratio is greater than 2 but less than 7, high-Mg calcite forms.

The formation of secondary carbonates including dolomite occurs when the Mg/Ca ratio is 7 to 15 (Muller, et.al., 1972) and when high-Mg calcite is available in the sediment. Folk and Land (1975) have calculated somewhat different precipitation fields for dolomite, calcite, and high Mg calcite in terms of salinity and Mg/Ca rations (Figure 53). In their illustration lake waters range from Ca/Mg ratios of 1:20 to 3:1 ppm. Dolomite can also be precipitated through an increase in the Mg/Ca ratio thru

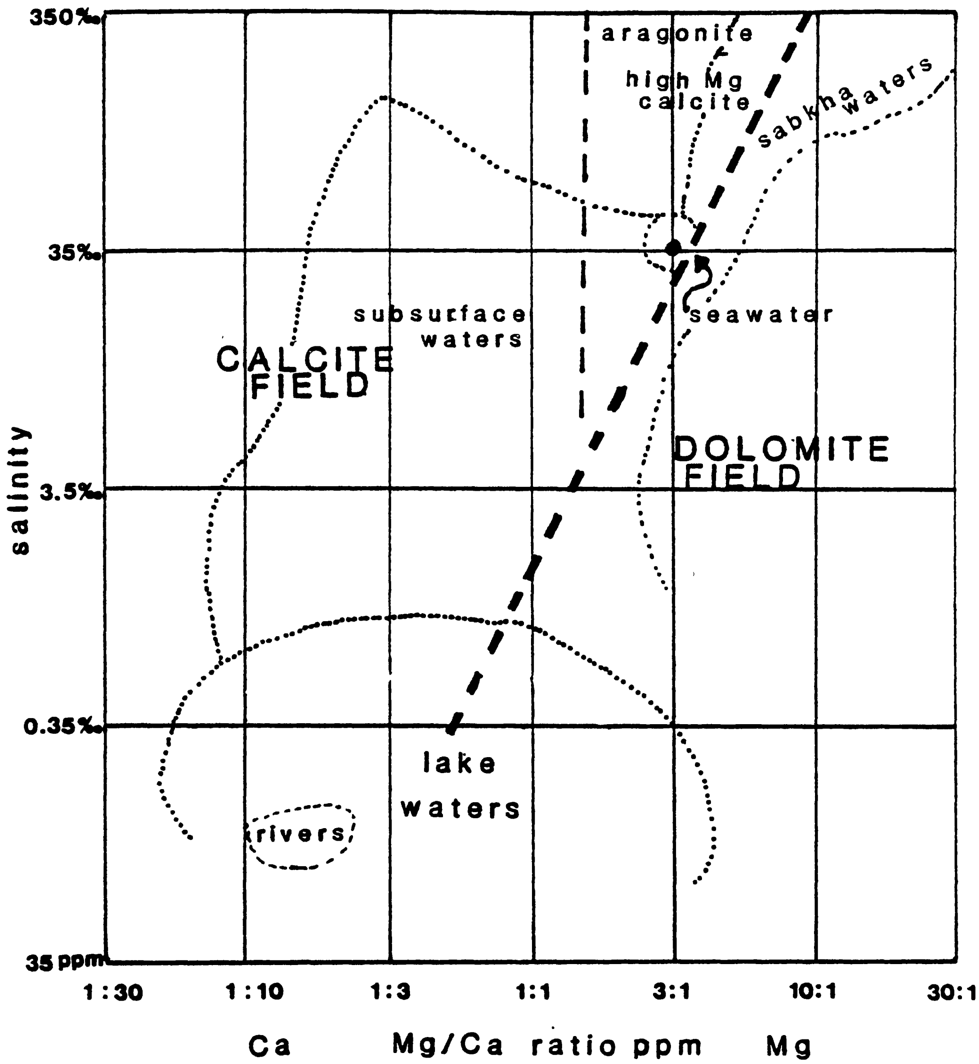


Figure 53. Calcite and Dolomite Precipitation Fields and Their Relationship to Lake Waters (After Folk and Land, 1975)

the influence of pore water (Tucker, 1981). There are two possible ways for this to occur. The first involves the leaching Mg from high Mg calcite, and the second is performed through the leaching of Mg which is absorbed on to clays in mudrock horizons (Kahle, 1965). Therefore dolomite in the basinal deposits could reflect local sources of Mg from high Mg calcite or from adjacent clays in the mudrock sequences of the deposits.

CHAPTER VI

PHOSPHATE-AN UNSOLVED PROBLEM?

Introduction

The presence of phosphate in lacustrine sediments is a rare occurrence. Lacustrine phosphate has been found in only four lake deposits (Bentor, 1980). All of these are saline and are located in the Rocky Mountain region, predominantly in the Green River Formation (Love, 1964). The phosphate beds are usually thin and contain very low amounts of phosphate. The dominant phosphate mineral in these deposits is apatite. The genesis of phosphate in ancient lake systems is problematic. Its origin as an inorganic primary precipitant versus a secondary replacive mineral is not fully understood. This chapter will attempt to derive an explanation and model for the presence of phosphate in the Orcadian Basin.

Phosphate Mineralogy

Most of the phosphate within sedimentary rocks is a variety of apatite. The most common varieties are represented by an isomorphous series with end member compositions of:

$Ca_5(PO_4)_3F$	Fluorapatite
$Ca_5(PO_4)_3Cl$	Chlorapatite
$Ca_5(PO_4)_3OH$	Hydroxyapatite
$Ca_5(PO_4,CO_3,OH)_3(F,OH)$?	Carbonate-apatite

Commonly, fluorapatites contain up to 10% carbonate ions which have subsituted for the phosphate ions (Blatt, et al., 1980). This type of phosphate is termed francolite and is the most common variety found in sedimentary rocks. The phosphate material in phosphate occurs as a cryptocrystalline or x-ray amorphous substance referred to as collophane. Hydroxyapatite is generally unstable in environments relative to fluorapatite (Blatt, et al., 1980). Before bones and teeth are buried they are relatively rich in hydroxl ions, but upon burial, groundwaters will infiltrate and replace the hydroxyl ions with fluorine ions within the crystal system (Blatt, et al., 1980).

Phosphorus in Lakes

Hutchinson (1957) is one of the early pioneers in the study of phosphate in lake systems. Phosphorus is one of the most ecologically important elements present in living organisms. Hutchinson (1957) stated that "the ratio of phosphorus to any other element in organisms tends to be dramatically greater than the ratio in the primary sources of the biological elements."

The catagories of phosphate discussed within the Hutchinson (1957) study include:

1. Soluble Phosphate Phosphorus
2. Acid-soluble Sestonic Phosphorus
3. Organic Soluble and Colloidal Phosphorus
4. Organic Sestonic Phosphorus

The vertical distribution of phosphorus in stratified lakes is generally due to an increase in the breakdown of soluble components within the hypolimnion. Phosphate in deeper waters is related to the fraction of soluble phosphate present, the fall in oxygen concentration with depth and an increase in ferrous iron.

Einsele (1937) postulated that the ratio of soluble phosphate to iron increases with depth. This hypothesis is assumed correct if the amount of iron is limited by turbulent downward diffusion of oxygen, and if the phosphate present is in amounts smaller than that of ferrous iron, so that ferricphosphate precipitates before any ferric-hyroxide forms (Einsele,1937). The conclusion drawn from this theory is that the appearance of large amounts of phosphate in deep waters is dependent upon the disappearance of the oxidized microzone along the mud surface (i.e., the existence of anoxic conditions).

The Phosphate Cycle

Later work, (Hutchinson, 1957) on the phosphorus cycle in lakes defined 7 main processes which led to stratification and phosphatization within lakes. The processes involved include:

1. Liberation of phosphorus into the epiliminion from the littoral zone (from the decay of littoral vegetation).
2. Uptake of phosphorus from the water by littoral vegetation.
3. Uptake of the liberated phosphorus by phytoplankton.
4. Loss of phosphorus as a soluble compound, from the phytoplankton, probably followed by slow regeneration of ionic phosphate.
5. Sedimentation of phytoplankton and other phosphorus-containing organisms, probably due largely to faecal pellets, into the hypolimnion.
6. Liberation of phosphorus from the material in the hypolimnion or at the sediment-water interface along the bottom.
7. Diffusion of phosphorus from the sediment into the water at a depth which lacks abundant oxygen.

This sequence of events applies to warm or summer seasonal periods in which algal influence is at its peak production. Liberation of phosphate from the previous season's algal development is primarily a winter or cool period phenonmena.

In lake waters, most phosphate is continuously reworked and recycled by life processes. The phosphorus is taken in by plants and then returned back to the water upon decay of the plant. Organisms which fed upon plants incorporate phosphate into their systems which is returned to the cycle through faeces and the death of the organism. Phosphorus is then returned to the lake by diffusion from the muds as the organic material decays (Figure 54).

Content of Phosphorus in Lakes

The total amount of phosphorus in lake varies from undetectable amounts of <1mg.m-3 (0.001 ppm) in Traunsee, Austria up to huge quanties of 78g.m.-3 (208 ppm) in the saline Goodenough Lake, British, Columbia (Hutchinson, 1957). These values are estimated from the near surface or epilimnetic waters of the lakes. The phosphorus content is generally higher in the stagnant hypolimnia of stratified lakes. Large quantities of dissolved phosphorus occur in brine lakes which are deficent in calcium and magnesium. Examples of brine lakes with high phosphorus values include Deep Springs Lake, Calif. (1,070-1,410 ppm PO4 or 349-469g. cm-3) and Alkali Valley, Oreg. (2,420 ppm PO4 or 788g. cm-3) (Bradley and Eugster, 1969).

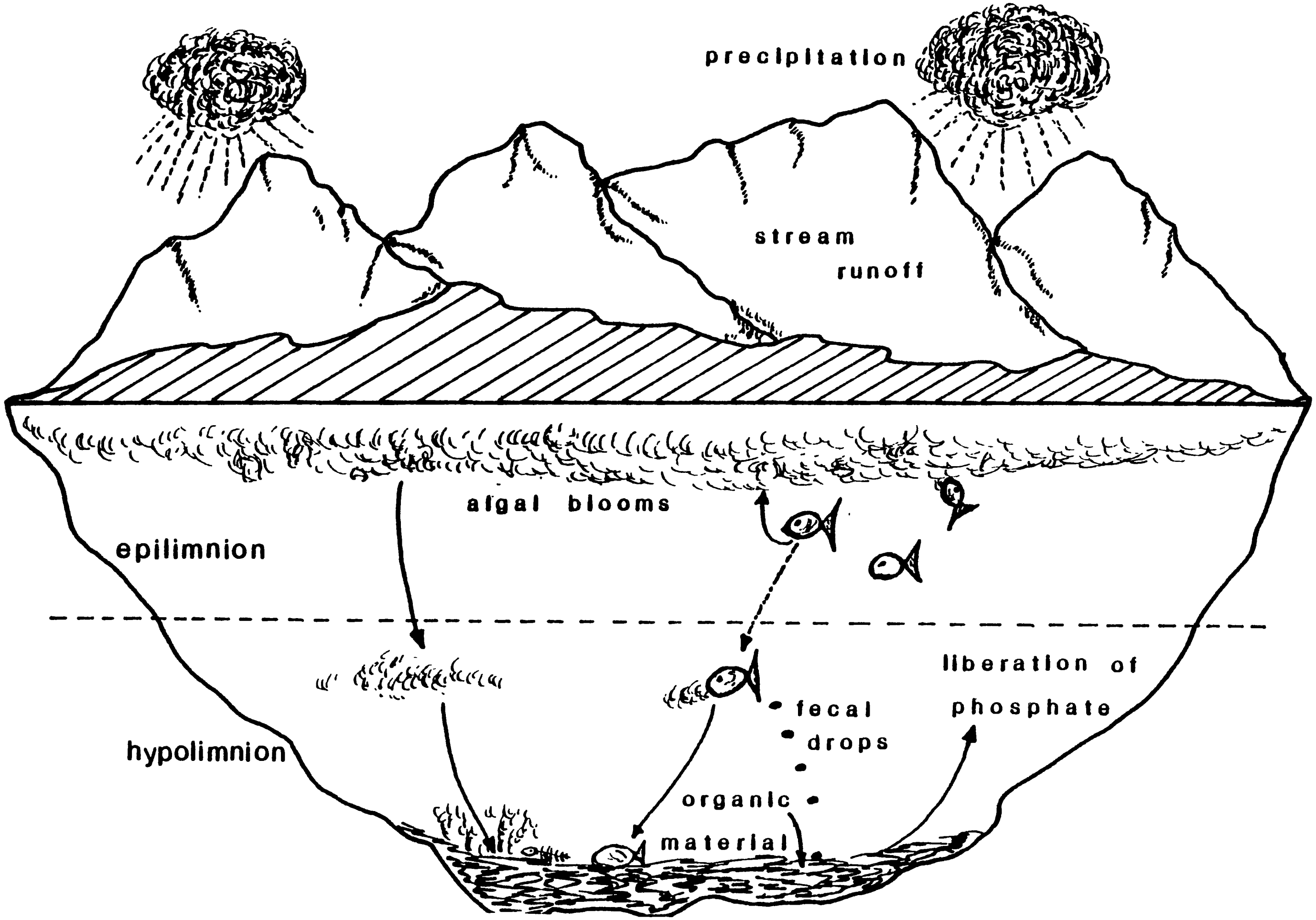


Figure 54. Schematic Illustration of the Phosphorus Cycle

Phosphate in the Green River Formation

Two members of the Green River Formation contain phosphatic sediments; the Wilkins Peak Member (Love, 1964), and the Gosiute Lake Brine Member (Bradley and Eugster, 1969). The following sequence of events for the formation of phosphate in Lake Gosiute is summarized from the results of Bradley and Eugster (1969).

Lake Gosuite was a meromict lake which contained a highly saline hypolimnion overlain by a calcium bicarbonate rich mixolimnion. As with most meromictic lakes, over extended time periods, the hypolimnion of Lake Gosuite became enriched with phosphorus. The enrichment occurred through the continuous infiltration of decayed organic material from the overlying waters. Eventually, the mixolimnion underwent a chemical change which resulted in the precipitation of calcite. The precipitation of the calcite was directly related to the large losses of CO_2 which occur during algal photosynthesis and/or through the progressive warming of the water. The important mechanism involved in this process is the means of bringing new calcite and Ca^{+2} ions into the hypolimnetic brine. This calcite reacted with the phosphate ions to form carbonate-apatite (or carbonate hydroxylapatite or carbonate fluorapatite). Secondly, the calcite reacted with magnesium and formed dolomite. The third stage of this scenario involved the excess calcite being preserved.

Love's (1964) richest phosphatic zone in the Wilkins Peak Member contained approximately 18.2 percent P205. The percentage of phosphate can be accounted for by direct precipitation of carbonate apatite in the same manner as that found in Lake Gosuite. Calculated rates of accumulation of phosphate are about 7.5 cm per every 500 years (Bradley and Eugster, 1969).

Phosphate in the Orcadian Lake

Phosphate in the Orcadian Basin has had little attention in the literature. Donovan (1971) has referred to the presence of phosphate as a form of collophane which is exhibited by fossil fish preserved in limestones. Coprolites were also examined for phosphate composition and were found to contain collophane as well (Donovan, 1971). Phosphatic pebbles and nodules were also collected and found to contain collophane. Donovan (1971) also noted slight recrystalization of collophane to cryptocrystalline apatite in a few of the compacted sediments (varves and laminations-?).

The phosphate found in this study occurs in two states. The first type of phosphate seen appears as a yellow-brown "dirty" deposit. This type is associated with the marginal laminations (varves) and occurs as pockets in both the marginal and basinal deposits (Figure 55). The second type of phosphate observed in the Orcadian Lake occurs as varves within the deep water

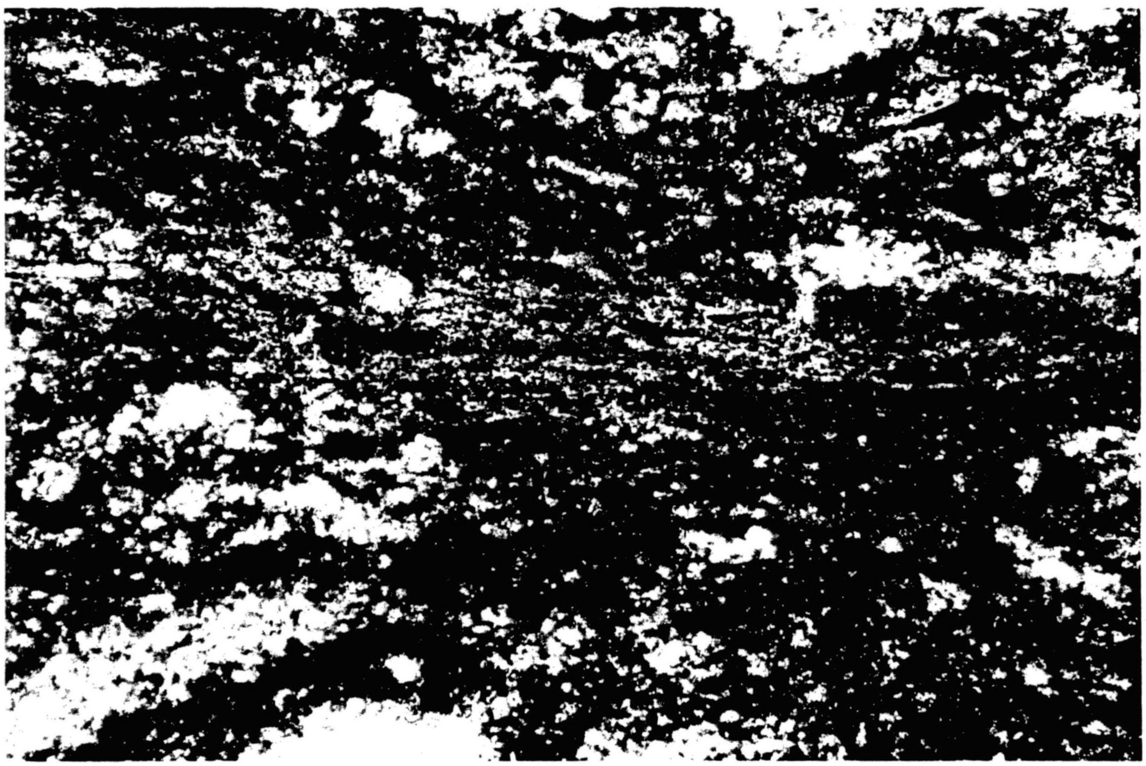


Figure 55. Phosphate Pockets in the Basinal and Marginal Deposits (X4-PP)

laminites (Figure 56). This phosphate is bright orange-brown in plane polarized light. These two different types of phosphate are believed to represent two completely different stages of phosphate formation.

The first type of phosphate (yellow-brown) is a cryptocrystalline material believed to be collophane. This material is termed collophane because the precise composition of the apatite present has not been established. The pockets of phosphate associated with the marginal and basinal varves are related to the presence of faecal matter (coprolites) and or fish remains.

The second type of phosphate is more complex and is believed to be a primary precipitation which took place while the basinal varves formed. The composition of this phosphate is carbonate apatite (as indicated by the x-ray diffraction peak). The variation in the phosphate is due primarily to the amount of phytoplankton and algal growth which occurred on the lake surface. The amount of soluble phosphate is greater with increasing depths due to decomposition and liberation of more soluble orthophosphates derived from the decay of organic material. The amount of phosphate formed at the bottom of the lake can be attributed to long periods of stagnation within the lake. Phosphatic enrichment of the muds during the decay of organic material probably produced a "gel" which slowly became richer in P2O5 while the lake remained

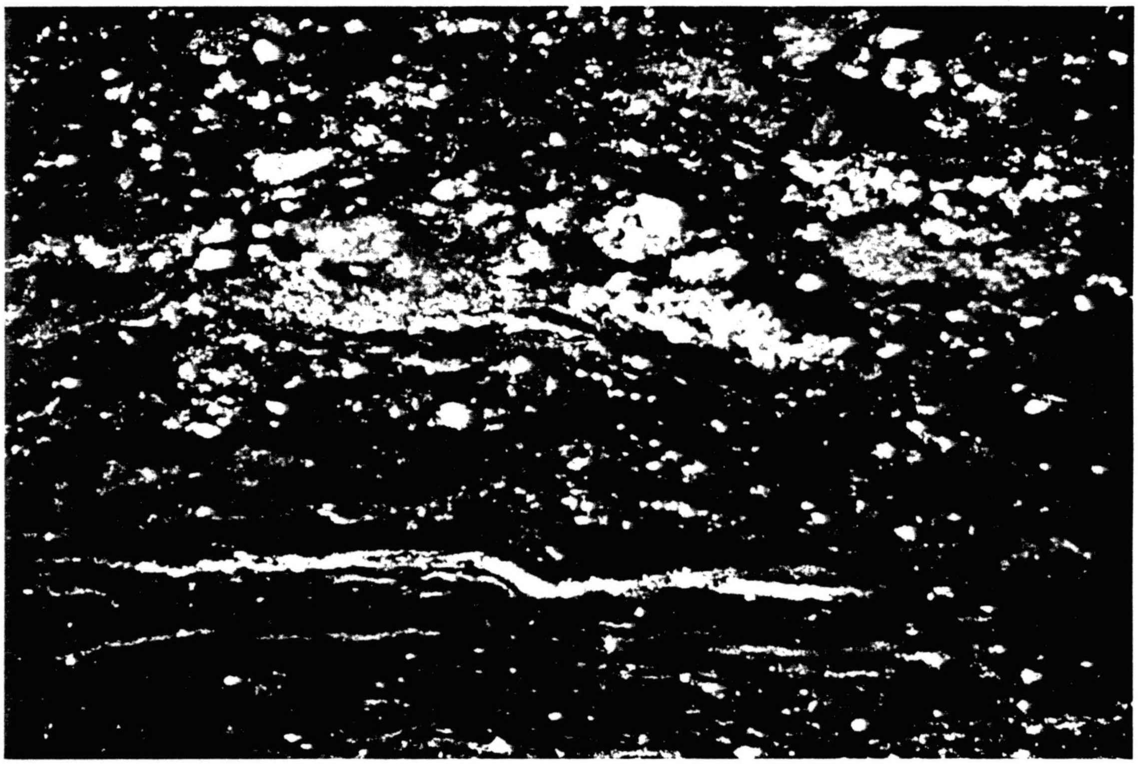


Figure 56. Phosphate in the Deepwater Laminites of the Basinal Deposits (X4-PP)

fairly deep. A low Eh in the sediments caused interstitial waters rich in phosphorus to form below the sediment-water interface. This was a direct result of leaching of phosphate from organic remains. Direct precipitation of apatite within the sediment followed.

The explanation of the origin of the phosphate in the Orcadian Basin is similar to that offered for the Green River Formation. The Green River Formation phosphate occurs in thin zones as does the Orcadian Basin phosphate. Since the amount of phosphate in the sediments is relatively small (traces to 10 percent in select areas), there must have been an inhibitor mineral or ion within the environment of formation. The Orcadian Lake may have been poor in phosphorus because while it was being stored in a calcium-saline-anoxic hypolimnion, phosphorus was being released (precipitated) very sparingly. The small amount of Ca +2 ions available at the bottom of the lake may have prohibited the profuse formation of carbonate apatite. This in turn caused the thin phosphatic varves to accumulate slowly over a long period of time.

CHAPTER VII

GEOCHEMISTRY OF THE ORCADIAN BASIN DEPOSITS

Geochemical Parameters

A geochemical analysis of the rocks of the Orcadian Basin was conducted as part of this study. Geochemical techniques included x-ray diffraction, total organic carbon, and isotope analysis using O18 and C13 standards. Atomic adsorption spectometry was attempted on the rocks but due to unforseen complications, analysis was not completed. X-ray diffraction was run on the samples to determine the major constituents as well as to determine differences in minerals present in the marginal facies versus the basinal facies. Total organic carbon percentages were run to determine the percentage of carbon as well as to delineate the difference between carbon content of the marginal as opposed to the basinal deposits. Isotope analysis was run to determine the origin of the deposits (marine or lacustrine).

X-Ray Diffraction Analysis

Procedure

The samples of the Orcadian Basin were x-rayed so that a more precise method of identifying the mineral species found in the basinal and marginal deposits could be attained. Twenty-six samples were run for x-ray diffraction analysis. Of these, nine were marginal deposits and seventeen were basinal deposits. The rocks were powdered for approximately two minutes in a Spex carbide-lined ball and cylinder. X-ray diffraction spectra were obtained using a Nicolet diffractometer with CüK radiation. Tube settings of 45 KV and 35 MA were used and each sample was scanned from 2-60 2θ degrees in increments of 0.5 degrees. The sample, mounted in an aluminum holder, was rotated during scanning to minimize the effects of preferred orientation. X-ray results appear in Appendix B.

The minerals were identified by comparing their d-spacings and 2θ values to those listed in: "Mineral Powder Diffraction File", compiled by the Joint Committee on Powder Diffraction Standards, 1980.

Analysis

To distinquish the main constituents in each of the samples, a graph was constructed. Sample number and minerals were used along the sides of the graph (Figure 57

Sample \ Mineral	Calcite	Dolomite	Illite	Carbonate Apatite	Montmorillonite	Quartz	Biotite	Chlorite	Carbonate Fluorapatite	K-Feldspar	Plagioclase	Hematite	Microcline	Albite	Na-Montmorillonite
RQB 1	●	●	●	●	●	●		●		●	●				
RQB 2	●	●	●	●		●		●		●	●				
RQB 3	●	●	●	●		●				●					
RQB 4	●	●		●		●			●	●			●		
RQB 5	●	●	●	●		●				●	●				
RQB 6	●	●	●	●		●			●			●		●	
ROB 7	●	●	●			●		●		●	●	●			
RQB 8	●	●	●	●		●		●	●	●	●	●			
RQB 10	●	●	●	●	●	●			●	●					
RQB 11	●	●	●	●		●					●	●			
RQB 12	●	●	●	●		●			●	●	●				
RQB 13	●	●	●	●	●	●				●					
ROB 14	●	●		●		●			●	●			●		
RQB 15	●	●	●			●			●				●		
A2	●	●		●		●			●	●				●	
A 3	●	●		●		●				●	●				

Basinal Deposits

Figure 57. Main Constituents of Basinal Deposits Based on X-Ray Diffraction

and 58). The samples were divided into basinal deposits (Figure 57) and marginal deposits (Figure 58). The most obvious difference between the two deposits is the amount of minerals seen in the basinal deposits as opposed to the marginal deposits. The basinal deposits show a greater variation in mineral types. This is due in part to the varves which contain a lot of clay and carbonaceous material as well as clastic debris. The marginal deposits contain only small amounts to zero percent clay and carbonaceous material. Dolomite was also more abundant in the basinal varves. This suggests that higher Ca/Mg ratios found in the deeper water sections of the lake (see Chapter V). The other mineral more prevalent in the basinal deposits is apatite (carbonate-apatite or carbonate fluorapatite). This is due in part to the formation requirements of apatite (see Chapter VI).

Total Organic Carbon

Procedure

Samples of the rocks in the Orcadian Basin were analyzed for the percent of total organic carbon. The method used is given in Appendix C. The procedure is a standard method used by the Oklahoma State Agronomy Department. Nineteen samples were tested to determine the percent of total organic carbon in the marginal and basinal deposits. Two fractions of each of the nineteen

Sample \ Mineral	Calcite	Dolomite	Illite	Carbonate Apatite	Montmorillonite	Quartz	Biotite	Chlorite	Carbonate Fluorapatite	K-Feldspar	Plagioclase	Hematite	Microcline	Albite	Na-Montmorillonite
TARB 4	●			●		●			●	●					
TARB 7	●		●	●		●		●	●	●					
TARB 9	●					●				●					
TARB 12	●	●				●				●		●			
TARB 14	●		●	●		●									
TARB 17	●		●			●	●			●				●	
TARB 22	●	●		●		●	●		●	●					
BA. 4 A	●	●				●				●					
BA 4 B	●	●	●			●									

Marginal Deposits

Figure 58. Main Constituents of Marginal Deposits Based on X-Ray Diffraction

samples were weighed out to approximately one gram. The samples were then run through the OSU argonomy procedure for soil organic matter. Results of the analysis appear in Appendix C. The percent of total organic carbon was calculated based on the formula in figure 59.

Analysis

Samples containing the prefix ROB or A are located in the basinal section of the lake. Samples with a prefix of TARB, BL, or BALIB are located along the margins of the lake.

The samples were plotted on graphs with axes of sample number (increasing stratigraphically) and total percent organic carbon (Figure 60, 61, and 62).

Overall, the basinal deposits contain higher percentages of total organic carbon (TOC) than do the marginal deposits. The basinal percentages of TOC range from .686 up to 4.14 whereas the marginal deposits have lower percentages ranging from .367 up to 2.12. Given the environmental interpretation offered above these values suggest that the influence of organic matter from algae is directly responsible for the high percentages of organic material associated with the basinal varves of the Orcadian Basin. Also the influence of water depth (i.e. stratification) and the activity of the water are important parameters. If the water activity was hostile (i.e. oxidation), then the organic matter was not well

CALCULATION OF TOC

Percent Total Organic Carbon

$$\% \text{ TOC} = .69 \left[\frac{(\text{Blank A} + \text{Blank B} + \text{Blank C})}{3} - \text{Sample} \right]$$

$$= (B - X) \times \text{Normality/Ferrous Sulphate} \times .00336 \times 100/\frac{\text{Sample}}{\text{Weight}} \times 1.33$$

B = Blank Average

X = Sample Used

1.33 = Fudge Factor (75% of C in sample is oxidized)

$$\% \text{ TOC} = \frac{.687\ (B - X)}{\text{Sample Weight}}$$

Figure 59. Calculation of Total Organic Carbon (O.S.U. Agronomy Dept.)

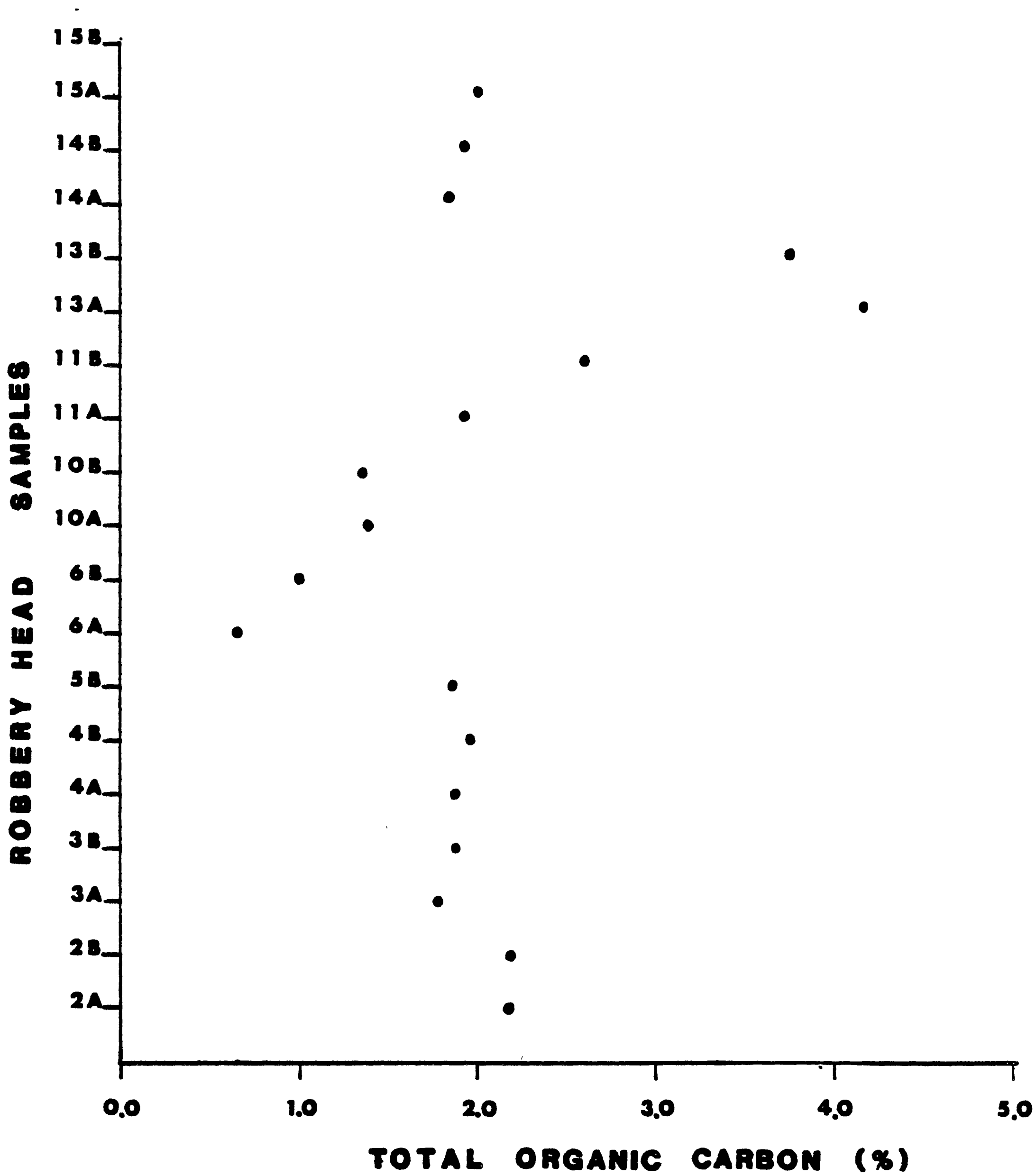


Figure 60. Robbery Head Plot of Total Organic Carbon in the Basinal Deposits

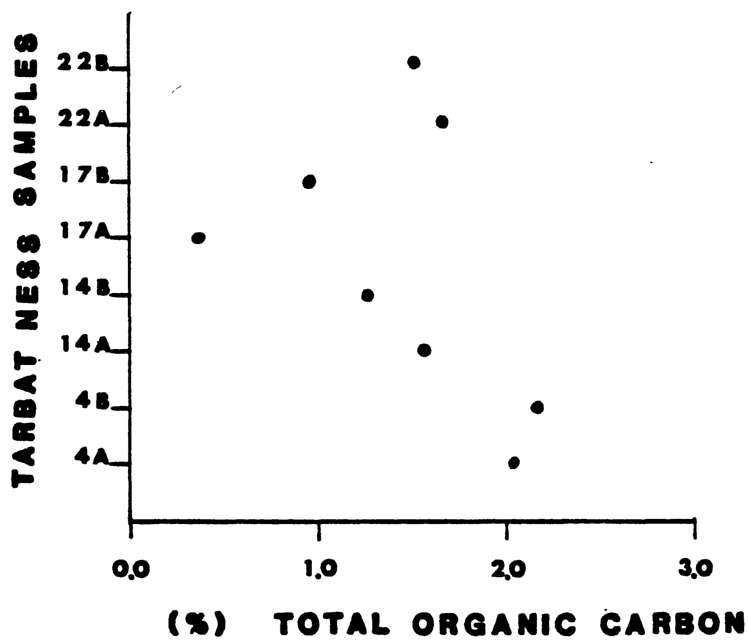
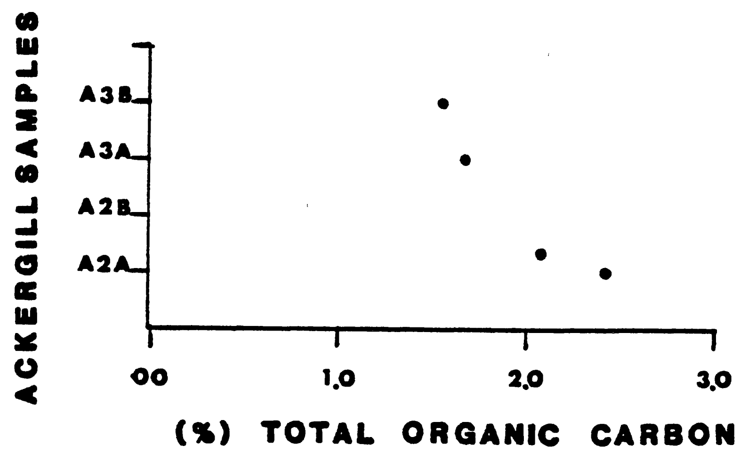


Figure 61. Tarbat Ness Plot of Total Organic Carbon in the Marginal Deposits



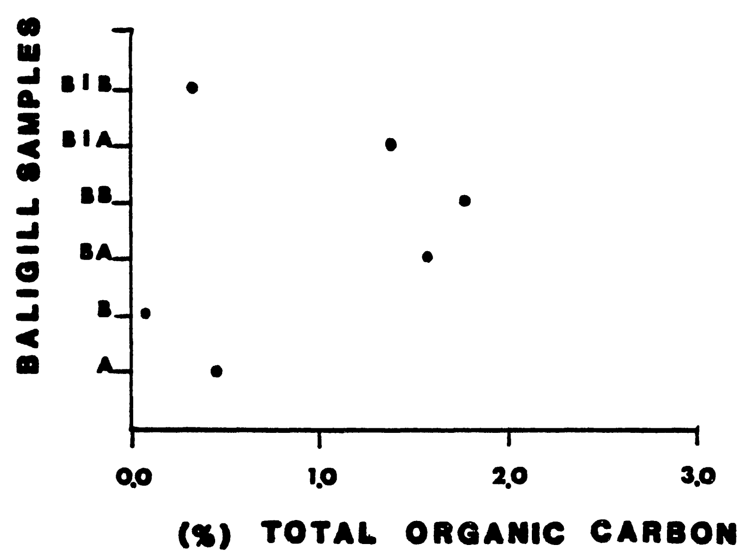


Figure 62. Baligill and Ackergill Plots of Total Organic Carbon

preserved.

The Robbery Head graph (Figure 60) illustrates an interesting correlation which may be related to seasonal variations. The lower (ROB 2-5) and the upper (ROB 14-15) remain fairly constant with percentages of TOC at approximately 1.8. This shows a constant influx of organic material into the system, suggesting its stability. The middle (ROB 6-13) samples show a variation in the percent of TOC. These samples range from 0.687 up to 4.14. The low values associated with the middle samples may due to a decrease in the amount of organic carbon entering the system, possibly indicating a warm to hot stage when algae were actively growing and reproducing. This "growth" period would restrict the amount of organic debris needed to form organic carbon. As the algae slowly died and filtered to the bottom, possibly during a cool to cold stage, this would have provided the necessary material to form organic carbon. It is now represented as varves in the basinal deposits.

A similar correlation can be observed in Tarbat Ness samples (marginal deposits). The influence and preservation of organic carbon in the marginal deposits is not as dramatic as that seen in the basinal deposits. This may inpart be due to the number of samples analysized but is probably due to the lack of organic material preserved. The hostile environment along the margins of the lake did not allow for the protection of the organic material from oxidation, wind, and or the destruction by clastic influx.

Isotope Analysis

Isotopes have been defined by Anderson and Arthur (1983) as atoms which contain nuclei made up of the same number of protons but a different number of neutrons. Oxygen (δ 18O) and Carbon (δ 13C) isotopes were used in this study. There are two standards used to report oxygen isotopic compositions, they are PDB and SMOW. The abbreviation PDB stands for belemnitella americana from the Cretaceous Pedee formation, South Carolina whereas SMOW stands for Standard Mean Ocean Water. The PDB is normally used in the analysis of sedimentary carbonates (as it is in this study). PDB is also the most accepted standard for reporting carbon isotopes. A brief introduction to freshwater carbonates will be included within this study, then an analysis of the Orcadian Basin isotope values will follow.

Freshwater Carbonates

Freshwater carbonate rocks show a wide variation in the ranges of carbon and oxygen isotope compositions (Figure 63). This is generally because freshwater is isotopically lighter than marine water (Hoefs, 1973). In some carbonates, the formation of the rock is related to

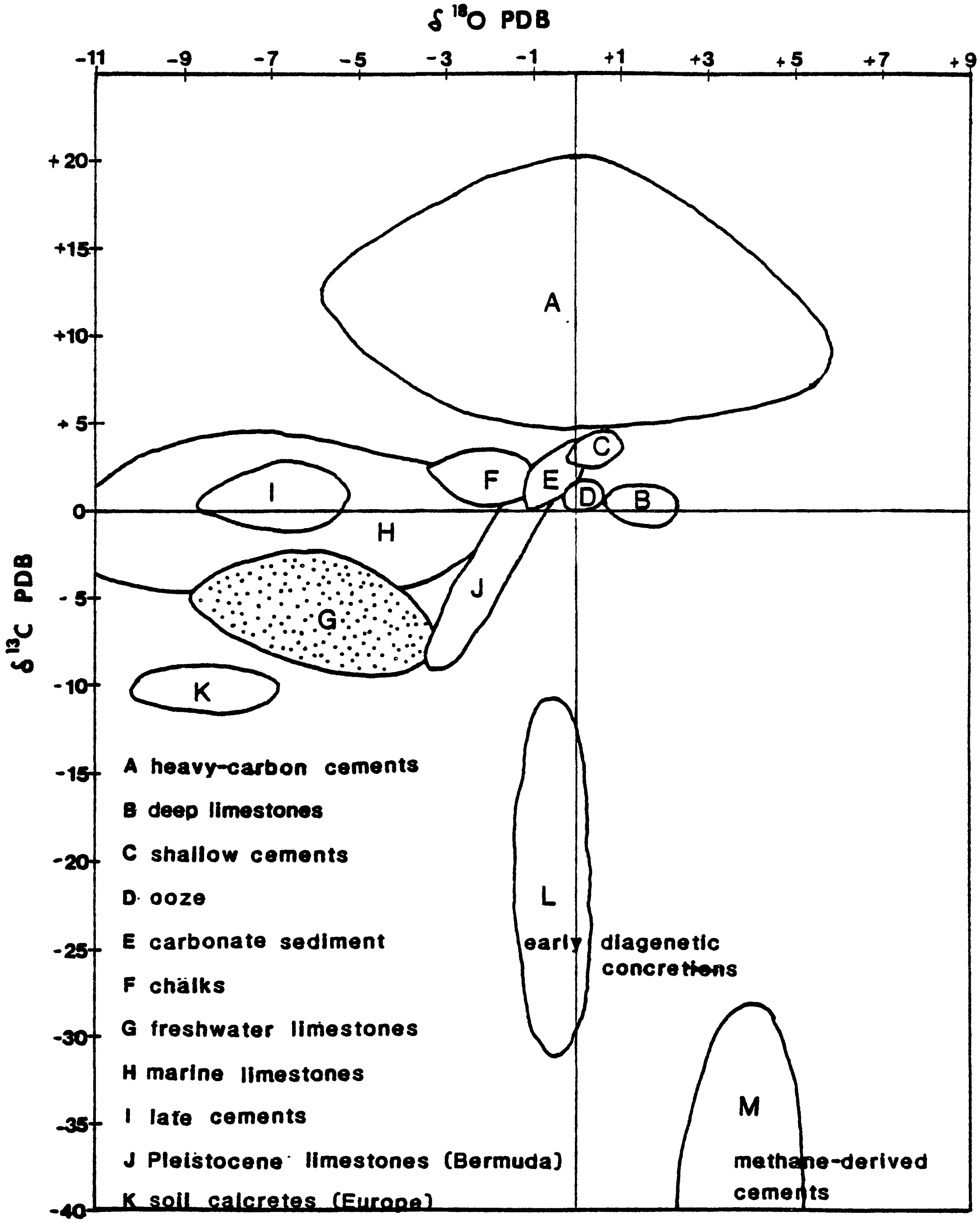


Figure 63. Range of Freshwater Carbonate Variations in Carbon and Oxygen Isotopes (After Hudson, 1977a)

Orcadian Basin Isotope Values

the CO_2 produced during oxidation of the organic matter (Figure 64).

Formation of tufas and freshwater limestones are formed as a result of a number of complex processes. The most important process involves the following reaction:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

Hudson (1977a) has summarized the importance of this process. In this reaction, one carbon atom is donated by the parent carbonate and one is supplied by the CO_2. This results in a precipitated bicarbonate solution which is moderately depleted in C13. A positive delta (δ) value delineates enrichment in the heavy isotope, whereas it is the opposite for a negative delta (δ) value. Hudson (1977a) has estimated the depletion to be approximately -12. If bicarbonate solutions of this type react with atmospheric CO_2 or organically derived CO_2, this will increase the C13 values above -12. C13 values increase with imput of atmospheric CO_2 because δC13 (-7) is in equilibrium with HCO_3^- which has a δC13 ranging from +1 to +2 at 20° C (Emrich et. al., 1970). Because of the variable influence by atmospheric CO_2 and or organically derived CO_2, freshwater limestones and tufas commonly display a wide range (-12 to +3) of C13 values (Keith and Weber, 1964).

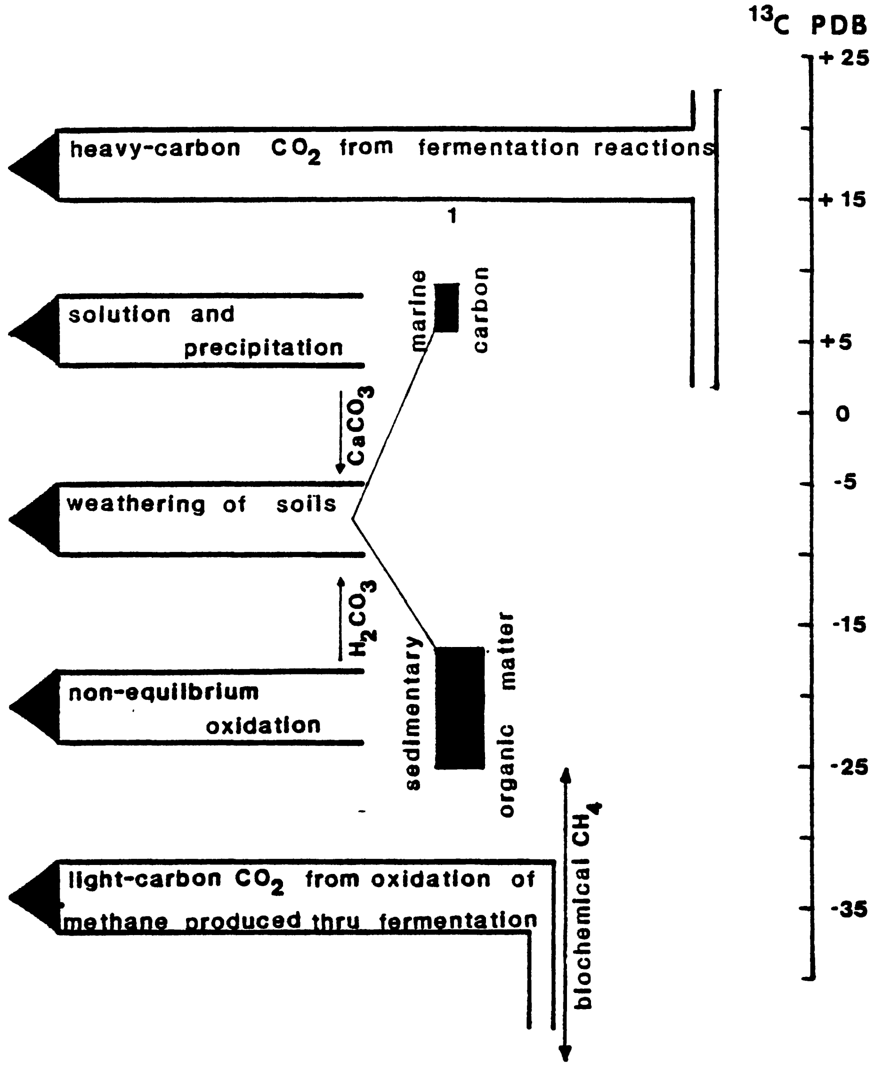


Figure 64. Oxidation of Organic Matter and Sedimentary Organic Matter (After Hudson, 1977a)

Twenty-eight samples from the Orcadian Basin were analysized isotopically using C13 and O18 parameters. These samples fall into five carbonate facies (Figure 65). The facies include basin margin deposits, laminites (basinal), dolostones, nodular limestones, and marlstones. The range of the five facies are variable. The basin margin deposits range from values of approximately -12 to -4 δ18O and -1 to -7 δ13C (Figure 66). The laminites range in value from -11 to -3 δ18O and -3 to +2 δ13C (Figure 67). The dolostones range from -4 to -7 δ18O and -7 to +4 δ13C (Figure 68). The nodular limestones are located between -8 to -4 δ18O and -1 to -4δ13C (Figure 69). The marl facies ranges from -11 to -5 18O and -7 to -3 δ13C (Figure 70).

All of these values plot within the freshwater limestones parameter (Figure 63). These deposits are not believed to be of marine origin because of the isotopic ranges of the rocks analysized. The conclusion drawn from this analysis is basically that the total iostopic range for freshwater carbonates is very large. This large spectrum reflects a variety of conditions found in lakes.

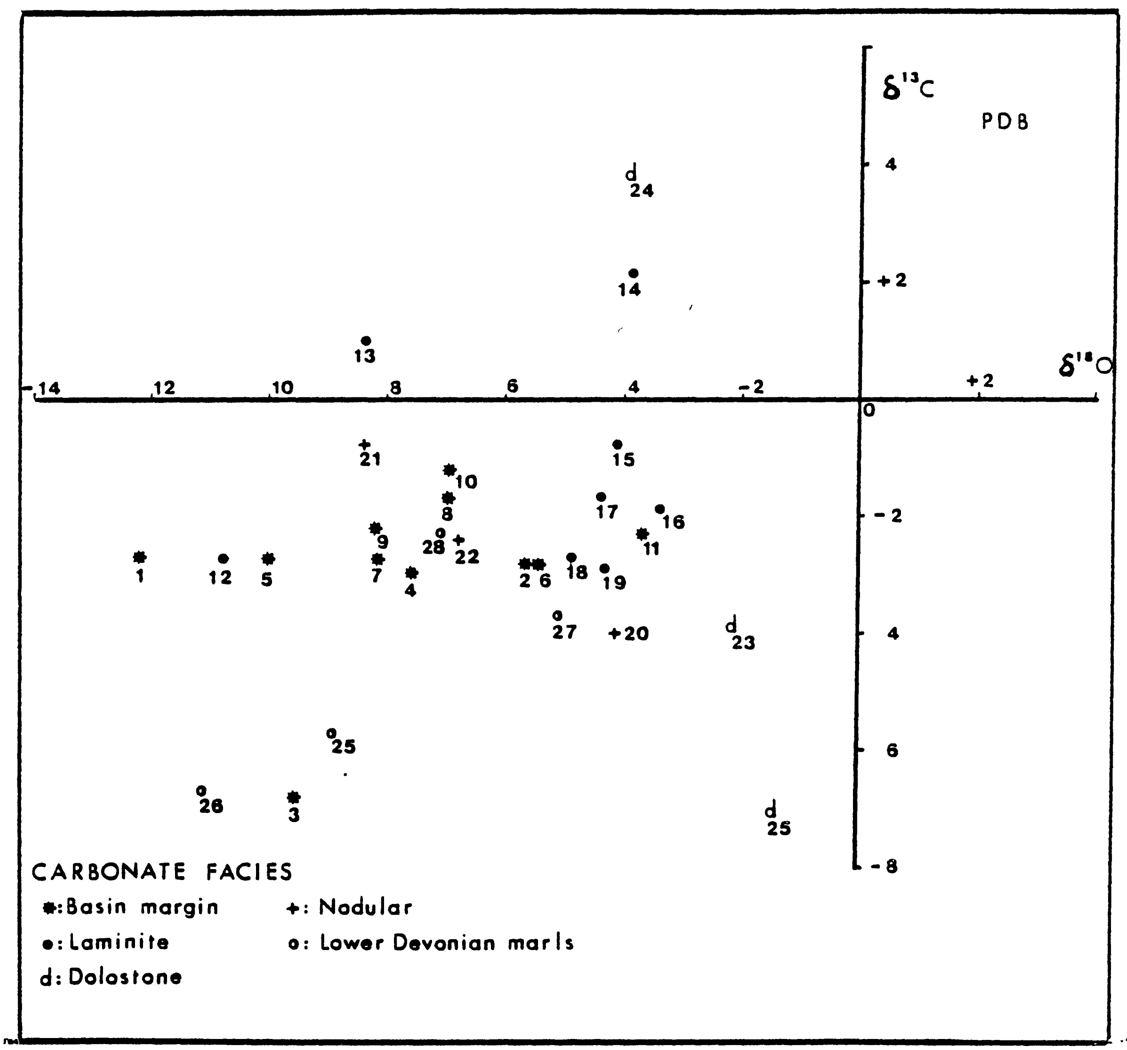


Figure 65. Carbon and Oxygen Isotope Plots of the Orcadian Basin Deposits.

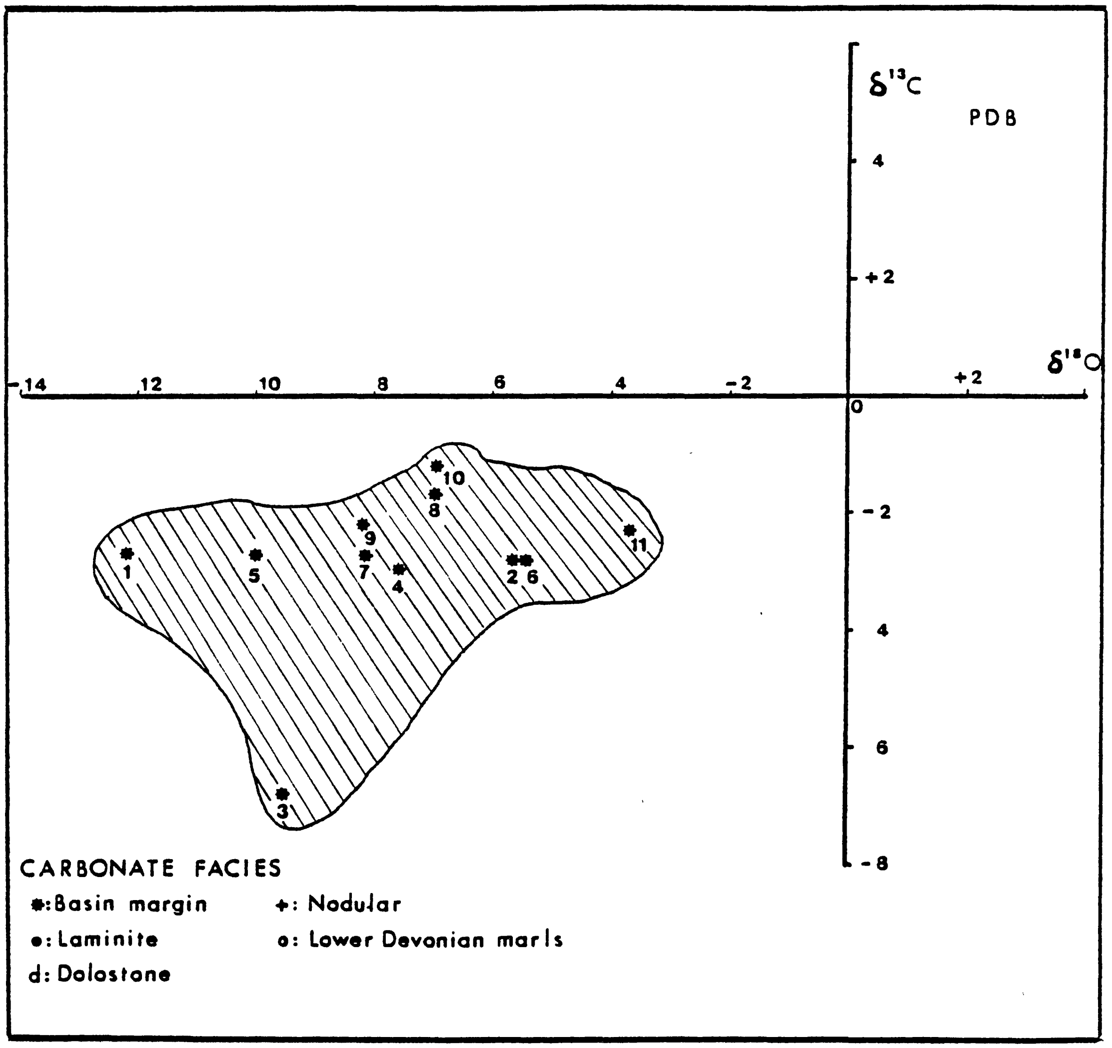


Figure 66. Carbon and Oxygen Isotope Plots of the Basin Margin Deposits

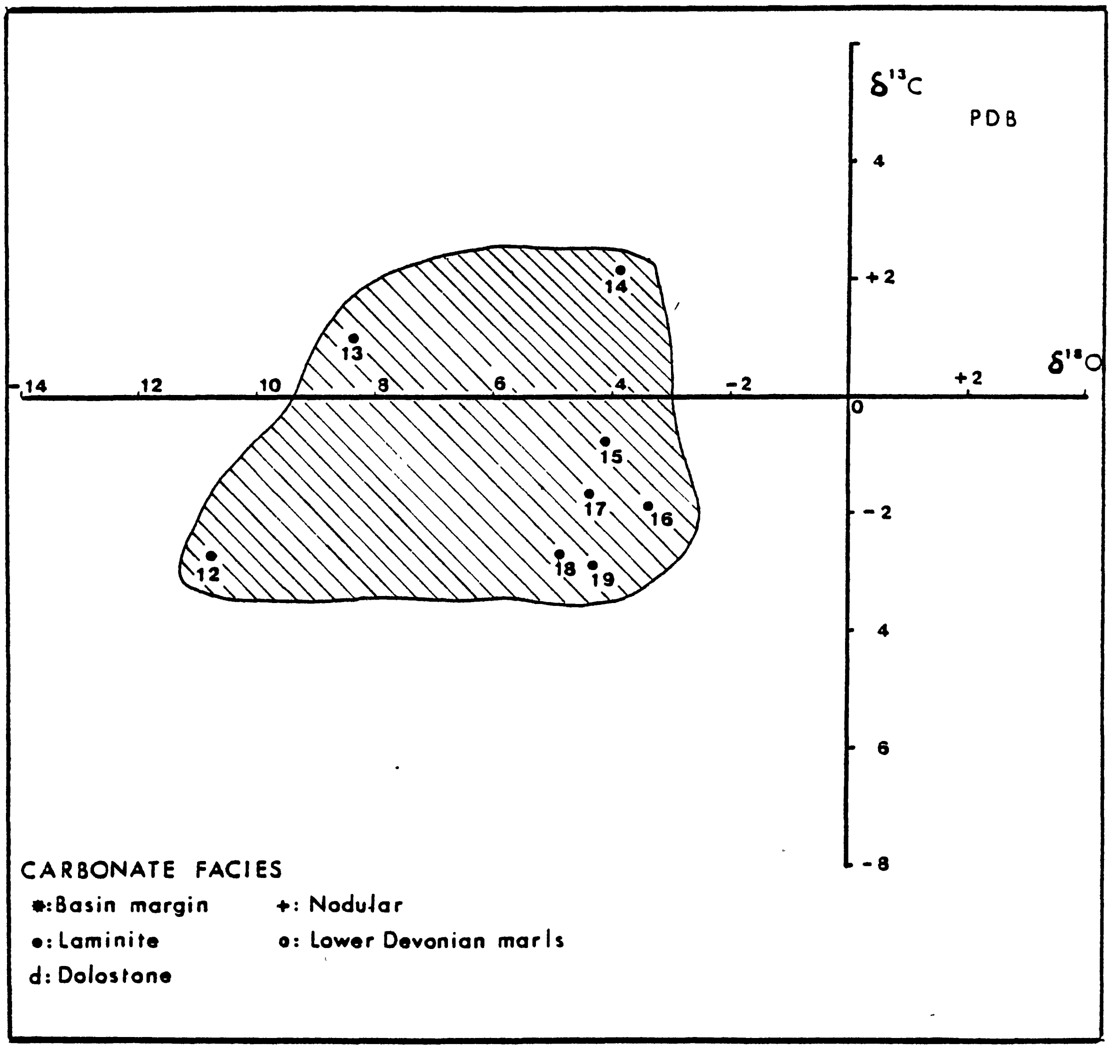


Figure 67. Carbon and Oxygen Isotope Plots of Orcadian Basin Laminites

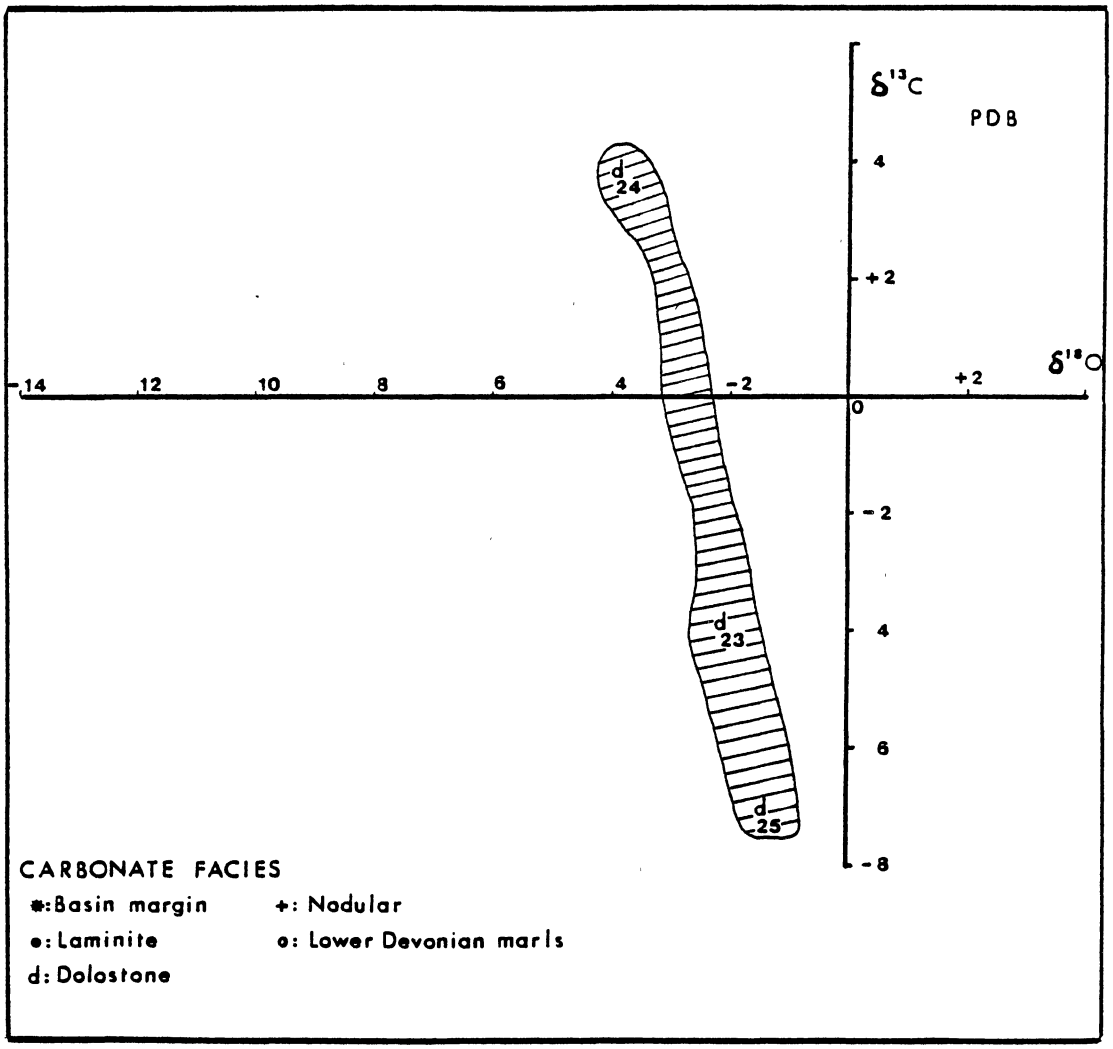


Figure 68. Carbon and Oxygen Isotope Plots of Dolostones

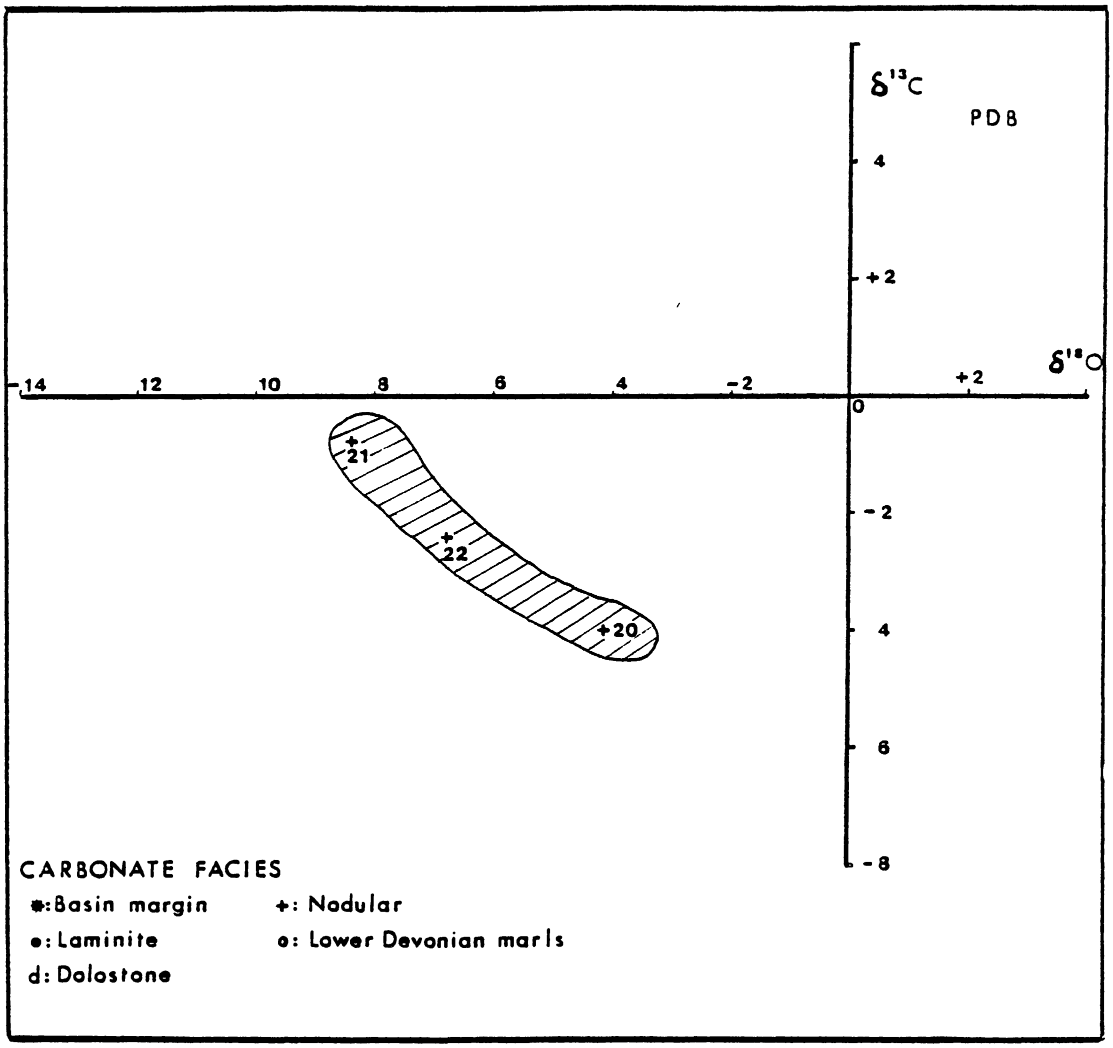


Figure 69. Carbon and Oxygen Isotope Plots of the Nodular Limestones

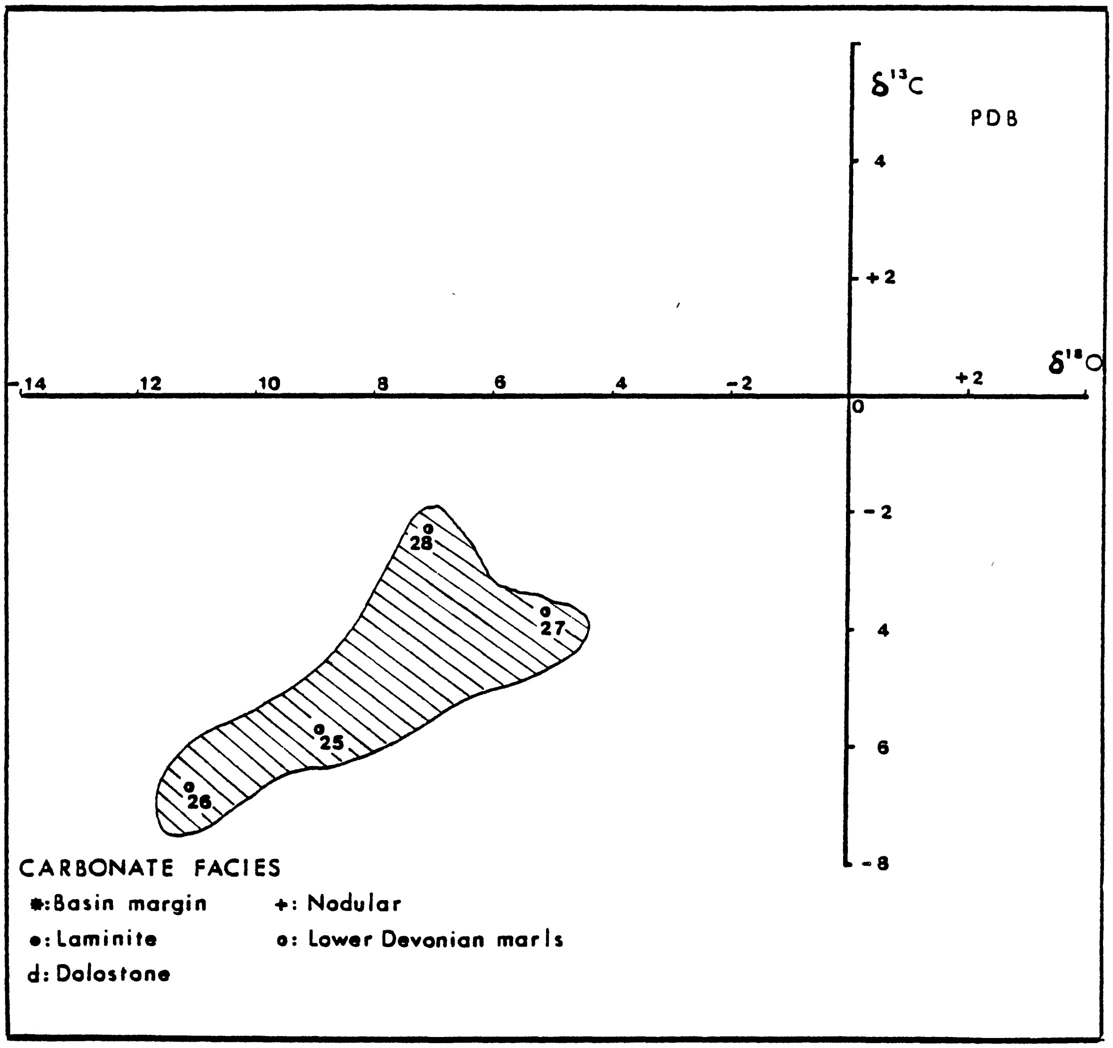


Figure 70. Carbon and Oxygen Isotope Plots of the Marlstones of the Devonian Orcadian Basin

CHAPTER VIII

DEPOSITIONAL ENVIRONMENTS

A Lacustrine Setting

The Orcadian Basin of Northern Scotland has been well documented as a lacustrine setting (Conybeare and Phillips, 1822; Murchinson,1859; Crampton and Carruthers, 1914; Donovan, 1975; Westoll, 1977; and Mykura, 1984). The combined results of petrologic analysis, isotopic analysis, and x-ray diffractometry have illustrated the variable conditions within this basin. Several separate but related depositional environments occur within the lake facies of the Orcadian Basin. This chapter will illustrate the variability and controls on the formation of the lake within the Orcadian Basin.

Lake Facies Variation

Environments within the lake of the Orcadian Basin range from deepwater facies to evaporitic facies. The characteristics of each of the facies will be described separately, but it must be noted that they are all related and control the formation of the lake recorded in The Orcadian Basin.

Early Stages of Lake Development

During the early stages of the Middle Devonian period, the Orcadian Basin was inundated by streams and rivers which erroded pathways across the basin. As the rivers and streams extended their banks, small floodplains developed. Small lakes were then formed through this process. As the lake level gradually rose during transgression, inflowing rivers alluviated their pathways, resulting in a decrease of sediment movement across the lake. As transgression continued, reworking and sorting of sediment by wind-generated processes produced symmetrical ripple marks. The lake underwent minor seasonal fluctuations in water level. The fluctuating water level resulted in subaerial desiccation of the lacustrine flats (Donovan, 1984). Stromatolites formed around the shallow lake margins. Since stromatolites are found in a variety of environments, they cannot be by themselves an indicator of water depth. Fannin (1969) noted though, that the combination of stromatolites and desiccation features suggests periods of fluctuating water levels.

As the transgression resumed and the lake level increased, the water cover became more stable. During this stage, subaqueous cracks (syneresis) developed due to the annual salinity rises caused by the "dry season" (summer?) (Donovan, 1984). These cracks were later infilled by coarse silt and sand during the "wet season" (winter?) period.

During the shallow stages of the lake, bottommuds and clastic debris underwent frequent stirring. The constant reworking of the sediment prohibited the deposition and formation of delicate laminations. Laminae found along the margins and in the shallower water facies are therefore incomplete and disrupted.

Deep Water Lake Development

The controls on the deep water facies are as follows:

1. Thermal Stratification
2. Water Depth
3. Ionic Concentration of the Lake Water
4. Presence or Absence of Saline Minerals
5. Climate of the Basin
6. Transgressive/Regressive Stages

Thermal stratification in lacustrine environments is a widespread phenomena. Thermal stratification in lakes begins shortly after spring when the cold water of the lake begins to warm. The combined influence of the surface heating of the water and the mixing from the wind produces a shallow layer of warm isothermal water. Below this layer, the thermocline develops as a result of the increase in the hydrostatic stability. The thermocline is the divider between the warm oxygenated layer termed the epilimnion and the cooler anoxic layer termed the hypolimnion. During the summer and early fall, the waters of the epilimnion consolidate and develop a uniform thermocline. As the climate cools off, the lake water cools and develops a layer of cool dense water at the surface. The layer of cooler water eventually sinks and combines with the warmer waters of the epilimnion. This process continues until the water temperature of the epilimnion is the same as the hypolimnion. Oxidation of the anoxic hypolimnion occurs through wind mixing and eventually forms an isothermally stratified lake.

When thermal stratification is well developed, algal blooms occur along the surface. The formation of the algal blooms leads to an increase in pH and a decrease in the amount of dissolved CO2 taken from the lake by the algae during photosynthesis. When both of these conditions are employed, the result is the preciptation of low-Mg calcite. As the algae die and sink to the bottom of the lake, their remains are left as organic material which form the organic carbon-rich layers along the bottom of the lake.

Rayner (1963) suggested that the formation of the "nonglacial" varves seen in the Orcadian Basin are due to three processes. The processes involved are summarized below:

1. Seasonal algal bloom which results in an increase in photosynthesis, a rise in the

pH of the water and the subsequent precipitation of carbonate

2. Algal decay and accumulation of material as organic matter on the lake bottom

3. The continuous or periodic accumulation of clastic debris from windblown sources.

The Orcadian Basin lake may have been a well stratified lake as indicated by the presence of fossil fish in an undisturbed state and by the lamination of the bottom sediments (Donovan, 1975). Nonglacial varves of this type are believed by Bradley (1973) to form only in "the quiet hypolimnion of lakes whose waters are, for one reason or another, permantly stratified."

The preservation of organic matter in the varved sediments of the basin requires a low-Eh environment (Figure 71). This will prevent the total oxidation of organic compounds to $CO2$ and $H2O$. Blatt et al. (1980) has defined the meaning of a low Eh to mean that the rate of the influx of organic matter to the area of deposition must be more than the quanity of oxygen available to oxidize it. During high water periods the Orcadian Basin was able to maintain quiet water conditions which enabled the preservation of organic matter now represented as varved sequences within the lake.

The amount of organic carbon produced and deposited within the lake is dependent upon where in the lake

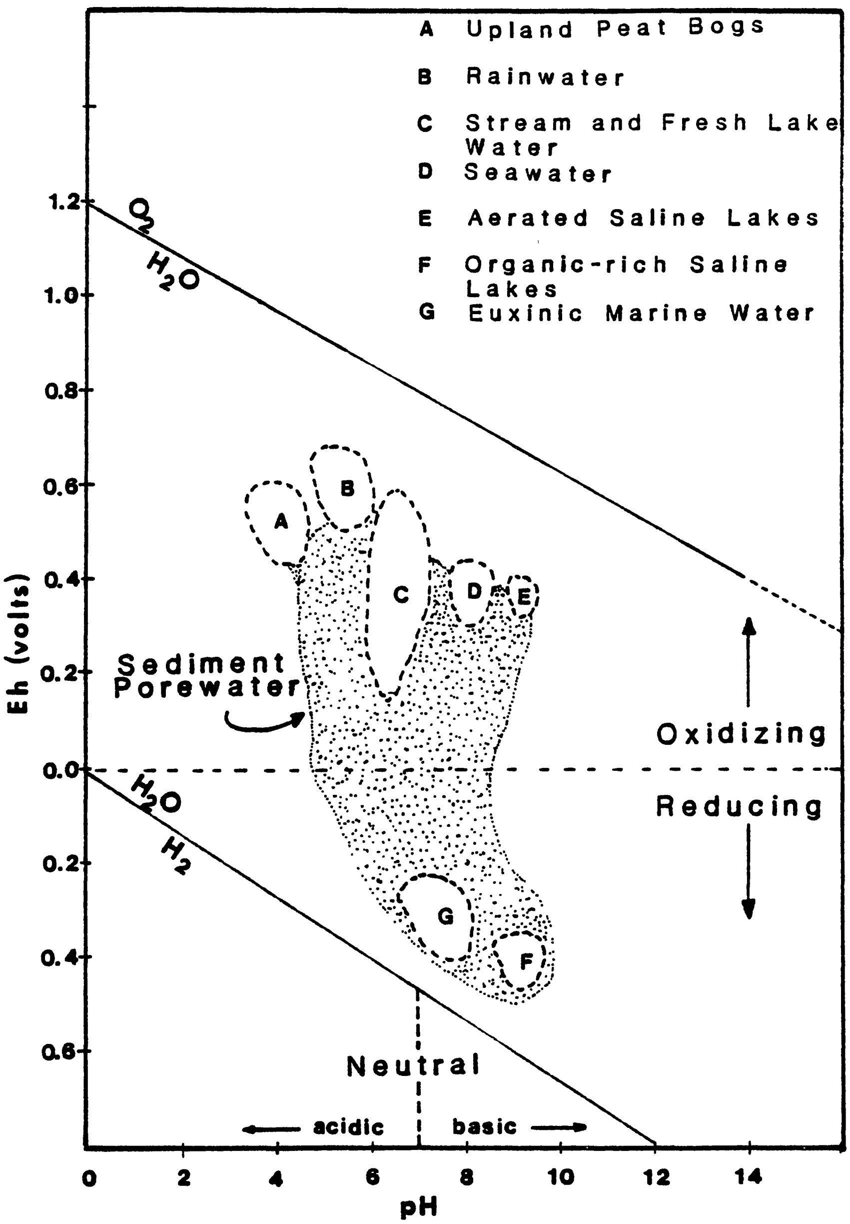


Figure 71. Eh-pH Diagram Illustrating Some of the Fields of Naturally Occurring Waters and Environments (After Baas-Becking et al., 1960)

deposition took place. In unstratified areas along the margins, most of the carbon would have been oxidized. Deeper waters in the center of the lake could have resulted in the thermocline acting as an organic fence which preserved the organic matter in the hypolimnion. The hypolimnion probably cooled the surface waters of the epilimnion and resulted in minor algal activity. The marginal areas which were warmer promoted the increase in algal growth which resulted in increases in the photosynthetic activity which ensued high pH values. These processes are directly associated with the amount of carbonate produced. The marginal facies have more carbonate and little organic carbon; whereas the basinal facies are richer in organic carbon. The disruptive and noncontinuous texture of the marginal laminae is due in part to the incomplete development of clastic laminae and to the disruption of birdseye structures (Donovan, 1975). The origin of the birdseye structures within the Orcadian Basin probably resulted from the decay of algae which produced gas bubbles or shrinkage during desiccation.

Transgressive/Regressive Stages

During transgressive stages within the lake basin, the lake margin occasionally coincided with the basin sequences. Figure 72 illustrates a sedimentation model for the effects of contraction and expansion on the lake basin. The time involved in a complete transgressive-

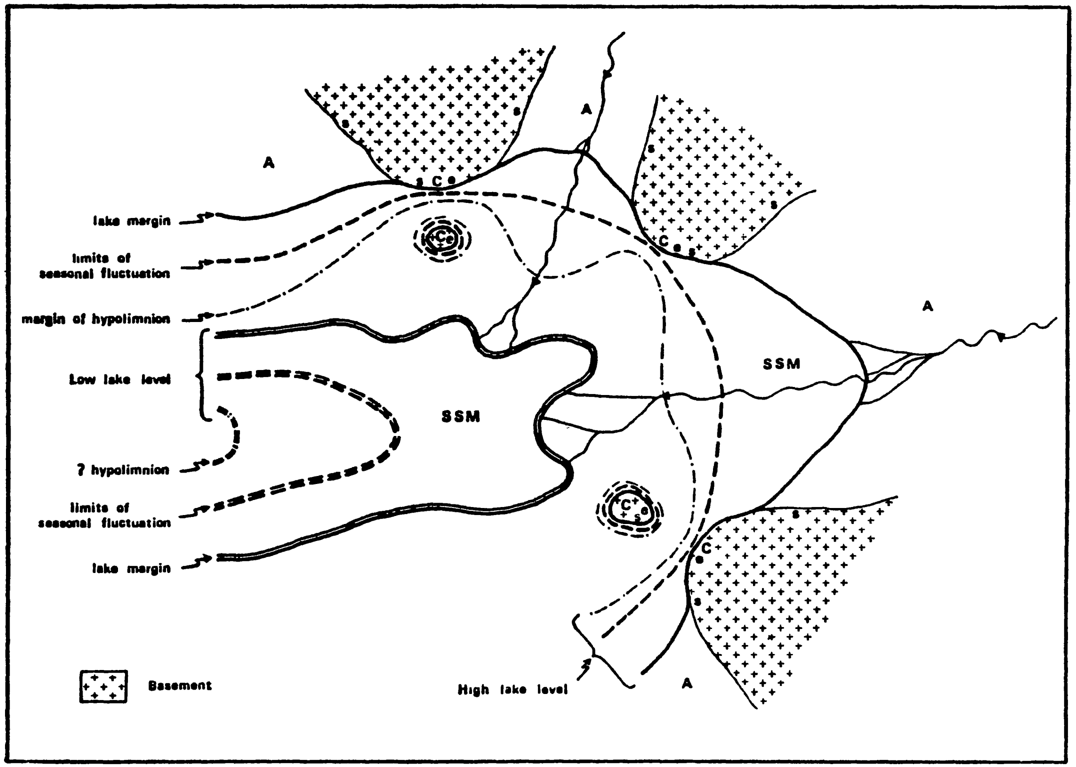


Figure 72. Sedimentation Model for the Expansion and Contraction of the Lake in the Orcadian Basin (From Donovan, 1975)

and the marginal topography was drowned. "Non-coincident" margins formed during low lake periods which resulted in exposure of the lake sediments. Subaerial exposure produced clastic-dominated margins and subaerially cracked sequences. Figure 72 illustrates a sedimentation model for the effects of contraction and expansion on the lake basin. The time involved in a complete transgressive-regressive sequence cannot be estimated accurately. Overall sedimentation rates within the basin are unstable and diastems tend to be absolute in base level cycles within enclosed basins (Donovan, 1980).

Similar transgressive-regressive cycles have been recognized in other ancient lake basins. These include the Eocene Green River Formation of Utah and Wyoming (Bradley, 1929; Picard and High, 1972) and the Triassic Lockatong Formation of New Jersey (Van Houten, 1964).

Fish Habitats and Distributions

Donovan (1980), has done a complete analysis of the fish populations and ecology of the lake found in the Orcadian Basin. A brief summary of this analysis will be included within this study. Fossil fish within this basin provide a useful stratigraphic zonation. Fish fauna within this basin comprise a variety of populations. Fish were subjected to a variety of environmental conditions including seasonal variations which resulted in annual fluctuations in temperature, oxygen-content, pH, food supply, salinity, availability of mineral nutrients as well as predation from other fish.

Westoll (1958) considered the effects of long term changes in transgressive-regressive cycles on fish populations. These cycles were thought to have possibily exerted a powerful influence on the fish faunas and conditions they had become adapted to. Donovan (1980) has elaborated upon this theme and has presented a population control model (Figure 73). Case 4 in the model represents the effects of hot, dry periods in the lake. During this stage, the water evaporated and became unable to support any fish fauna because of either excessive salinity or complete desiccation of the lake. More moderate regression (case 3) could have severly altered the environment and also reduced the fish population but may not have lead to mass extinction. Fish faunas in shallow waters would have been subjected to increased temperatures and muddy, unsettled water due to wind action along the shallow lake surfaces. Fish faunas are more susceptible to asphyxication in shallow lakes than in deeper water lakes. During periods of regression, if the conditions were not totally hostile to life, surviving fish could have developed and expanded during subsequent increases in water level. During transgressions, the lake may have expanded (case 1 or case 2) and filled (case 2) or overfilled the basin (case 1). In case 1, a faunal exchange or replenishment from a neighboring population

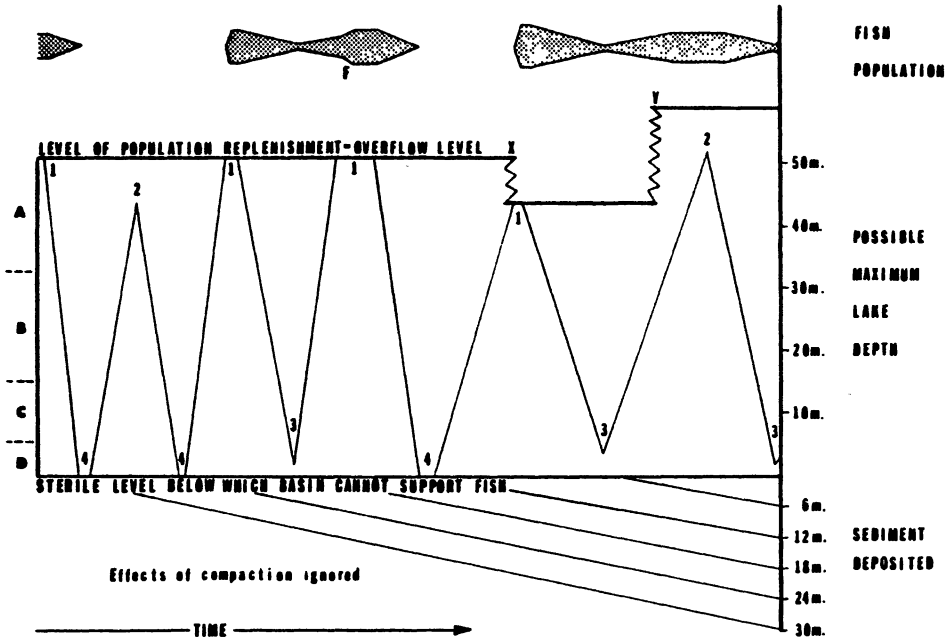


Figure 73. Population Control Model for Fish Faunas and Transgressive/Regressive Cycles (From Donovan, 1980)

could have occurred due to the overflow ofthe lake basin.

The last control on the population control model involves adjustments to the overflow level. These adjustments could have resulted from faulting and flexturing (isostatic variations) due to resulting sediment load (Walcott, 1970). or by isostatic adjustments resulting from the weight of the water in the lake. Crittendon (1963) discussed this phenomena in Lake Bonneville, by where the lake basin underwent "capture" by river piracy and or by blocking of overflow by lava flows which cutoff inflowing water.

The best developed "fish bed" in the Orcadian Basin is the Achanarras "limestone" in Caithness. This bed can also be correlated to zones in Shetland, Orkney, and around Moray Firth (Mykura, 1976; Donovan et al., 1974; Trewin, 1976; Wilson et al.,1935). The number of different species found at Achanarras attests to the incoming of new species which were not previuosly found in the basin. The invaison of the new and different fish faunas coincided with a major transgression and expansion of the lake. While some of the species and populations underwent extinction, others may have evolved through modifications in the environment. The alteration in characteristics of the fish fauna may have resulted in the migration of "new" fish species into adjacent basins during overflow periods. Therefore the evolution of fish in the Orcadian Basin was the result of periodic exchange of locally-induced features between adjacent ecosystems (Donovan, 1980).

Evaporitic Environments

At one point in the history of the Orcadian Lake, the lake level was reduced so drastically that a saline environment developed within the basin. Three conditions are necessary for the formation of an inland sabhka or playa (Eugster and Hardie, 1978). They are as follows:

1. outflow of water must be restricted (closed basin)
2. evaporation must exceed inflow
3. inflow must be in sufficent quanities as to maintain a standing body of water

All of these conditions appear to have occurred simulutanously within the Orcadian Lake.

Because of the selective removal of ions, mineral precipitation will dramatically influence the composition of inflowing waters into a closed basin. Eugster and Hardie (1978) have defined four main processes which can lead to supersaturation and consequent precipitation. They are as follows:

1. evaporative concentration
2. loss of gas such as CO_2
3. mixing of waters
4. temperature changes

Evaporitic minerals are common in ancient lake environments (Lake Lockatong, Triassic, New Jersey; Gosuite Lake, Eocene, Wyoming and Colorado; Searles Lake, Quaternary, California; and Green River Basin, Eocene, Wyoming and Utah). The best known ancient sequence and variety of evaporitic minerals is located in the Eocene Green River Formation in Utah and Wyoming (Bradley and Eugster, 1969; Eugster and Hardie, 1975; Surdam and Stanley, 1979; and Smoot, 1983).

One type of evaporitic mineral precipitated in the Orcadian Lake has a morphology similar to Gypsum. The crystals are 6-sided prismatic. The gypsum pseudomorphs (as they are referred to in Chapter V) have now infilled with calcite. The formation of gysum results from saturation of waters rich in carbonate and sulphate ions. Dolomitization is commonly associated with the precipitation of gypsum (Tucker, 1981). Further gypsum precipitation is induced as a result of the high Mg/Ca ratio. This high ratio releases calcium carbonate for continued gypsum precipitation. The crystals of gypsum occur within the deep-water laminations. Therefore they indicate the shallowing of the lake followed by the subsequent saturation of the waters by saline ions which resulted in the precipitation of gypsum.

Conclusion

As mentioned in the previous sections, the Orcadian Lake underwent a variety of seasonal, physical, and chemical changes. All of these changes and variations acted as processes which were responsible for the formation of numerous depositional environments found within the lake basin.

CHAPTER IX

CONCLUSION AND SUMMARY

The purpose of this thesis is to describe the environmental reconstruction of a Devonian Lake Basin in Northern Scotland. The interpretation was based on the use of geochemical data (isotope data, x-ray diffraction, and total organic carbon) and a petrographic analysis.

Two distinct depositional facies were contained within the Orcadian Basin of Northern Scotland. The first major facies within the Devonian lake was termed the marginal deposit. These deposits contained thinly laminated clastic and organic "non-glacial" varves or laminations, tufa deposits, and phosphate nodules. The marginal deposits were dominantly controlled by clastic influx which destroyed most of the laminations along the edges of the lake basin. The dominant minerals present in these sediments are quartz, calcite, dolomite, muscovite, hematite, and organic material. Minor constituents include tourmaline, pyrite and biotite.

The second depositional facies within the lake basin was termed the basinal deposits. These deposits were composed of varves, pseudomorphs, and a variety of minerals. The major mineral constituents within these deposits are quartz, calcite, dolomite, organic material, hematite, phosphate, illite, and muscovite. The minor mineral constituents are hydrocarbons, aegirine, tourmaline, biotite, and chlorite.

A goechemical analysis of the deposits included x-ray diffraction, total organic carbon, and isotope (180 and 13C) analyses. X-ray diffraction was run on the samples to delineate the major mineral constituents within the marginal versus the basinal deposits. The samples were plotted on graphs with axes of sample number and minerals. The basinal samples showed a grater variation in mineral types than the marginal samples. This was due in part to the larger amount of clay and carbonaceous material found within the basinal deposits. The difference in chemical conditions of the deeper water of the basinal deposits also resulted in a wider variation in mineral constituents.

Percent of total organic carbon was calculated for both marginal and basinal samples. The basinal deposits contained higher percentages of total organic carbon than did the marginal deposits. This is thought to have been a result of larger amounts of algal and phytoplanktonic material within the deeper sections of the lake.

The marginal and basinal deposits were analyzed using 180 and 13C isotope parameters. The isotope analysis was run to determine the origin of the deposits (marine or Lacustrine). Five carbonate facies were recognized within the rocks of the Orcadian Basin. These include basin margin deposits, laminites, dolostones, nodular limestones, and marlstones. The values attained for the deposits show a wide variation in the ranges of carbon and oxygen isotope compositions. This is generally due to frashwater being isotopically lighter than marine water. All the rock values analyzed plot within the Hudson (1977a) freshwater limestone parameter. The large spectrum of values in the deposits, reflects a wide variety of conditions under which the Orcadian lake formed.

The presence of phosphate within the Orcadian Lake deposits is problematic. Phosphate occurred in both the marginal and basinal sections. Most of the phosphate was associated with varved (laminated) sections, but some phosphate also occurred as fish fragments, coprolites, nodules, and as pebbles. The dominant phosphate mineral observed in the section was apatite. The phosphate is believed to have been derived from the decay and leaching of phosphate from algae and phytoplankton along the bottom of the lake during long periods of stagnation. Precipitation of the phosphate is believed to have been primarily a result of a calcium-saline-anoxic hypolimnion which inhibited the amount of Ca^{+2} ions entering the system. Over long periods of time, enough Ca+2 ions entered the phosphatic rich muds which resulted in the formation of carbonate apatite.

The marginal and basinal deposits compose the lake which formed within the Orcadian Basin. Within these two major facies are a variety of smaller subfacies. The subfacies were controlled by the depth and amount of water within the basin at any one time.

Environments within the lake of the Orcadian Basin range from deepwater facies to evaporitic facies. When the lake was full of water, or the lake level increased during transgression; the lake probably flourished with algae and fish fauna. This resulted in the formation of varved sequences through the deposition of organic material during the cooler seasons.

During low lake levels or regression, the influence of algae dramatically decreased due to the saline conditions of the lake. During the saline enrichment of the lake, evaporitic minerals were precipitated along the previously deposited sediments. During at least one point in time the lake underwent complete desiccation and produced subaerial cracks.

In conclusion, the deposits which formed in Northern Scotland around the area of Caithness are interpreted as a lake environment which contained numerous subfacies.

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APPENDIX A

MEASURED SECTIONS

Sample Number: Date:

Formation: Age:

Location: Classification:

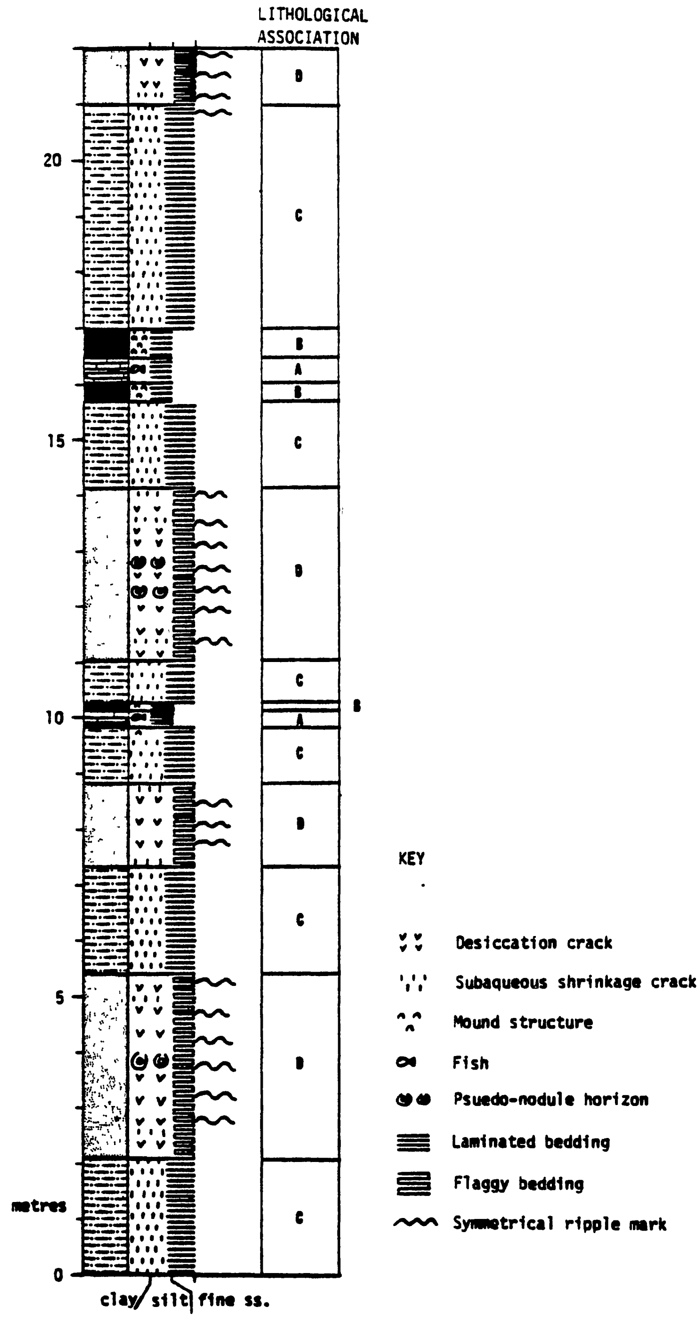
Description

Detrital Constituents	%	Size	Remarks
Quartz Monocrystalline			
Polycrystalline			
Feldspar a. plagioclase			
b. microcline			
c.			
Other Grains a.			
b.			
c.			
Carbonate Constituents			
a.			
b.			
Diagenetic Constituents Cement a. quartz			
b. calcite			
c. dolomite			
d. phosphate			
e. other			
Authigenic Clays			
a.			
b.			

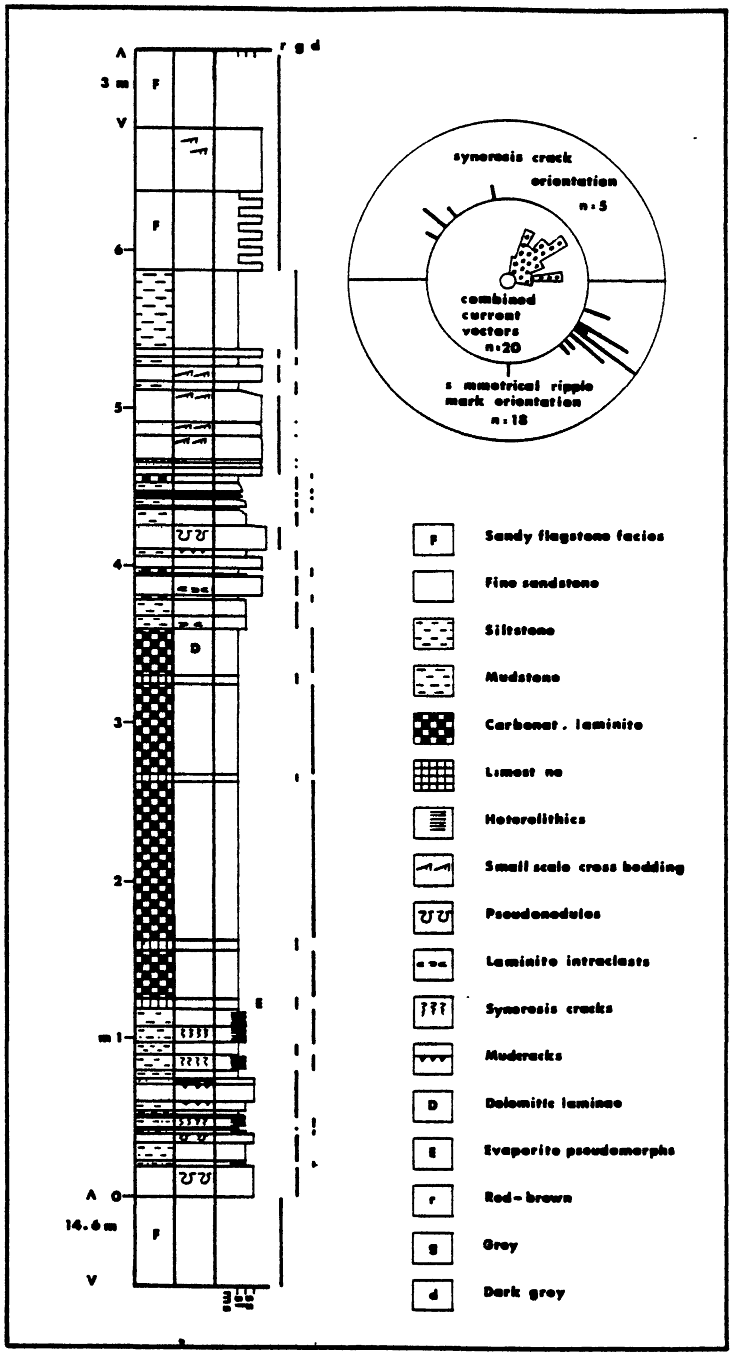
Texture

a. varves per quad
b. size of laminae
c. composition of varves
d. size of couplet

Remarks



LITHOLOGICAL ASSOCIATION
20
15
10
5
0
metres
clay/ silt fine ss.
KEY
Desiccation crack
Subaqueous shrinkage crack
Mound structure
Fish
Psuedo-nodule horizon
Laminated bedding
Flaggy bedding
Symmetrical ripple mark



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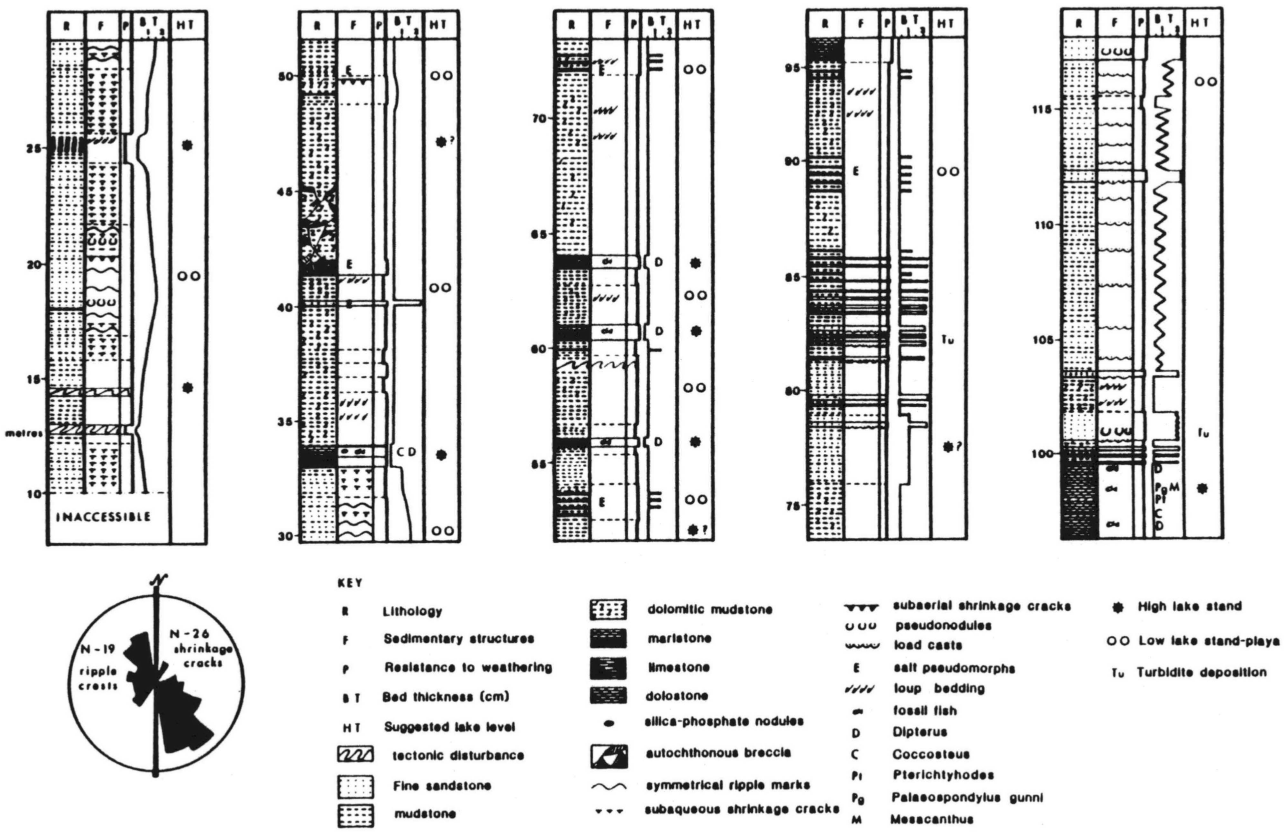
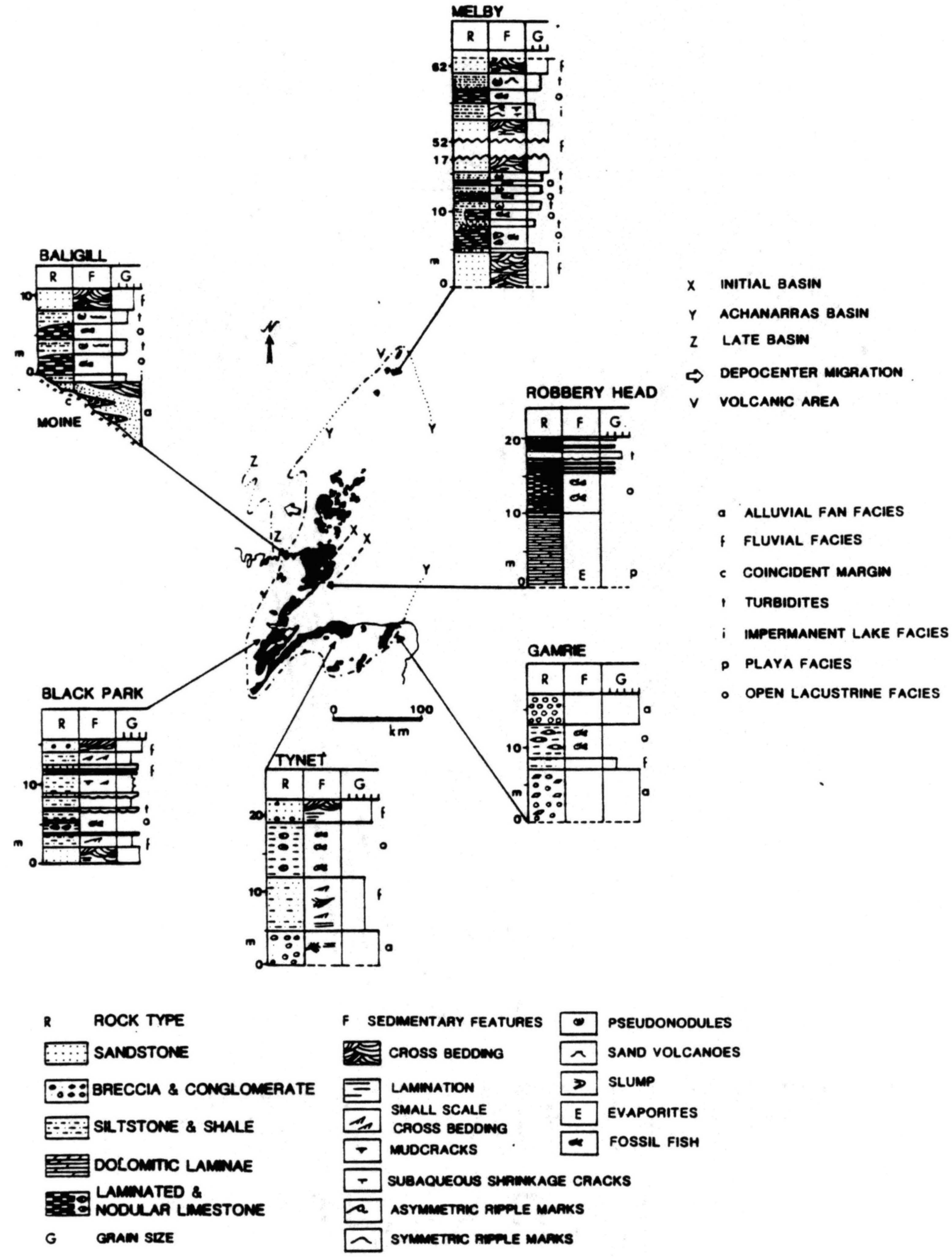
3 m
V
F
F
6
5
4
3
2
1
m
D
E
A 0
14.6 m
F
V
synaeresis crack
orientation
n: 5
combined
current
vectors
n: 20
s mmetrical ripple
mark orientation
n: 18
Sandy flagstone facies
Fine sandstone
Siltstone
Mudstone
Carbonat. laminite
Limest ne
Heterolithics
Small scale cross bedding
Pseudonodules
Laminite intraclasts
Synaeresis cracks
Mudcracks
Dolomitic laminae
Evaporite pseudomorphs
Red-brown
Grey
Dark grey


R
F
P
BT
HT
metres
INACCESSIBLE
N-19
ripple crests
N-26
shrinkage cracks
KEY
R Lithology
F Sedimentary structures
P Resistance to weathering
BT Bed thickness (cm)
HT Suggested lake level
tectonic disturbance
Fine sandstone
mudstone
dolomitic mudstone
marlstone
limestone
dolostone
silica-phosphate nodules
autochthonous breccia
symmetrical ripple marks
subaqueous shrinkage cracks
subaerial shrinkage cracks
pseudonodules
load casts
E salt pseudomorphs
loup bedding
fossil fish
D Dipterus
C Coccosteus
Pt Pterichtyhodes
Pg Palaeospondylus gunni
M Mesacanthus
High lake stand
OO Low lake stand-playa
Tu Turbidite deposition


MELBY
BALIGILL
MOINE
ROBBERY HEAD
BLACK PARK
TYNET
GAMRIE
R F G
km
X INITIAL BASIN
Y ACHANARRAS BASIN
Z LATE BASIN
DEPOCENTER MIGRATION
V VOLCANIC AREA
a ALLUVIAL FAN FACIES
f FLUVIAL FACIES
c COINCIDENT MARGIN
t TURBIDITES
i IMPERMANENT LAKE FACIES
p PLAYA FACIES
o OPEN LACUSTRINE FACIES
R ROCK TYPE
SANDSTONE
BRECCIA & CONGLOMERATE
SILTSTONE & SHALE
DOLOMITIC LAMINAE
LAMINATED & NODULAR LIMESTONE
G GRAIN SIZE
F SEDIMENTARY FEATURES
CROSS BEDDING
LAMINATION
SMALL SCALE CROSS BEDDING
MUDCRACKS
SUBAQUEOUS SHRINKAGE CRACKS
ASYMMETRIC RIPPLE MARKS
SYMMETRIC RIPPLE MARKS
PSEUDONODULES
SAND VOLCANOES
SLUMP
E EVAPORITES
FOSSIL FISH

APPENDIX B

X-RAY DIFFRACTION

X-RAY DIFFRACTION

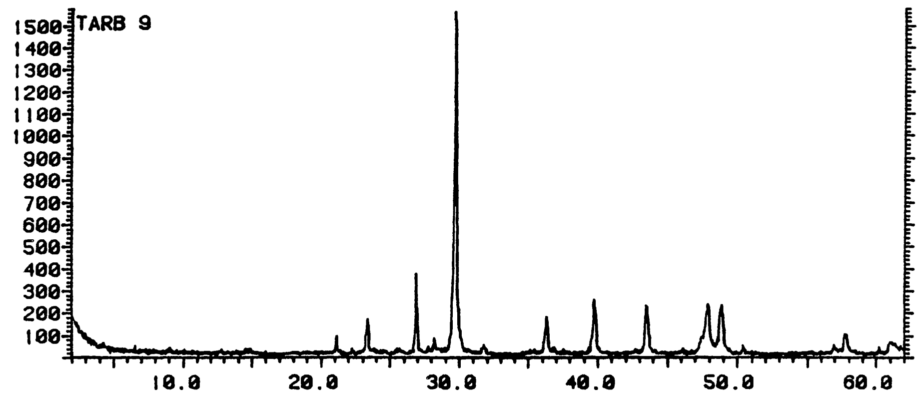
Mineral	Strongest Intensity 20
Quartz (high)	26.2
Quartz (low)	26.7
Montmorillonite	5.8
Illite	8.8
Biotite	8.8
Chlorite	6.2
Illite/Montmorillonite	3.4
Carbonate-Apatite	32.9
Carbonate-Fluorapatite	33.3
K-Feldspar	21.3
Plagioclase	22.0
Hematite	24.2
Albite	27.9
Microcline	27.5
Calcite	29.8
Dolomite	30.9
Na-Montmorillonite	7.4

X-RAY DIFFRACTION

Mineral	Relative Intensity	2θ	d-spacing
Montmorillonite	(5)	17.70	5.01
	-	5.89	15.0
	(6)	19.72	4.50
	(5)	29.57	3.02
Illite and Micas	(3)	17.77	4.99
	-	8.84	10.0
	(4)	19.86	4.47
	-	26.60	3.35
	(7)	34.91	2.57
	-	8.75 - 8.87	10.1 - 9.96
	(4)	17.73 -17.81	5.00- 4.98
Biotite	-	8.75	10.1
	(2)	17.73	5.00
	-	26.52	3.36
	(7)	33.69	2.66
	(5)	36.67	2.45
Chlorite	(7-3)	6.18 - 6.31	14.3 -14.0
	-	12.46	7.10
	-	18.80	4.72
	-	25.15	3.54
	-	31.72	2.82
Illite/Mont.		3.42	25.8
	(8)	7.12	12.4
	(4)	17.91	4.95
	(8)	19.86	4.47
	(5)	28.89	3.09
Carbonate Apatite	(10-6)	32.92- 32.07	2.72 -2.79
	(3)	25.89	3.44
	(10-8)	31.84	2.81
	(4)	39.88	2.26
	(1)	32.19 -32.92	2.78 -2.72
Carbonate Fluorapatite	(1)	33.30	2.69
	(2)	25.97	3.43
	(3)	29.28	3.05
	(10-5)	37.07	2.79
	(4)	40.25	2.24
Na-Montmorillonite	(2)	14.28	6.20
	-	7.12	12.4
	(2)	21.51	4.3
	(3)	28.79	3.10
	(2)	36.22	2.48

X-RAY DIFFRACTION

Mineral	Relative Intensity	2θ	d-spacing
K-feldspar	(6)	20.91 - 21.62	4.25 - 4.11
	(7)	21.30	4.17
	(1)	27.01	3.30
	(5)	23.59 - 23.79	3.77 - 3.74
	-	26.68 - 27.70	3.34 - 3.22
Plagioclase	-	22.05	4.03
	-	28.14 - 27.79	3.17 - 3.21
	(7)	30.61 - 30.29	2.92 - 2.95
	(5)	33.82	2.65
Hematite	(2)	24.25	3.67
	(1)	33.30	2.69
	(5)	35.77	2.51
	(2)	41.02	2.02
	(6)	54.20	1.692
Albite	(1)	27.96	3.19
	(6)	22.05	4.03
	(7)	24.31	3.66
	(6)	27.70	3.22
	(5)	28.33	3.15
Microcline	(1)	27.52	3.24
	(6)	21.05	4.22
	(2)	23.40	3.80
	(4)	27.10	3.29
	(2)	29.57	3.02
Calcite	-	29.37	3.04
	(1)	23.04	3.86
	(2)	39.34	2.29
	(2)	39.52	2.28
	(2)	43.07	2.10
Dolomite	-	30.94	2.89
	(1)	33.56	2.67
	(3)	41.22	2.19
	(1)	45.10	2.01
	(2)	51.14	1.78
Quartz (high)	(2)	20.46	4.34
	-	26.20	3.40
	(1)	35.92	2.50
	(1)	45.10	2.01
	(1)	46.62	1.83
Quartz (low)	(3)	20.85	4.26
	-	26.68	3.34
	(1)	36.67	2.45
	(1)	39.52	2.28
	(1)	50.20	1.817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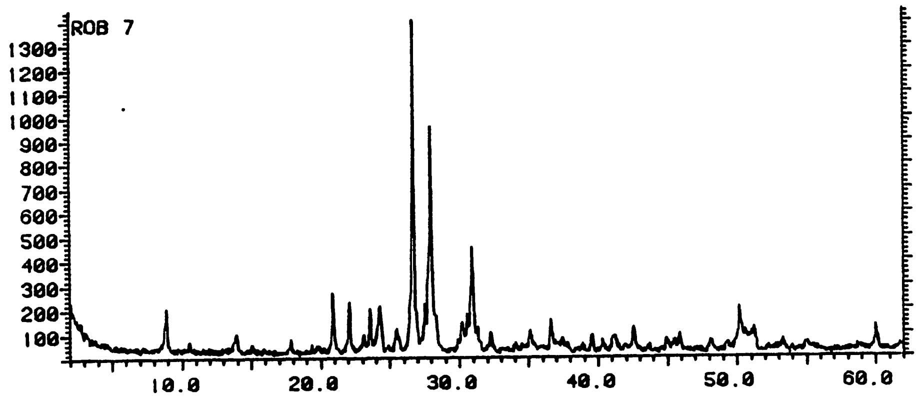
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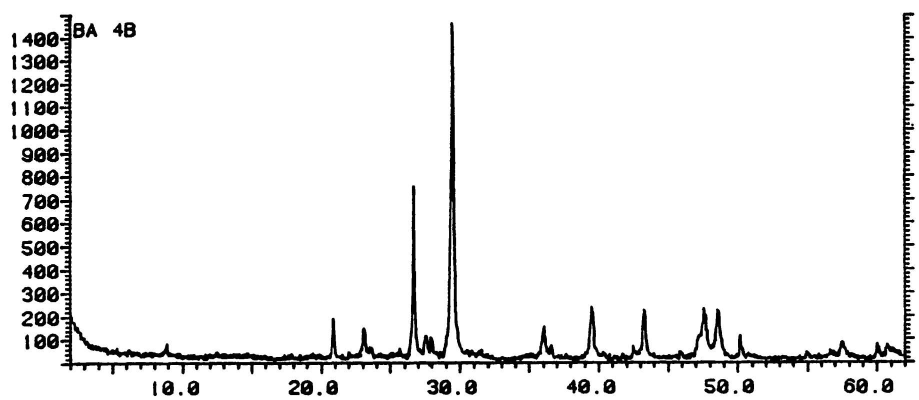
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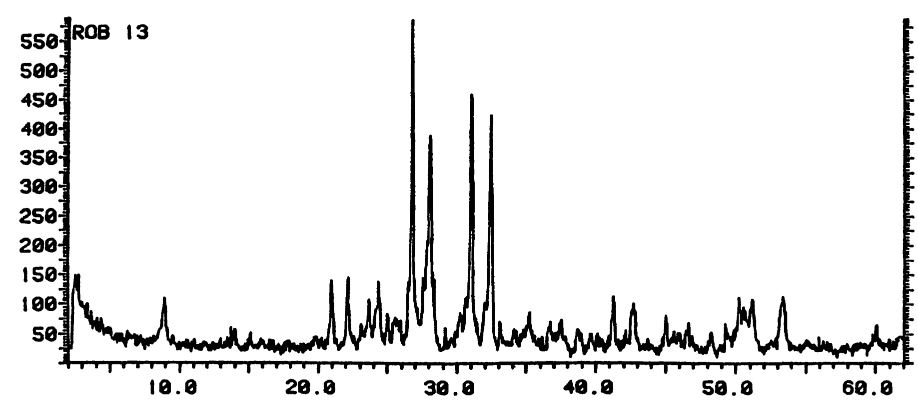
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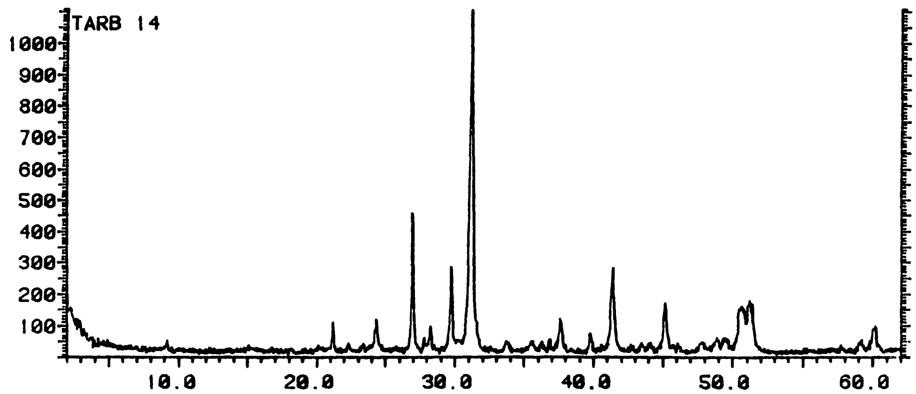
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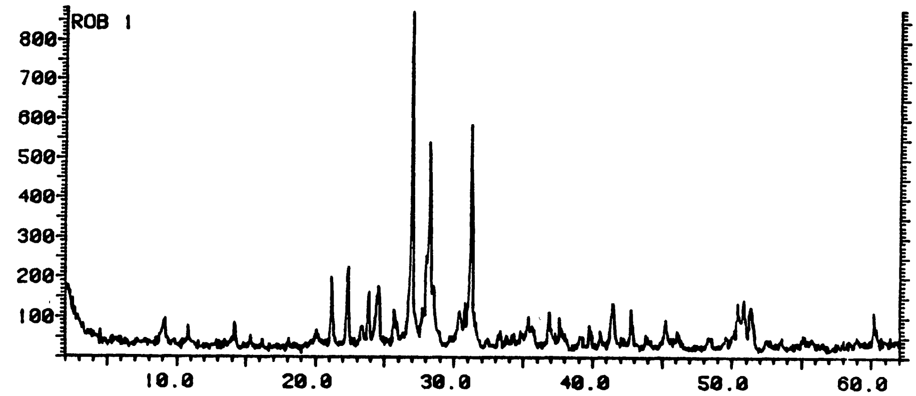
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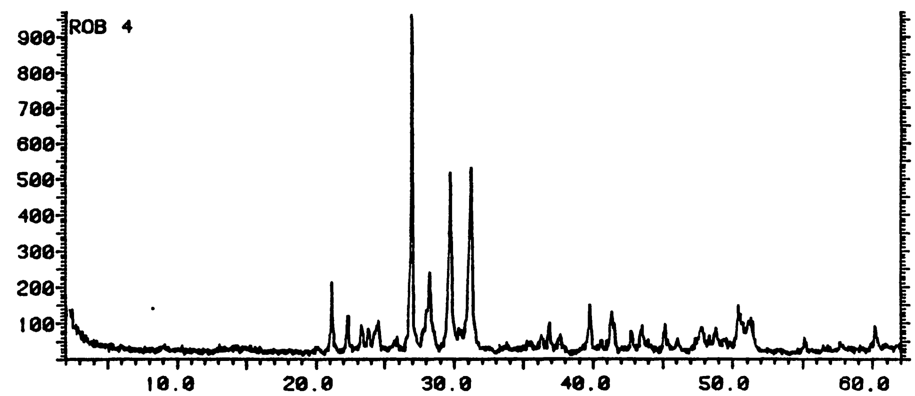
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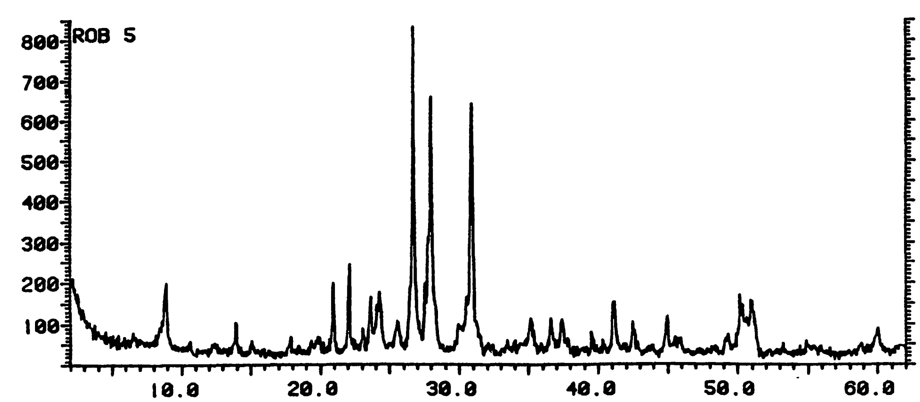
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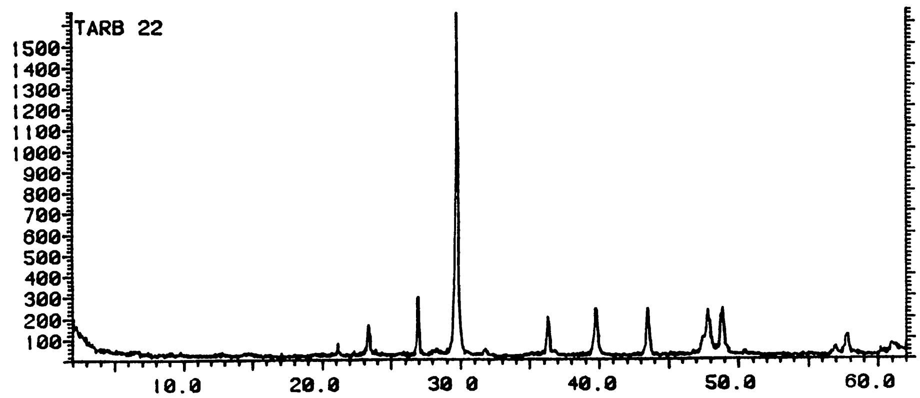
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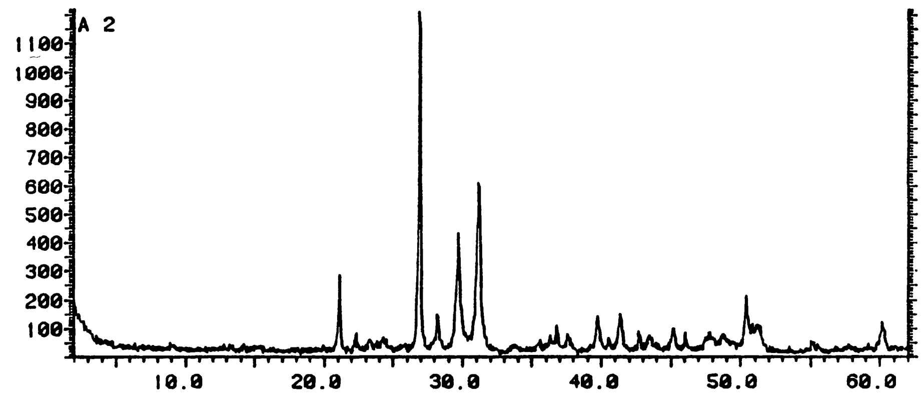
60.0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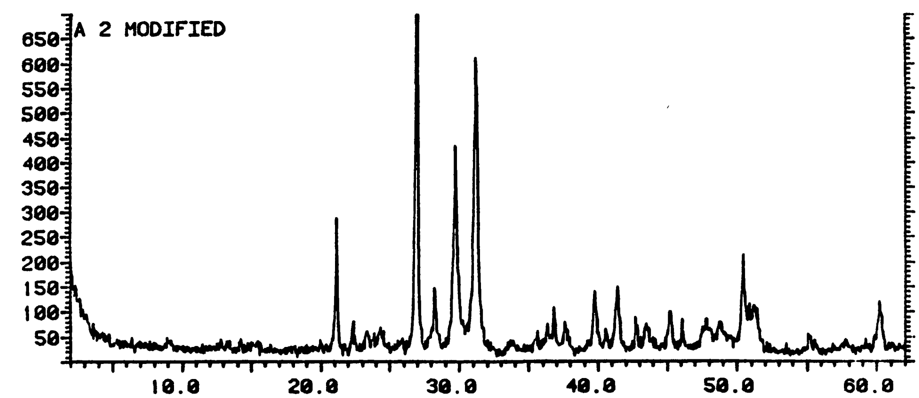
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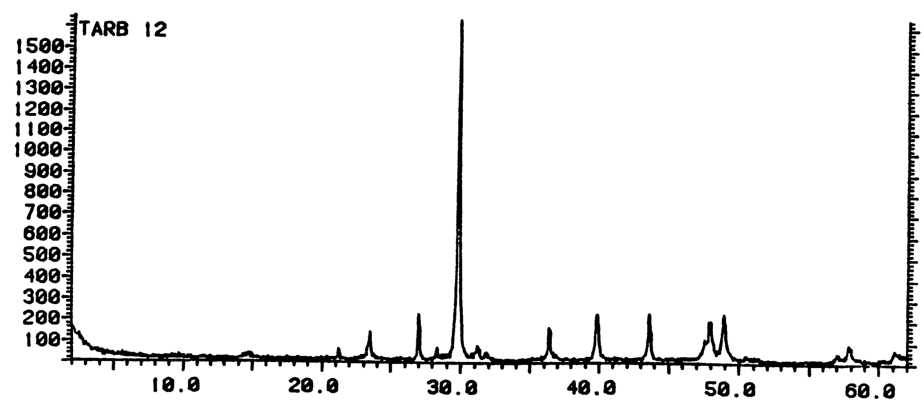
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1300
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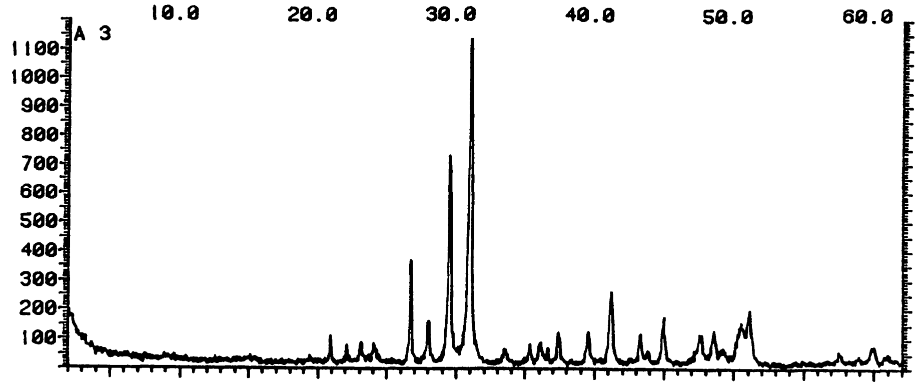
60.0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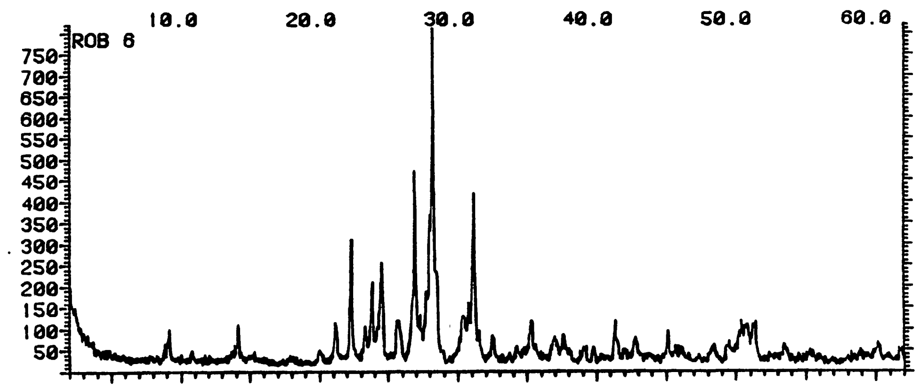
ROB 6
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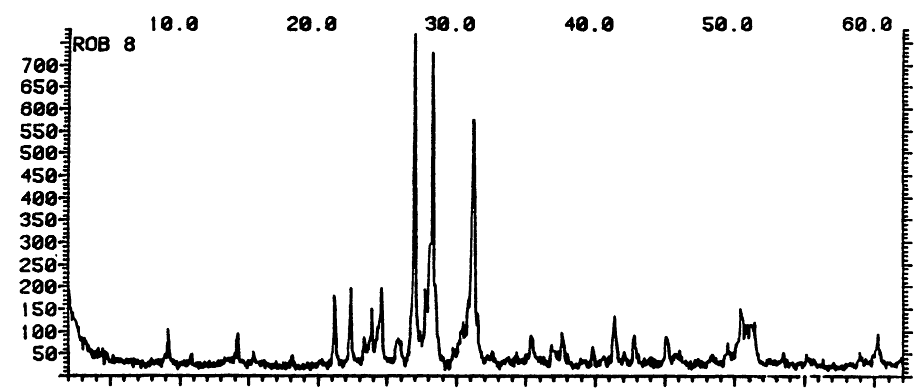
50


ROB 8
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100
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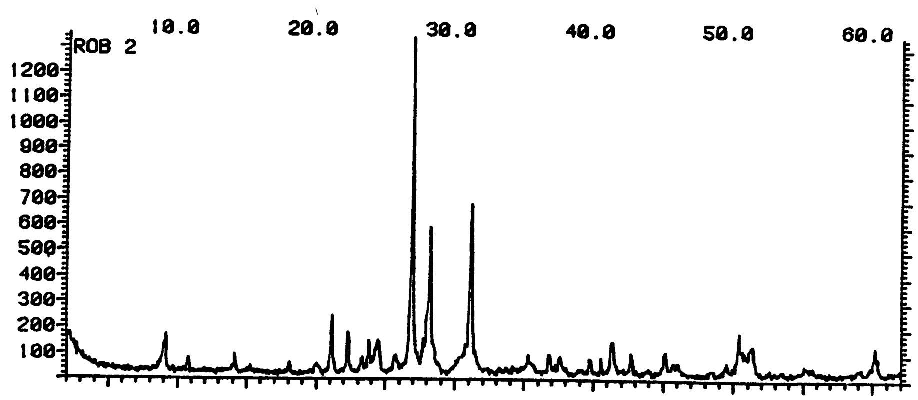
ROB 2
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20.0
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200
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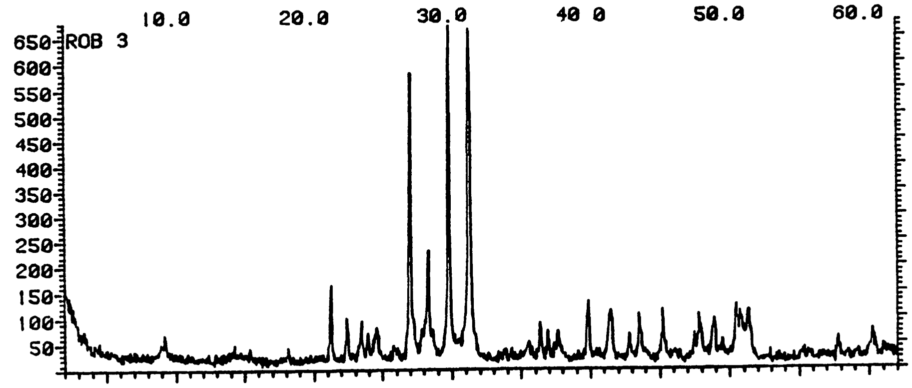
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20.0
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150
100
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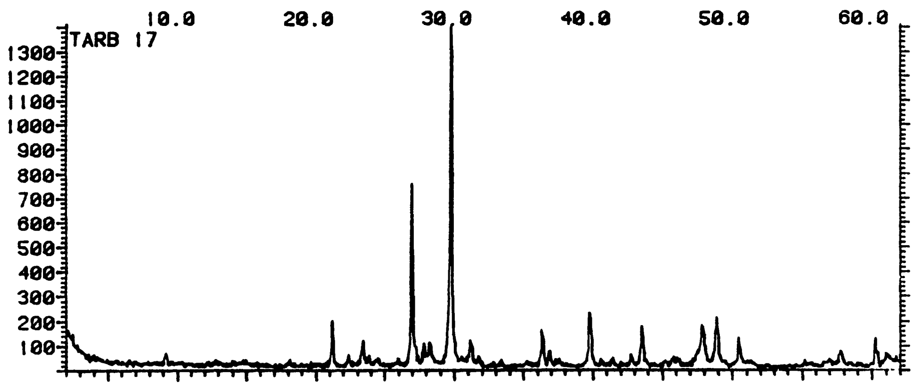
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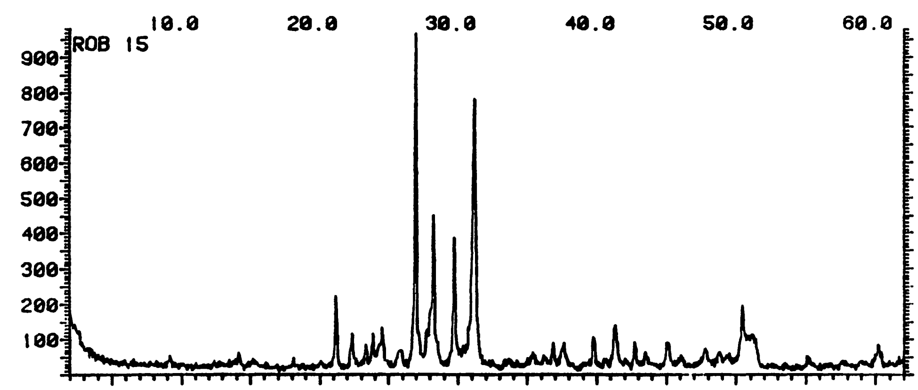
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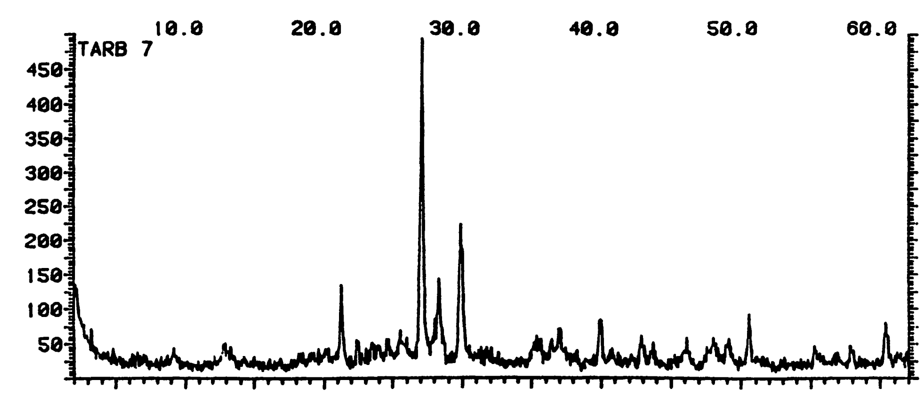
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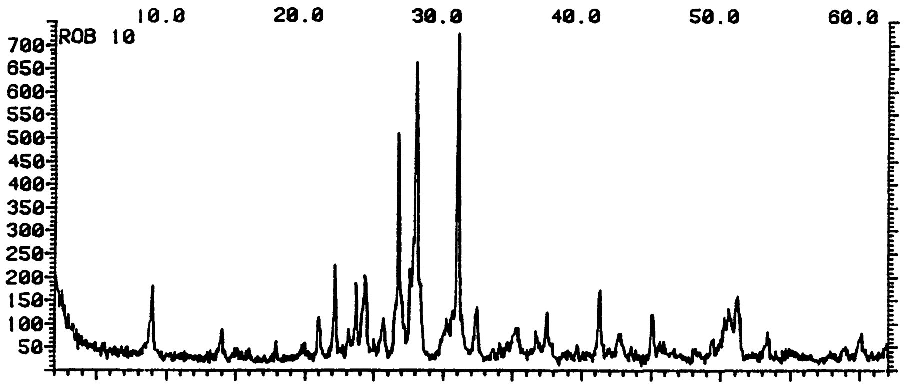
50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200
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100
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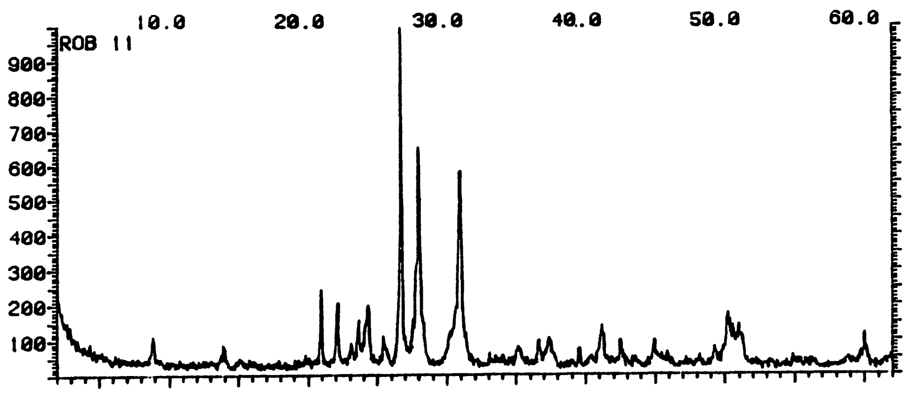
ROB 11
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50.0
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800
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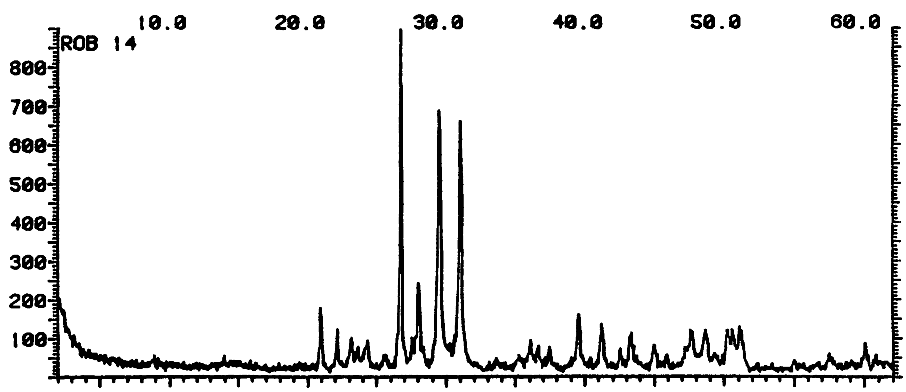
600
500
400
300
200
100


ROB 14
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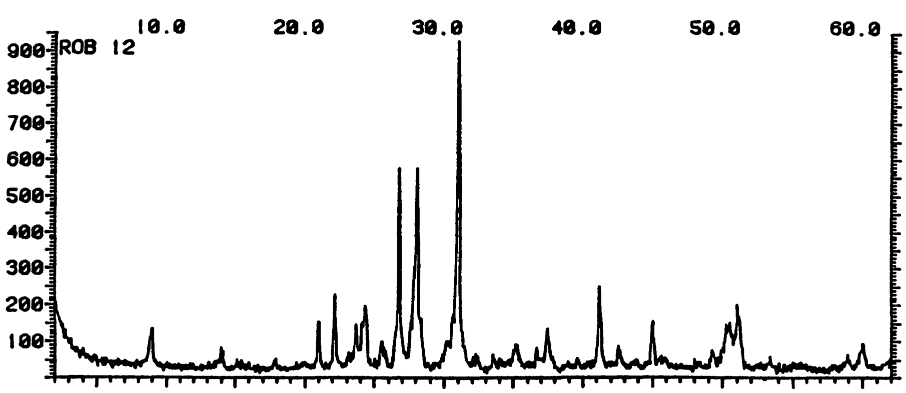
50.0
60.0
800
700
600
500
400
300
200
100


ROB 12
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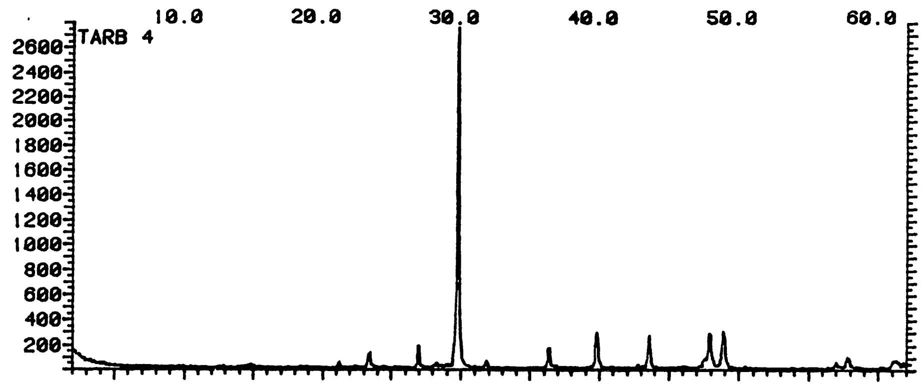
30.0
40.0
50.0
60.0
900
800
700
600
500
400
300
200
100


TARB 4
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2200
2000
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1000
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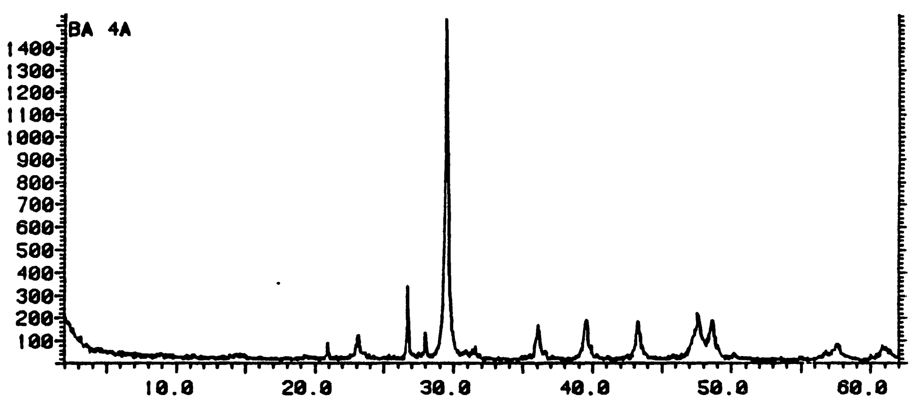
400
200


BA 4A
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1300
1200
1100
1000
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800
700
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500
400
300
200
100
10.0
20.0
30.0
40.0
50.0
60.0

APPENDIX C

TOTAL ORGANIC CARBON

TOTAL ORGANIC CARBON

Analysis #1

Sample	Weight A (gm)	Weight B (gm)
Bali A	1.16050	1.20107
A2	1.03920	1.36000
TARB 22	1.16311	1.17329
ROB 10	1.61823	1.50843
ROB 13	1.37625	1.54808
ROB 2	1.24144	1.04300

Analysis #2

A3	1.0013	1.12677
TARB 14	1.10989	1.26437
TARB 17	1.12119	1.28237
ROB 5	1.14072	1.19478
TARB 4	1.13956	1.26007
ROB 3	1.10757	1.25457

Analysis #3

ROB 11	1.29269	1.22912
ROB 15	1.12820	1.08155
ROB 4	1.06700	1.11034
ROB 14	1.11882	1.36000
ROB 6	1.46113	1.38804
Bali B	1.17025	1.12900
BL	1.38040	1.27135

TOTAL ORGANIC CARBON

Analysis #1

Sample Number		Initial(ml)	Final(ml)	Used(ml)	TOC(%)
Bali	B	10.3	20.5	10.2	.057
ROB2	A	20.1	26.5	6.4	2.15
ROB13	B	26.5	28.4	1.9	3.72
TARB22	A	28.5	36.0	7.5	1.65
ROB2	B	36.0	43.0	7.0	2.17
A2	B	43.0	49.3	6.3	2.02
ROB10	A	9.7	16.7	7.0	1.40
A2	A	24.1	31.3	7.2	2.40
TARB22	B	31.3	39.2	7.9	1.40
ROB13	A	39.3	41.3	2.0	4.14
Bali	A	8.4	18.0	9.6	.414
ROB10	B	16.7	24.0	7.3	1.36

Blanks

Blank Number	Initial(ml)	Final(ml)	Used(ml)
A	.1	10.4	10.3
B	18.0	28.3	10.3

Blank Average = 10.3 ml

Analysis #2

Sample Number		Initial(ml)	Final(ml)	Used(ml)	TOC(%)
A3	A	34.85	42.4	7.55	1.68
A3	B	3.9	11.4	7.50	1.52
TARB14	A	19.1	26.65	7.55	1.51
TARB14	B	11.4	19.1	7.70	1.24
TARB17	A	17.1	26.5	9.40	.367
TARB17	B	26.55	34.8	8.25	.937
ROB5	A	41.75	54.0	12.25	0.00
ROB5	B	10.35	17.1	6.75	1.86
TARB4	A	25.2	31.8	6.60	2.04
TARB4	B	33.8	39.9	6.10	2.12
ROB3	A	26.65	33.75	7.10	1.79
ROB3	B	42.45	49.0	6.55	1.88

Blanks

Blank Number	Initial(ml)	Final(ml)	Used(ml)
A	31.85	41.75	9.9
B	.20	10.35	10.15
C	39.9	49.9	10.0

Blank Average = 10.0 ml

TOTAL ORGANIC CARBON

Analysis #3

Sample Number		Initial(ml)	Final(ml)	Used(ml)	TOC(%)
ROB11	B	10.3	14.7	4.4	2.60
ROB4	B	14.7	20.6	5.9	1.95
ROB4	A	20.6	26.75	6.15	1.87
ROB15	A	26.75	32.4	5.65	2.07
ROB15	B	32.45	38.3	5.85	2.03
BL	B	38.3	46.8	8.5	.302
ROB6	A	40.95	48.55	7.6	.686
ROB14	B	8.8	14.0	5.2	1.94
ROB6	B	20.7	27.6	6.9	1.06
Bali B	B	14.55	20.7	6.15	1.77
ROB14	A	27.6	33.7	6.1	1.81
BL	A	34.7	41.0	6.3	1.37
Bali B	A	41.0	47.4	6.4	1.56
ROB11	A	21.85	27.3	5.45	1.91

Blanks

Blank Number	Initial(ml)	Final(ml)	Used(ml)
A	.25	10.25	10.0
B	.10	8.8	8.7
C	27.30	35.8	8.5

Blank Average = 9.06 ml

TOTAL ORGANIC CARBON

Robbery Head Formation

Sample Number		% Total Organic Carbon
ROB 2	A	2.15
ROB 13	B	3.72
ROB 2	B	2.17
ROB 10	A	1.40
ROB 13	A	4.14
ROB 10	B	1.36
ROB 11	B	2.60
ROB 4	B	1.95
ROB 4	A	1.87
ROB 15	A	2.07
ROB 15	B	2.03
ROB 6	A	.686
ROB 14	B	1.94
ROB 6	B	1.06
ROB 14	A	1.81
ROB 11	A	1.91
ROB 5	B	1.86
ROB 3	A	1.79
ROB 3	B	1.88

Tarbat Ness

Sample Number		% Total Organic Carbon
TARB 22	A	1.65
TARB 22	B	1.40
TARB 14	A	1.51
TARB 14	B	1.24
TARB 17	A	.367
TARB 17	B	.937
TARB 4	A	2.04
TARB 4	B	2.12

Miscellaneous Formations

Sample Number		% Total Organic Carbon
Bali	B	.057
A2	B	2.02
A2	A	2.40
Bali	A	.414
A3	A	1.68
A3	B	1.52
BL	B	.302
BL	A	1.37
Bali B	A	1.56
Bali B	B	1.77

PROCEDURE

1. Scoop 1 gm of soil sample into a 250 ml Erlenmeyer flask.
2. Add 10 ml Potassium Dichromate solution from an auto pipetter.
3. Add 10 ml concentrated Sulfuric Acid and shake soil-solution mixture.
4. After cooling (45 minutes), add 5 ml concentrated Phosphoric Acid and 50 ml of distilled water.
5. Add about 10 drops (1/2 ml) of Barium Diphenylamine Sulfonate indicator using a bulb pipette with 7 ml capacity.
6. Titrate to green color with the Ferrous Sulfate solution.
7. Run three blanks through the above procedure with each set. It is also advisable to run the first and last sample in duplicate to detect any variation in chemicals, etc.
8. Use the following formula to calculate % O.M.:

$$\% \text{ Organic Matter} = 0.69 \left(\frac{\text{Blank}^1 + \text{Blank}^2 + \text{Blank}^3}{3} - \text{Sample}\right)$$

where Blank 1, Blank 2, Blank 3 and sample are mls Ferrous Sulfate used in step 6.

SOIL ORGANIC MATTER CONTENT

Dissolve the ferrous sulfate in deionized water then add Sulfuric Acid slowly while mixing. After solution has cooled bring to final volume with deionized water. Use Sample Number as a guide to determine amount of Ferrous Sulfate solution required. Keep excess solution in a sealed vessel in the refrigerator for no more than a few days.

Sample # = # Unknowns + 3 Blanks

VITA

Kelley Ann Clinton Race

Candidate for the Degree of

Master of Science

Thesis: GEOCHEMICAL ANALYSIS AND ENVIRONMENTAL RECONSTRUCTION OF A DEVONIAN LAKE BASIN IN NORTHERN SCOTLAND

Major Field: Geology

Biographical:

Personal Data: Born in Manhatten Kansas, November 20, 1958, the daughter of John M. and Sue L. Clinton.

Education: Graduated from Greely High School, Cumberland, Maine, in May, 1977; attended the University of Maine at Presque Isle and Orono, Maine; received Bachelor of Science degree in Geology from the University of Oklahoma, Norman, Oklahoma in August, 1983; completed requirements for the Master of Science degree at Oklahoma State University in July, 1985.

Professional Experience: Teaching Assistant, Department of Geology, Oklahoma State University, May 1984 to July 1985.

Professional Organizations: Phi Kappa Phi (Honor Fraternity) American Association of Petroleum Geologists, Society of Economic Paleontologists and Mineralogists, Association of Women Geoscientists, Geological Society of America.