THE RELATIONSHIPS BETWEEN LIGHT HYDROCARBONS, CARBONATE DIAGENESIS, AND BASE METAL ORE DEPOSITS.

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ABSTRACT

This thesis is an investigation into the complex relationships between light hydrocarbons, carbonate diagenesis, and base metal ore deposits, inspired by previous research that indicated that base metal ores in carbonate hosts are surrounded by areas of elevated light hydrocarbon content.

The theoretical study of ore deposition and hydrocarbon formation and migration is accompanied by practical examination of the light hydrocarbon content of carbonate and non-carbonate rocks, with and without extensive mineralisation. The conclusion is drawn that light hydrocarbons, especially methane, are generated at the site of ore deposition, but that the control on whether the hydrocarbons form a detectable anomaly lies with the host lithology.

The nature of carbonate hosts is investigated through a series of experiments designed to simulate natural diagenesis. The results indicate that the diagenetic state of the host rock will determine whether any anomaly pattern is present around an orebody, by controlling the ease of migration of the light hydrocarbons, and the manner in which they are held within the rock.

The research therefore indicates that, while the processes which generate the light hydrocarbons are common

to many ore deposits, the formation of an extensive hydrocarbon anomaly around the deposit is probably exceptional.

Throughout this investigation, the potential use of the detection of light hydrocarbon haloes in mineral exploration is borne in mind. The evidence suggests that, while further research is required, there would seem to be many problems still to be overcome if such potential is to be realised.

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PART ONE

HYDROCARBON ANOMALIES AND MINERAL EXPLORATION

THE INVESTIGATION OF THE PHENOMENON OF LIGHT HYDROCARBON ANOMALIES AROUND CARBONATE HOSTED BASE METAL ORE DEPOSITS; THEIR GEOLOGICAL SIGNIFICANCE AND PROSPECTIVE USE IN MINERAL EXPLORATION.

CHAPTER ONE

INTRODUCTION TO THE CONCEPT OF HYDROCARBON ANOMALIES

The research described in this thesis is based on the discovery of characteristic patterns in the hydrocarbon content of rocks hosting certain base metal deposits. Since this is a relatively recent discovery, an explanation of the concepts involved is provided by way of introduction, as is a description of the type of ore deposit in question. The latter description sets limits on the processes which may act to control the hydrocarbon content of the host rocks, and so limits the scope of the hypothetical scenarios developed later in the thesis.

1.1. ORIGINAL RESEARCH

In 1981, J.S. Carter produced a Ph.D. thesis entitled 'The Connection between Gaseous Hydrocarbons and Lead - Zinc Mineralisation'. This was the result of research undertaken at Imperial College, and was inspired by previous theoretical and practical studies of the same subject (Dunsmore & Shearman 1977, Ferguson 1984). These studies suggested that light hydrocarbons, and especially methane, could be found in abnormally high concentrations in ore-bearing carbonates, due to the chemical reactions occurring during mineralisation. Carter's research was an experimental investigation of this phenomenon, involving the analysis of

gaseous hydrocarbons emitted by 770 samples of limestone, after crushing and heating. Samples from the North Pennine Orefield were found to contain 70% methane relative to other light hydrocarbons, compared to a value of about 35% outside the mineralised zone. Similar results were obtained from samples from the vicinity of Tynagh Mine, Ireland, and samples collected within the mineralised Carboniferous Limestone of the Mendip Hills (Carter 1981, p.71). Carter assumed that the gaseous hydrocarbons detected were related to those released during the formation of the lead-zinc sulphide deposits, and he concluded that the detection of such anomalously high methane values elsewhere could form the basis of a future method of mineral exploration. Research into this proposed exploration method has been continued at Mercury Hydrocarbons, Limerick, Ireland, by Carter and others, and has allowed refinement of both the method of analysis and the interpretation of results. Most recently a research grant was awarded by the C.E.C. Research and Development Group to Imperial College, to continue this research in conjunction with Mercury Hydrocarbons. This thesis presents the results of some of the research undertaken at Imperial College during the author's tenure of a Research Assistantship financed from the C.E.C. research contract.

1.1.1. Sampling, Analysis, and Interpretation.

In its simplest form, the light hydrocarbon anomaly consists of a high proprtion of methane in gases released by rocks sampled in the vicinity of mineralisation,compared to those from unmineralised areas. The use of the composition of the analysed light hydrocarbons from any region in a mineral exploration programme would obviously depend on the identification of any such anomaly. Samples should be taken in great enough numbers, and over a large enough area for the threshold at which gas compositions could be termed 'anomalous' to be decided statistically. A reconnaissance exploration programme would therefore be devised to give good sample coverage of the exploration area, though the precise nature of the sampling pattern would depend on the specific site.

The samples collected in the field should be free of vegetation, since any such contamination can cause misleading modification of the results, due to the release of hydrocarbons from the vegetation as the rock sample is prepared for analysis (Carter & Cazalet 1985, pA4). The preparation method itself is quite simple, and so is suitable for the large number of samples which would constitute a reconnaissance survey. The rock samples are coarsely crushed by means of a jaw crusher, and a weighed subsample of a certain range in grain size is sealed in a glass bottle. The bottle is heated in order to drive any hydrocarbons present in the crushed rock into the headspace. Analysis of the headspace

gas by gas chromatography identifies the different hydrocarbon components, and allows the proportions in which they are present to be calculated.

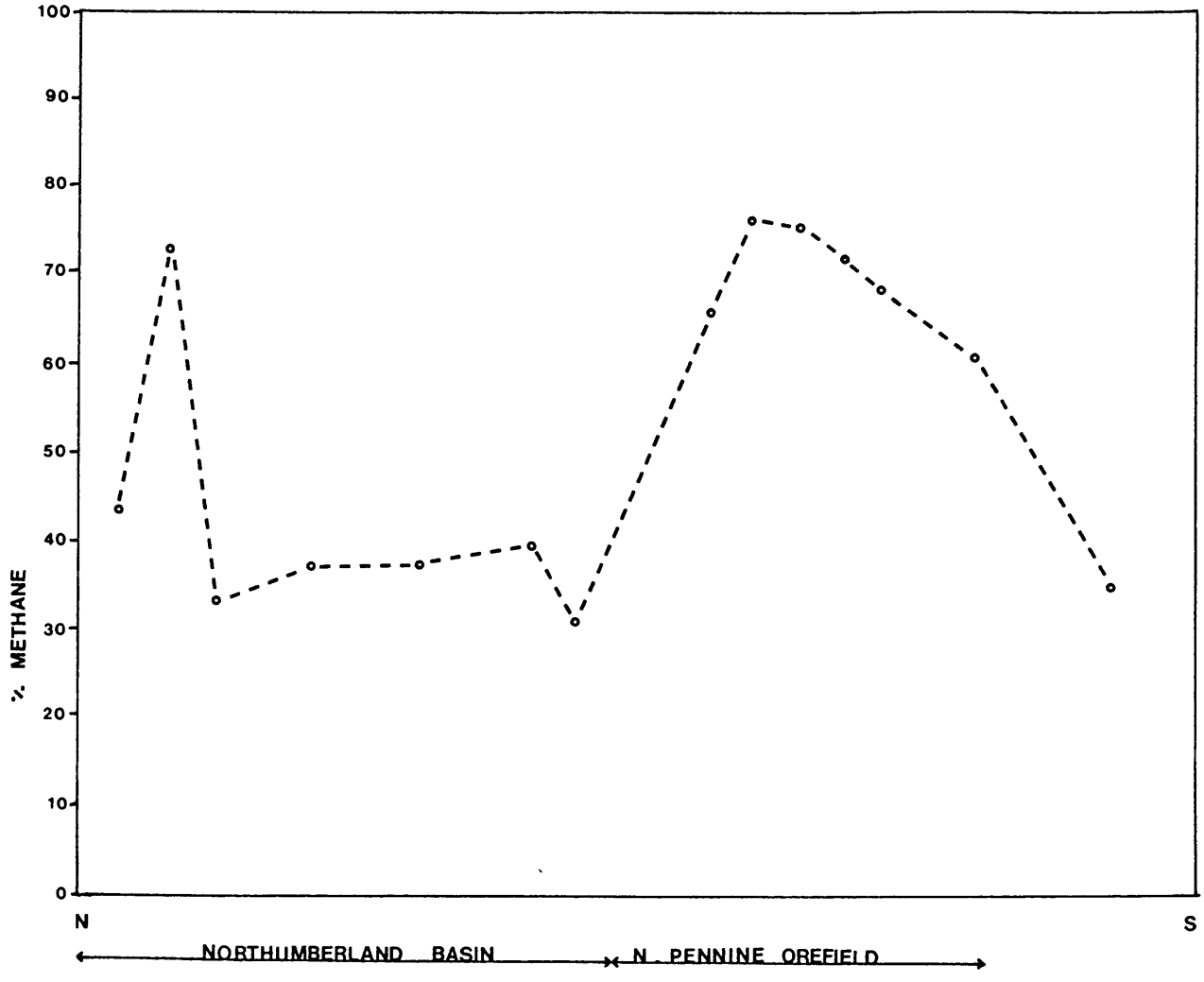
Interpretation of the results would usually begin with the mapping of patterns in the composition of the analysed hydrocarbons over the survey area. Plotting the percentage of methane in the analysed gas at each sample location would allow any area of higher than average methane value to be identified. Statistical analysis of the data would determine whether any such grouping of high values formed a significant anomaly, by taking into consideration variations in hydrocarbon composition throughout the exploration area, and anomaly threshold values in similarly surveyed areas of known mineralisation. The geological significance of any identified anomaly would then be investigated in greater detail, either by further application of the method outlined above, or by more target-specific exploration methods.

1.1.2 Surveys Completed and Results

At Mercury Hydrocarbons extensive studies have been completed which investigate many of the known economic ore deposits in the Carboniferous Limestone of Ireland, and also a number of smaller mineral occurrences. Carter's original work on the North Pennine Orefield showed a simple regional anomaly (Carter 1981, p.60). The percentage of methane in the detected hydrocarbons was found to be higher in the

Figure 1.1a: Variation in Methane Percentage across the North Pennine Orefield.

(after Carter 1981)



mineralised area than in the surrounding region (figure 1.1a). The pattern around the Irish base metal ore deposits was, however, found to be more complex. Again, there was a general increase in the methane percentage over the mineralisation, but the highest methane percentage values formed a halo around a central area in which the higher order hydrocarbon gases seemed to be enriched. Carter has proposed a scenario whereby he recognises concentric rings surrounding the central ore zone - the 'hydrocarbon haloes', with the heaviest hydrocarbons enriched at the centre, and methane, the lightest gas, forming the outermost halo. Outside the outer methane halo, the hydrocarbon values are said to fall away to the level of the regional background (figure 1.1b).

The size of the halo may be related to the size of the ore deposit it is associated with, as illustrated by the Irish base metal ore deposits. The deposit at Mallow is small, with reserve of four million tonnes or ore, grading 0.7% copper. The methane halo identified here is approximately one kilometre across, with only a small central zone close to the deposit, where heavier hydrocarbons predominate. The larger deposit at Navan (one hundred million tonnes of ore, grading 10% combined lead and zinc) has a larger methane halo, some fifteen kilometres or more across, with a strong concentration of heavier hydrocarbon gases at the centre. The halo patterns at Tynagh and at Silvermines have been shown to be between these extremes of size, as are the

Figure 1.1b: Hypothetical Cross Section through a Hydrocarbon Gas Anomaly.

(after Carter 1983)

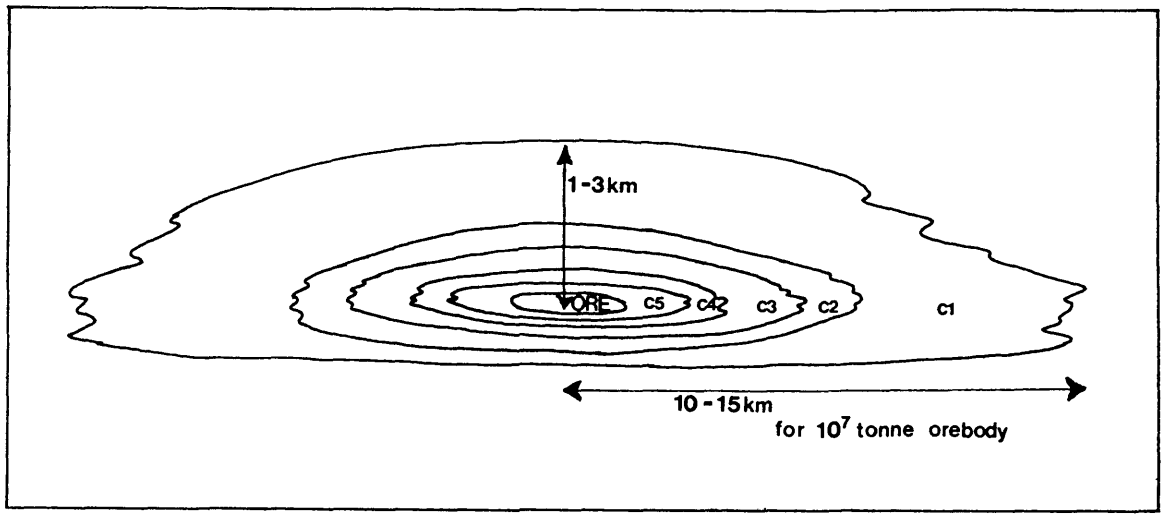
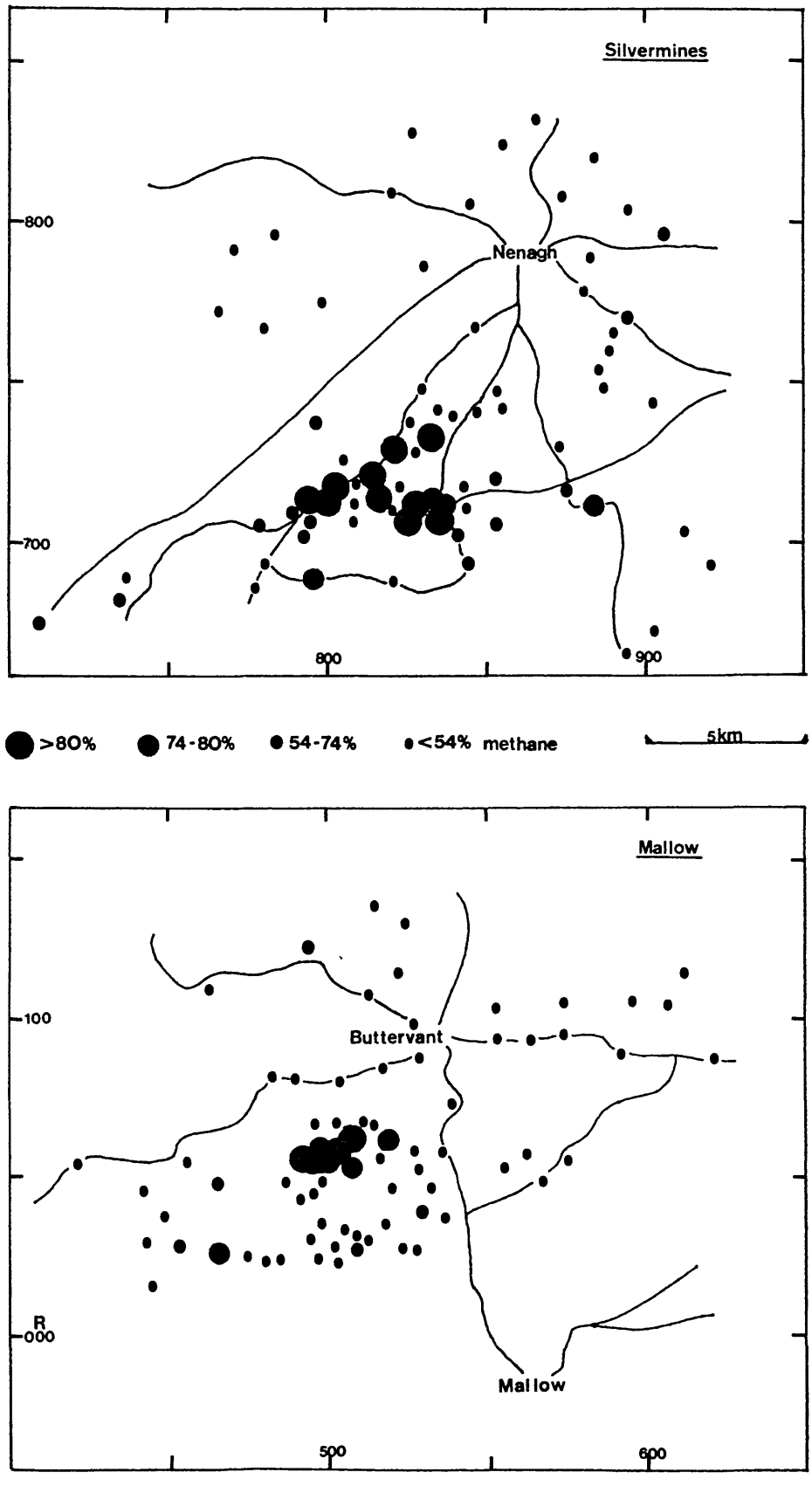


Figure 1.1c: Methane Anomalies around Irish Ore Deposits.

(after Carter & Cazalet 1984)



In both cases the location of the mineralisation is represented by high percentage methane values.

orebodies themselves (Carter & Cazalet 1984, p.17). Figure 1.1c is a reproduction of maps indicating the position and nature of methane haloes around two of the Irish deposits studied.

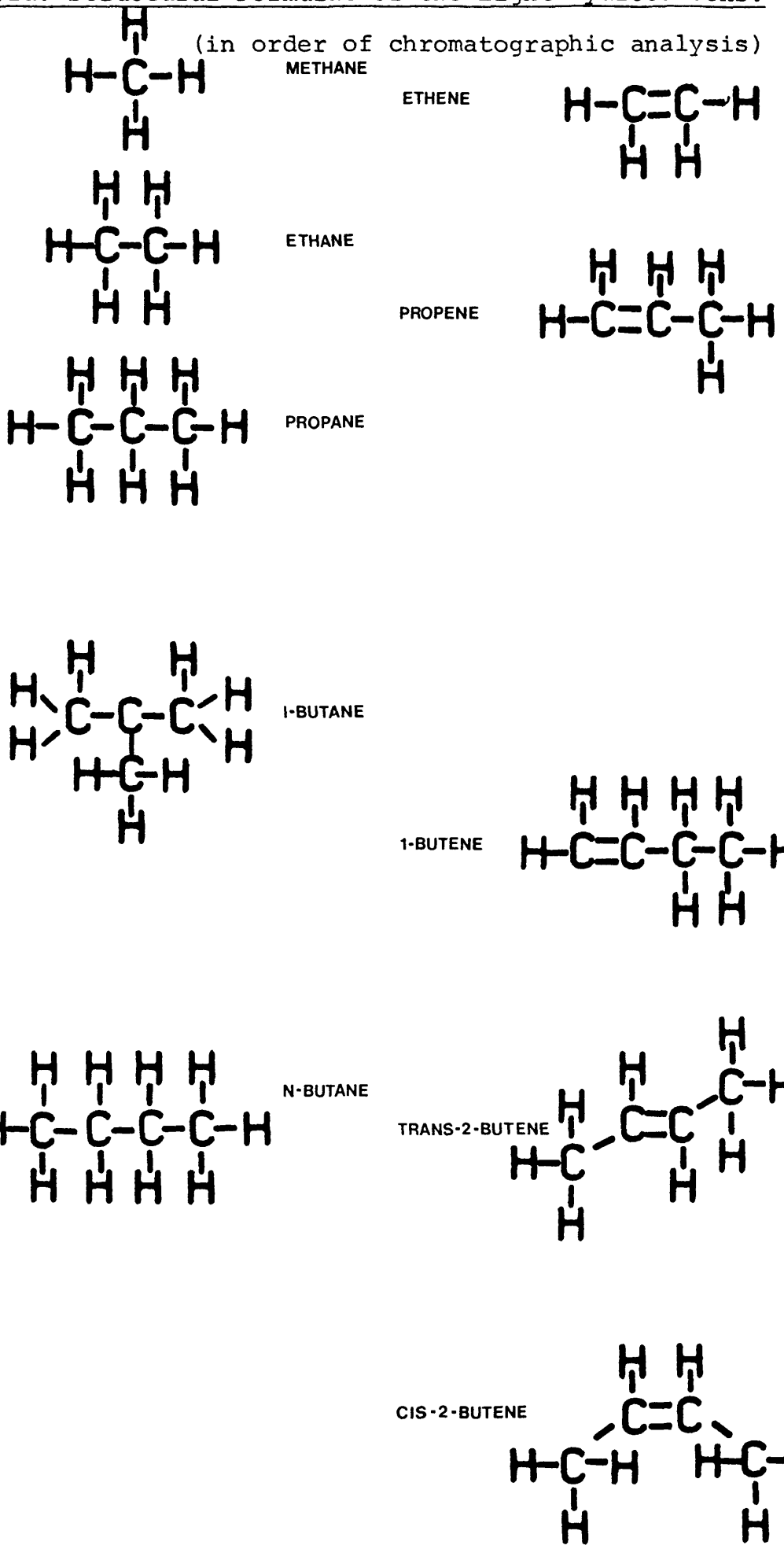
1.1.3. Hydrocarbon Composition

The hydrocarbons which are released on heating of the crushed rock sample have been identified as those members of the alkane and alkene series which are gaseous at room temperature. Methane is the dominant component of the light hydrocarbons in the gas samples, but gases up to C_4 (butane and butene) have been detected and analysed. The important hydrocarbon gases and their structural formulae are represented in figure 1.1d. Carter records the amount of higher order gases (e.g. pentane, pentene, hexane, etc.) as one combined component which he terms 'C5+'. The analytical system used at Imperial College, however, does not record a value for these higher order gases.

Apart from the positively identified hydrocarbon gases, certain other gases have been detected in the gas released on heating of the rock samples. These have not been identified with any certainty, but are now considered to be probable non-hydrocarbon contaminants.

Figure 1.1d: Structural Formulae of the Light Hydrocarbons.

(in order of chromatographic analysis)



1.1.4. Origin of Anomalies

Stated simply, the relationship between ore deposits and hydrocarbon content of the host rock is thought to develop from the ore-forming chemical reactions. Dunsmore & Shearman (1977) were the first to suggest that light hydrocarbons, especially methane, could be generated during the reduction of anhydrite by a reaction such as:

$CaSO_4$ + hydrocarbons → H_2S + H_2O + light hydrocarbons + bitumens

Such reduction of a sulphate source, which may be anhydrite, seawater sulphate etc., is necessary to produce sufficient sulphide for precipitation of ore minerals. Carter (1981, p.121) suggested that the light hydrocarbons thus produced would migrate outwards from the centre of mineralisation, forming the aforementioned anomaly pattern. The broad methane anomaly detected in the Northern Pennines he explained as being due to the migration of light hydrocarbons from numerous vein systems as ore deposition occurred (Carter & Cazalet 1984, p.18). The more distinct halo patterns described around deposits in the Irish Carboniferous were said to be due to the gases migrating at different rates from single centres of ore deposition. Methane, being the lightest gas, would travel faster than the other gases, to form the outer halo, the different rates of diffusion of the gases resulting in the overall pattern of concentric haloes.

The work presented here is therefore based on longstanding research by workers at Imperial College (Dunsmore & Shearman

1977, Carter 1981, Ferguson 1984), and more recently at Mercury Hydrocarbons (Carter & Cazalet 1984, 1985), and combines both experimental and theoretical studies, to provide further evicence on some of the many problems surrounding the hydrocarbon anomaly concept.

1.1.5. Problems Raised by Previous Research

In the attempt to develop a new mineral exploration technique it is necessary to understand the processes involved, so that the method can be developed and applied successfully. The detection of high methane percentage values, or a halo pattern in the hydrocarbon content of rocks hosting ore deposits provides a potential exploration tool. For it to be developed further, there are several problems raised by earlier research which need to be solved. Previous research concentrated on ore deposits of the Mississippi Valley type, i.e. carbonate hosted base metal ore deposits. It is necessary to know whether light hydrocarbon haloes are present around deposits of this type other than those in the Irish Carboniferous, or around deposits of other types. This is not only important for the applicability of the exploration method, but also for the geological controls on the hydrocarbon - ore deposit relationship. The theory of halo formation itself is difficult to prove, involving as it does such complex processes as sulphate reduction, hydrocarbon migration etc. The 'state of the art' knowledge of these subjects will, however, give some indication of the role of these processes in this situation.

It is also necessary to consider whether the hydrocarbon content of the rocks may depend on some process other than ore precipitation. It is possible that if, for instance, high heat flow were the controlling factor, then methane anomalies could be found in unmineralised areas, or associated with very minor mineralisation, as well as in the vicinity of major deposits. This could only be determined by the completion of extensive surveys in areas of different temperature gradients, and with different amounts of known mineralisation. While surveys of this type are outside the scope of the present investigation, evidence is presented concerning this problem. The problems associated with the effect of deformation and metamorphism on the hydrocarbon content of rocks are also discussed. If high heat flow (whether associated with ore deposition or not) is a controlling factor on hydrocarbon migration at the time of anomaly formation, it is reasonable to assume that high heat flow during metamorphism would also affect the nature of the anomaly.

Anomalously high methane percentages or hydrocarbon haloes detected around ore deposits have a potential use in mineral exploration. This potential, coupled with geological curiosity, ensures the type of investigation of the practical and theoretical problems raised which constitutes this thesis.

1.2. CARBONATE HOSTED LEAD - ZINC ORE DEPOSITS

The investigation of the relationship between ore deposition and hydrocarbons must begin with the study of the ore genetic system involved. Up to the present, most of the research has involved deposits of base metal ores in carbonate hosts. An understanding of the controls on and environment of deposition of such ores suggests factors which may also control the hydrocarbon content of the rock. This type of deposit, like many other types, was originally deemed to be due to magmatic or magmatic-related hydrothermal action. Gradually, however, the theories of epigenetic and syngenetic origin of ore deposits have come to the fore. At present it is considered that many ore deposits are part of the sediment pile, and formed by processes which occur in any sedimentary basin. The Mississippi Valley type of ore deposit consists of lead and zinc sulphides within carbonate host strata. The Pine Point district was the first in which these deposits were discussed as being a typical part of the evolution of a sedimentary basin, in much the same way as oil generation is thought to be. The source of the ore metals is present in the sedimentary prism within the basin. The mechanism for the flow of fluids out of such a basin are well documented for the case of oil migration; ore bearing fluids could migrate in the same manner. Basinal growth faults are thought to concentrate fluids migrating out of the basin into receptive marginal facies, in this case these are carbonates, and mechanisms for the precipitation of ore minerals also exist.

Figure 1.2a: Model of Formation of Mississippi Valley Type Ores.

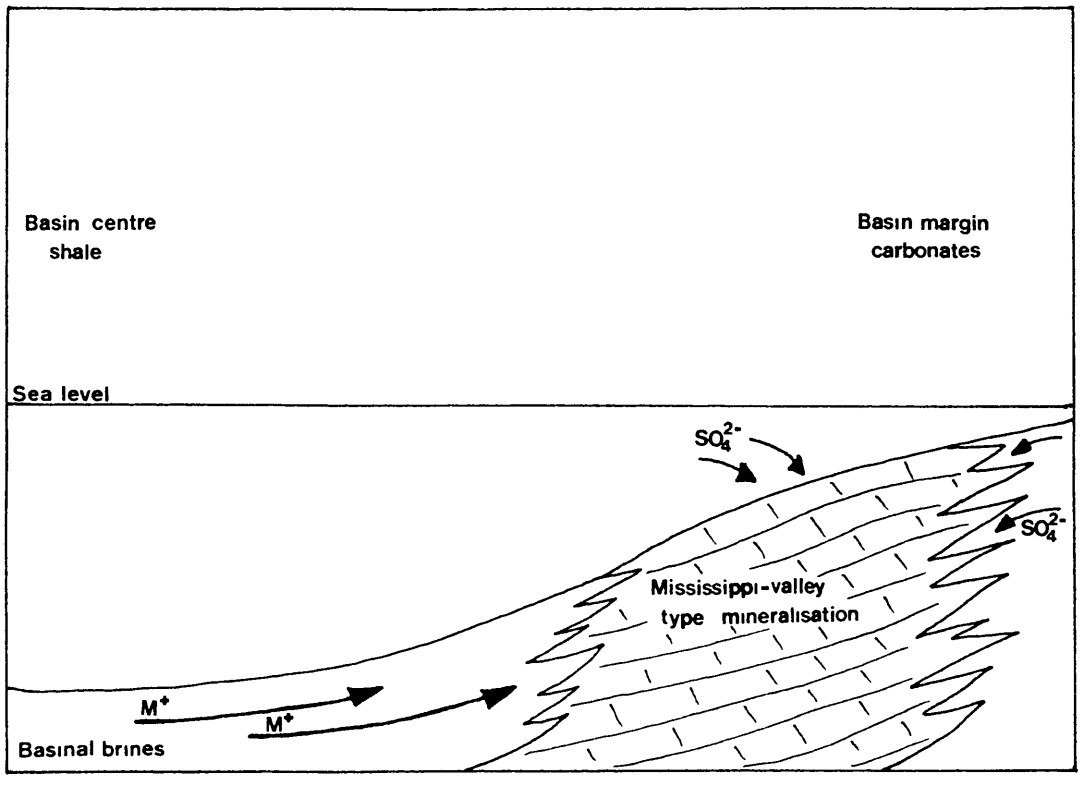


Figure 1.2a summarises this model; reference should be made to Morganti (1981) and Clemmey (in Brenchley & Williams (Eds.) 1985) for a full discussion of the position of this type of deposit in the range of sediment associated ores.

1.2.1. Components of the System

The elements of the ore genetic system comprise a source for the metal ions and the sulphide ions, a fluid to transport these from the source, a mechanism for reaction between them, and a receptive host rock. The host rocks for the type of ore deposit under discussion here are carbonates, and limestone and/or dolomite may be included, depending on the diagenetic condition of the rock. Generally, the rock will not have attained great age, and will be under relatively shallow cover, no more than a few hundred metres (Barnes in Barnes (Ed.) 1979, p.446). There may be some alteration of the host rocks prior to mineralisation by the first fluids to be flushed through them - the pre-ore fluids (Giordano & Barnes 1981, p.2202). These may thin or dolomitize the pre-existing carbonate, but there is little evidence that the mineralising fluids themselves have any such effect.

For precipitation of the metal sulphide ore minerals, the ore genetic system must contain base metal ions and reduced sulphur in solution. The sulphide will be present in solution as dissolved hydrogen sulphide, which will react with the metal ions at the site of ore deposition. Precipitation reactions

of this type may be due to the mixing of two fluids, one containing the metal ions and one the dissolved sulphide. Alternatively it has been suggested that both metal and sulphide ions may be transported in the same fluid to the site of ore deposition, where precipitation is caused by a change (possibly quite small) in the redox potential (Eh) or acidity (pH) of the environment.

The physical condition of the mineralising fluids must be determined by deduction from traces left in the geological record. Their temperature, for instance, has been calculated from fluid inclusion studies. Giordano & Barnes (1981) give the temperature of main stage Mississippi Valley type mineralisation as being in the range 100 - 150°C, with some temperatures as high as 200°C. Barnes (in Barnes (Ed.) 1979) gives the range of fluid inclusion deduced temperatures as 85 - 210°C for this type of deposit. The pressure will be relatively low, since the depth of burial of the host formation is small, but it must be high enough to prevent boiling. The pH conditions have been shown to be neutral to slightly acidic. Giordano & Barnes (1981) give the pH a range from pH 6.2 at 100°C to pH 5.6 at 200°C.

1.2.2. Fluid Flow

Theoretical analysis of the role of groundwater flow in the genesis of stratabound ore deposits in general has been undertaken by Garven & Freeze (1984). Their numerical

modelling of ore genesis by fluid flow considers the case of a mature sedimentary basin with gravity driven groundwater flow (as opposed to compaction driven flow). The mathematical model is tested by modelling the case for the Pine Point deposit (Garven 1985). This shows that a gravity driven flow system was capable of providing favourable flow rates, temperatures, and metal ion concentrations for ore formation there. The time interval involved, 0.5 to 5.0 ma, is close to that proposed for major deposits in the Wisconsin lead-zinc district, 0.25 ma (Hanor in Barnes (Ed.) 1979, p.163). These results do not preclude the possibility that driving forces other than gravity may be equally important; gravity driven flow was merely the choice made for the model. In all cases the time taken for ore deposition is unlikely to be controlled by the rate of fluid flow. It is more likely that the nucleation of the sulphide minerals and the kinetics of the precipitation reactions are the controlling factors. The ore minerals are probably slow to nucleate, with growth after nucleation proceeding rapidly, and often involving exponential reaction rates. Sweeney & Kaplan (1973) saw evidence of this during laboratory experiments on the formation of framboidal pyrite. These framboids grew on spherical nuclei, the fluid being 'seeded' with suitable nuclei. Once these nuclei were introduced, growth of the grains by further precipitation onto them was seen to be relatively rapid. The fluid flow rate then becomes important to continue the supply of material for precipitation; if this is rapid enough a major ore deposit

may then be formed in a geologically short period of time.

1.2.3. Metal Ions in Fluids

For verification of the above theory of ore precipitation it is necessary to identify a source for the metal ions in the fluids, and a method by which they are transported by these fluids. The ultimate source for the metals must be the mantle, from which they are incorporated into crustal rock sequences, derived from these rocks by weathering, and eventually introduced into the sedimentary prism (Clemmey in Brenchley & Williams (Eds.) 1985, p.231). Fluids migrating through and out of such sediments must have the ability to transport some metal ions. Practical observations of natural brines has been undertaken by many workers. Roedder (1968), for example, gives the concentrations of the metals which are of interest here in Salton Sea brines as being as high as 790ppm zinc and 85ppm lead. Seyfried & Bischoff (1977) carried out laboratory experiments, reacting seawater with basaltic glass, and attained concentrations of 45ppm iron and 20ppm manganese. These show the possible range in the natural system. Giordano & Barnes (1981, p.2201) suggest that for effective ore deposition, a minimum concentration of 10ppm for each base metal involved is necessary, and this figure now seems generally accepted.

There is more debate about the method by which the metal ions are transported. From fluid inclusion studies it seems that the fluids involved are usually sodium-calcium chloride brines, with low sulphate, and salinites in the range 100 - 300%

(Hanor in Barnes (Ed.) 1979, p.147), though each district will have a distinct temperature-related salinity. These brines are similar in nature (and origin) to those fluids associated with petroleum formation and known as 'oilfield waters' (Neumann et al 1981). It is known that there is often a strong association between sulphide deposits and organic matter, and there is a longstanding debate as to whether organic or inorganic complexes are the most important transport medium (Giordano & Barnes 1981, p.2207). It is known, for instance, that there are many organic compounds that form strongly-bonded soluble organometallic complexes, e.g. porphyrins, amino acids, carboxylates, and humic acids. The upper stability limit of these is 300°C, so they could be important in lower temperature deposits such as those studied here. Gardner (1974) studied sulphidic marine sediment waters on theoretical grounds, making calculations of the transport capabilities of complexes, based on their stability co-efficients. The results indicate that those organic complexes usually cited, e.g. those mentioned above, are probably not effective. Instead it is suggested that bisulphide and polysulphide complexes are far more important than the simple organic ligands. Giordano & Barnes (1979) studied typical Mississippi Valley type chemistry, and found that, along with chloride complexes, the bisulphide complexes are the most numerous, but their concentrations are several orders too low to form an ore deposit. Study of further inorganic and organic complexes from natural sources, e.g. oilfield brines, also

produced no single substance capable of producing the necessary concentrations of metal ions in solution. However, the authors suggest that the salicylate ion is capable of sufficient transport, at least for lead, to produce a sizeable ore deposit of this type. There is no evidence for the presence of salicylic acid in natural fluids, but crude oils and oilfield brines contain both phthalic acid and phenol. Since salicylic acid is a hybrid between the two, it is not outside the bound of possibility that it should occur naturally in the mineralising brine.

1.2.4. Sulphide in Fluids

For precipitation of sulphide ore minerals to occur, there must be a source of reduced sulphur with which the metal ions can react at the site of ore deposition. The accepted hypothesis is that hydrogen sulphide is produced by the reduction of calcium sulphate, which can be either that in seawater, or from the solution of anhydrite by formation waters at some stage in their evolution. The main debate, however, is over whether the sulphate reduction is a biochemical or a thermochemical reaction.

Reynolds & Goldhaber (1983) studied iron disulphide mineral production in relation to roll front uranium deposits. The minerals of interest to them were pre-ore pyrite, and ore stage pyrite and marcasite. The conclusion is drawn that bacterial sulphate reduction produced the sulphide for both the pre-ore and ore stage pyrite. The ore stage marcasite,

however, contains sulphide derived from elemental sulphur, or sulphur oxy-anions by abiogenic means. The authors conclude that the controlling factor is the abundance of organic matter present, with bacterial action being important where there is abundant organic matter, and abiogenic reactions being dominant where the quantity of organic matter present is small.

Walker et al (1983) studied the Coxco lead-zinc deposit in Northern Territory, Australia. This is a Proterozoic stratabound deposit in a karstic dolomite host. They conclude that the low temperature of the deposit, the ubiquitous association of organic matter with the sulphide, and the sulphur isotope ratios all suggest that sulphide was produced by sulphate reducing bacteria within the karst system. Such sulphate reduction occurring at the present time was observed by Ferguson et al (1983) offshore from a smelting complex in South Australia, where the waters are enriched in heavy metals. Bacterial sulphate reduction is strongly established, and with concomitant diagenetic reactions leads to dissolved sulphide, iron monosulphides, and trace quantities of pyrite. The high ratio of iron monosulphides to pyrite results from the rapid deposition of the surface layer, and, in deeper sediments, limitations to the oxygen supply.

Lord & Church (1984) studied cores from Delaware Bay salt marshes and found that sulphate reduction is part of the normal sequence of organic diagenesis, involving the

decomposition of organic matter. A major product of this sulphate reduction is pyrite which is the major sink of sulphide within the anaerobic sediments.

There is some support for the theory of abiogenic sulphate reduction e.g. Orr (1975), who states that organic matter alone without the presence of hydrogen sulphide will only reduce sulphate at a very high temperature. Orr states that the thermochemical reduction of sulphate, a reaction well documented at temperatures above 300°C, will also take place at temperatures of 175 - 200°C, which brings it just within the range of interest to this present study. Experimental work has shown that it is a process capable of taking place in geologically significant time, 22% sulphate reduction being obtained experimentally after 620 hours at 250°C (Orr 1975, p.589). In this case the rate of sulphate reduction is limited by the rate of diffusion or mass transfer processes, rather than by any inherently slow reaction kinetics. Inorganic sulphate reduction is therefore a possible precipitation mechanism, though it is thought that for most ore deposits bacterial sulphate reduction will be the dominant process.

1.2.5. The Role of Diagenesis

Organic diagenesis has already been cited as possibly important in ore genesis; the diagenesis of the host rocks themselves is of major importance. The division of 'exhalative'

base metal deposits into 'syngenetic' (i.e. contemporaneous with sedimentation) and 'epigenetic' (i.e. after lithification) can be considered as a measure of the diagenetic state of the host rock. The ore forming processes affecting the host in each case are the same, but the result will differ due to the effect of diagenesis. Badham (in Tarling (Ed.) 1981) suggests that the lead-zinc deposits of the Irish Carboniferous are intermediate in this range; i.e. they show features typical of both syngenetic and epigenetic mineralisation. Here again the nature and advancement of the diagenesis would be a controlling factor on the extent and nature of the mineralisation. Chartrand & Brown (1985) found a record of diagenesis and concurrent ore deposition in the Redstone Copper Belt of Canada. Of the three diagenetic stages they identify, the mineralisation occurs at the beginning of the second, prior to the sealing of fluid pathways due to the formation of neomorphic calcite. Diagenesis in this case probably prevented further mineralisation by the control of the permeability of the host strata. The diagenetic state of the host rock is therefore an important feature of the ore genetic system, as is the result of any diagenesis continuing during the period of ore deposition.

1.2.6. Summary

Mississippi Valley type ore deposits are formed by mineralising fluids moving through carbonate host rocks, which will be undergoing or will have undergone diagenesis at a

depth of up to a few hundred metres. The fluids will be high salinity brines, in a temperature range 100 - 200°C, and will be neutral or slightly acidic. The metal ions and sulphide ions may be carried in two chemically distinct brines, or they may be within the same brine. In the former case, ore precipitation is caused by mixing of the brines, in the latter case the cause is a change in the geochemical conditions. The pressure under which precipitation occurs is not great, due to the shallow level of the host rocks, but it must be great enough to prevent boiling. The base metal ions, leached from the sedimentary prism, must be at concentrations of greater than 10ppm for each metal in order to produce an ore deposit. They may be transported as inorganic complexes, e.g. chloride, polysulphide, or as complex organometallic compounds, e.g. salicylates. The hydrogen sulphide in the system is produced from sulphate, either from seawater or from dissolved anhydrite. The sulphate reduction is probably accomplished by sulphate reducing bacteria, though inorganic thermochemical reduction is also possible. The slowest process in the precipitation phase will be the nucleation of the metal sulphides. Once nucleated, the new mineral grains will grow rapidly by further precipitation, and a major lead-zinc deposit may be formed in a geologically short period of time.

All the processes of ore formation are characteristic features of sedimentary basins, acting in a situation which is favourable for them to concentrate minerals into an ore deposit.

Somewhere among these processes lies the explanation of the hydrocarbon content of the host rocks of these deposits. The aim of any further research should be to determine those processes which are the important controlling factors.

CHAPTER TWO

GAS CHROMATOGRAPHIC ANALYSIS FOR LIGHT HYDROCARBONS.

To allow further investigation of the phenomenon of light hydrocarbon anomalies, suites of samples from two new sites were collected, the sites being chosen with the aim of answering specific questions. One suite of samples, from the Mendip Hills, was analysed to determine whether the petrology of limestones affected their hydrocarbon content. The other suite of samples, from around the Aberfeldy baryte deposit, was analysed to discover whether any hydrocarbon anomaly could be detected in the highly metamorphosed non-carbonate host rock.

2.1. THE ANALYTICAL PROCEDURE.

The analysis of the suites of samples involved the crushing and seiving of the rock samples, after which a measured quantity of the crushed rock was sealed in a bottle. The bottle was then heated, and the headspace gas was analysed, since this should contain any light hydrocarbons driven off during the heating. The method of analysis was essentially that developed by Carter (1981), though some adaptations were made. The analysis was carried out by gas chromatography, a new Perkin Elmer model 8310 gas chromatograph system being used. Figure 2.1a is a fully annotated example of a typical gas chromatogram. The detail shown on this printout has been omitted from chromatograms reproduced later in the text, however the same pattern is followed by all.

2.1.1. Sample Collection

The samples collected were about fist-sized specimens and as fresh as possible, since any trace of vegetation was known to cause considerable contamination of the results. Weathering of the sample surface and the presence of any moss or lichen on the surface were recognised as indications that the sample could produce spurious results on analysis, due to the emission of hydrocarbon and non-hydrocarbon gases from the organic matter. The poor conditions of any such samples was noted in the field, so that their preparation could involve scrupulous cleaning, and so that their analysis could be given extra attention. The sample distribution depended on the nature of the sampling survey undertaken. The survey of the Mendips limestones comprised collection of samples of many different carbonate lithologies over a restricted area. The survey undertaken around the Aberfeldy baryte deposit, on the other hand, covered a much wider area, and, as far as the poor outcrop allowed, followed the plan of sample collection over a grid pattern typical of a reconnaissance exploration programme. The different types of sample collection programme are commensurate with the differing aims of the two surveys.

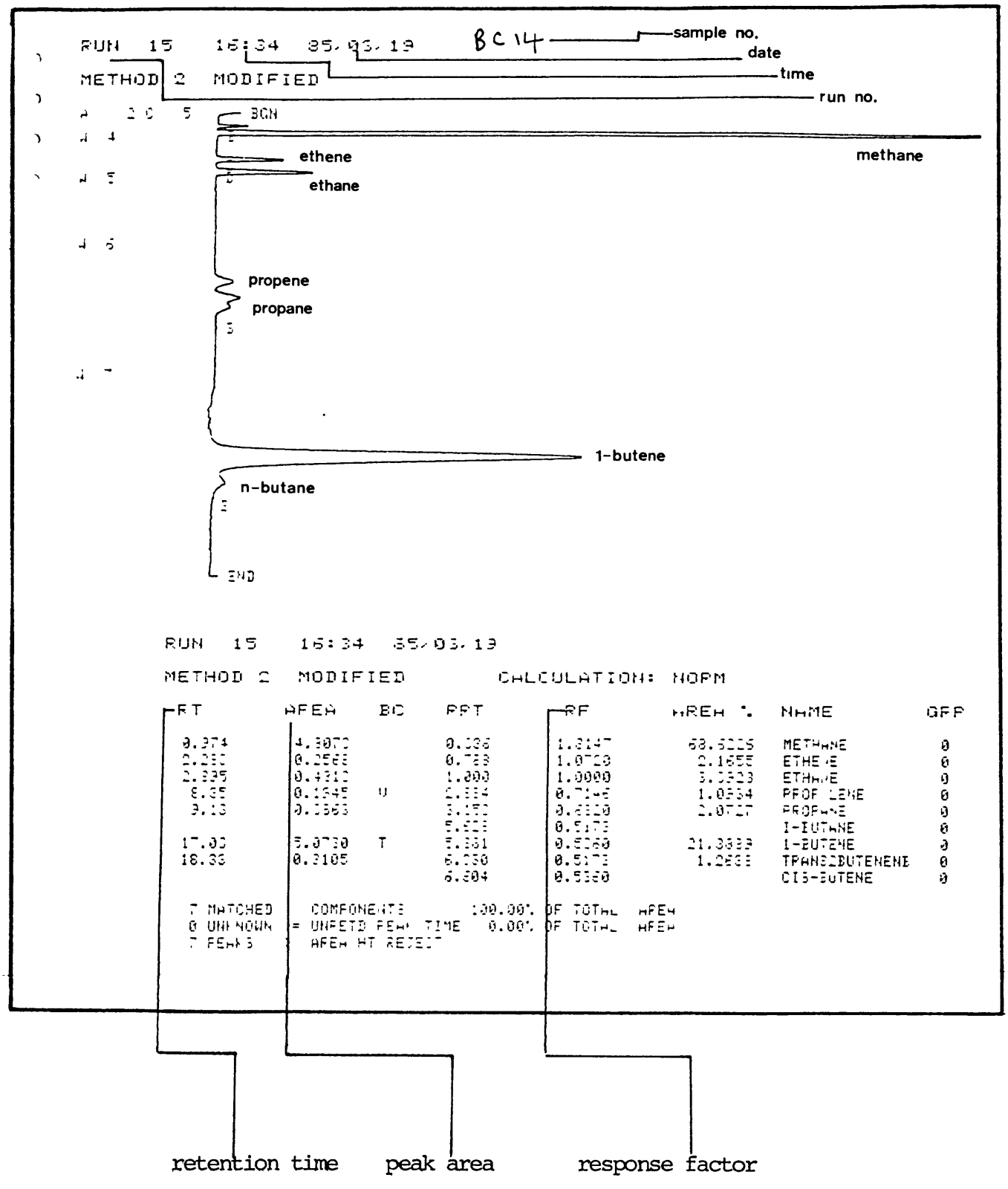
2.1.2. Sample Preparation

The sample to be analysed was first crushed, the rocks being split into small pieces prior to fine crushing to that any badly vegetated fragments could be discarded. The

remaining pieces were then put through a jaw crusher, the crushed rock was seived, and the 1 - 2mm size fraction was chosen for analysis. The restricted grain size range was an attempt to ensure the homogeneity of subsamples, and to avoid the possibility of subsamples being of different grade. It was known that homogeneous samples varying only in grain size have different hydrocarbon gas contents, due to the escape of some gas during crushing (Carter & Cazalet 1985, p.A3). After crushing and seiving, the fines were discarded, but the coarsely crushed material was retained for further crushing, in case the need arose.

Subsamples of the crushed rock were weighed out and sealed in a glass bottle, and the bottle was heated in a fan oven for 2½ hours at 200°C, and then left to cool to room temperature. The heating process caused hydrocarbons to be driven out of the crushed rock and into the headspace, and this headspace gas was then analysed. At the start of the research the bottles available for use in the analyses were 125ml. glass serum bottles. Different amounts of crushed rock obviously produce different amounts of gas, and it was found that if less than 15g of rock were used, the gas hardly registered on the chromatograph. Figure 2.1b shows the results of using 15g, 20g and 25g of the same crushed sample in the 125ml bottle. Of these the 25g sample gave the best result, and a sample of that size was really necessary to prevent dilution of the hydrocarbons emitted, by air already in the headspace, to an

Figure 2.1a: Example of Gas Chromatogram and Results Printout.

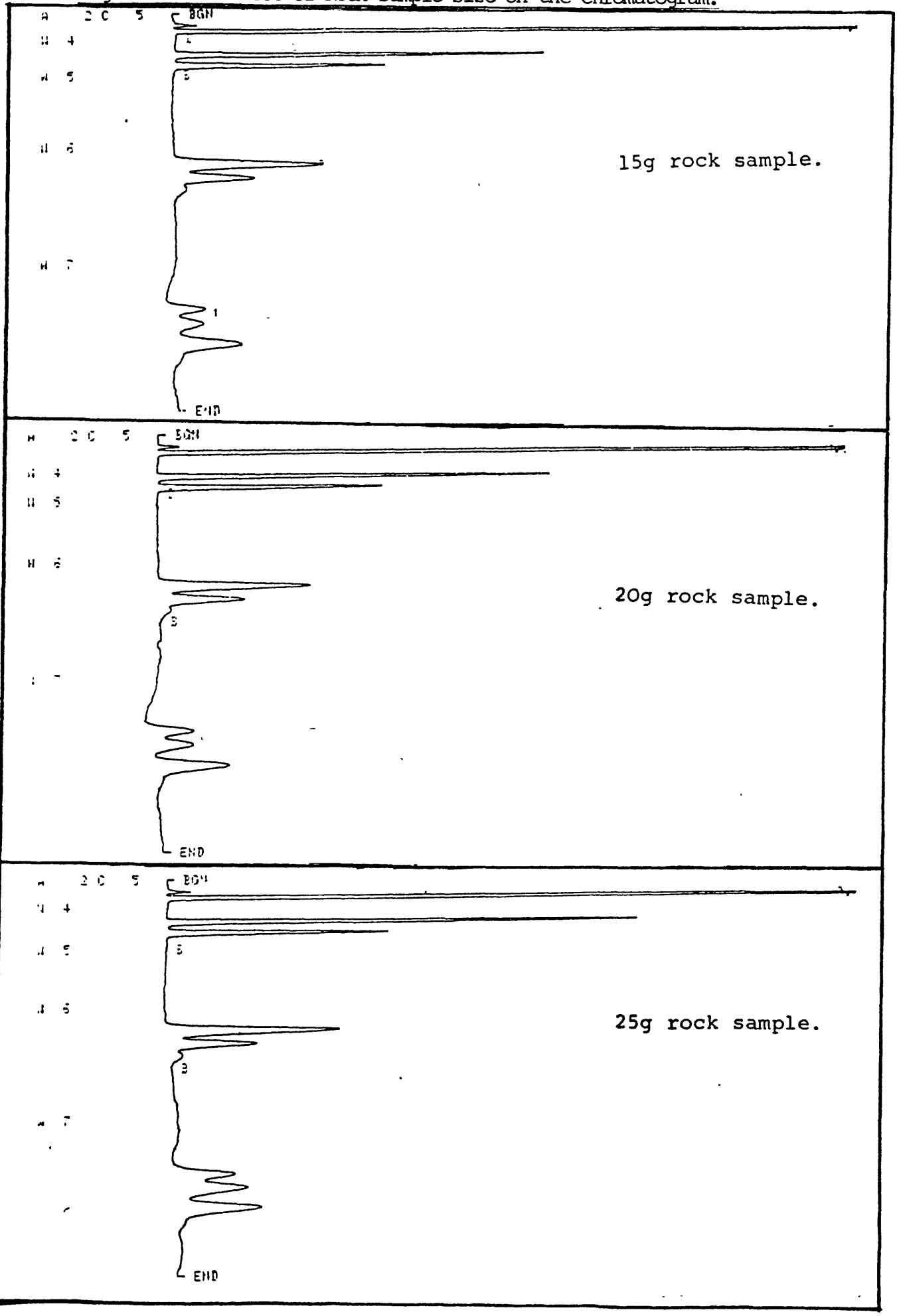


$$\text{AREA \% } (x) = \frac{\text{AREA}(x).\text{RF}(x)}{\Sigma(\text{AREA}(i).\text{RF}(i))}$$

unacceptable level. There were problems with using this size of sample, however. Firstly, the larger the volume of crushed rock, the more likely it was that some of the hydrocarbons would have remained within the rock volume and not escaped into the headspace. The second problem was probably more important and involved the availability of the sample. The original specimen, possibly quite small, was crushed, the fines were discarded, and the 1 - 2mm size fraction was chosen for analysis. Only a small proportion of the sample would fall into this category, perhaps not enough to make the duplicate 25g analyses that may have been necessary. It would be possible to crush down the coarser material to the required size, but all the time much would be unavoidably lost to fines. A smaller subsample was therefore considered preferable. 50ml glass serum bottles were obtained, and 10g subsamples of crushed rock were used, giving the same rock/bottle volume ratio as 25g in 125ml, but avoiding the attendant problems.

The glass bottles were sealed with a silicone rubber seal and an aluminium cap which were crimped into place. The seals had to be silicone rubber since the alternative, butyl rubber could generate hydrocarbons on heating. The aluminium caps had a central hole through which a hypodermic needle could be inserted to withdraw a sample of the headspace gas. Figure 2.1c is a representation of the sample preparation procedure and the equipment used.

Figure 2.1b: Effect of Rock Sample Size on the Chromatogram.



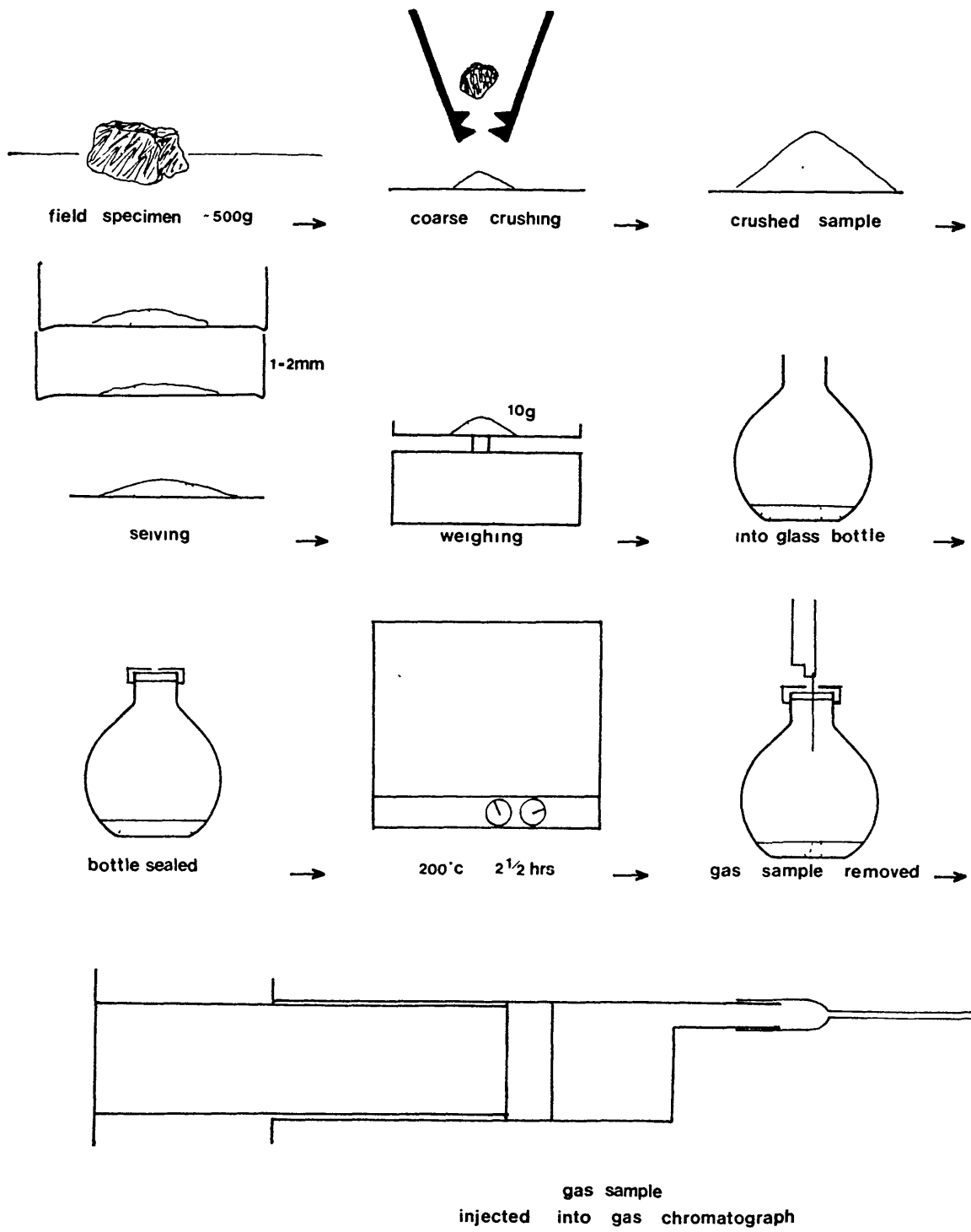
2.1.3. Analytical Procedure

After the weighed subsample had been sealed in the bottle, this was heated for 2½ hours at 200°C, and allowed to cool to room temperature. The headspace gas, containing hydrocarbons, was sampled by means of a syringe with a hypodermic needle, inserted through the bottle seal. A good supply of these needles was available, as was a piece of fine wire which was used to clear pieces of seal from the needle. Although such pieces of seal were very small, they could block the needle quite effectively, so preventing a full sample of gas being taken. A standard amount of gas was removed for each analysis; in this case 6ml was chosen. This was small enough to avoid inducing a partial vacuum in the bottle, but large enough to provide a full sample of gas for injection into the gas chromatograph column. The number of samples analysed per day depended on the time per analysis, which in turn depended on the conditions under which the chromatograph was being run (see section 2.1.4. - following). During this research two different sets of conditions were used, one giving an analytical run lasting twenty-five minutes, the other giving a run time of fifteen minutes, so the number of samples analysed per day varied accordingly. It was found to be most efficient if the bottles were heated in a batch in the late afternoon, allowed to cool overnight, and analysed the following day. Preliminary experiments showed that once the bottles had cooled to room temperature, they could be left as long as this before analysis, with no obvious effect on the analytical results.

2.1.4. Gas Chromatography

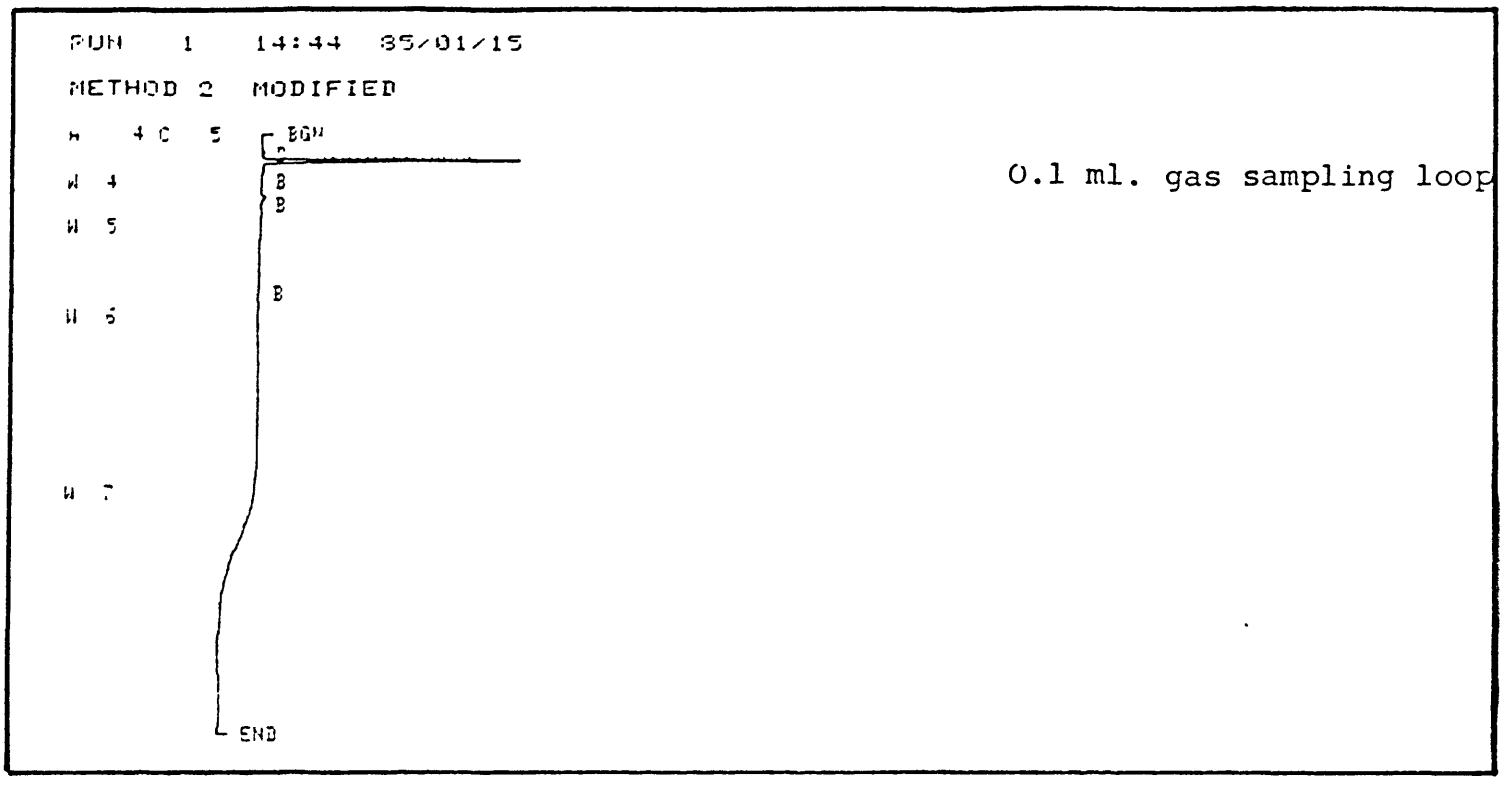
The method of analysis by gas chromatography depends on a certain amount of a mixture of gases being introduced onto the heated chromatographic column, separated into the constituent gases, and analysed by a flame ionisation detector. The first stage in setting up a successful analytical system was to introduce enough of the gas sample. The sample of headspace gas that had been taken into the syringe was introduced into the unheated injector of the chromatograph via a gas sampling loop. This loop was flooded with the gas from the syringe, and once it was full, the gas was injected from the loop onto the chromatograph column. This method ensured that precisely the same amount of gas was analysed on every analytical run. Two sizes of gas sampling loop were available, 0.1ml and 0.5ml, the size of the loop determining the amount of gas analysed. The choice of loop size depended on the concentration of hydrocarbons within the gas sample. For these analyses the concentration of hydrocarbons was often low, so the larger gas sampling loop was used, in order to introduce as much hydrocarbon as possible into the system, to ensure the gases would be present in concentrations well above the detection limit. Figure 2.1d illustrates the difference in analyses using the two sizes of gas sampling loop; these were two early tests, the low rock/bottle volume ratio being responsible for the poor quality of the chromatograms.

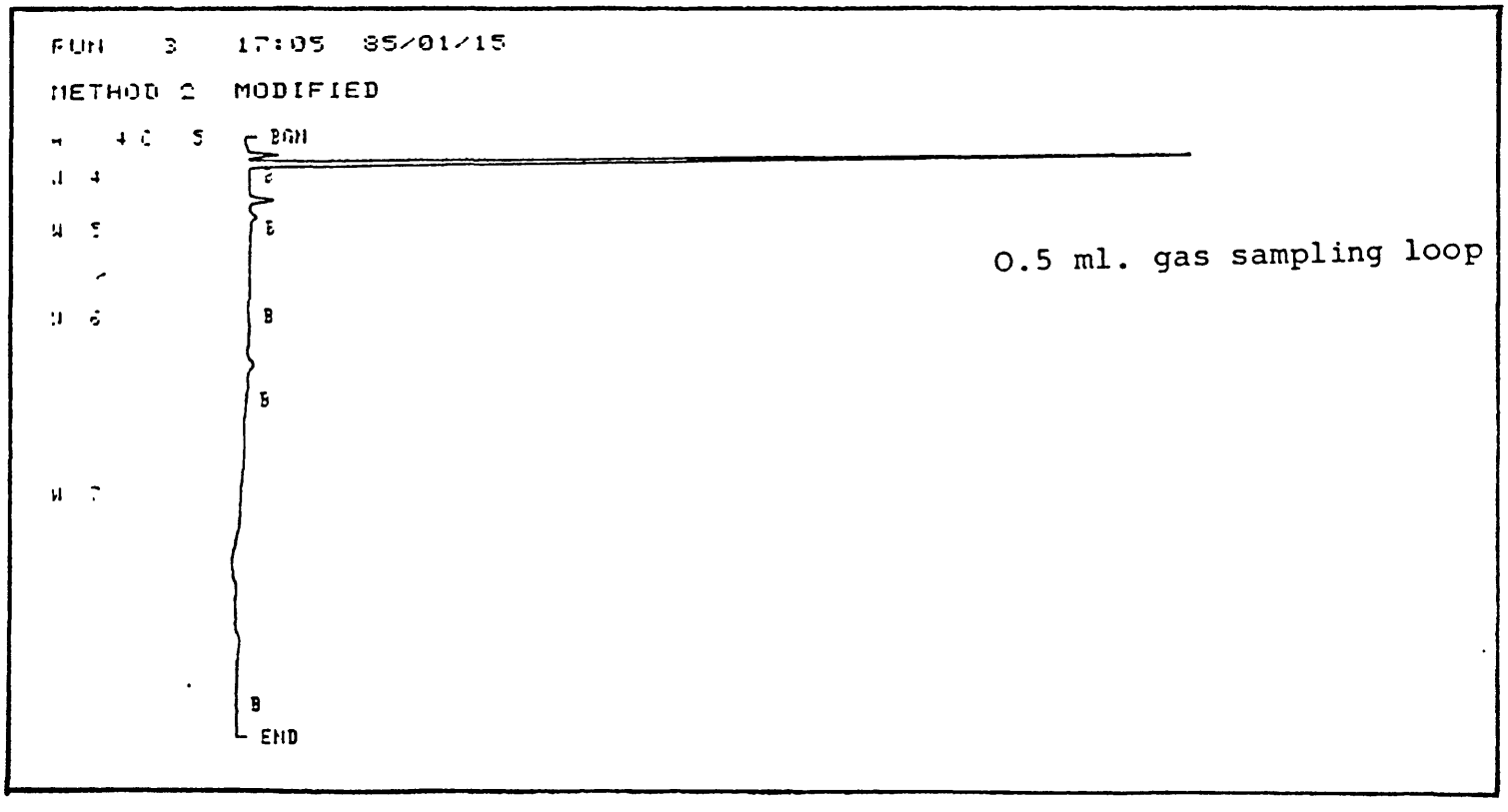
Figure 2.1c: Stages in the Preparation of Samples for Analysis.



Once the gas sampling loop had been opened onto the column, the analytical run began. The gas sample, a mixture of light hydrocarbons in air, was taken through the column by a steady flow of a carrier gas, which in this case was helium. The chromatographic column itself was two metres in length, and filled with a packing of 'Poropak Q' of 80 - 100 mesh size. As the gases flowed through the column they became separated due to their partition between the mobile and stationary phases, i.e. between the helium and the packing of the column. The gases of smallest molecular weight were able to travel more rapidly through the column than those with larger molecules. At the end of the column the gas mixture was therefore split into the separate gases, each of which had come through the column at a different rate. The gases passed through a hydrogen flame at the end of the column. This flame ionised the gases (flame ionisation detection), so producing an electrical pulse at the passage of every gas, a pulse which was translated into a peak on the chromatogram displayed on a V.D.U. or chart recorder. The amount of current producing these peaks could be altered (or 'attenuated') to change the apparent size of the peaks on the screen or printer, so that the whole chromatogram could be viewed at once. Altering the attenuation obviously caused only a cosmetic change in the chromatogram; the actual peak areas were not affected. The time taken for a gas to pass through the column, the 'retention time', was known to be constant for that gas under certain conditions. The gas chromatograph had been calibrated

Figure 2.1d: Effect of Sampling Loop Size on the Chromatogram.

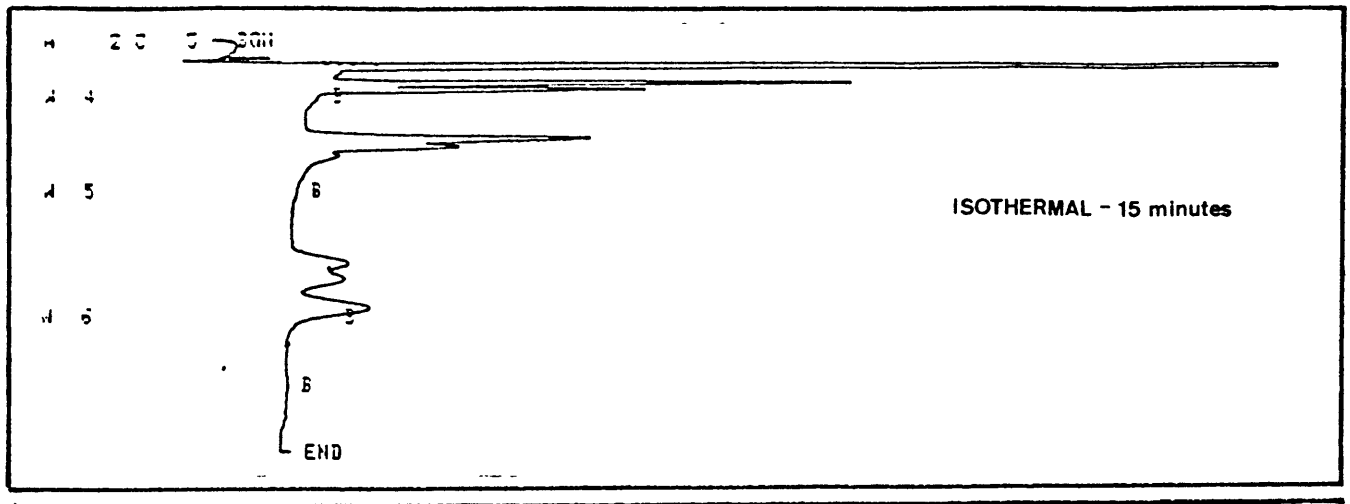


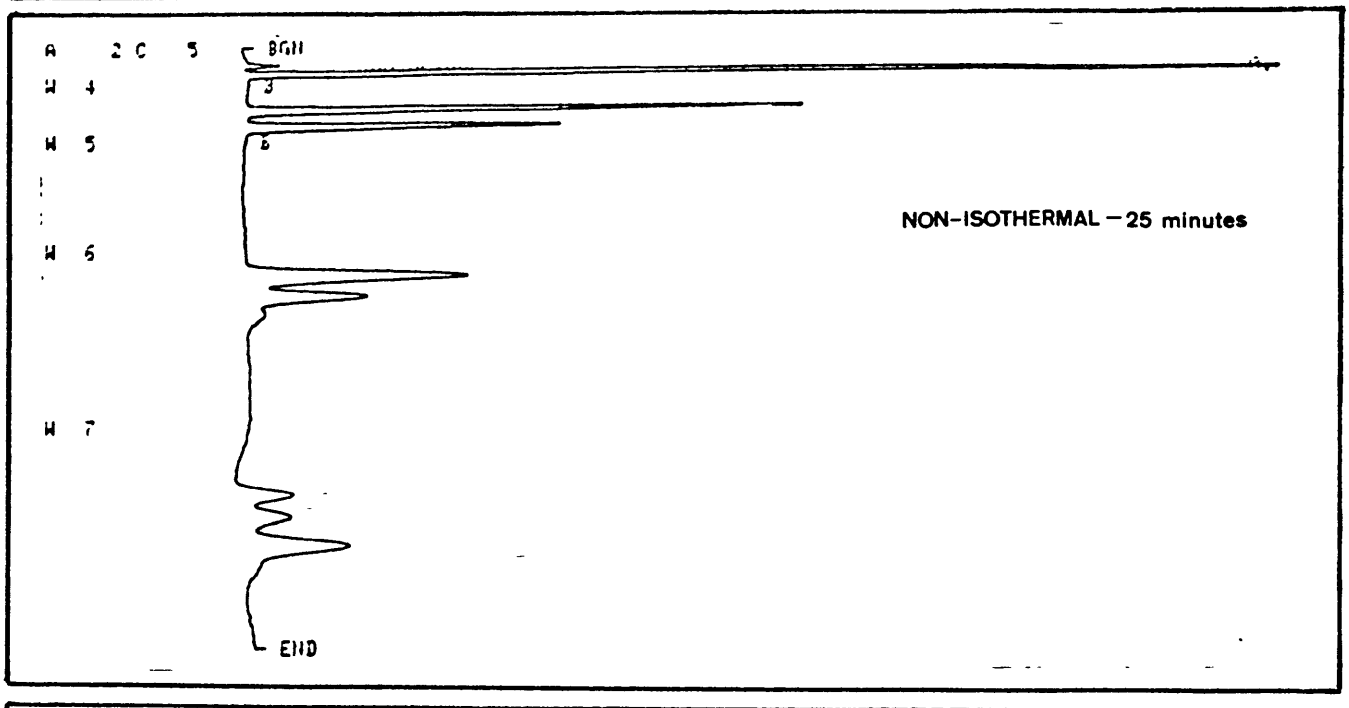


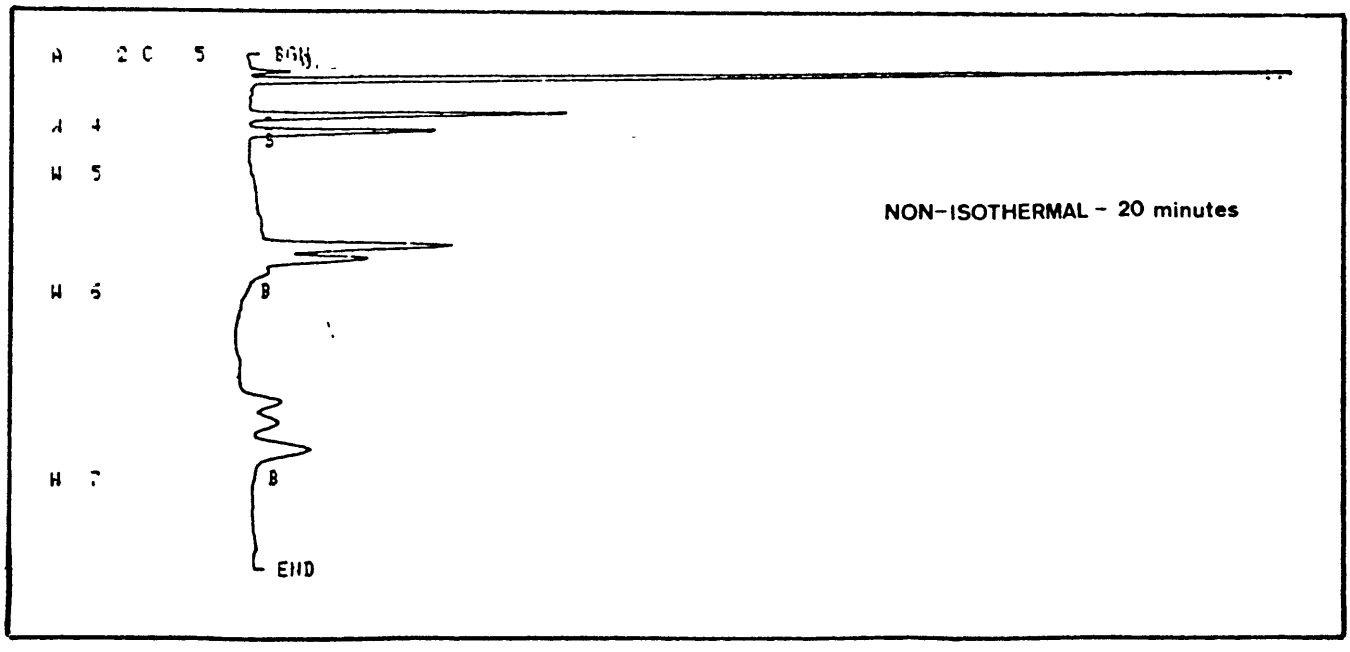
using standard gas mixtures containing known concentrations of the hydrocarbon gases, and identified the peaks caused by the passage of each gas by the retention times. A computerised integrator in the system calculated the area under each peak, and, from this information, the percentage of each component present.

During the analytical run, the chromatographic column was heated, and the temperature at which it was held was varied to produce different results. It was possible for the column to be at the same temperature throughout the analysis (isothermal running), or for the temperature to be changed (non-isothermal running). During isothermal running the column temperature was held at 130°C and the gases came through the column quickly. At this temperature analysis for gases up to and including the C_4 gases could be accomplished in fifteen minutes, but the resolution was poor,with gases not always being fully separated, two components sometimes giving a single merged peak. During non-isothermal running, the column began at one temperature, and was heated during the run to a higher temperature. The lenght of time at the steady temperatures, the temperatures themselves, and the ramp rate between them could be varied. This allowed conditions to be chosen where optimum separation of the gases could be accomplished in minimum time. Figure 2.1e illustrates the

Figure 2.1e: Different Running Conditions of Gas Chromatograph.







effect of different chromatograph running conditions on the analysis of gas from the same rock sample. The upper run was carried out under isothermal conditions at 130°C, and the gases were poorly separated. The central run had the column at 80°C for five minutes, ten minutes with a ramp rate of 5°C per minute, and ten minutes at 130°C. The time per analysis for these conditions was twenty-five minutes compared to fifteen minutes for the isothermal conditions, but the resolution can be seen to be much better. The lower non-isothermal run in figure 2.1e also began with the column at 80°C for five minutes, and ended with the column at 130°C for ten minutes. The ramp rate between these temperatures was greater, however, being 10°C per minute for five minutes. This gave a run time of twenty minutes per analysis, but again the accuracy of the analysis was sacrified to speed.

The two analytical surveys undertaken for this research had vastly different aims, and different chromatographic conditions were used in each case to suit those aims. The survey of the Mendips limestones attempted to relate the hydrocarbon content to the petrology of the samples (section 2.2.) so it was important to have details of all the gases present. For these analyses the non-isothermal method at the centre of figure 2.1e was used, since it gave the most accurate analyses. The second survey, of the Aberfeldy area, was an attempt to simulate the use of the detection of a methane anomaly in mineral exploration. The methane value was therefore of most importance, and the analyses were to be

done in as little time as possible. The speed of the isothermal method was therefore attractive, and the loss of resolution on the higher order gases was unimportant, since this did not affect the methane value. These samples were analysed isothermally at 130°C.

2.1.5. Data Treatment and Presentation

The gas chromatograph as set up was capable of identifying nine light hydrocarbon gases - those illustrated in figure 1.1d. The printout of results gave the area percentages of all of these gases, as well as the chromatogram peak from which the percentages were calculated. Not all of this data was used in the interpretation of results; it was reduced to certain key indices. These were the percentages of certain gases (e.g. methane, 1-butene) present in the analysed sample, and the total area under the chromatogram. This latter index was in arbitrary integrator units, but was proportional to the total amount of hydrocarbon present, and so allowed useful comparison between samples. The decision was made not to present the data as a 'parts per billion' value, calculated from the peak areas, as had been done in the past (Carter 1981, p.51). This decision was made on the basis of two factors: that the calculation used was at best an approximation, and that the resulting value was open to misinterpretation. The calculation used by Carter (1981) to convert the amount of hydrocarbons from integrator units to parts per billion used an approximate conversion factor.

This introduced an error, different for every gas, and while this was found to be small compared to the calculated values, it seemed better to avoid such error altogether. What appeared to be more important than this, however, was the ambiguity of the parts per billion value. Most results presented in this manner are absolute measures of concentration, e.g. parts of ionic copper per billion parts of pore water. The concentration of hydrocarbons as measured by the gas chromatograph was by its very nature not this sort of absolute value. The values given were not even a true measure of the amount of hydrocarbon emitted during heating, since the gas samples were allowed to cool and equilibrate before analysis. The values were certainly not a measure of the hydrocarbon within the crushed rock sample; it is not known what proportion of the total rock gas content is released by the method of sample preparation. The presentation of the results as a parts per billion value, suggesting a measure of hydrocarbons present in the rock, was therefore thought to be at best slightly ambiguous, and possibly misleading. It was decided to use the chromatogram peak areas, and the percentage values calculated from these as a simpler and more accurate way of presenting the data, rather than use a parts per billion value which was, after all, no more than a further mathematical derivation of the chromatogram peak area. For the record it should be noted that analysis of limestones from the Northern Pennines by the British Gas Corporation gave absolute values for the hydrocarbon content of the rocks

(Ferguson 1984, p.68). The values given for the concentration of methane in the rocks range from 1000ppb weight/weight to 50,000ppb W/W, and suggest the approximate range for absolute concentration in similar areas elsewhere.

At all times it was attempted to keep the data treatment and presentation as simple as possible. Maps were drawn up using the indices mentioned above, and where it was necessary to classify the data, a simple median and percentile method was followed. Details of the treatment of the data sets can be found in the appropriate sections: 2.2.3. for the Mendips survey, and 2.3.3. for the Aberfeldy survey.

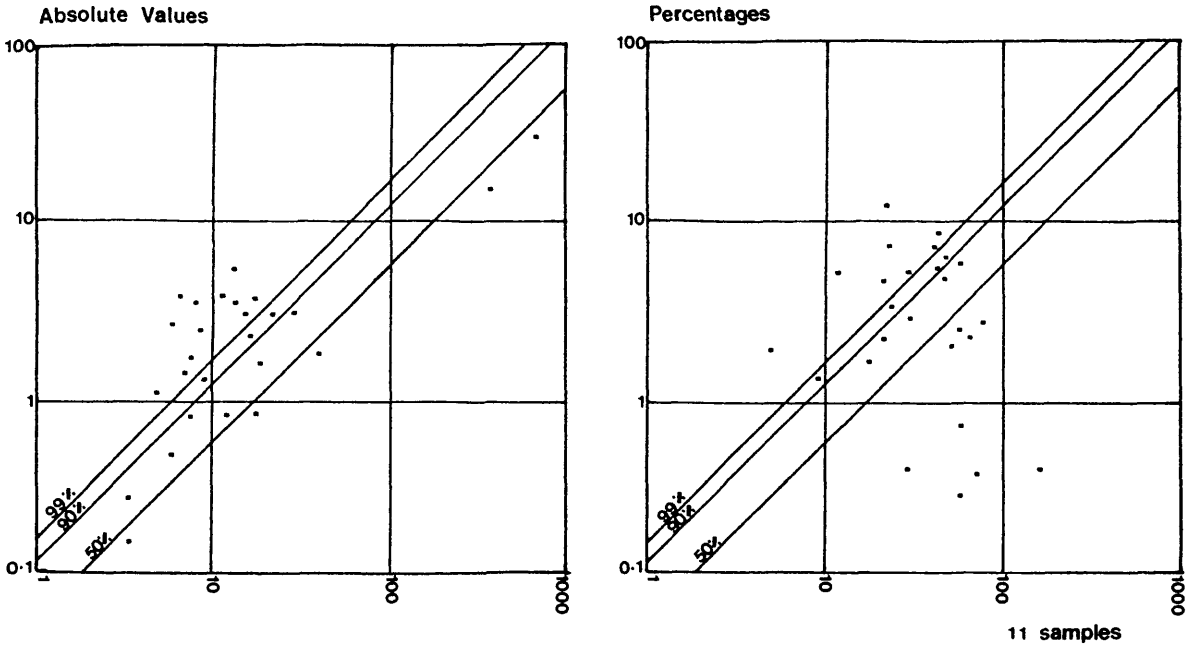
2.1.6. Analytical Quality Control

Quality control procedure involved randomisation of samples for analysis; bottle blanks and machine blanks; testing of calibration with standard gas mixtures; and duplicate analyses. From the latter procedure it was possible to form an idea of the precision of the analytical method. The method of Thompson & Howarth (1978) was followed in the collation of precision charts; the resulting charts form figure 2.1f. The duplicate analyses were used to calculate the mean of any variable and the difference between the duplicate results of the same variable. These were then used to plot on the chart. The charts used here are for ten percent precision with a coefficient of variation of 0.05, a high enough standard for any analytical method to be considered

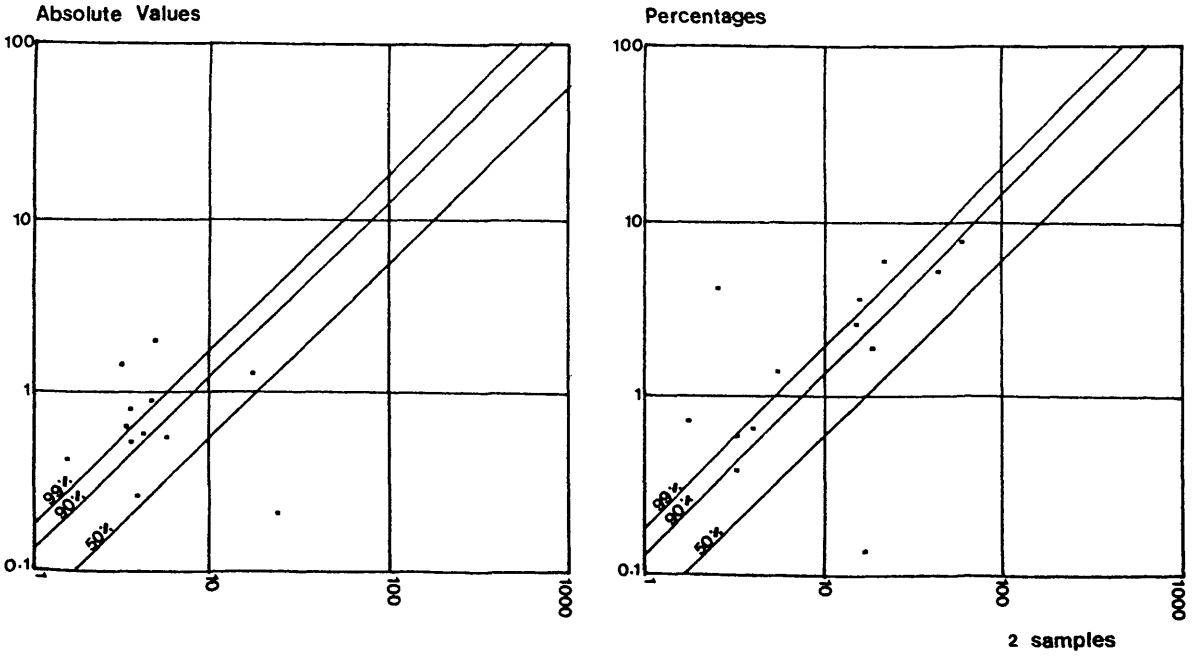
Figure 2.1f: Ten Percent Precision Charts.

(see also Appendix C)

NON-ISOTHERMAL CONDITIONS



ISOTHERMAL CONDITIONS

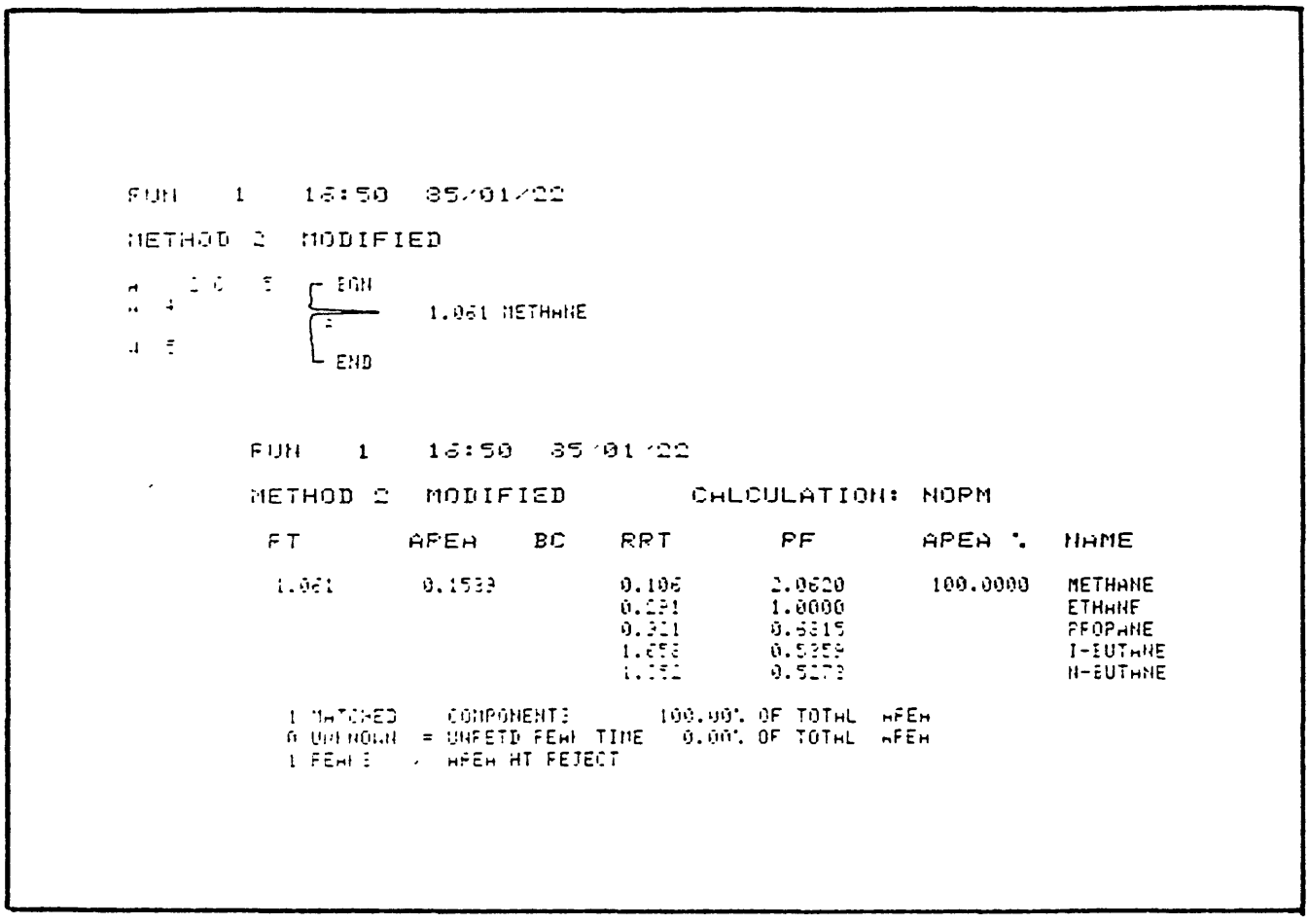


reliable. At 10% precision, 50% of the points plotted on the chart should lie below the 50% line etc. As can be seen from the charts, the precision of the absolute results was poor, but, while being still far from ideal, the precision of the percentage results was much better than the precision of the absolute results. This agreed with precision data from previous analyses of the same kind (Carter 1981, p.48), and stressed an important feature of these analyses. The single results should not be given any great importance; the overall pattern of the analyses, and comparative values were considered more important to study. By studying the results in this way it was hoped to avoid the problems caused by the general imprecision of the data.

The blank runs were undertaken either by heating a sealed bottle with no sample and analysing the headspace gas from this, or by running the gas chromatograph with no gas sample in it. In both cases the result was the same (figure 2.1g) - a small methane peak was all that was seen. Since this was the same for both types of blank it was assumed that this peak was formed by a small amount of gas remaining on the column between analyses. Since the quantity involved was negligible, and the same for every run, the effect of this carry-over was ignored.

The poor quality of the data was a result of the heterogeneity of the crushed rock sample, and error introduced during the analyses. Within a rock mass the hydrocarbons

Figure 2.1g: First Four Minutes of a Blank Run.



would be present in different concentrations depending on their presence in pore space, absorbed onto different mineral grains etc. The crushing of the rock, and the selection of a restricted size range for analysis was an attempt to render the crushed sample homogeneous, but even so some variation in the sample properties was to be expected. The method of weighing the subsamples on a top loading balance gave samples of 10g ± 0.5g, and the accuracy of this could obviously have been improved by using a chemical balance. As with the other stages of sample preparation and analysis it was considered more important to keep the method quick and simple, and the error in the results due to slight variations in the sample size was accepted. Slight differences in the dimensions of the bottles, and the temperature and duration of heating would also have some effect, though this would be small, and was largely unavoidable.

Some error is likely to be introduced by any analytical system, and when that system was running at high sensitivity, as was the chromatograph here, then that random error was likely to be all the more noticeable. However, such error was likely to be very small compared to that from other sources, and no systematic drift was ever noticed during the analyses.

The precision of the data could therefore probably have been improved by greater care during sample preparation etc., though the problem of sample heterogeneity could not easily have been solved. The random variations in the data were, however,

small compared to variations due to other effects, e.g. lithology etc. It was considered better to accept the limitations to the precision of the data, and to remember always to study the data sets as a whole, rather than attach any great importance to individual results.

2.1.7. Reproducibility of Results

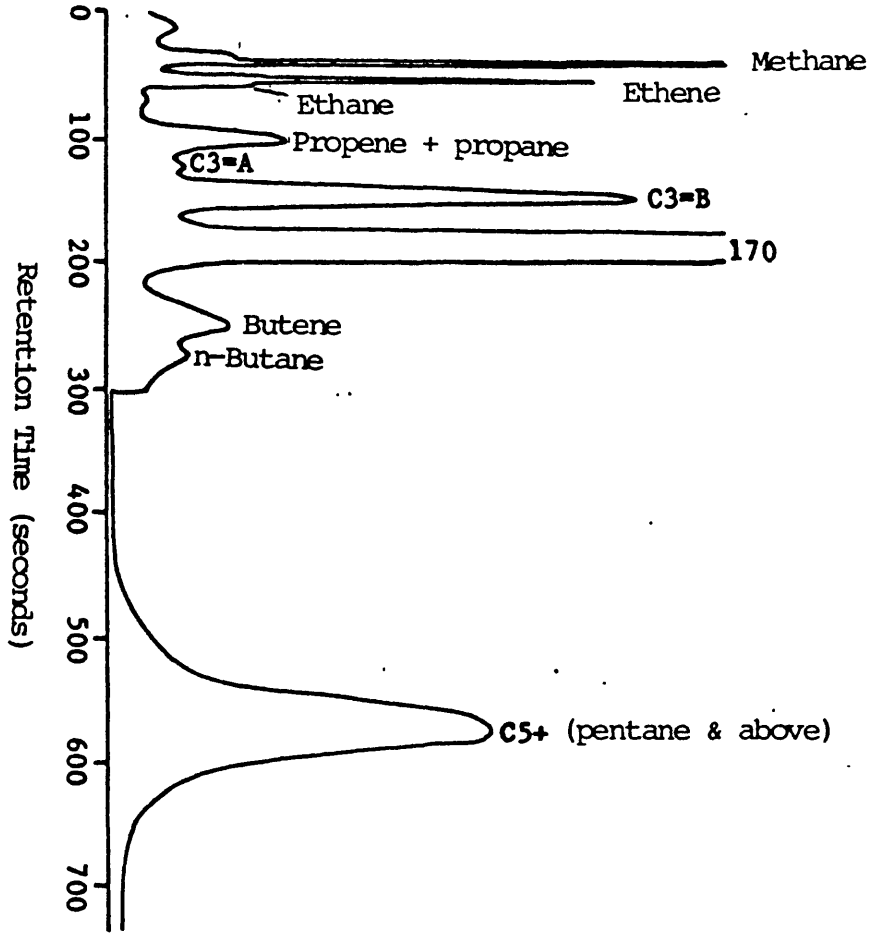
Some analyses carried out for this research were duplicated on the gas chromatograph at Mercury Hydrocarbons (see section 1.1.). It was considered important to do this to determine how compatible the two systems were since this is vital for the application of such analyses in mineral exploration. The gas chromatograph systems are of different makes, that at Imperial College being a Perkin-Elmer model 8310 gas chromatograph, and that at Mercury Hydrocarbons being a Pye-Unicam PU 4500. The latter chromatograph has a larger gas sampling loop (1ml as against 0.5ml) so that more gas goes onto the column; the injector is heated while that at Imperial College is not; and the carrier gas is nitrogen rather than helium; however the same length and packing of column are used in both systems. The aim of both chromatographs is the same, that is to separate mixtures of hydrocarbon gases into their constituents, and to identify and quantify these. The differences in the chromatograph specifications should not affect their ability to do this.

There were two differences in the manner of running of the chromatographs. At Mercury Hydrocarbons all the samples were analysed isothermally at 135°C, whereas, as has been described previously, at Imperial College both isothermal and non-isothermal conditions were used in the analyses for the present research. The second difference involves the fate of the gases of higher order than C_4. The Perkin-Elmer system used at Imperial College was not set up to identify any gas after cis-2-butene, the analytical run being terminated at that point. The Pye-Unicam system of Mercury Hydrocarbons had two packed columns, and when the C_4 gases had been flushed through the first column, the flow of carrier gas was reversed, and any remaining gas was flushed through the second column in the opposite direction. This was all emitted from the column as a single peak, known as the 'backflush peak'. The value for the gases of C_5 and above was not available to the present research, though this did not seem to be a great disadvantage; during the research the only samples encountered that contained significant amounts of higher order gases were those where the analyses was contaminated by gases emitted by traces of vegetation in the crushed rock sample.

If the presence of the backflush peak was ignored, it might be expected that the two chromatograph systems would have produced similar analyses. Instead of this some extraordinary differences were seen, not least in the presence in the analyses by Mercury Hydrocarbons of gas components which failed

Figure 2.1h: Gas Chromatogram Showing the Unidentified Gases.

(after Carter 1985)



to be detected by the system at Imperial College. These gases had appeared in most of the previous analyses undertaken at Mercury Hydrocarbons, and had been termed 'C3=A', 'C3=B' and '170', though they had never been identified. The chromatograph reproduced in figure 2.1h indicates how the first two gases were usually present in small quantities, while the latter, the '170' gas, could be a major constituent of the analysed gas. All these gases appeared between propane and i-butane, appeared more dominant in samples affected be vegetation, and had been included in the calculation of percentage values for the plotting of 'hydrocarbon halo' maps. The rocks analysed at Imperial College did not give any of these gases. It was suggested a certain amount of seasoning of a new column would be necessary before these gases would be detected (Carter 1984, pers.comm.); grass blades were used in place of rock samples to season the chromatograph at Mercury Hydrocarbons when it was first used. This procedure was not followed at Imperial College; should such conditioning be necessary, it was felt that the analysis of two hundred rock samples should accomplish this. In fact the only samples that did produce these gases on analysis were artificial limestones produced in pressure cells (as described in section 5.3.), and the charge material used for this; large amounts of the '170' gas was found on analyses of these samples. Full discussion on the nature of the gas is included in the appropriate section (section 5.3.3.); suffice it to say here that it is now considered that the '170' component is

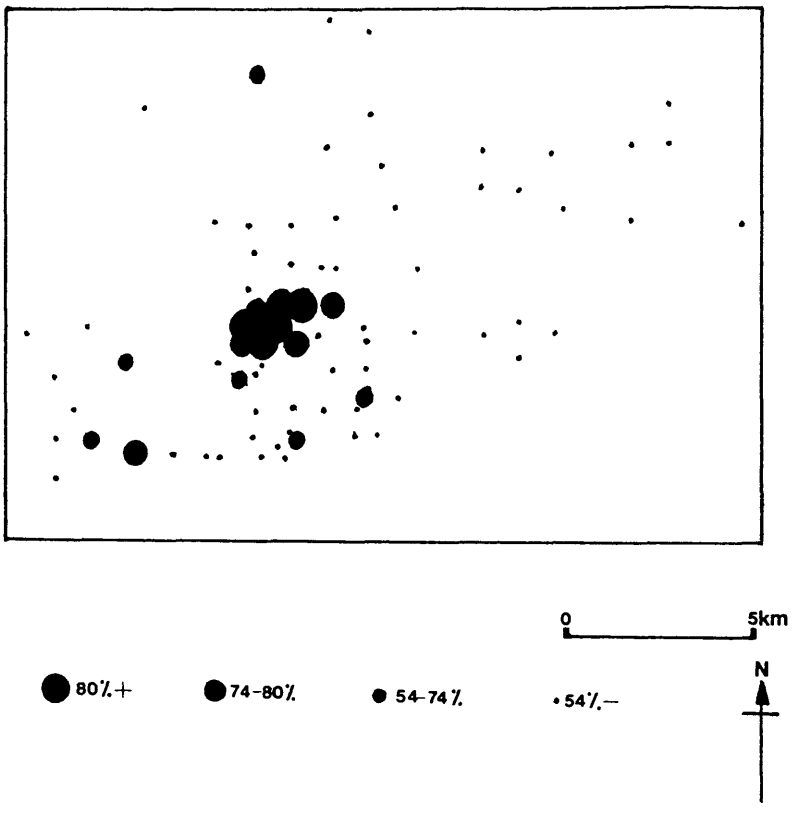
formaldehyde, generated by the heating of plant material, and that the other two gases are likewise non-hydrocarbons, which are contaminants rather than being part of the rock gas assemblages. It is possible that the treatment of the chromatograph at Mercury Hydrocarbons with grass samples (surely rich in formaldehyde) caused some of the gas to be adsorbed onto the machine, to be liberated piecemeal by passing hydrocarbon at every subsequent analysis. This, however, is merely conjecture. What is important is that it seems these gases were probably contaminants, and should therefore not have been included in the analytical data set as they had been in the past. Data available on two areas previously studied by Mercury Hydrocarbons were recalculated to omit the unidentified gases, in an attempt to ascertain whether their inclusion in the data had affected the identification of a hydrocarbon anomaly. The results are illustrated in figures 2.1i and 2.1j, and as can be seen the methane anomaly results were very similar, whether the unidentified gases were included or not, for both a mineralised and a non-mineralised area. This means that previous work in which these gases were included still stands, at least for the methane anomalies, though some doubt must be cast on the presence of halo patterns, in which values for these gases were often included in complex ratios.

The results of the duplicate analyses performed at Mercury Hydrocarbons were recalculated, omitting the backflush peak, and the unidentified gases, so that they could be better

Figure 2.1i:Methane Halo Around the Mallow Ore Deposit, Ireland.

(after Carter 1981)

Methane percentage- data including unidentified gas.



Methane percentage- data excluding unidentified gas.

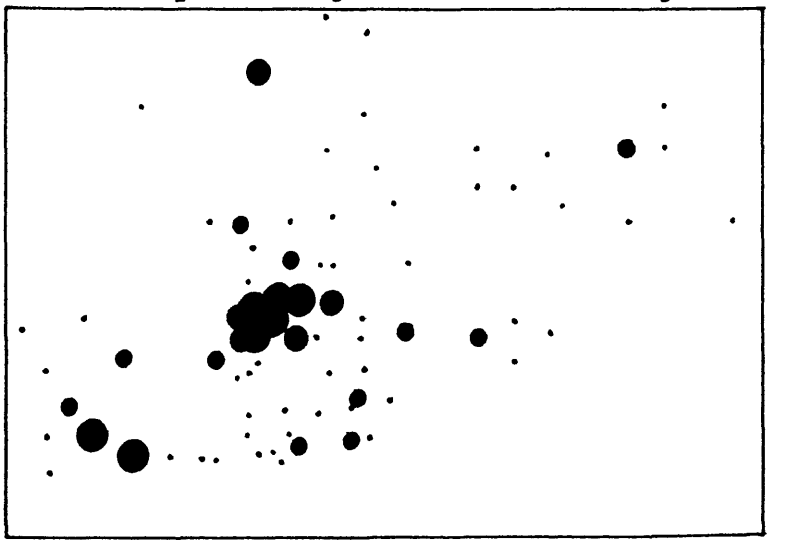
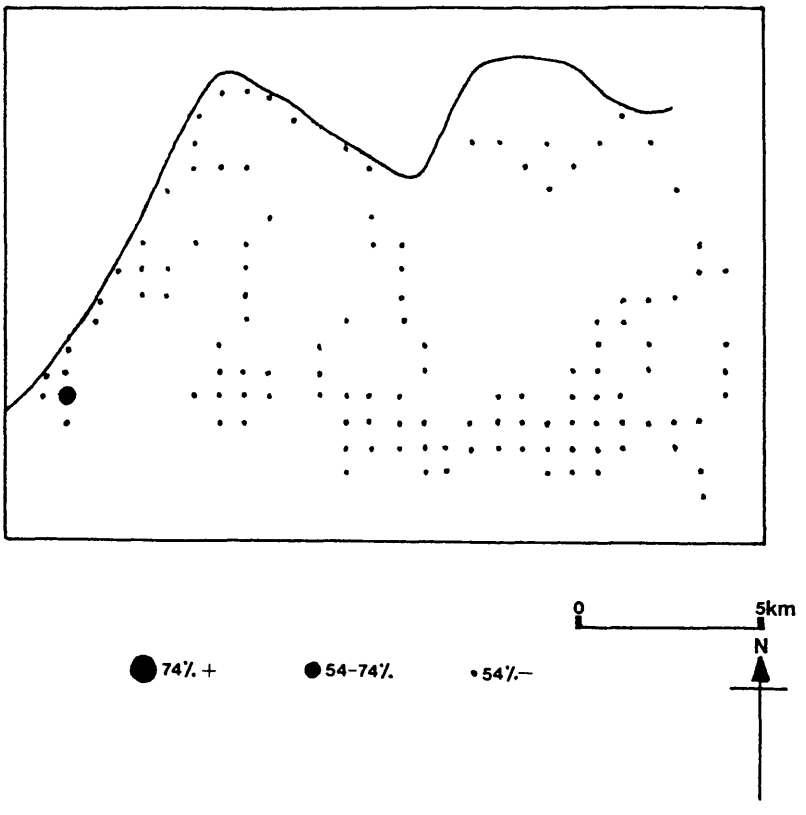


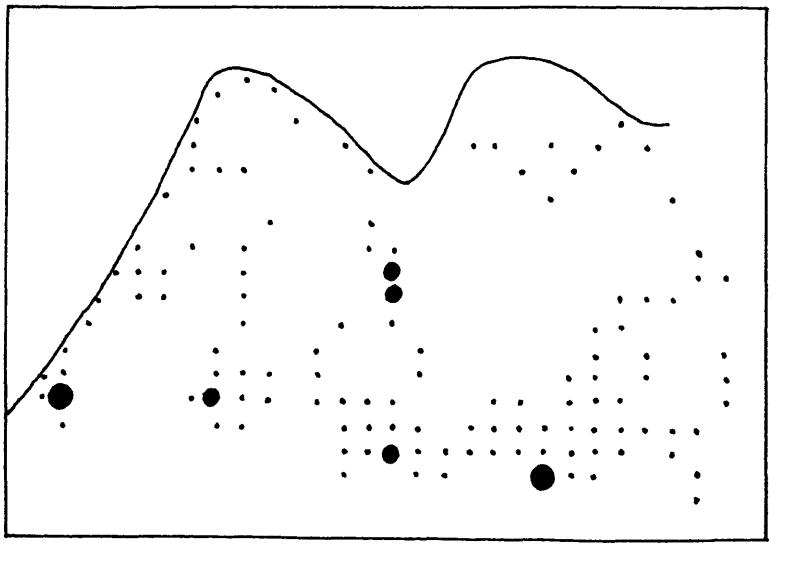
Figure 2.1j: Methane Content in an Unmineralized Area - The Burren, Ireland.

(after Carter 1983)

Methane percentage- data including unidentified gas.



Methane percentage- data excluding unidentified gas.



compared to the analyses undertaken at Imperial College. Table 2.1a gives the results of analysing the samples on the two systems, after this recalculation. The fundamental pattern was found to be the same, with a large methane peak, a secondary 1-butene peak, and the remaining gases subordinate to these. Sample B gave very similar results, but the other samples showed major differences which were a little hard to excuse. Taking the methane percentage, for instance, the difference between 57% and 64% (sample E) was considered negligible, since they would be likely to fall in the same class of data, so the difference would have no effect on any overall pattern. The differences between 41% and 70% (sample C) or between 66% and 83% (sample D) were more startling, since these values were considered likely to be in classes at the extremes of the range in methane values. The two chromatograph systems would therefore obviously produce different results for individual samples, and since there is no immediate explanation for the discrepancy between these particular systems, it must be assumed that any two chromatograph systems would similarly produce different results. It has, however, already been noted that the important information from the analyses came from the survey of many samples, and not from individual analyses. It is hoped, though by no means proven, that if a regional survey was undertaken by two systems, any methane anomaly present would be detected by both, though the details of the analyses might vary.

Table 2.1a Differences in Analysis by Two Chromatograph Systems.

	Sample A	Sample B	Sample C	Sample D	Sample E
Pye-Unicam System: (Dr.J.S.Carter)					
Methane %	53.98	61.64	41.04	65.79	63.83
Ethene %	3.49	3.72	1.25	1.16	9.05
Ethane %	6.35	0.97	17.77	5.22	1.57
Propene+ Propane %	9.26	4.09	16.83	0.30	10.99
i-Butane %	0.00	0.00	0.00	0.00	0.00
1-Butene %	26.91	29.58	16.02	27.52	11.78
n-Butane %	0.00	0.00	7.08	0.00	2.78
Perkin-Elmer System: (S.Goodman)					
Methane %	67.19	61.91	70.26	82.79	57.19
Ethene %	2.48	2.71	0.63	0.00	7.24
Ethane %	5.78	0.95	13.52	4.06	2.55
Propene %	3.45	1.86	0.43	0.00	5.21
Propane %	5.26	0.52	7.27	0.86	0.54
i-Butane %	0.00	0.00	2.08	0.00	0.00
1-Butene %	15.04	32.05	3.33	12.06	25.45
n-Butane %	0.80	0.00	2.50	0.24	0.00

Note: The upper set of results have been calculated from the full analysis which gave readings for the unidentified gases, and for the backflush peak. This was done to allow closer comparison of the two sets of results presented here.

2.1.8. Summary

Before the start of the analytical runs a considerable amount of time was spent on setting up the gas chromatograph for the most accurate analysis, and assembling all the necessary analytical equipment. A standard procedure was adopted and adhered to for the duration of the analyses, since any change in procedure, no matter how slight, may have had some effect on the analytical results. Duplicate analyses showed that the method is imprecise, but the analytical error was found to be small compared to variation in results due to other factors. More worrying than this was the difference in duplicate analyses performed on different chromatograph systems, a problem which deserves further consideration.

2.2. HYDROCARBON CONTENT OF THE MENDIPS LIMESTONES

About one hundred samples of unmineralised Carboniferous Limestone were collected from quarries in the Mendip Hills of Southern England. Previous work had suggested that the hydrocarbons detected in rocks in any area were not dependent on their lithology. This area was chosen for the collection of samples to test this theory since a wide variety of lithologies were available. Two large suites of samples were collected in Whatley Quarry (grid ref. ST7347), and Holcombe Quarry (grid ref. ST6649), and these were used to study the links between hydrocarbon content and lithology. A small suite of samples from Burrington Coombe (grid ref. ST4759) was also collected, as a reference suite.

The sample localities are shown in figure 2.2a.

2.2.1. Carboniferous Geology of the Mendips Area

The limestone sequences in the Mendips area are a consequence of the shallow marine conditions which dominated during the Lower Carboniferous. The formation of the Tintern Old Red Sandstone was brought to an end by the sinking of the area, causing the sea to spread from the South. The O.R.S. terrain over which it encroached was an area of little or no relief. The sediments show a gradual passage from sandstone through fossiliferous sandy limestones and shales to limestones deposited in clear and relatively shallow seas.

Figure 2.2a: Location of Quarries Sampled in the Mendip Hills.

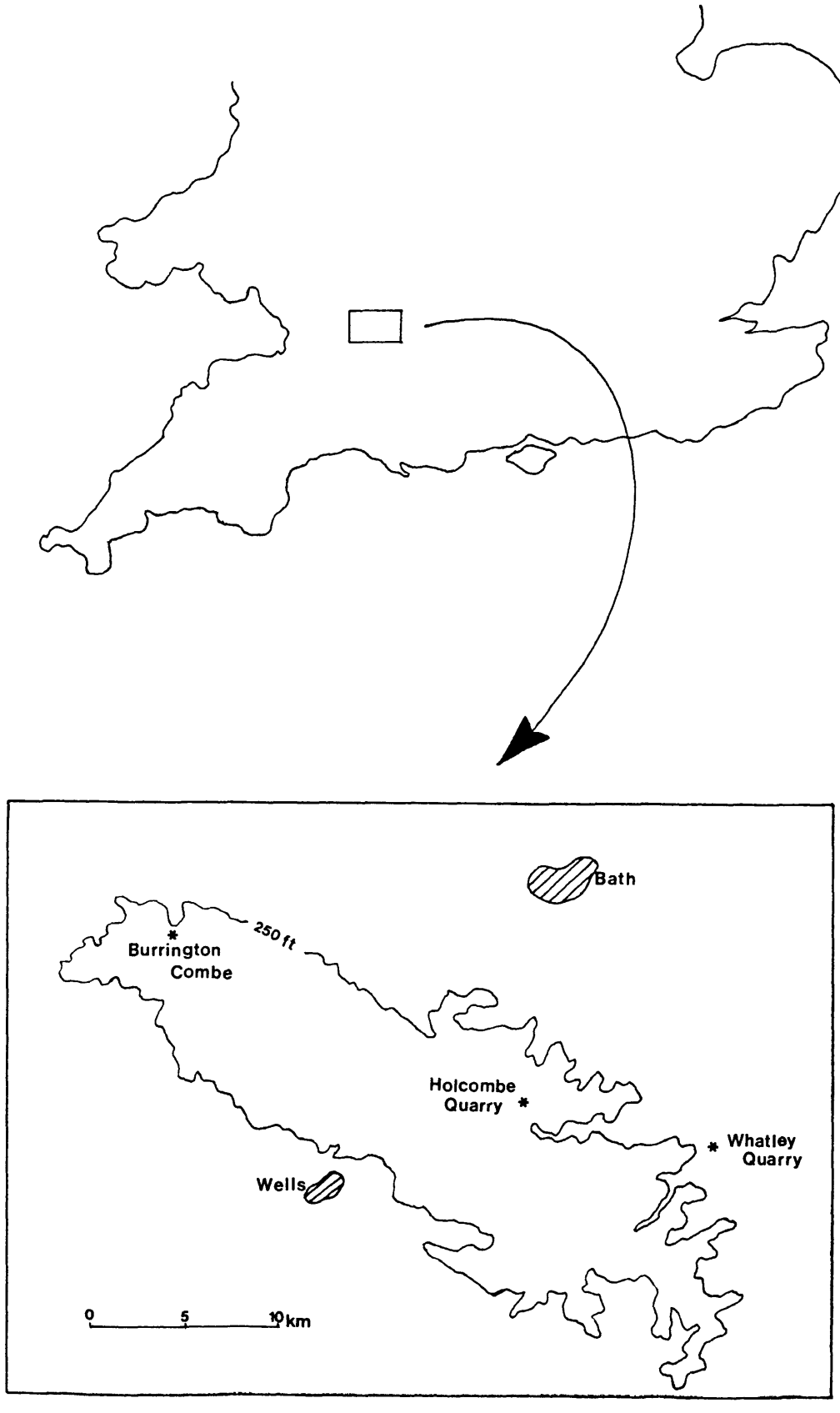


Table 2.2a: Carboniferous Limestone Stratigraphy.

Upper Carboniferous Limestone	Dibunophyllum Zone D	D3:Base of local Millstone Grit.
		D2:Upper Dibunophyllum Zone
		D1:Lower Dibunophyllum Zone
	Main Seminular Zone S	S2:Upper Seminular Zone
		S1:Lower Seminular Zone
	Upper Caninia Zone C2S1	C2:Upper Syringothyris Zone
Lower Carboniferous Limestone	Lower Caninia Zone C1	C1:Lower Syringothyris Zone Horizon δ
	Zaphrentis Zone Z	Z2:Upper Zaphrentis Zone
		Z1:Lower Zaphrentis Zone
	Cleistopora Zone K	K2:Upper Cleistopora Zone
		K1:Lower Cleistopora Zone
		Km:Passage Beds to O.R.S.

The sea remained deeper in the South than in the North throughout Carboniferous times. There were also local variations in sea level caused by movement along the Lower Severn Axis and the Bath Axis, so that contemporaneous sediments can show striking differences in lithology. Limestones deposited under normal marine conditions in this area are massive, frequently dark coloured, highly fossiliferous crinoidal limestones. Shallower water produced massive dolomites. In areas where the water was shallower still, and incompletely connected to the sea, lagoons produced calcite mudstones or chinastones, oolites, dessication breccias, pseudobreccias due to the recrystallisation of calcite mud, and algal limestones. There is also frequent penecontemporaneous dolomitisation. Extreme shallowing towards shorelines or current-swept shoals caused the lateral passage into grits, sandstones or conglomerates from the limestones.

In 1905 Arthur Vaughan subdivided the limestone into five groups, each named after a characteristic fossil of the coral-brachiopod assemblages. Table 2.2a shows these subdivisions.

The Carboniferous sequence in the areas of Holcombe Quarry and Whatley Quarry and at Burrington Coombe is shown in figure 2.2b. At Whatley the sequence exposed in the quarry extends from the base of the Black Rock Limestone to the middle of the Clifton Down Limestone, though at the time of

Figure 2.2b: Stratigraphy in the Sampling Areas.

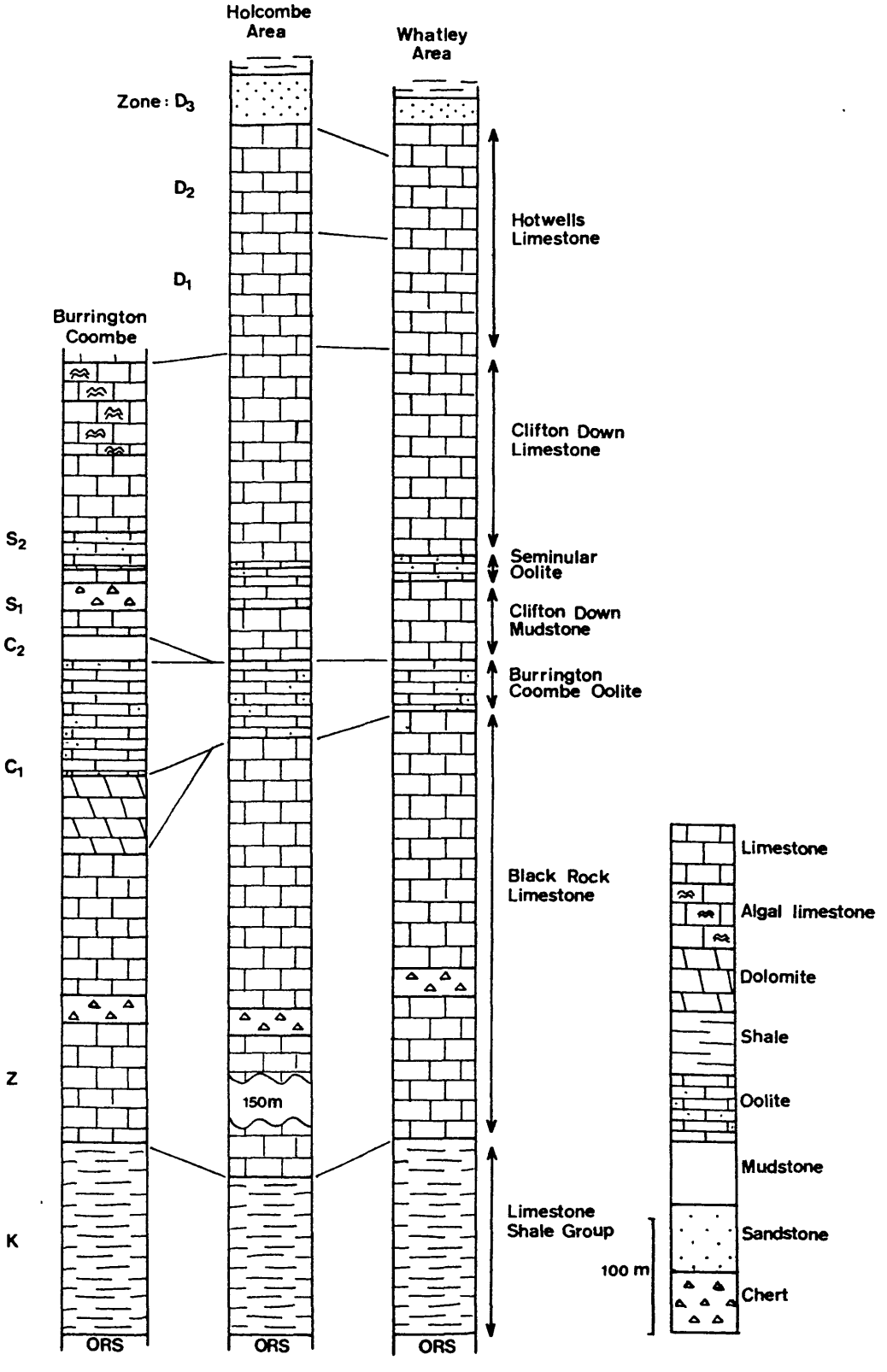
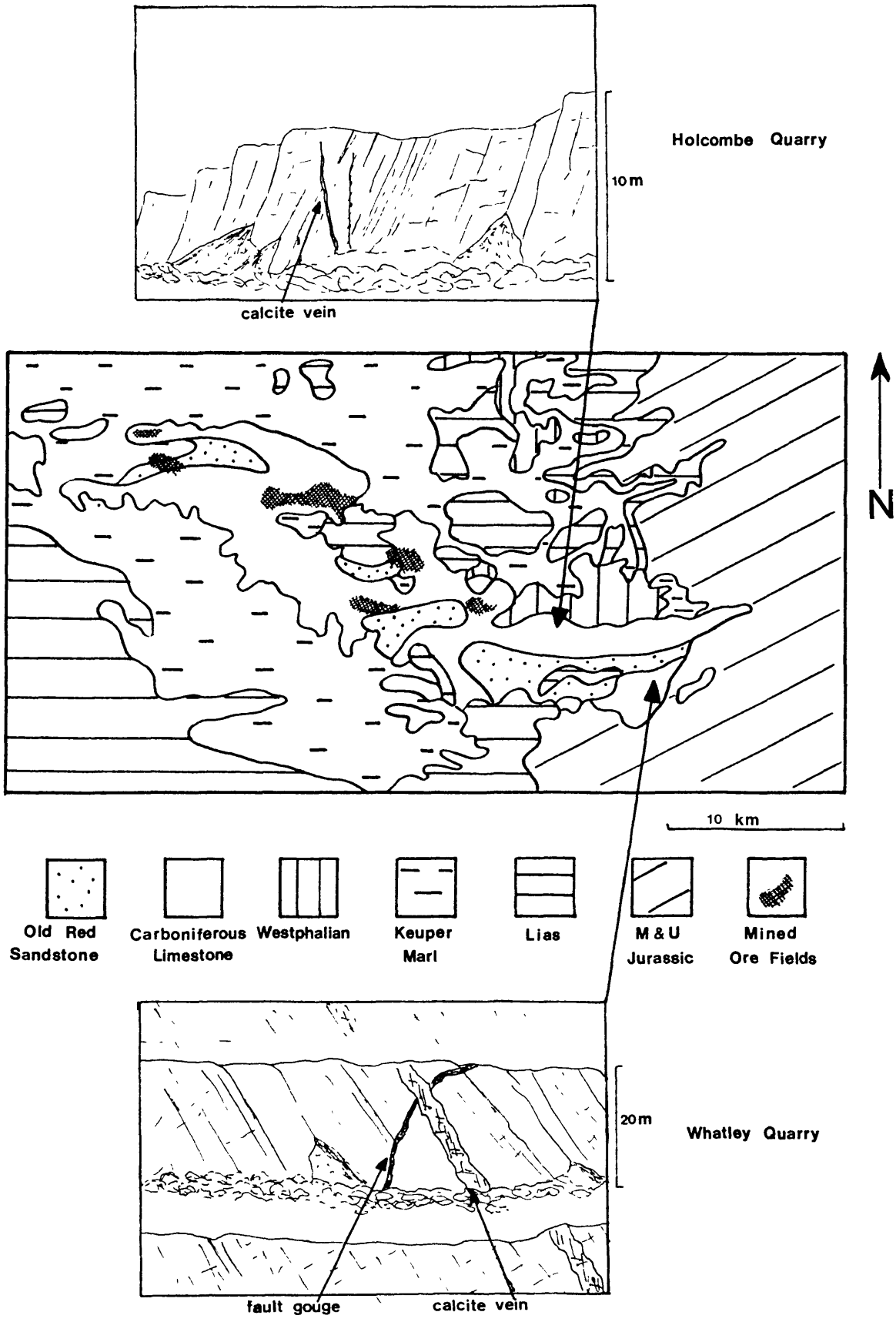


Figure 2.2c : Quarry Locations in Relation to Known Mineralisation.



sample collection access to the Black Rock sequence was restricted by the quarrying activity. At Holcombe Quarry the sequence is exposed from the Burrington Oolite through to the top of the Clifton Down Limestone. In both cases samples were collected with a view to obtaining as many examples of different carbonate lithologies as possible, rather than producing an exact series through the succession.

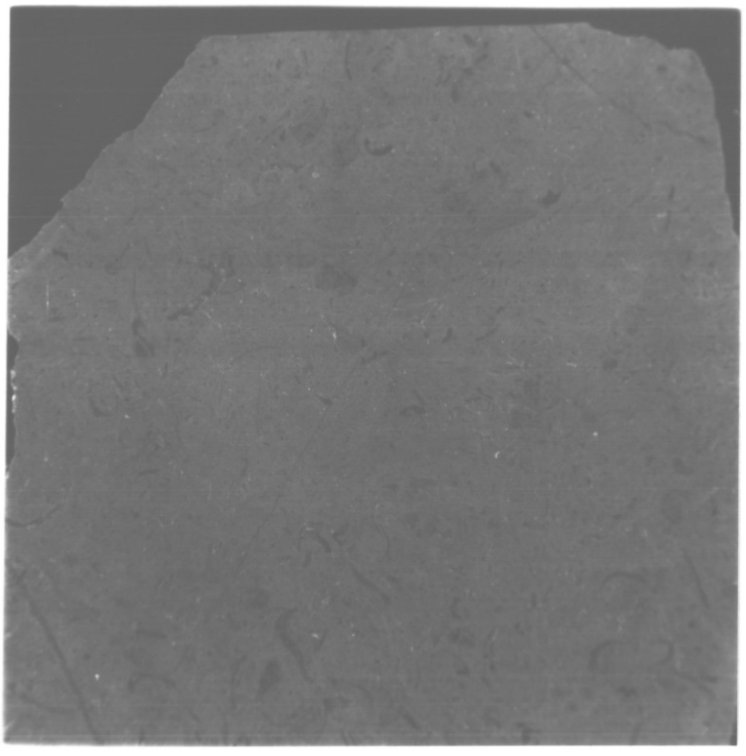
The Mendip Hills were at one time extensively mined, though at present there is no mining activity. The Carboniferous Limestone contained galena in veins or lodes with calcite and baryte gangue minerals (Kellaway & Welch 1948). Such veins occur throughout the Carboniferous Limestone, often following the strike of the beds, e.g. at Brentry, Priddy, Charterhouse and East Harptree. This type of mineralisation, i.e. veins rather than stratabound lenses, suggests that the Mendip Hills would be more likely to have a methane anomaly pattern similar to the North Pennine Orefield rather than the Irish Carboniferous Limestone. A general elevation of the methane content of the contained gases would be expected rather than any distinct anomalies around individual deposits. Figure 2.2c illustrates the location of the quarries sampled in relation to the known ore deposits in the vicinity,and the nature of the outcrop in the quarry faces.

2.2.2. Lithological Study of the Samples

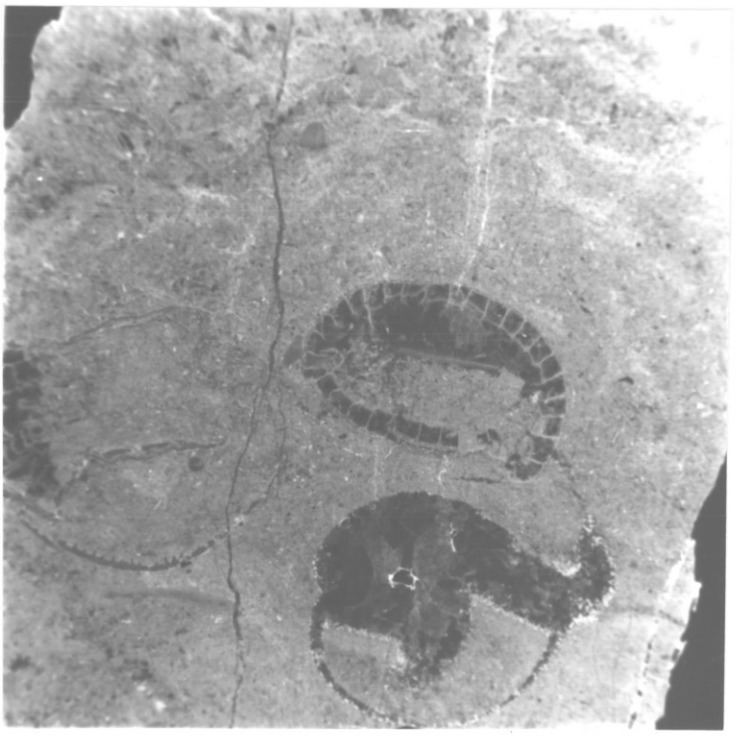
A total of one hundred and fourteen samples of the Mendips limestone were collected for lithological study and for analysis of their contained light hydrocarbons. One half of each sample was crushed for analysis, and the other half was used to produce a slide-mounted acetate peel (see Appendix A). The slide mounting of the peel allowed the petrology of the samples to be studied in great detail, so that it was possible to describe each slide in great petrological and palaeontological detail. However, since the aim of the study was to determine whether different lithologies could be related to different patterns in their hydrocarbon content, it was necessary to simplify both the subdivision of lithologies and the variation in the hydrocarbon content, so that the number of variables to be related to each other was of more manageable proportions. Thus the task of studying the petrology of the samples and classifying them was made simpler by the identification of certain key features. These features were then noted for each sample, so that only the more important aspects of the petrology could later be compared and contrasted. This gave a more flexible approach than one based on single classification (e.g. micrite, biosparite etc.), while still reducing the amount of information from that of a full petrological description. Appendix B contains the worksheets used in the petrological study.

Figure 2.2d: Examples of Petrology of Mendips Limestones.

Scale:×2



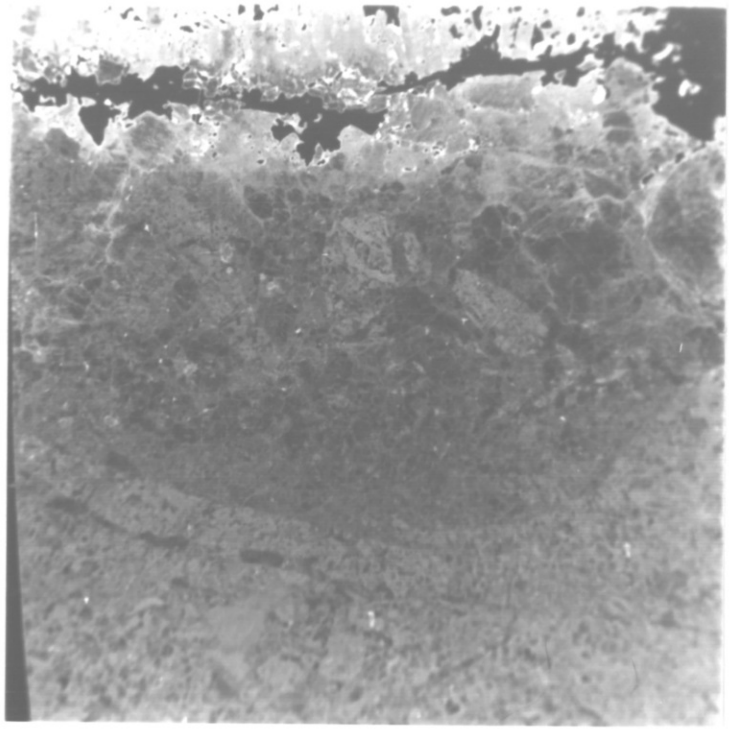
Sample HQ24: A poorly sorted fossiliferous limestone with brachiopod and gastropod fragments and abundant foraminifera.



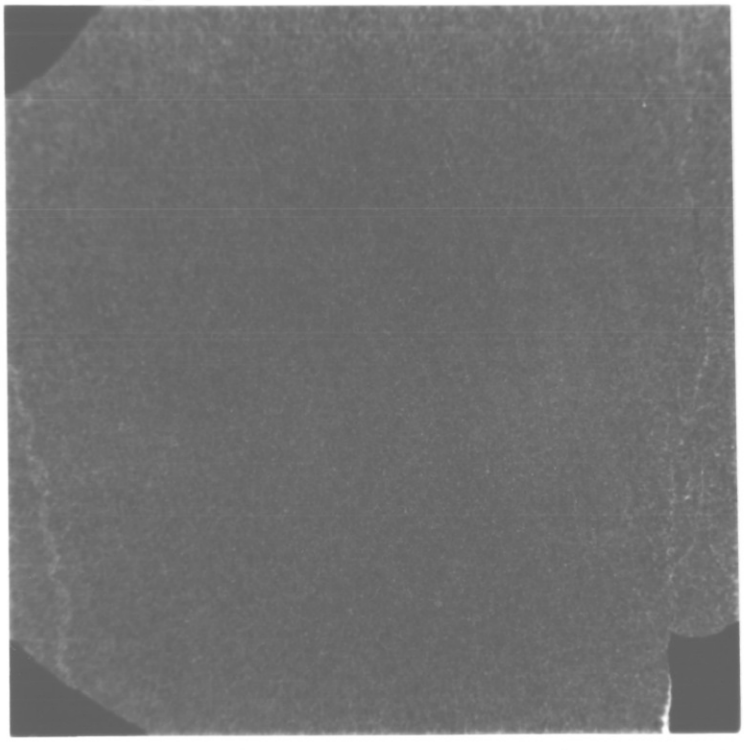
Sample WQ42: A coarse grained dark grey limestone, showing a complete gastropod shell with geopetal infilling; also fragmented corals, shell fragments and foraminifera.

Figure 2.2e: Examples of Petrology of Mendips Limestones.

Scale: × 2



Sample HQ23: A partly recrystallised limestone with sparry calcite cement between shell and coral fragments. The dark band at the top of the plate represents a calcite vein.



Sample WQ20: A recrystallised limestone (mid grey) showing regular grain size.

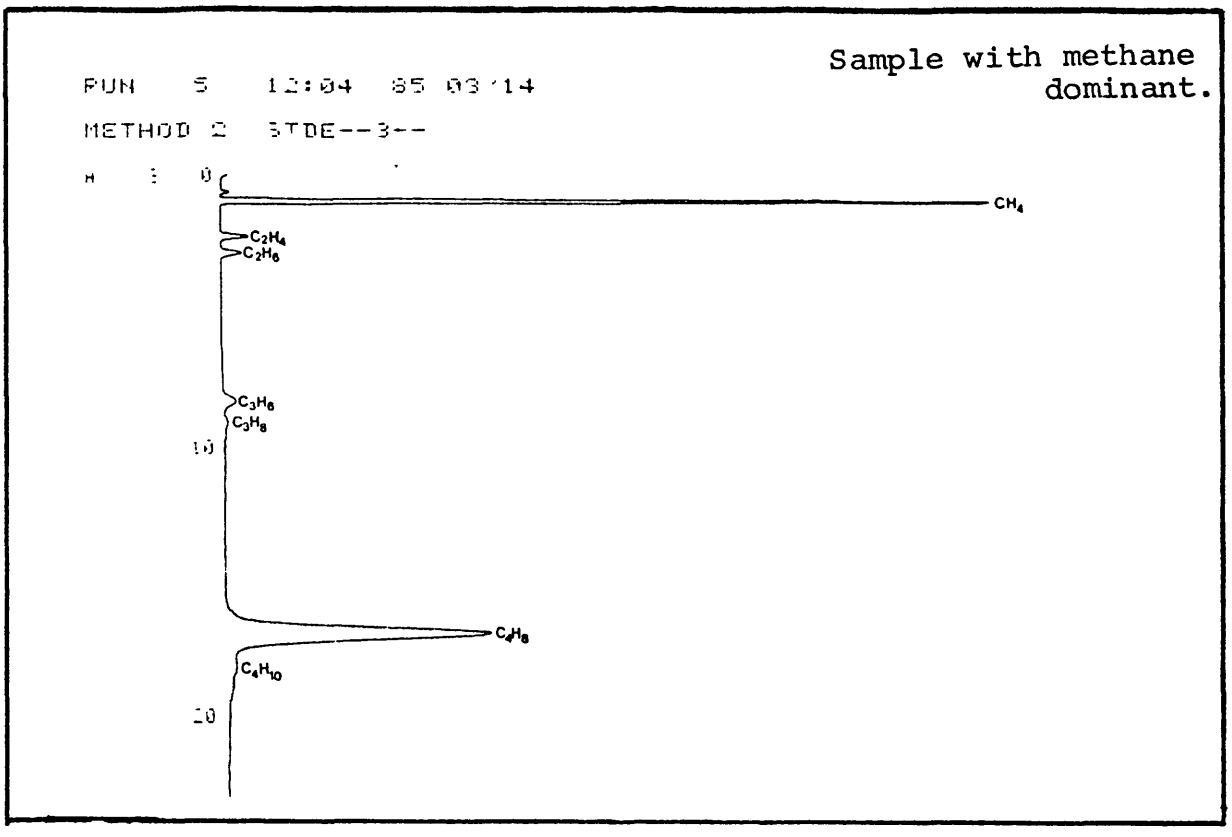
The features that were identified for each sample provided a full description of the sedimentology, and also those factors likely to be important for the migration of fluids through the rock. Such features included evidence of initial porosity, or late fluid movement, and were considered important for their possible effect of the migration of hydrocarbons. Once the hydrocarbon analyses were complete, the data was classified, and it was possible to use the petrological study sheets to determine whether there were any gross differences in the petrological characteristics of samples in different hydrocarbon data groups.

Figures 2.2d and 2.2e comprise plates of some of the samples, produced by projecting the acetate peels onto photographic paper. They illustrate the range of limestone lithology encountered during the survey.

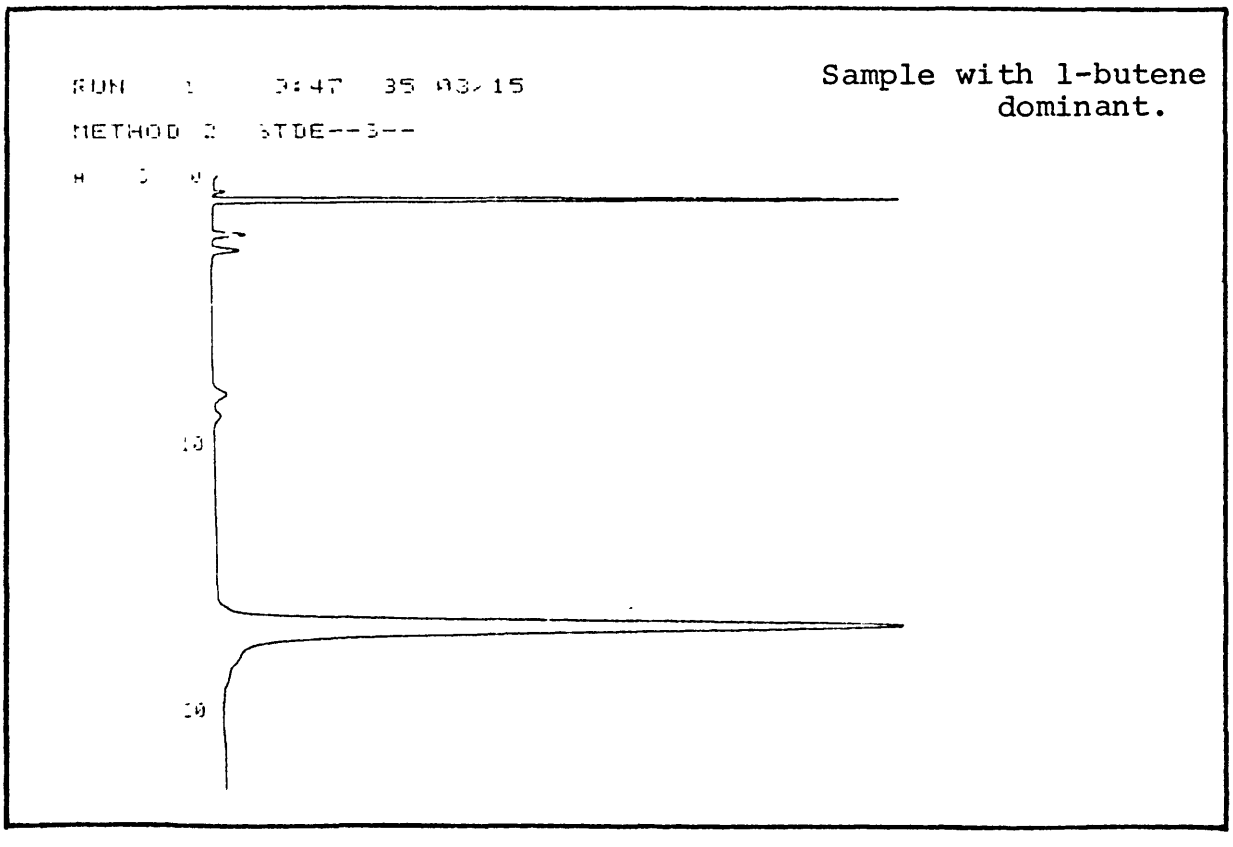
2.2.3. Gas Chromatography

The rock samples were prepared for analysis as described in section 2.1.2. The aim of the chromatorgraphic analysis was to identify all the components of the hydrocarbon gas released by the limestone samples on heating. The conditions for the gas chromatograph were therefore chosen to give maximum peak separation in as short a time as possible. A non-isothermal method was used, which gave good separation of the gases during a twenty-five minute analytical run. (see also section 2.1.4.). Nine gaseous components were identified

Figure 2.2f: Typical Chromatograms of Mendips Samples.

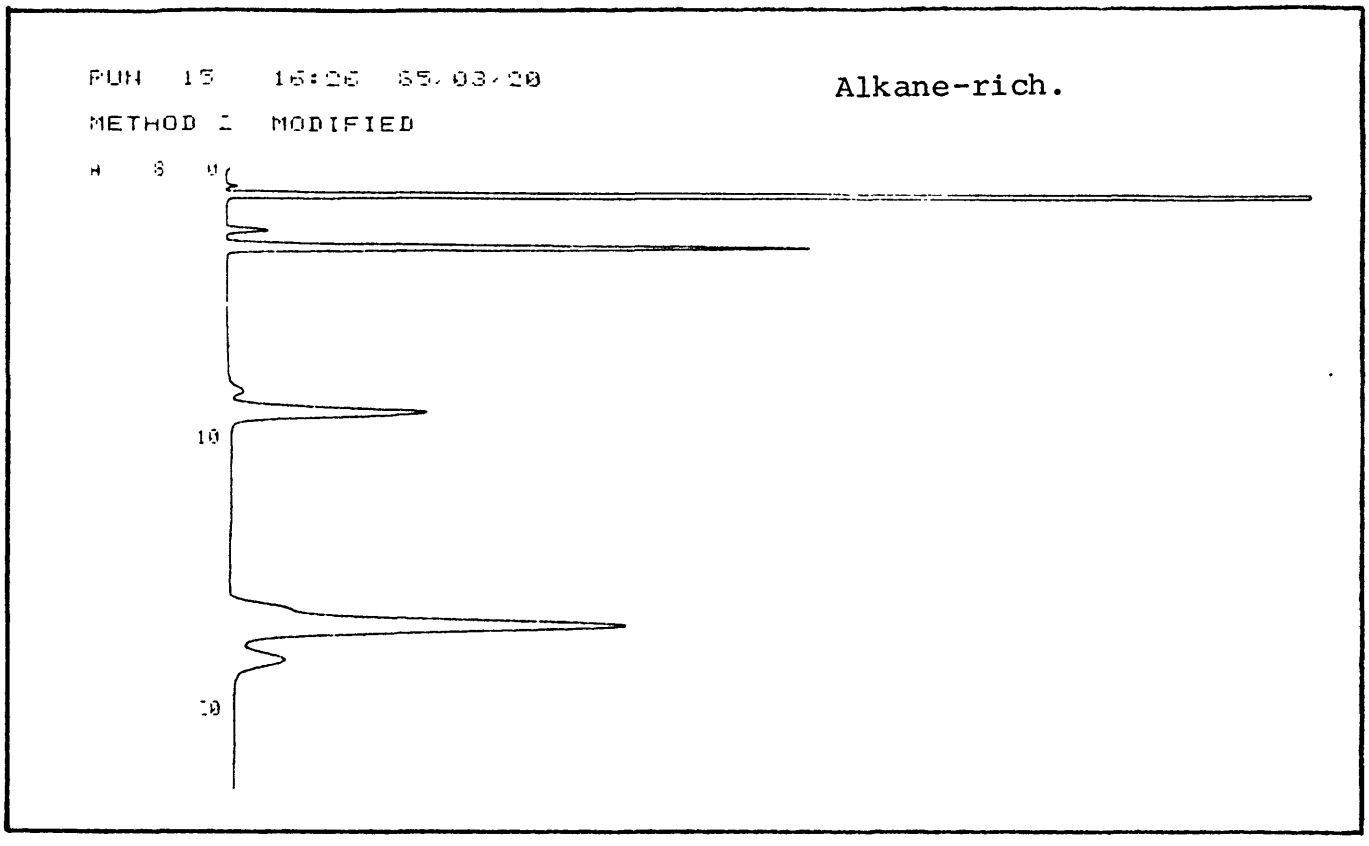


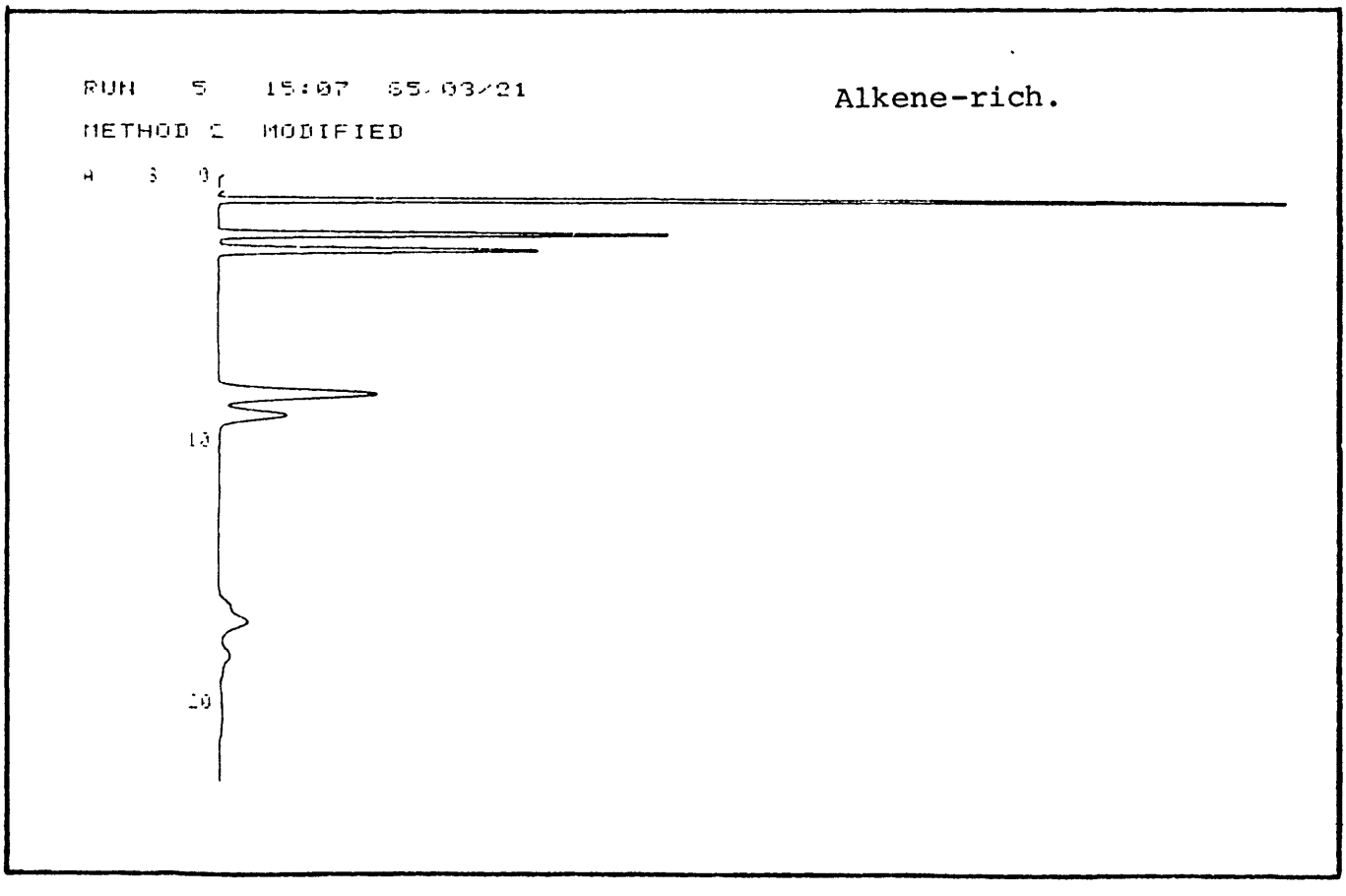
Sample with methane dominant.



Sample with 1-butene dominant.

Figure 2.2g: Chromatograms of Alkane-rich and Alkene-rich Samples.

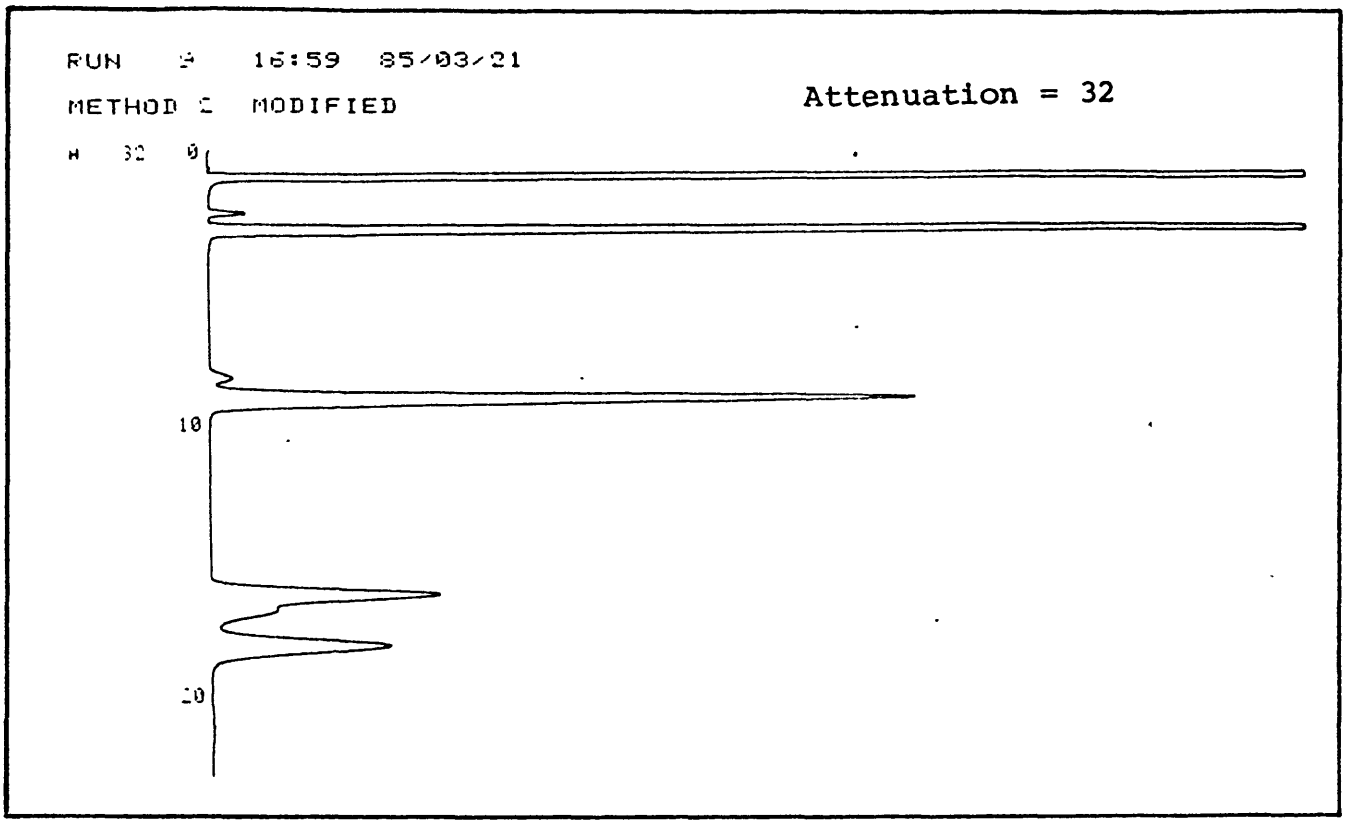




by the analyses, and of these, two were dominant; methane and 1-butene (full results form Appendix C). In the majority of cases, methane was the more abundant though in some cases the 1-butene formed the larger peak on the chromatogram (figure 2.2f). The percentages of these two gases in the total gas analysed were noted as important indices in the interpretation of the hydrocarbon data. An index was also devised to quantify the bias that was noticed, where some analyses showed a bias towards the alkane gases, and some towards the alkenes (figure 2.2g). The index ethane + propane peak area / ethene + propene peak area gave a value greater than one for those samples richer in alkanes, and less than one for those with a higher alkene content. It should be noted that this is a somewhat arbitrary division of the data, devised solely to quantify a feature of the analyses not shown by the other indices. Whether the value of the index has any meaning in itself remains to be discovered; and if it has, this is merely a fortuitous by-product of the decision to divide the data in this manner.

The final index used was the total area under the chromatogram, which gave a good comparative measure of the amount of hydrocarbon within the sample. Figure 2.2h illustrates the need for such a measure. The two chromatograms reproduced here show similar patterns of hydrocarbon composition, however one chromatogram is at attenuation of four, and one at thirty-two. This means that to produce chromatograms of the same

Figure 2.2h: Chromatograms Showing Differences in Total Area Value.



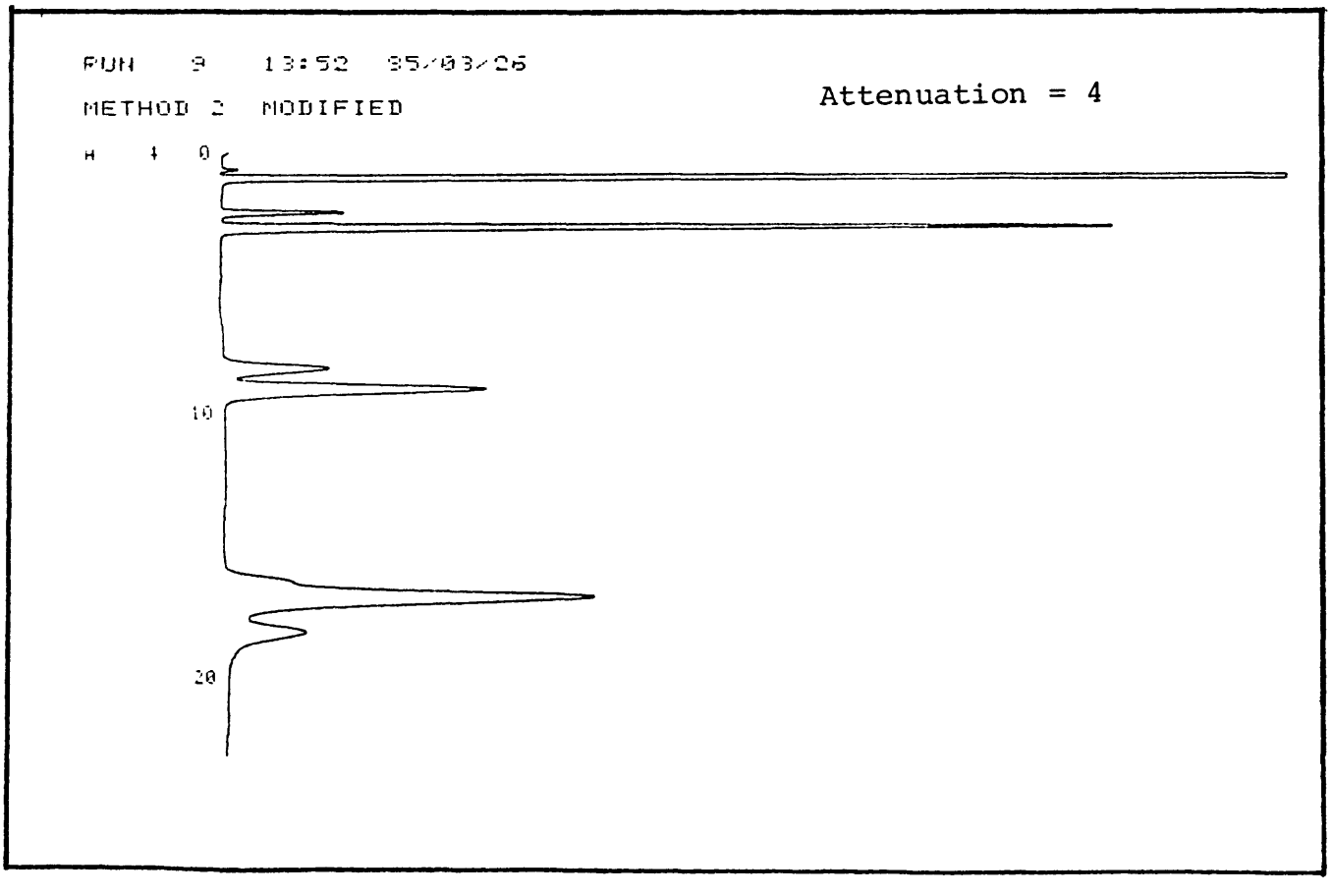


Table 2.2b: Values of Hydrocarbon Indices of Mendips Samples.

HQ	CH_4 %	C_4H_8 %	Area	Alkane/Alkene
1	59·30	33·19	11·57	0·00
1	66·26	26·49	16·96	0·16
2	73·92	16·18	9·75	1·33
3	48·94	46·21	21·11	0·61
4	85·77	4·74	45·48	19·07
5	67·21	23·00	10·11	0·79
5	74·75	20·83	18·69	0·39
5	60·47	31·36	16·04	0·78
6	73·38	5·90	9·97	0·72
7	55·83	28·02	21·50	1·21
8	63·66	27·35	24·01	0·79
9	68·48	17·70	59·65	11·22
10	78·20	11·99	17·05	17·72
11	54·41	28·01	16·37	0·82
12	48·29	39·34	7·19	0·91
13	74·41	11·22	8·47	0·19
13	72·79	16·74	9·79	0·08
14	73·44	21·96	6·60	0·25
14	65·18	27·73	8·50	0·29
15	74·09	12·10	21·15	1·85
16	30·41	65·54	27·01	0·44
17	53·37	41·01	26·25	3·48
18	59·62	33·90	35·37	4·87
19	38·11	56·68	35·11	0·73
20	69·62	24·55	16·16	2·98
21	84·55	12·03	10·60	0·32
22	52·88	42·28	14·94	0·46
23	55·67	31·71	28·91	0·38
24	62·24	29·12	29·97	2·02
25	58·53	34·06	16·97	0·46
26	52·13	35·71	29·79	0·32
27	82·75	11·11	38·83	13·74
28	81·44	11·15	40·64	22·18
29	29·13	67·25	22·05	0·12
30	60·77	30·86	19·00	0·58
31	58·34	30·79	28·07	11·66
32	77·20	11·30	20·62	8·16
33	89·04	5·30	62·36	13·03
34	79·47	13·14	24·46	6·47
35	73·39	14·13	20·40	2·98
36	57·16	33·25	17·60	5·07
37	59·62	34·29	21·67	2·77
38	66·80	27·79	11·28	1·74
39	70·87	18·63	20·01	9·70
40	59·00	31·94	46·31	3·85
41	73·81	20·02	13·00	2·60
42	80·79	13·42	25·93	6·58

WQ	CH_4 %	C_4H_8 %	Area	Alkane/Alkene
1	66·15	20·65	21·80	5·28
1	68·28	18·88	22·69	5·79
2	41·21	42·18	17·26	0·00
3	60·22	35·09	19·03	0·29
3	62·43	34·68	22·56	0·37
4	44·77	46·19	28·47	0·11
5	38·74	52·40	30·37	0·09
6	62·10	28·47	34·74	3·31
7	50·00	41·96	33·94	0·23
8	57·83	30·70	38·45	3·86
9	40·26	54·77	20·00	0·93
10	52·64	30·32	21·01	0·77
11	80·36	18·70	27·07	0·36
12	74·99	20·13	15·76	0·73
13	68·04	23·37	20·32	1·38
13	57·83	27·32	17·60	1·81
14	80·77	16·10	11·62	0·99
15	80·91	15·66	11·11	2·83
16	46·09	51·20	31·46	0·78
17	44·50	52·41	24·76	0·15
18	60·85	35·93	14·92	0·46
19	38·93	57·67	24·01	0·86
20	58·93	37·60	26·72	1·22
21	39·96	54·86	24·60	0·47
22	55·45	38·52	30·40	0·12
23	56·36	38·90	25·58	0·26
24	69·47	22·96	31·08	2·77
25	88·43	2·99	32·29	∞
25	85·56	5·18	29·09	32·01
26	26·38	62·77	33·84	0·11
27	59·31	20·03	14·33	0·62
28	87·88	7·41	17·56	0·03
29	35·70	54·54	25·86	0·12
30	53·47	2·54	28·27	0·72
31	81·77	13·84	15·34	2·26
32	78·09	20·48	14·52	1·36
33	60·55	35·81	15·27	0·26
34	61·82	35·02	25·40	0·42
35	68·09	26·06	18·30	0·72
36	31·08	64·16	38·82	0·22
37	67·19	15·04	19·32	1·89
38	57·22	32·96	13·25	0·15
39	71·64	25·55	17·66	1·53
40	61·91	32·05	17·85	0·33
41	63·56	21·22	26·64	3·63
42	72·36	4·74	117·38	23·58
43	64·39	5·91	26·41	1·49
44	54·35	34·41	11·27	0·11
45	67·21	13·25	59·80	15·21
46	70·26	3·33	96·19	20·42
47	33·42	3·83	14·28	0·14
48	71·75	8·10	44·60	6·89
48	70·26	9·59	42·90	4·41
49	82·79	12·06	28·52	3·00
50	32·22	34·21	24·05	0·06
51	25·25	56·95	48·98	0·13
52	49·90	42·56	23·88	0·76
53	34·48	57·41	27·29	0·31
54	48·87	30·24	20·70	0·38
55	57·19	25·45	8·91	0·24
56	81·19	0·00	826·00	40·73
56	80·74	0·00	714·70	50·19

scale, the trace of one of the chromatograms had to be amplified eight times. The factor of eight between the quantities of hydrocarbons involved would not have been identified by any of the other indices; the total area index is necessary to do this.

Table 2.2b gives the values of all the indices for each sample.

2.2.4. Spatial Trends in the Data

The samples all show the moderately high methane percentages of a mineralised region, though they lack the very high values associated with proximity to a major ore deposit. This had been predicted from knowledge of the local geology, and suggests a similarity to the case of the North Pennine Orefield (see figure 1.1a), another region of vein mineralisation. To determine whether there were any spatial trends in the data, the values of the indices were plotted up as across the quarry faces where they were collected; these plots form figures 2.2i and 2.2j. As can be seen from these, there appear to be no strong trends in the data at this scale. This is an advantage for the identification of relationships between the lithology and the hydrocarbon content, since it means that there is no regional trend to be taken into consideration when interpreting the results.

Figure 2.2i: Whatley Quarry Hydrocarbon Indices Plot.

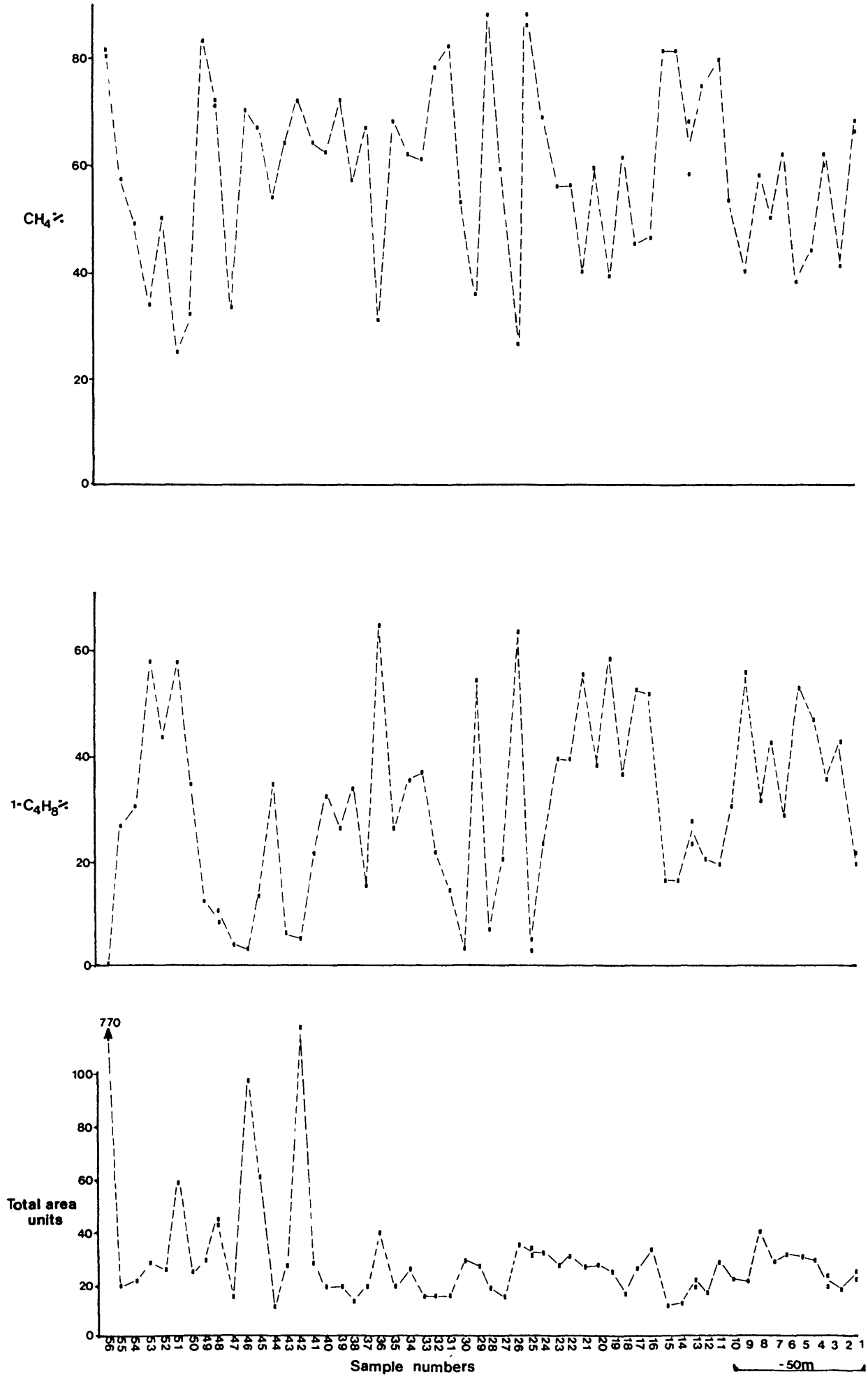
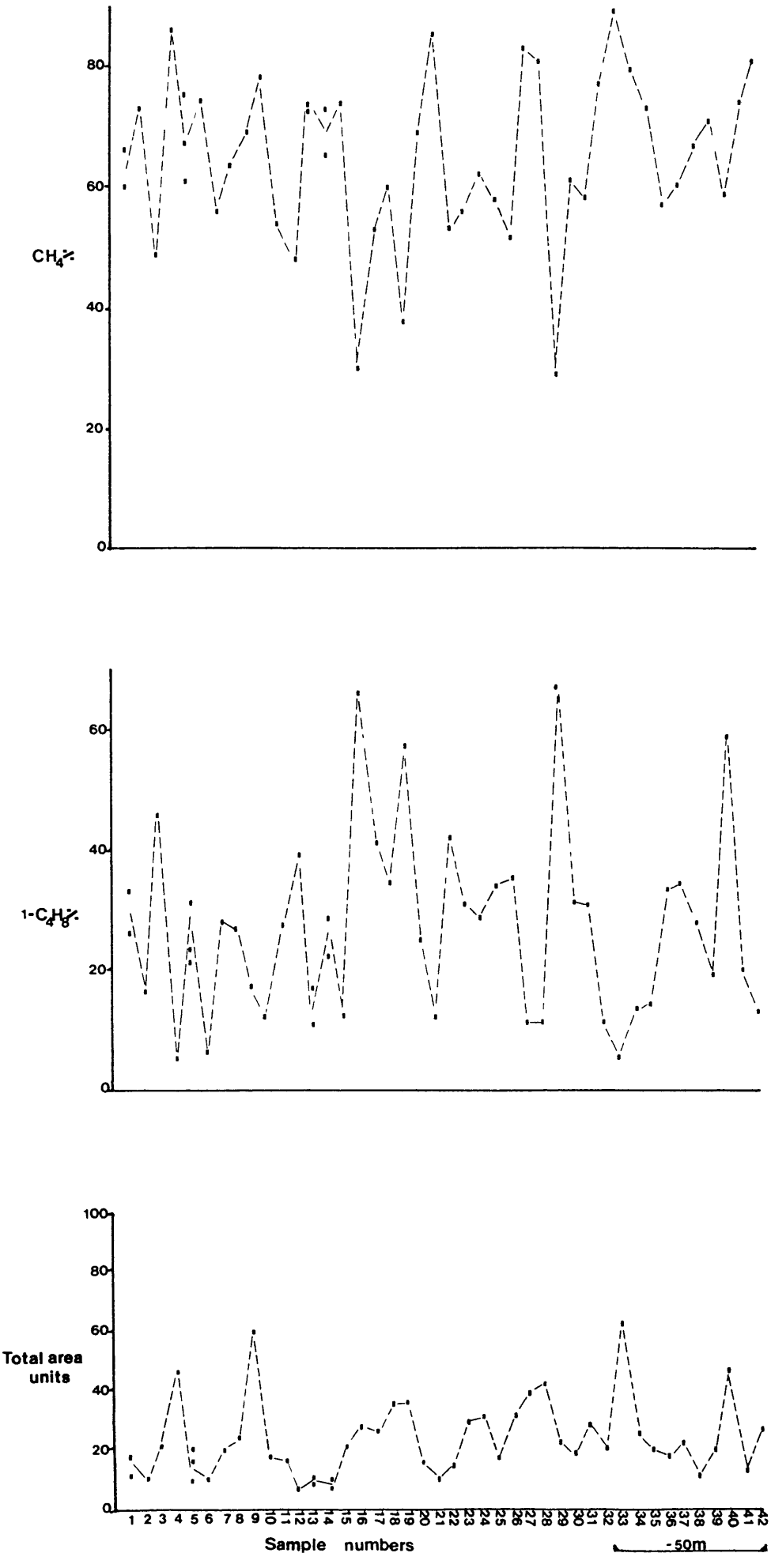


Figure 2.2j: Holcombe Quarry Hydrocarbon Indices Plot.



2.2.5. Lithology and Hydrocarbon Content

For each of the three numerical indices (methane percentage, 1-butene percentage and total area index) the range of values was divided into classes by ranking the data and using the median value and percentile classes either side of it. This was chosen in preference to a scheme of classification using the arithmetic mean and the standard deviation, since in each index group, there were one or two samples which had values very much higher or lower than the majority, by as much as an order of magnitude. The inclusion of these values in the calculation of the mean and standard deviation made a nonsense of the results and their interpretation. The choice was then either to omit such values from any calculation, or to use another classification method. The latter approach was chosen, in order to avoid introducing an element of subjectivity into the statistics. Thus, using the median and percentile method, the data for each of the three numerical indices was divided into ten classes, and the petrological characteristics of each class were compiled. Any trends present in the comparison of lithology and hydrocarbon content would have been detected by this method; the tables 2.2c, 2.2d and 2.2e show a method by which the data was compiled for the methane, 1-butene and total area indices respectively.

From these studies, only one trend could be identified with any certainty; that is that dolomitised samples gave

Table 2.2c:Methane Percentage - Lithological Characteristics of Classified Samples.

CH_4 group	1	2	3	4	5	6	7	8	9	10
CH_4% range	-35.70	-48.29	-54 35	-58 34	-61.33	-66 80	-70.87	-74.09	-80.97	-89.04
No. in group	9	10	10	10	10	10	10	10	10	9
Limestone	7	8	8	8	10	10	9	10	9	7
Dolomite		1	1	1						
Chert	1	1		1					1	
Vein calcite							1			1
Sandstone	1		1							
Fault gouge										1
<20% skeletal	8	7	7	6	8	4	4	4	6	4
20-40%		2	1	1		2	3	3		3
40-60%		1	1	3	2	4	1	3	2	1
>60% skeletal	1		1		1		2		2	
Oolitic		2		2	2	2	1		4	
Peletal		3	4	5	4	3	6	4	6	3
Mud grain size	3	1	2	2	3	2		4		2
Fine sand	3		2	2	2	1	1	2	1	
Sand	3	5	2	2	4	2		2		3
Coarse sand		3	3	3	1	5	9	2	9	4
Good sorting	5	5	5	3	7	3	3	5	4	2
Fair	1	1	3	3	1	3	2	2	1	3
Poor	1	3	2	3	2	4	4	3	4	2
Clast supported	1		1		1	2	3	1	4	
Matrix supported	6	7	9	9	8	8	6	9	5	7
Initial porosity	1	2	2	3	5	4	4	3	8	5
Fluid migration	6	7	7	6	6	6	4	7	7	7
Light grey	2	2	3	1	4	3	4	2	3	3
Mid grey	1		1	2	3	2	2	4	3	1
Dark grey	1	4	1	3		2	3	2	3	
Black	2	1	2	1	2	2		1		1
Brown	1	2	2	1						1
Pink		1		1		1				

Table 2.2d: 1-Butene Percentage - Lithological Characteristics of Classified Samples.

1-C_4H_8 group	1	2	3	4	5	6	7	8	9	10
C_4H_8% range	-5.90	-12.10	-16.18	-22.96	-28.01	-31.71	-34.89	-41.96	-54.77	-67.25
No. in group	9	10	10	10	10	10	10	10	10	9
Limestone	6	9	10	10	8	9	8	9	9	8
Dolomite							2		1	
Chert	1				1			1		1
Vein calcite	1				1					
Sandstone	1					1				
Fault gouge		1								
<20% skeletal	4	6	4	6	5	4	9	6	6	7
20-40%	4	2	1	1	3	3				1
40-60%	1	1	3	2	2	3	1	3	3	
>60% skeletal		1	2	1				1	1	
Oolitic		1	1	3	2		3	1	1	1
Pelletal	3	4	7	5	4	6	4	4	2	1
Mud grain size	1	3	1	1	3	1	5	2	2	3
Fine sand	1	1	2	1	1	3	1	1	1	2
Sand	1	3		1	1	2	2	5	5	3
Coarse sand	6	3	7	7	5	4	2	2	2	1
Good sorting	1	4	3	5	4	4	6	4	6	5
Fair	5	2	2	2	3	1	2	2	1	2
Poor	1	3	5	2	3	4	1	5	3	1
Clast supported		1	4	3	1		2	2	2	
Matrix supported	7	8	6	7	7	10	7	7	7	8
Initial porosity	3	6	5	6	4	3	4	2	1	2
Fluid migration	6	8	7	5	6	6	7	7	8	7
Light grey	3	2	2	4	3	1	5	2	3	3
Mid grey	1	1	5	2	3	2	1	3		1
Dark grey	1	1	3	2	1	4		1	3	1
Black	1	1		1	3	1	2	1	1	1
Brown		1					2	1	1	2
Pink								2	2	1

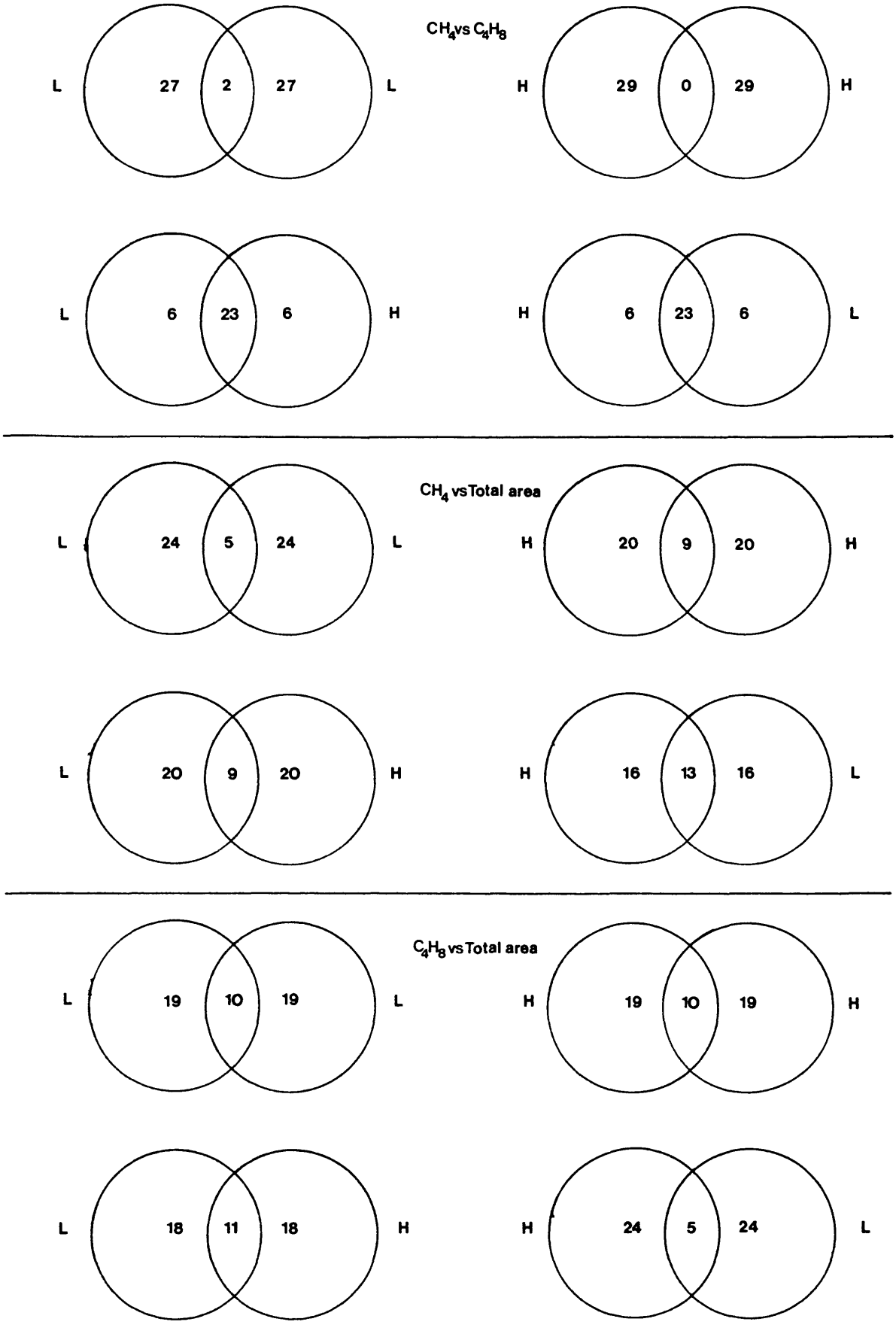
Table 2.2e: Total Peak Area - Lithological Characteristics of Classified Samples.

Total area group	1	2	3	4	5	6	7	8	9	10
Total area range	-11.27	-14.94	-17.56	-20.40	-22.25	-25.86	-28.27	-31.46	-43.75	-810.06
No. in group	9	10	10	10	10	10	10	10	10	9
Limestone	6	8	7	10	9	10	9	9	10	8
Dolomite	1	1	1							
Chert	1		1				1			1
Vein calcite	1							1		
Sandstone		1			1					
Fault gouge			1							
<20% skeletal	7	9	7	3	7	5	5	5	6	3
20-40%	1		1	2	1	1	1	2	3	3
40-60%	1	1	1	4	1	3	1	3	1	3
>60% skeletal			1	1	1	1	2			
Oolitic	1	1	2	3	2		1	1		1
Pelletal	4	3	3	6	4	4	4	4	4	5
Mud grain size	5	3	2	2	3		1	1	2	1
Fine sand	1	3	1	1	2		2	2	2	
Sand		2	2	1	1	7	1	4	3	2
Coarse sand	2	2	4	6	4	3	6	3	3	6
Good sorting	2	6	5	3	8	5	3	3	5	2
Fair	3	2		2		2	4	1	?	4
Poor	2	1	3	5	2	3	2	5	3	2
Clast supported	1	1	2	1	2	2	3	1		2
Matrix supported	6	8	5	9	8	8	6	8	10	6
Initial porosity		4	6	5	2	2	7	3	5	4
Fluid migration	8	7	8	5	5	8	7	7	5	6
Light grey	3	3	5	2	4	1	2	3	2	1
Mid grey	2	4	1	2		2	2	3	1	2
Dark grey	1	1		2	5	3	2	2	2	2
Black	1	1	1	2	1	2	2			2
Brown	1	1	2					1	2	
Pink						2		1	1	

consistently low total area values. This is due to the dolomitisation process in which the calcium carbonate precursor minerals are converted to dolomite. The conversion is achieved by partial dissolution and reprecipitation in the presence of waters of high magnesium concentration (Blatt et al 1980, p.530). During the dissolution stage, hydrocarbons held within the carbonate precursor would be released into solution, and would be free to move through the sediment pore space. Some of the hydrocarbons could be trapped within the new dolomitic material, but the evidence suggests that most would be lost in solution. The low hydrocarbon content of the dolomitised carbonates was therefore not an unpredictable result.

One other analysis worthy of note was that of sample WO28, a fault gouge formed of limestone rock flour, with veins of galena a few millimetres thick forming a stockwork through it. The methane percentage of the gases given off by this sample was high (89%), as would have been expected from a mineralised sample. Samples taken at either side of the fault, however, gave no indication of their proximity to this minor mineralisation. The explanation of this was thought to lie in the nature of the mineralised rock itself - a fine grained unconsolidated gouge. Any gas within this material would migrate prefentially along the fault plane, through the gouge, rather than into the lithified limestone of lower permeability at either side of the fault. The ease with

Figure 2.2k: Venn Diagrams Correlating Hydrocarbon Indices.



L=low value (groups 1-3); H=high value (groups 8-10)

See tables 2.2c-f

Table 2.2f: Lithological Characteristics of Samples Divided by the Alkane/Alkene Ratio.

Group	Alkane-Rich	Alkene-Rich
No. in group	43	55
Limestone	41	45
Dolomite		3
Chert	1	3
Vein calcite	1	1
Sandstone		2
Fault gouge		1
<20% skeletal	18	40
20-40%	9	6
40-60%	11	8
>60% skeletal	5	1
Oolitic	8	5
Pelletal	23	14
Mud grain size	2	18
Fine sand	5	9
Sand	8	15
Coarse sand	28	11
Good sorting	14	27
Fair	12	8
Poor	15	14
Clast supported	10	5
Matrix supported	31	43
Initial porosity	24	14
Fluid migration	22	43
Light grey	11	16
Mid grey	11	8
Dark grey	11	8
Black	5	7
Brown		7
Pink		5

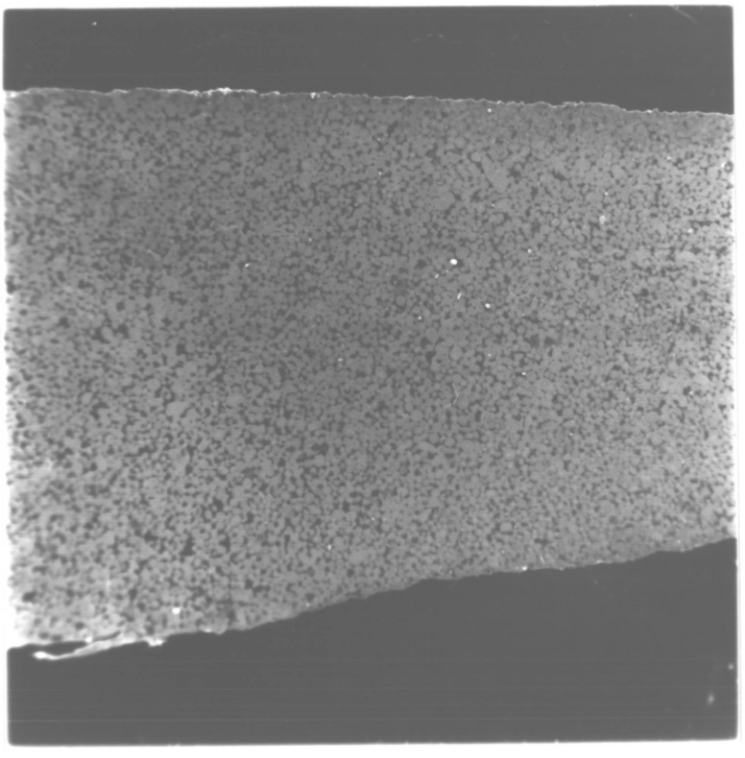
which the gases could move through such a gouge was supported by the low total area index, suggesting that only a small amount of gas remained within the rock sample.

For identification of any correlation between the hydrocarbon indices, the ranked data for each was divided into three broad classes, low, medium and high, based on the percentile divisions. Comparison of the class of a sample for each index then allowed identification of any relationship between the indices. The results are shown in figure 2.2k, illustrated by means of Venn diagrams. The only trend indicated by these is that those with higher methane percentages tended to have low 1-butene percentages, and vice versa, a predictable result when the analyses are known to be dominated by these two gases. Neither of these indices showed any correlation with the total area index.

The petrological characteristics of the samples divided into 'alkane-rich' and 'alkene-rich' groups were also studied (table 2.2f) and here there were some important trends. The alkane-rich samples tended to be more highly fossiliferous, typically coarse grained, poorly sorted limestones, often porous, or showing features of high initial porosity (figure 2.2l). The alkene-rich samples tended to be well sorted, finer grained limestones, often lime mudstones, without features due to high initial porosity, but often with suggestions of later fluid movement (figure 2.2m).

Figure 2.21: Examples of Alkane-Rich Lithologies.

Scale:×2



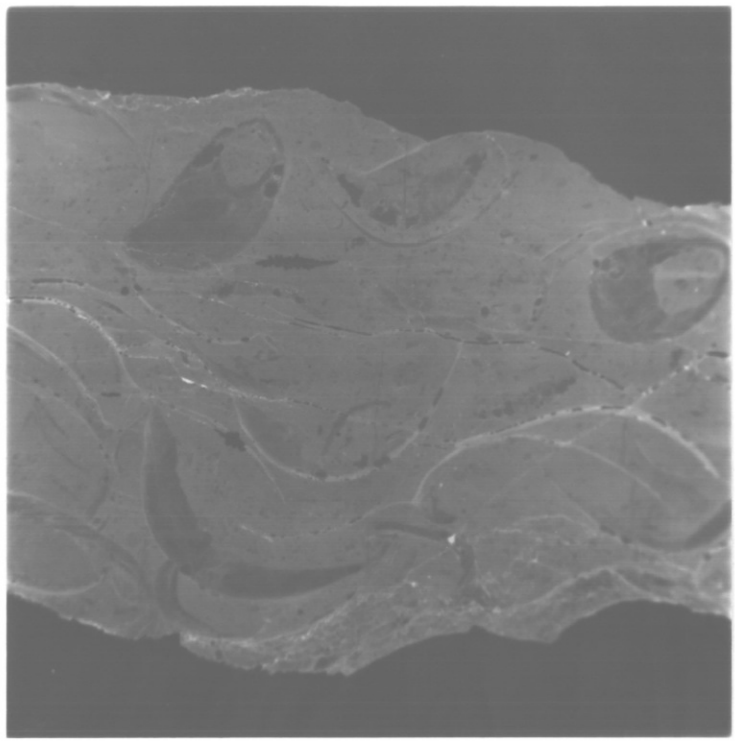
Sample HQ38: A porous light grey oolite with some rim cement.



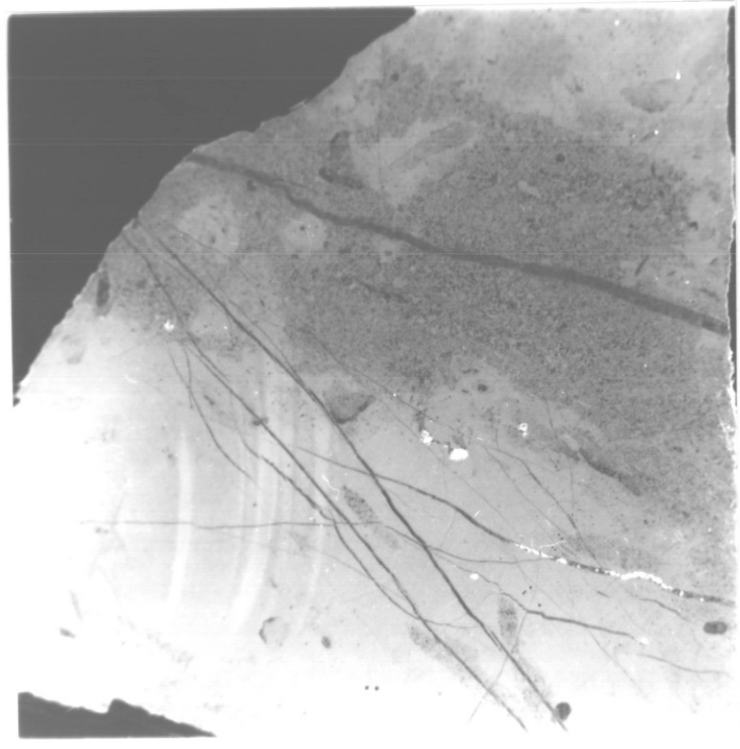
Sample HQ10: A highly fossiliferous coarse grained limestone with coarsely crystalline sparry cement.

Figure 2.2m: Examples of Alkene-Rich Lithologies.

Scale:×2



Sample WQ13: A black limestone with brachiopod shells and skeletal debris in a fine grained matrix; also some stylolites.



Sample HQ21: A light grey lime mudstone, slightly silicified, with some calcite veining.

2.2.6. Interpretation of Results ---

The major trend in the results, i.e. the gross lithological differences between alkane-rich and alkene-rich samples, can be explained by reference to the environment of sediment deposition represented by the different lithologies. The samples which released gases with a predominance of alkanes tended to be of a type associated with aerobic conditions and active water circulation (e.g. coarse grained fossiliferous, porous sediment). Those samples with a predominance of alkenes suggested sediment deposition in an anaerobic environment with little water circulation (e.g. deep water lime muds of low porosity). Assuming each environment to have the same potential for the deposition of organic matter from the water column, the preservation potential of this organic matter under the different depositional circumstances must be the control on the hydrocarbon content of the resultant rock. Degradation of organic matter will take place at different rates and by different reaction paths in aerated, water washed sediments, and in stagnant, anaerobic sediments. The products of organic degradation in each case would therefore be different, leading to a difference in the quantity and nature of the organic material incorporated in the sediments at the start of lithification. The relationship between this and the observed alkane-rich /alkene-rich bias could act in one of two ways. Firstly, it may be that during diagenesis and lithification, hydrocarbons were

generated from the organic matter, and that the nature of that retained in the anaerobic sediments tended to generate a greater proportion of the alkene gases. The alkenes are not a common constituent of natural systems, however, due to their great reactivity, and there is some doubt whether the alkenes could have survived through geological time, without reaction to form the corresponding, stable alkanes. The second possibility is that the analysed alkenes, and a certain amount of the alkanes, were generated from organic matter within the rock sample, during the heating phase of sample preparation. High order hydrocarbons, e.g. kerogen, are known to break down into simpler, light hydrocarbons on heating. The nature of the organic matter remaining in the rock sample, and available for reaction, would determine the composition of the hydrocarbons generated, and again this would have been determined by the environment of sediment deposition.

To investigate hydrocarbon generation on heating, an experiment was undertaken whereby a range of heating temperatures was employed on a number of subsamples of the same sample. The effect of the heating temperature on the amount of methane, total alkane and total alkene detected is shown in figure 2.2n. These graphs all show the same trend which is that followed by all the gas components when similarly plotted. There is first a gradual rise in the amount of gas released, then at about 100^{o}C the amount of gas begins to increase rapidly on a curved path. This is the type of trend

Figure 2.2n: Results of Experiment on Heating Temperature.

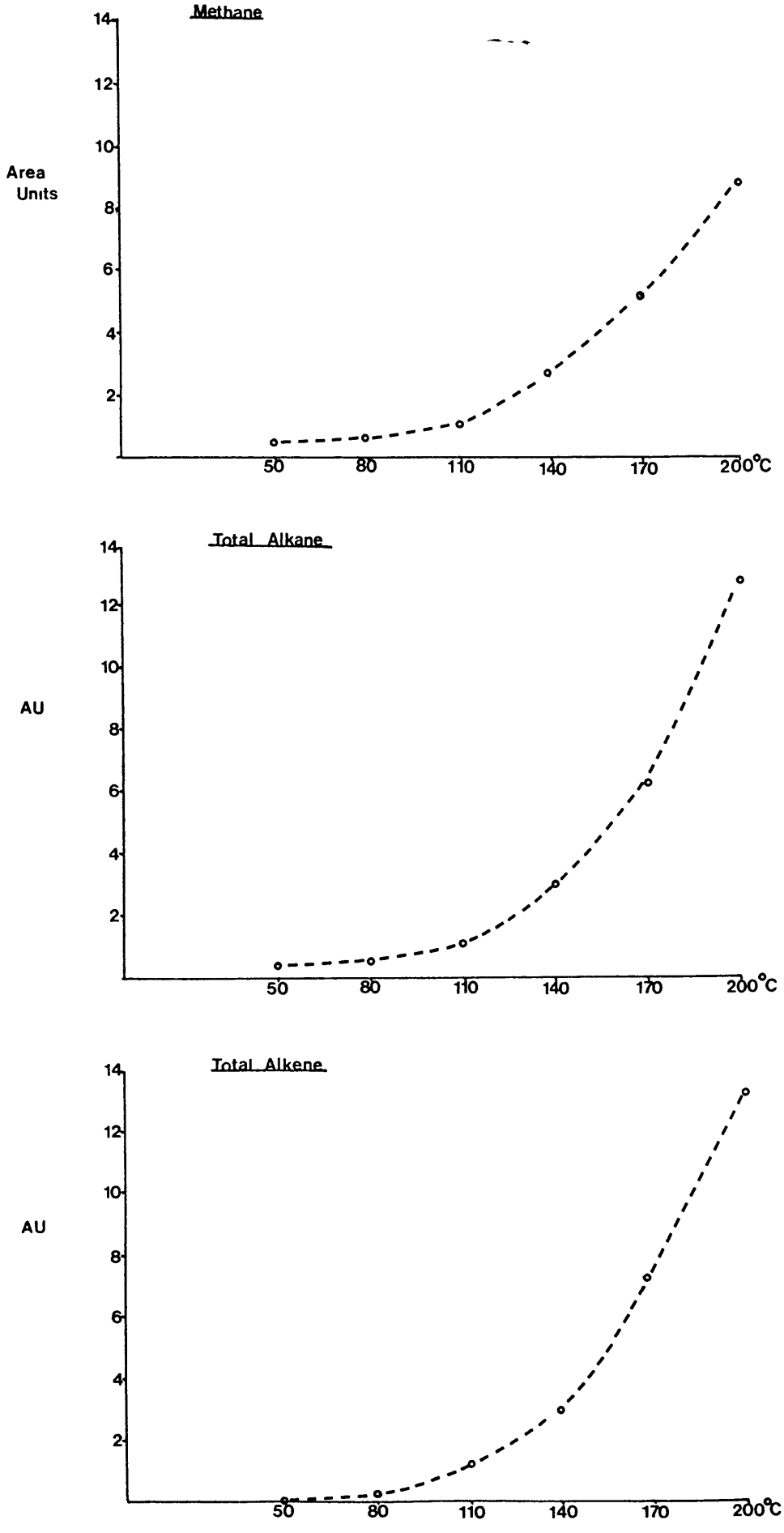
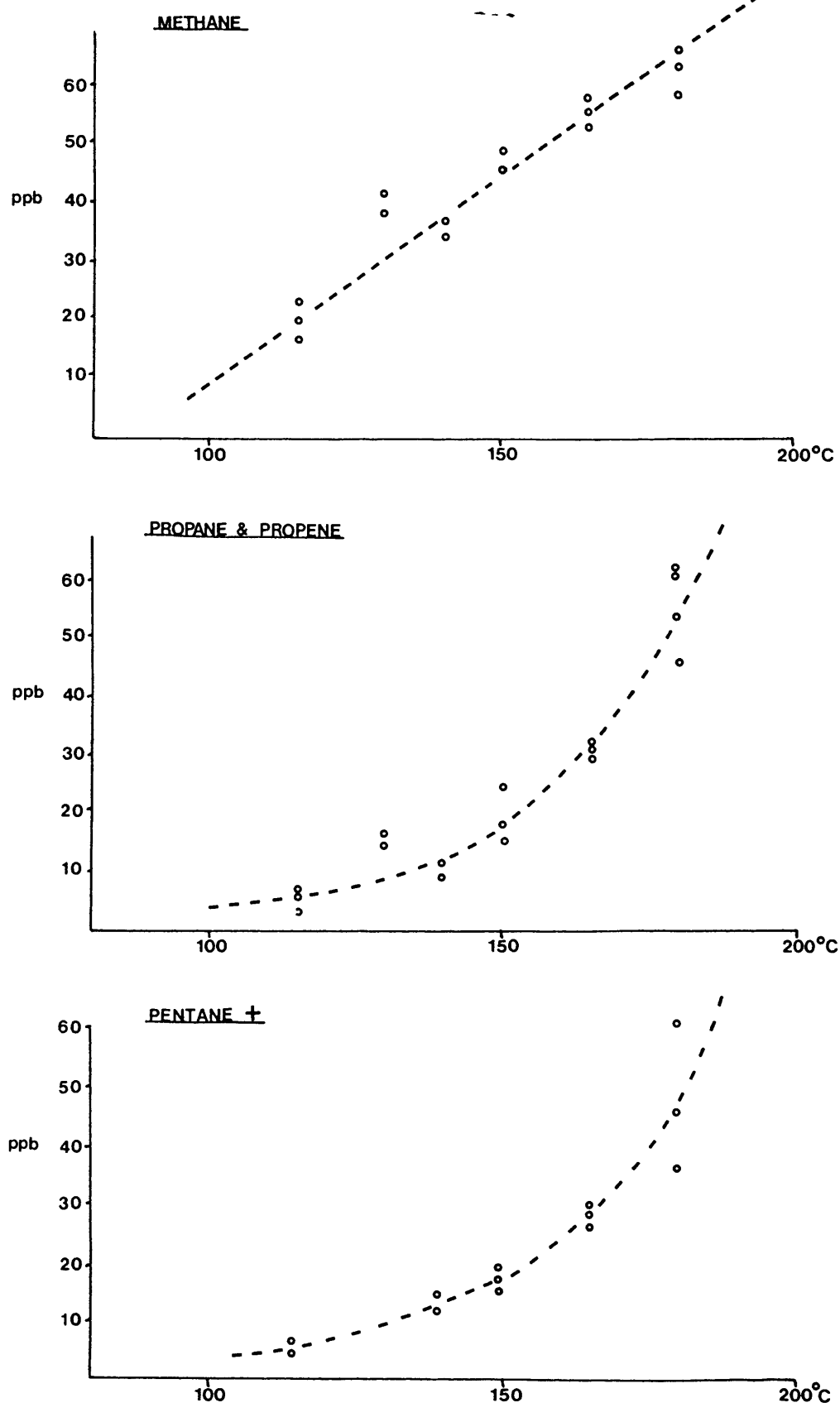


Figure 2.2o: Results of Dr.Carter's Heating Experiments.

(Carter 1981)



that would be expected if temperature dependant hydrocarbon generation were occurring during heating.

These results were compared to those from a similar experiment conducted on mineralised samples (figure 2.2o). The results are similar for propane, propene, and gases of pentane and above, but the results for methane are markedly different. The straight line relationship suggests a much simpler link between the amount of methane given off by a mineralised sample and the heating temperature. From this it can be deduced that in highly mineralised areas the large amount of methane introduced during the mineralisation process swamps the effect of methane generated during the heat extraction process. Data is not available for the other light hydrocarbons.

The petrological control on the light hydrocarbon content is therefore thought to be due to different types of organic diagenesis controlled by water circulation within the carbonate sediment. Whether the hydrocarbon content is affected directly or through an intermediate stage of hydrocarbon generation during sample heating cannot be determined. This effect will be visible in areas where there is general elevation of methane content due to widespread minor mineralisation. In areas close to major ore deposits it is likely that this production of hydrocarbons in situ will be swamped by the introduction of large volumes of methane due to the mineralisation reactions.

2.2.7. Summary

The study of the relationship between the hydrocarbon content of the limestones and their petrology identified only one trend, which was that different types of limestone produced different proportions of alkanes and alkenes on analysis. This theory was tested using the samples from Burrington Coombe, which had not been used in the original grouping of the data, and it was found that to some extent the hydrocarbons 'signature' could be predicted from the petrology. The presence of large quantities of alkene in some gas samples suggests that these may have been generated during heating of the crushed rock sample, since the alkenes are considered too reactive to form a large part of natural gases held in the rock. The proportions of alkanes and alkenes will depend on the early diagenetic conditions of the carbonate, as suggested by the different petrological features, whether or not there is generation from preserved higher order organic matter during the extraction process. In mineralised samples, the large amounts of introduced hydrocarbons, especially methane, will mean that any contribution by hydrocarbons generated in situ will be swamped. The petrological control on the hydrocarbons detected is therefore not a problem for the application of light hydrocarbon analyses in mineral exploration, though it would always be good field practise to select samples of similar petrology, as far as this is possible.

2.3. HYDROCARBONS AROUND A BARYTE ORE DEPOSIT, PERTHSHIRE

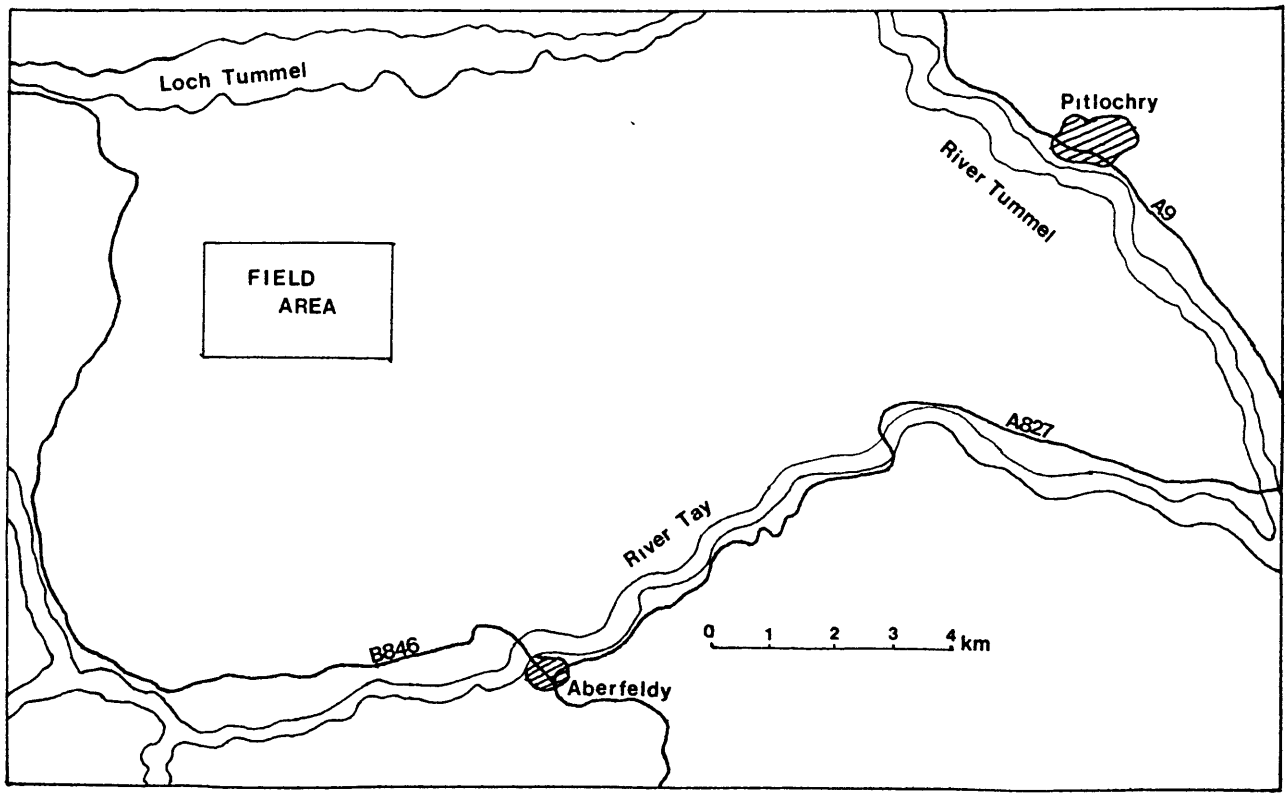
About 100 samples were collected from the area around a stratabound baryte orebody near Aberfeldy, Perthshire. The samples were analysed in a simulation of a mineral exploration programme to determine if such a method was applicable in this area, which was chosen since the mineralisation is hosted in black shale rather than carbonate. There has also been much deformation and metamorphism of the three major lithological units in the field area. These are all potential limits on the use of the hydrocarbon analyses as an exploration tool, and as such need to be investigated. In the field area it is possible to sample in detail over the ore horizon and the ore-bearing strata, as well as to sample over a larger area.

Figure 2.3a shows the location of the field area.

2.3.1. Geology of the Area

The Aberfeldy baryte deposit lies within metasediments of the Dalradian Group, which form an extensive belt across central Scotland. In the field area the regional tectonics have brought three major lithological units into juxtaposition. The Carn Mairg Quartzite, the oldest of these, is a mature white pebbly quartzite, probably a tidal shelf sediment. It grades up through muddy quartzite into a black schist unit, the Ben Eagach Schist. This would originally have been a black mud, deposited under anoxic conditions, and is now the unit which hosts the mineralisation; i.e. the massive bedded

Figure 2.3a: Location of the Aberfeldy Field Area.



baryte ore, and the sulphides, chert, muscovite schist and crystalline biotite-rich rock which are everywhere associated with it. These lithologies are indicative of an exhalative system, working at a time of slow sedimentation, this accounting for the lack of clastic dilution of the chemical sediments. The youngest of the three major units is the Ben Lawers Schist, a garnet mica schist which interfingers with the Ben Eagach Schist at its lower margin. The Ben Lawers Schist represents a return to oxygenic seafloor conditions, and the deposition of calcareous silts and muds.

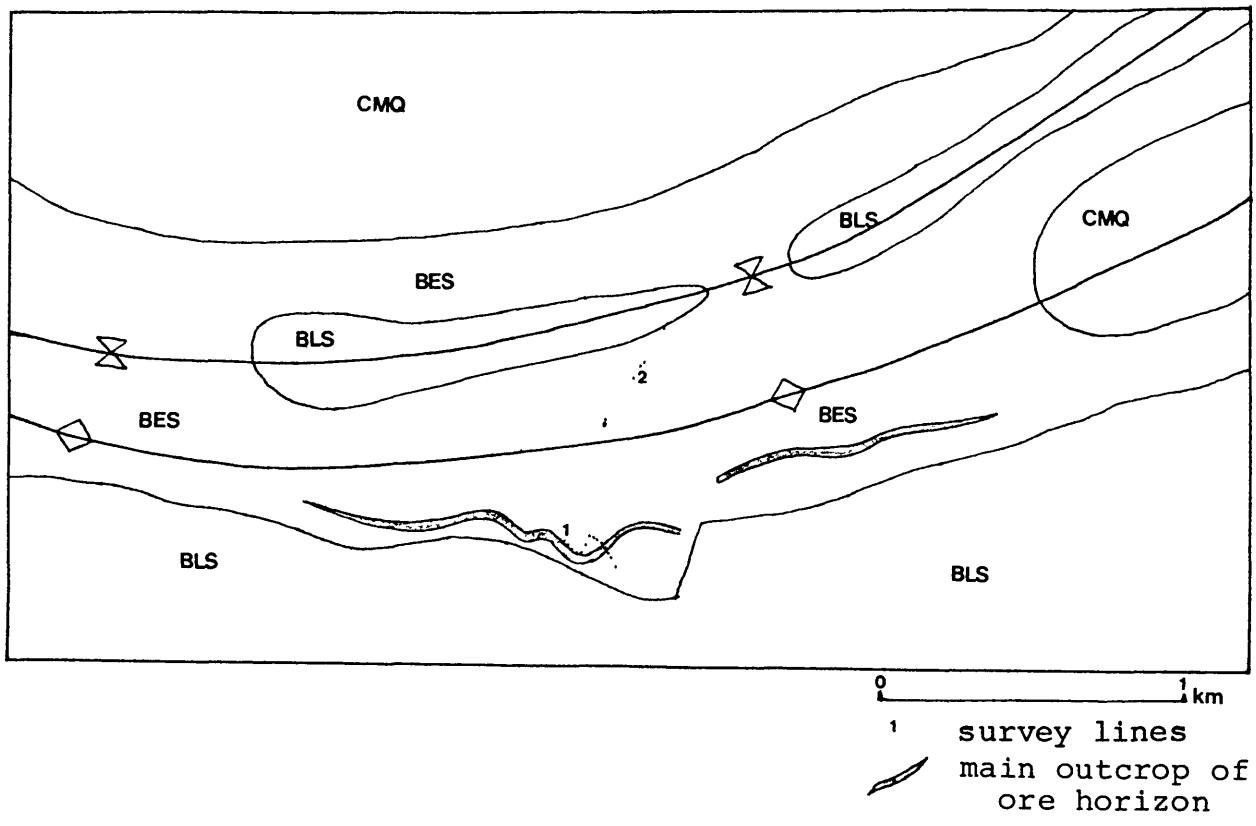
All these units are part of the lower limb of the Tay Nappe system, and as such have undergone a long history of deformation and metamorphism.

Figure 2.3b shows the geology of the field area.

2.3.2. Sampling Surveys Undertaken

Three sampling surveys were completed, each sampling on a different scale, and to a different purpose. Survey 1 comprised the collection of samples from the ore horizon itself. These included baryte, chert with sulphides, schist around the baryte etc. Survey 2 sampled the Ben Eagach Schist where this was exposed in a stream cutting. The orebody itself does not crop out in the stream, but the stream does intersect the cherts with disseminated sulphides which are the distal representatives of the ore horizon. Survey 3 formed a regional survey over

Figure 2.3b: Geology of the Aberfeldy Field Area.



Middle Dalradian Stratigraphy:

Unit	Ore Horizon
Ben Lawers Schist (BLS)	
Ben Eagach Schist (BES)	Hanging wall chert with sulphides Massive bedded baryte with sulphides Footwall chert with sulphides Chert and schist with sulphides Muscovite schist with pyrrhotite Biotite rich crystalline rock Muscovite schist with pyrrhotite
Carn Mairg Quartzite (CMQ)	

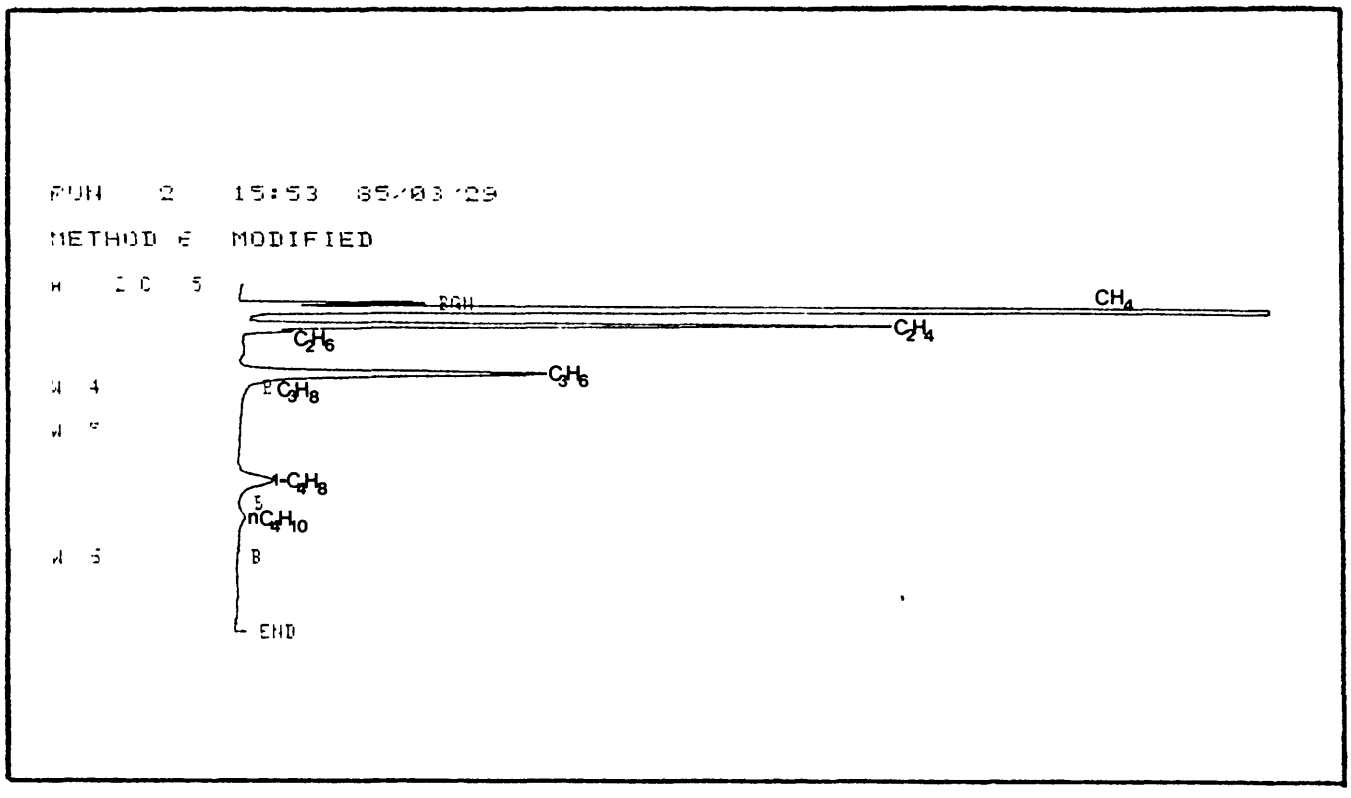
the whole field area, some 2km by 3km in extent. Samples were collected from all three major lithological units, and where outcrop allowed, a grid pattern was followed for the sample collection. It was hoped that the three surveys would indicate the quantity and nature of the hydrocarbons within the ore horizon, and whether the position of the ore could be detected by the hydrocarbon pattern within the host rock, or by the presence of an anomaly over a large area.

2.3.3. Gas Chromatography

The samples were prepared for analysis as described in section 2.1.2., with one minor variation. The baryte samples, having a very much higher specific gravity than the samples of the host rock, gave a very much smaller volume of crushed sample if the standard 10g was taken. Since the volume of the rock, rather than the mass, will determine the amount of hydrocarbon emitted, the amount of crushed baryte used for analysis was adjusted to be of similar volume to the 10g crushed host rock samples.

The aim of the gas chromatographic analysis was to identify and quantify the gases important in determining the position of the orebody, in the shortest time possible. This simulated the conditions under which gas chromatography would be used in an exploration programme. The methane percentage in the analysed gas was regarded as the most important index, since

Figure 2.3c: Typical Chromatogram of an Aberfeldy Sample.



from this it would be possible to determine whether any methane anomaly could be detected. The total area under the chromatogram was also recorded, to give a comparative measure of the amount of hydrocarbons within the samples. The values of the indices for all the samples are given in table 2.3a; the complete results are to be found in Appendix C. Since the methane content and the speed of the analysis were the important controls on the analysis, an isothermal method of running the chromatograph was chosen. This gave a time of fifteen minutes per analysis (cf. section 2.2.3.), but the reduction in turnaround time was accomplished at the expense of accuracy. The gases were not separated as well at the higher temperature, as when the non-isothermal method was used for the Mendips samples, and sometimes propene and propane formed a single merged peak. However, since the aim of the analyses was to quantify the methane content, this loss of resolution on the other gases was considered unimportant.

The hydrocarbon content of the samples varied from that of the Mendips limestones, most noticeably in the lack of the secondary 1-butene peak (figure 2.3c). The rocks have a long history of metamorphism, and any hydrocarbons generated at high temperatures or only loosely bound to the rock will already have been lost, during some metamorphic episode. It can therefore be assumed that the gases analysed are those most tightly bound to the host rock.

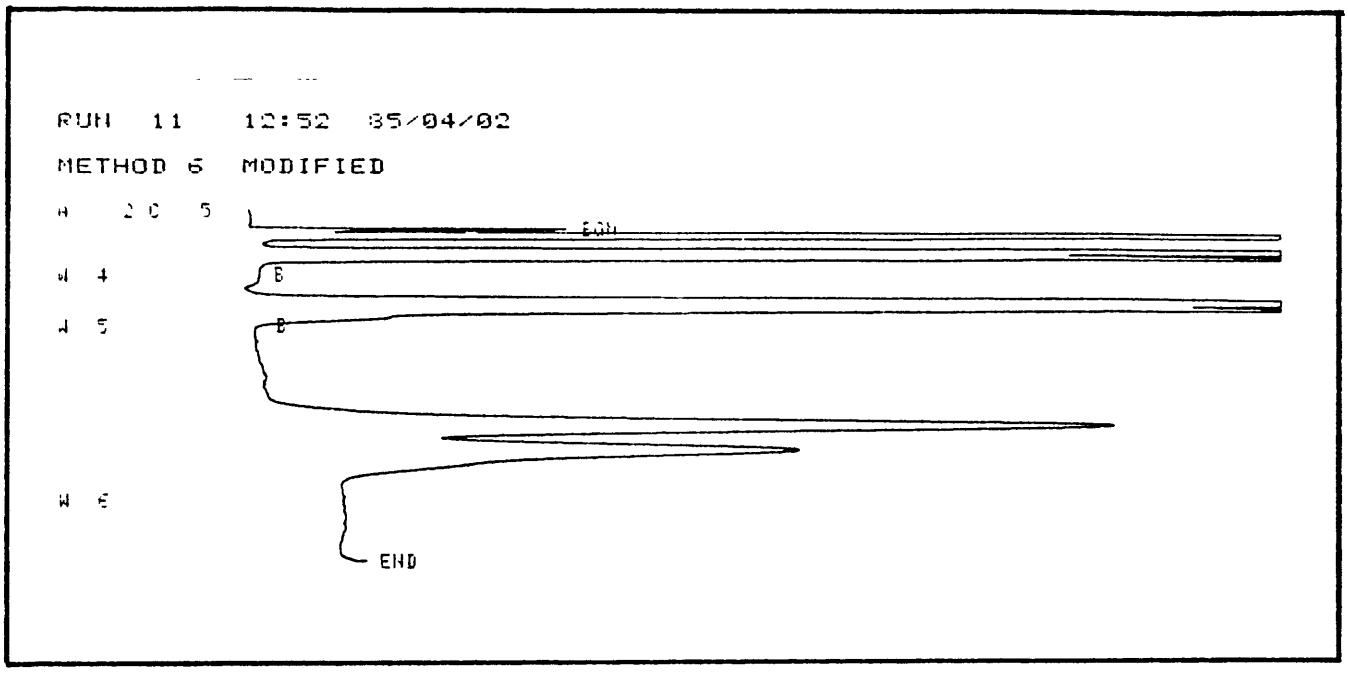
Table 2.3a: Values of Hydrocarbon Indices of Aberfeldy Samples.

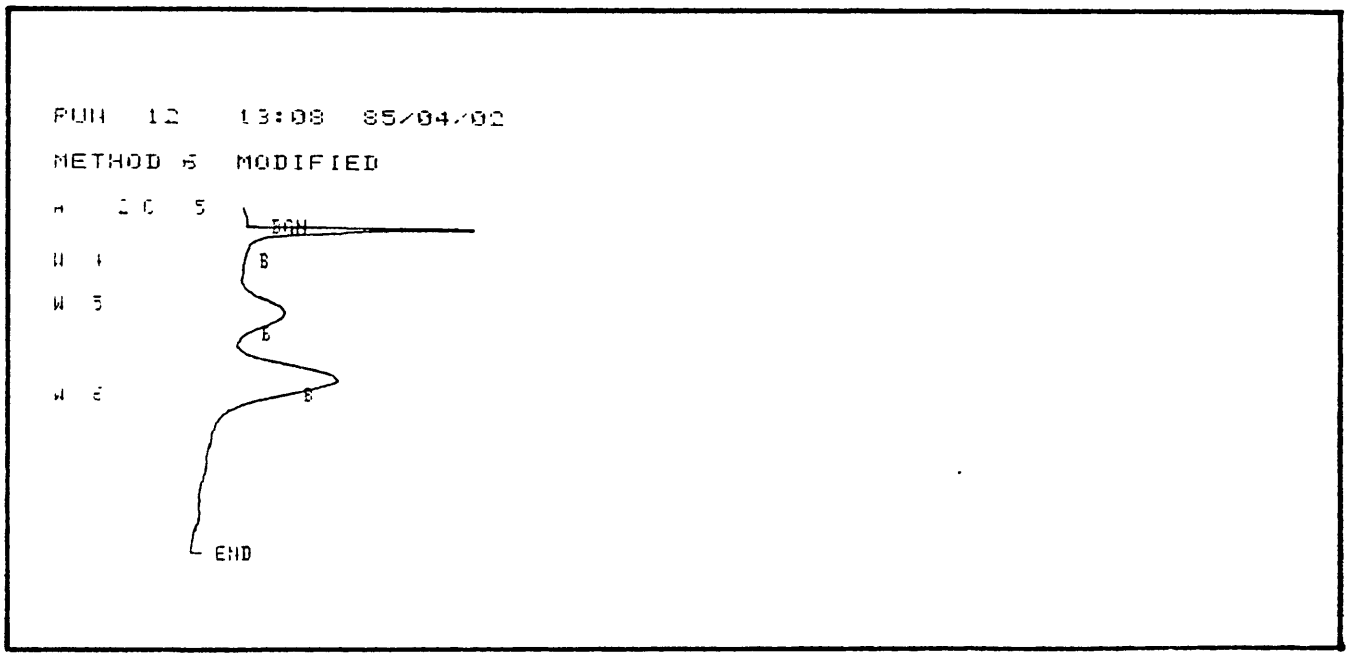
AB	CH_4%	Area	Survey	Unit
1	82·98	10·90	1	BES
2	92·81	14·86		"
4	95·68	27·49		"
5	95·04	23·35		"
6	93·38	13·82		"
7	92·24	9·59		"
22	56·86	13·33	2	BLS
23	84·57	6·21		"
26	60·69	8·78		BES
27	59·17	10·67		"
28	90·47	10·63		"
29	81·61	8·01		"
30	73·94	6·69		"
31	86·81	8·36		"
32	37·49	17·26		"
33	55·41	6·81		"
34	69·18	11·49		"
35	56·69	11·41		"
36	70·30	5·34		"
37	67·17	5·18		"
39	60·41	12·07		"
39	53·46	11·83		"
40	89·29	8·21		"
41	69·69	13·53		"
44	73·96	9·52		"
45	76·61	8·61		"
50	42·94	13·56		"
53	62·10	10·19		"
55	74·88	9·88		"
57	77·76	7·39		"
58	39·45	12·11		"
59	51·88	12·90		"
60	67·20	8·55		"
61	80·00	8·59		"
62	55·56	7·32		"
63	38·68	17·34		"
64	88·40	10·65		"
66	53·33	10·90		"
67	62·85	9·86		"
68	81·49	8·93	3	BLS
71	83·90	9·98		BES
73	50·34	9·75		"
75	83·65	13·98		"
77	55·29	12·42		BLS
84	72·54	10·74		CMQ
86	75·52	11·43		BES
89	47·90	11·86		BLS
93	66·69	13·75		BES
95	85·17	6·56		BLS
97	62·49	7·89		CMQ

2.3.4. Vegetation Contamination

The field area is one of poor exposure, with what outcrop there is often having a copious cover of mosses and lichens. This made the collection of fresh samples difficult, and sometimes it was necessary to take samples despite their attached vegetation. During sample preparation, an attempt was made to clean the samples, and after the samples had been split, only the cleanest fragments were chosen for crushing. Unfortunately, these attempts were not wholly successful, and the problem of contamination remained. The effect of such contamination was more pronounced when the chromatograph was run under isothermal conditions, as for the Aberfeldy samples, due to the carry-over effect. The trouble was caused by gases of C_5 and above emitted by vegetation attached to the rock samples, when the crushed rock was heated. The analytical runs were tailored to deal with gases up to C_4 only, so the higher order gases were not cleared from the column during a single analytical run, but were expelled from the column at the start of the next run. On the non-isothermal programme (under which the Mendips samples were analysed) the lower temperature at the start of the run caused the carried-over gases to be expelled slowly, forming broad peaks. The chromatograph considered these to be baseline drift, and they were compensated for, thus having no effect on the results of the analysis underway. On the isothermal programme, however, the column was hot at the start of the run, and the higher order gases that had been carried over formed distinct peaks.

Figure 2.3d: Chromatograms of Contaminated Sample and Following Blank Run.





These peaks interrupted the next analysis, and could only be prevented from doing this if a blank run was included after any such analysis, to clear the column. An example of a chromatogram produced by analysis of a vegetated sample is given in figure 2.3d, as is the following blank run.

The problem with vegetation contamination was therefore twofold; not only was the analysis of the vegetated sample itself invalidated by gases emitted by the vegetation, but the analysis of the following sample could also be badly affected.

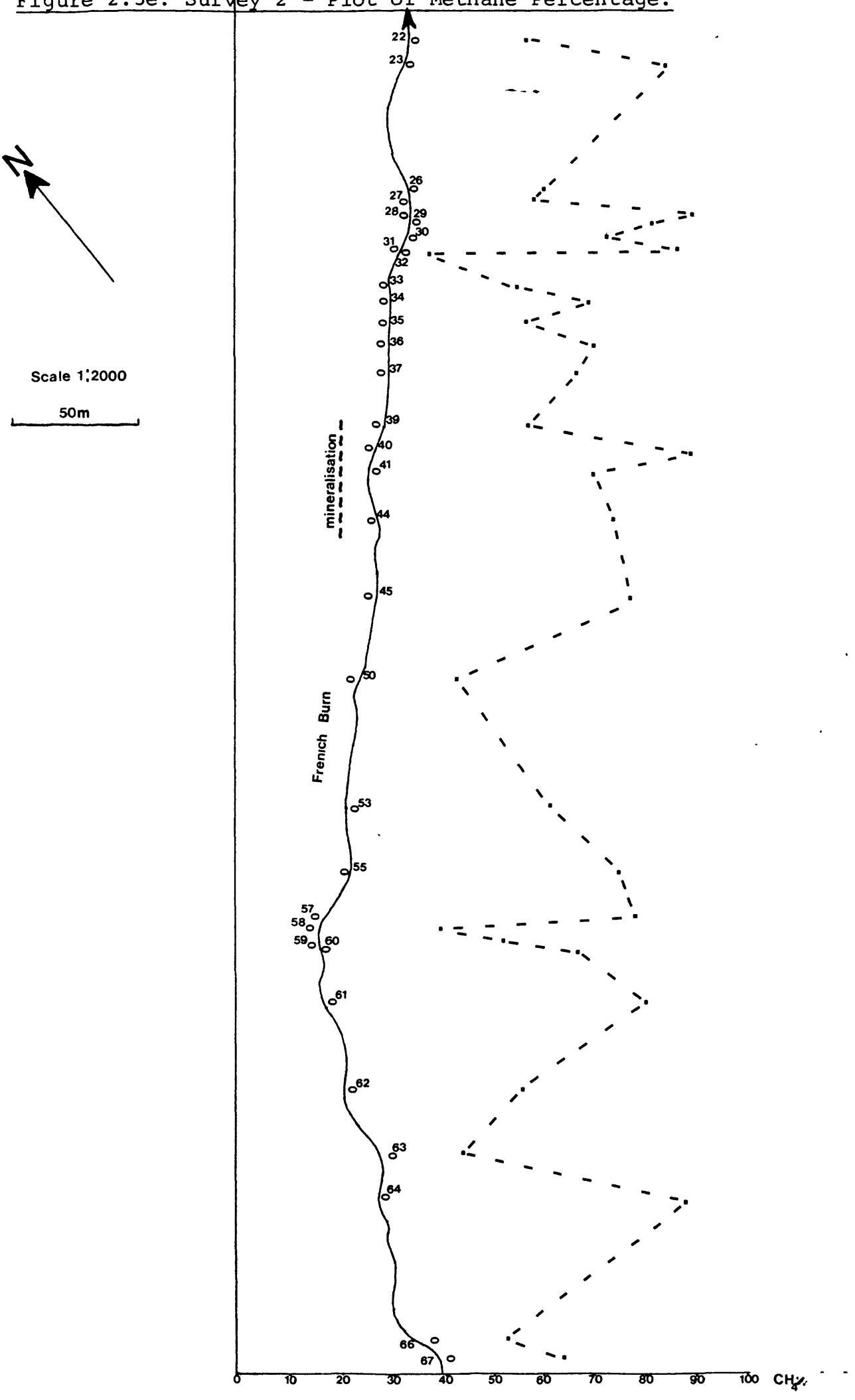
Several of the samples were obviously contaminated in this manner, and the problem remained as to how much reliance could be put in the remaining results. Some of the results from the stream survey (survey 2) were omitted through contamination, as were many of those from the regional survey (survey 3).

2.3.5. Results of the Surveys

Survey 1:

The samples of the ore horizon lithologies were fresh, coming from a road cutting made fairly recently, and there was therefore no problem with vegetation contamination. All the samples were found to contain higher than average total amounts of hydrocarbon, and very high methane percentage values, 82 - 96% of the analysed gas. Previous work suggests that the ore itself should be slightly lower in methane than the

Figure 2.3e: Survey 2 - Plot of Methane Percentage.



rocks just around it, in which the methane maximum usually occurs. It is, however encouraging that the samples are noticeably higher in methane; not only can they be distinguished from the surrounding rocks, but this also indicates that anomalous amounts of methane associated with ore deposits are not only a feature of carbonate host rocks.

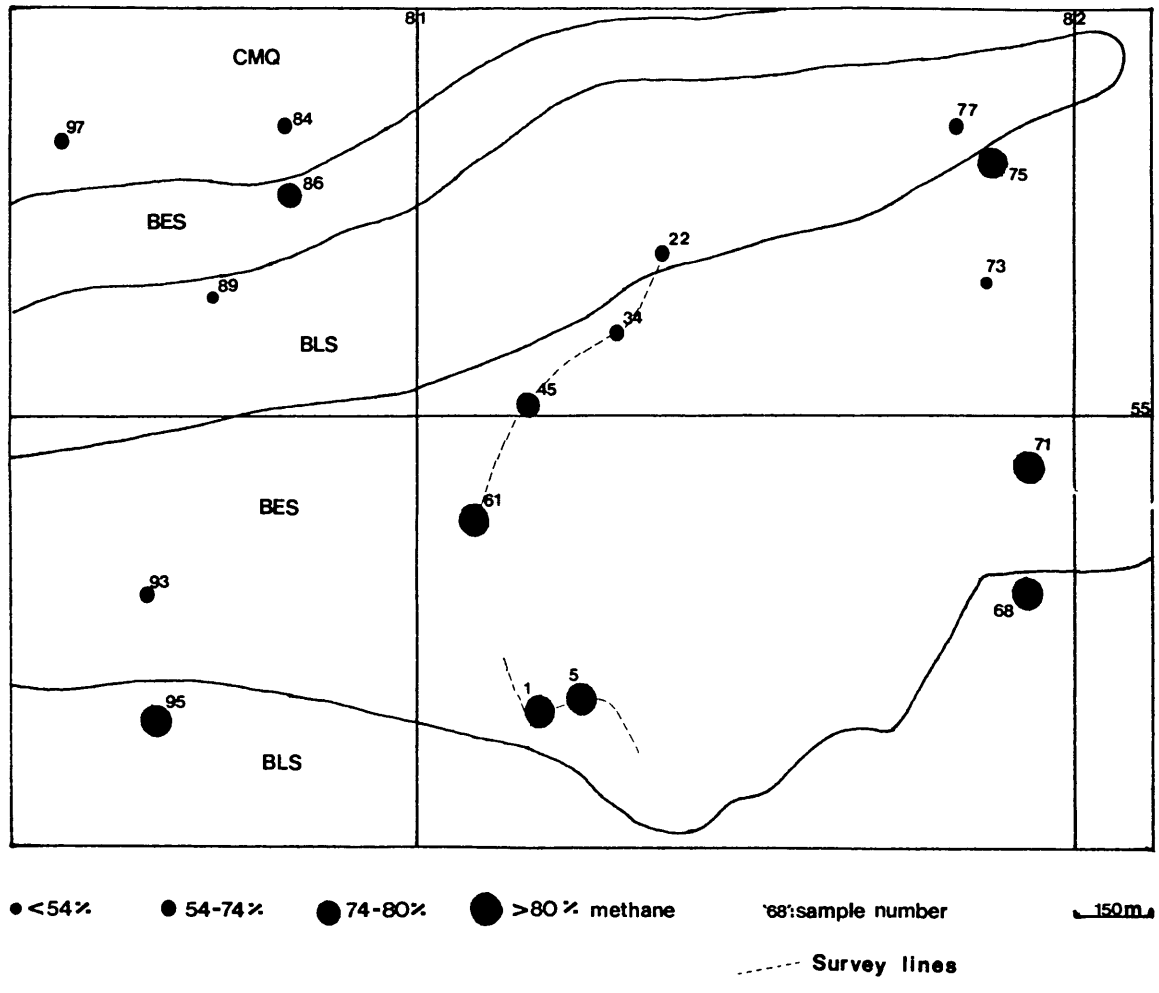
Survey 2:

The samples collected along the stream were all weathered to some extent, but in most cases careful cleaning during sample preparation ensured that the analyses were not contaminated. Those samples that did produce spurious results were omitted from the interpretation. The remaining results were plotted up along the section as shown in figure 2.3e. The mineralisation indicated is the distal equivalent of the ore horizon, and as such might be expected to have an effect on the hydrocarbon pattern along the section. As can be seen by figure 2.3e, although there is one high methane percentage value at this position, there is no way to distinguish this region from the rest of the section. Sampling on this scale would therefore not identify the location of a mineralised horizon, unless such sampling intersected the ore itself, when, as above, there would be a series of samples with consistently high methane percentage values.

Survey 3:

This regional survey, sampling all three lithological units, was unfortunately greatly affected by vegetation

Figure 2.3f: Survey 3 - Plot of Methane Percentage.



contamination, due in part to the schistose and easily weathered nature of many of the samples taken. The omission of results from the interpretation due to the contamination exacerbated the problem of poor survey coverage caused by the paucity of outcrop. The remaining results are plotted in figure 2.3f, and whilethese are more widely spaced than originally anticipated, due to the problem of contamination, the samples are still taken more frequently than the one sample per square kilometre suggested by Carter (1981, 1984) for a reconnaissance survey. All three lithological units have a similar range of hydrocarbon values, the percentage methane in the analysed gas being in the range 60 - 80%, slightly lower than in the ore horizon itself.

2.3.6. Interpretation of the Results.

From study of the results it seems that the position of the baryte ore or its distal equivalents (chert and sulphides) is not indicated by variations in the hydrocarbon composition on this scale. There is no pattern in the hydrocarbon content of the rocks which could be termed a 'halo' of the sort described around base metal deposits in the Irish Carboniferous Limestone (Carter & Cazalet 1985, p14). The concentric halo effect has been seen only around the Irish ore deposits, suggesting some peculiarity of the ore genetic system there which encouraged their formation. It is perhaps not surprising that no such haloes were found around the (very different) ore deposit near Aberfeldy. However, even in the absence of a hydrocarbon halo, the simpler methane

anomaly pattern would be expected, with higher methane values in the vicinity of the ore deposit. At first it appears that there is no obvious pattern in the results, however the range of methane percentage values recorded in this area is similar to that noted around other ore deposits, when the latter are studied on the same scale (Carter & Cazalet 1984, p14). It seems likely that the field area lies within a region of anomalous hydrocarbon content, and is not big enough in extent to cross into the region of background hydrocarbon values.

It might be expected that the'concertina'effect on the geology caused by the tectonic history of the region would have resulted in the anomaly being reduced in area, and possibly covered by the field area. This effect of the deformation would, however, be counteracted by the attendant metamorphism. It has already been noted that the long history of these rocks has led to a change in the composition of the contained hydrocarbons, for instance when compared to those of the Mendip Hills. It is likely that metamorphic events involving high temperatures and fluid movement would affect both the nature and distribution of the hydrocarbons in the rocks. The 'concertina' effect that the deformation of the region would have on the extent of the hydrocarbon anomaly would be balanced by the attendant metamorphic redistribution of the hydrocarbons throughout the region.

That the ore precipitation processes producing methane act during the precipitation of the baryte ore is indicated by the very high methane percentage values of the ore horizon. The difference between these values and those of the surrounding host rock suggests that the gases within the ore horizon itself avoided any metamorphic redistribution. Previous work on this ore deposit has shown that the baryte ore and surrounding sediments of the ore horizon lie within an envelope of cherts. These cherts have allowed preservation of delicate sedimentary features by causing the different strata of the ore horizon to deform as a single competent unit (Goodman 1982). It seems probable that these cherts also acted as a permeability barrier, so preventing the migration and redistribution of gases within the ore horizon.

2.3.7. Summary.

The main conclusion to be drawn from these results is that the hydrocarbons analysed from the rocks cannot be used to detect the position of the ore deposit by sampling on this scale. Problems are caused by the nature of the rock itself, the schistose and easily weathered nature of the rock giving rise to problems with vegetation contamination. The poor outcrop in this region means that it is not always possible to select an alternative sample site to avoid a weathered outcrop. The resulting restriction on the sample coverage poses difficulties for the use of hydrocarbon anomaly detection as an exploration tool, and the same must be true of many similar field areas.

The interpretation of the results also leads to the conclusion that in this area there is no hydrocarbon halo pattern. It does, however, seem probable that there is an anomaly pattern here. The samples in the field area, being taken within the confines of the anomalous region, have high percentage methane values; the field area was not large enough to sample rocks with background hydrocarbon compositions..

The results are of great importance for the information which they supply on the nature of the hydrocarbon pattern. The fact that there are hydrocarbons present at all indicates that these are indeed linked to the presence of the ore, and are not merely a feature of carbonate host rocks. The cause of the high methane content of the ore itself and the surrounding rocks is limited to those processes of ore formation which both carbonate hosted base metal deposits and shale hosted baryte deposits have in common. To determine which of these processes are important controls on the hydrocarbons, it is necessary to study the hydrocarbons htemselves, and their relationship to the processes of ore formation.

CHAPTER THREE

THE NATURE OF LIGHT HYDROCARBON ANOMALIES

The preceding research has established some of the controls on the nature of hydrocarbons within the rock e.g. lithology, petrology, metamorphic history, presence of ore etc. In order to understand these further, and the reasons for their control on the hydrocarbons, it is necessary to study the nature of hydrocarbon formation and migration, and the relationship of this to the ore-forming process.

3.1. THE FORMATION AND MIGRATION OF HYDROCARBONS

Due to the interest in and reliance on economic petroleum deposits, there is a wealth of published material available on this subject. This section is an attempt to select the relevant information from recent publications.

3.1.1. Definition of Petroleum and Hydrocarbons

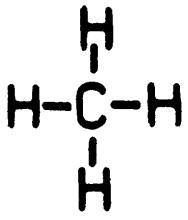
A brief definition of terms is perhaps necessary here, in order better to understand the subjects under study. Petroleum is a substance occurring naturally as semi-solids, liquids or gases, or mutual solutions of these (Chapman 1983, p.72). Petroleums are mixtures of hydrocarbons (i.e. compounds containing only carbon and hydrogen) and contaminant non-hydrocarbon compounds. The hydrocarbons comprise four groups; the alkanes (paraffins), cycloalkanes (naphthenes), aromatics, and naphthenoaromatics (complex hydrocarbons) (Neumann et al

Figure 3.1a: The Hydrocarbon Components of Petroleum.

ALKANES C_nH_{2n+2}

e.g. Methane

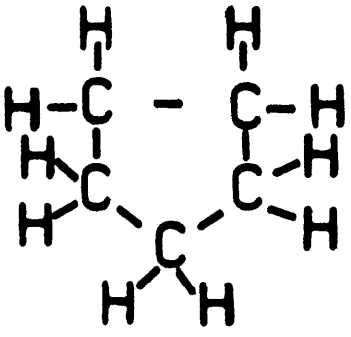
CH_4



CYCLOALKANES C_nH_{2n}

e.g. Cyclopentane

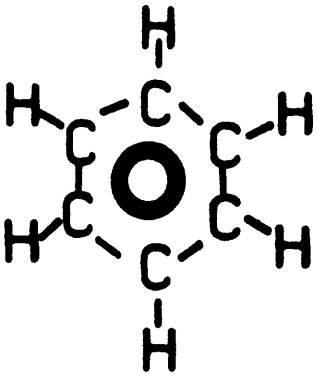
C_5H_{10}



AROMATICS

e.g. Benzene

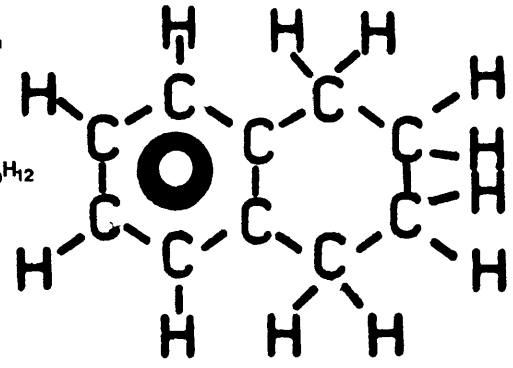
C_6H_6



NAPHTHENOAROMATICS

e.g. Tetralin

$C_{10}H_{12}$



1981, p.1). Each of these groups contains a series of compounds similar in molecular structure, though varying in the number of carbon and hydrogen atoms present (a homologous series). Figure 3.1a illustrates the structural formulae of examples from each series. Unsaturated hydrocarbons, such as alkenes, are not found in most petroleums, though natural gas may contain a few percent ethene. The non-hydrocarbon contaminants of petroleum include compounds of sulphur, oxygen, nitrogen and various metals, all in combination with hydrocarbon radicals.

Natural gases are those compounds of petroleum which are gaseous under standard pressure and surface environmental temperature. They may occur in close association with liquid petroleums, or may form separate deposits. Natural gas consists mainly of the gaseous hydrocarbons i.e. the lowest molecular weight members of the alkane series. The main component of the gas is methane (CH_4), though other members of the alkane series up to hexane (C_6H_{14}) will also be present. There may also be some non-hydrocarbon gases e.g. the inert gases nitrogen, helium and carbon dioxide. Table 3.1a lists the important hydrocarbons in natural gases, and table 3.1b gives the average composition of natural gas of European, African and American origin (after Neumann et al 1981, p.27).

This, then, is the substance to be considered; a mixture of gases, each formed from carbon and hydrogen, naturally occurring in the geological column. The generation of this

Table 3.1a:Important Hydrocarbons in Natural Gas.

Hydrocarbon	B.P.°C.	Formula
Methane	-161	CH_4
Ethane	-89	C_2H_6
Propane	-42	C_3H_8
n-Butane	-0.5	C_4H_{10}
i-Butane	-12	C_4H_{10}
n-Pentane	+36	C_5H_{12}
2-Methylbutane	+28	C_5H_{12}
2-2-Dimethylbutane	+9	C_6H_{14}

Table 3.1b: Average Composition of Natural Gases Of European, African and American Origin.

Component	Volume %
CH_4	81.5
C_2H_6	3.6
C_3H_8	2.0
C_4H_{10}	0.4
C_5H_{12}	0.2
C_5+	1.0
N_2	5.2
CO_2	4.6
H_2S	1.4
He	0.04

(after Neumann et al 1981)

gas, and its migration from the site of generation are both important factors in the investigation into hydrocarbon anomaly formation. The text by Tissot & Welte (1984) is the standard reference for petroleum generation and alteration in nature. A simplified view of the subjects is presented here, drawn from this source and others.

3.1.2. Petroleum Generation

Any sediment will undergo certain changes as it becomes compacted and lithified, such processes being generally termed 'diagenetic'. The changes affect all parts of the sediment, both the mineral grains and any organic material. Petroleum is the product of the diagenesis of organic compounds contained in organic matter that accumulated with fine grained sediment in an anoxic low energy environment (Chapman 1983, p.78). The environment must be anoxic to prevent the destruction of the organic matter by oxidation; the fine grained nature of the sediment and the low water energy will further restrict the circulation of oxidising waters.

Plankton and bacteria in the seawater column provide most of the organic matter, a mixture of fatty acids and proteins. These break down under the anaerobic conditions to produce alkanes. The green pigment chlorophyll, for instance, decomposes through hydrolysis to produce phytol ($C_{20}H_{39}OH$), which in turn can produce pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$), both common constituents of petroleum (Neumann et al 1981, p.34). The diagenetic changes in the organic matter take place under

the influence of heat, pressure and time, and clay catalysis may also be important. Early diagenesis removes the more volatile and soluble components, leaving an insoluble residue known as 'kerogen'. The kerogen may then be a further source of petroleum. The controls on petroleum generation are now well enough understood for it to be possible to model the process mathematically, and to quantify the petroleum formation and occurrence in a given sedimentary basin (Welte & Yukler 1981). The variables considered to be important input data are the heat flux, initial physical and thermal properties of the sediments, palaeobathymetric estimates (i.e. pressure gradients), sedimentation rate, and amount and type of organic matter. These properties of the sedimentary basin are considered the most important controls on the generation of petroleum.

The fine grained sediment, formed under anoxic conditions, that is considered the most likely sediment to retain organic matter throughout diagenesis, will eventually form a mudstone on lithification. Mudstones are known to be particularly good petroleum source rocks. Not only do they have this ability to preserve organic matter (Chapman 1983, p.207), but they will also tend to be formed away from any proximal source of sediment. The slow rate of clastic sedimentation will then allow the build-up of a suitably high concentration of organic matter within the sediment.

It is possible to document the effect of temperature and time on petroleum generation by examining known deposits

(Magara 1978); figure 3.1b illustrates the relationships. This suggests that, all other things being equal, temperature and time are to a certain extent interchangeable. Therefore, for a similar stage of petroleum generation to have been reached, a younger rock formation will need to have been heated to a higher temperature than a more ancient formation.

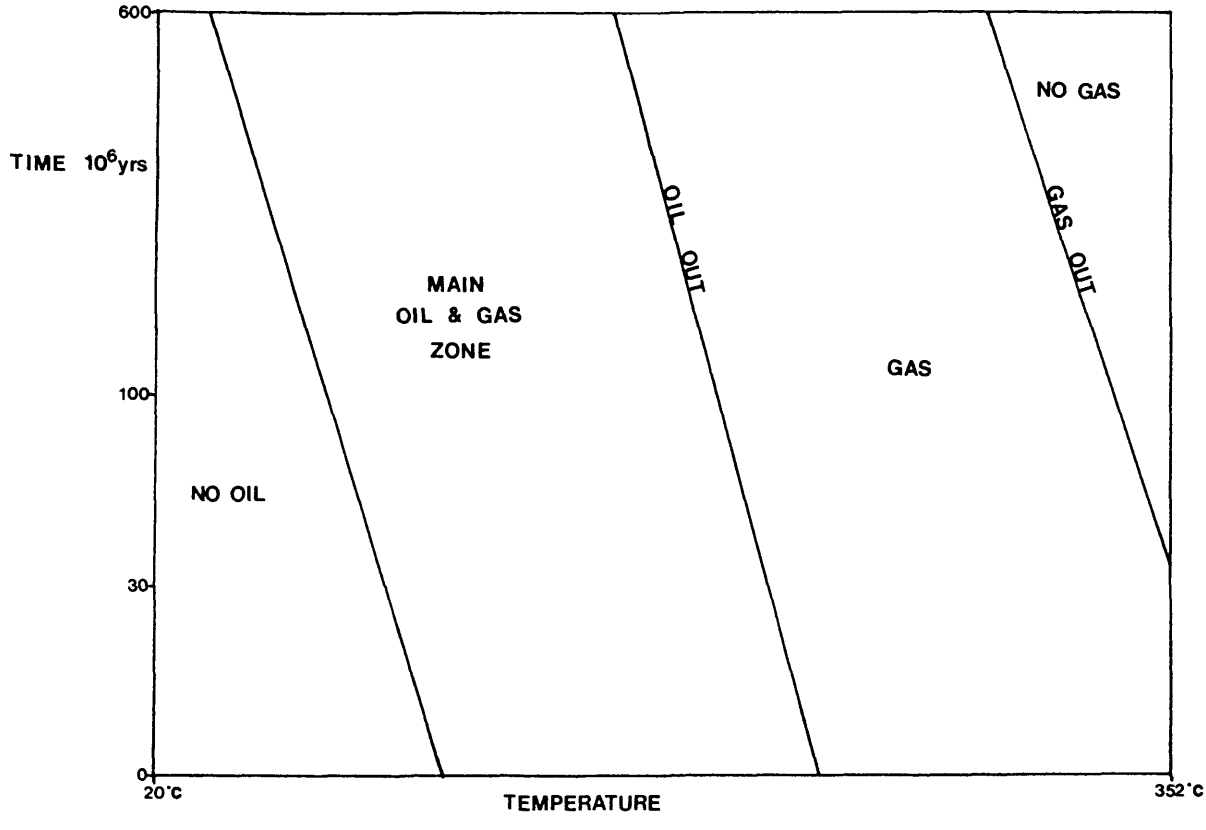
Most natural gas, including the hydrocarbon gases, is produced in the same way as the heavier petroleum components. (Tiratsoo 1972). The hydrocarbon gases are generally considered to be the gaseous phase of crude oil. This is not necessarily strictly true, but most petroleum deposits do have either gaseous hydrocarbons associated with them, or hydrocarbon gases dissolved in the liquid hydrocarbon. Methane can be formed by other methods, e.g. during coal formation, by magmatic action, by bacterial decomposition of organic matter etc. However only natural gas associated with petroleum or the processes of petroleum formation contains hydrocarbon gases other than methane.

3.1.3. Petroleum Migration

After generation of hydrocarbons in the source rock, this hydrocarbon may migrate from the source rock into a reservoir, eventually to form a hydrocarbon accumulation, provided the situation is favourable. This migration is split into two phases; primary migration from source rock to carrier bed, and secondary migration from carrier bed to reservoir.

Figure 3.1b: Temperature/Time Relationships of Petroleum Generation.

(after Magara 1978)



Migration paths taken during this time are a result of the permeability of the rock, and of fluid potential gradients (Chapman 1983, p.80). The secondary migration process, with hydrocarbons moving into the reservoir is generally well understood, being the result of the differences in density between the hydrocarbons and pore water. The hydrocarbons, being lighter, will move to the highest possible level within the reservoir, with the water beneath (Tissot 1984). There is still, however, much debate as to the nature of primary migration, that is, the expulsion of hydrocarbons from the source rock, and their transport through the adjacent carrier bed. This process is of prime importance in the study of methane anomalies, as this is in effect the study of hydrocarbons as they migrate. As the source rock is continually buried, overpressuring of the pore fluids will occur, causing an increase in internal pressure. This is accompanied by the thermal expansion of the pore water, in addition to volume expansion due to hydrocarbon generation. The partial transfer of the geostatic pressure from the solid rock to the enclosed fluid will cause microfracturing, forming hydrocarbon migration pathways through, or out of, the source rock. It is then possible for the hydrocarbons to move, though the form in which they move remains a problem.

Liquid hydrocarbons are not soluble enough in water for molecular solution to be an effective mechanism (Magara 1978). It has been proposed that the hydrocarbons are transported as soaps of organic acids in micellar solution. Again the problem

of solubility in water occurs, and there is no evidence of a great enough concentration of such micelles in natural systems. It is now generally accepted that the liquid hydrocarbon moves as a separate phase during primary migration (Tissot 1984, Magara 1978, Meissner 1978). The amount of organic matter migrating out of a source rock is small compared to the amount of water. The movement of this water probably influences and may well control the direction and effectiveness of hydrocarbon migration.

The migration of the gaseous hydrocarbons is easier to understand. The solubility of methane in fresh water increases from $0.7m^3m^{-3}$ at 35 bar to $5m^3m^{-3}$ at 700 bar, though it does decrease with increasing water salinity (Magara 1978). At great depths the quantities of gaseous hydrocarbons dissolved in pore waters may reach high values of around 5% by weight. This equals their solubility in oil (Jones 1980). Some of this gas will be released if the reservoir rock suffers a drop in pressure, such as that caused by tectonic upwarping, sudden faulting etc. (Perrodon 1983, p.85). Diffusion of light hydrocarbons through water-saturated pore space is an effective enough process to account for much gaseous primary migration (Leythauser et al 1982). In the case where there is a greater amount of gas present than that explicable by solution alone, formation of tiny bubbles has been postulated (McElvain in Heroy (Ed.) 1969). These bubbles would be small enough to be affected by molecular Brownian motion in the pore water, and so would be in perpetual random motion. The fact

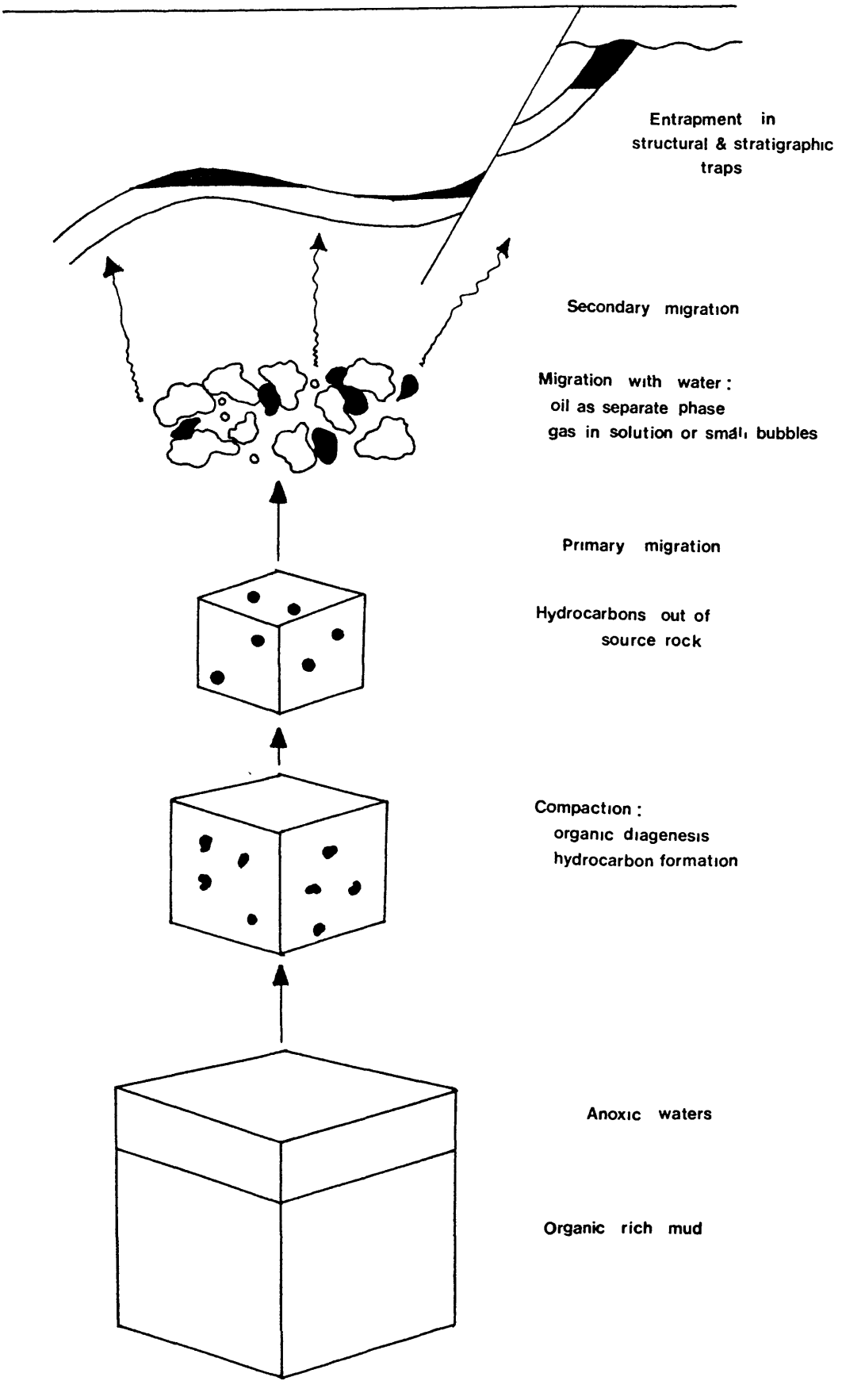
that they would be lighter than the surrounding pore fluid would give a vertical component to the motion, giving gradual mass migration.

There is therefore sufficient explanation of the migration of gaseous hydrocarbons through the source and carrier beds. Both gaseous and liquid hydrocarbons will be affected by the migration of water from the same beds, which will be occurring at the same time.

3.1.4. Summary

The processes of petroleum formation begins with the accumulation of planktonic and bacterial organic matter within fine sediment. Under anoxic bottom waters this escapes oxidation, and undergoes organic diagenesis during burial of the sediment. A combination of heat, pressure and time causes the formation of hydrocarbons, which eventually migrate out of the source rock and into the carrier bed. The movement of water is important for this migration, especially for the liquid hydrocarbons, which must migrate as a separate phase, not having the solubility of the lighter gases. Eventually a point may be reached where there is a permeability barrier preventing further migration. The hydrocarbon may then accumulate within the trap to form an economically viable deposit. The similarities to the ore genetic system discussed in section 1.2. should be noted. Both systems are normal features of any sedimentary basin, and in each case the presence of an economic deposit depends on some concentrating feature, rather than any particularly unusual geological event.

Figure 3.1c: The Generation, Migration and Entrapment of Petroleum.



3.2. HYDROCARBONS AND ORE DEPOSITS

The association between organic matter and ores has frequently been commented on, most often where heavy bitumen-like compounds are present in ores. The presence of a hydrocarbon anomaly near an orebody may be another facet of this association, or may be only marginally related. The possibilities must be investigated to derive any information on the formation of hydrocarbon anomalies.

3.2.1. Organic Matter and Ore Deposits

The carbonate hosted base metal ore deposits which form the main subject of this research have long been known to be associated with organic material, especially bitumens and liquid hydrocarbons. The presence of this material suggests a link between organic matter and ores, which led to the idea of the importance of bacterial activity in the geological system. The reduction of sulphate necessary to produce sufficient hydrogen sulphide for an ore deposit was said to be due to the action of sulphate reducing bacteria (Roedder in Brown (Ed.) 1967). An example of the application of this theory comes in the genetic history of the Saint-Privat baryte deposit in France, as described by Connan and Orgeval (1976). Their theory is that two fluids are involved, one carrying sulphate, and one metal ions. At the point of ore deposition the sulphate is reduced to hydrogen sulphide by the contemporaneous bacterial degradation of organic material within the host rock to bitumen. The precipitation caused by

the mixing of the metal rich brine with the sulphate/sulphide fluid results in baryte and sulphides, which trap the bitumen as they are formed. Bacterial sulphate reduction of this type has now been widely accepted as an ore genetic process, and has been invoked to explain the common association of ores with evaporite sulphate. Such evaporites would be a source of abundant sulphate for the bacteria to metabolize. It has been suggested that bacterial sulphate reduction is capable of producing only low-grade ores (Trudinger in Postgate & Kelly (Eds.) 1982, p.140), but the process certainly does play some part and may well be dominant (Clemmey in Brenchley & Williams (Eds.) 1985, p.232).

The process of bacterial sulphate reduction is well documented both in field observations (Reeburgh 1976; Goldhaber et al 1977) and in laboratory experiments (Davis & Yarborough 1966; Reeburgh 1980). The bacteria most commonly cited as important sulphate reducers are those of the Desulfovibrio desulfuricans type, which also oxidise hydrocarbons as part of the metabolic process. Methanogenesis caused by bacterial action is an equally important feature of the anaerobic decomposition of organic matter in sediments. The processes of sulphate reduction and methanogenesis were generally considered to be mutually exclusive, the sulphate reduction occurring at an early stage followed by methanogenesis. It has, however, been shown that these processes can occur simultaneously (Oremland & Taylor 1978), and that the rate of methanogenesis is increased if the sulphide in solution is

reduced. In a system where ore deposition was acting as a sink for the sulphides, it is therefore possible that both sulphate reducing and methanogenic bacteria would be agents of anaerobic organic diagenesis.

The organic matter in potential ore host sediments is therefore not only a part of the sediment pile, but also capable of aiding the production of sulphide and of methane on its bacterial decomposition. The sulphide so produced can precipitate ore minerals, causing the association between degraded organic matter and ore deposits.

3.2.2. Hydrocarbon in Ore Fluids

The ore genetic system responsible for the carbonate hosted base metal ore deposits is one in which basinal brines are expelled into the host strata at the basin margin (section 1.2.). The fluids contain high concentrations of metal ions derived from deep basinal shales, and are expelled due to compaction, to migrate through permeable strata to the basin margin. This system is very similar to that responsible for the generation and migration of petroleum (section 3.1). The metal ions and hydrocarbons are thought to come from the same type of source rock - deep basinal mudrocks. These organic rich sediments are known to concentrate metal ions (Park & McDiarmid 1975, p.429) as well as to produce hydrocarbons. It is therefore hardly surprising if hydrocarbons are present in metal bearing brines, nor that sulphides are sometimes found in oil and gas

reservoirs. Any basin is likely to have fine-grained sediments at its centre, and these will be anoxic if there is no mixing with aerated water. Compaction of such sediments will eventually lead to the expulsion of brines, containing both hydrocarbons and metal ions. Whether or not the fluid eventually forms an ore deposit or a hydrocarbon deposit will depend on the conditions within the basin, the concentrations of hydrocarbons and metals in the brine, and on the migration path. Even when the concentrations are great enough, the brine must ultimately reach a hydrocarbon trap or a sufficient source of sulphide to form one or other type of deposit, and in most cases there will be no productive outcome. Such a deposit is therefore an unusual occurrence; nonetheless, the process involved would be expected to occur in any sedimentary basin.

In the potential host sediment, anaerobic organic diagenesis could be established, with bacterial action causing decomposition of heavy hydrocarbons etc. These processes would act whether there was ore precipitation or not, and would be responsible for the levels of light hydrocarbons detected in analysed samples of rock from unmineralised areas. Previous work has suggested that the processes of sulphate reduction and methanogenesis are responsible for the large amount of methane at the site of ore deposition (Dunsmore & Shearman 1977; Carter 1981). It is suggested here that the action of bacteria on hydrocarbons introduced with the ore fluid, rather than pre-existing in the sediment, is responsible for the generation of the large amounts of gas detected at

anomalous sites. At the site of ore precipitation, sulphate reducing bacteria will be involved in the decomposition of organic matter, accompanied by some methanogenic bacteria. The bacteria, acting on hydrocarbons introduced in the mineralising fluid, will decompose them to simpler members of the series, and ultimately to carbon dioxide and water. The process of methanogenesis will therefore not be the only one producing light hydrocarbons at the site of ore deposition, the action of the sulphate reducers will also have this effect. Evidence from the hydrocarbon content of the rocks around ore deposits shows that the final effect is an increase in light hydrocarbons, especially methane.

3.2.3. Anomaly Formation

If the above hypothesis is correct, that hydrocarbons are introduced with the ore fluids and altered by the action of bacteria, it is still necessary to determine a method whereby the resulting light hydrocarbons can form the detected anomaly in the host rock. The continuing introduction of fluids at the site of ore deposition will tend to cause the hydrocarbons to migrate away from the ore. There may be bulk migration, with the pore fluid also being displaced, but the most important process may well be gaseous diffusion through saturated pore space (section 3.1.3.). The migration will, however, only occur where there is sufficient permeability in the surrounding host rock. Stegena (1961, p.450) modelled the case for light hydrocarbons migrating away from oil

reservoirs, and came to the conclusion that for reservoirs at great depth, or where the surrounding rocks were impermeable, no significant migration could take place within the life of the reservoir. Only in cases where the depth was not great and the host rock was permeable was the migration rate rapid enough to allow steady-state diffusion. This restriction on migration of the hydrocarbon gases must also apply to those gases produced at sites of ore deposition. In some cases where ore precipitation has occurred, there may be no large hydrocarbon anomaly, since insufficient time has elapsed for the hydrocarbons to have migrated through a highly compacted low permeability host rock. Where the permeability is generally low, the action of faults and fractures as migration conduits will also become more important, so that the anomaly may be displaced from the position of the orebody, and may thus reflect the tectonic style of the area, rather than the mineralisation (Jones & Drozd 1983, p.943). It is therefore important to understand the nature of the rock hosting the ore genetic system, so that the nature of the hydrocarbon anomaly can be investigated in detail. The gases, for instance, are known to be bound tightly in the rock, which is why high temperature heating is used in the analytical procedure. In addition, the anomalies are sharply defined, with a sudden change from high methane values to background levels, rather than the gradual change that would be expected from continual diffusion. For the solution to these problems, a study of the carbonate hosts was undertaken; the investigation of carbonates and carbonate diagenesis form the second part of this thesis.

3.2.4. Summary

A hypothesis is proposed whereby the fluids carrying metal ions to the site of ore deposition also transport a certain amount of hydrocarbons. These are introduced at the centre of precipitation, and altered by the ongoing bacterial activity, resulting in large volumes of the lightest components, especially methane, which then disperse away from the orebody. This migration, probably accomplished by diffusion where the permeability is great enough, causes the anomalous hydrocarbon content of the surrounding rock. An explanation is still needed for the form that the anomaly takes, and for its preservation through geological time.

PART TWO

CARBONATE DIAGENESIS

THE INVESTIGATION OF THE PROCESSES OF CARBONATE DIAGENESIS AND THE CONTROLS ON THESE BY SIMULATION OF THE NATURAL SYSTEM; IMPLICATIONS OF THIS FOR THE THEORY OF HYDROCARBON ANOMALY FORMATION

CHAPTER FOUR

INTRODUCTION TO CARBONATE DIAGENESIS & ITS EXPERIMENTAL SIMULATION

The first part of this thesis investigated the carbonate-hosted ores and their attendant hydrocarbon anomalies. This second part examines the carbonates themselves, and the processes by which the sediment is transformed into rock. This first chapter identifies the changes occurring in nature, and describes previous attempts to simulate these experimentally.

4.1. CARBONATE DIAGENESIS

'Diagenesis' can be defined as the sum of all the processes affecting a sediment while it is at or near the Earth's surface. Such processes act on the sediment to change its chemical and physical nature, eventually causing the change to consolidated rock, or lithification. Diagenetic processes are generally characterised by their low temperature and pressure, though they do grade up into the metamorphic processes, which can be recognised by a new assemblage of stable minerals.

For lithification of siliciclastic sediments, the action of increased heat and pressure may be necessary, but this is not so for carbonates. The onset of carbonate lithification occurs immediately following deposition, involving processes such as cementation, replacement with calcite, dissolution, replacement of original or diagenetic minerals with dolomite etc. Due to the high solubility of carbonate minerals in water containing carbon dioxide, and the variety of carbonate mineralogy and crystal

size, the carbonate sediments are highly susceptible to diagenesis. For example, in carbonate sediments, diagenesis can create, obliterate or completely modify the porosity, whereas clastic diagenesis plays only a minor part in the reduction of primary porosity by compaction and cementation.

All diagenetic reactions involve the sediment pore water to some degree, and are therefore at least partly controlled by its chemistry, its Eh (redox potential) and its pH (acidity/alkalinity).

4.1.1. Carbonate Mineral Transformations

The mineral phases involved are calcite, aragonite (both $CaCO_3$), magnesian calcite, and dolomite ($CaMg(CO_3)_2$). Magnesian calcite and aragonite are stable in surface seawater, but unstable in fresh water, where calcite is the stable phase. Early diagenesis involves the transformations between the different mineral phases, and the inversion of aragonite to calcite is particularly important. The dry, solid state reaction needs a temperature of 400°C, for below this it is slow even by geological standards (Bathurst 1975, p.239); the wet transformation is the one important in natural systems. The water present reduces the activation energy which must be exceeded if the reaction is to proceed. Chemical controls on this reaction involve the concentrations of other ions in solution; the divalent magnesium ion is the main inhibitor of calcite precipitation. Where it is present in high concentrations, aragonite may be precipitated as the stable

carbonate phase, rather than magnesian calcite. This is probably a surface effect, with the magnesium ion being absorbed onto pre-existing grains. The blocking of active sites on the calcite face will then prevent further growth. Similarly magnesium inhibits dolomite precipitation, and magnesian calcite may form instead. The highly ordered nature of the dolomite lattice means that it will grow much more slowly than the calcite, even though dolomite is the less soluble phase, and should therefore precipitate first. Strontium ions can also be incorporated into the carbonate lattice, being more abundant in aragonite, since the large strontium ion fits more easily into the aragonite lattice. The concentration of strontium in the pore water is therefore also a chemical control (Bathurst 1975, p.241).

The physical constraints on mineral transformations include pressure and solubility of the phases. The variation in the amount of carbon dioxide in solution depends on the exchange between water and atmosphere (i.e. water mixing), on the bacterial decomposition or organic matter, and on the reaction with pelagic calcium carbonate. On a large scale the turbulence and mixing of water masses is also important. Pressure is important only for deep burial or deep water conditions. The solubility of the carbonates increases with increasing hydrostatic pressure, and with pressure within the lattice; the latter leads to the pressure solution effects commonly seen in deep diagenesis. In deep water the

dissolution of carbonates occurs, giving rise to the concept of the carbonate compensation depth (Blatt et al 1980, p475). Above this there is a supply of carbonate material; at the compensation depth the rate of supply equals the rate of dissolution, and below the compensation depth dissolution is dominant. The level is difficult to fix, however, depending as it does on the physical constraints mentioned above.

A combination of physical and chemical conditions therefore controls the dissolution or precipitation of the carbonate phases, and the transformations between these.

4.1.2. Subaerial Diagenesis.

Subaerial exposure of carbonates gives ample opportunity for the exchange and movement of fluids within the sediment. Examples of this are carbonate beachrock flushed by tidal seawater, dissolution of exposed carbonate rock etc. There are three major environments where subaerial diagenesis takes place. These are the marine phreatic, fresh water phreatic and fresh water vadose zones, where 'phreatic' involves groundwater below the water table, and 'vadose' involves that between the water table and the ground surface. The differences between the zones lies in the amount of water available. In the vadose zone the water forms thin films around the sediment grains, held there by capillary forces (Blatt et al 1980 p.507), while in the phreatic zone there is saturation by the pore water. Cements in the vadose zone are therefore restricted to a thin layer, and tend to contain more strontium ions from dissolved aragonite (Pingitore 1976).

Only small amounts of magnesium can be introduced from elsewhere. In contrast, the cement formed in the phreatic zone contains less strontium, more magnesium, and the greater circulation of pore fluid ensures consistency of composition in the precipitated carbonates.

Any carbonate may have a complicated subaerial history, as has been found in the case of backreef terraces in Barbados. These marine carbonates have been exposed to all the subaerial diagenetic environments at some time due to the vertical migration of the fresh water lens (Bathurst 1975, p.322). The changing chemistry of the sediments is reflected in the changing chemistry of the pore waters. The recharge of this water can make the diagenetic history yet more complicated, though in areas where there is little recharge the carbonate - pore water system may approach equilibrium.

Subaerial diagenesis can lead to a carbonate rock with a porosity as low as 15%, compared to the 40% porosity typical of carbonate sediments. Deep burial diagenesis has its attendant pressure solution to act as a source of carbonate for the new cement. In the case of shallow diagenesis, the source is less easy to identify. Subaerial exposure will lead to dissolution of surface carbonate, and the waters containing this may percolate into the shallow subsurface, and precipitate carbonate there. Alternatively, evaporation of water at the surface may draw carbonate-rich pore water upwards by capillary action. There is proof of these processes in

natural systems, though they are by no means present in every case. The problem remains that of ancient limestones, few of the original minerals still exist, and about half the rock is new material introduced from elsewhere.

4.1.3. Subsea Diagenesis

Diagenesis of carbonates on the sea floor or just below is limited to a few processes only. The minerals will undergo little change until exposed to pore water of a different composition to that originally present. The large reservoir of seawater buffers any reaction, preventing such change in the pore water composition. Precipitates of aragonite and high-magnesium calcite will be formed, and though these are unstable with respect to low-magnesium calcite there is little evidence for large scale transformations on the sea floor. The composition of the substrate controls the composition of the diagenetic minerals to some extent, though beachrock of shelly silica sand cemented by aragonite, has been reported (Allen et al 1969). Fine grained cements may be precipitated in areas where the waters are saturated with respect to carbonate, and again this will tend to be high-magnesium calcite.

The activity of the sea floor fauna is important for mixing of the sediment, and boring organisms may cause micritisation, i.e. the formation of very fine lime mud. This fine grained material again has a composition related to

that of its host. It may be finely comminuted matter washed into the borings, though there is some evidence of precipitation in situ, for which the presence of organic matter may be a control.

The interstitial waters of shallow marine sediments affect the diagenetic processes, and the composition of these waters is largely detemined by organic activity. The increase in dissolved carbon dioxide with depth is due to metabolic activity rather than dissolution of carbonates (Presley & Kaplan 1968). Biological activity also affects sulphur speciation. Sulphate and sulphide decreases with depth, and eventually there is no dissolved sulphur in the interstitial fluid (Nissenbaum et al 1972). Changes such as these in the pore water chemistry have an effect on the nature of the diagenetic transformations.

Diagenesis on the sea floor is therefore a slow process, due to the constant composition of the saline pore fluid. The changes that do occur in this fluid, and so in the carbonate sediment, are a result of biological activity.

4.1.4. Cementation and Neomorphism

The diagenetic mineral transformations lead to lithification of the carbonate sediment to form a low-porosity carbonate rock. The physical processes involved in lithification are cementation and neomorphism. The two processes have similar overall results, and their effects may look similar in detail,

but they are quite distinct. Cementation involves the precipitation of new carbonate material - the cement - in pore space, so binding the grains together. Neomorphism is the physical change of pre-existing material, either by wet inversion of aragonite to calcite, or by recrystallisation.

The cementation process involves the competitive growth of new crystals of carbonate, so the cement crystals have plane faces, and increase in size away from the host grain. These features may also be found in neomorphic spar, but a cement can be distinguished by its multiplicity of generations, and by the greater number of triple junctions with one of the interfacial angles at 180°C. The rate and nature of cement growth, as well as its composition, is related to the substrate composition (Bathurst 1975). For the precipitation of cement to occur, it is necessary to have calcium carbonate phases of different solubility, and a flow of pore fluid. The latter is necessary to produce sufficient mass transport in solution, since ionic diffusion is too slow a process. Cementation at the seawater - sediment interface is slow, and needs frequent recharging of the saline pore water for it to proceed.

Of the neomorphic processes, the aragonite to calcite inversion has already been mentioned, the wet inversion being the only one kinetically able to proceed under these conditions. It is accomplished without the development of further porosity, and often with an increase in grain size - aggrading neomorphism (Adams et al 1984). Recrystallisation may also

increase the grain size, e.g. when micrite is replaced by neomorphic calcite spar. Neomorphic spar generally has irregular crystal boundaries, patchy grain size distribution, and frequent relict micrite and skeletal grains.

Aragonite bioclasts are usually preserved as calcite clasts with no trace of the original structure, through wholesale dissolution and replacement precipitation. Sometimes, however, inversion occurs in situ and the fine structure is preserved in the new calcite material. This is another form of neomorphism.

4.1.5. Summary

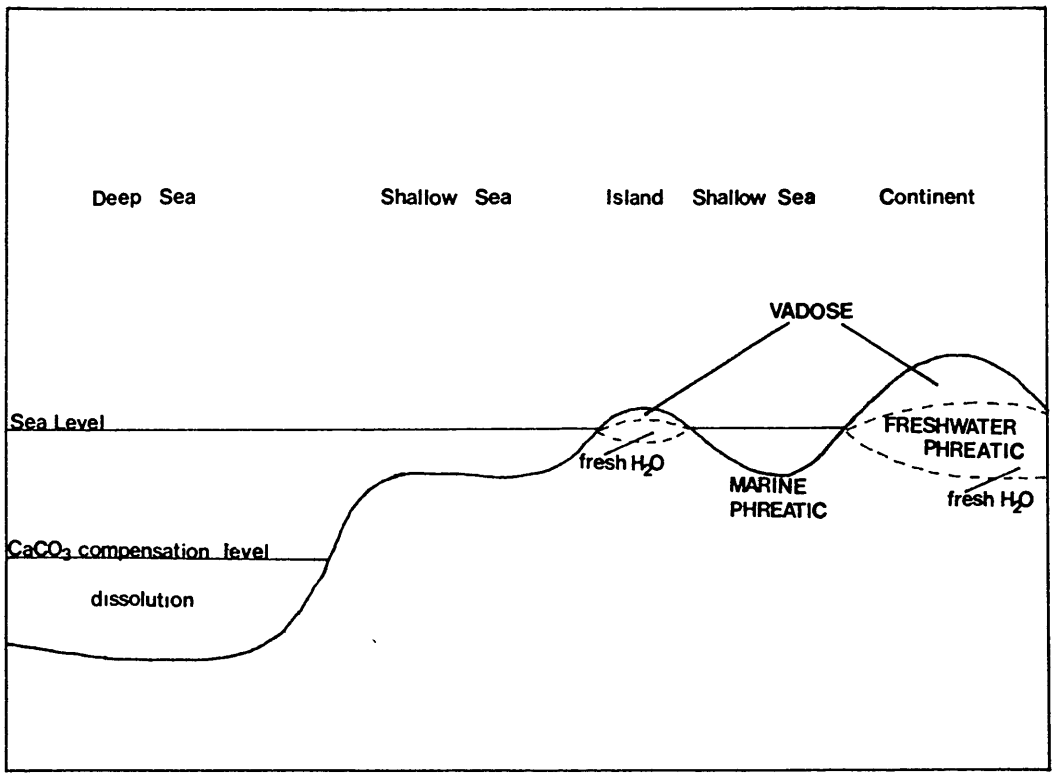
Diagenesis includes the changes that occur as a consolidated rock is formed from a sediment. This may occur after deep burial, and certainly for siliciclastic sediments higher temperature and pressure are important, but for carbonates most diagenesis occurs at a shallow level. Chemical transformation between the carbonate phases and reaction with the pore waters cause a change in the chemistry and mineralogy of the carbonates. Lithification is finally attained by this, through the processes of cementation and neomorphism.

For mathematical treatment of the processes of diagenesis reference should be made to Berner (1980), while Dickson (in Brenchley & Williams (Eds.) 1985) describes the petrographic and analytical methods of practical diagenetic investigation.

Figure 4.1a summaries the environments of carbonate diagenesis.

Figure 4.1a: Environments of Carbonate Diagenesis.

(after Blatt et al 1976)



4.2. PREVIOUS WORK ON EXPERIMENTAL DIAGENESIS

The experimental carbonate diagenesis which forms the bulk of the following sections is a continuation of that undertaken previously at Imperial College (e.g. Ferguson et al 1984). This work investigated the changes occurring when shallow diagenesis was simulated. Recent experimental work has also been undertaken on deep burial diagenesis (Bhattacharyya & Friedman 1984). A summary of the methods and results of all this recent research is presented here. In both cases the aim of the experiments was to simulate natural diagenesis by taking natural carbonate material and subjecting it to conditions under which diagenetic reactions might be expected to occur. In both sets of experiments the temperature was chosen to encourage these reactions to proceed, rather than to mimic natural conditions. Each experiment was conducted under sufficient hydrostatic pressure to prevent boiling, and for the burial diagenesis experiments a uniaxial force was also applied.

4.2.1. Equipment and Conditions

In both sets of experiments, ooid sands were used as an experimental charge. The regular size and composition of the ooids ensured homogeneity of multiple samples, so that the effects of starting composition could be ignored. This would not be the case it, for instance, a variety of samples of skeletal material were used. For the experiments on burial diagenesis, the spherical shape of the ooids and their internal

lamellae were useful in compaction studies. Any compaction of the sediment would be represented by deformation of this regular shape. In both cases the experimental charge was placed in a container within a steel pressure cell which was filled with water (either fresh or seawater). The cells were taken up to full temperature and pressure slowly, and reduced to ambient conditions slowly at the end of the run, to prevent any boiling of the pore fluid. For the experiments on shallow diagenesis, the temperature varied between 120°C and 210°C, and the pressure between 48 and 96 bars in different experimental runs (Ferguson et al 1984,p.247). The burial diagenesis experiments had a similar temperature range (150 - 200°C) and a similar hydrostatic pressure (72 bars). There was, however, an additional uniaxial pressure of between 800 and 1500 bars applied; pressures equivalent to overburden depths of 3.5 to 6.5km (Bhattacharyya & Friedman 1984, p.363).

Both experimental systems had methods of preventing the escape of the pore fluid, so that the experimental charge was saturated at all times. The experiments on shallow diagenesis ran for about twenty-eight days usually, whereas those on burial diagenesis ran for four days.

4.2.2. Analytical Method

A wide range of geochemical analyses were undertaken on the experimental material from the shallow diagenesis

experiments. Both the solid carbonate charge and the pore fluid (liquid and gas) were analysed. Gas chromatography was used to analyse gas given off when the cells were opened, and induction coupled plasma analysis was used for the pore water. The solid phase was investigated using X-ray diffraction, transmitted light microscopy, scanning electron microscopy etc., and it was also analysed for total organic carbon, soluble organic material etc. (Ferguson et al 1984, p.246). The nature and variety of these analyses reflects the interest in the detail of chemical changes during the experiments, and especially in the relationship between organic and inorganic reactions.

After the burial diagenesis experiments, the main feature of interest was the nature of compaction and deformation of the ooids. The solid sample, impregnated with epoxy resin, was studied by transmitted light microscopy. The various types of deformation seen in the section were then noted, statistics being compiled on their frequency etc. Measurements were also made on the initial and final porosities, and the reduction in bulk volume (Bhattacharyya & Friedman 1984, p.364). The nature of the analysis reflects the comparatively simple aim of these experiments.

4.2.3. Shallow Diagenesis - Results

The ooid samples, immersed in seawater for several weeks at high temperature and pressure, showed some interesting physical and chemical changes on analysis. Some of the

samples became cemented, the cement-type being dependant on the starting material. Ooids from the Bahamas developed rhombohedral calcite cement around the rims of unaltered ooids, while those from the Persian Gulf were often found to be completely recrystallised. No stages in between these extremes were detected, and it was suggested that the difference in organic content of the original material may be the cause (Ferguson et al 1984, p.265).

The charge material was found to have undergone the transformation from aragonite to calcite, as shown by analysis of the pore fluid. At the end of the run this fluid showed an increase in the concentration of calcium and strontium ions from the aragonite, and a decrease in magnesium and sulphur ions. Magnesium would be taken up on formation of calcite, and sulphur by anhydrite. The latter mineral was sometimes seen forming crystals in the pore space. Organic material was flushed out of the carbonate, and some was converted to humic acids and kerogen, though much remained essentially unaltered.

4.2.4. Burial Diagenesis - Results

At the end of the experimental runs the ooid samples showed appreciable compaction, but no cementation. When compared to the above experiments, it seems likely that the brevity of the runs (four days compared to twenty-eight) may be responsible for the lack of cementation. The noted compaction was accomplished by a reduction in porosity.

Those experiments having distilled water as pore fluid gave a uniform reduction in bulk volume and porosity. There was, however, a variation in these when the pore fluid was seawater, though the significance of this is unknown. Contacts between the ooids showed plastic deformation, with some pressure solution, and again the nature of the pore fluid had some effect, with the samples in seawater tending to have more plastic deformation. The action of pressure solution seemed to be encouraged by higher temperatures. The way in which the ooids had fractured was also noted, and again could be related to the nature of the pore fluid.

Although no cementation was achieved by these experiments, they still produced fabrics which are seen in natural carbonates which have been subjected to deep burial diagenesis (Bhattacharyya & Friedman 1984, p.369).

4.2.5. Summary

These experiments show that it is possible to simulate the effects of both shallow and deep diagenesis of carbonates. The extent to which the natural processes themselves are simulated is always in some doubt when the geological timescale is reduced to a matter of days or weeks. The experiments are, however, valuable in the planning of future experimental work, defining the equipment and the conditions to be used, and suggesting the focus of such work.

CHAPTER FIVE-

EXPERIMENTAL SIMULATION OF DIAGENESIS

Experiments were undertaken which sought to simulate the physical and chemical transformations occurring when a natural carbonate sediment undergoes diagenesis. It was hoped that the monitoring of these transformations would identify the important processes and reactions, and the controls on these. This chapter describes the experiments and the interpretation of their results.

5.1. EXPERIMENTAL METHOD AND TRANSFORMATION ACHIEVED

The equipment and conditions used in the experimentation were determined by similar research done previously (section 4.2.). All the experiments had the basic aim of investigating the diagenetic reactions achieved; in addition to this they sometimes provided information on facets of diagenesis not considered at the outset of the experimentation.

5.1.1. Equipment and Conditions Used

The experiments were carried out using stainless steel pressure vessels, which could be held at a predetermined hydrostatic pressure throughout the experimental runs. The pressure vessels were held at a constant temperature, either surrounded by a heated jacket or placed within an oven. The experimental charge (carbonate aragonite sediment) was placed within a 'PTFE' container, and this was placed in the pressure

vessel. The whole system was flooded with a standard seawater and sealed, so that the air was completely excluded at the start of the run. The carbonate sediment used as an experimental charge was either Bahamaian ooid sand, or detrital carbonate material, also from the Bahamas. Previous work had shown the ooid sand to be that most rapidly cemented.

Two pressure vessel systems were available, one containing four small cells, the other one large cell. The latter was modified to allow the pore waters to be flushed through the sample during the experimental run.

Previous experimentation had determined the conditions necessary for the successful simulation of diagenesis. The optimum conditions chosen for this work were a temperature of 200^{o}C, and a pressure of 69 bars (1000 psi). The temperature must be high enough to encourage the diagenetic reactions to take place, and the pressure must be high enough to prevent boiling of the pore waters. Temperature and pressure were monitored throughout the experimental runs to check that the equipment was functioning properly. The pressure reading also gave an indication of the onset of cementation, suddenly rising more sharply than is explicable by the effects of external factors. This is thought to be due to the precipitation of new carbonate material causing an increase in the internal pressure.

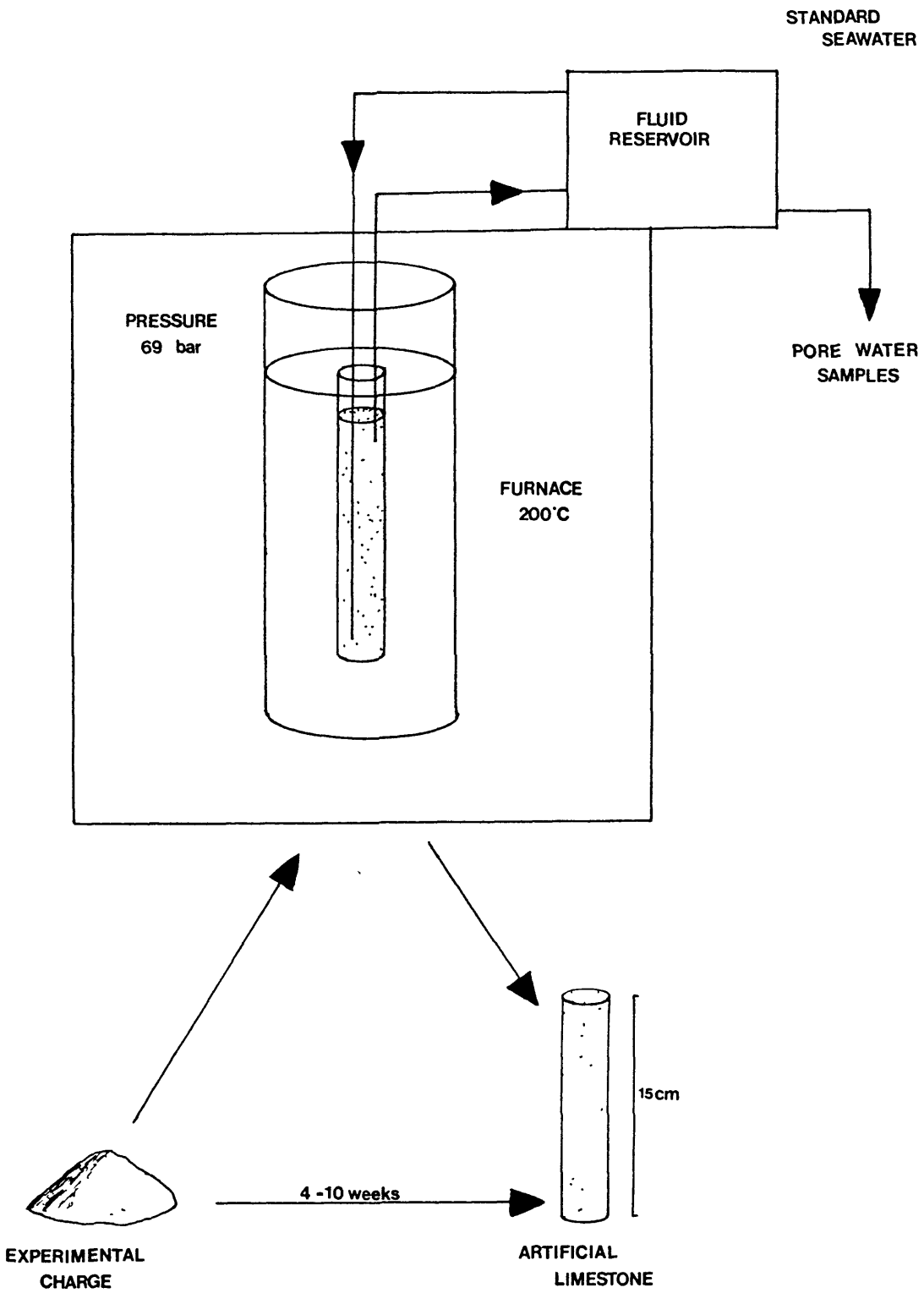
The experiments were allowed to run continuously for many weeks, the minimum time for the onset of cementation (indicated by the pressure increase) being three weeks. Indeed several experiments ran for a few months, when further experimentation was undertaken after cementation had been achieved. Pore water samples were drawn off for analysis regularly where possible, though in cases where the system was completely sealed the pore waters could only be analysed at the end of the experimental run. The cell with the facility for pore water circulation also allowed introduction of waters of different composition during the experiments.

Figure 5.1a is a representation of the experimental equipment used.

5.1.2. Analysis and Interpretation

The samples of pore water removed during the experimental runs or at the end of them were stored under refrigeration until they could be analysed. The induction coupled plasma technique used for analysis gave the concentrations of all the ions present in the pore waters. The samples taken regularly throughout experimental runs allowed trends in the concentration of certain ions to be detected. In the closed carbonate-pore water system, any such trends in the composition of the pore waters must be the reverse of corresponding trends in the composition of the carbonate. Monitoring the trends

Figure 5.1a: The Experimental Pressure Cell Equipment Used.



in the water composition therefore defined the general diagenetic changes in the carbonate charge. Full results of the analyses of the pore water samples form Appendix D.

The solid samples were inspected with a hand lens, though it is obvious to the naked eye whether any significant cementation has occurred. Some samples were also impregnated with epoxy resin, sectioned, and studied under the J.E.O.L. scanning electron microscope/microprobe. This allowed verification of the fact that changes in pore water composition reflect reverse changes in carbonate composition.

5.1.3. Experiments Undertaken

The primary aim of all the experiments was to produce an artificially cemented 'limestone' from the experimental charge of carbonate sediment. Monitoring of the experiments allowed determination of the reactions and transformations taking place. Different types of carbonate material, both ooid sand and detrital carbonate, were used as an experimental charge. The differences between the reactions of these to the applied diagenetic conditions were identified, and an explanation was proposed. Organic material was introduced into the carbonate charge to see if its presence affected the diagenetic reactions greatly. Experiments were undertaken where solutions in seawater of lead and zinc salts were introduced, to see whether these would precipitate out, and, if so, in what form. These experiments also showed what

Table 5.1a: Details of Experiments Undertaken.

Run no.	Sample no.	Composition	Run time	Result
1	1.1	detrital carbonate	4 weeks	uncemented
2	2.1	detrital carbonate	4 weeks	uncemented
3	3.1	detrital carbonate	10 weeks	uncemented
3	3.2	detrital carbonate	10 weeks	uncemented
3	3.3	detrital carbonate	10 weeks	uncemented
3	3.4	detrital carbonate	10 weeks	uncemented
4	4.1	ooid sand	10 weeks	cemented
5	5.1	ooid sand	10 weeks	cemented
6	6.1	ooid sand & algal mat	4 weeks	semicemented

Notes:

Run no.3 involved use of a four-cell pressure vessel, hence the four samples.

At the end of five weeks, after cementation of the samples had occurred, a solution of lead chloride in seawater was added to sample 4.1 (run 4), and a solution of zinc chloride in seawater to sample 5.1 (run 5).

effect such a change in the pore water composition would have on the diagenetic reactions. Finally, though no experiment was specifically designed to test this, the chemical buffering of the carbonate by the pore water was illustrated.

In total some nine samples were involved in six experimental runs (table 5.1a).

5.1.4. Chemical Changes

From the results of the analyses, a trend in the pore water composition could be seen. This trend was present in all the experiments, those that resulted in a cemented sample and those that did not. This trend involved the calcium, magnesium and strontium content of the pore water, as might be expected in a water-carbonate system. The magnesium content of the pore water decreased, and its content of calcium and strontium increased during the experimental runs. In terms of the carbonate composition this represents an uptake of magnesium, coupled with release of calcium and strontium ions into solution. This is due to the transformation of aragonite to calcite, and illustrates the difference in composition required by their different lattice morphologies, the effect discussed in section 4.1. for the natural system. Some of the original ooid sediment, and this material having undergone diagenesis were studied by S.E.M./microprobe, which showed that the proposed change in carbonate composition had indeed taken place, and X-ray diffraction study of the same

Figure 5.1b: Histograms of Pore Water Composition.

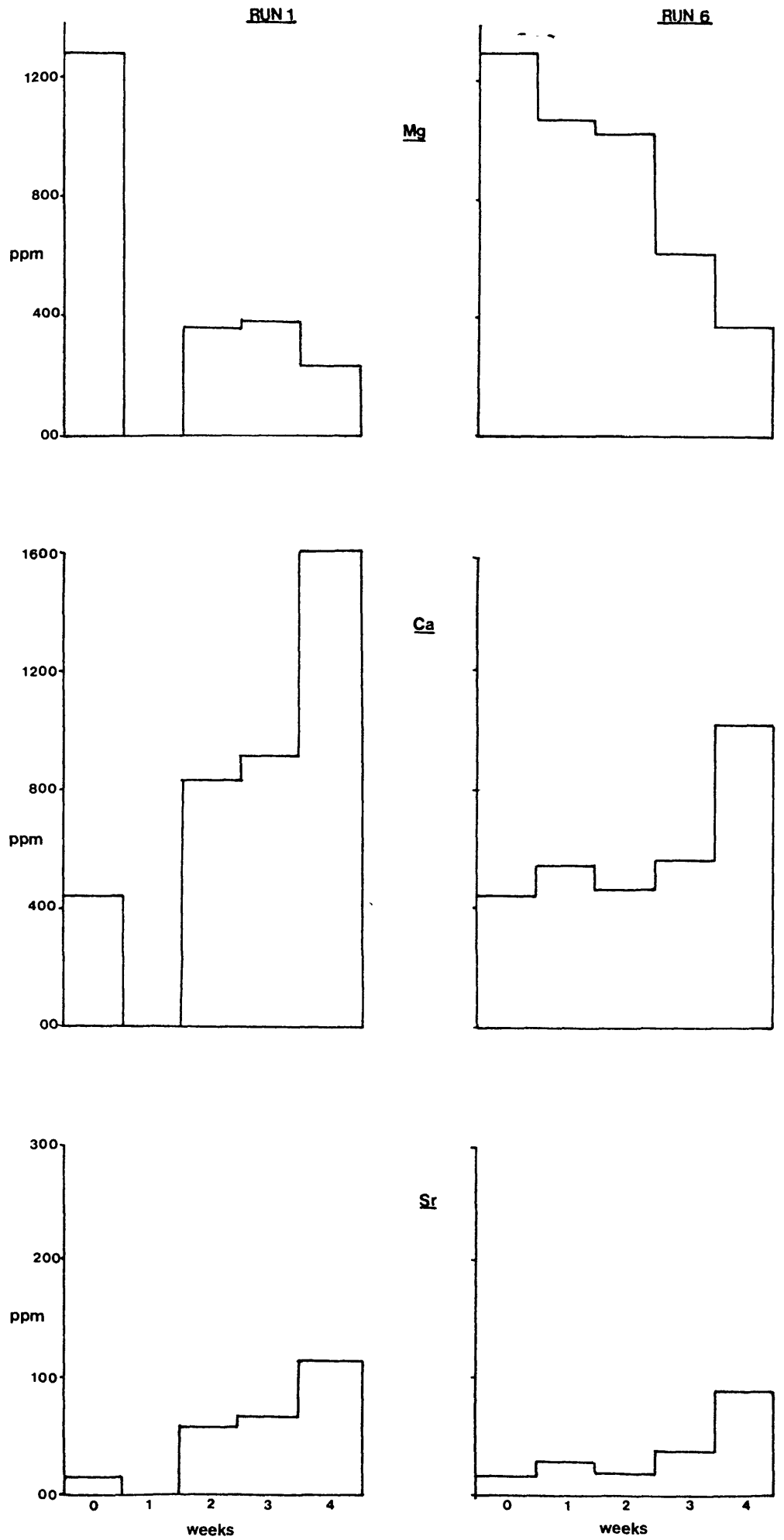
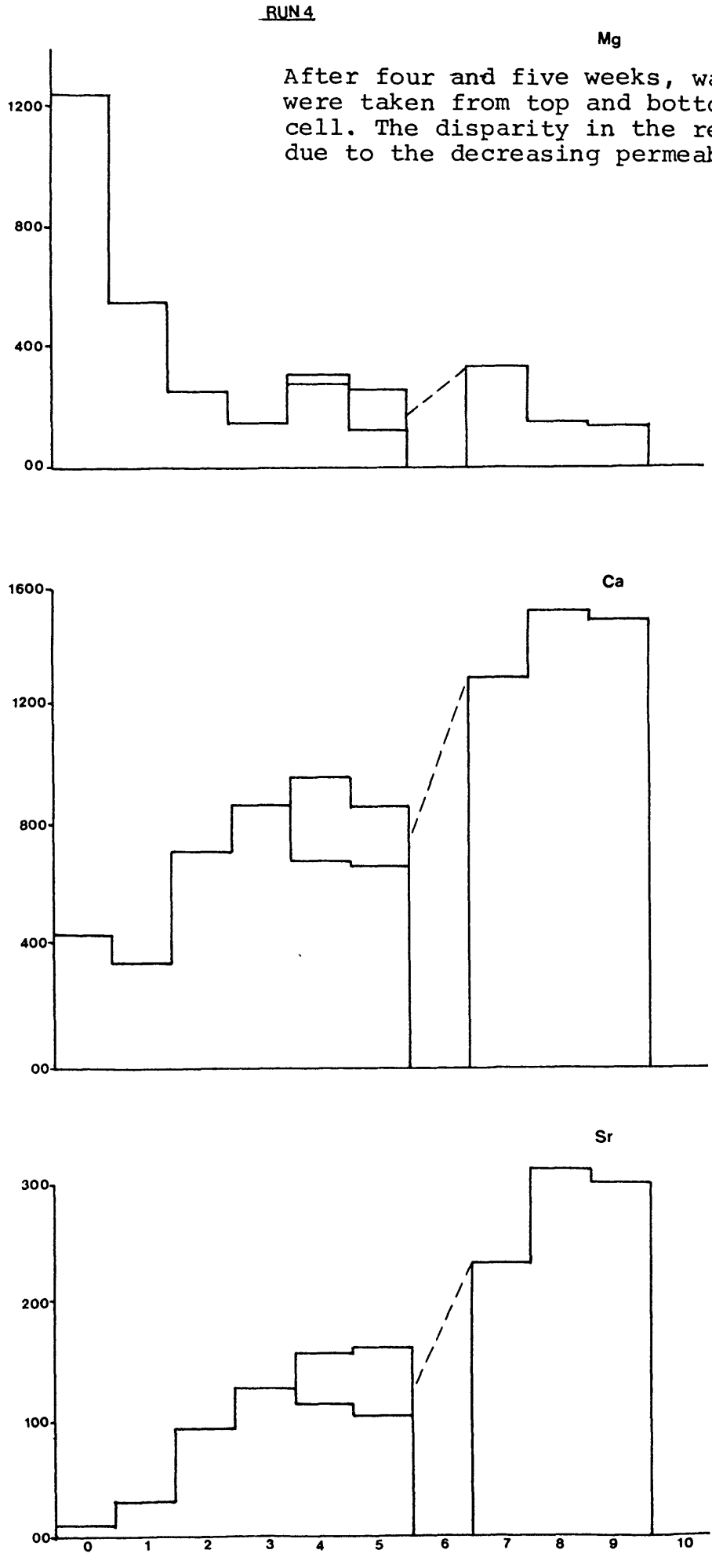


Figure 5.1c: Histograms of Pore Water Composition.



sample (sample 1.1) verified that this was due to the aragonite to calcite inversion.

The plotting of histograms of the raw data illustrates the change in the composition of the pore waters, as shown in figures 5.1b and 5.1c. To identify the general trend, it was found to be more useful to plot the molar ratios of strontium/calcium against magnesium/calcium (full results of these ratios and the method of their calculation are given in table 5.1b). The plot of these forms figure 5.1d; the general diagenetic trend identified here was followed by all experiments, whether or not cementation was achieved.

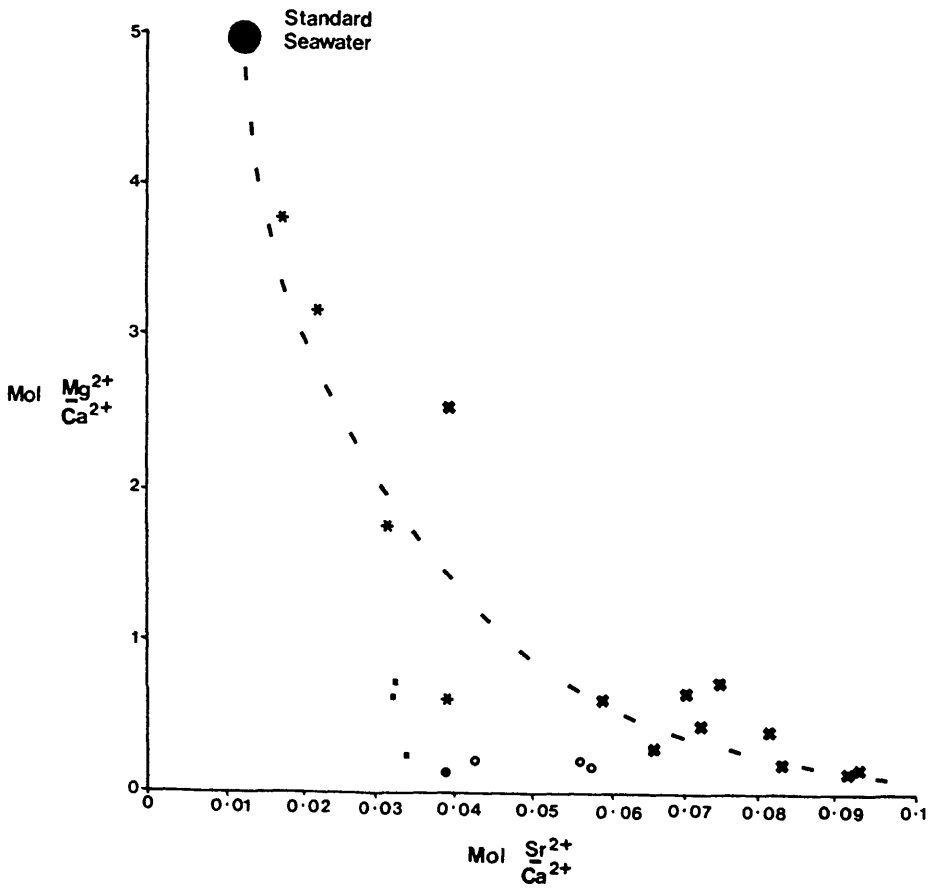
5.1.5. Physical Changes

Those samples which had undergone full cementation were obvious when they were removed from the pressure vessel. The carbonate grains adhered firmly together, and a slight increase in volume caused the sample to have a convex surface, and to be stuck firmly within the PTFE container. S.E.M./ microprobe analysis showed the cementation to be due to the precipitation of new carbonate material in the original pore space (sample 4.1). The reduction in porosity due to this cementation was calculated from the wet and dry weights of the sample at the end of the experimental run. From an original porosity of about 50%, the porosity was reduced to about 35% for cemented samples. (sample 4.1). Uncemented samples also showed some decrease in porosity, for instance to 46%

Table 5.1b: Values of Molar Ratios for all Samples.

Sample No.	Mol Mg/Ca	Mol Sr/Ca
1a	0·74	0·032
1b	0·69	0·032
1c	0·25	0·033
2a	0·13	0·038
3.1a	2·05	0·022
3.1b	3·08	0·019
3.1c	2·50	0·023
3.1d	0·85	0·034
3.1e	0·17	0·041
3.1f	2·31	0·024
3.1g	2·21	0·038
3.1h	1·99	0·042
3.2a	2·34	0·021
3.2b	3·05	0·019
3.2c	2·50	0·024
3.2d	1·70	0·030
3.2e	0·33	0·050
3.2f	0·76	0·045
3.2g	3·00	0·025
3.2h	2·44	0·031
3.3a	1·97	0·023
3.3b	2·64	0·023
3.3c	2·14	0·032
3.3d	1·42	0·041
3.3e	0·48	0·059
3.3f	0·56	0·060
3.3g	2·05	0·045
3.3h	2·08	0·045
3.4a	1·69	0·024
3.4b	1·67	0·027
3.4c	1·45	0·032
3.4d	1·56	0·033
3.4e	0·58	0·053
3.4f	0·45	0·038
4a	2·55	0·038
4b	0·62	0·058
4c	0·30	0·065
4d	0·49	0·071
4e	0·75	0·074
4f	0·67	0·070
4g	0·20	0·082
4h	0·41	0·081
4i	0·16	0·092
4j	0·15	0·091
5a	0·14	0·057
5b	0·17	0·056
5c	0·16	0·042
6a	3·19	0·021
6b	3·82	0·015
6c	1·78	0·031
6d	0·61	0·039
SWa	4·95	0·012
SWb	4·96	0·008

Figure 5.1d: Trend in Pore Water Composition as Samples Undergo Diagenesis.



$$\text{Mol}\frac{Mg^{2+}}{Ca^{2+}} = 1{\cdot}66666\ \frac{Mg\ (ppm)}{Ca\ (ppm)}$$

$$\text{Mol}\frac{Sr^{2+}}{Ca^{2+}} = 0{\cdot}45714\ \frac{Sr\ (ppm)}{Ca\ (ppm)}$$

(sample 2.1). This could be due to the onset of cement growth, invisible to the naked eye, or to an increase in volume during the aragonite to calcite inversion (aggrading neomorphism). S.E.M. study of uncemented samples did not detect any incipient cement growth, so the latter explanation is the more likely.

No measurements of absolute permeability were made, but the permeability of cemented samples was greatly reduced. This was indicated by the increasing difficulty of circulating pore water through the sample as cementation advanced, and by the difference in composition of pore water from the top and bottom of the sample after four weeks of Run 4 (figure 5.1c). A decrease in permeability was presumably also suffered by those samples with decreased porosity as discussed above, though this effect was too small to be registered by the equipment used.

5.1.6. Summary

The experiments undertaken simulated natural diagenesis in that they involved the transformation of the original aragonite to calcite, sometimes accompanied by the precipitation of a new carbonate cement. Monitoring these changes allowed a general diagenetic trend to be identified, with which further results could be compared.

5.2. CONTROLS ON DIAGENESIS

During the experimentation, the controls on the progress of diagenesis were illustrated by observed variations in the experimental charge, pore fluid and pressure vessel system. These variations were all within the possible scope of the natural system, and the effects seen reflected those to be expected in nature.

5.2.1. The Effect of the Charge Material

Three features were investigated as potential controlling factors on the diagenesis of different charge materials: the nature of the carbonate, the grain size, and the organic content.

Two types of carbonate material were used as an experimental charge; detrital skeletal material and ooids (table 5.2a). Both types of material were originally of aragonitic composition, and suffered the inversion to calcite during the course of the experimental runs. Only one type of material - the ooids - became cemented during the experiments. The onset of cementation was indicated initially by an increase in pressure about three weeks after the start of the experimental run, the sample would be partially cemented after four weeks (Run 6) and fully cemented after five weeks (Run 4). Detrital carbonates, on the contrary, did not show any signs of cementation after a similar length of time. The explanation of this behaviour lies with the small size and spherical

shape of the ooids, and the contrasting larger size and irregular shape of the detrital grains. These factors affect the nature of calcite precipitation (as when a cement is formed) due to the manner in which this is controlled. As discussed previously (section 4.1.1.), the magnesium content of the environmental water is the dominant control on calcite precipitation, since the magnesium ions become adsorbed onto active sites on the carbonate surface, thus preventing further precipitation of calcite. In any system, the greater the surface area of the pre-existing carbonate, the more magnesium can be removed from the fluid phase, and the more chance there will be for the precipitation of calcite to proceed. If the surface area of the carbonate is restricted, the active sites may be dominated by magnesium, so preventing calcite formation. In this case, the ooids are spherical, and so individually have a low surface area to volume ratio. They will, however, pack tightly into any container, much more so than the larger, irregularly shaped detrital grains. For the volume of the container (i.e. the pressure cell) the ooids will therefore present a far greater total surface area than the detrital material, due to their great numbers and ability to pack together. During the experiments the ooids would therefore be far more effective at removing magnesium from the pore fluid, so allowing precipitation of calcite to form the new cement. A second factor enhancing the opportunity for the ooids to become cemented is the greater number of grain to grain contacts in the ooid samples, again

due to the packing of the regular grains. Not only does the detrital material have fewer such contacts (along which reaction can occur) due to the irregular shape and poor packing of the grains, but much of the material tends to be plastered with small calcite crystals, which again will act to retard the calcite precipitation reactions.

For the present research, the ooids used came from the Bahamas, and these gave a calcite rim cement. Previous work involved the use of ooids from the Persian Gulf (Ferguson et al 1984) and these showed different cementation characteristics, becoming completely recrystallised, rather than merely cemented together (section 4.2). The explanation of this behaviour could also lie with the control of magnesium on calcite precipitation. The Persian Gulf ooids are very much smaller than those from the Bahamas, and so have an even greater total surface area to given bulk volume ratio. This presumably makes them highly efficient at removing the magnesium from the pore solution, hence allowing them to react so completely to form new calcitic material.

The effect of the presence of organic material in the experimental charge was investigated in Run 6. The charge for this run comprised approximately equal masses of ooids and algal mat material. The algal mat was sandwiched between layers of ooids in the pressure vessel, the experimental run lasting for four weeks. At the end of the run, the organic matter had undergone some degradation, producing an oily film

on the pore waters. The composition of the pore waters, however, plotted on the general diagenetic trend, showing that even when a high proportion of organic matter was present, the aragonite to calcite inversion would proceed as normal. Cementation also occurred to some extent; at the end of the four week run the sample was partially cemented, and would presumably have become fully cemented, had the experimental run been extended.

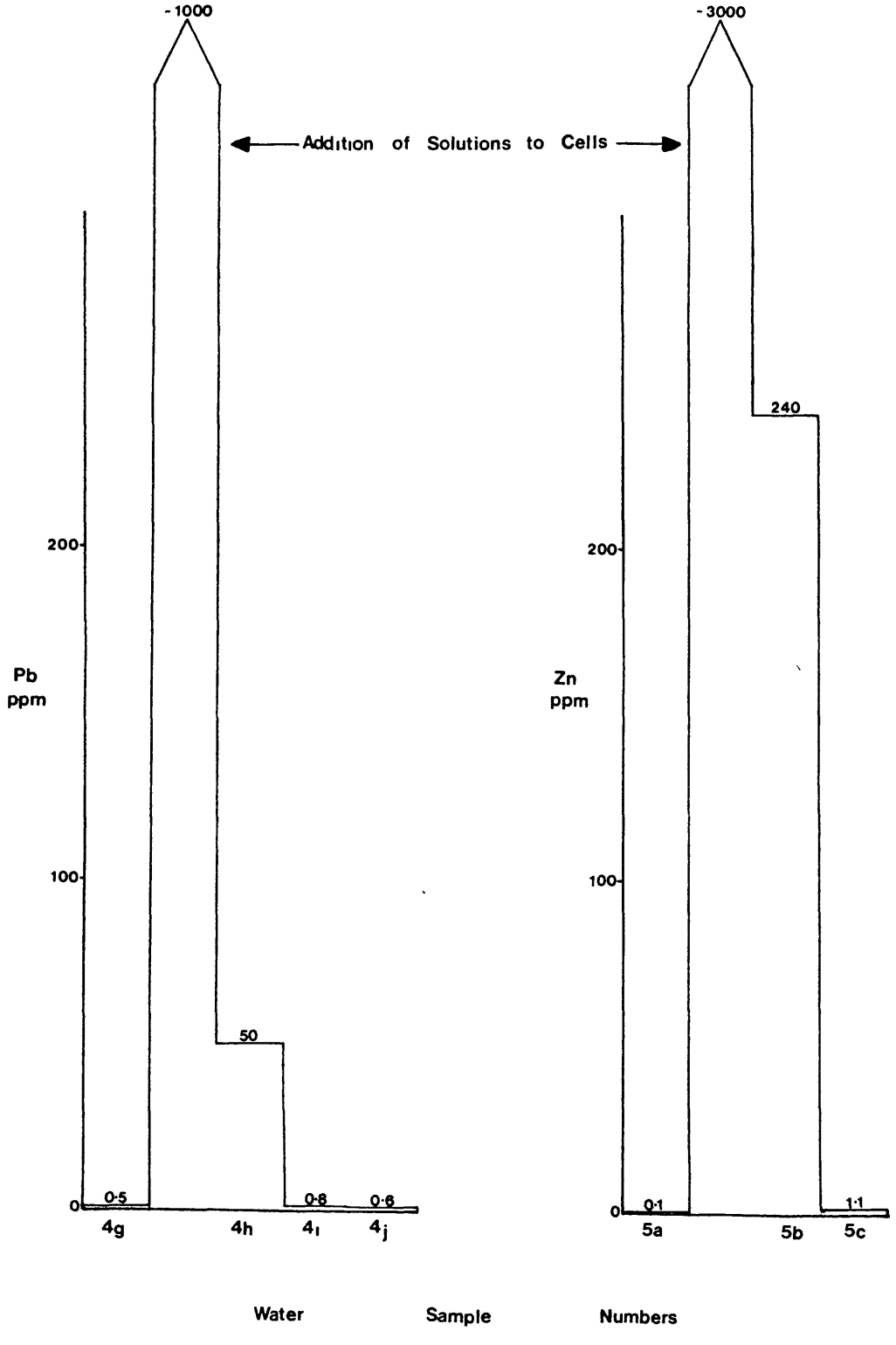
As might be expected, the nature of the charge material is seen to control the diagenetic reaction to a large extent. The grain size appears to be particularly important, controlling the amount of grain surface available to remove magnesium from solution, and, through that, controlling the rate at which the new calcite cement can be precipitated. The nature of the carbonate charge seems to have little effect on the aragonite to calcite inversion, and the presence of organic material seems to affect neither this nor the cementation.

5.2.2. The Effect of Pore Fluid Composition

When cementation had been achieved in samples 4.1 and 5.1, each after five weeks, solutions containing lead ions and zinc ions respectively were drawn into the system. The cells had by that time been under anaerobic, reducing conditions for some time, and it was hoped that it would be possible to investigate in what form the metals were precipitated, if indeed they were removed from solution at all. In the context of an

examination of the relationship between carbonate diagenesis and ore precipitation, it was also thought to be important to determine whether the introduction of solutions of very high metal ion concentrations had any effect on the ongoing diagenetic reactions. From analysis of water samples it was obvious that the metal ions disappeared from the pore waters over a number of weeks after their addition to the system (figure 5.2a). After five weeks, the metal ion content of the pore waters had dropped to background levels in both experiments. A segment of the solid sample, once dried and impregnated with epoxy resin, could be sectioned for study by the scanning electron microscope/microprobe, so that the sample could be searched for any sign of metallic precipitates. Small amounts of metal sulphides were detected, but these could well have been detrital mineral grains, and were not numerous enough to account for the fate of all the metal ions injected into the cell. To determine the probable fate of these ions it is necessary to consider the chemical system into which they were injected. At the time of their introduction, the aragonite to calcite inversion and cementation had been achieved, though the active components of the system would still be carbonate and water. At the start of the experimental runs, the reactions would proceed rapidly, the carbonate phase being unstable under the prevailing conditions. With increasing reaction, stability would be approached, and the reactions would slow down, until eventually, cementation having been achieved, a state of equilibrium would be reached between the carbonate and the pore water. This,

Figure 5.2a: Concentrations of Metal Ions in Solution.



however, does not necessarily mean that no further reaction would be taking place; rather that at equilibrium carbonate would be taken into the pore waters and precipitated out of it at equal rates. Under these conditions it seems likely that the metal ions would probably precipitate out of the pore waters as metal carbonates as part of the cement phase, since both lead and zinc form stable, insoluble carbonate compounds. It has been suggested that such precipitation of metal carbonates was the first stage in the formation of the base metal deposit at Navan, Eire, rather than the direct precipitation of metal sulphides. The first generation of metal bearing fluids are said to have precipitated metal carbonates, which were later sulphidized on the passage of a sulphide-bearing fluid through the rock (Kucha & Wieczoreck, 1984). This latter fluid also precipitated a second phase of metallic minerals directly as sulphides. The evidence suggests that this process of metal carbonate precipitation occurred in the experimental system, there being too little sulphide in solution to precipitate metal sulphides directly.

The high concentrations of metal ions introduced into the pore fluid had no noticeable effect on the carbonate diagenesis. The carbonate dissolution and precipitation reactions continued as usual after their introduction, as indicated by the lack of deviation from the normal diagenetic trend in the pore water composition on analysis.

5.2.3. The Buffering Effect of the Pore Fluid

None of the research previously presented here contains results from Run 3, which was carried out in the four-cell pressure vessel. The results from this ten week run are shown in the histograms in figure 5.2b, and in the graph of molar ratios in figure 5.2c. As can be seen, although the same general trends in composition were followed, the changes took place much more slowly, and did not proceed as far as for the other experiments. The explanation of this behaviour lies not with the charge material (detrital carbonate), nor with the pore fluid composition (standard seawater), but with the nature of the pressure vessel system. The four cell system contained cells which were much smaller than the alternative single cell rig, and though a large reservoir was available, the water was not circulated through the cells during the experimental runs. Each time a water sample was drawn off each cell for analysis, some of the standard seawater was drawn into the cell from the reservoir. In the case of the single large cell, the volume involved in the sampling would be very small in comparison to the total amount of pore water present, and there would be little resulting change in the overall pore water composition. For the smaller cells, however, a large proportion of the pore water was replaced with standard seawater every time a water sample was taken (i.e. every week). This flushing of the cells with waters approaching the original seawater composition meant that the

Figure 5.2b: Histograms of Pore Water Composition.

(cf. figs 5.1b,5.1c)

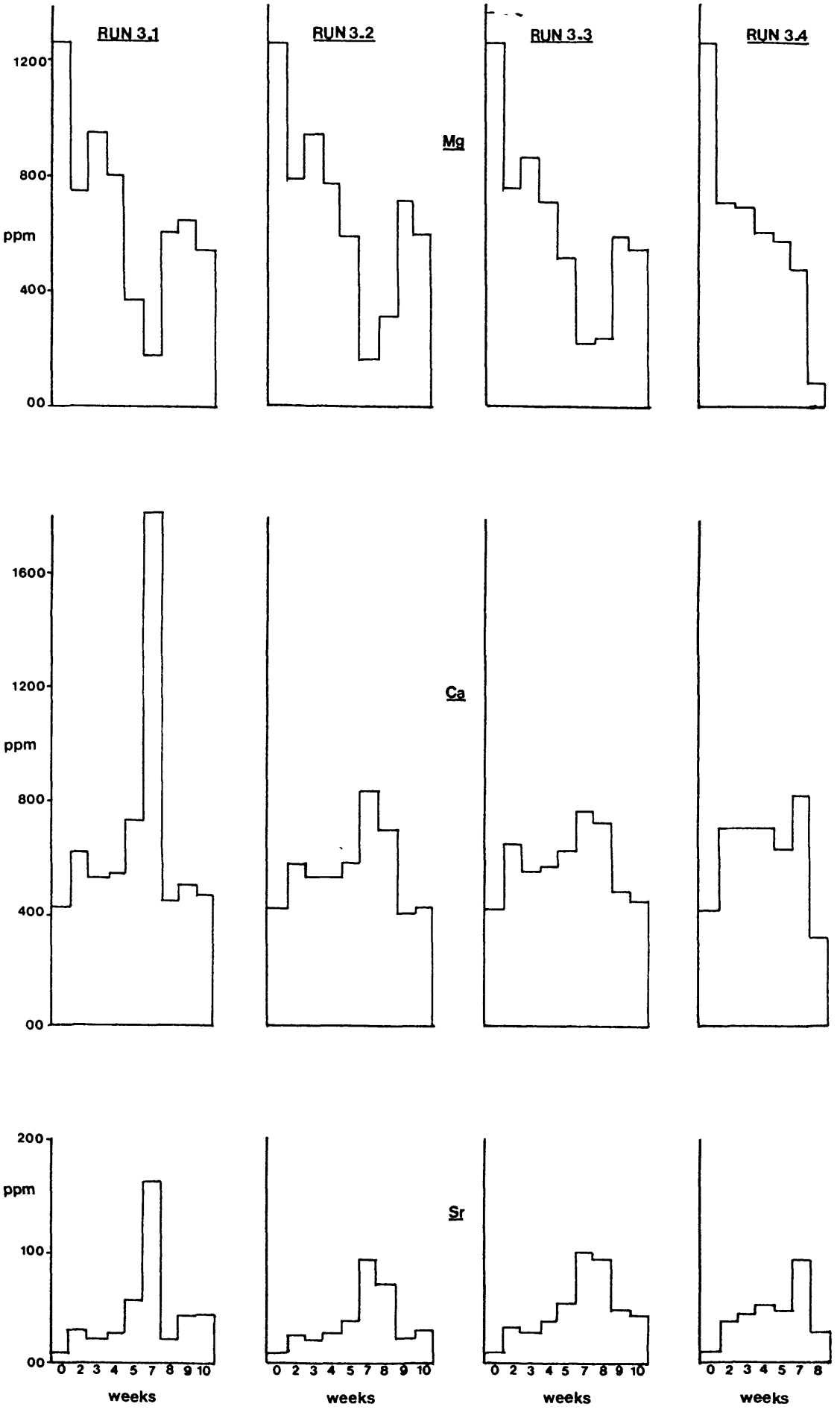
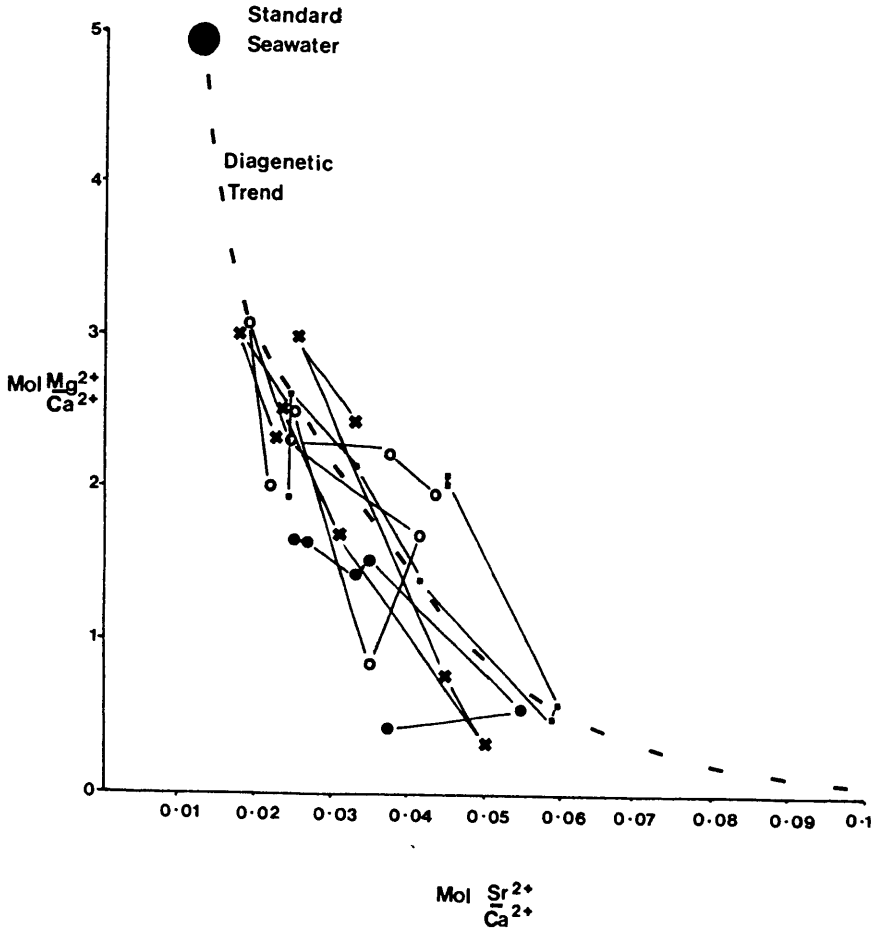


Figure 5.2c: Trend in Pore Water Composition.

(cf. fig.5.1d)



RUN 3.1 o
RUN 3.2 ✖
RUN 3.3 ▪
RUN 3.4 ●

diagenetic reactions never had the chance to proceed properly. Considering again the control of magnesium concentration in the waters on calcite formation, it is easy to illustrate how the diagenetic reactions might be prevented. At the start of the experimental run, the original carbonate charge would be able to take a certain amount of magnesium out of solution, allowing the diagenetic reactions to proceed. However, the next time a water sample was removed, more magnesium would be introduced in the drawn-in seawater. The carbonate phase, having already taken magnesium onto certain active sites, would then have to undergo this process again to reduce the amount in the pore fluid, thus leaving fewer active sites available for the processes of calcite formation. Each new influx of seawater would therefore inhibit diagenetic reactions further, with the carbonate-water system never able to equilibrate fully. This is an illustration of the buffering effect of the original pore water composition, and indicates the reason why marine carbonates show little early diagenesis, until they are no longer regularly flushed with seawater of the same composition as that they formed under.

5.2.4. Summary

The diagenesis of the carbonate samples proceeded in two stages; the aragonite to calcite inversion undergone by all samples, and cementation with new calcite rim cement. For this diagenesis to proceed it must be possible for the composition of the pore water, as well as that of the carbonate

to change during diagenesis. The high temperature under which the experiments were run encouraged the reactions, allowing the experiments to be completed on a timescale somewhat shorter than that available to natural systems. Cementation occurred only in samples formed of ooid sediment, due to the effect of shape, size and packing geometry on the total surface area available for reaction. These parameters will differ for all carbonate sediments, indicating that within the well defined framework of carbonate diagenesis there may be great variations in the details of the manner of the reactions and the rate at which they occur, in different carbonate sediments.

The diagenetic processes were not affected by the presence of a large amount of organic material (though this material suffered diagenetic changes itself), nor by the introduction of high concentrations of base metal ions in the pore fluid. In both cases, analysis of the pore waters showed no deviation from the general diagenetic trend. There was not enough sulphide in the system to precipitate the introduced metal ions as metal sulphides, though the carbonate salts which they would form instead would be susceptible to later sulphidisation.

The controls on the diagenetic reactions identified by the experimental work mirror those that have been observed elsewhere in the natural system.

5.3. DIAGENESIS OF ORGANIC MATTER IN CARBONATES

As has been mentioned previously, during diagenesis of a sediment compositional changes affect not only the mineral components, but also the organic matter in the sediment. The samples removed from the pressure vessels at the end of the diagenesis experiments were analysed for light hydrocarbons by the method described in section 2.1. The results illustrate the interaction between carbonate and organic matter during diagenesis, and confirm results from observations of natural systems.

3.1. Organic Diagenesis

The alteration of the organic matter in the sediment begins early after its deposition and proceeds rapidly before burial has had time to occur. Only a very small proportion of organic material survives decomposition and scavenging by other organisms to become part of the sediment pile. Diagenetic changes affecting the organic matter can be divided into those that take place at shallow depths, and those that take place once the sediment has undergone burial (Barnes et al 1984, p.104). At shallow depths the changes are biochemical, due to the action of living organisms (particularly bacteria) on the organic matter. After burial the bacterial action is much slower, and temperature and time become more important controlling factors. The diagenesis of the organic matter is progressive and irreversible. As this material is broken

down, the original proteins and carbohydrates are degraded to form monomers such as amino acids, which can then form fulvic and humic acids and kerogen. These processes involve the formation of compounds which are removed from the system, either through further reaction or dissolution and diffusion. The system therefore never reaches an equilibrium, but will continue until only a stable insoluble residue remains.

The early action of microorganisms will produce carbon dioxide and water in oxygenated sediment, and methane, carbon dioxide, hydrogen and water under anoxic conditions. This biogenic methane is the first hydrocarbon to be formed during organic diagenesis, and accompanies the start of the decay of organic matter. Hydrocarbons continue to be generated throughout organic diagenesis, especially after burial, when the sediment is subjected to increased temperatures. At first both liquid and gaseous hydrocarbons may be formed, but later, when only kerogen remains of the original material, only dry gas will be formed (Barnes et al 1984, p.110).

These processes will take place at the same time as the sediment itself is undergoing diagenesis. A marine carbonate sediment, like any other, will have a certain amount of organic matter associated with it (Blatt et al 1980, p.466). The change in pore water composition associated with shallow burial may be the start of the reducing conditions needed for the preservation of the organic material in the sediment.

Table 5.3a: Hydrocarbon Content of Samples.

(all values are peak areas in integrator units)

Sample	ooid sand	1.1	4.1	4.1	5.1	6.1
Run time	0 wks	4 wks	5 wks	10 wks	10 wks	4 wks
Methane	2·81	1·24	1·40	2·14	2·43	1·82
Ethene	0·94	2·54	1·28	1·54	1·38	3·08
Ethane	0·49	0·22	0·49	0·57	1·70	0·34
Propene	0·97	2·19	0·99	1·04	1·28	2·33
Propane	2·79	0·66	4·64	3·49	1·90	0·71
i-Butane	0·00	0·00	0·00	0·00	0·00	0·00
1-Butene	5·06	3·66	3·43	3·47	3·79	5·42
n-Butane	2·18	0·33	1·94	1·94	1·33	1·71
Total area	15·24	10·84	14·15	14·19	13·81	15·41

The processes of anaerobic degradation of the organic matter, and of carbonate diagenesis will then proceed rapidly and simultaneously as the sediment is progressively buried. The organic matter will break down to give kerogen, simple organic compounds and hydrocarbons (Barnes et al 1984, p.112) as the carbonate undergoes cementation and neomorphism.

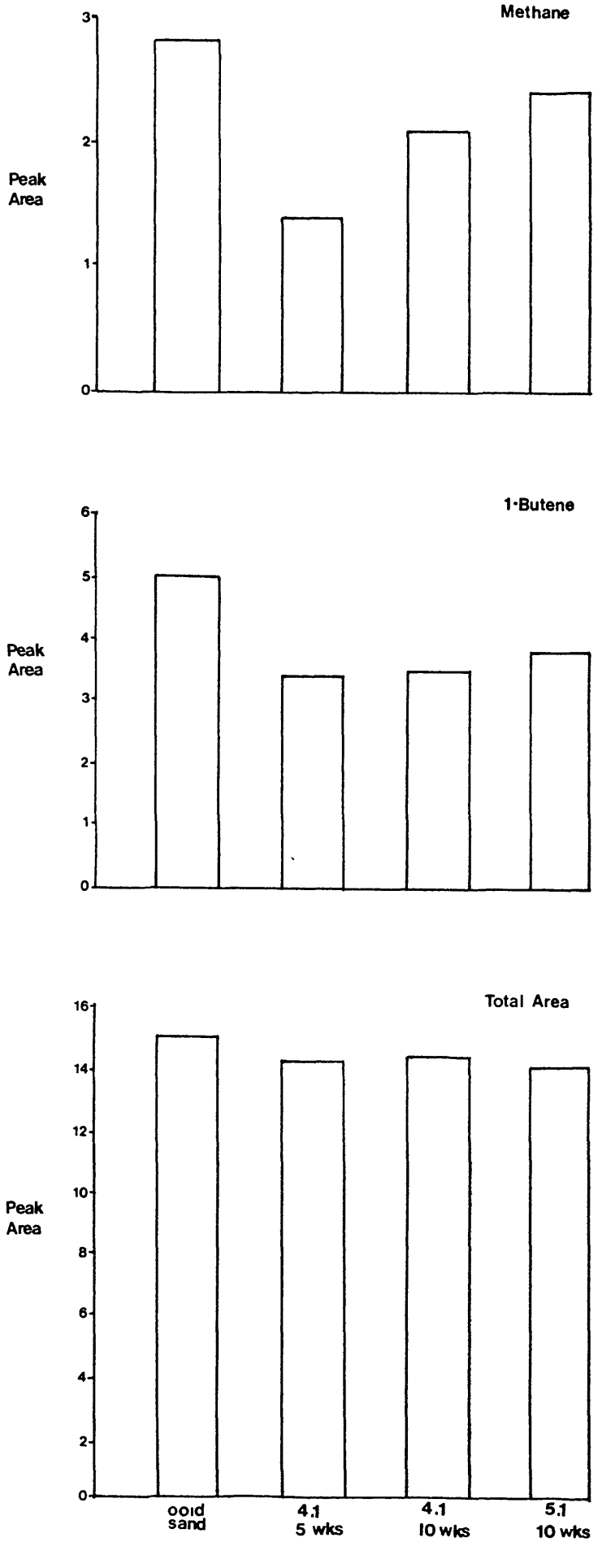
5.3.2. Hydrocarbons in Experimental Samples

The carbonate samples removed from the pressure vessels after Runs 1,4,5 and 6 were analysed for the hydrocarbon gases they emitted on heating. The gas chromatographic method developed for the analysis of crushed rock samples was used (section 2.1), though the pressure vessel samples were not crushed and seived. Those that were cemented were broken down gently, so that the cement was fractured, rather than the ooids themselves. This allowed comparison of the results of their analyses with those from the analysis of some of the original ooid sediment which had not been subjected to the diagenetic conditions.

The results of the analyses are presented in table 5.3a as chromatogram peak areas in integrator units. This allowed easier comparison of absolute amounts of each gas from one sample to another. The most obvious feature of the results is the variation in hydrocarbon content of samples of different starting materials. The sample formed of detrital carbonate (sample 1.1) contained less gaseous hydrocarbon than those

Figure 5.3a: Ooid Sediment Samples - Hydrocarbon Content.

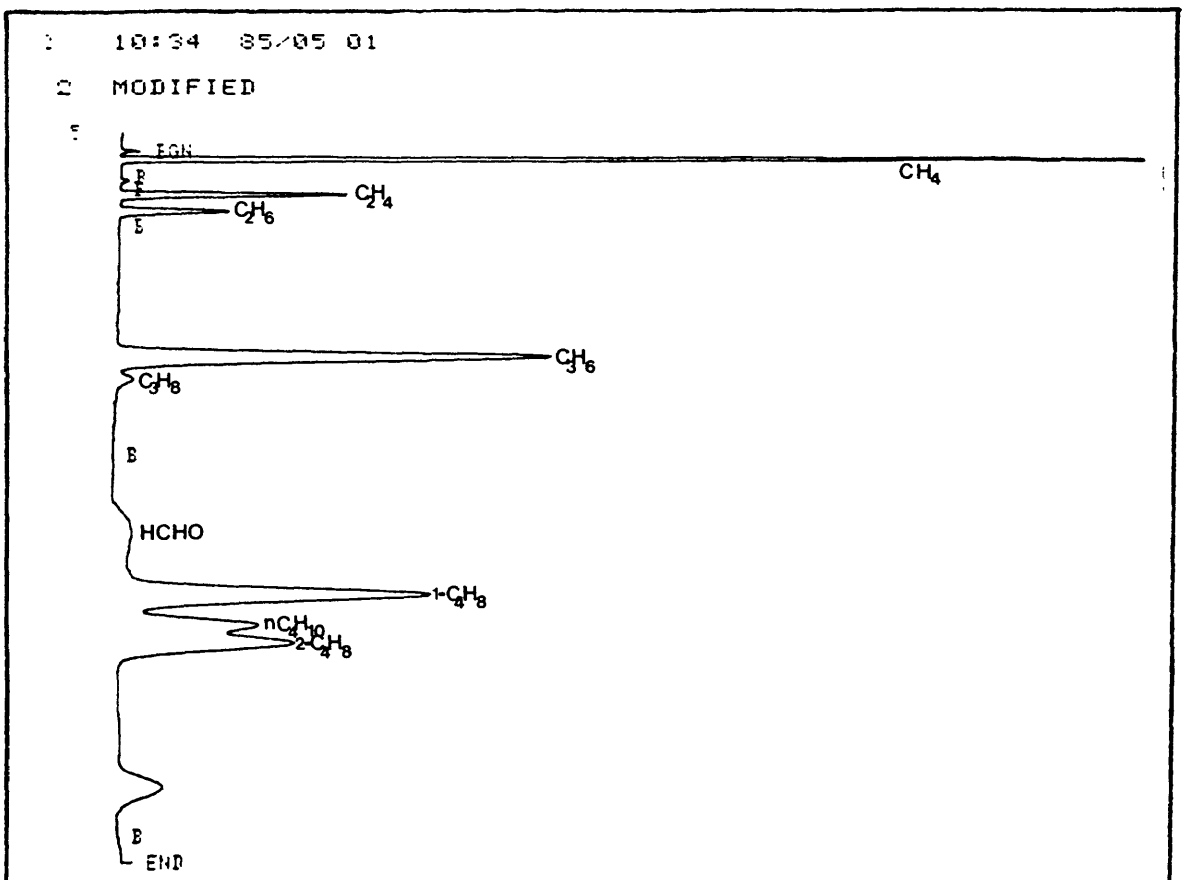
(all values in integrator units)



formed of ooid sediment (samples 4.1 and 5.1), and these in turn emitted less gas than the sample which also contained algal mat material during the experimental run (sample 6.1). The gases are produced by the diagenesis of the organic matter in the sample during the experiments, and by heating of the remaining organic matter during preparation for analysis. The order of hydrocarbon abundance as described above is also the order of abundance of organic matter within the sediment, able to produce such hydrocarbons. Results from the ooid sands before and after the experimental runs (figure 5.3a) show that there is a decrease in the amount of gaseous hydrocarbon analysed in the samples with continuing diagenesis. There is some suggestion that after an initial decrease, some of the gases increase slightly in abundance in some of the samples, trapping the hydrocarbon gas within the new cement.

That light hydrocarbons are generated during this type of experimental run, and lost to the pressure vessel atmosphere or the pore fluid has been shown during more recent research at Imperial College, and is illustrated by the chromatogram in figure 5.3b. The gas sample analysed to produce such a chromatogram is gas removed from a pressure cell during diagenesis experimentation; the facility to sample such gases and analyse them was not available at the time of the research presented here. The light hydrocarbons generated during organic diagenesis within carbonate sediments are important, as is their tendency to become trapped in the early carbonate

Figure 5.3b: Analysis of Hydrocarbons in Gas from Pressure Cells.



RUN 2 10:34 85/05/01

METHOD 2 MODIFIED CALCULATION: NORM

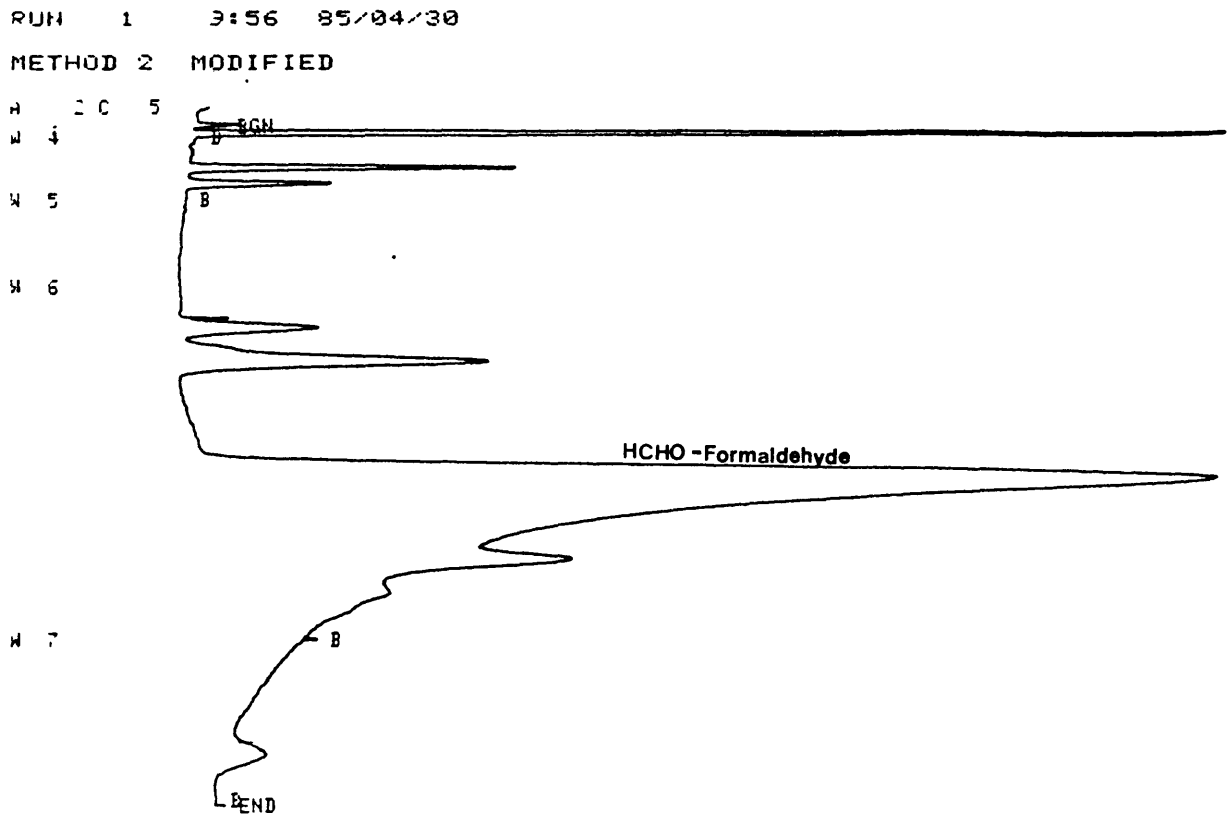
RT	AREA	BC	RRT	RF	AREA %	NAME	GPP
0.997	4.4615		0.343	1.8147	32.5670	METHANE	0
2.298	1.2488	T	0.751	1.0720	5.3850	ETHENE	0
2.905	0.7228		1.000	1.0000	2.9077	ETHANE	0
8.28	6.1634	T	2.850	0.7146	17.7165	PROPYLENE	0
9.08	0.3186		3.126	0.6820	0.8742	PROPANE	0
14.95	1.3070	T	5.145	1.0000	5.2575		
			5.528	0.5173		I-BUTANE	0
17.06	6.9220	T	5.880	0.5360	14.9376	1-BUTENE	0
18.23	2.9595	T	6.277	0.5173	6.1583	TRANS2BUTENENE	0
18.87	3.9524	U	6.497	0.5360	8.5216	CIS-BUTENE	0
24.20	1.4106		8.329	1.0000	5.6741		

8 MATCHED COMPONENTS 90.77% OF TOTAL AREA
2 UNKNOWN >= UNPETD PEAK TIME 9.22% OF TOTAL AREA
16 PEAKS ` AREA/HT REJECT

formed of ooid sediment (samples 4.1 and 5.1), and these in turn emitted less gas than the sample which also contained algal mat material during the experimental run (sample 6.1). The gases are produced by the diagenesis of the organic matter in the sample during the experiments, and by heating of the remaining organic matter during preparation for analysis. The order of hydrocarbon abundance as described above is also the order of abundance of organic matter within the sediment, able to produce such hydrocarbons. Results from the ooid sands before and after the experimental runs (figure 5.3a) show that there is a decrease in the amount of gaseous hydrocarbons detected in the samples with continuing diagenesis. There is some suggestion that after an initial decrease, some of the gases increase slightly in abundance in some of the samples. This would be due to the ongoing cementation reactions trapping the hydrocarbon gas within the new cement.

That light hydrocarbons are generated during this type of experimental run, and lost to the pressure vessel atmosphere or the pore fluid has been shown during more recent research at Imperial College, and is illustrated by the chromatogram in figure 5.3b. The gas sample analysed to produce such a chromatogram is gas removed from a pressure cell during diagenesis experimentation; the facility to sample such gases and analyse them was not available at the time of the research presented here. The light hydrocarbons generated during organic diagenesis within carbonate sediments are important, as is their tendency to become trapped in the early carbonate

Figure 5.3c: Chromatogram Showing Formaldehyde Peak.



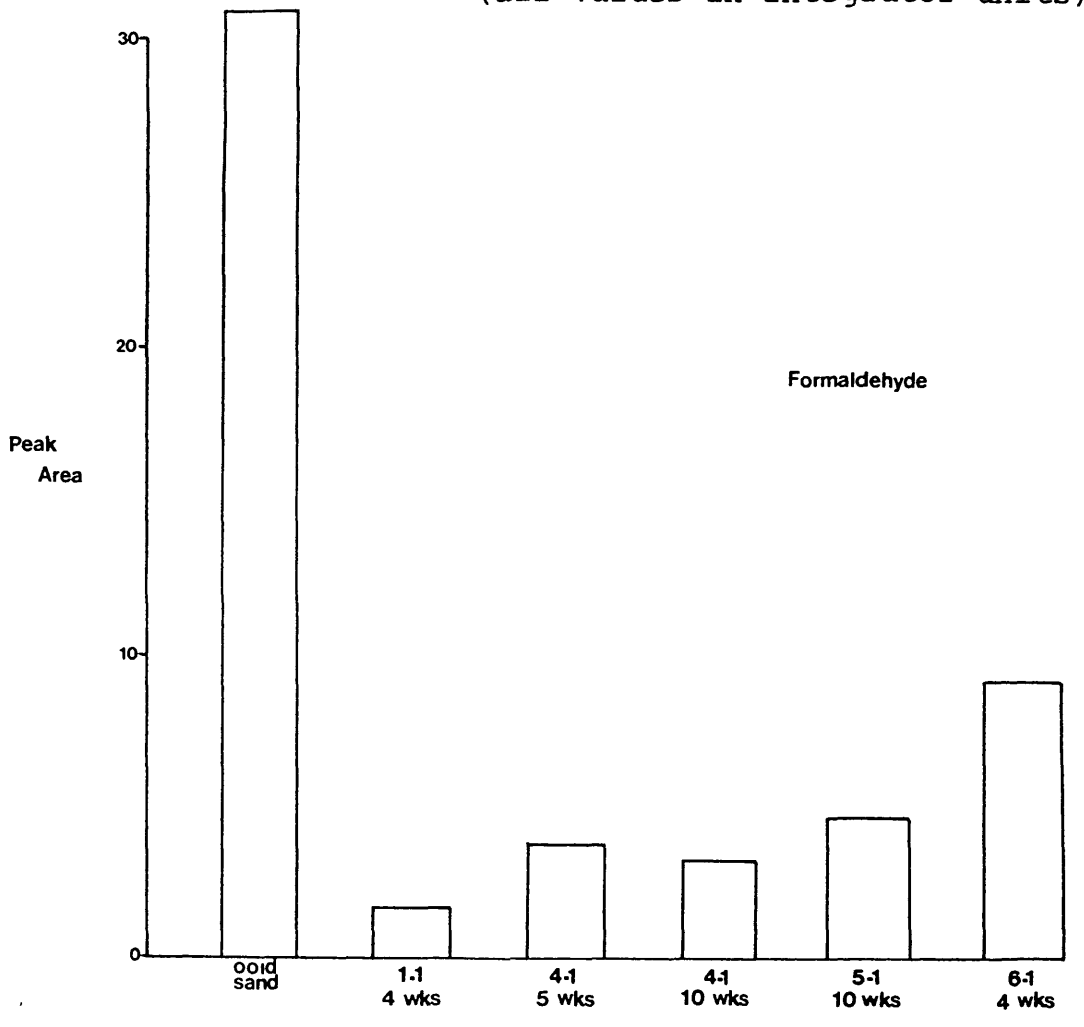
cements. In the natural system these hydrocarbons are those detected on analysis of limestones from unmineralised areas, where they give rise to the background levels of light hydrocarbons against which anomalies can be measured.

5.3.3. Formaldehyde in Experimental Samples

In addition to emitting simple light hydrocarbons, the samples also gave rise to other more complex gases. These appeared in the chromatographic analyses, and one in particular was present in copious quantities, especially in the case of the unaltered ooids, as illustrated by the chromatogram forming figure 5.3c. The gas, confirmed by analysis at Mercury Hydrocarbons to be the gas termed '170' (section 2.1.7.), was abundant in the analysis of the fresh ooid sand, and decreased in abundance as diagenesis proceeded (figure 5.3d). From the position of the gas in the chromatogram, it must have a boiling point between those of the gases at either side of it, i.e. propane and i-butane (-45°C and -12°C respectively). Of the simple organic compounds there are only two with boiling points within this range. These are dimethyl ether (methoxymethane) with a boiling point of -24°C, and formaldehyde (methanal) with a boiling point of -21°C (Stokes 1973, p.137). The ethers do not occur naturally, which makes it unlikely that dimethyl ether (CH_3-O-CH_3) is the identity of the gas. Formaldehyde (HCHO), however, is known to be present in the chlorophyll pigment of green plants, and is also a product of

Figure 5.3d: Formaldehyde Content of Samples.

(all values in integrator units)



Sample	ooid sand	1.1	4.1	4.1	5.1	6.1
Run time	0 wks	4 wks	5 wks	10 wks	10 wks	4 wks
Formaldehyde	31·40	1·40	3·61	3·16	4·44	9·06

the incomplete combustion of plant material. It is considered that the '170' gas is probably formaldehyde, formed by the heating of the organic matter in the carbonate sand, though this was difficult to prove experimentally.

That formaldehyde should be emitted by the experimental carbonate samples on heating is logical enough, but the problem remains as to the cause of the abundance of the gas in analyses of rock samples at Mercury Hydrocarbons. The implications of the identification of the gas to previous analysis undertaken at Mercury Hydrocarbons is discussed in section 2.1.7.; in addition it should be noted that, even after identification of the gas at Imperial College on analyses of the experimental samples, the gas was not detected in subsequent analyses of rock samples. The Perkin-Elmer chromatograph therefore did not come conditioned with the gas in the same way in which the Pye-Unicam chromatograph at Mercury Hydrocarbons would appear to have been.

The decrease in abundance of formaldehyde in the experimental samples with increased diagenesis reflects a decrease in the ability of the contained organic matter to generate the gas. This is another illustration of the way in which diagenetic alteration affects the nature of the organic content of a sediment. The complete lack of formaldehyde in the analysis of ancient oolites (Mendips samples, section 2.2) suggests that the ability to generate the gas is eradicated on prolonged diagenesis.

5.3.4. Summary

In addition to undergoing carbonate diagenesis, the samples of carbonate sediment illustrated diagenesis of their organic content. Analysis of the charge material and the samples after simulated diagenesis showed differences in the amounts of light hydrocarbon and of formaldehyde present. The light hydrocarbon content decreased, though there is some evidence that the onset of cementation caused retention of these hydrocarbons in the solid phase. The formaldehyde content was greatly decreased, and after prolonged diagenesis, the sediment will no longer generate this gas on heating. These changes illustrate the alteration of the organic matter which occurs at the same time as alteration of the carbonate host, as the sediment undergoes diagenesis.

PART THREE

CONCLUSIONS

THE RELATIONSHIP BETWEEN CARBONATE DIAGENESIS, BASE METAL ORE DEPOSITION, AND THE FORMATION OF LIGHT HYDROCARBON ANOMALIES, AND THE POTENTIAL OF THESE ANOMALIES IN MINERAL EXPLORATION.

THE RELATIONSHIP BETWEEN LIGHT HYDROCARBONS, CARBONATE DIAGENESIS, AND BASE METAL ORE DEPOSITS

The research presented in this thesis has investigated the phenomenon of light hydrocarbon haloes surrounding base metal ore deposits in carbonate hosts. This investigation has involved study of all three components of this system, and their inter-relation. From the evidence presented, a model for ore deposition is proposed which describes both the precipitation of ore and the formation of hydrocarbon anomalies in the carbonate host.

The geological system under consideration is that of a sedimentary basin undergoing subsidence and associated sedimentation. The centre of such a basin, under deep water and with little clastic input from the basin margin, is an ideal site for the accumulation of organic rich sediment, and under anoxic conditions a black mud will accumulate here. Such a sediment will contain a high proportion of organic matter undergoing anaerobic decomposition, and will also have a higher content of trace metals than sediments of different facies elsewhere in the basin. While these organic-rich sediments accumulate at the anoxic centre of the basin, the basin margin sediments will be deposited under aerobic conditions. Such sediments will include carbonate strata, for instance basin marginal reefs, and ooid sediments. Continued sedimentation at these locations results in shallow burial of the carbonates, and the buried sediments will

start to undergo diagenesis. During the first stages of this, mineral transformation will occur, and there may be formation of early calcite cement, but the porosity and permeability of the sediment will remain unimpaired.

With further sedimentation within the basin, the central sediments will become compacted, and their formation waters will be forced out as the pore space is reduced. These waters have the opportunity to dissolve minerals from their host sediments, and so have the composition of brines. Metal ions will be taken into solution from the sediment and transported in complex form as the brine migrates. The sediment at the centre of the basin will not at this stage be a fully mature petroleum source rock, though it has the potential to become one. It will, however, have generated some hydrocarbons, due to the onset of organic diagenesis and the anaerobic decomposition of the organic matter. The hydrocarbons produced, both liquid and gaseous, will migrate away from the basin centre with the movement of the basinal brine. This is particularly efficient for the removal of the gaseous hydrocarbons due to their high solubility (especially under pressure). The formation water of the sediments, given the composition of a brine by its content of dissolved salts and gases, will migrate out of the source sediment towards the margin of the basin. The driving force behind this migration may be the compaction of the sediments alone. There may be an additional force, for instance a temperature gradient due

to a deep heat source, or pumping due to seismic activity. In either case the result is the migration of a brine of elevated salinity and temperature, containing dissolved hydrocarbons and base metal ions, moving into the basin margin sediments. For the purpose of this discussion it is assumed that the base metal ions are present in great enough concentration to precipitate ore minerals if conditions are favourable.

The brine rises through fluid migration pathways to the basin margin, where it is expelled into the permeable carbonate strata. These sediments will be undergoing diagenesis, and if the Eh/pH conditions are suitable, bacterial sulphate reduction will already be established as a process of organic diagenesis. The reduction of sulphate to sulphide allows precipitation reactions to occur with the formation of metal sulphides from the metal ions dissolved in the introduced brine. Continued precipitation of the sulphides allows sulphate reduction to proceed by removing the reaction product from solution and so preventing the attainment of equilibrium. This removal of dissolved sulphide to the ore minerals will also encourage bacterial methanogenesis, which is usually restricted by dissolved sulphide. The bacteria (both methanogenic and sulphate reducing) usually act on organic matter within the sediment. The injection of basinal brines into the host carbonate will give these bacteria an alternative material to metabolize;

the hydrocarbon introduced in solution. The action of bacteria on these hydrocarbons will cause them to be decomposed into ever simpler members of the homologous series (and ultimately to carbon dioxide and water). The result of this process and the concurrent methanogenesis will be the generation of the lightest members of the hydrocarbon series at the site of ore deposition, and more especially the generation of methane.

As the ore precipitation reactions continue, the generation of gas will also proceed, and the gradient in partial pressure of gas in solution will encourage the gas to move away from the site of its generation. This migration will be attained by the diffusion of the gases through the water saturated pore space of the carbonate. The chromatographic pattern described around certain ore deposits (Carter 1983) is said to be due to the different rates of diffusion of the gases due to their different molecular size. Indeed, if this is so, then the methane will form the outermost halo, since the methane molecule is the smallest, and the gas will therefore diffuse faster than the other hydrocarbon gases. It would, however, seem likely that the predominance of methane in the rocks around an ore deposit could also be due to it being produced in greater volume during ore precipitation. The latter interpretation seems to be the more likely in the light of the fact that hydrocarbon haloes have been described in far fewer cases than those where only a higher than average percentage of methane

compared to other light hydrocarbons has been noted in rocks hosting ore deposits. All the time that this precipitation of ores and migration of gases is continuing, the carbonate sediment is undergoing diagenesis. The mineral transformations and processes of cementation are unaffected by the introduction of high concentrations of metal ions and hydrocarbons. As diagenesis continues, with the formation of new fabrics and new minerals, the hydrocarbon passing through the pore space will become arrested in its migration path. With lithification of the carbonate, the permeability will decrease, and the hydrocarbons will be prevented from moving from closed pore space. The hydrocarbons will also become trapped within the very structure of the newly forming minerals, tightly bound within the new rock. This process acting over the area of ore precipitation and hydrocarbon migration will 'freeze' the hydrocarbon pattern into the rock, so giving the typical elevated methane content around the ore deposit. It may be that in the vicinity of ore deposition the diagenesis of the carbonates proceeds more rapidly than elsewhere, stimulated by the higher temperature, and flushing by the basinal brines. The limit of the hydrocarbon anomaly i.e. where the methane content falls away to the level of the regional background can then be considered to represent a diagenetic front at the limit of the area affected by accelerated diagenesis. Where this is not the case, and the diagenesis continues at a steady rate throughout the area, the anomaly limit represents the distance the methane had migrated before being frozen into position by the progress of

diagenesis. In either case the result is an ore deposit in a carbonate host, surrounded by an area where the hydrocarbon gas content of the host rock differs from that elsewhere in the region, and is characterised by the high quantities of methane emitted when the rocks are crushed and heated.

Large ore deposits with long lived, vigorous systems of ore precipitation will produce more methane than smaller deposits. This will migrate further before being arrested, so producing a larger anomaly than those around smaller deposits. The processes described here will occur in all cases where ores are precipitated in similar manner; however carbonates will produce a cleaner anomaly pattern than clastic host rocks, due to the control of diagenesis. The speed at which carbonate diagenesis starts after sediment deposition, and the rapid reactions help to trap the hydrocarbons in situ as they migrate. The rapid formation of cement traps the hydrocarbons within the rock structure, so that they are released only by high temperature heating. Clastic sediments, with their slower diagenetic reactions, will not trap the hydrocarbons so effectively, and will tend to lose them easily, giving neither a satisfactory halo pattern nor samples suitable for analysis. The diagenetic state of the carbonate itself will also have an effect on the trapping of the hydrocarbons. If the carbonate is unconsolidated, gases will be able to pass continually through it, and equilibrium will be reached over a large area, preventing the formation of a restricted region over the orebody with anomalous hydrocarbon values. On the other hand, if diagenesis has proceeded to a

stage where the permeability of the carbonate is greatly restricted, then only very limited diffusion away from the orebody will occur, and again there will be no anomaly over the area.

The processes which act to produce the ore deposit and its surrounding halo are characteristic processes of any sedimentary basin. It is their interdependence which causes this intriguing phenomenon. For the ore to be formed, the basinal brine must contain a certain concentration of metal ions, and there must be sulphate reduction within the host. The bacterial action associated with this also causes generation of hydrocarbon gases at the site of, and concurrent with, ore deposition. The gases generated, dominantly methane, migrate through the carbonate host, and the diagenetic state of this host decides the nature of the ore deposit, and the form of the hydrocarbon anomaly surrounding it. Therefore, though the single processes may be common, it is their combination which is necessary to produce the unusual event.

THE USE OF LIGHT HYDROCARBONS IN MINERAL EXPLORATION

The investigation of the phenomenon of light hydrocarbons of anomalous compositions extracted from carbonates hosting ore deposits is made the more interesting since there is a potential application in mineral exploration. It is envisaged that during reconnaissance exploration samples of a possible host rock would be collected in a regular pattern over a large area. Analysis of these for light hydrocarbons should then determine the percentage of methane in the extractable light hydrocarbons which constitutes the regional background level, and any area where the methane percentage is noticeably higher than this. Any area with such anomalous methane values would then be the target for more detailed exploration. It now remains to discuss the implications of the research presented in this thesis for the use of methane anomalies in this manner.

The theory of formation of hydrocarbon anomalies described in the preceding Conclusion suggests that, due to diagenesis being a controlling factor, carbonate terrains are those most suited to the detection of such anomalies. The same processes of ore precipitation and methane generation will act when ores are deposited in clastic sediments, as shown by the high methane percentages of the Aberfeldy ore zone. However, clastic sediments will not give good anomaly patterns or retain the hydrocarbons as efficiently as the

carbonates. Within carbonate lithologies, the diagenetic state of the host at the time of ore precipitation will decide whether a clear anomaly pattern can be detected or not. This will depend on whether the permeability is high enough to allow hydrocarbon migration, and, if so, whether diagenesis proceeds rapidly enough to 'freeze' the hydrocarbons in situ as they migrate. The tectonic history of the host will also be important, the evidence being that deformation and metamorphism can redistribute any hydrocarbons, so destroying the methane halo effect. It would therefore seem that the most productive terrains in which to search for methane anomalies are undeformed carbonate terrains. Whether the relative timing of diagenesis and ore deposition allowed anomaly formation cannot be deduced from the study of the regional carbonate geology alone. This will only be discovered later after analysis of the carbonate samples. Carbonates do, of course, have the ability to generate some hydrocarbons on heating, due to their organic matter content. In heavily mineralised areas this hydrocarbon will be swamped by that introduced during the mineralisation process, especially methane. The first stage in the interpretation of the results from analysing a suite of samples must be the identification of regional background levels, and the determination of a level at which the percentage methane in the analysed sample is said to be anomalous. This first stage is necessary since, due to the geological controls on the hydrocarbon content, the regional background levels may vary

from one region to another, and what is classed as an anomalous reading in one region may represent background levels in another.

Any mineral exploration tool exploits certain characteristics of an ore deposit, in this case the composition of hydrocarbons extracted from the surrounding rock. It is, however, not enough to identify the characteristic features and to describe its causal relationship with the orebody. If a potential method is ever to be used as an exploration tool, it is also necessary to understand the problems with and restrictions upon that method. Knowledge of the limits under which a certain method can be used is of as much value as knowledge of the method itself. The detection of anomalous quantities of methane in carbonates is a potential exploration tool, but the constraints on it must be evaluated if it is to be correctly applied within its limits. If the constraints are poorly understood and an attempt is made to commercialise the method, it is possible that it could be used in an inappropriate situation and pronounced a failure through no fault of its own. Such a trial, having defined a problem, may also provide the means of solving it, but in a sense it will then be too late, and the name of the method will always carry the taint of a failed commercial introduction. To prevent this, the problems surrounding any exploration tool should be evaluated prior to its commercialisation. The methane anomaly method discussed in this thesis is a mineral

exploration tool in embryo form. The setbacks encountered during the course of this research are as important as the discussion of the ideal situation. The problems of using the hydrocarbon anomalies in exploration do not necessarily arise from the basic concept, nor from the analytical method, but from the application of the method in the real situation.

That the geological conditions affect the presence and detection of a hydrocarbon anomaly has already been noted. The method may be restricted to carbonate terrains, and even within this environment there will be variation due to the diagenetic state of the rock and the lithologies involved. During sample collection, the petrology of the sample should be noted so that similar samples can be collected throughout the field area, where possible. It will also be necessary to note any samples that may be contaminated by vegetation or deeply weathered. Some areas, for instance where outcrop is poor, may not be suitable for sampling, since vegetation contamination may prevent collection of a good suite of fresh samples. On a larger scale, whole regions may be unsuitable for the same reasons. An example of this would be tropical regions, where high temperatures and heavy rainfall cause luxuriant vegetation and deep chemical weathering. In such an area it would be very difficult to collect a suite of samples that did not give contaminated analyses. The climatic control which precludes the use of an exploration method based on hydrocarbon content in such areas will act in favour of such a method in other areas. Optimum conditions for the

preservation and detection of methane anomaly patterns in the rocks include low chemical weathering, and little vegetation. These are features of the arid regions of the world, and it would seem that both hot deserts and high arctic regions would provide good climatic conditions. The idenfification of well-developed methane anomalies, and hydrocarbon halo patterns, around Irish ore deposits (Carter & Cazalet 1984) suggests that, where outcrop is good enough for the collection of fresh samples, this method also has a potential application in more temperate latitudes. It should be noted that these ore deposits in the Irish Carboniferous Limestone are the only deposits where hydrocarbon haloes (as opposed to simple methane anomalies) have been described. It is possible that the fact that ore deposition and carbonate diagenesis proceeded together in this area resulted in the hydrocarbon pattern being more pronounced than in similar deposits with a different time interval between these episodes.

Having identified certain situations where it is unlikely that an exploration method based on methane anomalies could be applied, it is important to consider the analytical method as it would be used in suitable areas. Sample collection and preparation would be similar to the methods used for this research. Some geological training would be necessary for this, and a skilled operator would be needed to carry out the chromatographic analyses. The level of training of personnel to carry out the analyses is therefore no greater

than is necessary for comparable methods of geochemical and geophysicalexploration. The main problem associated with the analysis is the fact that different gas chromatograph systems have been shown to give different results from the analysis of the same sample. If the identification of methane anomalies is to be used in mineral exploration, then some standardisation of results is required. It is hardly feasible that only one operator and system are capable of identifying such anomalies, the results must be reproducible on different systems. The individual analyses need not be the same, but it must be possible to reproduce the same overall anomaly pattern on different systems. At present the ability to do this is by no means proven, and this problem should be investigated further, perhaps by the analysis of a suite of samples from an area of known mineralisation by different gas chromatographs. It is hoped that any methane anomaly would be detected by the different systems, though the patterns produced may differ in detail. Another feature of the analysis which should be investigated further is the presence of formaldehyde and other non-hydrocarbon gases in some analyses. These are now thought to be contaminant gases though they were for a long time included in the calculation of ratios, the plotting of results etc. This illustrates how vital it is to understand the method as fully as possible to prevent the generation of spurious data. For ease of interpretation the simplest index - the percentage of methane in the analysed gas - should be used to identify the anomaly

pattern. This avoids the possibilty that the data may be manipulated in complex ratios to give patterns of dubious significance. Once a methane anomaly has been shown to exist in a certain area, this anomaly can then be investigated by more detailed sampling. The analysis of the hydrocarbons emitted from the rocks in this area may show a pattern in gases other than the methane, though as has already been noted, the chromatographic halo patterns are found only under exceptional circumstances. The methane anomaly alone is the simplest and most reliable indication of the possible position of an ore deposit.

The detection of a methane anomaly, within these constraints, would then be used as part of an exploration programme as follows. After identification of a suitable region, for example one of good carbonate outcrop, samples would be collected in the field over a large regular grid (as far as the topography allowed). The samples would be studied petrologically, and analysed for light hydrocarbons. Of the results of these analyses, the percentage of methane in the analysed gas would be calculated, and plotted across the field area. This would allow identification of the background level of methane percentage, and of any areas where the methane percentage was noticeably higher than average. A more detailed suite of samples taken from any such area would then allow the methane anomaly to be plotted up in more detail. The centre of the anomaly could then be examined by other geochemical or geophysical means to determine whether there was a target suitable for exploratory drilling. With

investigation of many such areas, information gained from the surveys (whether or not any methane anomaly has been detected) should be collected to provide a large database, allowing the method to be scrutinised, so that alterations and improvements could be made.

In addition to being an interesting geological phenomenon, methane anomalies in ore-hosting carbonate rocks may have a practical application in mineral exploration. The problems which are outstanding at present fall into three categories: those relating to the geological conditions which restrict the potential use of such a method to certain areas; the fact that the limits to the use of the method are not as yet fully evaluated; the problems raised by the analytical method and the poor reproducibility of results. If such problems can be solved, then the economic state of the mineral exploration industry will decide whether the potential method is ever fully developed. It is to be hoped that further research and development is encouraged; not only is there a potentially useful exploration tool to be produced, but there is undoubtedly more to be discovered about the complex interdependence of carbonate diagenesis, base metal ore deposits, and their associated light hydrocarbons.

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APPENDIX A

PREPARATION OF A STAINED ACETATE PEEL OF A LIMESTONE.

APPENDIX A

PREPARATION OF A STAINED ACETATE PEEL OF A LIMESTONE

The preparation of acetate peels is a rapid and simple method for producing a slide allowing study of the limestone petrology in detail. The peel records an impression of the etched and stained rock surface on a thin sheet of acetate film. The correct procedure is as follows:

1. The rock sample is cut in half with a diamond saw, care being taken that any interesting structure is intersected by the line of the saw.

2. The cut face of the chosen half sample is smoothed for a few minutes on a diamond grinder.

3. The sample is 'lapped' with 600 silicon carbide and water on a glass plate. That is, all the grinding scratches are polished away using a rotary movement of the sample on the slurry-covered glass.

4. The sample is washed well with water and left to dry.

5. The sample is etched by holding the polished surface in a bath of 10% hydrochloric acid for fifteen seconds. The sample should be tilted slightly to allow bubbles of carbon dioxide to escape from beneath. The sample is then rinsed with water.

6. The sample is stained by holding the etched surface in a bath of the stain solution for 25 seconds. The stain is made by dissolving 2g. of Alazarian Red in 1000ml. of

0.2% hydrochloric acid. After staining, the sample is again rinsed with water.

7. The sample is left to dry with the cut face uppermost, by pressing the base of the sample into plasticine, if necessary. The cut face should be horizontal to prevent pooling of the stain, and should not be touched.

8. Once the sample is completely dry, the peel can be made. The sample is first titled slightly, and the surface is flooded with acetone.

9. As the surface is still wet, a piece of acetate film (0.008cm. thickness) is rolled onto it, so that no bubbles are left underneath.

10. This is left to dry; when dry the smell of acetone will have disappeared completely from the sample.

11. The acetate film is peeled off carefully, trimmed to size, and mounted, either between glass for microscope study, or in a slide mount for projection onto a screen.

N.B. Protective gloves should be worn throughout. The acetone vapour should not be inhaled.

APPENDIX B

WORKSHEETS FOR MENDIPS PETROLOGICAL STUDY.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sorting	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments

HOLCOMBE QUARRY.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sorting	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments
1	✓			5%.	Shell fragments			MUD	GOOD		✓		Stylolites	59.30 / 66.26	Light grey
2	✓			40%.	Rugose corals, coral + shell fragments, foraminifera		10%.	FINE SAND	POOR	✓			Stylolites	73.92	Mid grey
3	✓			10%.	Coral + shell fragments			MUD	GOOD		✓		Calcite veining	48.94	Light grey
4	✓			40%.	Rugose corals, brachiopods, + shell + coral debris			SAND	FAIR		✓		Stylolites	85.77	
5	✓			50%.	Brachiopod shells + shell fragments, crinoids, foraminifera			FINE SAND	POOR		✓	some spory cement	Calcite veining	74.75 / 67.21	Mid grey
6	✓			20%.	Brachiopods shell fragments, few crinoids			MUD	POOR		✓		Fe-stained stylolites, much shattered. Silicification.	73.38	
7	✓		†SOME BLACK CHERT	10%.	Foraminifera.			FINE SAND	GOOD		✓			55.83	Dark grey
8	✓			20%.	Shell fragments, foraminifera.		10%.	SAND	FAIR		✓		Stylolites	63.66	Mid grey
9	✓			10%.	Small shell fragments, foraminifera		30%.	COARSE SAND	GOOD		✓	spory cement		68.48	
10	✓			70%.	Whole rugose corals, large + small brachiopods, abundant foraminifera, shell + coral fragments.	10%.	10%.	COARSE SAND	POOR	✓		Spory cement (coarsely crystalline)	Some recrystallisation.	78.20	
11			BLACK CHERT		Microfossils e.g. forams preserved in chert			AMORPHOUS						54.41	NO peel. Black chert in limestone - diagenetic silicification
12			BLACK CHERT		ditto			AMORPHOUS						49.29	NO peel ditto
13	✓			10%.	Brachiopods, also shell fragments			MUD	GOOD		✓		Stylolites, vein calcite. Some silicification.	74.41 / 72.79	Light grey
14			VEIN CALCITE					COARSE CRYSTALS						65.18 / 73.44	NO peel
15	✓			10%.	Shell fragments, coral obscured by silicification.			SAND	GOOD		✓		Partly silicified. Calcite veining	74.09	Dark grey
16			GREY CHERT		Microfossils preserved in chert			MUD						30.41	NO peel diagenetic silicification of limestone.
17	✓			70%.	Brachiopod shells, shell + coral fragments, foraminifera		10%.	COARSE SAND	POOR	✓		Spory cement	Some recrystallisation.	53.37	Mid grey

HOLCOMBE QUARRY.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sorting	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments
18	✓			10%.	Shell fragments		10%.	FINE SAND	GOOD		✓	some sparry cement		59.62	Mid grey
19	✓			20%.	Brachiopod + gastropod fragments foraminifera.			COARSE SAND	POOR		✓			38.11	Brown-grey
20	✓			10%.	Foraminifera		70%.	COARSE SAND	GOOD		✓	Sparry cement still quite porous	Calcite veining	69.62	Light grey
21	✓						10%	MUD	FAIR		✓		Calcite veining some silicification	84.55	Light grey
22	✓			10%.	Gastropod + shell fragments			FINE SAND	FAIR		✓		some recrystallisation	52.88	Light grey
23	✓		+ VEIN CALCITE	20%.	Shell + coral fragments foraminifera		20%.	COARSE SAND	POOR		✓	sparry cement	Much recrystallisation, Calcite vein.	55.67	Mid grey
24	✓			40%.	Brachiopod + gastropod fragments, abundant foraminifera			SAND	POOR		✓			62.24	Mid grey
25	✓			5%.	Foraminifera.			MUD	GOOD		✓		Calcite veining Stylolites	58.53	Light grey
26	✓			10%.	Shell fragments - now indistinct.			SAND	POOR		✓		Limestone undergoing dolomitisation.	52.13	Brown
27	✓			30%.	Brachiopods, gastropods, shell fragments		30%.	SAND	POOR		✓	sparry cement Calcite infilling shells		82.75	
28	✓			10%.	Shell + coral fragments			COARSE SAND	GOOD		✓	some sparry cement	Patchy recrystallisation	81.44	
29	✓			10%.	Very small shell fragments.			MUD	GOOD		✓		Stylolites	29.13	Light grey
30	✓			50%.	Brachiopods, shell fragments, foraminifera		10%.	FINE SAND	POOR		✓		Stylolites.	60.77	
31	✓			10%.	Shell fragments, foraminifera.		70%	COARSE SAND	FAIR		✓	Sparry cement		58.34	
32	✓			40%.	Rugose coral, shell + coral fragments		10%.	COARSE SAND	POOR		✓	Sparry cement some overgrowths	Calcite veining	77.20	Dark grey
33	✓			30%.	Shell fragments, crinoids, foraminifera.		30%	COARSE SAND	FAIR		✓	Sparry cement		89.04	Block
34	✓			10%.	Foraminifera.		70%.	COARSE SAND	GOOD		✓	Sparry cement		79.47	Mid grey

HOLCOMBE QUARRY.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sorting	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments
35	✓			40%.	Small gastropods, shell fragments, crinoids, foraminifera.		20%.	COARSE SAND	FAIR		✓	Sparry cement.		73.39	Mid grey
36	✓			10%.	Shell fragments, foraminifera.	20%.	50%.	COARSE SAND	FAIR		✓	sparry cement still quite porous		57.16	Light grey
37	✓					90%.		COARSE SAND	GOOD	✓		Porous Sparry nm cement		59.62	Light grey oolite
38	✓					90%.		COARSE SAND	GOOD	✓		Porous Sparry nm cement		66.80	Light grey oolite
39	✓					50%.	20%.	COARSE SAND	GOOD		✓	Fairly porous Some sparry cement.		70.87	Light grey
40	✓			40%.	Brachiopods gastropods, shell fragments foraminifera.	10%.	20%.	SAND	POOR	✓		Sparry cement	Calcite vein	59.00	Black
41	✓			10%.	small shell fragments, foraminifera			SAND	GOOD		✓		Calcite vein	73.81	Mid grey
42	✓			60%.	Rugose coral, brachiopods, shell fragments, foraminifera.		10%.	COARSE SAND	POOR	✓		crystalline calcite infilling shells ex.	Stylolites	80.79	Dark grey

BURRINGTON COMBE.

NB no peels made of these samples.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sorting	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments
1	✓		VEIN CALCITE					COARSELY CRYSTALLINE					Vein	68.79	vein some 6cm in width. Laterally extensive. Light grey.
2	✓			20%	microfossils.			COARSE SAND	FAIR		✓		small veins of cc. mm in width.	71.43	Dark grey
3	✓			20%	microfossils			SAND	GOOD		✓				Mid grey
4	✓			30%	bivalves, shell debris microfossils	10%	10%	COARSE SAND	POOR	✓			some rex[n]	71.18	Light grey
5	✓							FINE SAND	GOOD					57.66	Dark grey fine grained lst. no obvious fossil content
6	✓			10%	fine debris			FINE SAND	GOOD		✓			47.29	Dark grey
7		✓						FINE SAND					dissolution	83.85	light brown sucrosic dolomite/ dolomitic limestone
8	✓							MUD	GOOD				Recrystallized. Stylolites.	50.15	Dark grey fine mica mudstone.
9	✓							FINE SAND	GOOD				cc veins on mm scale	61.43	light grey granular
10	✓			30%	shell debris, microfossils			SAND	FAIR		✓		cc veins on mm scale	56.69	mid-grey.
11	✓			30%	shell debris, microfossils		10%	SAND	FAIR		✓			69.21 / 69.73	Dark grey
12	✓			40%	shell fragments, coral fragments.		10%	COARSE SAND	POOR	✓				67.81	Mid-grey
13	✓							SAND	GOOD					54.98	Light grey Granular
14	✓			60%	microfossils bivalves + fragments		10%	SAND	POOR					68.62	Mid-grey fossiliferous.
15	✓			60%	fragments of solitary corals + other debris			V. COARSE SAND	POOR	✓			Extensive recrystallization	71.92	Light grey
16	✓			80%	coral + shell fragments			COARSE SAND	POOR	✓			Extensive recrystallization	74.41	Light grey

WHATLEY QUARRY.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sorting	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments
1	✓			70%.	Whole brachiopod shells, broken shell fragments, rugose corals, foraminifera		10%.	COARSE SAND	POOR	✓				66.15 / 68.28	Dark grey
2		✓						SAND	GOOD				Dolomitisation	41.21	Dolomitised lst.
3	✓			10%.	Small shell fragments			MUD	GOOD		✓		Calcite veining	60.22 / 62.43	Light grey fine-grained micrite
4	✓			50%.	Shell fragments coral fragments		10%.	COARSE SAND	POOR	✓				44.77	Dark grey Finely bedded - mm scale fining up sequences Intraclasts.
5	✓			5%	Foraminifera			MUD	GOOD		✓		Stylolites, cc veining	38.74	Light grey with fine banding
6	✓			20%.	Coral fragments, crinoid debris		20%.	COARSE SAND	POOR		✓	meritic rim cement	Calcite veining	62.10	Dark grey
7	✓							MUD	GOOD		✓		Stylolite, cc veining	50.00	Very light grey
8	✓			40%.	Whole brachiopod shells (large + small) Some foraminifera		10%.	SAND	FAIR		✓		Some recrystallisation	57.83	Dark grey
9	✓			50%.	Brachiopod + gastropod shells (whole + broken) Colonial coral Foraminifera			SAND	POOR		✓	Shell cavities	crystalline cc. infilling shell cavities	40.26	Dark grey
10	✓			30%.	Rugose corals		20%.	COARSE SAND	GOOD (OF MATRIX)		✓			52.64	Dark grey
11	✓					80%		COARSE SAND	GOOD	✓		Still highly porous Sparry cement		80.36	Light grey oolite
12	✓					80%		COARSE SAND	GOOD	✓		Highly porous Sparry cement	Small cc. veinlet		Light grey oolite
13	✓			50%.	Large brachiopod shells Also some shell fragments coral fragments foraminifera	5%.		COARSE SAND	POOR		✓			68.04 / 57.83	Black
14	✓							FINE SAND	GOOD		✓	Sparry cement	Some recrystallisation	80.77	Mid grey
15	✓			5%	Shell fragments	10%	70%.	COARSE SAND	FAIR		✓			80.91	Dark grey
16	✓			5%.	Shell fragments	20%	30%.	SAND	GOOD		✓	Sparry cement		46.09	Dark grey
17	✓							COARSE SAND	GOOD		✓		Recrystallised	44.50	Pink-grey

WHATLEY QUARRY.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sort	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments
18	✓			5%.	Foraminifera		80%	SAND	G		✓	Still porous Some sparry cement.			Mid grey
19	✓			5%.	Coral fragments Foraminifera.	20%	60%	SAND	GOOD		✓	Sparry cement	Calcite vein	38.93	Light grey
20	✓							SAND	GOOD		✓		Recrystallised	58.93	Mid grey
21	✓		↑ VEIN CALCITE	10%	Brachiopod + gastropod shells, foraminifera (cell recrystallised)			SAND	FAIR		✓		Much recrystallisation. cc veining + stylolites	39.96	Dark grey.
22	✓			40%.	Brachiopod shells (whole + broken), small gastropods, foraminifera, Solitary rugose coral.		10%.	FINE SAND	POOR		✓		Calcite veining	55.45	Pink-grey
23	✓			40%	Rugose corals (fragments) Shell fragments	10%		SAND	POOR		✓		cc veining	56.36	Dark grey
24	✓			20%.	Shell fragments - shape still visible through undergoing silicification			FINE SAND	FAIR		✓		Partially silicified.	69.47	Silicification causing light/mid grey banding
25			VEIN CALCITE					COARSELY CRYSTALLINE					Vein calcite	85.56 / 87.43	NO peel
26	✓			5%.	Rugose coral			FINE SAND	FAIR		✓		Partially dolomitised. Stylolites	26.38	Grey/brown
27	✓			10%.	Shell fragments, small brachopods + gastropods crinoids, foraminifera		5%.	MUD	FAIR		✓		Some crystalline cc in shells.	59.31	Black
28			FAULT GOUGE + Pb/Zn					MUD					Penetration PbS/ Fluid up fault plane.	87.88	NO peel Veins of calcite few mm. wide in brown calcareous fault gouge.
29	✓			80%.	Corals (internal structure recrystallised) shell fragments, crinoids. Foraminifera.			SAND	POOR	✓			Recrystallisation	35.70	Dark grey
30	✓			5%.	Shell fragments		10%.	COARSE SAND	FAIR		✓	Some sparry cement.	Recrystallisation. Calcite veining	53.47	Light grey
31	✓			30%.	Shell fragments, crinoids + foraminifera.		10%.	COARSE SAND	POOR		✓	Sparry Cement	Recrystallisation.	81.77	Light grey
32	✓			40%.	Crinoids, shell fragments		10%.	COARSE SAND	POOR		✓	Sparry cement overgrowths on some crinoids	Recrystallisation. cc veining	78.09	Mid grey
33	✓			10%.	Small shell fragments			SAND	GOOD		✓	Sparry Cement some overgrowths		60.55	White, chalky
34	✓			40%.	Corals (internal structure recrystallised) shell fragments, crinoids,		20%.	COARSE SAND	POOR	✓			Recrystallisation.	61.82	Pink-grey

WHATLEY QUARRY.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sorting	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments
35	✓			30%	Shell fragments, gasteropod, crinoids, foramin.fera.		20%	COARSE SAND	POOR		✓	Sparry cement	Fe-stained stylolites	68·09	Dark pink-grey
36	✓			5%	Shell fragments			SAND	GOOD		✓	Still porous		31·08	Pink-grey
37	✓			80%	Rugose coral (internal structure recd) shell fragments (brachiopod + gasteropod), foraminifera.			COARSE SAND	POOR	✓			Stylolit, Fe-staining Recrystallisation		Mid grey, with red Fe-staining.
38		✓		5%	Shell fragments			MUD	GOOD		✓		Dolomitised lst.	57·22	Light brown
39	✓			20%	Shell fragments, abundant foraminifera		10%	MUD	GOOD		✓			71·64	Black
40	✓		CHERTY		Few silicified microfossils			MUD					Red-stained stylolites silicification	61·91	NO peel Silicified + veins - little of original structure left
41	✓			40%	Broken corals, complete gasteropod shell, shell fragments, foraminifera			COARSE SAND	FAIR		✓	Geopetal in gasteropod shell		63·56	Dark grey
42	✓			20%	Rugose coral, shell fragments, foraminifera		10%	COARSE SAND	FAIR		✓	Sparry cement	Recrystallisation	72·36	Dark grey
43	✓			20%	Shell + coral fragments, foraminifera.			FINE SAND	FAIR		✓	Sparry cement	Calcite vein	64·39	Black
44		✓		10%	Shell + coral fragments, foraminifera		10%	MUD	FAIR		✓		Dolomitised lst. Fe-stained stylolites.	54·35	Brown-grey
45	✓			40%	Brachiopod shells + fragments coral (recrystallised) + foraminifera		20%	COARSE SAND	POOR	✓			Recrystallisation	67·21	Dark grey
46	✓			30%	Shell fragments			COARSE SAND	FAIR		✓			70·26	Mid grey
47			SST					FINE SAND						33·42	NO peel Dark grey fine sst. little internal structure.
48	✓			10%	Brachiopod shell, shell fragments, some coral.			MUD	GOOD		✓			70·26 / 71·35	Light grey
49	✓			10%	Shell fragments, foraminifera.			SAND	GOOD		✓	Sparry cement.	Calcite veining	82·79	Mid grey
50	✓							SAND	GOOD		✓		Stylolites	32·22	Black
51	✓							MUD	GOOD		✓		Much calcite veining - rock very shattered.		Mid grey

WHATLEY QUARRY.

No.	Lst.	Dol.	Other	Skel.	Fossil Type	Oolitic	Peletal	Grain Size	Sorting	Clast Supp.	Matrix Supp.	Evidence Initial Porosity	Evidence Fluid Movement	% CH_4	Comments
52	✓			40%	Colonial coral (Favosites)			SAND	GOOD		✓			49.90	Black Lst. with colonial coral
53	✓		VEIN CALCITE					FINE SAND	GOOD		✓		Crystalline calcite ppts in vugs	34.48	Black
54			SST					FINE SAND	GOOD		✓			48.87	Black
55	✓							MUD	GOOD		✓		Fe stained stylolites	57.19	Grey
56			WHITE CHERT					COARSELY CRYSTALLINE						81.19 / 80.74	NO peel. No evidence original carbonate structure recrystallised.

APPENDIX C

GAS CHROMATOGRAPH ANALYTICAL RESULTS

APPENDIX C

GAS CHROMATOGRAPH ANALYTICAL RESULTS.

Sample numbers:

HQ : Holcombe Quarry

BC : Burrington Coombe - all Mendips

WQ : Whatley Quarry

AB : Aberfeldy

All the tabulated values are percentages of total hydrocarbon, except the 'Total Area' value, which is given in integrator units.

In the Aberfeldy analyses, the isothermal conditions gave poor separation of the C_3 gases. There may therefore be propane present in analyses which appear to have none, but this has been included in the propene value.

Identity of Gases:

CH_4	: methane	$i\text{-}C_4H_{10}$	: isobutane
C_2H_4	: ethene	$1\text{-}C_4H_8$	: 1-butene
C_2H_6	: ethane	$n\text{-}C_4H_{10}$	: n-butane
C_3H_6	: propene	$t2\text{-}C_4H_8$	: trans-2-butene
C_3H_8	: propane	$c2\text{-}C_4H_8$	: cis-2-butene

See figure 1.1d for the structural formulae of these compounds.

Sample No.	CH_4	C_2H_2	C_2H_4	C_3H_6	C_3H_8	iC_4H_{10}	$1C_4H_8$	nC_4H_{10} $t2C_4H_8$	$c2C_4H_8$	Total Area.
HQ01	59.30	3.11	0.00	2.77	0.00	0.00	33.19	0.00	0.00	11.57
HQ01	66.26	3.63	0.37	1.78	0.41	0.00	26.49	0.00	0.00	16.96
HQ02	73.92	2.52	3.60	1.08	1.04	0.00	16.18	0.00	0.00	9.75
HQ03	49.94	1.93	0.51	0.00	0.40	0.00	46.21	1.23	0.79	21.11
HQ04	85.77	0.27	6.73	0.16	1.60	0.00	4.74	0.74	0.00	45.48
HQ05	60.47	1.68	2.19	1.42	0.44	0.00	31.36	2.45	0.00	16.04
HQ05	74.75	1.14	1.03	1.01	0.49	0.00	20.83	0.00	0.00	18.69
HQ05	67.21	2.18	2.10	1.52	0.77	0.00	23.00	1.48	0.00	10.11
HQ06	73.38	5.87	1.84	4.21	0.90	0.00	5.90	7.91	0.00	9.97
HQ07	55.83	3.41	4.41	2.55	2.58	0.00	28.02	2.46	0.00	21.50
HQ08	63.66	2.68	2.60	1.93	1.04	0.00	27.35	0.00	0.00	24.01
HQ09	68.48	0.40	6.29	0.28	1.58	0.00	17.70	5.26	0.00	59.65
HQ10	78.20	0.51	5.78	0.00	1.76	0.00	11.99	0.81	0.00	17.05
HQ11	54.41	5.58	4.68	2.57	1.71	0.00	28.01	1.76	0.00	16.37
HQ12	48.29	1.90	1.77	1.18	0.92	0.00	39.34	6.60	0.00	7.19
HQ13	74.41	5.03	0.89	5.25	0.98	0.00	11.22	1.82	0.00	8.47
HQ13	72.79	5.59	0.80	3.80	0.27	0.00	16.74	0.00	0.00	9.79
HQ14	73.44	1.40	0.83	1.05	0.00	0.00	21.96	0.00	0.00	6.60
HQ14	65.18	2.02	1.00	1.50	0.00	0.00	27.73	0.00	0.00	8.50
HQ15	74.09	2.72	5.93	1.56	1.90	0.00	12.10	1.07	0.00	21.15
HQ16	30.41	1.32	0.84	0.51	0.23	0.00	65.54	0.00	0.00	27.01
HQ17	53.37	0.71	2.97	0.40	0.88	0.00	41.01	0.00	0.00	26.25
HQ18	59.62	0.66	4.20	0.43	1.19	0.00	33.90	0.00	0.00	35.57
HQ19	38.11	1.56	1.37	1.09	0.54	0.00	56.68	0.00	0.00	35.11
HQ20	69.62	0.93	3.21	0.55	1.14	0.00	24.55	0.00	0.00	16.16
HQ21	84.55	1.05	0.61	0.65	0.00	0.00	12.03	0.00	0.00	10.60
HQ22	52.88	1.82	1.07	1.49	0.46	0.00	42.28	0.00	0.00	14.94
HQ23	55.67	3.27	1.72	4.05	1.06	0.00	31.71	2.52	0.00	28.91
HQ24	62.24	1.38	3.54	0.86	1.03	0.00	29.12	1.21	0.00	29.97
HQ25	58.53	2.42	1.45	1.73	0.48	0.00	34.06	0.00	0.00	16.97
HQ26	52.13	3.91	1.46	2.89	0.67	0.00	35.71	2.27	0.00	29.79
HQ27	82.75	0.19	4.04	0.15	0.81	0.00	11.11	0.70	0.00	38.83
HQ28	81.44	0.21	5.20	0.09	1.32	0.00	11.15	0.58	0.00	40.64
HQ29	29.13	1.87	0.43	1.33	0.00	0.00	67.25	0.00	0.00	22.05
HQ30	60.77	2.11	1.62	1.36	0.43	0.00	30.86	2.02	0.00	19.00
HQ31	58.34	0.82	5.44	0.00	2.37	0.00	30.79	2.24	0.00	28.07
HQ32	77.20	0.74	6.73	0.41	2.45	0.00	11.30	1.17	0.00	20.62
HQ33	89.04	0.23	4.00	0.13	0.73	0.00	5.30	0.39	0.00	62.36

Sample No.	CH_4	C_2H_2	C_2H_4	C_3H_6	C_3H_8	iC_4H_{10}	$1C_4H_8$	nC_4H_{10} $t2C_4H_8$	$c2C_4H_8$	Total Area
HQ34	79.47	0.59	4.77	0.37	1.45	0.00	13.14	0.00	0.00	24.46
HQ35	73.39	1.84	5.93	1.04	2.40	0.00	14.13	1.27	0.00	20.40
HQ36	57.16	1.39	4.28	0.00	1.56	0.00	33.25	1.21	0.00	17.06
HQ37	59.62	0.91	2.69	0.47	1.01	0.00	34.29	0.00	0.00	21.67
HQ38	66.80	1.11	2.28	0.60	0.67	0.00	27.79	0.00	0.00	11.28
HQ39	70.87	0.82	5.25	0.00	1.45	0.00	18.63	2.17	0.00	20.01
HQ40	59.00	0.63	3.42	0.59	1.37	0.00	31.94	2.21	0.00	46.31
HQ41	73.81	0.97	2.42	0.45	1.05	0.00	20.02	0.00	0.00	13.00
HQ42	80.79	0.44	3.65	0.24	0.87	0.00	13.42	0.00	0.00	25.93
BC01	68.79	5.55	1.01	2.89	0.00	0.00	20.52	0.00	0.00	11.83
BC02	71.43	4.95	0.81	2.92	0.46	0.00	16.98	1.52	0.00	15.20
BC03	69.79	2.36	0.76	1.80	0.58	0.00	24.71	0.00	0.00	13.98
BC04	71.18	1.27	2.07	0.00	0.53	0.00	24.95	0.00	0.00	17.18
BC05	57.66	1.53	0.79	0.78	0.37	0.00	38.86	0.00	0.00	18.78
BC06	47.29	4.64	0.53	1.70	0.00	0.00	44.89	0.00	0.00	22.60
BC07	83.85	4.26	1.28	3.06	0.00	0.00	3.21	1.97	0.00	4.73
BC08	50.15	5.17	0.00	2.63	0.47	0.00	38.57	1.98	0.00	23.38
BC09	61.43	1.88	0.74	0.68	0.00	0.00	33.95	0.00	0.00	16.47
BC10	56.69	2.11	1.52	0.68	0.00	0.00	37.35	0.00	0.00	15.31
BC11	69.73	3.11	2.08	0.00	0.78	0.00	24.29	0.00	0.00	16.54
BC11	69.21	2.14	1.46	1.11	0.94	0.00	24.33	0.00	0.00	18.03
BC12	67.81	2.58	1.57	1.39	0.82	0.00	24.42	0.00	0.00	14.13
BC13	54.98	2.17	0.69	1.14	0.65	0.00	39.44	0.00	0.00	23.48
BC14	68.62	2.17	3.39	1.09	2.07	0.00	21.39	1.26	0.00	11.46
BC15	71.92	1.12	12.75	0.47	5.63	0.00	6.30	1.81	0.00	56.56
BC16	74.4i	1.43	4.42	0.75	1.20	0.00	15.02	1.91	0.00	19.78

Sample No.	CH_4	C_2H_2	C_2H_4	C_3H_6	C_3H_8	iC_4H_{10}	$1C_4H_8$	nC_4H_{10} $t2C_4H_8$	$c2C_4H_8$	Total Area.
WQ01	66.15	1.18	6.42	0.57	2.44	0.00	20.65	1.89	0.00	21.80
WQ01	68.28	1.06	6.58	0.53	2.34	0.00	18.88	1.72	0.00	22.69
WQ02	41.21	5.62	0.00	10.99	0.00	0.00	42.18	0.00	0.00	17.26
WQ03	62.43	1.28	0.00	1.08	0.53	0.00	34.68	0.00	0.00	22.56
WQ03	60.22	2.00	1.33	0.94	0.47	0.00	35.09	0.00	0.00	19.03
WQ04	44.77	4.42	0.56	2.95	0.25	0.00	46.19	0.00	0.00	28.47
WQ05	38.74	4.83	0.42	3.35	0.26	0.00	52.40	0.00	0.00	30.37
WQ06	62.10	1.22	4.69	0.67	1.48	0.00	28.47	1.38	0.00	34.74
WQ07	50.00	4.12	0.86	2.49	0.57	0.00	41.96	0.00	0.00	33.94
WQ08	57.83	1.28	5.41	0.64	1.84	0.00	30.70	1.78	0.00	38.45
WQ09	40.26	2.30	1.97	0.24	0.47	0.00	54.77	0.00	0.00	20.00
WQ10	52.64	5.04	4.18	3.17	1.96	0.00	30.32	1.82	0.00	21.01
WQ11	80.36	0.50	0.26	0.19	0.00	0.00	18.70	0.00	0.00	27.07
WQ12	74.99	1.00	0.35	1.95	1.59	0.00	20.13	0.00	0.00	15.76
WQ13	68.04	1.86	3.63	1.04	1.47	0.00	23.37	0.00	0.00	20.32
WQ13	57.83	3.44	4.68	1.62	1.99	0.00	27.32	1.54	0.00	17.60
WQ14	80.77	1.05	1.03	0.56	0.49	0.00	16.10	0.00	0.00	11.62
WQ15	80.91	0.70	2.19	0.21	0.33	0.00	15.66	0.00	0.00	11.11
WQ16	46.09	0.89	0.96	0.62	0.24	0.00	51.20	0.00	0.00	31.46
WQ17	44.50	1.40	0.34	0.67	0.00	0.00	52.41	0.00	0.00	24.76
WQ18	60 85	1.53	1.06	0.64	0.00	0.00	35.93	0.00	0.00	14.92
WQ19	38.93	1.13	0.96	0.74	0.57	0.00	57.67	0.00	0.00	24.01
WQ20	58.93	0.85	1.33	0.39	0.21	0.00	37.60	0.00	0.00	26.72
WQ21	39.96	1.74	1.04	1.19	0.35	0.00	54.85	0.00	0.00	24.60
WQ22	55.45	3.27	0.72	2.04	0.00	0.00	38.52	0.00	0.00	30.40
WQ23	56.36	1.76	0.90	1.31	0.00	0.00	38.90	0.00	0.00	25.58
WQ24	69.47	1.15	3.65	0.67	1.31	0.00	22.96	0.79	0.00	31.08
WQ25	85.56	0.27	4.91	0.00	2.04	0.00	5.18	0.89	1.15	29.09
WQ25	88.43	0.00	5.14	0.00	2.24	0.00	2.99	0.87	0.00	32.29
WQ26	26.38	4.85	0.49	4.11	0.43	0.00	62.77	0.00	0.00	33.84
WQ27	59.31	7.38	4.90	4.72	2.34	0.00	20.03	1.32	0.00	14.33
WQ28	87.88	2.46	0.17	2.08	0.00	0.00	7.41	0.00	0.00	17.56
WQ29	35.70	3.98	0.46	2.35	0.28	0.00	54.54	1.78	0.00	25.86
WQ30	53.47	16.59	12.94	9.69	4.18	0.00	2.54	1.71	0.00	28.27
WQ31	81.77	0.72	1.98	0.34	0.42	0.00	13.84	0.00	0.00	15.34
WQ32	78.09	0.63	0.80	0.00	0.00	0.00	20.48	0.00	0.00	14.52
WQ33	60.55	1.42	0.51	0.47	0.00	0.00	35.81	0.00	0.00	15.27

Sample No.	CH_4	C_2H_2	C_2H_4	C_3H_6	C_3H_8	iC_4H_{10}	$1C_4H_8$	nC_4H_{10} $t2C_4H_8$	$c2C_4H_8$	Total Area.
WQ34	61.82	1.30	0.46	0.98	0.42	0.00	35.02	0.00	0.00	25.40
WQ35	68.09	1.31	1.23	1.46	0.77	0.00	26.06	0.00	0.00	18.30
WQ36	31.08	2.16	0.56	1.74	0.30	0.00	64.16	0.00	0.00	38.82
WQ37	67.19	2.48	5.78	3.45	5.26	0.00	15.04	0.80	0.00	19.32
WQ38	57.22	4.99	0.68	3.60	0.55	0.00	32.96	0.00	0.00	13.25
WQ39	71.64	0.73	1.04	0.00	0.00	0.00	25.55	0.00	0.00	17.66
WQ40	61.91	2.71	0.95	1.86	0.52	0.00	32.05	0.00	0.00	17.85
WQ41	63.56	1.78	7.43	1.16	3.05	0.00	21.22	1.22	0.00	26.64
WQ42	72.36	0.44	12.92	0.36	5.91	1.45	4.74	1.72	0.00	117.38
WQ43	64.39	5.17	9.48	4.70	5.15	2.19	5.91	2.39	0.00	26.41
WQ44	54.35	5.07	1.01	3.37	0.00	0.00	34.41	0.00	0.00	11.27
WQ45	67.21	0.71	10.93	0.42	5.58	0.00	13.25	1.90	0.00	59.80
WQ46	70.26	0.63	13.52	0.43	7.27	2.08	3.33	2.50	0.00	96.19
WQ47	33.42	29.24	4.07	23.79	3.12	0.00	3.83	2.54	0.00	14.28
WQ48	71.75	1.37	10.57	1.89	4.59	0.00	8.10	1.73	0.00	44.60
WQ48	70.26	1.21	10.98	1.06	4.73	0.00	9.59	1.87	0.00	42.90
WQ49	82.79	0.00	4.06	0.00	0.86	0.00	12.06	0.24	0.00	28.52
WQ50	32.22	8.23	1.04	7.80	0.00	15.82	34.21	0.00	0.00	24.05
WQ51	25.25	6.91	1.14	8.81	0.95	0.00	56.95	0.00	0.00	48.98
WQ52	49.90	2.47	2.29	1.82	0.97	0.00	42.56	0.00	0.00	23.88
WQ53	34.48	3.64	1.40	2.55	0.52	0.00	57.41	0.00	0.00	27.29
WQ54	48.87	4.76	1.98	2.34	0.67	10.24	30.24	0.00	0.00	20.70
WQ55	57.19	7.24	2.55	5.21	0.54	0.00	25.45	0.00	0.00	8.91
WQ56	81.19	0.15	10.90	0.15	4.50	1.82	0.00	1.30	0.00	826.00
WQ56	80.74	0.18	10.93	0.19	4.64	1.76	0.00	1.50	0.00	793.70

Sample No.	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_{10}	$1C_4H_8$	nC_4H_{10} $t2C_4H_8$	$c2C_4H_8$	Total Area.
AB01	82.98	10.07	0.91	5.64	0.00	0.00	0.00	0.40	0.00	10.90
AB02	92.81	2.23	0.89	3.76	0.00	0.00	0.31	0.00	0.00	14.86
AB04	95.68	1.84	0.68	1.73	0.00	0.00	0.08	0.00	0.00	27.49
AB05	95.04	1.73	0.57	2.00	0.00	0.00	0.51	0.14	0.00	23.35
AB06	93.38	1.31	0.00	1.92	0.00	0.00	3.39	0.00	0.00	13.82
AB07	92.24	1.94	0.00	2.71	0.00	0.00	3.11	0.00	0.00	9.59
AB22	56.86	8.65	5.56	9.84	0.00	0.00	16.43	2.67	0.00	13.33
AB23	84.57	4.28	0.87	6.79	0.00	0.00	2.45	1.04	0.00	6.21
AB26	60.69	12.51	6.72	13.56	0.00	0.00	4.79	1.74	0.00	8.78
AB27	59.17	9.75	5.40	15.53	0.00	0.00	6.93	3.21	0.00	10.67
AB28	90.47	6.31	1.25	1.55	0.00	0.43	0.00	0.00	0.00	10.63
AB29	81.61	5.73	1.24	6.78	0.00	0.00	3.49	0.39	0.00	8.01
AB30	73.94	10.57	2.11	10.34	0.00	0.00	2.34	0.70	0.00	6.69
AB31	86.81	4.42	0.87	5.48	0.00	0.00	1.57	0.84	0.00	8.36
AB32	37.49	25.86	3.62	30.58	0.00	0.00	1.01	1.45	0.00	17.26
AB33	55.41	21.46	1.13	20.61	0.00	0.00	0.00	1.39	0.00	6.81
AB34	69.18	15.61	1.63	11.28	0.00	1.75	0.00	0.55	0.00	11.49
AB35	56.69	15.54	2.06	22.11	0.00	1.83	0.00	1.78	0.00	11.41
AB36	70.30	14.29	0.00	13.53	0.00	0.00	0.89	0.99	0.00	5.34
AB37	67.17	20.28	2.46	7.45	1.40	0.00	0.00	1.24	0.00	5.18
AB39	60.41	21.17	1.47	14.67	0.00	1.15	0.00	1.15	0.00	12.07
AB39	53.46	21.06	2.09	20.74	0.00	0.69	0.00	1.95	0.00	11.83
AB40	89.29	3.68	0.82	5.23	0.00	0.00	0.95	0.00	0.00	8.21
AB41	69.69	15.98	2.21	10.65	0.00	0.65	0.00	0.83	0.00	13.53
AB44	73.96	10.16	2.06	9.50	0.00	0.00	3.39	0.86	0.00	9.52
AB44	65.21	12.30	2.42	12.50	0.00	4.98	0.00	1.51	0.00	10.83
AB45	76.61	10.58	1.85	9.10	0.00	1.25	0.00	0.62	0.00	8.61
AB50	42.94	17.53	10.65	15.88	0.00	0.00	8.82	4.17	0.00	13.56
AB53	62.10	11.76	5.88	17.17	0.00	0.00	1.09	2.00	0.00	10.19
AB55	74.88	11.67	4.22	8.59	0.00	0.00	0.00	0.64	0.00	9.88
AB57	77.76	8.13	3.61	8.77	0.00	0.00	1.13	0.62	0.00	7.39
AB58	39.45	35.55	2.96	20.89	0.00	0.45	0.00	0.70	0.00	12.11
AB59	51.88	30.48	3.20	12.67	0.00	0.85	0.00	0.93	0.00	12.90
AB60	67.20	11.40	3.04	12.37	0.00	0.00	3.62	2.36	0.00	8.55
AB61	80.00	9.39	0.86	7.95	0.00	1.23	0.00	0.57	0.00	8.59
AB62	55.56	22.14	1.47	19.39	0.00	0.00	0.00	1.46	0.00	7.32

Sample No.	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_{10}	lC_4H_8	nC_4H_{10} $t2C_4H_8$	$c2C_4H_8$	Total Area.
AB63	38.68	26.15	1.93	28.50	0.00	0.00	1.86	2.90	0.00	17.34
AB64	88.40	7.84	1.60	2.16	0.00	0.00	0.00	0.00	0.00	10.65
AB66	53.33	22.00	2.01	17.08	0.00	0.00	2.47	3.11	0.00	10.90
AB67	62.85	13.32	1.39	16.69	0.00	0.00	1.95	3.80	0.00	9.86
AB68	81.49	7.30	2.07	8.51	0.00	0.00	0.63	0.00	0.00	8.93
AB71	83.90	6.19	3.84	4.80	0.00	0.00	1.26	0.00	0.00	9.98
AB73	50.34	19.71	3.42	23.21	0.00	0.00	0.78	2.54	0.00	9.75
AB75	83.65	4.11	1.00	5.68	0.00	0.00	1.04	0.70	0.00	13.98
AB77	55.29	8.75	2.25	10.43	0.00	0.00	20.58	2.70	0.00	12.42
AB84	72.54	17.11	0.98	8.91	0.00	0.26	0.22	0.00	0.00	10.74
AB86	75.52	19.85	1.91	2.41	0.00	0.00	0.21	0.10	0.00	11.43
AB89	47.90	24.51	2.10	22.24	0.00	0.00	0.40	2.86	0.00	11.86
AB93	66.69	8.36	2.35	10.22	0.00	0.00	10.85	1.53	0.00	13.75
AB95	85.17	4.02	0.87	8.19	0.00	1.13	0.00	0.63	0.00	6.56
AB97	62.49	4.68	0.93	4.90	0.00	0.00	27.01	0.00	0.00	7.89

APPENDIX D

INDUCTION COUPLED PLASMA ANALYTICAL RESULTS

APPENDIX D

INDUCTION COUPLED PLASMA ANALYTICAL RESULTS

Water sample identities, and run time to removal of each water sample.

Sample no.	Run time
Run 1	start
1a	+1 week
1b	+2 weeks
1c	+3 weeks
Run 2	start
2a	+4 weeks
Run 3	start
3.1a	+2 weeks
3.1b	+3 weeks
3.1c	+4 weeks
3.1d	+5 weeks
3.1e	+7 weeks
3.1f	+8 weeks
3.1g	+9 weeks
3.1h	+10 weeks
3.2a	+2 weeks
3.2b	+3 weeks
3.2c	+4 weeks
3.2d	+5 weeks
3.2e	+7 weeks
3.2f	+8 weeks
3.2g	+9 weeks
3.2h	+10 weeks

Sample no.	Run time
Run 3 contd.	start
3.3a	+2 weeks
3.3b	+3 weeks
3.3c	+4 weeks
3.3d	+5 weeks
3.3e	+7 weeks
3.3f	+8 weeks
3.3g	+9 weeks
3.3h	+10 weeks
3.4a	+2 weeks
3.4b	+3 weeks
3.4c	+4 weeks
3.4d	+5 weeks
3.4e	+7 weeks
3.4f	+8 weeks
Run 4	start
4a	+1 week
4b	+2 weeks
4c	+3 weeks
4d	+4 weeks
4e	+4 weeks
4f	+5 weeks
4g	+5 weeks
4h	+7 weeks
4i	+8 weeks
4j	+9 weeks

Sample no.	Run time
Run 5	start
5a	+4 weeks
5b	+6 weeks
5c	+10 weeks
Run 6	start
6a	+1 week
6b	+2 weeks
6c	+3 weeks
6d	+4 weeks

Seawater Samples:

SWa

SWb

Sample No.	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba
1a	0.3	10179	386	2.9	0.0	356	804	56	0.2
1b	0.3	10306	388	2.2	0.0	382	919	65	0.2
1c	0.2	10011	363	3.3	0.0	241	1606	115	0.2
2a	0.2	10000	400	2.0	0.0	134	1740	146	0.5
3.1a	0.3	10000	400	2.0	0.0	750	610	29	0.1
3.1b	0.2	10000	380	2.0	0.0	960	520	21	0.1
3.1c	0.2	9500	360	2.0	0.0	810	540	27	0.1
3.1d	0.2	9400	360	2.0	0.0	370	730	55	0.2
3.1e	0.3	10000	380	2.0	0.0	181	1810	161	0.1
3.1f	0.2	6600	260	2.3	0.0	610	440	23	0.1
3.1g	0.2	7500	280	2.0	0.0	650	490	41	0.1
3.1h	0.2	6700	260	2.0	0.0	550	460	42	0.1
3.2a	0.3	10000	390	2.0	0.0	800	570	26	0.1
3.2b	0.2	10000	380	2.0	0.0	950	520	21	0.1
3.2c	0.2	9200	350	2.0	0.0	780	520	27	0.1
3.2d	0.2	9000	340	2.0	0.0	590	580	38	0.1
3.2e	0.3	9500	360	2.1	0.0	163	830	91	0.2
3.2f	0.2	8400	320	2.0	0.0	320	700	71	0.2
3.2g	0.1	6900	260	2.0	0.0	720	400	22	0.1
3.2h	0.2	6400	250	2.0	0.0	600	410	28	0.1
3.3a	0.3	10000	410	2.0	0.0	770	650	32	0.1
3.3b	0.2	9900	380	2.0	0.0	870	550	28	0.1
3.3c	0.2	9400	360	2.0	0.0	720	560	39	0.1
3.3d	0.2	9200	350	2.0	0.0	520	610	54	0.2
3.3e	0.3	9500	350	2.8	0.0	220	760	98	0.3
3.3f	0.2	8800	330	2.0	0.0	240	720	94	0.2
3.3g	0.2	7500	280	2.0	0.0	590	480	47	0.1
3.3h	0.1	6700	260	2.0	0.0	550	440	43	0.1

Sample No.	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba
3.4a	0.2	10000	400	2.0	0.0	710	700	36	0.1
3.4b	0.2	10000	390	2.0	0.0	700	700	41	0.1
3.4c	0.2	10000	380	2.0	0.0	610	700	49	0.1
3.4d	0.2	8600	330	2.0	0.0	580	620	45	0.1
3.4e	0.2	8500	320	2.0	0.0	280	810	93	0.2
3.4f	0.1	8900	380	2.0	0.0	83	310	26	0.1
4a	0.4	10000	450	2.0	0.0	550	360	30	0.1
4b	0.4	10000	450	2.0	0.0	270	730	93	0.3
4c	0.4	10000	440	2.0	0.0	160	880	125	0.3
4d	0.4	10000	510	2.0	0.0	290	980	153	0.4
4e	0.3	10000	410	2.0	0.0	310	690	111	0.3
4f	0.3	10000	380	2.0	0.0	270	670	103	0.1
4g	0.4	10000	430	2.0	0.0	107	870	156	0.3
4h	0.2	9900	370	2.4	0.0	320	1300	230	0.4
4i	0.3	10000	380	2.0	0.0	146	1540	310	0.3
4j	0.3	10000	380	2.0	0.0	139	1510	300	0.1
5a	0.4	10000	450	2.0	0.0	136	1610	200	0.1
5b	0.3	10000	390	2.0	0.0	270	2700	330	0.1
5c	0.2	9600	350	2.0	0.0	240	2500	230	0.1
6a	0.3	10000	450	2.0	0.0	1070	560	26	0.1
6b	0.2	9600	370	2.0	0.0	1030	450	15	0.1
6c	0.2	8200	320	2.0	0.0	610	570	38	0.1
6d	0.4	10000	490	2.0	0.0	370	1020	87	0.2
SWa	0.2	10179	391	2.6	0.0	1282	432	11	0.1
SWb	0.2	10000	380	2.0	0.0	1250	420	8	0.1

Sample No.	Al	La	Ti	V	Cr	Mo	Mn	Fe	Co	Ni
1a	0.5	0.2	2.1	0.1	0.2	0.5	0.2	0.4	0.1	0.4
1b	0.5	0.2	1.6	0.1	0.6	0.3	0.2	5.1	0.1	1.8
1c	0.5	0.2	0.6	0.1	0.1	0.5	0.2	0.4	0.1	0.3
2a	0.5	0.1	1.6	0.1	0.1	0.2	0.2	40	0.1	0.7
3.1a	0.8	0.1	1.$	0.1	0.6	0.3	0.2	19	0.1	2.8
3.1b	0.5	0.1	0.8	0.1	0.1	0.3	0.2	0.5	0.1	0.5
3.1c	0.5	0.1	1.1	0.1	0.1	0.2	0.2	0.4	0.1	0.4
3.1d	0.5	0.1	0.6	0.1	0.1	0.1	0.2	0.4	0.1	0.4
3.1e	0.5	0.1	0.6	0.1	0.1	0.2	0.2	0.4	0.1	3.6
3.1f	0.5	0.2	1.3	0.1	0.1	0.3	0.2	0.4	0.2	0.4
3.1g	0.5	0.1	0.6	0.1	0.1	0.3	0.2	0.4	0.1	2.5
3.1h	0.5	0.1	1.2	0.1	0.1	0.2	0.2	0.4	0.1	1.5
3.2a	0.5	0.1	0.6	0.1	0.9	0.3	0.2	15	0.1	1.7
3.2b	0.5	0.1	1.2	0.1	0.4	0.3	0.2	3.5	0.1	0.7
3.2c	0.5	0.1	0.6	0.1	0.3	0.2	0.2	6.2	0.1	1.3
3.2d	0.5	0.1	0.6	0.1	0.2	0.2	0.2	6.1	0.1	0.7
3.2e	0.5	0.2	0.8	0.1	0.1	0.2	0.2	0.4	0.1	0.7
3.2f	0.5	0.1	1.0	0.1	0.1	0.2	0.2	0.4	0.1	2.5
3.2g	0.5	0.1	1.0	0.1	0.1	0.3	0.2	0.4	0.1	2.0
3.2h	0.5	0.1	0.6	0.1	0.1	0.3	0.2	0.4	0.1	1.1
3.3a	0.5	0.1	1.5	0.1	0.2	0.2	0.2	12	0.1	1.7
3.3b	0.5	0.1	0.9	0.1	0.2	0.2	0.2	1.2	0.1	0.6
3.3c	0.5	0.1	0.6	0.1	0.1	0.2	0.2	1.9	0.1	0.9
3.3d	0.5	0.1	1.0	0.1	0.1	0.2	0.2	4.1	0.1	1.0
3.3e	0.5	0.2	0.6	0.1	0.1	0.3	0.2	0.4	0.1	1.1
3.3f	0.5	0.1	0.9	0.1	0.1	0.2	0.2	0.4	0.2	5.0
3.3g	0.5	0.2	1.4	0.1	0.1	0.3	0.5	0.4	0.2	5.0
3.3h	0.5	0.1	0.6	0.1	0.1	0.3	0.2	0.4	0.1	1.9

Sample No.	Al	La	Ti	V	Cr	Mo	Mn	Fe	Co	Ni
3.4a	0.5	0.1	1.1	0.1	0.2	0.2	0.2	6.2	0.1	1.1
3.4b	0.5	0.1	1.5	0.1	0.1	0.2	0.2	0.4	0.1	0.3
3.4c	0.5	0.1	0.6	0.1	0.1	0.2	0.2	0.4	0.1	0.1
3.4d	0.5	0.1	0.6	0.1	0.1	0.2	0.2	0.4	0.1	0.1
3.4e	0.5	0.1	1.3	0.1	0.1	0.2	0.2	0.4	0.2	0.1
3.4f	0.5	0.1	0.6	0.1	0.1	0.1	0.7	0.4	0.1	0.4
4a	0.5	0.1	0.6	0.1	0.1	0.2	0.2	11	0.1	1.8
4b	0.5	0.1	0.6	0.1	0.1	0.2	0.2	11	0.1	3.4
4c	0.5	0.1	0.6	0.1	0.1	0.2	0.2	9.5	0.2	3.8
4d	0.5	0.1	0.6	0.1	0.1	0.2	0.2	10	0.1	3.6
4e	0.5	0.1	0.6	0.1	0.3	0.2	0.2	0.4	0.1	0.6
4f	0.5	0.1	1.0	0.1	0.1	0.1	0.2	3.7	0.1	1.0
4g	0.5	0.1	0.6	0.1	0.2	0.1	0.2	3.1	0.1	0.4
4h	0.5	0.2	0.6	0.1	0.1	0.2	0.2	0.4	0.1	0.7
4i	0.5	0.2	0.6	0.1	0.1	0.2	0.2	0.4	0.1	0.5
4j	0.5	0.2	0.6	0.1	0.1	0.2	0.2	0.4	0.1	0.3
5a	0.5	0.1	0.6	0.1	0.2	0.1	0.2	45	0.1	0.7
5b	0.5	0.1	0.6	0.1	0.2	0.1	0.2	27	0.1	3.2
5c	0.5	0.1	0.6	0.1	0.1	0.3	0.2	41	0.1	1.9
6a	0.5	0.1	0.6	0.1	0.1	0.5	0.2	3.5	0.1	1.1
6b	0.5	0.1	1.0	0.1	0.1	0.4	0.2	0.4	0.2	0.2
6c	0.5	0.1	1.0	0.1	0.1	0.3	0.2	0.4	0.1	0.2
6d	0.5	0.1	0.6	0.1	0.1	0.5	0.2	0.5	0.1	0.2
SWa	0.5	0.2	1.5	0.1	0.1	0.7	0.2	0.4	0.1	0.1
SWb	0.5	0.1	0.6	0.1	0.1	0.5	0.2	0.5	0.2	0.2

Sample No.	Cu	Ag	Zn	Cd	Pb	P	S	B	As	Si
1a	0.3	0.1	0.5	0.2	0.5	3.1	91	7.4	0.5	40
1b	1.1	0.1	0.9	0.3	0.5	3.5	186	7.0	0.5	49
1c	0.5	0,1	0.1	0.1	0.5	2.8	524	7.0	0.5	73
2a	0.6	0.1	0.3	1.5	0.5	1.3	560	8.6	0.5	102
3.1a	0.2	0.1	2.2	6.2	0.5	1.0	520	11	0.5	20
3.1b	0.1	0.1	0.7	17	0.5	0.4	700	6.9	0.5	11
3.1c	0.1	0.1	0.9	19	0.5	0.5	590	7.3	0.5	13
3.1d	0.1	0.1	0.9	7.2	0.5	0.8	270	9.4	0.5	25
3.1e	0.1	0.1	0.1	0.1	0.5	0.9	850	9.7	0.5	14
3.1f	0.1	0.1	0.5	16	0.5	0.5	400	4.2	0.5	6
3.1g	0.1	0.1	1.2	14	0.5	0.5	460	4.3	0.5	11
3.1h	0.1	0.1	0.9	14	0.5	0.4	390	4.1	0.5	10
3.2a	0.1	0.1	0.3	1.2	0.5	0.6	580	8.8	0.5	17
3.2b	0.1	0.1	0.4	9.3	0.5	0.4	710	6.7	0.5	11
3.2c	0.1	0.1	0.9	13	0.5	0.5	580	7.0	0.5	13
3.2d	0.1	0.1	0.9	9.9	0.5	0.5	440	7.1	0.5	18
3.2e	0.1	0.1	0.8	0.1	0.5	0.7	112	9.4	0.5	28
3.2f	0.1	0.1	0.3	4.1	0.5	0.5	230	6.6	0.5	17
3.2g	0.1	0.1	0.4	11	0.5	0.4	510	3.5	0.5	5
3.2h	0.1	0.1	0.4	13	0.5	0.4	420	3.7	0.5	7
3.3a	0.1	0.1	0.6	5.4	0.5	0.9	560	8.5	0.5	18
3.3b	0,1	0.1	0.6	14	0.5	0.4	640	6.5	0.5	13
3.3c	0.1	0.1	0.8	15	0.5	0.7	520	6.6	0.5	14
3.3d	0.1	0.1	0.8	11	0.5	0.7	380	7.5	0.5	19
3.3e	0.1	0.1	0.5	3.7	0.6	1.1	156	8.4	0.5	25
3.3f	0.1	0.1	0.4	4.1	0.5	0.9	172	7.2	0.5	20
3.3g	0.1	0.1	0.4	11	0.5	0.4	420	4.7	0.5	8
3.3h	0.1	0.1	0.2	13	0.5	0.5	390	4.4	0.5	8

Sample No.	Cu	Ag	Zn	Cd	Pb	P	S	B	As	Si
3.4a	0.1	0.1	0.6	3.7	0.5	0.6	500	7.7	0.5	18
3.4b	0.1	0.1	0.2	5.8	0.5	0.4	520	7.1	0.5	21
3.4c	0.1	0.1	0.4	10	0.5	0.4	420	6.7	0.5	22
3.4d	0.1	0.1	0.3	12	0.5	0.4	410	5.5	0.5	20
3.4e	0.1	0.1	0.1	5.0	0.5	0.4	176	5.9	0.5	31
3.4f	0.1	0.1	0.2	0.6	0.5	0.5	155	2.7	0.5	2
4a	0.1	0.1	0.4	0.2	0.5	0.6	110	12	0.5	9
4b	0.1	0.1	0.7	0.3	0.5	0.6	62	12	0.5	14
4c	0.1	0.1	0.6	0.2	0.5	0.8	51	12	0.5	15
4d	0.1	0.1	0.8	4.4	0.5	0.8	169	13	0.5	19
4e	0.1	0.1	1.0	4.9	0.5	0.5	103	9.4	0.7	7
4f	0.1	0.1	0.4	3.8	0.5	0.4	135	9.2	0.5	10
4g	0.1	0.1	0.8	0.5	0.5	0.8	55	11	0.5	13
4h	0.1	0.1	1.7	0.1	50	1.0	450	10	0.5	11
4i	0.1	0.1	0.3	0.6	0.8	0.4	53	5.8	0.5	4
4j	0.1	0.1	0.2	0.5	0.6	0.4	36	6.1	0.5	5
5a	0.1	0.1	0.1	0.3	0.5	1.0	450	10	0.5	11
5b	0.1	0.1	240	4.0	0.5	0.5	410	5.4	0.5	2
5c	0.1	0.1	1.1	0.9	0.5	0.4	950	4.5	0.5	5
6a	0.1	0.1	4.1	9.9	0.5	4.8	570	15	0.5	9
6b	0.1	0.1	0.1	0.3	0.5	0.7	680	5.3	0.5	3
6c	0.1	0.1	0.6	9.2	0.5	1.0	400	5.9	0.5	9
6d	0.1	0.1	1.1	8.3	0.5	4.8	240	16	0.5	27
SWa	0.1	0.1	0.1	0.1	0.5	0.4	927	4.4	0.5	0.5
SWb	0.1	0.1	0.1	0.1	0.5	0.4	900	4.3	0.5	0.5