

A possible role for light hydrocarbons in Pb/Zn mineral exploration

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Abstract

A method of base metal exploration in sedimentary rocks which depends on detecting anomalous amounts of the light hydrocarbon gas methane in the host rocks has been applied in a number of orientation surveys in the British Isles and in Europe. The results of these studies are described, and the limitations of the method discussed. It is suggested that the principal difficulty lies in the extraction technique which is based on heating, and alternative methods are proposed. The preliminary results from these new methods are discussed and compared with those from the original study. A number of the samples analysed by the new methods are calcites of differing diagenetic origins. It is postulated that the differences in methane found in these samples may give a clue to the organic geochemistry of the rocks at the time when the calcites were deposited.

KEYWORDS: hydrocarbons, lead-zinc mineralization, base metal exploration, calcite.

Introduction

THE use of hydrocarbon gas geochemistry as a mineral exploration technique has developed from the idea of a strong genetic link between hydrocarbons and base metal deposits (Beales *et al.*, 1970; Hitchon, 1977) and the almost fortuitous results of work carried out by a team from the British Gas Corporation in the early 1970s (Ferguson, 1984, p. 67). The ideas and technique were developed further during research undertaken by Carter (1981) and subsequently tested in a commercial venture by Mercury Hydrocarbons Ltd, when some Irish lead/zinc deposits were examined. As a result of this funding was awarded by the C.E.C. (R & D subprogram on metals, Contract MSM-106-UK(N), which allowed further investigation in a joint project under the direction of the author, involving both staff of the Geology Department at Imperial College and Mercury Hydrocarbons Ltd. This phase of work was completed in 1984 and two reports compiled by Carter and Cazalet (1985) and Ferguson (1985), copies of which are available for reference from either the authors or direct from Brussels. The first part of the present paper gives a brief resumé of the work to the end of the contract, while the remainder is concerned with the early results of a further project being undertaken

at Imperial College with financial support from Cominco (Europe) Ltd. This latter work is an attempt to consider more objectively problems which arose in the earlier studies.

Until recently the approach to both field and laboratory sides of the study has largely been governed by the desire to develop a robust and relatively inexpensive primary mineral exploration technique which, as well as being reliable, can be performed quickly by well trained but not necessarily highly qualified staff. Although this approach sacrifices scientific accuracy for expediency, efforts have been made to minimize the adverse effects.

The technique is based on data obtained from the analysis of suites of rock samples, most of which have been restricted to limestones of various types collected from areas of expected or known mineralization and, as far as possible, the surrounding non-mineralized rocks of similar age and lithology. Samples used in the study have been taken either from surface outcrops or from cores obtained from shallow bore holes, and have been collected so as to minimize contamination from either vegetation or oily drilling fluids.

Prior to analysis, each sample is inspected for possible contamination not spotted in the field and where practical this is removed by trimming. Samples considered to be too badly contaminated are rejected. A small representative piece is put

to one side, to be used for petrological examination if required. The remainder is prepared by coarse crushing and sieving, collecting material between 4 and 1 mm for analysis (Carter and Cazalet, 1985, p. 5). The light hydrocarbon gases are released from the rock by heating. For this a known amount (usually 5 g) of the prepared sample is sealed in a 50 ml vaccine bottle. These are then heated in batches, in a forced convection oven at 200 °C for 2 hours. After cooling, a sample of the head space gas from each bottle is analysed by gas chromatography. The gases which are of special interest are the alkanes and alkenes in the range C1–C4. During the period of research several different instruments have been employed; at present a Perkin Elmer 8310 model gas chromatograph with a 2 m Poropack Q column (80–100 mesh) and flame ionization detector is being used.

The simplest method of interpreting the results of these gas analyses is by calculating the relative percentage of methane to the other hydrocarbons detected, plotting the values onto a base map and contouring. It has been found that mineralized areas are characterized by methane percentages greater than 60, although occasionally lower values are recorded. The results for the northern Pennine orefield and adjacent areas are summarized in the form of histograms, and illustrated in Fig. 1, which is based on Carter (1981, Figs. 3.8 and 3.10), updated by the addition of more recently obtained data.

In the work to date, where gas extraction is achieved by heating, contamination not detected at the sample preparation stage is frequently indicated by the occurrence of an unidentified component which we have designated '170'. Samples with greater than 100 ppb of this gas are rejected on the grounds of excessive contamination (Carter and Cazalet, 1985, Appendix p. A4). This is based on experimental evidence which suggests that this is the principal gas generated by the breakdown of vegetation such as grass or lichen by heating in a closed container.

Summary of the results of the early studies

If we adopt strict scientific criteria to the interpretation of the results, then the proposed method is unacceptable for many reasons. However its use as a primary mineral exploration technique does seem to have some merit. From our results, sampling on a 1/2 or 1 km grid, the method is capable of detecting target areas suitable for further detailed exploration. Although a broad

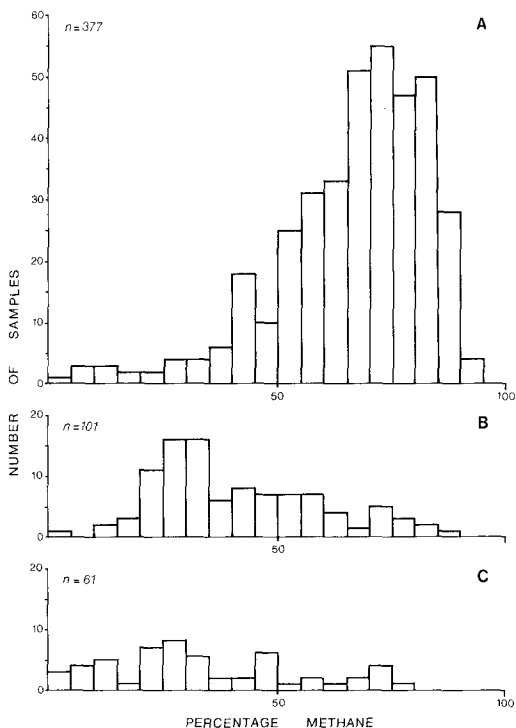


FIG. 1. Histograms showing the percentage methane, relative to the other light hydrocarbon gases, released from samples of limestone from the northern Pennines and adjacent areas, using the heating method of gas extraction. Numbers indicate sample size. A. Northern Pennine orefield. B. Northumberland. C. Ingleton, N. Yorkshire, area.

spectrum of light hydrocarbon gases are quantified during a survey, the relative amount of methane detected is probably the most easily interpreted feature of the data.

In our work we have concentrated on the analysis of carbonate rocks, although we have been able to show that other sedimentary rocks give comparable results (Carter and Cazalet, 1985, p. 48). Also, in a small number of limited studies, igneous and metamorphic rocks associated with mineralization have been found to give similar patterns, as for example at Aberfeldy (Goodman, 1986, p. 114). The choice of carbonate rocks as the principal material for analysis is based on the results of an earlier study in which it was demonstrated that rocks which contained even relatively small amounts of carbonate retained their hydrocarbons for long periods after sampling, whereas rocks which did not lost their gases within one or two days.

The heating method of gas extraction outlined is simple and inexpensive but is subject to a number of problems other than contamination. Two are important; these are reproducibility and the amount of unsaturated gases detected. The problem of reproducibility can be minimized by analysing the samples from a particular area of interest as one batch. This approach produces results which are internally consistent, but it can mean that detailed comparisons between areas may be problematic. However, since the differences in the methane ratio between mineralized and non-mineralized areas are relatively large as in the case of the Northern Pennine orefield (see Fig. 1), reproducibility has presented problems only in a limited number of cases.

The detection of unsaturated hydrocarbons is a more intractable problem. Considering their generally greater reactivity, it seems unlikely that they should occur naturally in the quantities found. It must therefore be concluded that they are generated as a consequence of the heating process, being the result of the breakdown of either higher hydrocarbons or kerogens, which are present in the rock and which may not be related to the mineralization process.

The original orientation surveys were centred on the northern Pennine orefield and adjacent areas (Carter, 1981; Carter and Cazalet, 1984; and Ferguson, 1984). Subsequently these findings have been confirmed and progress made in the study of other lead/zinc-producing areas. Carter and Cazalet have concentrated on a study of rocks associated with the Irish base metal deposits and, in particular, those of the Silvermines and Mallow prospects, and of the Burren (Carter and Cazalet, 1984 and 1985). In Ireland, in contrast to the single methane high obtained for the Northern Pennine orefield, both Silvermines and Mallow show extensive haloes of gases, with methane being the outermost and the heavier gases dominant nearest the ore deposit itself (Ibid. 1985, p. 46). Also, borehole data from a number of Irish prospects have produced evidence which suggests the existence of narrow pathways along which gases migrated (Ibid. 1985, p. 63). On a larger scale there is a major regional trend of the heavier saturated hydrocarbons toward the east of Ireland (Ibid. 1985, p. 65ff).

In France a survey in the area of Figeac showed the possibility of the extension of mineralization to the south of the known occurrences. This particular survey, carried out on a 2 km grid, showed the disadvantage of working on this scale (Ferguson, 1985, p. 66), which is too coarse to be of real value. Elsewhere in Europe, surveys in northern Spain and Sardinia (Ibid. p. 34ff) have proved

difficult to interpret, largely due to the fact that it was not possible to establish the background concentration of gases for the areas. Also, a particular difficulty in Sardinia resulted from the effects of tectonism (Ibid. p. 37). However, in both areas, large numbers of samples with anomalous amounts of methane were detected in rocks which are known to be mineralized.

Using data from a number of sources, including a suite of samples from the Carboniferous Limestone of the Mendip Hills, Somerset, it has been concluded that there is no close relationship between the gases detected and lithology (Ibid. p. 50; Carter and Cazalet, 1985, p. 47). The data obtained from the Mendip suite of carbonates lead to the conclusion that there might be a relationship between the alkane/alkene ratio and lithology (Goodman, 1986, p. 95). This conclusion unfortunately, is not substantiated by data from any of the other areas examined (Ferguson, 1985, p. 58).

Preliminary results of latest phase of study

Following on from the work described above, it was resolved to attempt to solve some of the problems outlined. In particular, the use of different methods to release the hydrocarbons from the rock is an essential part of this new project. Also of importance is the investigation of the occurrence of light hydrocarbon gases in the minerals such as fluorite or baryte associated with base metal ores and, in particular, in calcites of various origins which are found both associated with mineralization as well as in areas where it is absent. It is thought that any light hydrocarbon gases found in minerals of the orebody itself would enable deductions to be made about the nature of the reactions occurring during mineralization, while those found in calcite on the other hand might provide a link between mineralized and non-mineralized areas. Furthermore as the analysis of calcite is unlikely to be plagued by some of the problems associated with rocks, its use may provide a satisfactory alternative for exploration purposes.

As an alternative to heat extraction, development has been started on a dry grinding method based on a modification of the Tima Mill (Ferguson, 1985, p. 70). A stainless steel grinding pot has been constructed such that it can be sealed and samples of gas obtained from the interior by means of a simple seal which can be pierced by a hypodermic needle. The equipment is illustrated in Fig. 2. The technique is simple; a weighed amount of material is placed in the pot, the lid is screwed into place and the material ground for

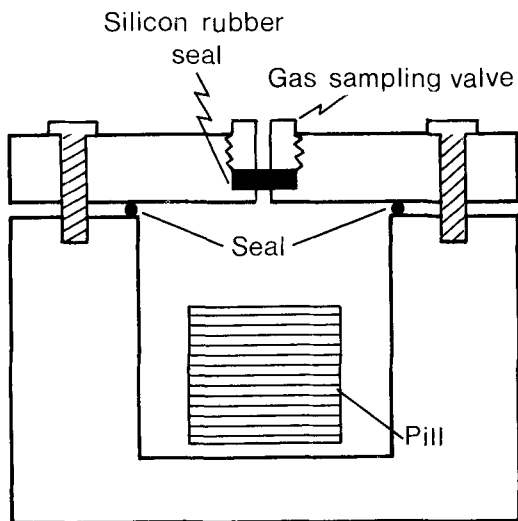


FIG. 2. Prototype of gas extraction equipment, based on the Tima Mill principle. The material used for construction is stainless steel.

approximately 30 minutes. The head space gas is then sampled and analysed in the normal way. Knowing the volume of the head space for the pot and the weight of rock crushed, the amount of gas released per gramme of rock can be calculated. The prototype will hold up to 30 g of rock. Experience suggests that for limestones and calcite a 15 g sample is adequate, although satisfactory results have been obtained from amounts as small as 0.5 g. It has been noted that grinding times of greater than 30 minutes produce a marked rise in temperature of the pot and its contents which, based on the evidence of the results from heat extraction, should be avoided.

Since most of our work has been concerned with carbonates, the possibility of using chemical extraction is also being investigated. The simple method of using dilute acid has one important drawback; unless elaborate precautions are taken to remove the carbon dioxide generated, the analytical system fails to detect any light hydrocarbon gases. More success has been obtained using the sodium salt of ethyl diamine tetra-acetic acid (E.D.T.A.). This method is extremely slow, but it can be speeded up by shaking. At present 2 g of crushed rock are used with 100 ml of 10% E.D.T.A. solution sealed in a 150 ml glass vaccine bottle and shaken for 18 hours or as long as required to dissolve the rock, after which the head space gas is sampled and analysed.

In order to be able to compare results with those obtained earlier, three methods of extraction are

being used with a freshly collected suite of samples from the Northern Pennines. Table 1 shows some early results which represent the analysis of a sample of experimentally-produced oolitic limestone. As can be seen there is reasonable agreement between duplicate sample runs for each of the two new methods, although there are differences between them. However there is a closer relationship between these two than with the results obtained by heating. This set of results shows relatively high amounts of unsaturated gases, which is to be expected given the nature of the material being analysed.

More recently, after some standardization of the methodology, we are getting more comparable and reproducible results using the new techniques. It does seem however that the inhomogeneity of the rocks is a major contributing factor to the differences observed between replicate samples. In an attempt to resolve this problem, further tests will be performed to assess the effect of crushing the rock to various size grades and using the new methods of gas extraction.

The problem of high alkane/alkene ratios and the effects of gases generated by the heating of the contaminating vegetation also seem to be resolved by the new techniques. Although high alkene ratios were to be expected in the sample of experimentally produced limestone (Table 1), it should be noted that even here the amounts of alkenes found by the heating method are somewhat reduced. A quick visual impression can be obtained by comparing the gas chromatograms obtained by using different extraction methods on the same sample. Fig. 3 shows two chromatograms, one obtained from heating and the other from grinding. The differences between the balance of alkanes and alkenes is very clear; attention is particularly drawn to the C₄ peaks where 1-butene dominates the chromatogram of the heated sample.

Another approach which allows an easy visualization of the differences is illustrated in Fig. 4, which shows a plot of ethane + n-butane against ethene + 1-butene for 10 samples where the gas was extracted by grinding and a similar number extracted by heating. There are clear differences between the two techniques, which are probably a direct result of heat extraction giving rise to high unsaturated gas ratios. The ten data points selected to represent the heating technique were taken at random from the total data set for the northern Pennines, after rejecting samples thought to be contaminated.

The analytical details for two samples of calcite which have been analysed by grinding and heating

Table 1. Comparison of results obtained by three methods of gas extraction.

| | Dry grinding | | EDTA | | Heat |
|-----------|--------------|-------|--------|--------|-------|
| | 1 | 2 | 1 | 2 | |
| Methane | 92.97 | 75.91 | 119.55 | 112.58 | 18.61 |
| Ethene | 6.50 | 4.92 | 0.00 | 0.00 | 11.59 |
| Ethane | 19.79 | 17.65 | 31.93 | 30.30 | 1.68 |
| Propylene | 4.21 | 3.16 | 0.00 | 0.00 | 10.76 |
| Propane | 9.74 | 8.32 | 14.54 | 11.35 | 10.00 |
| I-butane | 1.82 | 4.55 | 7.93 | 13.56 | 0.00 |
| N-butane | 5.06 | 4.87 | 6.65 | 9.23 | 13.68 |
| 1-butane | 5.85 | 5.73 | 0.00 | 0.00 | 57.30 |

Duplicate sample runs are reported for the new methods to give some idea of the reproducibility obtained. This sample is an experimentally-generated oolitic limestone (Sample Ref. Test XII). Values in ppbv/g sample.

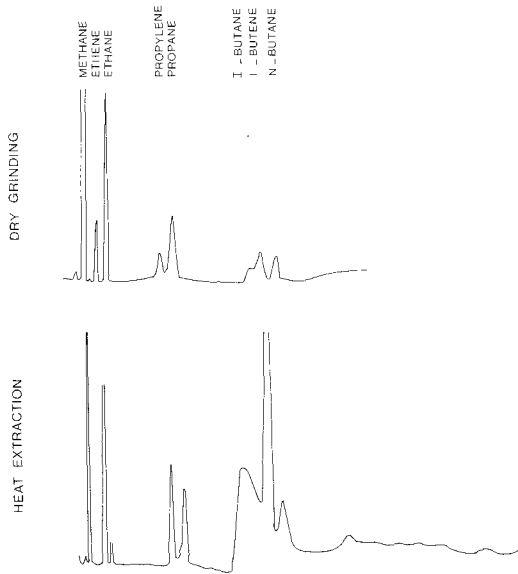


FIG. 3. Gas chromatograms obtained from a sample of artificially prepared oolitic limestone, extracted by two methods. Note the considerable differences in the balance of alkanes and alkenes. Vertical axis—retention time; horizontal axis—response. Equipment—Perkin Elmer 8310 G.C. with 2 m Poropak Q column (80–100 mesh) and F.I.D.

are given in Table 2. Again, it can be seen that there are differences in the balance of alkanes to alkenes and, more significantly, there are the differences in the total amount of gases released from the mineral. It is suggested on the basis of this and other data that the grinding method is probably more efficient in releasing gases from rock than heating. From the evidence of work

carried out using E.D.T.A. extraction, it seems likely that most of the gas is released by grinding.

Results obtained from the analysis of a number of samples of calcite, chosen to give a cross section of the data available, are presented in Table 3. In this data set are included results obtained from the analysis of calcite from two veins associated with mineralization in the Northern Pennine ore-field and one from a small vein carrying marcasite and calcite from Northumberland, as well as a small selection from other areas and possibly differing diagenetic origins. Two factors emerge from these data. Firstly, as expected, there are significantly larger amounts of methane in the calcites found in association with mineralization. Secondly, the samples from the non-mineralized areas show considerable differences when compared with each other. It is tentatively suggested that these differences may be highly significant and related to the mode and time of deposition of the calcite. For example the vug infill from Kirtlington, Oxfordshire, was probably deposited during the earliest stages of diagenesis of the host rock, whereas the drip stone from High Whittle, Northumberland, probably represents very late stage phenomena associated with the present day groundwater regime. It is likely that the remaining three calcites owe their origin to tectonic effects. If future work substantiates these findings it may be possible to use the analysis of light hydrocarbon gases in calcite to give some clue to the nature of the hydrocarbons circulating in the rocks at different times during their evolution.

Conclusions

Although the method of utilizing light hydrocarbon gas anomalies as a first-order mineral exploration technique has been shown to work

Table 2. Comparison of results obtained using the dry grinding and heating methods of gas extraction, for two calcite samples collected from different areas.

| | Calcite, N Craven Fault | | Calcite, Great Lst, Fourstones | |
|-----------|-------------------------|-------|--------------------------------|------|
| | Dry grind | Heat | Dry grind | Heat |
| Methane | 515.7 | 196.8 | 2850.8 | 45.2 |
| Ethene | 4.0 | 5.0 | 0.6 | 7.4 |
| Ethane | 8.8 | 0.9 | 153.2 | 2.5 |
| Propylene | 3.0 | 4.4 | 0.4 | 7.3 |
| Propane | 2.0 | | 71.6 | |
| I-butane | 1.1 | 0.0 | 12.0 | 0.0 |
| N-butane | 0.6 | 0.0 | 20.6 | 0.0 |
| l-butane | 0.0 | 3.8 | 0.0 | 35.9 |

Note that for the heating method propylene and propane are not separated and are recorded as a single value. Values in ppbv/g sample.

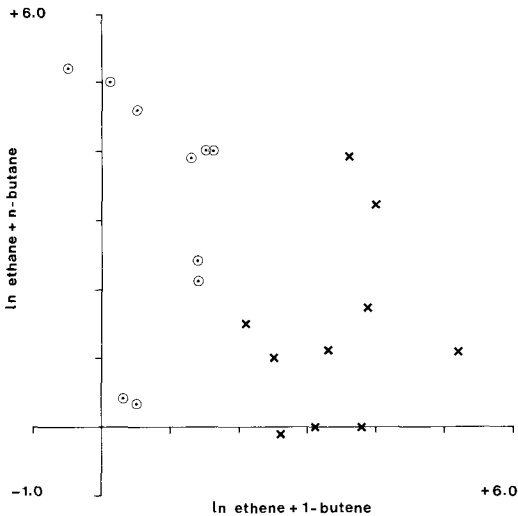


FIG. 4. Plot of ethane + n-butane against ethene + 1-butene for ten samples extracted using the heating method (crosses) and ten samples extracted using grinding (circles with dots). All samples from northern England. The use of the logarithmic scale is for clarity of presentation.

over a number of known mineral deposits in the British Isles and Europe, it does have a number of drawbacks and limitations. These are probably related to the heating technique used to extract the gases from the rock and are:

(1) Contamination: Minute quantities of vegetation adhering to samples can give rise to spurious results.

(2) Anomalous gases: Many samples show unexpectedly large amounts of unsaturated gases thought to be generated by heating, which causes the breakdown of higher hydrocarbons held in the rock.

(3) Reproducibility: This is poor and can be in part a consequence of the factors mentioned above, but is also likely to be affected by inhomogeneity in the samples themselves.

The present phase of research is directed toward reducing the effects of these problems by experimenting with alternative methods of extracting the gases from the rock, as well as the use of calcite as an alternative. The preliminary results of this work, which are described in the second part of this paper, lead to the following conclusions:

(1) Gas extraction: The two methods used appear to give better reproducibility. The amounts of unsaturated components detected are considerably reduced, as are the effects of contamination.

(2) Use of calcite: This appears to provide a satisfactory alternative to the use of rock in lead/zinc mineral exploration. More significant, however, may be the suggestion that the method could be used to detect changes in the hydrocarbons circulating in an area during different stages of its diagenetic and tectonic evolution.

Finally, it should be noted that it has not proved possible to discover where or how the gases detected are held in the rock with any degree of certainty. Most of the calcites whose analysis are reported in this paper are known to contain fluid inclusions. It is hoped that at some later stage a link between the inclusions and the gases detected might be established.

Table 3. Results of gas analysis of a number of samples of calcite, from mineralised and non-mineralised areas. Values in ppbv/g sample.

| | Mineralized | | | Non-mineralised | | | | |
|-----------|-------------|--------|--------|-----------------|-------|------|------|-------|
| | 1a | 2a | 3a | 1b | 2b | 3b | 4b | 5b |
| Methane | 2850.0 | 1020.6 | 3426.7 | 12.8 | 793.5 | 81.3 | 19.2 | 515.7 |
| Ethene | 0.6 | 0.9 | 2.9 | 1.4 | 1.1 | 2.5 | 0.9 | 4.0 |
| Ethane | 153.2 | 29.3 | 55.8 | 1.3 | 100.5 | 2.4 | 1.2 | 8.8 |
| Propylene | 0.4 | 6.8 | 2.4 | 0.3 | 0.0 | 1.6 | 0.0 | 3.0 |
| Propane | 71.6 | 0.0 | 6.0 | 1.0 | 86.9 | 1.1 | 0.3 | 2.0 |
| I-butane | 12.0 | 1.3 | 0.0 | 0.0 | 23.7 | 0.0 | 0.0 | 1.1 |
| N-butane | 20.6 | 1.1 | 0.9 | 0.2 | 30.3 | 0.4 | 0.0 | 0.6 |
| 1-butane | 0.0 | 0.0 | 1.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

- 1a calcite vein, Great Limestone, Fourstones, Northumberland
 2a calcite vein, Great Limestone, Killhope, Co. Durham
 3a calcite vein with mineralisation, just south of Cullernose Point, Northumberland
 1b drip stone, Great Limestone, High Whittle, Northumberland
 2b calcite vein, Great Limestone, Lowick, Northumberland
 3b calcite vein, Sandbanks Limestone, Dunstanburgh, Northumberland
 4b calcite vug infill, Kirlington, Oxfordshire
 5b calcite vein, associated with the North Craven fault, nr. Ingleton, Yorkshire

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