A RE-APPRAISAL OF THE CONTROLS OF NON-METALLIC GANGUE MINERAL DISTRIBUTION IN DERBYSHIRE

by

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Summary

Previous descriptions of the distribution of non-metallic gangue minerals are reviewed and inconsistencies between published maps are discussed. The distribution is consistent with deposition from mineralising fluids which tended to move laterally up-dip and whose flow was controlled by aquicludes, such as the toadstones and Edale Shales, and by the permeability of the host rocks. The mineralisation is shown to be episodic; an early and a later phase of calcite mineralisation is recognised and it is tentatively suggested that later stages of the barite-fluorite mineralisation were preferentially concentrated into horsts and anticlines. From time to time faults appear to have acted as hydrological barriers rather than channelways to mineralising fluids. Anomalies in the regular pattern of zoning are explicable by invoking a combination of structural control and successive periods of mineralisation. No attempt has been made to discuss the source, composition or physical chemistry of the mineralising fluids.

Definitions

The term "ore", "ore mineral" and "gangue mineral" are used in different senses by different authors. In this paper we attempt to restrict their use to the definitions given in the recently published, Penguin dictionary of Geology (Whitten and Brooks, 1972). Thus *ore* "is the sum and total of ore minerals, gangue minerals and country rock which constitute the material worked for the purpose of extracting metal from the ore mineral" and *gangue* is "that part of an ore deposit from which a metal or metals is not extracted. The loose use of the term gangue to denote the waste minerals is avoided. As Whitten and Brooks remark, some non-metallic gangue minerals such as barite and fluorite are valuable in their own right, and in spite of their commercial importance they are not ore minerals since metal cannot be extracted from them. By the definitions given above they must be regarded as gangue minerals if they are part of an ore deposit. The Derbyshire mineral deposits are no longer worked exclusively for ore minerals and thus strictly speaking are no longer ore deposits but ore minerals are still obtained as by-products and hence may still be regarded as ores.

The definition of an ore-field is more subjective. Dunham (1952) used the term Southern Pennine Ore-field and Ford and Ineson (1971), Ineson and Mitchell (1973) refer to the Derbyshire Ore-field. In this paper we have not tried to define the limits of the ore-field (or orefields) in the Southern Pennines but wish to emphasise that unless otherwise stated, this paper deals solely and exclusively with *Derbyshire* mineralisation.

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3 text-figs.

Introduction

Derbyshire has been exploited for many centuries for a number of the great variety of the minerals which it contains. Its history as a lead-mining area may extend back to at least Roman times, and continued with varying success through to its height of activity in the 18th and 19th centuries. After about 1880 the area declined in importance as regards lead production which ended with the closing of the Mill Close Mine in 1939. The detailed history of the industry is described by Ford, Rieuwerts *et alia* (1968).

The mineralisation is contained almost totally within the C_1 to D_2 Carboniferous Limestone sequence which consists of various limestones interbedded with "toadstone", a miner's term for a number of basaltic lava flows and sills along with tuffs and agglomerates. In the Matlock region the Geological Survey's maps define two main lavas - the Upper and Lower Matlock lavas, but Shirley (1949 and 1959) describes them as of limited extent and of importance only on a local scale. Traill (1939 and 1940) agrees with this view and records seven different toadstones and seventeen wayboards (horizons of settled volcanic dust or clay) within the workings of the Mill Close Mine at Darley Dale.

The limestone consists of many facies and is sometimes dolomitised, particularly in the southern part of the limestone outcrop. Dolomites have also been recorded from the Woodale and Eyam boreholes (Cope 1949 and 1973; Dunham 1973). The Eyam borehole proved anhydrite and thin mudstone bands interbedded with dolomites in the lower part of the Visean and throughout the 68 metres of Tournaisian rocks. Total thickness of the Carboniferous Limestone is uncertain. Based on evidence from the Woodale borehole (Cope 1949) estimates of up to 900 metres seemed reasonable but the Eyam borehole proved more than twice this thickness of Carboniferous Limestone, suggesting that the Woodale borehole either exhibits a condensed sequence over a basement high (Cope 1973) or the Precambrian age of the basement rocks is in doubt (Dunham 1973).

The structure of the Derbyshire Limestone outcrop is frequently referred to as a "dome" but this is an oversimplification of the truth. Superimposed on this basic structure are a number of folds. These are of particular importance along the eastern boundary of the limestone outcrop where they consist of a number of eastward pitching anticlines and synclines with approximately E - W axes. The limestones are well jointed and affected by faults which reveal mainly horizontal slickensides. However, some evidence of vertical movement is occasionally present. Shirley and Horsfield (1940) suggest that the structural pattern of the area was largely determined by the end of Carboniferous times, although some minor fault movements have occurred since.

During post-Carboniferous times these faults and joints have been mineralised by solutions to give the present day complex mineral distribution. The deposits range in size from the large rakes, sometimes over 20 m in width and of unknown depth, which extend for several kilometres usually in an E - W direction, to small veinlets or scrins perhaps only a millimetre or so wide. The larger fissures are usually within a few degrees of vertical in the limestone, although less steep in the igneous rocks. There are also mineral deposits called flats or pipes formed along bedding planes. These are usually in contact with an impervious layer of country rock. As well as emplacement in the open fissures and caverns, in many instances the limestone itself has been replaced by the mineralisation.

Estimates of the age of Pennine mineralisation have varied from Hercynian (Dunham 1952) to Tertiary (Trotter 1944), but recent work by Ineson and Mitchell (1973) has supported a number of previous suggestions, based on isotopic dating techniques, that the Derbyshire mineralisation took place intermittently over a long period. They suggest a series of mineralisation episodes occurring between 180 and 290 million years ago.

Nearly 100 minerals have been identified in Derbyshire (Ford and Sarjeant 1964), but most are rare and of no economic importance. The development of the ore-field up to the last century was due to the presence of workable quantities of galena in the mineral veins, although sphalerite, wad (manganese dioxide), cerussite, smithsonite and ochre have also been worked on a small scale. In the west near Ecton, in Staffordshire, chalcopyrite, malachite and azurite have been mined for copper.

However, these metallic ores form less than 10 per cent of the mineral contents of the veins, which were largely composed of fluorite, barite and calcite. These are collectively referred to as the gangue minerals. They were regarded by the old miners as waste and either left in the old workings or tipped on the surface nearby. Hence, much of the ore-field is marked to this day by old tips, some of which are overgrown, but many can be examined and provide indications of the minerals present beneath the ground. The demand for these gangue minerals, particularly fluorite and barite, has increased during this century. Consequently many of the lead veins have been re-opened and the tips re-worked. This activity has instigated renewed interest in the distribution of these minerals within the ore-field and is the subject of discussion in this paper.

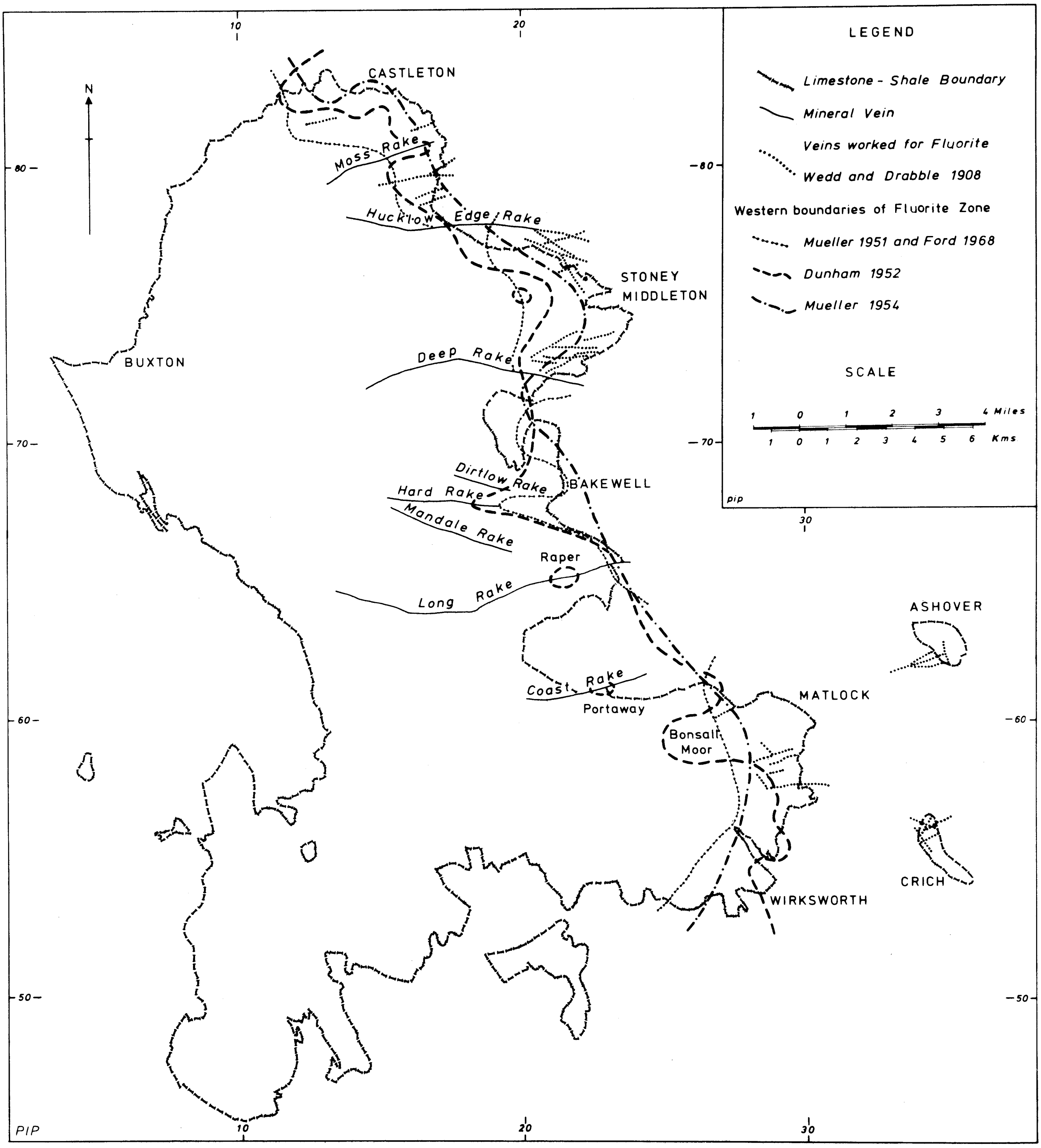
Discussion of previous work on the regional distribution of non-metallic gangue minerals

The mineral deposits of Derbyshire have been described by a number of writers during the past 200 years, but it is Wedd and Drabble (1908) who are usually credited with the first detailed account of any regional zoning of the gangue minerals. The fluorite-bearing veins described in their paper are shown in text-fig. 1. They claimed a change from calcite to barite to fluorite from west to east, so that fluorite supposedly occurs only near the eastern margin of the limestone outcrop.

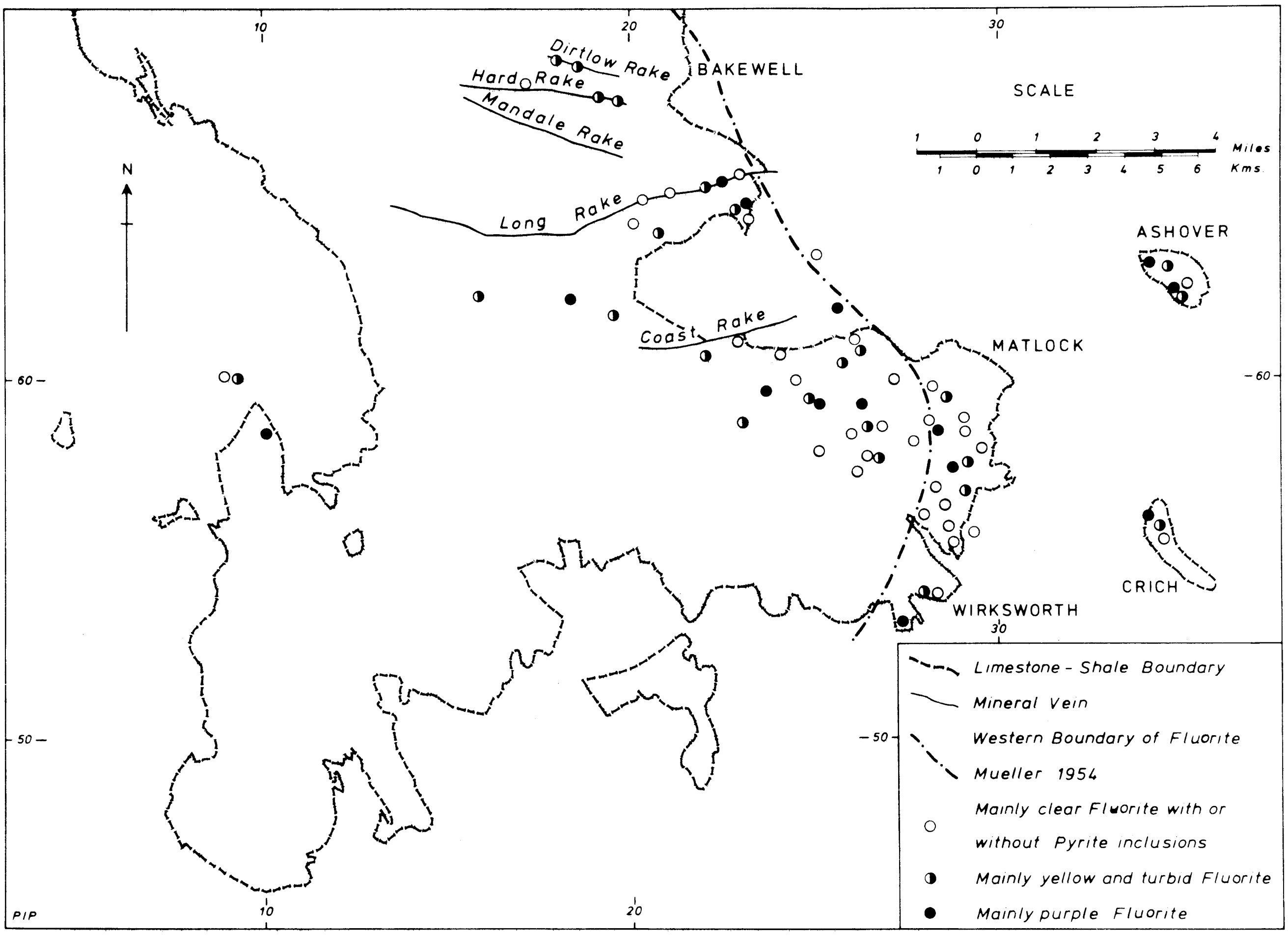
Shirley and Horsfield (1945) like Wedd and Drabble, discussed aspects of the stratigraphical and structural control of mineralisation but no other authors attempted to describe the regional distribution of gangue in Derbyshire before Mueller completed his thesis in 1951 and Dunham's Fluorspar Memoir was published in 1952. Mueller's maps are by far the most detailed work to date on the mineral distribution. His two most relevant works on the subject are his Ph.D. thesis (1951) and a later paper (1954). The map produced in the former is that published by Ford (1968) and Ford and Ineson (1971), which is erroneously described as "after Mueller 1954". In this initial map Mueller divides the ore-field into an eastern fluorite zone followed to the west by barite and calcite zones respectively. Furthermore he subdivides the fluorite zone into three subzones each with different types of fluorite, which are claimed to be due to variations of temperature of deposition. The high-temperature pyritic fluorite subzone is allegedly confined to within half a mile west of the limestone - shale boundary and top 100 m of the limestone succession. To the west of, and beneath this, according to Mueller, is the turbid fluorite subzone (Bradwell spar) followed by purple fluorite which supposedly extends "from the western extremities of the fluorite zone to the central areas of the limestone plateau so far as fluorspar is detectable in the veins". (Mueller, 1954).

Our detailed examinations of old tips and present workings reveals no such simple pattern of fluorite distribution. Most areas provide a mixture of fluorite types and a map of the dominant type at each locality has revealed no evidence of any zoning (see text-fig. 2). Neither is it true that only purple fluorite occurs west of the fluorite zone. Clear, turbid yellow and pyritic fluorites have all been found west of this zone. In fact, purple fluorite is by no means the most common form, although it is present at most exposures in small quantities. These occurrences are frequently just thin smears on the sides of joints rather than in the larger veins.

Fluid inclusion studies at the University of Leicester have failed to verify or disprove Mueller's contention that the pyritic, turbid and purple fluorite subzones indicate high, medium and low-temperature deposition respectively, although they do indicate much lower temperature (c. 80 - 120 °C) than Mueller envisaged. (Rogers personal communication, 1974).



Text-fig. 1. Western limit of fluorite according to various authors. Note that Mueller's western limit of fluorite is based on a 10% fluorite content yet in places it lies east of Dunham's line which is probably equivalent to a commercial limit of 40%.



Text-fig. 2. Varieties of fluorite.

Most of Derbyshire localities shown have either been worked for fluorite or are expected to be viable prospects. Only the most dominant variety at each locality is indicated. The map illustrates the impossibility of producing regional zones based on the varieties of fluorite and also shows how fluorspar workings have spread westward since Dunham and Mueller drew their western limits. Other isolated discoveries of fluorite occur south and west of the main group.

Mueller's three major zones on his 1951 map are defined by the percentage content of each gangue mineral. He also includes a pyritic calcite zone which occurs mainly in synclines, and three areas of "Ecton-type mineralisation" which are left undefined. He then published a second version of his map in 1954 in which the zones were not only defined by different percentage mineral content but did not coincide geographically with his original version. The new western boundary of the fluorite zone (text fig.1) which should coincide with 10 per cent fluorite in the major veins, presents three points of confusion:-

(i) It is further west than some of the veins mapped by Wedd and Drabble (1908) at which time the fluorite content must have been much greater than 10 per cent to make them economically viable.

(ii) In the Eyam and Mill Close Mine areas this western limit of fluorite is further east than two of his fluorite subzones.

(iii) The map published by Dunham (1952) shows the western limit of the then worked fluorite deposits which would coincide approximately with a 40 per cent fluorite content (text-fig.1). In places this is well west of Mueller's 10 per cent western limit and includes worked deposits at Bonsall Moor and Portaway Mine, etc., of which Mueller makes no mention.

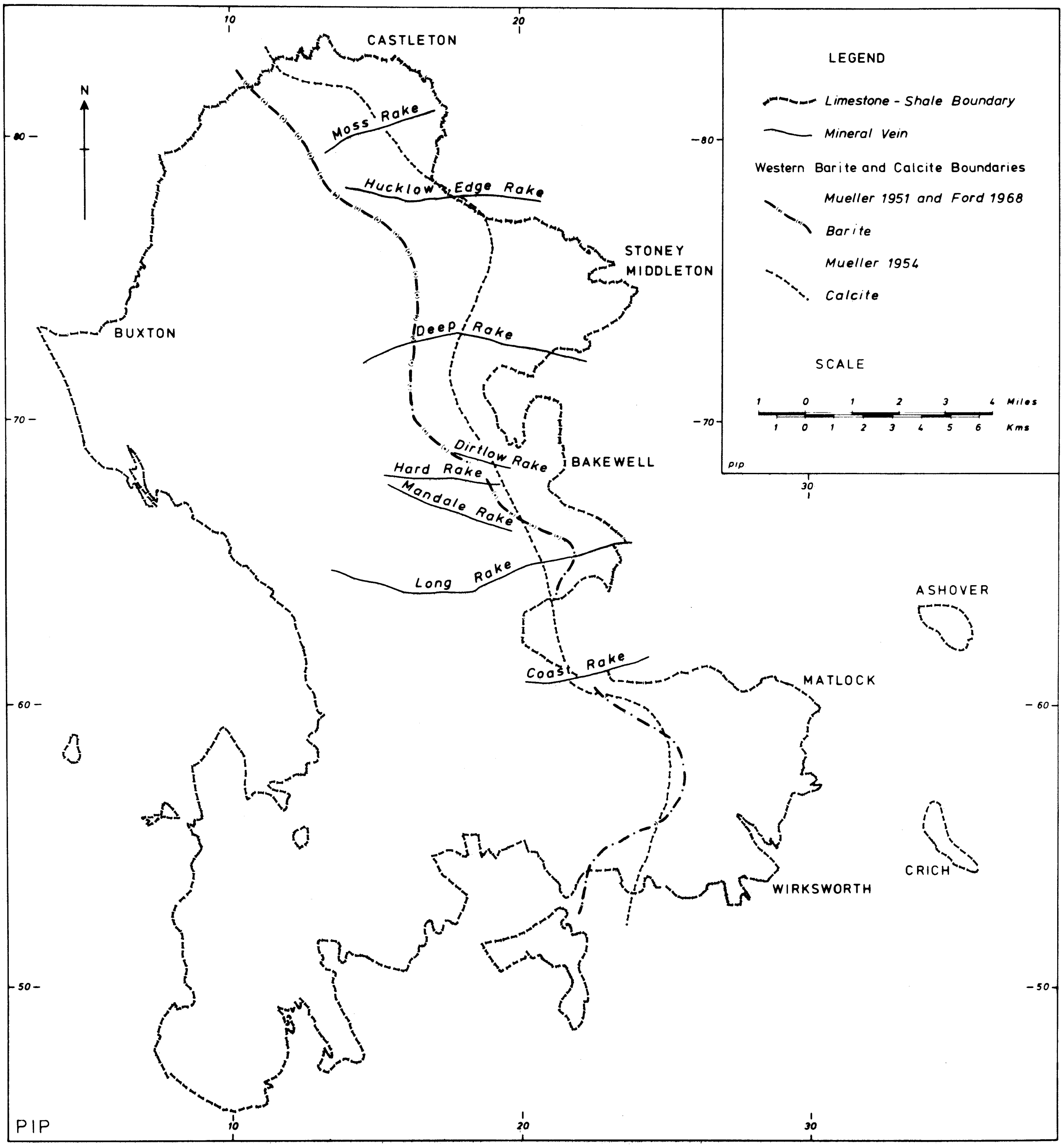
Since these publications, other viable deposits with more than 25 per cent fluorite have been discovered to the west of all these limits, e.g. in the Elton area of the Coast Rake.

In our opinion the work of Wedd and Drabble (1908) and Dunham (1952) provides valid evidence of the historical developments in the mining of fluorite in Derbyshire, but Mueller's western limit (1954) was probably incorrect when it was published and is certainly invalid now. It should no longer be used. Neither is there necessarily a steady decrease in fluorite percentage westwards from the limestone - shale contact. As will be explained later, areas of low fluorite content are known to the east of those with a much greater percentage.

Mueller is the only author to have defined barite and calcite zones to the west of a fluorite zone. There is again a discrepancy between the two versions of his map. The 1951 map shows the western limit of the barite zone to be substantially different from that in his 1954 map (text-fig. 3). This is particularly true in the north of the area where the former limit is on average 1 mile further west than the latter. It would also appear that several high-barite-content areas are to the west of at least one of these limits, e.g. Golconda Mine (249552).

The mineralogy of the so-called calcite zone is by no means simple, and various assemblages including calcite-barite, calcite-barite-galena, calcite-barite-fluorite, calcite-barite-fluorite-galena, as well as various ironstones and ochres, have been recorded. Although parts of some veins within Mueller's calcite zone contain more than the required 80 per cent calcite (e.g. Long Rake and Yokecliffe Rake), others contain very little (e.g. fluorite bearing veins on Bonsall Moor and north west of Youlgreave all of which were placed by Mueller in his calcite zone. Conversely the eastern part of Moss Rake, which as mapped by Mueller (1951 and 1954) is supposed to lie in the barite and fluorite zones, is now known to consist largely of calcite. In other veins (e.g. Long Rake at Nether Haddon and Great Rake at Riber Mine, Matlock Bath) Varvill (1959) claimed that the calcite content increases to the east rather than towards the west. On the northern part of the area Stevenson and Gaunt (1971 p. 308) comment with reference to the fluorite, barite and calcite zones, "the zones, however, should only be taken as a general illustration of the tendencies of gangue mineral development, there being many anomalies and reversals of the normal sequence".

The inclusion of the pyritic calcite zone in Mueller (1951) and Ford (1968) is also puzzling. Although some of the calcite from this zone is pyritic, much of it is not. Pyritic calcite is also found elsewhere. Perhaps Mueller himself had doubts about the validity of this zone as it was omitted from his 1954 paper, as were the areas of "Ecton-type mineralisation".



Text-fig. 3. Barite and calcite zones.

It would therefore appear that there is much confusion within the literature about mineral distribution in Derbyshire, and that a simple division of the area into zones based on percentage mineral content does not withstand close inspection. Indeed, it is rarely possible to quote the percentage composition of a mineral vein with any meaningful accuracy. Mueller claims to have derived his figures from a variety of sources including statistics supplied by a mining company and personal inspections of old workings etc. However, figures for hand-worked ore, machine-worked ore and original vein content could all be different for the same deposit, depending on the method of mineral extraction used. The results of examination of old workings could also depend on such factors as from what part of the workings was the gangue brought to the surface and in which part was it left below ground; whether the tips have been reworked for fluorite or barite by either mining companies or "hillockers", and from which part of the ore-dressing process the tip material was derived. Because of these factors any attempt to estimate the percentage content of most deposits should be regarded with suspicion.

Mueller's maps thus give a misleading and far too generalised idea of the distribution of gangue minerals in Derbyshire and in our opinion both his maps and his explanations need to be revised. However, the general impression of an east-west zoning with the bulk of the fluorite deposit in the east of the limestone outcrop is still broadly valid notwithstanding many anomalies.

Stratigraphical and Structural Control

All research workers, including Mueller, realised that the distribution of gangue minerals in Derbyshire was more complex than they had depicted on their maps. Most authors considered that the anomalies known to them could be explained by assuming that impermeable beds such as the volcanic layers and particularly the Edale Shales had capped and channelled uprising and westward migrating mineralising fluids into structural traps. Thus for example Wedd and Drabble (1908) concluded that fluorite occurred only in the top 600 feet of the limestone succession and tentatively suggested that it tended to be concentrated in the eastward-pitching anticlines. Mueller (1951 and 1954) accepted that the fluorite content of the veins decreases into the synclines and postulated that its place is taken by pyritic calcite (Mueller 1951 and Ford 1968). Shirley and Horsfield (1945) in a detailed study of the Eyam area claimed that the principal veins follow the anticlines and that where veins are oblique to the dip the ore-bearing off-shoots are on the up-dip side. Shirley (1948) later applied these principles to the Matlock area and to Mill Close Mine where "the 'main joint' carried little or no ore but the rich deposits were on its western or up-dip side". All these authors' observations thus tended to confirm the "mainly lateral up-dip movement of the mineralising fluids in the restricted spaces afforded between impermeable layers in the country rocks" (Dunham 1952).

In spite of the strong evidence for lateral up-dip movement from an eastern source, many exceptions have been noted. Wedd and Drabble's (1908) contention that "fluor-bearing limestone is always wholly above the lowest sheet of igneous rock and a large proportion above the highest igneous sheet" was confounded by the subsequent discovery and development of Low Mine (285574) below the Matlock Lower Lava and of fluorspar deposits further west in the Matlock anticline. The large proportions of fluorite which are currently being extracted from the Mill Close Mine dumps which have come from the Stanton Syncline show that fluorspar is not necessarily confined to the anticlines. Similarly recent mapping by officers of the Geological Survey has failed to confirm the importance of anticlinal control in the Matlock area (Smith *et al* 1968) and only partly confirms Shirley and Horsfield's (1945) opinions in the northern part of the limestone outcrop (Stevenson and Gaunt 1971). Moreover, recent mining in the Eyam area has demonstrated that probably monoclines rather than anticlines are associated with the main east-west veins (Ineson, personal communication, 1974). The excellent examples of mineralisation on the up-dip side of major feeders (Shirley 1948 and 1949) can be matched by examples of extensive mineralisation on the down-dip side of some east-west rakes (e.g. Long Rake) and similarly King (1966) and Ford (1967) have reported several instances of mineral deposits which appear to have formed from downward rather than upward movement often accompanied by collapse structures. An eastern source seems likely for almost all the Derbyshire gangue minerals, but Ecton and other Staffordshire deposits may be derived from a separate and possibly western source (c.f. Mueller 1954).

Our field observations suggest that notwithstanding the many exceptions there is an overall tendency for mineralisation to extend laterally up-dip, but in addition there is evidence that some of the major faults may sometimes have acted as hydrological barriers to mineralising fluids. We also find a tendency for the most highly coloured (? late stage) minerals to be preferentially concentrated in anticlines and the tops of up-faulted areas.

Good examples of both these types of structural control occur in the Matlock District. Here, as elsewhere in Derbyshire, the compositions of the mineral veins above and below the volcanic horizons are often significantly different suggesting that these aquicludes separated mineralising fluids of somewhat different composition and possibly different ages. Less obvious but nevertheless distinct mineralogical changes occur either side of major faults suggesting that they also from time to time acted as hydrological barriers. Thus, for example, fluorite is rare west of the Gulf Fault but common east of it, and silicification, purple fluorite and pink crystalline barite are common north of the Bonsall Fault and rare in the graben to the south. The upper beds of the Middleton Moor horst, the Matlock Anticline and the minor anticline near the Watts shaft at Mill Close Mine are the chief repositories of coloured gangue minerals, the graben between the Gulf and Bonsall faults and the Stanton Syncline being characterised by colourless transparent fluorite. Exceptions such as the silicified limestone near Slaley and the purple fluorite in the Ball Eye Mine (both south of the Bonsall Fault) do not invalidate the general tendencies outlined above but we do not know if similar tendencies characterise the whole of the Derbyshire ore-field.

Such structural control, exemplified by the Matlock district and to be described separately (Bagshaw, in preparation), strongly suggests that mineralising fluids during different episodes of mineralisation often followed different routes through the fissured limestones. Thus it is important to study the paragenesis of mineralisation in order to define the characteristics of each episode of mineralisation and, hopefully, deliminate the routes of each phase of mineralisation.

Lithological Controls

The most obvious and most easily overlooked fact about the Derbyshire mineralisation is that limestone and dolomite host rocks contain virtually all the gangue minerals: only trivial amounts, which are hardly ever in economic concentrations, occur in the interbedded volcanic rocks and mineralisation rarely extends into the intrusive dolerites and vent agglomerates. The overlying Edale Shales contain no known veins and appear to have acted as a blanket preventing rising mineralising fluids reaching favourable host rocks in the Millstone Grit Series. Leakage up faults may explain the scrins of barite on Alport Heights and other very rare coatings on joints which sporadically occur in the Millstone Grit. The more frequent though sporadic occurrence of barite and galena in the Permo-Trias of north-east Derbyshire and Nottinghamshire (Deans, 1961; Ineson *et al* 1972 and Taylor and Holdsworth, 1973) may also be due to leakage along faults which tapped mineralising fluids rising from the underlying Carboniferous Limestone, or alternatively they may be deposits from thermal waters which entered the Permo-Trias where the Permian unconformity overstepped the Edale Shales (Ford, 1969). Whatever the true explanation of mineral occurrences stratigraphically above the Carboniferous Limestone the overwhelming concentration of gangue minerals in the limestone seems due to the efficiency of the Edale Shales as a cap-rock.

If this is true no special lithological control by the limestone need be invoked but it is also true that on a world scale Mississipi Valley type mineralisation of which Derbyshire is a typical example, is predominantly confined to limestones in preference to other suitable reservoir rocks. The reason appears to be that in addition to being good aquifers, because of their primary porosity and brittle fracture, limestones are particularly susceptible to solution by acidic groundwaters and mineralising fluids and to dolomitisation, all of which tend greatly to increase the capacity of the reservoir. Moreover limestones and dolomites are more easily replaced by gangue minerals such as fluorite than are other rocks. In addition it may be true as suggested by Jackson and Beales (1967) that the carbonate rocks contain, prior to mineralisation, more components such as Ca^{++}, SO_4 and H_2S which contribute to the mineralisation than occur in other potential host rocks.

In Derbyshire, owing to the post-diagenetic character of the mineralisation, the primary porosity of the limestone is not an important lithological control except in such unusual circumstances as the fluorite deposits in the boulder bed at Treak Cliff, Castleton (Ford, 1969). Limestone lithology is a factor in determining which limestones are dissolved and which are replaced by gangue minerals such as fluorite. Structure hydrology and the distribution of aquicludes are other important factors but there is a tendency for the coarse-grained limestones to be preferentially replaced or dissolved (Traill, 1939). Stevenson and Gaunt (1971) for instance noted that the Bradwell Pipe had developed in the coarsest crinoidal limestone in the district and pipes, flats and irregular gangue mineral ore bodies are notably absent from the fine-grained limestones around Ashford and Bakewell.*

Claims that reef limestones are preferentially replaced are more difficult to substantiate and it seems to us that the replacement of reefs lying, as at Raper Mine, directly below the Edale Shales may be due to their position as structural "highs" rather than any intrinsic lithological features.

Although the primary porosity of the limestones is of little importance in controlling the location of gangue mineral deposits the secondary porosity resulting from *dolomitisation* is of prime importance. Many economically viable deposits are situated in dolomite and must have resulted from the comparative ease with which mineralising fluids could flow through the dolomite. Curiously these deposits tended to accumulate at the bottom of the dolomite whereas replacements tend to occur at the top of the limestone strata. This difference between limestones and dolomites will be discussed more fully in a later section. Many authors, for example Dunham (1952), have noted that the dolomitisation occurred before mineralisation possibly due to brines descending from the Zechstein sea, but it is also worth noting that the porosity of the dolomites is much greater than would be expected from the volume reduction resulting from the replacement of calcite by dolomite. Fluoritised dolomites which seem to have formed by simple pore-filling commonly have 20 - 25% CaF_2 contents. Therefore unless it escaped in surface springs very considerable amounts of calcium carbonate must have been added to the groundwater and been available for subsequent mineralisation.

Our researches have failed to indicate any relationship between the distribution of chert and mineralisation in Derbyshire. It could be argued that mineralisation is sparse in the chert rich limestones around Bakewell but conversely many cherty limestones are strongly mineralised elsewhere in Derbyshire. Recent research (Orme, unpublished data quoted by Orme and Ford 1971) "indicates that the bulk of the chert was produced during the earlier phases of the diagenetic evolution of the limestone, and in many instances before complete lithification of the carbonate host". Thus chert was formed before lead-zinc mineralisation began but metasomatic silicification, first described by Bemrose (1898) as "quartz rock" and "quartzose limestone" does appear to be intimately associated with mineralisation. Although quartz is rare in the Derbyshire mineral veins (Ford and Sarjeant, 1964) silicification is widespread particularly in the Matlock Anticline, Pindale and to a lesser extent north of Youlgreave along the Long Rake.

Silicification like dolomitisation must have similarly enhanced both the Ca^{++} and HCO_3 content of the groundwaters and it may be no coincidence that the walls of the Great Rake, Matlock, are silicified below the Matlock Lower Lava and at higher stratigraphical and structural horizons the vein is very rich in calcite. Like dolomitisation, silicification is confined to restricted areas in Derbyshire but unlike dolomitisation it reduces the porosity of the original limestone. It seems to have been formed from fluids rising through the limestone and often spreading laterally below toadstones and wayboards: silicification thus tends to reinforce the effectiveness of these rocks as cap-rocks to subsequent phases of mineralisation and quite thin wayboards when silicified may become effective barriers to fluorine-bearing mineralising fluids. But silicified limestones are brittle rocks and later earth movements

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* The Ecton and Clayton Pipes in Staffordshire are developed in basinal limestones many of which are very fine-grained but the mineralogy, structural and stratigraphical controls are so very different from the Carboniferous Limestone in *Derbyshire* and for this reason are not considered further in this paper.

may fracture them allowing mineralising fluids to pass through. Silicified limestones are therefore temporary barriers which modify the flow of mineralising fluids. Age relationships are uncertain but some silicified dolomites outcrop in the Griffe Grange and Carsington areas suggesting that silicification is later than dolomitisation. Our observations suggest that most of the silicification preceded the calcite-barite-fluorite mineralisation but some was contemporaneous with the early phases of barite-fluorite mineralisation (e.g. Raper Mine, Ineson and Al-Kufaishi, 1970).

Primary limestone lithology seems to be a factor in controlling the location of replacement deposits and solution of limestone but is of less importance than secondary alterations such as dolomitisation and silicification, but these only partly explain the non-uniform distribution of gangue minerals in Derbyshire limestones and dolomites. Other factors must be invoked to explain the lack of clear-cut zoning.

Paragenesis of gangue minerals

Schnellman and Willson (1947) suggested that the relatively poor zoning might be explained by successive periods of mineralisation and recent detailed studies of the paragenesis of small areas have tended to confirm their opinions. The most significant of these recent studies is that of Ineson and Al-Kufaishi (1970) who describe a paragenetic sequence at Raper Mine consisting of five stages of mineralisation separated by fracturing and brecciation. Their first stage of mineralisation consists of barite with little or no galena and no other gangue minerals. This was followed by fluorite-barite, 2 stages of fluorite only, and finally fluorite and later-stage barite. Evidence of similar multiphase mineralisation is so widespread in Derbyshire that it might well be a major reason for anomalies in the regional pattern of zoning. Zones of a later phase of mineralisation often overlap the zones of earlier phases and such overlapping may explain the reversals of the normal sequence of fluorite-barite-calcite noted by Stevenson and Gaunt (1971). Similarly, the patches of commercially viable fluorspar lying west of the main zone (Dunham 1952), and Ineson and Al-Kufaishi's early barite which precedes later fluorite-barite mineralisation at Raper, may also be explained by overlapping zones.

Implicit in this interpretation of the anomalies to Mueller's zones is the assumption that the east-west sequence of fluorite-barite-calcite zones is the normal sequence and moreover applies to each episode of mineralisation. But this is not necessarily true and in our opinion there is strong evidence of both early and late calcite mineralisation unaccompanied by either fluorite or barite.

The clearest evidence of early calcite mineralisation is in the Dirtlow Rake at Sheldon (Plate 6) where columnar calcite occurs in the clasts of a fault breccia within a vein currently being worked for fluorspar. Such unambiguous evidence of early calcite preceding fluorite-barite mineralisation is rare but columnar calcite on the outer margins of fluorspar veins is common throughout the Derbyshire ore field. Moreover, mining records indicate that both fluorspar and barite veins usually pass down into calcite and Varvill (1959) has claimed that several veins pass eastward into calcite. The westward and upward temperature-controlled fluorite-barite-calcite sequence is thus exceedingly difficult to substantiate when applied to the distribution of calcite. The evidence thus seems to favour an early calcite mineralisation preceding the main barite-fluorite mineralisation.

This early calcite was often accompanied by galena and more rarely by sphalerite. It usually, but not always, consists of rhombohedral calcite but sometimes, especially in the larger rakes, occurs as columnar crystals. The latter suggests rapid crystal formation of a rhombohedral form which had a direction of growth predominantly horizontal from the wall rock into the centre of the open fissure.

Many veins in Derbyshire show no evidence of early calcite mineralisation probably because many fissures were not open during this early episode. Nevertheless those fractures which were open were subjected to repeated hydraulic mineralisation (Phillips, 1972) and occasional brecciation. For example rhythmic deposition of columnar calcite and galena is a common feature of the wider veins and along the Long Rake brecciated columnar calcite cemented with rhomboidal calcite is not uncommon. Like the barite mineralisation at Golconda (Ford and King 1965) and the barite-fluorite mineralisation at Raper Mine (Ineson and Al-Kufaishi 1970) early calcite mineralisation seems to have been multiphasal.

A late calcite mineralisation, frequently, but not always, consisting of scalenochedra lining cavity walls and deposited on earlier mineralisations is a well recognised feature of the Derbyshire ore-field. It is not confined to any particular zone or area and is not accompanied by fluorite or barite.

Thus it appears that a paragenetic sequence of (i) early calcite, (ii) multiphase barite-fluorite, and (iii) late calcite may be widely applicable in Derbyshire. The multiphase barite-fluorite mineralisation needs further study. Mueller (1954, p. 529) noted that in the master veins blue fluorite though rare is "usually restricted to the youngest generations of hydrothermal minerals". Similarly at Raper Mine (Ineson and Al-Kufaishi 1970) the most brightly coloured varieties of both fluorite and barite are amongst the last minerals to crystallise and on Middleton Moor and elsewhere we find that pink crystalline barite is younger than the more earthy forms of barite such as "caulk". Unfortunately we are not certain that these observations apply throughout the orefield.

Doubt also exists about whether calcite is entirely restricted to the early and late phases of mineralisation. It is not part of the episodic mineralisation at either Raper Mine or Golconda and is confined to late cross-cutting veins in Conksbury Quarry, Youlgreave, but elsewhere rhythmic alternations of calcite and fluorite occur (e.g. Coalpit Rake and Great Rake near Matlock). The sequence fluorite-barite-calcite is common in many thin crustiform veins and scrins throughout Derbyshire but like the calcite-fluorite veins appears to be confined to the later stages of mineralisation. The evidence, on balance, suggests that most of the calcite in Derbyshire is confined to early and late stages of mineralisation but that some calcite was precipitated towards the end of the fluorite-barite multiphase mineralisation.

Review of some exceptions to the regular pattern of mineral zones

From the preceding sections it should be evident that we believe that most gangue mineral deposits in Derbyshire can be ascribed to deposition from mineralising fluids which migrated laterally up-dip: many exceptions to the regular pattern of calcite-barite-fluorite zoning can be explained by invoking a combination of structural control and successive periods of mineralisation. Each exception needs to be considered on its merits but the following examples may indicate our general approach:-

1. Fluorite veins which apparently pass eastward into calcite

Varvill (1959) claimed that some rakes which contained fluorspar above the upper lava pass eastward into calcite; amongst his examples were Long Rake east of Raper Mine and the Great Rake at the Riber Mine, Matlock. Our favoured opinion is that an early calcite mineralisation was confined to the down-dip parts of these veins and that subsequent reshearing and extension of the fractures allowed mineralising fluids to migrate further west up-dip above the uppermost lava and precipitate fluorite west of the calcite. In both examples the extent of the westward migration of these fluorite bearing fluids in the upper part of the limestone is unknown owing to erosion but it seems likely that they eventually became trapped under the unconformable Edale Shales. Alternatively some or all of the calcite may be later than the fluorite but either way it appears that the fluorite has preferentially precipitated in the up-dip reaches of the rake. Riber Mine is now closed but it is hoped that mining along the Long Rake will help to elucidate the pattern of mineralisation more adequately. Varvill (1959) also claimed that the Coast Rake became impoverished in fluorite eastwards - again down-dip.

2. Increases in the fluorite content of suites of veins in a contrary direction to Mueller's zones.

The best example is in the graben between the Bonsall and Gulf faults as mapped by Officers of the Geological Survey (see Matlock 2½ inch map). Here the fluorite content seems to increase substantially and barite decrease north-westward in the strata above the Matlock Upper Lava. Thus the barite-fluorite zones appear to be reversed hereabouts. South of the Via Gellia almost all veins seem to have contained less fluorite than veins north of the Via Gellia and currently grades of 60 per cent and more have been reported from the Whitelow mines towards the north western end of the graben. Smith *et al* (1967) have shown that the Matlock Upper Lava, which underlies the whole area, rises westward and therefore, if Smith's structural interpretation is correct, it seems possible that fluorine-bearing fluids percolating through the stockwork of fractured limestone were hemmed in by the Gulf and Bonsall faults as they moved up-dip and were eventually concentrated towards the north-western up-tilted end of the graben. A structural control of fluids migrating up-dip seems to explain this and other similar anomalies.

3. Ore-shoots, minor veins and replacements on the down-dip side of major rakes suggest a contrary movement of the mineralising fluids but it is argued (Firman in preparation) that most of these features result from either mineralisation during second-order shearing or the re-opening of second-order shearing or the re-opening of second-order shears by hydraulic fracturing (Phillips, 1972). The geometry of such ore-bodies therefore depends on the propagation of second-order faults and if these predominate on the down-dip side of a major feeder then mineralisation will also be concentrated on the down-dip side (e.g. south of the Long Rake).

4. Gangue mineral deposits in dolomite

Ford (1969) has described many deposits in the dolomites of south Derbyshire and concludes that there are few areas where the boundary between the limestone and dolomite is devoid of mineralisation. The largest of these deposits, such as the fluorspar at Masson Hill and barite at Golconda, show evidence of cavern formation both before and during mineralisation but many smaller deposits appear to be scrins with impregnations of the porous dolomite and show no evidence of collapse structure. Apart from a few rakes, mineralisation of the dolomite is rare anywhere other than near the limestone-dolomite boundary or resting on top of impermeable beds within the dolomite. Deposits commonly occur in hollows in the limestone-dolomite boundary and in general the distribution of much of the mineralisation suggests downward rather than upward percolation of the mineralising fluids. There is evidence therefore that laterally migrating fluids moving up-dip through the limestone tended to sink when they reached the dolomite: possibly they were chilled by or reacted with ground waters contained in the porous dolomites or alternatively the flow regime changed from laminar to turbulent flow as it passed into the more porous medium (see Firman, in preparation.)

Whatever the true explanation, mineralising fluids diffusing through the dolomites behaved differently from those in the relatively impermeable limestone.

5. Gangue mineral deposits resting on impervious toadstones

These types of deposits appear to have been formed from downward-percolating fluids but according to Ford (1969) they grade into other deposits which seem to fill pre-mineralisation karstic features, and include many of the famous "pipe deposits" of Derbyshire. If channelways and caverns were formed prior to mineralisation, it is to be expected that they would control the direction of flow of the mineralising fluids, which when hot, might rise and attack the cavern roofs causing roof collapse but on cooling might, as in the porous dolomites, flow down-dip instead of up-dip.

The evidence from all these examples thus suggests that although the broad overall distribution of the gangue minerals suggests a predominantly lateral and up-dip movement of the mineralising fluids, in the more porous and cavernous strata the fluids tended to move downwards.

In order adequately to explain the exceptions discussed above, the mechanism of flow through the limestone, dolomites, karstic features and the rakes needs much more detailed study. For example it is claimed that fractures may open at speeds approaching 1,000 feet per sec. (Price, 1968) so that under conditions of hydraulic mineralisation the rakes may have been filled with fluid almost instantaneously. Moreover the direction of flow of this fluid will depend on the direction of propagation of the fracture. Thus fluids filling the rakes might flow in the opposite direction to the mineralising fluids diffusing through the main body of the rock. Such considerations are beyond the scope of this paper but are to be considered elsewhere.

Recapitulation and Conclusions

This paper reviews previous descriptions of the distribution of gangue minerals in Derbyshire. Maps by Wedd and Drabble (1908) and Dunham (1952) depict stages in the development of fluorspar mining but the suggested western limit of fluorite has been superseded by the discovery of many lower-grade and a few high-grade ores west of Dunham's line. Mueller's more detailed illustrations of zoning in Derbyshire are critically discussed. Substantial differences between the two published versions of his map have led to confusion in the literature. Field work and paragenetic studies have failed to confirm Mueller's three-fold division of the "fluoritic zone" into pyritic, turbid and purple fluorite; his western limit of fluorite when compared with Dunham (1952) is likely to have been invalid when it was published in 1954 and his "calcitic zone" is reinterpreted as a relic of an early calcite mineralisation where it was not overlapped by later fluorite-barite mineralisation.

Mueller's concept of a fluorite zone in the east of the limestone outcrop succeeded westward by barite is considered to be broadly true but the junctions are by no means clear-cut. Paragenetic studies and K-Ar dating (Ineson and Mitchell 1973) show that the mineralisation was episodic and may therefore consist of several overlapping zones. It is important that in future the products of each episode of mineralisation should be identified and its distribution mapped separately, so that eventually maps can be produced which show the distribution of non-metallic gangue minerals deposited during each episode of mineralisation. One of us (Bagshaw) is attempting this difficult task and will publish his preliminary results separately.

We conclude that the principal controls of mineralisation are structural and stratigraphical; anticlines, horsts, the toadstones and the Edale Shales playing an important role in channelling and impounding mineralising fluids which were migrating laterally up-dip. Our views are therefore similar to those of Wedd and Drabble (1908), Shirley and Horsfield (1945) and Dunham (1952), but in addition we do have evidence that from time to time some of the major faults acted as hydrological barriers and that structural control may have been more effective in the later phases of barite-fluorite mineralisation, when the purple fluorites and pink barites were formed. Although most of the mineralising fluids tended to rise in the limestones there is evidence that they sank in the more porous dolomites before precipitating gangue minerals.

No attempt has been made, in this paper, to discuss the source, composition or physical chemistry of the mineralising fluids, and the distribution of non-metallic gangue minerals is consistent with deposition from cooling fluids from whatever source. The zones albeit poorly defined could be temperature-controlled as suggested by Mueller (1954), but if precipitation results from the reaction between chloride brines entering the host rock and sulphate-rich ground waters (c.f. Jackson and Beales 1967), then the distribution of barite may not be temperature-controlled but may depend on the distribution of sulphate-rich ground waters within the host rock. Similarly the distribution of sulphides could depend more on the availability of hydrogen sulphide generated and stored in the host rock than on the temperature of the mineralising fluids. Such considerations are beyond the scope of this paper but are to be the subject of a later one.

PLATE 6

Fig. A. Hand specimen from Dirtlow Rake near Sheldon with angular fragments of calcite set in a fluorite lacking calcite but with minor amounts of barite.

Fig. B. General view of the breccia in the Dirtlow Rake near Sheldon. Large rounded and sub-angular blocks of an early calcite mineralisation are set in a matrix of later fluorite with subordinate barite. About a metre above the hammer smaller angular fragments of the early calcite probably represent disruption of the rounded clasts.

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