A SEDIMENTARY BASIN EVOLUTION MODEL FOR ORE GENESIS IN THE SOUTH PENNINE OREFIELD

by

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Summary

The genesis of ore mineralisation in the South Pennine Orefield has been studied in the light of the sedimentological development of the Pennine and adjacent basins and a multi-stage genetic model is proposed in which three separate stages of ore precipitation are recognised:–

1. Base metal sulphides, especially framboidal pyrite, formed during the early diagenesis phase, sulphur being supplied by decomposition of organic matter and by sulphur-reducing bacteria, and metals by pore waters. The later mobilization of these sulphides could have provided rich sources of metal and sulphur for subsequent ore deposition.

2. During Permian and Triassic, the main stages of ore mineralisation in the orefield took place by episodic discharge of heated saline connate brines from deeply buried sediments near the centres of the adjacent basins. The ore fluids were generated by release of formation waters during compaction of sediments and clay dehydration of the shale units and had an outward and upward movement particularly from the North Sea basin to zones of lower pressure. The ore minerals precipitated behind a "front" of hydrocarbons over a temperature range of 50 to 150 °C. These temperatures were obtained by a combination of "normal burial" temperature and diagenetic exothermic reactions. Metals and sulphur were derived from more than one source.

3. During the uplift and weathering phase of the orefield secondary alteration minerals were formed and some early-formed minerals, especially galena and fluorite, were transported by groundwater circulatory system and re-deposited as residual sediments in caves.

Introduction

The South Pennine Orefield lies at the southern end of the north-south trending Pennine Hills in central England and consists of a plateau of about 90 km^2 of Lower Carboniferous (Dinantian) limestones, often bituminous, with dolomite, chert and inter-bedded basic igneous rocks. Although some 1600 metres of limestone have been penetrated by a deep borehole (Dunham, 1973), only the top 450 metres are exposed in the orefield and mining activity has been restricted to the top 300 metres of the limestone (Ford and Ineson, 1971). The ore mineralisation in the orefield consists of hundreds of fissure-fill veins (locally known as rakes and scrins) and stratiform ore bodies of void-filling or replacement character (known as pipes and flats) with galena, sphalerite and minor pyrite as the metallic minerals. More than 90 per cent of the ore bodies are made up of different proportions of calcite, fluorite and baryte as the principal ore minerals in the present-day exploitation of the orefield (Mostaghel, 1984). In contrast to the earlier periods of mining development, minor quantities of lead and zinc are raised only as by-products today. It has been estimated that between 3 and 4 million tons of lead concentrates and between ¼ and ½ million tons of zinc concentrates have been produced since mining began in the South Pennine Orefield during the Roman occupation of the British Isles (Ford and Rieuwerts, 1983).

Several authors (Mostaghel, 1984; Worley, 1978; Emblin, 1978; Ineson and Ford, 1982; Dunham, 1983) have given accounts of the evolution of ideas and hypotheses concerning the genesis of ore mineralisation in the South Pennine Orefield. These hypotheses range from a magmatic source for the ore fluids to a hydrothermal origin with igneous heat drive, a sabkha-type derivation, precipitation by downward percolation of Triassic ground waters, formation by up-dip movement of saline connate waters, and a sedimentary-diagenetic model of

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origin. From a review of the proposed genetic models of ore deposition in the orefield, however, it is possible to deduce that:

(1) no direct evidence has been found of a genetic relationship between the ore mineralisation in the orefield and igneous activities, and advocates of the magmatic-hydrothermal theories can do no more than postulate the hypothetical existence of magmatic bodies beneath the orefield; and (2) in recent years, a number of authors have advocated, with some variations, a sedimentary-diagenetic model involving connate brines from the basins to the east and west of the orefield. Although the source of the brines which entered the orefield from the west is thought to be the Cheshire Basin (Ineson and Ford, 1982), there is some controversy on the possible source of the brines which penetrated the limestones of the orefield from the east. Ford (1976), for example, suggested the North Sea Basin as the possible source of these brines but Robinson and Ineson (1979) and Brown *et al*, (1980) pointed out that this proposal requires the brines to travel up-dip over a distance of at least 160 km with no significant heat loss. Alternatively, the basinal sediments in the Gainsborough, Edale and Widmerpool Gulfs were proposed as the possible source of the brines responsible for ore mineralisation in the eastern margin of the orefield (Robinson and Ineson, 1979). However, as noted by Ineson and Ford (1982), "the Somerton Borehole on the Norfolk coast ... encountered mineralised ground in the Carboniferous Limestone at a depth of over 1000 m", and this tentatively supports the proposal that the North Sea Basin could have been the source of brines derived from the east.

A Dinantian North Sea Basin is itself an unproven hypothetical concept and is a generalization of what may be a group of basins and swells, now deeply buried beneath thick Upper Carboniferous, Permian and Mesozoic sediments. The lack of deep drilling information on anything older than the Westphalian precludes anything more than this simplified concept, though the Westphalian (Coal Measures) undoubtedly accumulated in a wide basin in the southern North Sea.

The origin of the galena-sphalerite-fluorite-baryte-calcite deposits of the South Pennine Orefield is here proposed to be best explained by a multi-facet sedimentary-diagenetic model, which relates ore deposition in the orefield to the sedimentological development of the adjacent basins, together with a combination and modification of several genetic models, namely refluxing brines, original deposition of the host rocks and the metals, leaching and secretion of metals by upward moving brines, downward and horizontal movement of groundwater and a karstic model with secondary enrichment and transportation processes.

Evolution of sedimentary rocks and ore deposition

The historical evolution of any sedimentary rock can be divided into four distinctly different phases: (1) sedimentation (the sedimentary particles are transported to the basin or directly precipitated from seawater); (2) early diagenesis—unconsolidated sediments are either in direct contact with seawater or seawater can penetrate between the grains into the sediment; (3) late diagenesis (direct contact with seawater is lost but the sediments are saturated by formation waters): increased temperatures and chemical reactions (commonly collectively called "hydrothermal activity") between grains and formation waters are the prime factors in causing late diagenetic changes; and (4) uplift and weathering (strata are uplifted above sea level and are exposed to chemical and mechanical erosion). These phases could all simultaneously be in progress during the course of development of a sedimentary basin unless sedimentation is totally terminated, and often sedimentary basins show repetition of sedimentation-diagenesis-erosion cycles as the result of marine transgressions and regressions.

In Figs. 1, 2 and 5, the paragenetic relationships in the South Pennine Orefield are contrasted with corresponding phases of evolution of the enclosing host rocks.

Structural History

An interpretation of Bouguer gravity anomalies (Maroof, 1976) suggested that the Carboniferous sediments were deposited on a basement which has a graben structure in which the central block of the basement is down-thrown relative to the northern and southern blocks. By analogy with the basement beneath carbonate platforms elsewhere, Miller and Grayson (1982) have suggested that the Derbyshire Dinantian rests on a tilted fault block, with the downthrown side beneath the Staffordshire basin and a dip-slope falling eastwards beneath the limestone massif. This model has been supported by seismic studies (Rogers, 1983; McDonald, 1984), though refuted by Smith *et al.* (1985) on the basis of unspecified "confidential" geophysical evidence. Smith *et al.* have suggested a series of westward tilted blocks with a NW-SE trend crossing such Hercynian structures as the Longstone Edge monocline obliquely. Gutteridge's (1983) analysis of the sedimentary history and thickness variations of the later Brigantian beds in the Monyash-Lathkill area clearly supports the Miller & Grayson-

Rogers-McDonald interpretation. So little is known of the structure of the basement and its possible effects on later sedimentation and structures that it must be discounted in any study of mineralization for the present.

The predominant structural element of the orefield is the Derbyshire "Dome" which is an asymmetrical anticline with a flat culmination trending north-south near the western margin of the limestone outcrop. This anticline is really formed of the westward culmination of a series of easterly plunging folds within both the limestones and the younger rocks. Some folding developed during sedimentation of the Lower Carboniferous limestones as shown by the development of lagoonal and reef environments on the anticlines and shallow basinal environments in the synclines (Ford, 1977). The folds of the limestone have mainly E-W and NW-SE trends except in the extreme SW where folds trend N-S. Some folds and faults were active during Dinantian sedimentation, and may have relationships to basement faults. Compressional reverse faults are locally associated with east-west asymmetrical folding, whereas some normal faults may be related to post-folding relaxation (Worley, 1978; Butcher, 1976). Both compressional and relaxation faults appear to have been re-activated and extended during mineralization (Firman, 1977). Deeply buried NW-SE growth faults have been proposed by Smith *et al.* (1985) though without evidence.

Periodically during Dinantian times, volcanic activity resulted in the extrusion of vesicular basalt lava flows, tuffs and ashes, with a few associated vents and rare sills. These were folded along with the limestones during the Hercynian orogeny. The relatively impervious basaltic volcanic rocks locally controlled the disposition of individual mineral deposits. A further period of structural deformation affected the area in the Miocene when the Alpine Orogeny produced faulting and gentle folding in the region (Frost and Smart, 1979).

Sedimentation and Diagenesis

Phase I: Sedimentation

A deep borehole at Eyam in the eastern side of the orefield penetrated 48 metres of Ordovician (?Llanvirn) mudstones (Dunham, 1973; Strank, 1985; Aitkenhead et al. 1985). These Ordovician mudstones are the oldest known sediments in the area, and overlying them are more than 1.8 km of Dinantian sediments, mostly limestone but with a minor group of anhydrites, dolomites and shales at the base. Apart from the latter the limestones were deposited in an association of basin, lagoon and reef environments. The Dinantian tends to be thicker in the east of the exposed orefield than in the west because: (*a*) sedimentation started earlier in the east; and (*b*) the basement surface occurs at a greater depth in the east (Maroof, 1976; Rogers, 1983; McDonald, 1984). Sedimentation continued during Upper Carboniferous times and it is estimated that the orefield was covered by 1.3 to 2.3 km of Namurian (Millstone Grit) and Westphalian (Coal Measures) sediments (Worley, 1978). However the thickness of the Carboniferous sediments under the North Sea is probably greater and the Dinantian is more deeply buried (Ford, 1976). Although sedimentation was resumed after the Hercynian movements during Upper Permian and Triassic times with some deposition of carbonates and sandstones over the orefield, little is known of the thickness of these beds or of any later sedimentation during the rest of the Mesozoic era (Ford, 1977). A late Tertiary sheet of clays, sands and gravels covered the orefield and is now preserved only in karstic solution-collapse "pockets" in the Dinantian limestones. Walsh *et al.*, (1972) estimated that in Lower Pliocene times a stratigraphic sequence of approximately 53 metres of Mio-Pliocene sediments (Brassington Formation), a few metres of Namurian shales and an insoluble residue of chert gravel lay horizontally on top of the Dinantian limestones and then sagged into solution cavities (Walsh *et al.*, 1972; Ford, 1972). The Pleistocene period has also seen the deposition of screes, sands, gravel, loess and boulder clays over parts of the orefield.

At least four major periods of hiatus occurred in sedimentation: (1) if any sediments were deposited during Silurian times they were removed by erosion before the Dinantian; (2) toward the end of the Dinantian period, some erosion took place especially on the northern, western and southern margins of the present orefield before the Upper Carboniferous seas and deltas covered the area; (3) a period of erosion during Lower Permian times resulted in removal of much of the Upper Carboniferous cover; and (4) the Permian dolomites and Triassic sandstones were removed from the orefield by erosion during the early Tertiary period.

As noted by Kent (1966), both the Millstone Grit and Coal Measure sediments, and probably the Lower Carboniferous limestones, thicken into the Central (=Pennine) Basin which probably resulted in eastward migration of fluids out of the Pennine Basin towards the North Sea Basin during later Carboniferous times. However, the structural upwarping of the South Pennines by the Hercynian Orogeny "inverted" the basin and reversed this migration so that since the end of the Carboniferous the potential fluid migration path has been westwards out of the North Sea basin (Ineson and Ford, 1982) and its subsidiary Edale, Gainsborough and Widmerpool "Gulfs". Expulsion of metal-enriched saline formation waters during compaction has also been proposed as a source for ore fluids by Smith *et al.*, (1985).

Phase II: early diagenesis

Early diagenetic changes occur from the sediment-sea-water interface to a depth of a few hundred metres (Berner, 1980). The more important changes include formation of framboidal pyrite, lithological changes and bacterial decomposition of organic matter.

Experimental studies and field observations (Sweeney and Kaplan, 1973; Farrand, 1970; Love, 1967; Park, 1967) show that microscopic metal sulphides, and especially framboidal pyrite, can form during early diagenesis even before compaction at the sediment-water interface, as the result of precipitation of metals in pore waters by sulphur supplied by decomposition of organic matter possibly by sulphur-reducing bacteria. The organic compounds in recent sediments play a key role in the formation and preservation of framboids in sedimentary environments (Farrand, 1970). Therefore the formation of framboids and small grains of pyrite should be considered the first stage of sulphide deposition in sedimentary rocks.

One of the important diagenetic changes of the calcareous sediments in the orefield is the formation of bedded chert and chert nodules in the Dinantian limestones. Chert formation is thought to be the result of siliceous organic activity (Wise and Weaver, 1974) and in the orefield it formed during the earlier phases of diagenetic evolution (Orme and Ford, 1970). Another important lithological change of the sediments deposited in the orefield is the transformation of unstable aragonitic mud and fossils into stable calcite during early diagenesis which is accompanied by partial expuslion of base metals (Ferguson *et al.*, 1975) and barium and fluorine from aragonite (Worley and Ford, 1977). Dolomitisation of the calcite mud is also accompanied by expulsion of metallic elements into formation waters and results in loss of volume and development of secondary porosity in limestones which may provide a favourable environment for precipitation of ore minerals.

Towards the end of the early diagenesis phase, sediments start to lose both their free formation waters and some absorbed waters (Wolf and Chilingarian, 1976) as the result of reduction in initial porosity of sediments due to compaction. Movement of the formation waters results in reactions which may cause precipitation of cementing materials between grains. These reactions involve dissolution, replacement and recrystallisation processes. It should be noted that, although the direction of compactive pore water movement during the early diagenetic phase is mainly vertical, as the depth of burial increases it may also have a lateral component to where permeability is higher (Berner, 1980).

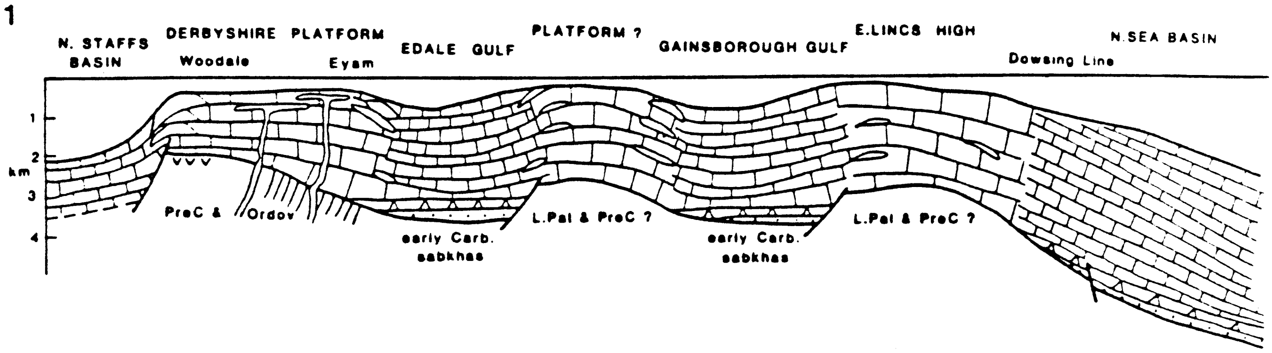
The most important diagenetic addition to the sediments deposited in the orefield was the formation and accumulation of hydrocarbons in these sediments, especially in the limestones (Pering, 1973). Many oil "shows" have been encountered in the colliery workings in the areas surrounding the orefield (Frost and Smart, 1979), and oil and gas have been discovered in commercial quantities in both Upper Carboniferous sediments and near the top of the Dinantian limestones (Smith *et al.*, 1967). The hydrocarbons are mostly present in the orefield in the form of asphalts, bitumen, pitch, or thick, heavy and unconsolidated oil. These hydrocarbons are sometimes localised in the limestones but often they are disseminated through the pore spaces of the carbonate rocks either in the matrix or as bonding material (Pering, 1973). Although the decomposition of organic matter results in formation of low-molecular-weight hydrocarbons during the early diagenesis phase, the transformation and thermal maturation of these hydrocarbons into polyhydrocarbons (petroleum) takes place during the late diagenesis phase (Hitchon, 1977; Bailey, 1977).

Phase III: late diagenesis

The late diagenesis phase is characterised by the slow compaction and maturation of sediments that results from overburden and hydrostatic pressures. It begins at a depth of a few hundred metres and continues to where sediments become completely lithified. Compaction results in concomitant expulsion of connate formation waters and will cease only when the sedimentary rocks are able to support the weight of the overlying sediments, and withstand hydrostatic pressures by their internal stability. Increase in depth of burial after this point results in initiation of metamorphism due to higher burial temperatures. After lithification, significant reduction in volume of these rocks may occur as the result of stylolitisation in consolidated carbonate rocks.

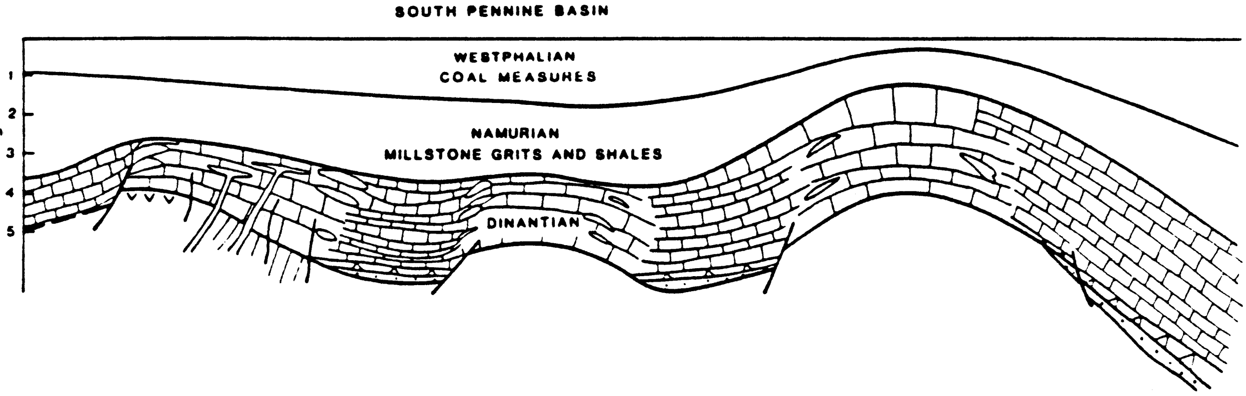
Due to differential depth of burial the compaction forces nearer the centre of sedimentary basins are greater than those nearer the margins and formation water expelled from the sediments is thought to move generally both upward and outward to zones of lower pressure (Ohle, 1959) carrying with it droplets of oil and gas (Beckmann, 1976). During this movement, which may cover hundreds of kilometres (Beckmann, 1976), formation water can become enriched in metals and other ingredients essential for ore mineralisation. In order to derive these ingredients from consolidated sedimentary rocks, Noble (1963) concluded that the fluids must be able to penetrate the rocks, be sufficiently reactive to leach metals and be able to move out of the leached rocks. During the late diagenesis phase formation (connate) water is already in the sedimentary units, in a position to leach individual particles, and is expelled as a natural consequence of compaction. Pre-compaction leaching of sedimentary units is probable because the chloride, sulphate and carbonate characters of the connate waters make them solvents for the ingredients needed in ore mineralisation. Thus, connate waters can be regarded as ore-forming fluids during the compaction of sediments.

1



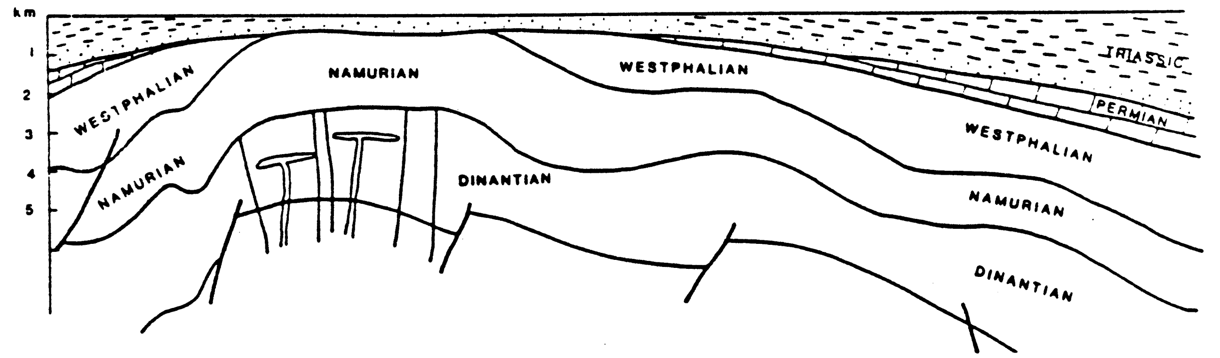
1. LOWER CARBONIFEROUS-SEDIMENTATION PHASE: deposition of a thick sequence of Dinantian limestones with anhydrite beds at the base developed particularly in "gulfs" between positive "highs"; formation of chert and dolomite in buried limestones; initiation of folds and faults bounding highs; episodic changes of sea level with alternating marine transgressions and regressions resulting in contrasting lithofacies of massive limestones on highs, marginal reefs, and shaly thin limestones in gulfs. Local eruption of lavas and tuffs within limestone sequence.

2



2. LATE CARBONIFEROUS-EARLY DIAGENESIS PHASE: deposition of a cover of thick Namurian Millstone Grit deltaic sandstones and shales followed by Westphalian Coal Measures swamp sediments. Thicknesses of clastic cover greatest in South Pennine and southern North Sea Basins. Early diagenesis in limestones yields framboidal pyrite and possibly other sulphides, particularly well-developed in basinal facies of gulfs. Petroleum formation is initiated and migration towards highs begins with loss of sediment formation waters. Volume reduction in sediments.

3



3. PERMO-TRIASSIC-LATE DIAGENESIS PHASE: partial removal of part of Westphalian and Namurian cover during structural inversion yielding South Pennine anticline, followed by dolomitic and clastic sedimentation in upper Permian and Triassic times. Hydrocarbons matured; movement of hydrocarbons and connate/formation waters to low pressure zones. Separation of hydrocarbons and connate waters towards basin margin where they are trapped beneath remaining Namurian cover. A front of liquid hydrocarbons is followed by ore-fluids depositing minerals in fracture systems and other voids; hydraulic fracturing re-opens wrench faults giving vein deposits; local fluoritization of host limestones; further volume reduction and compaction of sediments.

Fig. 1. Stages 1, 2 and 3 in the geological evolution of the South Pennine Orefield (see also Fig. 5, p. 220).

Maturation and accumulation of hydrocarbons

Hydrocarbons continue to form and mature during the late diagenesis phase. The maturation of hydrocarbons is largely a temperature-dependent phenomenon which occurs within a "liquid window" between the approximate temperatures of 60 to 150°C (Bailey, 1977; Macqueen and Thompson, 1978; Pudsey, 1973). During the primary migration (movement of fluids and hydrocarbons from a source sediment to a reservoir rock owing to compaction), hydrocarbons have similar outward and upward flow patterns to those of connate waters (Hunt, 1979). Price (1976) has shown that hydrocarbons and connate waters can exist, initially, as a single phase at high temperatures, but on raising the salinity, or decreasing the temperature, hydrocarbons will exsolve from solution. The ability of hydrocarbons to migrate also increases as increasing temperatures convert solids to liquids and liquids to gases (Hunt, 1979). Therefore, as the connate waters increase their salinity, and decrease in temperature on upward and outward migration, hydrocarbons, maturing at different depths in the sedimentary succession, would be separated, collected and, because petroleum is lighter than connate waters, pooled in front of the advancing connate brines. Hydrocarbons move in response to compactional and hydrostatic pressures supplied by connate brines. Eventually, the upward movements of these pools are stopped by stratigraphical and/or structural traps and oil and gas reservoirs accumulate within reservoir rocks (secondary migration; Hunt, 1979).

In the South Pennine Orefield the advancing hydrocarbons and connate brines were stopped by Edale Shales overlying the Dinantian limestones. Eventually, most of the hydrocarbons either moved upward along faults and fractures of the overlying rocks until they reached the surface and became oxidised, or, as the cover of the limestones was removed by erosion, they were exposed to oxidation and escaped into the atmosphere. Some of the hydrocarbons were trapped in both limestones and the overlying Upper Carboniferous sandstones where they formed small oil and gas reservoirs. The heavy fraction of the hydrocarbons formed bitumen deposits in the pores and cavities of the limestones especially below the Dinantian-Namurian boundary. The thermal alteration and oxidation of hydrocarbons also resulted in formation of scattered black bitumens in the orefield, especially within some ore deposits. The hydrocarbons in fluorites from the orefield are very similar in composition to those of hydrocarbons in the Edale Shales and the Dinantian limestones. This is consistent with mixing of the hydrocarbons from both sedimentary units, prior to crystallization of fluorite (Pering, 1973). Thus, both Dinantian limestones and the Upper Carboniferous Edale Shales were probable source rocks for hydrocarbon generation in the region including the orefield (Pering, 1973; Nooner *et al.*, 1973). Whilst it is difficult at first sight to see how the Edale Shales could form a cap-rock in the South Pennines and at the same time be the source rock, the same shale formation can do both if it is much more deeply buried and thus more matured in the basins to the east. Also, if stratigraphic "inversion" is taken into account, it may be that there has been a "two-pass" situation with the Edale Shales in the Pennine Basin being a source rock during later Carboniferous times, whilst their equivalents in the North Sea became the source rock in post-Carboniferous times. If the Dinantian lithofacies are more argillaceous in the deeper basins in contrast to the Derbyshire massif (as yet unproven by deep borings) then a single-pass contribution to hydrocarbon and ore-rich fluids could have occurred in post-Carboniferous times as a result of the Hercynian pressures.

As matured liquid hydrocarbons moved to low pressure zones at basin margins (i.e. the South Pennine Orefield) in front of the advancing connate brines, they were able to supply sulphur species for ore mineralisation. Pering (1973) found that "elaterite", a bitumen complex present in joints and fissures of the Dinantian limestones, contains 0.47 percent elemental sulphur. The black and brown bitumens from the Windy Knoll bitumen deposit in the north of the orefield also contain 1.01 and 1.64 percent sulphur, respectively (Pering, 1973). Additional elemental sulphur, produced by bacteria, could also have been generated in significant quantities in the Carboniferous sediments. Since hydrocarbons reached the orefield before the connate brines, they could have been retained within the sediments. Sulphur liberated from these hydrocarbons as H_2S would have enabled sulphide and sulphate minerals to precipitate from the metalliferous connate brines as these followed the same path taken by the earlier hydrocarbons. Being covered by thick shales, the carbonate rocks have the potential to trap both hydrocarbons and H_2S and this is considered to be a major factor controlling precipitation of sulphide minerals in carbonate environments (Beales and Jackson, 1968).

Depth of burial and palaeotemperature

The limestones of the orefield were covered by between 1.3 to 2.4 km of Namurian and Westphalian sediments prior to erosion during Lower Permian. The present thickness of the Dinantian sediments at Eyam on the eastern margin of the orefield is about 1.8 km (Dunham, 1973) and therefore, before Permian erosion, the lower beds of the Dinantian in the eastern side of the orefield were buried by up to 4.2 km of Carboniferous sediments, and later had about 1 km each of Permian and Triassic covers, so that by the end of Triassic times there could have been 6 km of cover on the Dinantian. These estimates are mostly based on the thicknesses of the

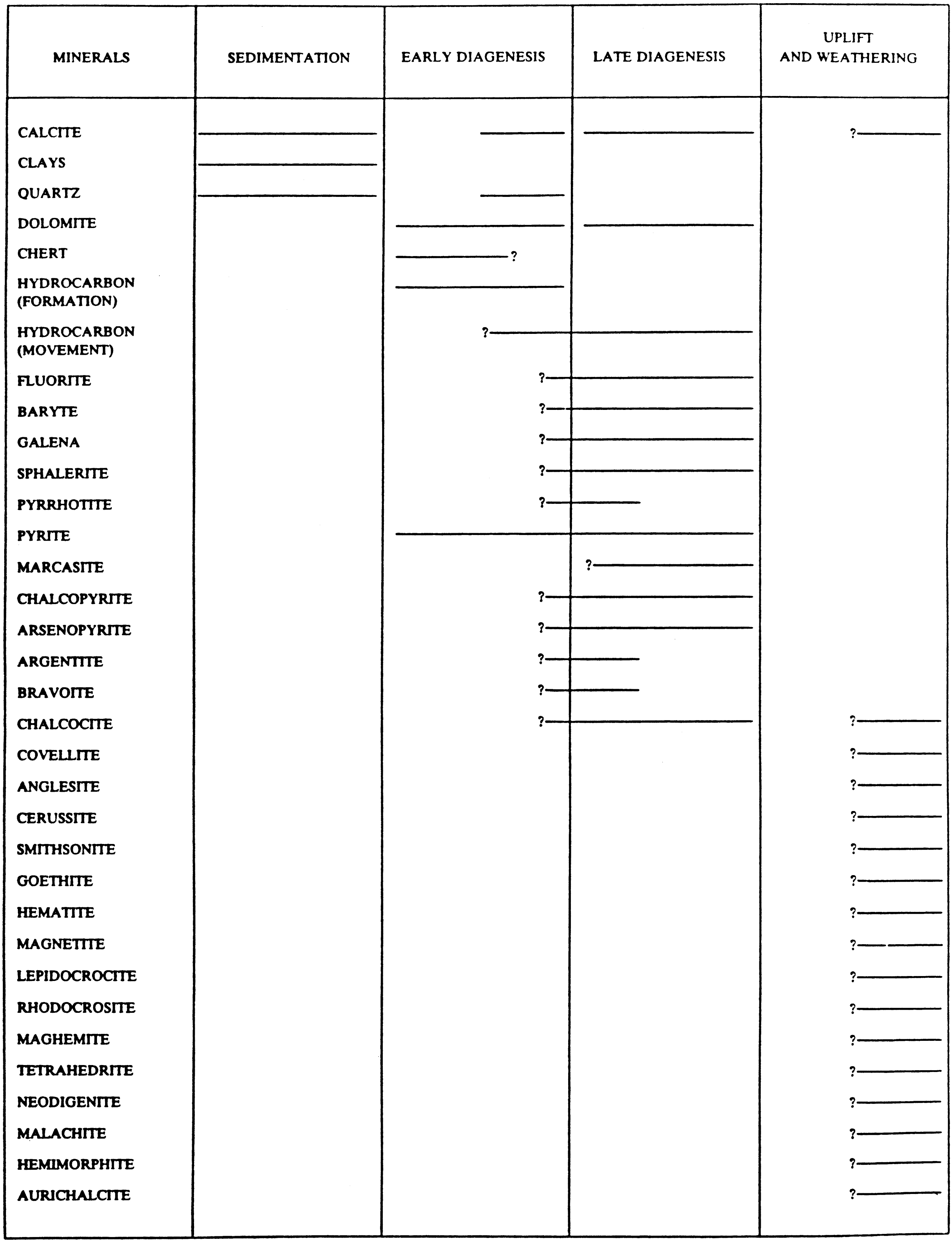


Fig. 2. Paragenesis of minerals, and hydrocarbon accumulation, in the South Pennine Orefield, as a function of evolution of the enclosing Lower Carboniferous strata.

lithified sedimentary units and should be adjusted to allow for the compaction and late diagenetic changes which occurred in all these units. These are loss of pore waters, dehydration of clay minerals as the result of progressive conversion of illite-poor mixed-layer illite/smectites to illite-rich mixed-layer illite/smectites, dissolution, cementation, dolomitisation and stylolitisation (Mostaghel, 1984).

Of these changes, stylolitisation is perhaps the most important one and can acount for as much as 50 percent reduction in volume of carbonate rocks (Glover, 1968). The carbonate rocks of the orefield contain numerous stylolites and microstylolites and the clay wayboards in the Carboniferous sediments are very rich in illite with 10 to 30 percent smectite (Walkden, 1972). If all the compaction and diagenetic changes produced a 25 percent loss of volume in the sedimentary column, then the depth of burial at the end of Carboniferous of the base of the Dinantian would be greater than 5 km in the eastern side of the orefield and considerably more in the North Sea.

Geothermal gradients of 7.3 °C/100 m in the uppermost least compacted sediments and 1.8 to 3.5 °C/100 m in the deeper buried sediments have been reported in the northern North Sea Basin (Cooper et al, 1975). A geothermal gradient of 2.5 °C/100 m for the whole sedimentary succession in the late Palaeozoic—early Mesozoic period would have resulted in connate waters, originating in or migrating from the Dinantian limestones under the North Sea having temperatures of more than 150 °C assuming a 6 km cover by the end of Triassic. These connate waters, moving upward and outward from the centre toward the basin margins, could have maintained a higher temperature than the host rocks at the sites of ore deposition in the orefield, if the rates of heat exchange to the walls of the migration paths were low. Also, additional heat may have been added by diagenetic chemical reactions governed by the first part of the Van't Hoff Law (Fairbridge, 1967), long-lived isotopes (Brown *et al.*, 1980), and exothermic biogeologic reactions involving bacteria and algae. Therefore, the formation temperatures of the ore minerals, estimated to range between less than 50 up to 150 °C (Mostaghel, 1984; Rogers, 1977; Smith, 1973; Atkinson, 1983; Atkinson et al, 1982) could have been achieved by a combination of "normal burial" temperatures and diagenetic, exothermic reactions.

Ore mineralisation

The model favoured by the authors is that during migration connate waters become enriched in salts as well as Pb, Zn, F and Ba. These essential ingredients of ore mineralisation became available as the result of leaching of different lithological units. The fluids were generated by expulsion of formation waters during compaction of sediments and clay dehydration of the shale units in the succession. The dominant salt components in the ore fluids were calcium and sodium chlorides (Atkinson, 1983). As the ore fluids reached the orefield, the ore minerals precipitated behind the preceding front of liquid hydrocarbons. The main controls of ore minerals are difficult to establish due to the episodic nature of ore mineralisation were structural, stratigraphical and lithological (Firman and Bagshaw, 1974). Faults, fractures, joints and stylolite seams provided channelways for migration of ore fluids. The effectiveness of the Upper Carboniferous Edale Shales, which overlie the Dinantian limestones as a cap-rock, has resulted in concentration of the ore minerals in the limestones and dolomites though not always in the highest carbonate beds. Although the precise paragenetic sequences of the ore mineralisation in the orefield and large local variations, the generalised regional paragenetic sequences indicate the following phases of ore deposition: early calcite-baryte-fluorite followed by the main phase of galena-sphalerite-iron and copper sulphide mineralisation followed by late calcite-baryte-fluorite precipitation (Mostaghel, 1984).

The ore fluids penetrated the orefield from two directions; one from the east, i.e. from the North Sea Basin, which was responsible for major and prolonged episodes of fluorite-baryte-calcite-galena-sphalerite mineralisation in the eastern and central parts of the orefield. Other fluids entered the orefield from the west and were responsible for localised mineralisation of lead, zinc and copper sulphide ore bodies in the western part of the orefield. These fluids are thought to have come from the Cheshire-Irish Sea Basin. In terms of metal concentration, copper was the dominant component in the fluids from the Cheshire-Irish Sea Basin whereas lead had a far greater concentration than the other metals in the fluids from the North Sea Basin. The ore fluids may have been responsible for reopening, by hydraulic fracturing, of pre-existing primary and secondary wrench faults (Firman, 1977). The precipitation of ore minerals from these fluids in faults and fractures resulted in formation of the rakes and scrins which form a substantial part of the ore mineralisation in the South Pennine Orefield. It is generally believed that chloride complexes are the most important transporting agents for metals under the conditions of formation of the ore deposits in the South Pennine Orefield (Anderson, 1975).

The ore mineralisation in the South Pennine Orefield was not the result of a single "surge" of ore fluids but the result of at least a partial two-pass migration system resulting in several separate episodic pulses of ore-forming solutions (Ineson and Al-Kufaishi, 1970; Ineson and Mitchell, 1973). The episodic expulsion of fluids may account for some mineral banding and, since episodic dewatering would be accompanied by a higher flow rate, variable and higher temperature of ore fluids in near-surface sites of ore deposition.

Source of metals

Although no systematic study has been made of metal concentration in the Carboniferous rocks, Monteleone (1973) found between 5 to 6560 ppm Ba and up to 1205 ppm Pb and 416 ppm Zn in 56 Carboniferous limestones from Leicestershire. Burek and Cubitt (1979) reported mean values of 15 ppm Pb and 209 ppm Zn in 15 dolomitic limestones and 31 ppm Pb and 16 ppm Zn in 15 limestone samples.

Harrison and Adlam (1985) summarized many hundreds of analyses as a mean Pb content of 17 ppm, range 0 to 2000, in non-dolomitized limestones, and a maximum of 10100 ppm in dolomitized beds, and a mean Zn content of 40 ppm, range 0–1750 ppm, in non-dolomitized beds, maximum 3800 in dolomitized beds. Values were highly variable between stratigraphic units and lithofacies with no clear pattern: the very high values in dolomites may reflect local dispersed ore deposits. In any case the values should not be taken to represent original concentrations of metals in the sediments owing to diagenetic redistribution.

By using a figure of 4 km for the average thickness of the Carboniferous sediments in the orefield and the western part of the North Sea, the volume of these sediments in an area 40 km long (the length of the orefield) and 300 km wide (from the centre of the orefield to the North Sea Basin in the east) is equal to $48\times10^3\,km^3$. By using an average density of 2.5 for all the rock types, the mass of these sediments in this area is 12×10^{13} metric tons. If this mass contains 10 ppm combined Pb and Zn, 12×10^8 metric tons of metal are present. If only 10 percent of the metals present in this mass was leached by connate waters, 12×10^7 metric tons of metal could be available for transportation to the sites of ore deposition. If 10 percent of this metal in solution actually precipitated, then 12×10^6 metric tons of metals (not sulphides) would have been formed in the orefield. The values used in these calculations are conservative and probably underestimates but they are realistic; thus the calculated tonnage of precipitated metals is almost 3 times the maximum estimated tonnage of extracted lead and zinc concentrates from the orefield.

Volcanic activities during the Carboniferous could also have enriched the metal concentration of the Carboniferous sea and the alteration of the igneous rocks in the orefield probably resulted in the release of some metals. Another possible source of metals is from the numerous tuff horizons deposited between the limestone beds (Walkden, 1972). Ineson (1970) reported a tuff horizon in Ladywash Mine containing on average 175 ppm Pb and 2500 ppm Zn.

Sources of sulphur

Sulphur isotope studies have shown that sulphur in galena, sphalerite and baryte was derived from more than one source (Coomer and Ford, 1975; Robinson and Ineson, 1979). Galenas from the South Pennine Orefield have sulphur isotope composition of −23.2 to 6.6‰ whereas the analysed sphalerite and baryte samples show a spread of −16.0 to 9.5‰ and 4.4 to 2.6‰, respectively. The observed sulphur isotope spread in the galenas is interpreted to be the result of mixing of biogenic H_2S (low sulphur isotope values) with H_2S derived from the reduction of sulphate (Robinson and Ineson, 1979). The sulphur isotope composition of baryte is also consistent with partial mixing of fresh-water sulphate and connate sea-water sulphate (Robinson and Ineson, 1979).

Anderson (1975) concluded that mixing of metal-ion solutions with reduced-sulphur species, supplied at the sites of ore deposition, caused the precipitation of sulphide ore assemblages. Reduced sulphur could be supplied by inorganic or bacterial reduction of sulphate, thermal degradation of hydrocarbons, and replacement of pre-existing sulphides (Anderson, 1975). In the South Pennine Orefield different generations of reduced sulphur were formed at shallow depths in the orefield and at greater depths in the North Sea which later moved to the orefield with migrating hydrocarbons. Additional sources of sulphur could have included localised sulphur and sulphate deposited with the sediments and biogenic production of sulphur in limestones during hydrocarbon generation. Mixing of sulphur from different sources, which have different isotopic ranges, with some isotopic disequilibrium and secondary exchanges can best explain the heterogeneity of the sulphur isotope compositions of the minerals in the orefield.

Smith *et al.*, (1985) have revived Llewellyn and Stabbins' (1968) hypothesis of a sulphate source in evaporitic beds in sabkha facies at the base of the Dinantian sequence particularly in the down-faulted troughs of the tilted fault-blocks. However, as the Eyam borehole (Dunham, 1973) shows that the anhydrite beds are still in place it is difficult to see how they could have been the source. If early Dinantian evaporites in the deeper and more highly matured basins to the east are postulated the problem may be resolved, but there is no direct evidence as yet.

Volume of ore fluids

Atkinson (1983) calculated that for an estimated 20 million tons of fluorite which formed in the orefield 17.38×10^3 km^3 of fluids containing 1 ppm CaF_2 are required. If the calculated volume of Carboniferous sediments in the orefield and the western part of the North Sea basin (48×10^3 km^3) contained, on average, 10 percent formation waters, then only 4.8×10^3 km^3 of fluids would have been released. The discrepancy between these two calculations becomes smaller if it can be shown that: (*a*) the calculated volume of sediments was greater than 48×10^3 km^3; (*b*) the volume of formation waters released from these sediments was greater than 10 percent; or, more likely, (*c*) the concentration of base metals, barium and fluorine in these fluids was greater than 1 ppm. If the fluids contained 10 ppm Pb, Zn, Ba and F then less than 2×10^3 km^3 of fluids are required to form the ore deposits in the orefield. In the sedimentary basin evolution model for carbonate-hosted lead-zinc deposits, unlike convecting heated brine models postulated for ore deposits such as volcanogenic massive sulphides, the ores are formed by fluids in a "one-pass" situation (Anderson, 1978). Therefore, since the ore-forming fluids have limited reservoirs (i.e. the basinal formation waters), they must have higher concentration of metals and be able to precipitate their minerals effectively when passing through a depositional site.

Causes of mineral deposition

The major causes of precipitation of galena and sphalerite in the orefield were fluid mixing and dilution (as deduced from the heterogeneity of the sulphur isotope compositions of sulphide minerals), decrease in temperature (due to upward movement of the ore-forming fluids from the deeper areas of the basin to the positive structures on the margins), and increase in reduced sulphur (supplied in the orefield by hydrocarbons, trapped H_2S in limestones, and in situ reduced sulphur and sulphate). The causes of fluorite precipitation and localisation may have included: (*a*) decrease in temperature in the flow direction; (*b*) availability of both calcium and fluorine ions; and (*c*) suitable depositional environments. However, the distribution and precipitation of baryte in the orefield was very much dependent on the availability of *in situ* sulphate-rich fluids (Firman and Bagshaw, 1974). The irregular distribution of calcite in the orefield (Mostaghel, 1983) may have been the result of precipitation of this mineral from fluids which were super-saturated with respect to calcium carbonate introduced by dissolution of the limestone host rocks.

Some general observations regarding the conditions of ore precipitation in the orefield can be made by calculating the thermodynamic behaviour of standard reactions between specific pairs of minerals (cf. Vaughan and Ixer, 1980).

A promising method is sphalerite geobarometry wherein the mole percent concentration of iron in sphalerite as seen in pressure/composition phase diagrams of minerals forming in the Fe-Zn-S system can be used to estimate the formation pressure of sphalerite but this is dependent on the sphalerite being demonstrably in equilibrium with pyrite and pyrrhotite.

It is, however, possible to define the limits of the physical conditions by using the presence or absence of certain mineral species in the orefield, as well as thermochemical data of different Fe minerals and the iron content of sphalerite from the orefield (Figs. 3 and 4).

Using these criteria, the shaded areas indicate the theoretical conditions under which sphalerite precipitated in the South Pennine Orefield. Figs. 3 and 4, based on Vaughan and Craig (1978) and Vaughan and Ixer (1980), can also be used to deduce the optimum chemical conditions at different temperatures; in particular, taking points in the centres of the shaded areas the sulphur and oxygen activities at 100 °C, during ore precipitation in the orefield, are estimated to be $10^{-22.7}$ atm and 10^{-58} atm respectively. For a temperature of 150 °C, the activities are somewhat higher: aS_2 is 10^{-19} atm and $a0_2$ is 10^{-50} atm. Fluid inclusion studies on gangue minerals (Rogers, 1977, Atkinson, 1983) suggest that most of the sulphides in the orefield precipitated between 100 and 150 °C and thus these calculations were performed only for this temperature range. The activity of CO_2 is estimated to be 10^{-3} atm at 100 °C and $10^{-1.5}$ atm at 150 °C (Fig. 4). These conditions are comparable with those in the North Pennine orefield (Vaughan and Ixer, 1980, Fig. 4).

Whilst these calculations place constraints on the conditions at the time of sphalerite precipitation, much more work is needed before the conditions of precipitation of other minerals can be similarly constrained.

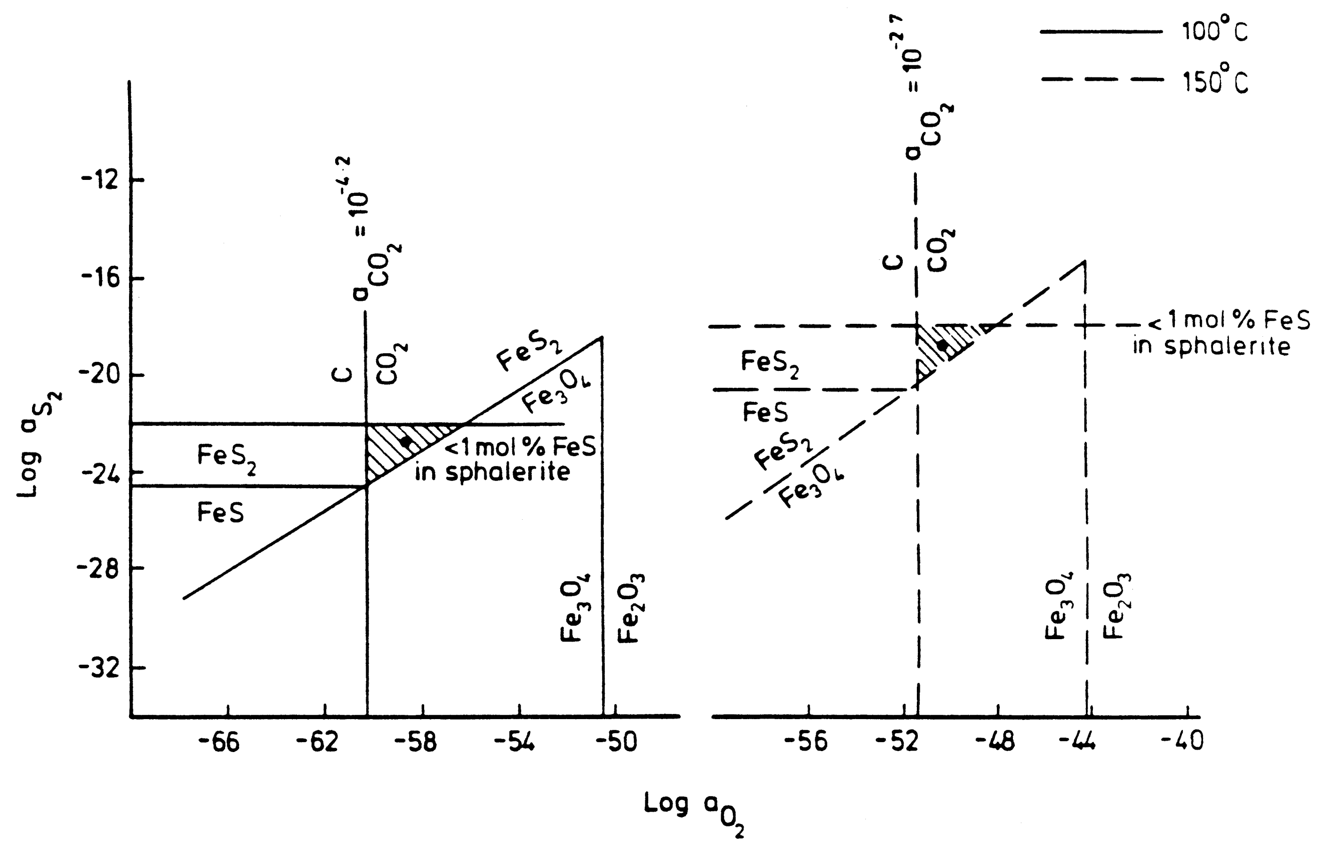


Fig. 3. Plots of Log a_{S_2}−Log a_{O_2} for the South Pennine ore assemblages at 100 and 150 °C (based on Vaughan and Craig, 1978, fig. 10.10). The shaded area constrains the conditions of precipitation of sphalerite in the South Pennines.

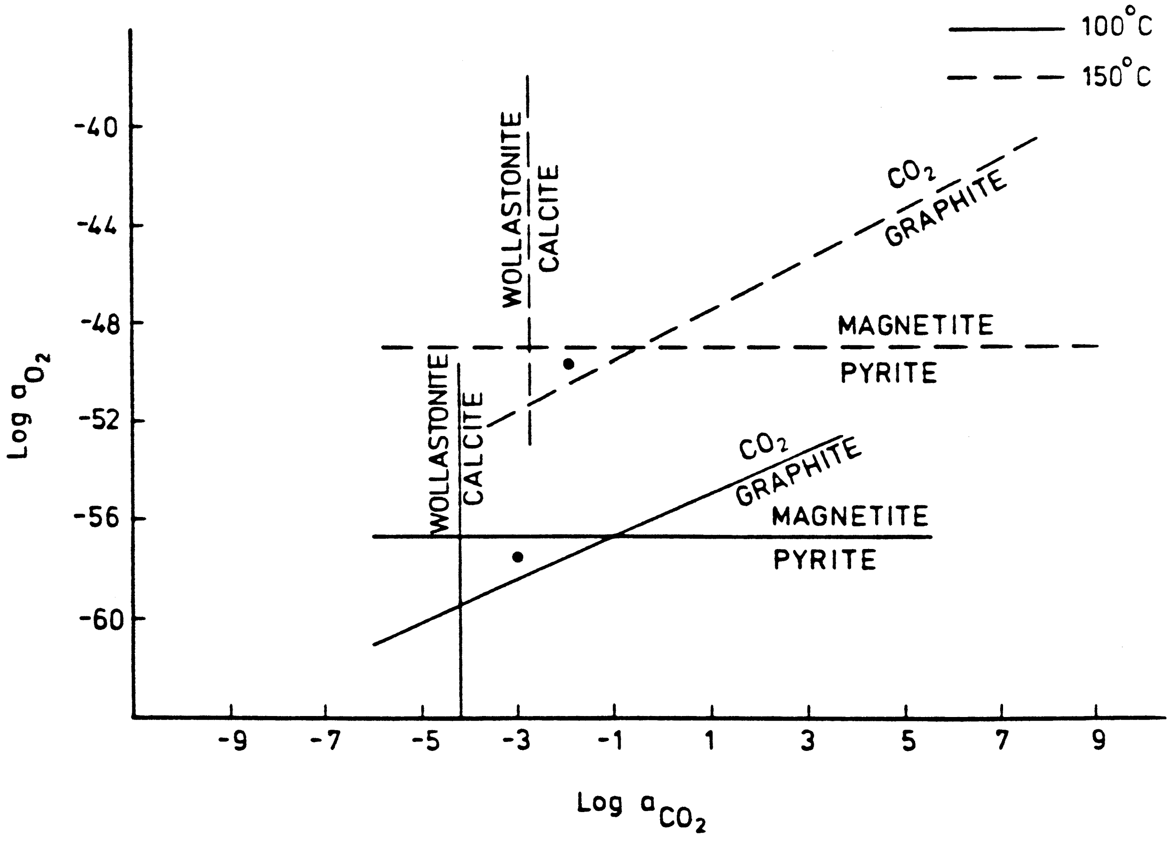


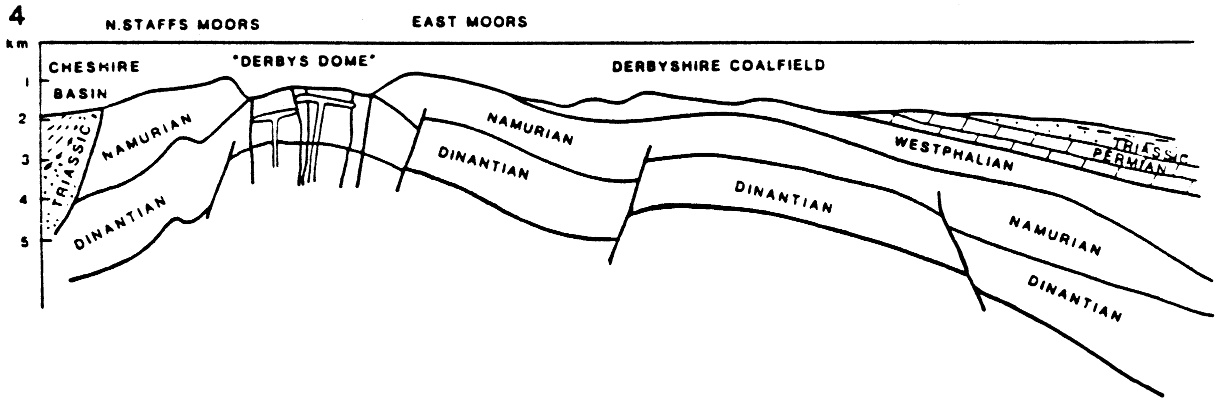
Fig. 4. Plots of Log a_{O_2}−Log a_{CO_2} for the South Pennine ore assemblages at 100 and 150 °C (based on Vaughan and Craig, 1978, fig. 10.10). The triangles with black spots indicate the conditions of precipitation of calcite and pyrite in the South Pennines.

Timing of ore mineralisation

A study of lead isotope ratios in galenas from the orefield has shown that the lead in these galenas is anomalous J-type and gives negative ages (Coomer and Ford, 1975). Isotope studies of metasomatised Carboniferous volcanic rocks have indicated that primary ore mineralisation (hydrothermal alteration of the basalts in the orefield) started at 290 million years before present in association with the Hercynian Orogeny and was followed by subsequent hydrothermal events at 280–265, 225, 170 and 130 m.y. before present (Fitch *et al.*, 1970). Ineson and Mitchell (1973) reported K-Ar dating of 34 samples of clay minerals, formed as the result of alteration of wall rock by mineralising fluids. The results showed ages from about 280 to 180 m.y. before present with major activities in early and late Permian and continuing activity to late Triassic. Therefore, it seems the ore mineralisation in the orefield started shortly after the Hercynian tectonic movements structurally "inverted" the orefield and continued intermittently into late Triassic times.

Phase IV: uplift and weathering

The host rocks in the South Pennine Orefield have been going through the final phase of evolution for some considerable geological time. The surface erosion and weathering phase starts when sedimentary rocks are uplifted above sea level and exposed to chemical and mechanical weathering. The most important characteristic of this phase is downward percolation of meteoric waters in permeable zones which results in internal chemical weathering of rocks, especially in carbonate rocks. The carbonate rocks in the orefield were exposed to weathering processes during at least some of the non-depositional periods (mid-Carboniferous, Lower Permian, earliest Triassic) and, almost continuously, since the late Mesozoic. Some of the groundwaters and springs in the orefield are considered to be thermal waters though with temperatures of less than 30 °C (Edmunds *et al.*, 1969). The higher than normal temperatures of these waters may be due to mixing of near surface meteoric waters with heated connate brines being expelled at the present time from the sediments beneath the Southern North Sea Basin (Ineson and Ford, 1982) or, as the result of long-lived isotopes and the high surface heat flow in the orefield (Brown *et al.*, 1980), the meteoric waters are heated to temperatures of around 30 °C without deeply circulating in the Dinantian limestones. The circulation of meteoric waters in the limestones has resulted in development of extensive cave systems in these rocks. Some of these cave systems, which probably had their initial developments during the first period of the Dinantian erosion in mid-Carboniferous times, provided palaeokarstic depositional sites for ore minerals that were precipitated from connate waters during the late diagenesis phase (Ford, 1977, 1984).



4. JURASSIC-HOLOCENE-UPLIFT AND WEATHERING PHASE: following limited cover by Mesozoic sediments these were removed as a result of mid-Tertiary renewal of uplift. Late Tertiary thin cover of Brassington Formation sand and clays, followed by further uplift. Development of karstic features; downward movement of meteoric waters and formation of secondary oxidized minerals, with transportation and deposition of derived minerals in caves etc. Late fluid expulsion from North Sea Basin establishes thermal springs.

Fig. 5. Stage 4 in the geological evolution of the South Pennine Orefield.

As far as the ore minerals in the orefield are concerned, the circulation of meteoric waters in the Dinantian limestones has resulted in: (*a*) formation of secondary alteration minerals (Fig. 5); (*b*) physical transportation of some minerals, especially fluorite and galena, with re-deposition in the residual sediments of some cave systems; (*c*) formation of secondary dispersion patterns of elements, derived from the ore deposits in the Dinantian rocks, in soils and superficial deposits on the orefield (Burek and Cubitt, 1979); and (*d*) leaching of the ore minerals and the host rocks which has a considerable effect on the chemistry of groundwaters near mineralised areas. Some limited transportation and re-deposition of ore minerals has resulted in minor residual and alluvial ore deposits at a few locations in the orefield.

Conclusions

It is proposed that the ore-forming fluids of strata-bound carbonate-hosted Pb-Zn deposits, such as those in the South Pennine Orefield, were formed as the result of interaction of many processes taking pace during the diagenesis of both their source and host rocks.

The Dinantian and early Namurian rocks of the Central Pennine Basin were deeply buried by late Carboniferous times with resultant expulsion of some formation water during diagenesis, but a stratigraphic inversion as a result of Hercynian tectonics made the formation waters from much more extensive, deeply buried and matured equivalent strata in the North Sea Basin and associated Gulfs available as ore-fluids, migrating to the basin margin in the South Pennines. Thereby a "one-pass" Carboniferous fluid became a more enriched "two-pass" fluid by Permo-Triassic times.

The ore minerals could have been precipitated in three stages: (*a*) as early generations of base metal sulphide during the early diagenesis phase which either remain preserved or broken down in later stages of sedimentological evolution of the enclosing rocks and provide additional sources of metal and sulphur; (*b*) during the late diagenesis phase when the main phase of ore mineralisation took place by episodic upward and outward circulation of heated saline connate brines generated by release of formation waters during compaction of sediments and clay dehydration; and (*c*) during the uplift and weathering phase when secondary alteration minerals were formed and some minerals from pre-existing ore deposits were transported by the groundwater circulatory system and re-deposited in residual sediments of some karst depressions and cave systems. The essential conditions for ore mineralisation include: availability of different ions in sufficient concentration for low-temperature ore deposition; availability of sulphur and sulphate species in the sites of ore deposition; an appropriate temperature range of 50 to 150 °C for thermal maturation of hydrocarbons and ore deposition; an appropriate depth of burial; suitable depositional sites and channelways in the host rocks; regional and local structural and lithological controls; availability of transporting agents for different ions and sulphur; presence of factors causing precipitation of ore minerals and a large source area for leaching of metals and decomposition of organic matters. The absence of these conditions would result in barren carbonate rocks.

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