Controls on mineralisation in the Cadeby formation (lower magnesian linestone)

Thesis

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CONTROLS ON MINERALISATION IN THE
CADEBY FORMATION
(LOWER MAGNESIAN LIMESTONE)

by

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Val II

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PART III

MINERALISATION
Part III

MINERALISATION

IIIA INTRODUCTION

Mineralised localities and brief descriptions of the mineralisation in the research are given in Appendix 1. Distribution of the localities is shown in Figure Al.1. Additional research on mineralisation in the Raisby Formation (lower Zl carbonate) of County Durham was carried out for comparative studies. Durham localities mentioned in the text are given at the end of Appendix 1.

In Part III of this thesis Chapter 8 describes the mineral assemblages and their association, if any, with host facies and their emplacement relative to diagenetic history. Chapter 9 contains evidence from stable and lead isotope determinations and Chapter 10 includes influences from the pre-Permian basement. Conclusions are in Chapter 11.

IIIB METHODS

Methods used in addition to those detailed in Part II are sulphur, carbon, oxygen and lead isotope determinations and attempted fluid inclusion studies. Sample preparation for stable isotopes, sample preparation and mass spectrometer operating conditions for
lead isotope determination are in Appendices 13 and 14. The value of cathodoluminescence in determining the relative age of mineralisation is summarised in Appendix 11 and the importance of magnesium affecting luminescence intensity is shown in Appendix 12.
CHAPTER 8

Mineral assemblages and their relation to facies and diagenesis

8.1 Introduction

In contrast to mineralisation in the Carboniferous carbonates of the neighbouring Pennine orefields (Dunham, 1948; Dunham, 1967; Ford, 1969; Smith, 1974; Smith, 1980) the mineralisation in the Cadeby Formation took place at many different times during the diagenetic history and it is often impossible to link episodes of mineralisation from one locality, or group of localities, to another. Several different assemblages of base metal sulphides and/or baryte are found. This chapter describes these assemblages and documents their host facies. The timing of mineralisation with respect to the diagenetic history is also detailed.

Mineralisation is demonstrably both pene-contemporaneous and mesogenetic. No unequivocably eogenetic mineralisation has been recognised. Penecontemporaneous mineralisation includes sphalerite, galena and baryte at different localities. Mesogenetic mineralisation can be grouped into three main assemblages; sulphides with little or no baryte, baryte with some sulphides and baryte-dominated assemblages. Mesogenetic mineralisation differs between areas; localities are therefore grouped
in areas for description and discussion. A few mineralised localities are solely fracture related, whereas others, no longer exposed, can only be surmised to be mesogenetic. The formation known to be enriched in base metals, the Marl Slate (Hirst and Dunham, 1963; Turner et al., 1978) does not crop out in the research area although present in the subsurface (Appendix 6, Log 11). No detailed research was done on this formation.

8.2 Penecontemporaneous mineralisation

8.2.1 Calcitised displacive anhydrite nodules

Sphalerite and marcasite with some baryte and galena are present in calcitised displacive anhydrite nodules at Rock Cottage Quarry, Wormald Green (Appendix 1, locality 6; Appendix 6, Log 9). The displacive anhydrite nodules grew in low energy wackestones and mudstones in lagoon facies of the Lower Member (3.2.10). Petrological evidence suggests calcitisation and concurrent mineralisation took place shortly after penecontemporaneous dolomitisation and before substantial burial of the sediments (Harwood, 1980). Sphalerite is concentrated in nodules or parts of nodules rich in dolomite muds; these muds
are contorted around subhedral sphalerite crystals (Fig. 8.1a), implying crystal growth took place whilst the muds were still soft. Sphalerite is honey-coloured with low iron content. Microprobe scans show little variation in iron content whereas cathodoluminescence does show some zoning in the crystals (Fig. 8.1b). Calcite-rich parts of the nodules show pseudomorphs after anhydrite (Harwood, 1980; Fig 5) and contain marcasite and some baryte (Harwood, 1980; Fig 8). Galena is a rare accessory mineral and is also found on isolated joint faces at the same stratigraphic level (Appendix 6, Log 9).

Interbedded black carbonaceous muds show rusty staining from recent oxidisation of iron sulphides; uncorrected base metal contents (Appendix 5, specimen 605) contain considerably higher zinc contents than the standard shale used (Appendix 5, specimen 998) or mean shale values (Turekian and Wedepohl, 1961). The amount of sulphide mineralisation in the nodules is similar to that expected were the metals derived from the surrounding sediments.

Minor quantities of fluorite are found as
Figure 8.1  

a  Sphalerite crystals in mineralised replaced displacive anhydrite, Rock Cottage Quarry, Wormald Green (SE 30465). Dolomitic muds are distorted around euhedral sphalerites, indicating sphalerite growth whilst muds were still soft. Field of view is 3.45mm.

b  Zoning in sphalerite crystal, Rock Cottage Quarry, Wormald Green (SE 304650). Cathodoluminescence. Field of view is 1.00mm.
Figure 8.1  c  Dolomite rhombs in replaced anhydrite nodules, Vale Road Quarry, Mansfield Woodhouse (SK 532648). Note smaller crystal size of host dolomite with some ?peloid ghosts (dashed line). Dolomite crystals within nodule are euhedral rhombs (~250μm) with calcite (stained) cement. Field of view is 3.45mm.
inclusions within some calcite crystals in the nodules. Fluorine can become
were still causing, penecontemporaneous
dolomitisation (4,5,2).

Beds at the same stratigraphic level are
not exposed in neighbouring quarries
(Appendix 6, Logs 7 + 8) so it is not
possible to assess the lateral extent of this
mineralisation. Two nearby borehole records
the Calvert Formation continues for over
16.5 metres below the possible intervals
at Wormald Drew. The section has no record of
no record of the fluorite mineral (3, 2, Smith,
para. egm. 1951).

Similar replacement calcitic amygdale nodules
are found near the top of the lagoon wacke-
stones and mudstones with elastic muds at
inclusions within some calcite crystals in the nodules. Fluorine can become concentrated in evaporites. Co-precipitation of calcite and fluorite is caused by high magnesium contents in the parent solution (Kitano and Okumura, 1973). Thus the presence of fluorite inclusions is indicative of both magnesium-rich solutions and evaporite precursors during calcite formation. The magnesium-rich solutions and evaporite precursors during calcite formation. The magnesium-rich solutions may have been those which had caused, and perhaps were still causing, penecontemporaneous dolomitisation (4.5.2).

Beds at the same stratigraphic level are not exposed in neighbouring quarries (Appendix 6, Logs 7 + 8) so it is not possible to assess the lateral extent of this mineralisation. From quarry borehole records the Cadeby Formation continues for over 16.8 metres below the present exposures at Wormald Green (Fig 3.19), but there is no record of the facies present (D. B. Smith, pers. comm., 1981).

Similar replaced displacive anhydrite nodules are found near the top of the lagoon wackestones and mudstones with clastic muds at
Vale Road Quarry, Mansfield Woodhouse (Appendix 1, locality 47; Appendix 6, Log 5). The nodules contain sphalerite and some marcasite, but in a matrix of dolomite rhombs and dolomite muds with little calcite. The dolomite rhombs within the nodules contrast with the dolomicrite host (Fig. 8.1c). The similarities of these nodules, in form, host facies and mineral assemblages, to those at Rock Cottage Quarry, suggests that they also result from sulphate reduction and replacement of anhydrite during penecontemporaneous diagenesis. Calcitisation is thought here to have taken place before dolomitisation was complete, with the dolomite subsequently replacing the calcitised anhydrite.

8.2.2 Stratabound galena

Galena as disseminated crystals, replacive cubes within carbonate mudstones, in bivalve molds and on irregular joint surfaces is found at the top of the clastic-rich sequence at Vale Road Quarry, above the sphalerite-rich replaced nodules (Appendix 6, Log 5). The galena horizon can be traced for over one square kilometre both within the quarry and from cores further west; the quarry managers use the occurrence of galena
in borehole cores as the base of the mud-free, and therefore exploitable, carbonates. Galena is the sole sulphide present; baryte has not been found. Galena is found at this upper junction of the clastic-rich sequence, the former "Lower Permian Marls" at many localities throughout the outcrop of the Cadeby Formation in Nottinghamshire (Fig. 8-2).

At Vale Road Quarry evidence of former evaporites is found both above and below the galena horizon but, whereas the lower evaporites were replaced (8.2.1), the upper ones have been dissolved (Fig. 6-8b). Replacement took place in an anoxic environment. Anoxic conditions are also implied by frequent plant fragments (Appendix 6, Log 5). Lack of replacement at the higher level suggests less reducing conditions during penecontemporaneous diagenesis of these beds. In the quarry springs now issue from immediately below the galena horizon; the mud-rich lower carbonates thus form a much less permeable sequence. Mineralisation along this boundary suggests inter-dependence of lithological change, oxic/anoxic environments and permeability differences.
Figure 8.2  Map showing distribution of mineralised localities in Nottinghamshire

▼ Whitwell localities

▲ Dispersed baryte mineralisation

★ Galena at boundary of main carbonates/siliciclastic carbonates

◇ Mineralisation at the top of the Cadeby Formation
baryte (Whitwell)
▲ baryte (dispersed)
♦ galena (Deans)
* galena (databound)
□ other mineralisation

Nottingham

10 km
The widespread occurrence of diffuse galena mineralisation at this diachronous boundary (1.2.2) suggests a penecontemporaneous age. Lead is possibly derived from the underlying anoxic clastics during early compaction and de-watering with sulphur from bacterial reduction of sea water sulphate, not necessarily in the form of evaporites. Galena on irregular joint faces may be from later remobilisation or, alternatively, these irregular joints could be early features, related to early preferential cementation within beds (3.2.8). Separation of galena and sphalerite mineralisation at Vale Road Quarry is possibly the result of differences in solubility, and hence further migration of lead complexes.

The galena mineralisation at Vale Road Quarry contrasts with many other occurrences in the area which contain baryte (Fig. 8.2). The baryte is associated with mesogenetic mineralisation (8.4.1); its absence at Vale Road Quarry supports a different, penecontemporaneous origin for the galena.

8.2.3 Hydraulic brecciation and baryte cementation
The existence of a vertical fissure breccia
immediately above a large flame structure in lagoon wackestones and packstones at Bedale Quarry, Well (Appendix 1, Locality 4) (Fig. 8.3a + b) gives evidence of both de-watering with vertical fluid expulsion and early cementation of some dolomites (Harwood, in press). Baryte and calcite are the only minerals present. De-watering of the underlying shales (bed 4) took place before lithification of bed 3. (Fig. 8.3b); the overlying dolomicrites (bed 2) must have been already lithified to form the breccia. Mineralisation was thus penecontemporaneous or eogenetic; the fluid expulsion was possibly triggered by a seismic shock (Harwood, in press).

The breccia is clast supported near the margins but matrix supported near the centre. Cementation must have been instantaneous to support the clasts. The small crystal size of the baryte substantiates this suggestion. The baryte is considered to originate from barium incorporation in the lattice of pre-existing gypsum crystals, both within the underlying black carbonaceous muds and, perhaps, from neighbouring calcitised gypsum crystals (4.5.3) (Harwood, in press). Baryte mineralisation elsewhere in the quarry lines existing voids (8.4.2); supply of barium was
Figure 8.3 Hydraulic brecciation of dolomite, Bedale Quarry, Well (SE 257812).

a Field photograph. Flame structure shown by lower arrow and breccia by upper arrow. Hammer is 0.35m long.

b Diagram of breccia and underlying beds from Harwood, in press.
1. dolomite breccia in baryte matrix
2. overlying dolomites
3. channel
4. calcareous and carbonaceous mudstones
5. penetrative flame structure
therefore not restricted to early diagenetic events.

8.3 Mesogenetic sulphide occurrences with little or no baryte

8.3.1 The Doncaster area

Galena mineralisation is found throughout the breccia at the top of the Upper Member in the Doncaster area (3.4.5) (Appendix 1, localities 18-29). Lead grades range from over 3% in selected specimens (e.g. Fig. 8.4a) to 0.26% combined Pb and Zn in a bulk sample through the thickest breccia to less than 0.1% in poorly mineralised specimens (Appendix 5, specimens 290-306). Galena is restricted to the breccia apart from at New Edington Brick Works Quarry (Appendix 1, locality 29) where it also occurs in void fills and thin veinlets at the top of the ooid grainstones and packstones (Fig. 8.4b). Some galena with calcite was also found on NE-SW trending joint faces in Lower Member packstones and grainstones at Sprotborough Quarry (Appendix 1, locality 26). Mineralisation within the breccia facies is a partial void fill and forms on top of, and is therefore later than, dolomite fringing cements and later dolomite (Fig. 8.4c) (4.5.8). Galena
Figure 8.4  
a  Galena on exposed surface of breccia, New Edlington Brick Works Quarry (SK 532986). Galena has partially altered to cerussite.

b  Galena and calcite in vug, New Edlington Brick Works Quarry (SK 532986). Vug may result from dissolution of evaporites; vug surrounds do not indicate this is a burrow (see Fig 4.13 c).
Figure 8.4  c  Galena between fringing cements in breccia facies, New Edlington Brick Works Quarry (SK 532986). Galena (opaque) grows on and between fringing cements; calcite later partially occludes porosity. Field of view is 3.45mm.
Mineralization was before calcite spar growth (Fig. 8.4c) and galena has since present in intercrystalline voids and moldic porosity in an underlying skeletal packstone bed in Upper Member shallow water siliciclastic dolomites (Fig. 8.5b). No sulphides are oxidized. Most dolomites are altered, particularly adjacent to pore margins, but show little ferroan dedolomitization. Mineralization therefore took place after dolomite alteration. The mineralised skeletal packstone bed can be traced for over a hundred metres within the quarry, although the overlying galena in veinlets and on irregular joint surfaces is very patchy.

8.3.3 Kirby in Ashfield

In one bed galena and sphalerite are present in intercrystalline voids in Lower Member.
mineralisation was before calcite spar
growth (Fig. 8.4c) and galena has since
been partially altered to cerussite
(Fig. 2.7b). No other sulphides nor baryte
were found. The dolomites show no alteration
nor dedolomitisation.

8.3.2 Linby

In one exposure at Linby (Appendix 1,
locality 66) galena and calcite are found
on joint surfaces (Fig. 8.5a) and marcasite
with galena, sphalerite and calcite are
present in intercrystalline voids and moldic
porosity in an underlying skeletal packstone
bed in Upper Member shallow water
siliciclastic dolomites (Fig. 8.5b). No
sulphides are oxidised. Host dolomites are
altered, particularly adjacent to pore margins,
but show little ferroan dedolomitisation.
Mineralisation therefore took place after
dolomite alteration. The mineralised skeletal
packstone bed can be traced for over a
hundred metres within the quarry, although
the overlying galena in veinlets and on
irregular joint surfaces is very patchy.

8.3.3 Kirby in Ashfield

In one bed galena and sphalerite are present
in intercrystalline voids in Lower Member
Figure 8.5  

a  Euhedral galena and calcite on joint surface, Linby (SK 537523).

b  Marcasite and calcite in moldic porosity in skeletal siliciclastic carbonate, Linby (SK 5375230. Marcasite (M) predates calcite void fill. Cathodoluminescence. Field of view is 2.2mm.
stalagmitic carbonates at Kirby in Ashfield (Appendix 1, Locality 51). Dolomites are subhedral to euhedral coarse rhombo (Fig.

3.3.4: The Sathy area

Sphalerite and magnesite (unidentified) were

subsurface (Appendix 7, Fig A7.3), parallel to the downthrow line. High artesian pressures within this zone has

expressed engineering problems in shaft
siliciclastic carbonates at Kirby in Ashfield (Appendix 1, Locality 51). Dolomites are subhedral to euhedral coarse rhombs (Fig. 4.19 a + b). Sulphides are present in areas where ferroan dedolomitisation has not taken place and sucrose ferroan dolomites are preserved in a calcite cement (Fig. 4.19 b + c). Galena does not corrode the sucrose dolomites (Fig. 4.19c) and formed after sucrose dolomite development. Local anoxic micro-environments were retained in mineralised areas and probably these prevented ferroan dedolomitisation.

8.3.4 The Selby area

Sphalerite and marcasite up to one centimetre across occur in voids in Lower Member patterned carbonates of the Selby coalfield (Appendix 1, locality 17; Appendix 6, log 11). Mineralisation occurred after formation of limpid dolomite overgrowths (Fig. 4.22). Sphalerite and marcasite are intergrown with large calcites with curved crystal faces ('baroque' calcites) (Fig. 8.6). The high porosity vuggy zone is up to 20 metres thick and can be traced for several kilometres in the subsurface (Appendix 7, Fig A 7.3), parallel to the palaeoshore line. High artesian pressure within this zone has presented engineering problems in shaft
Marcasite and calcite in patterned carbonates, Wistow Wood borehole (SE 567356). Note rounded crystal boundaries of 'baroque' calcite.
construction. Present day artesian fluids do not oxidize barite or such calcite; mineralisation may be of relatively recent origin from these fluids or their precursors.

3.4 Mesogenesis: Barite occurrences with some sulphides

8.4.1 The Nottinghamshire area

Vug fills, veinlets, intercrystalline cements
construction. Present day artesian fluids do not oxidise marcasite nor etch calcite; mineralisation may be of relatively recent origin from these fluids or their precursors.

8.3.5 Deans' mineralised localities

The northern mineralised localities (Appendix 1, localities 19, 25-27) recorded by Deans are related to the breccia facies at the top of the Upper Member (8.3.1). None of his recorded localities further south are now exposed (2.3.2., Fig. 2.4) (Appendix 1, localities 59, 61, 63-65, 67-69). Deans' descriptions indicate that mineralisation was mesogenetic and present immediately below the Ripon Formation. Host facies were peloid grainstone barriers and siliciclastic carbonates. The major control on location appears the less permeable nature of the overlying continental clastic succession (Deans, 1961). Galena is the major sulphide present, occurring with baryte, chalcopyrite, ashphalite and secondary cerussite and wulferite. Mineral grades are low throughout the localities.

8.4 Mesogenetic baryte occurrences with some sulphides

8.4.1 The Nottinghamshire area

Vug fills, veinlets, intercrystalline cements
and some replacive baryte are found throughout much of the outcrop in Nottinghamshire (Fig. 8.2). Host facies are Lower Member lagoon wackestones and mudstones (Appendix 1, localities 44, 48, 50, 55, 53, 56, 58). In the lagoon packstones and mudstones baryte commonly fills vugs formed after dissolution of displacive evaporites and partially replaces the surrounding dolomites. No baryte is found in the lagoon clastic-rich lower wackestones and mudstones but is found in the more oxic facies above the galena horizon (8.2.2) (Fig. 8.8). Where partially replaced, dolomite crystals are corroded by baryte; the preservation of limpid rims shows alteration pre-dated mineralisation (Fig. 8.7). Elsewhere, replacive baryte contains inclusions of iron oxides (Appendix 11, Figs. All.1 a + b). Here alteration and ferroan dedolomitisation must have taken place before baryte crystallisation. Baryte is also found as a pore-filling cement after dolomite alteration and ferroan dedolomitisation (Fig. 5.8a) and in veinlets.

Sulphides within the baryte are rare and are restricted to marcasite, pyrite and some galena. All are altered to hematite, goethite
Figure 8.7 Baryte replacing dolomite, Skegby (SK 501611). Baryte (dark) is corroding dolomite (D). Dolomite crystal has thin limpid rim after alteration. Cathodoluminescence. Field of view is 2.2mm.
Figure 8.8 Log of facies changes through the two sections at Clowne (SK 486757 and 486756) showing position of galena and baryte occurrences.
Leached evaporite nodules

Baryte

1 m

Galena

Skeletal wackestone
and cerussite in some places. Void-occluding calcite postdates baryte and sulphides (Appendix 12, Fig.A12.5a + b).

The baryte mineralisation therefore took place relatively late in the diagenetic history after dolomite alteration and, sometimes, after ferroan dedolomitisation. As altered dolomite crystals surround vugs formed after displacive evaporite alteration and mineralisation. The sulphate in the baryte is therefore not directly derived from Zechstein evaporites.

8.4.2 Mesogenetic baryte and marcasite/hematite/geothite mineralisation at Bedale Quarry. Well (Appendix 1, locality 4) lines pre-existing voids (Harwood, in press) (Appendix 11, Fig.A11.3) (Fig.8.9) Sedgwick (1829) also reports galena from the same area. Voids are sheet cracks and vugs after evaporite dissolution in dolomite lagon wackestones and mudstones (3.2.10). There is no baryte mineralisation in either primary or secondary limestones.

Void margins are lined with altered dolomites; alteration penetrated 1 to 2 centimetres into the dolomite so was not
Baryte with goethite in vugs, Bedale Quarry, Well (SE 257812). Vugs were probably sheet cracks. Goethite has corroded pyrite/marcasite cores.
Alteration is therefore related to fluid movement through the void spaces and, as mineralisation lines these voids (Fig. 2.9), may be related to the mineralising fluids. Ferroan dolomite crystals partially fill the mineralising voids (Fig. 2.1; Appendix I).

Analyses (Appendix I; Figs A1-2.6-a-e) show that the initial void-filling calcite was precipitated from magnesium-rich fluids, which may have been related to the later stages of dolomite alteration. Barite growth from void margins appears to have been initiated in, or before, the magnesium-rich calcite zone (Appendix I). Mineralisation was thus after dolomite alteration but before ferroan dolomitisation, in contrast with the contemporaneous barite mineralisation in the hydromorphic breccia (0.2.3; Harwood, in prep).
pervasive (Fig. 5.2). Alteration is therefore related to fluid movement through the void spaces and, as mineralisation lines these voids (Fig. 8.9), may be related to the mineralising fluids. Ferroan dolomite crystals partially line some vugs; in others not all dolomite crystals are subject to ferroan dedolomitisation (Fig. 5.5). Therefore, ferroan dedolomitisation took place after, or during the late stages of mineralisation, concurrent with marcasite oxidisation and he-matite/goethite growth. The presence of fluorite inclusions, first recognised by J. A. D. Dickson, in calcite zones close to the void margins, (Figs. 5.2 c + d) and subsequent micro-probe analyses (Appendix 12, Figs. A12.2 a – e) show that the initial void-filling calcite was deposited from magnesium-rich fluids, which may have been related to the later stages of dolomite alteration. Baryte growth from void margins appears to have been initiated in, or before, the magnesium-rich calcite zones (Appendix 11). Mineralisation was thus after dolomite alteration but before ferroan dedolomitisation, in contrast with the penecontemporaneous baryte mineralisation in the hydraulic breccias (8.2.3; Harwood, in press).
8.5 Baryte-dominated mesogenetic mineralisation

8.5.1 The Bramham area

Baryte replacing both evaporites and dolomite is found at many localities around Bramham (Fig. 8.10) (Appendix 1, localities 10-16). Baryte was recorded from the area by Versey (1925) and Barratt (1975). Barratt described baryte in the Namurian Follifoot and Plumpton Grits and the Cadeby Formation (Fig. 8.10). Where not exposed, baryte is in some places present as float in cultivated fields, as in the East Keswick region (Smith, 1974c; Barratt, 1975, p. 208). Baryte is present:

(i) with calcite and small amounts of oxidised marcasite in sites of original displacive anhyrdite nodules in supratidal carbonates (Fig. 3.16a + b).

(ii) in supratidal and intertidal carbonates, patch reefs and shallow water peloid packstones and grainstones as vug linings, joint coatings and irregular veinlets (Appendix 6, Log 1) (Barratt, 1975, Fig 6.6).

(iii) in supratidal and intertidal carbonates and grainstone barriers as large scale replacements of dolomite.

There is thus little facies control on this mineralisation.
Figure 8.10  Map of mineralised localities in the Bramham area
Small scale occurrences of baryte are
restricted to isolated evaporite
breakout lenses from thick and a
limestone unit (see Fig. 8.10),
the Lower Dolomite of the
Breciated Limestone member
(Fig. 8.11). To a larger extent
baryte containing veins and fissures
are known in other deposits, locally
in the Upper Stillingfleet Limestone.
Fluorite, celestite, and baryte (Fig. 8.11c)
have been collected from the larger
baryte veins and fissures
containing minerals. The baryte matrix
contains small amounts of celestite,
fluorite, and calcite. The baryte
mineralisation consists of small
cubes, up to 0.5 centimetres across, in a
baryte matrix. Baryte mineralisation debris
with traces of celestite (Appendix 1,
locality 12c), also records small
amounts of enargite, azurite, and
calcedonite, and barite (Fig. 8.11c).
Traces of calcite were present
in the flat in the pipeline trench. The
green copper carbonate recorded at nearby
Newton Kyme (Marshall, 1829) may have been in
the Brotherton Formation (Ej3 carbonate); no
traces remain today.
Small scale occurrences of baryte are restricted to replaced evaporite nodules; large scale replacements range from lenses (or flats) 30 centimetres thick and a metre or so long (Barratt, 1975, p. 208), through blocks of replaced fenestral dolomite, the Lower Dolomite of the Hampole Beds, (Fig. 8.11a) to a larger flat one metre thick by about 200 metres long exposed in a recent gas pipeline trench at Oglethorpe (Appendix 1, locality 13). The latter exposure also contained veins of pink and white colloform baryte up to 18 centimetres wide (Fig. 8.11b) and, in the host dolomite peloid grainstones, veins of fluorite, hematite with pyrite cores and baryte (Fig. 8.11c). Fluorite along vein margins pre-dates baryte crystallisation. Near Bramham village colourless fluorite cubes, up to 0.8 centimetres across, in a baryte matrix were found in excavation debris with traces of chalcopyrite (Appendix 1, locality 12c). Barratt (1975) also records small amounts of chalcopyrite, azurite and malachite; traces of malachite were present in the flat in the pipeline trench. The green copper carbonate recorded at nearby Newton Kyme (Marshall, 1829) may have been in the Brotherton Formation (EZ3 carbonate); no traces remain today.
Figure 8.11  

a  Fenestral dolomite replaced by baryte, Bramham (SE 426425). Lower Dolomite of Hampole Beds.

b  Colloform baryte from vein in baryte flat, Oglethorpe (SE 451430).
Figure 8.11c  Fluorite-baryte-calcite vein in dolomite, Oglethorpe (SE 451430). Fluorite cubes (yellow or colourless) are earliest mineral as on vein margin; main vein fill is calcite with some baryte (arrowed).
"Pseudo-pisoids" are formed by radiating baryte spheres (Fig. 8.12b). In other areas baryte crystal growth is present as inclusions along crystal outlines (Fig. 8.12c). Crystal form may continue unchanged through the inclusions or crystals may have a more mosaic texture within the hematite. Two or three influxes of iron inclusions have been defined. The inclusions may be due to three mechanisms:

(i) build up of iron within the barium-rich fluid until hematite solubility is exceeded; iron is then precipitated and baryte growth continues until iron build-up

(ii) periodic introduction of a second, iron rich, fluid or

(iii) "surfing" of inclusions in front of
The vertical limits of the extensive baryte flat at Oglesthorpe are controlled by two thin, (<3 centimetres), laterally extensive clay beds. As this exposure is near the top of the Upper Member (marls were found at the southern end of the trench) these clays were probably formed during periods of stillstand between dune migrations. The clays are now red-stained from hematite induration. Host dolomites are peloid and pisoid grainstones and packstones from the barrier facies. Baryte replacement in places centres within pisoids (Fig. 8.12a), elsewhere "Pseudo-pisoids" are formed by radiating baryte spherules (Fig. 8.12b). In other areas baryte crystal growth is present as inclusions along crystal outlines (Fig. 8.12c). Crystal form may continue unchanged through the inclusions or crystals may have a more mosaic texture within the hematite. Two or three influxes of iron inclusions have been defined. The inclusions may be due to three mechanisms: (i) build up of iron within the barium-rich fluid until hematite solubility is exceeded; iron is then precipitated and baryte growth continues until iron build-up (ii) periodic introduction of a second, iron rich, fluid or (iii) "surf-ing" of inclusions in front of
Figure 8.12  

a  Baryte replacing iron stained pisoids and peloids, Oglethorpe (SE 452428). Baryte in places replaces complete pisoid within outer envelope (dashed line). Baryte is not spherulitic. Field of view is 3.45mm.

b  Spherulitic baryte replacing dolomite, Oglethorpe (SE 451430). Dolomite where not replaced shows few peloids and no pisoids. Baryte is concentrically zoned and forms 'pseudo pisoids' in hand specimen. Field of view is is 3.45mm.
Figure 8.12  

**c** Inclusions of hematite (arrowed opaque) within coarse bladed baryte, Oglethorpe (SE 450431). Crystal form remains same after growth through inclusions. Later void (v) is calcite filled. Field of view is 3.45mm.

**d** Feathery baryte on end of coarse baryte laths, Oglethorpe (SE 450431). Feathery laths show preferred orientations (arrowed) which may be result of fluid flow paths. Later void (v) filled with calcite. Field of view is 2.2 mm.
rapidly crystallising baryte; when crystallisation rate slows down inclusions can be contained within the crystal. The second and third alternatives are perhaps more likely to result in changes in crystal form. He-matite is derived from the overlying red marls of the Ripon Formation.

The crystal form of the replacive baryte is dependent on the dolomite precursor. Where baryte replaces dolomicrite, spherulitic baryte is more common (Fig. 8.12b) although bladed baryte is sometimes present where spherulites coalesce. However, where a dolomicrospar or coarser dolomite is replaced, spherulitic baryte is rare and crystals are commonly bladed (e.g. Fig. 8.12a). Late baryte crystals, as a void fill, form feathery laths on the surface of larger bladed baryte. These laths are not radially orientated and perhaps indicate some direction of pore water flow (Fig. 8.12d). Voids are sometimes subsequently calcite filled although others remain open.

8.5.2 The Whitwell area

Baryte mineralisation in temporary exposures around Whitwell was described by Ineson et al. (1972) with isotope determinations by
Robinson and Ineson (1979) (Fig. 8.2) (Appendix 1, localities 36-42). Thin sections were lent by Dick Ineson. Baryte occurs as a void fill and replaces Upper Member peloid and pisoid grainstones and packstones of the barrier facies (3.4.2). Ineson et al., note that "shelly limestones" have not been substantially replaced by baryte; there is thus some degree of facies control. Baryte mineralisation is after eogenetic dolomitisation and is also later than the formation of limpid dolomite overgrowths which line some vugs. Marcasite is present between some bladed baryte crystals but is not common; there is no hematite. Ineson et al.; found galena crystals (two!) in a central vein. Baryte spherulites (Ineson et al., 1972, Fig. 3) are similar to those at Oglethorpe; centres of spherulites again are not always the centres of pisoids and some "pseudo-pisoids" result. Some coarse bladed concentrically banded baryte (e.g. Ineson et al., 1972, Figs. 4 and 7) contain ghosts of former dolomite structures, indicating these may not have been simple void-filling barytes, as previously deduced. Rapid crystal growth would allow incorporation of rare small dolomite inclusions in the baryte;
other inclusions would "surf" in front of the growing crystals and may be later flushed away if not incorporated in the crystal itself.

Lead mining was recorded at Whitwell in 1661 and there are ancient records of lead ores being found at Barlborough and Bolsover (Pilkington, 1789; Ineson et al., 1972). The depth of ore in the adit traced by Ineson is not known. Their descriptions of "galena in grey marl with irregular beds of marly limestone" from the Whitwell Wood borehole core (Eden et al., 1957, p. 224) suggests galena near the base of the Lower Member (7.2.2). Baryte and galena are found in the nearby working quarry (Appendix 1, locality 41) where baryte replaces dolomite and, with galena, occurs in a near-vertical vein (P. R. Ineson, pers. comm., 1980).

8.6 Mineralisation in fractures

Mineralisation solely within fractures is rare in the Cadeby Formation. Baryte-galena-fluorite mineralisation in a fault at West Tanfield was described by Lamming and Robertson (1968) (Appendix 1, locality 5). Host rocks are lagoon wackestones and mudstones; baryte is also found in vugs after displacive evaporite dissolution and on joint fac-es
for up to 5 metres from the fault. Smith et al., (1967) also record baryte and galena where the Cadeby Formation is faulted against the Ripon Formation (Appendix 1, locality 70) although this is no longer exposed.

8.7 Copper mineralisation

Copper was mined in the Cadeby Formation in the Farnham area in the late sixteenth century from shafts and galleries up to 16 yards (4.6 metres) deep (Marshall, 1856; Hunt, 1884) (Appendix 1, localities 7 + 8). Mining was discontinued due to frequent flooding of the galleries. Surface rocks are Upper Member ooid and peloid grainstone and packstone barriers; shaft depths indicate mineralisation was in the Lower Member. Copper, principally as carbonate, was mined "in small masses, seldom exceeding the size of a large potato" (Marshall, 1856). Prof. H. Versey (pers. comm., 1978) remembers a descent into the galleries after a shaft collapse in the 1920s. An unpublished I.G.S. report by Dr. T. Deans describes waste from the workings with chalcocite, bornite, corellite and malachite as replacements in nodules and on joint coatings. Copper mineralisation was therefore after dolomitisation and subsequent evaporite dissolution; vug and nodule descriptions suggest host rocks contained displacive evaporite nodules,
possibly in lagoon mudstones and wackestones.

Prof. H. V. Warren (written comm., 1980) tells of up to 0.1% Cu determined in soil sample traverses over drift-free hills of the Cadeby Formation around Franham, traverses over drift did not find anomalous copper. The method of copper determination is not known. A borehole record further east mentions 2'1" of hard limestone with pyrite and galena in Lower Member carbonates (Appendix 1, locality 9). It is possible that chalcopyrite with the pyrite was overlooked.

The copper mineralisation in this area is more extensive than previously realised. It is distinct from other mineralisation within the Cadeby Formation.

8.7 Mineralisation in the E21 carbonates in County Durham

Investigation of the mineralised localities of the Ferryhill area (Hirst and Smith, 1974) shows the host carbonate to be mainly Raisby Formation lagoon wackestones and mudstones. Halite pseudomorphs similar to those at Wormald Green (Fig.3.14b) were found at Rough Furze Quarry (Appendix 1, locality 71). Cathodoluminescence studies revealed that baryte at Rough Furze grew against anhydrite crystals (Appendix 11, Fig. All.4).
Sulphate was thus derived directly from in situ evaporites and not from dissolution of overlying evaporites as postulated by Hirst and Smith. Apart from the copper mineralisation at Raisby Hill (Appendix 1, locality 72) much of the mineralisation described fills vugs after displacive evaporites, is in sheet cracks, replaces the surrounding dolomite or is in fractures (auto-brecciation) very like those produced from the hydraulic fracturing associated with satin spar gypsum veining. The link with former evaporites is therefore very close.

8.9 Summary and conclusions

Mineralisation in the Cadeby Formation can be divided into two major groups, penecontemporaneous and mesogenetic; mineralisation rarely has a simple fault control. Penecontemporaneous mineralisation is low grade and confined to lagoon facies; metal amounts are in quantities that could be derived from the surrounding sediments. The penecontemporaneous mineralisation described has little economic potential. However, other areas of similar facies, where a potential hydrothermal source is present, may have a much greater economic significance.

Mesogenetic mineralisation falls into several characteristic assemblages; these, with their host
facies and mode of occurrence of minerals, are summarised in Table 8-1 together with penecontemporaneous mineralisation. Much mesogenetic mineralisation shows some facies control; Lower Member lagoon wackestones and mudstones which hosted displacive evaporite nodules contain more mineralisation than other facies (Fig. 8.13). In the subsurface, patterned carbonates form an excellent porous host for potential mineralising solutions (8.3.4). Some facies, including patch reefs and grainstone "domes", which form potential traps for ore solutions are unmineralised (3.5). In the Upper Member mineralisation is facies-restricted within the breccias (Fig. 8.14) but other occurrences are less facies dependent; Deans' localities are controlled by the overlying less-permeable Ripon Formation clastics. Only the major baryte replacement mineralisation is largely independent of facies (8.5.1 and 8.5.2) although associated minor baryte is controlled by evaporite occurrences (8.5.1).

Episodes of mesogenetic mineralisation cannot be definitely correlated between mineralised districts; Table 8-2 summarised the relative timing of mineralisation and diagenetic events. Although mineralisation is both penecontemporaneous and mesogenetic in displacive evaporite vugs (8.2.1, 8.4.1) mineralisation in vugs after replacive
<table>
<thead>
<tr>
<th>Mineral Assemblage</th>
<th>Location</th>
<th>Host Facies</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphalerite + marcasite + calcite + galena + baryte</td>
<td>Wormald Green</td>
<td>Lower Member lagoon wackestones + mudstones with displacive evaporites</td>
<td>Penecontemporaneous</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td>Mansfield Woodhouse</td>
<td>Lower Member; boundary of Lower clastic lagoon sequence and higher lagoon carbonates</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baryte + later calcite</td>
<td>Well</td>
<td>Lower Member lagoon wackestones and mudstones</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena + calcite</td>
<td>Doncaster</td>
<td>Breccias at top of Upper Member</td>
<td>Mesogenetic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena + sphalerite + marcasite + calcite</td>
<td>Linby</td>
<td>Skeletal packstone in Upper Member siliciclastic carbonates</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena + sphalerite</td>
<td>Kirby in Ashfield</td>
<td>Lower Member siliciclastic carbonates</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena + marcasite + calcite</td>
<td>Selby</td>
<td>Lower Member patterned carbonates</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena + baryte + asphaltite</td>
<td>Nottinghamshire</td>
<td>Upper Member grainstone barriers + siliciclastic carbonates</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baryte + galena + marcasite/Fe Oxides + later calcite</td>
<td>Nottinghamshire</td>
<td>Lower Member lagoon facies. Siliciclastic carbonates in both members</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baryte + marcasite/Fe oxides</td>
<td>Well</td>
<td>Lower Member lagoon wackestones + mudstones</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baryte + fluorite + copper minerals + hematite + calcite</td>
<td>Bramham</td>
<td>independent of facies</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baryte + galena + calcite</td>
<td>Whitwell</td>
<td>mostly in Upper Member grainstone barriers</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malachite + other copper minerals</td>
<td>Farnham</td>
<td>?Lower Member lagoon wackestones + packstones with evaporites</td>
<td></td>
</tr>
</tbody>
</table>
**TABLE 8-2**

**SUMMARY OF RELATIVE TIMING OF MINERALISATION TO DIAGENETIC EVENTS**

**SEDIMENT DEPOSITION**

<table>
<thead>
<tr>
<th>Feature</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penecontemporaneous Dolomitisation + Evaporite Formation</td>
<td>Mansfield Woodhouse</td>
</tr>
<tr>
<td>Evaporite Calcitisation</td>
<td>Wormald Green</td>
</tr>
<tr>
<td>Evaporite Calcitisation</td>
<td>Well (hydraulic breccia)</td>
</tr>
<tr>
<td>Eogenetic Dolomitisation</td>
<td>Deans localities</td>
</tr>
<tr>
<td>Pore Filling + Replacement by Anhydrite</td>
<td>Farnham</td>
</tr>
<tr>
<td>*Sucrose Dolomite Formation</td>
<td>Bramham</td>
</tr>
<tr>
<td>Leaching + Limpid Dolomite Overgrowths</td>
<td>Kirby in Ashfield</td>
</tr>
<tr>
<td>*Dolomite Alteration</td>
<td>Doncaster</td>
</tr>
<tr>
<td>*Ferroan Dedolomitisation</td>
<td>Whitwell</td>
</tr>
<tr>
<td>Leaching</td>
<td>Selby</td>
</tr>
<tr>
<td>*Dedolomitisation</td>
<td>Linby</td>
</tr>
<tr>
<td></td>
<td>Well</td>
</tr>
<tr>
<td></td>
<td>Nottinghamshire</td>
</tr>
<tr>
<td></td>
<td>baryte and sulphides</td>
</tr>
</tbody>
</table>

*In areas which do not contain these diagenetic features timing of mesogenetic mineralisation can only be shown to be later than eogenetic dolomitisation.*
Figure 8.13  Map showing facies distribution and mineralisation in the Lower Member.

- *stratabound galena mineralisation*
- ♦ other Lower Member mineralisation

Facies as for fig. 3.18
Figure 8.14  

Map showing facies distribution and mineralisation in the Upper Member.

▲ galena in breccia

♦ Deans' localities

▼ other Upper Member mineralisation

Facies as for Fig. 3.31
evaporation is rare. Gypsum and anhydrite with calcite are known from only two localities (Appendix 3: localities 5, and 4). The reason why carnallite is not clear as mesogeic mineralization is often considerably later than dissolution of explosive evaporites (6.4.1).

The facies and genetic history (and geochemistry) of the Carnallite Formation are determined by the nature of the solution fluids. It should be noted, however, that on the one hand, the isotope data are difficult to interpret; on the other hand, locations of mineralization vary considerably throughout the Carnallite Formation where, although there is little evidence that there was a significant amount, there is no mineral, and other controls on mineralization are variable due to the pre-Carnallite anhydrite and dolomitic base.

Fig 6.1: There are three general types of mineralization: (1) euhedral, (2) anhedral, and (3) interstitial. The euhedral mineralization is characterized by large, well-rounded crystals, while the anhedral mineralization is characterized by small, irregular crystals. The interstitial mineralization is characterized by small, irregular crystals that fill the spaces between larger crystals.
evaporites is rare. Galena and marcasite with calcite are known from only two localities. (Appendix 1, localities 6 and 4). The reason for this is not clear as mesogenetic mineralisation is often considerably later than dissolution of displacive evaporites (8.4.1).

The facies and diagenetic history (and hence porosity) of the Cadeby Formation thus provide some controls on mineral locations. They give little information however on the origin of the minerals involved. Isotope determinations were carried out to try to define these origins more closely (Chapter 9). Also, locations of mineralisation are not evenly distributed throughout the area (Appendix 1, Fig A1.1); there are large areas of the Cadeby Formation where, although exposure is of a similar amount, there is no mineralisation. This implies other controls on mineralised localities, possibly due to the pre-Permi-an basement (Chapter 10).
CHAPTER 9
ISOTOPE EVIDENCE

9.1 Introduction
Both stable and lead isotopes were measured for selected specimens in an attempt to gain information on the origin of the mineralisation. This chapter is divided into two parts, the first part containing results and discussion from stable isotopes whereas the second part considers lead isotopes. Stable isotope determinations concentrated on the mineralisation at Rock Cottage Quarry, Wormald Green (SE 304650) (8.2.1) (Harwood, 1980; Coleman and Harwood, 1980). Lead isotope measurements were from thirty galena specimens from Yorkshire, Nottinghamshire and County Durham; Marl Slate galenas were included for comparison.

9.2 Stable Isotopes

9.2.1 Techniques and results
Stable isotope determinations were carried out by Dr. M. Coleman at I.G.S., Gray's Inn Road. Techniques used are briefly described in Coleman and Harwood (1980). Results are given in Tables 9-1 and 9-2.

9.2.2 Discussion - sulphur isotopes
Determinations of both interbedded and replacive anhydrite both have similar values, which are within the range of Upper Permian sea water (Claypool et al., 1980, Fig. 9 + p.243). Fractionation between sea water sulphate and
<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Description</th>
<th>$\delta^{34}$ SCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>152</td>
<td>Gypsum interbedded with dolomite</td>
<td>+ 11.40</td>
</tr>
<tr>
<td>164</td>
<td>Gypsum after replacive anhydrite</td>
<td>+ 11.46</td>
</tr>
<tr>
<td>760</td>
<td>Baryte replacing supratidal fenestral dolomite (8.5.1)</td>
<td>+ 11.21</td>
</tr>
<tr>
<td>463</td>
<td>Baryte in mineralised replaced anhydrite nodule</td>
<td>+ 17.88</td>
</tr>
<tr>
<td>463</td>
<td>Sphalerite in mineralised replaced anhydrite nodule</td>
<td>- 21.92</td>
</tr>
<tr>
<td>463</td>
<td>Galena in mineralised replaced anhydrite nodule</td>
<td>- 15.10</td>
</tr>
<tr>
<td>456</td>
<td>Marcasite in mineralised replaced anhydrite nodule</td>
<td>- 29.44</td>
</tr>
<tr>
<td>456</td>
<td>Sphalerite in mineralised replaced anhydrite nodule</td>
<td>- 15.98</td>
</tr>
<tr>
<td>462X</td>
<td>Sphalerite in mineralised replaced anhydrite nodule</td>
<td>- 18.9</td>
</tr>
<tr>
<td>462X</td>
<td>Marcasite in mineralised replaced anhydrite nodule</td>
<td>- 30.7</td>
</tr>
<tr>
<td>462X</td>
<td>Baryte in mineralised replaced anhydrite nodule</td>
<td>+ 19.4</td>
</tr>
<tr>
<td>619</td>
<td>Baryte in vug after displacive evaporite dissolution (8.4.1)</td>
<td>+ 17.34</td>
</tr>
<tr>
<td>621X</td>
<td>Baryte in vug after displacive evaporite dissolution (8.4.1)</td>
<td>+ 23.2</td>
</tr>
<tr>
<td>673</td>
<td>Galena replacing dolomite (8.2.2)</td>
<td>- 32.3</td>
</tr>
<tr>
<td>644</td>
<td>Galena in veinlet with calcite (8.3.2)</td>
<td>- 8.51</td>
</tr>
<tr>
<td>523</td>
<td>Galena in void fill in sucrose dolomite (8.3.3)</td>
<td>- 8.06</td>
</tr>
<tr>
<td>304</td>
<td>Galena in breccia (8.3.1)</td>
<td>- 7.96</td>
</tr>
<tr>
<td>°Baryte, Chilton Quarry</td>
<td></td>
<td>+ 9.3</td>
</tr>
<tr>
<td>°Kupferschiefer anhydrite Sangerhaussen, D.D.R.</td>
<td></td>
<td>+ 10.8 (average value)</td>
</tr>
<tr>
<td>°Selenite porphyroblast, Billingham mine</td>
<td></td>
<td>+ 9.0</td>
</tr>
<tr>
<td>°Anhydrite, Billingham</td>
<td></td>
<td>+ 9.7</td>
</tr>
<tr>
<td>*Whitwell baryte</td>
<td></td>
<td>+ 15.7 - + 19.3</td>
</tr>
<tr>
<td>*Whitwell galena</td>
<td></td>
<td>+ 6.6</td>
</tr>
</tbody>
</table>
X  Values determined by F. Bokari, 1979

Ø  Solomon et al., 1971

*  Robinson and Ineson, 1980

Other values were determined by Max Coleman.
and evaporite sulphate is small; (Claypool (op. cit.) gives fractionation values of 1 to 2 \(\text{oo/oo}\). These results support an Upper Permian age of the inter-beded anhydrite and also imply that the replacive anhydrite is of the same age, or was formed by remobilisation of Upper Permian evaporites. Other determinations of Zechstein evaporites have yielded similar values (Table 9-1).

The baryte replacing dolomite from Bramham (8.5.1) has a \(\delta^{34}\)S value close to the evaporites. The sulphate in the baryte is thus thought to be derived directly from the evaporites although, because of preservation of the fenestral texture (Fig 8-10 a), it is unlikely that the dolomite was replaced by calcium sulphate before baryte replacement. Hirst and Smith (1974) surmised that the sulphate in the baryte mineralisation in County Durham was derived from dissolution of the overlying evaporites, using the data from Solomon et al. (1966) (Table 9-1). Petrographic observations (Appendix 11, Fig A11-4) show the baryte to have grown in contact with the evaporite. Thus the baryte mineralisation at Bramham and in County Durham, in part at least, derived the sulphate directly from Zechstein evaporites.

The sulphide and baryte samples from Wormald Green came from mineralised nodules in the lagoon
wackestones and mudstones (3.2.10, 4.5.2). Where the sulphides formed in equilibrium conditions, $^{34}$S values would increase in the order galena-sphalerite-marcasite (Ohmoto, 1972; Rye and Ohmoto, 1974). The sulphide pairs do not have this relationship (Table 9-1); they therefore grew under non-equilibrium conditions. High negative $^{34}$S values are characteristic of sulphate reduction. Abiotic reduction in these nodules is considered unlikely (Harwood, 1980); oxygen isotope results (9.2.3) indicate low temperatures during sulphate reduction and replacement by calcite. As desulphurisation of hydrocarbons produces isotopically heavier sulphides, bacterial action seems the most probable mechanism of sulphate reduction. The baryte sample from the same nodule has a $^{34}$S value of +17.88 o/oo. The large negative fractionation caused by bacterial sulphate reduction and sulphide formation may leave the remnant sulphate correspondingly enriched in $^{34}$S; the presence of probable anhydrite inclusions within the baryte (Harwood, 1980, Fig 8) suggests that this enrichment did take place.

Sulphur isotope values from barytes at Clowne and Whitwell are distinct from evaporite sulphate values (Table 9-1). Robinson and Ineson (1979) interpret these results as sulphate derived from connate brines of Lower Carboniferous sea water, which migrated up-dip from further east. However, recent determinations of Carboniferous sea water
sulphate (Claypool et al., 1980, p.224 and Table 1) are different from those used by Robinson and Ineson (Fig 9-1 a). The Whitwell results are nearer Jurassic sea water sulphate (Fig 9-16). The results may also represent diagenetically modified Upper Permian sea water sulphate. Fresh water sulphate is commonly much lighter than marine sulphate (Coleman, 1977) so there is little likelihood of a dominant meteoric influence.

Apart from the galena specimen from Mansfield Woodhouse, other Cadeby Formation Galenas have $\delta^{34}S$ averaging -9 o/oo (Table 9-1); their origin is therefore different from the bacteriological reduced sulphides, amongst which the Mansfield Woodhouse galena can be included. These $\delta^{34}S$ values may result from partial reduction of Zechstein sea water sulphate in a closed system; however, the consistancy of the values from widely spaced localities (Appendix 1, Fig A1-1) suggests a more common, but unknown origin.

9.2.3 Discussion - carbon and oxygen isotopes

Carbonate samples were from replaced displacive anhydrite nodules and of calcite spar from vugs resulting from dissolution of displacive evaporites (Table 9-2). The calcite spar is quite distinct from the other calcites (Fig 9-2) and is what would be expected from calcite
Figure 9.1

a  Plot of sulphur and oxygen isotopes (from Robinson and Ineson, 1979).

b  Plot of sulphur and oxygen isotopes with fossil sea water values

J  Jurassic sea water

T  Triassic sea water

P  Permian sea water

C  Carboniferous sea water
(a) 

Derbyshire orefield

Whitwell

Mixing

Oxygen isotope exchange

'Fresh-water' sulphate

Carboniferous sea-water sulphate

δ¹⁸O snow, %

δ³⁴S_CDT, %

(b) 

Derbyshire orefield

Whitwell

Mixing

Oxygen isotope exchange

'Fresh-water' sulphate

Carboniferous sea-water sulphate

δ¹⁸O snow, %

δ³⁴S_CDT, %

temperature
### TABLE 9-2

**CARBON-OXYGEN DETERMINATIONS**

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Description</th>
<th>( ^{13}\text{C}_{\text{PDB}} )</th>
<th>( ^{18}\text{O}_{\text{PDB}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>603</td>
<td>Calcite spar from vug after dissolution of replacive</td>
<td>- 4.95</td>
<td>- 7.27</td>
</tr>
<tr>
<td>454</td>
<td>Calcite spar from vug after dissolution of displacive anhydrite</td>
<td>- 2.64</td>
<td>- 7.02</td>
</tr>
<tr>
<td>463</td>
<td>Host dolomite</td>
<td>+ 5.56</td>
<td>- 2.31</td>
</tr>
<tr>
<td>463</td>
<td>Ferroan dolomite adjacent to displacive anhydrite nodule - separated from calcitised anhydrite</td>
<td>+ 5.20</td>
<td>- 5.11</td>
</tr>
<tr>
<td>463</td>
<td>Calcitised ferroan dolomite</td>
<td>+ 3.53</td>
<td>- 9.41</td>
</tr>
<tr>
<td>463</td>
<td>Calcitised anhydrite from nodule centre</td>
<td>+ 3.24</td>
<td>- 13.30</td>
</tr>
<tr>
<td>604</td>
<td>'Rounded' calcite in similar nodule</td>
<td>+ 2.28</td>
<td>- 13.57</td>
</tr>
</tbody>
</table>
Figure 9.2 Carbon/oxygen isotope plot.
precipitated from Quaternary or Recent ground water. The data from the carbonates from the mineralised nodules plot on a line (Fig 9-2). As calcite and dolomite were separated by their density differences where these two minerals were intergrown (Appendix 13) the samples of ferroan dolomite may be contaminated with calcite. However, the line is still defined by the remaining samples, both $^{13}C$ and $^{18}O$ becoming more negative with calcitisation of anhydrite.

$^{18}O$ values are dependent on (i) the origin of the precipitating pore water and (ii) the temperatures of formation of the calcite. Both addition of isotopically light water from a meteoric source and increased temperatures lead to depletion of $^{18}O$. Meteoric water addition is also suggested by sulphate reduction (4.5.2) although Spiro (1977) details no meteoric influence in single crystal calcites which replace gypsum. Temperatures of calcite precipitation can be calculated from $^{18}O$ results using the equation of Craig (1965) for calcite:

$$T = 16.9 - 4.21 (S_c - S_w) + 0.14 (S_c - S_w)^2$$ (9.1)

where $S_c = S^{18}O$ calcite and $w = S^{18}O$ water

and that of Fritz and Smith (1970) for dolomite:

$$T = 31.9 - 5.55 (S_d - S_w) = 0.17 (S_d - S_w)^2$$ (9.2)

where $S_d = S^{18}O$ dolomite
Table 9-3 gives the calculated temperatures of formation of calcites and dolomites for initial water $\delta^{18}O_{H_2O}$ values of 0 and -5 $^0/00$ smow. Calculated temperatures are low, suggesting bacterial reduction of the sulphate. Introduction of meteoric-derived waters would further reduce these values.

$\delta^{13}C$ values are influenced by bacterial action, which usually results in high negative values (-20$^0/00$ or less, Hudson, 1977). However, buffering of bacterial carbon by the surrounding carbonate-rich pore waters would result in only slight decreased in $\delta^{13}C$ (Fig 9.2).

Stable isotope determinations therefore support most of the inferences of the initial petrological study (Harwood, 1980).

9.3 Lead Isotopes

9.3.1 Methods and results

Lead isotopes were measured at Leeds University using the Aldermaston micromass 30 mass spectrometer. Sample preparation and operating conditions are given in Appendix 14. Results and precision are tabulated in Table 9-4 and plotted on Figures 9-3 a+b. Two samples had large errors (>0.5 Pb$^{206}/Pb^{204}$) and are not included in the results. The two-stage lead isotope evolution curve of Stacey and Kramers
### TABLE 9-3
CALCULATED OXYGEN ISOTOPE TEMPERATURES

Calculated temperature °C assuming:

\[ \delta^{18}O_{\text{H}_2\text{O}} = 0 \text{ / 00} \quad \delta^{18}O_{\text{H}_2\text{O}} = -5 \text{ / 00} \]

<table>
<thead>
<tr>
<th></th>
<th>(\delta^{18}O_{\text{H}_2\text{O}} = 0\text{ / 00} )</th>
<th>(\delta^{18}O_{\text{H}_2\text{O}} = -5 \text{ / 00} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Host dolomite</td>
<td>46</td>
<td>18</td>
</tr>
<tr>
<td>Ferroan dolomite</td>
<td>58</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>33</td>
</tr>
<tr>
<td>Calcitised dolomite</td>
<td>69</td>
<td>28</td>
</tr>
<tr>
<td>Calcitised anhydrite</td>
<td>98</td>
<td>62</td>
</tr>
<tr>
<td>Rounded calcite</td>
<td>100</td>
<td>63</td>
</tr>
</tbody>
</table>
1974) is also plotted on Figures 9-3 a and 6 to give an estimation of age of the leads.

9.3.2 Discussion

Results from the galena samples showed little or no radiogenic lead. Results clustered near ages of 220-100 Ma. (Figs 9-3 a+b). The Marl Slate leads show a distinct cluster with an older model age around 250 Ma on both plots. The only galena in the EZ1 carbonates to plot near the Marl Slate is that of Rough Furze Quarry, County Durham (Appendix 1, Locality 71). Other galenas, both from County Durham and the research area show no direct relationship to those in the Marl Slate.

Lead isotope ratios from Mississippi Valley Type ore deposits show heterogeneity and are usually highly radiogenic (Heyl et al., 1966). Where deposits are approximately the same age as the host rocks lead isotope compositions are more uniform and have the same common lead age as the wall rocks (Doe and Stacey, 1974). Following these guidelines, both the Marl Slate and, on a broader scale, the EZ1 carbonate galena leads are representative of the latter lead occurrences and are thus not typical of Mississippi Valley Type galenas. Values plot close to the common lead isotope two stage evolution curve proposed by Stacey and Kramers (1974).
### TABLE 9-4

**LEAD ISOTOPE DETERMINATIONS**

<table>
<thead>
<tr>
<th>Specimen Description</th>
<th>Pb(^{208}/^{204})</th>
<th>Pb(^{207}/^{204})</th>
<th>Pb(^{206}/^{204})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yorkshire and Nottinghamshire</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena in fracture, Marl Slate, Wistow Wood borehole</td>
<td>38.310 ± 0.018</td>
<td>15.604 ± 0.018</td>
<td>18.325 ± 0.017</td>
</tr>
<tr>
<td>Bedded Galena, base of Marl Slate, Wistow Wood borehole</td>
<td>38.165 ± 0.0075</td>
<td>15.574 ± 0.0077</td>
<td>18.300 ± 0.0077</td>
</tr>
<tr>
<td>Galena on joint surface, Vale Road Quarry</td>
<td>38.475 ± 0.011</td>
<td>15.630 ± 0.010</td>
<td>18.565 ± 0.009</td>
</tr>
<tr>
<td>Replacive galena, Vale Road Quarry</td>
<td>38.538 ± 0.013</td>
<td>15.653 ± 0.012</td>
<td>18.563 ± 0.012</td>
</tr>
<tr>
<td>Galena on joint surface, Vale Road Quarry</td>
<td>38.416 ± 0.021</td>
<td>15.615 ± 0.022</td>
<td>18.400 ± 0.021</td>
</tr>
<tr>
<td>Replacive galena cube, Vale Road Quarry</td>
<td>38.550 ± 0.028</td>
<td>15.665 ± 0.027</td>
<td>18.545 ± 0.026</td>
</tr>
<tr>
<td>Galena on joint surface, Vale Road Quarry</td>
<td>38.657 ± 0.022</td>
<td>15.559 ± 0.022</td>
<td>18.544 ± 0.021</td>
</tr>
<tr>
<td>Galena in replaced anhydrite nodule, Rock Cottage Quarry</td>
<td>38.241 ± 0.005</td>
<td>15.553 ± 0.005</td>
<td>18.431 ± 0.005</td>
</tr>
<tr>
<td>Galena in replaced anhydrite nodule, Rock Cottage Quarry</td>
<td>38.384 ± 0.009</td>
<td>15.573 ± 0.009</td>
<td>18.562 ± 0.009</td>
</tr>
<tr>
<td>Galena in replaced anhydrite nodule, Rock Cottage Quarry</td>
<td>38.641 ± 0.016</td>
<td>15.675 ± 0.015</td>
<td>18.484 ± 0.014</td>
</tr>
<tr>
<td>Galena on joint surface, Rock Cottage Quarry</td>
<td>38.550 ± 0.028</td>
<td>15.665 ± 0.027</td>
<td>18.545 ± 0.026</td>
</tr>
<tr>
<td>Galena in breccia, New Edlington</td>
<td>38.393 ± 0.004</td>
<td>15.615 ± 0.004</td>
<td>18.488 ± 0.004</td>
</tr>
<tr>
<td>Galena in vug, New Edlington</td>
<td>38.436 ± 0.009</td>
<td>15.639 ± 0.008</td>
<td>18.452 ± 0.008</td>
</tr>
<tr>
<td>Galena in small fractures, New Edlington</td>
<td>38.479 ± 0.008</td>
<td>15.612 ± 0.008</td>
<td>18.381 ± 0.008</td>
</tr>
<tr>
<td>Galena in breccia, New Edlington</td>
<td>38.445 ± 0.010</td>
<td>15.639 ± 0.009</td>
<td>18.428 ± 0.009</td>
</tr>
<tr>
<td>Galena in fracture with calcite, Linby</td>
<td>38.493 ± 0.028</td>
<td>15.648 ± 0.027</td>
<td>18.531 ± 0.027</td>
</tr>
<tr>
<td>Galena in joint with no calcite, Linby</td>
<td>38.391 ± 0.011</td>
<td>15.391 ± 0.011</td>
<td>18.483 ± 0.011</td>
</tr>
<tr>
<td>Galena round sucrose dolomite, Kirby in Ashfield</td>
<td>38.684 ± 0.013</td>
<td>15.709 ± 0.013</td>
<td>18.514 ± 0.013</td>
</tr>
<tr>
<td>Outside of galena crystal, West Tanfield</td>
<td>38.417 ± 0.009</td>
<td>15.644 ± 0.008</td>
<td>18.412 ± 0.008</td>
</tr>
<tr>
<td>(Laming and Robertson, 1968)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centre of galena crystal, West Tanfield</td>
<td>38.483 ± 0.019</td>
<td>15.637 ± 0.018</td>
<td>18.403 ± 0.018</td>
</tr>
<tr>
<td><strong>Durham</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena in Marl Slate, Old Middridge Quarry</td>
<td>38.331 ± 0.015</td>
<td>15.599 ± 0.013</td>
<td>18.277 ± 0.013</td>
</tr>
<tr>
<td>Galena in Marl Slate, Old Middridge Quarry</td>
<td>38.456 ± 0.027</td>
<td>15.641 ± 0.026</td>
<td>18.318 ± 0.026</td>
</tr>
<tr>
<td>Galena in vug after displacive anhydrite, Rough Furze Quarry</td>
<td>38.255 ± 0.016</td>
<td>15.583 ± 0.016</td>
<td>18.241 ± 0.015</td>
</tr>
<tr>
<td>Weathered galena in vug after displacive anhydrite, Rough Furze Quarry</td>
<td>38.374 ± 0.025</td>
<td>15.618 ± 0.023</td>
<td>18.275 ± 0.023</td>
</tr>
<tr>
<td>Galena cube in calcite, Chiton Quarry</td>
<td>38.398 ± 0.013</td>
<td>15.615 ± 0.012</td>
<td>18.390 ± 0.012</td>
</tr>
<tr>
<td>Pb(^{208}/\text{Pb}^{204})</td>
<td>Pb(^{207}/\text{Pb}^{204})</td>
<td>Pb(^{206}/\text{Pb}^{204})</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>38.778</td>
<td>15.728</td>
<td>18.491</td>
<td></td>
</tr>
<tr>
<td>± 0.021</td>
<td>± 0.020</td>
<td>± 0.02</td>
<td></td>
</tr>
<tr>
<td>38.594</td>
<td>15.640</td>
<td>18.546</td>
<td></td>
</tr>
<tr>
<td>± 0.010</td>
<td>± 0.010</td>
<td>± 0.010</td>
<td></td>
</tr>
<tr>
<td>38.451</td>
<td>15.628</td>
<td>18.396</td>
<td></td>
</tr>
<tr>
<td>± 0.017</td>
<td>± 0.016</td>
<td>± 0.016</td>
<td></td>
</tr>
<tr>
<td>38.553</td>
<td>15.657</td>
<td>18.530</td>
<td></td>
</tr>
<tr>
<td>± 0.013</td>
<td>± 0.013</td>
<td>± 0.013</td>
<td></td>
</tr>
</tbody>
</table>

Although the statistics suggest very high precision in some of these determinations, the value of 2s is more realistically nearer ±0.05. This value has been used as the minimum size of error bars on the plots.
Figure 9.3 a Pb 207/204/Pb 206/204 results

b Pb 208/204/Pb 206/204 results
The only locality where several results cluster is Vale Road Quarry (Appendix 1, Locality 47). The galena here is found with anoxic muds and carbonates which contain plant fragments (3.2.5; 8.2.2). The sulphide was probably derived from bacterial reduction of sulphate (9.2.2). Muds, particularly anoxic muds, contain more uranium than thorium. Uranium decay produces more radiogenic lead, increasing $\text{Pb}^{206}/\text{Pb}^{204}$ with respect to $\text{Pb}^{207}/\text{Pb}^{204}$ (Fig 9-3 a). A host clastic sediment could cause a lateral shift of the Vale Road Quarry galena leads, if they formed during early diagenesis. Interpolating backwards, these leads may have derived from values near the Marl Slate cluster (Fig 9-4). Thus the galenas here may be the lateral, more clastic equivalent of the Marl Slate/Kupferschiefer. Further research on the underlying carbonates may show similarities with the German Mutteloz, the carbonate lateral equivalent of the Kupferschiefer which was developed on basin highs (Herman, 1956; Paul, in press).

The lead isotope results from Vale Road Quarry are significantly above the two-stage growth curve (Fig 9-3 a). The isochron linking these results with those of the Marl Slate, when projected backwards, cuts the two stage growth curve at about 3b.y. (3000 Ma) (Fig 9-4). This suggests that some source of Archaen
Figure 9.4 Two-stage isotope evolution curve with Vale Road - Marl Slate isochron.
EXPLANATION

- Galenas IVI ≤ 100 m.y.
- Galenas IVI > 100 m.y.
- Feldspar leads IVI ≤ 100 m.y.
- Feldspar leads IVI > 100 m.y.

**Marl Slate - Vale Road isochron**

**Meteoritic isochron**
uranium-enriched lead was mixed with the Marl Slate leads in the Vale Road Quarry galenas.

Although also penecontemporaneous in origin, (8.2.1, 9.2) the lead results from the mineralised displacive anhydrite nodules show a wide spread of lead isotope ratios (Figs 9-3 a+b), implying the existence of an open system crystallisation recycling leads from many different sources. This supports the stable isotope data (9.2) and earlier inferences (4.5.2) that sulphate reduction took place with the influence of meteoric water. The results from the Doncaster area (Fig 9-3 a+b) also are spread. These galenas crystallised in voids in the breccia near an open fault system (10.2.1). Fluid fluctuation within the fault and associated pore systems is suggested by this scattered data.

The values for the galena specimen collected by Lamming and Robertson (1968) are considerably different from those published which gave a radiogenic age of -50 Ma. The values obtained in this study fall within the main cluster of EZ1 carbonate galenas with a conformable lead age.

Lead isotope values from the Derbyshire ore field have the same range as EZ1 carbonate leads (Figs 9-3 a+b) (Coomer and Ford, 1975) whereas values from the Closehouse mine in the Northern
Pennines show a relatively wider scatter (Figs 9-3 a+b) (Brazier, 1979). There is thus no single source of Pennine or Permian leads.

Four major points emerge from this study of Permian galena lead isotopes:

(i) lead isotope values determined give near conformable common lead ages and contain little or no radiogenic lead

(ii) Marl Slate galenas contain leads distinct from most of those in the overlying EZ1 carbonates, although a possible relationship exists with the penecontemporaneous galenas in more clastic beds at Vale Road Quarry.

(iii) Marl Slate and Vale Road galena lead isotopes are the only ones to cluster tightly; other values thus show no indication of a nearby lead deposit (Heyl et al., 1966).

(iv) the source of the leads for Pennine galenas is not distinct from those in the EZ1 carbonates.

9.4 Fluid inclusions

A note should be added here on the attempt to determine crystallisation temperatures from fluid inclusions in Cadeby Formation minerals. Although this resulted in calibration of the Chaixmeca fluid inclusion stage for the 0°-200°C temperature range no usable results were
obtained. Sphalerite crystals, although translucent, contained submicroscopic inclusions. Other evidence (8.2.1, 9.2) (Harwood, 1980) suggests penecontemporaneous sphalerite formed at low temperatures. Some baryte specimens were semi-opaque and contained many mineral inclusions (e.g. Harwood, 1980, Fig 8); translucent barytes had vapourless inclusions. Calcite also had vapourless inclusions, many of which showed evidence of leakage or necking, or both. Freezing data on calcite spar in vugs after evaporite dissolution gave low salinities. Freezing data from other minerals was not feasible. The fluorite crystals from the Bramham area (e.g. Fig. 8-10 c) were found late in the research. Thin sections show few fluid inclusions with small vapour bubbles; homogenisation temperatures have yet to be determined.
CHAPTER 10
The pre-Permian Basement

10.1 Introduction

Mineralised occurrences have a patchy distribution throughout the outcrop. There are large gaps where no exposures are mineralised (8.8; Appendix 1, Fig A1-1). East of the outcrop information is scarce and less reliable; the Cadeby Formation is seldom completely cored and mineralisation may be missed. The group of borehole records from I.G.S. memoirs (Appendix 1, localities 30-35, 45) may represent a fastidiousness on the part of the author in the original core logs. In general, many occurrences of minerals in bores and shafts for coal, hydrocarbons or water have been overlooked, so the absence of records of mineralisation in the sub-surface area is not necessarily significant. The sphalerite at Wistow Wood (8.3.4) was only discovered by chance within the shaft; the 9 inch diameter core contained only marcasite with calcite.

Other authors (notably Hirst and Smith, 1974 and Ineson et al., 1972) have remarked the importance of structural controls in the pre-Permian basement on EZ-1 carbonate mineralisation. Figure 10-1 shows that the three northern-most mineral districts; Farnham (8.7), Bramham (8.5.1) and Doncaster (8.3.1) overlie important basement structural trends and that the more frequent records in Nottinghamshire overly
Figure 10.1 Map showing major structures in the pre-Permian basement and mineralised localities.
several fold and fault structures and the eastwards extension of the Derbyshire massif. Basement heat flow may also stimulate hydrothermal circulation.

The pre-Permian basement is also important as a region of groundwater flow. Ford (1969) and Robinson and Ineson (1979) derive their metals for Derbyshire Pennine mineralisation from Carboniferous formation waters migrating up-dip from the east. These Carboniferous formation waters possibly moved up into the Cadeby Formation, may have been modified by Cadeby Formation formation waters or modified during the pre-Zechstein continental weathering. Basement formation waters moving through the Cadeby Formation may introduce mineralisation; they may also cause alteration of the dolomites. Thus basement structure and hydrology may have an important influence on both diagenesis and mineralisation in the Cadeby Formation.

10.2 Basement structure

10.2.1 The Farnham area

Figure 10-2 shows the outline geology of the Knaresborough and Farnham districts, taken partly from the 1874 Geological Survey map and memoir (Fox-Strangeways, 1908), partly from recent mapping by I.G.S. and partly from personal interpretation. The Cadeby Formation is generally exposed throughout the area, except for the Knaresborough Gorge, and is in places covered by a considerable thickness of glacial and post-glacial deposits (Dundas, 1981).
The Farnham anticline and the Knaresborough monocline (Fig 10-2) are the largest fold structures within the Cadeby Formation. The area also includes the pre-Permian Harrogate anticline which exposes Yoredale facies Carboniferous limestones in its core. The well known spa springs issue from the crest of the Harrogate anticline and from faults along its flanks. Carboniferous limestones also directly underly the Cadeby Formation at Ellenthorpe, near Boroughbridge (B.P. well records) (Fig 10-2). It was therefore encouraging to find that the previously known 'traces' of mineralisation in the area were more extensive than hitherto realised (8.7).

Farnham lies on the eastwards extension of the Craven Fault Belt. This fault felt forms the southern boundary of the Askriig Block (Fig 10-3) where it is associated with the mineralisation in the Grassington-Yarnbury and Greenhow fluorite-galena districts (Dunham, 1974); the fault belt has attracted attention from mineral exploration companies as a prime target for 'Irish-style' sulphide mineralisation.

North and east from Farnham are faults associated with the Coxwold-Gilling system, the continuation of the Howardian-Flamborough
Fault Belt which forms the northern boundary of the Market Weighton block (Kent, 1974; 1980) (Fig 10-3). The associated Easingwold fault may persist through the Vale of York to join the structures at Farnham or Knaresborough (A.C. Cooper, pers. comm.). The Howardian-Flamborough Fault Belt swings south east into the North Sea Dowsing fault system which forms the northeastern limit of the Mesozoic shelf (Kent, 1974). Further to the south east it joins the complex fault belt which crosses the Dutch North Sea and the Netherlands to link with the Rhine Valley Graben system (Kent and Walmsley, 1970; Kent, 1974).

Marie (1975, Fig 1B) showed that Rotliegendes sedimentation was influenced by the Flamborough-Dowsing Fault system. Taylor and Colter (1975, Fig 4A) show some evidence of the presence of the Market Weighton high during formation of the EZ3 evaporites. However carbonate/evaporite isopach data is distorted by massive replacement of carbonates by evaporites; thus although there is no published evidence, it is possible that the Market Weighton Block had some influence during Zechstein carbonate sedimentation.

The Craven Fault Belt and the Howardian-Flamborough-Dowsing Fault System therefore were
Figure 10.3  Major basement blocks and associated faults in Yorkshire (compiled from Kent, 1974 Figs 4 and 5 and personal interpretation).
active before and after Cadeby Formation sedimentation, with movement on the Howardian-Flamborough system continuing until after Upper Cretaceous (Kent, 1974; 1980). The two fault systems, which down throw in opposite directions (Fig 10-3), meet near the Farnham area. This junction area seems a good prospect for hydrothermal activity.

The Harrogate anticline is one of a series of northeast trending folds in the area. This may be a relict Caledonian trend, but is more likely to be conjugate folding associated with movement along the Craven Fault Belt (Fig 10-3). No mineralisation is known within the Harrogate anticline but there are records of up to eighty-eight spa springs yielding mineral waters of different compositions. Recorded compositions vary considerably within small areas and include hydrogen sulphide contents of up to 36.6 cm$^3$ l$^{-1}$ and barium chloride of around 100 ppm (Fox-Strangeways, 1908) although no baryte is recorded from the area. Sodium chloride content is high enough for evaporation works to have produced salt in the seventeenth century.

On a more regional scale, geophysical maps show two magnetic basement highs in the Ripon-Harrogate area (Fig 10-4 a) and a region of positive gravity anomalies (Fig 10-4 b), both
Figure 10.4

a Contours on the magnetic basement in central and south-east Yorkshire (from Kent, 1974, Fig 3).

b Residual gravity anomalies in central and south-east Yorkshire (from Kent, 1974, Fig 2).
suggesting a prominent fault structure in the region. The map shows a series of faults and folds, indicating a complex geological history. The map also highlights the presence of rocks such as limestone and sandstone, which are common in the area. The map is oriented with north at the top and includes a scale for distance.

The text mentions the east-west structural trends in the area, with the recognition of galena in the Spelle Hill core. This supports the idea that the area has been subjected to significant tectonic activity in the past.

South of the area, the Coal Measures dip gently eastwards and to the north the strike of the concealed coalfield is again north-south. No
suggesting a prominent basement structure in the area.

The intersection of the two fault belts, the Harrogate anticline with the continued presence of hot mineral springs and the geophysical anomalies all suggest that mineralisation within this area may be more than originally suspected. The presence of copper also differs from other mineral occurrences in the Cadeby Formation. Copper mineralisation further north at Middleton Tyas (Raistrick, 1936; Dunham, 1948) and Raisby Hall (Hirst and Smith, 1974) is also associated with major east-west structural trends. The recognition of galena in the Spellow Hill core (Appendix 1, locality 9) supports the inferences of hydrothermal activity within the region. Penecontemporaneous mineralisation at Wormald Green and at Well (8.2.1 and 8.2.3) may be associated with hydrothermal activity and movement along the fault zones (Harwood, in press p.8)

10.2.2 The Bramham area

The baryte mineralisation in the Bramham area (8.5.1) overlies the northern margin of the Coal Measures which here strikes east-west. South of the area the Coal Measures dip gently eastwards and to the north the strike of the concealed coalfield is again north-south. No
major basement feature is known which governs this change in strike, but two major structures in the area are more evident, the Wharfe anticline and the Osmondthorpe-Oglethorpe faults (Fig 10-5).

The Wharfe anticline plunges eastwards from the flanks of the larger Harrogate anticline. Springs originating from this structure are known at Wetherby (where they were used to fill a Roman bathing pool near the river banks) and Boston Spa and Thorpe Arch (Anderson, 1945). Baryte is found along the crest of the anticline (Fig 10-5; 8.5.1).

The Osmondthorpe-Oglethorpe faults trend southwest/northeast through Leeds and Tadcaster (Kent, 1974, Fig 4) with subsidiary northwest trending faults. Continuation of this fault system runs through York into the Howardian Fault at the northwest margin of the Market Weighton Block (Fig 10-3). In the Bramham area, individual faults have throws of up to 60 metres in the Carboniferous and some were reactivated in post-Permian times. Present day groundwater is restricted by two faults (Fig 10-5) although aided by others (Aldrick, 1978). Some of the fluorite mineralisation (Appendix 1, locality 12c) is found near the junction of two faults.
Figure 10.5 Structure and mineralised localities in the Bramham district.
No baryte is known further southwest along the fault system. This may be because of the lack of phosphate in the Coal Measures, suitable in the Brotherton Formation being derived from sedimentary sources. This area is also geologically anomalous by virtue of higher gravity readings and regional magnetic anomalies, possibly corresponding with a baryte mineralisation in the Brotherton Formation.

10.2.3 The structure and history of the Coal Measures in the area south of the Wharfe anticline and north of the Oglethorpe and Aberford is still uncertain. The main structure control features were investigated in the Geological Survey map and memoir (Mitchell, 1947). Detailed subsurface maps of coal measure structures are unavailable due to economic interests in obtaining data on hydrocarbons. Surface Coal Seam maps in the area are at present being re-mapped by the BGC. The mineralised localities in the Cadeby Formation lie in a zone of northeast-southwest orientation, in an extension of the Don monocline (Fig. 10-6). This is one of the largest structures in the area.
No baryte is known further southwest along the fault system. This may be because of the lack of sulphate in the host Coal Measures, sulphate in the Cadeby Formation being derived from the evaporites (9.2.2). This area is also underlain by a positive residual gravity anomaly (Fig 10-4 b) although there is no corresponding magnetic anomaly.

10.2.3 The Doncaster area

Galena mineralisation in the breccia at the top of the Upper Member (3.4.5; 8.3.1) was originally thought to be stratabound and have no relation to structure. However, galena only on the northeast-southwest trending joint faces in the Lower Member (Appendix 1, locality 26) showed some structural control so basement features were investigated.

Geological maps are based on the Barnsley Geological Survey map and memoir (Mitchell, 1947). Detailed subsurface maps of coal measure structures are unavailable due to economic interests in both coal and hydrocarbons. Surface Coal Measure Geology is at present being re-mapped by I.G.S. The mineralised localities in the Cadeby Formation lie in a zone of northeast-southwest faulting above the northeastwards extension of the Don monocline (Fig 10-6). This is one of the largest structures in the
Figure 10.6 Structure and mineralised localities in the Doncaster district.
Outcrop of Cadeby Formation

galena mineralisation

Δ Adwick

Bentley Colliery

North Don Fault

Don Monocline

South Don Fault

Sprotborough

Δ Doncaster

New Edlington

1 km

Yorkshire Coalfield with displacements of up to...
Yorkshire Coalfield with displacements of up to 600 metres. To the west of the Cadeby Formation outcrop the Don monocline overlies a magnetic basement high (Fig 10-4 a). Both gravity and magnetic anomalies show the Askern-Spital High (Figs 10-1, 10-4 a+b) which intersects the Don faults immediately north-east of the Cadeby Formation outcrop. The junction of these two basement structures may serve as a funnel for hydrothermal fluids. Present economic interests, however, are concentrating on hydrocarbon potential and it thus seems unlikely that this was a major hydrothermal conduit. The near-conformable common lead ages (9.3.2) do, however, suggest a hydrothermal source. It is thought that fluids migrated up the fault system to be trapped in the breccia horizon below the less permeable Ripon Formation. Sulphur was from a separate, reduced source (9.2.2).

10.2.4 The Whitwell area

The pre-Permian structure of the north Nottinghamshire area is transected by three east-south-east trending anticlines and associated faults (Fig 10-7). Baryte mineralisation in the Whitwell area is concentrated around the central, Whitwell, anticline which has an amplitude of around 300 metres. It is followed
Figure 10.7 Mineralised localities and basement structure in Nottinghamshire (constructed from Edwards, 1951).
Park Hall Fault (Eden et al., 1957, Fig 27), which has a throw of 100 metres in the Coal Measures, and 30 metres in the Cadeby Formation. This fault is thought to be unmineralised in the Coal Measures (Ineson et al., 1972) and is not exposed at surface in the Cadeby Formation. Lack of mineralisation in the Coal Measures may be due to the absence of available sulphate. The Whitwell vein parallels the Park Hall Fault and overlies the axial trace of the Whitwell anticline (Ineson et al., 1972) so there seems to have been some degree of structural control. No mineralised occurrences were found in the Cadeby Formation above the more northern, Kiverton anticline and fault zone, in spite of several outcrops and evidence of post-Permian folding (Eden et al., 1957, p.145). The Whitwell anticline does, however, continue into the Eakring structures (Fig 10-7) (Edwards, 1951) whereas there is no continuation of the Kiverton anticline. There are no underlying major basement structures nor geophysical anomalies.

10.2.5 North Nottinghamshire

South of Whitwell, mineralisation is dispersed throughout the area and shows little relation to basement structure (Fig 10-7). Basement fold structures trend more north-north-westwards around
the margins of the Derbyshire massif, an exception being the east-south-east trending Mansfield anticline. This anticline may have locally helped concentrate some of the baryte and sulphide mineralisation reported from the Teversal-Skegby area (8.4.1) (Aldred, 1969). Otherwise, mineralisation in the southern part of the Cadeby Formation outcrop has little obvious relation to basement structure.

10.3 Basement heat flow

Exploration for geothermal energy has detailed two areas of high basement heat flow within England and Wales (Brown et al., 1980), the more northern province extending across the outcrop of the Cadeby Formation (Fig 10-8). Brown et al. note that the Caledonian granites of northern Britain contain unusually high levels of heat producing elements which influence hydrothermal circulation long after granite emplacement. This fact has been well documented for the North Pennines by several lines of evidence, including isotope determinations (Solomon et al., 1971), fluid inclusions (Sawkins, 1966; Smith, 1974) and vitrinite reflectances (Creaney, 1980). High heat flow may stimulate hydrothermal fluid circulation through basement structures, resulting in mineralisation where fluid compositions are metal-rich and an adequate source of sulphide and/or sulphate exists.
Figure 10.8 Areas of high basement heat flow in the British Isles (from Brown et al., 1980).
The evaporites overlying the Caithy Formation have a low thermal conductivity and would have formed an effective insulating layer preventing further upwards migration of hydrothermal fluids. This probably comprised a composite cover comprising outcrop regions of evaporites, Maissite, and the Marl Slate. Temperatures due solely to the geothermal gradient are not likely to have exceeded about 80°C. However, the combined effect of geothermal and metamorphic heating would have been sufficient to produce temperatures in excess of 400°C (Cooper, 1975). Background temperatures were therefore likely to have been significantly higher than those of the Caithy Formation.

Zones of higher vitrinite reflectance in the Lower Devonian sediments of the Lower Meghrigheh (Figures 9 and 10) could represent possible hydrothermal conduits. Future research on vitrinite reflectance in these sediments and in the Carboniferous sediments further east, perhaps as far away as the North Sea Basin (Ford, 1969), may provide further evidence of hydrothermal activity in the Devonian period. Metals in the Alston Block mineralisation, however, are thought to have been leached from Lower Palaeozoic sediments and Carboniferous orophytic deposits are thought to originate from formation waters moving up-cip from these sediments. Further studies are needed to determine the exact source and migration pathways of these metals.
The evaporites overlying the Cadeby Formation have a low thermal conductivity and would have formed an effective blanket as well as preventing further upwards migration of fluids because of their effectiveness as a seal. Mesozoic cover probably comprised one or two kilometers in the outcrop region; temperatures due solely to the geothermal gradient are not likely, therefore, to have exceeded about 80°C. Vitrinite reflectivities from the Marl Slate of south Durham are in accord with a period of heating of perhaps 100Ma at low temperatures (ca 40°C) (Cooper, 1975). Background temperatures were therefore likely to have been low during burial of the Cadeby Formation. Zones of higher heating could represent possible hydrothermal conduits. Future research on vitrinite reflectances in the interbedded carbonaceous muds of the Lower Member (Appendix 6, Logs 5, 9 and 10) could define any such zones.

10.4 Formation water flow and metal origins

10.4.1 General considerations

Metals in the Derbyshire Carboniferous ore deposits are thought to originate from formation waters moving up-dip from Carboniferous sediments further east, perhaps as far away as the North Sea Basin (Ford, 1969). Metals in the Alston Block mineralisation, however, are thought to have been leached from Lower Palaeozoic sediments and
the Weardale granite by fluid circulation promoted by high heat flow (Dunham, 1970; Solomon et al., 1971). Mineralisation within the Cadeby Formation is of much lower grade and metals may come from a variety of sources; major mineralisation is of galena and baryte. Sources of lead, barium and sulphide/sulphate should thus be considered. Most recent models of mineralisation involve the mixing of two fluids, one bearing metal ions and the other carrying sulphate or sulphide on the same basis as the model envisaged for Pine Point mineralisation by Jackson and Beales (1967). Metal ions are thought to be carried in the fluids as soluble chloride complexes. Anderson (1975) and Beales (1975) have detailed chemical conditions of fluid mixing and metal sulphide precipitation.

10.4.2 Origin of sulphate/sulphide

The origin of sulphate where evaporite dissolution has not occurred before mineralisation presents little problem. Isotope determinations show some sulphate to be directly derived from evaporite sulphate (9.2.2). Some sulphides are also from bacteriogenically reduced sea water sulphate (9.2.2) (Coleman and Harwood, 1980). Where evaporite dissolution and dolomite alteration
has taken place before mineralisation, however, the sulphate/sulphide origin is less obvious. Dissolution of nearby overlying evaporites is likely to cause dedolomitisation (5.3) and there are no instances of mineralisation close to largely dedolomitised carbonates. Nor is it probable that fluids resulting from distal evaporite dissolution would provide an adequate source of sulphate as isotopes would then show domination of meteoric sources. Migration up-dip of evaporite-rich pore fluids from non-altered dolomites could provide sulphate although isotopic modification of the sulphate during mesogenesis and migration is necessary (9.2.2). Some sulphate may also be derived from Jurassic sea water (9.2.2). More isotope determinations are necessary from each of the various mineral assemblages (Table 8-1) before the sulphate or sulphide origins can be further defined.

10.4.3 Origin of Lead

The lead isotope ratios for Cadeby Formation and Derbyshire galenas are not consistent with an origin from Carboniferous formation waters without modification and lead re-cycling. The near-conformable ages indicate it is more likely some, at least, of the lead had a mantle origin in the Upper Permian or Lower
Triassic. This lead must have been introduced through basement fractures. The position of many of the ratios above the growth-line (Fig 9-3) does, however, indicate a possible input of Archaen lead (9.3.2).

10.4.4 Origin of barium

Barium is a common constituent of formation waters; it is also concentrated in some evaporite deposits. There are thus two possible origins of the barium for the common baryte mineralisation in the Cadeby Formation.

Turekian and Wedepohl (1961) list barium concentrations in formation waters (Table 10-1), with maximum values in the Carboniferous formation waters of Northern Europe and North America. Barium contents of up to 4180 ppm are found in formation waters of the Durham and East Midlands coalfields (Edmunds, 1975). Traces of barium are also recorded from the Yorkshire coalfield (Anderson, 1945) and baryte is known to precipitate from mine waters on the shaft linings of Bevercoates Colliery (R.E. Elliot in discussion with Ineson et al., 1972 p.148). Contact of barium-rich waters with a sulphate source would cause baryte precipitation under a range of conditions compatible with shallow burial and formation water chemistry.
Table 10.1 Barium concentration in formation waters

<table>
<thead>
<tr>
<th>Period</th>
<th>Country</th>
<th>Total No. of samples</th>
<th>No. of samples &gt; 1 ppm</th>
<th>Mean Ba conc. of samples with Ba &gt; 1 ppm</th>
<th>Maximum Ba conc. ppm</th>
<th>Analytical method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precambrian</td>
<td>U.S.A.</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>S</td>
<td>WHITE (1965)</td>
</tr>
<tr>
<td></td>
<td>U.S.A.</td>
<td>4</td>
<td>3</td>
<td>61</td>
<td>100</td>
<td>S</td>
<td>McGRAIN and THOMAS (1951)</td>
</tr>
<tr>
<td>Silurian</td>
<td>U.S.A.</td>
<td>1</td>
<td>1</td>
<td>320</td>
<td>320</td>
<td>S</td>
<td>McGRAIN and THOMAS (1951)</td>
</tr>
<tr>
<td></td>
<td>Canada</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>S</td>
<td>WHITE (1965)</td>
</tr>
<tr>
<td></td>
<td>Germany</td>
<td>2</td>
<td>1</td>
<td>1.1</td>
<td>W</td>
<td></td>
<td>FRESENIUS (see MICHEL 1963)</td>
</tr>
<tr>
<td></td>
<td>U.S.A.</td>
<td>37</td>
<td>21</td>
<td>828</td>
<td>2,000</td>
<td>S</td>
<td>POTI (1962)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13</td>
<td>7</td>
<td>700</td>
<td>W, S</td>
<td></td>
<td>PRICE et al. (1937), WHITE et al. (1963)</td>
</tr>
<tr>
<td></td>
<td>U.S.S.R.</td>
<td>73</td>
<td>67</td>
<td>971</td>
<td>S</td>
<td></td>
<td>HOSKINS (1947)</td>
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<td></td>
<td></td>
<td>69</td>
<td>12</td>
<td>828</td>
<td>2,000</td>
<td>S</td>
<td>KOZIN (1964)</td>
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<tr>
<td>Carboniferous</td>
<td>Belgium</td>
<td>1</td>
<td>1</td>
<td>347</td>
<td>347</td>
<td>S</td>
<td>CAMERMAN (1951)</td>
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<tr>
<td></td>
<td>Germany</td>
<td>4</td>
<td>3</td>
<td>1,007</td>
<td>1,250</td>
<td>S</td>
<td>JACOBSHAGEN and MÜNNICH (1964)</td>
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<td></td>
<td></td>
<td>249</td>
<td>46</td>
<td>1,006</td>
<td>2,860</td>
<td>W</td>
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<td></td>
<td></td>
<td>225</td>
<td>69</td>
<td>832</td>
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<td>152</td>
<td>38</td>
<td>798</td>
<td>2,000</td>
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<td>ANDERSON (1945), GIBSON (1963)</td>
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<tr>
<td></td>
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<td>152</td>
<td>112</td>
<td>447</td>
<td>5,530</td>
<td>W, S</td>
<td>PRICE et al. (1937)</td>
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<td></td>
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<td>77</td>
<td>34</td>
<td>265</td>
<td>1,080</td>
<td>S</td>
<td>POTI (1962), HOSKINS (1947)</td>
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<td></td>
<td></td>
<td>72</td>
<td>20</td>
<td>236</td>
<td>1,980</td>
<td>S</td>
<td>COLLINS (1969)</td>
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<td>20</td>
<td>190</td>
<td>S</td>
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<td>KOZIN (1964)</td>
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<tr>
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<td>U.S.S.R.</td>
<td>111</td>
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<td></td>
<td></td>
<td></td>
<td>HERMMANN (1961)</td>
</tr>
<tr>
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<td>S</td>
<td></td>
<td>WHITE et al. (1963)</td>
</tr>
<tr>
<td></td>
<td>U.S.A.</td>
<td>3</td>
<td>5.2</td>
<td>9.6</td>
<td>S</td>
<td></td>
<td>KOZIN (1964)</td>
</tr>
<tr>
<td></td>
<td>U.S.S.R.</td>
<td>48</td>
<td>5</td>
<td>73</td>
<td>S</td>
<td></td>
<td>PUCHELT (1967)</td>
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<tr>
<td>Jurassic</td>
<td>Germany</td>
<td>26</td>
<td>7</td>
<td>30</td>
<td>S, W</td>
<td></td>
<td>ASSARSON (1948)</td>
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<tr>
<td></td>
<td>Sweden</td>
<td>8</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>S</td>
<td>DUCKLEY et al. (1958), WHITE et al. (1963)</td>
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<tr>
<td></td>
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<td>24</td>
<td>14</td>
<td>72</td>
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<td>TUREKIAN and WEDEPOHL, (1961)</td>
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<td>59</td>
<td>S</td>
<td>BAILLY et al. (1961)</td>
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<td>U.S.A.</td>
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<td>37</td>
<td>150</td>
<td>S</td>
<td></td>
<td>BAILLY et al. (1961), WHITE (1965)</td>
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<tr>
<td></td>
<td>Quartermary</td>
<td>Poland</td>
<td>6</td>
<td>3.6</td>
<td>4</td>
<td>S</td>
<td>DOWGIALLO (1965)</td>
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<tr>
<td></td>
<td>Quartermary</td>
<td>U.S.A.</td>
<td>2</td>
<td>16</td>
<td>28</td>
<td>S</td>
<td>WHITE et al. (1963)</td>
</tr>
</tbody>
</table>
Present day formation waters in the Visean and Namurian show dilution over the eastwards extension of the Derbyshire massif (Fig 10-7) where structural trends bring them near to the sub-Permian unconformity (Downing, 1967; Downing and Howitt, 1969). Dilution decreases down-dip and must have resulted in displacement of some of the formation waters. F.W. Smith (pers. comm., 1979) notes that the diluted area underlies the southern zone of dispersed mineralised localities within the Cadeby Formation (Fig 10-7). He estimates that the quantities of barium present in this area could have come from displacement of these formation waters, if these waters had an average barium content of 625 ppm (c.f. Edmunds, 1975). Groundwater displacement could thus account for the dispersed baryte mineralisation, although it is unlikely to provide a sufficiently concentrated source for either the Whitwell or Bramham occurrences. The lack of dilution of the formation waters further north than Clowne (Downing and Howitt, 1969) may account for the absence of the dispersed baryte mineralisation to the north. Present day baryte precipitation demonstrates that mineralisation from formation waters is a viable hypothesis.
Davidson (1966), Lagny (1980) and Fuchs (1980), amongst others, note that many stratiform baryte deposits are associated with evaporites. Sea water contains 88ppb barium. Increase in salinity lowers the solubility co-efficient, so that for a concentration of 2.5 times normal sea water salinity, barium content is reduced to 60ppb (Fuchs, 1980). Fuchs also states that evaporitic barytes are usually characterised by high strontium contents, with values up to 7900ppm. However, as the sulphate in some Cadeby Formation barytes is from evaporites, this may also carry a high associated strontium content. Strontium content does not, therefore, give unequivocable evidence of barium origin. The barium in the larger-scale replacement baryte deposits at Bramham and Whitwell is, perhaps, more likely to have originated from re-mobilised barium-rich evaporites than that of the more dispersed baryte mineralisation. Fluid flow through basement and Permian fractures may have promoted this re-mobilisation, rather than being the source of the mineralising fluids.

10.4.5 Origin of other metals

Zinc and copper occurrences are not common in the Cadeby Formation. Copper is only
found in any quantity at Farnham where it seems to be related to major fracture systems and hydrothermal fluids (10.2.1). Zinc, as sphalerite, is most common in bacteriogenically replaced evaporite nodules (8.2.1) and may be concentrated by organic activity. Elsewhere, sphalerite is only present in minor quantities.

The pyrite/hematite/geothite at Bramham (8.5.1) is found directly below red marls. There seems little doubt that the iron was derived from the marls and, if so, must have descended into the area of baryte mineralisation. The dolomite beds above the mineralised flat are red-stained, also suggesting that the iron was re-mobilised from above. However, at present there is no unequivocable evidence of movement of either barium or sulphate with the iron.

10.5 Summary of basement controls on mineralisation

The spatial distribution of the more highly mineralised districts in the Cadeby Formation can be related to the underlying major basement structures. The dispersed mineralisation in the south of the outcrop, however, shows little relation to major structures and may result from upwelling, displaced formation waters.

The Cadeby Formation overlies a zone of high heat flow
which contains several known ore deposits. The large amount of void space in the Cadeby Formation, particularly in the evaporitic lagoon facies of the Lower Member, means that this formation should not be ignored in future mineral prospecting within the United Kingdom.
11.1 Thesis Conclusions

The occurrences of mineralisation within the Cadeby Formation are controlled by facies, diagenetic history and the pre-Permian basement. Facies control is demonstrated by penecontemporaneous and mesogenetic mineralisation in low energy lagoon facies of the Lower Member, where mineralisation is related to the former occurrence of evaporites. The galena in the breccia bed at the top of the Upper Member also shows facies control (Fig 11.1). Other facies, which form adequate traps, are poorly mineralised (8.8).

Mineralisation associated with penecontemporaneous diagenesis is restricted to lagoon facies and is of low grade (8.2). However, penecontemporaneous galena mineralisation is found at the same facies boundary over a wide area in Nottinghamshire (8.2.2) and replaced evaporites might be expected to be more widespread in the Ripon area (8.2.1). Local recent (21st November 1981) reports of 'gold' at depths of 15 metres in core sections for a new quarry at North Stainley (SE 28-76-) substantiate this suggestion.

Mesogenetic mineralisation is also facies controlled in places (8.3.1, 8.4.1). However, porosity, itself dependent on diagenesis, is the main factor in determining the exact location of mineralisation. Evaporite dissolution results in vugs and open pore
Figure 11.1  Mineralisation and facies relationships in the Cadeby Formation.
Lower Member moderate energy facies
Lower Member lagoon low energy facies
Upper Member breccia facies
other mineralisation in the Upper Member

Separate mineralised districts are defined. Most of these districts overly minor structures in the pre-Permian basement (Fig 1). The occurrences around Ropon are near the eastern continuation of the Craven Fault Belt and the western part of the Jurassic-Flamborough Fault system, while Doncaster localities above the Don monocline and east of Whitwell above the Whin Sill monocline. The Mansfield area and further south direct correlation with basement structure is difficult due to the high and low grade galena mineralisation at the base of the Lower Permian Limestone and several closely spaced structures in the Carboniferous. A distinction to these correlations are the intercalations of the Bramhope area where underlying Carboniferous appear minor. However, mineralisation in the Namurian plus the east-west strike of the Namurian boundary in the area may include some deeper basement lamination.
spaces during mesogenesis and telogenesis (6.4.2, 6.5.1), providing voids for mineral precipitation (Fig 11.2). Dolomite alteration, with or without ferroan dedolomitisation, (5.2.7) causes some increase in intercrystalline porosity allowing permeation of mineralising fluids. Modified primary porosity, although effective in the non-mineralised patch reefs (3.2.3), only carries mineralisation in the breccia facies (4.5.8, 8.3.1). Mesogenetic porosity in patterned carbonates is high and forms an attractive host for mineralisation (8.3.4), where metal-rich fluids are present.

Separate mineralised districts are defined. Most of these districts overly major structures in the pre-Permian basement (Fig 11.2). The occurrences around Ripon are near the eastward continuations of the Craven Fault Belt and the western part of the Howardian-Flamborough Fault system, the Doncaster localities above the Don monocline and those of Whitwell above the Whitwell anticline. In the Mansfield area and further south direct correlation with basement structure is difficult due to the widespread low grade galena mineralisation at the base of the Lower Magensian Limestone and several closely spaced structures in the Carboniferous. A major exception to these correlations are the baryte localities of the Bramham area where underlying Carboniferous appear minor. However, mineralisation within the Namurian plus the east-west strike of the Namurian-westphalian boundary in the area may include some deeper basement lineation.
Figure 11.2 The relationship between basement structure and types of mineralisation in the Cadeby Formation.

- mineralisation due to replacement of evaporites
- mineralisation in voids after evaporite dissolution
- mineralisation at top of Upper Member
- stratabound galena mineralisation
- other mineralisation
stable isotope determinations may either confirm or
destroy many of the arguments presented herein. More
sulphur isotope values would give additional information
on sulphate/sulphide origins.

Research on Zechstein carbonates in the subsurface in
England has been limited to confidential work by oil
companies or their consultants. Many subsurface cores
of Zechstein sediments are now released; I.G.S. also
hold core sections from some of their boreholes. No
published recent research has been done on the evaporites,
which constitute the major part of Zechstein sediments
in the subsurface. Thus the scope for research in
sedimentology and diagenesis in the subsurface is very
wide. Furthermore, the conclusions on mineralisation
reached during this research may have applications both
in other English Zechstein carbonates in the subsurface
and throughout the Zechstein Basin.
### APPENDIX 1

**OCCURRENCES OF MINERALISATION IN EZ1 CARBONATES**

Localities in this appendix are numbered and named. Grid references plus a brief description of the mineralisation and the original reference where relevant are also given.

<table>
<thead>
<tr>
<th>Locality No.</th>
<th>Name</th>
<th>Grid Reference</th>
<th>Description and Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cadeby Formation Localities</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Scorton borehole</td>
<td>SE 251988</td>
<td>Lower Member - some baryte in dolomite (Fowler, 1945)</td>
</tr>
<tr>
<td>2</td>
<td>Catterick area</td>
<td>SE 23-97</td>
<td>Lower Member - small amounts of vein galena present (Smith, 1977)</td>
</tr>
<tr>
<td>3</td>
<td>Saugdale Beck borehole</td>
<td>SE 534990</td>
<td>3589' - 3629'; baryte, fluorite. 3360' - 3369'; chert lenses with sphalerite and galena on joint surfaces (Fowler, 1944)</td>
</tr>
<tr>
<td>4</td>
<td>Bedale Quarry well</td>
<td>SE 266813</td>
<td>Lower Member - (a) baryte in breccia caused by dewatering (b) baryte in veinlets by collapse structures (c) baryte, hematite, marcasite and traces of galena in planar voids after evaporite dissolution. Fluorite traces in calcite.</td>
</tr>
<tr>
<td>5</td>
<td>West Tranfield</td>
<td>SE 282784</td>
<td>Lower Member - vein with fluorite and galena with baryte on neighbouring joint faces and infilling vugs (Laming and Robertson, 1957)</td>
</tr>
<tr>
<td><strong>Ripon-Farnham District</strong></td>
<td></td>
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</tr>
<tr>
<td>6</td>
<td>Wormald Green</td>
<td>SE 300650</td>
<td>Lower Member - sphalerite, calcite, baryte, galena and fluorite traces in replaced anhydrite nodules. Interbedded pyritic black muds.</td>
</tr>
<tr>
<td>7</td>
<td>Folly Hill, Farnham</td>
<td>SE 349608</td>
<td>Old copper mine area; chalcocite; chalcopyrite, bornite, covellite and some malachite.</td>
</tr>
<tr>
<td>8</td>
<td>Limekiln Hill, Farnham</td>
<td>SE 353603</td>
<td>Lower Member - old shaft with malachite on joint faces and infilling vugs.</td>
</tr>
<tr>
<td>9</td>
<td>Spellow Hill, borehole</td>
<td>SE 38176235</td>
<td>Lower Member - 2'1&quot; of hard limestone with pyrite and galena.</td>
</tr>
<tr>
<td><strong>Bramham district</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>East Keswick</td>
<td>SE 365454</td>
<td>Lower Member - baryte float in fields and baryte in stream sediments of R. Wharfe near Collingham (Barrett, 1975)</td>
</tr>
<tr>
<td>11</td>
<td>Linton</td>
<td>SE 385474</td>
<td>Lower Member - baryte in vugs in shelly facies.</td>
</tr>
<tr>
<td>12</td>
<td>Bramham (a)</td>
<td>SE 426425</td>
<td>Hampole Beds - bedded baryte replacing fenestral dolomite - not in situ - but veins and vug fills around same horizon (b) SE 427423</td>
</tr>
<tr>
<td>13</td>
<td>Oglethorpe</td>
<td>SE 450428-452434</td>
<td>Upper Member - pipeline trench. Baryte in veins and replacing dolomite - some hematite staining. Stratigraphic control by clay bands.</td>
</tr>
<tr>
<td>14</td>
<td>Newton Kyme</td>
<td>SE 46-44-</td>
<td>?Brotherton Formation - malachite traces infilling vugs (Marshall, 1829)</td>
</tr>
<tr>
<td>15</td>
<td>Aberford</td>
<td>SE 43-37-</td>
<td>Lower Member - baryte replacing dolomite - largely unexposed.</td>
</tr>
<tr>
<td>16</td>
<td>Barwick-in-Elmet</td>
<td>SE 410368</td>
<td>Base of Lower Member - baryte in vugs and veinlets in Lower Member and veinlets in Carboniferous sandstones (Barrett, 1975)</td>
</tr>
<tr>
<td>17</td>
<td>Wistow Wood shaft</td>
<td>SE 567356</td>
<td>Lower Member - cavernous dolomite with partial void fill of calcite, marcasite and some sphalerite.</td>
</tr>
<tr>
<td>Locality No.</td>
<td>Name</td>
<td>Grid Reference</td>
<td>Description and Reference</td>
</tr>
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<td>---------------------------</td>
</tr>
<tr>
<td>18</td>
<td>Long Lands Lane Bridge</td>
<td>SE 519080</td>
<td>Upper Member - 25cm of breccia with galena</td>
</tr>
<tr>
<td>19</td>
<td>Cusworth Park</td>
<td>SE 542035</td>
<td>Upper Member - galena below MPM contact (Deans, 1961)</td>
</tr>
<tr>
<td>20</td>
<td>Plaster Pits Wood</td>
<td>SE 539035</td>
<td>Upper Member - loose blocks of breccia with galena</td>
</tr>
<tr>
<td>21</td>
<td>Lovers Leap (1)</td>
<td>SE 545018</td>
<td>Upper Member - 5-10cm of breccia with galena and irregular base on peloid grainstones. White clay above.</td>
</tr>
<tr>
<td>22</td>
<td>Lovers Leap (2)</td>
<td>SE 546018</td>
<td>Upper Member - 18cm of breccia with galena on peloid grainstones. White clay (12cm) above.</td>
</tr>
<tr>
<td>23</td>
<td>Church Rein (1)</td>
<td>SE 548015</td>
<td>Upper Member - 6cm of breccia with little galena.</td>
</tr>
<tr>
<td>24</td>
<td>Church Rein (2)</td>
<td>SE 550015</td>
<td>Upper Member - galena below Ripon Formation contact with traces of asphaltite (Deans, 1961)</td>
</tr>
<tr>
<td>25</td>
<td>Sprotborough Quarry</td>
<td>SE 534017</td>
<td>Lower Member - galena on SW trending joint faces - not on others</td>
</tr>
<tr>
<td>26</td>
<td>Warmworth</td>
<td>SE 543009</td>
<td>Upper Member - galena below MPM with asphaltite traces (Deans, 1961)</td>
</tr>
<tr>
<td>27</td>
<td>Bentley Colliery</td>
<td>SE 570075</td>
<td>11'10&quot; dark grey limestone with pyrite and galena above 24'6&quot; strata on top of Coal Measures</td>
</tr>
<tr>
<td>28</td>
<td>New Edlington Brick Pit</td>
<td>SK 532986</td>
<td>Upper Member - galena in breccia for 62cm and in underlying peloid grainstones</td>
</tr>
<tr>
<td>29</td>
<td>Scartworth borehole</td>
<td>SK 532986</td>
<td>Calcite - sphalerite veins at 1118' and galena veinlets at 1888' (Smith et al., 1973)</td>
</tr>
<tr>
<td>30</td>
<td>Torworth borehole</td>
<td>SK 64959595</td>
<td>Lower Member - galena in joints 2' above base (Smith et al., 1973)</td>
</tr>
<tr>
<td>31</td>
<td>Barnby borehole</td>
<td>SK 6630364</td>
<td>Lower Member - sphalerite at 910' - 913'6&quot; (Smith et al., 1973)</td>
</tr>
<tr>
<td>32</td>
<td>Easton borehole</td>
<td>SK 71037810</td>
<td>Lower Member - sphalerite at 1255'8&quot; (Smith et al., 1973)</td>
</tr>
<tr>
<td>33</td>
<td>West Dayton borehole</td>
<td>SK 70247448</td>
<td>Upper Member - 2' of &quot;barytic&quot; dolomite 28' below Ripon Formation (Smith et al., 1973)</td>
</tr>
<tr>
<td>34</td>
<td>Markham Moor borehole</td>
<td>SK 7145573770</td>
<td>7' Upper Member - brown and grey limestone with a little galena and pyrite, 1129'6&quot; - 1132'7&quot;, 55' below Ripon Formation (Edwards et al., 1967)</td>
</tr>
<tr>
<td>35</td>
<td>Barlborough</td>
<td>SK 478777</td>
<td>Ancient record of lead ore (Ineson et al., 1972)</td>
</tr>
<tr>
<td>36</td>
<td>Bolsover</td>
<td>SK 473705</td>
<td>Upper Member - patches of baryte seen in limestone at surface (Eden et al., 1957)</td>
</tr>
<tr>
<td>37</td>
<td>Womble Hill, Clowne</td>
<td>SK 502763</td>
<td>Upper Member - baryte replacing pisolithic dolomite. Rare galena in baryte vein (Ineson et al., 1972)</td>
</tr>
<tr>
<td>38</td>
<td>Whitwell</td>
<td>SK 52-76-</td>
<td>Vugs in dolomite lined with galena, sphalerite and baryte; disseminated galena (Ford, in discussion of Ineson et al., Steetly Quarry bh).</td>
</tr>
<tr>
<td>39</td>
<td>Whitwell borehole</td>
<td>SK 548788</td>
<td>Baryte replacing dolomite with some galena in crystal vein (P.R. Ineson, pers. comm., 1979)</td>
</tr>
<tr>
<td>40</td>
<td>Whitwell Quarry</td>
<td>SK 5307542</td>
<td>Upper Member - road cutting to east of Marland Grips shows baryte in dolomite at surface below Ripon Formation</td>
</tr>
<tr>
<td>41</td>
<td>Marland Grips</td>
<td>SK 513753</td>
<td>Lower Member - galena in limestone/marl at base of main carbonates (Eden et al., 1957)</td>
</tr>
<tr>
<td>42</td>
<td>Whitwell Wood borehole</td>
<td>SK 524782</td>
<td>Lower Member - galena in shell bed at base of main carbonates with bladed baryte infilling vugs and replacing dolomite for 3m above.</td>
</tr>
<tr>
<td>43</td>
<td>Clowne</td>
<td>SK 48557570</td>
<td>Lower Member - specks of galena in bottom 2&quot; main carbonates (Smith et al., 1973)</td>
</tr>
<tr>
<td>44</td>
<td>Walkingbrook Wood borehole</td>
<td>SK 55367609</td>
<td>Lower Member - sphalerite crystals in dolomite band, 5' below main carbonates adjacent to fault (Smith, 1967)</td>
</tr>
<tr>
<td>45</td>
<td>Cross Hills borehole</td>
<td>SK 50866947</td>
<td>Lower Member - galena on joint faces and as replacive cubic at base of main carbonate. Sphalerite in replaced evaporite nodules in interbedded limestones and muds.</td>
</tr>
<tr>
<td>Locality No.</td>
<td>Name</td>
<td>Grid Reference</td>
<td>Description and Reference</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------------------</td>
<td>----------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>48</td>
<td>Newbound Farm</td>
<td>SK 485653</td>
<td>Lower Member - traces of baryte and galena at base of main carbonates in railway cutting</td>
</tr>
<tr>
<td>49</td>
<td>Dovedale Farm</td>
<td>SK 471563</td>
<td>Lower Member - galena in limestone bands near top of interbedded carbonates and muds (Aldred, 1969)</td>
</tr>
<tr>
<td>50</td>
<td>Meden Bank</td>
<td>SK 48416105</td>
<td>Lower Member - calcite, galena, siderite and baryte in fractures and &quot;impregnations&quot; (Aldred, 1969)</td>
</tr>
<tr>
<td>51</td>
<td>Kirkby-in-Ashfield</td>
<td>SK 502563</td>
<td>Lower Member - laminae of galena with sphalerite traces replacing dolomite.</td>
</tr>
<tr>
<td>52</td>
<td>Tile Kiln Wood borehole</td>
<td>SK 5543073130</td>
<td>Lower Member - thin vein of galena at 133', 79' below Ripon Formation (Edwards et al., 1967)</td>
</tr>
<tr>
<td>53</td>
<td>Skegby</td>
<td>SK 501611</td>
<td>Upper Member - baryte in vugs with pink and white baryte on joint surfaces and traces of oxidised galena. <em>Asphaltite</em></td>
</tr>
<tr>
<td>54</td>
<td>Healds Wood</td>
<td>SK 48876139</td>
<td>Lower Member - baryte in veinlets 'apparently near base' (Aldred 1969)</td>
</tr>
<tr>
<td>55</td>
<td>Stanton Hill</td>
<td>SK 482608</td>
<td>Lower Member - baryte in vugs and replacing dolomite around vugs over 100m.</td>
</tr>
<tr>
<td>56</td>
<td>Skegby Railway Cutting</td>
<td>SK 495614</td>
<td>Lower Member - baryte in vugs in bioturbated dolomite</td>
</tr>
<tr>
<td>57</td>
<td>Herrods Hill</td>
<td>SK 46996020</td>
<td>Lower Member - calcite and baryte veinlets and at SK 47006054 Basal Permian Breccia with 1 cm galena crystals (Aldred, 1969)</td>
</tr>
<tr>
<td>58</td>
<td>Robin Hood's Well</td>
<td>SK 490497</td>
<td>Lower Member - baryte veinlets and some replacive baryte near base main carbonates</td>
</tr>
<tr>
<td>59</td>
<td>Kirkby-in-Ashfield</td>
<td>SK 504550</td>
<td>Upper Member - top of Cadeby Formation with galena, malachite, wulfenite and asphaltite traces (Deans 1961). Now filled in</td>
</tr>
<tr>
<td>60</td>
<td>Annesley Tunnel</td>
<td>SK 510546</td>
<td>Upper Member - baryte with pyrite at Ripon Formation contact (Taylor and Elliot, 1971). Now filled in</td>
</tr>
<tr>
<td>61</td>
<td>Mansfield Quarry</td>
<td>SK 539600</td>
<td>Upper Member - galena cubes at Ripon Formation contact (Deans, 1961)</td>
</tr>
<tr>
<td>62</td>
<td>Clipstone Colliery Shaft</td>
<td>SK 597633</td>
<td>Upper Member - 1'3&quot; grey limestone and galena immediately below Ripon Formation</td>
</tr>
<tr>
<td>63</td>
<td>Limekiln Wood, Newstead</td>
<td>SK 536531</td>
<td>Upper Member - galena, wulfenite, asphaltite below Ripon Formation contact (Deans, 1961)</td>
</tr>
<tr>
<td>64</td>
<td>Woodsetts Cross Roads borehole</td>
<td>SK 557836</td>
<td>Upper Member - galena, cerussite, chalcopyrite at top of Cadeby Formation (Deans, 1961)</td>
</tr>
<tr>
<td>65</td>
<td>Papplewick</td>
<td>SK 545520</td>
<td>Upper Member - galena and pyrite in shell bed plus galena and calcite on joint faces 2-5m below Ripon Formation</td>
</tr>
<tr>
<td>66</td>
<td>Linby</td>
<td>SK 534521</td>
<td>Upper Member - galena at Ripon Formation boundary, now filled in</td>
</tr>
<tr>
<td>67</td>
<td>Hucknall</td>
<td>SK 530488</td>
<td>Upper Member - galena, cerussite, wulfenite, asphaltite in top 2&quot; below Ripon Formation, (Deans, 1961)</td>
</tr>
<tr>
<td>68</td>
<td>Springfield borehole</td>
<td>SK 545463</td>
<td>Upper Member - top few cm of Cadeby Formation with galena, wulfenite and asphaltite over 500 x 200 yds (Deans 1961)</td>
</tr>
<tr>
<td>69</td>
<td>Bulwell</td>
<td>SK 533452</td>
<td>Shattered zone with vein baryte and little galena where faulted against Ripon Formation. Some baryte replacing dolomite (Smith, 1967)</td>
</tr>
<tr>
<td>70</td>
<td>Sheepbridge Lane, Mansfield</td>
<td>SK 52726003</td>
<td></td>
</tr>
</tbody>
</table>

Marl Slate and Raisby Formation mineralisation, County Durham

<table>
<thead>
<tr>
<th>Locality No.</th>
<th>Name</th>
<th>Grid Reference</th>
<th>Description and Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>Rough Furze Quarry</td>
<td>NZ 318324</td>
<td>Baryte, flourite (fibrous and colourless cubes) and galena in displacive evaporite vugs (Hirst and Smith, 1974)</td>
</tr>
<tr>
<td>72</td>
<td>Raisby Hill</td>
<td>NZ 350348</td>
<td>Chalcopyrite, malachite and other copper minerals in brecciated dolomite (Hirst and Smith, 1974)</td>
</tr>
<tr>
<td>73</td>
<td>Old Middridge Quarry</td>
<td>NZ 248253</td>
<td>Galena in Marl Slate</td>
</tr>
<tr>
<td>74</td>
<td>Middridge Lime-Stone Quarry</td>
<td>NZ 255246</td>
<td>Galena and some baryte in vugs in dolomite. Traces of colourless flourite.</td>
</tr>
<tr>
<td>75</td>
<td>Chilton Quarry</td>
<td>NZ 300314</td>
<td>Baryte and calcite in vugs and autobrecciated dolomites with rare galena (Hirst and Smith, 1974; Fowler, 1957).</td>
</tr>
</tbody>
</table>
Figure A1-1 Location of mineralised localities in the Cadeby Formation.
APPENDIX 2

Preparation Methods for Whole Rock Analysis

(1) Specimens were broken and weathered surfaces removed.

(2) Crushing to approximately 2-3 mm was done in a mortar.

(3) 25g specimens were ground to -120 on the agate TEMA barrel. Total grinding time was about 20 minutes; specimens were redistributed in TEMA barrel every 3 to 5 minutes to prevent clogging, especially prevalent in evaporite-rich samples. Pure evaporite samples were hand ground throughout.

Trace elements were analysed using loose -120 powder; major elements were analysed using pellets.

(4) Pellets were made of 7g powder plus 11 drops of 2% PVA (poly vinyl alcohol) solution. Powder and solution were mixed thoroughly, them compressed in a mould under pressure of 11 tons.

(5) Pellets were dried at <100°C for several hours and stored in airtight plastic bags.

Several specimens were ground to different amounts (-90, -120 and -230) to see if this affected final analyses.

Reproducability was better on -120 than -90, especially for majors. Although grinding to -230 marginally improved this reproducability, the additional grinding time involved, plus the increased tendency of fine powders to clog, made this not
worthwhile.

Care was taken to homogenise powders throughout each stage.

Powders and pellets were analysed on a Phillips 1212 XRF spectrometer.
Wet Chemical Analysis and Insoluble Residue Determination

(a) Wet chemical analysis

Ten specimens were analysed by wet chemical analysis at the start of the project to provide internal dolomite and dedolomite standards. Analysis was for Ca, Mg, Fe$_2$O$_3$, SiO$_2$, Cu and P. Methods are detailed below:

1. 2g of -90 powdered specimens roasted in platinum crucible for ½ hour.
2. Powder transferred to evaporating dish, damped with H$_2$O and acidified with HCl. Remaining powder in crucible was dissolved with dilute HCl and washed into evaporating dish.
3. Solution was evaporated to dryness.
4. 7-8 mls of conc. HCl were added and solution warmed for a few minutes.
5. 50 mls hot water added; solution stood for 10 minutes with stirring.
6. Solution was then filtered and washed with warm 3% HCl and then warm water.
7. Residue was analysed for SiO$_2$ following Vogel (1962).
8. Residue was then fused in 1g Na$_2$CO$_3$, dissolved in HCl and washed into filtrate. Filtrate was made up to 500 ml.
(9) 25 ml of solution (from 8) were analysed for Ca + Mg (Pribil and Vesely. 1966).

(10) 12 ml of solution were analysed for Fe$_2$O$_3$ using the Dipyridyl titration method.

(11) 50 ml of solution were analysed for P using vanado-molybdate titration.

(12) A further 1g powder was analysed for total copper using a method modified from Hoste et al., (1953) by F. Buckley (written comm., 1977).

Results:

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>CaCO$_3$</th>
<th>MgO</th>
<th>MgCO$_3$</th>
<th>P$_2$O$_5$</th>
<th>Total Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>162</td>
<td>2.11</td>
<td>0.54</td>
<td>30.00</td>
<td>53.54</td>
<td>16.84</td>
<td>35.23</td>
<td>190</td>
<td>12</td>
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<tr>
<td>163</td>
<td>1.94</td>
<td>0.41</td>
<td>30.32</td>
<td>54.11</td>
<td>13.45</td>
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<td>225</td>
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<td>30.04</td>
<td>53.61</td>
<td>18.11</td>
<td>37.88</td>
<td>115</td>
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<td>13.64</td>
<td>0.64</td>
<td>24.88</td>
<td>44.40</td>
<td>18.07</td>
<td>37.80</td>
<td>450</td>
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<td>131</td>
<td>4.12</td>
<td>0.54</td>
<td>29.60</td>
<td>52.83</td>
<td>20.65</td>
<td>43.19</td>
<td>190</td>
<td>203</td>
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<tr>
<td>132</td>
<td>2.87</td>
<td>0.34</td>
<td>28.53</td>
<td>50.92</td>
<td>19.38</td>
<td>40.54</td>
<td>115</td>
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<td>134</td>
<td>3.47</td>
<td>0.24</td>
<td>28.96</td>
<td>51.69</td>
<td>19.67</td>
<td>41.14</td>
<td>115</td>
<td>24</td>
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<td>3.28</td>
<td>0.24</td>
<td>29.39</td>
<td>52.45</td>
<td>19.54</td>
<td>40.87</td>
<td>115</td>
<td>n.d.</td>
</tr>
<tr>
<td>101</td>
<td>4.33</td>
<td>0.76</td>
<td>43.95</td>
<td>78.40</td>
<td>6.33</td>
<td>13.24</td>
<td>225</td>
<td>18</td>
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<tr>
<td>151</td>
<td>34.83</td>
<td>2.59</td>
<td>12.86</td>
<td>22.63</td>
<td>1.76</td>
<td>3.68</td>
<td>475</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

(b) Insoluble residue determinations

20g of -120 powder for each specimen analysed by XRF was dissolved in 500 ml of 10% HCl over a heated water bath. Filter papers were weighed and solutions filtered and the residue dried and weighed. Care was taken that the filter paper was of equal dryness when weighing
before and after filtration. Hydrochloric acid was used in preference to acetic or humic acids because of (i) the total volume necessary and (ii) most specimens were of dolomite rather than limestone. Results are tabulated in Appendix 5 with whole rock XRF analyses.
APPENDIX 4

CALIBRATION OF XRF RESULTS

Pellets were analysed on the Philips 1212 XRF spectrometer, using the silver tube for Si, Ti, Al, Fe, Mn, Ca, Mg, S, Sr and Na and the tungsten tube for Zn, Pb, Cu and Ba. Standards used were two department internal limestones, pure gypsum (specimen 996) and the range of dolomites analysed by wet chemistry (Appendix 3). A further standard of 50% gypsum and 50% dolomite (specimen 134) was mixed for evaporite-dolomite specimens calibration. Mass absorption corrections for the standards were initially calculated using the data of Heinrich (1966) for CaO, MgO, Fe$_2$O$_3$ and SiO$_2$ and then further correction the results by continual alteration of the absorption data factors, using the Leeds computer programmes written by Mr. A. Gray, until XRF results were consistently near the chemical results. SrO was corrected on a separate programme for limestone-dolomite mixtures. Al$_2$O$_3$, TiO, S, Na$_2$O, Cu, Zn, Pb and Ba were corrected using calculated standard absorption factors (Table A4-1). CaO and MgO were further re-calculated as carbonates; S was re-calculated as SO$_4$ where evaporites were known to be present (Appendix 5). Precision of analyses is given in Table A4-2.

Reference:

<table>
<thead>
<tr>
<th>Element</th>
<th>Dolomite</th>
<th>Limestone</th>
<th>Evaporite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.89</td>
<td>1.09 Evaporite</td>
<td>1.05 Dolomite</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.3</td>
<td>1.12 Evaporite</td>
<td>0.95 Dolomite</td>
</tr>
<tr>
<td>MnO₂</td>
<td>1.12</td>
<td>0.8 Dolomite</td>
<td>1.05 Limestone</td>
</tr>
<tr>
<td>S</td>
<td>0.8</td>
<td>1.09 Limestone</td>
<td>0.95 Limestone</td>
</tr>
<tr>
<td>Na</td>
<td>1.09</td>
<td>0.92 Evaporite</td>
<td>0.92 Dolomite</td>
</tr>
<tr>
<td>Cu</td>
<td>1.51</td>
<td>0.64 Evaporite</td>
<td>0.64 Dolomite</td>
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<tr>
<td>Zn</td>
<td>1.49</td>
<td>0.63 Evaporite</td>
<td>0.63 Dolomite</td>
</tr>
<tr>
<td>Pb</td>
<td>1.50</td>
<td>0.64 Evaporite</td>
<td>0.64 Dolomite</td>
</tr>
<tr>
<td>Ba</td>
<td>1.50</td>
<td>0.64 Evaporite</td>
<td>0.64 Dolomite</td>
</tr>
</tbody>
</table>
## APPENDIX 5

### RESULTS OF WHOLE ROCK XRF ANALYSES AND INSOLUBLE RESIDUE (I.R.) DETERMINATIONS

Insoluble residues, oxides and sulphur (as both sulphide and sulphate) are given in weight percentage; base metals and barium are in p.p.m., n.d. = not determined; mineralised specimens are marked with an asterisk.

\[
\begin{align*}
X &= \frac{\text{CaCO}_3}{\text{CaCO}_3 + \text{Na}_2\text{CO}_3} \\
Y &= \text{Al}_2\text{O}_3 + \text{SiO}_2
\end{align*}
\]

<table>
<thead>
<tr>
<th>No.</th>
<th>11R</th>
<th>Sio2</th>
<th>TiO2</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Ba</th>
<th>Co</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>512</td>
<td>7.966</td>
<td>3.67</td>
<td>0.08</td>
<td>0.75</td>
<td>1.23</td>
<td>0.01</td>
<td>2.07</td>
<td>88.60</td>
<td>1.07</td>
<td>0.045</td>
<td>0.11</td>
<td>1</td>
<td>66</td>
<td>19</td>
<td>53</td>
<td>n.d.</td>
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<tr>
<td>527</td>
<td>7.417</td>
<td>3.86</td>
<td>0.08</td>
<td>0.77</td>
<td>1.30</td>
<td>0.03</td>
<td>4.09</td>
<td>88.56</td>
<td>1.54</td>
<td>0.028</td>
<td>0.07</td>
<td>1</td>
<td>56</td>
<td>18</td>
<td>55</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

### a. Primary limestones

### b. Dolomites

(i) Grainstone barriers
<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>I.R.</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>SrO</th>
<th>Na₂O</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Ba</th>
<th>Co</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>164</td>
<td>1.505</td>
<td>1.18</td>
<td>0.04</td>
<td>0.11</td>
<td>0.32</td>
<td>0.06</td>
<td>0.32</td>
<td>0.65</td>
<td>0.11</td>
<td>0.06</td>
<td>0.19</td>
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<td>10.5</td>
<td>67</td>
<td>9</td>
<td>4</td>
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</table>

(ii) granstone barrier (core sample)

(iii) siliciclastic carbonates

(iv) lagoon wackestones and mudstones

(v) lagoon wackestones and mudstones with former evaporites

(vi) breccia facies

(vii) patterned carbonates and other anoxic facies (core samples with no sulphate)

Secondary limestones

(i) dedolomites
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All logs in Appendix 6 use the following notation:

| Column 1 | Occurrence of mineralization or evaporite minerals related to sedimentary structures |
| Column 2 | Evaporite form or evidence of former evaporites |
| Column 3 | Bioturbation |
| Column 4 | Grain types and skeletal evidence |
| Column 5 | Sedimentary structures, and, where applicable, weathering profile |
| Column 6 | Brief description |
| Column 7 | Interpretation |
Symbols used in logs

Symbols used in logs

low angle cross lamination

ripple lamination

load structures

dewatering structures

desiccation cracks

fenestrae

solution breccia

intraclast breccia

concretion

crust

crust intraclasts

contorted bedding; soft sediment

contorted / autobrecciated bedding; lithified sediment

cryptalgal laminites

bivalve

brachiopod

brachiopod spine

algal coating

foraminifera

bryozoa

plant fragment

ooliths

pisoliths

Lingula

burrows

trails

slight bioturbation

moderate bioturbation
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>intense bioturbation</td>
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<td>⭐</td>
<td>'nests' of bioturbated pellets</td>
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<td>Mo</td>
<td>mottled dolomite</td>
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<td>⨄</td>
<td>displacive vugs</td>
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<td>⧨</td>
<td>replacive vugs</td>
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<td>⬥</td>
<td>partially filled</td>
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<td>⬦</td>
<td>empty</td>
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<td>⧧</td>
<td>gypsum pseudomorphs or casts</td>
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<td>⥧</td>
<td>halite pseudomorphs or casts</td>
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<tr>
<td>P</td>
<td>patterned carbonates</td>
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<tr>
<td>Ca</td>
<td>Calcite</td>
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<td>Ba</td>
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<td>G</td>
<td>Galena</td>
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</table>
Figure A6-1  Bramham, A1 section (SE 426425).
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<tr>
<td>Ca</td>
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</tbody>
</table>

**Hampole Beds**
- crypt-algal laminites with small dewatering structures, often eroded.
- Crusts of algal laminites blown in ooids

**Intertidal** - supratidal algal mats with blown in ooids

**Ca**
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**Bioturbated carbonate grainstones?**

**2m**

- Channel ooids + flat cross laminated ooids
- Ooids + pisoids; algae, desiccation cracks
- Crusts + autobrecciation

**Bioturbated grainstone**
- Storm channels + sheet flood on very shallow shelf
- Periodically exposed carbonate flats

**Massive bioturbated oolite**

**Bioturbated grainstone**

**?Storm sands**
Figure A6-2  Ingbarrow Farm, near Wetherby
(SE 390495)
Deepening upwards sequence:

- Increasing depth of water plus increasing energy of environment
- As oolite grainstones migrate into area as large shoals/sandwaves
- Intertidal flats of carbonate muds
- Sheet flood

- Hampole beds eroded by channel fill?

- Badly weathered thin mm-cm bedded dolomites
- Planar bedded grainstone
- Badly weathered thin mm-cm bedded dolomites with occasional grainstone lenses
- Bioclastic bivalve dolomite, bioturbated and channeled near top
- Thin mm-cm bedded fuze dolomites with channel grainstones, ripple laminated at base
- Weathered dolomitisation, contorted horizon
- Bioturbated dolomites passing into bivalve shoals - "Bakevellia bed". Dislocated valves
- Fine dolomites with prolific loading structures. Bioturbation 'nests' at one horizon.
- Horizontally laminated dolomites with occasional loading and ripple cross lamination. Burrows + trails near base with some bioclasts.
- Quartz grains in bottom 1-2 cm

Shallow subtidal low energy environment with high depositional rate of carbonates.

- Shallow subtidal environment, periodic current producing ripples; detritus from surrounding palaeohills at base.
Figure A6-3  Wetherby Railway cuttings (SE 309486).
More massive bedforms with pockets of bioturbation and isolated burrows.

Higher energy environment; subtidal, possibly in lee of offshore oolite barrier

Low angle dune bedding with trails and burrows, sometimes concentrated on discrete horizons.

Concentrations of bioturbation suggest periodic sedimentation.

Horizontal lamination. Thin contorted bed above shale with some circular vugs.

Sheet floods on flats - ?subtidal

Horizontal lamination with some circular vugs; Contorted parallel cross laminated bed overclay.

High intertidal-supratidal environment with evaporite formation and contortion of bedding.

Crust over horizontally bedded bioclastic horizon. Some trails Algal lamination

Wenn emergence on top of flood deposit.

Fine horizontally laminated strata, slightly cross cutting at base. Harder bands show parallel cross lamination and may contain circular vugs.

Tidal flats. Algal lamination in intertidal zone visible in places, especially near top. Shallow channels with parallel cross lamination and some flood sands. Circular vugs were sites of evaporite nodules which implies some supratidal emergence.

Soft dolomite/dedolomite above breccia with contorted fragments of dolomite and marls. Large vugs. Hard crust with burrows extending down from surface. Low angle small scale cross lamination with valves and trails. Contorted horizon.

Possible synsedimentary dissolution breccia, formed by dissolution of interbedded evaporites. Vugs secondary.

Dislocated valves Low angle small scale cross lamination with small scour and fill structures. Some trails channels with planar cross lamination. Possible rippled surfaces. Fragments of crusts near base.

Crust produced by emersion of surface - supratidal exposure. Shallow subtidal meandering channels on tidal flat. Contortion due to emersion and evaporation/water escape. Intertidal-shallow subtidal flats in meandering channel area. No development of algal mats due to continuously shifting sediment surface.
Massive bedforms often with convex-upwards surfaces.

Offshore oolite grainstone barrier build-ups.

Low angle dune bedding with some bioturbation.

Start of migration of offshore barrier into area

Convoluted bedding truncated by next bpd.

Supratidal sediments above Hampole "Discontinuity"

Contorted area with circular vugs

Soft dolomite/shale with vugs

Crust over algal laminations which contain isolated fragments of crusts.

Intertidal flat with algal mats. Exposure at top of unit to produce crust.
Figure A6-4 Linton (SE 386473).
bryozoan-rich horizons

bivalve banks with starred sand ripples which may show dewatering.

Crusts with overlying breccia horizons - intraclasts plus quartz grains. Rare horizons of evaporite vugs.

patch reef pillows; entirely subaqueous

periodically exposed and eroded bivalve shoals

beach rock
Figure A6-5

Vale Road Quarry, Mansfield Woodhouse (SK 532648).
Large scale convex upwards bedforms
loose fragments of fenestral dolomite
Red sandstone/dolomite with cross laminations and some loading structures
Migration of grainstone barriers into area outcrop of sandstone (possible supratidal exposure)
Fluvial derived quartz grains with dolomite fine intraclasts and cement.

bioturbated current laminated dolomite.
bioturbated grey bioclastic limestones/muddy dolomites interbedded muds and fine cross laminated dolomites with erosive bases passing into thin bedded grey dolomites muds ripple laminated dolomites cross laminated dolomites
subaqueous current grainstone
subtidal bioturbated carbonate muds
subtidal lagoonal carbonates with periodic current action (?storms) and stillstand events when only clastic deposition
increasing energy of environment - migration of tidal channel into area?
supratidal sediments with evaporite nodule growth periodic desiccation of lagoon.

vuggy horizon with voids and evaporite casts
succession of thin limestones with good fauna and intervening grey muds.

bioturbated, almost muddled grey limestones with some mud drapes
Algal coatings to bioclasts.
clear shallow lagoon environment with periodic influxes of mud during wet events. Algal coatings imply minimal sedimentation for long periods. No current action. Lagoonal sediments, subtidal, with frequent small clastic influxes little or no current action.

Algal coatings to bioclasts.
Figure A6-6 Skegby Railway cuttings (SK 494600).
LOG 6  DISUSED RAILWAY CUTTING, SKEGBY

Coarsely dolomitized throughout

cross laminated dolomites

concentrations following bedding horizons

bioturbated coarse dolomite with lip fill channels at top

two clays, with associated dewatering structures separated by cross laminated dolomite

Cross laminated channel dolomites

migration of grainstone shoal into the area

?possible algal mats rolled and redeposited during storm periods

subtidal passing to intertidal dolomites - shallowing upwards sequence

flovable-derived clays, loading during shallow subtidal environment. Channel sands between muds

shallow subtidal to exposed carbonate flats

shallow tidal grainstones

Repetitive beds with unidirectional low angle cross-lamination on top of ripple laminated channels. Bioturbation at base of units.

bioturbated dolomites with some concretion horizons and occasional channel grainstones. Some ripple cross-lamination.

Grainstones introduced, during high current action from reworking sand barriers. Bioturbation in quieter episodes.

Low energy carbonates of shallow-supratidal environment. Periodic migration of small tidal channels.

Intensely bioturbated dolomites with rare small channels. Contorted horizon plus evaporite nodules near base.

Deepening upwards sequence from contorted horizon and underlying evaporite nodules (supratidal) into bioturbated subtidal dolomite with small tidal channels.
Figure A6-7

Monkton Moor, old quarry (SE 306655).
LOG 7 MONKTON MOOR (old quarry)

- Deepening upwards sequence with increasing energy of environment as oolites migrate into area over Hampole Beds.
- Regression with inundation forming current laminated oolites, pisoliths between crust over oolites with crust intraclasts.
- Lagoonal barrier migrating into area and remaining in low angle cross laminated oolites; constant cross-lamination direction; some small scours; rare bioturbation.
- Ripple laminated bioturbated oolites.

Cross laminated oolites with increasing size of bedforms.
Figure A6-8 Monkton Moor, new quarry (SE 306653).
AG/II

LOG 8 MONKTON MOOR (new quarry)

sometimes massive
cross lamination ooids -
large scale cross
laminae

current intensity +
depth increasing,
upwards in subdivision.
Migrating sandwaves?

planar laminated ooids
ripple laminated ooids

Harnpole Beds: fenestrae, clays

Periodic regression

cross laminated ooids
ripple laminated ooids
and clay horizons

Migration of lagoon
barrier into area
oscillating currents in lee
of barrier. Clays deposition
in pluvial but quiet
(?storm free) periods.

ripple laminated
passing up into cross
laminated ooids

Goid barrier partially
migrating into area.

mottled dolomites
- bioturbated

Bioturbation in quiet
lagoon carbonates
Figure A6-9  Rock Cottage Quarry, Wormald Green (SE 304650).
**Log 9**

**Rock Cottage Quarry, Wormald Green**

- Planar bedded dolomites passing into cross lamination oolite grainstones
- Hampole Beds?
  - Cross laminated oolite grainstones
  - Deepening upwards sequence with increasing energy as grainstone shoals migrate into area
  - Periodic regression
  - Migration of lagoon barrier into area

- Thin dolomites with desiccation cracks. Bioturbation at top crust, evaporite nodules, smaller fenestrae and desiccation cracks, mud drapes
- Bioturbated dolomites with mud drapes passing into similar dolomites with open former evaporite nodules passing into planar evaporite nodule rich stratum.
  - Chart formation at one horizon
  - Replaced anhydrite nodules in bioturbated, fetid, dolomites
- Bioturbated irregularly bedded fine dolomites rare loading structures and mud drapes

- Periodic exposure of lagoon surface with eventual deeper subtidal dolomites and bioturbation
  - Periodic exposure with supratidal conditions developing and evaporite formation and mud drapes during subtidal conditions.
  - Shallowing upwards sequence from bioturbated lagoonal carbonates with mud influxes during wetter periods, as desiccation proceeds.
  - Evaporite nodule formation supratidal sediments
  - Supratidal conditions due to regression of lagoon from original subtidal carbonates. Evaporation evaporite nodule formation
  - Subtidal low energy lagoon environment
Figure A6-10  Bedale Quarry, Well (SE 257812).
LOG 10  BEDALE QUARRY, WELL

- **bioturbated thin dolomites, hardgrounds and carbonaceous muds**
- **planar bedded dolomites**: no internal structure visible
- **channels of dolomite**
- **black true limestones and prodolomites, inundation and no clastics**
- **limestone with gypsum pseudomorphs + dolomite crust**
- **thin bedded limestones and dolomites**
- **partially dolomitized limestones, bioturbated with many mud drapes. May pass laterally into carbonaceous muds**
- **black limestones - fossiliferous**
- **bioturbated thin dolomites, evaporite casts at one horizon and mudes, hardgrounds**
- **planar buff dolomites**
- **bioturbated thin dolomites, leading structures, muds, contortion and brecciation, few ripple cross laminations and some hardgrounds.**

**Shallow lagoon, quiet water with periods of stillstand**
- **subtidal environment with channelling - brief destruction of lagoonal barrier?**
- **planar bedded dolomites; destruction of no internal structure visible**
- **channels of dolomite**
- **black true limestones and prodolomites, inundation and no clastics**
- **limestone with gypsum pseudomorphs + dolomite crust**
- **thin bedded limestones and dolomites**
- **partially dolomitized limestones, bioturbated with many mud drapes. May pass laterally into carbonaceous muds**
- **black limestones - fossiliferous**
- **bioturbated thin dolomites, evaporite casts at one horizon and mudes, hardgrounds**
- **planar buff dolomites**
- **bioturbated thin dolomites, leading structures, muds, contortion and brecciation, few ripple cross laminations and some hardgrounds.**

**Subtidal lagoonal carbonates and muds**
**Quite shallow lagoon with areas of higher carbonate production and cementation. Clastic input periodic.**
**Events of no clastic input**
**Quiet shallow lagoon periodic exposure and periodic clastic influxes ?schizohaline**
**?storm deposits - sheet floods?**
**bioturbated lagoonal carbonates, quiet water with few current influxes, periodic near desiccation giving contorted sediments.**
**Periodic clastic influxes ?schizohaline**
Figure A6-11  Wistow Wood borehole (SE 567356).
massive anhydrite replaces ooids in places

crystalline laminates with evaporite rich horizons; some ooids increasing "marl" content

evaporite rich levels of core with rare and cross laminated ooids. Ooids throughout section. No evidence of exposure surfaces.

subaqueous: deepening sequences of shallow subtidal sands

intraclast breccia

emergence, or nearby emergence with reworking of clasts
increasing displacive evaporites, some ripple cross lamina

more restricted environment, evaporite rich but no evidence of supratidal sediments apart from evaporite nodules. Subaqueous but very shallow lagoon

Shallow water carbonates with mud deposition during stilllakes. Periodic near emergence evaporite formation. Low energy currents - lagoon in lee of protective barrier.

carbonates with bioturbation, some loading structures, muds, occasional shallowing upwards sequences, rare visible ooids and bivalves. Occasional displacive evaporites. Porosity occluded.

crusts overlying breccia horizons

periodic emergence, desiccation and storm reworking.

bioturbated and planar bedded carbonate muds

sheltered environment with bioturbation. Lagoon by analogy with other areas

ripple laminated and bioturbated carbonates

small current, relatively shallow water, protected environment

bivalves and ooids, no visible bedforms. Some discontinuous muds.

shallow water carbonates with occasional clastic influxes.

planar bedded ooids, some bioturbation

sheet flood with later subaqueous bioturbation patterned carbonates
patterned carbonates -

diagenetic facies due
to early reduction of

evaporites. Quiet water
fine carbonate muds
and evaporites; may be
partially emergent
(Fig 3.22) or intertidal.
Occasional storm

deposits of bivalves with
plant remains

fine grained
dolomites with
colour banding
from dark-light
areas. Loading
structures, some
bioturbation and
many partially
open voids.
Frequent open
fine irregular
joints.
Porosity good through
voids and joints.

Marl Slate

Basil Permian Sands
Appendix 7

The data for the following maps was supplied by Malcolm Pennington-George at NCB, Selby Project.
Fig. A7.1  Map of the Permian in the Selby coalfield area

(i) STRUCTURE CONTOURS
structure contours on the base of the Zechstein
Fig. A7.2   Map of the Permian in the Selby coalfield area

(ii) ISOPACHS
Fig. A7.3  Map of the Permian in the Selby coalfield area

(iii) VUG ABUNDANCE

(modified from the original map by Goosens, 1976)
vugs are in the lower 20 m of the Cadeby Formation mostly in patterned carbonates
Staining Techniques

Dual staining method for dolomite from J.A.D. Dickson (written comm., 1979)

Reactants used:
Solution 1: 800 cm\(^3\) of 2% HCl (vol/vol) made with distilled water.
Solution 2: 300 cm\(^3\) of Alizarin Red S (ARS) solution, comprising 0.5 grm ARS and 300 cm\(^3\) of 2% HCl (from Solution 1).
Solution 3: 200 cm\(^3\) of potassium ferricyanide (PF) solution, made with 4 grms PF with 200 cm\(^3\) of 2% HCl (from Solution 1).

Procedure:

(1) Wash slide with detergent to remove grinding oils.
(2) Etch for 45 secs in 2% HCl.
(3) Stain for 30-45 secs in solution of ARS and PF, mixed in the ratio 3:2.
(4) Stain for 10 secs in ARS solution.

Thin sections were washed between each stage with distilled water taking care not to rub off stain. Final drying was done as quickly as possible to avoid cracking of stain. Slides were covered by glass corner slip when dry.

Staining for calcites is modified by using 0.2% HCl.
throughout.

Resultant colours:

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<th>Mineral Type</th>
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<td>Non ferroan calcite</td>
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<tr>
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<td>purple</td>
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<tr>
<td>Non ferroan dolomite</td>
<td>colourless</td>
</tr>
<tr>
<td>Ferroan dolomite</td>
<td>blue</td>
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CATHODOLUMINESCENCE OPERATING CONDITIONS

Cathodoluminescence studies were done in the Geology Department at Nottingham University with the help of Tony Dickson and Madeleine Raven. Luminescence was produced from a cathode electron gun operating at 30 KV DC with a beam current of 400 µA. The specimens were smoothly polished thin sections enclosed in a vacuum chamber with purposely leaked air in a vacuum pressure of $10^{-1}$ torr. Some specimens had been previously coated with carbon for electron microprobe analysis. The vacuum chamber was attached to a Zeiss microphotometer. Exposure time average 5 minutes on ASA 400 film for earlier photographs, but a new camera with direct illumination allowed exposure time to be reduced to 30-50 seconds in 1980. Films were processed by enhanced development by Dave Jones at Nottingham.
APPENDIX 10

ELECTRON MICROPROBE OPERATING CONDITIONS, DRAWBACKS AND METHODS

A. Operating Conditions
Specimens used were polished thin sections with carbon coating. Measurements at Leeds were done with the Jeol JXA 50A electron microprobe with operating voltage of 15KV, specimen current of 20nA and a focussed beam. At the Open University, a Cambridge Microscan 9 electron microprobe was used with an operating voltage of 20KV, specimen current of 3nA and a defocussed beam of approximately 20μm diameter.

B. Drawbacks
Early point measurements were made at Leeds with the high specimen current. Calcite disintegrated rapidly during the count period of 30 seconds and dolomite showed slight disintegration in this time. In spite of later, separately computed, mass absorption corrections, dolomite gave consistently low totals (80-90%). Disintegration made it impossible to measure more than two elements (from the two spectrometers) at any one point. As later cathodoluminescence observations showed both calcites and dolomites were zoned (e.g. Fig 5-5 b) it was impossible to determine the composition of any one zone. High probe currents also give enhanced trace element contents; thus the few iron and manganese values which were obtained were suspect. Leeds had no standard
calcite and the dolomite standard had not been viewed with cathodoluminescence it was not known if it were zoned. With the low precision due to specimen decay, results for points measured at Leeds were therefore considered unusable.

The Open University microprobe had been calibrated for carbonates using British Museums standard calcite and dolomite. A secondary standard 'ankerite' was also used with a composition close to many ferroan dolomites (Table A10-1). Standards had not been viewed with cathodoluminescence. The low probe current (3nA) caused no specimen disintegration allowing total count times for individual points to last for 8-10 minutes (for 4 elements). Totals for dolomites were acceptable (limits of 95%-105% were chosen) although calcite results were nearer 100%. Statistics for low iron and manganese percentages were poor. Use of the 20µm unfocussed beam meant that analyses of dolomicrites had poor totals due to grain boundary interference. Also, small inclusions of ferric oxides in ferroan dedolomites (5.2.4) were included in the total. Average zone compositions could be determined.

C. Methods and Refinements

Best results were obtained by point analysis at the Open University and using the Leeds microprobe to semi-quantitatively scan across these points (e.g. Appendix 11, Fig A11-1d). Best scan results were obtained by specimen movement at 20µm/minute and chart flow of 20mm/minute.
Future refinements would include selection of non-zoned standards and determination of their compositions by atomic absorption spectrometry. J.A.D. Dickson also contains better results by using gold-coated specimens.
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APPENDIX 11

THE APPLICATION OF CATHDOLUMINESCENCE IN RELATIVE DATING OF MINERALIZATION IN THE CADEBY FORMATION

Cathodoluminescence techniques have been used mainly in studies of carbonate sedimentology and diagenesis, clastic diagenesis, and metamorphic growth of certain minerals; a recent view is given by Nickel. With cathodoluminescence, growth zones in crystals are revealed due to differences in trace element content: for example, in carbonates, the inclusion of Mn$^{2+}$ usually promotes luminescence whereas Fe$^{2+}$ may act as an inhibitor. Such growth zones are usually invisible in conventional thin sections, although, in carbonates, some zones may become visible by staining techniques. As cathodoluminescence requires polished thin sections the variation in elements across the differing zones may later be quantified by electron microprobe analysis.

This note is solely concerned with the interpretation of samples from various localities in the Permian EZ1 Carbonates and the possibility of determining the age of baryte and sulphide mineralization relative to various carbonate hosts and void fills. In Figures 1 to 4 the first photograph, (a), is taken with transmitted light whereas the second, (b), is with cathodoluminescence. Examples 1 to 3 all involve intergrowths of carbonate and baryte.

Example 1: Skegby, Notts. SK 501611. Figure 1a shows a group of dolomite crystals enclosed by non-luminescing baryte (B). An unaltered dolomite crystal (1) has a cloudy inclusion-rich
centre surrounded by a dark zone and an outer clear dolomite rim. Baryte laths in the dolomite are visibly replacive in hand specimen. Progressive replacement of the other dolomite crystals by baryte has occurred, with the baryte growth being initiated within the dark (iron oxide-rich) zone of the dolomites and corroding the cloudy core (2, 3) until only the clear, outer, limpid rim remains unreplaced (4). Although visible in transmitted light (Figure 1a), the corrosive features are more readily apparent with luminescence (Figure 1b).

Example 2: Well, North Yorks. SE 257812. Baryte crystals in calcite show no indication of relative age of growth under transmitted light (Figure 2a) but in Figure 2b the baryte crystals in the central rectangle cut across the calcite growth zones. If this occurred throughout it would be evidence of replacive growth, baryte developing after calcite formation. However, on examination of a larger area, (Figures 2a and 2b), it can be seen that the baryte crystals are centred on non-luminescing calcite near the vein margin. It is proposed that the baryte grew outwards from the vein margin zone and the non-luminescent zone. Baryte growth was ahead of that of calcite so that the later calcite zones 'lap-up' against the baryte laths (Figure 2b). The centre of the vein is filled with later, uniformly luminescing calcite. Thus, in this specimen, baryte and calcite growth were almost concurrent until baryte growth halted, the precipitating fluids becoming deficient in barium and/or sulphate. Calcite precipitation continued as a void fill.
Example 3: Wormald Greeh, North Yorks. SE 300650. Under transmitted light (Figure 3a) the textural evidence is ambiguous. In Figure 3b baryte can be seen to be present only in the central zone of the calcite crystal and is truncated by the less-luminescent outer zone. Baryte may have grown with the more luminescent calcite, or replaced it before growth of the outer zone. This again shows a later calcite-rich fluid depleted in barium and/or sulphate.

Example 4: Ferryhill, Co. Durham 10. NZ 318324. At some localities in the EZ1 Carbonates calcite crystals with rectangular outlines and re-entrant angles, sometimes containing inclusions of anhydrite, indicate direct replacement of displacive anhydrite by calcite 11. In transmitted light Figure 4a appears to be a further example of this, with later baryte growth surrounding the replacive calcite. But in Figure 4b the growth zones within the calcite show various nucleation sites and later growth zones within the rectangular outline, typical of a void fill. Thus the calcite has grown after the formation of baryte. The rectangular outlines indicate the baryte crystallized against the original anhydrite, further substantiating Hirst and Smith's proposal from sulphur isotope data that the baryte was intimately linked with co-existing evaporites. Later influx of less saline fluids caused dissolution of anhydrite with, at a subsequent date, growth of calcite into the resulting void.

Similar textural evidence can be used to determine the relative ages of sphalerite, galena, marcasite and fluorite with EZ1 Carbonates. The development of colour in some
fluorites with cathodoluminescence \(^{12}\) not only exhibits growth zones in the fluorites but also allows the detection of hitherto unnoticed small inclusions of fluorite within calcite crystals.

The preceding examples demonstrate that, whereas in transmitted light many textures are difficult to interpret correctly, with cathodoluminescence the additional information allows detection of growth zones and hence direction of growth, thus unravelling paragenetic sequences. Where it is evident that zonation was concurrent with mineralization, microprobe analysis of the same section will give evidence of the changing chemistry of the mineralizing fluids. In Mississippi Valley type deposits in Tennessee cathodoluminescence showed the formation of sulphides to have occurred at one particular stage during dolomite precipitation \(^{13}\) but, throughout the EZ1 Carbonates, mineralization has taken place several times during the sediment's history.

**Acknowledgement**

I would like to thank Dr. J.A.D. Dickson for help and guidance in using the cathodoluminescence microscope at Nottingham University, M. Nutting for many discussions on the Nottinghamshire Permian mineralization, and Dr. F.W. Smith for showing me the Ferryhill localities.
References


Figure A11-1  Dolomite rhombs with cloudy centres (c), iron oxide rich zone (f) and clear outer rim (r) being progressively replaced by baryte (B) in the order 1-2-3-4. 1a in transmitted light (TL) and 1b with cathodoluminescence (CL).
Figure A11-2  Baryte crystals (B) surrounded by calcite (C). Baryte nucleation on non-luminescent calcite zones (n). 2a TL, 2B CL.
Figure A11-3  Baryte (B) in central zone of calcite crystal (C) truncated (arrowed) by outer, less-luminescent zone. 3a TL, 3b CL.
Figure A11.4 Baryte (B) adjoining rectangular crystal form, originally anhydrite but now possessing a calcite void fill. 4a TL, 4b CL.
APPENDIX 12

The importance of magnesium content in calcites to degree of mineralisation in the Upper Persian Cadoby Formation was constructed a similar plot for dolomites. Research on mineralisation in the Upper Persian Cadoby Formation detailed a zone of non-luminous calcite adjacent to volcalcic dolomite. Further mineralisation were then made to see if this relationship could be traced further. In Figure 12-1 (a-e) both iron and manganese contents remain low (0-45) across both zones; both marginally increase in the brighter zone (Figure 12-2).
The importance of magnesium content in calcites to degree of cathodoluminescence intensity

Several authors have shown how Fe$^{2+}$ usually inhibits cathodoluminescence and that Mn$^{2+}$ promotes luminescence within carbonates (Sommer, 1972; Meyers, 1974; Oglesby, 1976; Pierson, 1977; 1981 and Fairchild, 1978). Oglesby (1976) has predicted mineral assemblages, calcite compositions and amount of luminescence as a function of pH and $p_e$. Fairchild (1978) has constructed fields of luminescent and non-luminescent zones in calcites and dolomites dependent on iron and manganese contents (Fig A12-1); Pierson (1977; 1981) has constructed a similar plot for dolomites. Research on mineralisation in the Upper Permian Cadeby Formation detailed a zone of non-luminescent calcite adjacent to a void margin (Appendix 11) (Figs. A12-2 a, b + c). Point analysis by electron microprobe showed this zone to have low iron and manganese contents but high magnesium (Table A12-1; point A). Microprobe scans across the zones (Fig A12-2 d+e) show that the high magnesium content is contained within the non-luminescent zone. Magnesium may thus be acting as an inhibitor to luminescence within this zone. Manganese:iron ratios increase in the brightly luminescing zone.

Further scans across zoned calcite crystals associated with mineralisation were then made to see if this relationship could be traced further. In Figure A12-3 (a-d) both iron and manganese contents remain low (<0.4%) across both zones; both marginally increase in the brighter zone (Figure A12-3 d).
Magnesium here increases in the more brightly luminescing zone, although totals remain below 1% MgCO₃. Where changes in luminescence were slight (Figure A12-4 a-c) zonal correlation with manganese and iron was slight (Figure A12-4 c). Magnesium content varied sharply between zones and increased (up to <1% MgCO₃) in the more brightly luminescent zone. In these two examples, therefore, magnesium contents of <2% apparently promoted luminescence.

In the final example, multiple zoning in a centripetal calcite void filling cement (Fig A-12-5 a-c), bright zones showed higher manganese contents (Fig A12-5 d). Magnesium was high in poorly luminescing zones near the void margin but in the more central, non-luminescent zone was, on average, lower than surrounding zones (<1% MgCO₃) (Fig A-12-5 d).

The evidence for magnesium influencing luminescence intensity is therefore equivocal. Change in magnesium content does correlate with zone margins in several examples (Figs A12-2 d+c, A12-3 d and A12-4 c). Moderate magnesium contents (<2% MgCO₃) are found in some luminescent zones. Higher magnesium content (>2% MgCO₃) apparently inhibit luminescence. Thus the presence of magnesium within the calcite lattice should not be overlooked and non-luminescent zones should not immediately be regarded as ferroan calcite.
References for Appendix 12


Sommer, S. F., 1972, Cathodoluminescence in carbonates.
1. Characterisation of cathodoluminescence from carbonate solid solutions
2. Geological applications
Chem. Geol., v. 9, p. 257-284.
### TABLE A12-1

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Figure A12-1  Luminescence of calcites and dolomites in terms of their iron and manganese concentrations (from Fairchild, 1978 and 1980, written comm.)
Figure A1-2  a+b  Non-luminescing calcite zone (N) with later more luminescent calcite. Baryte (B) apparently nucleates in or before non-luminescent zone. a: transmitted light (TL) b; cathodoluminescence (CL).
Figure A12-2  

c) Diagramatic representation of Figure A12-2 b. Baryte is orange. Probe scans along line w-x and y-z.

d) Semi-quantitative scan along w-x of A12-2 c showing variations in concentration of MgCO₃, FeCO₃ and MnCO₃. Points analysed are in Table A12-1.

e) Semi-quantitative scan along y-z of Fig A12-2 c showing variations in concentration of MgCO₃, FeCO₃ within zones.
Figure A12-3  a+b  Baryte in central zone of calcite crystal, truncated by outer, less-luminescent calcite zone. (arrowed).

a : TL

b : CL
Figure A12-3 c  Diagramatic representation of Figure A12-3 b. Baryte is orange. Probe scan along line x-y.

d  Semi-quantitative scan along x-y of Fig A12-3 c, showing variations on MgCO$_3$, FeCO$_3$, MnCO$_3$ and SrCO$_3$ within zones.
Figure A12-4

a  Faintly zoned calcite cement filling void after limpid dolomite overgrowths (D). Cathodoluminescence.

b  Diagramatic representation of Fig A12-4 a, showing calcite zones and dolomite. Probe scan along line x-y.

c  Semi-quantitative scan along x-y of Fig A12-4 b, showing variation of MgCO₃, MnCO₃ and FeCO₃ within zones. Iron peak is at crystal boundary.
Figure A12-5  a+b Zoned calcite centripetally filling vug after baryte (B) mineralisation.

a : transmitted light

b : cathodoluminescence
Figure A12-5  

c Diagramatic representation of Figure A12-5 b. Baryte is orange. Probe scan along line x-y. Zones are broadly grouped together in diagram.

d Semi-quantitative scan along x-y of Fig A12-5 c, showing variation in MgCO$_3$, FeCO$_3$ and MnCO$_3$ within zones.
APPENDIX 13

STABLE ISOTOPE SAMPLE PREPARATION

Sample amounts for stable isotope determinations were:

- Carbon + oxygen 30-40 mg
- Sulphur 20 mg

Samples were hard ground to -100.

Calcite-dolomite separations were done with heavy liquids:

Densities:
- Calcite 2.7 g/cm³
- Dolomite 2.85 g/cm³
- Ferroan dolomite 2.96 g/cm³ (Ca:Fe4:1)

TBE was diluted with ethanol orthophosphate until standard dolomite and calcite crystals were separated. 100ml of diluted solution was then added to the sample powder, shaken, left for a few minutes then centrifuged. The resultant powders were separated once more for purification. XRD traces were run to ensure good separation of calcite and dolomite.
APPENDIX 14

LEAD ISOTOPE SAMPLE PREPARATION AND MASS SPECTROMETER OPERATING CONDITIONS

A. SAMPLE PREPARATION

1. Samples of galena were hand scraped.

2. Small labelled beakers were cleaned with 6M HCl and left with acid on the hot plate for ½ hour. Beakers were then washed with distilled H₂O.

3. Small specks of galena with 6M HCl were added to beakers immediately.

4. Specimens were left to evaporate for approximately 1 hour.

5. 6M HCl and dilute HCl were added and small portion transferred to small beakers to dilute sample.

6. Specimens in small (50ml) beakers were evaporated then transferred to the lead-free laboratory (where atmospheric Pb contamination is minimal).

7. 2 to 3 drops of perchloric acid and some double distilled H₂O were added to each beaker.

8. Samples were evaporated nearly to dryness, the perchloric acid driving chloride ions and reducing Fe³⁺ to Fe²⁺. Samples fumed before final separation.

9. Double distilled water was added and sample loaded into an electrolytic cell which had been cleaned with concentrated HNO₃.

10. Lead was precipitated by anodic deposition for approximately ½ hour. The anode turned bronze as lead was deposited. Black anodes developed if the solution
had not been sufficiently diluted at stage 5. Filaments prepared from black anodes were overloaded and mass spectrometer runs were unstable.

11. The single rhenium ribbon filament was loaded using a lamp filament current. 1-2 drops of silica gel were mounted in the centre of the filament and allowed to evaporate slightly. The sample was dissolved in a drop of 2% HNO₃ and 0.1% H₂O and then transferred to the filament with a micropipette.

12. 3 drops of 1M H₃PO₄ and sublimed P₂O₅ were added and the filament allowed to dry at lamp current.

13. When dry, current was generally increased to 2 amp until the filament smoked and then momentarily increased to red heat. Filaments were then stored until use.

Samples were run on the Micromass 30 mass spectrometer using a filament current of 2.0-3.0 amps at 8.1 KV and 3.5 K gauss.

Peaks selected were:

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb 208</td>
<td>798</td>
</tr>
<tr>
<td>Pb 207</td>
<td>780</td>
</tr>
<tr>
<td>Pb 206</td>
<td>762</td>
</tr>
<tr>
<td>Pb 204.5 (background)</td>
<td>735.2</td>
</tr>
<tr>
<td>Pb 204</td>
<td>725.9</td>
</tr>
<tr>
<td>Pb 204.5 (background)</td>
<td>735.2</td>
</tr>
</tbody>
</table>

Ratios used to normalise ratios were:

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb 208/Pb 206</td>
<td>1.002</td>
</tr>
<tr>
<td>Pb 206/Pb 204</td>
<td>1.002</td>
</tr>
<tr>
<td>Pb 207/Pb 206</td>
<td>1.001</td>
</tr>
</tbody>
</table>

from standards run by Jam Kramers.


Aldred, K., 1969, Occurrences of galena and other minerals in the area West of Mansfield, Nottinghamshire: Mercian Geol. v.3, p.35-38.


Beales, F.W., 1975, Precipitation Mechanisms for Mississippi Valley-type Ore Deposits: Econ. Geol., v.70, p.943-948.


Butler, G.P., 1970, Secondary anhydrite from a sabkha - NW Gulf of California, Mexico: in Rau and Dellwig (Eds); Third Symposium on Salt, Northern Ohio Geol. Soc.


Pilkington, J., 1789. A view of the present state of Derbyshire, with an account of its most remarkable antiquities. 2nd edn. Marriot, Derby.


Rastall, R.H., 1943. The Cleveland Axis; Geol. Mag., v.80, p.30-36.


Stewart, F.H., 1951a. (The petrology of the evaporites of the Eskdale No. 2 boring, E. Yorks.) Part 2. The Middle Evaporite Bed; Mineral Mag., v.29, p.445-475.


Taylor, F. M. 1974. Permian and Lower Triassic landscapes of the E. Midlands; Mercian Geol., v.5, p.89-100.


