A

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FLUID INCLUSION STUDIES IN FLUORITE FROM THE
ASKIRGG AREA OF NORTH WEST YORKSHIRE

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GENERAL INTRODUCTION

A study of fluid inclusions in fluorite from the epigenetic mineralization in lower Carboniferous strata of the Askrigg block in the Northern Pennine Orefield has been made. The purpose of the study was to ascertain the nature, origin and significance of these inclusions and to obtain information concerning the temperature, salinity and chemistry of the environment of crystallization of these ore deposits. The information subsequently obtained can be used to place constraints on postulated theories of genesis of these deposits.

In Chapter 1 a short introduction to the study of fluid inclusions in minerals is given. The suitability for inclusion study of minerals from the Askrigg area is discussed in Chapter 2. A method for the preparation of polished samples is also described together with criteria for the recognition of inclusion types. The importance of the recognition of post-formational changes in inclusions such as leakage and necking-down is also stressed.

Chapter 3 contains a detailed geological outline of the ore deposits and a brief review of ideas regarding their genesis. Detailed homogenization studies have been performed on fluorite from numerous localities. The data obtained is then used to determine the minimum temperature of formation of the fluorites. The statistical evaluation of the significance of these results is also described together with details of the positive pressure correction applied to the results. The distribution of temperature in the orefield is described.

A detailed account of a freezing stage is presented in Chapter 4. The behaviour of fluid inclusions in fluorite on freezing is outlined together with detailed salinity measurements from various samples. The results obtained are then discussed in the light of other inclusion studies from similar deposits.
Chapter 5 contains a detailed appraisal of the analytical methods used to study the chemistry of fluid inclusions. The methods used to analyze leached portions of this inclusion fluid for sodium, potassium, lithium, magnesium, calcium, chloride, and sulphur are described. The chemistry of the ore-forming fluid in the light of these results plus other electronmicroprobe and atomic absorption studies is then discussed. The theories regarding the mode of transport of metals in the inclusion are reviewed in the light of fluid inclusion evidence.

The genesis of the ore deposits of the Mississippi Valley type in the light of fluid inclusion studies is discussed in Chapter 6. Comparison is made between the Askripp and other deposits of similar type and a possible genetic model is postulated for the Askripp block mineralization.
CHAPTER 1

INTRODUCTION

The Northern Pennine Orefield occupies about 4,000 square kilometres of Carboniferous rocks stretching from the Tyne valley in the north to the Craven district in the south (Dunham 1948). The area is divided into two main physiographic units by the Stainmore gap, the northern Alston block (Trotter and Hollingworth 1928) and the southern Askrigg block (Harr 1921). The lower Carboniferous rocks of these areas are extensively mineralized and for many centuries have been important sources of lead and zinc (Raistrick and Jennings 1965) (fig. 1.1).

The mineralization consists mainly of a galena-sphalerite-fluorite-baryte assemblage of typical epigenetic type. The problem of their genesis, their temperature of formation and the composition of the ore forming solution has been and still is the subject of much debate. The application of fluid inclusion techniques (Roedder 1972) to these deposits can provide valuable information as to the nature of this ore forming fluid. These techniques were successfully applied to the deposits of the Alston area by Sawkins (1966). It was thus felt to be necessary to apply them also to the Askrigg deposits. This present study is concerned with fluid inclusion studies on fluorites from the Askrigg area. The aim of the study is to provide information on the temperature, salinity, composition of the ore-forming fluid and ultimate genesis of these deposits.

1.1. Historical Development

When examined under a polarizing microscope, crystalline substances reveal small cavities containing a portion of the fluid medium from which the host material grew. These cavities represent growth irregularities in the host material in which some of the fluid present during crystallization has been trapped and hermetically sealed to produce what are known as fluid inclusions. Often neglected in the past, they are our prime source of information as to the nature of that medium and with careful study provide an insight into the operation of several important geological processes and allow us to estimate the temperature of crystallization of the host mineral.
The study of fluid inclusions has had a long and controversial history, earlier ideas and observations by Davy (1822), Brewster (1826) and especially Sorby (1858) being ignored and their significance dismissed. Modern studies of fluid inclusions really began with those of Lemmllein (1929) in the U.S.S.R. and Newhouse (1933) in the United States. This heralded the start of extensive studies of fluid inclusions in the U.S.S.R. (Ermakov 1950). In the United States, due mainly to the extensive work of Edwin Roedder, the study of fluid inclusions is now recognised as the important tool it undoubtedly is. Excellent reviews of the historical development of fluid inclusion studies are to be found in Harker (1971) and Roedder (1972) and they will not be repeated here.

1.2. Size and Volume of Inclusions

Fluid inclusions have been reported in a number of minerals from a wide variety of geological environments and appear to be ubiquitous in all crystalline substances. These inclusions are normally less than 0.01 mm in size, those greater than 0.1 mm are comparatively rare and inclusions greater than 1 mm in size are very rare. Some minerals with inclusions greater than 5 mm in size have been reported by numerous workers but these large inclusions, with 10 ml or even 100 ml of fluid, are exceptionally rare; normally the total fluid in a crystal or mineral grain is between 0.01 and 0.1 per cent. Electron microscopy has revealed large numbers of inclusions down to $2 \times 10^{-5}$ mm, see Sella and Deicha (1962, 1963) and Deicha and Sella (1963). The number of inclusions in any sample is usually inversely related to inclusion size, e.g. see fig. 1.2.

1.3. Shape of Inclusions

Most inclusions are irregularly shaped, some have a spheroidal or negative crystal morphology. The symmetry of the host mineral determines the negative crystal form of the inclusions; thus fluorite exhibits cubic cavities (fig. 1.3) whilst quartz and apatite exhibit hexagonal cavities.

The observed shape is not necessarily the original one as inclusion shape is a transient feature (Roedder 1968). Deposition of material from
the trapped fluid on to the cavity walls will tend to change the cavity shape to that having the minimum surface energy. The fact that the inclusion shape may have altered over time is of no great significance provided that the cavity has remained hermetically sealed, has not necked-down and has not changed significantly in volume.

1.4. Necking-Down of Inclusions

Necking-down is a process which has commonly occurred in large inclusions and due to its frequent occurrence its recognition is of paramount importance when studying inclusions. Failure to recognise this is probably the most common source of error in inclusion studies and can place their significance in serious doubt.

A large inclusion can in time separate into two or more smaller inclusions often with a differing gas/liquid ratio. This is often reflected in neighbouring inclusions of similar origin with quite widely varying homogenization temperatures, (Kelly and Turneaure 1970). It is quite common in fluorite from the Pensines (Sawkins 1966). This process of necking-down is shown diagrammatically in Fig. 1.4.

1.5. Leakage of Inclusions

The whole basis of fluid inclusion study rests on the assumption that the fluid in which the host mineral is growing is trapped in a cavity which is then hermetically sealed by further growth. Thus it is of the utmost importance to recognize if leakage has occurred, since temperature determinations are then invalidated and must be disregarded. Microfractures and tubes on the surface of the host crystal, in this case fluorite, have been detected by the writer using scanning electron micrography. Their significance is discussed later (section 2.5.3.) Mechanical sawing and grinding during sample preparation can cause leakage (Roedder 1967). Some inclusions do exhibit fractures and on heating often leak. Leakage from an inclusion is often evidenced by extremely high homogenization temperatures compared with cogenetic inclusions in the same crystal or by an increase in the size of the vapour bubble following an homogenization run on the heating stage.
The nature of the host mineral can radically affect the likelihood of leakage occurring. Soft cleavable minerals such as calcite and baryte are highly susceptible to leakage as are soluble minerals such as halite. Inclusions have been observed to leak under extreme pressure conditions in the laboratory (Kennedy 1950; Skinner 1953), evidence often cited against the validity of inclusion studies. However Roedder and Skinner (1968) have demonstrated that most inclusions in fact do not leak. The writer has observed leakage only on rare occasions in many thousand heating runs performed on polished plates of fluorite. They frequently occur near the surface of such plates and are presumably related to fractures produced during sample preparation.

1.6. The Classification of Inclusions

Various schemes, often elaborate, have been proposed for the classification of inclusions. They are usually purely descriptive being based on the ratios of phases present; vapour, liquid and solids (Yermakov 1965). They assume trapping from a homogeneous fluid which is not always the case in nature. The fact that heterogeneous systems have operated during geological time has been demonstrated by numerous workers (Roedder 1965; Roedder and Coombs 1967; Rankin 1973). Other schemes using homogenization behaviour, cause of trapping, degree of crystallinity, state of aggregation have been proposed (Roedder 1972). All these schemes are descriptive, but they are based on arbitrarily chosen features and they are of limited usefulness.

A genetic scheme is more desirable but unfortunately is rarely unambiguous. In the study of fluid inclusions the distinction between inclusions of primary and secondary origin is of paramount importance. A primary inclusion is one formed during the growth of the host crystal, whilst a secondary inclusion was formed by fracturing and subsequent recrystallization after the cessation of growth. A third important category that of the 'primary secondary' or 'pseudo-secondary' (Ermakov 1949) inclusions formed by fracturing and hermetic sealing during growth, such inclusions are very common in fluorite, (Roedder 1967).
1.7. The Trapping of Non Representative Samples of Fluid

If a crystal is growing in a heterogeneous system; for instance, vapour bubbles or oil globules in an aqueous fluid, trapping of samples of both these fluids may occur. Errors in the interpretation of this phenomenon can occur, especially when preferential wetting of immiscible fractions takes place. For example, immiscible oil globules are frequently reported in the fluid associated with fluorite-baryte-lead-zinc deposits. Sometimes these globules preferentially adhere to the growing surface of the crystal and are enclosed by the host to give apparently primary inclusions with no trace of the associated brine. Boiling of the aqueous phase can also lead to preferential wetting by vapour bubbles. Roedder and Coombs (1967) report boiling of a dense saline phase with subsequent trapping of immiscible globules of low density carbon dioxide rich vapour.

Most fluids also contain a large amount of solid particles in suspension which may settle on a growing crystal surface. Sometimes some of these particles may be trapped in a fluid inclusion giving the appearance of a daughter mineral. This is often the case with sulphide phases in fluorite. Daughter minerals usually occur in a regular phase ratio in oogenetic inclusions whilst the solid particles in contrast have widely varying phase ratios.

1.8. Methods Used in the Study of Fluid Inclusions

A multiplicity of techniques have been applied to the study of fluid inclusions, Roedder (1972) giving an extensive summary. Unfortunately none are universally applicable to give accurate, unambiguous results and they are beset by various, sometimes insurmountable, experimental problems.

Sample duplication is rarely achieved, due to the nature of the occurrence of primary inclusions. Ideally only large inclusions should be studied, but, as stated earlier, they are rare and prone to leakage.
Therefore a compromise often has to be made by studying the more abundant smaller inclusions in a large sample despite the attendant risk that these may have suffered contamination.

Optical techniques using polished plates or cleavage flakes can be applied to transparent minerals. Unfortunately most ore minerals are opaque and the optical study of fluid inclusions in them is usually restricted to transparent varieties of sphalerite, (Newhouse 1933).

Parameters of both liquid vapour and solid phases such as wetting characters, index of refraction, fluorescence can be assessed optically (Roedder 1972). The heating of inclusions on heating stages has long been used to obtain information on the temperature of formation of the mineral (Sorby 1858). Whether the sample in the heating stage is in air or oil there remains the problem of thermal gradients, often severe at higher temperatures. These must be evaluated if any significance is to be attached to the results. Decrepitation techniques have been widely applied but have severe limitations, one problem being the relation of temperatures of maximum decrepitation to the filling temperatures of primary or secondary inclusions. The freezing of inclusions using acetone and nitrogen gas as heat exchange mediums (Roedder 1962; Smith 1973) yields valuable results regarding the salinities of the fluid in the inclusions.

Chemical analyses of inclusion fluids, gases, solids, as stated above are beset by experimental difficulties, extreme care being needed with regard to contamination. Various microchemical techniques such as mass spectrometry, gas chromatography, flame photometry, spectrophotometry and neutron activation analysis have all been applied with mixed results (Roedder 1972). Fluid inclusions generally consist of a low viscosity liquid and a vapour bubble. The liquid is usually water with less than 10 per cent total dissolved salts which range from 0 to 50 per cent. The salts are predominately made up of the following ions: - Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, with lesser amounts of:-


Li⁺, Al³⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, HSO₄⁻, H₂CO₃⁻, and CO₃²⁻

When a gas is present it is usually CO₂ with varying amounts of H₂O (Roedder 1972).
THE RELATIONSHIP BETWEEN THE SIZE, VOLUME, AND WEIGHT OF A SPHERICAL FLUID INCLUSION.

[after Roedder 1958a]
Fig. 1.3.

PLATE SHOWING TYPICAL NEGATIVE CRYSTAL MORPHOLOGY OF PRIMARY INCLUSIONS IN FLUORITE

1.3.a. Primary fluid inclusion in fluorite, sample 152, Galloway Vein, Greenhow Hill. The inclusion here exhibits a stepped rectangular shape with marked striations on the inclusion walls.

1.3.b. Primary fluid inclusion in fluorite, sample 77, Escoe Hill, Craven. The inclusion exhibits a cubic negative crystal, enabling the volume of the vapour phase to be estimated.

1.3.c. Primary fluid inclusion in fluorite, sample 75, Escoe Hill, Craven. Here the inclusion is flattened in one dimension and cannot be used for volume estimations.

1.3.d. Primary fluid inclusion in fluorite, sample 180, Middle Vein, Grassington Moor. The cubic negative crystal is elongated in one direction giving a rectangular shape.

1.3.e. Primary fluid inclusion in fluorite, sample 75, Escoe Hill, Craven. An almost perfect square inclusion. Note the vapour bubble compressed onto the side of the inclusion. This indicates a highly saline fluid.

1.3.f. Primary fluid inclusion in fluorite, sample 83, Lolly Mine, Midderdale. The inclusion exhibits a marked rectangular shape and compressed vapour bubble.
PLATE SHOWING TYPICAL NEGATIVE CRYSTAL MORPHOLOGY OF PRIMARY INCLUSIONS IN FLUORITE.
A DIAGRAM ILLUSTRATING THE PROCESS
OF NECKING-DOWN IN FLUID INCLUSIONS.

THE INCLUSION COOLS FROM TRAPPING AT $T_5$ TO
$T_1$, FORMING INCLUSIONS A, B & C: ALL WITH DIFFERING
HOMOGENIZATION TEMPERATURES.
CHAPTER 2
THE CHOICE OF SAMPLES AND THE METHODS USED IN THIS INVESTIGATION

2.1. The Choice of Minerals

During the course of the present project the suitability for fluid inclusion study of various minerals occurring in the Pennine Orefields was assessed. The selection of suitable sample material is of vital importance to enable evaluation of the precision, accuracy and above all the significance of the results obtained. Fluid inclusion studies have severe constraints placed on them by the very nature of their occurrence in nature. The small sample size of the fluid, the compositional variation between host minerals and fluid inclusion, the possible multiplicity of origins and trapping irregularities all combine to render truly duplicate sample analyses virtually impossible. Differing sample requirements for the various techniques place important restrictions on what can be studied. Optical methods, including homogenization and freezing only need $10^{-13}$ g of sample in contrast to wet chemical methods such as flame photometry, spectrophotometry which need $10^{-3}$ to 1 g of sample fluid. A compromise thus has to be reached between these varying requirements, in the hope that it will have little effect on the significance of the results obtained.

In the Askrigg area, the mineralization consists of a dominant calcite-baryte gangue with subsidiary witherite and fluorite. The ore minerals are dominantly galena with subsidiary sphalerite, chalcopyrite and pyrite. Fluid inclusions were examined in the various gangue minerals. Fluorite was found to be the most suitable, the others are less satisfactory for a variety of reasons.

2.1.1. Baryte ($\text{BaSO}_4$) occurs widely as a massive, opaque, porous, nodular variety, often secondary after witherite and totally unsuitable for fluid inclusion study. Good tabular primary crystals are rare and they usually exhibit extensive fracturing and secondary inclusion development. Despite hours of patient searching only one sample was found which contained possible primary inclusions.
2.1.2. **Calcite** (CaCO$_3$) also occurs extensively as a massive, columnar variety usually forming an early phase in the mineralization. It is unfortunately only translucent even in very thin polished plates and is totally unsuitable. More suitable, transparent material is normally found as a later phase. Of this both massive and good crystal varieties are found. As in the case of baryte extensive fracturing and secondary inclusion development are common; unambiguous primary inclusions were not found. All fluid inclusions examined were predominantly monophase fluid filled cavities.

2.1.3. **Witherite** (BaCO$_3$) has predominantly secondary inclusions along fractures due to its soft cleavable nature. Any primary inclusions that were present have undergone extensive necking-down and are unsuitable for study.

2.1.4. **Fluorite** (CaF$_2$) from many ore fields has been extensively studied by various workers using fluid inclusion techniques. In many respects it is an ideal mineral for this purpose. It polishes well, occurs as good crystals enabling oriented sections to be cut and is transparent affording excellent observation of fluid inclusions. It often contains colour banding and bands of solid inclusions parallel to growth surfaces enabling primary inclusions to be positively identified.

In the Askrigg area fluorite has a limited zonal distribution in relation to calcite and baryte, (Dunham 1952). Fluorite often does exhibit secondary fracturing, but despite this and its restricted occurrence, it yielded the most consistent and useful results.

2.1.5. **Sphalerite** (ZnS) is very restricted in occurrence, being found normally as the dark black crystals known locally as "black jack". A massive brown to yellow variety also occurs which is transparent in thin polished section. Suitable fluid inclusions were not found in this variety.

2.2 Sample Selection

2.2.1. **Calcite** and **Baryte**. By far the easiest method to study fluid inclusions in these minerals was found to be with the use of cleavage
fragments, as their soft cleavable nature made mechanical sawing virtually impossible. In the case of baryte, individual crystals were used when they were sufficiently transparent. Calcite was normally crushed and individual pieces examined for suitable inclusions.

2.2.2. Fluorite, Sphalerite and Zitherite

When studying these minerals the predominant method was the use of polished plates cut from the individual crystal. It was found for fluorite that mechanical sawing was only possible on crystals greater than 1 mm in size. Crystals smaller than this were cleaned and studied individually in the same way as cleavage flakes of calcite or baryte. During the sawing process these minerals are very susceptible to shattering and tend to disintegrate very easily under a diamond blade. To combat this and also to allow the cutting of oriented slices parallel to growth directions, the minerals were set in a dental plaster prior to cutting. The minerals were placed in a silicone rubber mould and set with J.S. Stoneshard dental cement in batches of ten. The dental plaster took approximately thirty minutes to set into a very strong protective casing. These sections were then cut using a Q.3.2 diamond saw, manufactured by Meyer and Burger Ltd., Switzerland. Oriented sections were cut with a thickness of approximately three to four mm usually taking two from each specimen, more if it was of particular interest.

2.2.3. Preparation of Polished Samples

The three to four mm thick plates were then examined to select plates with inclusion rich areas for homogenization and other studies. Various methods of preparing polished sections for fluid inclusion study have been well reviewed by Harker (1971) in which a polishing method is described as developed by that author. During the early part of this study Harker's method was used but was, for a variety of practical reasons, found to be unsatisfactory. It is slow, lacks adequate sample control and produces sections polished on one side only.

(10)
With experience of the Leitz 1350 heating stage it was found desirable to have sections doubly polished to improve observation of the fluid inclusions. Consequently various methods were tried with the aim of producing doubly polished sections as quickly as possible and of a standard thickness, the importance of which has been stressed in Harker.

A method was subsequently developed using a Durener polishing machine and a diamond lap which has produced good results. As most of the fluid inclusions examined homogenized in the temperature range 80°C to 150°C the use of araldite resin is not precluded. At temperatures in excess of 300°C it is oxidized and renders the section opaque. The mineral plates are set in batches of thirty in cold setting Araldite resin using a silicone rubber mould. Cold setting Araldite is used to reduce any possible heat effects on the inclusions. The sections are then allowed to harden overnight.

The bottom surface is then lapped with 600 grade silicone carbide grit on a Logitech LP30 lapping machine made in Alexandria, Scotland, to obtain a planar surface. The sections are then ground on an Alba S.J.P. grinding wheel to obtain parallel surfaces about 2 mm thick and lapped again with 600 grit to remove any remaining saw marks. It is possible to prepare up to a hundred thick sections in this way quite easily in one day. The sections are then numbered by scratching with a sharp steel point and given a preliminary lap on Bramet 600 grade sandpaper with Hyprez fluid acting as a lubricant. This was found to cut down considerably on the actual time spent on the polishing machine.

The sections were then lapped on both sides on the Durener polishing machine using a twelve inch paper lap manufactured by Engis Ltd., with 6 - V 42 grade diamond paste and Hyprez fluid as a lubricant. Up to six sections can be mounted on the machine at any one time in special chucks manufactured in the Leicester University Geology Department Workshops.
Polishing normally takes between ten and fifteen minutes per side and in this manner anything up to sixty doubly polished plates could be produced in a day. The advantages of this method are the ease of production, rapid production rate, high quality polish of the finished product and standardization of section thickness for heating stage work. The use of a mechanical lapping machine did not produce any unwanted heating as heat generation was minimal, leakage of inclusions being rarely observed. The use of organic resin as a setting medium had no deleterious effect as homogenization temperatures rarely exceeded 150°C, well below its oxidation temperature.

2.4. Examination of Polished Sections for Suitable Fluid Inclusions

This perhaps is the most time consuming aspect of fluid inclusion study but it is very important, as the recognition of inclusion type is of paramount importance in any systematic study. Detailed optical examination was carried out using a Zeiss Standard Junior Polarmicroscope. A reflecting microscope was used to identify any solid sulphide phases present. Photomicrography of inclusions of interest was carried out at this stage using a Zeiss photomicroscope.

The identification of fluid inclusions as either primary, secondary, or pseudo-secondary in polished plates of approximate dimensions thirty by thirty mm was found to be relatively easy compared with using small plates of material. Areas of interest were marked on the surface using Indian Ink and then sawn from the mineral plate. This was achieved with a one in. diameter metal bonded diamond cutting disc 0.010 in thick manufactured by Diagrit Diamond Tools Ltd., Staplehurst, Kent. It was specially adapted to fit an old dental drill. This was hand held for maximum control of the cutting operation, using water cooling to prevent excessive heat generation.

The specimen size is governed by the 7.5 mm diameter object carrier of the Leitz 1350 heating stage. A sample of approximate five by five mm dimensions was found to be most suitable, study being possible on all of its area if desired.
2.5. Differentiation of Types of Inclusions

2.5.1. General Remarks  Fluorite commonly exhibits primary, secondary, and pseudo-secondary inclusions, fig. 2.1. It cannot be over stressed that these inclusion types must be distinguished, the whole validity of the study depending on their correct origins being elucidated. The criteria used in the distinction are not absolute and unfortunately are inapplicable in many cases, (Roedder 1965). Despite these obstacles fluid inclusions provide valuable insights into fluid systems operating in the geological past.

2.5.2. Distinction of Primary Inclusions

Any process that interferes with the growth of a crystal may cause the trapping of primary inclusions. Solid particles can frequently interrupt growth, hindering the nutrient supply at the point of contact. The crystal can grow around and enclose the particle, fluorite frequently traps sulphide and quartz grains in this way. In some cases fluid may be trapped in the lee of such solid particles, see fig. 2.2.

Changes in minor constituents in the fluid have been shown to affect crystal perfection, (Buckley 1951; Schlichta 1967). Large inclusions can also be formed at the centre of faces by temporary starvation relative to the faster growing edges (Zerfoss and Slawson 1956; Sheftal 1956). Inclusions can also be trapped on grain boundaries.

To identify an inclusion as definitely primary, the inclusion needs to be related to a former growth surface of a crystal (Roedder 1967b). In fluorite, colour bands parallel to faces of the cubic form and bands of solid particles provide excellent reference planes, see fig. 2.1. Primary inclusions normally exhibit some degree of random distribution, secondary inclusions being definitely related to fractures.

Negative crystal shape is frequently cited as proof of primary origin. Inclusion shape is, however, a transient feature (Roedder 1968a). Secondary inclusions can also assume negative crystal shapes in a healed fracture.
Negative crystal shape is common in fluorite typically in the larger inclusions, fig. 1.3. A variety of shapes being assumed from a basic cubic symmetry. Rounded or spherical primary inclusions are frequently found in fluorite, see fig. 2.3.

Scanning electron micrography of the crystal faces of fluorites reveals large numbers of "hopper" or cubic re-entrant surfaces, fig. 2.4. This represents the final growth surface of the fluorite crystal, often with a later calcite and barite phase present, see fig. 2.5. During growth of the crystal similar surfaces probably existed, if a portion of the fluid were then trapped and hermetically sealed, a negative crystal shaped primary inclusion would result. These provide possible examples of possible proto-inclusion sites.

The distinction of primary origin is thus not always unambiguous, sometimes in doubt and yet of critical importance. This paradox, however, can be resolved with patient observation, to yield valuable results placing important constraints on theories of ore genesis (Roedder 1967a). 2.5.3. Distinction of Pseudo-secondary and Secondary Inclusions.

All primary inclusions form during growth of the host mineral in contrast to secondary inclusions which are formed by fracturing and recrystallisation after the cessation of growth. Pseudo-secondary inclusions (Irmačov 1949) are formed by fracture during growth. Fluid at the rim enters and is trapped in the core of the crystal. Positive proof of pseudo-secondary origin is evidenced by healed cracks travelling to an abrupt end at a growth face in the crystal. Fluorite exhibits numerous curving fractures often parallel to the octahedral plane of probably pseudo-secondary origin, see fig. 2.6. and fig. 2.1. Secondary inclusions are found in fractures positively cutting across the edges of a crystal, see figs. 2.1. and 2.6.

Hydrothermal leaching can form pseudo-secondary inclusions cutting across growth zones. Long deep etch pits could produce tubular inclusions (fig. 2.6.) They are sometimes observed in fluorites in the oxidation zone.

(14)
The stresses causing both pseudo-secondary and secondary inclusion development include twinning, phase transitions, thermal shock and mechanical stress (Roedder 1967).

Scanning electron microscopy also revealed the development of cracks in the surface of fluorite crystals of probably secondary origin, see fig. 2.7. These outline a curved shape typical of secondary inclusion development in fluorite. They often exhibit stressed growth with elongate re-entrant faces. Secondary inclusion planes in fluorite are often severely necked-down indicating probable growth under stress.

The surfaces of some fluorites also exhibit holes, usually in the bottom of "hopper" faces (fig. 2.4.) These could either be due to hydrothermal leaching, a process noted earlier, or areas of possible leakage. This serves to underline the extreme care needed in the selection of primary inclusions for study.

2.5.4. Post-Formational Changes in Fluid Inclusions and the Selection of Inclusions for Examination

When studying fluid inclusions the basic assumption is made that trapping of an original homogeneous fluid has occurred. This assumption holds true unless trapping of a heterogeneous fluid is indicated by criteria outlined in section 1.6. Certain phase changes however do occur after trapping of this homogeneous fluid. The most obvious is the formation of a vapour bubble as the vapour pressure in the inclusion drops below that of the fluid on cooling, see fig. 2.8. for a diagrammatic representation of this phenomenon. Sorby (1858) postulated heating fluid inclusions until this vapour bubble homogenized to give the temperature of trapping, the basis of modern fluid inclusion geothermometry.

Yermakov (1950) recognized crystallization on the cavity walls due to the inclusion being saturated with respect to the host mineral. This normally involves very small amounts of material and its effects are small.
Immiscibility can also occur, for instance, the separation of gaseous and liquid carbon dioxide. Liquid carbon dioxide was never observed in the numerous inclusions studied, its presence during the mineralization has however been demonstrated in the North Pennine Orefield in the Alston area by Barker (1972).

An immiscible hydrocarbon phase has frequently been observed in numerous other Mississippi Valley type deposits (Roedder 1967). Inclusions in fluorite from the Askrigg area also contain an immiscible fraction. The present writer has often observed a clear slightly greenish oil trapped within inclusions. Another brown phase tended to occur as separate, usually rounded blebs often with a vapour bubble. This phase also tended to occur along fractures and cleavage directions.

The inclusion fluid is often saturated with other phases which on cooling crystallize as daughter minerals. Sodium and potassium chlorides are frequently found as daughter minerals. Carbonates, bicarbonates (Rankin 1973) and sulphides are often present. During the many observations made of fluid inclusions during this study the presence of daughter minerals was not noted. Some inclusions, however, did appear to have a sulphide daughter phase (fig. 2.9.). However these examples most probably represent trapping of solid sulphide floating in the crystallizing fluid and not crystallization after hermetic sealing. Their occurrence is very sporadic and they do not show the constant phase ratio indicative of daughter mineral formation. During homogenization runs a dark speck was noted in some fluid inclusions to which the vapour bubble preferentially adhered. This could be a sulphide daughter phase but the small size precluded positive identification. One inclusion displayed a bright rhombohedral, birefringent mineral of high relief between crossed polars, see fig. 2.9. This could be a possible carbonate daughter mineral.

Metastability is indicated by the failure to nucleate new but stable phases, especially on cooling.
Freezing studies have revealed gross supercooling, some inclusions would not freeze after immersion in liquid nitrogen for many hours. After homogenization runs on the heating stage numerous vapour bubbles fail to renucleate indicating metastability. Roedder (1967) comments on this phenomenon as indicating crystallization from pure solutions free of nuclei which would have enabled renucleation of the bubble to take place. Small rounded inclusions of less than ten microns in size never form vapour bubbles, again this is indicative of metastable conditions.

From the point of view of temperature determination the two most important post-formational changes are necking-down and leakage. These will be dealt with separately in the next two sections.

2.5.5. Necking-Down and Coalescence

Any inclusion of irregular shape and large surface area will, by recrystallization, try and obtain a more stable, spherical shape as this will have a lower free energy level, (Lemmlein 1956). Thus a large inclusion can form several smaller ones with varying phase ratios (fig. 1.4.). This can introduce large discrepancies in homogenization temperatures from adjacent inclusions, a feature noted in fluorites from the Pennines (Sawkins 1966). Such results must be disregarded as an indication of the temperature of formation of the host crystal. Necking-down is normally distinguishable by these effects, its presence must be detected, otherwise the whole validity of a fluid inclusion study must be in question.

Large numbers of primary inclusions in fluorite, particularly the larger ones, exhibit some degree of necking-down. They frequently have "tails" or thin appendages (figs. 2.10. and 2.11.). In some cases near-complete necking-down has occurred. Most of these large inclusions were found to be hermetically sealed, as they gave constant homogenization temperatures after repeated re-heating. The development of these tails was not found to have any significant bearing on the homogenization results obtained.
2.5.6. Leakage of Inclusions

Leakage is any process resulting in the movement of fluid into or out of inclusions after they formed. It is often promoted by inclusions being intersected by cracks and tubes in the host crystals. Complete leakage can be due to deformation and local metamorphic heating. The effects of diffusion tend to be minimised by its strong pressure-temperature dependency. Oxidation effects by groundwater are generally buffered by reaction with the sulphides present.

Numerous reports of leakage (Kennedy 1950; Skinner 1953; McCulloch 1959) were often used to discredit inclusion studies. Roedder and Skinner (1968) however, using controlled conditions, subsequently established its rarity. Leakage has been revealed in some inclusions studied in this investigation by anomalously high homogenization temperatures, some decrepitation and widely varying phase ratios after homogenization runs. Fluid inclusions can normally be heated to tens of degrees above their homogenization temperatures without inducing leakage (Harker 1971). The rare inclusions that did leak on heating tended to be found near to the surface of polished plates or near to cleavage cracks. Sawing and polishing cracks are probably responsible for most of the leakage of these near-surface inclusions.

Certain other inclusions exhibited irregular outlines and long, possibly fracture-bound margins (fig. 2.11). These inclusions tended to leak on heating and were not used in this study.

The results of a detailed application of the homogenization method to fluid inclusions in fluorite from the Askrigg area are to be found in Chapter 3. This allows the temperature of formation of these fluorites to be established. Detailed information regarding the salinity of the ore-forming fluid was gained using a freezing stage (see Chapter 4). The chemistry of the fluid was investigated using both flame photometry and spectrophotometry on a leach sample from crushed fluorite (Chapter 5)
The solid inclusions of sulphides found in abundance in fluorite were investigated using an electron microprobe. Atomic absorption analysis was performed on galenas and sphalerites for trace element content.

All these methods and the equipment used will be discussed further in the relevant section.
FIG. 2.1.

A DIAGRAM ILLUSTRATING THE MODE OF OCCURRENCE OF PRIMARY, SECONDARY AND PSEUDO-SECONDARY FLUID INCLUSIONS IN FLUORITE.
Fig. 2.2.

PLATE SHOWING TRAPPING OF PRIMARY INCLUSIONS BY SULPHIDE GRAINS

2.2.a. A primary fluid inclusion in fluorite, sample 159, Rodhill Vein, Appletreewick. The inclusion was formed by a cavity produced as growth was interrupted by the sulphide grain. Near the end of the formation of the inclusion more sulphide was also trapped.

2.2.b. A primary fluid inclusion in fluorite, sample 324, Rodhill Vein, Appletreewick. The trapping of the inclusion again resulted from growth being interrupted by the grain of sulphide.

2.2.c. A primary fluid inclusion in fluorite, sample 158, Inman Vein, Appletreewick. Here trapping has resulted from organic matter interrupting the crystal growth. The vapour bubble is obscured by the organic matter.

2.2.d. A primary fluid inclusion in fluorite, sample 158, Inman Vein, Appletreewick. Note the long tail produced by some necking-down. The vapour bubble is adhering to the large grain of sulphide, probably chalcopyrite.

Bar = 300 µ
FIG. 2.2.

PLATE SHOWING TRAPPING OF PRIMARY INCLUSIONS BY SULPHIDE GRAINS.

a.  

b.  

c.  

d.
PLATE SHOWING THE SHAPE OF TYPICAL PRIMARY INCLUSIONS IN FLUORITE

2.3.a. Negative crystal shaped primary inclusions in amber fluorite, sample 80, Lolly Mine, Nidderdale. The inclusions have a definite random distribution, constant phase ratios and are thus primary.

2.3.b. Rounded primary inclusions in purple fluorite, sample 172, Raygill Quarry, Lothersdale. The inclusions occur in a growth plane parallel to the cubic growth face of the host fluorite crystal.

2.3.c. Typical abundant, small, rounded primary inclusions in fluorite, sample 86, Seata Mine, Aysgarth, Wensleydale. The inclusions have a random distribution and the shape is tending to that of the minimum surface energy, i.e. a spherical shape.

2.3.d. A similar primary inclusion zone to that of 2.3.c. The polished section was cut across the growth zone to give the termination observed in the photograph.
FIG. 2.3.

PLATE SHOWING THE SHAPE OF TYPICAL PRIMARY INCLUSIONS IN FLUORITE.

a.    b.

c.    d.
Fig. 2.4.

PLATE SHOWING THE DEVELOPMENT OF "HOPPER" FACES ON THE SURFACE OF A FLUORITE CRYSTAL

2.4.a. Scanning electron micrograph of part of the surface of a fluorite crystal, Greenhow Rake, Greenhow Hill. The hopper faces are found in varying sizes, probably reflecting nutrient starvation in the final stages of growth.

2.4.b. Scanning electron micrograph of another area of the fluorite crystal. Note the coalescence of some hopper faces with others. This could be due to stresses during growth. Also note the coating of calcite crystals.

2.4.c. Scanning electron micrograph showing the marked coalescence of neighbouring hopper crystal faces.

2.4.d. Scanning electron micrograph of a large rectangular hopper face. This could well be an example of a "proto"-inclusion. If this cavity was isolated and subsequently trapped some fluid, a typical primary inclusion could be formed. Also note the extreme diversity of shape shown in neighbouring areas of hopper faces. This is a very similar occurrence to the distribution of negative crystal shaped fluid inclusions in fluorite.

Bar = 5 \mu
PLATE SHOWING THE DEVELOPMENT OF "HOPPER" FACES ON THE SURFACE OF A FLUORITE CRYSTAL.
Fig. 2.5.

PLATE SHOWING A FLUORITE CRYSTAL WITH A COATING OF CALCITE

Scanning electron micrograph of a large area of the surface of a fluorite crystal from Greenhow Hill, Yorkshire. The surface of the fluorite crystal is covered with a later coating of well developed calcite crystals. The hopper crystal faces occur in various sizes, all have the basic cubic symmetry. Some of these faces show a marked alignment indicating possible areas of stress during growth. Stresses during the growth of fluorite crystals often result in the formation of pseudo-secondary inclusions.
Plate showing a fluorite crystal with a coating of calcite.
Fig. 2.6.

**PLATE ILLUSTRATING SECONDARY AND PSEUDO-SECONDARY INCLUSIONS IN FLUORITE**

2.6.a. The typical rectangular pattern of secondary inclusion zones in a fluorite crystal from the Palfrey Vein, Grassington Moor.

2.6.b. A curving secondary inclusion zone cutting across the growth zones of the host crystal. The inclusion zone finally penetrates the edge of the crystal. Massive fluorite from the Gill Heads Vein, Appletreewick.

2.6.c. Small rounded pseudo-secondary inclusions in fluorite from the Palfrey Vein, Grassington Moor. The fluid inclusions terminate at a growth surface in the crystal and are thus pseudo-secondary.

2.6.d. Definitely secondary inclusions cutting across growth zones outlined by solid inclusions. The secondary inclusions were probably formed by hydrothermal leaching, fluorite crystal, Middle Vein, Grassington Moor.

2.6.e. Long tubes penetrating the fluorite crystal, again probably due to hydrothermal leaching. Fluorite crystal from Slanter Vein, Grassington Moor.

2.6.f. A long tubular inclusion which probably resulted from trapping of fluid by one of the hydrothermal leaching tubes seen in 2.6.g. Massive fluorite from Greenhow Rake, Greenhow Hill.

Bar = 1000 µm.
FIG. 2.6.

PLATE ILLUSTRATING SECONDARY AND PSEUDO-
SECONDARY INCLUSIONS IN FLUORITE.

a. b.

c. d.

e. f.
Fig. 2.7.

PLATE ILLUSTRATING THE DEVELOPMENT OF FRAGMENTS OF PROBABLE SECONDARY ORIGIN IN FLUORITE

2.7.a. Scanning electron micrograph of a fluorite crystal from Sun Vein, Greenhow Hill. Note the cracks containing probable secondary inclusions.

2.7.b. Scanning electron micrograph, an enlargement of 2.7.a. showing the cleavage crack penetrating deep into the surface of the fluorite crystal.

2.7.c. Scanning electron micrograph of an area of the crystal of 2.7.a. This shows the curving fracture so typical of secondary inclusion planes in fluorite. Also shown are numerous holes in the surface, probably due to some hydro-thermal leaching after growth had ceased.

2.7.d. Scanning electron micrograph, an enlargement of the fracture shown in 2.7.c. This shows the stressed appearance of the fluorite infilling the fracture. Secondary inclusions in fluorite frequently exhibit necking-down of a very similar pattern.

2.7.a, c. Bar = 200 μ
2.7.b, d. Bar = 20 μ
PLATE ILLUSTRATING THE DEVELOPMENT OF FRACTURES OF PROBABLE SECONDARY ORIGIN IN FLUORITE.
THE RELATIONSHIP BETWEEN MODE OF TRAPPING AND TEMPERATURE IN THE SYSTEM H₂O (after Roedder 1962)

FIG. 2.8

TEMPERATURE °C

FLUID

LIQUID & GAS

LIQUID

GAS

0 100 200 300 400

100% 80% 60% 40% 20% 0%

DEGREE OF FILL (AS PERCENT LIQUID)
The trapping of solid particles of sulphide (probably chalcopyrite) in fluid inclusions in purple fluorite from Easco Hill, Craven. The widely varying phase ratio of liquid to sulphide indicates these grains to be accidental and not daughter minerals.

A primary fluid inclusion from Grimes Groove Vein, Grassington Moor. This inclusion contains a high relief, rhombohedral inclusion of ? Carbonate. It also shows bright relief under crossed nicols (2.9.e.). This could be a daughter mineral but it was only found on one isolated occasion and again is probably an accidental inclusion.
FIG. 2.9.

PLATE SHOWING THE TRAPPING OF
NON-REPRESENTATIVE FRACTIONS
IN FLUID INCLUSIONS.

a.  

b.  

c.  

d.  

e.
Fig. 2.10.

PLATE ILLUSTRATING CHANGES SINCE TRAPPING

2.10.a. Primary fluid inclusion in fluorite from sample 86, Seata Mine, Aysgarth. This inclusion shows a thinner appendage due to post-formational changes.

2.10.b. Primary fluid inclusion in fluorite from sample 1, Gill Heads Vein, Appletreewick. Here the inclusion shows a long "tail".

2.10.c. A "tail" in an inclusion in fluorite, Escoe Hill, Craven. The inclusion has not undergone any necking-down or leakage and can thus be used in a heating study.

2.10.d. A negative cubic crystal with a small tail in fluorite, sample 108, Kettlewell, Wharfedale.

2.10.e. This inclusion in sample 152, Galloway Vein, Greenhow Hill shows the development of walls in the inclusion cavity. This represents a partial arrest of the process of necking-down. If it had proceeded further, two separate inclusions one with a vapour bubble, one without, would have been formed.

2.10.f. Fluid inclusion in sample 157, Forest Vein, Greenhow Hill. Here the process of necking-down and leakage has resulted in the formation of a smaller inclusion enclosed in a larger cavity. This inclusion is totally unsuitable for study.
FIG. 2.10.

PLATE ILLUSTRATING CHANGES SINCE TRAPPING.
Fig. 2.11.
PLATE ILLUSTRATING FURTHER CHANGES SINCE TRAPPING

These photographs represent the completion of the process of necking-down and leakage on fluid inclusions. All fluid inclusions shown are totally unsuitable for study as they are extremely prone to leakage.

2.11.a. Inclusion in sample 115, Galloway Vein, Greenhow Hill. Here the inclusion cavity has undergone slight necking-down which has resulted in the separation of inclusions with no vapour bubble.

2.11.b. Large inclusion in sample 115, Galloway Vein, Greenhow Hill. This inclusion has undergone some leakage of fluid, evidenced by the larger vapour bubble and numerous appendages.

2.11.c. Large inclusion in sample 157, Inman Vein, Appletreewick which has undergone marked post-trapping changes. Note the irregularly shaped inclusion produced and long fractures.

2.11.d. Large inclusion in sample 157, Inman Vein, Appletreewick with irregular outline and similar fracture bound edges.

2.11.e. Inclusion in sample 73, Escoe Hill exhibiting a large vapour bubble and long "tail" probably indicating some leakage. In fact this inclusion leaked on heating, giving progressively higher homogenization temperatures.

2.11.f. Inclusion in sample 108, Forest Vein, Greenhow Hill which has undergone complete leakage along the fracture in the host fluorite crystal.
FIG. 2.11.

PLATE ILLUSTRATING FURTHER CHANGES SINCE TRAPPING.

a.  

b.  

c.  

d.  

e.  

f.  

CHAPTER 3
HOMOGENIZATION STUDIES ON FLUORITES FROM THE ASKRIGG BLOCK

3.1. GEOLOGICAL ENVIRONMENT

3.1.1. The Stratigraphic Setting

The epigeanic mineral deposits of the Askrigg area occur in approximately 500 metres of Viséan and Namurian strata belonging to the Carboniferous system (Dakyns et al. 1890, 1891, Hudson et al. 1938; Edwards and Trotter 1954). There are five predominant facies types developed:

1. The massive Great Scar Limestone.
2. The reef limestone of the Craven District.
3. The cyclic limestone-shale-sandstone-coal sequences of the Yoredale beds.
4. The Bowland Shale.
5. The coarse sandstones and alternating marine bands of the Millstone Grit.

The stratigraphic setting is thus very similar to that of the Alston area, the more notable difference being the development of the massive Great Scar limestone in the lower horizons of the Askrigg area. The relationship between the limestone strata of the Alston and Askrigg ore-fields is taken from Rayner (1967), and shown diagrammatically in fig. 3.1.

TABLE 3 A THE MAIN LIMESTONE HORIZONS OF THE NORTHERN PENNINE OREFIELD

<table>
<thead>
<tr>
<th>STAGE</th>
<th>ASKRIGG ORFIELD</th>
<th>ALSTON ORFIELD</th>
<th>LIMESTONE GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>MAIN LIMESTONE</td>
<td>GREAT LIMESTONE</td>
<td>UPPER LIMESTONE</td>
</tr>
<tr>
<td></td>
<td>UNDERSEEN LST.</td>
<td>FOUR FASHION LST</td>
<td>GROUP</td>
</tr>
<tr>
<td></td>
<td>THREE YARD LST.</td>
<td>THREE YARD LST</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FIVE YARD LST.</td>
<td>FIVE YARD LST.</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>MIDDLE LST.</td>
<td>SQR LST. SHELL</td>
<td>MIDDLE LIMESTONE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>COCKLE SHELL LST.</td>
<td>GROUP</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SINGLE POST LST.</td>
<td></td>
</tr>
</tbody>
</table>

contd.

(20)
Table 3.A. contd.

<table>
<thead>
<tr>
<th>STAGE</th>
<th>ASKRIGG ORFIELD</th>
<th>LOWAN ORFIELD</th>
<th>LIMESTONE GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2</td>
<td>SIMONSTONE LST.</td>
<td>TYNEBOTTOM LST.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HARDRAW SC.R LST.</td>
<td>JEW LST.</td>
<td>LOWER LITTLE LST.</td>
</tr>
<tr>
<td>P1 D2</td>
<td></td>
<td>SHIDDY LST.</td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>GREAT SCAR LST.</td>
<td>ROBINSON LST.</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>MEINDERBY SCAR LST.</td>
<td>Lower Limestone Group</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td>BASEMENT BEDS</td>
</tr>
</tbody>
</table>

The beds of the Hillstone Grit facies rest unconformably on the Yoredale and massive limestone facies. The unconformity is scarcely developed in the north (Rowell and Scanlon 1957; Reading 1957) but becomes prominent southwards from Kettlewell, progressively cutting out lower beds until it finally rests on the Hargate End Limestone at Greenhow (Garwood and Goodyear 1924; Chubb and Hudson 1925; Dunham and Stubblefield 1944).

The stratigraphy plays an important role in localizing the mineralization in a number of preferred horizons or "bearing beds" (Phillips 1836). Each horizon acted as a trap for the mineralizing fluid with an impermeable shale member acting as a cap. These "bearing beds" include the Middle Limestone of Wensleydale and Grassington, the Grassington Grit, the upper part of the Great Scar Limestone and the strata between the Richmond Chert and Undersett Limestone of Swaledale. The more important impermeable shale members include the Bowland Shale, the Thirty Five Fathom Shale, the shale between the Richmond Chert and Crow Limestone and the basal shale of the Hillstone Grit. The stratigraphic control of these bearing beds on the mineralization is illustrated in fig. 3.2.

Lower Palaeozoic rocks occur in small faulted inliers along the northern side of the North Craven Fault (Hing and Wilcockson 1934) as the Chapel-le-Dale, Horton in Ribblesdale and Crummack Dale inliers.

(21)
Along the western side of the Dent Fault, Silurian rocks occur in east-west folds with small Ordovician inliers in the Howgill and Middleton Fells. These rocks are either fault bounded or overlain unconformally by Dinantian limestones and probably represent the basement of the Askrigg block.

The Ingletonian Series (Rastall 1907) consists of some 800 metres of isoclinally folded greywackes with some intrusive basic dykes (King 1932; Leedal and Walker 1950; Dunham et al. 1953). The Pre-Cambrian age assigned to the Ingletonian has long been in dispute. On recent evidence, O'Nions et al. (1973) postulate a possible Cambrian to up to 600 metres of the gray calcareous mudstone of the Coniston Limestone Series (Daleyns et al. 1891). The Silurian is present as 500 metres of limestones, calcareous shales, slates and greenish grits with a steep south-westerly dip.

During the Carboniferous period sedimentation on the Askrigg block was thin compared with the thick sequences developed in the flanking Craven, Bowland and Cleveland troughs. Breaks in sedimentation, uplift along the Middleton Tyas Anticline with associated faulting results in the probably maximum deposition of about 2000 meters of Carboniferous sediment. Extensive pre-Permian erosion followed and then a cover of Permian-Triassic rocks was deposited. In the Askrigg area in particular and in the Pennine ore fields in general, the age of the lead-zinc, fluorite-baryte mineralization is still in dispute (Moorbath 1962; Ineson and Mitchell 1972). It is essential to know the age of the mineralization to evaluate a positive pressure correction (section 3.3.).

Another important factor is the structural evolution before and during the mineralization. The salinity of the mineralizing fluid also affects the pressure correction applied (Lemlein and Kletsov 1956, 1961; Kennedy 1950b, 1954). Fortunately this can be evaluated by freezing point determinations (see chapter 4). Salinities in the Askrigg area were found to be in the range of 15 to 25 per cent equivalent by weight of sodium chloride. If the mineralization is indeed Permian-Triassic in age (Dunham 1944), the amount of this cover needs to be evaluated for the pressure correction.
to be applied. Subsequent Tertiary uplift, tilting and erosion imposes yet more uncertainties.

3.1.2. The Structural Setting.

The Askrigg block (Harr 1921; Hudson 1938) is one of the three major limestone massifs of the English Pennines. They all exhibit dominant block and basin control of sedimentation and subsidence. The fault and flexure bounded blocks are associated with marked gravity anomalies, epigenetic mineralization and Caledonian granitic intrusions at depth (Bott 1961, Dunham et al. 1965; Taylor pers. comm. 1974). The blocks consist essentially of shallow water Lower Carboniferous sediments. The intervening gulfs or basins are made up of deeper water sediments with up to three times the sedimentary thickness found in the blocks. The Askrigg block is bounded by the Bowland Trough to the south and the Cleveland and Ravenstonedale Gulfs to the east and west respectively (Kent 1966, 1974). The position of the Askrigg block in relation to the main structural features of the Pennines is shown in fig. 3.3. These blocks probably represent post-Caledonian adjustments and deep basement displacements (Bott 1967).

The Askrigg block itself comprises the area from the Craven Faults in the south, to Stainmore in the north, the main mineral veins and geology are shown in fig. 3.4. The western boundary is the north-north easterly trending Dent line (Dakyns et al. 1891) which consists of an easterly inclined, overfolded and faulted monocline. The North Craven Fault truncates the southern boundary of the Askrigg block and consists of a complex transcurrent fault system (Wager 1931; Anderson 1951).

The general north-south compressive Hercynian stress produced mild non-orogenic movements in the massifs. Contemporaneous movements produced non-sequences between the C1 and C2, S2 and S2-D1 beds of the Carboniferous beds (Hudson and Mitchell 1931). Movement during carboniferous D1 to P1 times has also been noted along the Mid-Craven Fault (Hudson 1933, 1944; Black 1958).
The main structural feature is the broad Sleightholme-Hiddleton Tyas anticline (Wells 1957) which terminates southwards against the Stockdale Monocline. Southwards from the Stockdale Monocline the rocks are gently folded into a half dome above the roof of the Wensleydale granite terminating as the Greenhow Hill and Skyreholme anticlines near to the Craven Faults (Anderson 1928; Dunham and Stubblefield 1944). In marked contrast intense folding occurred in the basin areas represented by the Clitheroe folds (Zarp et al. 1961) and Ribblesdale folds (Hudson and Mitchell 1937). wrench faulting in the basin areas with mainly north-east and north-west trends was developed with north-south faults associated with the monoclines (Moseley 1972). Reactivation of existing faults with uplift and the easterly tilting of the Askrigg area with resultant erosion occurred during the alpine orogenic movements.

3.1.3. The Style of Mineralization

The baryte-fluorite-base metal deposits of the Askrigg block are found in mineralized normal faults with dominant west north-west and east-west directions and subsidiary north-north-west and east-north-east trends. The mineral deposits are in the Askrigg block with a few isolated occurrences in the much faulted and folded Bowland Trough; the importance of the latter deposits will be discussed later in this chapter (section 3.9.).

Three main types of orebody are present in the Askrigg area, fissure veins, flats and pipe deposits. They are represented diagrammatically in fig. 3.5.

Fissure Veins

Fissure veins take the form of ribbon structures often with a banded mineral fill, their length many times greater than their depth and often with a variable dip of a few degrees from the vertical. The more important ore carrying faults commonly exhibit small vertical displacements, although displacements of up to 70 metres have been recorded (Bradley 1862).
Cross fissures are sometimes preferentially mineralized to give a constricted appearance to the vein, a feature common in the Greenhow area. Tensional stress acting along the strike of the bedding results in a "side-stopped" fissure, as in the case of the Gills Heads Vein, Appletreevick. These veins illustrate the typical character of remaining steep and open in the hard and brittle bearing beds whilst dipping more gently and closing in the softer shale beds.

Flats (Flattening).

Flat deposits take the form of bedding - controlled replacements in limestone. Examples are found at Lover Gill, Buckden Gavels Mine, Gill Shaft (Stump Cross) and more notably the galena-baryte deposit at Mussey Knott, Greenhow.

Pipes.

Pipes normally consist of irregular mineral masses usually found at the intersection, of a vertical fissure or joint with the limestones' bedding. They are found either immediately above or below a layer of lower porosity or solubility. Very common in the Greenhow Hill area (Varvill 1937), they are usually very rich in ore, examples include the Pendleton and Gill Shaft pipes.

Gulfs (Gulfs).

The Greenhow Hill area also exhibits a feature known as Gulfs or Gulphs. These are produced by swallow holes, sinks and caverns developed across productive veins by post-mineralization solution effects. They are filled with a debris of limestone, clay, sand and lumps of fluorite, galena and baryte, for example those on the Galloway Vein, Greenhow Hill.

The major minerals found in the deposits of the Askrigg area are summarized in tabular form in fig. 3.6. (after Dunham 1959).

The recorded output of lead concentrates during the period 1845-1938 totalled some 350,000 tons (Dunham 1944) with some 200,000 tons of baryte and 55,000 tons of fluorite produced from the gangue.
3.1.4. A Review of the Ideas on the Genesis of the Pennine Mineralization

The mineral deposits found in Lower Carboniferous strata in the Pennine orefields are part of a group known collectively as the Mississippi Valley type deposits (Heyl 1959; Brown 1967). These deposits share many common geological features but vary in detail from region to region (Heyl 1969). They are all stratabound orebodies usually with marked mineralogical zoning of ore, gangue and trace elements with a broadly simple galena-sphalerite-baryte-fluorite mineralogy. They occur to a large extent in carbonate host rocks, with subordinate sandstone, in cratonic platforms. They are often located on regional structural highs on the flanks of sedimentary basins associated with fractured domes and deep basement lineaments.

Fluid inclusion studies (Hall and Friedman 1963; Roedder 1967b) indicate deposition from concentrated sodium-calcium-potassium-chloride brines in the temperatures range of 70° to 200°C.

A multiplicity of origins have been postulated for these deposits; indeed the subject today is still one of lively debate. Their genesis has been variously assigned to a meteoric source (Sieboldenthal 1915) a magmatic alkali igneous source (Lindgren 1935), a lateral secretion source (Davidson 1965a, b), or a deeply circulating connate water source (Beales and Jackson 1966). The ideas of genesis of the deposits of the English Pennines have also undergone a radical re-examination in the light of recent discoveries (Sawkins 1966a; Solomon et al. 1971). The underlying supposed Hercynian granite of the Pennines (Bott and Haszum-Smit 1957; Bott 1961, 1967) was long thought to be the source of the deposits (Dunham 1934), until recent evidence (Dunham et al. 1965) confirmed a Caledonian age for this granite. Deposition from Permian brines of the seichstein Sea was postulated by Davidson (1966) whilst Sawkins (1966a) proposed mixing of connate waters and magmatic fluids.

A deep mantle source has been suggested for Derbyshire and Irish deposits.
on the basis of basaltic activity (Russell 1968) and a deep crustal source for the Askrigg deposits by Mitchell and Krouse (1971). Deeply circulating connate waters have recently been postulated for the Alston area by Solomon et al. (1971).

It was felt that by a detailed study of the temperature, salinity and chemistry of the ore fluid represented as fluid inclusions from the Askrigg area, more information could be presented to place constraints on these postulated origins. The genesis of these deposits in the light of the author's fluid inclusion studies will be discussed in much greater detail in Chapter 6.

3.2. THE LEITZ 1350 HEATING STAGE

The Leitz 1350 heating stage was used during this study to homogenize fluid inclusions in specially prepared doubly polished plates (section 2.3.). It consists essentially of a metal, water-cooled cell with a heating element. This is mounted on a polarizing microscope with a binocular head. A detailed account of the apparatus is to be found in Harker (1971).

3.2.1. Calibration of the Leitz Heating Stage.

Temperature readings were taken using a Pt-Rh thermocouple connected to a galvonometer which was calibrated by melting the following chemicals:

- 8-Hydroxyquinoline  73°C - 75°C
- Benzoic Acid       122.0°C
- n-Nitro p-aniline  147.5°C
- Ammonium Nitrate  169.0°C
- Dicyandiamide     207°C - 209°C

The scheme essentially is that of Harker (1971); details of chemicals for calibration at temperatures up to 900°C are contained in Rankin (1973). The chemicals were placed in capillary tubes on the heating element and the reading on the galvonometer when melting occurred was noted.
The ambient temperature was added to this reading and the result compared with the known melting point. The error in readings up to 200°C was of the order ± 2°C agreeing with both Harker and Rankin. The calibration scheme is shown in fig. 3.7. Sublimation was a problem with certain chemicals like acetonilide which were then discarded. Regular calibration checks were run to assure the validity of the homogenization temperatures obtained.

**Correction Factor:** To facilitate easy manipulation the galvanometer was set to zero at an ambient temperature of 23°C any changes in the ambient temperature were then monitored. The observed homogenization temperatures were corrected using Harker's equation:

\[
T_{\text{corr}} = T_{\text{obs}} + RT + 2°C
\]

where:
- \(T_{\text{corr}}\) = Corrected homogenization temperature.
- \(T_{\text{obs}}\) = Observed homogenization temperature.
- \(RT\) = Change in ambient temperature.
- \(RT_{\text{zero}}\) = 23°C

### 3.2.2. Heating Rates

All heating stages have the inherent problem of thermal gradients. The calibration sequence outlined above established the Leitz 1350 to have minimal thermal gradients up to 200°C, the temperature range of most of this study. Heating rate is critical in this respect, the faster it is the greater the thermal gradient produced. In any systematic fluid inclusion study, a compromise between time spent heating to ensure complete equilibrium and the need to study a representative number of inclusions has to be made. After experimentation the following technique of stop heating, following that recommended by Roedder (1962) was evolved. In a normal run of between thirty to forty-five minutes the temperature was raised quickly to 70°C and kept there for approximately ten minutes.
The inclusions were then heated at 1°C per minute until homogenization occurred. For samples with abundant inclusions runs of up to two hours were made. It was thus possible to make about six or seven homogenization measurements in a working day.

3.2.3. The Behaviour of Fluid Inclusions in Fluorite on Heating.

The observation of the homogenization temperature in some inclusions was found to be difficult. The vapour bubble would sometimes move into the dark edges of the inclusion walls and remain there, observation of its behaviour thus being impossible. Another problem was the occurrence of a small dark speck of probably sulphide in some inclusions as mentioned earlier (section 1.7.). If the vapour bubble adhered to this speck the homogenization point was often very difficult to distinguish.

However with doubly polished plates observation of most inclusions was excellent, a typical example is illustrated in fig. 3.8. After each run the diameter of the vapour bubble was checked using a micrometer ocular to detect any possible leakage (section 2.5.6.). The homogenization of the vapour bubble can be repeated a number of times and the diameter of the vapour bubble plotted against temperature, as a homogenization curve. The results are always constant if leakage has not occurred. Fig. 3.9, shows various examples of homogenization curves for fluid inclusions in fluorite from the Askrigg area.

3.3. POSITIVE PRESSURE CORRECTION

After the homogenization temperature of the fluid inclusion has been obtained on the heating stage, a positive pressure correction needs to be applied to the result (Roedder 1967a). If the fluid system responsible for depositing the ores had been open to the surface and confined hydraulically, boiling of the fluid would not have occurred. As stated earlier, the fluid inclusions in fluorite from the Askrigg
area are predominantly two phase gas-liquid inclusions, the vapour phase only occupying between five and ten per cent of the total volume. This is in stark contrast to the vapour dominated systems boiling under no confining pressure (Roedder and Coombs 1967).

The confining pressures operating on the fluid system consist of a lithostatic load, due to the amount of overburden and a hydrostatic one, from pore-fluid pressure in the host rock reservoir. The estimation of these two parameters is somewhat vague as little is known about the operation of either in geological systems.

In view of these uncertainties it was felt that it was not worthwhile assessing all the stratigraphical and structural possibilities necessary to estimate the actual amount of cover present during mineralization.

However, a positive pressure correction was needed as the Askrigg fluid inclusions gave no evidence of boiling of the hydrothermal fluid. In order to estimate the amount of cover present during the mineralization, a Permian age for the deposits was assumed (Dunham 1959). The Trollers Gill area, Appletreewick, contains the oldest Lower Carboniferous rocks exposed on the Askrigg block and is thought to occur just above the supposed Pre-Cambrian basement (Anderson 1928). A maximum possible cover of up to one kilometer was assumed for this area (Edwards and Trotter 1954). The cover of all other areas of mineralization was then estimated by reference to fig. 3.2.

The lithostatic pressure was estimated using the following equation:-

$$\text{pressure} = \text{density} \times \text{height} \times \text{gravitational acceleration}$$

$\text{kg m}^{-2} \times \text{kg m}^{-3} \times \text{m} \times \text{cm}^{-2} \times \text{s}^{-2}$

The average density for the Carboniferous rocks was taken as 2550 kg m$^{-3}$ using the data of Bott (1961).
The lithostatic pressure was computed and then converted to atmospheres.

In sediments, such as sandstones and limestones, where the load is carried by the mineral grains and gives rise to lithostatic pressure, any water in the pore spaces gives rise to a hydrostatic pressure. In near-surface, unconsolidated sediments, the pore-water pressure is merely that of the hydraulic head and increases with depth by about 1 atm for every 10 m of burial. If the pore-water pressure is defined as a ratio \(x\) of the lithostatic pressure, then under near-surface conditions \(x = 2.5\) this would be about 0.4. With burial and consolidation of the sediment, the porosity is reduced and if the pore-water cannot escape, then its pressure increases and approaches the lithostatic pressure.

As a result, measurements in deep wells have shown that \(x\) may exceed 0.8 (Phillips 1972). Table 1 in Phillips (1972) suggests that for the Askerg area with depths of 1-2 km it would be reasonable to assume a value of 0.5 for \(x\). If the hydrostatic pressure of the mineralizing fluid is assumed to be equal to the pore-water pressure then the pressure correction calculated from the lithostatic pressure must be reduced by a half as shown in Table 3B.

### Table 3B. The Positive Pressure Corrections Applied to the Hologenization Results

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>OLD GANG SHALEDale</td>
<td>609.6</td>
<td>150.9</td>
<td>10</td>
<td>75.5</td>
</tr>
<tr>
<td>GRASSINGTON MERELEYdale</td>
<td>712.0</td>
<td>176.3</td>
<td>20</td>
<td>83.2</td>
</tr>
<tr>
<td>LOLLY GREENHOWN</td>
<td>829.6</td>
<td>205.9</td>
<td>20</td>
<td>103.0</td>
</tr>
<tr>
<td>BUSHILL COPPERS GILL</td>
<td>1000</td>
<td>247.6</td>
<td>20</td>
<td>123.3</td>
</tr>
<tr>
<td>BASIN AREAS</td>
<td>1524.0</td>
<td>376.3</td>
<td>30</td>
<td>183.0</td>
</tr>
</tbody>
</table>

As a result, measurements in deep wells have shown that \(x\) may exceed 0.8 (Phillips 1972). Table 1 in Phillips (1972) suggests that for the Askerg area with depths of 1-2 km it would be reasonable to assume a value of 0.5 for \(x\). If the hydrostatic pressure of the mineralizing fluid is assumed to be equal to the pore-water pressure then the pressure correction calculated from the lithostatic pressure must be reduced by a half as shown in Table 3B.
2. Average density $= 2550 \text{ kgm}^{-3}$
3. Maximum assumed cover

- 1000 metres shelf
- 2000 metres basin

All the mineralizing solutions were assumed to have an average salinity of $20\%$ by weight of sodium chloride.

In view of the uncertainties involved a total correction of $15^\circ$C was added to the Wharfedale and Wensleydale mineralization, $8^\circ$C to that of Swaledale, $20^\circ$C to that of the basin areas.

3.4. **THE SIGNIFICANCE OF THE HOMOGENIZATION RESULTS**

3.4.1. **The Selection of Samples for Study.**

During the course of the present study some 600 polished plates were prepared and examined for fluid inclusions suitable the heating and freezing stages. Of these about fifty per cent were used, most of them had isolated primary inclusions numbering two or three per sample. Samples with greater than ten primary inclusions were rare but provided the most useful information.

As stated earlier (section 2.5.2) the distinction of definite primary inclusions is rarely unambiguous. In addition to this is the extra disadvantage of the paucity of inclusions suitable for study. Thus, apart from a few instances, a fair number of samples from one particular locality needed to be studied to obtain statistically viable results.

In single crystals, positive primary inclusions related to a growth zone will give a particular temperature, representing the stage of growth reached. These can also often be traversed by numerous planes of both pseudo-secondary and secondary inclusions (fig. 2.6.)

With massive fluorite deposits the problem is more acute as they were deposited over a range of temperature often with extensive fracturing.

An attempt was made systematically to examine one of these massive veins for thermal gradients, the Gill Heads Vein, Troller's Gill. The results were however, very disappointing.
During this study a minimum of five inclusions per sample was adopted to enable statistical tests to be applied, with an applied maximum of up to 100 inclusions per sample. Unfortunately most of the sampling had to be from old dumps, wherever possible samples were taken from veins exposed at surface or underground. As with all dump sampling one has not got complete sample control. One problem is to fit the dump sample into a paragenetic sequence and also to be sure of sampling from the same population each time.

3.4.2. Analysis of Variance

With these constraints on sampling the problem arises of assessing whether, in each sample, one has the same population from one fluorite generation deposited over a certain temperature range. To test the validity of the results gained an analysis of variance for a one-tailed test was applied.

This test, the F test, is based on the F probability distribution which is the theoretical distribution of values from random sampling of a normal population. The F distribution describes the probabilities of obtaining specified ratios of sample variances drawn from the sample population.

The variance is defined as the average squared deviation of all possible observations from the population mean.

\[
\text{Population Variance} = \sigma^2 = \frac{\sum_{i=1}^{n} (X_i - \mu)^2}{n}
\]

\(X\) = sample mean

\(\mu\) = population mean

\(n\) = No. of samples

\(\sigma^2\) = sample variance

\[F = \frac{\sigma^2}{\bar{\sigma}^2} \text{ larger variance}\]

\[F = \frac{\bar{\sigma}^2}{\sigma^2} \text{ smaller variance}\] 

(33)
The Null Hypothesis is proposed that the two or more samples are drawn from the same population with equal variance. If the F-ratio exceeds the computed value then they probably are from different populations. With a one tailed test certain basic assumptions are made as follows:- (a) each set of replicates represent random samples, (b) each parent population is normally distributed and has some variance. The analysis of variance is usually broken down into two component parts, the within sample variance and the variance among samples.

The F test is a rigorous statistical tool and was used extensively during this study. It was applied to verify sampling from one or more parent populations on a within sample scale and between different samples from one specific locality.

The fluorite samples with abundant inclusions had to be broken into smaller pieces to fit into the specimen carrier of the Leitz 1350 Heating stage (section 2.4). The F test was then applied to the samples to test the significance of the homogenization results obtained. For example: samples 448 (Yarnbury) and 64 (Old Vein, Appletreewick) both contained abundant inclusions measured in a total of three sections each.

The F test was applied to both with the following results:-

<table>
<thead>
<tr>
<th>SAMPLE NUMBER, SITUATION</th>
<th>NO. INOS.</th>
<th>MEAN°C</th>
<th>CALCULATED F RATIO 5% LEVEL</th>
<th>ACTUAL F RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>448/1</td>
<td>35</td>
<td>112.4857</td>
<td>F = 3.5 2.61 degrees of freedom</td>
<td>F = 1.7589</td>
</tr>
<tr>
<td>448/2</td>
<td>13</td>
<td>115.3846</td>
<td>F = 3.5 2.61 degrees of freedom</td>
<td>F = 1.7589</td>
</tr>
<tr>
<td>448/3</td>
<td>16</td>
<td>109.6875</td>
<td>F = 3.5 2.61 degrees of freedom</td>
<td>F = 1.7589</td>
</tr>
<tr>
<td>YARNBURY</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>448/1</td>
<td>35</td>
<td>112.4857</td>
<td>F = 3.5 2.61 degrees of freedom</td>
<td>F = 1.7589</td>
</tr>
<tr>
<td>448/2</td>
<td>13</td>
<td>115.3846</td>
<td>F = 3.5 2.61 degrees of freedom</td>
<td>F = 1.7589</td>
</tr>
<tr>
<td>448/3</td>
<td>16</td>
<td>109.6875</td>
<td>F = 3.5 2.61 degrees of freedom</td>
<td>F = 1.7589</td>
</tr>
<tr>
<td>OLD VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APY/21/3/2</td>
<td>41</td>
<td>118.3171</td>
<td>F = 3.5 2.62 degrees of freedom</td>
<td>F = 3.0000</td>
</tr>
<tr>
<td>21/3/3</td>
<td>8</td>
<td>124.0000</td>
<td>F = 3.5 2.62 degrees of freedom</td>
<td>F = 3.0000</td>
</tr>
<tr>
<td>21/3/4</td>
<td>16</td>
<td>114.9375</td>
<td>F = 3.5 2.62 degrees of freedom</td>
<td>F = 3.0000</td>
</tr>
</tbody>
</table>
Thus both samples upheld the Null Hypothesis and had no significantly differing variances between each section of the sample examined.

Most measurements however had to be performed not just on one but on a number of samples from one locality to obtain sufficient homogenization results. Here again the F test was applied to compare results. Most of the samples showed little variation between themselves and may be considered to have come from one population. Some however did show differences with F ratios greater than the expected value. This was generally restricted to samples exhibiting necking-down and with inclusions of doubtful primary origin. These results were then disregarded. The results of some of these F tests are summarized in table 3.10.

3.4.3. The Plotting of the Homogenization Results.

After the homogenization temperatures, corrected for room temperature, had been tested for variance, they were then plotted as histograms (e.g. fig. 3. 20.). Secondary inclusions normally homogenized at lower temperatures, often with some overlap into the lower temperature range of the primary inclusions (e.g. fig. 3. 14.). They represent a thermal event after growth had ceased, probably in the later vaning phases of the mineralization. Evidence from the freezing studies (Chapter 4) indicates low salinities of between one to five per cent equivalent by weight of sodium chloride possibly indicating an increasing dilution of the brines during the later stages of the mineralization by groundwaters. It should be noted however that secondary inclusion development can take place any time after the primary mineral growth has taken place. Secondary inclusion development was particularly evident in the oxidation zone, the Swaledale-Arkengarthdale area exhibiting numerous examples.

The primary and secondary inclusions were present as discrete populations.
The Primary inclusion populations were plotted on a log probability paper and exhibited remarkably little deviation (fig. 3.16. and fig. 3.22.) from the straight line of a normal population. Some necking-down was evident in the histogram plots, as in the example in fig. 3.14.

3.5. HOMOGENIZATION STUDIES IN THE GREENHOW HILL AREA

3.5.1. Introduction

The Greenhow Hill lead mining field occupies the watershed area between the valleys of the rivers Nidd and Wharfe, five kilometres to the west of Patley Bridge, Yorkshire (fig. 3.11.). Lead mining has been carried out there since Roman times (Raistrick 1927), its heyday being reached in the late Nineteenth Century (Dickenson 1970). No mining is carried out today except for small scale production of fluorite for metallurgical purposes. The area lies on the southern fringe of the askrigg block (Hudson 1938). The main structural feature is the Greenhow Anticline which is the northernmost of a series of sub-parallel folds (Hudson and Mitchell 1937) including the Skyreholme anticline (Anderson 1928). The Greenhow Hill Anticline trends in a north-easterly direction (Dunham and Stubblefield 1944) with a steeply dipping northern limb. The North Craven fault truncating the southern limb. Its amplitude has a maximum of some 300 metres with subsidiary basins and domes developed along the axis. The North Craven Fault forms the southern boundary. It consists essentially of a series of conjugate fractures with some lateral tear fault movement (Rager 1931). The northern boundary excluding Midderdale is the Bycliffe Vein fault system with a predominant north-westerly trend. This is the largest fault in the area with a throw of 80 metres to the south at Providence Mine, Ashfoldside Beck. It continues westwards to the Grassington Moor area, a distance of eleven kilometres.

(36)
The veins themselves occur in two main directions, an east-west sigmoid series and an east-north-east series with north-north-west and north-south cross veins (Dunham 1952). They occur in 500 metres of massive Carboniferous Limestone overlain unconformably by the Grassington Grit which progressively oversteps southwards down on to the Limestone succession (Garwood and Goodyear 1924). The mineralization occurs over a large stratigraphical range of 400 metres of the C_2S_1, S_2 and D_1 beds of the Carboniferous Limestone (fig. 3.12). The most heavily mineralized horizon is the Hargate End Limestone which always has a capping of shale (Dunham and Stubblefield 1944) illustrating the controlling influence of these shale horizons, a very common feature of the Yorkshire Orefield. Host mineralization is confined to the uppermost 80 metres of limestone, in direct relationship to the pre-Limestone Grit unconformity. However the Limestone Grit is mineralized at the Providence Mines, Ashfoldside Beck, probably due to the large throw of the Bycliffe Vein system. The fissure veins normally have a vertical extent of 30 to 60 metres. Veins have been worked at Greenhow at depths of 200 metres below surface due to the folding of the host formations.

3.5.2. Mineralization

The mineralization consists of a galena-calcite-baryte-fluorite association with subsidiary sphalerite in four main assemblages:

I Fluorite + Galena + Baryte e.g. Waterhole Veins
II Fluorite + Galena + Baryte e.g. Galloway Vein
III Baryte + Galena e.g. Providence Mines
IV Calcite + Galena e.g. Appletreewick Mines

There is a crude zoning sequence with fluorite centres at Burhill and Greenhow Hill. Galena is the dominant sulphide. It contains some silver in solid solution. Gold has been reported from the Jamie vein. Sphalerite is less common, being found mainly around the Providence Mines and in Nidderdale at the Lolly Mine.
The chief gangue mineral is calcite occurring as massive columnar varieties with typical nail head spar as a later phase. Baryte is predominantly a massive fine-grained, cream to red coloured "caulk" but also develops "cockscomb" tabular crystal varieties. Strontianite and ankerite have been reported from the Providence Mine system. Fluorite occurs typically as a colourless massive variety.

A greenish variety is found on Greenhow Rake, the green colour being due to the abundance of pyrite and chalcopyrite inclusions. Pale yellow amber varieties are found as late vug filling especially in the Lolly Mine and Providence Mines. Purple varieties are found in the Pendleton Pipe and Escoc Hill areas. When fluorite replaces the host limestone a typical deep purple variety is seen, especially in the Burhill area. Witherite is found at the Lolly Mine, Ramsgill. Dolomitization of the wall rocks of some veins is common, for example the Foxholes Vein. Secondary oxidation affects are represented by the development of hydrozincite, cerussite, goethite and other iron minerals.

As stated earlier, due to the difficulties of access to the majority of the veins, most samples of necessity had to come from old dumps. To establish a true paragenetic sequence from dump material is a difficult task. However, as a broad statement, it is reasonable to say that massive columnar calcite was deposited early in the mineralization followed by massive fluorite plus baryte often with late vug deposits of amber and purple fluorite. The paragenetic sequences of some mines in the Greenhow area are summarized in fig. 3.13.

3.5.3. Homogenization Results.

Homogenization studies were carried out on some 79 samples, 1000 primary and 402 secondary inclusions were examined (see Appendix A, Tables 1 and 2). A positive pressure correction of 15°C was added to the results (section 3.3.).

(38)
Homogenization studies on massive colourless fluorites from both Greenhow Hill and Burnhill indicate deposition in the temperature range 107°C to 164°C (figs. 3.14. to 3.16.) with mean temperatures of between 118°C and 158°C. At the Lolly lime results from both the amber and purple varieties occur in the more restricted range of 122°C to 151°C. The purple fluorite of the Escooe Hill mineralization occurs in the range 120°C to 146°C.

The homogenization results show the Greenhow Hill mineralization to have occurred over a broad temperature range of 107°C to 164°C. Reference to fig. 3.17. indicates that most of the veins studied were deposited over a narrower 30°C to 40°C range. The Greenhow Hill mineralization is thus seen to be of a lower temperature hydrothermal aspect.

3.6. HOMOGENIZATION STUDIES IN THE GRASSINGTON MOOR AREA

3.6.1. Introduction

This area embraces the other major fluorite occurrences in Upper Wharfedale and includes the mines of Rosedale and Kettlewell as well as those of Yarnbury and Grassington Moor (fig. 3.18 a and b). The mineralization occurs predominantly as narrow fissure veins in a gently easterly dipping platform of massive Carboniferous Limestone capped by shales and sandstones of the Millstone Grit series. The area occupies the south-western edge of the Askrigg block.

3.6.2. Mineralization

The Grassington Moor area has had an extensive mining history well documented in the writings of Raistrick (1927, 1938 a and b, 1973) and Dickenson (1972). The veins are normally mineralized faults and joints trending north-west and east-west, confined to two narrow belts (fig. 3.18a). These are the 1000 metre wide Grassington High Moor Group and the 400 metre wide Yarnbury Low Moor Group containing seven to eight veins.
Some of the veins occur in strong faults downthrowing up to 45 metres to the south (Dunham 1952), for example the Palfrey and Byron veins. The mineralization was usually confined to the Grassington or "Bearing Grit" but did however extend down to 50 metres from the top of the Middle Limestone. The Thirty Five Fathom Shale acted as an effective upper limit to the mineralization.

The stratigraphic succession at Grassington is as follows:

<table>
<thead>
<tr>
<th>HORIZON</th>
<th>Thickness in metres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Scar Grit</td>
<td>40</td>
</tr>
<tr>
<td>35 Fathom Shale</td>
<td>70</td>
</tr>
<tr>
<td>Top Grit</td>
<td>15 - 17</td>
</tr>
<tr>
<td>Shale</td>
<td>6 - 10</td>
</tr>
<tr>
<td>Bearing or Grassington</td>
<td>23</td>
</tr>
<tr>
<td>Grit</td>
<td></td>
</tr>
<tr>
<td>Shale</td>
<td>10</td>
</tr>
<tr>
<td>Grit</td>
<td>8</td>
</tr>
<tr>
<td>Shale</td>
<td>10</td>
</tr>
<tr>
<td>Middle Limestone</td>
<td>Base not seen</td>
</tr>
</tbody>
</table>

The Rosedale mines are found two kilometres to the north of Grassington as a series of east-west and north-west veins in a narrow 400 metre wide belt (Raistrick 1966). The mining was carried out in the Bearing Grits and Middle Limestone, up to 70 metres from the top of this horizon. Around Kettlewell the veins occur as narrow north-west and west-north-west fissures in massive Great Scar Limestone (fig. 3. 18 a.). Dolomitization is common with replacement flats well developed at Buckden Gavels Mine.

The sulphide mineralization consists of galena and sphalerite in a dominant calcite-baryte gangue with subsidiary fluorite, either colourless or amber (Table Xili Dunham 1952). Extensive secondary oxidation has taken place with the development of cerussite,
anglesite, smithsonite, homimorphite, aurichalcite and pyromorphite. Minimum, aragonite, ankerite, dolomite, and witherite are all present in small quantities. Prehnite is present as a primary mineral at High Mark, Measham (Raistrick 1938a). Bravoite is present around Kettlewell as solid inclusions in the fluorite.

A paragenetic sequence was again difficult to determine for the same reasons as at Greenhow. The sequence at Grassington is similar to that at Greenhow, the main differences are a larger presence of amber fluorite and an extensive secondary oxidation of all the primary minerals. A generalized paragenetic sequence is illustrated diagrammatically in fig. 3.19.

3.6.3. Homogenization Results.

The measurement of homogenization temperatures on 738 primary and 323 secondary inclusions was performed on 57 samples. The results are summarized in Appendix A, Tables 3 to 5, and shown diagrammatically in figs. 3.20 to 3.22. The homogenization results indicate deposition of colourless fluorite in the temperature range of 110°C to 159°C, the mean temperature range from 117°C to 150°C. The amber fluorite of the later vuggy phase was deposited in the temperature range of 105°C to 153°C, the mean temperatures occur in a narrower 113°C to 133°C range. The homogenization results on some 92 primary inclusions from the Middle Vein (fig. 3.20.) indicate deposition in the temperature range of 99°C to 114°C, which agrees with the 95°C to 114°C of Harker, 1971 (unpublished results – uncorrected for pressure).

In both the Mossdale and Kettlewell areas the colourless fluorite predominates as the main phase with minor vuggy amber fluorite. Fluorite deposition occurred in a much narrower temperature range than at Grassington; Mossdale has a temperature range from 92°C to 120°C, Kettlewell from 103°C to 142°C. The Grassington - Yarnbury area was extensively mined for lead whereas the other two areas were only sporadically worked, possibly reflecting the broader temperature range of deposition, shown in fig. 3.23.
3.7. HOMOGENIZATION STUDIES IN THE ENSLEYDALE AND DENTDALE AREA

3.7.1. Introduction

This area comprises the valleys of the Rivers Ure and Dent, and represents the next major occurrences of fluorite northwards from Wharfedale. The fluorite is restricted to certain centres, the Dentdale areas being located along the bounding Dent Fault Line. The deposits themselves are numerous but too small to justify any large scale mining activity. Unlike the Wharfedale areas, the host formation is not massive Great Scar Limestone, but the Middle and Upper Limestone Groups of the Yoredale Series (Philipps 1836). The more important areas of the fluorite mineralization include the Wet Grooves, Seata and Meld Head mines and are shown in fig. 3.24.

3.7.2. Mineralization

The mineralization is usually confined to the Upper Limestone Group with extensions from the base of the Middle Limestone to the top of the Ten Fathom Grit. The fissure veins mainly follow west-north-westerly and north-north-westerly directions. The paragenetic sequence is similar to that of the Wharfedale occurrences, (sections 3.5.2 and 3.6.2). A coarse amber variety of fluorite is especially well developed in the Wet Grooves - Seata mine area, with a late vugh development of purple-edged cubes of colourless fluorite. Primary tabular baryte crystals are well developed, one sample contained fluid inclusions (section 3.7.3). The late calcite deposited in vughs typically develops excellent crystals of the scalenohedral and rhombohedral sorts. Dolomitization of the mineral veins is very common, being especially well developed at Hartley Birkett and the Meld Heads Mine, Bensley. The fluorite gangue tends to be restricted to strata below 1,000 ft O.D. (Harpy 1941). When followed northwards, into higher strata it is replaced by a calcite - baryte - hemimorphite - barytocalcite gangue, well illustrated by the Keld Heads Vein.
3.7.3 Homogenization Results

A total of some 541 primary and 199 secondary inclusions in 35 samples were homogenized on the Leitz Heating stage. The results are summarized in Tables 6, 7; Appendix A, and shown diagrammatically in fig. 3. 22. and 3. 25.

The Wet Grooves area consists of an extensively faulted plexus of veins and strings in the Preston Grit. This continues southwards as a vein tending 60° to 85° west seen at Haw Bank, Seata Mine and a small east-west vein at West Burton (fig. 3. 24.).

The colourless fluorite found on the dumps was deposited at temperatures between 100°C to 154°C, the amber fluorite between 109°C and 146°C. Baryte from the dumps at Haw Bank yielded homogenization temperatures of between 125°C and 134°C.

Studies on colourless fluorite from the Keld Heads and Worton mines indicates lower temperatures of between 100°C and 124°C. This could however be due to insufficient data as fluorite with definitely primary inclusions was not found despite a rigorous search. The Dentdale occurrences of colourless fluorite were however consistent with the other Hensleydale results indicating deposition between 126°C and 153°C.

The mineralization of Hensleydale and Dentdale is therefore seen to have been deposited over the same temperature range as that of Wharfedale and Nidderdale. They are both seen to be low temperature hydrothermal mineral deposits.

3.8. Homogenization Studies in the Skiddale and Arkengarthdale Areas

3.8.1. Introduction

Mining has been carried out in this area since ancient times often using "hushing" to expose the mineral veins. The main period of activity was during the seventeenth to nineteenth centuries.
Load mining is no longer practised, some small scale working of old
dumps for baryte and fluorite, however, still continues. The main
centres of activity were the south Swaledale area around Grinton
separated by the Stockdale Fault from the north Swaledale and
Arkengarthdale areas, (fig. 3. 27.).

The Old Gang Vein complex is located on either side of Gunnerside
Gill and comprises two main veins. They are the Fr iar fold Vein
trending east-north-east and Old Rake trending east-west, which
diverge eastwards to Hard Level Gill. Mineralization is present
over some 250 metres of strata from the Undersett Limestone to the
Ton Fathom Grit but is heavily concentrated in the 20 - 25 metres of
the Main Limestone (Dakyns et al. 1891). The stratigraphic range
of the Swaledale mineralization is shown in fig. 3, 28.

The Fr iar fold Vein continues east to the Surrender Mines of
the Arkengarthdale Complex five kilometres to the north-west of Reeth.
The main veins of the area are the Blockside Vein, an east-north-easterly
trending fault with an 80 metre southerly downthrow and the variously
named Fell End - Dudgeons - Justice - Punchard Gill Vein, a west-north-
westernly trending fault downthrowing to the north.

The south Swaledale mineralization south of the Stockdale
Fault consists of predominantly west-north-west trending veins around
the Whiteside - Apedale - Harker mines area (fig. 3. 24.).
This represents the upward continuation into the oxidation zone of
the Wensleydale mineralization (Earp 1941). The dominant gangue is
a baryte - calcite - hemimorphite - witerite - aragonite assemblage,
fluorite being absent. The baryte is secondary after witerite which
reacted with sulphate ion produced from the oxidation of the sphalerite,
galena and marcasite. This material was found to be totally unsuitable
for fluid inclusion study (section 2. 1. 1.).
3.8.2. Mineralization

The bulk of the mineralization of the Old Gang - Arkengarthdale areas occurs in the oxidation zone. In consequence the gangue consists of a predominantly barite - calcite - aragonite - hemimorphite - barytocalcite assemblage with subordinate fluorite. Witherite is the main barium gangue mineral below the oxidation zone, barite above with its typical bushy growth and gabled crystal development. Galena is the main ore mineral and there is some evidence of increasing sphalerite content with depth. Fluorite occurs generally as amber coloured varieties in accessory amounts. As with the case of sphalerite it appears to increase with depth in the Old Gang area, illustrated by the following figures, quoted in Dunham and Dines (1945).

<table>
<thead>
<tr>
<th>Table 3.0. ANALYSES OF DOPES FROM THE OLD GANG MINE</th>
<th>BaSO₄</th>
<th>BaCO₃</th>
<th>CaCO₃</th>
<th>CaF₂</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old Rake East Shaft</td>
<td>45</td>
<td>1</td>
<td>17</td>
<td>8</td>
<td>.5</td>
<td>4</td>
</tr>
<tr>
<td>Old Rake West</td>
<td>51</td>
<td>1</td>
<td>17</td>
<td>4</td>
<td>.6</td>
<td>4</td>
</tr>
<tr>
<td>Friarfold Smithy</td>
<td>63</td>
<td>1</td>
<td>10</td>
<td>2</td>
<td>.75</td>
<td>3.5</td>
</tr>
<tr>
<td>Friarfold West</td>
<td>72</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>.75</td>
<td>3.5</td>
</tr>
<tr>
<td>New Whim Shaft</td>
<td>72</td>
<td>1</td>
<td>14</td>
<td>2</td>
<td>.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Forefield Shaft</td>
<td>44</td>
<td>4</td>
<td>29</td>
<td>8</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Surrender</td>
<td>15</td>
<td>32</td>
<td>-</td>
<td>19</td>
<td>1.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Fluorite is also very common in the Hungry Hushes area of Arkengarthdale near the crossing of the Blackwitho - Fell End and Friarfold - Blackside vein system.

3.8.3. Homogenization Results

A total of 382 primary and 494 secondary inclusions in 56 samples were homogenized on the Leitz heating stage. The results are summarized in Tables 6 and 7, Appendix A and shown diagramatically in figs. 3.29 and 3.30.
The veins in this area often contained a dark brown viscous hydrocarbon phase. It was usually found along cleavage fractures but in a few rare instances it was trapped as a definite primary inclusion in the fluorite. In one sample from the Martin Vein a couple of such inclusions were found to be suitable for study on the heating stage. They gave homogenization temperatures of 99°C consistent with those for fluid inclusions from this area.

The homogenization temperatures thus obtained indicate mineralization in the temperature range of 96°C to 153°C for amber and 96°C to 144°C for colourless fluorite. The mean temperatures are grouped in the range of 107°C and 130°C. The results from this area are thus consistent with other areas in the Askrigg block indicating low temperatures of formation. The next step is to consider them in relation to homogenization results from fluorites occurring in the Bowland Trough.

3.9. HOMOGENIZATION STUDIES ON FLUORITES OCCURRING IN THE BOWLAND TROUGH

3.9.1. Introduction and Mineralization

The mineralization occurs within the Ribblesdale Fold Belt which is a series of west-south-west trending anticlines and synclines (Darp et al. 1961). The Sykes Anticline forms the northern boundary, the Pendle Monocline the southern one (fig. 3.32). The mineralization is concentrated in an east-south-east belt parallel to the Barnoldswick Fault and near to the Clitheroe Fault, a post-riassic structure. It consists essentially of galena and pyrite in a matrix of creamy massive barite and white massive calcite, fluorite is normally present as an accessory mineral. Fluorite was found at two localities; Skeleron Mine, Rimington and Raygill Quarry, Lothersdale. At Rimington it was found in south-east trending veins in the Chatburn Limestone and was colourless but in the east-west Main Vein at Raygill it was purple in colour.
In both cases the fluorite was restricted to the cores of tightly folding anticlines in the Chetburn Limestone.

3.9.2. Homogenization Results

The homogenization temperatures of some 276 primary and 82 secondary fluid inclusions in six samples were measured. These indicated temperatures of deposition for the primary inclusions in the range 120°C to 179°C and 106°C to 116°C for the secondary inclusions, see Table 3.4, Appendix A and figs. 3.29 and 3.30. The mean temperatures are between 148°C and 153.5°C for the Rimington and Raygill areas respectively, thus indicating higher temperatures of deposition than the mineralization found on the Askrigg Block itself.

3.10. SUMMARY OF THE HOMOGENIZATION RESULTS FROM THE ASKRIGG BLOCK

During this study a total of some 233 polished sections were used on the heating stage yielding homogenization results from 3,000 primary and 1,500 secondary fluid inclusions. As stated earlier, (see section 3.3.) all the homogenization results were positively corrected for pressure by 8°C to 15°C.

The homogenization results indicate the minimum temperatures of deposition for fluorite to be in the range of 92°C to 159°C on the Askrigg block with temperatures of between 120°C and 179°C in the Bowland Trough. The mean homogenization temperatures fall in the temperature range of 104°C to 158°C. Most individual deposits had a temperature range of between 30°C to 50°C, see figs. 3.12, 3.17, 3.23, 3.26, and 3.32. Of the three main fluorite varieties found in the Askrigg area comparison of their mean homogenization temperatures in fig. 3.34 indicates the amber and purple varieties to have a more restricted but similar temperature range. The colourless variety is the main fluorite phase in the orefield and is found over the broadest temperature range.

The homogenization results thus indicate the Askrigg mineralization to be of a telethermal, low temperature aspect.
The range of temperature deposition agrees with homogenization results from other Mississippi Valley type deposits (Roedder 1967a) The available homogenization results from other British telethermal mineral deposits are compared in the following table:

**TABLE 3.D. COMPARISON OF BRITISH HOMOGENIZATION RESULTS**

<table>
<thead>
<tr>
<th>AREA/MINERAL</th>
<th>HOMOGENIZATION TEMP °C</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alston Block Fluorite</td>
<td>100 to 250°C</td>
<td>Sawkins 1966a</td>
</tr>
<tr>
<td>Barite</td>
<td>50 to 150°C</td>
<td>Sawkins 1966a</td>
</tr>
<tr>
<td>Fluorite</td>
<td>125 to 195°C</td>
<td>Smith 1973a</td>
</tr>
<tr>
<td>Askrigg Block Fluorite</td>
<td>92 to 159°C</td>
<td>Author</td>
</tr>
<tr>
<td>Bowland Trough Fluorite</td>
<td>120 to 179°C</td>
<td>Author</td>
</tr>
<tr>
<td>Derbyshire Block Fluorite</td>
<td>70 to 160°C</td>
<td>Author</td>
</tr>
<tr>
<td>Fluorite</td>
<td>60 to 140°C</td>
<td>Roedder 1967a</td>
</tr>
<tr>
<td>North Wales Fluorite</td>
<td>95 to 115°C</td>
<td>Smith 1973a</td>
</tr>
</tbody>
</table>

The mineral deposits of Cornwall associated with the Hercynian granitic plutons have homogenization temperatures in the range of 100°C to 450°C (Sawkins 1966b). The mineral deposits of the Carboniferous rocks in comparison are low temperature. However the Alston area still has a somewhat higher temperature range when compared to the other areas. This was confirmed by the author on Sawkin's material and from other localities in the area. Smith (1973) has also firmly established this higher temperature relationship. He also comments on the enrichment of rare earth elements, high hydrothermal silica content in the fluorites and postulates possible magmatic influences on the predominantly connate water origin proposed by Solomon et al. (1971). The similarities and differences between the various ore-fields in the light of fluid inclusion studies will be discussed in Chapter 6.
FIG. 3.1.
CORRELATION OF THE YOREDALE BEDS

[AFTER RAMSBOTTOM 1974]

N.  Alston Area  Kirby Stephen  Askrigg  Fountains Fell  Greenhow

S.  MAIN  UNDERSETT

3 or 5 YARD  MIDDLE  SIMONSTONE  GAYLE HAWES  COLDSTONES

Southerly thinning due to uplift of the southern edge of the Askrigg Block.
THE GEOLOGY, MINERAL VEINS AND FAULTS OF THE ASKIRIO BLOCK.
FIG. 3.5

DIAGRAM OF THE FORM OF THE ASKRIGG MINERAL DEPOSITS

A. CROSS-SECTION DEVONSHIRE VEIN

[After Dunham 1959]

B. A TYPICAL CROSS VEIN

C. THE DEVELOPMENT OF FLATS

D. PIPE DEPOSITS

[After Varvill 1920]

E. GULPHS or GULFS

F. SECTION HARGATE END VEIN

[From Dickenson 1970]
FIG. 3.6.

SUMMARY OF THE PRINCIPAL MINERALS OF THE ASKRIGG OREFIELD.

PR IMARY. 1. Sulphides.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>coarse, massive crystals; low Ag content, also as banded ore. Au in Jamie Vein.</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
<td>rare, brown massive variety.</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>often found as solid inclusions in fluorite.</td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu₅FeS₄</td>
<td></td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td></td>
</tr>
<tr>
<td>Bravoite</td>
<td>(Fe,Ni)S₂</td>
<td></td>
</tr>
</tbody>
</table>

2. Gangue.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>rare, usually small idiomorphic crystals.</td>
</tr>
<tr>
<td>Fluorite</td>
<td>CaF₂</td>
<td>typically amber, colourless.</td>
</tr>
<tr>
<td>Barytes</td>
<td>BaSO₄</td>
<td>tabular, platy crystals.</td>
</tr>
<tr>
<td>Witherite</td>
<td>BaCO₃</td>
<td>massive amber, colourless.</td>
</tr>
<tr>
<td>Baryto calcite</td>
<td>BaCO₃</td>
<td>mainly found in the Old Gang area.</td>
</tr>
<tr>
<td>Aragonite</td>
<td>CaCO₃</td>
<td>Calcite the dominant carbonate, the remainder are comparatively rare.</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaCO₃(Mg,Fe)CO₃</td>
<td></td>
</tr>
<tr>
<td>Ankerite</td>
<td>CaCO₃(Mg,Fe)CO₃</td>
<td></td>
</tr>
<tr>
<td>Chalbybite</td>
<td>FeCO₃</td>
<td></td>
</tr>
</tbody>
</table>

SECONDARY.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Secondary Oxidation From:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerussite</td>
<td>PbCO₃</td>
<td>Galena PbS</td>
</tr>
<tr>
<td>Anglesite</td>
<td>PbSO₄</td>
<td>Sphalerite ZnS</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>ZnCO₃</td>
<td></td>
</tr>
<tr>
<td>Hemimorphite</td>
<td>ZnSi₄O₂(OH)₂H₂O</td>
<td></td>
</tr>
<tr>
<td>Hydrozincite</td>
<td>2ZnCO₃.3Zn(OH)₂</td>
<td></td>
</tr>
<tr>
<td>Malachite</td>
<td>Cu₂CO₃(OH)₂</td>
<td>Bornite Cu₅FeS₂, Chalcopyrite Cu₅FeS₂</td>
</tr>
<tr>
<td>Azurite</td>
<td>Cu₃(CO₃)₂(OH)₂</td>
<td></td>
</tr>
<tr>
<td>Goethite</td>
<td>2Fe₂O₃H₂O</td>
<td>Pyrite Fe₂, Witherite BaCO₃</td>
</tr>
<tr>
<td>Barytes</td>
<td>BaSO₄</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 3.7.

CALIBRATION CURVE FOR THE
LEITZ 1350 HEATING STAGE.

TEMP. OBS. °C

MELTING POINT °C

- Ammonium nitrate
- n-nitro p-aniline
- Benzoic Acid
- 8-hydroxyquinoline
- Diacyno-diamide
- Observed
- Actual
3.8.a, shows the fluid inclusion at ambient temperature. On heating the inclusion shows the first noticeable change at 3.8.c. with a slight shrinkage of the vapour bubble. This proceeds slowly up to 3.8.h. when at 123°C the vapour bubble rapidly shrinks until at 3.8.k., 127°C, homogenization occurs.

After the fluid inclusion has been allowed to cool, the vapour bubble diameter is rechecked to ensure leakage has not occurred. This homogenization run thus indicates the fluid inclusion in question to have a minimum temperature of deposition of 150°C (corrected).
FIG. 3.8.

PLATE ILLUSTRATING THE HOMOGENIZATION BEHAVIOUR OF A PRIMARY FLUID INCLUSION

a. 19°C  b. 49°C  c. 69°C

d. 89°C  e. 104°C  f. 114°C

g. 121°C  h. 123°C  i. 124°C

j. 126°C  k. 127°C  l. 19°C

--- BAR = 100 μ
FIG. 3.9.

HOMOGENIZATION CURVES FOR TYPICAL PRIMARY INCLUSIONS IN FLUORITE FROM THE ASKRIGG AREA.
<table>
<thead>
<tr>
<th>Sample No. &amp; Loc.</th>
<th>No. P. Ings Measured</th>
<th>Mean °C</th>
<th>Calculated F Ratio, 5%</th>
<th>Actual F Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clouds 119</td>
<td>43</td>
<td>118.721</td>
<td>3.96</td>
<td>0.0066</td>
</tr>
<tr>
<td>120</td>
<td>46</td>
<td>118.304</td>
<td>1.87 df</td>
<td></td>
</tr>
<tr>
<td>State 86</td>
<td>40</td>
<td>119.825</td>
<td>3.95</td>
<td>0.5578</td>
</tr>
<tr>
<td>Mine 23</td>
<td>25</td>
<td>123.560</td>
<td>2.09 df</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>27</td>
<td>121.593</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kettle 185/1</td>
<td>21</td>
<td>96.952</td>
<td>4.08</td>
<td>1.0593</td>
</tr>
<tr>
<td>Well 185/2</td>
<td>22</td>
<td>102.000</td>
<td>1.44 df</td>
<td></td>
</tr>
<tr>
<td>Green-Row 162</td>
<td>60</td>
<td>116.917</td>
<td>3.92</td>
<td>0.1178</td>
</tr>
<tr>
<td>164</td>
<td>88</td>
<td>117.182</td>
<td>1.14 df</td>
<td></td>
</tr>
<tr>
<td>Claylay 112</td>
<td>7</td>
<td>130.857</td>
<td>5.12</td>
<td>3.5115</td>
</tr>
<tr>
<td>Vein 66</td>
<td>10</td>
<td>127.600</td>
<td>4.49</td>
<td>4.1068</td>
</tr>
<tr>
<td>Vein 66</td>
<td>8</td>
<td>124.500</td>
<td>1.16 df</td>
<td></td>
</tr>
<tr>
<td>Rodhill 158</td>
<td>8</td>
<td>111.500</td>
<td>4.16</td>
<td>2.0471</td>
</tr>
<tr>
<td>Vein 160</td>
<td>5</td>
<td>118.000</td>
<td>3.31 df</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>4</td>
<td>110.500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>18</td>
<td>114.889</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Douglas 72</td>
<td>8</td>
<td>111.875</td>
<td>4.38</td>
<td>0.0593</td>
</tr>
<tr>
<td>Hill 76</td>
<td>13</td>
<td>112.462</td>
<td>1.19 df</td>
<td></td>
</tr>
<tr>
<td>Middle 180/1</td>
<td>23</td>
<td>111.522</td>
<td>3.15</td>
<td>2.3725</td>
</tr>
<tr>
<td>Vein 180/2</td>
<td>9</td>
<td>110.778</td>
<td>2.62 df</td>
<td></td>
</tr>
<tr>
<td>136</td>
<td>33</td>
<td>112.546</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Old Hosp 4/2</td>
<td>20</td>
<td>109.550</td>
<td>4.20</td>
<td>2.5730</td>
</tr>
<tr>
<td>Vein 4/1</td>
<td>10</td>
<td>107.400</td>
<td>1.28 df</td>
<td></td>
</tr>
<tr>
<td>Burton 259</td>
<td>9</td>
<td>112.557</td>
<td>4.03</td>
<td>1.6833</td>
</tr>
<tr>
<td>Level 260</td>
<td>45</td>
<td>109.511</td>
<td>1.52 df</td>
<td></td>
</tr>
<tr>
<td>Surrender 302</td>
<td>30</td>
<td>112.557</td>
<td>4.00</td>
<td>1.1987</td>
</tr>
<tr>
<td>282</td>
<td>34</td>
<td>101.547</td>
<td>1.62 df</td>
<td></td>
</tr>
<tr>
<td>Hungry 478</td>
<td>6</td>
<td>106.833</td>
<td>4.45</td>
<td>2.3571</td>
</tr>
<tr>
<td>Huskies 484</td>
<td>13</td>
<td>100.462</td>
<td>1.17 df</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 3.11

MAP SHOWING THE PRINCIPAL VEINS, SAMPLING LOCALITIES AND GEOLOGICAL OUTLINE OF THE GREENHOW HILL AREA

LEGEND:

A. Greenhow

B. Appitree with
(south of Craven F.)

M.G. MILLSTONE Grit
Grit

GRASSINGTON
Grit

GRASSINGTON
Grit

TOL TOMPIT GATE
LST

CL COLDSTONES
LST

HEL HAREHAG END
LST

GHL GREENHOW HILL
LST

TL TIMPSON
LST.

M.G. MILLSTONE Grit

Grit

LOWER CARBONIFEROUS
Stake

Porcellanous
Limestone

VEIN

FAULT

ROAD

STREAM

SCALE:

0 1 2 Mile

GEOLOGY FROM: DUNHAM & STUBBLEFIELD 1944
ANDERSON 1938
THE STRATIGRAPHIC RANGE OF THE GREENHOW MINERALIZATION.
FIG. 3.13
PARAGENETIC SEQUENCES GREENHOW HILL AREA.

A. GREENHOW RAKE
   Massive Calcite
   Massive Colourless Fluorite + Galena
   Purple Fluorite

B. GALLOWAY VEIN
   Massive Calcite
   Massive Colourless Fluorite + Galena, Barytes
   Amber Fluorite
   Cockscob Barytes

C. LOLLY MINE, RAMSGILL
   Purple Fluorite
   Brown Massive Sphalerite
   Massive Barytes
   Galena
   Witherite
   Amber Fluorite

TIME →
FIG. 3.14.
HISTOGRAMS OF THE GREENHOW HILL MINERALIZATION.

% FREQ.

GREENHOW RAKE
S Inc., P Inc.

SUN VEIN
P Inc.

HARGATE END VEIN
P Inc.

GALLOWAY VEIN
S Inc., P Inc.

FIELDING VEIN
P Inc.

FOXHOLES VEIN
P Inc.

HOMOGENIZATION TEMPERATURE °C.

0 10 20 30 40
100 120 140
FIG. 3.15.

HISTOGRAMS OF THE APPLETREEWICK MINERALIZATION.

<table>
<thead>
<tr>
<th>% FREQ</th>
<th>GILL HEADS VEIN</th>
<th>JOYCE VEIN</th>
<th>ESCOE HILL</th>
<th>OLD VEIN</th>
<th>RODHILL VEIN</th>
<th>INMAN VEIN</th>
</tr>
</thead>
</table>

HOMOGENIZATION TEMPERATURE °C
FIG. 3.18.

PROBABILITY PLOTS GREENHOW HILL.

[Graphs showing probability plots with various data points and frequency distribution.]
FIG. 3.17.

THE TEMPERATURE RANGE OF THE GREENHOW-APPLETREEWICK MINERALIZATION.

TEMP. °C

160
150
140
130
120
110
100
90
80

APPLETREEWICK

GREENHOW

Gill Heads V

Greenhow R.

Hargate End V.

Forest V.

Foxholes V.

Sun V.

Fielding V.

Blackhill V.

Honley V.

Joyce V.

Old V.

Rodhill V.

Inman V.

Lolly (purple)

Lolly (amber)

Escoe
MAP OF THE VEINS AND SAMPLE LOCALITIES IN THE KETTLEWELL AREA

LEGEND:

- VEIN
- FAULT
- RIVER
- VILLAGE
- AREA COVERED BY FIG. 3.18

SCALE:

0 1 Mile

Figures and locations mentioned in the legend include:

- Middlemoor Pasture
- Middlesmoor
- Starbotton
- Starbotton Cam
- Coldstream Mine
- Hawkswick
- River Wharfe
- Providence Mine
- Hawkhawk Y
- Wharfedale Mine
- SE 470
- SE 400
**Fig. 3.19.**

**Diagrammatic Representation of the Paragenetic Sequence in the Grassington Area**

<table>
<thead>
<tr>
<th></th>
<th>Early Replacement</th>
<th>Main Mineralization</th>
<th>Vug Development</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Massive columnar calcite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Massive fluorite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Barytes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Amber fluorite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Nail head calcite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Galena</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Sphalerite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*TIME* →
FIG. 3.22

PROBABILITY PLOTS GRASSINGTON, WENSLEY.
FIG. 3. 23.
THE TEMPERATURE RANGE OF THE GRASSINGTON
MOSSDALE - KETTLEWELL MINERALIZATION.

TEMP °C
150
140
130
120
110
100
90

Grimes Groove V.
Cavendish V.
Bycliffe V.
Yarnbury
Stool V.
Slanter V.
Old Moss V. Middle V.
Ripley V.
Gnerness Groove V.
Palfrey V.
Grassington
Mossdale V. Moorhead V. Providence V.
Mossdale V.
Oddmere V.
K/10
K/14 - K/16
K/24 K/26
K/17
K/28

GRASSINGTON MOSSDALE KETTLEWELL
FIG. 3. 25.
HISTOGRAMS OF THE WENSLEYDALE MINERALIZATION.

% FREQ

WET GROOVES
COLOURLESS FLUORITE

SEATA MINE
COLOURLESS FLUORITE

WEST BURTON

P. Incs.

P. Incs.

P. Incs.

WET GROOVES
YELLOW FLUORITE

HAW BANK

KELD HEADS

P. Incs.

PS. Incs.

PS. Incs.

HOMOGENIZATION TEMPERATURE °C
FIG. 3.26.

THE TEMPERATURE RANGE OF THE DENTDALE AND WENSLEYDALE MINERALIZATION.

TEMP. °C

150

Seata (col)

140

Wet Grooves (col)

Haw Bank fluorite

130

Haw Bank barytes

120

W. Burton

Keld Heads V.

110

100

90

WENSLEYDALE

DENTDALE
FIG. 3. 28.

THE STRATIGRAPHY AND MINERALIZATION IN THE
SWALEDALE AND WENSLEYDALE AREAS.

PERMIAN Basal Conglomerate.

PICKERSETT EDGE GRITS

TAN HILL GRIT

CROW LST TEN FATHOM GRIT

LITTLE LST. MAIN LST

UNDERSETT LST.

MIDDLE LIMESTONE GROUP

THREE YARD LST. MIDDLE LST.

FIVE YARD LST. SIMONSTONE LST.

LOWER LIMESTONE GROUP

HARDRAW SCAR LST. GAYLE LST.

GREAT SCAR LST.
FIG. 3, 29.

HISTOGRAMS OF THE SWALEDALE MINERALIZATION.

**BUNTON LEVEL**

S. Incs.  P. Incs.

**DAM RIGG LEVEL**

P. Incs.

**MARTIN VEIN**

P. Incs.

**SURRENDER MOSS**

P. Incs.

**DAM RIGG VEIN**

P. Incs.

**MOULDS TOP MINE**

P. Incs.

% FREQ

HOMOGENIZATION TEMPERATURE °C
FIG. 3.30.
HISTOGRAMS OF THE SWALEDALE, DENTDALE & BOWLAND MINERALIZATION.
FIG. 3.31

PROBABILITY PLOTS SWALEDALE, BOWLAND TROUGH.
FIG. 3.32.
THE TEMPERATURE RANGE OF THE SWALEDALE AND BOWLAND TROUGH MINERALIZATION.

TEMP.°C
170
160
150
140
130
120
110
100
90

SWALEDALE
BOWLAND TROUGH

Rimington
Raygill
Turf Moor L.
Old R.
Bunton
Surrender Blackside V.
Hungry H.
Martin V.
DamRiggV
Moulds Top M.
DamRiggL
Black Hills H.
FIG. 3.33.

THE GEOLOGY, STRUCTURE AND VEINS OF THE BOWLAND TROUGH.

LEGEND:

PERMO-TRIAS.
PENDLE GRIT & MILLSTONE Grit
BOWLAND & WORTON SHALE GROUPS.
PENDLE SANDSTONE
CHATBURN LIMESTONE

SCALE:

0 1 2 3 Miles
FIG. 3.34
COMPARISON OF MEAN HOMOGENIZATION TEMPERATURES FOR DIFFERENT FLUORITE VARIETIES FROM THE ASKRIGG AREA.

MEAN HOMOG TEMP °C
160 GREENHOW
150 GRASSINGTON
140 SEATA / WET GROOVES
130 KETTLEWELL
120 MOSSDALE
110 KELD HEADS
100

COLOURLESS FLUORITE

AMBER FLUORITE

PURPLE FLUORITE

RAYGILL

GREENHOW

GRASSINGTON

SEATA

SWALEDALE

GREENHOW

GRASSINGTON

SEATA

SWALEDALE
CHAPTER FOUR
CHAPTER FOUR

FREEZING STUDIES ON FLUID INCLUSIONS FROM THE KAERING AREA

OF N. W. YORKSHIRE

4.1. Introduction

The freezing of the fluid present in fluid inclusions under experimental conditions is one of a variety of methods used to obtain a measure of the concentration of salts trapped as the fluid inclusions formed. This data can provide a valuable insight into the origin, possible mixing, wall rock alteration effects and diagenetic changes undergone by the trapped fluid. It can also be used to determine the salinity correction for homogenization results (Adetosoye and Lemmlein 1959; Sourirajan and Kennedy 1962). Other methods are available including the measurements of refractive indices, crushing in vacuo and extraction into a gas analysis line with subsequent analysis of the leachate using flame photometric and spectrometric methods. An extensive survey of all these methods is to be found in Roedder (1972).

The contents of very large inclusions can be simple extracted using a microdrill and syringe (Davy 1822) but these large inclusions are very rare, see section 1.2. Most inclusions are very small with minute amounts of fluid, often as little as \( 10^{-10} \) g. A reliable method is thus required to analyze the contents of these small inclusions. One of the few techniques available is one measuring the depression of the freezing point of the host fluid due to the presence of dissolved salts. The basic assumption of this freezing method used extensively in fluid inclusion studies, relies on the predominance of sodium chloride amongst the dissolved salts, a result verified by numerous inclusion analyses (Roedder 1972).

Various techniques of cooling inclusions under a microscope have been tried by a number of workers. Semi-quantitative results can be obtained by simply cooling with a drop of alcohol, acetone, ether or ethyl chloride.
More accurate results have been obtained using cooling stages mounted on a microscope, the low temperatures being obtained using a variety of heat exchange mediums. Cameron, Rowe and Weiss (1953) used cooled air; Roedder (1962) an acetone - dry ice mixture; Bazarov (1966) and Smith (1973) used cooled nitrogen gas whilst Henier and Hocart (1950) and Sawkins (1966) used a thermoelectric "Peltier" effect cooling stage.

During the earlier part of this study the merits of these various methods were assessed with regard to speed, reliability, ease of operation and economy. Following the recommendations of Roedder (1962) the combination of a rapidly thermostatically controlled acetone heat exchange medium was chosen. The operation of this freezing stage will now be described.

4.2. DESCRIPTION AND OPERATION OF THE COOLING STAGES USED IN THIS STUDY

The apparatus used consisted of a brass cooling cell mounted on a Leitz binocular medical microscope with a heat exchange unit and a circulating bath - thermostat (fig. 4.1.).

4.2.1. The Cell

This consists of a fifty mm diameter heavy brass cup with inlet and outlet pipes for the circulating acetone. Observation is through two polished quartz windows located at the top and bottom of the cell (fig. 4.2.). These are sealed with Teflon gaskets, the top retaining screws are tightened down with an allen key. A neoprene 0-ring is used as an extra seal at the top. The samples are placed on a glass plate and cemented by rubber solution. These plates are then placed on to an aluminium cage in the cell, held down by a strong spring to prevent flutter of the samples in the circulating acetone.

The cell is insulated by a tightly fitting asbestos cup which slots on to the mechanical stage of the microscope.
The mechanical stage is fitted with a vernier scale to facilitate easy location of appropriate inclusions. To prevent fogging of the glass windows dry air is introduced to both windows using a small air pump. The air is dried by passing through indicating silica gel. A sub-stage illuminator with a variable output is used and the inclusions are observed using Leitz long working range objectives.

4.2.2. Auxiliary Equipment Used.

The cell was mounted on a Leitz binocular microscope with a photographic attachment. The heat exchange unit, supplied by Lauda of West Germany (catalogue No. 6010), has a capacity of up to ten kilograms of dry-ice. Low temperature operation at -78°C is obtained using a methanol and dry-ice mixture. This was found to be far more suitable and economical than a dry-ice - acetone mixture. In a normal working day amounts of up to two to three kilograms of dry-ice were sufficient for twenty to thirty freezing runs.

Acetone cooled in this way is circulated using a Lauda Ultra thermostat, Type K2. Construction is of stainless steel with a bath capacity of three litres. The Simplex bearingless circulating pump has a fully variable output of up to eight litres a minute, the heater output is continuously variable up to 700 W. The temperature of the acetone in the bath is indicated by the reference thermometer, with a range of -70°C to + 40°C, the controlling contact thermometer is graduated in divisions of 0.1°C. The acetone is circulated through silicone rubber and flexible copper tubing suitable for low temperature operation. The tubing is well lagged to avoid excessive heat loss with several layers of aluminium foil and asbestos fibre.

4.2.3. Operation of the Equipment

The sample to be analysed is immersed in a Dewar flask with a mixture of dry-ice and acetone at -78°C to overcome the gross supercooling of fluid inclusions. Most of the inclusions studied would freeze after approximately thirty minutes immersion. Some however, would not freeze and these had to be placed in a liquid nitrogen bath at -196°C. Even after this severe treatment some inclusions would not
freeze and were therefore discarded. Whilst the inclusions are in the Dewar flask the rest of the system is cooled to -50°C. A cooling rate of 2°C per minute is easily obtained using the bath thermostat.

After the sample had been immersed for half an hour it is rapidly transferred to the cell at -50°C. After transfer cold acetone is circulated at -60°C for a period of up to five minutes to ensure complete freezing. The two lengths of flexible copper tubing located on either side of the cooling stage are necessary in order to allow the cell to be moved and shaken to remove any air bubbles remaining after transfer of the sample. If any air bubbles are present they interfere with the observation of the inclusion and consequently must be removed prior to making the freezing run. After the air bubbles have been eliminated and acetone rapidly circulated at -60°C, the temperature of the cell needs to be raised to establish the melting and freezing temperatures of the fluid inclusions.

To facilitate rapid reconnaissance runs a tap was fitted to the system which isolated the heat exchange unit (fig. 4.2.). This enabled the temperature of the cooling stage to be raised quickly and it also had the extra bonus of conserving dry-ice supplies. During a slower freezing run the temperature of the acetone is gradually raised using the heater and controlling the thermometer. The temperature is raised at about one degree °C per minute until first melting is reached and then raised at a rate of 0.5°C per minute. As the melting temperature is approached the temperature is dropped slightly to test the reversibility of the reaction the importance of which is discussed in section 4.3.3.

4.2.4. Calibration of the Freezing Stage.

After the system had been lagged and thoroughly tested for acetone leakage, the next step involves calibration of the freezing stage. In general most of the freezing runs were performed in the narrow temperature range of 0°C to -35°C compared to the broader temperature range of the homogenization runs (Chapter 3).
The need is thus for a far greater degree of precision, as a few degrees of error can make a marked difference to the salinity obtained (fig. 4.4.). A system of total immersion in the heat exchange medium, in this case acetone, was chosen in order to minimize thermal gradients.

Both the reference and contact thermometers of the freezing stage are located in the stainless steel bath. Despite a fast circulation of up to eight litres per minute with the Simplex pump, a thermal lag must still be present between the cell and the bath. The magnitude of this thermal lag was established using two independent calibration methods. The first method involves calibration with organic reagents of known melting point. The organic liquids were placed in small bore capillary tubes and sealed using an oxygen flame. Whilst the tubes were being sealed one end was immersed in a dry ice-acetone mixture to avoid any spurious heating effects on the liquid. A number of these liquids were then frozen in and the observed temperatures when freezing occurred were compared with their known melting points. The chemicals used and their melting points are as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Decane</td>
<td>-29.7</td>
</tr>
<tr>
<td>O-Xylene</td>
<td>-25.16</td>
</tr>
<tr>
<td>Quinoline</td>
<td>-15.9</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td>-13.0</td>
</tr>
<tr>
<td>Methyl Benzoate</td>
<td>-12.3</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>-9.60</td>
</tr>
<tr>
<td>Bytric Acid</td>
<td>-6.5</td>
</tr>
<tr>
<td>5% Sodium Chloride</td>
<td>-2.9</td>
</tr>
<tr>
<td>10% Sodium Chloride</td>
<td>-6.5</td>
</tr>
<tr>
<td>20% Sodium Chloride</td>
<td>-16.3</td>
</tr>
</tbody>
</table>

The calibration curve produced is shown in fig. 4.3. After several measurements had been obtained the experimental error was found to be generally better than $\pm 0.5^\circ$C.
Calibration was also performed using a Copper-Constanton thermocouple (British Standard No. 1828) and similar results were obtained.

4.3. THE BEHAVIOUR OF FLUID INCLUSIONS ON FREEZING

4.3.1. Sample Selection for Freezing Studies

Far more stringent sample requirements apply to freezing studies compared with those for homogenization studies. Great care is needed to select only samples that have a good polish with a mass as small as possible to overcome any thermal lag. A completely clear view of the fluid inclusion is a prerequisite as ice crystals have a low refractive index in water. Inclusions with dark borders and irregular shapes make observation difficult and they were not used in this study. Mineral plates with cleavage cracks were frequently rendered opaque by the acetone penetrating along the cracks. Larger inclusions were often seen to have leaked as they were usually totally opaque well above the melting point of other cogenetic inclusions. Thus only a small percentage of fluid inclusions are suitable for freezing studies, only first class material will provide meaningful results.

Another problem is to provide adequate illumination to observe the inclusions themselves (Roedder 1962). The freezing stage used in this study did not have a sub-stage diaphragm but had instead a variable light source mounted beneath the cell. Adequate results were obtained but photography was only possible with somewhat mixed results. This was to a large extent due to the acetone's facility to absorb water vapour from the atmosphere along with some dust particles and rubber solution used to make up the sample mosaics. This problem was overcome by changing the acetone daily and giving the system a good flushing out after each day's freezing runs.

4.3.2. Freezing and Metastability.

The freezing stage used in this study will reach temperatures as low as -60°C with few problems. Yet most fluid inclusions exhibit very stubborn metastability; they will not freeze at temperatures well
below their actual melting point. This supercooling was first noted by Sorby (1858) and is very common in fluid inclusions in fluorite. To overcome this the sample plates were immersed for periods of up to thirty minutes in an acetone-dry-ice mixture of liquid nitrogen (section 4.2.3.). Shattering of sample plates rarely occurred in liquid nitrogen even after extended immersion. It was usually the glass mounting slide which shattered. Hydrocarbon inclusions were extremely difficult to freeze; some would not freeze after many hours in liquid nitrogen. Freezing when it occurs is usually instantaneous occurring within a small temperature range of one to two tenths of a degree. The cause of this extreme supercooling is problematical but is probably due to a lack of suitable nuclei available for spontaneous nucleation. Roedder (1962) cites this as evidence for the ore-forming fluid to be a slow moving medium, most of the solid particles in suspension thus having settled out under gravity.

The gross composition of the fluid obviously determines which phase forms on freezing. In most fluid inclusions ice is formed as a low relief, low birefringent mush of platey crystals exhibiting parallel extinction and length fast characters. A volume increase takes place on freezing with a corresponding decrease on heating. Hydrohalite (NaCl.2H₂O) can form on freezing by the reaction of the liquid and sodium chloride. It is highly birefringent and exhibits incongruent melting up to 0.1°C. This one method of distinguishing daughter minerals of sodium and potassium chloride as the potassium salt will not form a hydrate on freezing. Hydrohalite was not observed in the fluid inclusions examined from the Askrigg area although it has been observed by the author in some fluid inclusions from the Derbyshire orefield. It has been noted in a few inclusions both in the Alston and North Wales areas by Smith (1973).
The liquid can also react with either carbon dioxide liquid or gas to form a hydrate, \( \text{CO}_2 \cdot 5 \text{H}_2\text{O} \) (Roedder 1972). It has a similar refractive index to that of water and is consequently difficult to observe. Its presence however is very important and provides a means of estimating the carbon dioxide partial pressure (Takenouchi and Kennedy 1965). Vapour bubbles which are not present at room temperature can form on freezing, a similar situation applies to sodium chloride daughter minerals.

The freezing of fluid inclusions can thus provide valuable information on the composition of the fluid medium. The next step is to establish how this composition is estimated from the frozen inclusions behaviour on heating to room temperature.

4.3.3. Determination of the First Melting and Freezing Temperatures

The frozen inclusion is normally totally opaque but on heating becomes translucent. This is caused by liquid forming on the ice crystals. The first melting temperature is obtained when this liquid forms in appreciable amounts. This usually takes place quickly over a small temperature range of 0.5°C. It is important to observe this first melting temperature as it indicates the presence of multicomponent systems, very common in geological fluid systems (section 1.8.). Fluid inclusions in fluorite from the Skrigg area had first melting temperatures as low as -40°C but were predominantly in the range of -24°C to 30°C (see Tables B.1.2. and 3., Appendix B). Detailed analytical work (Chapter 5) has substantiated these observations as potassium is present in fairly large amounts in the inclusion fluid in addition to sodium.

The freezing temperature itself is the point at which the last ice crystal melts under equilibrium conditions between growth and melting of the last crystal (Roedder 1962). At equilibrium a slight drop in the temperature will cause fresh growth of ice.
This property can also be used to see if melting has occurred when the
ice crystal has moved into a dark corner of an inclusion. The typical
behaviour on freezing of a fluid inclusion in fluorite is shown in
fig. 4.5.

4.4. FREEZING STUDIES ON GRASSINGTOON FLUORITES

4.4.1. Results from the Grassington - Greenhow area

The geology, mineralization and structural setting of these
deposits has been described previously (sections 3.5 and 3.6.) and will
not be repeated here. Due to various factors outlined in section 4.3.1.
only twenty four samples were found to be suitable for study on the
cooling stage. A total of 260 Primary inclusions were studied, the
results are summarized in Appendix B, tables B.1. and B.2.

The 133 primary inclusions from the Greenhow Hill area indicated
deposition from solutions with a wide compositional range of between
14 and 23 per cent sodium chloride by weight. The mean values are
grouped in the range from 15.30 to 22.45 per cent sodium chloride
equivalent by weight. At the Lolly Mine the early fluorite phase
was deposited from solutions with salinities of between 17 to 20 per
cent equivalent by weight of sodium chloride compared to the 21.5 to
23 per cent of the later amber fluorite phase, shown diagrammatically in
fig. 4.6. The 127 Primary inclusions from the Grassington Moor area
however show a more restricted compositional range of between 21 and 25
per cent equivalent by weight of sodium chloride. This is illustrated
diagrammatically for the Grassington Moor and Greenhow areas in fig. 4.7.

4.4.2. Results from the Kennedydale, Dentdale, Swaledale and
Bowland Trough Areas

The geology, mineralization and structural settings of these areas
have been described previously in sections 3.7., 3.8., and 3.9. Again
only certain of the samples used in the homogenization studies were found
to be suitable for the freezing stage. The results obtained are
listed in Tables B.2. and B.3., Appendix B.
In the Wensleydale area sixty primary inclusions were studied in
the Seata Mine and Wet Grooves areas. They had freezing temperatures
in the narrow range of from -22.2°C to -25.0°C, indicating a mean
salinity of 23.80 per cent equivalent by weight of sodium chloride.
Very similar results were obtained from Cloud End Fell, Dentdale, con­
firming a similar relationship noted previously for the homogenization
results (section 3.7.3.). The forty four inclusions studied showed a
range of freezing temperatures from -19.3°C to -24.5°C, a mean salinity
of 22.95 per cent equivalent by weight of sodium chloride.

The Swaledale and Arkengarthdale areas however provided more
suitable material. A total of 274 primary inclusions were studied from
thirteen localities. Freezing temperatures were obtained in the range
of -10.5°C to -24.0°C with mean salinities from 21.70 to 23.3 per
cent equivalent by weight sodium chloride. The freezing temperature
ranges for each locality is represented diagrammatically in fig. 4.8.
The results from both Wensleydale and Swaledale are compared using
histograms in fig. 4.9.

This similarity of freezing temperatures and salinity was also
confirmed on forty primary inclusions from the Skelerton Mine in the
Bowland Trough. Freezing temperatures were found in the range from
-15.7°C to 24.0°C with a mean salinity of 21.70 per cent equivalent
by weight of sodium chloride.

4.4.3. Discussion of The Freezing Results

During this study freezing results were obtained from 654 primary
inclusions in 41 samples from 34 different localities. Freezing temp­
eratures were obtained in the range from -9.75°C to -25.0°C with mean
salinities of between 15.30 to 24.65 per cent equivalent by weight of
sodium chloride. Similar results have been obtained from the .Jston
area (Sawkins 1966a; Smith 1973(a) and by the author), the Derbyshire
area (Roedder 1967a and by the author) and for the North Wales occurrences
(Smith 1973a).
The freezing studies in fluorites from the Askrigg area indicate a dense, saline brine as the ore fluid medium. The ore fluid has a mean salinity of 20 per cent equivalent by weight of sodium chloride. The homogenization temperatures of Chapter 3 indicate temperatures of formation of greater than 100°C. Using the data of Unterberg (1966) the ore fluid must have had densities in excess of 1.14 kg/m³. That is much denser than ordinary meteoric water. The ore fluid also exhibits metastability revealed as gross supercooling, indicating a marked lack of suspended matter available for spontaneous nucleation. Most inclusions exhibited low first melting temperatures indicating the presence of other salts, probably of potassium and calcium (Hall and Friedman 1963). Neither the hydrate of carbon dioxide or hydrohalite were detected on freezing, indicating the ore fluid to be undersaturated with regard to these phases. The range of salinities obtained, between 15.30 to 24.65 per cent equivalent by weight of sodium chloride are entirely consistent with freezing data from numerous other Mississippi Valley deposits (Nowhorse 1933; Roedder 1967b). This again demonstrates the striking similarity of both homogenization and freezing results for this type of deposit.

The freezing studies indicate freezing temperatures of between 0°C and -9.4°C. This indicates a salinity of 0 to 14 per cent equivalent by weight of sodium chloride (Roedder 1963). Fluid inclusions in post-magmatic fluorite associated with carbonatite emplacement from the Gregory Rift, Kenya were also examined on the freezing stage. A freezing temperature of -2°C was obtained, indicating a salinity of 3.5 per cent by weight of sodium chloride. The ore fluid responsible for the Askrigg mineralization is found from freezing studies to be on average a 3 molar solution of sodium chloride. This salinity is similar to that of Mississippi Valley-type deposits and well above that of normal hydrothermal-type deposits. Similar data led Hall and Friedman (1963) to suggest the presence of highly saline connate...
waters during the formation of Mississippi Valley-type deposits.

Any postulated theories of genesis for these deposits need to account for these observations of the presence of connate waters. It was thus felt that a detailed study of the chemistry of these fluids was necessary to test the validity of the freezing studies. A description of the microchemical techniques used and the results obtained is contained in the next chapter.
A description and usage of the equipment used is as follows:

(a) The Heat Exchange Unit containing up to ten kilograms of a dry-ice-methanol mixture.

(b) The Lauda Ultrathermostat K 2 Electronic with a stainless steel pump, heater control on the side and both contact and reference thermometers.

(c) The Leitz binocular microscope with photographic attachment (d) and sub-stage illumination with variable output (e). The freezing stage itself is a brass cell with inlet and outlet insulated flexible copper piping. The cell is tightened down with Allen screws on the top of the cell.

(f) The Dewar Flask containing an acetone-dry-ice mixture (or liquid nitrogen) to freeze the fluid inclusions. Transfer of sample plates from the Dewar Flask to the cell was performed as rapidly as possible, it usually took thirty seconds.
FIG. 4.2.

PLAN OF THE COOLING STAGE

HEAT EXCHANGER

CELL

BATH

Thermometers

CROSS-SECTION OF THE COOLING STAGE

1. BRASS CELL
2. ACETONE IN
3. QUARTZ DISC
4. TELON GASKETS
5. SCREWS
6. RING
7. ASBESTOS INSULATION
8. SAMPLE HOLDER
9. SAMPLE
10. LEITZ OBJECTIVE
11. LEITZ SPRING
12. MICROSCOPE STAGE
13. SUB MICROSCOPE STAGE
14. VERNIER SCREW
FIG. 4.4.
THE SYSTEM H₂O – NaCl [after Roedder 1962]

FREEZING TEMP. °C
+10
0
-10
-20
-30
0 5 10 15 20 23.3 25 30
WEIGHT % SODIUM CHLORIDE.

SOLUTION
NaCl + SOLUTION
ICE + SOLUTION
NaCl₂H₂O + SOLUTION
ICE + NaCl₂H₂O

-21.1 EUTECTIC POINT
4.5.a. and b. show the fluid inclusion cavity to be filled completely with an opaque mass of ice crystals. As the temperature is raised small quantities of water appear on the ice crystals at the first melting point of \(-31.5^\circ C\) at 4.5.c. After this melting of the ice crystals proceeds with larger quantities of liquid being formed. At 4.5. a. only a couple of ice crystals still remain and at 4.5.p at a temperature of \(-19.5^\circ C\), complete melting has occurred. This is the point of the final melting temperature and the amount of depression of the freezing point of the fluid is attained.
FIG. 4.5.

THE FREEZING BEHAVIOUR OF A FLUID INCLUSION IN FLUORITE FROM N.W. YORKSHIRE.

a. -50
b. -40
c. -31.5
d. -31

e. -29
f. -27
g. -23
h. -22

i. -21.5
j. -21.25
k. -21
l. -20.75

m. -20.5
n. -20
o. -19.75
p. -19.5
FIG. 4.8

HISTOGRAMS OF FREEZING RESULTS FROM THE GREENHOW—GRASSINGTON AREAS.

% FREQUENCY

GALLOWAY VEIN

LOLLY MINE

Early Purple Fluorite
Later Amber Fluorite

HARGATE END VEIN

GILL HEADS VEIN

YARNBURY

MIDDLE VEIN

FREEZING TEMPERATURE °C
Fig. 4.7.
The range of freezing temperatures and salinities in the Grassington Greenhow area.
FIG. 4.8.

THE RANGE OF FREEZING TEMPERATURES AND SALINITIES IN THE SWALEDALE, WENSLEYDALE AND BOWLAND AREAS.

<table>
<thead>
<tr>
<th>Location</th>
<th>Swaledale</th>
<th>Bowland Areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bunton L</td>
<td>26</td>
<td>55</td>
</tr>
<tr>
<td>Moulds Top Mine</td>
<td>39</td>
<td>37</td>
</tr>
<tr>
<td>Hungry Hushes</td>
<td>3</td>
<td>22</td>
</tr>
<tr>
<td>Old Rake</td>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td>Turf Moor L</td>
<td>62</td>
<td>11</td>
</tr>
<tr>
<td>Surrender M</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Dam Rigg L</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Martin V</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Dam Rigg M</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

WENSLEYDALE

<table>
<thead>
<tr>
<th>Location</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Grooves</td>
<td>37</td>
</tr>
<tr>
<td>Seata M.</td>
<td>23</td>
</tr>
<tr>
<td>Clouds</td>
<td>44</td>
</tr>
</tbody>
</table>

BOWLAND TROUGH

<table>
<thead>
<tr>
<th>Location</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skeleron M.</td>
<td>40</td>
</tr>
</tbody>
</table>

-5  -10  -15  -20  -25  °C
FREEZING TEMPERATURE

15  20  25  3
SALINITY AS EQUIVALENT % NaCl

SALINITY AS EQUIVALENT % NaCl
FIG. 4.9. HISTOGRAMS OF FREEZING RESULTS FROM THE WENSLEYDALE AND SWALEDALE AREAS.

% FREQ

-24  -25
-22
-23
-20
-19
-18
-17
-16

FREEZING TEMPERATURE °C

-24  -25

CLOUDS

SEATA MINE

WET GROOVES

MOULDS TOP MINE

OLD RAKE

BUNTON LEVEL FRIARFOLD RAKE
CHAPTER 5

THE GEOCHEMISTRY OF THE ORE-FORMING FLUID IN THE ASKRIGG AREA FROM STUDIES OF FLUID INCLUSIONS IN FLUORITE.

3.1. REVIEW OF THE ANALYTICAL METHODS USED TO STUDY FLUID INCLUSIONS

3.1.1. Introduction

Apart from the recent discoveries of areas with metalliferous brines in the Salton Sea (White, Anderson and Grubbs 1963), the Red Sea (Swallow and Crease 1965; Degens and Ross 1969) and the Cheleken Peninsular (Lebedev 1967), fluid inclusions still provide us with the only sample of the ore-forming fluid available from older ore deposits. Ideally a complete quantitative analysis for the contents of a single inclusion for the major trace constituents of the vapour, liquid and solid phases with isotopic ratios for hydrogen, sulphur, oxygen and carbon plus the $H^+$, $pH$ and $OH$ values is desirable. Unfortunately a quantitative approach is rarely attainable, at best only semi-quantitative or qualitative results can be obtained (Roedder 1972). Except for the study of large inclusions, no method or combination of methods will give accurate unambiguous results. Many methods have been tried but none are universally applicable, due to the varying occurrence of inclusions in a wide range of sample material. As stated earlier (section 1.2.) the larger fluid inclusions are rare and prone to leakage. A compromise thus has to be reached between the ease and accuracy of studying the rare larger inclusions and the greater abundance of the smaller inclusions. An important point to note here is that the volume of an inclusion is a function of the cube of its radius (fig. 1.2.). Thus when studying small inclusions, a relatively large sample volume is needed with attendant risks of increasing contamination, error and ambiguity. Sample duplication of primary inclusions is normally rarely attained as most fluids undergo some
change during growth, plus the added cumulative error of secondary inclusion development.

Methods applicable to the study of inclusions can be divided into non-destructive and destructive tests. Due to the extreme vagaries of the occurrence of inclusions, as much information as possible needs to be obtained from the better inclusions using a non-destructive tests before a destructive one is applied.

5.1.2. Non-Destructive Methods

The examination of fluid inclusions using a petrological microscope is perhaps the most time consuming aspect of the study but it is a very sensitive method yielding qualitative or semi-qualitative data. Inclusions can be studied using polished plates or slabs and cleavage fragments immersed in oil of similar refractive index (section 2.4.).

Composition of the Liquid Phase

Various important characters can be recognised which enable different fluids to be differentiated. These include the fluidity, allowing both glass and viscous oil to be distinguished from aqueous fluid. Water solutions are usually uncoloured whilst hydrocarbons are normally coloured yellow, green or brown. The wetting characteristics of a mixture of phases will always take up the minimum surface energy sequence of: host - glass - liquid H₂O - liquid CO₂ or oils - gaseous CO₂ and H₂O (Roedder 1972). Thus the vapour bubble is normally found in the immiscible oil phase in three phase fluid inclusions in fluorite. A few organic liquids can be identified by their fluorescence (Reese 1898), whilst liquid CO₂, CO₂ vapour, H₂CO₃⁻ and CO₃⁻ can all be recognised by their sharp infra-red absorption spectra (Cifrułak and Cohen 1969). The index of refraction can be estimated from the apparent relief versus that of the host mineral but it is extremely dependent on inclusion shape and the amount of salts present.
Brewster (1823) developed a technique for determining refractive indices using total reflection at the flat interface of the inclusion and host mineral. The thermal expansion and homogenization method (chapter 3) is particularly useful to identify liquid carbon dioxide from other phases (Brewster 1823), those inclusions with a small degree of liquid fill with homogenization with inversion (Ermakov 1950) and the presence of salt solutions (Sorby 1858). Critical phenomena are indicated by the fading of the miniscus on heating and the raising of the critical point of water by the presence of sodium chloride (Sourirajan and Kennedy 1962). The depression of the freezing point is a very useful property of inclusion fluids and has wide applications (Chapter 4). Inclusions can also be differentiated by their movement in a thermal gradient applied to the section (Roedder 1965b).

**Composition of the Solid Phases**

The presence of daughter minerals indicates the saturation of the fluid at the temperature of observation. It is important to distinguish the daughter minerals from accidental inclusions by using phase ratios but there is also the added danger of necking-down and metastability to be taken into account. Observation of petrographic properties such as colour, habit and refractive index are limited by the nature of the host mineral. Often daughter minerals exhibit well developed crystal faces enabling their crystal system to be identified (Rankin 1973). Opaque daughter minerals can sometimes be identified by their magnetic properties or the Curie temperature on the heating stage (Kelly and Turneaure 1970). If the daughter minerals can be separated, often with severe difficulty, analysis using an electron microprobe offers great promise (Dolomanova et al. 1966, 1968). Freezing of inclusions (Chapter 4) can lead to the development of ice, halite and carbon dioxide hydrate, often with the elimination of
metastability. The heating of daughter minerals in the inclusions can give much valuable information, especially regarding the solubility of the alkali chlorides. Potassium chloride has a coefficient of solubility eight times that of sodium chloride and in a mixture of the two it will dissolve preferentially in the fluid on heating.

Composition of the Gas Phase

Little information can be obtained by the non-destructive methods except estimates of densities from phase ratios in tubular inclusions, inversion densities on heating and the condensation of liquids on cooling.

5.1.3. Destructive Methods.

Various qualitative and semi-quantitative tests can be applied to fluid inclusions. The amount of liquid can be estimated by weight loss methods (Ermaakov and Ryaz 1957) or density measurements (Roedder 1963). The vapour pressure can be estimated by crushing in oil (Davy 1822; Roedder 1970a), especially the large volume expansion of carbon dioxide. The vapour bubbles will dissolve in a suitable fluid or react chemically with it. The presence of small amounts of hydrogen sulphide can often be detected by the human nose on crushing by their distinctive smell.

Composition of the Liquid Phase

Simple crushing and leaching of the inclusions is by far the most common method employed (Roedder 1972). Ideally all materials should be leached without contamination from the host mineral. Unfortunately this is rarely achieved and a compromise has to be reached, with corrections for the host mineral's solubility (Roedder et al. 1963; Hall and Friedman 1963). Decomposition followed by leaching has also been widely applied using a gas stream (Roedder 1958), in a vacuum (Wahler 1956; Roedder et al. 1963) and by the use of ball milling techniques (Fabor 1941,
Lamar and Shrode 1953). The leachate is then analyzed using special micro-chemical techniques developed for high precision, such as flame photometry, colorimetry (Roedder et al. 1963), spectrographic methods (Haffty and Pinckney 1967) and x-ray fluorescence techniques.

An important fact to bear in mind is that the leachate obtained is not the same as the original fluid. This is due to the unknown amount of the host mineral present in the fluid inclusion at the time of trapping. The samples must always be cleaned extensively as most cracks in the mineral will contain soluble salts not removed by simple washing. Electrolytic cleaning is recommended by Roedder (1958). Contamination from broken surfaces of the host mineral or from small impurities can be serious (Correns 1940). Loss of ions by absorption and contamination by laboratory glassware can also lead to crucial errors.

Composition of the Gas Phase

Most methods of extraction have their limitations and inherent errors as the evolved gas does not always come entirely from the vapour inclusions. Some material will be added by the evaporation of liquids and dissolved gases and from other sources such as impurities present in the equipment and specimen. Simple crushing in an inert gas stream with absorption and weighing (Pfaff 1971, Khitarov and Rengarten 1956) or simple weight loss (Sorby 1858) were first used. The application of vacuum techniques to inclusion analysis (Wright 1881; Barker 1965a and b; Elinson 1968a and b) is beset by the problem of gases produced by catalytic reactions (Wahler 1956). Vacuum ball milling (Elinson 1949, 1956) has also been used with some contamination noted from the carbide balls used (Goguel 1963; 1964) and errors due to gas absorption on the surfaces of the samples and apparatus (Kunkel 1950). Mass spectrometry has been applied recently with some success (Barker 1965a,b, 1966;
Ohmote 1968a and b, Krans 1968) but this method suffers from the inherent problems of gas fractionation and reaction with the exposed surfaces. Gas chromatography also offers great promise with its high precision (Giddings et al. 1968) and has wide future applications. Deuterium ratios have been successfully determined by crushing in vacuo, condensing in a cold trap and converting to hydrogen (Hall and Friedman 1963; Rye 1964, 1966).

5.2. METHODS USED TO STUDY ASKRI GG FLUORITES

5.2.1. Introduction

After applying the non-destructive methods to fluid inclusions in fluorite from the Askrigg area (Chapers 2, 3 and 4) the next step was to apply selected destructive methods to the analysis of those samples. The aim was to verify the freezing data of Chapter 4 and obtain geochemical parameters which have been obtained from other Mississippi Valley type deposits of similar temperature of formation (Chapter 3). Of particular interest in this respect is the sodium/potassium and chloride/sulphate ratios (Sawkins 1968) as possible genetic indicators for these ore deposits.

5.2.2. Sample Selection and Preparation

Samples with abundant primary inclusions used in both the homogenization and freezing methods were selected. Areas of interest were sawn from slabs of fluorite using a hand held diamond blade (section 2.4.). The observation of inclusions was made by applying oil of the same refractive index as fluorite to the surface of the slabs. The optimum size of the fluid inclusions was assessed optically and a preliminary crushing to obtain particles of less than one mm diameter was then performed. At this stage most secondary inclusions present would be destroyed as they occur on fractures and would thus be removed.

After the preliminary crushing the samples were washed repeatedly with deionized water.
Any carbonates and sulphides present were removed by boiling for four hours with concentrated hydrochloric and nitric acids and then with a five per cent solution of oxalic acid to remove any iron present. A heavy liquid separation using Clerici's solution was then performed to remove any particles of baryte associated with the fluorite.

The risk of severe contamination in the sample preparation has been stressed by Roedder (1958), the use of ordinary demineralized water is thus precluded. In the sample preparation polythene containers were used throughout and rubber gloves were worn to prevent sodium contamination. The samples were finally repeatedly washed for three days with frequent changes of deionized water in an electrodialysis cell. The cell was supplied by Shandon Southern Instruments Ltd., Camberly, Surrey. This washing should have by then selectively removed all soluble ions into the electrode compartments. The completion of the washing occurs when the conductivity of the solution is the same as that for pure water. The samples were then dried overnight at 80°C and placed in polythene containers.

A method using a combination of ball milling and leaching was developed, enabling a large number of samples to be crushed rapidly with a low contamination risk. The clean fluorite samples were placed in an agate ball mill, the Fritsch Pulverisette, supplied by Christen Ltd., Gateshead and were thoroughly crushed for thirty minutes. The crushed fluorite was then successively leached with 20 ml quantities of deionized water. Three leachates were normally taken, although a number of the larger samples required up to six leachings. The leachate was then rapidly filtered into polythene sample bottles for analysis. The filter used in the study needed to be absolutely free of soluble ions, so the use of filter paper was precluded due to their high chloride concentration.
content. A filter pad was prepared from glass fibre used in chromatography columns. The glass fibre was boiled in concentrated acid for two days and washed repeatedly with deionized water. After each crushing the filter pad and the agate ball mill were thoroughly washed with deionized water and acetone to avoid contamination. After the crushing, leaching and collection in the sample bottles, the samples were then ready for microchemical analysis.

5.3. ANALYSIS FOR THE ALKALINE METALS

5.3.1. Flame Photometry

This method offers great accuracy, speed and requires only a small sample volume. It is thus ideally suited to the determination of the small amounts of alkali metals found in fluid extracted from the inclusions.

A Flame Photometer, manufactured by Evans Electroselenium Ltd., Harlow, Essex was used in this study. For each analysis a 1 ml quantity of leachate was vaporised in the flame for sodium, potassium and lithium determinations. Regular calibration checks were made using standards prepared from the appropriate alkali chloride salt. Calibration curves were obtained using these standards and they are shown in fig. 5.1. After correction for the blank value, the concentration of the unknown solution was then obtained.

The detection limit for potassium was found to be 0.1 ppm and for sodium 0.01 ppm. As the concentration of potassium was normally low the interference of potassium in the flame during sodium determinations was thus at a very low level. This was subsequently verified by tests using various mixtures of sodium and potassium. Amounts of up to 5 ppm potassium were found to be tolerable in a sodium analysis.
5.3.2. Sodium and Potassium Results

Only the results for sodium and potassium will be presented here as the presence of lithium was not detected in any of the samples. The results for the flame photometry are summarized in tables 5.2 and 5.3. The results are presented as ratios as the ball milling technique will only produce semi-quantitative data. The ball milling also precluded analysis of the leachate for both calcium and fluorine. This is because of the unknown quantity of ions of the host mineral, fluorite, that will enter solution on crushing (Hall and Friedman 1963). The potassium/sodium ratios (by weight) range from values of 0.063 to 0.1500 with a mean value of 0.556. Comparison with other orefields and other varieties of waters is shown in fig. 5.4.

<table>
<thead>
<tr>
<th>AREA</th>
<th>MEAN K/Na</th>
<th>RANGE K/Na</th>
<th>SOURCE OF INFORMATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Formation Waters</td>
<td>0.049</td>
<td>0.1664 - 0.0001</td>
<td>White et al. 1963, 1965, Graf et al. 1966, Downing 1967, Anderson 1945</td>
</tr>
<tr>
<td>2. Volcanic Waters Geothermal areas</td>
<td>0.0207</td>
<td>0.1500 - 0.0001</td>
<td>White et al. 1963, Ellis 1967, Halgeson 1968, Lebedev 1967, Brewer et al. 1965</td>
</tr>
<tr>
<td>3. Mississippi Valley</td>
<td>0.0637</td>
<td>0.0926 - 0.0433</td>
<td>Hall and Friedman 1963, Roedder et al. 1963</td>
</tr>
<tr>
<td>4. Alston Fluorite Zone Baryte zone</td>
<td>0.1099</td>
<td>0.2128 - 0.0768</td>
<td>Sawkins 1966a, Smith 1975a</td>
</tr>
<tr>
<td>5. Askirgg area</td>
<td>0.0556</td>
<td>0.1500 - 0.0630</td>
<td>Author</td>
</tr>
<tr>
<td></td>
<td>0.0510</td>
<td>0.0854 - 0.0304</td>
<td>Smith 1973a</td>
</tr>
<tr>
<td>6. Derbyshire area</td>
<td>0.0168</td>
<td>0.346 - 0.0082</td>
<td>Author</td>
</tr>
<tr>
<td></td>
<td>0.0452</td>
<td>0.0666 - 0.0353</td>
<td>Smith 1973a</td>
</tr>
<tr>
<td>7. N. Wales Orefield</td>
<td>0.0677</td>
<td>0.1333 - 0.0459</td>
<td>Smith 1973a</td>
</tr>
<tr>
<td>8. Other ore deposits</td>
<td>0.0487</td>
<td>0.1368 - 0.0070</td>
<td>Roedder 1972, Tables 4, 5, 6</td>
</tr>
</tbody>
</table>
Reference to fig. 5.4. indicates the Askrigg mineralization fluid inclusions have a similar range of values to that of the Mississippi valley deposits but definitely enriched in potassium compared with formation waters. The Alston area generally has higher potassium levels in the ore-forming fluid, which probably indicates the higher temperatures of ore deposition (Sawkins 1966a) and possible magmatic influences (Smith 1973a). This is marked contrast to the Derbyshire orefield where a relative potassium deficiency is accompanied by lower homogenization temperatures (Roedder 1967b, author's unpublished results). Because of the semi-quantitative nature of these analyses and other factors (such as wall-rock interactions) comparisons with other more detailed analyses of fluid inclusions are only possible on a broad scale.

5.4. ANALYSIS FOR MAGNESIUM AND CHLORIDE

5.4.1. Magnesium Determination by the Titan Yellow Spectrophotometric Method

A number of direct colorimetric methods have been used to determine magnesium in solution. They usually involve absorption of a dye on colloidal magnesium hydroxide to form a colour lake. Some methods involve the use of soluble coloured compounds (Mann and Yoe 1957). In this study the colouring reagent Titan Yellow was used (Evans 1968).

The determination of magnesium by colorimetric methods is susceptible to interference by a number of other ions. To overcome this the ten ml. aliquot of solution was extracted in a five per cent solution of 8 quinolinol in chloroform in a mildly acidic solution (Mann and Yoe 1956). Most metallic ions form quinolnolates which are soluble in chloroform, the magnesium is unaffected under these conditions. Calcium interference is negligible in the presence of sucrose and can be tolerated up to levels of 110 ppm (Evans 1968). The titan yellow reagent is stabilized in the presence of glycerol and polyvinyl alcohol in an alkaline solution.
After extraction with 8-quinolinol the ten ml. aliquot of solution is added to ten ml. of titan yellow reagent and five ml. of an eight per cent solution hydroxide and then left for one hour. The amount of magnesium is then determined using a Spectronic 100 Spectrophotometer, manufactured by Bausch and Lomb Ltd., New York; absorption was then measured at 490 m\(\mu\). The readings are then compared with those of the standards on the calibration curve shown in fig. 5.5. The precision of the readings is in the range of 0.01 ppm.

5.4.2. Chloride Determination Using Colorimetric Methods

The chloride was determined as a thiocyanate complex in an acid solution following the methods of Swain (1956). A ten ml. aliquot of the sample was added to two ml. of mercuric thiocyanate in a methanol solution. To this was added one ml. of ferrie ammonium sulphate in a solution of 6N nitric acid. The absorption was then measured using the Spectronic 100 Spectrophotometer at a wave length of 470 m\(\mu\). Overall precision was again high at 0.01 ppm and the calibration curve shown in fig. 5.5. was obtained.

5.4.3. Chloride and Magnesium Results

The results for both chloride and magnesium are summarized in table 5.6. Comparison of the chloride/sodium weight ratios for different varieties of waters is shown in fig. 5.7. The Askrigg mineralization has a mean chloride/sodium ratio of 1.636 compared with a value of 2.00 for the Mississippi Valley area (Hall and Friedman 1963; Roedder et al. 1963); 2.058 for oilfield waters (White et al. 1963) and 1.755 and 2.175 for Carboniferous formation waters (Anderson 1945; Downing 1967). The Askrigg area thus has lower chloride values than the Mississippi Valley area, possibly due to the incomplete leaching of the samples. This figure still exceeds the chloride/sodium ratio of 1.542 for a normal sodium chloride brine.
This probably indicates the presence of calcium in solution as calcium chloride. The presence of calcium was detected in all the solutions using atomic absorption techniques. However, due to the uncertainties attached to the solubility of the host mineral fluorite on crushing, a correction factor could not be applied and these results could not be used (Hall and Friedman 1963).

Magnesium levels in the ore-forming fluids are given in table 5.6. and they are compared as magnesium/sodium ratios in fig. 5.7. The results are very similar to those for the Mississippi Valley area and for formation waters. Comparison of mean magnesium/sodium ratios indicate the following values:

- Formation waters 0.0893
- Volcanic waters 0.0150
- Carboniferous formation 0.08217 (Downing 1967)
- Mississippi Valley inclusions 0.09152
- Askri g inclusion s 0.152
- Derbyshire inclusions 0.131

The ratios of both the Derbyshire and Askrigg areas indicate enrichment of magnesium with respect to the published data from Carboniferous formation waters.

The presence of magnesium in the ore solution is thus seen to be an integral part of the mineralization. The samples were also investigated for the presence of sulphate using the method of Johnson and Nishita (1952). The sulphate is determined colorometrically as sulphide using methylene blue. Using this very sensitive method the detection of sulphide was possible down to levels of 0.3 ppm. Despite numerous analyses only one sample yielded detectable sulphide of 1.2ppm. This was probably due to a high concentration of solid sulphide inclusions in the sample concerned.
5.5. **PRELIMINARY STUDIES ON SOLID INCLUSIONS IN FLUORITE**

5.5.1. **Mode of Occurrence**

During the growth of fluorite crystals the trapping of extraneous solid particles present in the fluid medium frequently occurs. Due to their ubiquitous occurrence in fluorite it was felt that their study might provide further useful information on the processes operating during the mineralization. These solid particles outline the cubic growth zones and are important tools in the identification of primary inclusions.

Organic matter is sometimes present as dark brown material of irregular shape and rounded blebs. Quartz is frequently found as aggregates of euhedral crystals in amounts of normally not less than five per cent, and not greater than ten per cent (Dunham 1952). The sulphide inclusions are very common in fluorite and often impart a greenish colour, and one notable example is the fluorite from Greenhow Rake, Greenhow Hill. They occur in a variety of shapes from the long ribbons of chalcopyrite to euhedral triangular and square shaped pyrite inclusions. Inclusions of the main sulphide phases, galena and sphalerite, are present but are comparatively rare. This is in direct contrast to the abundance of both chalcopyrite and pyrite in fluorite crystals. The chalcopyrite inclusions often have crystal edges which have undergone secondary oxidation. The various types of sulphide inclusions found in fluorite from the Askrigg area are shown in fig.5.9.

5.5.2. **Electronmicroprobe Studies of the Sulphide Inclusions**

The electronmicroprobe provides an excellent method of studying these solid sulphide inclusions in fluorite. Due to the shallow penetration of the electron beam, inclusions for study had to be located on the surface of the polished plate.
The fragments of polished fluorite were cemented on to perspex discs enabling them to be easily positioned in the electron beam. Analysis performed on the Microscan 5 Electron microprobe supplied by Cambridge Instruments, Cambridge. The presence of nickeliferous pyrite was demonstrated in a number of specimens from previously unrecorded localities in Yorkshire including the Keld Heads Mine, and the Wharfedale Mine, Kettlewell and also in Lancashire at the Skelerton Mine, Rimington. These nickeliferous pyrites exhibit a marked compositional zoning, illustrated in figs. 5.10. and 5.11. There is a very striking negative zoning relationship between the iron and nickel contents. The nickel content can be up to as much as ten per cent but averages about five per cent. A summary of electron microprobe analyses on some of these sulphide inclusions is shown in table 5.12. The further study of these sulphide inclusions in fluorite could provide much more useful data and they are worthy of a further more detailed study.

5.6. TRACE ELEMENTS STUDIES ON THE MAJOR ORE MINERALS

5.6.1. Preparation of Samples

Ore minerals from the samples to be analysed were hand picked and to minimize contamination only fresh cleavage fragments were selected. The ore was picked off the sample using a vibrotool, and the fresh cleavage fragments were then selected using a binocular microscope. The cleavage fragments were then washed in acetone, carbon tetrachloride and deionized water successively. They were then crushed by hand in an agate pestle and mortar and sieved. The fraction between 350 and 235 microns was rechecked using a binocular microscope and then thoroughly cleaned. The final crushing was again in the agate pestle and mortar. The weighed samples were then digested in a mixture of concentrated nitric and hydrochloric acids and made up to a volume of 50 ml. for atomic absorption analysis.
5.6.2. Atomic Absorption Studies.

The solution subsequently obtained was then analyzed on an atomic absorption spectrophotometer, the 290 model, manufactured by Perkin Elmer of Norwalk, Connecticut. The solutions were examined for trace amounts of silver, copper, manganese, zinc (galena), strontium, nickel and chrome. Their concentrations were obtained by comparison with standards made up from the appropriate metal. Detection of all elements was possible down to levels of 0.1 ppm.

A total of fifty samples of both sphalerite and galena were determined for trace constituents, the results are presented as histogram plots in fig. 5.13. Of the trace elements determined in the samples, manganese was only present in small amounts of up to 23 ppm, most samples did not contain any at all. A similar situation applies to chromium with sporadic occurrences of up to 50 ppm. High levels of chromium are indicated in galenas from the Bowland Trough area and from the Dent Fault area. Nickel values are generally higher in the range of 0 to 420 ppm. The areas of high nickel values also correlate with the occurrence of nickeliferous pyrite inclusions in fluorite, such as in the Keld Heads and Kettlewell areas. Strontium values generally occur in the range of 0 - 200 ppm, with a few exceptions. These higher values probably represent some degree of baryte contamination as strontium is frequently found as a trace constituent in baryte. A similar situation exists for zinc values which mostly occur in the range of 0 to 500 ppm (see fig. 5.13). All samples show a marked enrichment in both copper and silver as trace constituents. High copper values are found in a few samples indicating possible intergrowths of galena with chalcopyrite.

The trace element analysis of the galenas and sphalerite indicate enrichment in silver, copper, zinc and nickel with subsidiary
chromium and strontium. The Bowland Trough area and the deposits along the Dent Fault exhibit higher concentrations of trace constituents when compared to the other deposits of the Askrigg block.

5.7. THE CHEMICAL NATURE OF THE ORE-FORMING FLUID IN THE ASKRIGG AREA

5.7.1. Fluid Inclusions as Samples of the Ore-Forming Fluid

Natural hydrothermal systems are incongruent mixtures of large numbers of different phases and components. Any chemical models postulated for the evolution of these hydrothermal systems into mineral deposits will have to account for a large number of controlling processes. These include the processes of deposition of the mineral assemblages, the paragenetic sequences developed, the replacement features and the development of mineralogical zoning. Fluid inclusions can provide a wealth of data pertinent to the evaluation of these conditions of formation and can apply important constraints on any postulated theories of genesis of the ore deposits.

The study of fluid inclusions in both ore and gangue minerals of the Mississippi Valley type deposits during the last decade has contributed much to our understanding of the processes responsible for these hydrothermal ore deposits. As the study of fluid inclusions has been the focus of a great deal of recent attention the question arises of how representative is the fluid inclusion as a sample of the ore-forming fluid. Various basic assumptions are made in the study of inclusions. Although not strictly valid in all cases the exceptions are generally few and of little significance (Roedder 1967b).

The first basic assumption is that the ore or gangue mineral must itself have crystallized from a fluid medium which represents the ore fluid.
Whole series of inclusion zones can be recognized in individual crystals from all stages of the paragenetic sequence. They are certainly not the "last residue" or "final spent fraction" of Ingerson (1954) as they provide samples of the ore fluid from all stages of growth. A small amount of precipitation does take place on the inclusion walls but its effect is insignificant.

The second assumption is that if re-entrant imperfections form on the surface of a growing crystal, it subsequently fills with a portion of the ore fluid. This portion of fluid is then trapped by the further growth to form a primary inclusion as a representative sample of the ore fluid at that moment of trapping. Slight compositional differences due to boundary layer effects and steep concentration gradients will be present but they are again of little significance. The recognition of both primary and pseudosecondary inclusions (section 2.5.) does suffer from some ambiguity which fortunately can be resolved with careful investigation.

The third basic assumption is that no material has been lost or gained, subsequent to the time of trapping. The importance of recognizing leakage, necking-down and other post-formational changes has been stressed in section 2.5.

5.7.2. The Chemistry of the Ore Fluid Trapped as Inclusions in Fluorite from the Askrigg area

In chapter 2 the suitability of using other gangue and ore minerals for inclusion study from the Askrigg area was assessed. Despite an exhaustive search only fluorite of the gangue minerals gave fluid inclusions suitable for study. The data thus obtained is for the ore-forming fluid associated only with the fluorite deposition. As both galena and sphalerite are usually found associated with fluorite it is reasonable to tentatively extrapolate these results to include all of the ore minerals. (77)
The composition of the ore-forming fluid may also change with time but Hall and Friedman (1963) noted a constant composition during the mineralization and this may well be the case during the Askrigg mineralization. The latter waning stages of the mineralization are probably represented by secondary inclusion development. The freezing studies of chapter 4 indicated these secondary inclusions to be very dilute solutions of low salinity compared with the very saline solutions of the main mineralization. The study of hydrothermal ore fluid in the Askrigg area was thus restricted to examining fluid inclusions in fluorite. The fluid inclusions trapped in fluorite crystals are assumed to be representative of the ore-forming fluid for reasons outlined above.

Only definite primary inclusion rich samples were used in this detailed chemical examination of the inclusion fluid. The more important areas of mining activity in the Askrigg area are located within the major fluorite occurrences. The ore minerals also occur with both calcite and baryte outside the fluorite areas. Monophase fluid inclusions were found in some of these minerals but were found to be unsuitable for study. A similar relationship of temperature zoning exists to that found by Sawkins (1966a) in the Alston area. Higher temperature fluorite centers are found with a lower temperature fringing baryte zone. By analogy with Sawkin's results the ore fluid in the baryte zone is presumed to be also of a lower salinity.

Thus the small amounts of fluid trapped in minute cavities in fluorite crystals provide the only available sample of the ore-
forming fluid in the Askrigg area. The microchemical tests performed on this fluid indicates the substantial presence of various ions in this solution. The results are by necessity only semi-quantitative yet they are comparable with quantitative data from other deposits (Hall and Friedman 1963).

The presence of large amounts of chloride and sodium ions with subordinate potassium and magnesium in the proportions of \( \text{Cl}^- \gg \text{Na}^+ \gg \text{K}^+ \gg \text{Mg}^{2+} \) was found. Calcium was also found to be present but the amount actually obtained on crushing the fluid inclusions could not be estimated (section 5.4.3.) Neither lithium nor sulphate ion (as sulphide) were detected in the samples analyzed. The analysis of the ore-forming fluid in the Askrigg area thus exhibits the startling consistency of results common to other Mississippi Valley type deposits. The ore-forming fluid is thus similar in many respects to the connate waters of the sodium - calcium - chloride type of oilfield brines, first noted by White (1958).

There exists strong similarities between the chloride/sodium and magnesium/sodium ratios (by weight) of the fluid inclusions and those of the formation waters (figs. 5.7. and 5.8.) There are however, notable differences in the amounts of potassium present. In most oilfield brines magnesium greatly exceeds the amount of potassium (White 1958). On the other hand inclusion fluids are enriched in potassium at levels equal to or just less than magnesium. Davidson (1966) explained this by citing magnesium abstraction during dolomitization of the wall rocks. This potassium enrichment is also revealed in the potassium/sodium ratios in fig. 5.4. The presence of potassium fixed as clay minerals, feldspar and mica has long been noted as characteristic of hydrothermal wall rock alteration.
This relative potassium enrichment has been used to postulate a magmatic influence on these connate fluids (Hall and Friedman 1963). Most ore deposits of definite magmatic influence do exhibit strong potassium enrichment in the inclusion fluids such as at Providencia, Mexico (Sawkins 1964; Rye and Haffty 1968). However the potassium could also have been contributed by the association of the fluid with evaporites (White, Hem and Waring 1963, table 27). The strong temperature dependency of this ratio has been stressed by White (1965). The work of Orville (1962, 1963) and Hemloy and Jones (1964) demonstrate increasing sodium relative to potassium in the fluid phase with decreasing temperature. This potassium discrepancy between the data from fluid inclusions and the ore field brines of chloride-sodium-calcium type could reflect the differing temperatures of formation. Most ore field brines have temperatures of around 50°C whilst the filling temperatures of fluid inclusions of Mississippi Valley type deposits indicate temperatures between 70°C and 200°C (Roedder 1972).

The analysis of the ore-forming fluid in the Askrigg area indicates the presence of ions in proportions very similar to other deposits of the Mississippi Valley type. The ore-forming fluid also contained lead, zinc and copper with varying amounts of silver, nickel, chromium, manganese and strontium. The ore-forming fluid thus exhibits a wide assemblage of different elements in solution. The mode of transport of these elements in solution has an important bearing on any discussion of their genesis. Using the chemical data from fluid inclusions various chemical models of transport have been postulated. They will now be discussed in the light of fluid inclusion evidence from the Askrigg area.
5.7.3. Models for the Mode of Transport of Metals to Form the Mississippi Valley Type Deposits

The chemical data obtained from the fluid inclusions indicates remarkably uniform conditions of formation from many different areas of these ore deposits. A "typical fluid inclusion analysis" conforms to the following pattern:

<table>
<thead>
<tr>
<th>Conc./ppm</th>
<th>Moles/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>57,100</td>
</tr>
<tr>
<td>K</td>
<td>2,700</td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>18,000</td>
</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2,400</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>124,600</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>3,300</td>
</tr>
<tr>
<td>B&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>107</td>
</tr>
</tbody>
</table>

Total dissolved salts 208,000
Water 792,000

This analysis is for fluid inclusions in a sphalerite from the Tri-state district, given in Roedder (1967b). These inclusion fluids are also capable of transporting large quantities of base metals in solution (Czamanske et al. 1963; Pinckney and Hefft 1970).

The ore fluid is thus on average a three molal solution of sodium chloride (indicated by freezing studies and chemical analysis) with varying amounts of other ions in solution. The fluid is sulphide deficient, the sulphur usually being present as sulphate. The metallic ions present must be in the form of complex ions due to the solubility considerations (Czamanske 1959) in the following formula:

\[ \text{M}^{2+} (\text{aq.}) + n \text{A}^{x-} (\text{aq.}) = \text{M}_n^{2-n} \text{A}_x \]

\[(81)\]
The metallic ion and ligand thus combine to form anion complexes. The predominant ligands available in ore solutions are $\text{Cl}^-$, $\text{HS}^-$, $\text{S}^{2-}$, and $\text{NH}_3^-$ (Barnes 1967) which form stable complexes. Barnes (1967), Harnes and Czamanske (1967) favour transport as bisulphido complexes of lead $\text{Pb(HS)}_3^-$, zinc $\text{Zn(HS)}_3^-$ and copper $\text{Cu(HS)}_4^{2-}$.

This is incompatible with fluid inclusion evidence and the presence of metalliferous sulphur deficient brines in the Salton Sea, Red Sea and Cheleken Peninsular (Tooms 1970). Some oxidation and loss of sulphur could have taken place on opening of inclusions but this is unlikely. Recent evidence by Nriagu (1970 a,b), Nriagu and Anderson (1971) indicates the stability of lead as the chloride complex $\text{PbCl}_4^{2-}$ below 200°C.

Studies of fluid inclusions in fluorite from the Askrigg area indicate a sulphur deficient concentrated sodium chloride brine present during the mineralization at elevated temperatures. This fluid is capable of carrying large amounts of ore metals and gangue minerals such as fluorite (Ellis and Iishon 1964, 1967; Strubel 1965), baryte and witherite (Townley et al. 1937; Garrolls et al. 1960) all important in the Askrigg area. This observation has to be reconciled with the lack of an obvious source of sulphur for the ore minerals and a source of fluorine and potassium for the gangue minerals. These and other factors pertinent to a consideration of the genesis of the ore deposits in the Askrigg area will be discussed in Chapter 6.
FIG. 5.1.
CALIBRATION CURVES FOR SODIUM, POTASSIUM.

GALVANOMETER DEFLECTION.

Sodium.

Potassium.
<table>
<thead>
<tr>
<th>SAMPLE NO. &amp; LOCATION</th>
<th>Na ppm</th>
<th>K ppm</th>
<th>K/Na RATIO</th>
<th>LEACHATE VOL. (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GREENHOW HILL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GREENDOW HILL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>col. fluor. 105,106</td>
<td>2.00</td>
<td>0.25</td>
<td>0.1250</td>
<td>40</td>
</tr>
<tr>
<td>GALLOWAY VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>112 col. fluor.</td>
<td>5.30</td>
<td>0.65</td>
<td>0.0815</td>
<td>60</td>
</tr>
<tr>
<td>GALLOWAY VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>152 col. fluor.</td>
<td>2.80</td>
<td>0.15</td>
<td>0.0186</td>
<td>60</td>
</tr>
<tr>
<td>SUN VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>209 col. fluor.</td>
<td>3.80</td>
<td>0.10</td>
<td>0.0260</td>
<td>60</td>
</tr>
<tr>
<td>PROVIDENCE MINE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>amber fluor.</td>
<td>2.10</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>LOLLY MINE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 amber fluor.</td>
<td>93.00</td>
<td>5.45</td>
<td>0.0590</td>
<td>60</td>
</tr>
<tr>
<td>83 purple fluor.</td>
<td>35.20</td>
<td>3.90</td>
<td>0.1010</td>
<td>60</td>
</tr>
<tr>
<td>GILLBREADS VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61 col. fluor.</td>
<td>37.10</td>
<td>0.50</td>
<td>0.0134</td>
<td>110</td>
</tr>
<tr>
<td>61</td>
<td>36.00</td>
<td>0.53</td>
<td>0.0184</td>
<td>130</td>
</tr>
<tr>
<td>157</td>
<td>5.60</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>INDIAN VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>318 col. fluor.</td>
<td>15.10</td>
<td>0.95</td>
<td>0.0630</td>
<td>60</td>
</tr>
<tr>
<td>JOYCE VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66 col. fluor.</td>
<td>4.60</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>WRIGHT VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>319 col. fluor.</td>
<td>1.10</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>RODHILL VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>158-160 col. fluor.</td>
<td>1.80</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>ESCOE HILL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72-74 purple fluor.</td>
<td>36.60</td>
<td>2.15</td>
<td>0.0587</td>
<td>80</td>
</tr>
<tr>
<td>GRASSINGTON MOOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YARNBURY</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>448 amber fluor.</td>
<td>3.50</td>
<td>0.10</td>
<td>0.0286</td>
<td>60</td>
</tr>
<tr>
<td>BYCLIFFE VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>174-177 amber fluor.</td>
<td>0.65</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>SLANTER VEIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>142 amber fluor.</td>
<td>2.30</td>
<td>0.10</td>
<td>0.0435</td>
<td>60</td>
</tr>
<tr>
<td>KETTLEFELL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KETTLEFELL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>228 col. fluor</td>
<td>1.50</td>
<td>0.15</td>
<td>0.1000</td>
<td>60</td>
</tr>
<tr>
<td>200 col. fluor</td>
<td>7.70</td>
<td>0.55</td>
<td>0.0714</td>
<td>60</td>
</tr>
<tr>
<td>185-189 col. fluor.</td>
<td>2.10</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>SAMPLE NO. LOCATION</td>
<td>Na ppm</td>
<td>K ppm</td>
<td>K/Na RATIO</td>
<td>LEACHATE VOL. ml.</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------</td>
<td>-------</td>
<td>------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>WENSLEYDALE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEATA NINE 86, 87. col. fluor.</td>
<td>7.0</td>
<td>0.40</td>
<td>0.0571</td>
<td>60</td>
</tr>
<tr>
<td>WERT GROOVES M. 101. col. fluor.</td>
<td>2.9</td>
<td>0.20</td>
<td>0.0690</td>
<td>60</td>
</tr>
<tr>
<td>WORTON NINE 422, 423. col. fluor.</td>
<td>7.3</td>
<td>0.25</td>
<td>0.0342</td>
<td>60</td>
</tr>
<tr>
<td>CLOUDS 119, 120. col. fluor.</td>
<td>0.35</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>BIRKETT FELL 412, 413. col. fluor.</td>
<td>3.2</td>
<td>0.35</td>
<td>0.1094</td>
<td>60</td>
</tr>
<tr>
<td>SWALEDALE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BUNTON LEVEL 259, 260. amber fluor.</td>
<td>6.05</td>
<td>0.90</td>
<td>0.0488</td>
<td>60</td>
</tr>
<tr>
<td>OLD RAKE 290. col. fluor.</td>
<td>9.1</td>
<td>0.40</td>
<td>0.0440</td>
<td>80</td>
</tr>
<tr>
<td>SURRENDER GROUND 302, 302. col. fluor.</td>
<td>2.1</td>
<td>n.d.</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>MARTIN VEIN 314. amber fluor.</td>
<td>1.75</td>
<td>0.05</td>
<td>0.0350</td>
<td>60</td>
</tr>
<tr>
<td>HUNGRY HUSHES 477, 478. col. fluor.</td>
<td>1.50</td>
<td>0.23</td>
<td>0.0648</td>
<td>80</td>
</tr>
<tr>
<td>SHELTON MINE 484. col. fluor.</td>
<td>0.35 n.d.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAN RIGG VEIN 276. col. fluor.</td>
<td>0.02</td>
<td>0.1000</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>TURF MOOR VEIN 507. amber fluor.</td>
<td>2.6</td>
<td>0.02</td>
<td>0.0577</td>
<td>60</td>
</tr>
<tr>
<td>BOWLAND TROUGH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SKELERON MINE 415, 415. col. fluor.</td>
<td>6.0</td>
<td>0.15</td>
<td>0.0250</td>
<td>60</td>
</tr>
<tr>
<td>RAUILL QUARRY 168 - 170. purple fluor.</td>
<td>6.5</td>
<td>0.65</td>
<td>0.1000</td>
<td>60</td>
</tr>
</tbody>
</table>
FIG. 5.4

COMPARISON OF K/Na RATIOS.

FORMATION WATERS.
(White 1963,1965; Graf 1966; Downing 1967; Anderson 1945)

MISSISSIPPI VALLEY AREA.
(Hall & Friedman 1963
Roedder et al. 1963)

VOLCANIC WATERS.
(White et al. 1963)

ASKRIGG BLOCK AREA.

OTHER ORE DEPOSITS.
(Roedder 1972)

ALSTON BLOCK AREA.
(Sawkins 1966)

POTASSIUM / SODIUM RATIO BY WEIGHT.
FIG. 5: CALIBRATION CURVES FOR CHLORIDE, MAGNESIUM.

Chloride:

Magnesium:

10 ppm  5 ppm  0 ppm

150 100 50

DEFLECTION
<table>
<thead>
<tr>
<th>SAMPLE LOCATION</th>
<th>CONCENTRATION 10 ml (ppm)</th>
<th>SAMPLE LOCATION</th>
<th>CONCENTRATION 10 ml (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl^-</td>
<td>Mg^2+</td>
<td></td>
</tr>
<tr>
<td>GREENHOW RAKE</td>
<td>2.65</td>
<td>0.30</td>
<td>KETTWELL K/6</td>
</tr>
<tr>
<td></td>
<td>2.80</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>GALLOWAY VEIN</td>
<td>3.00</td>
<td>0.37</td>
<td>SEATA MINE</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>SUN VEIN</td>
<td>N.a.</td>
<td>0.34</td>
<td>WET GROOVES</td>
</tr>
<tr>
<td>PROVIDENCE MINE</td>
<td>0.85</td>
<td>0.30</td>
<td>BRAITHEWAITE</td>
</tr>
<tr>
<td>LULLY MINE</td>
<td>4.09</td>
<td>0.72</td>
<td>WURTSON MINE</td>
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<tr>
<td>GILL HEADS VEIN</td>
<td>13.45</td>
<td>0.54</td>
<td>KELD HEADS MINE</td>
</tr>
<tr>
<td></td>
<td>26.65</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>INDIAN VEIN</td>
<td>0.85</td>
<td>n.d.</td>
<td>WEST BURTON</td>
</tr>
<tr>
<td>JOYCE VEIN</td>
<td>0.66</td>
<td>0.34</td>
<td>CLOUDS</td>
</tr>
<tr>
<td>WRIGHT VEIN</td>
<td>0.15</td>
<td>0.26</td>
<td>BIRCHETT HILL</td>
</tr>
<tr>
<td>RODHILL VEIN</td>
<td>0.90</td>
<td>0.22</td>
<td>RIMINGTON</td>
</tr>
<tr>
<td>ESCOE HILL</td>
<td>45.80</td>
<td>0.48</td>
<td>RAYGILL</td>
</tr>
<tr>
<td>YARNBURY</td>
<td>1.45</td>
<td>0.58</td>
<td>BURTON LEVEL</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIDDLE VEIN</td>
<td>19.20</td>
<td>1.17</td>
<td>OLD RAKE</td>
</tr>
<tr>
<td></td>
<td>2.48</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>BYCLIFFE VEIN</td>
<td>0.40</td>
<td>0.40</td>
<td>NORTH RAKE</td>
</tr>
<tr>
<td>SLANTER VEIN</td>
<td>2.00</td>
<td>0.24</td>
<td>SURRENDER GROUND</td>
</tr>
<tr>
<td>MOSSDALE</td>
<td>n.a.</td>
<td>2.23</td>
<td>MARTIN VEIN</td>
</tr>
<tr>
<td>KETTWELL K/16</td>
<td>0.90</td>
<td>0.26</td>
<td>HUNGRY HUSHES</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>KETTWELL K/24</td>
<td>6.70</td>
<td>0.34</td>
<td>DAM Rigg VEIN</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KETTWELL K/28</td>
<td>n.a.</td>
<td>0.22</td>
<td>TURF MOOR MINE</td>
</tr>
</tbody>
</table>
FIG. 5, 7.

COMPARISON OF Cl/Na RATIOS.

FORMATION WATERS.
(White 1963; 1965; Graf 1966)

MISSISSIPPI VALLEY AREA.
(Hall & Friedman 1963; Roedder 1963)

CARBONIFEROUS WATERS.
(Anderson 1945; Downing 1967)

ASKRIGG BLOCK.

CHLORIDE / SODIUM RATIO BY WEIGHT.
FIG. 5.8

COMPARISON OF Mg/Na RATIOS.

MISSISSIPPI VALLEY
(Hall & Friedman 1963, Roedder 1963)

AS KRIGG BLOCK.

FORMATION WATERS

CARBONIFEROUS WATERS
(Downing 1967, Anderson 1945)

% FREQUENCY
0 0.2 0.4 0.6
0 0.2 0.4 0.6
0 0.2 0.4 0.6
MAGNESIUM / SODIUM
RATIO BY WEIGHT.
Fig. 5.9.

PLATE SHOWING THE SOLID INCLUSIONS OF SULPHIDES IN FLUORITE.

5.9.a. A typical rounded pyrite inclusion in colourless fluorite, Greenhow Rake, Greenhow Hill.

5.9.b. A large inclusion of galena with the characteristic polishing grooves in colourless fluorite, Gill Heads Vein, Appletreewick.

5.9.c.d. Large rounded inclusions of chalcopyrite in colourless fluorite, Worton Mine, Bainbridge, Wensleydale. Here the chalcopyrite inclusions show a rim due to secondary oxidation.

5.9.e.f. Large high relief reticulate inclusions of nickeliferous pyrites in colourless fluorite from the Wharfedale Mine, Kettlewell.

Bar = 300 \( \mu \).
PLATE SHOWING THE SOLID INCLUSIONS OF SULPHIDES IN FLUORITE.
**Fig. 5.10.**

**ELECTRONMICROPROBE STUDIES ON SULPHIDE INCLUSIONS**

5.10.A  A large nickeliferous pyrite inclusion in fluorite from the Kold Heads Mine, Wensleydale. The inclusion is shown in reflected light in A.1. A six minute X-Ray Image scan for sulphur is shown in A.2. The marked zoning with respect to nickel is shown in A.3 as an X-Ray Image for a ten minute scan for nickel.

5.10.B  A sulphide inclusion in fluorite from the Gill Heads Vein, Appletreewick, shown in B.1 as the reflected light image. The larger lighter area is in fact chalcopyrite, the darker area pyrite. This was confirmed in B.2 with a six minute scan for iron which produced an X-Ray Image depleted in one area for iron. A subsequent ten minute scan for copper produced an X-Ray Image photograph (B.3.) revealing the sharp outline of the pyrite inclusion. This dual association of both pyrite and chalcopyrite is very common in sulphide inclusions in fluorite from the Askrigg area.
FIG. 5, 10. ELECTRONMICROPROBE STUDIES ON SULPHIDE INCLUSIONS.


2.

3.

2.

3.
FIG. 5.11. PROBE SCAN OF A PYRITE INCLUSION IN FLUORITE, KELD HEADS V. WENSLEY.
### Table 5.12 Summary of Electron Microprobe Analysis of Sulfide Inclusions in Fluorite from N.W. Yorkshire

<table>
<thead>
<tr>
<th>Sample No. &amp; Location</th>
<th>Sulfide Phase</th>
<th>No. Anal.</th>
<th>Atomic % Elements</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
<th>Cd</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 67 Middle V Moor</td>
<td>Pyrite</td>
<td>2</td>
<td>34.5</td>
<td>64.9</td>
<td>0.5</td>
<td>0.03</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite</td>
<td>4</td>
<td>28.2</td>
<td>52.2</td>
<td>19.3</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>2. 74 Esco Hill Craven</td>
<td>Pyrite</td>
<td>4</td>
<td>29.2</td>
<td>70.6</td>
<td>0.2</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite</td>
<td>4</td>
<td>23.8</td>
<td>57.3</td>
<td>18.9</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3. 233 Keld Heads Mine Wensley</td>
<td>Pyrite</td>
<td>17</td>
<td>37.1</td>
<td>49.3</td>
<td>0.3</td>
<td>4.80</td>
<td>-</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Bravoyite</td>
<td>2</td>
<td>38.1</td>
<td>61.5</td>
<td>0.1</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4. 461 Skelerton Mine, Rimington</td>
<td>Pyrite</td>
<td>3</td>
<td>32.9</td>
<td>67.1</td>
<td>-</td>
<td>0.02</td>
<td>0.01</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: The table provides a summary of electron microprobe analysis of sulfide inclusions in fluorite from N.W. Yorkshire, including sample numbers, locations, and atomic percentages of various elements (Cu, Ni, Zn, Cd, Mn).
FIG. 5.13.
HISTOGRAMS OF TRACE ELEMENT RESULTS FROM GALENAS AND SPHALERITES.

% FREQ

SILVER

STRONTIUM

COPPER

NICKEL

ZINC

CHROMIUM

CONCENTRATION ppm.
CHAPTER 6
GENESIS OF THE ORE DEPOSITS OF THE ASKRIGG BLOCK IN THE LIGHT
OF FLUID INCLUSIONS STUDIES

6.1. NATURE OF THE PROBLEM

The base metal deposits found in the Lower Carboniferous strata
of the Askrigg block represent a substantial concentration of these
elements in this particular area of the Earth's Crust. The compar­
ison of these concentrations is taken from Dunham (1974):-

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Zn</th>
<th>F</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Earth's Crust</td>
<td>0.0016</td>
<td>0.015</td>
<td>0.073</td>
<td>0.026</td>
</tr>
<tr>
<td>Old Gang Area</td>
<td>15</td>
<td>1</td>
<td>3.5</td>
<td>35.5</td>
</tr>
</tbody>
</table>

This concentration of elements has resulted from the operation
of the process of ore deposition due to the reaction between the ore
fluid and the mineral-logic environment. The lack of any high tem­
perature metamorphism in the wall rocks has established that this ore
fluid was at moderate temperatures.

The process of hydrothermal ore deposition can be ascribed
to four main evolutionary stages. The first is the source of the
ore fluids, be it a cooling magma, connate waters or weathering of
sedimentary rocks. Secondly the ore and other constituents then
have to be selectively concentrated into the hydrous phase under
favourable phsyio-chemical conditions. Thirdly, after concentration
a migration path is initiated (usually upwards) by pressure differ­
etials along which the ores are then transported. Finally, the ore
is then deposited in suitable host rocks by selective precipitation
due to physiso-chemical interactions with the new host environment.
The amount and variety of the orebody formed is a function of the
composition of the fluid at each stage of the process. Natural
hydrothermal systems are complex incongruent mixtures of numerous
elements. Helgeson (1970) describes them as a function of sixteen
important thermodynamic characters:-
The various processes operating during hydrothermal ore deposition include:

1. reversible/irreversible reactions,
2. metasomatic alteration of silicate and carbonate host rocks,
3. diffusion to and from reaction fronts in the wall rock,
4. bulk flow of liquid in the fracture system,
5. oxidation - reduction reactions,
6. cotectic, peritectic precipitation of minerals,
7. temperature and pressure changes.

Any postulated genetic model for ore deposition must therefore include some of these processes to account for the mineral assemblages produced and their attendant zonal, paragenetic and replacement features.

Geologists have tended to describe this hydrothermal process in the form of simple, end-member models. Each theory has had its adherents, with waxing and waning periods of popularity. Sandberger (1882) proposed lateral seepage as the dominant process whilst Posepny (1893) favoured a deeply circulating meteoric source. The views of Lindgren (1935) resulted in the dominance of the magmatic-hydrothermal school of thought. Recent attention has also focused on the epigenetic-syngenic debate (Dunham 1963). Undoubtedly some hydrothermal ore deposits can be described in terms of simple end-member processes. The origins, however, of numerous other hydrothermal ore deposits, the Mississippi Valley type in particular, have been the subject of much debate in recent years. It would seem to show that we need a multivariate approach to obtain valid genetic models in the light of much recent evidence regarding this important group of deposits (Brown 1967).
The study of fluid inclusions can provide important data on the density, temperature, salinity and composition of the ore fluid responsible for these deposits. Any theory of genesis for the deposit concerned must be compatible with the fluid inclusion evidence. An incompatible theory must therefore refute or otherwise account for the fluid inclusion evidence. With careful application fluid inclusion data does provide important constraints on theories of ore deposition. Indeed our understanding of the nature of the ore fluid has benefited greatly in recent years from fluid inclusion studies. In combination with studies of the isotopes of sulphur, hydrogen, oxygen and the present-day active geothermal systems, the theories of ore genesis are indeed undergoing a radical review.

6.2. A REVIEW OF MISSISSIPPI VALLEY TYPE DEPOSITS

6.2.1. The Main Geological Features

The majority of Mississippi Valley type deposits are stratabound occurring as discordant veins, pore and breccia infill with a marked preference for certain stratigraphic horizons. The Bearng or Grassington Grit of the Askrigg block is a good example of this phenomenon. They also tend to a stratiform aspect on a small scale, often occurring as concordant layers parallel to the bedding. As a group they are invariably found in a host of limestone, dolomite sedimentary units of predominantly Paleozoic age. Beales and Onasick (1970) estimated that up to 85 per cent of these deposits were located in carbonate hosts compared to only 6 to 7 per cent in sandstones. A basic palaeogeographic control is revealed by their frequent location in belts of elongate reef complexes, such as the Craven Reefs. These cratonic platform deposits usually exhibit mineralization in the crests and flanks of major domes or anticlines on the flanks of major sedimentary basins. These positive structural features thus provide the structural and stratigraphic traps as the point of least resistance for the escape of buried fluids under a considerable confining pressure.
Slight structural deformation usually accompanies the mineralization with deposition controlled by faults, fractures and folds. Deep lineaments, often extending into the basement act as foci where they intersect the carbonate strata (Heyl 1972).

Each district exhibits various types of localized ore occurrence, fig. 6.1. illustrates some of the more common ones. In the Skirrigg orefield the shale beds often act as important confining horizons, a similar situation applies to the toadstones and clay wayboards, both are volcanic horizons found in the Derbyshire orefield. The sulphide deposits themselves can exhibit highly variable forms on a fine scale, often manifested as areas of barren ground interspersed with areas of rich ore. From stratigraphic reconstructions the ore deposition is assumed to have occurred at depths not greater than one kilometer (White 1968). Where associated igneous rocks are found they are invariably alkaline in character (Brock and Heyl 1961).

The mineralogy is generally of a simple type but it must be noted that these deposits represent quite remarkable segregations of galena, sphalerite, fluorite and baryte in the Earth's Crust. Pyrite marcasite, and chalcopyrite are widespread accessory sulphide minerals in a gangue of calcite, aragonite, dolomite, quartz, siderite and ankerite (Ohle 1959). This simple gross mineralogy is often accompanied by areas locally enriched in various trace constituents. These include the sulphides of silver, cadmium, copper, cobalt, nickel and mercury (Heyl et al. 1959). The zonation of these deposits with respect to the ore, gangue and trace elements is a dominant feature, the Pennine orefields being notable examples. Enrichment of elements like iron, manganese, titanium, potassium, silicon, aluminium and magnesium occurs near to the ore. (Iweson 1969) has noted strontium depletion near to the Pennine mineral veins and a marked zirconium enrichment.

(86)
This essentially simple mineralogy however, belies the fact that these deposits can show important differences in lead and sulphur isotope ratios, mineralogy, trace element content, zonation and geologic settings (Ohle 1959; Heyl 1969). These differences probably reflect the permutation on a simple theme by a series of varied reactions during the evolutionary progress of the hydrothermal solution. Textural variations are common between deposits with polycrystalline masses, crustified veins, colloform textures and perfect crystal development as vugh fillings.

Isotope studies of both sulphur and lead in these deposits have produced somewhat conflicting results and consequent interpretations, especially in the Northern Pennine orefield. Mitchell and Krouse (1971) report a very narrow spread of $\delta^{34}S$ values between -0.6 to -3.8 per mil with a mean of -2.2 per mil for the sulphides. This is in direct contrast to the widespread of $\delta^{34}S$ values of -5.9 to 15.0 per mil for the sulphides and 17.1 to 20.9 per mil for baryte in the Aston orefield reported by Solomon et al. (1971). Most Mississippi Valley type deposits exhibit a broad $\delta^{34}S$ range (Ault and Kulp 1960). The Pine Point deposit however also exhibits a narrow $\delta^{34}S$ value (Sasaki and Krouse 1969). Greig et al. (1971) note increasingly negative $\delta^{34}S$ values upwards along and outwards from the Silvermines Fault. This is due to an increase of oxygen fugacity and pH away from the fault. They suggest a juvenile sulphur source and their diagram, reproduced here as fig. 6.2, provokes interesting parallels with the Alston block results.

The lead isotopes of Mississippi Valley type deposits usually exhibit slight variations within each deposit and often show a wide regional systematic variation (Brown 1967; Heyl 1969). These deposits also show enrichment in radiogenic lead to give the predominantly J lead ages (Heyl et al. 1966).
The Askrigg data of Mitchell and Krouse indicates a narrow isotopic range of J leads similar to Pine Point (Comming and Robertson 1969). Moorbath's (1962) data for the Alston Block, Derbyshire and Ireland was also recalculated and they show remarkable compatibility with that for Askrigg (fig. 6.3.)

These deposits thus exhibit very many common features and yet quite striking differences of structural setting, mineralogical zoning, trace element content and isotopic composition which can often occur between adjacent orefields (Heyl 1969).

6.2.2. A Review of Fluid Inclusion Studies

This particular group of deposits has been the attention of the most rigorous fluid inclusion analysis (Roedder 1972). The analyses performed indicate a quite remarkable consistency of results in numerous deposits from various localities.

Homogenization studies indicate temperatures of deposition from 70°C to 220°C, except the Irish deposits (Greig et al. 1971) have most deposits temperatures in the range of 100°C to 150°C. The homogenization results from various Mississippi Valley deposits are presented in table 6.4. The primary inclusions are generally of a two phase liquid - vapour variety, sometimes with the presence of immiscible oil globules. Pressure corrections applied to the results are generally small, indicating a shallow depth of emplacement. The salinities of the fluids vary between 15 to 30 per cent equivalent by weight of sodium chloride (Roedder 1963; 1967b; Hall and Friedman 1963) with an average of 20 per cent. Again these deposits are remarkably consistent in exhibiting very high saline fluids (chapter 4). Thus the fluid must also have had a density greater than the 1.0 kgm$^{-3}$ of water, often as high as 1.2 kgm$^{-3}$ (Roedder 1968b). The composition of this fluid is that of a calcium - sodium, chloride brine with (88)
Cl⁻ > Na⁺ > Ca²⁺ > K⁺ > Mg²⁺ > Br⁻ (Roedder 1967a) This brine as a 3 molar solution is quite capable of transporting large amounts of metals as chloride complexes (Czamanske et al. 1963; Pinckney and Haffty 1970). Study of isotopic ratios in the inclusion fluids, especially those of hydrogen and oxygen can provide important genetic information. The Mississippi Valley type deposits have isotopic ratios consistent with a pore-water origin (White 1973), compared to the predominantly magmatic influences of Providencia, Mexico (Rye 1964, Rye and O'Neill 1968).

The fluid inclusion studies on this group of deposits emphasise the remarkable consistency of the conditions of formation with regard to the temperature, salinity and composition of the ore fluid. All this evidence thus points to a common process of formation and genesis. To this must be added the proviso of local geological and structural differences along the evolutionary paths of the ore fluids.

6.3. FLUID INCLUSION STUDIES AND GENESIS OF THE ASKIRGG ORE DEPOSITS

The fluid inclusion studies of chapters 3, 4, and 5 reveal the presence of a hydrothermal fluid of quite remarkable compositional consistency. The ore-forming fluid was a low temperature saline fluid, four to ten times as saline as sea water. In chapter 5 the composition was found to be that of connate water similar to the calcium - sodium -chloride oilfield brine of White (1958). This type of ore fluid has also been demonstrated to contain quite large amounts of heavy metals (Czamanske et al. 1963; Pinckney and Haffty 1970) in the presence of very small amounts of sulphur.

The high salinities, temperatures, and general structural setting (Snyder 1967) are incompatible with a meteoric or syngentic source. However a syngentic origin by subsequent movement of elements during compaction and diagenesis is likely for numerous...
small occurrences of this type of deposit (Heyl 1968). For the large scale deposits however, we are generally dealing with a large scale regional process responsible for the introduction of these connate solutions into the host rocks. The combination of high salinities and low temperature is also incompatible with a direct magmatic derivation. To obtain a magmatic fluid of similar salinity requires a much higher temperature than is obviously present in these deposits (Roedder 1968b). The deuterium content of the inclusion fluids (Hall and Friedman 1963) also seems incompatible with a direct magmatic influence (Rye 1966). The evidence of isotopic ratios in inclusion fluids is however limited to a few deposits only, we need far more analyses before definite, firm conclusions can be placed on this evidence. The potassium enrichment of inclusion fluids was also thought to indicate a direct magmatic influence. This has since proved to be false, as the potassium/sodium ratio is usually dependent on the temperature (White 1965).

Comparison with present day connate waters of similar type (White et al. 1963) indicates calcium enrichment and magnesium depletion relative to present day ocean water. High chloride brines of similar composition are generally found in the deeper parts of sedimentary basins, with salinity increasing with depth of burial. White (1965) notes sulphatic waters dominant at depths up to 600 metres, bicarbonate waters are present to intermediate depths of 600 to 800 metres whilst chloride is dominant at depths of greater than 800 metres. A linear increase of concentration with depth has been widely noted in pre-Tertiary brines in undisturbed sedimentary basins through the world by Dickey (1969). Downing and Howitt (1969) report a similar salinity increase in depth in Carboniferous formation waters from the East Midlands.
The fluorspar content of modern formation waters also tends to show an increase with depth (Dunham 1970) from an average of 0.4 ppm in shallow waters to 3.24 ppm in deep formation waters. Modern formation waters are very dilute solutions of base metals (Rittenhouse et al. 1969). The formation of an ore deposit from these solutions thus requires an effective concentration mechanism.

The high salinities of formation waters can be produced by various mechanisms. Solution of evaporites by meteoric waters could provide the high salinities and also provide large amounts of potassium and barium (Davidson 1966), as would seem to be the case for the Salton Sea and Red Sea areas (White 1968). Concentrations can also be increased by membrane filtration by fine-grained sediments (White 1965). The negative fixed charges of the clay minerals montmorillonite and illite are balanced by absorbed exchangeable cations. An increase in both the calcium/chloride and calcium/sodium ratios is then produced by compaction of sediments in the direction of least pressure resistance. Early diagenetic changes between the pore-water and sediment are also important processes in brine evolution. As compaction proceeds a hydrostatic head is maintained by meteoric water at surface. The hydrostatic pressure is thus built up and when triggered results in the migration of brines in the direction of least pressure, that is to the basin's flanks (Dozy 1970), leaching metals from the host rocks in transit.

The ore fluid in the Askrigg area contains high concentrations of chloride in a predominantly sulphur deficient brine. As we have seen in section 5.7.3. from chemical considerations the metals must have been carried as chloride and not bisulphide complexes in the three molar sodium chloride brines. As noted in section 3.8. wetherite predominates as the major barium gangue mineral in the Swaledale/Arkengarthdale area. This reinforces the view of a barium rich, sulphate deficient solution as wetherite is
stable at pH 7, and at a carbon dioxide fugacity of 0.1 atmospheres when the sulphate content is less than $10^{-4}$ moles (Holland 1965). The source of sulphur is thus somewhat problematical as excess sulphur must be present to precipitate the galena and sphalerite. This mixing of a sulphide-rich solution derived from pyrite in the host rock and chloride brine was proposed by Lowenberg (1961). Non-biogenic reduction of sulphate by methane at low temperatures (Barton 1967) could be feasible as all constituents are present in the inclusion fluids:

$$
\text{CH}_4 + 2\text{ZnCl}_2 + \text{SO}_4^{2-} + \text{Mg}^{2+} + 3\text{CaCO}_3 \rightarrow \text{ZnS} + 2\text{Ca}^{2+} + \text{Mg(CO}_3\text{)}_2^{2+} + 2\text{Cl}^- + 2\text{HCO}_3^- + \text{H}_2\text{O}
$$

The organic reduction of sulphate by bacteria (Skinner 1967) has also been postulated. The marked preference of these deposits for carbonate host rocks has been cited by Beales and Onarick (1970) as due to the presence of large amounts of biogenic sulphur in 'sour' hydrogen sulphide rich pore-fluids. Mitchell and Krouse (1972) however state the narrow isotopic ranges obtained from galena as indicative of a juvenile source. This is in direct contrast to Solomon et al. (1972) who ascribe Carboniferous formation waters as the main source of sulphate. Recent evidence from Greig et al. on the Irish deposits indicates marked fractionation of an original juvenile source of sulphur which produces a pattern remarkably similar to the Alston orefield results of Solomon et al. (1971).

The temperature of the ore fluids is also a problem. If a normal geothermal gradient of 1°C per 30 metres burial is applied the Askrigg ore fluids must have attained depths of at least 6,000 metres before rising to the environment of ore deposition. Most of these ore bodies have been emplaced at shallow depths (White 1968) and they must therefore have had a
specific heat source. A higher depth of deposition could be assumed but this is unlikely. Heated brines in the adjacent basins could have been released and migrated rapidly upwards with little effective heat loss. Magmatic heat could have been supplied but there is little evidence of magmatic activity during the period in question in the Askigg block. Higher regional geothermal gradients related to mantle convection could have been present but are unlikely.

Concluding Remarks

It is of the utmost importance to bear in mind that fluid inclusion evidence can be used only to place constraints on postulated theories of ore genesis. The study of fluid inclusions present in the fluorite gangue from the Askigg area has provided new evidence on the temperature, salinity and aspects of the chemistry of the ore-forming fluid in that part of the Northern Pennine Orefield.

The homogenization temperatures and high salinities exhibited in the Askigg orefield are consistent with fluid inclusion data from other similar deposits (Roedder 1972). The ore deposits of the Northern Pennine orefield occur in a predominantly vein situation within a limestone and sandstone host in Upper Carboniferous strata. They exhibit a marked stratiform aspect, the mineralization is invariably located in a restricted vertical sense within bearing beds. This contrasts with the extensive pore and breccia infill of the Pine Point occurrence for example, which is also associated with widespread dolomitization. Dolomite and dolomitization are found in the Northern Pennine orefield but is by no means as ubiquitous as in the case of Pine Point. The study of the isotopes of sulphur and lead in both gangue and ore minerals from the Northern Pennine orefield has resulted in conflicting results. Solomon et al. (1971) indicate a broad spread of isotopic ratios for the Alston area whilst Mitchell and Krouse (1971) report J-type leads with a narrow isotopic spread from Greenhow Hill in the Askigg area. The significance of this isotope data with regard to the definition of Mississippi Valley-
type deposits is still a matter of debate (Brown 1967; Heyl et al. 1974) and illustrates the apparent regional nature of isotopic data within this large group of deposits. This contrasts with the marked gross similarity of homogenization temperatures, salinities and sodium-potassium ratios indicated by the fluid inclusion data from numerous deposits in very similar geological situations.

The presence of diversity of geochemical characters within adjacent orefields is well illustrated by evidence from the Northern Pennine orefield itself. The Alston area exhibits a higher temperature aspect, rare earth enrichment, a greater variety of mineral species, a broad spread of isotopic data and a larger area of discovered and worked mineralized ground, reflected in the greater mining activity of past and present. The Askrigg area however, has slightly lower homogenization temperatures, little rare earth enrichment, J-type leads, a smaller variety of mineral species and a more restricted mineralization reflected in the lesser amount of mining activity. Yet fluid inclusion studies by Sawkins (1966a), Smith (1973a) and the author indicate the ore-fluid in both areas to have been heated, connate waters in very similar geological conditions. This indicates both areas to have been affected by a common geological process yet with local geological conditions producing a certain amount of geochemical diversity.

The fluid inclusion studies indicate the ore-forming fluid for large numbers of Mississippi Valley type deposits to have been a chloride-rich sodium-potassium-calcium brine with small amounts of sulphur. A source of sulphur for these lead-zinc sulphide deposits is thus somewhat of a problem and has resulted in a number of contrasting hypotheses being postulated. The role of Permian evaporates, particularly anhydrite and gypsum, to provide the sulphide (as sulphate) and potassium has been postulated by Davidson (1966) but their effect has been discounted by Dunham (1966). The presence of evaporites in Carboniferous strata in close proximity and in the large amounts required has not been demonstrated in
the flanking Carboniferous basins of the Askrigg area.

The mineralizing brine was also heated to relatively high temperatures and the source of this heat is crucial to any postulated theory of origin. Magmatic heat is the obvious contender but magmatic activity and the presence of a higher geothermal gradient in the period in question has also not been demonstrated in the Askrigg area. Heat could also have been supplied by the inorganic or organic exothermic reduction of sulphate in the presence of hydrocarbons. The association of the Askrigg deposits with large hydrocarbon reservoirs has also not been demonstrated. Oil globules have been infrequently observed in the ore-field and bitumens are also present in the mineralized areas. They are however invariably found in very small amounts and would appear to be of minor importance only. Interest has recently focused on this problem (Dunsmore 1973) but this theory requires the close proximity of anhydrite deposits to the mineralized areas in conjunction with extensive dolomitization and large amounts of hydrocarbons. Neither of these requirements would appear to fit the available evidence from the Askrigg area.

The presence of base metal ions in oilfield waters of similar type to the inclusion fluids has been reported (Rittenhouse et al. 1969; Hitchon et al. 1971). These base metal ions however are present in low concentrations when compared to the extremely high concentrations reported in analyses of fluid inclusions (Czamanske et al. 1963; Pinckney and Haffty 1970). Hirst (1970) reports that shale deposits can easily provide sufficient base metal quantities to form an ore deposit. An effective concentrating mechanism for these base metal ions is thus required to equate these two observations. An alternative is to invoke large amounts of fluid flow of waters with low metal concentrations to form an ore deposit. Metals could also have been selectively added to the brine during diagenesis of the host sediments but this aspect needs further experimental evaluation.

The source of large amounts of both fluorine and barium for the
Northern Pennine ore deposits has also been a matter of debate. Sawkins (1966a) postulated a source in nearby coalfield waters whilst Solomon et al. (1971) favour a local formation water source. Both fluorine and barium are elements associated extensively with acid igneous activity and perhaps some magmatic contributions either directly or indirectly by the leaching of the granitic basement cannot be ruled out on the available evidence. Diagenetic processes in the basins could also provide these elements to the brine but the extent of this contribution is difficult to assess.

To summarize then the available evidence for a possible genetic theory, the observed characteristics of the Askrigg mineralization need to be reconciled with the additional fluid inclusion evidence. The ore-forming fluid was a very saline, heated, sodium-potassium-(calcium)-chloride sulphur (or sulphate)-deficient brine with a similar composition to oilfield waters. A model of mixing of two fluids, one chloride rich, the other sulphide rich, is thus postulated to explain all features of the Askrigg mineralization.

On the basis of this new fluid inclusion evidence deeply circulating connate waters from the flanking Craven and Cleveland Basins are postulated as the main ore-forming fluid medium. Higher homogenization temperatures have been recorded in the Craven Basin and this observation lends support to a theory of heated brines squeezed out of the flanking sedimentary basins. The higher temperatures of the ore-forming fluid were probably obtained by descent of the brines to depths of up to 6 kilometers. The high salinities were probably obtained by processes such as membrane filtration. The base metals were probably leached from the host sediments and carried in solution predominantly as chloride complexes. Diagenetic change in the host sediments also probably played an important role. Its effect though is difficult to estimate from the semi-quantitative fluid inclusion analyses available from the Askrigg area. The brines then migrated through suitable aquifers to the flanks of the sedimentary basin in response to compaction pressures and density differentials. Pulses of brine flow could also have been triggered by faulting and other tectonic activity. The basic
gravitational drive resulted in upward migration via suitable sandstone aquifers and channelways such as folds and faults. These fluid transport routes were probably complex with shale damming, palaeokarst features, blanket sands and local permeability throats all adding to diversify the fluid flow. The heated brines entered the area of least pressure resistance, the ore environment and mixed with a local sulphide-rich brine. The ore and gangue minerals were deposited in response to dilution, temperature loss and oxidation reactions at the chloride/sulphur brine interface.
The postulated process is shown diagrammatically in fig. 6.5.

However, this simple hypothesis of the mixing of two solutions does require large volumes of solution. For the Askrigg area, taking the fluorite reserves at one million tons, something in the region of $10^{18}$ gm of water is required, using the data of Holland (1967). The polyphase nature of the mineralization however indicates repeated influxes of solution spread over a long time span (Ineson and Mitchell 1973).

The location of all the major fluorite occurrences away from the central Wensleydale granite along major fractures at the edges of the block is probably related to the unfractured nature of this granite. In comparison to the Woardale granite with the megafraction of the Burtonford Disturbance allowing the granite to act as the structural channelway for the ascending fluids.

The contrasts in temperature and trace element content of fluorite from the adjacent Askrigg and Alston orefields stresses the need for a multivariate approach to their genesis. Contributions from a magmatic source of heat, metals, and trace elements cannot be ruled out for the Alston area (Smith 1973a) or the Mississippi Valley area itself (Heyl 1969). The data of Mitchell and Krouse (1972) point to a juvenile source for some of the sulphur and lead in the Groenhow area indicating some magmatic contributions.

The conclusions reached from the fluid inclusion studies indicate the need for a multivariate approach to the genesis of this type of deposit. Some form of mixing of two different connate fluids is required to explain all the features of the mineralization. Further avenues of research should include a detailed quantitative analysis of the inclusion fluids with particular reference to the isotopes of hydrogen, oxygen and sulphur. More data is also

(97)
required on the distribution of sulphur and oxygen isotopes in baryte and galena in relation to the major mineralized faults in the light of recent discoveries in Ireland by Grieg et al. (1971). The shales of the flanking sedimentary basins were probably the main source of the ore metals. Detailed whole rock analysis is needed to either verify or disprove this statement. The presence of quite substantial amounts of nickel in pyrite inclusions in fluorite establishes the need for further research on this topic. A magmatic contribution to the fluids cannot be ruled out on the available evidence. However, White (1973) stresses the diverse origins of most hydrothermal deposits and the variety of simple end-member models. The thermodynamic parameters of the mixing of sulphur-rich and sulphur-deficient brines with respect to zoning and precipitation mechanisms also need to be critically evaluated.
FIG. 6.1.
IDEALIZED DIAGRAM OF SOME LOCATIONS OF THE
MISSISSIPPI VALLEY DEPOSITS. (after Callahan 1967)

Solution collapse breccia
Thinning collapse structure
Reef
Drape
Talus
Mud bank
Shale damming
Facies change
BASEMENT.
SURFACE
UNC.
FIG. 6.2.
The isotopic variation of baryte and pyrite at 250°C, Mogul Mine (Greig et al. 1971)

-30
-32
-34
-36
-38
-40

LOG $f_{O_2}$

-26
-15
0
+11
+26

$baryte$

$\delta^{34}S_{py}$
$\delta^{34}S_{bar}$

 hematite

magnetite

pyrite

juvenile source

pyrrhotite

graphite

PH
FIG. 6.3.
COMPARISON OF LEAD ISOTOPE RATIOS.

DATA FROM: Heyl 1969,
Greig et al. 1971.

NON-RADIgenic LEADS

RADIogenic \( ^{187} \text{Pb} / ^{204} \text{Pb} \) LEADS

Mississippi Valley

Irish Deposits

Pennine Orefields

Vesuvius lead
<table>
<thead>
<tr>
<th>AREA</th>
<th>MINERAL</th>
<th>HOMOGENIZATION TEMP. RANGE °C</th>
<th>SOURCE</th>
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<td>ZnS</td>
<td>115 - 135</td>
<td>Newhouse 1933</td>
</tr>
<tr>
<td>Missouri</td>
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<td>90 - 135</td>
<td>Schmidt 1962</td>
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<td>ZnS I</td>
<td>83 - 120</td>
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<tr>
<td>Kansas and Oklahoma</td>
<td>ZnS II</td>
<td>83 - 105</td>
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</tr>
<tr>
<td></td>
<td>Dolomite</td>
<td>76 - 96</td>
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<td></td>
<td>Calcite</td>
<td>52 - 68</td>
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<tr>
<td>Kentucky</td>
<td>Zns</td>
<td>70 - 95</td>
<td>Newhouse 1933</td>
</tr>
<tr>
<td>Illinois</td>
<td>Zns</td>
<td>75 - 121</td>
<td>Bailey and Cameron 1951</td>
</tr>
<tr>
<td>(Cave-in rock)</td>
<td>CaCO₃</td>
<td>61 - 115</td>
<td>Grogan &amp; Schode 1952</td>
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<td></td>
<td>CaF₂</td>
<td>113 - 129</td>
<td>Freas 1961</td>
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<tr>
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<td>ZnS I</td>
<td>84 - 103</td>
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<td></td>
<td>Qtz I</td>
<td>81 - 105</td>
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<td>CaF₂ II</td>
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<td>ZnS₂ II</td>
<td>81 - 92</td>
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<td>E. Tennessee</td>
<td>Qtz</td>
<td>195 - 207</td>
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<td>CaF₂</td>
<td>115 - 125</td>
<td>Heyl et al. 1966</td>
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<td>J.C. Tennessee</td>
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<td>Calcite</td>
<td>82 - 149</td>
<td>Roedder 1971</td>
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<td>E. Tennessee</td>
<td>Zns, CaF₂</td>
<td>72 - 132</td>
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<td></td>
<td>Dolomite</td>
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<tr>
<td></td>
<td>Qtz</td>
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<td></td>
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<tr>
<td>C. Tennessee + C Kentucky</td>
<td>CaF₂ Zns</td>
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<td><strong>UPPER MISSISSIPPI VALLEY</strong></td>
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<td>Wisconsin</td>
<td>Zns</td>
<td>80 - 105</td>
<td>Newhouse 1933</td>
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<tr>
<td>Wisconsin</td>
<td>CaCO₃</td>
<td>50 - 79</td>
<td>Bailey and Cameron 1952</td>
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<td>CaCO₃II</td>
<td>71 - 74</td>
<td>Erickson 1965</td>
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<td></td>
<td>CaCO₃III</td>
<td>47 - 63</td>
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<td></td>
<td>CaCO₃IV</td>
<td>46 - 56</td>
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<td><strong>PINE POINT, NORTH WEST TERRITORIES</strong></td>
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<td></td>
<td>Dolomite</td>
<td>140 - 360</td>
<td>Campbell 1966</td>
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<tr>
<td></td>
<td>Zns</td>
<td>51 - 97</td>
<td>Roedder 1968b</td>
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A HYPOTHETICAL SECTION OF THE ASKRIGG BLOCK IN LATE PERMIAN TIMES SHOWING A GENETIC MODEL FOR THE MINERALIZATION.
APPENDIX A

SUMMARY OF HOMOGENIZATION RESULTS FROM FLUID INCLUSIONS IN FLUORITE FROM THE ASKIRK BLOCK.

LIST OF TABLES.

A.1. APPLETREHOOK AREA.
A.2. GREENHOW HILL AREA.
A.3. CRASSINGTON MOOR AREA.
A.4. YARNBURY, MOSSDALE AND BOWLAND TROUGH AREAS.
A.5. KETTLEWELL AREA.
A.6. WENSLEYDALE AREA.
A.7. SWALEDALE, CLOUDS AND HARTLEY BIRKETT AREAS.
A.8. ARKENGARTHDALE AREA.

N.B. 1. All results in °C.
2. Experimental error ± 2°C
3. All results positively corrected for pressure.
<table>
<thead>
<tr>
<th>SAMPLE LOC. &amp; DESCRIPTION</th>
<th>NO.</th>
<th>TYPE &amp; TEMP. RANGE °C</th>
<th>MEAN °C</th>
<th>S.D.</th>
<th>S.E. PRESS.</th>
<th>CORR.</th>
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<tr>
<td>ESCOE HILL L. purple fluor.</td>
<td>6</td>
<td>46 P 105 to 131°C</td>
<td>113.696</td>
<td>6.77</td>
<td>0.99</td>
<td>128.696</td>
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<tr>
<td>OLD VEIN colourless fluorite</td>
<td>70 P 93 to 139°C</td>
<td>117.700</td>
<td>8.54</td>
<td>1.02</td>
<td>132.700</td>
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<tr>
<td>RODHILL VEIN colourless fluorite</td>
<td>19 P 105 to 125°C</td>
<td>113.158</td>
<td>6.89</td>
<td>1.53</td>
<td>128.158</td>
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<tr>
<td>INIAN VEIN colourless fluorite</td>
<td>11 P 99 to 129°C</td>
<td>111.091</td>
<td>9.99</td>
<td>3.01</td>
<td>126.091</td>
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<td>HONLEY VEIN colourless fluorite</td>
<td>14 PS 111 to 115°C</td>
<td>112.857</td>
<td>0.95</td>
<td>0.25</td>
<td>127.857</td>
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<tr>
<td>NEWCASTLE R. col. fluorite</td>
<td>39 S 91 to 121°C</td>
<td>109.077</td>
<td>9.09</td>
<td>1.46</td>
<td>124.077</td>
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<tr>
<td>BRIGHT VEIN col. fluorite</td>
<td>25 S 87 to 118°C</td>
<td>109.920</td>
<td>10.92</td>
<td>2.18</td>
<td>124.920</td>
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<tr>
<td>1. GILL HEADS V col. fluorite</td>
<td>44 P 97 to 133°C</td>
<td>117.795</td>
<td>8.69</td>
<td>1.31</td>
<td>132.795</td>
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<tr>
<td></td>
<td>45 S 94 to 116°C</td>
<td>106.667</td>
<td>5.31</td>
<td>0.79</td>
<td>121.667</td>
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<tr>
<td>2. GILL HEADS V col. fluorite</td>
<td>36 P 102 to 119°C</td>
<td>108.333</td>
<td>8.69</td>
<td>1.36</td>
<td>123.333</td>
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<td></td>
<td>23 S 86 to 108°C</td>
<td>96.697</td>
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<td>3. GILL HEADS V all col. fluorite</td>
<td>30 P 102 to 145°C</td>
<td>118.727</td>
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<td>10 S 97 to 99°C</td>
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<td>0.21</td>
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<td>4. GILL HEADS V all col. fluorite</td>
<td>109 P 107 to 137°C</td>
<td>117.716</td>
<td>9.41</td>
<td>0.90</td>
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<td></td>
<td>10 S 102 to 105°C</td>
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<td>1.0</td>
<td>0.32</td>
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<tr>
<td>5. GILL HEADS V all col. fluorite</td>
<td>4 P 119 to 131°C</td>
<td>127.500</td>
<td>5.75</td>
<td>2.87</td>
<td>142.500</td>
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<tr>
<td>JOYCE VEIN col. fluorite</td>
<td>31 P 111 to 131°C</td>
<td>121.000</td>
<td>5.49</td>
<td>0.98</td>
<td>136.000</td>
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<td>SAMPLE LOCALITY &amp; DESCRIPTION</td>
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<td>S.D.</td>
<td>S.E.</td>
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<tr>
<td>HILLTOP VEIN col. fluor.</td>
<td>13</td>
<td>P</td>
<td>113 to 130°C</td>
<td>122.769</td>
<td>10.31</td>
<td>2.86</td>
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<td>GREENHILL RANCH col. fluor.</td>
<td>152</td>
<td>PS</td>
<td>106 to 126°C</td>
<td>117.099</td>
<td>4.61</td>
<td>0.37</td>
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<td>GULLOY VEIN col. fluor.</td>
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<td>101 to 133°C</td>
<td>121.361</td>
<td>8.15</td>
<td>1.36</td>
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<td>FOREST VEIN col. fluor.</td>
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<td>P</td>
<td>138 to 145°C</td>
<td>143.667</td>
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<tr>
<td>WATRHOLE VEIN col. fluor.</td>
<td>19</td>
<td>S</td>
<td>83 to 115°C</td>
<td>101.737</td>
<td>11.54</td>
<td>2.65</td>
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<tr>
<td>GILLFIELDS HILL col. fluor.</td>
<td>43</td>
<td>PS</td>
<td>96 to 113°C</td>
<td>104.465</td>
<td>5.59</td>
<td>0.85</td>
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<td>SUN VEIN col. fluor.</td>
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<td>P</td>
<td>105 to 122°C</td>
<td>122.000</td>
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<td>PENDLETON PIPE col. fluor.</td>
<td>21</td>
<td>S</td>
<td>90 to 91°C</td>
<td>89.190</td>
<td>3.43</td>
<td>0.74</td>
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<td>LOLLY HINE amber fluor.</td>
<td>71</td>
<td>P</td>
<td>107 to 136°C</td>
<td>118.535</td>
<td>8.63</td>
<td>1.03</td>
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<td>LURGATE END col. fluor.</td>
<td>18</td>
<td>P</td>
<td>99 to 149°C</td>
<td>120.945</td>
<td>11.98</td>
<td>2.82</td>
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<td>FIELDING VEIN col. fluor.</td>
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<td>PS</td>
<td>99 to 110°C</td>
<td>110.432</td>
<td>7.08</td>
<td>1.07</td>
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<td>FOXHOLES VEIN col. fluor.</td>
<td>58</td>
<td>P</td>
<td>104 to 128°C</td>
<td>116.224</td>
<td>11.44</td>
<td>1.50</td>
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<tr>
<td>RODHILL VEIN col. fluor.</td>
<td>6</td>
<td>S</td>
<td>76 to 94°C</td>
<td>85.833</td>
<td>7.44</td>
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<td>JAMIE VEIN col. fluor.</td>
<td>16</td>
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<td>83 to 103°C</td>
<td>95.875</td>
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<td>105 to 112°C</td>
<td>109.146</td>
<td>2.81</td>
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<td>CRAYVEN CROSS col. fluor.</td>
<td>22</td>
<td>PS</td>
<td>105 to 118°C</td>
<td>116.955</td>
<td>2.72</td>
<td>0.58</td>
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</table>

## Table 1

**Homogenization Results from the Grassington Moor Area.**

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<tr>
<td>CAVENDISH VEIN 4</td>
<td>18 P</td>
<td>col. fluor.</td>
<td>132 to 137°C</td>
<td>135.222</td>
<td>1.55</td>
<td>0.37</td>
<td>150.222</td>
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<td></td>
<td>56 S</td>
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<td>80 to 114°C</td>
<td>101.000</td>
<td>7.01</td>
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<td>SLANTER VEIN 3</td>
<td>31 P</td>
<td>amber fluor.</td>
<td>91 to 94°C</td>
<td>92.333</td>
<td>1.53</td>
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<td></td>
<td>3</td>
<td></td>
<td>102 to 123°C</td>
<td>105.097</td>
<td>3.77</td>
<td>0.68</td>
<td>120.097</td>
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<td>STOOL VEIN 2</td>
<td>26 P</td>
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<td>110 to 135°C</td>
<td>119.846</td>
<td>4.78</td>
<td>0.94</td>
<td>134.846</td>
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<td></td>
<td>15 PS</td>
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<td>102 to 107°C</td>
<td>103.400</td>
<td>1.72</td>
<td>0.44</td>
<td>118.400</td>
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<td>RIPLEY VEIN 1</td>
<td>33 PS</td>
<td>col. fluor.</td>
<td>95 to 105°C</td>
<td>102.242</td>
<td>2.33</td>
<td>0.41</td>
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<td>PALMY VEIN 1</td>
<td>55 P</td>
<td>amber fluor.</td>
<td>92 to 101°C</td>
<td>98.127</td>
<td>2.99</td>
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<td>BYCLIFFE VEIN 4</td>
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<td>col. fluor.</td>
<td>110 to 138°C</td>
<td>118.348</td>
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<td></td>
<td>56 S</td>
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<td>84 to 108°C</td>
<td>102.214</td>
<td>3.97</td>
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<tr>
<td>OLD MOSS VEIN 2</td>
<td>31 P</td>
<td>amber fluor.</td>
<td>90 to 114°C</td>
<td>109.806</td>
<td>3.52</td>
<td>0.63</td>
<td>124.806</td>
</tr>
<tr>
<td>GRIFFS GROOVE 3</td>
<td>19 P</td>
<td>col. fluor.</td>
<td>114 to 144°C</td>
<td>125.211</td>
<td>8.94</td>
<td>2.05</td>
<td>140.211</td>
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<td>VEVIN 6</td>
<td>16 S</td>
<td></td>
<td>80 to 104°C</td>
<td>93.525</td>
<td>3.27</td>
<td>2.07</td>
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<tr>
<td>MIDDLE VEIN 6</td>
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<td>99 to 114°C</td>
<td>109.994</td>
<td>4.08</td>
<td>0.43</td>
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<tr>
<td></td>
<td>20 S</td>
<td></td>
<td>83 to 96°C</td>
<td>89.550</td>
<td>4.66</td>
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<td>MEAN°C</td>
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<td>PRESS.</td>
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<td>--------</td>
<td>------</td>
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<tr>
<td>BELLERS SHAFT 6</td>
<td>62 P</td>
<td>96 to 135°C</td>
<td>112.08</td>
<td>8.31</td>
<td>1.06</td>
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<td>38 S</td>
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<td>4.85</td>
<td>0.79</td>
<td>112.737</td>
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<tr>
<td>MAIN DUMPS 2 INCLINE</td>
<td>10 P</td>
<td>95 to 106°C</td>
<td>100.900</td>
<td>4.25</td>
<td>1.35</td>
<td>115.900</td>
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<td>13 P</td>
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<td>101.769</td>
<td>1.79</td>
<td>0.50</td>
<td>116.769</td>
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<td>7 S</td>
<td>93 to 118°C</td>
<td>111.000</td>
<td>8.43</td>
<td>3.10</td>
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<td>MOSSDALE VEIN</td>
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<td>93 to 105°C</td>
<td>94.368</td>
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<td>109.368</td>
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<td>MAIN V. COL.</td>
<td>15 P</td>
<td>85 to 102°C</td>
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<td>3.46</td>
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<td>OLD MEREDO VEIN</td>
<td>19 P</td>
<td>87 to 105°C</td>
<td>89.320</td>
<td>6.20</td>
<td>3.42</td>
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<td>SKILLERON MINES</td>
<td>5 P</td>
<td>103 to 156°C</td>
<td>128.441</td>
<td>12.19</td>
<td>1.52</td>
<td>143.441</td>
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<td>RAYGILL MAIN</td>
<td>51 P</td>
<td>100 to 152°C</td>
<td>133.596</td>
<td>10.09</td>
<td>0.82</td>
<td>148.596</td>
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<tr>
<td>V. LOTHERSDALE</td>
<td>71 S</td>
<td>88 to 96°C</td>
<td>93.017</td>
<td>2.85</td>
<td>0.34</td>
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A.5.
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<th>DESCRIPTION</th>
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<th>SD.</th>
<th>S.E.</th>
<th>PRESS.</th>
<th>CURTAIN</th>
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<tbody>
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<td>PROVIDENCE MINE 2</td>
<td>col. flor.</td>
<td>30 S 75 to 99°</td>
<td>86.767</td>
<td>7.77</td>
<td>1.42</td>
<td>101.767</td>
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<td>DOMBE R GILL 4</td>
<td>col. flor.</td>
<td>54 P 95 to 108°</td>
<td>103.685</td>
<td>3.53</td>
<td>0.48</td>
<td>118.685</td>
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<tr>
<td>MIDDLESDOOR 1</td>
<td>col. flor.</td>
<td>48 S 81 to 109°</td>
<td>91.583</td>
<td>6.70</td>
<td>1.26</td>
<td>106.583</td>
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<tr>
<td>MIDDLESDOOR 1</td>
<td>col. flor.</td>
<td>10 P 90 to 100°</td>
<td>96.100</td>
<td>3.25</td>
<td>0.60</td>
<td>111.100</td>
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<td>MIDDLESDOOR 3</td>
<td>col. flor.</td>
<td>11 P 98 to 126°</td>
<td>110.909</td>
<td>9.67</td>
<td>2.96</td>
<td>125.909</td>
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<td>col. flor.</td>
<td>10 S 95 to 105°</td>
<td>104.000</td>
<td>3.16</td>
<td>1.00</td>
<td>119.000</td>
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<tr>
<td>COLDSTREAK MINE 2</td>
<td>col. flor.</td>
<td>17 S 88 to 99°</td>
<td>89.588</td>
<td>3.74</td>
<td>0.91</td>
<td>104.588</td>
<td></td>
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<tr>
<td>COLDSTREAK MINE 3</td>
<td>col. flor.</td>
<td>15 P 101 to 127°</td>
<td>105.733</td>
<td>8.00</td>
<td>2.07</td>
<td>120.733</td>
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<td>SCARFADALE MOOR 1</td>
<td>col. flor.</td>
<td>6 S 85 to 99°</td>
<td>91.833</td>
<td>6.59</td>
<td>2.69</td>
<td>116.833</td>
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<tr>
<td>SCARFADALE MOOR 1</td>
<td>col. flor.</td>
<td>13 P 93 to 103°</td>
<td>99.154</td>
<td>2.91</td>
<td>0.61</td>
<td>115.154</td>
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<tr>
<td>STARBOTTON CAI 2</td>
<td>col. flor.</td>
<td>17 S 110 to 121°</td>
<td>113.291</td>
<td>2.37</td>
<td>0.57</td>
<td>128.291</td>
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<tr>
<td>STARBOTTON CAI 1</td>
<td>col. flor.</td>
<td>10 P 95 to 110°</td>
<td>103.500</td>
<td>6.95</td>
<td>2.20</td>
<td>118.500</td>
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<tr>
<td>STARBOTTON CAI 2</td>
<td>col. flor.</td>
<td>51 P 88 to 110°</td>
<td>102.000</td>
<td>3.97</td>
<td>0.56</td>
<td>117.000</td>
<td></td>
</tr>
<tr>
<td>STARBOTTON CAI 2</td>
<td>col. flor.</td>
<td>29 P 94 to 109°</td>
<td>100.172</td>
<td>4.14</td>
<td>0.77</td>
<td>115.172</td>
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<tr>
<td>STARBOTTON CAI 4</td>
<td>col. flor.</td>
<td>53 P 93 to 119°</td>
<td>102.755</td>
<td>5.57</td>
<td>0.76</td>
<td>117.755</td>
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<tr>
<td>TABLE 4.6.</td>
<td>HANOVERIZATION RESULTS FROM THE MANSFIELD AREA.</td>
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</tr>
<tr>
<td>SAMPLE LOC. &amp; NO.</td>
<td>TYPE &amp; TEMP. RANGE °C</td>
<td>TAN°C</td>
<td>S.D.</td>
<td>S.E. PRESS.</td>
<td>CORPOR.</td>
<td></td>
<td></td>
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<tr>
<td>SLATE MINE</td>
<td>col. fluor.</td>
<td>7</td>
<td>106 to 139°C</td>
<td>122.267</td>
<td>6.26</td>
<td>0.72</td>
<td>137.267</td>
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<tr>
<td></td>
<td>amber fluor.</td>
<td>11</td>
<td>115 to 121°C</td>
<td>116.727</td>
<td>1.68</td>
<td>0.51</td>
<td>133.727</td>
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<tr>
<td>WEST GROOVES M.</td>
<td>col. fluor.</td>
<td>9</td>
<td>107 to 123°C</td>
<td>116.842</td>
<td>1.72</td>
<td>1.04</td>
<td>131.842</td>
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<tr>
<td></td>
<td>amber fluor.</td>
<td>8</td>
<td>93 to 105°C</td>
<td>96.375</td>
<td>5.53</td>
<td>1.95</td>
<td>111.375</td>
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<td></td>
<td>41</td>
<td>94 to 109°C</td>
<td>110.585</td>
<td>9.56</td>
<td>1.49</td>
<td>125.585</td>
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<tr>
<td>WALL BANK LEVEL</td>
<td>purple edged fl.</td>
<td>55</td>
<td>86 to 125°C</td>
<td>107.016</td>
<td>10.50</td>
<td>1.43</td>
<td>122.018</td>
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<tr>
<td></td>
<td>clear baryte</td>
<td>15</td>
<td>110 to 119°C</td>
<td>115.250</td>
<td>3.72</td>
<td>0.95</td>
<td>130.250</td>
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<tr>
<td>WORSTON MINE</td>
<td>col. fluor.</td>
<td>3</td>
<td>101 to 109°C</td>
<td>104.667</td>
<td>4.34</td>
<td>1.12</td>
<td>119.667</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>63 to 109°C</td>
<td>93.243</td>
<td>8.19</td>
<td>1.35</td>
<td>108.243</td>
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<td>WILD NEADS M.</td>
<td>col/purple fl.</td>
<td>18</td>
<td>85 to 100°C</td>
<td>91.056</td>
<td>3.30</td>
<td>0.77</td>
<td>106.056</td>
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<tr>
<td></td>
<td>32</td>
<td>88 to 109°C</td>
<td>103.469</td>
<td>4.69</td>
<td>0.63</td>
<td>117.469</td>
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<tr>
<td>WEST BURTON</td>
<td>col/purple fl.</td>
<td>20</td>
<td>93 to 103°C</td>
<td>97.300</td>
<td>2.30</td>
<td>0.51</td>
<td>112.300</td>
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<td>13</td>
<td>79 to 93°C</td>
<td>91.077</td>
<td>4.73</td>
<td>1.31</td>
<td>106.077</td>
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<tr>
<td>BRAINTWALLITE</td>
<td>amber/col. fluor.</td>
<td>17</td>
<td>75 to 103°C</td>
<td>89.353</td>
<td>9.57</td>
<td>2.32</td>
<td>104.353</td>
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A. 7.
# Table 4.7
HOMOGENIZATION RESULTS FROM SALTLEAD, CLOUDS, HARTLEY, BIRKETT AND ARING RUTHALL AREAS

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<th>SAMPLE LOG &amp; NO.</th>
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<th>TEMP. RANGE °C</th>
<th>MEAN °C</th>
<th>S.D.</th>
<th>S.E.</th>
<th>PRESS. CORR.</th>
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<tbody>
<tr>
<td>CLOUD END FELL 2</td>
<td>col. fluor.</td>
<td>113 to 138°C</td>
<td>118.740</td>
<td>5.04</td>
<td>0.57</td>
<td>130.740</td>
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<tr>
<td>HARTLEY BIRKETT 5</td>
<td>FELL col. fluor.</td>
<td>100 to 114°C</td>
<td>105.154</td>
<td>3.708</td>
<td>0.73</td>
<td>120.254</td>
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<td></td>
<td></td>
<td>111 to 114°C</td>
<td>112.000</td>
<td>0.378</td>
<td>0.09</td>
<td>127.000</td>
</tr>
<tr>
<td>BUNNIN LEVEL</td>
<td>KIRKPOOLD RAKE 5</td>
<td>95 to 126°C</td>
<td>109.927</td>
<td>6.44</td>
<td>0.57</td>
<td>117.927</td>
</tr>
<tr>
<td></td>
<td>amber and purple</td>
<td>73 to 97°C</td>
<td>93.8144</td>
<td>5.61</td>
<td>1.20</td>
<td>100.314</td>
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<td>OLD RAKE 5</td>
<td>col/purple fluor.</td>
<td>109 to 136°C</td>
<td>122.142</td>
<td>11.49</td>
<td>4.35</td>
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<td>SURRENDER MINES</td>
<td>MALRPOOLD RAKE 4</td>
<td>89 to 119°C</td>
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<td>0.83</td>
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<td>col. fluor.</td>
<td>91 to 115°C</td>
<td>96.348</td>
<td>3.50</td>
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<td>104.348</td>
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<td>NORTH RAKE MINES</td>
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<td>78 to 116°C</td>
<td>103.083</td>
<td>11.92</td>
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<td>DAM RIGG MINES  5</td>
<td>amber/col. fluor.</td>
<td>97 to 107°C</td>
<td>99.667</td>
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<td>0.86</td>
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<td>69 to 104°C</td>
<td>95.580</td>
<td>9.32</td>
<td>1.86</td>
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<td>amber fluor.</td>
<td>89 to 115°C</td>
<td>102.205</td>
<td>5.66</td>
<td>0.85</td>
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<td>CUPPERTHILITE MINES col. fluor.</td>
<td>92 to 113°C</td>
<td>102.029</td>
<td>6.22</td>
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A. 8.
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<th>TEMPERATURE °C</th>
<th>S.D.</th>
<th>S.E. PRESS. CORRTN.</th>
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<td>HUNGRY HUSHES 3</td>
<td>amber &amp; col. fl.</td>
<td>90 to 125°C</td>
<td>102.714</td>
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<td>83 to 99°C</td>
<td>93.316</td>
<td>4.73</td>
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<td>BLACKS HILLS</td>
<td>col. fluor.</td>
<td>102 to 133°C</td>
<td>115.000</td>
<td>7.68</td>
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<tr>
<td>HUSHES</td>
<td></td>
<td>78 to 115°C</td>
<td>91.127</td>
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<td>STODART HUSH 3</td>
<td>col. flor.</td>
<td>68 to 89°C</td>
<td>70.667</td>
<td>8.87</td>
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<td>SUN DAH HUSH 1</td>
<td>col. flor.</td>
<td>73 to 114°C</td>
<td>88.222</td>
<td>15.58</td>
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<td>DAH RIGG LEVEL 4</td>
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<td>95 to 105°C</td>
<td>100.929</td>
<td>3.91</td>
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<td>69 to 102°C</td>
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<td>7.77</td>
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<tr>
<td>MOULDS TOP HIDE 2</td>
<td>amber flor.</td>
<td>88 to 119°C</td>
<td>111.083</td>
<td>6.67</td>
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<td>MOULDS LEVEL 2</td>
<td>col. flor.</td>
<td>93 to 101°C</td>
<td>97.556</td>
<td>3.58</td>
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<td>STAPLE WHIN 2</td>
<td>SH. FT col. fl.</td>
<td>76 to 101°C</td>
<td>90.435</td>
<td>6.65</td>
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<td>TURF MOOR LEVEL 1</td>
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<td>75 to 105°C</td>
<td>86.566</td>
<td>9.90</td>
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<td>UNDERLEVE 4</td>
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<td>101 to 145°C</td>
<td>122.100</td>
<td>15.57</td>
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<td>AMENGARNDALE SIDE 3</td>
<td>col &amp; amber fl.</td>
<td>120°C</td>
<td>120.000</td>
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<td>78 to 111°C</td>
<td>103.038</td>
<td>11.62</td>
</tr>
<tr>
<td>JUSTICE LEVEL 1</td>
<td>col. flor.</td>
<td>68 to 113°C</td>
<td>99.525</td>
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<td>75 to 104°C</td>
<td>91.733</td>
<td>8.91</td>
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APPENDIX B.

SUMMARY OF FREEZING STAGE RESULTS FROM FLUID INCLUSIONS IN FLUORITE FROM THE ASKRIGG BLOCK

LIST OF TABLES.

B.1. GREENHOW - APPLETRIEVICK AREA.
B.2. GRASSINGTON MOOR - WENSLEYDALE AREA.
B.3. SWALEDALE AND BOWLAND TROUGH AREAS.

N.E. 1. All results in °C
      2. Experimental error - 0.5 °C
TABLE B.1

FREEZING RESULTS FROM THE GREENHILL HILL AND ANTHERBURY AREAS OF N.Y. YORKSHIRE.

<table>
<thead>
<tr>
<th>SAMPLE NO. &amp; LOCATION</th>
<th>EUTECTIC RANGE - °C</th>
<th>MEAN-°C</th>
<th>S.D.</th>
<th>MEAN 1ST MELTING - °C</th>
<th>NO. &amp; TYPE</th>
<th>NaCl</th>
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<tr>
<td>100, FOREST V.</td>
<td>20.0 to 20.3</td>
<td>20.08</td>
<td>0.06</td>
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<td>112, 152, GILLGORY V.</td>
<td>16.1 to 19.0</td>
<td>17.28</td>
<td>0.55</td>
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<tr>
<td>209, SUN V.</td>
<td>15.3 to 16.3</td>
<td>15.70</td>
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<td>106, GREENHILL RANK</td>
<td>12.7 to 13.3</td>
<td>12.50</td>
<td>0.80</td>
<td>22.00</td>
<td>3 P</td>
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<td>322, HARGETS END V.</td>
<td>16.8 to 17.5</td>
<td>16.99</td>
<td>0.27</td>
<td>20.79</td>
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<td>31, OLD V.</td>
<td>9.7 to 15.5</td>
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<td>318, INMAN V.</td>
<td>17.9 to 19.0</td>
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<td>66, JOYCE V.</td>
<td>12.5 to 20.5</td>
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<td>61, 63, GILL HEADS V.</td>
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<td>19.46</td>
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<td>23.03</td>
<td>19 P</td>
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<td>16.5 to 18.0</td>
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<td>74, 75 ESCOE HILL LEVEL</td>
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<td>18.95</td>
<td>0.61</td>
<td>23.50</td>
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<td>80, 83, LOLLY HINE</td>
<td>14.0 to 21.2</td>
<td>18.13</td>
<td>2.56</td>
<td>26.11</td>
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<td>448, YARNBEY</td>
<td>18.0 to 20.5</td>
<td>18.86</td>
<td>0.90</td>
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<td>127, RIPPLE VEIN</td>
<td>24.2 to 24.5</td>
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<td>180 MIDDLE VEIN</td>
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<td>20.83</td>
<td>0.62</td>
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<td>175 BYCLIFFE VEIN</td>
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<td>-</td>
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<td>144, STOOL VEIN</td>
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<td>410 HOSDALE</td>
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<td>200, KETTLE WELL</td>
<td>22.0 to 22.6</td>
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<td>31.94</td>
<td>8.P</td>
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<td>229, COLD STRIKE</td>
<td>21.5 to 21.8</td>
<td>21.87</td>
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<td>101, WET GROOVES</td>
<td>22.8 to 25.0</td>
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<td>86, SEAT LINE</td>
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<td>119, CLOUDS</td>
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<td>259, 260 BUNTON LEVEL</td>
<td>19.1 to 23.3</td>
<td>21.49</td>
<td>1.34</td>
<td>33.17</td>
<td>26 P</td>
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<td>279, OLD RAKE</td>
<td>20.0 to 22.5</td>
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<td>0.72</td>
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<td>500, HOULD TOP H.</td>
<td>20.0 to 22.7</td>
<td>21.34</td>
<td>0.75</td>
<td>30.62</td>
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<td>476, 484 HUNGRY HUSHES</td>
<td>10.3 to 23.2</td>
<td>19.76</td>
<td>3.49</td>
<td>32.15</td>
<td>32 P</td>
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<td>507, TURF NOOR LVL.</td>
<td>19.4 to 23.0</td>
<td>20.69</td>
<td>0.92</td>
<td>25.07</td>
<td>62 P</td>
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<td>302, 282 SURGENDER GROUND</td>
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<td>19.68</td>
<td>1.57</td>
<td>31.73</td>
<td>55 P</td>
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<td>493, 496 DAM RIGG LEVEL</td>
<td>17.8 to 22.4</td>
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<td>1.46</td>
<td>25.09</td>
<td>22 P</td>
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<td>314, MARTIN VEIN</td>
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<td>16 P</td>
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<td>280, DAM RIGG VEIN</td>
<td>20.1 to 23.2</td>
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<td>32.05</td>
<td>11 P</td>
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<td>416, SKELETON MIN.</td>
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<td>2.30</td>
<td>37.04</td>
<td>40 P</td>
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