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A Chemical and Isotopic Study of
Fluid Inclusions from the Northern
Pennine Orefield

by

G. R. Moore B.Sc.

A Thesis submitted for the
Degree of Doctor of Philosophy in
the University of Durham

December 1980

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A Chemical and Isotopic Study of fluid inclusions
from the Northern Pennine Orefield

by G. R. Moore

The present study was undertaken to investigate the origin of the mineralising fluids and mechanisms of ore deposition with particular reference to the fluorite/barite mineral zonation.

Fluid inclusions in fluorite, barite and quartz provided the principal material for analysis. Quantitative measurement of the inclusion gases, including water, was carried out by decrepitation (thermal rupture) under vacuum. The decrepitated material was subsequently leached with deionised water and the leachate analysed for Na, K, Ca, Sr, Mg, Cu, Zn, Fe and Mn by flame photometry and atomic absorption spectrometry; and Cl, F and Br by pyrohydrolysis and neutron activation analysis. Hydrogen isotope analysis on the inclusion fluids showed a greater depletion in deuterium for barite than for fluorite and quartz. This work was complemented by oxygen and strontium isotope studies.

It is concluded that the mineralising fluids originated from sediments in the deep basins to the north, south and east of the Alston block. During compaction of the sediments the pore fluids underwent filtration producing two chemically and isotopically distinct fluids. The filtered high level SO_4 -rich fluid migrated laterally, while the residual fluid at depth mixed with dehydration water released during montmorillonite-illite conversion to produce a Ca-Na-Cl brine rich in metals. This deeper component, similar in chemistry to the fluorite/quartz inclusion fluids, migrated upwards through the cupolas of the Weardale granite in response to tectonic re-adjustment in the basement and anomalous high heat flow in the region. Deposition of fluorite and quartz was caused by cooling and slight pH changes in the fluids. In contrast barite deposition was controlled by mixing of the two fluids. Chemical analysis and solubility data support the proposed mechanisms of mineral deposition.

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C H A P T E R O N E

1.1. Geology of the Northern Pennines

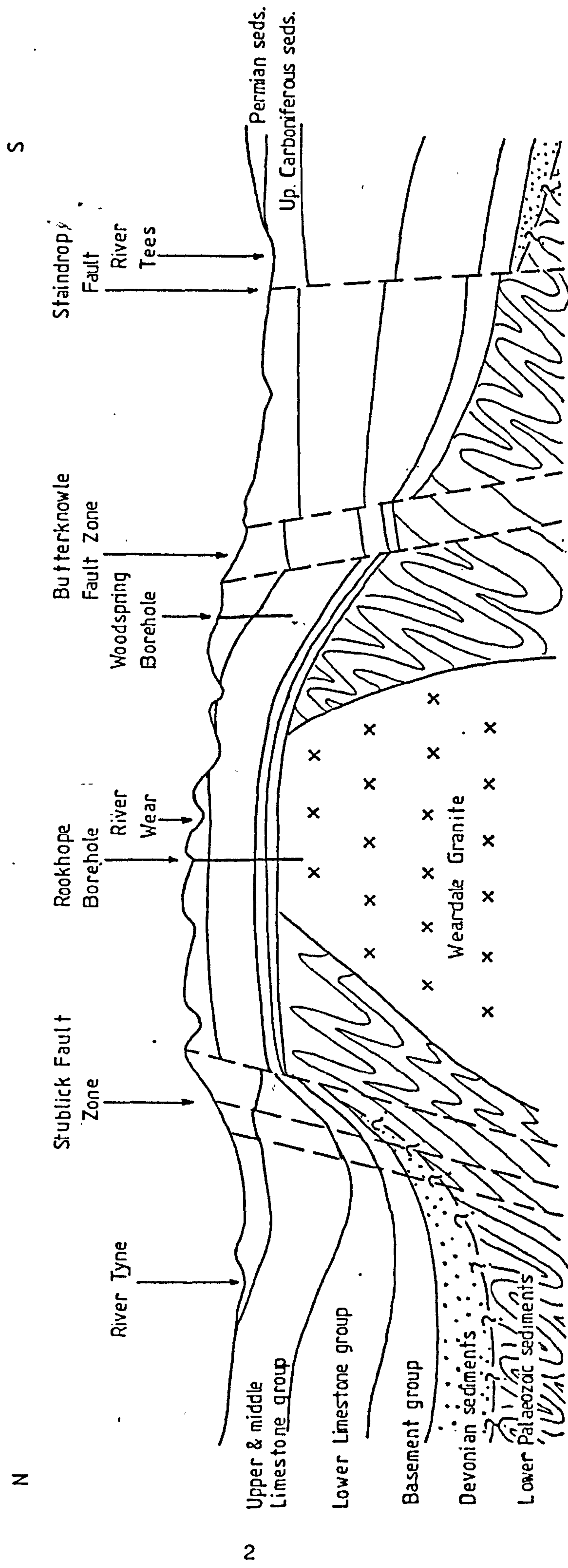
The Northern Pennine Orefield is located in north-east England and covers an area of approximately 1500 km² extending from Alston to Durham and Hexham to North Stainmore.

The geology of the area has been described by many workers, (Dunham, 1948; Johnson, 1960; 1967) and is summarised in Taylor et al., (1971). The area is underlain by Lower and Upper Carboniferous sediments, unconformably overlying folded Lower Palaeozoic rocks and a granite batholith. The Lower Carboniferous sequence consists of a basal conglomerate overlain by cyclic sequences of limestone, shale, sandstone and seat-earth. In the east of the area the 'Millstone Grit Series' overlies these cyclothems and is in turn overlain by Upper Carboniferous Coal Measures, which are still worked for coal. The thickness of the sediments is variable. On the stable 'Alston Block' they vary between 700 and 1,200 m. The sediment thicknesses increase to 2,300 to 4,000 m in the northern and southern troughs of Northumberland and Stainmore, Fig. 1.1. Outwards from the block the limestone bands thin and become argillaceous mudstones while the sandstones and shales increase producing the main lithologies in the sequence.

Igneous rocks found in the area are generally in the form of dolerite sills, notably the Great Whin Sill and Little Whin Sill. These sills were intruded in the Late Carboniferous to Early Permian times, but no evidence of their feeder has been found. Throughout the orefield the Whin Sills transgress to different horizons, but on the whole they form a sheet dipping to the east. The Great Whin Sill occupies its lowest strati-



Fig.1.1.1 Cross section across the Northern Pennines from north to south.



graphic horizon in the region of Upper Teesdale, where it is also thickest. The sill transgresses upwards away from this area reaching higher stratigraphic horizons to the north and east of Teesdale.

The other igneous body of importance is the unexposed Weardale granite proved by borehole under Rookhope. The general shape of the granite and its culminations have been modelled from Bouguer Anomalies, (Bott, 1967). High granite cupolas are found under the Rookhope area and east of the Great Sulphur Vein, Fig. 1.2.

The Alston block is surrounded on three sides, north, south and west by major fault zones whose earlier mobilisation has caused the block to tilt towards the east. Some of these faults lie along old Caledonian lines of weakness which were reactivated during the Hercynian Orogeny (Late Carboniferous - Early Permian) and the Alpine Orogeny (Tertiary) to produce the present structure.

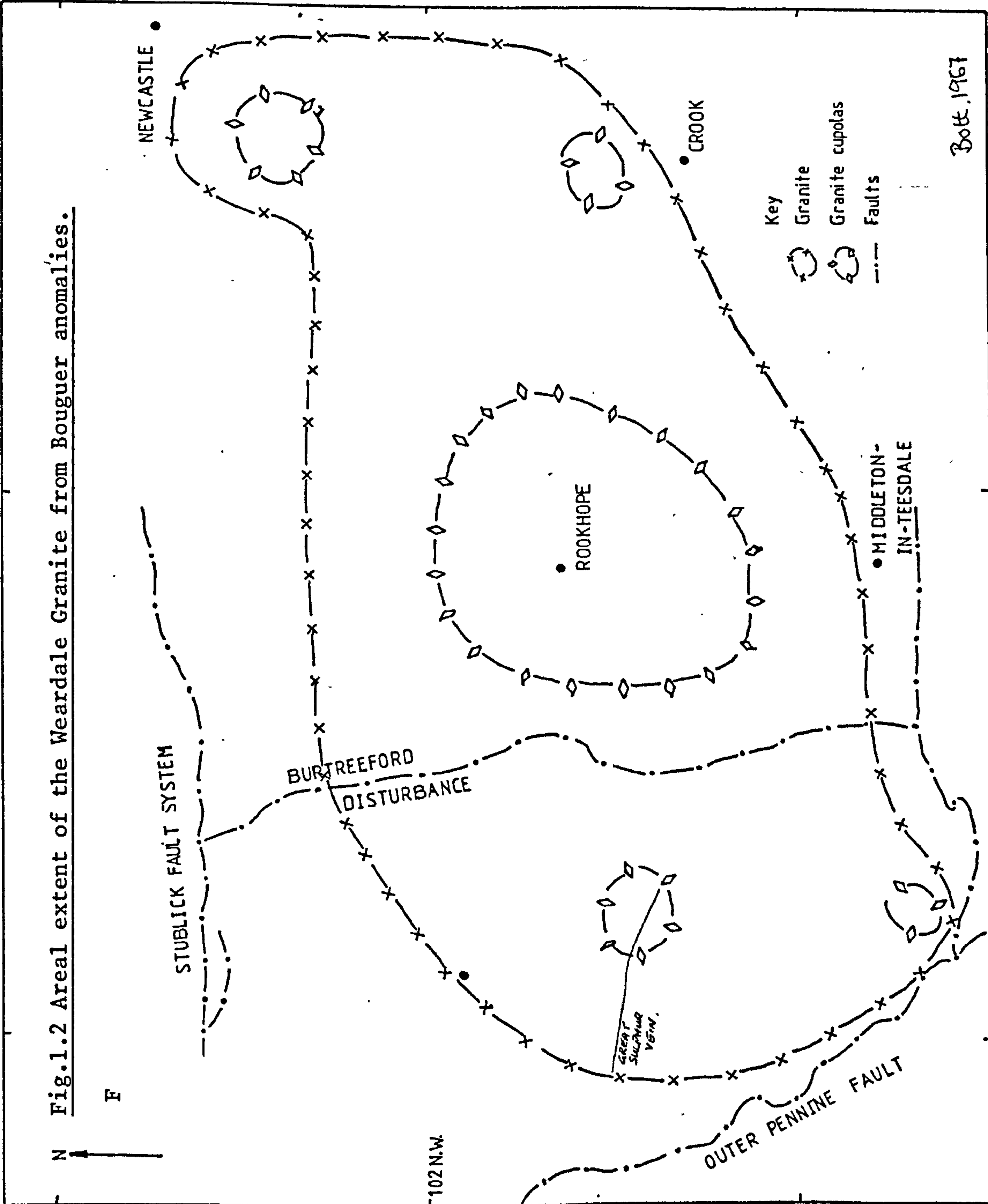
During the Hercynian Orogeny further faulting and minor folding was produced. The faults form three main sets. The first, trending E.N.E., are normal tension faults, the second, orientated N.N.W., are thrust faults and the third, E-W to E.S.E. faults also known as quarter point faults, are sinistral tear faults. The main folding at this time is represented by the Burtreeford Disturbance, an east facing monocline.

Further geological and structural information can be found from various works on the area, Dunham, (1948); Taylor et al., (1971); Edwards et al., (1975).

1.2. Mineralisation in the Northern Pennine Orefield

The lead, zinc, iron, barium and fluorine mineralisation

Fig.1.2 Areal extent of the Weardale Granite from Bouguer anomalies.



Boile, 1967

of the Northern Pennine Orefield is mainly found in steeply dipping faults, forming veins. Conformable replacement bodies or 'flats' also occur to a limited extent.

Dunham (1948), described the mineralisation in great detail. He suggested that the orefield could be subdivided into two mineral zones, a central fluorite zone and a peripheral barium mineral zone, Fig. 1.3. In the central zone fluorite is the dominant non-metallic mineral, but quartz is also present. In the peripheral zone barite and witherite dominate the non-metallic minerals. Further subdivision was possible using the sulphide minerals. Dunham, (1948) proposed five zones, Fig. 1.4. They are:-

- 1) Chalcopyrite + galena $\pm$ sphalerite
- 2) Galena $\pm$ sphalerite
- 3) Galena + sphalerite
- 4) Galena
- 5) Barren of sulphides

Fig. 1.4. also shows the Burtreeford Disturbance which seems to divide the orefield into two contrasting parts. The area to the west being richer in sphalerite than the area to the east.

The mineral veins cover most of the Alston block but are particularly abundant over the granite cupolas, Fig. 1.5. The veins mainly occupy the E.N.E. trending normal faults with additional occurrence of minerals in open cavities along the E-W trending faults. The faults generally form open cavities in hard beds, limestones and sandstones and are closed in the softer beds, shales. The mineralisation thus has the form of ribbon veins, (Dunham, 1948; Smith, 1974).

Fig.1.3 The fluorite and barite mineral zones from Dunham, (1948).

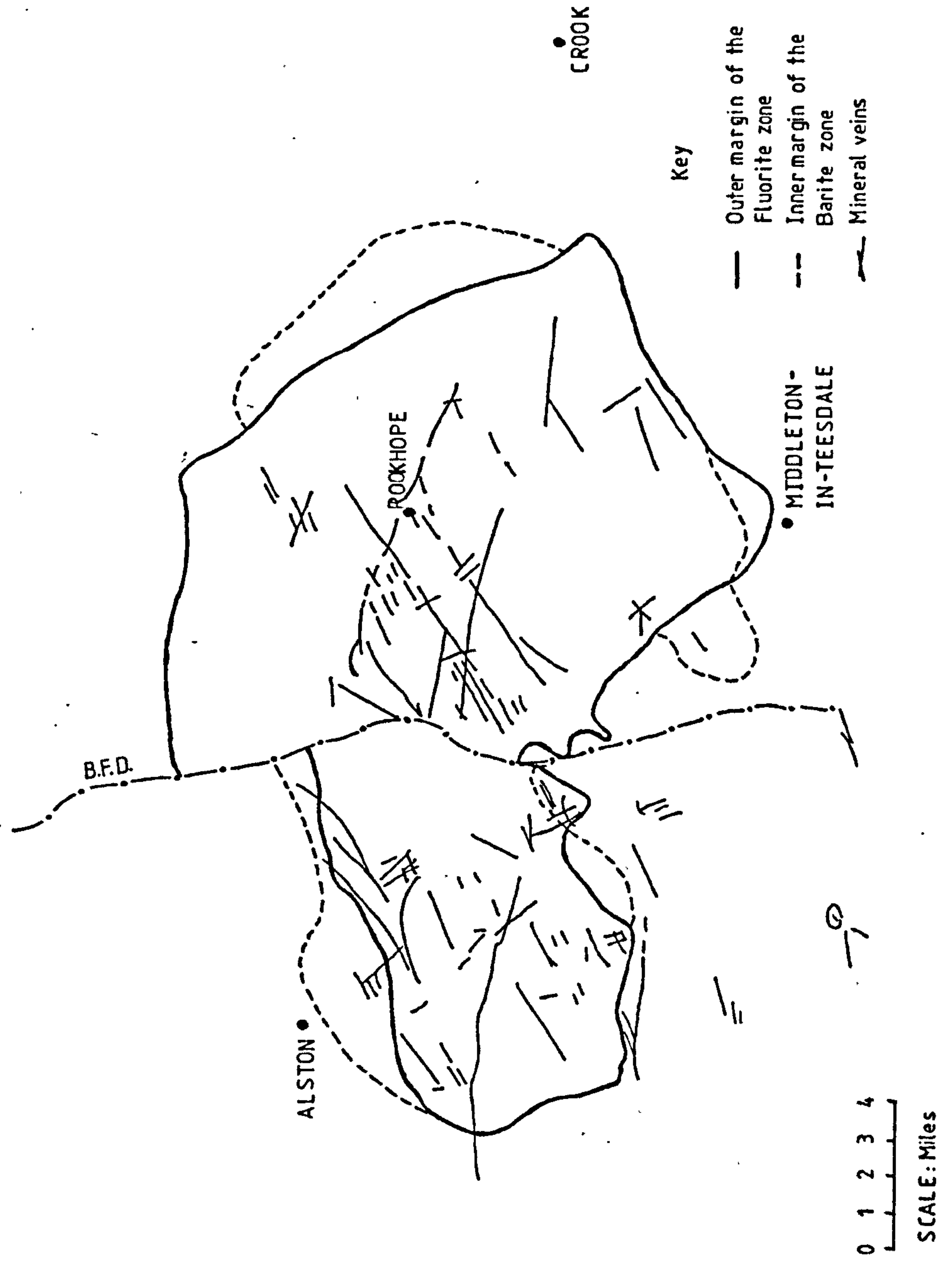


Fig.1.4 The sulphide mineral zonation in the Northern Pennines.

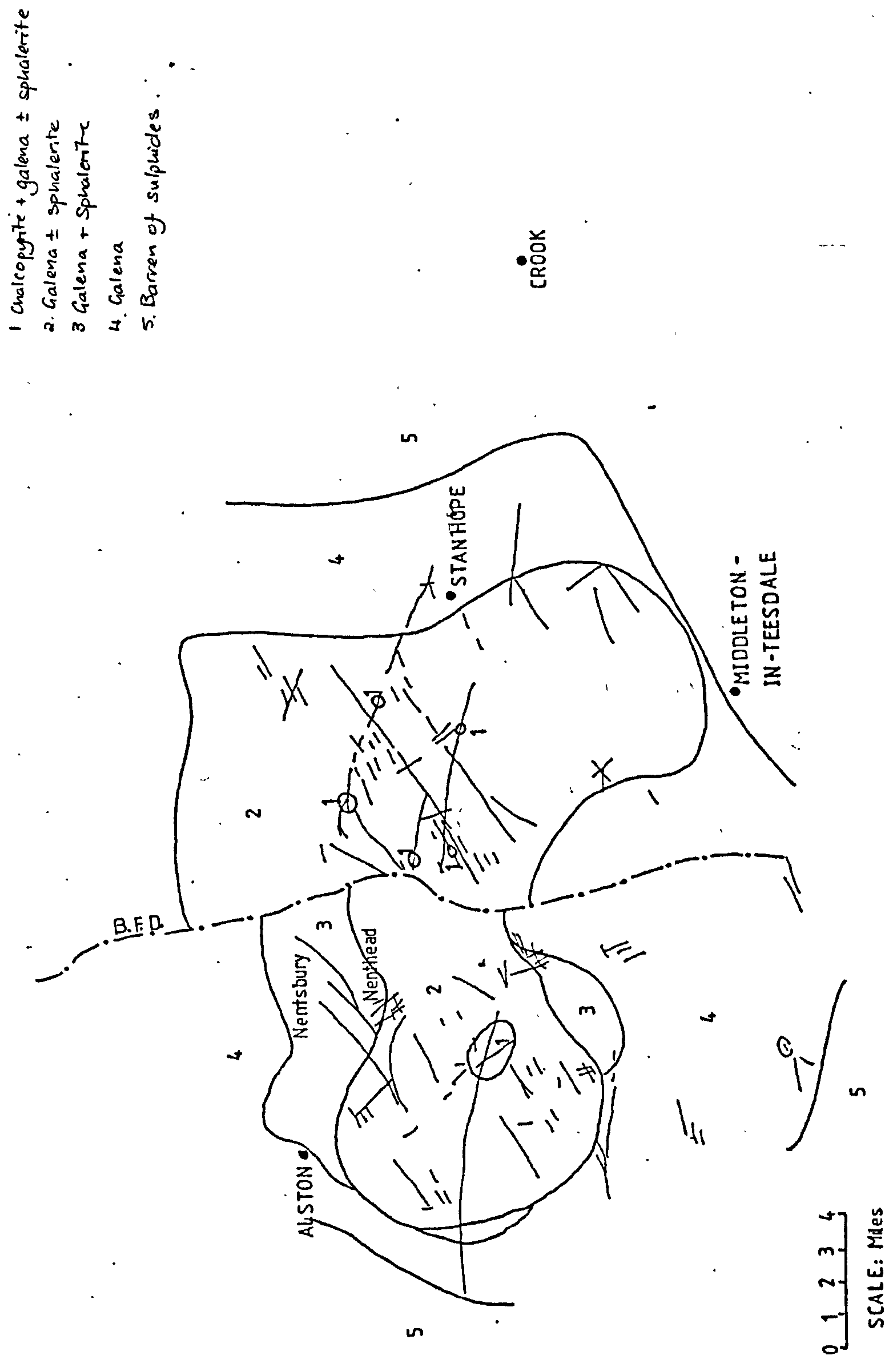
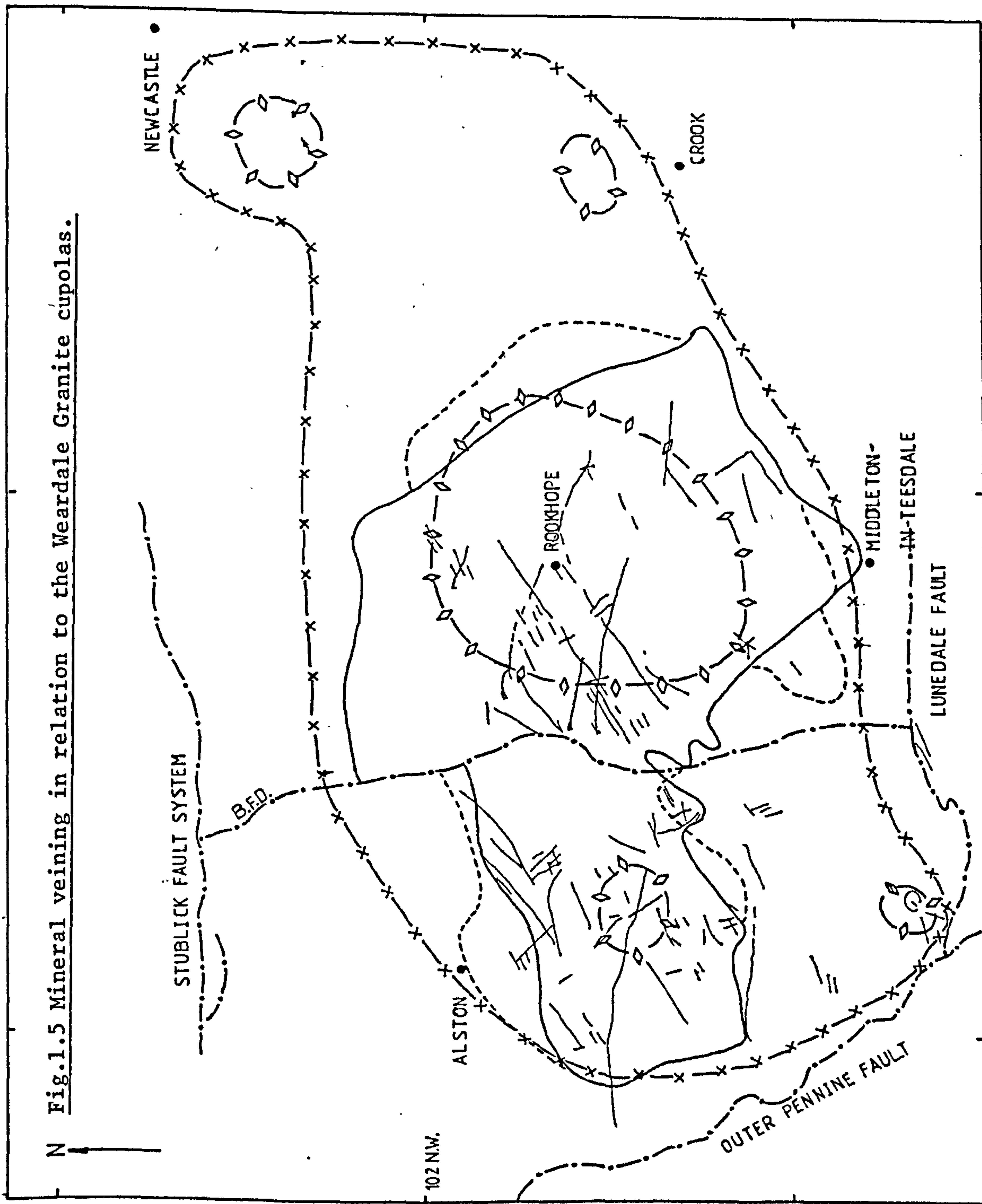


Fig.1.5 Mineral veining in relation to the Weardale Granite cupolas.



The veins are generally filled by banded ore with the ore minerals growing inwards from the wallrocks. This banding is generally of the green and purple varieties of fluorite. Quartz is found as wall rock incrustations, interbanded with the fluorite and as late stage cross-cutting microveining. Sulphides are generally found as discontinuous bands parallel with the main vein-banding.

1.3. Mechanisms of formation

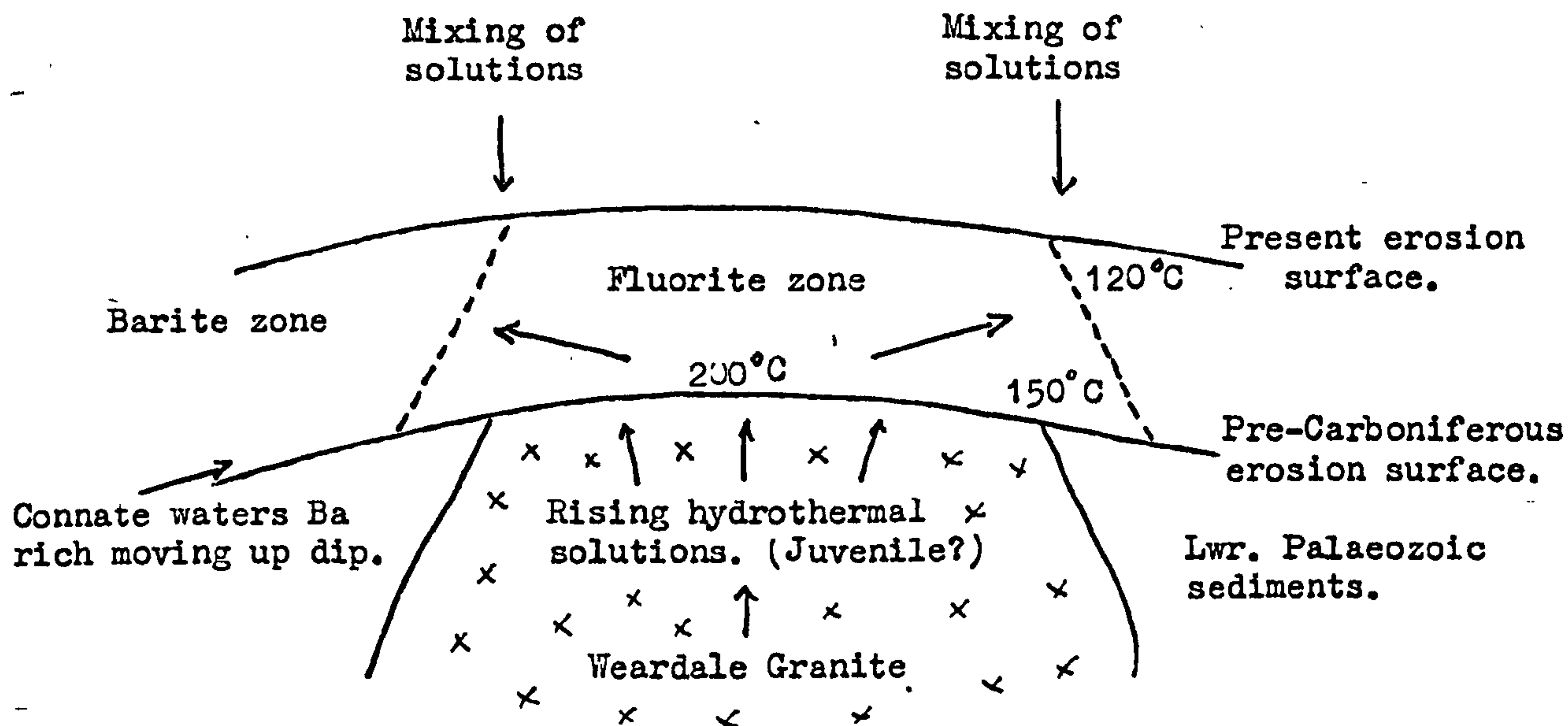
The genesis and evolution of the mineralisation has been debated for many years. Two main hypotheses have been proposed, that of Sawkins (1966), and that of Solomon, Rafter and Dunham (1971). More recent work has attempted to clarify the situation.

Sawkins (1966) based his model on a study on fluid inclusion data relating to quartz, fluorite and barite. He proposed that the zonal distribution resulted from mixing of two ore solutions. One solution was of magmatic hydrothermal origin and localised to the Weardale Granite cupolas. This solution was rich in metal ions, chloride, fluoride and sulphate and as it moved upwards and outwards from the granite came into contact with a second solution. This solution was a barium-rich connate brine containing reduced sulphur species, which had migrated up-dip from the surrounding sedimentary basins. Quartz and fluorite deposition from the magmatic fluid, resulted from cooling. Sulphides were precipitated where the two solutions met, as was the barite which formed as a result of cooling of the mixed solution, Fig. 1.6.

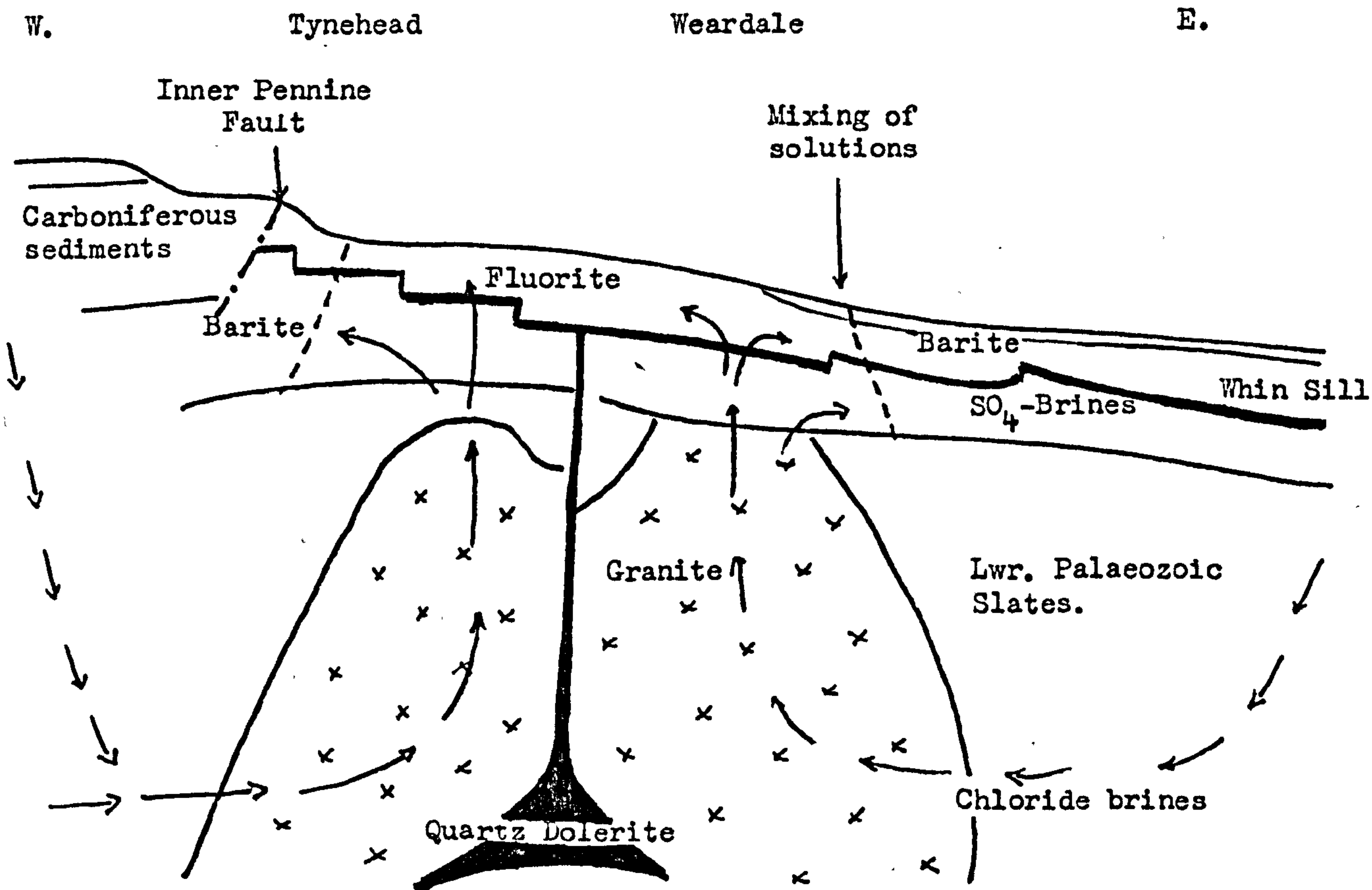
Soloman, Rafter and Dunham (1971) based their model on a study largely on sulphur and oxygen isotope data from sulphates

Fig.1.6 Mechanisms of formation for the Northern Pennine orefield.

Sawkins 1966.



Solomon, Rafter and Dunham 1971.



and sulphides. They proposed a mixing hypothesis involving two solutions both of connate formation water origin. The $\delta^{34}\text{S}$ values obtained for barite were found to be very similar to those of Lower Carboniferous evaporites. The first solution, a chloride rich brine had descended through Carboniferous sediments and had undergone membrane filtration. During this process sulphate was reduced to sulphide and metal ions were leached from the sediments. At depth the brine was heated and began to ascend. The Whin Sill, ^{and Granite} was suggested as the heat source driving the convective rise of the fluids. The other solution was a shallow sulphate rich brine present in the Carboniferous sediments. It originated either from trapped Carboniferous sea water or from meteoric water modified by solution of Carboniferous evaporites. The Cl^- and metal rich brine deposited fluorite due to cooling, and where it came into contact with the sulphate rich solution the Eh and pH conditions were favourable for the precipitation of sulphides and barite, Fig. 1.6.

Further work on the subject has tended to favour one or the other of these two mechanisms. (Smith, 1974; Russell and Smith, pers. comm.) Several points are still not satisfactorily explained.

1.4. Aims of the present work

The aim of the present work was to study the origin and mechanism of formation of the ore minerals in the Northern Pennine Orefield. Thus inclusion fluids from a variety of minerals were analysed using wet chemical methods and isotope work. Quantitative extraction and analysis of these fluids was necessary and involved much new development work.

Extraction by decrepitation, in a vacuum system, was used to obtain gas analyses which were later used for interpretation of the pH of the fluid. The extraction procedure was also necessary for hydrogen isotope work on the actual fluids. Conversely oxygen isotope work was only carried out on the mineral and hence necessitated correction to obtain a value for the inclusion fluid. These results were then used for interpretation of the origin and evolution of the ore fluid. Work on strontium isotopes of the fluorite mineralisation and its host rocks were also incorporated into this provenance study.

The chemical composition of the fluids was studied by leaching the decrepitated material and analysing the leachates obtained, by a variety of chemical methods. Generally the concentrations of elements were in the lower portion of the sensitivity ranges for the instruments. The results were then recalculated to give the actual fluid inclusion composition and were consequently used for the study of the causes of mineral deposition.

The above work was also used to determine why the two main non-metal mineral zones are almost mutually exclusive and why large amounts of sulphide mineralisation occurs at or near the junction of the zones.

Further work involving other chemical parameters and isotope compositions, for the fluids, is necessary to clarify the suggested proposal for the origin, evolution and deposition of the Northern Pennine Orefield.

C H A P T E R T W O

2.10. Fluid inclusions

Fluid inclusions are microscopic droplets of fluid preserved in naturally occurring minerals. The vacuoles, containing the fluid, form during growth of the mineral around irregularities or impurities. There are usually more than one generation of fluid inclusions in any one sample, those present most commonly being primary and secondary inclusions. These two main genetic groups of inclusions have been observed in many studies but their criteria of definition are far from absolute, (Roedder, 1967).

2.11. Primary fluid inclusions

Primary inclusions are produced by any process that interferes with the primary growth of a perfect crystal such that it traps fluid. They may form in one of the following ways:-

- a) Rapid dendritic growth of crystals producing irregular re-entrants within which fluid is trapped.
- b) Dis-orientated growth of crystals on a fractured seed crystal. This causes fluid to be trapped between developing crystal faces.
- c) Solid particle impurities deposited on the surface of a perfect crystal. The crystal develops around the impurity, where growth is unhindered, thus enclosing vacuoles filled with fluid centred on the impurity.

These methods produce primary inclusions which are in general related to growth zones or crystal shape. They often form series of inclusions parallel to particular forms such as

(100) in fluorite. Single inclusions are also relatively common.

Other criteria often allocated to primary inclusions are perfect negative crystal shapes and the occurrence of euhedral crystal faces projecting into vugs. These are, however, not absolute criteria as the morphology may produce irregular, amoeboid and branching shapes as well as regular, spherical, tabular and negative crystal forms.

Primary inclusions range in size from fractions of a micron in diameter to several tens of millimetres. However inclusions larger than 100 μm are rare.

Primary inclusions are useful because they represent the original fluid from which the minerals were formed.

2.12. Secondary fluid inclusions

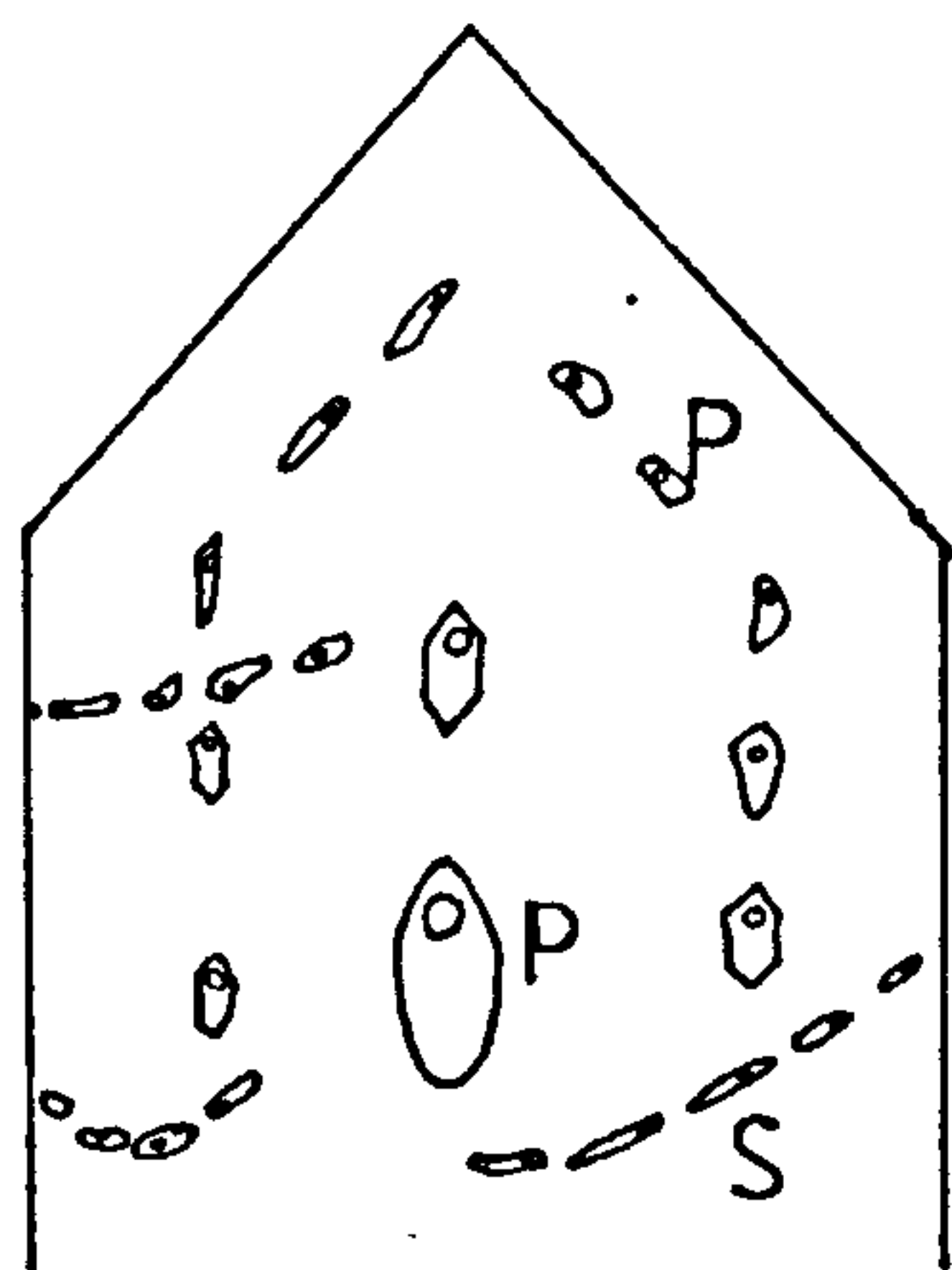
Secondary inclusions are formed, after complete crystallisation of the host mineral, by production of fractures or cleavages, along which any fluids present may pass. Passage of the fluid along the fractures results in dissolution and recrystallisation of the original mineral during which time inclusions of a different age, concentration and/or composition to the primaries are trapped in the mineral.

There may be a temporal overlap between the formation of primary inclusions, and secondary inclusions trapped near the core of the crystal, due to fracturing of the mineral during growth, Fig. 2.1.

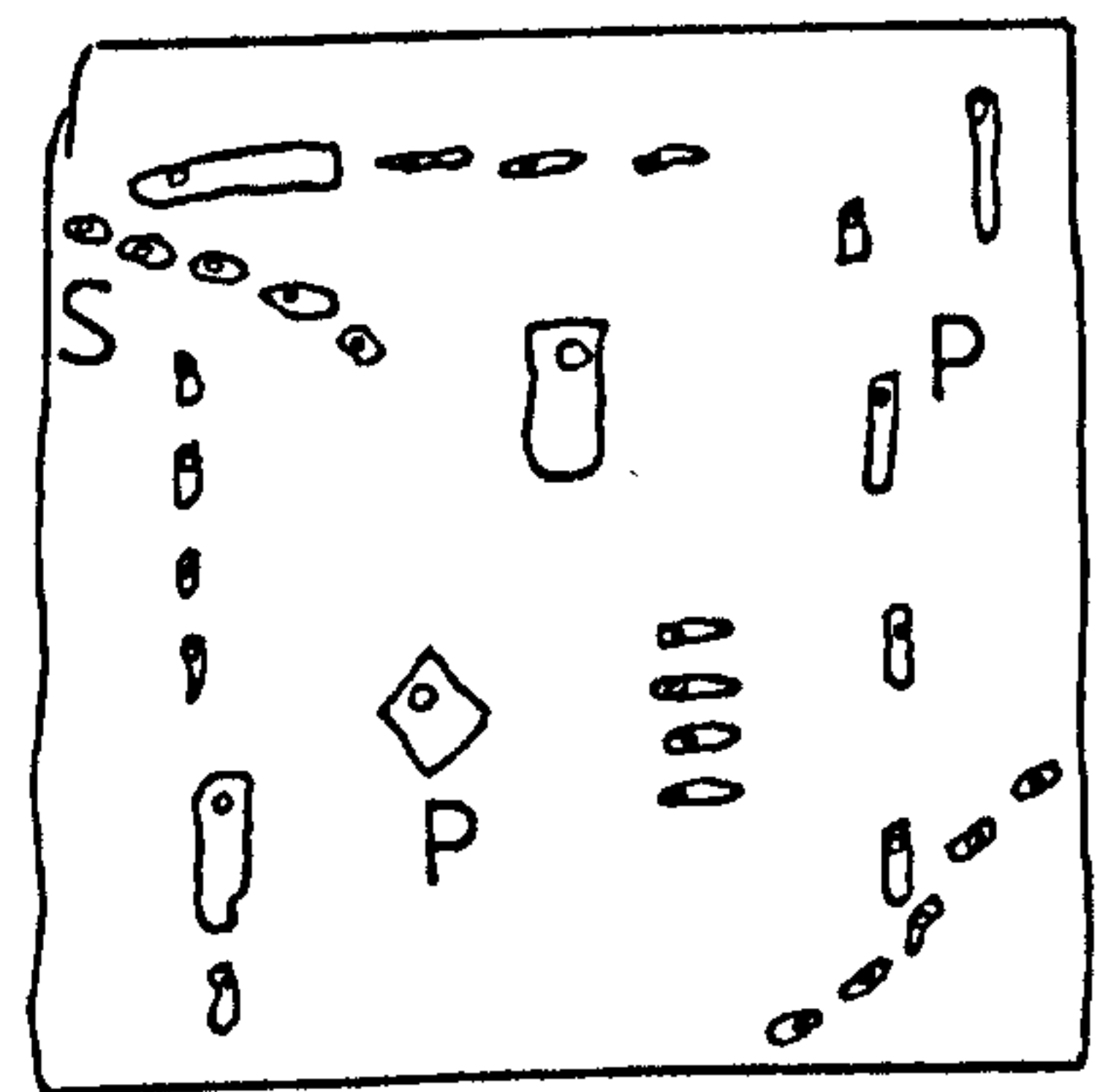
2.13. Composition of inclusions

The composition of an inclusion depends on the physical and chemical nature of the fluid medium at the time of trapping, (Rankin, 1978). During cooling of a liquid magma

Fig.2.1 Idealised distribution of primary and secondary fluid inclusions.

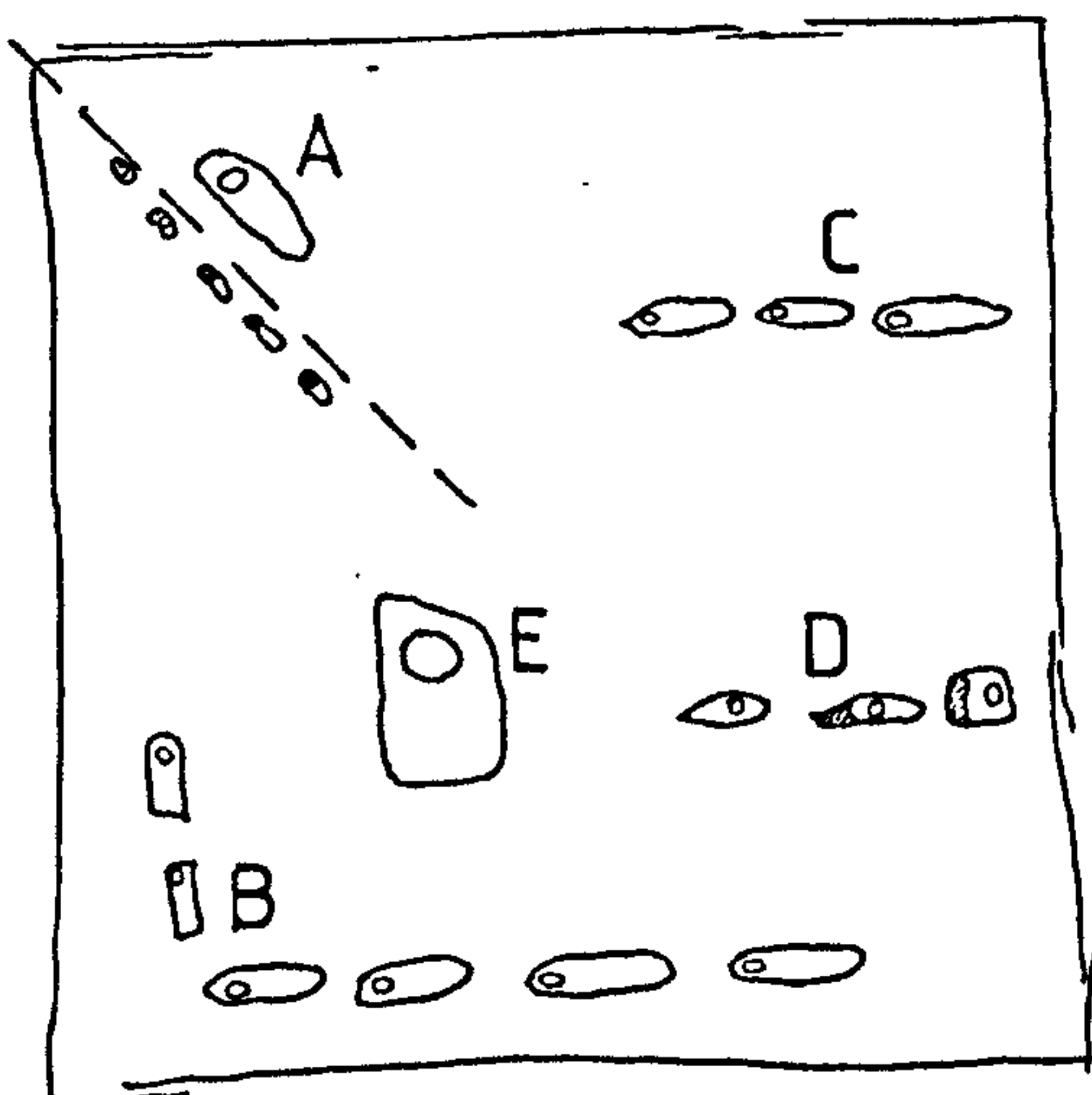


Quartz: Section parallel to the c-axis



Fluorite

Inclusions: P = Primary
S = Secondary



- A Along or parallel to twin planes
- B Along growth zones parallel to crystal faces
- C Associated with pre-existing etch pits
- D Associated with trapped solid phases
- E As relatively large isolated cavities

solid glass or crystal melt inclusions may form. However, in most hydrothermal deposits the inclusions contain either a single phase (liquid, gas or solid sulphide crystals) or multiple phases. These generally contain one or more liquids and a gas. At room temperature solutions oversaturated with respect to a compound may produce daughter crystals of that compound.

In hydrothermal minerals the most common variety of fluid inclusion contains an aqueous fluid with or without a gas bubble or solid particles present. These inclusions are composed of an aqueous solution which may contain many or few inorganic ions. The inclusion often contains a mobile vapour bubble, formed as a result of cooling from the original trapping temperature to room temperature. This is due to the differential thermal contraction of the host crystal and the contained fluid.

With concentrated brines the inclusions may contain daughter minerals, in addition to the aqueous solution and vapour bubble. These minerals only form when the concentration of the solution became saturated with respect to a specific salt. This usually occurs as a result of decrease in temperature to room temperature which is known to cause most inorganic salts to become less soluble. Thus a concentrated solution of >23 wt% NaCl. would produce daughter crystals of halite since this is the composition of a saturated solution of sodium chloride at room temperature.

Inclusion fluids are seldom pure single salt solutions and generally contain other salts which may exceed their own saturation points on cooling. This may result in the appearance of several daughter minerals within one inclusion. The

Most common types of daughter minerals are halite (NaCl), sylvite (KCl) and anhydrite (CaSO_4).

Solid phases incorporated into the inclusions at the time of formation, termed 'captive' minerals, are distinguished from daughter minerals by their erratic distribution and variable size in relation to the size of the inclusion. Their failure to dissolve in the fluid on heating indicates that they are not representative of the composition of the inclusion.

Aqueous inclusions are by far the most common variety found in hydrothermal minerals although carbon-dioxide rich inclusions, hydrocarbon-bearing inclusions and gaseous inclusions have also been recognised, Fig. 2.2, Plate 2.1.

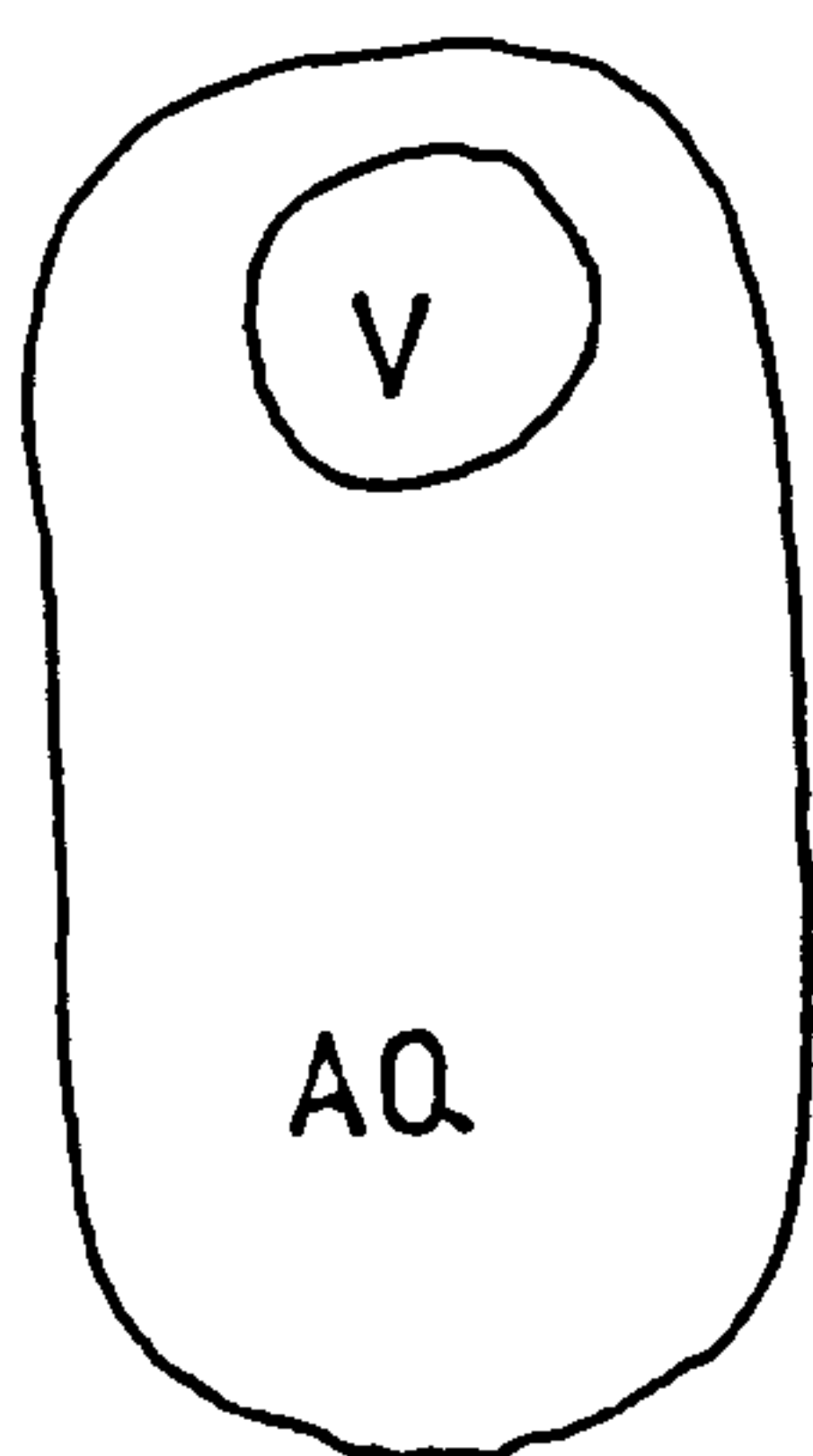
Carbon dioxide rich inclusions containing liquid carbon dioxide liquid with carbon dioxide gas have been observed, (Roedder, 1963). More complex inclusions may contain carbon dioxide gas and liquid together with an aqueous solution. These inclusions can be distinguished by the higher negative relief of liquid CO_2 relative to the aqueous solutions in the host mineral.

Hydrocarbon-bearing inclusions containing either bitumen or oil are less common, but can be recognised by their colour, and fluorescence under u.v. illumination. Methane rich inclusions are more difficult to identify. Hydrocarbon-bearing inclusions have been noted in association with the lead-zinc deposits of the Cave-in-rock district of Illinois, (Freas, 1961).

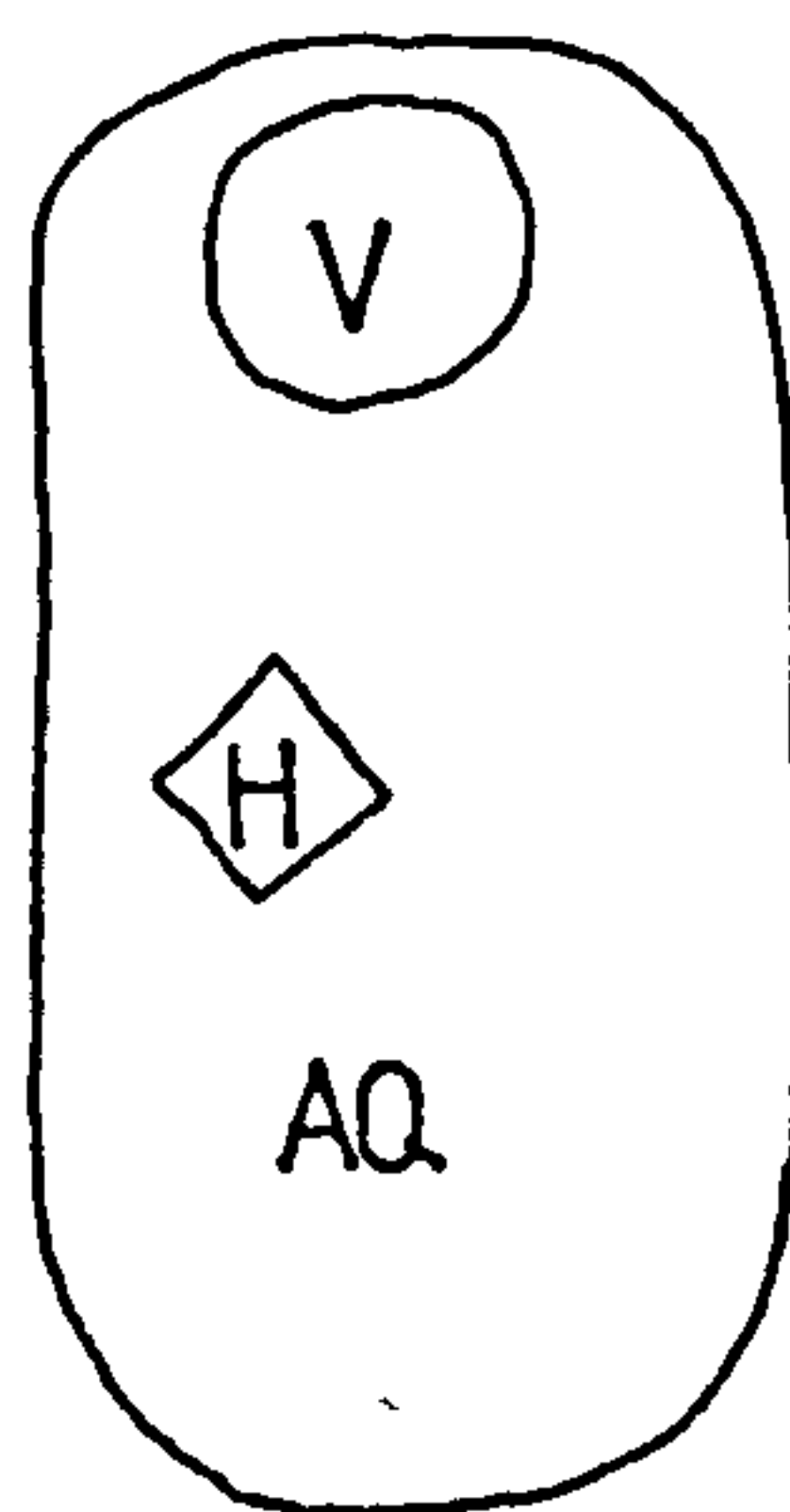
The other type of inclusion mentioned above is the gaseous inclusion. These are most frequently formed where the minerals have been deposited from a heterogeneous 'boiling' fluid.

Fig.2.2 Composition of fluid inclusions.

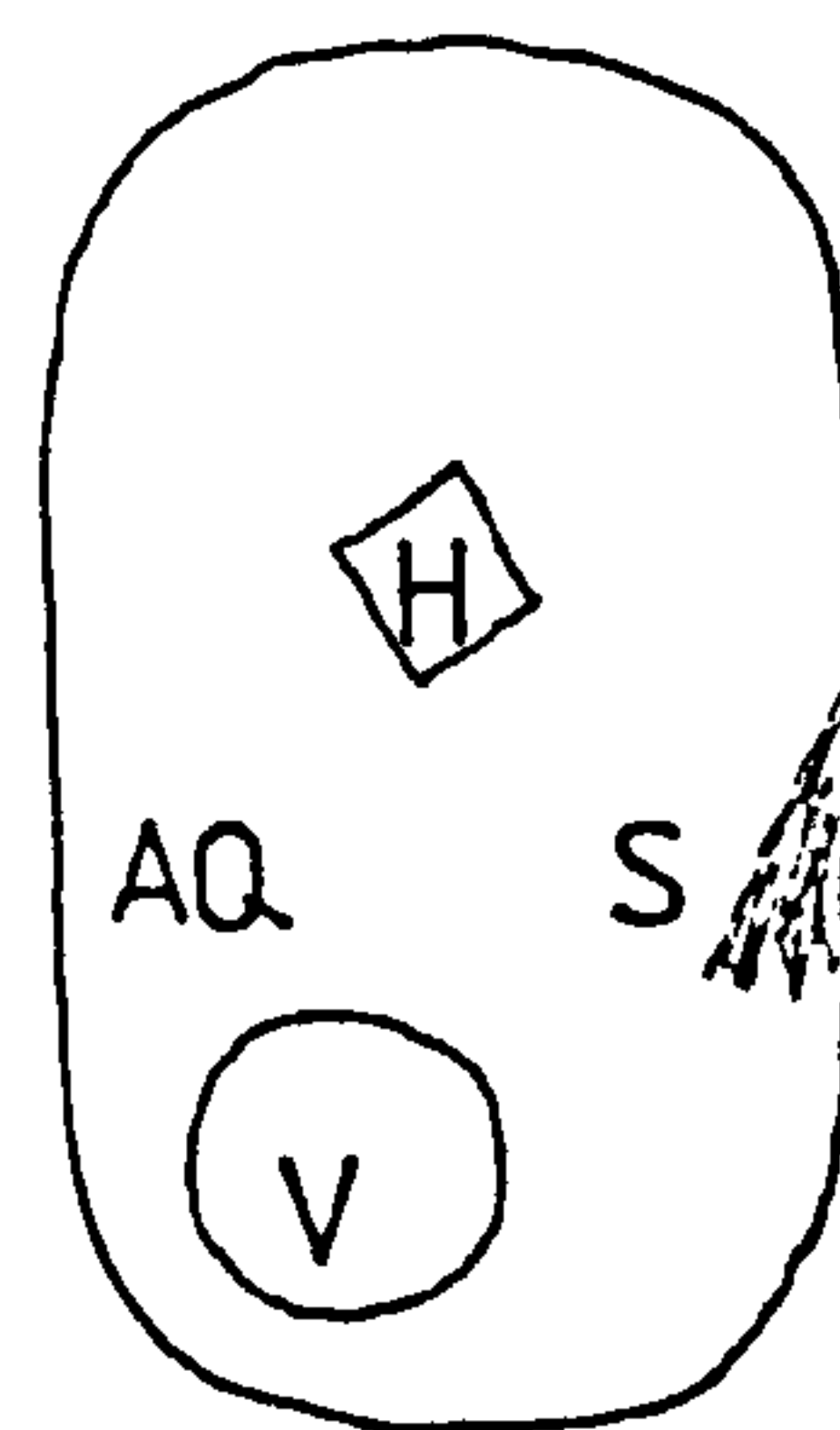
Aqueous Inclusions



With a vapour
bubble

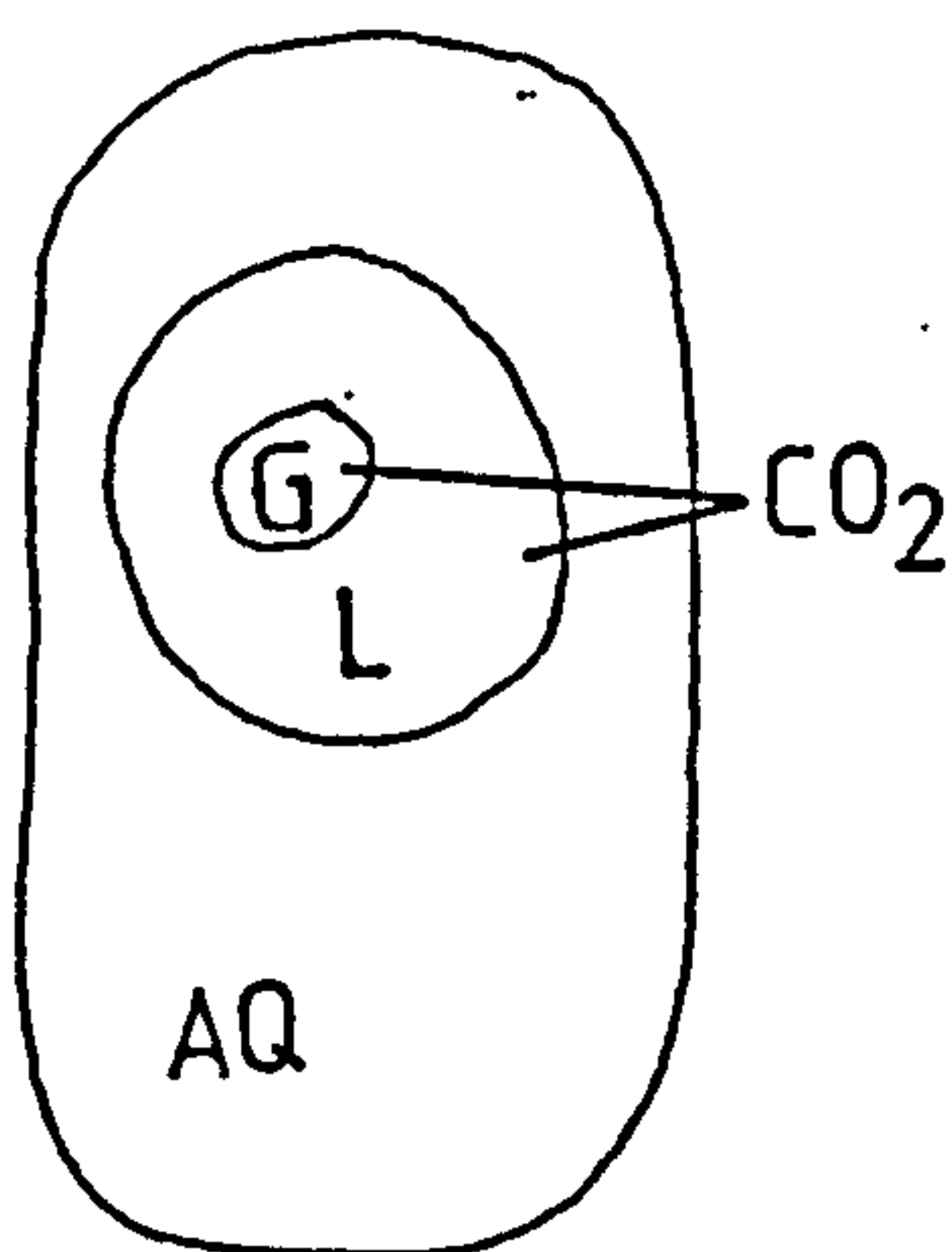


With a vapour bubble
and a daughter mine-
ral $> 23 \text{ wt\% NaCl}$

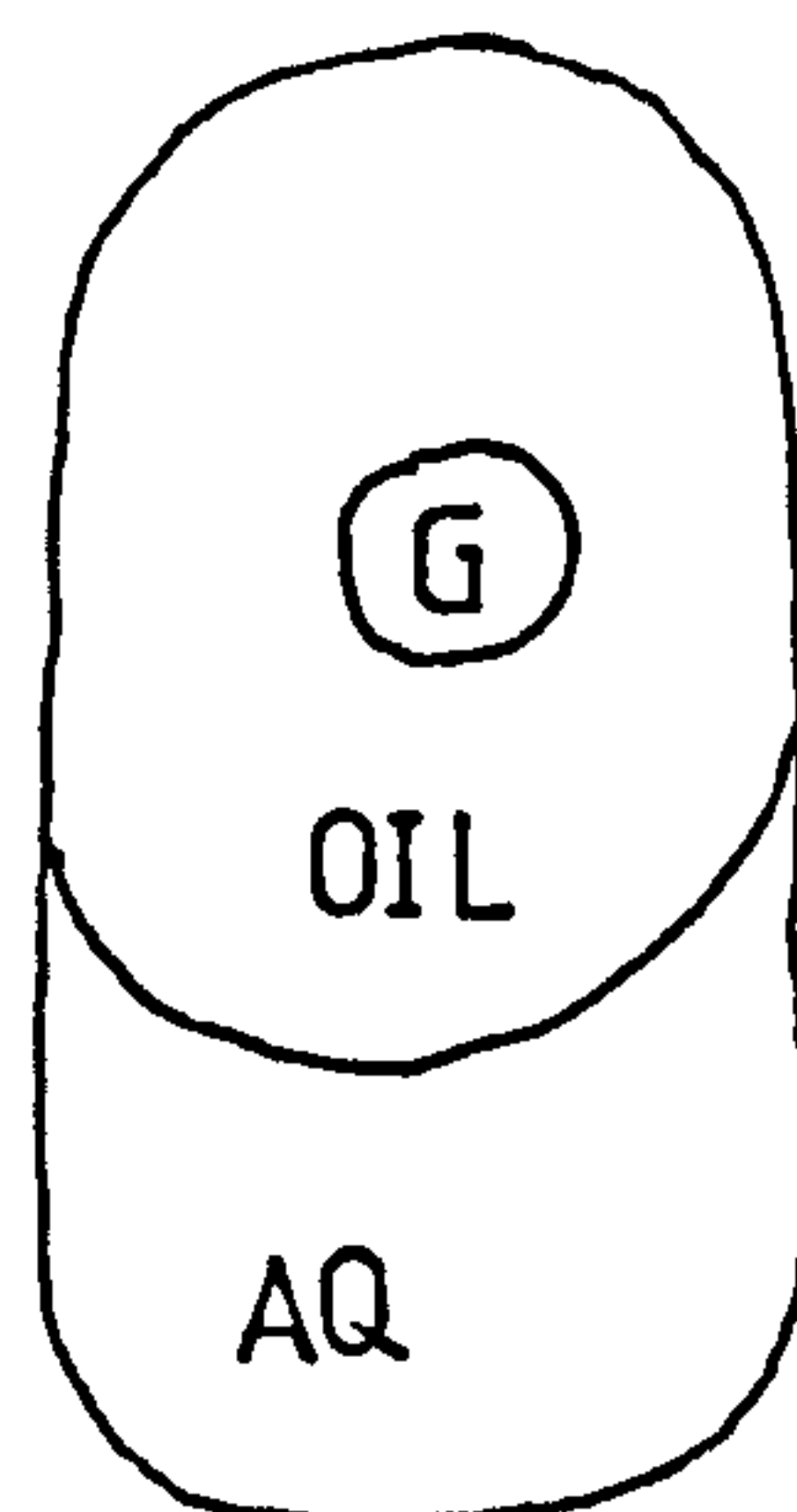


With a vapour bubble,
daughter mineral and
sulphide impurity

Other Inclusions



Carbon dioxide and
aqueous inclusion

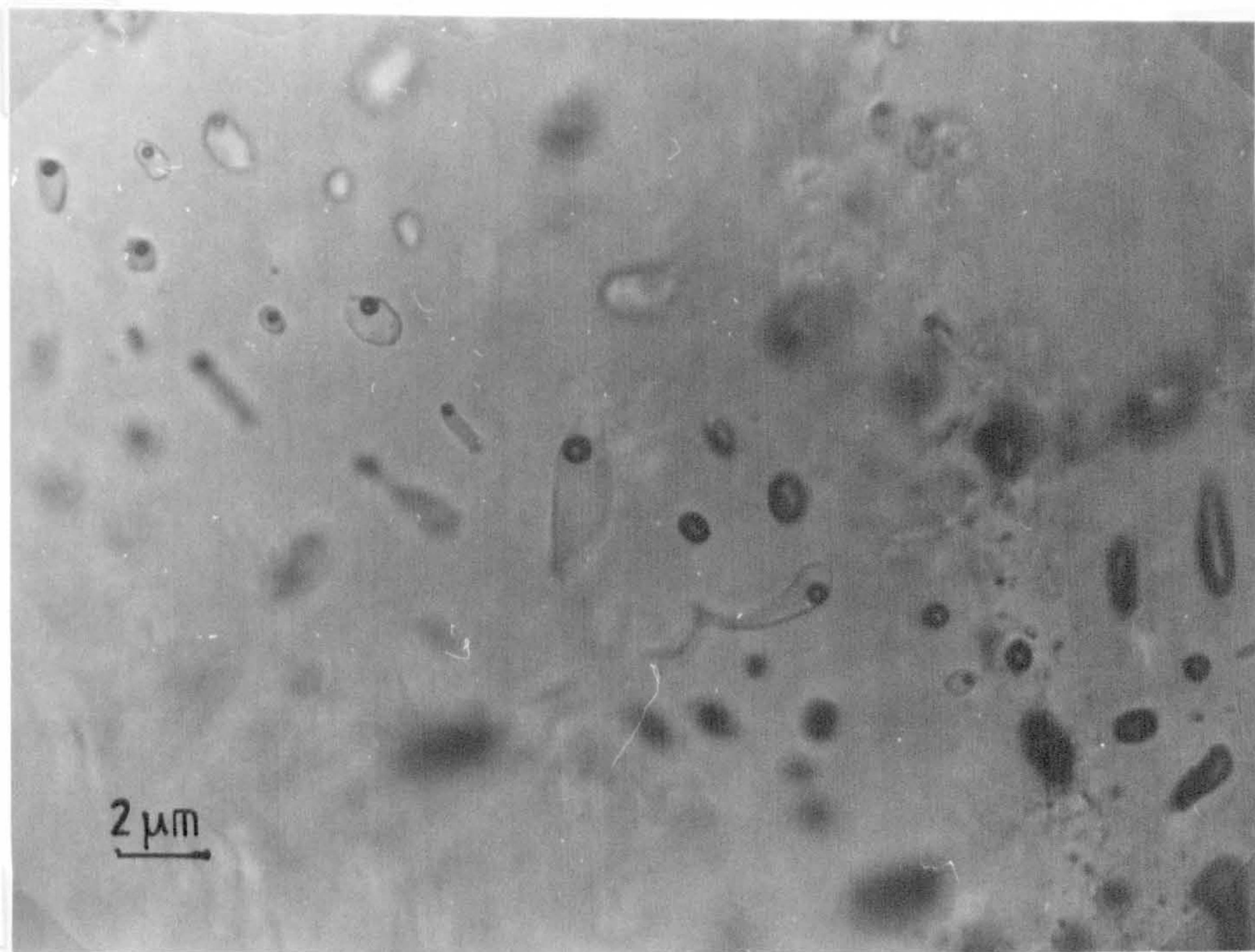


Hydrocarbon
bearing inc-
lusion

Key

AQ	Aqueous fluid
V	Vapour bubble
H	Halite crystal
S	Sulphide impurity
G	Gas
L	Liquid

Plate 2.1 Different types of inclusions.



Two phase aqueous fluid inclusions in fluorite.

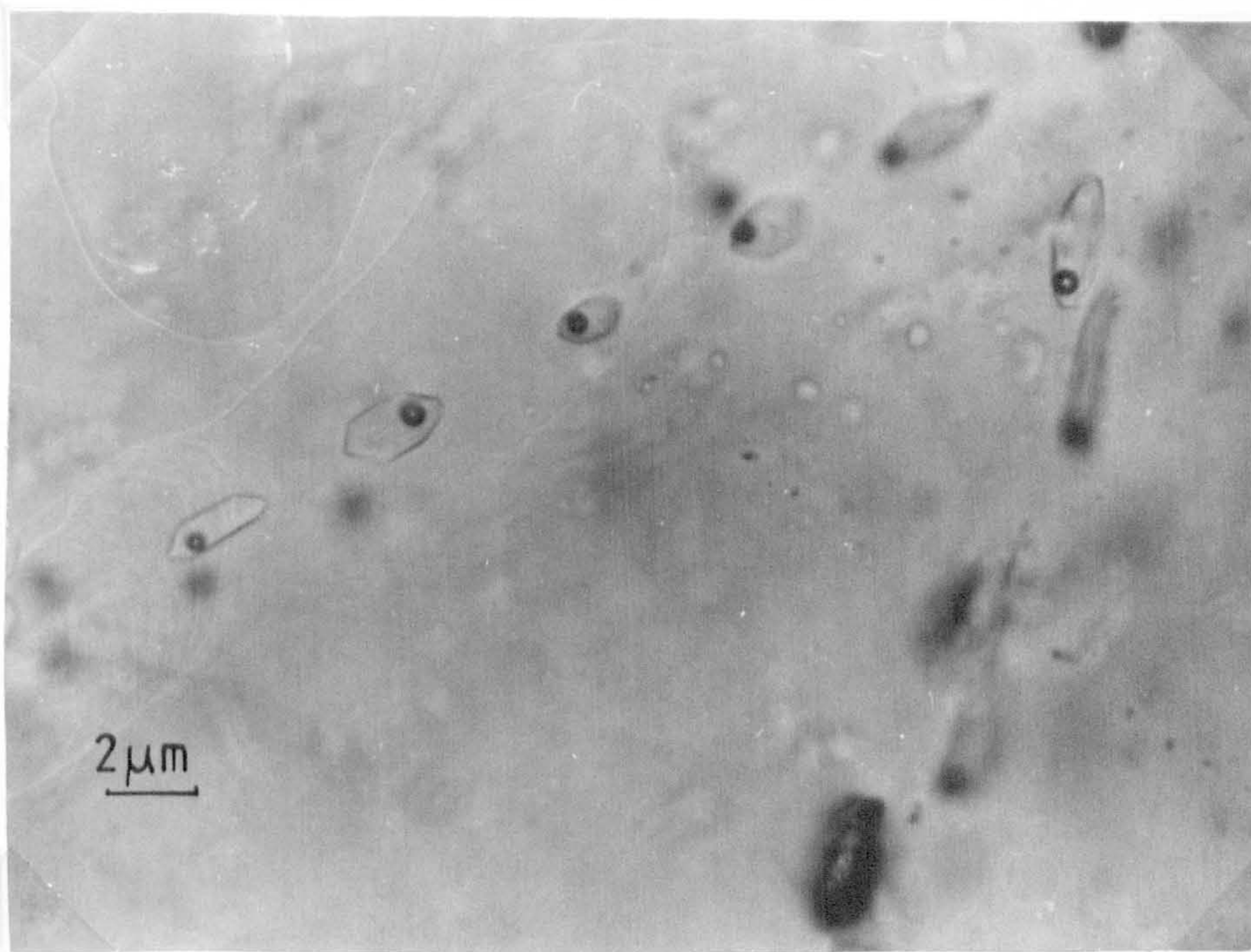
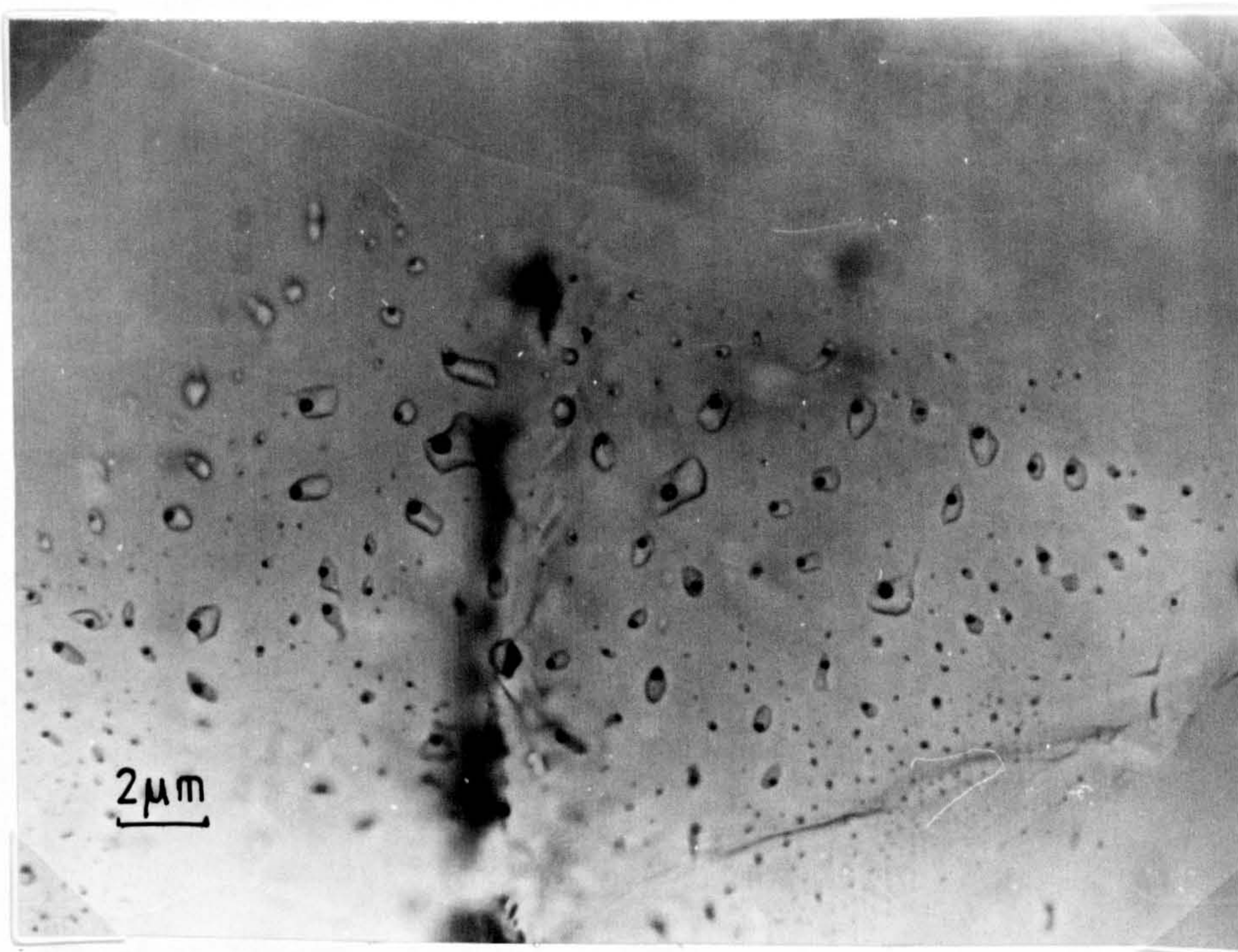


Plate 2.1 continued.

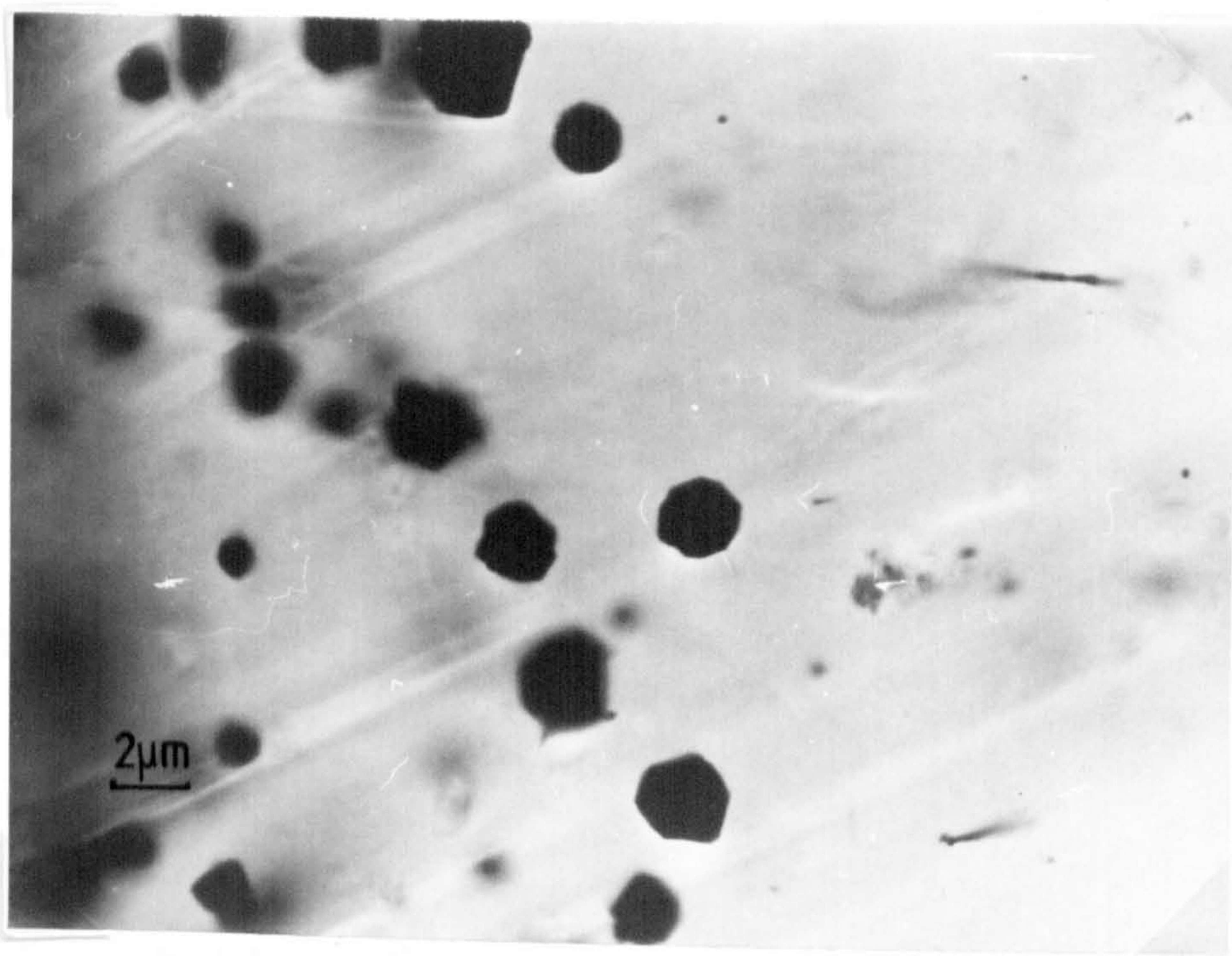


Zones of aqueous fluid inclusions in fluorite.



Oil and aqueous inclusions in fluorite.

Plate 2.1 continued.



Solid sulphide inclusions.



Other varieties of inclusions less common in hydrothermal minerals are glass and crystal melt inclusions. These are more likely in minerals formed during magmatic crystallisation.

2.20. Inclusions present in minerals from the Northern and Southern Pennine Orefields

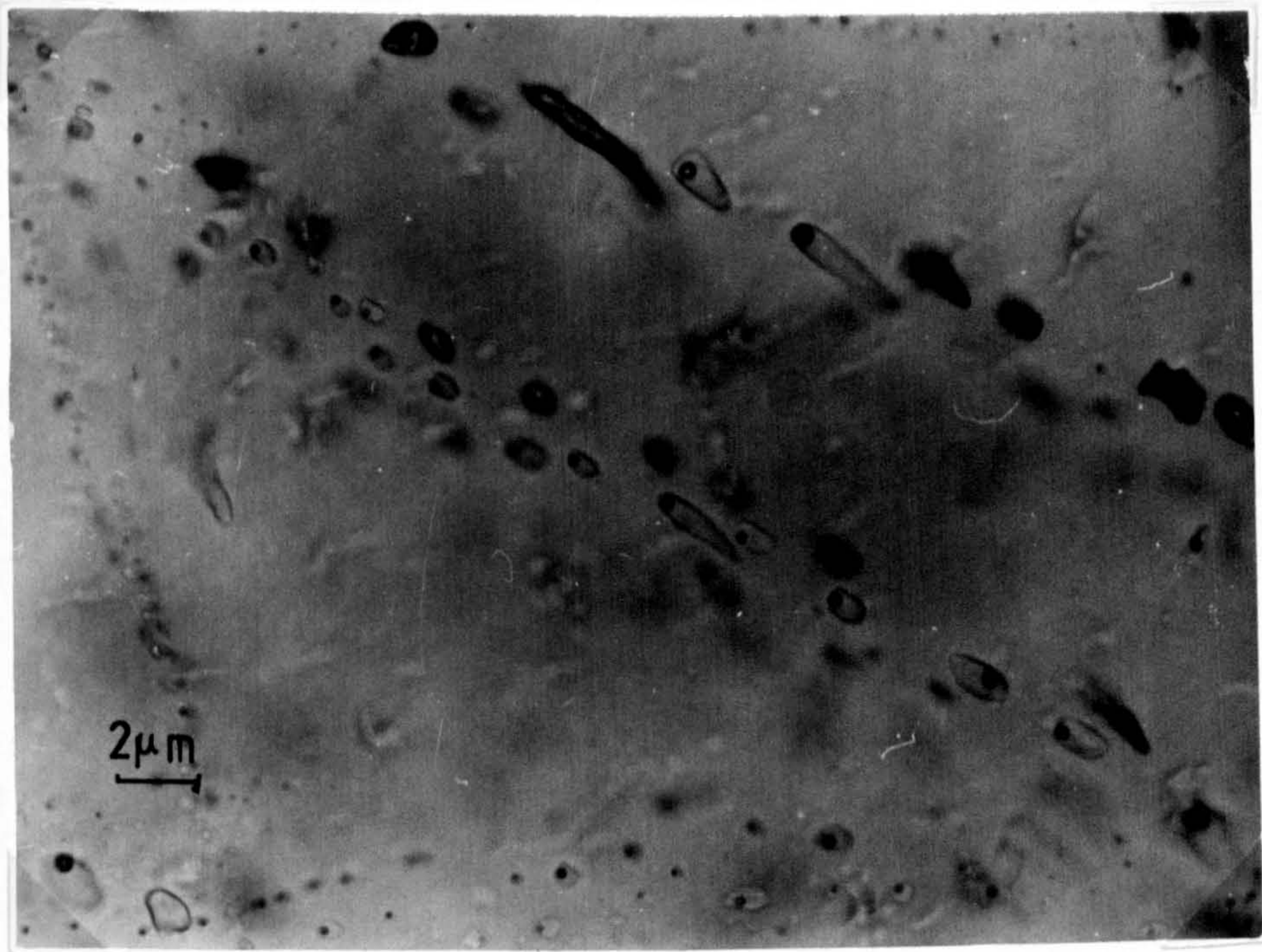
The minerals used in this study were fluorite, quartz and Barite. Variations in inclusion type were observed both within and between the different minerals, Plate 2.2.

Fluorite, the principal mineral, was generally rich in inclusions, mainly of primary rather than secondary origin. Their size ranged from a few microns, usually found in large numbers as planar arrays up to 100 μm , as single or small clusters of inclusions. Rare samples from Heights Mine on the Northern Pennine Orefield have macro-inclusions, 10 mm in length, and are clearly visible to the naked eye. The inclusions found in fluorite are all aqueous inclusions, containing a vapour bubble and occasionally a daughter mineral. One Derbyshire fluorite provided hydrocarbon inclusions in addition to composite hydrocarbon/aqueous fluid inclusions, Plate 2.2.

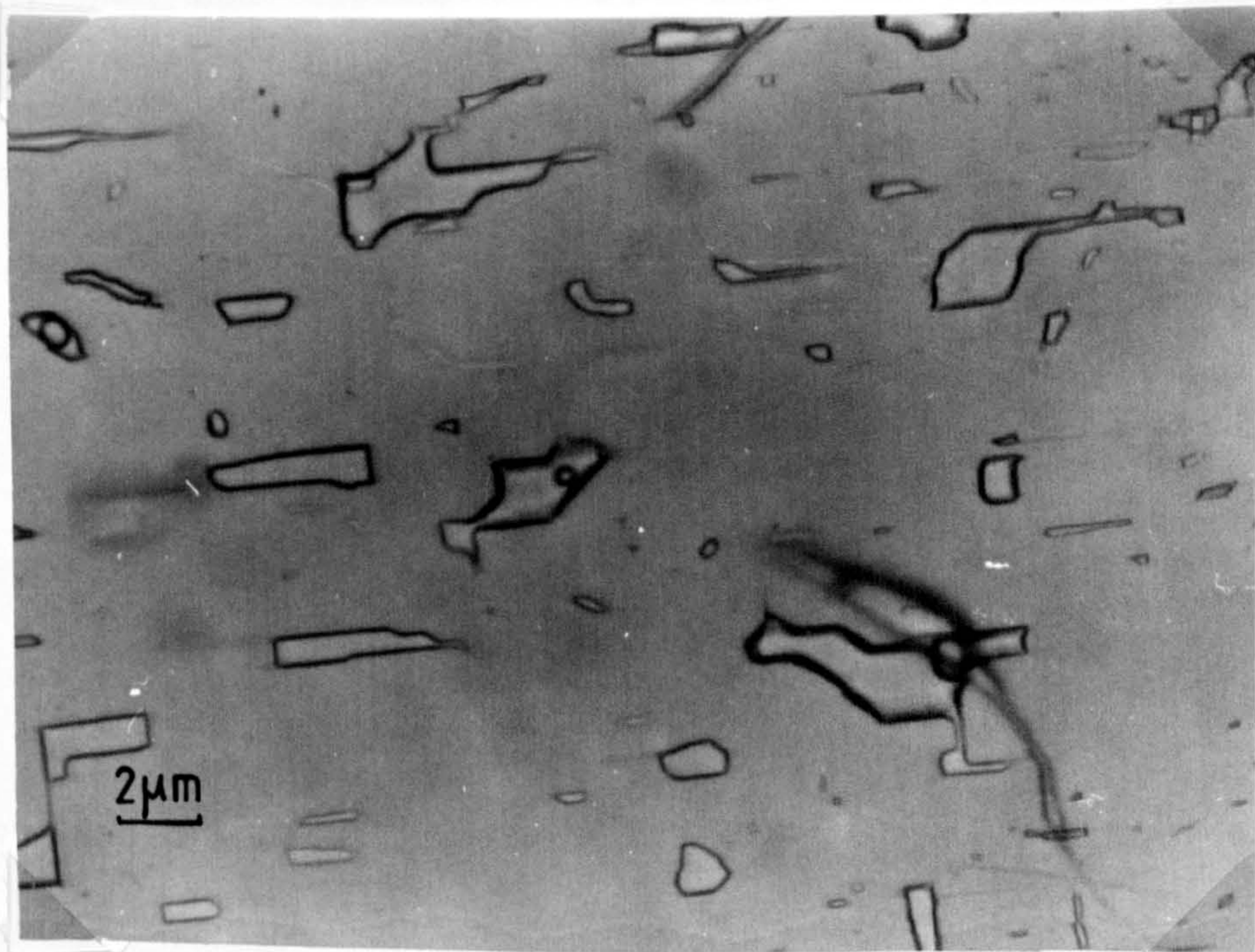
Inclusions in quartz were found to be very similar to those in fluorite but generally smaller in size.

The barite samples contained almost exclusively single phase aqueous inclusions, only a few having a vapour bubble. The shape of the inclusions tended to be more irregular, and necked inclusions were common.

Plate 2.2 Examples of inclusions in minerals from the Northern
and Southern Pennine Orefields.



Zones of aqueous fluid inclusions in fluorite.

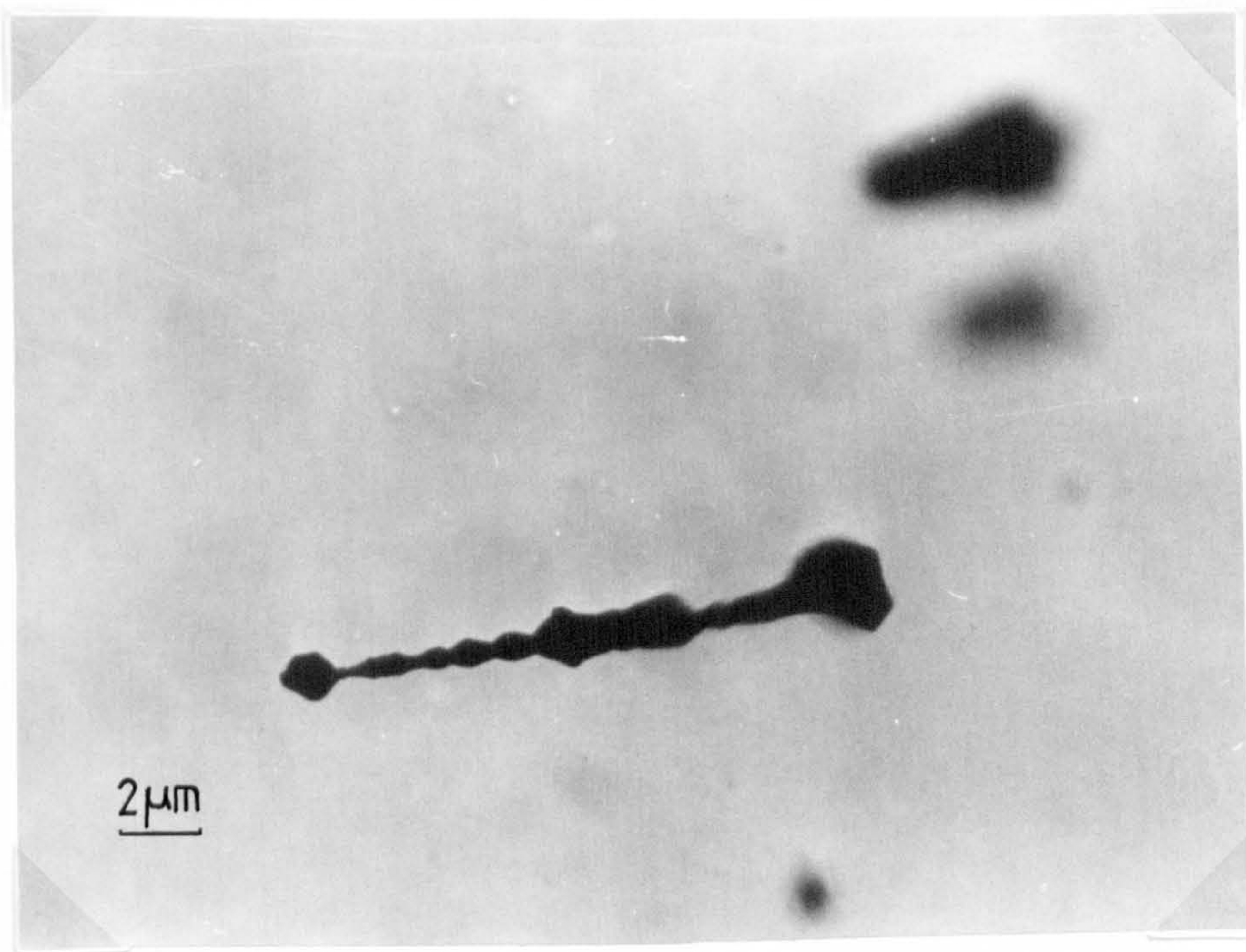


Aqueous fluid inclusions in barite.

Plate 2.2 continued.



An oil and aqueous fluid inclusion in fluorite.



Solid sulphide inclusions in fluorite.

2.30. Optical observation of fluid inclusions

For the optical observation of fluid inclusions, two methods of preparation were used.

The first method involved the preparation of double-sided polished plates. These were produced by casting the mineral in polyester resin and then casting it in araldite. A slice of mineral was then cut from the hardened araldite-mineral block and polished on both sides. The thickness of the polished plate was approximately 0.5 mm. Individual fluid inclusions within these mineral plates were examined using a Leitz binocular microscope with high-power objectives, (max. magnifications X500). The plates enabled freezing and heating work to be carried out on both large ($>100\text{ }\mu\text{m}$) and small ($<30\text{ }\mu\text{m}$) inclusions.

An alternative sample preparation method was used for the rapid checking of inclusion density. This involved breaking large pre-cleaned fragments of the mineral into smaller chips approximately 2-5 mm in diameter. These were then immersed in deionised water, to reduce problems of light scattering from irregular surfaces, and examined at (X50) magnification using a stereo microscope. Refractive index liquids were not employed since they would have increased the problem of sample decontamination prior to chemical analysis. This technique allowed one to observe zones of inclusions plus larger single inclusions. The inclusions varied from $20\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$, in diameter, most being $20\text{--}30\text{ }\mu\text{m}$. The chips were useful for the rapid checking of the abundance of inclusions in the material, but could not generally be used for thermometric analysis of inclusions because of surface irregularities, except where cleavage fragments were available.

2.40. Thermometric analysis of fluid inclusions

Thermometric analysis involves the controlled heating and freezing of inclusion fluids to produce reversible phase changes. These are of use in the interpretation of the temperature and salinity of the fluids at the moment of trapping.

Polished plates of fluorite and quartz and thin cleavage plates of barite were sufficiently transparent to enable study of fluid inclusions at X500 magnification on a Leitz binocular microscope. This microscope was equipped with a combined heating-freezing stage, designed by Dr. T. J. Shepherd, (Appendix 1). Previous work by Smith, (1974), who used his own stage, was mainly confined to homogenisation temperatures for the Northern Pennine fluorites, although some freezing data was also obtained. The present study has used many of Smith's original samples and only a few gaps remained in the data relating to fluorite homogenisation temperatures. Additional data for quartz and barite from the orefield were, however, necessary.

2.41. Heating Techniques

Heating experiments on fluid inclusions were first carried out by H. C. Sorby in 1858. He based his work on the assumption that at the time of closure of the inclusions the contents would be homogeneous. As the host crystal cooled separation of the homogeneous phase into two or more heterogeneous phases would occur. Reversing the process by heating the inclusions from room temperature, should produce a homogeneous phase at the temperature at which the inclusions were trapped. This can be related to the minimum formation temperature of the host crystal providing the inclusions are primary, (Roedder, 1967).

Most studies have been carried out on two-phase inclusions containing a small vapour bubble and co-existing aqueous fluid. These inclusions usually homogenise to a liquid phase, any daughter minerals dissolving below the final temperature of homogenisation. Sometimes the exact temperature at which the vapour bubble disappears can be difficult to measure. This occurs when the tiny bubble moves into a 'dark' corner of an inclusion and is thus obscured from view, Fig. 2.3, Plate 2.3.

Inclusions containing $> 60\%$ vapour usually homogenise to a gas phase, but have not generally been used for temperature measurement owing to the difficulty in recognising the moment of homogenisation. (i.e. problems of internal reflection)
Fig. 2.3.

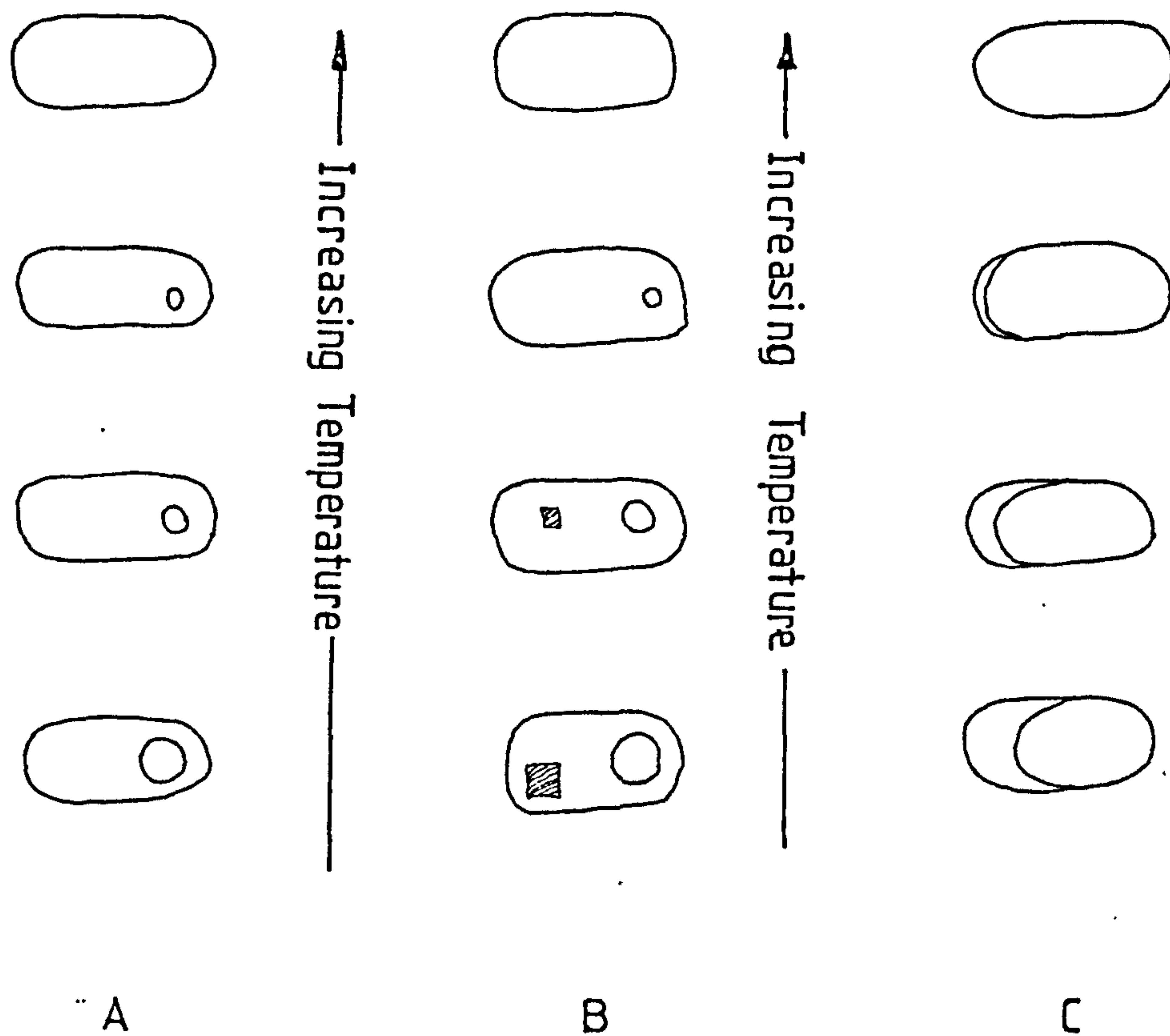
A wide range of homogenisation temperatures may occur for inclusions 'necked' due to later recrystallisation, which have leaked during heating. Such problems can be overcome by careful selection of inclusions and where possible by the measurement of at least 5 - 10 individual inclusions in the same specimen, and the repeat of each measurement.

Formation temperatures can be calculated from homogenisation temperatures by applying the appropriate pressure correction factor for the observed salinity, (Appendix 1).

2.42. Freezing Techniques

Freezing data on saline fluid inclusions can be used to estimate the total salt content of the inclusions. By measuring the depression of the freezing point with respect to pure water the concentration of dissolved salts, expressed as weight percent sodium chloride equivalents, can be derived. Consideration of the system $\text{NaCl-H}_2\text{O}$, Fig. 2.4., shows that solutions

Fig.2.3 Various types of homogenisation.

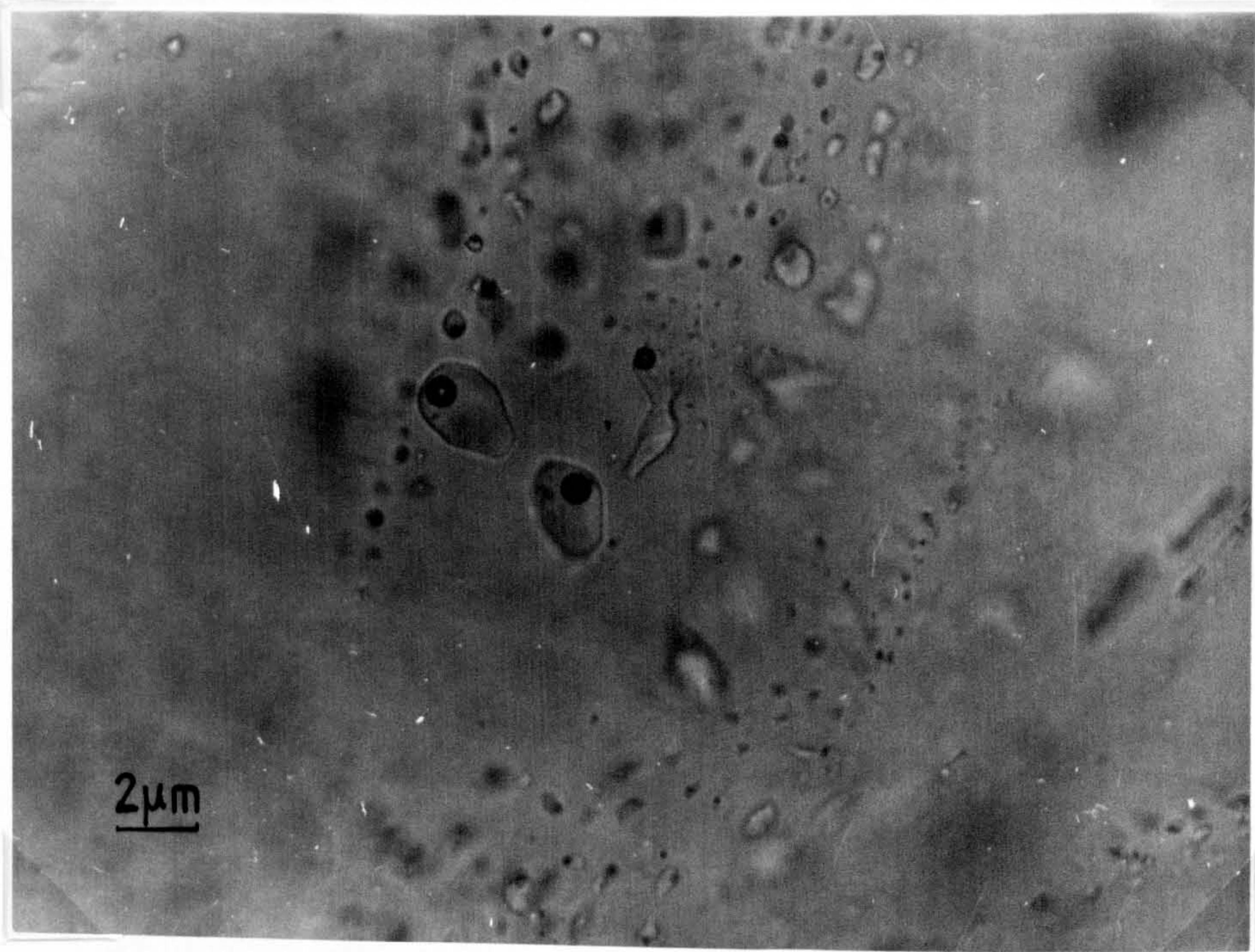


A: To a liquid

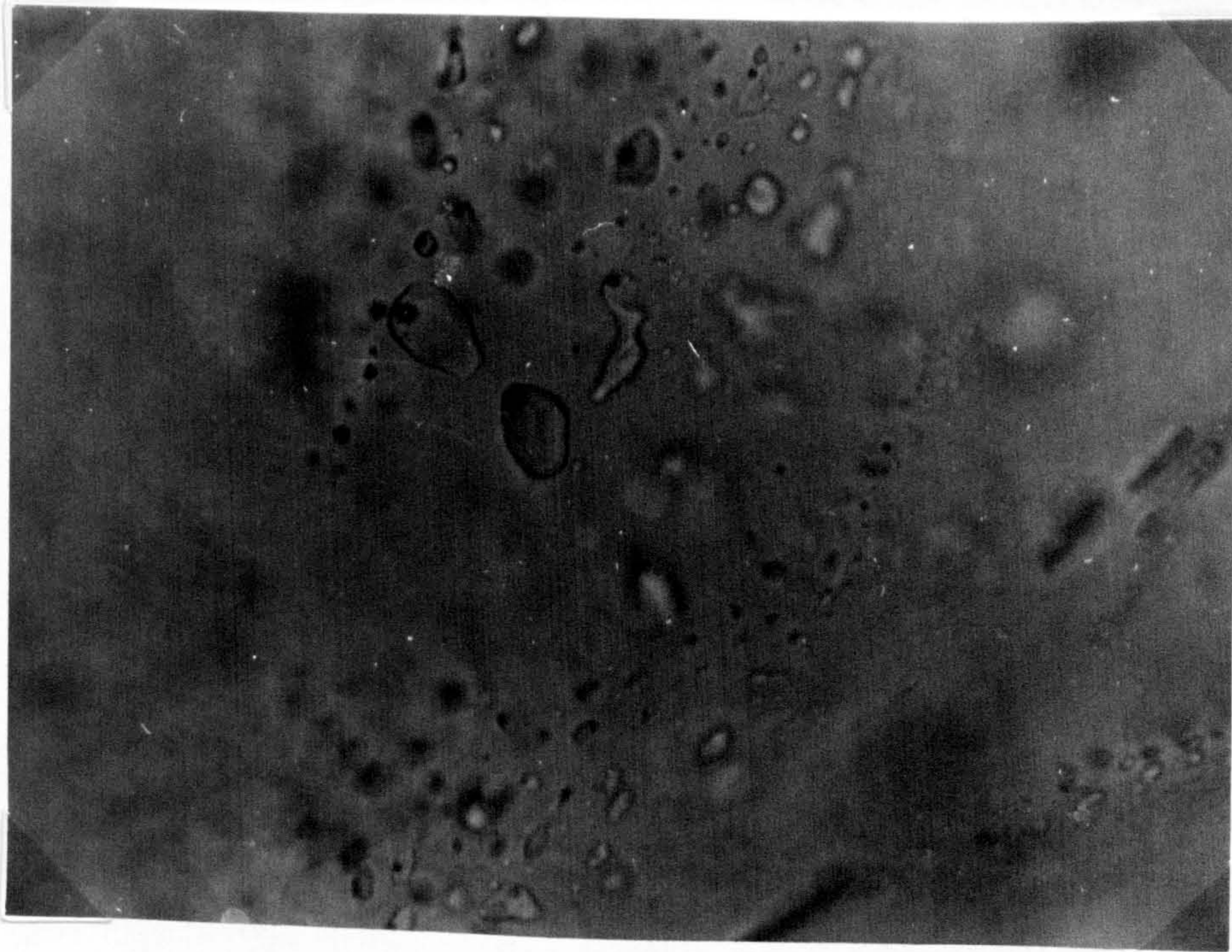
B: To a liquid with the solution of a daughter mineral

C: To a gas

Plate 2.3 Homogenisation of a two phase inclusion in fluorite
to a single phase.

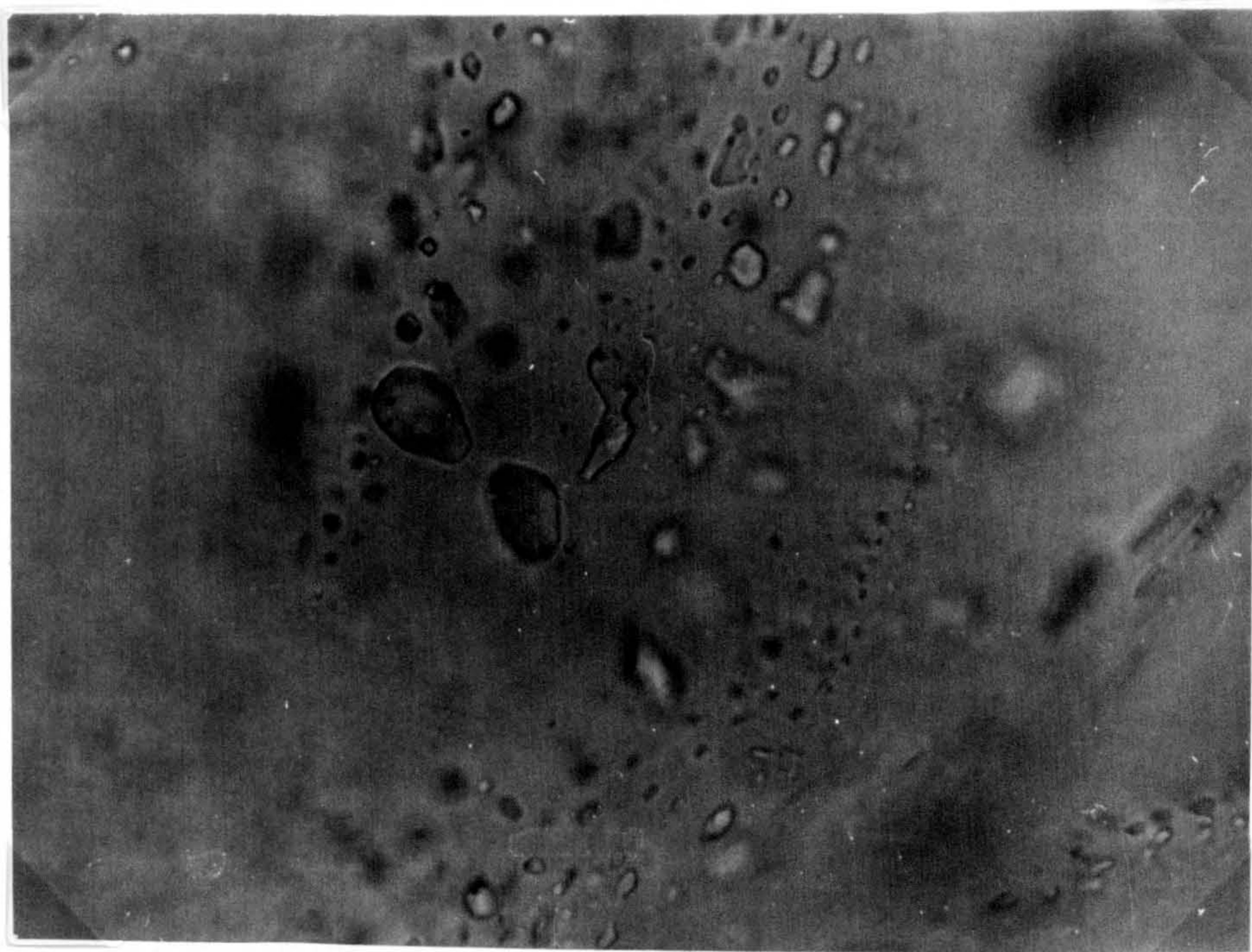


Room temperature.

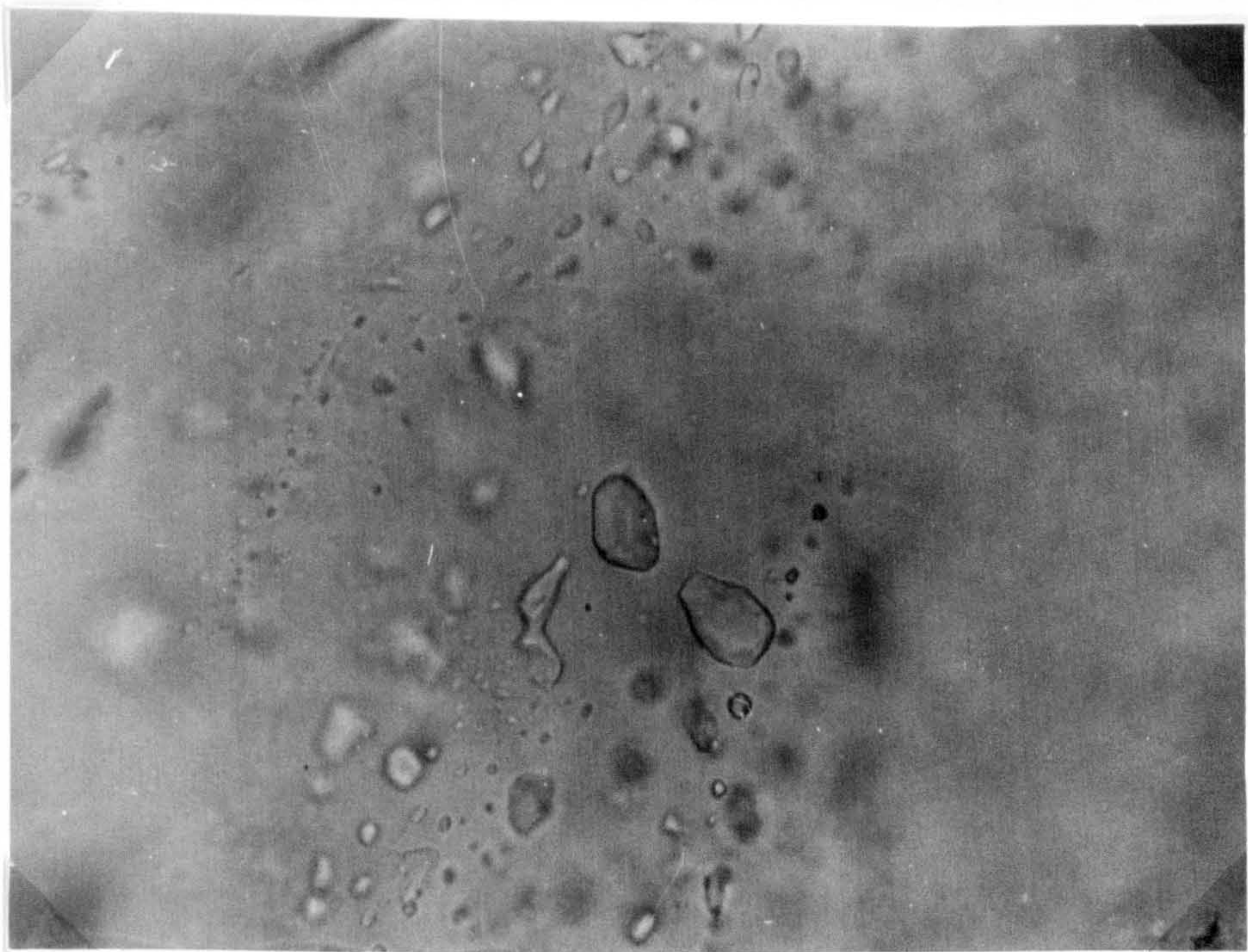


Temperature = 106.0 °C

Plate 2.3 continued.



Temperature = 130.9°C .



Temperature = 143.5°C , Temperature of homogenisation.

with salinities in the range 0 - 23.3 wt.% NaCl will give a freezing point depression of between 0 - 21.1 °C. The upper level of NaCl concentration, 23.3 wt% refers to the saturation level of one molar NaCl at room temperature, and produces a freezing point depression of 21.1 °C. Freezing point work has been modelled on the NaCl-H₂O system since it has been found that NaCl generally predominates over other salts in fluid inclusions, (Roedder, 1962; Shepherd, pers. comm.).

To incorporate higher sodium chloride equivalent salinity values the phase diagram has been extended by recording the incongruent melting of hydro-halite NaCl.2H₂O, (Roedder, 1963; Shepherd, pers. comm.) or by allowing for sodium chloride crystals precipitated during cooling. Hydro-halite can be distinguished from ice by its higher birefringence and incongruent melting point of +0.1 °C.

Thus for a two phase system, (NaCl-H₂O), the eutectic point and last melting point of the ice are required to obtain an idea of the fluid composition, Fig. 2.5. The measured eutectic point will indicate how close the fluid composition is to the NaCl-H₂O system, and the last melting point of the ice will give the NaCl composition of the solution.

However if a third salt is present the initial melting point or three phase eutectic will be decreased as below:-

System	3 phase - Eutectic
NaCl-KCl-H ₂ O	-22 °C
NaCl-CaCl ₂ -H ₂ O	-55 °C
NaCl-MgCl ₂ -H ₂ O	-35 °C

Addition of further phases to the above systems complicate the melting sequences and as very little experimental work has

Fig.2.4 The NaCl-H₂O system.

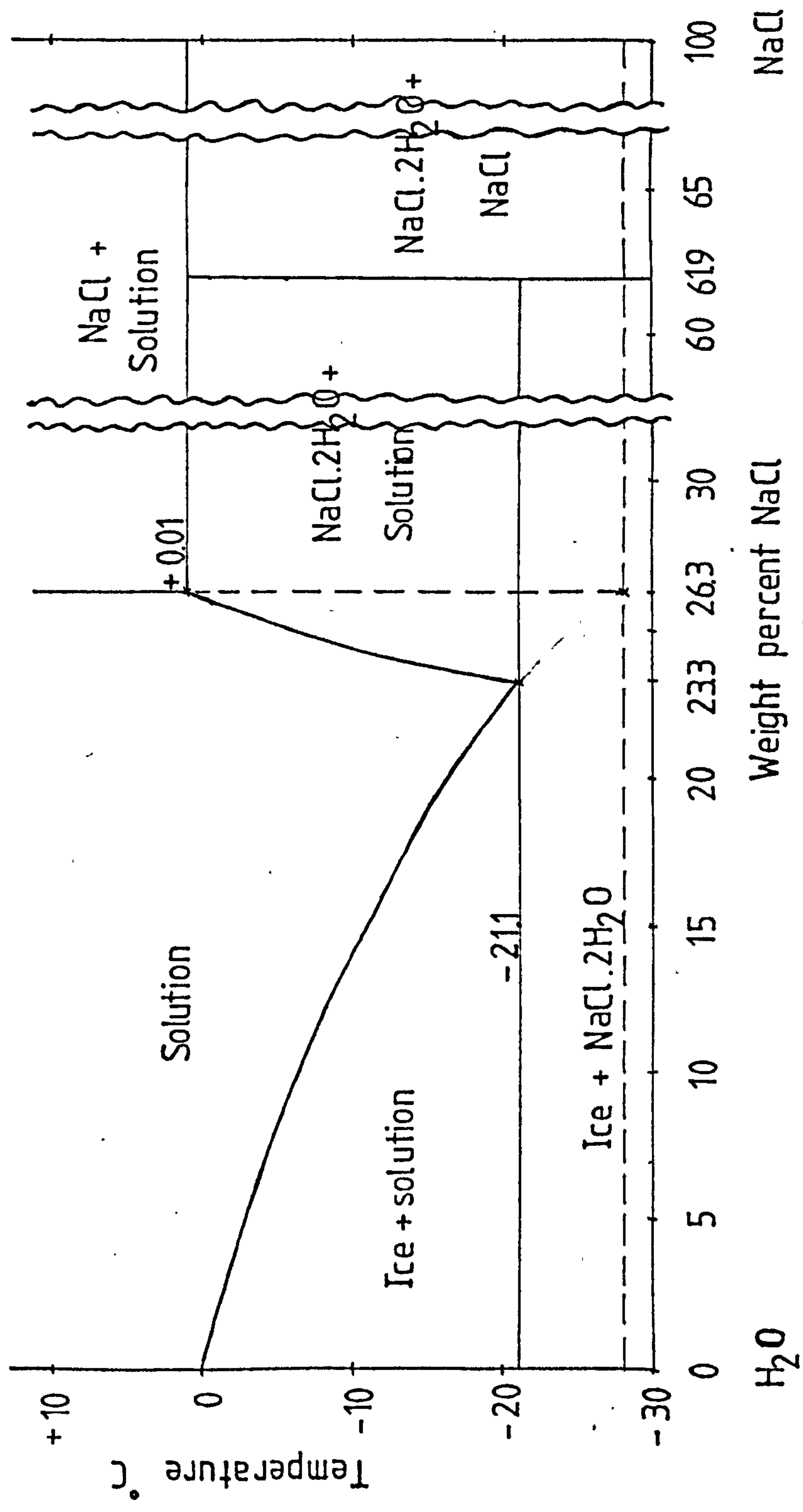
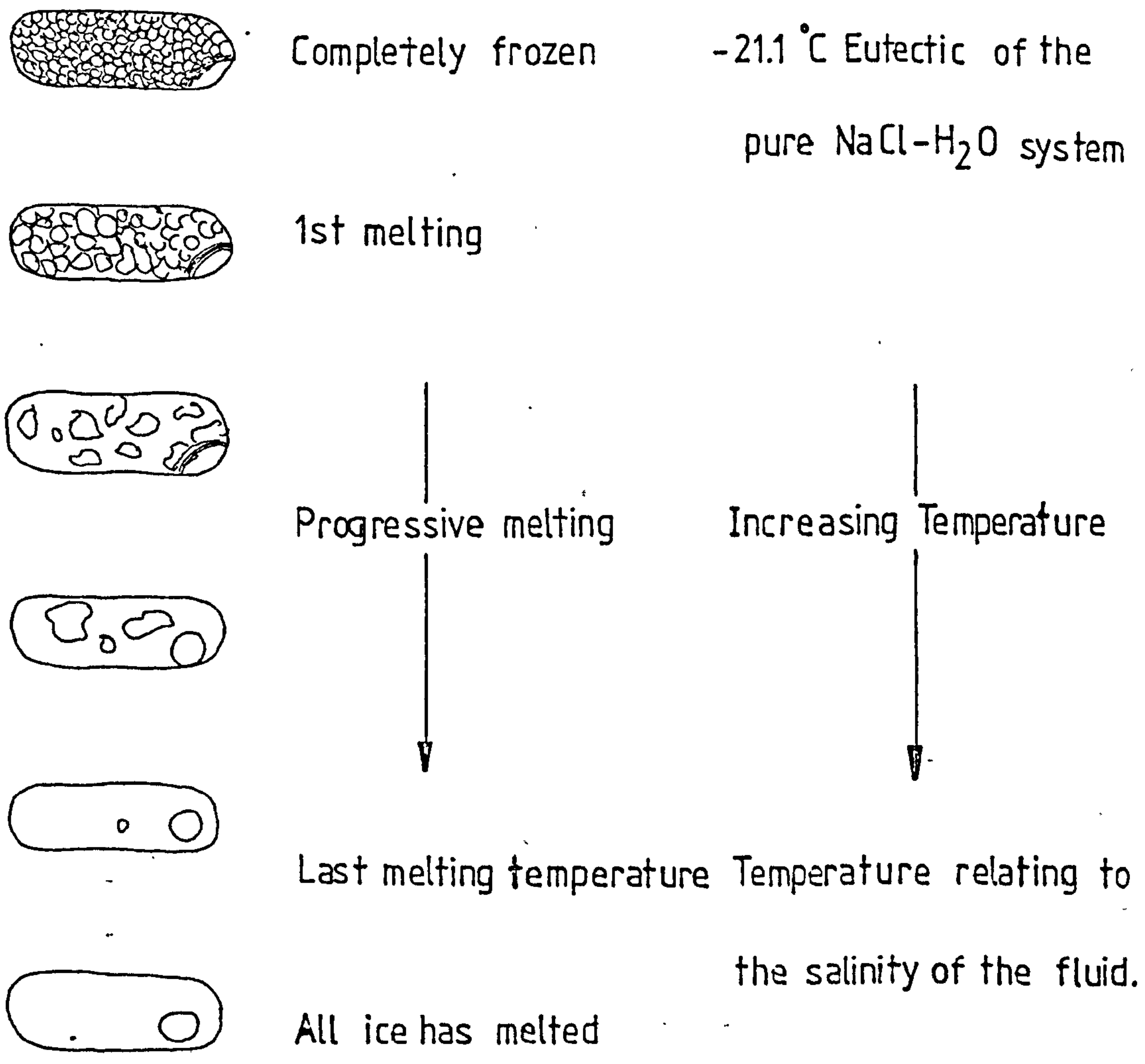


Fig.2.5 Behaviour of the frozen contents of an aqueous fluid inclusion (10wt.% NaCl) on warming.



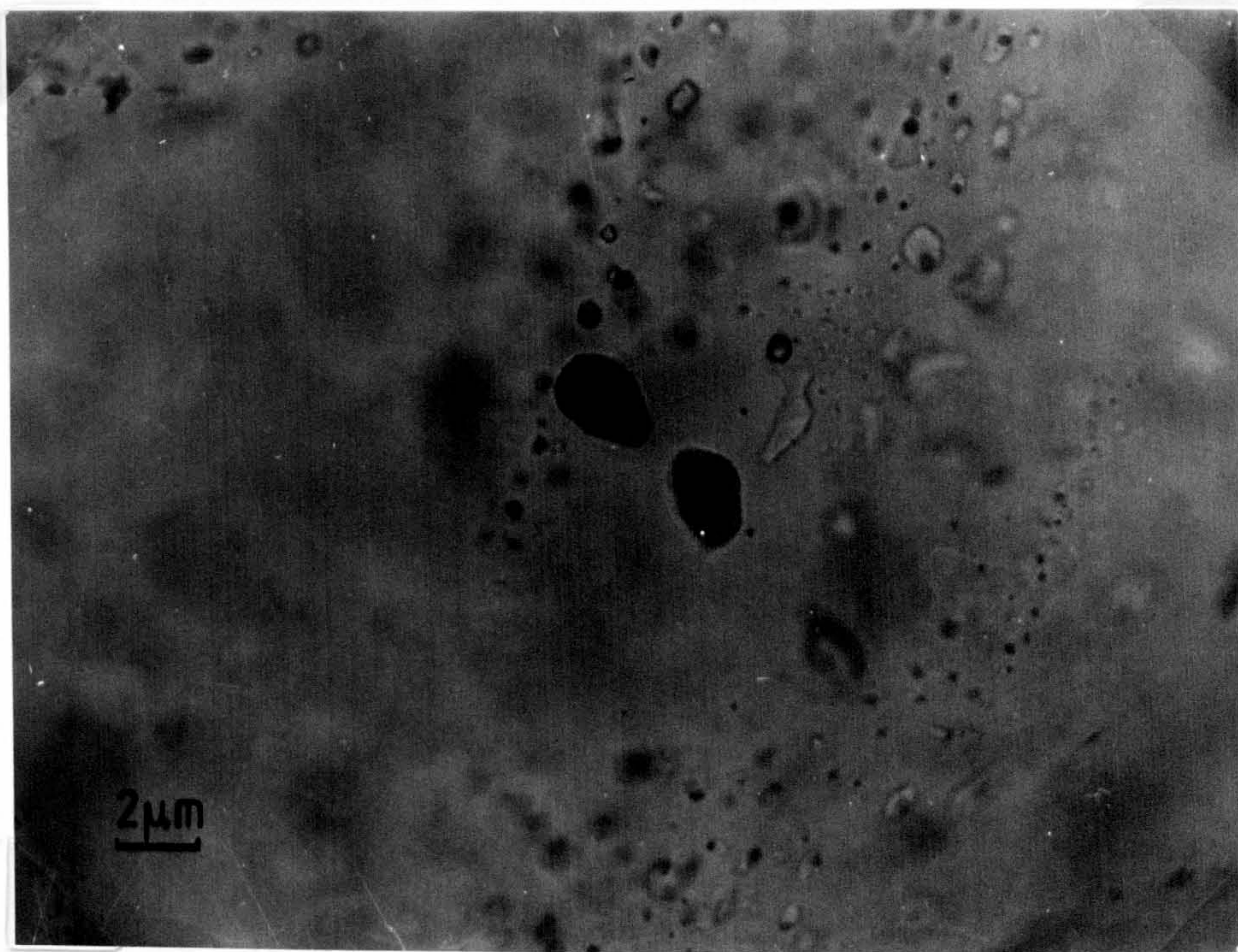
been carried out, the above three phase systems were used in connection with very low initial melting points. During warming of these systems hydrohalite and ice undergo simultaneous melting, the hydrohalite disappears before the ice and hence gives rise to two distinct melting points. Using these values, the initial melting point and a ternary phase diagram the composition of the fluid can then be calculated, Plate 2.4.

Freezing of monophasic inclusion fluids often nucleates vapour bubbles due to the metastable state of the solution, (Roedder, 1963).

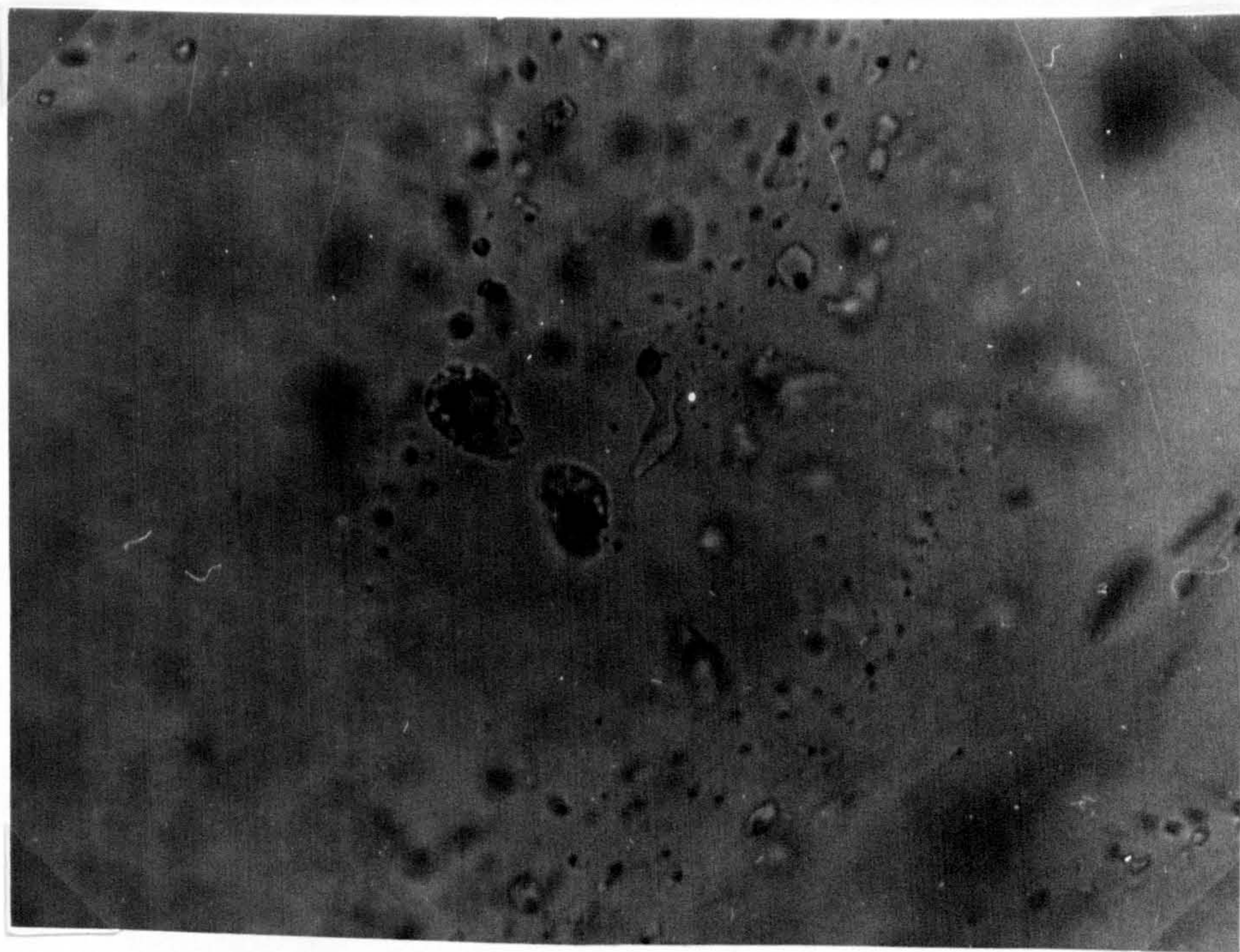
Freezing of oil-bearing inclusions do not give clear melting points although they are obviously crystalline at -35°C and in some cases at -5°C . Most of these inclusions were totally fluid around 0 to $+2.0^{\circ}\text{C}$. The aqueous solutions found in these oil-bearing inclusions produced freezing data approximately the same as surrounding aqueous inclusions. The oil was thus considered to be in the form of immiscible droplets which moved with the ore fluid. The oil-water ratio in individual adjacent inclusions was found to vary widely, in support of this view, (Freas, 1961; Roedder, 1963).

In the present study problems related to supercooling were overcome by the use of nitrogen gas pre-cooled in liquid nitrogen (temperature -196°C). This allowed fast cooling from room temperature to -150°C within 1 - 2 minutes. (Roedder, 1962; Shepherd, pers. comm.).

Plate 2.4 Warming a frozen two phase inclusion to room temperature
to study the salinity of the fluid.

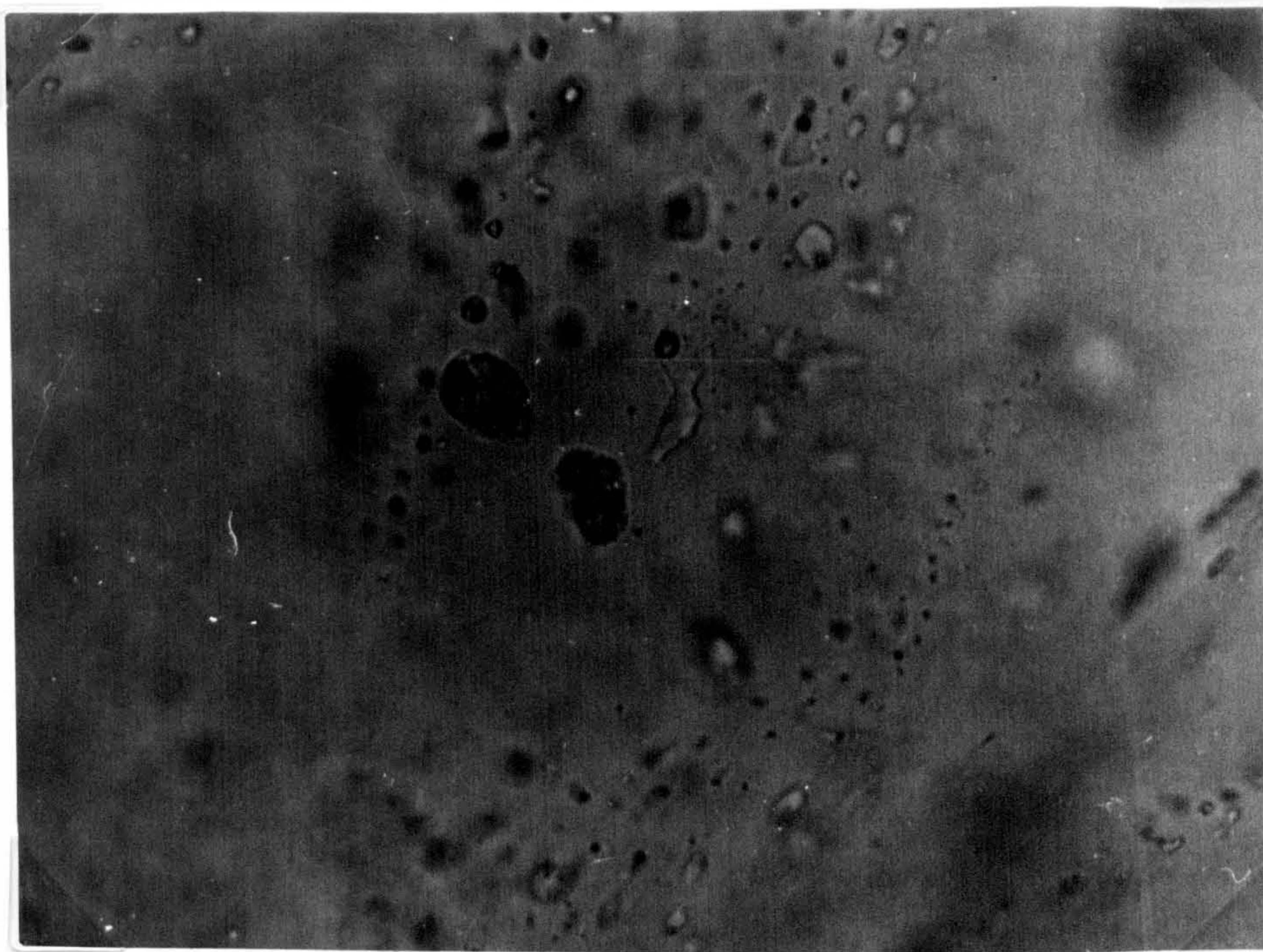


Totally frozen, temperature = -79.3°C .

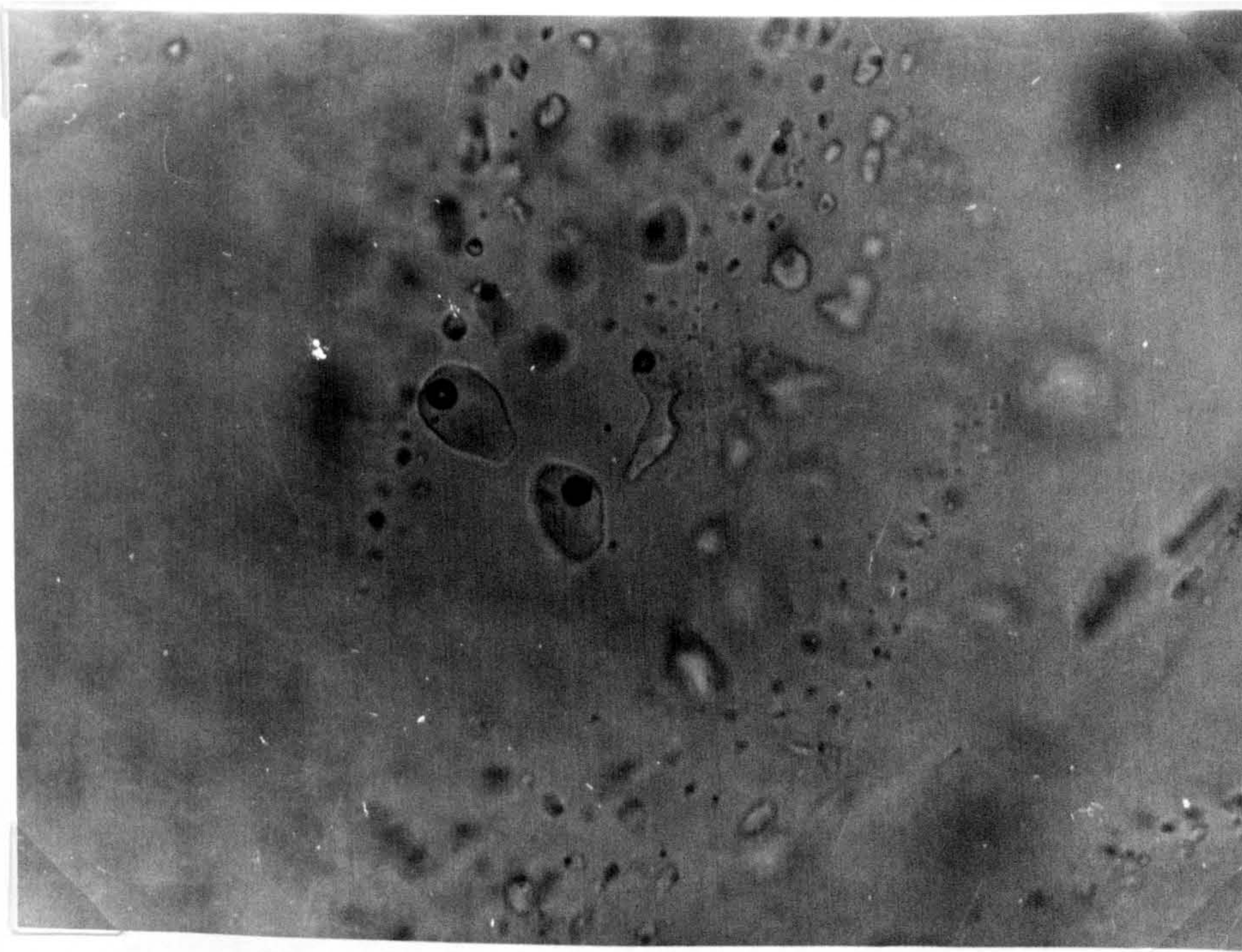


Two phases present: ice and hydro-halite. Temperature = -33.3°C .

Plate 2.4 continued.



Ice remains, all hydro-halite has melted. Temperature= -24.1°C .



Room temperature.

2.50. Thermometric analysis of inclusion in minerals from the Northern and Southern Pennine Orefields

2.51. Previous Work . .

Subsequent to the original thermometric work by Sawkins (1966), on the Northern Pennine Orefield, similar studies have been carried out on both the Northern and Southern Pennine Orefields by Smith (1974, 1975), Rogers (1977)^{Bailey (1977)} and Small (1978).

Sawkins' work was based on the whole Northern Pennine orefield, covering different coloured fluorites as well as quartz, calcite and barite. From the homogenisation data he was able to estimate temperature ranges for the various phases of mineral formation, Table 2.1. Less detailed freezing work demonstrated salinities equivalent to ~ 20 wt% NaCl, in both the quartz and fluorite.

Smith (1974) examined several hundred samples mainly fluorite and quartz from veins in the Northern Pennine fluorite zone. Homogenisation temperatures were related to position in the vein systems both along strike and at depth. By comparison his coverage of the barite zone was scanty. The data showed that in general quartz formed at temperatures overlapping but somewhat higher than fluorite; but that both were formed at higher temperatures than the surrounding barite. The ranges given by Smith (1974) are summarised in Table 2.1. They show good agreement with Sawkins' data and have within sample variation of ± 5 °C.

In 1975 Smith completed a more detailed study of the Groverake Vein system, with sampling at 1 metre intervals along the vein, and from several different levels within Groverake mine. This detailed study outlined higher temperature feeder

TABLE 2.1

Summary of Previous homogenisation temperatures for fluid inclusions in gangue minerals from the Northern and Southern Pennine Orefields

Northern Pennines

Mineral	Sawkins, (1966)	Smith, (1974), (1975).
Fluorite	120 ^o -220 ^o C	143 ^o -216 ^o C
Quartz	110 ^o -190 ^o C	115 ^o -190 ^o C
Late Calcite	78 ^o -84 ^o C	-
Barite	<129 ^o C	-

Southern Pennines

Mineral	Smith, (1974)	Rogers (1977)
Fluorite	70 ^o -128 ^o C	69 ^o -184 ^o C

zones at certain points along the vein, two of which could be linked to intersections by the Red and Burtree-pasture veins. Further though less detailed work was also carried out on the Slitt and White Vein Systems.

Freezing point data was obtained by Smith (1974); (1975), but on a smaller number of samples. The ice-melting point of primary inclusions was within the range -16°C to -23°C which is equivalent to 19.5 to 24 wt % NaCl. Temperatures below the eutectic temperature of the pure NaCl-H₂O system (-21.1°C), indicate the presence of other ions in solution; most probably calcium. Secondary inclusions from the same samples produced equivalent weight percent NaCl between 7 and 15%, thus suggesting more dilute solutions during the later stages of mineral deposition.

The Southern Pennine work by Smith (1974) and Rogers (1977) produced similar data. Smith (1974) found lower temperatures of homogenisation for the Derbyshire fluorites than those of the Northern Pennines, though he did no freezing work on this material. Rogers (1977) also showed that the range of homogenisation temperatures contained low values but found a wider range, in that his uppermost value of 184°C fell near the uppermost values of the Northern Pennine fluorites. Freezing work gave a range from 18 - 24 wt % NaCl. This also compared favourably with the Northern Pennine fluorite inclusions, Table 2.1.

These studies thus produced new data on the Northern and Southern Pennine inclusion fluids and provided important information on the temperatures of formation and probable salinity of the ore fluids. Secondary inclusions also indicated that the solutions became more dilute with time.

2.52. Present Work

The present thermometric work was carried out to expand the knowledge of quartz and barite temperatures of homogenisation and salinities.

Work on quartz required double-sided polished plates. These were prepared at I.G.S. by Mr. G. Brumby. Barite yielded plenty of small thin cleavage plates which were easy to work with. The stage used was designed by Dr. T. J. Shepherd and has been described in Appendix 1.

Heating work provided the ranges of homogenisation temperatures shown in Table 2.2. The values are uncorrected for pressure, but since this correction is presumed small, $<15^{\circ}\text{C}$, they may be used uncorrected on a comparative basis. The data indicate that barite formed over the range 140°C to 80°C , while quartz showed a higher range from 189°C to 108.8°C . Some Derbyshire fluorite gave values between 80°C and 100°C supporting Smith's (1974) work, and indicating that the Derbyshire orefield may well have been formed at overall lower temperatures than the Northern Pennine Orefield.

For the heating work on barite it was necessary to use different cleavage plates from the same sample to obtain a range of values for the homogenisation temperature. Repeated heating of the sample caused dissolution of the inclusion walls and as the material was not totally reprecipitated on cooling alteration of the initial fluid composition occurred. This resulted in a steady increase in the homogenisation temperature as illustrated by three runs on a barite from Ettersgill which gave consecutive homogenisation temperatures of 82 , 91.9 and 100.2°C . This affect could also be due to

TABLE 2.2

Homogenisation temperatures for samples run during
the present analyses

	Sample	Homogenisation temperature °C
Barite	R19	89.5
	R20	144.8
	R120	95.5
	R121	90.9
	R123	95.6
	5206	89.8
	6210	115.0
	6476	123.9
	6477	87.7
	6522	130.8
	6587	92.4
	20725	136.6
	20839	82.9
Quartz	6480	137.1
	6666	108.8
	414	143.7
	4416	122.1
	418	189.0 (Shepherd per. comm)
	419	188.0 " "
	424	147.2
	1018	126.9
	R101.1	150.9
	R102.3	138.4
Fluorite	R28	151.7
	R39	82.5
	R50	100.6
	R74	85.6

slight but progressive leakage. A further phenomenon found with the barite inclusions was that random inclusions would homogenise at temperatures far above the normal values. These inclusions on cooling were seen to have an increased vapour bubble size, which was related to leakage.

Freezing work was only carried out on barite and fluorite samples. The barite work was generally done before the heating runs, because freezing the sample was found to nucleate vapour bubbles in otherwise monophase inclusions. This nucleation was due to the metastability of the solutions within the inclusions.

The work on the barite produced results which suggested the presence of large amounts of major salts other than NaCl. This was indicated by the very low initial melting points (or eutectic points) obtained, in the range -60 to -30 °C averaging around -47 °C. These values were compared with the known three phase eutectics mentioned above, and it was suggested that the other major salt involved was CaCl_2 . A ternary phase diagram was used, to describe the melting sequence observed, Fig. 2.6., having been derived from work by Yanat'eva et al., (1946) and Crawford et al., (1979 a;b). Two distinct last ice melting points were observed which related to the melting of hydrohalite and ice, Table 2.3. The phases were distinguished by their different refractive indices. The diagram showed that when the inclusion fluid was warmed to room temperature from a frozen state, the fluid composition passed through an initial melting point or eutectic, E, Fig. 2.6. This would have been close to -55 °C, (Yanat'eva et al., 1946; Crawford et al., 1979 a; b). The fluid composition then passed along

Fig.2.6 Ternary phase diagram for the system $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$.

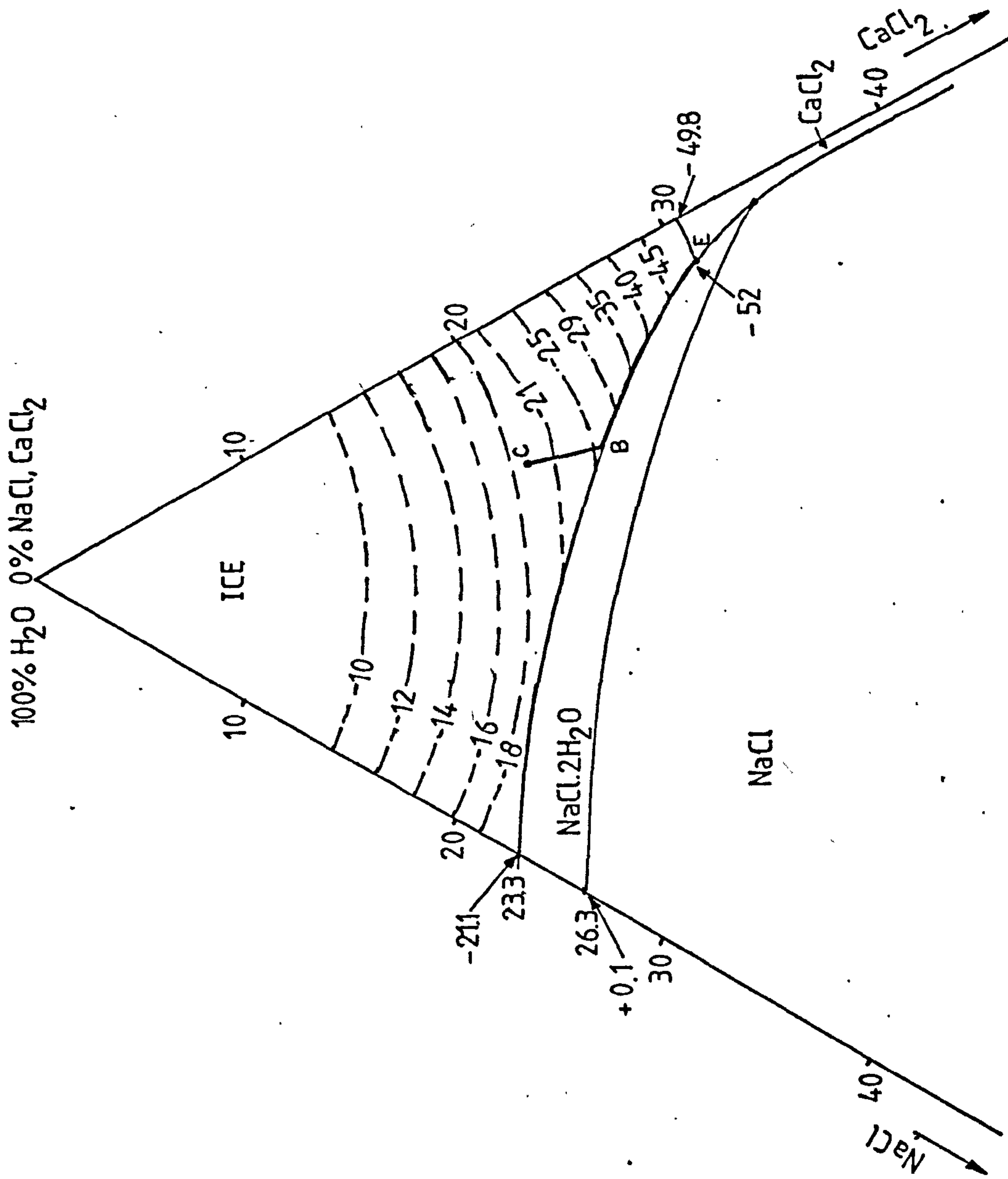


TABLE 2.3

Freezing data obtained in the present study

<u>Sample</u>	<u>Catectric</u> <u>°C</u>	<u>Last Ice mpt.</u> <u>°C</u>	<u>Hydrohalite mpt.</u> <u>°C</u>
<u>Barite</u>			
R19	-47.5	-20.1	-
R20	-46.7	-20.1	-
R121	-63.5	-13.1	-29.4
6210	-49.0	-22.0	-
6476	-46.7	-14.7	-26.0
6477	-46.7	-21.4	-27.2
6522	-38.7	-19.1	-26.0
6587	-44.0	-19.4	-26.1
20725	-48.9	-19.5	-26.6
20839	-47.0	-18.4	-27.7
<u>Fluorite</u>			
R28	-37.9	-20.0	-
R39	-73.7	-33.2	+ 1.56
R50	-47.1	-20.4	+ 0.90
R74	-46.6	-22.2	-

the liquidus from E to B, while hydrohalite and ice melted. At B, all the hydrohalite would have melted. Further warming then caused the remaining ice to melt, its final melting point being at C. This point thus represented the chemical composition of the fluid, assuming the approximation of the three phase system. To find C both the last melting point of the hydrohalite and ice were required. Results of the freezing work were thus used to calculate inclusion fluid compositions, Table 2.3., and Table 2.4.

Freezing work on fluorites followed the two phase system of NaCl-H₂O and some samples indicated the presence of hydrohalite, Table 2.3.

One sample of fluorite containing oil-bearing inclusions, from the Odin Vein, Derbyshire, was also studied by freezing methods. Complicated melting sequences were encountered and conclusive interpretation was impossible because of the limited experimental work on hydrocarbon systems, (Reamer et al., 1944; Swanenberg, 1979).

The temperature and salinity data are collated in Tables 2.2, 2.3, 2.4 and in Appendix 5, both past and present homogenisation temperatures are shown with the chemical and isotopic work. Some samples do not have homogenisation temperatures because it was considered that sufficient data had been obtained to give an overall picture of the areal distribution.

TABLE 2.4

Chemical concentrations equivalent to the freezing data

<u>Sample</u>	<u>NaCl.</u> <u>wt.%</u>	<u>CaCl₂</u> <u>wt.%</u>
<u>Barite</u>		
R19	22.0	-
R20	22.0	-
R121	4.2	15.9
6210	23.6	-
6476	13.8	28.0
6477	7.6	9.8
6522	6.6	30.4
6587	15.5	55.7
20725	5.8	21.6
20839	2.4	4.8
<u>Fluorite</u>		
R28	22.5	-
R39	> 26.0	-
R50	22.2	-
R74	23.8	-

C H A P T E R T H R E E

3.10. Introduction to Chemical Analysis

Studies on the salt composition of inclusion fluids were first carried out by H. C. Sorby in 1858. Later work by Roedder (1958) and Roedder et al. (1963), improved techniques. Prior to these studies, work on the gas composition of inclusions was done by Davy (1822) and later by Todd (1956). Todd's work on glass blisters indicated the ease with which gases could be analysed using mass spectrometry. He measured the amounts present by observing pressure rises in known volumes. Gas separation was achieved by using various cold traps. Solid carbon dioxide was shown to freeze water, whilst liquid nitrogen forced carbon dioxide and sulphur dioxide to condense. Non-condensable gases-measured were, oxygen, nitrogen, carbon monoxide, argon and hydrogen. This was later applied to fluid inclusions, (Barker, 1966).

Later work by Roedder et al. (1963) incorporated this technique to measure released volatiles from crushed mineral samples. The samples were crushed under vacuum, with the released volatiles being collected and measured. Leaching with deionised water was then carried out to redissolve salts, on the mineral, left by evaporation of the inclusion fluids. Analysis of salts incorporated the use of flame photometry and colourimetry. This particular study formed the basis of further work in this field.

Decrepitation, or thermal rupturing of samples, had also been used to release volatiles from inclusion fluids. Roedder et al. (1963), however suggested that this method may be prone

to large errors, due to chemical reactions occurring at the decrepitation temperatures; thereby disturbing the original chemical equilibrium of the gases.

Previous studies on the Northern and Southern Pennine ore minerals employed crushing and leaching methods. Volatile measurements were not made and thus ratios and not absolute values were obtained for the major salts. Sawkins (1966), measured Na:K ratios for quartz, (8 - 11), fluorite (6 - 13) and barite (15 - 46). The fluorite Na:K ratios are comparable to those of Smith (1974), (4 - 13) who also, measured ratios. For Southern Pennine ore minerals Rogers (1977), used the above techniques and obtained a wider range of Na:K ratios from 29 to 122. This indicated that the fluids were very deficient in potassium compared to the Northern Pennine fluids.

The present work was carried out to provide absolute concentrations for the various anions and cations in the inclusion fluids.

3.20. Preparation of samples

Prior to analysis of the inclusion fluids, the samples were rigorously cleaned of extraneous dirt and surface ionic contamination. Hand specimens were scrubbed and washed before being broken down into chips of 2-6 mm diameter. These were checked optically, using a stereo-microscope of 50X magnification, selecting only those chips with a high inclusion abundance. Later this process was eliminated, as, it was considered too time consuming for the benefit gained.

Further cleaning involved boiling the chips in 30% nitric acid for an hour, followed by two rinses in boiling deionised water. Most surface impurities, including ions, were thus removed.

Final clean up was achieved in electrolytic cells, which removed ion impurities from the fractures and cleavage planes in contact with the surface and also salts from inclusions ruptured or broken during preliminary crushing. (Roedder, 1958; Roedder et al., 1963). The cells were pyrex U-tubes containing deionised water into which were immersed platinum electrodes. A D.C. voltage of 60 volts was placed across the electrodes to bring about the electrolytic cleaning process. The water was changed once a day for the first week and then twice a week for the following one to three weeks. The process was continued until the conductivity of the solution, in the cells, had reached a steady value. This was generally higher than the conductivity of pure deionised water. The process was found to take two to four weeks.

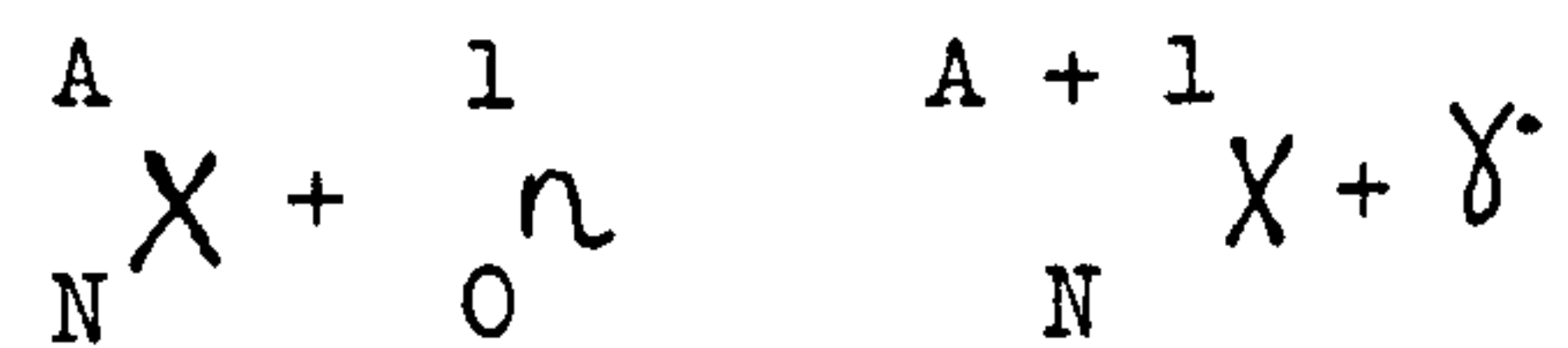
The chips were dried at $\sim 110^{\circ}\text{C}$ on watch glasses under infra-red lamps. Samples were then stored in clean labelled self-sealing polythene bags, ready for use.

3.30. Non-destructive chemical analysis

It is preferable to be able to analyse inclusion fluids by non-destructive methods since, several different analytical techniques can then be carried out on the same inclusions. The two principal methods of non-destructive analysis are thermometric analysis, mentioned above, and neutron activation analysis.

Neutron activation analysis entails irradiating samples with neutrons, and measuring the intensity of the characteristic radioactivity induced in the elements. The outer columns of a nuclear reactor, of the natural or enriched uranium type, are used to intersect the flux of slow or thermal neutrons.

These bombard the sample bringing about (n, γ) reactions, whereby the neutron is captured and γ -radiation is emitted. Neutron capture converts many elements into radioactive isotopes, the decay of which can be measured.



Thus a stable atom of mass number A , of the element X , is transformed into an isotope of mass number $A + 1$, which may be either stable or radioactive. The radioactive isotopes follow the normal law of radioactive decay. High activity and sensitivity may be obtained for a given weight of an element if the flux of the reactor and the activity cross-section of the element, are high. Samples with high relative abundance or elements with low atomic weights also have high sensitivity. Gamma-radiation emitted during decay may be measured on gamma-spectrometers and compared with similar decays for known standards. Thus quantitative analysis can be carried out. (Kruger, 1971; Smales and Wager, 1960).

Use of this technique on intact inclusion fluids from a rare-earth element deficient fluorite was carried out by Wickham and Khattab, (1972). They were able to measure Na, Cl, Br and some lanthanides in the fluorite. They showed that Na:Br ratios were fairly constant for several portions of the same hand specimen, but that Na:La ratios were very variable. This was thought to be due to Lanthanum in the fluorite lattice, where it substitutes for calcium. The Na, Cl and Br concentrations were however attributed to the inclusion fluids and checks were made by extraction of fluids and remeasurement of these

concentrations. This method thus seemed suitable for analysis of inclusion fluids without their actual extraction. Wickham and Khattab also suggested the possibility of measuring iodine and potassium concentrations by this method.

Two fluorite samples were cleaned and prepared as above and sent to the Herald Reactor Centre, at Aldermaston, for testing. 20-30 mg of the sample were weighed out into polythene phials which were placed in aluminium irradiation cans, 3 inches long by one inch in diameter, ready for irradiation. The first irradiation was for 30 minutes at a flux of $4 \times 10^{12} \text{ n.cm}^{-2} \text{ s}^{-1}$. Counting commenced using a gamma-spectrometer counter after allowing an extra 30 minutes for 'cooling'. The radioactive isotopes ^{24}Na , ^{38}Cl , ^{82}Br and I with short lived nuclides, were measured. A second irradiation of 4 hours duration, at the same flux, $4 \times 10^{12} \text{ n.cm}^{-2} \text{ s}^{-1}$, was then carried out to enable the measurement of Cs and Rb.

The results from two samples of fluorite showed much higher concentrations of rare earth elements, (Europium and Dysprosium) than those of Wickham's fluorite. These interfere and blanket the lesser emissions of Na, K, Cl, Br and I from the sample. The blanketing effect was due to the long half-life activities of the rare-earth elements, Europium for example, having several γ -spectrometry lines due to decays of 30 minutes and 9 hours.

Because of these interference problems posed by the rare earth elements, it was impossible to use this procedure, of non-destructive analysis, on the Northern Pennine Fluorites. Destructive analysis was thus utilised as the most viable procedure.

3.40. Destructive Analysis

Samples may either be crushed or decrepitated to release the contents for subsequent analysis.

3.50. Crushing Techniques

Crushing of samples may be carried out in various media, including vacuum. If crushing is done in air, gas or oil, volatiles are generally lost and leaching of the non-volatile matter only permits the results to be expressed as a ratio, rather than as absolute values. If however the samples are crushed under vacuum the volatiles can be collected and measured. Further leaching of the sample produces results which can then be related back to the original weight of inclusion fluid.

Crushing techniques carried out by Roedder et al. (1963), incorporated vacuum crushing. They used soft copper tubes, 8 inches long and $\frac{5}{8}$ inches in diameter, which were welded at one end; tubing $\frac{7}{8}$ inches diameter was used for larger samples. Once the sample had been weighed into the tube the upper section of the tube was squeezed together, and connected to a vacuum line, modified from that of Friedman (1953). The sample tube was evacuated to a pressure of 10^{-5} mm of mercury, and isolated from the vacuum pump after leakage checks were carried out. A hydraulic press was used to crush the sample by compression of the copper tube. To allow easier passage of gases, the flattened section of the tube was then squeezed open, from the sides, and warmed to about 80 °C. This ensured complete evaporation of the released inclusion fluids. The volatiles from the inclusions were condensed in a liquid nitrogen cold trap.

A different method of crushing was developed by Shepherd (pers. comm.), which also used a vacuum line. Samples were

placed in vertically orientated steel tubes, sealed at one end, along which an iron alloy tungsten-carbide tipped plunger could be moved. Movement of the plunger was effected by solenoid magnets placed in series, such that when turned on they attracted the plunger, moving it upwards. When turned off the plunger would fall crushing the material beneath it. The process was repeated several times. Yield of fluids depended on the extent of disintegration of the sample.

A disadvantage of both the above methods is that volatiles are often adsorbed onto the freshly ground material surfaces, (Piperov et al., 1979). Warming to 200 °C is therefore necessary to desorb the more polar gases.

3.60. Decrepitation techniques

The decrepitation technique is useful for analysis of inclusions with homogenisation temperatures below 300 °C and was thus used extensively in the present study.

Decrepitation or thermal rupture of inclusions is brought about by heating minerals to temperatures in excess of the inclusion homogenisation temperatures, (Scott, 1948; Roedder, 1958). This causes the internal pressure of the liquid in the inclusion to increase to a point where it is greater than the strength of the enclosing host mineral. Physical destruction of the mineral results, releasing volatiles present in the inclusions. Generally it is possible to release and collect all of the inclusion fluids in a vacuum line, but unfortunately some volatiles may also be evolved by desorption and by chemical reactions developed at high temperatures, (Piperov et al., 1979). Desorption has been eliminated mainly by outgassing the sample and vacuum line prior to decrepitation. Chemical

reactions have been kept to a minimum by using the lowest possible temperature to achieve complete release of fluid; (e.g. temperatures greater than 600 °C were found to cause decomposition of solid sulphide impurities). Hence 600 °C was the uppermost decrepitation temperature.

Half inch bore silica glass tubes approximately 12 cm length were used as decrepitating vessels. They held a maximum of 7 grams of fluorite, normally 3-4 grams being used for analysis. The tubes were connected to a vacuum line, Fig. 3.1., (Appendix 2) and evacuated to a pressure of less than 10^{-3} mTorr. To heat the tube, a furnace, 15 cm long, was constructed of resistance wire coiled around a 1.5 cm bore silica glass tube. The furnace was calibrated using a Chromel/Alumel thermocouple. The central 4-5 cm of the furnace gave a relatively even temperature, but this decreased rapidly towards the ends of the tube. Initial work used the decrepitation tube in a horizontal orientation and it was necessary to place a glass slug in front of the sample to inhibit migration of exploding material into the vacuum line. This was similar to apparatus described by Piperov et al. (1979). Later work incorporated the decrepitation tube in a vertical orientation so that exploding material fell back to the base of the tube, Fig. 3.1.

The best decrepitation temperature for fluorite samples was obtained by measuring the evolution of hydrogen gas, converted from fluid inclusion water, during linear heating, with the temperature being raised at 10 °C per minute. Fig. 3.2. is drawn from the chart recordings, during the decrepitation of six samples of fluorite; the gas being measured at constant

Fig.3.1 Vacuum line used for the quantitative extraction of inclusion fluids.

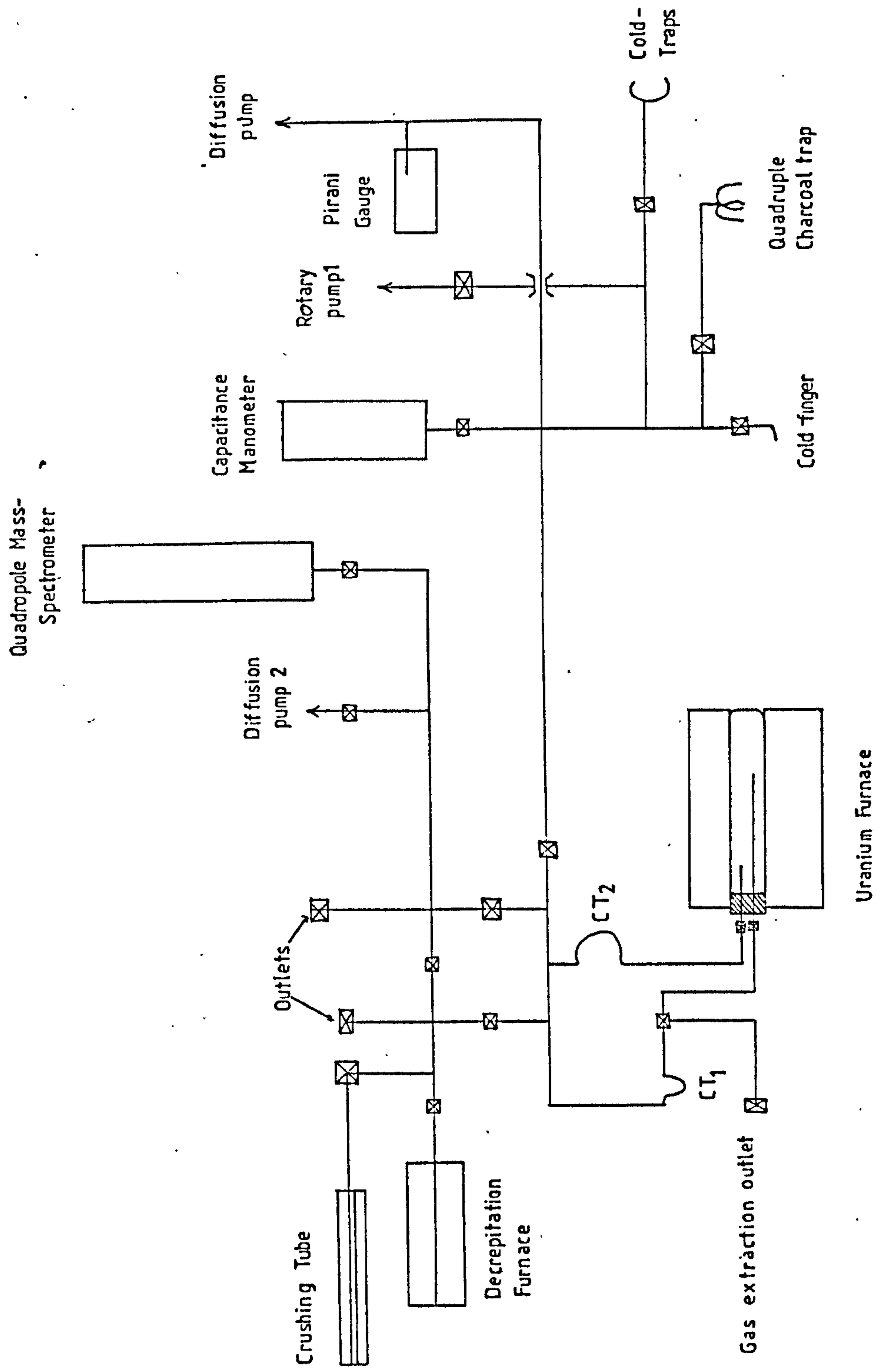
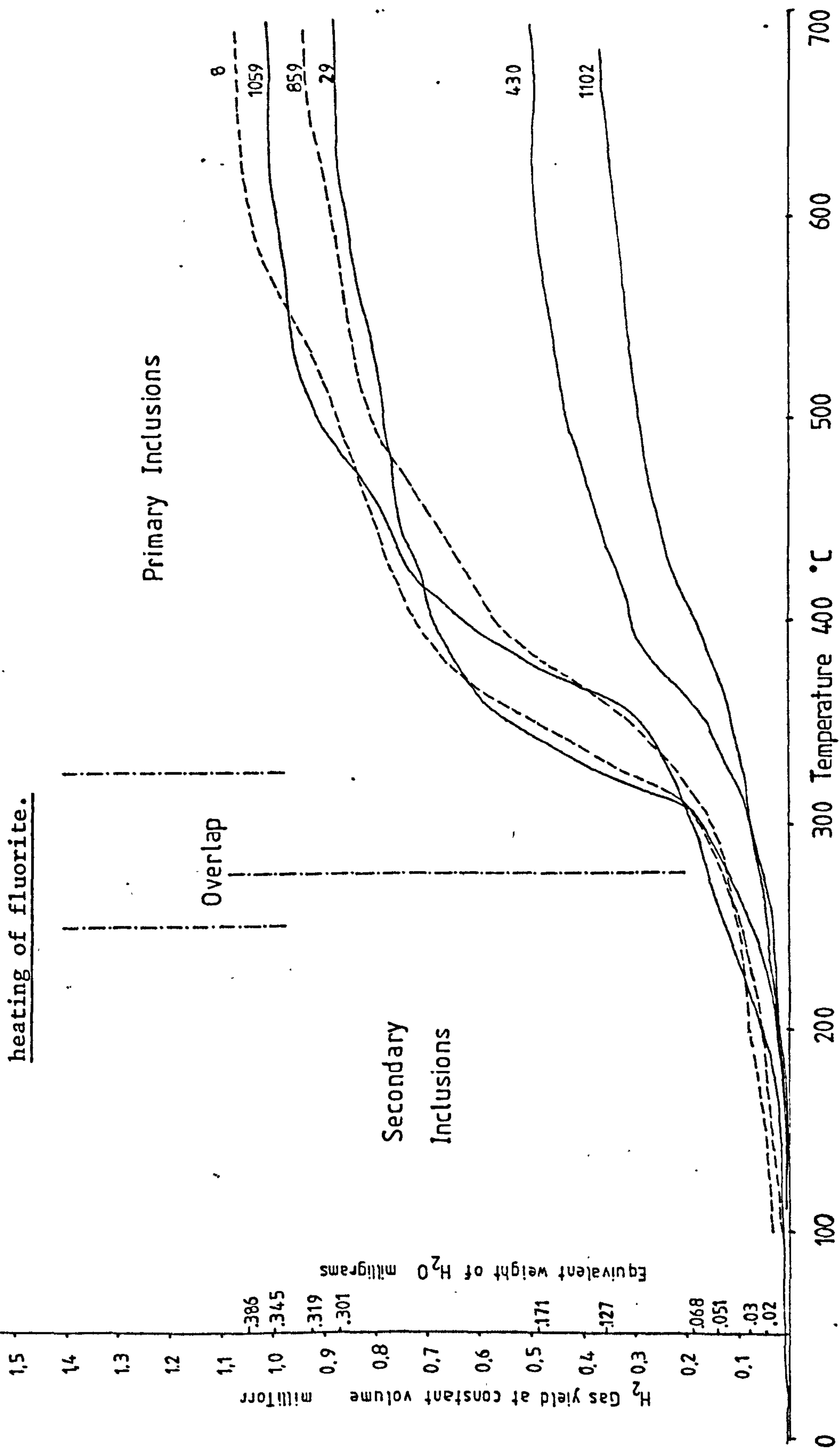


Fig.3.2 Evolved water versus decrepitation temperature during linear



volume. Experimentation indicated that decrepitation temperatures of 580 °-600 °C produced the most satisfactory release of fluid from inclusions in fluorite. However heating in excess of 610 °C resulted in decomposition of sulphide impurities to yield hydrogen sulphide. Sulphide impurities were therefore kept to a minimum in the sample. Calcite impurities were eliminated by initial cleaning and hence problems due to their decomposition were not encountered. Quartz samples, free from sulphides, were decrepitated at 600 °-630 °C. Barite samples decrepitated easily at 400 °-440 °C and thus no decomposition problems were encountered.

Relative decrepitation of primary and secondary inclusions was also observed. From the results it was considered that secondary inclusions would have decrepitated by 275 °C. Thus measurement of the hydrogen pressures at 275 ° and 600 °C enabled the percentage of the total water due to secondary inclusions to be calculated, Table 3.1. For the six samples run the percentage, at 275 °C was between 7.8 and 17.1, Table 3.2. Secondary inclusion fluids may however be released up to 300 °C depending on the sample. An overlap with the release of primary inclusion fluids would thus be encountered. Due to the difficulty in separating the two types of inclusion fluids, for individual samples, the contents of both primary and secondary inclusions were not collected separately.

Prior to decrepitation samples were outgassed under vacuum, at approximately 80 to 100 °C, to remove any surface moisture accrued during storage. After isolating the vacuum pump the furnace, stabilised at 600 °C was placed over the decrepitation tube and left for fifteen minutes, during which time volatiles were collected in a liquid nitrogen cold trap.

TABLE 3.1

Gas analysis of the amount of water released at specific
decrepitation temperatures indicative of primary and
secondary inclusions fluids

	Hydrogen Concentrations Pressure (Milli Torr) in the total volume of the extraction line = 296.6 cm ³			Water Equivalent Concentrations		
	T 275°C	T 300°C	T 610°C	H ₂ O(mg) at 275°	H ₂ O at 300°	Total H ₂ O at 610°
8	0.140	0.175	1.058	0.051	0.063	0.386
430	0.052	0.080	0.490	0.021	0.030	0.171
859	0.065	0.150	0.925	0.025	0.055	0.319
1059	0.162	0.190	0.999	0.059	0.068	0.345
1102	0.052	0.070	0.359	0.021	0.026	0.127
R29	0.125	0.170	0.870	0.045	0.061	0.301

The hydrogen pressures were converted to equivalent weights of water by equations in appendix 2. The above values were obtained from the chart recordings; fig. 3.2. Estimates of the secondary inclusion fluid content as a percentage of the total water collected are given in Table 3.2.

TABLE 3.2

Percentage of secondary fluid present at the specified temperatures

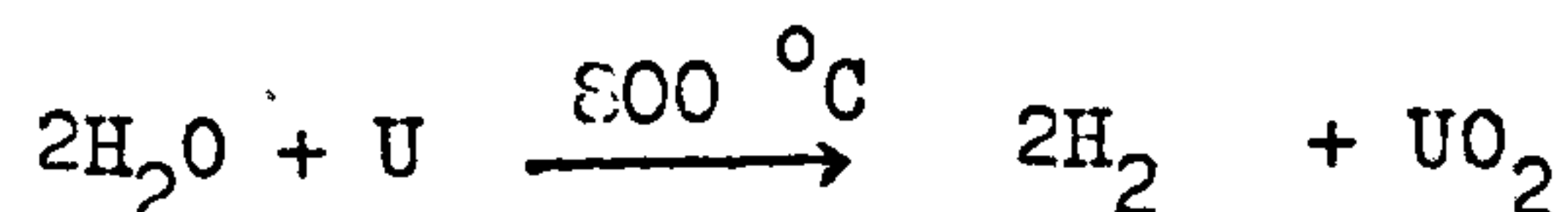
Sample	secondary fluid % of total fluid.	
	at 275°C	and 300°C
8	13.2	16.3
430	12.3	17.5
859	7.8	17.2
1059	17.1	19.7
1102	16.5	20.5
R29	15.0	20.3

At 275°C the percentage of secondary inclusion fluid ranges from 7.8% to 17.1%. At 300°C this range is 16.3% to 20.5%. Separation of the two inclusion fluids is quantitatively difficult as the results show that although some secondary inclusion fluids may be completely released at decrepitation temperatures of 250°C, others may not reach this stage until above 300°C.

After removal of the furnace the equipment was left for a few minutes to ensure that all volatiles released from the inclusions had been extracted from the sample. Once the decrepitation procedure was complete the sample was isolated from the trapped volatiles. The above procedure was used for fluorite, quartz and barite.

3.70. Gas Analysis

The volatiles released into the high vacuum extraction line were collected in a liquid nitrogen cold trap at a temperature of -196°C . At this temperature water, carbon dioxide and most sulphurous gases are condensed, but not nitrogen, oxygen, carbon monoxide, argon and hydrogen (Todd, 1956; Weast, 1977). Once decrepitation was complete the non-condensable gases were allowed to expand into a known volume of the line, where their pressure was measured using a capacitance manometer. This device has an accuracy to 10^{-3} mTorr. After this gas fraction had been pumped away, the liquid nitrogen trap was replaced by an acetone-solid CO_2 trap at a measured temperature of -75°C . After thermal equilibration, the CO_2 gas was then expanded into a second known volume, where its pressure was measured as before. The trap was then allowed to reach room temperature and the water vapour evolved was passed slowly over uranium metal at 800°C , converting the water to hydrogen via the reaction.



This section of the line was kept at 70 to 80°C by the use of heating tapes wrapped around the pipe work which minimised the adsorption of water.

The hydrogen was then expanded into a known volume and its pressure measured. From measured pressures, the volumes and weights of non-condensable gases, CO_2 and H_2O could be calculated, Appendix 2.

Two fluorite samples were run for analysis of primary and secondary inclusion volatiles. The sample was decrepitated at a temperature of 275°C to obtain volatiles relating to the secondary inclusions. After chemical analysis and drying the samples were decrepitated at a temperature of 600°C to obtain volatiles relating mainly to the primary inclusions. From the samples 430 and R28, the secondary inclusion fluid weight calculated, was found to be 17.7% and 9.6% respectively of the weight calculated for the primary inclusion fluids. Carbon dioxide was also measured. Sample 430 had an anomalously high value for CO_2 concentration for the primary inclusions compared to that of the secondary inclusions. Sample R28, however, showed CO_2 concentrations approximately the same.

Further detailed gas analysis was carried out on a Derbyshire fluorite sample using a quadropole mass-spectrometer. Previously Barker, (1966), had shown that the major volatile of inclusion fluids from the Northern Pennine fluorites was water, followed by CO_2 . Small amounts of hydrogen (H_2), methane (CH_4) and carbon monoxide (CO), were also found to be present in every analysis.

The Derbyshire fluorite was decrepitated and the volatiles collected in the liquid nitrogen cold trap. The non-condensable gases (approximately $5.22 \times 10^{-8} \text{ cm}^3$ at s.t.p.) were bled into the quadropole mass-spectrometer through a molecular leak where the pressure was maintained at 6.2×10^{-6} Torr. From the resultant mass spectrum, background measurements were taken before

and after each peak, with peak heights being measured for the different atomic masses. Once the peaks had been corrected for background, the relative amounts of each gas component ~~was~~ ^{were} calculated, Appendix 2. Standard tables for the cracking patterns and sensitivity factors of the various gases were used to work out relative amounts of each gas associated with specific atomic masses. Masses measured were 2, 12, 13, 14, 15, 16, 17, 18, 28, 40 and 44, which yielded information concerning the gases methane (CH_4), hydrogen (H_2), nitrogen (N_2), and argon (Ar). The technique was semi-quantitative because for precise gas analyses one requires the cracking pattern and sensitivity factors for the particular instrument. These were not available and the final results were obtained by optimising the values to ensure reasonable agreement between the major and minor masses. These quantities were then related to the total amount of non-condensable gases present and hence the CO_2 and H_2O concentrations.

3.80. Salt Analysis

Chemical analysis of the actual fluid inclusions is generally impossible due to the extremely small quantities available, (e.g. 1 mg or μl of water from 3-4 grams of fluorite). Accordingly salt analyses were carried out on leachates from decrepitated material.

3.81. Leaching procedures

Leaching with water or dilute acids dissolved soluble salts left on the material after evaporation of the inclusion fluid during decrepitation. The leachates were then analysed by the most appropriate chemical method for the anions and

cations considered.

Roedder et al. (1963), used deionised water and filtering processes. They added 10 ml of deionised water to their crushed material and swirled the mixture for one minute after which it was decanted through filter paper and collected. Two or three additional leachates were taken in a similar manner and added together before analysis.

In the present study the decrepitated samples were leached using two 5 ml aliquots of deionised water, each being shaken vigorously in an ultrasonic vibrator for 20 minutes before being centrifuged and pipetted into the same clean polypropylene bottle for storage. The leachates were acidified with 0.5% nitric acid to prevent adsorption of metal ions on to the walls of the bottles during storage. Prior to leaching all equipment was cleaned using boiling 30% nitric acid followed by two rinses of hot deionised water.

3.82. Principal Analytical Techniques

As the concentrations of elements present in the leachates were low, the number of useful chemical techniques available were limited. For measurement of the major ions sodium and potassium, flame photometry was considered the most useful technique. Atomic absorption spectrometry was considered the most useful technique for measuring other anions in both major and trace concentrations. Measurement of the halides was achieved by use of neutron activation analysis and pyrohydrolysis. However, sulphate detection methods were found to be unreliable at the concentrations present in the leachates. Rare-earth elements were measured by the X-ray fluorescence techniques employed in most laboratories.

Thus the two main methods of analysis used were flame photometry and atomic absorption spectrometry; each of which is based on a different theoretical concept.

In flame photometry the addition of salts to a flame causes the element atoms to become excited due to absorption of energy. This energy is then emitted at specific wavelengths as the atoms fall back to lower energy states. The amount of energy in the form of light emitted is proportional to the number of atoms that are excited and thus gives a measure of the concentration of the emitting element (Herrman and Alkemade, 1963). Sodium and potassium were measured by flame photometry because they produce simple spectra with a few strong lines.

An E.E.L. 170 digital flame photometer was used for the analysis with lithium as an internal standard. A reasonable quantity of sample for analysis was obtained by adding 1 ml of leachate to 2 ml of 200 ppm lithium solution and 1 ml of de-ionised water. Standards were also made up to contain 100 ppm lithium. Two ranges of standard solutions were used, 0 to 2.4 ppm. and 0 to 24 ppm. The upper range produced a good linear calibration graph, but the lower range gave curved calibration graphs. All samples were initially run on the lower range and samples above this range were then measured on the the higher range. This was only necessary for sodium. The readings obtained were corrected by using the calibration graphs, before being converted to concentrations in the fluid inclusions, Appendix 2. Concentrations were calculated for sodium and potassium as well as their equivalents in weight percentages of NaCl and KCl.

Atomic absorption spectrometry is based on the absorption

of energy by ground state atoms. It is found that substances dispersed as vapours, possess the property of absorbing their own characteristic radiation. Thus a radiation beam of an element will be absorbed by any ground state atoms of that element, passing through the beam from an external source. Reduction in the intensity of the beam gives a measure of the amount of ground state atoms of the element present. This is proportional to the concentration of the element in the external source. Atomic absorption spectrometry has a high sensitivity for most elements due to the general lack of spectral and chemical interference. It is thus a good technique for the analysis of trace and major elements, (Elwell and Gidley, 1962; Angino and Billings, 1972).

Atomic absorption spectrometry was used for the analysis of copper, iron, manganese, magnesium, zinc and strontium in leachates from fluorite samples and additionally, calcium in quartz and barite samples. To minimise interference from calcium during zinc and magnesium analysis of fluorite leachates; the samples and standard solutions were spiked with 0.25 ml of a 20% lanthanum solution. Calibration graphs were then drawn for each element. The specific operating conditions for each element are set out in Appendix 2, and the optimum aspiration rate for the samples was set at 5 ml per minute. The sample solution passed up the inlet tube into an atomisation chamber, where it was atomised and sucked into the flame. Duplicate runs for each element were made and standard solutions were rechecked after every third sample. A blank of deionised water, spiked with lanthanum, was run between every sample or standard solution measurement. Attempts at measuring other elements showed that lead, cobalt, and nickel were below the

limit of detection. Barium determination involved different flame conditions (nitrous oxide), not available at the time. Calcium was measured in leachates from quartz and barite which had been acidified with 0.5% nitric acid, but had not been spiked with lanthanum. The detection limits and sensitivities are given in Appendix 2.

Using these methods a separate comparative study was made of the chemical composition of primary and secondary inclusion fluids, for two fluorite samples (430 and R28). Secondary inclusion fluid concentrations were related to the weight of water produced by decrepitating the fluorite at a temperature of 275 °C. Redecreptation, at a temperature of 600 °C, and leaching of the sample plus analysis, produced the values for primary inclusion fluids. All analyses were treated in the same manner as described above to obtain initial fluid inclusion concentrations.

3.83. Other Analytical Techniques

Other useful analytical techniques included neutron activation analysis of leachates and chlorine and fluorine analysis of quartz samples. However, analysis for the sulphate content of leachates proved unviable and checks on the rare-earth contents of several fluorites by x-ray fluorescence analysis were not conclusive.

Neutron activation analysis was carried out on leachates, after it was found that non-destructive neutron activation analysis was unviable. Previous activation analysis of leachates had been carried out by several people. The first, Czamanske et al. (1963), used activation analysis to measure copper, manganese and zinc concentrations in extracted leachates.

Puchner and Holland (1966), incorporated this technique adding to the elements measured in leachates obtained from hydrothermal quartz fluid inclusions. Horn and Wickman (1973), measured the Na/K ratios of inclusion fluids; Rubidium (Rb) and Cesium (Cs), were also detected. Work by Krupka et al. (1977) used a new technique which involved separation of Na, from the solution, after it had been measured. This enabled K concentrations to be measured more accurately.

The elements analysed in the present work were Na, K, Cl, Br, I, Cs and Rb. The decrepitated samples were leached with 5 ml of deionised water and acidified with 0.5% nitric acid. Only one leach was used. The leachate was then sucked into a clean polypropylene bottle with an extended pipette-type neck. A cool flame was used to seal the neck of the bottles which were then sent to Aldermaston for irradiation and analysis.

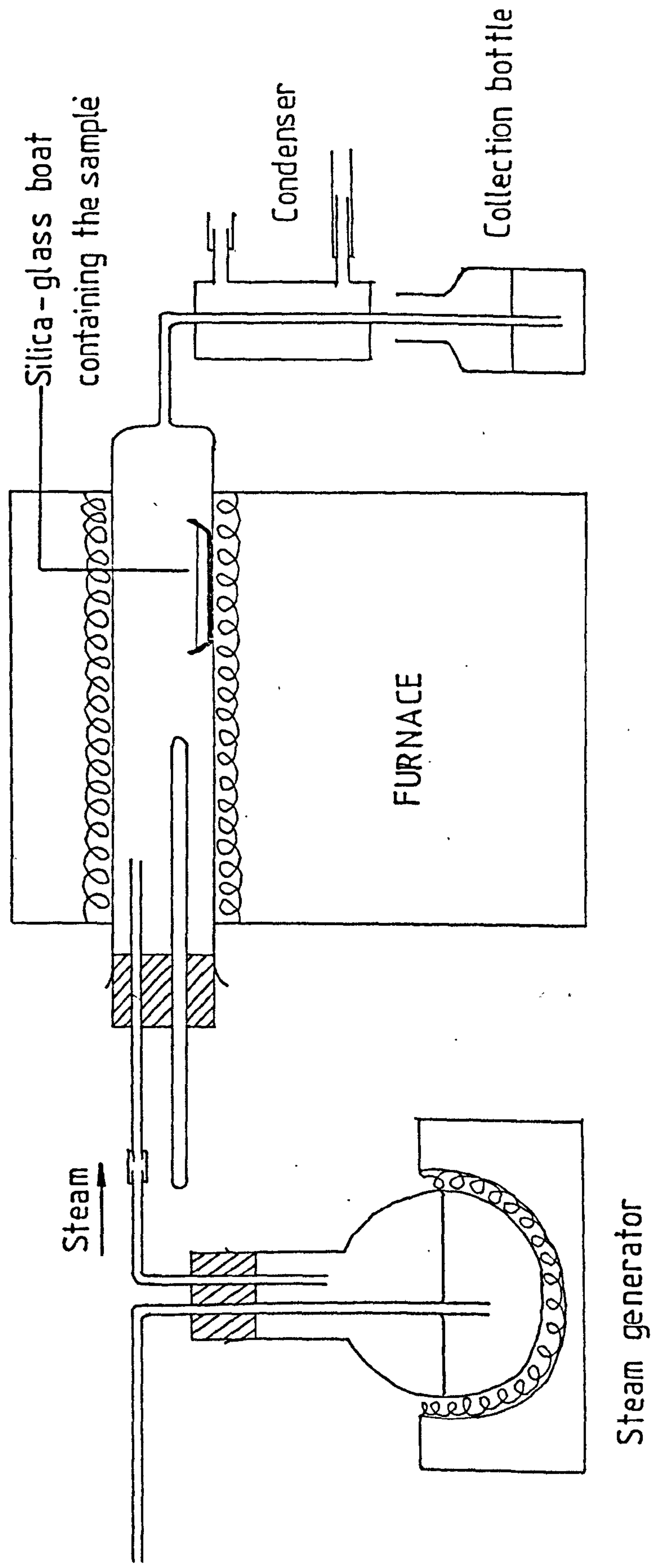
At the reactor centre the bottles were weighed and placed in aluminium cans, with standard solutions, for irradiation. The first irradiation of 30 minutes, at a flux of $4 \times 10^{12} \text{ ncm}^{-2} \text{ s}^{-1}$, was followed by cooling for 30 minutes before counting commenced. Measurement was carried out for Cl, Br, I, Na and K at this point. The samples were then irradiated for 4 hours with the same flux. After 'cooling' for 24 hours, counting was carried out for Cs and Rb. The results were then converted to concentrations in the fluid inclusions, using an approximation of the weight of inclusion fluid obtained from previous measurements on the same sample, Appendix 2. The analysed elements all produced (n, γ) reactions. Their estimation required relatively high natural abundances, $\frac{1}{2}$ lives which could be measured in minutes or hours, relatively good intensity of γ -emission and

neutron cross-sections between 0.4 and 15 barnes, Appendix 2.

Pyrohydrolysis was used to measure chlorine and fluorine concentrations in fluid inclusions from quartz samples. Originally it was intended to measure chlorine and fluorine directly in leachates from quartz using ion electrodes. However, the presence of elements such as silica, iron and aluminium in the leachate, produced interference with the ion electrode measurement. Pyrohydrolytic distillation was thus used to provide a solution of Cl^- and F^- free from aluminium, silica and iron for use with these electrodes. This involved heating the sample in a furnace, with a flux of vanadium pentoxide to induce chlorine and fluorine gas emission. The gases were then collected during transfer by steam through an alkali solution. This solution was buffered, using nitric acid, to eliminate OH^- interference and the formation of associated ionic species, before measurement, (Branch, 1979).

Quartz samples, as small chips, were rigorously cleaned to remove any carbonates and sulphides present, using ultra-violet light, any fluorite present was also removed by hand-picking. Once cleaned the quartz was crushed in steel tubes to a diameter of mesh 150#. Half a gram of sample, accurately weighed, was added to 2.5 grams of vanadium pentoxide, the flux. The mixture was ground together in an agate mortar and pestle, and vigorously shaken mechanically in a stopped specimen bottle, to ensure homogeneity. One gram of the mixture was weighed accurately into a pre-cleaned silica glass boat and placed in a tube furnace at 650-700 °C, Fig. 3.3. The furnace was raised to a temperature of 800 °C and held there for 35 minutes. An air-flow of 120 Lh^{-1} and steam flow of 0.5 ml min^{-1} were used

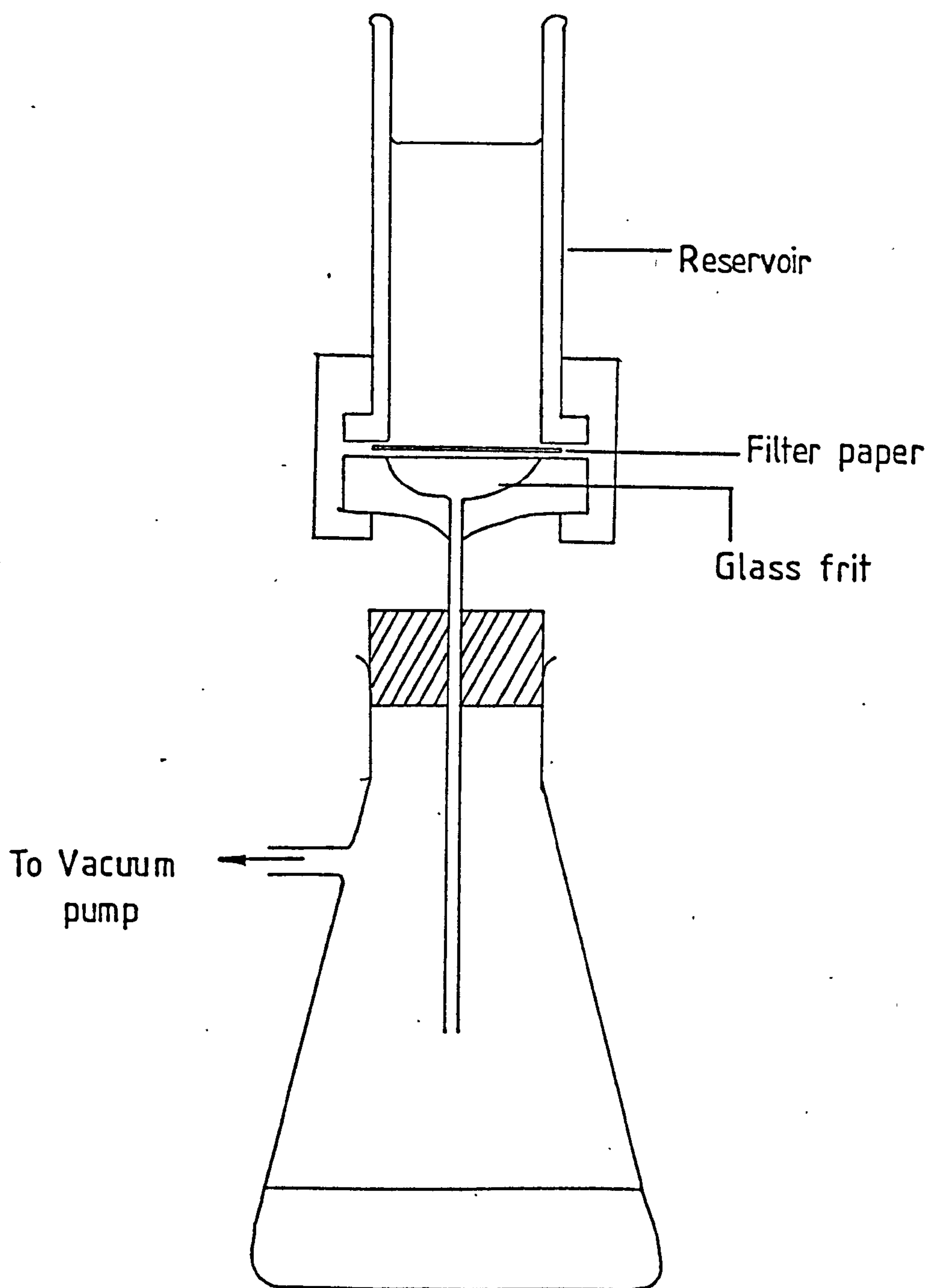
Fig.3.3 Apparatus used for chloride and fluoride analysis of quartz samples.



to take up gases produced during pyrohydrolysis. The distillate was collected in 5 ml of 0.2 M sodium hydroxide solution. This was allowed to cool before being transferred to a 100 ml polythene beaker together with washings, and was diluted to 45 ml with deionised water. Dropwise acidification of the solution with nitric acid was carried out until the pH was between 5.5. and 6.5. The solution was then transferred to a 50 ml flask and diluted to the mark. After setting up and calibrating the ion electrodes, the concentrations of Cl^- and F^- in the distillate was measured and converted to concentrations in the inclusion fluids, Appendix 2.

Analysis of sulphate was investigated due to interest in the cation content of the inclusion fluids of fluorite. It was however, thought to be present in only very small amounts. The method used involved the precipitation of the sulphate as the barium salt, which was then collected on filter papers and analysed by X-ray Fluorescence techniques for barium radiation. This was then recalculated to give the SO_4 concentration (Luke, 1968). 0.5 ml of leachate, prepared as above, were mixed with an ethanol-pH buffer solution of barium chloride, sodium acetate and glacial acetic acid. This was spiked with $0.25 \mu\text{l}$ of $20 \mu\text{l}$ S^{2-} solution to give a spiked equivalent of $5 \mu\text{g}$ S^{2-} . The mixture was stirred continuously for 10 minutes. A $0.6 \mu\text{m}$ filter paper disc, type Millipore B.D.W.P. 02500, was placed on an ethanol washed glass frit and overlain by a reservoir which was clamped into position. The filter paper was washed with 2-3 ml of 50% ethanol solution using a vacuum pump suction system, Fig. 3.4. The sample solution was poured into the reservoir allowing slow passage

Fig.3.4 Apparatus used for collection of precipitated sulphate
on to filter papers from the sample solution.



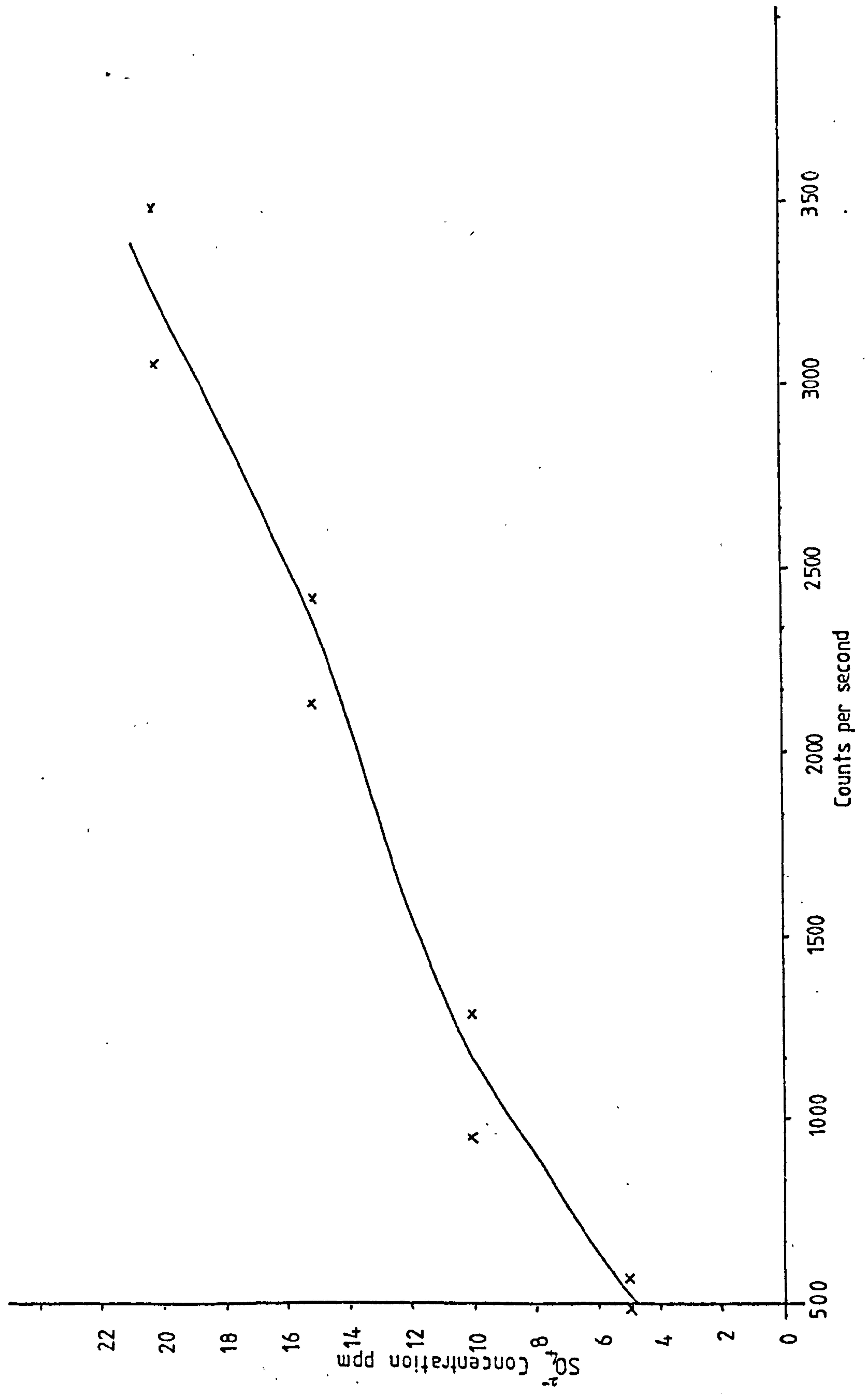
through the filter paper. 2 ml of 50% ethanol solution were used as washings, and when the filter paper was dry, 5-10 ml of 50% ethanol solution were used to rinse the reservoir. The filter paper was allowed to dry completely before analysis by X-ray fluorescence.

For the x-ray fluorescence analysis a tungsten target and LiF_{220} analysing crystal were used. A chromium backing disc was employed to improve the excitation of the barium $L\alpha$ radiation peak being measured. Interaction of the tungsten x-rays with the disc produced radiation due to iron and chromium which then helped excite the $L\alpha$ radiation on their passage back through the sample, thus improving the measurement of the $L\alpha$ radiation. 40 second counts were made using a flow counter at 20 positions of 85.50° , 87.16° and 88.50° . After adjusting for dead time corrections, calibration graphs were drawn up using standards prepared as above, Fig. 3.5. and Appendix 2.

Rare Earth Element Analysis was carried out by Mr. D. Bland at the I.G.S., using x-ray fluorescence techniques, to check concentrations previously measured by Smith, (1974). The samples were prepared as powders of 30# mesh grain-size, by grinding in an alumina ball mill. Further grinding of 4 grams of sample with one gram of elvisite powder binder was then carried out to a mesh grain size of 60-120#. The powder was then pressed at 30 tons per square inch into $1\frac{3}{8}$ inch diameter dies.

A standard of Derbyshire fluorite, previously shown to be rare-earth element deficient was prepared as above and spiked with 77 ppm Yttrium, 130 ppm cerium and 49 ppm Lanthanum, using spec. pure oxides. The accuracy of the spike was $\pm$ 2-4 ppm.

Fig.3.5 Calibration graph for the sulphate analysis.



The samples and standards were run on a Siemens x-ray fluorescence spectrometer. The conditions and wavelengths used are shown in Tables 3.3. and 3.4. 20 chart recordings were analysed for results, Fig. 3.6a and b.

A remeasurement of Smith's original samples was attempted although the use of different binders and different x-ray fluorescence spectrometer conditions prevented a direct duplication of results.

3.90. Analytical Results

3.91. Gas Analysis

The results show that the inclusions contain mainly water, 0 to 5 weight % CO_2 and very small amounts of non-condensable gases. Detailed mass spectrometric analysis indicated that the non-condensable gases consisted mainly of methane, hydrogen, nitrogen and argon, Table 3.5. The CO_2 and water shown in the analysis cannot be attributed to the non-condensable gases and probably originates from the unbaked section of the line into the Quadropole mass spectrometer. A small amount of the hydrogen may also be derived from dissociation of water on the filament. However the CH_4 , N_2 , Ar and most of the H_2 are more likely to have been the dissolved gases in the inclusion fluids, as their solubility is quite high in brines even allowing for 'salting out'.

Every attempt was made to reduce the errors associated with the gas analysis. Initial outgassing removed any water accrued by the sample during storage, in addition to volatiles adsorbed on to the vacuum line walls. Maximum temperatures were kept below 610°C to avoid chemical reactions such as the breakdown of sulphides to produce sulphurous gases. Carbonates were

Table 3.3 Radiation peaks used in Rare Earth element analysis

Element	Radiation	Wavelength
Ce	$L\beta^1$	2.356 Å
Nd	$L\alpha$	2.370 Å
La	$L\alpha$	2.655 Å
Y	$K\alpha$	0.831 Å

Table 3.4 Standard Conditions for the Seimens X-ray fluorescence spectrometer

1) Conditions constant for all elements analysed:-

Tube: Tungsten

Crystal: LiF_{220}

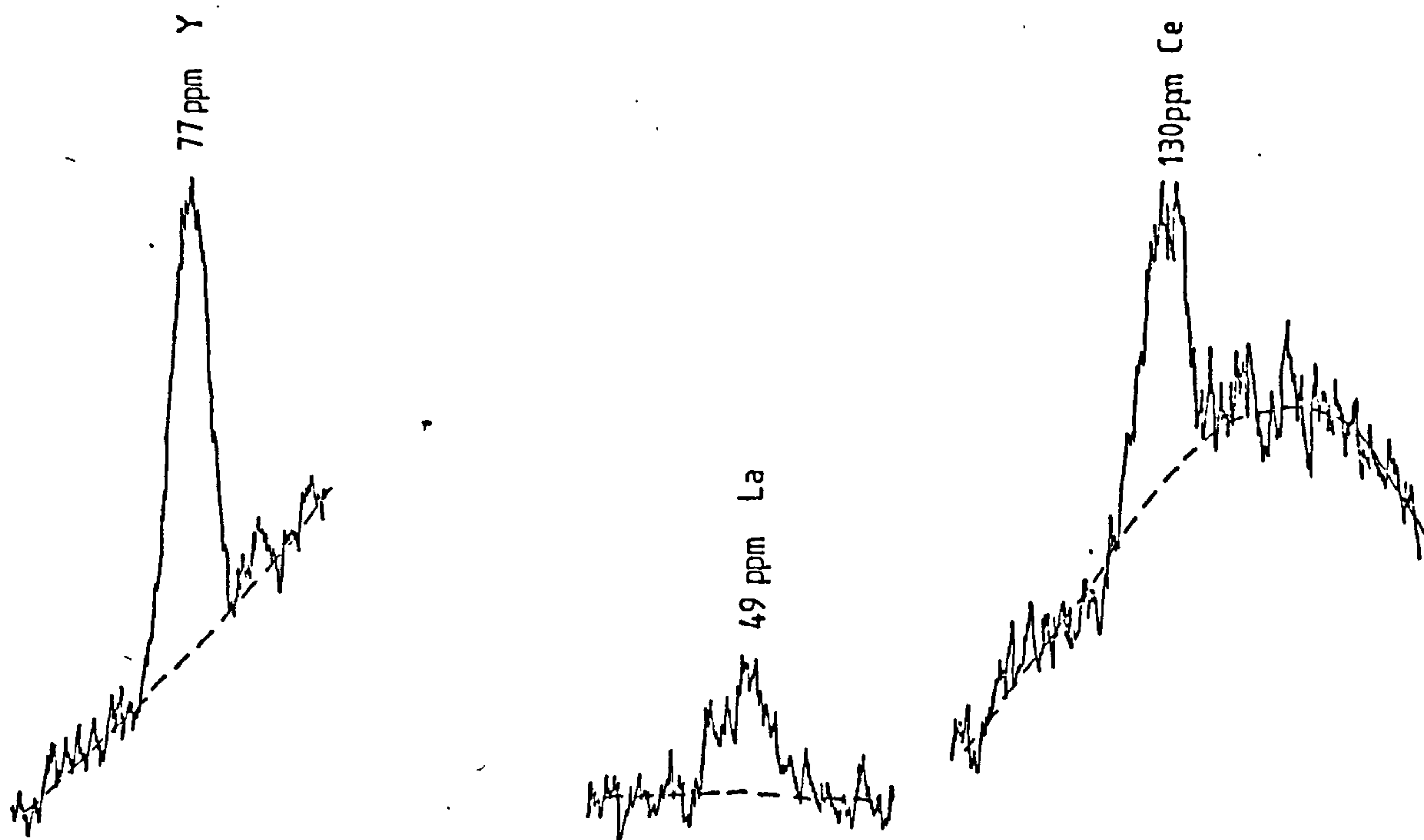
Scan Rate: $\frac{1}{2}^\circ \text{ min}^{-1}$

Count Time: 4 secs.

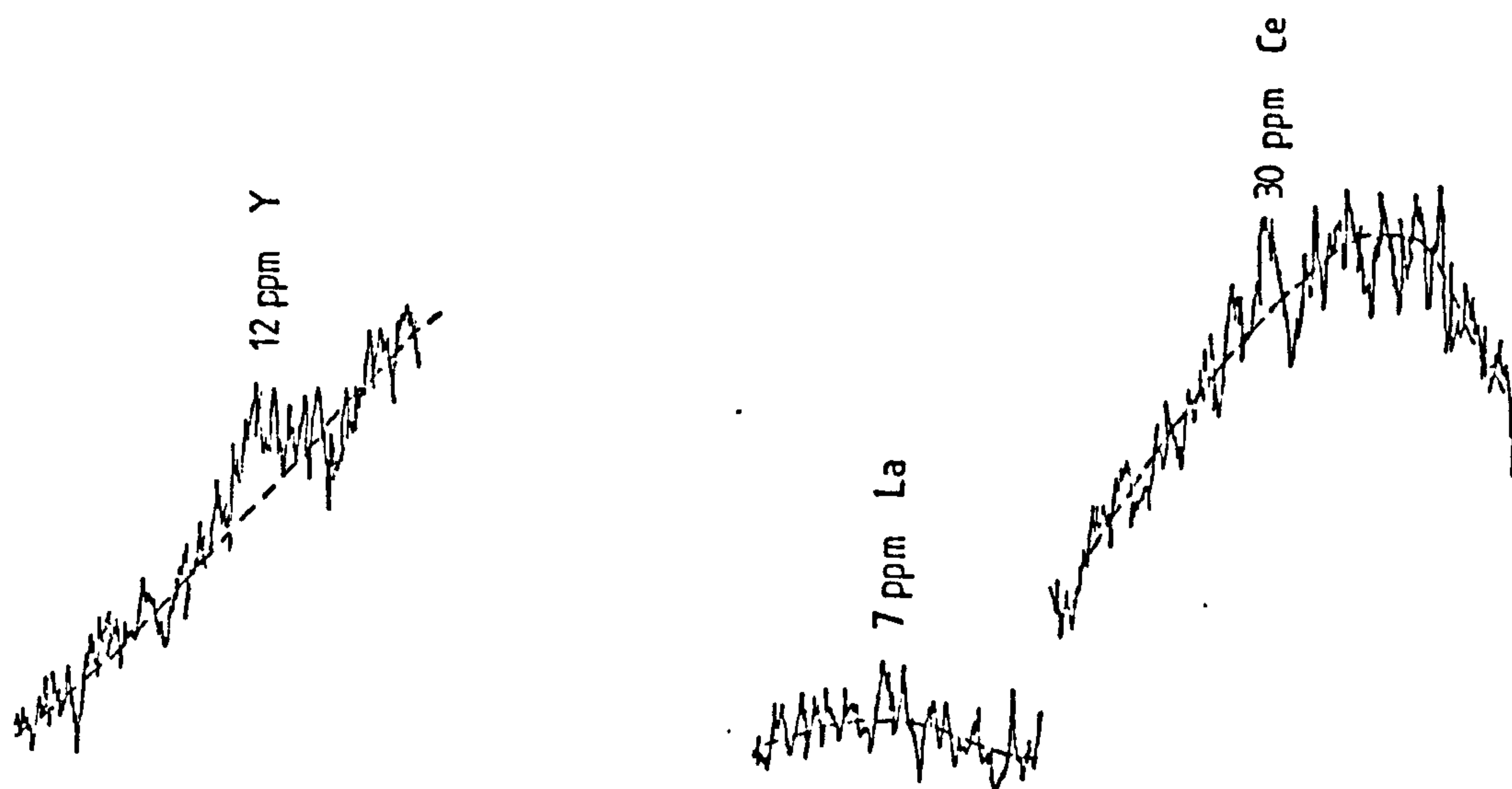
2) Conditions varying for the elements analysed:-

Element	Voltage Kv	Current mA	Full Scale Deflection cs^{-1}
Y	60	32	4×10^2 to 2×10^4
Ce, La, Nd	45	70	1×10^2

Fig.3.6a 20 chart recording for X-ray fluorescence analysis of rare earth elements; the standard before and after spiking.



The standard after spiking.



The standard before spiking.

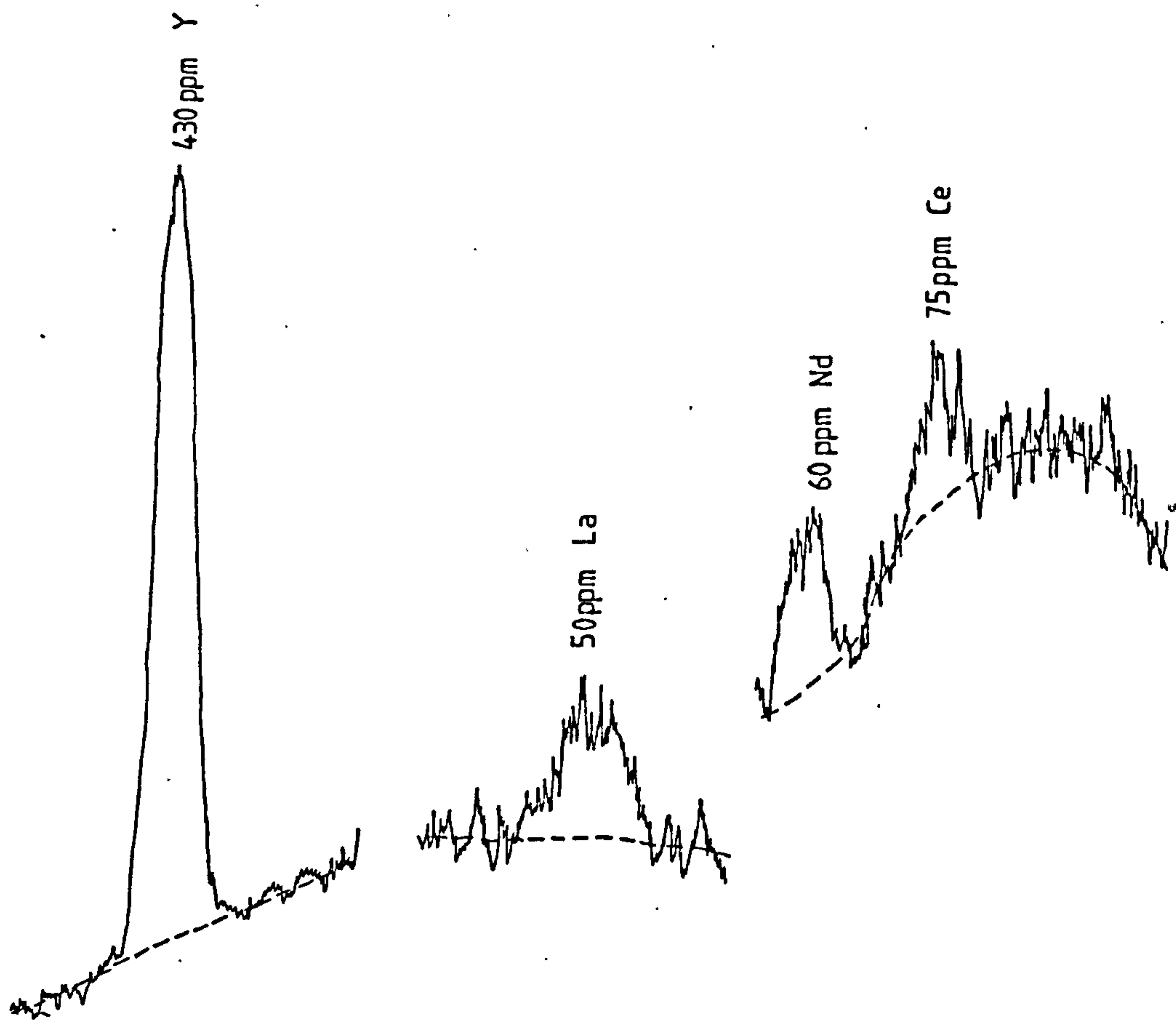


Fig.3.6b A sample rich in rare earth elements.

TABLE 3.5 Quadropole Mass Spectrometer Gas analysis
of a Derbyshire Fluorite Sample

Non-condensable Gas	% of Total Non-condensable gas	Vol.at stp. $\text{cm}^3 \times 10^{-8}$	Ratio against CO_2
Methane (CH_4)	19.18	1.192	.0604
Nitrogen (N_2)	21.95	1.364	.0691
Hydrogen (H_2)	55.20	3.428	.1736
Argon (Ar)	.04	0.002	.0001
Carbon dioxide (CO_2)	.011	0.006	.0003
Water (H_2O)	3.48	0.215	.0109
Total	99.99	6.207	

CO_2 and H_2O are not non-condensable gases but originate from out-gassing of the unbaked line to the quadropole mass-spectrometer.

Volume of N.C. (total) = $5.22 \times 10^{-8} \text{ cm}^3$ (S.T.P.)

Volume of CO_2 = $19.750 \times 10^{-8} \text{ cm}^3$ (S.T.P.)

Weight of CO_2 = 0.009×10^{-3} grams.

Weight of H_2O = 1.150×10^{-3} grams.

ratio $\text{CO}_2:\text{H}_2\text{O}$ (weights) = .0078

N.C.: CO_2 (volume) = .264

removed by acid washing. Thus errors are most likely to result from incorrect volume measurements in the vacuum line. Those measurements were repeatedly checked; only the uranium furnace showing any variation. This is due to the fact that hydrogen is absorbed on to the uranium in the furnace at 800 °C. The affect is quite marked at low hydrogen pressures, but becomes negligible at higher pressures. The affect cannot be eliminated by use of a different gas for estimating volumes, due to the fact that it is necessary to use hydrogen over hot uranium in order to preserve the integrity of the activated uranium surface. Thus a correction curve was constructed, using different hydrogen pressures, to enable calculation of the percentage of pressure to be added to the measured pressure and thus correct for hydrogen absorption, Appendix 2.

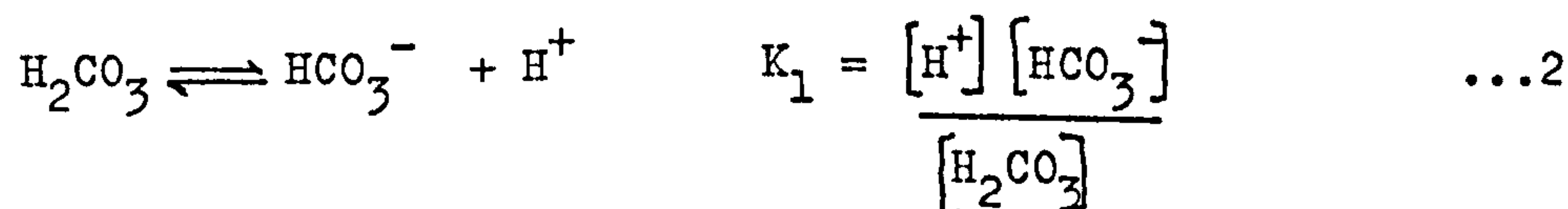
3.92. pH calculation

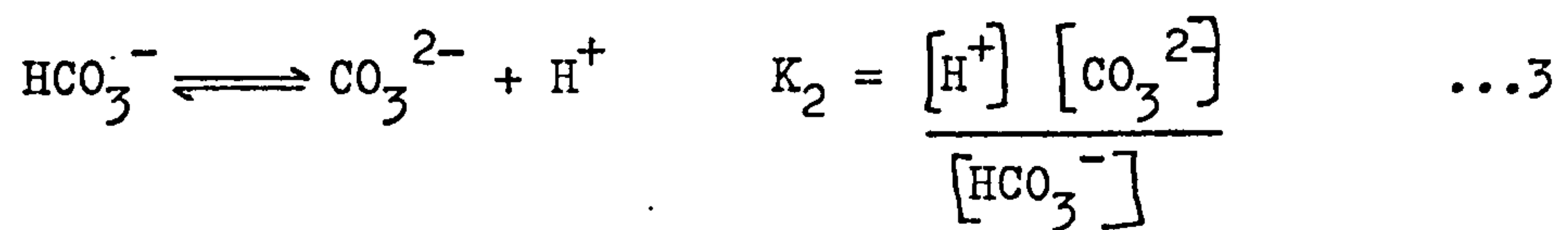
The CO₂, water ratios found for each sample were used in connection with temperature values and salt contents of the inclusion fluids to derive pH values for the fluids.

The pH values were derived from the weak acid (H₂CO₃) content of the inclusion fluids.

$$[H_2CO_3] = \left[\frac{CO_2/H_2O \text{ ratio} \times 10^3}{44} \right] \text{ moles L}^{-1} \text{ of } CO_2 \quad \dots 1$$

Derivation of the pH used the dissociations of carbonic acid taken from Krauskopf, (1979). The dissociations are:-





Thus the total carbonate concentration will be represented by:-

$$\Sigma \text{CO}_3 = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad \dots 4$$

For equilibrium the solution must be electrically neutral, such that positive charge = negative charge or:-

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad \dots 5$$

The ~~water~~ water dissociation must also be satisfied.

$$[\text{H}^+][\text{OH}^-] = 10^{-14} = K_w \quad \dots 6$$

Helgeson (1969), showed that at 25 °C and up to 300 °C the value of K_2 is 10^4 times smaller than K_1 . Thus the $[\text{H}^+]$ contribution from the second dissociation will also be very small compared to that from the first dissociation. $[\text{CO}_3^{2-}]$ concentration derived from the second dissociation will therefore also be very small. Three assumptions were thus made:-

Assumption 1: $[\text{CO}_3^{2-}]$ concentration in equations 3 and 4 is negligible compared to the $[\text{H}_2\text{CO}_3]$ and $[\text{HCO}_3^-]$ concentrations.

Assumption 2: $[\text{OH}^-]$ concentration will be small relative to $[\text{H}^+]$ since an acid is being dissolved in water.

Therefore from equation 5.

$$[\text{H}^+] = [\text{HCO}_3^-] \quad \dots 7$$

from equation 2 and substituting equation 7

$$K_1 = \frac{[H^+]^2}{[H_2CO_3]} \quad \dots 8$$

from equation 4 and substituting equation 7

$$\leq CO_3 = [H_2CO_3] + [H^+] \quad \dots 9$$

Assumption 3: As H_2CO_3 is a weak acid, the $[H^+]$ concentration from dissociation of $[H_2CO_3]$ is probably small in comparison with the concentration of undissociated molecules. Thus $[H^+]$ in equation 9 can probably be neglected giving

$$\leq CO_3 = [H_2CO_3]$$

Ellis and Golding's (1963) work was used to show that all the CO_2 present in the inclusions would be totally dissolved and 'salting out' does not occur. Using the salting out coefficients provided it was possible to show what mole fraction of CO_2 would be dissolved in a particular NaCl solution at a particular temperature and pressure.

The mole fraction of CO_2 was given by

$$\text{mole fraction } CO_2 = \frac{\text{Fugacity of } CO_2}{K_o^S}$$

where K_o^S is the solubility of CO_2 in a salt solution and is found using the following equation

$$Km = \log \left[\frac{K_o^S}{K_o} \right] \quad \begin{array}{l} \text{Sechenov equation.} \\ \text{(Ellis and Golding, 1963)} \end{array}$$

where K = salting out factor

m = molality of the solution

K_0 = solubility of CO_2 in water (Henry's Law constant)

Assuming a fugacity of $\text{CO}_2 = 0.1$ to 1.0 units. The mole fraction of CO_2 that can be dissolved was calculated and compared to the mole fraction of CO_2 calculated from equation 10 for the fluid inclusions. All CO_2 in the inclusions will thus be dissolved, Table 3.6. Thus the pH can be calculated from:

$$\text{pH} = -\log [\text{H}^+] = \frac{1}{2} (\log K_1 + \log [\text{H}_2\text{CO}_3])$$

3.93. Flame photometry and Atomic absorption spectrometry Results

Given the general inhomogeneity of the samples, flame photometry and atomic absorption spectrometry determinations yielded fairly reproducible results on duplicate runs. Each run involved two consecutive 5 ml deionised water leachates, as it was shown that the majority of salts were removed after the second leach. Acid leachates were not used, even though they showed slightly greater yields, because of the possibility of contamination from acid soluble solid sulphide inclusions in the fluorite, Table 3.7.

The flame photometry determinations gave a mean of 10% analytical variation of duplicate analyses of sodium and 17% analytical variation for those of potassium. For the atomic absorption spectrometric analyses the mean analytical variation was greater, from 28% to 43%, for the different elements, Table 3.8. This higher analytical variation is probably due to the lower concentrations of elements (Cu, Zn, Mg, Mn and Fe) in the leachates. However for some of the duplicate runs totally different concentrations are found as indicated by the

Table 3.6 Comparison of the mole fractions of CO₂ soluble in salt solutions of different concentrations at different temperatures and pressures, with the mole fractions calculated for the inclusion fluids

Mole fractions of CO₂ at a P_{CO₂} = 1.0

Temperature:-	100 °C	150 °C	200 °C
Water	192	161	156
0.5 M NaCl	164	129	127
1.0 M NaCl	136	108	104
2.0 M NaCl	93	78	72

Mole fractions of CO₂ at a P_{CO₂} = 0.1 ~~atm~~

Temperature	100 °C	150 °C	200 °C
Water	19	16	15
0.5 M NaCl	16	13	13
1.0 M NaCl	14	11	10
2.0 M NaCl	9	8	7

The mole fraction range of the fluid inclusions is between 7.5 and 0.081 for all but three samples for the temperature range of 82.5 °C to 189 °C and a NaCl concentration between 0.1 and 5.5 M.

Calculation of the mole fraction is given by:-

$$\text{mole fraction CO}_2 = \frac{\left[\frac{\text{weight CO}_2}{\text{molecular weight CO}_2} \right]}{\left[\frac{\text{weight H}_2\text{O}}{\text{molecular weight H}_2\text{O}} + \frac{\text{weight CO}_2}{\text{molecular weight CO}_2} \right]} \times 100$$

--10

TABLE 3.7.

Comparative acid and water leachate concentrations

Sample	Leachate	Sodium		Potassium	
	Aliquot	Acid	D. Water	Acid	D. Water
244	1	39.0	30.0	3.0	2.6
Fluorite	2	12.0	3.6	-	-
	3	8.0	1.6	-	-
	4	-	-	-	-
	Total	59.0	35.2	3.0	2.6
1070	1	39.0	25.0	4.0	2.0
Fluorite	2	14.0	4.0	1.6	-
	3	9.0	1.6	-	-
	4	-	-	-	-
	Total	62.0	30.6	5.6	2.0

All concentrations are in ppm.

Table 3.8 Concentration ranges and percentage analytical variations in inclusion fluids from fluorite, barite and quartz

Element	Northern Pennine		Derbyshire		Northern Pennine		Northern Pennine		Percentage Analytical		
	Fluorites		Fluorites		Barite		Quartz		Mean	Analytical Variation	Range
CO ₂ :H ₂ O	.002 -	.536	.007 -	.332	.007 -	.338	.002 -	.017	28		0 - 81
Na	14.6 -	129.8	13.1 -	110.8	2.8 -	70.7	16.1 -	53.5	10		1 - 39
K	1.62 -	14.71	0.76 -	7.26	0.63 -	10.43	1.79 -	13.52	17		0 - 53
Cu	0.01 -	10.47	0.03 -	13.2	0 -	4.03	0.10 -	11.62	43		1 - 38
Zn	0.03 -	14.57	0 -	11.71	0.09 -	3.72	0.05 -	0.79	34		1 - 96
Mg	0.08 -	9.90	0.33 -	1.67	0.10 -	12.99	0.05 -	0.20	28		0 - 89
Mn	0.03 -	7.18	0 -	0.41	0.02 -	7.36	0 -	0.06	35		0 - 80
Fe	0.05 -	21.8	0.20 -	11.06	0 -	5.80	0.15 -	2.24	43		3 - 92
Sr	0.20 -	3.68	0.68 -	8.63	0.6 -	153.90	0.34 -	1.88	-		-
Ca	-	-	-	-	6 -	494	25 -	484	-		-

Table 3.8 cont.

nb. all values other than $\text{CO}_2:\text{H}_2\text{O}$ ratios are $\times 10^3$ ppm

Calculation of Percentage Analytical Variation

$$\% \text{ variation} = \frac{\sigma}{\bar{x}} \times 100$$

where σ is the standard deviation

$\bar{x}$ is the mean value of replicate analysis

$$\text{The mean variation} = \frac{\sum \% \text{ variations}}{n}$$

where $\sum \% \text{ variation}$ is the sum of percentage variations

and n is the number of sample errors used.

range of percentage analytical variation to 96%. This may be attributed to sulphide mineral inclusions which were partially dissolved during leaching. In these cases the lower values have been used in later interpretation.

These element concentrations have been converted to molalities of chloride complexes to give an indication of their amounts in solution and for use in interpretation, Table 3.9.

Work was also carried out on primary and secondary inclusion fluids using samples 430 and R28, Table 3.10. The absolute concentrations of the different elements shows some variability between primary and secondary inclusion fluids. However the high Cu, Zn and Fe concentrations found in the secondary inclusions may be due to solid sulphide leaching during ultrasonic vibration of the decrepitated material with the leachate. This is carried out before the primary inclusions are extracted. Thus to find whether the fluids are similar ratios were calculated between different elements, Table 3.11. It can be seen from the salinity ratios, Na/K, NaCl/KCl and K/Mg, that the primary inclusions are relatively more concentrated, by up to a factor of two, than the secondary inclusions. The metal element concentrations however look to be very similar, at least for sample 430. Values for sample R28 have probably been influenced by leaching of solid sulphide inclusions. Therefore it would seem that the secondary inclusions represent a diluted version of the primary inclusions.

3.94. Neutron Activation Analysis Results

Neutron activation analysis of leachates produced data for sodium, chlorine and bromine. Potassium, rubidium, cesium and iodine were below the limits of detection. Table 3.12 gives

Table 3.9 Concentrations in molalities of the major cations as chloride complexes in inclusion

fluids from fluorite, barite and quartz samples

Element	Northern Pennine		Derbyshire		Northern Pennine		Northern Pennine	
	Fluorite		Fluorites		Barite		Quartz	
NaCl	1.0	- 5.5	0.8	- 3.0	0.1	- 3.200	1.4	- 2.5
KCl	.09	- .35	0.05	- 0.20	0.05	- .27	0.1	- .35
CaCl ₂	-	-	-	-	0.2	- ~15.0	0.3	- ~15.0
MgCl ₂	0.003	- 0.42	0.01	- 0.07	0.004	- 0.56	0.002	- 0.008
SrCl ₂	0.002	- 0.04	0.008	- 0.10	0.007	- 2.44	0.004	- 0.022
CuCl ⁺	0.0002	- 0.17	0.0005	- 0.21	0.00	- 0.064	0.002	- 0.19
ZnCl ₂	0.0005	- 0.23	0.00	- 0.18	0.001	- 0.057	0.0008	- 0.01
FeCl ⁺	0.0009	- 0.40	0.005	- 0.20	0.00	- 0.0001	0.003	- 0.04
or FeCl ₂	0.0009	- 0.41	0.005	- 0.20	0.00	- 0.0001	0.003	- 0.04
MnCl ₂	0.0006	- 0.07	0.00	- 0.007	0.0004	- 1.800	0.00	- 0.001

All concentrations are in molalities = mols per kg H₂O. Molalities for NaCl, KCl, CaCl₂ and SrCl₂ incorporated density values from the Handbook of Chemical and Physical Constants (Weast, 1977). All other chloride complex molalities were calculated assuming the density of the solution was 1.00 kgL⁻¹

Table 3.10 Comparison of primary and secondary inclusion fluids in
Northern Pennine fluorites

Element	Sample 430		Sample R28	
	Secondary F.I. concentrations	Primary F.I. concs.	Secondary F.I. concentrations	Primary F.I. concs.
H ₂ O (mg)	0.398	2.251	0.342	3.566
CO ₂ / H ₂ O	0.001	0.005	0.006	0.006
Na 10 ³ ppm	48.30	58.60	68.20	52.70
K 10 ³ ppm	6.03	3.91	7.02	4.04
NaCl wt%	11.40	13.60	14.50	12.4
KCl wt%	1.14	0.74	1.33	0.76
Cu 10 ³ ppm	2.76	1.76	11.99	0.84
Zn 10 ³ ppm	5.28	2.62	9.32	1.32
Mg 10 ³ ppm	1.51	0.51	0.79	0.43
Mn 10 ³ ppm	3.27	0.31	1.17	0.11
Fe 10 ³ ppm	11.81	1.20	4.97	0.20

In samples 430 and R28, the relative weight of water for each type of inclusion, gives the secondary inclusion fluids as 17.7% and 9.6% respectively, of the primary inclusion fluids.

Table 3.11. Comparison of elemental ratios for secondary and
primary inclusions

ratio	sample 430		sample R28	
	Secondary F.I.	Primary F.I.	Secondary F.I.	Primary F.I.
Na/K	8.01	19.99	9.00	13.04
NaCl/ KCl	10.00	18.38	10.90	16.32
K/Mg	3.99	7.67	8.89	9.40
Cu/Zn	0.52	0.67	1.29	0.64
Fe/Mn	3.61	3.87	4.25	1.82
Zn/Fe	0.45	2.18	1.88	6.60

(n.b. Sample numbers as for table 3.7)

data for the few samples analysed, with the calculated concentration of NaCl and any excess Cl^- left in solution. This is probably taken up as CaCl_2 . The chlorine bromine ratio can also be calculated and gives a range from 125 to 380. Sea water's ratio is 292 with river and lake water generally equal to or greater than this. No duplicate runs were carried out. Errors due to overlapping radiation peaks were mainly eliminated by the use of multiple irradiations as described above.

3.95. Results of Pyrohydrolysis

Pyrohydrolyses provided data for Cl^- and F^- on most of the quartz samples, Table 3.13. Errors associated with the technique are mainly due to incomplete removal of fluorite from quartz (e.g. the Slitt Vein.). Otherwise contamination was kept to a minimum. Calculation procedures involved two major assumptions which relate closely to the estimation of errors. The first is, that the one gram of mixture used for analysis from the 1.5 grams made up, contained the sample in the ratio $z/z + y$, where z was the number of grams of sample used and y was the number of grams of vanadium pentoxide. The second assumption rests on prior calculation of the weight of inclusion fluid contained in one gram of quartz, Appendix 2.

3.96. Sulphate analysis results

The sulphate analysis showed that the amount of sulphate being precipitated from the sample solution, even after spiking, was within the experimental error of the calibration curve. The technique though suitable for other materials was thus considered too insensitive for the low sulphate levels in the fluorites.

Table 3.12 Neutron activation analysis of fluid inclusion

leachates

Sample	Na	Cl	Br	Cl/Br	NaCl	Cl ⁻ excess
250	51.7	102.3	0.62	165	131.2	22.71
270(1)	49.9	96.6	0.35	276	126.8	19.7
441	121.5	189.8	1.52	125	308.6	2.6
806	60.5	121.6	0.48	253	135.5	39.4
807	62.1	131.9	0.60	220	157.7	36.2
993	101.6	147.2	1.11	133	243.0	-
1013	57.6	114.1	0.30	380	146.3	25.3
1044	54.0	103.0	0.48	215	137.3	19.7
1102	91.3	189.6	1.12	169	231.8	48.9

All concentrations are measured in 10^3 ppm

Table 3.13 Chlorine and fluorine analyses of quartz inclusion
fluids using pyrohydrolysis

Sample	Location	Cl ⁻ ppm in fi. x 10 ⁺³	F ppm in fi. x 10 ⁺³	Cl ⁻ /F ⁻
414	Great Sulphur Vein	264.3	9.91	26.7
416		121.6	4.05	30.0
416rpt		121.5	4.05	30.0
418		351.1	19.15	18.3
419		191.1	9.05	21.1
424		637.5	22.50	28.3
R101.1	Slitt	54.8	1,911.50	0.03
R102.3	Vein	45.3	900.30	0.05

The Slitt Vein quartz samples are thought to have been contaminated with fluorite, whereas the Great Sulphur Vein samples are free from fluorite.

3.97. Results of rare earth element analysis by X-ray fluorescence

X-ray fluorescence analysis of duplicates of Smith's samples by Bland indicated that the Cerium peak was subject to interference by a second order calcium $K\alpha$ radiation, Fig. 3.7. The results obtained are compared to Smith's analyses in Table 3.14. Smith's actual sample pellets were not analysed as they were thought to be of too coarse grain size to be truly homogeneous. Homogeneous samples are necessary due to the small depth of penetration, 0.1 mm of the radiation, when measuring Ce, Nd, and La. This obviously shows that reproduction of the actual results obtained by Smith, is unviable due to the differences in pellet preparation and machine conditions. However the yttrium analyses seem to show similar trends, Fig. 3.8. Also Smith's results have been shown to be useful for ore exploration in the Groverake Mine and thus must have internal reproducibility. On this basis Smith's yttrium work has been incorporated into the present study.

Fig.3.7 Interference of the Cerium peak by a second order Calcium
K α radiation.

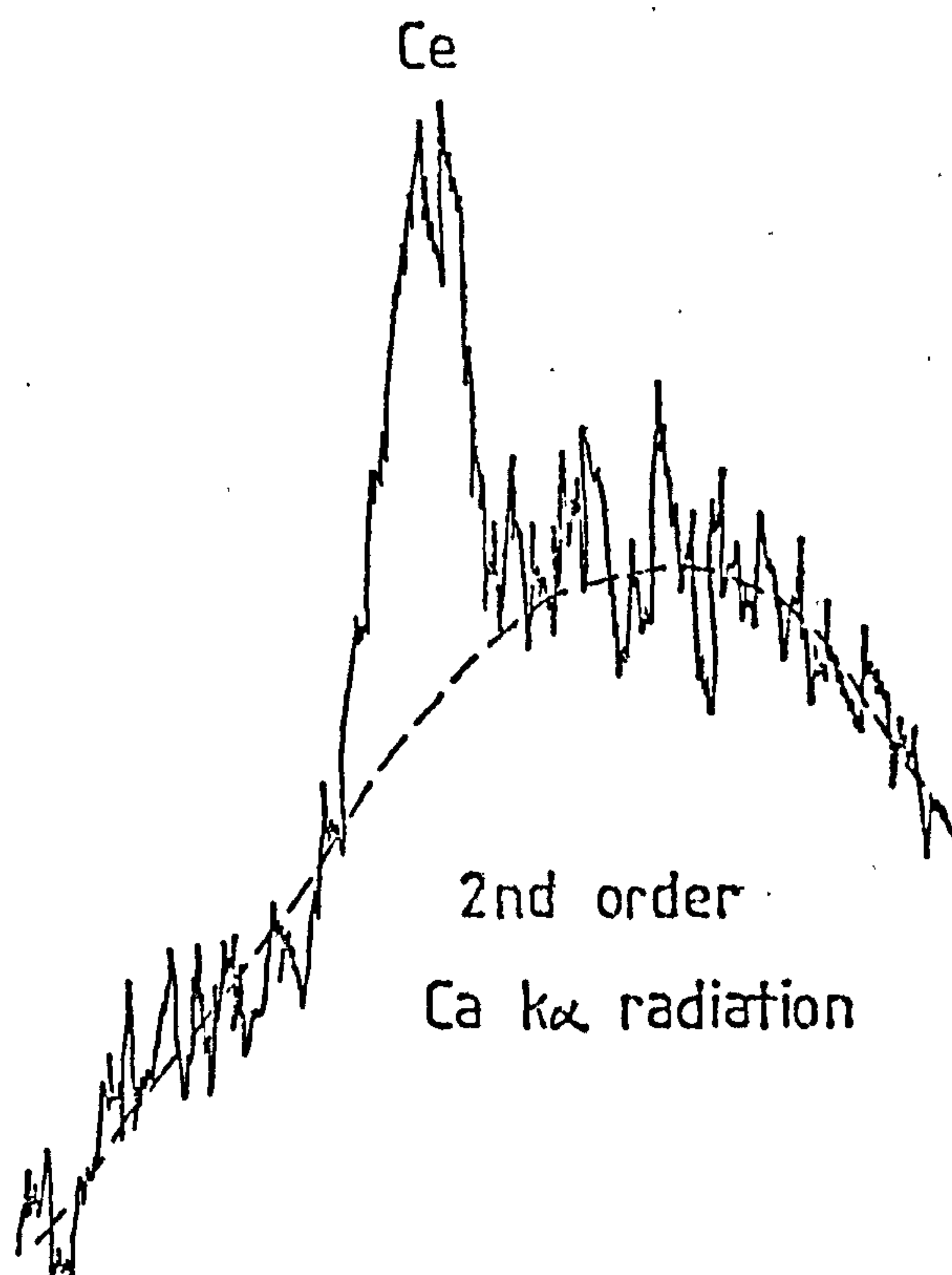


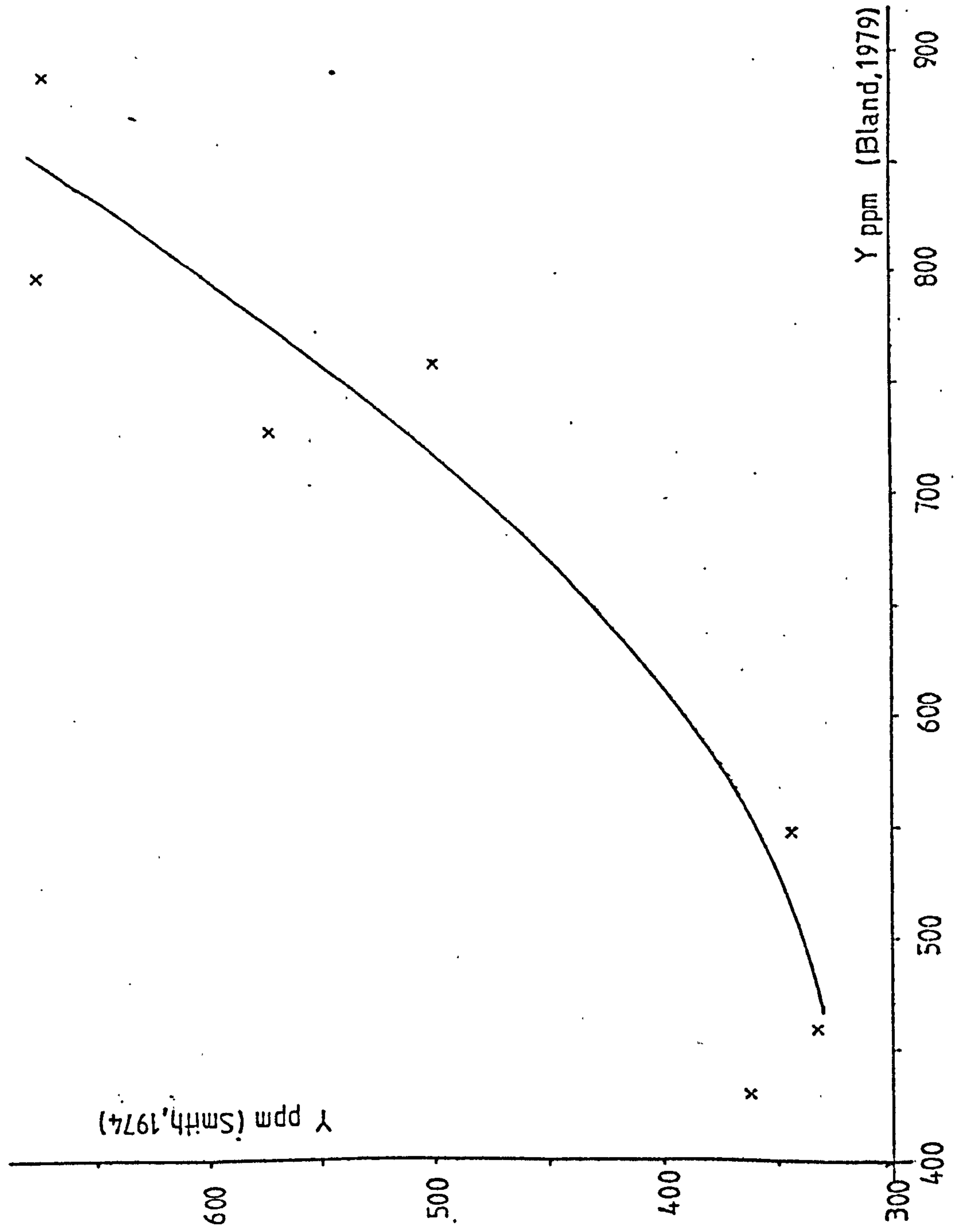
Table 3.14 Rare-earth element concentrations of fluorites from
the Northern Pennine Orefield by x-ray fluorescence
analysis

Sample	Ce		La		Yt		Nd
	Smith	Bland	Smith	Bland	Smith	Bland	Bland
250	117	140	66	110	344	550	120
277	196	110	86	90	500	760	210
330	162	75	92	50	362	430	60
442	92	25	54	50	673	890	-
876	79	-	32	5-15	676	800	90
892	53	20	24	30	572	730	50
1031	166	75	82	65	336	460	80

All concentrations are in ppm.

Fig.3.8 Comparison of Yttrium concentrations obtained by Smith(1974) and Bland(1979) on

similar samples.



C H A P T E R F O U R

4.1. Application of stable isotopes to the study of hydrothermal ore deposition

Deuterium-hydrogen isotopes have been used by many workers together with Oxygen 18/16 isotopes, because they are sensitive parameters relating to the origin and evolution of different types of waters.

Hydrogen isotope work has been carried out on natural waters since 1953 (Friedman, 1953), complementary work on oxygen isotopes was also started in 1953 by Epstein and Mayeda. Progression from this led to combined D/H and O^{18}/O^{16} studies on waters (Friedman and Woodcock, 1957; Craig, 1961 a; Friedman et al., 1964; Halevy and Payne, 1967; Sakai and Matsubaya, 1974). More recently work has focussed on formation waters and oilfield brines. (Clayton et al., 1966; Hitchon and Friedman, 1969; Kharaka and Berry, 1973; Fleischer et al., 1977).

In 1963 Roedder et al., applied Friedman and Woodcock's (1957) ideas on D/H work to fluid inclusion analysis. They crushed the sample to release the inclusion water which was then converted to hydrogen, by passage over hot uranium, before analysis.

Oxygen isotope work on fluid inclusions has not been expansive. Most workers relying on mineral analyses which were then corrected to give the equivalent $\delta^{18}O$ for water in equilibrium with the mineral, using fractionation factors.

This work on mineral analysis was first done on oxides and silicates, using bromine pentafluoride to release the oxygen from the mineral lattice. The oxygen was then converted to CO_2

for analysis on the mass spectrometer (Clayton and Mayeda, 1963). Sharma and Clayton, (1965), developed a technique for analysis of carbonates using phosphoric acid and this was followed with work on sulphates by Holser and Kaplan, (1966), and Rafter, (1967). The BrF_5 method was also used for analysis of milligram quantities of fluid, (O'Neil and Epstein, 1966), but this procedure was not whole-heartedly adopted, most workers continuing to analyse oxygen derived from the mineral lattices, in preference.

During this time much work was carried out to derive fractionation factors for the different mineral-water pairs. This was also necessary for fluid inclusion interpretation. (Lloyd, 1968; Bottinga, 1969; Mizutani and Rafter, 1969; Deines, 1970; Kusakabe and Robinson, 1977).

The primary standard used for hydrogen and oxygen isotope analysis is the Atomic Energy standard of Standard Mean Ocean Water, S.M.O.W. For CO_2 work other standards are often used, (Craig, 1957; 1961 b.)

Work on mineral deposits has thus incorporated many of the above techniques. Actual water analysis of fluid inclusions has been done to obtain δD values, whereas mineral oxygen analysis has been carried out with the aid of fractionation factors, to derive the $\delta^{18}\text{O}$ water.

In 1966, Rye, analysed for δD in fluid inclusions from minerals of the lead-zinc deposits, Providencia Mexico. He and his co-workers followed this in 1968, (Rye and O'Neil). with oxygen isotopic analysis of carbonates. They proposed, from the results that the ore fluid had remained approximately constant during ore deposition and had originated from a

magmatic source. The ranges found were $\delta D = -5.8$ to -8.3% and $\delta^{18}O = 6.4$ to 7.9% .

Also in 1966, Garlick and Epstein worked on the copper deposits of Butte, Montana. They showed the main stage quartz to have a $\delta^{18}O = +10\%$ and later stage carbonates to have $\delta^{18}O = -2$ to 0% . Interpretation of this led them to suggest that the ore solution was predominantly of magmatic origin, with late stage additions of meteoric ground water causing the depletion in $\delta^{18}O$.

Further work on hydrothermal mineral deposits was done at Cave-in-rock, Illinois, (Hall and Friedman, 1963), Bluebell Mine, British Columbia, (Ohmoto and Rye, 1970), Darwin silver-lead-zinc deposits in South California (Rye and Hall, 1971; Rye et al., 1974), Casapalca silver-lead-zinc deposits of Peru (Rye and Sawkins, 1974), and the Kuroko deposits of Japan, (Ohmoto and Rye, 1974; Hattori and Sakai, 1979). A summary of the work done on Mississippi Valley type deposits is given by Heyl et al., (1974) and Taylor's, (1974) paper compares isotopic data obtained on a wide variety of waters and minerals.

4.2. Previous stable isotope work on the Northern Pennine Orefield and present objectives

With regard to the Northern Pennine Orefield a small amount of oxygen and sulphur isotope work has been carried out on barite and sulphides, (Soloman, Rafter and Dunham, 1971). They concluded that the sulphur values obtained for the sulphate were indicative of Carboniferous sea water sulphate. The sulphide mineral sulphur isotopes also suggested a sedimentary origin rather than a magmatic source. Oxygen isotope work was also carried out on the sulphates.

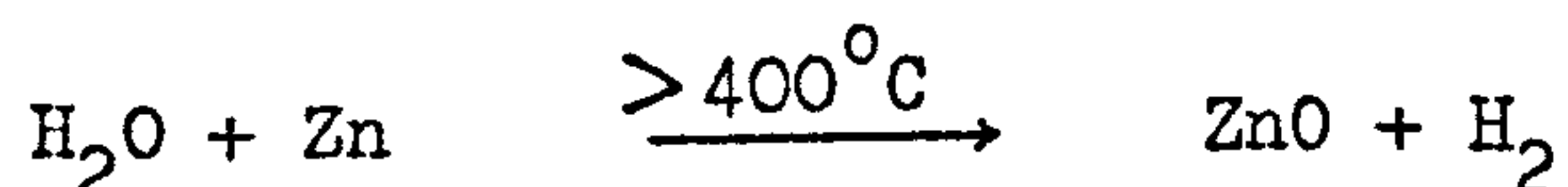
More recently, a small amount of sulphur isotope work has been carried out on minerals from the Closehouse Barite mine. (Sarah Brazier, pers. comm)

In the present study the stable isotopes of water were used to try and define further limits on the origin and evolution of the ore fluids. Hydrogen isotope work was carried out on water from fluid inclusions in quartz, fluorite and barite. In the course of the work it was necessary to carry out significant amounts of new development work, particularly with regard to the preparation of H_2 gas for D/H analysis, (section 4.5.). With respect to oxygen isotope work, analysis of quartz samples was done. A value for the ore fluid was obtained by using fractionation factors. Oxygen isotope values for barite were taken from Solomon, Rafter and Dunham's (1971) work, although no hand specimens were available.

4.3. Preparation of standards for D/H work

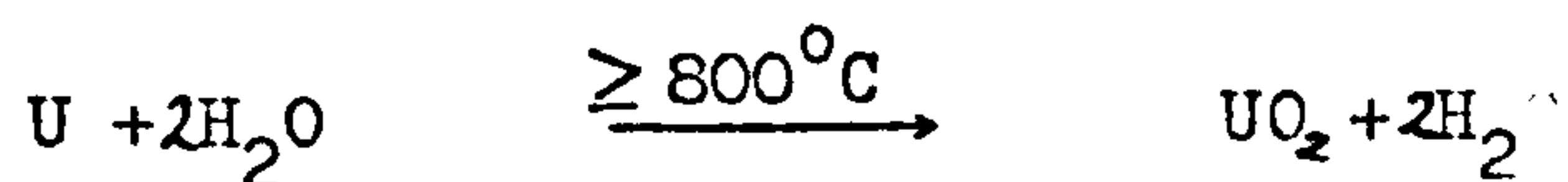
A variety of standards were used including the International Atomic Energy Standards, (Vienna Standard Mean Ocean Water, S.M.O.W.; Standard light Antarctic Precipitate, S.L.A.P.; NBS-18), (Craig, 1961 b), gypsum and deionised water. However all samples were related to SMOW in the final results.

Preparation of the standards mainly involved the use of zinc for the direct reduction of water to hydrogen, (Friedman, 1953).



Uranium used by most other workers was only used in the present study for a few samples, (Friedman and Woodcock, 1957).





Zinc used in the above reaction was obtained in the mesh grain size range of 30 to 60#. Prior to use it was cleaned with dilute nitric acid, then rinsed twice with deionised water and finally with acetone. It was then outgassed under vacuum for six hours at a temperature of 300°C .

Preparation of the standards involved leaching 5-10 μl aliquots of standard water on to 0.5 grams of outgassed zinc, contained in a glass reaction tube. The transfer was carried out under dry nitrogen to exclude atmospheric water. After freezing the water down in a liquid nitrogen trap the tube was then evacuated to 10^{-3} mTorr and sealed before removal from the extraction line. The vessel was heated to 420°C for $\frac{1}{2}$ to $\frac{3}{4}$ hour until the reaction was complete, shown by the production of a zinc bloom around the upper section of the tube.

Gypsum was also used as a standard, Appendix 3. At about 350°C gypsum undergoes total dehydration releasing two moles of water for every mole of CaSO_4 , (Sofer, 1978). Before dehydration the gypsum was stored in a dessicator for 24 hours. A known weight of the gypsum was then loaded into a silica-glass tube and connected to the glass section of the extraction line.

After evacuation and degassing the gypsum at 50°C , the temperature was raised to 400°C and the released water rapidly transferred to an evacuated reaction vessel containing zinc granules, previously outgassed at 100°C . Transfer was achieved using a liquid nitrogen trap on the collection vessel while all intermediate sections of the line were warmed to prevent adsorption of water. The whole process normally took about 15 minutes. The zinc was then reacted by heating to 420°C as

for the standard water. Gypsum was used as a standard because the method used to obtain hydrogen was similar to that adopted for the analysis of hydrogen from inclusion fluids.

4.4. Preparation of inclusion fluids for D/H analysis

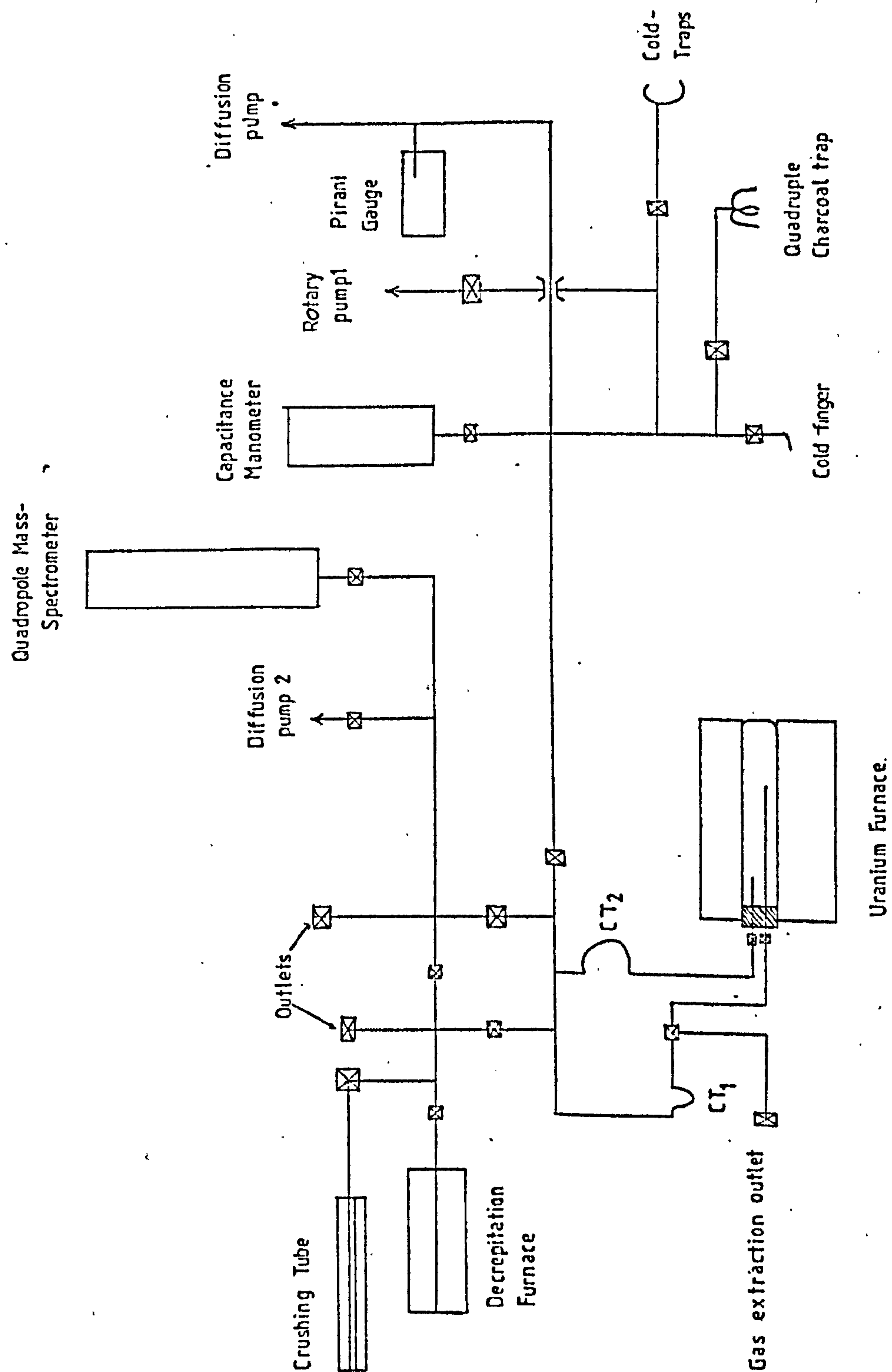
Using the fluid yields obtained for the chemical analysis of the fluid inclusions, an appropriate weight of sample was loaded into a silica glass tube. After evacuation and outgassing at 80 to 100 °C, the temperature was raised to 600 °C and decrepitation initiated. The water released was transferred to an evacuated reaction vessel containing outgassed zinc, as for the gypsum standards. (Transfer time approximately 10 mins.) Before sealing the reaction vessel any non-condensable gases were pumped away. The liquid nitrogen trap was then replaced by an acetone-dry ice trap, which allowed one to pump away similar traces of CO₂ and SO₂. To minimise the risk of SO₂ contamination, samples containing appreciable sulphide impurities were hand picked before decrepitation. This reduced the amount of SO₂ produced by thermal decomposition. The zinc was then reacted at 420 °C as before.

4.5. Development of small volume/direct zinc reduction methods for standards and inclusion fluids

The procedures described above for the preparation of inclusion fluids for D/H analysis was the subject of much development work. Incomplete reaction of the water with the zinc, and isotopic fractionation during water transfer proved severe problems to overcome.

Initially the main stainless steel extraction line was used, Fig. 4.1., but poor reproducibility of standards both

Fig.4.1 Vacuum line used for the quantitative extraction of inclusion fluids.



of gypsum and water was obtained. The observed isotopic fractionation (depletion in D) was thought to be due to water absorption and memory effects at cold spots on the line. Subsequently the entire transfer section was kept at 110 ° to 130 °C using heating tapes. This produced little improvement.

Atmospheric water vapour contamination was suspected and subsequent water standards were loaded onto the zinc under dry nitrogen. This ultimately proved to be a significant factor, Table 4.1., but did not eliminate the immediate fractionation problem. Finally it was decided to rebuild the relevant sections of the extraction line in glass, at the same time reducing the transfer volume, Fig. 4.2. This greatly improved reproducibility both for the water and gypsum standards. A comparative study of water reacted with zinc in closed vessels and water reduced over hot uranium at 800 °C was done. Subsequent collection of the evolved hydrogen demonstrated an isotopic difference between the two methods. δD values for the zinc reaction were more depleted in D, but for each method the differences between standards were constant, Table 4.2. The reason for this difference remains unanswered and will require further study.

Capillary tubes containing the standard waters were also tried but it was found that an equivalent reproducibility was achieved by injecting water directly onto the zinc under dry N_2 gas.

Two gypsum standards were tested, one showing non-reproducibility, was found to contain very tiny blebs of hematite after study under the microscope and thus was not used further. No appreciable difference was encountered on comparing results obtained from coarse and fine grained gypsum standards.

Table 4.1 Comparison of δD results obtained by spiking
S.M.O.W. onto zinc under dry air and dry
nitrogen

	Dry air ‰	Dry nitrogen ‰
S.M.O.W.	-5.0	-5.7
	-2.2	-8.0
	-5.0	-7.9
	-6.8	-6.6
	+0.7	-8.1
	-4.8	-8.0
	+0.2	
	+0.1	
	-0.2	
	-0.1	
	-0.2	
Average	-2.1	-7.4
Std. Deviation	$\pm 3\%$	$\pm 1\%$

Fig.4.2 Glass vacuum line extension used for extraction of inclusion fluids for δD analysis.

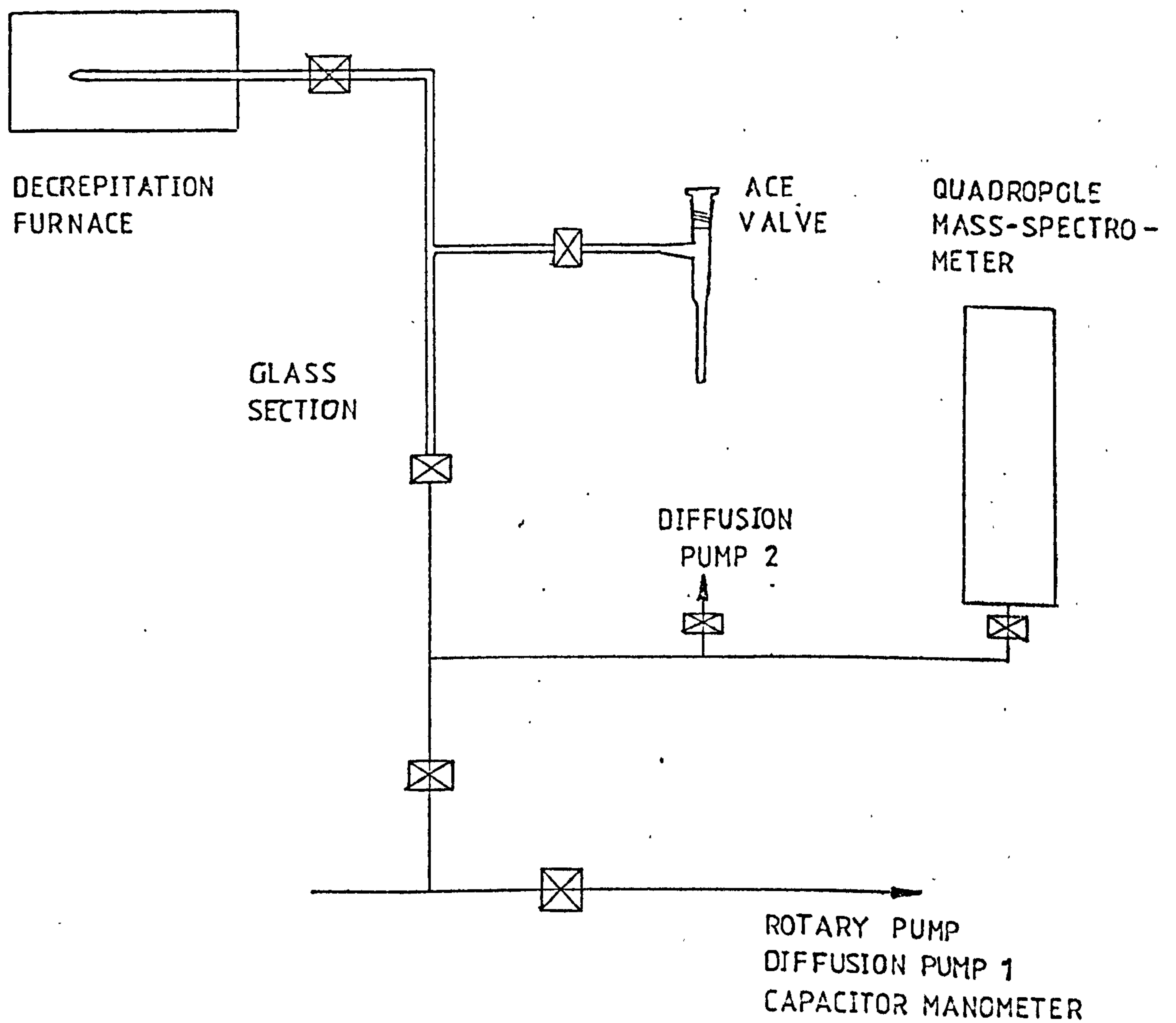


Table 4.2 Comparison of results obtained by direct injection of
water onto zinc, conversion through the uranium furnace
and transfer through the glass line

Standard Water	Injection . into Ace Valve (under dry air)	Uranium Furnace	Transfer through glass line
S.M.O.W.	+0.2 +0.1 -0.2 -0.1	-0.7 -2.1	+1.4
Average	0.0	-1.4	+1.4
S.L.A.P.	-397.5 -396.6 -400.8	-394.5 -390.8	-392.3 -395.6
Average	-398.3	-392.7	-394.0
G.I.S.P. 90	-183.9	-176.5	-182.8
Average	-183.9	-176.5	-182.8
S.L.A.P. - S.M.O.W.	-398.3	-391.3	-395.4
G.I.S.P. 90 - S.M.O.W.	-183.9	-175.1	-184.2

Reproducibility for the standards injected under dry nitrogen gas and transferred through the glass line to a glass breakseal or reaction vessel with vacuum stopcock, containing zinc granules, was checked. Results showed the reproducibility to be good, ~~Table 4.2~~. Direct injection of the standard water onto zinc under dry nitrogen gas was also tested and gave similar results of good reproducibility. Thus for ease of standard preparation the direct injection method was resorted to. Having checked the glass extraction line by use of standards, samples were then run in a similar manner to the gypsum standards.

4.6. Mass Spectrometer Optimisation procedures for D/H analysis

The mass spectrometer used for D/H analysis was a Siamese micromass MM602C with an on line calculator and chart recorder. This is a double collector mass spectrometer used for collecting positive ions of mass 2, and 3 for calculation of the 3:2, DH:H₂ ratio. Optimisation was carried out to obtain maximum sensitivity and stability of the ion beam, during the mass analysis.

The magnet was employed to bend the ion beam and hence acquire good sensitivities. Source parameters such as accelerator voltage, electron energy, ion repeller and high potential (ΔH) were altered to reduce the effect of H₃⁺ interference due to the reaction:



The main aim being to acquire the highest major peak value for the highest DH/H₂ ratio. Runs were made with the sample and reference gases at the same pressure and major

peaks to ensure the same percentage contribution of H_3^+ to each gas.

Thus after optimisation of the mass spectrometer eight duplicate runs of both the reference gas and sample gas were obtained for use in the final δD calculation for each sample.

Corrections and calculations used to obtain the δD results are shown in Appendix 3.

4.7. Preparation of standards and samples for Oxygen isotope work

A bromine pentafluoride method was used for both quartz standards and samples, (Clayton and Mayeda, 1953). This involved the breakdown of quartz by the BrF_5 to release oxygen which was then converted to CO_2 for mass-spectrometer analysis.

The samples of quartz were cleaned and ground to -30# mesh grain size for use. Approximately 10 mg of sample were loaded into nickel reaction vessels, Fig. 4.3. and outgassed under vacuum at 250 °C for two hours.

A measured volume of BrF_5 was then added and the reaction was allowed to run at 550 °C for approximately ten hours. After completion, liquid nitrogen traps were placed over the vessels, to condense all gases except the oxygen released. Subsequently the oxygen from each vessel was passed over hot charcoal to produce CO_2 which was collected in pre-cleaned outgassed glass transfer vessels with vacuum stopcocks, Fig. 4.4. This vessel was then removed ready for analysis on the mass-spectrometer. Five samples and one standard being run at any one time.

Fig.4.3 Vacuum line for the extraction of oxygen from quartz for $\delta^{18}\text{O}$ analysis.

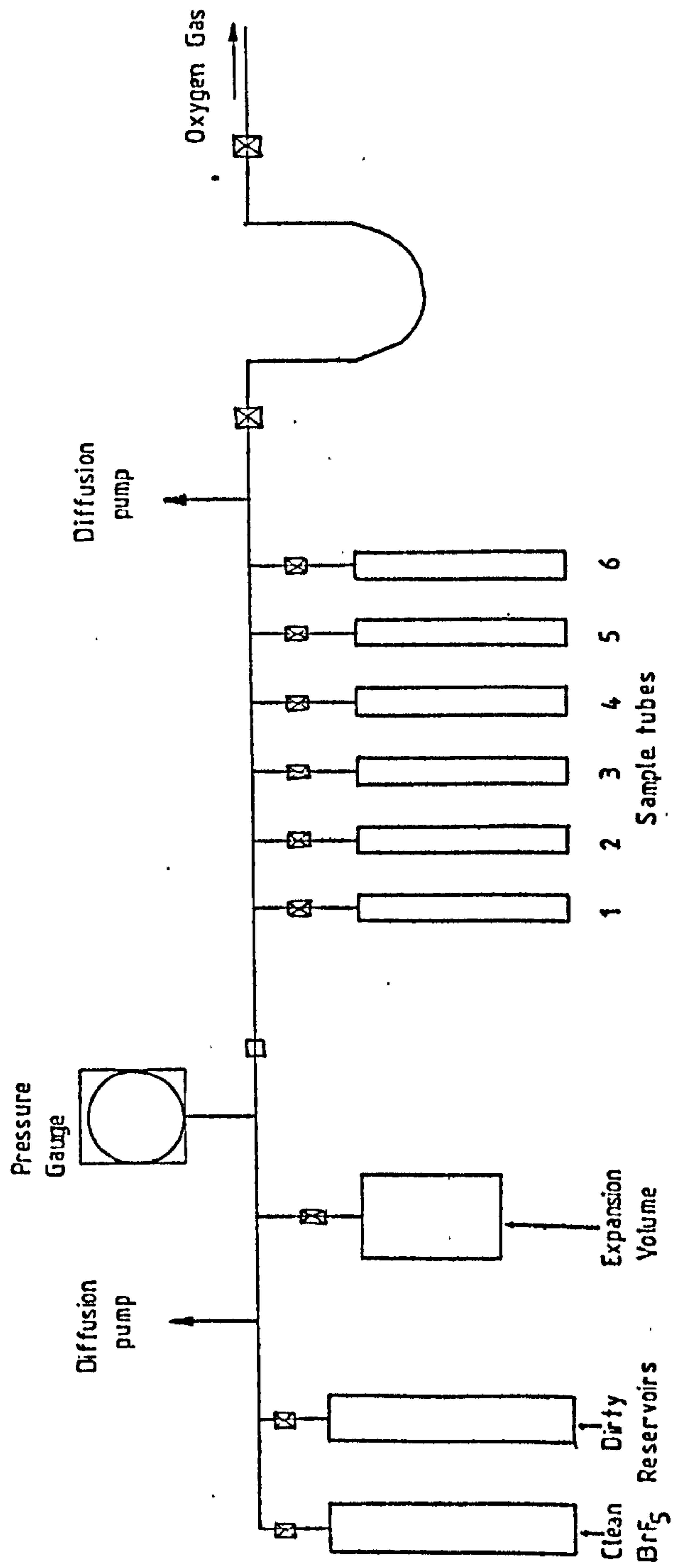
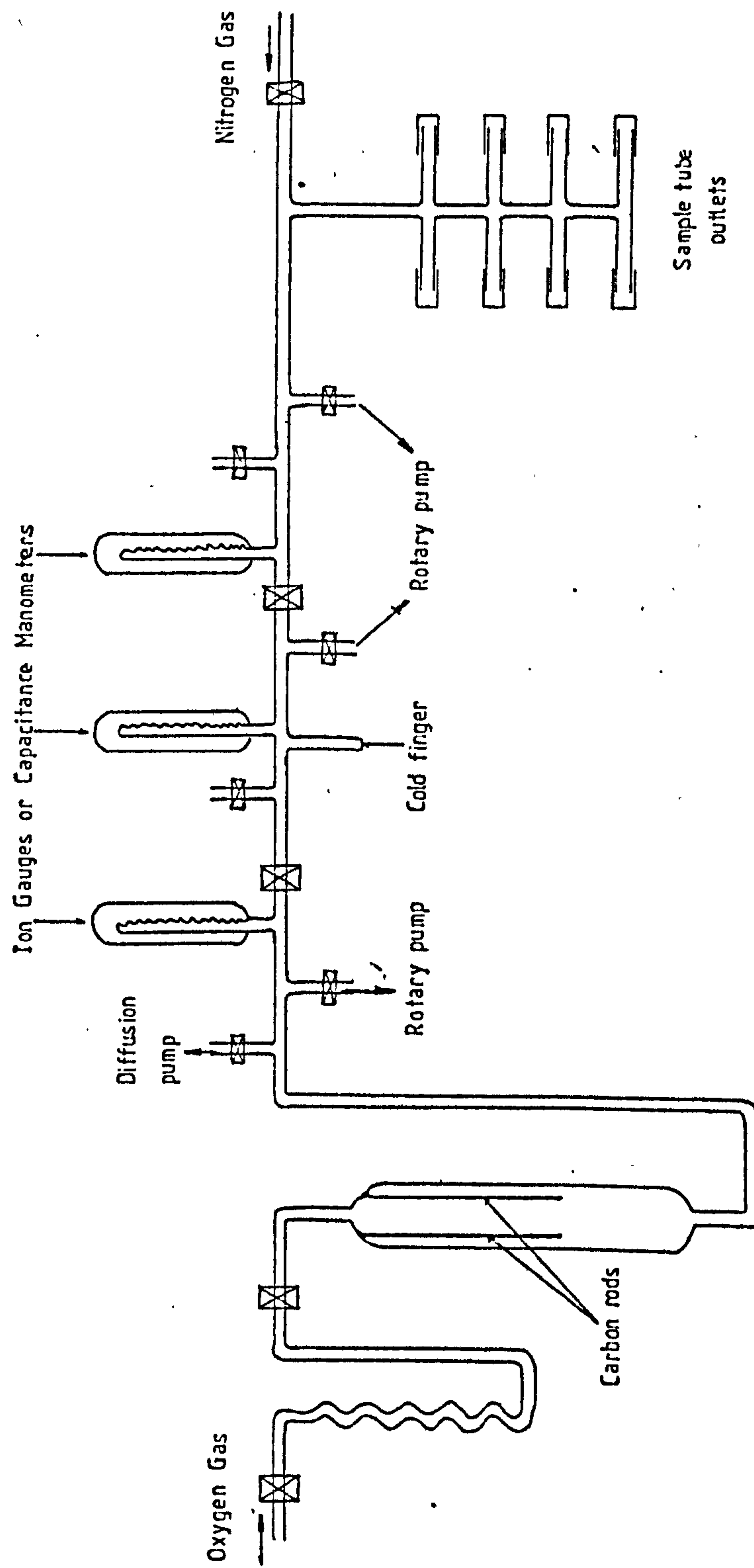


Fig.4.4 Vacuum line for the conversion of the extracted oxygen to carbon dioxide.



4.8. Mass Spectrometer Optimisation procedures for O^{18}/O^{16} analysis

The mass spectrometer used for these analyses was the micromass MI903 with an on-line calculator and chart recorder. This is a triple collecting mass spectrometer used for collecting positive ions of masses 44, 45 and 46, for calculation of the ratios 45:44 and 46:44. These two ratios are then used to calculate values for carbon $^{13}/^{12}$ and oxygen $^{18}/^{16}$, (Craig, 1957).

Optimisation involved finding the maximum peaks of masses 45 and 46 and maximum ratios 45/44 and 46/44. Alteration of the magnet, accelerating voltage and source parameters was employed to reach maximum optimisation. International standards used for these analyses were NBS-28, a quartz standard and PDB, a carbonate standard, which were then corrected to S.M.O.W.

Corrections necessary to derive the final values are given in Appendix 3.

4.9. Results of D/H and O^{18}/O^{16} analysis

Results of δD values for inclusion fluids from all the minerals studied are given in Appendix 5 with the chemical analyses. These results give the ranges of δD for the different minerals shown in Table 4.3. Oxygen isotopic analyses of quartz samples are given in Table 4.4. and Table 4.5 gives the barite values taken from Solomon, Rafter and Dunham, 1971.

Recent work has shown that the isotopic composition of a water is affected by salts dissolved in it (Taube, 1954; Sofer and Gat, 1972). Sofer and Gat's (1972), work provided an equation for correction of the oxygen isotope values derived from the minerals, Appendix 3. They found that concentrated salt solutions tended to produce an increase in the $\delta^{18}O$

Table 4.3 δD ranges of the Northern

Pennine Minerals

Mineral	δD range ‰		
Fluorite	-46.0	to	+8.0
Quartz	-51.0	to	-28.0
Barite	-106.0	to	-48.0
Derbyshire Fluorite	-100.0	to	-8.0

Table 4.4 $\delta^{18}\text{O}$ and δD values obtained
for quartz samples

Sample	$\delta^{18}\text{O} \text{ ‰}$	$\delta\text{D} \text{ ‰}$
414	-1.87	-37.0
418	+4.25	-29.0
419	+0.49	-34.0
424	-1.97	-28.0
R101.1	+2.43	-43.0
R102.3	+0.25	-51.0
1018	+2.14	-41.0
6480	+0.20	-37.0
6666	-3.09	-50.0

$\delta^{18}\text{O}$ values have been corrected for
Quartz-water fractionation and salinity
affects.

Table 4.5 $\delta^{18}\text{O}$ and δD values obtained
for barite samples

Sample	$\delta^{18}\text{O} \text{ ‰}$	$\delta\text{D} \text{ ‰}$
R20	+7.73	-67.0
R120	-1.66	-49.0
R121	-0.68	-56.0
R123	-1.17	-59.0
6476	+3.38	-58.0
6477	-1.39	-49.0
6522	+3.47	-48.0
20725	+3.85	-59.0
20839	-4.91	-106.0

compared to that of pure water. The effect of Ca, Mg and K salt concentrations was marked, but that of sodium seemed negligible.

All $\delta^{18}\text{O}$ values from quartz samples were therefore corrected accordingly using previously measured chemical compositions and homogenisation temperatures to obtain the final results shown in Table 4.4.

The barite hand specimens used by Solomon, Rafter and Dunham were not available for further temperature and chemical work, but samples from the same deposits were analysed to obtain rough estimates of the approximate chemical composition and homogenisation temperatures of the fluid inclusions. The barite $\delta^{18}\text{O}$ values obtained were thus converted to equivalent water values (Kusakabe and Robinson, 1977) and corrected for salt effects, Appendix 3, to obtain the results in Table 4.5.

Salinity effects on the δD values are probably similar to those on $\delta^{18}\text{O}$ but no work has at present been done on this subject.

Further discussion of the interpretation of these results is given elsewhere.

4.10. Strontium Isotope Work

Strontium isotope studies have three main uses. The first, radiometric dating, is used by many workers for studying co-magmatic suites of rocks. The second utilises strontium as a tracer of the magmatic rocks related to ore deposits, whilst the third uses the isotopic composition of the strontium in the ore minerals themselves, to determine the source of the strontium. (Hedge, 1974). Because strontium occurs in important hydrothermal minerals such as fluorite, calcite and barite, where it replaces either Ca or Ba in the crystal lattice it can be used as a geochemical tracer for these elements, (Reesman, 1963). Therefore both host rocks and minerals should be measured to provide a satisfactory comparison.

Strontium isotope variations are due to the radioactive decay of Rb^{87} to Sr^{87} and thus it is necessary to measure the Rb/Sr ratio in a sample and correct the measured $^{87}\text{Sr}/^{86}\text{Sr}$ for this decay. This ratio is normally measured by X-ray fluorescence analysis (Turek et al., 1972).

The primordial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the earth is estimated to have been 0.699 but this has now risen to 0.703 in modern mantle derived rocks, (Hedge, 1974). Crustal rocks however generally have a Rb/Sr ratio one order higher than mantle rocks and thus their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increases at a higher rate than the associated mantle rocks.

Very little work has been carried out on mineral deposits, most work being directed to radiometric dating. Some work has however been carried out on sedimentary carbonate rocks and calcareous fossils, to determine the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic variation for sea-water through Phanerozoic and Cenozoic time.

(Peterman et al., 1970; Dasch et al., 1971; Veizer and Compston, 1974; Tremba et al., 1975). Other work has been carried out on formation waters and oilfield brines, (Chaudhuri, 1978; Sunwall and Pushkar, 1979; Sass and Starinsky, 1979).

4.11. Aim

The aim of the present work was to use strontium isotopes as a tracer for Ca, in the fluorite mineralisation and its host rocks. Though Sr^{2+} (1.13Å) has a greater ionic radius than Ca^{2+} (0.99 Å), and thus substitutes for Ca only in 8-fold co-ordinated lattice positions the substitution is sufficient to permit the use of strontium as a tracer.

4.12. Sample preparation of the host rocks

As representative samples of the host rocks to the mineralisation, fresh samples of limestone and shale were obtained from the Rookhope Borehole core. The Weardale Granite having previously been analysed by Holland and Lambert, (1972).

The rocks were initially prepared by cleaning in water, drying and then breaking into 5 cm squares using a rock splitter. Further crushing to obtain chips in the order of 2 mm diameter was carried out with a jaw crusher. An alumina disc grinder was then employed to reduce the sample to a mesh size of 30# to 60 # . Finally a terna was used to produce powders of -200 microns grain size.

For x-ray fluorescence analysis 20 grams of the powder was mixed with 3 ml of 5% noviol solution (Poly vinol alcohol) and pressed in dies at 15 tons per sq. inch to produce pellets. After drying naturally these pellets were ready for analysis.

To obtain strontium in solution, for strontium isotopic

analysis, free from rubidium and with as low calcium content as possible ion exchange columns, containing dowex 50 resin, 8% cross linked, were used. For limestone samples, 0.25 grams of sample were placed in a beaker with 10 ml of ultra-pure deionised water. 6N hydrochloric acid was added dropwise to the solution and when effervescence had stopped one or two more drops were added to ensure complete dissolution of the sample. The solution was then evaporated to dryness. For shale samples, 0.25 grams of sample were dissolved in 5 ml of concentrated nitric acid and 10 ml of concentrated hydrofluoric acid. After warming to complete dissolution, the solution was evaporated to dryness. Both shales and limestone were then taken up in 5 ml of 2.5 M HCl before being centrifuged. One ml aliquots of the solution were passed through the columns and collected. The strontium elutant was then reloaded onto the column for a second pass to remove Ca. The samples obtained were evaporated to dryness, ready for mass spectrometric analysis.

4.13. Sample preparation of the fluorite

The procedure for fluorite dissolution involved a boric acid/6 N HCl dissolution. (1 g : 100 ml; boric acid : 6 N HCl). (Dolezal et al., 1968).

The fluorite samples, as cleaned chips, were weighed out in 1 gram quantities into pre-cleaned glass beakers, to which 20 ml of the boric-HCl acid solution, was added. After warming for $\frac{1}{2}$ hour the solution was discarded and the chips washed and dried. Contaminants from the fluorite surface were thus kept to a minimum by removal of the outer layer of fluorite. A further 20 ml of acid solution was then poured over the reweighed chips and warmed for $2\frac{1}{2}$ hours. This solution was decanted into clean

beakers with washings and evaporated to dryness. The procedure produced between 0.6 and 0.8 grams of dissolved fluorite in the solution, found by weighing the fluorite chips prior to and after the second acid dissolution.

The evaporated aliquot was taken up in 10 ml of 6 N HCl, evaporated to dryness, redissolved in 5 ml of 2.5 M HCl and centrifuged. One ml of the solution was then loaded onto the prepared ion exchange columns to remove Ca. Only one pass, of the solutions, through the exchange columns was necessary as the deposit left after evaporating the elutant to dryness indicated that the calcium content was low.

Fluorites were also checked by x-ray fluorescence the procedure being similar to that of the host rocks after thorough grinding of the sample to -200 μ microns grain size.

4.14. Analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr

Strontium isotope compositions ($\text{Sr}^{87}/\text{Sr}^{86}$) were measured on a Micromass MM30 solid source mass spectrometer, with an on line calculator. The strontium ion beam was produced from a single tantalum filament loaded with aqueous sample solution and ortho-phosphoric acid.

The sample solution was made by addition of 20 μ l of ultra-pure deionised water to the evaporated sample. To this was added one drop of orthophosphoric acid.

Five samples were run on the above system together with the Eimer and Amend Strontium isotope standard. The latter gave $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70803 ± 0.00004 (2 std. err.) for the MM30; (Rundle, 1979).

For analysis of Rb/Sr ratios standard x-ray fluorescence

methods were used. Whole rock and fluorite sample pellets were run on a Phillips PW/450 automatic x-ray fluorescence spectrometer. The Rb and Sr concentrations were calculated using the Mo Compton scatter peak as a measure of the mass absorption coefficient. (Turek et al., 1977). The Rb/Sr work was carried out to correct for the decay of ^{87}Rb to ^{86}Sr .

The standard used in the analysis was GSP-1. The Rb/Sr weight ratio obtained was then converted to the $^{87}\text{Rb}/^{86}\text{Sr}$ atomic ratio by the equation

$$\frac{^{87}\text{Rb}}{^{86}\text{Sr}} = \left[\frac{\text{Rb}}{\text{Sr}} \right] (0.27835) \left(9.4318 + \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)$$

(Appendix 3 gives the derivation), (Brooks and Derbyshire, pers. comm.).

An isochron plot was then made by plotting $\text{Rb}^{87}/\text{Sr}^{86}$ against $^{87}\text{Sr}/^{86}\text{Sr}$, Fig. 4.5.

4.15. Results

Mass spectrometer results of $^{87}\text{Sr}/^{86}\text{Sr}$ were generally good with standard deviations of runs in the range .00011 to .00041 and two standard errors of the runs in the range .00004 to .00022, Table 4.6.

The fluorite samples were only run once because they gave low standard deviations and 2 std. errors. For each sample 20-50 measurements were taken to calculate the final ratio value.

Some of the whole rock sample runs were aborted before the desired number of runs were completed due to beam instability. These were therefore repeated and the measurements obtained were added to previous good results to achieve between 15 and 30 runs

Fig.4.5 Isochron plot of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope data obtained for the host rocks of the Northern

Pennine mineralisation.

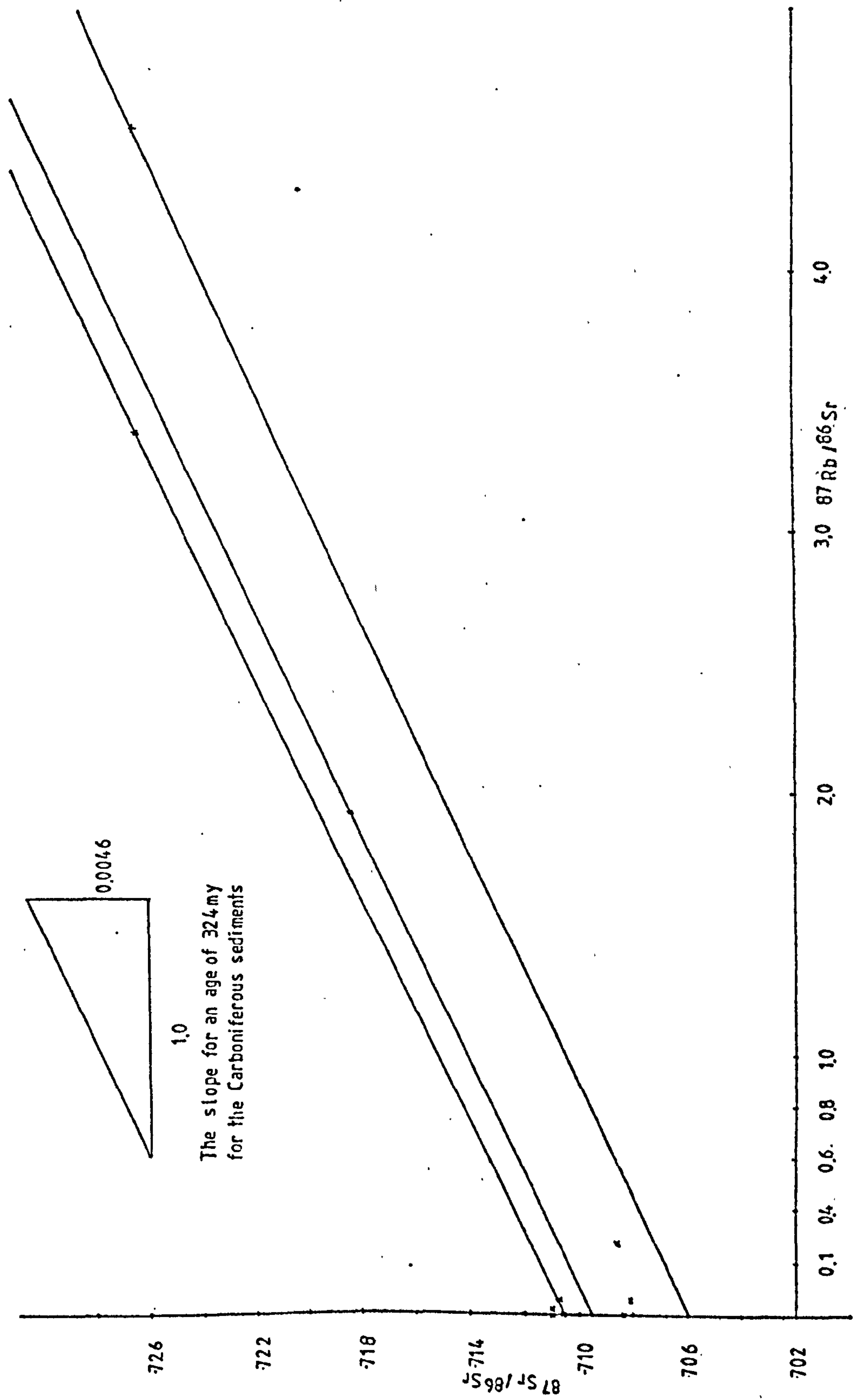


Table 4.6 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope results

Sample	Location	$^{87}\text{Sr}/^{86}\text{Sr}$	Std. Deviation	2 std. error
<i>Fluorite</i>				
165	Red Vn.	.71117	.00023	.00009
243	Wolfeleugh New Vn.	.71095	.00017	.00007
244	Wolfeleugh New Vn.	.71109	.00021	.00014
263(1)	Wolfeleugh Old Vn.	.71114	.00013	.00006
310	Greencleugh Vn.	.71147	.00022	.00013
316	Greencleugh Vn.	.71120	.00026	.00008
442	Groverake Vn.	.71122	.00015	.00006
451	Groverake Vn.	.71084	.00026	.00015
467	North Fulwood Vn.	.71111	.00016	.00006
<i>Host Rocks.</i>				
R108	Melmerby Scar Lst. 1200'	.71061	.00016	.00006
		.71065	.00017	.00006
R109	Melmerby Scar Lst- breccia. 1170'	.70855	.00012	.00005
		.70860	.00011	.00004
R110	Mudstone. 1000'	.71836	.00025	.00010
R113	Jew Limestone 686'	.70807	.00012	.00005
		.70798	.00018	.00012
R114	Scar Lst. 478'	.70826	.00016	.00006
R115	Shale. 436'	.72635	.00036	.00009
R117	Four Fathom Lst. 200'	.70828	.00011	.00004
		.70827	.00012	.00007
R118	Shale. 112'	.72623	.00041	.00022

All whole rock samples were obtained from the Rookhope Borehole.

for the final ratio value calculation. The limestones tended to give better runs than the shales. The shales also gave higher $^{87}\text{Sr}/^{86}\text{Sr}$ values due to the contribution of radiogenic strontium⁸⁶.

To correct for radiogenic Sr^{86} , the $\text{Rb}^{87}/\text{Sr}^{86}$ ratio was used, Table 4.7. By plotting $^{87}\text{Rb}/^{86}\text{Sr}$ against $^{87}\text{Sr}/^{86}\text{Sr}$ isochrons could be fitted to the points assuming an age for the rocks of 324 myrs. (Lower Carboniferous period). The isochrons were drawn using the slope from the following equation. (Faure and Powell, 1972; Faure, 1977; Steiger and Jager, 1977).

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}}_{\text{pres}} = \frac{^{87}\text{Sr}}{^{86}\text{Sr}}_{\text{orig}} + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda t} - 1)$$

where t is the age of the sample and $\lambda = 1.42 \times 10^{-11}$.

Only the shale values were corrected for addition of radiogenic strontium as all other samples had negligible rubidium concentrations. The ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the different samples are given in Table 4.8.

Radiogenic dating previously carried out on the Weardale Granite provides present day $^{87}\text{Sr}/^{86}\text{Sr}$ values of between 0.7432 and 0.7862 and an initial ratio of 0.7060. (Lambert and Holland, 1972). From these results it is possible to calculate the isotopic composition of the granite 324 myrs. ago Fig. 4.6. This gives an average value of 0.7190 for the range of values, see Table 4.8, for comparison with present work.

Table 4.7 $^{87}\text{Rb}/^{86}\text{Sr}$ Isotope results

<u>Sample</u>	<u>Rb/Sr weight ratio</u>	<u>$^{87}\text{Rb}/^{86}\text{Sr}$</u>
243	.00733	.02069
244	.00067	.00189
263(1)	.00417	.01177
310	.00347	.00980
316	.00294	.00830
442	.00303	.00855
451	.01578	.04455
467	.00148	.00418
R108	.00104	.00294
R109	.09477	.26750
R110	.67578	1.90920
R113	.01910	.05391
R114	.00689	.01945
R115	1.19819	3.38792
R117	.00077	0.00217
R118	1.61323	4.56137

Table 4.8 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ranges for the minerals and rocks
from the Northern Pennines

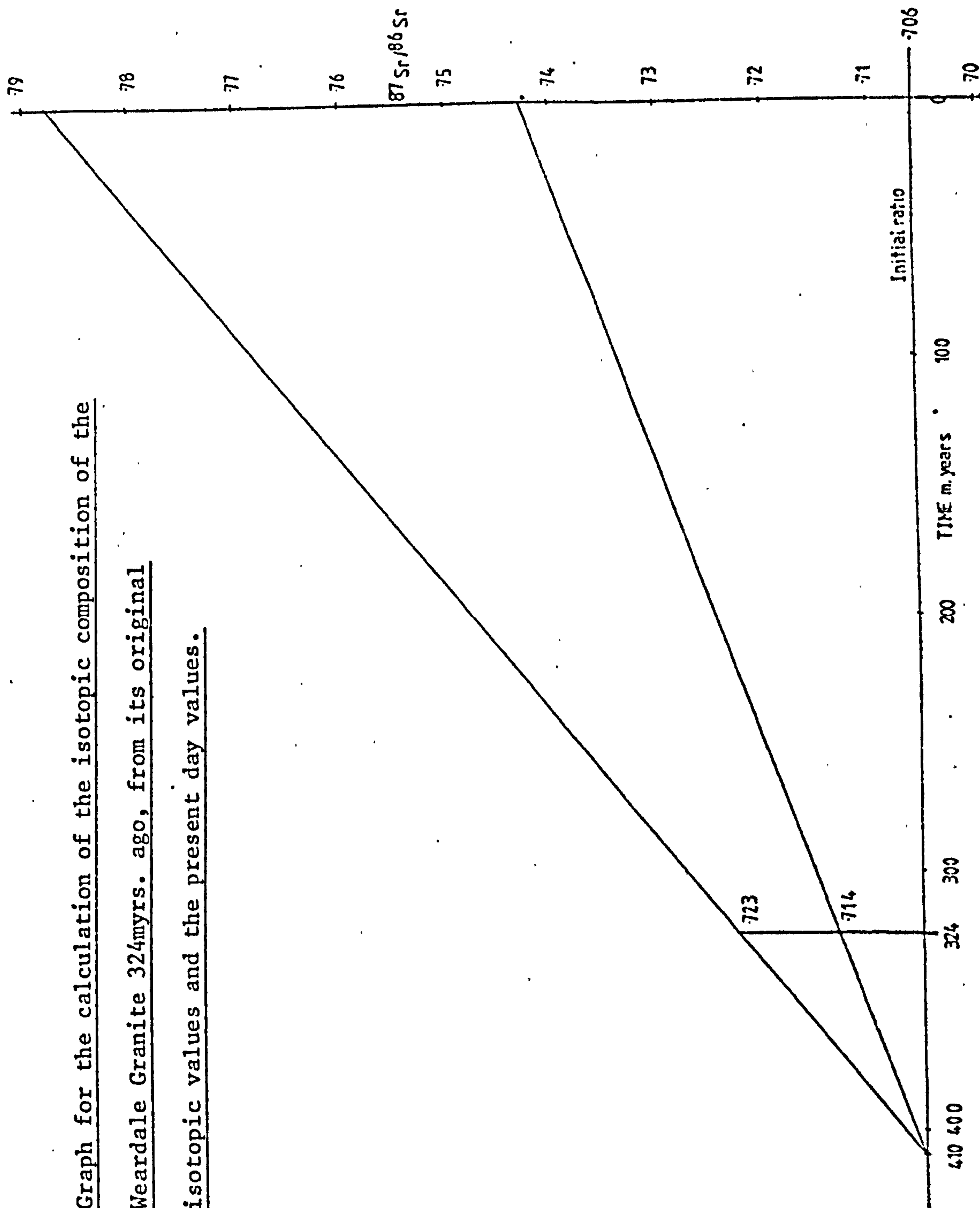
Sample	$^{87}\text{Sr}/^{86}\text{Sr}$
Fluorite	.71084 - .71147
Limestone	.70798 - .71061
Shale	.7060 - .7106
Weardale Granite	.714 - .723

Where the shale range is derived from fig. 4.5
and the Weardale granite range from fig. 4.6.

Fig.4.6 Graph for the calculation of the isotopic composition of the

Weardale Granite 324myrs. ago, from its original

isotopic values and the present day values.



CHAPTER FIVE

Mineralisation in the Northern Pennines

5.10. Introduction

The present work was done to investigate the mechanisms of formation of the minerals of the Northern Pennine Orefield.

Hydrogen isotope work on the inclusion fluids and oxygen isotope work on quartz and barite are used to provide information for interpretation of the origin and evolution of the ore fluid. Strontium isotope tracer work and sulphur isotope data from Solomon, Rafter and Dunham, (1971), are also incorporated into the provenance study.

The gas and chemical composition of the inclusion fluids are used to obtain pH values for the solution. These are then used with available solubility data in pH-log fO_2 plots to investigate how the ions are transported in solution and the cause of their deposition.

5.20. Origins of the fluids

Data obtained on strontium isotope ratios in the host rocks and the fluorite mineralisation, show that the Carboniferous limestone and shales have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of .70738 to .71061 and .7060 to .7106 respectively. The limestone values in particular, probably represent the seawater values of the Carboniferous period, but both sets compare well with available data from Peterman et al. (1970), and Viezer and Compston (1974), Table 5.1. Shales, composed largely of detrital material, would normally have ratios higher than the range shown in Table 5.1, since they would generally

Table 5.1 Strontium isotope results and comparison with previous estimations of the sea water ratio

Present work: results

	$^{87}\text{Sr}/^{86}\text{Sr}$ range	Std. Deviation
Limestone	.70798 to .71061	± 0.00018
Shale	.7060 to .7106	± 0.00041
Granite	.714 to .723	-
Fluorite	.71084 to .71147	± 0.00026

Previous work: Strontium isotopic composition of sea water

Period	Peterman et al. (1970)	Veizer + Compston (1974)
Permian	.7072 to .7078	-
Carboniferous	.7075 to .7093	.7077 to .7085
Devonian	.7080	-

only assume a marine water ratio after high temperature (170-200 °C) alteration and dehydration, of montmorillonite to illite. According to Dasch (1969) and Perry et al. (1974), the strontium isotope ratios would then have become more homogeneous and acquired a range closer to that of seawater. The mean value of $^{87}\text{Sr}/^{86}\text{Sr}$ for the Weardale Granite is .719. Strontium isotope ratios in fluorite occupy the narrow range of .71084 to .71147, which is slightly above those of the limestones and shales but below that of the granite.

The above data suggest that the fluorite was deposited from a fluid which originated in marine sediments but which had not undergone complete lithification. Possible sources are the Lower Carboniferous sedimentary basins to the north, south and east of the Alston Block. In these basins the sequences of sandstones, shales and limestones are 2 to 4 times as thick as on the Alston Block, with thicknesses of 2,300 m to 4,000 m and 1,000 m to 1,300 m respectively, Fig. 5.1, Table 5.2.. The shales in the sequences are mainly composed of mixed-layer clay minerals, illite and chlorite, and thus any original montmorillonite must have been converted to these minerals. (Bott and Masson-Smith, 1957; Johnson, 1960; 1967; Bott 1967; Johnson and Marshall, 1971).

Investigation of the isotopes of hydrogen and oxygen was therefore undertaken in an attempt to further define the origins of the ore fluids. Fig. 5.2 shows plots of δD against $\delta^{18}\text{O}$ for fluids of different type. The meteoric water line originally defined by Craig (1951a) as

Fig.5.1 Cross section across the Northern Pennines from north to south.

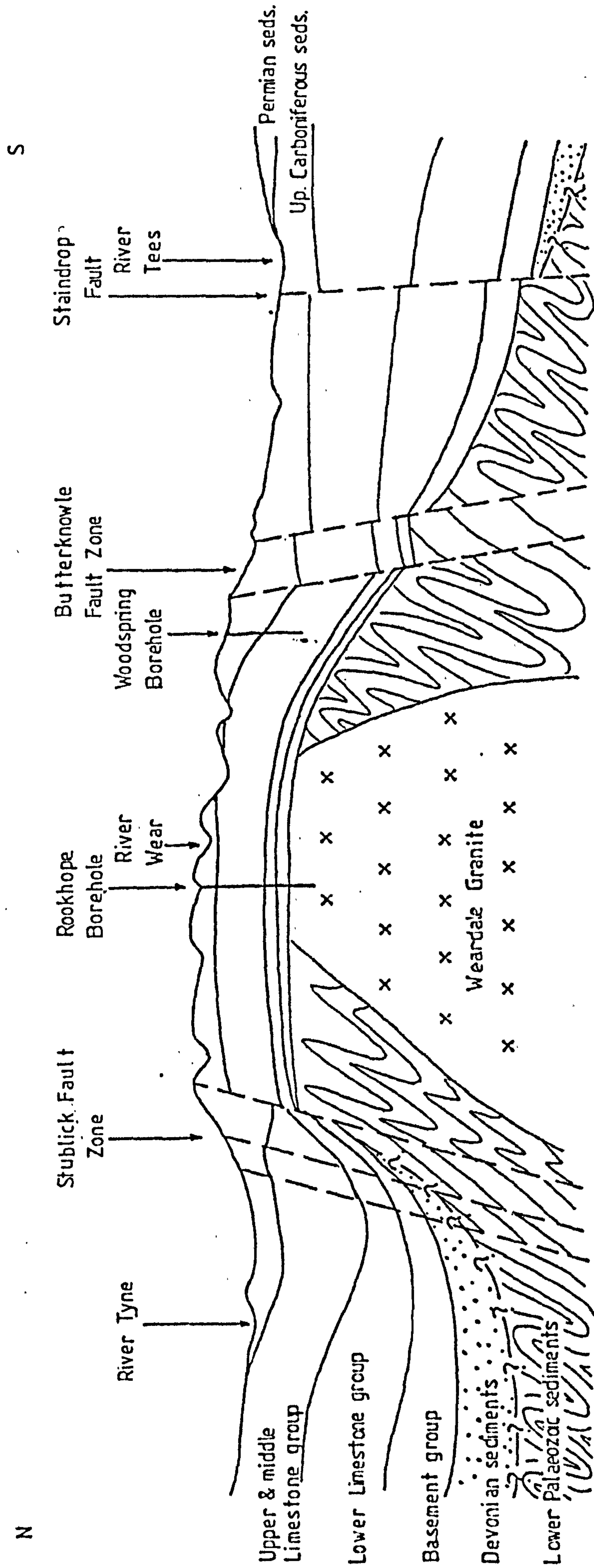


Table 5.2 Geology of the Alston block and the troughs to the north and south

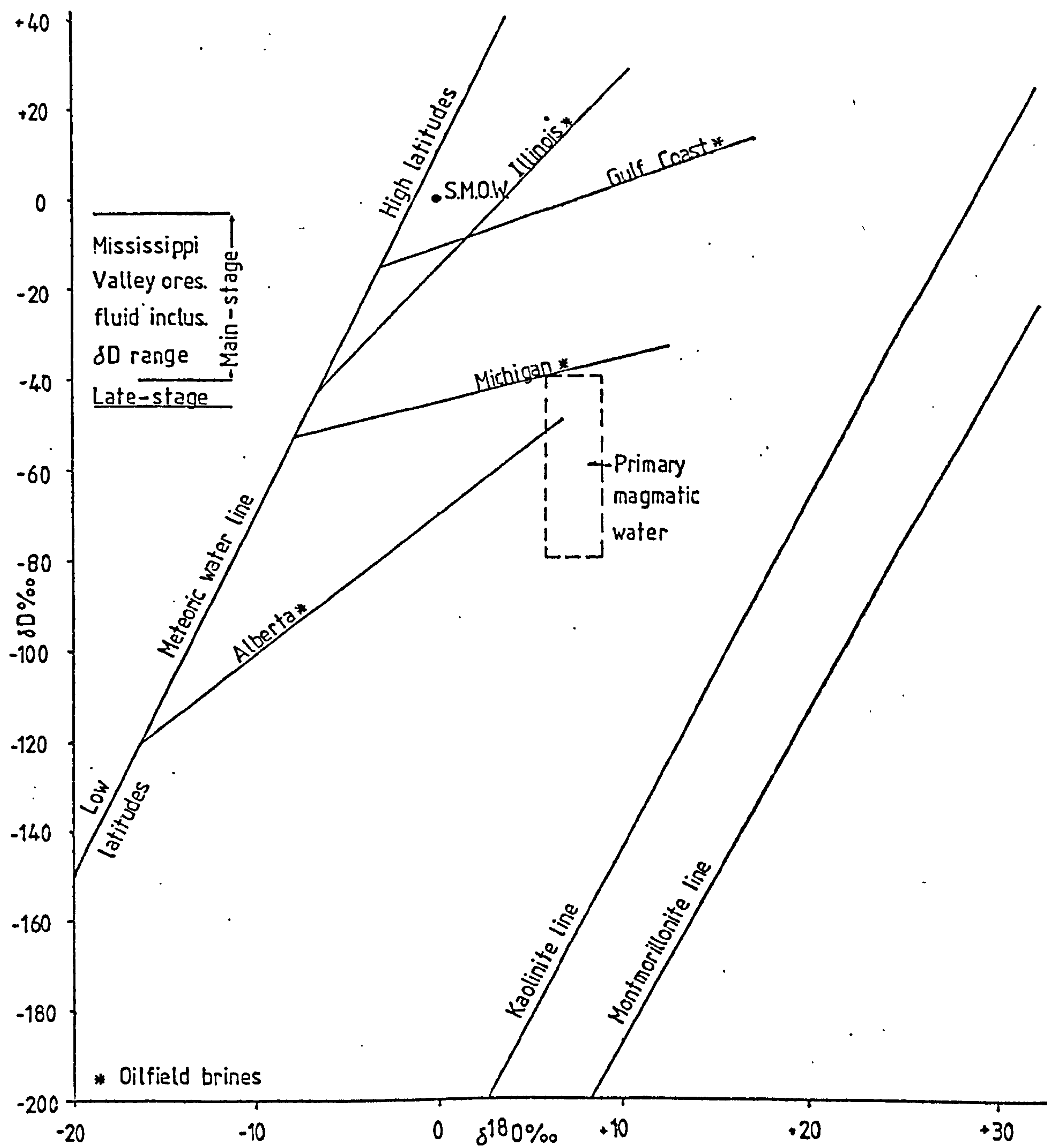
Northumberland Trough (N)			Alston block		Stainmore and N. Yorkshire trough(S)	
Stage	Thickness	Lithology	Thickness	Lithology	Thickness	Lithology
Permian	-	-	-	-	↑	Lower magnesian lime- stone, marl slate yellow sands ~~~~~ Millstone grit and coal measures
Upper Carboniferous	100 m ↑	Millstone grit and coal measures	80-100 m ↑	Millstone grit (if present)		
Lower Carboniferous	2,300 m -3,000 m	Upper, middle and lower Limestone facies:- Thin limes- tones, thick shales and sandstones. Cyclothermic sedi- ments.	700 m - 1,200 m	Upper Limestone facies:- mainly lime- stones and shales. Middle Limestone facies:- Cyclothermic sediments, thinner limestones.	4000 m	Upper and middle lime- stone facies:- Cyclo- thermic sediments, mainly shales and sand- stones. Lower Limestone facies:- sandstones and shales

Table 5.2 cont.

Stage	Thickness	Lithology	Thickness	Lithology	Thickness	Lithology
Lower Carboniferous	↓	Lower facies: greater amounts of shales. Basement Group:- yellow and grey shales.	↓	Lower Limestone facies:- mainly limestones and shales Basement group:- conglomerates, sandstones and shales.	↓	thin limestones. Basement Group:- basal conglomerates.
Devonian		Red sandstone		-		Red sandstone
Lower Palaeozoic		Ordovician and Silurian folded, metamorphic sediments.		Folded metamorphosed Ordovician and Silurian sediments.		Folded metamorphic Ordovician and Silurian sediments.

Fig.5.2 Plot of δD versus $\delta^{18}O$ for different types of fluids.

(Taylor,1974)

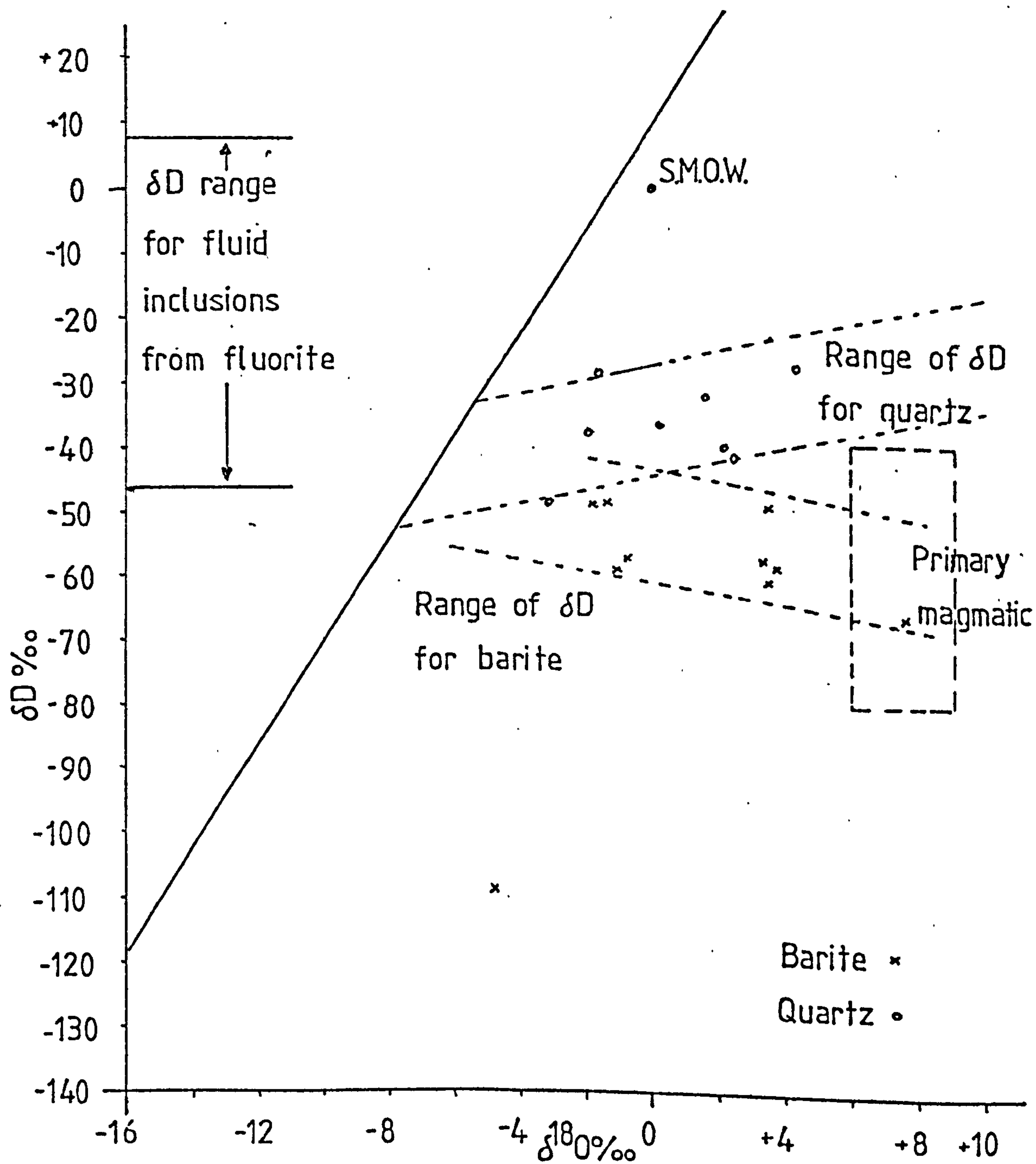


$\delta D = 8 \delta^{18}O + 10$, reflects the changes of δD and $\delta^{18}O$ due to atmospheric precipitation at differing latitudes. Latitudes between 0° (the equator) and 25° north or south have δD values between 0‰ and -30‰. Higher latitudes have more negative δD values. The altitude at which the precipitation falls may also produce a depletion of up to 20‰ in δD . (Lawrence and Taylor, 1971).

δD and $\delta^{18}O$ values for inclusion fluids from the Northern Pennines have been plotted on Fig. 5.3. Both δD and $\delta^{18}O$ values were obtained for quartz and barite but only δD values were measured for fluorite. The first impression from Fig. 5.3. is that quartz inclusion fluids were derived from a meteoric source with $\delta D = -35$ ‰. Barite inclusion fluids, on the other hand, seem to have been derived from mixing of magmatic water, with δD of -65‰, and meteoric water with δD of -43‰.

Meteoric water at the time of ore deposition is thought to have had a δD range of 0‰ to -15‰. This is derived from the suggestion made by Faller and Briden (1978) that the palaeolatitude of northern England at this time was between $15^\circ S$ and $12.5^\circ N$ of the equator. Sea water has a δD value of 0‰. Slightly more depleted δD values, up to -30‰, may have been produced in rainfall on the Caledonian mountains to the north of the Alston block and Northumberland Trough, due to altitude effects. However, the inclusion data include δD values that are too low for direct involvement of meteoric water and a different origin must be sought. Assuming an initial water composition of $\delta D = -15$ ‰ to 0‰ and $\delta^{18}O = -3$ ‰ to 0‰, a method for significant

Fig.5.3 Plot of δD versus $\delta^{18}O$ for the inclusion fluid
values obtained during the present work.

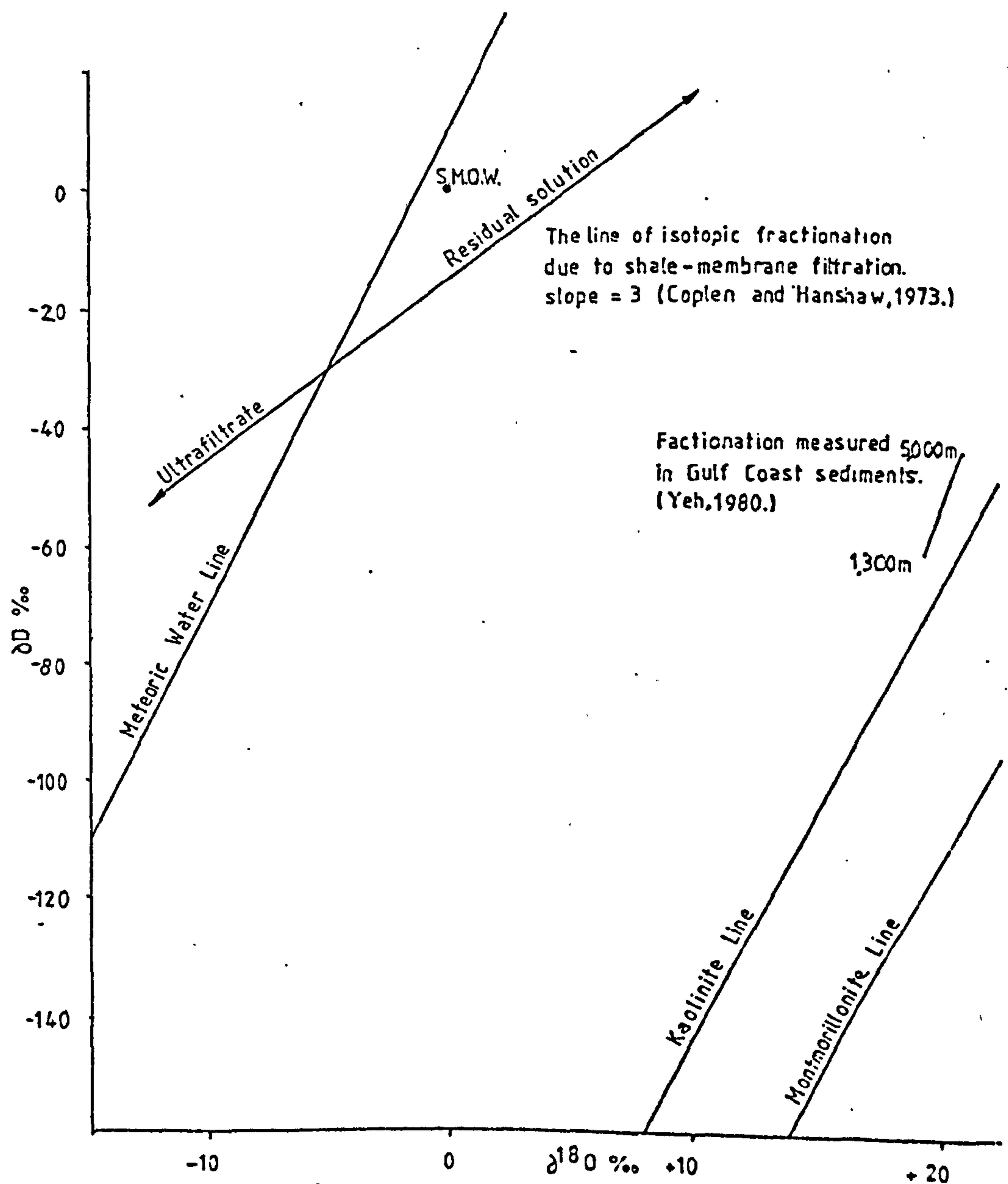


depletion of δD in the fluids is required to obtain the observed ranges. The data has a larger spread in δD than $\delta^{18}O$ which is unusual for simple water-rock interaction.

A process shown to produce greater depletion of deuterium than ^{18}O is the expulsion of fluids through semi-permeable membranes. (Coplen and Hanshaw, 1973; Yeh 1980). Coplen and Hanshaw's experimental work indicated an average fractionation of δD three times greater than that of $\delta^{18}O$, due to adsorption of water molecules onto clay minerals during passage through the membrane. They suggested that the extent of isotopic fractionation would be increased if the salinity of the fluids was high and the membranes were thicker. Hydraulic gradient changes were found to have little or no effect Coplen and Hanshaw (1973), also noted that considerable oxygen isotope exchange, between the fluid and rock, took place at temperatures above 50 °C. This was found to counteract the fractionation of oxygen isotopes due to ultrafiltration, Fig. 5.4.

Yeh, (1980) demonstrated an increase in δD with depth in Gulf Coast sediments. Over the depth interval from 5,000 m to 1,300 m the value of δD changed from -45‰ to -66‰ while $\delta^{18}O$ values only showed a change of 1 to 2‰. Thus as the pore water was expelled upwards it became more depleted in δD . Yeh proposed that the 20‰ fractionation in the hydrogen isotopes was due to membrane filtration, while the oxygen isotopes had undergone exchange with their surrounding rocks counteracting the fractionation effect. (Yeh and Savin, 1977). Ultrafiltration therefore seems a feasible process to obtain the ranges measured for inclusion fluids from the Northern

Fig.5.4 The isotopic fractionation that occurs to fluids which undergo membrane filtration, according to Coplen and Hanshaw (1973) and Yeh (1980).



Pennine ore minerals.

Thus, assuming a sedimentary origin for the ore fluids, their evolution involves three distinct phases of fluid production. They are:-

- 1) The release of 10-40% of the original pore fluid by the initial compaction process. This fluid is then lost to the surface.
- 2) The production of shale membranes which cause filtration and fractionation of pore fluids rising through them. Thus producing a second modified fluid at shallow depths above the membranes.
- 3) The third fluid is produced from dehydration coupled with chemical and physical alteration of montmorillonite to illite at depths greater than 2,600 m.. This would produce a further fluid at depth below the membranes, which could then mix with residual pore water from phase 2.

Initial compaction, to depths of about 1,300 m releases 10-15% of the pore water from sandstone and 30-40% of the pore water from shales. This is lost to the surface, or sediment-water interface.

Further compaction, and reduction in shale porosity to 35%, would result in the formation of semi-permeable membranes. Pore fluids released below these membranes pass upwards through them, and undergo fractionation. They become depleted in δD and $\delta^{18}O$, according to the trend determined by Coplen and Hanshaw (1973). At the same time water-rock interactions would produce oxygen isotope exchange, leading to enrichment of $\delta^{18}O$ in the fluids. The affects of both

trends can be resolved both for the residual pore water and for the filtered pore water, Fig. 5.5. The resolved trend for the filtered pore water will be similar to the trend shown by Yeh (1980), producing major δD depletions after passage through successive membranes. The overall affect on $\delta^{18}O$ will be minor. If the first fluid expelled by the process has an initial isotopic composition similar to sea water, its evolution might be along path (1a), as indicated in Fig. 5.5. The residual fluid would meanwhile change isotopic composition along path (1b). Further expulsion of pore fluids through the membrane must involve fluids with initial compositions lying along path (1b). A second stage could be illustrated in Fig. 5.5 by path (2a) for the filtered pore water, the residual fluid continuing to evolve along path (1b). Continuing expulsion of fluids through the membranes is reflected by paths (3a) and (4a). It is of course impossible to measure the extent of δD depletion along any of the paths (1a), (2a), etc. This will depend on the extent of ultrafiltration and hence on the number and thickness of the shale membranes through which the fluids have passed. These may increase with time, and thus it is possible that later ultrafiltrates, such as (4a), may be more depleted in δD than the earlier ones (1a), as indicated schematically in Fig. 5.5.

Fig. 5.5 assumes that the original pore fluid was sea water, but it is more likely that it contained some meteoric water. A compositional triangle can be drawn for the original pore fluid which will enclose the value of sea water, ($\delta D = 0\text{‰}$, $\delta^{18}O = 0\text{‰}$), and the compositional range of

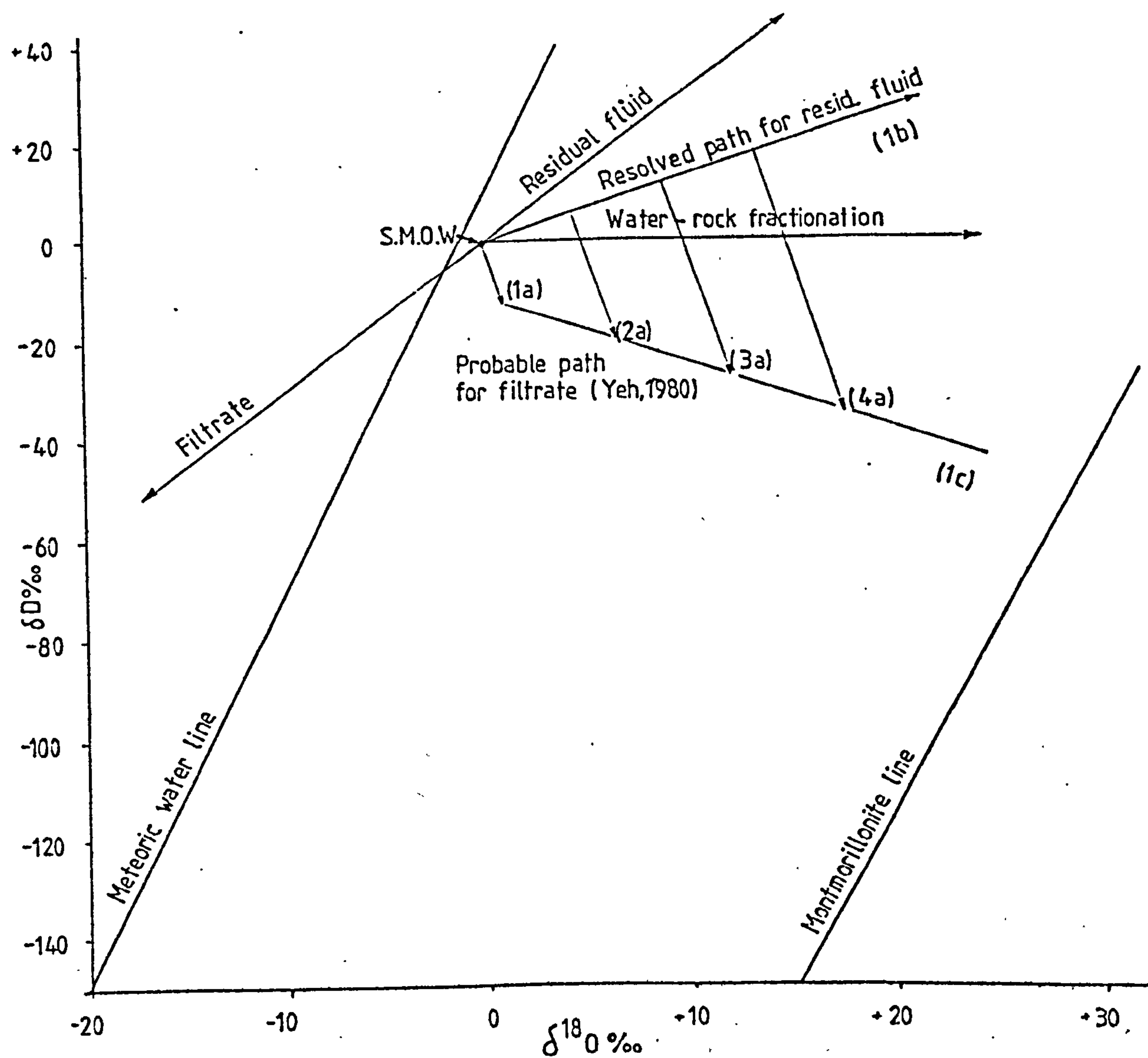


Fig.5.5 Application of the affect of membrane filtration on pore fluids to those from Carboniferous sediments undergoing compaction, assuming the original fluid to be sea water.

meteoric water, from $\delta D = 0$ to -15% with its equivalent $\delta^{18}O$ range. Fig. 5.6 shows the evolution of the mixed pore water as it undergoes membrane filtration. The resolved trends, $(1a^1)$ and $(1b^1)$, for the filtered and residual fluid were derived from an original pore fluid of $\delta D = -15\%$ (totally meteoric water). They were produced in a similar manner to those of Fig. 5.5. The original pore fluid could thus have two extremes in isotopic composition: one composed of sea water with a δD of 0% and the other composed of meteoric water with a δD of -15% . In most cases the original pore fluids would lie between these extremes and an equivalent range of isotopic compositions would be acquired by the resulting filtered and residual fluids. Fig. 5.6 shows the possible range for the deep seated residual pore fluids, bounded by $(1b)$ and $(1b^1)$. Similarly the filtered fluid would be bounded by the limits $(1c)$ and $(1c^1)$, as set by the lines $1a$ to $4a$ and $1a^1$ to $5a^1$. Figs. 5.5 and 5.6 are of course schematic in the sense that expulsion of fluids through the membrane is illustrated as a series of pulses. The process would in all probability, be a continuous one with both expelled and residual fluids evolving steadily with time. This process would thus generate a fluid at shallow depths with a very depleted range of δD .

At depths of greater than 2,600 m and at temperatures between 150 and 200 $^{\circ}C$ a fluid is released from the breakdown and conversion of montmorillonite to illite. On mixing this with the residual pore fluid a third resulting fluid of variable isotopic composition is formed. The water released by the montmorillonite is likely to be fractionated compared

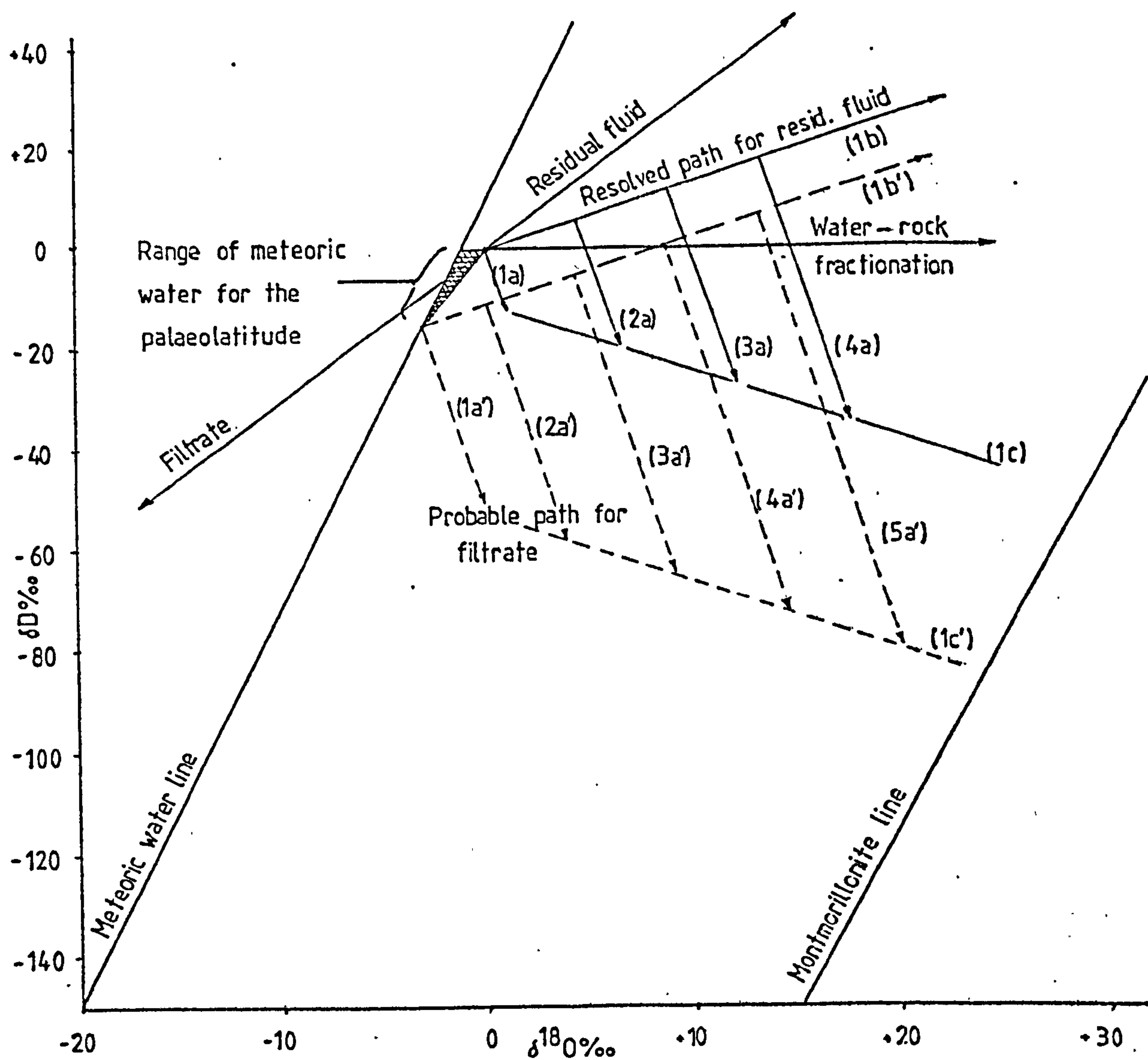


Fig.5.6 The affect of membrane filtration on the above pore fluids
assuming they had a variable original composition between
sea water and meteoric water of $\delta D = -15\%$.

to the residual pore water, and will probably have a composition along the montmorillonite line derived by Savin and Epstein, (1970). Fig. 5.7. shows the range of isotopic compositions resulting from mixing of the residual pore fluid within the range bounded by (1b) and (1b¹), with the water derived from dehydration of montmorillonite, (e.g. V and Z). The isotopic composition obtained from the mixture, using residual pore fluids derived from seawater ($\delta D = 0\%$), will depend on the proportion of each fluid and will lie within the triangular zone defined by S.M.O.W., Y and Z. With the residual pore fluid derived from meteoric water, ($\delta D = -15\%$) a similar triangular zone, V, W, and X, can be drawn. Thus the fluid resulting from a 1:4 mixture of dehydration water to residual pore fluid lies between the limits (1d) and (1d¹) which depend on whether the original pore fluid was sea water or meteoric water.

These limits indicate the probable ranges of δD and $\delta^{18}O$ for a solution generated at depth by this process. They are similar to those analysed in the fluorite and quartz inclusions.

Graf et al., (1966) have shown that selective ion filtration occurs when solutions pass through a charged membrane. This affect was thus studied with regard to the possible changes in chemical composition of the original fluid.

Initial compaction of the sediments released pore fluids which were lost to the surface. Further compaction initiated membrane filtration, which produced a segregation of elements between the residual fluid and the filtered fluid, Fig 5.8. Neutral species and small cations would pass through

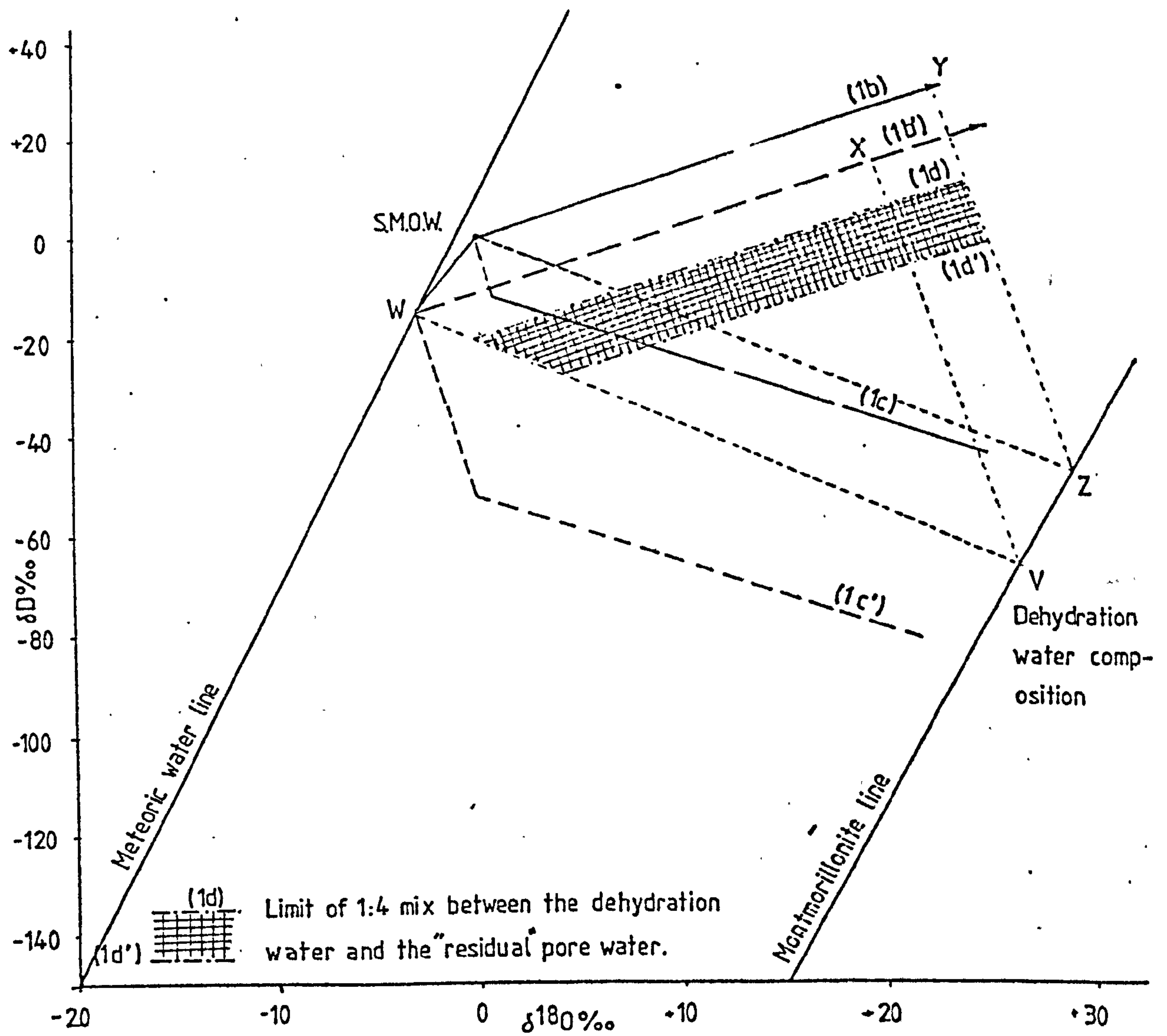
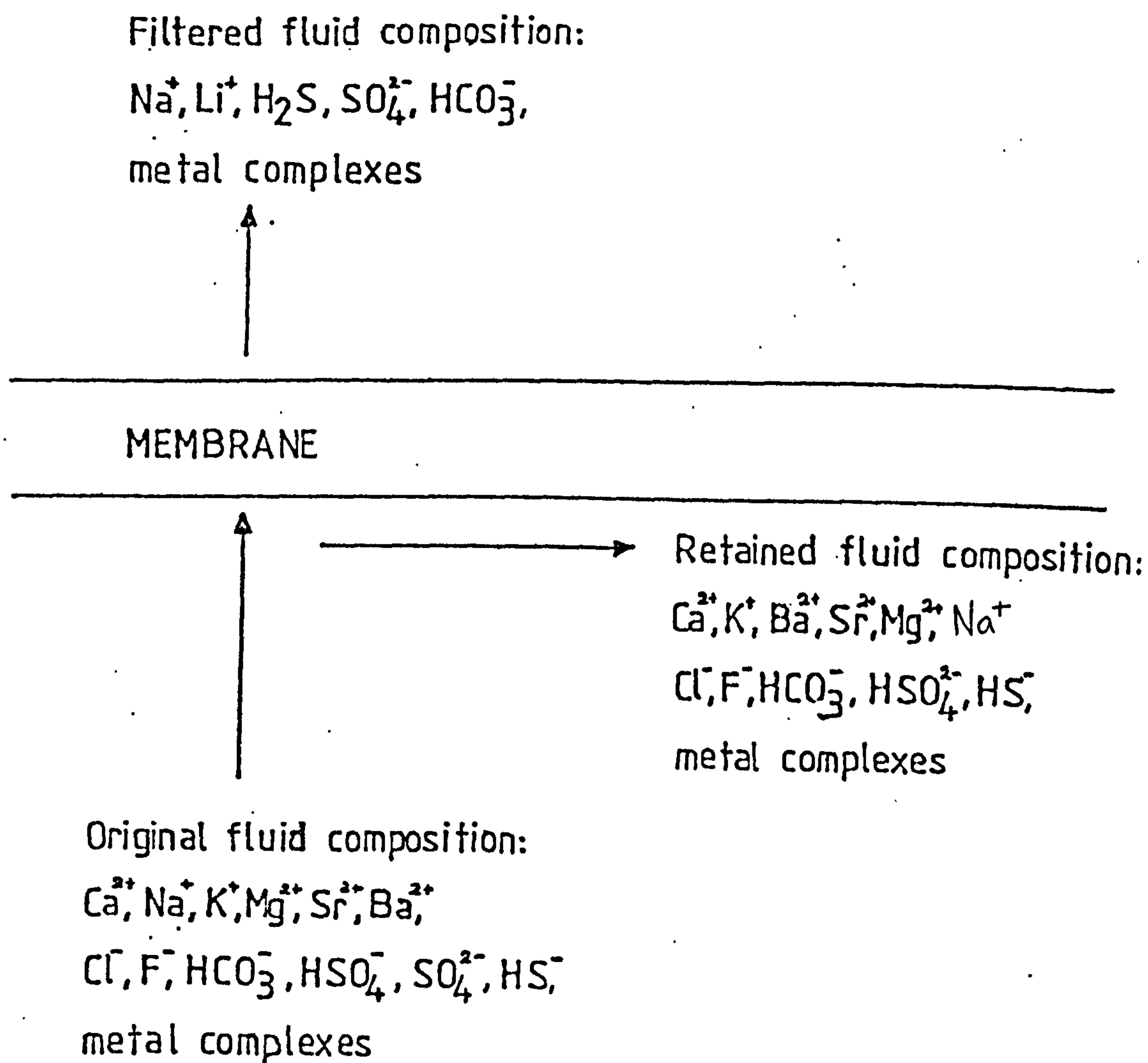


Fig.5.7 The range of isotopic compositions of a fluid produced by mixing residual pore water with water derived from the dehydration of montmorillonite.

Fig.5.8 The possible range in chemical composition of two fluids,
a filtered fluid and a residual fluid, produced from an
original pore fluid which had undergone membrane filtration.



the membrane in the filtered fluid, while most of the anions and large cations were retained in the residual fluid, (White, 1965). The two fluids would thus develop different chemical compositions. The shallow, filtered fluid would be concentrated in H_2S , Na^+ , Li^+ , ZnCl_2 , CuCl , and $\text{Pb}(\text{HS})_2$, (neutral species and small cations), whereas the deep, residual fluid below the membrane, would be richer in Cl^- , F^- , Ca^{2+} , Mg^{2+} , Ba^{2+} and Sr^{2+} as well as containing some HS^- and S^{2-} . Large negative or positive metal complexes, such as PbCl_4^{2-} , FeCl_2^+ and the bisulphide complexes $\text{Cu}(\text{HS})_3^{2-}$, and $\text{Zn}(\text{HS})_3^{2-}$ would also have been retained. The latter fluids are thought to be comparable to those of the fluorite and quartz inclusion fluids. During the evolution of both fluids, elements may have been leached from the host rocks, the amount and variety would depend on the rock composition, Table 5.3. Metallic elements are likely to have been leached from shales and would form negatively charged and neutral complexes in solution. Additional Sr, Mg and Ba are more likely to have come from limestones, thus the solutions, both near the surface and at depth, may have similar metal and minor element concentrations although their major components will be different. Local variations of trace elements will, however, occur due to local variations in the host rocks and original pore fluids. (Vaughan and Ixer, 1980). The near surface solutions may also have contained SO_4 leached from Lower Carboniferous evaporite deposits.

The third phase of fluid production involved the diagenetic change of montmorillonite to illite and chlorite. Potassium and magnesium from the residual pore fluid, will

Table 5.3 Chemical composition of Sedimentary Rocks.

(Collins, 1975)

Element	Shale conc. ppm.	Sandstone conc. ppm.	Limestone conc. ppm.
Na	9,700	3,300	370
K	27,000	11,000	2,700
Ca	22,300	39,500	304,500
Mg	14,800	7,100	47,700
Cl	trace	trace	200
Br	-	-	-
S	2,600	2,800	1,100
F	510	-	250
Sr	170	<26	425 to 765
Ba	460	170	120
Si	272,800	367,500	24,200
Rb	300	273	-
Al	81,900	25,300	4,300
Fe	47,300	9,900	4,000
Zn	200 to 1000	<20	<50
Cu	192	-	20.2
Pb	20	20	5 to 10
Mn	620	trace	385

be fixed by the mineral whereas Na and Ca will be released into the solution by this process, (Millet, 1970). The decrease in $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio from 2.59 to 1.64 in the minerals may also result in the release of silica into solution (Greensmith et al., 1971). Small amounts of heavy metals may also be released into the solution during this process.

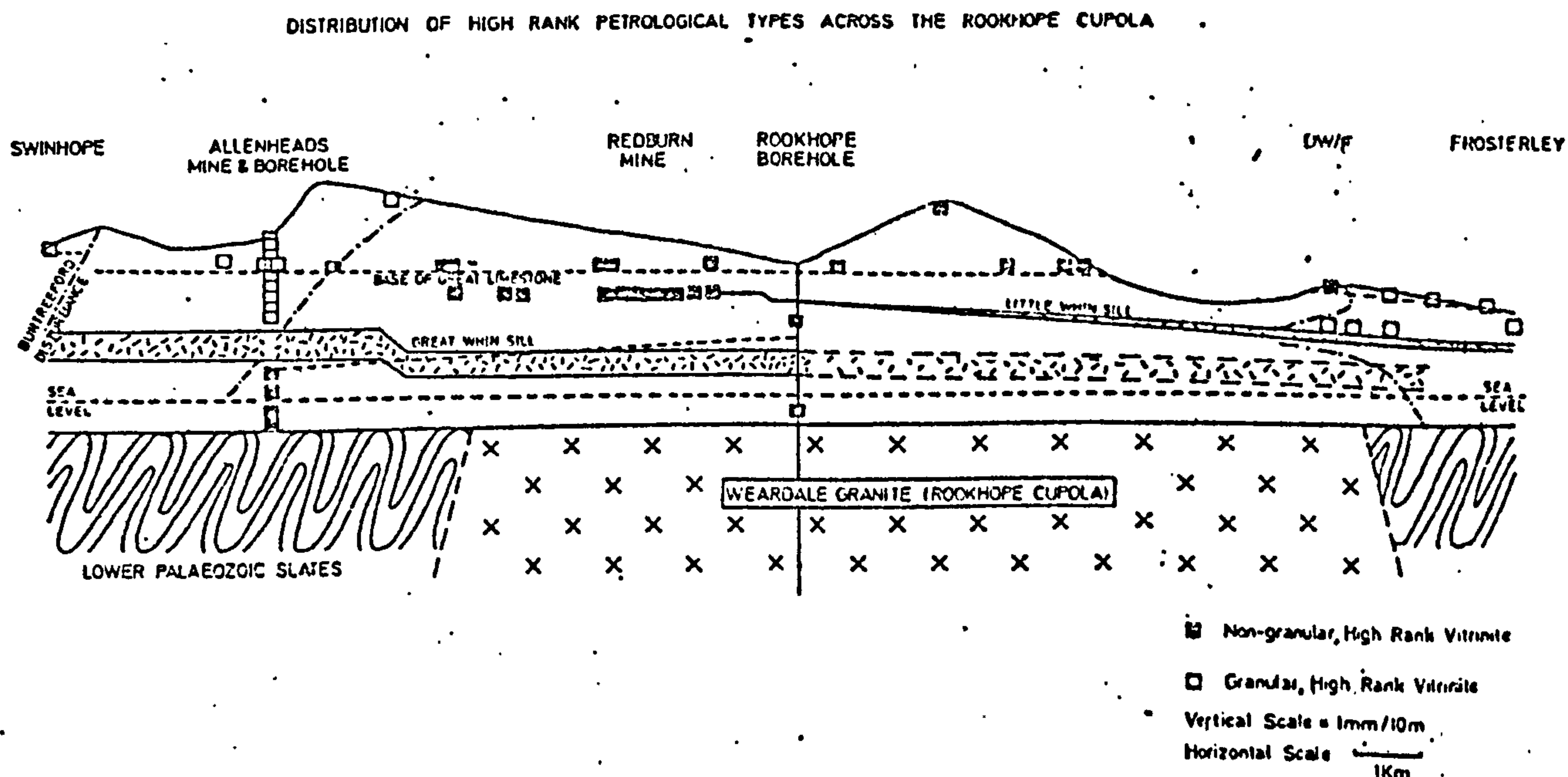
The above model thus provides a means for obtaining two solutions. The one at a shallow depth being a sulphate rich, barium poor solution and very depleted in δD , whereas the other at a greater depth being similar to the fluorite-quartz inclusion fluids.

5.30. Migration of fluids

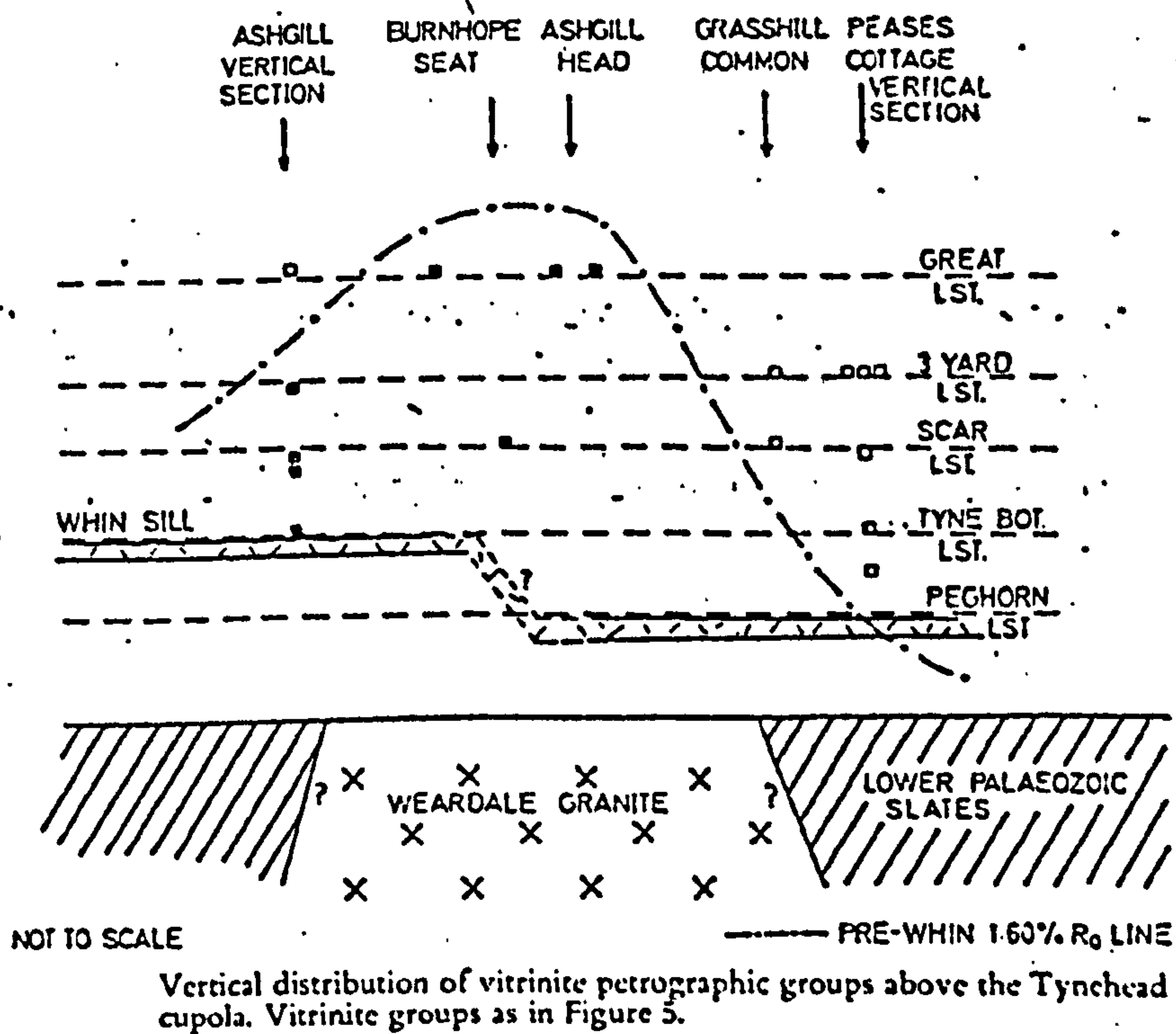
From the above process a dynamic system of fluid movement would have developed, since at the same time the Hercynian orogeny was causing faulting and folding in the area, opening conduits along which the fluid migration could take place. Thus the near-surface fluids migrated laterally up dip into the sediments of the Alston Block, while at depth geopressure systems were set up and caused the deeper fluids to be expelled along intermittently open fault structures. Migration along such structures would have allowed the fluids to enter the Lower Palaeozoic rocks and the Weardale Granite.

Creaney (1980), in a study of coal ranks, has shown that high heat flow was being directed through the Weardale Granite cupolas, under Rookhope and Tynehead, at this time, Fig. 5.9. This localised heat flow would have enhanced and directed the flow of the deep seated fluid upwards, through open conduits, towards the surface.

Fig.5.9 The use of coal ranks to show high heat flow from the
Weardale Granite cupolas under Rookhope and Tynehead,
(Creaney,1980).



Vertical distribution of vitrinite petrographic groups above the Rookhope cupola.



5.40. Transport of elements in solution

A brief review of the mechanisms for transporting ions in solution is necessary to understand how the constituents of the Northern Pennine minerals were carried to their sites of deposition. Most previous work has suggested that the elements are transported either as anions, cations, molecules or chloride and bisulphide complexes.

Chemical analysis has shown that the fluorite and quartz inclusion fluids are Na-Ca-Cl brines carrying small amounts of CO_2 , used for pH calculations, and very small concentrations of sulphide ions. Barite inclusion fluids are more acidic and less saline, and probably also contain some SO_4^{2-} .

Recent publications by Nordstrom and Jenne (1977) and Richardson and Holland (1979 a and b), indicate that fluorite is mainly transported in solution as CaF . Additional fluorine may be carried as neutral or positively charged complexes of the form NaF , Na_2F^+ , KF and MgF_2 , if these ions are present in sufficient quantities in the solution. Extra calcium is carried as CaCl_2 with minor CaCO_3 and CaSO_4 , thus the quantities of Ca and F transported by this method are more than sufficient to produce large fluorite deposits. Transportation of quartz will generally be in the form of neutral molecules such as H_4SiO_4 , (Anderson and Burnham, 1965). At 200°C approximately 300 ppm SiO_2 will be transported, but below this temperature the concentration falls. Even less barite can be transported in the solution as BaSO_4 at this temperature and it is likely that mutually exclusive solutions of Ba^{2+} and SO_4^{2-} were necessary to transport the constituents of barite, (Blount, 1977). Helgeson (1964; 1969)

showed that metal ions were generally carried as either chloride or bisulphide complexes.

Anderson (1973; 1975) suggested that chloride complexes such as CuCl^+ , FeCl , FeCl^+ , ZnCl_2 and PbCl_4^{2-} were most stable at temperatures below 300°C in Ca-Na-Cl rich brines. Crerar and Barnes (1976) also proposed that CuCl would be present. Bisulphide complexes only became dominant in solutions containing high levels of reduced sulphur, (Barnes 1967; 1969), but they may also occur in sulphate rich solutions. Barnes, (1979) considered that the most stable bisulphide complexes at temperatures below 300°C would be $\text{Cu}(\text{HS})_3^{2-}$, $\text{Zn}(\text{HS})_3^{2-}$ and $\text{Pb}(\text{HS})_2$.

The inclusion fluids of fluorite and quartz, analysed in the present study, indicate a chemical composition suitable for the transport of fluorite, assuming sufficient Ca and F are present in the solution. No chemical analysis has been made of the levels of Si, Ba and SO_4^{2-} in the inclusion fluids. Metal concentrations in the solutions were found to be relatively high, and sufficient Cl^- for complex formation is generally present irrespective of whether the NaCl and CaCl_2 are dissociated in the solution, Table 5.4.

5.50. Factors causing mineral deposition

Four main factors have been shown to cause deposition:-

- 1) Changes in temperature
- 2) Changes in pH
- 3) Changes in pressure
- 4) Mixing of solutions

Table 5.4 Cl composition required in the ore solution for complex formation

Element	Fluorite	Quartz	Barite
Cl^-	1.34 - 6.61	3.88 - 49.72	-
NaCl	1.00 - 5.50	1.40 - 2.50	0.10 - 3.20
KCl	0.09 - 0.35	0.10 - 0.35	0.05 - 0.27
CaCl_2	-	0.30 - 15.00	0.20 - 15.00
MgCl_2	0.003 - 0.42	0.002 - 0.008	0.004 - 0.56
SrCl_2	0.002 - 0.04	0.004 - 0.022	0.007 - 2.44
CuCl	0.0002 - 0.17	0.0020 - 0.19	0 - 0.0640
ZnCl_2	0.0005 - 0.23	0.0008 - 0.01	0.001 - 0.0570
FeCl_2	0.0009 - 0.41	0.0030 - 0.01	0 - 0.0001
Cl^- required for Saline Elements	1.10 - 6.77	2.112 - 32.92	0.58 - 39.47
Cl^- required for metal complexes	0.0025 - 1.22	0.0088 - 0.28	0.001 - 0.1212
Cl^- total required	1.103 - 7.99	2.121 - 33.19	0.581 - 39.591
Cl^- in excess	0.237 - ?	1.76 - 16.53	?

The table assumes one mole of Cl^- is required by one mole of x and two moles of Cl^- are required by one mole of y, where x = Na, K, Cu, Zn and y = Ca, Mg, Sr, Fe.

5.51. Changes in temperature

Temperature variation in the Northern Pennine Orefield has been studied by Smith (1974). He suggested that cooling was due to heat exchange between the fluid and surrounding rocks, the affect being greatest where the flow rate was lowest. Lower flow rates were postulated for horizontal cavities in comparison to vertical feeder zones where the flow rate would have been much faster. Smith (1974) also showed that the flow was turbulent rather than laminar, which would have increased the loss of heat from the fluid. Temperature gradients varied over the area, decreasing away from feeder zones, and towards the surface. The early phase minerals were also found to have higher formation temperatures than later phase minerals.

5.52. Changes in pH

Changes in pH are mainly produced by loss of CO_2 from the solution, and by wall-rock interactions. Dunham(1948), Ineson (1969, 1972) and Smith (1974), have shown that there are three main types of wall-rock reactions in the Northern Pennines.

The first of these involved interactions between the fluids and the Weardale granite, and produced minor amounts of sericitic wall rock alteration tending slightly, with the presence of minor kaolinite, towards intermediate argillic alteration. The interaction is very limited in extent and little or no leaching of the granite has taken place, (Smith, 1974,p.74).

Early silicification of the limestone wall rocks

minimised subsequent ~~xy~~ fluid/rock interactions by isolating one from the other. However, as shown by the production of replacement ore-bodies or 'flats', small amounts of limestone/fluid interaction have taken place.

The third type of wall-rock alteration was that associated with the Whin Sill, (Ineson, 1972). Here, CO_2 and K were lost from the solution during the production of 'White Whin'. This consists of quartz, carbonates, pyrite, kaolinite and K feldspar; no micas are present. Other clay minerals were formed and include montmorillonite-illite mixed-layer clay and illite. Leaching during alteration locally released Na, Mg, Si and F^- to the solution.

pH changes of between one and two units, from 4.5 to 3.0, are shown by the calculations presented in Chapter 3. They can be attributed to loss of CO_2 from the solution. Wall rock alteration, particularly limestone alteration, was kept to a minimum after initial silicification had isolated the host rocks, and although local leaching of the Whin Sill occurred it was quantitatively insignificant.

5.53. Changes in Pressure

Smith (1974) concludes that the maximum pressure gradient in the Northern Pennine orefield was 275 bars over a depth of 520 m. He suggested that the pressure of the brines at depth was close to lithostatic pressure but at the surface was close to hydrostatic pressure. Between these two extremes there was generally a gentle decrease in pressure. Localised constriction of the conduits caused sudden increases in fluid pressure, and the decrease in pressure of the solution as it passed into the low pressure area

beyond may have given rise to an increase in precipitation. Changes in pressure are thus only of local importance in the deposition of minerals.

5.54. Mixing of Solutions

Previous work on the Northern Pennine orefield suggested that mixing of two solutions had a role in ore deposition. (Sawkins, 1966; Solomon, Rafter and Dunham, 1971; Smith, 1974). However, these authors concluded that there was very little evidence for extensive mixing.

There are several possible combinations of solutions which might mix in an orefield. They are:-

- a) Two brines of the same salinity and temperature
- b) Two brines of the same salinity but different temperature or visa versa.
- c) Two brines, each saturated with respect to different minerals.

Mixing according to (a) would produce no change in temperature or salinity of the overall solution. However when two solutions of either different salinity or temperature are mixed the resulting solution would have a value for its salinity or temperature, between those of the original solutions. Also, when two brines saturated with respect to different minerals are mixed, the solution produced will either have become undersaturated with respect to both minerals or undergone some chemical reaction. This may result in decreased or increased precipitation of minerals.

5.60. Changes in mineral solubility

5.61. Quartz Solubility

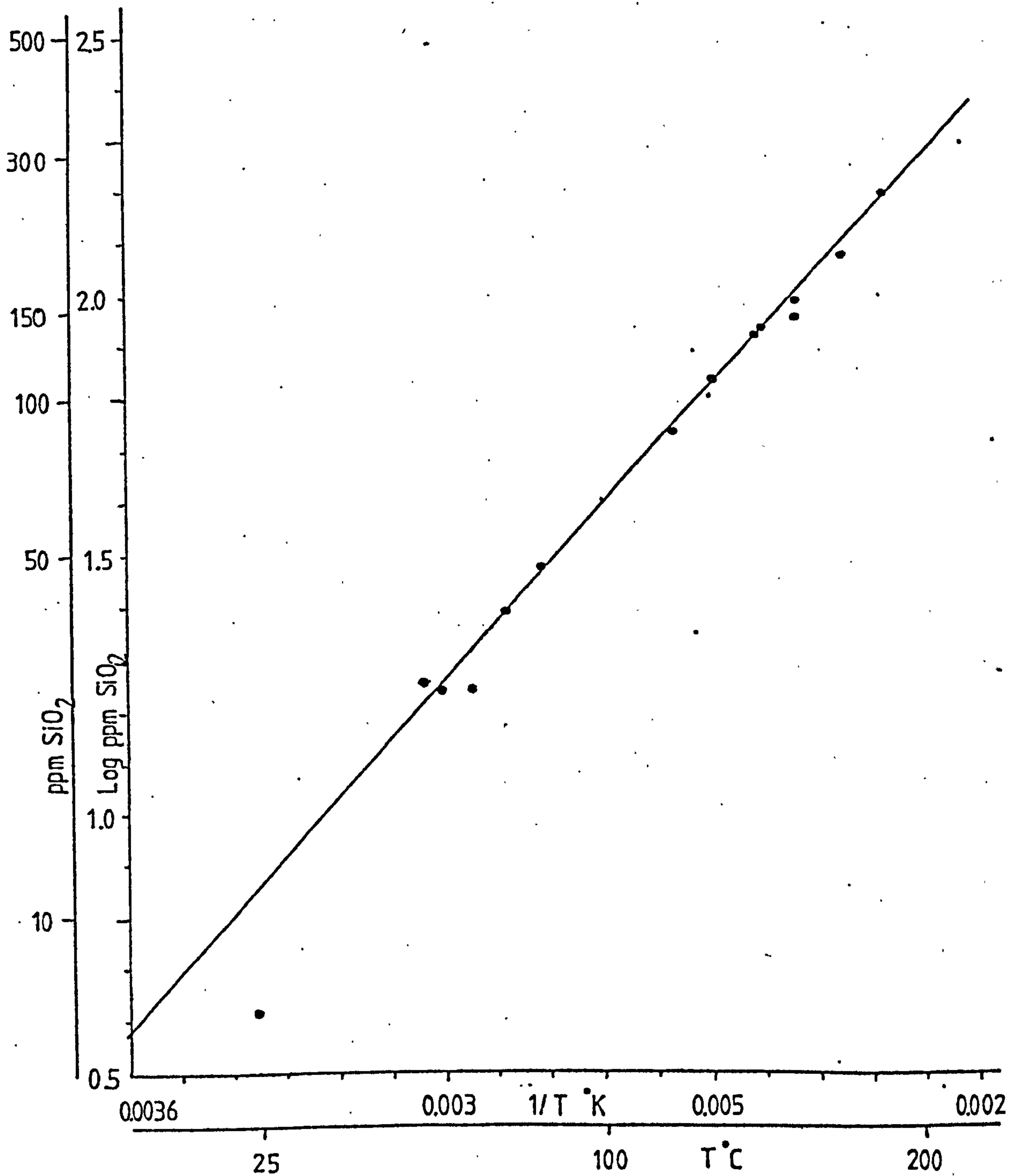
Quartz solubility decreases with decreasing temperature, as shown by Krauskopf (1979), Fig. 5.10. The relationship shows that at temperatures below 200 °C less than 300 ppm SiO_2 will be soluble in pure water, and at 100 °C only about 70 ppm will be soluble. Thus with higher concentrations of SiO_2 in the ore solution significant precipitation should occur on cooling. In NaCl solutions of greater than 1 M concentration, the solubility of silica decreases even faster with temperature, (Anderson and Burnham, 1965). Pressure changes and pH variations below a pH = 9 have little or no affect (Krauskopf, 1979), while the affects of mixing two solutions have not been studied.

The most likely cause of quartz deposition in the Northern Pennines is therefore cooling of the ore-fluids.

5.62. Fluorite solubility

Fluorite deposition may also occur due to cooling. A decrease in temperature, at constant pH and NaCl concentration, will produce a decrease in the stability of fluorine complexes and hence release fluoride ions. This produces an increase in the amount of CaF_2 in the solution which may cause the solution to become oversaturated and result in fluorite deposition. When the NaCl concentration is >1.0 M a decrease in temperature will lead to a proportional decrease in the solubility of fluorite, but if the NaCl concentration is <1.0 M the decrease in temperature will initially produce an increase in fluorite solubility, to

Fig.5.10 Solubility of silica as a function of temperature; plotted as log. ppm. SiO_2 against the reciprocal of the absolute temperature, (Krauskopf,1979).



100 °C, and then a decrease in solubility below this temperature, Fig. 5.11. (Richardson and Holland, 1979a; b). An increase in pH of the solution from 3 to 5, will result in a decrease in fluorite solubility from 32 to 20 mg CaK₂H₂O at a temperature of 100 °C, Fig. 5.12.

Mixing of two ore-solutions can produce varying changes in fluorite solubility. Addition of a dilute solution, to one saturated in fluorite, at the same or lower temperature, will result in undersaturation of the solution and a halt in deposition of fluorite. If, however, a concentrated fluorite solution was added to a similar solution at the same or lower temperature, oversaturation of the solution would result and fluorite deposition would be increased. (Richardson and Holland, 1979a).

Deposition of fluorite in the Northern Pennine orefield was therefore probably caused by cooling of the fluid and changes in pH, due to loss of CO₂ from the fluid. This assumes that sufficient Ca²⁺ and F⁻ were originally present in the solution.

5.63. Barite solubility

Barite is generally only sparingly soluble in chloride brines, but its solubility may be increased by high concentrations of CaCl₂ and MgCl₂. In NaCl solutions of >1.0 M a decrease in temperature will lead to a proportional decrease in barite solubility, however, in solutions of <1.0 M NaCl barite solubility decreases above 150 °C and below 100 °C, remaining almost constant between these temperatures. Thus only small amounts of barite are likely

Fig.5.11 Solubility of fluorite as a function of temperature in NaCl solutions,

(Richardson and Holland,1979a).

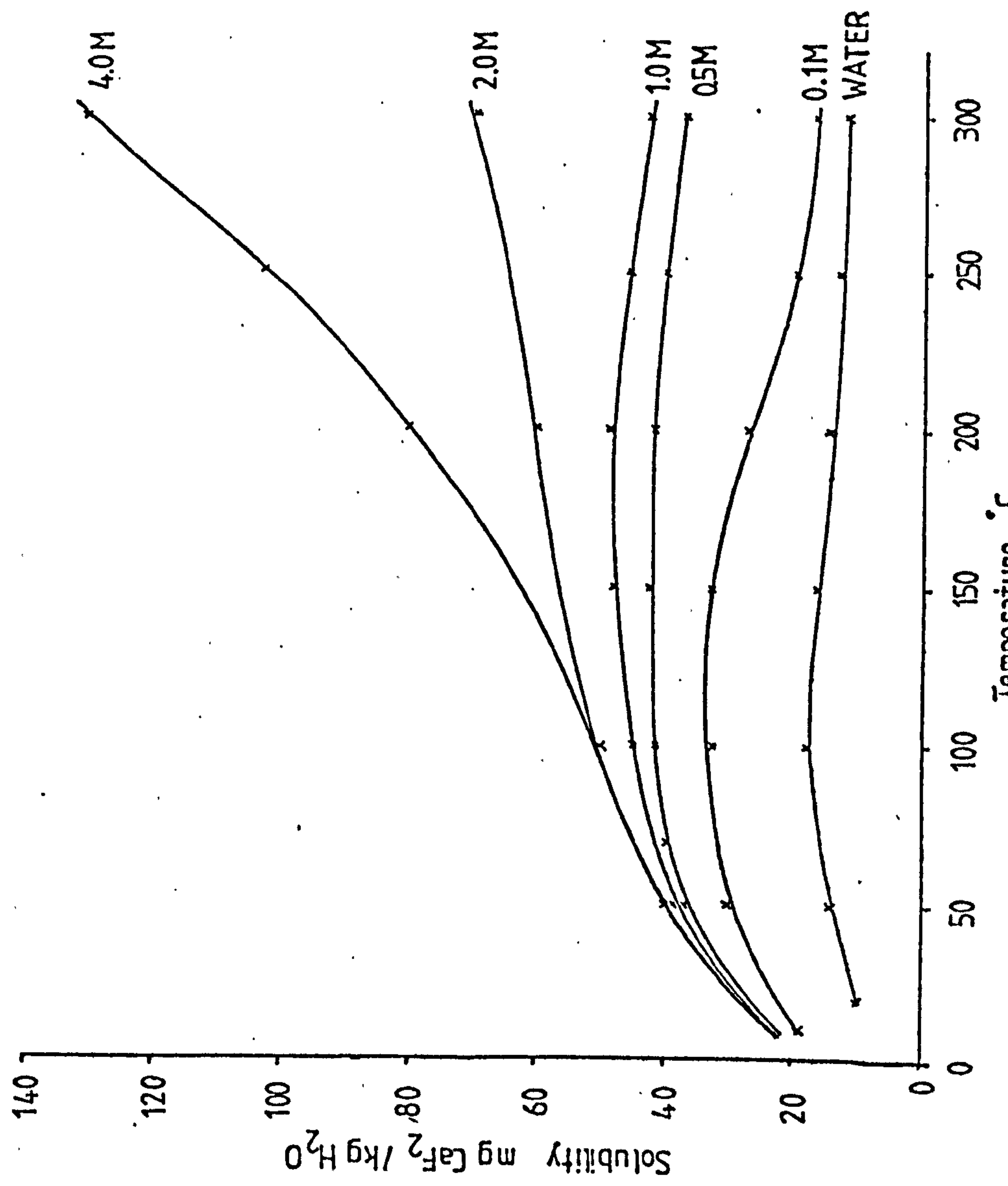
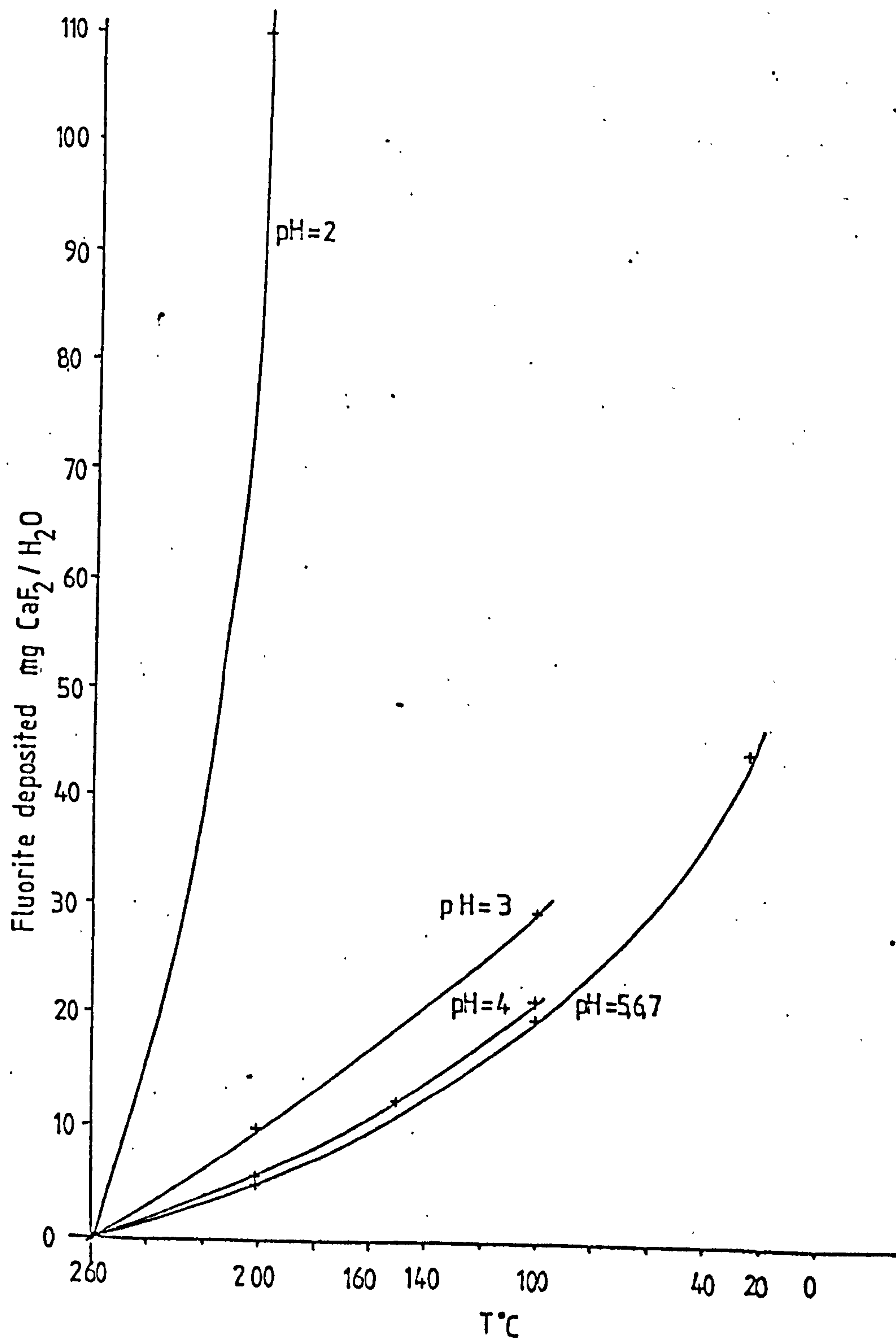


Fig.5.12 The quantity of fluorite precipitated by cooling NaCl solutions at varying pH values, (Richardson and Holland,1979b).



to be deposited due to cooling (Malinin et al., 1969; Blount, 1977). The affect of pH changes is unknown, while decreases in pressure have the same affects on barite solubility as decreases in temperature, but to a lesser extent.

Mixing of two solutions can produce large variations in barite precipitation. A Ba^{2+} -rich solution if mixed with a solution containing SO_4^{2-} at constant temperature, will precipitate barite. Similar precipitation would result from mixing a solution containing Ba^{2+} and S^{2-} with one of a higher oxygen fugacity, at constant temperature and pressure.

Therefore only small amounts of barite will be deposited from a cooling solution, deposition of larger amounts requiring the mixing of two solutions of different composition.

5.64. Metal Sulphide Solubility

Metal ions may be transported as either chloride or bisulphide complexes. The affect of temperature on the stability of both types of complex will be greater at high temperatures and a decrease in stability will be produced by a decrease in temperature. This releases metal ions into solution which then react with reduced sulphur resulting in the precipitation of metal sulphides (Crerar and Barnes, 1976). Changes in pH will cause major changes in the stability of metal chloride or sulphide complexes, (Anderson, 1973, 1975). For chloride complexes an increase in pH will result in a large decrease in their stability and metal sulphide will be precipitated until the reduced sulphur has been consumed. A decrease in pH

is however necessary for reduction in stability of bisulphide complexes, (Barnes, 1979).

An ore fluid containing metal chloride complexes will precipitate metal sulphides on mixing with another solution providing that the initial solution undergoes dilution of its Cl concentration, increase of its reduced sulphur concentration, or a decrease in oxygen fugacity, (Anderson, 1973; Barnes, 1979). Conversely an ore fluid containing metal bisulphide complexes will precipitate metal sulphides on mixing with another solution only if the initial solution undergoes dilution of its reduced sulphur concentration or if its oxygen fugacity is increased.

Small amounts of metal sulphides will thus be precipitated by cooling, but larger amounts may form due to variations in pH. Mixing of two solutions also provides a method for extensive precipitation of sulphides.

5.70. Mineral Deposition in the Northern Pennines : Fluorite Zone

In the fluorite zone three major mineral assemblages are represented by:-

- a) Quartz, chalcopryrite and pyrite
- b) Fluorite, chalcopryrite and galena with or without quartz
- c) Fluorite, galena and sphalerite with or without quartz.

Fluorite and quartz were deposited from a single, original fluid which may have been locally variable. This conclusion derives from data described above (Sect. 5.20), and on similarities in chemical composition between inclusion

fluids from quartz and fluorite, tested by the Mann Whitney U test, Appendix 4. The fluid inclusions show similar levels of K, Sr, Cu, Zn and Fe and concentrations with closely overlapping ranges for δD , Na, CO_2 and Mg. The compositional ranges are shown in Table 5.5. The composition of the fluorite inclusion fluids is compatible with a solution capable of depositing fluorite assuming that sufficient Ca^{2+} and F^- were present.

To find out why fluorite deposition halted during quartz precipitation, a comparison was made of the concentration of $CaF_2(aq.)$ in the quartz inclusion fluids with that necessary for deposition of fluorite. Fluorine and calcium analyses in these inclusions were recalculated to give the maximum $CaF_2(aq.)$ composition of the fluid, assuming that either all the fluorine or all the calcium was used, Table 5.6. These values are compared with those obtained from Fig. 5.11 for solutions of different salinities which are saturated with fluorite. The results show that the fluids in quartz taken from fluorite veins, contain Ca and/or F in excess of that necessary for deposition of fluorite, except for sample 6666. Contamination by fluorite cannot be ruled out, and thus the data probably indicate that the $CaF_2(aq.)$ concentration of the fluid was probably just below the saturation level, as no fluorite was deposited. The silica concentration, however, must have exceeded its saturation level probably due to slight cooling, to produce the quartz veins.

Table 5.6 shows that generally the quartz from the Great Sulphur Vein carries inadequate $CaF_2(aq.)$ in solution for fluorite deposition. All $CaF_2(aq.)$ thus remains in solution

Table 5.5 Chemical composition of fluid inclusions in the northern
Pennine minerals

Element	Fluorite	Quartz	Barite
Na	14,600 - 129,800	16,100 - 53,500	2,800 - 70,700
K	1,620 - 14,710	1,790 - 13,520	630 - 10,430
Ca	-	25,000 - 484,000	6,000 - 494,000
Mg	80 - 9,900	50 - 200	100 - 12,990
Cl	96,600 - 189,800	45,300 - 637,500	-
Br	300 - 1,520	-	-
S	< 100	-	-
F	-	4,000 - 22,500	-
Sr	200 - 3,680	340 - 1,880	60 - 153,900
Fe	50 - 21,800	150 - 2,240	0 - 5,800
Zn	30 - 14,570	50 - 790	90 - 3,720
Cu	10 - 10,470	10 - 11,620	0 - 4,030
Mn	30 - 7,180	0 - 60	20 - 7,360
Y	334 - 890	-	-

All concentrations are shown in ppm and have been taken from results shown in Chapter 3.

Table 5.6 Aqueous CaF_2 concentrations in Quartz inclusion fluids

a) Quartz-fluorite veins

Sample	Temperature $^{\circ}\text{C}$	NaCl M	pH	CaF_2 * 10^{-3}gL^{-1}	CaF_2 ** 10^{-3}gL^{-1}
R101.1	151	1.81	4.42	56.0	442.2
R102.3	138	1.43	4.19	48.0	272.7
1018	127	2.45	4.27	54.0	399.3
6480	137	1.97	4.15	55.0	150.0
6666	109	1.86	4.10	51.0	48.7

Both CaF_2 (aq) concentrations are in 10^{-3}gL^{-1}

b) Great Sulphur Vein

Sample	Temperature $^{\circ}\text{C}$	NaCl M	pH	CaF_2 * 10^{-3}gL^{-1}	CaF_2 ** 10^{-3}gL^{-1}
414	143	1.42	4.13	48.0	22.79
416	122	2.39	4.34	53.0	16.65
418	189	2.03	4.19	59.0	78.71
419	188	2.04	4.92	59.0	37.20
424	147	2.03	4.22	56.0	42.48

* CaF_2 concentration calculated from fig. 5.11

** CaF_2 concentration calculated from chemical analyses (Chapt. 3).

while quartz was deposited in this area.

Small amounts of sulphide minerals were deposited throughout the zone, contemporaneously with the fluorite and quartz. The quartz/fluorite inclusion fluids have concentrations of metal ions varying from 10 ppm to 22,000 ppm. These are in excess of the 10 ppm accepted as the lower limit of metal ion concentration necessary for appreciable metal sulphide precipitation, (Anderson, 1973).

Comparisons of the metal concentration with temperature and sodium content (as an indicator of salinity and Cl^- concentration) should indicate whether sulphide deposition was dependent on either one of these solution parameters. Very low correlation coefficients between the two variables and the metal concentration, indicated that the parameters had little or no apparent affect on the metal concentration. Thus precipitation of the sulphides appears not to be controlled by changes in temperature and salinity. However, precipitation of small volumes of metal sulphides may be masked by the large concentrations of metal ions in the solution. Samples at closer intervals were taken across a vein and show that generally the metal concentration decreased with salinity, (i.e. with respect to Na and K). Metal concentration was also found to vary with δD and fluorite colour-banding trends, although samples 100.5 and 100.6, produce some anomalous values, Figs. 5.13 and 5.14. Metals were therefore probably transported as metal chlorides and Table 5.4 shows that sufficient chloride was present in the solution to account for the complexes.

The mineral assemblages were thus used to predict the

Fig.5.13 The variation of iron, zinc, copper and sodium across the south lens of the Slitt vein, 240 level.

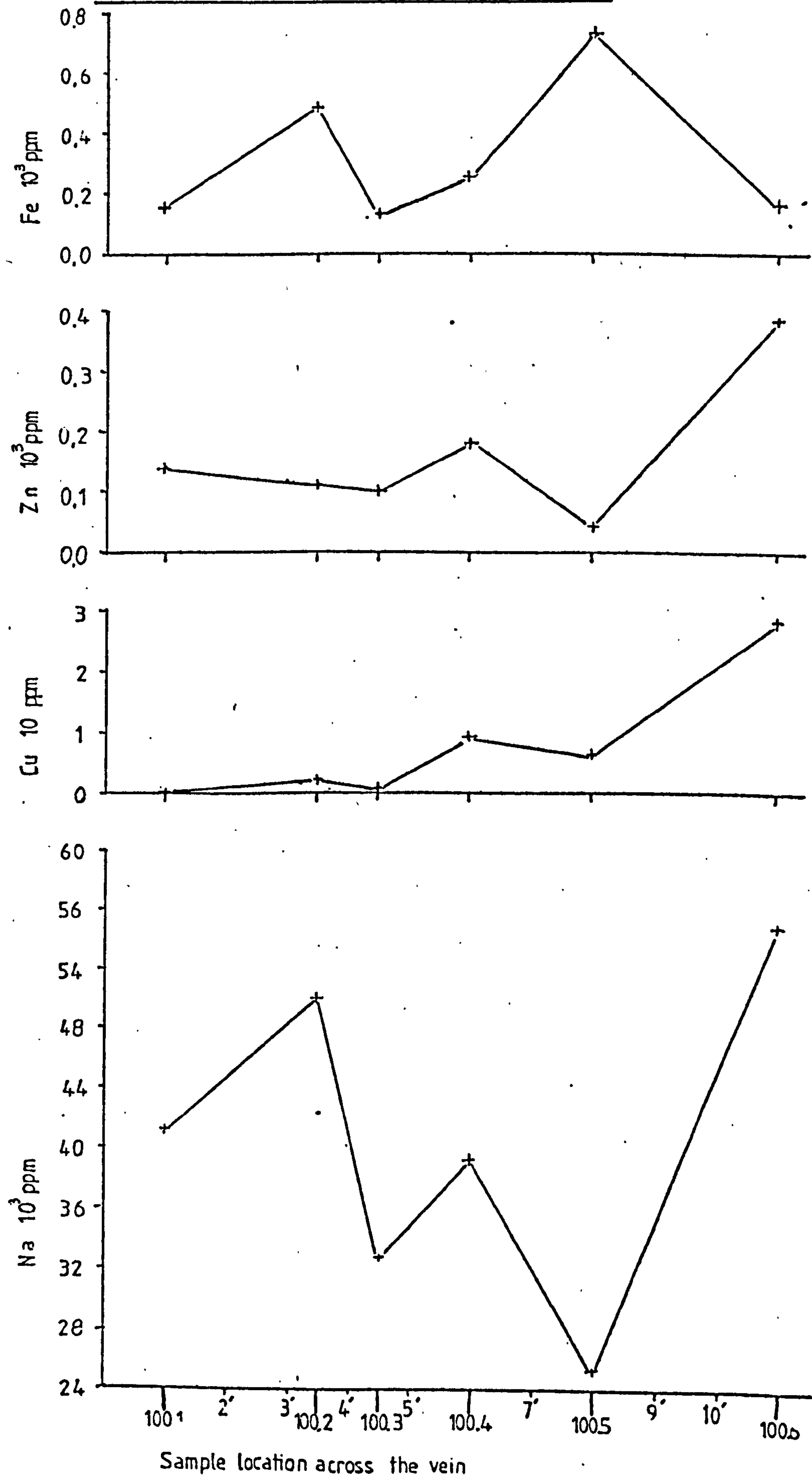
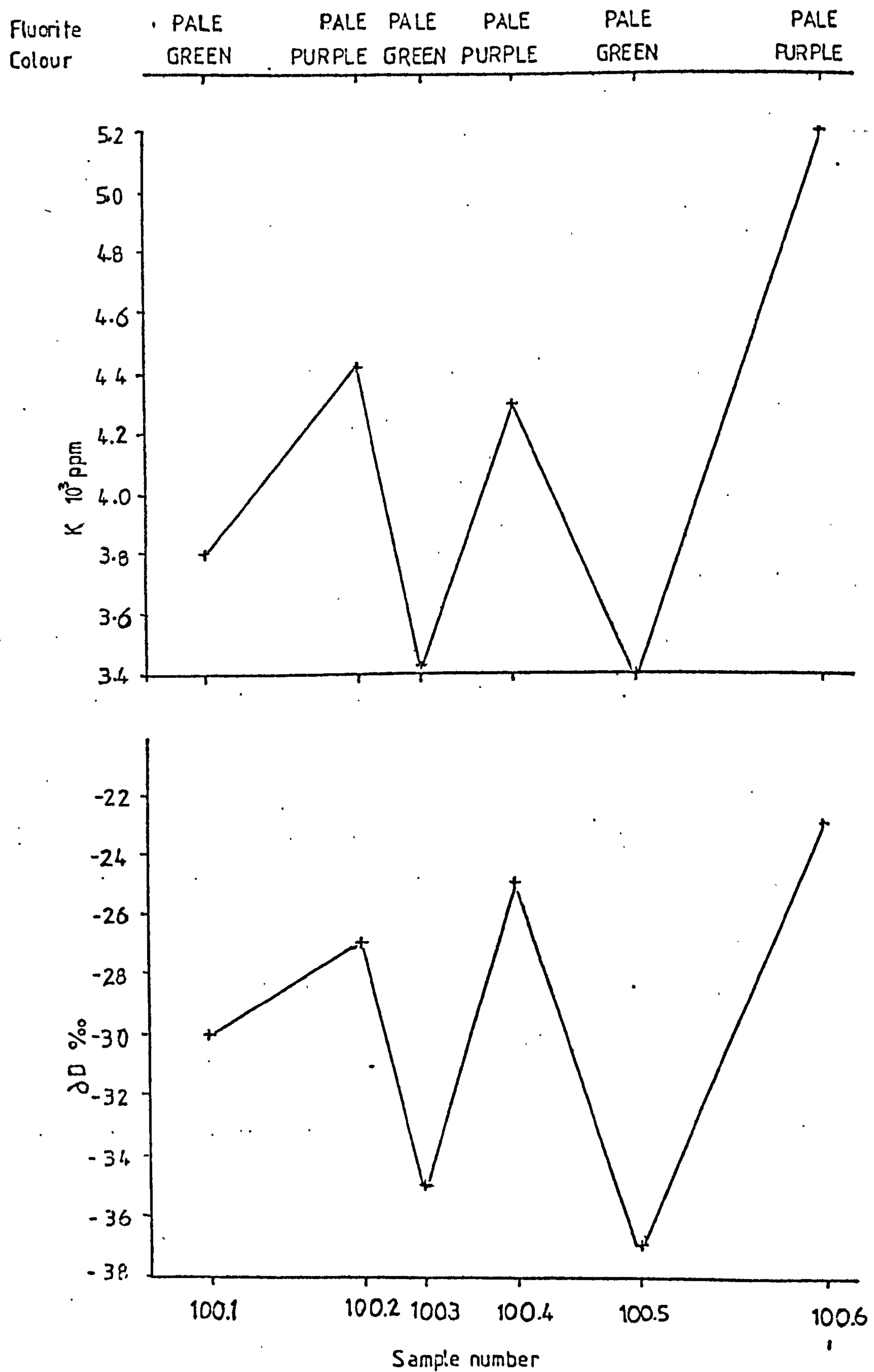


Fig.5.14 The variation of colour, potassium and δD across the south lens of the Slitt vein, 240 level.



limits of other parameters of the fluid, such as the fugacities of oxygen and sulphur. The calculations, and method of construction of the pH-log fO_2 plots, are described in Appendix 4. (Bailey, 1977).

Fig. 5.15 is a pH-log fO_2 plot for the phase one mineralisation of quartz, chalcopyrite and pyrite, at a temperature of 200 °C; the relevant constants are shown in Table 5.7. The limits of log fO_2 are governed by the mineral assemblages. The presence of chalcopyrite (cp) and pyrite can be used to give an upper limit, at the chalcopyrite-pyrite-bornite boundary, of -41.7. Additionally, the presence of pyrite will set the lower log fO_2 limit to the pyrite-siderite boundary at -48.8. This can be increased however, due to the presence of CO_2 in the samples. Thus by letting $\log fCO_2 = -1.0$, the log fO_2 must be greater than -44.5, Fig. 5.15. These upper and lower limits for log fO_2 will then define the log fS_2 and provide physical and chemical information on the fluid, Table 5.8. Copper and iron will be precipitated continuously while the solutions carry greater than 10 ppm or 10^{-5} m, providing sufficient reduced sulphur was also present in solution. Lead and zinc may be transported by the solution but their deposition will be limited due to their lower concentrations. Fig. 5.15 also shows that the solution would deposit fluorite if sufficient amounts of Ca^{2+} and F were present in the solution.

Fig. 5.15, also includes the stability field of the fluid responsible for the phase two mineralisation of fluorite, chalcopyrite, galena and minor sphalerite, at 200 °C. Similar limits for log fO_2 were found for this phase as for phase one

Fig.5.15 pH-log. f_{O_2} plot for the fluid producing the three phases of mineralisation in the fluorite zone, at a temperature of 200°C.

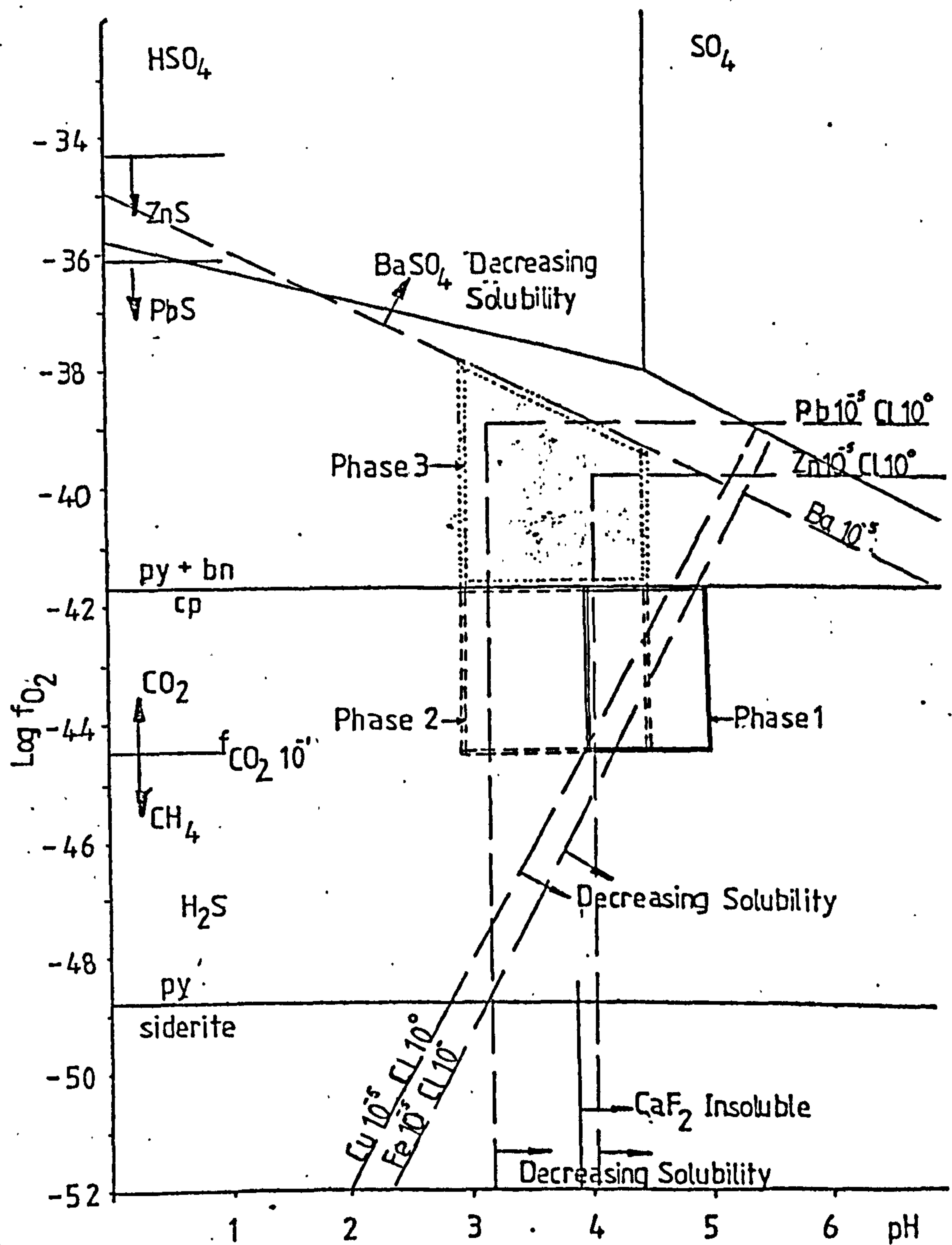


Table 5.7. Activities of elements used in pH log fO_2 plot calculations
for solutions up to 3 M. NaCl

Element	Range of Concentration used (Activity)	Range of conc. found by experiment (m).
Total Sulphur ΣS	0.01	$< .10$
Total Carbon dioxide ΣCO_2	0.1 - 1.0	0.05 - 4.2
Total Calcium ΣCa	0.1 - 7.0	0.2 - 15.0
Total Potassium ΣK	0.3	0.0 - 0.3
Total Chloride ΣCl	0.1 - 1.0	0.1 - 3.0

For mineral precipitation in ore quantities 10^{-5} m is the minimum concentration required.

Metal (Cu, Zn, Fe, Pb)	10^{-5} m
Reduced Sulphur (S^{2-})	10^{-5} m
Fluorine (F^-)	10^{-5} m
Barium (Ba^{2+})	10^{-5} m

Table 5.8 Summary of log fO_2 -pH plot results for the fluorite zone

Temperature 200 °C

	log fO_2 range	log fS_2 range
Phase 1	-41.7 to -44.5	-10.65 to -13.45
phase 2	-41.7 to -44.5	-10.65 to -13.45
phase 3 (pH = 3.0)	-37.9 to -41.7	-6.85 to -10.65
(pH = 4.5)	-39.4 to -41.7	-8.35 to -10.65

Temperature 150 °C

phase 3 (pH = 3.0)	-43.3 to -48.5	-7.31 to -12.51
(pH = 4.5)	-44.8 to -48.5	-8.81 to -12.51

Temperature 100 °C

phase 3 (pH = 3.0)	-51.7 to -56.0	-9.43 to -13.73
(pH = 4.5)	-52.8 to -56.0	-10.53 to -13.73

although the pH was lower and the Cl^- and Zn^{2+} concentrations were higher. The solubility boundary for fluorite again lies within the pH range and hence deposition of fluorite will proceed. Occasional redissolution may occur when quartz is deposited. Metal sulphides should be precipitated fairly continuously, in small amounts, depending on the reduced sulphur content of the solution and the variation in pH.

Phase three, the main phase of mineralisation, differs from phase two in that no chalcopyrite is present. Hence the lower limit of $\log f_{\text{O}_2}$ will be set by the chalcopyrite-bornite-pyrite boundary of -41.7, Fig. 5.15. The upper limit can be set by the stability field boundaries of galena and sphalerite (-34.3) but will be further restricted by the absence of barite.

The solubility boundary of barite, at a Ba^{2+} concentration of 10^{-5}M and SO_4^{2-} concentration of 10^{-2}M , gives an upper limit that varies with pH, Table 5.8. Within the defined field fluorite will be deposited continuously, with galena and sphalerite, but copper and most of the iron will remain in solution. The stability field for the fluid responsible for phase three can be determined for temperatures of 150°C and 100°C , Fig. 5.16 and Fig. 5.17, Table 5.8. At 150°C the solubilities of the minerals were similar to those at 200°C , but occur at lower $\log f_{\text{O}_2}$ levels. At 100°C , the natural sulphur field appears over the calculated pH range and, as no natural sulphur was present in phase three, the stability field for the phase three mineralisation will be greatly reduced compared to that at 150°C . The data shown in Table 5.8, indicate that the

Fig.5.16 pH-log. f_{O_2} plot for the fluid producing the phase three mineralisation in the fluorite zone, at a temperature of 150°C.

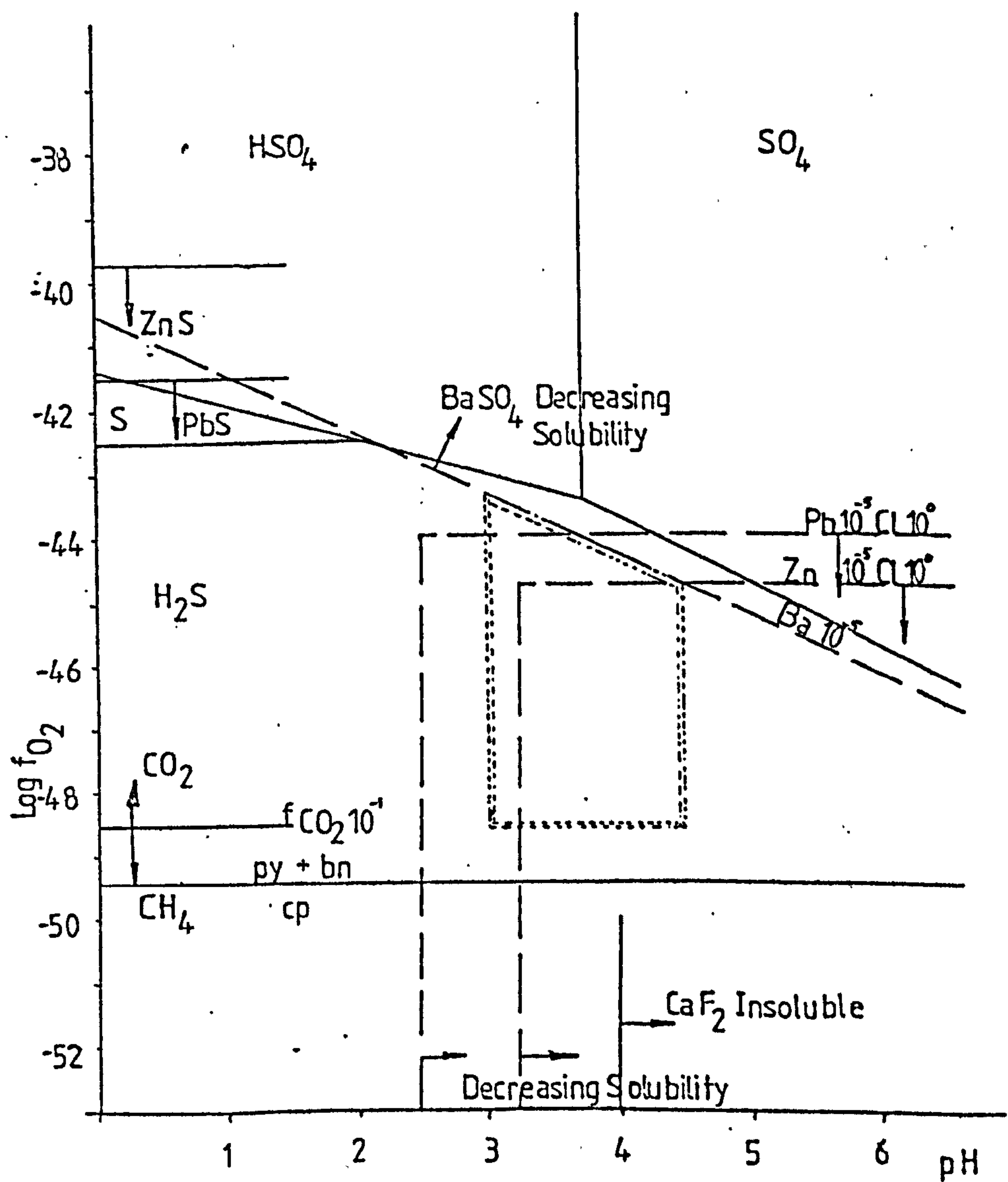
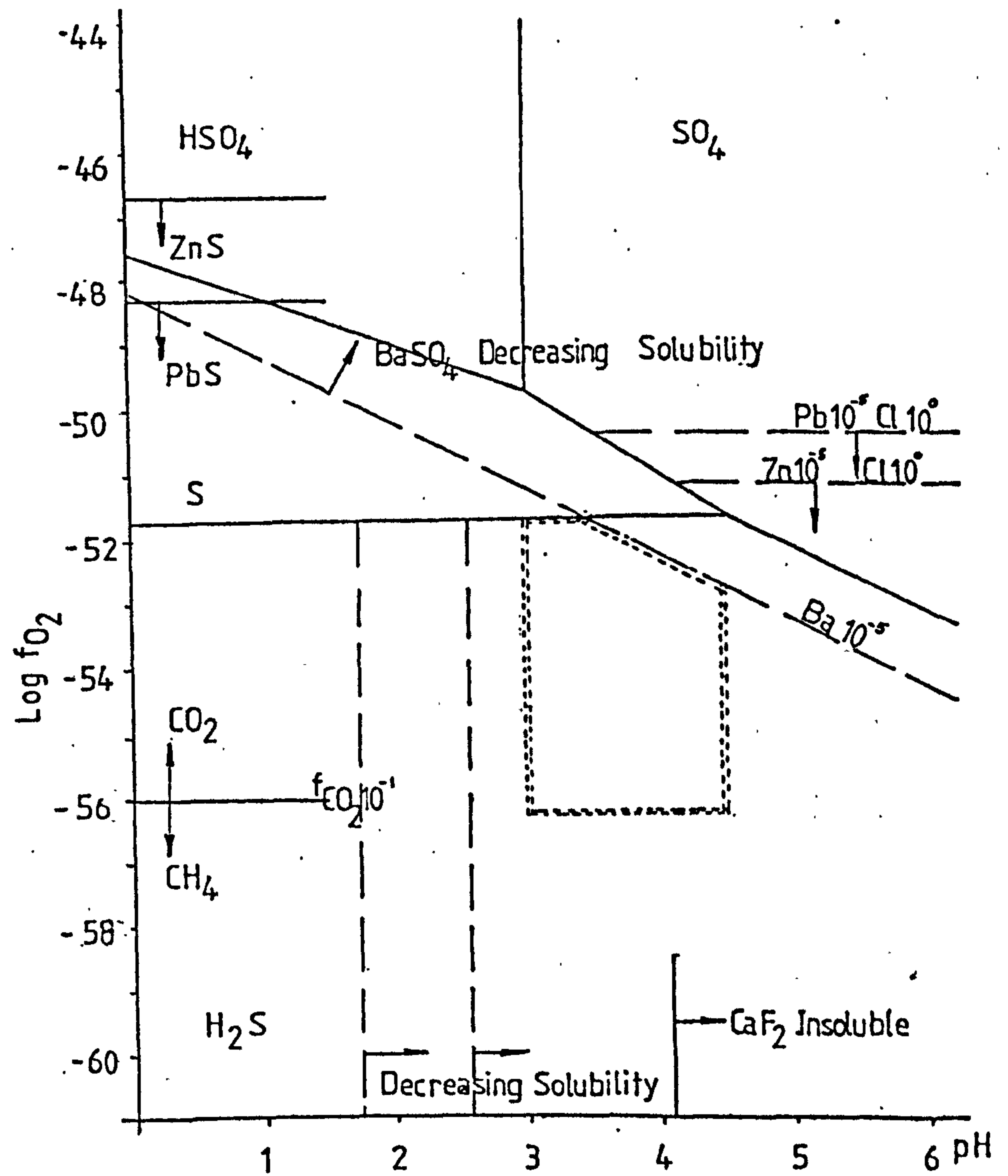


Fig.5.17 pH-log. f_{O_2} plot for the fluid producing the phase three mineralisation in the fluorite zone, at a temperature of 100°C.



fugacities of oxygen and sulphur increased initially as the mineralisation changed from phase one to phase three, but as the temperature decreased during phase three mineralisation the fugacity was also found to decrease. The fugacity of sulphur is controlled by the oxygen fugacity and visa versa and this decrease with temperature may indicate that sulphur was being fixed as metal sulphides precipitated throughout the duration of the main phase of mineralisation. Decreasing $\log f_{O_2}$ and temperature, have already been shown to increase metal sulphide precipitation from chloride complexes and increasing pH from 3 to 4.5 will also favour metal sulphide precipitation.

5.71. Barite zone

In the barite zone the mineral assemblage is barite galena and sphalerite with or without pyrite.

Blount (1977) showed that only a few millimoles of barite would be deposited by decreasing the temperature and pressure of a $BaSO_4$ solution. He proposed that barite was mainly deposited by mixing two solutions.

Thus the barite inclusion fluids are thought to represent a mixture of fluids. From section 5.1. two solutions were derived from the combined affects of membrane filtration and montmorillonite dehydration. One, a deep seated fluid, was shown to be similar to the fluorite-quartz inclusion fluids. The other was a SO_4 -rich brine which was very depleted in deuterium and migrated to shallow depths. It is thus proposed that the barite inclusion fluid represents a mixture of these two fluids resulting in the observed range in δD .

Mann-Whitney 'U' tests indicated that the δD , salinity, and temperature of the barite inclusion fluids are different from those of the quartz and fluorite inclusion fluids, Appendix 4.

The solubility of fluorite was studied in the barite inclusion fluids, to determine why fluorite was not precipitated from the mixed fluids of this zone. Calcium concentrations were used because no fluoride analyses had been carried out. They indicated, in all but two cases, that there was sufficient Ca^{2+} in solution to produce fluorite, Table 5.9. The limiting factor must be the fluoride concentration. The high concentrations of Sr and Mg in the barite inclusion fluids will also cause the fluorite to become more soluble due to complexing, while lowering of the pH may have produced HF complexing and hence increased fluorite solubility. Although no abrupt change in pH is found, the barite inclusion fluids are generally more acidic than those from fluorite and quartz. The original, SO_4^{2-} -rich solution at shallow depth must thus have been more acidic than the deep-seated fluid, to produce this decrease in pH.

Comparison of metal concentrations with temperature and salinity (Na), show that changes in these parameters have no major affect on the concentration of the metal complexes in solution. Small amounts of precipitation however, may be masked again by the large overall concentrations of metal ions in solution. Sampling at closer intervals is needed to detect the changes producing this precipitation. Also if the barite inclusion fluid represents the resulting concentration after mixing of two solutions, the metal concentrations

Table 5.9 Aqueous CaF_2 concentration in barite inclusion fluids

Barite Sample	Temperature °C	NaCl M	pH	CaF_2 * 10^{-3} gL^{-1}	Ca ** 10^{-3} gL^{-1}	Ca *** 10^{-3} gL^{-1}
R120	96°	0.12	3.66	33.0	16.94	8.7
R121	91	0.75	4.39	44.0	22.6	64.8
20725	137	1.07	4.50	47.0	24.1	92.6
R123	96	1.05	4.38	45.0	23.1	33.4
6522	131	1.22	4.38	47.0	24.1	139.8
6587	92	3.15	3.58	48.0	24.6	381.4
6476	124	2.74	3.51	53.0	27.2	127.4
6477	88	1.41	3.95	44.0	22.6	38.5
5206	90	1.31	3.61	44.0	22.6	401.6
6210	115	1.01	3.17	47.0	24.1	493.5
R19	90	3.30	3.53	46.0	23.6	288.8
R20	145	3.12	4.47	58.0	29.8	226.1
20839	83	0.41	3.01	41.0	21.0	17.9

* CaF_2 concentration calculated from fig. 5.11

** Ca concentration calculated from *

*** Ca concentration calculated from chemical analyses (Chapt. 3)

of the shallow fluids have probably been swamped by the metal concentration from the fluorite and quartz fluids.

Figs. 5.18 and 5.19 are pH-log fO_2 plots for the mixed solution at temperatures of 150 °C and 100 °C. The pH ranges shown are derived from the barite inclusion fluid analyses and are probably slightly higher than those of the original shallow fluids. The latter are assumed to have contained SO_4^{2-} and/or HSO_4^- , and thus the mixed fluid must also contain these anions to produce the barite and sulphides. The mixed fluid must thus have a stability field at least partially within these aqueous sulphur fields. The lower oxygen fugacity limit, at 150 °C, was defined by the barite solubility/insolubility boundary representing a minimum Ba^{2+} concentration of $10^{-5}m$. The upper limit was set by the boundary representing $10^{-5}m$ reduced sulphur in the solution. This assumes that no reduced sulphur was added from an external source, as it was probably provided by the reduction of SO_4^{2-} in the solution at shallow depth. The pH and log fO_2 values obtained are shown in Table 5.10. Within these pH limits fluorite should be deposited and its absence must indicate insufficient CaF_2 in solution. Again the probability of a lower pH for the shallow fluid, before mixing, will also help to increase the fluorite solubility after mixing.

At 100 °C the lower and upper limits again correspond to the parameters defined above, but the field is reduced by the overlap of the natural sulphur stability field, Fig. 5.19. The mixed solution thus showed a decrease in oxygen fugacity with temperature. Metal chloride complexes may

Fig.5.18 pH-log. f_{O_2} for the mixed solution producing the barite zone mineralisation, at a temperature of 150 °C.

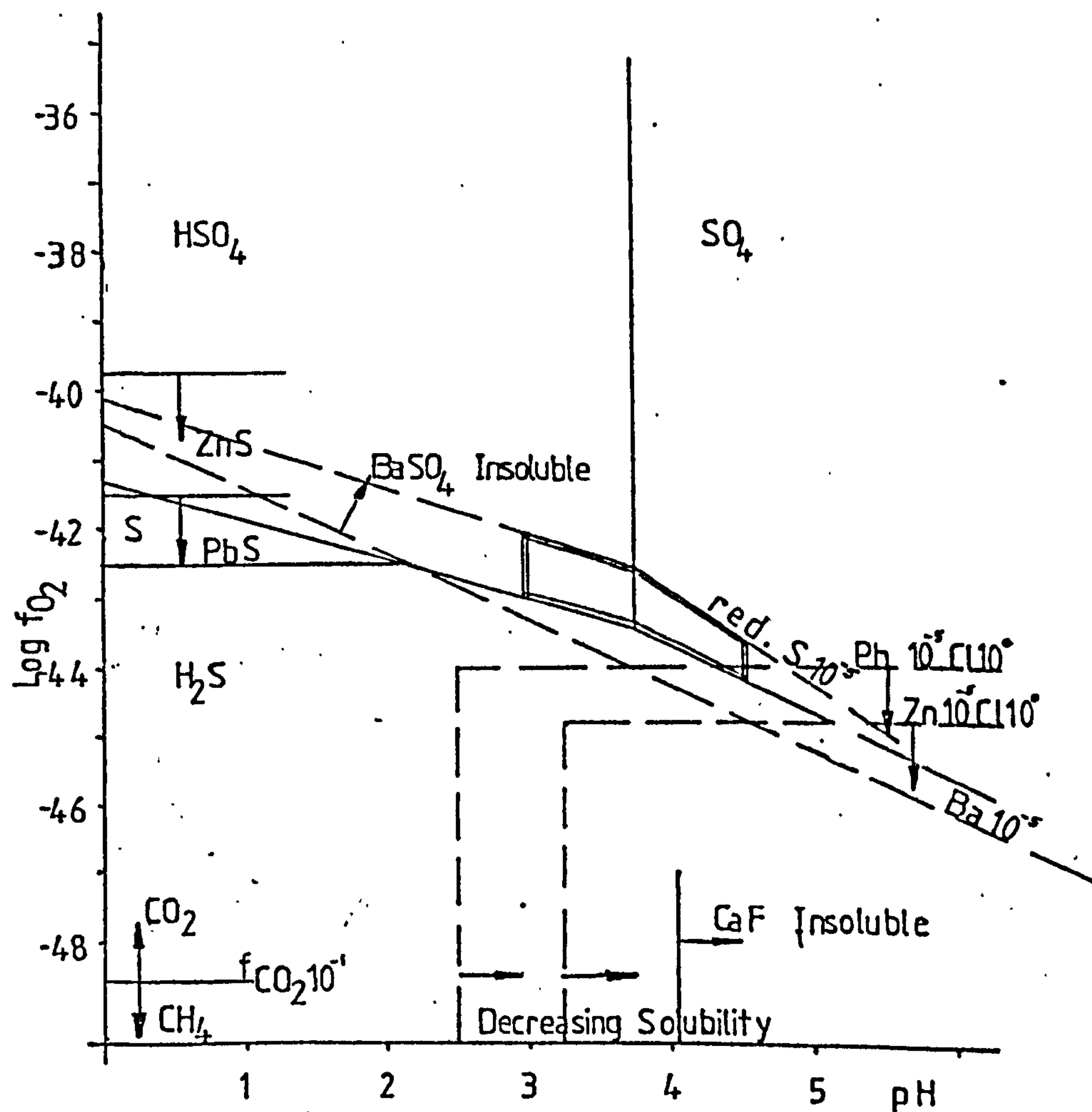


Fig.5.19 pH-log. f_{O_2} plot for the mixed solution producing the barite zone mineralisation, at a temperature of 100°C.

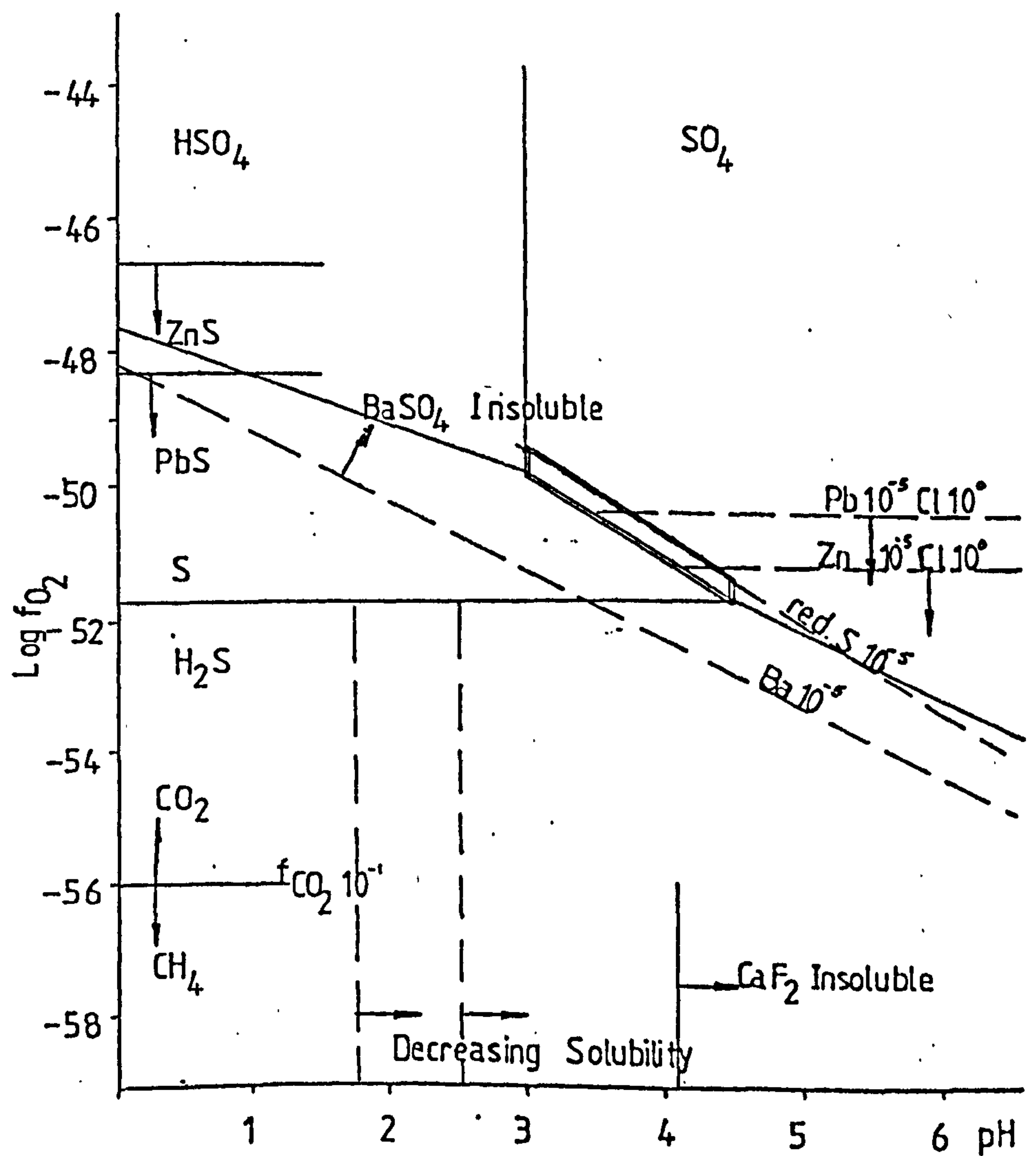


Table 5.10 Summary of $\log fO_2$ - pH results for the barite zone

Temperature 150 °C

	$\log fO_2$	$\log fS_2$
pH = 3.0	-42.0 to -43.0	-6.01 to -7.01
pH = 4.5	-43.5 to -44.2	-7.51 to -8.21

Temperature 100 °C

pH = 3.0	-49.8 to -49.5	-7.53 to -7.23
pH = 4.5	-51.7 to -51.4	-9.43 to -9.13

have been precipitated by decreasing temperature or removal of reduced sulphur from the solution which would lead to the decrease in oxygen fugacity. Bisulphide complexes would only have been precipitated by a decrease in temperature and pressure as decrease in the oxygen fugacity leads to bisulphide complexes becoming more soluble.

5.72. Junction Zone

The junction zone represents the area where the barite and fluorite zones become mutually exclusive. It must therefore be the area where the two solutions start to mix. However, good field evidence is lacking.

Work on the solubility of the various minerals supports a mixing hypothesis. A halt in fluorite deposition will be caused by a decrease in pH and in-sufficient F^- in the solution. Work shows, that to increase the solubility of fluorite quickly, mixing of two solutions is necessary. The more acidic shallow SO_4 -rich solution, undersaturated with respect to fluorite, will when mixed with a solution saturated in fluorite produce the required halt in fluorite deposition.

With regard to barite deposition, Blount (1977) had shown that mixing of two solutions, one rich in Ba^{2+} and the other in SO_4^{2-} would produce large quantities of barite. A similar process was proposed by Hirst and Smith (1974) to produce the barite mineralisation in the Lower Magnesian Limestone, near Ferryhill, and is proposed here for the barite mineralisation in the Northern Pennines.

Thus barite deposition, by the above process, will be

instantaneous where the two solutions meet. At the same time the solution will become undersaturated with respect to fluorite.

The two minerals will thus be found in close proximity along the vein channels where the two solutions first start to mix. Barren zones are encountered where fault conduits are absent. In some areas, (i.e. Nentshead and Nentsberry), both fluorite and barite mineralisation are absent, but sulphides are present, (Dunham, 1948). This may occur where SO_4^{2-} -rich solutions have encountered reducing conditions such that the SO_4^{2-} has been reduced. In these areas the mixing of a solution carrying Ba^{2+} and fluorite with one rich in reduced sulphur will precipitate large quantities of metal sulphides but little or no barite or fluorite.

Metal sulphides are, in general found to be present in large quantities in the junction area, and as no abrupt temperature changes are evident their precipitation must rely on changes in the pH, the oxygen and sulphur fugacity, or the chemical composition of the solution. Log $f\text{O}_2$ -pH diagrams used in sections 5.71 and 5.72, indicate that the oxygen and sulphur fugacities of the shallow SO_4^{2-} solutions and the fluorite solutions were different due to the changes seen for the mixed solution or barite inclusion fluids. Major precipitation of metal sulphides from metal chloride complexes will thus occur due to dilution, increased fugacity of oxygen and sulphur and changes in pH. The reduced sulphur necessary for deposition of sulphides must come from reduction of SO_4^{2-} in the barite solutions.

Hence the sharp demarcation of the fluorite and barite zones may be explained by the mixing of two solutions; one rich in SO_4^{2-} and some metals and the other a Ca-Na-Cl brine rich in Ba^{2+} and metals. Increased sulphide deposition close to the zone also supports this hypothesis.

C H A P T E R S I X

The conclusions drawn from the above study are based on new data on the chemical and isotopic composition of fluid inclusions in quartz, fluorite and barite and incorporates previous data on sulphur isotopes by Solomon, Rafter and Dunham (1971), and on homogenisation temperature and rare earth element contents of fluorite by Smith (1974).

The mineralisation has previously been considered to result from mixing of two fluids. Sawkins (1966), and Smith (1974) have both suggested mixing of formation waters and magmatic fluid, whereas, Solomon, Rafter and Dunham (1971) proposed a sedimentary origin for both fluids.

The present work suggests that sedimentary pore fluids have undergone membrane filtration to produce two distinct ore-fluids. These fluids have migrated into the sedimentary rocks of the Alston block where their migration was controlled by the regional fault pattern and the heat flow directed through the Wear-dale Granite. Minerals were deposited from the cooling fluids in the open fracture system in the Carboniferous rocks. A sharp junction between the barite and fluorite mineralisation indicates the point of mixing of the two solutions.

The geology of the Alston block and surrounding areas has been discussed in Chapters 1 and 5. It indicates that the sedimentary troughs to the north, south and east provide suitable thicknesses of shales and sandstones to generate sufficient fluid for the mineralisation. Palaeogeographical work by Faller and Briden (1978) indicates that the area was between 15°S and 12.5°N of the equator during Lower Carboniferous to early

Permian times. This gives an estimated range δD in the original pore fluid of 0 to -15%.

Compaction of the sedimentary basins which provided the ore-fluids, involved three stages of fluid release. The first release of pore-fluid occurred during initial compaction to a depth of 1,300 m, when 30 to 40% of the pore water from the shales was lost to the surface.

The second stage occurred after further compaction, and production of semi-permeable shale membranes. Pore fluid with an original composition between 0% and -15% δD was released from rocks below the membranes and became modified by the filtration effect of the membrane. Two fluids were thus produced, one was expelled upward through the membrane, while the other was retained as residual pore water. The fluid expelled was highly fractionated (i.e. depleted), with respect to δD and can be represented on a δD , $\delta^{18}O$ plot by a zone of values. This is because of the original variability of the isotopic composition of the pore fluids (Chapter 5). The filtration effect on $\delta^{18}O$ was less marked due to normal water-rock interactions. The expelled fluid had a modified chemical composition, being rich in Na, Li, and H_2S . Other elements such as metal ions may have been added to the fluid by leaching of sediments. SO_4^{2-} may also have been added due to leaching of evaporites. Thus a shallow depth SO_4^{2-} -rich fluid, was generated, which subsequently mixed with the quartz-fluorite fluid to produce the solution represented in the barite inclusion fluids.

A third stage was necessary to produce the deep-seated fluids. This involved the chemical and physical alteration

and dehydration of montmorillonite to illite. In this process K and Mg were fixed by illite and chlorite, while Na, Ca and Si were released to the pore fluid from the montmorillonite. The deep-seated fluid was produced by addition of this clay dehydration water to the residual pore fluid, formed in stage two. This deep fluid will be comparatively enriched in δD compared to the shallow SO_4^{2-} fluid although its isotopic composition will be variable, (Chapter 5). Chemically the solution will be a Ca-Na-Cl brine rich in Ba^{2+} and heavy metals. It will be comparable to the fluorite-quartz inclusion fluids if the latter can be assumed to contain Ba^{2+} .

Thus sediment compaction will produce two fluids, one similar in composition to the fluorite and quartz inclusion fluids, and the other a shallow-depth fluid which was more depleted in δD than the barite inclusion fluids.

Strontium isotope ratios were also used, and further support a sedimentary source for the ore fluids.

During the evolution of these fluids at the end of the Carboniferous and beginning of the Permian, the Hercynian orogeny was producing structural changes. Reactivation of old Caledonian fault trends and initiation of new fault movements produced the structures seen today. Open fault conduits acted as pathways for lateral migration of the fluids into the Alston Block. The deep fluids, under higher pressures, were forced along the conduits into the Lower Palaeozoic basement rocks and the Weardale Granite. At the same time, reheating of the granite produced high heat flow through its cupolas. This directed the deeper fluids upwards through the granite, towards the surface, resulting in deposition of minerals and

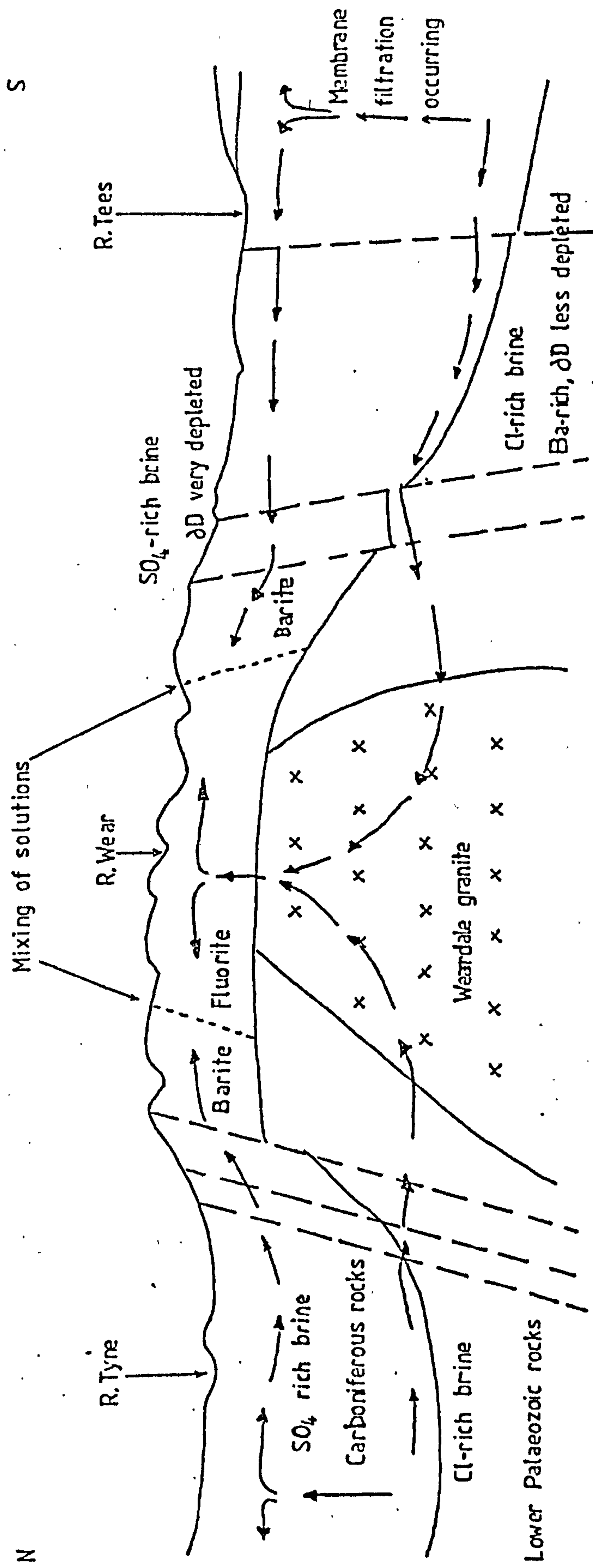
mixing with the high level fluid.

During migration of the Ca-Na-Cl brine, fluorite was carried as CaF_2 (aq.). Additional fluorine was probably carried complexed to Na, K, Hg and minor H. Calcium was also transported as CaCl_2 , CaCO_3 and CaSO_4 . Quartz was carried in the form of H_4SiO_4 or $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and metals were mainly complexed with chlorine. In the near surface fluids SO_4^{2-} , Na, Ca and metal chlorides were present.

Deposition of the minerals is best discussed in terms of the barite and fluorite mineral zones. The fluorite solutions were directed upward through the granite cupolas under Rookhope and Tynehead, Fig. 6.1. Deposition of the fluorite and quartz was mainly due to cooling and changes in pH. Cooling was achieved by loss of heat to the conduit wall rocks. It was also dependent on the rate of flow, faster flow producing less heat loss and hence little cooling. Changes in pH were due to loss of CO_2 , rather than to reaction with the wall rocks because the wall rocks had previously been isolated by silicification. Smith (1974) has also shown progressive cooling from the early to late phase of mineralisation which may be due to a decrease in heat flow from the granite. Variation in the chemical composition of the ore solution must have occurred during deposition, because elements were continually being lost and gained by the solution. This is indicated by the dissolution textures found in some fluorite veins, as well as by the banding of different coloured fluorites with quartz.

Sulphide deposition in these veins was dependent on the amount of reduced sulphur present in the solution. Thus although increases in pH will decrease the chloride complex

Fig.6.1 The mechanism of formation for the Northern Pennine ore minerals proposed from present work.



solubility, the minerals will only be deposited sporadically, parallel to the main mineral banding.

In the peripheral barite zone minor deposition may have resulted from cooling of the near surface fluid. The main barite and sulphide mineralisation however, will occur where the fluorite rich and SO_4^{2-} rich solutions met. At this point instantaneous precipitation of barite and undersaturation of fluorite would result. Barren areas are generally those where faulting is almost absent. A few areas show major sulphide mineralisation but no fluorite or barite (e.g. Nentsberry and Nenthead). These must indicate mixing of the metal rich fluorite solution with a solution rich in reduced sulphur. The latter may have been produced by reduction of the SO_4^{2-} rich solution during its passage through the sediments.

Sulphide minerals are also found in large quantities near the boundaries of the two zones. They would have been precipitated as a result of the mixing process between the solution rich in fluorite and one rich in SO_4^{2-} . Changes in chemical composition, dilution of Cl^- concentrations, changes in gas fugacities, and pH increases, would all have had an affect on the metal chloride complexes, which may have caused major 'dumping' of minerals.

The processes described above, thus provide a mechanism capable of explaining the observed distribution of minerals in the Northern Pennines. Further work is, however, necessary to clarify the situation. Barium and SO_4^{2-} analyses of fluorite and quartz inclusion fluids would provide evidence for and against the above mechanism. $\delta^{18}\text{O}$ values for the fluorite inclusion fluids would also enhance the present work.

Appendix 1: Fluid Inclusion Geothermometry

Al.1 Heating and freezing apparatus

The stage used is shown in Fig. Al.1. It is a dual purpose heating and freezing stage useful over the range +600 °C to -180 °C. Small samples are supported on a metal block inside a temperature controlled chamber, the temperature being measured by a thermocouple in contact with the sample.

In the freezing mode oxygen free nitrogen, pre-cooled with liquid nitrogen, is circulated through the chamber. The temperature is then raised by use of a resistance heater within the metal block, mentioned above. Above room temperature the coolant gas flow is stopped, and the required temperature is achieved by use of the heater alone.

Calibration of the stage was by standard melting point substances, Table Al.1.

Al.2 The Pressure Correction (ΔT)

The homogenisation temperature, shown in all results, is a minimum value for the true trapping temperature, T . A correction ΔT , which is pressure dependent, is therefore necessary, when dealing with large pressure domains.

At the temperature of homogenisation, T_h , when the vapour bubble disappears, the internal vapour pressure of the inclusion is equal to the vapour pressure of the solution. Thus, for any given salinity and brine density, T_h is constant regardless of temperature and pressure. However the degree of brine compressibility determines the original trapping pressure, and the pressure corrections can only be found if an estimate of this

Fig.A1.1 Freezing - Heating stage.

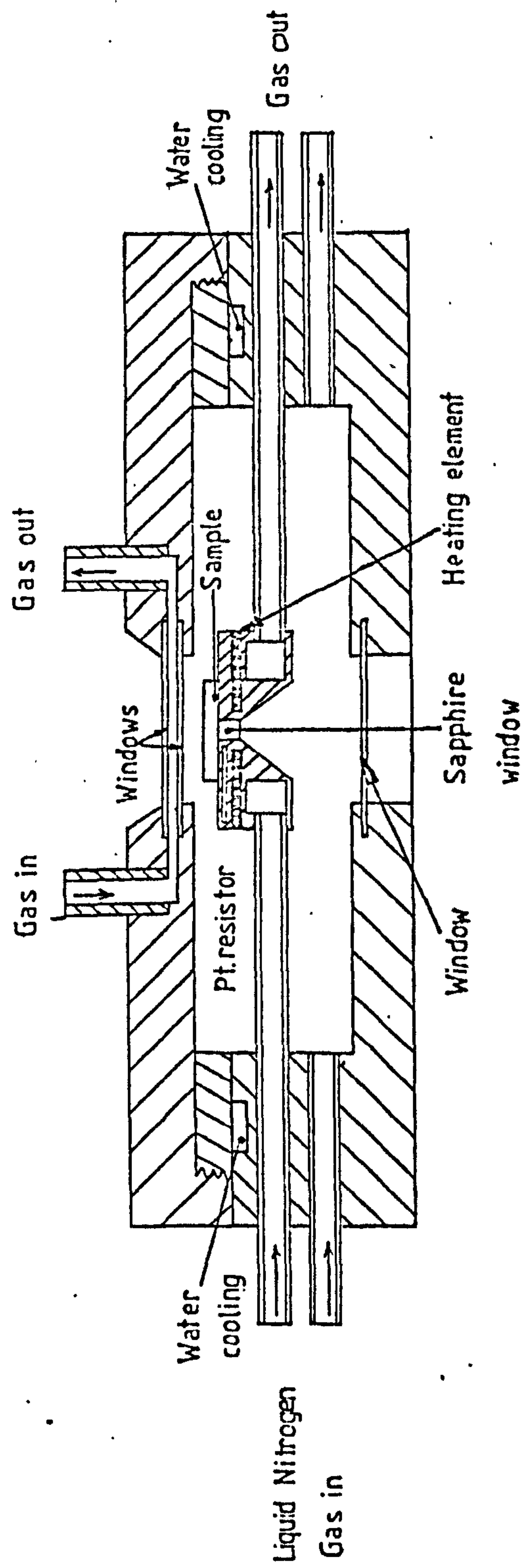


Table A1.1 Calibration Standards for the heating-freezing stage

Organic compound	melting point °C
Hexadecane	+17.5
Pentadecane	+10.0
Tetradecane	+5.86
Tridecane	-5.5
Dodecane	-9.6
Decane	-29.7
Nonane	-51.0
Octane	-56.8
Heptane	-90.6

At temperatures from +100 °C to 600 °C Tempilaq temperature indicating liquids were used to calibrate the stage.

pressure is available. The corrected trapping temperature, T , may however be inaccurate and imprecise as a result of incorporating the factor ΔT , around which there is a high degree of uncertainty. (Smith, 1974). For the present work the correction was not used.

A1.3 Temperature and salinity results

The results acquired during Smith's (1974) study, and the present work are summarised with the chemical and isotopic composition of the fluids in Appendix 5.

Freezing data obtained during this study are shown in Table A1.2.

Table A1.2 Heating and freezing data obtained on barite and fluorite

<u>samples</u>				
Sample	T _{homog.}	Eutectic	Last ice melting point	Hydrohalite melting point
Barite				
R19	89.5	-47.5	-20.1	-
R20	144.8	-46.7	-20.1	-
R121	90.9	-63.5	-13.1	-29.4
6210	115.0	-49.0	-22.0	-
6476	123.9	-46.7	-14.7	-26.0
6477	87.7	-46.7	-21.4	-27.2
6522	130.8	-38.7	-19.1	-26.0
6587	92.4	-44.0	-19.4	-26.1
20725	136.6	-48.9	-19.5	-26.6
20839	82.9	-47.0	-18.4	-27.7
Fluorite				
R28	151.7	-37.9	-20.0	-
R39	82.5	-73.7	-33.2	+1.56
R50	100.6	-47.1	-20.4	+0.90
R74	85.6	-46.6	-22.2	-

All temperatures are in °C.

Appendix Two

A2.10. Vacuum extraction line

The vacuum extraction line shown in Fig. A2.1. was used in the present work. Prior to analysis all volumes were calculated at their running temperatures. They gave the following figures:-

	Volume. cm ³
Cold Trap 1. (CT ₁)	92.65
Cold Trap 2. (CT ₂)	129.00
Uranium Furnace (UF)	49.00
Primary Measuring Volume (PMV) }	82.00
Cold Finger (F) }	
Quadruple Graphite trap (QGT)	8.00

Thus the Total measuring volume was.

$$CT_1 + CT_2 + (PMV + CF) + UF = T.M.V. = 352.65$$

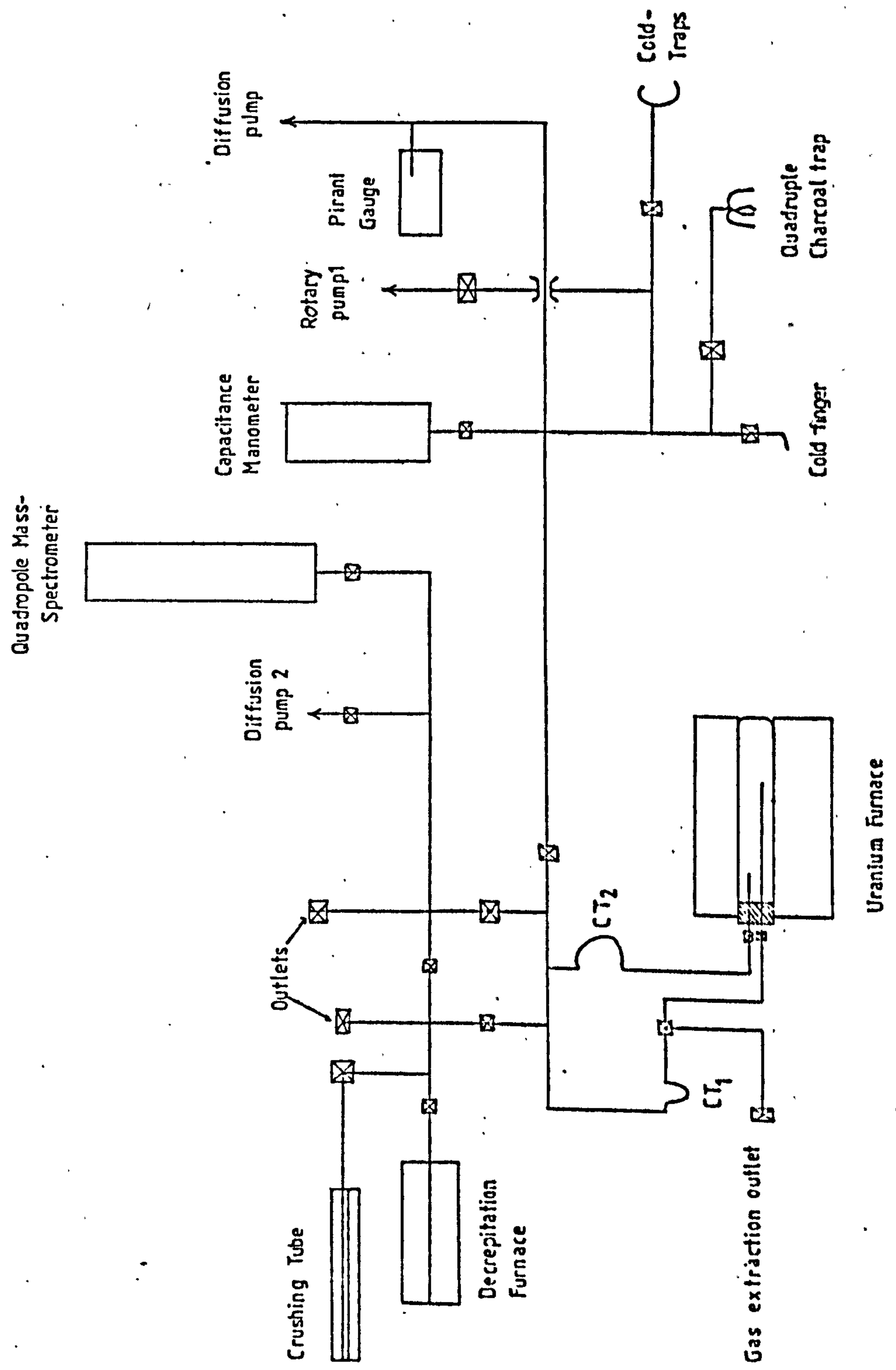
These values are used in the following gas analysis sections for calculations of the amounts of the different gases.

A2.20. Calculations required for the chemical analysis of inclusion fluids

Calculations required to produce the results given in Appendix 5, depend on initial gas analysis of the decrepitated samples, in terms of weight of water and CO₂ extracted. These values then form the basis of the calculation of fluid inclusion concentrations from leachate analysis.

Standard solution and optimal conditions required for the chemical analyses are given in section A2.40.

Fig.A2.1 Vacuum line used for the quantitative extraction of inclusion fluids.



A2.21. Calculation of the weight of inclusion fluid

The ideal gas law is:-

$$PV = nRT \quad (\text{Atkins, 1978}) \quad \dots(1)$$

where P = pressure Nm^{-2} (Newton metre⁻²)

V = volume m^3 or 10^3cm^3

n = nos. moles of gas

T = temperature $^{\circ}\text{K}$ (295°K)

R = gas constant = $8.31441 \text{ NmK}^{-1} \text{ mol}^{-1}$

In the present study pressure is measured in milliTorrs thus conversion factors are required:-

$$1 \text{ atm} = 760 \text{ Torr} = 1.01325 \times 10^5 \text{ Nm}^{-2}$$

$$1 \text{ mTorr} = \frac{1.01325 \times 10^5 \times 10^{-3}}{760}$$

Substituting into equation 1.

$$n = \frac{\left[\frac{P \times 1.01325 \times 10^2}{760} \right] \left[V \times 10^{-3} \right]}{8.31441 \times 295}$$

$$n = 5.44 \times 10^{-8} \times P \times V. \text{ moles of gas} \quad \dots(2)$$

To find the weight of gas the number of moles of gas must be multiplied by the molecular weight. Thus equation 2 becomes:-

$$\text{Weight of } \text{H}_2 = 544 \times 10^{-8} \times P \times V \times \text{mol.wt.}(\text{H}_2) \text{ grams} \quad \dots(3)$$

The weight of water is given by:-

$$\text{Weight of H}_2\text{O} = \text{weight of gas} \times \frac{\text{mol.wt H}_2\text{O}}{\text{mol.wt H}_2} \quad \dots(4)$$

Thus equation (3) becomes:-

$$\text{Weight H}_2\text{O} = 5.44 \times 10^{-8} \times P \times V \times 2 \times \frac{18}{2} \text{ grams} \quad \dots(5)$$

As the volume has previously been calculated, and the pressure of the extracted gas measured, the weight of the inclusion fluid can be calculated.

At low gas pressures a correction is necessary due to absorption of hydrogen in the uranium furnace. The percentage pressure correction is shown in Fig. A2.2, and equation 5 becomes:-

$$\text{Weight H}_2\text{O} = (5.44 \times 10^{-8} \times 18 \times PV) + (5.44 \times 10^{-8} \times 18 \times PV \times \% \text{ correction}) \quad \dots(6)$$

A2.22. Calculation of the volume and weight of CO₂

This calculation uses Boyles Law, which states:-

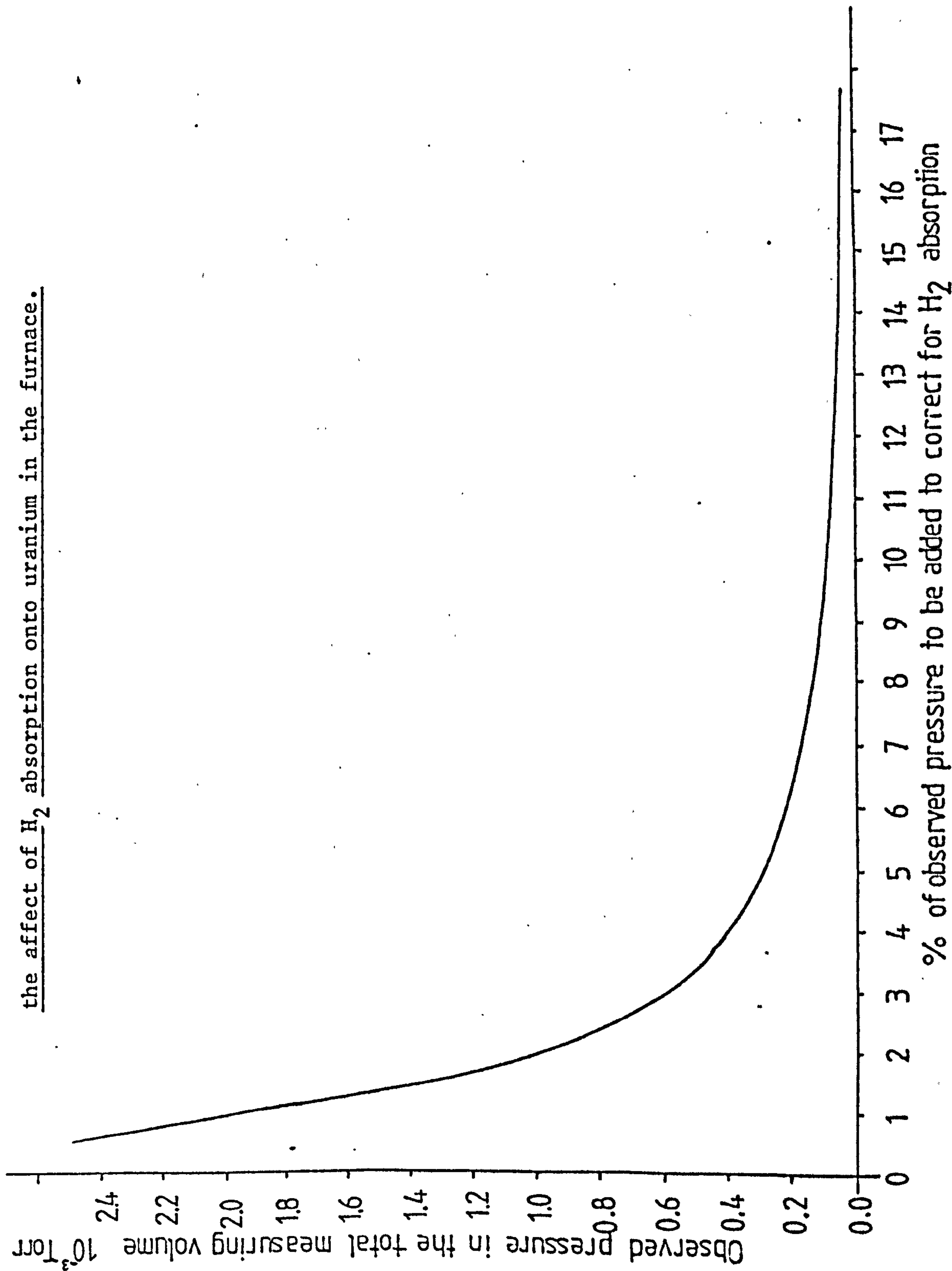
$$PV = \text{constant}$$

$$\text{or } P_1V_1 = P_2V_2 \text{ at constant temperature}$$

Taking P_1V_1 to be the values at s.t.p. and P_2V_2 the values when the gas is extracted, the following relationship is derived

$$V_1 = \frac{P_2V_2}{P_1} = \frac{P_2 \times 10^{-3} \times \text{Primary measuring vol.}}{760}$$

Fig.A2.2 The percentage pressure correction to be added to measured H_2 pressure to eliminate the affect of H_2 absorption onto uranium in the furnace.



$$V_1 = \frac{P_2 \times 10^{-3} \times 82}{760} \text{ moles} \quad \dots(7)$$

To find the volume of the gas in cm^3 the standard 22.4 cm^3 volume of one mole of gas is applied.

$$V_1 = \frac{P_2 \times 10^{-3} \times 82}{760} \times \frac{1}{22.4} \text{ cm}^3 \quad \dots(8)$$

The weight of the gas is then given from multiplication by the molecular weight.

$$\text{Weight CO}_2 = \frac{P_2 \times 82}{760} \times \frac{10^{-3}}{22.4} \times 44 \text{ grams}$$

$$\text{Weight CO}_2 = 0.2119 \times 10^{-3} \times P \text{ grams} \quad \dots(9)$$

Calculation of the $\text{CO}_2:\text{H}_2\text{O}$ ratio by weight is thus given by division of the result from (9) by the result from (6).

A2.23. Calculation of the volume of non-condensable gases

The procedure used to calculate the volume of CO_2 again applied, substituting values of pressure (in Torrs) equivalent to the non-condensable gas volumes.

$$V_1 = \frac{P \times \text{Tot. volume used}}{760} \times \frac{10^3 \text{ cm}^3}{22.4} \quad \dots(10)$$

The ratio of non-condensable gases to CO_2 is calculated from the results of (10) divided by (8).

A2.24. Calculation of trace gas analysis

Results are given in Table A2.1. Calculations were made from mass-spectra cracking patterns, Table A2.2. The

Table A2.1 Trace Gas Analysis

Mass	Background $\times 10^{-6}$ Torr	Sample $\times 10^{-6}$ Torr	True sample $\times 10^{-6}$ Torr
2	0.210	4.00	3.790
12	0.028	0.15	0.122
13	-	0.13	0.130
14	0.006	0.90	0.894
15	0.013	5.20	5.187
16	0.028	5.60	5.572
17	0.042	0.14	0.098
18	0.100	0.80	0.700
28	0.230	4.70	4.470
29	0.005	-	-
39	-	-	-
40	-	0.01	0.010
44	0.009	0.04	0.031

TABLE A2.2. Mass spectra cracking patterns.

[illegible]

masses marked with an asterix Table A2.3, represent the starting masses taken for calculation of each of the gas components. Thus 0.031 milli Torr of mass 44 is equivalent to 100% CO₂ and 0.002 of mass 12 is equivalent to 6% of the CO₂ total. From Table A2.2, it can be seen that mass 28 represents 100% N₂ and CO. However it is more likely that N₂ is present than CO. A small amount of CO may be produced from the source but will be negligible. CO₂ and H₂O are not non-condensable gases and must therefore originate from outgassing of the unbaked line to the quadropole mass-spectrometer.

After estimations of the amounts of gases corrections were made for the sensitivity of the gauge to the different gases. Calibration factors for a general ionisation gauge are shown in Table A2.4. Corrections were calculated using the following equation.

$$\text{True press} = \text{calibration factor} \times \text{measured pressure} \quad \dots(11)$$

The total non-condensable pressure was $0.003 \times 10^{-3} \text{ T}$ and hence the gas components were scaled to this pressure by the following equation.

$$\begin{aligned} \text{Pressure equivalent in non-} &= \frac{\text{True press.} \times 0.003 \times 10^{-3}}{\text{Total true pressure}} \\ \text{condensable gas total.} & \end{aligned} \quad \dots(12)$$

$$= \frac{0.003 \times \text{True Pressure}}{20.318 \times 10^{-6}}$$

Boyles Law was again used to find the volume of these

Table A2.3 Derivation of gas components

Mass	CO ₂	Sample remainder	CH ₄	remainder	H ₂ O	remainder
2		3.790	.167	3.623	.005	3.618
12	.002	.120	.134	-		-
13		.130	.429	-		-
14		.894	.869	0.025		0.025
15		5.184	4.639	0.548		0.548
16	.003	5.569	*5.569	-	.008	-
17		0.098	0.067	0.031	.161	-
18		0.700		0.700	*.700	-
28	.004	4.466		4.466		4.466
40		0.000		0.010		0.010
44	*.031	-		-		-

Table A2.4 True pressures of trace gases

Gas	Pressure measured $\times 10^{-6}T$	Calibration Factor	True Pressure $\times 10^{-6}T$	% Total Press. Non-condensibles
CH ₄	5.569	0.7	3.898	19.18
N ₂	4.466	1.0	4.466	21.98
H ₂	3.618	3.1	11.216	55.20
Ar	0.010	0.9	0.009	0.04
CO ₂	0.031	0.7	0.022	0.11
H ₂ O	0.700	1.01	0.707	3.48
Total			20.318	99.99

Table A2.5 Volumes of trace gases

Gas	Pressure equivalent $10^{-3}m$ Torr.	Volume $10^{-8}cm^3$	Vol. N.C./CO ₂ ratio
CH ₄	0.576	1.192	0.0604
N ₂	0.659	1.364	0.0691
H ₂	1.656	3.428	0.1736
Ar	.001	0.002	0.0001
CO ₂	.003	0.006	0.0003
H ₂ O	.104	0.215	0.0109

gases at s.t.p. This allowed the trace gas : CO₂ ratio to be calculated, Table A2.5.

Major gas components were calculated as above, giving:-

N.C.	=	0.003 mT.	Vol	=	$5.22 \times 10^{-8} \text{ cm}^3$	
CO ₂	=	.041 mT.	V ₁	=	$19.75 \times 10^{-8} \text{ cm}^3$	wt = 0.009 mg
H ₂	=	3.396 mT.	wt	=	1.15 mg (H ₂ O)	

The ratios of N.C. : CO₂ and CO₂ : H₂O are respectively 0.264 and 0.0078.

A2.30. Calculation of element concentrations from leachates

During analysis the following parameters were measured:

- final leachate concentration (ppm)
- dilution factor of aliquot from leachate
- amount of deionised water used initially in leaching
- conversion of leachate volume (cm³ to litres)
- weight of inclusion fluid for each individual sample.

The fluid inclusion concentrations were calculated for all methods of chemical analysis, the different analytical techniques requiring different calculations, as below:

A2.31. Flame Photometry

A 1 ml aliquot of the original 10 ml leachate was diluted to 4 ml. The concentrations of Na and K in the inclusion fluid are given by:-

$$\text{Concentration of element} = \frac{\text{concentration final leachate} \times 4 \times 10^3}{\text{weight fluid inclusion}}$$

Values of Na or K, in ppm, were converted to NaCl or KCl ppm by:-

$$\text{Concentration MCl (ppm)} = \text{M concn. (ppm)} \times \frac{\text{molecular weight MCl}}{\text{molecular weight M}}$$

where M = Na or K, and the atomic weights of Na, K and Cl are 22.99, 39.10 and 35.45 respectively.

To convert the MCl ppm values to weight percentage graphs were used from data given in Weast (1977), Fig. A2.3. and Fig. A2.4.

A2.32. Atomic Absorption Spectrometry

Analyses for metallic elements were carried out on the 10 ml leachates without further dilution. The concentration in the inclusion fluid was thus:-

$$\text{concn. metal (ppm)} = \frac{\text{final leachate concn.} \times 10 \times 10^3}{\text{weight of fluid inclusion}}$$

A2.33. Neutron Activation analysis

Only one leach of 5 ml was taken for each sample thus the element concentrations found were derived from:-

$$\text{concn. metal} = \frac{\text{final leachate concn.} \times 5 \times 10^3}{\text{weight of fluid inclusion}}$$

A2.34. Pyrohydrolytic Analysis

Calculations made in the analysis of chlorine and

Fig.A2.3 Graph for the conversion of NaCl ppm to NaCl weight percent.

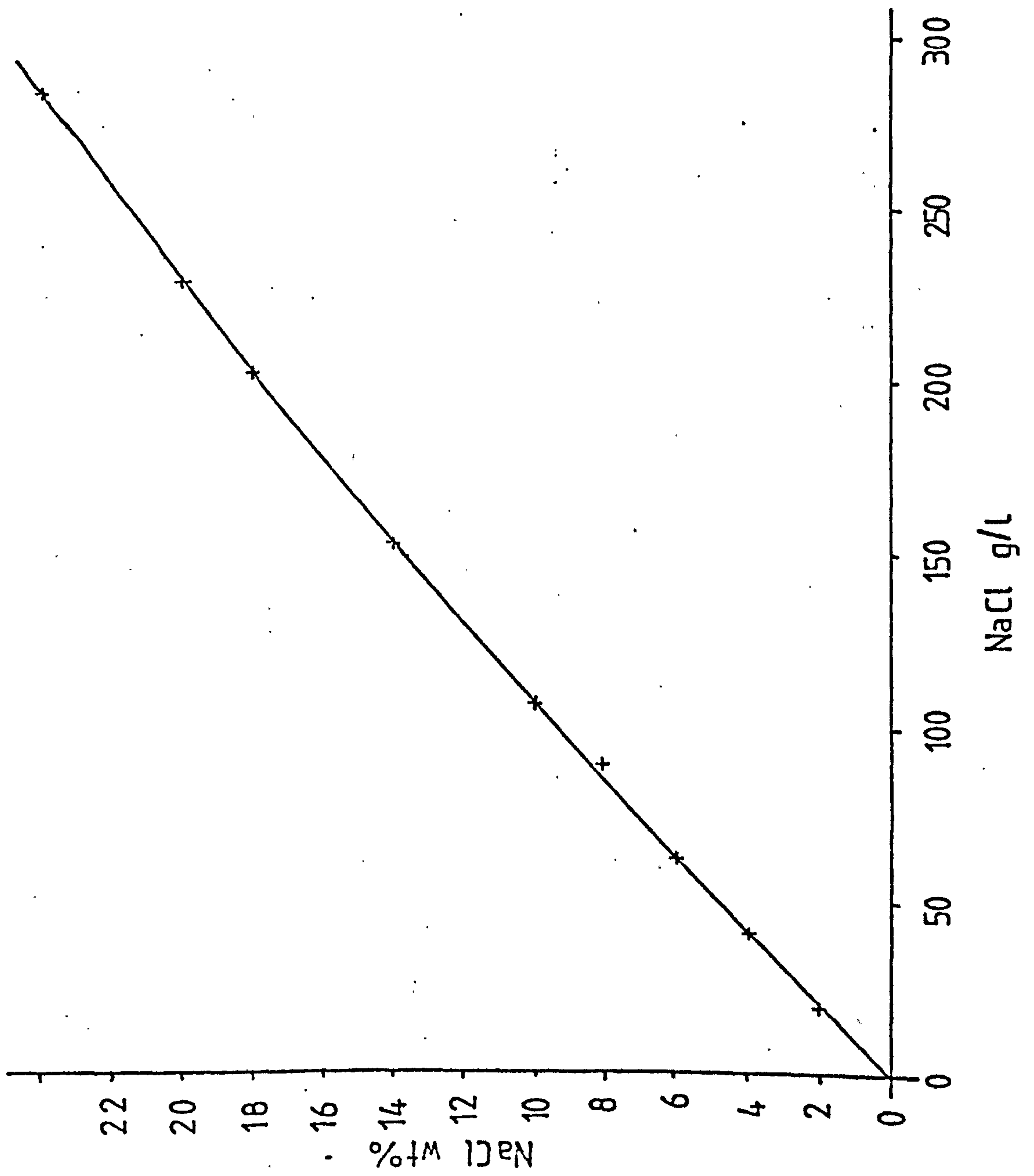
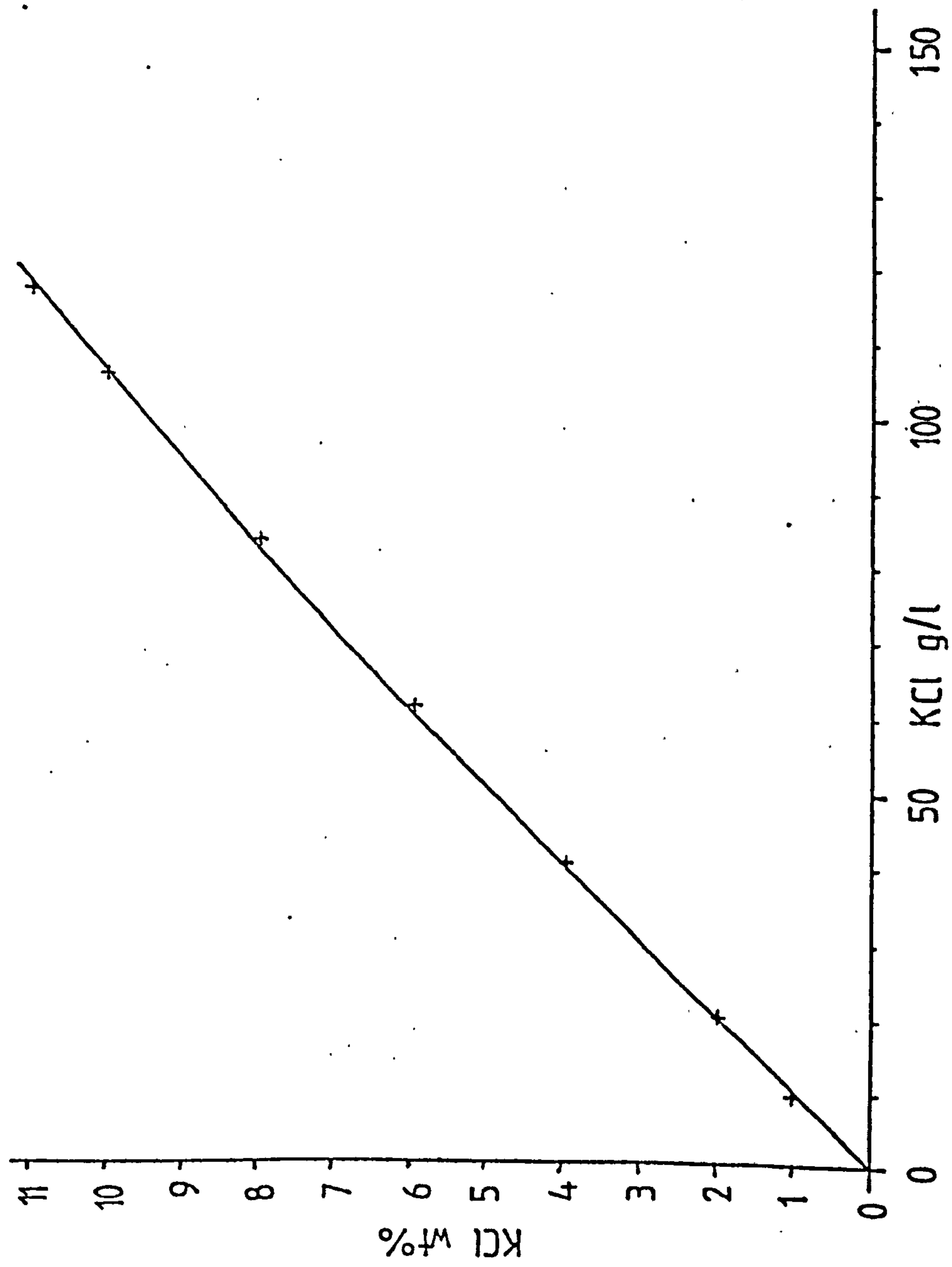


Fig.A2.4 Graph for the conversion of KCl ppm to KCl weight percent.



fluorine involved several assumptions:

- (i) The flux mixture was made up of z grams of sample and y grams of V_2O_5 and it was assumed that the 1 gram of mixture analysed would contain the sample in the ratio $z/z + y$ where $z + y = 1.5$ gram
- (ii) The Cl and F were collected in 50 ml of distillate and it was assumed that the concentration of elements in 1 ml of the distillate was $(c \times 50)$ where c was the concentration of the element measured (ppm).

The amount of sample used must therefore have produced the Cl/F concentration in 1 ml of distillate and thus the concentration of Cl or F in one gram of sample would be.

$$\text{concentration (per gram sample)} = c \times 50 \times \frac{z + y}{z}$$

The last assumption was that the amount of inclusion fluid throughout a sample was approximately constant and thus previous gas analyses could be used to estimate the amount of fluid applicable to each sample.

Therefore the Cl or F concentration in the inclusion fluids will be given by

$$\text{concentration Cl/F (ppm)} = 50 \times C \times \left\{ \frac{z + y}{z} \right\} \times \frac{10^3}{w}$$

where w is the estimated weight of inclusion fluid in 1 gram of sample.

All results are given in Table A2.6.

Table A2.6 Pyrohydrolytic Analysis Results

Sample	aCl ⁻	aF ⁻	z	y	$\frac{z + y}{z}$	w
414	.40	.015	.2460	1.2498	6.080	0.46
416	.15	.005	.2500	1.2500	6.000	0.37
416 rpt	.15	.005	.2502	1.2500	5.996	0.37
418	.55	.030	.2500	1.2500	6.000	0.47
419	.95	.045	.2502	1.2500	5.996	1.49
424	.85	.030	.2500	1.2500	6.000	0.40
R101.1	.15	5.23	.2503	1.2500	5.994	0.82
R102.3	.15	2.98	.2500	1.2500	6.000	0.993

Concentrations in the fluid inclusions

Sample	Cl ⁻ ppm x 10 ³	F ppm x 10 ³	Cl ⁻ /F
414	264.3	9.91	26.7
416	121.6	4.05	30.0
416 rpt	121.5	4.05	30.0
418	351.1	19.15	18.3
419	191.1	9.05	21.1
424	637.5	22.50	28.3
R101.1	54.8	1,911.50	0.03
R102.3	45.3	900.30	0.05

A2.35. Sulphate Analysis Corrections

Standards of known concentration were run to obtain calibration graphs for calculation of sample concentrations. Peak heights and backgrounds were measured and sloping back-ground corrections carried out. Dead time corrections were also applied.

The correction for sloping backgrounds, required $b_1 > b_2$,

$$\text{background } b = b_2 + (b_1 - b_2) \left[\frac{\text{abs } (2\theta_p - 2\theta_{b1})}{\text{abs } (2\theta_{b1} - 2\theta_{b2})} \right]$$

with b_1 and b_2 the backgrounds measured and b the corrected background. The 2θ values are those used for the peak and backgrounds during measurement, and abs 2θ values are the angle of peak multiplied by the counts measured at that position.

The dead time correction for the peak height is:-

$$p^* = \frac{p}{1 - P/t.t^*}$$

where p and p^* are the measured and corrected peaks respectively, t is the time interval and t^* is the dead time constant. For the equipment used the dead time constant = 1.4×10^{-6} secs. After calculating the above the count rate, r , could be calculated from the following.

$$r = \frac{p^* - b}{t}$$

Calibration graphs of concentration (SO_4^{2-}) against count rates per sec. were then drawn.

A2.40. Solutions and conditions needed for atomic absorption spectrometry

Standard conditions on the 1L453 atomic absorption spectrometer, for the different elements studied are shown in Table A2.7. Table A2.8., shows the sensitivities and optimal ranges for the different elements.

Standard solutions were made up for each element in the following ways:-

a) Calcium

2.7693 grams of CaCl_2 were weighed out and dissolved in deionised water. The solution was then made up to one litre.

b) Copper

Concentrated nitric acid was added to 1.000 grams of copper until it dissolved. Deionised water was then added to make one litre.

c) Iron

Similar to copper only using 1.000 grams of iron filings.

d) Magnesium

Using 1.000 grams of magnesium granules. Otherwise similar to copper.

e) Manganese

3.601 grams of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in deionised water and diluted to one litre.

f) Strontium

2.415 grams of $\text{Sr}(\text{NO}_3)_2$ were dissolved in deionised water and diluted to one litre.

g) Zinc

1.000 grams of zinc were dissolved in conc. nitric acid

Table A2.7 Standard conditions on the 1L.453 atomic absorption
spectrometer for different elements

Element	Lamp	P.M.	Slit	Wavelength	Flame
	Current	Voltage	Width		(Fuel-acetylene)
	mA.	V.	μ m.	n.m.	
Ca	7	530	320	422.7	Stoichiometric
Cu	5	530	320	324.7	Stoichiometric
Fe	9	620	160	248.3	Lean
Mg	4	530	320	285.2	Stoichiometric
Mn	5	530	320	279.5	Rich
Sr	7	530	320	460.7	Rich
Zn	5	530	320	213.9	Rich

Table A2.8 Sensitivities and Optimal ranges for atomic absorption
spectrometry

The likelihood of being able to measure an element depends on the sensitivity and optimal range for the particular element.

Element	Sensitivity g ml ⁻¹	Optimal Range g ml ⁻¹
Ca	0.05	0.02 - 10
Cu	0.05	0.02 - 10
Fe	0.10	0.05 - 20
Mg	0.005	0.003 - 1
Mn	0.03	0.03 - 6
Sr	0.07	0.07 - 16
Zn	0.01	0.01 - 2
Ba	>0.20	0.20 - 80
Co	0.06	0.10 - 14
Ni	0.05	0.05 - 11
Pb	0.20	0.20 - 3

Ba analysis requires a nitrous oxide flame.

and diluted with deionised water to one litre.

A2.50. Neutron Activation Analysis: Isotopic Information

The isotopes measured by neutron activation, to enable calculation of element concentrations are shown in Table A2.9. Various parameters are also given such as the $\frac{1}{2}$ life, the natural abundance, the gamma energy emitted and its relative intensity as well as the activity cross-section of the element.

Table A2.9 Isotopic information used for neutron activation analysis (Weast, 1977)

Isotope	natural abundance	Radioactive Isotope	Half-life	Energy emitted	relative intensity	Thermal neutron capture cross-section
	%			Kev	%	(Barnes)
⁸¹ ₃₅ Br	49.5	⁸² Br	6.1 m	776.5	83	3.00
³⁷ ₁₇ Cl	24.5	³⁸ Cl	37.3 m	2,167.6	100	0.43
¹³³ ₅₅ Cs	100.0	¹³⁴ Cs	2.9 h	604.7	98	2.66
¹²⁷ ₅₃ I	100.0	¹²⁸ I	25.1 m	442.9	17	6.20
⁴¹ ₁₉ K	6.9	⁴² K	12.4 h	1,524.0	100	1.30
²³ ₁₁ Na	100.0	²⁴ Na	15.0 h	1,368.7	100	0.40
⁸⁷ ₃₇ Rb	27.8	⁸⁸ Rb	17.8 m	1,835.9	100	0.12

where m = minutes

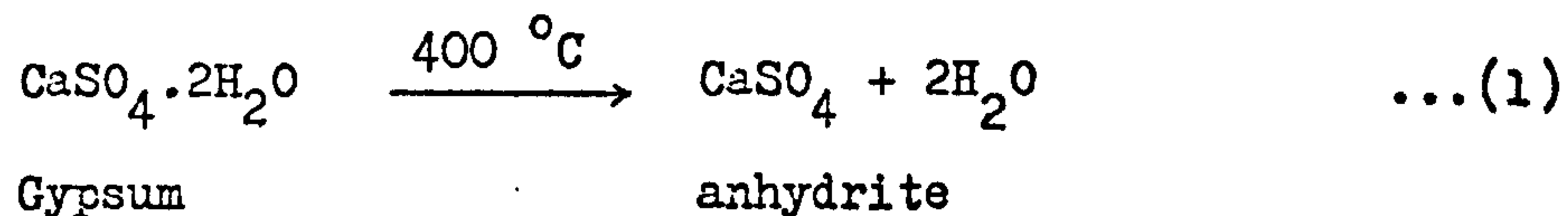
h = hours

Appendix 3

A3.1. Gypsum Standards

- (1) GP1 - A high purity standard - which is white and massive. It comes from Watford in Somerset, and is a useful δD standard.
- (11) GP2 - A less pure standard of the white massive variety. It contains blebs of hematite. It produces unreproducible δD values and was not used further.

The Gypsum dehydration reaction used was:



The relevant atomic weights are

Ca = 40.08	CaSO_4	= 120.14
S = 32.06	$2\text{H}_2\text{O}$	= 36.00
O = 16.00	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	= 156.14

Thus the above equation (1) gives:-

1 mole of gypsum dehydrates to give off 2 moles of H_2O
or 156.14 grams of gypsum dehydrates to give off 36 grams
of H_2O . $\therefore$ 1 gram of gypsum will give $\left[\frac{36}{156.14} \right]$ or .2306 grams

of H_2O . This calculation was necessary to find how many grams of gypsum provided 5 to 10 mgs of water for analysis.

Prior to dehydration, surface moisture is removed by use of a dessicator for 24 hours and outgassing at 40°C

under vacuum.

A3.2. δD calculation and corrections

Ratios of DH/H_2 for samples against references are obtained by mass spectrometer analysis. These are converted to δD by the following equation.

$$\delta D = \left[\frac{DH/H_2 \text{ samp.}}{DH/H_2 \text{ ref.}} - 1 \right] 10^3 \quad \dots(2)$$

where the ratios represent the average of eight runs. These measurements must, however, be corrected for H_3^+ contributions and cross-talk corrections.

H_3^+ is produced when H_2 and H^+ combine in the source and the contribution is given by:-

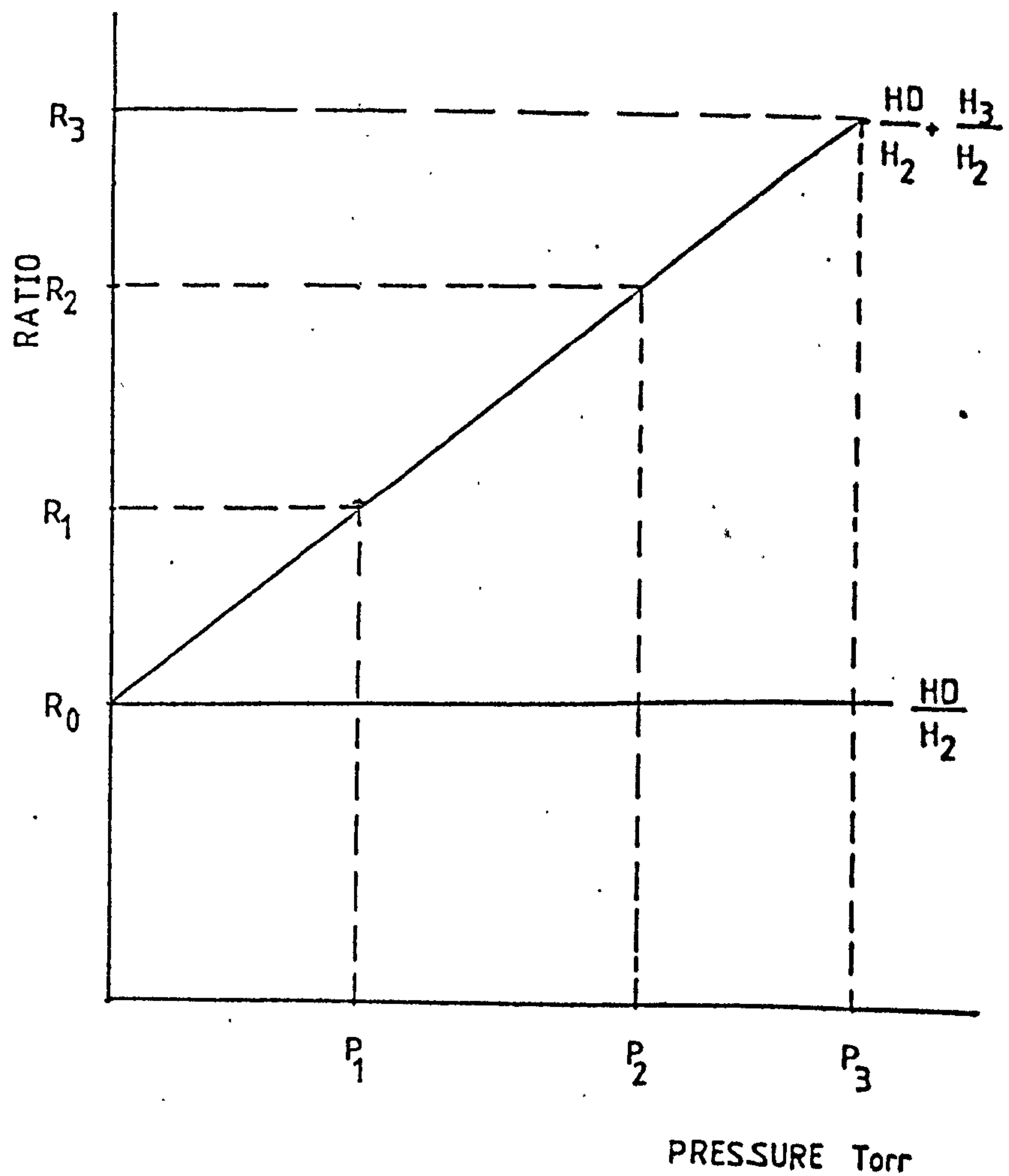
$$\left[\frac{DH}{H_2} \right]_{\text{meas.}} = \left[\frac{DH}{H_2} \right]_{\text{True}} + \left[\frac{H_3^+}{H_2} \right] \quad \dots(3)$$

To find the true ratio the H_3^+ contribution must be subtracted from the measured ratio. Hence it is necessary to find H_3^+/H_2 . The H_3^+ contribution is dependent on the pressure of the gas and increases in pressure result in H_3^+ increases. At any given pressure the H_3^+ contribution is represented by:-

$$\left[H_3^+/H_2 \right]_{p_1} = \left[\text{major peak} \right]_{p_1} \times \text{slope} \quad \dots(4)$$

The slope can be calculated by measuring major peaks and DH/H_2 ratios at three different pressures, Fig. A3.1. If no H_3^+ were present the ratio would remain the same, however its change may be found by calculation of the slope

Fig.A3.1 The affect of the H_3^+/H_2 contribution on the DH/H_2 ratio as a function of pressure.



$$Y = mX + c$$

$$R_1 = mP_1 + c$$

$$R_3 = mP_3 + c$$

$$\text{The slope, } m = \frac{R_3 - R_1}{P_3 - P_1}$$

m = slope, ie. the H_3 contribution at any P and R
 c = the basic ratio R_0

between the values. The correction for H_3^+ contribution can then be made by combining equations 3 and 4.

$$\left[\frac{DH}{H_2} \right]_{\text{true}} = \left[\frac{DH}{H_2} \right]_{\text{meas.}} - \left[\text{maj. peak} \times \text{slope} \right] \dots(5)$$

A further correction necessary is the x talk correction. This is due to leakage of gas from the sample side to the reference side of the mass spectrometer, and visa versa, during analysis.

$$\delta D_{\text{corr}} = \delta D_{\text{meas}} - \frac{(\text{Tot\% crosstalk} \times \delta D_{\text{meas}})}{1000} \dots(6)$$

where the % cross talk for one side is given by

$$\% \text{ cross-talk}_{\text{ref-samp}} = \frac{\text{Background}_2 - \text{Background}_1 \times 100}{\text{major peak of ref.}} \dots(7)$$

B_1 = background of sample side before gas allowed into reference side

B_2 = background of sample side after reference gas input (i.e.leakage).

The total cross talk percentage is

$$\text{Total \% cross talk} = \% \text{ cross talk}_{\text{ref-samp}} + \% \text{ cross talk}_{\text{samp-ref}} \dots(8)$$

Lastly the measured $\delta D_{\text{samp-ref}}$ must be corrected to S.M.O.W. to obtain $\delta D_{\text{samp-SMOW}}$. The following equation is used.

$$\delta D_{\text{samp-SMOW}} = \delta D_{\text{samp-ref}} + \delta D_{\text{ref-SMOW}} + 10^3$$

$$\left[\delta D_{\text{samp-ref}} \cdot \delta D_{\text{ref-SMOW}} \right] \dots (9)$$

where δD refers to equation 2. and samp. ref and S.M.O.W. refer to sample, reference and standard mean ocean water.

A3.3. Correction of $\delta^{18}\text{O}$ for Quartz samples

The mass spectrometer results were generated in the form of ratios of masses:-

$$\frac{45}{44} = \frac{C^{13}_O^{16} + C^{12}_O^{16}_O^{17}}{C^{12}_O^{16}_O^{16}} \dots (10)$$

$$\frac{46}{44} = \frac{C^{12}_O^{18}_O^{16} + C^{12}_O^{17}_O^{17} + C^{13}_O^{16}_O^{17}}{C^{12}_O^{16}_O^{16}} \dots (11)$$

Using Craig's (1957) method these were then recalculated to produce $\delta^{18}\text{O}$ values relative to NBS-28 and $\delta^{13}\text{C}$ values relative to PDB. The oxygen values are then converted to SMOW by the following equation.

$$\delta^{18}\text{O}_{\text{samp-SMOW}} = \delta^{18}\text{O}_{\text{sample-NBS-28}} + \delta^{18}\text{O}_{\text{NBS-28-SMOW}} + 10^3 \left[\delta^{18}\text{O}_{\text{samp-NBS}} \cdot \delta^{18}\text{O}_{\text{NBS-SMOW}} \right] \dots (12)$$

$$\text{where } \delta^{18}\text{O}_{\text{samp-NBS-28}} = \left[\frac{O^{18}/O^{16}_{\text{samp}}}{O^{18}/O^{16}_{\text{NBS-28}}} - 1 \right] 10^3 \dots (13)$$

Once in terms of SMOW, the results were corrected for fractionation between Quartz and water. Taylor's (1974), fractionation factor derived from Clayton et al.'s (1972), value, was used.

$$10^3 \ln \alpha_{\text{Qtz-Water}} = 3.57 \times \frac{10^6}{T^2} - 2.73 \quad \dots(14)$$

where T = Temp. °K and α = fractionation factor.

The fractionation factor is related to $\delta^{18}\text{O}$ by the equation

$$\alpha = \frac{1 + 10^3 \cdot \delta^{18}\text{O}_{\text{Quartz}}}{1 + 10^3 \cdot \delta^{18}\text{O}_{\text{Water}}} \quad \dots(15)$$

Thus by using equations (14) and (15) the $\delta^{18}\text{O}$ water can be calculated. This gives the values shown in Table A3.1.

A3.4. Correction for Salinity affects

Previous work had shown that salts in a solution produced fractionation of the isotopes. Thus Sofer and Gat's (1972) equation was used to correct for this. Results are shown in Table A3.1.

$$\left[\frac{\delta_o - \delta_m}{1000 + \delta_m} \right] 10^3 = 1.11 M_{\text{Mg}} + 0.47 M_{\text{Ca}} - 0.16 M_{\text{K}} \quad \dots(16)$$

where δ_o = $\delta^{18}\text{O}$ value salinity corrected

δ_m = $\delta^{18}\text{O}$ value previously measured and corrected
for Qtz. fractionation

M = molality of the element chlorides such that

$$M = \frac{1000 \times (\text{conc. of element} \times 10^{-3})}{\text{mol. wt. compound} \left[(1000 \times \text{density of solute}) - (\text{conc. of element} \times 10^{-3}) \right]} \quad \dots(17)$$

Table A3.1 Oxygen isotope results for quartz samples

Sample	$\delta^{18}\text{O}_{\text{Quartz}}$	$\delta^{18}\text{O}_{\text{Water}}$	$\delta^{18}\text{O}_{\text{inclusion fluid}}$
414	+16.068	-1.98	-1.87
416	+14.668	-5.56	-
418	+16.758	+2.63	+4.25
419	+13.557	-0.60	+0.49
424	+13.758	-3.81	-1.97
R101.1	+16.575	-0.70	+2.43
R102.3	+17.681	-0.83	+0.25
1018	+18.194	-1.57	+2.14
6480	+17.918	-0.74	+0.20
6666	+18.552	-3.38	-3.09

All results are in ‰

Table A3.2 Oxygen isotope results for barite samples

Sample	$\delta^{18}\text{O}_{\text{Barite}}$	$\delta^{18}\text{O}_{\text{Water}}$	$\delta^{18}\text{O}_{\text{inclusion fluid}}$
R20	+12.6	+4.46	+7.73
R120	+13.2	-1.77	-1.66
R121	+13.2	-1.48	-0.68
R123	+12.6	-1.58	-1.17
6476	+13.2	+1.68	+3.38
6477	+13.2	-1.87	-1.39
6522	+12.6	+1.58	+3.47
20725	+13.2	+2.67	+3.85
20839	+11.0	-5.12	-4.91

A3.5. Correction of $\delta^{18}\text{O}$ for barite samples

$\delta^{18}\text{O}_{\text{barite}}$ values were obtained from Solomon Rafter and Dunham's work (1971). To obtain $\delta^{18}\text{O}_{\text{water}}$ values fractionation factors from Kusakabe and Robinson (1977) were used.

$$10^{-3} \ln \alpha_{\text{Barite-water}} = \frac{3.01 \times 10^5 - 7.3}{T^2} \quad \dots(18)$$

$$10^{-3} \ln \alpha_{\text{Barite-1M NaCl}} = \frac{2.64 \times 10^6 - 5.3}{T^2} \quad \dots(19)$$

After the water values had been obtained the salinity correction equation (above) from Sofer and Gat (1972) was used to give the values in Table A3.2.

A3.6. Rubidium-Strontium isotopic ratio calculation

The following equation was used to calculate the isotopic ratio of Rb to Sr from the weight ratio measured by x-ray fluorescence techniques.

$$^{87}\text{Rb}/^{86}\text{Sr} = \text{X.R.F. Rb/Sr} \cdot [0.27835 (^{87}\text{Sr}/^{86}\text{Sr} + 9.4318)] \quad \dots(20)$$

This equation represents the following

$$\frac{^{87}\text{Rb}}{^{86}\text{Sr}} = \frac{\text{total Rb}}{\text{total Sr}} \cdot \left[\frac{\text{Rb}^{87}}{\text{Total Rb}} \right] \cdot \left[\frac{\text{Total Sr}}{\text{Sr}^{86}} \right] \quad \dots(21)$$

In terms of masses this may be written as:-

$$\frac{87}{86} = \frac{\text{Total Rb}}{\text{Total Sr}} \cdot \left[\frac{87}{85 + 87} \right] \cdot \left[\frac{88 + 87 + 86 + 84}{86} \right] \quad \dots(22)$$

$$= \frac{\text{Total Rb}}{\text{Total Sr}} \cdot \left[\frac{87}{85} + \frac{87}{87} \right] \cdot \left[\frac{88}{86} + \frac{87}{86} + \frac{86}{86} + \frac{84}{86} \right] \quad \dots(23)$$

These mass ratios can be obtained from Steier and Jager, (1977).

$$\begin{aligned} \text{Rb}^{85}/\text{Rb}^{87} &= 2.59265 & \text{Sr}^{86}/\text{Sr}^{88} &= 0.1194 \\ \text{Sr}^{84}/\text{Sr}^{86} &= .056584 \end{aligned}$$

substituting in (23) gives:-

$$\frac{87}{86} = \frac{\text{Total Rb}}{\text{Total Sr}} \left[\frac{1}{2.59265 + 1} \right] \left[\frac{1}{.1194} + \frac{87}{86} + 1 + 0.056584 \right] \quad \dots(24)$$

$$\text{or } \frac{\text{Rb}^{87}}{\text{Sr}^{86}} = \frac{\text{Total Rb}}{\text{Total Sr}} \cdot \left[.27835 \right] \cdot \left[9.4318 + \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right]$$

Appendix 4

A4.1. The Mann-Whitney 'U' test

The Mann-Whitney 'U' test is a non-parametric statistical test used for comparing two independent groups of random observations. The null hypothesis states:-

H_0 : The two random groups are drawn from a common population.

The alternative hypothesis is:-

H_1 : The two random groups are drawn from different populations.

The test procedure is based on assigning ranks to all the observations, such that ranks are in increasing magnitude for the combined groups. If the populations differ, most of the low ranks will fall in one group, (and the high ranks in the other).

The 'U' statistic is

$$U = W_n - \frac{[N(2) (N(2) + 1)]}{2}$$

where W_n = Wilcoxon two sample rank sum statistic
(or the sum of ranks assigned to the group
with the smaller number of observations).

N = number of observations

(1) (2) = the number corresponding to the first or
second group

For the test $N(1) > N(2)$. When $N(1)$ and $N(2)$ are large the Mann Whitney U statistic approximates to a normal distribution, and using this approximation, the null hypothesis is rejected if the attained significance level is smaller than the desired level of significance. (i.e.

0.01 or 99% significance level). The attained significance level is given by the area under a standard normal distribution to the right of the value, and is thus equal to:-

$$\frac{[U - \text{mean}(U)]}{\sqrt{\text{var}(U)}} = \text{attained significance}$$

$$\text{where mean } (U) = \frac{N(1) \cdot N(2)}{2}$$

$$\text{and var } (U) = \frac{N(1) \cdot N(2) \cdot [N(1) + N(2) + 1]}{2}$$

When tied observations appear a rank averaging method is used to assign ranks to the tied observations. (Univ. Michigan, 1976, Gibbon, 1977). Mann-Whitney tests relevant to the text are given in Table A4.1.

Table A4.1 Results of the Mann Whitney U test on data obtained on
the fluorite quartz and barite inclusion fluids

Quartz fluids versus fluorite fluids.

Parameter	significance	Acceptance or rejection of the Null Hypothesis
K	0.6578	accepted
Cu	0.9796	accepted
Temperature	0.0710	accepted
CO ₂ :H ₂ O	0.0023	rejected
δD	0.0000	rejected
Na	0.0000	rejected
Mg	0.0000	rejected

Barite fluids versus fluorite fluids.

Temperature	0.0006	rejected
δD	0.0000	rejected
Na	0.0000	rejected
K	0.0005	rejected
Sr	0.0000	rejected
CO ₂ :H ₂ O	0.0574	accepted
Zn	0.7102	accepted
Mg	0.4814	accepted
Mn	0.0775	accepted

Table A4.1 cont.

Null hypothesis:- The two random groups are drawn from a common population.

The significance level used for rejecting the null hypothesis was .0050 or 99.5%.

A4.2. Thermodynamic calculations for the production of pH-log fO₂ plots

Using pH values and chemical data on the mineral species from Appendix 5, pH-log fO₂ plots were drawn to obtain oxygen and sulphur fugacity limits for each stage of the mineralisation. The diagrams were calculated at the relevant solution temperatures for a 3 m NaCl solution with activities mainly provided from the present chemical analyses, Table A4.2.

Methods of calculating stability fields have been described by Holland, (1965), Barnes and Kullerud, (1961), Garrels and Christ, (1965), and Bailey (1977). Equilibrium constants are generally available, those absent having been calculated using data from Helgeson (1969), all those used being shown in Table A4.3. The equations and derivations used are shown below with the number 1, 2, 3 etc. instead of the equation being used in Table A4.3.

A4.21. Aqueous Sulphur Species

The important sulphur species in aqueous solutions at the relevant physico-chemical conditions are HSO₄⁻, SO₄²⁻, H₂S and HS⁻, (Barnes and Czamanske, 1967). The equations used to calculate the stability fields are as follows:-



Table A4.2 Activities of elements used in pH-log fO_2 plot

calculations for solutions up to 3 M NaCl

Element	Range of concentration used (Activity)	Range of concentration by experiment
Total Sulphur ΣS	0.01	<.10
Total Carbon dioxide ΣCO_2	0.1 - 1.0	0.05 - 4.2
Total Calcium ΣCa	0.1 - 7.0	0.2 - 15.0
Total Potassium ΣK	0.3	0.0 - 0.3
Total Chloride ΣCl	0.1 - 1.0	0.1 - 3.0

For the minimum amount of mineral precipitated in ore quantities
the following is required 10^{-5} m

Metal (Cu, Zn, Fe, Pb)	10^{-5} m
Reduced Sulphur (S^{2-})	10^{-5} m
Fluorine (F^-)	10^{-5} m
Barium (Ba^{2+})	10^{-5} m



For the field boundary of $\text{HSO}_4^-/\text{SO}_4^{2-}$ the conditions will be equivalent to:-

$$\log K_1 = \log a_{\text{SO}_4^{2-}} - \text{pH} - \log a_{\text{HSO}_4^-}$$

However at the boundary $a_{\text{SO}_4^{2-}} = a_{\text{HSO}_4^-}$

$$\therefore \log K_1 = -\text{pH}$$

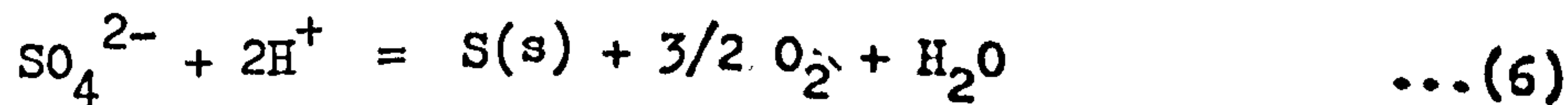
Similarly for the $\text{H}_2\text{S}/\text{HSO}_4^-$ boundary:-

$$K_2 = \log a_{\text{HSO}_4^-} - \text{pH} - \log a_{\text{H}_2\text{S}} - 2 \log f\text{O}_2$$

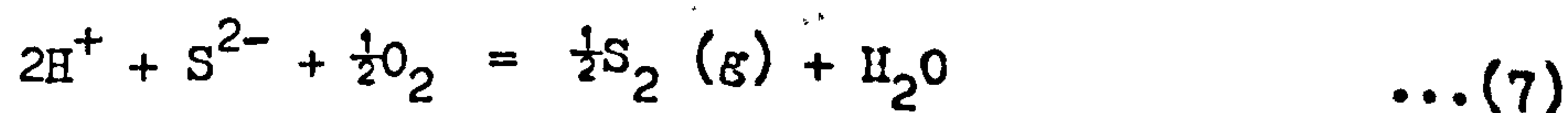
and as $a_{\text{HSO}_4^-} = a_{\text{H}_2\text{S}}$

$$K_2 = -\text{pH} - 2 \log f\text{O}_2$$

Equations 3, 4, and 5 can also be converted, to forms of equations based on K, pH and $\log f\text{O}_2$, in the above manner, and thus the relevant boundaries can be drawn on the pH-log $f\text{O}_2$ plots. To find the boundaries for the solid or liquid sulphur field further equations were necessary. For the $\text{SO}_4^{2-}/\text{S}$ boundary:-

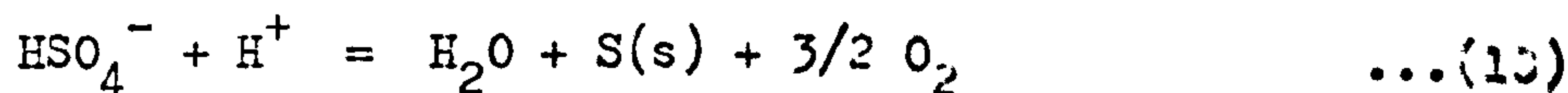


This equation was derived from 7 - $\frac{1}{2}(8)$ - 9 where those numbers refer to:-





For the HSO_4^-/S boundary the following equation was derived by additions of equation (1) and (6).



The $\text{H}_2\text{S}/\text{S}$ boundary required:-



which was derived from $(12 - 8)\frac{1}{2}$.



Thus to obtain the field boundaries in physico-chemical terms, calculations of the following type were necessary.

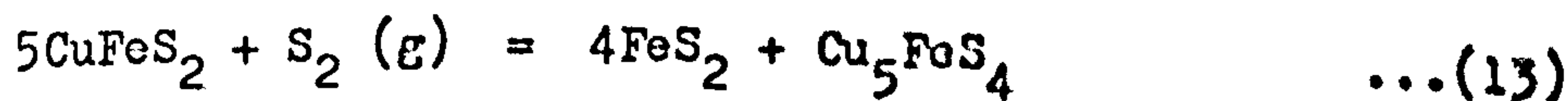
e.g. Equation (6)

$$\log K_6 = 3/2 \log f\text{O}_2 - \log a_{\text{SO}_4^{2-}} + 2\text{pH}$$

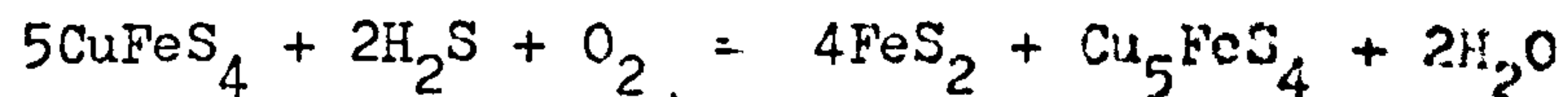
K_6 and pH are known, $a_{\text{SO}_4^{2-}} = 10^{-2}$ and therefore the $\log f\text{O}_2$ can be calculated.

A4.22. Stability fields of iron minerals

The stability fields of chalcopyrite, pyrite and siderite were calculated and plotted. The chalcopyrite/pyrite + bornite boundary is given by:-



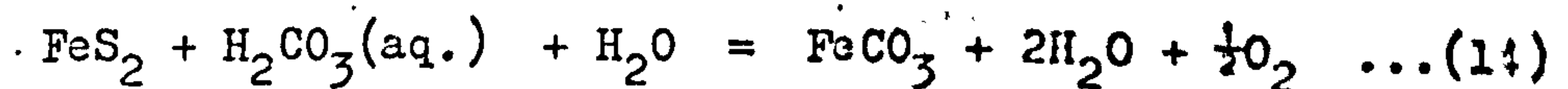
In the hydrogen sulphide field this is equivalent to:-



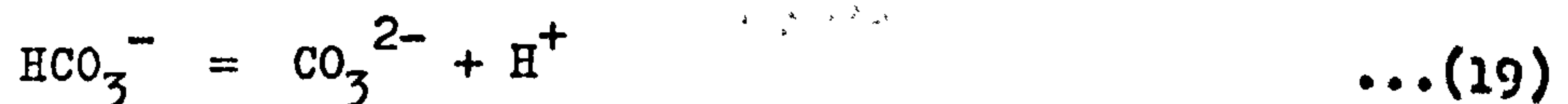
This was derived from addition of equations (12) and (13) in physico-chemical terms is represented by:-

$$\log K_{13} + \log K_{12} = -2\log a_{\text{H}_2\text{S}} - \log f_{\text{O}_2}$$

For the pyrite-siderite boundary the following equation is necessary:



which is derived from $15 - 4 - \frac{1}{2}(12) - 16 - 17 + 18 + 19$.



As these equilibrium constants are known, the stability fields of pyrite and chalcopyrite can be found. The chalcopyrite stability field extends into the other aqueous sulphur fields and using other equations its position can be found if necessary.

A4.23. Stability field of Graphite

Graphite although not present may be associated with the fluid in the form of CO_2 and CH_4 . Thus estimation of its stability field, and those of CO_2 and CH_4 , are necessary:





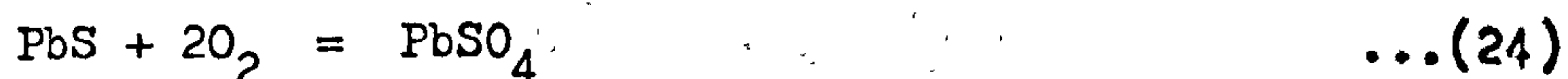
Equation (21) was derived from 20-22 + 23.



The values of $\log fO_2$ can be calculated from the equilibrium constant and $\log fCO_2$ values shown in their relevant tables.

A4.24. Stability field of Galena and Sphalerite

As Galena and Sphalerite are the main sulphide minerals of the ore field their stability fields were studied. The equations being:-



In terms of physico-chemical parameters these are:-

$$\log_{24/25} = -2 \log fO_2$$

The equations are derived from 24 = 26 - 27 + 9 and

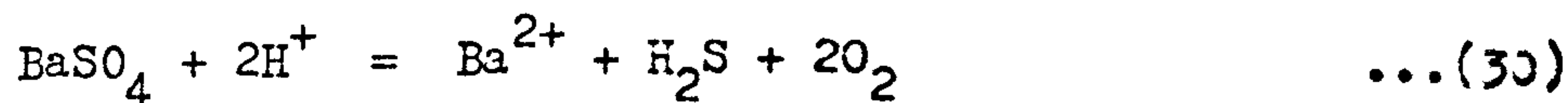
27 = 30 - 31 + 9, with the new equations given below:-



A4.25. Barite insolubility-solubility boundary

This boundary was necessary to give the limits at which barite in ore quantities occurred. (10^{-5} wt %).

The equation is given for the H_2S field, values for the other sulphur fields may be found using different equations.



$$\text{where } \log K_{30} = \log a_{Ba^{2+}} + \log a_{H_2S} + 2 \log fO_2 + 2pH$$

The equation was derived from: $30 = 31 - 3$



A4.26. Fluorite insolubility-solubility boundary

Fluorite being the other main non-sulphide mineral, was useful for its solubility-insolubility boundary, given by:-



$$\text{or } \log K_{32} = \log a_{Ca^{2+}} + 2 \log a_{HF} + 2pH$$

The activities of Ca^{2+} and F^- are shown in Table A4.1. The equation was derived from:- $32 = 33 + 2(34)$



The equilibrium constants for equation 34 were derived by thermodynamic principles, (Krauskopf, 1979).

$$\log K = \frac{-\Delta G}{2.303RT}$$

$$\text{and } \Delta G = \Delta H^0 - 0.001T\Delta S.$$

Where ΔG = Free Energy

ΔH = Change in Heat of Enthalpy

ΔS = Change in Heat of Entropy

T = Temperature $^{\circ}\text{K}$

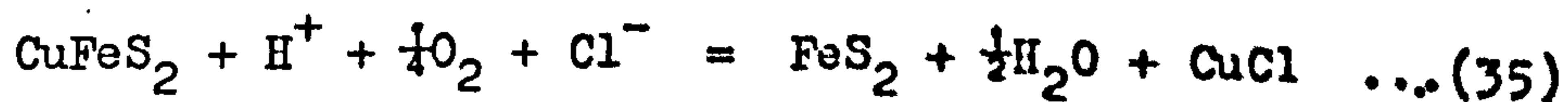
R = Gas Constant

All values were taken from Helgeson (1969), and Krauskopf, (1979).

A4.27. Chalcopyrite and pyrite solubilities

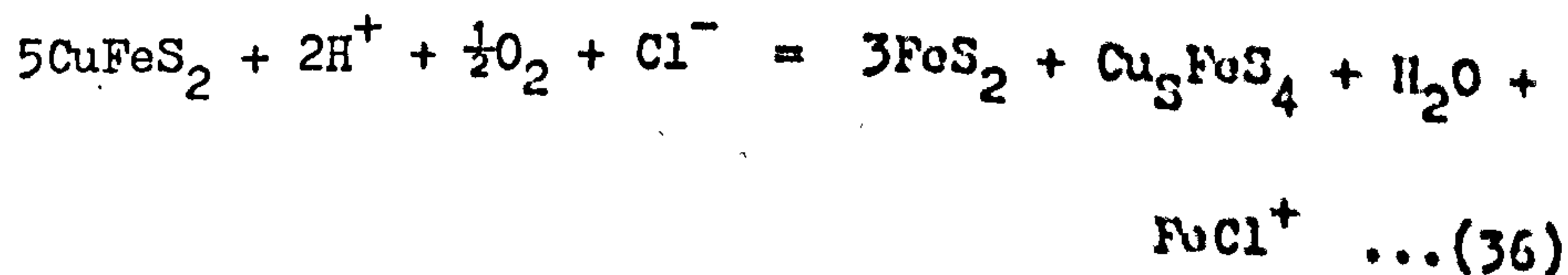
The solubility of 10^{-5}m of the above sulphides was required to check for solubility of these elements in the ore fluids. The relevant equations were taken from Crerar and Barnes (1976), and their equilibrium constant values were extrapolated to lower temperatures.

For chalcopyrite the equation is:-



$$\text{or } \log K_{35} = \log a_{\text{CuCl}} + \text{pH} - \frac{1}{4}\log f\text{O}_2 - \log a_{\text{Cl}^-}$$

For pyrite the equation is:-



$$\text{or } \log K_{36} = \log a_{\text{FeCl}^+} + 2\text{pH} - \log a_{\text{Cl}^-} - \frac{1}{2}\log f\text{O}_2$$

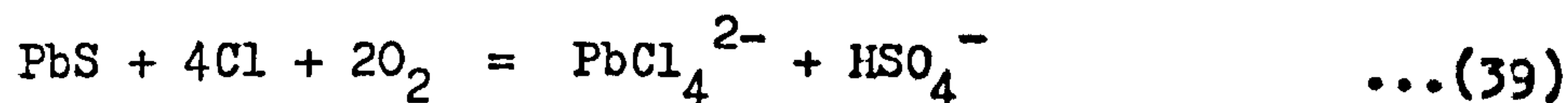
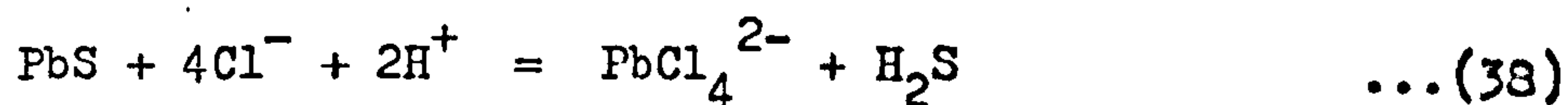
equation is derived from: $36 = 13 + 7 + 15 - 37$



The metal chloride concentrations used are 10^{-5}m , which is the minimum limit for ore deposition.

A4.28. Galena Solubility

The solubility of galena depends on the aqueous sulphide field considered. The relevant equations needed for the H_2S and HSO_4^{2-} fields are (38) and (39).



These are derived from $38 = 28 - 4 - 16 - 40$

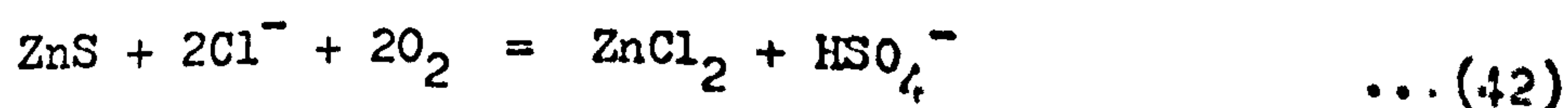
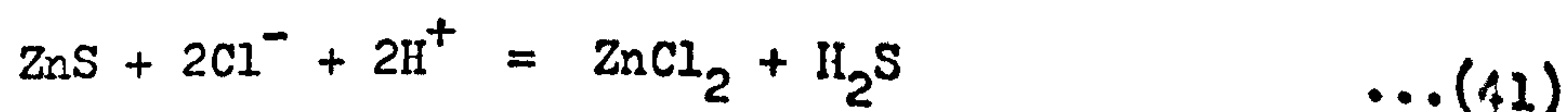
and $31 = 5 + 26 - 1 - 16 - 40$, where (40) is:-



Physico-chemical parameters can be derived for equations (38) and (39) in a similar way to previous calculations.

A4.29. Sphalerite Solubility

The solubility of sphalerite is similar to that of galena but occurs at slightly different physico-chemical conditions. In the H_2S and HSO_4^{2-} fields the following equations are necessary:-



These are derived from $41 = 28 - 43 - 16 - 4$ and
 $42 = 28 - 43 - 16 - 1 + 5$, where (43) is:-



Table A4.3 Equilibrium Constants used in thermodynamic calculations

Equation Number	Log of Equilibrium Constant			Reference
	100 °C	150 °C	200 °C	
1	-2.99	-3.74	-4.49	Crerar + Barnes 1976
2	97.30	83.05	71.62	Helgeson, 1969
3	94.31	79.31	67.13	"
4	-6.63	-6.72	-6.96	"
5	100.93	86.03	74.09	"
6	-66.50	-56.10	-47.90	Present work
7	41.54	37.33	34.05	Helgeson, 1969
8	-9.40	-6.50	-3.50	Barnes + Kullerud, 1961
9	112.70	96.68	83.74	Helgeson, 1969
10	-69.50	-59.80	-52.40	Present work
11	27.84	23.25	19.28	"
12	46.27	39.99	35.05	Helgeson, 1969
13	16.86	13.41	10.68	Crerar + Barnes, 1976
14	-39.61	-33.41	-28.40	Present work
15	-30.17	-26.60	-24.19	Helgeson, 1969
16	-11.78	-10.62	-9.57	"
17	-11.95	-12.86	-14.05	"
18	-6.45	-6.73	-7.08	"
19	-10.16	-10.29	-10.68	"
20	55.21	47.54	43.55	Bailoy, 1977
21	-56.82	-52.87	-45.38	Present work
22	1.97	2.07	2.06	Helgeson, 1969
23	-110.06	-98.34	-86.87	Bailoy, 1977

Table A4.3 cont.

Equation	Log of Equilibrium Constant			Reference
	100 °C	150 °C	200 °C	
24	96.6	83.01	72.26	Present work
25	93.4	79.47	68.53	"
26	-23.96	-21.93	-20.36	Helgeson, 1969
27	-7.86	-8.26	-8.88	"
28	-22.48	-21.01	-19.81	"
29	-3.20	-3.80	-4.60	"
30	-103.53	-88.65	-76.89	Present work
31	-9.22	-9.34	-9.76	Helgeson, 1969
32	-1.82	-1.92	-2.22	Present work
33	-9.20	-9.66	-10.26	Helgeson, 1969
34	-3.69	-3.87	-4.02	Present work
35	10.75	10.30	10.00	Crerar + Barnes, 1976
36	31.17	28.12	25.64	Present work
37	-2.94	-3.98	-5.10	Helgeson, 1969
38	-3.50	-2.02	-0.63	Present work
39	93.80	81.00	71.00	"
40	-2.05	-2.57	-3.20	Helgeson, 1969
41	-1.94	-0.48	+1.12	Present work
42	95.35	82.57	72.74	"
43	-2.13	-3.19	-4.40	Helgeson, 1969

5.1. Location of samples

Samples were acquired from areas throughout the Pennine orefield, both the fluorite and barite zones. However some areas provided more samples than others due to greater concentration of mineral veins or easier access. Hence the fluorite zone is considerably better sampled than the barite zone.

Table 5.1. gives the location and map reference for the samples used as well as the colour and mineral type. Fig. 5.1. shows the position of the groverake vein samples at different levels in the Groverake Mine. Fig. 5.2 indicates the geographic position of the fluorite samples along veins. The barite and most of the quartz samples are not shown.

Table A5.1 Location of Samples

Sample	Mineral	Map ref.	Location
R19	Barite	3890.5291	Ettersgill
R20	Barite	3763.5228	Murton, Nr. Scordale
R21	Witherite	4175.5505	Anfield Plain, Nr. Stanley
R119	Barite	3847.5227	Closehouse Mine
R120	Barite	3847.5226	"
R121	Barite	3848.5227	"
R122	Barite	3850.5228	"
R123	Barite	3710.5320	Silverband. Gt. Dun Fell. Westmorland
5206	Barite	3774.5452	Nentsberry Mine, Cumberland.
6210	Barite	3773.5451	"
6476	Barite	4219.5420	New Brancopeth Colliery
6477	Barite	4219.5421	"
6522	Barite	3710.5319	Silverband. Gt. Dun Fell, Westmorland
6587	Barite	3710.5320	"
20725	Barite	3842.5226	Closehouse Mn. Sub-level above SFMS Drift
20839	Barite	3815.5305	Rods Voin, Cow Green Reservoir
414	Quartz	3710.5387	Great Sulphur Vein
416	Quartz	3715.5386	"
418	Quartz	3720.5385	"
419	Quartz	3725.5383	"
424	Quartz	3730.5381	"

Table A5.1 cont.

1018	Quartz	3985.5409	Red Vein
R101.1	Quartz	3929.5386	Slitt Vein, South lens, 240 level
R102.3	Quartz	3929.5386	"
6216	Quartz	3941.5432	Boltsburn Mine
6480	Quartz	3705.5418	Rotherhope Foll Mine flats
6666	Quartz	3860.5410	Copt. Clough Vein, Sedling Mine
1	Fluorite - Green	3901.5442	Groverake Vein, 60 FMS level
3	"	3901.5442	"
8	"	3901.5442	" , 50 FMS level
11	"	3900.5442	" , 60 FMS level
430	Fluor. - Green/Purple	3895.5442	" , 50 FMS level
433	Fluorite - White	3896.5442	" , "
441	Fluorite - Purple	3898.5442	" "
442	"	3898.5442	" "
443	"	3898.5442	" "
451	Fluorite - Green	3899.5442	" "
480	Fluorite - Purple	3901.5442	Groverake Vein, 60 FMS level
847	Fluorite - Green	3897.5442	" , Firestone Drift
851	"	3898.5442	" "
853	"	3898.5442	" "
858	"	3899.5442	" "
859	Fluor. - Green/Purple	3899.5442	" , Jakes Sublevel, Firest.Drift
860	Fluorite - Green	3899.5442	" , Firestone Drift

Table A5.1 cont.

873	Fluorite - Green	3897.5442	Groverake Vein, 30 FMS level
875	Fluorite - Purple	3897.5442	"
876	"	3899.5442	"
885	Fluorite - Green	3897.5442	"
887	Fluor. - Green/Purple	3901.5442	" , Firestone Drift
890	Fluorite - Purple	3900.5442	" "
892	"	3900.5442	" "
897	Fluor. Purple/Green	3900.5442	" "
921	Fluorite - Green	3896.5442	" 30 FMS level
929	"	3897.5442	Groverake/Red Vn. inter- section. Firest. Drift
310	Fluorite - Purple	3882.5446	Greencleugh Vein. Frazars Hushes.
311	"	3885.5445	"
312	"	3887.5445	"
314	"	3898.5442	Greencleugh/Red Vein intersection
316	Fluor. Purple/Green	3891.5443	Greencleugh Vein, Frazars Hushes.
330	Fluorite - Purple	3879.5444	"
165	"	4007.5401	Red Vein, Rogerwell Hush
277	Fluorite - Green	3970.5415	" , Stanhopeburn Mine 17th level
398	"	3944.5423	" , Redburn Mine
R25	"	3934.5429	Rookhope Borehole, 591'
R26	"	3934.5429	" , 606'
R28	"	3934.5429	" , 689'
R29	"	3934.5429	" , 694'
R31	"	3934.5429	" , 942'

Table A5.1 cont.

243	Fluorite - Purple	3896.5432	Wolfcleugh New Vein
244	"	3898.5432	"
259	"	3904.5434	Wolfcleugh Old Vein
262	"	3898.5432	"
263(1)	"	3897.5431	"
265	"	3896.5430	"
256	"	3917.5441	Greenwells Vein
257	"	3919.5442	"
250	Fluorite - Purple	3921.5434	Rispey Vein, Rispey Syke levels
251	"	3922.5435	"
252	"	3924.5437	"
254	"	3917.5432	"
233	Fluorite - White	3941.5432	Boltsburn Vein (E. Mine)
170	Fluor. Green/Purple	3999.5399	Ridleys Vein - E. Ashes Quarry
467	Fluorite - Purple	3916.5417	North Fulwood Vein, High Fulwood Mine.
607	Fluor. Purple/Green	3879.5397	North Slitt Vein, Black- dene Mine 195' level
812	Fluor. Green/Purple	3928.5387	South Slitt Vein, Black- dene Mine, Haul. level
993	Fluorite - Purple	3915.5390	Slitt Vein, Siders level
999	Fluorite - Purple	3901.5392	"
1012	Fluorite - Green	3920.5388	" , Cammock Eales Mine
1013	Fluor. White/Green	3921.5389	"
1021	Fluorite - White	3894.5396	High Slitt Vein
1056	Fluorite - Purple	3875.5398	Slitt Vein. Elmford Mine
1058	Fluorite - White	3869.5396	Ironstone Quarry. Elm- ford Cleugh/Bell Hill

Table A5.1 cont.

R99.1	Fluor. Purple/Green	3933.5385	Slitt Vein, North lens. 240' level
R99.2	"	3933.5385	"
R99.3	"	3933.5385	"
R99.4	Fluorite - Purple	3933.5385	"
R99.5	Fluor. Purple/Green	3933.5385	"
R100.1	Fluor. White/Green	3929.5386	" , South lens. 240' level
R100.2	Fluorite - Purple	3929.5386	"
R100.3	Fluor. White/Green	3929.5386	"
R100.4	Fluorite - Purple	3929.5386	"
R100.5	Fluor. White/Green	3929.5386	"
R100.6	Fluorite - Purple	3929.5386	"
R101.2	Fluorite - White	3929.5386	"
R101.3	Fluor. White/Green	3929.5386	"
R102.1	"	3929.5386	"
R102.2	Fluorite - Purple	3929.5386	"
1007	Fluorite - Green	3872.5392	Blackdene Vein (Mine)
1031	Fluorite - Purple	3873.5398	Wearhead Vein
1025	Fluor. Purple/Green	3885.5397	Old Fall Vein. Silverdykes
1067	Fluorite - Purple	3878.5389	Old Fall Vein. Sunny-side Opencut
1068	"	3880.5391	"
1070	"	3882.5392	Old Fall Vein, level-gate Working
1071	"	3884.5395	Old Fall Vein. Sike Opencut
1072	"	3884.53960	"
1073	"	3875.5392	Lodgefield Vein. New-house Qu. Opencut

Table A5.1 cont.

1075	Fluorite - Purple	3881.5395	Lodgefield Vein, Silverdykes
1076	"	3882.5396	"
1078	Fluorite - White	3883.5396	"
760	Fluor. Purple/Green	3854.5381	Barbary Mine
762	Fluorite - Purple	3860.5378	Low Groveheads Vein
1044	Fluorite - Yellow	3969.5470	Sandyford Vein, White- heaps Mine
1050	Fluorite - Purple	3942.5459	Ferney Gill Vein, Whiteheaps Mine
1052	"	3946.5462	Florence Vein. Burn- hopehead drift
1059	"	3955.5463	White Vein. White- heaps Mine
270	"	3893.5403	Longsyke Vein, Middle- hope Old Mine
775	Fluorite - White	3887.5343	Swinhopehead Vein
806	Fluorite - Purple	3852.5426	Claypath Vein, Greenfield Hush
807	"	3855.5454	Old Vein, Allenheads
828	Fluorite - Yellow	3797.5075	Kirby Stephen, Hartley Birkett Hill
984	Fluorite - Purple	3989.5383	Coves Vein
1102	"	3859.5417	Burtree Pasture Vein
348	Fluorite - Yellow	4343.3561	Great Rake/Hard Rake, Glory Mine, Crich
544	Fluorite - White	4349.3618	Gregory Vein. Ashover
547	"	4352.3622	Spencers/Sawland Rake, Ashover
555	"	4356.3626	Milltown Quarry, Ashover
570	Fluor. Yellow/White	4287.3592	King Shaft, Bonsall- Masson

Table A5.1 cont.

571	Fluor. White/Yellow	4287.3589	Opencut, Bonsall-Masson
574	Fluorite - White	4285.3585	Great Rake, Bonsall-Masson
575	Fluorite - Yellow	4223.3654	Long Rake, Youghreave-Alport
578	Fluorite - White	4222.3734	Waterhole Mine
580	"	4229.3734	Brightside Mine
581	Fluorite - Purple	4134.3834	Odin Vein, Odin Gorge Opencut, Castleton
R1	Fluorite - White	4219.3775	Hucklow Edge Vein, Ladywash Mine
R5	"	4351.3619	Sawland Rake, Ashover
R35	"	4178.3782	Milldam Mine, Great Hucklow
R38	Fluor. Purple/Yellow	4134.3834	Odin Vein, Odin Gorge Opencut, Castleton
R39	Fluorite - Purple	4135.3831	Treak Cliff Craggs and Mine
R48	"	4162.3817	Moss Rake, Smalldale
R51	Fluor. Purple/White	4341.3556	Hard Rake, Crich
R53	Fluorite - White	4344.3554	Crich, Opencut
R64	Fluor. White/Yellow	4354.3620	Milltown Quarry, Ashover
R74	Fluorite - Yellow	4278.3599	Oxclose Mine, Matlock

Fig.A5.1 Groverake vein sample locations at different levels in the Groverake Mine.

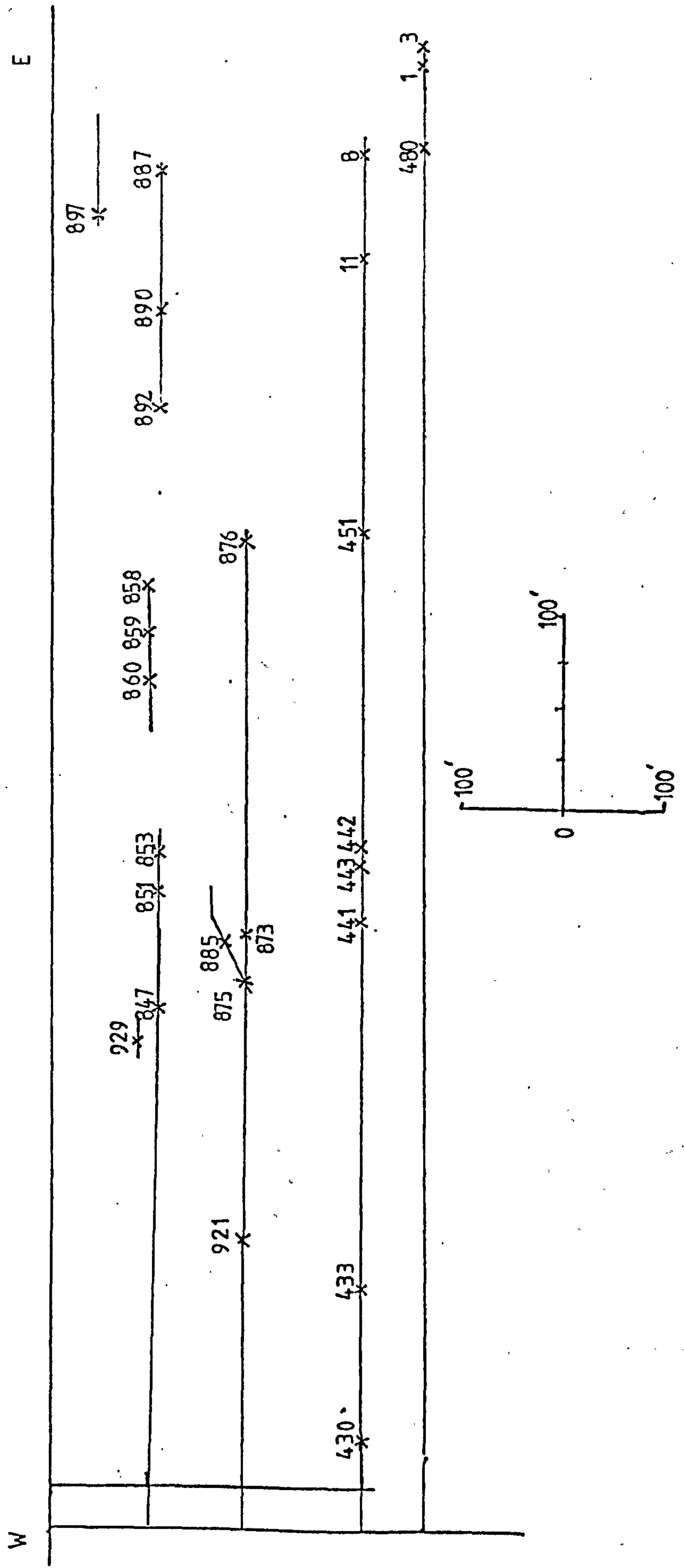
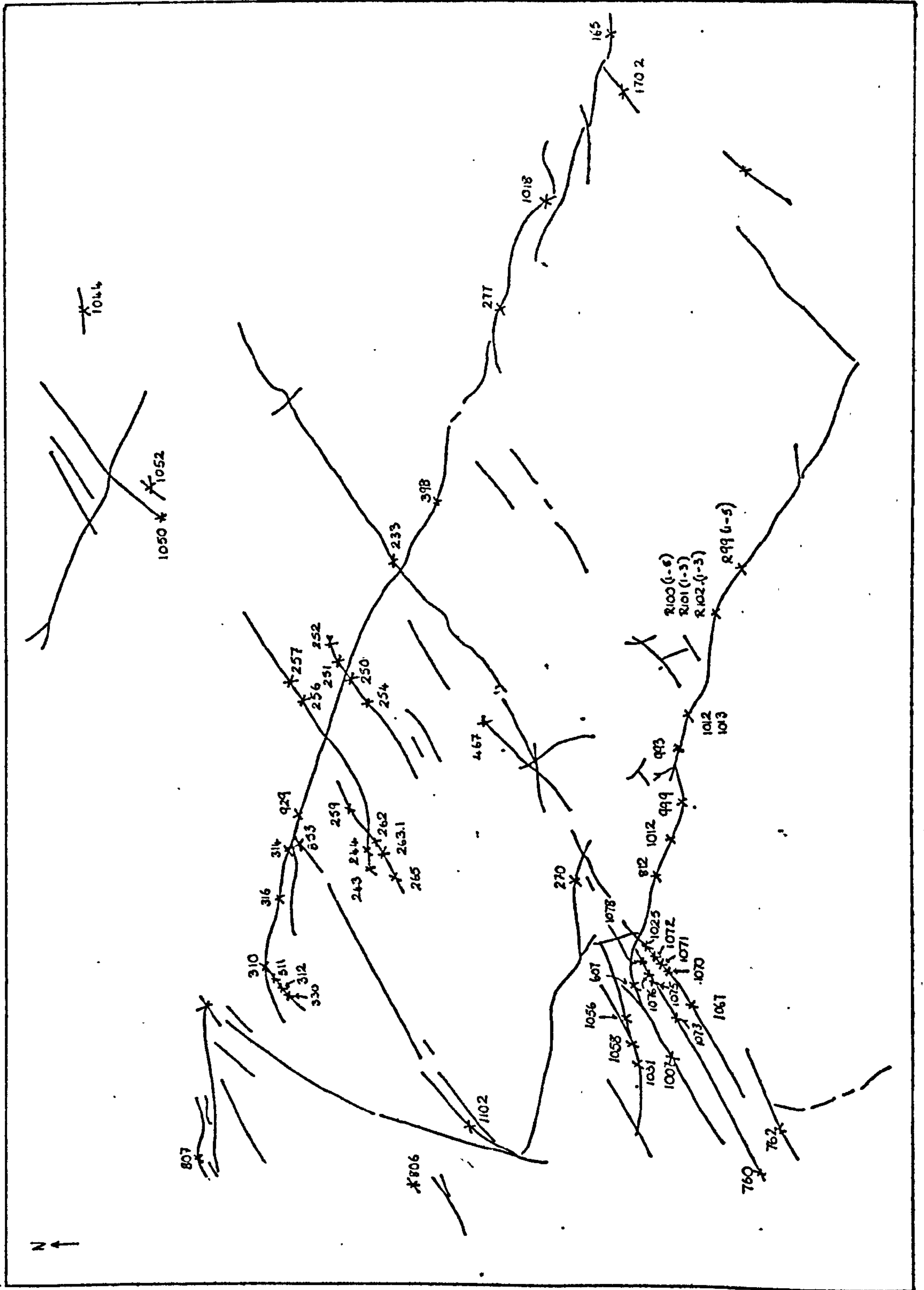


Fig.A5.2 Location map of fluorite samples in the Northern Pennines.



5.2. Isotopic and geochemical results obtained.

The results shown in Tables 5.3 and 5.4 are average values for each element on each sample taken from duplicate or triplicate analyses.

Table 5.3 represents results for the temperature of homogenisation, δD and salinity elements obtained on the inclusion fluids. Table 5.4 gives the metal and Yttrium concentrations of the fluids and fluorite respectively as well as the calculated pH values.

Other results obtained for a limited number of samples were given in Chapters 3 and 4. These include chlorine, fluorine, bromine and rare-earth element analyses as well as $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ isotopic results.

Table 5.2 gives the units used for each parameter shown in Tables 5.3 and 5.4. Where -0.0 has been used in these tables, it represents samples which were either not analysed for a particular parameter or were below the limit of detection for a particular parameter.

Table A5.2 Units for the chemical and isotopic parameters shown
in Tables 5.3 and 5.4

Parameter	Unit
Table 5.3	
Temperature	°C
DH : H ₂ (δ D)	‰
all other ratios	-
Na, K, Ca	10 ³ ppm
NaCl, KCl	wt. %
Table 5.4	
Mg, Sr, Cu, Zn, Mn, Fe	10 ³ ppm
Y	ppm
Tot. metal	10 ³ ppm
pH	-

2)

[illegible][illegible][illegible][illegible][illegible]

0
C:
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:
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Figure 1. Schematic representation of the experimental design. The subjects were divided into two groups: the control group (C) and the experimental group (E). The control group (C) was divided into two subgroups: the control group (C) and the control group (C). The experimental group (E) was divided into two subgroups: the experimental group (E) and the experimental group (E). The control group (C) was divided into two subgroups: the control group (C) and the control group (C). The experimental group (E) was divided into two subgroups: the experimental group (E) and the experimental group (E).

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DH: H2

[illegible][illegible]

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