

Fluid inclusion studies on the Ecton Hill copper deposits, north Staffordshire

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Abstract

Thermometric and D-ICP analysis of fluid inclusions in calcite and fluorite show that the fluids responsible for extensive carbonate-hosted copper mineralization in the Ecton Hill area were low-temperature (< 100 °C), high-salinity (19.5 to 23 wt. % NaCl equivalents) brines strongly enriched in calcium (mean Ca:Na wt. ratio = 1.9). Compared with the fluids responsible for classical 'Mississippi Valley type' lead-zinc deposits elsewhere in the south Pennine orefield, the Ecton ore-fluids were of lower temperature and slightly more enriched in potassium. Despite these subtle differences, the data are consistent with a basinal brine model for ore genesis in this western part of the orefield similar to that envisaged for the remainder of the orefield. These Ca-Na-K-Cl, copper-bearing brines were most probably derived from the Cheshire basin located to the west of the Derbyshire Dome.

KEYWORDS; fluid inclusions, Ecton Hill copper deposits, north Staffordshire.

Introduction

THE South Pennine or Derbyshire orefield is the southernmost of three orefields within the English Pennines (Dunham, 1983). At its western margin, in the vicinity of Ecton and Mixon, once extensive but now largely worked-out areas of copper mineralization are known to have occurred. The predominance here of copper over lead and zinc sulphides is atypical of the orefield as a whole where lead-zinc-fluorite-baryte mineralization dominates, and a different origin to that proposed for these classical, carbonate-hosted, 'Mississippi-Valley-Type' lead-zinc deposits (Mostaghel, 1985) in the area might be envisaged.

Detailed fluid inclusion studies have already been undertaken throughout much of the orefield (Rogers, 1977; Atkinson *et al.*, 1982), with the notable exception of the copper-mining area at Ecton where only one fluid inclusion homogenization temperature of 77 °C from Waterbank mine has so far been reported (Atkinson *et al.*, 1982). In order to determine whether the cupriferous fluids at Ecton differed markedly from those responsible for mineralization elsewhere in the orefield we report here on the results of an integrated thermometric and geochemical study of fluid inclusions in calcite and fluorite from the Ecton mine area. These data permit further discussion of the source of

ore-fluids responsible for copper mineralization in the western part of the orefield.

Geology and mineralization

The Ecton Hill copper deposits are located on the western margin of the Derbyshire Dome within a folded series of Dinantian limestones (Fig. 1a). These sediments are surrounded by younger mudstones and sandstones which form part of the Ecton Hill Anticline (Aitkenhead *et al.*, 1985). At one time the Ecton Hill copper deposits were amongst the richest in Europe but mining operations ceased in 1891 (Robey and Porter, 1972). Underground workings at Ecton were mainly centred on a series of irregular, pipe-like bodies where mineralization occurred largely as a result of open-cavity filling. The Ecton pipe is the largest of these bodies with a vertical extent of some several hundred metres. The total tonnage of ore extracted from the Ecton mines is estimated at between 100 000 and 150 000 tons with grades of the order of 15% copper (Robey and Porter, 1972). Small vein deposits, worked in the past mainly for galena, also occur in the immediate vicinity of the pipes. Further details of the geology and mineralization are provided by Critchley (1979) and Astrop (1987).

The dominant hypogene sulphides are chalcopyrite and pyrite with lesser amounts of galena.

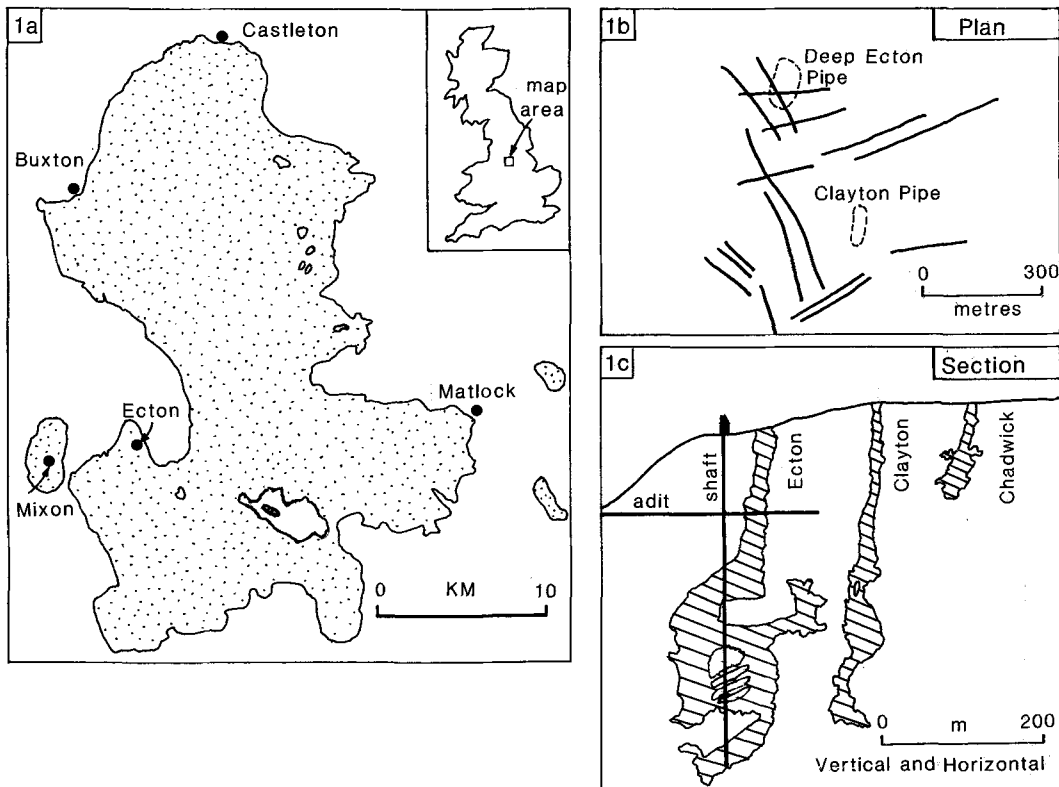


FIG. 1. Location and geological setting of the Ecton copper pipes. (a) Dinantian formations of the Derbyshire Dome (stippled area) and the location of Ecton and Mixon, modified from Aitkenhead *et al.* (1985). (b) Mineral veins and projected position of the Ecton and Clayton Pipes at Ecton Hill. Modified from Robey and Porter (1972). (c) Section through the copper pipe deposits of Ecton Hill showing the vertical extent of the workings (hatched). After Robey and Porter (1972).

Calcite is the main gangue mineral often occurring as large (> 10 cm), transparent crystals lining cavity walls within the pipe. Chalcopyrite is often included in, or associated with, calcite. Supergene sulphide alteration has been extensive with the development of a range of secondary iron and copper minerals.

Samples studied

Samples of calcite for fluid inclusion studies were collected from accessible underground workings at Ecton mine and also from dump material. A single sample of fluorite was included in this study. Sample descriptions and locations are provided in Table 1.

Fluid inclusion descriptions

Optical examination showed that the fluid inclusions could be divided into three main types on the

basis of size, shape and distribution throughout the sample (Fig. 2):

Type 1 are flat, two-phase aqueous inclusions with a small vapour bubble. They occur either in planar groupings of somewhat elongate inclusions averaging 20 to 30 μm in size or as larger irregular-shaped cavities up to about 50 μm .

Type 2 are flat, monophasic aqueous inclusions. They are usually associated with Type 1 inclusions and are of similar size and shape.

Type 3 are three-dimensional, two-phase aqueous inclusions with a small vapour bubble. They appear to be more isolated and larger (up to 150 μm) than types 1 and 2 inclusions.

The relative abundance of types 1, 2 and 3 are typically about 75, 24 and 1% respectively. Classification of inclusions into primary, pseudosecondary and secondary types is based on the criteria of Roedder (1984). Type 3 inclusions are thought to be primary, type 1 are either secondary or, more likely,

TABLE 1 Locations and descriptions of samples studied

Sample Number	Mineral	Location/Description
RM1	Calcite	Typical gangue calcite from the Ecton Pipe comprising large (10cm.) blocky, zoned crystals. From raise between Salts Level and Deep Ecton Level.
RM2	Calcite	From dumps below hillocks near Ecton Engine Shaft. Assumed to have come from the Ecton Pipe.
RM5	Calcite	As above
RM6	Calcite	Nail head spar associated with crustiform chalcocopyrite from the top of the Ecton pipe collected just below Salts Level.
RM11	Fluorite	Cubic crystals (2mm) from a crustiform fluorite sample collected from the Chadwick mine dumps

NOTE : Four additional samples of gangue calcite from the Ecton Pipe were also analysed by D-ICP ; RM 7,8,9,10.

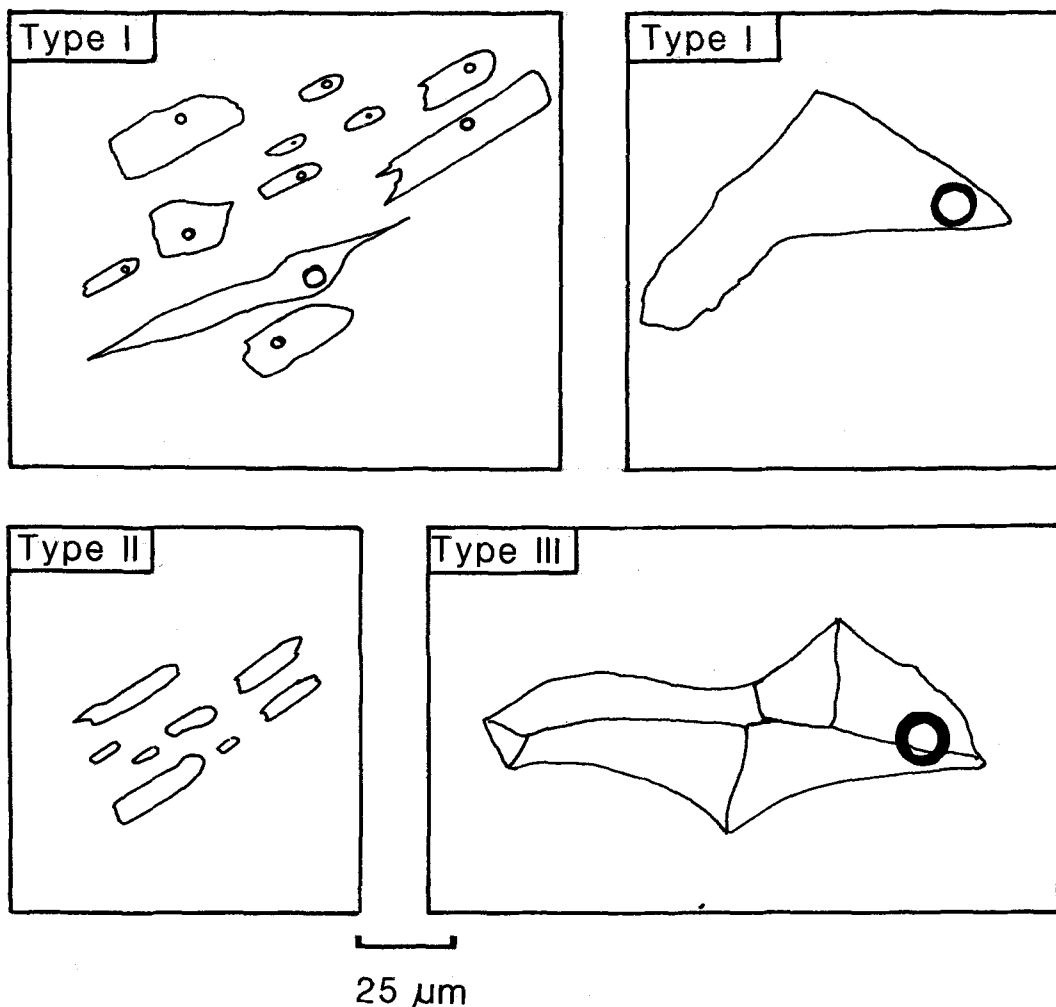


FIG. 2. Sketches showing typical fluid inclusion types in calcite and fluorite from the Ecton Hill deposits.

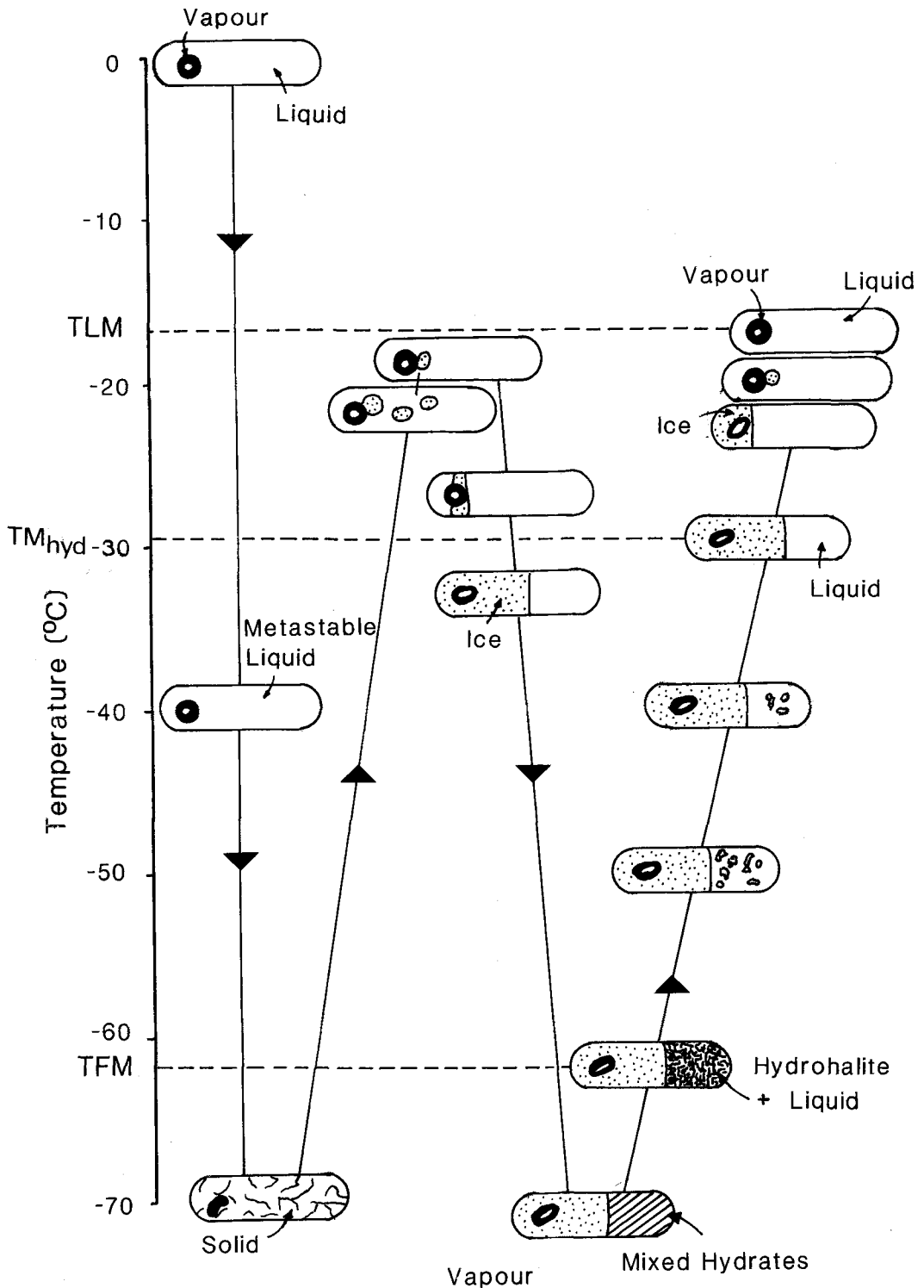


FIG. 3. A typical heating/cooling run used to determine the temperatures of first melting (TFM), hydrohalite melting (TM_{hyd}) and last ice melting (TLM). After freezing the inclusion is heated until only one ice crystal remains. On cooling ice continues to grow as a single crystal filling most of the cavity and mixed hydrates fill the remainder. First melting occurs in the hydrate part of the inclusion and hydrohalite and ice remain in separate parts of the inclusion, facilitating the measurement of the appropriate melting temperatures TM_{hyd} and TLM.

pseudosecondary, and type 2 are metastable or necked-down versions of type 3. Subsequent thermometric analysis showed that type 3 and type 1 inclusions are indistinguishable. Type 2 inclusions were not included in the thermometric analysis.

Analytical methods

Microthermometric analysis was carried out on doubly polished wafers some 0.5 mm thick using a Linkam TH600 microscope heating and freezing stage. Experimental procedures are outlined by Shepherd *et al.* (1985). Where possible the following phase transitions were recorded:

1. Temperature of first melting (TFM); the point at which the first sign of liquid appears upon heating a previously frozen inclusion.
2. Temperature of salt hydrate melting (TMhyd); the hydrate is presumed to be $\text{NaCl} \cdot 2\text{H}_2\text{O}$ (hydrohalite) and typically forms small, irregular-shaped grains of low relief within the aqueous fluid.
3. Temperature of last ice melting (TLM); the last crystal of ice, characterized by its typically rounded appearance, always melted after hydrohalite in these inclusions.
4. Temperature of homogenization (TH); vapour/liquid homogenization was always into the liquid phase.

The parameters TFM, TMhyd and TLM provide information on the salinity and Ca/Na ratios of the fluid. TH provides information on fluid density and an estimate of fluid trapping temperature. A typical heating/freezing run is shown schematically in Fig. 3. Care was always taken to ensure that TLM occurred in the presence of a vapour bubble. Unless this precaution was taken, metastable and therefore erroneous transition temperatures might be recorded (Rankin and Criddle, 1985).

Analysis of Na:K ratios by D-ICP

The Na:K weight ratios in the inclusion fluids were determined on 0.5 g samples of carefully cleaned and graded (0.5 to 2.0 mm) material using the Decrepitation-linked, Inductively Coupled Plasma emission spectroscopic method (D-ICP) described by Alderton *et al.* (1982) and outlined by Shepherd *et al.* (1985). Other elements capable of analysis using the D-ICP method were not considered here, partly because of the considerable spectral line overlaps that occur when large amounts of calcium are introduced into the plasma as decrepitated mineral fragments, and partly because their concentration is too close to background to be meaningful.

Summary of results

Homogenization temperature data ($\pm 2^\circ\text{C}$) for 102 type 1 and 3 inclusions are summarized in Table 2. The three disproportionately high values shown in brackets are thought to be due to necking-down or leakage, and are consequently of little significance. The grand mean excluding these three values is 79°C .

Paired TMhyd and TLM data ($\pm 0.3^\circ\text{C}$) are presented in Table 3. The parameter TFM is notoriously difficult to determine with any great accuracy because of the subjectivity involved in deciding upon the exact temperature at which the inclusion starts to melt. The temperatures reported in Table 3 are therefore only an approximation with an accuracy probably no better than 5°C .

Duplicate D-ICP results for Na and K for each of the five samples on which detailed thermometric analysis was carried out are shown in Table 4 together with results for a further four samples (RM7,8,9,10). The 'ppm' values refer to equivalent parts per million in the decrepitate for a particular element based on standard calibration procedures

TABLE 2 Summary of homogenisation temperature data

Sample Number	Mineral	Th Range °C	Mean Th	Number Studied
RM1	Calcite	77 - 85 (151)	82	20
RM2	Calcite	64 - 87 (107)	77	21
RM5	Calcite	58 - 90	80	24
RM6	Calcite	72 - 85 (122)	77	20
RM11	Fluorite	73 - 97	81	17

Bracketed figures were assumed to be due to necking down and were not included in the estimation of mean Th values

TABLE 3 Summary of TFM, TMhd and TLM data

Sample	Inclusion Type	TFM °C	TMh °C	TLM °C
RM1 (Calcite)	I	-68	-31.9	-16.2
	I	-70	-34.2	-16.2
	III	-63	-23.7	-15.5
RM2 (Calcite)	III	-67	-33.3	-15.5
	III	-65	-27.7	-16.2
	III	-61	-28.4	-15.4
	III	-60	-26.5	-15.6
RM5 (Calcite)	III	-51	-30.9	-16.4
	I	-58	-31.3	-15.6
	III	-70	-28.9	-16.6
	III	-70	-30.7	-16.0
	III	-51	-30.2	-17.8
RM6 (Calcite)	III	-55	-31.0	-17.3
	I	-58	-29.2	-17.8
	I	-62	-32.6	-17.8
RM6 (Calcite)	III	-53	-23.7	-16.9
	I	-64	-25.2	-16.8
	I	-65	-26.1	-16.8
RM11 (Fluorite)	III	-68	-28.7	-21.1

for nebulized solutions (Thompson and Walsh, 1983). It is not possible to determine the absolute concentration of a particular element in the deprecipitate because the actual amount of inclusion fluid entering the plasma is unknown. Hence it is far more meaningful to present the results in terms of Na:K weight ratios. With two exceptions (RM2 and RM6), reproducibility is moderately good. Significantly, it is two of the above samples (RM2.1 and RM6.1) which showed the lowest overall potassium responses. Because these responses are so close to background it is probable that the resultant K:Na ratios are in error. Excluding these two points from the data set the K:Na weight ratios range from 0.27 to 0.021 (mean = 0.067).

Discussion and interpretation of thermometric data

Salinity estimates based upon the TLM data presented in Table 3 and on the model NaCl-H₂O system (Potter *et al.*, 1978) define a tight grouping between 19.5 and 23 wt. % NaCl equivalents (mean = 20.5 wt. % NaCl equivs.). First melting temperatures below -51 °C differ markedly from the eutectic temperatures of -20.8 °C for the system NaCl-H₂O and -22.9 °C for the system

NaCl-KCl-H₂O. These temperatures are, however, much closer to the eutectic temperatures of between -49.5 °C and -57 °C for CaCl₂- and MgCl₂-bearing brines (data summarized by Shepherd *et al.*, 1985). Sodium and calcium are likely to be the dominant monovalent and divalent cations in the majority of crustal fluids, so it is possible to interpret the freezing results in terms of the simple system NaCl₂-CaCl₂-H₂O for which data are available (Borisenko, 1977).

TABLE 4 Summary for D-ICP results for Na and K

Sample Number	Na eppm	K eppm	K : Na wt.
RM1.1	11.8	3.2	0.270
RM1.2	12.6	3.1	0.250
RM2.1	15.4	0.4	(0.026) *
RM2.2	14.4	1.2	0.084
RM5.1	39.5	1.6	0.040
RM5.2	26.4	0.9	0.030
RM6.1	40.5	0.6	(0.008) *
RM6.2	67.9	1.7	0.025
RM7.1	42.5	2.8	0.066
RM7.2	43.0	2.3	0.053
RM8.1	30.4	0.7	0.023
RM8.2	55.6	1.7	0.031
RM9.1	43.0	1.4	0.033
RM9.2	38.3	2.0	0.051
RM10.1	51.3	1.1	0.021
RM10.2	42.5	1.6	0.040
RM11.1	74.4	2.4	0.032
RM11.2	50.6	1.3	0.026

* Samples showing poor reproducibility for K:Na also show lowest responses for K. Bracketed values therefore considered erroneous.

By locating the melting paths of individual inclusions on the appropriate ternary phase diagram it is possible to fix the NaCl:CaCl₂:H₂O weight ratio of the inclusion fluids in the manner described by Shepherd *et al.* (1985). In all instances it was assumed that the transition at TLM was due to hydrohalite rather than antarcticite melting, simply because it is highly unlikely that crustal fluids would be so enriched in calcium as to be in the antarcticite + liquid field. Results based on the present study are shown in Fig. 4. The CaCl₂/NaCl weight ratio ranges from 0.9 to 5.2. The mean value of 2.06 corresponds to a mean Ca:Na weight ratio of 1.9.

The TH data (Table 2) represent minimum trapping temperatures and require a positive 'pressure correction' to convert them into true trapping temperatures. Rogers (1977) assumed an average depth of mineral formation throughout the South Pennine orefield of about 1 km and only applied a pressure correction of 11 °C to his data. Presumably this estimate was based on hydrostatic rather than lithostatic pressures. A pressure correction corresponding to a burial depth of about 1 km is not unreasonable for the Ecton area and a similar

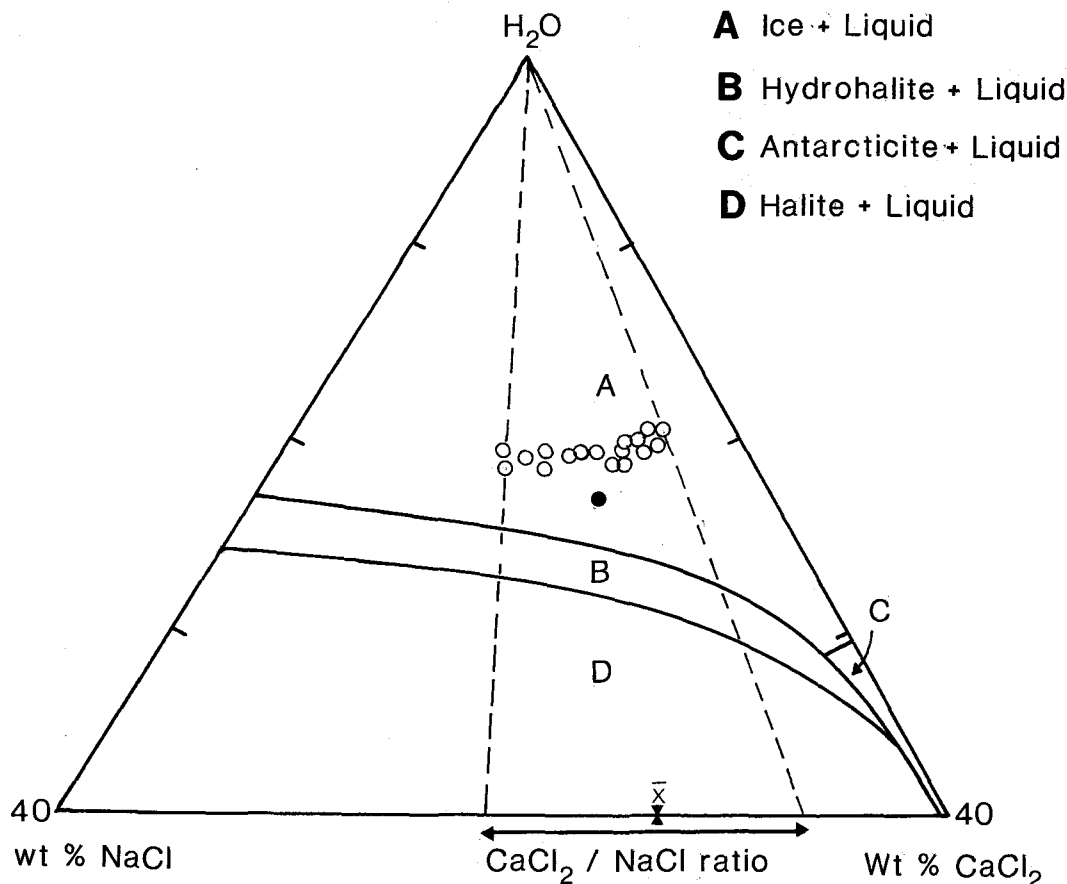


FIG. 4. Compositions of Ecton Hill fluid inclusions in the system NaCl-CaCl₂-H₂O as defined by thermometric data presented in Table 3 and the procedure outlined by Shepherd *et al.* (1985). Phase boundaries and stability fields A, B, C, D after Borisenko (1977).

correction might be added to the present data, increasing from about 10 to 27 °C if pressure was lithostatic rather than hydrostatic (Potter, 1977).

From the combined TH and salinity data it is further possible to estimate an overall density of the orefluids at Ecton at about 1.16 kg/m³, again based on the model NaCl-H₂O system (Potter, 1977).

Comparison of results

Results obtained by Rogers (1977) for presumed primary and pseudosecondary inclusions in fluorite from the South Pennine orefield, together with the corresponding summary of results for Ecton Hill, are presented in Table 5.

Overall salinities are similar but homogenization temperatures appear to be somewhat lower for the Ecton samples. Atkinson *et al.* (1982) have sum-

marized largely unpublished alternative fluid inclusion data for fluorite from the Derbyshire orefield and suggest that Rogers' homogenization temperatures may be too high. These authors suggest that average TH values for fluorite should be between 75 and 110 °C rather than between about 75 and 150 °C as determined by Rogers (1977). Despite these discrepancies the mean homogenization temperatures for the Ecton calcite samples (77 to 82 °C) are still at the lower end of the average fluorite temperatures in the remainder of the orefield. The possibility that calcite is later in the overall paragenesis is untenable because the mean temperatures for fluorite samples reported here (RM11, 81 °C) and by Atkinson *et al.* (1982) for Waterbank mine (77 °C) are within the same temperature range.

About half of the Ecton samples display K:Na

TABLE 5 Comparison of fluid inclusion data for the Ecton Hill samples and the remainder of the orefield.

Source of Data	DERBYSHIRE OREFIELD	ECTON HILL	
	Rogers (1977)	This Work	
Mineral Studied	Fluorite	Calcite	Fluorite
Uncorrected Th range °C	80 - 166	72 - 87	73 - 97
Salinity wt. % NaCl equiv.	18 - 25	19 - 21	23
K : Na wt. ratio	0.008 - 0.035	0.021 - 0.27	0.026 - 0.032
Ca : Na wt. ratio	Not determined	0.82 - 4.83	2.1

Note : See text for comments on the validity of Rogers' data in the light of unpublished data reported by Atkinson *et al.* (1982)

ratios within the range reported by Rogers (1977) but the remainder appear to be much more enriched in potassium (K:Na ratios up to 0.25). Unfortunately, comparable data on the Ca:Na contents of inclusion fluids in the remainder of the orefield are lacking, though Atkinson *et al.* (1982) do indicate that these were similarly enriched in calcium. Both the K:Na and the Ca:Na ratios of inclusions in the Ecton fluorite sample are indistinguishable from those in the calcites.

Source of the mineralizing fluids at Ecton

Several theories have been proposed to explain ore genesis throughout the South Pennine orefield (see reviews by Dunham, 1983; Mostaghel and Ford, 1986; Brown *et al.*, 1987). A basinal brine model, or refinements thereof, involving the expulsion of metalliferous brines derived from surrounding sedimentary basins into ore structures within the Derbyshire Dome has proved one of the most popular (Dunham, 1983; Mostaghel and Ford, 1986). To explain the occurrence of copper and associated mineralization in the Ecton area it has been suggested (Mostaghel and Ford, 1986) that these formed from eastward-moving fluids expelled from the Cheshire-Irish-Sea basin to the west of the orefield. It has been further suggested that sandstone-hosted stratabound copper deposits located at the margins of Triassic basins in Cheshire and Staffordshire may be linked in some way to the copper deposits at Ecton (Allen, 1982). In the eastern and central parts of the orefield, where the bulk of the lead-zinc-fluorite mineralization occurs, other sedimentary basins are thought to be

the source of the mineralizing fluids. A possibility is the North Sea basin as originally envisaged by Ford (1976), but a derivation from the basinal sediments in the Gainsborough, Edale and Widmerpool Gulfs seems more likely since these are much closer to the site of mineralization (Rogers, 1977; Ineson and Ford, 1982).

Whatever the source of these lead-zinc-rich fluids the available fluid inclusion evidence suggests that their physico-chemical properties differed only slightly from eastward-moving, copper-enriched fluids believed to be derived from the Cheshire basin. The Ecton fluids were cooler and rather more enriched in potassium than the fluids responsible for lead-zinc fluorite mineralization elsewhere in the orefield. The slightly lower temperatures of the Ecton mineralization may reflect the shallower depth of generation of fluids within the Cheshire basin compared with other sedimentary basins discussed above, rather than lower geothermal gradients in the area. Lower source temperatures are however incompatible with the higher K:Na ratios of the fluids if it is assumed that these have interacted with feldspar-bearing rocks in the source region. Experimental and theoretical studies have shown that the K:Na ratios of crustal fluids, admittedly above about 150°C, are controlled by relatively simple fluid-rock interactions involving feldspar alteration (Truesdell, 1984). These reactions are largely temperature-controlled and under equilibrium conditions form the basis of several empirical alkali geothermometers used in geothermal exploration (*op. cit.*). As temperature increases so should the potassium content of the fluid. Below about 150°C ion exchange reactions, involving clay

minerals, become more important, and the K:Na ratios may no longer accurately reflect equilibration temperatures (Truesdell, 1984). However, this argument would also hold for the orefluids from all the sedimentary sources considered above. An alternative explanation for the higher potassium contents of Ecton orefields is that marine evaporation processes and resulting evaporite sequences may have been rather more important in the Cheshire basin than in other sedimentary basins elsewhere in the area. This general idea of potassium enrichment of orefluids through interaction with evaporites is not new. Davidson (1966) originally proposed it to explain the high K:Na ratios in fluid inclusions from the North Pennine orefield. Robinson and Ineson (1979) have also suggested on the basis of S-isotopic evidence the possibility that Sabkha-type fluids were involved in ore formation in the Derbyshire orefield.

The pronounced calcium enrichment of the Ecton fluids is also noteworthy but entirely compatible with the concept of a basinal brine model for ore genesis since modern-day oilfield and basinal brines (Carpenter *et al.*, 1974) are similarly enriched. No doubt further enrichment would occur as these fluids interacted with Carboniferous limestones, resulting in fluids where Ca > Na.

Conclusions

The Ecton copper deposits and their inclusion fluids have many features in common with classical 'Mississippi Valley Type Deposits' (Ohle, 1980; Sangster, 1983), the main difference being the predominance of copper over lead and zinc. The fluid inclusion evidence shows that fluids responsible for extensive carbonate-hosted copper mineralization in the area were low-temperature (less than 100 °C), high-density, high-salinity brines with an average Ca:Na:K weight ratio of 1.9:1:0.07. The physical and chemical properties of these fluids are comparable to modern-day, metalliferous basinal and oilfield brines (Carpenter *et al.*, 1974) and therefore support a basinal brine model for ore genesis in this part of the orefield.

Brines believed to have been derived from the Cheshire-Irish-Sea basin (Mostaghel and Ford, 1986) appear to have had slightly lower temperatures and were slightly more enriched in potassium compared to their counterparts responsible for Pb-Zn-fluorite-baryte mineralization elsewhere in the orefield. The fact that these fluids deposited copper rather than lead and zinc in the Ecton area probably reflects differences in the initial metal ratios in the source rocks, rather than major differences in the physical and chemical properties of the orefluids derived from different sources.

Acknowledgements

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