

A

THESIS

entitled

SOME ASPECTS OF FLUID INCLUSION GEOTHERMOMETRY WITH
PARTICULAR REFERENCE TO BRITISH FLUORITES

submitted for the degree of

DOCTOR OF PHILOSOPHY

in the

FACULTY OF SCIENCE OF THE UNIVERSITY OF LEICESTER

by

ROGER STUART HARKER

B.Sc. (Leicester)

April, 1971

UMI Number: U378535

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI U378535

Published by ProQuest LLC 2015. Copyright in the Dissertation held by the Author.
Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against
unauthorized copying under Title 17, United States Code.



ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

X753062436



THESIS
4086/6

ABSTRACT

The development of fluid inclusion geothermometry is described from its nineteenth century beginnings down to the present time. A method for the preparation of samples for fluid inclusion work and the experimental technique using the Leitz 1350 heating stage are described.

The problems involved in obtaining representative geothermometric data are outlined. When a sample consists of well-formed crystals it is relatively easy to determine the thermal history of the sample but not so with massive material. A preliminary investigation was undertaken to assess the variation of data obtained from different sections cut from the one sample and on arbitrary grounds a minimum number of sections and of temperature measurements is suggested so that approximately representative data may be obtained.

An investigation of the relationship between filling temperatures of fluid inclusions and the thickness of the enclosing section is described. It was found that on reducing the thickness of a section, the filling temperatures of inclusions decreased. Statistical tests showed the decrease in filling temperatures to be significant and it is suggested that the rate of heating adopted by the writer is too fast to allow equilibrium between the inclusion and the heating stage to be achieved and that the observed filling temperatures are somewhat higher than the actual filling temperatures.

A preliminary investigation into the problems of leakage in fluid inclusions is described. Experiments showed that moderate overheating above the filling temperature of an inclusion did not cause leakage but that heating to 100°C. above the filling temperature usually induced leakage. A theory that over-heating may cause fluid to migrate into inter-atomic spaces and that, on cooling, this fluid may move back into

the inclusion cavity was not proved.

All the recent published works on British geothermometry are reviewed and the published data are compiled as an appendix.

CONTENTS

Acknowledgements.

Introduction.

Chapter 1. An Historical Review of Fluid Inclusion
Geothermometry.

1.1. Introduction.

1.2. The Period 1800-1880.

1.3. The Period 1880-1940.

1.4. Recent Work.

1.4.1. Techniques and Instrumentation of Fluid
Inclusion Studies.

1.4.2. Classification of Inclusions, their
Significance and the Interpretation
of Data obtained from them.

1.4.3. Filling Temperatures and their Correction
for Pressure and for the Concentration of
the Included Fluid.

1.4.4. Changes in Volume and Shape of Fluid
Inclusions since entrapment.

1.5. Conclusions.

Chapter 2. The Preparation of Sections of Minerals for
Fluid Inclusion Work.

2.1. Introduction.

2.2. Method of Sample Preparation.

Chapter 3. Experimental Procedure.

3.1. Introduction.

3.2. Calibration Procedure.

3.3. Rate of Heating.

3.4. The Correction of Filling Temperatures to compensate
for Variations in the Ambient Temperature.

3.5. Conclusions.

Chapter 4. The Range of Filling Temperatures of Fluid Inclusions within Single Samples.

- 4.1. Introduction.
- 4.2. Variations of Filling Temperatures of Inclusions within single Samples.
- 4.3. Conclusions.

Chapter 5. The Relationship between Filling Temperatures of Inclusions and Variations in the Thickness of the Sections containing them.

- 5.1. Introduction.
- 5.2. Historical Considerations.
- 5.3. Preliminary Investigation of the Variation of Filling Temperatures with the Thickness of Sections.
- 5.4. Statistical Investigation of the Variation of Filling Temperatures with the Thickness of Sections.
- 5.5. Conclusions.

Chapter 6. A Preliminary Investigation into Leakage, caused by overheating, of Fluid Inclusions in Fluorite.

- 6.1. Introduction.
- 6.2. Experimental Procedure.
- 6.3. Conclusions.

Chapter 7. General Conclusions.

APPENDICES

- Appendix 1. The Leitz 1350 Heating Stage.
- Appendix 2. Descriptions of the Samples used in the present Study.
- Appendix 3. Descriptions of the Inclusions.
- Appendix 4. Geothermometric Data.
- Appendix 5. The data obtained from the Experiment described in Chapter 5.
- Appendix 5a. The Mathematical Procedure for Student's t Test.
- Appendix 5b. The Mathematical Procedure for Student's t Test modified by Winer (1962) for Correlated Observations.
- Appendix 6. A Review of the Recent Published Work on British Geothermometry.
- Bibliography.

ACKNOWLEDGEMENTS

The writer would express his sincere thanks to the Natural Environment Research Council for financial assistance during the early part of this study.

At the University of Leicester, Professor P.C. Sylvester-Bradley is to be thanked for making available the facilities which made this study possible; Dr. A.M. Evans for his supervision of the work and for his valuable suggestions, criticisms, assistance and encouragement; Mr. P. Matkovitz for his advice in the preparation of samples and Mrs Mary Cutting for undertaking the difficult task of typing this thesis.

Sincere thanks are due to the staff of Geevor Tin Mines, Ltd., particularly to Mr. D.H. Batchelor, Managing Director, and Mr. K. Gilbert, Manager, for making possible the numerous visits to the mine and to Mr. J. Trembath and Mr. R. Barstow of the Sampling Department for their invaluable assistance in underground sampling. Thanks are also due to Dr. B. Mathias, geologist at South Crofty Mine, for kindly donating several samples.

Finally, the writer would express his deep gratitude to his wife for her advice on statistical tests and for her constant encouragement and patience during the work.

INTRODUCTION

It was the writer's intention, at the beginning of this work in January, 1968, to make a geothermometric study of some of the tin-bearing lodes at the Geevor Mine, St. Just, Cornwall. It was hoped that it would be possible to trace the thermal history of selected lodes by studying the inclusions in samples from each of the phases of mineralization described by Garnett (1962). It was also hoped that, by sampling a known phase of mineralization from one lode, on several levels and at several points on each level, a thermal gradient, if one existed, would become apparent.

Before such a project could be undertaken, it was necessary for the writer to become familiar with the methods of fluid inclusion geothermometry and in particular with the Leitz 1350 heating stage, which had been made available to him. In the absence of detailed descriptions of methods of sample preparation, some time was spent in developing a suitable technique. There followed a period during which the writer became familiar with fluid inclusions, with the various types of inclusion i.e. primary, secondary and pseudosecondary and with their behaviour on heating. The Leitz 1350 heating stage was calibrated to the writer's satisfaction using organic reagents of known melting points.

During this preliminary work it was found that only quartz and fluorite, from the Geevor Mine, were suitable for inclusion studies and that quartz was not universally usable. Cassiterite and tourmaline were unsuitable, the former because of the small grain size and dark colour, the latter because of the apparent lack of inclusions.

During the period of familiarization, several points of interest arose related to the method of fluid inclusion geothermometry, which the writer felt worthy of investigation. The samples from Geevor Mine, which

had been collected over a two year period prior to 1968 with a view to a geochemical and mineralogical study, were largely unsuitable for geothermometric work and this led the writer to devote about two years of part-time work to some aspects of the fluid inclusion geothermometric method rather than to a systematic study of the Geevor Mine. The work to be described here comprises mainly a preliminary study of the effects on the filling temperature of aqueous saline fluid inclusions of the thickness of the sections containing the inclusions, a study of the variation of filling temperatures within a sample and also a short study of the effects of heating inclusions above their filling temperatures and thereby inducing leakage. Most of this work was conducted on fluorites from various British localities, from Cornwall to the Northern Pennines. The results of these investigations are by no means startling, but the writer hopes they may be accepted as small contributions to the sum total of knowledge pertaining to fluid inclusions in minerals.

During this work, a small number of topographical data was accumulated. Some of these are new and add a little to the total of British geothermometric data. These results are presented as an appendix to this thesis. Also presented as an appendix is a compilation of all the published British data obtained during the last thirty years. Compared with the amount of work which has been published on American, Russian and European geothermometry, work on British material has been very sparse and in view of this, the writer feels justified in pointing to avenues of future research into the geothermometry of British minerals. Avenues of future research into the techniques of fluid inclusion geothermometry are outlined in the body of the text of this thesis.

In view of the apparent lack of interest, in Britain, in fluid inclusion geothermometry, the writer makes no apology for the fairly lengthy historical review in the hope that it might stimulate some interest in the subject. It will be noted that very few papers from the European school

have been reviewed. When American or Russian papers are consulted, it will be noticed that the European school has been largely ignored. The writer, while still a novice and hardly in a position to criticize, found that, on the whole, the European authors had few original contributions to offer other than large amounts of topographical data. The writer does not wish to imply that the accumulation of topographical data is without value, on the contrary, these data are the substance of knowledge of the ore-forming processes, but rather that, from the writer's point of view, contributions to the techniques of inclusion geothermometry are at present of more interest. It is to be hoped that the near future will see an increase in the methodical accumulation of British topographical data, and an upsurge in interest in the subject because, after all, Britain was the birth-place of fluid inclusion geothermometry.

1. AN HISTORICAL REVIEW OF FLUID INCLUSION GEOTHERMOMETRY

1.1. Introduction.

Fluid inclusion geothermometry has gained widespread acceptance only during the last thirty years. Whereas the fundamental principles of the method were first recognized in the eighteen twenties and firmly established in 1858, it was not until the nineteen forties that researchers seriously turned their attention to it. Two schools developed in parallel; one in the U.S. and the other in the U.S.S.R. These schools worked in isolation until the mid-nineteen fifties when Russian publications became available in English translation. While each school was critical of the other, in their isolation they had each developed and refined the method to a closely comparable extent. From the late nineteen fifties, international scientific cooperation and communication has greatly enhanced the development of fluid inclusion geothermometry. To further this cooperation, an international body, the Commission on Ore-Forming Fluids in Inclusions (COFFI), was formed in 1968 under the auspices of the International Association on the Genesis of Ore Deposits, which it is hoped, will coordinate research in this field.

1.2. The Period 1800-1880.

The existence of fluid inclusions in a number of minerals had been known for some time prior to 1800 but published reports of their detailed examination did not begin until the eighteen twenties.

Davy (1822) was the first to realize the potential of fluid inclusions as geothermometers and geobarometers. The main part of his paper described the analysis of the fluids from large inclusions in quartz from Schemnitz in Hungary and from Guanaxuato in Mexico.

Also, he described the mechanism of the development of a vapour bubble in an inclusion, pointing to the possible use of such inclusions in determining the temperature of formation of the host mineral. However, he also grasped the fundamental drawback to their use, namely that great imponderable, the confining pressure. ". . . . no exact conclusions can be drawn from the apparent degree of contraction of the water; particularly as water is much more compressible than was formerly imagined; and the volume of water, however high its temperature, must be influenced by the pressure to which it is exposed; so that a certain compressing weight may not only impede, but altogether counteract the expansive force of the heat." While Davy thus underestimated the value of fluid inclusions, he considered them to afford support to the Huttonian, or Plutonist, school of geological thought.

Davy's paper was closely followed by that of Brewster (1823) in which the existence of inclusions was noted in several new minerals and in some artificially grown crystals. While finding them of interest optically and physically, Brewster did not consider fluid inclusions of great significance to applied geology.

Sorby (1858) laid the foundation for modern fluid inclusion geothermometry. In his classic paper, he described the development of fluid inclusions in artificially grown crystals and found their several characteristics to compare very closely with those of inclusions in natural minerals. He fully appreciated the significance of fluid inclusions as possible self-registering geothermometers and he also understood the problems inherent in their use. The greatest problem in determining the temperature of formation of a mineral is the estimation of the effect of the confining pressure. Sorby clearly described the problem and constructed a formula to overcome it. He assumed that most igneous rocks solidified at about 360°C . and the

difference between the filling temperature of inclusions, estimated from their degree of filling, and 360°C . was the effect of pressure. From the expansion characteristics of a saline solution of concentration thought to correspond to that of the fluid in inclusions, he was able to estimate the pressure, in terms of feet of overlying rock, necessary to depress the filling temperature below the assumed 360°C .

The problem of pressure is but one of the factors governing the use of fluid inclusions in geothermometry. Sorby recognized most of them. It must be assumed, first of all, that the fluid exactly filled the cavity at the time of its entrapment. Sorby demonstrated this in artificial crystals. It must be assumed that the inclusions have remained hermetically sealed since the time of their entrapment, i.e. that leakage has not taken place, either out of, or into, the inclusion. Sorby was of the opinion that leakage is rare and when it has occurred, it can be seen to have occurred. The volume of an inclusion must be assumed to be unchanged since entrapment or the change must be assumed to be insignificant. Sorby regarded this point as of minor importance in so far as the compressibility of minerals is far less than that of aqueous solutions. Similarly, Sorby considered the deposition of host mineral, from the solution, on the walls of the inclusion to be of little significance. These factors are what have become to be known as the basic assumptions of Sorby.

Since the time of Sorby, several further factors have become important. Of these, the most important is the distinction between primary and secondary inclusions; indeed, this distinction is of the utmost importance in any study of fluid inclusions. The presence of carbon dioxide in some inclusions can have a pronounced effect on the thermometric data obtained and it is only of recent years, in the light of pressure-volume-temperature studies of the system $\text{H}_2\text{O}-\text{CO}_2$, that the influence of carbon dioxide has been fully evaluated.

Having described the underlying theory of fluid inclusion geothermometry, Sorby demonstrated its validity in the laboratory. Davy and Brewster had already discovered that the fluid in most inclusions was an aqueous solution of several alkali chlorides and sulphates and Sorby confirmed these findings, adding hydrochloric acid to the list. He was of the opinion that the fluid in inclusions in vein quartz contained about 15 wt. per cent of dissolved salts and upon this assumption he constructed a formula for the estimation of the filling temperature, having determined experimentally the expansion characteristics of such solutions as compared with pure water. The validity of his formula was born out by the direct comparison of the calculated filling temperature and the experimentally determined temperature (on a heating state). This temperature is higher for an inclusion of an aqueous saline solution of a certain degree of filling than for an exactly comparable inclusion of pure water. But even this higher temperature gives only a minimum temperature of formation unless the confining pressure was no greater than the vapour pressure of the fluid.

In the latter part of his paper, Sorby estimated the confining pressures of several igneous rocks, notably elvans and granites in Cornwall and the Aberdeen granite.

Sorby's work did not win instant acclaim. Ten years later, Phillips (1868) published a work on the gold-quartz veins of California. In this paper, he described the construction of a heating stage, probably similar to that used by Sorby, pointing out its limitations. The greatest of these was the relatively low (185°C.) maximum temperature obtainable. He found fluid inclusions to be very common in the vein quartz but only rarely were they usable and it was necessary to select such material "as may be more than ordinarily crystalline, or to operate on thin fragments of crystals (from) ... drusy cavities". This appears to

be the first recorded comment on the difficulties attendant upon the selection of samples. A single quartz crystal from the Mariposa vein gave filling temperatures ranging from 121°C . to 185°C . and higher. Phillips merely recorded these figures, drawing no conclusions from them.

Ward (1875) attempted to estimate the confining pressures, and hence the depth of burial at the time of formation, of several granitic bodies in the Lake District. In the preparation of sections, he noted that leakage often occurred. He used Sorby's formula for the estimation of pressure but conceded that the solidification temperature of 360°C . for quartz was by no means certain and that the discrepancies in his results may have been in part due to variations in the total salt concentrations of the fluids.

Phillips (1875) again described his heating stage and its inherent limitations. In outlining Sorby's method of calculating filling temperatures from the degree of filling, he pointed out the difficulty encountered when the inclusions were of irregular shape. Also, he noted the occurrence of single phase inclusions in some of the quartz he examined. Thus, the variability of filling temperatures obtained from a single crystal and the subjective method Sorby advocated for the selection of inclusions for study led Phillips to the conclusion that "all such calculations must necessarily be fallacious". Phillips quoted Zirkel as having said that the filling temperatures of fluid inclusions were "so very doubtful as to afford no certain data, although it would otherwise be of great value to geologists".

Allport (1876) was also critical of Sorby's ideas. He noted the abundance of fluid inclusions in quartz of varied origin and also the variability of the degree of filling of inclusions within a single crystal. Assuming that the inclusions were completely filled at the time of their entrapment and that the bubble was solely the result of contraction of

the fluid on cooling, then the degree of filling should be constant in all crystals in any small portion of rock. Because the degree of filling was by no means constant, Allport found it "difficult to see the value of any calculations based on such data."

The criticism and scepticism levelled at fluid inclusion geothermometry by Phillips, Zirkel and Allport destroyed any remaining interest in the method at that time.

A review of the state of knowledge pertaining to fluid inclusions at the end of the nineteenth century is convenient at this point. Fluid inclusions were known to exist in a wide range of minerals of hydrothermal, igneous and metamorphic origin. The majority of these inclusions had been found to be aqueous solutions containing Na^+ , K^+ , Ca^{++} , Cl^- and SO_4^{--} ions. Sorby recorded the presence of free hydrochloric acid in some inclusions in vein quartz from Cornwall and Davy described gaseous inclusions in quartz from Minas Gerais, Brazil. These latter probably contained carbon dioxide. Davy also described the occurrence of hydrocarbon in some inclusions in quartz from Dauphine, France.

It had been demonstrated that when crystals grow at elevated temperatures, the fluid trapped in cavities in the crystals completely fills the cavities at the temperature of entrapment. On cooling to room temperature, the fluid contracts to yield a partial vacuum which is filled with vapour from the fluid. Thus, normal two-phase inclusions contain a liquid phase and a mobile vapour bubble. By analogy, it was accepted that fluid inclusions in natural minerals had formed in a similar manner.

If a mineral formed under pressure conditions no greater than the vapour pressure of the fluid from which it was growing, then the temperature at which the vapour phase of inclusions disappeared (the filling

temperature or the temperature of homogenization) should closely approximate the original temperature of formation. However, should the original pressure be greater than the vapour pressure of the fluid medium, then the filling temperature will be lower than the temperature of formation. The difference between the filling temperature and the true temperature of formation will be in simple and direct proportion to the excess of the pressure of the system over the vapour pressure of the crystallizing medium.

Knowledge regarding the pressure-volume-temperature characteristics of water and aqueous saline solutions was in an elementary state. It was known that pure water expanded to a greater degree on heating than did salt water solutions and remarkably precise measurements of the differences had been made. The effect of the variable compressibility of pure water and salt water solutions on the filling temperatures of fluid inclusions was appreciated. If two inclusions occurred with identical vapour-liquid ratios (degrees of filling) one containing pure water, the other an aqueous saline solution, then the filling temperature of the inclusion containing pure water would be lower than that of the inclusion with the aqueous saline solution. The magnitude of the difference is in direct proportion to the concentration of salts in the aqueous solution.

The problem of whether an inclusion has remained hermetically sealed since the time of its entrapment and whether it has undergone any physical or chemical change since that time was fully appreciated. Sorby's opinion on these points has already been mentioned. Sorby also noted that moderate overheating, above the filling temperature, did not induce leakage. Ward (1875) recorded the frequent occurrence of leakage during sample preparation. But general opinion held that this was not an insurmountable problem and where it had occurred, those inclusions which had leaked could be distinguished from those which had

not, largely on the evidence of abnormally low degrees of filling compared with the majority of inclusions in a section. The problem of leakage has received considerable attention down to the present time.

A problem which was not appreciated by the nineteenth century workers was that of the differentiation between fluid inclusions of primary and of secondary origin. All inclusions were regarded as of primary origin and large variations in degrees of filling within single crystals were, thus, difficult to explain. The lack of a plausible explanation of this phenomenon was the greatest single factor militating against a general acceptance of the concept of fluid inclusion geothermometry during the nineteenth century.

1.3. The Period 1880-1940.

From the eighteen eighties to the nineteen twenties, the literature on fluid inclusions is extremely sparse. At the beginning of the new century, two papers appeared by Königsberger (1901) and Königsberger and Müller (1906) in which a modification of Phillips' heating stage was described. The maximum temperature obtainable with this device was 260°C. Königsberger and Müller determined the filling temperatures of quartz crystals from Alpine-type veins from several localities, stating that their data were accurate to within $\pm 15^{\circ}\text{C}$. From three Swiss localities, inclusions in quartz gave filling temperatures in the range 199°C. to 229°C.

It would appear that a further twenty years elapsed before the subject was taken up again. Holden (1925) recorded some filling temperatures in Smoky quartz and amethyst from Alpine-type veins in an attempt to estimate the pressure at the time of formation. Two smoky quartz crystals gave filling temperatures in the range 125°C. to 135°C., and an amethyst crystal gave 150°C.

In 1929, Lemmlein published on the occurrence of secondary inclusions in minerals. This paper may be regarded as marking the beginning of modern fluid inclusion geothermometry. In distinguishing between inclusions of primary origin and those developed subsequent to the formation of crystal, Lemmlein eliminated the cause of the doubt held by Phillips, Zirkel and Allport. The distinction of primary inclusions from secondaries gave a new meaning to earlier recorded and apparently erratic data. The concept of primary and secondary inclusions added a new dimension to fluid inclusion geothermometry and whereas it solved many of the old problems, it created a whole host of new ones in its wake, not the least of these being how to distinguish primaries from secondaries. Fluid inclusion geothermometry acquired a new "basic assumption", namely that primary inclusions can be distinguished from those of secondary or subsequent origin.

Newhouse (1933) was the first to conduct a systematic study of fluid inclusions with a view to determining the temperatures of deposition of the host minerals. In an earlier paper (1932) he had summarized the then existing data on the composition and concentration of fluid inclusions and, in the light of Lemmlein's, findings, discussed the significance of inclusions of primary and secondary origin. He described the criteria for their differentiation as then accepted and pointed to the difficulties encountered in many cases.

Using a heating stage comprising a paraffin bath and mercury thermometers, Newhouse (1933) studies several thousands of inclusions in blende of several generations from some eight localities in the Mississippi Valley and from several foreign localities. This work set the pattern for future geothermometric studies of ore deposits.

The form of Newhouse's paper has been followed by a great majority of subsequent workers. The state of knowledge to that time was reviewed,

then the basic assumption of fluid inclusion geothermometry were stated and discussed in the context of the study being undertaken. The technical details of the method used in the work were described and the magnitude of the errors estimated. In order that future workers might judge the validity and accuracy of geothermometric data, every study should be conducted in a similar manner to this.

1.4. Recent Work.

The work of Lemmlein and Newhouse set the study of fluid inclusions on a firm base. During the nineteen forties and fifties, interest in the subject expanded rapidly in two main schools, namely in Russia and in the United States, and with a smaller school in France. The techniques of fluid inclusion geothermometry were developed and refined considerably; the chemistry of the fluids attracted a great deal of attention in affording evidence of the nature of the ore-forming media; pressure-volume-temperature relations of pure water and aqueous saline solutions were more accurately defined, thus enabling the determination of temperatures of formation of greater precision.

During these years the Russian and American schools advanced the study of fluid inclusions on very similar lines but completely isolated from each other. Separate development was the result of poor interchange of scientific ideas between the two countries. Russian literature was difficult to obtain and it was not until 1950 that the work of the Russian school, during the previous ten years, was published. This work, presented as a monograph by Yermakov, was not available in English translation until 1965. From 1956, Russian work began to appear in English in the journal "Geochemistry", the translated form of "Geokhimiya". Whereas the translation of Russian papers is not an impossible task, it can be difficult and costly, consequently the publication of such material in English made the assessment of Russian fluid inclusion studies

much simpler.

An understanding of the development of the study of fluid inclusions from the nineteen forties to 1970 can best be gained by dividing the subject into four fairly distinct parts.

1.4.1. Techniques and Instrumentation of Fluid Inclusion Studies.

Until 1948, the thermometric study of fluid inclusions had been a visual process involving the direct observation of inclusions on heating under the microscope. Several types of heating stage were used, all of which appear to have been constructed by the workers themselves to their own specifications.

Heating stages can be divided into two types, the immersion type and the atmospheric type. The early workers, with the exception of Königsberger, used the immersion type of stage which involved the immersion of the slice of mineral in a bath of liquid, the liquid acting as the heat exchange medium. A variety of liquids were used. As previously noted, the nineteenth century workers used liquid paraffin which placed a severe limitation on the temperature attainable. Later workers adopted silicone oil whose refraction index can be varied to approximate that of the mineral to be studied. (Grogan and Shrode, 1952). Silicone oil has the added advantage of being usable at relatively high temperatures, i.e. in excess of 300°C.

The basic construction of an immersion type heating stage comprises a bath of liquid with a transparent bottom, an insulating jacket with a transparent top, a temperature measuring device such as a mercury thermometer or a thermocouple and a finely controllable heating element, the whole of which assemblage must be capable of attachment to the stage of a microscope. The relative advantages of the immersion type stage over the atmospheric type are as follows: The mineral sections do not

require a high polish to allow the observation of inclusions when immersed in a liquid of similar refractive index. The problem of thermal gradients within the stage is not so great as in the atmospheric type. Provided the hot junction of the thermocouple, or the bulb of the thermometer, is in very close proximity to the section, the problem of thermal gradients is minimal. However, with the atmospheric type, unless the temperature measuring devices are in physical contact with the section, considerable differences can occur between the actual filling temperature of an inclusion and the temperature recorded by the instrument. This problem, in relation to the Leitz 1350 heating stage, will be discussed at length in chapter 3.

Of the disadvantages attendant upon the use of the immersion type stage may be noted the messiness involved in the manipulation of sections and the necessity of partially or wholly dismantling the apparatus when changing sections.

The atmospheric type heating stages involve the heating of mineral sections in air. This type of stage comprises a perforated platform on which to place the section, a heating element in close proximity to this platform and a thermocouple in contact with the platform. This apparatus is enclosed in an insulating cell with transparent top and bottom to permit the observation of the section and the transmission of light. The transparent top of the cell is usually removable to allow easy access to the specimen platform. Manipulation of this type of apparatus is more easily accomplished than with the immersion type. The major disadvantage, as noted above, is the development of thermal gradients.

The atmospheric type of heating stage was first described by Königsberger and Müller (1906). This instrument could reach a temperature of 400°C. However, for some inexplicable reason it was not developed and later workers continued to use the immersion type with its inherent

disadvantage of a low maximum temperature. It was not until 1941 that the atmospheric type gained acceptance. Yermakov (1950) gave a detailed description of the instrument used by the Russian workers during the nineteen forties and descriptions of modifications of the basic design have appeared from time to time in the Russian literature. During the last twenty years there have been notable advances in design and of recent years such stages have become available commercially. In the vanguard of their manufacture is E. Leitz of Germany with three models, the Leitz 350 (Roedder, 1968) the Leitz 1000 (Rye, 1966) and the Leitz 1350 used by the present writer.

Heating stages of the visual type permit the determination of the filling temperatures of only a few inclusions at any one time. Thus, studies using this method must, of necessity, be extremely time-consuming. A group of workers at the University of Toronto considered this to be a major limiting factor in the widespread use of fluid inclusion geothermometry. They noted that when fluid inclusions are heated above their filling temperatures, they burst and that their bursting is accompanied by an audible noise. On the assumption that the difference between the filling temperature and the bursting or decrepitation temperature of a group of inclusions can be determined, it was put forward that the mere heating of a coarsely crushed sample and the recording of the temperature of maximum decrepitation would give a close estimate of the filling temperature of the inclusions in the sample. Opaque minerals could be studied by this method, whereas the visual method is limited to transparent minerals.

This was the basis of the decrepitation technique first described by Scott (1948) and further developed by Peach (1949) and by Smith and Peach (1949). At first, changes in the rates of decrepitation were noted by means of a stethoscope attached to the heating chamber but, later, automatic recording devices were developed. These latter

eliminated the subjectiveness inherent in the manual technique.

Whereas the decrepitation method of geothermometry was enthusiastically adopted in the U.S.S.R., the American school was more reserved in its acceptance and the small French school does not appear to have had success with it until 1965 (Pulou et al, 1970). The problems posed by this new technique gave rise to a fairly large volume of literature, for example, Kennedy (1950), Yermakov (1950), Stephenson (1952), Zakharchenko et al (1958) and Kostyleva and Labuntsov (1958). The most serious problem lies in the interpretation of the data. The method makes no distinction between primary and secondary inclusions, which distinction is one of the fundamental principles of geothermometry. Cameron, Rowe and Weis (1953), working on pegmatitic quartz, were critical of the decrepitation method in that the results can only be significant "..... when bursting can be correlated precisely with the various types of inclusions and when the effects of primary inclusions are not masked by those of secondary inclusions".

The problem of "overshoot", or the difference between filling temperatures and decrepitation temperatures, presents difficulties as this varies with the position of an inclusion within a mineral fragment; this difference will be less for inclusions close to the surface and greater for those deep within a fragment where they have to overcome the strength of a greater thickness of the mineral.

In certain instances, the converse of "overshooting" occurs. Naumov and Malinin (1968) described the decrepitation characteristics of inclusions with high gas contents (CO_2 , H_2S , H_2 , N_2 etc.). On heating an inclusion containing an appreciable quantity of gas, the internal pressure increases much more rapidly than in an aqueous saline inclusion and consequently decrepitation may occur before the filling temperature is reached. Touray (1968) noted that decrepitation sometimes

occurred below 100°C . and that a specimen of anhydrite and one of calcite, collected underground, decrepitated at a temperature not much above the ambient. Also, Sushchevskaya and Ivanova (1967) obtained a decrepitation temperature of 120°C . for a sample of quartz while the filling temperature, obtained visually from the inclusions which survived, was of the order of 280 to 285°C ; they attributed the discrepancy to a high CO_2 content. Thus, before a decrepitation study is undertaken, the inclusions must be examined visually to determine whether gas is present or not. Where gas is present, or is likely to be present, the decrepitation technique should be used with reserve.

The low temperature decrepitation of gas-rich inclusions may explain the findings of Blais (1953). In a study of a gold-quartz deposit in Quebec, he found that the gold-bearing vein quartz was characterized by decrepitation temperatures from 75° to 120°C . and that in barren quartz, decrepitation commenced above 130°C . It could be postulated that the gold values can be correlated with the gas content of the inclusions in the quartz gangue.

As a consequence of "overshooting" and its converse, the data obtained by the decrepitation method are less precise than those obtained by the visual method but exponents of decrepitation point out that the visual method only gives readings from relatively few inclusions whereas decrepitation presents the sum of many thousands or even millions of inclusions and, hence, yields more truly representative data. Critical appraisals of the decrepitation technique have been given by Ingerson (1955) and Roedder (1967). The principal advantage of the decrepitation geothermometer is its rapidity but of recent years its main use would appear to be restricted to the study of opaque minerals.

As fluid inclusion geothermometry developed, interest in the chemistry of inclusion fluids grew as fluid inclusions are, in most

cases, the only samples available of the actual mineral-forming medium. Roedder (1967b) summarized the then state of knowledge of the chemistry of fluid inclusions. Because of the technical difficulties involved in the quantitative analysis of inclusion fluids, a rapid technique to give approximate quantitative data of total salt concentrations in inclusions was sought.

The freezing point of water is depressed by the addition of nonvolatile solutes and as normal aqueous inclusions are, in fact, inclusions of aqueous saline solutions, it was early postulated that by measuring the freezing points of such inclusions, an estimate could be obtained of the total salt concentration of the solution. Sorby (1858) attempted this but was confounded by supercooling phenomena. Of recent years Deicha (1950) made an attempt, as did Cameron, Rowe and Weis (1953) and Weis (1953). Yermakov (1950) suggested it as a future line of investigation and Little (1960) tried the technique but found frosting up of the equipment a problem.

Roedder (1962) was the first to develop the technique successfully. In his paper he described the theoretical aspects of the freezing method and gave a detailed description of the instrument which he built. Roedder's success led to the widespread use of this new method of study of fluid inclusions and most worthwhile studies published since that time have included a section on freezing data. Roedder followed up his descriptive paper with a presentation of the data he had so far obtained on material from a variety of geological environments and an interpretation of those data (Roedder 1963)..

A description of a freezing stage will not be given here. It is sufficient to say that a freezing stage is analogous to a heating stage. This is true to such an extent that Roedder's instrument could be used for both freezing and heating. The preparation of sections for

use in a freezing stage is exactly the same as for use in heating studies.

The detection of gases in fluid inclusions can often be a difficult task. It is generally accepted that fluid inclusions, particularly those occurring in high temperature minerals, were entrapped at pressures greater than one atmosphere. If such an inclusion, containing a gas, is pierced at atmospheric pressure the gas may be expected to expand. Deicha (1950) developed a technique for the observation of this expansion. Basically the technique involved the crushing of inclusion-bearing mineral fragments in a drop of oil between glass plates on the microscope stage and observing any gas bubbles which appear. Deicha's instrument became available commercially but the technique does not appear to have been widely accepted. A detailed appraisal of the technique and a detailed description of a crushing stage is given by Roedder (1970).

The foregoing has been a brief review of the development of the equipment used in the direct study of fluid inclusions. In parallel with this development has been the development of more refined techniques for the chemical analysis of the contents of inclusions.

Qualitative data are relatively easy to obtain and such data have been published from the very beginning of interest in fluid inclusions. The data of Newhouse (1932) are probably the most reliable of those of the early workers. From time to time, the fluid from exceptionally large inclusions has been analyzed quantitatively; Davy (1822) was the first to publish such data. However, large inclusions are the exception rather than the rule and in systematic work they can rarely be used. In the majority of minerals, the average diameter of fluid inclusions is only a few hundredths of a millimeter and in order to obtain a sufficient volume of fluid for quantitative work, relatively large volumes of mineral must be crushed. This gives rise to the problem of distinguishing between fluids of primary and secondary origin.

The necessity for such a distinction needs no elaboration other than to say that the fluids from primary and secondary inclusions can have very different compositions.

Roedder (1958) described a method for the quantitative analysis of the fluids released on decrepitating relatively large amounts of mineral. The amount of water obtained was determined by passing it through a gas absorption train and the salts were determined, both quantitatively and qualitatively, by a process of very careful leaching and microanalysis. Ames (1958) quickly adopted Roedder's method in analyzing fluids from a group of minerals from New Mexico. However, the major drawback to this method, as mentioned above, was the impossibility of distinguishing primary fluid from secondary fluid. To overcome this problem, Roedder et al (1963) described a technique whereby very small, selected portions of crystals could be cut, containing only the desired type of inclusion and whereby the contents of these inclusions could be determined quantitatively. Details of the procedure will not be given here.

Interest in the isotopic compositions of inclusion fluids began in the nineteen fifties when Friedman (1953) and Friedman and Smith (1958) described a technique for the determination of the deuterium content of natural waters and published data from their findings. Roedder et al (1963) made use of this method and since then Rye (1966), Dontsova and Naumov (1967) and Rye and O'Neil (1968), among others, have extended isotopic studies to oxygen and carbon with interesting and significant results.

Roedder (1967a; 1967b) reviewed and discussed the various methods available for determining the composition of fluid inclusions.

1.4.2. Classification of Inclusions, their significance
and the interpretation of data obtained from them.

Sorby's simple fourfold classification of inclusions found in minerals, namely liquid, gas, glass and stone, was **not** questioned or modified for some eighty years. The greatly increased interest in the subject during the nineteen forties led to more refined and detailed systems of classification, particularly as the result of the recognition of numerous sub-classes within Sorby's broad framework. In the monograph by Yermakov (1950) an excellent classification is given which subdivides Sorby's four groups into some sixteen sub-classes. Smith (1954) put forward a fivefold classification which clarified that of Sorby, and discussed the significance of the various divisions. While Smith's classification is chronologically later than Yermakov's, the latter was not generally available until 1965. Thus, in effect, the classification of Smith preceeded that of Yermakov as far as most non-Russian workers are concerned.

A detailed appraisal of all the classes and sub-classes of inclusions in minerals is beyond the scope of this brief review. However, for the sake of completeness some mention must be made of them.

Solid inclusions in minerals, the stoney inclusions of Sorby, are of two types, clastic and crystalline. Clastic inclusions represent fragments of rocks and minerals which settled on to growing crystal faces by gravity and were enclosed by the growing crystal material (type 3 of Smith). Crystalline inclusions are small crystals of a foreign mineral which nucleated and grew upon the growing face of the host crystal; growth of the host was more rapid than that of the foreign crystal and hence the latter became enclosed, (type 4 of Smith).

Solidified inclusions, or Sorby's glassy type and in part his stoney type, occur only in the minerals of magmatic rocks. These may be

included in Smith's type 1. They include two broad divisions, glassy and crystalline. The latter represent small globules of magma which solidified slowly, within cavities in already solidified crystals, to assume a crystalline structure. The glassy type were similar globules of magma which solidified rapidly without attaining crystallinity. In many ways these latter are analogous to the aqueous type described below. As with the aqueous type, glass inclusions are divisible into three - single-phase, two-phase (glass-gas) and multiphase. The glassy type is restricted to the phenocrysts of effusive rocks. The present writer has found only two modern references to work on inclusions of this type: Roedder (1965) and Naumov (1969). The latter author described the determination of homogenization temperatures of gas-glass inclusions in quartz phenocrysts by a method analogous to the heating stage study of fluid inclusions. Roedder (1965) was not concerned so much with the glass inclusions in olivine nodules in basalts as with the carbon dioxide which the inclusions contained.

Gaseous inclusions (Smith's type 2 in part) are of two major types: chiefly gaseous and gas-liquid. By Yermakov's definition a fluid inclusion containing more than 50 vol. per cent of the gas or vapour phase is a gaseous inclusion. Only rarely are inclusions observed wholly filled with gas. Gaseous inclusions are characteristic of pegmatitic minerals and minerals formed by sublimation.

The fourth major group of inclusions, of particular importance in geothermometry, is the liquid type (Smith's type 1). This group is divisible into three; aqueous, carbon dioxide and hydrocarbon. Carbon dioxide and hydrocarbon inclusions, whilst occasionally very abundant, are of relatively minor importance to geothermometry. By Yermakov's definition, aqueous inclusions must contain more than 50 vol. per cent of the liquid phase. The aqueous subgroup is itself divisible into three, namely single phase, two phase and multiphase.

In aqueous inclusions, one of the phases is always liquid, usually an aqueous saline solution. The most common second phase is a bubble of the vapour of the liquid. A variety of other phases and components has been recognized; most commonly a third phase comprises small crystals of a daughter mineral such as halite or sylvite, indicative of supersaturation of the solvent at room temperature. Several different daughter minerals may be present in the one inclusion. Tourmaline, hematite, selenite, halite, sylvite, hydrated sodium silicate, hydrous ferrous chloride, elpasolite (K_2NaAlF_6), cryolite, fluorite, etc. have been recognized along with numerous unidentified substances either singly or in various combinations from various localities. Lyakov (1967) described the occurrence of as many as fourteen different crystals in a single inclusion in a pegmatitic smoky quartz and Kelly and Turneaure (1970) reported twenty six different types in Bolivian material, their being most varied and abundant in the early-formed quartz and cassiterite. While inclusions containing both water and carbon dioxide are, in some instances, quite abundant, they will be described in the subgroup of carbon dioxide inclusions.

Hydrocarbon inclusions are relatively rare but where they occur they can be very abundant. Davy (1822) was the first to describe this type. Their composition ranges from heavy bituminous material to light paraffin-like substances. Two phases, liquid and vapour, are most common; single phase inclusions are rare. The most frequently quoted example of this type are from the fluorite deposits of Illinois; less well known examples include the "Blue John" fluorite of Castleton, Derbyshire and the quartz crystals of Herkimer County, New York (Herkimer Diamonds).

Inclusions containing carbon dioxide are of two types; those containing carbon dioxide alone and those containing both carbon dioxide and aqueous solution. In the latter, the ratio of carbon

dioxide to aqueous solution varies considerably. Pure carbon dioxide inclusions commonly comprise two phases at room temperature, liquid and gas. On warming above 31.1°C. (the critical temperature of carbon dioxide) homogenization occurs, either to the liquid or the gas phase, depending on the density of the entrapped carbon dioxide. Inclusions containing both carbon dioxide and aqueous solution commonly contain three phases at room temperature, liquid carbon dioxide, carbon dioxide gas and liquid aqueous solution. As liquid water and liquid carbon dioxide have low mutual solubility, they form separate liquid phases and as water is a polar compound and carbon dioxide is not, the water phase clings to the walls of the inclusion and the liquid carbon dioxide surrounds the central gas bubble (Roedder, 1965). At 31.1°C. or lower (Roedder, 1965), partial homogenization takes place to yield a two-phase situation, liquid aqueous solution and liquid or gaseous carbon dioxide. According to Smith (1954) carbon dioxide-bearing inclusions have not been observed to contain daughter crystals which suggests a low salinity for the aqueous component. Roedder (1965) observed small crystals of, apparently, spinel in essentially carbon dioxide inclusions in olivine-bearing nodules from basalts and Kelly and Turneure (1970) recorded the occurrence of occasional traces of daughter salts in Bolivian quartz and cassiterite.

The classification of fluid inclusions according to physical types reviewed above is open to further refinement and as research progresses, doubtless refinements will be made. A generic classification is much simpler and is unlikely to be complicated in the future. Lemmlein (1929) was the first to recognize the existence of secondary fluid inclusions in minerals and the division of inclusions into primary and secondary categories did much to ease the problems of interpreting geothermometric data. A third category or division was described by Yermakov (1950) which he termed primary-secondary or

pseudosecondary.

Secondary inclusions are generally considered to have developed after the crystallization of the host mineral has ceased, by fracturing and healing of the host. Fracturing and healing of the host crystal can occur while crystallization is still in progress, so that planes of apparently secondary inclusions may penetrate the core of the crystal and the fluids present chemical and thermometric data identical to the fluids from undoubted primary inclusions in the outer zones of the crystal. Healed fracture or cleavage planes containing fluid inclusions may sometimes be seen to terminate abruptly before they reach the outer surface of a crystal; this is the only really positive criterion for the recognition of pseudosecondary inclusions. Roedder (1967) reviewed a mechanism for the formation of pseudosecondary inclusions first put forward by Barton et al (1963). This mechanism was described as "hydrothermal leaching". Mineral deposition may sometimes be interrupted by brief periods during which dissolution of the already precipitated material occurs. Such dissolution is seldom uniform and leads to the development of etch pits which may penetrate several growth zones. Etch pits may be sealed off by further growth of the crystal, thereby entrapping a pseudosecondary inclusion.

The generic classification of fluid inclusions is, thus, now a threefold one and in any study of inclusions it is essential, for the unambiguous interpretation of the data, that the three categories are recognized.

Fluid inclusions represent samples, albeit minute, of the media from which the host minerals were deposited. With the exception of fumarolic and hot spring fluids, inclusion fluids are the only samples available to geologists of the ore-forming media. Fluid inclusions must, thus, be of inestimable value in throwing light upon the

chemical composition, temperature and state of aggregation of the ore-forming fluids.

Mention has already been made of the significance of solid and solidified inclusions. Of particular interest to the geologist is the significance of the liquid and gaseous types.

Knowledge of the chemistry of the ore-forming fluids can be gained by the analysis of the inclusion fluids. Early attempts at such analyses have already been described. The modern techniques were reviewed by Roedder (1967b). It remains here to outline the evidence which fluid inclusions afford of the physical properties of the ore-fluids.

The appearance of fluid inclusions at room temperature and their behaviour on heating provide evidence of the state of aggregation of the ore-forming fluids. The simplest case is the single phase aqueous inclusion. Sorby considered that this type represented deposition from a low temperature aqueous solution; Yermakov (1950) considered it to represent a solution temperature of not more than 50°C. and subsequent workers are in agreement.

Two phase and multiphase inclusions yield evidence of two main types, namely of the temperature of mineral deposition and of the state of aggregation of the mineralizing fluid, whether it was in the liquid state, the gaseous state or in a state with intermediate properties.

It is accepted that the filling temperature of a two phase or multiphase aqueous inclusion is indicative only of a minimum temperature of formation of the host mineral and that a positive correction for pressure must be applied. The magnitude of such corrections as deduced from the pressure-volume-temperature relations of water and aqueous solutions will be discussed later in this chapter.

With regard to evidence of the state of aggregation of the ore fluids, the way in which homogenization occurs is the most important

criterion, a criterion which is still somewhat controversial. Homogenization of two phase aqueous inclusions is of three types, homogenization to the liquid phase, homogenization to the gaseous or vapour phase and homogenization by the fading of the phase boundaries, the factor governing which is the degree of filling as observed at room temperature. Inclusions with a degree of filling greater than 50 per cent, that is, in which the liquid phase occupies more than 50 vol. per cent of the cavity, homogenize to the liquid phase by the concurrent expansion of the liquid and contraction of the vapour bubble. Minerals containing inclusions of this type are generally considered to have grown from liquid water solutions of varying temperature and concentration, that is, from hydrothermal solutions.

Aqueous inclusions with a degree of filling of about 45 per cent homogenize by a fading of the phase boundary, sometimes preceded by a slight contraction of the vapour phase. This is the least common of the three types of homogenization. Ingerson (1947) showed that if an inclusion of pure water possessed the correct ratio of liquid to vapour at room temperature, then on heating, the phase boundary would disappear at the critical temperature of water. Cameron, Rowe and Weis (1953) considered the temperature of fading of the phase boundary to be the critical temperature of the included fluid and Kelly and Turneure (1970) stated that this type of homogenization occurs when an inclusion has the critical degree of filling; they suggested that inclusions of this type indicate mineral deposition from a boiling fluid with the simultaneous entrapment of both liquid and vapour in the inclusions.

Inclusions with a degree of filling of less than about 45 per cent homogenize to the vapour phase by the expansion of the vapour bubble. General agreement is lacking as to the interpretation of this phenomenon. Yermakov (1950) is of the opinion that homogenization to the vapour

phase indicates deposition from super-critical water vapour or gaseous solutions and ascribes such minerals to the pneumatolytic group. Smith (1949) was of a similar opinion when he studied the filling temperatures and mode of homogenization of inclusions in some Cornish ore and gangue minerals (see Appendix 6). However, as they all homogenized to the liquid phase, he considered them to be of hydrothermal origin even though the temperature of formation he obtained was higher than the critical temperature of water. Kennedy (1950) criticized Smith on this point and appeared to be firmly convinced that any ore-forming solution at a temperature higher than 373°C . (the critical temperature of water) must be in the gaseous state and hence give rise to pneumatolytic deposits and inclusions homogenizing to the vapour phase, despite earlier work (Kennedy, 1944) in which he considered it pointless to advocate the existence of a gas or liquid state of aggregation in moderately deep seated fluid systems. In reply to Kennedy, Smith (1950) maintained his hypothesis of the mode of homogenization and suggested that the critical density of a fluid should be taken as the dividing line between hydrothermal and pneumatolytic minerals, not the critical temperature and in a later paper (Smith, 1954a) he concluded that water and aqueous saline solutions under normal geothermobaric conditions have liquid-like rather than gas-like properties. Takenouchi and Kennedy (1965) concluded that there can be no sharp temperature boundary, such as 373°C ., between the regions of pneumatolytic and hydrothermal mineral deposition.

Discussions such as the above described lead into the concepts of critical phenomena, pressure-volume-temperature relations of aqueous solutions and the like, which will be considered later in this chapter. Suffice it here to say that there can be no sharp dividing line between minerals of hydrothermal and of pneumatolytic origin or rather between hydrothermal and pneumatolytic ore-forming solutions, but that a

continuous series must exist between minerals formed from low temperature, strictly liquid, aqueous solutions and minerals formed from strictly gaseous, high temperature, aqueous solutions and that it is convenient to draw an arbitrary division between minerals containing inclusions homogenizing to the liquid phase and those containing inclusions homogenizing to the vapour phase. It is only for the sake of convenience that one is justified in calling the former hydrothermal and the latter pneumatolytic.

It may be noted at this point that, in certain cases, inclusions have been described from one and the same crystal exhibiting homogenization both to the liquid and to the vapour phase (Smith and Little, 1959). Kelly and Turneure (1970) interpreted such an occurrence in Bolivian tin veins as indicative of boiling of the ore-forming fluid, some inclusions having trapped the liquid phase and others the vapour phase and both types yielding similar filling temperatures. In such a case, the vapour pressure of the ore-forming fluid is equal to the confining pressure of the system and the filling temperatures of the inclusions are equal to the true temperature of formation. This is one of the few cases in which an accurate temperature of formation can be obtained.

Occasionally, additional information about the nature of the mineral-forming fluid can be deduced. Roedder (1965b) described the occurrence of two-phase aqueous inclusions interspersed with single phase hydrocarbon inclusions in fluorite from southern Illinois. The relatively low temperature of formation deduced from the filling temperatures of the aqueous inclusions leaves no doubt as to the liquid nature of the ore fluid. The hydrocarbon inclusions are interpreted as droplets of oil which adhered to the growing faces of the crystals. Thus, the mineralizing fluid is considered to have been an immiscible mixture of brine and oil droplets.

In cases such as the above and in the case of a majority of moderate to low temperature mineral deposits, the physical state of the mineral-forming medium is not difficult to envisage. It is in the realms of high temperature deposits, such as pegmatites and skarns, that difficulties arise.

As mentioned above, carbon dioxide inclusions are of two major types, those containing carbon dioxide alone and those containing carbon dioxide and water. The latter type may contain other gases such as hydrogen, nitrogen and methane. Maslova (1961) described gas-water inclusions in which the gas consisted of up to 94 per cent hydrogen sulphide. The major division is approximately reflected by the geological environments of the minerals containing carbon dioxide inclusions. Pure carbon dioxide inclusions appear to be restricted to minerals of volcanic origin (Roedder, 1965, and Touray, 1968). Roedder (1965) described pure carbon dioxide and carbon dioxide-water inclusions in olivine-bearing nodules in basalts from some seventy world-wide localities. Touray (1968) recorded the occurrence of pure carbon dioxide inclusions in olivine, diopside, bronzite and anorthosite. The occurrence of inclusions of almost pure carbon dioxide is considered indicative of a silicate fluid containing droplets of immiscible, dense, super-critical carbon dioxide which attached themselves to growing crystal faces and became entrapped (Roedder, 1965).

Pure carbon dioxide inclusions are of little use in geothermometry but they can be used as geobarometers. Roedder (1965) determined the approximate pressure at the time of entrapment of carbon dioxide inclusions in olivine-bearing nodules by estimating visually the phase ratios at known temperatures and, using known phase data for the carbon dioxide system, the density of filling was calculated. From the density of filling, the approximate pressure was obtained from the data of Kennedy (1954).

Inclusions containing both carbon dioxide and water occur in minerals from more diverse geological environments. Minerals of volcanic origin may contain such inclusions, as noted above. Touray (1968) observed them in quartz and potash feldspars from granites and in apatites from carbonatites. Probably the most common occurrence is in pegmatitic and high temperature hydrothermal minerals (Smith and Little, 1959). Cameron, Rowe and Weis (1953) described their occurrence in pegmatitic quartz and beryl; Little (1960) observed them in "normal vein" type cassiterite; Zakharchenko (1964) listed their occurrence in pegmatitic topaz, fluorite and apatite and Touray (1968) extended the list to include calcite and anhydrite. Tugarinov and Naumov (1969) stated that H_2O-CO_2 inclusions had been found in blende, magnesite, huebnerite, realgar and orpiment. However, inclusions of carbon dioxide and water are not found universally in pegmatites. Weis (1953) commented on their absence from minerals in some Black Hills pegmatites.

Controversy exists as to the significance of H_2O-CO_2 inclusions with regard to the state of aggregation of the mineralizing fluid. Yermakov (1950) considered them to throw no light on the problem of the state of aggregation and stated that they were unsuited for thermometric analysis. However, he admitted at that time that the Russian school had had little experience of H_2O-CO_2 inclusions and he was, perhaps, too hasty in dismissing them as of no value. Smith (1954a) was of the opinion that carbon dioxide under "normal geothermobaric conditions" would have more the properties of a liquid than of a gas and Garrels and Richter (1955) demonstrated the relatively high solubility of carbon dioxide in water at high temperatures and pressures from which it may be postulated that at great depth and at high temperature and pressure, carbon dioxide and water may exist as a homogeneous, dense, single-phase fluid. On rising from depth, with a concomittant decrease in pressure and possibly

temperature, two immiscible phases may separate; a nearly pure carbon dioxide phase and a phase consisting essentially of water and containing only minor carbon dioxide. They pointed out that the homogenization of H_2O-CO_2 inclusions is not entirely caused by the expansion of the liquid water phase but is due, at least in part, to the dissolution of carbon dioxide in the water as the temperature increases.

Cameron, Row and Weis (1953) described three modes of total homogenization in H_2O-CO_2 inclusions dependant upon the density of the included fluids, but they did not consider their significance. After a prolonged discussion on the philosophy of inclusion geothermometry, they concluded that "... nothing in the nature of a fluid inclusion at room temperature or in its behaviour when heated tells us whether they have formed under supercritical or subcritical conditions from single-phase or two-phase systems". However, Smith and Little (1959) in their study of H_2O-CO_2 inclusions, were less pessimistic. They proposed a classification based on the modes of homogenization in some respects similar to that of Cameron, Rowe and Weis; three modes of partial homogenization from the three-phase to the two-phase condition were recognized and three modes of total homogenization, from the two-phase to the one-phase condition. The two-phase to one-phase transformation was said to be unrelated to the preceding three-to two-phase change. Smith and Little were of the opinion that evidence of the state of aggregation of the mineralizing fluid could be obtained by observing the phase ratios of H_2O-CO_2 inclusions at room temperature. When all the primary inclusions in a crystal exhibit identical ratios, formation from a single phase fluid is indicated. The filling temperatures of such inclusions will be lower than the temperature of formation. When essentially aqueous inclusions are found together with carbon dioxide-rich inclusions, a two-phase fluid is indicated, that is, partition has taken place in an originally homogeneous multicomponent fluid

to yield a water-rich phase and a carbon dioxide-rich phase, some inclusions having trapped the water-rich phase, some the carbon dioxide-rich phase and others possibly having trapped a quantity of both phases. Smith and Little postulated that when aqueous and carbon dioxide-rich inclusions occur together the phase ratios at room temperature are similar throughout the sample, the filling temperature is equal to the temperature of formation, but that the filling temperatures of inclusions which have trapped some of both phases, indicated by erratic phase ratios at room temperature, are higher than the temperature of formation. This hypothesis has not been widely questioned but nor has it been widely accepted, possibly in view of the comparative rarity of H_2O-CO_2 inclusions. Of recent years, Kelly and Turneaure (1970) have applied the idea in their study of Bolivian tin deposits.

Takenouchi and Kennedy (1965) elaborated on the ideas of Garrels and Richter (1955) in a study of the solubility of carbon dioxide in aqueous saline solutions at elevated temperatures and pressures. They found that the solubility of carbon dioxide decreased with an increase in the salt concentration and considered it unreasonable to expect large quantities of carbon dioxide to be dissolved in mineralizing fluids of high salt concentrations. An originally homogeneous magmatic emanation containing carbon dioxide and appreciable quantities of salts, on cooling, will separate into a CO_2-H_2O -rich phase and an $H_2O-NaCl$ rich phase. As partition is to be expected in a CO_2-H_2O system (Garrels and Richter, 1955) the addition of salts to the system will enhance such partition. The low solubility of carbon dioxide in saline solutions explains the observations of Smith (1954a) that carbon dioxide-bearing inclusions did not contain daughter salts.

From the above brief review, it may be concluded that some evidence may be derived from H_2O-CO_2 inclusions as to the nature of the

mineralizing fluid, whether a homogeneous fluid or an immiscible mixture of fluids, but with regard to the state of aggregation of the fluid or fluids, problems arise analogous to those encountered with aqueous saline fluid inclusions.

1.4.3. Filling Temperatures and their correction for pressure
and for the concentration of the included fluid.

The most serious drawbacks to the fluid inclusion geothermometric method are the effects of pressure and of concentration of solution on the filling temperature of an inclusion. Both problems were recognized by Sorby (1858) but, even in the light of currently available data, they are not yet fully resolved. The effect of the concentration of solution upon the filling temperature of an inclusion is the lesser of the two problems. It has long been accepted that pure water expands more rapidly on heating than an aqueous salt solution and, consequently, that for a given degree of filling, an inclusion of pure water will yield a filling temperature lower than that of an inclusion of a salt solution. It would appear relatively simple to establish experimentally the elevation of filling temperatures caused by varying concentrations of salt solutions; from such data and from the degree of filling of the inclusion it should be possible, assuming the pressure at the time of formation to have been no greater than the vapour pressure of the solution, to estimate the concentration of the included solution.

Whereas the effect of the concentration of solution on the filling temperature can be relatively easily established, the effect of pressure at the time of formation is less easily evaluated. It is generally agreed that, at high pressure, a greater mass of fluid will be compressed into an inclusion of given volume than at a lower pressure, the temperature remaining constant, and, consequently, that the inclusion formed at the higher pressure will record a lower filling temperature

than that formed at the lower pressure. The problem in geothermometry is how to determine, in quantitative terms, the depression of filling temperatures caused by pressure.

A third problem arises from a combination of the above, namely the problem of critical phenomena in geological environments. This has already been considered briefly in relation to the state of aggregation of the mineral-forming fluids as deduced from the behaviour of fluid inclusions on heating. The critical constants of an aqueous solution vary with the concentration and composition of the solution and the filling temperature of an inclusion of an aqueous solution is in part determined by the critical constants, as will be shown below. The problem of critical phenomena necessitates the study of the pressure-volume-temperature relationships of aqueous saline solutions.

The following is a chronological review of selected papers pertaining to the problems outlined above.

Ingerson (1934) reviewed the state of knowledge of critical and supercritical phenomena to that date. Hannay and Hogarth (1879) were the first to study such phenomena. They demonstrated that non-volatile solutes were soluble in supercritical gases; the solubility was governed by the density of the solvent and by the temperature, the density, in turn, being governed by the pressure. Hannay found that at constant pressure, the solubility increased with increase in temperature. Centnerszwer (1903) established that non-volatile solutes raised the critical temperature of the solvent in proportion to the concentration and that the critical temperature of a mixture (or solution) of two volatile substances was lower than that of either component. From this work, Ingerson concluded that the elevation of the critical temperature of water by the addition of non-volatile solutes may be counteracted by the presence of volatile solutes. Thus, a natural hydrothermal solution, containing both NaCl and CO₂ may have a critical temperature very close

to that of pure water. He described the data of Schröber (1929) on the elevation of the critical temperature of water by the addition of alkali halides.

Morrey and Ingerson (1937) concluded that concentrated aqueous solutions may not have a critical temperature but that up to 15 wt. per cent of non-volatile solutes will raise the critical temperature of a solution to no higher than 500°C.

Kennedy (1944) attempted to determine the "hydrothermal solubility" of silica. He concluded that the denser a gas, the more like a liquid solvent it behaves and demonstrated that at 380°C. and 1000 atm., H₂O gas is denser than H₂O liquid at 370°C. and 200 atm. Kennedy considered it of little point to advocate the existence of gas or liquid at such high a pressure as 1000 atm.

In 1947, Ingerson presented a series of diagrams to show the relation between the degree of filling of an inclusion and the filling temperature both for pure water and for a 10 per cent NaCl or KCl solution, the latter part compiled from the data of Schröber; the relation of filling temperature, pressure and temperature of formation for inclusions of pure water; the temperature correction to be added to the critical temperature of water for solutions of NaCl or KCl up to 12 wt. per cent concentration and a diagram to show the pressure correction to be added to the filling temperature of an inclusion to compensate for depth of burial of up to ten kilometers. He pointed out that the estimation of pressure can usually be little more than an intelligent guess. This was a most valuable contribution to fluid inclusion geothermometry and it enabled workers, for the first time, to make quantitative allowance for pressure when amassing geothermometric data.

Kennedy (1950) re-measured the press-volume-temperature relationships of water and revised the correction curves of Ingerson (1947). He

presented two diagrams, one to show temperature of formation when pressure can be estimated and the filling temperature is known, the other to show the pressure corrections to be added to filling temperatures to compensate for depth of burial. In their lower regions, Kennedy's diagrams are in fair agreement with those of Ingerson but not so in their upper regions. Above about 250°C., Kennedy's pressure corrections are consistently higher than Ingerson's. It was pointed out that the correction curves were for pure water and that if the inclusion fluids contained non-volatile solutes, then the corrections would be somewhat smaller and, conversely, if volatile components were present, the corrections would be greater. Kennedy found, experimentally, that a water inclusion formed at 360°C. and 440 bars and one formed at 555°C. and 2120 bars both exhibited a filling temperature of 325°C.; the density of water at 360°C. and 440 bars is equal to that of water at 555°C. and 2120 bars.

Smith (1954) considered the critical temperature and pressure to be limits neither of the gaseous nor of the liquid state of aggregation of a fluid and that water and aqueous saline solutions under normal geothermobaric conditions would have liquid-like properties.

Weis (1953) pointed out that the expansion curves for salt solutions lie on one side of the expansion curve for pure water and the expansion curve for H₂O-CO₂ solutions on the other. This was the equivalent of saying that salt solutions expand, on heating, less rapidly than pure water and therefore yield higher filling temperatures for a given degree of filling. He made note of Keevil's data (1942) on the vapour pressure of saturated NaCl and KCl solutions and pure water at 500°C. The vapour pressure of pure water at this temperature is far higher than that of either solution.

Cameron, Rowe and Weis (1953) described the processes which take place within an inclusion on cooling from the temperature of formation to

room temperature. Various types of behaviour may be expected, depending on the temperature of formation and on the density of the fluid. It was assumed, in all cases, that the fluid completely filled the cavity at the time of entrapment. The simplest case is that of a subcritical liquid which, on cooling, shrinks and a vapour phase appears. If the fluid is supercritical, behaviour on cooling depends on the density of the fluid. When the density is higher than the critical density, the fluid passes into the liquid phase on cooling below the critical temperature and the liquid still fills the cavity; the vapour phase appears at a considerably lower temperature when the liquid has been able to contract sufficiently. On re-heating, the behaviour of such an inclusion is indistinguishable from that of a normal subcritical inclusion. The data of Kennedy (1950) were used to illustrate this point. Cameron et al. put forward three possible types of behaviour of inclusions formed from supercritical fluid below the critical density. Where the density is only slightly less than the critical, on cooling below the critical temperature, a liquid phase will appear which does not completely fill the cavity. On cooling to room temperature, this liquid phase diminishes. Re-heating causes the liquid to expand but before filling is complete, the phase boundary disappears. At a certain density (unspecified by Cameron et al.) cooling below the critical temperature causes shrinkage of the liquid phase which is compensated by the condensation of the vapour phase. Re-heating is accompanied by no change in the liquid-vapour ratio but at the critical temperature the phase boundary disappears. Where the density is considerably lower than the critical, the liquid phase expands as cooling continues to room temperature. Re-heating in this type is accompanied by an expansion of the vapour phase to completely fill the cavity at the temperature of homogenization.

Kennedy (1954) determined the pressure-volume-temperature relationships for CO_2 up to 1000°C . and 1400 bars. He noted that CO_2

lowers the critical temperature of solutions and so is a factor in determining whether the mineralizing solutions were gaseous or liquid but Smith (1954a) stated that there was no evidence that gases as such were of consequence in the formation of mineral deposits. Kennedy's work made available data on CO_2 , permitting for the first time, the objective assessment of the effect of CO_2 in fluid inclusions.

Lemmllein (1956) presented a diagram, constructed by Lemmllein and Klevtsov, to show the variation of filling temperature with the degree of filling for NaCl solutions of various concentrations, along with the curve for pure water. This work was complementary to that of Ingerson and Kennedy. From this diagram, if the degree of filling can be estimated and if the filling temperature is known, the approximate concentration of the inclusion fluid can be determined.

Koltun (1958) described a method, devised by Kalyuzhnyi, for determining the pressure of formation from pairs of inclusions, one of each pair rich in CO_2 and the other in H_2O . In the field of the combined pressure-volume-temperature diagram for CO_2 and H_2O , the pressure and temperature of formation are determined by the point of intersection of the isochores corresponding to the characteristics of the two inclusions.

Klevtsov and Lemmllein (1959) observed that fluctuation in pressure had a greater effect on the filling temperatures of inclusions than had variations in salinity. They presented experimental data in support of their statement.

Lemmllein and Klevtsov (1961) noted that the capacity for expansion of aqueous salt solutions decreased rapidly with increase in concentration. They presented six pressure correction diagrams for aqueous NaCl solutions of 5, 10, 15, 20, 25 and 30 per cent concentration. Again, their work is complementary to that of Kennedy (1950b).

Sourirajan and Kennedy (1962) determined experimentally the critical

temperatures of NaCl solutions of up to 26 wt. per cent concentration. They found the curve to be almost a straight line from 374°C and zero wt. per cent NaCl to 700°C. and about 26 wt. per cent NaCl. The critical pressure for similar solutions ranged from about 220 bars for pure water to about 1240 bars for 26 wt. per cent NaCl. It was found that the solubility of NaCl in H₂O gas increased with increase in pressure and temperature and above 600°C the solubility increased very rapidly.

Takenouchi and Kennedy (1965) found that even with high partial pressures of CO₂, liquids exist in the system H₂O-NaCl at temperatures and pressures above the critical for pure water.

Samoylovich and Khetchikov (1968) presented limited data for the systems H₂O-CaCl₂, H₂O-LiCl and H₂O-NH₄Cl.

Naumov and Malinin (1968) described a method for determining the pressure of formation from H₂O-CO₂ inclusions which involved knowledge of the internal pressure at the point of partial homogenization (62-70 atm.) and the pressure necessary to start mass decrepitation (given as 850 atm. for quartz). Heating stage measurements of the temperature of partial homogenization, the temperature of complete homogenization and the temperature of the start of mass decrepitation were then required. These data were plotted on the combined pressure-volume-temperature diagram for H₂O and CO₂ and in the case of the temperature of complete homogenization being higher than that of the start of mass decrepitation, a straight line extrapolation to the temperature of complete homogenization allowed the pressure of formation to be read. They justified the straight line extrapolation by reason of experimental evidence from the system H₂O-CO₂ where almost straight lines were obtained. They claimed the error involved in this method to be no greater than 10 per cent.

Tugarinov and Naumov (1969) noted that the pressure corrections for

salt solutions are smaller than for pure water but that for aqueous solutions of low concentration (<10 per cent) the corrections differ little from those for pure water. They concluded that where the inclusion fluids are known to be dilute, it is permissible to use the data for pure water.

From the foregoing review, it can be seen that during the past forty years or so, the total of knowledge pertaining to the problems of corrections of filling temperatures of fluid inclusions for pressure and concentration has increased considerably. It is now possible, by using the currently available analytical techniques and by referring to the appropriate pressure-volume-temperature data, to evaluate accurately the effects of concentration of solution on the filling temperatures of inclusions. In certain instances it is possible to determine the pressure at the time of formation as in the case of an ore-fluid which can be shown to have been boiling, in which case the confining pressure was equal to the vapour pressure of the solution and in the case of inclusions containing both water and CO_2 and pairs of inclusions, the one containing water and the other CO_2 ; these latter two are comparatively new ideas which emanated from the Russian school and should, perhaps, be accepted with some reservation for the present. However, instances such as these are comparatively rare and in the vast majority of cases it is not possible to determine the pressure although it is possible to obtain an accurate correction factor to be added to the filling temperature to compensate for the pressure if the pressure were known. Accurate correction factors are to be desired but they are of limited value when the pressure itself cannot be estimated with comparable accuracy. The estimation of pressure at the time of formation is still the greatest drawback to the fluid inclusion method of geothermometry and until this problem can be overcome it is not possible to make truly objective comparisons between thermometric data from widely separated localities.

However, when a single mineral deposit is under consideration it is probably permissible to ignore the factor of pressure and to regard the data obtained as comparable within themselves.

1.4.4. Changes in volume and shape of fluid inclusions since entrapment.

One of the basic assumptions of the fluid inclusion geothermometric method is that there has been no change in the ratio of cavity volume to liquid volume since the time of entrapment (Weis, 1953). In a normal two-phase aqueous inclusion, the volume of the vapour phase represents the difference between the contraction of the mineral and the contraction of the aqueous solution on cooling. The very presence of a vapour phase at room temperature indicates that the contraction of the fluid has been greater than that of the host mineral. On heating to the filling temperature, the liquid expands more rapidly than the host mineral and so fills the inclusion cavity. In the majority of cases, the observed filling temperature is lower than the true temperature of formation, and consequently, at the filling temperature the host mineral will not have expanded to the precise volume it occupied at the time of its formation. The result of this discrepancy will be a further lowering of the filling temperature below the temperature of formation. However, the difference in volume of an inclusion cavity at the filling temperature compared with its volume at the temperature of formation is very small and the difference between the temperature of formation and the filling temperature resulting from this difference in volume is negligible compared with the difference between the two temperatures caused by the pressure at the time of formation. Thus, the error caused by changes in the volume of the inclusion cavity may be safely disregarded (Sorby, 1858).

Changes in cavity volume as a result of deposition of solutes upon the cavity walls is another problem which must be taken into account.

Yermakov (1950) discussed this problem at length, particularly the problem of the deposition of "cognate substance," that is, the substance of the host mineral. The present writer does not consider this to be a problem of any significance. A primary fluid inclusion usually represents an area of non-deposition upon the face of a growing crystal. At the moment of trapping, a volume of fluid containing in solution a certain amount of host substance becomes completely enclosed and hermetically sealed. The host substance dissolved in the fluid will at some time be deposited upon the walls of the cavity in crystallographic continuity with the host crystal. The amount of deposition cannot be very great as the volume of the enclosed fluid is only very small and the writer does not consider this deposition to be a significant source of error in the fluid inclusion geothermometric method.

Similarly, the changes in volume caused by the precipitation of "daughter minerals" are not a significant source of error as the "daughter minerals" usually redissolve before the filling temperature is reached. In the case where the "daughter minerals" dissolve at a temperature higher than the filling temperature, the temperature of their dissolution represents a minimum temperature of formation, just as the filling temperature of an inclusion containing no "daughter minerals" is a minimum temperature of formation in the majority of cases. The problems of changes in inclusion cavity volumes have been discussed by Roedder (1967b).

Changes in the shape of inclusions as a result of the recrystallization of the host mineral bounding the inclusion cavity can introduce serious errors into the geothermometric method if they are disregarded. Peach (1951) noted the fairly common occurrence of pairs of inclusions with dissimilar degrees of filling some times connected by a capillary canal. He considered them to result from recrystallization since the time of formation by the solution of the host mineral in certain parts of an

inclusion and deposition in other parts during cooling. The vapour bubble resulting from shrinkage of the liquid may be positioned at one end of the inclusion and recrystallization may cause the inclusion to be divided. As cooling progresses, the vapour bubble already formed, and now trapped in one of the inclusions, continues to expand and a bubble develops in the other inclusion. At room temperature, the liquid-vapour ratios of the two inclusions may be markedly different and the filling temperatures obtained from them have no bearing on the temperature of formation. Roedder (1967b) termed this phenomenon "necking down" and presented a diagram to describe its mechanism.

Lemlein (1956) observed "necking down" and changes in shape in artificially formed secondary inclusions in halite and sodium nitrate. Irregularly shaped inclusions have high free surface energies and it is in the nature of crystalline substances to achieve a state of minimum free surface energy. The consequence of this is that material forming a convex or plane surface is more readily soluble than the same substance forming a concave surface and in a closed system, may migrate from convex or plane surfaces to concave surfaces. Thus, ideally, an irregular cavity will change to a spherical cavity of similar volume if sufficient time is allowed for the achievement of equilibrium. In readily soluble minerals, such as halite, the process is very rapid and can be observed experimentally but most of the ore and gangue minerals are not readily soluble. In the case of the latter, geological time is required to attain equilibrium and commonly it can be seen that equilibrium has not yet been reached in minerals studied at the present time.

Roedder (1967b) showed that spherical shapes were not necessarily the equilibrium configuration but that negative crystals may be the end result of the healing of a fracture plane. Negative crystals are cavities bounded by crystallographically orientated walls; the writer has observed cubic and rectangular cavities in fluorite and hexagonal cavities

in quartz.

In geothermometric studies of fluid inclusions, it is essential that the phenomenon of "necking down" should be recognized. If a group of inclusions is found with dissimilar degrees of filling in a section where the majority of inclusions have a fairly uniform degree of filling, then the possibility of "necking down" should be considered (Sawkins, 1966b). Inclusions which have undergone or are suspected of having undergone "necking down" cannot be used as geothermometers.

With regard to distinguishing primary and secondary inclusions, one of the old criteria of primary origin, namely negative crystal shape, must now be accepted with caution in the light of the findings of Roedder (1967b). Roedder amplified his views on the shapes of fluid inclusions in a paper, which was, unfortunately, published as an abstract only, presented at the C.O.F.F.I. symposium (section 1.1.) in Prague in 1968.

It may be concluded, here, that changes in the ratios of the volumes of inclusion cavities and inclusion liquids since the time of entrapment are of little significance and may be disregarded as a major source of error in fluid inclusion geothermometry. However, changes in the shape of inclusions since their formation, resulting in "necking down", cannot be so easily dismissed; failure to recognize such changes can lead to serious error in geothermometric studies.

1.5. Conclusions.

The foregoing has been an attempt to trace the development of fluid inclusion geothermometry from its nineteenth century beginnings to the present day. From this review, it will have been noticed that the majority of the modern developmental work was carried out by the American and the Russian schools. The European school has made relatively few technical contributions and modern work in Britain, of any description, has been very limited.

Historical reviews and monographs of fluid inclusion chemistry and geothermometry have been published by Ingerson (1947), Yermakov (1950), Smith (1953), Correns (1954), Deicha (1955), Ingerson (1955) and Roedder (1967a and 1967b).

A great majority of the recently published works have been topographical studies and an attempt at their review has not been possible. It appears that certain types of mineral deposits have received especial attention, particularly the Mississippi Valley-type deposits in the U.S., the rock crystal bearing pegmatites in the U.S.S.R. and the Alpine-type veins in Europe. In Britain, the bulk of the published work has been devoted to the Hercynian tin deposits of the south-west of England.

At the present time, the value of fluid inclusion geothermometry and chemistry is largely academic although from time to time an economic application is found. As fluid inclusions represent samples of the ore-forming media, it is to be expected that their study will help in solving some of the problems associated with ore-formation. The work of Billings, Kesler and Jackson (1969) may be cited as an excellent example of the application of fluid inclusion studies to the problems of ore genesis and Sawkins (1966b) put forward a plausible theory for the formation of the ores of the Northern Pennines in the light of the evidence from fluid inclusions.

The economic application of fluid inclusion studies has so far been rather limited. Blais (1953) described a fairly rapid method whereby auriferous quartz could be distinguished from barren quartz, using the decrepitation technique. Bradshaw and Stoyel (1968) advocated the possible use of geothermometry in the exploration of zoned metalliferous deposits, using Cornwall as an example, and numerous Russian workers have studied the geothermometry of piezo-optical crystal quartz with a view to establishing exploration guides (Laz'ko, 1957; Piznyur, 1957; Puzanov, 1958; Venediktov, 1958; Elinson and Polykovskiy, 1967, and many others).

As a geological tool, the study of fluid inclusions is of a value which cannot be denied. As the techniques improve and the problems are solved, its value will increase greatly. Over the past fifty years, fluid inclusion geothermometry has gained widespread acceptance, the evidence for which lies in the exponential growth of the published literature. It remains now for that growth to include Britain.

2. THE PREPARATION OF SECTIONS OF MINERALS

FOR FLUID INCLUSION WORK

2.1. Introduction.

The methods of preparation of mineral sections for fluid inclusion studies have received only brief mention in the published literature. Sorby (1858) mounted thin sections on glass slides with Canada balsam in much the same manner as petrological thin sections are prepared. Twenhofel (1947) cut sections 1 mm thick but made no mention of polishing, whereas Yermakov (1950) pointed out that a thorough polish was essential for minerals of high refractive index and that semi-transparent minerals required polishing on both surfaces. He did not recommend the use of sections thicker than 5 mm as greater thickness would interfere with the uniform heating of the sections and cause the development of thermal gradients. Yermakov suggested that the final polish should be on a smooth, cloth covered board using chromic oxide.

Subsequent workers were divided in opinion as to the necessity of polishing one or both sides of the sections. Cameron, Rowe and Weis (1953) found that the frosted, unpolished lower surface of a section provided a diffuse illumination against which inclusions could be more clearly seen than against a polished lower surface. Kelly and Turneure (1970) used sections polished on both surfaces.

In some cases, the polishing of sections has proved unnecessary. For instance, where cleavage flakes are used, the cleaved surface is often sufficiently smooth to permit the observation of inclusions within the body of the flake (Kelly and Turneure, 1970). Where silicone oil heating stages are used, polishing is not required. Grogan and Shrode (1952) cut slices of fluorite 2.5 mm thick and heated them in silicone oil of similar refractive index to fluorite. When very

small crystals are being used, cutting and polishing is sometimes unnecessary and Kelly and Turneaure (1970) found that natural crystal faces were often sufficiently transparent to be used without further preparation.

The physical operation of polishing has rarely been described in detail. The majority of workers have favoured a hand method, either on glass or on cloth, using various abrasives such as alumina, jewellers rouge, chromic oxide, tin oxide or diamond dust. Stress has been laid on the necessity of polishing by hand to prevent the generation of excessive heat which could cause overheating and leakage of inclusions with low filling temperatures.

Most workers seem to have favoured a method of polishing where the slice of the mineral is physically held in the hand whereas Freas (1961), Schmidt (1962) and Erickson (1965) mounted their slices on bakelite blocks with "Duco" cement (presumably an organic resin); after polishing, the slices were removed from the bakelite blocks by soaking in acetone. This use of organic resin has a serious drawback which will be described below.

In chapter 5 of this thesis, it is stated that the thickness of the sections used in this study was usually determined in an arbitrary fashion, there being no hard and fast rules governing the choice of thickness. The literature reveals the use of sections varying in thickness from 0.2 to 5.0 mm. The most obvious criterion in deciding the thickness is the clarity of the minerals to be used. All previous workers appear to agree that the more opaque the mineral the thinner must be the section and vice versa. The choice of thickness must be determined by each worker for the material in hand, but a standard thickness should then be adopted for each mineral to be studied.

In preparing sections for fluid inclusion work, several factors

must be taken into consideration. The most important of these is the avoidance of excessive heating. If heating takes place such that a temperature is achieved higher than the temperature of filling of the inclusions, leakage may occur, the consequences of which are described in chapter 6. The initial slicing of the sample is usually conducted using diamond saws, most of which, to-day, are supplied with adequate cooling systems. The subsequent lapping of slices is usually by hand on glass with silicon carbide grit and water, the latter acting as lubricant and coolant. It is in the final polishing stage that the problem of heating becomes more critical. Mechanical lapping on cloth with diamond dust is wont to generate heat. Consequently this final operation should be conducted slowly by hand.

The degree of polish which must be achieved is governed by the transparency of the mineral, but in all cases there is a minimum below which the section will not be usable. The choice of whether to polish one or both surfaces of a section is also somewhat arbitrary but in the case of deeply coloured and semi-transparent minerals, double polishing is often required. In some cases, where the inclusions are known to have low filling temperatures, lacquering of the surfaces may be sufficient. The use of small, untreated crystals and cleavage flakes has already been noted but it should be pointed out that lapping of the lower surfaces of such crystals and flakes may be necessary to achieve an even contact with the heating surface or specimen platform of the heating stage.

Lacquering of sections and mounting sections for polishing using organic resins can, in certain circumstances, be undesirable. The first sections prepared in Leicester University for the use of the writer were made by the standard procedure for the preparation of polished sections of ores. The slices were set in bakelite rings

in Araldite resin and, after polishing, they were removed from the Araldite and soaked in acetone to remove any adhering resin. These first sections were of early-formed quartz from Geevor Mine, Cornwall, and the inclusions contained therein had filling temperatures in excess of 300°C . On heating to about 300°C , the sections began to turn brown and eventually became totally opaque as a result of the oxidation of the small amount of resin which had not been removed from the section by washing in acetone. It was found to be almost impossible to remove every last vestige of resin from the sections. Thus, the writer concludes that when sections are to be heated in air, as in using the Leitz 1350 heating stage, and when high filling temperatures are to be expected, the use of organic substances in the preparation of sections should be avoided.

2.2. Method of Sample Preparation.

The initial slicing of the samples is conducted on a diamond saw (Type Q.S.2. manufactured by Meyer and Burger Ltd., Steffisburg, Switzerland). The slices cut from all samples are about 2 mm thick, irrespective of transparency. If the sample is small, a number of slices may be necessary to ensure that sufficient inclusions will be found. In this case, the Q.S.2. now can be set to cut automatically any number of slices of exactly the same thickness up to a maximum of eighty.

After cutting, the slices require lapping to remove saw-marks and to ensure a planar surface. The procedure adopted for this process depends on the physical size of the slices. If they are very small and difficult to hold in the fingers, they must be mounted in some way. The writer developed a technique whereby these small slices are set in rapid setting dental plaster in a 40 mm diameter bakelite ring of the type used in preparing polished sections of ores. Several slices can

be mounted in one ring. Initial lapping, with 600 grade silicon carbide grit is carried out on an automatic lapping machine (Unilap, manufactured by Speedlap Corporation, Spokie, Illinois). This lapping machine can be set to operate for any given length of time. For quartz, the writer found three to four minutes sufficient and for fluorite about two minutes. Heat generation during this operation is minimal as there is adequate fluid ("Glyconol" antifreeze and water in the ratio 1:1) in the system to act as a coolant. As many as sixteen bakelite rings of slices can be lapped simultaneously. When the slices are large enough to be hand held, the bakelite rings are not required and initial lapping is carried out by placing the slices loose upon the lapping machine.

After lapping with 600 grade silicon carbide grit, the slices are lapped by hand on a glass plate with 800 grade grit. For both quartz and fluorite, three to four minutes' lapping is sufficient. This hand operation is more time consuming than the previous one. As in the previous operation there is no great heat generation.

The final polishing is achieved on a slowly rotating, paper-covered lap using gamma alumina and a small amount of water. The generation of some heat is unavoidable at this stage as, for best results, the lap has to be fairly dry. In the case of hand-held slices, excessive heating can be detected through the finger tips and when the slices are mounted in bakelite rings it is merely necessary, from time to time, to touch the partially polished surface against the palm of the hand. Three to four minutes' lapping is usually sufficient to achieve a good polish on quartz and two to three minutes for fluorite. With hand-held slices it is easy to examine them under the microscope to adjudge the degree of polish and if it is insufficient, further lapping can easily be undertaken. However, with mounted slices this is more difficult as re-lapping after removal from the bakelite rings

necessitates re-mounting and re-lapping from the 600 grade silicon carbide stage. Slices are removed from the plaster in the bakelite rings by the use of a hammer and a small cold chisel. Adhering plaster is easily removed by washing in cold water.

The writer is satisfied that insufficient heat is generated to cause leakage of inclusions during all the above operations. Most primary inclusions can tolerate overheating by some tens of degrees without leaking and leakage was rarely observed by the writer in any of the current work.

In the above method of preparing sections, no control of the thickness was exercised. The thickness required cannot be determined until polishing has been carried out. In a suite of samples of a particular mineral, the thickness used was decided by the most opaque sample in the suite and that thickness was adopted as the standard for that mineral in that suite of samples. The significance and necessity of standardizing the thickness is described in chapter 5. To obtain the required thickness the polished slices are lapped by hand on glass with 240 grade silicon carbide. This lapping gives a frosted lower surface of the type advocated by Cameron, Rowe and Weis (1953). In the case of reasonably transparent quartz and fluorite, the writer found polishing of both surfaces of a section to be unnecessary. This afforded a saving in the time taken preparing sections.

By the above procedure it is possible to prepare more than 20 hand-held slices or bakelite rings of slices in a normal working day. This rapid technique has now been adopted as standard procedure for the preparation of sections for fluid inclusion work in the Department of Geology at Leicester University.

3. EXPERIMENTAL PROCEDURE

3.1. Introduction.

It is necessary, in any study of fluid inclusions involving the use of a heating stage, to assess the error inherent in the equipment to be used. The difference between the true temperature of filling of a fluid inclusion and the temperature recorded by the measuring instrument must be evaluated. The magnitude of this difference varies from one heating stage to another; particularly does it vary between the immersion type and the atmospheric type, the latter usually producing the greater discrepancies.

Roedder, Heyl and Creel (1968) found rather large thermal gradients to exist between the heating element, the thermometer and the sample chamber in the Leitz 350 heating stage. The writer is not familiar with this instrument but assumes it to be similar to the Leitz 1350 model. Consequently, the writer expected to find thermal gradients to exist within the Leitz 1350 stage and, to evaluate such gradients, a procedure of calibration, using organic reagents of known melting point, was adopted on the advice of Roedder (personal communication).

3.2. Calibration Procedure.

The heating assembly of the Leitz 1350 heating stage (Appendix 1) consists of a sapphire glass object carrier set upon a metal platform or object carrier support into which is set the hot junction of a thermocouple, the whole of which is surrounded by a ceramic heating cartridge. As the hot junction of the thermocouple does not come into contact with the sample, but only touches the sapphire glass object carrier, a difference between the temperature recorded by the thermocouple and the true temperature within the sample may be expected; the

thermocouple should record a higher temperature, commensurate with the thermal lag between it and the sample.

The cold junction of the thermocouple is at room temperature so that the temperature recorded on the measuring instrument (a galvanometer) is the difference between room temperature and the temperature within the heating chamber. The zero on the galvanometer scale represents room temperature ($20-23^{\circ}\text{C}$) and as a first step in obtaining a true temperature reading, the room temperature must be added to the recorded temperature. A fine adjusting screw on the galvanometer allows the instrument to be set at zero for any given room temperature; if, for example, it is set at zero when the room temperature is 23°C . and the temperature falls to, say, 20°C ., the needle of the instrument will indicate a negative temperature, ideally -3°C . The converse is also true. To compensate for this variation, two alternatives present themselves, either to adjust the instrument for every slight change in the room temperature or to establish a correction factor to be applied to the readings. The writer chose the latter course.

The calibration made use of organic reagents of known melting points for the low temperature range and an inorganic substance for the high temperature range. The reagents were:-

8 - hydroxyquinoline,	M.P.	73 - 75°C .
Acetanilide,	M.P.	115 - 116°
Ascorbic Acid,	M.P.	190 - 192°
Dicyandiamide,	M.P.	207 - 209°
Barium Nitrate,	M.P.	593°

Two methods were used in an attempt to measure the melting temperature of the reagents. The first was to place crystals of the reagents directly upon the sapphire glass object carrier and the second was to seal a quantity of each reagent in a short length of capillary tube and to place

the tube on the object carrier (Roedder, Heyl and Creel, 1968). Both methods have their drawbacks.

Crystals placed directly upon the object carrier sublimed to some degree before the melting temperature was reached and the sublimate condensed on the quartz cover plate thereby obscuring the vision. However, the quartz cover plate can be rotated through 360° and as one area became obscured, the plate was turned to a clean area. Anthracene (M.P. 217°C) was tried initially but this reagent sublimed completely before melting.

There are two drawbacks to the use of capillary tubes. The first is the difficulty of sealing the tube without causing the reagent to oxidize. Five to seven millimetres is the maximum length of tube which can be used in the Leitz 1350 heating stage. One end of such a length is sealed in a bunsen flame and a small quantity of the reagent is inserted into the tube. The open end of the tube is then sealed in a bunsen flame whereupon the reagent melts and migrates to the cool end of the tube where it may undergo oxidation if the sealing is not performed very rapidly. If the reagent has been oxidized, it cannot be used for melting point determinations.

The second drawback is the poor contact a capillary tube makes with the object carrier. At best, the contact is along a narrow strip the length of the tube but often, in sealing the tube, the ends become somewhat bulbous or dumb-bell shaped, in which case contact with the object carrier is limited to two points only. As a result of such poor contact, a thermal gradient exists between the object carrier and the capillary tube. This drawback is further aggravated by the sublimation of the reagent from the lower side of the tube and its condensation on the upper side with the result that during repeat readings, the thermal gradient is made greater. The magnitude of the thermal gradients resulting from the use of capillary tubes can be seen from a comparison of Fig. 3.1. with Fig. 3.2. In consequence of these drawbacks, the capillary tube

method was dismissed in favour of the simpler placing of the reagents directly upon the object carrier.

In determining the melting temperatures of the various reagents, the temperature of the beginning of melting was read. In all cases, complete melting occurred over a range of three or four degrees. On cooling after melting, supercooling was almost invariably observed. The rate of heating used during the calibration was the same as that used throughout the whole of the present work. The rate is described below (section 3.3.).

When crystals of the reagents were placed directly upon the object carrier, the melting temperatures recorded were, in all cases, very close to the expected temperatures, namely the melting point minus the room temperature (Fig. 3.1.). As the melting points of the reagents used were themselves somewhat variable, a figure of $\pm 2^{\circ}\text{C}$. was necessary to allow for the error inherent in the calibration. Thus, at this stage, assuming that the galvanometer has been set at zero for a given room temperature, the true temperature may be obtained by adding the room temperature to the observed temperature and adding the error factor of $\pm 2^{\circ}\text{C}$.

3.3. Rate of Heating.

The thermal conductivity of most minerals is poor and it is to be expected that thermal gradients will be set up, on heating a mineral section, between the base of the section, which is in contact with the object carrier, and the interior of the section. On this assumption, it may be expected that the temperature recorded by the instrument will be somewhat higher than the temperature within the section. In order to minimize this discrepancy, a very slow rate of heating should be adopted, whereby the mineral section is given the opportunity to achieve the temperature of the object carrier support which is the part of the heating assembly whose temperature is actually measured by the thermocouple. A

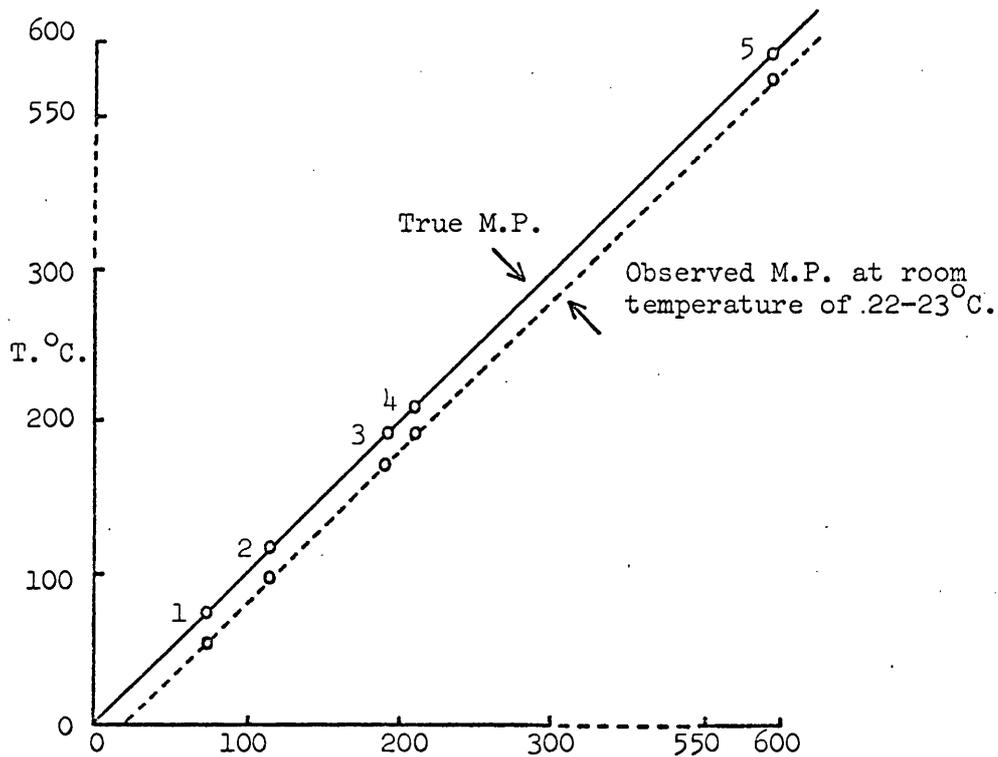


Fig.3.1. Diagram to illustrate the difference between the true melting points of the reagents and the observed melting points when crystals of the reagents were placed directly upon the object carrier.

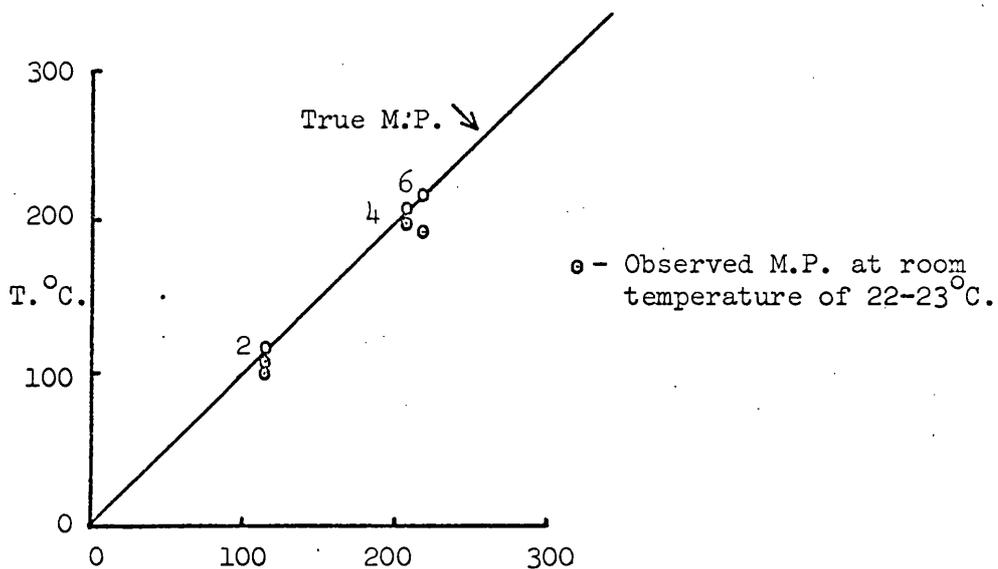


Fig.3.2. Diagram to illustrate the difference between the true melting points of the reagents and the observed melting points when crystals of the reagents were sealed in capillary tubes.

- | | |
|-----------------------|-------------------|
| 1. 8-Hydroxyquinoline | 4. Dicyandiamide |
| 2. Acetanilide | 5. Barium Nitrate |
| 3. Ascorbic Acid | 6. Anthracene |

very slow rate of heating is acceptable in theory and in studies which involve the measurement of only a few fluid inclusions. However, in a systematic study, which may involve the measurement of many hundreds or even thousands of filling temperatures, very slow heating is not feasible and a compromise must be reached commensurate with the required accuracy and with the time available.

Yermakov (1950) emphasized the necessity of a slow and uniform rate of heating and stated that the same rate should be used for the same type of inclusions in a given mineral from a given locality. He considered it preferable to determine the optimum rate of heating empirically. The average time taken for a homogenization run was found, by Yermakov, for low temperature inclusions to be about one hour whereas with high temperature inclusions a run may take four to five hours. Cameron, Rowe and Weis (1953) found a heating rate of 10 to 15°C. per minute satisfactory and they claimed to obtain results accurate to within 2½°C. Freas (1961) and Schmidt (1962) adopted a rate of 6-8°C. per minute whereas Erickson (1965) claimed to have used a heating rate of 1°C. per three to four minutes. From these few references, it can be seen that it is impossible to state a definitive rate of heating for fluid inclusion studies. Obviously, the slower the rate the more accurate the results but there is a point at which the increased accuracy is outweighed by the increase in the time taken; the larger the number of inclusions to be measured, the sooner is this point reached.

An hour for one run, postulated by Yermakov (1950), is acceptable in a systematic study provided several inclusions in the section can be measured during that hour. Four to five hours for a run is only worth while if quite a large number of inclusions, say about twenty, can be measured and it is seldom that twenty inclusions are found within one field of view of the microscope. A rate of heating of ten to fifteen degrees per minute, adopted by Cameron, Rowe and Weis (1953) is, in the

opinion of the writer, a reasonable rate consistent with the accuracy required in a large scale, systematic study of high temperature minerals and six to eight degrees per minute for low to moderate temperature minerals is also reasonable. One degree per three to four minutes claimed by Erickson (1965) is far too slow if anything but a small number of inclusions are to be measured.

The problem confronting the writer, at the beginning of his studies of fluid inclusions, was to establish a rate of heating which would provide reasonable accuracy of results and be economical of time. To this end, a fairly rapid rate of heating was tried on fluorite, from the Geevor Mine, whose inclusions homogenized in the range of 200 to 300°C. A rapid run, taking four to five minutes, was conducted to establish an approximate filling temperature. If the filling temperature was, say, approximately 250°C., it would be determined accurately as follows; 100°C. would be achieved in about two minutes, 200°C. in a further four or five minutes and thereafter the rate would decrease to about two degrees per minute for the last ten degrees or so. Thus, a run would take about fifteen minutes. Duplicate runs took less time than this as cooling to room temperature was not required; as soon as the vapour bubble reappeared, usually some tens of degrees below the filling temperature, heating could be recommenced. Every filling temperature determination in the writer's work was repeated at least once to confirm the validity of the result. If a determination could not be duplicated to within one degree, it was discarded. This happened but rarely and only when leakage had occurred.

To test the accuracy of filling temperature determinations by this rapid rate of heating, a simple experiment was conducted. Fluorite from 10 Foot Wall Branch Lode, Geevor Mine, was chosen and a single, large, clearly defined and easily locatable two-phase inclusion was selected. The filling temperature was measured ten times by the method described above and the temperature was found to vary from 213 to 214°C.

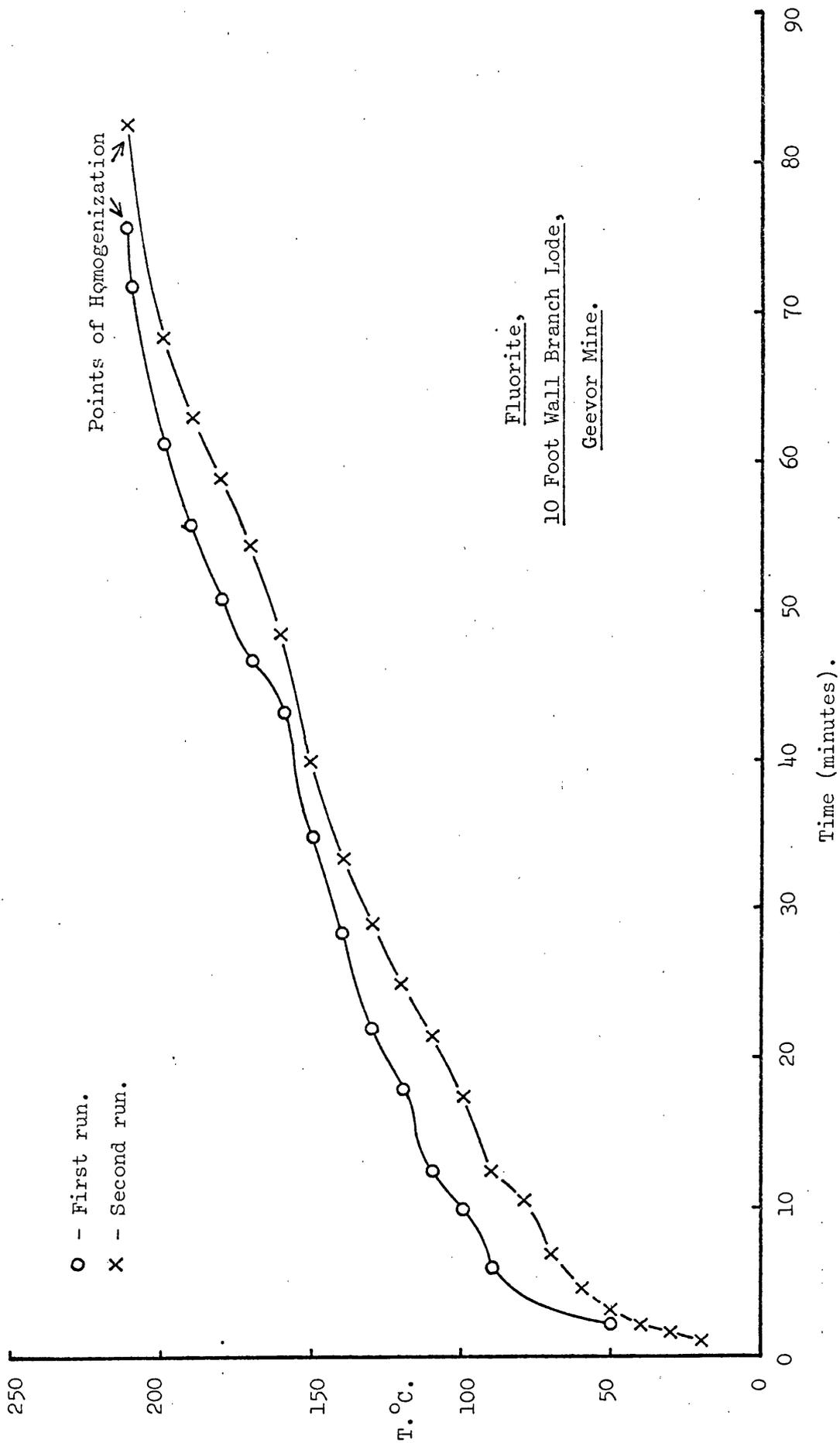


Fig.3.3. Diagram to illustrate the very slow rate of heating described in section 3.3.

with a mean of 213.5°C . The rapid runs were followed by two very slow runs (Fig. 3.3.) which gave a filling temperature of 211.5°C . Thus, it was concluded that the rapid rate of heating yielded filling temperatures which were a little high and a more accurate figure could be obtained by subtracting two degrees from the observed temperature.

At this stage it can be seen that a multiple correction factor must now be applied to all observed reading, namely the factor derived in section 3.2. and the above. To the observed readings must be added the room temperature minus two degrees, the whole accurate to $\pm 2^{\circ}\text{C}$. The correction required to compensate for variation in room temperature when the instrument is not continually adjusted will now be considered.

3.4. The correction of filling temperatures to compensate for variations in the ambient temperature.

Nowhere in the literature has the writer found mention of the variation of filling temperatures with variations in the ambient temperature. During the work described in chapter 5, it was noticed that the filling temperatures of "control inclusions" varied inversely with the temperature of the laboratory, that is, the higher the room temperature the lower were the filling temperatures. It was necessary to evaluate this variation and to this end a small experiment was conducted.

Whereas one thermometer had previously been kept in the working area of the small optical laboratory, a second thermometer was now introduced and the room temperature was taken as the mean of the readings of the two thermometers. The galvanometer was set at zero at a room temperature of 23.5°C . (the then usual temperature for the laboratory). Two sections of fluorite from 13 North Pig Lode, Geevor Mine, were taken and a single, clearly defined two-phase inclusion was chosen from each. The filling temperature of the inclusion in one of the sections was measured when the room temperature was 23.5°C ., after which the laboratory was heated

by means of an electric convector heater. Several hours were allowed for the temperature of the equipment to reach equilibrium with the temperature of the laboratory and the filling temperature of the inclusion was redetermined. Over several days the laboratory was alternately heated and allowed to cool and the filling temperature of the inclusion was measured at various times. A similar experiment was conducted on the second section and the results from both sections are presented graphically as Figs. 3.4 and 3.5. Ideally, the two parts of the diagrams should be mirror images of each other.

From the results, the inverse relationship between room temperature and filling temperature is clearly seen. With the exception of point X in Fig. 3.4, the readings of room temperature and filling temperature correlate very closely. Point X is anomalous and the writer offers no explanation other than to suggest that equilibrium may not have been achieved and that the galvanometer, containing the cold junction of the thermocouple, may still have been warm some time after the room temperature had fallen.

It may be concluded that if the room temperature changes after the instrument has been set at zero, the filling temperatures of inclusions can be corrected by adding or subtracting the difference between the actual room temperature and the room temperature at which the instrument was set at zero. If the room temperature rises, the correction is positive and if it falls, the correction is negative.

3.5. Conclusions.

In fluid inclusion studies involving the measurement of the filling temperatures of many hundreds and sometimes thousands of inclusions, a relatively rapid rate of heating must be adopted in order to complete the work in a reasonable length of time. The writer has shown, to his own satisfaction, that with the Leitz 1350 heating stage a rapid rate of

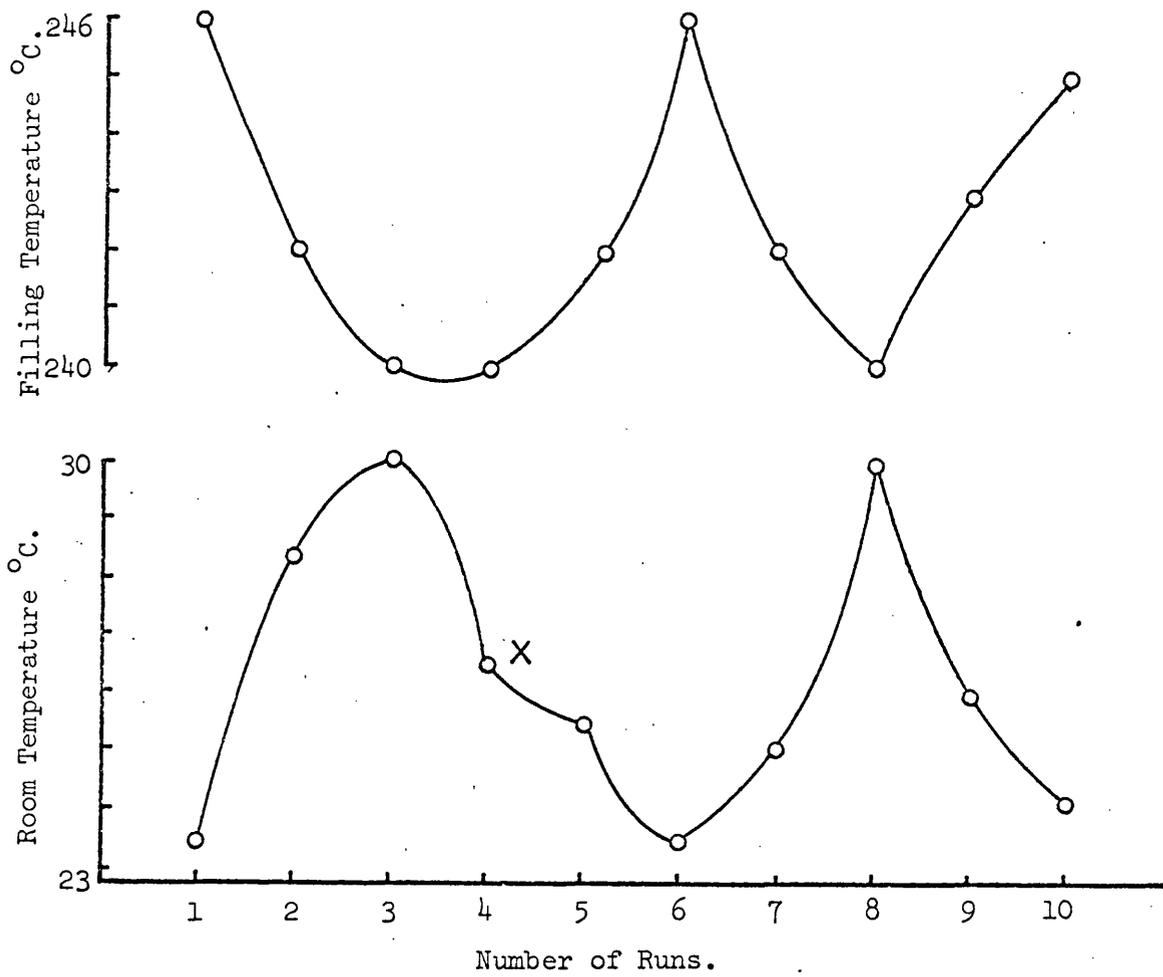


Fig.3.4. Diagram to illustrate the relationship between filling temperature and room temperature. Green fluorite, 13 North Pig Lode, Geevor Mine.

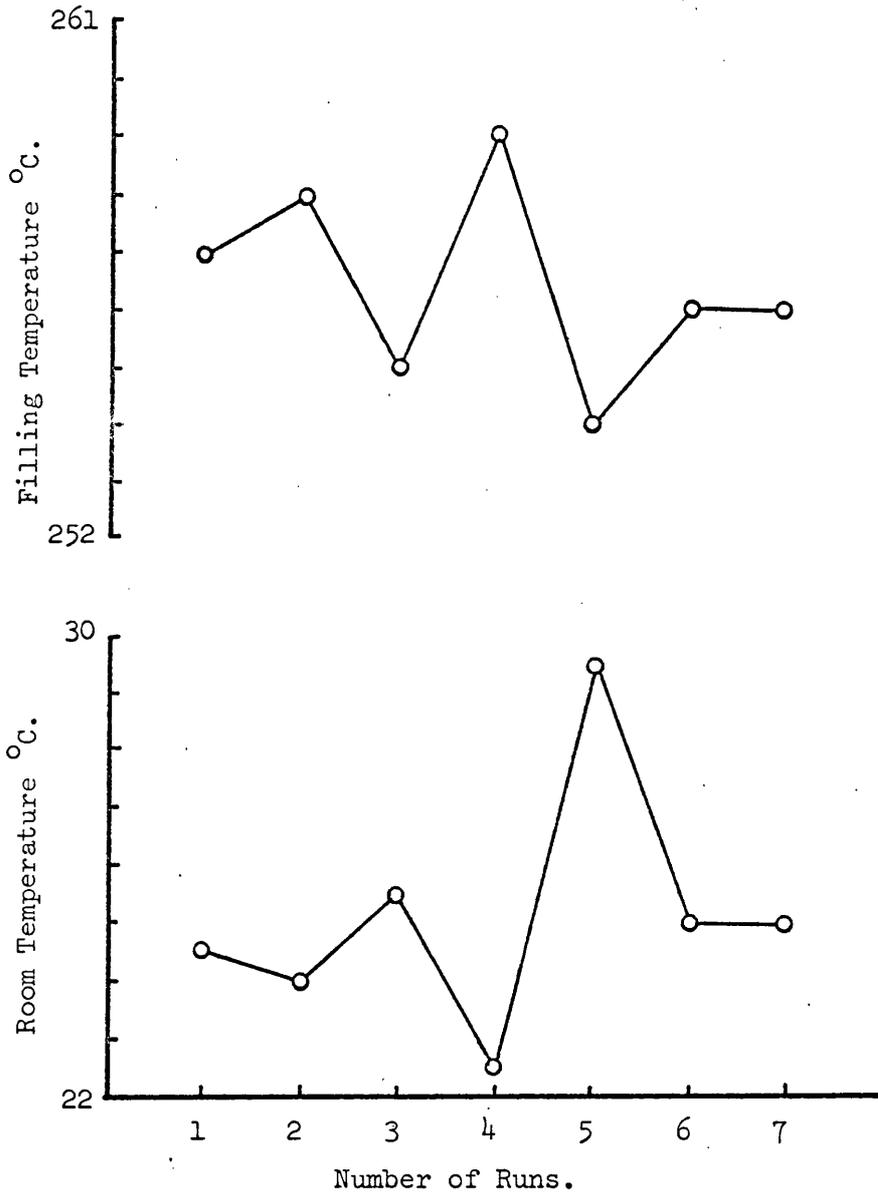


Fig.3.5. Diagram to illustrate the relationship between filling temperature and room temperature. Green fluorite, 13 North Pig Lode, Geevor Mine.

heating gives very precise and acceptably accurate results (3.3). The precision is determined by the reproducibility of the results and the accuracy by the closeness of the results from rapid and slow rates of heating.

To the readings obtained from the use of the Leitz 1350 heating stage, a compound correction factor must be applied. The first part of this factor is the addition of the room temperature at which the galvanometer was set at zero (3.2); then the difference between that room temperature and the actual room temperature at which the reading was taken must be added or subtracted as the case may be (3.4). After this, two degrees must be subtracted to compensate for the difference between the results of slow and rapid heating (3.3). Finally, the corrected filling temperature now obtained is accurate to within $\pm 2^{\circ}\text{C}$. These corrections may be summarized in the equation.

$$T_{\text{F corrected}} = T_{\text{F obs}} + R.T._{\text{zero}} \pm \Delta R.T. \pm 2^{\circ}\text{C}.$$

where $T_{\text{F corrected}}$ = corrected filling temperature

$T_{\text{F obs}}$ = observed filling temperature

$R.T._{\text{zero}}$ = room temperature at which galvanometer was set at zero

$\Delta R.T.$ = difference between $R.T._{\text{zero}}$ and actual room temperature.

4. THE RANGE OF THE FILLING TEMPERATURES OF FLUID INCLUSIONS

WITHIN SINGLE SAMPLES

4.1. Introduction.

It is uncommon to find a mineral crystal the whole of which was formed at a single fixed temperature. Natural crystal growth in the hydrothermal environment may be presumed to have been a slow process and it is to be expected that fluctuations occurred in the temperature of the mineralizing solution during the growth of a single crystal. It is widely accepted that hydrothermal mineral deposition took place as the temperature of the mineral-forming medium decreased and that commonly the core of a crystal was formed at a higher temperature than the periphery. Fluid inclusion geothermometry makes possible the study of the thermal history of minerals and such studies have shown that single crystals were commonly formed over a range of temperatures. The range of temperatures may be determined by the filling temperatures of the earliest formed primary inclusions and the last formed pseudosecondaries (Yermakov, 1950). A single filling temperature is characteristic of only one single moment in the growth of a crystal.

It is a relatively easy task to trace the thermal history of a single well-formed crystal. Twenhofel (1947) was the first to describe the thermal history of a crystal and Yermakov (1950) presented several such descriptions. A detailed thermal study of a crystal is to be commended but geothermometry should aim at determining the thermal history of a mineral deposit rather than of a single crystal from it. A prerequisite of such detailed studies is the availability of well-formed crystals. However, very often well-formed crystals represent only the later stages of mineral deposition. Generally, the bulk of a mineral deposit is in a massive form and it is extremely difficult to decide which part of an

anhedral grain was deposited first. Whereas with a single crystal it is often possible to equate a particular temperature with a particular zone, with massive material this is not possible and the temperature of formation, as deduced from fluid inclusion studies, must be expressed as a range of temperature. The published data of Sawkins (1966a, 1966b) are so presented.

Bradshaw and Stoyel (1968) could be criticized for publishing only the maximum filling temperatures of their samples but from their point of view the maxima were all that were required. It would have involved them in just a little more work to have included the range of temperatures which they obtained. The writer would criticize further on the grounds that the maximum temperature obtained by one operative from one sample may be different from that obtained by another operative from the same sample or from another sample from the same locality (see section 4.2.).

The question which now presents itself is what is the minimum number of fluid inclusions which must be measured in order to obtain a representative characterization of the thermal range of a given sample. Ideally, the filling temperatures of every primary and pseudosecondary inclusion in the sample should be measured. However, this is far from feasible and a compromise must be reached. Section 4.2. described some observations made by the writer on the variation of filling temperatures of inclusions within samples from the Geevor Mine and in section 4.3. an attempt is made to equate these variations with the minimum number of measurements necessary to obtain representative data.

4.2. Variations of filling temperatures of inclusions within single samples.

The filling temperatures recorded in this section are the raw data; the correction factor described in chapter 3 has not been applied.

The first fluorite examined by the writer was massive purple material

from 10 Foot Wall Branch Lode, Geevor Mine. A small polished slice was broken in half and the filling temperatures of probable primary inclusions in each half were measured. Forty inclusions were measured in one half and thirty in the other and the mean values were noticeably different. It was decided, by means of statistical tests, to determine whether the observed difference was likely to be due to chance variations within the sample or to a systematic difference between the two inclusion populations. Student's t test was selected as most suitable for testing the significance of the difference between two means. The mathematical procedure is outlined in Appendix 5a. The relevant data are presented in Table 4.1.

Table 4.1. Statistical data of the filling temperatures of inclusions in purple fluorite from 10 Foot Wall Branch Lode.

	Section No. 1.	Section No. 2.
No. of inclusions measured (n)	40	30
Range of filling temperatures	172-210°C.	193-220°C.
Mean filling temperature (\bar{x})	193°C.	210°C.
Standard deviation (s)	9.7	7.6

From the data in Table 4.1., the value of t was found to be 8.1 and as the value of t for 68 degrees of freedom at the 0.01 level is 3.67, the difference ($\bar{x}_2 - \bar{x}_1$) is significant at the one per cent level. In fact, the difference of 17°C. between the two means is highly significant and the likelihood of its occurring by chance is less than one in one hundred. Thus it seems likely that it is a real difference and not just a difference caused by the experimental error of $\pm 2^\circ\text{C}$. described in chapter 3. Regular calibration using dicyandiamide during this and the subsequent experiments revealed no variation in the instrument's performance.

A similar experiment was conducted on massive green fluorite from 10 Borehole Lode, Left Hand Vein. The relevant data are presented in Table 4.2.

Table 4.2. Statistical data of the filling temperatures of inclusions in green fluorite from 10 Borehole Lode, Left Hand Vein.

	Section No. 1.	Section No. 2.
No. of inclusions measured (n)	20	20
Range of filling temperatures	347-357	337-349
Mean filling temperature (\bar{x})	350	343
Standard deviation (s)	3.6	4.5

By the procedure already described, the value of t was found to be 17, whereas t for 38 degrees of freedom at the 0.01 level is only 2.71. The difference of 7°C . between the two means is, thus, highly significant at the one per cent level and unlikely to have occurred by chance.

To test the reproducibility of these results, the experiment was repeated. A sketch had been made of each inclusion and the first half of the section was re-run with the results of the previous run written in beside the sketches. As a result of this, a subconscious effort may have been made to obtain the same results. This showed itself in the new results where no difference was greater than $\pm 2^{\circ}\text{C}$. and nine of the twenty readings were identical. The new mean filling temperature was again 350°C .

To eliminate any subjectivity, with the second half of the section the previously obtained results were recorded by a disinterested party and the figures erased from beside the sketches. By this means, the inclusions could be identified but the previously obtained filling temperatures were unknown. The repeat measurements differed from the

originals by 0 to -4°C .; none were higher than the originals. The new mean filling temperature was 341°C .

The experiments indicate that a difference exists between the mean filling temperatures of sections of massive fluorite taken adjacent to each other. The statistical treatment of the data indicates that the observed means are significantly different and unlikely to be due to chance variations in sampling.

From this, it would seem that when massive material is to be used for fluid inclusion work, no two sections from one sample are likely to yield exactly comparable data, unless there is some evidence of zoning in the material whereby orientated sections may be prepared.

In comparison with massive material, closely comparable results should be obtained from separate sections cut from freely grown crystals. A comparison of the data obtained from two sections of quartz from 10 C Lode, Geevor Mine, shows this to some extent. A striking feature of the C Lode is the late quartz "leader" which can be traced over more than 2000 ft. of strike length and from No. 8 Level down to No. 14 Level. This last formed quartz is often freely crystallized and the crystals are often zoned. The preparation of orientated sections was, thus, relatively easy. Two slices were cut parallel to the c-axis of a crystal and sections were taken from the same zone in each slice. The filling temperature data from two of these sections are given in Table 4.3.

From these data, the value of t was found to be 2.8. The value of t for 29 degrees of freedom at the 0.01 level is 2.75. Thus, the difference of 4°C . between the two means is significant, but the significance is not as great as in the fluorite.

Table 4.3. Statistical data of the filling temperatures of inclusions
in freely grown quartz from 10 C Lode,

	Section No. 1.	Section No. 2.
No. of inclusions measured (n)	20	11
Range of filling temperatures	242-254	238-249
Mean filling temperature (\bar{x})	248	244
Standard deviation (s)	3.75	3.80

The difference of 4°C . in the mean filling temperatures of two sections of quartz from the same zone in a crystal is in part attributable to the experimental error of $\pm 2^{\circ}\text{C}$. described in section 3.3. A further contributory factor is the thickness of the two sections; each section was taken from a different slice and the thickness of the slices was not controlled. In chapter 5 it will be shown that the filling temperatures of fluid inclusions vary with the thickness of the sections containing them. As the two sections studied were of slightly different thicknesses, a difference in the mean filling temperatures is to be expected. The writer is satisfied that in the case of the freely grown quartz, the observed difference in the mean filling temperatures is more apparent than real.

The differences observed in the two samples of fluorite (17°C . for 10 Foot Wall Branch Lode and 7 or 9°C . for 10 Borehole Lode, Left Hand Vein) cannot be accounted for entirely by the above explanations. The experimental error of $\pm 2^{\circ}\text{C}$. is, undoubtedly, a contributory factor but the thickness is not, as in both cases the two sections were obtained by breaking a large section in half and, hence, the thicknesses were identical. The explanation must lie in the relative positions of the sections in the crystals and as neither crystal faces nor zoning were evident in the material used, it was not possible to determine from

which part of a crystal the sections came. On the assumption that the cores of crystals are likely to have been formed at higher temperatures than the peripheries, it is suggested that the sections which yielded the higher filling temperatures were nearer the cores of the crystals.

4.3. Conclusions.

It was noted in section 4.1. that the filling temperatures of inclusions within a single crystal usually show a range of values and in section 4.2. it was shown that the mean filling temperatures of inclusions in sections taken adjacent to each other, and hence only a few millimetres apart, can exhibit significant differences. When freely grown crystals are used, it is often possible to equate a given filling temperature with a certain zone in the crystal and a detailed thermal history of the crystal may thus be described, but this is not generally possible where only massive material is available. It has become customary, in fluid inclusion geothermometry, to record the range of filling temperatures obtained from a sample and the question which arises is; how representative is the observed range?

When the sample consists of a single, well-formed crystal, it is necessary merely to measure the filling temperatures of inclusions in the core and in the periphery of the crystal to obtain a representative range. However, when the sample is a hand specimen of a mineral in massive form, how can such a representative range be established? The sample is sliced and suitable inclusions are sought before the slice is broken into working sections. When the slice has been broken into sections and one section contains a large number of suitable inclusions, it is tempting to measure the filling temperatures of those inclusions alone and to regard those data as representative of the sample. It was shown in section 4.2. that those data are not necessarily representative and this tempting practice should be avoided. Several sections should

be studied and several inclusions in each section should be measured.

On quite arbitrary grounds, the writer would recommend that at least four sections should be studied from each sample and that a total of at least twelve inclusions should be measured. The value of some of the published data, where only two or three inclusions were measured per sample, is doubtful although in many instances such sparse data are presented only as a guide to the expected temperatures and are included for the sake of completeness. Examples of this practice may be found in Sawkins' paper (1966b). In advocating the measurement of at least twelve inclusions per sample it should be borne in mind that the greater the number, the more truly representative is the range of temperatures obtained and the maximum number is determined by the time available for the work. As many measurements should be made as the time will allow.

In conclusion, the writer would point to the value of a future line of research which might investigate, on a statistical basis, the minimum number of fluid inclusion measurements required to yield a reliable estimate of the range of filling temperatures for a sample.

5. THE RELATIONSHIP BETWEEN FILLING TEMPERATURES OF INCLUSIONS

AND VARIATIONS IN THE THICKNESS OF THE SECTIONS CONTAINING THEM

5.1. Introduction.

The thickness of the polished sections used in fluid inclusion geothermometry has received little attention throughout the history of the development of the method. In none of the literature has there been given any definitive statement of the optimum thickness for the various minerals, merely vague statements to the effect that thick sections can be used for transparent minerals and thinner sections for translucent ones.

The maximum thickness of section which can be used on the Leitz 1350 heating stage is 3 mm. In preliminary work by the writer, no particular attention was paid to the thickness of sections other than to ensure that they were less than 3 mm. In slicing the specimens, a thickness of approximately 2 mm. was aimed for, but a variation of ± 0.3 mm. was common. During the polishing of the sections, particularly during the initial lapping with 600 grade silicon carbide, the sections were reduced in thickness by a variable amount, depending on the mineral; for instance fluorite was reduced to a greater extent than quartz. Thus, the thickness of the sections prepared by the writer varied between one millimeter and two millimeters.

While testing the reproducibility of results from adjacent slices from a single quartz crystal, from 10 C Lode East, Geovor Mine, the filling temperatures obtained from two-phase inclusions probably of secondary origin in the second section, from the same zone in the crystal, were consistently higher than those obtained from the first. The second section was rather thick and it was thought that it might have been in contact with the quartz cover plate of the heating stage. However, this was not the case and another explanation had to be sought. This second

section was reduced to the thickness of the first by grinding on a glass plate with 240 grade silicon carbide and the filling temperatures of the inclusions were re-measured. The mean value of the filling temperatures of twenty inclusions in the first section was 132°C . and the mean for the re-run, at reduced thickness, of the second section was now also 132°C . Thus, it was apparent that the thickness of the section had some effect in the filling temperatures obtained by the method adopted by the writer and described in chapter 3 of this thesis.

5.2. Historical Considerations.

In his study of fluid inclusions, Sorby (1858) used thin sections of minerals, mounted on glass slides with Canada balsam. Later workers used polished thick sections of variable thickness. Yermakov (1950) considered 5 mm. to be the maximum for transparent minerals and 0.2 to 0.5 mm. for the semitransparent specimens, with an optimum somewhere between two and three millimeters. Smith (1953) did not consider the thickness of sections to be critical except that the greater the concentration of inclusions, the thinner the section should be. He found thicknesses of the order of 0.5 to 3.0 mm. to be usually satisfactory. Freas (1961) adopted a standard thickness of one millimeter while Schmidt (1962) used a thickness of 0.5 to 0.75 mm. and Erickson (1965) prepared sections between two and three millimeters thick. The last three authors all worked on similar material from the Mississippi Valley and Illinois lead-zinc deposits. More recently, Roedder (1968) used sections from 0.1 to 1.5 mm. and Roedder et al (1968) prepared "doubly polished plates, several millimeters thick" while Kelly and Turneure (1970) used sections of 1 mm. and less.

From this it can be seen that no great importance has been attached to the thickness of sections and that no attempt was made, other than by Schmidt, at standardization. The governing criterion appears to have been the transparency of the minerals studied. It must be assumed,

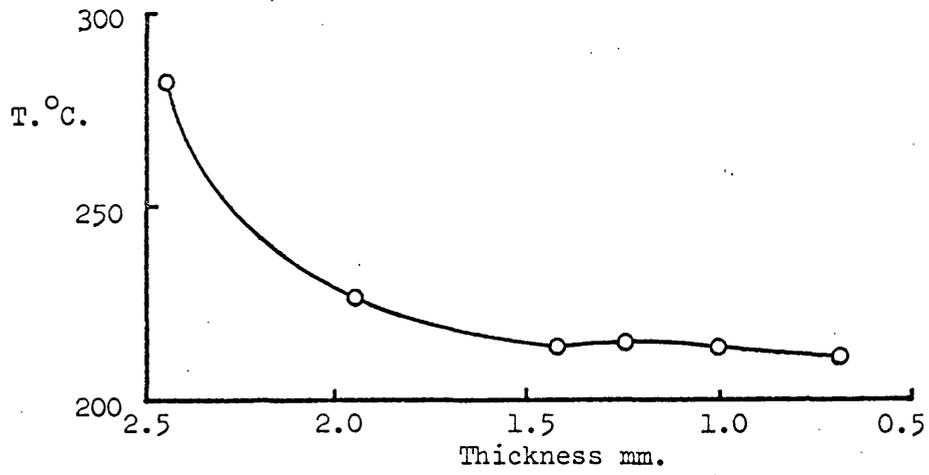
although it is by no means certain, that a uniform thickness was adopted by each writer for each mineral species. If this assumption is incorrect, then the results obtained by previous workers may be in error to a small extent as will be indicated by the following description of work undertaken by the present writer.

5.3. Preliminary investigation of the variation of filling temperatures with the thickness of sections.

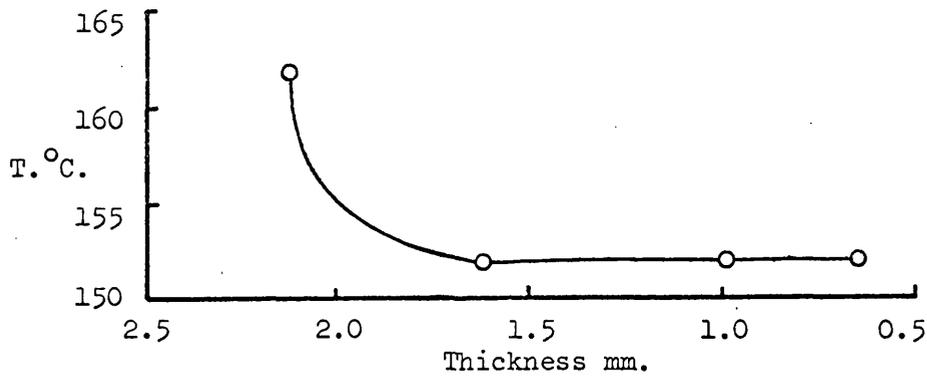
As described above, it was by accident that a variation in the filling temperatures, of two-phase liquid inclusions in quartz, with the thickness of the section was observed. To determine whether such a variation really existed or whether the observed variation was merely a chance occurrence, a small pilot experiment was designed.

Five sections of quartz were prepared with thicknesses ranging from 1.6 mm. to 2.4 mm., four from 10 C Lode East and one from 13 Boscawell Lode West, Geevor Mine. In each section, one or two inclusions were chosen, in the upper half of the section, on the grounds of their clarity of definition, relatively large size and ease of location, irrespective of their origin, primary or secondary. The thickness of each section was measured accurately with a micrometer and the inclusion or inclusions to be studied were sketched and their approximate locations in the section described to permit their re-location in later runs.

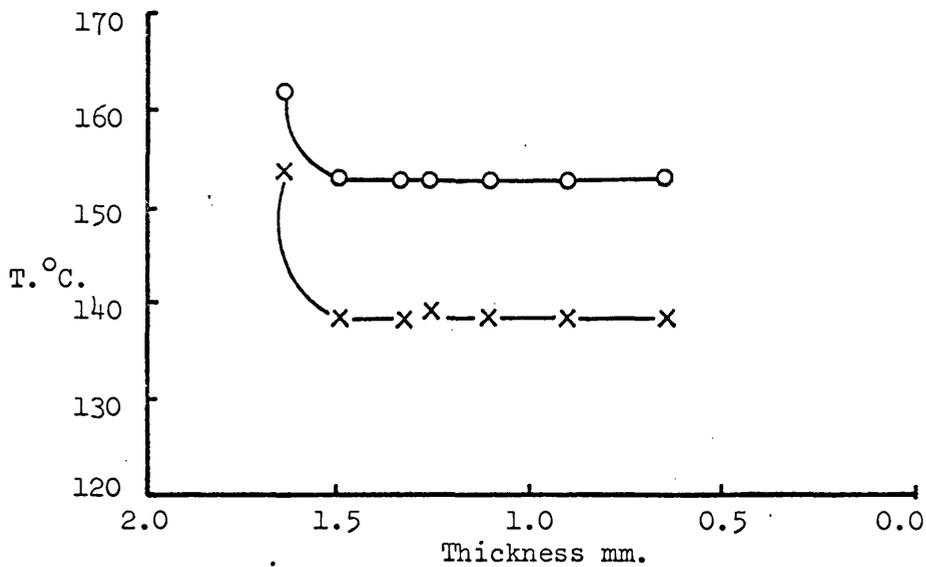
The filling temperatures of the inclusions at the initial thicknesses of the sections were determined using the rate of heating adopted throughout the writer's work (see chapter 3). After these initial determinations, the sections were reduced in thickness by grinding by hand on a glass plate using 240 grade silicon carbide. As previously noted (section 2.2.) in the majority of cases, polishing of the lower surfaces of the sections was found to be unnecessary, the surface given by grinding with 240 grade silicon carbide allowing the transmission of



Quartz, 10 C Lode, Geevor Mine.

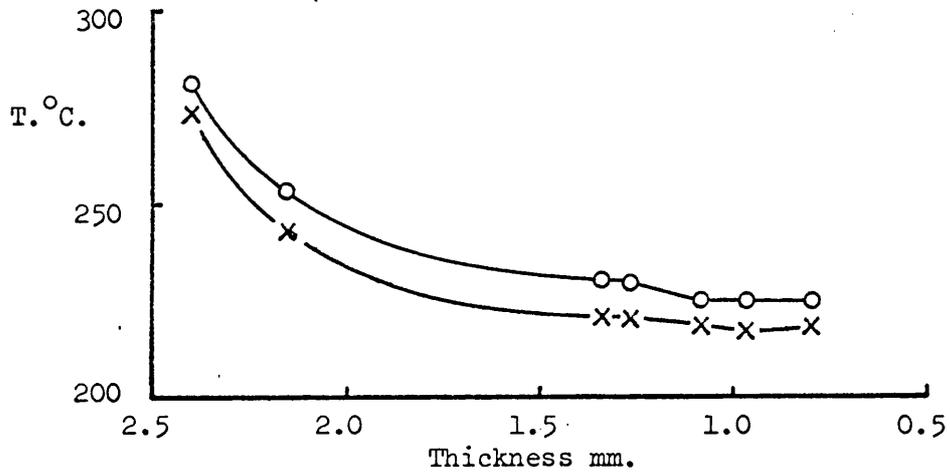


Quartz, 10 C Lode, Geevor Mine.

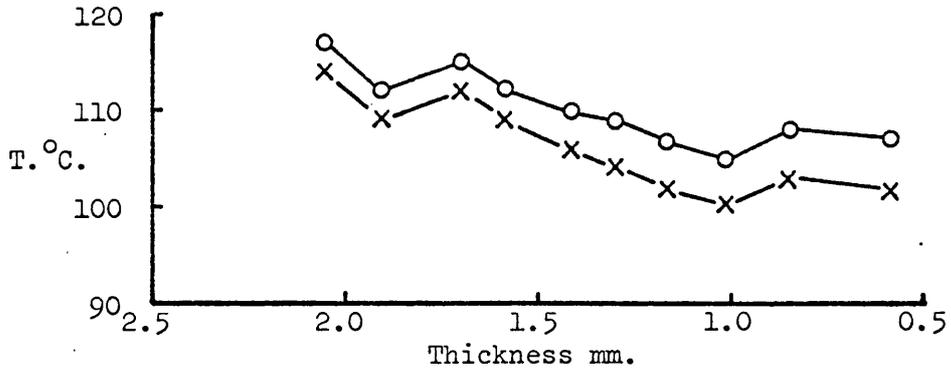


Quartz, 10 C Lode, Geevor Mine.

Fig. 5.1a. Diagram to show the relationship between filling temperatures and the thickness of sections.



Quartz, 10 C Lode, Geevor Mine.



Quartz, 13 Boscawell Lode, Geevor Mine.

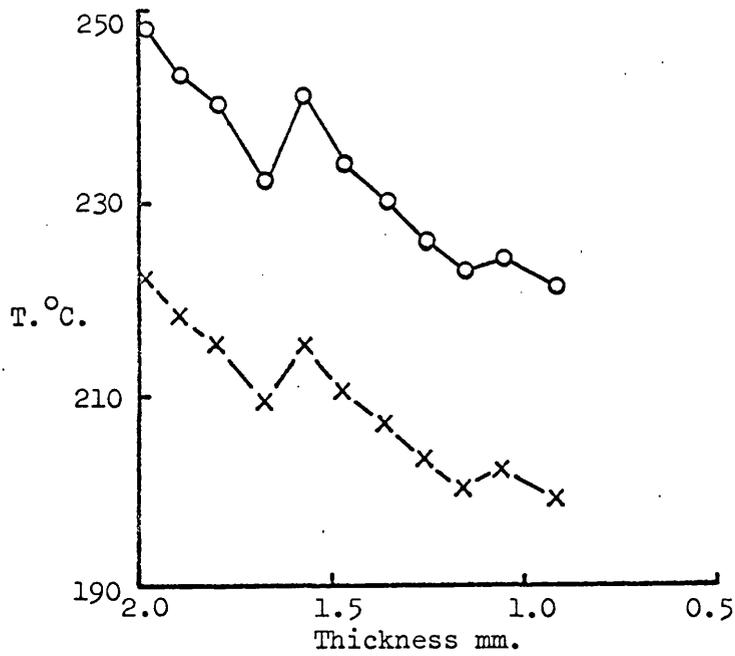
Fig. 5.1b. Diagram to show the relationship between filling temperature and the thickness of sections.

sufficient light. Two of the sections were reduced by approximately 0.5 mm. and the other three by approximately 0.2 mm. Redetermination of the filling temperatures showed a noticeable decrease in all cases. The sections were then further reduced in thickness by increments down to 0.6 to 0.7 mm. (the magnitude of these increments can be determined from the accompanying diagrams, Fig. 5.1a and 5.1b.

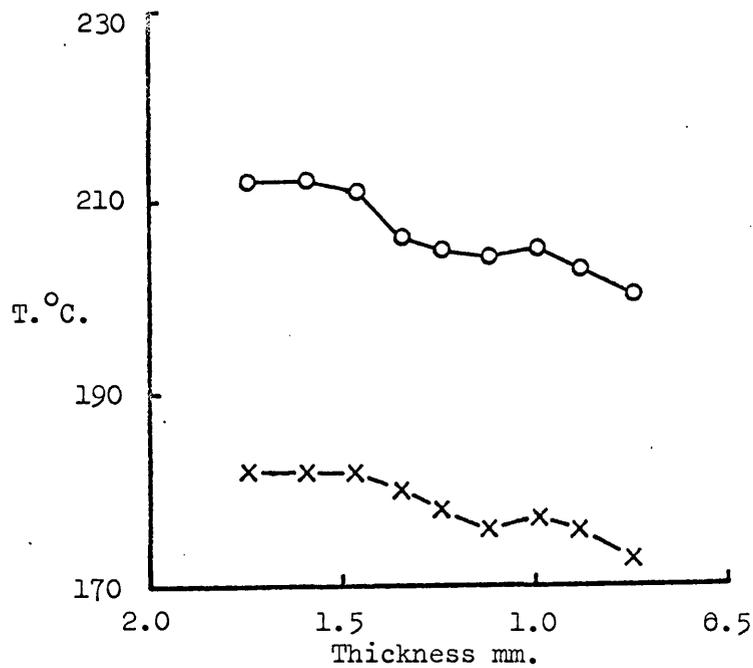
Six inclusions in four sections of quartz from 10 C Lode East showed a rapid decrease in filling temperature with initial decrease in thickness but below approximately 1.5 mm. no further decrease occurred. Four of the inclusions showed decreases of several tens of degrees, whereas the other two exhibited decreases of smaller magnitude. In the case of the section from 13 Boscanswell Lode West, the initial decrease was not as great, but, again, a flattening of the curve took place below about 1.5 mm.

That such curious and consistent results should be obtained from quartz, suggested that it might be worth conducting a similar experiment on fluorite. Four sections were prepared, three of purple fluorite from 10 Foot Wall Branch Lode and one of green material from 10 Borehole Lode, Left Hand Vein, Geevor Mine. The inclusions to be used were chosen on similar criteria to those in the quartz described above and the sections were reduced in thickness by increments of approximately 0.1 mm. and the results plotted graphically (Figs. 5.2a and 5.2b).

The behaviour of the filling temperatures of the inclusions in fluorite differed from that of those in quartz, in that the decrease was somewhat variable. The greatest difference was noted in the sample from 10 Borehole Lode, Left Hand Vein, where the inclusion studied gave a filling temperature of 416°C . at a thickness of 2.21 mm.; whereas at a thickness of 0.70 mm., the same inclusion yielded a temperature of 333°C . (Fig. 5.2b). This is by far the greatest difference recorded

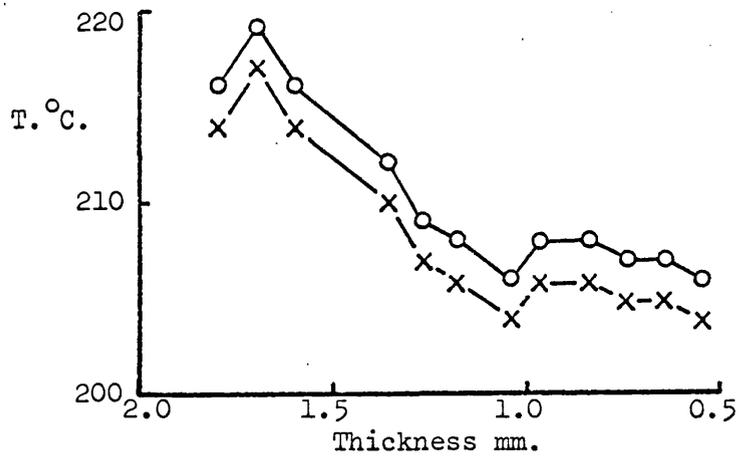


Fluorite, 10 Foot Wall Branch Lode, Geevor Mine.

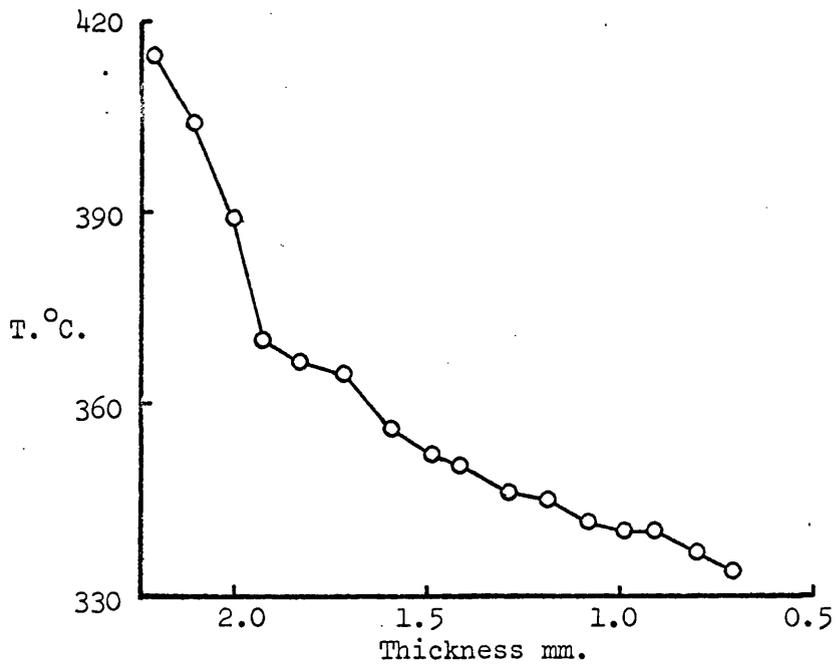


Fluorite, 10 Foot Wall Branch Lode, Geevor Mine.

Fig.5.2a. Diagram to show the relationship between filling temperatures and thickness of sections.



Fluorite, 10 Foot Wall Branch Lode, Gevor Mine.



Fluorite, 10 Borehole Lode, Left Hand Vein, Gevor Mine.

Fig. 5.2b. Diagram to show the relationship between filling temperatures and thickness of sections.

by the writer and as the difference is several times greater than any of the others, it may prove to be anomalous. Lack of time has not permitted a repetition of the experiment on this material.

Again, the behaviour of fluorite appears to differ from that of quartz in that whereas quartz showed a flattening of the curve below about 1.5 mm., fluorite showed a progressive decrease with decrease in thickness down to the point where the sections disintegrated on further grinding. The curves obtained for fluorite were not as smooth as those for quartz but this might be a reflection of the number of points on each curve. In the first section of fluorite from 10 Foot Wall Branch, Lode, there is a large increase in the filling temperatures of both inclusions in the reduction from 1.65 to 1.55 mm. A jump of 9°C. in the case of the inclusion showing the higher filling temperature is greater than any observed as a result of variation in room temperature and if the curve is taken to run between the previous and the subsequent temperatures, a discrepancy of 5°C. is still rather large to explain on these grounds. It might be postulated that the thermal gradients described by Roedder et al (1968) as inherent in the Leitz heating stages be the cause of this anomaly. However, the calibration of the Leitz 1350 stage, described in section 3. suggests that large gradients do not exist.

The two small experiments here described did not provide enough data for a statistical analysis of the significance of the apparent difference between the filling temperature of an inclusion in a thick section and that of the same inclusion in a thinner section. It was, therefore, decided to conduct further work on this problem.

5.4. Statistical investigation of the variation of filling temperatures with the thickness of sections.

In order to determine the reality of the variations observed, a

previously run section of quartz, containing a number of easily determinable inclusions was chosen from 10 C Lode East. During the previous run, eleven inclusions yielding fairly close filling temperatures had been measured. The mean filling temperature was 244°C ., the mode 243°C . and the range 11°C .

Table 5.1. The variation of filling temperatures in quartz with the thickness of the sections. 10 C Lode, Geevor Mine.

(Raw data - instrumental correction factor not applied).

Inclusion No.	Thickness of Section (mm.).		
	2.130	1.680	1.030
1	248	238	228
2	241	230	220
3	238	229	220
5	243	227	218
8	240	228	217
9	249	238	226
10	247	236	223
11	240	223	218
n	8	8	8
Range	238-249	223-238	217-228
\bar{x}	$243(\bar{x}_1)$	$231(\bar{x}_2)$	$221(\bar{x}_3)$
s	4.20	5.57	4.04

In reducing the thickness of the section by increments, several of the inclusions were lost, either by their being ground away or by their being rendered unusable by changes in the light transmission properties of the section. At the end of the experiment, only eight of the eleven remained. The data obtained from this experiment are presented in Table 5.1.

As in chapter 4, Student's t test was used to determine the significance of the observed differences in filling temperatures. The mean filling temperatures of the three runs were designated \bar{x}_1 , \bar{x}_2 and \bar{x}_3 and the values of t for the differences $(\bar{x}_1 - \bar{x}_2)$, $(\bar{x}_2 - \bar{x}_3)$ and $(\bar{x}_1 - \bar{x}_3)$ were, respectively, 4.8, 4.1 and 10.6, all of which are greater than t at the one per cent level of significance for seven degrees of freedom (3.50).

From the statistical treatment of the data obtained from this small experiment, the previously noted apparent decrease in the filling temperatures of inclusions with decrease in the thickness of the section containing them has, thus, been shown to be significant and it is unlikely that the observed differences between the mean filling temperatures occurred by chance.

Further reduction of the test section, from 1.030 mm. to 0.910 mm., lowered the mean filling temperature of the eight inclusions by 1°C. This difference is not of any significance as it is well within the limits of experimental error. A change in the ambient temperature during the run could easily account for such a small variation. Variations of greater magnitude were observed on the flat parts of the curves obtained during the earlier work described in section 5.3.

Having established to the satisfaction of the writer that variations occur in the filling temperatures of fluid inclusions with changes in the thicknesses of the enclosing sections, it was decided to test the significance of these variations still further and to try and establish some idea of the magnitude of the variations in minerals from different localities. Previously, quartz and fluorite from the Gevor Mine, Cornwall, had been used and whereas it did not appear likely that the observed phenomenon would be confined to minerals from this one locality, it was deemed necessary to confirm this thought by testing materials from other

parts of Britain.

A mineral which was of widespread occurrence, was easy to prepare and which contained abundant easily usable two-phase liquid inclusions was required. The mineral which most readily fulfills these requirements is fluorite and therefore samples were obtained from various sources representing the following localities:-

Weardale, Co. Durham

Scordale, Westmorland

Grassington, Yorkshire

Appletreewick, Yorkshire

Wheal Mary Ann, Cornwall

South Crofty Mine, Cornwall

Geevor Mine, Cornwall

Descriptions of the samples and their localities are given in Appendix 2.

Several thick slices were cut from each sample and one surface on each slice was polished in the manner described in section 2.2. The slices were then examined for usable inclusions and eleven small sections from each sample, containing at least one usable inclusion per section, were cleaved from the slices. These several sections were then reduced to approximately two millimetres thickness. One inclusion in each section was chosen, as described above, a sketch made to enable its re-location and its filling temperature measured at the initial thickness of two millimetres. Ten of the sections from each sample were reduced in thickness by increments of 0.25 to 0.5 mm. until each section was approximately one millimetre thick. The eleventh section was used as a control.

It was hoped that ten inclusions from each sample could be measured. However, inclusions in some of the samples were so few that spare sections were not available to make up the numbers in case of loss. Of the eight

samples, only two lasted throughout the experiment with ten inclusions; the others lost inclusions by grinding, breakage or complete loss of the section. However, it is believed that these losses will not lead to serious errors in the analysis and interpretation of the results.

During the initial run of the ten sections from each sample, the sections were numbered from one to ten in the order of their use. The control section was numbered eleven. In the subsequent runs, after reduction in thickness, the order of reading was randomized using the random number tables of Fisher and Yates (1953). It was hoped that randomization would help eliminate any subjective bias which may have developed. The control section was run at various times during the sequence; usually it was used as the first run of each day and run at various times during the day. Variations in the filling temperatures of the control inclusions could usually be correlated with variations in the ambient temperature. The galvanometer had previously been set at zero when the room temperature had been 22.5°C . For example, at the beginning of a session, the room temperature was relatively low, and filling temperatures obtained were relatively high. As the session progressed and the room warmed up, albeit only by a few degrees, filling temperatures became progressively lower. Towards the end of the experiment, the use of the control inclusion was dispensed with, in favour of recording the ambient temperature at the time of each run.

The full data obtained from this experiment are presented as Appendix 5 of this thesis. The data of interest to the present discussion are given in the accompanying Table 5.2.

The significance of the observed differences was determined by means of Student's *t* test modified for correlated observations as described by Winer (1962) and outlined in Appendix 5b.

The values of t_{obs} for the eight samples studied are presented

in Table 5.3. In all cases, the value of t_{obs} is greater than t at the one per cent level of significance for the appropriate number of degrees of freedom. Therefore, the observed differences are statistically significant and unlikely to have occurred by chance.

The data presented in Table 5.2. are the raw data; the instrumental correction factor has not been applied. When the correction factor is applied, the observed differences still remain significant at the one per cent level, but the differences expressed as percentages of the initial filling temperatures are generally lower than before the correction was applied (Appendix 5.). The percentage differences in the raw data range from 4.06 to 10.55, whereas, in the corrected data, the range is 5.61 to 7.35 per cent. It is noticeable from these figures that the higher the initial filling temperature, the greater is the difference on reducing the thickness of the section.

Table 5.1. The variation of filling temperatures of inclusions in quartz with the thickness of the sections. 10 C Lode, Geevor Mine.

(Raw data - instrumental correction factor not applied).

Inclusion No.	Thickness of Section (mm)		
	2.130	1.680	1.030
1	248	238	228
2	241	230	220
3	238	229	220
5	243	227	218
8	240	228	217
9	249	238	226
10	247	236	223
11	240	223	218
n	8	8	8
Range	238-249	223-238	217-228
\bar{x}	243 (\bar{x}_1)	231 (\bar{x}_2)	221 (\bar{x}_3)
s	4.20	5.57	4.04

Table 5.2. Summary of statistical data (uncorrected).

Locality	No. of Inclusions	Mean Filling Temps		\bar{d}	$\sum d$	$\sum d^2$
		2mm.	1mm.			
<u>Geevor Mine</u>						
13 North Pig Lode	10	241.1	216.7	24.4	244	6186
12 Simms Lode	9	201.3	186.7	14.6	131	1973.
<u>South Crofty Mine</u>						
<u>Wheal Mary Ann</u>	8	123.7	117.7	5.0	40	216
<u>Grassington</u>	8	80.5	72.9	7.6	61	497
<u>Appletreewick</u>	8	83.3	77.1	6.25	50	354
<u>Scordale</u>	9	111.1	99.2	11.9	107	1343
<u>Weardale</u>	8	132.5	119.6	12.9	103	1559

\bar{d} = Mean difference

$\sum d$ = Sum of the differences from the mean

$\sum d^2$ = Sum of the squares of the differences

Table 5.3. The values of t_{obs} calculated from the data of Table 5.2.

Locality	Ld^*	s_d^2	s_d^2/n	t_{obs}^*
<u>Geevor Mine</u>				
13 North Pig Lode	2324	25.82	1.61	15.1
12 Simms Lode	596	8.28	0.96	15.1
<u>South Crofty Mine</u>				
<u>Wheal Mary Ann</u>	128	2.62	0.28	17.5
<u>Grassington</u>	225	4.55	0.57	13.3
<u>Appletreewick</u>	332	5.93	0.85	7.3
<u>Scordale</u>	638	8.86	0.99	12.0
<u>Weardale</u>	1863	33.26	2.04	6.3

* See Appendix 5b.

5.5. Conclusions.

It has been shown in section 5.4. that the filling temperature of a two-phase fluid inclusion varies with the thickness of the section containing it, when a rapid rate of heating is used. The observed difference between the filling temperature of an inclusion in a thick section and the filling temperature of the same inclusion in a thin section has been shown, statistically, to be significant. In all the samples of fluorite and quartz studied by the writer, a reduction in the thickness of the sections gave rise to a decrease in the filling temperatures of the inclusions. An attempt must now be made to account for the observed differences and a number of possibilities present themselves.

In all the examples given, the difference between the filling temperature of an inclusion in a section about two millimetres thick and in a section about one millimetre thick was several times greater than the experimental error described in chapter 3. An experimental error of $\pm 2^{\circ}\text{C}$. cannot account for observed differences ranging from 6° to 24°C .

Constant reheating of a mineral may cause slight re-ordering of the crystal lattice accompanied by a slight decrease in the volume of the specimen. If shrinkage of the specimen were to take place without loss of fluid from the inclusions, the volume of fluid in an inclusion would remain constant but the size of the cavity would decrease, thereby lowering the filling temperature of the inclusion. However, in the writer's preliminary work, several sections of fluorite were reheated several tens of times without any noticeable effect; therefore, this possible explanation may be discounted.

Dana (7th. Ed. Vol. II, 1951) lists fluorite with a water content as high as 2.40 wt. per cent. Probably, most of this water is contained in fluid inclusions but it is likely that at least a small amount is

contained in inter-atomic spaces and in imperfections in the crystal lattice (section 6.1.). Reheating of a specimen may cause the inter-atomic fluid to migrate into the inclusion cavities, thereby increasing the volume of fluid and lowering the filling temperature. Alternatively, the pressure exerted upon the specimen during grinding may cause movement of the fluid into areas of lower pressure, viz the partially filled inclusion cavities, a diffusion process analogous to that obtaining during rock metamorphism and described by Ramberg (1952). To test this idea, it would be necessary to subject a section of fluorite to the pressure exerted during grinding but without the grinding action.

In the Leitz 1350 heating stage, the mineral sections are heated from below and it may be suggested that reheating causes fluid to migrate upwards through the section from inclusion to inclusion, thereby causing inclusions in the upper layers of sections to give lower filling temperatures. However, this mechanism would be expected to take place on reheating a section of constant thickness and as noted above, reheating of sections several tens of times did not give rise to a lowering of the filling temperatures of the inclusions. It will be shown in chapter 6 that leakage or the migration of fluid into or out of inclusion cavities in insoluble minerals is a rare phenomenon and that considerable overheating above the filling temperature is necessary to induce such leakage.

In the opinion of the writer, the following tentative explanation of the observed phenomenon is the most probable and should be investigated further. The rate of heating adopted by the writer throughout the current work and described in chapter 3 gives rise to readings which are high by some 2°C . when compared with a rate of heating taking up to an hour and a half to reach the filling temperature. This discrepancy of 2°C . is the result of the poor thermal conductivity of the minerals studied and it is possible that even a slow rate of heating

taking an hour and a half is too fast to allow the section to reach equilibrium with the hot junction of the thermocouple.

In all the experiments described in section 5.3., the measured inclusions were situated just below the polished upper surfaces of the sections. In a section two millimetres thick almost two millimetres of mineral must achieve the same temperature as the hot junction of the thermocouple in order to obtain a true filling temperature reading. In a section one millimetre thick, less than one millimetre of mineral requires heating and it would seem logical that, by using a standard rate of heating, the observed filling temperature of an inclusion in a section one millimetre thick would be nearer the true filling temperature and lower than the observed filling temperature of an inclusion in a two millimetre section. It is suggested here that the observed variation in the filling temperature of an inclusion with variation in the thickness of the mineral section is caused mainly by the difference in the magnitude of the thermal lag between the hot junction of the thermocouple and the fluid inclusion. This hypothesis may be investigated by conducting a series of very slow heating runs of four to five hours duration as postulated by Yermakov (1950) or even or longer duration. Such an investigation would have been undertaken by the writer had time allowed.

It would appear from this work that the thermal gradient between the interior of a section and the hot junction of the thermocouple in the Leitz 1350 heating stage is much greater than had previously been realized. The difference of 2°C . found between a rapid run and a slow run pointed to the existence of a gradient but it was not a true indication of the magnitude of that gradient. However, provided that the data required from a geothermometric study are relative rather than absolute and that the same rate of heating is used throughout the study, the thermal gradient is not a great cause for alarm. If absolute filling

temperatures are required, it is necessary to determine the magnitude of the gradient by conducting a series of very slow runs.

The work described above leads the writer to conclude that in a geothermometric study, a standard thickness of section for each mineral is an absolute prerequisite in order to obtain comparable data. It has been shown that the filling temperatures of inclusions in two millimetre sections can differ from those in one millimetre sections by as much as seven per cent. If the range of filling temperatures of a sample is determined by the use of sections of variable thickness, the observed range may be greater than the actual range and the writer thus considers variation in the thickness of sections to be a potential source of error in fluid inclusion geothermometry.

6. A PRELIMINARY INVESTIGATION INTO LEAKAGE, CAUSED BY OVERHEATING, OF FLUID INCLUSIONS IN FLUORITE

6.1. Introduction.

The problem of leakage and its effects on the validity of fluid inclusion geothermometry was recognized by Sorby (1858). It is one of the basic assumptions of inclusion geothermometry that the inclusions being studied have neither lost nor gained fluid since the time of their entrapment. This is a very obvious point, the significance of which needs no elaboration.

Throughout the history of fluid inclusion geothermometry, the problem of leakage, whether it can be seen to have occurred, whether it is likely to have happened and so on, has recurred innumerable times. Indeed, no study of fluid inclusions is complete without some consideration of the problem as it applied to the material being studied.

Sorby (1858) appreciated the effect leakage might have on the validity of geothermometric data. His opinion has already been mentioned (see section 1.2.). Ward (1875) recorded a very important point, in his observation of the occurrence of leakage during sample preparation.

In almost every subsequent study of fluid inclusions, at least some consideration has been given to the problem. As much evidence has been put forward in favour of leakage as the greatest drawback to inclusion thermometry as has been offered to negate the idea. Most of the evidence, both for and against, has been ably summarized by Roedder and Skinner (1968). In their paper they list, in chronological order, most of the published evidence since 1949 supporting both arguments.

Several workers in the early nineteen fifties conducted experiments to induce leakage of fluid both into and out of inclusions. Grunig,

reported by Kennedy (1950a), and Skinner (1953), working on fluorite and quartz respectively, induced leakage into inclusions by subjecting them to high external pressures under water. This inward leakage was manifested in a lowering of the filling temperatures. Several other workers, at this time, noted the outward leakage of inclusions as a result of heating above the filling temperature.

Overheating of aqueous inclusions, homogenizing to the liquid phase, causes a great increase in the internal pressure and this can cause the migration of fluid either by the development of fine fissures adjoining the cavity, particularly in minerals with good cleavages such as calcite, fluorite and topaz, or by migration through the crystal structure (Kalyuzhnyi, 1958). This latter mechanism would seem possible in view of the work of Joffe (1928) in which interlineage gaps were found in crystals measuring from 100 to 1000 Å across and when it is remembered that the water molecule is only 2.8 Å in diameter. Whereas outward leakage as a result of overheating is a proven and accepted fact, the migration of fluid into inclusions as a result of high external pressure is not so certain.

Richter and Ingerson (1954) were critical of Skinner's, Kennedy's and Grunig's idea of leakage occurring during geological time as a result of temperature and pressure gradients. They repeated part of Skinner's work using laboratory grown quartz crystals containing inclusions of known filling temperatures. Overheating indicated no leakage other than that which was visible along fractures, that is, there was no migration along lineages. By analogy, they considered inward migration of fluids unlikely. Kalyuzhnyi (1958) still maintained that migration of fluid through the crystal structure should be theoretically possible, but found no evidence of it on subjecting quartz to high pressures under water for periods longer than those used by Skinner. Moderate overheating of topaz for a long period did not cause leakage. Roedder

and Skinner (1968), not satisfied with the available evidence, conducted a similar but more refined experiment to that of Skinner (1953) and found no evidence of inward leakage. They concluded that "Where leakage has occurred, either in nature or in the laboratory, it is generally recognizable and hence those few inclusions or samples that have leaked can be readily eliminated from further study". Tugarinov and Naumov (1969) confirmed the conclusions of Roedder and Skinner by subjecting quartz, calcite and blende to high pressures under water for periods of time twenty five times longer than those in Skinner's original experiments.

Whereas leakage is acknowledged as but a minor problem in the relatively insoluble minerals such as quartz, fluorite, topaz etc., it has been shown to be a major problem in easily soluble minerals such as halite, sylvite and carnallite. Leakage is a potential problem in minerals with open crystal structures such as the zeolites (Yermakov, 1950; Kalyuzhnyi, 1958).

Sorby noted that halite crystals grown at room temperature contained inclusions completely filled with mother liquor immediately after they were grown and that after a few days vapour bubbles appeared. Yermakov (1950) repeated this observation and the present writer observed the same phenomenon in halite crystals two weeks old. It would appear that hygroscopic minerals, such as halite, possess a property whereby water molecules migrate through the crystal lattice or along lineages. In the case of such migration from a fluid inclusion, the present writer advocates the descriptive term "autoleakage". Such a mechanism would solve the problems discussed by Dreyer, Garrels and Howland (1949). They found that the filling temperatures of inclusions in bedded halite suggested a temperature of formation in the region of 70 to 100°C. and they considered it unlikely that a marine environment would attain such a temperature; they put forward the idea that heat of crystallization or exothermic reactions could give rise to apparently high temperatures of

formation. Peach (1949~~8~~) was critical of the interpretation presented by Dreyer, Garrels and Howland and postulated recrystallization at a geologically later time and at an elevated temperature as the explanation. In view of the evidence of "autoleakage", the present writer suggests that this might be the cause of the apparently anomalously high filling temperatures of the inclusions in halite. It would seem, on the available evidence, that reliable thermometric data cannot be obtained from easily soluble evaporite minerals.

6.2. Experimental Procedure.

During preliminary work by the writer, on fluorite from 10 Borehole Lode, Left Hand Vein, Geevor Mine, a group of two phase aqueous inclusions gave filling temperatures ranging from 233°C. to 239°C. Two other inclusions in the same section yielded filling temperatures of 303°C. and 304°C. After measuring the high temperature inclusions, two of the lower temperature inclusions were re-measured and higher filling temperatures were recorded of 245° and 262° (Table 6.1.).

Three days later, these same inclusions yielded filling temperatures of 237°C. and 258°C. respectively. The difference of four degrees, between 262°C. and 258°C., may be explained by the error inherent in the Leitz 1350 heating stage or by variations in the ambient temperature (which was not recorded at this time) or by a combination of both. However, the difference of eleven degrees, between 248°C. and 237°C., cannot be explained on these grounds, particularly as in all previous and subsequent work, any variation in the filling temperature of an inclusion, whatever the cause, was found to be almost exactly reflected by all the other inclusions in the same section. The explanation which immediately came to mind was that on overheating, the fluid had migrated into the crystal structure of the fluorite and after a period of time at a lower temperature, the fluid had migrated back into the inclusion cavity. On

cooling to room temperature, a partial vacuum would be created within the inclusion cavity and a gradient would be set up between the external atmosphere pressure and the negative pressure within the inclusion. If fluid was capable of migrating into the crystal structure, it could be advocated that air could also penetrate the structure. Assuming that, on overheating, the fluid had entered the crystal structure and that it had not left the system, that is, it had not been forced out on to the surface of the section where evaporation would have taken place, the relatively high external atmospheric pressure could possibly have caused the fluid to migrate down the pressure gradient back into the inclusion cavity.

In order to test this hypothesis an experiment was designed in which a number of sections of fluorite, from 13 North Pig Lode, Geevor Mine and from Roskear South Lode, 360 fm. Level, South Crofty Mine, were taken, one inclusion in each section chosen and careful overheating conducted. The inclusions to be used were chosen for their large size, their clarity, the ease with which they could be re-located and for their depth within the section. The sections were about 1.5 mm. thick.

Table 6.1.

Inclusion No.	A	B
1	236 ^o C.	248
2	237	262

A = Original filling temperature

B = New filling temperature after heating to 305^oC.

Table 6.2.

Section No.	Original Filling Temp.	Overheated to	Time in Minutes	New Filling Temp.
13NP1A	269	300	30	269
13NP2A	257	315	40	257
13NP6A	207	297	30	207
13NP5A	255	325	4	259

Table 6.3.

A.

Section No.	Date	Original Filling Temp.	Overheated °C	Minutes	New Filling Temp.
S.C.1A	16.9.70	153	253	1	206
S.C.2A	17.9.70	200	300	2	219
13NP3A	10.9.70	138	238	1	217

B.

Section No.	Date	Filling Temp.	Section No.	Date	Filling Temp.
S.C.1A	17.9.70	204	S.C.2A	19.9.70	219
	19.9.70	204		18.10.70	221
	8.10.70	205		19.1.71	220
	19.1.71	206	13NP3A	11.9.70	217
				19.1.71	216

Moderate overheating caused leakage in only one out of the first four sections used, as can be seen from Table 6.2. That overheating by 90°C. for thirty minutes did not cause leakage, whereas overheating by 70°C. for four minutes did is explained by variations in the degree of fracturing of the sections. The inclusion which leaked may have been in close proximity to, or have been intersected by, a fracture plane or an incipient cleavage plane, whereas the others must have been in areas of undisturbed fluorite.

Heating to 100°C. above the filling temperature rapidly induced leakage in three sections (Table 6.3A). The degree of leakage was by no means uniform in the three inclusions observed and uniformity was not to be expected as the degree of fracturing varied from section to section and within the sections. The filling temperatures of the inclusions were redetermined after a day or so and after about four months and in no case was a decrease observed, the filling temperatures varying very slightly but remaining within the limits of error inherent in the method employed (Table 6.3B).

6.3. Conclusions.

From the data obtained, it may be concluded that migration of fluid back into the inclusion cavity did not take place. However, from so few data it is not permissible to draw definite conclusions. This pilot study was intended as a guide to further work on this aspect of leakage but lack of time has prevented the writer from undertaking such work.

An expanded study on the above lines should aim at obtaining data from a larger number of inclusions and samples, say ten inclusions from each of three or four samples. Fracture-free material should be chosen and the sections prepared with a thickness of over 2 mm. The inclusions chosen should be at a depth of about 1 mm. from the top surface of the

section and only slight leakage should be induced in order to minimize the possibility of the fluid's reaching the surface of the section.

If the phenomenon of migration of fluid back into an inclusion can be proved, new light will be thrown upon the problem of changes within inclusions subsequent to their entrapment, particularly with regard to changes caused by thermal metamorphism. If the phenomenon is disproved, then a fruitless line of investigation will have been eliminated. In either case, the results will be of value to future researchers.

7. GENERAL CONCLUSIONS

In chapter 1, the history of fluid inclusions geothermometry was traced from its nineteenth century beginnings down to the present time. Emphasis was placed upon the development of techniques and upon the knowledge to be gained, from fluid inclusions, of the nature of ore-forming fluids. Whereas Britain was the birth-place of fluid inclusion geothermometry, very little work has been done in this field since the turn of the century. An upsurge of interest began in the nineteen forties, mainly in America and in the U.S.S.R. and these two schools were largely responsible for the modern development of the techniques of geothermometry. A smaller school grew up in Europe, centred in Paris, where emphasis has been placed upon the acquisition of topographical data. There has been a notable lack of interest in Britain and it is hoped that by describing the history of the subject and by pointing to possible avenues of investigation, enthusiasm for fluid inclusion geothermometry may be aroused among British geologists.

There is a notable lack, in the published literature, of descriptions of the techniques employed in preparing mineral sections for fluid inclusion studies. Deicha (1970) and Pulou et al (1970) considered the publication of technical information to be of importance and Deicha (1970) stressed the need for the free interchange of ideas and information; it is felt that the publication of chapter 2 as a technical note would be of value to future workers. In this chapter, the method of preparing mineral sections, developed by the writer, is described. When minerals are to be heated in air, as opposed to their being heated in liquid, the sections require a fairly high polish to permit the observation of fluid inclusions within them. It was generally found, by the writer, that only the upper surface of a section needed to be polished; the lower surface, lapped with 240 grade silicon carbide, provided a diffuse illumination

against which inclusions could be more clearly seen than against a polished surface. There can be no definitive statement of the thickness to which sections must be prepared; the maximum thickness is determined by the most opaque sample in the suite and it is necessary to adopt a standard thickness for a given mineral from a given locality for the reason described in chapter 5.

The experimental procedure was described in chapter 3. At the commencement of a study of fluid inclusions it is necessary to calibrate the equipment and to establish empirically the optimum rate of heating. This rate must be maintained throughout the study. The heating stage used by the writer was a Leitz 1350 model and as Roedder et al (1968) reported large thermal gradients in the Leitz 350 heating stage, it was essential that the writer determine the magnitude of those gradients in the Leitz 1350 model. To this end, a calibration procedure using organic reagents of known melting points, was adopted and an experiment conducted to assess the magnitude of the error arising from the relatively rapid rate of heating used throughout the study. In a systematic study, involving the measurement of the filling temperatures of several hundreds or even thousands of fluid inclusions, a rapid heating rate is essential. By comparing the filling temperatures obtained in runs lasting about 15 minutes and those obtained from the same inclusions in runs of an hour and a half, a correction factor was established. Calibration of the instrument by means of organic reagents produced a further correction factor and a third factor was determined which made allowance for changes in the ambient temperature. The compound correction factor which must be added to all readings obtained from the Leitz 1350 heating stage in a run of 15 minutes' duration may be summarized thus:-

$$T_F \text{ corrected} = T_{Fobs.} + R.T. \text{ zero} \pm \Delta R.T. \pm 2^\circ C.$$

where $T_F \text{ corrected}$ = corrected filling temperature.

$T_{Fobs.}$ = observed filling temperature.

- R.T._{zero} = room temperature at which galvanometer was set at zero.
- Δ R.T. = difference between R.T._{zero} and actual room temperature.

In chapter 4, some of the problems of sampling are described. It is generally accepted that hydrothermal mineral deposition took place under conditions of fluctuating temperature and commonly under conditions of decreasing temperature. In order to describe the thermal history of a given mineral or phase of mineralization in an ore deposit, it is necessary to determine the range of temperature under which the mineral formed. A single temperature measurement gives only a single point in the range and is, consequently, of little value.

When a sample consists of a well-formed crystal, it is a relatively easy matter to describe its thermal history but in the more common case, where only massive material is available, difficulties arise. It has been shown that when a polished section of massive material (quartz or fluorite) is broken in half, the mean filling temperature of the inclusions in one half is, on statistical grounds, significantly different from the other. It is, thus, apparent that the filling temperature data obtained from measuring the inclusions in a single small working section cut from a massive sample are not necessarily representative of the sample. To obtain representative data, it is necessary to measure the filling temperatures of inclusions from several sections from different positions in the sample and the writer suggests, on arbitrary grounds, that at least four sections should be studied and a minimum of twelve inclusions measured for each sample. Ideally, every inclusion in a sample should be measured but this is rarely possible and it is suggested that a fruitful line of investigation might be to determine, on statistical grounds, the minimum number of measurements necessary to obtain a truly representative thermal range.

Chapter 5 describes the relationship between the thickness of a mineral section and the filling temperatures of the fluid inclusions contained therein. During the work described in chapter 4, it was noticed that the filling temperatures of inclusions varied with the thickness of the section; the thicker the section, the higher were the filling temperatures of the inclusions. The statistical treatment of the data obtained from several experiments showed a correlation between thickness and filling temperatures. In the case of quartz the filling temperatures were shown to decrease as the thickness of the section was reduced from more than two millimetres to about 1.5 mm. Below about 1.5 mm., the filling temperatures remained constant, even on reduction of the section to 0.5 mm. However, with fluorite, filling temperatures decreased continuously with reduction in thickness from about two millimetres down to about 0.5 mm. An experiment was conducted on fluorites from several British localities in order to augment the initial findings and in an attempt to evaluate the magnitude of the variations. Fluorite from eight localities was obtained. In all cases, reduction of the thickness of the sections was accompanied by a decrease in the filling temperatures of the inclusions. In reducing the thickness of the sections from approximately two millimetres to approximately one millimetre, the ^{mean} filling temperatures were seen to fall by an amount ranging from 5.6 to 7.3 per cent. Statistical tests showed the observed decreases to be significant.

Several possible reasons may be put forward to account for the observed phenomenon but in the opinion of the writer the most likely explanation is to be found in the thermal gradient in the Leitz 1350 heating stage. It was shown in chapter 3 that the filling temperature of an inclusion measured during a run taking ninety minutes was 2°C. lower than that of the same inclusion measured during a rapid run of fifteen minutes. This was accounted for by the thermal lag between the hot junction of the thermocouple and the inclusion resulting from the poor

thermal conductivity of the mineral. The writer suggests that even a run taking ninety minutes is too rapid to allow equilibrium to be achieved between the thermocouple and the interior of the mineral section. In a section two millimetres thick, a greater mass of mineral must be heated in order to measure the filling temperatures of inclusions than in a section only one millimetre thick. Consequently, the thermal lag must be greater in the thicker section and the filling temperatures of inclusions higher than in a thinner section. The writer concludes that the thermal gradient between the interior of a section and the hot junction of the thermocouple in the Leitz 1350 heating stage is greater than had previously been realized. The difference of 2°C. between a rapid run and a slow run showed that a gradient existed but it did not indicate the true magnitude of that gradient. However, provided that the data required from a geothermometric study are relative rather than absolute and that the experimental conditions remain constant throughout the study, the thermal gradient is not a great cause for alarm.

The principal conclusion to be derived from chapter 5 is that a standard thickness of section for each mineral in a geothermometric study is an absolute prerequisite if truly comparable data are to be obtained. If the thickness of sections is allowed to vary, then the observed range of filling temperatures may be greater than the actual range and, thus, variation in the thickness of sections is a potential source of error in fluid inclusion geothermometry.

In chapter 6, some of the problems concerning leakage of fluid inclusions are discussed and a preliminary investigation into leakage induced by overheating is described. It is suggested that by heating an inclusion above its filling temperature, thereby causing fluid to migrate out of the inclusion cavity, some of the fluid may pass into inter-atomic and lineage spaces within the crystal lattice rather than into fracture planes, and that on cooling the section, the partial vacuum set up in the

inclusion cavity might be sufficient to cause a pressure gradient between the inter-atomic and lineage spaces and the inclusion cavity. If such a gradient were set up, fluid in the inter-atomic and lineage spaces may migrate back into the inclusion cavity and so lower the filling temperature of the inclusion to its original level. To test this hypothesis, several inclusions in fluorite were subjected to overheating whereby fluid was forced out of the cavities and the filling temperatures were, thus, raised. The filling temperatures were re-measured after several days and again after several months but no significant changes were observed and it was concluded that migration of fluid back into the cavities did not occur. However, this was only a pilot study; an extended study on similar lines would be of value. If the phenomenon of migration of fluid back into an inclusion can be proved, new light will be thrown upon the problem of changes within inclusions subsequent to their entrapment, particularly with regard to changes caused by thermal metamorphism. If the phenomenon is disproved, then a fruitless line of investigation will have been eliminated.

To summarize briefly, the writer would stress that in fluid inclusion geothermometry it is essential to calibrate the heating stage, to evaluate the thermal gradients which may exist within it, to adopt a standard rate of heating and a standard thickness of mineral section and, finally, to measure the filling temperatures of sufficient inclusions to obtain representative data.

APPENDIX 1The Leitz 1350 Heating Stage

The following description of the Leitz 1350 Heating Stage is taken from lists 515-73a/Engl. and 515-74/Engl.R. of E. Leitz (Instruments) Ltd., by the kind permission of A.H. Elder, Manager, Instruments Division (London).

The heating equipment was mounted upon the stage of a Leitz Dialux-Pol binocular microscope. By the use of Periplan GF 12.5x eye pieces and a UMK 50/0.60 objective, a magnification of about 780x was achieved. This was the magnification most commonly used in the present study. Only occasionally were lower magnifications used when the UMK 50/0.60 objective was changed for a UM 32/0.30, a UM 20/0.33 or a UM 5/0.10 objective which gave, respectively magnifications of 500x, 312.5x and 78x.

General Description.

The Leitz 1350 water-cooled, microscope heating stage was designed for observations in both transmitted and reflected light. It is attached to the microscope stage by means of two screws and is heated by a low voltage current through a finely adjustable transformer. The interchangeable heating cartridge contains a metal support for sapphire-glass, sintered alumina or platinum object carriers, and, in addition, platinum crucibles can be inserted for the study of melts. The sample is screened by a quartz-glass disc which can be rotated through 360° ; if the area above the sample becomes steamed up, it can be replaced by a clean portion of the surface through a small turn of the disc. The disc also provides a gas-tight seal, permitting observation in a protective gas atmosphere. A thermocouple is used for the measurement of the temperature, which is recorded on a "0.5 quality" standard galvanometer with a reading range of up to $1600^{\circ}\text{C}.$, graduated in 10° intervals. Heating above $1350^{\circ}\text{C}.$ should be strictly

avoided. Two centring screws, which permit the orientation of the sample, are situated in the bottom part of the stage, and two levelling screws serve to align the sample parallel to the surface of the microscope stage.

The entire equipment is illustrated in Fig. Al.1. (For the purposes of the photograph, the galvanometer is standing on end; in the working position it lies flat upon the bench).

The Structural Elements.

(The numbers in parentheses correspond with those in the cut-away diagram in Fig. Al.2).

1. The Vessel.

Two screw connections for the current supply for the measuring instrument (7), sockets for the cooling of the bottom part of the heating stage (5 and 22) and sockets for the protective gas supply (4 and 23) are located on the exterior of the double-walled vessel. The vessel walls have holes for the thermocouple and the two current leads, ceramically insulated against shorting. Two quartz-glass discs (2 and 10) provide gas-tight seals for the top and bottom of the vessels.

2. Heating Element and Water-cooling Mechanism.

The interchangeable heating cartridge (17) has a ceramic thread for the screwing-in of the platinum-rhodium heating wire. The heating wire has an average life of over 50 hours at the maximum continuous temperature of 1350°C. A metal support (18) is fitted to the top end of the heating cartridge for the sapphire-glass object carrier (19). This support carries the hot junction of the thermocouple.

The water for cooling enters the lower part of the stage by one of the sockets (5) and leaves by the other whence it passes into the upper

part of the stage (5). The water finally leaves the system by the socket at the opposite side of the stage (22).

3. Thermocouple and Measuring Instrument.

The heating stage is supplied with a platinum-rhodium thermocouple which is metal-joined to form a unit with the object carrier support. This form of heat transfer ensures reliable measurements of the effective temperature close to the sample. A galvanometer with a reading range of up to 1600°C . serves as a measuring instrument. Continuous heating of the stage in excess of 1350°C . should be avoided.

4. Centring Devices.

A centring device is built into the bottom part of the stage with an adjustment range of ± 3 mm. for the orientation of the sample. This is operated by means of two screws, only one of which is illustrated (15). Two levelling screws (16) allow the sample to be aligned parallel with the surface of the microscope stage.

5. Upper Part of Stage.

The double-walled upper part of the stage can be removed to permit cleaning and the interchange of heating cartridges. This carries the upper quartz-glass disc (2) held in place by the leaf-spring (3). The leaf-spring presses the disc against a rubber ring (20) thereby ensuring a gas-tight seal. An adjustable slide stop (1) above the quartz-glass disc can be used as an additional radiation screen.

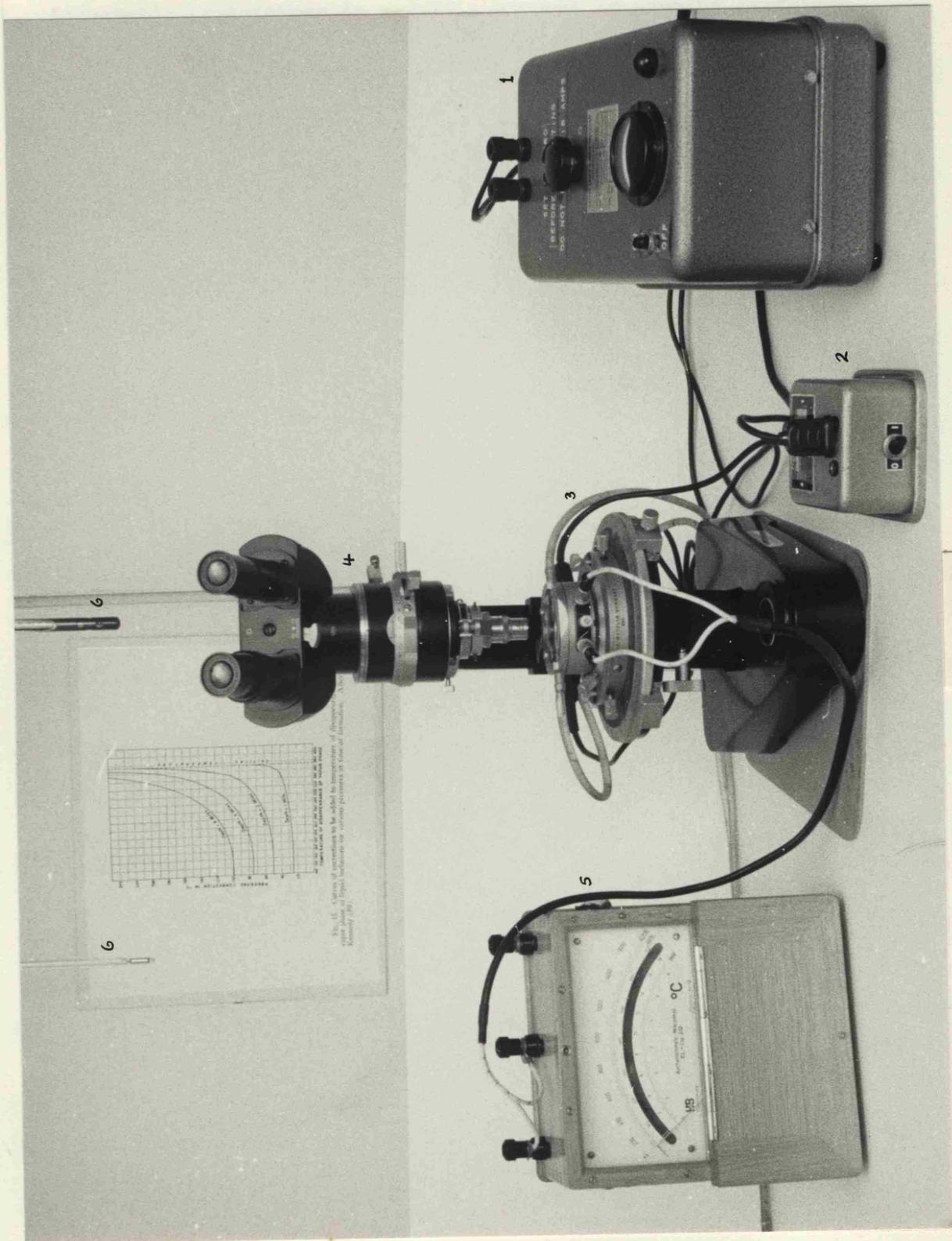


Fig. AL.1.

Key to Fig. A1.1.

1. Adjustable transformer to regulate current to heating cartridge.
2. Transformer to regulate current to microscope lamp.
3. Leitz 1350 Heating Stage.
4. Leitz Dialux-Pol binocular microscope.
5. Galvanometer capable of measuring up to 1600°C.
6. Mercury thermometers.

1. Spoon diaphragm stop
2. Quartz plate
3. Leaf spring
4. Protective gas socket
5. Sockets for cooling water
6. Rubber ring
7. Current connection
8. Round cord ring
9. Clamping screw
10. Quartz plate
11. Clamping ring
12. Round cord ring
13. Milled nut for the thermo-element
14. Connection "Measuring instrument"
15. Milled screw for orientating the object
16. Milled screw for the horizontal alignment of the object
17. Heating cartridge
18. Object carrier support with thermo-element
19. Object carrier
20. Round cord ring
21. Diaphragm stop
22. Socket for cooling water
23. Socket for protective gas

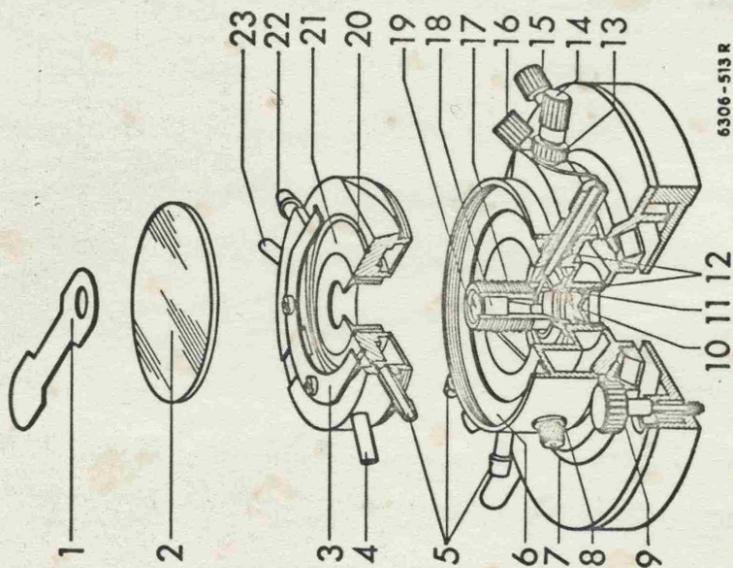


Fig. Al.2. Cut-away diagram of the Leitz 1350 Heating Stage.

APPENDIX 2Descriptions of the samples used in the present study

Sample No. 1. Fluorite, Coronation Lode, No. 15 Level, Geevor Mine.

(85 ft. from X-cut to No. 2 Branch Lode).

Massive purple fluorite intergrown with massive milky quartz with minor interstitial chalcopyrite. Occasionally some of the larger anhedral grains of fluorite exhibited zoning as alternating purple and colourless bands. The sample was taken from the last-formed part of the lode which consisted of a nine inch quartz vein with a central cavity. The fluorite occurred as patches within the quartz and as a selvedge on either side of the vein. The quartz-fluorite vein was bounded on either side by quartz-tourmaline with minor chalcopyrite and cassiterite.

Sample No. 2. Fluorite, Coronation Lode, No. 15 Level, Geevor Mine.

(210 ft. from X-cut from Victory Shaft).

Massive purple fluorite, intergrown with massive milky quartz from the last-formed part of the lode, as in sample No. 1. The quartz-fluorite vein was here seven to eight inches wide and bounded on either side by quartz-tourmaline lode material.

Sample No. 3. Fluorite, Coronation Lode, No. 15 Level, Geevor Mine.

(200 ft. from X-cut from Victory Shaft).

Massive purple and greenish fluorite intergrown with massive milky quartz as in samples Nos. 1 and 2. The quartz-fluorite vein was six to seven inches wide at this point.

Sample No. 4. Fluorite, Borehole Lode, No. 14 Level, Geevor Mine.

(Approximately 600 ft. east of X-cut).

Patches of massive green to grey fluorite in a chlorite-hematite-

cassiterite lode material. An abundance of earthy hematite obscured the details of the lode along this level.

Sample No. 5. Fluorite, North Pig Lode, No. 13 Level, Geevor Mine.

(Approximately 80 ft. south of Victory Shaft).

Massive yellow-green to greyish fluorite intergrown with arsenopyrite, pyrite and chalcopyrite. This sample was collected by a member of the mine staff and its relationship to the lode was not recorded.

Sample No. 6. Fluorite, Simms Lode, No. 12 Level, Geevor Mine.

(Approximately 40 ft. east of the 45° incline).

Massive grey-green fluorite intergrown with chlorite, earthy hematite and cassiterite. As in sample No. 4, the earthy hematite obscured the details of the structure of the lode.

Sample No. 7. Fluorite, Foot Wall Branch Lode, No. 10 Level, Geevor Mine.

(Precise locality not recorded).

Massive purple fluorite intergrown with massive milky quartz. The sample was taken from the last-formed part of the lode but the relationship of this material to the rest of the lode was not recorded at the time of sampling.

Sample No. 8. Fluorite, Borehole Lode, Left Hand Vein, No. 10 Level, Geevor Mine.

(At junction of Left Hand Vein with Borehole Lode proper).

Massive, transparent grass-green fluorite forming the cores of partially freely-grown cubo-octahedral crystals whose outer parts were purple. These crystals occurred in a clay-filled vugh containing freely grown pyrite, quartz and cassiterite, the latter as very small crystals. The intimate association of the minerals suggested contemporaneity. The colour of the green fluorite was very even, with no suggestion of zoning.

Sample No. 9. Fluorite, Borehole, Left Hand Vein, No. 10 Level, Geevor Mine.

(At junction of Left Hand Vein with Borehole Lode proper).

Purple, cubo-octahedral crystals with green cores (sample No. 8).

Zoning was quite marked in this sample. Cubic growth surfaces exhibited very thin layers of deep purple colouration and each layer was only a few microns thick. The intervening areas were usually colourless. From the surface of the crystals to a depth of a few millimetres, the zoning was less regular tending to be patchy with blue areas as well as purple. The purple colouration appeared to have been caused by the deposition of minute discrete particles of colouring matter. The particles were less than one micron in diameter and suggested intermittent deposition of colloidal material upon the growing surfaces of the crystals. Many of the zones were only one or two particles deep but still showed intense colouration. It was not possible to determine the cause of the green colouration of the cores of the crystals.

Sample No. 10. Quartz, C Lode, No. 9 Level, Geevor Mine.

(160 ft. west of X-cut 9E5).

Massive milky to clear quartz intergrown with small amounts of chalcopyrite, arsenopyrite, tourmaline and fluorite. At this locality the lode was split into a four inch vein of massive quartz etc. (the sample) and a two inch quartz "leader", separated by four inches of hard, reddened granite.

Sample No. 11. Quartz, C Lode, No. 10 Level, Geevor Mine.

(East of X-cut, footage not recorded).

The sample was taken from the last-formed, central quartz "leader" which here comprised a six inch vein with a central vugh lined with hematite-coated quartz crystals. The pyramid faces of the crystals were freely grown whereas the prism faces formed compromise growth surfaces with

each other.

Sample No. 12. Quartz, C Lode, No. 10 Level, Geevor Mine.

(25 ft. west of X-cut).

Central quartz "leader", very similar to No. 11.

Sample No. 13. Quartz, C Lode, No. 11 Level, Geevor Mine.

(East of X-cut, at end of drive).

Central quartz "leader", very similar to Nos. 11 and 12.

Sample No. 14. Quartz, Boscawell Lode, No. 13 Level, Geevor Mine.

(West of X-cut, no footage recorded).

Freely grown, transparent quartz crystals up to three inches long from a vugh about the middle of the lode. The crystals were coated with "micromicaceous" hematite, the abundance of which obscured the relationship of the vugh with the rest of the lode.

Sample No. 15. Fluorite, Roskear South Lode, South Crofty Mine.

(360 fm. Level. Exact locality not recorded).

Massive green fluorite. The sample consisted of a single hand specimen of pure fluorite; no other minerals were present. Details of its association with the lode were not available.

Sample No. 16. Fluorite, Wheal Mary Ann, Menheniot.

Massive, bluish, transparent fluorite from the dumps at Wheal Mary Ann. The dumps contained bluish, yellow, greenish and purple Fluorite, some with minor galena, chalcedonic silica and a slatey country rock.

Sample No. 17. Fluorite, Scordale, Westmoreland.

Freely crystallized amber fluorite collected from the dump below

the portal of the Horse Level. The dump material contained amber fluorite, massive white baryte, galena and several varieties of country rocks. Pyromorphite and other secondary minerals were found in small amounts.

Sample No. 18. Fluorite, Middle Vein, Grassington Moor, Yorkshire.

Massive colourless fluorite associated with galena. The sample was collected from dump material consisting of baryte, fluorite, calcite, hemimorphite and galena. The country rocks were fossiliferous limestone, shale and sandstones of the Millstone Grit series.

Sample No. 19. Fluorite, Inman Vein, Appletreewick, Yorkshire.

Massive, colourless to yellowish transparent fluorite with subhedral galena. The Inman Vein ranges from a few inches to fifteen feet in width, in a country rock of grey Carboniferous Limestone. Wallrock alteration is restricted to a few inches to two feet of dolomitization, rendering the limestone buff in colour. The mineralogy of the vein at the sample locality consisted of an intergrowth of massive fluorite and galena, the latter partially oxidized to cerussite. Some of the fluorite contains inclusions of sulphide, probably pyrite. Vughs lined with well-formed fluorite crystals and infilled with yellow-brown clay occurred sporadically throughout the vein.

Sample No. 20. Fluorite, Weardale, Co. Durham.

Massive purple fluorite, Probably dump material. Locality not known.

APPENDIX 3Descriptions of the InclusionsSamples Nos. 1 to 9. Fluorite, Geevor Mine.

Three major types of inclusions have been distinguished in the fluorite from the Geevor Mine.

1. Probable primary inclusions; these occur as randomly distributed subhedral to euhedral negative crystals, typically elongated but not showing obviously cubic symmetry. Fig. A3.1 illustrates this type of inclusion.

2. Probable pseudosecondary inclusions; these occur as planes of inclusions, sometimes orientated along cleavage directions. Their shapes are very similar to those of the probable primaries and their filling temperatures fall within the range of the probable primaries also. Fig. A3.2 illustrates their typical shapes. All the inclusions in a given plane show a constant orientation.

Daughter crystals were found only very rarely in the probable primary and probable pseudosecondary inclusions. However, an as yet unidentified third phase was often observed in both types. This third phase usually became noticeable on cooling, after a homogenization run, when the vapour bubble had just reappeared. It would be seen as a minute bubble or droplet of an immiscible fluid moving rapidly about the vapour bubble as though trying to penetrate it. After a time this small third phase would settle down and become stationary; it would remain stationary on re-heating to the filling temperature and still be visible at a considerably higher temperature. Six of the inclusions illustrated in Fig. A3.1 and three of those in Fig. A3.2 contain the third phase.

3. Probable secondary inclusions; these are irregularly shaped, often amoeboid inclusions occurring in planes corresponding to the cleavage directions of the fluorite. They are characterized by a wide range of

degrees of filling; single-phase inclusions were not infrequently observed in close proximity to inclusions with very high vapour contents, indicative of necking down.

Multiphase inclusions containing one or more solid phases were noticeably more common among the probable secondary inclusions than among the probable primaries and pseudosecondaries. Fig. A3.3 illustrates examples of multiphase secondary inclusions. Whereas the probable primary and pseudosecondary inclusions were highly three-dimensional, the probable secondaries were usually very flat and when viewed from the side, they sometimes appeared as a bubble and a crystal joined by a thin line (Fig. A3.4).

Necking down was frequently observed in all three major types of inclusions. Examples are illustrated in Figs. A3.5 and A3.6.

A fourth type of inclusion was occasionally found in the fluorite of 15 Coronation Lode; these were small, two-phase negative crystals, usually of tetrahedral habit with a random distribution and most probably of primary origin (Fig. A3.7). This type was very similar to the probable primary inclusions found in the fluorite from South Crofty Mine (sample No. 15), illustrated in Fig. A3.7 also.

Samples Nos. 10 to 13. Quartz, Geevor Mine.

The details of zoning in the crystals applies to sample No. 13 but the descriptions of the inclusions apply to all the samples.

The outermost zone of the crystals was white and opaque, the opacity caused by a hyperabundance of inclusions, both fluid and solid. The outermost zone was not usable for geothermometric work. The penultimate zone was colourless and transparent and was devoid of inclusions; the boundary with the opaque outer zone provided some measurable two-phase inclusions of irregular shape. Negative crystals were not observed, nor were multiphase inclusions although petrographic thin sections of the

same material contained oval to spherical inclusions with an aqueous phase, a vapour bubble and a cubic daughter crystal.

The transparent zone was preceded by a milky, translucent zone and this by a variably clear to milky core with hematite on the compromise growth surfaces. Irregularly shaped two-phase inclusions were abundant in these zones, some distributed randomly and others arranged in rows or planes which sometimes intersected each other; the former were regarded as primary and the latter as secondary. Not infrequently, groups of inclusions showed very variable degrees of filling and sometimes single-phase inclusions were found in such groups which may be attributable to necking down. Fig. A3.8 is a drawing of a group of inclusions showing variable degrees of filling found in the core of a crystal.

Sample No. 14. Quartz, Geevor Mine.

The freely grown crystals were clear with faintly milky growth zones. Basal sections were cut and inclusions were found to be fairly abundant in the milky parts but large areas of the clear quartz were barren. Irregularly shaped two-phase inclusions occurred in rows parallel to the crystal faces and these were considered to be primary. However, a very wide range of filling temperatures (170° to 350°C) was obtained which suggested either wide-spread necking down or a mixture of primaries, secondaries and probably also pseudosecondaries. The data obtained from these inclusions have not been recorded.

One section from the sample contained a plane of sharply faceted hexagonal negative crystals. The plane was not orientated crystallographically and so it was thought to be a healed fracture, and the inclusions to be of secondary origin. The negative crystals showed a constant orientation corresponding approximately with the faces of the host crystal.

Generally, the inclusions in quartz from Geevor Mine were smaller and less clearly defined than those in fluorite. Consequently, it was more

difficult to obtain filling temperature data from quartz than from fluorite.

Sample No. 15. Fluorite, South Crofty Mine.

Examples of the probable primary inclusions are illustrated in Fig. A3.7. They occurred as randomly distributed negative crystals often of tetrahedral habit. Planes of probable pseudosecondary inclusions of similar size and shape to those in the Geevor fluorite were observed. Highly irregularly shaped secondary inclusions, some containing daughter crystals, were also present.

Sample No. 16. Fluorite, Wheal Mary Ann.

Two types of inclusions were distinguished in this material.

1. Probable primary inclusions; these occurred as randomly distributed subhedral to euhedral negative crystals (Fig. A3.9). Only rarely were daughter crystals observed.

2. Probable secondary inclusions; most of the sections studied contained a fine tracery of veils of minute rounded inclusions, one micron and less in diameter. Occasionally, some were large enough to have their filling temperatures measured: the filling temperatures were much lower than those of the probable primary inclusions.

Sample No. 17. Fluorite, Scordale, Westmoreland.

This material was transparent and fluid inclusions were very sparsely distributed. It was not possible to distinguish with certainty primary inclusions from secondaries. All the inclusions were highly irregular in shape (Fig. A3.10a) and randomly distributed and their filling temperatures fell within a fairly limited range. In consequence they were considered to be of probable primary origin. The filling temperature range obtained by the writer was somewhat higher than that obtained by Sawkins (1966b) from fluorite from the same locality. One inclusion was observed by the writer

to contain an opaque, solid phase which, in reflected light appeared brassy-yellow in colour and was thought to be a sulphide (Fig. A3.10b).

Sample No. 18. Fluorite, Grassington, Yorkshire.

Two distinct types of inclusion were found in this clear, unzoned material:

1. Randomly distributed negative crystals, seldom cubic but more usually rectangular or L-shaped (Fig. A3.11a). These were considered to be primary inclusions.

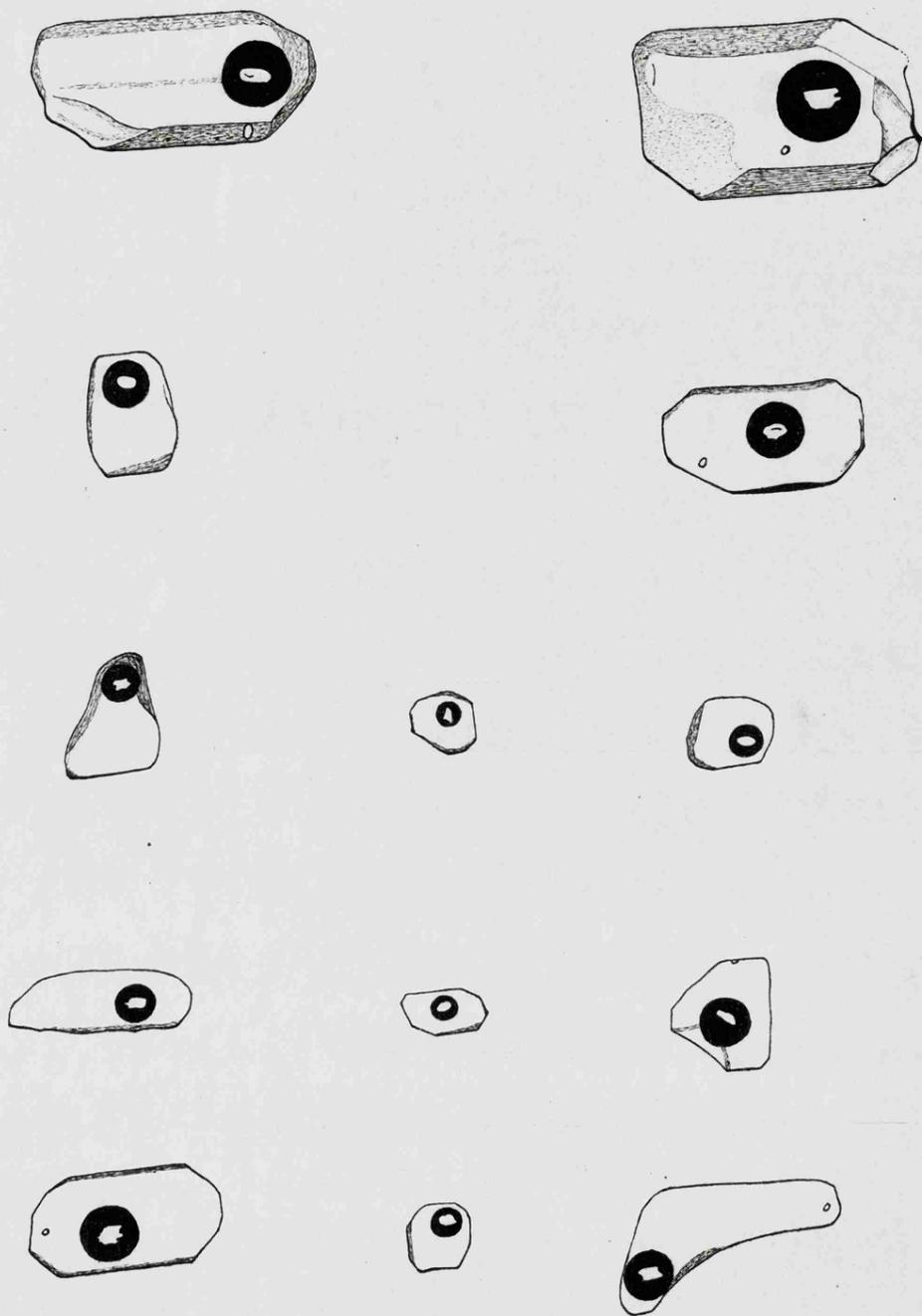
2. Veils and curving planes of irregularly shaped, usually elongate inclusions, generally much smaller than the negative crystals. The examples illustrated in Fig. A3.11b are larger than the average. These were considered to be secondary and their filling temperatures augmented this view by their being lower than those of the probable primaries.

Sample No. 19. Fluorite, Appletreewick, Yorkshire.

As in sample No. 18, two types of inclusions were distinguished; randomly and sparsely distributed negative crystals (Fig. A3.12) probable of primary origin and highly irregularly shaped inclusions in planes corresponding to cleavage directions which were considered to be secondary. These latter are not illustrated.

Sample No. 20. Fluorite, Weardale, Co. Durham.

It was not possible to distinguish primary inclusions from secondaries in this sample. All the inclusions were very irregularly shaped and the sample proved to be most unsatisfactory from the point of view of obtaining topographical data, the more so as it was not localized. It was used in the study of the variation of filling temperatures with the thickness of sections (chapter 5), but the data have not been recorded in Appendix 4 as they were not thought to be reliable.



0.1mm.

Fig. A3.1. Probable primary inclusions in purple fluorite,
15 Coronation Lode, Geevor Mine.

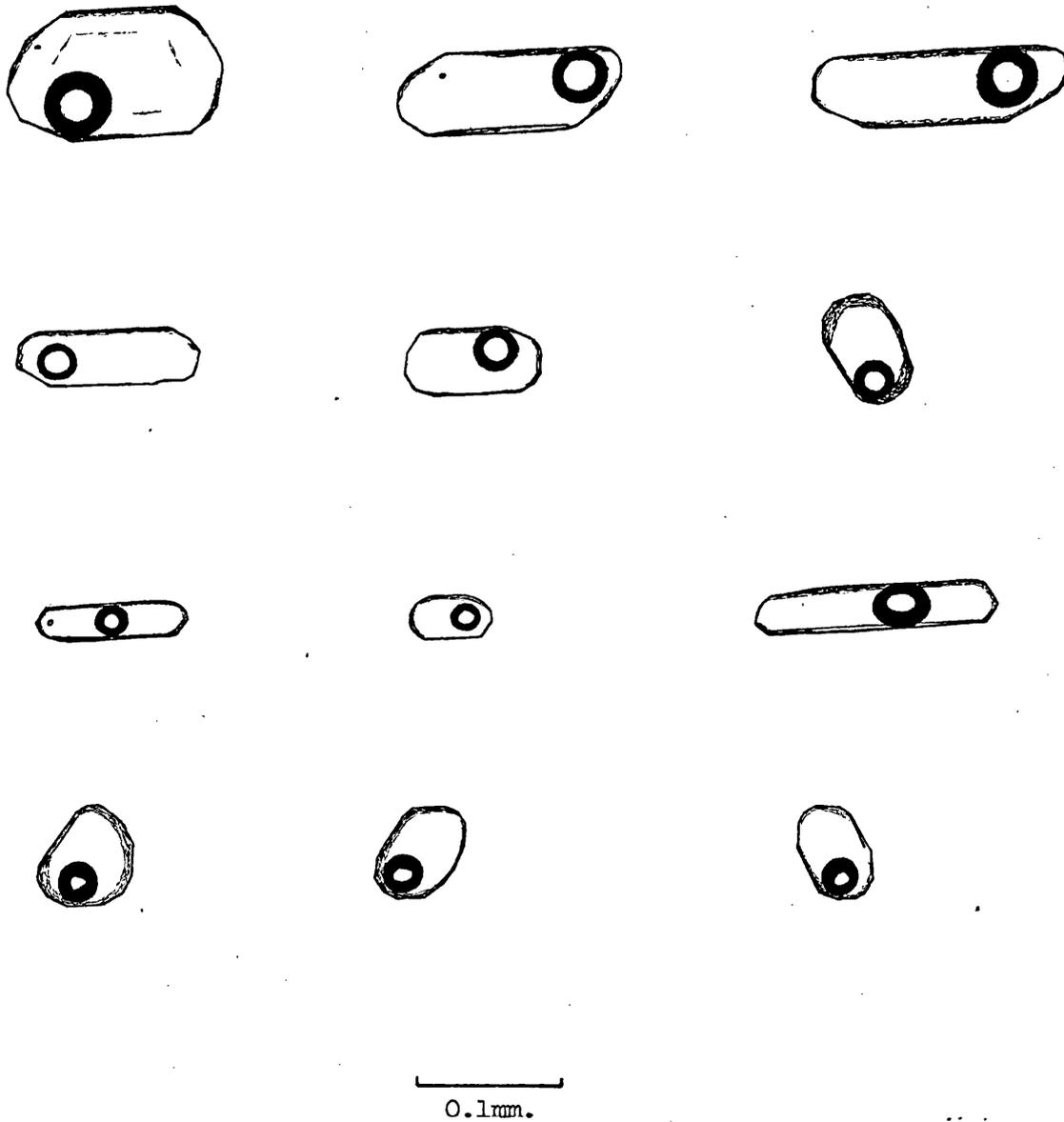
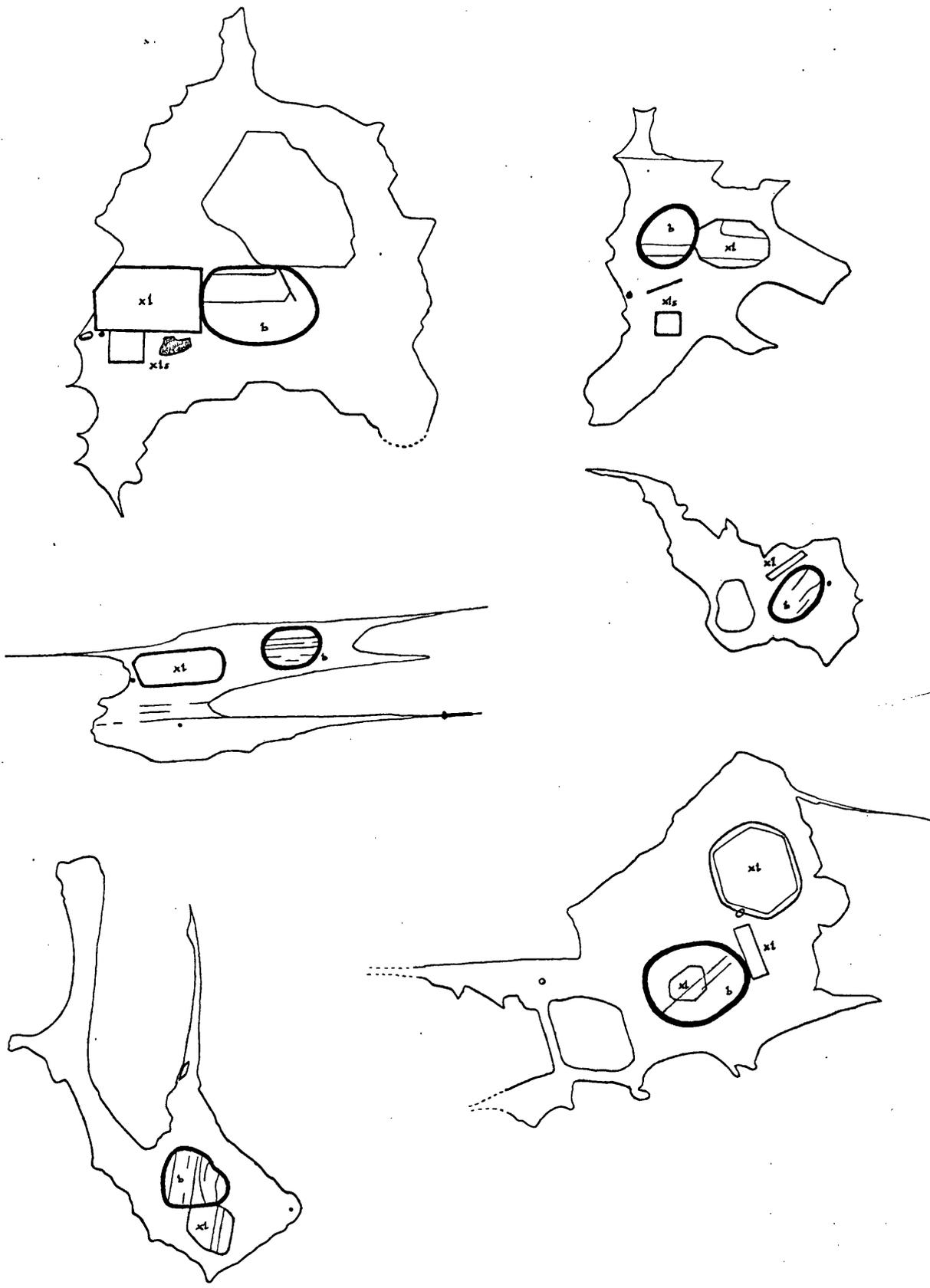


Fig.A3.2. Probable pseudosecondary inclusions in fluorite.
12 Simms Lode, Geevor Mine.



0.1mm.

Fig.A3.3. Multiphase secondary inclusions in fluorite,
10 Borehole Lode, Left Hand Vein, Geevor Mine.

xl - daughter crystal,
b.- vapour bubble.

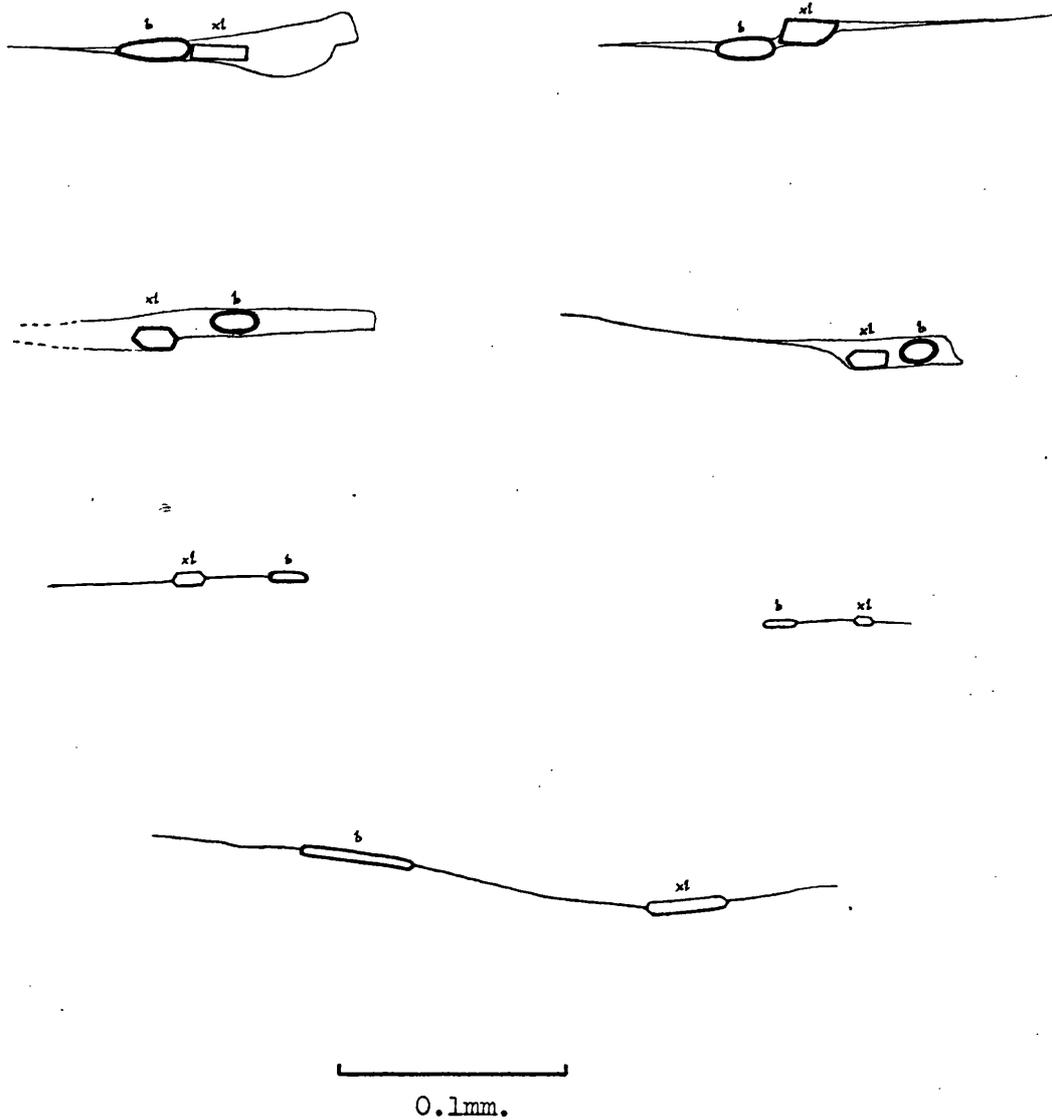
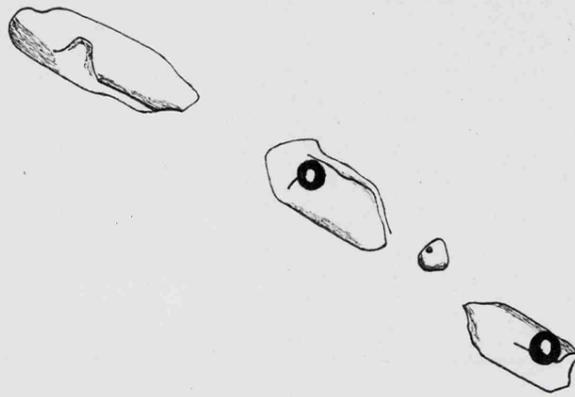


Fig.A3.4. Multiphase secondary inclusions in fluorite.
 10 Borehole Lode, Left Hand Vein, Geevor Mine.

xl - daughter crystal
 b - vapour bubble.



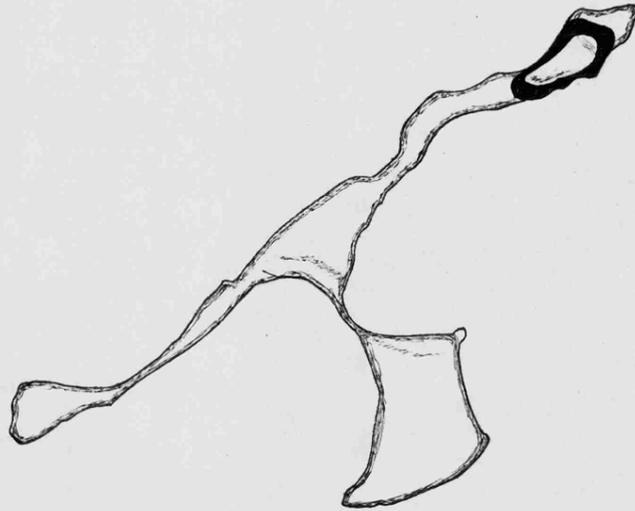
13 North Pig Lode, Geevor Mine.



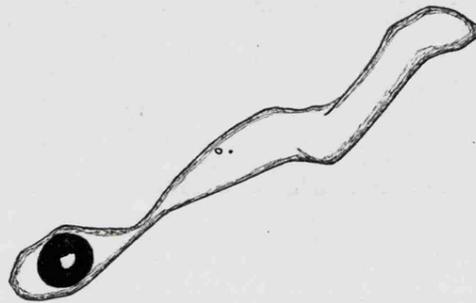
0.1mm.

Roskear South Lode, South Crofty Mine,
360fm. Level.

Fig.A3.5. Necking down of inclusions in fluorite.



0.1mm.



13 North Pig Lode, Geevor Mine.

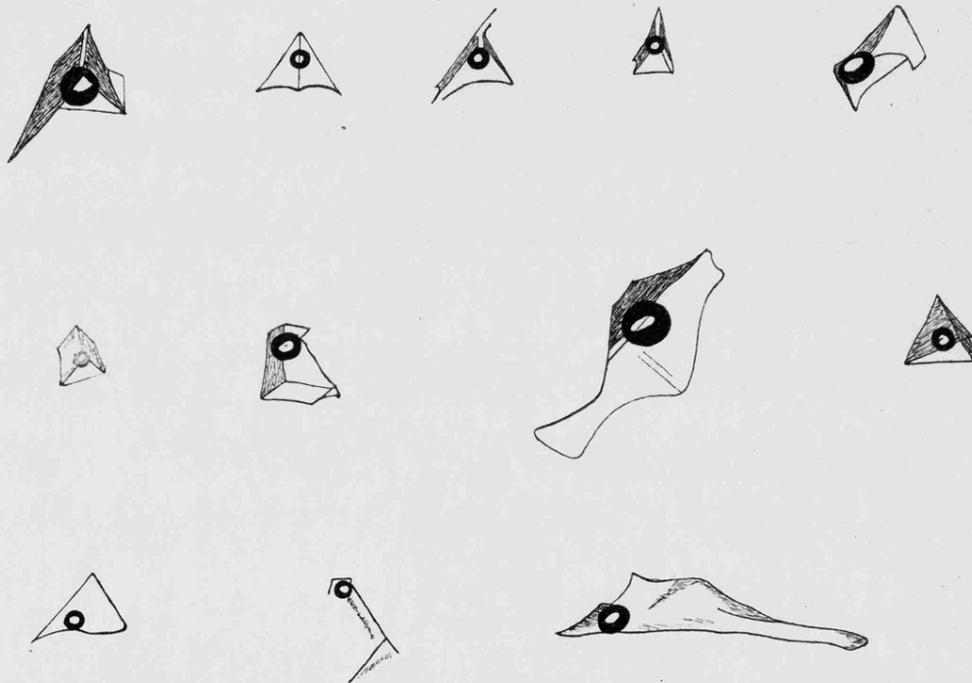


12 Simms Lode, Geevor Mine.

Fig.A3.6. Incipient necking down of inclusions in fluorite.



15 Coronation Lode, Geevor Mine.



0.1mm.

Roskear South Lode, South Crofty Mine,
360fm. Level.

Fig.A3.7. Probable primary inclusions in fluorite.

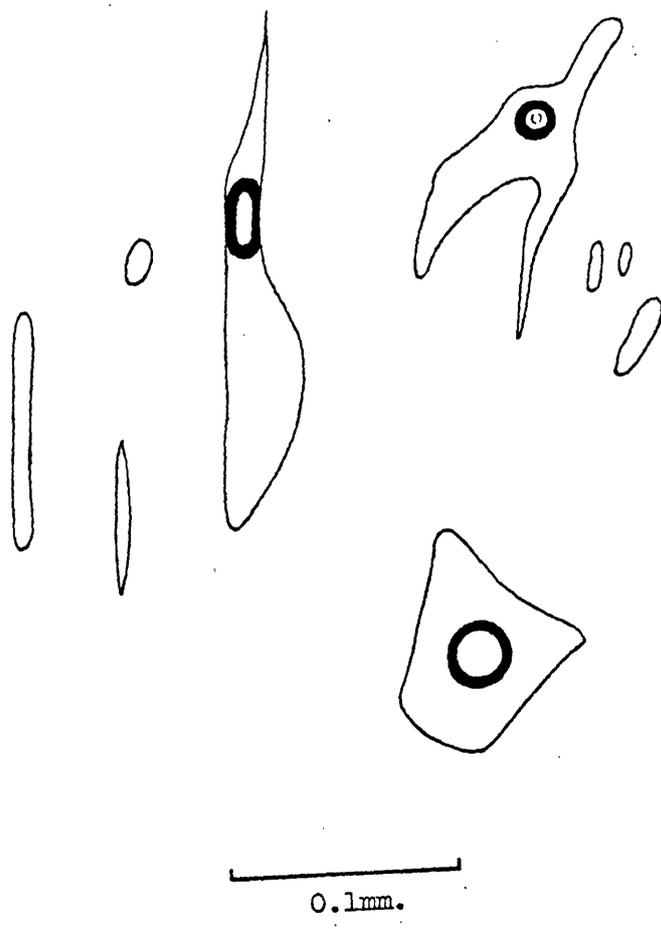
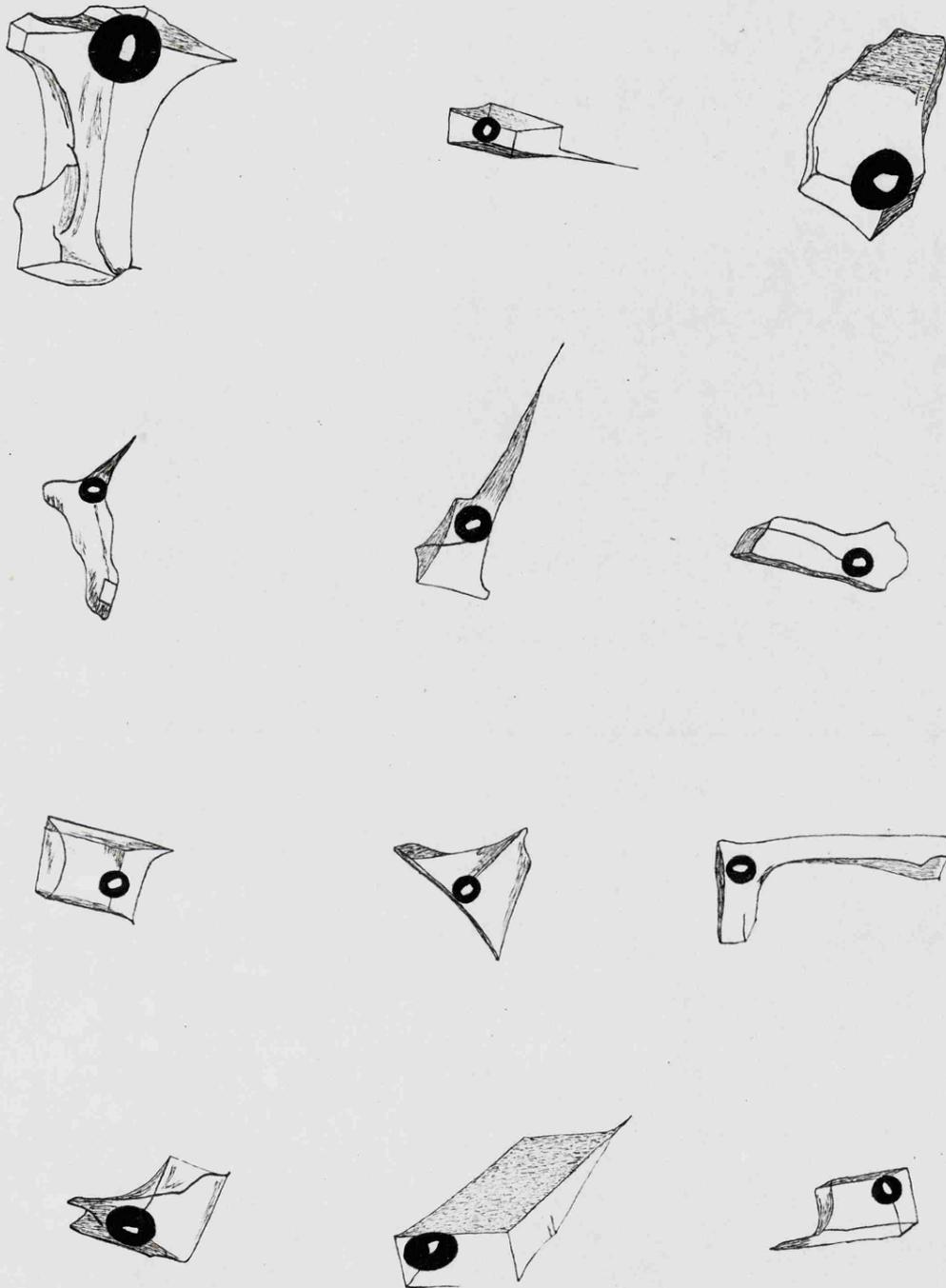


Fig.A3.8. Probable primary inclusions in quartz which have undergone necking down. 11 C Lode, Gevor Mine.



0.1mm.

Fig.A3.9. Probable primary inclusions in fluorite.
Wheal Mary Ann, Menheniot, Cornwall.

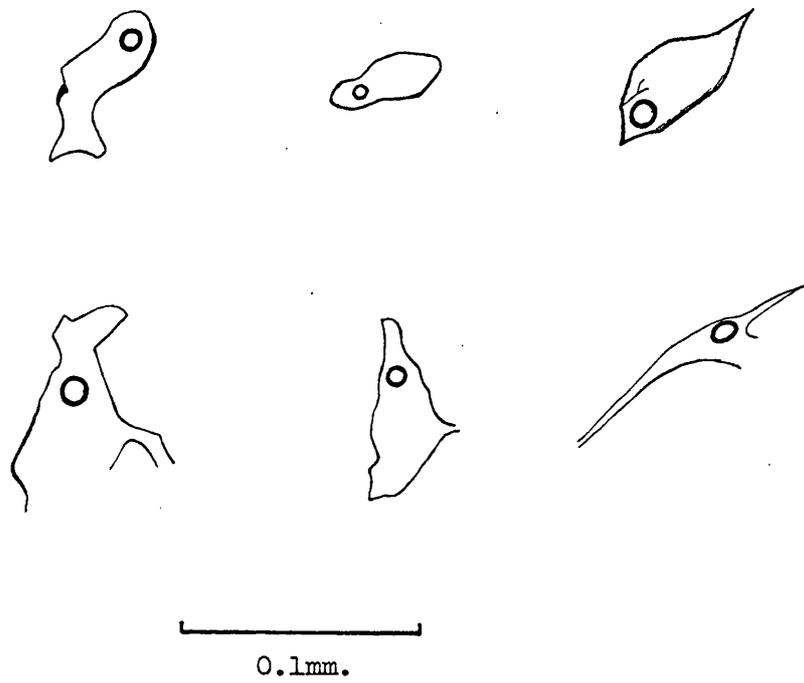


Fig.A3.10a. Probable primary inclusions in fluorite.
Scordale, Westmoreland.



Fig.A3.10b. Probable primary inclusion in fluorite,
containing a crystal of sulphide.
Scordale, Westmoreland.

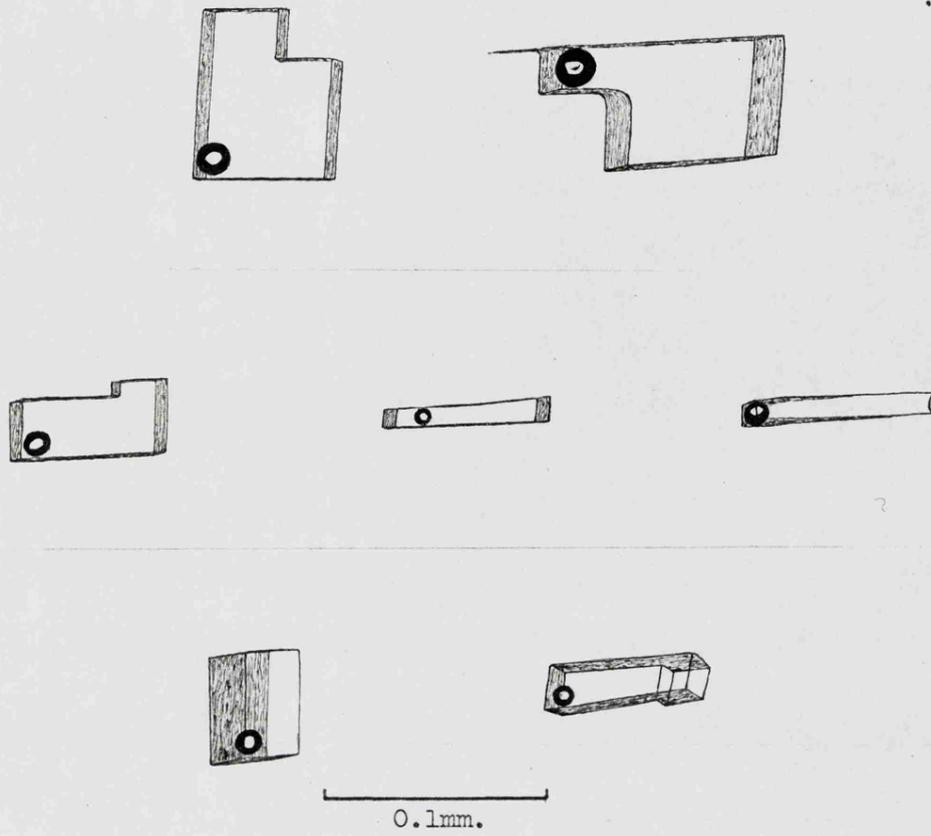


Fig.A3.11a. Probable primary inclusions in fluorite.
Middle Vein, Grassington, Yorkshire.

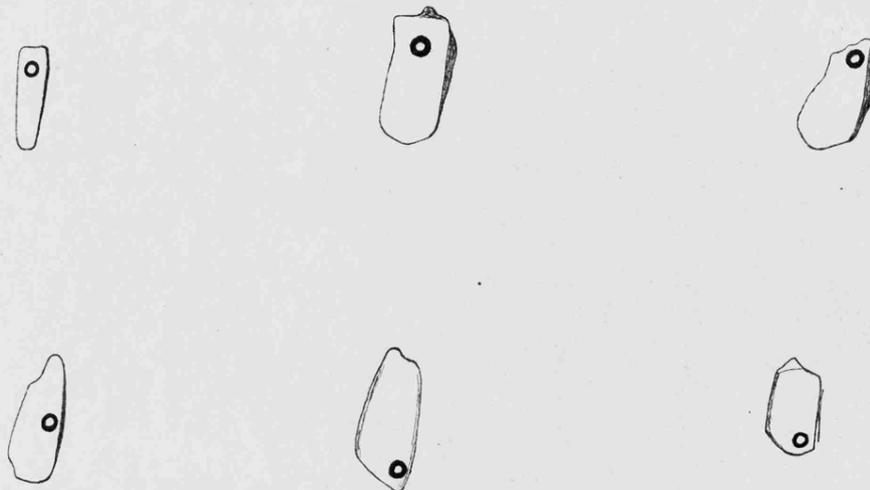
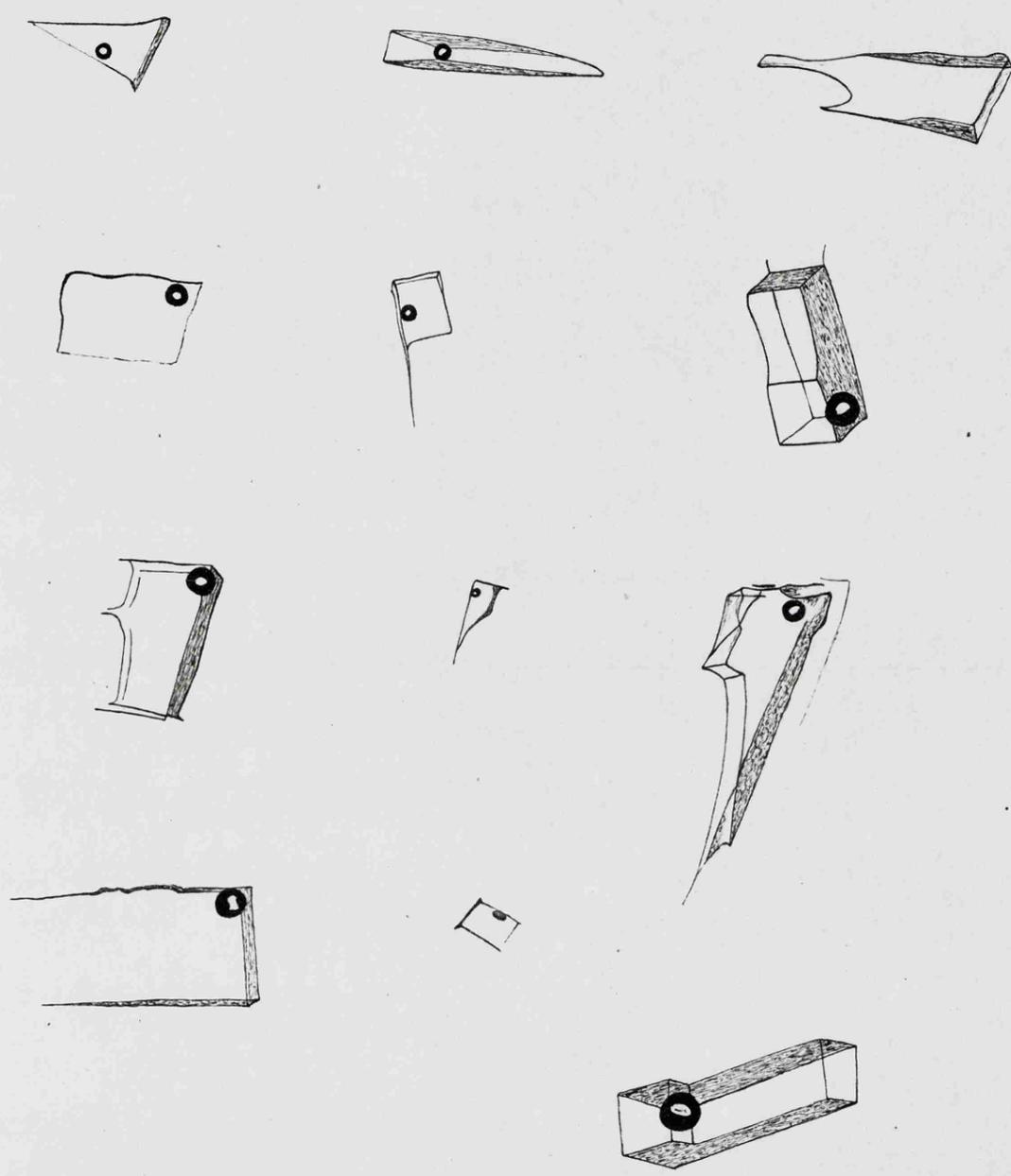


Fig.A3.11b. Probable secondary inclusions in fluorite.
Middle Vein, Grassington, Yorkshire.



0.1mm.

Fig.A3.12. Probable primary inclusions in fluorite.
Inman Vein, Appletreewick, Yorkshire.

APPENDIX 4

Geothermometric Data.

(Instrumental correction factor applied, but uncorrected for pressure).

Geevor Mine, St. Just, Cornwall.

Sample No.	Locality	Description	Type	No.	Range
1.	15 Coronation Lode	Purple fluorite with quartz, and chalcop- yrite	P	23	237-264
2.	15 Coronation Lode	Purple fluorite with quartz and chalcop- yrite	P	34	202-243
3.	15 Coronation Lode	Purple fluorite with quartz, and chalcop- yrite	P	15	211-248
4.	14 Borehole Lode	Green fluorite with chlorite.	P	50	310-335
5.	13 North Pig Lode	Green fluorite associated with arsenopyrite, pyrite and chalcopyrite	P	20	280-301
6.	12 Simms Lode	Grey-green fluorite with chlorite and ea earthy hematite	P	20	276-293
7.	10 Foot Wall Branch Lode	Purple fluorite	P&PS	70	192-240
8.	10 Borehole Lode Left Hand Vein	Green fluorite with cassiterite, pyrite & quartz	P	40	357-377
9.	10 Borehole Lode Left Hand Vein	Purple fluorite with cassiterite, pyrite & quartz	P	50	317-347
10.	9 C Lode	Quartz with tourmaline and chalcopyrite	P	21	290-323

Sample No.	Locality	Description	Type	No.	Range
11.	10 C Lode	Comb quartz leader	S	40	142-162
		Comb quartz leader (core)	P	20	262-274
		Comb quartz leader (edge)	P	20	225-248
		Comb quartz leader (core)	P	11	258-269
12.	10 C Lode	Comb quartz leader	S&PS	23	158-204
13.	11 C Lode	Comb quartz leader	P	17	242-269
14.	13 Boscaswell Lode	Freely grown late quartz	S	7	118-132
<u>Other Localities</u>					
15.	South Crofty Mine	Green fluorite	P	9	297-314
16.	Wheal Mary Ann	Blue fluorite	P	20	134-150
		Colourless-yellowish fluorite	P	14	130-144
		Purple fluorite	P	12	99-113
17.	Scordale, Westmoreland	Amber fluorite	P	20	126-139
18.	Grassington, Yorkshire	Colourless fluorite	P	19	95-114
		Colourless fluorite	S	10	88- 94
19.	Appletreewick, Yorkshire	Colourless fluorite	P	20	96-113

APPENDIX 5The Data obtained from the Experiment described in
Chapter 5.

Where possible, two sets of data are presented for each sample; the raw data and the corrected data. In three cases, the corrected data are not available.

Abbreviations used in the tables:

Th = Thickness of section in millimetres.

T_F = Filling temperature of the inclusion in $^{\circ}\text{C}$.

R.T. = Room temperature in $^{\circ}\text{C}$.

d = Difference between the two readings.

d% = Difference between the readings expressed as a percentage of the initial reading.

13 North Pig Lode, Geevor Mine, Cornwall.

(Primary and Secondary Inclusions)

Raw Data.

Section No.	Th	T _F	Th	T _F	d.	d%.
1	2.015	125	1.000	108	17	13.60
2	1.985	279	1.005	249	30	10.75
3	2.010	171	1.000	154	17	9.99
4	1.975	297	1.000	270	27	9.09
5	2.000	288	1.000	265	23	7.99
6	1.930	306	1.010	274	32	10.45
7	2.005	271	1.005	245	26	9.59
8	2.010	284	1.000	252	32	11.26
9	2.000	174	1.000	157	17	9.95
10	2.000	216	1.000	193	23	10.65
Means		241.1		216.7	24.4	10.10

The filling temperature of the control inclusion varied between 249 and 252°C. throughout the experiment and the room temperature was not recorded. The galvanometer was set at zero at a room temperature of 23°C. at this time, consequently corrected filling temperatures may be obtained by adding $21 \pm 1.5^\circ\text{C}$. to the observed readings. As both primary and secondary inclusions were used in this experiment, it was considered that no useful purpose would be served by presenting corrected data.

12 Simms Lode, Geevor Mine, Cornwall.

(Primary and Secondary Inclusions)

Raw Data.

Section No.	Th	T _F	Th	T _F	d.	d%
1	1.995	212	1.000	195	17	8.01
2	2.025	240	0.950	222	18	8.50
3	1.990	211	1.000	196	15	7.10
5	1.945	252	1.000	234	18	7.14
6	2.015	205	1.000	192	13	6.34
7	1.935	176	1.020	160	16	9.09
8	1.935	209	1.000	198	11	5.26
9	2.010	129	1.005	118	11	8.51
10	1.965	178	0.950	166	12	6.74
Means		201.3		186.7	14.6	7.22

The filling temperature of the control inclusion varied between 298 and 301°C. throughout the experiment and the room temperature was not recorded. The Galvanometer was set at zero at a room temperature of 23°C., consequently corrected filling temperatures may be obtained by adding 21⁺ 1.5°C. to the observed readings. As both primary and secondary inclusions were used in this experiment, it was considered that no useful purpose would be served by presenting corrected data.

Roskear South Lode, South Crofty Mine, Cornwall.

(Secondary Inclusions)

Raw Data

Section No.	Th	R.T.	T _F	Th	R.T.	T _F	d.	d%
1	2.005	22.0	151	1.000	24.0	138	13	8.61
2	2.025	21.5	158	1.005	24.0	139	19	12.02
4	2.035	23.0	141	1.000	23.0	131	10	7.09
5	2.020	23.0	158	1.000	24.0	146	12	7.59
6	2.010	22.5	144	1.005	23.5	131	13	9.02
7	2.000	23.5	151	1.005	24.0	138	13	8.61
8	2.035	23.0	156	0.990	23.5	144	12	9.09
9	2.015	23.5	143	1.000	24.5	130	13	9.09
10	2.030	24.0	152	1.000	23.0	141	11	7.23
11	2.000	24.0	140	1.000	23.0	130	10	7.14
Means			149.4			136.8	12.4	8.28

Corrected data; galvanometer set at zero at 23°C.

Section No.	Th	T _F	Th	T _F	d.	d%
1	2.005	171	1.000	161	10	5.84
2	2.025	178	1.005	161	17	9.55
4	2.035	162	1.000	152	10	6.17
5	2.020	179	1.000	168	11	6.14
6	2.010	165	1.005	153	12	7.27
7	2.000	172	1.005	160	12	6.97
8	2.035	177	0.990	165	12	6.78
9	2.015	165	1.000	153	12	7.27
10	2.030	174	1.000	162	12	6.89
11	2.000	162	1.000	151	11	6.78
Means		170.5		158.6	11.9	6.96

Wheal Mary Ann, Menheniot, Cornwall.

(Primary Inclusions)

Raw Data

Section No.	Th	T _F	R.T.	Th	T _F	R.T.	d.	d%
1	2.000	116	22.5	0.990	111	21.5	5	4.31
2	1.995	120	26.0	1.000	115	23.0	5	4.16
4	2.005	130	26.5	1.000	125	22.5	5	3.84
5	2.005	116	25.5	0.965	113	21.5	3	2.59
6	2.000	121	26.0	1.010	118	23.0	3	2.48
7	2.015	130	26.0	1.000	123	23.0	7	5.39
8	2.040	119	26.5	0.980	114	22.5	5	4.20
10	2.010	130	25.0	1.005	123	22.0	7	5.39
Means		122.7			117.7		5	4.06

Corrected data; galvanometer set at zero at 24°C.

Section No.	Th	T _F	Th	T _F	d.	d%
1	2.000	140	0.990	131	9	6.42
2	1.995	144	1.000	136	8	5.55
4	2.005	154	1.000	146	8	5.19
5	2.005	140	0.965	133	7	5.00
6	2.000	145	0.010	139	6	4.14
7	2.015	154	1.000	144	10	6.49
8	2.040	143	0.980	135	8	5.59
10	2.010	153	1.005	143	10	6.53
Means		146.6		138.3	8.25	5.61

Middle Vein, Grassington, Yorkshire.

(Mostly Primary Inclusions)

Raw Data

Section No.	Th	R.T.	T _F	Th	R.T.	T _F	d.	d%
1	1.990	24.5	79	1.000	25.0	70	9	11.4
2	1.990	25.0	95	1.075	24.0	85	10	10.5
3	1.990	25.5	79	0.980	25.0	74	5	6.3
6	1.995	23.0	67	1.000	25.0	57	10	14.9
7	1.985	23.5	86	1.000	25.0	77	9	10.4
8	1.990	24.0	82	0.995	24.5	75	7	8.5
9	1.985	24.5	77	1.000	25.0	72	5	6.5
10	1.980	24.5	79	1.000	24.5	73	6	7.6
Means			80.5			72.9	7.6	9.4

Corrected data; Galvanometer set at zero at 24°C.

Section No.	Th	T _F	Th	T _F	d.	d%
1	1.990	101	1.000	93	8	7.9
2	1.990	118	1.075	107	11	9.3
3	1.990	102	0.980	97	5	4.9
6	1.995	88	1.000	80	8	9.1
7	1.985	108	1.000	100	8	7.4
8	1.990	104	0.995	98	6	5.8
9	1.985	100	1.000	95	5	5.0
10	1.980	102	1.000	96	6	5.9
Means		102.8		95.7	7.1	6.9

Inman Vein, Appletreewick, Yorkshire.

(Mostly Primary Inclusions)

Raw Data

Section No.	Th	T _F	Th	T _F	d.	d%
1	1.980	63	0.985	60	3	4.75
2	2.000	84	1.000	79	5	5.95
3	1.995	96	1.000	87	9	9.04
4	2.000	80	1.000	71	9	11.25
7	1.975	92	1.000	86	6	6.43
8	2.030	75	0.980	67	8	10.66
9	2.015	83	1.000	80	3	3.61
10	2.005	94	0.985	87	7	7.44
Means		83.3		77.1	6.2	7.49

Data corrected according to readings of control inclusion.

(Galvanometer set at zero at 22°C.)

Section No.	Th	T _F	Th	T _F	d.	d%
1	1.980	83	0.985	78	5	6.02
2	2.000	104	1.000	98	6	5.77
3	1.995	116	1.000	107	9	7.75
4	2.000	100	1.000	92	8	8.00
7	1.975	112	1.000	107	5	4.46
8	2.030	95	0.980	88	7	7.37
9	2.015	103	1.000	99	4	3.88
10	2.005	114	0.985	107	7	6.14
Means		103.3		97.0	6.3	6.17

Scordale, Westmoreland.

(Primary Inclusions)

Raw Data

Section No.	Th	T _F	Th	T _F	d.	d%
1	2.045	121	1.000	109	12	9.91
2	1.970	107	1.000	94	13	12.15
3	2.010	107	0.960	96	11	10.28
4	2.005	100	1.005	88	12	12.00
5	1.990	118	0.950	104	14	10.86
7	2.040	120	0.965	102	18	15.00
8	?	110	1.005	102	8	7.27
9	2.010	109	1.000	99	10	9.17
10	2.000	108	0.980	99	9	8.33
Means		111.1		99.2	11.9	10.55

Data corrected according to readings of control inclusion.

(Galvanometer set at zero at 22°C.)

Section No.	Th	T _F	Th	T _F	d.	d%
1	2.045	141	1.000	131	10	7.09
2	1.970	127	1.000	116	11	8.66
3	2.010	127	0.960	119	8	6.30
4	2.005	121	1.005	110	11	9.09
5	1.990	137	0.950	127	10	7.30
7	2.040	140	0.965	124	16	11.43
8	?	131	1.005	125	6	4.58
9	2.010	128	1.000	121	7	5.47
10	2.000	129	0.980	121	8	6.20
Means		131.2		121	9.7	7.35

Weardale, Co. Durham.

(Primary and Secondary Inclusions)

Raw Data

Section No.	Th	T _F	Th	T _F	d.	d%
2	1.840	145	0.965	137	8	5.52
3	1.945	150	1.000	140	10	6.66
6	1.945	103	1.005	94	9	8.73
7	1.900	138	1.010	112	26	18.84
8	1.635	125	0.995	113	12	9.60
9	1.605	122	0.980	107	15	12.29
10	1.845	136	0.900	123	13	9.56
11	1.890	141	0.940	131	10	7.09
Means		132.5		119.6	12.9	9.74

At the time this sample was examined, no record was kept of the room temperature and the control section (No. 11) had to be used to make up the numbers of inclusions. Consequently, no corrections were possible and the data have not been recorded in Appendix 4.

APPENDIX 5a.The Mathematical Procedure for Student's t Test.

1. Calculate the combined variance. (V_c)

$$V_c = \frac{(s_1^2 \times n_1 - 1) + (s_2^2 \times n_2 - 1)}{n_1 + n_2 - 2}$$

2. Calculate the combined standard deviation. (S.D._c)

$$S.D._c = \sqrt{V_c}$$

3. Calculate the standard error of the difference. ($\bar{x}_1 - \bar{x}_2$)

$$S.E. = S.D._c \sqrt{1/n_1 + 1/n_2}$$

4. Calculate t.

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{S.E.}$$

APPENDIX 5b.The Mathematical Procedure for Student's t Test, modified
by Winer (1962) for Correlated Observations.

Data required:

- a. The mean difference, \bar{d} .
- b. The sum of differences $\sum d$.
- c. The sum of the squares of the differences $\sum d^2$.

1.
$$L_d = n \sum d^2 - (\sum d)^2$$

2.
$$s_d^2 = \frac{L_d}{n(n-1)}$$

3.
$$t_{\text{obs}} = \frac{\bar{d}}{\sqrt{s_d^2/n}}$$

APPENDIX 6A review of the recent published work on British geothermometry.

Britain may honestly be claimed as the birth-place of fluid inclusion geothermometry. Davy (1822) pointed to the possible use of fluid inclusions as self-registering thermometers and Sorby (1858) adopted the idea and laid the foundation for the modern development of the method. In the latter half of the nineteenth century, a number of workers attempted to use fluid inclusions as geothermometers but not with great success (Ward, 1875; Phillips, 1875; Allport, 1876). Since that time, very little interest has been shown, in Britain, in geothermometry. The following is a review of the published works which have appeared since fluid inclusion geothermometry gained general acceptance as a valid geological tool. The second part of this section is a compilation of the published data obtained from British material.

Smith (1949) appears to have been the first, in recent times, to use British material for a geothermometric study. He put forward the hypothesis that the mode of homogenization of aqueous fluid inclusions is indicative of the state of aggregation of the ore-forming fluid. In practical terms, he postulated that homogenization to the liquid phase is indicative of a hydrothermal ore-solution (liquid) and homogenization to the vapour phase indicates a pneumatolytic fluid (gas). To test this hypothesis on material which had been regarded as of pneumatolytic origin, Smith chose quartz, tourmaline and cassiterite from the St. Austell area of Cornwall and also chalcopyrite, quartz and wolfram from the Camborne district. In all cases, the inclusions in the transparent minerals were observed to homogenize to the liquid phase and from this, Smith concluded that the Cornish tin-tungsten ores were of hydrothermal origin. The filling temperatures of the minerals were determined by the decrepitation method and they were corrected for pressure, assuming a depth of burial of two miles, according

to the diagram of Ingerson (1947). These data are presented in the second part of this section.

Little (1960), in a reconnaissance study of inclusions in cassiterite and associated minerals from world-wide localities, presented data on material from several Cornish localities. Whereas his data are of value in the context of his study, few are of great value to British topographical geothermometry. The present writer would criticize the work on two points. The first is that of some twenty-two Cornish samples taken, filling temperatures measurements were made on only five. Little presented temperature data of three types, the first an estimate of the filling temperature obtained by estimating the bubble-cavity ratio at room temperature and from that ratio the filling temperature was obtained from the pressure-volume-temperature data for water. The second was a calculated determination whereby the bubble-cavity ratio of suitably shaped and sized inclusions was measured with a micrometer ocular and the filling temperature derived from the pressure-volume-temperature data for water. Finally, the filling temperatures of inclusions in selected samples were measured visually on a heating stage. In the Cornish material, where all three methods of obtaining the filling temperatures were used, there was considerable discrepancy between the estimated or calculated filling temperature and the measured filling temperature and, thus, the data from seventeen of the twenty-two samples are somewhat unreliable.

The second criticism lies in the recording of the sample localities. Only five of the twenty-two samples were localized to the mine, two to the parish and the remaining fifteen were given merely as "Cornwall". Furthermore, four of the five samples, the filling temperatures of whose inclusions were actually measured, were given in the locality "Cornwall". From the view point of accumulating topographical geothermometric data, Little's contribution is of less value than it might otherwise have been, but from Little's point of view the additional topographical information

was unnecessary.

Sawkins (1966a) presented the results of a preliminary investigation into the geothermometry of the Cornish metalliferous lodes by the study of the inclusions in quartz, fluorite and, where possible, blende. The filling temperatures of over 200 inclusions from 24 samples were determined on a heating stage. The localities were given fairly precisely; usually the name of the mine but occasionally only the parish was given. However, even a parish is more useful than Little's "Cornwall". Sawkins' data were consistent with the generally held views on mineral zoning in Cornwall (Dines, 1956; Hosking, 1963) in that the highest filling temperatures obtained were from quartz associated with cassiterite and lower temperatures were obtained from post-cassiterite quartz, quartz and/or fluorite with chalcopyrite, post-chalcopyrite quartz and quartz associated with blende. The lowest temperatures of all were obtained from fluorite associated with galena. Complementary to the geothermometry, freezing studies of inclusions from selected samples provided approximate data on the total salt concentration of the inclusion fluids, expressed as equivalent weight per cent sodium chloride. These showed a wide and inconsistent variation from about 50 equiv.wt. per cent down to 2 equiv.wt. per cent. Similarly the sodium to potassium ratios, determined by flame photometry, showed a wide variation. These chemical data could not be correlated with the temperature data. Sawkins made no attempt to apply a pressure correction to his temperature data.

Bradshaw and Stoyel (1968) favoured the application of fluid inclusion geothermometry to mineral exploration to which end they measured the filling temperatures of over 1000 inclusions in samples from 185 mineral vein localities in Cornwall. Samples were collected from the dumps of thirteen mines in a traverse from Cligga Head to the St. Day area. The highest filling temperature from each sample was plotted and an isothermal contour map was constructed. The contours showed close agreement with the

mineral zones advocated by Dines (1956) and others. Similarly the temperature data correlated closely with the mineralogy in that the highest temperatures were obtained from cassiterite and from quartz associated with cassiterite and the lowest from quartz with galena, as previously noted by Sawkins (1966a).

A study of the Pryce's lode - Tincroft South lode system at the South Crofty mine revealed an increase in filling temperature of the inclusions in fluorite with depth of the order of 10°C per 300 ft. Bradshaw and Stoyel concluded that, as the metals which characterize the well established zonal arrangement in Cornwall have well-defined filling temperature ranges, it may be possible to use "... filling temperature data in mineral exploration in order to predict if the sampling level is in the optimum temperature zone for mineralization or if a relatively deeper or shallower level should be investigated".

Sawkins (1966b) investigated the geothermometry of the Northern Pennine orefield by the heating-stage study of fluid inclusions in fluorite, calcite and baryte. He also investigated the total salt concentration and the sodium to potassium ratios of the inclusion fluids. He found that fluorite was deposited in the temperature range of 200°C to 100°C ., quartz in the range $200+^{\circ}\text{C}$. down to 120°C . and baryte in the range 130°C . to below 50°C . Late calcite in the central part of the fluorite zone was deposited at about 80°C . By analogy, pyrrhotine appeared to have been deposited at temperatures above 160°C . and galena and blende from 200°C . to less than 100°C . The temperature data suggested to Sawkins that hotspots occurred within the fluorite zone centred on Rotherhope Fell, the Great Sulphur Vein, Whiteheaps Mine and in the area which includes Stotsfieldburn, Stanhopeburn, Black Dene and Sedling mines in Weardale; these are heavily mineralized areas which probably represent feeder zones through which the hydrothermal solutions ascended.

The freezing data indicate relatively high salinities for the solutions,

which did not fluctuate markedly during the deposition of fluorite and quartz. Both the salinity data and the sodium to potassium ratios compare closely with those of the Mississippi Valley deposits (Roedder et al, 1963; Hall and Friedman, 1963).

The sodium to potassium ratio of present day sea-water is 29 and it is unlikely that it will have changed significantly since Carboniferous times. Sea-water trapped in sediments eventually becomes connate water and it evolves in the direction of an increasing sodium to potassium ratio as potassium is constantly being fixed by the reconstitution of degraded clay minerals. The average sodium to potassium ratio of connate brines encountered in the Durham coalfield is 703 and most recorded connate brines have ratios greater than 50. The low sodium to potassium ratio (6.8 to 12.4) of the inclusion fluids in the fluorite zone of the Northern Pennine orefield suggest that the hydrothermal solutions were not of connate origin. The sodium to potassium ratio in baryte, particularly in late stage crystals is significantly higher than in quartz and fluorite (15.3 to 46). Sawkins presented two possible explanations; either the sodium to potassium ratio of the hydrothermal solutions was changing at source, or that increasing amounts of connate water similar to that now found in the Durham coalfield were mixing with the hydrothermal solutions during the later stages of mineralization, that is, during the period of baryte deposition.

Sawkins also put forward an interesting and apparently plausible explanation for the zoning of the mineralization in the Northern Pennine Orefield.

For the sake of completeness, it should be noted that Roedder (1965), working on olivine-bearing nodules from basalts of world-wide origin, noted the occurrence of carbon dioxide inclusions in olivine from the basalt of Calton Hill, Derbyshire. At room temperature, these inclusions consisted of a single liquid phase and only on cooling to $3.24 \pm 0.08^{\circ}\text{C}$. did a

shrinkage bubble appear. Thus, the density of the liquid carbon dioxide was very high, probable as high as 0.89 gm. per cm³. Roedder obtained the approximate pressure at the time of entrapment by the extrapolation of the data of Kennedy (1954), assuming a temperature of formation in the region of 110 to 1200°C. The pressure required to trap liquid carbon dioxide of the density found at Calton Hill would probably be in the region of 5000 bars, representing about 16 kilometres of overlying magma or rock.

Thus, there have been only five published fluid inclusion geothermometric studies of British mineral deposits, four of which were concerned with the relatively high temperature Hercynian mineralization of Cornwall and the fifth with the moderate to low temperature Hercynian mineralization of the Northern Pennines. It can be seen from this that the systematic accumulation of topographical data is in its infancy as far as Britain is concerned and that there is scope for a vast amount of further work.

Although Cornwall has so far received the most attention, the potential of the county is far from exhausted. The working mines in Cornwall, Geevor, Levant, South Crofty, Pendarves, The Janes and Mount Wellington, should afford excellent opportunities for detailed geothermometric studies of the mineralization. The Cornish lodes are very often of a crustiform nature, each pulse of mineralizing fluid having deposited a recognizable layer of minerals. Study of the fluid inclusions in each of these layers, at one locality, should facilitate the understanding of the thermal history of the ore fluids. Also the study of inclusions from a particular phase of mineralization in a lode, sampled on several levels and at several points on each level, will prove or disprove the existence of thermal gradients. A thermal contour diagram of a lode compared with a tin-value diagram may show some correlation in which case fluid inclusion geothermometry may prove to be useful in mineral exploration. Bradshaw and Stoyel (1968) conducted a pilot study on these lines at South Crofty.

Besides such detailed studies, there are areas of Cornwall and Devon which have not yet been looked at. The parishes of St. Erth and St. Hilary, notable for their lead production, have received no attention. The lead-antimony area of North Cornwall remains virgin. The stockworks of the Mulberry Mine and Hemerdon Ball are worthy of attention as are the fairly numerous pegmatite deposits in Cornwall, and the skarn-type mineralization on the north side of Dartmoor should prove of interest.

Sawkins' (1966b) work on the Northern Pennines covered the area fairly comprehensively and other than filling in topographical details, not a great deal of fundamental work is here required. However, detailed studies of the veins in the working mines of the type outlines above for Cornwall, should prove rewarding. It remains for Sawkins' work to be extended to cover the central and southern Pennines, notably to the Swaledale-Wensleydale-Wharfedale district of Yorkshire and to the Derbyshire Peak District.

There is potential for useful geothermometric work in the Lake District. Of particular interest would be a study of the Caldbeck Fells area where two distinct types of mineralization intersect; the older tungsten-molybdenum mineralization of the Carrock Mine and the younger copper-lead mineralization of Roughton Gill and Dry Gill intersect in Brandy Gill, above Carrock Mine. A fluid inclusion study of the West Cumberland hematite deposits may throw light on the problems of ore genesis encountered there.

The lead-zinc fields of North Wales, Shropshire and Central Wales have not been investigated, nor have the Alpine-type veins of Snowdonia and as far as the present writer is aware, no fluid inclusion studies have been conducted on the many and varied Scottish mineral deposits.

It may be concluded that whereas Britain was the birth-place of fluid inclusion geothermometry, the use of this valuable geological tool in Britain is still in its infancy; a great amount of work is required before it attains adulthood.

Smith, F.G., 1949. Econ. Geol. Vol. 44, p.p. 624-625.

"Laboratory testing of pneumatolytic deposits."

Locality	Mineral	Filling Temperature uncorrected	Filling Temperature corrected for 2 miles depth
St. Austell	Tourmaline	345°C.	390°C.
	Cassiterite	345	390
	Quartz	329	370
South Crofty	Quartz	293	345
	Wolfram	242	265
Tincroft	Chalcopyrite	261	280

Little, W.M. 1960. Econ. Geol. 55, p.p. 485-509

"Inclusions in cassiterite and associated minerals."

Geothermometric data, uncorrected for pressure.

Locality	Mineral	Type of Inclusion	Filling Temperatures			
			Estimated T ^o C.	$\frac{\text{Vol. inc.}}{\text{Vol. liq.}}$	Calculated T ^o C.	Measured T ^o C.
S. Terras Mine	Quartz	H ₂ O P, very few	-	-	-	-
		(Smokey) H ₂ O-CO ₂ , complex	330	-	-	395
S. Crofty Mine	Cass- iterite	H ₂ O P (?)	250	1.22	230	-
S. Crofty Mine	Quartz	H ₂ O P (?)	280	1.45	310	-
St. Austell	"Capped" quartz from granite	H ₂ O S (?)	-	-	-	-
		complex	-	-	-	-
S. Terras Mine	Quartz	H ₂ O S (?) few	-	-	-	-
		(Amethyst H ₂ O P (?) few	230	-	-	-
		"Complex" numerous	-	-	-	-
S. Crofty Mine	Cass- iterite	H ₂ O P (?)	250	1.29	260	-
S.W. Cornwall	Quartz from cross- course	H ₂ O S (?)	130	+	-	-
		H ₂ O P (?)	260	-	-	-
		"Complex"	-	-	-	-
St. Austell	Axinite	H ₂ O P	280	1.43	300	-
Castle-an- Dinas	Quartz	H ₂ O P (?) some with salt crystals and anisotropic crystals	250	-	-	-
		H ₂ O-CO ₂ (?)	-	-	-	-
Cornwall	Sphalerite	H ₂ O P (?)	100	-	-	-
	Quartz	H ₂ O P (?) a few with anisotropic crystals	140	-	-	-
Cornwall	Fluorite	H ₂ O S (?)	130	-	-	-
	Quartz	H ₂ O P (?) some with salt crystals	300	-	-	-

Little (1960) continued.

Cornwall	Quartz	H ₂ O S (?) few	-	-	-	-
		H ₂ O P some with salt and anisotropic crystals	300	-	-	-
		H ₂ O-CO ₂ P	-	-	-	-
Cornwall	Quartz	H ₂ O S (?)	-	-	-	-
		H ₂ O P (?) some with salt and anisotropic crystals	300	-	-	-
Cornwall	Fluorite	H ₂ O S (?)	150	-	-	252
		H ₂ O P (?) some with salt and anisotropic crystals	270	1.40	300	398
Cornwall	Quartz from granite	H ₂ O S (?)	130-300	-	-	-
Cornwall	Cassiterite	H ₂ O P (?)	300	1.35	290	388
Cornwall	Cassiterite	H ₂ O P (?)	-	-	-	499
Cornwall	Sphalerite	H ₂ O P (?)	180	1.11	170	-
Cornwall	Wolframite	H ₂ O S (?)	-	-	-	-
		H ₂ O P (?)	280	1.24	235	-
Cornwall	Cassiterite	H ₂ O P (?) some with salt crystals	250	1.22	230	358
		H ₂ O-CO ₂ (?) a few	-	2.34	-	-
Cornwall	Quartz	H ₂ O S (?)	-	-	-	-
		H ₂ O P (?)	275	1.33	280	409
		H ₂ O-CO ₂ (?)	-	-	-	-
		Tourmaline	-	-	-	-

Little (1960) continued.Summary of observed filling temperatures of H₂O inclusions.

Locality	Mineral	Filling Temperatures	No. of inclusions
Cornwall	Cassiterite	355-381	3
	Quartz	389-429	8
Cornwall	Fluorite	240-264 S (?)	9
	Fluorite	391-405	
Cornwall	Cassiterite	388	3
	Cassiterite	484-514	10

Sawkins, F.J. 1966(a). Trans. I.M.M. 75 p.p. B109-B112

"Preliminary fluid inclusion studies of the mineralization associated with the Hercynian granites of Southwest England."

Geothermometric data, uncorrected for pressure.

Locality	Description	No. of inclusions	Type	Filling T. °C.
Penlee Quarry	Quartz contemporaneous with SnO ₂	4	P	435-440
Penlee Quarry	Quartz associated with pyrite	9	PS	286-309
Polgooth, St. Austell	Quartz, just post-cassiterite	10	P	305-312
Geevor Mine	Quartz, post-cassiterite	23	P	300-314
Penlee Quarry	Quartz from N-S cross-course	15	PS	298-314
Geevor Mine	Quartz, post-cassiterite	3	PS	273-276
St. Day	Quartz, associated with chalcopyrite	11	P&PS	250-290
St. Day	Large, late quartz crystal-core	9	P	221-238
St. Day	Large, late quartz crystal-edge	3	P	176-180
Wheal Friendship	Quartz associated with orthoclase and pyrite	20	PS	248-256
Botallack	Late quartz	18	P	221-248
Botallack	Late quartz	7	PS	235-256
Geevor Mine	Fluorite	8	P	184-206
Geevor Mine	Fluorite	5	PS	174-184
Lambriggan	Quartz, pre-sphalerite	13	P	208-226
Lambriggan	Sphalerite-low iron	4	PS	150-170
Menheniot	Colourless fluorite - post-galena	12	P	127-146
Menheniot	Colourless fluorite - post-galena	6	P	115-122
Trewavas Head	Quartz	5	P	263-284
Trewavas Head	Quartz	6	FSorS	160-179

Sawkins, (1966a) continued

Trewavas Head	Zoned purple fluorite	18	P	115-146
?probably South Crofty	Green fluorite containing tiny blebs of chalcopyrite	14	P	256-270
St. Austell clay pits	Quartz	15	P	245-251
St. Austell clay pits	Quartz	6	P	295-300

Salinity data.

Locality	Description	No. of inclusions	Equiv. wt. % NaCl.
Penlee Quarry	Quartz associated with cassiterite	6	50
Geevor Mine	Quartz, post cassiterite	3	26
Penlee Quarry	Quartz from N-S cross-course	4	26
Polgooth, St. Austell	Quartz, post-cassiterite	7	4.2
Wheal Friendship	Quartz	3	18.2
?probably South Crofty	Green fluorite	7	12.8-13.5
Lambriggan	Quartz, pre-sphalerite	3	2.0- 3.0
St. Austell clay pits	Quartz	6	2.6- 3.4
St. Austell clay pits	Quartz	2	4.6

Sawkins, (1966a) continued.Na/K ratio data.

Locality	Description	Na/K
St. Day	Quartz associated with chalcopyrite	10.4
?probably South Crofty	Green fluorite	9.5
Menheniot	Colourless fluorite	6.7
Poolgooth, St. Austell	Quartz, post-cassiterite	3.0
Geevor Mine	Quartz, post cassiterite	12.3
Penlee Quarry	Quartz from N-S cross-course	11.6
Wheal Friend- ship	Quartz	17.9
St. Day	Quartz, post chalcopyrite	6.25
Menheniot	Colourless fluorite	9.4
Geevor Mine	Fluorite	6.8
Mary Tavy	Quartz associated with arsenopyrite	16.0
St. Austell clay pits	Quartz	2.8

Bradshaw, P.M.D. and Stoyel, A.J., 1968. Trans. I.M.M. 77, p.p. B144-152.

"Exploration for blind orebodies in southwest England by the use of geochemistry and fluid inclusions."

Geothermometric data, uncorrected for pressure. Samples mostly of quartz and fluorite with a few cassiterites and blends.

Locality	Highest filling temperature recorded.
Cligga Head	374 (approx)
Trevaunance Mine	394
Tywarnhayle Mine	261
Wheal Charles	233
Hallenbeagle Mine	181
Pednandrea Mine	336
Creegbrawse Mine	290
Penstruthal Mine	270
Wheal Tretharrup	226
United Mines (western part)	268
United Mines (eastern part)	296
Great Wheal Baddern (S.W. part)	202
Great Wheal Baddern (N.E. part)	231

Pryce's lode - Tincroft South lode system, South Crofty Mine.

(Highest filling temperatures obtained from inclusions in fluorite.)

Approx. depth from surface	Highest Filling Temperature
No. 1. 1000ft.	264
2. 1150	265
3. 1150	260 (100ft. E. of No.2.)
4. 1740	280
5. 1900	279
6. 1900	280 (150ft. E. of No.5.)
7. 1900	285 (400ft. E. of No.5.)

Sawkins, F.J., 1966(b). Econ. Geol. 66 p.p. 385-401.

"Ore deposition in the Northern Pennine orefield, in the light of fluid inclusion studies."

Geothermometric data, corrected for pressure by the addition of 11°C.

Locality	Description	Type	No. of inclusions	Temperature range
<u>Black Dene Mine</u>				
Black Dene Vein	Green fluorite	P	7	171-176
Black Dene Vein	Purple fluorite	P	10	155-158
Black Dene Vein	Quartz	P	3	143-153
Black Dene Vein	Quartz	P	12	135-139
Black Dene Vein	Late purple fluorite	P	13	152-161
Black Dene Vein	Late purple fluorite	P	4	135-137
Black Dene Vein	Purple-green zoned fluorite	P	4	165-171 early
Black Dene Vein	Purple-green zoned fluorite	P	8	142-148 late
Slitt Vein	Late calcite	P	43	78-84
Slitt Vein	Late purple fluorite	P	3	127-131
<u>Stanhopeburn Mine</u>				
Red Vein	Purple fluorite	P	26	168-190
Red Vein	Purple fluorite	P	6	148-151
Red Vein	Bluish fluorite	P	2	178-183
Red Vein	Quartz	S	2	121-126
<u>Stotsfieldburn Mine</u>				
Red Vein	Green fluorite	P	10	163-167
Red Vein	Bluish fluorite	P	19	165-181
Red Vein	Bluish fluorite	S	9	148-153
Red Vein	Purple fluorite	P	16	161-166
Red Vein	Quartz	P	7	144-150
Red Vein	Quartz	P	4	153-155
Red Vein	Purple fluorite	P	13	158-174

Sawkins, (1966b) continued.Rookhope Borehole

Depth	900ft.	Green fluorite	PS	7	146-162
	900ft.	Green fluorite	P	9	152-169
	1355ft.	Colourless fluorite	P	8	146-160
	1562ft.	Greenish fluorite	P	7	140-160
	900ft.	Green fluorite	PS	12	145-164

Groverake Mine

Greencleugh Vein	Green fluorite	P	13	158-167
Greencleugh Vein	Green-purple zoned fluorite	P	3	170-171
Greencleugh Vein	Quartz	P	2	151-154
Greencleugh Vein	Quartz	S	4	131-144
Red Vein	Purple fluorite	P	17	170-186

Boltsburn Flats

	Green-purple zoned fluorite	P	10	140-148
--	-----------------------------	---	----	---------

Heights Vein South

	Purple fluorite	P	9	153-157
	Purple fluorite	P	4	149-154

Allenheads Flats

	Purple fluorite	P	8	134-145
	Purple fluorite	P	4	127-130
	Yellow fluorite	P	11	126-133

Whiteheaps Mine

Poor Vein	Green fluorite	P	14	170-177
Poor Vein	Green-purple zoned fluorite	P	13	155-157
Red Vein	Green fluorite	S	6	145-150
Red Vein	Purple fluorite	P	13	145-153
Red Vein	Purple fluorite	P	5	163-168

Sawkins, (1966b) continued.Great Sulphur Vein

Quartz	P	6	181-188
Quartz	PS	7	175-188
Quartz	P	8	200-216

Sedling Mine

Purple fluorite	P	13	156-165
Green fluorite	P	4	157-175
Purple fluorite	P	5	141-156
Colourless fluorite	P	6	147-149
Purple fluorite	S&PS	12	132-153

Rotherhope Fell

Quartz	PS	3	181-182
Purple fluorite	P	5	135-147
Purple fluorite	P	10	128-155
Purple fluorite	P	2	139-143
Pale purple fluorite	P&PS	16	118-132

Nentsberry Mine

Clear baryte	P	7	126-129
--------------	---	---	---------

Smithergill Head

Purple fluorite	PS	4	148-170
-----------------	----	---	---------

Garigill Area

Purple fluorite	P	4	128-135
Quartz	P	2	143-151

Greencastle Area

Quartz	PS	6	140-143
--------	----	---	---------

Lodgesyke-Manorgill Vein

Purple fluorite	P	15	129-135
-----------------	---	----	---------

Sawkins, (1966b) continued.Pike Law Veins

Purple fluorite	S	2	130-131
Purple fluorite	P	9	156-164
Purple fluorite	S	2	130-131
Purple fluorite	PS	9	156-164

Stanhope, S. of river

Purple fluorite	P	16	132-153
-----------------	---	----	---------

Nenthead Area

Yellow fluorite	P	3	117
Yellow fluorite	P	5	130-136

Coalcleugh Mine (dump)

Colourless fluorite	P	7	110-116
Purple fluorite	P	6	122-124

Cross Fell Area

Cashwell Vein	Purple fluorite	P&PS	12	139-158
Cashwell Mine Vein	Purple-green fluorite	P	11	130-154
Cashwell Vein	Purple-green fluorite	P	7	132-145
Scordale Mine	Yellow fluorite	P	4	121-130
Greenlaws Vein	Purple fluorite	P	9	118-128
Greenlaws Vein	Yellow fluorite	P	14	115-128
Greenlaws Vein	Purple fluorite	P	10	120-130

Eggleshope Area

Purple fluorite	P	10	130-136
Purple fluorite	P	11	118-134

Sharnberry Area

Purple fluorite	P	13	125-128
-----------------	---	----	---------

Sawkins, (1966b) continued.

Salinity data.

Locality	Description	Corrected Filling Temp.	Ice Point	Equiv. wt. % NaCl
<u>Heights Vein South</u>				
	Pale purple fluorite	155	-17.2	20.7
<u>Stotsfieldburn Mine</u>				
Red Vein	Purple fluorite	174	-17.8	21.1
<u>Stanhopeburn Mine</u>				
Red Vein	Bluish fluorite	183	-17.8	21.1
<u>Black Dene Mine</u>				
Black Dene Vein	Purple fluorite	156-158	-19.5	22.2
<u>Sedling Mine</u>				
	Quartz	165	-20	22.5
<u>Pike Law</u>				
	Purple fluorite	157	-21	23
<u>Allenheads</u>				
	Purple fluorite	128	-17	20
<u>Greenlaws</u>				
	Purple fluorite	121	-17	20
<u>Rotherhope Fell</u>				
	Purple fluorite	153	-17.5	20.5
<u>Stanhopeburn Mine</u>				
Red Vein	Purple fluorite	186	-17	20

Sawkins, (1966b) continued.

Na/K ratios of fluid inclusions in Pennine minerals

Locality	Description	Concentration in Na ppm	Filtrate K ppm	Na/K
FLUORITE ZONE				
Great Sulphur Vein	Massive quartz	67	5.9	11.4
Black Dene Vein	Green fluorite	35	5.8	6.9
Black Dene Vein	Quartz crystals	15	1.2	12.4
Greencleugh Vein	Purple-green fluorite	50	5.2	9.6
Slitt Vein	Purple fluorite	7.5	1.1	6.8
Whiteheaps Mine	Quartz associated with galena	38	4.75	8.0
INTERMEDIATE ZONE				
Swinhope Mine	Blende crystal	67.5	6.2	10.9
BARYTE ZONE				
Closehouse Mine	Massive baryte associated with galena	81	5.3	15.3
Silverband Mine	Late baryte crystal	43	1.4	31
Silverband Mine	Large baryte crystal	15	0.75	20
New Brancepeth Vein	Baryte crystal	50	1.2	42
Nentsberry Mine	Baryte crystals	32.5	0.7	46

BIBLIOGRAPHY

- ALLPORT, S. (1876). On the metamorphic rocks surrounding the Land's End mass of granite. Q.J.G.S. Vol. 32, p.p. 407-427.
- AMES, L.L. (1958). Chemical analyses of the fluid inclusions in a group of New Mexico minerals. Econ. Geol. Vol. 53, p.p. 473-480.
- BARTON, P.B. Jr., BETHKE, P.M., AND TOULMIN, P. (1963). Equilibrium in ore deposits. Min. Soc. America, Special Paper 1, p.p. 171-185.
- BILLINGS, G.K., KESLER, S.E. AND JACKSON, S.A. (1969). Relation of zinc-rich formation waters, Northern Alberta, to the Pine Point ore deposit. Econ. Geol. Vol. 64, p.p. 385-391.
- BLAIS, R.A. (1953). Structural and decrepitation features of the gold mineralization at the O'Brien Mine, Quebec. Econ. Geol. Vol. 48, p. 616.
- BRADSHAW, P.M.D. AND STOYEL, A.J. (1968). Exploration for blind orebodies in southwest England by the use of geochemistry and fluid inclusions. Trans. Inst. Min. Metall. (Sect. B: Appl. earth sci.), Vol. 77, p.p. B144-B152.
- BREWSTER, D. (1823). Fluids in the cavities of minerals. Edinburgh Phil. Jour. Vol. 9, p.p. 94-107.
- CAMERON, E.N., ROWE, R.B. AND WEIS, P.L. (1953). Fluid inclusions in beryl and quartz from pegmatites of the Middletown district, Connecticut. Am. Mineral. Vol. 38, p.p. 218-262.
- CENTNERSZWER, M. (1903). Über kritische Temperaturen der Lösungen. Zeit für Phys. Chem. Vol. 46, p.p. 427-501.
- CORRENS, C.W. (1954). Flüssigkeitseinschlüsse mit gasblasen als geologische thermometer. Geol. Rundschau, Vol. 42, p.p. 19-34.
- DANA'S SYSTEM OF MINERALOGY, (1951). Ed. by C. Palache, H. Berman and C. Frondel. 7th Edition, Vol. 2. John Wiley and Son, London and New York.

- DAVY, H. (1822). On the state of water and aëriiform matter in cavities found in certain crystals. Phil. Trans. p.p. 367-376.
- DEICHA, G. (1950). Essais par écrasement de fragments minéraux pour la mise en évidence d'inclusions de gaz sous pression. Soc. franc. mineral. Bull. Vol. 73, p.p. 439-445.
- DEICHA, G. (1955). Les Lacunes des Cristaux et leurs Inclusions Fluides. Masson et Cie, Paris.
- DEICHA, G. (1970). Expansion actuelle des recherches sur les inclusions et le problème de leur coordination future. Schweiz. Min. Pet. Milleilurgen, Vol. 50, p.p. 3-12.
- DINES, H.G. (1956). The metalliferous mining region of south west England. Mem. Geol. Surv. Gt. Br. 2 vols., 795 pp.
- DONTSOVA, E.I. AND NAUMOV, G.B. (1967). Determination of temperature of formation of hydrothermal quartz by oxygen isotope ratio. Translated in Geochem. Internat. Vol. 3, p.p. 469-473.
- DREYER, R.M., GARRELS, R.M. AND HOWLAND, A.L. (1949). Liquid inclusions in halite as a guide to geologic thermometry. Am. Mineral, Vol. 34, p.p. 26-34.
- ELINSON, M.M. AND POLYKOVSKIY, V.S. (1967). Composition of gases in the solutions responsible for deposition of rock-crystal veins in skarns. Translated in Geochem. Internat. Vol. 4, p.p. 108-114.
- ERICKSON, A.J. (1965). Temperatures of calcite deposition in the Upper Mississippi Valley lead-zinc deposits. Econ. Geol. Vol. 60, p.p. 506-528.
- FISHER, R.A. AND YATES, F. (1953). Statistical Tables. Oliver and Boyd, London.
- FREAS, D.H. (1961). Temperatures of mineralization by liquid inclusions, Cave-in-Rock fluorspar district, Illinois. Econ. Geol. Vol. 56, p.p. 542-556.

- FRIEDMAN, I. (1953). Deuterium content of natural waters and other substances. *Geochim. et Cosmochim. Acta*, Vol. 4, p.p. 89-103.
- FRIEDMAN, I. AND SMITH, R.L. (1958). The deuterium content of water in some volcanic glasses. *Geochim. et Cosmochim. Acta*. Vol. 15, p.p. 218-228.
- GARNETT, R.H.T. (1962). The geology and mineralization of the Geevor Tin Mine, Cornwall. Unpublished Ph.D. thesis, Univ. of London.
- GARRELS, R.M. AND RICHTER, D.H. (1955). Is carbon dioxide an ore-forming fluid under shallow-earth conditions? *Econ. Geol.* Vol. 50, p.p. 447-458.
- GROGAN, R.M. AND SHRODE, R.S. (1952). Formation temperatures of Southern Illinois bedded fluorite as determined from fluid inclusions. *Am. Mineral.* Vol. 37, p.p. 555-566.
- HALL, W.E. AND FRIEDMAN, I. (1963). Composition of fluid inclusions, Cave-in-Rock fluorite district, Illinois, and upper Mississippi valley zinc-lead district. *Econ. Geol.* Vol. 58, p.p. 886-911.
- HANNAY, J.B. AND HOGARTH, J. (1879). On the solubility of solids in gases, I. *Proc. Royal Soc. London*, Vol. 30, p.p. 178-188.
- HOLDEN, E.F. (1925). The cause of colour in smoky quartz and amethyst. *Am. Mineral.* Vol. 10, p.p. 203-252.
- HOSKING, K.F.G. (1963). The major characteristics of primary zoning in the south west of England. *Symp. Problems Postmagmatic Ore Deposition*, Prague. Vol. 1, p.p. 329-332.
- INGERSON, E. (1934). Relation of critical and s-percritical phenomena of solutions to geologic processes. *Econ. Geol.* Vol. 29, p.p. 454-470.
- INGERSON, E. (1947). Liquid inclusions in geological thermometry. *Am. Mineral.* Vol. 32, p.p. 375-388.
- INGERSON, E. (1955). Methods and problems of geologic thermometry. *Econ. Geol.* 50th Anniversary Vol. pt. 1, p.p. 341-410.
- JOFFE, A.F. (1928). *The Physics of Crystals*. McGraw-Hill.

- KALYUZHNYI, V.A. (1958). In reference to hermetic sealing of liquid inclusions. See Yermakov (1950) for English translation.
- KEEVIL, N.B. (1942). Vapour pressure of aqueous solutions at high temperatures. Jour. Am. Chem. Soc. Vol. 64, p.p. 841-850.
- KELLY, W.C. AND TURNEAURE, F.S. (1970). Mineralogy, paragenesis and geothermometry of the tin and tungsten deposits of the Eastern Andes, Bolivia. Econ. Geol. Vol. 65, p.p. 609-680.
- KENNEDY, G.C. (1944). The hydrothermal solubility of silica. Econ. Geol. Vol. 39, p.p. 25-36.
- KENNEDY, G.C. (1950a). "Pneumatolysis" and the liquid inclusion method of geologic thermometry. Econ. Geol. Vol. 45, p.p. 533-547.
- KENNEDY, G.C. (1950b). Pressure-volume-temperature relations in water at elevated pressures and temperatures. Am. Jour. Sci. Vol. 248, No. 8, p.p. 550-564.
- KENNEDY, G.C. (1950c). A portion of the system silica-water. Econ. Geol. Vol. 45, p.p. 629-653.
- KENNEDY, G.C. (1954). Pressure-volume-temperature relations in CO₂ at elevated temperatures and pressures. Am. Jour. Sci. Vol. 252, p.p. 225-241.
- KLEVTSOV, P.V. AND LEMMLEIN, G.G. (1959). Pressure corrections for the homogenization temperatures of aqueous NaCl solutions. Akad. Nauk. SSSR., Doklady 128, p.p. 1250-1253. (in Russian).
- KOLTUN, L.I. (1958). Special features of the origin of the Lebedinoye gold-ore deposit ascertained on the basis of inclusions in minerals. See Yermakov (1950) for English translation.
- KÖNIGSBERGER, J. (1901). Die Minerallagerstätten im Biotitprotogin des Aarmassivs. Neues Jahrbuch für Min. Vol. 14, p.p. 43-119.
- KÖNIGSBERGER, J. AND MÜLLER, W.J. (1906). Versuche über die Bildung von Quarz und Silikaten. Centralblatt für Mineralogie, Geologie und Paläontologie, p.p. 339-372.

- KOSTYLEVA, Y.Y. AND LABUNTSOV, V.A. (1958). Studies of the decrepitation of quartz and the universal decrepitation amplifier-recorder. See Yermakov (1950) for English translation.
- LAZ'KO, Y.M. (1957). Certain genetic features of the Kurumkan deposit ascertained by means of mineraloothermometric analysis. See Yermakov (1950) for English translation.
- LEMMLEIN, G.G. (1929). Sekundare Flüssigkeitseinschlüsse im Mineralien. Zeit. Krist. Vol. 71, p.p. 237-256.
- LEMMLEIN, G.G. (1956). Formation of fluid inclusions in minerals and their use in geological thermometry. Translated in Geochemistry, 1956, No. 6, p.p. 630-642.
- LEMMLEIN, G.G. AND KLEVTSOV, P.V. (1961). Relations among the principal thermodynamic parameters in a part of the system $H_2O-NaCl$. Translated in Geochemistry, No. 2, p.p. 148-158.
- LITTLE, W.M. (1960). Inclusions in cassiterite and associated minerals. Econ. Geol. Vol. 55, p.p. 485-509.
- LYAKHOV, Y.V. (1967). Mineral composition of multiphase inclusions in morion from pegmatites of Volynia. Translated in Geochem. Internat. Vol. 3, p.p. 618-625.
- MASLOVA, I.N. (1961). Ultramicrochemical investigation of compositions of the liquid and vapour phases in two-phase inclusions in quartz from Volynia. Translated in Geochemistry, No. 2, p.p. 190-195.
- MORAY, G.W. AND INGERSON, E. (1937). The pneumatolytic and hydrothermal alteration and synthesis of silicates. Econ. Geol. Vol. 32, p.p. 607-761.
- NAUMOV, V.B. AND MALININ, S.D. (1968). A new method for determining pressure by means of gas-liquid inclusions. Translated in Geochem. Internat. Vol. 5, p.p. 382-391.

- NAUMOV, V.B. (1969). Thermometric investigations of quenched magma inclusions in the quartz phenocrysts of rhyolites. Translated in *Geochem. Internat.* Vol. 6, p.p. 379-383.
- NEWHOUSE, W.H. (1932). The composition of vein solutions as shown by liquid inclusions in minerals. *Econ. Geol.* Vol. 27, p.p. 419-436.
- NEWHOUSE, W.H. (1933). The temperature of formation of the Mississippi Valley lead-zinc deposits. *Econ. Geol.* Vol. 28, p.p. 744-750.
- PEACH, P.A. (1949a). A decrepitation geothermometer. *Am. Mineral.* Vol. 34, p.p. 413-421.
- PEACH, P.A. (1949b). Liquid inclusions in geothermometry. *Am. Mineral* Vol. 34, p.p. 460-461.
- PEACH, P.A. (1951). Geothermometry of some pegmatite minerals of Hybla, Ontario. *Jour. Geol.* Vol. 59, p.p. 32-38.
- PHILLIPS, J.A. (1868). Notes on the chemical geology of the gold-fields of California. *Phil. Mag.* Vol. 36 pt. 2, p.p. 321-336.
- PHILLIPS, J.A. (1875). The rocks of the mining districts of Cornwall and their relation to metalliferous deposits. *Q.J.G.S.* Vol. 31, p.p. 319-345.
- PIZNYUR, A.V. (1957). Genetic relation of quartz veins in the Barsukchi deposit and granitic intrusions as indicated by inclusions in minerals. See Yermakov (1950) for English translation.
- PULOU, R., de CROIZANT, J. AND GRITTI, C. (1970). Enregistreur decrepitemetrique applique a la determination des temperatures de depot des mineraux. *Schweiz. Min. Pet. Mitteilungen* Vol. 50, p.p. 59-66.
- PUZANOV, L.S. (1958). Homogenization temperatures of inclusions in crystal quartz from the Ol'gino deposit, the Far East. See Yermakov (1950) for English translation.
- RAMBERG, H. (1952). *The Origin of Metamorphic and Metasomatic Rocks.* Univ. of Chicago Press, Chicago, Illinois, U.S.A.

- RICHTER, D.H. AND INGERSON, E. (1954). Some considerations regarding liquid inclusions as geologic thermometers. *Econ. Geol.* Vol. 49, p.p. 786-789.
- ROEDDER, E. (1958). Technique for the extraction and partial chemical analysis of fluid-filled inclusions from minerals. *Econ. Geol.* Vol. 53, p.p. 235-269.
- ROEDDER, E. (1962). Studies of fluid inclusions I: Low temperature application of a dual-purpose freezing and heating stage. *Econ. Geol.* Vol. 57, p.p. 1045-1061.
- ROEDDER, E. (1963). Studies of fluid inclusions II: Freezing data and their interpretation. *Econ. Geol.* Vol. 58, p.p. 167-211.
- ROEDDER, E., INGRAM, B. AND HALL, W.E. (1963). Studies in fluid inclusions III: Extraction and quantitative analysis of inclusions in the milligram range. *Econ. Geol.* Vol. 58, p.p. 353-374.
- ROEDDER, E. (1965a). Liquid CO₂ inclusions in olivine-bearing nodules and phenocrysts from basalts. *Am. Mineral.* Vol. 50, p.p. 1746-1782.
- ROEDDER, E. (1965b). Evidence from fluid inclusions as to the nature of the ore-forming fluids. Symposium "Problems of Postmagmatic Ore Deposition," Prague, Vol. 2, p.p. 375-384.
- ROEDDER, E. (1967a). Composition of fluid inclusions. In *Data of Geochemistry*, U.S. Geol. Surv. Prof. Paper 440 JJ.
- ROEDDER, E. (1967b). Fluid inclusions as samples of ore fluids in "Geochemistry of Hydrothermal Ore Deposits," ed. H.L. Barnes, Holt, Rinehart and Winston, New York.
- ROEDDER, E., HEYL, A.V. AND CREEL, J.P. (1968). Environment of ore deposition at the Mex-Tex Deposits, Hansonburg District, New Mexico, from studies of fluid inclusions. *Econ. Geol.* Vol. 63, p.p. 336-348.

- ROEDDER, E. (1968). Temperature, salinity, and origin of the ore-forming fluids at Pine Point, Northwest Territories, Canada, from fluid inclusion studies. *Econ. Geol.* Vol. 63, p.p. 439-450.
- ROEDDER, E. AND SKINNER, B.J. (1968). Experimental evidence that fluid inclusions do not leak. *Econ. Geol.* Vol. 63, p.p. 715-730.
- ROEDDER, E. (1970). Application of an improved crushing microscope stage to studies of the gases in fluid inclusions. *Schweiz. Min. Pet. Mitteilungen.* Vol. 50, p.p. 41-58.
- RYE, R.O. (1966). The carbon, hydrogen, and oxygen isotopic composition of the hydrothermal fluids responsible for the lead-zinc deposits at Providencia, Zacatecas, Mexico. *Econ. Geol.* Vol. 61, p.p. 1399-1427.
- RYE, R.O. AND O'NEIL, J.R. (1968). The O^{18} content of water in primary fluid inclusions from Providencia, north-central Mexico. *Econ. Geol.* Vol. 63, p.p. 232-238.
- SAMOYLOVICH, L.A. AND KHETCHIKOV, L.N. (1968). Pressure corrections to the homogenization temperatures of aqueous salt solutions. Translated in *Geochem. Internat.* Vol. 5, p.p. 1184-1189.
- SAWKINS, F.J. (1966a). Preliminary fluid inclusion studies of the mineralization association with the Hercynian granites of Southwest England. *Trans. Inst. Min. Metall. (Sect. B: Appl. earth sci.)*, Vol. 75, p.p. B109-B122.
- SAWKINS, F.J. (1966b). Ore genesis in the North Pennine Orefield in the light of fluid inclusion studies. *Econ. Geol.* Vol. 61, p.p. 385-401.
- SCHMIDT, R.A. (1962). Temperatures of mineral formation in the Miami-Picher district as indicated by liquid inclusions. *Econ. Geol.* Vol. 57, p.p. 1-20.
- SCHRÖER, E. (1929). Untersuchungen über den kritischen Zustand, IV. *Zeit. für Phys. Chem.* Vol. 142, p.p. 365-390.

- SCOTT, H.S. (1948). The decrepitation method as applied to minerals with fluid inclusions. *Econ. Geol.* Vol. 43, p.p. 637-654.
- SKINNER, B.J. (1953). Some considerations regarding liquid inclusions as geologic thermometers. *Econ. Geol.* Vol. 48, p.p. 541-550.
- SMITH, F.G. (1949). Laboratory testing of "pneumatolytic" deposits. *Econ. Geol.* Vol. 44, p.p. 624-625.
- SMITH, F.G. AND PEACH, P.A. (1949). Apparatus for the recording of decrepitation in minerals. *Econ. Geol.* Vol. 44, p.p. 449-451.
- SMITH, F.G. AND OTHERS. (1950). "Pneumatolysis" and the liquid inclusion method of geologic thermometry. (A reply to G.C. Kennedy). *Econ. Geol.* Vol. 45, p.p. 582-587.
- SMITH, F.G. (1953). *Historical Development of Inclusion Thermometry.* Univ. Toronto Press, Toronto, Ontario.
- SMITH, F.G. (1954a). Composition of vein-forming fluids from inclusion data. *Econ. Geol.* Vol. 49, p.p. 205-210.
- SMITH, F.G. (1954b). Discussion of "Some considerations regarding liquid inclusions as geologic thermometers." *Econ. Geol.* Vol. 49, p.p. 331-332.
- SMITH, F.G. AND LITTLE, W.M. (1959). Filling temperatures of H₂O-CO₂ fluid inclusions and their significance in geothermometry. *Can. Mineral.* Vol. 6, pt. III, p.p. 380-388.
- SORBY, H.C. (1858). On the microscopical structures of crystals, indicating the origin of minerals and rocks. *Q.J.G.S.* Vol. 14, p.p. 453-500.
- SOURIRAJAN, S. AND KENNEDY, G.C. (1962). The system H₂O-NaCl at elevated temperatures and pressures. *Am. Jour. Sci.* Vol. 260, p.p. 115-141.
- STEPHENSON, T.E. (1952). Sources of error in the decrepitation method of study of liquid inclusions. *Econ. Geol.* Vol. 47, p.p. 743-750.

- SUSHCHEVSKAYA, T.M. AND IVANOVA, G.F. (1967). Composition of mineralizing solutions of some wolframite deposits of Eastern Transbaykaliya, based on a study of gas-liquid inclusions. Translated in *Geochem. Internat.* Vol. 5, p.p. 885-891.
- TAKENOUCI, S. AND KENNEDY, G.C. (1965). The solubility of carbon dioxide in NaCl solutions at high temperatures and pressures. *Am. Jour. Sci.* Vol. 263, p.p. 445-454.
- TOURAY, J.C. (1968). Recherches geochemiques sur les inclusions avec CO₂ liquide. *Bul. Soc. francais Min. Crist.* Vol. 91, p.p. 367-382.
- TUGARINOV, A.I. AND NAUMOV, V.B. (1969). Thermobaric conditions of formation of hydrothermal uranium deposits. Translated in *Geochem. Internat.* Vol. 6, p.p. 89-103.
- TWENHOFEL, W.S. (1947). The temperature of crystallization of a fluorite crystal from Luna County, New Mexico. *Econ. Geol.* Vol. 42, p.p. 78-82.
- VENEDIKTOV, S.N. (1958). Thermometric investigations of vein quartz and crystal quartz from quartz veins of the Dzhezkazgan-Ulutan District. See Yermakov (1950) for English translation.
- WARD, J.C. (1875). On the granitic, granitoid and associated metamorphic rocks of the Lake District. *Q.J.G.S.* Vol. 31, p.p. 568-602.
- WEIS, P.L. (1953). Fluid inclusions in minerals from zoned pegmatites of the Black Hills, South Dakota. *Am. Mineral.* Vol. 38, p.p. 671-697.
- WINER, B.J. (1962). *Statistical Principles in Experimental Design.* McGraw-Hill, London.
- YERMAKOV, N.P. (1950). Research in mineral-forming solutions, Kharkov, U.S.S.R.; Univ. of Kharkov Press (in Russian). Transl. (along with other material dated 1957-1958) in Yermakov, N.P., and others, 1965, Research on the nature of mineral-forming solutions, with special reference to data from fluid inclusions. Vol. 22 of International Series of Monographs in Earth Sciences, Pergamon Press, Oxford.

ZAKHARCHENKO, A.I., LAZAREVICH, N.S., MOSKALYUK, G.I. AND MOSKALYUK, A.A.

(1958). A simplified automatic thermosonic recorder. See Yermakov (1950) for English translation.

ZAKHARCHENKO, A.I. (1964). Physicochemical conditions and processes of formation of granitic pegmatites. Translated in Geochem. Internat. No. 6, p.p. 1057-1067.