FLUID INCLUSION GEOTHERMOMETRY IN FLUORITE
FROM GAYS RIVER, NOVA SCOTIA
AND BOAT HARBOUR, NEWFOUNDLAND

by

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CHAPTER 1

Introduction

INTRODUCTION

The genesis of Mississippi Valley type deposits (hereforth M.V.T.D.) remains a controversy because of the lack of quantitative data on some important parameters. Temperature of formation and the salinity of the ore fluids represent two very important variables in the evaluation of genetic models for these deposits. This thesis contributes the first fluid inclusion data on two carbonate hosted deposits, the Gays River, Nova Scotia base metal deposit and the Boat Harbour, Newfoundland fluorite occurrence. These data are discussed in the light of the geochemical behavior of fluorite in the hydrous system NaCl - $CaCl_2$ - $MgCl_2$, which may be relevant for M.V.T.D. environments.

Mississippi Valley Type Deposits (M.V.T.D.)

> "Mississippi Valley type base metal ore deposits are strata-bound in nearly horizontal carbonate rocks lacking congruent tectonic structures which might control their localization. Commonly they are remote from post-host rock igneous intrusives and through going plumbing systems which might serve respectively as a source and conduit for mineralizing solutions. They are further characterized by an association with dolomite in many instances; by relatively simple mineralogy and by textures which indicate the dominant process of mineralization was filling and not replacement. Sulfide and carbonate mineral detritus locally are present in the breccia matrix of some of them".
>
> \- Callahan, 1967

Depending upon the area of occurrence, carbonate-hosted lead-zinc deposits are described as "Alpine" in Europe and as "Mississippi Valley type" in North America. Major occurrences in North America include the Tri-State (situated on the border of Missouri-Kansas-Oklahoma), the Appalachian (eastern United States and Canada), and the Kentucky-Illinois fluorspar regions (Figure 1). The recently delineated MacKenzie Valley lead-zinc district, which includes Pine Point, extends from the Northern Canadian Cordillera in British Columbia, eastward to Saskatchewan (Sangster and Lancaster, 1976).

Collectively, these carbonate-hosted base metal deposits exclude skarns and other replacement deposits (Sangster, 1976). Common to most Mississippi Valley type deposits is the mineralogical association with dolomite, and less frequently with limestone.

However, occurrences in sandstone, shale and conglomerate are not unknown.

Although spatial relationships to reefs, facies changes, basin margins and basement topography can be established, the limiting factor necessary for the development of most Mississippi Valley type deposits is the existence of a thick carbonate sequence (Sangster, 1976). A climate suitable for the formation of carbonate sediments (ie. warm waters) can be determined by paleogeography. Stanton (1972) states that paleogeography can be considered the primary regional control of lead-zinc carbonate occurrence.

A characteristic feature of M.V.T.D. is the existence of ore bodies that are approximately parallel with bedding. The term "stratiform" implies no genetic implications and is, therefore, the most suitable term for description.

According to Callahan (1967), features controlling the localization of these deposits are derivatives of paleophysiography:

A. Specific sedimentary environments related to the topographic relief on an unconformity below

B. Solution collapse breccias and structures related to an unconformity above

C. Facies changes not clearly related to an unconformity (Figure 2).

Time distribution of the Mississippi Valley type deposits range from limited Precambrian occurrences to significant deposits from Cambrian to Cretaceous, with the exception of the Silurian.

Figure 1

Distribution of lead-zinc (barite-fluorite) deposits in carbonate rocks relative to sedimentary basins in North America:

1. Metaline area (M. Cambrian)
2. Kootenay Arc (L. Cambrian)
3. Monarch-Kicking Horse (M. Cambrian)
4. Pine Point (M. Devonian)
5. Bankeno (M. Ordovician)
6. Strathcona Sound (Proterozoic)
7. Upper Mississippi Valley (M. Ordovician)
8. Central Missouri (Ordovician)
9. Tri-State (Mississippian)
10. Southeast Missouri (U. Cambrian)
11. Eastern Tennessee (L. Ordovician)
12. Central Kentucky (M. Ordovician)
13. Austinville, Virginia (L. Ordovician)
14. Friedensville, Pennsylvania (L. Ordovician)
15. Bruce Peninsula--Niagara Escarpment (M. Silurian)
16. Gays River (Mississippian)
17. Newfoundland Zinc (L. Ordovician)

(after Sangster, 1970).

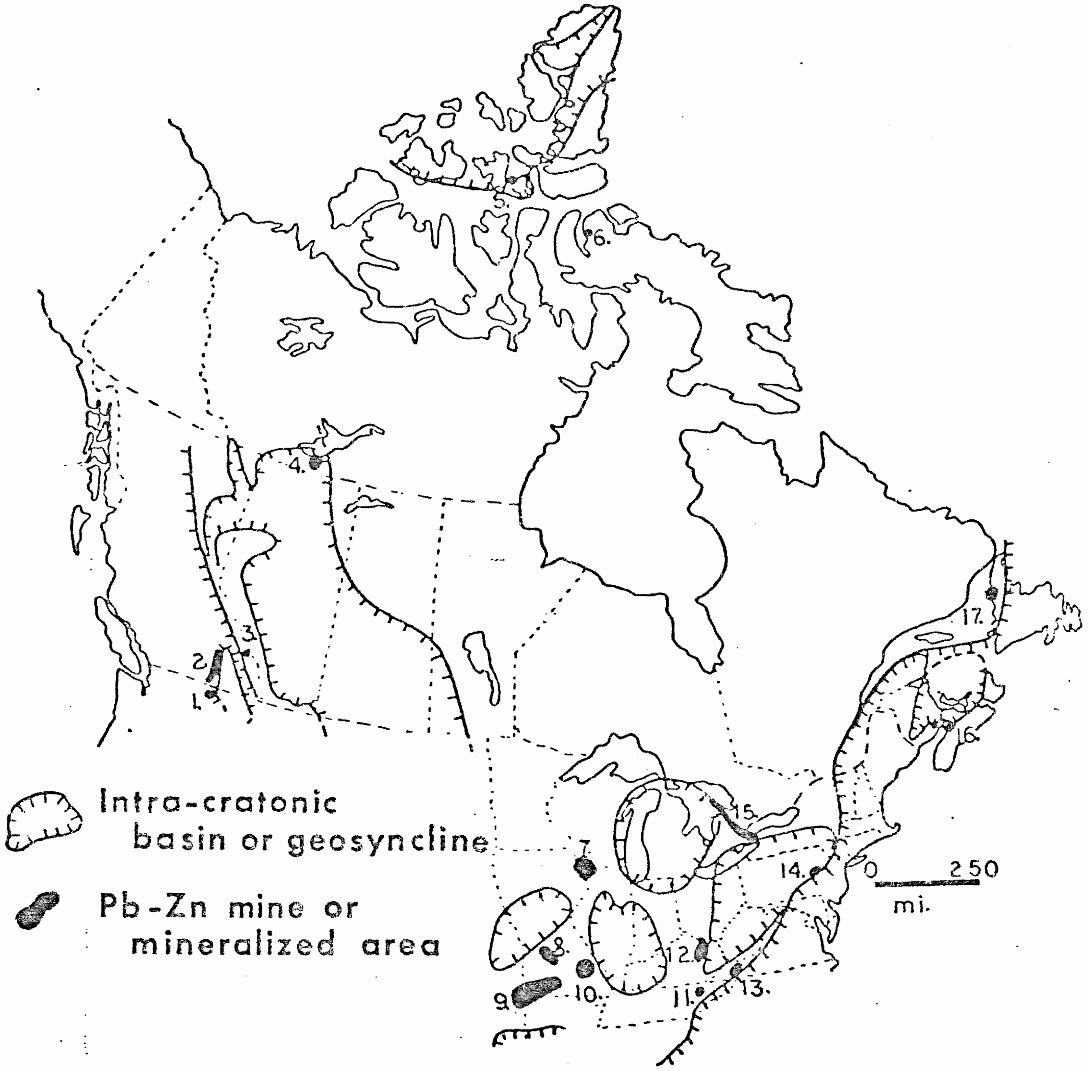
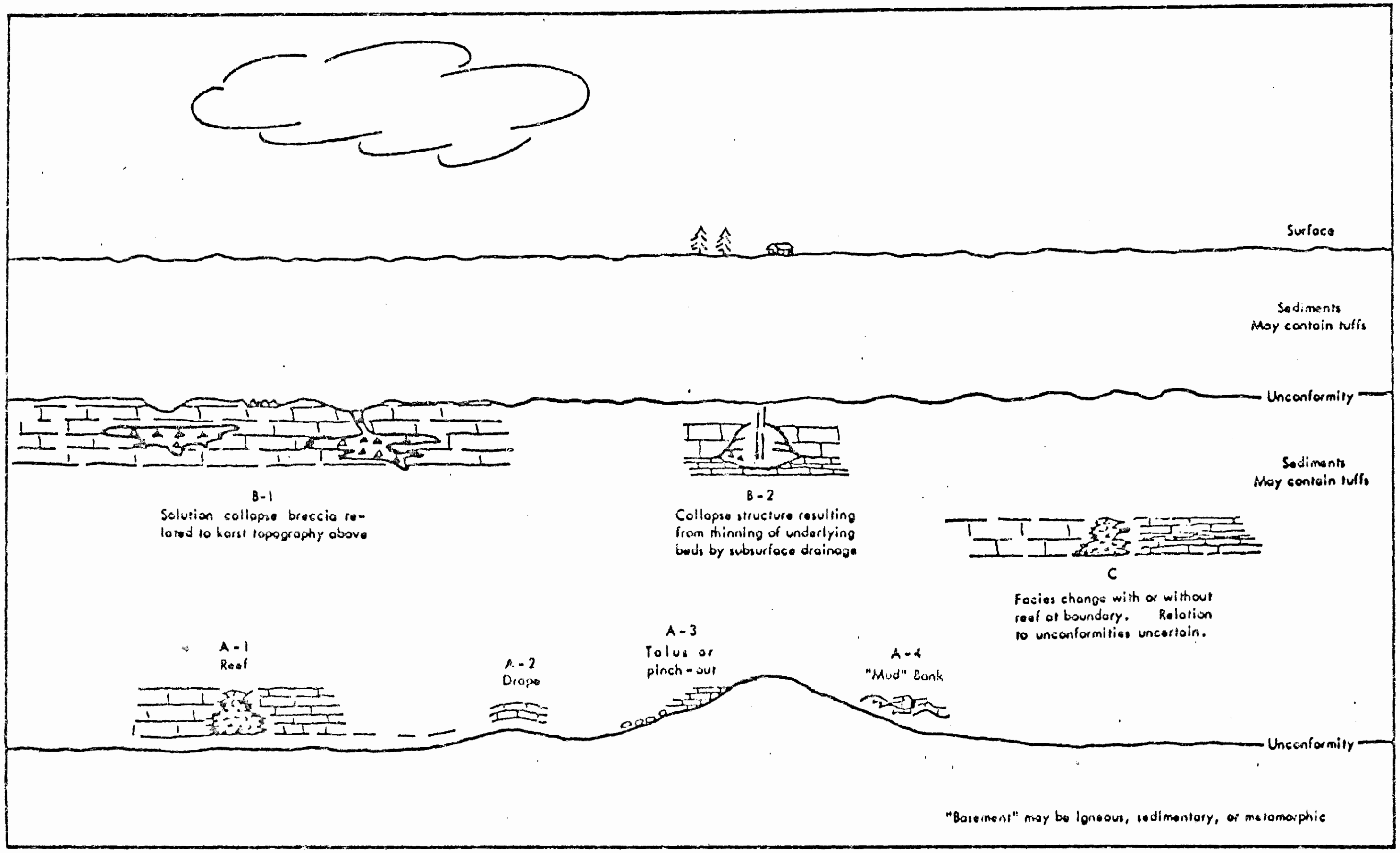

Intra-cratonic basin or geosyncline
Pb-Zn mine or mineralized area
1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.
15.
16.
17.
0
250
mi.

Figure 2

Idealized vertical section illustrating the range of geological situations in which Mississippi Valley type deposits are known to occur.

(from Callahan, 1967).


Surface
Sediments
May contain tuffs
Unconformity
Sediments
May contain tuffs
B-1
Solution collapse breccia related to karst topography above
B-2
Collapse structure resulting from thinning of underlying beds by subsurface drainage
C
Facies change with or without reef at boundary. Relation to unconformities uncertain.
A-1
Reef
A-2
Drape
A-3
Talus or pinch-out
A-4
"Mud" Bank
Unconformity
"Basement" may be Igneous, sedimentary, or metamorphic

Mineralogy

Galena, sphalerite, barite and fluorite constitute the ore minerals of Mississippi Valley type deposits. They represent a distinct segregation within the earth's crust of lead, zinc, barium and fluorine (Stanton, 1972). Sulfide accessories include pyrite and marcasite, with occasional minor amounts of chalcopyrite. Mineralization is typically described as open space fillings (ie., vugs, cavities, fractures).

Calcite, aragonite, dolomite and quartz are the most common non-metallic gangue minerals. Siderite and colloform silica may also occur. In comparison to other lead-zinc sulfide deposits, Mississippi Valley type do not host appreciable amounts of silver, and other precious metals are absent (Behre Jr., 1967). Bituminous matter (ie.,resins, asphaltenes, hydrocarbons) is commonly associated with these deposits.

Genesis

Mississippi Valley type stratiform ore bodies are classified as syngenetic, epigenetic or diagenetic. Evidence supporting syngenetic origin includes (Snyder, 1967):

A. uniform mineralization at a given stratigraphic position or within a restricted stratigraphic interval, and

B. close, but widespread correlation between mineralization and particular sedimentary lithologies, facies and features

In favour of epigenetic origin are extensive mineralization of post-depositional structures; changes in extent and grade of ore; open space filling, either of fissures or along bedding; district-wide lack of close control by sedimentary features; and relation of the ore to tectonic structures. On the basis of the criteria mentioned above, Snyder (1967) defines the major lead-zinc deposits of the Mid-Continent United States as epigenetic.

Diagenesis occurs in the sediment during and prior to lithification. The process of diagenesis involves deposition of metals with the host sediments accompanied by recrystallization, rearrangement and limited migration. Renfro (1974) attributes the formation of evaporite-associated stratiform metalliferous deposits to both syngenesis and diagenesis in coastal sabkhas.

Paleomagnetism has been used to date mineralization of M.V.T.D. Beales et. al. (1974, p. 222) concluded of the Newfoundland Zinc Mine hosted in Lower Ordovician dolomite that "hosts and ores have statistically indistinguishable remnant magnetization . . . therefore, the emplacement of the ores seems to be close, in a geological time sense, to the deposition of the host. A time span of less than 25 m.y. is likely to encompass both the formation of the host and ore."

Accurate determination of the age of mineralization relative to the host rock would reduce the numerous theories of the genesis of Mississippi Valley type deposits.

Current Working Hypothesis

The current working hypothesis establishes Mississippi Valley lead-zinc deposits as a product of normal sedimentary basin evolution during the late stages of diagenesis (Anderson, 1978; MacQueen, 1979).

When viewed in this context, the analogy between M.V.T.D. and petroleum deposits becomes quite apparent. Critical to the deposition of both ore and oil is the existence of a source, subsequent migration and eventual precipitation or trapping within suitable geologic environments. It should be mentioned, however, that ore and oil are not deposited together.

Mississippi Valley type deposits are usually situated towards basinal edges or between basins, in generally unmetamorphosed and tectonically undisturbed rocks. During the evolution of a large sedimentary basin, dewatering generates great volumes of water. These waters, rich in petroleum and metals, migrate to the host carbonate rocks at the basin edge.

The transport of metals in brines is determined by the reduced sulfur content of the brines. Transport occurs readily in brines containing no reduced sulfur (ie., all sulfur occurs as sulfate ions and various sulfate complexes) (Anderson, 1978). The metals occur dominantly as chloride complexes.

Beales and Hardy (1979) state that nearby evaporite deposits provide a local sulfur source, thus enhancing the chances of ore formation in basins. The presence of sulfide ore in apparently sulfate-free host rocks (ie., dolostone) may indicate a former sulfate abundance. Reduction of sulfate by organic reducing agents, commonly gas or oil, is the most probable intermediate step (Beales and Hardy, 1979). Evaporite solution produces collapse breccias in the carbonates, the lithology that most commonly hosts the mineralization.

Purpose and Scope of Thesis

The purpose of this thesis is to evaluate fluorite, an ubiquitous mineral constituent of Mississippi Valley type deposits, with respect to temperature and salinity of the hydrothermal ore-bearing solutions. The chemical and physical parameters of fluorite deposition are investigated and the paragenesis determined. Detailed mineralogy, ore petrology and discussion of diagenesis and genetic models are out of the scope of this thesis.

Organization of Thesis

Chapter Two is a discussion of the mineral fluorite in Mississippi Valley type deposits. Precipitation mechanisms of fluorite are considered in the light of experimental data from the literature. Chapter Three describes the techniques used in fluid inclusion geothermometry and the assumptions upon which it is based. Photomicrographs of fluid inclusions in fluorite from Boat Harbour and Gays River are included here. The regional and local geology of the study areas Boat Harbour and Gays River are outlined in Chapter Four. Mineralization and paragenesis for each area are discussed. Daniel's Harbour, Newfoundland is included in this Chapter. Chapter Five contains sample descriptions and microprobe analysis, photographs, fluid inclusion data (ie., homogenization temperatures and salinities), laboratory methods and observations. Chapter Six is a discussion of the significance of these data and of the chemical and physical parameters involved in fluorite deposition. Other fluid inclusion studies are reviewed and compared. Conclusions and recommendations for future work are found in Chapter Seven.

CHAPTER 2

Fluorite

FLUORITE (CaF_2)

Introduction

Crystallography

Fluorite crystallizes in the isometric system ($4/m\ \bar{3}\ 2/m$). It usually occurs in simple cubes, but often as penetration twins on a cube-diagonal twinning axis (Figure 3). The tetrahexahedron form is less common (Figure 3). Fluorite crystals generally occur in cleavable masses. Euhedral crystals have square outlines. Fluorite, however, usually forms massive aggregates made of crystals and fills spaces between other minerals. The crystal faces are smooth to rough or etched.

Cleavage

Fluorite cleavage is perfect octahedral {III}. The cleavage usually occurs at two intersecting lines at oblique angles of 70° and 110°, or at three intersecting lines of 60° and 120°.

Fluorite is determined by its cubic crystals and octahedral cleavage.

Colour

The colour of fluorite varies widely. It is most commonly light green, yellow, bluish-green or purple. Other colours include white, rose, blue, brown and clear. The colour in some fluorite results from the presence of a hydrocarbon. Single crystals and massive aggregates demonstrate colour banding or zonation. Fluorite crystals can be split open easily to display numerous zones of colour, indicating the shape of the crystal in earlier stages of growth.

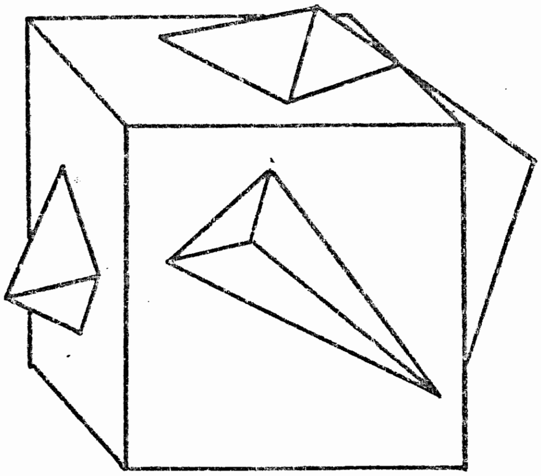
Occurrence

Fluorite is a common vein mineral. It is usually found in hydrothermal veins as either the chief mineral or as a gangue mineral with metallic ores. Fluorite is common in limestone and dolostone. It is associated with a variety of minerals including calcite, dolomite, gypsum, celestite, barite, quartz, galena, sphalerite, cassiterite, topaz, tourmaline and apatite.

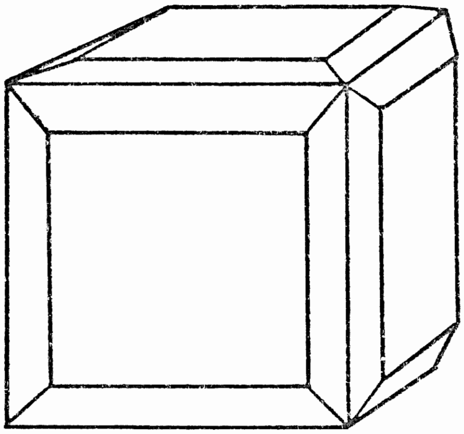
Figure 3

Fluorite a) Penetration twin
b) Cube and tetrahexahedron

A



B



Fluorite in Mississippi Valley Type Deposits (M.V.T.D.)

Fluorite is a common and occasionally abundant primary mineral in some of the stratiform galena-sphalerite-fluorite-barite Mississippi Valley type deposits (M.V.T.D.). The term fluorspar refers to the mineral fluorite (CaF_2). Fluorite occurs either in veins or as fine disseminations and crystal aggregates in the host carbonate.

Many of the fluorite-barite deposits in the eastern parts of the Mississippi Valley lie along major basement lineaments or at the intersections of lineaments (ie., mineralization is related to major structures). An east-trending lineament that extends approximately along the 38th parallel of latitude from western Virginia to south-central Missouri (Heyl, 1974), is the most important commercially. The Illinois-Kentucky and central Kentucky districts lie along this lineament at its intersection with other major structures.

The Illinois-Kentucky fluorspar district is the largest producer of fluorite in the United States. The deposits occur in sedimentary rocks of Middle-Late Mississippian and Early Pennsylvanian age (Trace, 1974). The ore consists primarily of calcite and fluorite, with lesser amounts of sphalerite, galena and barite. The fluorspar occurs either as veins along a series of northeast-trending, steeply dipping normal fault zones or as bedding replacement deposits along certain horizons of Mississippian age (Trace, 1974). It is generally considered that the deposits are epigenetic and that the ore elements were carried upward by hot connate water as a result of deep-seated igneous activity.

Fluorite in Hydrothermal Systems

In Mississippi Valley type deposits where fluorite constitutes the primary ore mineral, an understanding of the probable deposition mechanism(s) may be helpful in the location of new deposits or ore horizons. Where fluorite occurs as a gangue mineral, the mechanism of fluorite deposition is relevant to the study of the deposition of the ore minerals.

During the formation of fluorite deposits, fluorite is precipitated from hydrothermal solutions as a consequence of:

1. changes in the temperature and pressure of the ore fluid along the flow path
2. mixing of two or more fluids of different chemical composition
3. interaction of the ore-forming fluids with wall rocks

(Richardson & Holland, 1979b)

A decrease in temperature in the flow direction remains the most acceptable, although yet unproven, mechanism of fluorite deposition in Mississippi Valley fluorite deposits (Richardson & Holland, 1979b).

Fluorite is one of the many sparingly soluble salts which occur in hydrothermal deposits. In aqueous solutions, fluorite is at least partly ionized. Its solubility is, therefore, affected by the presence of other electrolytes. The amount of fluorite dissolved or precipitated is a function not only of the temperature, pressure, and the ionic strength of a given hydrothermal solution, but also of the pH and the ratio of the concentration of calcium and magnesium to that of fluoride ion in solution (Barnes, 1979).

Richardson & Holland (1979a; 1979b) have conducted solubility experiments of fluorite ore deposits which formed between 100 and 260 degrees C. The major ions present in the fluorite-depositing solutions were restricted to Ca^{2+}, Na^+, K^+, Mg^{2+}, Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, H_2S, H^+ and F^-. In brines containing "normal" concentrations of NaCl, $CaCl_2$ and $MgCl_2$, nearly all of the fluoride is present as a constituent of CaF^+, MgF^+ and NaF complexes (Richardson & Holland, 1979b).

Temperature Changes

The solubility of fluorite in most aqueous solutions is a function of temperature. Fluorite solubility decreases with decreasing temperature; consequently, fluorite tends to precipitate with decreasing temperature (Strübel, 1965; Richardson & Holland, 1979a). Dilute ($<$1.0M) NaCl or KCl solutions are an exception to this rule. In such dilute solutions, the solubility of fluorite goes through a maximum of about 100 degrees C (Richardson & Holland, 1979b)

Figure 4 defines the quantity of fluorite that precipitates from NaCl solutions of various concentrations as they are cooled from 260 to 25 degrees C. Richardson & Holland (1979b) demonstrate by these solubility experiments that:

i. the quantity of fluorite precipitated increases with the salinity of the fluids

ii. the solubility of fluorite changes most rapidly with temperature in the lower temperature ranges (for all the ionic strengths)

iii. as 0.5M and 0.1M NaCl solutions are cooled from 260 degrees C, they first become undersaturated with respect to fluorite, and until they have cooled to temperatures below 100 degrees C, do not begin to precipitate fluorite

Figure 4

The quantity of fluorite precipitated by cooling NaCl solutions of varying ionic strengths from 260° C to 25° C. Negative amounts of fluorite deposition indicate fluorite dissolution.

(from Richardson & Holland, 1979b).

Figure 5

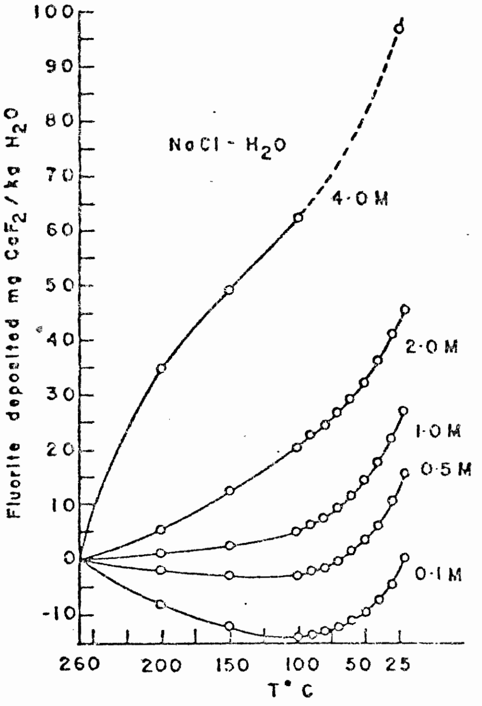
The quantity of fluorite precipitated by cooling NaCl - $CaCl_2$ - H_2O solutions with an ionic strength of 2.0 M from 260° C to 25° C.

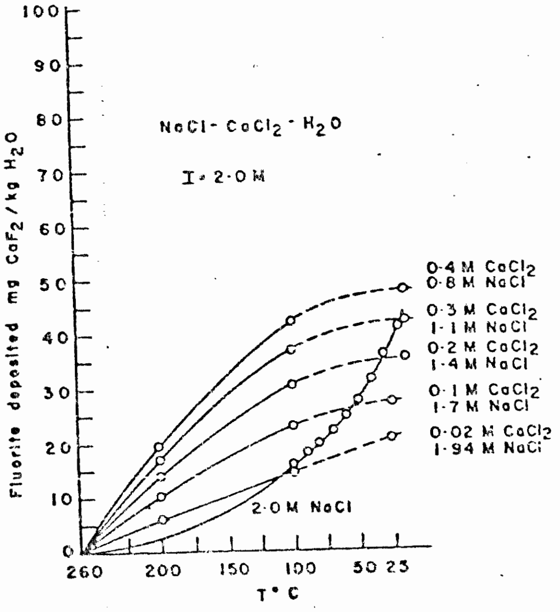
(from Richardson & Holland, 1979b).

Figure 6

The quantity of fluorite precipitated by cooling NaCl - $CaCl_2$ - H_2O solutions with an ionic strength of 4.0 M from 260° C to 25° C.

(from Richardson & Holland, 1979b).


NaCl - H_2O
4·0 M
2·0 M
1·0 M
0·5 M
0·1 M
Fluorite deposited mg CaF_2 / kg H_2O
100
90
80
70
60
50
40
30
20
10
0
-10
260
200
150
100
50
25
T° C


NaCl - $CaCl_2$ - H_2O
I = 2·0 M
0·4 M $CaCl_2$ 0·8 M NaCl
0·3 M $CaCl_2$ 1·1 M NaCl
0·2 M $CaCl_2$ 1·4 M NaCl
0·1 M $CaCl_2$ 1·7 M NaCl
0·02 M $CaCl_2$ 1·94 M NaCl
2·0 M NaCl
Fluorite deposited mg CaF_2 / kg H_2O
100
90
80
70
60
50
40
30
20
10
0
260
200
150
100
50
25
T° C

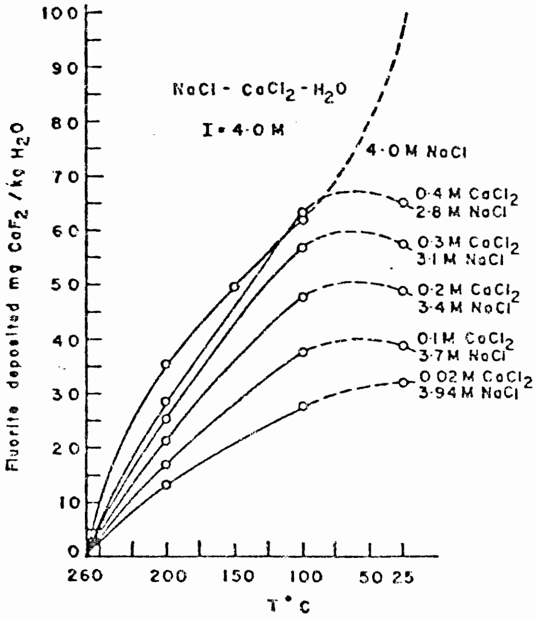

NaCl - $CaCl_2$ - H_2O
I = 4·0 M
4·0 M NaCl
0·4 M $CaCl_2$ 2·8 M NaCl
0·3 M $CaCl_2$ 3·1 M NaCl
0·2 M $CaCl_2$ 3·4 M NaCl
0·1 M $CaCl_2$ 3·7 M NaCl
0·02 M $CaCl_2$ 3·94 M NaCl
Fluorite deposited mg CaF_2 / kg H_2O
100
90
80
70
60
50
40
30
20
10
0
260
200
150
100
50
25
T° C

Figure 7

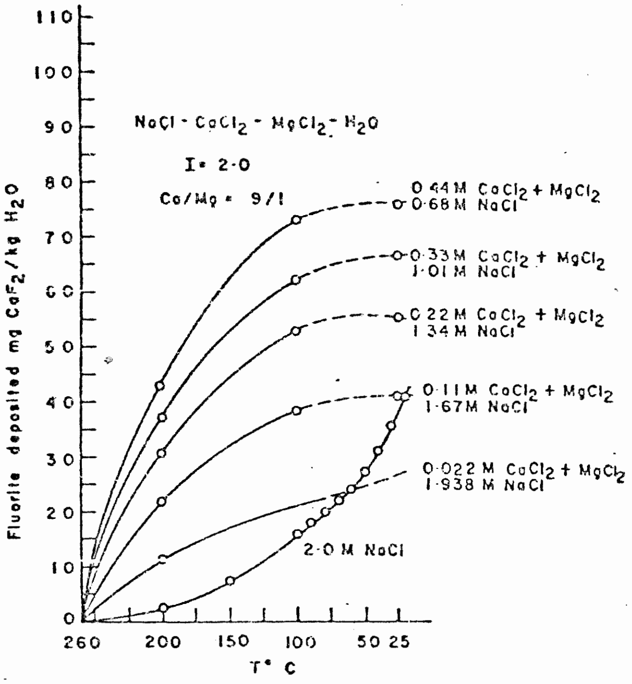
The quantity of fluorite precipitated by cooling NaCl - $CaCl_2$ - $MgCl_2$ - H_2O solutions with a Ca/Mg ratio of 9/1 and an ionic strength of 2.0 M from 260 ° C to 25 ° C.

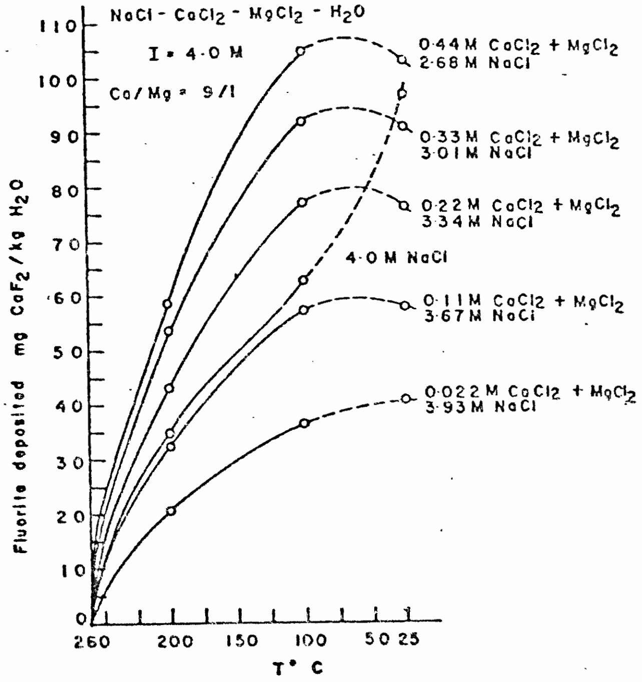
(from Richardson & Holland, 1979b).

Figure 8

The quantity of fluorite precipitated by cooling NaCl - $CaCl_2$ - $MgCl_2$ - H_2O solutions with a Ca/Mg ratio of 9/1 and an ionic strength of 4.0 M from 260 ° C to 25 ° C.

(from Richardson & Holland, 1979b).


NaCl - CaCl$_2$ - MgCl$_2$ - H$_2$O
I = 2·0
Ca/Mg = 9/1
0·44 M CaCl$_2$ + MgCl$_2$
0·68 M NaCl
0·33 M CaCl$_2$ + MgCl$_2$
1·01 M NaCl
0·22 M CaCl$_2$ + MgCl$_2$
1·34 M NaCl
0·11 M CaCl$_2$ + MgCl$_2$
1·67 M NaCl
0·022 M CaCl$_2$ + MgCl$_2$
1·938 M NaCl
2·0 M NaCl
Fluorite deposited mg CaF$_2$/kg H$_2$O
0
10
20
30
40
50
60
70
80
90
100
110
260
200
150
100
50 25
T° C


NaCl - CaCl$_2$ - MgCl$_2$ - H$_2$O
I = 4·0 M
Ca/Mg = 9/1
0·44 M CaCl$_2$ + MgCl$_2$
2·68 M NaCl
0·33 M CaCl$_2$ + MgCl$_2$
3·01 M NaCl
0·22 M CaCl$_2$ + MgCl$_2$
3·34 M NaCl
4·0 M NaCl
0·11 M CaCl$_2$ + MgCl$_2$
3·67 M NaCl
0·022 M CaCl$_2$ + MgCl$_2$
3·93 M NaCl
Fluorite deposited mg CaF$_2$/kg H$_2$O
0
10
20
30
40
50
60
70
80
90
100
110
260
200
150
100
50 25
T° C

Richardson & Holland (1979b) also report on solubility experiments conducted for solutions containing $CaCl_2$ or ($CaCl_2$ + $MgCl_2$) in addition to NaCl. The curves in Figures 5 - 8 indicate that the amount of fluorite precipitated per kilogram of solution increases with the Ca (or Ca + Mg) concentration and with increasing ionic strength except in solutions containing very little $CaCl_2$ (Richardson & Holland, 1979b).

In pure NaCl solutions (Figure 4) precipitation of fluorite with decreasing temperature results from changes in the value of the solubility product of fluorite with temperature and from the strength of the complex NaF (Richardson & Holland, 1979b). Deposition of fluorite from NaCl - $CaCl_2$ - $MgCl_2$ solutions in addition is dependent upon the stability of the CaF^+ and MgF^+ complexes with decreasing temperature. The complexes CaF^+, MgF^+ and NaF all become less stable with decreasing temperature; on cooling, they release free fluoride ions which can combine with calcium to precipitate fluorite (Richardson, 1979a).

Changes in Pressure

Upward movement of fluids is accompanied by a corresponding decrease in confining pressure. The solubility of most gangue minerals, (quartz, calcite, barite, dolomite and anhydrite) decreases as pressure is decreased (Holland, 1967). MacDonald & North (1974) have determined that fluorite behaves similarly.

The majority of fluorite deposits are in the vertical range of 100-500m. This corresponds to a pressure decrease of only 10-50atm (hydrostatic gradient) (Richardson & Holland, 1979b). The general agreement is that changes in fluorite solubility with pressure in hydrothermal solutions are negligible in comparison to temperature related solubility changes in concentrated brines or dilute solutions.

Mixing of Fluids

Mixing of two or more fluids of different chemical composition represents a probable mechanism for fluorite precipitation (Hall & Friedman, 1963; Heyl et al, 1974). Possibilities for interaction include:

i. Meteoric water mixing with a concentrated brine at the same temperature (ie., dilution at a constant temperature)

ii. Meteoric water mixing with a concentrated brine at a different temperature (ie., dilution plus cooling)

iii. Two brines of different chemical composition mixing isothermally or non-isothermally

(Richardson & Holland, 1979b)

Mixing can produce solutions which are either undersaturated or supersaturated with respect to fluorite. Richardson & Holland (1979b) outline the most important parameters as temperature, salinity, and calcium and fluoride concentration of the fluids prior to mixing.

The mixing of a calcium rich brine with a fluoride rich brine appears the most obvious mechanism for precipitating fluorite. The example most frequently cited is the interaction of calcium-bearing connate waters with deep solutions carrying fluoride of volcanic origin (Hall & Friedman, 1963).

Interaction with Wall Rocks

Fluorite precipitation can result from interactions of hydrothermal (ore-forming) solutions with host rocks. Changes in pH and in the calcium and magnesium concentrations of hydrothermal solutions induce fluorite deposition.

Fluorite is quite soluble in acid solutions. A pH change from acid to nearly neutral can lower the solubility of fluorite by as much as 100 mg CaF_2/kg H_2O (Richardson & Holland, 1979a). At 200 degrees C the solubility of fluorite in a 2.0M NaCl solution at a pH of 5 is 63 mg CaF_2/kg H_2O; whereas, its solubility at 200 degrees C in a 2.0M NaCl solution at a pH of 3 is 104 mg CaF_2/kg H_2O (Richardson & Holland, 1979b) (Figure 9).

The pH of hydrothermal solutions is generally >3 at 200 degrees C (Richardson & Holland, 1979b). Since the pH of ore-forming fluids of Mississippi Valley type deposits was probably 4-5 at 200 degrees C, the authors conclude that it is, therefore, unlikely that pH changes produced significant precipitation of fluorite.

Hydrothermal solutions entering a limestone host rock dissolve calcite, thereby increasing the calcium concentration of the host rock. Such an increase in calcium concentration in a pure NaCl solution can lead to fluorite precipitation (Richardson & Holland, 1979a).

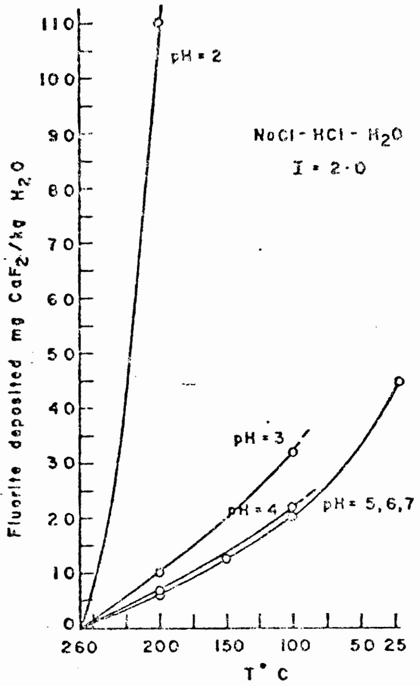
The solubility of fluorite increases with increasing magnesium and calcium concentrations in solution. Therefore, a decrease in the calcium or magnesium concentration by precipitation of calcium and/or magnesium minerals may lead to fluorite deposition (Richardson & Holland, 1979b).

Fluorite precipitation may also be attributed to dolomitization of limestone. Since MgF^+ is more stable than CaF^+, a reduction in the magnesium concentration, although accompanied by an equivalent increase in the calcium concentration, can cause precipitation of fluorite. (Richardson & Holland, 1979b).

Figure 9

The quantity of fluorite precipitated by cooling NaCl solutions at varying pH values from 260 °C to 25 °C.

(from Richardson & Holland, 1979b).


110
100
90
80
70
60
50
40
30
20
10
0
Fluorite deposited mg CaF_2/kg H_2O
pH = 2
NaCl - HCl - H_2O
I = 2.0
pH = 3
pH = 4
pH = 5, 6, 7
260
200
150
100
50
25
T° C

Summary

In summary, the formation of fluorite deposits may result from changes in temperature and pressure along the flow path of hydrothermal solutions, from fluid mixing, or from the interaction of hydrothermal solutions with wall rocks. It should be noted that although each mechanism of fluorite precipitation has been discussed separately, the most realistic interpretation may involve the interaction of two or more of the mechanisms as previously outlined.

CHAPTER 3

Fluid Inclusions

FLUID INCLUSIONS

Introduction

The existence of fluid inclusions was first noted and described by Robert Boyle in 1672. Today fluid inclusions represent an important geological tool in the study of ore formation. Fluid inclusions supply valuable data concerning the temperature, pressure and composition of the geological environments in which they were formed or trapped. They are successfully used as geothermometers, geobarometers and in the determination of ore fluid densities.

Fluid inclusion studies of Mississippi Valley type deposits have established that the ores were deposited by highly saline brines, up to ten times the salinity of sea water. Temperatures during mineral deposition range from 80° to 150° C, and occasionally up to 200° C (Roedder, 1967).

Crystals, whether natural or man-made, that have grown from an aqueous solution, characteristically contain fluid inclusions. The white colouration in calcite and quartz is due to the presence of abundant fluid inclusions. Densities may exceed one billion inclusions per cubic centimeter. However, such minuscule inclusions may comprise only 0.1 volume percent of the sample (Roedder, 1972;1962).

Fluid inclusions exhibit a variety of morphologies: spherical, ovoid, tubular, "negative" crystal shape and irregular forms (Figure 10). Ranging in diameter from less than one micron to a few centimeters, fluid inclusions rarely exceed 1 mm in size (Roedder, 1972). According to Roedder (1967), fluid inclusions could actually represent single dislocations within crystals (2 Å).

Deicha (1975) refers to inclusions as macroscopic if they exceed 1 mm in size, microsopic if they fall within the size range 1 mm to 1 um, and nanoscopic if they are less than 1 mm.

Two phases are generally present in fluid inclusions: the liquid phase (H_2O or CO_2) and the gas phase (CO_2 or H_2O vapour) represented by the bubble. Some inclusions are composed of two immiscible liquids or of a gas phase only (Roedder, 1972).

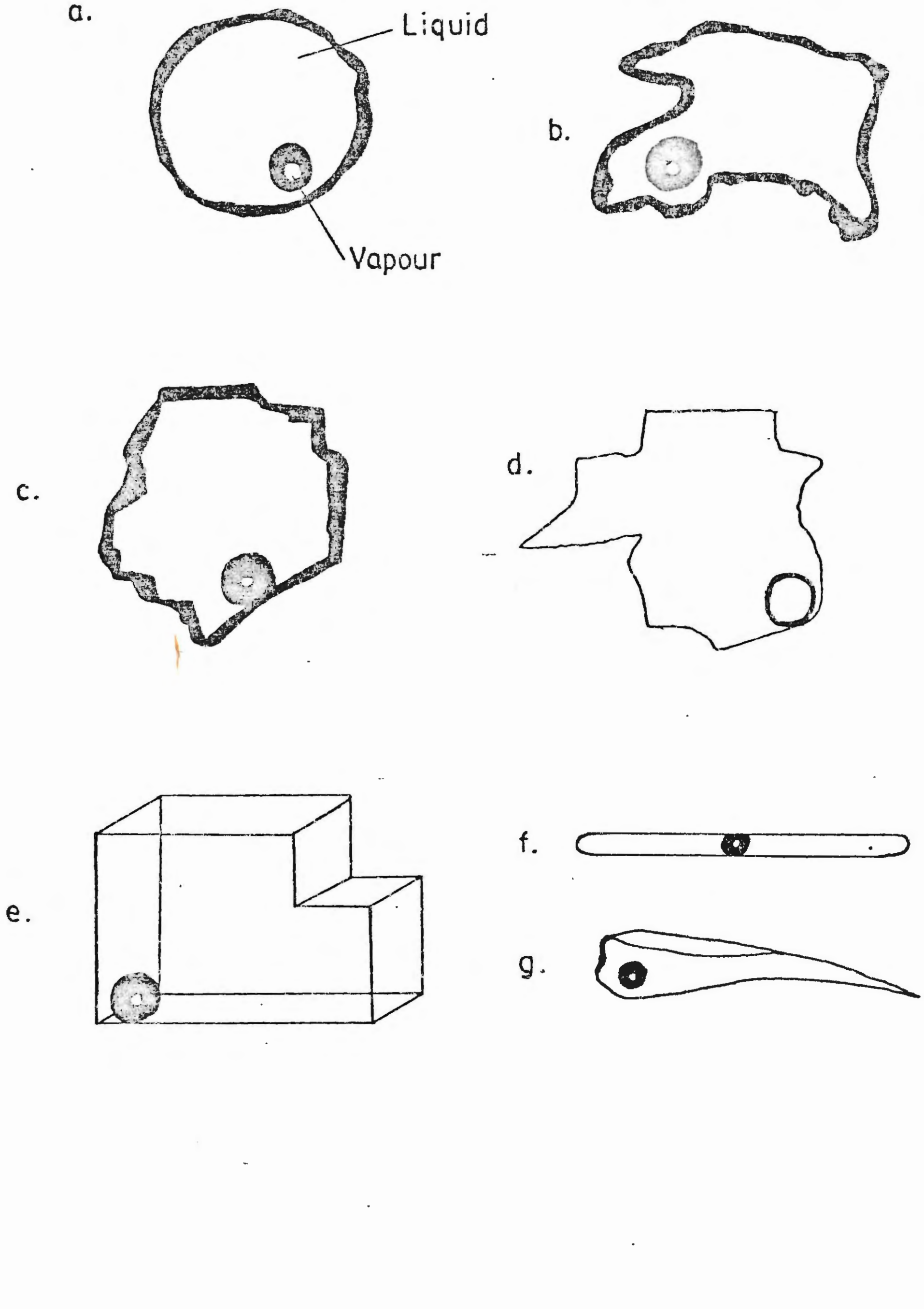
The predominant component of the liquid phase is water. Sodium and chloride are the most abundant ions, with lesser amounts of sulfate ($SO_4^{=}$), carbonate ($CO_3^{=}$), and bicarbonate (HCO_3^{-}). Roedder (1979) outlines the relative abundance of ions in fluid inclusions of Mississippi valley type deposits as $Cl > Na > K > Mg > B$. Heavy metals in the fluids rarely exceed one percent (Roedder, 1972).

Both the concentration and composition of the fluids depend upon the geological environment of formation. The total amount of dissolved salts may range from nearly fresh water to very concentrated brines. The presence of daughter minerals (ie., salt crystals formed from inclusion fluids after trapping) is indicative of salt rich fluids trapped at elevated temperatures (Roedder, 1972). Cooling of such a salt rich solution precipitates salt crystals.

Figure 10

Some common morphologies of fluid inclusions in fluorite.
a) spheroidal; b) irregular; c) semi-regular, faceted;
d) flattened, irregular; e) negative crystal (cubic);
f) tubular; g) tapered. Note that all inclusions are two-phase (vapour-liquid). The vapour bubble in (d) is flattened.

(redrafted from Rankin, 1978).


a.
Liquid
Vapour
b.
c.
d.
e.
f.
g.

Assumptions on which Fluid Inclusion Data are based

1. If a crystal of an ore mineral (or a gangue mineral known to be cogenetic with the ore) grows from a fluid medium, irregularities in the growth process can cause the trapping of small amounts of this medium within the crystal.
2. The fluid trapped is a representative sample of the ore fluid at the moment of trapping.
3. Significant quantities of material are neither lost nor gained from the inclusions after trapping.

(Roedder, 1976)

Classification of Fluid Inclusions

Fluid inclusions represent imperfections in the crystal structure of the host mineral. Criteria based on occurrence and growth patterns are utilized to classify inclusions as primary, secondary and pseudosecondary (Appendix 1).

Primary inclusions form simultaneously with the surrounding host crystal. Dendritic or skeletal crystal growth, followed by solid, perfect growth that covers the imperfect region, entraps primary inclusions. The presence of an immiscible liquid or gas bubble during crystal growth may also trap fluid inclusions.

Secondary inclusions form after growth has terminated, during the spontaneous healing of post-depositional fractures within a crystal. A fracture represents an increase in surface energy within the crystal structure, and is, therefore, eliminated by solution and growth processes (Roedder, 1972). Secondary inclusions are frequently more abundant in the crystal structure than are primary inclusions. Whereas primary fluid inclusions contain samples of the fluid in which the crystal grew, secondary fluid inclusions consist of a later fluid which may be unrelated to the ore fluid (Roedder, 1976).

Pseudosecondary inclusions are formed by fracturing and rehealing during the growth of the host crystal. Roedder (1976) states that inclusions found along healed fractures (ie., along cleavage directions in fluorite and sphalerite) are not necessarily secondary.

The common distribution of the three genetic classes of fluid inclusions in a fluorite crystal is illustrated in Figure 11. The following photomicrographs (Figures 12-17) are of two-phase fluid inclusions in purple fluorite from Boat Harbour, Newfoundland (samples SE - 1, SE - 2, SE - 3, SE - 4) and Gays River, Nova Scotia (samples ZGR - 1, ZGR - 2).

Figure 11

Diagrammatic representation of the distribution of P, PS and S inclusions in a section through a cubic crystal of fluorite. Secondary and pseudosecondary (S and PS) inclusions occur in planes which traverse growth zones. Primary (P) inclusions occur either as isolated cavities, unrelated to fractures, or in planes parallel to, and within, growth zones.

(redrafted from Rankin, 1978).

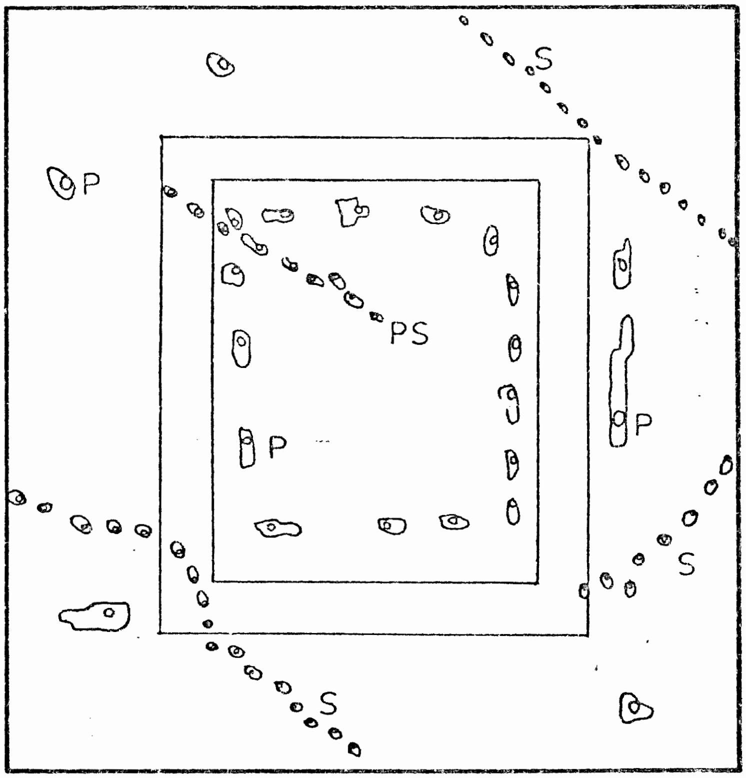
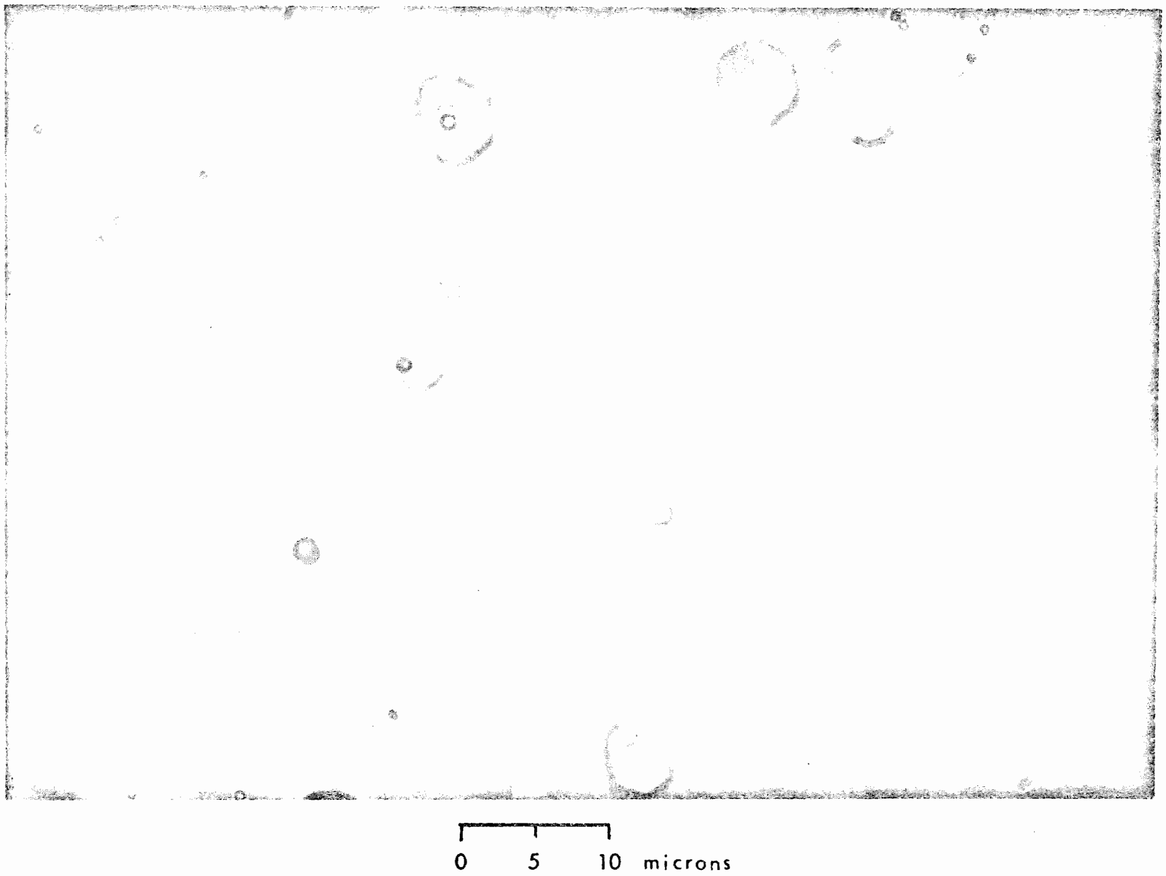

S
P
PS
P
P
S
S

Figure 12 (SE - 4)

A field of primary inclusions arranged in several planes within the crystal. Morphologies range from spheroidal to semi-regular or faceted.

Figure 13 (ZGR - 2)

A large primary inclusion of negative crystal shape. Only one face is outlined (ie., the remainder of the inclusion lies within a deeper level of the crystal).


0
5
10 microns

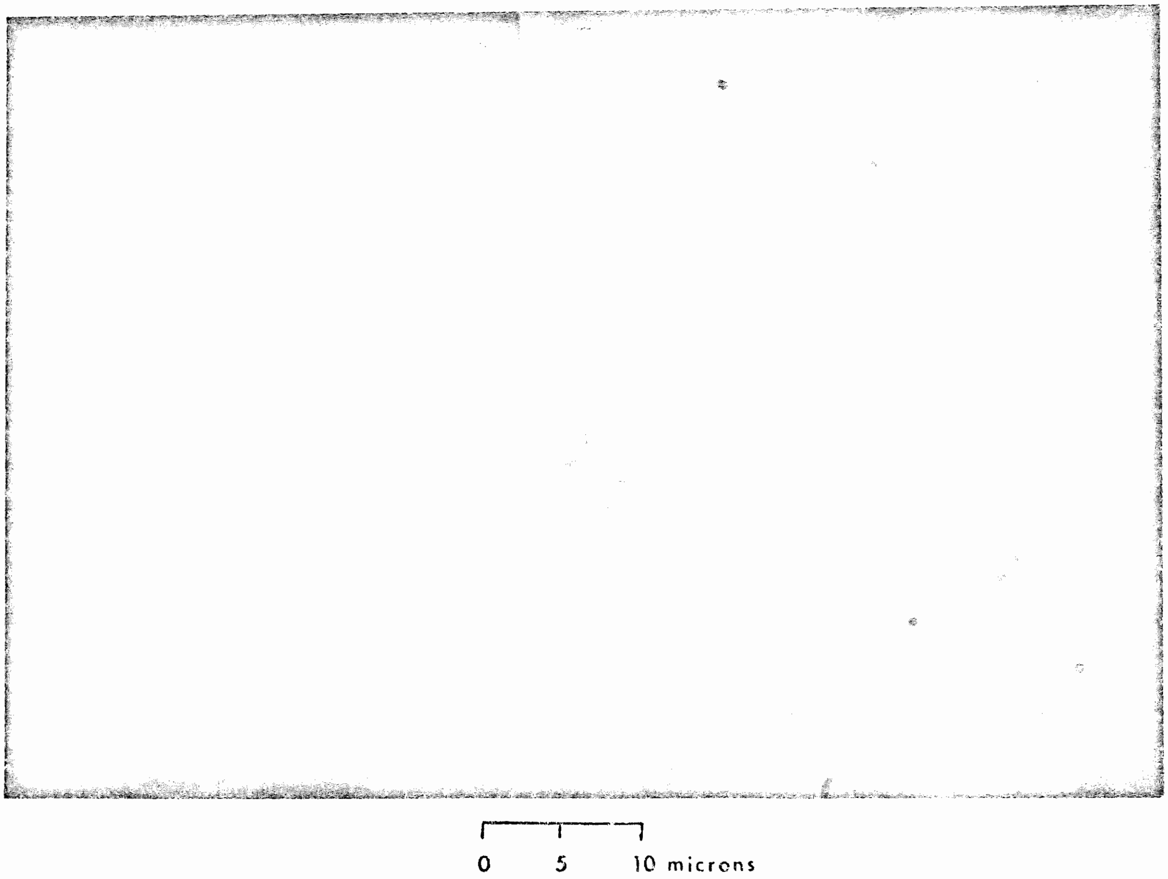
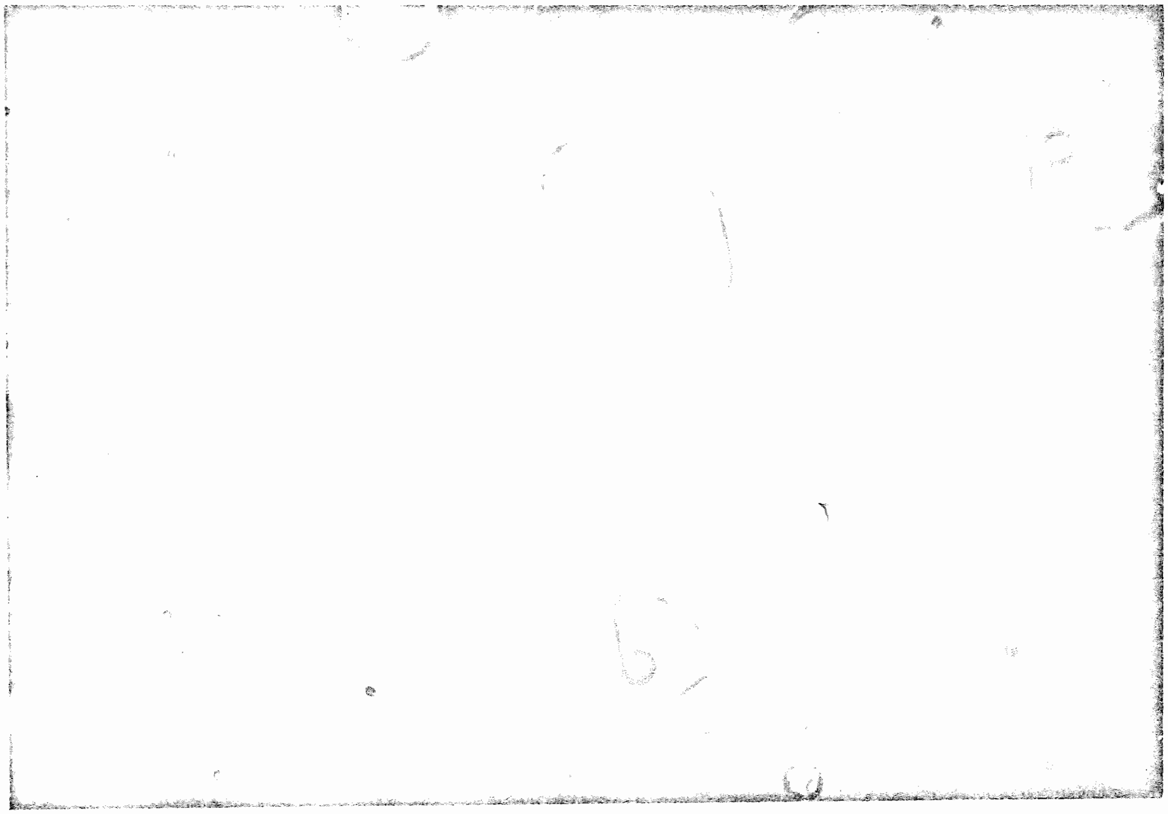

0
5
10 microns

Figure 14 (SE - 1)

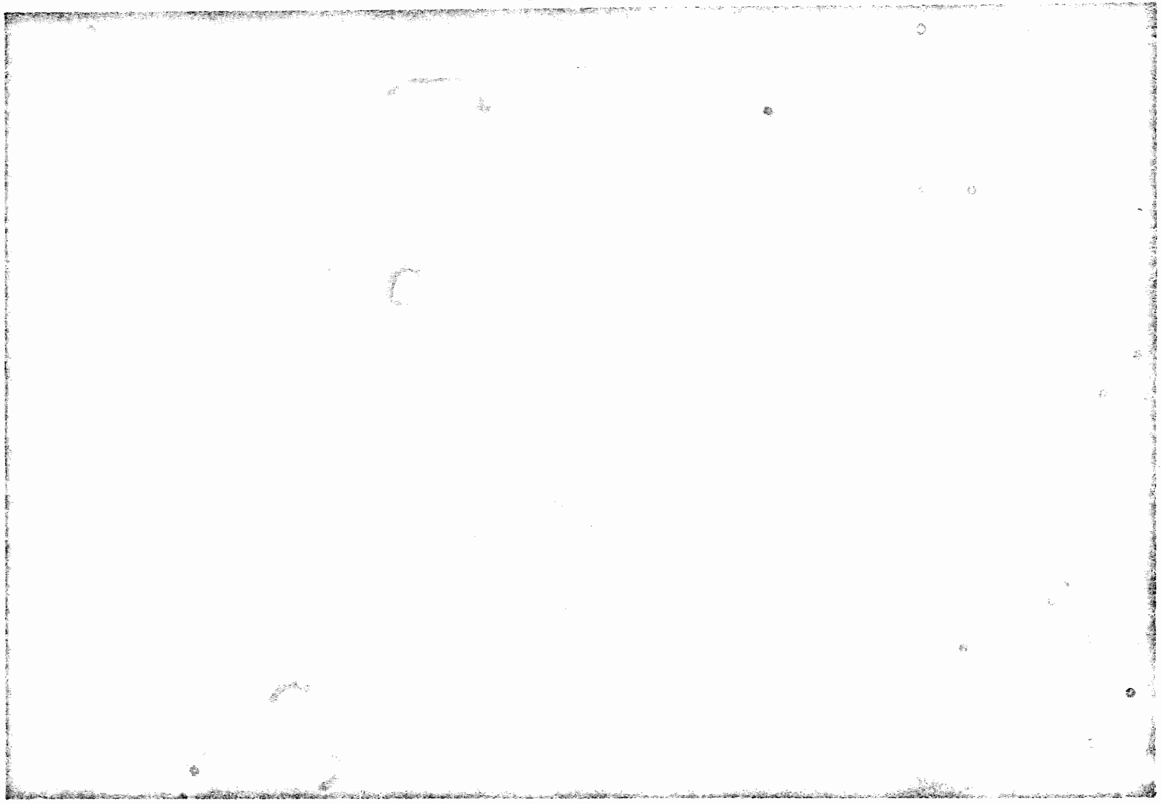
Several large primary inclusions. Morphologies range from roughly spheroidal to semi-regular or faceted.

Figure 15 (ZGR - 1)

An isolated primary inclusion with a tapered, somewhat elongated shape.



0 5 10 microns



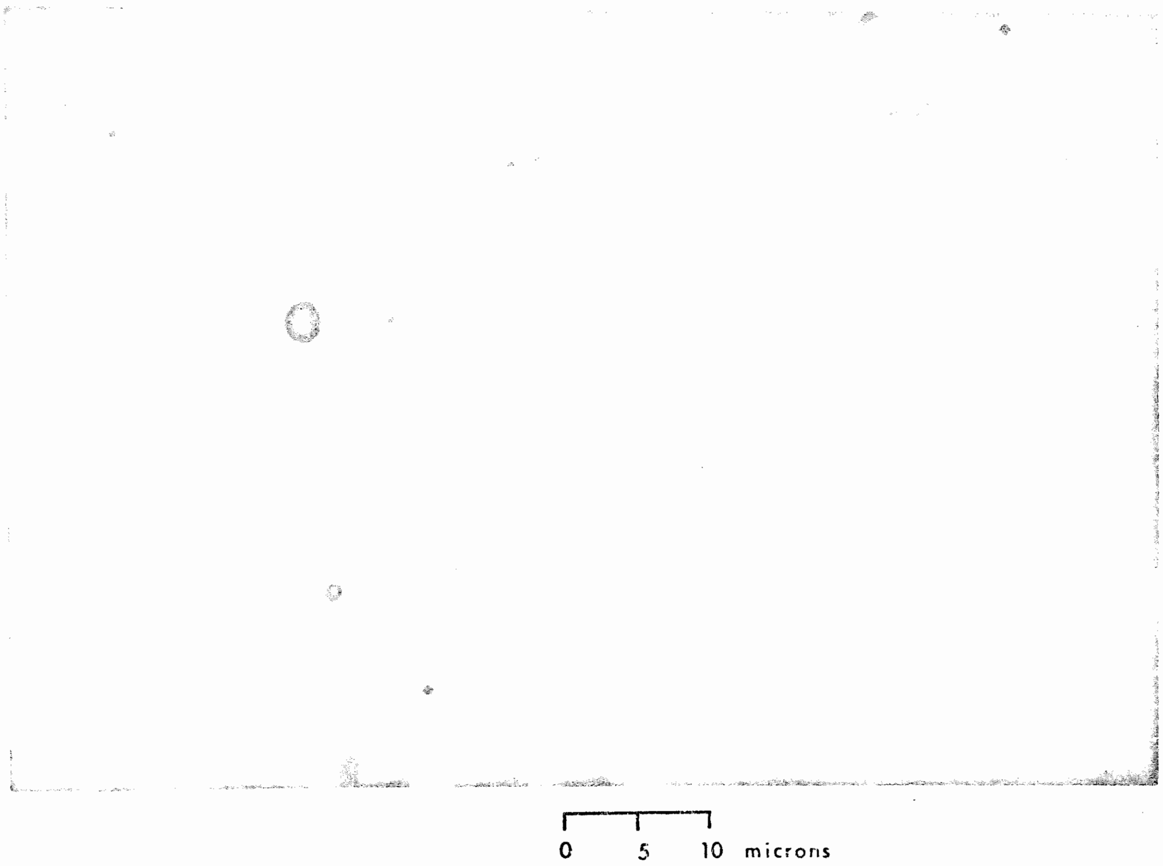
0 5 10 microns

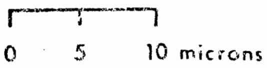
Figure 16 (SE - 2)

Several large primary inclusions ranging in shape from spheroidal to rectangular.

Figure 17 (SE - 3)

An elongated primary inclusion with a large bubble (gas phase). The inclusion is in the process of "necking down".


0
5
10 microns


0
5
10 microns

Geothermometry

In two-phase fluid inclusions, the gas bubble represents differential shrinkage from the original temperature of trapping to the temperature of observation (Roedder, 1972). The relative size of the bubble, therefore, provides a visual estimate of the temperature of trapping. Low temperature rock formation produces characteristically small bubbles or none at all in comparison to large bubbles formed at high temperatures (Roedder, 1962).

Heating of the inclusion until the bubble disappears (ie., the fluid phase expands to fill the inclusion) yields the homogenization or filling temperature. The apparent gas/liquid ratio is greatly affected by inclusion shape; inclusions that appear different may have the same homogenization temperatures (Roedder, 1976).

The homogenization temperature does not equal the true trapping temperature in all cases. If an inclusion traps a homogeneous liquid that is in equilibrium with its vapor (ie., it is on the "boiling curve", line A - C.P., Figure 18), or traps a homogeneous vapor that is in equilibrium with the liquid (line B - C.P., Figure 18), then the experimentally determined temperature equals the true trapping temperature (Roedder, 1972). Most commonly, the pressure on the fluid at the time of trapping is greater than that given by the line A - C.P. - B, and the homogenization temperature is lower than the true trapping temperature (Roedder, 1972). A pressure correction must then be added to the homogenization temperature. Therefore, the homogenization provides only a minimum temperature of fluid trapping.

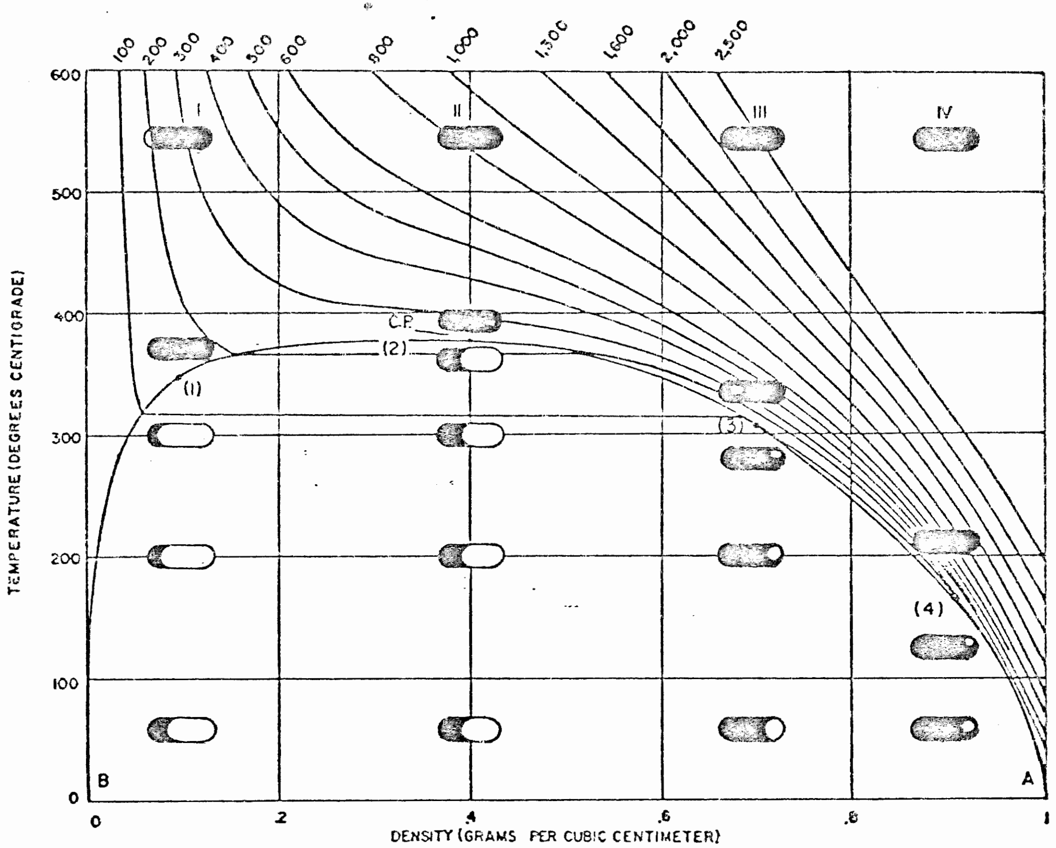
A further complication results from the position of the curve A - C.P. - B (shown for pure water). The presence of salts in the fluid raises the curve significantly.

Figure 18

Thermal behaviour of four inclusions (four vertical rows of capsules) that have different liquid-vapour densities is superimposed on the phase diagram for pure water. C. P. refers to the critical point. The thin curving lines are isobars, connecting points of equal pressure (given at the top, in atmospheres).

(from Roedder, 1972).

note: the liquid-vapour ratio is defined as volume of liquid/volume of liquid plus volume of gas.


100
200
300
400
500
600
800
1,000
1,300
1,600
2,000
2,500
I
II
III
IV
C.P.
(1)
(2)
(3)
(4)
A
B
600
500
400
300
200
100
0
0
.2
.4
.6
.8
1
TEMPERATURE (DEGREES CENTIGRADE)
DENSITY (GRAMS PER CUBIC CENTIMETER)

Salinity

The salinity of the ore fluid is most readily determined from the equilibrium freezing temperature of the fluid inclusion. Depression of the freezing point of the fluid with a microscope freezing stage yields the freezing temperature. A semi-quantitative measure of the salt concentration in the fluid inclusions is obtained from the freezing temperature. However, some uncertainty exists in salinity measurements based on the depression of the freezing point for mixed salt solutions.

According to Roedder (1976) the salinity of Mississippi Valley ore fluids usually exceeds 15 wt. percent salts, and frequently exceeds 20 wt. percent salts. The absence of daughter crystals of NaCl in these deposits implies appreciable amounts of ions other than Na and Cl (Roedder, 1976).

Density

Fluid inclusions enable the accurate determination of the density of ore bearing fluids. If the relative volumes of liquid and gas phases are measured at room temperature (by using geometrically regular inclusions), and if the salinity is known (from freezing experiments), the denisity of the originally homogeneous fluid can be calculated (Roedder, 1976). Average fluid inclusion densities (ie., the density of the fluids at the time of trapping) of Mississippi Valley deposits are found to be greater than 1.0 g/cm^3, and are frequently as high as 1.1 g/cm^3 (Roedder, 1976).

CHAPTER 4

Study Areas

GAYS RIVER, NOVA SCOTIA

Introduction

The Gays River base metal deposit, situated within the Maritimes Carboniferous Basin, represents the Nova Scotian equivalent of a Mississippi Valley type deposit. A dolomitized reef complex of Lower Carboniferous (Windsor) age hosts this lead-zinc deposit.

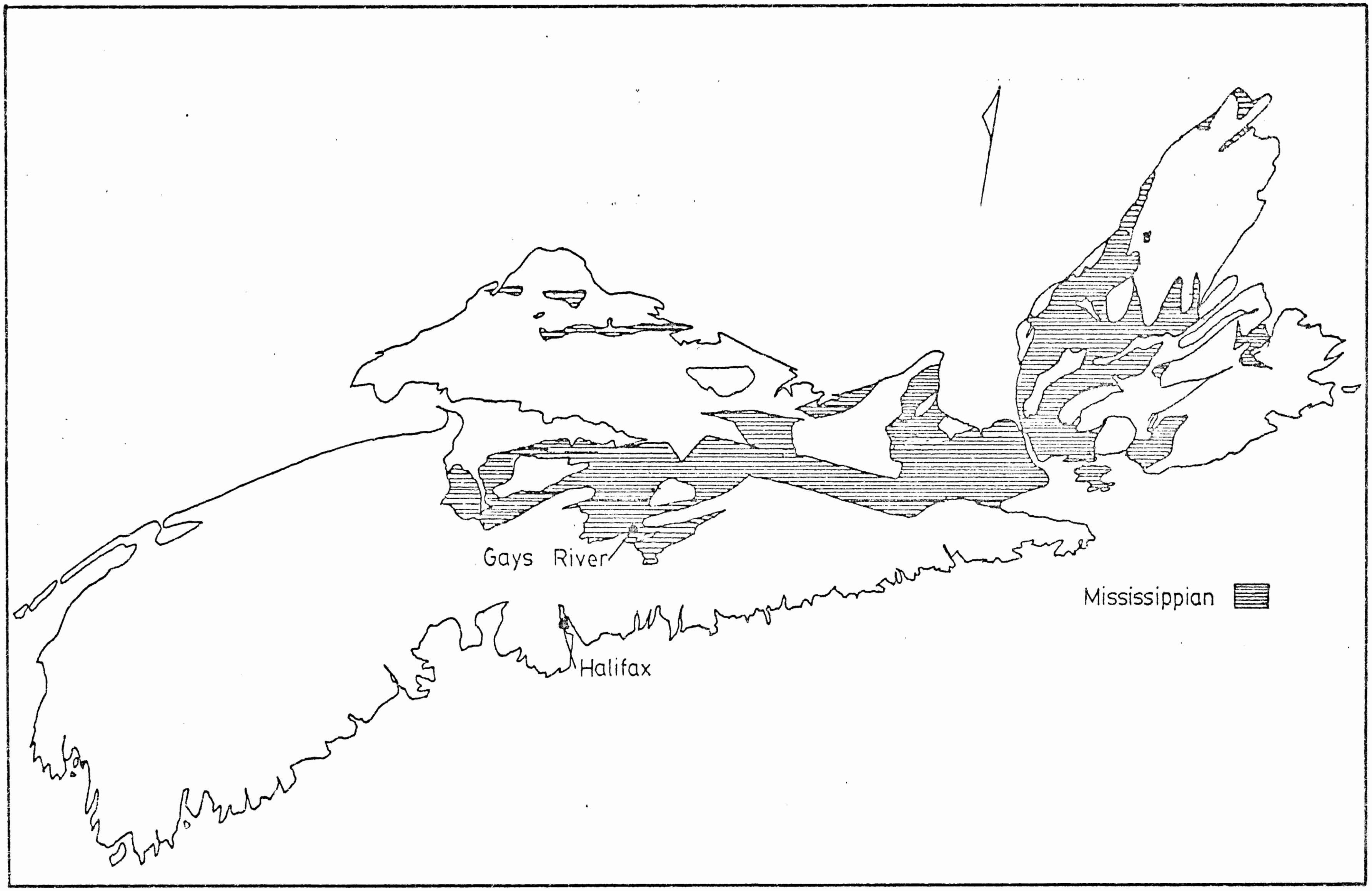
Developed around pre-Carboniferous topographic highs, the reef complex straddles a chain of islands between two Carboniferous mini-basins. MacEachern & Hannon (1974) state that the Gays River deposit is analagous to a barrier reef between two ancient seas. The Musquodoboit Basin lies to the south; the Shubenacadie Basin to the northwest. Evaporites of gypsum and anhydrite flank either side of the reef complex.

Location

The Imperial Oil owned Gays River lead-zinc deposit is located in central Nova Scotia, 11 kilometers southeast of Shubenacadie and 50 kilometers northeast of the Port of Halifax (45° 02' North 63° 22' West) (Figure 19).

Figure 19

Location of Gays River base metal deposit. The Mississippian of Nova Scotia is outlined.


Gays River
Halifax
Mississippian ▤

Regional Geology

The Maritimes Carboniferous Basin is situated at the northeastern boundary of the Appalachian physiographic province. The basin evolved early in the Mississippian in response to crustal adjustments following the Acadian orogeny. Sedimentation during the Mississippian and Pennsylvanian consisted of shales, sandstones and conglomerates, and evaporites and carbonates in ascending order of frequency. The existence of carbonate reefs and thick accumulations of evaporites suggest that the Windsor climate was generally warm and arid.

The Carboniferous rocks are mainly undisturbed (ie., minor post-depositional tectonism has occurred). The underlying pre-Carboniferous basement rock is composed of the Cambro-Ordovician Meguma Group.

The Meguma Group consists of 20,000 - 35,000 feet of quartzites, slates and shales. The lower unit, the Goldenville Formation, comprises approximately two-thirds of the total thickness. The Goldenville Formation consists of arkosic quartzites with minor greywacke and slates. The upper unit, the Halifax Formation, conformably overlies the Goldenville Formation. It is composed of slates and shales with minor quartzite. Extensive regional metamorphism of the Group has occurred. The entire group has been tightly folded, forming northeast-southwest trending anticlines and synclines.

Local Geology

The Gays River lead-zinc deposit is hosted by a dolomitic reef complex of Lower Carboniferous (Windsor) age. The carbonates developed over a pre-Carboniferous paleotopographic high, forming a barrier between two ancient seas. The reef complex straddles two Carboniferous mini-basins; the Musquodoboit Basin to the south and the Shubenacadie Basin to the northwest.

An angular unconformity exists between the basement rocks (Meguma Group) and the overlying Windsor carbonates. This contact is market by a thin "paraconglomerate". The clasts of the paraconglomerate consist of Meguma quartzites and slates, and range in size from small pebbles to large tabular cobbles (Taylor, 1977). This Basal unit or paraconglomerate is cemented with carbonate.

The carbonate sequence overlies the paraconglomerate. On the basis of geometery and paleontological evidence, MacEachern & Hannon (1974) have established a fore-reef area, reef crest, reef proper and a back-reef area (Figure 20).

The lithologic units within the reef as described by MacEachern and Hannon (1974) are as follows:

1. Recrystallized micritic dolomite - this is a dolomitic mud which has been recrystallized to give it a more or less sugary texture.

2. Micritic skeletal dolomite - these are shell horizons, made up mainly of brachiopod shells within a matrix of micritic dolomite.

3. Coral-bearing dolomite - this unit consists of tabulate coral (syringopora) colonies with micritic dolomite trapped between corals. The coral-bearing dolomite occurs at the reef crest.

4. Algal dolomite - these are nodular calcareous algae that form a "mat" or bed in the reef proper. Because almost all of the reef has been recrystallized (limestone to dolomite), much of what we are referring to as micritic dolomite may indeed be algal dolomite.

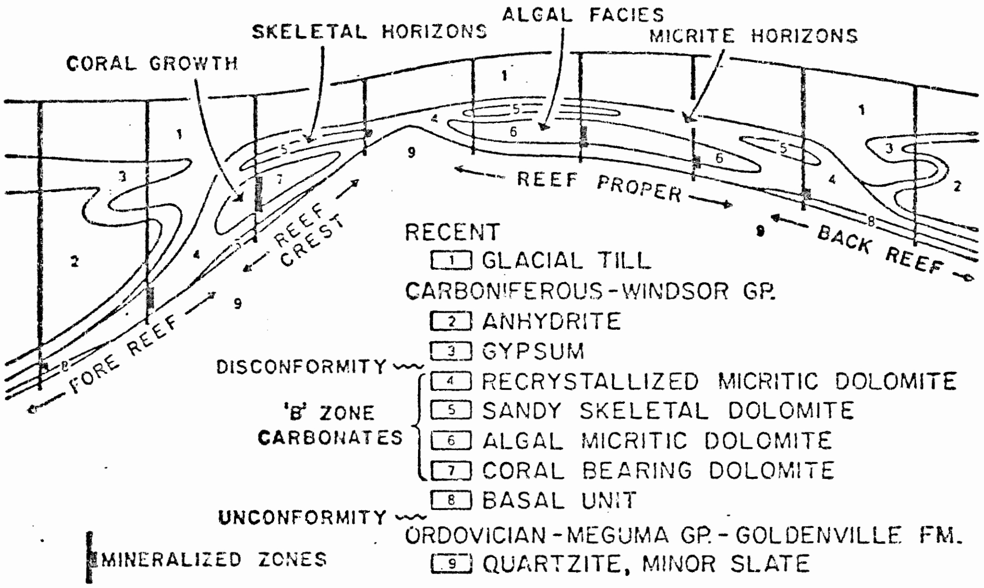
As mentioned previously, a thick evaporite unit flanks both sides of the reef complex. The evaporite unit is slightly disconformable to the reef. It consists of a core of anhydrite, rimmed by a thin alteration zone of gypsum (MacLeod, 1975). Halite rich anhydrite is not uncommon. The carbonate complex is generally undeformed. Overlying glacial till is 35-60 meters thick.

Figure 20

Gays River Section - Idealized

(from MacEachern & Hannon, 1974).

GAYS RIVER SECTION - IDEALIZED



Mineralization

The economic mineralization consists predominantly of the lead and zinc sulfides, galena and sphalerite. Galena and sphalerite comprise about 99.5 percent of the metallic minerals in the deposit; marcasite and chalcopyrite constitute the remainder. The gangue minerals are dolomite and calcite with minor amounts of fluorite and barite. The fluorite occurs at the evaporite-dolomite contact; the barite at the base of the Basal Unit (MacEachern & Hannon, 1974).

The sphalerite is honey-yellow in colour and is found in fine grained aggregates, disseminations, veinlets and irregular masses. Massive sphalerite horizons up to five feet in thickness may be directly related to the sinkholes of the flanks of the reef (MacEachern & Hannon, 1974). Although the galena occurs disseminated with sphalerite, its distribution is more restricted to open spaces (ie., fractures, vugs, stylolites). Both the sphalerite and galena display open space filling and host rock replacement.

The fluorite is coarsely crystalline and occasionally grows as well-developed cubic crystals lining irregular cavities in the dolomite. It ranges in colour from transparent to purple to black; the purple and black varieties being the most common. Felderhof (1978) describes a specimen which contained approximately 15 percent fluorite filling cavities and replacing dolomite.

Pore spaces utilized by the mineralization consisted of interparticle, sheltered, fenestral, intraskeletal, fracture, and moldic porosity (MacLeod, 1975). The sulfides act as cements during diagenesis.

Paragenesis - Gays River

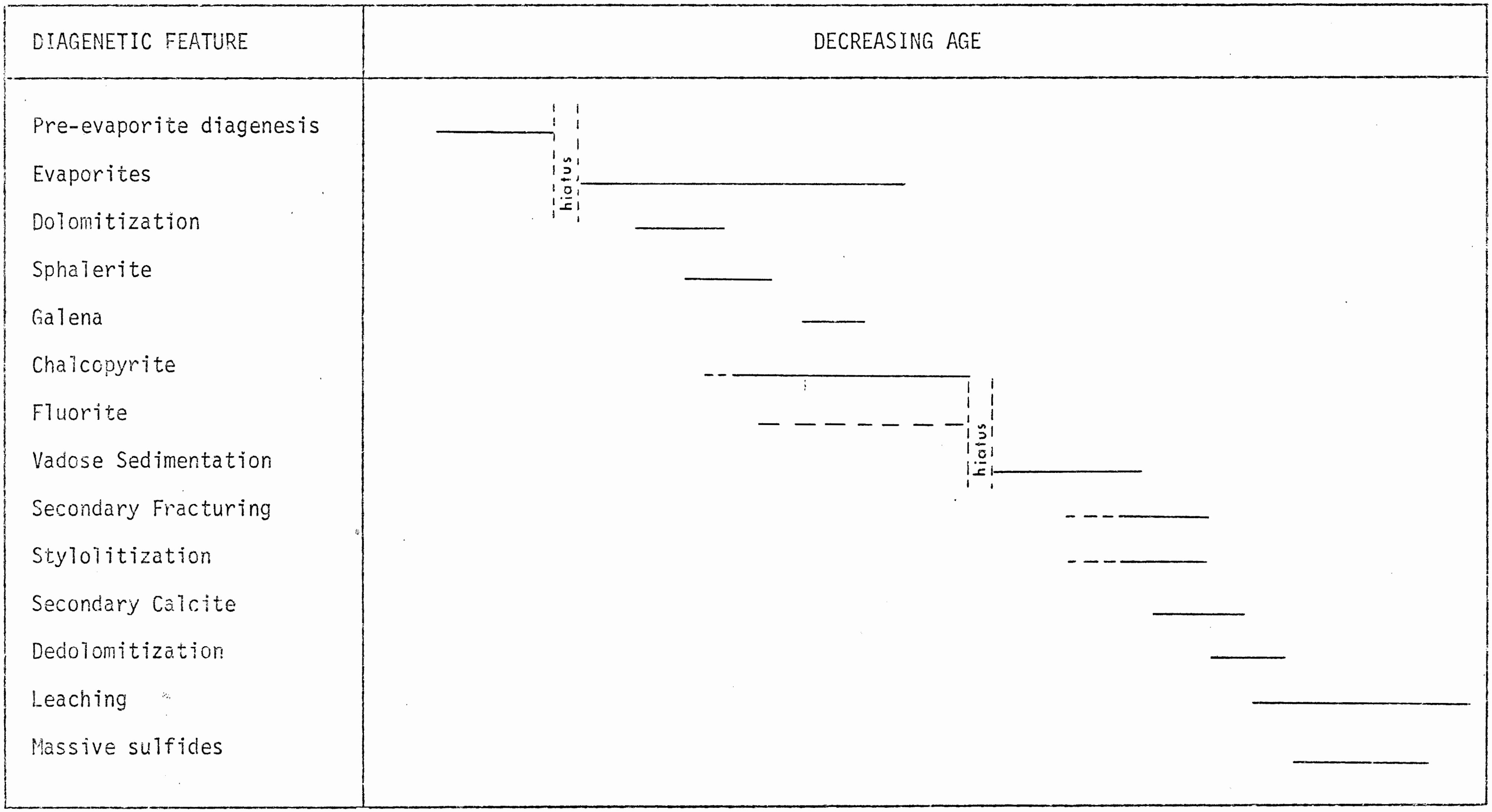
The paragenesis of the sulfide minerals and the associated barite and fluorite has been established by MacLeod (1975) on the basis of macroscopic and microscopic petrographic relationships (Table 1). Pyrite and marcasite deposition occurred prior to the sphalerite and galena. MacLeod (1975) states that "the generation of iron sulfides occurred distinctly earlier than and separated from, via a time hiatus, the economic sulfides."

MacLeod (1975) supports his paragenetic sequence with petrographic relationships:

1. a hypidiomorphic grain of sphalerite surrounded by a mass of galena, indicating that galena post-dates the sphalerite.
2. sphalerite occurs lining a fenestral cavity, the remainder of which is filled by galena
3. chalcopyrite occurs rimming galena, between galena and sphalerite, and within sphalerite
4. fluorite is found rimming sphalerite
5. barite occurs within the massive secondary sulfide zone; therefore, its primary relationship could not be determined

TABLE 1

Diagenetic Sequence Gays River
(modified from MacLeod, 1975)



NEWFOUNDLAND STUDY AREAS
Boat Harbour, Daniel's Harbour

Introduction

Western Newfoundland is situated along the western margin of the Appalachian Orogen. The sedimentary platform of the Great Northern Peninsula consists of a Cambro-Ordovician sequence of clastics and carbonates. Various depositional environments that existed during the initial rifting, expansion and contraction of the Proto-Atlantic Ocean, are represented on this platform.

The carbonates of the Great Northern Peninsula represent ideal host rocks for lead-zinc deposits of Missisippi Valley type. On the property of Newfoundland Zinc Mines Ltd. at Daniel's Harbour, 5.4 million tons of 7.7 percent zinc have been delineated (Fielder, 1970). Widespread small showings of lead and zinc occur elsewhere on the peninsula. Many have been correlated stratigraphically with the Newfoundland Zinc Mine. Interesting to note is the existence of two petroleum showings on the western platform (Figure 21).

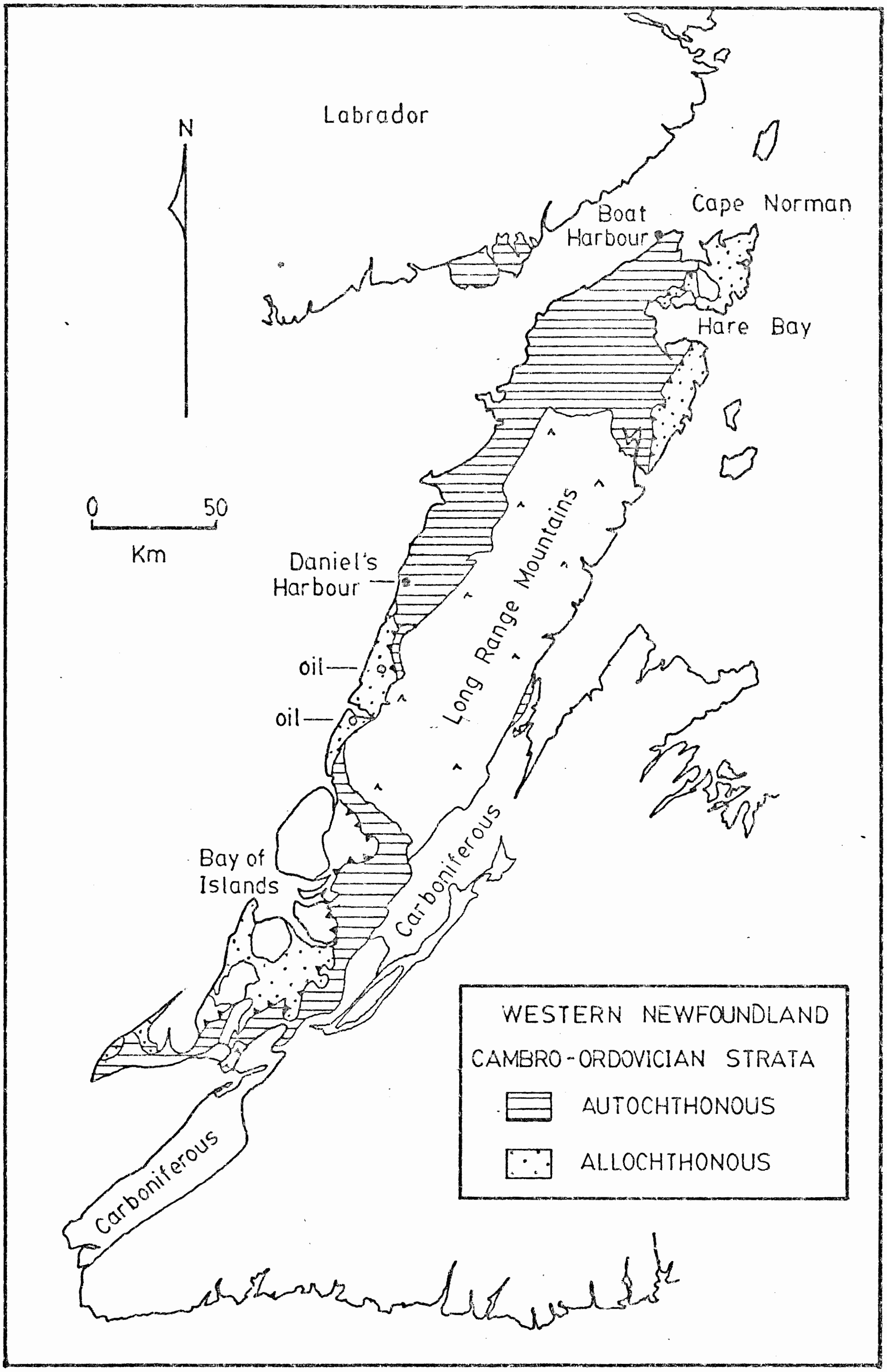
Regional Geology

The Cambro-Ordovician platform extends along the west coast of the Great Northern Peninsula from the Port au Port peninsula to Cape Norman, a distance of over 400 kilometers. The western platform is composed of three contrasting sub-units: an inlier of Precambrian basement, an autochthonous cratonic cover, and an allochthonous transported sequence.

The Long Range Mountains consist of uplifted Precambrian (Grenville) gneisses, schists and granites. The mountains form the core of the Great Northern Peninsula. The autochthonous cratonic cover (Cambro-Ordovician) consists of flat-lying to moderately deformed stable shelf carbonates and clastics. The autochthon rests unconformably upon, or in fault contact with the Grenville inlier. Two immense Taconic Klippen rest structurally upon the autochthon shelf sequence. The Klippen consist of Cambro-Ordovician clastic and volcanic rocks. The allochthonous Klippen represent a transported sequence of continental slope to basin deposits that was thrust westward during the Taconic Orogeny in the Middle Ordovician. An ophiolitic suite overlies the transported clastic sequences at Hare Bay (Figure 21). Transported (heavy - such as ophiolitic rock) sheets did not surpass or overlay the carbonate platform of the Daniel's Harbour or Boat Harbour areas (S. Stouge, personal communication).

Figure 21

Western Newfoundland indicating areas of autochthonous and allochthonous Cambro-Ordovician strata.


Labrador
N
0
50
Km
Boat Harbour
Cape Norman
Hare Bay
Daniel's Harbour
oil
oil
Long Range Mountains
Bay of Islands
Carboniferous
Carboniferous
WESTERN NEWFOUNDLAND
CAMBRO-ORDOVICIAN STRATA
AUTOCHTHONOUS
ALLOCHTHONOUS

Stratigraphy of the Cambro-Ordovician

The Cambrian sequence consists of the Hawkes Bay Quartzite formation, which was deposited as an extensive sublittoral and littoral sand flat during the upper Lower Cambrian (Knight, 1977). Limestone and dolomitized limestones, representative of deposition on an open marine shelf, comprise the overlying Micrite formation of upper Middle Cambrian age. A shallowing of the shelf seas during the Upper Cambrian produced thick intertidal-supratidal dolostones and stromatolites of the Dolomite formation (Knight, 1977).

The Ordovician carbonate succession of the Great Northern Peninsula is subdivided into six lithostratigraphic units: the Unfortunate Cove, the Watts Bight, the Catoche, the Diagenetic Carbonate and the Siliceous Dolomite formations, which comprise the Lower Ordovician St. George Group. The St. George Group is overlain conformably by the Middle Ordovician Table Head Formation limestones, the sixth lithostratigraphic unit.

This disconformity separating the St. George Group and Table Head Formation is believed to be conformable (Knight, 1977). Dolomitization fronts have previously been misinterpreted as the "disconformity" in places.

Boat Harbour

Location

The fluorite occurrence at Boat Harbour was discovered by the Newfoundland Department of Mines and Resources in 1977 during the regional geologic mapping of the Cambro-Ordovician rocks of the Great Northern Peninsula. Boat Harbour is located on the northern tip of the peninsula, 8 kilometers southwest of Cape Norman (51° 35' north 56° 00' west) (Figures 21, 22).

Stratigraphy - Boat Harbour

The Catoche formation outcrops in a section 125 meters thick at Boat Harbour (Figure 23). The formation is composed predominantly of rubbly weathering blue-black micritic limestone with occasional dolomitic limestone and dolostone (Knight, 1977). The limestone contains a diverse fauna that includes trilobites, brachiopods, ostracods, crinoid ossicles, coiled and spiral gastropods, and straight and semicoiled cephalopods.

Stromatolites are present in the lower half of the section. The stromatolites form isolated and interconnected mounds which vary from 30-120 cm in height and up to 300 cm in diameter. Depressions separating the stromatolite heads are filled by dolomitic limestones (Knight, 1977).

Intensely bioturbated micrites have been preferentially dolomitized. Sparry white dolomite is abundant. The dolostone may be described as approaching a "pseudobreccia". The rock is mottled grey and dark grey crystalline dolomite, with the mottling due to the bioturbation. Fluorite is found in the pseudobreccia, in association with the sparry white dolomite. The stromatolitic horizons are spatially related to the mineralization (ie., the pseudobreccia dolostone occurs between the stromatolite mounds).

The Catoche formation is overlain by the Diagenetic Carbonates. Since the carbonates have been radically altered by secondary processes and diagenesis that was possibly transgressive to the stratigraphy, no formal status is proposed for the unit (Knight, 1977). The Diagenetic carbonates at Boat Harbour have a sharp, transgressive but sometimes faulted contact with the underlying Catoche formation. The dolomites vary between very vuggy, dark grey, bituminous, calcareous dolomites containing sparry dolomite filled veins, and fine to coarsely crystalline, brown-grey dolomite which is massive, vuggy, or criss-crossed by a honeycomb of weathering-resistant spar-filled fractures (Knight, 1977). The rocks are termed pseudobreccias.

Figure 22

Location and regional stratigraphy of Boat Harbour.

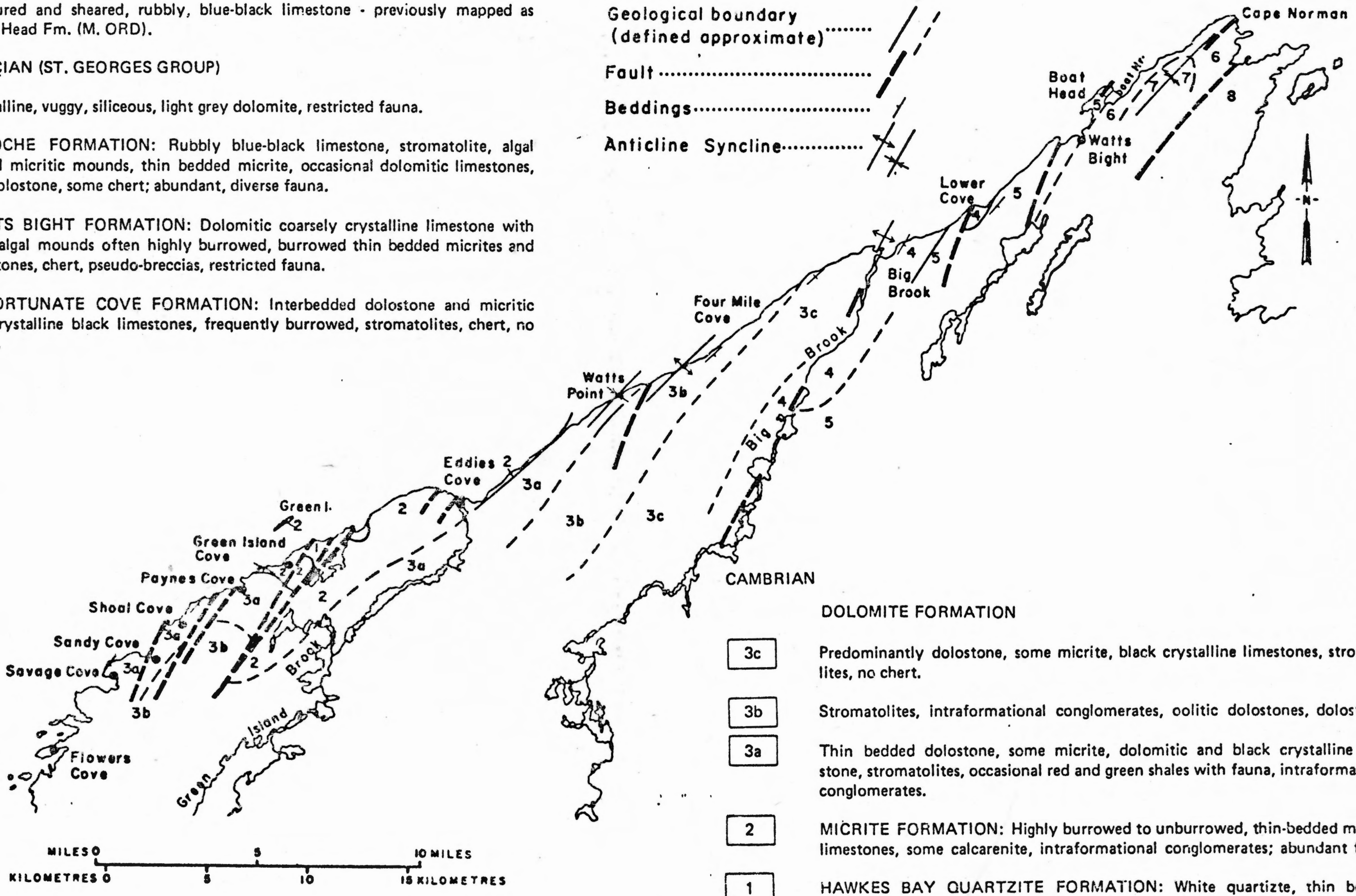
(from Knight, 1977).

UNIT

8	Fractured and sheared, rubbly, blue-black limestone - previously mapped as Table Head Fm. (M. ORD).

LOWER ORDOVICIAN (ST. GEORGES GROUP)

7	Crystalline, vuggy, siliceous, light grey dolomite, restricted fauna.
6	CATOCHE FORMATION: Rubbly blue-black limestone, stromatolite, algal bound micritic mounds, thin bedded micrite, occasional dolomitic limestones, and dolostone, some chert; abundant, diverse fauna.
5	WATTS BIGHT FORMATION: Dolomitic coarsely crystalline limestone with large algal mounds often highly burrowed, burrowed thin bedded micrites and dolostones, chert, pseudo-breccias, restricted fauna.
4	UNFORTUNATE COVE FORMATION: Interbedded dolostone and micritic and crystalline black limestones, frequently burrowed, stromatolites, chert, no fauna.



CAMBRIAN

DOLOMITE FORMATION

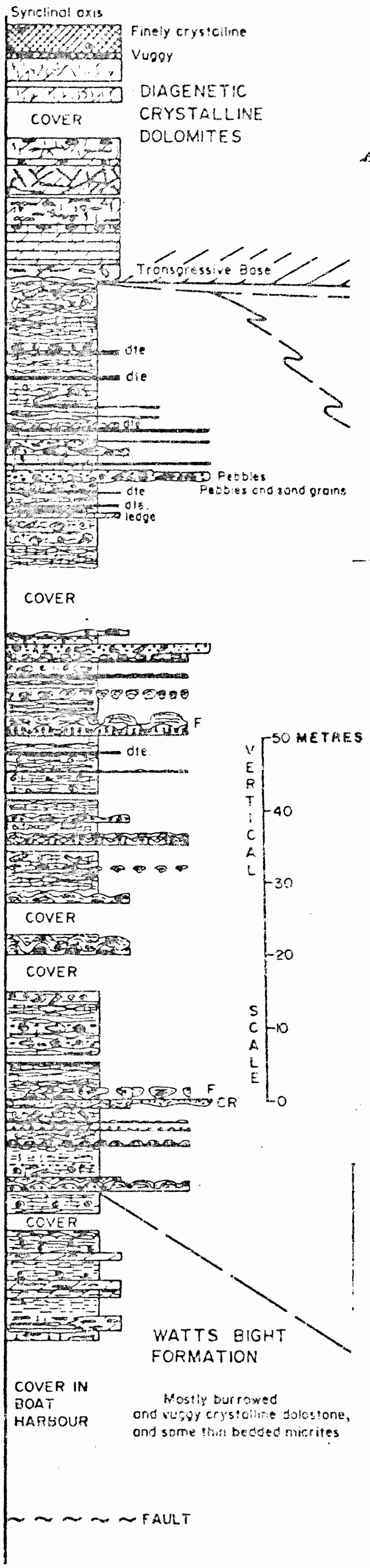
3c	Predominantly dolostone, some micrite, black crystalline limestones, stromatolites, no chert.
3b	Stromatolites, intraformational conglomerates, oolitic dolostones, dolostones.
3a	Thin bedded dolostone, some micrite, dolomitic and black crystalline limestone, stromatolites, occasional red and green shales with fauna, intraformational conglomerates.
2	MICRITE FORMATION: Highly burrowed to unburrowed, thin-bedded micritic limestones, some calcarenite, intraformational conglomerates; abundant fauna.
1	HAWKES BAY QUARTZITE FORMATION: White quartizte, thin bedded micrite, glauconitic sandstone, rusty burrowed, dirty sandstone (equivalent to Hawkes Bay Quartzite Formation).

Figure 23

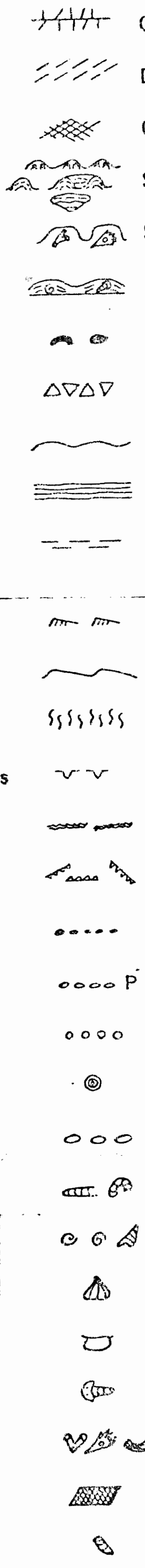
Local stratigraphy of Boat Harbour indicating fluorite occurrences.

(from Knight, 1977).

BOAT HARBOUR



LEGEND



Crystalline dolomitic limestones

Dolostone (all other units lacking this symbol are limestone)

Crystalline dolomite

Stromatolites

Sponge Mounds

Bio-micrite mounds

Chert

Breccia (usually secondary)

Erosional surfaces

Thin bedding, often lenticular or nobbly

Lamination

Cross Lamination

Ripple marks

Bioturbation or mottling

Mudcracks

Vugs or cavities

Veins

Intraclasts

P Pellets

Ooliths

Oncolites

Pebbles

Straight and semicoiled cephalopods

Coiled and spiral gastropods

Brachiopods

Ostracods

Trilobites

Sponges

Receptaculites

Crinoid Ossicles

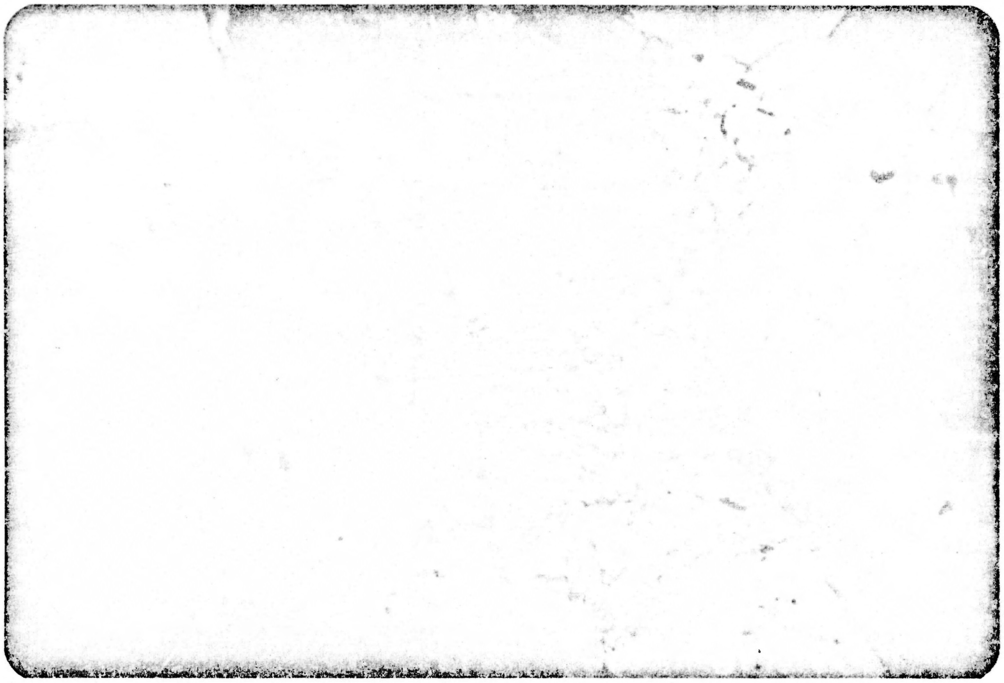
Abbreviations:

P	Pellets
CA	Calcarenite
CR	Calcirudite
dte	dolomitic
XB	Crossbedding
Sp	Sponge
F	Fluorite

Paragenesis - Boat Harbour

1. Preferential dolomitization of a burrowed limestone (of the Catoche formation) between stromatalitic micrite mounds to produce a lithology approaching a pseudobreccia.
2. Sparry white dolomite fills in open spaces (ie., fractures, vugs, cavities) of the dolomite host rock.
3. Fluorite deposition is the last phase of mineral deposition, filling in any remaining open spaces. (N.B. Fluorite did not proceed the sparry white dolomite because it occurs within the white dolomite and is not spatially related to the grey dolomite host).

The following Figures 24-26 are photographs of Boat Harbour samples which demonstrate the spatial relationship between the dark grey dolomite host rock, the sparry white dolomite, and the purple fluorite.



Daniel's Harbour

The carbonate succession in the Daniel's Harbour area includes the St. George Group and the overlying conformable Table Head Formation. The sphalerite mineralization occurs within the Massive Dolomite unit of the St. George Group.

The stratigraphic column as outlined by Fish (1974):

Table Head Formation
Disconformity (N.B. conformable Knight, 1977)
St. George Group
- Siliceous dolomite
- Dark-grey dolomite
- Grey dolomite
- Grey-tan dolomite
- Dolomitized limestone
- Razor limestone

The Massive Dolomite consists of three distinct lithologies: the Grey-tan pseudobreccia, the Grey pseudobreccia and the Upper dark-grey dolomite. The ore is contained in the Grey-tan and Grey pseudobreccias. It occurs as tabular, sub-parallel bodies of pseudobreccia 1 to 5 feet thick and laterally continuous over distances greater than 1,000 feet (Hartlein & Blecha, 1975). The pseudobreccia horizons alternate with 2 to 10 feet thick bands of the parent Grey-tan or Grey Dolomite. This cyclic alternation of pseudobreccia and massive dolomite suggests a bedding sequence; however, the pseudobreccias are not mechanical, but solution breccias (Fish, 1974; Hartlein & Blecha, 1975).

The ore is confined to the pseudobreccias and is absent from their massive dolomite counterparts, except for disseminated flecks and cross-cutting sparry white dolomite veins that originate from the pseudobreccias. This supports the theory that the sphalerite required pre-existing voids for deposition (Hartlein & Blecha, 1975).

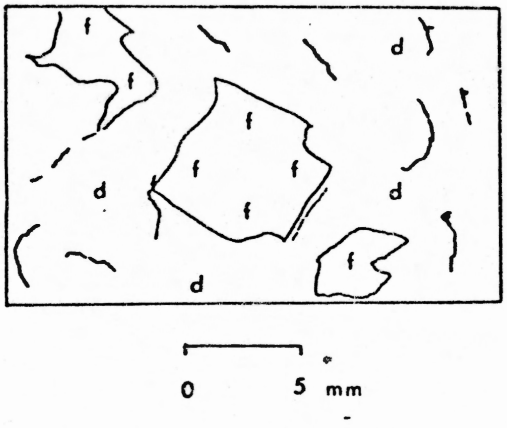


Figure 25 Sample SE - 1

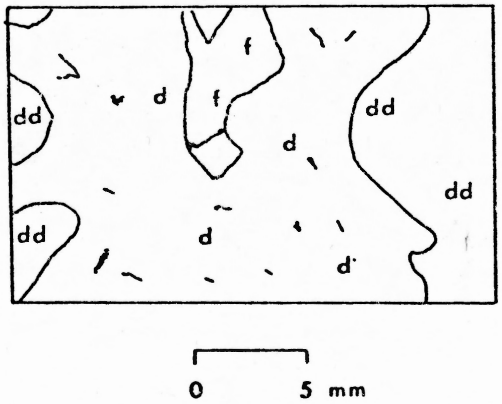


Figure 26 Sample SE - 3

Figures 24 - 26

Photographs of Boat Harbour samples which demonstrate the dark grey dolomite (dd), the sparry white dolomite (d) and the purple fluorite (f).

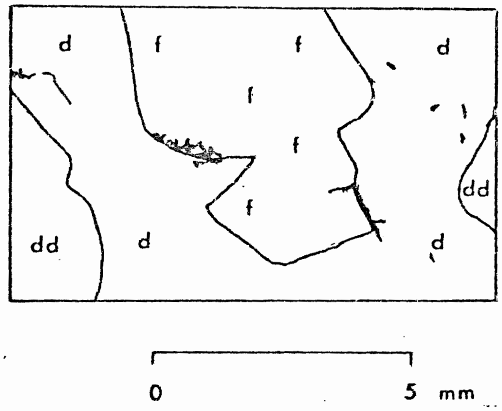


Figure 24 Sample SE - 2

The sphalerite ore is coarsely crystalline and forms in colloform masses. Trace minerals (less than one percent) include galena, pyrite and marcasite. The gangue consists of sparry white dolomite with traces of calcite and bituminous residue.

Paragenesis - Daniel's Harbour

1. Dolomitization of fine-grained unburrowed limestone and bioturbated limestone produced alternating tight, finely crystalline dolomites and vuggy, coarsely crystalline dolomites (Collins & Smith, 1975; Knight, 1977). This diagenesis produced a mottled dolomite.
2. Pseudobreccia formation by Karst solution - micrite dissolution and open space filling by sparry white dolomite (Collins & Smith, 1972; 1975).
3. Sphalerite preceeded white dolomite and grew in colloform fashion around dolomote mottles or nuclei (Collins & Smith, 1972).
4. Sphalerite emplacement was followed by that of white dolomote, which filled in open spaces (Collins & Smith, 1972).
5. A period of detrital sphalerite deposition occurred, filling in any remaining open spaces (Collins & Smith, 1972).

CHAPTER FIVE

Results

RESULTS

Sample Description

Boat Harbour, Newfoundland

Samples SE - 1, (SE - 1), SE - 2, SE - 3, and SE - 4 were all collected from the continuous flat-lying outcrop along the coast. The rock consists of a dark grey, finely crystalline, thinly laminated dolomite with sparry white dolomite filling fractures and cavities. The lithology can be described as approaching a pseudobreccia. Microprobe analysis has determined that the chemical compositions of the dark grey dolomite and the sparry white dolomite are fairly uniform (Table 2, Figure 29). The fluorite mineralization occurs within the sparry white dolomite (ie.,fluorite is surrounded by the dolomite). Fluorite crystals range from medium to dark purple and from 1 mm to 7 mm in diameter. The crystals are predominantly euhedral (cubic) with terminated faces (Figures 27, 28). Fluorite constitutes one to two percent of the rock. Microprobe analysis revealed the presence of minor disseminated pyrite $\ll$ one percent.

Daniel's Harbour, Newfoundland

The samples were collected in the Newfoundland Zinc Mine from the pseudobreccia horizon of the Grey Dolomite unit. The sphalerite is honey-orange, coarsely crystalline and comprises approximately 40 percent of the sample. Sparry white dolomite forms the gangue. Traces of black bituminous residue line vugs of sphalerite and sparry white dolomite.

Table 2

MICROPROBE ANALYSIS OF DARK GREY DOLOMITE AND SPARRY WHITE DOLOMITE BOAT HARBOUR

		(WT. %)
Dolomite Standard	Mg	13.10
	Ca	21.73
1. Dark	Mg	12.64
	Ca	21.24
2. White	Mg	12.79
	Ca	20.39
3. Dark	Mg	12.48
	Ca	21.21
4. White	Mg	12.64
	Ca	20.71
5. Dark	Mg	12.60
	Ca	21.71
6. White	Mg	12.65
	Ca	20.43

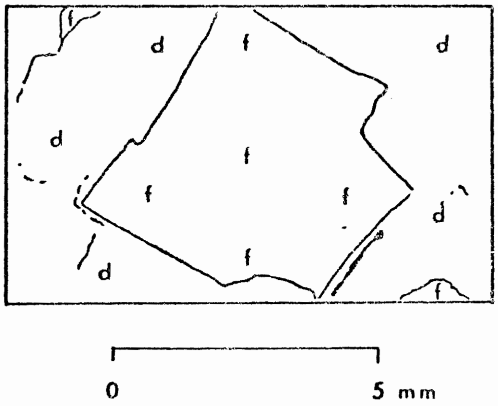


Figure 27 Boat Harbour fluorite (SE - 1)

- euhedral, cubic crystal with terminated crystal faces.

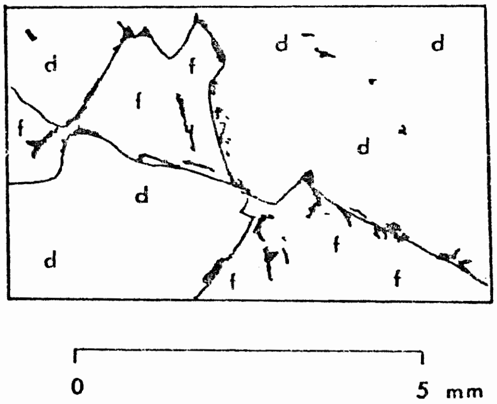
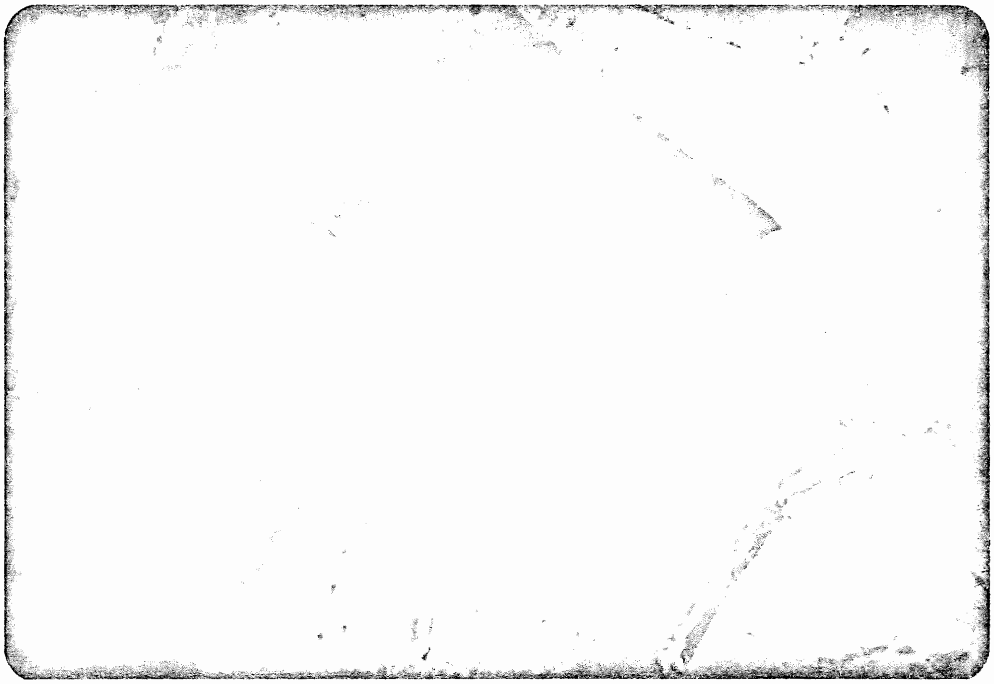


Figure 28 Boat Harbour fluorite (SE - 4)

- euhedral, cubic crystals.



Gays River, Nova Scotia

Samples ZGR - 1 and ZGR - 2 were collected from the upper levels of the decline at the Gays River Mine. The lithology is a "micritic skeletal dolomite" (MacEachern & Hannon, 1974). The rock consists of fossil shells bound within a matrix of finely crystalline grey micritic dolomite. Clear to white calcite is also present in minor amounts ($<$10 percent). Sphalerite, galena, and fluorite mineralization occurs in fenestral, interparticle and intraskeletal pore spaces - sphalerite 10 percent; galena 5 percent; fluorite 5 percent. The sphalerite is honey-yellow and occurs as anhedral crystal aggregates and disseminations in the rock. The galena and fluorite are similarly distributed. Average crystal size is 1-2 mm. Fluorite ranges in colour from transparent to purple.

Microprobe analysis of fluorite colour zonation in sample ZGR - 1 (Table 3, Figure 30) determined that the purple and clear zones had approximately identical chemical compositions (ie., the clear was not calcite). The dark grey dolomite also contained fluorite, suggesting that fluorite is perhaps more abundant than is apparent in visual inspection. The mine geologist at Gays River indicates that fluorite is a rare mineral (Bill Palmer, personal communication). However, since the fluorite occurs in colours other than purple (ie., black, clear), it may be overlooked.

Table 3

MICROPROBE ANALYSIS OF PURPLE-CLEAR-PURPLE ZONATION IN FLUORITE AND OF DARK GREY DOLOMITE ZGR - 1		
		(WT. %)
Calcite Standard	Ca	40.04
1. Purple	Ca	54.43
2. Clear	Ca	54.33
3. Clear	Ca	54.74
4. Dark Dolomite	Ca	53.27
5. Dark Dolomite	Ca	52.73

Composition and Structure

Calcite $CaCO_3$	Ca	40.0 wt.%
	CO_3	60.0 wt.%
Fluorite CaF_2	Ca	51.3 wt.%
	F_2	48.7 wt.%

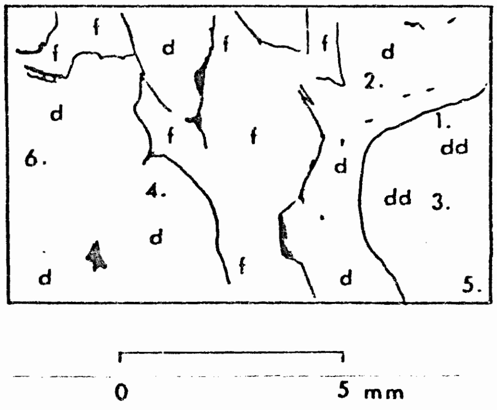


Figure 29 Boat Harbour fluorite (SE - 3)

- numbers 1 - 6 refer to microprobe analysis (Table 2).

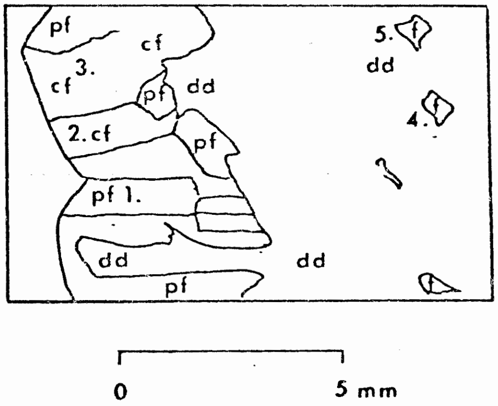
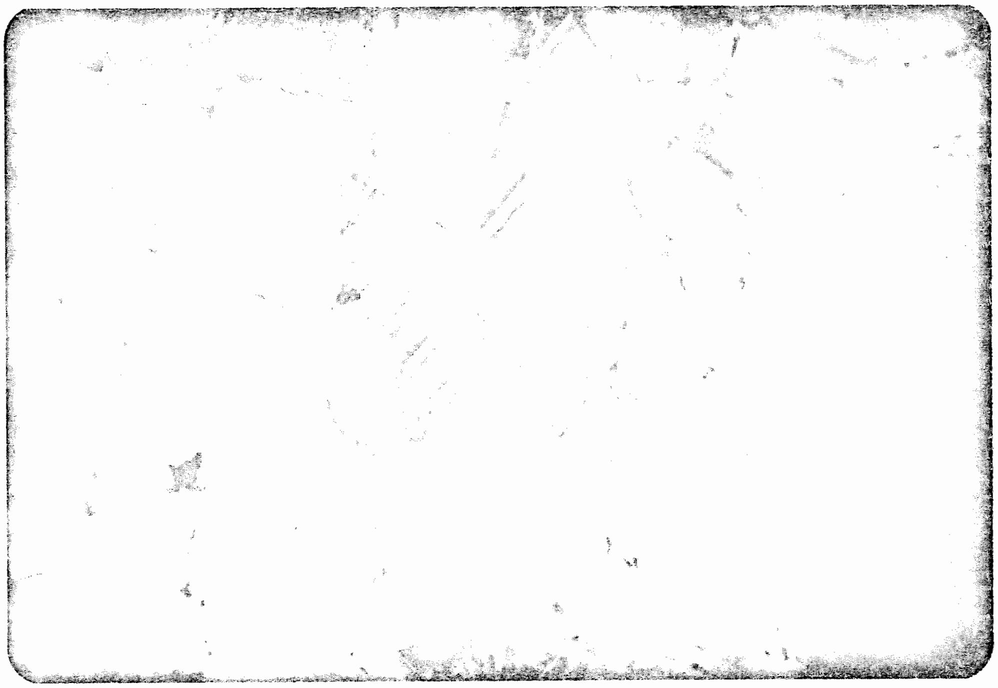


Figure 30 Gays River banded fluorite (ZGR - 1)

- (pf) is purple fluorite and (cf) clear fluorite. Numbers 1 - 5 refer to microprobe analysis (Table 3).



Laboratory Method

Sample Selection

Large crystal size aids in establishing the necessary criteria to determine fluid inclusion origin (ie., primary, secondary, pseudosecondary). Fluorite samples ranging from approximately 1 mm to 7 mm in diameter were examined from Gays River and Boat Harbour. Clear to white calcite from Gays River was also examined for fluid inclusions. The honey-orange sphalerite from Daniel's Harbour and the honey-yellow sphalerite from Gays River proved too opaque for fluid inclusion work. Irregularities within the sphalerite crystals also reduced their optical clarity.

Heating Procedure

Doubly polished plates (thin-sections) of approximately 1 mm in thickness were prepared. Hand polishing of the thin sections produced poor optical properties and necessitated the use of the index of refraction of fluorite n = 1.434. An approximate index liquid for fluorite is kerosene n = 1.45. The doubly polished samples prepared by machine yielded the most optimum optical properties.

Prior to heating and cooling experiments, the sample plates were photographed and then removed from the glass slides by dissolution of the epoxy (balsam) in acetone. The sample plates were then sectioned to fit into the heating and cooling stages.

The heating stage used in the experiments was built by Milton Graves (1976) and subsequently modified by Dr. M. Zentilli. A nickelchromium versus nickel-aluminum thermocouple was utilized. Calibration of the thermocouple against the known melting temperatures of organic compounds ensured accurate temperature measurements within the heating stage.

The inclusions were repeatedly taken through their homogenization temperatures so that a representative homogenization temperature could be determined. This involved a double run to confirm the initial result. An anomalous homogenization temperature would indicate previous rupturing of an inclusion.

Observations

All of the inclusions homogenized to a liquid phase, indicating that the fluid originally trapped in the inclusion was a liquid. Since many inclusions could be observed simultaneously, the range of homogenization temperatures could be obtained.

The homogenization temperature for Gays River fluorite was in the range 134° to 150° C; Gays River calcite in the range 170° to 174° C. The homogenization temperature for Boat Harbour fluorite was in the range 127° to 159° C.

The majority of inclusions from each deposit exhibited consistent homogenization temperatures, while a few did have scattered higher temperatures. Occasional higher temperatures may have resulted from leaking or stretching during sample preparation or during heating. The general rule that high temperature inclusions contain larger bubbles than low temperature inclusions (Roedder, 1972;1962), held true for the majority of the experiments.

The fluorite inclusions from Boat Harbour and Gays River had liquid-vapour densities in the range of 0.90 to 0.95. The overlapping temperature ranges for fluorite from Boat Harbour and Gays River demonstrate the relationship between bubble size and homogenization temperature. Calcite inclusions from Gays River with liquid-vapour densities of 0.90 had substantially higher homogenization temperatures than the fluorites (Figure 34).

Differences between primary, secondary and pseudosecondary inclusions were determined in the Gays River fluorite. Trails of inclusions occurring within the same plane yielded homogenization temperatures in the range 149° to 164° C in comparison to the overall average of 134° to 150° C. On the basis of criteria established by Roedder (1979) (Appendix 1), these inclusion trails were classified as secondary. Inclusions in Boat Harbour fluorite which showed anomalously high homogenization temperatures (ie., 170°C) were categorized as secondary. These data were excluded and the mean value calculated for n = 27 (Figure 32).

Overheating of fluid inclusions increases the pressure (vapour pressure of the water solution). The build-up of pressure in large inclusions or in planes of many small ones, causes a series of small explosions. The sample decrepitates or cracks. This phenomenon was recorded in several of the Boat Harbour fluorite samples: SE - 3 at 128° C, SE - 2 at 131° C. Decrepitation occurred along certain planes in the fluorite crystals. Fluids were observed moving within these planes (ie., looked like water moving under ice). In one instance, the explosion was so great that the entire sample chip shot out of field of view.

During the heating experiments some of the gas bubbles moved quickly back and forth or circled the perimeters of the fluid inclusions. Movement of the bubbles was also observed during photography of the inclusions. This type of movement has been termed "Brownian" (Roedder, 1962).

A small percentage of the inclusions from Gays River and Boat Harbour ($<$ 10 percent) possibly contained one solid phase (ie., daughter crystals). The existence of solid phases was not positively identified due to the small size. The "solids" appeared only as points of light due to the contrast of their index of refraction with that of the liquid.

Freezing Procedure

Depression of the freezing point of the fluid depends upon the salt concentration. The higher the salt concentration, the lower the freezing point of the fluid. This temperature was determined by freezing the inclusion solid, then gradually warming it while observing it through the microscope. Two freezing runs were conducted to verify results.

The fluid inclusions were frozen by a jet of compressed gas. The gas was cooled as it passed through piping immersed in liquid nitrogen. Each run was supercooled to -65° C.

The frozen mass of solid ice and salt crystals becomes opaque. The initial melting temperature occurs when the first of the solid components melts. A further increase in temperature melts more of the solids. The freezing temperature is that temperature at which the last ice crystals melt.

Theoretically, the freezing temperature should equal the temperature at which the first ice crystal forms on cooling (Roedder, 3). However, this is not the case. Mississippi Valley type inclusions commonly show gross supercooling (ie., the inclusions must be cooled considerably below their freezing point before the growth of ice crystals begins). Crystals containing salt crystals or other crystals exhibit supercooling. Due to the supercooling phenomenon, it was necessary to cool the inclusions to -65° C and then warm upwards to the melting point.

Observations

Daughter crystals (halite?) formed from the fluid during the cooling experiments. The frozen inclusions consisted of a granular mass of ice and salt crystals. Ice crystals were observed to nucleate around the gas bubble and then grow outward to fill the entire inclusion. Upon melting, the bubbles were liberated, moving around the inclusion in the fluids.

Photographic Procedure

The main objective of photography was to obtain clarity of image of the fluid inclusions which were situated at various depths within the fluorite crystals (ie., in various planes), while retaining some indication of external morphology.

The purpose of the entire plate photography was to demonstrate the spatial relationship between host rock, gangue and ore minerals. The paragenetic sequence could, therefore, be determined. Kerosene oil immersion was used in the photography of thin sections. Colour banding or growth zonation in sample ZGR - 1 (Figure 30) was of particular interest.

Figure 31

Histogram for frequency distribution of CaF_2 fluid inclusion temperature - Gays River, Nova Scotia.

n = 31
$\bar{x} = 142 \pm 8°$ C

$CaCO_3$ Gays River Mine, Nova Scotia
°C
173.5
172.0
173.0
167.0
172.0
173.0
171.0
171.5
174.0
177.0
174.0
169.0
173.5
171.5
170.0
n = 15 $x = 172 \pm 2°$ C

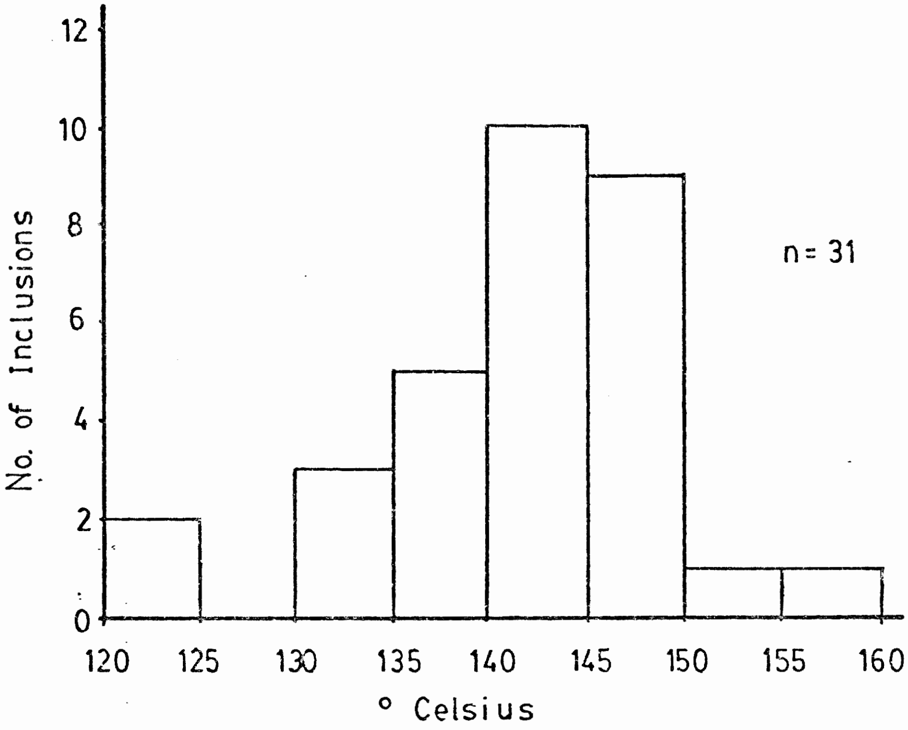

No. of Inclusions
0
2
4
6
8
10
12
n= 31
120
125
130
135
140
145
150
155
160
° Celsius

Figure 32

Histogram for frequency distribution of CaF_2 fluid inclusion temperature - Boat Harbour.

$n = 27$
$\overline{x} = 143 \pm 16\ °C$

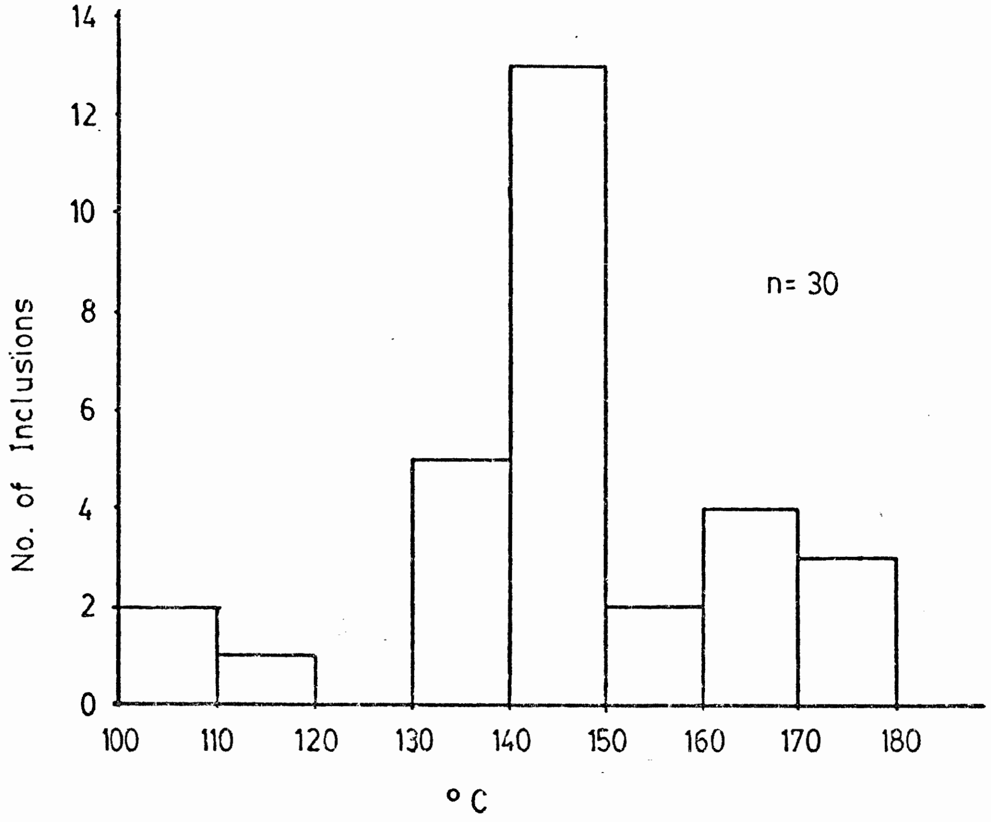

14
12
10
8
6
4
2
0
No. of Inclusions
n= 30
100
110
120
130
140
150
160
170
180
° C

Figure 33

Plot of the concentrative properties of aqueous NaCl solution.

(graphed from Table 53, Wolf & Brown, 1966).

Gays River	A.	-19° C initial melting	B.	-17° C initial melting
		-17° C total melting		-13° C final melting
		NaCl wt.% 20.4		NaCl wt.% 17.0
Boat Harbour	A.	-26° C initial melting	B.	-25° C initial melting
		-18° C total melting		-17° C final melting
		NaCl wt.% 21.2		NaCl wt.% 20.4

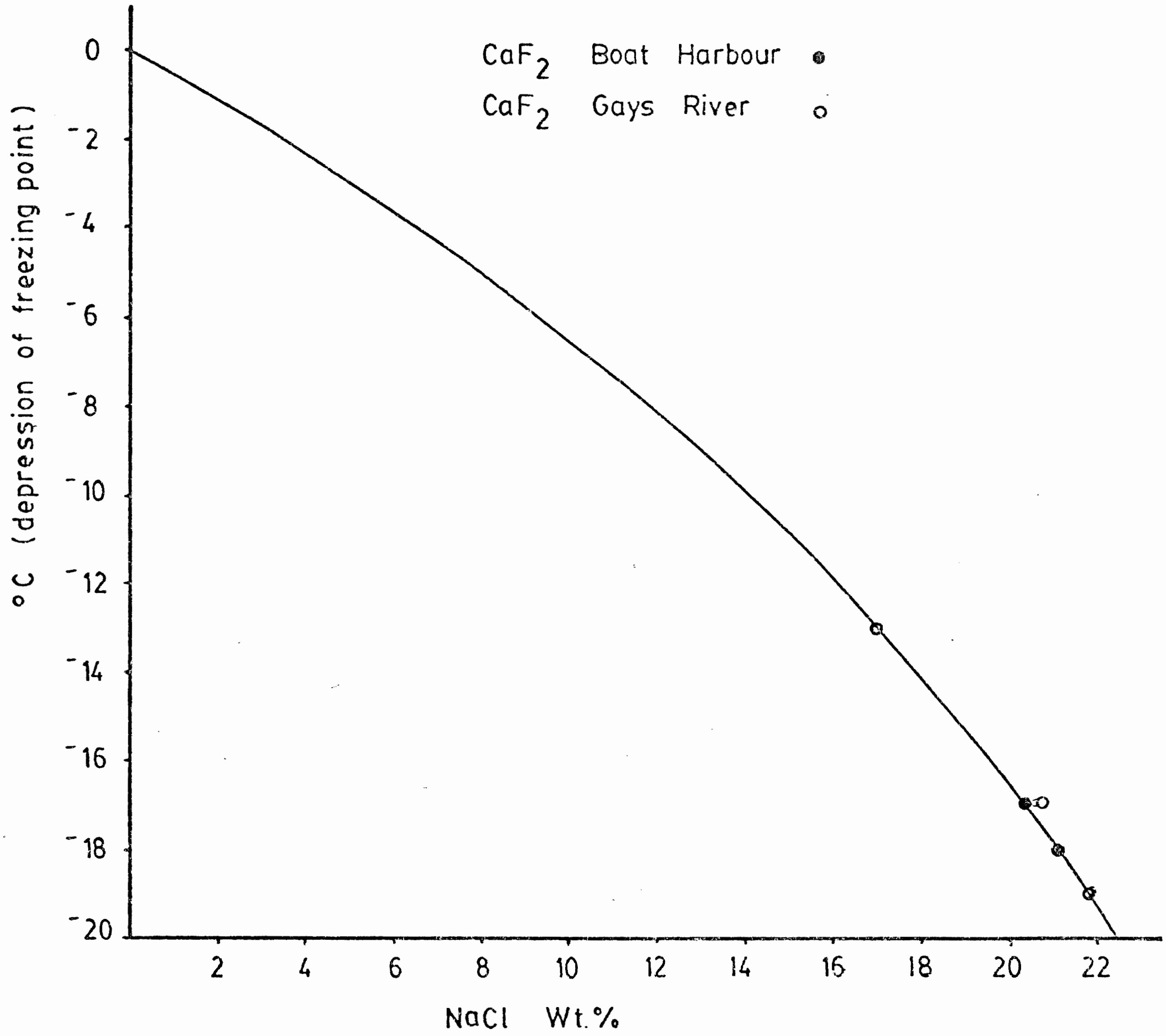
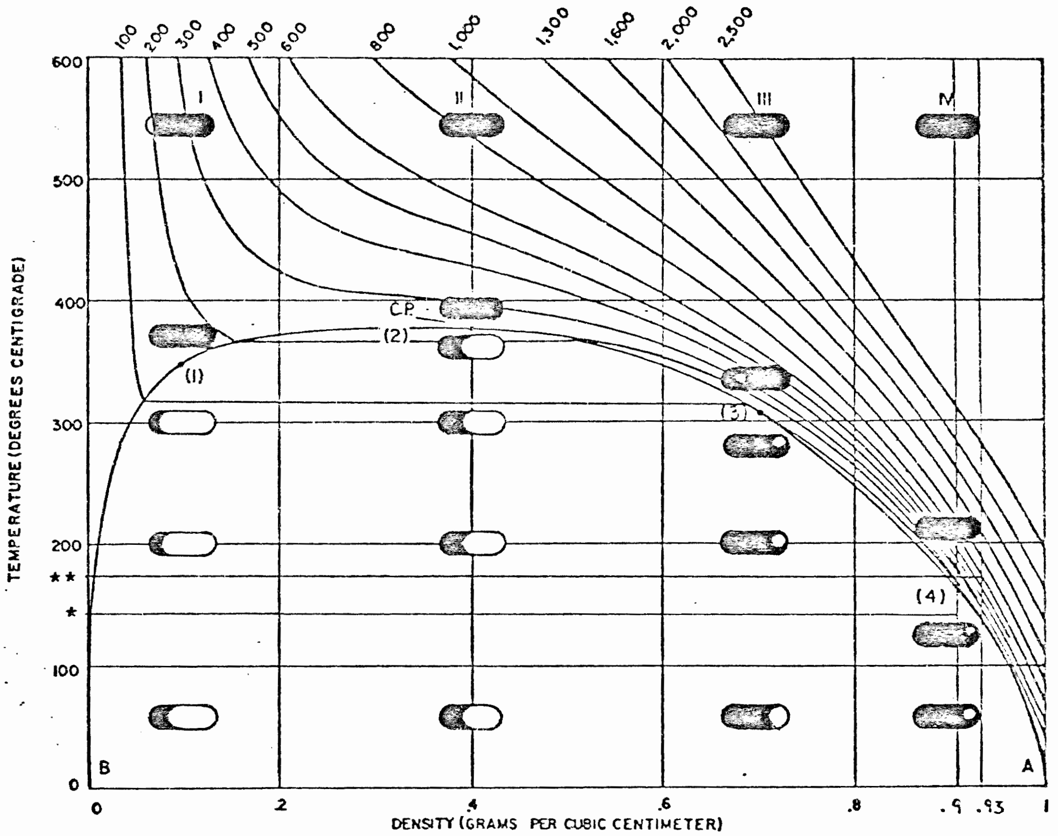

CaF$_2$ Boat Harbour ●
CaF$_2$ Gays River ○
°C (depression of freezing point)
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
2
4
6
8
10
12
14
16
18
20
22
NaCl Wt.%

Figure 34

Gays River calcite and fluorite liquid-vapour densities superimposed on diagram.

** calcite 172 ± 2° C

* fluorite 142 ± 8° C


100
200
300
400
500
600
800
1,000
1,300
1,600
2,000
2,500
I
II
III
IV
C.P.
(1)
(2)
(3)
(4)
B
A
600
500
400
300
200
**
*
100
0
TEMPERATURE (DEGREES CENTIGRADE)
0
.2
.4
.6
.8
.9
.93
1
DENSITY (GRAMS PER CUBIC CENTIMETER)

CHAPTER SIX

Discussion

DISCUSSION

Pressure Correction

In fluid inclusion geothermometry, corrections of homogenization temperature for pressure existing at the time of inclusion formation in the crystal are of great importance. As mentioned previously, the homogenization temperature represents the minimum temperature of formation. A confining pressure essentially decreases the size of the vapor phase (ie., the bubble becomes smaller) of the fluid inclusion, producing a lower homogenization temperature. Pressure corrections entail estimating the time of mineralization and the depth of burial (hence the pressure) at which the mineralization occurred.

Gays River, Nova Scotia

Pressure corrections may be required for the Gays River fluorite and calcite homogenization temperatures. The Gays River reef complex is Lower Carboniferous (Windsor) in age, and was deposited in the Maritimes Carboniferous Basin. At present, only 35-60 m of glacial till overlies the reef complex. However, the remainder of the Carboniferous may have been deposited over the reef complex and subsequently eroded away. Extrapolation of stratigraphy by Hacquebard (1964) indicates that approximately 3.6 kilometers of Upper Carboniferous terrestrial strata could have overlain the Gays River deposit.

The fluorite inclusions have liquid-vapor densities of 0.90 - 0.95 and the calcite inclusions have liquid-vapor densities 0.90 (Figure 34). Burial to 3.6 km depth by Upper Carboniferous sediments would produce approximately 350 atmospheres of hydrostatic pressure. Pressure correction of the fluorite is from 142 ± 8 ° C to 157 ± 8° C, and the calcite from 172 ± 2° C to 185 ± 2° C (Figure 35).

The Smithfield lead-zinc deposit, Middle Stewiacke, occurs in Windsor limestones and limestone conglomerates. Walker (1978) determined the mean temperature of formation for sphalerite, calcite and barite to be 138 ° C. Applying the same stratigraphic estimate of 3 to 4 kilometers to the Smithfield deposit, Walker (1978) calculated 1,000 atmospheres of lithostatic pressure. The resulting pressure correction for the mineralization was as high as 250 ° C.

If lithostatic pressure is calculated for the Gays River deposit, approximately 1,080 atmospheres would correct the homogenization temperatures of fluorite from 142 ± 8° C to 188 ± 8° C and the calcite from 172 ± 2° C to 228 ± 2° C (Figure 36).

In comparison to lithostatic pressure, the pressure of the overlying rock column, hydrostatic pressure assumes that pore fluids in the rock have free connections with the earth's surface ($P_{\text{hydrostatic}}$ $P_{\text{total (lithostatic)}}$). Hydrostatic pressure correction is the most realistic approximation for both the Gays River and Smithfield deposits, as only three to four kilometers of Carboniferous sediments may have overlain the two areas.

Review of Figure 37 shows that Mississippi Valley homogeniation temperatures are generally 100-150 ° C, and rarely as high as 200 ° C. The uncorrected values for Gays River and Smithfield fall well within the upper range of homogenization temperatures summarized in Figure 37. Hydrostatic pressure corrections for Gays River also fall within the upper range. Lithostatic pressure correction yields anomalously high homogenization temperatures and is the less acceptable correction method.

Hydrostatic pressure is applied on the assumption that the Upper Carboniferous was in fact deposited over the Windsor carbonates. There exists no definite evidence of this episode at Gays River. The second assumption involved is that the mineralization occurred after deposition of the Upper Carboniferous; whereas the mineralization may have been early epigenetic (ie., occurred prior to Upper Carboniferous deposition), or may have happened after the Upper Carboniferous was eroded away.

MacLeod (1975) states that sulfide mineralization at Gays River appears to closely follow dolomitization of the carbonates. Consequently, the mineralization is early epigenetic, and most probably occurred prior to deposition of the Upper Carboniferous.

Beales et. al. (1974) have dated Daniel's Harbour mineralization by paleomagnetism. The host and ore have statistically indistinguishable remnant magnetization, indicating that the ore emplacement is close, in geological terms, to the deposition of the host. The authors estimate that a time interval of less than 25 million years separates the formation of the host and ore.

Within this context, the early epigenetic mineralization at Gays River is presumably closely related in time with the formation of the host. It is, therefore, suggested that pressure corrections are not required, and that the previously determined homogenization temperatures for Gays River fluorite and calcite are representative.

Figure 35

A hydrostatic pressure correction of 350 atmospheres is applied to the Gays River calcite and fluorite having liquid-vapour densities of 0.90 and 0.93 respectively.

** calcite 185 ± 2° C

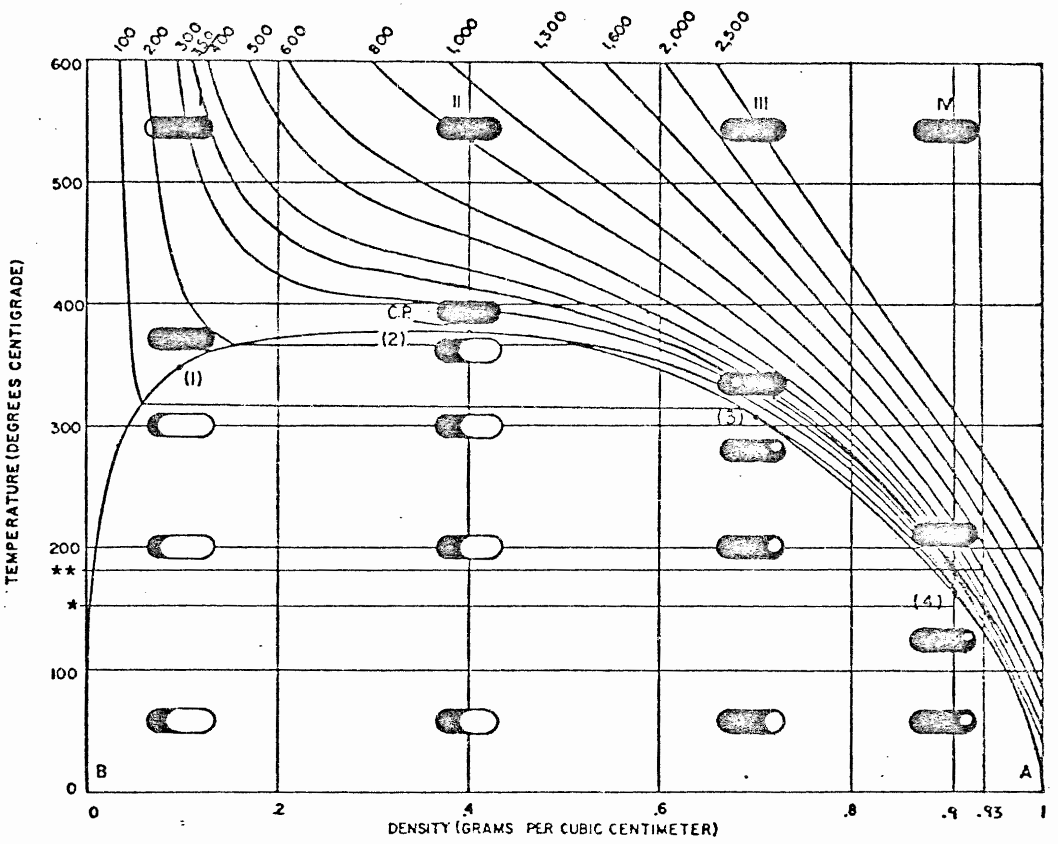
* fluorite 157 ± 8° C

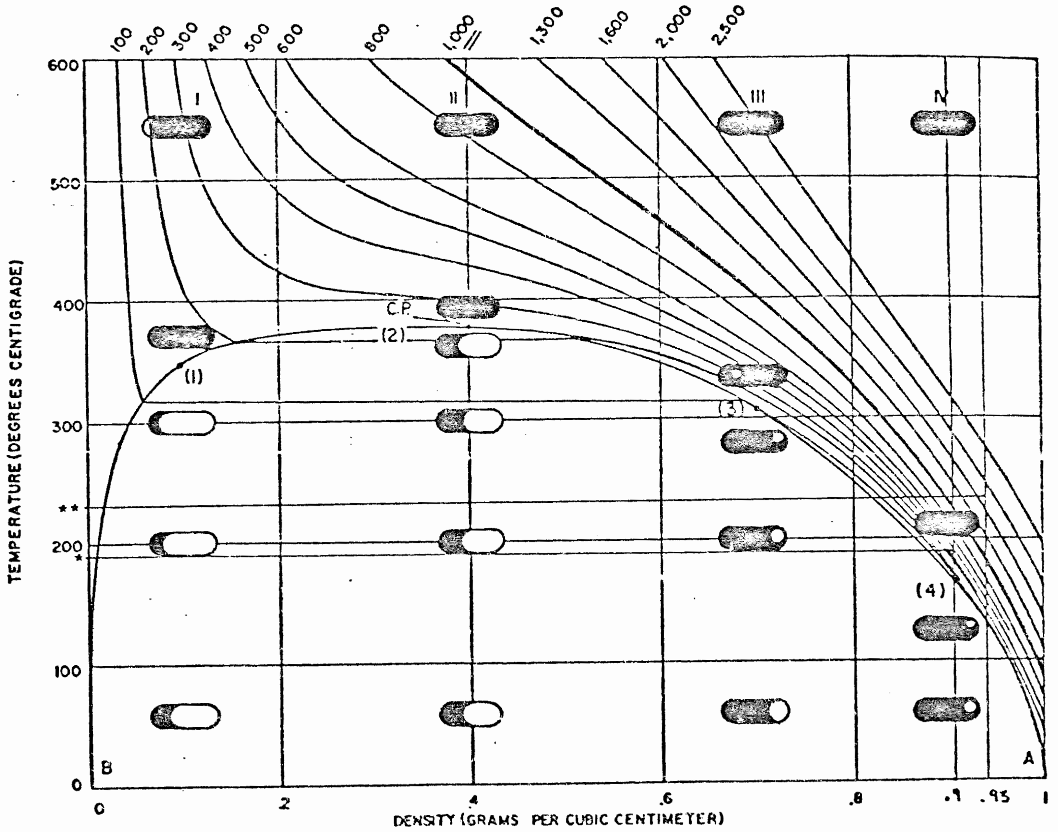
Figure 36

A lithostatic pressure correction of 1,080 atmospheres is applied to the Gays River calcite and fluorite having liquid-vapour densities of 0.90 and 0.93 respectively.

** calcite 228 ± 2° C

* fluorite 188 ± 8° C


100
200
300
350
400
500
600
800
1,000
1,300
1,600
2,000
2,500
I
II
III
IV
C.P.
(2)
(1)
(3)
(4)
600
500
400
300
200
**
*
100
0
TEMPERATURE (DEGREES CENTIGRADE)
B
A
0
2
.4
.6
.8
.9
.93
1
DENSITY (GRAMS PER CUBIC CENTIMETER)


100
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(2)
(1)
(3)
(4)
600
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400
300
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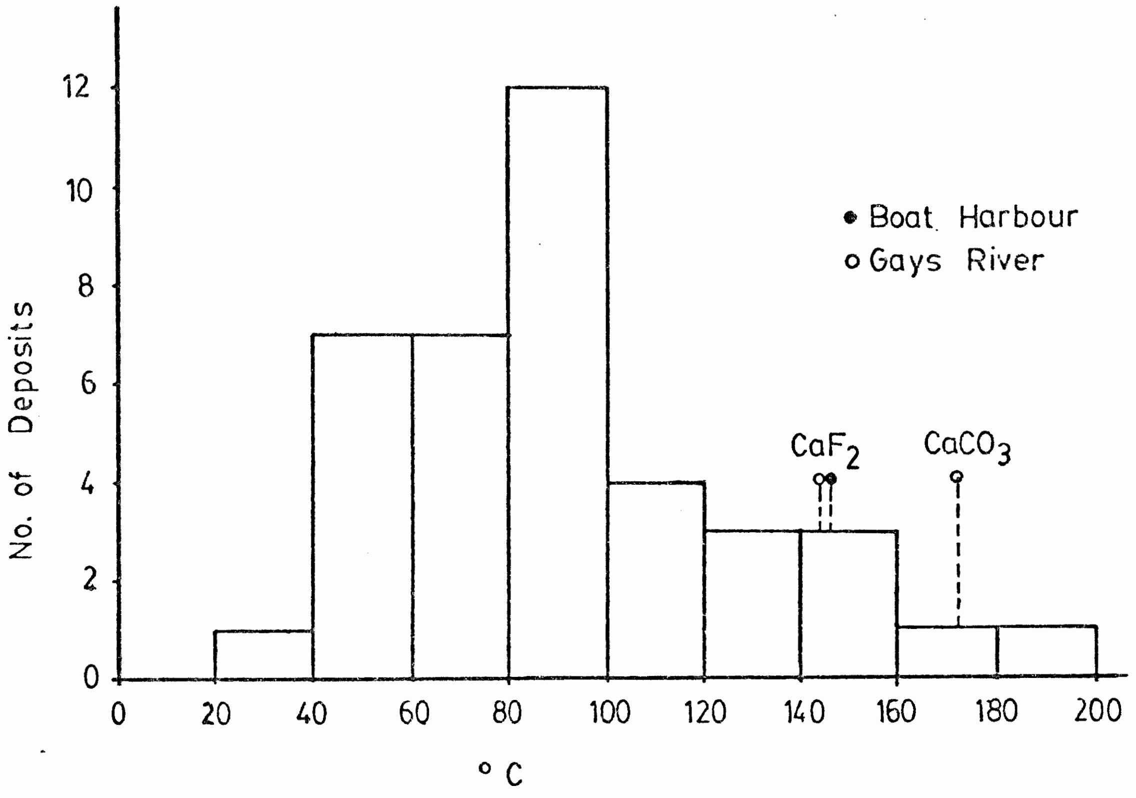
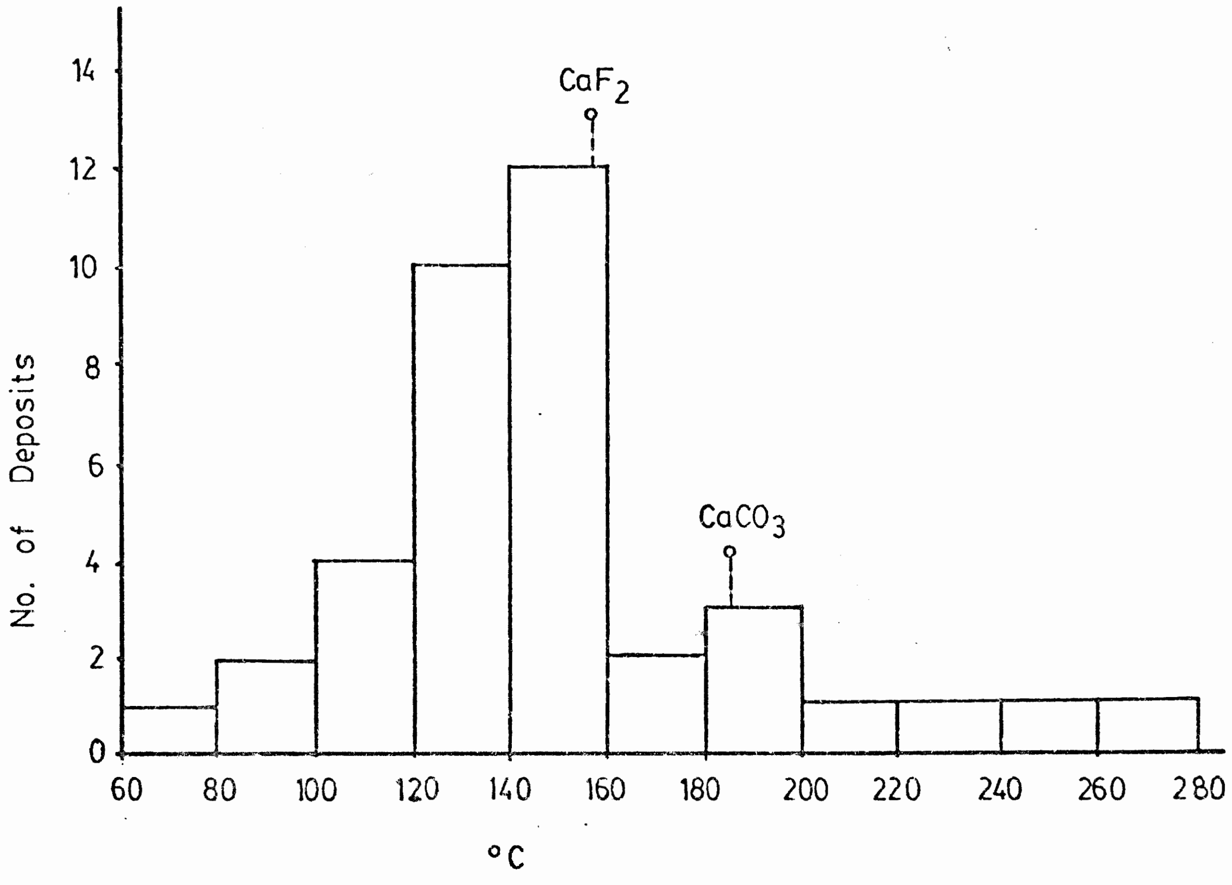
200
*
100
0
TEMPERATURE (DEGREES CENTIGRADE)
B
A
0
2
.4
.6
.8
.9
.93
1
DENSITY (GRAMS PER CUBIC CENTIMETER)

Figure 37

Minimum and maximum homogenization temperatures on inclusions in major Mississippi Valley type deposits and possibly related occurrences.

(graphed from Table IV, Roedder, 1976).


No. of Deposits
0
2
4
6
8
10
12
0
20
40
60
80
100
120
140
160
180
200
°C
● Boat Harbour
○ Gays River
CaF_2
$CaCO_3$


No. of Deposits
0
2
4
6
8
10
12
14
60
80
100
120
140
160
180
200
220
240
260
280
°C
CaF_2
$CaCO_3$

Boat Harbour, Newfoundland

Pressure correction for the homogenization temperature of the Boat Harbour fluorite is not necessary. As stated earlier, transported (heavy - such as ophiolitic rocks) sheets did not surpass or overlay the Boat Harbour area (S. Stouge, personal communication). The platform carbonates as such were unaffected by the westward moving Klippen. Rocks of Silurian, Devonian and Carboniferous age are absent from the Great Northern Peninsula (Fogwill, 1970). Carboniferous sediments are restricted to two long, relatively narrow troughs in west Newfoundland (Figure 21).

Stouge (1980) bases the above statement on colour changes in conodonts which reflect temperature increases. The author formulates a Conodont Alteration Index (CAI), which is an expression of temperatures induced on the host rocks by the amount of overload. The CAI at Boat Harbour is 1½: 50-90 ° C (Appendix 2).

Therefore, the homogenization temperature of 143 ± 16 ° C for fluorite mineralization represents a realistic temperature of formation.

Physical and Chemical Parameters

Pressure and temperature at the time of ore formation represent two important physical parameters to be considered. Fluid inclusions are successfully used as geobarometers and geothermometers. The salinity of the ore solution is essential in the determination of the chemical parameters of the geologic environment of trapping. The specific chemical constituents of the ore fluids, although frequently unknown, are fundamental in the overall understanding of hydrothermal ore-bearing solutions. Theoretical experimentation of fluorite in hydrothermal systems involves a restriction of the ionic species to facilitate interpretation.

Fluorite is sparingly soluble in water, more soluble in solutions containing sodium or calcium chloride, and very soluble in acid solutions (Richardson & Holland, 1979a). The amount of fluorite dissolved or precipitated is a function not only of the temperature, pressure and the ionic strength of a given hydrothermal solution but also of the pH and the ratio of the concentration of calcium and magnesium to that of fluoride ion in solution (Barnes, 1979).

During the formation of fluorite deposits, fluorite is precipitated either as a consequence of changes in temperature and pressure along the flow path of hydrothermal solutions or due to fluid mixing, or as the result of the interaction of hydrothermal solutions with wall rocks (Richardon & Holland, 1979b).

The quantity of fluorite that is precipitated increases with the salinity of the fluids. The salinity of Mississippi Valley type ore fluids usually exceeds 15 wt.% salts, and frequently exceeds 20 wt.% salts (Roedder, 1976).

Depression of the freezing point below $^{-}21.1°$ C, the temperature that pure NaCl can lower the freezing point, indicates the presence of other salts in solution. The absence of NaCl daughter crystals at room temperature in such salinities, also indicates salts other NaCl. Gays River salinities ranged from 17.0 to 20.4 wt.%; those of Boat Harbour from 20.4 to 21.2 wt.%. The exact composition of these salts is unknown. However, it can be assumed that since the mineralizing fluids were moving through dolomite ($CaMgCO_3$) host rock, $CaCl_2$ and $MgCl_2$ are probably present in solution.

Deposition of fluorite from the NaCl - $CaCl_2$ - $MgCl_2$ system is dependent upon the stability of the CaF^+, MgF^+, and NaF complexes, all of which become less stable with decreasing temperature (Richardson & Holland, 1979a). The solubility of fluorite increases with increasing magnesium and calcium concentration in solution.

With reference to the paragenetic sequence at Boat Harbour, the host rock was initially dolomitized and brecciated. Mineralizing solutions, perhaps originally NaCl in composition, entered the host rock, dissolving calcium and magnesium. Precipitation of sparry white dolomite, possibly due to fluid mixing, pH, temperature or pressure changes, decreased the solubility of fluorite. The interval between the precipitation of the sparry white dolomite and the fluorite was most likely accompanied by a temperature decrease. As mentioned previously, the presence of bituminous matter may be related to mineral precipitation in these types of deposits.

In the Gays River reef complex, dolomitization of the host rock occurred prior to mineral deposition. Fluorite occurs throughout the paragenetic sequence of sulfide metal deposition (Table1). It is found rimming sphalerite crystals. Fluid inclusion studies on sphalerite should, therefore, yield higher homogenization temperatures than those for fluorite. At Gays River, the homogenization temperature of calcite is 172 ± 2 ° C, whereas that for fluorite is 142 ± 8 ° C.

The saline hydrothermal solution was rich in lead, zinc, iron and fluoride. It probably increased in calcium and magnesium concentration during migration through the host rock. Precipitation of calcite out of solution at 172 ± 2 ° C effectively reduced the fluorite solubility. A decrease in the temperature of the mineralizing fluid followed, with the subsequent deposition of fluorite at 142 ± 8 ° C.

The hydrothermal solution at Gays River is chemically more complex than that of Boat Harbour, which precipitated only fluorite. Therefore, other unforeseen factors may have influenced the sequence and concentrations of mineral deposition.

Source of the Hydrothermal Solutions

The source of these heated brines remains in contention. White (1967) proposes that such brines are heated to high temperatures in adjacent basins and released into channel ways. The brines migrate to sites of ore deposition. This appears quite feasible for the Gays River deposit which is flanked by two thick units of salt-rich evaporites. The evaporites are believed by some to be the source of the mineralizing fluids. The presence of selenite, which crystallized out of a solution supersaturated from gypsum, supports this theory for Gays River (MacLeod, 1975). However, recent work on lead isotopes (Zentilli et. al., 1980) suggests that the lead in the Gays River deposit probably originated from the Ordovician basement rocks.

At Daniel's Harbour, Newfoundland, evidence implies the past existence of a now eroded evaporite sequence. No evaporites are associated with the platform carbonate rocks of the Great Northern Peninsula.

MacQueen (1976) indicates that sulfides could be precipitated in carbonate traps from oil-field brines through interaction with reduced sulfur (H_2S) from previously migrated oil and natural gas. Two oil showings occur on the carbonate platform in Newfoundland (Figure 21), but are not in close proximity to either Daniel's Harbour or Boat Harbour. Organic (bituminous) matter is present in the Gays River, Daniel's Harbour and Boat Harbour deposits.

CHAPTER SEVEN

Conclusions & Recommendations For Future Work

CONCLUSIONS

General

This thesis indicates that fluid inclusion studies of fluorite appear to provide a useful indication of the temperature and salinity of the hydrothermal solutions during late (post-ore) stages of mineralization in Mississippi Valley type deposits. Experimental data on the solubility of fluorite in the hydrous system NaCl - $CaCl_2$ - $MgCl_2$ is probably a relevant system to consider for the precipitation of fluorite from hydrothermal solutions migrating through dolomitized carbonates.

Gays River, Nova Scotia

1. The homogenization temperature of fluid inclusions in calcite from the Gays River base metal deposit averages 172 ± 2 ° C.
2. Fluid inclusion data for fluorite indicate an average homogenization temperature of 142 ± 8 ° C.
3. Calcite crystallized earlier than fluorite in the Gays River deposit; both calcite and fluorite appear to have crystallized later than the sulfides.
4. The salinity of the hydrothermal ore solution ranged from 17.0 to 20.4 wt. percent dissolved salts.
5. The hydrothermal solution originated either from the adjacent evaporite units or from the underlying basement rocks.

Boat Harbour, Newfoundland

1. The homogenization temperature of fluid inclusions in fluorite from the Boat Harbour fluorite occurrence averages 143 ± 16° C.
2. Sparry white dolomite precedes fluorite in the paragenetic sequence.
3. The salinity of the hydrothermal fluoride-bearing solution ranged from 20.4 to 21.2 wt. percent dissolved salts.
4. The source of the hydrothermal solution is not known.

RECOMMENDATIONS FOR FUTURE WORK

Temperature of formation and the salinity of the ore fluids represent two very important parameters in the evaluation of Mississippi Valley type deposits. The following studies would provide valuable data on the genesis of M.V.T.D.:

1. Fluid inclusion geothermometry should be performed on sphalerite from the Gays River deposit. It is predicted that the homogenization temperature for sphalerite should lie between those determined in this study for calcite (172 ± 2° C) and fluorite (142 ± 8° C).
2. The homogenization temperature of barite from the Gays River deposit should be determined and the results compared with values obtained by Walker (1978) for barite at the Smithfield deposit, Nova Scotia.
3. Fluid inclusion geothermometry should be performed on sphalerite and dolomite from the Daniel's Harbour Zinc mine. Results should be compared with those of Boat Harbour (this thesis).

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Appendix One

Criteria for the Origin of Fluid Inclusions

(Modified from Roedder, 1979)

Criteria for primary origin

1. Based on occurrence in a single crystal with or without evidence of direction of growth or growth zonation.
   - A. Occurrence as a single (or a small three-dimensional group) in an otherwise inclusion-free crystal
   - B. Large size relative to that of the enclosing crystal e.g., with a diamter~≥0.1 that of crystal, and particularly several such inclusions.
   - C. Isolated occurrence, away from other inclusions, for a distance of~≥5 times the diameter of the inclusion.
   - D. Occurrence as part of a random, three-dimensional distribution throughout the crystal
   - E. Disturbance of otherwise regular decorated dislocations surrounding the inclusion, particularly if they appear to radiate from it
   - F. Occurrence of daughter crystals (or accidental solid inclusions) of the same phase(s) as occur as solid inclusions in the host crystal or as contemporaneous phases.

2. Based on occurrence in a single crystal showing evidence of direction of growth:
   - A. Occurrence beyond (in the direction of growth), and sometimes immediately before extraneous solids (the same or other phases) interfering with the growth, where the host crystal fails to close in completely. (Inclusion may be attached to the solid or at some distance beyond, from imperfect growth).
   - B. Occurrence beyond a healed crack in an earlier growth stage, where new crystal growth has been imperfect.
   - C. Occurrence between subparallel units of a composite crystal
   - D. Occurrence at the intersection of several growth spirals, or at the center of a growth spiral visible on the outer surface.

E. Occurrence, particularly as relatively large, flat inclusions, parallel to an external crystal face, and near its center (ie., from "starvation" of the growth at the center of the crystal face), e.g., much "hopper salt".

F. Occurrence in the core of a tubular crystal (e.g., beryl). This may be merely an extreme case of previous item.

G. Occurrence, particularly as a row, along the edge from the intersection of two crystal faces.

3. Based on occurrence in a single crystal showing evidence of growth zonation (as determined by color, clarity, composition, X-ray darkening, trapped solid inclusion, etch zones, exsolution phases, etc.).

   A. Occurrence in random, three-dimensional distribution, with different concentrations in adjacent zones (as from a surge of sudden, feathery or dendritic growth).

   B. Occurrence as subparallel groups (outlining growth directions), particularly with different concentrations in adjacent growth zones, as in previous item.

   C. Multiple occurrence in planar array(s) outlining a growth zone (Note that if this is also a cleavage direction, there is ambiguity).

4. Based on growth from a heterogeneous (i.e., two-phase), or a changing fluid.

   A. Planar arrays (as in 3-C), or other occurrence in growth zones, in which the compositions of inclusions in adjacent zones are different (e.g., gas inclusions in one and liquid in another, or oil and water).

   B. Planar arrays (as in 3-C), in which trapping of some of the growth medium has occurred at points where the host crystal has overgrown and surrounded adhering globules of the immiscible, dispersed phase (e.g., oil droplets or steam bubbles).

   C. Otherwise primary-appearing inclusions of a fluid phase that is unlikely to be the mineral-forming fluid, e.g. mercury in calcite, oil in fluorite.

5. Based on occurrence in hosts other than single crystals.
   - A. Occurrence on a compromise growth surface between two nonparallel crystals. (These inclusions have generally leaked, and could also be secondary).
   - B. Occurrence within polycrystalline hosts, e.g., as pores in fine grained dolomite, cavities within chalcedony-lined geodes ("enhydros"), vesicles in basalt, or as crystal-lined vugs in metal deposits or pegmatites. (These latter are among the largest "inclusions" and have almost always leaked).
   - C. Occurrence in noncrystalline hosts (e.g., gas bubbles in amber; vesicles in pumice).

6. Based on inclusion shape or size.
   - A. In a given sample, larger size and/or equant shape.
   - B. Negative crystal shape -- this is valid only in certain specific samples and is a negative criterion in others.

7. Based on occurrence in euhedral crystals, projecting into vugs (suggestive, but far from positive).

Criteria for secondary origin

1. Occurrence as planar groups outlining healed fractures (cleavage or otherwise) that come to the surface of crystal (note that movement of inclusions with recrystallization can cause dispersion)

2. Very thin and flat; in process of necking down.

3. Primary inclusions with filling representative of secondary conditions.
   - A. Located on secondary healed fracture, hence presumably refilled with later fluids.
   - B. Decrepitated and rehealed following exposure to higher temperatures or lower external pressures than at time of trapping; new filling may have original composition but lower density.

Criteria for pseudosecondary origin

1. Occurrence as with secondary inclusions, but with fracture visibly terminating within crystal.

2. Generally more apt to be equant and of negative crystal shape than secondary inclusions is same sample (suggestive only).

3. Occurrence as a result of the covering of etch pits cross-cutting growth zones.

Appendix Two

GOVERNMENT OF NEWFOUNDLAND AND LABRADOR
DEPARTMENT OF MINES AND ENERGY

13 Febr., 1980 ST. JOHN'S

Susan R. Eaton
Department of Geology
Sir James Dunn Building
Dalhousie University
Halifax N.S. B3H 3J5

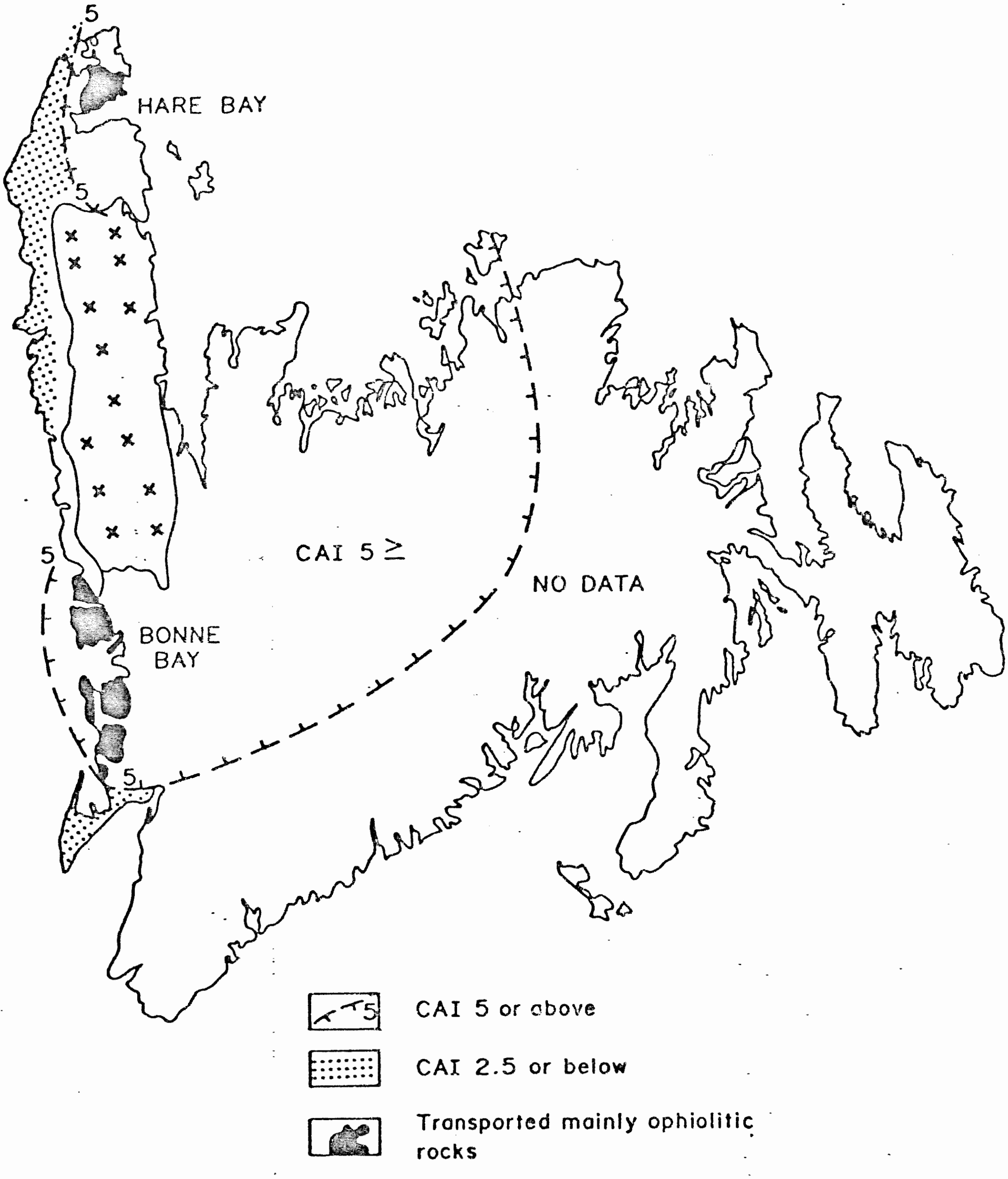
Dear Susan:
Thank you very much for your letter on your fluid inclusion geothermometry on the Daniels Harbour and Boat Harbour material. At this late stage of your thesis it must suffice for you to know that transported (heavy - such as ophiolitic rocks) sheets did not surpass or overlay the Daniels Harbour or Boat Harbour areas. Thus it should not be necessary for you to correct for pressure. Fault activities and secondary dolomitisation may have minor influences, but these parametres may be beyond the limit of resolution of your technique (?).

Personally, I have dealt with temperatures induced on the carbonates in the two areas. The technique is based on the color changes of conodonts (phosphatic microfossils of unknown zoological affinity). The conodonts change their color from amber to black with increasing temperature. This is called conodont alteration index (CAI), and it is an expression of temperatures induced on the host rocks by the amount of overload. CAI 1 indicate temperatures mainly below 50°C. CAI 1½: 50-90°C, CAI 2: 60-140°C CAI 3: 110-200°C, CAI 4: 190-300°C and CAI 5: over 300°C. The enclosed illustration indicate the distribution of CAI's in Newfoundland. For your specific information - the Daniels Harbour area has an CAI of 1-1½ and the Boat Harbour area is 1½.

I hope the information is in accordance with yours. I will be in Halifax to May, and would be interested to hear more about your results. Send my best wishes to Dr. R. Jamieson, and good luck with your thesis.

Yours

Svend Stouge
Project Geologist


5
HARE BAY
5
CAI 5 ≥
NO DATA
5
BONNE BAY
5
5
CAI 5 or above
CAI 2.5 or below
Transported mainly ophiolitic rocks

Appendix Three

CONCENTRATIVE PROPERTIES OF AQUEOUS SOLUTIONS

53 SODIUM CHLORIDE, NaCl

MOLECULAR WEIGHT = 58.45

RELATIVE SPECIFIC REFRACTIVITY = .797

A % by wt.	D^{20}_{20}	C_s g/l	M g-mol/l	C_w g/l	$(C_o - C_w)$ g/l	$(n - n_o) \times 10^4$	n	Δ °C	S g-mol/l
.00	1.0000	.0	.000	998.2*	.0	0	1.3330	.00	.000
.50	1.0035	5.0	.086	996.8	1.5	9	1.3339	.30	.086
1.00	1.0071	10.1	.172	995.3	3.0	18	1.3347	.59	.172
1.50	1.0107	15.1	.259	993.8	4.5	26	1.3356	.89	.259
2.00	1.0143	20.2	.346	992.2	6.0	35	1.3365	1.19	.346
2.50	1.0178	25.4	.435	990.6	7.6	44	1.3374	1.49	.435
3.00	1.0214	30.6	.523	989.0	9.2	53	1.3382	1.79	.523
3.50	1.0250	35.8	.613	987.4	10.8	61	1.3391	2.10	.613
4.00	1.0286	41.1	.703	985.7	12.5	70	1.3400	2.41	.703
4.50	1.0322	46.4	.793	984.1	14.2	79	1.3409	2.72	.793
5.00	1.0359	51.7	.885	982.3	15.9	88	1.3417	3.05	.885
5.50	1.0395	57.1	.976	980.6	17.6	96	1.3426	3.36	.976
6.00	1.0431	62.5	1.069	978.8	19.4	105	1.3435	3.69	1.069
6.50	1.0468	67.9	1.162	977.0	21.2	114	1.3444	4.02	1.162
7.00	1.0504	73.4	1.256	975.2	23.1	123	1.3453	4.36	1.256
7.50	1.0541	78.9	1.350	973.3	24.9	131	1.3461	4.70	1.350
8.00	1.0578	84.5	1.445	971.4	26.8	140	1.3470	5.05	1.445
8.50	1.0615	90.1	1.541	969.5	28.7	149	1.3479	5.41	1.541
9.00	1.0652	95.7	1.637	967.6	30.6	158	1.3488	5.78	1.637
9.50	1.0689	101.4	1.734	965.6	32.6	167	1.3496	6.10	1.734
10.00	1.0726	107.1	1.832	963.6	34.6	175	1.3505	6.54	1.832
11.00	1.0801	118.6	2.029	959.6	38.7	193	1.3523	7.33	2.029
12.00	1.0876	130.3	2.229	955.4	42.8	211	1.3541	8.16	2.229
13.00	1.0952	142.1	2.432	951.1	47.1	228	1.3558	9.03	2.432
14.00	1.1028	154.1	2.637	946.7	51.5	246	1.3576	9.93	2.637
15.00	1.1105	166.3	2.845	942.3	56.0	264	1.3594	10.88	2.845
16.00	1.1182	178.6	3.056	937.7	60.6	282	1.3612	11.88	3.056
17.00	1.1260	191.1	3.269	933.0	65.3	300	1.3630	12.93	3.269
18.00	1.1339	203.7	3.486	928.2	70.1	318	1.3648	14.04	3.486
19.00	1.1418	216.6	3.705	923.3	75.0	336	1.3666	15.21	3.705
20.00	1.1498	229.6	3.927	918.2	80.0	354	1.3684	16.45	3.927
22.00	1.1660	256.1	4.381	907.9	90.3	391	1.3721	19.18	4.381
24.00	1.1825	283.3	4.847	897.1	101.1	428	1.3758		4.847
26.00	1.1993	311.3	5.325	885.9	112.3	466	1.3796		5.325

H W (S + L)

(Table 53, Wolf & Brown, 1966)

Appendix Four

Homogenization and freezing temperatures on inclusions in major Mississippi Valley-type deposits and possibly related occurrences

District, mine, or occurrence*[1]	Homogenization temperature, °C			Freezing data*[14]			Reference
	minimum*[2]	maximum	accepted best range or value*[3]	minimum salinity*[2]	maximum salinity*[4]	accepted best range or value*[3]	
Aachen, West Germany, Zn	125	140					Roedder, unpublished data
Alabama, Ba	73	91					Hughes and Lynch (1973)
Bytom, Poland, Zn			100–120*[11]				Roedder, unpublished data
Cartagena, Spain, Pb–Zn				−7.9	−9.4	−9.2	Roedder (1963)
Central Kentucky, Zn	60	140	110	−2.5	−35	−15–20	Roedder (1971a)
Central Missouri, Ba–Pb–Zn	80	110		−10	−24	−22	Leach (1973)
Central Tennessee, Zn	50	140	110	−7.5	−30	−20	Roedder (1971a)
Central Tennessee, Zn	64	151	90–120				De Groodt (1973)
Derbyshire, England, F	70	140		−15	−22		Ford (1969)
				−13	−23	−15–20	Roedder (1967b)
East Tennessee, Zn	100	280*[6]	194*[6]				Miller (1969)
	60	175*[6]	100–150	−7.5	−32	−10–30	Roedder (1963, 1971a)
	89	135	114				Larson et al. (1973)
Friedensville, Pa., Zn				−12	−26		Roedder (1967b)
Guatemala, Pb–Zn	50	150					Kesler and Ascarrunz-K (1972)
Hansonburg, N. Mex., Pb–Ba–F	140	195	160–180	−7	−13	−10	Roedder et al. (1968)
Ireland, Keel mine, Pb–Zn	176	185		−7.3	−8.0		Roedder, unpublished data
Ireland, Keel mine, Pb–Zn			175				Patterson (1970, in Morrissey et al., 1971)
Ireland, Mogul, Pb	150	275	225				Greig et al. (1971)
Ireland, Silver mines, Pb–Zn	190	250					Greig et al. (1971)
Laisvall, Sweden, Pb	83	223*[6]	100–150	−19.7	−1.05*[7]	−23–27	Roedder (1968c)
Missouri, Ba–Zn	<50*[13]	115		(5–10)*[15]	(23)		Leach (1971)
Missouri, Pb–Zn–Ba	<40*[15]	110		(4–10)*[15]	(>22)		Leach (1973)
New Lead Belt, Missouri, Pb	82	145	90–120	−10.6	−28.2	−22	Roedder, unpublished data
Northern Arkansas, Zn	83	132			(>22)		Leach (1973)
Northern Arkansas, Ferndale limestone*[16]	85	170	110–150	(5)	(25)		Nelson (1973)
Northern Arkansas, Rush Creek, Zn	114	169*[17]					Potter (1970)
North Pennines, England, Pb–Zn–F	88	150					Harker (1971)
North Pennines, England, Pb–Zn–F	99	205	130–160	−17.2	−21		Sawkins (1966)
North Pennines, England, Pb–Zn–F				−17	−24	−20	Roedder (1967b)
Picher (Tri-State) Pb–Zn				−23.0	−23.4		Roedder (1963)
Picher (Tri-State) Pb–Zn	115	135					Newhouse (1933)
Picher (Tri-State) Pb–Zn	83	120					Schmidt (1962)
Pine Point N.W.T., Can., Pb–Zn	51	97		−12	−35*[8]	−25	Roedder (1968a)
Polaris deposit, N.W.T., Can., Pb–Zn	52	131	52–105				Jowett (1972)
Santander, Spain, Pb–Zn				−12.5	−12.9		Roedder (1963)
Sardinia, Litopone Ba			<40*[12]				Roedder, unpublished data
Southeast Missouri Pb belt				−6.5*[5]	−23.5*[5]		Roedder (1967b)
Southern Illinois, F–Pb–Zn	84*[10]	172	140				Grogan and Shrode (1952)
Southern Illinois, F–Pb–Zn	122	144	130				Pinckney and Rye (1972)
Southern Illinois, F–Pb–Zn	70*[10]	129					Freas (1961)
Southern Illinois, F–Pb–Zn	139	153	142–145				Roedder et al. (1963)
Southern Illinois, F–Pb–Zn				−15.6	−19.0		Hall and Friedman (1963)
Southern Illinois, F–Pb–Zn				−14.5	−23.4	−15–20	Roedder (1963, 1967b)
Sweetwater, Tenn., Ba*[9]	109	198					Nadeau (1967)
Sweetwater, Tenn., Ba*[9]	52	130	96	−5	−11		Roedder (1967b, 1971a)
Timberville, Va., Zn	140	150		−13	−23		Roedder (1967b, 1971a)
Tri-State Pb–Zn	83	120			(>22)		Leach (1973)
Upper Miss. Valley, Pb–Zn	80	105					Newhouse (1933)
Upper Miss. Valley, Pb–Zn	75	121					Bailey and Cameron (1951)
Upper Miss. Valley, Pb–Zn				−2.9*[5]	−3.1*[5]		Hall and Friedman (1963)
Upper Miss. Valley, Pb–Zn	46*[5]	74*[5]					Erickson (1965)
Upper Miss. Valley, Pb–Zn						−20	Roedder (1967b)

*[1] See original reference for details on samples, locality and geology; only data on sphalerite, fluorite, or barite are listed unless otherwise stated; no data on decrepitation listed.

*[2] Data on *known* secondary inclusions are excluded.

*[3] Given only where appropriate.

*[4] As −21.1° is the minimum liquidus temperature (eutectic) in the system NaCl–H_2O, temperatures below this must have salts other than NaCl.

[*5] Late calcite only.

[*6] This has been shown to be incorrect – see Larson et al. (1973).

[*7] This inclusion had a $NaCl \cdot 2H_2O$ liquidus, hence, it was very strongly saline.

[*8] Some as high as –10° had a $NaCl \cdot 2H_2O$ liquidus and hence were very strongly saline.

[*9] Data only on fluorite cogenetic with barite.

[*10] Oil inclusions.

[*11] Estimated, from tiny oil inclusions in sphalerite and brine inclusions in associated carbonates.

[*12] Estimated, as all inclusions are full of liquid at room temperature.

[*13] This temperature obtained only on calcite and barite; sphalerite temperatures were 108–115°.

[*14] Values in parentheses are salinities (NaCl % equiv.).

[*15] Low values obtained on barite.

[*16] Possibly the same brine that formed the northern Arkansas zinc district?

[*17] These homogenization temperatures are believed to be approximately 30°C too high, because of thermal gradients in the heating stage (R.W. Potter, personal communication, 1974).

(Table IV, Roedder, 1976)