GEOLOGIC. FLUID INCLUSION

AND STABLE ISOTOPE STUDY

OF A CARBONATE-HOSTED

LEAD DEPOSIT AT PEMBROKE

(GLENBERVIE), COLCHESTER

COUNTY, NOVA SCOTIA

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Mark Anthony Peter Ponsford

Submitted in partial fulfillment of the requirements for the degree of Bachelor of Science (Honours)

DALHOUSIE UNIVERSITY
HALIFAX, NOVA SCOTIA, CANADA
APRIL 25, 1983



DALHOUSIE UNIVERSITY

Department of Geology

Halifax, N.S. Canada B3H 3I5

Telephone (902) 424-2358 Telex: 019-21863

DALHOUSIE UNIVERSITY, DEPARTMENT OF GEOLOGY

B.Sc. HONOURS THESIS

Author: Mark Anthony Peter Ponsford

TITLE: GEOLOGIC, FLUID INCLUSION AND STABLE ISOTOPE STUDY OF A CARBONATE - HOSTED LEAD DEPOSIT AT PEMBROKE (GLENBERVIE), COLCHESTER COUNTY, NOVA SCOTIA.

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The Pembroke (also Glenbervie) prospect is a carbonate-hosted lead deposit located at 45°17'05" North Latitude and 62°56'15" West Longitude in Colchester County, Nova Scotia. The deposit is stratabound within the Macdonald Road Formation limestone of the Lower Carboniferous Windsor Group, a sequence of cyclic marine carbonates, evaporites and red-beds. Coarse-grained galena occurs in calcite veinlets as well as filling interskeletal and intraskeletal pores created by abundant fossil brachiopods.

Homogenization temperatures obtained from fluid inclusions in mineralized calcite indicate that the minimum temperature of crystallization was 214.8°C.

Oxygen and carbon isotope data for mineralized calcite indicate mean values of $\int_{SMOW}^{+} 19.08_{SMOW}$ and $\int_{PDB}^{+} 1.38_{PDB}$ respectively. Mineralization resulted in isotopic exchange, lowering the original ^{18}O and ^{13}C values of the host limestone.

The mineralizing event probably occurred during the Maritime Disturbance (Pennsylvanian) when high geothermal gradients accompanied the dewatering of evaporites, the resulting brines leaching the underlying Ordovician metasediments and transporting metals to favourable sites of deposition along the Horton-Windsor contact.

ACKNOWLEDGMENTS

I am grateful to my supervisor, Dr. Marcos Zentilli, who gave his time and provided valuable assistance and constructive criticism on this thesis. The assistance of Dr. Sam Akande, Dr. F. Medioli, Dr. G. C. Milligan, Dr. Paul Schenk and Mr. Gordon Brown was greatly appreciated. I am also grateful to Dr. Peter Reynolds for the many hours he spent analysing the samples and for his help with interpreting the data. My sincere thanks go to John Macleod and Esso Minerals Canada who made the thesis possible by allowing full access to their files and granting permission to sample and study the cores.

CHAPTER 1 INTRODUCTION

The occurrence of galena at Pembroke has been known for many years but the origin of the deposit is poorly understood. The structural geology and stratigraphy of the area provide important controls on the extent and distribution of mineralization. A map of the structural geology of the area was modified from work done by J. Macleod (1979) in light of new information from diamond drill holes and reinterpretation of air photograghs. Eleven diamond drill hole cores were relogged by way of permission from Esso Minerals Canada Ltd.. Diamond drill hole GB-15 best represents the complete stratigraphy of the area. Fourteen samples of representative rock units were taken from this drill core and these were slabbed and polished in an attempt to better define the stratigraphic sequence of the faulted and folded rocks of the map area.

The fossil assemblage of the mineralized carbonate at Pembroke was determined by the author in order to positively identify and correlate this limestone formation.

Fluid inclusion geothermometry and stable isotope work was conducted to determine the temperature and nature of mineralizing fluids at the deposit in an attempt to construct a genetic model for ore deposition.

1.1 General Statement

This study describes the geological setting, mineralogy, fluid inclusion geothermometry and carbon and oxygen isotope composition of the carbonate-hosted Pb deposit at Pembroke. An attempt is made to explain the genesis of the deposit in terms of the evolution of the Carboniferous basin.

1.2 Location and Access

The Pembroke Pb prospect is located 130 kilometres by road NE of Halifax at 45° 17' 05" North Latitude and 62° 56' 15" West Longitude in Colchester County, Nova Scotia (figure 1.1). Access can be gained by travelling 90 kilometres north from Halifax to Brookfield on route 102. Take exit 12 east at Brookfield on route 289 and travel 30 kilometres to Stewiacke Cross Roads. The prospect is located 6 kilometres north of Stewiacke Cross Roads near the village of Pembroke (Glenbervie). The area is easily accessible over paved, secondary and bush roads.

1.3 History and Previous Work

The lead showing at Pembroke has been known since before 1877, when it was mapped by Hugh Fletcher of the Geological Survey of Canada. Before 1931, many test pits, trenches and one shallow shaft with tunnels were dug on the property. In 1931, a sample of several tons

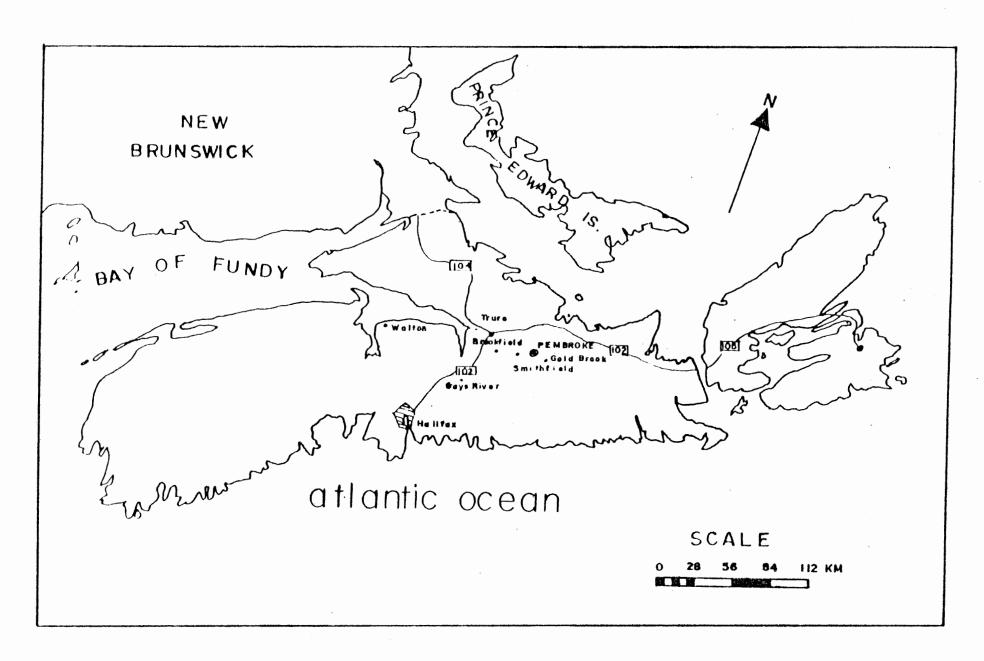


Figure 1.1 Location of the Pembroke deposit.

of limestone from the dump was taken and found to average 13.7% Pb. In 1952, Minda Scotia, a subsidiary of Mindus Corporation, drilled 3 holes directly over the mineralization. Dome Exploration drilled 5 holes (NS series) in the area in 1959. The area was mapped at a scale of 1:63,360 by D. G. Benson of the Geological Survey of Canada in the following year. Canex Aerial Exploration Limited carried out geochemical soil sampling, geological mapping and a resistivity survey over the area in 1974. During 1974-1975, Amax Exploration Inc. drilled 5 holes (G series). In 1976, Esso Minerals Canada Ltd. carried out reconnaissance geology and geochemistry and in 1977 drilled 4 holes (GB-15 to GB-18). Esso drilled 6 more holes (GB-19 to GB-25) on the property in 1978. The area has recently been mapped by P. S. Giles and R. C. Boehner of the Nova Scotia Department of Mines and Energy on a scale of 1:50,000.

1.4 Objectives and Scope

The purpose of the thesis was to describe and document the structural geology, stratigraphy, mineralogy and ore paragenesis of the deposit. Fluid inclusion geothermometry was conducted with the intent of determining the temperature of ore deposition. Carbon and oxygen isotope study was undertaken with the aim of gaining a better understanding of the isotopic history and possible origin of the mineralizing fluids. An interpretation of the depositional history

of the host rocks, however, was beyond the scope of the present study.

1.5 Physiography and Air Photograph Interpretation

Relief in the area is gentle with a maximum elevation difference of 50 metres. The Pembroke River flows from higher ground in the north and empties into the Stewiacke River, located further south of the map area. Glacial till, averaging 40 metres in thickness, blankets the map area, making outcrops scarce and rendering exploration difficult. Geological units, however, are easily recognizable on air photographs by differences in elevation and/or vegetative cover. Swampy lowlands and karst topography often define the presence of carbonates and evaporites. Sink holes are only developed in thick sequences of gypsum or anhydrite. These sink holes are not necessarily recent features. Akande (1982) has demonstrated that sink holes bordering the Gays River Pb-Zn mine, located only 40 kilometres to the SW, are Early Cretaceous in age.

The linear path of streams and the presence of lineaments on air photographs indicate the position of geological contacts and faults. Three major sets of faults strike approximately 30°NE, 60°NE and 80°NE.

Synclines of the folded Carboniferous strata form ridges which roughly trend from NW to SE.

CHAPTER 2 GEOLOGY AND STRATIGRAPHY

- 1 Regional Geology

Pre-Carboniferous basement rocks in the region include slates and quartzites of the Ordovician Meguma Group which have been intruded by granitic plutons of unknown age, the nearest of which lies 11 kilometres east of the prospect. The Meguma Group metasediments outerop 5 kilometres southeast of the prospect where a northeast trending ridge, termed the Wittenburg Massif, presently separates two Carboniferous basins of deposition. Wittenburg Massif parallels the strike of the Meguma sediments, which were intensely folded and metamorphosed to greenschist facies during the Acadian Orogeny (Devonian). Two Carboniferous depositional basins, the Shubenacadie in the north and the Musquodoboit in the south, form part of a complex rift valley system, the Fundy Basin, which was probably formed by basement subsidence and block faulting (Schenk, 1967).

Within the Shubenacadie Basin, red and grey siltstones, shales, sandstones and conglomerates of the Lower Carbon-iferous Horton Group unconformably overlie the Meguma Group basement. These terrestrial sediments have been partly derived from the Meguma Group metasediments (Bell, 1929) and may have been specifically derived from the Wittenburg Massif (Benson, 1960). The Horton Group attains

a maximum thickness of 1.3 kilometres (Bell, 1929).

Cyclic marine carbonates, evaporites and red beds of the Windsor Group (Lower Carboniferous) lie concordantly on the Horton Group clastics (Giles, 1979). A significant diastem exists between the Horton and Windsor Groups (Giles, 1979). The maximum thickness of the Windsor Group in the Shubenacadie basin is 762 metres (Giles, 1979).

The Pembroke prospect is located on the northeastern edge of the Shubenacadie Basin, near the contact between Horton and Windsor Groups. Windsor Group carbonate is the host for galena mineralization.

Grey mudstone and shale with intercalated gypsum, anhydrite and halite of the Canso Group (Upper Carboniferous) conformably overlie the Windsor Group. The Canso Group, however, is not present within the immediate study area. A table of formations taken from Giles and Boehner (1978) is presented in figure 2.I.

In general, Carboniferous strata are gently folded and intensely faulted.

2.2 Paleontology of Mineralized Carbonate

The fossil content of the limestone at the Pembroke deposit was identified by the author and placed into the faunal range chart (figure 2.2) proposed by Bell (1929) and revised by Moore and Ryan (1976). It should be stressed that the faunal range chart does not represent the age

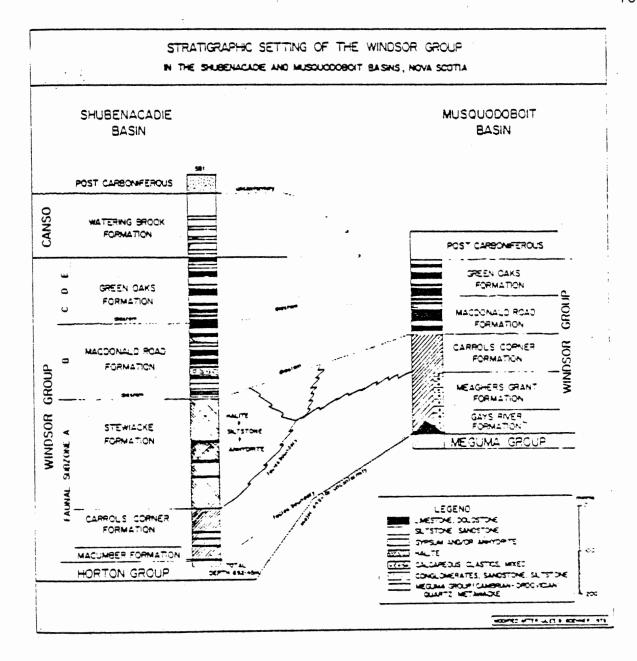


Figure 2.1 Stratigraphic setting of the Windsor Group in the Shubenacadie and Musquodoboit Basins, Nova Scotia.

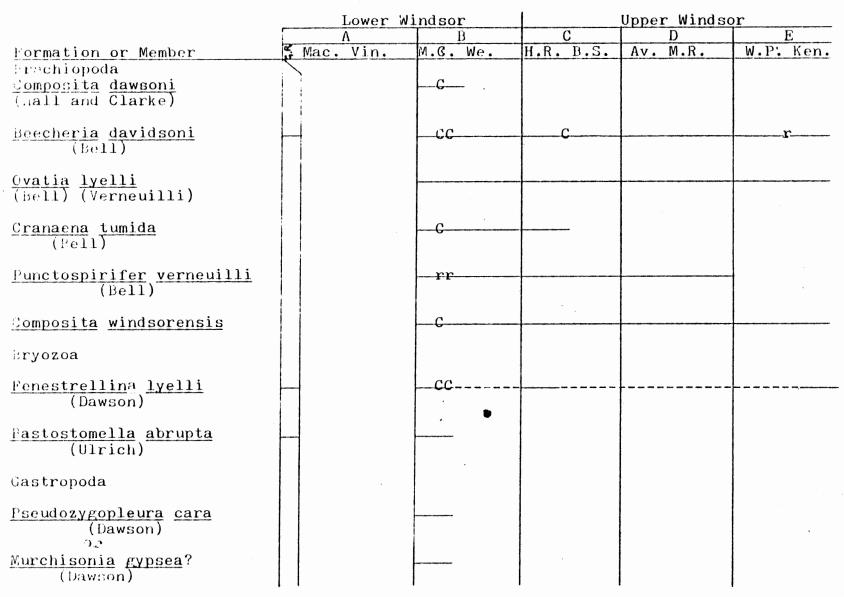


Figure 2.2 Faunal range chart of the Windsor Group showing the fossil content of the mineralized carbonate at Pembroke.

Abbreviations to Accompany Figure 2.2

Gays River Formation G.R. Mac. Macumber Formation Vin. Vinland Formation M.C. Miller Creek Formation Wentworth Formation We. Herbert River limestone H.R. Brooklyn station limestone B.S. Av. Avon limestone Meander River limestone M.R. Wallace point limestone W.P. Kennetcook and Musquodoboit Ken.

R.R. - very rare

c.c. - very common

limestones

c - common

r - rare

limitations of each species, only their absence or presence in each faunal zone. Environmental factors, such as water depth, salinity and paleotopography may therefore be of utmost importance in determining the faunal content of each zone.

Other less abundant fauna, not mentioned in the chart, include crinoids and foraminifera. Corals are notably absent. Bell (1929) attributes their absence to often inhospitable conditions of the Windsor sea. Corals are particularly sensitive to changing salinities, temperatures and water depths.

Bell (1929) recognized five macrofaunal zones within the Windsor Group which he termed subzones A to E. The subzones were further divided into formations or members. The mineralized limestone at Pembroke can be grouped into Bell's lower B subzone, the Miller Creek Formation.

The Miller Creek formation has recently been grouped into the lithologic unit termed the Macdonald Road Formation, shown in figure 2.1.

2.3 Local Stratigraphy

The stratigraphy of the map area is best represented by diamond drill hole GB-15. This drill hole, which is located 260 metres west of the deposit, contains the thickest and most complete section of carbonate drilled to date. The core was relogged by the author and 14 samples were taken. These were slaped, polished and

described, the results of which are presented in figure 2.3. Dunham's (1962) textural classification system (figure 2.4) was the standard terminology used to describe the carbonate rock types.

Description of individual lithologies of diamond drill hole GB-15 are as follows:

Horton Group- The Horton Group consists of red and grey micaceous sandstone and siltstone with occasional coalified plant remains.

Windsor Group

Macumber Formation - This formation consists of dark grey, sandy, unfossiliferous, finely laminated mudstone. This formation is indicative of a shallow subtidal environment and may represent an event of sudden marine transgression (Schenk, 1967). This lithology is often extensively veined and brecciated by gypsum and is therefore usually characterized by zones of low core recovery.

Carrols Corner Formation- Evaporites characterize this formation. Anhydrite is usually massive with large (model of the decrease) selenite porphyroblasts. Thin interbeds of shale are also common. Where gypsum is present, it is usually laminated. These laminations are assumpting interestly folded.

Macdonald Road Formation - This formation consists of numerous limestones and dolomites of various lithologies. Limestones are dark grey to black but often weather to a light grey colour. Bryozoans are the most abundant

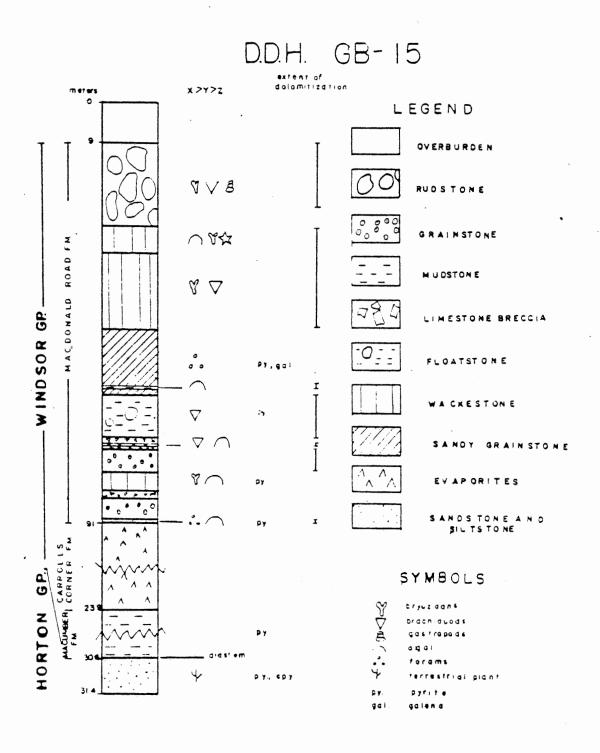


Figure 2.3 Stratigraphy of diamond drill hole GB-15.

	All original bo	Autochthonous limestones original components organi- cally bound during deposition							
Less tha	n 10° u > 2	mm com	ponents	Greate 10° • > compo	2 mm	By organ- isms	By organ- isms	By organ- isms	
	ains lime r < .03 mm		No lime mud			which act as baffles	which encrust and bind	which build a rigid frame-	
Mud su	pported	c.	ain	Marada	> 2 mm	barnes	onid	work	
Less than 10% grains 1> 03 mm < 2 mm	Greater than 10% grains		am orted	Matrix sup- ported	ponent sup- ported				
Mud- stone	Wacke- stone	Pack- stone			Rud- stone	Baffle- stone	Bind- stone	Frame- stone	

Figure 2.4 Dunham's classification system for carbonate rocks (taken from Dunham 1962).

fauna. These are often selectively dolomitized. Dolomitized limestone is light brown to buff in colour. Abundant calcite veinlets post-date dolomitization.

Limestone breccia consists of angular clasts of up to 2 centimetres in diameter which are cemented by calcite and hematite. These may be solution collapse features as indicated by the presence of red vadose silt (Macleod, 1979).

A sandy grainstone lithology is an important host for mineralization. This limestone consists of algal-coated, sand-sized grains of quartz, rock fragments and carbonate. Calcite veinlets are common. Traces of galena can be observed within these veinlets. This rock type is identical to the main mineralized lithology (sample P-8) located at the deposit.

2.4 Local Structural Geology

A possible SE-plunging syncline of Horton and Windsor Group rocks is preserved in a graben structure which is separated in the north and south by major faults. The faults trend roughly in E-W and SW-NE directions. Horton Group sediments outcrop to the east and south. The only mineralized outcrop in the area occurs in the Macdonald Road Formation limestone and is located at the old mine site. The reader is referred to Map 1 (folded in pocket).

Systems used by various workers to describe drill core vary greatly from company to company and with the

year that drilling was undertaken. A standardized system was therefore necessary to integrate information from all drill holes in the area. This system was used in the preparation of geological cross-sections (folded in pocket).

CHAPTER 3 MINERALOGY AND ORE PARAGENESIS

3.1 Calcite

Three types of calcite are present within mineralized host rocks at Pembroke. They are as follows:

type 1- fibrous calcite cement

type 2- blocky geopetal calcite

type 3- blocky veinlet calcite

Type 1 calcite is a fibrous fringe cement which radiates with c-axes perpendicular to the rims of the fossil constituents. The crystals are equigranular, averaging 700 microns in length and a few microns in width. Crystals are light brown and what slucest under plain polarized light. Type 1 calcite probably formed as a result of early diagenesis. This calcite is unrelated to galena mineralization. It does, however, reduce the original porosity of the host from 35% to as low as 10%.

Type 2 calcite fills interskeletal and intraskeletal voids between or within fossil brachiopods or between algal-coated grains. This blocky calcite is clear to milky in appearance, often having a bluish tinge.

Type 3 calcite occurs in small veinlets, usually only a few millimetres in width. These veinlets are randomly orientated, their direction often controlled by host porosity. Veinlets follow for the same and cross-cut type 1 calcite. Type 3 and type 2 calcite are similar

in appearance and probably cogenetic in origin. The fact that veinlet calcite commonly appears to feet geopetal calcite is further evidence for this.

Type 1, 2 and 3 calcites fill open spaces; no replacement features were observed.

3.2 Sulfides

Galena is the only economic mineral at the Pembroke deposit. It is found associated with type 2 and 3 calcite where it occurs as randomly distributed aggregates of euledral cubes. Sphalerite is notably rare. Minute specks were observed by geologists who originally logged the core but the present author was unable to find sphalerite in hand samples or drill core. Sphalerite was found, however, in a doubly-polished thin section of sample P-14 by using reflected light microscopy. The sphalerite was recognized by the presence of red internal reflections and by having a reflectance of 17 as measured with a microphotometer. In this case, sphalerite occurs as intergrowths with galena (figure 3.1). Pyrite, which is commonly found disseminated within the Horton and Windsor strata, is absent in type 1, 2 and 3 calcite. Chalcopyrite, barite and fluorite are common minerals within carbonate-hosted base metal deposits of the Windsor Group of Nova Scotia. They are, however, notably absent at Pembroke.

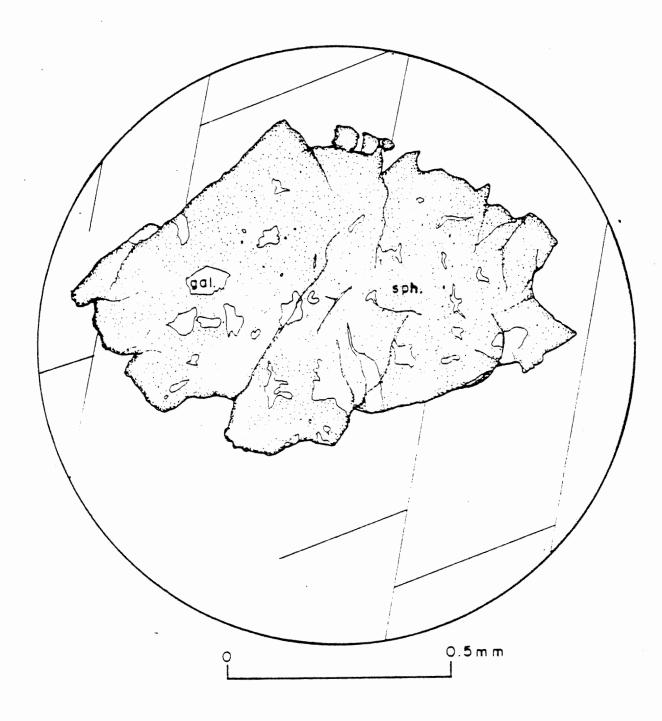


Figure 3.1 Small sphalerite crystal (sph.) with inclusions and intergrowths of galena (gal.) as seen under reflected light. The crystal occurs 1: type 2, geopetal calcite.

3.3 Stylolites

Stylolites are sutured contacts which form by dissolution and redistribution of calcite due to increased stresses This process of pressure solution may form stylolites during load or deformation compaction (Friedman, 1978). They tend to form in a plane perpendicular to the direction of compaction and as a result usually form along bedding surfaces. Stylolites observed from samples taken from the Pembroke Deposit and from drill core are aligned parallel to the bedding planes. This is also the case for beds which now dip at up to 60 degrees from the horizontal. It is therefore likely that the event which caused the folding of the Windsor strata occurred after the formation of stylolites. Thin sections of samples collected from the dump clearly show that stylolites cross-cut and often offset type 1, 2, and 3 calcite . Galena mineralization is also concentrated as an insoluble product along these sutured contacts. Emplacement of type 2 and 3 mineralized calcites must have occurred before the stata were folded. Folding probably occurred during the Late Carboniferous Maritime Disturbance (apx. 300m.y. B.P.) (Reynolds et. al., 1981).

3.4 Sample Descriptions

3.4a Sample P-8, Sandy Grainstone

Location: ore dump at Pembroke deposit

Hand Specimen: This sample consists of grey carbonate which is highly mineralized with galena (up to 20%) and often takes on the appearance of massive ore. A "stockwork" of mineralized calcite veins cross-cuts the carbonate in a random fashion. Detrital carbonate and siliclastic grains range in size from less than one millimetre to up to one centimetre in diameter.

Thin Section: (figure 3.2)

Rounded grains of various lithologies are present within this sample. They include:

- 48% carbonate grains (C) including shell fragments, foraminiferal tests and crinoid stems.
- 40% quartz (Q)
- 10% rock fragments (R)
- 2% quartz with subgrains (QS)

All constituents are coated with a fossilized rim of algae. Micrite is notably absent. Type 3 calcite veinlets (3) act as feeders for type 2 calcite (2) intergrain porosity. Galena tends to be concentrated in intergrain pores rather than in veinlet systems.

Environment of Deposition: This limestone was deposited in a high energy, nearshore environment where a supply of clastic sediments persisted.

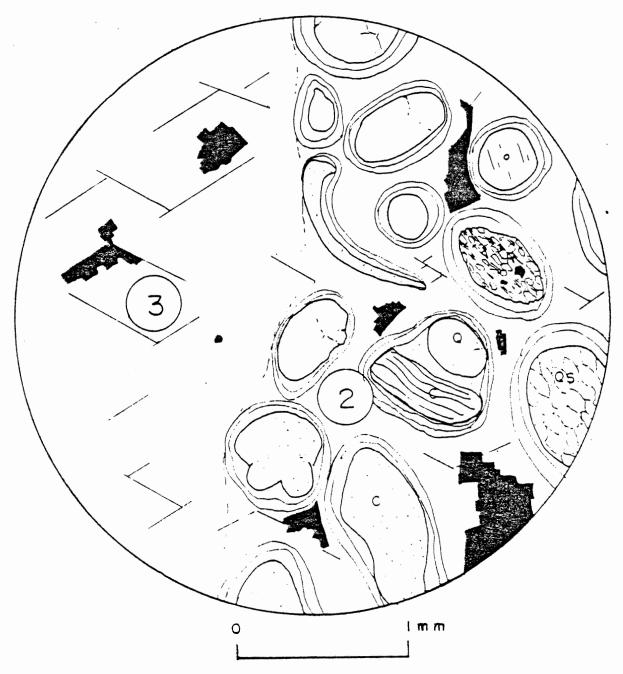


Figure 3.2 Sample P-8, Sandy Grainstone

- 2 mineralized type 2 calcite
- 3 mineralized type 3 calcite
- Q quartz , R rock fragment
- C carbonate ,opaques-galena
- Q3- quartz with subgrains

3.4b Sample P-5, Brachiopod Rudstone

Location: outcrop at the Pembroke deposit.

<u>Hand specimen</u>: Sample P-5 is a highly fossiliferous dark grey limestone containing small, randomly orientated calcite veinlets which are mineralized with galena.

The limestone gives off a petroliferous odour when struck with a hammer.

Thin section: (figure 3.3)

Brachiopods are the prominent fauna of this sample; bryozoans being second in abundance. The constituents are in grain support with marine silt partially filling interskeletal and intraskeletal porosity and indicating the "way up" direction of the beds. This silt is composed of shell fragments, crinoid ossicles, foraminifera and pellets. The pellets are not compacted. Early cementation by type 1 (1) fibrous calcite may be responsible for their preservation.

Type 2, mineralized, blocky calcite occupies intraskeletal pores (2a) created by fossil brachiopods and interskeletal pores (2b) between fossils and below umbrella structures.

The coarse-grained galena usually defines a "way up" direction roughly parallel to that indicated by geopetal silt.

Veinlets (3) are usually a few millimetres in width.

These cross-cut fossils and type 1 calcite cement. The

veinlets sometimes act as feeders for type 2 calcite pores.



Figure 3.3 Sample P-5, Brachiopod Rudstone

- 1 type 1 calcite
- 2a- mineralized type 2 calcite occupying
 an intraskeletal pore.
- 2b- mineralized type 2 calcite occup,ing
 an interskeletal pore.
- 3 type 3 calcite ,opaques-galena
- S stylolite

Stylolites (S) parallel bedding planes, bisecting all previous structures, including the mineralized calcite.

Galena is often concentrated as an insoluble product along these stylolites.

Environment of Deposition

The brachiopod shells of this limestone are usually intact, with brachidia which often project in an excellent state of preservation. Stratification is usually absent although slight sorting of shell sizes was observed in a similar sample. Marine conditions must have been sufficiently turbulent to disperse the silt, but not so turbulent and/or persistant that the shells became abraded and broken. The brachiopod rudstone was probably deposited below normal wave base but where storm conditions did have some effect in reworking the bottom sediments.

3.5 Paragenesis

In summary, the paragenetic sequence is as follows:

- 1) type 1 calcite
- 2) type 2 and 3 calcite mineralized with galena and minor sphalerite
- 3) stylolite formation
- 4) folding of strata

3.6 Extent of Mineralization

Galena mineralization is confined to limestone of

the Macdonald Road formation. The deposit can therefore be classified as stratabound. A 3 centimetre size fragment of mineralized limestone breccia was recovered from diamond drill hole GB-17, located 450 metres west of the mineralized outcrop. Mineralized calcite surrounding the angular clasts is similar in appearance to the type 3 calcite, previously described. Traces of galena have also been observed in calcite veinlets located at the 61 metre depth in diamond drill hole GB-15. This calcite is also similar to the type 3 calcite. These veinlets cross-cut a sandy grainstone lithology which is identical to that which is highly mineralized at the old mine site. This lithology is referred to as calcareous sandstone in cross-sections at the back of the thesis. Galena mineralization has not been observed eastward of the old mine site.

Tiny specks of sphalerite are often sporadically distributed in trace amounts in the host limestone proximal and distal to the old workings.

CHAPTER 4

FLUID INCLUSION GEOTHERMONETRY

4.1 Introduction

Fluid inclusions result from some process that interferes with the growth of perfect crystals. Variation in the growth rate or chemistry of the precipitating fluid may trap a representative sample of the fluid from which the crystal grew. These are referred to as primary inclusions. Primary inclusions are usually 10-100 microns in diameter and tend to be roughly spherical to irregular in shape. An inclusion generally consists of a gas or vapour bubble having a volume much less than that of the liquid. The bubble results from differential contraction of a single phase fluid and host crystal upon cooling (Roedder, 1962b). Common ions present within fluid inclusions include: Na+, Cl-, K+, Ca+2 and SO, -2. A third solid phase may be present, especially if the salinity of the fluid is high. A hydrocarbon phase may also be present as is the case for fluid inclusions in fluorite of the Gays River Pb-Zn deposit (Akande, 1982).

Secondary inclusions form by modification of primary inclusions and therefore do not represent a sample of the fluid from which the crystal grew. They may be formed by:

- 1) rehealing of cracks
- 2) later refilling
- 3) leakage
- 4) necking down

Leakage may occur due to tectonic deformation or even when grinding during sample preparation. A change in bubble size after a heating run usually indicates leakage. Most inclusions, however, do not leak in natural situations (Roedder, 1963).

Necking down occurs when an inclusion separates into two smaller inclusions. Necking down is recognized by inclusions with irregular shapes and anomalous temperatures and bubble sizes.

Inclusions may also be formed in fractures created while the crystal is still growing. These are referred to as "Pseudosecondary Inclusions" and may give anomalous temperatures; however, they often yield the same temperatures as primary inclusions (Roedder, 1962b).

The temperature at which the fluid and gas bubble of a primary inclusion homogenize into a single phase is referred to as the filling temperature and is interpreted to represent the minumum temperature of the fluid from which the crystal precipitated. Pressure corrections can be introduced to refine the actual temperature of entrapment. However, an independent measure of the pressure is needed (such as a stratigraphic thickness), but this requires that the age or timing of mineralization is known. A correction for salinity can also be made. The salinity of a fluid inclusion is determined by freezing the inclusion, the freezing point being proportional to the salinity

of the fluid (Roedder, 1962a). Since time was limited, such an experiment was not performed. The possible corrections for salinity are, however, discussed briefly in the following text.

4.2 Procedure

Doubly polished thin sections of mineralized and unmineralized type 1 and 2 calcite were prepared by the author with assistance from Mr. Gordon Brown, of Dalhousie University. The sections were then placed into a microscope heating stage. Glass plates of the heating stage served as insulation but greatly reduced the optical quality. Resolution also decreased with increase in temperature due to heating of the objective. A microscope equiped with an optic fiber illuminator was therefore necessary to observe the inclusions. Temperature was determined by placing a thermocouple of nickel-aluminum next to the section. Accuracy of the thermocouple was checked by heating organic solids of known melting point.

Isolated primary inclusions of geometrically regular shape were chosen. These were heated slowly until the liquid and gas phases homogenized, at which time the temperature was recorded. The temperature was also recorded when the vapour bubble reappeared on cooling. The procedure was repeated several times. Temperatures were recorded and averaged to determine the filling temperature of each

inclusion. The size of the vapour bubble was noted before and after a heating run as a check for leakage.

4.3 Observations

Inclusions in calcite were small, ranging in size from 1 to 13 microns with a mean of 6 microns. Roughly spherical primary inclusions were fairly abundant although many showed evidence of leakage or necking down. Most inclusions consisted of two phases, a liquid phase and a vapour phase. The vapour bubble usually occupied approximately 3 to 5 percent of the inclusion. A third solid phase was apparent in some inclusions of both type 2 and type 3 calcite. The solid phase is probably halite as evidenced by its high relief and cubic habit. When heated, the solid disappeared before the filling temperature was reached and did not reappear when cooled. Vapour bubbles displayed rapid movement when the inclusions were heated even slightly. This "Brownian Movement" is indicative of dense saline brines (Roedder, 1962b).

4.4 Data

The results are displayed in figure 4.1. Filling temperatures obtained from 29 inclusions have been plotted on a frequency histogram (figure 4.2). The data display a good normal distribution with mean of 214.8°C and standard deviation of 12.3. Temperatures range from 210.1°C to 219.5°C at the 95 percent confidence level.

FLUID INCLUSION FILLING TEMPERATURES

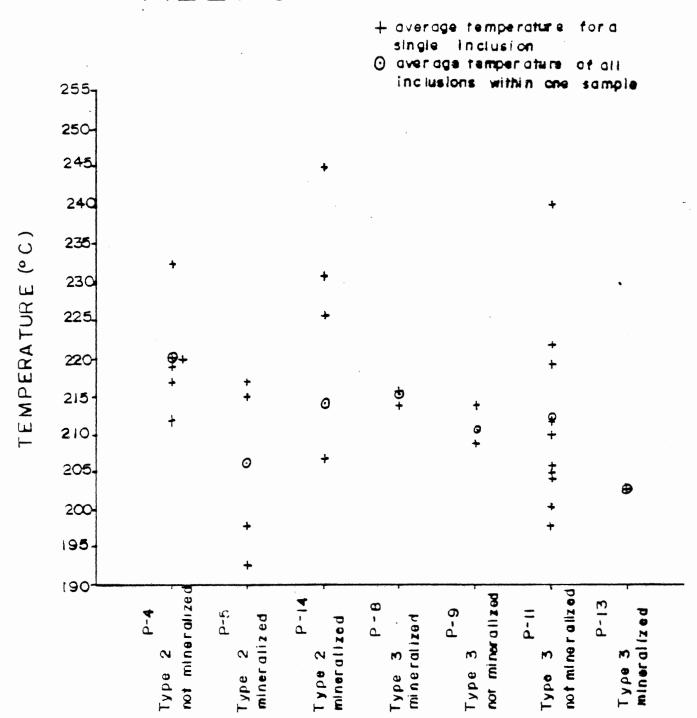


Figure 4.1 Homogenization temperatures of fluid inclusions.

FREQUENCY HISTOGRAM FOR FLUID INCLUSION FILLING TEMPERATURES

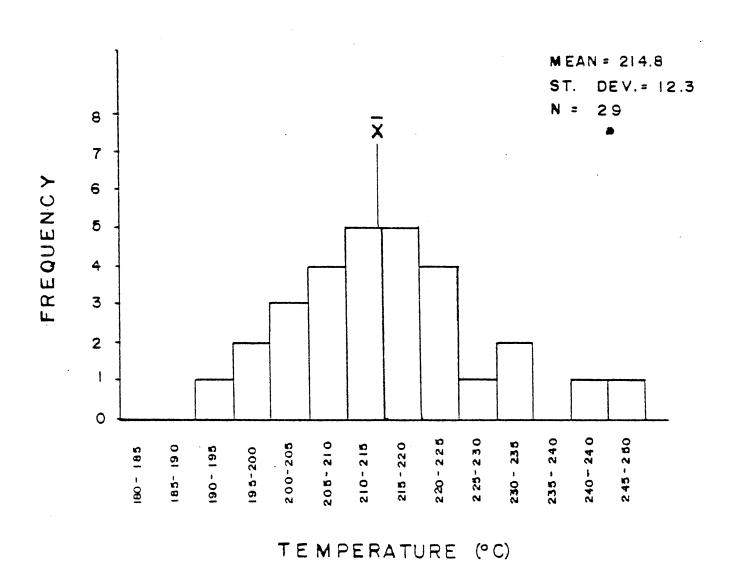


Figure 4.2 Frequency histogram of fluid inclusion filling temperatures showing good normal distribution.

4.5 Constraints on Boiling-Calculation of Minimum Hydrostatic Pressure

The absence of coexisting gas-rich and gas-poor aqueous inclusions is good evidence that fluids were not boiling at the time of trapping (Roedder 1962b). This is the case for fluid inclusions at Pembroke. An estimation of the confining pressure or hydrostatic pressure and thus the minimum thickness of overlying strata or the water depth at the time of mineralization can therefore be determined from the fluid inclusion filling temperatures. This assumes that the fluids were freely connected to the surface and that abnormal fluid pressure did not exist. The salinity of the fluids also affects the estimation. The relationship between salinity, depth (confining pressure) and fluid temperature is demonstrated in figure 4.3, taken from Haas (1971). A mean temperature of 214.8°C for fluid inclusions from Pembroke is plotted. Although the salinity of the mineralizing fluids is not known, it is likely that the salinity did not exceed 25 wt.% NaCl. With this assumption in mind, the depth of the water column must have been at least 175 metres to prevent the fluids from boiling. If the deposit is of syngenetic origin, ore deposition must have taken place at depths greater than 175 metres below sea level. This seems unlikely, especially since it has previously been demonstrated that the mineralized carbonate was probably deposited in a shallow water environment. With this consideration in mind, the measurement probably

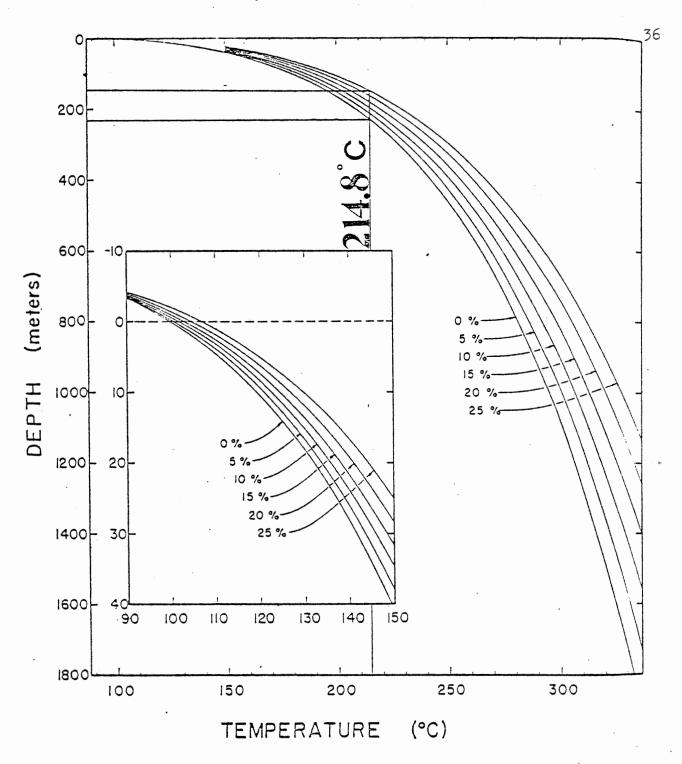


Figure 4.3 Boiling-point curves for H2O liquid of variable salinities (wt.% NaCl). A temperature of 214.8°C, obtained from fluid inclusions, is plotted. The graph shows the range of depths (hydrostatic pressures) which would be required to prevent solutions of this temperature and of variable salinities from boiling.

represents the minimum thickness of overlying strata at the time of mineralization.

4.6 Pressure Correction

The increase in confining pressure has a net effect of decreasing volume of the vapour phase of the inclusion, which in turn yields a lower temperature of crystallization. A pressure correction must therefore be applied to refine the temperature of entrapment determined from fluid inclusions. Such a correction must, however, involve the estimation of the stratigraphic thickness of overlying units. Hacquebard (1970)extrapolated a thickness of 3.6 kilometres of Upper Carboniferous strata for an area near Gore, located 58 kilometres WSW of Pembroke. This is equal to a pressure of 900 bars. He based his calculation on the reflectance of vitrinite (0.84% Ro and 0.96% Ro) from coaly debris in the Horton Group sediments. Since the age or timing of the mineralizing event is not known, only a correction for maximum pressure can be applied. The salinity of the fluid inclusions also affects this estimate somewhat. If a salinity of 1 wt.% NaCl is taken, a pressure correction of 900 bars would require a temperature correction of *74°C. (Potter, 1977). A salinity of 25 wt.% NaCl would require a correction of *84°C under the same pressure conditions. The maximum temperature of the mineralizing fluids could therefore have been as high as 299°3, but this is unlikely.

CHAPTER 5 OXYGEN AND CARBON ISOTOPE GEOCHEMISTRY

5.1 Introduction and Terminology

The following discussion was principally compiled from Faure (1977) and Taylor (1967, 1974).

Oxygen is the most abundant element in the earth's crust; it is composed of three stable isotopes, 16 O, 18 O. The relative abundances are as follows:

 $16_0 = 99.763\%$

170 = 0.0375%

 $^{18}_{0} = 0.1995\%$

Carbon has two stable isotopes:

 $12_{\rm C} = 98.89\%$

13c = 1.11%

The isotopic composition of a substance is expressed as a ratio; $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$. These ratios can be converted to a delta (\int) value as below:

$$\int x = \frac{R \text{ sample} - R \text{ standard}}{R \text{ standard}} 1000$$

where $R_{sample} = {}^{18}0/{}^{16}0$ or ${}^{13}C/{}^{12}C$ of the sample and $R_{standard} = {}^{18}0/{}^{16}0$ or ${}^{13}C/{}^{12}C$ of the standard. The PDB standard, named after the Peedee Belemnite formation of North Carolina, was used. ${}^{018}PDB$ values were converted to SMOW or standard mean ocean water as follows:

 $\int ^{18}0_{SMOW} = 1.03086_{DDB} + 30.86$

The difference in vibrational frequencies between

 18 O and 16 O and between 13 C and 12 C is the principle behind oxygen and carbon isotopic study. For example, since 16 O is a lighter isotope than 18 O, it tends to be preferentially evaporated from seawater, thus enriching the atmosphere in 16 O and depleting seawater in 16 O. For this reason, seawater tends to be enriched in 18 O, giving higher positive 18 OSMOW values. With the use of carbon and oxygen isotopes, it is therefore often possible to determine the environment from which a substance was derived and its history of isotopic exchange.

The oxygen and carbon isotopic composition of host rock and allochthonous calcite from Pembroke was determined for the purpose of:

- a) selecting isotopic groupings which may correspond to separate phases of calcite emplacement.
- b) obtaining isotopic information about the mineralizing fluids and to interpret the history of isotopic exchange.

5.2 Procedure

Nine samples of mineralized and apparently unmineralized type 2 and 3 calcite were selected along with five samples of mineralized host rock. One calcite vein containing sphalerite mineralization was taken from the Gold Brook prospect, located 8 kilometres SE of Pembroke and hosted in Meguma Group metasediments of Ordovician age. Calcite samples were hand crushed and impurities were carefully separated with the aid of a binocular microscope. Brachiopods from the host rock samples were chosen and crushed for analysis. All rock samples were sifted with a 125 micron screen (120 mesh), the finest fraction being used for analysis.

Isotopic compositions were determined by Dr. Peter Reynolds with the use of a vacuum line and mass spectrometer, located at Dalhousie University. 1-2 milligrams of carbonate were placed into a reaction vessel which was kept at a constant temperature of 50°C. 100 percent phosphoric acid was added to the sample and allowed to react. Water and carbon dioxide vapour evolves from the reaction chamber. The water vapour was extracted in a section of the vacuum line which was cooled to -93°C. CO2 was collected in a coolant bath of liquid nitrogen, located in a separate section of the vacuum line. The gaseous CO2, which contains all of the isotopes of carbon and oxygen, is then pumped into a double-collecting ratio mass spectrometer where it is compared to a laboratory standard. In this case, the standard being from the Carrara marble (cm). The mass spectrometer utilizes a magnetic field to separate the various isotopes. These isotopes become ionized in the mass spectrometer and as a result are deflected by the magnetic field to various degrees, depending on the

isotope mass number.

Measurements were expressed in mass ratios of 45/44 and 46/44 where

$$44 = 12_{C} 16_{0} 16_{0}$$
 $45 = 13_{C} 16_{0} 16_{0}$
 $46 = 12_{C} 16_{0} 18_{0}$

These values were converted to the PDB standard by using the following equations:

$$\int_{0}^{18} c_{\text{m}} = 1.001 \int_{0}^{46} + 9.6 \times 10^{-3} \int_{0}^{45} \int_{0}^{18} c_{\text{m}} = \int_{0}^{18} c_{\text{m}} - 1.19$$

$$\int_{0}^{13} c_{\text{m}} = 1.067 \int_{0}^{45} + 0.03384 \int_{0}^{46} \int_{0}^{45} c_{\text{m}} + 2.79$$

The precision of the measurements is approximately $^{\pm}$ 0.1 per mil 18 0 and 13 0.

5.3 Data

The data are presented in table 1 of the appendix. A plot of $\int^{18} 0 \, \mathrm{SMOW}$ versus $\int^{13} 0 \, \mathrm{CpDB}$ is shown in figure 5.1. The mean isotopic composition of seven brachiopod shells, analysed by Akande (1982), is plotted for comparison. The samples were taken from the Miller Brook limestone quarry and belong to the Macdonald Road formation.

5.3a Unaltered Limestone

Samples of unaltered limestone, analysed by Akande (1982), have $\int^{18} 0 \, \text{SMOW}$ values which range from $^+24.49$ to

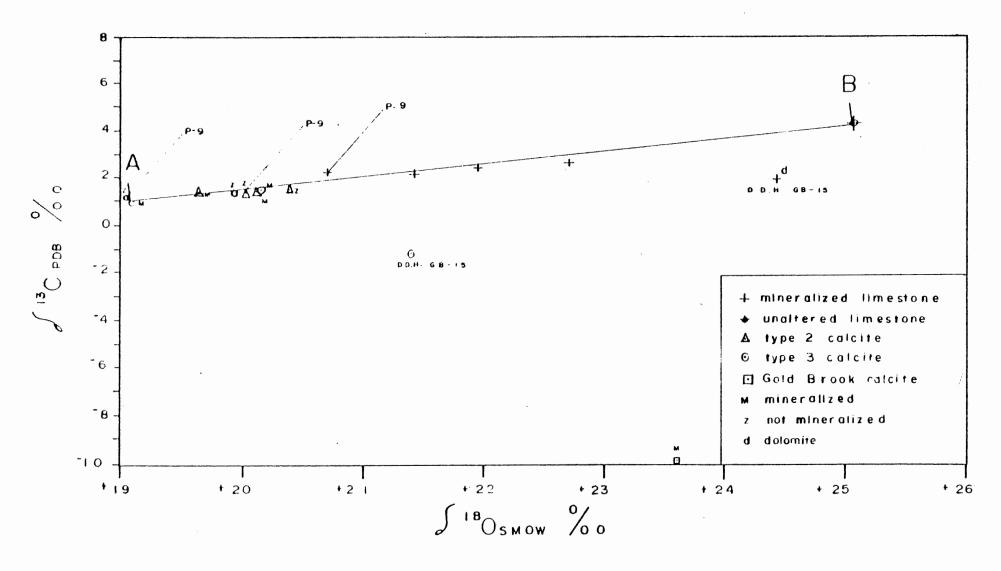


Figure 5.1 Oxygen and carbon isotope composition of host rock and calcite.

+26.39 per mil with mean of 25.05 ± 0.7 per mil. These values deviate slightly from values established for Carbon-iferous seawater. Possible explanations are as follows:

- the isotopic composition of shelly material is species dependent
- 2) the temperature and/or salinity of the seawater may have been anomalous in the depositional environment
- diagenesis may have altered the original isotopic composition

The variation of brachiopod species used in the analyses may provide for differences in isotopic composition.

The species of brachiopod used in each sample is therefore noted in table 2 of the appendix.

5.3b Unmineralized Dolomite and Calcite Vein of D.D.H. GB-15

Buff coloured dolomite was sampled from 30.8 metres depth in diamond drill hole GB-15. The sample was predominantly composed of skeletal grainstone of unknown composition. This lithology was not found at the Pembroke deposit and probably lies stratigraphically higher than the mineralized limestone. A \int^{180} SMOW value of $^{+}$ 24.41 is comparable, although somewhat depleted in the heavier 0^{18} isotope, to values obtained by Akande (1982) for unaltered limestones of this formation. \int^{13} CPDB values are, however, notably less than those of unaltered limestone. This depletion

in the heavier isotope of carbon may be related to dolomitization.

A 1 centimetre wide veinlet of blocky calcite, which appears to cut this dolomite, was also analyzed. This veinlet has a $\int^{18} O_{SMOW}$ value of $^{+}21.40$ and a $\int^{13} C_{PDB}$ value of $^{-}1.17$. Emplacement of this calcite and isotopic exchange with the dolomite host may be responsible for the depletion of the latter in the heavier isotopes. This calcite should not be confused with that which is mineralized at the 61 metre depth of the same drill hole.

5.3c Gold Brook Mineralized Calcite

A 1cm wide vein of calcite was obtained from the Gold Brook prospect. This prospect is located 7.9 kilometers at azimuth 106° from the Pembroke deposit (see location map, map1). The sample was taken from 59.3 metres depth in diamond drill hole 224-15. The reader is referred to the unpublished B.Sc. thesis by Jenner (1982). The vein is composed of clear yellow calcite, mineralized with light yellow sphalerite, and cuts pyrite-rich slate of the Ordovician Meguma Group. This sample was analyzed, suspecting that the Meguma Group may have been the source for mineralization at Pembroke. A \$180SMOW value of *23.61 and \$13CpdB value of *9.85 were obtained. This sample is extremely depleted in the heavier \$13C\$ isotope with respect to samples analyzed from Pembroke. It can be concluded that

this calcite is not related to the type 2 or 3 calcites. Gold Brook calcite is therefore considered as a separate phase, unrelated to mineralization at Pembroke.

5.3d Altered Limestone

Altered limestone was taken from outcrop and dump rocks located at the prospect. Brachiopods of known species were used when available. $\int ^{18} o_{SMOW}$ values showed a broad range from $^{+}20.70$ to $^{+}22.70$ with mean of $^{+}21.69$. $\int ^{13} c_{PDB}$ values range from $^{+}2.15$ to $^{+}2.65$ with mean of $^{+}2.37$. A linear relationship between $\int ^{18} o_{SMOW}$ and $\int ^{13} c_{PDB}$ is evident; $\int ^{18} o_{SMOW}$ values increasing with increase in $\int ^{13} c_{PDB}$ values. The isotopic composition of the mineralized limestone is intermediate between the type 2 and 3 calcite and the unaltered limestone.

5.3e Type 2 and 3 Calcite

 in the heavier isotopes and may be superficially grouped separately from the type 3 calcite.

No distinction is observed between mineralized and unmineralized calcite. It is suspected that visible mineralization was only concentrated in favourable locations along veinlets or in selected geopetal structures. The fact that mineralized "zones" are often encountered in "barren" veinlets is further evidence for this.

5.4 Discussion

Isotopic relationships between type 2 and type 3 calcite, the altered limestone and the unaltered limestone indicate that isotopic exchange between these groupings has probably occurred. Line A-B, indicated on figure 5.1, appears to be a path of isotopic exchange.

Altered limestone samples have isotopic compositions intermediate between type 2 and 3 calcite (the ore fluids) and unaltered limestone. Depletion in the heavy isotopes of altered limestone may be caused by:

- 1) isotopic fractionation due to elevated temperatures
- 2) the degree of interaction of the ore fluids with the host limestone
- diagenesis

Hall and Friedman (1969) studied isotopic relations in carbonate-hosted Pb-Zn deposits of the Upper Mississippi Valley and Tri-state districts. They found systematic

decreases in \int^{18} 0 and \int^{13} C values of limestone and dolomite host rock with proximity from the ore. This was attributed to diminishing isotopic fractionation with increase in temperature. It was assumed that the ore fluids, at a given temperature, were in isotopic equilibrium with the host rock and that isotopic exchange was complete. The isotopic composition of the altered host rock was therefore temperature dependent and not related to the degree of interaction with the mineralizing fluids. $\int_{0.000}^{18} 0.000$ and $\int_{0.000}^{19} 0.000$ values for altered limestone at Penbroke tend to spread along the path A-B. This may reflect differences in the paleotemperature to which each sample was heated during mineralization. The spread of type 2 and 3 calcites along the line A-B could also be explained by temperature gradients. fact that type 2, geopetal calcite is spread further along the line A-B than veinlet calcite would suggest a lower temperature of emplacement for the type 2 calcite. relationship is seen, however, between temperatures obtained from fluid inclusions and the isotopic composition of each sample.

The degree to which mineralizing fluids have interacted with the host limestone may better explain the isotopic variations. This would assume that isotopic equilibrium for a given temperature had not been reached. Sample P-9 (see figure 5.1) best explains this concept. Type 2 and 3 calcite and the host carbonate were all analysed

separately within this sample. A systematic depletion in the heavy isotopes along the path B-A from altered limestone to type 2 calcite to type 3 calcite is apparent. This implies that the type 2 calcite has undergone greater isotopic exchange with the host rock than the type 3 calcite, since temperature is no longer a factor. Type 2, geopetal calcite probably originated from fluids filtering through the host limestone from type 3 veinlet systems. This would result in the increased interaction of type 2 calcite with the host rock, thus accounting for the difference in isotopic composition between type 2 and type 3 calcite.

Whatever the explanation, it appears that present isotopic compositions have resulted from isotopic exchange between the mineralizing fluids and the host limestone.

Friedman (1964) has demonstrated the effects of fire shorter diagenesis on the isotopic composition of skeletal sands from Bermuda. He found that dissolution of aragonite and high-magnesian calcite followed by precipitation of calcite as interparticle cement or mold filling resulted in an enrichment in the lighter isotopes of carbon and oxygen.

Diagenesis of the host limestone at Pembroke is apparent and resulted in the emplacement of the type 1 calcite cement. Diagenesis, however, probably had little effect in depleting the heavier isotopes of host rock from Pembroke since diagenesis does not explain the diversity

in isotopic composition among samples of altered limestone.

The isotopic composition of type 2 and 3 calcite represents the isotopic composition of the calcite for a specific temperature; this temperature being 214.8°C or higher. Mineralized calcite may have been derived from dissolution and fractionation of the host carbonate or fractionation of basinal brines. The resulting ore fluids would be depleted in the heavier isotopes due to isotopic fractionation induced by elevated temperatures.

CHAPTER 6 ORIGIN OF ORE DEPOSITION

6.1 Summary of Characteristics

A summary of characteristics of the Pembroke deposit are as follows:

- stratabound mineralization confined to the Macdonald Road Formation limestone of the Lower Carboniferous Windsor Group
- 2) the minimum temperature of mineralizing fluids was 214.8°C
- 3) fluids were probably dense, saline, basinal brines
- 4) mineralized calcite was emplaced after lithification of the host limestone but before maximum compaction and folding
- 5) galena is the only sulfide present, apart from traces of sphalerite
- 6) coarse-grained galena occurs in calcite veinlets as well as filling interskeletal and intraskeletal pores

Characteristics 2, 4 and 6 above suggest an epigenetic origin for ore deposition.

6.2 Source of Fluids

The mineralized fluids at Pembroke were probably

derived from heated basinal brines. Akande (1982) has suggested that brines released during the conversion of gypsum to anhydrite at elevated temperatures and pressures were a likely source for fluids responsible for mineralization at the Gays River Pb-Zn deposit. The great abundance of evaporites within the Shubenacadie Basin could supply enormous volumes upon dewatering. Akande points out that fluid release would lead to fluid overpressuring since the brines could not escape through the impermeable evaporite caprock.

6.3 Source of Metals

Boyle (1972) has suggested that fluids responsible for mineralization at the Walton Pb-Zn-Ba mine (see location map) have leached metals from the underlying Horton Group sandstones and shales. Akande (1982), however, presents strong evidence to suggest that lead from the Gays River mine was derived from the Meguma Group basement. He found a genetic relationship between basement alteration and mineralization whereby altered fault zones in the basement rocks coincided with massive sulfide veins in the overlying carbonate. Pb-isotope determinations preformed by Zentilli (1981) indicate that galena samples obtained from Walton, Gays River and Pembroke all have Ordovician model ages, similar to the age of the Meguma Group basement rocks.

only 8 kilometres ESE of the Pembroke deposit, is evidence for anomalous concentrations of Pb and Zn in the Meguma Group.

6.4 Genetic Model

The genetic model proposed by Akande (1982) for mineralization at Gays River can be successfully applied to mineralization at Pembroke. The model involves dewatering of evaporites which results in overpressured basinal brines within the Horton Group. These brines, which are slightly acidic, travel along faults and fractures in the underlying Meguma Group basement rocks where metals are leached. A very high geothermal gradient or the presence of a magma chamber at depth would be necessary to heat the brines to the high temperatures determined from fluid inclusions. These metal-rich solutions would then travel up dip to the basin margins where favourable conditions for ore deposition are encountered. Such favourable conditions include: reducing conditions, increased pH, the presence of sulphur, high porosity, high permeability and low temperatures. The presence of bitumen in this limestone, as evidenced by the petroliferous odour given off when struck with a hammer, may have created reducing conditions. High porosity and relatively high permeability are also present. pH would be increased due to interaction of the ore fluids with the carbonate. Interaction between one fluids and host rock would also result in isotopic exchange, depleting the host carbonate in the heavier isotopes of oxygen and carbon.

Still remaining, is the problem of how the fluids came into contact with the limestone. The mineralized limestone lies stratigraphically above almost 150 metres of impermeable evaporites. This limestone was probably in contact with the Horton Group during the mineralizing episode. Pre-mineralization faulting is a likely explanation. The possibility of a basement high of Horton Group rocks, however, can not be ruled out. A basement high may exist east of the deposit. Diamond drill hole NS-7, drilled by Dome Exploration Ltd., may have encountered such a high. This hole encounted 105 metres of carbonate at which point 7 metres of red and grey sandstone, shale and arkose were encounted before the drilling was stopped. These clastics were logged as the Horton Group by Dome geologists because of the similarity of this lithology to the Horton Group in the area.

6.5 Timing of Mineralization

Mineralization at Pembroke occurred after lithification of the host limestone and at sufficient depths to prevent the fluids from boiling. It occurred prior to major compaction and stylolite formation and before the folding event. The folding event probably occurred during the late stages of the Maritime Disturbance (Late Carboniferous). It is likely that mineralization occurred during the Maritime Disturbance when the geothermal gradient was

high. This would coincide with the late stages of evaporite dewatering.

CHAPTER 7 CONCLUSIONS

Galena mineralization at Pembroke is confined to the Macdonald Road formation limestone of the Lower Carboniferous Windsor Group. Coarse-grained galena occurs in calcite veinlets as well as filling interskeletal and intraskeletal pores often created by abundant fossil brachiopods.

Fluid inclusions in mineralized calcite homogenize at 214.8°C, indicating the minimum temperature of crystal-lization and suggesting an epigenetic origin for the deposit.

Mean \int^{18} OSMOW values of +19.08 and \int^{13} CPDB values of +1.38 indicate that mineralizing fluids may have been the result of fractionation of basinal brines due to elevated temperatures. Mineralization resulted in isotopic exchange, lowering the original \int^{18} O and \int^{13} C values of the host carbonate.

One can speculate that the mineralizing event, which occurred before major compaction (stylolite formation) and folding, was accommodated by a high geothermal gradient, probably during the Maritime Disturbance (Pennsylvanian). Dewatering of evaporites, due to increased pressures and temperatures, may have resulted in overpressured basinal brines. The brines could have leached the underlying Ordovician metasediments with subsequent transport of metals to favourable sites along the Horton-Windsor contact.

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APPENDIX

Sample #	Composition and type	Location	Mineralization	(C)	\$ 0 18 POB	50 smou	Fossil used
P-13 VM	calcite veinlet	Pembroke	galena	+ .94	-11.43	+19.08	
P=9GN	geopetal calcite	Pembroke	not mineralized?	+1.45	-10.51	+20.03	
FVN	calcite vein	DDH-GB-15	not mineralized	-1.17	- 9.18	+21.40	
P-9VN	calcite veinlet	Pembroke	not mineralized?	+1.16	-11.47	+19.04	
P=911	limestone host (brachiopod Rudstone)	Pembroke	altered	+2.25	- 9.86	+20.70	Unknown brachiopod
P- 15HM	limestone host (brachiopod Rudstone)	Pembroke	altered	+2.15	- 9.17	+21.41	Unknown
P-5HM	limestone host (brachiopod Rudstone)	Pembroke	altered	+2.44	- 8.63	+21.96	Ovatia lyelli
FIId	dolomite host (skeletal grainstone)	DDH-GB-15	not altered	+2.01	- 6.26	+24.41	Unknown
P-14HM	limestone host (brachiopod Rudstone)	Pembroke	altered	+2.65	- 7.92	+22.70	Ovatia lyelli
P-11VN	calcite veinlet	Pembroke	not mineralized	+1.42	-10.61	¥19.92	'
P-4GN	geopetal calcite	Pembroke	not mineralized	+1.60	-10.17	+20.38	
P-8VM	calcite vein .	Pembroke	mineralized	+1.54	-10.40	+20.14	
P-3GM	geopetal calcite	Pembroke	mineralized	+1.52	-10.42	+20.12	
P-5GM	geopetal calcite	Pembroke	mineralized	+1.41	-10.87	+19.65	
224-15	calcite vein	Gold Brook	sphalerite	-9.85	- 7.03	+23.61	·

Table I Description and carbon and loxygen isotopic composition of samples from Pembroke and Gold Brook.

SAMPLE NUMBER	LOCATION .	DESCRIPTION	IDENTIFICATION	δ ¹³ c _{PDB°/}	δ ¹⁸ 0 _{SMOW} %
S-001	Miller's Quarry	Brachiopod from the Miller limestone	Composita windsorensis	+ 3.61	+ 24.63
S-002	Miller's Quarry	Brachiopod from the Miller limestone	Composita windsorensis	+ 4.49	+ 24.49
s-003	Miller's Quarry	Brachiopod from the Miller limestone	Dielasma davidsoni	+ 4.55	+ 25.08
S-004	Miller's Quarry	Brachiopod from the Miller limestone	Spirifena vernuili	+ 4.20	+ 24.62
S-005	Miller's Quarry	Brachiopod from the Miller limestone	Spirifena vernuili	+ 4.47	+ 24.57
s-006	Miller's Quarry	Brachiopod from the Miller limestone	Productus lyelli	+ 4.47	+ 25.56
S-007	Miller's Quarry	Brachiopod from the Miller limestonc	Productus lyelli	+ 4.38	+ 26.39
Range of δ^{18} 0	+24.49 to +26.39	Mean δ^{18} 0	SMOW = 25.05 ± .7 per mi	.1	
Range of $\delta^{13}C$	+ 3.61 to + 4.55	Mean $\delta^{13}C_1$	PDB = + 4.31 ± .3 per mi	.1	

Table 2 Description and carbon and oxygen isotopic composition of unaltered limestone from the Miller Brook limestone quarry.

