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Résumé de l'article

Cet article présente les résultats d'une étude microthermométrique d'inclusions fluides dans la dolomite (pre-minéralisation), la sphalérite (syn-minéralisation), la calcite et le quartz authigènes (syn- et post-minéralisation) du dépôt de Zn-Pb de Gays River et de ses environs non minéralisés. Les données de la température d'homogénéisation (T_h) et de la salinité du dépôt indiquent que pendant la précipitation d'une part majeure de la sphalérite et d'une faible part de la calcite et du quartz, un fluide de haute température (200°C) et salinité (27% poids en équivalent NaCl) se serait mélangé avec un fluide de plus basse température ($T_h=107-147^\circ\text{C}$) et salinité (24% poids en équivalent NaCl), i.e. celui qui a dolomitisé les carbonates et saturé leur pores avant la minéralisation. Pendant la précipitation de la plus grande part de la calcite et d'une faible part de la sphalérite, un troisième fluide, de plus faible salinité (<20% poids en équivalent NaCl) et température ($T_h<90^\circ\text{C}$), a affecté le système hydrothermal et s'est mélangé avec les deux fluides préexistants. Un mode de mélange similaire est observé dans les régions non minéralisées. Un groupe d'inclusions fluides dans la calcite (du dépôt et des régions non minéralisées) ont des salinités très basses (0.4-14 poids en équivalent NaCl) et des T_h variables (60-246°C). Ces résultats sont interprétés comme des artefacts dus à des fuites et à un remplissage par les fluides tardifs de basse salinité.

Fluid evolution and mixing in the Gays River carbonate-hosted Zn-Pb deposit and its surrounding barren areas, Nova Scotia*

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This paper presents the results of a microthermometric study of fluid inclusions in authigenic dolomite (pre-ore), sphalerite (syn-ore), calcite and quartz (syn- to post-ore) from the Gays River Zn-Pb deposit and its surrounding barren carbonates. Homogenization temperature (T_h) and salinity data from the deposit indicate that during precipitation of most sphalerite and minor calcite and quartz, a high-temperature ($\geq 200^\circ\text{C}$), high-salinity (≥ 27 wt. % NaCl eq.) fluid mixed with a fluid having lower temperature ($T_h = 107\text{--}147^\circ\text{C}$) and salinity (24 wt. % NaCl eq.), i.e., the fluid that dolomitized the carbonates and saturated their pores before mineralization. During precipitation of most calcite and minor sphalerite, a third fluid with lower salinity (< 20 wt. % NaCl eq.) and temperature ($T_h < 90^\circ\text{C}$) affected the hydrothermal system and mixed with the two pre-existing fluids. A similar mixing trend has been observed for the barren areas. A group of fluid inclusions in calcite (both from the deposit and barren areas) have very low salinities (0.4–14 wt. % NaCl eq.) and variable T_h (60–246°C); these results are interpreted as artifacts due to leaking and refill by late, low-salinity fluids.

Cet article présente les résultats d'une étude microthermométrique d'inclusions fluides dans la dolomite (pré-minéralisation), la sphalérite (syn-minéralisation), la calcite et le quartz authigènes (syn- à post-minéralisation) du dépôt de Zn-Pb de Gays River et de ses environs non minéralisés. Les données de la température d'homogénéisation (T_h) et de la salinité du dépôt indiquent que pendant la précipitation d'une part majeure de la sphalérite et d'une faible part de la calcite et du quartz, un fluide de hautes température ($\geq 200^\circ\text{C}$) et salinité ($\geq 27\%$ poids en équivalent NaCl) se serait mélangé avec un fluide de plus basses température ($T_h = 107\text{--}147^\circ\text{C}$) et salinité (24% poids en équivalent NaCl), i.e. celui qui a dolomitisé les carbonates et saturé leur pores avant la minéralisation. Pendant la précipitation de la plus grande part de la calcite et d'une faible part de la sphalérite, un troisième fluide, de plus faibles salinité ($< 20\%$ poids en équivalent NaCl) et température ($T_h < 90^\circ\text{C}$), a affecté le système hydrothermal et s'est mélangé avec les deux fluides préexistants. Un mode de mélange similaire est observé dans les régions non minéralisées. Un groupe d'inclusions fluides dans la calcite (du dépôt et des régions non minéralisées) ont des salinités très basses (0.4–14 poids en équivalent NaCl) et des T_h variables (60–246°C). Ces résultats sont interprétés comme des artefacts dus à des fuites et à un remplissage par les fluides tardifs de basse salinité.

INTRODUCTION

The Gays River Zn-Pb deposit, located in southern Nova Scotia (Fig. 1), is one of several base metal deposits hosted by the basal Windsor carbonates (Early Carboniferous) along the southern margin of the Late Devonian - Permian Maritimes Basin. In previous studies of the deposit, fluid inclusions have been used to investigate the nature of the hydrothermal fluids and the physicochemical conditions during mineralization (Akande and Zentilli, 1984; Ravenhurst *et al.*, 1989; Kontak, 1992). These studies have shown that the ore-forming fluids were hot ($> 200^\circ\text{C}$), hypersaline brines (> 23 wt. % NaCl eq.) (Akande and Zentilli, 1984; Ravenhurst *et al.*, 1989; Kontak, 1992), that were probably derived from the central part of the Maritimes Basin (Ravenhurst *et al.*, 1989).

Although fluid inclusions have been extensively studied in the deposit, several problems remain unsolved. Firstly, a wide range of homogenization temperatures and salinities have been reported, and the reason for this variation

remains unexplained. Homogenization temperatures range from 90 to $> 210^\circ\text{C}$ in sphalerite and from 70 to $> 250^\circ\text{C}$ in calcite (Kontak, 1992), or from 158 to 219°C in sphalerite, 167 to 178°C in ore-stage calcite and 132 to 147°C in post-ore calcite (Akande and Zentilli, 1984; Ravenhurst *et al.*, 1989). Salinities of fluid inclusions vary from 23 to 25 wt. % NaCl equivalent in calcite to 23 to 35 wt. % NaCl equivalent in sphalerite (Kontak, 1992). Secondly, the compositional systems of the inclusion fluids, except for a few fluid inclusions (Kontak, 1992), have not been determined due to incomplete freezing data, and the relationship between homogenization temperatures and salinities has not been established. Thirdly, in contrast to extensive investigations of fluid inclusions in the deposit, fluid inclusions from the barren surroundings have only received cursory study (Savard, 1992). Consequently, little is known about fluids which circulated in the barren areas and their relationship to fluids in the deposit. Finally, a more recent study (Kontak *et al.*, 1994) indicates that a group of fluid inclusions in authigenic quartz (?) and calcite have relatively low salinities (< 1 to 15 wt. %

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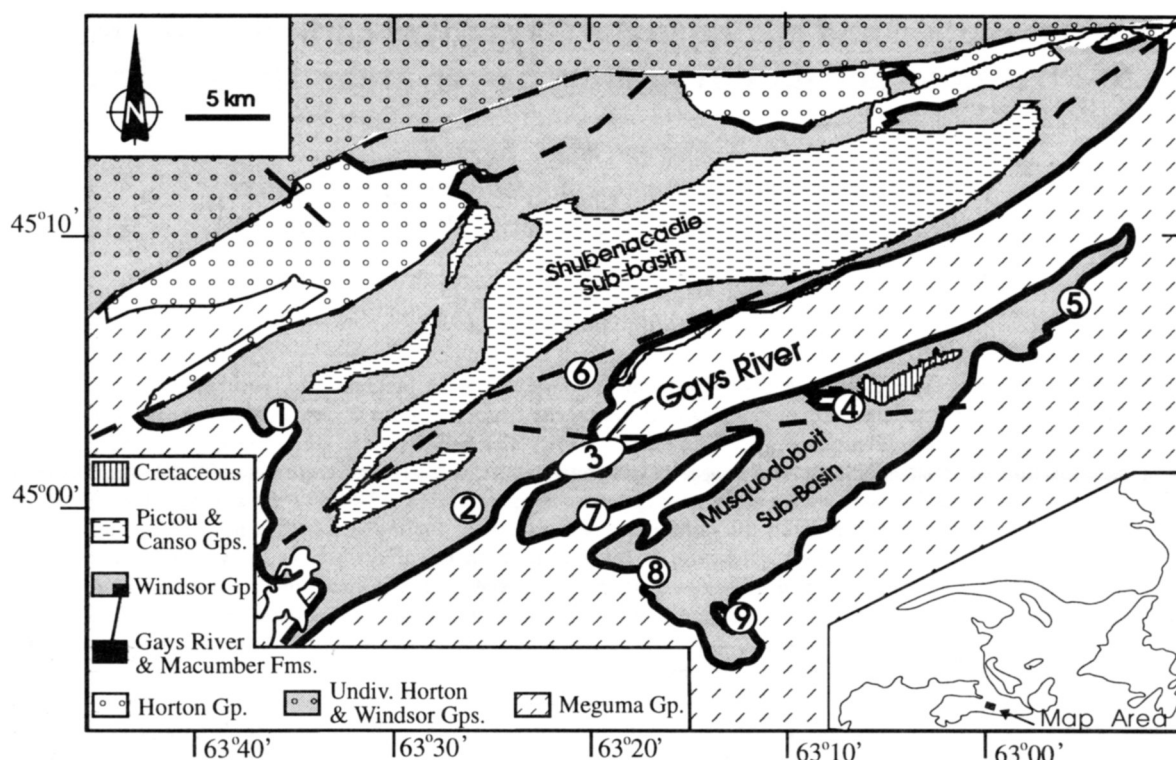


Fig. 1. Geological map of Shubenacadie and Musquodoboit sub-basins (simplified from Giles and Boehner, 1982) showing sample locations.

NaCl eq.) and variable homogenization temperatures. The nature of these low salinity fluids and their relationship with the high-salinity brines have not been investigated.

From previous studies described above it appears that more than one fluid was involved in the hydrothermal system of the Gays River deposit, but the relationships between these different fluids remain unclear. The objective of this paper is to examine the thermal and compositional characteristics of the fluids that have affected the Gays River deposit and its surrounding barren areas through a systematic microthermometric study of fluid inclusions from pre-, syn-, to post-ore minerals, and to explain some of the problems previously outlined, especially the wide range of salinity and homogenization temperature.

GEOLOGICAL SETTING

The Gays River Zn-Pb deposit is hosted by dolostones of the Gays River Formation (Viséan), which unconformably overlies a basement high of metasedimentary rocks of the Meguma Group. The basement high is the boundary between the Shubenacadie sub-basin to the northwest, and the Musquodoboit sub-basin to the southeast (Fig. 1). In lows of the two sub-basins, deeper water carbonates equivalent to the Gays River Formation belong to the Macumber Formation which rests on Upper Devonian-Lower Carboniferous clastic rocks of the Horton Group. Carbonates of the Gays River and Macumber formations are covered by evaporites of the Carrolls Corner and Stewiacke formations and locally, by fine clastics of the Meaghers Grant Formation. A

schematic representation of the stratigraphy in the Gays River region is illustrated in Figure 2.

The mineralization in the Gays River deposit occurs both as replacement (massive ore) and pore-space filling (disseminated ore) of host-rock dolostones. The massive ore represents the high-grade part of the deposit, and is located at the dolostone-evaporite contact, in fine wackestones and packstones of the northwestern flank of the Gays River carbonate mound. The disseminated ore is of relatively low grade, and occurs mainly beneath the massive ore (Kontak, 1992).

SAMPLES AND PETROGRAPHY

Nineteen samples from the deposit (area 3, Fig. 1) and twenty samples from the surrounding barren areas (1-2 and 4-9, Fig. 1) were selected for fluid inclusion studies. Most samples from the deposit are from the low-grade part, because the replacive sphalerite from the high grade part is fine grained and does not contain fluid inclusions suitable for microthermometric study.

Petrographic study of the samples indicates a paragenetic pattern similar to that established by Savard (1991, 1992): marine limestones were pervasively replaced and then cemented by dolomite prior to Zn-Pb mineralization, and calcite, fluorite, and barite mainly post-date (partly overlap) sphalerite and galena. Some authigenic quartz, post-dating dolomite and contemporaneous with associated calcite, was found during this study. The paragenetic sequence, modified after Savard (1991, 1992), is summarized in Figure 3.

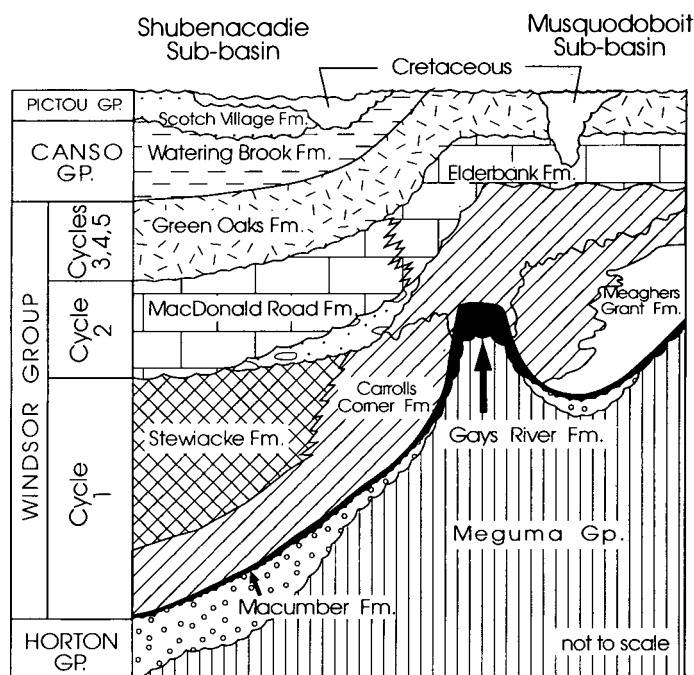


Fig. 2. Schematic representation of the stratigraphy of the Windsor Group around the Gays River deposit (after Giles and Bochner, 1982).

Fluid inclusions were studied in dolomite, sphalerite, calcite, and authigenic quartz. Dolomite occurs as cement in primary pores or as replacement of limestones. Dolomite cement typically occurs as small euhedral crystals on the wall of pores, and always pre-dates sphalerite and galena where a direct relationship between them can be observed (see also Savard, in press). Fluid inclusions in dolomite cement will be used to characterize the pre-ore fluid regime (fluid inclusions in the cloudy core of dolomite cement may have been inherited from the replacive precursor).

Sphalerite and galena occur in primary pores preserved through dolomitization and in subsequent fractures with or without associated calcite (Fig. 4A, B, C). They can totally fill a pore, or coat walls with calcite occupying the remaining pore space (Fig. 4B). In these cases, calcite may be broadly considered as being partly contemporaneous with, but mainly post-dating, sphalerite and galena. Calcite also occurs in pores or fractures without associated sulfides (both in the deposit and barren areas), in which case its timing with respect to mineralization is unknown. Under cathodoluminescence, most calcite is uniformly dull (bright when there are many inclusions), but some crystals are zoned and seem to be earlier than uniform crystals. However, no consistent cathodoluminescent distinction can be established between ore-stage and post-ore calcites. It is likely that precipitation of the uniform calcite started during, and continued after mineralization. Therefore, calcite is generally treated as a syn- to post-ore mineral. In a few cases in the deposit, calcite fills fractures that clearly post-date sphalerite-galena-calcite assemblage (Fig. 4D, E). These late calcite veins do not contain dolomite, sphalerite or galena, and are considered to be the true post-ore products. Fluid inclusions in

Host Minerals	Pre-ore	Syn-ore	Post-ore
Dolomite cement	—		
Sphalerite		—	
Galena		—	
Calcite (CL-zoned)			—
Calcite (CL-dull)			—
Authigenic quartz			—

Fig. 3. Paragenetic sequence (modified from Savard, 1991, 1992). Only the minerals from which fluid inclusions were studied are listed. The timing of petrographic elements is given relative to ore minerals (sphalerite and galena).

late calcite veins are used to characterize the post-ore fluid regime.

Quartz is frequently observed in our samples, and in most cases it is well rounded and shows undulatory extinction. With such attributes, it is classified as detrital, probably derived from metamorphic rocks. In one sample from the deposit, quartz crystals are clear, euhedral, have unique extinction and fill pores. Such quartz is classified as authigenic. It clearly post-dates dolomite cement, and appears to be contemporaneous with associated syn- to post-ore calcite (Fig. 4F).

FLUID INCLUSION TYPES AND OCCURRENCES

Two compositional types of fluid inclusions have been observed: (1) aqueous inclusions, and (2) hydrocarbon inclusions, including crude oil and methane. Hydrocarbon inclusions are rare, and were observed only occasionally in CL-zoned calcite (both in the deposit and barren areas) and fluorite. Crude oil inclusions have a brown color and comprise a liquid and a vapor phase at room temperature. Methane inclusions comprise a vapor phase at room temperature and nucleate a liquid phase during cooling which homogenizes to vapor at temperatures between -87 and -74°C . The higher temperature (-74°C) may imply minor CO_2 . Because of their limited number, hydrocarbon inclusions will not be further considered in this paper.

Aqueous inclusions are abundant in most samples examined. Both primary (and pseudosecondary) and secondary types were observed. Only the primary or pseudosecondary type of inclusions according to the criteria of Roedder (1984) was selected for microthermometric study. The occurrences of these inclusions are described below.

Fluid inclusions in dolomite are commonly small ($\leq 8 \mu\text{m}$) and comprise two phases (liquid + vapor) at room temperature. They occur in the cloudy core regions (inherited from replacive dolomite) of euhedral crystals with a clean rim (Fig. 5A), or are randomly distributed in three dimensions throughout a crystal. Fluid inclusions in sphalerite comprise two phases (liquid + vapor) at room temperature.

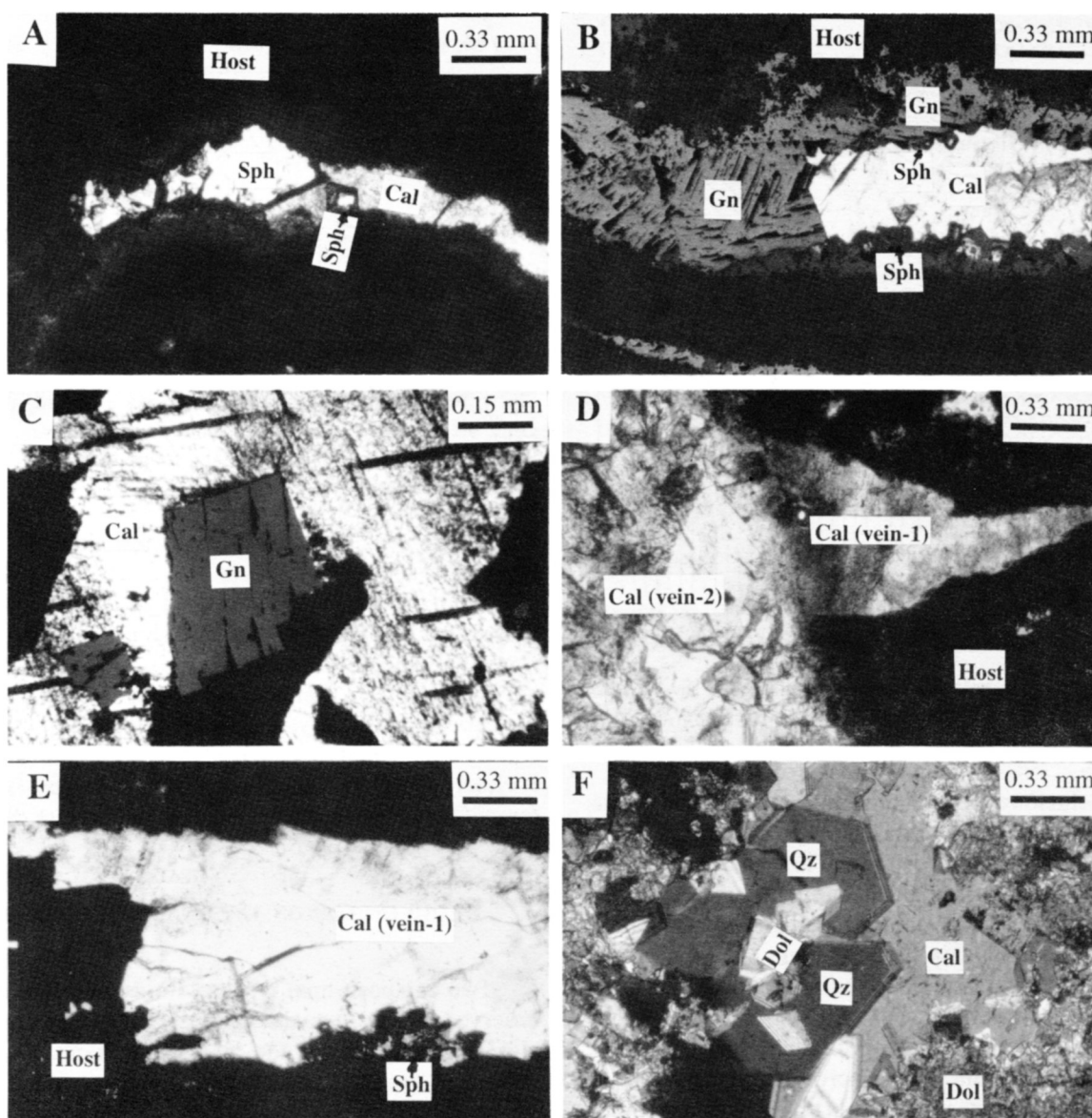


Fig. 4. Photomicrographs showing (A) euhedral sphalerite and calcite fill a fracture (calcite may be partly contemporaneous with sphalerite) (core: GR-191; sample: No.734); (B) sphalerite, galena and calcite fill a pore (sphalerite post-dating some galena and pre-dating calcite; galena partly post-dating sphalerite and partly contemporaneous with calcite) (U-625; No.907); (C) galena associated with calcite in a vein (contemporaneous) (U-637; No.806); (D) a late calcite vein cuts a calcite with minor sphalerite (continuation of the same fracture shown on (E)) and host rocks with disseminated sphalerite, galena and calcite (U-637; No.943); (F) authigenic quartz post-dating dolomite and contemporaneous with calcite (GGR-112; No.306). Dol = dolomite; Sph = sphalerite; Gn = galena; Cal = calcite; Qz = authigenic quartz.

They occur in clusters lacking fracture control (Fig. 5B) or are isolated (Fig. 5C). Fluid inclusions in syn- to post-ore calcite comprise two phases (liquid + vapor) or, less commonly, three phases (liquid + vapor + halite). They are randomly distributed in three dimensions (Fig. 5D) or occasionally occur along growth zones. Fluid inclusions in late calcite veins typically comprise only one phase (liquid) (Fig. 5E), and are randomly distributed. The absence of vapor bubble in the inclusions likely indicates low trapping temperature and natural metastability (failure to nucleate a vapor bubble) (Roedder, 1984). Fluid inclusions in authigenic quartz are rare. They comprise two phases (liquid + vapor) and occur in clusters lacking fracture control (Fig. 5F).

ANALYTICAL METHOD

Microthermometric measurements of fluid inclusions were performed on a U.S.G.S. Heating-Freezing Stage. The stage has been calibrated to a precision and accuracy of $\pm 0.1^\circ\text{C}$ with synthetic fluid inclusions provided by Fluid Incorporated. Homogenization temperatures were measured for each selected fluid inclusion in a chip of sample prior to cooling runs, in order to avoid the effect of stretching caused by fluid freezing. For monophasic fluid inclusions from late calcite veins, however, cooling runs were first performed to force the nucleation of vapor bubble. The homogenization temperature of such inclusions can only be used as the maxi-

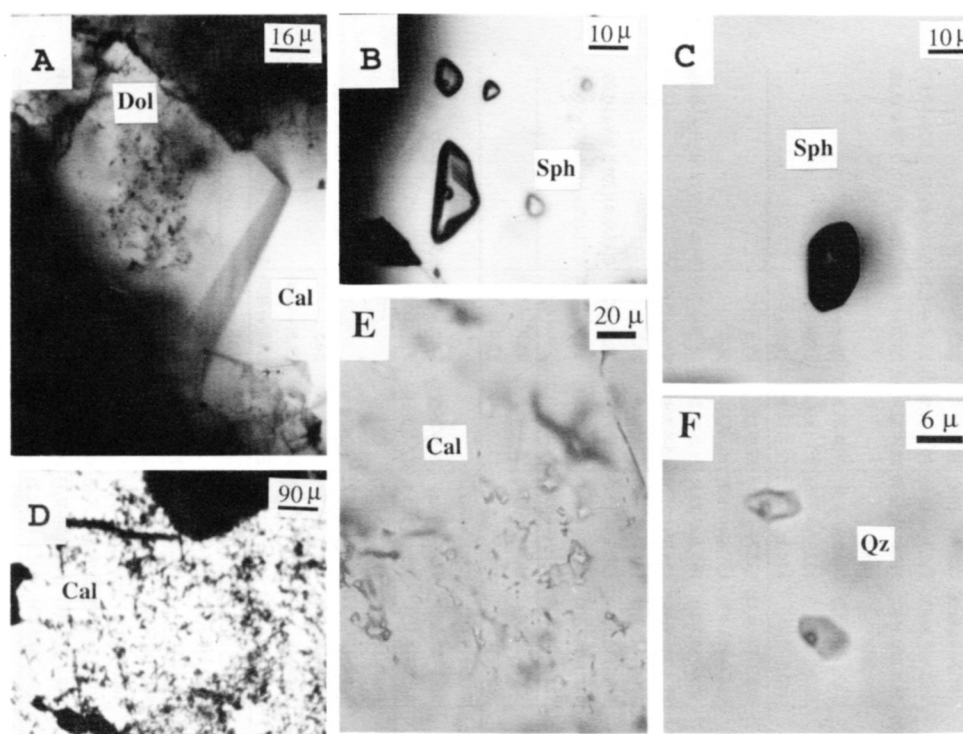


Fig. 5. Photomicrographs showing (A) fluid inclusions in the core of a dolomite crystal with an inclusion-free rim (NM-8; No.313); (B) a cluster of fluid inclusions in sphalerite (U-643; No.898); (C) an isolated fluid inclusion in sphalerite (GR-256; No.217); (D) randomly distributed fluid inclusions in CL-dull calcite (GGR-7; No.811); (E) monophasic fluid inclusions in a late calcite vein (U-637; No.943); (F) a small cluster of two fluid inclusions in authigenic quartz (GGR-112; No.306). Abbreviations of minerals are the same as in Figure 4.

mum value because artificial stretching has likely taken place. Melting temperatures (first melting, ice, hydrohalite, and halite melting temperatures, where applicable and observable) were measured for about one fifth of the inclusions for which homogenization temperature data have been obtained. All cathodoluminescence observations were performed after microthermometric measurements had been completed.

MICROTHERMOMETRIC RESULTS

Microthermometric results are summarized in Table 1. Homogenization and melting temperatures as well as compositional data calculated from melting temperatures are described following the paragenetic order of the host minerals (dolomites, sphalerite, syn- to post-ore calcite, authigenic quartz, and late calcite veins) for the deposit and barren areas respectively.

Melting temperatures and estimate of composition and salinity

First melting temperatures (Table 1) fall into two groups: one ranges from -68.7 to -49.9°C, and the other, from -33.8 to -26.5°C. The first group of fluid inclusions generally froze and the vapor bubble was slightly deformed at temperatures between -90 and -65°C. The first melting temperature of this group of inclusions can be measured with a precision of $\pm 2^\circ\text{C}$. By contrast, the second group of fluid inclusions froze at temperatures around -40°C and the vapor bubble

was significantly squeezed. The first melting temperature of this group of inclusions was generally difficult to measure due to its low salinity. The measured values merely reflect temperatures at which melting processes started to be observable and the actual first melting temperatures could be lower than observed.

The first group (named Aq-1) can be approximated by the $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system. The first melting temperatures of such system are usually within 3°C of the eutectic temperature (-52°C) if stable salt hydrates form during cooling, but they may be as low as -80°C if there are metastable salt hydrates (Davis *et al.*, 1990). The second group (named Aq-2) may belong to the $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system too, but because the salt concentration is very low and the melting temperatures of salt hydrates cannot be detected, it is approximated by the $\text{H}_2\text{O}-\text{NaCl}$ system in the following calculation of salinity. These approximations do not exclude the possible presence of other cations such as K^+ and Mg^{2+} , but Na^+ and Ca^{2+} are generally much more important in fluid inclusions from carbonate-hosted Pb-Zn deposits as indicated by quantitative analyses (e.g., Roedder, 1967; Haynes and Kesler, 1987).

The melting sequence after first melting depends on the composition of the fluid in inclusions. For Aq-2 inclusions, ice is the next (and last) observable phase to melt. Melting temperatures of ice can be measured with a precision of $\pm 0.2^\circ\text{C}$. For Aq-1 inclusions, three sequences of melting were observed: (1) hydrohalite - ice; (2) ice - hydrohalite (as illustrated in Fig. 6); and (3) ice - hydrohalite - halite. In the

Table 1. Microthermometric results of fluid inclusions from the Gays River deposit and its surrounding barren areas.

	Area	Host	Stage	Type	Tm-1st (- °C)		Tm-HH (- °C)		Tm-H ₂ O (- °C)		Tm-H (°C)		Th (°C)		Salinity (wt%)		NaCl/(NaCl+ CaCl ₂)	
					Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
					(Number)	(Std. Dev.)	(Number)	(Std. Dev.)	(Number)	(Std. Dev.)	(Number)	(Std. Dev.)	(Number)	(Std. Dev.)	(Number)	(Std. Dev.)	(Number)	(Std. Dev.)
Ore Deposit	3	Dol	1	Aq-1	53.4(1)	53.4			24.6(1)	24.6			107.2-146.8(26)	129.4(+/-10.6)	24.3(1)	24.3		
		Sph	2	Aq-1	50.2-68.7(27)	54.9(+/-4.1)	2.4-28.7(12)	23.2(+/-7.3)	16.2-29.0(33)	24.0(+/-1.9)			92.2-197.8(47)	136.3(+/-18.8)	19.2-26.9(33)	23.8(+/-1.2)	0.45-0.69(12)	0.57(+/-0.07)
		Cal-d	2,3	Aq-1	50.9-62.4(9)	55.1(+/-3.7)	21.9-31.5(9)	24.3(+/-2.9)	14.7-32.8(16)	21.3(+/-4.1)	140.1-148.1(4)	144.0(+/-4.3)	56.4-200.1(82)	117.0(+/-30.4)	18.4-32.7(19)	24.2(+/-4.6)	0.32-0.90(10)	0.70(+/-0.18)
		Cal-z	2,3	Aq-1									140.2(1)	140.2				
		Qz	2,3	Aq-1	57.7-59.8(2)	58.8(+/-1.5)			30.5-31.4(2)	31.0(+/-0.6)			142.2-149.7(2)	146.0(+/-5.3)	26.0-26.1(2)	26.1(+/-0.1)		
		Cal-d	3(?)	Aq-2	26.5(1)	26.5			0.3-9.9(16)	1.7(+/-2.4)			60.2-245.9(17)	137.2(+/-50.5)	0.5-13.9(16)	2.7(+/-3.4)		
		Cal-d	3	Aq-1	>32.4	>32.4			10.7-15.8(5)	12.8(+/-1.9)			<70.2	<70.2	14.7-19.3(5)	16.7(+/-1.7)		
Barren Areas	1	Dol	1	Aq-1	54.6(1)	54.6			20.8(1)	20.8			110.2-150.6(12)	132.7(+/-11.9)	22.9(1)	22.9		
		Sph	2	Aq-1	57.9(1)	57.9			27.6(1)	27.6			128.6-173.4(5)	151.8(+/-16.2)	26.17(1)	26.2		
		Cal-d	2,3	Aq-1	50.4-57.4(6)	55.5(+/-2.7)	21.2-22.0(3)	21.7(+/-0.4)	12.0-25.2(14)	19.1(+/-4.1)			60.6-155.1(24)	105.2(+/-22.3)	16.0-25.2(14)	21.3(+/-2.9)	0.89-1.00(3)	0.93(+/-0.06)
		Cal-d	3(?)	Aq-2	32.3-33.8(2)	33.1(+/-1.1)			0.3-6.0(8)	2.9(+/-2.3)			82.4-246.9(9)	124.8(+/-52.5)	0.5-9.2(8)	4.6(+/-3.6)		
	2	Dol	1	Aq-1	58.0(1)	58.0			23.8(1)	23.8			120.3-145.9(6)	134.1(+/-8.7)	24.1(1)	24.1		
		Cal-d	2,3	Aq-1	49.9-56.9(23)	53.3(+/-1.8)	2.8-29.0(15)	21.0(+/-6.9)	18.5-27.9(25)	23.6(+/-2.2)	127.7-168.8(6)	150.6(+/-14.4)	80.6-182.5(84)	128.3(+/-19.4)	20.9-31.5(27)	25.5(+/-3.1)	0.44-0.83(19)	0.70(+/-0.09)
		Cal-z	2,3	Aq-1	52.8-63.0(5)	60.1(+/-4.1)	16.0-23.8(6)	17.6(+/-3.0)	23.7-24.0(6)	23.8(+/-0.1)			148.1-237.3(8)	183.7(+/-40.7)	24.0-25.3(6)	25.0(+/-0.5)	0.72-0.73(6)	0.73(+/-0.01)
		Cal-d	3(?)	Aq-2					0.2-0.8(4)	0.5(+/-0.3)			121.5-249.6(4)	187.1(+/-53.5)	0.4-1.4(4)	0.9(+/-0.5)		
	4	Cal-d	2,3	Aq-1	51.2-56.0(3)	53.0(+/-2.6)			21.5-25.4(4)	22.8(+/-1.8)			100.2-224.4(19)	153.0(+/-30.8)	23.1-25.3(4)	23.9(+/-1.0)		
		Cal-d	3(?)	Aq-2					9.0(1)	9.0			268.5(1)	268.5	12.9(1)	12.9		
	5	Dol	1	Aq-1									93.5-117.4(5)	105.5(+/-8.8)				
		Cal-d	2,3	Aq-1	52.3-58.1(2)	55.2(+/-4.1)	8.6-9.2(2)	8.9(+/-0.4)	16.7-22.0(5)	19.7(+/-2.3)			65.2-157.6(23)	97.4(+/-30.6)	19.9-25.5(5)	22.7(+/-2.6)	0.90(2)	0.90
		Cal-d	3(?)	Aq-2	28.4(1)	28.4			0.4-1.3(5)	0.7(+/-0.4)			94.2-157.1(5)	125.7(+/-25.1)	0.7-2.2(5)	1.3(+/-0.6)		
	6	Dol	1	Aq-1									112.4-161.4(19)	138.2(+/-13.1)				
		Cal-d	2,3	Aq-1									106.2-157.2(12)	135.5(+/-14.2)				
	7	Dol	1	Aq-1					25.1(1)	25.1			126.3-132.8(3)	129.5(+/-3.3)	24.5(1)	24.5		
		Sph	2	Aq-1	51.7(1)	51.7			23.0-24.0(2)	23.5(+/-0.7)			110.6-152.8(8)	135.3(+/-15.8)	23.2-23.8(2)	23.5(+/-0.4)		
		Cal-d	2,3	Aq-1	50.4-55.6(3)	52.5(+/-2.8)	26.2(1)	26.2	23.6-26.5(4)	25.0(+/-1.3)			80.6-145.8(19)	117.5(+/-19.1)	23.6-24.9(4)	24.1(+/-0.7)	0.57(1)	0.57
	8	Cal-d	2,3	Aq-1	58.4(1)	58.4			25.6(1)	25.6			140.0-173.9(12)	157.1(+/-10.4)	24.5(1)	24.5		
	9	Cal-d	2,3	Aq-1									88.8-146.7(6)	123.0(+/-19.7)				
		Cal-d	3(?)	Aq-2					0.2(1)	0.2			182.0(1)	182.0	0.4(1)	0.4		
	barren areas as a whole	Dol	1	Aq-1	54.6-58.0(2)	56.3(+/-2.4)			20.8-25.1(3)	23.2(+/-2.2)			93.5-161.4(45)	132.0(+/-14.8)	22.8-24.5(3)	23.8(+/-0.8)		
		Sph	2	Aq-1	51.7-57.9(2)	54.8(+/-4.4)			23.0-27.6(3)	24.9(+/-2.4)			100.6-173.4(13)	141.7(+/-17.4)	23.2-26.2(3)	24.4(+/-1.6)		
		Cal-d	2,3	Aq-1	49.9-58.4(38)	53.8(+/-2.4)	2.8-29.0(22)	20.2(+/-7.0)	12.0-27.9(53)	22.1(+/-3.5)	127.7-168.8(6)	150.6(+/-14.4)	60.6-224.4(199)	126.0(+/-27.0)	16.0-31.5(55)	23.9(+/-3.2)	0.44-1.00(25)	0.74(+/-0.12)
		Cal-z	2,3	Aq-1	52.8-63.0(5)	60.1(+/-4.1)	16.0-23.8(6)	17.6(+/-3.0)	23.7-24.0(6)	23.8(+/-0.1)			148.1-237.3(8)	183.7(+/-40.7)	24.0-25.3(6)	25.0(+/-0.5)	0.72-0.73(6)	0.73(+/-0.01)
		Cal-d	3(?)	Aq-2	28.4-33.8(3)	31.5(+/-2.8)			0.2-9.0(19)	2.0(+/-2.5)			82.4-268.5(20)	147.5(+/-57.2)	0.4-12.9(19)	3.2(+/-3.7)		

Areas 1-9 are shown in Figure 1. Dol = dolomite; Sph = sphalerite; Cal-d = CL-dull calcite; Cal-z = CL-zoned calcite; Qz = authigenic quartz. Stage 1: pre-ore; stage 2: syn-ore; stage 3: post-ore. Aq-1: fluid inclusions with low first melting temperatures and high salinities; Aq-2: fluid inclusions with high first melting temperatures and low salinities. Tm-1st = first melting temperature; Tm-HH = hydrohalite melting temperature; Tm-H₂O = ice melting temperature; Tm-H = halite melting temperature; Th = homogenization temperature.

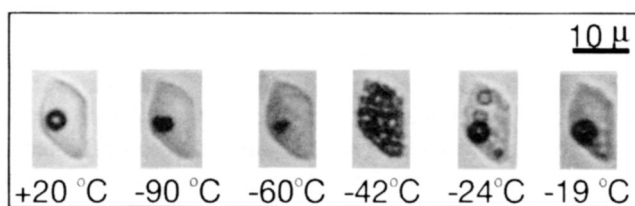


Fig. 6. Photomicrographs showing melting sequence of an aqueous inclusion in CL-zoned calcite (CK-17, No. 549). The inclusion froze at -90°C and started melting at -60°C . At -42°C , ice (dark) and hydrohalite (bright) crystals can be well differentiated; at -24°C , only a few ice crystals coexist with hydrohalite (ice completely melted at -23.8°C), and at -19°C , the only solid phase is hydrohalite (hydrohalite completely melted at -16°C).

first case, the melting temperature of hydrohalite can be measured with a precision of $\pm 2^{\circ}\text{C}$, and the melting temperature of ice can be measured with a precision of $\pm 0.2^{\circ}\text{C}$. In the second case, both melting temperatures of ice and hydrohalite can be measured with a precision of $\pm 0.5^{\circ}\text{C}$. In the third case, the melting temperatures of ice and halite can be measured with a precision of $\pm 0.5^{\circ}\text{C}$ and $\pm 2^{\circ}\text{C}$ respectively, but the melting temperature of hydrohalite was difficult to measure.

Both Aq-1 and Aq-2 inclusions are plotted on a H_2O - NaCl - CaCl_2 diagram (Fig. 7) compiled from the data of Williams-Jones and Samson (1990) and Oakes *et al.* (1990). Aq-2 inclusions lie on the H_2O - NaCl binary system. Aq-1 inclusions are located within the H_2O - NaCl - CaCl_2 ternary system by using the melting temperatures of various phases with the technique described by Williams-Jones and Samson (1990). $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ weight ratios were graphically estimated from the diagram (Fig. 7). The potential error of $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratio introduced by uncertainty on hydrohalite melting temperature in the above-described sequence 2 (i.e., precision = $\pm 2^{\circ}\text{C}$) is about 0.1 to 0.2. For Aq-1 inclusions which plot in the ice + liquid area (Fig. 7) and for all Aq-2 inclusions, salinities were calculated using melting temperatures of ice and $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios (= 1.0 for Aq-2 inclusions) with the equation 2 of Oakes *et al.* (1990). For Aq-1 inclusions for which the last (ice) melting temperature was measured but the second (hydrohalite) melting temperature was not measured, the average $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratio of the same type of fluid inclusions in the same mineral was used to calculate salinities. In the case of dolomite and authigenic quartz, no fluid inclusions have been measured for hydrohalite melting temperature due to their small size, and salinities were calculated by assuming that hydrohalite and ice melted at the same temperature. The errors introduced by this assumption are negligible. For Aq-1 inclusions which plot in the areas of hydrohalite + liquid or halite + liquid, salinities were graphically estimated from Figure 7, i.e., equal to $\text{NaCl wt. \%} + \text{CaCl}_2 \text{ wt. \%}$.

Dolomites (pre-ore stage)

Most fluid inclusions in dolomites did not freeze even when cooled to liquid nitrogen temperature. The few inclu-

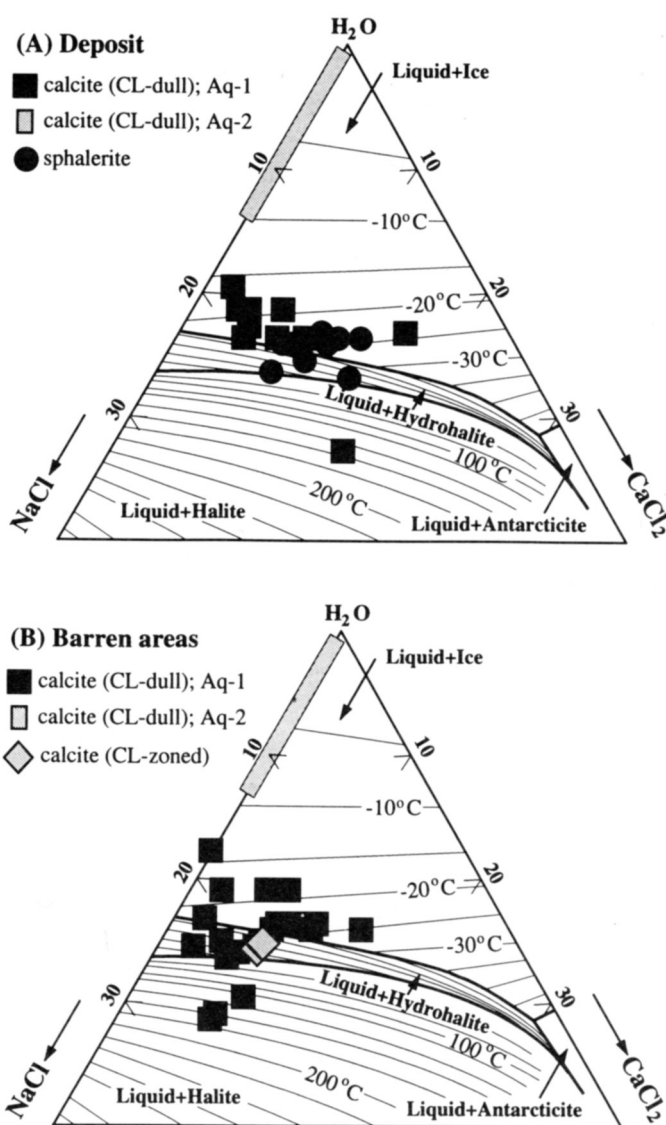


Fig. 7. Ternary diagrams showing composition of aqueous inclusions approximated by the H_2O - NaCl - CaCl_2 system (isotherms are compiled from Oakes *et al.*, 1990 and Williams-Jones and Samson, 1990) for the deposit (upper) and barren areas (lower).

sions which did freeze show first melting temperatures ranging from -58.0 to -53.4°C (Aq-1). The small size of the inclusions made it impossible to measure the melting temperature of hydrohalite, so $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios cannot be estimated. Salinities range from 21.9 to 24.1 wt. % NaCl equivalent. Homogenization temperatures range from 107.2 to 146.8°C for the deposit and from 93.5 to 161.4°C for the barren areas (Fig. 8).

Sphalerite (ore stage)

Fluid inclusions in sphalerite show first melting temperatures ranging from -68.7 to -50.2°C (Aq-1). A few inclusions did not freeze when cooled to liquid nitrogen temperature. Bulk salinities range from 19.2 to 26.9 wt. % NaCl equivalent for the deposit and from 23.2 to 26.2 wt. % NaCl equivalent for the barren areas. $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios

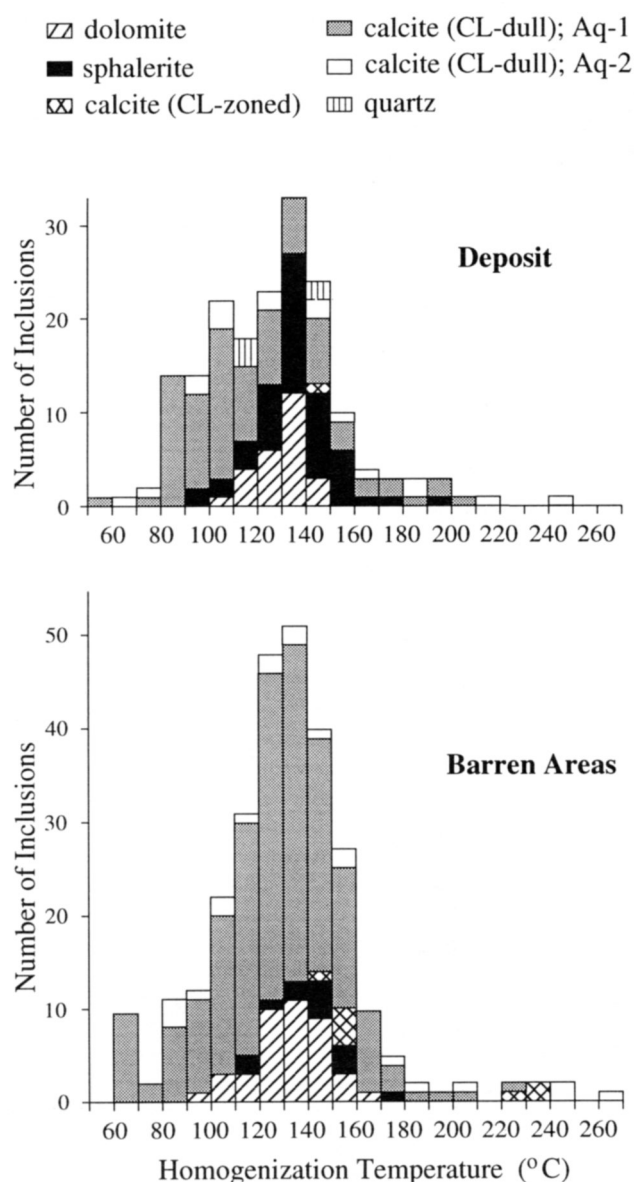


Fig. 8. Histograms of homogenization temperatures of fluid inclusions from the deposit (upper) and barren areas (lower).

range from 0.45 to 0.69 for samples from the deposit, but no data have been obtained for the few inclusions studied in sphalerite from the barren areas. Homogenization temperatures range from 92.2 to 197.8°C for the deposit and from 110.6 to 173.4°C for the barren areas (Fig. 8).

Calcite (syn- to post-ore stage)

Most fluid inclusions studied are from CL-dull calcite, and a few are from CL-zoned calcite. Fluid inclusions in CL-zoned calcite (from barren areas) show first melting temperatures ranging from -63.0 to -52.8°C (Aq-1). Bulk salinities range from 24.0 to 25.3 wt. % NaCl equivalent, and NaCl/(NaCl+CaCl₂) ratios range from 0.72 to 0.73. Homogenization temperatures range from 148.1 to 237.3°C. Fluid inclusions in CL-dull calcite (both from the deposit and barren areas) belong to two groups: one with first melting temperatures ranging from -62.4 to -49.9°C (Aq-1), the other

with first melting temperatures ranging from -33.8 to -26.5°C (Aq-2). In general, both types of fluid inclusions occur in the same sample, but either Aq-1 or Aq-2 dominates in individual crystals. However, there is no petrographic distinction between crystals which host Aq-1 or Aq-2 inclusions. Moreover, it is not uncommon that both Aq-1 and Aq-2 inclusions occur in the same crystal. Bulk salinities, NaCl/(NaCl+CaCl₂) ratios, and homogenization temperatures of Aq-1 inclusions range from 18.4 to 32.7 wt. % NaCl equivalent, 0.32 to 0.90, and 56.4 to 200.1°C for the deposit, from 16.0 to 31.5 wt. % NaCl equivalent, 0.44 to 1.00, and 60.6 to 224.4°C for the barren areas. Bulk salinities and homogenization temperatures of Aq-2 inclusions range from 0.5 to 13.9 wt. % NaCl equivalent and 60.2 to 245.9°C for the deposit, and from 0.4 to 12.9 wt. % NaCl equivalent and 82.4 to 268.5°C for the barren areas.

Authigenic quartz (syn- to post-ore stage)

Only two workable fluid inclusions were found in authigenic quartz in a sample from the deposit. First melting temperatures are -57.7 and -59.8°C (Aq-1). Melting temperatures of ice are -30.5 and -31.4°C. Melting temperatures of hydrohalite cannot be measured. Assuming that hydrohalite and ice melted at the same temperatures, bulk salinities are estimated to be 26.0 and 26.1 wt. % NaCl equivalent. Homogenization temperatures are 142.2 and 149.7°C.

Late calcite veins (post-ore)

Fluid inclusions in late calcite veins are usually monophasic. A few fluid inclusions nucleated a vapor bubble after one or two runs of cooling. These inclusions homogenize at temperatures between 44.2 and 70.2°C. As pointed out above, these temperatures can only be used as the maximum values. First melting temperatures were difficult to measure, but appear to be <-32°C. One inclusion clearly shows a first melting temperature of -56.9°C. Ice-melting temperatures vary from -15.8 to -10.7°C, and salinities vary from 14.7 to 19.3 wt. % NaCl equivalent.

A group of monophasic, highly irregular fluid inclusions in calcite from barren areas shows salinities <5 wt. % and homogenization temperatures probably <50°C, and is interpreted to represent the latest fluids (James Reynolds, personal communication, 1994). This group of inclusions was not detected in the late calcite veins in the present study, but it is likely that it records a very late, low-temperature, low-salinity fluid, which might have infiltrated and diluted some earlier fluid inclusions, resulting in low salinities and variable T_h (Aq-2), as will be discussed below.

DISCUSSION

The microthermometric results documented above indicate that multiple fluids have been present during the evolution of the hydrothermal systems of the Gays River deposit and its surrounding barren areas. The compositional and thermal characteristics of fluids in different evolution stages

and the relationships of different fluids in individual stages are discussed in this section.

Fluid evolution from pre-, syn-, to post-ore stages

According to the relative chronology determined by petrography, the evolution of fluid systems in the Gays River deposit is broadly divided into three stages, i.e., pre-, syn-, and post-ore stages (Fig. 3). The pre-ore stage had a long history and we only studied the fluids in the late period of this stage, i.e., the fluids present during dolomitization. Fluids present during the ore stage are represented by fluid inclusions in sphalerite. Fluid inclusions in calcite (except in late vein calcite) and authigenic quartz are astride the syn-ore and post-ore stages. Fluids obviously post-dating the ore stage are recorded by fluid inclusions in late calcite filling fractures.

For the barren areas, such a division of fluid evolution stages relative to mineralization is difficult because sphalerite and galena are not commonly seen in the samples. However, from the petrographic relationships observed in the few samples that contain sphalerite and galena, it seems reasonable to assume that the dolomites in the barren areas are coeval to those in the deposit (pre-ore), and that the calcite is broadly contemporaneous with the syn- to post-ore calcite in the deposit.

The thermal and compositional evolution of fluids is highlighted on a homogenization temperature versus salinity plot of fluid inclusions, hosted by minerals belonging to different stages (Fig. 9). Fluid inclusions in dolomites (pre-ore) are characterized by median salinity and homogenization temperature. Although freezing data have been obtained for only a few fluid inclusions in dolomite and a small range of salinity is indicated, the homogenization data indicate a span of temperature of about 70°C (Table 1). We propose that a fluid with progressively increasing temperature was present during dolomitization in accordance with isotopic geochemistry (Savard, in press). Fluid inclusions in sphalerite (syn-ore) have a significant range of salinities and homogenization temperatures (both higher and lower than those in dolomite cement), indicating that more than one fluid may have been involved during precipitation of sphalerite. Fluid inclusions in calcite and authigenic quartz (syn- to post-ore, except in late calcite veins) partly overlap, but mainly have lower salinities and homogenization temperatures than those in sphalerite. Fluid inclusions in late calcite veins have the lowest homogenization temperatures and relatively low salinities.

A group of fluid inclusions (Aq-2) in calcite have significantly lower salinities than other inclusions and have variable homogenization temperatures. These inclusions, although they can occur with Aq-1 inclusions in the same sample or even in the same calcite crystal, do not show any mixing trend with the high-salinity inclusions (Aq-1). Instead, they appear to depart from the low-salinity, low-temperature late fluid (lower left corner, Fig. 9) and form a horizontal trend (trend 3?, Fig. 9). Although it cannot be petrographically confirmed, it is likely that this group of

fluid inclusions has leaked and been re-filled by late, low-salinity fluids.

The general trend of fluid evolution, as shown in Figure 9, may be summarized as follows. In the pre-ore stage, fluids had moderate salinities and temperatures (trend 1, Fig. 9). In the main stage of mineralization, the mineralizing fluids had higher salinities and temperatures than the pre-ore fluids (trend 2, Fig. 9). During the waning stage of mineralization and post-ore stage, fluids had lower salinities and temperatures than the two previously infiltrated fluids (trend 3, Fig. 9).

Fluid mixing during and after mineralization

The wide range of homogenization temperatures and salinities of fluid inclusions in sphalerite and syn- to post-ore calcite suggests that more than one fluid has been involved during the precipitation of sphalerite and calcite, both within the deposit and in the barren areas. Variability of fluid inclusion homogenization temperatures and salinities has been reported in many other carbonate-hosted Pb-Zn deposits, e.g., the Viburnum Trend in southeast Missouri (Roedder, 1977; Rowan and Leach, 1989) and the Nanisivik deposit in Baffin Island (Arne *et al.*, 1991). This variability has been interpreted as evidence for mixing of several fluids during mineralization (e.g., Rowan and Leach, 1989; Shelton *et al.*, 1992).

The positive correlation between homogenization temperatures and salinities of fluid inclusions in sphalerite and calcite from the Gays River deposit and its surrounding barren areas (Fig. 9), suggests that fluid mixing was likely the cause of the variability of homogenization temperature and salinity. Based on the study of petrography, a scenario of two stages of mixing can be envisaged. First, during precipitation of most sphalerite and minor calcite, a high-temperature ($\geq 200^\circ\text{C}$), high-salinity (≥ 27 wt. % NaCl eq.) fluid mixed with a fluid having relatively low temperature ($T_h = 94$ – 161°C) and salinity (23–24 wt. % NaCl eq.), i.e., the dolomitizing fluid which saturated pores before mineralization (Mixing A, Fig. 9). This fluid mixing event is likely the result of post-Windsor faulting (Savard *et al.*, 1995): hot, fast incoming fluids travelling along faults mixed with diagenetic background fluids.

During precipitation of most calcite and minor sphalerite, a third fluid with lower salinity (< 20 wt. % NaCl eq.) and temperature ($< 90^\circ\text{C}$) mixed with the hydrothermal and diagenetic fluids. This late fluid eventually dominated in the post-ore stage, as indicated by fluid inclusions in late calcite veins.

Figure 9 shows that a small number of fluid inclusions in calcite (Aq-1), both from the deposit and barren areas, have significantly higher salinities than the others. These inclusions contain a halite crystal at room temperature. Their high salinities may be related to a local source enriched in NaCl.

The correlation between homogenization temperatures and NaCl/(NaCl+CaCl₂) ratios is very weak (Fig. 10, left side). Although it is likely that the high-temperature, high-

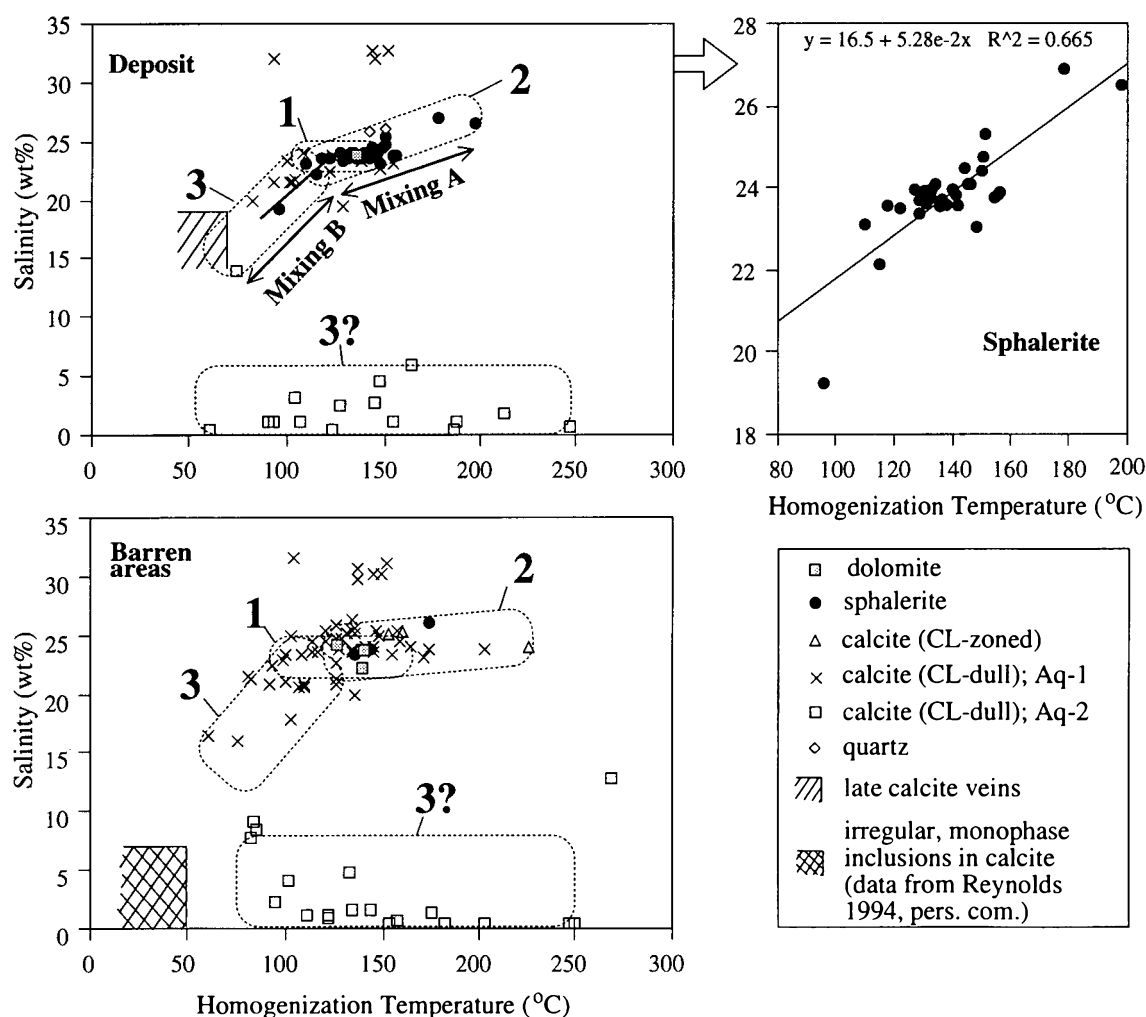


Fig. 9. Homogenization temperature versus salinity diagrams showing thermal and compositional evolution of fluids from pre-, syn-, to post-ore stages and mixing trends for the deposit (upper) and barren areas (lower). 1 = pre-ore stage; 2 = main stage of mineralization; 3 = waning stage of mineralization and post-ore stage; 3? = syn- to post-ore stage fluid inclusions leaked and re-filled by late low-salinity fluids.

salinity fluid had a lower $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratio than the low-temperature, low-salinity end member, some processes other than fluid mixing must have influenced the $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios. One of the possibilities is fluid-rock interaction producing in situ source of Ca^{2+} during the massive replacement of carbonates by sulfides.

Comparison between the deposit and barren areas

Fluid inclusions from the deposit and barren areas show similar compositions, ranges of homogenization temperatures, bulk salinities, and mixing trends. This indicates that fluid mixing took place in the deposit and in the barren areas as well. A consequent implication is that fluid mixing does not necessarily constitute a mineralizing process in the studied region.

A comparison of $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios of Aq-1 fluid inclusions between the deposit and barren areas (Fig. 10, right side), indicates that the fluids from which sphalerite precipitated were relatively more Ca-enriched than the fluids precipitating calcite at the deposit and in its surround-

ing barren areas. Haynes and Kesler (1987) found the same trend by using SEM energy dispersive analysis of decrepitate of fluid inclusions from the East Tennessee and Pine Point Pb-Zn districts. They showed that $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios of fluid inclusions are consistently lower in sphalerite and ore-stage dolomite than in barren dolomite. The low $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios of fluid inclusions in sphalerite from the low-grade part of the Gays River deposit are likely caused by Ca^{2+} enrichment, due to massive replacement of carbonates by sulfides which produced the high grade ore.

A comparison of fluid inclusion, homogenization temperatures between the deposit and barren areas (see Table 1) does not show a thermal gradient around the deposit. A similar situation has been reported for the Viburnum Trend Pb-Zn district in southeast Missouri (Rowan and Leach, 1989). This is in contrast to previous organic matter and clay mineral studies which show a heat anomaly around the Gays River deposit (Héroux *et al.*, 1994). One exception is the east end of the Musquodoboit sub-basin (5, Fig. 1) where the lowest fluid inclusion, homogenization temperatures are recorded (Table 1), which is consistent with the lowest Ro

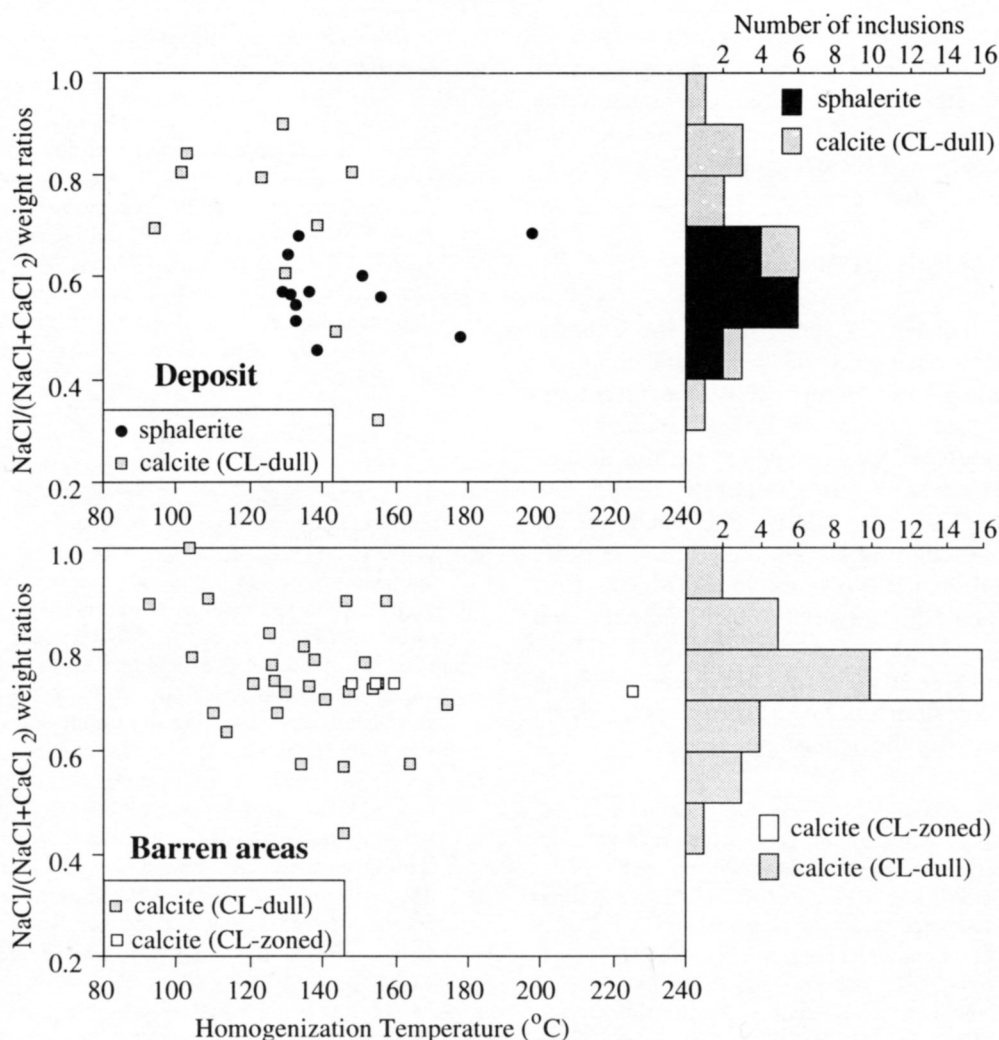


Fig. 10. Homogenization temperature versus $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratio diagrams (left) and histograms of $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios (right) for the deposit (upper) and barren areas (lower).

values of organic matter (Héroux *et al.*, 1994). The different thermal patterns indicated by fluid inclusions and organic matter perhaps suggest that the deposit and the barren areas had different fluid-rock thermal relations. Sangster *et al.* (1994) discussed three types of thermal relations between host rocks and the mineralizing fluids of MVT deposits, i.e., $T_{\text{fluid}} = T_{\text{host}}$, $T_{\text{fluid}} > T_{\text{host}}$, and $T_{\text{fluid}} < T_{\text{host}}$. It is likely that the ore-forming fluid flow in the Gays River deposit was intensive and focused so that the host rocks were heated and attained thermal equilibrium with the hot fluid ($T_{\text{fluid}} = T_{\text{host}}$), whereas such a thermal equilibrium was not attained in the barren areas ($T_{\text{fluid}} > T_{\text{host}}$), probably due to dispersive or less intensive, high-temperature fluid flow.

CONCLUSIONS

We have documented the thermal and compositional characteristics of fluids in three evolution stages of fluid systems in the Gays River deposit and its surrounding barren areas. The major findings and conclusions are summarized as follows.

(1) Fluids in the Gays River deposit and its surround-

ing barren areas evolved from relatively intermediate salinity and temperature in the pre-ore stage, through higher salinity and temperature in the main stage of mineralization, to low salinity and temperature in the waning stage of mineralization and post-ore stage.

(2) Fluid mixing took place during precipitation of sphalerite and most calcite, both in the deposit and barren areas. During precipitation of most sphalerite, a metal-carrying fluid with high temperature ($\geq 200^\circ\text{C}$) and high salinity (≥ 27 wt. % NaCl eq.) mixed with background, dolomitizing fluids, which saturated porosity of the Gays River carbonates before mineralization. During the waning stage of mineralization and precipitation of most calcite, a fluid with relatively low salinity and low temperature affected the hydrothermal system and mixed with other pre-existing fluids. That fluid mixing took place both in the deposit and barren areas indicates that fluid mixing did not necessarily lead to mineralization.

(3) The fluids from which sphalerite precipitated had lower $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ ratios than fluids precipitating calcite. This may be related to in situ addition of Ca^{2+} released during replacement of carbonates by massive sulfides.

(4) No thermal gradient has been indicated by fluid in-

clusion, homogenization data, in contrast to previous organic matter and clay mineral studies which show a heat anomaly around the deposit. The different thermal patterns indicated by fluid inclusions and organic matter perhaps suggest that the deposit and the barren areas had different fluid-rock thermal relations.

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