

CARBON AND OXYGEN ISOTOPE GEOCHEMISTRY OF CALCITE FROM THE JUBILEE Zn-Pb DEPOSIT, CAPE BRETON ISLAND

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ABSTRACT

The Jubilee Zn-Pb deposit, Nova Scotia, is one of many similar prospects hosted within Early Carboniferous limestones in the Maritime region of eastern Canada. At Jubilee, laminated limestone is overlain by transitional, interstratified limestone and anhydrite, with massive anhydrite capping the sequence. Mineralization is stratabound and hosted within the Pembroke breccia, which probably formed as a result of dissolution of anhydrite interbeds within carbonate host-rock. Mineralized-matrix breccia is the main host of the ore, and contains pyrite, marcasite, sphalerite, galena and barite, in addition to calcite. Liquid hydrocarbons and solid bitumen are abundant, particularly within sulfide-rich domains, and also occur as inclusions within sphalerite and barite. Carbon and oxygen isotope values have been obtained for five varieties of calcite from the Jubilee deposit: (1) finely laminated, unmineralized host limestone (pelsparite), $\delta^{18}\text{O}$ between +26.3 and +27.1‰ SMOW, $\delta^{13}\text{C}$ between +0.4 and +2.2‰ PDB, (2) early diagenetic calcite, $\delta^{18}\text{O}$ = +29.1‰, $\delta^{13}\text{C}$ = +1.4‰, (3) micritic to sparry calcite (replacement of anhydrite?), locally associated with minor, disseminated sulfides, $\delta^{18}\text{O}$ between +24.3 and +25.5‰, $\delta^{13}\text{C}$ between -24.0 and -22.8‰, (4) main ore-stage, breccia-cementing calcite, $\delta^{18}\text{O}$ between +23.9 and +24.7‰, $\delta^{13}\text{C}$ between -27.1 and -24.9‰, and (5) post-mineralization, drusy calcite, $\delta^{18}\text{O}$ between +21.6 and +22.5‰, $\delta^{13}\text{C}$ between -23.4 and -23.2‰. Using the isotopic data for calcite from Groups 3 and 4, and previously reported results on fluid inclusions (90–150°C), an average $\delta^{18}\text{O}$ value of $+9 \pm 3\text{‰}$ was calculated for the mineralizing fluid. This value is typical of an evolved basinal brine, as has been suggested for other deposits in the area. However, the $\delta^{13}\text{C}$ values (-27.1 to -22.8‰) of calcite from Groups 3, 4 and 5 are much lower than ore-stage calcite from the other deposits in the region (-10 to +3‰). Anhydrite dissolution, association of hydrocarbons with sulfides, and very low $\delta^{13}\text{C}$ values for most secondary calcite at Jubilee together suggest coupled oxidation of hydrocarbons, reduction of sulfate and precipitation of calcite at the site of mineralization. Contribution of inorganic carbon (e.g., from dissolution of host limestone) was very limited during calcite precipitation associated with mineralization.

Keywords: Jubilee Zn-Pb deposit, stable isotopes, hydrocarbons, brines, genesis, Nova Scotia.

SOMMAIRE

Le gisement à Zn-Pb de Jubilee, en Nouvelle-Écosse, est un parmi plusieurs indices semblables ayant comme hôte les calcaires carbonifères précoces des provinces maritimes de l'Est du Canada. À Jubilee, les calcaires laminés sont recouverts d'une séquence transitionnelle interstratifiée de calcaire et d'anhydrite, et ensuite d'une anhydrite massive. La minéralisation, qui est conforme à la stratigraphie, se trouve dans la brèche de Pembroke, qui serait due à la dissolution des interstratifications d'anhydrite dans la séquence de carbonates. Une brèche à matrice minéralisée, roche-hôte de la plupart du minerai, contient pyrite, marcasite, sphalérite, galène et barytine, en plus de la calcite. Les hydrocarbures liquides et le bitumen solide y sont abondants, surtout dans les amas de sulfures, et sont de plus inclus dans la sphalérite et la barytine. Nous avons déterminé les valeurs isotopiques du carbone et de l'oxygène pour cinq variétés de calcite: 1) roche-hôte non minéralisée, à laminations fines (pelsparite): $\delta^{18}\text{O}$ entre +26.3 et +27.1‰ SMOW, $\delta^{13}\text{C}$ entre +0.4 et 2.2‰ PDB, 2) calcite diagénétique précoce, $\delta^{18}\text{O}$ +29.1‰, $\delta^{13}\text{C}$ 1.4‰, 3) calcite micritique à transparente (due à la dissolution de l'anhydrite?), localement associée à de faibles concentrations de sulfures disséminés: $\delta^{18}\text{O}$ entre +24.3 et 25.5‰, $\delta^{13}\text{C}$ entre -24.0 et -22.8‰, 4) stade principal de formation du minerai, ciment calcitique de la brèche: $\delta^{18}\text{O}$ entre +23.9 et +24.7‰, $\delta^{13}\text{C}$ entre -27.1 et -24.9‰, et 5) calcite tardive par rapport à la minéralisation: $\delta^{18}\text{O}$ entre +21.6 et +22.5‰, $\delta^{13}\text{C}$ entre -23.4 et -23.2‰. D'après les données isotopiques pour la calcite des groupes 3 et 4, et les résultats d'études antérieures des inclusions fluides (90–150°C), nous préconisons une valeur moyenne de $9 \pm 3\text{‰}$ pour le rapport $\delta^{18}\text{O}$ du fluide responsable de la minéralisation. Cette valeur est typique des saumures évoluées des bassins sédimentaires, et des autres gisements de cette région. Toutefois, le rapport $\delta^{13}\text{C}$ de la calcite des groupes 3, 4 et 5 (entre -27.1 et -22.8‰) est beaucoup plus faible que dans la calcite typique des assemblages minéralisés des autres gisements de la région (entre -10 et +3‰). La dissolution de l'anhydrite, l'association des hydrocarbures avec les sulfures, et les valeurs très faibles du rapport $\delta^{13}\text{C}$ pour la plupart de la calcite secondaire à Jubilee témoigneraient d'un couplage de l'oxydation des hydrocarbures, la réduction du sulfate, et la précipitation de la calcite au cours de la minéralisation. La contribution de carbone inorganique, dû par exemple à la dissolution du calcaire encaissant, aurait été très limitée pendant la formation de la calcite associée à la minéralisation.

(Traduit par la Rédaction)

Mots-clés: gisement de Zn-Pb, Jubilee, isotopes stables, hydrocarbures, saumures, genèse, Nouvelle-Écosse.

INTRODUCTION

Carbon and oxygen isotope data are presented here for secondary calcite from the Jubilee Zn–Pb deposit, Nova Scotia (5.2% Zn, 1.4% Pb; Hein *et al.* 1991). This deposit, located on the Iona Peninsula of Cape Breton Island, is one of many Zn–Pb or Pb–Zn prospects within the Early Carboniferous (Viséan-aged, 348–336 Ma) limestones of the Maritime region in eastern Canada (Fig. 1). These occurrences have attracted much attention because of their variable styles of mineralization, their association with evaporite sequences, and their apparent genetic differences from more typical Mississippi-Valley-type deposits. Recently, it has been suggested that some of the mineralization was associated with deep-water vent communities (von Bitter *et al.* 1990).

Stable isotope data have been reported for similar carbonates from the Gays River, Pembroke and Smithfield Pb–Zn deposits (Fig. 1) in the Maritimes (Akanke & Zentilli 1984, Ravenhurst *et al.* 1987, 1989). These authors concluded that: (i) the mineralizing fluids were hot, basinal brines, (ii) the metals were

derived from adjacent clastic rocks of basement provenance, (iii) Viséan carbonate was the dominant source for carbon and sulfur, but sulfur also was derived from the voluminous Mississippian evaporites within the section, and (iv) sulfate was carried by the fluids and reduced at the site of mineralization. Mineralization likely occurred *circa* 330 to 300 Ma, as indicated by results of fission track, K–Ar and Rb–Sr dating (Ravenhurst *et al.* 1989, Arne *et al.* 1990).

Evidence for chemosynthetic communities (*e.g.*, fossil tubes, serpulid and spirorbid worms, conularids, brachiopods, bryozoa and ostracods) at hydrothermal vents associated with carbonate mounds has been reported by Schenk *et al.* (1990) and von Bitter *et al.* (1990); the associated sulfide mineralization has been interpreted to result from hydrothermal venting during mound formation. Such mounds have been reported in parts of Macumber Formation of the lower Windsor Group in Nova Scotia and New Brunswick, the Codroy Group in Quebec and Newfoundland, and the Parleeville Formation in New Brunswick (von Bitter & Plint-Geberl 1982, Dix & James 1988, 1989, McCutcheon 1988, von Bitter *et al.* 1990).

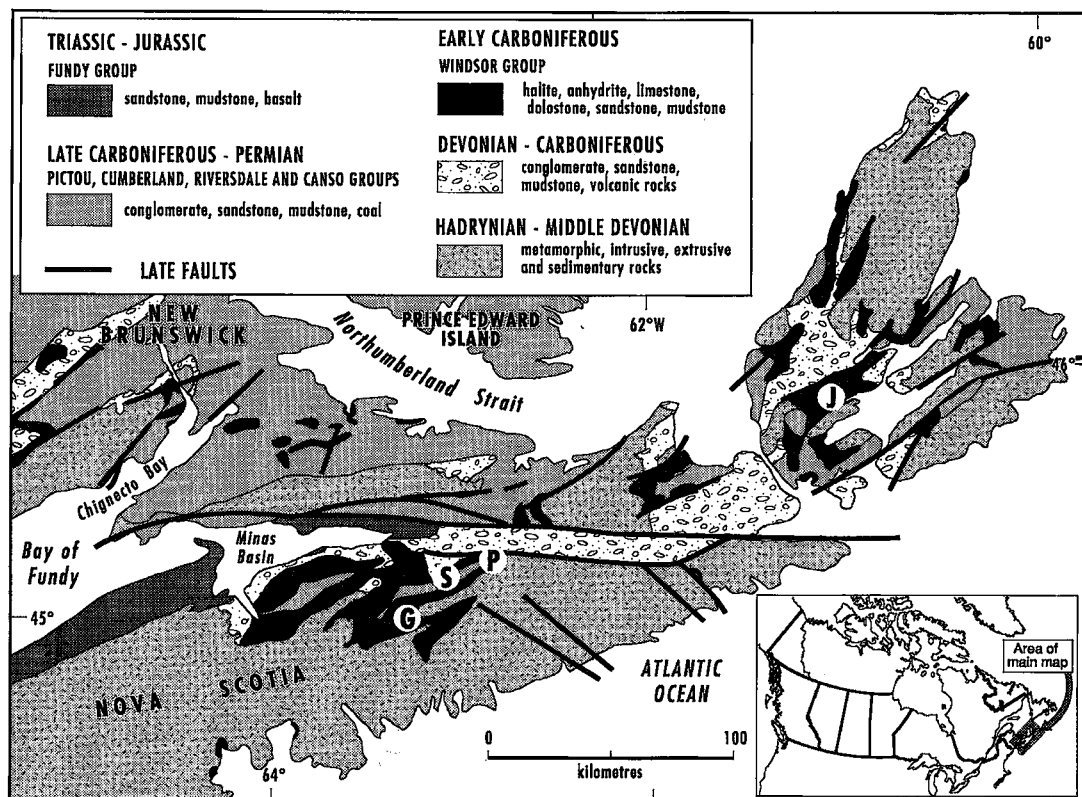


FIG. 1. General geology and location of the Jubilee (J), Smithfield (S), Pembroke (P) and Gays River (G) deposits (after Boehner *et al.* 1989).

At Jubilee, no fossil tubes have yet been identified. We present evidence here that (i) supports a basinal origin for a rather low-temperature (~100–150°C) metal-bearing brine, and (ii) strongly favors an organic source of carbon (hydrocarbons) for secondary calcite that crystallized as one product of *in situ* reduction of sulfate during mineralization.

GEOLOGY OF THE JUBILEE DEPOSIT

The Jubilee deposit was first explored in the early 1930s. Further exploration during the late 1930s and mid-1940s failed to delineate a substantial orebody

(Hein *et al.* 1991). The most recent efforts in exploration consisted of extensive diamond drilling during the 1970s by the Texam Joint Venture, and by Falconbridge in 1990. The deposit contains >0.5 million metric tonnes of 6.6% Zn-Pb.

The Jubilee deposit is hosted within Early Carboniferous (Visean-aged, 348–336 Ma), laminated limestones of the Macumber Formation, in the basal portion of the Windsor Group (Ravenhurst *et al.* 1989, Hein *et al.* 1991). The Macumber Formation has a sharp disconformable contact with the underlying Tournaisian-aged (360–350 Ma) Horton Group (Hamblin 1988, 1992; Ravenhurst *et al.* 1989). In the

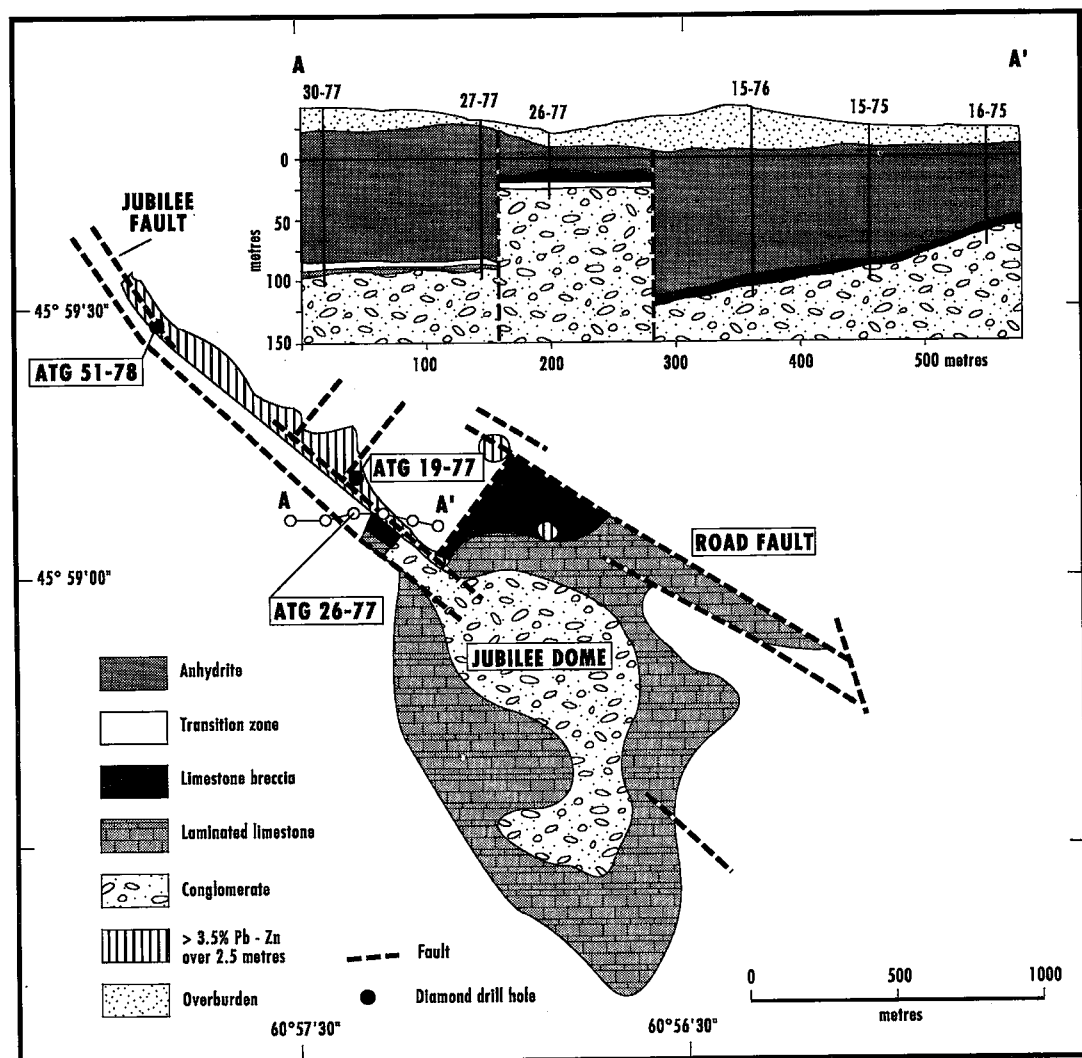


FIG. 2. Surface geology and cross-section of the Jubilee deposit (modified after Hein *et al.* 1991). Samples were analyzed from cores ATG 51-78, ATG 19-77 and ATG 26-77.

vicinity of the Jubilee deposit, the Horton Group is commonly recognized as the "upper" Horton or Ainslie Formation (Hamblin 1988); drill-core intersections consist of ungraded to massive conglomerate, with pebbly sandstone (Hein *et al.* 1991). The top of the Macumber Formation consists of interstratified limestone and anhydrite, capped by massive anhydrite (Fig. 2).

Sedimentary features within the Macumber Formation suggest that the limestone was deposited below wave base and may have been resedimented by slumping, debris flows or turbidity currents (Hein *et al.* 1991). The finely laminated limestone contains some beds with high concentrations of peloids, bioclastic debris (molluscan and bryozoan shell fragments), and very fine-grained, disseminated pyrite. Pyrite–marcasite sulfidization along bedding planes is restricted to more micritic and sparry laminae in the limestone.

The Pembroke breccia is the major host of the ore at the Jubilee deposit, and lies structurally above, or replaces, the Macumber Formation (Hein *et al.* 1991). The breccia has been interpreted as a karstic collapse-breccia, an evaporite-solution breccia, an intraclast storm deposit, and the product of hydrofracturing related to mineralization (Clifton 1967, Schenk 1984, Ravenhurst *et al.* 1989). According to Hein *et al.* (1991), the brecciation at Jubilee mostly resulted from dissolution of anhydrite laminae. Since remnants of anhydrite have not been observed in the breccia, this interpretation requires that dissolution or replacement of anhydrite was complete. Localized occurrences of karstic collapse-breccia were also noted by Hein *et al.* (1991), particularly in the northwestern portion of the study area (drill-core ATG-51–78, Fig. 2).

Two main breccia rock-types have been defined at Jubilee by Hein *et al.* (1991): "rock-matrix" breccia and "mineralized-matrix" breccia. "Rock-matrix" breccia contains clast-supported, chaotically distributed, centimeter-sized, subrounded to angular fragments of the Macumber Formation. Most clasts retain their original laminated texture, and have not been significantly recrystallized. According to Hein *et al.* (1991), the clasts have fallen into space created by dissolution of evaporite interbeds and interlaminae. Matrix material consists most commonly of finely comminuted rock fragments derived from the Macumber Formation.

The rock-matrix breccia is generally better developed in cores that contain some mineralization. Even more highly mineralized portions of the deposit, represented by most of the material described in this paper, consist of "mineralized-matrix" breccia. In the samples studied here, the rock fragments have been extensively recrystallized, and commonly contain finely disseminated sulfides. Anhydrite is absent. True matrix material was not observed. Instead, the recrystallized fragments are cemented by equant, sparry cal-

cite or fibrous and locally radial-fibrous calcite (0.05 to 1 mm), together with sulfides.

Circular structures (on the millimeter scale) also are present in some breccia samples. Some of these features arise from concentric alteration of inclusion-poor and slightly finer-grained, inclusion-rich aggregates of calcite crystals. Others result from filling of vugs by equigranular, fibrous calcite capped by sulfides (see "Mineralization"). No textural evidence was obtained to suggest that these features originated as biogenic oncolites or were related to the formation of bacterial mats associated with deep-water vents.

The Jubilee deposit is cut by a series of NNW-trending fault zones, of which the Jubilee and Road Faults are the most significant (Fig. 2). These faults bound a NW-trending horst. Interfingering of Horton Group and Macumber Formation lithologies, and dramatic changes in bed thickness and facies within both carbonate and clastic rocks near the Jubilee Fault, suggest that synsedimentary movement occurred during deposition of the uppermost Horton Group and continued during formation of the Macumber Formation limestones. The Jubilee Fault remained active during deposition of the interlaminated limestones and anhydrite, but was inactive during deposition of the thick anhydrite that caps the sequence (Hein *et al.* 1991).

The Pembroke breccia is associated with a decrease in abundance of the interstratified limestone–anhydrite sequence, an observation compatible with preferential dissolution of the anhydrite interbeds, and the "reaccumulation" of undissolved limestone. Although the Pembroke breccia is not a fault breccia, the unit is thickest and most heavily mineralized adjacent to the Jubilee Fault. Hence, the location of the fault may have played a secondary role in the creation of the breccia. Hein *et al.* (1991) proposed that the Jubilee Fault controlled evolution of the Jubilee deposit throughout its history. Fluids venting along the fault during sedimentation provided nutrients that led to enhanced accumulation of biogenic carbonate during sedimentation; later, during diagenesis, the fault acted as a conduit (confined by the impermeable cap of anhydrite) for formation waters, hydrocarbons and mineralizing fluids that entered the system.

MINERALIZATION

The mineralized-matrix breccia is the main host to the ore. Besides calcite, it contains: (i) pyrite intergrown with and replacing marcasite, (ii) zoned pyrite, (iii) honey-colored sphalerite that occurs as fine-grained disseminations within sparry calcite cement and recrystallized fragments (Figs. 3a, b), and that is most commonly associated with galena and barite along fractures and in clots (Fig. 3c), and (iv) pyrite – marcasite – galena intergrowths that cap vug-lining, sparry to fibrous calcite. Pyrite can also occur as subhedral grains within recrystallized fragments of the

host rock. Barite is paragenetically late, and commonly occurs as a wispy filling of pore space, together with sphalerite and galena, or in late veinlets.

Liquid hydrocarbons fill much of the remaining porosity, including joint planes, and solid bituminous

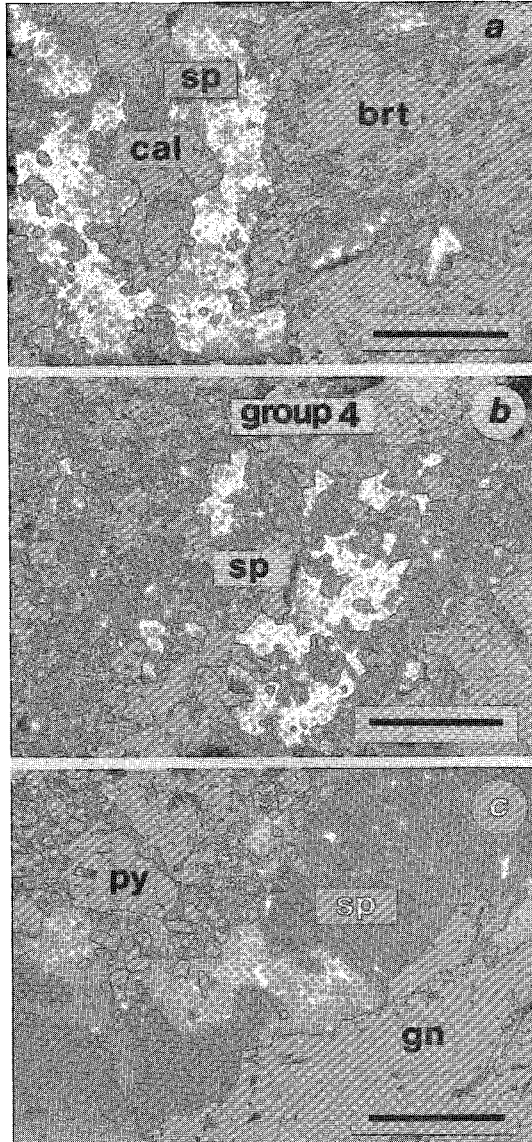


FIG. 3. a. Barite (brt) associated with sparry calcite (cal) and sphalerite (sp), plane-polarized light. b. Sparry calcite cement (Group 4) with interlocking sphalerite (sp), plane-polarized light. c. Ore-stage sphalerite (sp) and galena (gn) with gangue comprised of pyrite (py), barite and calcite; calcite and barite appear as the darkest grey tones in this reflected-light photomicrograph. Scale bar in all photomicrographs: 0.50 mm.

matter is present throughout the section, particularly within sulfide-rich domains. Hydrocarbon and bitumen inclusions are present in sphalerite and barite (Hein *et al.* 1991), indicating that an organic liquid entered the system at least as early as the beginning of mineralization.

Five varieties of calcite have been recognized in the thin sections. From earliest to latest, these groups are: (1) unmineralized pelsparite (Fig. 4a), (2) early diagenetic calcite that comprises the circular microstructures (Fig. 4b), (3) micritic to sparry calcite (pseudosparr) (Fig. 4c), (4) fibrous and locally radial-fibrous or sparry calcite that cements the breccia, and is most strongly associated with sulfide mineralization (Figs. 3b, 4d, e), and (5) medium- or coarse-grained, drusy calcite that postdates mineralization (Fig. 4f). Dolomite, in particular the white sparry variety typical of other Pb-Zn deposits in the region and Mississippi-Valley-type deposits in general, was not observed.

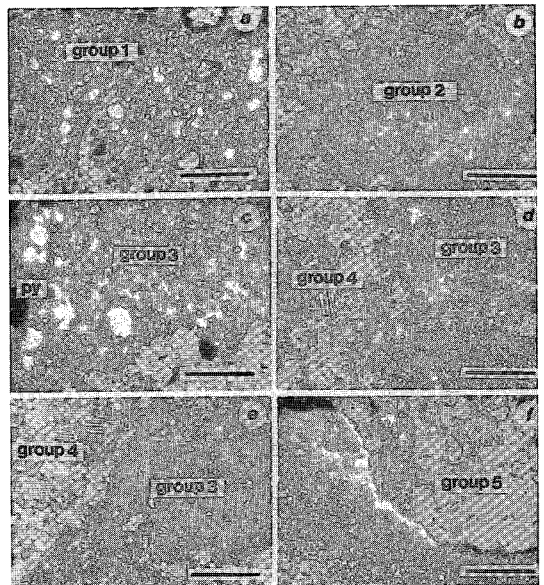


FIG. 4. a. Unmineralized pelsparite with bioclastic debris (Group 1). Scale bar: 0.50 mm. b. Portion of an early diagenetic, circular microstructure that contains Group-2 calcite. Scale bar: 0.50 mm. c. Pseudosparr (Group 3) and associated pyrite that probably replaced a fragment of limestone. Sparry calcite (Group 4) is present in the lower right of the photomicrograph. Scale bar: 0.50 mm. d. Interlocking sparry calcite cement (Group 4) and brecciated Group-3 pseudosparr. Scale bar: 0.50 mm. e. Pseudosparr (Group 3) and sparry calcite cement (Group 4). Scale bar: 0.25 mm. f. Portion of a vug lined by late, drusy calcite (Group 5) formed within Group-3 calcite. Scale bar: 0.25 mm. All photomicrographs in plane-polarized light.

ANALYTICAL METHODS

The carbonate host-rock and the various groups of secondary calcite were sampled from thin section slabs using a high-speed, precision drill equipped with either a burr or diamond-tipped bit. The bit size (1 to 2 mm) was appropriate to prevent contamination between different types of calcite during microsampling. Mineralogical purity of separates was checked using X-ray diffraction.

For isotopic analysis, 10–15 mg samples were reacted with orthophosphoric acid at 25°C for twelve hours in evacuated tubes (McCrea 1950). The evolved CO₂ was purified using cold traps at the appropriate temperatures to eliminate possible contamination from H₂O and SO₂. The carbon and oxygen isotope data were obtained using an DAAC-upgraded VG Micromass 602C mass spectrometer, and are reported in the usual δ -notation relative to V-PDB (carbon) and V-SMOW (oxygen).

RESULTS

The stable isotope results for calcite are listed in Table 1 and illustrated in Figure 5. Three samples of finely laminated pelsparite (Group 1) from outside the ore zone have $\delta^{18}\text{O}$ values of +26.3 to +27.1‰ (mean +26.8‰), and $\delta^{13}\text{C}$ values of +0.4 to +2.2‰ (mean +1.3‰), and lie in the middle of the range for "unaltered" Mississippian marine carbonates (Keith & Weber 1964, Wadleigh & Veizer 1992).

One sample of Group-2 calcite (circular microstructures) has values of $\delta^{18}\text{O}$ (+29.1‰) and $\delta^{13}\text{C}$ (+1.4‰) similar to the carbonate host-rock. Because the Group-

2 calcite is banded on the <0.5 mm scale (Fig. 3b), the microsample analyzed contains several laminae. A second sample has a similar $\delta^{18}\text{O}$ value (+26.3‰), but a much lower $\delta^{13}\text{C}$ value (−12.5‰). Re-examination of this sample showed that the Group-2 microstructure had been brecciated, and partially infilled by sparry calcite from Group 4.

The micritic to sparry calcite (Group 3) has values of $\delta^{18}\text{O}$ (+24.3 to +25.5‰, mean +24.7‰) and $\delta^{13}\text{C}$ (−24.0 to −22.8‰, mean −23.3‰) that cluster together tightly. The $\delta^{13}\text{C}$ values are much lower than those obtained for other deposits from this region (Fig. 5). The Group-4 calcite cement, which is most strongly associated with sulfide mineralization, has similar values of $\delta^{18}\text{O}$ (+23.9 to +24.7‰, mean +24.2‰) to Group 3, but the $\delta^{13}\text{C}$ values (−27.1 to −24.9‰, mean −26.2‰) are lower. Careful microsampling ensured that the difference in isotopic composition between calcite from Groups 3 and 4 is real. The late-stage, drusy calcite (Group 5) has values of $\delta^{18}\text{O}$ (+21.6‰) and $\delta^{13}\text{C}$ (−23.2‰) that plot at the end of the general trend of increasing $\delta^{13}\text{C}$ with decreasing $\delta^{18}\text{O}$ exhibited by Group-4 calcite (Fig. 5). Calcite intergrown with barite in one sample (J151–90A) also contains pyrite, and traces of sphalerite, but texturally it is most closely associated with Group 5. Its values of $\delta^{18}\text{O}$ (+22.5‰) and $\delta^{13}\text{C}$ (−23.4‰) support this interpretation.

DISCUSSION

Pb–Zn mineralization within the extensive Early Carboniferous limestones extends from central Nova Scotia northeastward to Newfoundland, and represents

TABLE 1. OXYGEN AND CARBON ISOTOPE COMPOSITIONS OF CALCITE

Sample	*Mineralogy	Description	Group	$\delta^{18}\text{O}$ ‰	$\delta^{13}\text{C}$ ‰
J154-90A	cal, tr qtz, py	unmineralized pelsparite	1	26.9	2.2
J154-90B	cal, tr qtz, py	unmineralized pelsparite	1	26.3	0.4
J154-90C	cal, tr qtz, py	unmineralized pelsparite	1	27.1	1.4
J152-90B	cal, tr py	early diagenetic calcite in concentric microstructures	2	29.1	1.4
J152-90A	cal, tr py	early diagenetic calcite in concentric microstructures + sparry calcite	2, 4	26.3	−12.5
J157-90A	cal, tr qtz	micritic calcite (pseudospar)	3	24.8	−23.3
J157-90D	cal, tr qtz	micritic calcite (pseudospar)	3	25.5	−24.0
J150-90	cal	micritic calcite (pseudospar)	3	24.3	−22.0
J153-90A	cal, tr qtz	micritic calcite (pseudospar)	3	24.2	−22.8
J157-90B	cal	sparry calcite cement	4	23.9	−24.9
J157-90C	cal	sparry calcite cement	4	24.6	−26.9
J159-90A	cal	sparry calcite cement	4	23.7	−25.6
J159-90B	cal, tr qtz	sparry calcite cement	4	24.6	−27.1
J159-90C	cal, tr qtz	sparry calcite cement	4	24.7	−26.3
J151-90B-i	cal	fibrous to radial-fibrous calcite	4	23.8	−26.4
J151-90B-ii	cal	fibrous to radial-fibrous calcite	4	24.4	−26.2
J151-90B-iii	cal	fibrous to radial-fibrous calcite	4	24.0	−25.9
ATG-51-78	cal	drusy calcite	5	21.6	−23.2
J151-90A	cal, py, brt, sp	vug-filling sparry calcite	5?	22.5	−23.4

Group 1: unmineralized limestone; Group 2: diagenetic calcite; Group 3: "recrystallized" limestone clasts in breccia; Group 4: ore-stage calcite; Group 5: post-ore, vug-filling calcite. tr = trace; cal = calcite; qtz = quartz; py = pyrite; brt = barite; sp = sphalerite.

*Mineralogy of microsample used for isotopic analysis, as determined by X-ray diffraction.

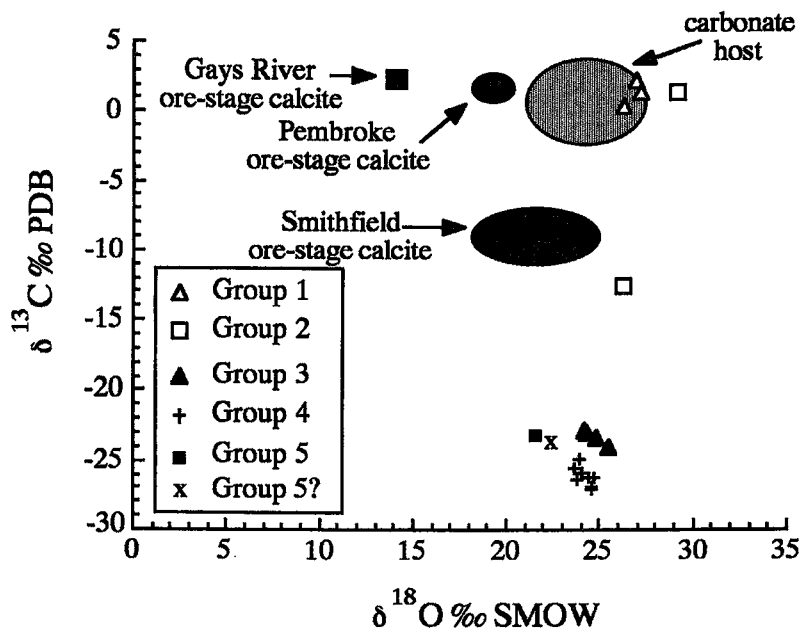


FIG. 5. Carbon and oxygen isotope compositions of Group-1 to -5 calcite samples from the Jubilee deposit. Fields for host carbonate and ore-stage calcite from the Gays River, Pembroke and Smithfield deposits also are shown (from data in Ravenhurst *et al.* 1989).

a significant, post-Acadian (*circa* 300 Ma) metallogenic event or events (Ravenhurst *et al.* 1989, Arne *et al.* 1990, Savard 1991). The deposits formed within transgressive deep or shallow marine limestones that disconformably or unconformably overlie continentally derived clastic rocks. The mineralogy of the ore and gangue is simple, with little variation among deposits. Galena and sphalerite are the main ore minerals. The gangue consists of pyrite, marcasite, calcite, barite, anhydrite, selenite and fluorite.

The Jubilee deposit can be usefully compared with the Gays River, Pembroke and Smithfield Pb–Zn accumulations (Fig. 1). The Gays River deposit (~12 million metric tonnes of 7% Pb–Zn) is hosted within the flank of a dolomitized carbonate bank that unconformably overlies quartz metawackes of the Meguma Group, and is overlain and bordered by beds of anhydrite. Ore zones at Gays River are dominated by stratiform, disseminated, and locally massive domains of sulfide that cut lithological contacts and follow carbonate textures as open-space fillings and sulfide replacements (Akande & Zentilli 1984, Kontak 1992). The Pembroke Pb deposit is characterized by galena that occurs in calcite veins, and by post-ore, vug-lining calcite (Ravenhurst *et al.* 1989). The Smithfield deposit (0.5 million metric tonnes of 6% Pb–Zn) is most similar to the Jubilee; it is a Pb–Zn–Cu–Ba occurrence hosted within the brecciated limestone of the Lower Windsor Group that disconformably over-

lies the clastic rocks of the Horton Group (Ravenhurst *et al.* 1989).

Savard (1992) has suggested that diagenetic, pre-mineralization dolomite precipitated in the Gays River Formation from saline brines at 60–105°C. Fluid-inclusion data for ore-stage calcite at Gays River suggest that temperatures peaked at 167–178°C; lower temperatures (132–165°C) were obtained for fluid inclusions from post-ore calcite, fluorite and barite (Akande & Zentilli 1984, Ravenhurst *et al.* 1989). Higher temperatures are indicated for the Pembroke deposit (160–250°C) (Ravenhurst *et al.* 1989). At Smithfield, crystallization of ore-stage calcite occurred at 140 to 172°C (Ravenhurst *et al.* 1989). In all cases, fluid-inclusion data indicate that the ore-forming fluids were saline (≥ 24 equivalent wt.% NaCl) (Akande & Zentilli 1984, Ravenhurst *et al.* 1989). The $\delta^{18}\text{O}$ values calculated for the ore-forming fluids (uncorrected for salinity) using the temperature data and compositions of the host calcite (after Friedman & O'Neil 1977) are typical of basinal brines: Gays River +3‰, Pembroke +10‰, and Smithfield +8‰.

Only limited fluid-inclusion data are available for the Jubilee deposit. Stewart (1978) reported temperatures in excess of 300°C for sphalerite and barite. However, Hein *et al.* (1991) argued that fluid/vapor ratios for two-phase inclusions in sphalerite are much more consistent with those known for Gays River and Pine Point, and indicate temperatures of crystallization

of approximately 150°C. Furthermore, their primary fluid-inclusion measurements for late-stage barite at Jubilee give an average temperature of homogenization of 89°C (range 82–98°C; Hein *et al.* 1991). If ore-stage calcite (av. $\delta^{18}\text{O} +24.2\text{‰}$) crystallized between 90° and 150°C, $\delta^{18}\text{O}$ values (uncorrected for salinity) of $+9 \pm 3\text{‰}$ can be calculated for the brine. Such values are most like those obtained for the Smithfield and Pembroke deposits, rather than Gays River. The Jubilee and Smithfield deposits, in particular, show the greatest similarity, not only in temperature of ore formation, calculated composition of the fluid, and stable isotope composition of the ore-stage calcite (Fig. 5), but also in size (~0.5 million metric tonnes), grade (6% combined Pb–Zn) and style of mineralization (*i.e.*, hosted by limestone breccia).

Organic carbon and in situ reduction of sulfate

The available $\delta^{13}\text{C}$ data for the Gays River, Smithfield and Pembroke deposits ($-10 < \delta^{13}\text{C} < +3\text{‰}$, Fig. 5) contrast sharply with the much lower values (-27.1 to -22.8‰) obtained at Jubilee for calcite from Group 3, Group 4 (main ore-stage) and Group 5 (post-ore). The former results have been interpreted to indicate variable addition of organic carbon to the inorganic carbon involved in crystallization of ore-stage calcite (Ravenhurst *et al.* 1989). However, only the Smithfield deposit shows a consistent shift toward the strongly negative $\delta^{13}\text{C}$ values that characterize the Jubilee deposit, and that indicate emergence of organic carbon as the dominant reservoir during formation of ore-stage calcite.

Low- $\delta^{13}\text{C}$ values like those observed at Jubilee may indicate that calcite formed by oxidation of methane seeps on the sea floor. For example, Matsumoto (1990) reported values of -33.2 to -26.1‰ for calcite presumed to have formed by microbial oxidation of methane at a hydrocarbon seep offshore of Baffin Island. However, because of the very low $\delta^{13}\text{C}$ values of biogenic methane, carbonates resulting from methane oxidation generally have much lower and commonly more variable values: Gulf of Alaska, -53.2‰ (Barnes *et al.* 1982), off-shore New Jersey, -60 to -49‰ (Hathaway & Degens 1969), offshore Oregon and Washington, -66 to -22‰ (Ritger *et al.* 1987), and the North Sea, -62 to -52‰ (Hovland *et al.* 1987). Bicarbonate produced during anaerobic oxidation of methane may have even lower values of $\delta^{13}\text{C}$ (by 2 to 14‰) than the methane from which it formed (Whiticar *et al.* 1986, Raiswell 1987).

Mixing of CO_2 produced by (i) oxidation of methane and (ii) dissolution of host carbonate ($\delta^{13}\text{C} \approx +2\text{‰}$) could produce the depletion in ^{13}C at Jubilee, but only if an invariant and fortuitously appropriate proportion of carbon were contributed from each reservoir. A more appropriate source would be oxidation of liquid hydrocarbons, which typically have

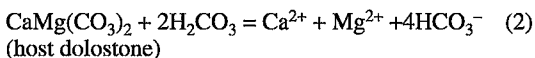
average $\delta^{13}\text{C}$ values near -28‰ (Stahl 1979). In an analogous situation, $\delta^{13}\text{C}$ values as low as -26.6 to -25.8‰ are known for calcite cements in the Trenton limestone, northwestern Ohio, a unit that is a major producer of oil and gas, and also contains small occurrences of Pb–Zn mineralization (Haefner *et al.* 1988).

At Jubilee, the physical evidence for dissolution of pre-existing laminae of anhydrite plus the ubiquitous association of hydrocarbons with sulfides collectively suggest that the low $\delta^{13}\text{C}$ values of Groups 3, 4 and 5 calcite may have resulted from coupled reduction of sulfate and oxidation of hydrocarbon at the site of mineralization. This reaction probably occurred in a fashion similar to that described by Anderson & Garven (1987),



where CH_4 is used *only* in a general sense to represent hydrocarbons. Whether the reaction at Jubilee was mediated by microbial processes is not obvious from the data that we have collected.

Ghazban *et al.* (1990) invoked such a reaction to explain $\delta^{13}\text{C}$ values as low as -12‰ for white sparry dolomite associated with mineralization at the Nanisivik Pb–Zn deposits, Baffin Island. However, following the model of Anderson & Garven (1987), they noted that the carbon incorporated into the sparry dolomite was derived from two sources, (i) hydrocarbons ($\delta^{13}\text{C} \approx -28\text{‰}$) and (ii) host dolostone ($\delta^{13}\text{C} \approx +2\text{‰}$). Dissolution of the dolostone host proceeded as a consequence of acidity produced during the sulfate-reduction process:



Hence the carbon-isotope composition of sparry dolomite that ultimately precipitated in this setting reflected the proportion of CO_2 derived from each source plus the dolomite- CO_2 fractionation at the temperature(s) of crystallization. This model (in modified form) could be invoked to explain the carbon-isotope results for ore-stage calcite from the Smithfield deposit.

However, the much lower $\delta^{13}\text{C}$ values of Groups 3, 4 and 5 (-27.1 to -22.8‰) from the Jubilee deposit strongly suggest that crystallization of this calcite occurred within a largely closed system with respect to inorganic carbon. Carbon was derived almost entirely from hydrocarbons with little input of inorganic carbon from host limestones (av. $\delta^{13}\text{C} +1.4\text{‰}$). Whereas coupled oxidation of hydrocarbons and dissolution-replacement of sulfate laminae in the host rock may have been closely associated with formation of the low- ^{13}C calcite at Jubilee, it is not necessary or even feasible to invoke large-scale dissolution of the host limestone.

Anderson & Garven (1987) have noted that gypsum or anhydrite can be replaced directly by calcite at low

temperatures (<200°C) provided that the sulfate is simultaneously reduced to H_2S , and that the H_2S is not precipitated immediately by base metals. Such a scenario could explain the $\delta^{13}\text{C}$ values (av. -23.3‰ ; Fig. 5, Table 1) for the Group-3 calcite, most of which crystallized prior to the main stage of sulfide precipitation. Assuming a $\delta^{13}\text{C}$ value of about -28‰ for the CO_2 produced from complete oxidation of the hydrocarbon, the Group-3 calcite results are consistent with the equilibrium carbon-isotope fractionation between calcite and CO_2 at about 100°C ($1000\ln\alpha \approx +5\text{‰}$; Deines *et al.* 1974).

The shift to the still lower $\delta^{13}\text{C}$ values (by ~ 2 to 3‰ ; Fig. 5) of the main ore-stage calcite (Group 4) may be an artifact of the small sample-population, but it may have further significance. Anderson & Garven (1987) noted that precipitation of metal (M) sulfides in such deposits is accompanied by the liberation of H^+ ,



which, in turn, could cause dissolution of carbonate host-rocks (and creation of solution-collapse breccias). At Jubilee, however, the very low $\delta^{13}\text{C}$ values of Group-4 calcite (av. -26.6‰ ; Table 1) probably rule out substantial involvement of carbon from such sources (*e.g.*, Group-1 or -2 limestone; $\delta^{13}\text{C}$ between $+0.4$ and $+2.2\text{‰}$). Instead, release of H^+ may have caused species such as HCO_3^- to become a dominant

product of oxidation of hydrocarbon in the ore fluids. Within the limits of current understanding (Emrich *et al.* 1970, Deines *et al.* 1974, Mook *et al.* 1974, Robinson 1975), a carbon-isotope fractionation ($1000\ln\alpha$) of about $+1$ to 3‰ can be anticipated between calcite and HCO_3^- at temperatures typical of ore deposition at Jubilee. Ore-stage calcite (*i.e.*, Group 4), with a $\delta^{13}\text{C}$ value of about -26‰ , would be the expected product of complete (-28‰) oxidation of hydrocarbons.

The very low $\delta^{13}\text{C}$ values of the post-ore, Group-5 calcite (-23.4 , -23.2‰) are very similar to those obtained for the Group-3 calcite. Whereas this stage of calcite precipitation also was dominated by carbon mostly derived from hydrocarbons, cessation of sulfide precipitation may be reflected in the return to slightly higher values of $\delta^{13}\text{C}$. In this case, however, other explanations may be more appropriate, since the Group-5 calcite has significantly lower $\delta^{18}\text{O}$ values ($+21.6$, $+22.5\text{‰}$) than either Group 3 or 4 ($+23.7$ to $+25.5\text{‰}$) (Table 1), and plots on a trend that describes the inverse relationship between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of Group-4 calcite (Fig. 6). A similar correlation also exists for Group-3 calcite (Fig. 6).

This behavior may indicate that the system was not entirely closed to carbon of inorganic origin. The observed trends on Figure 6 can be explained by introduction of a small fraction of low- ^{18}O water that car-

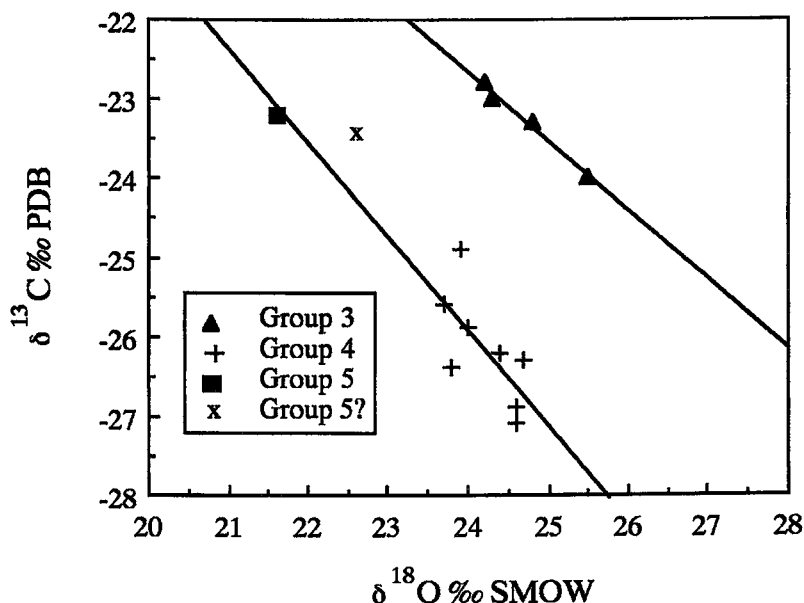


FIG. 6. Carbon and oxygen isotope results for Groups-3, -4 and -5 calcite samples from the Jubilee deposit. Linear regression lines are shown for Groups-3 and -4 calcite. The two data points for Group 5 (post-ore, drusy calcite) plot at the low- ^{18}O , high- ^{13}C end of the general trend observed for Group 4 (main ore-stage calcite).

ried carbon of inorganic origin (*i.e.*, $\delta^{13}\text{C} \approx 0\text{‰}$). If so, the results for Group-5 calcite suggest that external contribution of inorganic carbon (carried by surface-derived meteoric water), while remaining very small, increased from Group 4 to 5. Perhaps notably, the Group-5 sample is from the drill-core (ATG-51-78) that intersected the portion of the Jubilee deposit interpreted by Hein *et al.* (1991) to be a karstic collapse-breccia (Fig. 2). Alternatively, similar patterns for siderite from the Keno Hill Ag-Pb-Zn district were interpreted to reflect consumption of water during production of CO_2 and CH_4 from graphite in a closed system (Lynch *et al.* 1990). A modified version of this scenario (involving liquid hydrocarbons rather than graphite) might be possible at Jubilee, at least during the latter stages of calcite crystallization, once the local supply of sulfate (*i.e.*, anhydrite) had been exhausted.

Although insufficient data exist to distinguish among these and other possibilities, we can note that the lower $\delta^{18}\text{O}$ values for Group-5 calcite cannot be easily explained simply as a temperature effect. Fluid-inclusion data for Jubilee (*i.e.*, for late barite) suggest that temperatures were declining (rather than rising) following mineralization, similar to the pattern observed for post-ore calcite at Gays River, Pembroke and Smithfield deposits (Akande & Zentilli 1984, Ravenhurst *et al.* 1987, 1989).

CONCLUSIONS

The limited scope of this study does not permit presentation of a comprehensive model for mineralization at Jubilee. However, two significant comments concerning the mineralization process are possible. First, the $\delta^{18}\text{O}$ values ($+9 \pm 3\text{‰}$) of the ore-forming fluid(s) are most characteristic of an evolved basinal brine, like that proposed for the Smithfield and Pembroke deposits. Second, the $\delta^{13}\text{C}$ values (-27.1 to -22.8‰) of secondary calcite (Groups 3, 4 and 5) most closely associated with mineralizing fluids are substantially lower than those obtained for other Pb-Zn deposits of Carboniferous age in the Maritimes (-10 to $+3\text{‰}$). Evidence for dissolution of anhydrite, the ubiquitous association of hydrocarbons with the sulfides, and the very low $\delta^{13}\text{C}$ values of calcite can be linked in a model of coupled oxidation of hydrocarbons and reduction of sulfate close to the site of mineralization. The secondary calcite formed in an almost completely closed system, in that the carbonate species required to precipitate calcite were derived almost entirely from hydrocarbons. Only limited input of inorganic carbon (*e.g.*, dissolution of host limestone) is permitted. In this scenario, the Jubilee deposit represents the low-temperature, hydrocarbon-rich end-member in the spectrum of related styles of Pb-Zn mineralization present in the Early Carboniferous Maritime limestones.

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