Synthesis of Mississippi Valley-type lead-zinc deposit potential in northern Alberta and southern Northwest Territories

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Abstract: This paper discusses and integrates results of a research project investigating the resource potential of Mississippi Valley-type lead-zinc mineralization in northern Alberta and southern Northwest Territories. The source, flow path, and timing of fluid movement, and the relation of these fluids to mineralization are examined.

Pre-ore isotopic signatures and fluid inclusion analyses of samples collected in Pine Point district affirm an early episode of dolomitization associated with precipitation from seawater at very shallow depths. Ore-stage carbonate deposits display numerous petrographic and diagenetic features indicating a deeper subsurface or burial environment. Saddle dolomites and sphalerites at Pine Point display fluid inclusion-filling temperatures exceeding levels solely related to maximum burial depths of host strata beneath Paleozoic cover. Continuous recycling of magnesium-rich connate brine by thermal convection fluid flow provides a feasible mechanism for extensive and regional development of hydrothermal dolomite and paleokarst in porous limestone overlying dense dolostone.

Résumé : Le présent article examine et intègre les résultats d'un projet de recherche portant sur la possibilité de trouver des minéralisations de plomb-zinc de type Mississippi-Valley dans le nord de l'Alberta et le sud des Territoires du Nord-Ouest. La source, le trajet d'écoulement et la chronologie des mouvements des fluides, ainsi que la relation entre ces fluides et la minéralisation, font également l'objet d'un examen.

Les signatures isotopiques antérieures à la minéralisation et les analyses des inclusions fluides présentes dans des échantillons prélevés dans le district de Pine Point confirment l'existence d'un épisode précoce de dolomitisation associé à la précipitation à partir de l'eau de mer à de très faibles profondeurs. Les dépôts carbonatés de la phase de minéralisation présentent de nombreuses caractéristiques pétrographiques et diagénétiques qui témoignent d'un milieu de subsurface ou d'enfouissement plus profond. Les dolomites en forme de selle et les sphalérites à Pine Point donnent des températures de remplissage par des inclusions fluides qui dépassent les niveaux uniquement associés aux profondeurs d'enfouissement maximales des strates hôtes sous la couverture paléozoïque. Le recyclage continuel de la saumure connée riche en magnésium par des flux de convection thermique représenterait un mécanisme possible pour la formation régionale de dolomite hydothermale et de paléokarsts dans du calcaire poreux sus-jacent à de la dolomie dense.

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INTRODUCTION

A relatively undisturbed succession of sedimentary rocks dominated by marine carbonate strata of the cratonic platform of the Western Canada Sedimentary Basin (WCSB) hosts sporadic occurrences of lead-zinc mineralization. Significant concentrations of Mississippi Valley-type (MVT) mineralization have been discovered and exploited in the Great Slave Plain region of Northwest Territories at the world-class Pine Point mineral deposit. This volume contains a series of scientific papers discussing carbonate petrography and diagenesis, isotope geochemistry, paleotemperature regimes, mineralizing and dolomitizing fluid characteristics, stratigraphic and structural frameworks associated with mineralization, paragenesis, timing of mineralization, and fluid inclusion systematics in the Pine Point district and surrounding area. Information and data collected from these studies provide a framework in which to compare diagenetic and hydrothermal events associated with mineralization at Pine Point with observed characteristics of carbonate strata in regions elsewhere in the project area. The purpose of this synthesis paper is to integrate the results of these studies into a discussion on the movement of ore-bearing solutions and the subsequent precipitation of ore minerals at Pine Point, and evaluate the potential for similar MVT mineralization external to the Pine Point mine site. A genetic model for deposition of MVT lead-zinc (Pb-Zn) deposits in Devonian carbonate in the region is proposed based on these studies.

GEOLOGICAL SETTING

Phanerozoic strata in the Interior Plains of the WCSB consist of a northeasterly tapering wedge of supracrustal rocks overlapping the western extension of the Precambrian craton (Porter et al., 1982; Price, 1994; see Figure 1 in Introduction paper by Hannigan (2006) for WCSB and project area locations). The wedge of sediments thickens southwestward from zero at the craton/Phanerozoic boundary to near 6 km adjacent to the deformed belt of the Cordilleran Orogen (Porter et al., 1982; Wright et al., 1994). Filling the WCSB are two major sedimentary successions of approximately equal volume derived from distinct tectonic settings. The older succession consists of Upper Proterozoic to mid-Jurassic, dominantly marine sediments. These easterly derived rocks were deposited on a stable passive continental margin by means of oceanward progradation (Podruski et al., 1988). This episodic transgressive and regressive miogeoclinal succession predominantly consists of open-marine platformal carbonate deposits, basinal shale, and restricted evaporitic sediments. In the project area, the succession is expressed on the surface by lower Middle Devonian to Upper Devonian marine platformal, basinal and evaporitic strata (Fig. 1, 2). In the subsurface of the western portion of the project area, Devonian strata are overlain by a Carboniferous carbonate platform succession. The ‘cratonic platform’ succession was buried by a second major sedimentary succession consisting of shallow-marine and nonmarine strata of Late Jurassic to Tertiary age. The younger succession is westerly derived and was deposited by cratonward progradation of clastic detritus from an evolving Cordilleran Orogen. The accretion of exotic terranes onto the western continental margin of North America during the Middle Jurassic to Early Tertiary time period (Monger and Price, 2000) drove the development of the Cordilleran Orogen (Porter et al., 1982). The accretionary process produced an overriding mass of thrust sheets resulting in the formation of the foreland basin to the east (Price, 1994). Nonmarine Cretaceous clastic sediments were deposited in the west and southwest portions of the project area (Fig. 1, 2). The thrust sheets provided detritus to fill the foreland basin and produced a tectonic load on the western margin of the basin causing the cratonic platform succession to tilt southwestward toward the continental margin (Podruski et al., 1988). Several cratonic arches evolving prior to or during sedimentation profoundly affected environments of deposition, resulting in complex sedimentary facies patterns adjacent to these basement highs (Peace River and Tathlina arches in project area, Fig. 1).

Host rocks for MVT mineralization in northern Alberta and southern Northwest Territories are carbonate strata within the older cratonic platform sediment wedge. Although much of WCSB is underlain by carbonate of Cambrian, Devonian, or Carboniferous age, the predominant carbonate succession occurring in the project area is of Devonian age. Devonian carbonate deposits occur at or near the surface in the northern and eastern parts of the project area (Fig. 1, 2), establishing these strata as viable targets for effective exploration and development. There are little or no pre- and post-Devonian carbonate strata in these areas. Characteristic MVT deposit features such as karst and paleokarst development, dolomitization, and genetic associations with evaporites and hydrocarbons are present in the Pine Point mining district (Fig. 2) (In this paper, Pine Point district refers to the region of southern Northwest Territories covered by Fig. 2; the Pine Point property or mine site is indicated by the green polygon adjacent to the southeastern shore of Great Slave Lake on Fig. 2). The host rocks at Pine Point are Middle Devonian reef complex and platformal carbonates. Mineralization is epigenetic, and occurs as open-space cavity-fills and local replacements of carbonate. Within the mid-Devonian Givetian carbonate succession, a narrow linear buildup of carbonate up to 200 m thick formed the Presqu’ile barrier (Fig. 1; Kyle, 1981; Rhodes et al., 1984). The barrier separates two depositional subbasins: the Mackenzie subbasin to the north, where shale and argillaceous limestone were deposited; and the Elk Point subbasin to the south, where evaporite and lesser carbonate were laid down. The barrier complex exposed on the surface within the Pine Point mine area dips gently to the west, and is traceable in the subsurface through the southern portion of Great Slave Plain in Northwest Territories and through northwestern Alberta into northeastern British Columbia. Skall (1975) demonstrated that subtle tectonic adjustments along three N65°E hinge lines were responsible for the development of paleokarst

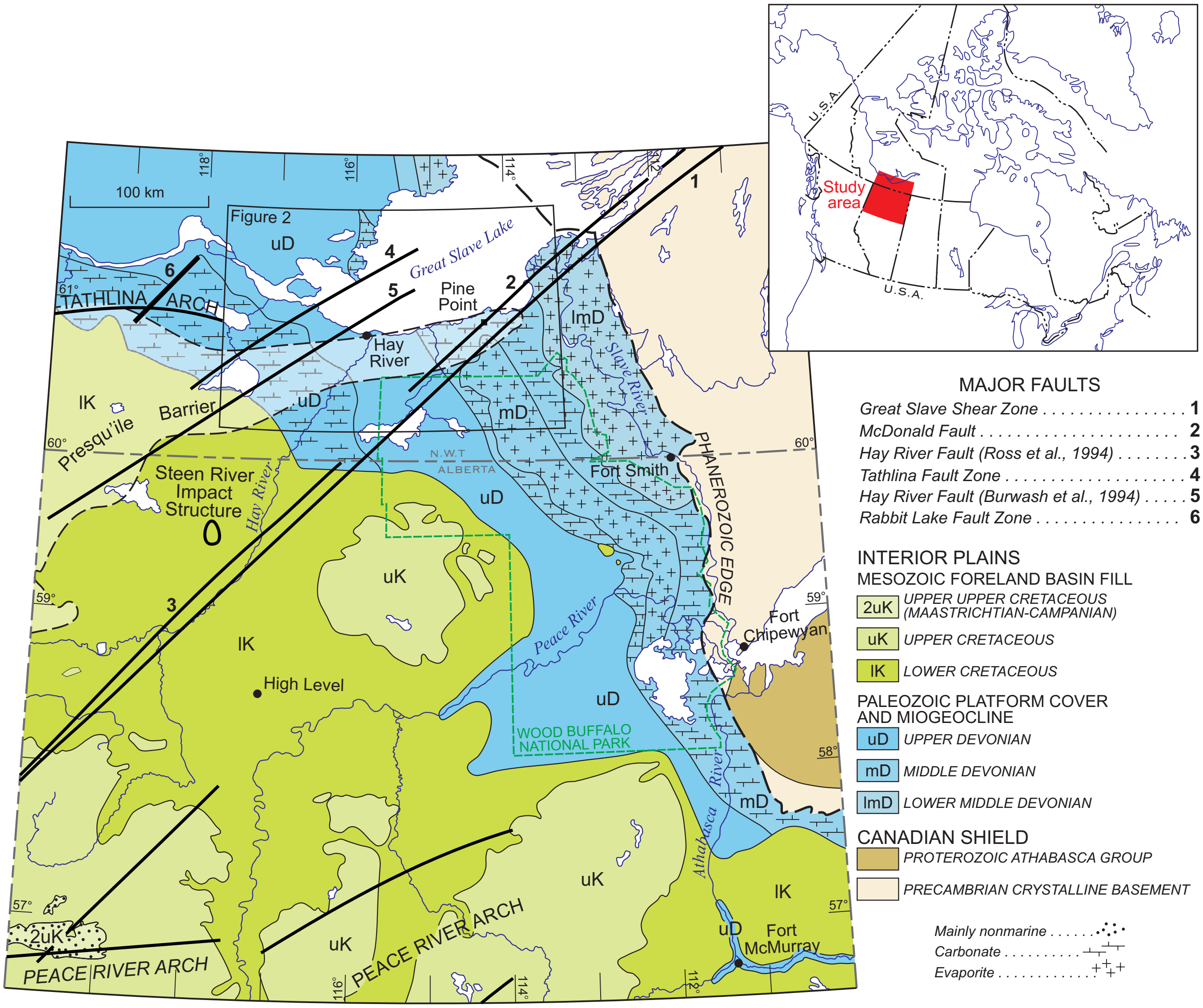

Figure 1. Bedrock geology and regional tectonics of TGI project area. Location of Presqu'ile barrier and Tathlina and Peace River arches are shown. *Modified from* Morrow et al. (2006) and Wheeler et al. (1996). Outline of Figure 2 is shown.

and numerous paleoenvironmental facies within and adjacent to the barrier. The hinge lines seem to be approximate projections of the underlying Precambrian McDonald–Great Slave fault system, although Skall (1975) pointed out that the trends of the hinge lines and fault system are not parallel. The hinges trace lines of weakness where preferential karstification, coarse-grained dolomitization (Presqu'ile dolomite) and mineralization are concentrated. A more detailed discussion of the regional geology and stratigraphic and structural framework of the project area is presented in the Introduction paper by Hannigan (2006).

MINERAL DEPOSITS AND SHOWINGS

About 95 per cent of the more than 820 lead and/or zinc deposits and showings listed by Hannigan (2005a) in the project area are hosted in carbonate strata (in this paper, a deposit is a naturally occurring mineral body that is wholly or partly of economic value whereas a showing is an occurrence of visible mineralization or geochemical anomaly that is of uneconomic value). The definitive classification of the Pine Point mineral deposit as belonging to the Mississippi Valley-type style of mineralization (see Leach and Sangster, 1993; Sangster, 1996) suggests that carbonate-hosted lead and zinc occurrences elsewhere in the project area are likely

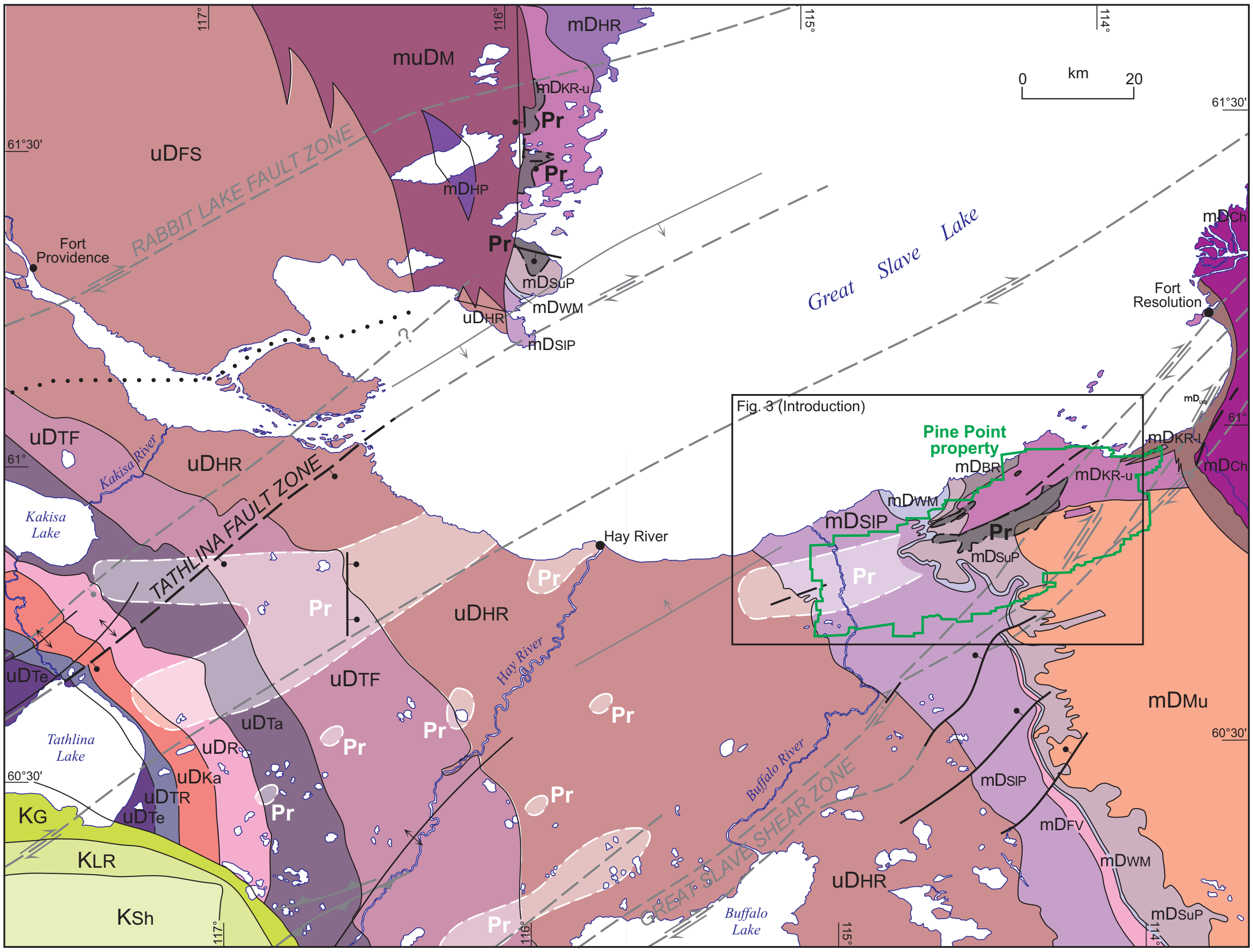

Figure 2. A geological map of the Pine Point district (*adapted from* Okulitch, 2006). Surface (black) and interpreted subsurface (grey) geological contacts and structures are shown. Presqu'ile dolostone in Pine Point minesite area (dark grey) *from* Rhodes et al. (1984). Subsurface distribution of Presqu'ile dolostone (white) *from* Janicki (2006). Outline of Figure 3 of Introduction paper by Hannigan (2006) is shown.

MVT-type because of similar host rocks and depositional environments (also, *see* Macqueen, 1997 for background information on a joint Geological Survey of Canada-Alberta Mineral Development Agreement project on the mineral potential of Alberta). The remaining 5 per cent of lead-zinc accumulations in the project area are classified as stratiform sediment-hosted-type accumulations apropos to their occurrence in shale or sandstone. One hundred orebodies distributed over 1600 square kilometres have been drill-delineated in the Pine Point mining camp (*see* Fig. 3 in Introduction paper by Hannigan, 2006 for orebody locations). The former orebodies and mineral deposits at Pine Point have been extensively studied. Their characteristics are representative of essential critical elements that should be incorporated in any future exploration strategy elsewhere in the project area. Therefore, a discussion of these orebodies and their characteristics in the Pine Point mining camp and district is required.

Deposit distribution

All MVT deposits or orebodies in the Pine Point district are hosted in middle Devonian Givetian carbonate strata within and adjacent to a dolomitized carbonate barrier complex. Carbonate units hosting ore include the Upper Keg River Member (or Pine Point Group) and Sulphur Point Formation within the barrier, Muskeg Formation of the back-barrier, Buffalo River Formation of the fore-barrier, and strata deposited on top of the barrier (Watt Mountain and Slave Point formations) (Fig. 7 and 9 in Introduction paper by Hannigan, 2006). Most individual orebodies occur in multiple formations and are closely associated with a major diagenetic facies called the Presqu'ile dolomite (*see* Fig. 2 for Presqu'ile dolomite distribution in Pine Point district).

Most of the 100 known Pb-Zn deposits or orebodies in the Pine Point district are hosted by more than one carbonate stratal unit. Thirty-nine of these orebodies partly or wholly occur in the Upper Keg River Member (Pine Point Formation of Rhodes et al., 1984), 82 are hosted by the Sulphur Point Formation, 22 occur in the Muskeg Formation, 20 are found in the Buffalo River Formation, 32 partly occur in the Watt Mountain Formation, and 12 are hosted by the Slave Point Formation (Hannigan, 2005a). The Sulphur Point Formation hosts in whole or in part the majority of orebodies at Pine Point mine site. In the Pine Point district (outside of Pine Point and Great Slave Reef properties), there are an additional 92 occurrences of visible lead and zinc mineralization in Middle and Upper Devonian carbonate strata (Hannigan, 2005a). Thirty-nine of these occurrences are hosted in the Slave Point Formation, whereas 23 are found in the Sulphur Point Formation, 12 in Upper Keg River Member, six in Lower Keg River Member, two in Watt Mountain Formation, one in Buffalo River Formation, eight in Hay River Formation and one in Twin Falls Formation.

Orebodies in Pine Point district are preferentially distributed along zones of weakness or hinge lines where extensive interconnected paleokarst networks developed at the lower limit of Presqu'ile-type coarse dolomitization of upper barrier porous limestone (Fig. 3 and 9 in Introduction paper by Hannigan, 2006). The paleokarst networks are most extensively developed along two major linear features called the North and Main trends, where Presqu'ile dolomitization was pervasive (Fig. 3 in Introduction paper by Hannigan, 2006). The South trend is less well-defined, consisting of only a limited number of scattered orebodies accompanied by very little Presqu'ile dolomitization. In the Pine Point district, 57 deposits are distributed along the Main trend, 36 occur in the North trend and 7 are located along the South trend (Fig. 3 in Introduction paper by Hannigan, 2006).

Grade and tonnage

Individual orebodies in the Pine Point mining camp ranged in size from less than 100 000 tonnes to near 17.5 million tonnes of average grade of 2.0% Pb and 6.2% Zn in the largest prismatic orebody with the mine designation of X-15 (Table 1). Figure 3 illustrates the grade-tonnage distribution for orebodies with reported proven reserves as well as produced orebodies according to orebody type and trend. Not all Pine Point orebodies are shown because of unavailability of reserve or production information. However, an estimation of remaining geological resource on the Pine Point property was determined and is depicted. Figure 3 also indicates indirectly the mine development strategy at Pine Point. Large orebodies

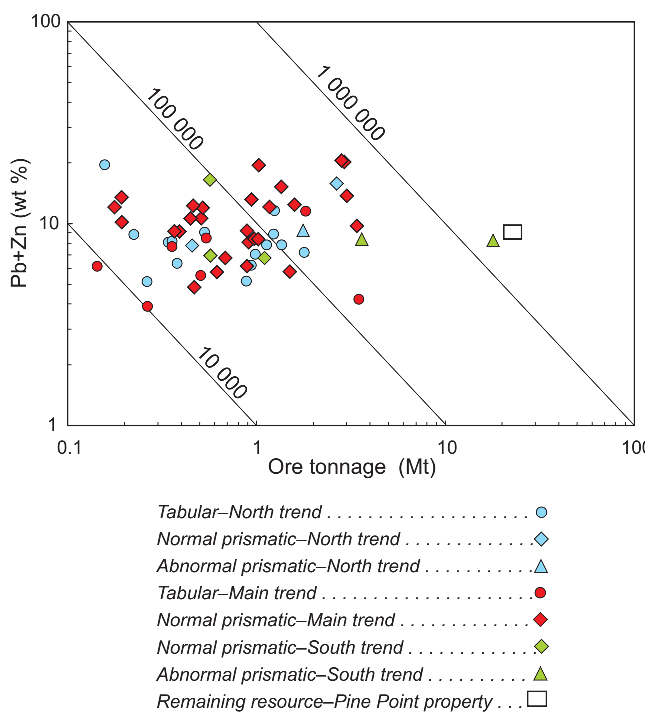

Figure 3. Grade versus tonnage plot of produced individual orebodies at Pine Point according to major mineralized trend and orebody type (production data supplied by D. Rhodes of Teck-Cominco). Estimated grade and tonnage of the remaining resource in the Pine Point district is depicted.

Contents

Table 1. Pine Point District orebodies

Orebody	Host formation	Orebody type	Tonnes produced	Production grade Pb (%)	Production grade Zn (%)	Produced Pb Tonnes	Produced Zn Tonnes	Reserves Tonnes	Reserves Year	Grade of reserves Pb (%)	Grade of reserves Zn (%)	Dimensions Length (m)	Dimensions Width (m)	Dimensions Thickness (m)
A. Pine Point property														
A-55	Slave Point, Watt Mountain, Sulphur Point, Upper Keg River	abnormal prismatic	1,550,830	3.0	7.6	46,525	117,863	1,814,000	1980	2.5	6.8	130	130	14
A-70	Slave Point, Watt Mountain, Sulphur Point, Upper Keg River	normal prismatic	2,289,360	4.5	10.4	103,021	238,093	2,539,600	1981	5.0	11.3	215	110	7–53
G-03/H-02	Slave Point, Watt Mountain, Sulphur Point	normal prismatic	0			0	0	907,000	1978	2.3	6.0			
HZ	Sulphur Point		0			0	0							
I-46	Upper Keg River	normal prismatic	389,870	5.1	4.2	19,883	16,375							
I-65	Sulphur Point, Upper Keg River	normal prismatic	194,510	3.8	11.1	7,391	21,591	200,000	1984	3.9	8.1	190	130	
J-44	Sulphur Point	normal prismatic	1,282,230	5.9	9.8	75,652	125,659							
J-68	Sulphur Point		0			0	0							
J-69	Sulphur Point, Upper Keg River	normal prismatic	854,770	1.2	5.2	10,257	44,448							
K-32	Sulphur Point	tabular	0			0	0					300	25–100	3–6
K-35	Sulphur Point	tabular	0			0	0					800	50–300	5–10
K-48	Sulphur Point		0			0	0							
K-51	Sulphur Point	normal prismatic	0			0	0							
K-53	Sulphur Point	normal prismatic	468,900	3.7	9.3	17,349	43,608							
K-57	Sulphur Point, Upper Keg River	normal prismatic	1,564,540	6.5	5.2	101,695	81,356	1,632,600	1981	7.0	5.6	350	15–130	10–50
K-60	Sulphur Point	tabular	0			0	0					790	190	
K-62	Sulphur Point, Upper Keg River	normal prismatic	1,001,590	3.6	4.8	36,057	48,076					190	100	
K-66	Sulphur Point	tabular	0			0	0					360	130	
K-68	Sulphur Point	tabular	0			0	0					695	150	
K-77	Sulphur Point	normal prismatic	511,120	6.4	6.4	32,712	32,712							
L-27	Sulphur Point, Muskeg	tabular	0			0	0					820	350	3–10
L-30	Sulphur Point, Muskeg	tabular	262,170	1.1	2.8	2,884	7,341					250	100	3–5
L-35	Sulphur Point, Muskeg	tabular	0			0	0					150	50	
L-36	Sulphur Point, Muskeg	tabular	0			0	0					1450	50–400	2.5–10

Data derived from Thorpe (1966); Padgham et al. (1974); Gibbins et al. (1977); Hurdle and Gibbins (1978); Gibbins (1978, 1987, 1990); Kyle (1981); Alldrick et al. (1981); Carter (1983); Goodwin et al. (1983); Rhodes et al. (1984); Brophy (1984, 1987); Randall et al. (1985); Turner (2002); Hannigan (2005a); and D. Rhodes (pers. comm.).

Table 1. (cont.)

Orebody	Host formation	Orebody type	Tonnes produced	Production grade Pb (%)	Production grade Zn (%)	Produced Pb Tonnes	Produced Zn Tonnes	Reserves Tonnes	Reserves Year	Grade of reserves Pb (%)	Grade of reserves Zn (%)	Dimensions Length (m)	Dimensions Width (m)	Dimensions Thickness (m)
A. Pine Point property														
L-37	Sulphur Point, Muskeg	tabular	3,417,550	1.0	3.4	34,176	116,197					900	375	4–12
L-65	Sulphur Point		0			0	0							
M-40	Sulphur Point	tabular	350,870	2.2	5.5	7,719	19,298							3–15
M-48	Sulphur Point		0			0	0							
M-52	Sulphur Point, Muskeg	normal prismatic	455,260	3.5	7.6	15,934	34,600					120	80	
M-62	Sulphur Point	tabular	0			0	0					1500	200	
M-63	Sulphur Point	tabular	0			0	0					1500	200	
M-64	Sulphur Point, Upper Keg River	normal prismatic	178,460	4.9	8.0	8,745	14,277	153,283	1984	3.4	9.0	43	27	2–48
M-67	Sulphur Point	tabular	0			0	0					650	300	
N-31	Sulphur Point	tabular	505,200	1.6	4.1	8,083	20,713					350	100	
N-32	Sulphur Point	tabular	1,862,070	3.4	8.4	63,310	156,414					350	100	
N-33	Sulphur Point	tabular	0			0	0							
N-36	Sulphur Point		0			0	0							
N-38	Sulphur Point, Muskeg	normal prismatic	1,182,110	4.9	7.4	57,923	87,476					250	150	
N-42	Sulphur Point, Muskeg, Watt Mountain	normal prismatic	2,959,680	5.3	9.5	156,863	281,170					490	180	<28
N-50	Sulphur Point		0			0	0							
N-81	Slave Point, Watt Mountain, Sulphur Point, Muskeg, Upper Keg River	normal prismatic	2,699,950	7.0	14.1	188,997	380,693	2,700,000	1984	7.0	12.0	260	76	11–100
N-99	Slave Point, Watt Mountain, Sulphur Point	normal prismatic	0			0	0							
N-204	Upper Keg River	tabular	0			0	0		1984	3–4% Pb+Zn	3–4% Pb+Zn	2000	1000	2–15
O-28	Muskeg	normal prismatic	1,483,870	2.0	3.7	29,677	54,903							
O-32	Sulphur Point, Muskeg	normal prismatic	375,970	2.8	6.4	10,527	24,062							
O-42	Sulphur Point, Muskeg, Watt Mountain	normal prismatic	2,742,720	8.8	11.6	241,359	318,156					335	185	<30
O-53	Sulphur Point, Muskeg	normal prismatic	0			0	0					250	70–110	
P-24	Sulphur Point	normal prismatic	496,640	3.5	7.6	17,382	37,745	454,000	1985	3.7	7.6			
P-29	Muskeg	normal prismatic	476,120	1.6	3.3	7,618	15,712							

Table 1. (cont.)

Orebody	Host formation	Orebody type	Tonnes produced	Production grade Pb (%)	Production grade Zn (%)	Produced Pb Tonnes	Produced Zn Tonnes	Reserves Tonnes	Reserves Year	Grade of reserves Pb (%)	Grade of reserves Zn (%)	Dimensions Length (m)	Dimensions Width (m)	Dimensions Thickness (m)
A. Pine Point property														
P-31	Muskeg	normal prismatic	604,760	2.2	3.6	13,305	21,771							
P-32	Muskeg	normal prismatic	694,980	3.2	3.5	22,239	24,324							
P-41	Sulphur Point	normal prismatic	196,140	2.1	8.3	4,119	16,280	140,600	1986	2.2	8.0			
R-61	Sulphur Point, Muskeg	normal prismatic	1,034,540	1.6	5.2	16,553	53,796	1,242,590	1974	10.4% Pb+Zn	10.4% Pb+Zn	190	100	
R-67	Sulphur Point, Muskeg	normal prismatic	0			0	0							
S-65	Sulphur Point, Muskeg	normal prismatic	575,550	1.2	5.7	6,907	32,806					190	55	
T-37	Upper Keg River	tabular	358,960	2.1	6.3	7,538	22,614							
T-58	Sulphur Point, Muskeg	normal prismatic	563,310	4.5	12.6	25,349	70,997	544,200	1975	17% Pb+Zn	17% Pb+Zn	130	95	75
V-90	Upper Keg River	tabular	0			0	0							
W-17	Muskeg, Upper Keg River	abnormal prismatic	3,515,400	2.0	6.1	70,308	214,439	3,537,300	1981	2.0	6.2	440	350	30–75
W-85	Slave Point, Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	normal prismatic	0			0	0					300	150	5–20
X-15	Muskeg, Upper Keg River	abnormal prismatic	17,474,260	2.0	6.2	349,485	1,083,404	9,070,000	1975	10% Pb+Zn	10% Pb+Zn	800	400	20–30
X-17	Upper Keg River	normal prismatic	44,910	1.5	6.3	674	2,829							
X-49	Upper Keg River	tabular	0			0	0							
X-51	Buffalo River, Upper Keg River	tabular	1,203,980	2.2	6.7	26,488	80,667					800	50–133	
X-52	Buffalo River, Upper Keg River	tabular	1,104,080	1.6	6.3	17,665	69,557					400	83–133	
X-53	Buffalo River, Sulphur Point, Upper Keg River	tabular	1,231,940	2.7	9.2	33,262	113,338					770	67–300	3–13
X-54/ X-55	Buffalo River, Sulphur Point	tabular	216,130	2.1	6.7	4,539	14,481					830	30–100	
X-56/ X-57	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	1,319,580	1.6	6.3	21,113	83,134					670	30–170	4–23

Data derived from Thorpe (1966); Padgham et al. (1974); Gibbins et al. (1977); Hurdle and Gibbins (1978); Gibbins (1978, 1987, 1990); Kyle (1981); Alldrick et al. (1981); Carter (1983); Goodwin et al. (1983); Rhodes et al. (1984); Brophy (1984, 1987); Randall et al. (1985); Turner (2002); Hannigan (2005a); and D. Rhodes (pers. comm.).

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Orebody	Host formation	Orebody type	Tonnes produced	Production grade Pb (%)	Production grade Zn (%)	Produced Pb Tonnes	Produced Zn Tonnes	Reserves Tonnes	Reserves Year	Grade of reserves Pb (%)	Grade of reserves Zn (%)	Dimensions Length (m)	Dimensions Width (m)	Dimensions Thickness (m)
A. Pine Point property														
X-58	Watt Mountain, Buffalo River	tabular	0			0	0							
X-59	Watt Mountain, Buffalo River	tabular	0			0	0							
X-61	Watt Mountain, Sulphur Point, Buffalo River	tabular	0			0	0							
X-62	Watt Mountain, Sulphur Point, Buffalo River	tabular	0			0	0							
X-64	Watt Mountain, Sulphur Point	tabular	0			0	0							
X-65	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	0			0	0					630	30–280	
X-68	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	0			0	0							
X-71	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	0			0	0							
Y-53	Sulphur Point, Upper Keg River	tabular	967,710	1.5	5.6	14,516	54,192					1130	67–167	1.5-3
Y-54	Sulphur Point	tabular	263,840	1.3	4.0	3,430	10,554					270	70–200	
Y-55	Sulphur Point	tabular	0			0	0					370	30–130	
Y-60	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	512,490	2.1	7.3	10,762	37,412							
Y-61	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	549,040	3.5	9.3	19,216	51,061	1,814,000	1984	1.8	5.5	490–520	15–150	2-22
Y-62	Watt Mountain, Sulphur Point, Buffalo River	tabular	0			0	0					515	50–100	
Y-65	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	149,770	7.0	12.9	10,484	19,320							
Y-72	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	0			0	0							
YBM	Buffalo River, Upper Keg River	tabular	0			0	0	306,680	1968	1.7	6.0			
Z-53	Sulphur Point, Watt Mountain	tabular	380,520	1.4	5.0	5,327	19,026					300	75	
Z-57	Sulphur Point	tabular	827,870	1.1	4.2	9,107	34,771					430	50–270	

Contents

Table 1. (cont.)

Orebody	Host formation	Orebody type	Tonnes produced	Production grade Pb (%)	Production grade Zn (%)	Produced Pb Tonnes	Produced Zn Tonnes	Reserves Tonnes	Reserves Year	Grade of reserves Pb (%)	Grade of reserves Zn (%)	Dimensions Length (m)	Dimensions Width (m)	Dimensions Thickness (m)
A. Pine Point property														
Z-60	Sulphur Point		0			0	0							
Z-61	Upper Keg River		0			0	0							
Z-64	Watt Mountain, Sulphur Point, Buffalo River, Upper Keg River	tabular	913,470	1.4	5.1	12,789	46,587					850	30–550	
B. Great Slave Reef property														
O-556	Slave Point, Watt Mountain, Sulphur Point, Upper Keg River	normal prismatic	0			0	0	949,000	1982	4.3	4.2	245	110	0.5–52
P-499	Slave Point, Watt Mountain, Sulphur Point, Upper Keg River	normal prismatic	0			0	0	876,000	1982	2.9	6.5	60	90	3–70
R-190	Slave Point, Watt Mountain, Sulphur Point, Upper Keg River	normal prismatic	0			0	0	1,013,000	1983	6.3	12.7	120–170	80	2–45
V-46	Slave Point, Watt Mountain, Sulphur Point	tabular	0			0	0	522,000	1976	3.0	5.5	100-180	40–140	1–30
W-19	Sulphur Point, Upper Keg River	tabular	0			0	0	141,000	1976	0.4	5.9	275	45–90	1–10
X-25	Slave Point, Watt Mountain, Sulphur Point	normal prismatic	0			0	0	3,265,000	1985	2.6	7.1	120–560	140	2–63
Z-155	Slave Point, Watt Mountain, Sulphur Point, Upper Keg River	normal prismatic	0			0	0	907,000	1985	5.5	7.2	183	168	2–78
	Total tonnes		64,259,590			2,006,914	4,515,878							

Data derived from Thorpe (1966); Padgham et al. (1974); Gibbins et al. (1977); Hurdle and Gibbins (1978); Gibbins (1978, 1987, 1990); Kyle (1981); Alldrick et al. (1981); Carter (1983); Goodwin et al. (1983); Rhodes et al. (1984); Brophy (1984, 1987); Randall et al. (1985); Turner (2002); Hannigan (2005a); and D. Rhodes (pers. comm.).

close to the millsite (along the Main and South trends, *see* Fig. 3 in Introduction paper by Hannigan, 2006) were developed first. Along these trends, normal prismatic and abnormal prismatic deposits, which are chimney-like, vertically elongate orebodies most often containing greater tonnages and grades, were most amenable to the open-pit mining method. The recognition of tabular deposits (elongate flat-lying orebodies) later in the exploration cycle precluded immediate development because of generally lower grade and tonnage (Fig. 3) as well as their stratal location deeper within the carbonate succession (see below for orebody relationships with carbonatehosting strata). Figure 3 reveals that abnormal prismatic deposits (modern karst or sinkhole deposits) generally contain the greatest tonnages and grade. Normal prismatic deposits (paleokarst-related deposits) constitute intermediate grade/tonnage orebodies, and were developed regardless of tonnage and grade along the Main and South trends. Tabular deposits (also paleokarstic) of lowest grade and tonnage were developed along the North and Main trends, regardless of tonnage and grade, later in the exploration cycle after exhaustion of higher-grade prismatic orebodies. Tonnage and grade distribution are similar along each trend. Because of the southwest dip of the strata, orebodies were preferentially developed on the eastern portion of the Pine Point property earliest because of their proximity to surface.

Deposits averaged 1.32 million tonnes (Mt) of ore grading near 7.0 per cent Zn and 3.0 per cent Pb (district average in Fig. 4). Metal contents of individual orebodies ranged from 0.4 to 8.8 per cent Pb and 2.8 to 14.1 per cent Zn (Fig. 4). The iron content of individual orebodies ranged from less than 0.5 to near 10.5 per cent; the district average is near 3.5 per cent (Kyle, 1981). Total geological resource (produced resource and remaining proven reserves) for the Pine Point district is estimated by the author to be near 94.5 Mt. The Pb/(Pb+Zn) ratios of Pine Point district orebodies range from 0.06 to 0.56 with a district average of 0.26. Orebodies of the normal prismatic variety are generally lead-rich, averaging about 0.35. There is also a distinct lead richness associated with Main Trend normal prismatic orebodies averaging near 0.37, whereas normal prismatic orebodies in the North and South trends average near 0.25. Tabular and abnormal prismatic orebodies present in all trends are relatively zinc-rich, averaging near 0.25 (Fig. 4).

Weighted averages of lead and zinc in various orebodies from the upper (Sulphur Point–Slave Point buildup) and lower (Keg River buildup) portions of the Presqu'ile barrier indicate weak vertical metal zoning. In the upper barrier, a weighted average of the Pb/(Pb + Zn) ratio is 0.20, indicating that these orebodies are slightly richer in zinc than orebodies of the lower barrier (0.26). Kyle (1981) reported a district-wide pattern of metal zoning as determined from ore-reserve data at that time. The pattern showed a Pb/(Pb+Zn) increase from about 0.2 in the southeast to near 0.5 in the northwest in zones parallel to the Main and North trends. New information collected in this study, partly derived from ore data collected to the southwest of Kyle's (1981) study,

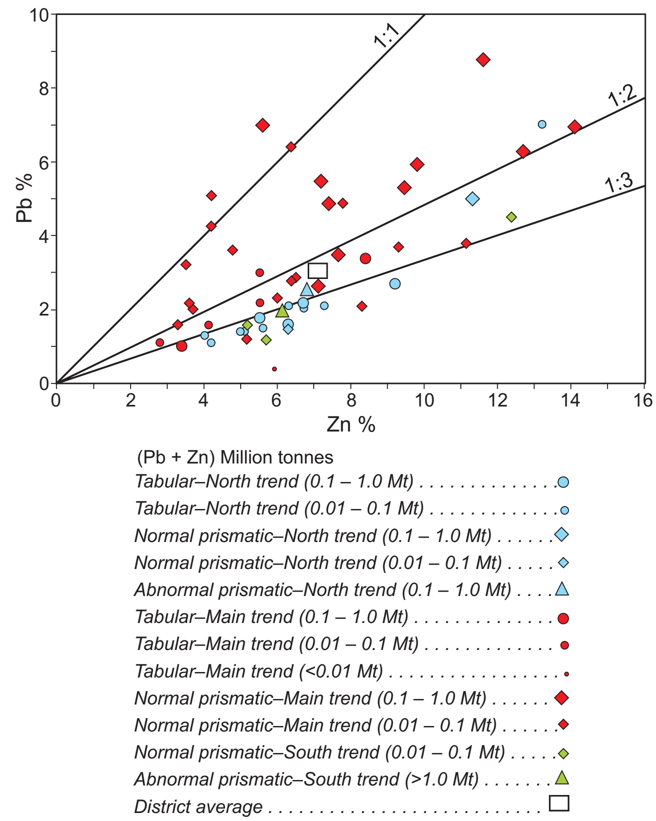

Figure 4. Weight per cent of Pb and Zn in major orebodies at Pine Point according to mineralized trend, orebody type, and tonnage (tonnages supplied by D. Rhodes of Teck-Cominco). The district average is also shown.

reveals the ratio decreasing southwesterly to near 0.2. A weighted average calculation of the Pb/(Pb+Zn) ratio on orebodies along the entire length of the Main Trend reveals a consistent ratio (0.36), indicating there is no district-wide lateral zoning pattern.

Deposit morphology

Nature of sulphide bodies

Rhodes et al. (1984) cited karstification of the barrier as a major control for ore deposition at Pine Point. They pointed out that the trend and geometry of these paleokarst bodies are similar to the orebodies and thus, strongly related. At Pine Point, karst refers to both surface and subsurface solution features and pore space. The mineralization is pervasive in interconnected paleokarst networks. The networks are mainly developed in the porous barrier complex along the North and Main hinge zones and are directly related to distinct lithofacies. At Pine Point, karstification not only occurs along these distinct trends but is also embodied in four, distinct, karstic orebody types: tabular, prismatic, abnormal prismatic and B-spongy type (Rhodes et al., 1984). These orebody types are illustrated in Figure 10 of Introduction paper by

Hannigan (2006). Ore deposition is strongly controlled by discrete stratal horizons, although individual prismatic orebodies are discordant.

Tabular karst is the more common and widespread solution network in the Pine Point district. This karstic network occurs along a crude stratabound horizon that coincides with the base of the Presqu'ile dolomite near the Sulphur Point/Upper Keg River contact (Fig. 10 in Introduction paper by Hannigan, 2006). The tabular ore deposits are elongate, flat-lying bodies associated with an interconnected network of karst channels (see Fig. 5, where an example of stratabound karstic or breccia dolostone is shown representing a potential host for tabular-type orebodies). These karst channels can attain thicknesses up to 12 m and widths up to 240 m (Rhodes et al., 1984).

Most past production at the Pine Point mine exploited normal prismatic deposits, which are associated with major cavity dissolution and prismatic openings extending upward from the tabular horizon (Fig. 10 in Introduction paper by Hannigan, 2006; Rhodes et al., 1984). These local zones of enhanced dissolution appear to coincide with areas of greater lithological weakness where more intense jointing and fracturing increased porosity and permeability. Dissolution caused sagging and collapse of the overlying strata, sometimes affecting up to 100 m of stratigraphy. These collapse structures seem to be related to structurally elevated areas (ridges or domes). The collapse process allowed the resedimentation of the openings by clastic carbonate ranging from well-laminated internal sediments to breccias incorporating surrounding and overlying material at and above the tabular karst horizon (Rhodes et al., 1984). The breccias show fine fragmentation at the base of the cavity structures and grade upward into coarser and fewer distorted fragments. The finer grained internal sediments and overlying breccias contain the sulphide mineralization.

There is a type of karstic structure of similar geometry to normal prismatic bodies that does not root in the tabular ore horizon. These abnormal prismatic orebodies are separate karstic features from the dominant paleokarst network hosting tabular and normal prismatic deposits. It is believed that these abnormal structures or unconsolidated collapses formed as a result of tabular or prismatic bodies originally hosted in overlying strata collapsing into underlying strata. The original host strata are missing as a result of erosion. The

Figure 5. A dolomite boulder from rubble pile at Pine Point mine site. Very porous partly-cemented rubble packbreccia layer underlain by laminated dolostone strata. (Field classification of breccia fabrics from Morrow (1982) adopted in this description. A partly-cemented rubble packbreccia represents a fabric in which fragments of chaotic orientation are largely in contact and partly cemented). Abundant rock dissolution in the stratabound packbreccia horizon produced breccia-moldic cavities subsequently cemented by white sparry or saddle dolomite. The breccia layer, a horizon of enhanced porosity and permeability, may form tabular karst structures commonly hosting tabular sulphide concentrations at Pine Point. The laminated dolostone probably exhibits original fabric due to dissolution and cementation of selected laminae. Photo by D. W. Morrow (GSCC photo number 4784-1).

abnormal orebodies are affected by continuing dissolution and are thought to represent modern karst or sinkholes (Rhodes et al., 1984; Fig. 10 in Introduction paper by Hannigan, 2006). Some of these modern sinkhole structures are mineralized (e.g. X-15 and W-17 orebodies).

The B-spongy mineralization ore habit (i.e. disseminated mineralization restricted to the porous horizon called the B-spongy member (Rhodes et al., 1984)) has only been discovered in one orebody at Pine Point. The N-204 orebody is located near the northeastern corner of the property where the B-spongy member is near the surface (Fig. 3 and 10 in Introduction paper by Hannigan, 2006). The B-spongy member consists of fine-grained dolomite containing fossil moldic porosity. On the eastern part of the property, this open porosity is accompanied by fine crackle brecciation (Rhodes et al., 1984). Dissolution in this horizon produced substantial vuggy, fracture and intergranular porosity. Mineralization is disseminated in the moldic and breccia porosity.

Dimensions of orebodies

Dimensions of the 100 known orebodies in the Pine Point district vary from 40 to 2000 m in length, 15 to 1000 m in width and 0.5 to 100 m thick (Table 1). Tabular orebodies range in length from 100 to 2000 m, in width from 15 to 1000 m and are one to 30 m thick. Normal prismatic orebodies vary in length from 40 to 560 m, in width from 15 to 185 m and in thickness from 0.5 to 100 m. Abnormal prismatic orebodies show dimensions of 130 to 800 m length, 130 to 400 m width and 14 to 75 m thickness.

Mineralogy

Mineralization at Pine Point consists of sphalerite, galena, marcasite, and pyrite with associated native sulphur and bitumen and local pyrrhotite, celestite, barite, gypsum, anhydrite, and fluorite (Kyle, 1981). The sphalerite grade is generally greater than galena, usually near 2:1, but this ratio varies widely among the orebodies (Fig. 4). Gangue minerals are dolomite and calcite. Common ore textures in the district are disseminations, banded encrustations, crystalline galena and sphalerite, and colloform sphalerite. The sulphide concentrations commonly have abrupt contacts with barren host rocks. Mineralization occurs as replacement of karst-filling internal sediments and breccia, open-space filling, and peripheral disseminations in vuggy porosity. The highest-grade mineralization seems to be restricted to karstic structures hosting the greatest amount of internal sediment fill (Rhodes et al., 1984). The most typical host lithology for ore-grade mineralization is the coarse-grained vuggy Presqu'ile dolomite. The orebodies occupy the most permeable portion of the highly porous Presqu'ile barrier complex.

Typical sulphide textures at Pine Point include open-space filling of breccias, fractures and vugs (Fig. 6). Massive replacements of host rocks, internal sediments and sulphide

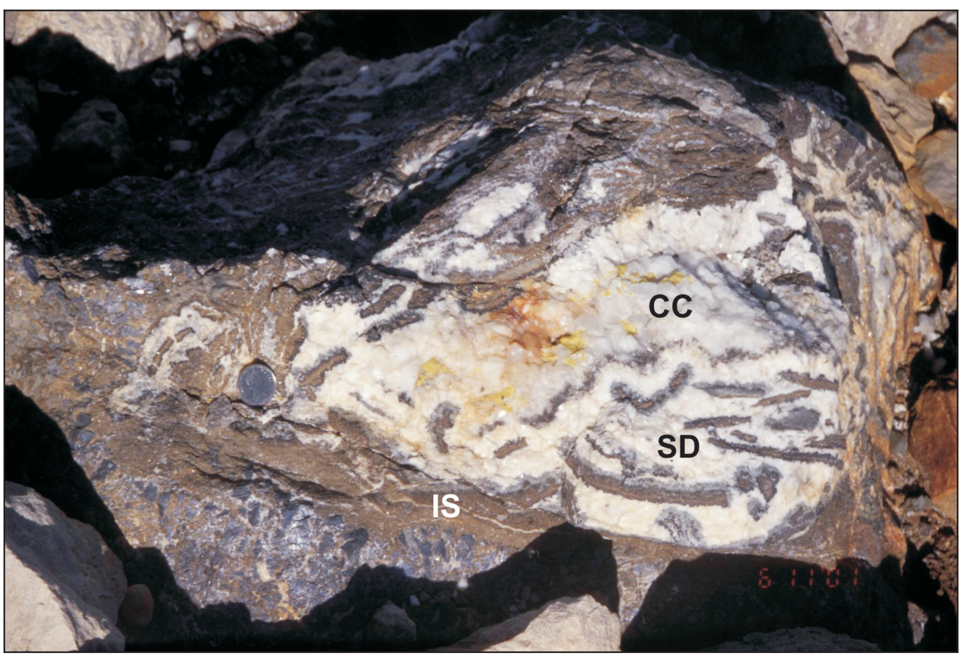

Figure 6. Ore from the Pine Point mine. Collapse breccia containing open-space filling white sparry dolomite (SD) surrounding broken angular fragments of dolomitic internal sediment impregnated by fine-grained dark brown sphalerite. Late white and coarse calcite (CC) with associated native sulphur fill the core of the former cavity. Fine-grained dark brown sphalerite replaces a laminated sandy interval on the floor (?) of the cavity. The internal sediment layer (IS) is underlain by coarse-crystalline matrix dolomite containing abundant fine- to coarse-crystalline galena (GSCC photo number 4784-2).

disseminations also occur in the Pine Point district. Much of the sulphide occurs as very fine-grained laminated aggregates of botryoidal or colloform sphalerite commonly intergrown with dendritic or skeletal galena (Leach and Sangster, 1993).

Alteration mineralogy and chemistry

The MVT deposits in the Pine Point district feature such diagenetic processes as dolomitization, recrystallization, dissolution and hydrothermal brecciation.

Dolomitization and recrystallization

At Pine Point, dolostone is differentiated into three main dolomite types: fine- to medium-crystalline matrix or replacement dolomite, coarse-crystalline matrix dolomite (Presqu'ile) and coarse-crystalline white dolospar (saddle dolomite) (Skall, 1975; Kyle, 1981; Krebs and Macqueen, 1984; Rhodes et al., 1984).

Much of the lower carbonate succession in the Presqu'ile barrier has been recrystallized to a fine- to medium-crystalline matrix dolomite on a property-wide basis (Krebs and Macqueen, 1984). Sedimentary structures and fossils are recognizable, although fossils have been leached forming moldic porosity. The dolostone consists of a very uniform mosaic of fine-grained dolomite crystals.

As discussed above, much of the coarse-crystalline Presqu'ile dolomite is contained largely in the Sulphur Point Formation and locally in part of the Upper Keg River Member. It rarely occurs above the disconformity into overlying Watt Mountain and Slave Point formations (Krebs and Macqueen, 1984). In contrast to the fine-crystalline dolomite, the original fabrics of the precursor carbonate are destroyed or occur as relicts (Krebs and Macqueen, 1984). The vuggy habit is characteristic of this dolomite and vugs range in size from several millimetres to a few centimetres, and locally up to metre-sized cavities. The vugs are filled or partly lined with white dolomite, calcite, sulphides, bitumen and/or native sulphur: these vug-fills are clearly post-Presqu'ile dolomite accumulations. Isolated remnants of limestone are preserved in the upper barrier complex of the Sulphur Point Formation within coarse-crystalline dolomite, contrasting from the underlying pervasive fine-crystalline dolostone succession. The contacts between coarse-crystalline dolomite and limestone remnants are sharp, irregular and transect bedding (Kyle, 1981). The main areal distribution of Presqu'ile dolomite on the Pine Point property follows the North and Main hinges where they also reach their maximum thickness.

The third dolomite type present at Pine Point is the white 'vein' dolosparite or saddle dolomite cements occurring in association with infilled solution cavities and ore. This dolomite type also occurs as white specks or crystals developed as a mottled pattern in the Presqu'ile dolomite. The dolomite is widespread, coarse-crystalline and possesses curved crystal faces and cleavage. Under cross-polarized light, it exhibits sweeping extinction and contains abundant inclusions. The saddle dolomite has complex age relationships with ore, varying from pre-ore, syn-ore to post-ore (Krebs and Macqueen, 1984). Regardless of the age relationships of the dolomite, the fluid inclusion filling temperatures of the dolomite suggest a 'hydrothermal' origin. Hot ascending solutions, possibly derived from deeply-buried Precambrian faults, heated the groundwater in these open fractures and voids and precipitated these dolomite cements (Krebs and Macqueen, 1984).

A discussion of the genesis of these various dolomite types are presented in the Introduction paper by Hannigan (2006).

Dissolution and brecciation

Internal karstification and collapse occurred during pre-ore dissolution and during the main ore-mineralization stage. It is impossible to differentiate the magnitude of dissolution that occurred in each stage. During pre-ore dissolution, undolomitized remnants of limestone were dissolved between the dolomitized fractures and fragment margins (Krebs and Macqueen, 1984). This dissolution process resulted in the development of cellular carbonate containing voids of different shapes and sizes separated by thin walls of fine-grained dolomite. The resultant breccia-moldic porosity formed both boxwork and zebra dolomite at Pine Point (Dunsmore, 1973). Internal sediments were deposited at the bottom of voids during this pre-ore dissolution stage.

The enigmatic zebra dolomite that is often intimately associated with MVT mineralization is not necessarily a dissolution phenomenon. Wallace et al. (1994) proposed that zebra textures were formed as a consequence of fracturing and sheet cavity development of unaltered carbonate with, in some cases, solution of cavity margins, followed by replacement by diagenetic dolomite and penecontemporaneous cementation. Nielsen et al. (1998) observed clear, inclusion-poor saddle dolomite cements interlayered with white, inclusion-rich and dark to black replacement dolomite and invoked the formation of zebra dolomite and MVT mineralization by an overpressured fluid system.

During the main ore-mineralization stage, further solution processes enlarged older dissolution macropores and created new collapse structures, thus preparing the brecciated host rock for subsequent sulphide mineralization and internal sediment filling (Krebs and Macqueen, 1984). Boundaries between massive orebodies and barren dolomite are generally sharp and distinct (Skall, 1975; Kyle, 1977, 1981). In the peripheral zones of larger collapse centres, well-developed fractures and veins occur parallel and oblique to bedding planes, indicating an increase of brecciation intensity as the mineralized zone is approached (Krebs and Macqueen, 1984). These fractures and veins are lined with white, coarse-crystalline saddle dolomite. The veins and fractures commonly form a halo around central mineralized collapse zones. Similarly, calcite flooding produced halos around many orebodies at Pine Point, giving the carbonate host rocks within these halos a coarsely granular appearance. Interior to these calcite flooding zones, very fine calcite and coarse-crystalline white sparry dolomite veins and vug-fillers are present.

Other alteration features

Soft sticky bitumen masses, commonly with associated heavy oil, and altered solid splintery bitumens with conchoidal fracture commonly occur in the Pine Point district. The heavy oil fills remnant voids and vugs in Presqu'ile dolomite. Many levels of the barrier complex show an intense impregnation by bitumen where small pores have been filled by droplets (Krebs and Macqueen, 1984). Near some orebodies, hydrocarbons have been altered to splintery pyrobitumen forming irregular concentrations in large vugs and glossy globules as well as thin coatings on carbonate crystals (Macqueen and Powell, 1983; Powell and Macqueen, 1984). Fluid inclusion studies of dolomite and sphalerite in the district reveal a population of inclusions filled with petroleum (N. Wilson, *pers. comm.,* 2004).

Lithogeochemical patterns have been mapped in the Pine Point district (Turner et al., 2002). One such pattern depicts the combined densities of the major metallic elements generally associated with MVT deposits; that is, iron, lead and zinc. At Pine Point, Fe-Pb-Zn anomalous zones display pronounced concentric distributions around orebodies in the Upper Keg River Member and Sulphur Point Formation. The geochemical patterns and anomalous zones are represented by density contours of various elements dependent on the number and threshold of anomalous samples. They are not dependent on the absolute concentration of an element in a given sample. The anomalous zones decrease gradationally from maximum density, coincident with high-grade prismatic cores to barren country rocks. The anomalies are widespread in Upper Keg River and Sulphur Point units, negligible in Watt Mountain Formation, and are confined to major collapse solution features in the Slave Point Formation. Also, on the Main trend, Fe-dispersion highs tend to be displaced north of the deposits. At the deposit scale, Fe is most widely distributed, Zn is intermediate and Pb occurs near the centre of the orebodies. Sr distribution is very irregular, but spatially overlaps the deposits (Turner et al., 2002).

Silicification is characteristic of MVT deposits in the classical Tri-State district and northern Arkansas district of south-central United States (Leach and Sangster, 1993) but was not observed in the Pine Point district.

PARAGENESIS

A detailed paragenetic sequence in the Pine Point district and along the Presqu'ile barrier was difficult to surmise because of the highly variable areal distribution and scale of diagenetic events. Despite these difficulties, Krebs and Macqueen (1984) established a comprehensive paragenetic sequence for the Pine Point mineral property and Qing (1991) refined and presented a generalized paragenesis for the entire Presqu'ile barrier (Fig. 7).

The diagenetic features that occur in carbonate rocks along the Presqu'ile barrier developed in three depositional environments: submarine, subaerial, and subsurface or burial. Submarine features include micrite envelopes, micrite, syntaxial cement, fibrous cement, and fine-crystalline to medium-crystalline dolomite (Qing, 1991, 1998). Subaerial diagenesis includes the precipitation of minor local pendant cements, as well as dissolution and brecciation. Submarine and subaerial diagenetic events precede the main sulphide or ore mineralization stage. The most significant diagenetic alteration within the barrier complex was brought about by large-scale dissolution, due to the invasion of hydrothermal fluids into the subsurface subsequent to burial (Krebs and Macqueen, 1984; Qing, 1991; Qing and Mountjoy, 1992, 1994a, b). Subsurface diagenesis occurring during the ore and post-ore stage intervals produced blocky sparry calcite cement, compaction and stylolitization features, coarse-crystalline and saddle dolomite, sulphide mineralization, late-stage calcite, fluorite, anhydrite, native sulphur, and bitumen (Fig. 7).

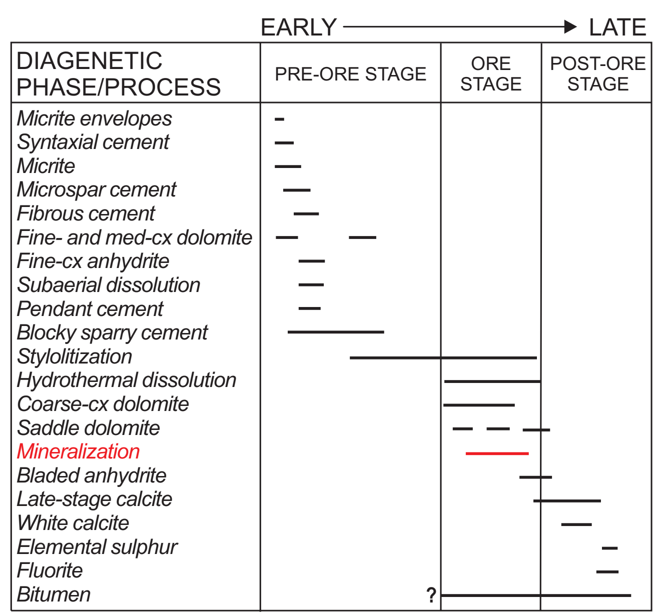

Figure 7. Paragenetic sequence at Pine Point. Pre-ore, ore, and post-ore stage diagenetic phases and processes are depicted. *Adapted from* Krebs and Macqueen (1984) and Qing (1991). Abbreviation: cx = crystalline.

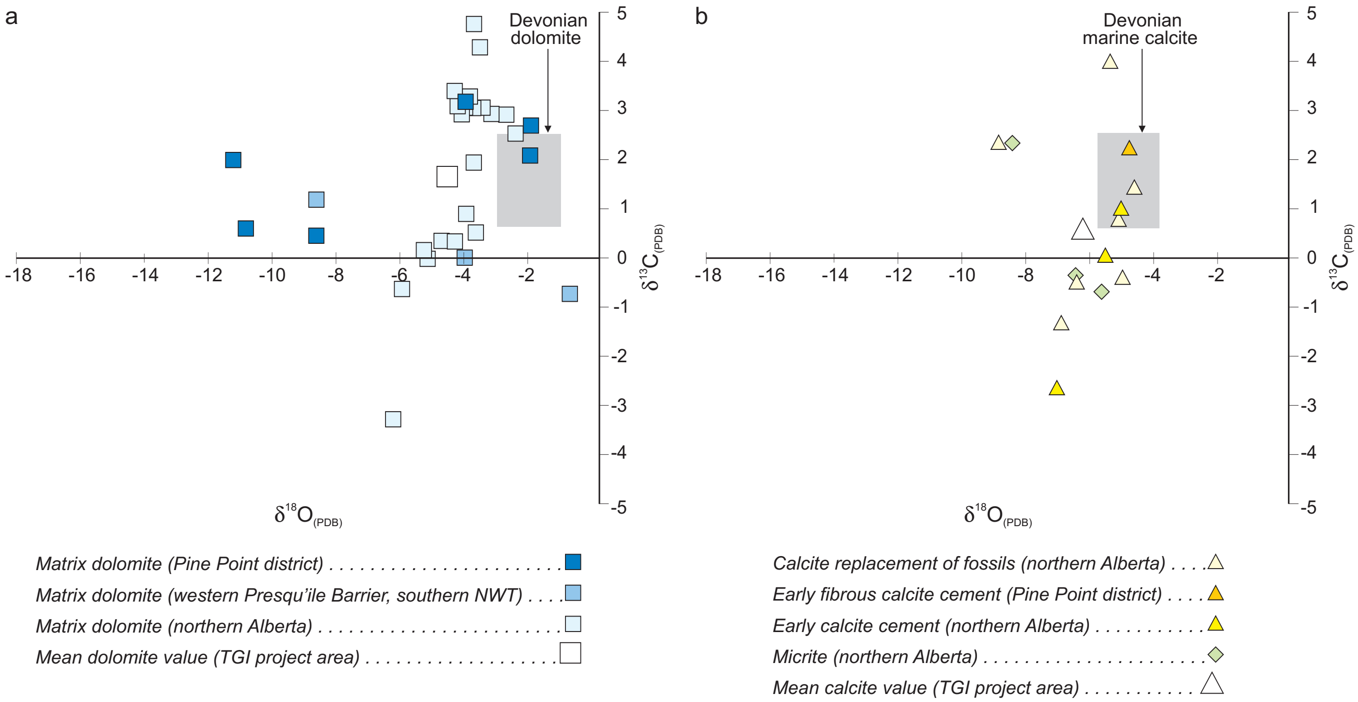

Figure 8. $\delta^{13}C_{PDB}$ versus $\delta^{18}O_{PDB}$ cross plots for pre-ore carbonate phases in the project area. a. Isotope data of fine- to medium-crystalline matrix dolomite clearly predating mineralization. b. Isotope data of calcitic fossils, early calcite cements, and limestone or micrite. Samples from Pine Point district, western Presqu'ile barrier and northern Alberta are depicted. Hypothetical Devonian marine calcite and dolomite fields are *from* Knauth and Roberts (1991) and Hurley and Lohmann (1989), respectively. Mean dolomite and calcite values show minor depleted oxygen and comparable carbon isotopic values to hypothetical Devonian marine dolomite and calcite fields. Data *from* Rice and Lonnee (2006) and Coniglio et al. (2006).

PRE-ORE CONDITIONS

Dissolution

Prior to the sulphide mineralization stage at Pine Point, porosity and permeability were enhanced in the hinge areas by a combination of Presqu'ile dolomitization and pre-ore dissolution. Dissolution of undolomitized limestone remnants took place between dolomitized fissures, fractures and fragment margins (Krebs and Macqueen, 1984). Interconnecting voids of various shapes and sizes developed, enhancing both the porosity and permeability in the region. The presence of boxwork dolomite and internal sediment at the bottom of cavities clearly indicates that openings formed by dissolution were present prior to the ore stage (Dunsmore, 1973; Krebs and Macqueen, 1984). Kyle (1981) speculated that horizons of increased porosity and permeability were created adjacent to zones of increased dissolution such as macropores or caves. The macropores were formed by extensive solution of limestone in the phreatic zone by meteoric water flow rather than seepage through a bypass from the overlying vadose zone. The meteoric water was not saturated with calcite, thus permitting dissolution.

Once meteoric water became saturated with calcite, porosity enlargement ceased. This may account for the limited lateral extent of these horizons in the lower Presqu'ile barrier (Kyle, 1981). These enhanced porous and permeable zones that were formed in the pre-ore stage, were subsequently occluded by saddle dolomite, sulphide minerals, calcite, bitumen, or native sulphur. Most of the smaller, millimetre-sized vugs also occurring in the Presqu'ile dolomite were likely formed by the dolomitization process rather than by dissolution (Krebs and Macqueen, 1984).

Stable isotopes

Conditions prior to sulphide mineralization in the TGI project area are recorded by fine- to medium-crystalline dolomite, fine-grained micrites, and early calcite cement phases. Figure 8 and Table 2 summarize the stable isotopic signatures obtained from collected samples throughout the project area. The isotopic signatures are differentiated on the basis of carbonate phase (dolomite, micrite, calcite replacement of fossils, or calcite cement) and location (Pine Point district, western Presqu'ile barrier in southern Northwest Territories, and northern Alberta).

In the Pine Point district (area encompassed by Fig. 2), the stable isotopes ^{18}O and ^{13}C of unaltered fine- to medium-crystalline matrix or replacement dolomite are similar to, or slightly to moderately depleted with respect to, hypothetical

Contents

Table 2. Geochemical characteristics of carbonates in project area

Carbonate type	Location	Formation(s)	Stable Isotopes (PDB) (‰)							Radiogenic Isotopes			
			n	$\delta^{18}O$ (range)	$\delta^{18}O$ (mean)	$\delta^{18}O$ (s.d.)	$\delta^{13}C$ (range)	$\delta^{13}C$ (mean)	$\delta^{13}C$ (s.d.)	n	$^{87}Sr/^{86}Sr$ (range)	$^{87}Sr/^{86}Sr$ (mean)	$^{87}Sr/^{86}Sr$ (s.d.)
A. Pre-ore carbonate													
Fine- to medium-crystalline matrix dolomite	Pine Point district	Upper Keg River/ Slave Point	6	-11.2 to -1.9	-6.43	4.29	0.5 to 3.2	1.85	1.1	3	0.70846–0.70932	0.70877	0.000485
Fine- to medium-crystalline matrix dolomite	Western Presqu'ile barrier	Keg River	3	-8.6 to -0.8	-4.47	3.92	-0.7 to +1.2	0.17	0.96	2	0.70836–0.70890	0.70863	0.000382
Fine- to medium-crystalline matrix dolomite	Northern Alberta	Grosmont/Mikkwa/ Jean Marie/Keg River	22	-6.1 to -2.4	-4.11	0.93	-3.1 to +4.8	1.95	1.88	21	0.70795–0.71025	0.70841	0.000623
Calcite replacement of fossils	Northern Alberta	Grosmont/Mikkwa	7	-8.8 to -4.7	-6.04	1.45	-1.3 to +4.0	0.91	1.85	5	0.70807–0.70835	0.70819	0.000129
Fibrous calcite cement	Pine Point district	Sulphur Point	1	-4.9	-4.9	0	2.2	2.2	0				
Early calcite cement	Northern Alberta	Grosmont/Mikkwa	3	-7.1 to -5.1	-5.93	1.04	-2.7 to +0.9	-0.6	1.87	2	0.70807–0.70811	0.70809	0.000028
Micrite	Northern Alberta	Mikkwa	3	-8.4 to -5.6	-6.8	1.44	-0.7 to +2.4	0.43	1.71	3	0.70831–0.70862	0.70847	0.000155
B. Ore-stage carbonate													
Coarse-crystalline matrix dolomite	Pine Point district	Upper Keg River/ Sulphur Point/Slave Point/Muskeg/ Watt Mtn	33	-12.7 to -7.0	-10.28	1.39	-0.9 to +2.6	0.71	1.03	14	0.70816–0.70852	0.70832	0.000096
Saddle dolomite	Pine Point district	Keg River/Sulphur Point/ Slave Point/ Muskeg	38	-13.0 to -7.2	-10.26	1.39	-2.44 to +11.8	0.98	2.06	21	0.70813–0.71045	0.70847	0.000545
Coarse-crystalline matrix dolomite	Western Presqu'ile barrier	Keg River/Slave Point	3	-13.2 to -7.3	-10.83	3.12	0.7 to 1.9	1.47	0.67	2	0.70892–0.71119	0.71006	0.001606
Saddle dolomite	Western Presqu'ile barrier	Keg River/Sulphur Point/Slave Point	4	-11.2 to -8.7	-10.1	1.04	-0.9 to +0.7	-0.03	0.72	2	0.70855–0.70909	0.70882	0.00038
Coarse-crystalline matrix dolomite	Great Slave Shear Zone	Keg River	4	-8.88 to -8.19	-8.56	0.29	1.64 to 2.59	2	0.45	3	0.70874–0.70977	0.70936	0.000548
Coarse-crystalline matrix dolomite	Northern Alberta	Mikkwa	1	-4.3	-4.3	0	3.4	3.4	0	1	0.70818	0.70818	0
Saddle dolomite	Northern Alberta	Keg River/Methy/ Grosmont	3	-6.4 to -4.2	-4.97	1.24	-1.7 to +2.6	0.6	2.17	1	0.70843	0.70843	0
Late-stage calcite cements	Pine Point district	Upper Keg River/ Sulphur Point/ Slave Point	8	-15.3 to -4.9	-8.79	3.14	-17.4 to +3.0	-5.18	5.91	2	0.71337–0.71551	0.71444	0.001513
Late-stage calcite cements	Northern Alberta	Keg River/Methy/ Slave Point/Grosmont/ Mikkwa/Jean Marie	10	-15.1 to -5.9	-12.99	2.64	-24.2 to +3.8	-9.88	9.73	9	0.70813–0.70901	0.70847	0.000263

Data derived from Coniglio et al. (2006); Paradis et al. (2006); Rice and Lonnee (2006).
s.d. = standard deviation

Devonian marine dolomite (Devonian dolomite box in Fig. 8a; Coniglio et al., 2006). Similar relationships were observed in previous studies (Qing, 1991, 1998). A single early fibrous calcite cement was sampled at Pine Point. Its stable isotope values are -4.9 and +2.2 per mil for $\delta^{18}O_{PDB}$ and $\delta^{13}C_{PDB}$, respectively (Table 2; Coniglio et al., 2006). This result is located within the Middle Devonian calcite field (Fig. 8B).

In northern Alberta and southern Northwest Territories, fine-crystalline to medium-crystalline matrix dolomite, early calcite cement and precursor micritic limestone show similar relationships (Fig. 8; Coniglio et al., 2006; Rice and Lonnee, 2006). West of Pine Point district on the Presqu'ile barrier in southern Northwest Territories, pre-ore carbonate phases were collected and sampled. The fine-crystalline to medium-crystalline matrix dolomite show mean stable isotopes of -4.47 per mil $\delta^{18}O_{PDB}$ and +0.17 per mil $\delta^{13}C_{PDB}$ (Table 2; Coniglio, et al., 2006) which are significantly depleted with respect to the hypothetical Devonian dolomite field (Fig. 8a).

Stable isotopic mean values of Middle Devonian Sulphur Point dolomicrite, and fine- to medium-crystalline matrix dolomite from the Rainbow oil and gas field in northwestern Alberta, adjacent to the Great Slave Shear Zone, are -9.97 per mil $\delta^{18}O_{PDB}$ and -0.08 per mil $\delta^{13}C_{PDB}$ (Lonnee and Al-Aasm, 2000). Their most enriched oxygen value plots near the hypothetical Devonian dolomite field but most values are significantly depleted with respect to hypothetical dolomite. Lonnee and Al-Aasm (2000) interpret that Sulphur Point matrix dolomite and dolomicrite at Rainbow are significantly recrystallized and the reset stable isotopes do not represent original dolomite geochemistry. Samples of early fine-crystalline matrix dolomite of the Keg River Formation were also examined at Rainbow (Qing, 1986; Qing and Mountjoy, 1989). Intermediate depletion of oxygen (mean, -7.65‰ $\delta^{18}O_{PDB}$) and enrichment of carbon (mean, +1.97‰ $\delta^{13}C_{PDB}$) were observed in these rocks. Submarine fibrous calcite cement in the Keg River Formation at Rainbow have stable isotope values near the Devonian marine calcite field (Qing, 1986).

Similar pre-ore conditions with respect to ^{18}O stable isotopes were recorded in early micrite, dolomite and calcite phases collected elsewhere in northern Alberta; that is, in areas distant from underlying basement shear zones and carbonate barrier complexes (Theriault and Hutcheon, 1987; Rice and Lonnee, 2006). Isotope values of ^{13}C show greater variance compared to samples along the Presqu'ile barrier and the hypothetical Devonian marine calcite field (Fig. 8b, Table 2).

The regional mean values for stable isotopes in all unaltered pre-ore dolomite throughout the entire project area are -4.59 per mil $\delta^{18}O_{PDB}$ and +1.76 per mil $\delta^{13}C_{PDB}$ (n=31; Fig. 8a). Generally, dolomites are oxygen-depleted but are similar in carbon isotopic values to hypothetical marine Middle Devonian dolomite. Among early calcite phases occurring as fossil replacements, early submarine cements, or micrites, the stable isotopes range from -8.8 to -4.7 per mil $\delta^{18}O_{PDB}$ and -2.7 to +4.0 per mil $\delta^{13}C_{PDB}$ (n=14; Fig. 8b). Calcite fossil fragments, early cements and micrites are slightly oxygen- and carbon-depleted with respect to Devonian marine calcite.

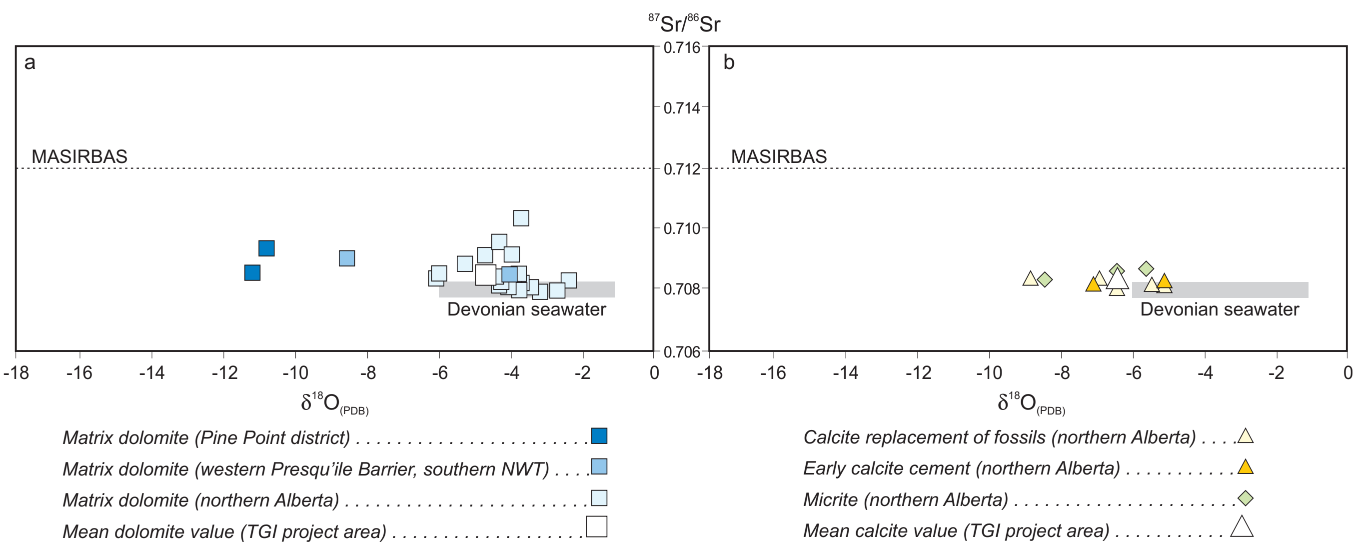

Figure 9. $^{87}Sr/^{86}Sr$ versus $\delta^{18}O_{PDB}$ cross plots for pre-ore carbonate phases in the project area. **a.** Isotope data of fine- to medium-crystalline matrix dolomite clearly predating mineralization. **b.** Isotope data of calcitic fossils, early calcite cements, and limestone or micrite. Samples from Pine Point district, western Presqu'ile barrier and northern Alberta are shown. Middle Devonian seawater values are *from* Veizer et al. (1999). Maximum Sr isotope ratio of basinal shale (MASIRBAS) is *from* Machel and Cavell (1999). Data *from* Rice and Lonnee (2006) and Coniglio et al. (2006).

Radiogenic isotopes

Radiogenic strontium isotopes (^{87}Sr) of pre-ore carbonate phases generally do not depart greatly from Devonian seawater and all plot below the strontium ratio ($^{87}Sr/^{86}Sr$) of 0.7120 that defines the regional background of the "Maximum Strontium Isotope Ratio of Basinal Shale" (MASIRBAS; Machel and Cavell, 1999; Fig. 9; Table 2). In the Pine Point district, matrix dolomite samples have a mean $^{87}Sr/^{86}Sr$ of 0.70877 (Table 2; Fig. 9a). Qing (1998) reported a general increase of $^{87}Sr/^{86}Sr$ according to crystal size (mean fine-crystalline ratio, 0.70797; mean medium-crystalline ratio, 0.70843). Coniglio et al. (2006), however, did not observe this trend. In fact, their work revealed an opposite trend of strontium ratios according to crystal size (mean fine-crystalline ratio, 0.708917; mean medium-crystalline ratio, 0.70846). In southern Northwest Territories within Presqu'ile barrier west of the Pine Point district, strontium ratios are similar to ratios from the Pine Point district (Table 2). In northern Alberta at Rainbow field, pre-ore matrix dolomite of the Sulphur Point Formation reveals a mean $^{87}Sr/^{86}Sr$ value of 0.70882, similar to Pine Point dolomite (Lonnee and Al-Aasm, 2000). Samples collected in northern Alberta from the Grosmont, Mikkwa, Jean Marie, and Keg River formations show $^{87}Sr/^{86}Sr$ values in fine- to medium-crystalline matrix dolomite ranging from 0.70795 to 0.71025 (Rice and Lonnee, 2006; Fig. 9a). These results contrast moderately with values from the Pine Point district in that there is a greater variance of radiogenic strontium in northern Alberta and fine-crystalline dolomite is slightly more radiogenic than medium-crystalline dolomite.

Micrites and early calcite phases (cements and calcitic fossils) show $^{87}Sr/^{86}Sr$ similar to matrix dolomite at Pine Point and in northern Alberta (Fig. 9b; Table 2). Rice and Lonnee's (2006) micrite and early-stage calcite sampling program in northern Alberta demonstrates slightly more radiogenic strontium than Devonian seawater (Fig. 9b). At Rainbow, strontium ratios of micrites and early calcite cements are slightly less radiogenic than matrix dolomite (Lonnee and Al-Aasm, 2000).

Over the entire project area, the regional mean strontium value for unaltered dolomite is 0.70847 (Fig. 9a). Similarly, $^{87}Sr/^{86}Sr$ of micrites, calcitic fossils and early calcite cements across the complete project area have a mean value of 0.70826 (Fig. 9b). These regional ratios are similar to or slightly more radiogenic than the Middle Devonian seawater signature.

Fluid inclusions

Aqueous fluid inclusion assemblage homogenization temperatures (Th) of pre-ore dolomite in the Pine Point district range from 97 to 104°C (Fig. 10; Table 3; Turner, 2006). Most of these inclusions are primary two-phase liquid-vapour hypersaline-type with occasional monophase liquid inclusions. Petroleum fluid inclusions were also observed at Pine Point and they homogenized at temperatures between 108 and 135°C (Fig. 10b; Table 3; Hannigan, 2005b). No final ice-melting temperatures were measured in the petroleum inclusion assemblages. Individual petroleum inclusions show distinctive fluorescence characteristics dependent on thermal maturities of the oils: green fluorescent inclusions homogenized between 110 and 120°C and orange fluorescent inclusions homogenized between 85 and 115°C (N. Wilson, *pers. comm.*). In northern Alberta at Rainbow, aqueous inclusions in recrystallized fine- to medium-crystalline matrix dolomite of the Sulphur Point Formation show a similar range of Th as those of the Pine Point district (90 to 113°C; Lonnee and Al-Aasm, 2000). Lonnee and Al-Aasm (2000) also observed that medium-crystalline dolomite generally had higher Th's than fine-crystalline dolomite. At the Oak gas field in northern Alberta, a fine-crystalline dolomite aqueous fluid inclusion assemblage from the Upper Devonian Wabamun Formation exhibits significantly greater Th, averaging near 130°C (Fig. 10a; Table 3; Hannigan, 2005b) indicating higher precipitation temperatures.

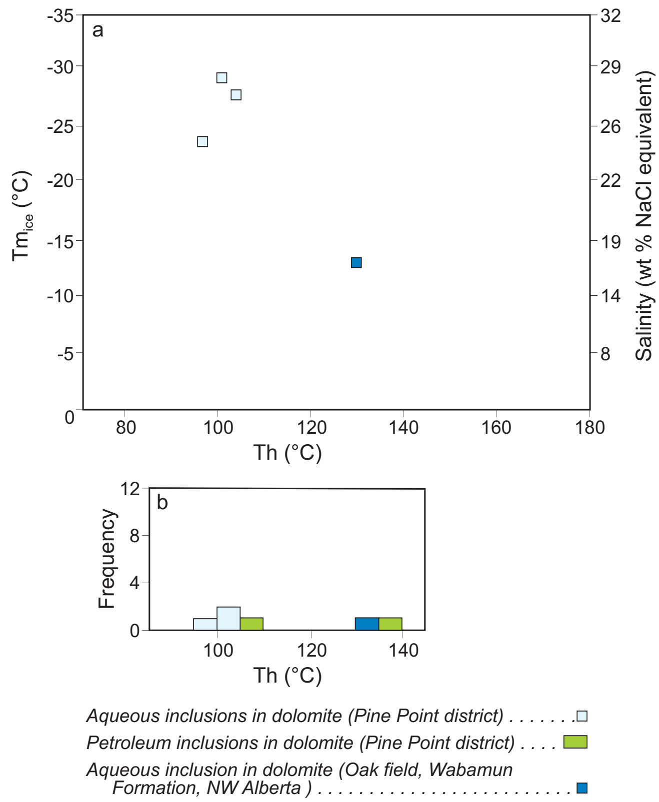

Figure 10. Fluid inclusion microthermometric data for pre-ore carbonate phases in the project area. **a.** Cross plot of homogenization temperatures (Th) versus final melting temperatures (Tm_{ice}) with equivalent salinities of primary aqueous fluid inclusion assemblages in matrix dolomite. Samples from Pine Point district and northern Alberta. **b.** Histogram distribution of homogenization temperatures (Th) of primary aqueous and petroleum fluid inclusion assemblages in pre-ore matrix dolomite. Data *from* Turner (2006), Coniglio et al. (2006), and Paradis et al. (2006).

Table 3. Thermal characteristics of carbonates and sulphides in project area (fluid inclusion assemblages)

Mineral phase	Location	Formation(s)	Microthermometry (aqueous) n	Microthermometry (aqueous) T_h (°C)	Microthermometry (aqueous) T_m (°C)	Salinity (wt% NaCl-equiv)	Microthermometry (petroleum) n	Microthermometry (petroleum) T_h (°C)
A. Pre-ore carbonate								
Fine- to medium-crystalline matrix dolomite	Pine Point district	Upper Keg River/ Muskeg/ Slave Point	3	97.0 to 104.0	-23.7 to -29.1	25 to 29	2	108.0 to 135.0
Fine- to medium-crystalline matrix dolomite	Northern Alberta	Keg River/Methy	1	130.9	-13	17		
B. Ore-stage and post-ore mineral phases								
Sphalerite	Pine Point district	Upper Keg River/ Sulphur Point/ Slave Point	9	60.0 to 108.0	-22.2 to -33.0	23 to 30		
Coarse-crystalline matrix dolomite	Pine Point district	Upper Keg River/ Sulphur Point/ Slave Point	6	95.5 to 126.0	-13.6 to -32.5	18 to 31		
Saddle dolomite	Pine Point district	Keg River/ Sulphur Point/ Slave Point/ Muskeg	13	86.0 to 112.5	-18.5 to -30.6	21 to 30	1	100.0 to 110.0
Saddle dolomite	Western Presqu'ile barrier	Upper Keg River	1	109			1	120.0 to 125.0
Sphalerite	Great Slave Shear Zone	Keg River	1	116				
Saddle dolomite	Northern Alberta	Grosmont	1	124.4				
Late-stage calcite cements	Pine Point district	Upper Keg River/ Sulphur Point/ Slave Point	14	62.0 to 109.0	-0.7 to -11.2	1 to 16		
Late-stage calcite cements	Western Presqu'ile barrier	Upper Keg River	1	101	-9.6	13		

T_h: Homogenization temperatures
T_m: Final ice-melting temperatures
Data derived from Turner (2006); Coniglio et al. (2006); Paradis et al. (2006); and N. Wilson (pers. comm.).

Final ice-melting temperatures (Tm_{ice}) of aqueous fluid inclusion assemblages in pre-ore dolomite at Pine Point range from -23.7 to -29.1°C (Fig. 10a; Table 3; Turner, 2006). This range corresponds to salinities of 25 to 29 weight per cent NaCl equivalent. Salinity, on the other hand, is much reduced in pre-ore dolomite in northern Alberta, where it is 17 weight per cent NaCl equivalent at Oak gas field (Fig. 10a; Hannigan, 2005b). Eutectic temperatures at Oak range between -45 and -50°C, indicating a dominant brine composition of $CaCl_2$-H_2O (Hannigan, 2005b).

Nature of pre-ore dolomitizing fluid

The isotopic and fluid inclusion data at Pine Point and throughout the project area collectively suggest that fine-crystalline and medium-crystalline dolomite formed penecontemporaneously from Middle Devonian seawater at or just below the seafloor, before lithification of the evaporite deposits. Qing (1998) observed that oxygen isotopes in the Pine Point district are more depleted, and strontium isotopes slightly more radiogenic than Middle Devonian seawater in medium-crystalline dolomite. This observation suggests neomorphic alteration by later hydrothermal fluids at somewhat elevated temperatures in the subsurface (Qing, 1998). Fluid inclusion analyses of pre-ore medium-crystalline matrix dolomite at Pine Point revealed elevated homogenization temperatures and two-phase inclusions, pointing to a dolomitization event in the subsurface.

Further afield in northern Alberta, similar relationships were observed among early, fine-crystalline dolomite and later, medium-crystalline matrix dolomite. Heaviest $\delta^{18}O_{PDB}$ values are associated with the earliest dolomite phase, usually occurring within the Devonian dolomite seawater field indicating precipitation from seawater or evaporitic seawater at very shallow depths. Depletion of oxygen isotopes associated with an increase in crystal size indicate elevated crystallization temperatures likely caused by burial diagenesis or by recrystallization. Therefore, prior to ore precipitation, dolomitizing waters were more saline, slightly more radiogenic and at higher temperatures than marine waters, all indicative of a burial setting (Allan and Wiggins, 1993).

ORE-STAGE CONDITIONS

The evolution from pre-ore to ore-stage conditions at Pine Point is marked by a transition from pre-ore fine- to medium-crystalline matrix dolomite and early calcite cements, to ore-stage, coarse-crystalline, Presqu'ile matrix vuggy dolomite and associated saddle dolomite. This shift in dolomite type is associated with significant changes in isotopic and thermal characteristics of the host rock.

Stable isotopes

Oxygen isotopes of coarse-crystalline matrix vuggy dolomite are more depleted than isotopes measured in pre-ore matrix dolomite in the Pine Point district (Qing, 1991; Coniglio et al., 2006; Paradis et al., 2006; Fig. 11a; Table 2). Carbon isotope levels are similar to or slightly enriched compared to pre-ore dolomite. Presqu'ile matrix dolomite samples collected within or adjacent to orebodies on the Pine Point and Great Slave Reef properties are slightly enriched in oxygen isotopic signatures compared to other coarse-crystalline matrix dolomite in the district (mean, -9.08‰; Fig. 11a).

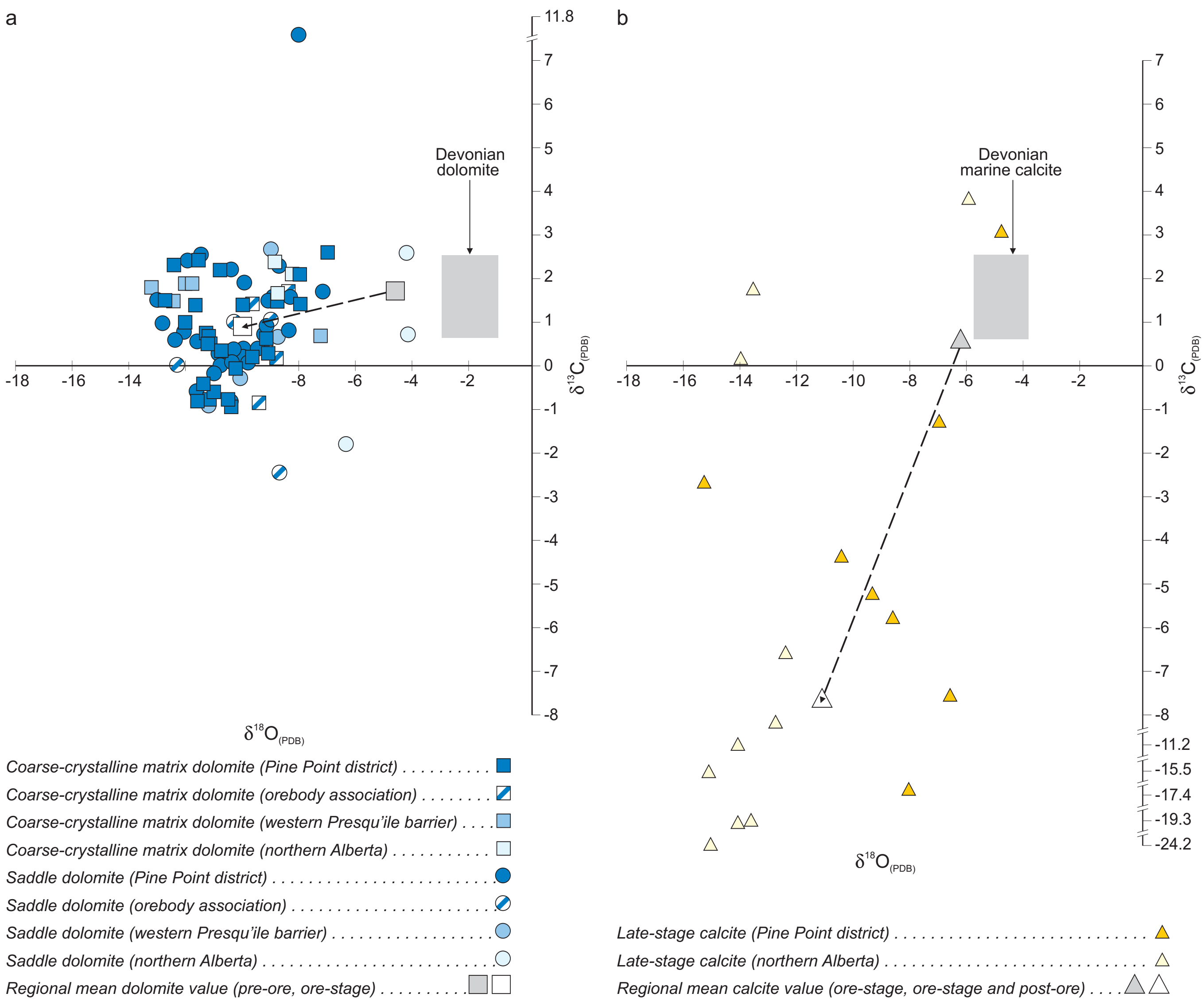

Figure 11. $\delta^{13}C_{PDB}$ versus $\delta^{18}O_{PDB}$ cross plots for ore-stage dolomite and ore-stage and post-ore calcite phases in the project area. **a.** Isotope data of coarse-crystalline matrix dolomite and saddle dolomite associated with mineralization event. **b.** Isotope data of late-stage calcite cements. Samples from Pine Point district, western Presqu'ile barrier and northern Alberta are shown. Mineralized dolomite samples are distinguished by blue slash. Hypothetical Devonian marine calcite and dolomite fields are *from* Knauth and Roberts (1991) and Hurley and Lohmann (1989), respectively. Ore-stage dolomite values show depleted oxygen-18 with respect to pre-ore matrix dolomite phases. Ore-stage and post-ore calcite values are depleted in both oxygen and carbon isotopes with respect to pre-ore calcite. Data *from* Coniglio et al. (2006), Paradis et al. (2006), and Rice and Lonnee (2006).

Carbon isotopes, however, are similar. Saddle dolomite samples at Pine Point have stable oxygen isotopic signatures similar to coarse-crystalline matrix dolomite samples (Fig. 11a, Table 2; Qing, 1991; Coniglio et al., 2006; Paradis et al., 2006). Carbon isotopes show a greater variance in saddle dolomite. Saddle dolomite samples retrieved proximally to or within orebodies give mean values of -9.91 per mil $\delta^{18}O_{PDB}$ and -0.01 per mil $\delta^{13}C_{PDB}$. These ore-related dolomites are slightly enriched in ^{18}O and depleted in ^{13}C compared to the Pine Point district average, which is -10.26 and 0.98 per mil for $\delta^{18}O_{PDB}$ and $\delta^{13}C_{PDB}$, respectively (Table 2).

Ore-stage Presqu'ile coarse-crystalline matrix and saddle dolomite, occurring in the Presqu'ile barrier at greater depth in the subsurface west of Pine Point, show depleted oxygen isotopic signatures compared to Pine Point dolomite (Table 2; Coniglio et al., 2006). Saddle dolomite samples are similar (Fig. 11a; Table 2). Both dolomite types show greater oxygen depletion than pre-ore phases in this region.

In northern Alberta, coarse-crystalline matrix dolomite and sparry dolomite show similar relationships. At Rainbow oil and gas field in northern Alberta adjacent to the Great Slave Shear Zone, Sulphur Point and Keg River sparry or saddle dolomite show depleted oxygen and carbon isotopes (Qing, 1986; Lonnee and Al-Aasm, 2000). Sulphur Point saddle dolomite at Rainbow is more depleted in ^{18}O than Keg River saddle dolomite. The isotope values are similar to Pine Point isotopic signatures. Coarse-crystalline and saddle dolomite were sampled adjacent to the Great Slave Shear Zone in the Keg River Formation at Slavey Creek between Rainbow and Pine Point (Paradis et al., 2006). The samples show isotope values ranging from -8.88 to -8.19 per mil for $\delta^{18}O_{PDB}$ and +1.64 to +2.59 per mil for $\delta^{13}C_{PDB}$ (mean, -8.56‰, and mean, +2.0‰, respectively, n=4; Table 2). The mean values show an enrichment in oxygen and carbon, although they are within the range of Pine Point ore-stage dolomite.

Sparry and coarse-crystalline dolomite in northern Alberta not directly associated with mineralization or basement shear zones are significantly enriched with respect to oxygen as compared to other similar dolomites in the project area (Table 2; Fig. 11a; Theriault and Hutcheon, 1987; Rice and Lonnee, 2006).

The mean values for ore-stage coarse-crystalline and sparry dolomite for the entire project area are -9.95 per mil $\delta^{18}O_{PDB}$ and +0.91 per mil $\delta^{13}C_{PDB}$ (n=86; Fig. 11a). The ore-stage regional mean value is depleted in oxygen isotope and slightly depleted in carbon isotope with respect to pre-ore stage dolomite (Fig. 11a).

Late-stage calcite cements were partly precipitated during the ore-stage, but these cements are also related to post-ore diagenetic events (Fig. 7). The mean value for all late-stage calcite in the entire study area is -11.12 per mil for $\delta^{18}O_{PDB}$ and -7.79 per mil for $\delta^{13}C_{PDB}$ (n=18; Table 2; Fig. 11b; Coniglio et al., 2006; Rice and Lonnee, 2006). This regional mean value is significantly depleted in both oxygen and carbon isotopes with respect to pre-ore calcite (Fig. 11b). The highly depleted ^{18}O values typify precipitation at relatively high temperatures; that is, greater than 100°C. Significant depletion of ^{13}C indicates the incorporation of oxidized organic carbon, generally attributed to the process of thermochemical sulphate reduction.

Radiogenic isotopes

Similar to pre-ore carbonate phases, $^{87}Sr/^{86}Sr$ in ore-stage dolomite generally does not depart greatly from Devonian seawater, and all dolomite samples plot below the MASIRBAS regional background level (Fig. 12a). In the Pine Point district, coarse-crystalline Presqu'ile matrix dolomite exhibits an $^{87}Sr/^{86}Sr$ ratio varying from 0.70816 to 0.70852 (Table 2; Coniglio et al., 2006; Paradis et al., 2006). The mean ratio for this dolomite is 0.70832. Saddle dolomite in the Pine Point district shows isotopic characteristics similar to coarse-crystalline matrix dolomite. The $^{87}Sr/^{86}Sr$ ratio ranges from 0.70813 to 0.71045 (Fig. 12a; Table 2; mean, 0.70847; Coniglio et al., 2006; Paradis et al., 2006). These 'late-stage' dolomite phases (except for one sample; 0.71045) do not display significant input of radiogenic strontium (>0.7100), unlike most late-stage dolomitic phases in the Western Canada Sedimentary Basin. This non-radiogenic signature at Pine Point may be caused by recycling of Devonian strontium, possibly from pressure solution of Devonian carbonate. Presqu'ile coarse-crystalline and saddle dolomite samples associated with orebodies do not display significant radiogenic strontium isotope deviation from other, nonmineralized dolomite in the Pine Point district (orebody association represented by symbols with a blue slash in Fig. 12a).

There is a general increase of radiogenic strontium in ore-stage Presqu'ile matrix and saddle dolomite in the deeper subsurface of the Presqu'ile barrier west of the Pine Point district (mean; 0.70944; Fig. 12a; Table 2). The westerly increase in radiogenic strontium content along the Presqu'ile barrier is attributed to deeply circulating dolomitizing and mineralizing fluids interacting with fine-grained siliciclastic rocks in the northern Rocky Mountains. The siliciclastic rocks are rich in radiogenic strontium contained in the alkali feldspars (Morrow et al., 1990). The reduction eastward of radiogenic strontium may be caused by a number of factors, such as dilution by less radioactive water at shallower depths in the barrier, incorporation of less radiogenic strontium from nonradioactive Devonian limestone, or mixing with fluids from a separate source (Mountjoy et al., 1992).

Strontium isotopic signatures from ore-stage dolomite proximal to major basement faults, including matrix and saddle dolomite along the Great Slave Shear Zone in northern Alberta, have a mean $^{87}Sr/^{86}Sr$ value of 0.70936, similar to the average ratio of western Presqu'ile barrier (Paradis et al., 2006). In northern Alberta, distant from major basement faults, the mean $^{87}Sr/^{86}Sr$ value of a range of ratios for ore-stage dolomite is 0.70831, classifying these ratios as distinctly nonradiogenic (Table 2).

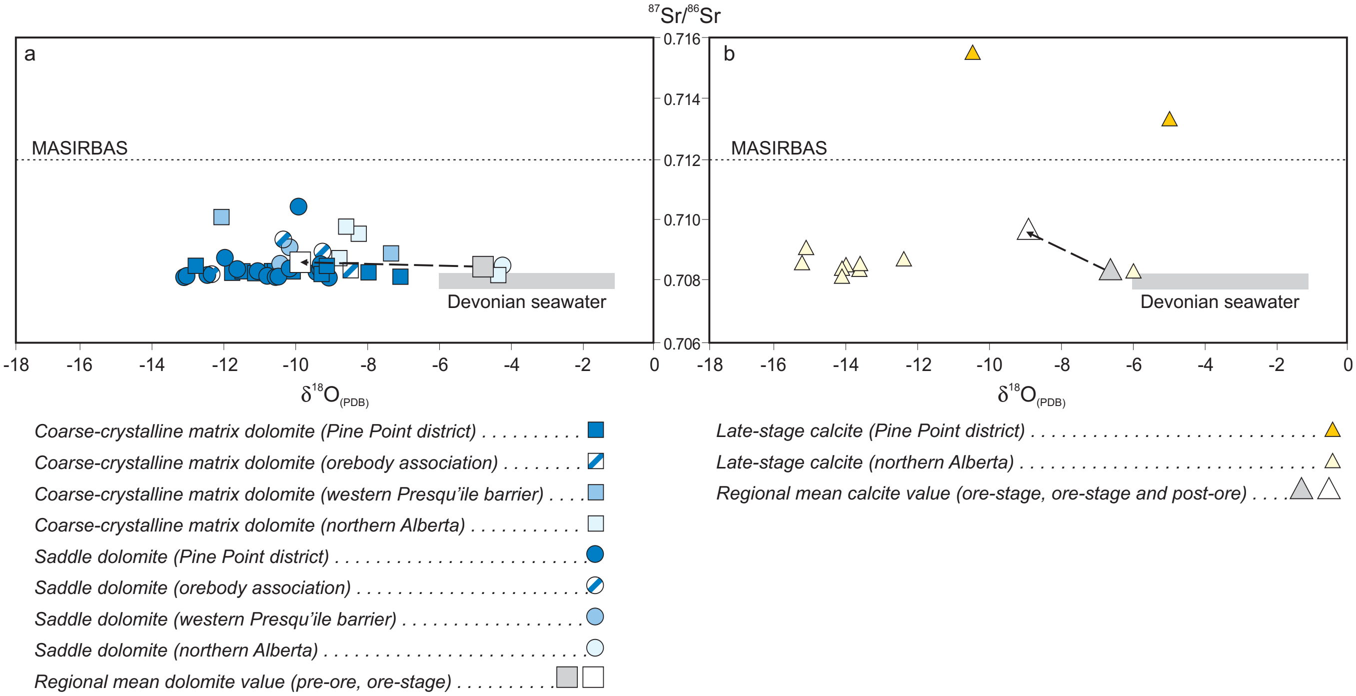

Figure 12. $^{87}Sr/^{86}Sr$ versus $\delta^{18}O_{PDB}$ cross plots for ore-stage dolomite and ore-stage and post-ore calcite phases in the project area. **a.** Isotope data of coarse-crystalline matrix dolomite and saddle dolomite clearly associated with ore-stage diagenetic events are displayed. **b.** Isotope data of late-stage calcite cements clearly associated with ore-stage or post-ore diagenetic events are displayed. Samples from Pine Point district, western Presqu'ile barrier and northern Alberta are shown. Mineralized dolomite samples are distinguished by blue slash. Middle Devonian seawater values are *from* Veizer et al. (1999). Maximum Sr isotope ratio of basinal shale (MASIRBAS) is *from* Machel and Cavell (1999). Ore-stage dolomite values show depleted oxygen-18 and similar strontium isotope values with respect to pre-ore matrix dolomite phases. Ore-stage and post-ore calcite values are depleted in oxygen-18 isotopes and are radiogenic with respect to pre-ore calcite. Data *from* Coniglio et al. (2006), Paradis et al. (2006), and Rice and Lonnee (2006).

Over the entire project area, $^{87}Sr/^{86}Sr$ isotopes of matrix and saddle dolomites vary from 0.70813 to 0.71119 (mean, 0.70856; n=44; Fig. 12a). The mean ratio for late-stage dolomite is slightly radiogenic compared to the average strontium ratio of pre-ore dolomite (0.70847).

Late-stage calcite cements have $^{87}Sr/^{86}Sr$ values ranging from 0.70813 to 0.71551 (Table 2; Coniglio et al., 2006; Rice and Lonnee, 2006). In the Pine Point district, late-stage calcite samples exhibit a mean ratio of 0.71444, considerably more radiogenic than the ore-stage dolomite phases as well as early calcite phases (Fig. 12b; Table 2). These calcites are also more radiogenic than late-stage calcite cements in northern Alberta distant from basement shear zones (mean, 0.70847). The Pine Point late-stage calcite cements represent carbonate phases formed by fluids undergoing more extensive water-rock interactions than fluids precipitating dolomite and early calcite. Mountjoy et al. (1992) observed this relationship throughout the Western Canada Sedimentary Basin and suggested that the common association of this calcite with anhydrite indicates that they were likely derived from basinal brines. However, one can argue that the highly radiogenic character of strontium in calcite and ore-stage dolomite at Pine Point and along the Great Slave Shear Zone are related and are derived from parent fluids emanating upward from radioactive basement terranes and mixing with basinal brine. McNutt et al. (1990) noted that present-day surface waters on the Canadian Shield can be highly radiogenic and these ^{87}Sr-enriched waters may have mixed with basinal brine, thereby forming the carbonate phases.

Fluid inclusions

In the Pine Point district, homogenization temperatures (Th) of primary aqueous inclusion assemblages in sphalerites vary from 60 to 108°C (Table 3; Fig. 13; Turner, 2006). These fluid inclusion filling temperatures likely represent minimum temperatures of the ore-forming solution, because the most suitable inclusions for Th determination occur within later, slow-forming coarse sphalerite crystals. Homogenization temperatures, therefore, would be biased toward lower temperatures assuming that temperature decreases during ore deposition (Krebs and Macqueen, 1984). Higher temperature banded and botryoidal fine-crystalline sphalerite crystals generally do not contain suitable fluid inclusions for the accurate determination of filling temperatures (Anderson, 1975; Kyle, 1977). Final ice-melting temperatures (Tm_{ice}) of the sphalerite inclusions range from -22.2 to -33°C corresponding to salinities of 23 to 30 weight per cent NaCl equivalent.

Fluid inclusion assemblage measurements in coarse-crystalline matrix and saddle dolomite at Pine Point display higher Th values (86–126°C; Table 3), but similar salinities (18 to 31 wt % NaCl-equiv.; Fig. 13) to sphalerites (Coniglio et al., 2006; Paradis et al., 2006; Turner, 2006). At Pine Point, average salinities are 27 wt.% NaCl equivalent for sphalerite and 25.5 wt.% NaCl equivalent for dolomite (Turner, 2006). The presence of hydrohalite ($NaCl \bullet 2(H_2O)$) with melting temperatures ranging between -40 and -56°C at Pine Point indicates that the salt hydrates are dominantly composed of $CaCl_2$ (Turner, 2006). Homogenization temperatures of a petroleum inclusion assemblage were also measured in saddle dolomite at Pine Point. The late low-salinity primary petroleum inclusions were trapped between 100 to 110°C (Table 3), within the Th range of aqueous fluid inclusions in saddle dolomite. Eutectic temperatures (Te) near -55°C indicate that matrix and saddle dolomite as well as sphalerite at Pine Point were formed from highly saline $NaCl-CaCl_2$ fluids (Crawford, 1981; Turner, 2006).

At Pine Point, fluid inclusions hosted in sphalerite have salinities and final melting temperatures comparable to inclusions in coarse-crystalline matrix and saddle dolomite. The inclusions in dolomite, however, have greater Th values than that of sphalerite inclusions. Although Th's are not alike, the similar melting temperatures indicate the formation fluids precipitating the sphalerite and dolomite at Pine Point were likely equivalent (Allan and Wiggins, 1993). The difference in Th of fluid inclusions hosted in dolomite and sphalerite was brought about by internal overpressuring caused by burial. Under overpressured conditions, inclusions in dolomite are more likely to stretch because of the relative low strength of cavity walls in carbonate as compared to sphalerite. When simple stretching occurs, the inclusion's fluid does not leak, but the pressure-temperature conditions do change because of the increase in cavity volume. This greater volume in the stretched inclusions produces higher Th. Samples that have undergone simple stretching show great variability in Th, but Tm remains the same (Goldstein and Reynolds, 1994).

Primary inclusions in late-stage calcite at Pine Point indicate formation from lower salinity NaCl fluids (Tm range, -0.7 to -11.2°C; equivalent to salinities of 1 to 16 wt % NaCl-equiv.; Table 3; Fig. 13a; Turner, 2006). These fluid inclusion measurements suggest that some mixing with less saline, possibly meteoric, fluids took place later in the paragenetic sequence when this calcite was precipitated. Homogenization temperatures are generally lower than those of the saddle and coarse-crystalline matrix dolomite, although the range significantly overlaps the dolomite data. Calcite homogenization temperatures are similar to sphalerite fluid inclusion-filling temperatures but they are less saline (Table 3).

West of Pine Point district on the Presqu'ile barrier, homogenization temperatures in saddle dolomite are generally much higher (mean, 137°C), fluids are less saline (10-28% wt.% NaCl eq.) and are dominantly NaCl- and

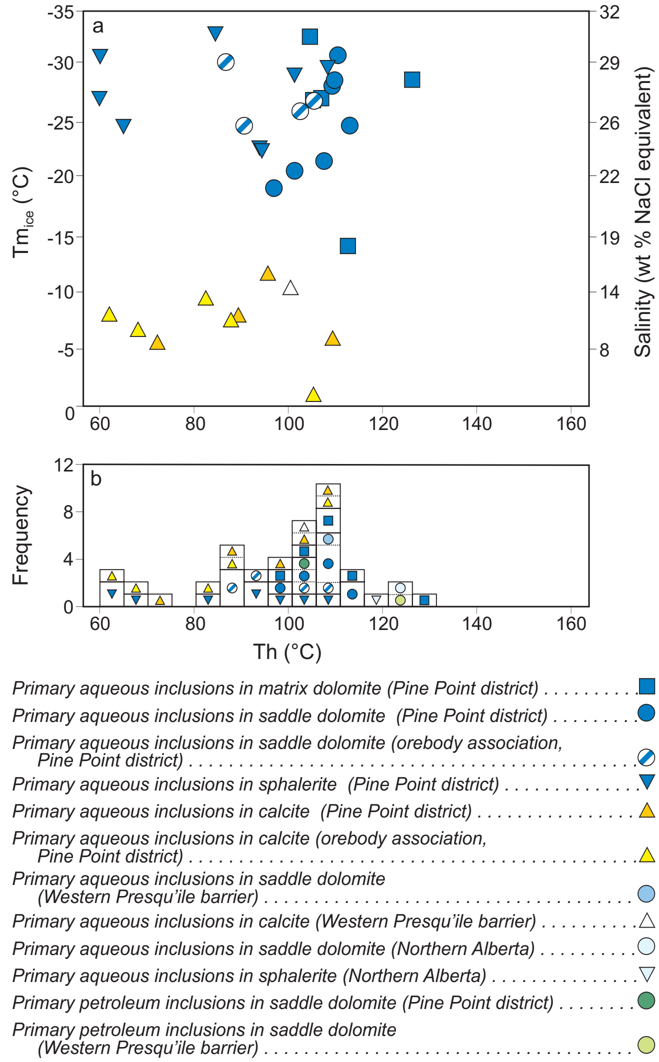

Figure 13. Fluid inclusion microthermometric data for ore-stage carbonate and sulphide phases and post-ore calcite phases in the project area. Mineralized samples are distinguished by blue slash. **a.** Cross plot of homogenization temperatures (Th) versus final melting temperatures (Tm_{ice}) with equivalent salinities of primary aqueous fluid inclusion assemblages in matrix dolomite, saddle dolomite, sphalerite, calcite, fluorite and anhydrite. Samples from Pine Point district and western Presqu'ile barrier. **b.** Histogram distribution of homogenization temperatures (Th) of primary aqueous and petroleum fluid inclusions in ore-stage and post-ore mineral phases. Samples from Pine Point district, western Presqu'ile barrier and northern Alberta. Data *from* Turner (2006), Coniglio et al. (2006), and Paradis et al. (2006).

$CaCl_2$-rich with subordinate KCl and $MgCl_2$ (Paradis et al., 2006) compared to saddle dolomite at Pine Point. Qing and Mountjoy (1994a) indicated that saddle dolomite cement in the western Presqu'ile area contains primary two-phase (aqueous vapor-liquid) fluid inclusion assemblages with Th's significantly greater than saddle dolomite cements at Pine Point. Saddle dolomite in the Keg River Formation of northwestern Alberta shows intermediate Th between Pine Point and western Presqu'ile saddle dolomites and comparable Tm_{ice} to these dolomites (Aulstead and Spencer, 1985).

Aqueous fluid inclusion assemblages of saddle dolomite in the Sulphur Point Formation at Rainbow in northwestern Alberta possess the highest range of Th's in the project area. Homogenization temperatures vary from 142.3 to 194.6°C (mean, 172°C; Lonnee and Al-Aasm, 2000). Salinities of these assemblages range from 10.5 to 13.5 weight per cent NaCl-equivalent. These data indicate that hot, slightly saline brines were responsible for precipitating this dolomite in the Sulphur Point Formation at Rainbow. Coarse-crystalline matrix dolomite at Rainbow shows lower Th and slightly reduced Tm compared to saddle dolomite (Lonnee and Al-Aasm, 2000).

Nature of dolomitizing and mineralizing fluids and environment of deposition

Characterization of parent fluids of coarse-crystalline dolomite, saddle dolomite and sulphide minerals in the Pine Point district by means of stable isotope and radiogenic isotope analyses is useful in defining the nature and components of the hydrothermal mineralizing fluid. Ore-stage dolomite and sphalerite are characterized by lower $\delta^{18}O_{PDB}$, slightly depleted $\delta^{13}C_{PDB}$, and similar $^{87}Sr/^{86}Sr$ values compared to pre-ore carbonate phases in comparable regions of the project area (Fig. 11, 12). Depletion of $\delta^{18}O_{PDB}$ indicates that higher temperature formation waters precipitated the carbonate and/or sulphide minerals. A comparison of homogenization temperatures of matrix dolomites confirms the increase of precipitation temperatures during ore-stage (Fig. 10, 13). Ore-stage coarse-crystalline matrix dolomite and saddle dolomite likely precipitated from fluids of similar composition because of their close spatial association and similar isotopic values. Initial and final melting temperatures in primary aqueous fluid inclusion assemblages in coarse-crystalline matrix and saddle dolomites, and sphalerites indicate that mineralizing fluids were hypersaline brines of the $NaCl$-$CaCl_2$-H_2O salt-water system. A spatial trend was defined by Qing (1991) where $\delta^{18}O_{PDB}$ values of saddle dolomite decrease westward along the Presqu'ile barrier from an average near -9.0‰ at Pine Point to about -14.0‰ in northeastern British Columbia. This decrease in $\delta^{18}O$ value was attributed to a westward increase of temperature of the dolomitizing fluid. The same trend was also observed with respect to the homogenization temperatures of fluid inclusions in saddle dolomite (92 to 178°C downdip and westward). Qing and Mountjoy (1994a) observed that $^{87}Sr/^{86}Sr$ ratios gradually increase westward from 0.7083 for saddle dolomite at Pine Point to 0.7095 in northeastern British Columbia. Turner (2006) observed a small increase of Th in sphalerite and dolomite from the eastern Pine Point property to Great Slave Reef, Hay West and Windy Point properties to the west and northwest, confirming a slight westward depletion of ^{18}O. The depleted $\delta^{18}O_{PDB}$ and high $^{87}Sr/^{86}Sr$ isotopic values along the western portion of the WCSB proximal to the Rocky Mountains are generally ascribed to higher temperature dolomitizing fluids and the influence of siliciclastic sources, respectively. These fluid characteristics were often attributed to sedimentary and tectonic burial during the Late Devonian to Carboniferous Antler Orogeny, the Late Jurassic to Early Cretaceous Columbian Orogeny or Late Cretaceous to Tertiary Laramide Orogeny, and fluid drive was related to topographic recharge or tectonic compression models (Garven and Freeze, 1984; Oliver, 1986). An alternative dolomitizing and/or mineralizing fluid flow mechanism in the region could be long-lived deep convective circulation occurring during late Paleozoic time (Anderson and Macqueen, 1988; Morrow, 1998). The convective cell circulation introduces, to previously lithified and permeable carbonate strata, hydrothermal solutions channelled along intrabasinal faults from Precambrian basement. Mountjoy et al. (1992) speculated the eastward decrease in radiogenic strontium supports the concept of basinal brines, which contain the Sr-signature of shale found in the deep basin to the west, migrating through a carbonate aquifer eastward and updip progressively adding local nonradiogenic Sr as a result of water-rock interaction.

Work completed in this project challenges these identified isotopic trends and shows rather variable and inconsistent spatial distribution of stable and radiogenic isotopes (Coniglio et al., 2006; Paradis et al., 2006). The non-mineralized sulphide-free dolomite does not show a westward decrease in $\delta^{18}O$ values and mineralized dolomite actually displays a westward increase. A significant increase of $^{87}Sr/^{86}Sr$ in close proximity to the Great Slave Shear Zone suggests a key role ascribed to the shear zone by providing a site for upward circulation of hydrothermal fluids from basement and precipitation of hydrothermal dolomite and sulphides in overlying porous carbonates (Paradis et al., 2006).

Petrological, geochemical, and fluid inclusion characteristics of ore-stage coarse-crystalline and saddle dolomites throughout the region indicate that they were formed in the subsurface. Since burial dolomitization normally occurs subsequent to sediment deposition and lithification, subsurface dolomite typically crosscuts depositional fabrics, formational boundaries, and unconformities. These crosscutting relationships were commonly observed in the project area. Burial-type dolomite is generally medium to very coarse crystalline and commonly contains saddle dolomite with two-phase aqueous fluid inclusions (Allan and Wiggins, 1993). In partly dolomitized rocks, coarse-crystalline dolomite and saddle dolomite replace blocky sparry calcite cement previously precipitated in the subsurface environment. The dolomite phases also postdate stylolites and overlap mineralization. Because of higher temperatures of precipitation, burial dolomite generally displays a greater depletion of $\delta^{18}O_{PDB}$ than near-surface dolomite. Burial dolomite commonly contains two-phase aqueous fluid inclusions of high salinity and elevated homogenization temperature and also may contain fluorescent petroleum inclusions. Although ore-stage dolomite at Pine Point is non-radiogenic and non-ferroan, burial dolomite may contain radiogenic isotopes in circumstances where dolomitizing brines interact with K-feldspars in siliciclastic sediments or basement rocks. Similar processes enrich many burial dolomites with certain trace elements such as Fe and Mn. Radiogenic and Fe- and Mn-rich coarse-crystalline and saddle dolomite occur west of Pine Point. Burial dolomite is also often associated with accessory minerals such as sphalerite, galena, fluorite and marcasite; all these accessory minerals are present at Pine Point.

In saddle dolomite and sphalerite crystals, fluid-inclusion filling temperatures (Th) exceed values attributed solely to their maximum burial depth in the barrier complex under Paleozoic cover. During late Paleozoic time, the barrier complex in the Pine Point district was thought to have been buried under approximately 1500 m of Paleozoic cover (Krebs and Macqueen, 1984). At this depth and assuming a geothermal gradient of 30°C/km, the resulting burial temperature should have been near 60°C, much lower than measured Th. Burial alone could not have produced the observed fluid-inclusion filling temperatures of the saddle dolomite. Other thermal sources must have been present in the Pine Point region (Krebs and Macqueen, 1984). Investigation of thermal maturity of organic matter at Pine Point (Macqueen and Powell, 1983) indicates a substantial contrast between thermally immature indigenous organic material in country rock carbonate and mature to overmature bitumen proximal to and within orebodies, demonstrating that thermal anomalies were present here and were directly associated with Pb-Zn mineralization.

Late-stage calcite cements are depleted in $\delta^{18}O_{PDB}$ and $\delta^{13}C_{PDB}$ values compared to pre-ore calcite phases (Fig. 11b). The depletion of $\delta^{18}O_{PDB}$ attests to higher temperatures brought about by burial. Final fluid inclusion melting temperatures indicate the calcite parent fluids were not as saline as dolomitizing fluids and consisted dominantly of NaCl-H_2O-type brines. Homogenization temperatures in late-stage calcite usually average about 10°C lower than those of saddle dolomite at the same location (Qing, 1991). Coniglio et al. (2006) suggest that reduced salinity in the blocky calcite was brought about by the mixture of the subsurface brines with meteoric fluids. The strong $\delta^{13}C_{PDB}$ depletion represents possible organic degradation reactions such as thermochemical sulphate reduction, methane oxidation, or decarboxylation (Coniglio et al., 2006). Late-stage calcite is considerably more radiogenic than pre-ore calcite (Fig. 12b). The source of radiogenic strontium is not clear, but Mountjoy et al. (1992), suggested that extensive water-rock interaction as well as the close association with anhydrites resulting in precipitation from residual brines, may have enriched the fluids with ^{87}Sr.

NATURE OF TRANSPORTING FLUID

Based on available production and reserve information, the Pine Point district contained original base metal reserves of approximately 95 million tonnes of ore averaging about 3.0% Pb and 7.0% Zn at the cutoff grade of 2% (Pb+Zn) (Natural Resources Canada, 2005). A reasonable estimate of metal resource from sub-economic occurrences and undiscovered orebodies in the district may be an additional 1.2 Mt (million tonnes) of Pb and 3.3 Mt of Zn (Kyle, 1981). Ore in the district also contains Fe averaging near 3.5% and likely contains about 13.6 Mt of sulphur in the form of sulphide, exclusive of native sulphur also present throughout the barrier (Kyle, 1981). The common metals in the mineralizing solution were Pb, Zn, and Fe and they are present in a ratio of 2:5:3 (Kyle, 1981). Cu, Mn, and Cd locally occur as trace elements in the common sulphides (Kyle, 1977; Gleeson and Gromek, 2006), but separate minerals have not been recognized containing these metals.

The relatively low temperatures (compared to many other mineral deposit types) and high salinities associated with fluid inclusions in Pine Point dolomite and sphalerite are characteristic of MVT deposits and indicate derivation from deeply buried basinal fluids affected by low-temperature diagenetic or metasomatic processes rather than from magmatic or volcanogenic sources. Chemical analyses of fluid inclusions in carbonate-hosted deposits in the Pine Point district indicate that mineralizing solutions were dense brines dominated by chlorine, sodium, calcium, potassium and magnesium in decreasing order of abundance (Kyle, 1981; Leach and Sangster, 1993). The bulk of the fluids have Cl/Br values that are less than seawater indicating that the fluids are Br-enriched (Gleeson and Gromek, 2006). These Br-rich fluid inclusions suggest that the parent fluids evolved from highly evaporated seawater rather than common seawater. Dominant cations are sodium and calcium with measurable subordinate amounts of potassium and magnesium (Haynes and Kesler, 1987). These Na and Ca-rich brines are similar in chemistry to oilfield brines (Kyle, 1981; Leach and Sangster, 1993). K/Na values of fluid inclusions in the MVT deposits are greater than the ratios found in oilfield brines, however, which suggest either that MVT ore fluids are more evolved from seawater or are at least partly composed of interstitial fluids from evaporite beds enriched in residual K (Anderson and Macqueen, 1988).

Brine springs in northern Alberta were sampled along the Athabasca River near Fort McMurray and in Wood Buffalo National Park (Grasby, 2006). Saline springs in these areas are characterized by compositions dominated by NaCl with high levels of sulphate and Ca. Waters in the Wood Buffalo region are saturated with respect to halite and gypsum, whereas Fort McMurray fluids are typically undersaturated in these minerals, which is consistent with the lack of evaporites in the latter area. The chemistry of these modern springs displays significant differences with respect to sampled Devonian formation waters in northern Alberta and in the Pine Point area (Connolly et al., 1990a, b; Tesler, 1999). The conservative ion ratio of Br/Cl in Devonian formation waters indicates original seawater evaporating past halite saturation, thereby producing a Br-enrichment. The spring waters, however, show low Br/Cl values suggesting derivation by dissolution of halite (Grasby, 2006). Fluid inclusions in Pine Point ore minerals display significant loss of Na (Gleeson and Gromek, 2006). This chemistry contrasts with Devonian waters, which show near equal molar concentrations of Na and Cl.

In northern Alberta, Hitchon (1993) discovered significant concentrations of Zn and Pb in modern saline formation waters emanating from the Middle Devonian Keg River Formation suggesting a possible undiscovered ore-source in the area. However, Hitchon (1993) did not believe these modern metal-rich formation waters are similar to fluids responsible for lead and zinc mineralization at Pine Point because of the major difference in the lead-zinc ratio (orebodies at Pine Point have Pb:Zn ratios ranging from 1:1.7 to 1:2.6 whereas Devonian formation waters in the Keg River Formation in northern Alberta range from 5.5:1 to 0.6:1; Hitchon, 1993). Grasby (2006) indicates Pb and Zn concentrations of modern formation waters are an order of magnitude lower than formation waters in Paleozoic units (Hitchon, 1993). The range of Zn/Pb is similar to that documented in Hitchon (1993), but a distinct difference was noted in the two study areas. The springs in the Fort McMurray area showed zinc concentrations much greater than concentrations at Wood Buffalo (Grasby, 2006). Generally, geochemical signatures of modern waters are quite different than Devonian formation brines, suggesting that recent formation waters in northern Alberta are not related to mineralization processes at Pine Point.

SOURCE OF METALS

Similarities between oilfield brines and parent fluids forming dolomite and sulphide in MVT deposits and the general spatial association of hydrocarbon accumulations and sulphide deposits indicate a plausible linkage between the two accumulation types. This linkage suggests that carbonate-hosted Pb-Zn deposits are precipitated by normal sedimentary basinal processes (Beales and Jackson, 1966, 1968; Jackson and Beales, 1967; Dunsmore, 1973; Anderson and Macqueen, 1988). Implicit in basinal evolution is the notion that hydrocarbons or metals were extracted from an original source rock, migration of petroleum or metals took place in solution, and petroleum pools accumulated or metal sulphide deposits precipitated at appropriate ‘trapping’ sites. Petroleum source beds are commonly organic-rich, fine-grained clastic sediments. Normally, organic-rich shale is also enriched in trace metals, and metal supply at Pine Point may have been derived from Devonian black shale situated in the Mackenzie subbasin directly north of the Presqu’ile barrier complex. Jackson and Beales (1967) proposed that a dewatering process, brought about by compaction of deeply buried shale, expelled large amounts of water, which transported released metals in solution to precipitation sites in porous carbonate units of the barrier complex. If the shale in Mackenzie subbasin were a metal source, one would expect the presence of a large-scale and widespread lateral metal zonation pattern at Pine Point, where metal concentrations decrease away from the subbasin. However, lead and zinc zonation patterns seem to be restricted along the Main and North hinge lines (Kyle, 1981). Macqueen and Ghent (1975) and Macqueen et al. (1975) reported anomalous zinc contents in dark shale samples along a transect through the Mackenzie subbasin. Lead contents, however, are very low in most of these transect samples, suggesting that a separate source is required for the anomalous lead concentrations at Pine Point. Also, many other trace elements such as uranium are anomalous in the black shale (Macqueen et al., 1975), suggesting that these shale units are too complex a metal source to correlate directly with the relatively simple mineralogical suite occurring in orebodies at Pine Point.

Another possible metal source may be trace metals in adjacent or nearby Devonian evaporite successions such as the underlying Chinchaga Formation or the coeval Muskeg Formation found south of the Presqu’ile barrier. Thiede and Cameron (1978) investigated trace metal concentrations found in the Middle Devonian Elk Point evaporite sequence of the WCSB. Basinal processes such as evaporite compaction and dehydration of gypsum to anhydrite led to solution of the evaporite succession by groundwater. Lead and zinc concentrations in Elk Point evaporite deposits are several orders of magnitude greater than in seawater (Thiede and Cameron, 1978). During evaporation processes, lead and zinc occurring as solid phases in gypsum or anhydrite were mobilized by the dissolution of gypsum or anhydrite by connate waters, making these waters highly saline and metal-rich. Changes in the chemical environment along the flow path led to precipitation of the metals in the barrier complex at Pine Point. Krebs and Macqueen (1984) objected to an evaporite source for metals at Pine Point because of insufficient thickness and volume of Chinchaga and Muskeg evaporitic formations in the district to account for the large resource of lead and zinc sulphides at Pine Point.

A third potential source for metals at Pine Point may be the Devonian carbonate deposits themselves. In many MVT deposits, metal character seems to be related to the lithology of the aquifer, commonly a carbonate unit, through which the fluids migrated. In carbonate-hosted MVT deposits, ore deposits are typically zinc-rich. The metals might have been released by aqueous solution during replacement of aragonite to low-Mg calcite and high-Mg calcite to dolomite (Anderson and Macqueen, 1988). However, these necessary mineralogical replacements occur too early in the proposed paragenetic sequence (Fig. 7) to be properly applied to the sulphide mineralization event at Pine Point (Krebs and Macqueen, 1984).

Metals can also be introduced to the barrier by upward-circulating hydrothermal solutions originating in Precambrian basement (Campbell, 1966, 1967). The northeast-trending deep-seated reactivated Precambrian Great Slave Shear Zone–McDonald fault system may be an opportunistic site for a gravitationally buoyant mass of metal-rich hot solutions to migrate upward into the highly fractured and brecciated collapse zones within the Presqu'ile barrier complex. These hot solutions may directly engender the thermal anomalies noted at Pine Point. The ascending solutions produced hydrothermal dolomite halos around collapse zones and led to the formation of hydrogen sulphide from pre-existing host rocks (Krebs and Macqueen, 1984). Morrow et al. (2006) and MacLean (2006) illustrate numerous subparallel basement faults and an orthogonal fault system that may represent sites of enhanced hydrothermal fluid circulation.

A distinct homogeneous non-radiogenic lead isotope signature characterizes the sulphides in the Pine Point district and those along the Great Slave Shear Zone–McDonald fault system, which suggests either a single source for the lead, or thorough mixing after extraction from several sources (Cumming et al., 1990; Paradis et al., 2006).

SOURCE OF SULPHUR

Approximately 15 million tonnes of sulphur are present as sulphides at Pine Point (Kyle, 1981). This volume does not include the sulphur also occurring in large quantities as native sulphur and sulphates. Native sulphur and sulphur in sulphates have uncertain associations with the orebodies (Kyle, 1981). Since sulphur plays a critical role in the precipitation of sulphides, its ultimate source is an important aspect of ore genesis.

Most subsurface brines have low quantities of sulphur, usually in the form of sulphates, rather than the reduced sulphur variety needed to precipitate sulphides. Sulphur isotopes of galena, sphalerite, marcasite and pyrite from Pine Point orebodies show a narrow range of variation (average of +20.1‰ $\delta^{34}S_{CD}$ with a standard deviation of 2.6; Sasaki and Krouse, 1969). Sverjensky (1986) reported sulphur isotopes for ore fluids depositing galena and sphalerite as +22‰ and +23‰, respectively. Middle Devonian anhydrite present in the adjacent Elk Point subbasin to the south of the barrier complex has mean $\delta^{34}S_{CD}$ values of +19 to +20‰, very similar to values determined for sulphides. These narrow sulphur isotope ranges are consistent with derivation from a single source or several sources that have been well homogenized. Evans et al. (1968) indicated that $\delta^{34}S_{CD}$ values at Pine Point are very similar to oils in the WCSB. The most reasonable source for sulphur in Pine Point sulphides is seawater sulphate (Sasaki and Krouse, 1969; Dunsmore, 1973). The uniform sulphur isotopic composition in the sulphides eliminates biogenic sulphate reduction as a possible ore-precipitating mechanism, because that process is characterized by large isotopic fractionation (Krebs and Macqueen, 1984). Powell and Macqueen (1984) demonstrated that some bitumen participated in thermochemical sulphate reduction (TSR) to produce H_2S. They also showed that the amount and degree of alteration of bitumen more than account for the reduced sulphur species at Pine Point. Grasby et al. (2002) speculated that TSR may have formed H_2S elsewhere in the basin that subsequently migrated to the site of ore deposition; because thermal maturation measurements of organic-rich facies proximal to orebodies indicate that these rocks were not buried deep enough to experience temperatures required for TSR.

MECHANISMS OF FLUID FLOW

Recent advances in understanding large-scale fluid flow within the crust and sedimentary basins have established that most MVT mineral districts are the product of regional- or subcontinental-scale hydrological movements. MVT deposits were formed by warm, saline, aqueous solutions similar to oilfield brines that migrated in sedimentary basins through aquifers in platform-carbonate sequences toward the basin peripheries. To effect this movement of solutions, several models of fluid flow have been postulated.

The sedimentary-diagenetic origin model was proposed by Jackson and Beales (1967) using the Pine Point deposit as their primary example. The model is based on the theory that basinal-derived fluids or brines acquire heat, metals and other solutes during the migration process and deposit sulphides in the host carbonate when conditions are favourable for precipitation. Fluid drive was generated by sediment compaction and movement of the fluids was sustained by porosity variations. The movement of warm brine from well-compacted sediments into strata of higher porosity is very similar to the process of migration of petroleum from their source beds along permeable conduits or strata to various trap configurations. Jackson and Beales' (1967) model speculated that fluids acquire their metals through brine leaching and the metals are transported by means of chloride or organic complexes. The metals in the solution precipitate when hydrogen sulphide is encountered. Nearby evaporites (Muskeg Formation at Pine Point) filter hydrogen sulphide into the migration route and thermogenic sulphate reduction occurs at the site of mineral precipitation in the presence of petroleum. Fluid inclusions residing in sphalerite, carbonate and fluorite of MVT deposits in general, are remarkably similar from deposit to deposit and are equivalent to brines found in petroleum wells. They always have densities greater than one g/cm^3, exhibit salinities usually greater than 15 weight per cent salts, contain concentrated solutions of Na and Ca chlorides, and carry organic matter in the form of methane or oil-like droplets (Anderson and Macqueen, 1988).

Cathles and Smith (1983) and Bethke (1985) demonstrated that the steady-state compression or compaction of basinal sediments invoked in Jackson and Beales' (1967) burial compaction model does not provide sufficient rates of discharge to produce the heat necessary for the elevated temperatures recorded in fluid inclusions of the host rocks. One possible mechanism to overcome this problem is the process of releasing fluids episodically in overpressured zones of compacting sediments (Cathles and Smith, 1983). This model does require, however, rapid sedimentation and swift transport of fluids through the aquifers, thereby producing the thermal anomalies prevalent in the ore districts. A significant constraint applied to these compaction-driven fluid-flow systems requires that mineral deposits only originate at an early stage in the geological history of the basin (Anderson and Macqueen, 1988), not likely the situation interpreted at Pine Point.

Another mechanism of formation fluid-flow that may be appropriate with respect to regional MVT mineralization in certain basins is the topographically driven fluid-flow model conceptualized by Garven and Freeze (1984). This model proposes recharged groundwater in the uplifted orogen on the flank of the basin migrating downward through shale units into the underlying carbonate unit by cross-formational fluid flow (see Fig. 4 in Introduction paper by Hannigan, 2006). As the fluid migrates updip through the deep portion of the basin along the carbonate aquifer, it acquires heat and dissolved components. The fluids or brines are eventually discharged by means of this immense hydrothermal circulation system on the basin's cratonic flank. Metals leached from source units in the shale spread throughout the basin, but concentrate at the discharge end where conditions are most favourable for precipitation of ore. Garven (1985) proposed that fluid flow migrated along the Presqu'ile barrier in a northeast direction from the recharge area in the Cordillera on the western margin of the basin, through a carbonate aquifer updip into the shallow discharge area near the outcrop or shallow subcropping margin of the aquifer on the northeast side of the basin (*see* Fig. 4 in Introduction paper by Hannigan, 2006). This model suggests fluid circulation was initiated as a result of the Cretaceous–Tertiary Laramide Orogen and mineralization took place during or in the immediate aftermath of that tectonic episode. Later work by Nesbitt and Muehlenbachs (1994, 1995), Root (2001) and Nelson et al. (2002) refuted this Laramide MVT mineralization event, and speculated instead that mineralization and dolomitization in the WCSB were likely associated with the Late Devonian-Early Mississippian Antler Orogeny.

Another means of moving large volumes of dolomitizing solutions through large rock masses is the hydrothermal convection model (Fig. 14; Morrow et al., 1990; Morrow, 1998). Convection is driven by buoyancy forces related to temperature and salinity variations. The continual vertical recycling of connate formational fluids derived from halite-saturated residual brines in the Elk Point subbasin provides greater opportunity for coarse open-space-filling dolospar crystals, such as saddle dolomite, to grow (Morrow, 1998). There is more than enough Mg present in the Elk Point evaporite deposits to form all Devonian dolomite in the WCSB (Shields and Brady, 1995). In this fluid flow model, fluid inclusion and isotopic paleotemperatures reflect basement depth gradients. The hotter paleotemperatures recorded in the western Presqu'ile barrier and in northeastern British Columbia are thought to be related to deeper convective circulation due to greater depth to relatively impermeable basement in latest Devonian time. The Presqu'ile dolomite at Pine Point displays vertically oriented, chimney-like breccia bodies cemented by white sparry dolomite and containing laminated internal sediments. Upward and downward fluid flow may be focused preferentially along fault zones (Fig. 14; Morrow et al., 1990). Nelson et al. (2002) discussed the applicability of this thermal convection model to the distribution of both volcanogenic, sedimentary exhalative and MVT deposits such as Robb Lake and Pine Point in the WCSB.

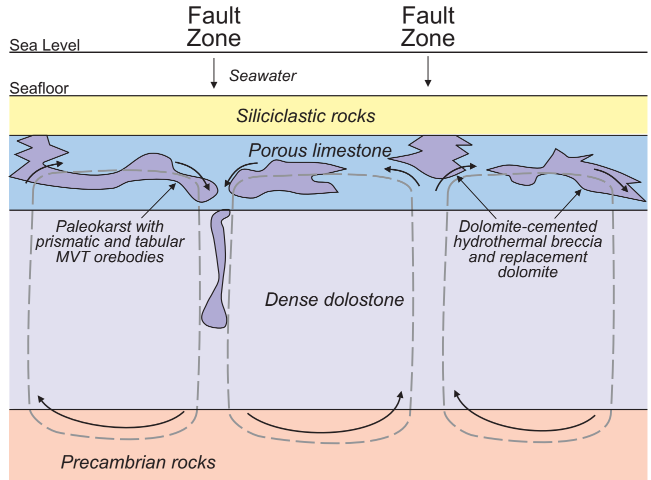

Figure 14. Schematic cross-section through part of a regional convection system within a typical Paleozoic sedimentary succession in the Western Canada Sedimentary Basin. Dense peritidal calcareous dolostone is overlain by porous limestone and capped by fine-grained siliciclastic rocks. Stratiform dolomite-cemented breccia forms within upper subhorizontal parts of the convective flow path. In regions of strong upward flow, dolomite breccias extend upward to the upper contact of the limestone with overlying, less permeable siliciclastic rocks. Upward and downward flow may be focused preferentially along fault zones (*from* Morrow, 1998).

SULPHIDE PRECIPITATION AND CONCENTRATION

The fluid-flow models cited above give appropriate mechanisms for the delivery of metal-bearing fluids to the site of deposition, but there remains a need to define the chemical processes required to precipitate the sulphides. Possible models are the reduced sulphur model, the sulphate reduction model and various fluid mixing models (Leach and Sangster, 1993).

The reduced sulphur model assumes that metals and reduced sulphur are transported together in the same fluid. Sulphide deposition is achieved by means of cooling, dilution of the brine by meteoric waters or less saline groundwater, or by changes in pH (Anderson, 1975; Anderson and Macqueen, 1988; Leach and Sangster, 1993). Sverjensky (1984) indicated that pH values of 4.5 or lower are required for reduced sulphur and metals to be transported in the same fluid. These acidic conditions are incompatible if the fluid is transported through a carbonate aquifer as proposed in the topographic recharge fluid-flow model. Anderson (1975) indicated that metal solubilities are too low in solutions containing reduced sulphur for metal transport to occur. Evidence consistent with ore deposition by means of the reduced sulphur model is the presence, in some instances, of district-wide uniform colour-banding in sphalerites (McLimans et al., 1980). This feature suggests that local sources of sulphur external to the fluid likely do not occur, since individual sources would not produce such a consistent feature (McLimans et al., 1980). This so-called ‘sphalerite stratigraphy’ was not observed at Pine Point, however. Similarly, the uniform sulphur isotope composition of ore sometimes observed in MVT districts may indicate a single metal/sulphur-bearing fluid. However, the uniform sulphur isotope compositions may also signal the presence of well-homogenized mineralizing fluids.

The sulphate reduction model is based on the premise that reduced sulphur concentration is increased at the deposition site as a result of sulphate reduction processes (Leach and Sangster, 1993). The model requires delivering both metal and sulphate to the precipitation site, where methane or other organic matter are present. The organic matter reduces the sulphate to precipitate the sulphides. The spatial association of evaporites and bitumen in some MVT deposits (such as Pine Point; Powell and Macqueen, 1984) indicate that biogenic or thermogenic sulphate reduction are feasible mechanisms (Machel, 1989). The lack of significant isotopic fractionation of sulphur isotopes in sulphides, sulphates and native sulphur eliminates biogenic sulphate reduction as a relevant chemical process.

Mixing models imply that sulphide is supplied at the site of deposition where the metal-rich brine is mixed with a H_2S-rich fluid (Anderson and Macqueen, 1988; Leach and Sangster, 1993). The mixing of fluids produces high degrees of supersaturation, large chemical and/or concentration gradients and relatively rapid rates of precipitation of sulphides. These chemical processes result in precipitation of fine-grained, dendritic, and colloform ores, all of which are found at Pine Point. Fluid mixing can also yield large crystals if the chemical gradients are small and mixing is very slow, as for example, by means of diffusion of H_2S through the wall-rock. Adams et al. (2000) demonstrated that mixing of two fluids may have taken place at Pine Point as a result of distinctive shifts in the chemistry of the parent fluid at the ore deposit site. Major differences in fluid inclusion homogenization temperatures, salinities, brine composition and ^{18}O enrichment all favour the introduction of a second fluid to the hydrological system at Pine Point.

TIMING OF MINERALIZATION

As a result of remarkable advances in dating of MVT deposits in the last 10 years, genetic links between MVT deposits and regional- to global-scale tectonic events were established (Leach et al., 2001). Most MVT deposits in North America formed during contractional tectonic events associated with the amalgamation of Pangea in the Devonian to Permian time interval and the accretion of exotic terranes onto the western margin of North America in Cretaceous to Tertiary time.

The timing of mineralization in MVT deposits is particularly difficult to determine because of a number of factors. These include the occurrence of MVT deposits in stable tectonic areas, precluding the use of geological field observations of post-ore events in order to determine relative timing of mineralization; the lack of magnetic minerals in the strata, making paleomagnetic methods untenable; and the lack of igneous material or feldspars in the immediate region from which one can apply radiometric dating methods. Despite these restrictions, numerous studies have been completed discussing the timing of the mineralization episode at Pine Point. The paleomagnetic method of dating MVT stratabound ore deposits was attempted at Pine Point (Beales et al., 1974). In this paper, it was concluded that magnetic intensities were too low subsequent to demagnetization to lead to any specific conclusions with respect to the age of mineralization. Another attempt using the paleomagnetic technique was described in a paper by Symons et al. (1993), who speculated that the observed remanent magnetism provided a cluster of magnetic measurements with respect to a unique pole position. This pole position indicates that ores at Pine Point are Late Cretaceous to Eocene in age, suggesting that metal-rich brines were possibly forced into the Presqu’ile barrier during the Laramide orogeny. Enkin et al. (2000) observed that all carbonate rocks in the Rocky Mountain thrust belt and foreland area were remagnetized in Late Cretaceous-Early Tertiary time, and any paleomagnetic remanent magnetism is not preserved. This Late Cretaceous-Early Tertiary remagnetization event (Gillen et al., 1999) has been recognized elsewhere in the WCSB extending eastward into the Elk Point subbasin of Saskatchewan (Koehler et al., 1997). Identical poles were found in unaltered limestone and secondary dolomite, so the remagnetization event is not directly related to the dolomitization episode or the sulphide mineralizing event. Thus, there must be some doubt with respect to the accuracy of paleomagnetic age determinations from strata affected by this regional remagnetization event.

Cumming et al. (1990) studied lead isotopes in the Pine Point district and observed a remarkable lead isotope homogeneity occurring throughout the area. The lead isotopes at Pine Point conform to the normal or N-type leads giving model ages near that of the host rocks (Baadsgaard et al., 1965; Cumming and Robertson, 1969; Kyle, 1977, 1981).

The distinct homogeneous character allows one to utilize the single-stage lead-evolution model procedure for age determination of lead precipitation. This method gives a mineralization age of 290 Ma. This Late Pennsylvanian age is younger than the host rocks but much older than the Laramide tectonic event. Cumming et al. (1990) also noted that Pine Point leads are much less radiogenic than those reported in Devonian carbonate-hosted Pb-Zn deposits in the Cordillera to the west. This difference in lead isotope signature likely specifies unique paleogeographic positions for the two lead types, indicating separate and distinct mineralization events, fluid sources, and fluid pathways in the two regions.

Apatite fission-track analysis in the Pine Point district was undertaken by Arne (1991) in order to determine the regional thermal history of the region. The analysis and frequency distribution of annealed fission-track lengths in apatite revealed that a heating event occurred subsequent to the deposition of Devonian rocks. The heating event, attributed to deep burial, reached its maximum during Cretaceous time before a subsequent cooling episode took place when the deeply buried Devonian strata were uplifted and eroded. The maximum attained paleotemperatures fall in the same range of estimated temperatures of ore formation, suggesting that these deposits formed during deep burial in Cretaceous time. This interpretation indicates that convective transport of heat is not necessary as heat is generated solely by deep burial.

Rb-Sr dating of sphalerites in the Pine Point district define an age of 361± 13 Ma indicating that mineralization occurred shortly after deposition of the Middle Devonian host carbonate (Nakai et al., 1993). This age is not consistent with the tectonic-driven fluid-flow model of Garven (1985) ascribing dolomitization and accompanying mineralization to effects generated by Laramide Cordilleran deformation, but is consistent with fluid flow and mineralization brought about by tectonic compression during the Late Devonian-Mississippian Antler Orogeny on the western margin of the continent (Nelson et al., 2002).

GENETIC MODEL

The most popular models for the formation of hydrothermal dolomite and the associated MVT sulphide minerals in the WCSB involve fluid flow related to topographic recharge or tectonic compaction initiated by either the Cretaceous-Tertiary Laramide or Devonian-Mississippian Antler orogenies (Garven, 1985; Qing and Mountjoy, 1992, 1994a; Machel et al., 1996; Root, 2001). Another model—thermal convection—has been proposed as an alternative mechanism for the movement of dolomitizing and mineralizing fluids in the basin (Morrow, 1998; Morrow et al., 2002; Nelson et al., 2002). Fluid movement by convection is initiated by high heat flow or paleogeothermal gradients producing vertically oriented cells where constant recycling of connate Mg-rich formation brines provide sufficient opportunity for extensive and regional development of hydrothermal dolomite in porous limestone overlying dense dolostone (Fig. 14). Stratiform dolomite-cemented breccias (tabular paleokarst) form in the upper subhorizontal portions of the convective cells. In areas of upward movement possibly associated with fault zones, chimney-like dolomite bodies extend upward from the tabular horizons to the upper contact of porous limestone with overlying, less permeable siliciclastic rocks (prismatic paleokarst).

Morrow (1998) argued against topographic recharge or tectonic compaction fluid flow forming Manetoe and related Presqu'ile hydrothermal dolomite in the region. The fact that regional dolomite such as Presqu'ile dolomite is saturated by connate hypersaline brines (Bachu, 1995, 1997; Spencer, 1987) indicates that this dolomite was not flushed by meteoric water as required by topographic recharge. Morrow (1998) argued that an important factor not satisfactorily reconciled in the tectonic compaction model is the extreme amount of fluid focusing required to support the fluid inclusion-filling temperatures measured in hydrothermal dolomite. Warming of updip carbonate aquifers to measured fluid inclusion temperatures requires flow rates an order of magnitude greater than inferred flow rates envisaged in the compaction flow model.

Similar to topographic recharge and tectonic compaction models, the thermal convection model requires a very large volume of magnesium-rich fluid to pass through precursor limestone to form large masses of dolostone. Since the convective system continually recycles brines through the carbonate strata, there is improved potential for more complete open-space dolomite cementation (saddle dolospar) to take place. The other models permit only one pass of the brine through the system, thus lowering substantially the potential for open-space cementation (*see* Anderson and Macqueen, 1988; their Figure 6; for discussion on the relationships among flow rate, fluid volumes, concentration change and time for deposition of MVT ore).

Qing and Mountjoy (1994a) invoked the topographic recharge model to explain the progressive westward increase of Th in dolomite along the Presqu'ile barrier. They suggested that this increase, along with similar trends in oxygen and strontium isotopes, is consistent with west-to-east updip groundwater flow during the Laramide Orogeny. Morrow (1998) speculated that hotter paleotemperatures observed in the western region may alternatively be caused by deeper convective circulation brought about by greater depths to impermeable Precambrian basement in late Paleozoic time.

Prominent northeast-trending extensional faults and the paleokarst system development in the Presqu'ile barrier at Pine Point greatly eased the evolution of a cross-formational flow system which produced the extensive array of convection cells. In the convectional flow regime, the fluid inclusion and isotope paleothermometers reflect basement depth gradients rather than regional fluid flow from recharge to discharge areas. Convection in Western Canada may have been initiated by high heat flow in late Paleozoic time related to times of rifting (Morrow et al., 1993; Feinstein et al., 1996; Nelson et al., 2002). Convection flow commonly forms brecciated hydrothermal dolomite masses that are stratiform in lower Middle Devonian limestone over broad areas. In certain areas, such as Pine Point, the hydrothermal dolomite also extends upwards through the Sulphur Point and Slave Point limestone to contacts in overlying shale. These chimney-like hydrothermal dolomite bodies are sites where upward flow of dolomitizing solutions was particularly vigorous, which may be preferentially associated with regional basement faults (Fig. 14).

The location of Pine Point deposits adjacent to the MacDonald–Great Slave Lake fault system and other Pb-Zn occurrences along subparallel northeast-trending faults suggests a key role for structural control of orebodies in the Pine Point district (Campbell, 1966; 1967; Morrow et al., 2006; Pană, 2006; Paradis et al., 2006). Two distinct lead isotope populations were recognized in the project area, a Cordilleran carbonate trend and a Pine Point cluster (Paradis et al., 2006). The Cordilleran carbonate lead trend is found in the Rocky Mountain MVT belt, western Presqu'ile barrier and Peace River Arch area of west-central Alberta. The Cordilleran carbonate signature is interpreted as representing a mixture of ordinary upper crustal lead and anomalous radiogenic lead derived from siliciclastic sources. The second lead isotope population, called the Pine Point cluster, is much less radiogenic than the Cordilleran carbonate population (Paradis et al., 2006). The Pine Point cluster does not seem to be related to the Cordilleran miogeocline. Nelson et al. (2002) suggested the Pine Point lead cluster represents a typical lead signature for Devonian-Mississippian northern hemisphere continental environments. Mineralized Pb and Zn samples collected along the Great Slave Shear Zone in northwestern Alberta, an area where the Cordilleran lead signature was anticipated to occur, give a Pine Point lead signature, implying an important structural control for sulphide mineralization (Paradis et al., 2006). The Pine Point lead signature was also encountered in the Cordova Embayment of the western Presqu'ile barrier in northeastern British Columbia, another area where the Cordilleran carbonate lead signature was expected (Paradis et al., 2006). Morrow et al. (2006) mapped major northeast-trending faults in this region. The source of the 'Pine Point lead' is speculated to be from rocks in the Precambrian basement that have been leached by fluids circulating in deep fault structures rather than from shale leached by recharging topographic fluids in the Cordilleran miogeocline (Paradis et al., 2006). The presence of radiogenic strontium and hot, slightly saline brines in saddle dolomite along these same structures suggest upward movement of fluids from basement.

EXPLORATION METHODS IN THE PINE POINT DISTRICT

Favourable geological features

Regional attributes

Sangster (1983) and Leach and Sangster (1993) indicated that one of the most distinctive characteristics of MVT deposits is their great geological and geochemical diversity. Diagnostic and permissive geological features established during the extensive and long-lived exploration history at Pine Point should be applicable to discovering new MVT deposits in the district as well as farther afield in the WCSB. Strata of exploration interest are carbonate successions developed on the flanks of large and deep sedimentary basins. Unconformities and paleokarsts are important diagnostic features to examine in these favourable strata. Arching or flexing of the underlying basement produces topographic highs on the basement surface. These highs may define zones of increased fluid movement or heat flow. Basement faults can provide escape routes for metal-bearing fluids and conduits for increased heat flow. MVT deposits are commonly found in dolostone sequences associated with evaporitic strata and organic matter. Carbonate fronts dividing basinal shale and platform carbonate are important features to map. Other associated features representative of potential MVT mineralization are highly permeable zones such as reefs or abundant open-fractures or faults, white sparry dolomite associated with the vuggy dolostone, and collapse breccias. All of these favourable indicators are present at Pine Point.

Local attributes

In addition to the set of general exploration criteria listed above, a further refinement of favourable geological attributes has been established in the Pine Point district. A primary exploration strategy might include follow-up along the hinge lines on the Pine Point property and along their projected extensions to the west of the property, since previous exploration along those trends at Pine Point had been extremely successful. The North and Main major trends are most important and economical because of the number and quality of orebodies. Seven additional orebodies were discovered on the Main Trend to the west of Pine Point property in the Great Slave Reef property, but no orebodies have been discovered as yet along the North trend in this area. These trends are coincident with two distinct zones of preferential and pervasive Presqu'ile dolomitization localizing the development of paleokarst networks (Rhodes et al., 1984). Within these major karst networks are continuous linear solution channels that developed at the base of the Presqu'ile dolomite and are associated with specific lithofacies in the barrier complex. These linear channels or subtrends are tabular karst networks that locally develop prismatic features often directly associated with paleotopographic ridges manifested on top of the Upper Keg River Member. The subtrends are associated with fossiliferous buildups or bioherms in the Upper Keg River Member and Sulphur Point Formation (Rhodes et al., 1984). Approximately 70 per cent of the prismatic orebodies at Pine Point are found along the Main trend; prismatic orebodies tend to be higher-grade at Pine Point than tabular deposits. On the Main trend, two of three subtrends are dominantly prismatic and facies-controlled. Prismatic orebodies on the northern or PB subtrend are always associated with a Pine Point (Upper Keg River) high and related development of a Sulphur Point bioherm. They are also situated just north of the pinchout of the C-horizon of the Muskeg Formation (a thin dolomite layer in the evaporite succession extending north from the back-barrier into the barrier where it pinches out). The second dominantly prismatic subtrend along the Main Trend is the southern or BC trend developed at the triple-point where the Muskeg, Sulphur Point and Upper Keg River stratigraphic units are juxtaposed. The central subtrend along the Main trend (CC subtrend) hosts semicontinuous runs of tabular ore and, less commonly, thickened tabular and prismatic orebodies (Rhodes et al., 1984).

Additional local exploration criteria observed in the Pine Point district include: 1) dolostone is not common in the Slave Point Formation, but where it does occur, it is almost always near mineralization; 2) tabular orebodies tend to follow bioclastic beds such as floatstone and rudstone in the Sulphur Point Formation; 3) 'presqu'ilized' dolomite and white sparry dolomite vugs and veins are present only near ore in the Watt Mountain Formation, and 4) blue-grey dolomite is closely associated with both tabular or prismatic ore. Recent work by Turner et al. (2003) indicates that blue-grey dolomite along with other carbonate alteration types exhibit unique spectral signatures in the Pine Point mining camp. Turner et al.'s (2003) study also determined that blue-grey dolomite contains greater sulphide concentrations compared to its white counterpart, and commonly envelops orebodies. It was also observed that disseminated lead and zinc sulphides generally are uncommon in the Slave Point Formation, but their rare occurrences almost always indicate proximity to prismatic ore deposits. Another observation on the Slave Point Formation pointed out that crackle brecciation is rare, but is fairly extensive directly over prismatic orebodies. Tabular orebodies, however, do not have these sizeable crackle zones. At Pine Point, the highest grade of base metal mineralization occurs in karst structures hosting the greatest amount of infilling internal sediment (Rhodes et al., 1984). In prismatic orebodies, internal sediments are thicker near the base of the karst network where tabular karst begins.

Surficial geochemistry

Most MVT deposits have minor geochemical signatures because of the limited primary dispersion of elements bounded in sphalerite and galena into surrounding carbonate rocks (Lavery et al., 1994). When weathering of the sulphides occurs and minerals such as limonite, cerussite, anglesite, smithsonite, hemimorphite, and pyromorphite are formed, the soil and stream sediments surrounding these deposits may contain anomalous concentrations of Pb, Zn, or Fe. At Pine Point, lead and zinc geochemical dispersion surveys in lake sediments, soils and tills were undertaken (Brabec, 1983). Zinc gives larger and more contrasting anomalies in lake sediments and soils; however, not all zinc anomalies are associated with an orebody. Major shale units, especially organic-rich ones, give zinc background values similar in magnitude to anomalies associated with orebodies (Macqueen and Ghent, 1975; Hannigan, 2005b). This same shale usually has relatively low lead contents. Therefore, areas of composite lead-zinc anomalies may indicate Pb-Zn sulphide mineralization.

Geophysics

Regional techniques

Geophysical techniques (airborne and ground) have been successfully utilized in certain MVT districts to indirectly delineate mineralization criteria such as faults or host rock configurations as well as to directly detect sulphide orebodies. Seismic, magnetic and gravity surveys have been successful in detecting basement highs beneath thick sedimentary successions. Basement topography is often influential in the migration of ore fluids by focusing upward flow through these highs. Deposits at Pine Point are situated above or near basement highs influencing the development of facies trends, paleokarsts and faults in the overlying Phanerozoic succession. Airborne magnetic surveys were successfully employed in the southeast Missouri district to delineate buried Precambrian topography (Leach et al., 1995). Aeromagnetic, resistivity and gravity surveys are also useful in mapping lineaments that may prove to be faults. Radarsat and Landsat imagery are additional important tools for lineament identification.

Other potential geophysical methods for detecting MVT deposits are magnetic, gravity, reflection seismic, and borehole surveys. Dissolution and breccia formation commonly produce substantial sagging and collapse of overlying strata, sometimes an indirect indication of mineralization, which can be identified by reflection seismic methods. Seismic and gravity methods are also useful for delineating subsurface topography and faults.

Property-scale techniques

The open-space-filling nature of MVT ore, where gangue minerals and sphalerite interrupt conducting paths between conductive minerals, generally produces poor responses in electrical geophysical surveys such as self-potential (SP) and electromagnetic (EM) (Lajoie and Klein, 1979). Sphalerite is nonconductive and nonpolarizable. Calcite and dolomite are nonconductive and have very low chargeability. Galena, marcasite and pyrite, on the other hand, are electrically conductive minerals. At Pine Point, induced polarization (IP) proved to be a powerful exploration tool for finding orebodies, but only when sufficient conducting minerals occur. If an orebody consists dominantly of sphalerite, with low abundance of galena, marcasite, or pyrite, the IP response is generally too weak for positive identification. Most of the Pine Point MVT deposits discovered to date contain sufficiently high concentrations of conducting minerals to be good IP targets. There may be a number of undetectable sphalerite-rich orebodies (with respect to IP geophysics) that have not been discovered as yet in the Pine Point region. Chargeability anomalies at Pine Point are generally in the order of 10 milliseconds above background (Lajoie and Klein, 1979). Normal background variations of chargeability in volcanic terranes, for example, are of this magnitude, so 10 milliseconds above background is not detectable in these areas. The success of the IP method at Pine Point, however, depends greatly on the uniform low chargeability background of the host carbonates. Lajoie and Klein (1979) also demonstrated that weak variations of chargeability in IP surveys can sometimes be correlated with changes in lithology.

In some MVT ore deposits, such as Pine Point, there are small amounts of the weakly magnetic iron sulphide mineral, pyrrhotite, associated with pyrite and marcasite mineralization. Because Pine Point is situated in the auroral zone, where severe magnetic storms are commonplace, the weak magnetic signature associated with pyrrhotite-bearing orebodies may not be discernable. Gravity has been proven to be useful as a complementary tool with IP in locating sphalerite-rich orebodies at Pine Point, because of the significant contrast in density between sphalerite and its gangue minerals. Since sphalerite is nonpolarizable, orebodies containing sphalerite with very small amounts of conducting minerals would not be detectable by IP alone. The degree of porosity, often directly associated with mineralization, can vary significantly in the host rock at Pine Point. Lajoie and Klein (1979) indicated that this high contrast in porosity may be detectable by gravity surveys. Differentiation of porous and nonporous horizons can also be detected by borehole geophysical logs, specifically, sonic and density geophysical survey logs.

MINERAL PROSPECTIVITY MAPPING

Mineral prospectivity mapping in the Pine Point district was evaluated conceptually by applying the previously discussed critical genetic attributes and features controlling the location of MVT deposits to empirical evidence of mineralization, such as orebodies, visible lead and/or zinc mineralization in outcrop and core, and anomalous geochemical soil and rock occurrences. Various diagnostic and permissive criteria related to fluid-flow pathways, depositional traps and fluid outflow zones were analyzed in the district in order to derive a mineral potential or prospectivity map (Fig. 15). All of these criteria were derived either directly from geological and structural data or indirectly by means of geophysical and geochemical data. Five categories of mineral potential were defined dependent on the number of critical diagnostic features. Single diagnostic features that are repeated in an area (for example, intersection of faults) also increased the prospectivity on the map. It was not possible, however, to assign a weighting of critical features based on their relative importance, with respect to location of potential mineral deposits.

Critical components of a regional-scale MVT system are all related to fluid flow during dynamic basin evolution. The five components that describe a regional hydrothermal system include energy, ligand source, metal source, and transport pathways and trap zones (D'Ercole et al., 2000). The first three components cannot be predicted because of the unresolved controversy of the nature of these sources in the genetic models. Transport pathways and trap zones, however, can be predicted, and these particular components are related to specific structural and stratigraphic features associated with MVT ore deposition. Specific geological features associated with these mappable components include major basement lineaments and faults that may have acted as structural conduits for migration of ore fluids. Garven and Freeze (1984) indicated that in some cases, certain geological units such as carbonate deposits act as aquifers. Basement highs are zones along which fluids are restricted from further lateral flow and thus represent possible depositional sites. Basement highs are also responsible for localization of reef growth, which are often potential host rocks for MVT mineralization. Fluid outflow or discharge is measured by mineralogical zoning of ore or alteration minerals around the deposit. Alteration zones at Pine Point are rather narrow and quite abrupt and dispersion is limited (Skall, 1975; Kyle, 1981). At the regional district scale, the zones are insignificant and were not incorporated into the metallogenic map.

Specific diagnostic criteria for MVT mineralization at Pine Point include: 1) proximity to faults and fractures, 2) proximity to major basement lineaments, 3) spatial relationship to subsurface basement highs, 4) areas of anomalously high concentrations of base metals in bedrock or soil, 5) occurrences of reefal carbonate barrier complexes on carbonate platforms, and 6) spatial locations of paleokarst networks, and 7) Presqu'ile dolomitization (Table 4). Permissive criteria for mineralization at Pine Point include: 1) their relation to carbonate aquifers, 2) proximity to evaporites, 3) relationships with carbonate or shale aquicludes or caprocks, 4) associations with hydrocarbons, specifically pyrobitumen, and 5) marcasite and pyrite haloes. Outcrop of potential host carbonate deposits versus subcrop (6) was also considered to be an important permissive criterion in mapping prospectivity because of their widely varying potential mining costs (Table 4).

The above criteria were spatially combined with known ore deposits, lead and/or zinc occurrences and soil anomalies (as listed in Hannigan, 2005 b) to produce a MVT mineral prospectivity map of the Pine Point district (Fig. 15). Five categories of prospectivity were defined. High prospectivity

Figure 15. A mineral prospectivity map of the Pine Point district (map-area identical to that in Fig. 2). Potential rating based on a combination of known mineral occurrence and number and intensity of various diagnostic and permissive factors recognized in the area that are directly or indirectly related to MVT mineralization. See text for further discussion.

represents areas containing orebodies or visible mineral occurrences with an additional four to seven diagnostic or permissive factors. High to moderate prospectivity indicates areas of geochemical anomalies and/or four to seven factors. Moderately prospective areas have three diagnostic or permissive factors, low to moderate two factors, and low prospective areas have one or no factors.

The most significant factor outweighing all other criteria is the presence of lead and /or zinc sulphide mineralization in the form of orebodies or visible mineral occurrences. The remaining diagnostic factors were considered to be of intermediate importance. Permissive factors represent the least important criteria for MVT mineralization at Pine Point. Further refinement of the relative importance of each factor would require an intimate knowledge of the strategy employed by explorationists at Pine Point in each of their exploration programs, their individual drill targets, and the

Table 4. Diagnostic and permissive criteria applicable to critical components of Pine Point MVT mineralization

Diagnostic criteria
• MVT mineralization in orebodies or visible occurrences
• Near areas of anomalous concentrations of Pb or Zn in soils or bedrock
• Presqu'ile dolomitization
• Proximal to or within faults and fractures
• Near major basement lineaments
• Spatially related to basement highs
• Proximal to or within reefal carbonate barrier complexes on carbonate platforms
• Proximal to paleokarst networks
Permissive criteria
• Relation to carbonate aquifers
• Proximity to evaporite successions
• Relation to aquiclude cap-rocks
• Association with hydrocarbons
• Marcasite and/or pyrite haloes
• Proximity to surface (outcrop vs. subcrop)

rate of success in finding new orebodies with respect to specific diagnostic or permissive factors. This knowledge is not available, so it is not possible to refine any further the relative importance of specific individual factors.

Figure 15 suggests significant potential in the immediate Pine Point mine site along the Main, North and South hinge zones continuing farther west under Upper Devonian carbonate cover along the trend of the Main Hinge (*see* Fig. 2 of this paper and Fig. 3 in Introduction paper by Hannigan, 2006 for geographic and hinge zone locations). Areas of high potential are also indicated in the Heart Lake area and near Pte. Desmarais on the southern shore of Great Slave Lake. Significant MVT potential is also expected in the Slave Point/Windy Point/Sulphur Bay area on the southwestern shore of Great Slave Lake. High to moderate potential is observed in the Escarpment Lake area, along the Hay River and in the Tathlina Lake area. A significant area of high to moderate potential is also interpreted in the Moraine Point area of southwestern Great Slave Lake. Significant regions of moderate potential surround the Pine Point mining camp, encompass the lower Hay River and occur in proximal areas to major fault zones in the western portion of the district underlain by the Presqu'ile barrier.

Insufficient information was available to extend this mineral prospectivity mapping exercise to areas beyond the Pine Point district, principally because of the widespread scattered sampling density over a very large area of northern Alberta in the WSCB. Work completed in northern Alberta (Rice and Lonnee, 2006) indicate that insufficient diagnostic criteria are present for effective mapping of MVT mineral potential using the method described above. However, Pană (2006; his Fig. 21) presents prospective areas of basement strain-related hydrothermal dolomitization with potential MVT mineralization in Alberta, with respect to major basement faults, shear zones and buried reef trends. Extensive geochemical sampling along approximately 200 km of Devonian carbonate exposure in the Athabasca, Clearwater and Peace river systems in northern Alberta, commonly described as representing the classical discharge area of the Alberta Basin, revealed low MVT potential (Eccles and Pană, 2003). This lack of significant metallic concentration in areas of discharge would refute the basinal fluid flow model for metal concentration if present fluid flow is representative of past fluid-flow, and may confirm the relationship of dolomitization and metallic concentration to fluid movement along vertical fractures (Eccles and Pană, 2003). Although the Pb and Zn metallic concentrations were low in these Devonian outcrop exposures in northern Alberta, significant Fe-concentrations in the form of local, thin iron-rich layers on top of the Devonian succession and numerous iron- and sulphide-rich nodules at the base of the overlying bitumen-rich McMurray Formation, are intimately associated with vertical fracture zones.

SUMMARY

1. The synthesis and metallogenic analysis of MVT mineralization in the TGI project area were accomplished by means of the establishment of source, flow-path and timing of dolomitizing and mineralizing fluid movement and the relation of these fluids to the regional stratigraphic and structural framework.
2. At Pine Point, orebodies are generally restricted to zones of weakness or hinge lines where extensive networks of interconnected paleokarst developed. Within these paleokarstic networks prismatic and tabular ore accumulations were deposited in hydrothermally derived dolomite breccias. The most typical host lithology for MVT orebodies at Pine Point is the coarse-grained vuggy Presqu'ile dolomite, an extensive, diagenetic, secondary dolomite facies that was formed relatively late in the paragenetic history of the Presqu'ile barrier complex.
3. Pre-ore conditions of carbonate phases in the project area indicate early dolomite formed penecontemporaneously at or just below the seafloor from Middle Devonian seawater. Shallow burial conditions prevailed during the time of medium-crystalline dolomitization.
4. The ore-stage coarse-crystalline vuggy matrix Presqu'ile dolostone, secondary saddle dolomite, open-space filling cements, and sphalerite and galena sulphide crystals are characterized by lower $\delta^{18}O_{PDB}$, slightly depleted $\delta^{13}C_{PDB}$ and similar $^{87}Sr/^{86}Sr$ isotopic values at Pine Point. The depleted $\delta^{18}O_{PDB}$ indicative of higher precipitation temperatures is confirmed by elevated fluid inclusion homogenization temperatures. Final melting temperatures show that formation fluids were hyper-

saline brines and eutectic or initial melting temperatures suggest they were fluids derived from the $NaCl-CaCl_2-H_2O$ salt system.

5. Previous studies delineated a broad westward decrease of $\delta^{18}O_{PDB}$ with a related increase of Th, along with an increase of $^{87}Sr/^{86}Sr$ within the Presqu'ile barrier. These geochemical trends are attributed to higher temperature dolomitizing fluids and the influence of siliciclastic sources, respectively. Data from this project challenges these identified trends and displays rather variable and inconsistent spatial distribution of stable and radiogenic isotopes.

6. A significant increase of $^{87}Sr/^{86}Sr$, proximal to the Great Slave Shear Zone, suggests that a key role is attributable to the shear zone in that it provided a favourable site for the upward circulation of hydrothermal fluids from basement and precipitation of hydrothermal dolomite and sulphides in overlying porous carbonate rocks.

7. Ore-stage dolomite formation postdated deep burial because of crosscutting relationships with depositional fabrics, formational boundaries, and unconformities, the replacement of blocky sparry calcite cement previously formed in the subsurface, the crosscutting of stylolites, depleted $\delta^{18}O_{PDB}$ values meaning higher precipitation temperatures attributable to burial, and the presence of two-phase fluid inclusions and fluorescent petroleum inclusions.

8. Generally, fluid inclusion filling temperatures in ore-stage dolomite and sphalerite are too high to be attributed solely to burial, indicating that thermal anomalies are necessary in regions of enhanced MVT mineral potential.

9. Post-ore calcite shows depleted $\delta^{18}O_{PDB}$ and $\delta^{13}C_{PDB}$ compared to pre-ore calcite. The higher temperatures associated with depleted $\delta^{18}O_{PDB}$ can be attributed to burial, but the fluid inclusion melting temperatures indicate a less saline fluid of contrasting brine composition ($NaCl-H_2O$). Homogenization temperatures in late-stage calcite are about 10°C cooler than those of saddle dolomite present at the same location. The reduced salinity may have been brought about by late mixing of meteoric water.

10. Chemical analyses of fluid inclusions in sphalerite and dolomite indicate that the transporting fluid consisted of dense brine derived from highly evaporated seawater, similar to oilfield brines. However, the K/Na cation mole ratios in these fluid inclusions are greater than in oilfield brines, suggesting the ore-stage dolomite fluids are more evolved than evaporated seawater and are composed of interstitial fluids derived from evaporite beds that are enriched in residual K.

11. Lead isotope values in the region exhibit two distinct populations: a Cordilleran carbonate trend interpreted as a mixture of upper crustal lead and siliciclastic-derived anomalous radiogenic lead, and a 'Pine Point' cluster of much less radiogenic and homogeneous isotopes. Two areas where the Cordilleran carbonate lead population were expected because of their geographic location, are proximal to the Great Slave Shear Zone in northwestern Alberta, and within the Cordova Embayment of northeastern British Columbia. Lead isotope results from galena and sphalerite samples from these two locations are remarkably consistent with the 'Pine Point' cluster, suggesting at least some degree of structural control with respect to Pb-Zn mineralization in the region.

12. The metals at Pine Point were likely derived from upwelling hydrothermal solutions originating in the basement and focused along fault zones directly forming the thermal anomalies. Sulphur was likely derived from seawater sulphate.

13. Fluid flow of dolomitizing solutions possibly took place by means of the thermal convection model, where buoyancy forces related to temperature and salinity variations formed individual crossformational convection cells. An attractive aspect of this model is that continuous vertical recycling of connate brines provided ample opportunity for the development of open-space dolomite cements. This dolomite was derived from halite-saturated residual brines from evaporite beds in the Devonian Elk Point subbasin.

14. Mineral prospectivity or metallogenetic mapping completed in the Pine Point mineral district depended on identification of critical components of the regional-scale MVT system related to fluid flow during dynamic basin evolution. Predictions of transport pathways and trap zones were completed and were related to specific diagnostic structural and stratigraphic features such as major basement lineaments and faults, carbonate aquifers and overlying siliciclastic aquitards, basement highs restricting lateral fluid flow and providing sites for possible reef growth, and the spatial locations of the paleokarst network and Presqu'ile dolomite development. Permissive criteria such as proximity to evaporite beds, association with hydrocarbons and marcasite and pyrite haloes were also incorporated into the metallogenic map.

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