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Dating and Duration of Fluid Flow and Fluid–Rock Interaction

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Contents

Geochemical constraints on the origin and timing of palaeofluid flow in the Presqu'ile barrier reef, Western Canada Sedimentary Basin

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Abstract: The Mississippi Valley-type ore deposits at Pine Point are spatially and genetically associated with saddle dolomite cements. The origin and timing of fluid flow that produced these ore deposits are, therefore, constrained by paragenesis and geochemistry of the saddle dolomite cements. Because saddle dolomites occur continuously across the sub-Watt Mountain unconformity, dolomitization and associated mineralization must have occurred after the sub-Watt Mountain exposure during burial. The lateral continuity of saddle dolomite along the barrier for 400 km suggests that dolomitization and mineralization were probably associated with the lateral fluid migration along the barrier reef.

From northeastern British Columbia to Pine Point, over a lateral distance of 400 km, saddle dolomites display remarkable trends of decreasing $^{87}Sr/^{86}Sr$ ratios (0.7106 to 0.7081) and homogenization temperatures of fluid inclusions (178°C to 92°C) with a corresponding increase in $\delta^{18}O$ values (−16‰ to −7‰ PDB). These regional trends suggest that hot, radiogenic basinal fluids moved eastward up-dip along the Presqu'ile barrier reef. The movements of basinal fluids were probably related to tectonic compression and sedimentary loading on the western margin of the Western Canada Sedimentary Basin during either the late Devonian–early Carboniferous (Antler Orogeny) or the Jurassic–early Tertiary (Columbia–Laramide Orogenies).

The δD values of aqueous fluid inclusions from Pine Point dolomite are very low (−80‰ SMOW to −100‰ SMOW) compared with that of Devonian seawater (−10‰ SMOW) suggesting an input of some Columbia–Laramide meteoric waters. If the low δD values are caused by a mixture of fluids from primary inclusions containing Devonian seawater with secondary inclusions that formed later during the Columbia–Laramide Orogenies, the fluid migration and associated dolomitization and mineralization could be interpreted as late-Devonian events. However, if the measured fluids were mostly from the primary inclusions, the low δD values indicate an entrapment of some Columbia–Laramide meteoric waters with Devonian formation waters at the time of dolomitization. This would suggest a Jurassic to early Tertiary age for dolomitization, which is supported by similar low δD values of present-day Devonian formation waters that consist of a mixture of Laramide meteoric waters and original connate brines. The light δD values of Pine Point dolomite inclusions could also occur as a result of reaction of fluids with organic matter associated with generation of oil and gas, which occurred at the maximum burial during the Laramide Orogeny.

When sedimentary rocks are buried beneath thrust sheets, pore fluids and those derived from hydrated minerals may be expelled and injected into adjacent foreland basins via fracture and regional aquifer systems (Oliver 1986). These tectonically expelled fluids may play an important role in the diagenesis, mineralization, and hydrocarbon accumulation in sedimentary basins (e.g. Dorobek 1989; Qing & Mountjoy 1992, 1994*a*, *b*; Montañez 1994; Nesbitt & Muehlenbachs 1994; Machel *et al.* 1996).

Mississippi Valley-type (MVT) ore deposits at Pine Point are hosted in carbonate rocks of the Middle Devonian Presqu'ile barrier reef, which extends from outcrops at Pine Point westward for about 400 km into the sub-surface of northeastern British Columbia where its present burial depth is up to 2 km. In spite of a number of studies on the MVT deposits at Pine Point during the past 20 years, there is no general consensus on the precise timing of mineralization. The timing of mineralization was broadly constrained as late Devonian by Rb–Sr dating (Nakai *et al.* 1993), Pennsylvanian to Permian by lead isotope dating (Kyle 1981; Cumming *et al.* 1990), Late Cretaceous to early Tertiary by fission track dating (Arne 1991) and palaeomagnetic data (Symons *et al.* 1993). Garven (1985, 1986) used numerical modelling to show that topography-driven basinal brines flowing eastward along the Presqu'ile barrier reef at rates of 1–5 m per year were capable of producing Pine Point MVT deposits during the late Cretaceous to early Tertiary. Because the sulphide minerals at Pine Point are spatially and genetically associated with saddle dolomite cements,

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a regional petrographic study and geochemical analysis of these saddle dolomites along the Presqu'ile barrier reef may provide additional information in our understanding of fluid flow responsible for Pb–Zn deposits at Pine Point.

The purpose of this paper is to investigate the origin and timing of the fluid flow in the Presqu'ile barrier reef using existing geochemical and geological information. The guiding rationale for this study is that there should be internal consistency among different types of data with respect to any particular model for the fluid migration and associated dolomitization and mineralization. The primary data sources are Qing & Mountjoy (1992, 1994*a*, *b*) for O and Sr isotopes and fluid inclusion homogenization temperatures of dolomite cements from the Presqu'ile barrier reef (Table 1), Nesbitt & Muehlenbachs (1994) for δD values of fluid inclusion from Pine Point dolomite cements, Connolly *et al.* (1990) for H and Sr isotopes of formation waters from central Alberta, and Knauth & Roberts (1991) for H isotopes of halite-hosted fluid inclusions from the Western Canada Sedimentary Basin. Details concerning methods for data acquisition and data reporting are contained in these publications.

Geological setting

The Middle Devonian Presqu'ile barrier reef is located in the northern part of the Western Canada Sedimentary Basin (Fig. 1). It is about 400 km long and 20 to 100 km wide, extending from outcrops in the Northwest Territories into the sub-surface of northeastern British Columbia (Fig. 1). Pine Point is located at the east end of the barrier reef (Fig. 1), where carbonate rocks host more than 80 individual MVT ore bodies (Skall 1975; Kyle 1981, 1983; Krebs & Macqueen 1984; Rhodes *et al.* 1984; Qing & Mountjoy 1994*a*, *b*). The development of the Presqu'ile barrier reef restricted seawater circulation in the southern part of the Western Canada Sedimentary Basin during Middle Devonian time (Williams 1984). As a result, evaporites and carbonates were deposited south of the barrier reef in the Elk Point Basin, whereas normal marine shales and argillaceous carbonate were deposited north of the barrier reef (Fig. 1).

The McDonald Fault Zone underlies the southeastern part of the Presqu'ile barrier reef (Fig. 1). This fault zone is a major tectonic feature of the Canadian Precambrian Shield and forms the boundary between the Slave and

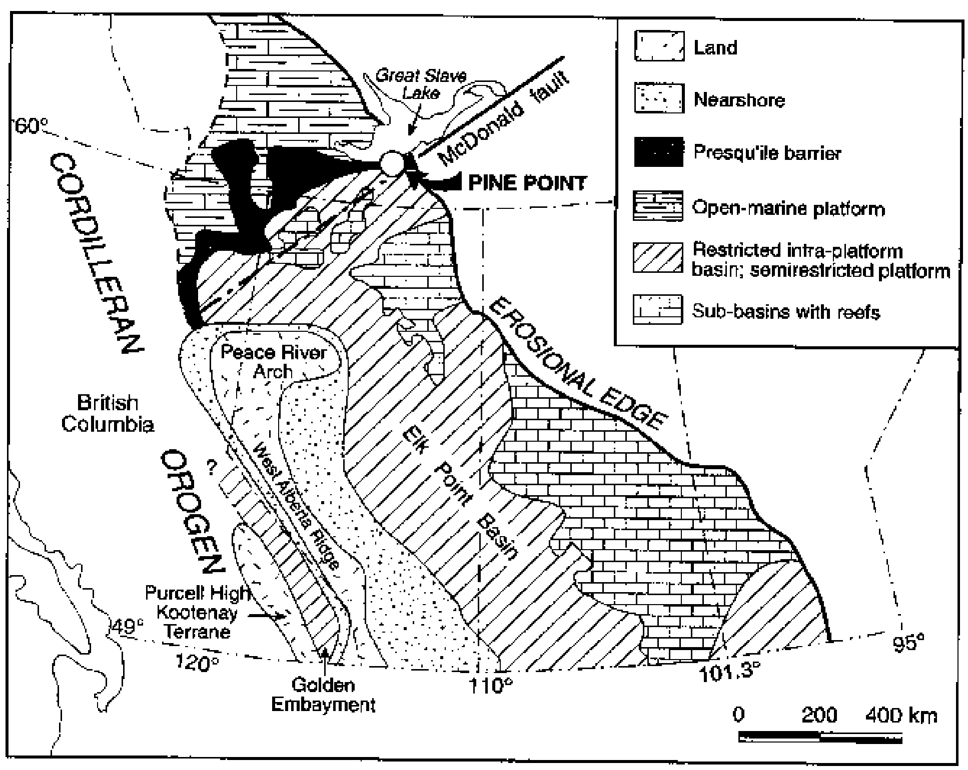

Fig. 1. Simplified regional geological map of the Western Canada Sedimentary Basin during Middle Devonian. The Presqu'ile barrier extends from outcrops in the Pine Point area westward into the sub-surface of Northwest Territories and northeastern British Columbia (modified after Qing & Mountjoy 1994*a*).

Table 1. *Analytical data of saddle dolomite cements from the Presqu'ile barrier reef*

Location	Depth (m)	Longitude	$\delta^{18}O$	$\delta^{13}C$	$^{87}Sr/^{86}Sr$	Avg. Th (st. dev.)
Samples from Pine Point						
Pit-M64	open pit	114.4	−10.42	−0.29		
Pit-M64	open pit	114.4	−10.27	−0.35	0.70831	
Pit-M64	open pit	114.4	−10.47	−0.72		
Pit-M64	open pit	114.4	−9.57	0.42		
Pit-M64	open pit	114.4	−9.54	0.72	0.70840	
Pit-P77	open pit	114.4	−10.05	−0.11	0.70818	
Pit-P77	open pit	114.4	−9.02	0.12	0.70818	
Pit-T37	open pit	114.4	−8.92	1.52		
Pit-T37	open pit	114.4	−7.32	1.11		
Pit-T37	open pit	114.4	−7.36	1.20		
Pit-X15	open pit	114.4	−9.59	0.70		
Pit-X15	open pit	114.4	−8.03	−0.11		
Pit-X51	open pit	114.4	−8.30	1.27		
Pit-X51	open pit	114.4	−8.07	1.13		
Pit-X51	open pit	114.4	−8.32	1.53		
Pit-X51	open pit	114.4	−7.03	1.24		
Pit-X51	open pit	114.4	−7.77	1.62		
Pit-X51	open pit	114.4	−8.01	1.69		93 (4.6)
Pit-X53	open pit	114.4	−9.41	1.18		
Pit-X53	open pit	114.4	−7.71	1.18		
Pit-X53	open pit	114.4	−8.52	1.08		
Pit-Y53	open pit	114.4	−8.43	1.22	0.70816	
Pit-Y56	open pit	114.4	−8.15	1.45		
Pit-Y56	open pit	114.4	−8.07	1.61		
Pit-P24	open pit	114.4	−9.21	0.56		99 (9.6)
Pit-P24	open pit	114.4	−9.40	0.54		
Pit-N81	open pit	114.8	−7.38	0.42		
Pit-N81	open pit	114.8	−8.51	0.19	0.70821	106 (6.8)
Pit-N81	open pit	114.8	−10.39	0.13		
Pit-N81	open pit	114.8	−10.22	−0.40	0.70807	
Borehole-2822	106.4	114.9	−8.88	0.14		
Borehole-2822	77.1	114.9	−10.76	−1.22		
Borehole-2822	86.0	114.9	−11.12	−0.91		
Borehole 2822	83.8	114.9	−10.04	−0.55	0.70847	
Samples from Northwest Territories						
Hay River, E30	225.6	115.8				116 (6.0)
NWT PET Escarpment L No.1, A77	470.9	116.2	−10.99	−2.24		
General Grude Ranvik Reef, G15	279.2	116.3	−12.35	−0.20	0.70850	112 (2.2)
NWT Desmarais Lake 1, C19	478.2	116.8	−12.78	1.66	0.70839	114 (7.6)
Tathlina Lake, D50	578.8	117.2	−12.30	[illegible] (24.6)		
H.B. Cameron, A-05	1417.9	117.5	−10.56	0.20		
Placid Wood W. Tathlina, K48	937.3	117.9	−12.03	−0.24	0.70859	
Pacific Cameron, M05	1277.4	118.3	−11.82	−1.[illegible] (5.9)		
Wilkinson Redknife River No 2, E33	984.2	119.4	−12.77	−1.25	0.70918	140 (13.5)
Union Pan Am Trainor, O72	1783.7	120.2	−16.01	−0.08	0.70895	144 (13.8)
Union Pan Am Trainor, O72	1784.9	120.2	−15.50	0.08		
Samples from north-eastern British Columbia						
b-22-b/94-P-10	1905.6	120.5	−13.28	−1.53		168 (26.1)
d-37-b/94-I-7	2042.8	120.5	−13.12	−0.53		154 (26.7)
c-09-d/94-P-06	2267.4	121.3	−13.02	−2.59	0.70942	
b-40-a/94-P-05	2143.4	121.3	−14.47	−3.38		
b-40-a/94-P-05	2148.2	121.3	−14.13	−3.45		
b-40-a/94-P-05	2148.2	121.3	−13.61	−2.31	0.70920	
b-40-a/94-P-05	2119.0	121.3	−12.89	−0.50		164 (7.2)
b-40-a/94-P-05	2124.8	121.3	−13.23	−1.34	0.70955	179 (20.8)
b-40-a/94-P-05	2134.5	121.3	−13.87	−3.65		
b-40-a/94-P-05	2141.2	121.3	−13.06	−1.22		
c-60-e/94-I-11	2022.0	121.4	−14.91	0.03	0.71060	

The reproducibility is 0.1‰ for oxygen and carbon isotopes, and 0.0025% for Sr isotopes (see Qing & Mountjoy, 1994*a* for analytical details)

Churchill tectonic provinces (Ross *et al.* 1991). Based on aeromagnetic data, it can be traced from the Canadian Shield into the sub-surface of the Northwest Territories, northwestern Alberta, and northeastern British Columbia (Jones 1980; Ross *et al.* 1991) (Fig. 1). It has been speculated that this basement fault system might have played a role in transmitting diagenetic fluids for dolomitization and mineralization at Pine Point (e.g. Campbell 1966; Skall 1975; Krebs & Macqueen 1984; Hitchon 1993). The role of this fault zone during Devonian sedimentation was questioned by Rhodes *et al.* (1984) because the strata immediately beneath the barrier are 'of uniform thickness without any signs of vertical displacements'. However, small-scale movements may have occurred along or across the McDonald Fault system during Devonian time, leading to the formation of some fractures in parts of the Presqu'ile barrier reef, thus enhancing its role as a regional fluid conduit system (Skall 1975).

Diagenetic paragenesis and spatial distribution

Saddle dolomites (also called sparry dolomite cement or white dolomite cement) in the Presqu'ile barrier reef are regionally extensive, late-stage diagenetic products, which occur mainly as cement in vugs and fractures in coarse-crystalline massive replacement dolomites (Fig. 2A). In hand specimens, saddle dolomite cements have a distinctive white colour and usually consist of coarse (millimetre-sized) dolomite crystals. The crystal shape ranges from rhombohedral to symmetrical saddle forms. Saddle dolomite has a diagnostic sweeping extinction pattern under cross-polarized light, and a dull red cathodoluminescence.

At Pine Point, saddle dolomites are associated closely with sulphide minerals, filling vugs and breccias in the coarsely crystalline replacement dolomites (Skall 1975; Kyle 1981, 1983; Rhodes *et al.* 1984; Krebs & Macqueen 1984; Qing & Mountjoy 1994*a*, *b*). Extensive dissolution vugs and breccias developed in the Presqu'ile barrier reef as a result of meteoric water influence during sub-Watt Mountain sub-aerial exposure and later invasion of the hydrothermal fluids during burial (Kyle 1981, 1983; Rhodes *et al.* 1984; Krebs & Macqueen 1984; Qing & Mountjoy 1994*b*). These dissolution vugs and breccias are typically filled first with pre-ore saddle dolomite cement, followed by early-stage sulphide minerals (e.g. colloform sphalerite, Fig. 2B). In some cases, saddle dolomite with a mixture of crystalline galena or sphalerite precipitated after earlier saddle dolomite in vugs and fractures (Fig. 2C). Locally, the pre-ore saddle dolomite and sulphide minerals are fractured and filled with post-ore saddle dolomite (Fig. 2B). The sulphide minerals commonly are followed by post-ore saddle dolomites that fill most of the remaining vugs and fractures. Finally, some vugs and breccias are filled with late-stage coarse-crystalline calcite and pyrobitumen. The timing of saddle dolomite precipitation, therefore, overlaps with Pb–Zn mineralization at Pine Point.

At Pine Point, saddle dolomites and associated mineralization occur most commonly in the upper part of the barrier reef in the Sulphur Point Formation. In the western part of the Pine Point property, where the strata above the Watt Mountain unconformity are preserved, saddle dolomites and sulphide minerals extend locally above the unconformity into the Watt Mountain and the lower part of the Slave Point Formations (Fig. 3). Clearly, dolomitization occurred after sub-Watt Mountain exposure (Qing & Mountjoy 1994*a*, *b*). Furthermore, the lack of significant occurrence of saddle dolomite and sulphide minerals in the regional carbonate platform (the Keg River Formation), which occurs immediately beneath the Presqu'ile barrier reef, discounts the credibility of the hypothesis that mineralizing hydrothermal fluids rose vertically through the McDonald Fault Zone in the vicinity of Pine Point area (e.g. Hitchon 1993). The lateral continuity of saddle dolomite along the barrier for 400 km and its occurrences mostly in the Sulphur Point Formation suggest that dolomitization and associated mineralization were probably associated with lateral fluid migration along the barrier reef (Qing & Mountjoy 1992, 1994a).

Geochemistry of saddle dolomite and basin fluids

Oxygen and strontium isotopes, and homogenization temperatures of fluid inclusions were analysed for the saddle dolomite cements (Table 1; Fig. 4). The obtained data display distinct regional trends from northeastern British Columbia, eastward along the Presqu'ile barrier reef, to Pine Point (Fig. 4). Saddle dolomites from the deeper sub-surface of northeastern British Columbia have lower $\delta^{18}O$ values, ranging from −15‰ to −13‰ PDB (Fig. 4A). The $\delta^{18}O$ values of saddle dolomite cements gradually increase eastward along the Presqu'ile barrier reef, and reach −7‰ PDB at Pine Point (Fig.

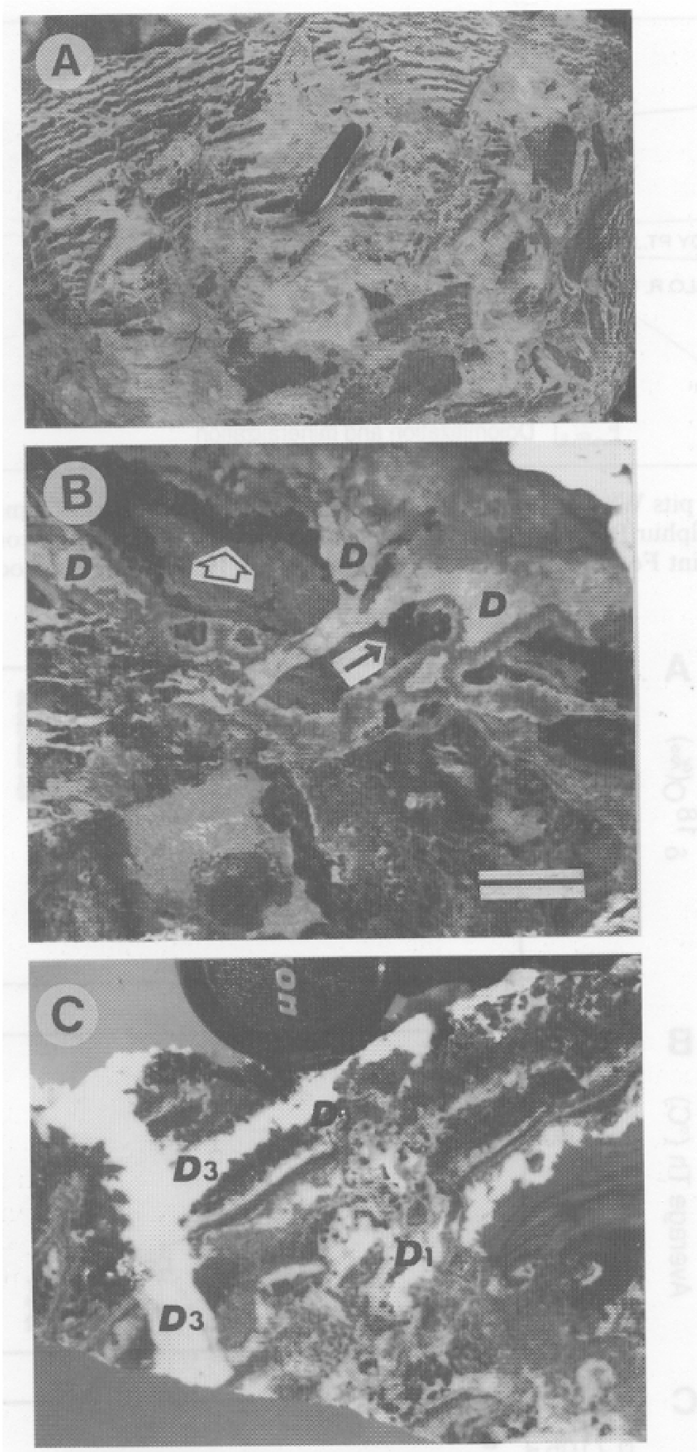

Fig. 2. Petrographic features of saddle dolomites and associated sulphide minerals (from Qing & Mountjoy 1994*a*). (**A**) Vugs and fractures in coarse-crystalline dolomite (grey) are filled with saddle dolomite (white), forming a 'zebra' texture. Location: Sulphur Point Formation, pit X53, Pine Point. Swiss knife for scale. (**B**) Vugs and fractures in colloform sphalerite (dark bands, arrows) are filled with saddle dolomite (D), indicating that dissolution, brecciation and dolomitization postdate mineralization. Location: Sulphur Point Formation, pit M64, Pine Point. Scale bar 15 cm. (**C**) Dissolution vugs and fractures filled with saddle dolomites (D1, D2 and D3) and sulphide minerals. Some saddle dolomites (D1) precipitated prior to, some (D2) are mixed with, and some (D3) postdate sulphide minerals. Location: Sulphur Point Formation, Pit X53, Pine Point. Camera lens cap for scale.

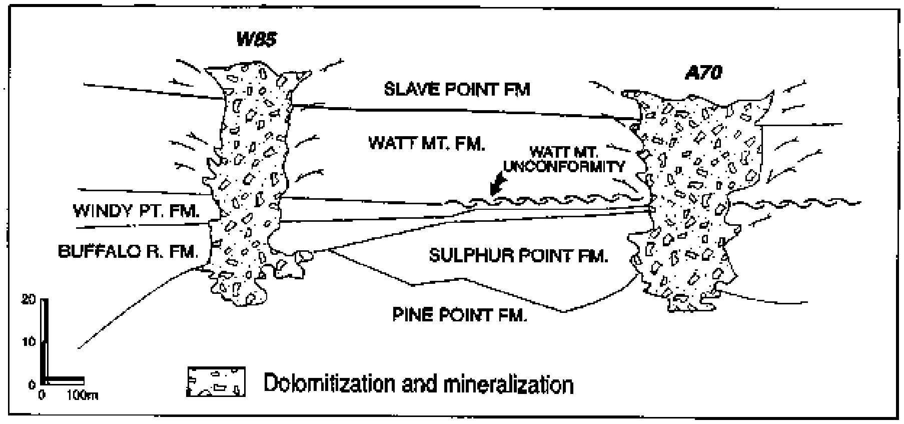

Fig. 3. Cross-section of pits W85 and A70, schematically illustrating zones of dolomitization and mineralization that extend from the Sulphur Point Formation, across the sub-Watt Mountain unconformity, into the Watt Mountain and Slave Point Formations (from Qing & Mountjoy 1994*a*) which is modified after Rhodes *et al.* (1984)).

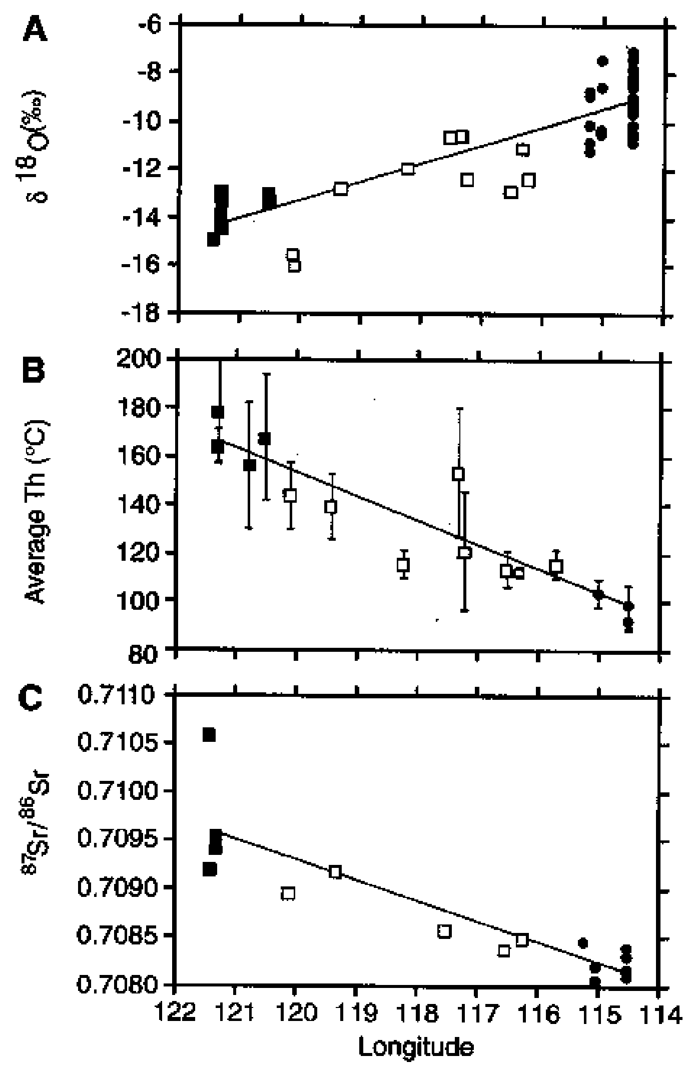

Fig. 4. Cross-plots of (A) $\delta^{18}O$ (PDB), (B) homogenization temperatures (Th), and (C) $^{87}Sr/^{86}Sr$ of saddle dolomite cements vs. longitude. Dots are Pine Point samples, open squares are samples from Northwest Territories, and solid squares are samples from northeastern British Columbia (modified after Qing & Mountjoy 1992, 1994*a*).

4A). This $\delta^{18}O$ trend is interpreted to be caused by dolomite precipitation at decreasing temperatures eastward along the barrier reef, as indicated by decreasing homogenization temperatures of saddle dolomite fluid inclusions.

Two-phase (aqueous liquid–vapour) primary fluid inclusions were analysed from 14 saddle dolomite samples from 13 localities. The average homogenization temperatures of fluid inclusions in saddle dolomite samples decrease eastward along the Presqu'ile barrier reef from 178°C in northeastern British Columbia to 92°C at Pine Point (Fig. 4B). Because these homogenization temperatures exceed the maximum burial temperatures of the Presqu'ile barrier reef (Qing 1991; Mountjoy & Amthor 1994), dolomitization and associated mineralization at Pine Point, therefore, represent a regional hydrothermal event (Skall 1975; Macqueen & Powell 1983; Krebs & Macqueen 1994; Qing & Mountjoy 1994*a*, *b*; Rhodes *et al.* 1984).

In northeastern British Columbia, the $^{87}Sr/^{86}Sr$ ratios of four saddle dolomites are the most radiogenic, ranging from 0.7094 to 0.7106 (Figs 4 and 5). These values are much more radiogenic than the $^{87}Sr/^{86}Sr$ ratios of Middle Devonian seawater (0.7078 to 0.7081) reported by Burke *et al.* (1982) (Fig. 5). Eastward up-dip along the Presqu'ile barrier reef, the $^{87}Sr/^{86}Sr$ ratios of saddle dolomites gradually decrease, to about 0.7081 at Pine Point (Fig. 4C), which is close to the $^{87}Sr/^{86}Sr$ ratios of Middle Devonian seawater. Connolly *et al.* (1990) analysed Sr isotopes of Devonian formation waters from Central Alberta about 500 km south of the Presqu'ile barrier reef. These waters were sampled from petroleum boreholes at depth ranging approximately from 1000 m to 1700 m. Thirteen Sr isotope analyses of these Devonian formation waters range from 0.70872 to 0.71285 (mean 0.7103), which overlap the values of saddle dolomite from northeastern British Columbia that were sampled from similar distances relative to the Cordilleran disturbed belt (Fig. 5).

The systematic isotopic analyses of fluid inclusions hosted in different ages of halites by Knauth & Roberts (1991) suggested that Devonian seawater had a δD value of approximately −10‰ SMOW (Fig. 6). Thirty-one measurements of halite-hosted fluid inclusions from the Muskeg and Prairie Formations of the Western Canada Sedimentary Basin yielded δD values from −7 to −77‰ SMOW (mean −28.7‰ SMOW). These δD values are distinctly higher than the δD values of dolomite-hosted fluid inclusions from Pine Point (−80 to −100‰ SMOW) reported by Nesbitt & Muehlenbachs (1994) (Fig. 6). The δD values of 12 present-day Devonian formation waters from central Alberta range from −58 to −104‰ SMOW (mean −82‰ SMOW) (Connolly *et al.* 1990), overlapping with δD values of fluid inclusions from Pine Point dolomites (Fig. 6). However, the δD values of formation waters from Upper Cretaceous strata range from −99 to −127‰ SMOW, which are distinctively lower than those of Pine Point dolo-

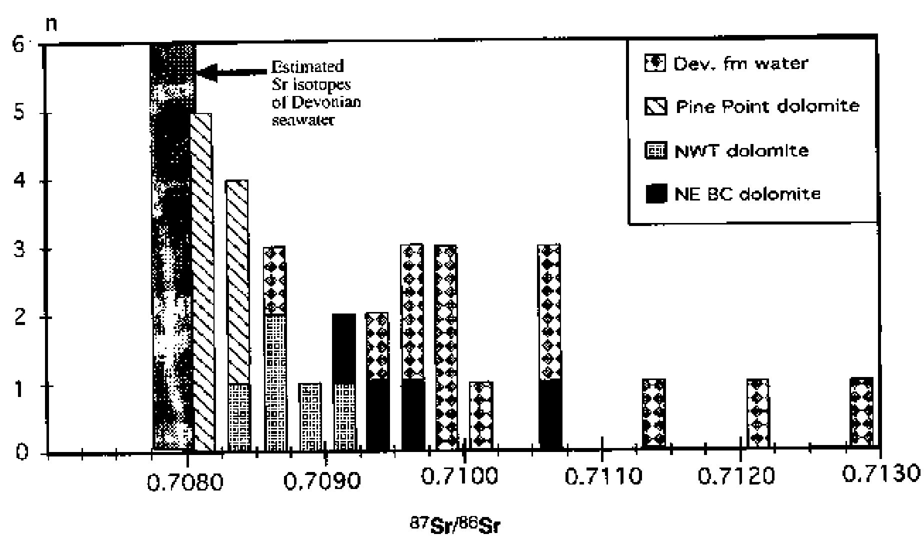

Fig. 5. Histogram of Sr isotopes for Presqu'ile saddle dolomite cement from Pine Point, Northwest Territories, and northeastern British Columbia. The Sr isotopes of Devonian formation waters from Central Alberta were based on Connolly *et al.* (1990). The $^{87}Sr/^{86}Sr$ ratios of Middle Devonian seawater were estimated in the range of 0.7078 to 0.7081 according to Burke *et al.* (1982). Note that the Sr isotopes of formation waters partially overlap those of dolomites from northeastern British Columbia that were sampled from similar burial depth as formation waters.

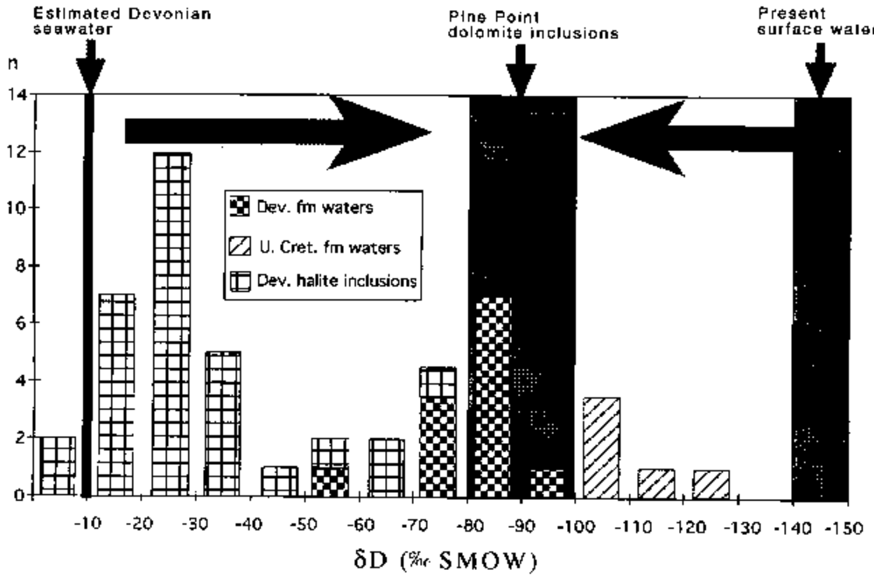

Fig. 6. Histograms of δD values for Devonian and Upper Cretaceous formation waters (data from Connolly *et al.* 1990) and Devonian halite-hosted inclusions (data from Knauth & Roberts 1991). The background values of Pine Point dolomite fluid inclusions come from Nesbitt & Muehlenbachs (1994), the present surface waters of central Alberta from Hitchon & Friedman (1969), and Devonian seawater from Knauth & Roberts (1991). The low δD values of Pine Point dolomite inclusions can be interpreted as a result of mixing of some Columbia–Laramide meteoric waters with the original Devonian basinal brines, but they do not offer a unique solution to the timing of fluid migration and associated dolomitization and mineralization at Pine Point as they could come from either primary or secondary inclusions (see text for further discussion).

mite inclusions but higher than δD values of present surface waters (−134‰ to −163‰ SMOW) from rivers and lakes from central Alberta (Hitchon & Friedman 1969; Fig. 6).

Discussion

Oliver (1986) suggested that fluids can be expelled from continental margin sediments and injected into adjacent foreland basins by tectonic compression when sedimentary rocks are buried beneath thrust sheets in zones of convergence. Tectonic-driven fluid flow can play an important role in diagenesis, mineralization, and hydrocarbon accumulation in sedimentary basins (Oliver 1986). Numerical calculations by Ge & Garven (1989, 1992, 1994) suggested that tectonic compression can create fluid flow in foreland basins, at maximum rates on the order of centimetres per year. The propagation of thrusting across the foreland wedge could ultimately result in the displacement of deep basinal fluids over long distances, although the volume of fluid migration is relatively small compared with topography-driven flow (Ge & Garven 1989).

The recent compilation of formation data in this part of the Western Canada Sedimentary Basin let Bachu (1997) conclude the following important points: (1) the present-day fluid flow is at steady state and driven by the present-day topography; (2) the flow in Devonian aquifers is an open system from the recharge area in the south-west at the fold belt to the discharge area in the north-east at Great Slave Lake; (3) the flow rates are much higher in the Presqu'ile barrier reef than elsewhere in the Western Canada Sedimentary Basin, because of extremely high core-plug and well-scale porosity and permeability measurements (up to 44% and 20×10^{-12} m^2, or 20 darcys, respectively) in the Presqu'ile barrier reef relative to the lower values for the platform carbonates and siliclastic aquifers (6–18% and 1–18 md, respectively). This suggests that focused flow probably occurs along the barrier reef (Bachu 1997). The origin and timing of fluid flow in the Presqu'ile barrier reef can be constrained by the geochemistry of saddle dolomite cements and basinal fluids.

Implication of $\delta^{18}O$, Th, and $^{87}Sr/^{86}Sr$ data

When hot fluids were expelled from deeply buried sediments and/or crystalline basement into the barrier reef during tectonic compression and sedimentary loading, the temperatures in the conduit might have increased. This would explain why the homogenization temperatures of saddle dolomite fluid inclusions exceed the maximum burial temperatures. Numerical simulations of the thermal constraints on overthrusting and topographically driven fluid-flow systems suggest that a significant amount of heat can be transported up-dip in adjacent sedimentary basins, provided the fluid flows are channelled and focused along regional conduit systems (Garven 1985, 1989; Deming *et al.* 1990; Deming & Nunn 1991; Nunn & Deming 1991; Deming 1992). The Presqu'ile barrier reef, therefore, appears to be able to act as a deeply buried regional palaeoconduit system, focusing and channelling basinal fluids during dolomitization and mineralization. As the fluids moved up-dip and eastward along the Presqu'ile barrier reef, they gradually cooled, resulting in decreases in homogenization temperatures and increases in $\delta^{18}O$ values of saddle dolomites (Fig. 4A, B). The hydrogeology study by Bachu (1997) also suggested that the high flow rates and the focused flow along the Presqu'ile barrier reef had advective effects on the terrestrial heat transport to the surface, leading to higher than normal burial temperatures and geothermal gradients in the Great Slave Lake area.

The eastward decrease of the $^{87}Sr/^{86}Sr$ ratio (Fig. 4C) suggests that ^{87}Sr-enriched fluids were probably derived from clastic successions down-dip, to the west, in the Lower Cambrian and the Upper Proterozoic and/or the underlying crystalline basement (Mountjoy *et al.* 1992). When ^{87}Sr-rich tectonically driven brines moved up-dip along the Presqu'ile barrier reef, they would become progressively less radiogenic as they mixed gradually with less radiogenic ambient connate/formation waters at shallower levels, or exchange with less radiogenic marine carbonates. This would explain the eastward decrease in $^{87}Sr/^{86}Sr$ ratios of saddle dolomite cements along the Presqu'ile barrier reef (Fig. 4C). The study by Machel *et al.* (1996) on Devonian carbonates in the Obed area on the south side of Peace River Arch indicated that ^{87}Sr-rich tectonic brines were expelled from the Rocky Mountain thrust belt into the Western Canada Sedimentary Basin during the Laramide Orogeny, which resulted in precipitation of dolomite and calcite cement with high $^{87}Sr/^{86}Sr$ ratios. The Sr isotopes of present-day Devonian formation waters from central Alberta, according to Connolly *et al.* (1990), vary from 0.70872 to 0.71285. These values are distinctively higher than those of coeval Devonian seawater (Fig. 5) and can be interpreted as a result of input of tectonically expelled ^{87}Sr-enriched fluids that ascended via faults from the Cambrian shales and the Precambrian basement (Connolly *et al.* 1990; Mountjoy *et al.* 1992; Machel *et al.* 1996). Although $^{87}Sr/^{86}Sr$ ratios of these Devonian formation waters are distinctively higher than those of Pine Point dolomites, they overlap those dolomites from northeastern British Columbia that were sampled from similar distances relative to the Cordilleran disturbed belt (Fig. 5), suggesting that the Devonian formation waters can precipitate dolomites with Sr isotope values observed in the Presqu'ile barrier reef.

The eastward decrease in fluid inclusion homogenization temperatures and Sr isotopes, in conjunction with the increase in oxygen isotopes, from northeastern British Columbia to the Pine Point area therefore suggest a large-scale migration of hot and radiogenic basinal fluids up-dip from southwest to northeast along the Presqu'ile barrier reef. Such a large-scale migration of basinal fluids was probably related to tectonic compression, and sedimentary loading on the western margin of the Western Canada Sedimentary Basin. Several major periods of tectonic compression and sedimentary loading occurred on the western margin of the Western Canada Sedimentary Basin. The earliest of these, the Antler Orogeny (Late Devonian–Early Carboniferous) occurred during shallow burial of the Presqu'ile barrier reef (Root 1993; Savoy & Mountjoy 1995). The next major tectonic event is the Columbia orogeny during Late Jurassic to Early Cretaceous time. The most dramatic tectonic event, the Laramide Orogeny, took place during deep burial of the barrier reef from the Late Cretaceous to Early Tertiary. Large-scale, eastward fluid migration in the Presqu'ile barrier reef could have occurred during the Antler Orogeny from Late Devonian to Early Carboniferous time, and/or during the Columbia–Laramide Orogenies from the Late Jurassic to Early Tertiary.

Implication of δD data

The δD values of Pine Point dolomite fluid inclusions were measured by Nesbitt & Muehlenbachs (1994) in order to provide further constraints on origin and timing of fluid flow and associated dolomitization and mineralization at Pine Point. The δD values of fluid inclusions in Pine Point dolomites (−80 to −100‰ SMOW) are extremely low compared to approximately −10‰ SMOW for Devonian seawater based on analyses of Middle Devonian halite-hosted fluid inclusions from the Western Canada Sedimentary basin (Knauth & Roberts 1991; Fig. 6). Among others, three possible scenarios that could lead to the low δD values of Pine Point dolomites are discussed in the following sections, including: (1) strongly evaporated Devonian seawater; (2) mixing of Devonian seawater with deuterium-depleted meteoric water; and/or (3) incorporation of organic-derived hydrogen into dolomitizing fluids during thermal maturation of organic matter and generation of oil and gas.

During the initial evaporation of seawater, the lighter isotopes are preferentially removed and the residual fluid becomes enriched in ^{18}O and D. However, upon further evaporation to more than 4×, the residual seawater evolves along an isotope trajectory towards progressively lower δD and $\delta^{18}O$ values as discussed by Knauth & Beeunas (1986). Because halite precipitation begins at about 11 × and continues to 65 ×, the $\delta^{18}O$ and δD values of fluids from which halite precipitates are highly variable; and could be lower than coeval seawater depending on the degree of evaporation. The fluids in halite inclusions, interpreted as connate brines that were trapped at the time of halite precipitation or during early diagenesis, therefore provide valuable information on the isotopic composition of ancient evaporate brines (Knauth & Beeunas 1986). The δD values of 31 halite-hosted fluid inclusion samples from Middle Devonian Muskeg and Prairie Formations in the Western Canada Sedimentary Basin range from −7 to −77‰ SMOW (mean −28.7‰ SMOW) (Knauth & Roberts 1991). These values are obviously too high to account for δD values of Presqu'ile dolomite (−80 to −100‰ SMOW) (Fig. 6). Therefore, it seems unlikely that the low δD values in Pine Point dolomites were attributed to the evaporatic Devonian seawater.

Another possibility for the low δD values in Pine Point dolomites is the influence of meteoric water. As isotopic composition of meteoric water reflects the latitude and altitude of precipitation, they can be utilized to determine the palaeogeographic position of sedimentary basins and to further constrain the origin and possible timing of palaeofluid flows in the basins (Nesbitt & Muehlenbachs 1994, 1995; Qing & Mountjoy 1995). During Late Devonian to Early Mississippian time, the Western Canada Sedimentary Basin was situated within 0° to 15° of the equator (Habicht 1979) (Fig. 7A). Taking −10‰ SMOW as a δD value for Devonian seawater (Knauth & Roberts 1991), the δD value of meteoric waters at sea level in the Western Canada Sedimentary Basin would be about −20 to −30‰ SMOW during Late Devonian to Early Mississippian time (cf. Craig & Gordon 1965). Mixing of these meteoric waters with Devonian seawater should result in a mixing trend with δD values from −10 to −30‰ SMOW, significantly higher than those of Pine Point dolomite inclusions (Fig. 6).

The low δD values of inclusion fluids in the Pine Point dolomites are unlikely to be due to the altitude effect from the inferred Purcell high

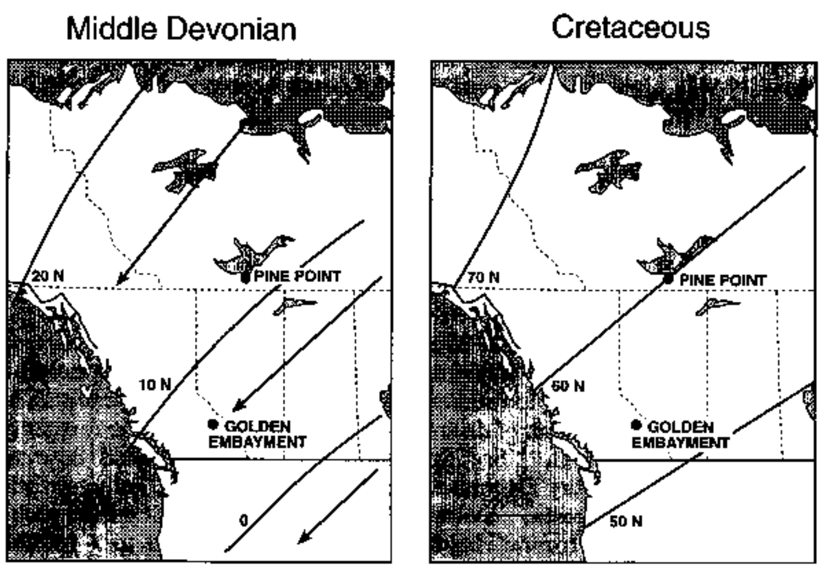

Fig. 7. (**A**) Estimated palaeolatitude and surface wind directions (arrows; Campbell 1987) of western North America during Middle Devonian time. (**B**) Estimated palaeolatitude of western North America during Cretaceous time (modified after Habicht 1979).

and Kootenay terranes as suggested by Nesbitt & Muehlenbachs (1995) because of the following considerations. Firstly, as there was about 400 km of separation between the Presqu'ile barrier reef and the Purcell high and Kootenay terranes (Fig. 1), it is not clear how and when the meteoric waters from these terranes could get into the barrier reef. Secondly, the trade wind during the Devonian was from northeast to southwest in the Western Canada Sedimentary basin (Campbell 1987; Fig. 7a). The rain-shadow effect of the Purcell high and Kootenay terranes, which could result in lower δD values in rainwater, should occur in the down-wind direction on the southwest side of these terranes, instead of the up-wind side in the Golden Embayment. Thirdly, the relative proportion of meteoric water from the Purcell high and Kootenay terranes that eventually reached the Golden Embayment as ground water would be limited because: (1) the amount of precipitation at high altitude is only a small fraction of that along the coastal areas; (2) depending on the drainage system, Golden Embayment could have collected only a portion of meteoric water from these landmasses; and (3) much of the high-altitude meteoric water may have evaporated en route to the Golden Embayment owing to the regional arid climate in the Western Canada Sedimentary Basin, as demonstrated by the presence of extensive contemporaneous evaporates in the basin. The major influence of meteoric water, if any, would have come mostly from precipitation along the coastal areas with relatively high δD values. Based on the above considerations of the δD values of Devonian seawater, palaeogeographic location, regional climate, and presumed trade winds in the Western Canada Sedimentary Basin, it seems unlikely that the low δD values of fluid inclusions of Pine Point dolomite were caused by mixing of meteoric water with seawater during Late Devonian to Early Mississippian time.

From Devonian to Triassic time, the Western Canada Sedimentary Basin remained mostly within 30° of the palaeoequator (Habicht 1979). According to Knauth & Beeunas (1986), the δD value of seawater has, since Permian time, been similar to that of present-day seawater. The corresponding average δD values of meteoric waters in the Western Canada Sedimentary Basin, depending on its topography, should be in the range of −30 to −60‰ SMOW, which are still too high to account for −80 to −100‰ SMOW of Pine Point dolomites. The Western Canada Sedimentary Basin moved to approximately its present high latitude (about 50° N to 60° N) during Jurassic time and has stayed at these high-latitude positions to the present time (Fig. 7n). The δD values of present surface waters from rivers and lakes in Alberta, which reflect the δD values of present-day precipitation, range from −134 to −163‰ SMOW (Fig. 6; Hitchon & Friedman 1969). The δD values for syn- or post-Laramide Orogenic fluids range from −115 to −155‰ SMOW (Nesbitt & Muehlenbachs 1994). The low δD values (−100 to −127‰ SMOW) of present-day formation water from Upper Cretaceous strata were interpreted as a result of influence of modern meteoric waters in the upper portion of the sedimentary succession (Fig. 6; Connolly *et al.* 1990). The δD values of Pine Point dolomite inclusions, therefore, can be interpreted as a result of mixing of some Columbia–Laramide meteoric waters with the original Devonian basinal brines (Fig. 6). Two major tectonic events occurred in the Western Canada Sedimentary Basin since Jurassic time: the Columbia Orogeny from the Late Jurassic to Early Cretaceous and the Laramide Orogeny from the Late Cretaceous to early Tertiary. Either or both could have provided the driving force for eastward fluid flow in the basin.

As the δD values of fluid inclusions reported by Nesbitt & Muehlenbachs (1995) were measured from bulk dolomite samples, these inclusions would have included primary as well as secondary ones (cf. Roedder 1984; Goldstein & Reynolds 1994). The signature of Columbia–Laramide meteoric waters, therefore, could come from either primary inclusions or secondary inclusions, leading to two different interpretations on the timing of fluid migration and dolomitization. If the low δD values of Pine Point dolomite-hosted inclusions reflect a mixture of fluids from primary inclusions containing Devonian seawater and secondary inclusions that formed later during the Columbia–Laramide Orogeny, the fluid migration and associated dolomitization and mineralization could be interpreted as a late-Devonian event. However, if the measured fluids were mostly from primary inclusions, these low δD values can be interpreted as a result of mixing of some Columbia–Laramide meteoric waters with Devonian formation waters at the time of dolomitization (Fig. 6), supporting a Jurassic to early Tertiary age for the dolomitization at Pine Point. This interpretation is also supported by overlapping of the δD values of Pine Point dolomite inclusions with present-day Devonian formation waters (Fig. 6), which were interpreted as a mixture of meteoric waters as a result of Laramide tectonism and original Devonian connate brines (Connolly *et al.* 1990).

Finally, the low δD values of Pine Point dolomite inclusions could occur as a result of incorporation of organic-derived hydrogen into dolomitizing fluids during thermal maturation of organic matter and generation of oil and gas. Recent study of δD values of fluid inclusions hosted in the sphalerite, fluorite and barite from MVT deposits in the southern Appalachians suggested that the δD values of basinal fluids can be significantly lowered if these fluids interacted with organic matter (Kesler *et al.* 1997). At the Pine Point mining property there is a highly diverse suite of natural bitumens ranging from liquid heavy oils to solid bitumens which were interpreted to be formed during thermal alteration, biodegradation and thermochemical sulphate reduction of organic matter (Macqueen & Powell 1983; Fowler *et al.* 1993). These processes could have released lighter hydrogen from organic matter to ambient fluids, resulting in the low δD values of the dolomite-hosted inclusions. According to Bachu (1997), only the deepest rocks adjacent to the western part of the Presqu'ile barrier reef reached the oil and gas window at maximum burial during the Laramide Orogeny. If the low δD values of Pine Point dolomite inclusions are due to the reaction of fluids with organic matter during generation of oil and gas, the timing of such fluid formation would probably be late Cretaceous during the Laramide Orogeny.

Conclusions

Petrographic study indicates that MVT deposits at Pine Point are associated spatially and genetically with saddle dolomite cements, which locally cut across the sub-Watt Mountain unconformity and overlap with sulphide mineral precipitation. Thus, dolomitization and associated sulphide mineralization must have occurred after the sub-Watt Mountain exposure during burial. The lateral continuity of saddle dolomite along the barrier for 400 km but the lack of it in the Keg River Formation at Pine Point, which occurs immediately beneath the barrier reef, suggest that dolomitization and associated mineralization were probably associated with the lateral fluid migration along the barrier reef rather than fluids that rose vertically through the McDonald Fault Zone in the vicinity of the Pine Point area.

From northeastern British Columbia to Pine Point, there is a general trend of decreasing $^{87}Sr/^{86}Sr$ ratios and fluid inclusion homogenization temperatures with corresponding increase of $\delta^{18}O$ values of saddle dolomite cements. Such a geochemical trend can be attributed to an eastward migration of hot and radiogenic basinal fluids as a result of tectonic compression and sedimentary loading on the western margin of the Western Canada Sedimentary Basin. Several major periods of tectonic compression and sedimentary loading occurred on the western margin of the Western Canada Sedimentary Basin, including the early Antler Orogeny that occurred at shallow burial during Late Devonian to Early Carboniferous, and the Laramide Orogeny which took place during deep burial from the Late Cretaceous to Early Tertiary.

The low δD values in Pine Point dolomite-hosted fluid inclusions (−80 to −100‰ SMOW) could result from: (1) mixing of Devonian seawater with deuterium-depleted meteoric water; and/or (2) incorporation of organic-derived hydrogen into dolomitizing fluids during thermal maturation of organic matter and generation of oil and gas. Based on the considerations of the δD values of Devonian seawater, palaeogeographic location, regional climate, and presumed trade winds in the Western Canada Sedimentary Basin, it seems unlikely that the low δD values of fluid inclusions in Pine Point dolomite were caused by mixing of meteoric water with seawater during Late Devonian to Early Mississippian time.

The low δD values of Pine Point dolomite inclusions can be interpreted as a result of mixing of some Columbia–Laramide meteoric waters with the original Devonian basinal brines. If the low δD values of Pine Point dolomite inclusions occurred as a result of mixing of primary inclusions containing Devonian seawater with secondary inclusions that formed later during the Columbia–Laramide Orogeny, the fluid migration and associated dolomitization and mineralization could be interpreted as late-Devonian events. However, if the measured fluids were mostly from the primary inclusions, these low δD values can be interpreted as a result of mixing of some Columbia–Laramide meteoric waters with Devonian formation waters at the time of dolomitization, supporting a Jurassic to early Tertiary age for the dolomitization at Pine Point. This interpretation is also supported by similar low δD values of present-day Devonian formation waters that were interpreted as a mixture of Laramide meteoric waters and original connate brines.

The low δD values of Pine Point dolomite inclusions could also occur as a result of reaction of fluids with organic matter associated with generation of oil and gas, which occurred at the maximum burial during the Laramide Orogeny. The present data set provide constraints, but not a unique solution to the timing of fluid migration and associated dolomitization and mineralization at Pine Point. This controversy can be resolved by further improved resolution of sampling, separating primary fluid inclusions from secondary ones.

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