Petrography and geochemistry of early-stage, fine- and medium-crystalline dolomites in the Middle Devonian Presqu'ile Barrier at Pine Point, Canada

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ABSTRACT

The petrography and geochemistry of fine- and medium-crystalline dolomites of the Middle Devonian Presqu'ile barrier at Pine Point (Western Canada Sedimentary Basin) are different from those of previously published coarse-crystalline and saddle dolomites that are associated with late-stage hydrothermal fluids. Fine-crystalline dolomite consists of subhedral to euhedral crystals, ranging from 5 to 25 μm (mean 8 μm). The dolomite interbedded with evaporitic anhydrites that occur in the back-barrier facies in the Elk Point Basin. Fine-crystalline dolomite has $\delta^{18}O$ values between −1·6 to −3·8‰ PDB and $^{87}Sr/^{86}Sr$ ratios from 0·7079–0·7081, consistent with derivation from Middle Devonian seawater. Its Sr concentrations (55–225 p.p.m., mean 105 p.p.m.) follow a similar trend to modern Little Bahama seawater dolomites. Its rare earth element (REE) patterns are similar to those of the limestone precursors. These data suggest that this fine-crystalline dolomite formed from Middle Devonian seawater at or just below the sea floor.

Medium-crystalline dolomite in the Presqu'ile barrier is composed of anhedral to subhedral crystals (150–250 μm, mean 200 μm), some of which have clear rims toward the pore centres. This dolomite occurs mostly in the southern lower part of the barrier. Medium-crystalline dolomite has $\delta^{18}O$ values between −3·7 to −9·4‰ PDB (mean −5·9‰ PDB) and $^{87}Sr/^{86}Sr$ ratios from 0·7081–0·7087 (mean 0·7084); Sr concentrations from 30 to 79 p.p.m. (mean 50 p.p.m.) and Mn content from 50 to 253 p.p.m. (mean 161 p.p.m.); and negative Ce anomalies compared with those of marine limestones. The medium-crystalline dolomite may have formed either (1) during shallow burial at slightly elevated temperatures (35–40 °C) from fluids derived from burial compaction, or, more likely (2) soon after deposition of the precursor sediments by Middle Devonian seawater derived from the Elk Point Basin.

These results indicate that dolomitization in the Middle Devonian Presqu'ile barrier occurred in at least two stages during evolution of the Western Canada Sedimentary Basin. The geochemistry of earlier formed dolomites may have been modified if the earlier formed dolomites were porous and permeable and water/rock ratios were large during neomorphism.

INTRODUCTION

Dolomites in the Middle Devonian (Givetian) Presqu'ile barrier host one of the world's largest Mississippi Valley-type (MVT) deposits (Rhodes *et al.*, 1984). In the subsurface of the North-west Territories and north-eastern British Columbia, these dolomites are also important hydrocarbon

reservoir rocks (e.g. Collins & Lake, 1989). Understanding the origin and distribution of different dolomites in the Presqu'ile barrier is therefore of great economic importance for both mining and oil industries. As massive replacement dolomites commonly occur in the Western Canada Sedimentary Basin and some of these are important hydrocarbon reservoirs (Morrow, 1982; Machel & Mountjoy, 1987), a better understanding of dolomitization will be useful to predict the spatial distribution of dolomite reservoirs elsewhere in the basin.

Dolomite has been interpreted to have formed in many different environments by various fluids (Land, 1985; Machel & Mountjoy, 1986; Hardie, 1987). These include: (1) evaporitic marine brines in sabkha environments (e.g. Adams & Rhodes, 1960; Patterson & Kinsman, 1982); (2) freshwater/seawater in mixing zones (e.g. Badiozamani, 1978; Humphrey, 1988; Humphrey & Quinn, 1989); (3) normal seawater in subtidal environments (e.g. Saller, 1984); and (4) various fluids in subsurface environments (e.g. Mattes & Mountjoy, 1980; Aulstead & Spencer, 1985; Machel & Mountjoy, 1987; Aulstead *et al.*, 1988; Qing & Mountjoy, 1989; Machel & Anderson, 1989; Mountjoy & Amthor, 1994). Dolomites formed in different diagenetic environments can be recognized by their petrography, spatial distribution, geochemical and isotopic signatures due to variations in fluid-driving mechanisms, temperature and chemical compositions of the dolomitizing fluids (Land, 1985; Machel & Mountjoy, 1986; Hardie, 1987).

The Presqu'ile barrier in the Western Canada Sedimentary Basin offers a good opportunity to study various massive replacement dolomites. Four types of dolomites are identified in the Presqu'ile barrier (Qing, 1991; Qing & Mountjoy, 1990). In paragenetic sequence, they are fine-, medium-, and coarse-crystalline replacement dolomites, and saddle dolomite cements. 'Fine-crystalline dolomite' of previous studies (Jackson & Beales, 1967; Skall, 1975; Kyle, 1981, 1983; Krebs & Macqueen, 1984; Rhodes *et al.*, 1984) is here divided into fine- and medium-crystalline dolomites based on their different petrographic textures, lithofacies associations, and geochemistry (Qing, 1991). Because the coarse-crystalline and saddle dolomites have been discussed in previous publications (Qing & Mountjoy, 1992, 1994a,b,c), this paper focuses on the petrography and geochemistry of fine- and medium-crystalline dolomites, and compares them with late-stage coarse-crystalline and saddle dolomites.

GEOLOGICAL SETTING

The Middle Devonian Presqu'ile barrier is located in the northern part of the Western Canada Sedimentary Basin (Fig. 1). It is a linear carbonate reef complex at least 400 km long with a width ranging from 20 km to 100 km. It extends from outcrops in the Northwest Territories near Pine Point into the subsurface of north-eastern British Columbia (Fig. 1). The thickness of the Presqu'ile barrier is about 200 m in the Pine Point area. The development of the Presqu'ile barrier restricted seawater circulation in the Elk Point Basin during Middle Devonian time. As a result, evaporites and carbonates were deposited south of the barrier in the Elk Point Basin, whereas normal marine sediments were deposited north of the barrier (Fig. 1). Pine Point is located towards the east end of the barrier (Fig. 1), where various dolomite rocks host more than 80 individual MVT ore bodies.

A major basement fault, the McDonald Fault, occurs in the Pine Point area (Rhodes *et al.*, 1984; Krebs & Macqueen, 1984) (Fig. 1). Based on aeromagnetic data, the McDonald Fault can be traced from the Canadian Shield into the subsurface of the Western Canada Sedimentary Basin (Jones, 1980; Ross *et al.*, 1991) (Fig. 1). The McDonald Fault may have been reactivated during Middle Devonian or post Devonian times and played a role in conducting the diagenetic fluids for late stage dolomitization and mineralization (e.g. Campbell, 1966; Skall, 1975; Krebs & Macqueen, 1984), although there is no definitive evidence to support this. The role of the McDonald Fault during Middle Devonian time was questioned by Rhodes *et al.* (1984) because strata immediately beneath the barrier are 'of uniform thickness without any signs of vertical displacement'.

The regional geology at Pine Point and diagenetic processes have been described in details by Jackson & Beales (1967), Skall (1975), Kyle (1981, 1983), Krebs & Macqueen (1984), Rhodes *et al.* (1984), Qing (1991), Qing & Mountjoy (1990, 1994a,b,c). The following is a brief summary of the stratigraphy and diagenesis of the Presqu'ile barrier. The Keg River Formation represents a regional shallow-water platform that underlies the barrier (Fig. 2). It consists of grey-brown dolostones with abundant crinoid and brachiopod fragments. The carbonate barrier itself comprises the Pine Point and overlying Sulphur Point Formations (Fig. 2). Both were originally deposited as marine limestones that since have been variably dolomitized to medium- and
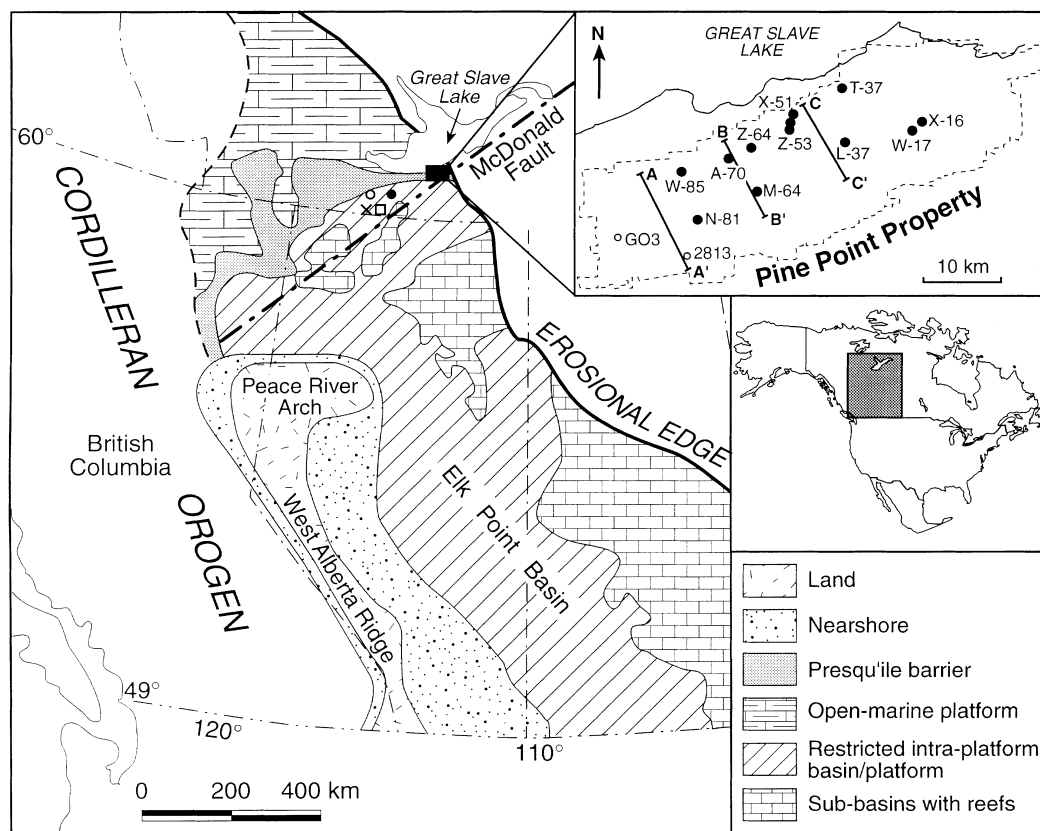
Fig. 1. Simplified regional geological map of the Western Canada Sedimentary Basin during the Middle Devonian. The Presqu'ile barrier outcrops in the Pine Point area west of the Canadian Shield. It extends westward into the subsurface of Northwest Territories and north-eastern British Columbia where its present burial depths are 2000–2300 m. Fine-crystalline dolomites were also sampled from 4 wells west of Pine Point: the open square is Cameron Hills F-51; the open circle, Pan Am Cameron C-22; solid dot, Murphy Alexandra Fall J-26; and cross, Cameron A–05. The insert map shows Pine Point property with locations of open pits (solid dots) and three traverses (A–A', B–B', and C–C') that were studied for lithofacies and spatial distribution of dolomites. The stratigraphy and dolomite distribution of A–A' section are shown in Fig. 2.

coarse-crystalline dolomites. The Pine Point and Sulphur Point Formations grade southward into fine-crystalline dolomite and anhydrite of the Muskeg Formation, deposited in the Elk Point Basin. To the north of the barrier marine shales and carbonates of the Buffalo River and Windy Point Formations interfinger with and onlap the north flank of the Presqu'ile barrier. The Presqu'ile barrier was subaerially exposed shortly after it developed, forming the sub-Watt Mountain unconformity. This unconformity is developed over a wide area in the northern part of the Western Canadian Basin (Meijer-Drees, 1988). The unconformity is overlain by the Watt Mountain Formation, which consists primarily of green, silty, pyritic shales, locally alternating with nodular and argillaceous limestones or dolostones, limestone breccia, and minor amounts of anhydrite (Rhodes *et al.*, 1984).

The diagenetic features in the carbonate rocks of the Presqu'ile barrier (Fig. 3) have been interpreted to have occurred in submarine, subaerial and subsurface environments (Qing, 1991; Qing & Mountjoy, 1990). Submarine diagenetic features include: micrite envelopes, micrite, syntaxial cement, microspar cement, fibrous cement, and fine crystalline dolomite. Subaerial diagenesis formed minor, localized pendant cements, and dissolution and brecciation (Qing & Mountjoy, 1994b). The most significant alteration, however, was produced by basinal and hydrothermal fluids during burial (Krebs & Macqueen, 1984; Qing, 1991; Qing & Mountjoy, 1990, 1992, 1994a,b,c). Subsurface diagenesis resulted in blocky sparry calcite cement, compaction and stylolitization, coarse-crystalline and saddle dolomites, white calcite, sulphide mineralization, and late-stage calcite, fluorite, and bitumen.
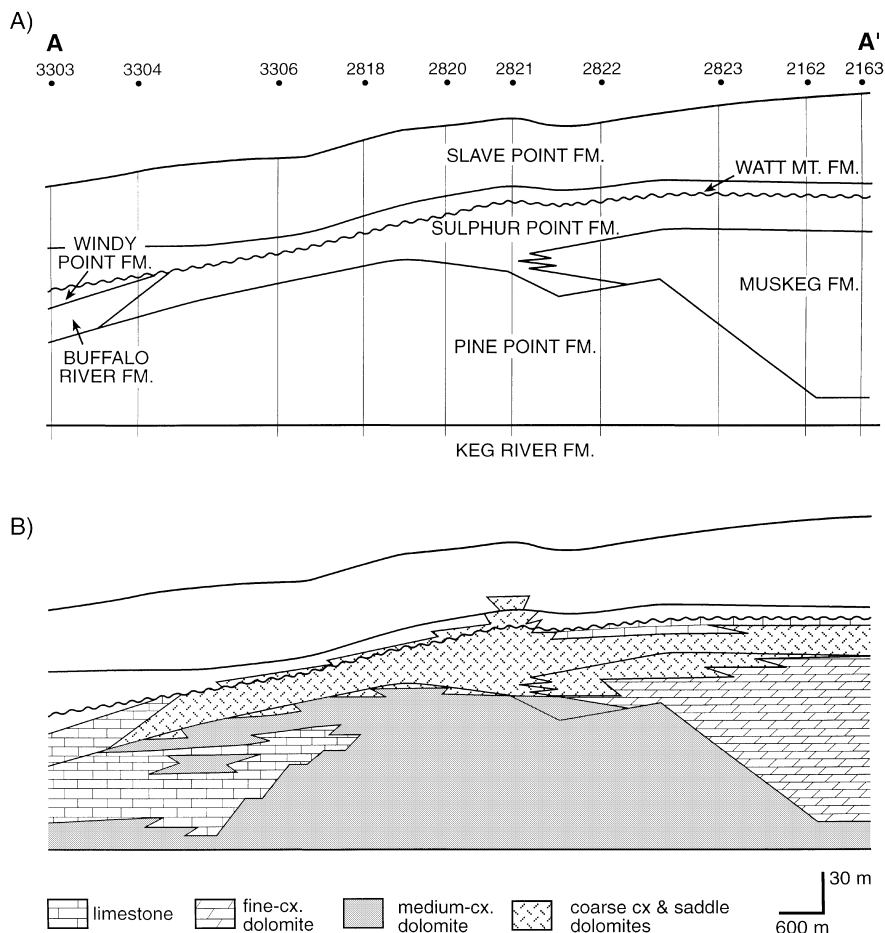
A)

B)

Fig. 2. Stratigraphy and dolomite distribution of traverse A-A′ in the western part of Pine Point property (see Fig. 1 for location) based on core examination. The numbers are borehole numbers of Pine Point Mines and the thin vertical lines are cored intervals. (A) Stratigraphy of Presqu'ile barrier at Pine Point. (B) Generalized spatial distribution of different types of dolomites. Modified after Rhodes *et al.* (1984) and Qing and Mountjoy (1994a).

METHODS

At Pine Point, a number of open pits and a series of drill holes from three representative traverses were systematically studied and sampled, and the spatial distribution of the various dolomites mapped (Figs 1 and 2). Core samples from four wells from the downdip, subsurface portion of the Presqu'ile barrier, west of Pine Point were studied and sampled (Fig. 1). Approximately 160 thin sections were studied and all were stained with alizarin-red S and potassium ferricyanide (Dickson, 1965). 100 thin sections were also studied using cathodoluminescence (CL) and representative samples were studied with a scanning electron microscope (SEM).

For carbon and oxygen isotope analyses, powdered carbonate samples ranged from 0·2–0·5 mg were drilled from polished slabs using 100 μm diameter drills. These samples were roasted at 380 °C under vacuum for 1 hr to remove organic matter. Samples were then reacted with anhydrous phosphoric acid at 55 °C for about 10 min for calcite and about 1 hr for dolomite. This was
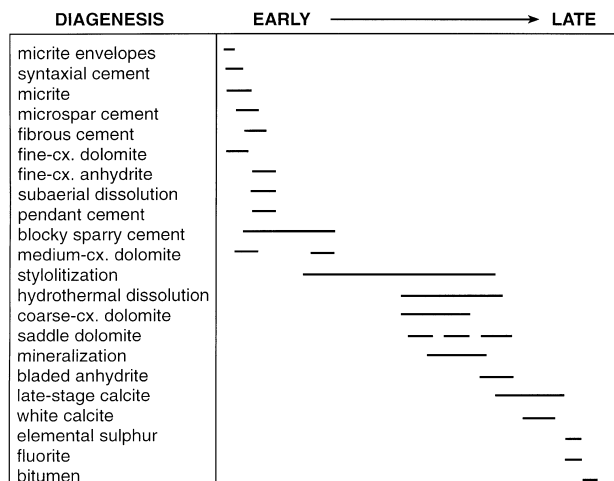

Fig. 3. Diagenetic paragenesis of the Presqu'ile barrier determined from petrographic study of samples from open pits and cores. Abbreviation: cx. = crystalline. Modified from Qing and Mountjoy (1990).

done in an on-line gas extraction system connected to an inlet of a VG 602E mass spectrometer. All the analyses were corrected for ^{17}O (and reported

in parts per thousand (‰) relative to the Pee Dee Belemnite (PDB) standard). Analytical precision was monitored through daily analysis of powdered carbonate standards and maintained to better than 0·1‰ (1 σ) for both $\delta^{18}O$ and $\delta^{13}C$.

For Sr isotope analyses, ≈ 5–15 mg samples were crushed in a stainless steel mortar prior to chemical dissolution. The dolomite samples were leached in 0·5 N HCl to extract Sr. Sr was extracted from the leachate with 2·5 N HCl using standard cation exchange techniques. The samples were loaded as $SrCl_2$ on a single Ta filament and were analysed using a VG 354 thermal ionization mass spectrometer. An error of ± 0·0025% has been calculated for the data, which is the average 2σ error for the internal precision of a single analysis. The average value of the NBS 987 standard during the course of the study was 0·71022. The isotopic ratios of samples were normalized against this value (Mountjoy *et al.*, 1992).

Major (Ca and Mg) and trace elements (Sr, Na, K, Mn, Fe, and Ba) were analysed using an atomic absorption spectrometer (AAS). Powdered dolomite samples (0·5 g) were dissolved in 10 mL 8% HCl solutions, which were filtered with ashless paper and then analysed. The detection limits were: Sr 6 p.p.m., Na 5 p.p.m., K 10 p.p.m., Mn 2 p.p.m., Fe 6 p.p.m., and Ba 40 p.p.m. The reproducibility for duplicates was better than three relative percentage. The stoichiometry of dolomites is calculated from major element concentrations.

REE concentrations were determined, using an inductively coupled plasma mass spectrometer (ICP-MS). Samples (0·1 g) were digested in 1 N HNO_3 and analysed by ICP-MS using the method of standard additions to correct for matrix effects. The reproducibility is within ± 2%. The detection limits and reagent blanks are from 0·001 p.p.m. for Yb to 0·026 p.p.m. for Sm. Identification of REE fractionation was made by normalizing the sample REE concentration to average chondritic meteorites, making the data comparable to previous studies on ancient dolomites (e.g. Graf, 1984; Banner *et al.*, 1988a,b; Dorobek & Filby, 1988).

PETROGRAPHY AND SPATIAL DISTRIBUTION

Fine-crystalline dolomite

Fine-crystalline dolomite is found only in the back-barrier facies in the Muskeg Formation on the south side of the Presqu'ile barrier based on the core examination of three traverses from eastern, central, and western part of Pine Point property and of selected wells in the adjacent subsurface (Figs 1 and 2). It is interbedded with evaporitic anhydrite in the Elk Point Basin. Fine-crystalline dolomite is either brown or grey in hand sample (Fig. 4a). Fossils and sedimentary structures are well-preserved while fractures and vugs are usually filled with fine-crystalline anhydrite (Fig. 4b).

Fine-crystalline dolomite consists of subhedral to euhedral crystals, ranging from 5 to 25 μm (mean 8 μm) with plane extinction (Fig. 4c). Crystal size gradually increases (to 100 μm) towards orebodies, suggesting possible neomorphism and/or recrystallization by later mineralizing fluids. Under the SEM, fine-crystalline dolomite consists of euhedral crystals with smooth and uncorroded crystal surfaces (Fig. 4d). Micro, intracrystalline pores (1–10 μm) are rare and porosity is low because of the interlocking texture.

Medium-crystalline dolomite

Medium-crystalline dolomite is the most abundant type of dolomite in the Pine Point area. It occurs mainly in the southern lower part of the barrier in the Pine Point Formation (Fig. 2b) which is in direct contact with evaporitic anhydrite and fine-crystalline dolomite of the Muskeg Formation in the Elk Point Basin. In the Pine Point area, there are two layers of porous sucrosic medium-crystalline dolomite: one at the base of the Pine Point Formation, the B Spongy Member of Rhodes *et al.* (1984); the other occurring just below the coarse-crystalline dolomite.

Medium-crystalline dolomite is medium to dark brown. Fossil and sedimentary textures are generally recognizable (Fig. 5a), while dissolution vugs and fractures are locally developed (Fig. 5b) and part filled by minor amounts of late-stage saddle dolomite or anhydrite cements. Medium-crystalline dolomite is composed of anhedral to subhedral dolomite crystals (150–250 μm, mean 200 μm), with well defined crystal boundaries (Fig. 5c). In contrast to the coarse-crystalline dolomite that commonly displays undulatory extinction (Qing & Mountjoy, 1994a), these dolomites have plane extinction. Some medium-crystalline dolomite crystals have clear rims toward the pore centres (Fig. 5c). Medium-crystalline dolomite is generally red/orange under CL, but bright orange blotches occur
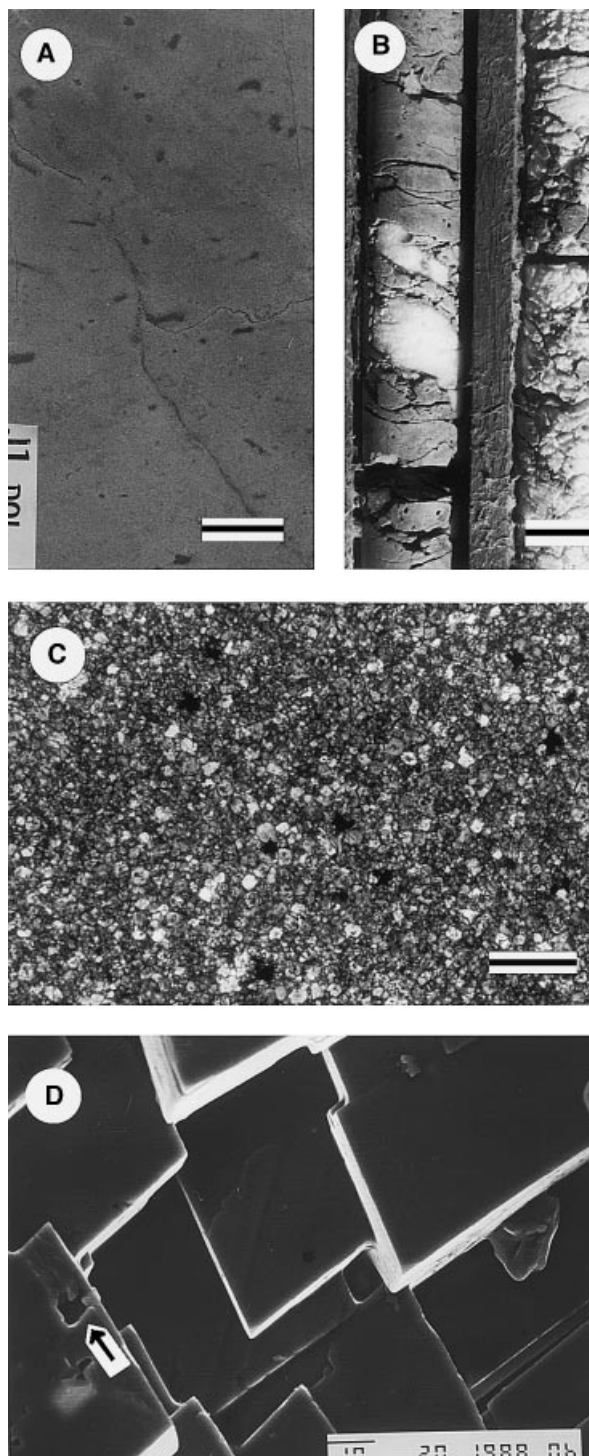
Fig. 4. Petrographic features of fine-crystalline dolomite. (A) Hand sample of fine-crystalline dolomite. Location: Muskeg Formation, Pine Point diamond drill hole 2162, 614 ft. Scale in cm. (B) Fine-crystalline dolomite with anhydrite nodules and interlayer. Location: Muskeg Formation, Pine Point diamond drill hole 2162, 645 ft. Scale in cm. (C) Thin section photomicrograph of fine-crystalline dolomite with anhedral dolomite crystals ranging from 15 to 25 μm. Location: Muskeg Formation, well C-22, 3192 ft. Scale bar 200 μm. (D) SEM photomicrograph of fine-crystalline dolomite. Euhedral dolomite crystals have smooth and uncorroded surface with rare micro intracrystal pores (arrow). Location: Muskeg Formation, Pine Point diamond drill hole 2162, 645 ft. Scale bar 10 μm.

GEOCHEMISTRY

Oxygen and carbon isotopes

Three fine-crystalline dolomites sampled from the Muskeg Formation in the subsurface of the Elk Point Basin had $\delta^{18}O$ values from −1·6 to −3·8‰ PDB and $\delta^{13}C$ from 0·27–1·7‰ PDB (Fig. 6). However, fine-crystalline dolomite sampled around orebodies at Pine Point, hereafter termed 'altered, fine-crystalline dolomites' has lower $\delta^{18}O$ values (−6·7 to −7·9‰ PDB) (Fig. 6). Twenty-one medium-crystalline dolomite samples yield $\delta^{18}O$ values from −3·7 to −9·4‰ PDB (mean −5·9‰ PDB) and $\delta^{13}C$ from 0·6–2·5‰ PDB. Their $\delta^{18}O$ values are distinctly more negative than fine-crystalline dolomite (Fig. 6). Two brachiopod shell fragments from the Sulphur Point Formation have $\delta^{18}O$ values of −3·8 and −4·2‰ PDB and $\delta^{13}C$ of 1·8 and 1·9‰ PDB, respectively (Fig. 6).

Sr isotopes

The Sr isotope data reveal a general increase in $^{87}Sr/^{86}Sr$ ratios from fine-crystalline to medium-crystalline dolomites (Fig. 7). Three fine-crystalline dolomites yield $^{87}Sr/^{86}Sr$ ratios of 0·7079–0·7081 (Fig. 7). One sample of primary anhydrite associated with these fine-crystalline dolomite has a $^{87}Sr/^{86}Sr$ ratio of 0·7078. However, two altered fine-crystalline dolomites sampled adjacent to orebodies at Pine Point have slightly higher $^{87}Sr/^{86}Sr$ ratios (0·7082 and 0·7083) (Fig. 7). One of three medium-crystalline dolomites has $^{87}Sr/^{86}Sr$ ratio of 0·7081, overlapping with those of the fine-crystalline dolomite but the other two are more radiogenic (0·7085 and 0·7087, respectively) than those of fine-crystalline dolomites (Fig. 7).

along some crystal boundaries. Under SEM (Fig. 5), medium-crystalline dolomite consists of anhedral–subhedral crystals with variable amounts of intra- and inter-crystalline porosity, suggesting possible dissolution by later diagenetic fluids.
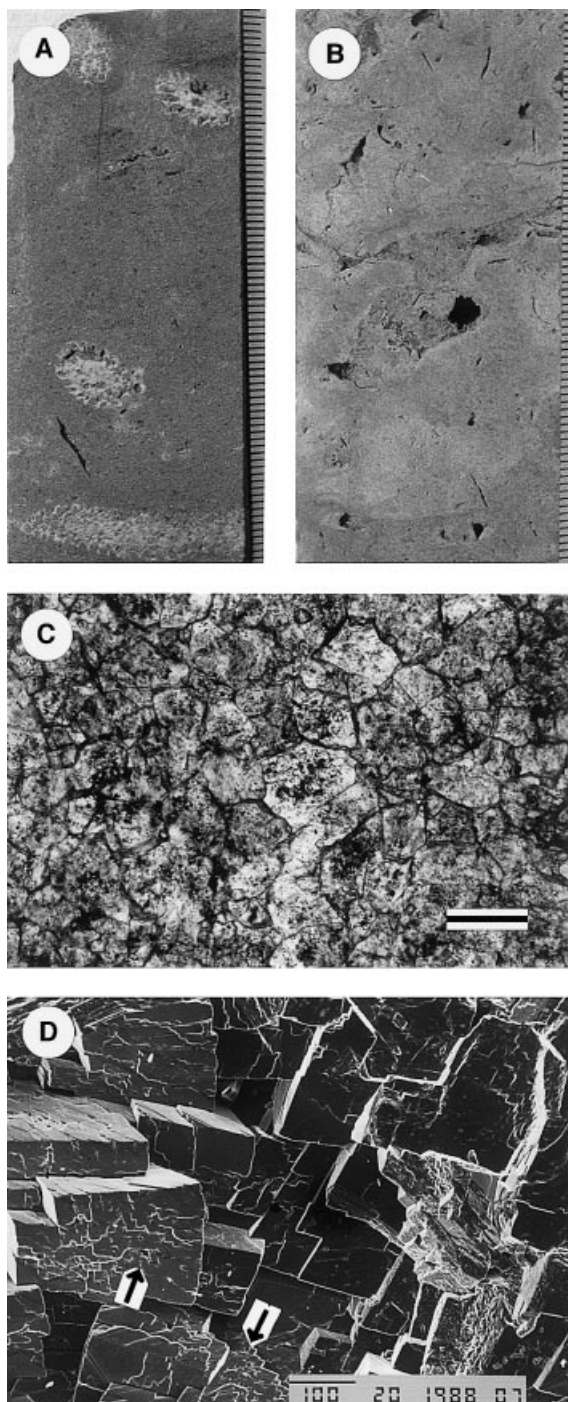
Fig. 5. Petrographic features of medium-crystalline dolomite. (A) Core sample of medium-crystalline dolomite with well preserved dolomitized fossil fragments. Location: Pine Point Formation, Pine Point diamond drill hole 2813, 530 ft. Scale in cm. (B) Core sample of medium-crystalline dolomite with moldic and vuggy porosity. Location: Pine Point Formation, Pine Point diamond drill hole 2813, 870 ft. Scale in cm. (C) Thin section photomicrograph of medium-crystalline dolomite. Some crystals have cloudy centres and clear rims, suggesting possible neomorphism or recrystallization. Location: Pine Point Formation, Pine Point diamond drill hole 2813, 642 ft. Scale bar 200 μm. (D) SEM photomicrograph of medium-crystalline dolomite. Subhedral dolomite crystals have variable amounts of intracrystal pores (arrows). Location: Pine Point Formation, Pine Point diamond drill hole 2813, 530 ft. Scale bar 100 μm.

(mean 86 p.p.m.) (Fig. 8). The Sr concentrations in medium-crystalline dolomite range from 30 to 80 p.p.m. (mean 50 p.p.m.) and Mn content from 50 to 253 p.p.m. (mean 161 p.p.m.). Therefore, there is a general trend of decrease in Sr and increase in Mn content from fine-crystalline to medium-crystalline dolomites (Fig. 8).

Rare earth elements

Three fine-crystalline dolomites (Muskeg Formation) are enriched in light REE but depleted in Eu, decreasing in concentration from La to Lu (Fig. 9a). The REE patterns of two of these samples
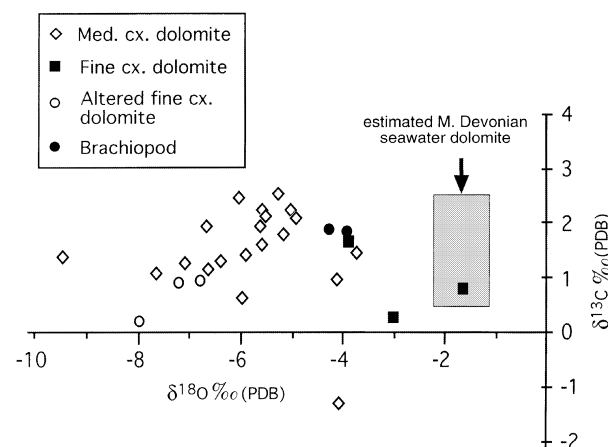

Fig. 6. Cross plot of $\delta^{18}O$ and $\delta^{13}C$ values for: (1) fine-crystalline dolomite (2) altered, fine-crystalline dolomite associated with mineralization, and (3) medium-crystalline dolomite. The possible $\delta^{18}O$ and $\delta^{13}C$ values of Middle Devonian seawater dolomite were calculated assuming a temperature of 20 °C and $\delta^{18}O$ values Middle Devonian seawater of −2·0 to −3‰ SMOW (see text for discussion).

Trace elements

Forty-five dolomite samples were analysed for major (Ca and Mg) and trace elements (Sr, Na, K, Mn, Fe, and Ba). Only Sr and Mn display covariation (Fig. 8); other elements show no clear covarying trends. Fine-crystalline dolomite has Sr concentrations from 55 to 225 p.p.m. (mean 105 p.p.m.) and Mn content from 25 to 160 p.p.m.
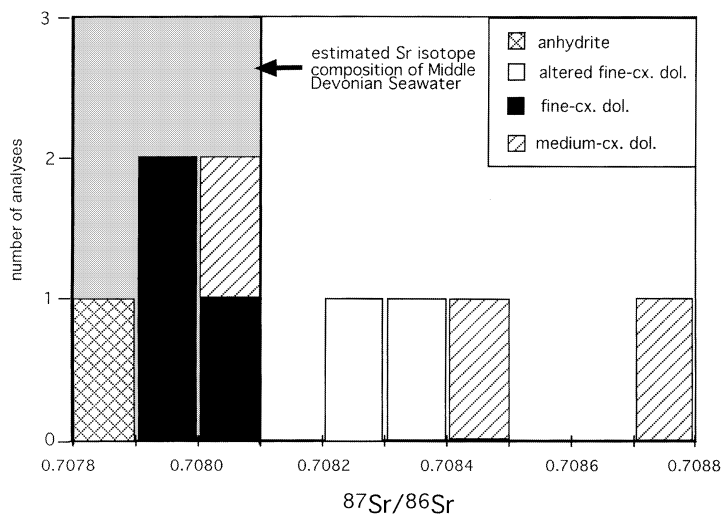
Fig. 7. $^{87}Sr/^{86}Sr$ ratios of dolomites and anhydrite in the Presqu'ile barrier. The best estimated $^{87}Sr/^{86}Sr$ ratio of Middle Devonian seawater, according to Burke *et al.* (1982), ranges from 0·7078–0·7081.
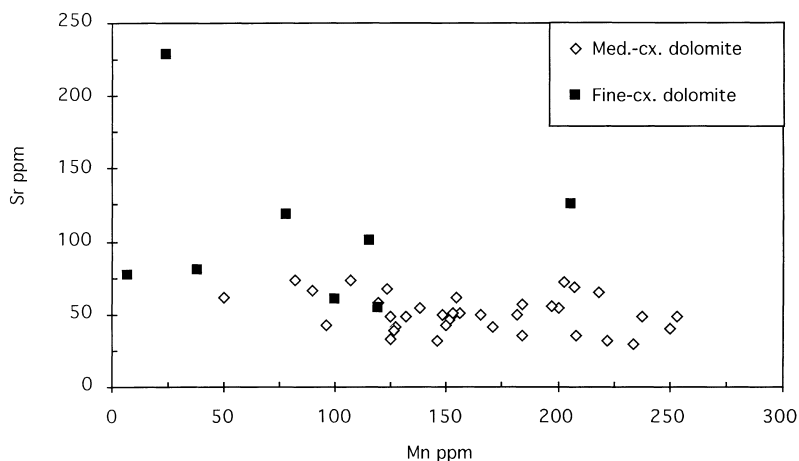

Fig. 8. Cross plot of Sr and Mn concentration for fine-crystalline and medium-crystalline dolomites.

are similar to those of marine limestone samples from Pine Point (Fig. 9a), while the REE pattern of the third is similar to those of medium-crystalline dolomites, with a negative Ce anomaly (Fig. 9a).

REE patterns of five medium-crystalline dolomite samples from the Pine Point Formation in the Pine Point property differ from those of the marine limestone and most fine-crystalline dolomites. Relative to chondrite, the REE contents decrease from La to Sm, are nearly constant from Gd to Tm, and decrease again from Yb to Lu (Fig. 9b). Medium-crystalline dolomites also have negative Ce anomalies compared with those of marine limestones (Fig. 9b).

DISCUSSION AND INTERPRETATION

The combined petrography, spatial distribution, diagenetic paragenesis, and geochemical data suggest the following interpretation.

1 Fine-crystalline dolomites are restricted to the back-barrier facies and are interbedded with Muskeg evaporitic anhydrites of the Elk Point Basin. Because the Muskeg Formation evaporites have low porosity and permeability and are regarded as a regional aquiclude (e.g. Bachu, 1997), large-scale fluid migration, a requirement for massive dolomitization (e.g. Land, 1985), seems unlikely. This suggests that the fine-crystalline dolomite formed penecontemporaneously at or just below the sea floor from seawater before lithofication of these evaporitic deposits.

2 Because the Western Canada Sedimentary Basin was located within 30° of the palaeo-equator from Devonian to Triassic time (Habicht, 1979), the average temperature for Devonian seawater was assumed to be 20 °C. Using $\delta^{18}O$ values measured from brachiopod shells from Pine Point area (−3·85 and −4·21‰ PDB, Fig. 6) and a temperature of 20 °C, the calculated $\delta^{18}O$ value of Middle Devonian seawater is about −2·0
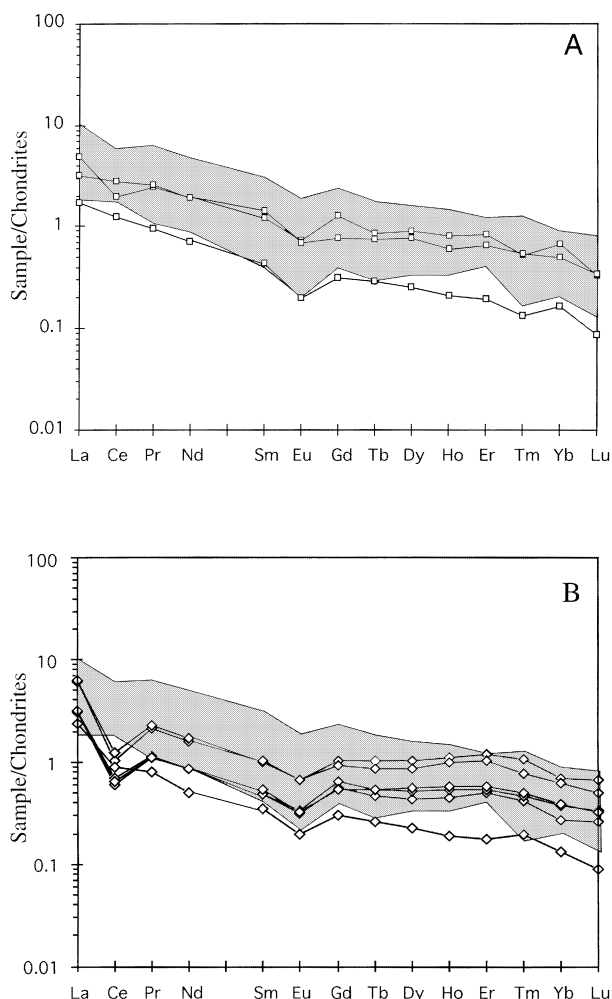
Fig. 9. (A) REE patterns of three fine-crystalline dolomites sampled from the Muskeg Formation in drill cores about 5 km south of the Presqu'ile barrier where the influence of late-stage hydrothermal fluids is minimal. (B) REE patterns of 5 medium-crystalline dolomites from the Pine Point Formation. Shaded area in (A) and (B) represents the REE patterns of marine limestones from Presqu'ile barrier.

to $-3‰$ Standard Mean Ocean Water (SMOW), using Friedman & O'Neil (1977) equation. This value is comparable with the estimated $\delta^{18}O$ value of $-2‰$ SMOW for Devonian seawater based on a larger sample set by Popp *et al.* (1986). The $\delta^{18}O$ values of dolomite precipitated in bulk solution equilibrium with this Middle Devonian seawater at a temperature of 20 °C should range from $-1·2$ and $-2·2‰$ PDB, calculated using an equation of Land (1985). The heaviest $\delta^{18}O$ of the unaltered fine-crystalline dolomite is $-1·58‰$ PDB, which falls within the range of calculated Middle Devonian seawater dolomite (Fig. 6), suggesting that the dolomitizing

fluids for fine-crystalline dolomites were probably Middle Devonian seawater.

3 Analysis of marine carbonates indicates that the $^{87}Sr/^{86}Sr$ ratio of oceans has varied systematically throughout Phanerozoic time, but has apparently been constant in the open ocean at any given time (Burke *et al.*, 1982). As the isotopic fractionation of Sr during carbonate precipitation is negligible, the Sr isotopic composition of marine carbonates are assumed to represent those of seawater at the time of deposition (Veizer, 1983). Therefore, unaltered Middle Devonian marine carbonates should have a $^{87}Sr/^{86}Sr$ ratio similar to Middle Devonian seawater, which is estimated to be between $0·7078$ and $0·7081$ (Fig. 7) (Burke *et al.*, 1982). The $^{87}Sr/^{86}Sr$ ratios of unaltered fine-crystalline dolomite range from $0·7079–0·7080$. These values are within the range of the estimated $^{87}Sr/^{86}Sr$ ratio of Middle Devonian seawater (Fig. 7), also suggesting that the dolomitizing fluids were Middle Devonian seawater.

4 From a study of Miocene marine dolomites from Little Bahama Bank, Vahrenkamp & Swart (1990) suggested that the amount of Sr in dolomite is related to both the Sr content of the dolomitizing fluids and the stoichiometry of the dolomite crystals. A dolomite with 50–51 mol % $CaCO_3$ precipitating in equilibrium with seawater should have a Sr content of about 50–70 p.p.m., but a nonstoichiometric marine dolomite with 60 mol percentage $CaCO_3$ could have a Sr content as high as 250 p.p.m. The Sr concentrations of Pine Point fine-crystalline dolomite range from 55 to 225 p.p.m., and follow the same trend as Little Bahama seawater dolomites (Fig. 10), suggesting that fine-crystalline dolomite may have formed from fluids with Sr^{2+}/Ca^{2+} ratios similar to those of modern seawater.

5 The REE patterns of two of the three fine-crystalline dolomite samples are similar to those of the marine limestone samples (Fig. 9), suggesting that either the fine-crystalline dolomite may have formed from fluids with similar REE characteristics as marine limestones, and/or that the REE patterns of the precursor limestones were not significantly altered during/after dolomitization.

Thus, the fine-crystalline dolomite probably formed from Middle Devonian seawater at or just below the sea floor. Those sampled near the Pine Point orebodies, however, have been altered by later diagenetic fluids during mineralization as indicated by their larger crystal size, lower $\delta^{18}O$ values ($-6·7$ to $-7·9‰$ PDB), and slightly higher $^{87}Sr/^{86}Sr$ ratios ($0·7082–0·7084$).
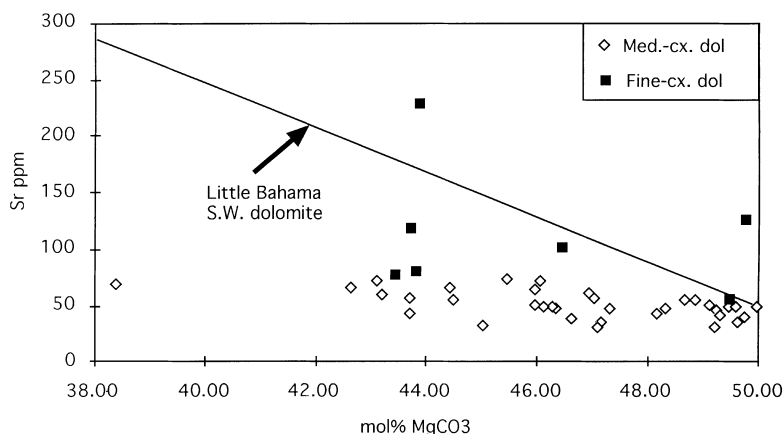
Fig. 10. Cross plots of Sr (p.p.m.) and mol percentage MgCO$_3$ for fine-crystalline and medium-crystalline dolomites. The trend line is for Miocene marine dolomites from Little Bahama Bank (Vahrenkamp & Swart, 1990).

For the medium crystalline dolomite, the data constrain but do not prove an unequivocal origin. The medium-crystalline dolomite has δ^{18}O values lower than calculated δ^{18}O values for dolomite precipitated in equilibrium with Middle Devonian seawater. The lower δ^{18}O values could have originated from compaction fluids of Middle Devonian seawater parentage during shallow to intermediate burial at slightly elevated temperatures. Such fluids would have δ^{18}O values similar to seawater, or slightly heavier as a result of recrystallization of the rock matrix in pore fluids of seawater parentage (Machel & Anderson, 1989). Taking the highest δ^{18}O value of −3·7‰ PDB as the possible original δ^{18}O signature of medium-crystalline dolomite and −2 to −3‰ SMOW as representative of Middle Devonian seawater, the temperature during dolomitization would be about 35–40 °C (calculated using the equation of Land, 1985). Using an average geothermal gradient of 30 °C km^{-1}, the burial depth of dolomitization would be 500–700 m. Based on the reconstructed burial history of the Presqu'ile barrier at the Pine Point (Mountjoy & Amthor, 1994), medium-crystalline dolomite would have occurred during the late Devonian time. This interpretation is also supported by the Sr isotope data. Medium-crystalline dolomite has slightly higher ^{87}Sr/^{86}Sr ratios than Middle Devonian seawater (Fig. 7), suggesting burial dolomitizing fluids with slightly radiogenic Sr isotopes.

The REE patterns of medium-crystalline dolomite differ from those of the precursor limestones, suggesting a high water/rock ratio during dolomitization (cf. Banner *et al.*, 1988a,b). The negative Ce anomalies in the REE patterns of medium-crystalline dolomite compared with those of precursor limestones (Fig. 9b) indicate a relative depletion of Ce in the dolomitizing fluids. The negative Ce anomalies commonly occur in the natural oxidizing waters (e.g. in seawater), because the solubility of Ce^{4+} is low in the oxidizing environment and is removed preferentially with authigenic Fe-Mn oxides or scavenged by particulate matter (e.g. Elderfield *et al.*, 1981; DeBaar *et al.*, 1985). The negative Ce anomalies in the medium-crystalline dolomite therefore could suggest (1) an oxidizing condition *during* dolomitization, or (2) removal of Ce from dolomitizing fluids in an oxidizing environment *before* dolomitization. If later is the case, the medium-crystalline dolomite would have inherited the negative Ce anomaly from dolomitizing fluids regardless of whether dolomitization occurred in an oxidizing or reducing environment. Because the similarity between the smaller ionic radius of Mg and the ionic radii of the heavy REE (Graf, 1984; Dorobek & Filby, 1988), dolomite should be enriched in heavy REE relative to calcites. The enrichment of heavy REE in the medium crystalline dolomite relative to the precursor limestones may therefore have resulted from the larger distribution coefficients of heavy REE for dolomite than calcite.

An alternative interpretation is that medium-crystalline dolomite formed soon after sedimentation of the Pine Point Formation by Middle Devonian seawater derived from the Elk Point Basin (Skall, 1975; Kyle, 1981, 1983; Rhodes *et al.*, 1984; Krebs & Macqueen, 1984). This interpretation is based primarily on the spatial distribution and geochemical trends of medium-crystalline dolomite. Medium-crystalline dolomite occurs mostly in the southern lower part of the Presqu'ile barrier in the Pine Point Formation (Fig. 2b). The absence of medium-crystalline dolomite in the upper part of the barrier does not appear to be due to lower porosity and permeability because the upper part of the barrier was intensively dolomitized to coarse-crystalline
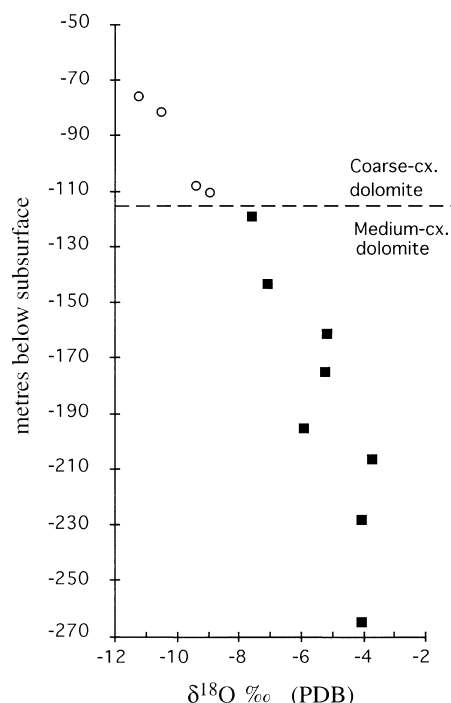
Fig. 11. The δ^{18}O profile of medium- and coarse-crystalline dolomites from borehole 2813, Pine Point. Medium-crystalline dolomite closer to the medium/coarse crystalline dolomite boundaries have lower δ^{18}O values, suggesting that medium-crystalline dolomite probably have been modified by later diagenetic fluids that precipitated coarse-crystalline dolomite.

dolomite during later diagenesis (Qing & Mountjoy, 1994a). Thus, the restriction of medium-crystalline dolomite to the southern lower part of the barrier suggests dolomitizing fluids may have

been derived from the Elk Point Basin to the south of the barrier.

If medium-crystalline dolomite was formed by Middle Devonian seawater, it should have geochemical signatures of Middle Devonian seawater, similar to the fine-crystalline dolomite discussed above. However, its geochemistry is different (lower δ^{18}O values, slightly higher ^{87}Sr/^{86}Sr ratios, and relatively low Sr but high Mn concentrations). This difference could have been caused by neomorphic alteration during later burial diagenesis. Dolomites can form as a Ca-rich, poorly ordered metastable phase, which would experience crystal enlargement and chemical modification during progressive stabilization (Land, 1985; Mazzullo, 1992). Unless earlier formed dolomites have a low porosity and permeability, their initial geochemical properties can be altered at elevated temperatures in the subsurface (Land, 1985; Mazzullo, 1992). This could be the case for the medium-crystalline dolomite at Pine Point, which is generally porous and permeable and regarded as part of a regional aquifer (Bachu, 1997). It occurs immediately beneath the massive coarse-crystalline dolomite and Pb-Zn minerals that were related to the hydrothermal fluids (Krebs & Macqueen, 1984; Rhodes *et al.*, 1984; Qing & Mountjoy, 1994a,b). The medium-crystalline dolomite therefore could have been neomorphosed by later hydrothermal fluids at elevated temperatures in the subsurface. Some medium-crystalline dolomite crystals have cloudy centres and clear rims (Fig. 5) and some have blotchy of bright orange (CL) suggesting
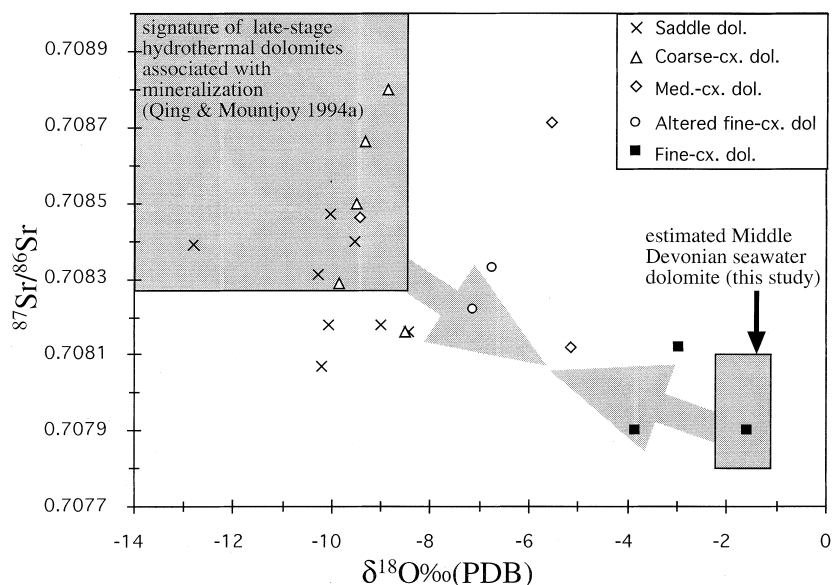

Fig. 12. Cross plot of ^{87}Sr/^{86}Sr ratios and δ^{18}O values of various dolomites associated with Presqu'ile barrier. The geochemical signatures of medium-crystalline and altered fine-crystalline dolomites can be interpreted as a mixture of two end members, one represents Devonian seawater signatures, and the other corresponds to hydrothermal fluids associated with late-stage dolomitization and mineralization.

neomorphism by later diagenetic fluids (cf. Banner *et al.*, 1988a,b).

Neomorphism is also indicated by the gradual lowering of $\delta^{18}O$ values for medium-crystalline dolomites when approaching the medium/coarse crystalline dolomite contact at borehole 2813 from the Pine Point area (Fig. 11). The $\delta^{18}O$ value of medium-crystalline dolomite remains almost constant at about $-4\text{\textperthousand}$ PDB for samples from 30 m below the medium/coarse crystalline dolomite contact. However, near the contact $\delta^{18}O$ value of medium-crystalline dolomite displays a gradual shift towards lower values (Fig. 11). At the medium/coarse crystalline dolomite contact, the $\delta^{18}O$ value of medium-crystalline dolomite reaches $-7\cdot6\text{\textperthousand}$ PDB, a value very close to that of the adjacent coarse-crystalline dolomite (Fig. 11). This suggests that $\delta^{18}O$ values of medium-crystalline dolomite may have been modified or reset by later diagenetic fluids that were responsible for the formation of coarse-crystalline dolomite.

Alteration and modification of medium-crystalline dolomite by later diagenetic fluids are also supported by cross plotting $^{87}Sr/^{86}Sr$ ratios and $\delta^{18}O$ values of various types of dolomites associated with the Presqu'ile barrier (Fig. 12). A general trend of progressively decrease in $\delta^{18}O$ with a corresponding increase in $^{87}Sr/^{86}Sr$ ratios from fine-crystalline, to medium-crystalline, coarse-crystalline and saddle dolomites occurs (Fig. 12). Two end members are evident in these dolomites. One is the unaltered fine-crystalline dolomite, that has the lowest $^{87}Sr/^{86}Sr$ (0·7079) and the highest $\delta^{18}O$ values ($-1\cdot6$ to $-3\cdot8\text{\textperthousand}$ PDB), representing dolomitization by the Middle Devonian seawater. The other end member (coarse-crystalline and saddle dolomites) has the most radiogenic $^{87}Sr/^{86}Sr$ ratios and lowest $\delta^{18}O$ values and characterizes dolomitization associated with late-stage hydrothermal fluids (see Qing & Mountjoy, 1994a for details). Medium-crystalline dolomite and the altered fine-crystalline dolomite near the orebodies have $^{87}Sr/^{86}Sr$ ratios and $\delta^{18}O$ values between these end members (Fig. 12) consistent with early dolomitization by Middle Devonian seawater later modified by hydrothermal fluids.

CONCLUSIONS

Fine-crystalline dolomite associated with the Middle Devonian Presqu'ile barrier at Pine Point

is interpreted to have formed penecontemporaneously at or just below the sea floor from Middle Devonian seawater, because: (1) it is interbedded with evaporitic anhydrites in the back-barrier facies; (2) its oxygen isotopes and Sr isotope compositions are similar to dolomites precipitated from Middle Devonian seawater; (3) and its Sr concentration and mol percentage $CaCO_3$ follows the same trend as do Little Bahama Bank seawater dolomites.

Medium-crystalline dolomite probably formed during shallow burial by fluids derived from compaction based on its lower $\delta^{18}O$ values slightly radiogenic $^{87}Sr/^{86}Sr$ ratios relative to the fine crystalline dolomite, and different REE patterns from the limestone precursors. An alternate interpretation is that medium-crystalline dolomite formed soon after deposition by Devonian seawater from the adjacent Elk Point basin, but was altered at higher temperatures by the later diagenetic fluids. This is supported by the restriction of medium-crystalline dolomite to the southern lower part of the Presqu'ile barrier, which is in direct contact with evaporites in the Elk Point Basin. If so, its geochemical signatures can be interpreted as mixture of two end members: one from Devonian seawater; and the other from hydrothermal fluids associated with late-stage dolomitization and mineralization.

This study indicates that dolomitization in the Middle Devonian Presqu'ile barrier occurred in at least two stages in different diagenetic environments during evolution of the Western Canada Sedimentary Basin. The geochemistry of earlier formed dolomites could have been modified if they were porous and permeable and water/rock ratio was large during neomorphism.

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