Mississippi Valley-type (MVT) Pb-Zn potential in Middle and Upper Devonian carbonate deposits of northeastern Alberta, and implications for future exploration based on diagenesis and isotope geochemistry

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Rice, R.J. and Lonnee, J., 2006: Mississippi Valley-type (MVT) Pb-Zn potential in Middle and Upper Devonian carbonate deposits of northeastern Alberta, and implications for future exploration based on diagenesis and isotope geochemistry; *in* Potential for Carbonate-hosted Lead-zinc Mississippi Valley-type Mineralization in Northern Alberta and Southern Northwest Territories: Geoscience Contributions, Targeted Geoscience Initiative, (ed.) P.K. Hannigan; Geological Survey of Canada, Bulletin 591, p. 117–148.

Abstract: Middle and Upper Devonian carbonate deposits in northeastern Alberta were investigated in outcrop and core for their Mississippi Valley-type (MVT) lead and zinc potential. A detailed petrographic study indicates that many, but not all, of the diagenetic products associated with the Pine Point – Presqu'ile Barrier deposits were found. Isotopic analysis of the rocks suggests the diagenetic fluid(s) responsible for dolomitization in the area was modified Devonian seawater. Stable isotope data from the Mikkwa Formation at Harper Creek, and the Methy Formation at Whitemud Falls, fall within, or are marginal to similar studies on the Pine Point – Presqu'ile Barrier deposits. $^{87}Sr/^{86}Sr$ values from the Mikkwa Formation at Harper Creek and Vermilion Chutes show some similarities to Pine Point dolomite data. Overall, the integrated data do not rule out the possibility of MVT Pb-Zn deposits in northeastern Alberta, but do not support exploration at the sites examined.

Résumé : Nous avons procédé à l'étude de dépôts carbonatés du Dévonien moyen et supérieur, dans le nord-est de l'Alberta, par l'examen d'affleurements et de carottes afin de déterminer leur potentiel pour des gisements de plomb-zinc de type Mississippi-Valley. D'après une étude pétrographique détaillée, nous avons trouvé bon nombre des produits diagénétiques (mais pas tous), associés aux gisements de Pine Point et de la barrière de Presqu'ile. L'analyse isotopique des roches donne à penser que le ou les fluides diagénétiques responsables de la dolomitisation dans la région étaient de l'eau de mer dévonienne modifiée. Les données sur les isotopes stables de la Formation de Mikkwa, au ruisseau Harper, et de la Formation de Methy, aux chutes Whitemud, sont conformes à ou en marge d'études similaires sur les gisements de Pine Point et de la barrière de Presqu'ile. Des valeurs du rapport $^{87}Sr/^{86}Sr$ obtenues pour la Formation de Mikkwa au ruisseau Harper et aux chutes Vermilion présentent des similitudes avec les données sur la dolomite de Pine Point. Dans l'ensemble, les données intégrées n'excluent pas la possibilité que des gisements de plomb-zinc de type Mississippi-Valley existent dans le nord-est de l'Alberta, sans toutefois soutenir l'exploration dans les sites étudiés.

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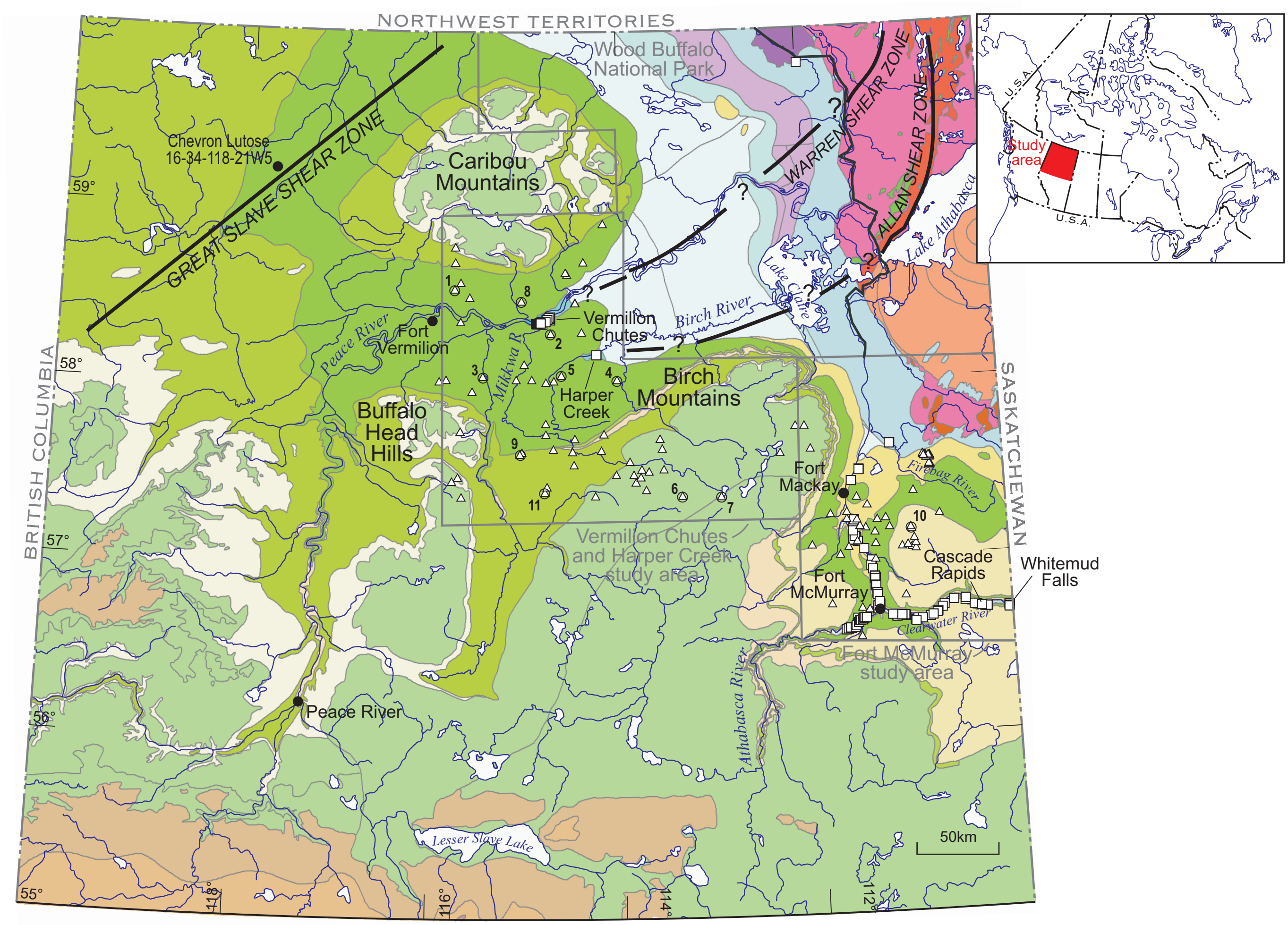
INTRODUCTION

The province of Alberta, although well known for its hydrocarbon resources, has received less recognition for its non-fuel mineral resource potential. This situation has improved somewhat in recent years with the discovery of diamondiferous kimberlite pipes (Carlson et al., 1998), an awareness of the potential for microdisseminated gold-silver-copper (Abercrombie and Feng, 1997), and a renewed interest in uranium exploration (Ruzicka, 1997) in the northern region of the province. However, as indicated in Olson et al. (1994), the mineral potential is not restricted to these commodities. This issue was addressed by the Canada-Alberta agreement on mineral development (1992–1995) (see Macqueen, 1997) and recently by the jointly funded Targeted Geoscience Initiative (TGI) program. The presence of relatively shallow carbonate bedrock in northeastern Alberta, and its proximity to the Pine Point lead-zinc mining district in the Northwest Territories (NWT), prompted the Alberta Geological Survey to partner in a TGI project to investigate the Mississippi Valley-type (MVT) carbonate-hosted lead-zinc potential of northern Alberta and the southern NWT.

The presence of lead (Pb) and zinc (Zn) mineralization in the Western Canada Sedimentary Basin in Alberta has been known since roughly 1890, when claims were staked at the Eldon prospect on Panorama Ridge west of the Bow River in Banff National Park. At approximately the same time, galena was discovered in carbonate deposits near Baker Creek on the west flank of Castle Mountain east of the Bow River. These occurrences and others (Spray Lake, Oldman River) are found in outcrop in the fold-and-thrust belt along the southwestern margin of the province. In addition to being reviewed in Godfrey (1985), these occurrences are also discussed by Pană (2006), with a focus on their structural control. More recently, as a result of hydrocarbon exploration, Pb-Zn occurrences are known to occur in subsurface carbonate deposits from central and northwest Alberta, but can be at depths exceeding 1000 m. Elsewhere in this volume, Pană (2006, his Fig. 21) the locations of surface and subsurface carbonate-hosted Pb-Zn occurrences in Alberta are presented. While it has been speculated that they could be MVT Pb-Zn mineralization, the genesis of these occurrences has not been formally established.

Carbonate rocks in Alberta range in age from Cambrian to Jurassic, but the principal sequences are Middle Devonian to Mississippian, with the main exposures found in the



fold-and-thrust belt. Outside of the fold-and-thrust belt, exposures in northeast Alberta (excluding Wood Buffalo National Park) are restricted to: 1) outcrop along the Clearwater and Athabasca rivers, and selected tributaries; 2) on the Peace River at Vermilion Chutes; 3) near the mouth of the Mikkwa River at its confluence with Peace River several kilometres downstream of Vermilion Chutes; and, 4) along Harper Creek at, and near, its confluence with Lambert Creek (Fig. 1). Only sparse evidence of Pb-Zn mineralization exists at these locations. Prior exploration at Vermilion Chutes (Gulf Minerals, 1975) returned up to 0.1% Zn, but follow-up work appears not to have been done. Also, Carrigy (1959) reported an isolated occurrence of galena at Whitemud Falls on the Clearwater River.

This paper presents diagenetic and isotopic data gathered from Middle and Upper Devonian carbonate deposits in northeastern Alberta. The study was designed to evaluate the potential for Mississippi Valley-type Pb-Zn mineralization in this region of the province. This objective is addressed through a comparison of the diagenetic and isotopic characteristics of potential host rocks with the carbonate units hosting the Pine Point deposits in the Northwest Territories. The study incorporated both a field and core program, and involved only Devonian-aged carbonate rocks, as they constitute nearly all (excepting the Mississippian Banff Formation) the carbonate bedrock underlying the northeastern plains of Alberta. Data from the 2001–2002 field program are presented elsewhere (Adams and Eccles, 2003;

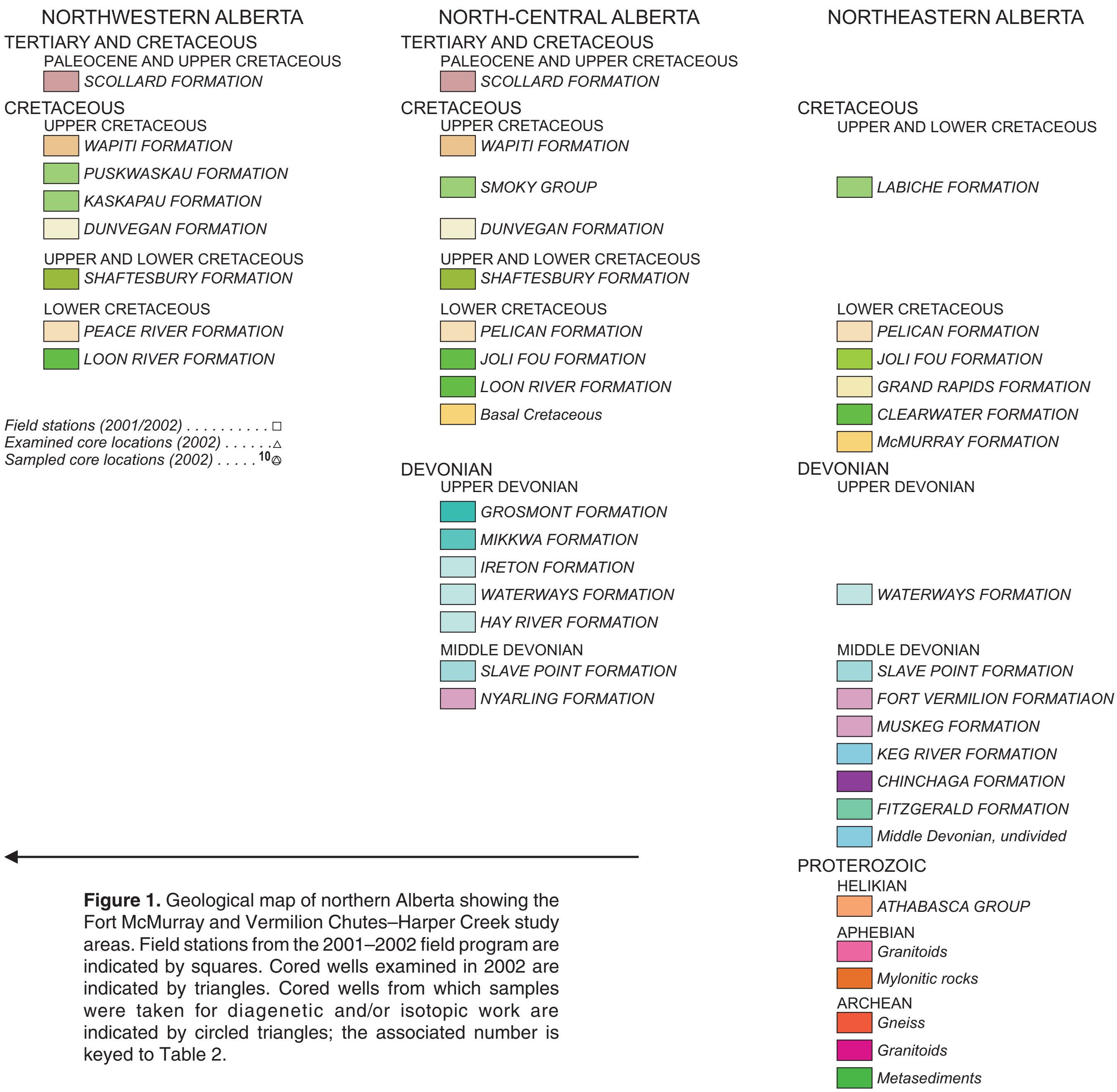


Figure 1. Geological map of northern Alberta showing the Fort McMurray and Vermilion Chutes–Harper Creek study areas. Field stations from the 2001–2002 field program are indicated by squares. Cored wells examined in 2002 are indicated by triangles. Cored wells from which samples were taken for diagenetic and/or isotopic work are indicated by circled triangles; the associated number is keyed to Table 2.

Buschkuehle, 2003; Pană, 2003; Eccles and Pană, 2003; Waters and Rice, 2003). Results of the 2002 core program are presented in Rice and Zerbe (2003). An interim summary of this study is given in Rice (2003).

This study did not encounter new Pb-Zn mineralization; however, the carbonate rocks at, or in the region of, all known reports of Pb-Zn mineralization were investigated (e.g. Vermilion Chutes, Whitemud Falls, Wood Buffalo National Park; see below). In the case of Vermilion Chutes, zinc-zap was utilized for the possible location of secondary Zn minerals without success. Carbonate rocks along the Athabasca River near Fort Mackay were also investigated, as this is the region where the most recent subsurface discovery was reported (see below). Despite the lack of new visible mineralization, selected samples from the field and core programs were submitted for trace element analysis. The results are presented in Eccles and Pană (2003), and Rice and Zerbe (2003), respectively. No economic values were returned. The study did not involve the comparison of mineralized Alberta samples, from outside of the study areas, to Pine Point ore. This comparison is included in Paradis et al. (2006).

As this study was geared to defining areas with greater potential for mineable carbonate-hosted MVT deposits, a primary consideration was depth to carbonate bedrock. Northeastern Alberta was chosen for this reason as opposed to northwestern Alberta, where the carbonate sequences are at considerable depths in the basin. It was also selected because it represents a more basin-marginal setting overlying possible southwesterly extensions of significant basement shear zones from the Precambrian Shield of northeastern Alberta (Fig. 1). Both basin-marginal settings and structural trends are known to be important regional controls with respect to the clustering of MVT deposits (Leach and Sangster, 1993). Since the scope of the study was restricted to northern Alberta, carbonate deposits in areas of known Pb-Zn occurrences in the thrust-faulted sequences of southwestern Alberta (mostly in Banff National Park) were not investigated. The most prospective region for MVT Pb-Zn deposits in northeastern Alberta occurs in Wood Buffalo National Park. The carbonate bedrock here is closest to the Pine Point mining district, is at or near surface and there are also old reports of galena from this area (see below). Only limited geological examination and selected sampling within the park was undertaken as part of this study, as park policies do not permit exploration.

As defined by Leach and Sangster (1993), Mississippi Valley-type (MVT) Pb-Zn deposits are a varied family of epigenetic ores that occur dominantly in dolostone with Pb and Zn as the main commodities. While a unifying genetic model cannot be developed for MVT districts (100's–1000's km^2), some general distinguishing characteristics for this deposit type do exist. Abbreviated from Leach and Sangster (1993), the most important characteristics of MVT deposits are as follows:

1. The host rock is predominantly dolostone.
2. They are epigenetic, strata-bound, and not associated with igneous activity.
3. They occur at relatively shallow depths in platform carbonate sequences in basin-marginal positions.
4. They occur in relatively undeformed to thrust-faulted foreland basin settings.
5. MVT districts contain geological features that promote upward migration of the ore-bearing fluids; such features include basement highs, breccias, faults, and facies trends including shale edges.
6. They are typically associated with thermal anomalies; i.e. while ore deposition temperatures are low (75°–200°C) they are greater than can be explained by local geothermal gradients.
7. The dominant minerals are sphalerite, galena, pyrite, marcasite, dolomite, calcite, and quartz.
8. Alteration types consist of host rock dolomitization, brecciation, and dissolution and the dissolution and recrystallization of clay and feldspar; dissolution of host rocks is especially important.
9. The ore fluids can be characterized as dense basinal brines with 10–30 wt.% salts.
10. Their isotopes indicate that reduced sulphur and metals are derived from crustal sources.
11. Sulphide mineral textures are highly varied and ores can be coarse-crystalline to fine grained and range from disseminated to massive.

Earlier reviews of this deposit type are listed in Leach and Sangster (1993). Subsequent important contributions include Sangster (1996), Leach et al. (2001), and Bradley and Leach (2003). The more recent significant improvements in our understanding of this deposit type stem from advances in their age-dating (see Leach et al., 2001) and from a better understanding of tectonic control (see Bradley and Leach, 2003). Leach et al. (2001) considered a direct connection between the formation of MVT mineralization and orogenic events, with deposits clustered in Devonian–Permian time associated with the assembly of Pangea, and in Cretaceous–Tertiary time during the polyphase Laramide orogeny. During these periods they (ibid.) favoured topographically driven models for moving large volumes of fluids through platform carbonate hydrologically connected to the deformation belt. Bradley and Leach (2003) investigated the relationship between MVT mineralization and type of orogenic foreland. They (ibid.) concluded that this does not exert a first-order control on the presence or absence of MVT deposits and proposed a tectonic model for collisional forelands that stressed the importance of lithospheric flexure in the localization of MVT districts.

GEOLOGICAL SETTING OF NORTHEASTERN ALBERTA

The study region in northeastern Alberta is situated between 56°30' and 59° north latitude and 110° and 116° west longitude (Fig. 1). It is part of the Alberta Basin, a subbasin of the Western Canada Sedimentary Basin. This region is covered by extensive glacial deposits of varying thickness and is characterized by low relief and poor bedrock exposure. Elements of principal relief are the Caribou and Birch mountains and Buffalo Head Hills, with the main drainage systems encircling the Peace, Athabasca and Clearwater rivers (Fig. 1).

The Phanerozoic bedrock geology of the Western Canada Sedimentary Basin in this region (i.e. northeastern Alberta) extends from Middle Devonian clastic, evaporite, and minor carbonate deposits in the Lower Elk Point Group unconformably overlying Proterozoic metasediments and crystalline basement, to Lower to Upper Cretaceous clastic deposits of the Labiche Formation (Fig. 1). The Middle and Upper Devonian carbonate succession (Fig. 2) forms a west-dipping wedge that lies at a burial depth of 1300 m in the west and outcrops onto the Canadian Shield about 150 km east of Fort McMurray. As mentioned above, exposures of the carbonate rocks occur at or near surface along the Athabasca, Clearwater, and Peace rivers, and their tributaries. In general, the stratigraphic units are flat lying to weakly tilted and display only gentle warping; however, they may be locally faulted to varying degrees, especially in areas of dissolution of underlying Elk Point Group evaporite deposits.

The carbonate rocks in the study area have been described by MacDonald (1955), Crickmay (1957), Norris (1963), Cutler (1983), and most recently by Buschkuehle (2003). The Middle and Upper Devonian sequences comprise four groups: the Elk Point, Beaverhill Lake, Woodbend, and Winterburn groups (Fig. 2).

Lower Elk Point Group rocks consist of interbedded redbed, evaporite (mostly containing halite), shallow-marine clastic and minor carbonate units and they attain thicknesses of up to 300 m in the subbasins. This succession, which includes Basal Red Beds, Ernestina Lake, Cold Lake, and Chinchaga formations (Fig. 2), was deposited within a restricted, shallow, epicontinental sea. The successions thin dramatically through depositional onlap to near zero over positive features such as the Tathlina Arch in southern Northwest Territories and the Peace River Arch in west-central Alberta (Reinson et al., 1993).

The Upper Elk Point Group represents the initial open-marine inundation of the Alberta Basin (Campbell, 1992a) and reaches a maximum thickness of about 400 m. This group is subdivided into the dolomitic Methy Formation and the salt-bearing Prairie Formation in northeastern Alberta, with the former being equivalent to the carbonate units of the Keg River and Winnipegosis formations in other parts of the Alberta Basin (Fig. 2). The reefal carbonate deposits of the

SYSTEM	GROUP	FORMATION			MEMBER
UPPER DEVONIAN	WINTERBURN	*REDKNIFE* (88 max)			*Jean Marie* (15+)
UPPER DEVONIAN	WOODBEND	*GROSMONT* (230 max)	*IRETON* (250 max)		*Hondo* (140 max)
UPPER DEVONIAN	WOODBEND	*MIKKWA* (30 max)	*IRETON* (250 max)		
UPPER DEVONIAN	WOODBEND	*COOKING LAKE* (90 max)	*HAY RIVER* (396 max)		
MIDDLE TO UPPER DEVONIAN	BEAVERHILL LAKE	*WATERWAYS*			*Mildred* (43)
					Moberly (60±)
					Christina (27±)
					Calumet (31±)
					Firebag (52±)
MIDDLE DEVONIAN	BEAVERHILL LAKE	*SLAVE POINT* (30 max)			
MIDDLE DEVONIAN	BEAVERHILL LAKE	*FORT VERMILION* (37 max)			
MIDDLE DEVONIAN	BEAVERHILL LAKE	*WATT MOUNTAIN* (19 type)			
MIDDLE DEVONIAN	UPPER ELK POINT	*PRAIRIE/MUSKEG* (237/270 max)			
MIDDLE DEVONIAN	UPPER ELK POINT	*METHY* (34+)	*KEG RIVER* (322 max)	*WINNIPEGOSIS* (113 max)	
MIDDLE DEVONIAN	LOWER ELK POINT	*CHINCHAGA* (76 max)			
MIDDLE DEVONIAN	LOWER ELK POINT	*COLD LAKE* (79 max)			
MIDDLE DEVONIAN	LOWER ELK POINT	*ERNESTINA LAKE* (23 max)			
MIDDLE DEVONIAN	LOWER ELK POINT	*Basal Red Beds*			

Thicknesses in metres, from Norris (1963) and Glass (1990)

Examined in core . . . . *Examined in outcrop* . . . .

Figure 2. Generalized Devonian stratigraphy for northern Alberta *from* Buschkuehle (2003) (*after* Norris, 1963). Stratigraphic units addressed in this paper are shaded.

Methy and Keg River formations were deposited in a tropical, shallow-marine environment. In the study area, most of the Methy/Keg River carbonate succession occurs as isolate reefs overlying open-marine ramp carbonate rocks in the La Crete subbasin (Chow et al., 1995). Near the western portion of the study area, the La Crete basin is bounded by a shelf margin that continues westward as a widespread carbonate bank or platform (Chow et al., 1995). Subsequent increased evaporation rates led to the deposition of the Prairie evaporite deposits and terminated reef growth in these formations. Prairie Formation evaporite does not outcrop in the study area and abundant dissolution has occurred over wide parts of the Alberta Basin east of the present-day fault scarp. To the north, a laterally equivalent carbonate and anhydrite called the Muskeg Formation is present. Although historically the dolomitic shale of the Watt Mountain Formation has been included as the youngest unit in the Upper Elk Point Group, work by Meijer Drees (1988) and Williams (1984) shows a major unconformity at the base of the Watt Mountain Formation representing either an erosional event or an initial transgressive deposit. Therefore, in this paper, the Watt Mountain Formation is assigned to be part of the overlying Beaverhill Lake Group.

The Beaverhill Lake Group, constituting the uppermost stratigraphic unit in the Fort McMurray region, overlies the Upper Elk Point Group. The Beaverhill Lake Group includes the Watt Mountain, Fort Vermilion, Slave Point, and Waterways formations, and can reach a total thickness of at least 240 m in the Alberta Basin (Fig. 2). All formations occur in the subsurface in the study area but the Waterways Formation represents the sole Beaverhill Lake unit that also outcrops. Unconformably overlying the Muskeg/Prairie evaporitic succession in the subsurface are the widespread, dominantly siliciclastic strata of the Watt Mountain Formation. Next in the succession are evaporite rocks of the Fort Vermilion Formation that underlie interbedded platformal limestone, dolostone, and shale of the Slave Point Formation, which in turn underlie the Waterways Formation consisting of five members: the Firebag, Calumet, Christina, Moberly, and Mildred (Fig. 2). Each member contains differing amounts of carbonate and shale, attributable to the intercalation of platform carbonate and deeper water facies (Campbell, 1992b). All but the Mildred Member are exposed along the Athabasca and Clearwater rivers.

The Beaverhill Lake Group is overlain by the Woodbend Group, which is divisible into the Cooking Lake, Hay River, Mikkwa, Ireton, and Grosmont formations (Fig. 2). The Woodbend Group may be up to 350 m thick in central parts of the Alberta Basin and up to 460 m to the northwest, but only a few metres of the Mikkwa and Grosmont formations outcrop in the Vermilion Chutes-Harper Creek region of the study area. The outcrops consist of shallow-marine and basinal carbonate and shale, with occasional, isolated reefs.

The Winterburn Group in turn overlies the Woodbend Group, which in the study area is represented only in the subsurface by the silty, argillaceous, dolomitic, and locally biostromal, shallow-marine limestone of the Jean Marie Member of the Redknife Formation (Fig. 2).

SUMMARY OF CARBONATE-HOSTED LEAD-ZINC INVESTIGATIONS IN ALBERTA

A series of four internal files at the Alberta Geological Survey consisting of selected correspondence with prospectors (Alberta Research Council, 1969), and reports by Green (1957), Holter (1973), and Godfrey (1985) constitute a review of the early carbonate-hosted Pb-Zn investigations in Alberta. The earliest known occurrences (Baker Creek, Eldon, Spray Lake, Oldman) are in the fold-and-thrust belt of southwest Alberta and are reviewed in Godfrey (1985), from which most of the following information is obtained. Except for the Oldman deposit, little technical information is available on these occurrences.

The history of Pb-Zn mineral exploration in Alberta begins in the late nineteenth century with discoveries of galena mineralization near Baker Creek on Castle Mountain, and of copper-lead-zinc mineralization at the Eldon showing on Panorama Ridge. Both are within Banff National Park on opposite sides of the Bow River, approximately half the distance between Lake Louise and Eisenhower Junction (see Godfrey, 1985, his Fig. 3). Some mining did occur during the First World War at Baker Creek, and a small community known as Silver City was developed to support the effort. The mineralization here occurs in black dolomite, veined by white coarse dolomite, of the Middle Cambrian Cathedral Formation. The Eldon showing was visited by R. Green of the Alberta Research Council (see Green, 1957) and is referenced in Evans (1965, Evans et al., 1968). It also produced a small amount of ore during the First World War. In his notes, Green (1957) refers to minor Cu mineralization and pockets of galena occurring in quartz veins within dolomite. Sphalerite, chalcopyrite, galena, and pyrite with quartz and siderite gangue were noted from the adit dump. Evans (1965) suggested that the host rock is Lower or Middle Cambrian and that it is cut by an east-striking shear zone.

As stated in Godfrey (1985), there is no known literature on the Spray Lake showing. Its location is roughly indicated in Holter (1977, his Fig. 8).

The Oldman River Pb-Zn occurrence is the best known of the early showings, with results published in Holter (1973, 1977). Depending on the source, the occurrence was initially discovered either by the Stony Indian, King Bearspaw, early in the twentieth century (Peaks of the Canadian Rockies internet website) or by a group of hunters in 1912 (Holter, 1977). It lies at the headwaters of the Oldman River at approximately 2290 m on the east slope of Mount Gass along the eastern flank of the High Rock Range (lsd. 13, sec. 35, twp. 13, rge. 6, W 5th mer.; NTS 82J/02; UTM 663036E, 5555234N (upper adit), 663008E, 5555268N (lower adit), NAD 27, zone 11). The occurrence is also discussed in Norris (1958) who described the mineralization as occurring approximately 50 ft. (15 m) below the top of the Upper Devonian Palliser Formation in an upper and lower zone, approximately 10 ft. (3 m) and 30 ft. (9 m) thick, respectively, developed along minor splays from the underlying Lewis Thrust. This report also states that no other similar occurrences were found in the map area. Two adits currently exist at the site, which Western Canadian Collieries worked during 1953 and 1954. The most meaningful assay results are from a bulk sample of unknown size taken from the portal of the upper adit: 31.5 % Pb, 7.3 % Zn, trace Au, and 2.2 oz/short ton Ag. The mine realized a total of $390 for the sale of 10 tons of ore.

Instances of surface discoveries in the Interior Plains of Alberta are limited, although occasionally landowners inform of finding galena in rock piles, or elsewhere, on their fields. The first published occurrence by Carrigy (1959) reported a single occurrence of galena filling a small cavity associated with the dolomitization of the Middle Devonian Methy Formation at Whitemud Falls on the Clearwater River. At roughly the same period, there are accounts of hand samples with Pb-Zn mineralization reportedly found in Wood Buffalo National Park (see Godfrey, 1985, p. 4). The most recent known surface discovery is associated with exploration conducted by Gulf Minerals at Vermilion Chutes on the Peace River in northeastern Alberta (Gulf Minerals, 1975). Metadata acquired for this property indicate that sampling returned 0.1 % Zn from the Upper Devonian Grosmont Formation, which is both vuggy and petroleum-stained at this location. Follow-up work apparently did not occur.

The subsequent history of carbonate-hosted Pb-Zn investigations in Alberta is dominated by subsurface discoveries associated with hydrocarbon exploration at depths excessive for mining. Undoubtedly, numerous instances of Pb and/or Zn mineralization would be encountered if the records of petroleum companies that have been, or are, active in Alberta were searched. This would be more than just a daunting task, and was not attempted during this study. An early indication of the presence of Pb and Zn in subsurface carbonate is found in the Annual Report of the Research Council of Alberta for 1952, which includes reports of sphalerite from both the Duhamel and New Norway fields in central Alberta (see Alberta Research Council, 1953). Up to 15% Zn over 7.5 ft. (2.3 m) was reported for a well in the New Norway field. In the same Annual Report it was also mentioned that a list of base metal sulphides had been made from the files of Imperial Oil Company. Attempts to locate this list were unsuccessful. Similarly, Haites (1960) reported sphalerite from the Duhamel field, as well as from the Upper Devonian Leduc Formation in most of the wells of the New Norway and Malmo fields, on the same reef trend as Duhamel. He also included reports of sphalerite in the Bonnie Glen and Wizard Lake fields on a different reef trend and suggested a structural control over the development of both trends.

Aware of the numerous subsurface Pb-Zn occurrences in carbonate of central Alberta, the provincial government sponsored two subsurface studies in the north of the province, where in some areas, such as northeastern Alberta, carbonate bedrock is much closer to, or at surface. The first study was performed by Dubord (1987) who completed a literature appraisal of the MVT Pb-Zn potential for the Alberta Research Council. Although this study involved core examination, and resulted in a list of 18 wells with Pb-Zn mineralization, the cores were not logged or sampled for analysis. In a subsequent, more comprehensive study undertaken as part of the Canada-Alberta Mineral Development Agreement, Turner and McPhee (1994) completed considerable core logging with trace element analyses. Unfortunately, the only significant result from the trace element work was 3.1% Zn and 0.05% Pb over 20.7 m (including 5.1% Zn and 0.03% Pb over 10.8 m, and 6.9% Zn and 0.05% Pb over 2.6 m) in faulted and dolomitized Keg River Formation at approximately 1300 m depth in the Chevron Lutose 16-34-118-21W5 well, which is located proximal to the Great Slave Shear Zone in northwestern Alberta (Fig. 1). The maximum Zn value for this interval exceeded 9.99% (no repeat analysis). The mineralization associated with this value occurred in zones of intense fracturing up to 1 m thick with very little host rock alteration, minor sparry dolomite, and up to 20% fine-crystalline pyrite in fractures. The style of mineralization associated with values up to 3.76 % Zn consisted of a dusting of the core with disseminated fine sphalerite.

In addition to government sponsored subsurface studies, there is also mineralization reported from mineral exploration diamond drilling activities. De Paoli (1997) has reported microscopic Pb, Zn, and Cu mineralization from carbonate rocks in the Fort Mackay region of northeastern Alberta.

DATA COLLECTION AND METHODS

Field program

As discussed above, carbonate exposures are limited in northeastern Alberta. As a result, two study areas incorporating three regions of bedrock exposure were selected for fieldwork (Fig. 1). Sedimentological, mineralogical, and structural data were collected during a 2001–2002 field program. A GIS summary of the fieldwork is given in Waters and Rice (2003).

Fort McMurray study area

The Fort McMurray study area consists of outcrops along the Clearwater and Athabasca rivers and their tributaries (Fig. 1). These outcrops were generally accessible by boat, although for some locations, such as Whitemud Falls on the Clearwater River, a helicopter was required.

The exposed rocks along the Clearwater River between Fort McMurray and Cascade Rapids belong to the Waterways Formation. Rocks of the Methy Formation are exposed at Cascade Rapids and farther to the east at Whitemud Falls.

Outcrops of the Moberly Member, Waterways Formation occur along the Athabasca River both southwest and north of Fort McMurray (Fig. 1). Several exposures of the Methy Formation were accessed by road and boat along the Firebag River, which joins the Athabasca from the east north of Fort Mackay.

Vermilion Chutes and Harper Creek study area

The Vermilion Chutes and Harper Creek study area consists of outcrops on the Peace River and Harper Creek-Birch river drainage system, respectively (Fig. 1). On the Peace River, carbonate bedrock is exposed only in the area of Vermilion Chutes. It is also exposed along the lower 1 to 2 km of the Mikkwa River, which joins the Peace River from the south several kilometres east of Vermilion Chutes. Exposures at Vermilion Chutes were accessed by jet boat, and those on the Mikkwa River by a combination of jet boat and all terrain vehicle, from Fort Vermilion. The only exposures of the Upper Devonian Grosmont Formation in northern Alberta occur on the north bank of the Peace River at the lower chutes. The underlying Upper Devonian Mikkwa Formation is more extensively exposed over several kilometres, mainly along the north bank of the Peace River, between the upper and lower chutes. It is also well exposed (accessible by all terrain vehicle and boat from the lower chutes) along the smaller Mikkwa River.

Harper Creek lies roughly 37 km to the southeast of Vermilion Chutes (Fig. 1), and was accessed by helicopter from Fort McMurray. Exposures of the Mikkwa Formation were examined at the confluence of Harper and Lambert creeks, as well as roughly 3 km east of this location on the north bank of Harper Creek.

Core program (2002)

A core study was conducted at the Alberta Energy and Utilities Board, Core Research Centre, Calgary, and at the Mineral Core Research Facility, Edmonton, from June to September 2002. One hundred and thirteen (113) cores from 90 wells or drillholes were logged and selected samples collected for petrographic examination, and trace element and isotope geochemistry (Rice and Zerbe, 2003). Of the total number of wells examined, only eleven contained diagenetic features that were selected for isotope analyses (see Table 2). This study was undertaken to examine the carbonate strata in the subsurface in the two larger study areas shown in Figure 1 beyond the river exposures inspected in the preliminary field study. In the Fort McMurray study area, conventional petroleum and oil sand wells east and west of the Athabasca River were included. In the Fort Vermilion and Harper Creek study area, wells on the southern flank of the Caribou Mountains and the northern flank of the Birch Mountains were included. As mentioned previously, this region contains the southwesterly projection of two major shear zones from the Precambrian Shield in northeastern Alberta (Fig. 1) and it incorporates a number of other northeast-trending potential structural lineaments identified by Pană et al. (2001). Some of the potential structures align along the northern flank of the Birch Mountains, on-strike with the axis of Lake Athabasca, and possibly define a regional structural trend.

ANALYTICAL METHODS

Transmitted light petrography

All thin sections were impregnated with blue epoxy for porosity determination and half-stained with potassium ferricyanide and alizarin red S according to Dickson (1966), enabling visual identification of calcite and dolomite phases. They were examined under transmitted light (plane-polarized and cross-polarized) on an Olympus BH-2 petrographic microscope.

Cathodoluminescent petrography

For cathodoluminescent petrography, a cold cathode Luminsoscope™ made by PATCO Inc. was used in conjunction with the petrographic microscope described above in the petroleum geology research laboratory at the Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta. The operating conditions were maintained at 14–16 kV and 0.5 mA under a vacuum of 30–50 millitorr to provide consistency of results. Photomicrographs were taken with a Minolta SLR camera using Kodak Ektachrome 35mm tungsten slide film at an exposure setting of +1 eV.

Stable and radiogenic isotopes

Thirty isotope powders were collected from the 2001–2002 outcrop samples, and nineteen were collected from 2002 core program samples.

Stable isotopes (carbon, oxygen)

Oxygen and carbon stable isotope powders were collected from calcite, dolomite, and anhydrite samples using a hand-held dental drill. The powders were reacted in vacuo with 100% pure phosphoric acid for at least 4 hours at 25°C for calcite and 72 hours at 25°C for dolomite. The evolved CO_2 gas was analyzed for isotopic ratios on a Finnigan mass spectrometer at the Isotope Science Laboratory, Department of Physics and Astronomy, University of Calgary. Values of oxygen and carbon isotopes are reported in per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard. Precision was better than 0.05 ‰ for both $\delta^{18}O$ and $\delta^{13}C$.

Radiogenic isotopes (strontium)

Strontium isotopes were analyzed on identical powder splits from the samples analyzed for stable isotopes. Strontium isotope analyses were performed by Geospec Consultants Ltd., Edmonton, using conventional cation exchange chromatography and Thermal Ionization Mass Spectrometry (TIMS). All data were normalized for instrumental fractionation to a value of $^{86}Sr/^{88}Sr = 0.1194$, and are presented relative to a value of 0.710245 for the NIST Standard reference Material SRM987 Sr isotope standard. The average value of $^{87}Sr/^{86}Sr$ determined for SRM987 over the course of the analyses was 0.710257. All Sr isotope data presented here have uncertainties (expressed as 2 Standard Errors) lower than 0.000020.

FORMATION DESCRIPTIONS

During the 2001 field program, stratigraphic sections were measured in the Methy, Waterways, Mikkwa, and Grosmont formations. The sections, and accompanying sedimentological descriptions, are presented in Buschkuehle (2003). The Waterways Formation is not discussed here as it displayed little dolomitization and therefore had less potential to host MVT Pb-Zn mineralization. The carbonate sequences seen in outcrop are essentially flat lying and only locally display low-amplitude, long-wavelength warping in some river exposures. They are fractured and jointed, but are not commonly faulted. Additional stratigraphic units sampled during the 2002 core program were the Keg River

(Methy Formation equivalent) and Slave Point formations, and the Jean Marie Member of the Redknife Formation. A brief summary of each formation examined in outcrop is provided below modified from Buschkuehle (2003). Complete lithological descriptions of carbonate core was not the emphasis of the subsurface program, rather it was the identification and sampling of relevant diagenetic features. Consequently, only the sampled carbonate phase is described (see Tables 1 to 3) and formal formation descriptions for these units are not included.

Middle Devonian Methy Formation, Upper Elk Point Group

The Methy Formation outcrops along the Clearwater and Firebag rivers (Fig. 3). On the Clearwater River, it is well exposed at Whitemud Falls, attaining a maximum thickness of approximately 10 to 12 m. At this location, the formation consists of a basal, light grey, fossiliferous, dolomitic limestone bank overlain by a yellow-grey, calcareous dolostone containing crinoids and bulbous to tabular stromatoporoids. The succeeding overlying unit contains up to 3.5 m of a very porous, pervasively dolomitized reefal bank with floating, bulbous stromatoporoids and paleokarst. The uppermost unit is a 1 to 2 m thick grainy, sucrosic, dolomitic limestone with scattered crinoids. The Methy Formation represents a fore-reef to reef environment in moderately to highly agitated water. Porosity values can be as high as 25%. Calcite cement is common in vugs and fractures, and scattered, very minor saddle dolomite also occurs.

Upper Devonian Mikkwa Formation, Woodbend Group

The Mikkwa Formation outcrops at three locations: 1) on the Peace River at Vermilion Chutes, 2) in the lower 1 to 2 km of the Mikkwa River, and 3) along Harper Creek (Fig. 4). Its maximum exposed thickness is approximately 6 m. The basal unit is a light grey to reddish, fossiliferous, dolomitic limestone overlain by a 1 m thick reddish-grey, brachiopod-rich limestone. The succeeding exposed units consist of 0.4 m of reddish-grey nodular limestone, 1 m of variegated reddish-grey nodular mudstone to wackestone, 1 m of yellowish-grey brachiopod-rich dolostone, and a massive, up

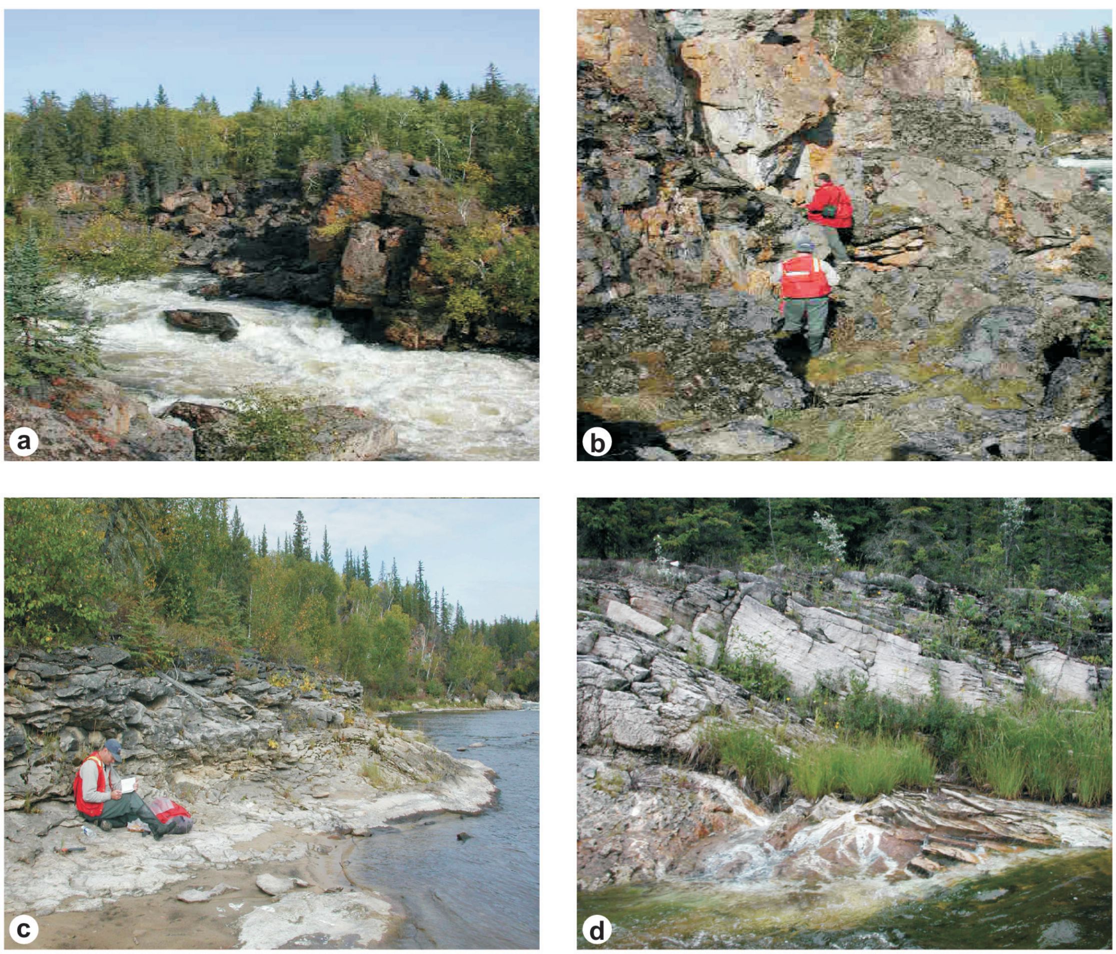


Figure 3. Middle Devonian Methy Formation at Whitemud Falls, Clearwater River (**a**, **b**, **c**) and on the Firebag River (**d**), Fort McMurray study area. *Modified from* Buschkuehle (2003).

to 2 m thick, yellow reefal dolostone with minor crinoids but abundant rugose and colonial corals. The uppermost unit is highly porous with extensive moldic porosity due to coral dissolution. At Vermilion Chutes these moulds are often hydrocarbon-stained and contain calcite and/or dolomite cements.

Upper Devonian Grosmont Formation, Woodbend Group

The Grosmont Formation is exposed on the Peace River only at Vermilion Chutes, where it is approximately 2 m thick and gradationally overlies the Mikkwa Formation (Fig. 4). A basal 0.6 m thick, grey, dolomitic coral framestone with colonial and rugose corals in growth position is succeeded by a nodular (cm-size) yellow to grey dolostone. This grades to an uppermost fossiliferous reefal fabric-selective dolostone displaying laminar to wavy lamination and abundant crinoids, corals, and stromatoporoids. Fossil dissolution has created extensive moldic and vuggy porosity that increases downward toward the Mikkwa Formation. Hydrocarbon staining occurs and also increases toward the Mikkwa Formation. Previous industry exploration by Gulf Minerals (1975) returned 0.1% Zn from the Grosmont Formation at this location, but no Pb-Zn occurrences were observed here despite the liberal application of zinc-zap.

DIAGENESIS

A petrographic diagenetic study of the Middle and Upper Devonian carbonate deposits in the two study areas was conducted as a prelude to isotopic investigation. Samples from both the field and core programs were examined. The following discussion follows stratigraphic order, from oldest to youngest.

Middle Devonian Methy and Keg River formations, Upper Elk Point subgroup

Methy Formation

Three (3) samples from the Methy Formation at Whitemud Falls were examined (C-406494–406496).

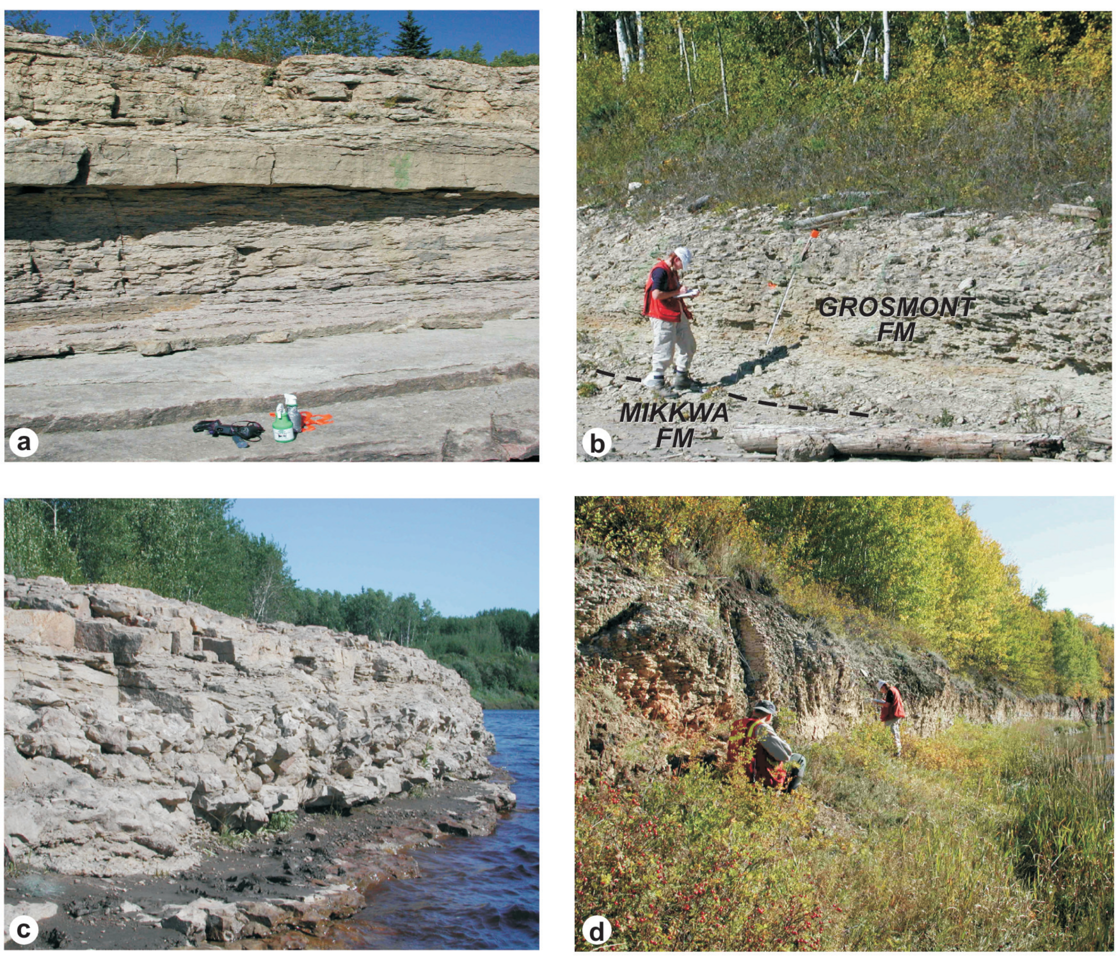


Figure 4. Upper Devonian Mikkwa (**a**) and Grosmont formations (**b**); Vermilion Chutes, Peace River, and the Mikkwa Formation near the mouth of the Mikkwa River (**c**), and at Harper Creek (**d**). *Modified from* Buschkuehle (2003).

All samples from the Methy Formation are completely dolomitized and original depositional textures could not be discerned. Three distinct diagenetic phases are visible in thin section. These precipitated subsequent to significant burial (i.e. >600 m). Very fine-crystalline matrix dolomite pervasively replaces the original limestone matrix. Under CL, this matrix dolomite displays a relatively homogenous dull red colour, and bright red rims adjacent to vuggy pores. Later diagenetic events include infilling of secondary vuggy pores by bitumen, and the precipitation of iron-rich sparry calcite cement. However, no evidence of MVT mineralization, such as saddle dolomite or Pb-Zn sulphides, exists.

Keg River Formation

Fourteen (14) thin-sections from core and one (1) from outcrop in the Keg River Formation were examined (C-421176–C-421187, C-421189, C-421194, and C-421197). Selected photomicrographs for these are shown in Figure 5 (refer to Table 2 for the well names and locations).

One sample (C-421197) of the Keg River Formation was collected from outcrop on the Salt River in Wood Buffalo National Park. It consists of a packstone with abundant brachiopods, crinoids, ostracodes, and bryozoans, characteristic of the Keg River Formation throughout the northern reaches of the Alberta Basin. There is no evidence of significant diagenesis within this sample (Fig. 5a).

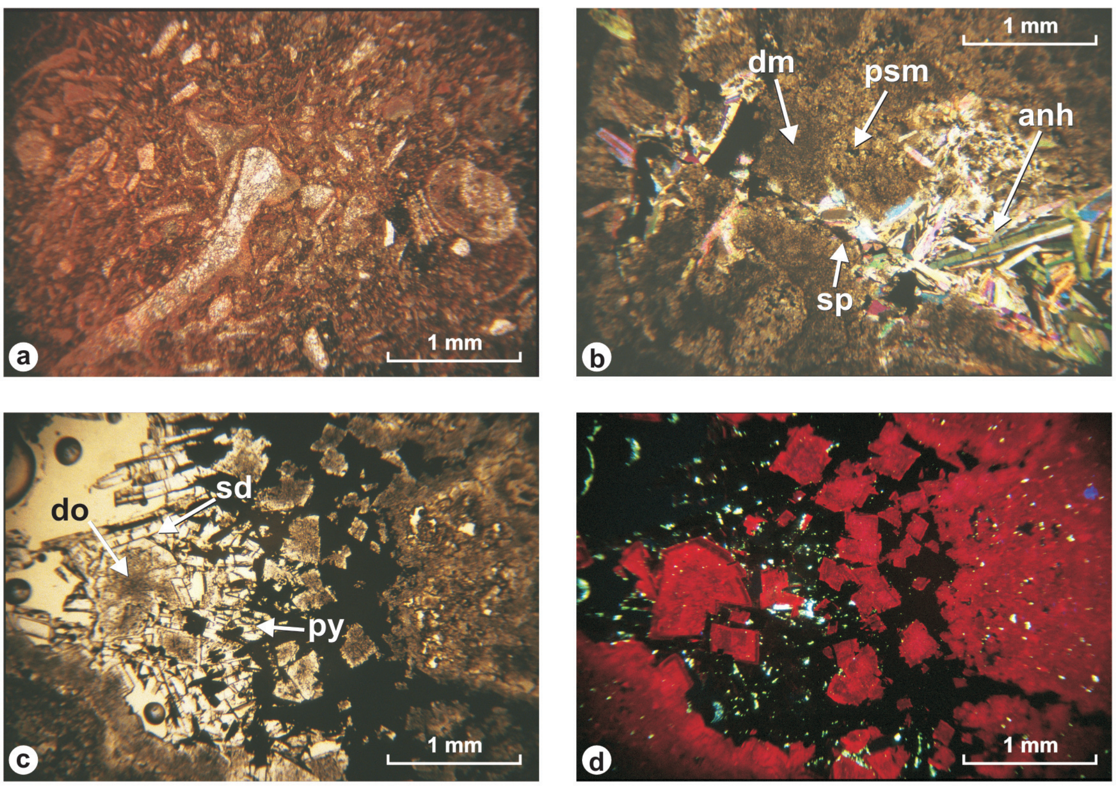


Figure 5. Transmitted light (**a**, **b**, and **c**) and cathodoluminescent (**d**) photomicrographs of the Keg River Formation in core. **a.** An unaltered brachiopod-crinoid-ostracode-bryozoan packstone (C-421197). **b.** Dolomicrite (dm) replacing the original ostracode/peloidal grainstone. Dolomicrite was recrystallized to fine-crystalline planar-s matrix dolomite (psm). Anhydrite (anh) precipitated along fractures and stylolites crosscut the two dolomite phases. Sulphide mineralization (sp) postdates the anhydrite, and precipitates along stylolites and as a porosity-occluding phase (C-421186). **c, d**. Fine- to medium-crystalline planar-s dolomite replacing an original bryozoan floatstone. Closer to the centre of the vug, coarse-crystalline matrix dolomite (do) and saddle dolomite (sd) have precipitated. Any remaining secondary porosity has been partly cemented by anhydrite and late-stage fibrous sulphide (pyrite/marcasite) mineralization (py). Under cathodoluminescent light, the matrix shows dull to bright luminescence. The saddle dolomite cement shows a typical dull red core surrounded by a bright zone, a dull/non-luminescent zone, and finally, another bright zone. Only those crystals that show the last two luminescent zones display sweeping extinction (C-421181).

In contrast to the field sample, core samples from the Keg River Formation show several diagenetic stages. The earliest stages of diagenesis include the precipitation of fine-crystalline, needle-like anhydrite and the replacement of micrite by very fine-crystalline, micron-scale dolomite, termed dolomicrite (Fig. 5b). The presence of needle-like anhydrite along fractures and stylolites crosscutting the dolomicrite suggests precipitation occurred after burial, and is not depositional. Dolomicritization, on the other hand, could have occurred penecontemporaneously or from the movement of seawater or evaporative brine during shallow burial.

The next diagenetic phase was the formation of fine-crystalline planar-s matrix dolomite (Sibley and Gregg, 1987). The planar-s matrix dolomite replaces the remaining micrite in the original limestone. Dolomicrite was also recrystallized to fine-crystalline planar-s dolomite. Following formation of the planar-s matrix dolomite, stylolitization of the host rock occurred. Even though stylolitization can occur at any depth following burial, it is generally accepted that chemical compaction occurs during intermediate burial: probably at depths of between 470 and 830 m (Lind, 1993). This indicates that the matrix dolomite formed during relatively shallow burial (<830 m), probably during Middle to Late Devonian time. Following dolomitization, slender laths of anhydrite precipitated along fractures and stylolites. Crosscutting relationships also indicate the sulphide mineralization (pyrite) postdates the anhydrite. This sulphide phase occurs along stylolites and solution seams, and occludes much of the remaining porosity in the host dolomite (Fig. 5c, d). Following dolomitization, late-stage equant calcite cement precipitated along fractures and in vugs.

Middle Devonian Slave Point Formation, Beaverhill Lake Group

One (1) thin-section from core in the Slave Point Formation was examined (C-421188; refer to Table 2 for the well name and location).

There is no evidence of dolomitization from the single sample examined from the Slave Point Formation. This is not unusual for this formation. The reason(s) for this are unknown, but may be due to the impermeable nature of the micritic matrix. This would reduce the flow of potential dolomitizing fluids. In general, where the Slave Point is extensively dolomitized, there is a relationship to tectonic activity and faulting (e.g. Ladyfern gas field), the location of lateral permeability barriers, or a combination thereof, such as the Clarke Lake gas field of northeastern British Columbia where dense brines ascend, potentially along faults, at the edge of the platform because of the relatively impermeable nature of the adjacent shale basin (Lonnee and Machel, 2004a, b).

In this sample, there is little evidence to suggest any relationship to Pine Point-type mineralization. The host rock is a non-dolomitized brachiopod-crinoid floatstone with primary intraparticle porosity lined by an early, likely marine, isopachous cement. A thin layer of sulphides precipitated after the isopachous cement, and any remaining shelter porosity was occluded by iron-rich, drusy, equant calcite cement, likely precipitated following burial. Other late-stage diagenetic phases typical of Pine Point were not found in this sample.

Upper Devonian Mikkwa Formation, Woodbend Group

One (1) sample from the Mikkwa Formation at Harper Creek was examined (C-406461). Photomicrographs from sample C-406461 are shown in Figure 6.

The original stromatoporoidal limestone has been partly to completely replaced by later, euhedral, fine- to medium-crystalline matrix dolomite (Fig. 6a, b), and then was succeeded by fracturing and pore-filling saddle dolomite cements (Fig. 6c, d).

Under cathodoluminescence, this sample shows some of the most complex crystal zoning of the whole suite of thin sections. Photos a and b show the incomplete replacement of the micritic portion of the host rock by matrix dolomite. The two phases of matrix dolomite (i.e. fine- and medium-crystalline) most likely precipitated concurrently. This is evident by the fact that both phases show identical zoning patterns under CL. The fine-crystalline dolomite shows at least five distinct bright- to dull or non-luminescent concentric zones. In the medium-crystalline dolomite, the five zones from the fine-crystalline dolomite are generally present, as well as a minimum of two additional concentric zones. The first of these two additional zones is a brightly luminescent phase that in some cases is the last, obvious concentric zone. The last zone develops a pattern more characteristic of oscillatory zoning, where rapid changes in the chemistry of the fluid or redox conditions occur. In Photo b, this last stage precipitates inward toward the micrite as a broad non-luminescent band. The latest carbonate phase to precipitate was saddle dolomite. Under cathodoluminescence, the saddle dolomite exhibits mostly non- to dull luminescence, and occurs as an overgrowth on the last stage of matrix dolomite (Fig. 6c, d).

Two (2) samples from the Mikkwa Formation at Vermilion Chutes were examined (C-421004, C-421161). Selected photomicrographs from these samples are shown in Figures 6e and 6f.

One sample from the Mikkwa Formation is an *Amphipora*-crinoid lime rudstone replaced by fine-crystalline matrix dolomite (Fig. 6e). Cathodoluminescent zoning in the dolomite is similar to that seen in the Mikkwa Formation at Harper Creek. Figure 6f shows a high-magnification view of the fine-crystalline matrix dolomite. In the centre of some of the dolomite crystals is a very small crystal that shows three to four bright to non-luminescent concentric zones. These zones are overgrown by two wider zones that alternate between bright and non-luminescent. The final zone is a bright luminescent cement that infills all remaining intercrystalline porosity. In samples showing only partial limestone replacement, the fine-crystalline dolomite appears to mimic what may have been large crinoid fragments. A later phase of dolomite cement replaced the matrix between the original fossils or clasts. The latest diagenetic phase to precipitate was a non-luminescent, sparry calcite cement that completely occluded all remaining porosity. The other sample from the Mikkwa Formation at Vermilion Chutes is a tabular stromatoporoidal framestone with abundant radiaxial marine calcite cements. In this sample, there was no significant replacement of the original limestone by dolomite. Also, remaining pores

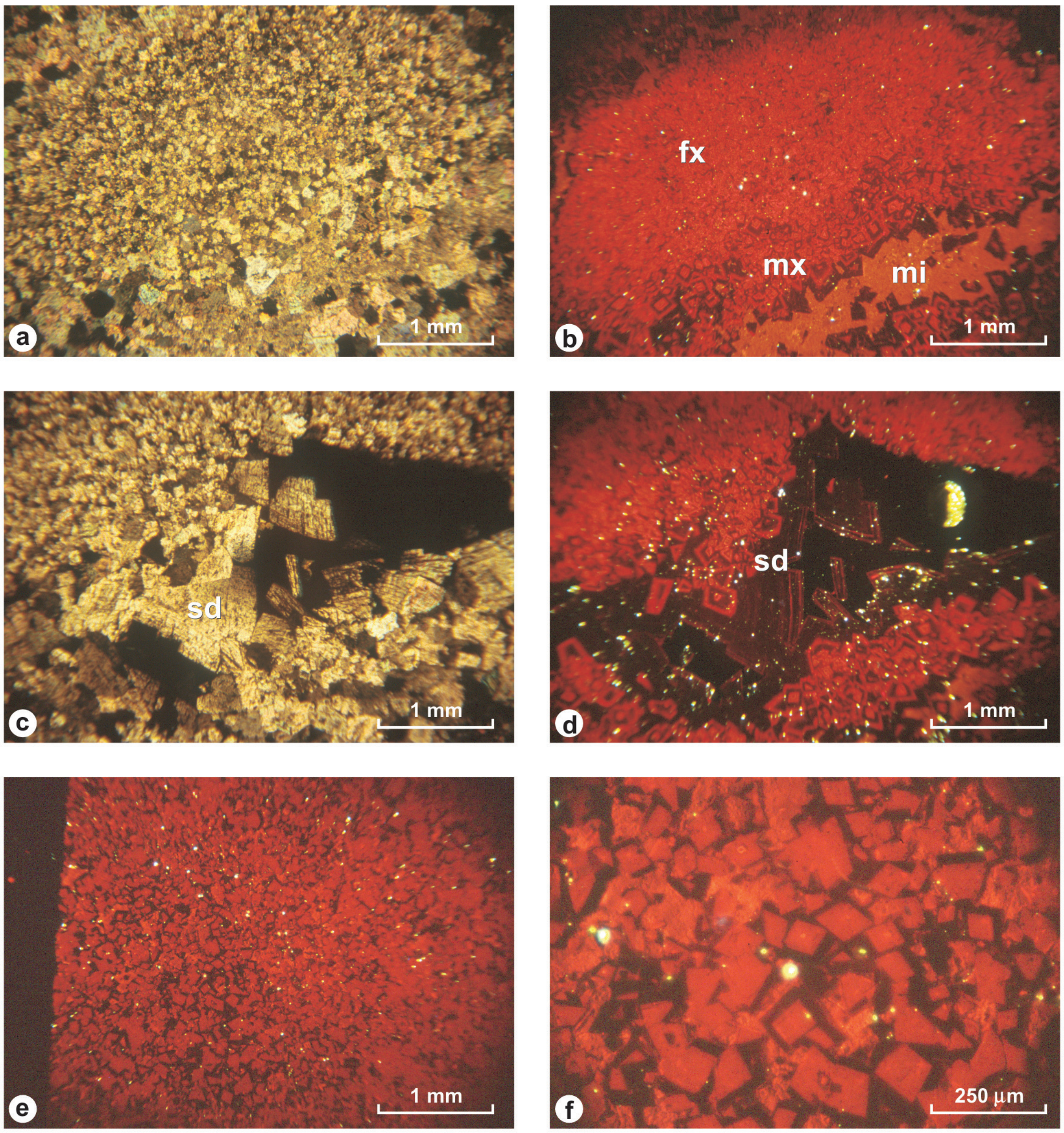


Figure 6. Transmitted light (**a** and **c**) and cathodoluminescent (**b**, **d**, **e,** and **f**) photomicrographs of the Mikkwa Formation at Harper Creek and Vermilion Chutes, Peace River: **a, b.** A transition zone between fine-crystalline matrix dolomite (fx) and medium-crystalline matrix dolomite (mx). The fine dolomite shows at least five distinct cathodoluminescent zones; the medium dolomite shows at least seven zones. Dolomitization is terminated by a coarse, non-luminescent phase. The bright zone (mi) represents original micrite that has not been replaced (C-406461). **c, d.** Late-stage saddle dolomite (sd) lining a vug. Euhedral non-luminescent dolomite from photo b is also present as a 'seed' crystal for saddle dolomite overgrowth (C-406461). **e, f.** Complete replacement of the original lime matrix by fine- to medium-crystalline matrix dolomite. Photo **f** (40x) shows original fine-crystalline dolomite 'seed' crystals with later overgrowths. The 'seed' crystals show luminescent patterns similar to those of the Mikkwa Formation at Harper Creek (C-406461; Fig. 6b, d). Later growth is represented by two wide cathodoluminescent zones and a final, bright dolomite infill (C-421004).

in the sample were not filled with either saddle dolomite or sulphides, both of which contribute supporting evidence for late-stage MVT mineralization potential.

Upper Devonian Grosmont Formation, Woodbend Group

Two (2) samples from the Grosmont Formation at Vermilion Chutes were examined (C-421001, C-421003).

Both samples from the Grosmont Formation were originally coral framestones. One thin section shows the well-developed colonial rugose coral *Medusaephyllum woodmani* with primary intraskeletal porosity filled by iron-poor to iron-rich (dark zones under CL) marine calcite cements. Dolomite replacement of this sample is not fabric selective, with both primary cements and original micrite replaced by fine- to medium-crystalline matrix dolomite. Under high magnification CL, this phase shows a minimum of eight concentric zones that range from bright to dull or non-luminescent. The centres of the matrix dolomite crystals show much the same patterns as those of samples from the Mikkwa Formation at Harper Creek, possibly reflecting the influence of similar fluid(s). However, in this sample, we do not see the large pore-filling and -lining dolomite cements with oscillatory zoning. If these dolomites are related, this difference could indicate either that hydrodynamics of the region changed during the late-stages of dolomite precipitation, that fluids were acting in a ‘closed’ system, or that fluid chemistry or redox conditions changed from one location to the other, so that later, coarse-crystalline dolomite would not precipitate. No other late-stage or MVT diagenetic phases are seen in the sample.

One (1) thin-section (C-421247) was examined from core in the Grosmont Formation. Photomicrographs from this sample are shown in Figure 7 (refer to Table 2 for the well name and location).

This sample of the Grosmont Formation is the only example that shows all the major late-stage diagenetic phases similar to Pine Point. However, there is no evidence of sulphides in the sample. The original limestone matrix of the Grosmont Formation was replaced by fine- to medium-crystalline planar-e matrix dolomite (Fig. 7a). Any remaining secondary porosity in this sample was cemented by clear saddle dolomite. Under cathodoluminescence, the matrix dolomites apparently display a relatively uniform red colour (Fig. 7b). The pore-filling saddle dolomite shows a very faint dull to non-luminescent zonation under CL. Under higher magnification, the fine-crystalline matrix dolomites show dull luminescent cores with bright rims (Fig. 7c, d). The coarser dolomite displays multiple oscillatory zonations with generally bright cores, grading into dull midsections, and an outer, thick, bright luminescent rim. The non- to dull luminescent saddle dolomites nucleated on the coarse matrix dolomites. The saddle dolomite displays alternating non-to dull luminescent zonation. Subsequent to formation of both the planar matrix dolomite and saddle dolomite, any remaining porosity was occluded by late-stage, blocky calcite cement (Fig. 7e, f).

Upper Devonian Jean Marie Member, Redknife Formation

Three (3) thin-sections were examined from core in the Jean Marie Member (C-421190, C-421191, C-421193; refer to Table 2 for the well name and location).

Examination of the thin-sections suggests that many of the late-stage diagenetic phases visible at Pine Point are not present (Qing and Mountjoy, 1994; Coniglio et al., 2006). The Jean Marie Member shows the earliest phases of partial to complete matrix dolomitization, as well as late-stage calcite and sulphide precipitation. However, late-stage coarse matrix dolomite and saddle dolomite characteristic of large-scale base metal deposits are not present.

In all thin-sections, fine-crystalline planar-e to planar-s matrix dolomite partly replaces the original micritic matrix. Later sulphides occur as cement along fractures and/or completely replace the micrite in some locations. Under cathodoluminescence, the original micrite matrix has a uniform orange colour, whereas the matrix dolomite displays a relatively homogenous dull red colour. The sulphides are found as non-luminescent blebs scattered throughout the sections.

ISOTOPE GEOCHEMISTRY

Stable ($\delta^{13}C$, $\delta^{18}O$) and radiogenic ($^{87}Sr/^{86}Sr$) isotope data for the field and core programs are presented (Fig. 8, 9) and interpreted in this section, organized stratigraphically from oldest to youngest formations (Keg River and Methy formations are stratigraphically equivalent). Field and core isotope powder samples are listed in Tables 1 and 2 respectively. Table 3 lists the analytical results.

Middle Devonian Keg River Formation, Upper Elk Point Subgroup

Thirteen (13) isotope powders were obtained from the Keg River Formation in northeastern Alberta. Twelve (12) samples were taken from subsurface core samples, and one (1) from outcrop on the Salt River in Wood Buffalo National Park.

One isotope powder was drilled from early diagenetic nodular (‘chicken wire’) anhydrite. This sample (C-421178) was analyzed only for strontium isotopes. The resulting value of 0.70789 indicates that the anhydrite was most likely the result of precipitation from Devonian seawater (see Fig. 9). This interpretation was obtained from the global Sr isotope age curve based on $^{87}Sr/^{86}Sr$ ratios of marine carbonate rocks (Burke et al., 1982). Burke et al.’s (1982) curve gives a best estimate of the $^{87}Sr/^{86}Sr$ ratio of seawater as a function of geological age.

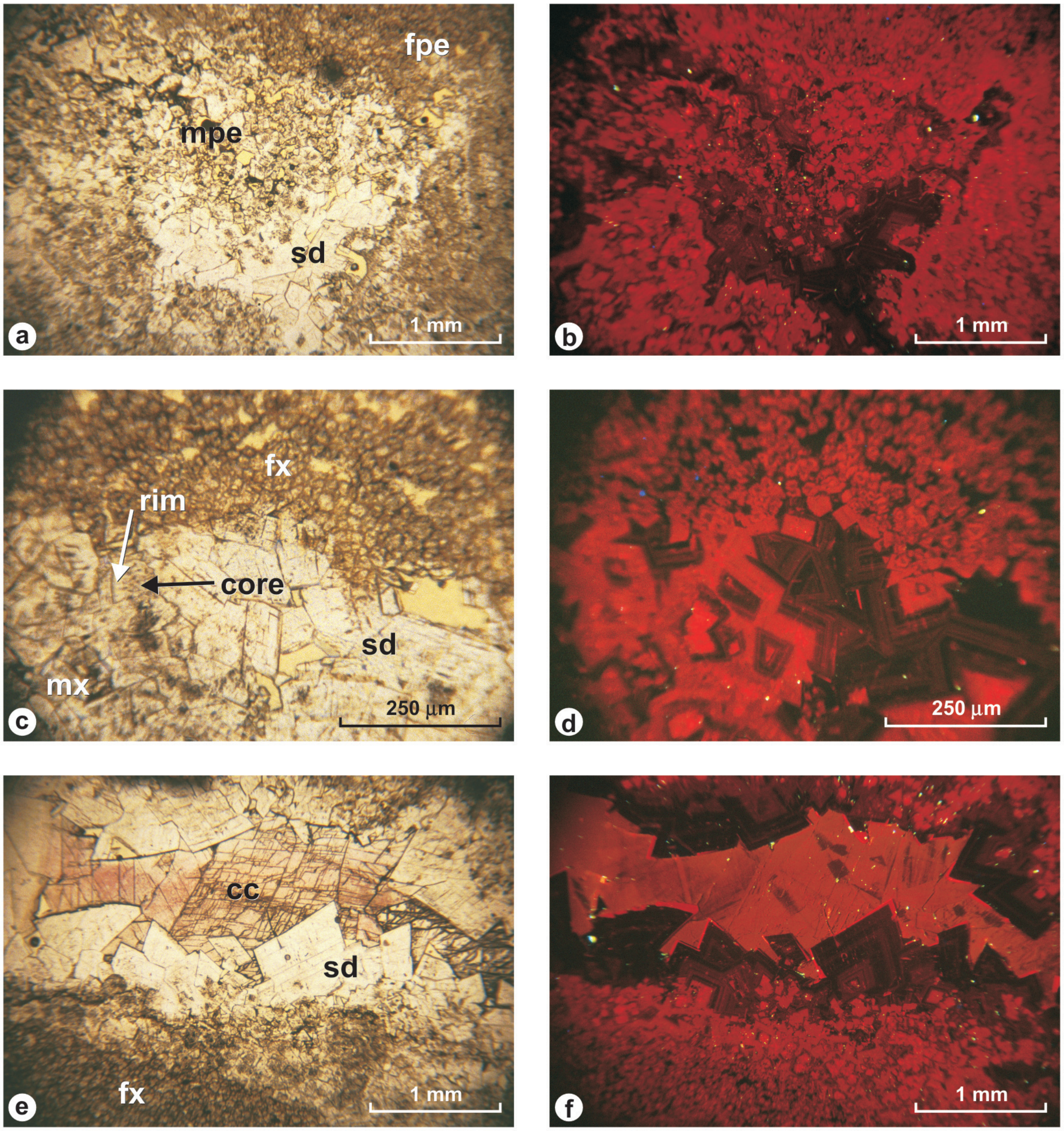


Figure 7. Transmitted light (**a**, **c,** and **e**) and cathodoluminescent (**b**, **d,** and **f**) photomicrographs of the Grosmont Formation in core (Sample C-421247): **a, b.** Fine- to medium-crystalline planar-e matrix dolomite (fpe and mpe, respectively) replacing the original matrix. The matrix dolomite generally displays cloudy cores and clear overgrowth rims. Any remaining porosity was cemented by clear saddle dolomite (sd). Under cathodoluminescent light, the matrix dolomite displays a relatively uniform red colour. The later saddle dolomite shows a very faint dull to nonluminescent zonation under cathodoluminescent light. **c, d.** Fine- (fx) to medium-crystalline (mx) matrix dolomite, clearly showing the cloudy cores and clear rims. The fine-crystalline matrix dolomite shows dull luminescent cores with bright rims. The coarser dolomite displays multiple oscillatory zonation with generally bright cores grading into dull midsections and finally terminated by thick bright rims. The non- to dull luminescent saddle dolomite (sd) used the coarser matrix dolomite as a ‘seed’ onto which it precipitated. The saddle dolomite displays alternating nonluminescent to dull luminescent zonation. **e, f.** Late-stage blocky calcite cement (cc) occluding any remaining porosity subsequent to precipitation of both the planar matrix dolomite (fx) and saddle dolomite (sd). Under cathodoluminescent light, saddle dolomite growth is terminated by a very bright rim. Late-stage calcite shows a relatively uniform orange colour throughout.

Contents

Table 1. Isotope powders collected from 2001 and 2002 field samples

Sample	Formation	Location	Longitude (NAD 83)	Latitude (NAD 83)	Name	Phase	Description	$\delta^{13}C$/ $\delta^{18}O$	^{87}Sr/ ^{86}Sr
C-406461	Mikkwa	Harper Creek	114.2725588	58.19504592	limestone	micrite (fossil)	stromatoporoidal limestone	X	X
	Mikkwa	Harper Creek	114.2725588	58.19504592	calcite vein	burial calcite	fracture-filling calcite	X	X
	Mikkwa	Harper Creek	114.2725588	58.19504592	matrix dolomite	matrix dolomite	fine-crystalline replacement dolomite	X	X
C-406463	Mikkwa	Harper Creek	114.2725588	58.19504592	calcite	burial calcite	loose calcite crystals (from fracture)	X	X
C-406499	Mikkwa	Harper Creek	114.27255	58.19504	stromatoporoid	micrite (fossil)	stromatoporoid (majority of thin section)	X	X
		Harper Creek	114.27255	58.19504	limestone	micrite	micrite (near calcite vein in thin section)	X	X
		Harper Creek	114.27255	58.19504	calcite	burial calcite	fracture/vug-filling calcite	X	X
C-406500	Mikkwa	Harper Creek	114.27255	58.19504	limestone	micrite (fossil)	bulk sample (stromatoporoid)	X	X
C-421001	Grosmont	Vermilion Chutes	114.87341	58.3772	calcite	micrite (fossil)	calcite - coral (*Medusaephyllum woodmani*)	X	X
		Vermilion Chutes	114.87341	58.3772	Fe-calcite	marine calcite	iron-rich calcite from coral	X	
C-421002	Grosmont	Vermilion Chutes	114.87341	58.3772	matrix dolomite	matrix dolomite	fine-crystalline matrix dolomite	X	X
		Vermilion Chutes	114.87341	58.3772	thamnopora	matrix dolomite	bitumen-coated dolomite. Not in section	X	X
		Vermilion Chutes	114.87341	58.3772	crinoid	micrite (fossil)	syntaxial calcite	X	
C-421003	Grosmont	Vermilion Chutes	114.87341	58.3772	matrix dolomite	matrix dolomite	fine-crystalline replacement dolomite	X	X
		Vermilion Chutes	114.87341	58.3772	vug dolomite	saddle dolomite	medium-crystalline dolomite in vugs	X	X
C-421004	Mikkwa	Vermilion Chutes	114.87089	58.37742	matrix dolomite	matrix dolomite	fine-crystalline replacement dolomite	X	X
		Vermilion Chutes	114.87089	58.37742	sucrosic dolomite	matrix dolomite	medium-crystalline dolomite (left side of slide)	X	X

Table 1. (cont.)

Sample	Formation	Location	Longitude (NAD 83)	Latitude (NAD 83)	Name	Phase	Description	$\delta^{13}C$/ $\delta^{18}O$	^{87}Sr/ ^{86}Sr
C-421161	Mikkwa	Vermilion Chutes	114.86557	58.376352	limestone	micrite	micritic limestone (bottom of slide)	X	X
		Vermilion Chutes	114.86557	58.376352	stromatoporoid	micrite (fossil)	tabular stromatoporoid (lower part of section)	X	X
		Vermilion Chutes	114.86557	58.376352	matrix dolomite	matrix dolomite	fine-crystalline dolomite (brown part of slide)	X	
		Vermilion Chutes	114.86557	58.376352	radiaxial calcite	early calcite cement	fibrous calcite (marine cement)	X	X
		Vermilion Chutes	114.86557	58.376352	blocky calcite	early calcite cement	calcite cement near vug and left side of slide	X	X
C-421162	Mikkwa	Vermilion Chutes	114.86557	58.376352	limestone clast	micrite	micritic limestone (red coloured clasts)	X	X
		Vermilion Chutes	114.86557	58.376352	matrix dolomite	matrix dolomite	fine-crystalline replacement dolomite matrix	X	X
		Vermilion Chutes	114.86557	58.376352	brachiopod shell	micrite (fossil)	unaltered calcite cement from brachiopod shell	X	
C-406494	Methy	Clearwater	110.0639	56.68987	dolomite	matrix dolomite	replacement matrix dolomite	X	X
C-406495	Methy	Clearwater	110.06406	56.69054	matrix dolomite	matrix dolomite	replacement matrix dolomite	X	X
		Clearwater	110.06406	56.69054	vug calcite	saddle dolomite	coarser-crystalline dolomite lining vugs	X	
C-406496	Methy	Clearwater	110.06394	56.69061	matrix dolomite	matrix dolomite	replacement matrix dolomite	X	X
		Clearwater	110.06394	56.69061	Fe-calcite	burial calcite	fracture-filling iron-rich calcite cement	X	
C-421197	Keg River	Salt River, WBNP	111.9665635	59.81810378	calcite	burial calcite	fracture-filling calcite spar	X	X

Table 2. Thin sections and isotope powders collected from 2002 core samples

Sample	Depth (m)	UWI	Name	#	Longitude (NAD 83)	Latitude (NAD 83)	Formation	Spl. No.	Phase	$\delta^{13}C/\delta^{18}O$	$^{87}Sr/^{86}Sr$
C-421176	965	8-20-110-11W5	Gulf AEC Beaver Ranch	1	115.7883198	58.56295182	Zama (Keg River)	3760-1	matrix dolomite	X	X
C-421177	971	8-20-110-11W5	Gulf AEC Beaver Ranch	1	115.7883198	58.56295182	Zama (Keg River)				
C-421178	767.3	1-28-107-5W5	Mutex IOE Mikkwa	2	114.7574636	58.31452951	Keg River	3762-1	anhydrite		X
								3762-2	matrix dolomite	X	X
C-421179	980.7	6-31-104-9W5	Shell et al. Tall Cree	3	115.4814507	58.07151765	Keg River	3763-1	fine-crystalline matrix dolomite	X	X
C-421180	982.3	6-31-104-9W5	Shell et al. Tall Cree	3	115.4814507	58.07151765	Keg River	3764-1	medium-crystalline matrix dolomite	X	X
C-421181	739.3	4-26-104-1W5	Mutex IOE EDRA	4	114.0547682	58.05176654	Keg River	3765-1	matrix dolomite	X	X
								3765-2	white, coarse dolomite	X	
C-421182	831.9	15-31-104-4W5	Chevron Amoco Harper	5	114.6456906	58.07895769	Keg River	3766-1	matrix dolomite	X	X
C-421183	843.1	15-31-104-4W5	Chevron Amoco Harper	5	114.6456906	58.07895769	Keg River	3767-1	matrix dolomite	X	X
C-421184	751.4	4-26-104-1W5	Mutex IOE EDRA	4	114.0547682	58.05176654	Keg River				
C-421185	844.9	15-31-104-4W5	Chevron Amoco Harper	5	114.6456906	58.07895769	Keg River				
C-421186	847.6	15-31-104-4W5	Chevron Amoco Harper	5	114.6456906	58.07895769	Keg River	3770-1	matrix dolomite	X	X
C-421187	1190.5	14-05-097-21W4	Mutex IOE Seaforth	6	113.3835421	57.39321265	Keg River				
C-421188	802.6	6-2-97-19W4	Dome Home Liege	7	112.9784143	57.38524127	Slave Point	3772-1	late-stage calcite	X	X
C-421189	780.6	15-27-109-7W5	GPD Noel et al Jean D'Or	8	115.0723583	58.49772445	Keg River	3773-2	matrix dolomite	X	X
C-421190	257.42	4-03-100-7W5	Calstan Senex Creek	9	115.0646459	57.64490061	Jean Marie	3774-1	late-stage calcite	X	X
C-421191	257.44	4-03-100-7W5	Calstan Senex Creek	9	115.0646459	57.64490061	Jean Marie				
C-421193	257.71	4-3-100-7W5	Calstan Senex Creek	9	115.0646459	57.64490061	Jean Marie	3777-1	matrix dolomite	X	X
								3777-2	late-stage calcite	X	X
C-421194	350.7	6-23-94-7W4	Chevron Steepbank	10	111.0162452	57.16671728	Keg River	3778-1	late-stage calcite	X	X
C-421247	571.35	10-13-97-6W5	Chevron Steepbank	11	114.8226769	57.42064034	Grosmont	3800-1	late-stage calcite	X	X
								3800-2	medium-crystalline matrix dolomite	X	X
								3800-3	fine-crystalline matrix dolomite	X	X

thin section only

\# well number keyed to Fig. 1

Table 3. Analytical results for field and core isotope powder samples

Sample	Phase	Type	$\delta^{13}C$	$\delta^{18}O$	$^{87}Sr/^{86}Sr$
Keg River					
C-421178	anhydrite	core			0.70789
C-421176	matrix dolomite	core	+2.5	-2.4	0.70826
C-421178	matrix dolomite	core	+2.9	-3.2	0.70789
C-421179	fx matrix dolomite	core	+3.1	-4.3	0.70814
C-421180	mx matrix dolomite	core	+3.1	-4.1	0.70803
C-421181	matrix dolomite	core	+2.9	-4.2	0.70795
C-421182	matrix dolomite	core	+3.1	-3.5	0.70796
C-421183	matrix dolomite	core	+3.1	-3.8	0.70796
C-421186	matrix dolomite	core	+3.1	-3.5	0.70799
C-421189	matrix dolomite	core	+2.9	-2.7	0.70796
C-421181	saddle dolomite	core	+2.6	-4.3	
C-421194	late-stage calcite	core	-24.2	-15.0	0.70901
C-421197	late-stage calcite	field	-11.2	-14.0	0.70813
Methy					
C-406494	matrix dolomite	field	+4.3	-3.5	0.70798
C-406495	matrix dolomite	field	+1.9	-3.8	0.70814
C-406496	matrix dolomite	field	+3.3	-3.9	0.70806
C-406495	saddle dolomite	field	-1.7	-6.4	
C-406496	late-stage calcite	field	-8.2	-12.7	
Slave Point					
C-421188	late-stage calcite	core	-15.5	-15.1	0.70854
Mikkwa					
C-421161	micrite	field	-0.4	-6.4	0.70847
C-421162	micrite	field	-0.7	-5.6	0.70862
C-406499	micrite	field	+2.4	-8.4	0.70831
C-421161	micrite - fossil	field	+0.8	-5.1	0.70808
C-421162	micrite - fossil	field	+1.4	-4.7	
C-406499	micrite - fossil	field	+2.4	-8.8	0.70830
C-406500	micrite - fossil	field	-1.3	-6.9	0.70835
C-406461	micrite - fossil	field	+4.0	-5.4	0.70814

Sample	Phase	Type	$\delta^{13}C$	$\delta^{18}O$	$^{87}Sr/^{86}Sr$
Mikkwa					
C-421161	early calcite	field	-2.7	-7.1	0.70811
C-421161	early calcite	field	+0.9	-5.1	0.70807
C-421161	matrix dolomite	field	-0.1	-5.2	
C-421162	matrix dolomite	field	+0.4	-4.4	0.70840
C-421004	matrix dolomite	field	+0.2	-5.3	0.70879
C-421004	matrix dolomite	field	+0.4	-4.7	0.70917
C-406461	matrix dolomite	field	+4.8	-3.8	0.70831
C-406499	late-stage calcite	field	+1.7	-13.5	0.70845
C-406461	late-stage calcite	field	+3.8	-5.9	0.70823
C-406463	late-stage calcite	field	+0.1	-13.9	0.70841
Grosmont					
C-421001	micrite - fossil	field	-0.5	-6.4	0.70807
C-421002	micrite - fossil	field	-0.4	-5.0	
C-421001	early calcite	field	0.0	-5.6	
C-421247	mx matrix dolomite	core	+3.4	-4.3	0.70818
C-421247	fx matrix dolomite	core	+3.4	-4.3	0.70957
C-421002	matrix dolomite	field	-0.6	-6.0	0.70845
C-421002	matrix dolomite	field	+0.5	-3.7	0.71025
C-421003	matrix dolomite	field	+0.9	-4.0	0.70905
C-421003	saddle dolomite	field	+0.9	-4.2	0.70843
C-421247	late-stage calcite	core	-6.6	-12.3	0.70871
Jean Marie					
C-421193	matrix dolomite	core	-3.1	-6.1	0.70831
C-421190	late-stage calcite	core	-19.3	-13.5	0.70836
C-421193	late-stage calcite	core	-19.4	-14.0	0.70838

$\delta^{13}C$ and $\delta^{18}O$ values reported in per mil relative to the VPDB standard
$^{87}Sr/^{86}Sr$ values reported relative to the NIST 987 standard
fx = fine crystalline
mx = medium crystalline

Nine (9) powders were drilled from matrix dolomite samples for isotopic analysis. All of the Keg River matrix dolomite samples have $\delta^{18}O$ values that range from -4.3 to -2.4 ‰ VPDB and $\delta^{13}C$ values between +2.5 and +3.1 ‰ VPDB. The oxygen isotopes have a mean value of -3.5 ‰ VPDB. Depending on the value of hypothetical marine dolomite that is used for comparison, the mean value of -3.5‰ matches or is very slightly depleted with respect to theoretical values. Of note, however, is that the accepted precision and reproducibility of stable isotope analyses is about +/- 0.5 ‰ VPDB. Based on the stable isotope data obtained from the matrix dolomite, there appears to be no significant statistical variation in the data. As a result of the lack of variation, no regional trend can be predicted for either the oxygen or carbon isotopes. The same nine matrix dolomites were analyzed for $^{87}Sr/^{86}Sr$, and their values ranged between 0.70789 and 0.70826. Based on the observed spread of the values, and the standard error of the analysis, there is no statistical variation in the dataset. The stable and radiogenic isotope data suggest that the matrix dolomites were the result of replacement by seawater or evaporative seawater at very shallow burial depths. This would indicate that the matrix dolomite from the Keg River Formation is an early diagenetic product. Both the stable and radiogenic isotope values show a Devonian seawater signature (i.e. $\delta^{18}O$ = -5.8‰ to -1.0‰ VPDB; $\delta^{13}C$ = +1‰ to +3.5‰ VPDB; $^{87}Sr/^{86}Sr$ = 0.7080 to 0.7085; hypothetical marine dolomites and calcites in Fig. 8 and 9), although the oxygen isotopes are slightly depleted with respect to Middle Devonian marine dolomite. This suggests that the matrix dolomite is either reflecting formation at ambient temperatures during shallow burial (i.e. 200–300 m), or exhibiting the effects of re-equilibration during burial.

One (1) powder of white saddle dolomite cement was obtained from the Keg River Formation (C-421181). Because of the limited volume of sample available, only stable isotope analysis was conducted. The $\delta^{18}O$ value for this sample is -4.3 ‰ VPDB and the $\delta^{13}C$ value is +2.6 ‰ VPDB. These values are almost identical to those obtained from the host matrix dolomite in the same sample (-4.2 and +2.9 ‰, respectively). The isotope values from the saddle dolomite are only slightly depleted with respect to hypothetical marine dolomite. Considering the similarity between the matrix and saddle dolomite, this suggests that the saddle dolomite was precipitated during pressure solution of matrix dolomite and the remobilization of Mg into open space (e.g. moldic/interparticle porosity) at temperatures between 60 and 100°C (reflecting the range of possible fluid compositions between seawater and evaporative seawater).

Two (2) samples of late-stage calcite were obtained from the Keg River Formation for isotopic analysis (C-421194 and C-421197). Stable isotope data from both samples are significantly different from the matrix and saddle dolomite phases discussed above. The $\delta^{18}O$ values are -15.0 and -14.0 ‰ VPDB and the $\delta^{13}C$ are -24.2 and -11.2 ‰ VPDB. In terms of the oxygen isotope values, these highly depleted numbers are typical of precipitation at relatively high temperatures (i.e. >100°C). The carbon isotope values are much more depleted in the core sample (C-421194) versus the outcrop sample (C-421197); however, both of these values tend to indicate the incorporation of oxidized organic carbon. The presence of oxidized carbon in carbonate is generally attributed to the process of thermochemical sulphate reduction (TSR). The late calcite cements have $^{87}Sr/^{86}Sr$ values of 0.70813 and 0.70901. The lower value, from the outcrop sample, is similar to the matrix dolomites discussed above (i.e. the value is typical of precipitation by Devonian seawater). The more enriched value, however, cannot be explained using Devonian seawater. This subsurface sample is most likely reflecting the infiltration of meteoric or basement fluids (i.e. fluids interacting with high-Sr basement rocks) during deep burial (>1–2 km). These samples are well below MASIRBAS (Maximum Strontium Isotope Ratio for Basinal Shale, of Machel and Cavell, 1999) though, eliminating any possibility of basinal shale as the conduit or source for the fluids. Therefore, the source of radiogenic strontium in the Keg River Formation was probably the result of K-feldspar dissolution in the underlying crystalline basement or Lower Devonian sandstone.

Middle Devonian Methy Formation, Upper Elk Point Subgroup

Five (5) isotope powders were obtained from the Methy Formation of northeastern Alberta from outcrops in the Fort McMurray study area.

Three (3) powders were drilled from matrix dolomite (C-406494–C-406496). The $\delta^{18}O$ values for these samples ranged between -3.9 and -3.5 ‰ VPDB; with essentially no variation. The $\delta^{13}C$ values showed more variation, ranging from +1.9 to +4.3 ‰ VPDB. Both sets of stable isotope values for the Methy Formation fall within a similar range to that exhibited by the Keg River Formation. Each of the three samples was also analyzed for their $^{87}Sr/^{86}Sr$ values. Again, the resulting data are identical to those from the Keg River Formation, values ranging between 0.70798 and 0.70814. Results of the radiogenic strontium analysis suggest that the matrix dolomite was precipitated from Middle Devonian seawater or evaporative seawater. Similar to the Keg River matrix dolomite, the stable isotope results point to formation either at slightly elevated temperatures or re-equilibration during burial. The spread in the $\delta^{13}C$ values for the matrix dolomite can be attributed to fermentation and/or methanogenesis. Assuming low water-rock ratios, the dolomite is likely incorporating the $\delta^{13}C$ from the original limestone it is replacing and, therefore, limestone deposited or transported to basin settings versus reef or platform environments will show varying degrees of $\delta^{13}C$ enrichment.

One (1) powder of saddle dolomite cement (C-406495) was obtained from the Methy Formation. This sample was analyzed only for stable isotopes because of a limited sample volume. The $\delta^{18}O$ value for this sample is -6.4 ‰ VPDB and the $\delta^{13}C$ value is -1.7 ‰ VPDB. Unlike the saddle dolomite from the Keg River Formation, values from the Methy

Formation are not identical to those obtained from the matrix dolomite. Figure 8 shows that this sample lies close to the field for Pine Point dolomites (i.e. the QM-SD and CCD field, which is derived from Qing and Mountjoy (1994) representing their saddle dolomite (SD) and coarse-crystalline dolomite (CCD) stable isotope results). The spread in the $\delta^{18}O$ values of the Pine Point–Presqu'ile data field is attributed to an increase in temperature westward, because of deeper convective circulation (Coniglio et al., 2006). In the case of the Methy Formation, this sample was collected at the surface, and therefore, the $\delta^{18}O$ value is reflecting precipitation at temperatures below 100°C, similar to values obtained from the Pine Point property.

One (1) sample of late-stage calcite (C-406496) was obtained from the Methy Formation for isotopic analysis. Stable isotope data from this sample are significantly different from the matrix and saddle dolomite phases discussed above. Results of the $\delta^{18}O$ and $\delta^{13}C$ analyses were -12.7 and -8.2 ‰ VPDB, respectively. These values are very similar to those obtained from the Keg River Formation in Wood Buffalo National Park (C-421197). Therefore, this sample is reflecting precipitation at relatively high temperatures (i.e. >100°C), under the effects of thermochemical sulphate reduction, resulting in the light $\delta^{13}C$ value. Strontium isotope values were not obtained for this sample; hence, no real interpretation of the fluids can be made.

Middle Devonian Slave Point Formation, Beaverhill Lake Group

One (1) isotope powder sample was collected from the Slave Point Formation in northeastern Alberta (C-421188).

Both stable and radiogenic isotopes were analyzed for late-stage calcite cement from the Slave Point Formation. The $\delta^{18}O$ and $\delta^{13}C$ values are -15.1 and -15.5 ‰ VPDB, respectively. These values are similar to those found in the late-stage calcite cements from the Keg River Formation discussed above. This sample is therefore reflecting the influence of TSR and temperatures greater than 100°C. The value from

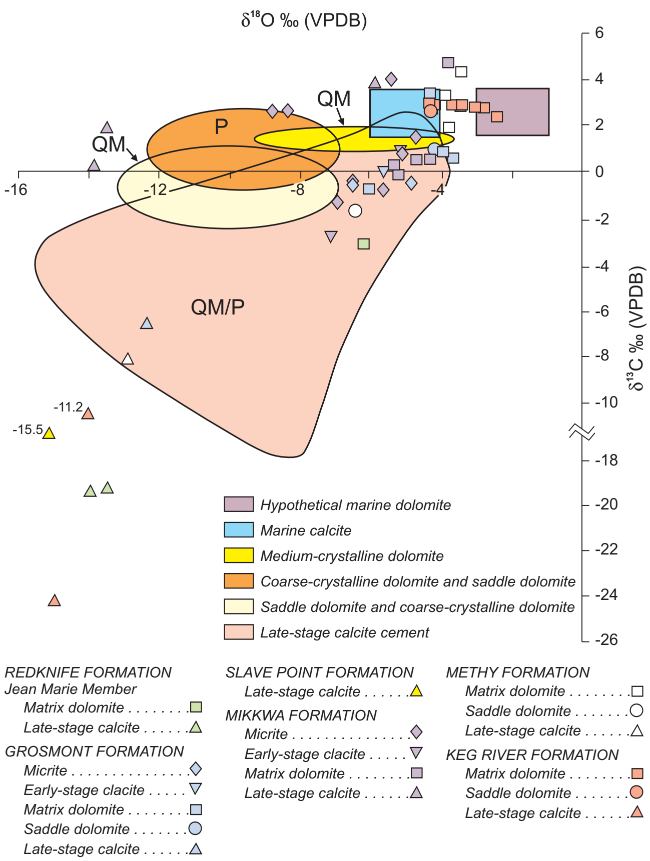


Figure 8. $\delta^{13}C$ versus $\delta^{18}O$ cross plot for diagenetic phases in the Keg River, Slave Point, Grosmont, Mikkwa, and Methy formations and the Jean Marie Member of the Redknife Formation of northeastern Alberta. Devonian marine calcite and hypothetical marine dolomite values are from Knauth and Roberts (1991). Values from both Pine Point and the subsurface Presqu'ile Barrier (east of Tathlina Lake) are from Qing and Mountjoy (1994, 1998); values exclusively from the Pine Point area are from Paradis et al. (2006). QM = Qing and Mountjoy, 1994, 1998; P = Paradis et al. (2006); VPDB = Vienna Pee Dee Belemnite.

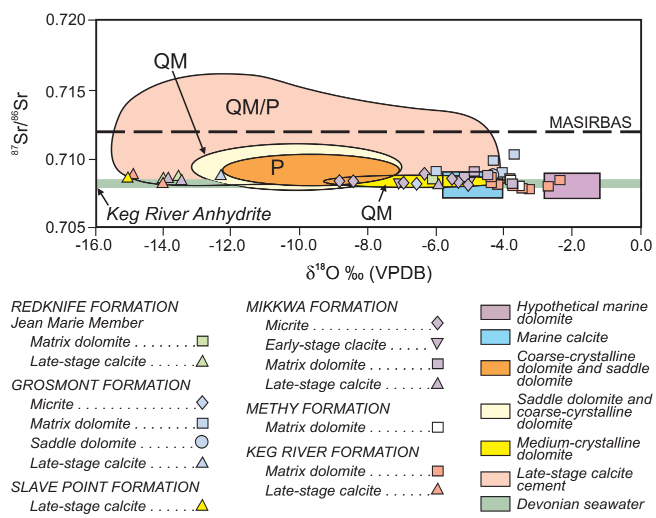


Figure 9. $^{87}Sr/^{86}Sr$ versus $\delta^{18}O$ cross plot for diagenetic phases in the Keg River, Slave Point, Grosmont, Mikkwa, and Methy formations and the Jean Marie Member of the Redknife Formation of northeastern Alberta. Devonian marine calcite and hypothetical marine dolomite values are from Knauth and Roberts (1991). Values from both Pine Point and the subsurface Presqu'ile Barrier (east of Tathlina Lake) are from Qing and Mountjoy (1994, 1998); values exclusively from the Pine Point area are from Paradis et al. (2006). QM = Qing and Mountjoy, 1994, 1998; P = Paradis et al. (2006); VPDB = Vienna Pee Dee Belemnite. Values of $^{87}Sr/^{86}Sr$ for Devonian seawater are from Burke et al. (1982), Veizer (1983) and Denison et al. (1997). Note: Devonian seawater 'field' represents absolute values for strontium; oxygen limits are not shown. MASIRBAS (MAximum Strontium Isotope Ratio for BAsinal Shale) is from Machel and Cavell (1999).

the $^{87}Sr/^{86}Sr$ analysis of 0.70854 is only slightly enriched in ^{87}Sr with respect to Devonian seawater. Therefore, it would appear that this relatively late-stage cement is reflecting precipitation from slightly modified Devonian seawater during deep burial (>1–2 km). Burial at this depth range may be a direct result of tectonic loading to the west (i.e. Cordilleran foreland succession), thereby placing a time constraint on precipitation of late-stage calcite cement.

Upper Devonian Mikkwa Formation, Woodbend Group

Eighteen (18) isotope powders were obtained from the Mikkwa Formation of northeastern Alberta from outcrops in the Vermilion Chutes and Harper Creek study area.

Eight (8) powders were drilled from various limestone components in the Mikkwa Formation. These included three (3) samples of micrite and five (5) samples of fossils (e.g. brachiopods, stromatoporoids) (Table 3). All powders were analyzed for their stable isotopic composition; all samples, except one (1) brachiopod, were analyzed for their radiogenic strontium composition. The $\delta^{18}O$ values for these samples ranged from -8.8 to -4.7 ‰ VPDB, whereas $\delta^{13}C$ values displayed a range from -1.3 to +4.0 ‰ VPDB. The $^{87}Sr/^{86}Sr$ ratios from the limestone components varied from 0.70808 to 0.70862. The isotope results indicate that some of the samples have experienced minor recrystallization as a result of the conversion of high-magnesium calcite and/or aragonite to more stable low-magnesium calcite. The isotope geochemistries of the other samples reflect precipitation from Devonian seawater.

Two (2) samples of early calcite cement (both powders obtained from Sample C-421161) were collected for isotopic analysis. The $\delta^{18}O$ values of this phase are -7.1 and -5.1 ‰ VPDB. The $\delta^{13}C$ analyses show slightly more variation, with values of -2.7 and +0.9 ‰ VPDB. The stable isotope composition of one of the samples (i.e. radiaxial calcite cement) is characteristic of marine calcite in the Devonian. The other early calcite cement (i.e. mosaic calcite) has textural and geochemical characteristics that suggest it was precipitated from Devonian seawater subsequent to shallow burial. The slightly depleted stable isotope values are representative of a slight increase in temperature, possibly as little as 10°C, and the inclusion of isotopically heavy CO_2 due to either methanogenesis or bacterial sulphate reduction. The narrow range of values from the $^{87}Sr/^{86}Sr$ analyses also suggests precipitation from Upper Devonian (Frasnian) seawater (0.70807 and 0.70811). Therefore, petrographic and geochemical characteristics of the early calcite cement phases suggest precipitation from Devonian seawater either in the marine realm or subsequent to shallow burial.

Five (5) powders were drilled from matrix dolomite samples for isotopic analysis. The matrix dolomite samples have $\delta^{18}O$ values that range from -5.3 to -3.8 ‰ VPDB and $\delta^{13}C$ values of between -0.1 and +4.8 ‰ VPDB. The oxygen isotope values have a mean of -4.7 ‰ VPDB. This value is roughly 2 ‰ more negative than what would be expected from the hypothetical marine dolomite (Fig. 8) during the Devonian. The stable isotope values from the matrix dolomites are, however, identical to the values obtained from the limestone components: the result of recrystallization without change in the geochemistry. Four of the five matrix dolomite samples were analyzed for $^{87}Sr/^{86}Sr$, and values ranged from 0.70831 to 0.70917. Similar to the stable isotopes, two of the matrix dolomite samples show no significant change in $^{87}Sr/^{86}Sr$ from the limestone components. However, the other two samples have more radiogenic values, indicating a minor contribution of enriched ^{87}Sr. The stable and radiogenic isotope data suggest that the matrix dolomites were formed from seawater or slightly modified seawater subsequent to burial. Assuming that the oxygen isotopes are representative of an increase in ambient temperature, and not re-equilibration, modelling suggests that the matrix dolomite was precipitated at temperatures of between 50 and 80°C. This result signifies precipitation at burial depths of greater than 1000 m, or by hydrothermal fluids during shallow burial.

Three (3) samples of late-stage blocky calcite were obtained from the Mikkwa Formation for isotopic analysis. The $\delta^{18}O$ values range from -13.9 to -5.9 ‰ VPDB and the $\delta^{13}C$ values from +0.1 to +3.8 ‰ VPDB. Stable isotope data of two samples are significantly different from the matrix dolomite phase discussed above; the other shows only a slight negative shift in $\delta^{18}O$. Similar to the burial and late-stage calcites from the other formations examined in this study, the oxygen isotope values tend to suggest precipitation from fluids at relatively high temperatures (i.e. >100°C). However, unlike the other formations, the carbon isotope values from the Mikkwa Formation do not show the characteristic negative shift attributed to thermochemical sulphate reduction. Instead, the $\delta^{13}C$ values from the Mikkwa burial calcites reflect the incorporation of internally derived carbon, either through pressure solution or recrystallization in a local system where fluid movement is slow and transport of ions insignificant. The burial calcite cements have $^{87}Sr/^{86}Sr$ values of 0.70823 to 0.70845, which fall within the range of expected Upper Devonian (Frasnian) seawater (i.e. 0.7080 to 0.7085; Burke et al., 1982), similar to the early calcite cement and limestone components discussed above. The lack of radiogenic strontium and depletion in $\delta^{13}C$ suggests that the Mikkwa Formation did not experience large-scale fluid migration during its diagenetic history.

Upper Devonian Grosmont Formation, Woodbend Group

Ten (10) isotope powders were obtained from core and field samples of the Grosmont Formation in northeastern Alberta.

Two (2) powders were drilled from fossil components in the Grosmont Formation (Table 3). The $\delta^{18}O$ values for these samples were -6.4 and -5.0 ‰ VPDB, with $\delta^{13}C$ values of -0.5 and -0.4 ‰ VPDB, respectively. A $^{87}Sr/^{86}Sr$ ratio of

0.70807 was obtained from one of the samples. The oxygen isotope results suggest minor recrystallization of these fossils or re-equilibration with burial fluids. The slightly negative carbon isotopes are characteristic of Frasnian seawater, prior to the positive Famennian shift (Wang et al., 1996; Joachimski et al., 2002). Similar to the Mikkwa Formation, the fossils of the Grosmont Formation were recrystallized as a result of a high-magnesium or aragonite content. The strontium isotope result suggests the fluid responsible for recrystallization was Devonian seawater (Fig. 9).

One (1) sample of early calcite cement was obtained for isotopic analysis. The stable isotope values for this phase were -5.6 and 0.0 ‰ VPDB for $\delta^{18}O$ and $\delta^{13}C$, respectively. The strontium isotope ratio of this sample was not analyzed. The textural and geochemical characteristics of this sample suggest precipitation in a shallow-burial environment, under reducing conditions, by Devonian seawater.

Five (5) powders were drilled from matrix dolomite samples for isotopic analysis. The matrix dolomite samples have $\delta^{18}O$ values that range from -6.0 to -3.7 ‰ VPDB and $\delta^{13}C$ values from -0.6 to +3.4 ‰ VPDB. These results are slightly depleted with respect to hypothetical Devonian marine dolomite (Fig. 8). The $^{87}Sr/^{86}Sr$ ratios for all the samples show significant variation (Table 3). One sample of matrix dolomite (C-421002) has a value of 0.70845, whereas another matrix dolomite from the same sample has a value of 0.71025. The stable and radiogenic isotope data suggest that the matrix dolomite originally formed from the seawater or evaporative seawater, and was subsequently recrystallized following interaction with an external fluid, accounting for the radiogenic signature.

One (1) powder of saddle dolomite cement (C-421003) was obtained from field samples of the Grosmont Formation. The $\delta^{18}O$ value for this sample is -4.2 ‰ VPDB and the $\delta^{13}C$ value is +0.9 ‰ VPDB. Similar to the saddle dolomite from the Keg River Formation, these values are almost identical to those obtained from some of the matrix dolomites. A $^{87}Sr/^{86}Sr$ isotope ratio of 0.70843 was obtained from this sample. The stable isotope values suggest precipitation at temperatures of between 60 and 90°C, depending on the initial oxygen isotope composition of the fluid (i.e. seawater or evaporative seawater). The strontium isotope ratio lies very close to expected Devonian seawater, and is identical to the values from the second phase of matrix dolomite discussed previously. Together, the isotope data suggest precipitation of the Grosmont Formation saddle dolomite subsequent to deep burial (>1000 m).

One (1) sample of late-stage calcite (C-421247) was obtained from the Grosmont Formation for isotopic analysis. Stable isotope data from this phase are consistent with most of the other late-stage calcite cements discussed for the Keg River, Slave Point, Mikkwa, and Methy formations, and the Jean Marie Member of the Redknife Formation, with a $\delta^{18}O$ value of -12.3 ‰ VPDB and a $\delta^{13}C$ value of -6.6 ‰ VPDB (Table 3). The oxygen isotope value is significantly depleted in $\delta^{18}O$, consistent with precipitation from fluids at relatively high temperatures (i.e. >100°C). The carbon isotope values are also depleted; not by as much as the other late-stage calcite cements analyzed, but enough to indicate precipitation from a dominantly TSR-driven process. The late-stage calcite cement was also analyzed to determine its $^{87}Sr/^{86}Sr$ value. The value of 0.70871 is also consistent with the strontium isotope values obtained from the late-stage calcite cements from the other formations studied. Therefore, the fluid responsible for precipitation of this phase in the Grosmont Formation was most likely evaporative Devonian seawater containing dissolved sulphate derived from the anhydritic Hondo Member of the Grosmont Formation (Cutler, 1983). This fluid would have been a requirement to satisfy the thermochemical sulphate reduction process, and probably precipitated the late-stage calcite cement during burial as a result of formation of the Cordilleran foreland succession.

Upper Devonian Jean Marie Member, Redknife Formation

Three (3) isotope powders were obtained from core in the Jean Marie Member of northeastern Alberta. All three of the samples were collected from a depth of approximately 260 m in the Calstan Senex Creek 4-3-100-7W5 well (see Table 2).

Both $\delta^{18}O$ and $\delta^{13}C$ values obtained from the matrix dolomite show 'significant' depletion with respect to hypothetical Devonian marine dolomite (Fig. 8). The oxygen value of -6.1 ‰ VPDB is typical of most matrix dolomites from the Western Canada Sedimentary Basin, precipitated by modified seawater at depths of 500 to 1500 m and temperatures between 50 and 70°C (Mountjoy and Amthor, 1994). The carbon isotope value of -3.1 ‰ VPDB reflects the contribution of oxidized organic carbon. Slightly depleted carbon values such as this may reflect the contribution of oxidized carbon, either through continuous water-rock interaction in an open system or through TSR. The likely explanation in this case is probably open-system water-rock interaction, as TSR dolomites generally display significantly more depleted $\delta^{13}C$ values. Radiogenic strontium isotopic analysis for the Jean Marie matrix dolomite (0.70831) indicates that the fluid responsible for precipitation was not significantly different or modified from Devonian seawater. This interpretation fits with the possibility that the matrix dolomite was formed at moderate burial depths by modified seawater, most likely during the latest Paleozoic.

Two (2) samples of late-stage calcite were obtained from the Jean Marie Member for isotopic analysis. Stable isotope data from both samples are significantly different from the matrix dolomite phase discussed above. The $\delta^{18}O$ values are -14.0 and -13.5 ‰ VPDB with corresponding $\delta^{13}C$ values of -19.4 and -19.3 ‰ VPDB. Neither of these isotopes shows any significant statistical variation when analytical errors are considered. In terms of the oxygen isotope values, these highly depleted numbers are typical of precipitation at relatively high temperatures (i.e. > 100°C). The carbon isotope values are also significantly depleted, similar to the Keg

River late-stage calcites, indicating precipitation from a dominantly TSR-driven process. TSR requires temperatures of about 100 to 140°C (Machel, 1987), conditions that could only have occurred during maximum burial resulting from tectonic loading to the west during the formation of the Cordilleran foreland succession.

COMPARISON WITH PINE POINT – PRESQU'ILE BARRIER

Summary of the Pine Point mining district emphasizing stratigraphy, age of mineralization, diagenesis, and isotopes

The stated objective of this study is the diagenetic and isotopic comparison of potential host carbonate deposits from northeastern Alberta to the carbonate units hosting the Pine Point deposits. As such, it is relevant to briefly review these characteristics for Pine Point before presenting the northeastern Alberta data. Rhodes et al. (1984) carefully documented the Pine Point orebodies, and it is from this work that most of the summary data below are derived.

Stratigraphy

The Middle Devonian Pine Point or Presqu'ile barrier complex consists of two superimposed carbonate buildups. The lower buildup, developed within the Pine Point Formation, represents two-thirds of the barrier and is a flat, lensoid body of mainly carbonate sand and mud created from skeletal organisms. The upper buildup developed in the overlying Sulphur Point Formation, is a tabular body consisting of local bioherms and related bioclastic limestone and carbonate sand.

Most of the mineralization at Pine Point occurs in two main paleokarst networks, known as the Main and North trends, developed within the lower limits of the Presqu'ile dolomite. This is a coarse-crystalline dolomite predominantly replacing the Sulphur Point Formation but also straddling the contact with the underlying Pine Point Formation. As shown in Rhodes et al. (1984, his Fig. 3), the Pine Point Formation conformably overlies the Keg River Formation and is laterally transitional into the evaporite, limestone and dolostone of the back-barrier Muskeg Formation. A wedge of shale and lesser carbonate flanking the north side of the barrier complex or fore reef making up the Buffalo River Formation lies conformably on the Pine Point Formation. As currently used however, the term Pine Point refers essentially to a fossiliferous dolostone that includes several formations extending from the top of the Chinchaga Formation to the base of the Watt Mountain Formation, and therefore includes the upper and lower Keg River Formation as well as the Sulphur Point Formation. The Pine Point Formation, as described by Rhodes et al. (1984), attains a maximum thickness of 175 m and consists of a variety of limestone lithofacies that are commonly dolomitized. The basal unit is a 12 to 18 m thick biostromal floatstone known as the B Spongy Member, interpreted as representing a regional marine shoaling following the deposition of platform carbonate of the Keg River Formation. Above this member, a carbonate sediment bank was deposited, consisting of a variety of interfingering lithofacies that generally follow a south-to-north progression of floatstone, clean bioclastic grainstone, fine grainstone, or wackestone and mudstone, and black, highly bituminous, laminated mudstone, reflecting a northward progradation caused by differential subsidence of the barrier and an adjoining deeper water area to the north.

The Sulphur Point Formation in the Pine Point region reaches a maximum thickness of 65 m and consists of a light cream to white limestone and its coarsely dolomitized equivalent. Sulphur Point lithofacies are distinctly lighter coloured than Pine Point carbonate units. The Sulphur Point Formation is unconformably overlain by siliciclastic and carbonate deposits of the Watt Mountain Formation and is both underlain and transitional into the Pine Point and Muskeg formations. The formation is characterized by lateral and vertical lithofacies variations that can be broken down into four general lithofacies: stromatoporoidal boundstone, clastic grainstone, bioclastic limestone and laminated algal limestone, and pelletoidal grainstone. Depositional settings represented by the formation include patch reef, lagoonal, subtidal, and supratidal.

Age of mineralization

The age of the Pb-Zn mineralization at Pine Point is contentious and the choice indicates the tectonic setting in which the mineralization occurred. A concise overview of the conflicting paleomagnetic and radiometric data central to the debate is provided in Symons et al. (1996) and Leach et al. (2001). In summary, the choice is between a Mid-Late Cretaceous to Paleocene age supported by paleomagnetic data and indicating a peripheral foreland basin setting associated with a Laramide collisional orogen, or a Devonian age, supported by Rb-Sr radiometric data on sphalerite, implying a retroarc foreland basin setting associated with an Antler Andean-type orogen. Additional support for a Laramide age is also found in Adams et al. (2000). Symons et al. (1996) proposed a possible resolution by suggesting the mineralization could be composite in age, a result of separate Antler and Laramide fluid events.

Diagenesis

Rhodes et al. (1984) did not present a diagenetic paragenesis for the Pine Point–Presqu'ile barrier. Qing and Mountjoy (1994) did develop a paragenetic sequence of diagenetic events for the Pine Point area (see below). Rhodes et al. (1984) did, however, distinguish two main dolomite types on the basis of grain size: fine crystalline and coarse crystalline (Presqu'ile). The distribution of dolomite phases was controlled by the amount of carbonaceous and argillaceous impurities, with the cleaner Sulphur Point lithofacies being coarsely dolomitized and the dirtier Pine Point rocks finely dolomitized. Much of the Pine Point Formation was finely dolomitized but primary features were not obscured to the extent that lithofacies could not be distinguished. Presqu'ile-style dolomitization affected 60–70% of the Sulphur Point Formation in the barrier complex, and while it has largely obscured the primary limestone textures, subdivisions of dolomite textures corresponding to primary lithofacies can still be distinguished, allowing depositional settings to be determined.

In addition to the fine and Presqu'ile dolomitization that occurs in the Pine Point barrier complex, there is also a much later, coarse-crystalline, white dolomite found in association with solution cavities and ore that is not to be confused with Presqu'ile dolomite. Later fluids related, or subsequent, to the ore fluids precipitated this white vein dolomite.

Isotopes

No isotopic data on the Pine Point–Presqu'ile barrier complex were provided in Rhodes et al. (1984). The bulk of isotopic data available for Pine Point are presented in Qing and Mountjoy (1994) and Paradis et al. (2006). This isotopic data are summarized diagrammatically in Figures 8 and 9.

Comparison of isotopic and diagenetic data

Stable and radiogenic isotope data (Fig. 8, 9, respectively) obtained from field and core samples are discussed separately, relative to that for the Pine Point–Presqu'ile Barrier. A comparison of the diagenetic sequence observed in northeastern Alberta with that published for the Pine Point–Presqu'ile Barrier by Qing and Mountjoy (1994) is presented in Fig. 10.

Field data

Cathodoluminescent and petrographic observations from the 13 field samples indicate that only 6 diagenetic phases identified by Qing and Mountjoy (1994) are present (Fig. 10). These phases include fine- and medium-crystalline matrix dolomite, blocky sparry calcite cement, saddle dolomite, late-stage calcite, and bitumen. However, none of the samples shows evidence of all six phases together, likely an indication that the fluids responsible for mineralization at Pine Point have not infiltrated these samples. In the case of Pine Point, the MVT mineralization (i.e. galena, sphalerite) is genetically related to hydrothermal dissolution of the host coarse-crystalline dolomite and saddle dolomite precipitation. There was evidence of saddle dolomite precipitation in samples C-406495 (Methy Formation, Whitemud Falls, Clearwater River) and C-421003 (Grosmont Formation, Vermilion Chutes). All of the field samples, except for the Keg River sample from Wood Buffalo National Park, show

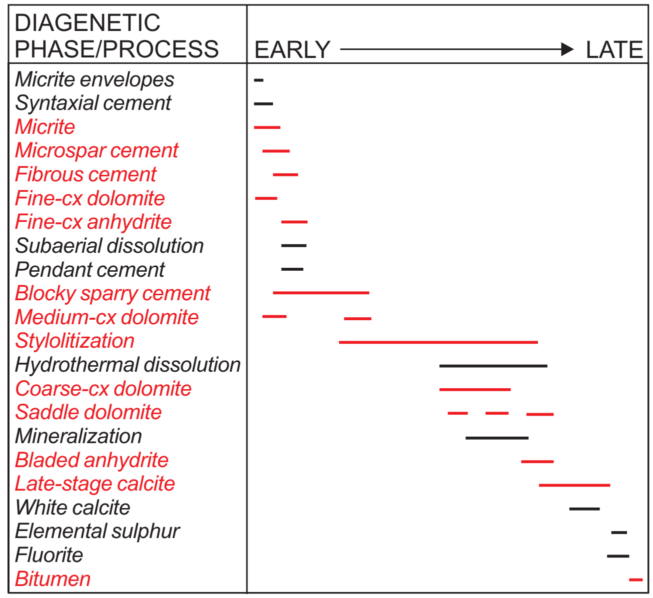


Figure 10. Diagenetic paragenesis of the Presqu'ile barrier derived from the petrographic study of open pits and cores, including Pine Point, *from* Qing and Mountjoy (1994). Phases in red indicate the diagenetic phases that were observed in this study.

evidence of matrix dolomitization. This is obviously an important first step in allowing the infiltration of later-stage mineralizing fluids due to an increase in porosity and permeability. (In these rocks, porosity and permeability are higher in dolostone relative to precursor limestone because of strengthening of the rock framework; thus, retarding compaction.) As well, samples from the Methy Formation at Whitemud Falls on the Clearwater River show evidence of the very late diagenetic phases, namely, bitumen and late-stage calcite cements. However, late-stage metal-bearing fluids have apparently not infiltrated these samples (recall from above however, that Carrigy (1959) has reported galena in a single small cavity at this location).

Stable isotopes of the matrix dolomite collected in the field show that the majority plot within 2‰ of the expected marine dolomite field (Table 1, Fig. 8). One exception was a single sample from the Grosmont Formation (Sample C-421002, $\delta^{18}O$ = -6.0‰ VPDB, $\delta^{13}C$ = -0.6‰ VPDB). The values that plot near the marine dolomite field may suggest precipitation from fluids that were at or near seawater composition. The $\delta^{18}O$ values for matrix dolomite plot near the least depleted end of the medium-crystalline dolomite field from Pine Point (Qing and Mountjoy, 1994; QM-MCD in Fig. 8), suggesting precipitation from fluids of similar composition and/or temperature. Dissimilar $\delta^{13}C$ values, however, may be the result of dolomitization by extraformational fluids that were not buffered by the host limestone, or methanogenesis in the case of the samples enriched in $\delta^{13}C$. Strontium isotope values from the matrix dolomites are, for the most part, within the range expected for Middle to Upper Devonian seawater.

Two samples from the Grosmont and one from the Mikkwa plot above 0.709, indicating the contribution of extra-formational strontium. There are similarities between the matrix dolomite samples from the field and those from Pine Point, most notably, strontium ratios at or near Devonian seawater levels. Unfortunately, when the entire isotope dataset is compared, there appears to be no genetic relationship between matrix dolomites from this study and those at Pine Point.

Two samples of saddle dolomite were analyzed for stable isotopes, one from the Methy Formation, and the other from the Grosmont Formation. The result obtained from the Grosmont sample is identical to those from the matrix dolomite samples discussed above. Both the stable and radiogenic isotope results from this sample suggest precipitation as a burial cement, reflecting re-distribution of Mg through chemical compaction, similar to the Nisku dolomite from West Pembina (Machel, 1987). The sample from the Methy Formation is significantly more depleted in $\delta^{18}O$, with a value of -6.4 ‰ VPDB. Unlike the Grosmont sample, this result may indicate precipitation from relatively high-temperature fluids. Unfortunately, a $^{87}Sr/^{86}Sr$ analysis is not available for this sample. Regardless, the stable isotope values from the Methy sample are similar to those obtained from saddle dolomite at Pine Point.

Five (5) samples of late-stage calcite cements were analyzed from the Keg River, Methy, and Mikkwa formations. Four of the five samples show significant depletion in $\delta^{18}O$ compared to Devonian marine calcite. The only exception is one sample from the Mikkwa Formation (C-406461, Table 3). In terms of $\delta^{13}C$, three of the late-stage calcite cements are depleted with respect to Devonian marine calcite. In general, the oxygen values range between -14 and -12 ‰ VPDB. This suggests precipitation at elevated temperatures. Typically, values of this order occur following burial to depths greater than 2000 m, the result of loading due to the Cordilleran foreland succession. The heavier-oxygen calcite sample from the Mikkwa Formation is only slightly depleted with respect to Devonian seawater, and probably precipitated at relatively shallow burial depths. Two of the calcite cements have carbon isotope values that are extremely depleted when compared to seawater, or even to dolomite samples from Pine Point. These samples, and even some from Pine Point, reflect precipitation under the effects of thermochemical sulphate reduction. Radiogenic strontium analyses were conducted only on samples from the Keg River and Mikkwa formations. Similar to both the matrix and saddle dolomites, most of the values plot in or just slightly above Devonian seawater. A closer look at Figure 9 shows that these values are similar to values obtained from Pine Point/Presqu'ile dolomite samples. The similarities between the Sr isotopes of the field samples and Pine Point are encouraging; nonetheless, an unequivocal genetic relationship to Pine Point cannot be made based on the quantity of data available.

Core data

Cathodoluminescent and transmitted-light petrography conducted on the 24 core samples indicate that most of the diagenetic phases (as opposed to only six in the field samples) identified by Qing and Mountjoy (1994) are present (Fig. 10). These phases include fine- and medium-crystalline matrix dolomite, fine-crystalline lath anhydrite, saddle dolomite, bladed ('pile of brick') anhydrite, late-stage calcite, and bitumen. It is generally accepted that mineralization only occurs where the majority of these phases are present in the host rock. However, as for the field samples, none of the core samples show evidence of all the important mineralizing phases together. Of the thin-sections examined, only those from the Keg River and Grosmont formations show characteristics typical of the Pine Point MVT deposit.

The most encouraging samples came from the Middle Devonian Keg River Formation. These samples showed evidence of matrix dolomite, anhydrite precipitation, saddle dolomite, late-stage calcite, bitumen, and scattered pyrite mineralization. The single sample from the Grosmont Formation shows extensive development of matrix dolomite, saddle dolomite and late-stage calcite. However, the matrix dolomite has low porosity, reducing the reservoir (i.e. hydrocarbon), and hence, mineralization potential. Samples from the Slave Point Formation and Jean Marie Member of the Redknife Formation show very little potential for Pb-Zn mineralization.

Stable and radiogenic isotopes show that the majority of the matrix dolomite samples that were analyzed plot near or within the marine calcite and marine dolomite fields. The only exception is the single sample of matrix dolomite from the Jean Marie Member (C-421193, Table 3). Data that plot near the marine calcite/dolomite boxes tend to suggest precipitation from fluids that were at or near seawater composition during the Devonian. When compared to Pine Point, the majority of the isotope values for matrix dolomite show enrichment in $\delta^{18}O$ (Fig. 8). In terms of strontium ratios, the matrix dolomites from the Jean Marie Member, Redknife Formation, and the Keg River and Grosmont formations all have values similar to Devonian seawater values (Fig. 9). However, a comparison of both the stable and radiogenic isotope values suggests that the matrix dolomites from this core study are not genetically similar to those at Pine Point.

One sample of saddle dolomite from the Keg River Formation was analyzed for stable isotopes (C-421181, Table 3). Values obtained from this sample are identical to those from the matrix dolomite samples discussed above. Similarly, these values indicate possible precipitation from modified Devonian seawater. However, the oxygen value suggests that the saddle dolomite was not precipitated from a fluid at temperatures characteristic of deep burial. Even saddle dolomite samples from Pine Point, which have been interpreted as having formed very close to the surface, have oxygen isotopes below -7 ‰ VPDB. This suggests that the saddle dolomite from the Keg River Formation is a burial cement reflecting re-distribution of Mg through chemical compaction, similar to the Nisku dolomite from West Pembina (Machel, 1987).

Six (6) samples from late-stage calcite cements were analyzed from the Jean Marie Member, Redknife Formation, and the Keg River, Slave Point, and Grosmont formations. All of the samples show significant depletion in both oxygen and carbon stable isotopes (Fig. 8). Oxygen values around -14 ‰ VPDB indicate precipitation at elevated temperatures. These values occur following burial to depths greater than 2000 m; during or subsequent to Laramide orogenesis. All six calcite cement samples have carbon isotope values that are extremely depleted when compared to seawater, and even dolomite samples from Pine Point. Carbon isotope values below -11 ‰ VPDB indicate the contribution of oxidized carbon. Values such as these are generally attributed to thermochemical sulphate reduction. This interpretation has also been used to explain the formation of late-stage calcite cements at Pine Point (Qing and Mountjoy, 1994; Coniglio et al., 2006). In terms of the radiogenic strontium analyses conducted on these late-stage calcite cements, most of the values plot in or just slightly above Devonian seawater, similar to the dolomite samples (Fig. 9). These values are similar to values obtained from Pine Point/Presqu'ile dolomite samples. However, without data for late-stage dolomite phases (i.e. saddle dolomite) from the four formations, a genetic relationship with Pine Point cannot be confirmed or discounted.

SUMMARY

The problem facing the explorationist in northeast Alberta is one of finding a blind MVT deposit, that is, a buried deposit with little or no direct evidence of its presence. Any attempt to evaluate the carbonate-hosted Pb-Zn (MVT) potential of the region is plagued by the problems of poor exposure and by the exclusion of carbonate deposits underlying Wood Buffalo National Park, with their favourable shallow depths and basin-margin position, from meaningful investigation. The amount of rock available for examination during this study, from the combination of river exposures and subsurface core, is extremely small relative to the size of the region. For this reason, the data gathered cannot be considered as sufficient to evaluate the entire area. It would be poor judgement, therefore, to consider the results herein as a final statement on the region's Pb-Zn potential.

Field areas

Those areas that were the focus of the field program are summarized below with respect to features relating to the potential for MVT Pb-Zn occurrences.

Vermilion Chutes, Peace River

The Vermilion Chutes region on the Peace River lies on-strike with the southwestward extension of the Warren Shear Zone in the Precambrian Shield of northeastern Alberta. The possible extension of this structure may give the area a regional structural control that could be considered favourable for localizing MVT deposits. Saddle dolomite was identified microscopically in the Grosmont Formation. Strontium isotopes for the Mikkwa Formation plot marginal to the Pine Point field. Both the Mikkwa and Grosmont formations display bitumen staining and moderate to good porosity. It was in the Grosmont Formation that Gulf Minerals (1975) collected a sample that contained 0.1% Zn.

Harper Creek

The Mikkwa Formation at Harper Creek is faulted and has associated coarse fracture-filling calcite. This location lies on the possible southwestern extension of the Allan Shear Zone in the Precambrian Shield. Similar to the Grosmont Formation at Vermilion Chutes, the Mikkwa Formation contains microscopic saddle dolomite, but does not contain bitumen. Stable isotopes for the formation plot both in, and marginal to, the Pine Point–Presqu'ile field. Strontium isotopes plot marginal to the Pine Point field.

Whitemud Falls, Clearwater River

At Whitemud Falls, the Methy Formation is locally faulted and hematite altered, but displays no late-stage coarse calcite veining as seen in the Mikkwa Formation at Harper Creek. It has locally well-developed porosity, reaching 25–30% in specific horizons. Saddle dolomite was identified both in outcrop (once in a very small cavity) and microscopically. Bitumen was not visible in outcrop, but present microscopically. Carrigy (1959) reported galena in a single small cavity at Whitemud Falls. Stable isotopes for the Methy dolomite plot marginal to the Pine Point–Presqu'ile field.

Diagenesis and isotopes

Field areas

1. None of the samples show the whole range of diagenetic phases evident at Pine Point, likely an indication that the fluids responsible for Pine Point have not infiltrated these samples.
2. The most encouraging sample (C-406461), obtained from the Mikkwa Formation at Harper Creek, contained late-stage diagenetic saddle dolomite cement, known to be associated with Pb-Zn mineralization at Pine Point.

3. The only evidence for the very late diagenetic phases similar to those found at Pine Point are in samples from the Methy Formation, at Whitemud Falls on the Clearwater River. At this location, bitumen and late-stage iron-rich calcite cements plug the pore spaces.
4. The remainder of the samples show varying degrees of replacement by matrix dolomite. When the cathodoluminescent zones within the dolomite across the study area are compared, there appears to be a relationship between the fluid(s) that was/were responsible for matrix dolomite precipitation.
5. Bitumen is found only in small quantities within the samples. As the interaction between hydrocarbons and sulphide-bearing fluids is generally invoked as the cause for mineralization at Pine Point, significant quantities of Pb-Zn minerals are not expected.
6. Both stable and radiogenic isotope data indicate that the diagenetic fluids have evolved from Devonian seawater or evaporative seawater. The stable isotope data that lie within, or close to the Pine Point – Presqu'ile fields are all from early (calcite cement and micrite) and burial calcite phases along a fault in the Mikkwa Formation at Harper Creek. Stable isotope data from saddle dolomite (C-406495) in the Methy Formation at Whitemud Falls also falls on the margin of the Pine Point/Presqu'ile saddle dolomite–coarse crystalline dolomite field.

Core samples

1. None of the core samples show the whole range of diagenetic phases present at Pine Point, suggesting that Pine Point fluids may not have invaded the carbonate sequence of northeastern Alberta.
2. The most encouraging samples were from the Middle Devonian Keg River Formation. These samples showed evidence of matrix dolomite, anhydrite precipitation, saddle dolomite, late-stage calcite, bitumen, and scattered sulphide (pyrite) mineralization.
3. The single sample from the Grosmont Formation shows extensive development of matrix dolomite, saddle dolomite, and late-stage calcite. However, the matrix has low porosity, reducing the reservoir (i.e. hydrocarbon), and hence, mineralization potential.
4. Samples from the Slave Point Formation and Jean Marie Member of the Redknife Formation show very little potential for Pb-Zn mineralization because of the lack of many of the diagenetic features found at Pine Point.
5. Bitumen is found only in small quantities within the samples.
6. Stable isotope data from both matrix and saddle dolomite in all formations indicate precipitation from modified Devonian seawater at very shallow burial depths.
7. Late-stage calcite cements incorporated oxidized organic carbon, and were precipitated via thermochemical sulphate reduction at elevated temperatures.
8. Strontium isotopes suggest that the fluids responsible for precipitation of the dolomite and calcite were likely not related to those at Pine Point and along the Presqu'ile Barrier.

CONCLUSIONS

This study did not encounter any new Pb-Zn occurrences, or any of the classic MVT features displayed in the Pine Point deposits of the southern Northwest Territories. The data summarized above indicate minor similarities with the Pine Point deposits in some of the core samples, and at each of the Vermilion Chutes, Harper Creek, and Whitemud Falls field areas. Having said this, the integrated data are not strong enough to propose any of these areas as exploration targets. Neither do the data rule out the possibility that MVT Pb-Zn deposits could exist elsewhere within the region (for example, the 0.1% Zn anomaly reported by Gulf Minerals (1975) at Vermilion Chutes has apparently not been explained). The presence of diagenetic phases characteristic of MVT deposits worldwide, and select isotope results comparable to the Pine Point–Presqu'ile Barrier, suggest that fluids responsible for diagenesis in the Middle and Upper Devonian carbonate deposits of northeastern Alberta may be genetically related to fluids responsible for MVT mineralization at Pine Point.

RECOMMENDATIONS FOR FUTURE WORK

Since MVT Pb-Zn exploration in northeastern Alberta amounts in large part to searching for blind deposits, the choice of geophysical techniques is very important. In this regard, it is recommended that the techniques proposed by Klein (2000) be considered; specifically, a combination of induced polarization/resistivity techniques and reflection seismic on the deposit-scale, coupled with aeromagnetic and gravity data to delineate larger structures that might localize MVT deposits on a more regional scale.

This project has improved upon previous evaluations of the MVT Pb-Zn potential of northern Alberta by employing a multidisciplinary approach. As a recommendation for future work, it is suggested that the subject of an overlap between hydrocarbon accumulations and MVT deposits be formally investigated, as proposed by Sangster (2002). Alberta is particularly well suited for such a study because of its huge amount of publicly available subsurface geological data accumulated from decades of hydrocarbon exploration. The interpretation of data compiled on a select number of relevant parameters (e.g. spatial coincidence, sulphur source, fluid migration, temperature, brine salinities) could result in the definition of a set of exploration guidelines that could then be used to search the petroleum industry dataset for locations with enhanced MVT potential.

ACKNOWLEDGMENTS

This paper represents part of the Alberta Geological Survey's contribution to the federally sponsored Targeted Geoscience Initiative project 232-110-010009 (Potential for Carbonate-Hosted Pb-Zn (Mississippi Valley-Type) deposits in northern Alberta and southern Northwest Territories). The project was a two-year (2001–2003) co-operative effort between the Alberta Geological Survey, Edmonton, Alberta, the Geological Survey of Canada, Calgary, Alberta and the C.S. Lord Northern Geoscience Centre, Yellowknife, Northwest Territories.

In addition to the senior author, Alberta Geological Survey personnel involved in the MVT project were J.J Adams, B.E. Buschkuehle, D.R. Eccles, E.C. Grunsky, D.I. Pană, and E.J. Waters. T.A. Zerbe contributed significantly to the project as a geological assistant for the field and core programs. C. Kehoe provided able office assistance. N. Blundon and D. Magee assisted with GIS and drafting. G. Hoffman, Northwest Labs, Calgary is thanked for information on the availability of additional core in the Fort McMurray region. Discussions with Don Sangster at the initial and intermediate stages of this project provided insight, direction and ideas regarding future work on MVT Pb-Zn mineralization in Alberta. Jack Wendte, Geological Survey of Canada, Calgary and Don Sangster, North Gower, Ontario are thanked for their formal reviews of the manuscript.

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