

**Geochemistry of formation waters, northern Alberta,  
Canada: their relation to the Pine Point ore deposit**

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**Abstract** - The source of the ore fluid which gave rise to the Pine Point Zn-Pb deposit has been controversial for many years. Although classified as a Mississippi Valley type deposit, a source from geothermal fluids rising from the Precambrian basement was also considered. None of the authors of these various studies had the benefit of determinations of both Pb and Zn in at least one of the proposed fluid sources. A new data base of nearly 200 detailed analyses of formation waters from northern Alberta helps to resolve this controversy.

Formation waters from northern Alberta, and possibly throughout the western Canada sedimentary basin, are unusual, if not unique, in having dominantly Pb>Zn. This is the same proportion as is found in brines from the exposed Canadian Shield, but is in marked contrast to formation waters from other sedimentary basins close to Mississippi Valley type ore deposits and to geothermal fluids at Cheleken and Salton Sea. Although analyses of formation waters with Pb>Zn can be manipulated to produce Zn>Pb deposits by means of water-rock reactions, the low-pH conditions are seldom met with in sedimentary basins. It has proved impossible to derive a Zn>Pb deposit from a formation water with Pb>Zn using SOLMINEQ.88, at least under conditions comparable to the deposition of the Pine Point ore. Therefore, formation waters were not the source of the metals at Pine Point.

Because there are no data on the composition of the geothermal fluid which gave rise to the Pine Point ore deposit, circumstantial and indirect evidence must be amassed to support such an origin. This information includes (1) the observations respecting Pb and Zn in formation waters from northern Alberta, (2) the very homogeneous and non-radiogenic character of the Pb isotopes in galena, (3) the past and present thermal anomaly along the Great Slave Lake Shear Zone, (4) the time of deposition of the ore (Famennian) with respect to possible overburden and reservoir temperatures at that time, and (5) the distribution of sphalerite and galena in the subsurface in relation of major crustal discontinuities and normal faults cutting the crystalline basement.

Exploration for other Zn-Pb deposits should therefore focus attention on two features: (1) the location of suitable shear zones and faults up which geothermal fluids might have migrated; and (2) the location of appropriate brines or at least saline formation waters with H<sub>2</sub>S, although there is no compelling reason why the ore fluid should be saline.

Finally, Pine Point differs in a fundamental way from other Mississippi Valley type ore deposits inasmuch as the ore fluid was of geothermal origin. This would suggest that Pine Point should be designated a new mineral deposit type.



## **PART A. PRELIMINARY SUMMARY OF FORMATION WATER CHARACTERISTICS**

## INTRODUCTION

**PINE POINT** in the Northwest Territories was the site of one of the most successful mining operations in the history of North America (Gibbins, 1988). Yet today the mine is closed, not because the ore reserves are depleted but because of low product demand combined with the opening of large high-grade deposits elsewhere in the world. There was a flurry of papers in the late 1960s and early 1970s reporting research work carried out on the rocks, minerals and fluids of the Pine Point region. Since that time there have been few studies specific to the Pine Point region, although similar stratabound ore deposits have been described from the 'adjacent' (~500 km southwest) thrustfold belt of the Western Canada sedimentary basin.

The Pine Point ore deposit belongs to the class called Mississippi Valley type. They are also known as carbonate-hosted Zn deposits, and more specifically as Appalachian Zn (Briskey, 1986). There are literally hundreds of papers dealing with the various aspects of Mississippi Valley type ore deposits and it is quite irrelevant to review them here. The most important of these papers which refer directly to Pine Point include Campbell (1966), Jackson and Beales (1967), Skall (1975), Kyle (1977, 1981), Rhodes et al. (1984) and Krebs and Macqueen (1984), all of whom described various aspects of the stratigraphy, structure, dolomitization, karstification, mineralogy and paragenesis of this deposit. Krebs and Macqueen (1984) provided an excellent summary of the prior literature on the Pine Point ore deposit.

With respect to the origin of the Mississippi Valley type ores there is an equally voluminous literature. Krebs and Macqueen (1984) have reviewed that portion of the literature that applies to Pine Point, and have listed ten features which need to be explained in any scenario on the origin of the deposit. The source of the ore fluid centres on either formation waters from deep in the sedimentary basin or hydrothermal fluids ascending from the basement. Yet of the many authors, including this one, who have proposed the involvement of formation waters, not one has had available a data base of formation water analyses which included the two main elements present in the ores, namely, Zn and Pb. Without this information it is impossible to show, unequivocally, that formation waters were involved in the origin of the Pine Point ores. Equally, advocates of a hydrothermal fluid source cannot justifiably exclude formation waters without this key information. This paper attempts to resolve this dilemma.

Basically, the Zn-Pb ore deposit at Pine Point is stratabound in secondary M. Devonian (M. and U. Givetian) dolostones created by Mg-rich brines refluxing through the carbonates of a barrier-complex. The complex was made more acceptable for brine flow by penecontemporaneous slumping, fracturing and small-throw faulting combined with late Givetian paleokarst development. Details of the geological characteristics are given in Table 1.

The host rock dolomite and ore minerals (sphalerite and galena) have been studied using geochemical, isotope and fluid inclusion techniques (see Table 2). It seems likely that about 100-125 Ma after deposition of the Pine Point Group (age ~380 Ma) the main ore minerals were deposited in the already existing coarse dolomite facies from waters

Table 1. Geological characteristics of the Pine Point ore deposit

Characteristic	Reference
<b>GENERAL</b>	
<u>Model type</u> Appalachian Zn (synonyms: Mississippi Valley type; carbonate-hosted Zn)	(1)
<u>General description</u> Stratabound deposits of sphalerite and minor galena in primary and secondary voids of favourable beds or zones in thick platform dolostone and limestone	(1)
<b>PINE POINT</b>	
<u>Tectonic setting</u> Interior continental platform margin. Middle Devonian (Givetian) tectonic movements controlled growth of a barrier complex, with penecontemporaneous hinge zones accompanied by slumping, fracturing and faulting. These lines of weakness were enhanced by late Givetian paleokarst development -- which provided conduits for later Mg-rich brines (from back reef evaporite pans) which produced the coarse dolomite of the host Presqu'île facies	(2)
<u>Stratigraphy and lithology</u> Hay River Fm. (Frasnian): shale, open marine Slave Point Fm. (U. Givetian): O/P. sandy micrite to micritic sand (shallow platform), 35 m N. micritic limestone (tidal flat), 15 m M. limey shale and limestone, 10 m * Watt Mountain Fm. (U. Givetian): L. fine micritic limestone and waxy green shale (restricted environment), 10-15 m * Pine Point Gp. (M. Givetian): K. coarsely crystalline vuggy dolomite (Presqu'île facies), max. 70 m * J. dense to sucrosic dolomite (back reef facies), max. 145 m H/I. limestone (gastropod and <u>Amphipora</u> facies), max. 35 m G. dark green basinal shale ( <u>Buffalo River</u> shale), up to 60 m F. dense bituminous limestone ( <u>Tentaculites</u> facies), max. 30 m E. massive sucrosic dolomite (clean arenite facies), max. 45 m D. fine to dense fragmental dolomite (organic barrier facies), up to 30 m C. massive limestone (shallow fore-reef facies) B. sucrosic dolomite (off-reef facies), max. 60 m * Keg River Fm. (L. Givetian): A. sucrosic dolomite with shale markers (marine platform), ~70 m	(2)

\* Although the Presqu'île facies (K) is the dominant host for the ore, all starred units contain some ore material. Occasionally, specks and veins of galena, sphalerite and iron sulphides can also be observed in the shales of the Keg River Fm. (Skall, 1975); likewise there are sporadic disseminated iron sulphides, as well as rare specks of sphalerite and galena in Facies H and I (Skall, 1975).

References: (1) Briskey (1986); (2) Skall (1975).

Table 2. Geochemical characteristics of host rock and ore deposit minerals, Pine Point

Characteristic	Reference
<b>HOST ROCKS</b>	
<u>Dolomite</u> 1. Supratidal and early diagenetic finely crystalline dolomite (all or part of facies A, B, D, E, F and J; see Table 1): precipitation of CaSO <sub>4</sub> and CaCO <sub>3</sub> (Muskeg Fm.) in back reef evaporite pans left Mg-rich brines which flowed downward and seaward, dolomitizing permeable limestones in their paths	(1)
δ <sup>18</sup> O values between -1 and -4‰ (PDB), >5 mol % CaCO <sub>3</sub> in excess, and up to 700 ppm Na in impurities	(2)
2. Late diagenetic coarsely crystalline dolomite characteristic of the Presqu'île facies (K; see Table 1): associated with fracture porosity along two main hinge zones resulting from later, warm Mg-rich brines converting the remaining vulnerable limestone (lower, earlier dolomite remained unaffected)	(1)
δ <sup>18</sup> O values between -7 and -12.5‰ (PDB), <5 mol% CaCO <sub>3</sub> in excess, and <200 ppm Na in impurities	(2)
<b>MINERALIZATION</b>	
<u>Sphalerite</u> Predominantly fine-grained with celloform structure, although much massive crystalline material also occurs. Collorform variety occurs frequently in massive (vertical) but rarely in tabular ore bodies. The Pb:Zn ratio is 1:1.7 for massive and 1:2.6 (or greater) for tabular ore bodies	(1,3)
Sphalerite is Ag-poor, with Cu:As ratio about the same as tennantite (not found)	(4)
Fluid inclusion studies suggest sphalerite formed from very saline brines at temperatures in the range 50°-100°C	(5)
Sulphur isotopes of sphalerite and galena (δ <sup>34</sup> S mean +20.1‰; σ ±2.6‰; n=118) indicate a source of S from M. Devonian sea water SO <sub>4</sub>	(6)
<u>Galena</u> Appears to follow the earliest sphalerite but from then on co-precipitation seems to have occurred	(3)
Lead isotopes fall close to the mantle growth curve and indicate that the Pb came from a homogeneous source with a model age about 250-275 Ma, appreciably younger than the M. Devonian host rocks	(7)

References: (1) Skall (1975); (2) Fritz (1971); (3) Jackson and Beales (1967); (4) Sangster (1968); (5) Roedder (1968); (6) Sasaki and Krouse (1969); (7) Cumming and Robertson (1969).

at a temperature in the range 50-100°C. Studies of the Fe content of sphalerites indicate a minimum temperature of formation of ~100°C (Evans et al., 1968). The S in the ore minerals originated from M. Devonian sea water SO<sub>4</sub>, based on S isotope studies, but the source of the metals could be contemporary carbonates or shales (see Table 3). Neither the precise source of the metals nor the exact mode of transportation in the waters has been ascertained.

Table 3. Geochemical characteristics of host and possible source rocks at and near the Pine Point deposit

Characteristics			Reference
<u>Carbonate host rocks</u> Collected from 1 m to ~ 2 km from ore body. Mean (n=35) Zn 354 ppm, Pb 65 ppm, Cu 3 ppm; on a Cu-Pb-Zn ternary diagram the average is close to the average composition of the ore (6.8% Zn, 2.9% Pb)			(1)
<u>Laterally equivalent shales and/or mudstones</u> Collected from cores in northwest line up to 225 km from Pine Point (n=12)			(2)
	Range	Mean	
Zn (ppm)	56-3216	790	
Pb (ppm)	0-82	15 (8 samples=0)	
Cu (ppm)	24-716	117 (n=11)*	
S (%)	0.4-2.1	1.26	
C <sub>org</sub> (%)	1.4-30.1	8.3	
<u>Muskeg Fm.</u> Well at 7-32-109-8-W6M from 1765.1-1765.4 m (all values in ppm) Zn 54, Pb<5, Cu 17, Ag 0.5, Cd 16, Mo 13, C <sub>org</sub> (%) 0.560, extractable organics 1120 ppm			(3)

\*(Macqueen, pers. commun.)

References: (1) Sangster (1968); (2) Macqueen et al. (1975); (3) Hitchon (unpublished).

Despite the importance attributed to formation waters as potential carriers of Zn and Pb, there exist only two published data sources for Zn in Alberta formation waters and one for both Zn and Pb (see Table 4). None is entirely satisfactory for elucidating the source of the sphalerite and galena at Pine Point, but individual analyses are of interest and value. The calculations of Billings et al. (1969) and the more recent numerical modelling study of Garven (1985) suggest that Zn concentrations in formation waters generally <10 mg/l (and even as low as 1 mg/l) could account for the Pine Point

Table 4. Summary of statistics on selected trace elements in formation waters from Alberta

Trace elements			Reference
<b>Northern Alberta</b>			(1)
About 40 formation waters from M. Devonian strata 350 km southwest of Pine Point were studied; general characteristics as follows (values in mg/l):			
	<b>Range</b>	<b>Mean</b>	
Total dissolved solids	91,000-306,000	143,000	
Zn	0.01-290	18.9	
Cu	0.02-0.52	0.10	
Fe	0.01-3.1	0.5	
Mn	0.04-65	5.9	
Analytical difficulties prevented the determination of Pb			
<b>Alberta Basin</b>			(2,3)
Major investigation of formation waters selected to represent the volume-weighted composition in the western Canada sedimentary basin; general characteristics as follows (values in mg/l):			
	<b>Range</b>	<b>Volume-weighted mean</b>	
Total dissolved solids	Freshwater - ~300,000	46,400	
Zn	0.0-27.5	0.30	
Cu	0.02-0.44	-	
Fe	<0.01-87.0	-	
Mn	<0.04-52.0	0.32	
Analytical difficulties prevented the determination of Pb			
<b>Swan Hills area</b>			(4)
Thirty-three detailed analyses reported in Appendix B of a study on deep waste injection; samples range from M/U Devonian to top of L. Cretaceous. Range of selected trace elements as follows (values in mg/l):			
Zn	<0.05 (n=20) to 7.3		
Pb	<0.1 (n=6) to 63		
Cu	<0.1 (n=23) to 0.6		
Fe	<0.1 (n=18) to 42		
Mn	<0.1 (n=14) to 20		

References: (1) Billings et al. (1969); (2) Hitchon and Friedman (1969); (3) Hitchon et al. (1971); (4) Hitchon et al. (1989).

ore deposit within reasonable geological times (0.5 to 5 Ma) and paleotemperatures in the range 60° to 100°C.

An important geochemical consideration, however, is the relation of Pb and Zn in formation waters to the production of a Zn-Pb deposit with the ratios of Pb-Zn ranging from 1:1.7 to 1:2.6 or greater, depending on the geometry of the ore body (see Table 2). Examination of the individual analyses in Hitchon et al. (1989), summarized in Table 4, shows that there are 29 analyses in which it is possible to determine the relative concentrations of Pb and Zn using both actual determinations and the fact that one of these trace metals may be below detection. Of these 29 analyses, 23 have Pb>Zn and only 6 have Zn>Pb. Where it is possible to calculate the Pb-Zn ratio, the values range from 0.09 to 18, with some of the higher ratios in the M/U Devonian Beaverhill Lake Group. Clearly, this presents a dilemma; not only is the general Pb-Zn ratio in the 'wrong' direction, albeit in stratigraphic units that are not likely carrier beds for formation waters producing the Pine Point deposit, but the Swan Hills area is far to the south of the region believed to contain the 'source' formation waters for Pine Point (see Hitchon, 1971, Fig. 5). The resolution lies in a new data base of formation waters from northern Alberta with many trace elements determined (including Pb and Zn), and the development of a realistic mechanism for producing a Zn-Pb deposit from formation waters with Pb>Zn. It is the intention of this paper to describe and evaluate the new data base, and to see if it is possible to produce the Pine Point ore deposit from these formation waters.

#### DATA BASE AND DATA PROCESSING

Effectively all formation water analyses in the files of the Alberta Energy Resources Conservation Board are 'standard' analyses in which 'Na' is determined as the difference between the analyzed anions and cations, therefore including accumulated analytical and other errors; rarely are trace elements reported. As such, these analyses are of limited utility (Hitchon, 1984; Bachu et al., 1987; Hitchon et al., 1987), and certainly not generally suitable for studies of trace elements in formation waters or water-rock interaction.

Ideally, two things are required if a formation water analysis is to be of value to petroleum or mineral exploration, or to studies of water-rock interaction. First, the sample should be partially analyzed in the field and aliquots preserved for subsequent laboratory analysis. Second, appropriate minor and trace elements should be determined, and a complete analysis made of major elements so that a proper ionic (charge) balance can be determined. Few analyses from Alberta meet both requirements, and of those that do it is clear that at least some are not even representative of the in situ formation water because of a variety of effects such as contamination with water floods.

The study area (Fig. 1) was defined as Alberta north of 55°N (Tp 70 and northward). The entire Phanerozoic section was considered during the preliminary phase, although emphasis was ultimately concentrated on Givetian and older stratigraphic units. Recent studies of the hydrochemistry (Hitchon, 1990, 1991) and hydrogeology (Hitchon et al., 1990b; Bachu et al., 1993) of the southern part of the study area make consideration of the entire Phanerozoic section less onerous than might appear at first sight (see Fig. 1).

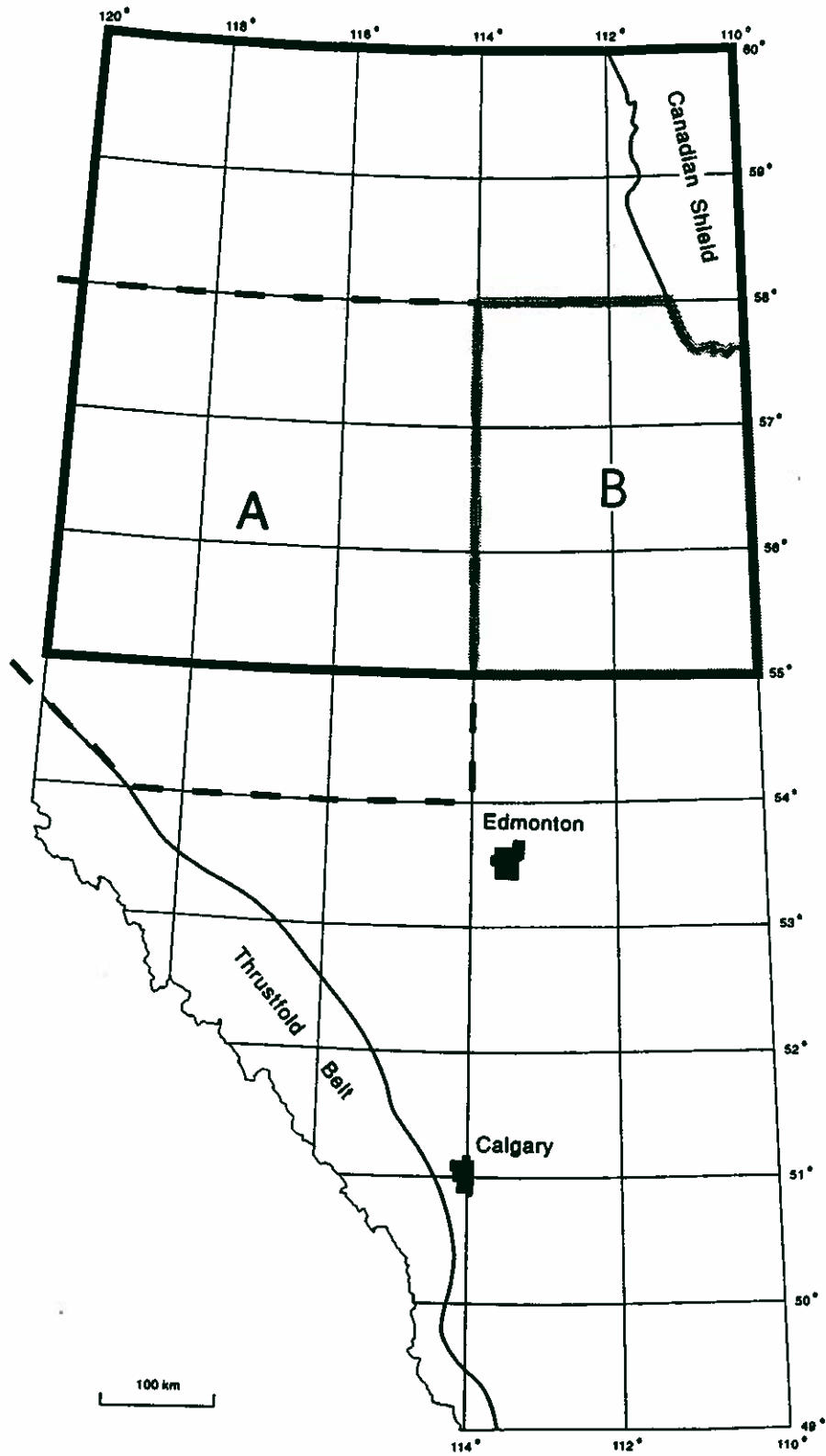


Figure 1. Study area showing recent hydrogeological evaluations of the Phanerozoic section: A. Peace River Arch (Hitchon, 1990; Hitchon et al., 1990b); B. Northeast Alberta (Hitchon, 1991; Bachu et al., 1993)



The only suitable published analyses within the study area are nine from Hitchon et al. (1971) from a variety of producing fields; while they were carefully sampled, only some trace elements were subject to field preservation.

Unpublished analyses used in this study comprise two groups. A so-called D-series are formation waters collected by the author in the summer of 1972 from Devonian and Pre-Devonian oil and gas fields throughout Alberta and northeastern British Columbia. Eight of the 40 fields sampled were from the study area. The samples were collected under optimum conditions with temperature, pH, Eh and alkalinity determined in the field, and aliquots treated for preservation of trace elements as appropriate. Special samples were also taken for stable isotope measurements. Limited information is also available on the associated natural gas and/or crude oil, as pertinent. Trace elements were determined by a variety of methods, including atomic adsorption, inductively coupled plasma (ICP) and specific ion electrode.

The major portion of the data base comprised the so-called RCAH-series (Research Council of Alberta Hitchon -series). These samples were collected in 1975-1977 through a cooperative project with the Energy Resources Conservation Board. All were from drillstem tests of then currently drilled wells. The produced formation water was subsampled by the operating company for the Energy Resources Conservation Board and the Alberta Research Council, though it was clear from the descriptions on the provided plastic containers that the position of the sample taken for the Energy Resources Conservation Board in the recovery was not always the same as that taken by the companies for their own 'standard' analyses. Often this made effectively little difference when the analyses were subsequently compared but it did allow a check to be made against samples for which a significant loss of CO<sub>2</sub> had resulted in possible precipitation of calcium carbonate prior to trace element determination. Major components were determined by the Energy Resources Conservation Board, and selected minor and trace elements by the Alberta Research Council. The majority of the trace elements were determined by Chemical and Geological Laboratories Ltd. of Edmonton using ICP methods.

The RCAH-series samples were collected under a wide variety of conditions, they were untreated in the field, and often several weeks elapsed before they could be treated for preservation of trace elements. As a result, CO<sub>2</sub> loss was sometimes significant, even to the extent of precipitation of calcium carbonate. Normally, formation waters with CO<sub>3</sub> present are mud-contaminated or, less commonly, have been subject to extensive CO<sub>2</sub> loss due to delay in analysis (see discussion in Hitchon et al., 1990a, Appendix 1). Because the 'standard' analysis reported by the operating company was made within a day or two of sampling, it acted as a check with respect to possible extensive CO<sub>2</sub> loss, and consequent calcium carbonate precipitation, in the RCAH-series samples. Thus only analyses without evidence of excessive CO<sub>2</sub> loss were included in the data base, even though they may report some CO<sub>3</sub>. Where the RCAH-series samples fell in the areas studied by Hitchon (1990, 1991) they were also checked against the regional trend maps and if anomalous were rejected. Table 5 shows that of the 511 unpublished and published detailed analyses available in the study area more than half were rejected because of their being incomplete (e.g. a major component not determined), mud filtrate

Table 5. Processing of formation waters

Procedure	No. of analyses	
Original data set	511	
Rejected (incomplete analyses)	32	(6.3%)
Rejected (mud filtrate or KCl mud contamination; not representative of regional trends)	247	(48.3%)
Entered into electronic data base and verified	232	(45.4%)
Rejected (charge balance >15%)	35	(6.8%)
Final data set for detailed evaluation	197	(38.6%)

contaminated, or not representative of the regional trends in the Peace River Arch and northeast Alberta study areas. A total of 232 analyses were entered into the electronic Alberta Geological Survey Well Data Base, and verified. They were then run through the computer program SOLMINEQ.88 (Kharaka et al., 1988), and those with a charge balance >15% were rejected. Table 6 shows that most (~55%) charge balances were <5%.

In order to compensate for the loss of CO<sub>2</sub> and to determine the mineral solubility characteristics at formation temperatures two procedures were carried out. First, the formation temperature was calculated from the depth of the drillstem test, and the integral regional geothermal gradient and annual ground temperature from Bachu and Burwash (1993). Second, the CO<sub>2</sub> option in SOLMINEQ.88 was used to add back CO<sub>2</sub> until the solution was saturated with respect to calcite. The SOLMINEQ.88 runs on which information for this study is based therefore reflect solutions saturated with calcite at formation temperature.

SOLMINEQ.88 reports the saturation of the water sample with respect to a large suite of minerals in terms of the Gibbs free energy difference ( $\Delta G_{diff}$ ) between the actual and equilibrium states of the mineral. A positive value of  $\Delta G_{diff}$  indicates that the mineral should precipitate from the water; a negative value of  $\Delta G_{diff}$  indicates that the mineral should dissolve in the water;  $\Delta G_{diff}=0.0$  indicates that the mineral is in equilibrium with the water. The calculation is strictly an equilibrium calculation. If the water is supersaturated with respect to the mineral, the mineral may not precipitate because of kinetic considerations. However, the greater the supersaturation, the more likely it is to precipitate. In order to provide an indication of the degree to which any specific mineral is saturated in the formation waters under consideration, the classification of  $\Delta G_{diff}$  shown in Fig. 2 will be used throughout this paper, rather than reporting the actual  $\Delta G_{diff}$  values. This is purely a convenience for the purposes of this paper.

Table 6. Discrepancy in charge balance by stratigraphic unit

Stratigraphic unit	Total analyses	Discrepancy in charge balance			
		Class A <5%	Class B 5-10%	Class C 10-15%	Class D >15% (discarded)
U. Cretaceous					
Belly River Fm.	1				1
Doe Creek Ss.	1	1			
L. Cretaceous					
Viking Fm.	21	9	9	2	1
Upper Mannville Gp.	11	4	2	3	2
Lower Mannville Gp.	45	20	11	6	8
Jurassic-Nordeg Mbr.	1	1			
Triassic					
Baldonnel Fm.	4	3	1		
Charlie Lake Fm.	8	5			3
Halfway Fm.	1	1			
Diaber Gp.	12	8	1		3
Permian-Belloy Fm.	7	1	2	1	3
Carboniferous					
Rundle Gp.	27	14	8	1	4
Pekisko Fm./U. Banff Fm.	8	5	2	1	
Devonian					
Wabamun Gp.	10	5		3	2
Winterburn Gp.	2	1			1
Leduc Fm./Grosmont Fm.	7	6		1	
Beaverhill Lake Gp.	13	6	1	1	5
Watt Mountain Fm.	6	3	2		1
Sulphur Point Fm.	8	8			
Muskeg Fm.	3	2		1	
Keg River Fm.	26	22	3	1	
Granite Wash	10	6	3		1
	232	131	45	21	35

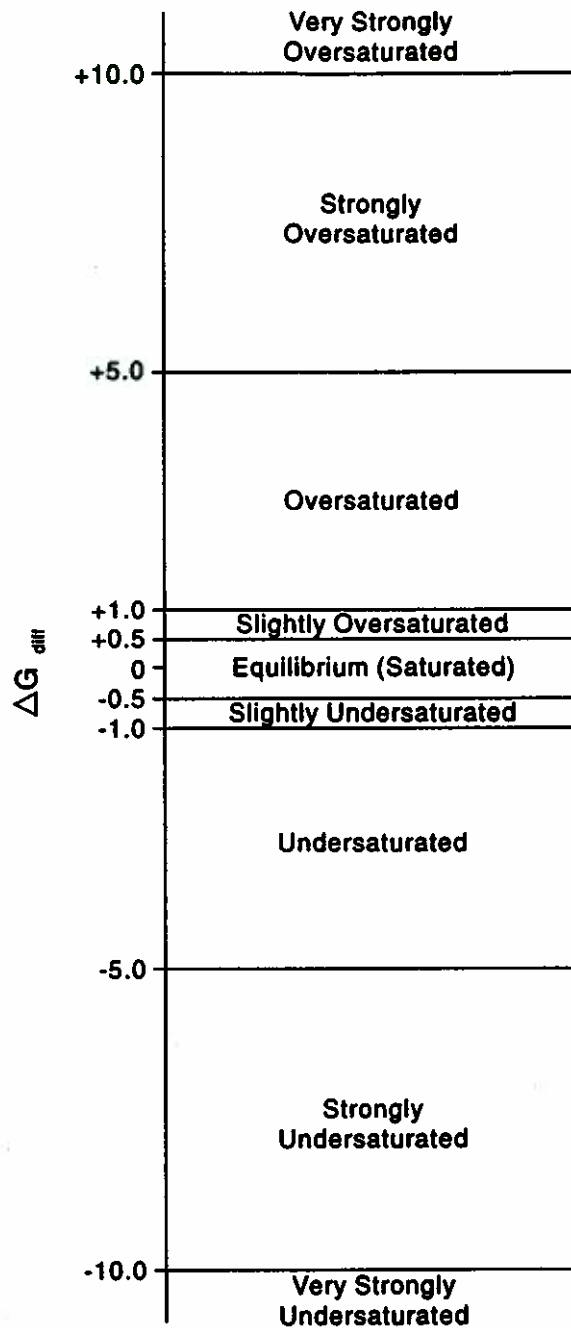


Figure 2. Classification of  $\Delta G_{diff}$  values determined by SOLMINEQ.88 in terms of mineral saturations

The final data base for detailed evaluation therefore comprises 197 samples ranging throughout the study area in stratigraphic units from the Upper Cretaceous (Turonian) to Pre-Middle Devonian Granite Wash. Figures 3-12 show the distribution of the samples by major stratigraphic units. Within the limitations noted above, this suite of formation water analyses is representative of the respective stratigraphic units.

## FORMATION WATER CHARACTERISTICS

### General

Based on hydrochemical reports for the southern portion of the study area (Hitchon, 1990, 1991), and the generally similar compositional variations within the data set prepared for this study, the following general observations can be made about the entire study area.

Salinity ranges from fresh water to 320,000 mg/l in the samples studied, although up to 380,000 mg/l has been reported in the Peace River Arch area. Salinity distribution maps for Pre-Cretaceous aquifers have salinity trends generally parallel to the structure contours, and show higher salinity with increased depth, hence increased temperature. This pattern may be modified by the presence of halite or by high permeability trends within individual aquifers. Both of these modifications result in relatively higher salinity for comparable depths. Salinity may also be modified by incursion of fresher waters from overlying aquifers.

Distribution patterns for Na, Cl, Ca and Mg closely resemble that for salinity, and as a broad generalization for any specific aquifer, the higher salinity area has a relatively lower  $\text{HCO}_3$  content compared to the lower salinity area. Sulphate is high in aquifers in which anhydrite is present, and may range up to 5500 mg/l; otherwise,  $\text{SO}_4$  generally shows no obvious regional trends.

Formation waters in the eastern part of the Elk Point hydrostratigraphic unit from near the updip edge of the Prairie aquiclude are similar to those of saline springs in the valley of the Athabasca River, which have been shown (Hitchon et al., 1969) to originate from solution of evaporites by meteoric water.

Based on the hydrochemical and hydraulic connections shown for the Peace River Arch and northeast Alberta areas (Hitchon, 1990, 1991; Hitchon et al., 1990b; Bachu et al., 1993) it is clear that no hydrostratigraphic unit younger than the Devonian is likely associated directly with the aquifer(s) feeding the Pine Point ore deposit. Further, attention should most reasonably be directed toward units older than the Ireton aquitard. Accordingly, the general characteristics of formation waters in post-Ireton aquifers will be dealt with only rather briefly. Specific attention will be directed to Pb, Zn, Fe, Mn, Sr, Ba and F, as well as saturations with respect to the most likely mineral occurrences for each element e.g. cerussite ( $\text{PbCO}_3$ ), smithsonite ( $\text{ZnCO}_3$ ), siderite ( $\text{FeCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ), celestite ( $\text{SrSO}_4$ ), strontianite ( $\text{SrCO}_3$ ), barite ( $\text{BaSO}_4$ ), witherite ( $\text{BaCO}_3$ ) and fluorite ( $\text{CaF}_2$ ). When considering pre-Ireton aquifers a complete characterization will be presented.

All except two formation waters were undersaturated to very strongly undersaturated with respect to halite (NaCl). The two exceptions came from the Keg

River aquifer, had  $\Delta G_{\text{diff}}$  values of -0.64 (slightly undersaturated), and were closely associated with thick sections of the Prairie Formation halite.

All formation waters from Cretaceous and Jurassic aquifers, as well as many samples from the Triassic Baldonnel and Diaber aquifers, the Belloy aquifer, some formation waters from the Rundle and Pekisko/U. Banff aquifers, and all samples from the Upper Devonian subcrop regions were undersaturated with respect to anhydrite ( $\text{CaSO}_4$ ). All formation waters from the Triassic Charlie Lake and Halfway aquifers were only slightly undersaturated with respect to anhydrite. Saturation or slight undersaturation with respect to anhydrite characterized formation waters from the Rundle, Wabamun, Winterburn, Leduc, Slave Point, Watt Mountain, Sulphur Point, Muskeg, Keg River, U. Cambrian and Granite Wash aquifers.

All formation waters were oversaturated with respect to dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ); it is suspected that the few samples showing only slight oversaturation could be the result of a low determination of Mg rather than an approach to saturation.

With very few exceptions, the formation waters show saturation or slight over- or undersaturation with respect to quartz ( $\text{SiO}_2$ ). Bearing in mind that silica was not preserved in the field (except for the D-series samples), it is reasonable to interpret these  $\Delta G_{\text{diff}}$  values in terms of quartz saturation in all the formation waters.

Although Al was reported in some samples the true value can only be measured following field filtration through 0.1  $\mu\text{m}$  filters. When a value for Al was reported the SOLMINEQ.88 calculations invariably show that the formation waters are strongly or very strongly oversaturated with respect to illite, kaolinite and K-smectite, and generally oversaturated or strongly oversaturated with respect to albite and K-feldspar. The  $\Delta G_{\text{diff}}$  values for anorthite vary widely and only this feldspar will be discussed in the following aquifer descriptions.

#### Colorado aquitard system

The only sample from this aquitard system (Fig. 3) is from the Doe Creek aquifer (see Hitchon et al., 1971, Table 2, no. 28). The formation water is undersaturated with respect to smithsonite, saturated with respect to rhodochrosite, but the high Fe content (11.7 mg/l) results in oversaturation with respect to siderite.

#### Paddy-Viking aquifer

The twenty samples from this aquifer all occur in the southern part of the study area (Fig. 4). Thirteen out of sixteen of the samples have  $\text{Pb} > \text{Zn}$  (both elements were below detection in four samples) and most of the formation waters are undersaturated or slightly undersaturated with respect to cerussite, and all are undersaturated with respect to smithsonite. All are undersaturated with respect to fluorite (F 0.22-4.1 mg/l, mean 0.8 mg/l, median 0.6 mg/l, n=17). Most samples are oversaturated or saturated with respect to barite and undersaturated with respect to witherite (Ba 0.43 - >200 mg/l, mean 34 mg/l, median 15 mg/l, n=18). Contents of Fe (max. 2.7 mg/l) and Mn (max. 0.4 mg/l) are generally very low and the formation waters were undersaturated with respect to both siderite and rhodochrosite. Strontium was in the range 6.6-67 mg/l (n=20) and all

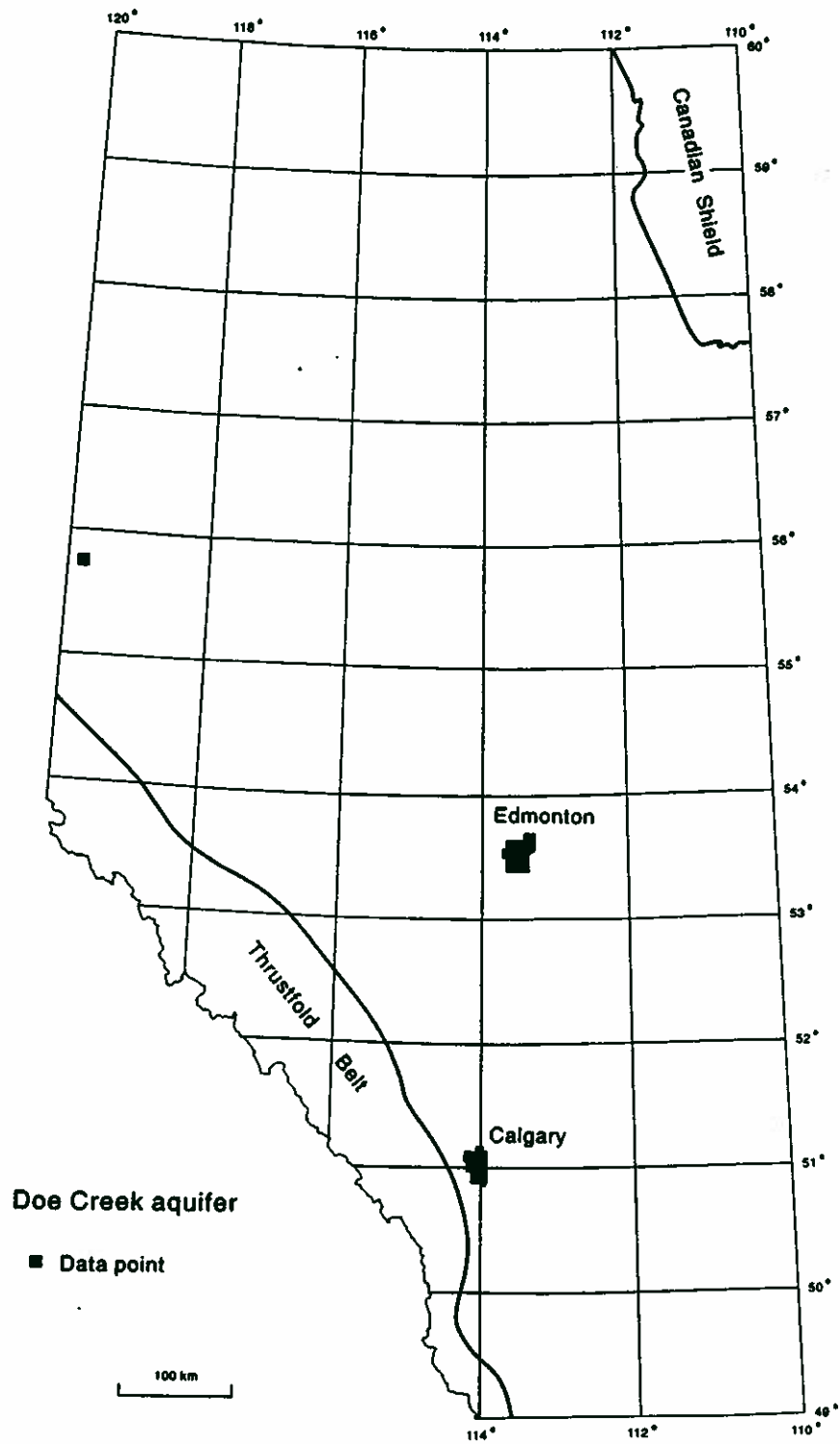


Figure 3. Colorado aquitard system: Data distribution, Kaskapau aquitard, Doe Creek aquifer (n=1)

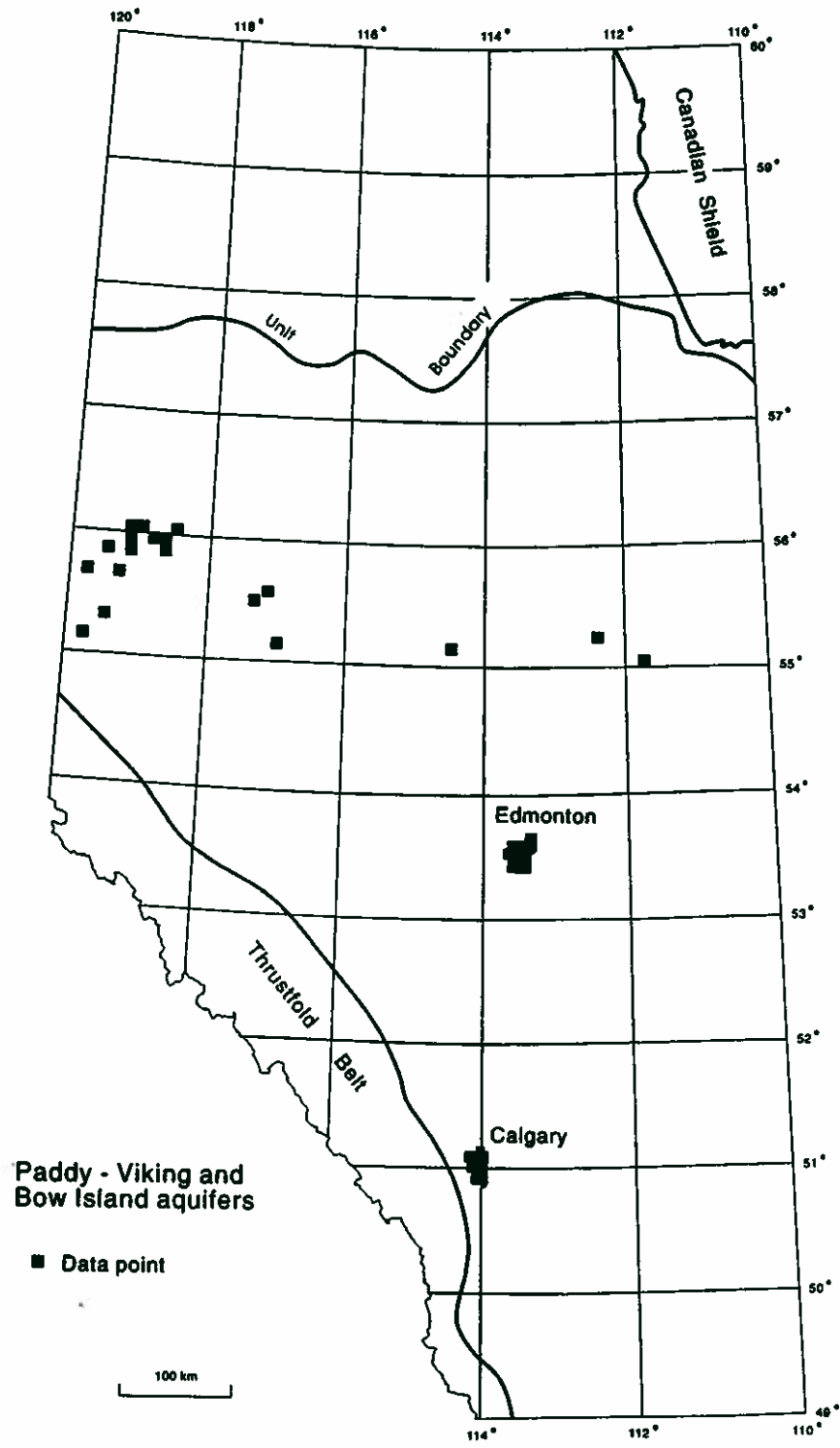


Figure 4. Paddy-Viking aquifer: Data distribution (n=20)



formation waters were undersaturated with respect to celestite and mostly saturated or slightly undersaturated with respect to strontianite. Aluminium was determined on only one sample which showed anorthite to be in equilibrium ( $\Delta G_{\text{diff}}=0.4$ ) with the formation water.

#### Upper Mannville aquifer

Most of the nine samples from this aquifer occur along the southern margin of the study area (Fig. 5). Out of five samples,  $\text{Pb} > \text{Zn}$  in four, and the formation waters were mostly saturated with respect to cerussite and undersaturated with respect to smithsonite. Most formation waters were undersaturated with respect to fluorite (F 0.38-2.2 mg/l, mean 0.7 mg/l, median 1 mg/l,  $n=9$ ) and generally saturated or slightly oversaturated with respect to barite and undersaturated with respect to witherite (Ba 0.3-13 mg/l, mean 2.9 mg/l, median 1.6 mg/l,  $n=9$ ). Contents of Fe (max. 0.05 mg/l) and Mn (max. 0.03 mg/l) are very low; formation waters were undersaturated with respect to both siderite and rhodochrosite. All formation waters were undersaturated with respect to celestite and undersaturated or slightly undersaturated with respect to strontianite (Sr 1-32 mg/l, mean 11 mg/l, median 6 mg/l). The only sample with Al determined showed undersaturation ( $\Delta G_{\text{diff}}=-1.3$ ) with respect to anorthite.

#### Lower Mannville aquifer

Formation water samples from this aquifer are widely scattered across the study area (Fig. 6) with one sample (RCAH 89-475; 2-28-94-9-W4) from the outcrop area north of Fort McMurray. Out of 25 samples,  $\text{Pb} > \text{Zn}$  in 22, and all formation waters were undersaturated with respect to smithsonite; saturation with respect to cerussite varied from undersaturated to oversaturated with the majority being at saturation. The range of F in the formation waters was 0.38-7.1 mg/l (mean 1.3 mg/l, median 1.1 mg/l,  $n=33$ ); the majority of the samples in the range 0.38-1.8 mg/l F were undersaturated or slightly undersaturated with respect to fluorite, but the sample with 7.1 mg/l F was oversaturated with respect to fluorite ( $\Delta G_{\text{diff}}=1.2$ ). Most formation waters were saturated or slightly oversaturated with respect to barite and mostly undersaturated with respect to witherite (Ba 0.2-680 mg/l,  $n=35$ , but 70% were  $<5$  mg/l). All formation waters were undersaturated or slightly undersaturated with respect to celestite, and mostly slightly undersaturated or undersaturated with respect to strontianite (Sr 0.2-95 mg/l, mean 23 mg/l, median 5 mg/l). Contents of Fe and Mn were generally  $<1$  mg/l (two extreme values of Fe were 3.4 and 27 mg/l) and out of 25 samples,  $\text{Fe} > \text{Mn}$  in 70% of the cases. All formation waters were undersaturated with respect to both siderite and rhodochrosite. For the six formation waters in which Al was reported, all showed highly variable saturations with respect to anorthite ( $\Delta G_{\text{diff}}=+4.7$  to  $-3.9$ ).

#### Fernie aquitard

There is only one sample from this hydrostratigraphic unit, from the Nordegg aquifer (see Fig. 7). Many of the trace elements of interest were below detection (Pb, Zn, Fe, Mn) but F was 1.3 mg/l, Sr 46 mg/l and Ba 4.4 mg/l. The formation water was undersaturated or slightly undersaturated with respect to celestite, strontianite, witherite, fluorite and anorthite, and saturated with respect to barite.

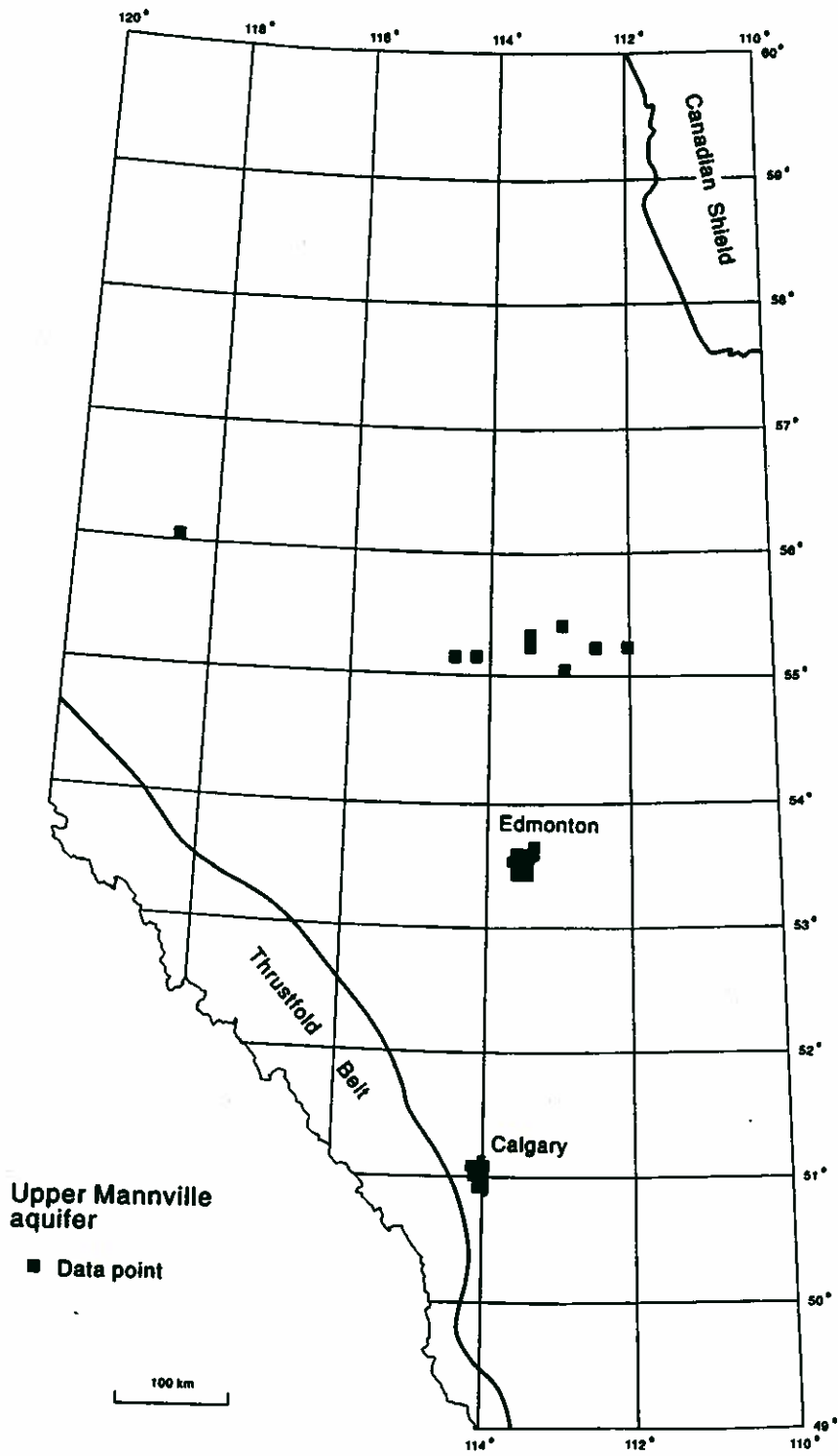


Figure 5. Upper Mannville aquifer: Data distribution (n=9)

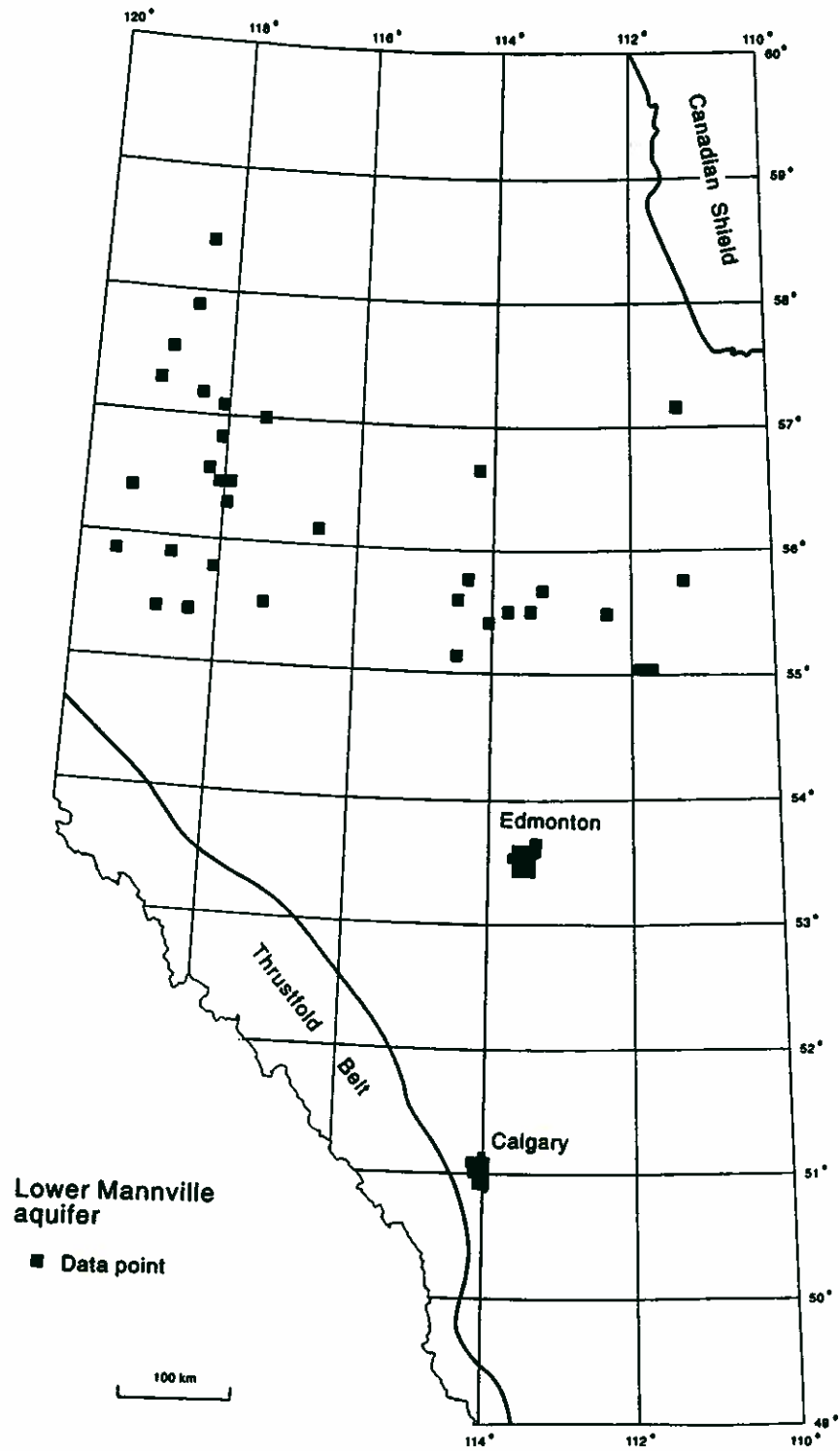


Figure 6. Lower Mannville aquifer: Data distribution (n=37)

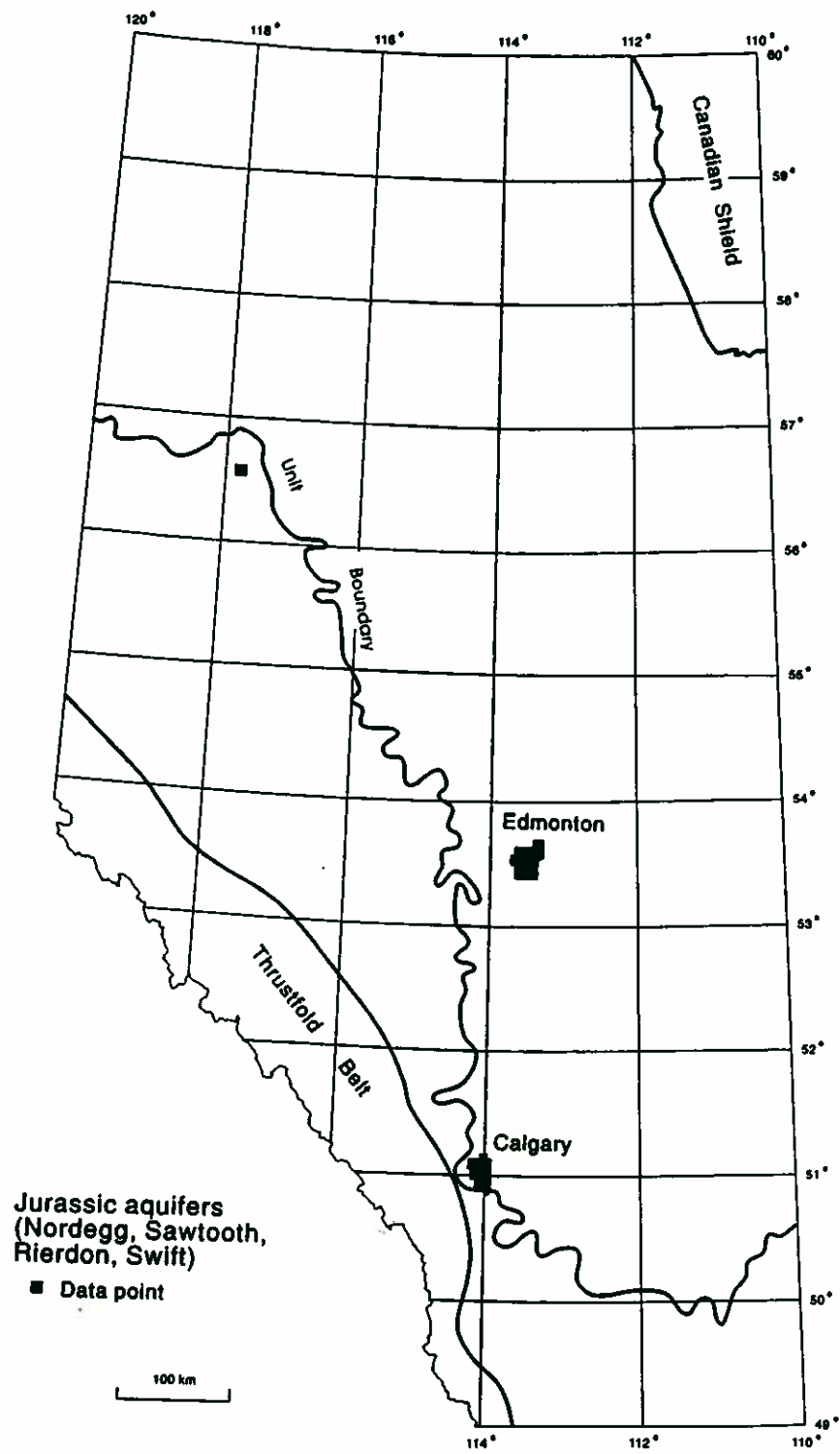


Figure 7. Fernie aquitard: Data distribution, Nordegg aquifer (n=1)

### Baldonnel aquifer

Four formation waters came from the Triassic Baldonnel aquifer (Fig. 8A), and their close spatial relation results in generally similar characteristics for many components: salinity (38,000-86,000 mg/l), Na (13,000-29,000 mg/l), K (280-1060 mg/l), Ca (250-1500 mg/l), Mg (150-450 mg/l), Sr (16-43 mg/l), Li (16-60 mg/l), Cl (19,000-47,000 mg/l), SO<sub>4</sub> (3600-4900 mg/l), NH<sub>3</sub> (110-230 mg/l, n=3) and pH at reservoir temperature (5.94-6.77). The very high SO<sub>4</sub> is a reflection of the underlying Charlie Lake Formation anhydrite, and has resulted in low contents of both Sr and Ba (0.08 mg/l, and below detection in three samples). The formation waters are all slightly undersaturated with respect to celestite, undersaturated with respect to strontianite, and the sample reporting Ba is saturated with respect to barite and strongly undersaturated with respect to witherite. The contents of Pb were in the range 0.8-2 mg/l, Zn was below detection in all samples, and Pb>Zn in all cases. Most formation waters were undersaturated with respect to cerussite and close to saturation with respect to fluorite (F 1.2-2.8 mg/l). Iron and Mn were generally below detection limits.

### Charlie Lake aquifer

Figure 8B shows the distribution of the five formation water samples from the Charlie Lake aquifer. The salinity of the northernmost sample (85,000 mg/l) is considerably less than the narrow salinity range for the other four samples (140,000-148,000 mg/l). This dichotomy is reflected in most of the other components. The content of SO<sub>4</sub> is very high (1750-2930 mg/l) and as a result Sr is low (38-100 mg/l) and Ba very low (0.23-0.56 mg/l, below detection in two samples); all formation waters are slightly undersaturated with respect to celestite, undersaturated with respect to strontianite, strongly undersaturated with respect to witherite, and saturated with respect to barite. The maximum contents of Zn and Pb are 13 mg/l and 9.6 mg/l, respectively, with Zn>Pb in three samples and Pb>Zn in the other two; all formation waters were undersaturated with respect to both cerussite and smithsonite. The contents of Fe and Mn were mostly below detection; Mn>Fe in two samples in which this relation could be determined. Saturation with respect to fluorite was very variable ( $\Delta G_{\text{diff}}=0.01$  to  $-2.2$ ) though the content of F was in a relatively narrow range (0.3-2.5 mg/l, mean 1.5 mg/l, median 1.8, n=5). The one formation water for which Al was reported was oversaturated with respect to anorthite.

### Halfway aquifer

Only one formation water came from the Halfway aquifer (Fig. 8C). It has a fairly high salinity (180,000 mg/l) with correspondingly high contents of most major components. The very high SO<sub>4</sub> (2590 mg/l) reflects the overlying Charlie Lake Formation anhydrite; consequently Sr (105 mg/l) and particularly Ba (0.5 mg/l) are low, with slight undersaturation with respect to celestite, undersaturation with respect to strontianite, strong undersaturation with respect to witherite, and saturation with respect to barite. The formation water is undersaturated with respect to both cerussite (Pb 1.2 mg/l) and smithsonite (Zn 4.7 mg/l), and is oversaturated with respect to anorthite ( $\Delta G_{\text{diff}}=2.9$ ).

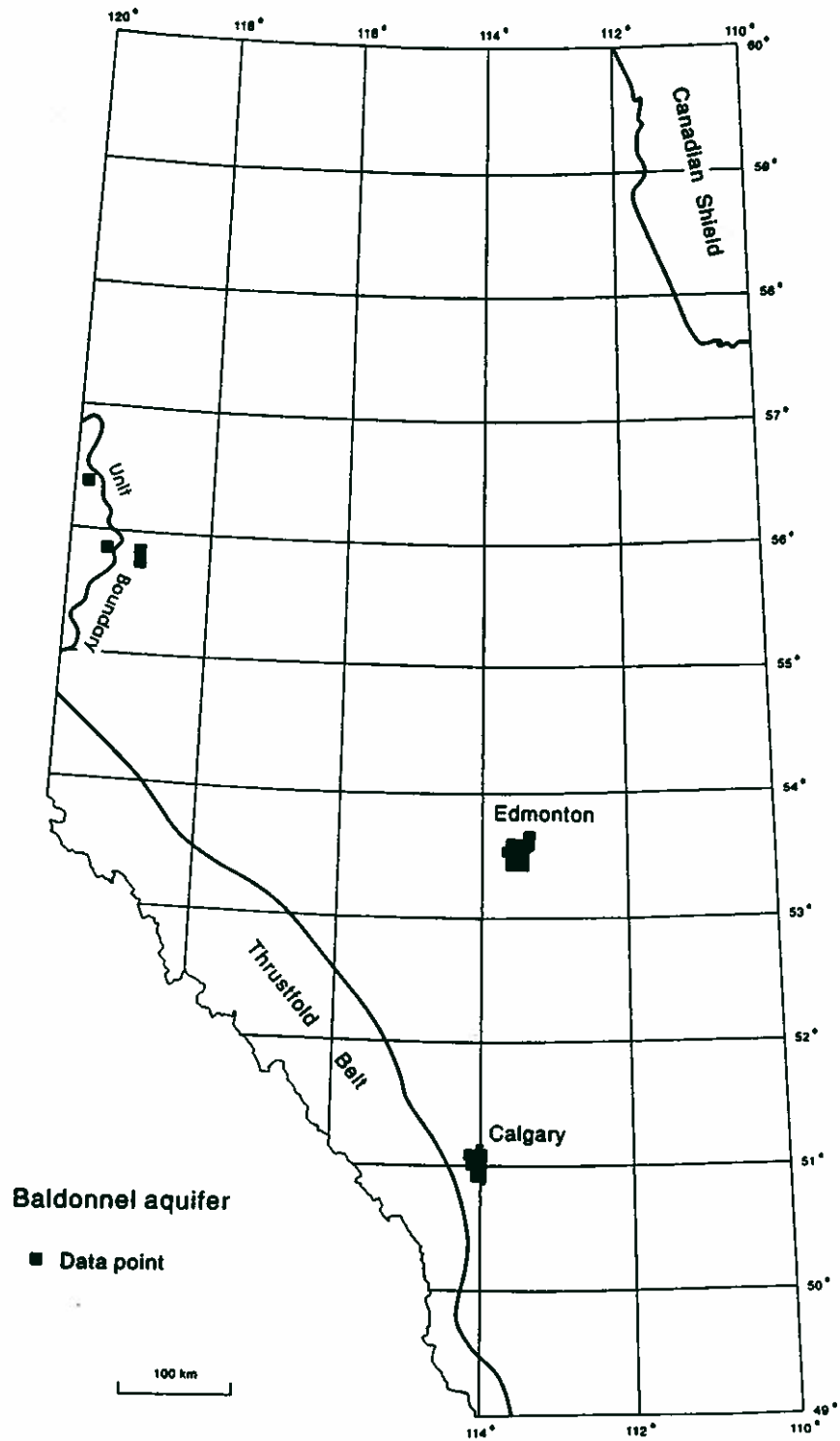


Figure 8A. Rundle-Permo-Triassic aquifer system: A. Data distribution, Baldonnel aquifer (n=4)

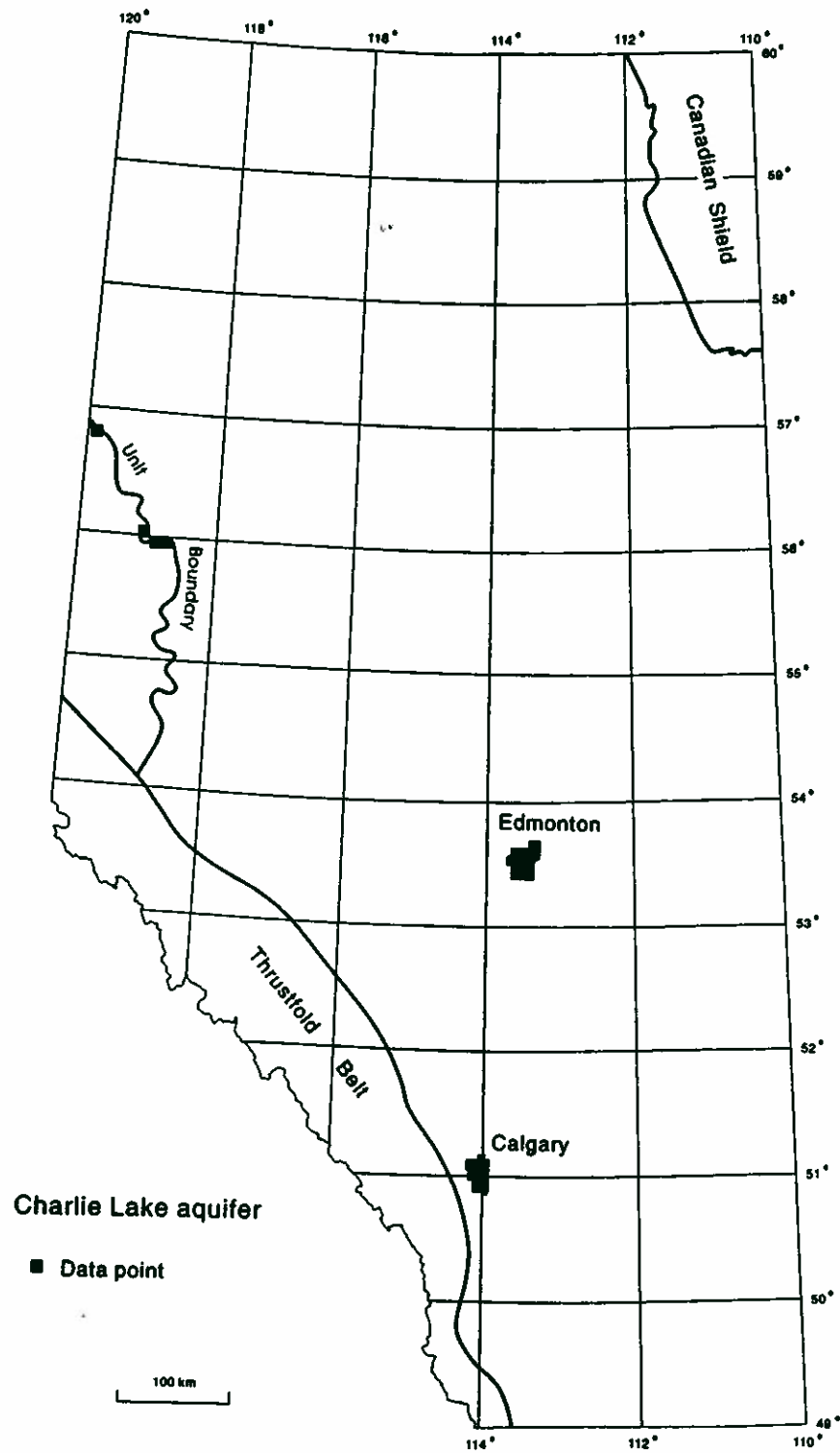


Figure 8B. Rundle-Permo-Triassic aquifer system: B. Data distribution, Charlie Lake aquifer (n=5)

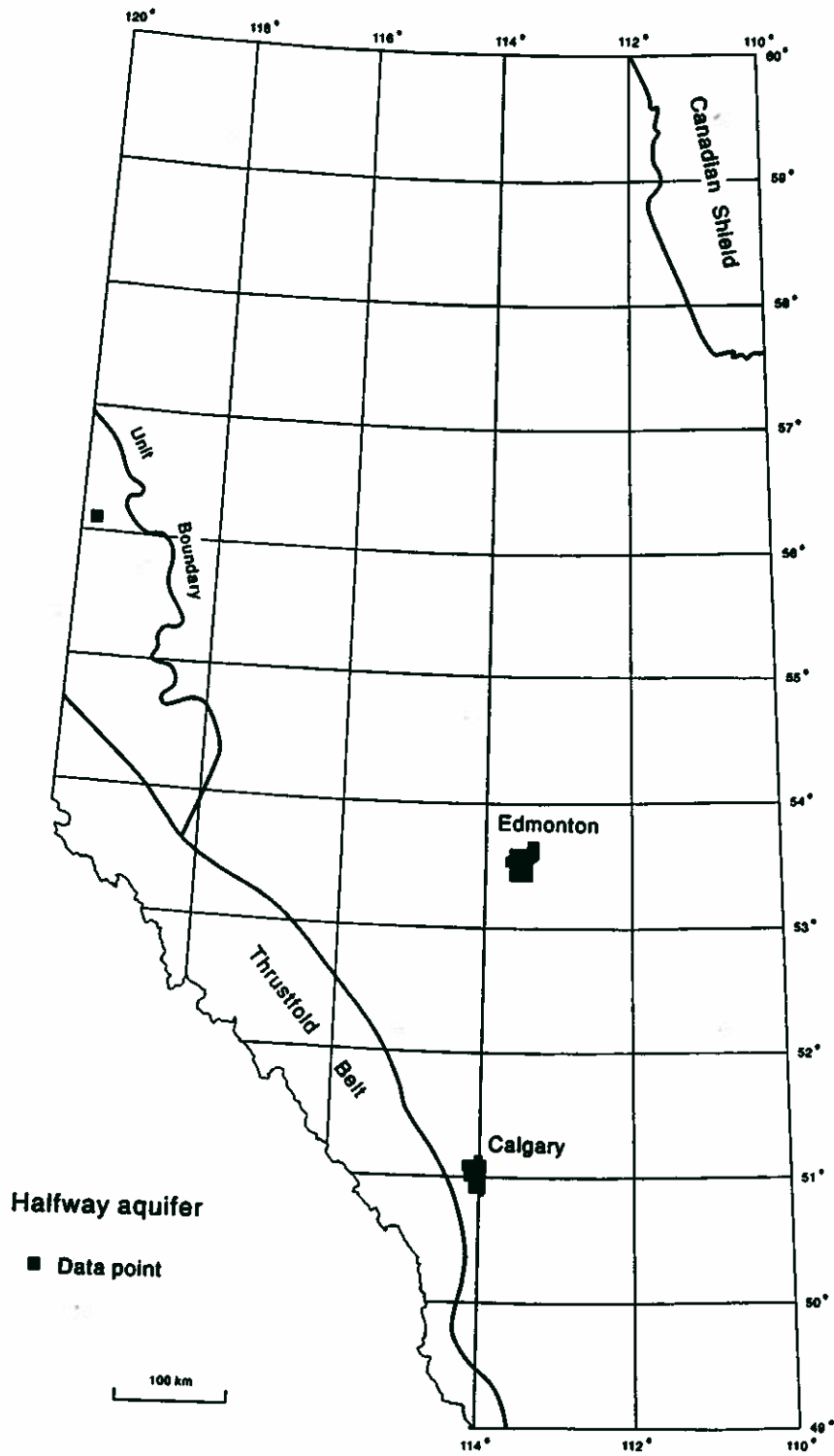


Figure 8C. Rundle-Permo-Triassic aquifer system: C. Data distribution, Halfway aquifer (n=1);



### Diaber aquifer

The distribution of the nine formation waters from the Diaber aquifer is shown in Fig. 8D. As might be expected for such a wide areal distribution, there is considerable variation in composition. The northernmost sample is the least saline (42,000 mg/l), with the others falling in the salinity range 69,000 to 139,000 mg/l. There are corresponding amounts of the major components. In the northernmost sample  $\text{SO}_4$  is low (23 mg/l) with a high content of Ba (27 mg/l), whereas in the other samples the respective ranges are 760-1320 mg/l  $\text{SO}_4$  and 0.5-1.8 mg/l Ba; all formation waters are saturated or slightly oversaturated with respect to barite. All formation waters were undersaturated with respect to both celestite and strontianite (Sr 39-156 mg/l, mean 82 mg/l, median 66 mg/l). The maximum content of Zn was 3.5 mg/l, with most samples having Zn below detection limits. Lead ranged up to 26 mg/l, though it was mostly <5 mg/l. Most formation waters were undersaturated with respect to both cerussite and smithsonite. Four samples had  $\text{Pb} > \text{Zn}$  and two had  $\text{Zn} > \text{Pb}$ . Iron and Mn were generally below detection limits. The content of F ranged from 0.13-3 mg/l (mean 1.8 mg/l, median 2 mg/l,  $n=7$ ), and saturation of the formation waters with respect to fluorite was highly variable ( $\Delta G_{\text{diff}} = -3.7$  to 0.68), with most being close to saturation. Aluminium was reported only in the northernmost sample, which was slightly undersaturated ( $\Delta G_{\text{diff}} = -0.51$ ) with respect to anorthite.

### Belloy aquifer

Figure 8E shows the distribution of the four formation water samples from the Belloy aquifer. Two samples have  $\text{Zn} > \text{Pb}$ , one has  $\text{Pb} > \text{Zn}$ , and all three have  $\text{Mn} > \text{Fe}$ ; the other ratios were indeterminate. The maximum contents of these elements are Zn 8.5 mg/l, Pb 2.2 mg/l, Mn 2.5 mg/l and Fe 0.38 mg/l. The content of F ranges from 1.45 to 3.4 mg/l (mean 2.1 mg/l,  $n=4$ ). The formation waters have very low contents of Ba (0.07-3 mg/l, mean 1.2 mg/l,  $n=4$ ). All formation waters are undersaturated with respect to cerussite, smithsonite, rhodochrosite and siderite, generally undersaturated with respect to celestite and strontianite, strongly undersaturated with respect to witherite, and saturated with respect to barite and fluorite.

### Rundle aquifer

The 23 formation water samples from the Rundle aquifer are found mainly along the west-central margin of the study area (Fig. 8F). Maximum contents of Zn and Pb were 32 mg/l and 58 mg/l, respectively. Out of 17 samples, 13 had  $\text{Pb} > \text{Zn}$  and the formation waters were generally undersaturated with respect to both cerussite and smithsonite. Iron was generally <1 mg/l (max. 1.1 mg/l) and Mn ranged up to 6.9 mg/l; 16 of 19 samples had  $\text{Mn} > \text{Fe}$ . Most formation waters were undersaturated with respect to both siderite and rhodochrosite, as well as fluorite, although only slightly so in a few instances for the latter mineral. Contents of F were in the range 0.8-2.6 mg/l (mean 1.5 mg/l, median 1.3 mg/l,  $n=17$ ). Fifteen samples reported Ba in the range 0.18-7.2 mg/l (mean 2.2 mg/l,  $n=15$ ) but one formation water had 70 mg/l; all formation waters were saturated with respect to barite and undersaturated or strongly undersaturated with respect to witherite. Strontium was in the range 13-143 mg/l (mean 81 mg/l, median 68 mg/l), with the formation waters generally undersaturated or slightly undersaturated

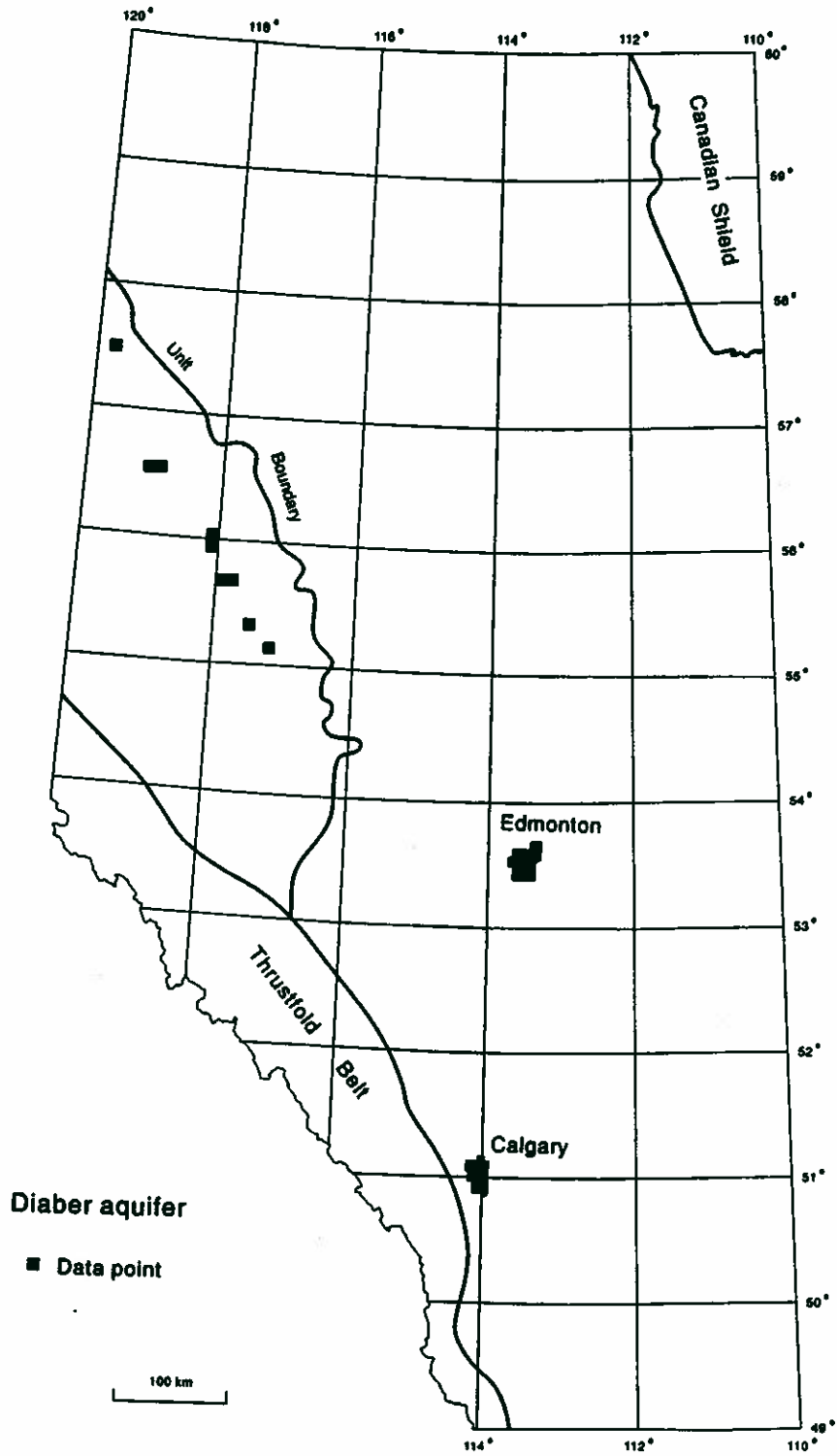


Figure 8D. Rundle-Permo-Triassic aquifer system: D. Data distribution, Diaber aquifer (n=9)

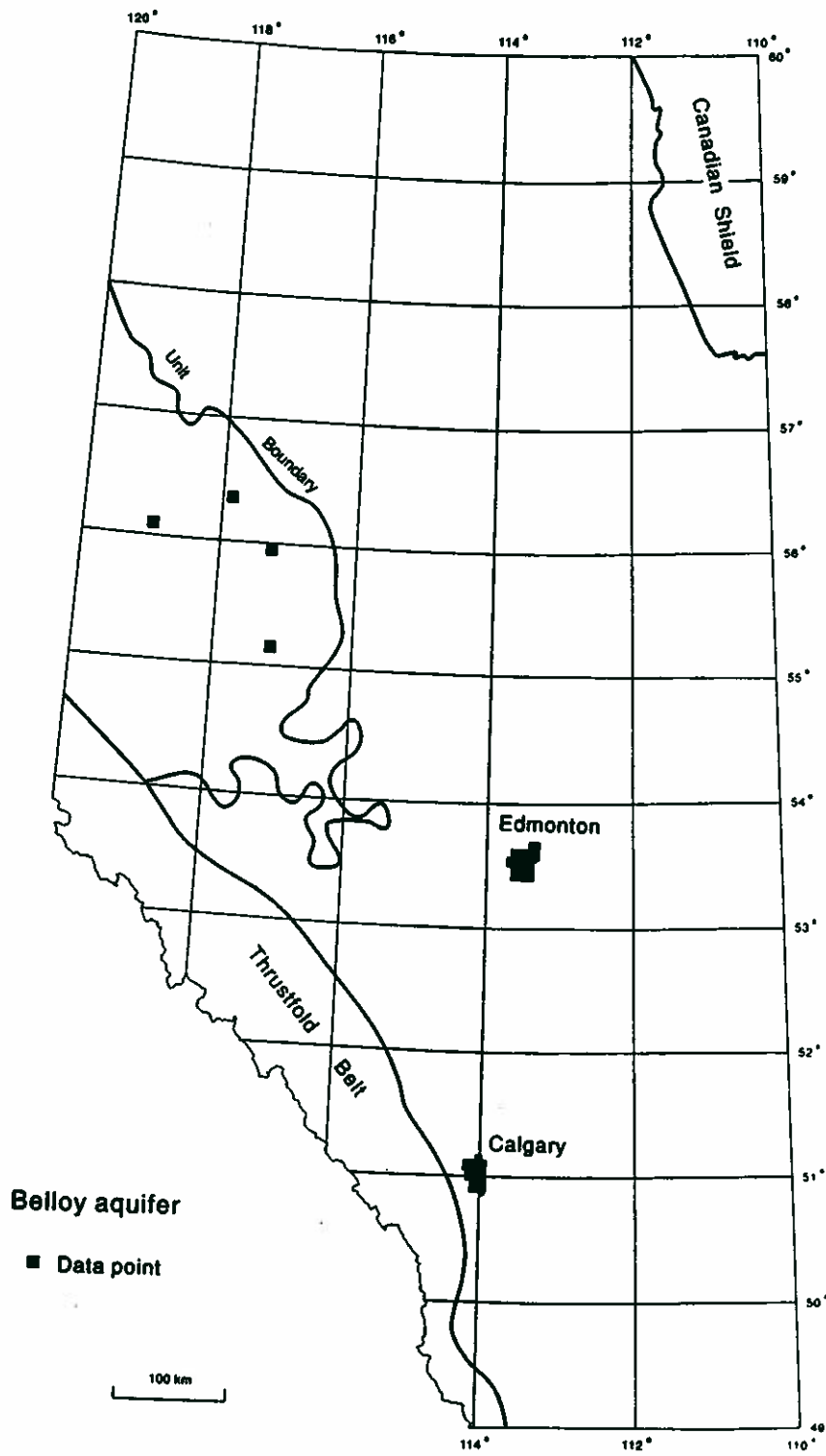


Figure 8E. Rundle-Permo-Triassic aquifer system: E. Data distribution, Belloy aquifer (n=4)

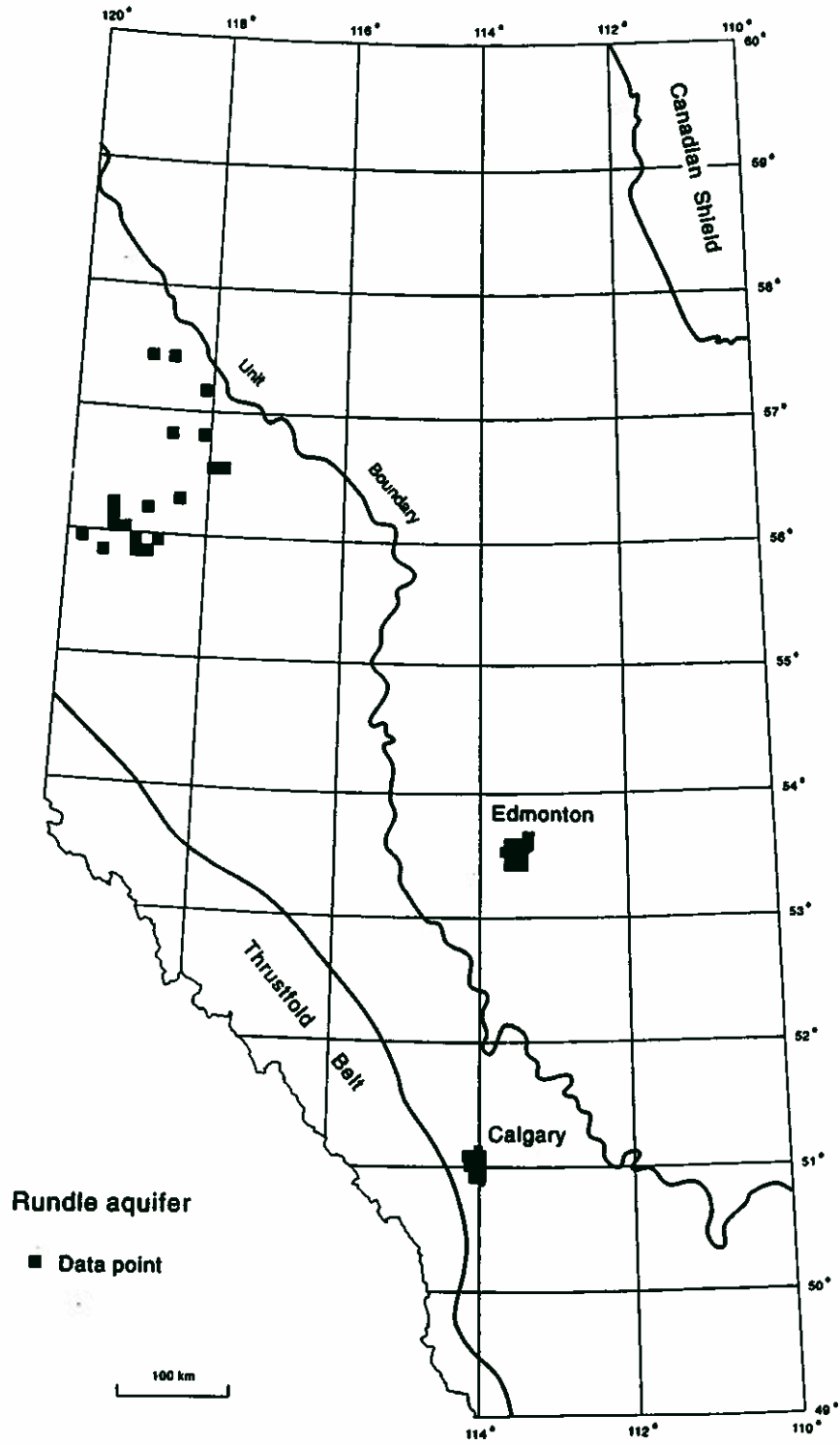


Figure 8F. Rundle-Permo-Triassic aquifer system: F. Data distribution, Rundle aquifer (n=23)

with respect to both celestite and strontianite. Where Al was determined the saturation with respect to anorthite varied from undersaturated to oversaturated.

#### Pekisko-Upper Banff aquifer

The majority of formation water samples from the Pekisko-Upper Banff aquifer are from the subcrop region (Fig. 8G). With the exception of one sample with 6.4 mg/l Zn, the contents of Zn and Pb were all <1 mg/l, with Pb>Zn in five of seven cases. Despite the very low contents of Pb, a few formation waters were slightly oversaturated or saturated with respect to cerussite; all were undersaturated with respect to smithsonite. Except for one sample, the contents of Fe and Mn were all <1 mg/l with all formation waters undersaturated with respect to both siderite and rhodochrosite. The amount of F never exceeded 2 mg/l, with all formation waters slightly undersaturated or undersaturated with respect to fluorite. The content of Ba was very variable (Ba 0.1-120 mg/l) without obvious regional trends, and all formation waters except one were saturated to oversaturated with respect to barite. The content of Sr was also very variable (Sr 0.4-300 mg/l), and all formation waters were undersaturated with respect to celestite and generally undersaturated with respect to strontianite, although the sample with 300 mg/l Sr was saturated with respect to strontianite. The only sample reporting Al was oversaturated with respect to anorthite.

#### Wabamun aquifer

One formation water sample from the Wabamun aquifer is from the subcrop region, and the other seven are from the southeast flank of the Peace River Arch (Fig. 9A).

The subcrop sample has a salinity of 28,000 mg/l, with pH 6.76 at formation temperature (21°C). The low SO<sub>4</sub> (33 mg/l) is accompanied by 8.8 mg/l Ba and the formation water is slightly oversaturated with respect to barite and undersaturated with respect to witherite. Most trace metals were below detection, except Pb 0.3 mg/l, Cu 0.05 mg/l and As 1.4 mg/l. The formation water is slightly undersaturated with respect to cerussite, undersaturated with respect to celestite and slightly undersaturated with respect to strontianite (Sr 31 mg/l), and undersaturated with respect to fluorite (F 0.7 mg/l).

The spatial closeness of the seven formation waters near the Peace River Arch results in rather narrow ranges for most components including salinity (182,000-265,000 mg/l), Na (49,000-69,000 mg/l), K (1560-3730 mg/l), Ca (16,000-27,500 mg/l), Mg (1180-3800 mg/l), Sr (450-1120 mg/l), Ba (1.8-4.6 mg/l), Cl (110,000-166,000 mg/l), Li (39-115 mg/l), NH<sub>3</sub> (91-239 mg/l) and pH at formation temperature (5.18-5.91). Contents of Zn range up to 43 mg/l (below detection in four samples) and of Pb up to 22 mg/l (below detection in two samples). The ratio of these metals was Pb>Zn in four samples and Zn>Pb in two samples. All formation waters were strongly to very strongly undersaturated with respect to both cerussite and smithsonite. Fluorine was determined in six samples, with a rather narrow range but high content (F 3.4-7 mg/l, mean 4.9 mg/l, median 4.8 mg/l); formation waters were variously slightly undersaturated to slightly oversaturated with respect to fluorite. Because contents of SO<sub>4</sub> were high (320-1330 mg/l), Ba was low and most formation waters were saturated to slightly

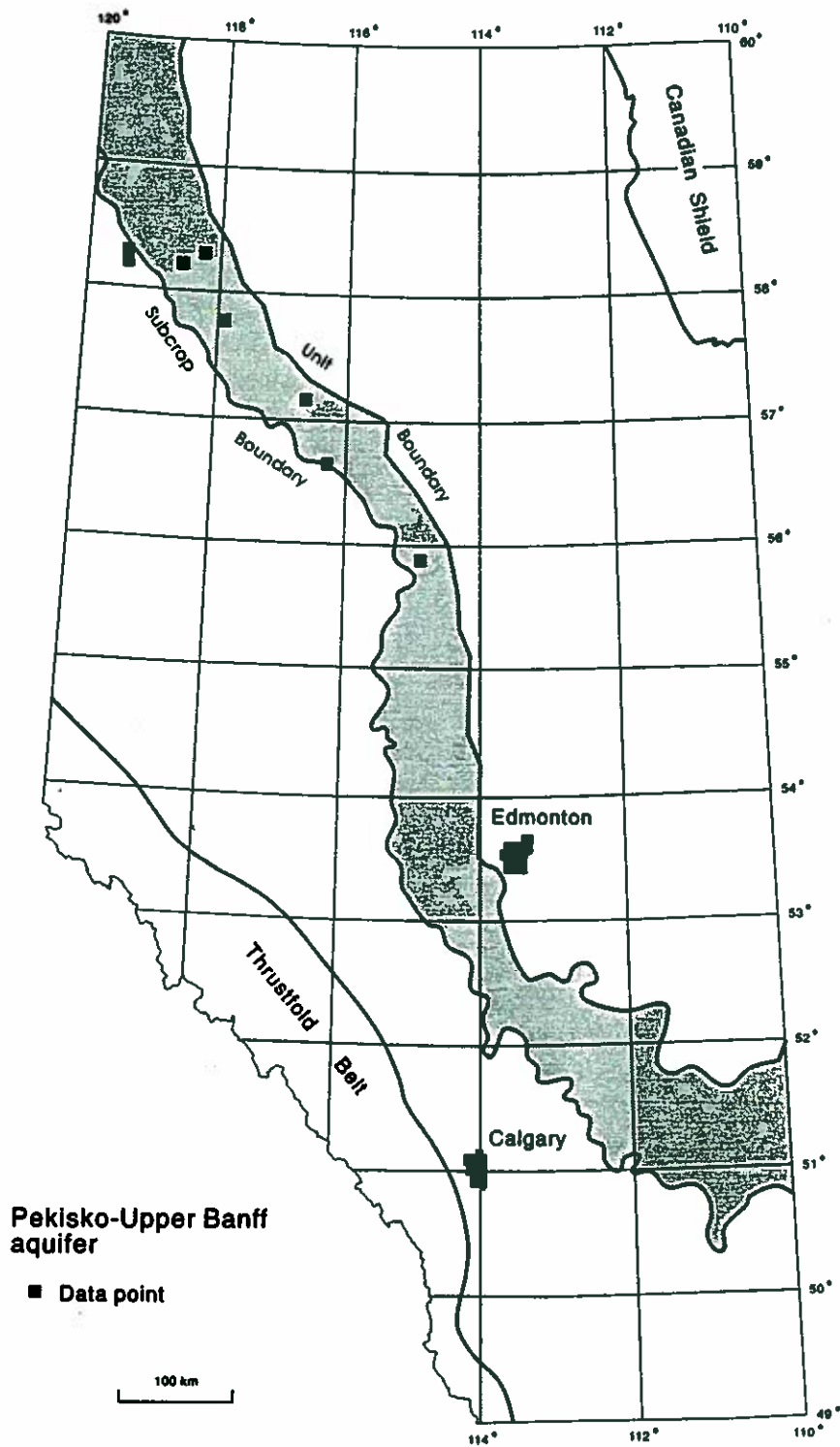


Figure 8G. Rundle-Permo-Triassic aquifer system: G. Data distribution, Pekisko-Upper Banff aquifer (n=8)

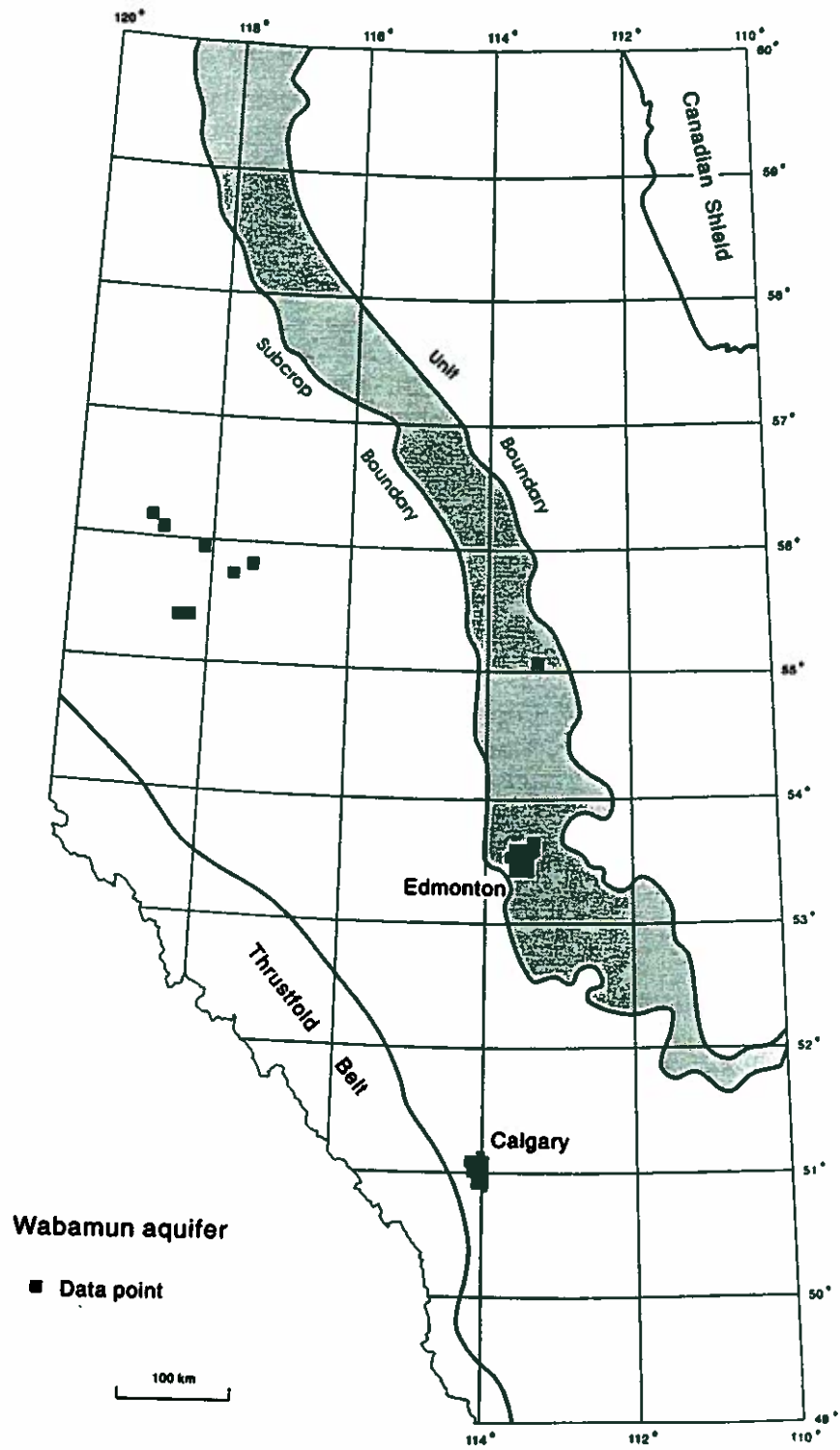


Figure 9A. Wabamun-Winterburn aquifer system: A. Data distribution, Wabamun aquifer (n=8)

oversaturated with respect to barite and strongly undersaturated with respect to witherite. The formation waters were generally slightly undersaturated to undersaturated with respect to celestite, but all were undersaturated with respect to strontianite. The majority of formation waters had Mn>Fe, with contents of these metals ranging up to 10 mg/l Mn and up to 5 mg/l Fe; all the waters were undersaturated or strongly undersaturated with respect to both rhodochrosite and siderite. The formation waters were oversaturated to strongly oversaturated with respect to anorthite.

#### Winterburn aquifer

The only sample of formation water from the Winterburn aquifer is from the subcrop region (Fig. 9B). Salinity is 14,600 mg/l and pH 6.79 at formation temperature (18°C). Trace element contents were generally low, as expected; Pb 0.7 mg/l (Pb>Zn), Fe 0.08 mg/l, Cu 0.17 mg/l, As 0.9 mg/l. The formation water is slightly oversaturated with respect to barite (SO<sub>4</sub> 63 mg/l, Ba 2 mg/l), but undersaturated with respect to witherite, and is slightly oversaturated with respect to cerussite, but slightly undersaturated with respect to fluorite (F 2.4 mg/l). It is undersaturated with respect to both celestite and strontianite.

#### Grosmont aquifer

There is only one sample of formation water from the Grosmont aquifer, from the subcrop area (Fig. 10A). Salinity is 24,000 mg/l and pH 6.33 at formation temperature (18°C). As expected, trace element contents were low: Pb 1 mg/l (Pb>Zn), Cu 0.05 mg/l. The formation water was slightly oversaturated with respect to barite (SO<sub>4</sub> 145 mg/l, Ba 2.1 mg/l) and cerussite, but saturated with respect to fluorite (F 1.68 mg/l); it was undersaturated with respect to celestite, strontianite and witherite.

#### Leduc aquifer

Six formation waters from the Leduc aquifer all come from the carbonate reef complex fringing the Peace River Arch (Fig. 10A). Their close spatial position results in rather narrow ranges for most components including salinity (206,000-256,000 mg/l), Na (47,000-67,000 mg/l), K (1800-3500 mg/l), Li (40-100 mg/l), Ca (18,000-25,000 mg/l), Mg (1650-3400 mg/l), Sr (545-900 mg/l), Ba (3.6-5.6 mg/l), Cl (128,000-158,000 mg/l), NH<sub>3</sub> (93-244 mg/l, n=4) and pH at formation temperature (4.92-5.63). Contents of Zn range up to 225 mg/l (although Zn is generally <1 mg/l) and Pb up to 9.1 mg/l; two samples have Pb>Zn and two have Zn>Pb. The formation waters are generally strongly undersaturated with respect to both cerussite and smithsonite, and generally undersaturated to strongly undersaturated with respect to siderite and rhodochrosite (max. Fe 41 mg/l, max. Mn 12 mg/l; Fe>Mn in three cases and Mn>Fe in three cases). Sulphate was generally high (295-1000 mg/l) and Ba low, with most formation waters saturated with respect to barite and strongly undersaturated with respect to witherite. Formation waters were all undersaturated with respect to strontianite but ranged from undersaturated to saturated with respect to celestite. Fluorine was only determined in two samples (each ~3.25 mg/l), both of which are saturated with respect to fluorite.



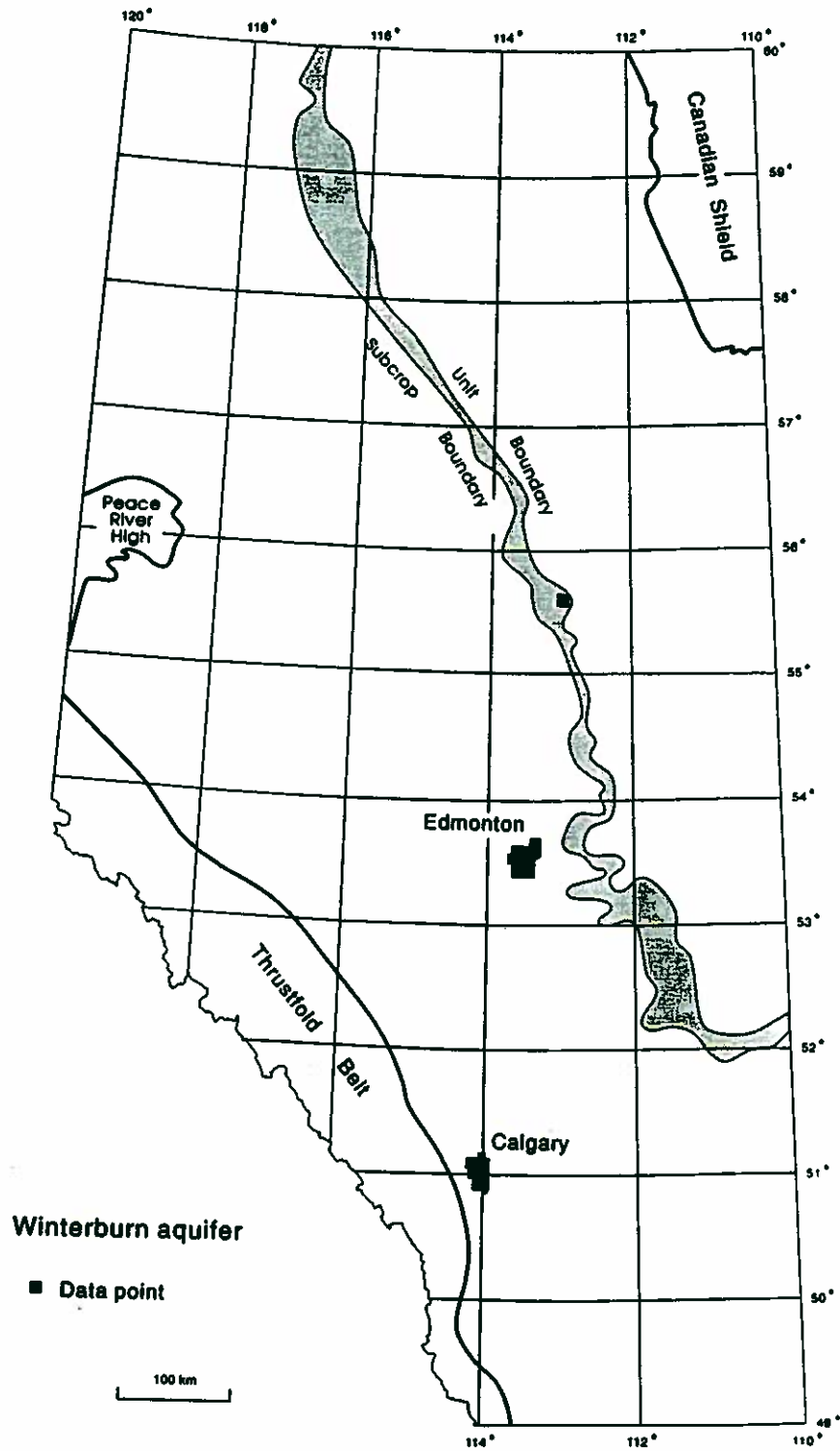


Figure 9B. Wabamun-Winterburn aquifer system: B. Data distribution, Winterburn aquifer (n=1)

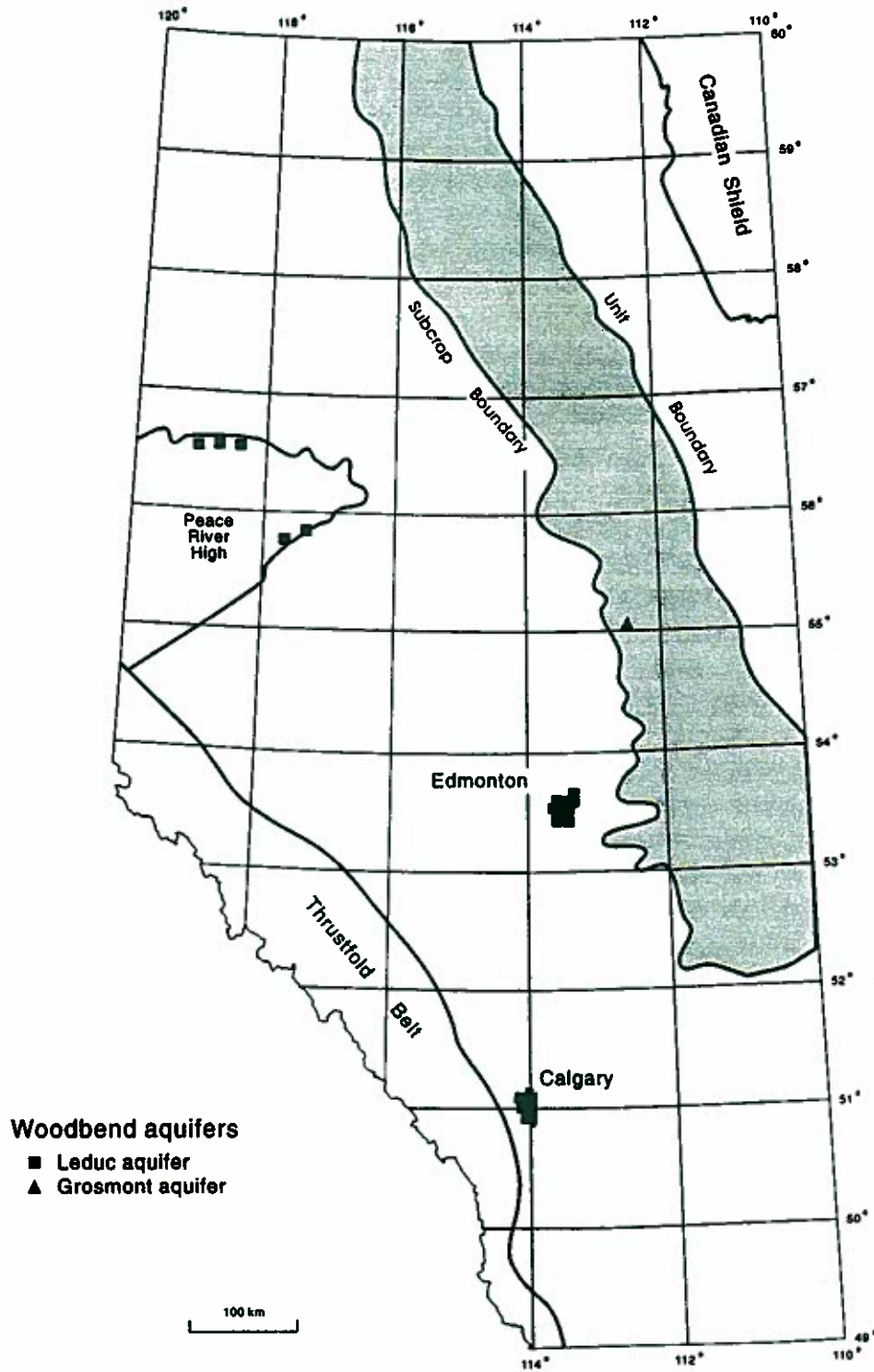


Figure 10A. Ireton aquitard and Beaverhill Lake aquifer system: A. Data distribution, Grosmont aquifer (n=1) and Leduc aquifer (n=6)

Formation waters for which AI was determined are strongly oversaturated with respect to anorthite in one case but saturated or only slightly oversaturated in two others.

### Beaverhill Lake aquifer

For the purpose of this review, the Beaverhill Lake aquifer will be considered in two parts, the Slave Point aquifer north of the Peace River Arch and the Swan Hills aquifer south of the Peace River Arch. In fact, these two aquifers are hydraulically continuous (Hitchon et al., 1990b; Bachu et al., 1993). Figure 10B shows the distribution of the formation waters in the study area, all except the southernmost one being in the Slave Point aquifer. In addition to the southernmost sample from the Swan Hills aquifer, eight other formation waters (not plotted in Fig. 10B) from the Swan Hills carbonate complex were used in this study; they were selected and checked in a manner similar to those from the study area. The Slave Point aquifer primarily comprises limestones with minor shale, and the Swan Hills aquifer is dominantly dolomite with minor anhydrite downdip.

Table 7 is a comparison of the average and range of chemical composition of formation waters from these two aquifers. The Swan Hills aquifer contains formation waters with significantly higher contents of many components, compared to the Slave Point aquifer, suggesting increased water-rock reactions due to the generally higher temperatures. However, the content of some components is mainly controlled by mineral solubilities; for example, while there is, on average, more Ba in the deeper, hotter, formation waters of the Swan Hills aquifer, a plot (Fig. 13) of the barite saturation index against  $\text{SO}_4$  content shows that  $\Delta G_{\text{diff}}$  is close to equilibrium over a very wide  $\text{SO}_4$  range, corresponding also to a wide temperature range. A similar plot (not shown) of the saturation index of fluorite against Ca content suggests that the content of F is governed by the solubility of fluorite in the formation water, though there is considerably more scatter about the equilibrium line than is the case for barite saturation.

With respect to the Slave Point aquifer, the content of Zn ranges up to 60 mg/l and Pb up to 15 mg/l, with Zn>Pb in four cases and Pb>Zn in three samples. Where it could be determined, the Pb:Zn ratio varied from 0.003 to 2.2 (n=4) without any obvious areal trend. All formation waters were undersaturated or strongly undersaturated with respect to both cerussite and smithsonite. For all formation waters, Mn>Fe and the majority were undersaturated with respect to both siderite and rhodochrosite. In the Slave Point aquifer the formation waters are slightly undersaturated with respect to celestite, whereas in the Swan Hills aquifer the formation waters generally exhibit undersaturation with respect to celestite. All formation waters are undersaturated with respect to strontianite, and strongly undersaturated with respect to witherite.

In the Swan Hills aquifer, the maximum contents of Zn and Pb were 10.5 mg/l and 63 mg/l, respectively, with Pb>Zn in seven samples and Zn>Pb in one sample. The Pb:Zn ratio varied from 0.56 to 18 (mean 6.9, n=5). There is therefore the hint that the contents and proportions of these two metals may differ between the Slave Point and Swan Hills aquifers.

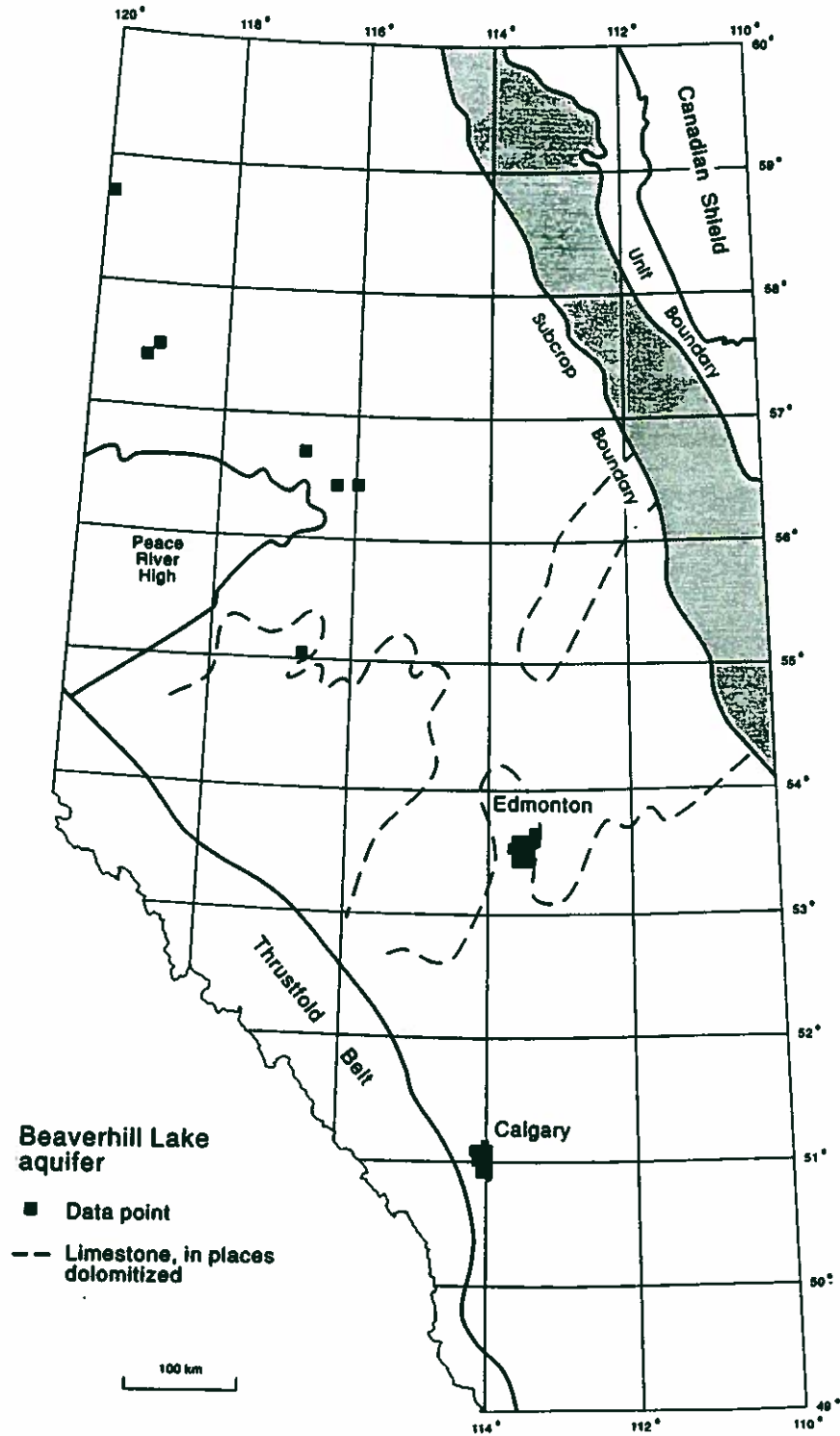


Figure 10B. Ireton aquitard and Beaverhill Lake aquifer system: B. Data distribution, Beaverhill Lake aquifer (n=8)

**Table 7. Comparison of chemical composition (mg/l) of formation waters from the Slave Point aquifer north of the Peace River Arch with those from the Swan Hills carbonate complex south of the Peace River Arch**

	Slave Point aquifer (n=7)		Swan Hills carbonate complex (n=9)	
	Mean	Range	Mean	Range
Salinity (mg/l)	152,000	(100,000-180,000)	190,000	(140,000-230,000)
Na	44,000	(28,000-56,000)	58,000	(40,000-74,000)
K	650	(450-1250)	3100	(750-5350)
Li	31	(17-47)	64	(26-130)
Ca	11,300	(6000-17,000)	10,700	(2000-24,000)
Mg	1500	(100-2500)	1300	(200-3000)
Sr	310	(210-440)	380	(70-680)
Ba	1.5	(0.8-3.1)	4.3	(0.7-3.6)(n=7)
Cl	92,000	(58,000-110,000)	115,000	(84,000-140,000)
Br	320	(235-370)	320	(175-450)
I	15	(7-28)	21	(5-47)
F	2.5	(1.4-4.4)(n=4)	4.2	(2.6-6.2)(n=6)
SO <sub>4</sub>	840	(600-1300)	600	(200-900)
NH <sub>3</sub>	95	(50-135)	440	(180-1000)(n=7)
B	38	(23-90)	143	(74-260)
Zn	20.4	(1.3-60)(n=5)	3.8	(0.06-10.5)(n=7)
Pb	6.7	(0.2-15)(n=6)	18.5	(1.9-63)(n=7)
Cu	0.23	(0.18-0.28)(n=2)	0.36	(0.09-0.68)(n=7)
Fe	0.66	(0.3-0.9)(n=3)	7.8	(0.36-42)(n=7)
Mn	3.4	(1.4-6.5)	7.2	(0.1-20)(n=8)
pH (at formation temperature)	5.98	(5.62-6.13)	5.62	(5.29-6.02)
Formation temperature (°C)	58	(38-80)	90	(76-110)

Four formation waters from the Slave Point aquifer in which AI was determined are oversaturated with respect to anorthite, in contrast to two formation waters from the Swan Hills aquifer which are undersaturated with respect to anorthite.

#### Watt Mountain aquifer

Five formation water samples from the Watt Mountain aquifer are confined to a small area southeast of the Peace River Arch (Fig. 11A); as such, their compositions are similar (average values: salinity 195,000 mg/l; Na 50,000 mg/l; K 930 mg/l; Li 70 mg/l; Ca 18,800 mg/l; Mg 3550 mg/l; Sr 390 mg/l; Ba 2.5 mg/l; Cl 120,000 mg/l; SO<sub>4</sub> 920 mg/l; NH<sub>3</sub> 75 mg/l). Zinc was below detection in three samples, and the average Pb content was 8.9 mg/l (4-12 mg/l; n=5); all samples had Pb>Zn and were undersaturated or strongly undersaturated with respect to both cerussite and smithsonite. Contents of Fe were variable (0.89-56 mg/l, mean 13 mg/l, n=5) but Mn was within fairly narrow limits (3-5.2 mg/l, n=5); all formation waters were undersaturated with respect to both siderite and rhodochrosite. Because of the high contents of SO<sub>4</sub> (665-1560 mg/l, n=5), Ba contents were low (1.8-3.4 mg/l, mean 2.5 mg/l, n=5), and all formation waters were saturated or slightly oversaturated with respect to barite (Fig. 13) and strongly undersaturated with respect to witherite. Formation waters were generally slightly undersaturated with respect to celestite and all were undersaturated with respect to strontianite. Most formation waters were undersaturated with respect to fluorite. Formation waters in which AI was determined show highly variable saturation values with respect to anorthite.

#### Sulphur Point aquifer

Figure 11B shows that the eight formation water samples from the Sulphur Point aquifer are confined to a small area in extreme northwestern Alberta. Most components fall in a narrow range with average values as follows: salinity 106,000 mg/l; Na 30,000 mg/l; K 1500 mg/l; Li 43 mg/l; Ca 6900 mg/l; Mg 1000 mg/l; Sr 295 mg/l; Ba 1.2 mg/l (n=3); Cl 68,000 mg/l; SO<sub>4</sub> 730 mg/l; NH<sub>3</sub> 130 mg/l (n=3). The content of Zn ranged from less than detection in two samples to 40 mg/l (median 4.7 mg/l, n=6); Pb was only determined in three samples (max. 2.8 mg/l). Copper was <0.1 mg/l, Fe<1.5 mg/l, and Mn generally in the narrow range 1-5 mg/l. The formation waters were undersaturated or strongly undersaturated with respect to cerussite, smithsonite, siderite, rhodochrosite, strontianite and witherite. Two samples were saturated with respect to fluorite, and three with respect to barite (Fig. 13). All formation waters were saturated to undersaturated with respect to celestite.

#### Muskeg aquifer

Only three of the formation waters in the data base came from the Muskeg aquifer (Fig. 11C). The two samples from northwestern Alberta are more saline than the average of formation waters in the overlying Sulphur Point aquifer by about 50% (for salinity, Na, Li, Ca, Mg, Cl), with nearly double the content of K but about 10% less SO<sub>4</sub>. The third sample, from the eastern edge of the Peace River Arch, is similar to the average Slave Point aquifer sample (Table 7), at least as far as major components are concerned. The content of Pb was 23 mg/l but Zn was below the detection limit. Both Br (9 mg/l) and I

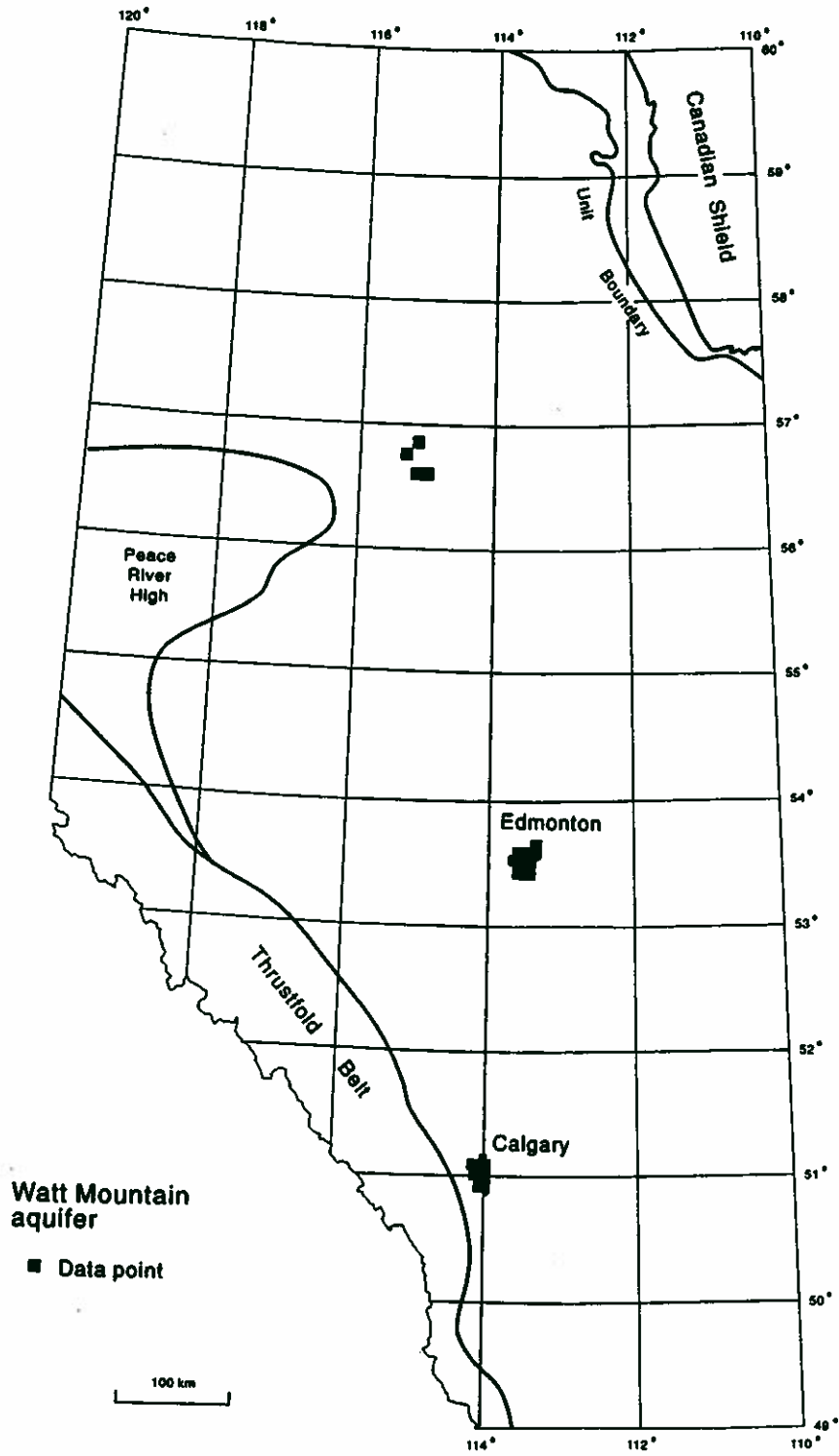


Figure 11A. Muskeg-Watt Mountain aquitard system: A. Data distribution, Gilwood aquifer (n=5)

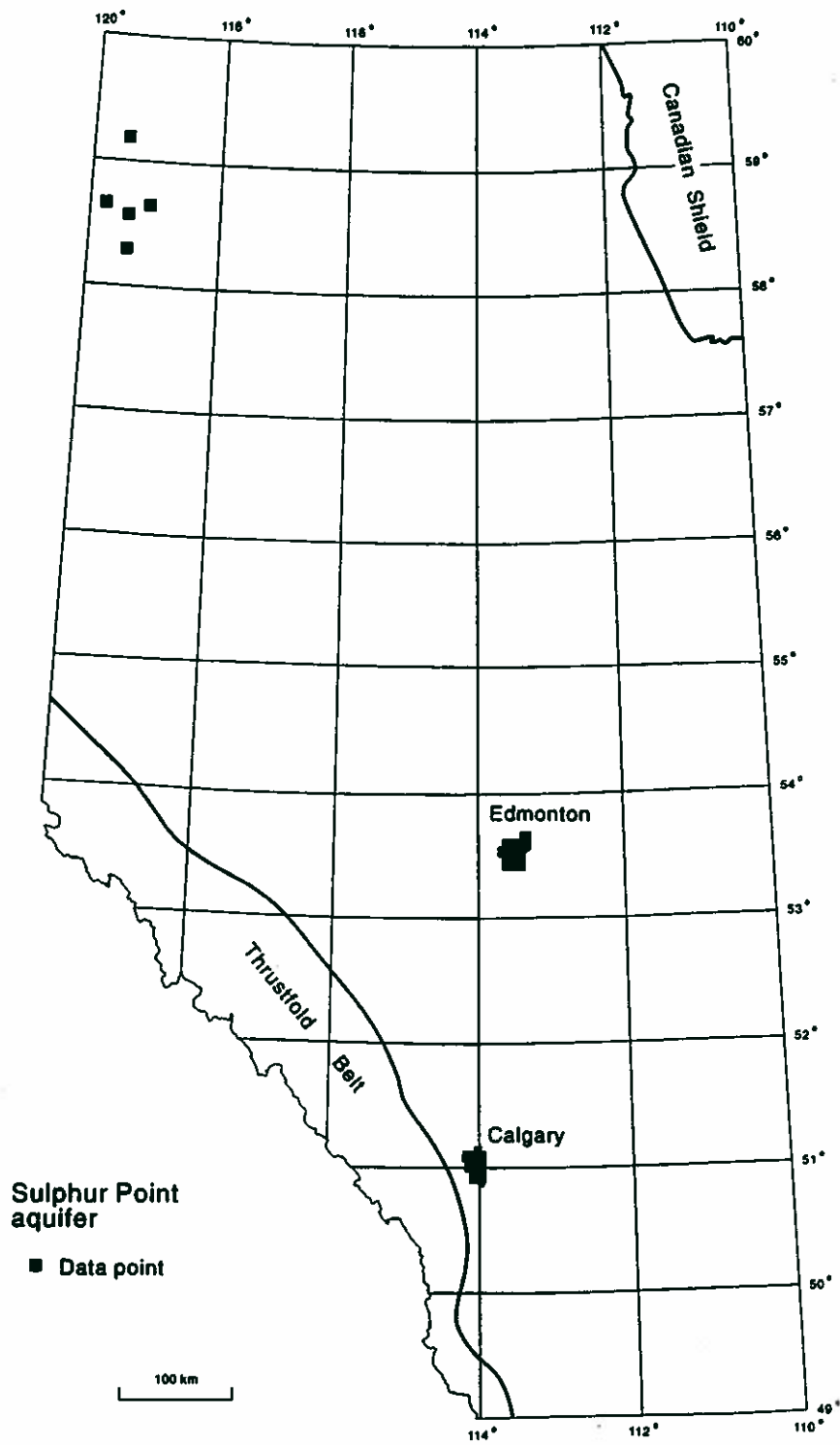


Figure 11B. Muskeg-Watt Mountain aquitard system: B. Data distribution, Sulphur Point aquifer (n=8)



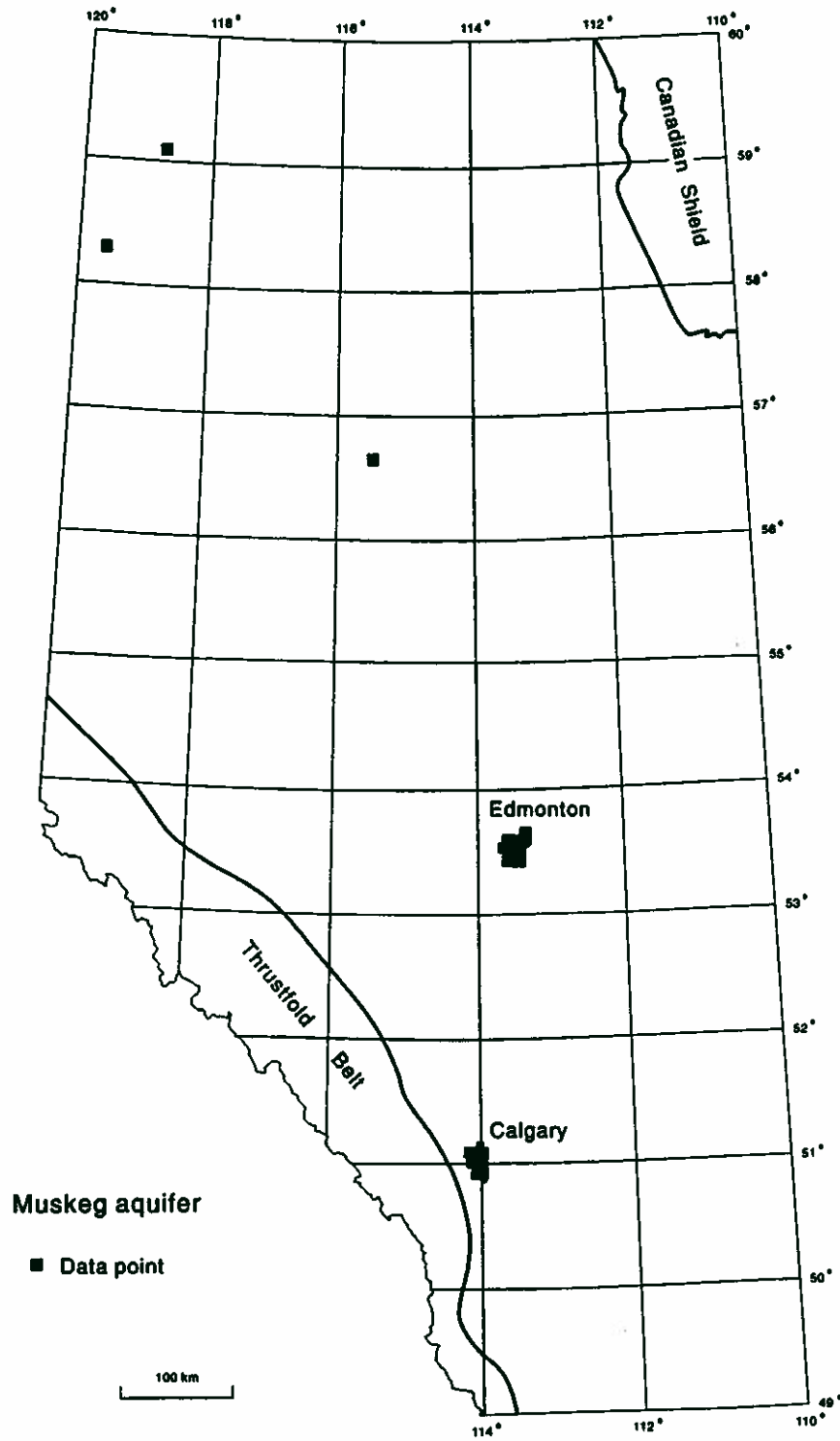


Figure 11C. Muskeg-Watt Mountain aquitard system: C. Data distribution, Muskeg aquifer (n=3)

(2 mg/l) were particularly low. The formation waters were undersaturated or strongly undersaturated with respect to cerussite, smithsonite, siderite, rhodochrosite, strontianite and witherite, and generally slightly undersaturated with respect to celestite. Barite and fluorite were at saturation in the formation waters. The formation water in which Al was determined was undersaturated with respect to anorthite.

### Keg River aquifer

Formation water samples from the Keg River aquifer are widely distributed across northern Alberta (Fig. 12A). This results in a fairly wide range in chemical composition (Table 8). The only other detailed formation water analysis from the Keg River aquifer is from southern Alberta and its location (6-1-19-7W4 Mer) and composition (Table 8) are provided for interest and comparison.

Fourteen formation water analyses from the Keg River aquifer in northwestern Alberta are compared in Table 9 with analyses from the overlying Muskeg and Sulphur Point aquifers in the same region. There is a broad increase with depth in the contents of most major components and some minor components, although the differences are far less than the range for the entire Keg River aquifer (Table 8). In this same region the content of Zn is highly variable (less than detection in two samples, range 0.3-98 mg/l, mean 15 mg/l, median 2.7 mg/l, n=14). Lead was only detected in three samples (Pb 2.5-55 mg/l, mean 23 mg/l) with Pb>Zn in all cases. The formation waters were undersaturated or strongly undersaturated with respect to cerussite, smithsonite, siderite and rhodochrosite (max. Fe 1.1 mg/l, max. Mn 8.2 mg/l).

The twelve formation water analyses from the central part of the study area (Fig. 12A) exhibit a very wide range in composition, depending on whether they are close to the outcrop, at depth near the Peace River Arch, or influenced strongly by the overlying Prairie Formation halite. Zinc was below detection in one third of these formation waters and exhibited a wide composition range in the remainder (Zn 0.3-91 mg/l, mean 19 mg/l, median 7.3 mg/l). Lead was determined in nine samples (below detection in two; range Pb 3.4-360 mg/l, mean 57 mg/l, median 6.8 mg/l), with Pb>Zn in five samples and Zn>Pb in three samples. The formation waters were undersaturated or strongly undersaturated with respect to cerussite, smithsonite, siderite and rhodochrosite (max. Fe 64 mg/l, max. Mn 27 mg/l).

The majority of formation waters from the Keg River aquifer are undersaturated with respect to strontianite and strongly undersaturated with respect to witherite; celestite is commonly slightly undersaturated and barite saturated. The  $\Delta G_{\text{diff}}$  values for fluorite exhibit a wide range, but most are oversaturated or slightly oversaturated.

### Granite Wash aquifer

Figure 12B shows the distribution of formation water samples from the Granite Wash aquifer, all of which lie immediately east of the Peace River Arch. Comparison with the composition of formation waters in the overlying aquifers in the same area (Table 10) shows a trend of increasing salinity and many major and minor components with depth, although  $\text{NH}_3$  appears to decrease with depth. Again, the trace metal data show great variability.

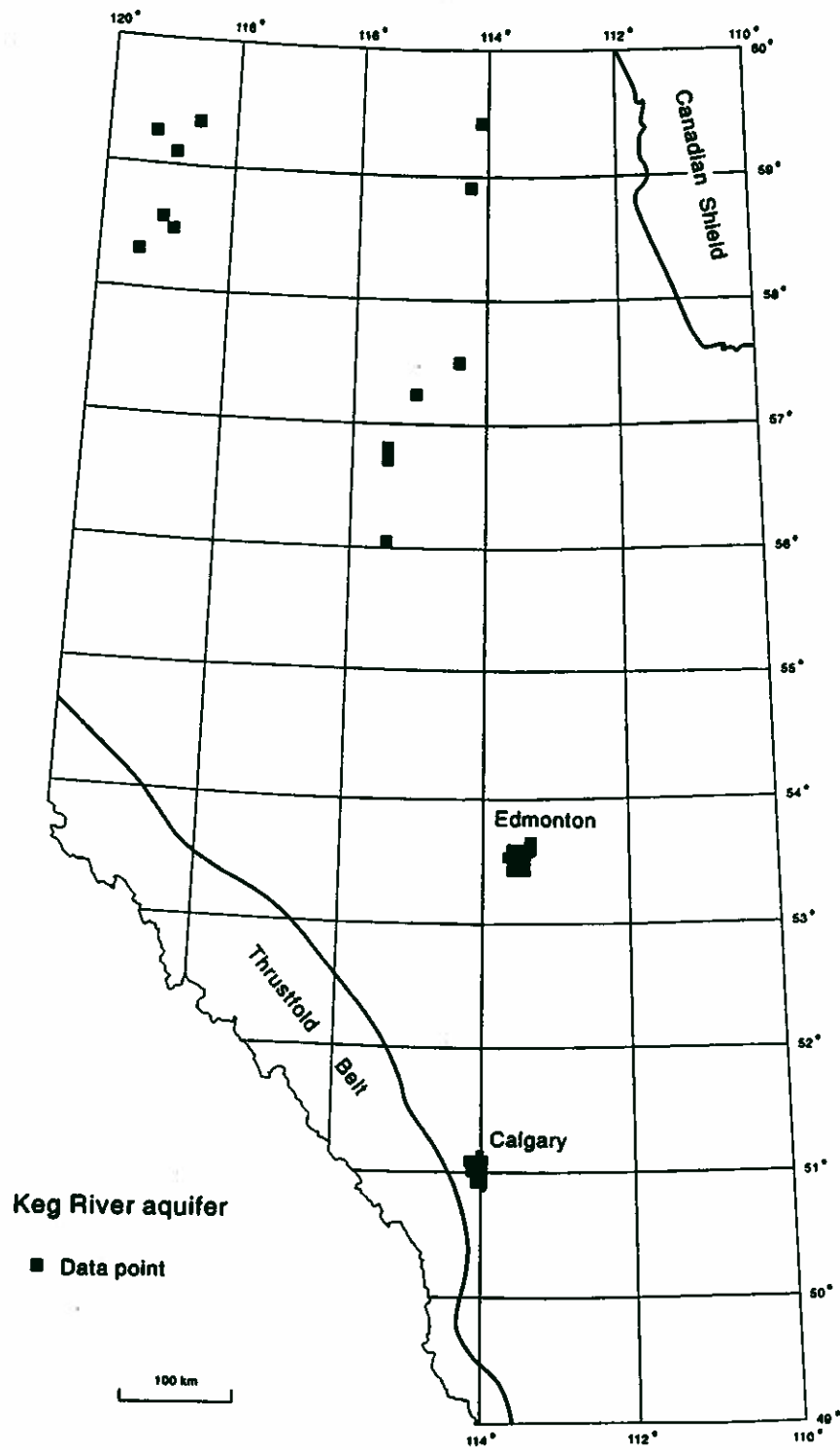


Figure 12A. Keg River-Granite Wash aquifer: A. Data distribution, Keg River aquifer (n=26)

Table 8. Chemical composition (mg/l) of formation waters from the Keg River aquifer of northern Alberta (n=26)

	General statistics				Winnipegosis aquifer (southern Alberta)
	Minimum	Mean	Median	Maximum	
Salinity (mg/l)	107,000	171,000	171,000	319,000	322,000
Na	31,000	50,000	44,000	101,000	86,400
K	400	1,650	1,500	5,000	1,900
Li	0.7	38	38.5	95	76
Ca	2,100	11,500	11,000	28,000	29,000
Mg	290	1,450	1,450	2,500	3,930
Sr	78	321	320	676	570
Ba (n=9)	0.49	1.6	1.0	4	3.9
Cl	64,000	104,000	107,000	194,000	199,510
Br (n=12)	16	429	344	760	1,313
I (n=12)	3	9.3	11.5	13	13
F (n=10)	2.1	2.8	3.0	5.5	0.46
SO <sub>4</sub>	485	1,430	1,075	6,450	377
NH <sub>4</sub> (n=11)	51	226	71	1,150	73.2
B (n=12)	16	77	31	260	25
Zn (n=20)	0.24	16.5	3.1	98	2.7
Pb (n=10)	2.5	47	7.7	360	25
Cu (n=19)	0.04	0.4	0.12	1.9	1.8
Fe (n=19)	0.09	4.2	0.94	64	1.3
Mn (n=22)	0.26	4.2	3.6	27	1.4

Table 9. Comparison of mean chemical compositions (mg/l) of formation waters from the Sulphur Point, Muskeg and Keg River aquifers, northwestern Alberta

	Sulphur Point aquifer (n=8)	Muskeg aquifer (n=2)	Keg River aquifer (n=14)
Salinity (mg/l)	106,000	160,000	148,000
Na	30,000	45,000	42,000
K	1,500	2,800	2,400
Li	43	65	46
Ca	6,900	10,000	10,100
Mg	1,000	1,300	1,400
Sr	295	355	385
Ba	1.2(n=3)	0.4(n=1)	2.8(n=3)
Cl	68,000	98,000	89,000
Br	200.(n=3)	512.(n=1)	475.(n=3)
I	4.(n=3)	13.(n=1)	6.(n=3)
F	3.(n=3)	-	4.8(n=2)
SO <sub>4</sub>	730	640	1010
NH <sub>4</sub>	130.(n=3)	670.(n=1)	670.(n=3)
B	88.(n=3)	215.(n=1)	220.(n=3)
Zn	9.6(n=6)	1.2(n=1)	15.(n=12)
Pb	2.5(n=2)	3.(n=1)	23.(n=3)
Cu	0.05(n=5)	0.24	0.18(n=11)
Fe	0.3(n=7)	0.9	0.6(n=12)
Mn	2.4	3.8(n=1)	2.7(n=13)

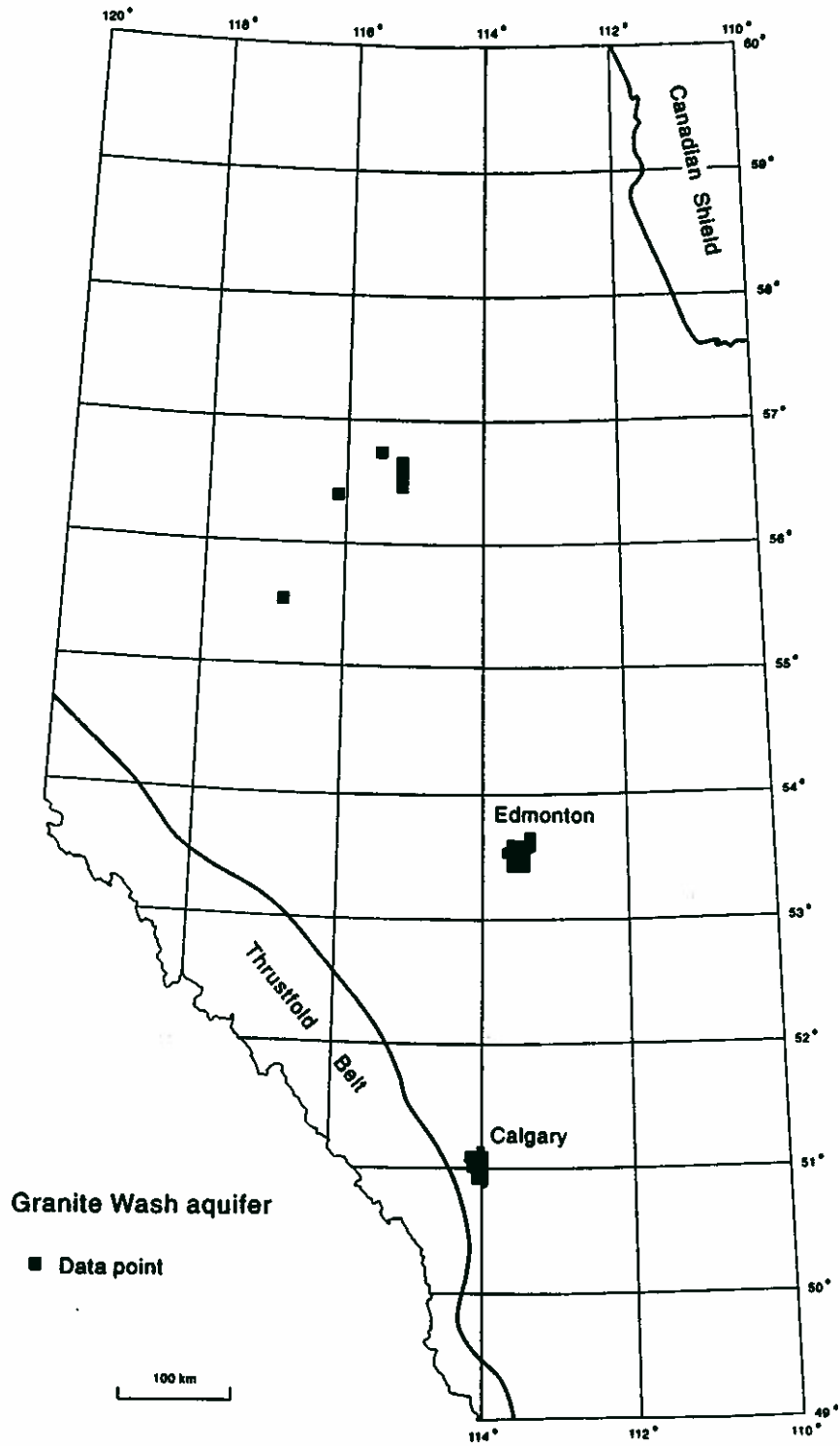


Figure 12B. Keg River-Granite Wash aquifer: B. Data distribution, Granite Wash aquifer (n=9)

Table 10. Comparison of mean chemical compositions (mg/l) of formation waters from the Slave Point, Watt Mountain, Keg River and Granite Wash aquifers immediately east of the Peace River Arch

	Slave Point aquifer (n=4)	Watt Mountain aquifer (n=5)	Keg River aquifer (n=9)	Granite Wash aquifer (n=9)
Salinity (mg/l)	172,000	195,000	203,000	216,000
Na	50,000	50,000	57,000	59,000
K	570	930	870	950
Li	24	70	38	29
Ca	14,300	18,800	16,300	21,300
Mg	1,700	3,550	1,780	2,000
Sr	295	390	305	460
Ba	1.1	2.5	1.(n=6)	2.1(n=7)
Cl	104,000	120,000	124,000	131,000
Br	340	475	415	480
I	12	5	10	11
F	1.9(n=3)	1.9(n=4)	2.7(n=8)	6.8(n=5)
SO <sub>4</sub>	1,000	920	1,070	800
NH <sub>3</sub>	79	75	61.(n=8)	63.(n=6)
B	24	27	29	26
Zn	32.(n=3)	2.6(n=2)	25.(n=5)	18.4(n=5)
Pb	5.6	8.9	57.(n=7)	12.6(n=7)
Cu	0.2(n=2)	1.1(n=4)	1.0(n=5)	0.6(n=7)
Fe	0.7(n=3)	13	17.(n=4)	28.(n=8)
Mn	3.4	4	6.7(n=8)	15

Although the maximum content of Zn is 82 mg/l, it was below detection in four out of nine samples. The sample with the maximum content of Zn also contained the maximum content of Pb (38 mg/l). Six samples had Pb>Zn with only one (the sample with maximum contents of both trace metals) having Zn>Pb. The majority of formation waters were undersaturated with respect to cerussite and strongly undersaturated with respect to smithsonite.

One sample contained 22 mg/l F, with  $\Delta G_{\text{diff}}$  for fluorite of 3.2, although the determination could be an analytical error. The range and mean content of F in four other samples were 1.7-4.6 mg/l and 3 mg/l, respectively ( $\Delta G_{\text{diff}}$  for these four samples was in the range -0.89 to 1.5), effectively similar to that of formation waters from the overlying Keg River aquifer (2.1-3.2 mg/l, mean 2.7 mg/l) and Watt Mountain aquifer (1.2-3.0 mg/l, mean 1.9 mg/l).

The contents of Fe (0.68-87 mg/l, mean 28 mg/l, median 3.7 mg/l) and Mn (3.5-51 mg/l, mean 15 mg/l, median 13 mg/l) contrast strongly with these same metals in the

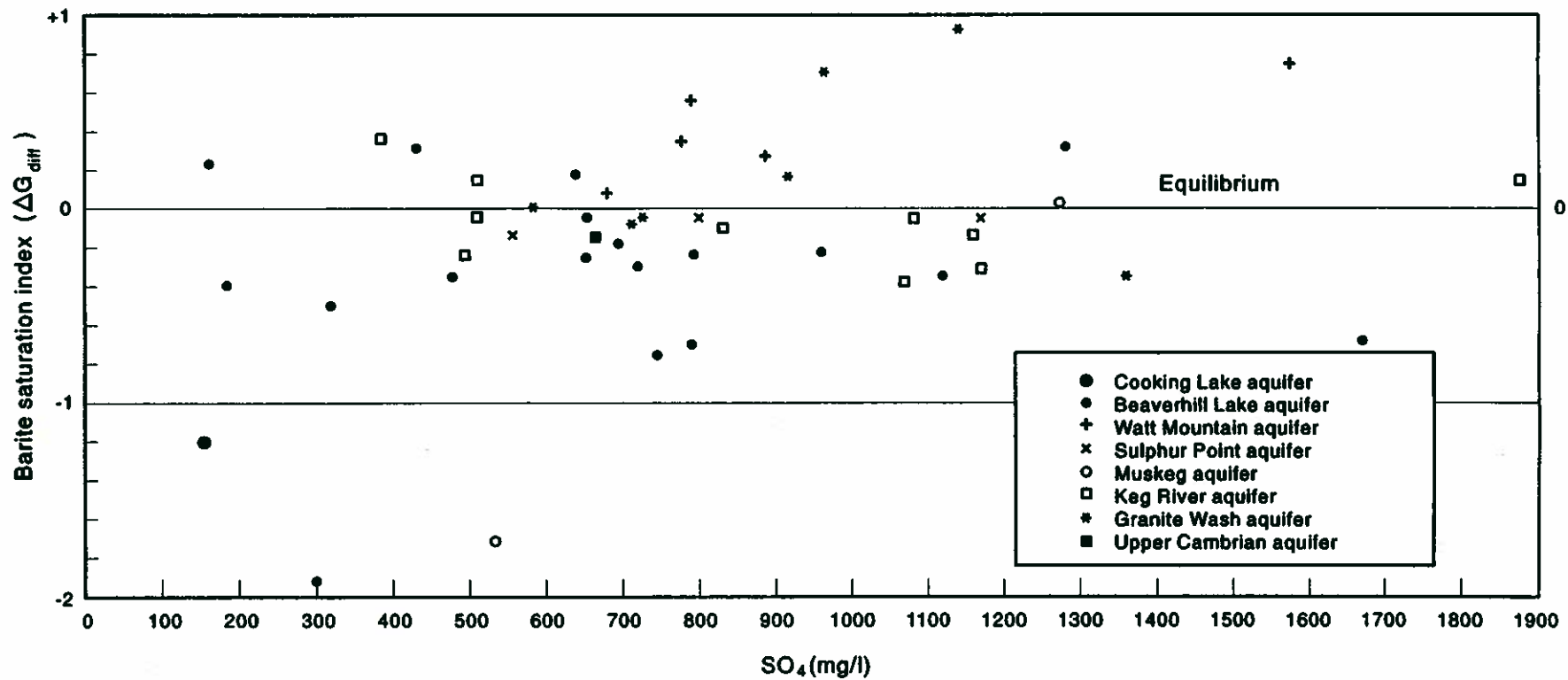


Figure 13. Plot of barite saturation index ( $\Delta G_{diff}$ ) against  $SO_4$  content (mg/l) of formation waters from Upper and Middle Devonian and Granite Wash aquifers, northern Alberta

overlying Keg River aquifer (Fe: four out of nine samples below detection, 1.1-64 mg/l, mean 17 mg/l, median 1.3 mg/l; Mn: one sample below detection, 1.2-27 mg/l, mean 6.7 mg/l, median 4.1 mg/l). Clearly, the Granite Wash formation waters are overall richer in both Fe and Mn, with the majority in both aquifers having Mn>Fe. In the Granite Wash aquifer, the formation waters are all undersaturated with respect to siderite, and undersaturated or strongly undersaturated with respect to rhodochrosite.

The formation waters are generally slightly undersaturated with respect to celestite, commonly undersaturated with respect to strontianite, and always strongly undersaturated with respect to witherite.

## SUMMARY

The Introduction to the section on formation water characteristics summarized the composition trends for the major components from previous studies and the saturation indices for major minerals from the present data base. The present summary is concerned mainly with five trace elements (Pb, Zn, Ba, Sr, F) and the way they and the saturation indices of their most important minerals vary over the hydrostratigraphic column. In order to synthesize the data better, the information previously presented is now summarized in six tables by hydrostratigraphic units. Figure 14 shows the hydrostratigraphic terminology used in this study, based on Hitchon et al. (1990b) and Bachu et al. (1993).

### Lead

As a general observation, the average content of Pb in formation waters from northern Alberta increases with depth (temperature, salinity) from <1 mg/l in Cretaceous aquifers to mean values >5 mg/l in pre-Cretaceous, dominantly carbonate, aquifers (Table 11); median values show a similar relation. Maximum values are <5 mg/l in Cretaceous aquifers and >10 mg/l in pre-Cretaceous aquifers. The change from dominantly carbonate to dominantly arenaceous aquifers seems to have a quite sharp and striking effect on the Pb content of formation waters. At the same time there is a distinct difference in the saturation indices of cerussite in formation waters from Devonian aquifers (dominantly undersaturated and strongly undersaturated) and those from Cretaceous aquifers (dominantly saturated). Formation waters from the Rundle-Permian-Triassic aquifer system exhibit intermediate features. The three  $\Delta G_{\text{diff}}$  values in the Wabamun-Winterburn and Grosmont aquifers classified as saturated or slightly oversaturated are all from formation waters in subcrop areas (therefore less saline at lower temperatures).

### Zinc

The content of Zn in formation waters and the  $\Delta G_{\text{diff}}$  values of smithsonite (Table 12) exhibit trends similar to that for Pb and the  $\Delta G_{\text{diff}}$  values for cerussite. Mean and median values for Zn are <1 mg/l in Cretaceous aquifers and the formation waters are all undersaturated with respect to smithsonite. In Devonian aquifers the mean and median contents of Zn are generally >3 mg/l and the formation waters are mostly strongly



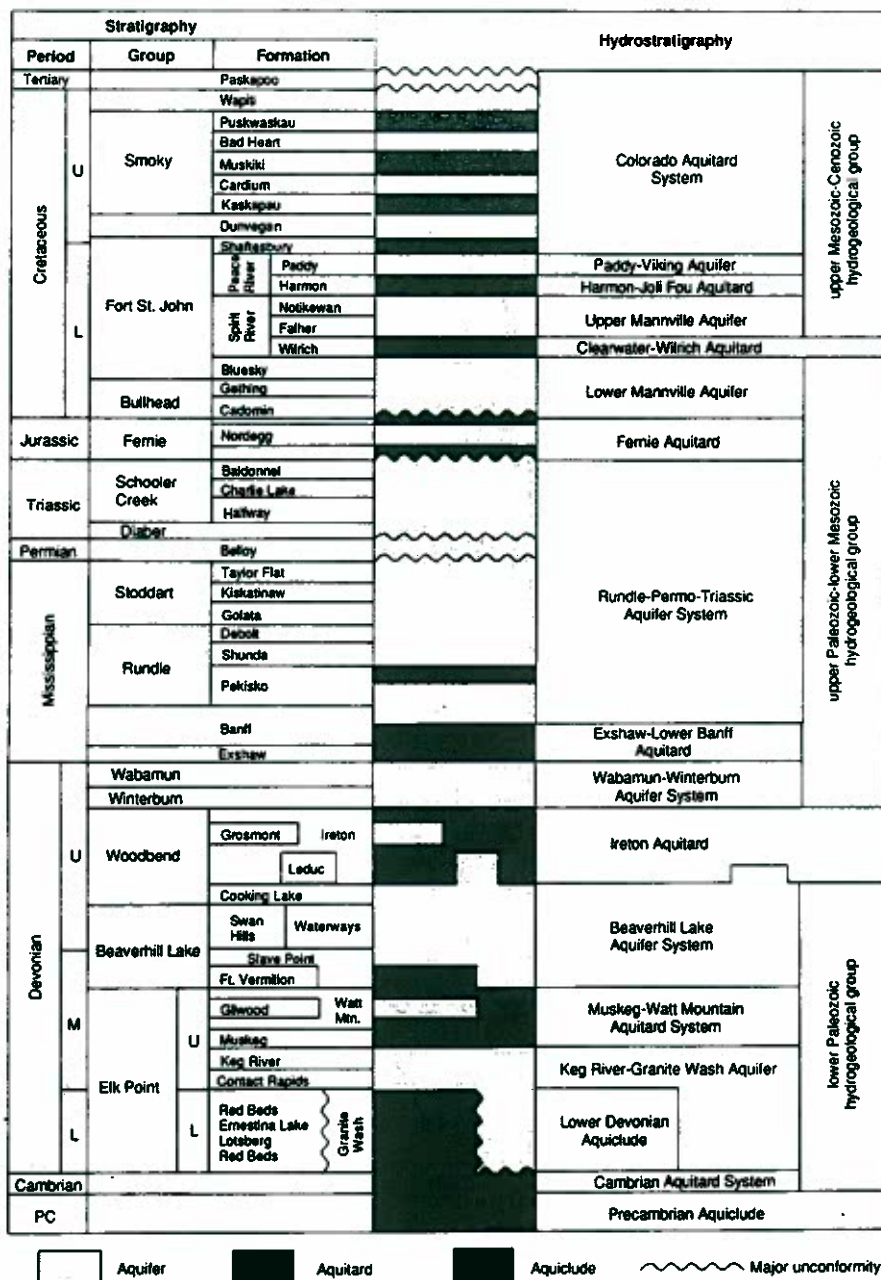


Figure 14. Hydrostratigraphy of northern Alberta (from Hitchon et al., 1990b, Table 1)

Table 11. Summary of Pb content (mg/l) and  $\Delta G_{diff}$  values for cerussite in formation waters from northern Alberta

Hydrostratigraphic unit	No.	Pb (mg/l)				$\Delta G_{diff}$ Cerussite*						
		Min.	Mean	Median	Max.	VSt USat	St USat	USat	SI USat	Sat	SI OSat	OSat
Paddy-Viking	15	0.2	0.5	0.5	1.0			1	3	10	1	
Upper Mannville	4	0.2	0.5	0.6	0.7					3	1	
Lower Mannville	23	0.08	0.9	0.5	3.9			3	2	12	4	2
Rundle-Permo-Triassic	39	0.1	7.3	2.0	58		2	26	8	1	1	1
Wabamun-Winterburn	7	0.3	8.5	7.0	22	1	4			1	1	
Grosmont	1			1.0							1	
Beaverhill Lake	10	0.2	6.6	6.1	15		5	5				
Watt Mountain	5	4	8.9	10	13		2	3				
Sulphur Point-Muskeg	4	2.2	7.8	2.9	23		1	3				
Keg River-Granite Wash	17	2.5	33	8.3	360		6	11				

- \* OSat = Oversaturated ( $\Delta G_{diff}$  +1.0 to +5.0)  
 SI OSat = Slightly oversaturated ( $\Delta G_{diff}$  +0.5 to +1.0)  
 Sat = Saturated ( $\Delta G_{diff}$  +0.5 to -0.5)  
 SI USat = Slightly Undersaturated ( $\Delta G_{diff}$  -0.5 to -1.0)  
 USat = Undersaturated ( $\Delta G_{diff}$  -1.0 to -5.0)  
 St USat = Strongly undersaturated ( $\Delta G_{diff}$  -5.0 to -10.0)  
 VSt USat = Very strongly undersaturated ( $\Delta G_{diff}$  > -10.0)

Table 12. Summary of Zn content (mg/l) and  $\Delta G_{\text{diff}}$  values for smithsonite in formation waters from northern Alberta

Hydrostratigraphic unit	No.	Zn (mg/l)				$\Delta G_{\text{diff}}$ Smithsonite*		
		Min.	Mean	Median	Max.	VSt USat	St USat	USat
Paddy-Viking	5	0.22	0.6	0.3	1.9			5
Upper Mannville	1			0.2				1
Lower Mannville	7	0.03	0.2	0.2	0.47			7
Rundle-Permo-Triassic	22	0.08	6.8	3.4	32		6	16
Wabamun-Winterburn	3	1.5	22	20	43	2	1	
Beaverhill Lake	10	0.11	35	8.2	225	2	7	1
Watt Mountain	2	1.7	2.6	2.6	3.4		2	
Sulphur Point-Muskeg	7	0.16	8.4	4.2	40		6	1
Keg River-Granite Wash	25	0.24	17	3.0	98	3	20	3

- \* USat = Undersaturated ( $\Delta G_{\text{diff}}$  -1.0 to -5.0)  
 St USat = Strongly undersaturated ( $\Delta G_{\text{diff}}$  -5.0 to -10.0)  
 VSt USat = Very strongly undersaturated ( $\Delta G_{\text{diff}}$  >-10.0)

undersaturated with respect to smithsonite. Again, the Rundle-Permo-Triassic aquifer system has some intermediate features.

#### Lead-zinc ratio

Table 13 presents information on the Pb:Zn ratio, where this could be calculated. Also shown is the relation of Pb and Zn where account was taken of values below detection limits but where, obviously, no Pb:Zn ratio could be calculated. It was possible to determine the relation of Pb and Zn in nearly 70% of the samples in the data base, of which 75% had Pb>Zn and 25% Zn>Pb. However, the proportion of samples with Pb>Zn varied from 85% for formation waters in Cretaceous aquifers to 70% for formation waters in pre-Cretaceous aquifers; the meaning and significance of this is not clear. The mean calculated Pb:Zn ratio does not appear to vary much from one hydrostratigraphic unit to another, and when all samples are considered (n=41) the Pb:Zn ratio varies over four orders of magnitude (0.003 to 30) with a mean of 2.7 and a median value of 0.8.

#### Barium

The information in Table 14 shows that although the range in content of Ba in formation waters varies widely from one aquifer to another, >80% have  $\Delta G_{\text{diff}}$  values in the narrow range -1.0 to +1.0 (slightly undersaturated, through saturated, to slightly oversaturated). This implies control of the content of Ba by the saturation of the formation water with respect to barite (see Fig. 13). Thus the content of Ba is a direct reflection of the  $\text{SO}_4$  content of the formation waters (Table 15), which explains the wide range in Ba contents depending on the  $\text{SO}_4$  content. Effectively all formation waters are undersaturated to strongly undersaturated with respect to witherite (Table 14), and although there is a change from mostly strongly undersaturated in Devonian aquifers to undersaturated in Cretaceous aquifers (with the Rundle-Permo-Triassic aquifer system showing intermediate features), it is clear that it is saturation with respect to barite and not witherite which controls the Ba content of formation waters in northern Alberta.

#### Strontium

The content of Sr in formation waters from northern Alberta (Table 16) varies widely (0.2-1120 mg/l), but as with several other trace and minor elements there is a strong contrast between the contents in formation waters in Cretaceous aquifers (mean 23 mg/l) and Devonian aquifers (mean 395 mg/l), with the Rundle-Permo-Triassic aquifer system having an intermediate mean Sr content of 76 mg/l. Formation waters from Devonian aquifers are mainly slightly undersaturated or saturated with respect to celestite and undersaturated with respect to strontianite. In contrast, formation waters from Cretaceous aquifers are dominantly undersaturated with respect to celestite and slightly more than half have  $\Delta G_{\text{diff}}$  values in the range -1.0 to +1.0. Again, formation waters from the Rundle-Permo-Triassic aquifer system show intermediate features. This means that control on the content of Sr is by means of different Sr-minerals, depending on the hydrostratigraphic unit -- or more precisely, on parameters such as  $\text{SO}_4$  content (see Table 15) and dissolved  $\text{CO}_2$  species. Table 17 summarizes the calculated pH at formation temperature (and calcite saturation) by hydrostratigraphic unit. For most (75%)

Table 13. Relation of Pb and Zn in formation waters from northern Alberta

Hydrostratigraphic unit	Pb>Zn		Zn>Pb	
	Pb:Zn	Indeterminate	Pb:Zn	Indeterminate
Paddy-Viking	2.1	12	0.2	2
Upper Mannville		4		1
Lower Mannville	2.7,3.4,30	19	1.0	2
Rundle-Permo-Triassic	1.3,1.5,1.7, 1.7,2.6,17	23	0.02,0.07, 0.09,0.26, 0.3,0.38, 0.66,0.74, 0.75,0.8	4
Wabamun-Winterburn	15	4	0.08	1
Grosmont		1		
Beaverhill Lake	2.2	4	0.003, 0.03,0.17, 0.3,0.57	1
Watt Mountain	2.4,2.9	3		
Sulphur Point-Muskeg		3	0.4	
Keg River-Granite Wash	1.0,1.4, 4.0,5.2,5.5	9	0.28,0.46, 0.63	1

Table 14. Summary of Ba content (mg/l) and  $\Delta G_{diff}$  values for barite and witherite in formation waters from northern Alberta

Hydrostratigraphic unit	No.	Ba (mg/l)				$\Delta G_{diff}$ Barite*					$\Delta G_{diff}$ Witherite*				
		Min.	Mean	Median	Max.	USat	St USat	Sat	SI OSat	OSat	VSt USat	St USat	USat	SI USat	Sat
Paddy-Viking	8	0.43	34	15	84			4	3	11			17	1	
Upper Mannville	9	0.3	2.9	1.6	13			4	3	2			9		
Lower Mannville	35	0.2	42	3.4	680		4	16	9	6			32	2	1
Nordegg	1			4.4				1					1		
Rundle-Permo-Triassic	40	0.08	9.7	1.0	120		2	32	2	4		23	17		
Wabamun-Winterburn	9	1.8	3.8	3.1	8.8			6	3			7	2		
Grosmont	1			2.1					1				1		
Beaverhill Lake	10	0.8	2.5	1.9	5.6			10				10			
Watt Mountain	5	1.8	2.5	2.4	3.4			3	2			5			
Sulphur Point-Muskeg	5	0.4	1.0	0.8	1.5	1		4				5			
Keg River-Granite Wash	16	0.42	1.8	1.4	4.5			14	2		1	15			

- \* OSat = Oversaturated ( $\Delta G_{diff}$  +1.0 to +5.0)
- SI OSat = Slightly oversaturated ( $\Delta G_{diff}$  +0.5 to +1.0)
- Sat = Saturated ( $\Delta G_{diff}$  +0.5 to -0.5)
- SI USat = Slightly undersaturated ( $\Delta G_{diff}$  -0.5 to -1.0)
- USat = Undersaturated ( $\Delta G_{diff}$  -1.0 to -5.0)
- St USat = Strongly undersaturated ( $\Delta G_{diff}$  -5.0 to -10.0)
- VSt USat = Very strongly undersaturated ( $\Delta G_{diff}$  >-10.0)

Table 15. Summary of SO<sub>4</sub> content (mg/l) of formation waters from northern Alberta

Hydrostratigraphic unit	No.	SO <sub>4</sub> (mg/l)			
		Min.	Mean	Median	Max.
Paddy-Viking	20	5	40	16	137
Upper Mannville	9	17	68	64	148
Lower Mannville	37	3	58	42	255
Nordegg	1			46	
Rundle-Permo-Triassic	54	7	1400	1170	4900
Wabamun-Winterburn	9	33	445	438	1330
Grosmont	1			145	
Beaverhill Lake	14	295	695	640	1264
Watt Mountain	5	665	920	770	1560
Sulphur Point-Muskeg	11	489	760	730	1250
Keg River-Granite Wash	35	248	1270	943	6444

Table 16. Summary of Sr content (mg/l) and  $\Delta G_{diff}$  values for celestite and strontianite in formation waters from northern Alberta

Hydrostratigraphic unit	No.	Sr (mg/l)				$\Delta G_{diff}$ Celestite*				$\Delta G_{diff}$ Strontianite*				
		Min.	Mean	Median	Max.	St USat	USat	SI USat	Sat	St USat	USat	SI USat	Sat	SI OSat
Paddy-Viking	20	6.6	27	24	67		20				3	12	5	
Upper Mannville	9	1.0	11	6	32		9				5	4		
Lower Mannville	37	0.2	23	5	95	3	34				20	13	3	1
Nordegg	1			46			1					1		
Rundle-Permo-Triassic	54	0.4	76	67	300		31	22	1		39	13	2	
Wabamun-Winterburn	9	6.6	555	660	1120		3	4	2		7	2		
Grosmont	1			19			1				1			
Beaverhill Lake	14	210	470	450	900		1	12	1		14			
Watt Mountain	5	375	390	380	410			4	1		5			
Sulphur Point-Muskeg	11	170	310	320	393		3	5	3		11			
Keg River-Granite Wash	35	78	360	350	735		5	22	8	2	33			

- \* SI OSat = Slightly oversaturated ( $\Delta G_{diff}$  +0.5 to +1.0)
- Sat = Saturated ( $\Delta G_{diff}$  +0.5 to -0.5)
- SI USat = Slightly undersaturated ( $\Delta G_{diff}$  -0.5 to -1.0)
- USat = Undersaturated ( $\Delta G_{diff}$  -1.0 to -5.0)
- St USat = Strongly undersaturated ( $\Delta G_{diff}$  -5.0 to -10.0)



Table 17. Summary of pH at formation temperature

Hydrostratigraphic unit	No.	Calculated pH				
		4.0-4.9	5.0-5.9	6.0-6.9	7.0-7.9	8.0-8.9
Doe Creek	1				1	
Paddy-Viking	20			6	14	
Upper Mannville	9			1	8	
Lower Mannville	37		1	29	6	1
Nordegg	1			1		
Rundle-Permo-Triassic	54		9	44	1	
Wabamun-Winterburn	8		6	2		
Grosmont	1			1		
Beaverhill Lake	14	1	9	4		
Watt Mountain	5	2	3			
Sulphur Point-Muskeg	11	2	7	2		
Keg River-Granite Wash	33	1	24	8		

formation waters in Devonian aquifers the dominant dissolved  $\text{CO}_2$  species will be  $\text{H}_2\text{CO}_3\text{aq}$ . In contrast,  $\text{HCO}_3^-$  will be effectively the only dissolved  $\text{CO}_2$  species in formation waters from Cretaceous aquifers. These differing chemical features explain the change in mineral control on the content of Sr in these formation waters.

### Fluorine

As noted previously, the content of F in formation waters is controlled by the saturation with respect to fluorite. The  $\Delta G_{\text{diff}}$  values (Table 18) for 75% of formation waters from Devonian aquifers fall in the range -1.0 to +1.0 (slightly undersaturated, through saturated, to slightly oversaturated). This contrasts with >80% of formation waters from Cretaceous aquifers which are undersaturated with respect to fluorite. Once more, formation waters from the Rundle-Permo-Triassic aquifer system show intermediate features. As a general observation, formation waters from Devonian aquifers contain higher contents of both F and Ca; this is possible because a significant portion of the F occurs as the  $\text{MgF}^+$  complex.

### Conclusion

The information presented so far relates specifically to the present situation in the northern part of the Alberta Basin. It is clear that none of the present formation waters could give rise, directly, to the Pine Point Zn-Pb deposit. However, it is important to have reviewed the entire Phanerozoic succession as will become apparent later.

The next part of this study addresses the question of how a Zn-Pb deposit can be derived from formation waters with  $\text{Pb} > \text{Zn}$ , with specific emphasis on present formation waters in the pre-Ireton aquifers. This will be done using the computer code SOLMINEQ.88.

Table 18. Summary of F content (mg/l) and  $\Delta G_{diff}$  values for fluorite in formation waters from northern Alberta

Hydrostratigraphic unit	No.	F (mg/l)				$\Delta G_{diff}$ Fluorite*				
		Min.	Mean	Median	Max.	USat	SI USat	Sat	SI OSat	OSat
Paddy-Viking	17	0.22	0.8	0.6	4.1	16		1		
Upper Mannville	9	0.38	0.7	1.0	2.2	7	1	1		
Lower Mannville	33	0.38	1.3	1.1	7.1	26	5	1		1
Nordegg	1			1.3		1				
Rundle-Permo-Triassic	45	0.13	1.5	1.5	3.4	15	12	16	2	
Wabamun-Winterburn	8	0.7	4.0	4.3	7.0	1	1	4	2	
Grosmont	1			1.68				1		
Beaverhill Lake	12	1.4	3.5	3.3	6.2	1		9	2	
Watt Mountain	4	1.19	1.9	1.8	3.0	2	1	1		
Sulphur Point-Muskeg	3	1.9	2.6	2.3	3.6			3		
Keg River-Granite Wash	15	1.7	4.2	3.0	22	2	1	1	6	5

- \* OSat = Oversaturated ( $\Delta G_{diff}$  +1.0 to +5.0)  
 SI OSat = Slightly oversaturated ( $\Delta G_{diff}$  +0.5 to +1.0)  
 Sat = Saturated ( $\Delta G_{diff}$  +0.5 to -0.5)  
 SI USat = Slightly undersaturated ( $\Delta G_{diff}$  -0.5 to -1.0)  
 USat = Undersaturated ( $\Delta G_{diff}$  -1.0 to -5.0)

**PART B. FORMATION WATERS AS A POSSIBLE SOURCE OF THE ORE**

## INTRODUCTION

PART A of this report dealt with the general characteristics of formation waters in northern Alberta. The formation waters fell into three groups (1) those from Cretaceous aquifers, (2) an intermediate group from Triassic, Permian and Carboniferous aquifers, and (3) those from Devonian aquifers. Formation waters from Devonian aquifers were characterized by generally higher salinity and temperature, and elevated contents of Pb and Zn. In northern Alberta, 75% of formation waters have Pb>Zn, with no preference for Zn>Pb anywhere in the stratigraphic column. In the Keg River and Granite Wash aquifers, which are hydraulically connected to the Pine Point aquifer, the areal distribution of the Pb:Zn ratio shows no discernable trends, with the distribution appearing to be random. Shales laterally equivalent to the Pine Point Formation and the carbonate host rocks have Zn>Pb. Because of these facts it was concluded that none of the present formation waters could give rise, directly, to the Pine Point Zn-Pb deposit.

This part of the report will consider what geochemical manipulations would be necessary to produce a Zn-Pb ore deposit from formation waters dominantly with Pb>Zn. Included will be the generally accepted view that mixing of two fluids is required to form Mississippi Valley type ore deposits. Aspects to be considered are (1) details of the deposition conditions at Pine Point based on fluid inclusion, chemical and isotope data, (2) manipulations of formation water analyses using the computer code SOLMINEQ.88, (3) the composition and temperature of the two end members of a mixing scenario, and (4) the results of the mixing model.

## DEPOSITIONAL CONDITIONS

### Temperature

Information on the ore-bearing fluid comes from several sources. With respect to the temperature of deposition, fluid inclusions in sphalerite suggest the range 50-100°C (Roedder, 1968), a range generally confirmed by a study of the Fe content of sphalerite (Evans et al., 1968). Aulstead and Spencer (1985) studied fluid inclusions in dolomite, fluorite and anhydrite cements in the Keg River Formation of northwestern Alberta, 300 km downdip from Pine Point. They implied a thermal anomaly in that area on the basis of homogenization temperatures in the general ranges 105-125°C for dolomite, 105-140°C for fluorite, and 105-220°C for anhydrite. In their calculations they assumed the depth and geothermal gradient at the time of maximum burial. They used a present geothermal gradient of 31°C/km. A recent study by Bachu and Burwash (1993) indicates that many (6 out of 9) of the locations sampled by Aulstead and Spencer (1985) are within or close to small areas with present geothermal gradients of a least 40°C/km. Using the maximum depths of burial assumed by Aulstead and Spencer (1985) and a geothermal gradient of 42°C/km, the maximum temperatures to which some of their samples have been subjected are at least 124°C and up to ~134°C in the deepest sample; these calculations assume the present geothermal gradient is the same as that at the time of maximum burial. What is suggested here is that at least some of the

homogenization temperatures for dolomite and fluorite can be accounted for without invoking a thermal anomaly. The situation for anhydrite remains anomalous, however.

Ore deposition at Pine Point took place during Pennsylvanian time according to many authors, when the Pine Point area was covered only by Upper Devonian and Carboniferous strata, since removed by erosion. Extrapolation of the isopachs of these missing strata into the Pine Point area (Fig. 15), based on the cross-section in Garven (1985), suggests that perhaps no more than 1500 m of sediments lay over the Pine Point ore deposition site by the end of the Pennsylvanian. Even using the present high geothermal gradients in the area of at least 40°C/km (Bachu and Burwash, 1993), the in situ temperature of the Keg River aquifer would be 60°C, at a maximum, at the time of ore deposition. Clearly, the system requires the input of heat.

Bachu and Burwash (1991) carried out a regional-scale analysis of the geothermal regime in the western Canada sedimentary basin and concluded that the characteristics indicated a conduction-dominated system. Evidence included regional variations in radiogenic heat production by basement rocks and the basin-scale average permeability of the aquifers at around the threshold for passing from a convective to a conductive system -- which feature is emphasized by the layered aquicludes and aquitards which retard vertical flow. Most features of the integral geothermal gradient pattern at the regional, intermediate and local scales can be accounted for by regional variations in basement heat production. Only along the cratonic edge of the basin in southeast Manitoba and northeast Alberta-Northwest Territories do the high geothermal gradients not correlate with radiogenic heat production by basement rocks. The cause could be just insufficient data, particularly in the north. In Manitoba, although data are scarce, the Archean basement is known for its low content of radiogenic elements. This same cause could apply along the Great Slave Lake Shear Zone, with loss of radioactive elements during shearing. Another cause, process related, could be indeed convection of terrestrial heat by formation waters.

From their study it seems clear that at the present time the convection of terrestrial heat by formation waters is a possibility only in southeast Manitoba and northeast Alberta-Northwest Territories, and even in these areas other causes for the high integral geothermal gradients are more plausible. During the Pennsylvanian, however, the average permeability of the strata in the basin would be greater and convection of heat by formation waters cannot be ruled out. On this basis it remains reasonable to consider hot (deep) formation waters as capable of supplying the heat input at Pine Point at the time of ore deposition.

### Salinity

Fluid inclusion data may also be used to estimate the salinity of the ore-bearing fluid. On the basis of fluid inclusions in sphalerite, Roedder (1968) indicated a salinity of 4.5 molal NaCl equivalent (~260,000 mg/l). Values as low as 1 molal NaCl equivalent were found for late calcite. Downdip, in the area studied by Aulstead and Spencer (1985), ionic strengths of solutions in fluid inclusions in dolomite were in the range 3.65-4.95; comparable ionic strengths were 3.15-3.40 for fluorite and 3.48-4.35 for anhydrite.

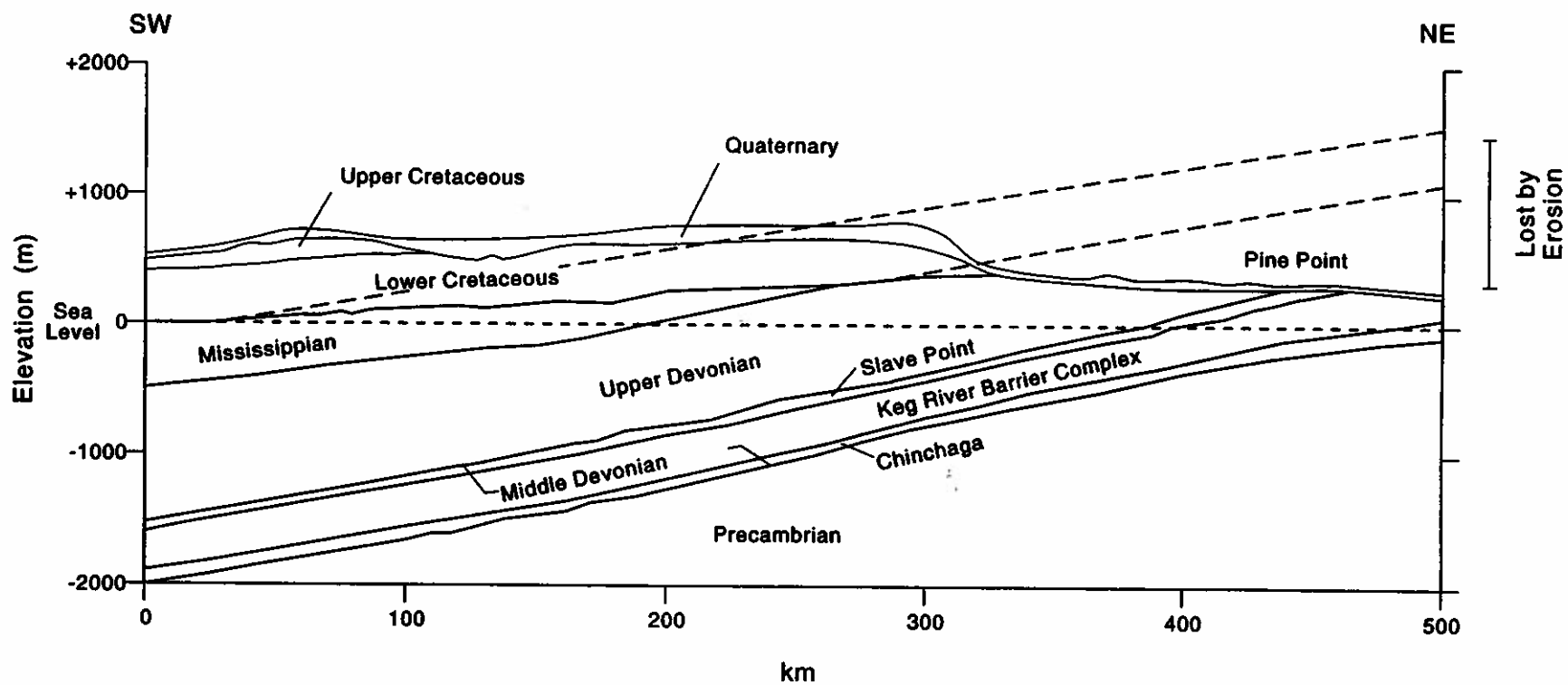


Figure 15. Cross-section along the Presqu'île barrier reef from Fort Nelson, British Columbia to Pine Point, NWT (from Garven, 1985)

They inferred a multicomponent salt system composed predominantly of  $\text{MgCl}_2$ - $\text{CaCl}_2$ - $\text{NaCl}$  based on eutectic temperatures measured in the inclusions. Ionic strengths in the range 3.0-5.0 correspond roughly to salinities of 150,000-250,000 mg/l. Thus a salinity of about 250,000 mg/l is reasonable for the ore-bearing fluid.

As a general observation in the Peace River Arch area, the salinity of formation water is mainly controlled by temperature, and hence shows a direct relation with depth, except where influenced by contact with evaporites or downward moving meteoric water (Hitchon et al., 1990b). In the Keg River aquifer, high salinity (up to 380,000 mg/l, Hitchon, 1990) occurs in formation waters coincident with the halite beds of the underlying Lotsberg Formation and the overlying Prairie Formation. These evaporite beds are found on the southeast side of the Presqu'île carbonate complex almost throughout its length. Certainly, without the influence of evaporites, normal formation water salinity at a temperature of only 60°C would be far lower than 250,000 mg/l. Therefore, the influence of evaporites on the salinity of the Pine Point ore fluid cannot be ruled out.

### Geochemistry

In addition to temperature and salinity constraints, two geochemical conditions need to be considered. First, the S in the sphalerite and galena originated from M. Devonian sea water  $\text{SO}_4$  (Sasaki and Krouse, 1969). This could be a direct link (unlikely, given water-rock reactions between the time of deposition of the host rock and the time of ore deposition) or most probably through the contribution of dissolved M. Devonian anhydrite to the salinity of the ore-bearing fluid. Second, the Pb in the galena has a mantle source (Cumming and Robertson, 1969). There is no implication as to the route of the Pb, which could be direct or indirect.

### SOLMINEQ.88

As noted in Part A, the nearly 200 formation water analyses used in this study were checked for ionic balance using the computer code SOLMINEQ.88 (Kharaka et al., 1988). In addition, the  $\text{CO}_2$  option in SOLMINEQ.88 was used to add back  $\text{CO}_2$  until the solution was saturated with respect to calcite at reservoir temperature. Thus all information on mineral saturations and pH presented in Part A relate to calcite saturation at formation temperature. The computer code can also be used to adjust an analysis for missing components provided information is available on the formation mineralogy and the general speed of kinetics of the minerals present. For example, if  $\text{SiO}_2$  was not determined it can be added to the analysis in increments until quartz saturation is reached, assuming the analysis was a formation water from a rock containing quartz. Likewise, missing Al can be added to reach saturation for a common clay mineral such as montmorillonite or illite. Another option in SOLMINEQ.88 is the mixing of two fluids in any given proportion. The program calculates the proportional temperature and composition and then computes the distribution of species and mineral saturation in the mixture in the normal manner. However, even if both end members are adjusted for, say, calcite saturation, the mixture is not so adjusted. To adjust the mixture it is necessary to re-enter the composition of the mixture and specify the  $\text{CO}_2$  option. The next section of this report is the result of more than 325 separate runs on SOLMINEQ.88.



## END MEMBER CHARACTERISTICS

### General

Although it is only possible to guess at the composition of the end members in a mixing scenario, there is sufficient information to place constraints on them because of what is known about the final product, namely, the Pine Point ore deposit. The most commonly advocated scenario is the contact of a hot saline formation water without H<sub>2</sub>S and carrying the metals, with a formation water, probably cooler and less saline at the basin margin, with abundant H<sub>2</sub>S. This is the first situation to be examined.

### Formation water

Two formation waters from the Keg River aquifer were selected for detailed study, each with relatively high contents of Pb and Zn. The first (RCAH93-1273A) came from the Rainbow area close to the subsurface extension of the Presqu'île barrier reef on which Pine Point is located (Fig. 16). It has a Pb:Zn ratio of 5.5, the highest in the Keg River aquifer (Table 13). The second (RCAH116-374D) lies just updip of the Peace River Arch and has a Pb:Zn ratio of 0.6. Complete analyses are given in Table 19.

Aluminum was below detection in each analysis. As far as could be determined, no published papers dealing with the Keg River Formation report the composition of the argillaceous beds associated with this dominantly carbonate unit. Pelzer (1966) indicated that about half the minerals in the basal portion of the Besa River shale near Clarke Lake in northeastern British Columbia comprised illite; this basal section of the Besa River shale is stratigraphically equivalent to the carbonates of the Presqu'île barrier complex. Accordingly, Al was added to these two analyses to reach equilibrium with illite at reservoir temperature. Likewise the content of SiO<sub>2</sub> was adjusted to quartz saturation at reservoir temperature. The computed amounts were:

RCAH93-1273A 73°C, SiO<sub>2</sub> 10.8 mg/l, Al 0.027 mg/l

RCAH 116-374D 36°C, SiO<sub>2</sub> 3.35 mg/l, Al 0.0105 mg/l

Given that about 1.5 km of sedimentary rocks have been eroded from this part of northern Alberta, the maximum temperature to which each of the above formation waters has been subjected can be calculated from the present geothermal gradient, with the following results:

RCAH93-1273A Geothermal gradient 38°C/km, maximum temperature 125°C

RCAH116-374D Geothermal gradient 25°C/km, maximum temperature 75°C

These higher temperatures require adjustments to the amounts of Al and SiO<sub>2</sub> needed to reach saturation with illite and quartz, respectively, as follows:

RCAH93-1273A 125°C, SiO<sub>2</sub> 38 mg/l, Al 0.053 mg/l

RCAH116-374D 75°C, SiO<sub>2</sub> 11 mg/l, Al 0.0043 mg/l

Tables 20 and 21 show the  $\Delta G_{\text{diff}}$  values for selected minerals for RCAH93-1273A and RCAH116-374D, respectively, for saturation with calcite, illite and quartz at the specified temperatures. Within each temperature set the first column shows the  $\Delta G_{\text{diff}}$  values at calcite saturation without adjustment for illite and quartz saturation e.g. 1.42 for dolomite at 73°C (Table 20). The second column shows the  $\Delta G_{\text{diff}}$  values for saturation

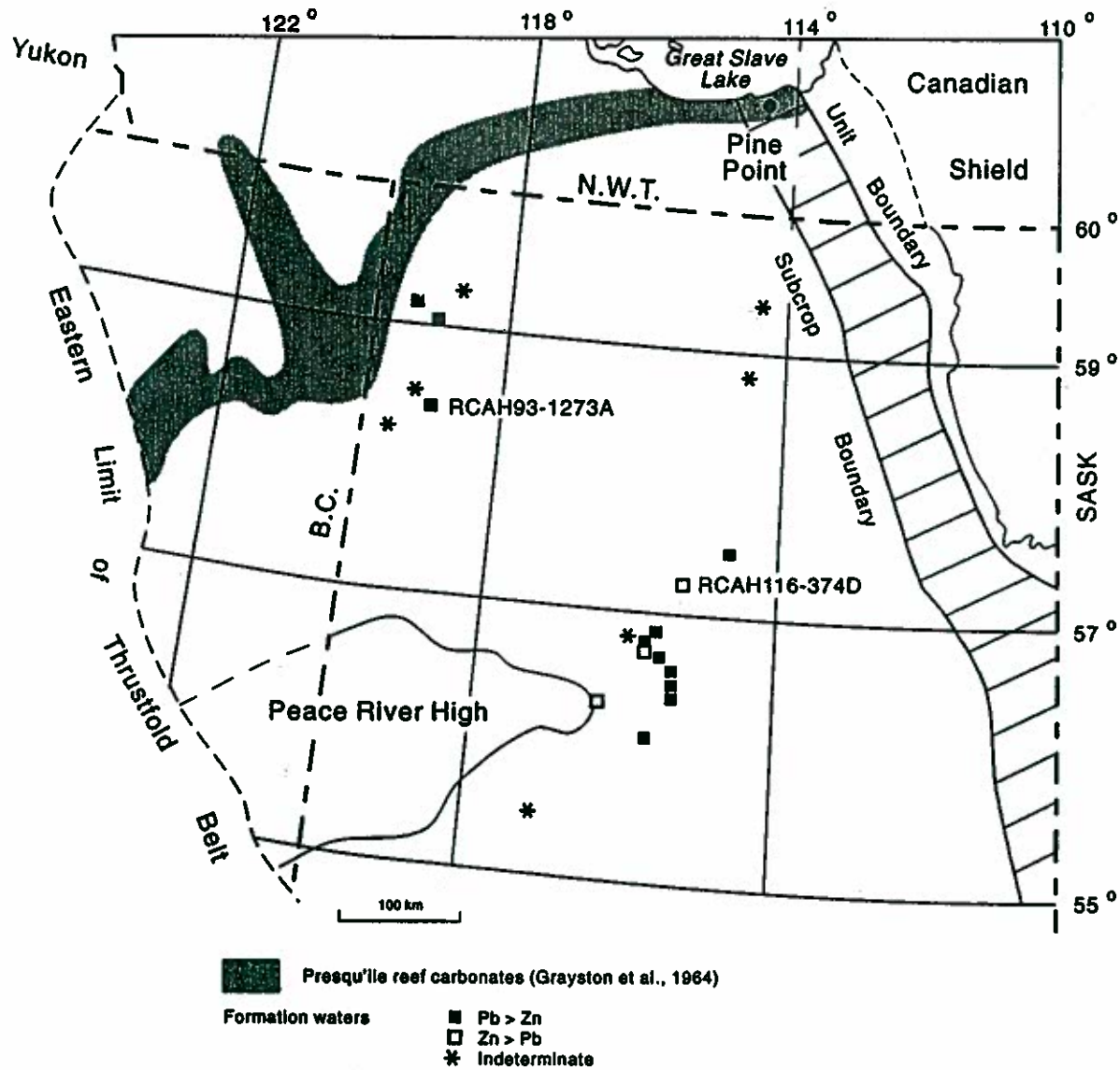


Figure 16. Keg River aquifer, northern Alberta and adjacent areas, showing: (1) location of the samples studied in the fluid mixing model; and (2) the proportions of Pb and Zn in formation waters in the Keg River and Granite Wash aquifers

Table 19. Chemical composition (mg/l), physical properties and production data for formation waters from the Keg River aquifer used in the mixing model.

	RCAH93-1273A	RCAH116-374D
Location	3-28-109-6-W6M	10-18-95-7-W5M
Depth (m)	1701.4-1713.0	1239.3-1252.7
Source	DST 1	DST 1
Recovery	832.1 m sul sw	914.4 m sw
Li	54	25
Na	60400	75200
K	2200	585
Mg	960	1440
Ca	14800	11100
Sr	430	195
Ba	3	0.52
Al	<2	<3
Cu	0.56	0.72
Ag	<2	2
Zn	10	16
Pb	55	10
Fe	1.1	1.5
Mn	22	<0.5
As	17	22
B	155	16
PO <sub>4</sub>	22	29
NH <sub>3</sub>	249	56.8
SiO <sub>2</sub>	12	19
F	5.5	2.7
Cl	115400	126,600
Br	16	327
I	3	3
SO <sub>4</sub>	484	1870
HCO <sub>3</sub>	204	158
Total solids (calc.)	196210	217440
Total solids (110°C)	216190	257240
Total solids (ign.)	194740	223060
Cations (anal., meq/l)	3519.6	3967.0
Anions (anal., meq/l)	3269.7	3613.9
Cations (calc., meq/l)	3239.4	3606.5
Anions (calc., meq/l)	2974.6	3249.4
pH (laboratory)	6.94	7.25
pH (calc., formation temp.)	5.50 (73°C)	6.01 (36°C)
Density (15.56°C)	1.1353	1.1529
Refractive index (25°C)	1.3653	1.3696

Additional determinations: RCAH93-1273A (Cr=1.7; Mo=2.6; Ni=2.0; Se=20; Ti=0.7; V=1.3).  
RCAH116-374D (Co=1.2; Cr=2.1; Mo=3.7; Ni=2.8; Se=22; Ti=0.8; V=1.7).

Table 20. RCAH93-1273A:  $\Delta G_{diff}$  values for selected minerals, variously adjusted for saturation with respect to calcite, illite and quartz, and addition of H<sub>2</sub>S, at formation temperature (73°C) and maximum burial temperature (125°C)

	Calcite saturation at 73°C				Calcite saturation at 100°C				Calcite saturation at 125°C				
		Illite and quartz saturation				Illite and quartz saturation				Illite and quartz saturation			
		1 mg/l H <sub>2</sub> S	10 mg/l H <sub>2</sub> S			1 mg/l H <sub>2</sub> S	10 mg/l H <sub>2</sub> S			1 mg/l H <sub>2</sub> S	10 mg/l H <sub>2</sub> S	100 mg/l H <sub>2</sub> S	
Calcite (CaCO <sub>3</sub> )	0.02				0.06				0.01				
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	1.42				2.15				2.56				
Strontianite (SrCO <sub>3</sub> )	-2.05				-2.19				-2.48				
Witherite (BaCO <sub>3</sub> )	-6.63				-7.03				-7.49				
Siderite (FeCO <sub>3</sub> )	-3.53				-3.99				-4.31				
Rhodochrosite (MnCO <sub>3</sub> )	-4.46				-5.12				-6.96				
Cerussite (PbCO <sub>3</sub> )	-4.05			-4.25	-5.30			-5.47	-6.60		-6.03	-8.71	
Smithsonite (ZnCO <sub>3</sub> )	-7.81	-7.95	-9.05	-6.69	-7.01	-7.65	-7.96	-6.03	-8.39	-9.43			
Anhydrite (CaSO <sub>4</sub> )	-0.78				-0.42				0.01				
Celestite (SrSO <sub>4</sub> )	-1.08				-1.04				-0.99				
Baite (BaSO <sub>4</sub> )	-0.22				-0.55				-0.78				
Hallite (NaCl)	-1.74				-1.66				-2.00				
Fluorite (CaF <sub>2</sub> )	1.33				0.39				-0.53				
Apatite (Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH)	16.7				16.4				16.4				
Quartz (SiO <sub>2</sub> )	0.08	0.01			-0.43	0.00			-0.91	0.01			
Albite (NaAlSi <sub>3</sub> O <sub>8</sub> )	-	0.32		0.29	-	0.47		0.37	-	0.62		0.35	0.04
Anorthite (CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> )	-	-6.80		-6.61	-	-5.56		-5.76	-	-4.62		-5.15	-5.76
K-Feldspar (KAlSi <sub>3</sub> O <sub>8</sub> )	-	1.45		1.41	-	1.29		1.20	-	1.12		0.86	0.54
Illite (K <sub>2</sub> Mg <sub>16</sub> Al <sub>12</sub> Si <sub>28</sub> O <sub>108</sub> (OH) <sub>2</sub> )	-	0.09		0.03	-	0.02		-0.14	-	0.01		-0.44	-0.99
Kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> )	-	2.81		2.77	-	2.45		2.35	-	2.36		2.09	1.76
K-Smectite (K <sub>2</sub> Al <sub>2</sub> Si <sub>20</sub> O <sub>70</sub> (OH) <sub>2</sub> )	-	0.41		0.36	-	0.17		0.03	-	0.16		-0.20	-0.63
Chalcocite (Cu <sub>2</sub> S)	-	-	7.31	9.47	-	-	4.36	6.31	-	-	1.28	2.87	4.58
Pyrite (FeS <sub>2</sub> )	-	-	3.63	7.42	-	-	3.45	6.95	-	-	3.74	6.77	10.07
Galena (PbS)	-	-	6.75	8.71	-	-	6.55	8.35	-	-	6.13	7.84	7.36
Sphalerite (ZnS)	-	-	3.51	4.56	-	-	3.40	4.54	-	-	2.92	4.23	4.85
pH at formation temperature	5.50	5.50	5.50	5.49	5.37	5.37	5.37	5.35	5.18	5.18	5.18	5.11	5.03

- Not calculated

Table 21. RCAH116-374D:  $\Delta G_{diff}$  values for selected minerals, variously adjusted for saturation with respect to calcite, illite and quartz, and addition of H<sub>2</sub>S, at formation temperature (36°C) and maximum burial temperature (75°C)

	Calcite saturation at 36°C				Calcite saturation at 75°C				
		Illite and quartz saturation				Illite and quartz saturation			
			1 mg/l H <sub>2</sub> S	10 mg/l H <sub>2</sub> S			1 mg/l H <sub>2</sub> S	10 mg/l H <sub>2</sub> S	100 mg/l H <sub>2</sub> S
Calcite	0.06				0.01				
Dolomite	1.17				1.93				
Strontianite	-1.98				-2.42				
Witherite	-6.80				-7.69				
Siderite	-2.74				-3.18				
Cerussite	-3.66			-4.09	-5.37			-5.69	-10.3
Smithsonite	-4.93			-7.06	-7.69			-9.21	-11.5
Anhydrite	-0.44				-0.12				
Celestite	-0.66				-0.77				
Barite	0.17				-0.61				
Halite	-1.25				-1.52				
Fluorite	0.88				-0.53				
Apatite	16.5				18.6				
Quartz	1.07	0.00			0.38	0.01			
Albite	-	0.66	0.42		-	0.83			0.24
Anorthite	-	-7.88	-8.36		-	-6.23			-7.41
K-feldspar	-	1.36	1.12		-	0.86			0.27
Illite	-	0.05	-0.43		-	0.01		-0.03	-1.03
Kaolinite	-	3.19	2.83		-	2.82			2.17
K-smectite	-	0.46	0.03		-	0.25			-0.59
Chalcocite	-	-	10.9	14.2	-	-	7.04	9.87	12.3
Pyrite	-	-	3.31	9.04	-	-	3.35	8.34	13.1
Galena	-	-	5.74	8.64	-	-	5.30	7.81	5.56
Sphalerite	-	-	4.25	5.53	-	-	3.58	4.98	5.03
pH at formation temperature	6.01	6.01	5.97	5.97	5.68	5.68	5.68	5.68	5.52

- = Not calculated

with respect to calcite, illite and quartz -- with the blanks indicating no significant change from the value in the first column at that temperature. The third to fifth columns reflect the effects of added H<sub>2</sub>S -- with the blanks again indicating no significant change from the column to the left.

For the carbonate, sulphate, halide and phosphate minerals, the effects of the addition of Al for illite saturation, SiO<sub>2</sub> for quartz saturation or H<sub>2</sub>S are negligible except for increased undersaturation with respect to cerussite and smithsonite on the addition of H<sub>2</sub>S. The effects due to increased temperature are significant, however, with dolomite becoming more saturated compared to the other carbonates which become more unsaturated. Likewise, anhydrite becomes more saturated whereas celestite shows little change and barite becomes more unsaturated. There is increased undersaturation with respect to halite and fluorite, but apatite shows increased saturation. Put another way, dolomite, anhydrite and apatite are more stable at higher subsurface temperatures. At the respective formation temperatures all the silicate minerals have positive  $\Delta G_{diff}$  values, except anorthite which exhibits strong undersaturation. Increased temperature results in more stable plagioclase and less stable K-feldspar, although anorthite remains undersaturated even at 125°C. Addition of H<sub>2</sub>S, especially at 100 mg/l, reduces the stability of all the silicates.

All the formation water-temperature combinations show oversaturation or strong oversaturation with respect to the sulphide minerals, even at H<sub>2</sub>S concentrations as low as 1 mg/l. Thus, galena and sphalerite will precipitate out at even very low H<sub>2</sub>S contents, with sphalerite having the lower  $\Delta G_{diff}$  value at all the conditions considered in Tables 20 and 21. This observation means that if less H<sub>2</sub>S is present than is necessary to precipitate out all the Pb and Zn, galena will be the preferred precipitate, depending on the exact kinetics involved. In the case of RCAH93-1273A, with 55 mg/l Pb and 10 mg/l Zn, 9.05 mg/l H<sub>2</sub>S is needed to neutralize all the Pb as PbS and 5.21 mg/l H<sub>2</sub>S is needed to neutralize all the Zn as ZnS. Thus, 10 mg/l H<sub>2</sub>S could conceivably be used up by first precipitating all the Pb as PbS, leaving only 0.95 mg/l H<sub>2</sub>S to be used in precipitating ZnS. This would result in an ore body with a Pb:Zn ratio of 30 and 3.39 mg/l Zn still in solution. In the case of RCAH116-374D, with 10 mg/l Pb and 16 mg/l Zn, the respective neutralizing amounts of H<sub>2</sub>S are 1.65 mg/l and 8.34 mg/l; i.e. 10 mg/l H<sub>2</sub>S would precipitate out all the Pb and Zn in this sample (23.8 mg ZnS and 11.6 mg PbS, for a Pb:Zn ratio of 0.6). With 75% of formation waters having Pb>Zn it is obvious that no amount of manipulation of these formation water compositions at the mineral saturation states indicated and at their temperatures of maximum burial can produce the effect required i.e. an ore deposit with Zn>Pb. Movement of the formation waters without H<sub>2</sub>S and subsequent mixing with a formation water containing H<sub>2</sub>S still remains a potentially viable option.

### Metal transport

In addition to calculating the saturation with respect to various minerals, SOLMINEQ.88 also computes the distribution of aqueous species at the composition, temperature and pressure specified. Table 22 shows the molecular weights of the Pb and

Table 22. Molecular weights of Pb and Zn complexes and percent metal in the complex as used in SOLMINEQ.88 (Kharaka et al., 1988, Table 1A)

Complex No.	Formula	Mol. wt.	Pb (%)	Complex No.	Formula	Mol. wt.	Zn (%)
25	Pb <sup>2+</sup>	207.190	100.0	27	Zn <sup>2+</sup>	65.370	100.0
148	PbCl <sup>+</sup>	242.643	85.4	158	ZnCl <sup>+</sup>	100.823	64.8
149	PbCl <sub>2</sub>	278.096	74.5	159	ZnCl <sub>2</sub>	136.276	48.0
150	PbCl <sub>3</sub> <sup>-</sup>	313.549	66.1	160	ZnCl <sub>3</sub> <sup>-</sup>	171.729	38.1
151	PbCl <sub>4</sub> <sup>2-</sup>	349.002	59.4	161	ZnCl <sub>4</sub> <sup>2-</sup>	207.182	31.6
152	PbSO <sub>4</sub>	303.252	68.3	162	ZnSO <sub>4</sub>	161.432	40.5
238	PbAce <sup>+</sup>	266.235	77.8	244	ZnAce <sup>+</sup>	124.415	52.5
239	Pb(Ace) <sub>2</sub>	325.280	63.7	245	Zn(Ace) <sub>2</sub>	183.460	35.6
240	Pb(Ace) <sub>3</sub> <sup>-</sup>	384.325	53.9	264	ZnOxy	153.388	42.6
262	PbOxy	295.208	70.2	280	ZnSuc	181.442	36.0
278	PBSuc	323.262	64.1	290	Zn(HS) <sub>2</sub>	131.514	49.7
286	Pb(HS) <sub>2</sub>	273.334	75.8	291	Zn(HS) <sub>3</sub> <sup>-</sup>	164.596	39.7
287	Pb(HS) <sub>3</sub> <sup>-</sup>	306.416	67.6	292	ZnHCO <sub>3</sub> <sup>+</sup>	126.387	51.7
288	PbCO <sub>3</sub>	267.199	77.5	293	ZnOH <sup>+</sup>	82.377	79.4
289	PbOH <sup>+</sup>	224.197	92.4	294	Zn(OH) <sub>2</sub>	99.385	65.8
				295	ZnHSOH	115.449	56.6

Ace=Acetate; Oxy=Oxylate; Suc=Succinate.

Zn complexes considered by SOLMINEQ.88, together with the percentage by weight of metal in each complex. Table 23 shows the amount of each Pb and Zn complex in RCAF93-1273A at saturation with respect to calcite, illite and quartz, without H<sub>2</sub>S, at both formation temperature (73°C) and the temperature of maximum burial (125°C). The weight of Pb and Zn in each complex was obtained using the data in Table 22.

Two features are clear from the data in Table 23. First, the majority of Pb and Zn is held as chloride complexes, mostly PbCl<sub>4</sub><sup>2-</sup> and ZnCl<sub>4</sub><sup>2-</sup>. Second, increased temperature has only minimal effect on the amount of Pb and Zn carried as chloride complexes. Table 24 shows that the addition of 1 mg/l H<sub>2</sub>S at formation temperature to RCAF93-1273A, again adjusted for saturation with calcite, illite and quartz, has almost no effect on the distribution of Pb in the various complexes, whereas the effect on the distribution of Zn is more marked, with up to nearly one-fifth being held as the ZnHSOH complex. At the higher temperatures achieved during maximum burial the effect of the addition of 1 mg/l H<sub>2</sub>S (not shown) is similar to that at the lower temperature i.e. there is only a small effect due to temperature on both metals, a negligible effect due to H<sub>2</sub>S for Pb, but a more marked change with respect to the presence of the ZnHSOH complex for Zn. With 100 mg/l H<sub>2</sub>S (Table 24), 92.7% of the Pb is held in the Pb(HS)<sub>2</sub> complex and only 5.3% as PbCl<sub>4</sub><sup>2-</sup>; 76.8% of the Zn is held in the ZnHSOH complex, 6.5% as Zn(HS)<sub>2</sub> and only 15.9% as ZnCl<sub>4</sub><sup>2-</sup>.

As might be expected, for formation waters with Zn>Pb (Table 25) the effects of temperature are still minimal. The data in Table 26 illustrate in a little more detail the effects of 1, 10 and 100 mg/l H<sub>2</sub>S on RCAF16-374D at 75°C, with adjustments for calcite, illite and quartz saturation. At 1 mg/l H<sub>2</sub>S there is essentially no effect on the distribution of the Pb complexes, but as with RCAF93-1273A there is now nearly 12% of the ZnHSOH complex. The Pb(HS)<sub>2</sub> complex is dominant at 100 mg/l H<sub>2</sub>S and the ZnHSOH complex is dominant at only 10 mg/l H<sub>2</sub>S.

Another feature of interest in all the combinations considered in Tables 23 to 26 is that increased temperature (Tables 23 and 25) reduces the amount of ionic Pb and Zn, as does increased amounts of H<sub>2</sub>S at constant temperature (Table 26). Precipitation of these metals is governed by the saturation indices of their respective sulphides, however, but the Pb<sup>2+</sup>/Zn<sup>2+</sup> ratio provides a clue as to the relative proportions of the initial precipitates.

From the above computations it is clear that Pb and Zn move mainly as chloride complexes in hot saline formation waters. While they may also move as other types of complexes in the presence of H<sub>2</sub>S, the high positive ΔG<sub>diff</sub> values imply precipitation of the metal sulphides if anything other than minute amounts of H<sub>2</sub>S are present. A scenario can be envisaged in which small amounts of H<sub>2</sub>S could strip out metal sulphides en route to a main ore deposition site, but because the ΔG<sub>diff</sub> value of sphalerite is almost half that of galena, galena will be the preferred precipitate. However, as will be noted later, sphalerite, rather than galena, is the dominant mineral deposited en route to Pine Point along the carbonate barrier complex of the Keg River Formation. We must therefore continue to consider movement of the metals in hot saline formation waters without H<sub>2</sub>S, and see if the Pb:Zn ratio can be changed by mixing at the site of ore deposition.



Table 23. Distribution of Pb and Zn among aqueous complexes in RACH93-1273A, illustrating the effect of temperature

Conditions	Calcite, illite and quartz satn. at 73°C			Calcite, illite and quartz satn. at 125°C		
	Complex (mg/l)	Pb (mg/l)	% total Pb	Complex (mg/l)	Pb (mg/l)	% total Pb
Total Pb	55 mg/l			55 mg/l		
Pb <sup>2+</sup>	0.0796	0.0796	0.1	0.0480	0.0480	<0.1
PbCl <sup>+</sup>	0.9761	0.8336	1.5	0.8490	0.7251	1.3
PbCl <sub>2</sub>	5.481	4.0833	7.4	6.565	4.8909	8.9
PbCl <sub>3</sub> <sup>-</sup>	9.992	6.6047	12.0	13.45	8.8905	16.2
PbCl <sub>4</sub> <sup>2-</sup>	72.98	43.3501	78.8	67.76	40.2494	73.2
PbSO <sub>4</sub>	0.0002	0.0001	<0.01	0.0001	0.0001	<0.01
PbCO <sub>3</sub>	0.0657	0.0509	0.1	0.2503	0.1940	0.3
PbOH <sup>+</sup>	0.0263	0.0243	<0.1	0.0308	0.0285	<0.1
			Σ99.9			Σ99.9
Total Zn	10 mg/l			10 mg/l		
Zn <sup>2+</sup>	0.0141	0.0141	<0.1	0.0024	0.0024	<0.1
ZnCl <sup>+</sup>	0.2217	0.1437	1.4	0.3047	0.1974	2.0
ZnCl <sub>2</sub>	0.2756	0.1323	1.3	0.2715	0.1304	1.3
ZnCl <sub>3</sub> <sup>-</sup>	0.5347	0.2037	2.0	0.3188	0.1215	1.2
ZnCl <sub>4</sub> <sup>2-</sup>	30.13	9.521	95.2	30.26	9.5622	95.6
ZnSO <sub>4</sub>	0.0001	<0.0001	<0.1	<0.0001	-	-
ZnHCO <sub>3</sub> <sup>+</sup>	0.0003	0.0002	<0.1	<0.0001	-	-
ZnOH <sup>+</sup>	<0.0001	-	-	<0.0001	-	-
Zn(OH) <sub>2</sub>	<<0.0001	-	-	<<0.0001	-	-
			Σ99.9			Σ100.1

Table 24. Distribution of Pb and Zn among aqueous complexes in RCAH93-1273A, illustrating the effect of temperature and added H<sub>2</sub>S

Conditions	Calcite, illite and quartz satn. at 73°C			Calcite, illite and quartz satn. at 125°C		
	55 mg/l			55 mg/l		
Total Pb	Complex (mg/l)	Pb (mg/l)	% total Pb	Complex (mg/l)	Pb (mg/l)	% total Pb
Pb <sup>2+</sup>	0.0795	0.0795	0.1	0.0035	0.0035	<<0.01
PbCl <sup>+</sup>	0.9755	0.8330	1.5	0.0615	0.0525	0.1
PbCl <sub>2</sub>	5.477	4.0804	7.4	0.476	0.3546	0.6
PbCl <sub>3</sub> <sup>-</sup>	9.986	6.6007	12.0	0.976	0.6451	1.2
PbCl <sub>4</sub> <sup>2-</sup>	72.94	43.3264	78.8	4.92	2.9225	5.3
PbSO <sub>4</sub>	0.0002	0.0001	<<0.01	<0.0001	-	-
PbCO <sub>3</sub>	0.0657	0.0509	0.1	0.0174	0.0135	<0.1
PbOH <sup>+</sup>	0.0263	0.0243	<0.1	0.0016	0.0015	<0.01
Pb(HS) <sub>2</sub>	0.0437	0.0331	<0.1	67.29	51.0058	92.7
Pb(HS) <sub>3</sub> <sup>-</sup>	<<0.0001	-	-	0.0060	0.0041	<<0.01
			Σ99.9			Σ99.9
Total Zn	10 mg/l			10 mg/l		
	Complex (mg/l)	Zn (mg/l)	% total Zn	Complex (mg/l)	Zn (mg/l)	%total Zn
Zn <sup>2+</sup>	0.0116	0.0116	0.1	0.0004	0.0004	<0.01
ZnCl <sup>+</sup>	0.1817	0.1177	1.2	0.0505	0.0327	0.3
ZnCl <sub>2</sub>	0.2259	0.1084	1.1	0.0450	0.0216	0.2
ZnCl <sub>3</sub> <sup>-</sup>	0.4383	0.1670	1.7	0.0528	0.0201	0.2
ZnCl <sub>4</sub> <sup>2-</sup>	24.69	7.802	78.0	5.019	1.5860	15.9
ZnSO <sub>4</sub>	<0.0001	-	-	<0.0001	-	-
ZnHCO <sub>3</sub> <sup>+</sup>	0.0002	0.0001	<0.1	<0.0001	-	-
Zn(OH) <sup>+</sup>	<0.0001	-	-	<0.0001	-	-
Zn(OH) <sub>2</sub>	<<0.0001	-	-	<<0.0001	-	-
Zn(HS) <sub>2</sub>	0.0001	<0.0001	<0.1	1.304	0.6481	6.5
Zn(HS) <sub>3</sub> <sup>-</sup>	<<0.0001	-	-	0.0344	0.0137	0.1
ZnHSOH	3.186	1.8033	18.0	13.56	7.6750	76.8
			Σ100.1			Σ100.0

Table 25. Distribution of Pb and Zn among aqueous complexes in RCAH116-374D, illustrating the effect of temperature

Conditions	Calcite, illite and quartz satn. at 36°C			Calcite, illite and quartz satn. at 75°C		
	10 mg/l			10 mg/l		
	Complex (mg/l)	Pb (mg/l)	% total Pb	Complex (mg/l)	Pb (mg/l)	% total Pb
Pb <sup>2+</sup>	0.0125	0.0125	0.1	0.0099	0.0099	0.1
PbCl <sup>+</sup>	0.1543	0.1318	1.3	0.1332	0.1138	1.1
PbCl <sub>2</sub>	0.5558	0.4141	4.1	0.8040	0.5990	6.0
PbCl <sub>3</sub> <sup>-</sup>	1.720	1.1369	11.4	1.700	1.1237	11.2
PbCl <sub>4</sub> <sup>2-</sup>	13.98	8.3041	83.0	13.71	8.1437	81.4
PbSO <sub>4</sub>	0.0002	0.0001	<0.01	0.0001	0.0001	<<0.1
PbCO <sub>3</sub>	0.0014	0.0011	<0.1	0.0110	0.0085	0.1
PbOH <sup>+</sup>	0.0027	0.0025	<0.1	0.0052	0.0048	<0.1
			Σ99.9			Σ99.9
Total Zn	16 mg/l			16 mg/l		
	Complex (mg/l)	Zn (mg/l)	% total Zn	Complex (mg/l)	Zn (mg/l)	%total Zn
Zn <sup>2+</sup>	0.1068	0.1068	0.6	0.0142	0.0142	<0.1
ZnCl <sup>+</sup>	0.4352	0.2820	1.7	0.2630	0.1704	1.0
ZnCl <sub>2</sub>	0.6771	0.3250	2.0	0.3407	0.1635	1.0
ZnCl <sub>3</sub> <sup>-</sup>	2.547	0.9704	6.0	0.7516	0.2864	1.8
ZnCl <sub>4</sub> <sup>2-</sup>	45.37	14.3369	89.6	48.70	15.3892	96.2
ZnSO <sub>4</sub>	0.0015	0.0006	<0.01	0.0002	0.0001	<<0.01
ZnHCO <sub>3</sub> <sup>+</sup>	0.0016	0.0008	<0.01	0.0002	0.0001	<<0.01
ZnOH <sup>+</sup>	0.0001	0.0001	<<0.01	0.0001	<0.0001	<<0.01
Zn(OH) <sub>2</sub>	<<0.0001	<<0.0001	<<0.01	<<0.0001	<<0.0001	<<0.01
			Σ99.9			Σ100.0

Table 26. Distribution of Pb and Zn among aqueous complexes in RCAH116-374D, illustrating the effect of H<sub>2</sub>S at 75°C

Conditions	Calcite, illite and quartz satn. at 75°C 1 mg/l H <sub>2</sub> S			Calcite, illite and quartz satn. at 75°C 10 mg/l H <sub>2</sub> S			Calcite, illite and quartz satn. at 75°C 100 mg/l H <sub>2</sub> S		
	10 mg/l			10 mg/l			10 mg/l		
Total Pb	Complex (mg/l)	Pb (mg/l)	% total Pb	Complex (mg/l)	Pb (mg/l)	% total Pb	Complex (mg/l)	Pb (mg/l)	% Total Pb
Pb <sup>2+</sup>	0.0089	0.0089	0.1	0.0082	0.0082	0.1	<<0.0001	-	-
PbCl <sup>+</sup>	0.1332	0.1197	1.1	0.0838	0.0714	0.7	0.0001	0.0001	<0.1
PbCl <sub>2</sub>	0.8038	0.8088	8.9	0.5048	0.5760	5.8	0.0008	0.0004	<0.1
PbCl <sub>3</sub> <sup>-</sup>	1.700	1.1227	11.2	1.088	0.7050	7.1	0.0012	0.0008	<0.1
PbCl <sub>4</sub> <sup>2-</sup>	13.71	8.1437	81.4	8.811	5.1148	61.1	0.0099	0.0068	0.1
PbSO <sub>4</sub>	0.0001	0.0001	<0.1	0.0001	0.0001	<0.1	<<0.0001	-	-
PbCO <sub>3</sub>	0.0110	0.0085	0.1	0.0089	0.0083	<0.1	<<0.0001	-	-
PbOH <sup>+</sup>	0.0062	0.0048	<0.1	0.0032	0.0030	<0.1	<<0.0001	-	-
Pb(HS) <sub>2</sub>	0.0021	0.0016	<0.1	4.908	3.7210	37.2	13.18	8.8004	89.8
Pb(HS) <sub>3</sub> <sup>-</sup>	<<0.0001	-	-	<0.0001	-	-	0.0065	0.0037	<0.1
			Σ100.8			Σ100.0			Σ100.0
Total Zn	16 mg/l			16 mg/l			16 mg/l		
	Complex (mg/l)	Zn (mg/l)	% total Zn	Complex (mg/l)	Zn (mg/l)	% total Zn	Complex (mg/l)	Zn (mg/l)	% Total Zn
Zn <sup>2+</sup>	0.0125	0.0125	0.1	0.0018	0.0018	<0.1	0.0001	-	-
ZnCl <sup>+</sup>	0.2322	0.1806	0.9	0.0232	0.0180	0.1	0.0008	0.0008	<0.1
ZnCl <sub>2</sub>	0.3008	0.1444	0.9	0.0378	0.0181	0.1	0.0012	0.0008	<0.1
ZnCl <sub>3</sub> <sup>-</sup>	0.8835	0.2828	1.8	0.0834	0.0318	0.2	0.0027	0.0010	<0.1
ZnCl <sub>4</sub> <sup>2-</sup>	42.89	13.5848	84.9	8.407	1.7086	10.7	0.1738	0.0548	0.3
ZnSO <sub>4</sub>	0.0002	0.0001	<0.1	<0.0001	-	-	<<0.0001	-	-
ZnHCO <sub>3</sub> <sup>+</sup>	0.0002	0.0001	<0.1	<0.0001	-	-	<<0.0001	-	-
ZnOH <sup>+</sup>	<0.0001	-	-	<0.0001	-	-	<<0.0001	-	-
Zn(OH) <sub>2</sub>	<<0.0001	-	-	<<0.0001	-	-	<<<0.0001	-	-
Zn(HS) <sub>2</sub>	<0.0001	-	-	0.0188	0.0078	<0.1	1.181	0.5870	3.7
Zn(HS) <sub>3</sub> <sup>-</sup>	<<0.0001	-	-	0.0001	<0.0001	<0.1	0.2240	0.0888	0.6
ZnHSOH	3.312	1.8746	11.7	25.11	14.2123	88.8	28.98	15.2504	95.4
			Σ100.1			Σ100.8			Σ100.0

## Second fluid

Based on the assumption that the Pb and Zn were carried by hot saline formation waters in the absence of  $H_2S$ , then the properties of the second fluid must include the presence of  $H_2S$ . The temperature and salinity can be variable so long as the final mixture generally corresponds to the ore fluid limits outlined previously. The maximum temperature of the second fluid is constrained to  $60^\circ C$ , the maximum subsurface temperature at Pine Point in the Pennsylvanian. Salinity can be any value up to saturation with halite and anhydrite at  $60^\circ C$ ; the maximum salinity of formation waters in the Keg River aquifer is 380,000 mg/l.

Within these general limitations it was decided to use a variety of modern surface waters from northern Alberta and the Northwest Territories, which had a wide range in salinity from fresh water to nearly 330,000 mg/l total dissolved solids. Two samples were from saline springs where chemical and isotope evidence implied dissolution of halite and anhydrite (Hitchon et al., 1969). A sample from the Salt River (Reeder et al., 1972) with 18,000 mg/l total dissolved solids also owed its salinity to dissolution of halite and anhydrite. Table 27 shows the analyses of these five surface waters, and Table 28 the  $\Delta G_{diff}$  values for common minerals at ambient temperatures. Note that Mission Spring is effectively saturated with respect to halite at ambient temperatures.

## MIXING RESULTS

Many mixing sets were run, including some for which the results were not expected to match the postulated ore fluid but were designed to understand the processes which might yield a  $Zn > Pb$  ore deposit from a  $Pb > Zn$  product mixture.

The first set of runs (Table 29) used sample RCAH93-1273A as the hot saline formation water, adjusted for calcite, quartz and illite saturation at  $125^\circ C$ . The five surface waters were mixed at their ambient temperatures. The top three lines in Table 29 show the proportions of formation water, Pb and Zn in the four mixtures and two end members. Each of the five sets includes data on the temperature, salinity, the contents of ionic Pb and Zn, the  $Pb^{2+}/Zn^{2+}$  ratio, and the pH of the mixture. Several features are of interest. First, there are *apparent* changes in the  $Pb^{2+}/Zn^{2+}$  ratio, which are accompanied by major changes in pH. Second, in general, the amounts of  $Pb^{2+}$  and  $Zn^{2+}$  are highest in the cooler moderately saline waters, and lowest in the hot saline and very dilute waters. It is quite unlikely that the second fluid would be at the ambient temperatures of the modern surface waters and so the complete sets were rerun at  $60^\circ C$  (Table 30). Note that now the temperature of each mixture is fixed for all combinations. At these higher temperatures the pH values are more realistic and no  $Pb^{2+}/Zn^{2+}$  values are below unity. There is, however, a general trend for an approach to  $Zn > Pb$  with decreased salinity, although at the salinities indicated the ratio is always  $> 1.5$ .

The composition of the mixtures in bold in Table 29 were re-entered into SOLMINEQ.88 and the  $CO_2$  option invoked. This adjusted the composition of the mixture to calcite saturation, which is what would be expected in nature. The results (Table 31) show that for the 20:80 mixture with La Saline the true subsurface  $Pb^{2+}/Zn^{2+}$  ratio is 1.35

Table 27. Chemical composition (mg/l), physical properties and ancillary data for modern surface waters used in the mixing model

	M-6*	M-7*	M-8*	La Saline **	Mission Spring**
Location	60° 44'N, 114° 56'W	60° 3'N, 112° 47'W	59° 51'N, 111° 58'W	-	-
Source	Buffalo River (198.1 m asl; ~47x10 <sup>3</sup> l/s)	Little Buffalo River (228.6 m asl; ~250 l/s)	Salt River (198.1 m asl; ~30 l/s)	nr. Athabasca River	nr. Slave River
Li	<0.005	0.21	0.031	0.96	0.26
Na	4.8	27.2	8350	25600	133000
K	1.1	2.0	7.7	64	82
Mg	5.8	36.5	68.5	456	458
Ca	22.6	261.0	607	1830	1020
Sr	0.04	1.8	7.3	37	29
Cu	0.004	0.002	0.003	0.11	0.07
Zn	0.005	0.004	0.004	0.05	0.05
Fe	0.07	0.02	0.01	0.11	0.01
Mn	<0.001	<0.001	0.002	<0.04	0.80
U	0.0006	0.0014	0.017	n.d.	n.d.
B	0.036	0.154	0.393	n.d.	n.d.
PO <sub>4</sub> (ortho, ftd.)	0.03	0.01	n.d.	n.d.	n.d.
NO <sub>3</sub>	0.14	<0.01	0.06	n.d.	n.d.
SiO <sub>2</sub>	2.8	3.7	1.2	n.d.	n.d.
F	0.11	0.51	0.50	n.d.	n.d.
Cl	2.3	28.4	9450	40200	191000
SO <sub>4</sub>	17.2	561	1332	4780	3850
HCO <sub>3</sub>	78.4	222	183	351	124
Total solids (calc.)	133.61	1145.05	18009.58	73317.23	329564.19
Cations (anal., meq/l)	1.845	17.306	312.500	1244.984	5876.528
Anions (anal., meq/l)	1.684	16.147	297.309	1241.201	5469.603
Cations (calc., meq/l)	1.800	13.719	299.031	1153.564	5195.415
Anions (calc., meq/l)	1.638	12.560	283.839	1149.783	4788.442
pH (laboratory)	n.d.	n.d.	n.d.	7.51	7.08
pH (field, sampling temp.)	7.50 (17.5°C)	7.80 (18.3°C)	8.00 (22.0°C)	n.d.	n.d.
Density (15.56°C)	1.0001	1.0008	1.0124	1.049	1.206
Conductivity (µmho/cm)	185.3	1580	n.d.	0.102	0.0314

n.d.= Not determined

Additional determinations: M-6 Ni<0.002; PO<sub>4</sub> (ortho, ftd.) 0.01; PO<sub>4</sub> (Σ, unftd.) 0.25

M-7 Ni<0.002; PO<sub>4</sub> (ortho, ftd.) 0.01; PO<sub>4</sub> (Σ, unftd.) 0.04

M-8 Ni < 0.02

La Saline Rb 0.12; Br 14; I trace

Mission Spring Rb 0.22; Br 46; I 1

\*from Reeder et al. (1972, Table 3)

\*\*from Hitchon et al. (1969, Table 1)

Table 28. Saturation indices ( $\Delta G_{diff}$ ) for selected minerals at ambient temperatures in the modern surface waters used in the mixing model

	$\Delta G_{diff}$				
	M-6	M-7	M-8	La Saline	Mission Spring
Calcite ( $\text{CaCO}_3$ )	-1.0	1.1	1.3	1.6	0.07
Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ )	-1.1	2.6	3.2	4.4	1.8
Strontianite ( $\text{SrCO}_3$ )	-4.0	-1.2	-0.7	-0.2	-1.4
Siderite ( $\text{FeCO}_3$ )	-1.8	-2.0	-2.6	-1.5	-1.5
Rhodochrosite ( $\text{MnCO}_3$ )	n.d.	n.d.	-3.5	n.d.	-3.9
Smithsonite ( $\text{ZnCO}_3$ )	-4.6	-4.0	-4.3	-3.5	-7.9
Anhydrite ( $\text{CaSO}_4$ )	-4.0	-1.2	-1.3	-0.6	-1.6
Celestite ( $\text{SrSO}_4$ )	-5.2	-1.6	-1.5	-0.6	-1.4
Halite ( $\text{NaCl}$ )	-12.6	-10.3	-4.1	-2.6	-0.4
Fluorite ( $\text{CaF}_2$ )	-3.8	-1.1	-1.2	n.d.	n.d.
Apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ )	1.8	6.0	n.d.	n.d.	n.d.
Quartz	-0.3	-0.2	-0.8	n.d.	n.d.

n.d.=Not determined

Table 29. Mixing RCAH93-1273A (calcite, quartz and illite saturation at 125°C) with modern surface waters at ambient temperatures

Formation water (%)	100	80	60	40	20	0
Pb (mg/l)	55	44.49	33.76	22.79	11.55	-
Zn (mg/l)	10	8.09	6.14	4.15	2.10	all <0.05
<b>Buffalo River (M-6)</b>						
Temperature (°C)	125	103.5	82	60.5	39	17.5
Salinity (mg/l)	196236	158759	120506	81391	41307	134
Pb <sup>2+</sup> (mg/l)	0.0480	0.2072	0.2636	0.0427	0.0002	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.7171	1.1850	0.9575	0.0001	0.0047
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	0.29	0.22	0.04	2.0	-
pH	5.18	6.88	8.63	9.72	11.8	7.50
<b>Little Buffalo River (M-7)</b>						
Temperature (°C)	125	103.7	82.3	61	39.6	18.3
Salinity (mg/l)	196236	158944	120833	81968	42095	1145
Pb <sup>2+</sup> (mg/l)	0.0480	0.2059	0.2435	0.0390	0.0002	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.6794	1.1340	0.9028	0.00015	0.0031
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	0.30	0.21	0.04	1.3	-
pH	5.18	7.14	8.67	9.73	11.75	7.80
<b>Salt River (M-8)</b>						
Temperature (°C)	125	104.4	83.8	63.2	42.6	22
Salinity (mg/l)	196236	162034	127182	91616	55254	18010
Pb <sup>2+</sup> (mg/l)	0.0480	0.1909	0.2139	0.0391*	0.00021	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.4956	0.8171	0.7794*	0.00025	0.0030
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	0.39	0.26	0.05	0.84	-
pH	5.18	6.98	8.59	9.62	11.6	8.0
<b>La Saline</b>						
Temperature (°C)	125	105	85	65	45	25
Salinity (mg/l)	196236	172316	148087	123526	98612	73317
Pb <sup>2+</sup> (mg/l)	0.0480	0.1487	0.1349	0.0318	0.0004	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.3223	0.4307	0.4181	0.0008	0.0194
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	0.46	0.31	0.08	0.5	-
pH	5.18	7.43	8.65	9.62	11.34	7.51
<b>Mission Spring</b>						
Temperature (°C)	125	103.6	82.2	60.8	39.4	18
Salinity (mg/l)	196236	224246	251537	278149	304139	329564
Pb <sup>2+</sup> (mg/l)	0.0480	0.0502	0.0220	0.0087	0.0026	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.1857	0.0832	0.0334	0.0100	0.00015
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	0.27	0.26	0.26	0.26	-
pH	5.18	5.48	5.54	5.64	5.84	7.20

\*No convergence in 100 iterations during species distribution; results may be in error



Table 30. Mixing RCAH93-1273A (calcite, quartz and illite saturation at 125°C) selected modern surface waters (60°C; with calcite saturation)

Formation water (%)	100	80	60	40	20	0
Temperature (°C)	125	112	99	86	73	60
Pb (mg/l)	55	44.49	33.76	22.79	11.55	-
Zn (mg/l)	10	8.09	6.14	4.15	2.10	all <0.05
<b>Buffalo River (M-6)</b>						
Salinity (mg/l)	196236	158759	120506	81391	41307	134
Pb <sup>2+</sup> (mg/l)	0.0480	0.1682	0.3304	0.6530	0.9408	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.0514	0.1165	0.2885	0.5504	0.0039
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	3.3	2.8	2.3	1.7	-
pH	5.18	5.29	5.43	5.62	5.93	7.36
<b>Little Buffalo River (M-7)</b>						
Salinity (mg/l)	196236	158944	120883	81968	42095	1145
Pb <sup>2+</sup> (mg/l)	0.0480	0.1680	0.3296	0.6440	0.8350	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.0513	0.1163	0.2879	0.5484	0.0028
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	3.3	2.8	2.2	1.5	-
pH	5.18	5.32	5.48	5.69	5.95	6.50
<b>Salt River (M-8)</b>						
Salinity (mg/l)	196236	162034	127182	91616	55254	18010
Pb <sup>2+</sup> (mg/l)	0.0480	0.1570	0.2822	0.4991	0.6328	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.0476	0.0970	0.2099	0.3731	0.0019
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	3.3	2.9	2.4	1.7	-
pH	5.18	5.32	5.48	5.70	6.00	6.60
<b>La Saline</b>						
Salinity (mg/l)	196236	172316	148087	123526	98612	73317
Pb <sup>2+</sup> (mg/l)	0.0480	0.1255	0.1709	0.2181	0.2155	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.0371	0.0547	0.0781	0.0925	0.0054
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	3.4	3.1	2.8	2.3	-
pH	5.18	5.33	5.47	5.61	5.77	5.94
<b>Mission Spring</b>						
Salinity (mg/l)	196236	224246	251537	278149	304139	329564
Pb <sup>2+</sup> (mg/l)	0.0480	0.0417	0.0186	0.0076	0.0023	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.0112	0.0048	0.0019	0.0006	<<0.0001
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	3.7	3.9	4	3.8	-
pH	5.18	5.23	5.31	5.43	5.67	6.63

Table 31. Examples of the effect of adjusting mixtures of RCAH93-1273A (calcite, quartz and illite saturation at 125°C) and two surface springs (ambient temperatures) for calcite saturation at the respective mixing temperature

		Not adjusted	Adjusted for calcite saturation
RCAH93-1273 (20%) and La Saline (80%) 45°C, 98612 mg/l salinity			
	Pb <sup>2+</sup> (mg/l)	0.0004	0.2531
	Zn <sup>2+</sup> (mg/l)	0.0008	0.1869
	Pb <sup>2+</sup> /Zn <sup>2+</sup>	0.5	1.35
	pH	11.34	5.35
RCAH93-1273A (80%) and Mission Spring (20%) 103.6°C, 224246 mg/l salinity			
	Pb <sup>2+</sup> (mg/l)	0.502	0.0268
	Zn <sup>2+</sup> (mg/l)	0.1857	0.0024
	Pb <sup>2+</sup> /Zn <sup>2+</sup>	0.27	11.2
	pH	5.48	5.41

and the pH a more realistic 5.35. Similarly, the 80:20 mixture with Mission Spring now has a pH of 5.41 and the Pb<sup>2+</sup>/Zn<sup>2+</sup> ratio approaches more closely that of the parent hot saline formation water.

Among the modern surface waters only La Saline and Mission Spring have salinities which when mixed with RCAH93-1273A produce a potential ore fluid of approximately the correct salinity. Thus the remainder of the mixing runs discussed here will be limited to mixtures with these two surface water end members. As expected based on the information in Table 20, the adjustment of the saline surface waters to quartz saturation (Table 32) or quartz and illite saturation (not shown) had no effect on the proportions of ionic Pb and Zn or on the pH when mixed with RCAH93-1273A. Although not a viable option based on earlier discussions, two mixing sets were run (Table 33) with 100 mg/l H<sub>2</sub>S added to RCAH93-1273A. As expected, the amounts of Pb<sup>2+</sup> and Zn<sup>2+</sup> are much lower, as is the pH, compared with runs without H<sub>2</sub>S. The Pb<sup>2+</sup>/Zn<sup>2+</sup> values <1 are false, as can be seen in Table 34 where the mixture in bold in Table 33 was re-entered into SOLMINEQ.88 and values recalculated for calcite saturation at the mixing temperature (112°C).

The final data set using RCAH93-1273A and the two saline springs are runs with 100 mg/l H<sub>2</sub>S added to the saline springs, similar to the generally accepted model (Table 35). At no combination is Zn<sup>2+</sup>>Pb<sup>2+</sup>.

Formation water RCAH116-374D was used in mixing runs as an example of a potential ore fluid with Zn>Pb. It was not necessary to match all the runs made with

Table 32. Mixing RCAH93-1273A (calcite, quartz and illite saturation at 125°C) with selected modern surface waters (calcite and quartz saturation at 60°C)

Formation water (%)	100	80	60	40	20	0
Temperature (°C)	125	112	99	86	73	60
Pb (mg/l)	55	44.49	33.76	22.79	11.55	-
Zn (mg/l)	10	8.09	6.14	4.15	2.10	<0.05
La Saline						
Salinity (mg/l)	196236	172319	148091	123533	98621	73329
Pb <sup>2+</sup> (mg/l)	0.0480	0.1255	0.1709	0.2181	0.2155	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.0371	0.0547	0.0781	0.0925	0.0054
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	3.4	3.1	2.8	2.3	-
pH	5.18	5.33	5.47	5.61	5.77	5.94
Mission Spring						
Salinity (mg/l)	196236	224248	251540	278152	304144	329570
Pb <sup>2+</sup> (mg/l)	0.0480	0.0417	0.0186	0.0076	0.0023	-
Zn <sup>2+</sup> (mg/l)	0.0024	0.0112	0.0048	0.0019	0.0006	<<0.0001
Pb <sup>2+</sup> /Zn <sup>2+</sup>	20	3.7	3.9	4	3.8	-
pH	5.18	5.23	5.31	5.43	5.67	6.63

Table 33. Mixing RCAH93-1273A (calcite, quartz and illite saturation, 100 mg/l H<sub>2</sub>S, 125°C) with modern saline springs (calcite and quartz saturation at 60°C)

Formation water (%)	100	80	60	40	20	0
Temperature (°C)	125	112	99	86	73	60
Pb (mg/l)	55	44.49	33.76	22.79	11.55	-
Zn (mg/l)	10	8.09	6.14	4.15	2.10	<0.05
La Saline						
Salinity (mg/l)	196336	172400	148155	123577	98644	73329
Pb <sup>2+</sup> (mg/l)	0.0035	0.00014	0.0001	0.00008	0.00007	-
Zn <sup>2+</sup> (mg/l)	0.0004	0.00017	0.00009	0.00004	0.00002	0.0054
Pb <sup>2+</sup> /Zn <sup>2+</sup>	8.75	0.8	1.1	2	3.5	-
pH	5.03	5.16	5.32	5.49	5.69	5.94
Mission Spring						
Salinity (mg/l)	196336	224324	251596	278188	304161	329570
Pb <sup>2+</sup> (mg/l)	0.0035	0.0002	0.0002	0.0002	0.00017	-
Zn <sup>2+</sup> (mg/l)	0.0004	0.00028	0.00022	0.00015	0.00006	<<0.0001
Pb <sup>2+</sup> /Zn <sup>2+</sup>	8.75	0.7	0.9	1.3	2.8	-
pH	5.03	5.04	5.10	5.20	5.41	6.63

Table 34. Example of the effect of adjusting a mixture of RCAH93-1273A (calcite, quartz and illite saturation, 125°C, 100 mg/l H<sub>2</sub>S) and Mission Spring (calcite and quartz saturation at 60°C) for calcite saturation at the mixing temperature

		Not adjusted	Adjusted for calcite saturation
RCAH93-1273 (80%) and Mission Spring (20%) 112°C, 224324 mg/l salinity			
	Pb <sup>2+</sup> (mg/l)	0.0002	0.0012
	Zn <sup>2+</sup> (mg/l)	0.00028	0.00018
	Pb <sup>2+</sup> /Zn <sup>2+</sup>	0.7	6.6
	pH	5.04	5.18

Table 35. Mixing of modern spring waters (calcite and quartz saturation, 100 mg/l H<sub>2</sub>S at 60°C) with RCAH93-1273A (calcite, quartz and illite saturation at 125°C)

Formation water (%)	0	20	40	60	80	100
Temperature (°C)	60	73	86	99	112	125
Pb (mg/l)	-	11.33	22.49	33.48	44.3	55
Zn (mg/l)	<0.05	2.1	4.12	6.11	8.07	10
H <sub>2</sub> S (mg/l)	100	79.3	59.0	39.1	19.4	0
La Saline						
Salinity (mg/l)	73429	98699	123589	148127	172336	196236
Pb <sup>2+</sup> (mg/l)	-	0.00007	0.0006	0.0050	0.0347	0.0480
Zn <sup>2+</sup> (mg/l)	<<0.00001	0.000006	0.00003	0.0002	0.0008	0.0024
Pb <sup>2+</sup> /Zn <sup>2+</sup>	-	11.6	20	25	43	20
pH	5.82	5.71	5.56	5.41	5.28	5.18
Mission Spring						
Salinity (mg/l)	329670	304227	278217	251585	224271	196236
Pb <sup>2+</sup> (mg/l)	-	0.00003	0.00028	0.0022	0.0139	0.0480
Zn <sup>2+</sup> (mg/l)	<<0.00001	0.000003	0.00002	0.0001	0.0005	0.0024
Pb <sup>2+</sup> /Zn <sup>2+</sup>	-	10	14	22	27.8	20
pH	6.67	5.91	5.63	5.42	5.27	5.18

RCAH93-1273A and only the following were made. Table 36 shows that when mixed with the water from La Saline the  $Pb^{2+}/Zn^{2+}$  remains  $<1$  and decreases steadily at lower salinities and temperatures. The mixture in bold in Table 36 was re-entered and adjustment made for calcite saturation at the mixing temperature. As can be seen (Table 37) there was little difference in the  $Pb^{2+}/Zn^{2+}$  ratio, and certainly nothing like the changes seen with RCAH93-1273A. Finally, Table 38 gives results for mixing when La Saline had 100 mg/l  $H_2S$  added. The amounts of ionic Pb and Zn are extremely low, as anticipated and there is no fundamental change in the  $Pb^{2+}/Zn^{2+}$  ratio. Results with Mission Spring are as expected.

Table 36. Mixing of RCAH116-374D (calcite, quartz and illite saturation at 75°C) with La Saline (calcite, quartz and illite saturation at 60°C)

Formation water (%)	100	<b>80</b>	60	40	20	0
Temperature (°C)	75	<b>72</b>	69	66	63	60
Salinity (mg/l)	217435	<b>189459</b>	161091	132304	103064	73329
Pb	10	<b>8.06</b>	6.09	4.10	2.07	-
Zn	16	<b>12.91</b>	9.78	6.59	3.35	0.05
$Pb^{2+}$	0.0099	<b>0.0165</b>	0.0238	0.0327	0.0353	-
$Zn^{2+}$	0.0142	<b>0.0413</b>	0.0645	0.0994	0.1297	0.0054
$Pb^{2+}/Zn^{2+}$	0.7	<b>0.4</b>	0.37	0.33	0.27	-
pH	5.68	<b>5.69</b>	5.71	5.77	5.84	5.94

Table 37. Effect of adjusting mixture 80:20 RCAH116-374D and La Saline for calcite saturation at the mixing temperature

		Not adjusted	Adjusted for calcite saturation
RCAH116-374D (80%) and La Saline (20%) 72°C, 189459 mg/l salinity			
	$Pb^{2+}$ (mg/l)	0.0165	0.0147
	$Zn^{2+}$ (mg/l)	0.0413	0.0243
	$Pb^{2+}/Zn^{2+}$	0.4	0.6
	pH	5.69	5.69

Table 38. Mixing of RCAH116-374D (calcite, quartz and illite saturation at 75°C) with La Saline (calcite, quartz and illite saturation at 60°C with 100 mg/l H<sub>2</sub>S)

Formation water (%)	100	80	60	40	20	0
Temperature (°C)	75	72	69	66	63	60
Salinity (mg/l)	217435	189476	161127	132360	103141	73429
H <sub>2</sub> S (mg/l)	0	19.3	39.0	58.9	79.3	100
Pb	10	8.06	6.09	4.10	2.07	-
Zn	16	12.91	9.78	6.59	3.35	0.05
Pb <sup>2+</sup>	0.0099	0.00025	0.00002	<<0.0001	<<0.0001	-
Zn <sup>2+</sup>	0.0142	0.00041	0.00008	0.00002	<0.0001	<<0.0001
Pb <sup>2+</sup> /Zn <sup>2+</sup>	0.7	0.6	0.25	-	-	-
pH	5.68	5.51	5.57	5.63	5.71	5.82

### INTERPRETATION

The distribution of Pb and Zn in formation waters in northern Alberta has been examined thoroughly and the observation that 75% of the formation waters have Pb>Zn seems sound. In the Keg River aquifer there is no pattern to the distribution of the Pb:Zn ratio in formation waters, and indeed it appears that there is no stratigraphic or areal preference for Zn>Pb anywhere in the stratigraphic column. On this basis it is reasonable to assume that it is unlikely that present formation waters could have given rise, directly, to the Pine Point ore deposit.

The contents of Pb and Zn in some of the formation waters from the Keg River aquifer are high enough for them to be considered as a potential ore source, were it not for the proportion of these metals in many of the samples. Computations using SOLMINEQ.88 failed to change, significantly, the proportions of Pb<sup>2+</sup> to Zn<sup>2+</sup> in a formation water with Pb>Zn, although the trends suggest that this might be possible in certain conditions -- which, incidentally, are not within the limits of deposition of the Pine Point ore as determined from fluid inclusion, isotope and geochemical data. For a formation water with Zn>Pb there are many conditions which could yield a Zn>Pb deposit; because of the much lower  $\Delta G_{diff}$  values for sphalerite compared with galena under a wide variety of possible mixing conditions, galena will be the initial sulphide deposited, as is the case at Pine Point (see comments in Table 2). The SOLMINEQ.88 runs revealed that although Pb and Zn are mainly held as chloride complexes in the saline formation waters other complexes dominate in the presence of H<sub>2</sub>S. This means that, as commonly suggested, the ore metals must be transported in a solution without H<sub>2</sub>S and it is at the ore-deposition site that the metals come in contact with reducing conditions. Mixing models using SOLMINEQ.88 under a variety of conditions failed to produce Pb<sup>2+</sup>/Zn<sup>2+</sup> ratios which would yield a Zn>Pb deposit, except when Zn>Pb in the hot saline formation water.

The final conclusion must be that it seems highly unlikely that present formation waters could have yielded the Pine Point ore deposit. One may speculate that in

Pennsylvanian time the formation waters were dominantly Zn>Pb but there is no apparent justification for such a contention. Further, because the salinity and other properties of formation waters are temperature dependent (with some exceptions such as the presence of evaporites or infiltration of meteoric water) it could well be that the contents of trace metals were much lower in Pennsylvanian time. Put another way, the present high contents of Pb and Zn in Devonian aquifers may be, in part, a reflection of water-rock reactions at the time of maximum burial.

The conclusion that formation waters were not the source of the metals in the Pine Point ore deposit is almost anathema to one who has advocated such a scenario for many years! It does, however, bring forward another scenario which will be dealt with in Part C of this report and which, if correct, has considerable implications for exploration.

**PART C. SOURCE OF THE PINE POINT ORE FLUID**



## INTRODUCTION

Mississippi Valley type ore deposits were classified by Briskey (1986) as either Southeast Missouri Pb-Zn or Appalachian Zn (carbonate-hosted Pb-Zn and carbonate-hosted Zn, respectively). They form a continuum and in a general way define a larger class of geologically complex stratabound carbonate-hosted deposits containing variable proportions of Pb and Zn. None cited by Briskey (1986) was a pure end-member deposit. Therefore, if their trace metals originated from formation waters, one should expect both Pb and Zn to be present. Indeed, it might be reasonable to assume that the formation waters giving rise to a Zn>Pb deposit would also have Zn>Pb. This would be an especially valid assumption in a mixing model scenario in which all the trace metals were precipitated at the ore-deposition site by H<sub>2</sub>S. However, with respect to Pine Point, the conclusion reached in the first two parts of this report indicated that formation waters from northern Alberta were not the source of the metals at Pine Point. Two fundamental questions arise from this conclusion: (1) are the formation waters of northern Alberta somehow unique with respect to their contents of Pb and Zn?; and (2) if so, what other source is likely for these metals? This part of the report will attempt to answer both questions and suggest an exploration strategy for the search for similar Zn-Pb deposits in Alberta.

### Pb-Zn RATIO IN FORMATION WATERS

As noted above, many authors, including this one, have cited formation waters as the source of Pb and Zn in Mississippi Valley type ore deposits without benefit of the appropriate trace metal determinations. A search of the more recent literature revealed that appropriate data were available for several basins (Table 39). Only in the northern Alberta Basin are formation waters characterized by Pb>Zn. Equally interesting is the fact that all brines from the Canadian Shield have Pb>Zn. This is additional support for an origin of the Canadian Shield brines from formation waters in strata since removed from the shield by erosion. Clearly, formation waters in northern Alberta, and probably those throughout the western Canada sedimentary basin, are unusual, perhaps unique, in their proportions of Pb and Zn. It is completely beyond the scope of this report to speculate on the reason for this characteristic.

Determinations of Pb and Zn are also available for brines from two geothermal areas (Table 39) where the brines have been suggested as possible ore-bearing fluids. The majority have Zn>Pb. This observation implies that a source of the metals at Pine Point from geothermal brines cannot be ruled out, even though geothermal brines are not present now in northern Alberta. There is no information on Pb and Zn in modern hot springs from western Canada which could conceivably serve as an analogue. Thus evidence for a source of the Zn and Pb at Pine Point from geothermal brines must be deduced from other types of information.

Table 39. Proportions of Pb and Zn in formation waters and geothermal brines

Location	No. of Samples			Reference
	Pb>Zn	Zn>Pb	Insufficient Data	
<u>Formation waters</u>				
Alberta	101	34	62	This study
Arkansas	1	10	11	Carpenter and Trout (1978), Carpenter (1979)
Michigan (southern)	-	2	3	Carpenter (1979)
Mississippi (central)	-	73	8	Carpenter et al. (1974)
Mississippi (Salt Dome basin)	-	18	-	Kharaka et al. (1987)
<u>Geothermal brines</u>				
Cheleken	3	8	-	Lebedev and Nikitina (1968)
Salton Sea	-	3	-	Muffler and White (1969), McKibben et al. (1987)
<u>Canadian Shield brines</u>	12	-	-	Frape and Fritz (1987)

### GEOHERMAL FLUID SOURCE FOR THE PINE POINT ORE

In the absence of an analysis of the geothermal ore-bearing fluid, other than whatever information can be garnered from fluid inclusion studies, evidence for an ore source from a geothermal fluid must be circumstantial. Indirect evidence is the inability of the majority of present formation waters to yield a Zn>Pb deposit within the limits proscribed from studies of fluid inclusions. Previous discussion related to the supposed temperature at the time of ore deposition concluded that the system required the input of heat. If formation waters did not yield the trace metals then it seems unlikely that they supplied the heat. Therefore, (1) the absence of a correlation between high geothermal gradients and radiogenic heat production by basement rocks observed along the Great Slave Lake Shear Zone by Bachu and Burwash (1991), and (2) the fluid inclusion evidence of Aulstead and Spencer (1985) for a thermal anomaly 300 km downdip from Pine Point both point to a long-term geothermal anomaly along this zone of weakness. This suggests that hot fluids rising through this shear zone could be the source of the Pine Point ores. As first observed by Campbell (1966), there is a strong relation between the location of the various ore bodies and the McDonald fault system, which is the surface manifestation of the underlying shear zone.

Geochemical evidence is likewise circumstantial. Cumming et al. (1990) found that the Pb isotopes of galena from Pine Point were remarkably uniform over a mineralized area of several hundred square kilometres. Further, they were nonradiogenic and contrasted markedly with Pb isotopes reported for Devonian carbonate-hosted Pb-Zn deposits of the Mackenzie platform to the north. Indeed, as noted by Nakai et al. (1993), the homogeneity and nonradiogenic Pb isotope compositions of galena from the Pine Point district are quite different from those of galena-rich mid-continent Mississippi Valley type deposits such as the Tri-State district. The difference could be explained if the Pine Point ore fluid was of deep-seated origin because the Pb in the other Mississippi Valley type deposits is believed to come ultimately from sedimentary rocks such as shales or carbonates, likely a mixed source with respect to Pb isotopes. The ore fluid need not have a high salinity, and probably did not, because the salinity and S isotopes could most easily be supplied by brines from the Keg River aquifer which would be near saturation with respect to halite and anhydrite due to the adjacent evaporites.

The earlier discussion on the age of the ore suggested a Late Pennsylvanian age, based on Pb isotopes (Cumming and Robertson, 1969; Cumming et al., 1990). Using Rb-Sr dating of sphalerite, Nakai et al. (1993) suggested an age of  $361 \pm 13$  Ma, or the end of the Late Devonian (Famennian). Neither date is close to the postulated date of maximum hydraulic heads in basinal formation waters related to the early Cenozoic Cordilleran deformation (Garven, 1985). But it must be noted that if the ore source was geothermal fluids rising along the Great Slave Lake Shear Zone it is only necessary to have the "Presqu'ileized" dolomite in place with saline formation waters containing H<sub>2</sub>S for an ore site to be ready for the appropriate heat and trace metals. An analogy with some deep sea 'smokers' comes to mind, though the pressures and geochemistry differ.

## SUMMARY

For almost three decades, discussion on the origin of the Zn>Pb ore deposit at Pine Point has swung from a deep-seated source along the adjacent fault system to a source from formation waters deep in the sedimentary basin. Most authors recognized the need for an input of heat and metals, with or without implying a mixing model. Yet no one, not even the present author, had the benefit of determinations of both Zn and Pb in at least one of the proposed sources of the metals.

Using a new data base of detailed analyses of formation waters in northern Alberta it has been shown that 75% of them have Pb>Zn. Not only does the proportion of these metals differ markedly from that found in formation waters in other sedimentary basins close to or containing Zn-Pb Mississippi Valley type deposits, but it differs from geothermal brines such as those at Chelekan and Salton Sea, also believed to be ore fluids. The only comparable suite of brines is from the Canadian Shield. Thus the northern Alberta Basin, and probably the western Canada sedimentary basin, may be unique with respect to Pb and Zn in formation waters.

But apart from this special feature of these formation waters, it has proved impossible to derive a Zn>Pb ore from formation water with Pb>Zn, at least using the SOLMINEQ.88 computer code. Sverjensky (1984), in an elegant study, showed Zn-rich

and Pb-rich phases could be deposited from formation waters by means of sequences of reactions with aquifer minerals. Simplistically, sandstones correlated with Pb-rich ores and carbonates with Zn-rich ores. However, pH values needed to be of the order of 4.5, somewhat below the range found for most Keg River and Granite Wash formation waters after adjustment for calcite saturation at formation temperature (Table 17). If, instead of adjusting for calcite saturation at reservoir temperature the adjustment is made with respect to dolomite saturation, the pH of the two test samples fell to 4.44 and 5.08 for RCAH93-1273A and RCAH116-374D, respectively. At these conditions calcite is undersaturated and illite strongly undersaturated. As noted by Sverjensky (1984), such very low pH values allow the transport of small but significant quantities of metals as chloride complexes in the presence of dissolved H<sub>2</sub>S. Based on the data in Table 17 such very low pH values would be far from the norm for any aquifer likely to contain possible ore-bearing formation waters. And still unexplained would be (1) the unusual Pb isotope characteristics and (2) the heat input needed, bearing in mind that the age-dating using sphalerite now places the time of ore-deposition at late Famennian. Overburden at Pine Point at that time might have been as low as 1 km (Fig. 15); this implies a source of the formation waters even farther away in the basin where overburden was even greater and was sufficient to yield the ore-deposition temperature.

None of the above arguments is conclusive on its own, but the consensus is that the source of heat and metals was from geothermal fluids arising along the Great Slave Lake Shear Zone in Late Devonian time. At the site of the ore deposit these fluids met saline formation waters containing H<sub>2</sub>S which came from the adjacent evaporites. This scenario is consistent with (1) a nonradiogenic mantle source for the Pb; (2) a heat anomaly along the shear zone, which is reflected to the present day; (3) the close relation of the individual ore deposits to the Macdonald fault; (4) the common Zn>Pb proportions in present geothermal fluids; (5) the need to dispense with extra long distance travel of formation waters because of the earlier timing of ore deposition and hence lower overburden at the time; (6) the possibly unique nature of formation waters in northern Alberta with respect to the proportions of Pb and Zn and the difficulty of deriving a Zn>Pb deposit except at very low pH values which would be quite unusual; (7) a source of the S from Middle Devonian sea water SO<sub>4</sub>; and (8) highly saline fluid inclusions resembling almost saturated evaporite brines.

## SIGNIFICANCE FOR EXPLORATION

In a scenario in which the source of the ore at Pine Point was formation waters, exploration for further deposits would include, but would not be limited to: (1) determination of the present regional geochemical characteristics of the formation waters; (2) evaluation of the present hydrogeological and geothermal regimes; and (3) extrapolation of these geochemical, geothermal and hydrogeological aspects back to the time of deposition to determine the loci of other deposits.

In the scenario suggested by the present study attention has to be focussed on: (1) the location of suitable shear zones and faults up which geothermal fluid might have migrated; and (2) the location of appropriate brines or at least saline formation waters with

H<sub>2</sub>S, although there is no compelling reason why a "second Pine Point" should have a saline ore fluid.

Traces of sphalerite and galena are common in many sedimentary basins, especially in association with carbonate rocks. Hitchon (1977) showed the distribution of Pb and Zn occurrences in Devonian strata of Alberta and adjacent regions of British Columbia and the southern Northwest Territories. Figure 17 expands on this study, with specific reference to Alberta. At first glance the distribution is random, but is in fact mostly related to major crustal discontinuities. Ross and Stephenson (1989) have described the basement structure of Alberta and the three crustal discontinuities which segment the basement, namely, from north to south, the Great Slave Lake Shear Zone, the Snowbird Tectonic Zone (and associated Thorsby Low), and the Vulcan Low. Five occurrences of sphalerite in Keg River and Muskeg aquifers lie on or close to the Great Slave Lake Shear Zone, as does Pine Point. In central Alberta four sphalerite occurrences in Woodbend aquifers lie close to the Thorsby Low, as does a sphalerite and galena occurrence in the Winterburn Group. Indeed, the carbonate reefs of the Rimbey-Meadowbrook reef chain are apparently associated with the Thorsby Low and the Rimbey Arc (Ross and Stephenson, 1989). These two major crustal discontinuities thus appear to account for more than half the occurrences so far recorded. Faults involving the crystalline basement are known on the Peace River Arch (Osadetz, 1989), and while not of the same significance as the three major crustal discontinuities it is interesting to note that the only two reported occurrences of sphalerite in Wabamun aquifers outside the thrustfold belt are found in the Peace River Arch where Wabamun strata lie unconformably on Precambrian basement and close to faults in the crystalline basement. All other occurrences remain unexplained, although the Oldman River galena and sphalerite lie in fault zones in the thrustfold belt of southern Alberta (close to the Vulcan Low).

Osadetz (1989) has noted that three types of faults occur throughout the southern Interior Platform: (1) normal faults observed or inferred to cut crystalline basement (e.g. on the Peace River Arch); (2) normal faults that do not reach basement; and (3) reverse faults that are Laramide compressive structures. Therefore, exploration should be concentrated first on major crustal discontinuities and second on normal faults which cut the crystalline basement. Until more information is available on fluid inclusions in some of the sphalerite occurrences shown in Fig. 17 it is problematic whether a secondary criterion should be the presence of saline formation waters. However, consideration should always be given to the presence of H<sub>2</sub>S in the formation waters in the Phanerozoic aquifers at the time of ore deposition. Of critical importance to confirming this concept outside the Pine Point area would be Pb isotopes on galena. If found along a major crustal discontinuity they should show mantle characteristics, be nonradiogenic, and probably close in isotope ratios to the Pine Point samples.

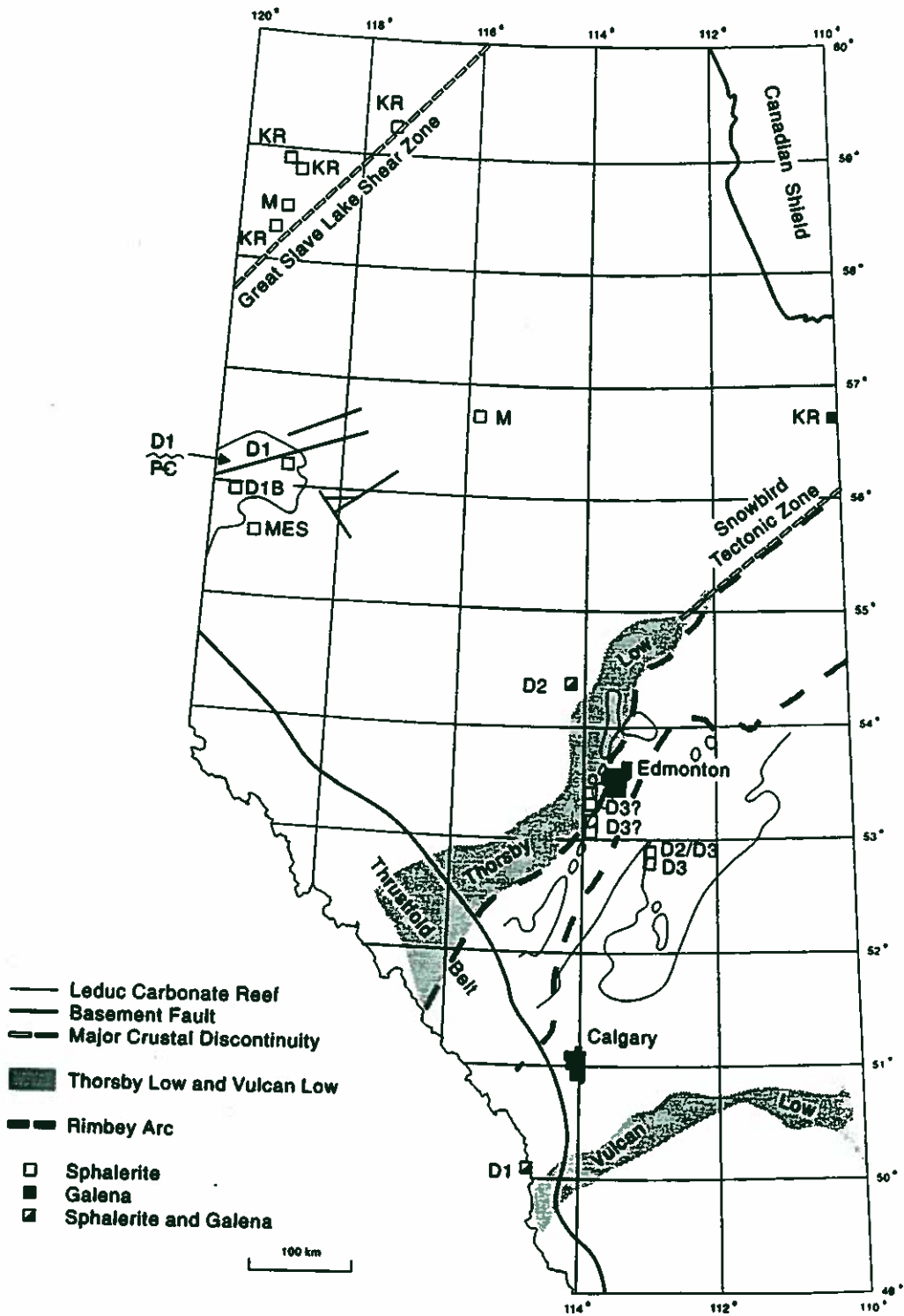


Figure 17. Location of sphalerite and galena in Phanerozoic rocks in Alberta; based on Hitchon (1977), Holter (1977), Carrigy (1959) and Dubord (1988). In addition to these sulphide minerals, smithsonite has been recorded from the Duhamel field (see Discussion in Hitchon, 1977, p. 22). KR=Keg River Fm.; M=Muskeg Fm.; D3=Woodbend Gp.; D2=Winterburn Gp.; D1=Wabamun Gp. or Palliser Fm.; D1B=Wabamun-Banff transition; Mes=Mesozoic (see Dubord, 1988). Major crustal discontinuities from Ross and Stephenson (1989). Basement faults in the Peace River Arch from the Basement Map of North America

## PINE POINT: A NEW MINERAL DEPOSIT TYPE

It is beyond the scope of this report to evaluate the many characteristics of Mississippi Valley type Pb and Zn deposits and to determine if the inclusion of Pine Point in this type is valid. It seems to the author that the extensive dolomitization found in the Devonian of the Alberta Basin may be relatively rare in a platform-type setting such as is found in western Canada. It might also be more than coincidence that many of the strongly dolomitized trends seem related to underlying basement structures. If this proves to be the case, then one may speculate that Pine Point differs in a fundamental way from other Mississippi Valley type deposits inasmuch as although there is a coincidence with the basinal setting of other Mississippi Valley type deposits the source of the metals is so different as to warrant a separate deposit type. Indeed, if the ore at Pine Point results from geothermal fluids ascending along the Great Slave Lake Shear Zone and meeting brines in the lowermost Phanerozoic strata, then there is no reason why similar deposits should not be found elsewhere along the same shear zone in the Canadian Shield. The brines are present -- all that is needed is an appropriate host aquifer. The association of Pb and Zn occurrences in the Canadian Shield with a major crustal discontinuity would be the strongest evidence for reclassifying Pine Point.

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