

# Brine springs of northern Alberta

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**Abstract:** Twenty-six brine springs discharging from Paleozoic carbonate deposits were sampled along the eastern edge of the Alberta Basin from two regions, Fort McMurray and Wood Buffalo National Park. Geochemical data indicate that the springs originate as an influx of meteoric and glacial waters that have come into contact with, and dissolved, halite deposits. The trace metal geochemistry indicates that these waters have interacted with carbonate rocks that have moderate to low base metal content, particularly for the Wood Buffalo region. This suggests that mineralization could be more widespread than recognized. However, there are data gaps between the national park boundary and Pine Point mine site, where mineralization could occur.

**Résumé :** Nous avons échantillonné 26 sources d'eau saumâtre émergeant de roches carbonatées paléozoïques dans deux régions en bordure de la marge est du bassin de l'Alberta, soit Fort McMurray et le parc national Wood Buffalo. Les données géochimiques indiquent que les sources ont comme origine un apport d'eaux météoriques et glaciaires qui sont venues en contact avec des dépôts de halite et les ont dissous. La géochimie des métaux-traces indique qu'il y a eu interaction entre ces eaux et des roches carbonatées à teneur en métaux communs variant de modérée à faible, en particulier dans la région du parc national Wood Buffalo. Cela porte à croire que la minéralisation pourrait être plus étendue qu'il ne l'a été reconnu. Toutefois, on manque de données pour la région qui s'étend entre la limite du parc et le site minier de Pine Point, où la minéralisation pourrait se trouver.

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## INTRODUCTION

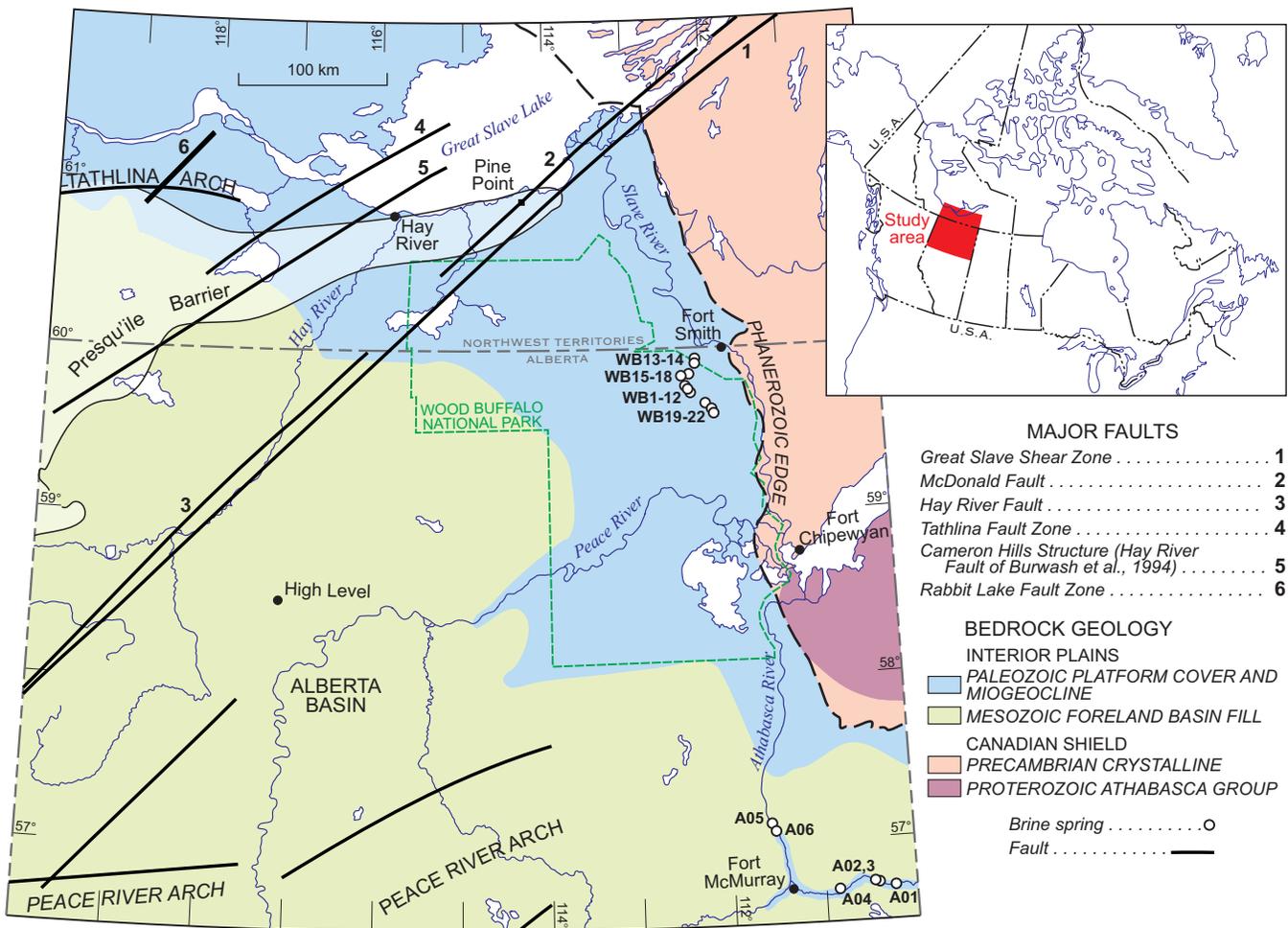
The Alberta Basin has a complex fluid-flow history that evolved through time. Present-day Paleozoic carbonate deposits are characterized by a topography driven, basin-scale flow system, with recharge in north-central United States and discharge along the northeastern edge of the Alberta Basin (Bachu, 1995; Grasby and Chen, 2005) (Fig. 1). Discharge from the basin is characterized by discrete brine springs in the Fort McMurray and Wood Buffalo areas (Fig. 1, 2) flowing from Devonian outcrop belts.

The Pine Point Zn-Pb district is hosted in the updip edge of the Middle Devonian Presqu'ile barrier complex, along the eastern erosional edge of the Alberta Basin. If these discharging fluids have interacted with mineralization on the way to the surface, then anomalous metal concentrations may indicate undiscovered resources. Given the lack of either water or petroleum wells in this region, these springs provide the best opportunity to sample such basinal fluids.

## REGIONAL GEOLOGY

The Alberta Basin is a subsbasin of the Western Canada Sedimentary Basin (WCSB), forming a trough inboard of the Canadian Cordillera north and west of the Bow Island Arch (not depicted on Fig. 1). The basin initiated during late Proterozoic rifting of the North American craton and developed a passive margin succession of Middle Cambrian to Middle Jurassic carbonate and evaporite deposits, with some intervening shale (Porter et al., 1982). In Late Jurassic time, accretion of allochthonous terranes to the western margin of the North American continent led to the development of a clastic shale-dominated foreland basin succession (Price, 1994). The Canadian Rockies foreland fold-and-thrust belt formed as a result of the Laramide Orogeny during Late Paleocene to Early Eocene time, corresponding to maximum burial of the Alberta Basin.

The regional-scale hydrostratigraphy of the Alberta Basin is illustrated in Figure 3 (after Bachu, 1995). In simplified terms, the major Paleozoic aquifer systems are the basal



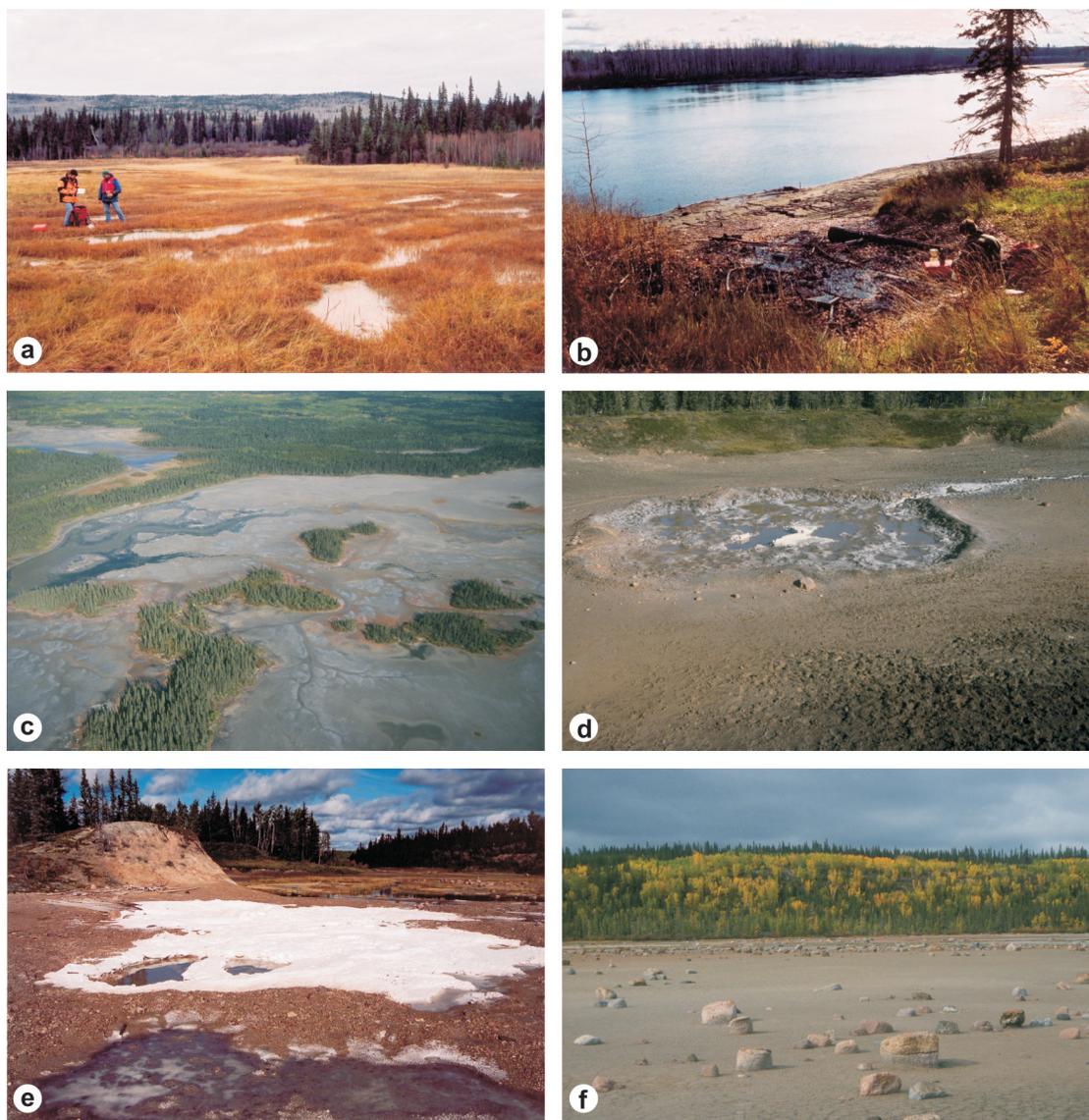
**Figure 1.** Simplified geological map of northeastern Alberta (northern extent of the Western Canada Sedimentary Basin). Locations of saline springs in this study are shown.

Cambrian sandstones, and Devonian through to Mississippian carbonates. The Mesozoic section is characterized by thick sequences of basinal shale that form regional aquitards. These are locally, and sometime regionally, punctuated by sandstone aquifers.

Extensive research has been carried out on the paleoflow system of the Alberta Basin, including specific focus on modelling movement of fluids related to formation of the Pine Point ore deposit (e.g. Garven, 1985; Adams et al., 2000; Adams, 2001). The modern-day Alberta Basin is characterized by a series of different flow systems depending on position in the basin and stratigraphic level. However, the dominant, present-day, basin-scale flow is a south-to-north

topography-driven system in the Paleozoic succession (Bachu, 1995; Anfort et al., 2001), with discharge in north-eastern Alberta (Fig. 1). Discharge from the Alberta Basin occurs along outcrop belts of Devonian carbonate in north-eastern Alberta (Fort McMurray and Wood Buffalo areas) as saline springs, with salinities ranging from 20 to 320 g/l (Fig. 2). Surface waters in these areas commonly show anomalous Na-Cl levels, suggesting discharge is more diffuse than just that emanating from the obvious spring sites (Environment Canada, unpublished data; Hitchon et al., 1969).

Previous studies have proposed that deposition of Zn-Pb ore minerals at Pine Point was related to basin-scale movement of formation waters either during the Late



**Figure 2.** Field photographs of saline spring discharge sites. **a.** Marshlands around saline spring along the Clearwater River; **b.** discharge site along the Athabasca River; **c.** aerial view of salt flat in Wood Buffalo region; **d.** saline spring discharge site and surrounding mudflat; **e.** halite deposits forming around spring discharge site; and **f.** mudflat associated with saline spring.

TERTIARY		<i>Scollard-Paskapoo Aquifer</i>	
CRETACEOUS	UPPER	<i>Battle Aquitard</i>	
		<i>Horseshoe Canyon Aquifer</i>	
		<i>Bearpaw Aquitard</i>	
		<i>Belly River Aquifer</i>	
		<i>Lea Park Aquitard</i>	
		<i>Milk River Aquifer</i>	
	LOWER	<i>Colorado Aquitard</i>	
		<i>Upper Mannville Aquifer</i>	
		<i>Clearwater Aquitard</i>	
	JURASSIC		<i>Lower Mannville Aquifer</i>
UPPER	<i>Jurassic Aquitard</i>		
	MIDDLE		
	LOWER		
TRIASSIC			
PERMIAN	UPPER	<i>Mississippian-Jurassic Aquifer</i>	
	LOWER		
PENNSYLVANIAN			
MISSISSIPPIAN	UPPER		
	LOWER		<i>Exshaw-Banff Aquitard</i>
DEVONIAN	UPPER		<i>Upper Devonian Aquifer</i>
			<i>Ireton Aquitard</i>
			<i>Middle - Upper Devonian Aquifer</i>
	MIDDLE		<i>Prairie Aquitard</i>
			<i>Winnipegosis Aquifer</i>
	LOWER	<i>Elk Point Aquiclude</i>	
SILURIAN			
ORDOVICIAN	UPPER	<i>Cambrian Aquitard</i>	
	MIDDLE		
	LOWER		
CAMBRIAN	UPPER		
	MIDDLE		<i>Basal Aquifer</i>
PRECAMBRIAN			<i>Aquiclude</i>

**Figure 3.** Simplified hydrostratigraphy of the Alberta Basin (after Bachu, 1995).

Devonian–Early Mississippian Antler Orogeny (e.g. Nesbitt and Muehlenbachs, 1994; Mountjoy et al., 1999), the Cretaceous–Tertiary Laramide Orogeny (e.g. Garven, 1985; Adams et al., 2000), or may be related to Devonian–Mississippian back-arc rifting events (Nelson et al., 2002).

## DESCRIPTION OF SPRING DISCHARGE SITES

Brine springs were sampled in two geographic locations, in the Fort McMurray and Wood Buffalo areas (Fig. 1). Brine springs in the Fort McMurray area are found where Paleozoic carbonate rocks are exposed along the Athabasca and Clearwater rivers (Fig. 2a, b). All the springs discharge close to river level, and outflow channels typically run less than 10 m before entering the main river (Fig. 2b). As the discharge is near main rivers and the flow tends to be channelized, the saline water has only minor impact on the surrounding landscape. Springs in the Fort McMurray area typically have associated gas discharge (dominantly nitrogen with CO<sub>2</sub> and methane), with one site in particular (A01) having very active effervescence. The smell of hydrogen sulphide gas was common at these sites.

Springs in the Wood Buffalo area all discharge along the base of a roughly north-south-trending escarpment, and all flow east to form tributaries of the Salt River. The landscape immediately around the discharge sites is characterized by extensive mudflats barren of any vegetation, with the exception of scattered, salt-tolerant species (Fig. 2c–f). These mudflats grade into grasslands and then to the more typical boreal forest of the region. The Wood Buffalo spring outlets themselves are typically characterized by large deposits of halite (Fig. 2e), which are reported by Park staff to grow up to 2 m high during dry periods. Some lower salinity springs (approx. 60g/l) do not have halite deposits but show development of extensive cyanobacterial mats within the outflow channels. These mats are not present at higher salinity sites. Red iron-oxide deposits are characteristic of most spring sites.

## METHODS

For this study, 26 springs, representing the majority of major discharge sites, were sampled. Numerous other smaller and lower salinity outlets are also known in the region but were not sampled as they likely represent more modern meteoric water.

Samples were collected, and unstable parameters (temperature, pH, dissolved HS<sup>-</sup>) were measured in situ within 0.5 m of the discharge site. For chemical analyses, water samples were passed through 0.45 µm filters and stored in the dark at 4°C in HDPE (high-density polyethylene) bottles until

analyzed. Samples for cation analyses were acidified with ultrapure nitric acid to pH less than 2. Samples for O and D isotope analyses were collected in glass bottles.

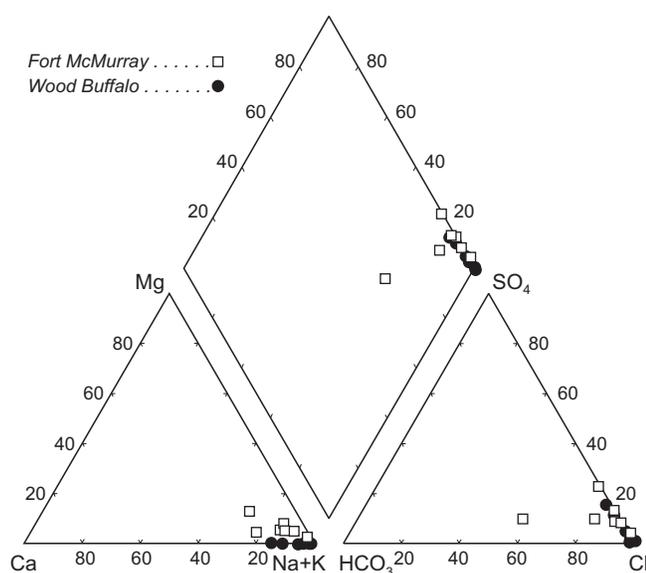
Chemical analyses were conducted at the Geological Survey of Canada. Alkalinity was determined by a standard end-point titration. Anions were measured by ion liquid chromatography and cations were measured by ICP-ES (Inductively Coupled Plasma Emission Spectrometer). Analytical error in concentration measurements was estimated to be less than 2%. Chemical analyses for Na, Cl, and Br were conducted by neutron activation following methods outlined by Duke and Rostron (pers. comm., 2005) at the University of Alberta.

## RESULTS AND ANALYSIS

### Major ion chemistry

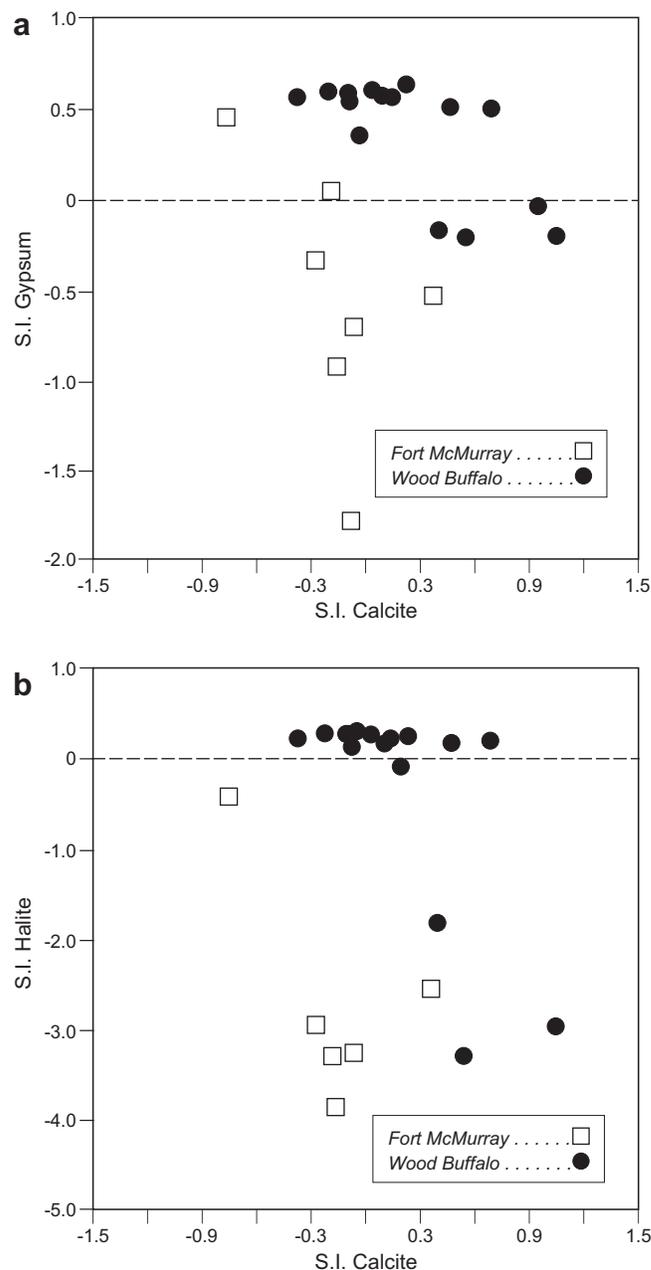
The total dissolved solids (TDS) content of spring water samples varied widely, from 403 to 321 000 mg/l (Table 1). Springs in the Wood Buffalo area typically had higher TDS contents (average 188 200 mg/l) than those from the Fort McMurray area, which were significantly lower (ranging from 1330 to 214 000 mg/l, but averaging near 45 000 mg/l). One sample from the Fort McMurray area taken from an abandoned flowing well contained significantly higher TDS (214 000 mg/l – A05). The “La Saline” spring along the Athabasca River, which was not sampled in this study, is reported to have TDS values of 71 400 mg/l (Borneuf, 1983).

Saline springs in the study area are characterized by a Na-Cl-dominated composition (Fig. 4). Sulphate and Ca levels are generally high as well (16 to 6419 and 36 to 1753 mg/l,



**Figure 4.** Piper diagram showing Na-Cl-dominated major ion chemistry of saline springs in the Fort McMurray and Wood Buffalo regions.

respectively; Table 1). Total alkalinity values (measured by  $\text{HCO}_3^-$  content) range from 100 to 1860 mg/l and are generally higher in lower-salinity Fort McMurray springs (Table 1). Figure 5 shows that waters from the Wood Buffalo region are typically saturated (calculated using Pitzer equations) with respect to halite and gypsum, whereas saturation with respect to calcite is variable. In the Fort McMurray area, the springs are typically undersaturated with respect to the above minerals, consistent with the lack of precipitates at these sites.



**Figure 5.** Plot of saturation indices of calcite versus a. gypsum and b. halite. Plots show that saline springs in the Wood Buffalo region are typically saturated or oversaturated with respect to gypsum and halite. With the exception of the flowing well at site A05, relatively lower salinity springs from Fort McMurray tend to be undersaturated.

Table 1. Analytical data for springs

Sample number	Latitude	Longitude	Date sampled	O <sub>2</sub> mg/l	Redox pot. mV (not converted to NHE)	H <sub>2</sub> S mg/l	TDS mg/l	pH	Temp °C	Ca mg/l	Mg mg/l	Na mg/l
Fort McMurray												
A01	56°44.082'	110°28.255'	Oct. 16/01	0.5	-263.1	5.8	18,904	6.74	6.1	537	182	6200
A02	56°45.022'	110°30.925'	Oct. 16/01	1	-129.8	7.6	1,330	7.33	5.9	68	29	320
A03	56°45.111'	110°31.859'	Oct. 16/01	9.3	115.3	n.p.	13,200	7.09	2.3	333	171	4127
A04	56°43.041'	110°44.057'	Oct. 16/01	3.9	-10.1	n.p.	7,200	6.83	4.4	222	68	2195
A05	57°11.358'	111°37.740'	Oct. 17/01	0.5	-95.7	9.38	214,000	5.85	7.2	1730	447	79200
A06	57°39.942'	111°25.837'	Oct. 18/01	1.06	-119	13	14,200	6.8	5.1	858	111	4029
WB01	59°53.328'	112°16.422'	Sept. 16/02	4.2	69.1	n.p.	316,000	6.3	12.9	1273	146	122000
WB02	59°53.639'	112°16.698'	Sept. 16/02	3	117.2	n.p.	314,000	6.03	2.5	1272	145	121000
WB03	59°54.666'	112°20.270'	Sept. 16/02	4.2	116.6	n.p.	314,000	6.27	2.1	1284	145	121000
WB04	59°54.785'	112°20.954'	Sept. 16/02	n.a.	95.6	n.p.	313,000	6.68	19.5	1356	230	121000
WB05	59°55.006'	112°21.358'	Sept. 16/02	n.a.	129.9	n.p.	306,000	6.56	8.8	1315	157	118000
WB06	59°55.107'	112°21.273'	Sept. 16/02	n.a.	124.6	n.p.	321,000	6.21	10.2	840	97	124000
WB07	59°48.762'	112°07.966'	Sept. 16/02	3.8	45.1	n.p.	403	9.02	18.1	36	37	15
WB08	59°50.046'	112°09.934'	Sept. 17/02	2.5	142.2	n.p.	308,000	6.46	7.2	1195	205	119000
WB09	59°50.720'	112°12.130'	Sept. 17/02	10.9	119.1	n.p.	67,200	7.44	1	963	62	22640
WB10	59°50.921'	112°12.337'	Sept. 17/02	n.a.	93.2	n.p.	20,200	8.29	1.7	690	35	6720
WB11	59°50.705'	112°15.227'	Sept. 17/02	n.a.	123	n.p.	13,300	7.61	2	650	32	3860
WB12	59°57.968'	112°24.012'	Sept. 18/02	n.a.	115	n.p.	317,000	6.08	10.6	1236	170	120000
WB13	59°58.388'	112°23.693'	Sept. 18/02	n.a.	113	n.p.	304,000	6.58	9.8	1313	169	117000
WB14	59°58.224'	112°23.852'	Sept. 18/02	n.a.	-150	n.p.	306,000	6.24	9	1254	169	118000
WB15	59°57.828'	112°24.113'	Sept. 18/02	n.a.	117	n.p.	309,000	5.9	4.7	1256	181	118000
WB16	59°57.738'	112°24.206'	Sept. 18/02	n.a.	120	n.p.	3,300	7.69	2.4	591	52	220
WB17	59°57.482'	112°24.382'	Sept. 18/02	n.a.	184	n.p.	312,000	6.15	6.6	1268	169	121000
WB18	59°57.133'	112°24.679'	Sept. 18/02	n.a.	178	n.p.	270,000	6.29	9.6	1753	188	102900
WB19	59°47.451'	112°00.408'	Sept. 19/02	4	-110	n.p.	10,900	6.61	8.8	510	30	3190
WB20	59°47.824'	112°00.650'	Sept. 19/02	1.4	-245	n.p.	8,770	7.01	9.6	420	44	2510
WB21	59°49.203'	112°02.696'	Sept. 21/02	3.8	132.5	n.p.	4,960	7.1	3.7	340	37	900
WB22	59°47.333'	112°02.211'	Sept. 21/02	1.3	129.7	n.p.	2,020	6.86	2.5	180	36	140

Notes: Negative values indicate results below the given detection limit; n.a.: not analyzed; n.p.: not present

Table 1. (cont.)

Sample number	K mg/l	SO <sub>4</sub> mg/l	Cl mg/l	HCO <sub>3</sub> mg/l	Si ppb	Br mg/l	I mg/l	Mn ppb	Pb ppb	Cu ppb	Fe ppb	Ba ppb	Zn ppb	As ppb	Al ppb
A01	15.2	1765	9847	358	3100	5	n.a.	29.0	0.09	12.0	-60	13	21	-0.2	11.0
A02	5.3	88	402	412	3100	1	n.a.	3.80	-0.05	0.8	-3	150	10	1.5	16.0
A03	22.0	928	7217	393	3600	4	n.a.	470	0.14	8.8	-60	30	14	-0.2	15.0
A04	4.4	539	3516	645	2900	2	n.a.	160	0.11	4.1	120	52	14	-0.2	11.0
A05	57.0	5727	126300	155	2500	30	n.a.	49.0	0.13	37.0	-60	19	25	-0.2	25.0
A06	10.0	2500	6421	243	7100	<.5	n.a.	45.0	0.12	10.0	210	13	13	6.7	89.0
WB01	65.5	4987	187000	215	1600	5.6	<.76	230	42.0	24.0	-60	42	-50	-10.0	10.0
WB02	63.0	4845	186000	192	1400	6.1	<.71	230	77.0	25.0	-60	36	76	-10.0	10.0
WB03	65.4	4850	186000	201	1800	4.9	<.77	270	80.0	33.0	-60	38	80	-10.0	12.0
WB04	80.0	4680	185000	214	1900	9.6	<.75	200	66.0	29.0	-60	30	-50	-10.0	-10.0
WB05	66.4	4662	182000	245	1800	5.6	<.74	200	74.0	34.0	-60	40	120	-10.0	12.0
WB06	47.5	4441	191000	195	1400	2.7	<.82	140	103.0	30.0	-60	45	60	-10.0	12.0
WB07	21.0	16	13	265	1200	<.05	n.a.	3.00	0.56	4.9	10	140	-1	0.9	5.5
WB08	60.4	5332	182000	157	1500	5.6	<.76	380	70.0	37.0	-60	29	100	-10.0	16.0
WB09	12.0	2937	40306	266	2300	<.05	n.a.	64.0	10.0	29.0	77	36	68	-10.0	11.0
WB10	4.5	2038	10500	214	1600	0.33	<.15	13.0	2.20	13.0	9	21	-10	-2.0	11.0
WB11	4.1	1779	6730	286	3100	0.37	<.11	4.60	0.36	7.2	4	16	2	-0.2	5.1
WB12	65.5	5005	190000	179	1600	4.4	<.77	130	42.0	31.0	110	40	130	-10.0	-10.0
WB13	60.2	5187	180000	99.5	1700	3.9	<.77	280	48.0	33.0	-60	43	74	-10.0	13.0
WB14	64.0	4992	181000	148	1600	5.5	<.78	120	39.0	27.0	250	34	110	-10.0	15.0
WB15	68.8	4983	184000	182	1600	5.4	<.75	120	39.0	36.0	-60	38	130	-10.0	17.0
WB16	1.5	1431	530	470	3200	<.05	n.a.	0.44	0.12	2.4	6	24	-1	0.2	6.6
WB17	70.0	4972	184000	184	1600	4.4	<.68	150	46.0	31.0	-60	40	-50	-10.0	-10.0
WB18	69.0	6419	158700	282	1700	3.50	n.a.	160	42.0	29.0	-60	47	-50	-10.0	25.0
WB19	2.2	1368	5060	745	2500	0.17	<.15	9.10	-0.05	5.6	45	20	13	-0.2	2.9
WB20	2.1	1369	4082	347	2700	n.a.	n.a.	13.0	-0.05	5.0	52	24	-1	0.2	6.0
WB21	1.7	691	1126	1860	2300	n.a.	n.a.	3.20	-0.05	4.1	31	28	510	0.2	4.4
WB22	0.96	264	77.5	1320	2700	n.a.	n.a.	0.11	-0.05	1.1	-3	69	840	-0.2	1.2

Fort McMurray

Wood Buffalo

Table 1. (cont.)

Sample number	Se ppb	Ni ppb	Cr ppb	Cd ppb	B ppb	U ppb	Ag ppb	Mo ppb	Sr ppb	Ti ppb	Be ppb	Bi ppb	Co ppb	Cs ppb
Fort McMurray														
A01	-1	14.0	2.0	-0.1	1600	-0.05	-0.05	-0.1	12000	-20	-1	-0.05	1.20	0.08
A02	-1	2.1	2.4	0.1	480	-0.05	-0.05	-0.1	1400	-1	-1	-0.05	0.22	-0.05
A03	-1	9.1	3.0	-0.1	1000	-0.05	-0.05	-0.1	11000	-20	-1	-0.05	0.80	-0.05
A04	-1	6.0	2.2	0.1	-320	-0.05	-0.05	-0.1	3600	-20	-1	-0.05	0.59	-0.05
A05	-1	61.0	12.0	-0.1	7900	-0.05	-0.05	-0.1	31000	-20	-1	-0.05	3.50	1.30
A06	-1	23.0	3.7	0.1	710	-0.05	-0.05	-0.1	12000	-20	-1	-0.05	2.10	0.06
WB01	-100	69.0	27.0	-5.0	3200	12	-3.00	33.0	-20	-20	-50	-3.00	4.00	-3.00
WB02	-100	71.0	28.0	-5.0	3000	14	-3.00	39.0	-20	-20	-50	-3.00	3.00	-3.00
WB03	-100	75.0	24.0	-5.0	4400	19	-3.00	32.0	-20	-20	-50	-3.00	4.00	-3.00
WB04	-100	74.0	21.0	-5.0	3900	19	-3.00	22.0	-20	-20	-50	-3.00	4.00	-3.00
WB05	-100	70.0	22.0	-5.0	3500	13	-3.00	13.0	-20	-20	-50	-3.00	4.00	-3.00
WB06	-100	63.0	22.0	-5.0	2300	9	-3.00	18.0	-20	-20	-50	-3.00	4.00	-3.00
WB07	-1	1.1	-0.1	-0.1	45	0.35	-0.05	0.5	-1	-1	-1	-0.05	0.10	-0.05
WB08	-100	66.0	22.0	-5.0	2400	19	-3.00	20.0	-20	-20	-50	-3.00	4.00	-3.00
WB09	-100	15.0	10.0	-5.0	730	7.00	-3.00	20.0	-20	-20	-50	-3.00	-3.00	-3.00
WB10	-20	24.0	2.0	-1.0	440	3.00	-0.50	7.0	-2	-2	-10	-0.50	1.00	-0.50
WB11	-1	13.0	0.7	-0.1	1100	2.00	-0.05	5.4	-1	-1	-1	-0.05	0.81	-0.05
WB12	-100	73.0	22.0	-5.0	3700	15	-3.00	15.0	-20	-20	-50	-3.00	3.00	-3.00
WB13	-100	87.0	20.0	-5.0	3600	17	-3.00	18.0	-20	-20	-50	-3.00	4.00	-3.00
WB14	-100	62.0	17.0	-5.0	3800	13	-3.00	8.0	-20	-20	-50	-3.00	3.00	-3.00
WB15	-100	74.0	19.0	-5.0	3900	16	-3.00	9.0	-20	-20	-50	-3.00	3.00	-3.00
WB16	-1	14.0	-5.0	-0.1	250	5.20	-0.05	2.4	-1	-1	-1	-0.05	0.73	-0.05
WB17	-100	75.0	21.0	-5.0	4000	17	-3.00	10.0	-20	-20	-50	-3.00	3.00	-3.00
WB18	-100	61.0	18.0	-5.0	3300	15	-3.00	15.0	-20	-20	-50	-3.00	3.00	-3.00
WB19	-1	9.3	0.6	0.1	300	0.45	-0.05	1.1	-1	-1	-1	-0.05	0.62	-0.05
WB20	-1	8.1	0.9	-0.1	170	0.12	-0.05	1.1	-1	-1	-1	-0.05	0.65	-0.05
WB21	-1	13.0	0.4	-0.1	130	5.10	-0.05	1.6	-1	-1	-1	-0.05	0.49	-0.05
WB22	-1	9.7	0.2	-0.1	30	5.50	-0.05	0.8	-1	-1	-1	-0.05	0.25	-0.05
Wood Buffalo														

Notes: Negative values indicate results below the given detection limit; n.a.: not analyzed; n.p.: not present

Table 1. (cont.)

Sample number	Ga ppb	Li ppb	Rb ppb	Sb ppb	Sc ppb	Tl ppb	V ppb	In ppb	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ V-SMOW	$\delta\text{D}_{\text{H}_2\text{O}}$ V-SMOW	$\delta^{34}\text{S}_{\text{SO}_4}$ V-CDT	$\delta^{34}\text{S}_{\text{HS}}$ V-CDT	$\delta^{13}\text{C}_{\text{DIC}}$ V-PDB	$^{13}\text{C}_{\text{CH}_4}$ V-PDB	$^{13}\text{C}_{\text{CO}_2}$ V-PDB
A01	-0.05	280	15.0	-0.05	-20	-0.05	-0.05	-0.05	-22.8	-175	20.9	-19.8	-12.6		
A02	-0.05	63	4.80	-0.05	-1	-0.05	-0.05	-0.05	-20.7	-157	20.8	0.0	-12.9		
A03	-0.05	480	11.0	-0.05	-20	-0.05	-0.05	-0.05	-22.4	-167	23.9	n.p.	-11.0		
A04	-0.05	200	2.60	-0.05	-20	-0.05	-0.05	-0.05	-16.6	-128	26.2	n.p.	-11.9		
A05	0.39	780	62.0	-0.05	-20	-0.05	-0.05	-0.05	-25.1	-188	19.0	-21.3	-5.5	-53.1	-1.1
A06	-0.05	120	9.40	-0.05	-20	-0.05	-0.05	-0.05	-19.4	-148	20.5	-25.3	-11.2	-53.1	-14.9
WB01	-3.00	140	35.0	-3.00	-20	-3.00	-3.00	-3.00	-20.3	-166	15.4	n.p.	-4.5		
WB02	-3.00	130	34.0	-3.00	-20	-3.00	-3.00	-3.00	-20.9	-166	16.5	n.p.	n.a.		
WB03	-3.00	130	34.0	-3.00	-20	-3.00	-3.00	-3.00	-20.5	-163	15.1	n.p.	n.a.		
WB04	-3.00	190	41.0	-3.00	-20	-3.00	-3.00	-3.00	-20.2	-162	15.2	n.p.	-6.4		
WB05	-3.00	140	38.0	-3.00	-20	-3.00	-3.00	-3.00	-19.6	-159	14.5	n.p.	-1.4		
WB06	-3.00	97	30.0	-3.00	-20	-3.00	-3.00	-3.00	-17.7	-146	15.7	n.p.	n.a.		
WB07	-0.05	12	0.81	0.13	-1	-0.05	0.49	-0.05	-12.4	-121	-3.3	n.p.	n.a.		
WB08	-3.00	140	36.0	-3.00	-20	-3.00	-3.00	-3.00	-20.1	-163	15.0	n.p.	n.a.		
WB09	-3.00	32	8.80	-3.00	-20	-3.00	-3.00	-3.00	-19.3	-154	16.9	n.p.	n.a.		
WB10	-0.50	19	3.20	-0.50	-2	-0.50	-0.50	-0.50	-20.0	-154	17.9	n.p.	-10.2		
WB11	-0.05	24	2.30	0.10	-1	-0.05	-0.05	-0.05	-19.7	-154	17.9	n.p.	-10.3		
WB12	-3.00	170	40.0	-3.00	-20	-3.00	-3.00	-3.00	-20.3	-165	14.2	n.p.	-11.5		
WB13	-3.00	160	33.0	-3.00	-20	-3.00	-3.00	-3.00	-20.2	-163	14.8	n.p.	n.a.		
WB14	-3.00	160	27.0	-3.00	-20	-3.00	-3.00	-3.00	-20.3	-161	13.5	n.p.	-10.4		
WB15	-3.00	180	40.0	-3.00	-20	-3.00	-3.00	-3.00	-20.4	-164	15.6	n.p.	-10.4		
WB16	-0.05	14	1.20	0.11	-1	-0.05	-0.05	-0.05	-19.5	-154	16.4	n.p.	-10.2		
WB17	-3.00	170	41.0	-3.00	-20	-3.00	-3.00	-3.00	-20.5	-162	14.5	n.p.	-11.0		
WB18	-3.00	140	33.0	-3.00	-20	-3.00	-3.00	-3.00	-20.6	-161	15.1	n.p.	-10.5		
WB19	-0.05	14	1.30	-0.05	-1	-0.05	-0.05	-0.05	-19.5	-151	18.3	n.p.	-11.1		
WB20	-0.05	25	0.69	0.10	-1	-0.05	-0.05	-0.05	-15.2	-128	18.2	n.p.	-12.7		
WB21	-0.05	9	0.98	-0.05	-1	-0.05	-0.05	-0.05	-22.4	-156	14.4	n.p.	-10.3		
WB22	-0.05	5	0.46	-0.05	-1	-0.05	-0.05	-0.05	-20.4	-157	8.4	n.p.	-11.3		

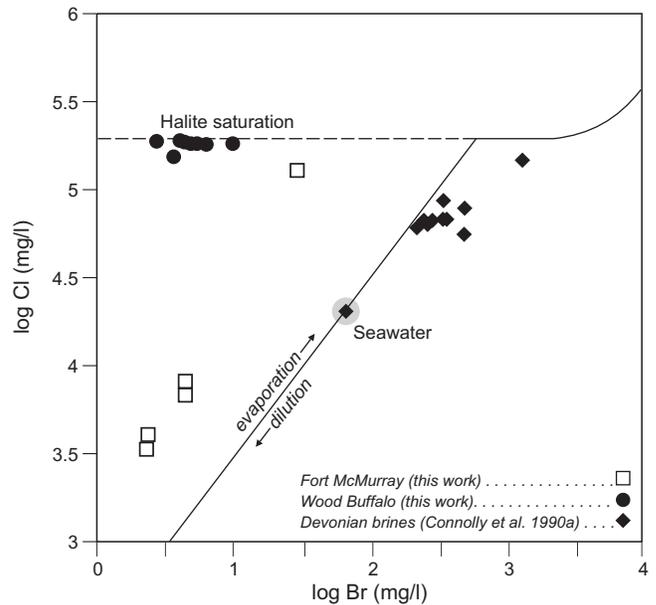
### Conservative ion ratios

Figure 6 plots conservative ions Br versus Cl for the brine springs and compares them with Devonian formation waters from the deep central part of the Alberta Basin (Connolly et al., 1990a). Also, the evaporation/dilution trajectory for seawater is depicted (Carpenter, 1978). Figure 6 shows that Devonian formation waters fall either on, or to the right of, the evaporation/dilution line. This was interpreted as Devonian basin brines originating from seawater that evaporated past halite saturation, leading to Br-enrichment (e.g. Connolly et al., 1990a; Simpson, 1999). Spring waters all plot to the left (Br-depleted) of the evaporation/dilution trend, showing a significantly different chemical signature from deep-basin brines or Pine Point mineralizing fluids (Gleeson and Gromek, 2006; Tesler, 1999). As halite typically excludes Br from the crystal structure, these low Br/Cl brines suggest that the salinity of the spring waters originated through dissolution of halite (Carpenter, 1978). Springs from the Wood Buffalo area are all at, or near, halite saturation, whereas only the flowing well sample (A05) is near halite saturation in the Fort McMurray area. All other springs from Fort McMurray area fall on a dilution trajectory suggesting that these springs originate as halite-saturated waters that have been mixed and diluted by lower TDS waters.

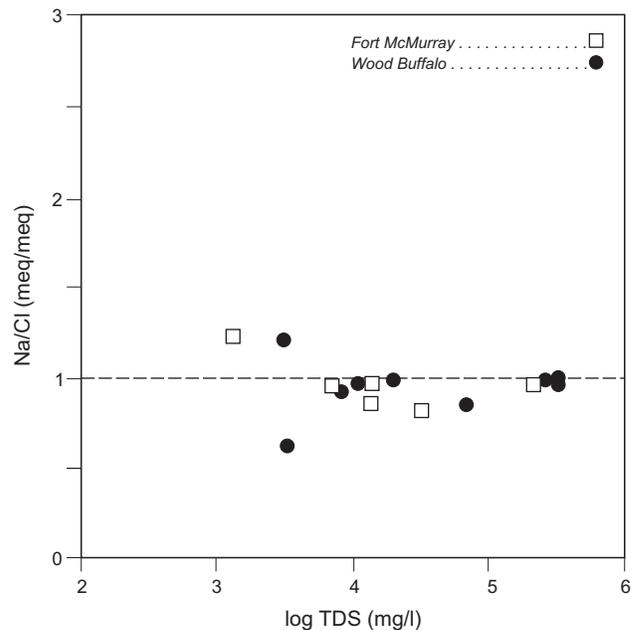
Saline springs in the study area have Na/Cl molar ratios close to one (Fig. 7), which is again indicative of halite dissolution. In contrast, deep basin brines of Devonian strata in the Alberta Basin have Na/Cl molar ratios typically less than 0.8 (Connolly et al., 1990a; Simpson, 1999). Similar to Cl/Br ratios discussed above, these data indicate that the spring waters are unrelated to brines in stratigraphically equivalent deep-basin Devonian carbonate deposits, and support the interpretation of evaporite dissolution by meteoric water. Similarly, brine springs have chemistry distinct from fluid inclusion data for Pine Point ore minerals, which show significant loss of Na (Gleeson and Gromek, 2006).

### O and D stable isotope data

Brines in deep-basin Devonian carbonate deposits have high  $\delta D$  and  $\delta^{18}O$  values and plot to the right of the global meteoric water line, consistent with the interpretation that they represent residual evaporated seawater (Connolly et al., 1990b; Simpson, 1999; Spencer, 1987). In contrast, we see in Figure 8 that brine springs fall along the local meteoric water line (LMWL) for Fort Smith (IAEA/WMO, 1998), with values that are close to the mean average for precipitation ( $\delta^{18}O$  of -20.1‰ and  $\delta D$  of -156‰ relative to V-SMOW). Springs from Wood Buffalo are tightly clustered, suggesting a common water source. In contrast, springs from Fort McMurray area show a broader spread along the LMWL. The  $\delta^{18}O$  values of spring waters tend to decrease with increasing Cl concentration, down to a low of -25‰. Values near -25‰ are significantly lower than average precipitation in the area and it has been argued that they represent subglacial influx into



**Figure 6.** Plot of Br vs. Cl concentrations for saline springs and Devonian formation waters. The evaporation/dilution trajectory from Carpenter (1978) is shown for reference. Note that saline springs have a distinctly different conservative ion behaviour than Devonian brine (from Connolly et al., 1990a). Waters plotting in the Cl-enriched field suggest halite dissolution as a source of salinity (see text).



**Figure 7.** Plot of Na/Cl molar ratio versus TDS, showing a near 1:1 relationship between Na and Cl for all springs except the ones with the lowest TDS content.

the eastern margin of the sedimentary basin (Grasby and Chen, 2005). This is consistent with the mixing dilution interpretation based on water chemistry above.

## S stable isotope data

In high sulphate springs at both Fort McMurray and Wood Buffalo areas, the  $\delta^{34}\text{S}$  values in dissolved sulphate vary from 15 to 20‰ (relative to V-CDT) (Fig. 9; Table 1), similar to the range expected for Devonian evaporite deposits (Claypool et al., 1980) and those observed in Middle Devonian units of the WCSB (e.g. Ueda et al., 1987). This is consistent with the data discussed above suggesting that the dominant source of salinity is related to evaporite dissolution. A diverging trend shows the Wood Buffalo springs decreasing in  $\delta^{34}\text{S}$  and the Fort McMurray ones increasing. The increasing trend at Fort McMurray may suggest a greater degree of biological sulphate reduction at lower sulphate concentrations, resulting in a kinetic isotopic shift of sulphur in the remaining sulphate to higher values. In contrast, the Wood Buffalo trend likely represents a mixing relation between sulphate derived from evaporates such as gypsum or anhydrite in high-sulphate springs and sulphate derived from sulphide oxidation in lower sulphate springs. In either case, more detailed work would be required to elucidate the cause of these trends.

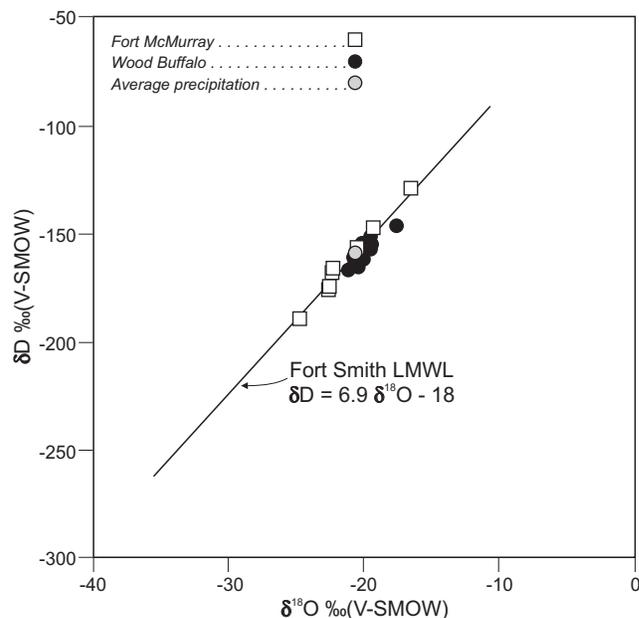
The Fort McMurray springs have detectable hydrogen sulphide. The  $\delta^{34}\text{S}$  values of  $\text{H}_2\text{S}$  vary from -20 to -25‰ (V-CDT; Table 1) suggesting an origin through bacterial sulphate reduction. This is noticeably different from  $\delta^{34}\text{S}$  values of sulphides from Pine Point, averaging at +20. 1‰ (Sasaki and Krouse, 1969).

## Trace Element data

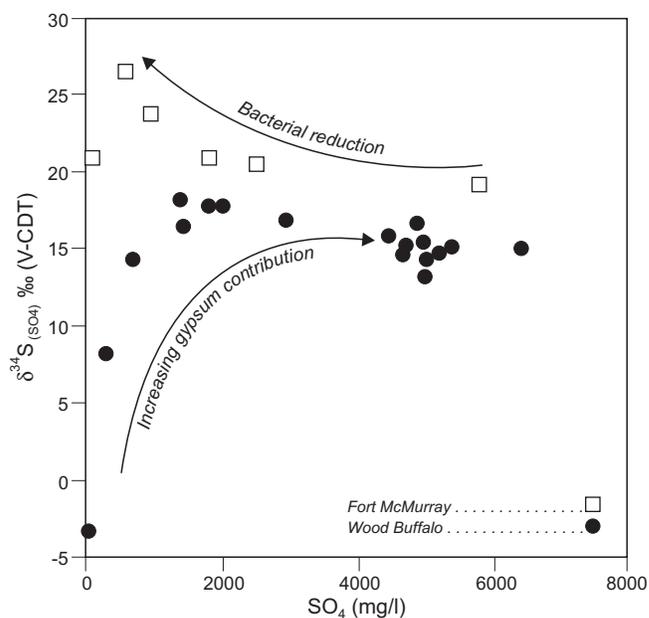
Pb was detected in 23 samples with a maximum value of 103 ppb, averaging near 34 ppb. Zn was detected in 20 samples with a maximum value of 840 ppb and an average of 121 ppb. In both cases, these concentrations are an order of magnitude lower than the range observed in formation waters from lower Paleozoic carbonate units (Fig. 10; Hitchon, 1993). The range of values for the Zn/Pb ratios (0.6 to 233) are similar to those observed by Hitchon (1993); however, there is a distinct difference between the two study areas. Wood Buffalo spring waters have Zn/Pb ratios ranging from 0.6 to 6.8, close to the average values for Paleozoic formation waters (2.7, Hitchon, 1993). In contrast, the Fort McMurray area always has Zn concentrations greater than Pb, with Zn/Pb ratios ranging from 100 to 233 (an order of magnitude greater than the highest values observed in formation waters). It was argued by Hitchon (1993) that average formation water values with low Zn/Pb ratios would not be able to precipitate the Zn-Pb ore deposits characteristic of Pine Point. It is interesting to note, however, that the Fort McMurray samples, while having significantly lower metal concentrations than

Pine Point, have the higher Zn/Pb ratios, more consistent with the theoretical fluid composition required for ore deposition at Pine Point.

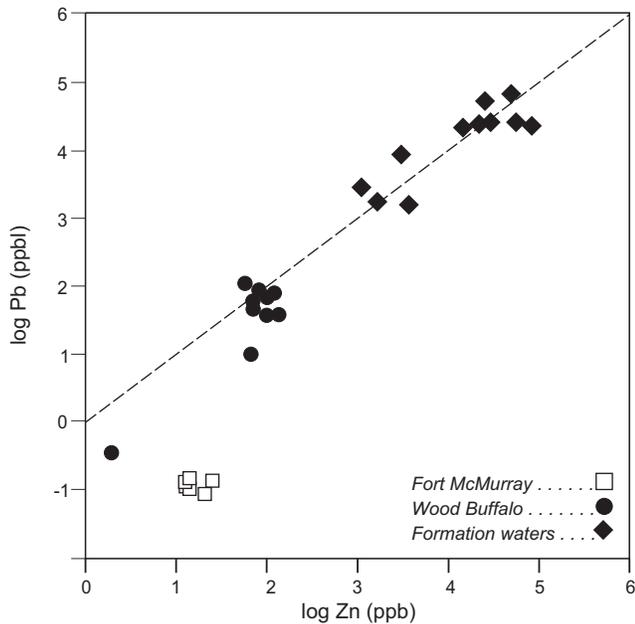
With respect to all samples, Zn and Pb do not show any statistically meaningful correlation with each other (correlation coefficient of 0.64). Zn does not show significant correlation with other ions whereas Pb shows significant correlation with Na, Cl, and  $\text{SO}_4$ , which all vary as a function of



**Figure 8.** Plot of  $\delta^{18}\text{O}$  versus  $\delta\text{D}$  for spring waters. Also shown is the local meteoric water line (LMWL) for Fort Smith, Northwest Territories (from IAEA/WMO, 1998).



**Figure 9.** Plot of  $\delta^{34}\text{S}$  versus sulphate concentration for brine springs (see text for discussion).



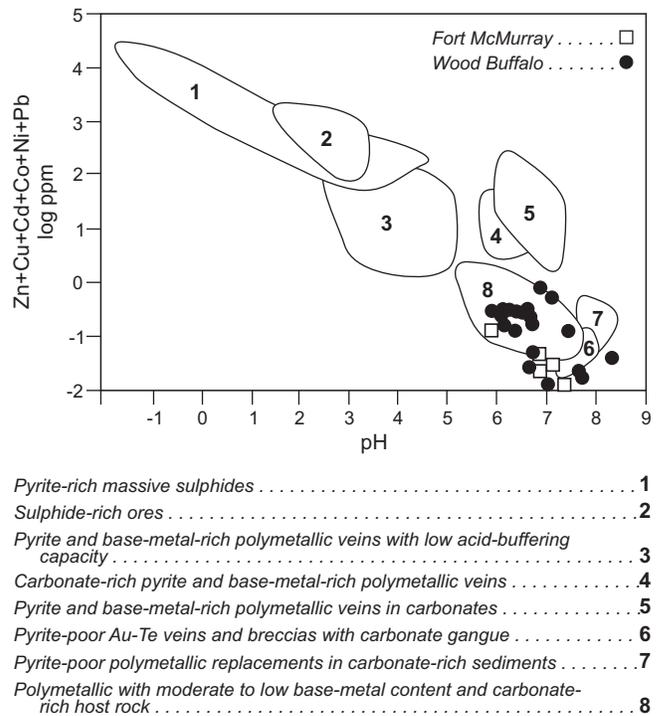
**Figure 10.** Plot of dissolved Zn versus Pb for brine springs in the study area along with data for formation waters from the Alberta Basin (from Hitchon, 1993).

TDS. The Cl<sup>-</sup> ion activity is likely the strongest control on Pb concentrations through enhanced solubility brought about by the formation of PbCl complexes.

Given the data above, suggesting that the saline springs originate as an influx of meteoric water, it was deemed reasonable to plot trace metal chemistry on a Ficklin diagram (Ficklin et al., 1992; Plumlee et al. 1994). The diagram compares our samples with fields defined for waters draining known mineral deposit types (Fig. 11). Most of the Wood Buffalo springs, and one spring from Fort McMurray, plot in the field for moderate to low base-metal content in carbonate-hosted sediments (Fig. 11). The remainder of the springs plot outside any defined fields, suggesting that these waters have not interacted with substantial base-metal mineralization.

## DISCUSSION AND CONCLUSIONS

Stable isotope and geochemical data indicate that brine springs in the Wood Buffalo and Fort McMurray areas originate as an influx of meteoric water that has come into contact with, and dissolved, halite deposits, producing waters of high salinity. Based on stable isotope composition and evidence for Pleistocene dissolution of the eastern edge of the Prairie evaporite, Grasby and Chen (2005) interpreted these springs as related to a reflux of subglacial meltwater. This suggests that they are a relatively recent phenomenon unrelated to mineralization processes at Pine Point.



**Figure 11.** Ficklin Diagram (Ficklin et al., 1992) showing net base metal concentration for spring waters along with fields for waters draining known ore deposit types.

Geochemical signatures (Br/Cl and Na/Cl ratios) indicate that salinity in these springs is derived from halite dissolution and is distinct from both basinal brines and ore-forming fluids characterized by fluid inclusion studies (Gleeson and Gromek, 2006). Coniglio et al. (2006) provide evidence for two stages of cementation: an initial phase involving highly saline Ca-Cl<sub>2</sub> brines related to ore mineralization, and a later, post-mineralization, lower saline NaCl-type water. While it is possible that this later fluid could be related to the brine spring waters observed today, there are no timing constraints to verify this inference. Recent modelling work by Adams et al. (2004) suggest the potential of underpressure developing in formation fluid-flow along the eastern margin of the Alberta basin responding to erosion, which may have led to a similar flow reversal earlier in the basin history.

The trace metal geochemistry of the spring waters, particularly for the Wood Buffalo region, indicates that they have interacted with carbonate rocks that have moderate to low base-metal content. This suggests that mineralization could be more widespread than recognized. However, these data are primarily within the national park area and there is little information available between the park boundary and the Pine Point site. Fluid sampling, as part of any exploration drilling activity, may prove useful in defining trace metal concentrations in waters of that region.

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## ACKNOWLEDGMENTS

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Peter Errman and Kathleen Bradford provided assistance with fieldwork. John Duke's help with neutron activation analyses of high salinity waters is appreciated.

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