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Brines in the Carboniferous Sydney Coalfield, Atlantic Canada

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Abstract

Formation waters within Upper Carboniferous sandstones in the sub-sea Prince and Phalen coal mines, Nova Scotia, originated as residual evaporative fluids, probably during the precipitation of Windsor Group (Lower Carboniferous) salts which underlie the coal measures. Salinity varies from 7800 to 176,000 mg/l, and the waters are Na–Ca–Cl brines enriched in Ca, Sr and Br and depleted in Na, K, Mg and SO_4 relative to the seawater evaporation curve. Br:Cl and Na:Cl ratios suggest that the brine composition corresponds to an evaporation ratio of as much as 30. The brines lie close to the meteoric line on H/O isotopic plots but with a compositional range of $\delta^{18}O$ from −4.18 to −6.99 and of δD from −42.4 to −23.5, distant from modern meteoric or ocean water. Mine water composition contrasts with that of nearby salt-spring brines, which are inferred to have originated through dissolution of Windsor Group evaporites by modern meteoric waters. However, a contribution to the mine waters from halite dissolution and from Br in organic matter cannot be ruled out. Present concentrations of several elements in the brines can be explained by water–rock interaction. The original Windsor brines probably moved up into the overlying coal-measure sandstones along faults, prior to the Late Triassic. The high salinity and irregular salinity distribution in the Phalen sandstones suggests that the brines have undergone only modest dilution and are virtually immobile. In contrast, Prince waters show a progressive increase in salinity with depth and are inferred to have mixed with surface waters. Basinal brines from which these modern formation fluids were derived may have been important agents in base-metal and Ba mineralisation from the mid-Carboniferous onwards, as saline fluid inclusions are common in Zn–Pb sulphide deposits in the region. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Coal has been mined since the 1600s in the Maritimes Basin of Atlantic Canada, and the main economic seams are found in the Sydney Basin (Fig. 1). Because the coal seams subcrop close to the Atlantic coast and dip seaward, the currently active Prince and Phalen Mines (Fig. 2), as well as many former mines, extend several kilometres offshore and up to 900 m below the sea floor. The mines are operated by the Cape Breton Development Corporation (CBDC).

Water inflows have occasionally been a problem during subsurface mining in the coalfield (Haites, 1951). Sudden, large inflows of variably saline water into the subsea Phalen Mine in 1992 (Cape Breton

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Development Corporation, 1994) prompted investigation of the regional groundwater system, in view of pumping costs and potential hazard to miners and equipment. Concern was expressed that some water might have originated from the overlying ocean, and more than 3000 water analyses have been obtained to date from the collieries. Access to mine panels (areas mined during longwall retreat) has allowed collection of formation water (natural groundwater) dripping from exposures and boreholes in the working roof, at depths up to nearly 700 m below sea level. Because the roof drips were collected prior to panel mining, they provide unusually reliable samples of deep groundwaters, without risk of contamination by drilling fluids or mixing of waters from different levels — a common problem in oilfield and aquifer samples. The most saline waters are Na–Ca–Cl brines with salinity more than 5 times that of sea water.

Sedimentary rocks are generally deposited with connate waters (original pore waters) at or below seawater salinity, but basinal pore waters are commonly more saline than seawater (Hanor, 1994). Although many constituents can be concentrated through water–rock reactions, Cl is essentially non-reactive (conservative), and only a limited number of mechanisms can produce brines with Cl concentrations several times that of seawater (Fontes and Matray, 1993a; Hanor, 1994). The most commonly invoked mechanisms for brine generation are reflux of residual evaporative fluids, halite dissolution, and hyperfiltration (Hanor, 1994). Key criteria for deciding between these alternatives include Na:Cl and Br:Cl ratios of the fluids and their O and H

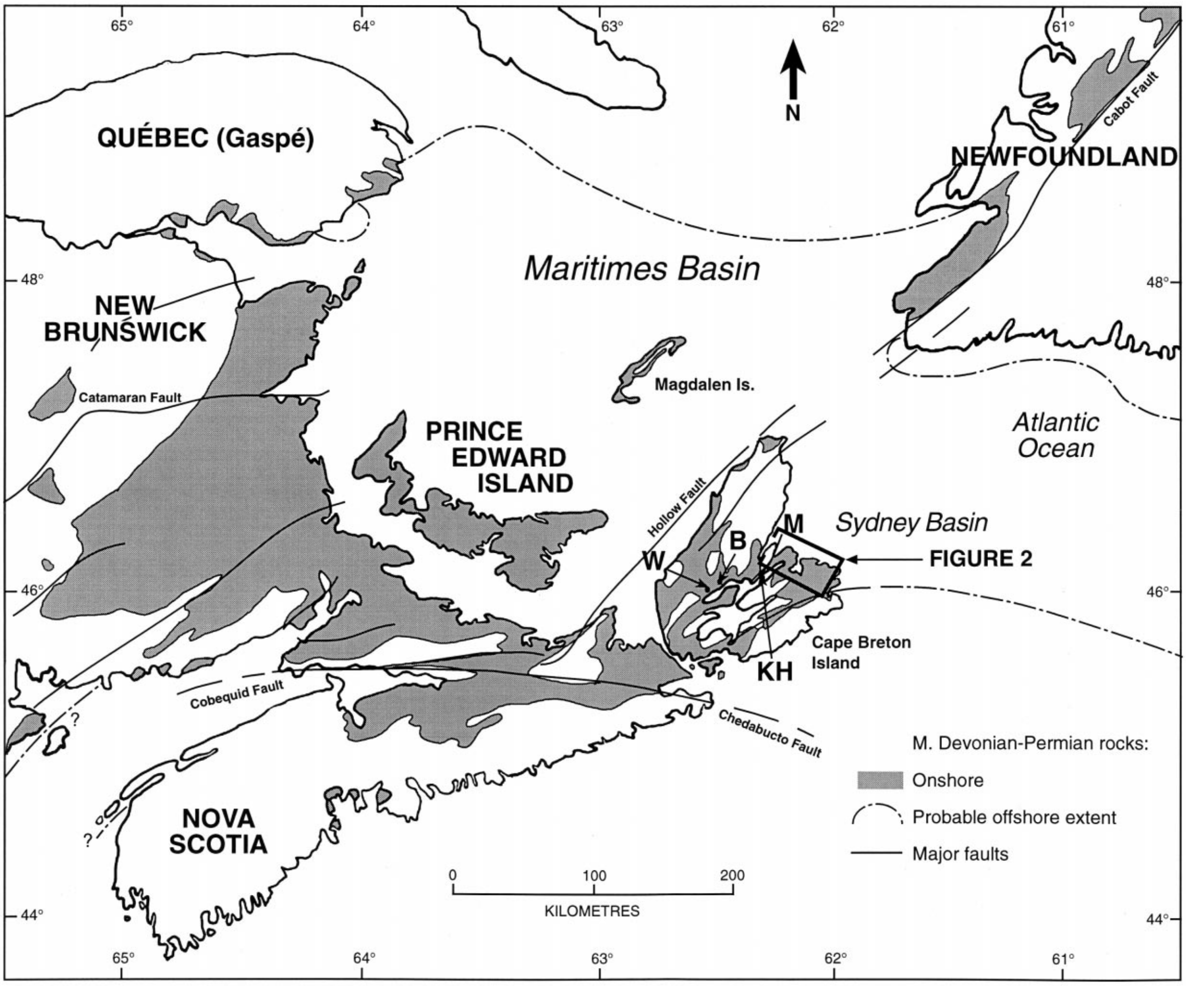

Fig. 1. Maritimes Basin of Atlantic Canada to show the distribution of Middle Devonian to Permian rocks. M = Mountain Fault; B and W = Bucklaw and Wycocomagh salt springs; KH = Kempt Head drill hole in the Sydney Basin.

isotopic ratios. Bromine and Cl are conservative in most water/rock reactions and are especially useful for determining water origins.

The present study investigates the origin of the mine formation waters, to provide insight into the hydrogeology of the Sydney Coalfield at intermediate depths under the coastal zone and to assist in mine planning. Salt springs are common in Carboniferous bedrock areas of the Maritimes Basin, and salt-spring chemical data were compiled, and new samples collected, for comparison with sub-sea brine samples. To the authors' knowledge, the present study is the first to examine in detail formation brine origins within the Maritimes Basin, although Frape and Fritz (1987) reported a brine sample from the Magdalen Islands (Fig. 1). The geological source of the brines are discussed and the timing of their migration into the coal measures. The paper also contributes to the understanding of mineral deposits in the region, for brines have been reported from fluid inclusions in ores and other minerals at many localities within the Maritimes Basin.

2. Geological background

The Maritimes Basin (Fig. 1) is a complex of depocentres across Atlantic Canada that originated in the mid-Devonian following the Acadian Orogeny. The Sydney Basin is a major depocentre of the Maritimes Basin, and is located in northeastern Nova Scotia (Cape Breton Island) and under the adjacent Atlantic Ocean (Fig. 2).The stratigraphic succession of the Sydney Basin (Fig. 3) follows regional patterns (Gibling et al., 1987; Gibling, 1995). The Horton Group is up to 800 m thick onshore, and consists mainly of alluvial fan/plain conglomerates and sandstones. The overlying Windsor Group is up to 1000 m thick and comprises 5 large-scale cycles of interstratified marine and continental sedimentary rocks (Boehner, 1986). The group includes hundreds of metres of marine anhydrite, gypsum and halite, with minor potash salts, well documented in the Kempt Head drill hole (Fig. 1). Mudstones, fossiliferous limestone and dolomite are prominent in the upper part of the group. Windsor diapirs are widely distributed both onshore and offshore in Atlantic Canada (e.g. Langdon and Hall, 1994), and salt springs are commonly associated with Windsor Group outcrops. The Windsor Group is overlain by about 200 m of lacustrine and fluvial strata of the Mabou Group. The Horton Group was deposited within a series of fault-bounded, extensional basins, and the Windsor and Mabou Groups probably represent subsequent thermal subsidence. Local evaporite occurrences are present in the Horton Group (Howie, 1988) and the Mabou Group (Boehner, 1986).

The Upper Carboniferous Morien Group rests on Lower Carboniferous rocks with angular unconformity (Fig. 3), linked to deformation associated with the onset of the Alleghanian Orogeny in eastern North America (Gibling, 1995). Locally, the topmost Windsor strata comprise brecciated carbonate and clastic rocks, up to 180 m thick, possibly a solution breccia (Boehner, 1986). The basal South Bar Formation comprises about 1 km of braided-fluvial sandstones and conglomerates, with minor shales and a few economic coals.

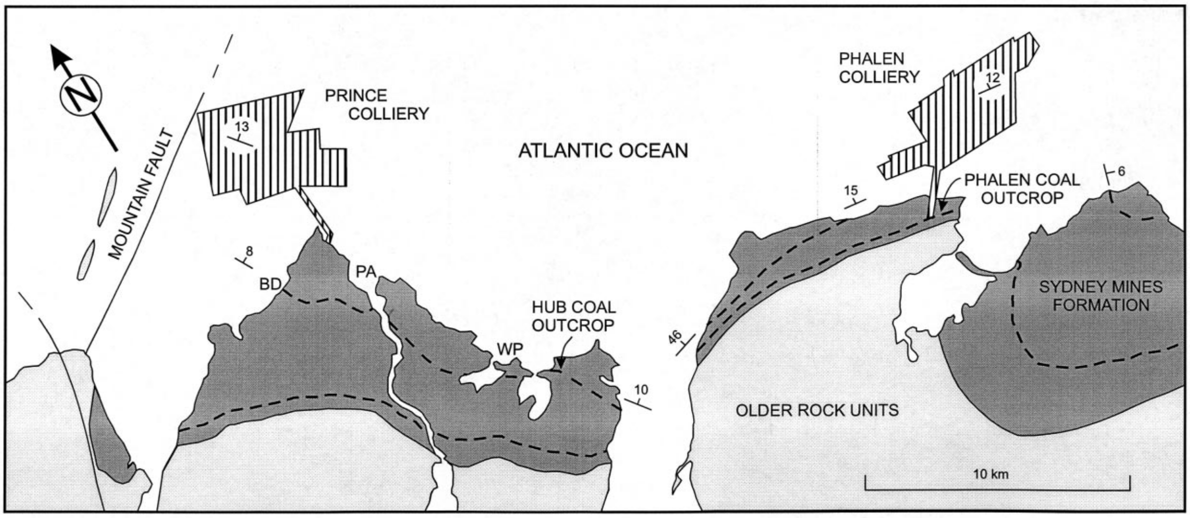

Fig. 2. Location of the sub-sea Phalen and Prince Collieries which work the seaward-dipping Phalen and Hub Seams, respectively, of the Sydney Mines Formation. The Bridgeport Anticline lies just east of the Phalen Mine, as indicated by stratal dips.

The overlying Sydney Mines Formation, of principal interest for this study, is Westphalian D to Stephanian in age and about 1000 m thick. It contains numerous economic coals that can be traced throughout the onshore and adjacent offshore part of the basin (Gibling and Bird, 1994). The coals are associated with grey shales, bay-fill sandstones, and channel sandstones up to 30 m thick, deposited in alluvial to restricted-marine environments, and evidence for marine influence is provided by the high-S coals and the presence of agglutinated foraminifera in associated shales. The channel sandstones are commonly incised through grey shales down to the tops of major coals (Naylor et al., 1996). Intercalated alluvial plain strata include calcretes and red paleosols with evidence for strongly seasonal conditions (Tandon and Gibling, 1997). The Waddens Cove Formation is a local, predominantly red facies equivalent to the previous formations. Offshore, overlying unnamed red-beds up to about 1000 m thick are ascribed to the Pictou Group.

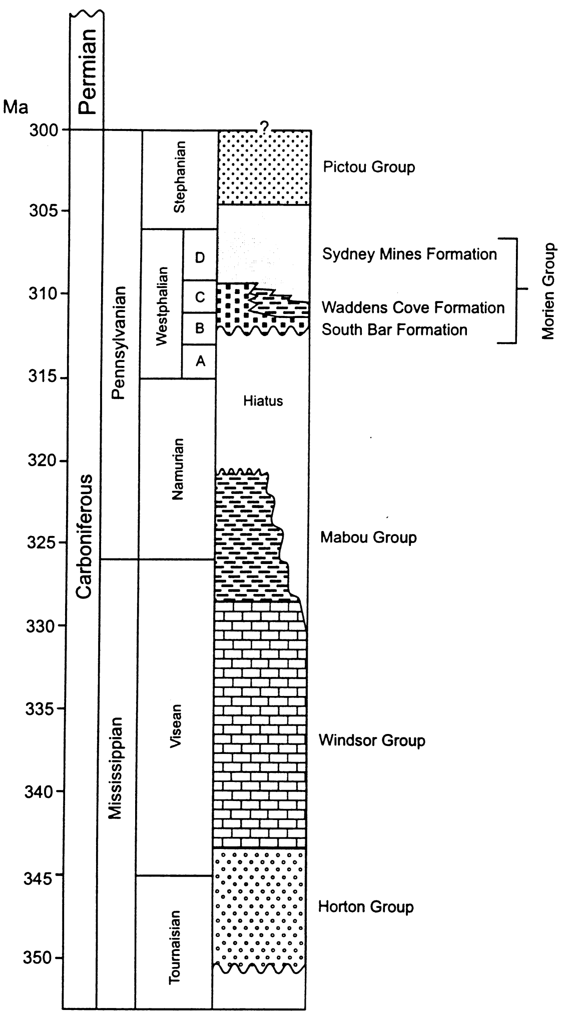

Fig. 3. Generalised stratigraphic column for the Carboniferous fill of the Sydney Basin onshore. Radiometric ages from Okulitch (1995). Modified from Gibling et al. (1987).

The Morien Group strata are gently folded into broad synclines and anticlines, with some anticlinal axes centred over structural highs in underlying basement rocks (Precambrian to Devonian). The strata mostly dip at low angles with local areas of steeper dips (Fig. 2). Faults are not prominent but are present locally, and some mines have experienced fault problems (Haites, 1951). The Sydney Basin is bounded by NE- to E-trending faults that run sub-parallel to the basement highs, and a basin-bounding fault, probably a strand of the Mountain Fault (Figs. 1 and 2), lies north of the Prince Mine and cuts the coal measures. Some faults that cut Lower Carboniferous rocks are overlapped by the coal measures, indicating a mid-Carboniferous or earlier phase of fault activity, whereas other faults have clearly moved subsequent to coal measure deposition. Several areas where the coal measures are faulted or folded, including the Mountain Fault and the Bridgeport Anticline near the Phalen Mine, are compressional zones that were probably active during the later Permian (Gibling et al., 1999). Salt structures are apparently rare in the Sydney Basin where Windsor Group strata appear to be regularly bedded. The basin was undergoing inversion by Late Triassic times, as indicated by apatite fission track studies (Grist et al., 1995), and Lower Cretaceous strata rest upon Carboniferous rocks in central Cape Breton Island (Dickie, 1987) and in the offshore Sydney Basin south of Newfoundland.

3. Sample groups and analysis

3.1. Water types

Formation waters, defined as waters within the pores of deeply buried rock (Drever, 1988), were collected from braced drivages (roadway tunnels) within the mine prior to significant coal extraction, when fracturing in the surrounding rock had been minimal. Samples were drips emanating from overlying roof sandstone or from boreholes intersecting sandstone, and are assumed to be in situ formation waters that have undergone little mixing or modification. Although the authors report relatively few samples, it is stressed that these samples have been carefully screened in consultation with CBDC staff, and represent an unusually reliable sub-surface suite. In both the Phalen and Prince Mines, samples were obtained from a single channel-sandstone aquifer (~30 m and 13 m thick, respectively) that locally cuts the mined coal. Phalen sandstones average 7% porosity and 0.08 millidarcies permeability (90 samples), whereas Prince sandstones average 15% porosity and 9.2 millidarcies (5 samples).

Gob waters are sampled from collection points that drain mined-out areas ("gobs"). Sydney coal is extracted by the retreat longwall method, where drivages encompass a reserve block and coal is extracted progressively toward the main slope beneath movable roof supports. As the supports move forward, the roof collapses behind the working face, allowing waters to drain through fractures into the "gob". The "gobs" are exposed to varying degrees of aeration, and waters may represent mixtures from panels mined at different times. They have undergone chemical reactions with mine rock that the formation waters have not, and may contain formation waters from several stratal levels mixed with the products of mine-rock reactions and fluids from operating machinery.

Strong evidence was reported in the Cape Breton Development Corporation (1994) report that inflows in the Phalen Mine are derived principally from the overlying, drowned workings of the Lingan Mine. The evidence includes good correlation between the initial flooding of Lingan and the onset of inflows into Phalen, and patterns of salinity and chemical variation through time following individual inflow events. This hypothesis is corroborated by the more extensive study carried out during the present project and reported elsewhere. Consequently, Phalen "gob" waters were not used in this study as they are mixed with waters (mainly modified meteoric waters) from the overlying Lingan workings. Prince "gob" waters probably originated principally from the thick sandstone just above the coal and, in view of the absence of overlying workings, are included as a separate population in this study. ADI Nolan Davis (1993) noted that waters from the shallow Lingan A mine section showed chemical similarity with modern seawater, but that deeper Lingan and Phalen waters showed little similarity to seawater. In addition, ^{3}H was detected in Lingan and Phalen inflow waters, indicative of a very recent source, whereas samples identified as formation waters contained no detectable ^{3}H (ADI Nolan Davis, 1993).

3.2. Collection and analysis

Waters in the Phalen and Prince Mines have been sampled routinely by CBDC since 1986, and additional samples were collected from mines and salt springs during this study. Samples collected during this study were filtered through 0.45 μm filters and stored in Nalgene polypropylene bottles. Temperature was measured at all locations using a standard thermometer. Eh and pH were measured at the salt spring locations, but could not be measured within the mine due to restrictions on taking equipment underground: they were measured at the surface immediately after collection. Samples collected by mine geologists at relatively shallow depths prior to the initiation of this study were no longer available, and formation water samples among this suite could not be duplicated because the near-surface sandstones have dried out during subsequent deeper mining. Thus, a full data set is not available for all samples.

Major and trace element analysis was conducted at Environmental Services Laboratory, Sydney, a CAEL accredited laboratory, using standard methods (American Water Works Association, 1989). Samples were split, filtered, acidified and analysed within two days of collection. The concentration of total dissolved solids (TDS, in mg/l) was calculated as the ionic sum of major and minor constituents (Na, K, Ca, Mg, Fe, Sr, Cl, SO_4 and 0.6 alkalinity), not including trace elements.

Bromine was measured by Philips Analytical Services Corporation, Halifax, Nova Scotia, a CAEL accredited laboratory, using ICP-MS (Long and Martin, 1991). Samples were preserved to $pH < 2$ with HNO_3, and Br was monitored at 79 and 81 amu, both of which are relatively free from interferences in a HNO_3 matrix. Precision was 0.0033 mg/l and the detection limit was 0.05 mg/l.

Oxygen, H and S isotope ratios were measured at the Environmental Isotope Laboratory, University of Waterloo, Ontario. Oxygen isotope ratios were determined using CO_2 equilibration (Epstein and Mayeda, 1953; Fritz et al., 1986), and H isotopic values were determined using Zn reduction (Coleman et al., 1982). Both methods employed conventional gas-source mass spectrometry, and results are reported with respect to the SMOW standard (Craig, 1961). Sulphur isotope analysis was carried out following combustion of SO_4 with a solid oxidant (Yanagisawa and Sakai, 1983), and laboratory procedures are described in Heemskerk (1993). Precision was 3‰ for D, 0.2‰ for ^{18}O in water, 0.5‰ for ^{18}O in SO_4, and 0.2‰ for ^{34}S.

$^{87}Sr/^{86}Sr$ isotope ratios were measured at Department of Geology, McMaster University, Ontario, on a VG354 mass spectrometer. All samples were leached with excess warm 6 M HCl and then rinsed before dissolution. The average value of NBS 987 during an earlier data acquisition was 0.710248 ± 0.000024 (2 SDM). Isotopic ratios were normalised for within-run fractionation to $^{87}Sr/^{86}Sr$ ratio of 0.1194.

Historical salt spring data for localities across Nova Scotia were collected by Cole (1930), and analyses were reported as weight of total solids with % of each species. The concentration of each component was converted to mg/l from the percentage value. The Whycocomagh and Bucklaw salt springs are close to the Sydney Basin (Fig. 1; locations given in Cole, 1930, and Boehner, 1986) and were resampled.

Table 1
Geochemical analyses of water samples from salt springs in Nova Scotia[a]

Sample Location	Sample ♯	Na	K	Mg	Ca	Sr	Fe	Cl	SO_4	Br	Ba	HCO_3	TDS	pH	$\delta^{18}O$	δD	$\delta^{34}S$	$\delta^{18}O(SO_4)$	$^{87}Sr/^{86}Sr$
DAL SPP-1 (Whycocomagh)	SSP-1	3300	15.6	5.0	51.2	0.6	0.02	5288	116.6	1.4	66	85.8	8829	7.9	−9.53	−61.74	12.28	8.64	
DAL SSP-2 (Bucklaw)	SSP-2	26200	108.5	43.0	1575.0	24.3	0.04	44850	4400.0	5.0	53	40.9	77225	7.7	−8.95	−61.2	14.40	11.48	0.7078
Kennetcook	33	1878	11.1	31.6	835.8			2981	2027.9				7900						
Kennetcook	34	7834	14.6	131.2	947.7			11839	3020.5			24300							
Kennetcook	35	6687		87.4	832.0			9580	2685.3				20800						
Otter Brook	36	1118		1.6	799.8			1763	1747.2				6000						
Walton	13	6698	40.7	19.3	1097.8			10546	2405.4				21400						
Walton	32	7430	53.0	19.3	1178.5			11650	2679.9				24100						
Oxford	9	3691	11.9	14.5	978.1			5823	2240.0				13200						
Oxford	10	7418	27.0	33.8	841.5			11693	1899.0				22500						
Oxford	10A	8087	19.6	34.3	833.0			12586	1984.5				24500						
Hartford-Hansford	7	4513	52.2	53.8	26.1			7480	2598.2				16300						
Hartford-Hansford	12	6615	1.9	39.7	415.8			10794	378.0				18900						
Hartford-Hansford	14	2592	15.6	9.2	46.2			4128	14.9				7100						
Hartford-Hansford	15	6109	33.1	29.4	702.9			9566	1698.3				18400						
Black River	11	27543	111.0	44.4	799.2			43179	1147.0				74000						
Roslin	8	2900	35.0	23.7	898.4			4780	2107.5				11300						
Kemptown-Cochester	29	10547	77.8	28.8	313.9			15719	1699.2				28800						
Salt Springs	28	20557	175.8	82.0	1254.0			33754	1037.2				58600						
Antigonish	21	14650	57.3	61.7	1437.7			22778	220.5				44100						
Antigonish	22	6854	19.2	91.6	824.3			10778	2061.8				21300						
Antigonish	26	22617	72.1	59.0	1637.5			35115	4028.3				65500						
Antigonish	27	12844	52.8	86.7	1131.0			20335	2394.0				37700						
Clendyer	38	11300	19.5	61.8	663.0			17752	1374.8				32500						
Pomquet	23	5894	28.2	107.2	579.0			8556	2564.3				18800						
Pomquet	24	13573	44.8	52.9	1400.1			21038	3414.7				40700						
Pomquet	25	2657	13.6	12.8	177.6			4188	368.0				8000						
Orangedale	18	10403	19.6	84.8	1356.2			16476	3022.0				32600						
Bucklaw	16	20119	40.8	64.1	1579.9			31418	3556.3				58300						
Whycocomagh	17	1218	2.6	8.6	66.0			1949	29.7				3300						
Baddeck	19	18225	105.0	85.0	555.0			28825	825.0				50000						
Baddeck	20	8288	49.6	42.5	250.2			13211	2709.3				23600						

[a] All data in mg/l, apart from pH and isotopic data. Numbered salt spring samples are from Cole (1930), recalculated to mg/l, and TDS values are as shown in the original report. Two additional samples (DAL notation) were collected during the present study, with TDS values calculated as described in the text. Spaces in data table indicate that analyses are not available.

Table 2
Geochemical analyses of water samples from Phalen and Prince Mines[a]

Sample ♯	Mine Section	Depth	Na	K	Mg	Ca	Sr	Fe	Cl	SO_4	Br	Ba	Alkalinity	TDS	pH	$\delta^{18}O$	δD	$\delta^{34}S$	$\delta^{18}O(SO_4)$	$^{87}Sr/^{86}Sr$
Phalen mine (formation water)																				
CBDC-589	3 WWF	435	40200	160	4400	21300		22.4	110000	11.0			1.0	176154	5.3					
CBDC-664	2 CB	611	38000	179	3220	15700	882.0	46.4	101945	1.0			0.4	160032	5.4					
CBDC-665	2 CB	611	41050	195	3390	15800	794.0	33.4	103834	1.0			0.4	165156	6.0					
PH-441	2 CB	610	40150	212	2825	13800	1006.0	30.0	94257	1.0		475	0.4	152328	5.5					
CBDC-845	6 ET	505	32750	200	3800	16000	1080.0	3.0	96126	1.0		323	0.4	150010	5.9					
CBDC-646	6 ET	508	43000	240	4200	17000	860.0	24.0	104955	1.0		421	0.4	170333	5.8					
CBDC-648	6 EB	542	40000	191	2600	13000	1210.0	5.2	96814	1.0		860	23.2	153885	5.8	−4.18	−28.6			
PH-407	6 ET	505	37300	210	3570	17100	1000.0	8.0	100788	1.0			20.8	160045	5.9					
PH-1229	7 ET	557	41000	224	2780	15600	1082.0	6.7	103716	1.0			49.9	164490	9.1					
PH-976	8 ET	612	41150	225	2360	12400	818.0	24.0	95828	8.9			26.7	152883	5.9					
PH-1200	8 EB	646	41900	204	2540	11700	1305.0	35.8	96754	1.9			56.6	154528	6.0					
PH-2264	8 ET	625	43000	209	2650	12300	2080.0	26.2	98362	1.0		975	43.3	158701	5.8					
PH-1611	9 ET	657	41950	216	2515	12550	840.0	33.8	97050	1.0		1160	0.4	155207	5.3					
PH-1612	9 ET	657	46450	246	2460	13000	862.0	32.2	97828	1.0		1150	13.1	160938	5.6					
PH-2835	9 ET	654	45800		2550	12450	2025.0	35.6	97135	2.7			25.0	160067	5.5					
PH-2841	9 ET	654	46700		2630	12800		32.8	97605	6.4			29.0	159849	5.9					
PH-2847	9 ET	654	46450		2630	12700		29.8	98546	1.0			68.3	160447	5.5					
Dal PH 3 S	3 S	692	41200	199	2690	12000	2030.0	27.2	97780	1.0	935		7.8	155980	5.1	−4.63	−23.47			0.7114
CBDC-663	3 S	690	40600	214	2370	11400	844.0	27.8	95525	1.7			20.2	151046	5.7					
PH-697	3 S	690	42100	225	2490	12300	724.0	28.8	98919	1.0			26.8	156852	5.7					
PH-2606	3 S	692	37450		2070	10425		36.6	83746	1.0			19.6	133776	5.4					
PH-2621	3 S	692	40400		2110	8910		80.4	87200	1.0			0.4	138754	4.9					
PH-2850	3 S	692	43450		2725	12300		24.8	96956	5.7			0.4	15551	4.8					
Prince mine (formation water)																				
CBCD-518	4 WWF	192	2650	52	93	345		0.02	4700	2.4		2.3	177.0	7950	7.9					
Dal Pr 4D	4 Decline	331	11900	108	1145	4345	82.3	4.5	30230	< 1	150	21	31.5	47840	7.9	−5.48	−31.31			0.7102
CBCD-559	4 Decline	266	5200	81	294	1030		0.9	11200	12.0			160.0	17918	8.1					
CBCD-43	8 WT	205	3200	64	175	463		6.8	6100	2.0			210.0	10139	7.7					
CBCD-594	9 WWF	234	5590	90	402	1370		2.5	11100	3.0			76.0	18606	7.5					
CBDC-602	9 WWF	241	4830	72	302	991		0.4	10000	2.0			140.0	16285	7.6					
CBDC-676	14 WB	313	11100	93	1135	4090	62.6	5.1	27105	3.6		12.2	44.9	43627	6.7					
PR 3	15 WBL	280	10580		958	3320	54.6	7.5	24500	3.7	130	25	105.0	39488	7.3					
Prince mine (gob water)																				
CBDC-571	5 WB	215	6770	104	660	1900		32.0	15600	1420.0			1.0	26490	2.7					
CBDC-570	6 WWF	220	7230	112	830	1900		197.0	16700	1870.0			1.0	28843	2.9					
DAL Pr 7WB	7 WB	224	5615	67	871	2025	30.3	187.0	13440	2235.0	63	< 0.05	0.4	24473	2.6	−6.99	−42.38			
DAL Pr 10WB	10 WB	266	8070	126	1290	2535	42.5	712.0	20550	2313.0	100	0.11	0.4	35643	4.0	−6.9	−42.41			0.7101
Dal Pr 12 WB	12 WB	290	10700	153	1625	4280	65.9	149.0	27950	1633.0	130	0.16	0.4	46561	4.4	−5.71	−36.57	10.84	3.05	
CBDC-673	13 WT x-cut ♯ 3	260	9000	180	1120	2800	40.2	19.8	21330	1978.7		0.07	36473	5.2						
CBDC-674	13 WT x-cut ♯ 3	260	8640	163	1060	2675	61.6	28.4	21830	1983.5		0.07	3.5	36447	5.6	−4.42	−29.42	17.24	9.13	
CBCD-677	12 WWF	284	9170	140	1305	3535	48.8	43.2	22425	1584.6		0.16	0.4	38256	4.5					
CBDC-679	13 WT x-cut ♯ 2	270	10175	174	1473	3470	46.2	95.4	24318	2063.7		0.05	0.4	41821	3.1					
CBDC680	13 WT x-cut ♯ 3	260	9000	159	1163	3018	37.4	39.4	21410	1678.8		0.08	23.1	36522	5.9	−4.33	−30.27	18.02	10.32	
CBDC-681	13 WT x-cut ♯ 2	270	9145	164	1265	2760	40.0	79.4	20815	1810.0		0.08	0.4	36081	5.2					
CBDC-684	14 WT x-cut ♯ 1	294	11400	141	1470	3210	451.0	24.6	225242	1914.8		0.07	0.0	43858	4.9					

[a] All data in mg/l, apart from pH and isotopic data. Mine section indicates location within mine panels. Depth in metres below sea level. See text for definition of “formation” and “gob” waters. Spaces in data table indicate that analyses are not available.

The compositions of 32 salt-spring waters and 43 mine waters are shown in Tables 1 and 2 and illustrated in the graphs of Figs. 4–11. The sea water evaporation curve of Fontes and Matray (1993a) is shown for reference, with the onset of precipitation of key minerals. In view of the great variability in salinity observed in the present study, with most samples greatly exceeding the salinity of sea water, the term "brine" is used for saline fluids without specific concentration limits (see discussions in Carpenter, 1978, and Hanor, 1994).

4. Salt spring waters

4.1. Results

Salt-spring samples are Na–Ca–Cl–SO_4 waters that

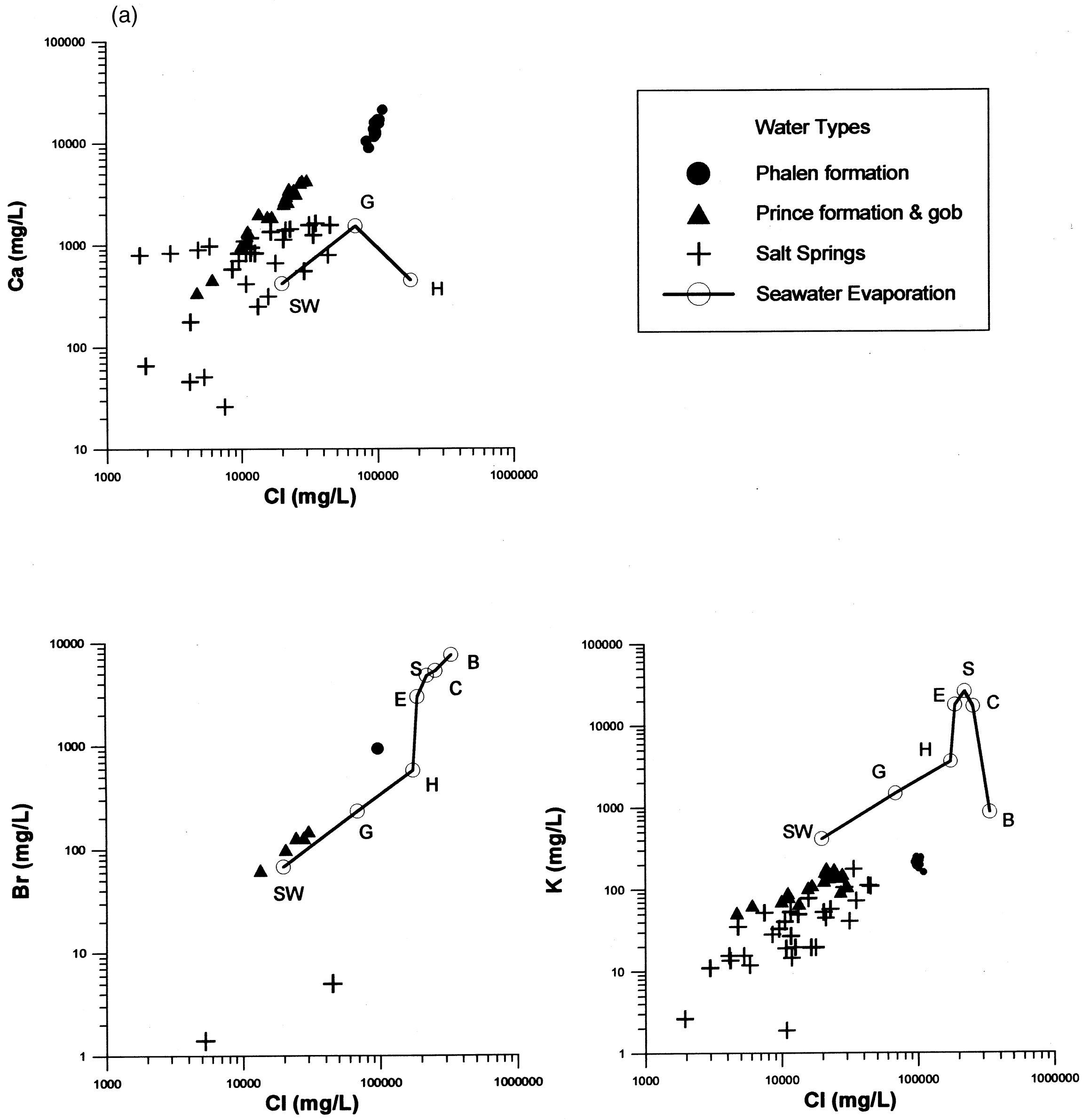

Fig. 4. Major ions of mine and salt spring waters, plotted against Cl. Seawater evaporation trajectory from Fontes and Matray (1993a): SW = sea water composition; G, H, E, S, C and B refer to point of precipitation of gypsum, halite, epsomite, sylvite, carnallite and bischofite, respectively. See text for explanation of "formation" and "gob" waters.

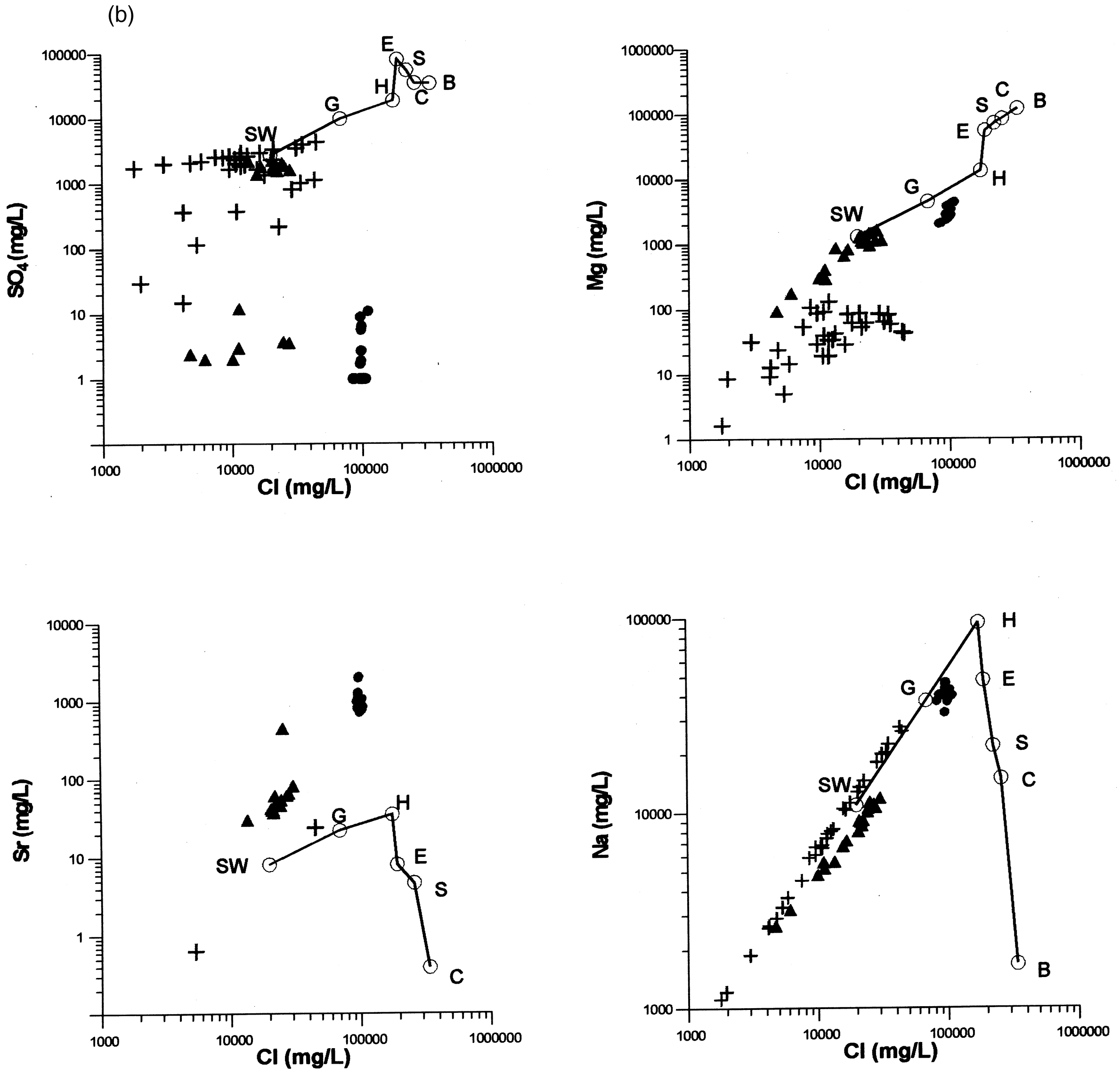

Fig. 4 (*continued*)

show TDS values from 3300 to 77,225 mg/l (Table 1). Cole (1930) found that Br values were below the detection limit, which was not reported. For the two resampled salt springs, both Br concentrations and Br:Cl ratios are much lower than expected for evaporated seawater (Figs. 4 and 5). The salt spring suite plots consistently above the seawater evaporation curve on a graph of Na against Cl (Fig. 4). Sodium enrichment is also shown in the plot of Na/Cl against Cl (Fig. 5, in which Cl serves as a proxy for salinity), where salt spring samples approximate a 1:1 molar ratio. Calcium and SO_4 show little correlation with Cl (Fig. 4) but show a moderate degree of correlation with each other (Fig. 6). The waters are depleted in K and Mg with respect to the evaporation curve, and two Sr analyses plot below and slightly above the curve (Fig. 4).

Hydrogen and O isotopic values plot close to the local rainwater mean (Fig. 7). One $^{87}Sr/^{86}Sr$ isotope measurement of 0.70775 was obtained (Fig. 8). $\delta^{34}S$ values are 12.3–14.4‰ and $\delta^{18}O(SO_4)$ values are 8.64–11.48‰ (Fig. 9).

4.2. Interpretation

The salt spring solutes are inferred to have originated from dissolution of Windsor evaporites. Dissolution of halite by circulating groundwaters typically generates Cl-rich brines with a high (~1:1) Na:Cl molar ratio (Fontes and Matray, 1993b). Halite excludes most Br during precipitation but contains ~30–260 ppm Br depending on the salinity of the evaporating water (Rittenhouse, 1967; McCaffrey et al., 1987; Fontes and Mattray, 1993a). Boehner (1986, Appendix 2) recorded 8–179 ppm of Br in 205 Windsor evaporite samples (mainly halite) from the Hants-Colchester area of mainland Nova Scotia, with most samples ≫30 ppm. Typical Br:Cl ratios from halite dissolution are much lower than those in brines at the onset of halite precipitation (Richter and Kreitler, 1986; Fontes and Matray, 1993a).Thus, halite dissolution should produce a low Br:Cl ratio relative to that of highly evaporated seawater. Halite dissolution, especially within diapirs, has been widely invoked to account for the elevated salinity of basinal waters in the Gulf of Mexico (Moldovanyi and Walter, 1992; Land and Macpherson, 1992; Hanor, 1987, 1994).

The poor correlation of Ca and SO_4 with Cl indicates that Ca is not balanced by Cl. Instead, the moderate correlation of Ca with SO_4 supports an origin from dissolution of Windsor Ca sulphates, and this inference is further supported by the similarity of S isotopic values with those of Windsor anhydrite. The single $^{87}Sr/^{86}Sr$ analysis is similar to the ratio inferred for Visean seawater (Smalley et al., 1994) and to that

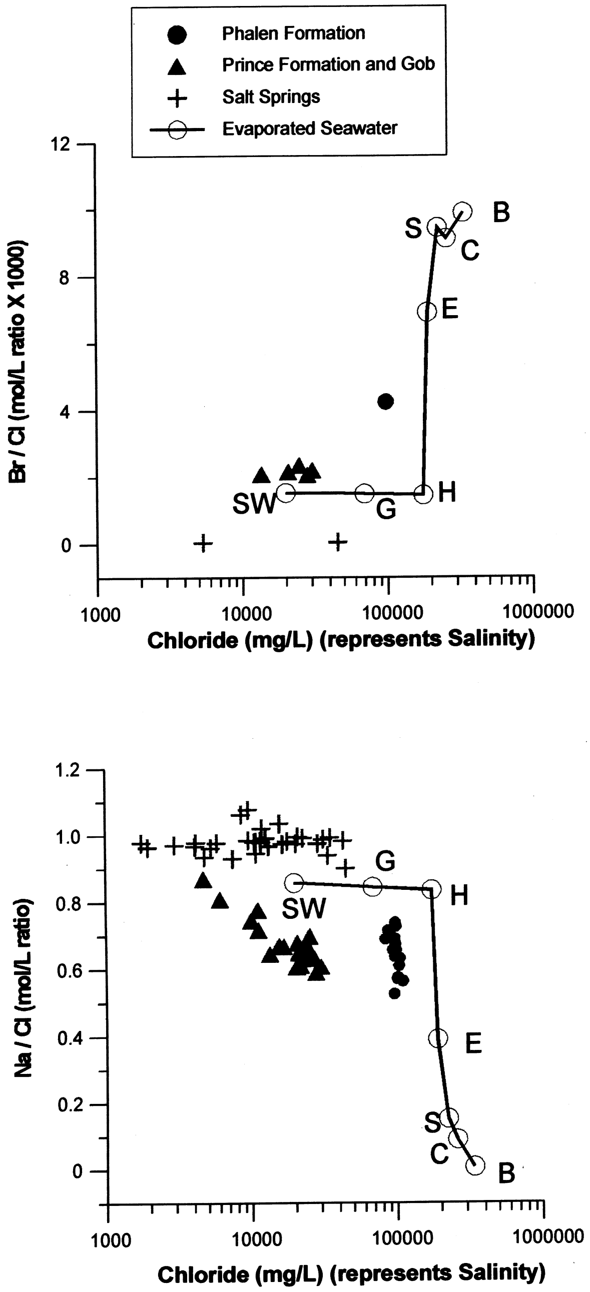

Fig. 5. Br/Cl and Na/Cl ratios (molar) of mine and salt spring waters, plotted against Cl. Seawater evaporation trajectory from Fontes and Matray (1993a).

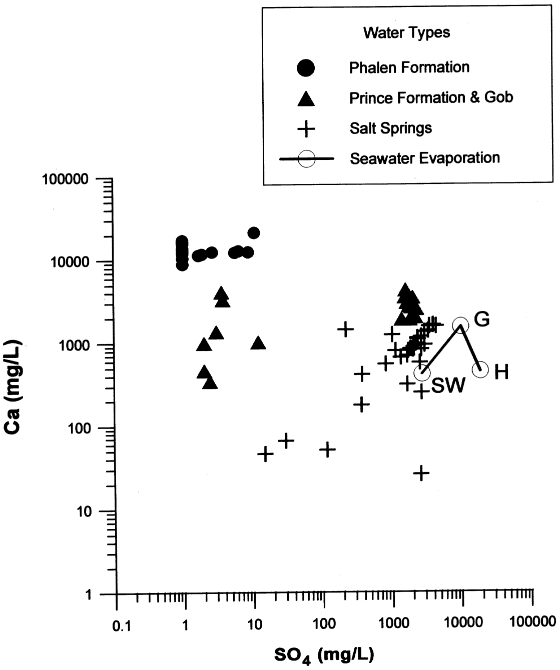

Fig. 6. Calcium in mine and salt spring waters, plotted against SO_4. Seawater evaporation trajectory from Fontes and Matray (1993a). The high-SO_4 mine waters are Prince "gob" waters.

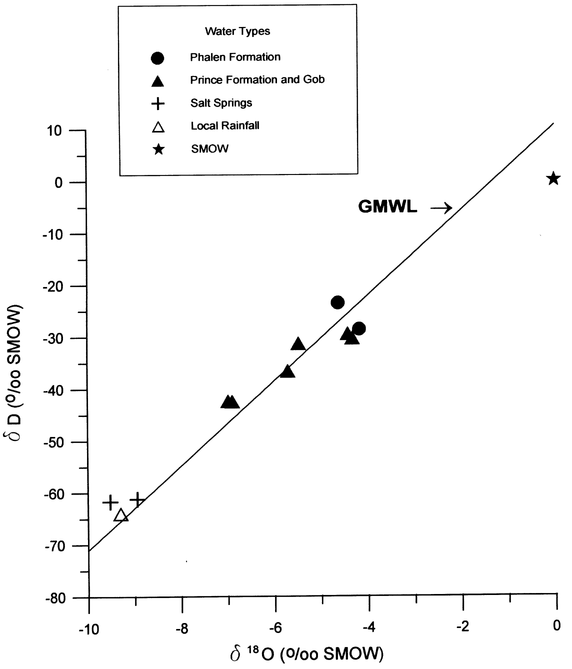

Fig. 7. Hydrogen and O isotopic ratios for mine and salt spring waters, in relation to Global Mean Water Line (GMWL) and Standard Mean Ocean Water (SMOW). GMWL and SMOW from Drever (1988).

measured for some Windsor carbonates (Savard et al., 1996), and also supports a Windsor source. Low Mg and K concentrations relative to the evaporation curve probably reflect the low proportion of Mg or K salts available for dissolution within the Windsor evaporite column. The close correspondence of H and O isotopic values with those of rainwater suggests that the salts were dissolved by modern meteoric waters.

5. Mine waters

5.1. Results

TDS values for Phalen formation water range from 133,740 to 176,094 mg/l for samples from 435 to 692 m depth (Table 2). TDS values for the shallower Prince formation water are much lower, ranging from 7949 to 47,834 mg/l, broadly comparable to "gob" waters at 24,470 to 46,556 mg/l (Table 2). Bromine is enriched relative to the seawater evaporation curve (Fig. 4), and Prince waters plot in a straight line sub-parallel to the curve. Br:Cl ratios plot above the evaporation curve, and are highest for the Phalen sample (Fig. 5). Sodium is balanced by Cl, as indicated by a well-defined linear trend in Fig. 4, but Na is depleted relative to the evaporation curve. The Na:Cl ratio shows a considerable range at near-constant Cl levels for Phalen waters and a well-defined trend with increasing Cl for Prince waters (Fig. 5), and the most saline Prince samples have Na:Cl ratios similar to Phalen samples.

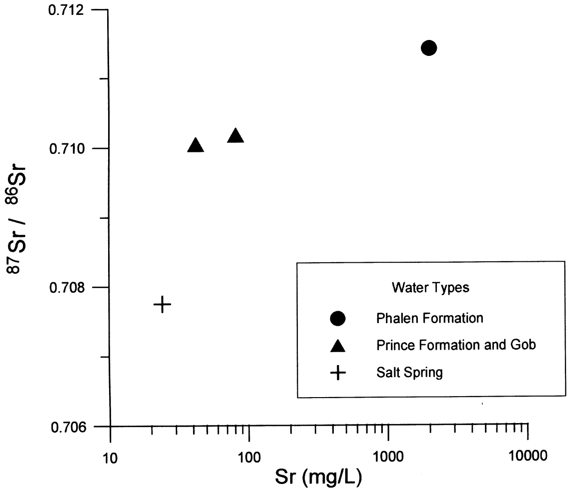

Fig. 8. $^{87/86}$Sr isotopic ratios for mine and salt spring waters, plotted against Sr.

Both Ca and Sr are enriched relative to the evapor-

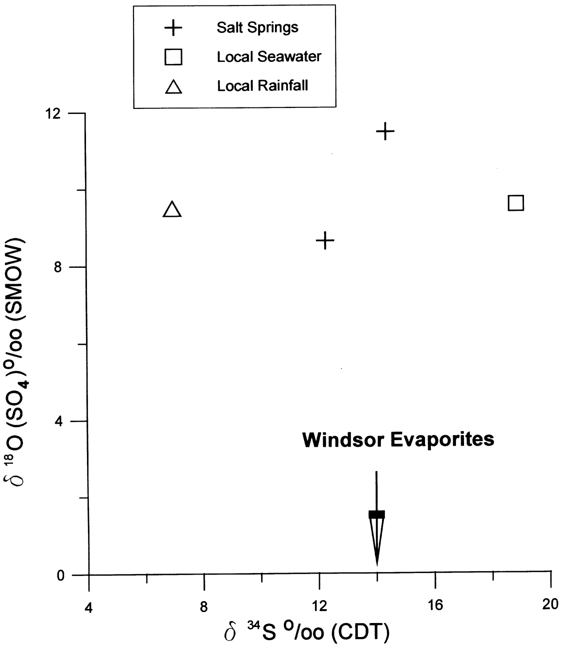

Fig. 9. Oxygen and S isotopic ratios for sulphates in salt spring and other local waters. The arrow indicates the average S isotopic value for Windsor anhydrite samples from the Kempt Head drill hole (Fig. 1), as reported by Gibling et al. (1989), who did not report isotopic values for O in SO_4.

ation curve whereas Mg and K are depleted (Fig. 4) and SO_4 is severely depleted (Figs. 4 and 6). Sulphate-rich Prince waters are all "gob" samples that also show increased Fe and decreased pH (Table 2), almost certainly due to pyrite oxidation within the "gob".

Hydrogen and O isotope values plot on or near the GMWL with H values between −23 and −42‰, and O values between −4 and −7‰ (Fig. 7). Heavy isotopes are generally enriched to a modest degree in more saline waters. $^{87}Sr/^{86}Sr$ is relatively high compared with salt-spring waters (Fig. 8), and the 3 mine samples show an increase in radiogenic Sr with increasing Sr and salinity.

5.2. Interpretation

The mine water chemistry is interpreted in relation to the 3 main models for solute concentration (see Introduction).

5.3. Seawater Evaporation Model

As noted above, Br is largely excluded from the halite structure, and thus evaporation of seawater past the point of halite precipitation results in a residual brine that has a high Br:Cl ratio relative to seawater (Carpenter, 1978; McCaffrey et al., 1987). The high Br content and high Br:Cl ratio of the Sydney mine waters favour an evaporative residue interpretation, as inferred for numerous other basinal brines (Egeberg and Aagaard, 1989; Connolly et al., 1990; Fontes and Matray, 1993b; Nativ, 1996). Halite precipitation reduces the Na:Cl ratio of residual fluids (e.g. Nativ, 1996), and the low Na:Cl ratios of the mine waters are also in accord with an evaporative origin.

The relationship between these two ratios is explored in a plot of Br/Cl against Br/Na (Walter et al., 1990) in Fig. 10. The brines lie within the zone ascribed to sea-water evaporation by Kesler et al. (1995). However, Chi and Savard (1997) noted that mixtures of evaporative brines and fluids derived from halite dissolution converge strongly towards the high-Br evaporative brines, and that mixed fluids with as little as 10–20% of original evaporative brine could still plot within the seawater evaporation zone. Thus, mixing of Sydney evaporative brines with fluids derived from halite dissolution cannot be ruled out.

Dilution of brines by meteoric water lowers the ab-

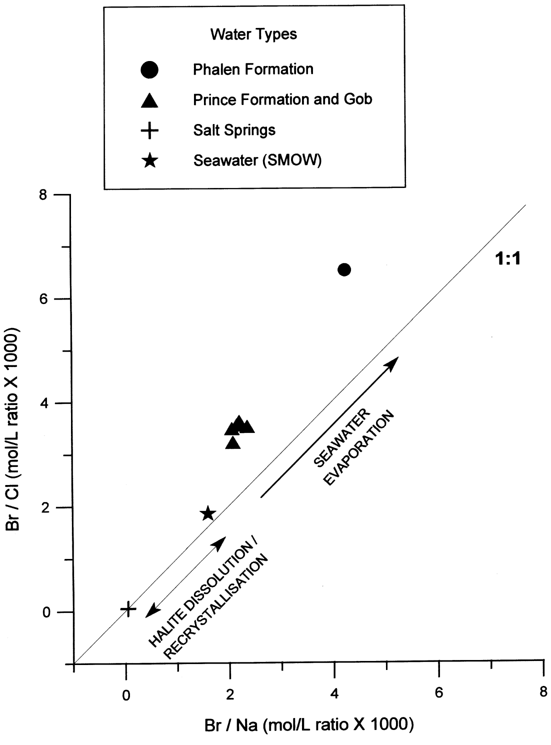

Fig. 10. Br/Na plotted against Br/Cl (molar ratios) for brine and salt spring samples. Geochemical trends (arrowed) modified from Kesler et al. (1995). The salt spring data point represents two samples with low Br contents.

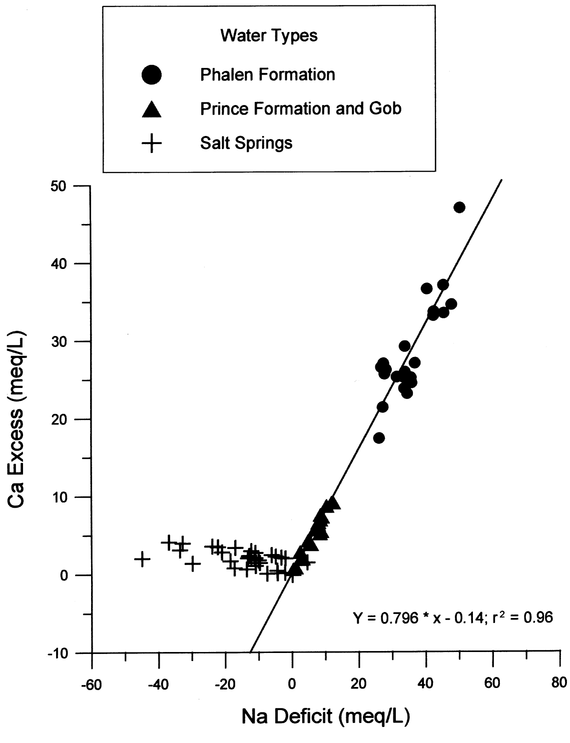

Fig. 11. Ca excess plotted against Na deficit for brine and salt spring samples. Parameters from Davisson et al. (1994) and Davisson and Criss (1996). Seawater composition used in calculation from Drever (1988).

solute concentrations but does not affect the solute ratios. Egeberg and Aagaard (1989) used the Br:Cl ratio to estimate the degree of evaporation experienced by North Sea basinal brines prior to dilution, by comparison with the seawater evaporation curve. They assumed that the brines had been diluted by meteoric water and that Br and Cl are conservative. Using similar reasoning, the evaporation ratio of the Sydney brines prior to dilution can be calculated for Phalen waters (30–32) and Prince waters (15–18). This evaporation level is well within the zone of halite precipitation, but below the concentration required for Mg salts (McCaffrey et al., 1987; Hanor, 1994), and corresponds well with the evolutionary stage of preserved Windsor salt deposits at Sydney (Boehner, 1986).

Evaporation initially enriches the remaining water in heavy isotopes (^{18}O, ^{2}H), so that evaporated seawater generally plots to the right of the GMWL (Lloyd, 1966; Sofer and Gat, 1975). The isotopic plot for the mine waters is problematic for an evaporative interpretation because the water samples plot very close to and, in some cases, slightly above the GMWL. Careful re-analysis of some samples confirmed these apparently anomalous results. Considering the isotopic data alone, modern meteoric water (local rainfall) is ruled out as a sole source, but mixing between modern meteoric and seawater would be possible. A single source of older (warmer than present) meteoric water with higher isotopic values is also possible. However, the highly elevated salinity of most samples (greater than sea water) rules out such explanations. Because the cation evidence outlined above strongly supports an evaporative origin, possible means of reconciling the isotopic signature with other geochemical evidence are set out below:

1. As seawater evaporates, the H and O isotopic values initially increase but eventually loop down and back toward the GMWL, probably due to the increased proportion of water involved in hydration spheres around cations (Knauth and Beeunas, 1986). Thus, a hooked isotopic trajectory is observed on H–O plots in progressively evaporated seawater.This results in highly evaporated waters that are generally depleted in ^{2}H and either enriched or depleted in ^{18}O relative to Standard Mean Ocean Water (SMOW) (Knauth and Beeunas, 1986). However, a much greater degree of evaporation than that deduced above from Br content would be necessary to bring isotopic values close to the GMWL.
2. Dilution by meteoric water could have moved the evaporative values back toward the line. Such dilution could have taken place during the evaporative cycle (Pierre et al., 1984) or during geologically recent times. The samples might thus lie on a mixing line between an evaporative residue to the right of the GMWL and a meteoric composition located on or close to the line. Such an explanation is difficult to apply to the concentrated Phalen waters which, at present TDS values of up to 176,000 mg/l, can have undergone only modest dilution (the most saline brine known has a concentration of 643,000 mg/l: Hanor, 1994).
3. Where modern inland seas evaporate into dry continental air, the ^{2}H excess is significantly greater than the worldwide average of 10‰ (e.g. 37 in the eastern Mediterranean), creating local lines above the GMWL (Gat and Carmi, 1970). Present-day isotopic values for the mine waters might lie in the evaporative field for such parent meteoric waters and would, by coincidence, lie close to the GMWL. Secular change in oceanic isotope composition could have changed the position of the GMWL through time, but such change is debatable (e.g. Land and Lynch, 1996).
4. Brines in Tennessee are interpreted by Nativ (1996) as seawater evaporative residues but plot above or on the GMWL. Nativ (1996) suggested that SO_4 was reduced to H_2S through the breakdown of ^{2}H-enriched organic matter. The H_2S could have exchanged with the brines, increasing their ^{2}H values (Friedman and O'Neil, 1977; Frape and Fritz, 1982). Whereas there is little evidence of H_2S gas in the Phalen and Prince mines, a similar exchange could have occurred between water and CH_4 as the mine sandstones are CH_4 reservoirs (Aston et al., 1990). Ravenhurst et al. (1989) studied isotopic data from saline fluid inclusions in mineral deposits within the Maritimes Basin, and noted that several values plotted above the GMWL, which they explained by interaction with organic components.

Sr isotope values are higher than inferred seawater levels since the Cambrian (Smalley et al., 1994), and are much higher than Windsor evaporite values (Savard et al., 1996) and the salt spring sample. This observation is discussed later.

5.4. Halite Dissolution Model

The strongest line of evidence against halite dissolution as an explanation for the mine-water chemistry is the contrast between mine and salt-spring waters evident in all the chemical plots (see, for example, Fig. 10). In particular, mine waters are enriched in Br (Fig. 4), which does not support halite dissolution. Bromine can be incorporated into brines through the preferential dissolution of relatively soluble evaporites precipitated during extreme evaporation (Hanor, 1987; Fontes and Matray, 1993a), but to date, only small amounts of highly evolved evaporites (carnallite and minor sylvite) have been found in Sydney Basin cores (Boehner, 1986). Bromine enrichment in fluids can occur during slow halite recrystallization, where Br is excluded from the crystal lattice, and this may explain high Br:Cl ratios in brines thought on other grounds to have originated from halite dissolution (Land and Prezbindowski, 1981; Moldovanyi and Walter, 1992). Recent literature (Fontes and Matray, 1993a) casts doubt on the effectiveness of halite recrystallization as a method of concentrating significant amounts of Br. Additionally, Br content of Windsor halite (Boehner, 1986) is mostly considerably greater than the 30 ppm cited by Fontes and Matray (1993a) for the onset of halite precipitation, implying that Windsor halite has undergone only modest recrystallisation and Br loss.

The mine waters show low Na:Cl values (Fig. 5), and substantial water–rock interaction would be required to modify original high Na–Cl waters generated by halite dissolution. As discussed below, the authors believe that some water–rock interaction has taken place. Evaporite dissolution should have been mediated by meteoric water, as inferred on isotopic evidence for salt-spring waters. The mine waters fall close to the GMWL approximately halfway between SMOW and local rainwater, and this composition could represent fluids from earlier geological time.

In summary, there is strong evidence against halite dissolution as a major cause of salinity generation for the mine waters, although some geochemical trends are consistent with halite dissolution. As noted above in the discussion of Fig. 10, a considerable contribution of fluid derived from halite dissolution cannot be ruled out, especially in view of the local evidence for solution brecciation of Windsor rocks.

5.5. Hyperfiltration Model

Hyperfiltration concentrates solutes during the passage of fluid through a semi-permeable, non-fractured membrane under a high hydrostatic pressure differential (Graf, 1982). A membrane such as shale allows preferential passage of ions depending on factors that include ionic radius, charge, temperature, pressure and membrane material (Kharaka and Berry, 1973; Kharaka and Smalley, 1976). Solutes are concentrated on the high pressure (inflow) side of the membrane. This process may also cause fractionation of isotopes such as ^{18}O and ^{2}H, generating heavier isotopic values on the inflow side (Graf et al., 1966; Kharaka and Carothers, 1986; Phillips and Bentley, 1987). Hyperfiltration has been applied especially to basins that contain overpressured zones or that lack evaporites (Graf, 1982).

It is currently difficult to evaluate this model for the Sydney brines. Large head differences are generally found in basins with large elevation differences or that have overpressured shales. Neither of these conditions applies to the Sydney Basin. Land (1995) inferred that hyperfiltration is not occurring at the present day in Gulf of Mexico overpressured zones where thick shale and large pressure differences should provide ideal conditions, and many other workers have questioned the ability of hyperfiltration to produce significant brines under natural or experimental conditions (Schwartz and Muehlenbachs, 1979; Knauth and Beeunas, 1986; Hanor, 1987, 1994; Demir, 1988; Egeberg and Aagaard, 1989; Fontes and Matray, 1993a). Hyperfiltration may have contributed to salinity elevation locally.

5.6. Other mechanisms

Various organisms are known to concentrate Br (see reviews in Edmunds, 1975, 1996), which might have been released from the host organic matter during maturation of the coal-bearing strata, as suggested for Texas brines by Means and Hubbard (1987). No Br analyses are available for Sydney coals and organic-rich shales to explore this possibility, which cannot be ruled out as a contributing factor. However, an organic source for Br leaves unexplained the very high salinity and Cl content of the brines, which are more readily explained by evaporative concentration.

Three additional methods for generating basinal brines were suggested by Hanor (1994). Firstly, brines in subsurface rocks of the Canadian Shield and other cratonic areas (Frape and Fritz, 1987) may have obtained Cl and Br from halogen-bearing minerals such as some hornblendes and biotites (Kamineni, 1987; Edmunds et al., 1987), although some basement brines may have originated by recharge from evaporative Proterozoic and Paleozoic basins (Gascoyne et al., 1987; Bottomley et al., 1994). Secondly, marine aerosols may be blown inland and contribute solutes to meteoric groundwater (Jones et al., 1994). Thirdly, basinal fluids may evaporate into gas accumulations in the subsurface, leading to increased salinity (Hanor, 1994). These 3 methods have not been widely cited for sedimentary basins, and are difficult to evaluate for the Sydney Coalfield.

6. Modification of the original brines

Sydney brines are enriched in Ca and Sr and depleted in Na, Mg, K and SO_4 relative to the modern seawater evaporation curve (Fig. 4), as noted in other basinal brines (e.g. Egeberg and Aagaard, 1989). Assuming a residual brine origin for most of the ions in the Sydney samples, changes in cation proportions are most readily explained by water–rock interaction within the host sandstones and/or during passage through adjacent rock units. As noted by Hanor (1994), the general covariance of K, Mg, Ca and Sr with Cl in basinal fluids (noted also in the Sydney mine waters) provides strong evidence that these elements are "buffered" by reactions with the rock body.

The relationship between the Na deficit and Ca excess in basinal fluids was explored by Davisson and Criss (1996) using two parameters:

$$\mathrm{Ca_{excess}} = [\mathrm{Ca_{meas}} - (\mathrm{Ca/Cl})_{\mathrm{sw}}\,\mathrm{Cl_{meas}}]\,2/40.08$$

$$\mathrm{Na_{deficit}} = [(\mathrm{Na/Cl})_{\mathrm{sw}}\,\mathrm{Cl_{meas}} - \mathrm{Na_{meas}}]\,1/22.99$$

where measured (meas) ion concentrations in mg/l are related to those of seawater (sw), and the numerical constants convert the results to meq/l.They showed that a wide variety of basinal brines plotted with a high degree of correlation along a Basinal Fluid Line, the slope of which indicates a net cation exchange ratio of 2 Na for 1 Ca, and suggested that original Na-rich brines have been modified principally through albitization of plagioclase (see also Land and Prezbindowski, 1981). Fig. 11 shows that these two parameters are well correlated for Phalen and Prince brines, in contrast to local salt-spring waters.

Plagioclase grains in Phalen sandstones have An contents less than 5%, and skeletal K-feldspars and perthites show lamellae, patches and cross-cutting veins of albite with similar low An contents (Gibling and Nguyen, 1999). This suggests that albitization has affected feldspars at the level of the Sydney Mines Formation. However, sandstones that were cemented by calcite early in diagenesis contain K-feldspars with albite patches, suggesting that at least some albite was formed prior to or in the earliest stages of burial, for example during deuteric activity in the source plutons (Lee and Parsons, 1998). Feldspathic sandstones and conglomerates are prominent in the thick Carboniferous succession below the Sydney Mines Formation, and have undergone burial to depths expected for albitisation of plagioclase (Fisher and Land, 1986).

Other water–rock reactions have probably influenced the present brine composition. Magnesium depletion may reflect dolomitisation (Carpenter, 1978; Stoessel and Moore, 1983), as dolomite is present in Windsor and Mabou Group carbonates (Savard, 1991; Crawford, 1996) and as a local cement in the South Bar Formation (M.R. Gibling, unpublished data). Dolomitisation of Sr-bearing carbonates could have generated some of the excess Sr observed in the waters (Fig. 4). Skeletal K-feldspar and perthite grains in Phalen sandstones suggest that K may have been added to the brines during diagenesis. However, K is depleted relative to the seawater evaporation curve, and may have been lost through formation of illite — a pore fill in the mine sandstones and component of Sydney Basin shales (Gibling et al., 1985; Gibling and Nguyen, 1999).

The $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios are very high in contrast to values for Paleozoic carbonates, including basal Windsor carbonates. High Sr isotope ratios have been used in several basins to infer that fluids moved through "basement" rocks enriched in radiogenic Sr (Egeberg and Aagaard, 1989; Banner et al., 1989; McNutt et al., 1987; Mountjoy and Qing, 1992). Within the Maritimes Basin, high Sr isotope ratios of phases have been noted in mineralised zones and explained by the passage of fluids through immature siliciclastic sediments of the Horton Group or underlying basement rocks (Ravenhurst et al., 1989; Savard et al., 1996; Sangster et al., 1998; Savard and Chi, 1998). This is a possibility also for the Sydney brines. The large $^{87}\mathrm{Sr}$ excess could also reflect the diagenetic dissolution of Rb-rich K-feldspars in sandstones of the Sydney Mines Formation. $^{87}\mathrm{Sr}$ may also be enriched in evaporitic fluids during or shortly after formation due to reaction with silicates or addition of Sr from continental waters entering the basin, or through $\mathrm{CaSO_4}$ dissolution (Fontes and Matray, 1993b).

Seawater evaporative residues are initially high in $\mathrm{SO_4}$, whereas the mine waters that have not travelled through the "gob" have very low $\mathrm{SO_4}$ values (Fig. 4). Sulphate may undergo reduction to sulphides in the presence of organic matter, and pyrite is common in the mine rocks and in the Sydney Basin strata generally. Much of the pyrite is framboidal and early diagenetic in origin, but some is present as large nodules, on coal cleats, and along basal sandstone surfaces, probably formed during deep burial. Additionally, galena coats some cleat surfaces (S. Forgeron, pers. comm.), and Pb and Zn sulphides are present as tiny crystals in diagenetic carbonates in mine sandstones (Gibling and Nguyen, 1999). It is suggested that sulphide formation at depth contributed to the decrease in $\mathrm{SO_4}$ values of the brines.

7. Source and emplacement of mine brines

The brine-hosting Sydney Mines Formation was deposited in an alluvial to restricted-marine setting. The red alluvial strata formed under seasonal conditions, but no salt deposits or other firm indications of hypersalinity are known. Thus, salinity of connate waters could have varied from fresh to normal marine, but is unlikely to have achieved the salinity levels of the Phalen brines. Minor evaporites are present in the Horton and Mabou Groups, but the Windsor Group contains the only thick and regionally extensive evaporite sequence preserved within the Maritimes Basin. Permian strata in Europe and the western USA contain thick evaporite successions, but no evaporites have been identified in the Pictou Group overlying the coal measures of Atlantic Canada. Although Triassic Argo Formation salts were deposited in rift basins along the Atlantic margin (Grant et al., 1986), they are not known within the Maritimes Basin. The Cretaceous ocean may have covered the mine areas as marine Cretaceous strata are present nearby, but they are not known to include evaporitic facies. Late Quaternary seawater may have covered the area during highstands, depending on isostatic factors and the rate of coastline retreat. It is concluded that, although marine waters may have entered the Upper Carboniferous strata at various times during and after deposition, the Windsor Group was the predominant source of the evaporitic brines. Remnant brines from halite (and potash) precipitation would have been denser than local groundwater and could have recharged adjacent porous aquifers, in a manner analogous to the recharge observed below Australian saline lakes (Macumber, 1992).

Brine-filled fluid inclusions, or mineral isotope data consistent with saline fluids, have been identified in several Zn–Pb sulphide and barite deposits within the Maritimes Basin (Ravenhurst et al., 1989; Armstrong et al., 1993; Chi and Savard, 1995; Chi et al., 1995; Savard et al., 1996; Kontak, 1998). Ages and palaeomagnetic evidence (Pan et al., 1993; Kontak et al., 1994) suggest that some brine-mediated mineralisation took place during the Pennsylvanian, possibly linked to a tectonically driven fluid expulsion event (Ravenhurst et al., 1989). These studies strongly implicate the Windsor Group as the Sydney brine source. It is noted that, although they may originally have been enriched in metals, both Phalen and Prince formational brines have very low metal contents: <0.1 mg/l Pb (5 samples), <2.65 mg/l Zn, and <0.28 mg/l Cu (13 samples). However, Ba is up to 1160 mg/l in Phalen formation waters (7 samples) and up to 25 mg/l in Prince formation waters (4 samples), and Ba-rich samples have low SO_4 concentrations (Table 2). A similar inverse relationship between Ba and SO_4 was noted in brines near mineralised areas of NE England by Edmunds (1975), who suggested that Ba is taken up into waters in the absence of SO_4 but precipitated as barite where Ba and SO_4 waters mix.

If residual Windsor fluids are the source of the mine brines, how and when might they have reached their present, stratigraphically elevated position? At Sydney, the Morien Group rests unconformably on the Windsor Group (Fig. 3), and the Phalen and Prince strata are about 1–2 km above the evaporite column. Evaporite diapirs have not been identified in seismic profiles in the Sydney Basin offshore, and upward motion of salts relative to the coal measures cannot be invoked

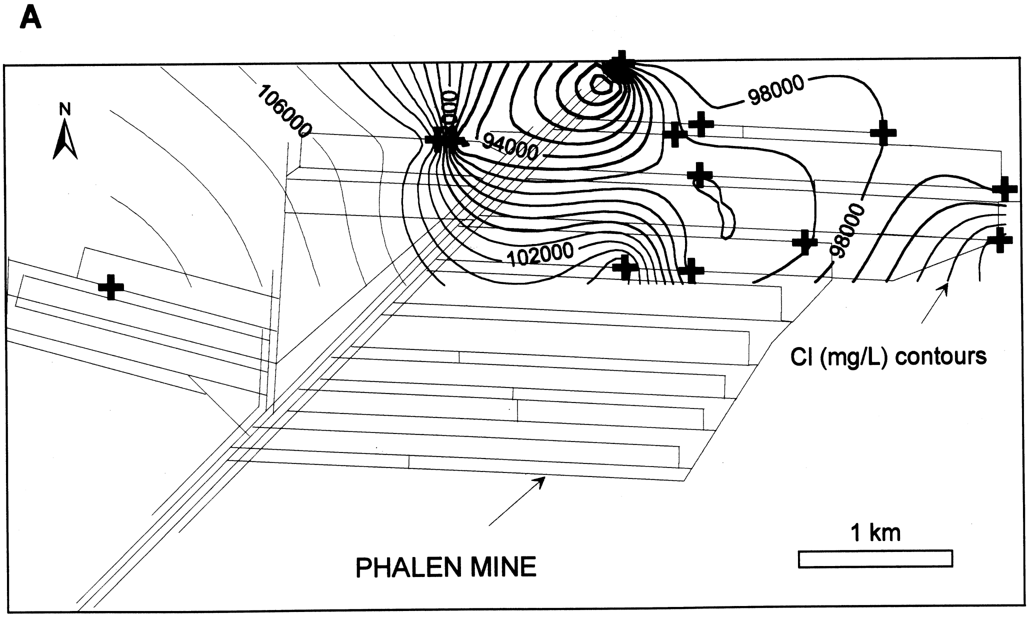

Fig. 12. Contour maps of Cl concentration in water samples (mg/l) from Phalen (A) and Prince (B) Mines. Sample locations are marked by crosses; 23 samples are represented for the Phalen Mine, with closely adjacent samples averaged, and 7 samples for the Prince Mine (depth is known but not location for CBDC-43). Positions of longwall mining panels are also shown. Depth to coal increases to the NE (sub-parallel to the Cl contours) in the Prince Mine and to the north in the Phalen Mine.

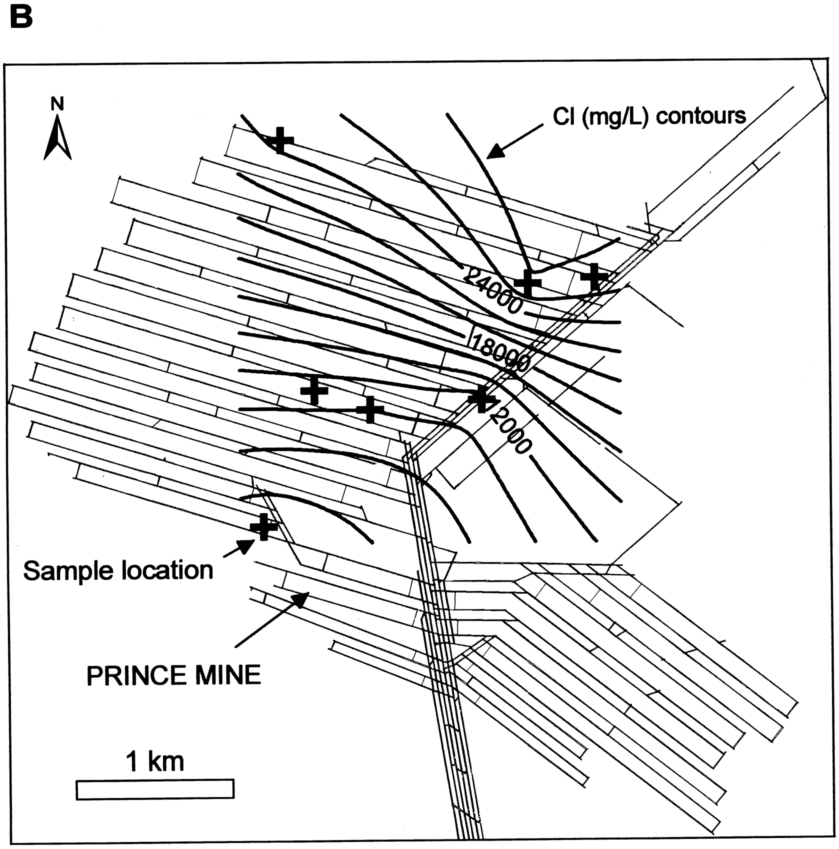

Fig. 12 (*continued*)

as a mechanism to bring the units into juxtaposition. Upward movement of water can occur along faults (e.g. Moldovanyi and Walter, 1992; Nesbitt and Muehlenbachs, 1995), and the modest dilution of the Phalen brines favours travel along faults where only minor mixing with less saline formation water would have occurred. Faults are present within the onshore mining area, and some have elevated Windsor Group strata relative to Morien Group strata. Both mid-Carboniferous and Permian deformation phases are probable (Gibling et al., 1999). The Mountain Fault borders the Prince Mine, and the Bridgeport Anticline, possibly associated with some faulting, borders the Phalen Mine area (Fig. 2). Brine-related sulphide mineralisation in the Maritimes Basin is commonly focussed within fault zones (Ravenhurst et al., 1989; Armstrong et al., 1993). The timing of brine emplacement in the mine sandstones is not known, however, the Sydney Basin was undergoing inversion by the Late Triassic, and Carboniferous strata elsewhere in Cape Breton were subaerially eroded prior to the Early Cretaceous. The authors speculate that Windsor brines entered Phalen sandstones during deep burial, probably before the Late Triassic.

The most saline Phalen waters appear to have suffered only modest mixing since emplacement, as noted above, and must be considered virtually immobile. The apparent absence of a systematic salinity variation within the Phalen sandstone aquifer (Fig. 12A) suggests minimal mixing with updip meteoric or ocean waters and limited communication within the sandstone. In contrast, the relatively uniform increase in salinity with depth in the Prince sandstone aquifer (Fig. 12B) suggests mixing with updip meteoric or marine waters (Gibling et al., 2000).These different salinity distributions may reflect the shallower depth at the Prince Mine, allowing younger waters to move downdip through the sandstones. Hydrologic isolation of low-permeability parts of aquifers is common

(Schwartz and Muehlenbachs, 1979; Domenico and Robbins, 1985; Nativ, 1996).

8. Conclusions

1. Formation brines within Upper Carboniferous sandstones in the subsea Prince and Phalen Mines, Nova Scotia, are inferred to have originated principally as evaporative residual fluids from the precipitation of Windsor Group (Lower Carboniferous) salts. Br:Cl ratios suggest that the brine composition corresponds to an evaporation ratio of as much as 30, within the zone of halite precipitation. Some degree of mixing with fluids derived from halite dissolution, as well as a Br contribution from organic matter, cannot be ruled out. Water–rock reactions have probably modified the original brine composition, leading to enrichment in Ca and Sr and depletion in Na, K and Mg with respect to the seawater evaporation curve. The brine samples correlate well on a Na deficit/Ca excess diagram, consistent with Na/Ca exchange during albitisation of plagioclase. The brines lie close to the meteoric line on H/O isotopic plots but distant from local meteoric water. Similar brines are likely to be encountered during hydrocarbon exploration in the Maritimes Basin of Atlantic Canada.
2. In contrast, Nova Scotia salt-spring brines originated through dissolution of Windsor Group evaporites by modern meteoric waters. This inference is supported by severe Br depletion, Na:Cl molar ratios near unity, and H and O isotopic values near those of recent meteoric water. Their chemical attributes contrast strongly with those of the mine waters.
3. The original Windsor brines probably recharged adjacent strata and subsequently moved upward into the overlying coal-measure sandstones along faults. They may have entered the sandstones during deep burial, probably before the Late Triassic. The high salinity and irregular salinity distribution in the low-permeability Phalen sandstones suggests that these brines are virtually immobile and suffered little dilution during and following emplacement. In contrast, the more dilute Prince mine waters show a progressive increase in salinity with depth and are inferred to have mixed with surface waters, due in part to the shallower depth of the Prince sandstones.
4. Saline fluid inclusions are common in Zn–Pb sulphide deposits (some as old as the mid Carboniferous) within the Maritimes Basin of Atlantic Canada. The formation brines documented here are rich in Ba, and barite deposits are common in the region. The authors suggest a link between the basinal brines documented here and some phases of metal transport and emplacement within the basin.
5. The present analysis confirms conclusions from earlier geochemical work (ADI Nolan Davis, 1993) that brines in the deep subsea Phalen and Prince mines are basinal in origin and not derived from modern seawater.

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References

ADI Nolan Davis, 1993. Origin of saline groundwater entering the Phalen 6E Panel, September 1993. Unpubl. report to Cape Breton Development Corporation.

American Water Works Association, 1989. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington DC, USA.

Armstrong, J.P., Longstaffe, F.J., Hein, F.J., 1993. Carbon and oxygen isotope geochemistry of calcite from the Jubilee Zn–Pb deposit, Cape Breton Island. Can. Mineral. 31, 755–766.

Aston, T., Kullmann, D., Barron, K., 1990. Modeling of outbursts at No. 26 Colliery, Glace Bay, Nova Scotia. Part 1: Outburst History and field data. Mining Sci. Technol. 11, 253–260.

Banner, J.L., Wasserburg, G.J., Dobson, P.F., Carpenter, A.B., Moore, C.H., 1989. Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri. Geochim. Cosmochim. Acta 53, 383–398.

Boehner, R.C., 1986. Salt and potash resources in Nova Scotia. Dept. Mines Energy, Bull. 5, 346.

Bottomley, D.J., Gregoire, D.C., Raven, K.G., 1994. Saline groundwaters in the Canadian Shield: Geochemical and isotopic evidence for a residual evaporite brine component. Geochim. Cosmochim. Acta 58, 1483–1498.

Cape Breton Development Corporation, 1994. Phalen Colliery Risk Assessment Report, Vol. 1.

Carpenter, A.B., 1978. Origin and chemical evolution of brines in sedimentary basins. In: Johnson, K.S., Russell, J.R. (Eds.), 13th Industrial Minerals Forum, Okla. Geol. Surv. Cir., 79, pp. 60–77.

Chi, G., Savard, M.M., 1995. A preliminary microthermometric study of the Sugar Camp, Yankee Line, and MacPhails Brook Pb–Zn showings, Cape Breton Island, Nova Scotia. Geol. Surv. Can., Current Res. 1995-D, 53–58.

Chi, G., Savard, M.M., Heroux, Y., 1995. Constraints from fluid-inclusion data on the origin of the Jubilee carbonate-hosted Zn–Pb deposit, Cape Breton, Nova Scotia. Can. Mineral 33, 709–721.

Chi, G., Savard, M.M., 1997. Sources of basinal and Mississippi Valley-type mineralizing brines: mixing of evaporated seawater and halite-dissolution brine. Chem. Geol. 143, 121–125.

Cole, L.H., 1930. The salt industry of Canada. In: Can. Dept. Mines, Mines Branch No. 716.

Coleman, M.L., Shepherd, T.J., Durham, J.J., Rouse, J.E., Moore, G.R., 1982. Reduction of water with zinc for hydrogen isotope analysis. Anal. Chem. 54, 993–995.

Connolly, C.A., Walter, L.M., Baadsgaard, H., Longstaffe, F.J., 1990. Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. II. Isotope systematics and water mixing. Appl. Geochem. 5, 397–413.

Craig, H., 1961. Standard for reporting concentrations of deuterium and oxygen 18 in natural waters. Sci. 133, 1833.

Crawford, T.L., 1996. Carbonates and associated sedimentary rocks of the Upper Visean to Namurian Mabou Group, Cape Breton Island, Nova Scotia: evidence for lacustrine deposition. Atlantic Geol. 31, 167–182.

Davisson, M.L., Presser, T.S., Criss, R.E., 1994. Geochemistry of tectonically expelled fluids from the northern Coast ranges, Rumsey Hills, California, USA. Geochim. Cosmochim. Acta 58, 1687–1699.

Davisson, M.L., Criss, R.E., 1996. Na–Ca–Cl relations in basinal fluids. Geochim. Cosmochim. Acta 60, 2743–2752.

Demir, I., 1988. Studies of smectite membrane behavior; electrokinetic, osmotic, and isotopic fractionation processes at elevated pressures. Geochim. Cosmochim. Acta 52, 727–737.

Dickie, G.B., 1987. Cretaceous deposits of Nova Scotia. In: Nova Scotia Dept. Mines Energy Paper 86-1.

Domenico, P.A., Robbins, G.A., 1985. The displacement of connate waters from aquifers. Geol. Soc. Am. Bull. 96, 328–335.

Drever, J.I., 1988. The Geochemistry of Natural Waters, 2nd ed. Prentice Hall.

Edmunds, W.M., 1975. Geochemistry of brines in the Coal Measures of northeast England. Trans. Inst. Min. Metall. 84, B39–B52.

Edmunds, W.M., 1996. Bromine geochemistry of British groundwaters. Mineral. Mag. 60, 275–284.

Edmunds, W.M., Kay, R.L.F., Miles, D.L., Cook, J.M., 1987. The origin of saline groundwaters in the Carnmenellis Granite, Cornwall (UK): Further evidence from minor and trace elements. In: Fritz, P., Frape, S.K. (Eds.), Saline Water and Gases in Crystalline Rocks, Geol. Assoc. Can. Spec. Paper, vol. 33, pp. 127–143.

Egeberg, P.K., Aagaard, P., 1989. Origin and evolution of formation waters from oil fields on the Norwegian shelf. Appl. Geochem. 4, 131–142.

Epstein, S., Mayeda, T.K., 1953. Variations of the $^{18}O/^{16}O$ ratio in natural waters. Geochim. Cosmochim. Acta 4, 213–224.

Fisher, R.S., Land, L.S., 1986. Diagenetic history of Eocene Wilcox sandstones, South-Central Texas. Geochim. Cosmochim. Acta 50, 551–561.

Fontes, J.C., Matray, J.M., 1993a. Geochemistry and origin of formation brines from the Paris Basin, France. 1. Brines associated with Triassic salts. Chem. Geol. 109, 149–175.

Fontes, J.C., Matray, J.M., 1993b. Geochemistry and origin of formation brines from the Paris Basin, France. 2. Saline solutions associated with oil fields. Chem. Geol. 109, 177–200.

Frape, S.K., Fritz, P., 1982. The chemistry and isotopic composition of saline groundwaters from the Sudbury Basin, Ontario. Can. J. Earth Sci. 19, 645–661.

Frape, S.K., Fritz, P., 1987. Geochemical trends for groundwaters from the Canadian Shield. In: Fritz, P., Frape, S.K. (Eds.), Saline Water and Gases in Crystalline Rocks. Geol. Assoc. Can. Spec. Paper, vol. 33, pp. 19–38.

Friedman, I., O'Neil, J.R., 1977. Compilation of stable isotope fractionation factors of geochemical interest, Data of Geochemistry, 6th ed., Fleischer, M., US Geol. Surv. Prof. Paper, vol. 440-KK.

Fritz, P., Frape, S.K., Drimmie, R.J., Heemskerk, A.R., 1986. Reply: Water–rock interaction and chemistry of groundwaters from the Canadian Shield. Geochim. Cosmochim. Acta 50, 1561–1563.

Gascoyne, M., Davison, C.C., Ross, J.D., Pearson, R., 1987. Saline groundwaters and brines in plutons in the Canadian Shield. In: Fritz, P., Frape, S.K. (Eds.), Saline Water and Gases in Crystalline Rocks, Geol. Assoc. Can. Spec. Paper, vol. 33, pp. 53–68.

Gat, J.R., Carmi, I., 1970. Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area. J. Geophys. Res. 75, 3039–3048.

Gibling, M.R., 1995. Upper Paleozoic Rocks, Nova Scotia. In: Williams, H. (Ed.), Geology of the Appalachian–Caledonian Orogen in Canada and Greenland, Geol. Surv. Can. Geology of Canada, vol. 6, pp. 493–523.

Gibling, M.R., Bird, D.J., 1994. Late Carboniferous cyclothems and alluvial paleovalleys in the Sydney Basin, Nova Scotia. Geol. Soc. Amer. Bull. 106, 105–117.

Gibling, M.R., Nguyen, M.H., 1999. Diagenetic and burial history of Sydney Basin sandstones. In: Gibling, M.R., Martel, A.T., Nguyen, M.H. (Eds). Geology and Hydrogeology of the Subsea Mining District, Sydney Coalfield, Nova Scotia. Centre for Marine Geology, Dalhousie University, Technical Report 14, 3–1 to 3–74.

Gibling, M.R., Boehner, R.C., Rust, B.R., 1987. The Sydney Basin of Atlantic Canada: An Upper Paleozoic strike-slip basin in a collisional setting. In: Beaumont, C., Tankard, A.J. (Eds.), Sedimentary Basins and Basin-forming Mechanisms, Can. Soc. Petrol. Geol. Memoir, vol. 12, pp. 269–285.

Gibling, M.R., Rust, B.R., Aksu, A., 1985. Mudrocks of the Pennsylvanian Morien Group, Sydney Coalfield: mud deposition and early diagenesis on an alluvial plain. Geol.

Assoc. Can. Annual Meeting, Program with Abstracts 10, A21.

Gibling, M.R., Zentilli, M., McCready, R.G.L., 1989. Sulphur in Pennsylvanian coals of Atlantic Canada: geologic and isotopic bedrock evaporite source. Int. J. Coal Geol. 11, 81–104.

Gibling, M.R., Pascucci, V., Williamson, M.A., 1999. The Sydney Basin of Atlantic Canada: a polycyclic Upper Paleozoic history. Geol. Soc. Am. Northeastern Section, Abstracts with Programs 31, A18.

Gibling, M.R., Martel, A.T., Nguyen, M.H., Kennedy, A.M., Shimeld, J., Baechler, F., Forgeron, S., Mackenzie, B., 2000. Fluid evolution and diagenetic history of a Carboniferous channel sandstone in the Prince Colliery, Nova Scotia, Canada. Bull. Can. Petrol. Geol., in press.

Graf, D.L., 1982. Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines. Geochim. Cosmochim. Acta 46, 1431–1448.

Graf, D.L., Meents, W.F., Friedman, I., Shimp, N.F., 1966. The origin of saline formation waters. Illinois State Geol. Soc. Cir. 397, 60.

Grant, A.C., McAlpine, K.D., Wade, J.A., 1986. Offshore geology and petroleum potential of Eastern Canada. Energy Exploration and Exploitation 4, 5–52.

Grist, A.M., Ryan, R.J., Zentilli, M., 1995. The thermal evolution and timing of hydrocarbon generation in the Maritimes Basin of eastern Canada: evidence from apatite fission track data. Can. Soc. Petrol. Geol. Bull. 43, 145–155.

Haites, T.B., 1951. Some geological aspects of the Sydney coalfield with reference to their influence on mining operations. Transactions Can. Inst. Mining Metal. 54, 215–225.

Hanor, J.S., 1987. Origin and migration of subsurface sedimentary brines. Soc. Econ. Paleont. Mineral. Short Course 21, 247.

Hanor, J.S., 1994. Origin of saline fluids in sedimentary basins. In: Parnell, J. (Ed.), Geofluids: Origin, Migration and Evolution of Fluids in Sedimentary Basins, Geol. Soc. Spec. Publ., vol. 78, pp. 151–174.

Heemskerk, A.R., 1993. Sulphur $^{34}/^{32}$ determination. Env. Isotope Lab., Department of Earth Sciences, University of Waterloo, Ontario.

Howie, R.D., 1988. Upper Paleozoic evaporites of southeastern Canada. Geol. Surv. Can. Bull. 380, 120.

Jones, B.F., Hanor, J., Evans, W.R., 1994. Sources of dissolved salts in the central Murray Basin, Australia. Chem. Geol. 111, 135–154.

Kamineni, D.C., 1987. Halogen-bearing minerals in plutonic rocks; a possible source of chlorine in saline groundwater in the Canadian Shield. In: Fritz, P., Frape, S.K. (Eds.), Saline Water and Gases in Crystalline Rocks, Geol. Assoc. Can. Spec. Paper, vol. 33, pp. 69–79.

Kesler, S.E., Appold, M.S., Martini, A.M., Walter, L.M., Huston, T.J., Kyle, J.R., 1995. Na–Cl–Br systematics of mineralizing brines in Mississippi Valley-type deposits. Geology 23, 641–644.

Kharaka, Y.K., Berry, F.A.F., 1973. Simultaneous flow of water and solutes through geological membranes. I. Experimental investigation. Geochim. Cosmochim. Acta 37, 2577–2603.

Kharaka, Y., Carothers, W.W., 1986. Oxygen and hydrogen geochemistry of deep basin brines. In: Fritz, P., Fontes, J.C. (Eds.), Handbook of Environmental Geochemistry, pp. 305–360.

Kharaka, Y.K., Smalley, W.C., 1976. Flow of water and solutes through compacted clays. Amer. Assoc. Petrol. Geol. Bull. 60, 973–980.

Knauth, L.P., Beeunas, M.A., 1986. Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters. Geochim. Cosmochim. Acta 50, 419–433.

Kontak, D.J., 1998. A study of fluid inclusions in sulfide and nonsulfide mineral phases from a carbonate-hosted Zn–Pb deposit, Gays River, Nova Scotia, Canada. Econ. Geol. 93, 793–817.

Kontak, D.J., Farrar, E., McBride, S.L., 1994. $^{40}Ar/^{39}Ar$ dating of fluid migration in a Mississippi Valley-type deposit: The Gays River Zn–Pb deposit, Nova Scotia, Canada. Econ. Geol. 89, 1501–1517.

Land, L.S., 1995. Na–Ca–Cl Saline Formation Waters, Frio Formation (Oligocene), South Texas, USA — Products of Diagenesis. Geochim. Cosmochim. Acta 59, 2163–2174.

Land, L.S., Lynch, F.L., 1996. $\delta^{18}O$ values of mudrocks: More evidence for an ^{18}O-buffered ocean. Geochim. Cosmochim. Acta 60, 3347–3352.

Land, L.S., Macpherson, G.L., 1992. Origin of saline formation waters, Cenozoic section, Gulf of Mexico Sedimentary Basin. Amer. Assoc. Petrol. Geol. Bull. 76, 1344–1362.

Land, L.S., Prezbindowski, D.R., 1981. The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, USA. J. Hydrol. 54, 51–74.

Langdon, G.S., Hall, J., 1994. Devonian-Carboniferous tectonics and basin deformation in the Cabot Strait area, eastern Canada. Amer. Assoc. Petrol. Geol. Bull. 78, 1748–1774.

Lee, M.R., Parsons, I., 1998. Microtextural controls of diagenetic alteration of detrital alkali feldspars: a case study of the Shap Conglomerate (Lower Carboniferous), northwest England. J. Sediment. Res. 68, 198–211.

Lloyd, R.M., 1966. Oxygen isotope enrichment of seawater by evaporation. Geochim. Cosmochim. Acta 30, 801–815.

Long, S.E., Martin, T.D., 1991. Determination of trace elements in waters and wastes by inductively coupled plasma — mass spectrometry. Method 200.8, US Env. Protection Agency, Cincinnati, Ohio.

Macumber, P.G., 1992. Hydrological processes in the Tyrrell Basin, southeastern Australia. Chem. Geol. 96, 1–18.

McCaffrey, M.A., Lazar, B., Holland, H.D., 1987. The evaporation path of seawater and the coprecipitation of Br^- and K^+ with halite. J. Sediment. Petrol. 57, 928–937.

McNutt, R.H., Frape, S.K., Dollar, P., 1987. A strontium, oxygen, and hydrogen isotopic composition of brines, Michigan and Appalachian Basins, Ontario and Michigan. Appl. Geochem. 2, 495–505.

Means, J.L., Hubbard, N., 1987. Short-chain aliphatic acid anions in deep subsurface brines: A review of their origin, occurrence, properties, and importance and new data on their distribution and geochemical implications in the Palo Duro Basin, Texas. Org. Geochem. 3, 177–191.

Moldovanyi, E.P., Walter, L.W., 1992. Regional trends in water chemistry, Smackover Formation, Southwest

Arkansas: Geochemical and physical controls. Amer. Assoc. Petrol. Geol. Bull. 76, 864–894.

Mountjoy, E.W., Qing, H., 1992. Strontium isotopic composition of Devonian dolomites, Western Canada Sedimentary Basin: significance of sources of dolomitizing fluids. Appl. Geochem. 7, 59–75.

Nativ, R., 1996. The Brine Underlying the Oak-Ridge Reservation, Tennessee, USA — Characterization, Genesis, and Environmental Implications. Geochim. Cosmochim. Acta 60, 787–801.

Naylor, R., MacNeil, D.J., Kennedy, C.M., 1996. Stratigraphy, sedimentology and depositional environments of roof rock in the Phalen Colliery, Sydney Coalfield. Nova Scotia Department of Mines and Energy, Report of Activities, 1–11.

Nesbitt, B.E., Muehlenbachs, K., 1995. Geochemical studies of the origins and effects of synorogenic crustal fluids in the southern Omineca Belt of British Columbia, Canada. Geol. Soc. Amer. Bull. 107, 1033–1050.

Okulitch, A.V., 1995. Geological time scale, 1995. Geol. Surv. Can., Open File 3040 (National Earth Science Series, Geological Atlas).

Pan, H., Symons, D.T.A., Sangster, D.F., 1993. Paleomagnetism of the Gays River zinc-lead deposit, Nova Scotia: Pennsylvanian ore genesis. Geophys. Res. Lett. 20, 1159–1162.

Phillips, F.M., Bentley, H.W., 1987. Isotopic fractionation during ion filtration. I. Theory. Geochim. Cosmochim. Acta 51, 683–696.

Pierre, C., Ortlieb, L., Person, A., 1984. Supratidal evaporitic dolomite at Ojo de Liebre Lagoon: mineralogical and isotopic arguments for primary crystallization. J. Sediment. Petrol. 54, 1049–1061.

Ravenhurst, C.E., Reynolds, P.H., Zentilli, M., Krueger, H.W., Blenkinsop, J., 1989. Formation of Carboniferous Pb–Zn and barite mineralization from basin-derived fluids, Nova Scotia, Canada. Econ. Geol. 84, 1471–1488.

Richter, B.C., Kreitler, C.W., 1986. Geochemistry of salt water beneath the Rolling Plains, north-central Texas. Groundwater 24, 735–742.

Rittenhouse, G., 1967. Bromine in oil-field waters and its use in determining possibilities of origin of these waters. Amer. Assoc. Petrol. Geol. Bull. 51, 2430–2440.

Sangster, D.F., Savard, M.M., Kontak, D.J., 1998. Sub-basin-specific Pb and Sr sources in Zn–Pb deposits of the lower Windsor Group, Nova Scotia, Canada. Econ. Geol. 93, 911–919.

Savard, M.M., 1991. A preliminary report on the relationship between mineralization and carbonate diagenesis in the Gays River Formation, Nova Scotia. Geol. Surv. Can., Paper 91-1D, 147–156.

Savard, M.M., Lynch, G., Fallara, F., 1996. Burial diagenesis model for the Macumber Formation on Cape Breton Island — implications for the tectonic evolution of the Windsor Group. Atlantic Geol. 32, 53–64.

Savard, M.M., Chi, G., 1998. Cation study of fluid inclusion decrepitates in the Jubilee and Gays River (Canada) Zn–Pb deposits — characterization of ore-forming brines. Econ. Geol. 93, 920–931.

Schwartz, F.W., Muehlenbachs, K., 1979. Isotope and ion geochemistry of groundwaters in the Milk River Aquifer, Alberta. Water Resour. Res. 15, 259–267.

Smalley, P.C., Higgins, A.C., Howarth, R.J., Nicholson, H., Jones, C.E., Swinburne, N.H.M., Bessa, J., 1994. Seawater Sr isotope variations through time: A procedure for constructing a reference curve and correlate marine sedimentary rocks. Geol. 22, 431–434.

Sofer, Z., Gat, J.R., 1975. The isotopic single composition of evaporating brines: effect of the isotopic activity ratio in saline solutions. Earth Planet. Sci. Lett. 26, 179–186.

Stoessel, R.K., Moore, C.H., 1983. Chemical constraints and origins of four groups of Gulf Coast reservoir fluids. Amer. Assoc. Petrol. Geol. Bull. 67, 896–906.

Tandon, S.K., Gibling, M.R., 1997. Calcretes at sequence boundaries in Upper Carboniferous cyclothems of the Sydney Basin, Atlantic Canada. Sediment. Geol. 112, 43–67.

Walter, L.M., Stueber, A.M., Huston, T.J., 1990. Br–Cl–Na systematics in Illinois basin fluids: constraints on fluid origin and evolution. Geol. 18, 315–318.

Yanagisawa, F., Sakai, H., 1983. Thermal decomposition of barium sulfate–vanadium pentoxide–silica glass mixtures for preparation of sulfur dioxide in sulfur ratio measurements. Anal. Chem. 55, 985.