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The origin and evolution of Canadian Shield brines: evaporation or freezing of seawater? New lithium isotope and geochemical evidence from the Slave craton

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Abstract

New chemical and isotopic data for deep seated calcium chloride brine from the Miramar Con gold mine, Yellowknife N.W.T., strongly suggest that the brine salinity is of marine origin. Diagnostic marine properties include uniformly elevated Br/Cl ratios typical of seawater concentrated beyond halite saturation, and Li/Br ratios (0.0254–0.0325) and δ^6Li compositions (-32.1 to -36.3‰) similar to seawater (-32.3‰). The mean δ^6Li for all mine water samples of -35.1‰ may reflect minor uptake of Li by secondary minerals. This interpretation is supported by analyses of altered metabasalt from fault zones which is enriched in Li but depleted in δ^6Li (-14.7 to -15.6‰) relative to the unaltered metabasalt (-5.4‰). The mechanism responsible for concentrating the hypersaline brine end member is not unequivocal as evidence exists to support both evaporative and cryogenic processes. On the one hand, the Devonian sedimentary record in the Great Slave Lake region, in conjunction with Yellowknife brine isotopic compositions (δ^2H and $\delta^{34}S_{SO_4}$) that are similar to various Devonian fluids, support an evaporative origin. On the other hand, the Na/Cl–Br/Cl relationship in the brine strongly suggests a cryogenic mechanism. Regardless of the concentrative mechanism, the chemical data indicate that the Yellowknife parent brine was concentrated 28- to 30-fold relative to seawater. The extreme depletion of Mg and enrichment of Ca in the brines, accompanied by Sr/Ca ratios similar to that of seawater, are accounted for by dolomitization of an aragonite-rich marine sediment by the brine before infiltration into the crystalline basement rocks. Subsequent alteration of silicate minerals in the shield added additional Ca and Sr to the brine as indicated by their radiogenic ^{87}Sr/^{86}Sr ratios (up to 0.7147). Based on mineral balance calculations, the major mineral products of the cryogenic and evaporitic concentration and evolution paths are significantly different. The cryogenic evolution results in some 15% mirabilite, 60% hydrohalite, and 18% dolomite whereas the major minerals formed from the evaporitic evolutionary sequence are 36% halite, 8% gypsum,

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17% dolomite, and 30% albite. The great similarity between the calcium chloride brine from Yellowknife and other such Canadian Shield brines indicates that they may share a common marine origin.

Keywords: Lithium; Isotopes; Shield; Brines; Seawater

1. Introduction

Hypersaline brines are common in deep mines across the Canadian Precambrian Shield, as well as in several other deep continental terrains, but their origin has remained enigmatic. These solutions may reach total salinities as high as 300 g/l and are calcium chloridic ($Ca > [SO_4 + HCO_3]$). Two major questions related to the origin of the brines are:

(a) What was the source, or sources, of their dissolved salts?

(b) How have the brines reached their salinity and present composition?

Two possible sources for the salts found in Ca-chloride brines are seawater and/or the host rocks. Because chemical modification of deep groundwaters is very likely irrespective of its source, the main research efforts of this study were directed towards the identification of the source of chloride and bromide, which are less sensitive to water/rock interactions than their complementary cations. Once the question of a ‘marine’ vs. a ‘non-marine’ origin for the salinity is settled, processes affecting the chemical and isotopic evolution of the brines can be identified.

Most students of the deep Canadian Shield brines (e.g., Frape et al., 1984; Frape and Fritz, 1987; Kamineni, 1987; Kamineni et al., 1992) proposed that the major solutes were leached from the crystalline host rocks over prolonged geologic time scales. The elevated $^{87}Sr/^{86}Sr$ ratios observed favor water/rock interaction (McNutt et al., 1990). Yet, the extremely high concentrations of chloride and bromide in the brines make crystalline host rocks a less likely source for the high salinity encountered therein. Moreover, Ca-chloride brines similar in composition to the Canadian waters are very common in deep-seated sedimentary terrains, where a ‘crystalline’ (i.e., silicate mineral) origin is out of the question. Rather, a marine source for all of these cases has been advocated (Carpenter et al., 1974; Starinsky, 1974; Carpenter, 1978; Wilson and Long, 1993a,b). Seawater has also been proposed as the source of the dissolved salts in the Canadian Shield brines by two research groups. Bottomley et al. (1994) proposed Paleozoic seawater as the source of the brines, which achieved their high salinity via evaporation. These dense, residual brines later infiltrated into underlying Precambrian basement rocks. Herut et al. (1990) have shown that such brines could also have formed through the freezing of seawater. Both models require subsurface migration of the brines from their site of formation, whether that involved only vertical infiltration or also lateral flow. The flow of marine evaporitic residual brines through fault and shear systems has been summarized by Bottomley et al. (1994) who concluded that the dense liquids have probably been residing within the shield for hundreds of millions of years.

Bein and Arad (1992) studied the hydrology of cryogenic brines and concluded that long distance migration of the residual brines is possible particularly near coastal areas when, during glacial periods, an advancing glacier overrides a landlocked inland sea. Although marine transgressions following the last Wisconsin deglaciation of northern Canada some 10^4 years ago did not encroach into areas where most existing deep mines are located, including the Yellowknife area, (Dyke and Dredge, 1989; Dredge and Cowan, 1989), this may not have been the case during earlier glaciations. For example, two late Proterozoic glaciations of the area are recorded by glaciomarine deposits in the Windermere Supergroup in the Mackenzie Mountains (N.W.T.) west of Yellowknife (Aitken, 1991).

Recently, we had the opportunity to study in detail the isotope geochemistry of mine waters at depths of up to 1600 m in the Miramar Con gold mine, Yellowknife, N.W.T. An earlier work (Frape et al., 1984) demonstrated that brines in the Yellowknife area are amongst the most concentrated brines found on the Canadian shield and thus this site would be ideal for additional investigations into the question of their origin. Moreover, the development of precise Li-isotope measurement techniques (Chan, 1987) is providing a new tool to constrain the source of the solutes in shield brines. Although this paper focuses on the origin of the Yellowknife brine and its evolution, we hope that the criteria and principles developed here may be extended and applied to other shield sites.

2. Geological setting

Yellowknife is situated within the Yellowknife volcanic belt in the southwestern part of the Archean Slave Structural Province of the Precambrian Shield in the Northwest Territories, Canada (Fig. 1). At the Miramar Con mine, gold is mined from shear zones

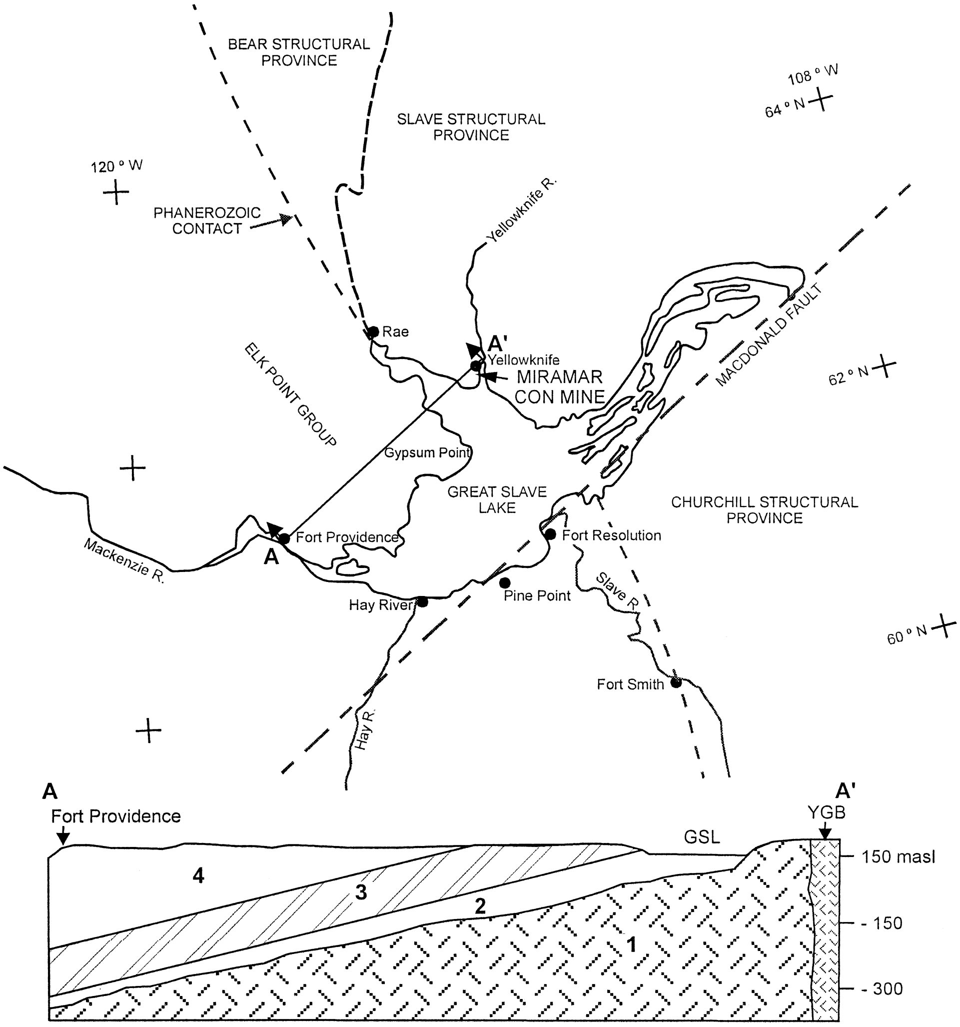

Fig. 1. Location of Yellowknife and major regional geological features. Section A–A′ shows the simplified geology between the Yellowknife Greenstone Belt (YGB) and Ft. Providence. (1) Precambrian granitic rocks, (2) Cambrian–Ordovician clastics, (3) Lower-Middle Devonian evaporites (Mirage Point and Chinchaga Formations), (4) Middle-Upper Devonian carbonates and shales.

in approximately 2.6–2.7 Ga old metabasalts of the Yellowknife Bay Formation of the Kam Group (Helmstaedt and Padgham, 1986; Isachsen and Bowring, 1994). These rocks have been intruded by the 2.6 Ga old Western Granodiorite batholith (Van Breemen et al., 1992) which outcrops approximately 2 km west of the mine site. Metamorphic grade ranges from the greenschist to upper amphibolite facies. Both the formations and shear zones show sinstrel displacements of up to several tens of kilometers along northwesterly trending transcurrent faults of probable Proterozoic age (Fig. 2). These faults also truncate several east–west trending faults that are important pathways for groundwater flow into the mine workings (Douglas, 1997).

The nearest outcrops of Phanerozoic sedimentary rocks of the Western Canada Sedimentary Basin occur about 75 km northwest of Yellowknife near the community of Rae and 50 km to the southwest near Gypsum Point on the western shore of the

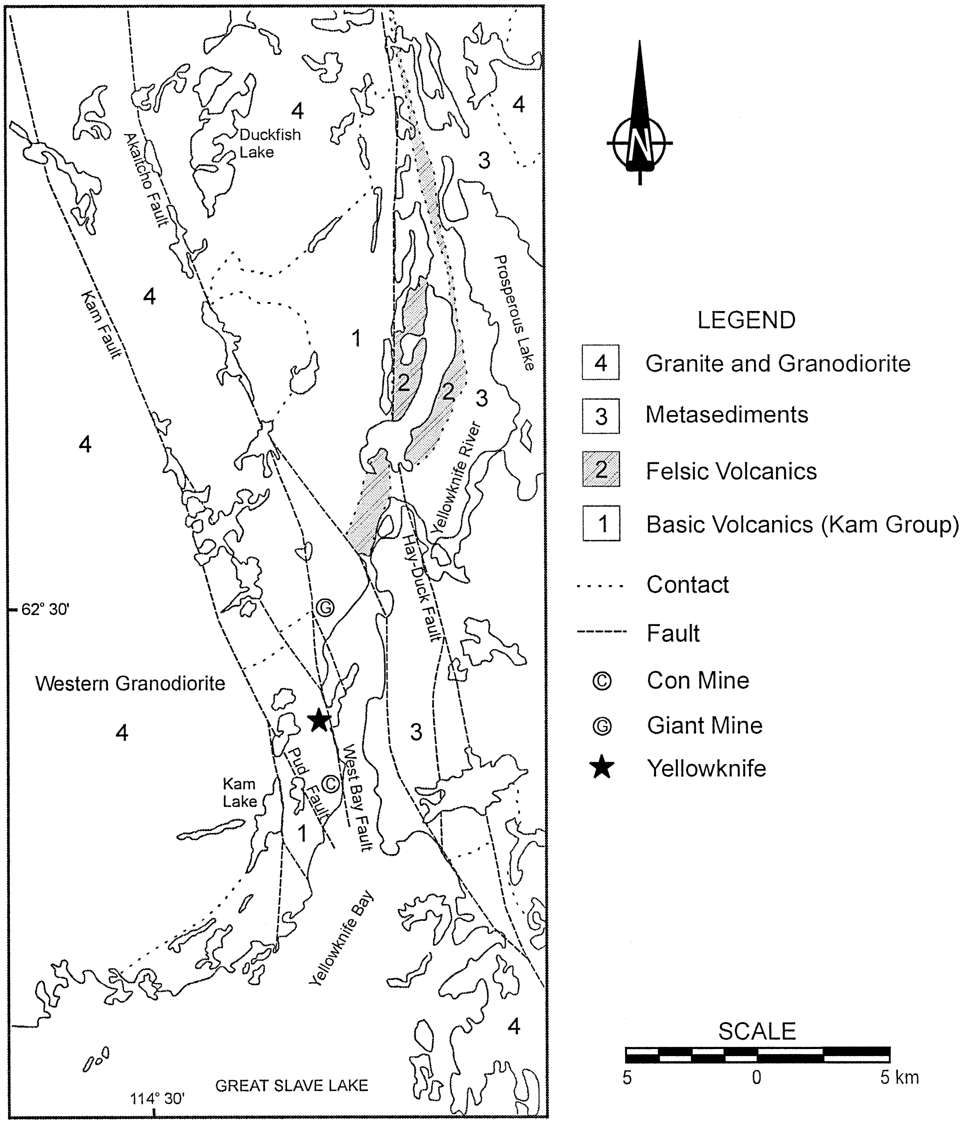

Fig. 2. Simplified geology of the Yellowknife area showing the location of the Miramar Con mine (modified after Helmstaedt and Padgham, 1986).

North Arm of Great Slave Lake (Fig. 1). These rocks consist of dolomite, shale and gypsum of the Middle Devonian Mirage Point Formation of the Lower Elk Point Group. Salt deposits occur within the Mirage Point Formation near the western end of Great Slave Lake (Meijer Drees, 1986). Middle Devonian dolomites also occur along the south shore of Great Slave Lake including the Keg River Formation (or its equivalent the Muskeg Formation of northern Alberta) which hosts Mississippi Valley Type lead–zinc deposits at Pine Point (Fig. 1). All these formations were deposited in sub-basins that comprised a northwestern extension of the Lower Elk Point Basin which was initiated in the Lower Devonian and which was succeeded in the Middle Devonian by the Upper Elk Point Basin. Halite and anhydrite deposits of the Upper Elk Point Prairie Evaporite Formation occupy an extensive area of central Saskatchewan and east–central Alberta and are lateral equivalents of the Upper Keg River Formation. These extensive evaporite deposits formed under tropical climatic conditions when Yellowknife was situated within about 10° of the equator during Lower to Middle Devonian time (Heckel and Witzke, 1979).

The present position of the contact between the Elk Point Basin and the Precambrian Shield is the result of post-Devonian tectonics and erosion. However, it is likely, based on regional stratigraphic considerations, that the Elk Point seas at times covered large areas of northern Saskatchewan and western and central regions of the Northwest Territories (Williams, 1984). It is therefore probable that Middle Devonian marine sediments were deposited over much of the Slave Province. This interpretation is supported by the recent identification of Middle Devonian marine limestone xenoliths in the Jericho kimberlite which intrudes the Slave craton about 400 km northeast of Yellowknife (Cookenboo et al., 1998). Conodont fossils in these xenoliths suggest that the seawater from which these limestones precipitated was, at times, of above normal temperature and salinity.

3. Analytical procedures

Water samples for chemical analyses were collected in 1-l plastic bottles and analyzed at the Geology Dept., Hebrew University of Jerusalem. The samples were filtered through Whatman #40 filter paper and diluted with deionized water to the optimal concentration ranges of the analytical procedures. Na, K, Li, Mg, Ca, Sr, Ba, SO_4 (as S), Si and B were analyzed by inductively coupled plasma atomic emission spectrometry (ICPAES) using a Perkin-Elmer Optima-3000 spectrometer, with a Segmented-array Charge-coupled-device Detector (SCD). Chloride and Br were analyzed by flow injection (FIA) on a 5-channel Lachat model QE FIA machine. Optical detection was deployed after reacting the chloride with mercuric-thiocyanate in the presence of Fe^{3+} ions (Lachat Instruments, 1990). Bromide was oxidized by chloramine-T to bromine which was then reacted with phenol-red to produce bromophenol blue (Lachat Instruments, 1993 # 30-135-21-1-A). The ICP analyses were carried out in triplicate and the FIA analyses were run in duplicate. Spiked standards served for post-run drift correction and data reduction of both the ICP and FIA analyses, by a home-made computer program. Bicarbonate was determined by acidimetric (0.02 N HCl) titration of a 50-ml aliquot of the undiluted sample, using the BDH ‘4460’ graded-step pH indicator.

The following precision, in %RSD, has been calculated for the various analytes: Na (± 0.5), K (± 0.5), Li (± 1.5), Mg (± 0.5), Ca (± 0.5), Sr (± 0.5), Ba (± 1), SO_4(± 5), Si (± 2), B (± 1.5), Cl (± 1.5), HCO_3 (± 2.0). Because of spectral interference by Ca in low sulphate, high salinity samples, sulphate was analyzed by ion chromatography (Dionex) at the University of Ottawa with a precision of 5%.

Rock samples were completely dissolved in an ultrapure 5:1 HF–$HClO_4$ acid mixture. After digestion, the salts were converted to perchlorates by addition of $HClO_4$ and redissolved in sub-boiling water. Li concentrations were determined by flame emission spectrometry, using a standard addition technique to eliminate matrix effects. Strontium concentrations were determined by ICP spectrometry.

Oxygen-18 and deuterium analyses were performed on a VG Sira-12 and a VG 602E mass spectrometer, respectively, in the Geology Dept., University of Ottawa. The ^{18}O and ^{2}H results are expressed in conventional delta per mil notation (δ‰) relative to the Standard Mean Ocean Water (V-SMOW) standard. The overall precision (2σ) of the $\delta^{18}O$ analyses is $\pm 0.1‰$. Oxygen isotope measurements for saline samples have been corrected for compositional effects using the equations of Sofer and Gat (1972). Deuterium analyses were performed on H_2 prepared by the zinc reduction technique. Saline samples were firstly filtered during vacuum distillation to remove hydrated salts. Precision (2σ) of the δ^2H analyses is $\pm 1.5‰$.

Sulphate was precipitated with $BaCl_2 \cdot 2H_2O$ as $BaSO_4$ and the $\delta^{34}S$ values were determined by mass spectrometric analysis of SO_2 produced by reacting $BaSO_4$ with a Cu/Cu_2O–quartz mixture in quartz vessels at 1100°C. Results are reported with respect to the Canon Diablo Troilite standard and have a precision of $\pm 0.2‰$. The ^{18}O contents of the sulphates were determined by graphite combustion at the Dept. of Earth Sciences, University of Waterloo using methods described by Fritz et al. (1994). Results are reported relative to V-SMOW with a precision of $\pm 0.5‰$ or better.

Tritium was analyzed at the Dept. of Earth Sciences, University of Waterloo by direct liquid scintillation counting of an Instagel-water cocktail on electrolytically enriched samples. The precision of this technique is ± 0.8 T.U. (tritium units).

Lithium isotopic compositions were determined at the Dept. of Geology and Geophysics, Louisiana State University by thermal ionization of lithium tetraborate following procedures described by Chan (1987) and Chan et al. (1992). This technique yields a precision of better than 1‰ in the δ^6Li value. Isotopic ratios are expressed as δ^6Li relative to the NBS isotope standard L-SVEC:

$$\delta^6\mathrm{Li} = \left(\left({}^6\mathrm{Li}/{}^7\mathrm{Li}\right)_{\mathrm{sample}}/\left({}^6\mathrm{Li}/{}^7\mathrm{Li}\right)_{\mathrm{std}} - 1\right)1000$$

where $({}^6\mathrm{Li}/{}^7\mathrm{Li})_{\mathrm{std}} = 0.083062 \pm 0.000054$ as determined by replicate analyses.

A single analysis of surface water from Yellowknife Bay was made by using a more sensitive mass spectrometric method because of the low Li concentration in this sample (1.8 μg/l). In this technique, lithium phosphate is used as the ion source. The chemical separation and mass spectrometric procedures are described in You and Chan (1996). Intercalibration between the phosphate and the tetraborate methods indicates an agreement of about 1‰.

Strontium was separated from brine samples by standard ion chromatography procedures. Isotopic measurements were made on a 90° sector thermal ionization mass spectrometer (Finnigan Mat 262), at Louisiana State University, using double Re filaments. Data were acquired using simultaneous collection with multiple Faraday cups. The reported $^{87}Sr/^{86}Sr$ values are normalized to $^{86}Sr/^{88}Sr = 0.1194$. The in-run precision (2σ) is better than ± 0.00001. Replicate analyses of the NBS 987 standard give an average $^{87}Sr/^{86}Sr$ ratio of 0.71026 ± 0.00001.

4. Results

4.1. Chemical compositions

Representative chemical and isotopic analyses of mine water samples collected from drifts at depths of 701 m to 1616 m (Fig. 3) are presented in Tables 1 and 2, respectively. Most of the samples were collected from flowing boreholes but two samples are from flowing ditches that are used to drain mine inflows from the drift and one sample is of a seep into the mine shaft. Repeat analyses are shown for samples from four boreholes (B3457, B5316, B6709 and B7126) collected several months apart. Electrical charge balances are better than about 3% except for the sample from borehole B646. This may in part be due to a very high concentration of arsenic in this sample (about 170 mg/l) which could have been in the form of the arsenate anion at the time of the analysis.

Whole rock Li and Sr concentrations and isotopic compositions are presented in Table 3. Sample CSR-2 is fresh metabasalt but two of the samples, CSR-1 and CSR-3, are altered metabasalts from fault zones. All three samples were collected from drill core on the 1067 m level. CSR-4 is a granodiorite outcrop sample from the adjacent Western Granodiorite batholith (Fig. 2).

In terms of the predominant ions, most of the mine water samples are of the Ca/Cl type, except for Y5 and B9362 which are of the Na–Ca/Cl type, and exhibit increasing salinity with depth. These results are consistent with those of previous investi-

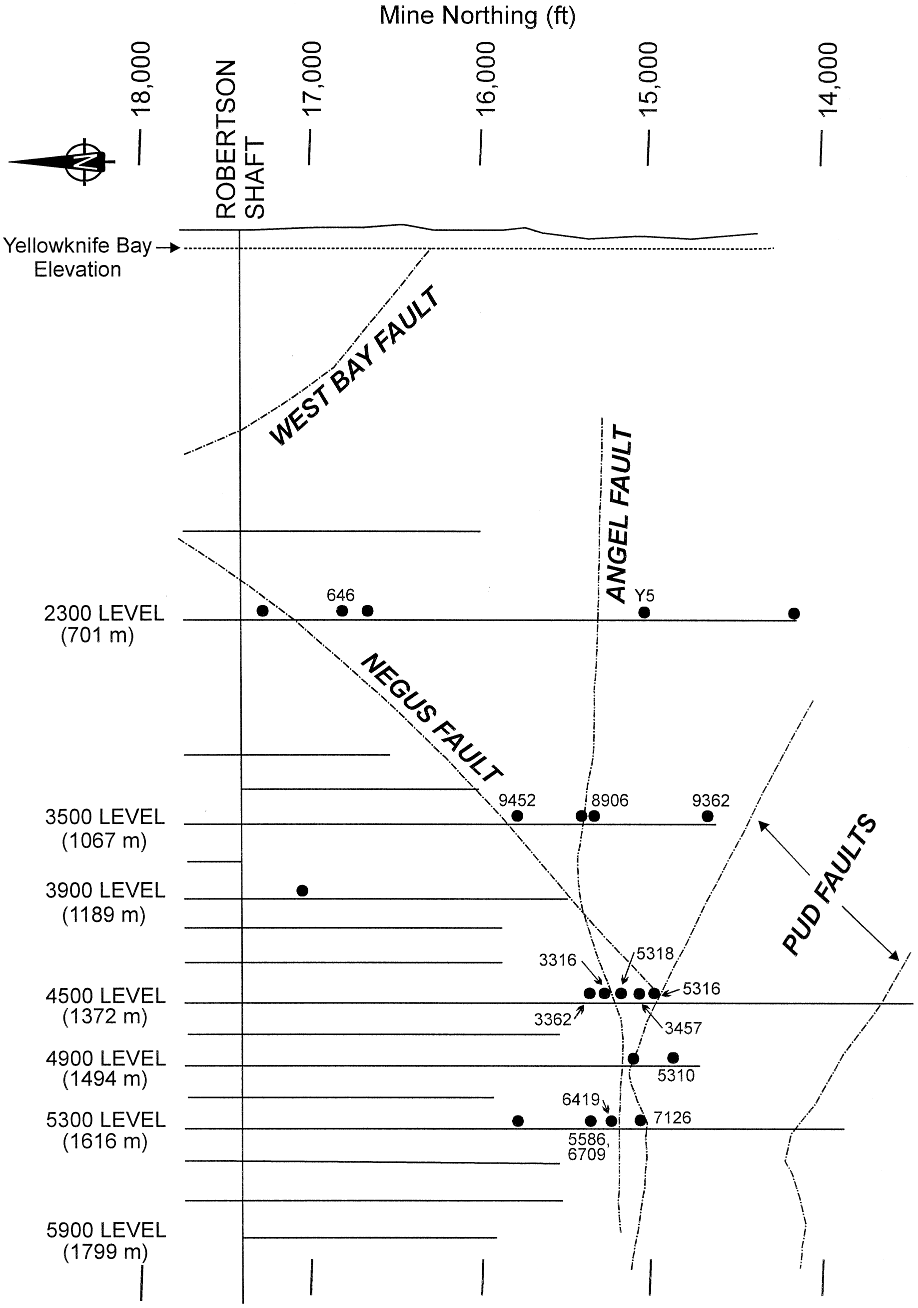

Fig. 3. Northeast–southwest cross-section through the Miramar Con mine showing borehole sampling locations, drifts and major faults.

gations at this site (Frape et al., 1984; Frape and Fritz, 1987). However, the brine samples collected from the 1616-m level are the deepest and most saline yet reported for the Yellowknife area.

Because of the overwhelming role of chloride in these liquids it is reasonable to discuss the chemical composition of the Canadian Shield brines relative to the seawater abundance of chloride. Table 4 shows

Table 1
Chemical composition of Miramar Con mine waters

Borehole # and depth (m)	Ca	Mg	Na	K	Sr	Cl	Br	SO_4	Alkalinity (as HCO_3)	Si	B (ug/l)	Li (ug/l)	Ba (ug/l)	pH	C.B.[a] (%)
Y5—701 m	728	75	995	7.8	11.0	2015	14.0	1168	256	5.2	1285	99	68	6.8	0.4
B646—701 m	268	68	195	5.1	4.0	309	2.0	514	256	9.7	504	49	145	6.7	8.0
Seep—793 m	2265	324	1585	12.5	30.0	6471	54.0	880	112	17.5	2321	230	111	7.7[b]	1.5
B8906—1067 m	194	32	205	2.9	4.0	388	2.0	113	425	11.2	659	39	23	6.9	2.6
B9362—1067 m	2095	40	2614	10.3	38.0	7136	55	640	20	9.1	2076	218	65	7.4	1.6
B9452—1067 m	2405	150	1990	13.0	52.2	7164	65	726	98	9.9	1584	558	101	7.0	0.2
B?—1189 m	20,598	136	10,650	61.0	350	52,084	450	290	15.0	6.1	1581	1353	1078	6.8[b]	1.0
Ditch—1311 m	7938	287	5477	33.4	175	22,332	198	460	44	5.2	788	276	428	7.2[b]	1.5
B3316-4—1372 m	48,997	260	22,005	176	838	123,066	1103	489		6.9	3085	2775	2563		0.4
B3362—1372 m	28,968	233	13,887	108	504	69,798	645	408	27	8.0	1555	1763	1507	5.6	2.4
B3457-1—1372 m	3037	57	2858	13.8	60	9266	76	300	22	7.3	1788	265	350	7.4[b]	2.4
B3457-2—1372 m	3767	63	3339	17.1	71	11,235	88	628	27	8.0	1598	328	214	6.0	1.3
B5316-1—1372 m	18,396	301	10,341	74.8	407	48,104	436	210	15	5.5	1385	837	2328	6.6[b]	1.3
B5316-2—1372 m	18,576	306	10,564	75.2	409	49,429	445	440	15	5.6	1774	950	2340	6.5	0.5
B5318—1372 m	14,408	145	7404	55.9	251	36,510	323	476	51	11.2	1622	805	801	6.3	0.7
B5310—1494 m	23,892	241	13,970	81.9	436	60,633	515	701	10	5.4	1636	1644	2537	7.2	2.8
ditch—1494 m	48,055	217	22,169	177	815	120,548	1071	57	15	4.1	1985	2844	5414	6.2[b]	0.2
B5586-4—1616 m	73,010	222	30,558	285	1247	174,134	1544	229	26	2.3	4744	3827	8993		1.0
B6419—1616 m	74,468	290	31,453	265	1282	177,954	1615	83	5	3.5	3714	3652	14,872	6.6	0.0
B6709-3—1616 m	76,136	319	32,459	292	1349	178,140	1474	93	11	1.4	3772	3975	15,895	6.7	2.2
B6709-4—1616 m	79,574	278	32,838	304	1419	188,440	1682	130	31	1.7	4732	3718	17,069		1.2
B7126-1—1616 m	72,755	231	30,219	258	1181	172,822	1615	123	5	2.1	3699	4205	9764	6.8	1.0
B7126-3—1616 m	69,715	223	29,997	259	1176	160,122	1543	122	10	1.6	3402	4349	8917	6.9	3.2
B7126-4—1616 m	73,789	198	30,670	278	1249	174,582	1567	247	28	1.5	3724	3975	8418		1.2

Concentrations are in mg/l unless otherwise indicated.

[a] Charge balance (%).

[b] Lab pH.

Table 2
Isotopic compositions of Miramar Con mine waters

Borehole # and depth (m)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	^{3}H T.U.[a]	$\delta^{6}Li$ (‰)	$\delta^{34}S_{SO_4}$ (‰)	$\delta^{18}O_{SO_4}$ (‰)	$^{87}Sr/^{86}Sr$
Y5-701 m	−20.8	−167	19.6	−33.7	11.2	7.7	0.708713
B646-701 m	−19.5	−152	26	−34.6	4.1	−5.4	0.713466
seep-793 m							0.707777
B8906-1067 m	−19.3	−156	19.3	−33.4	10.5	1.7	0.712012
B9362-1067 m	−20.9	−163	16.4	−35.5	26.3	9.0	0.712724
B9452-1067 m	−19.7	−156	24.6	−34.2	17.5	6.2	0.710964
B?-1189 m				−38.4			0.714340
ditch-1311 m							0.707559
B3362-1372 m	−18.3	−135	11.8	−35.4	21.6	6.6	0.714059
B3457-1-1372 m							
B3457-2-1372 m	−20.6	−165	18.7	−35.2	23.8	8.7	0.712822
B5316-1-1372 m				−33.9			0.712285
B5316-2-1372 m	−19.1	−139	10.7	−36.0	23.3	7.6	0.712321
B5318-1372 m	−19.1	−143	21.2	−40.1	19.7	5.4	0.714065
B5310-1494 m	−20.1	−141	4	−35.2	25.6	8.2	0.713492
ditch-1494 m				−36.3			0.714383
B6419-1616 m	−14.0	−67		−34.7			0.714305
B6709-3-1616 m	−13.3	−64	1.1	−32.1	26.1		0.714233
B7126-1-1616 m	−14.5	−68		−32.3			0.714740
B7126-3-1616 m	−14.2	−74	< 0.8	−35.4	25.7	7.7	0.714745

[a] T.U. = tritium units.

two groups of solutes which emerge from this comparison, the typically depleted and the typically enriched ions relative to chloride compared to their marine ratios. The various solutes are sorted in the table according to their enrichment factor (E.F.), from the most depleted ion, SO_4 (E.F. = 0.008) to the most enriched one, Ca (E.F. = 19.8).

Four important characteristics of the Yellowknife brine are displayed in Table 4. These are: (a) The very narrow range of variation ($< \pm 10\%$) of the $(M_i/Cl)_{brine}$ ratios of more than half of the solutes analyzed (K, Na, Li, Br, Sr and Ca); (b) Considering the absolute ionic concentrations of the respective samples (Table 1), it becomes evident that the main depletion-enrichment process(es) involved large-scale loss of Mg, SO_4 and Na, which was compensated by a massive gain of Ca; (c) Two pairs of ions belonging to the enriched group, Li and Br, and Sr and Ca, display very similar enrichment factors (2.56, 2.65 and 18.3, 19.8, respectively) with Li/Br and the Sr/Ca ratios very close to those of modern seawater ($Li/Br = 2.94 \times 10^{-2}$ vs. 2.86×10^{-2} and $Sr/Ca = 8.45 \times 10^{-3}$ vs. 7.81×10^{-3}, for seawater and the Yellowknife brine, respectively); (d) The strongly depleted sulfate ion shows the noisiest relationships to chloride ($\pm 97.6\%$) about the respective average ratio. Sulphate concentrations are highly variable, with some of the highest occurring in the shallower

Table 3
Li and Sr chemical and isotopic data for three metabasalt samples from the 1067-m level of the Miramar Con mine and a granodiorite outcrop sample of the Western Granodiorite batholith

Sample #	Rock	Li (ppm)	$\delta^{6}Li$	Sr (ppm)	$^{87}Sr/^{86}Sr$
CSR-1	altered metabasalt (Angel fault zone)	35.0	−15.6	65.0	0.71813
CSR-2	fresh metabasalt	14.9	−5.4	201.3	0.70501
CSR-3	altered metabasalt (Negus fault zone)	62.2	−14.7	33.2	0.71452
CSR-4	granodiorite (Western Granodiorite batholith)	14.0	−20.8	107.4	0.78441

Table 4
Enrichment factors, relative to seawater, of several ions in the nine most saline ($> 10^5$ mg/l Cl) Yellowknife brine samples

Ratio	Average	%RSD ($\pm 1\sigma$)	Seawater ratio	Enrichment factor
Depleted solutes				
SO_4/Cl	0.00042	97.6	0.0509	0.008
Mg/Cl	0.00226	18.9	0.0964	0.023
K/Cl	0.00141	5.0	0.0185	0.076
B/Cl	0.00007	14.6	0.0008	0.090
Na/Cl	0.276	2.4	0.854	0.32
Enriched solutes				
Li/Cl	0.000116	9.0	0.000045	2.56
Br/Cl	0.00405	2.9	0.00153	2.65
Sr/Cl	0.00289	4.0	0.000158	18.3
Ca/Cl	0.370	2.8	0.0187	19.8

The data are given in moles. The enrichment factors are calculated as $(M_i/Cl)_{brine}/(M_i/Cl)_{seawater}$ where M_i denotes the concentration of solute i.
Seawater ratios were calculated from Broecker and Peng (1982, Tables 1–6).

mine levels, partly due to the infiltration of sulfate-rich mine tailings pond water along major, high hydraulic conductivity, near vertical fault zones. Temporal mixing trends and spatial pathways have been discussed in detail by Douglas (1997).

4.2. Isotopic compositions

4.2.1. Oxygen and hydrogen

The $\delta^{18}O$ and δ^2H data from Table 2, as well as results for other isotope samples collected from the mine site during the present study, including local surface waters, are plotted in Fig. 4. Also shown on this plot is the Global Meteoric Water Line ($\delta^2H = 8\,\delta^{18}O + 10$), a Local Meteoric Water Line ($\delta^2H = 7.5\,\delta^{18}O - 4.9$) based on an isotopic record for precipitation at Fort Smith N.W.T. (Fig. 1), (Michel, 1986), and a hypothetical generic Canadian Shield brine end member composition based on the convergence of

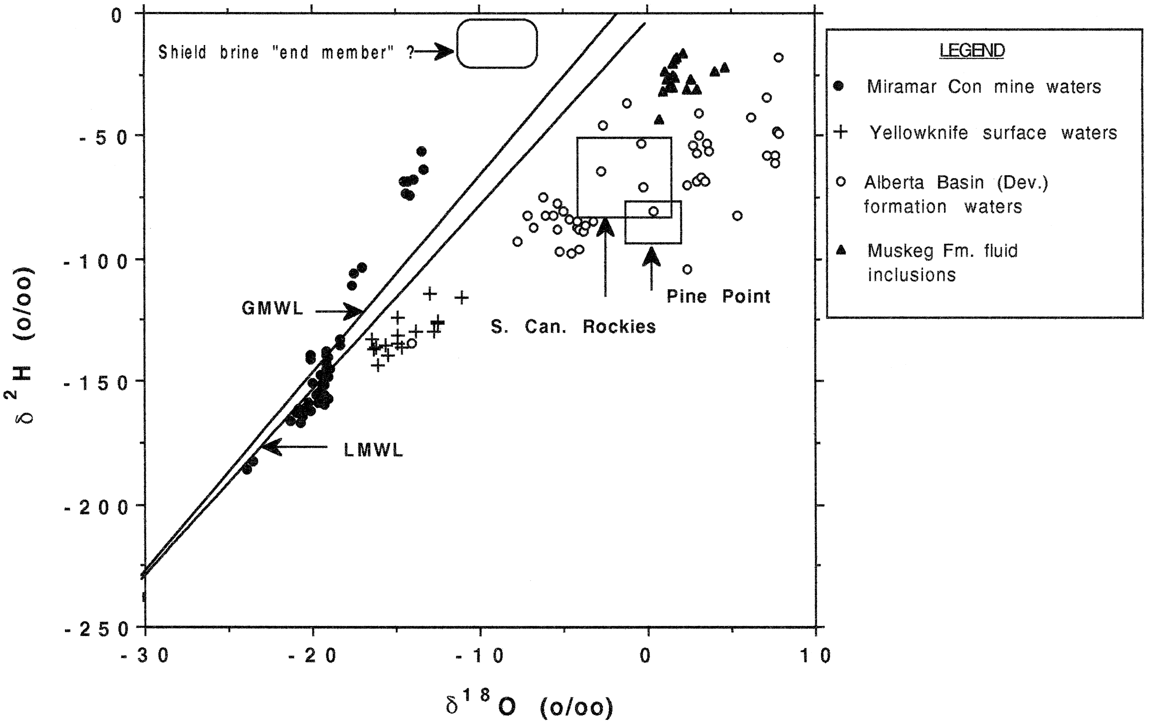

Fig. 4. Plot of the $\delta^{18}O$ and δ^2H compositions of Miramar Con mine waters and local surface waters with respect to the Global Meteoric Water Line (GMWL) and a Local Meteoric Water Line (LMWL) for Fort Smith, N.W.T. Also shown are the isotopic compositions of various brine fluids from the Alberta Basin and a hypothetical shield brine end member (see text).

extrapolated ^{18}O–^{2}H data for mine waters from Yellowknife, Thompson (Manitoba) and Sudbury (Ontario) (Frape and Fritz, 1987). The Yellowknife mine waters exhibit a wide range in $\delta^{18}O$ and $\delta^{2}H$ values of about 7‰ and 100‰, respectively, and define a mixing trend between meteoric water and an apparently ^{2}H-enriched (or ^{18}O-depleted) brine 'end member' that plots to the left of the Global Meteoric Water Line (Fig. 4). Surface waters tend to plot to the right of the meteoric water line because of evaporative isotopic enrichment. Relatively fresh mine waters at Yellowknife tend to lie closer to the Local Meteoric Water Line for Fort Smith than to the Global Meteoric Water Line suggesting that the Fort Smith precipitation data are a better approximation of the isotopic composition of present day groundwater recharge at Yellowknife. The presence of ^{3}H in most of the mine waters confirms that the meteoric component of these samples is of recent origins (i.e., less than about 40 years old) and that this recent infiltration has penetrated the mine workings to depths of at least 1370 m. This mixing with recent meteoric waters has been induced by hydraulic depressurization of the mine over its 50-year operating history. However, no tritium was detected in the brine sample from borehole B7126 on the 1616-m level indicating that post-bomb recharge has not yet infiltrated to the deepest levels of the mine.

4.2.2. Lithium

Despite the extreme variation in the concentrations of Li in the Yellowknife waters (40–4350 μg Li/l, Table 1), the $\delta^{6}Li$ values (Table 2) vary over a relatively narrow range from −32.1‰ to −40.1‰ with a mean value of −35.1‰. These values are similar to or slightly heavier than present day seawater ($\delta^{6}Li = -32.3 \pm 0.5$‰, Chan and Edmond, 1988). An analysis of a core sample of metabasalt from a borehole drilled on the 1067-m level containing 15 ppm Li, yielded a much lighter $\delta^{6}Li$ value of −5.4‰ (Table 3), which is similar in isotopic composition to MORB (Chan et al., 1992). In contrast, two altered metabasalt samples from fault zones in the same core are enriched in Li and ^{7}Li, relative to unaltered metabasalt, having Li concentrations of 35 and 62 ppm and $\delta^{6}Li$ compositions of −15.6‰ and −14.7‰, respectively. The granodiorite sample from the adjacent Western Granodiorite batholith (Fig. 2) has a similar Li concentration as the fresh metabasalt but has a significantly heavier $\delta^{6}Li$ of −20.8‰.

4.2.3. Strontium

Miramar Con mine waters have $^{87}Sr/^{86}Sr$ ratios of between 0.707559 and 0.71475 (Table 2), with the deepest, most concentrated brine samples having amongst the most radiogenic ratios. These results are similar to those previously reported by McNutt et al. (1990). Local surface waters have much lower Sr concentrations. An analysis of Yellowknife Bay surface water (part of Great Slave Lake) yielded a Sr concentration of only 78 μg/l with a radiogenic $^{87}Sr/^{86}Sr$ ratio of 0.725166.

Obviously, the high $^{87}Sr/^{86}Sr$ ratios measured in the brine samples could not have been supported by seawater, irrespective of its age (Burke et al., 1982). Hence, the brines must have reacted with silicate minerals to account for their radiogenic ratios. Support for this conclusion is provided by the relatively uniformly radiogenic ratios for the brine samples from the deepest level of the mine (1616 m). These samples are sufficiently Sr-rich that any contribution of radiogenic Sr to them from fresh, near surface waters is negligible. Although the host metabasalt has a relatively low $^{87}Sr/^{86}Sr$ ratio of 0.70501 (Table 3), its mafic minerals (amphiboles and micas) may have significantly higher ratios. Furthermore, the nearby Western Granodiorite batholith has a relatively radiogenic whole rock $^{87}Sr/^{86}Sr$ ratio of 0.784405.

4.2.4. Sulphur

The $\delta^{34}S$ compositions of the dissolved sulphate in mine water samples collected from the 1372-m level and below (Table 2) range from 19.7 to 28.3‰ and are similar to those previously reported by Fritz et al. (1994) for Miramar Con mine brines. Within this population there is no evidence for sulphur isotopic enrichment due to dissimilatory sulphate reduction. If anything, the higher sulphate concentrations tend to be richer in ^{34}S. A few samples collected above the 1372-m level have high sulphate concentrations that are due to the infiltration of sulphate-rich surface water from the tailings ponds. This is evident from their lower $\delta^{34}S$ and $\delta^{18}O$ values that are the result of the recent oxidation of sulphides, primarily pyrite, that commonly occur in the gold-quartz ore veins and which have $\delta^{34}S$ values in the range of 0 to +5‰ (Wanless et al., 1960).

The $\delta^{34}S$ values of the deep sulphate samples from the 1372-m level and below are similar to or heavier than the present day seawater sulphate value of about 20‰ but are typical of the global record for marine sulphates from the Devonian period (Claypool et al., 1980). More locally, Claypool et al. (1980) reported $\delta^{34}S$ values of 15.1‰ and 22.6‰ for two gypsum samples from the Devonian Mirage Point Formation near Gypsum Point (Fig. 1), and Ueda et al. (1987) reported $\delta^{34}S$ values ranging from 18 to 25‰ for trace sulphate in dolomites of the Rainbow Member of the Keg River Formation in northwestern Alberta. However, the $\delta^{18}O$ of the sulphate in the brine samples from the 1372-m level and below is in the range of 5 to 10‰, significantly lower than the $\delta^{18}O$ range for Devonian evaporites (12 to 19‰). Fritz et al. (1994) have suggested that the original ^{18}O of this sulphate may have been altered as the sulphate attempted to achieve isotopic equilibrium with an ^{18}O depleted shield brine end member ($\delta^{18}O = -9 \pm 2$‰) at temperatures of 100–200°C. This is much higher than the mine water temperature at the 1616-m level (25°C) and suggests that these brines infiltrated to much greater depths earlier in their history.

5. Discussion

5.1. The source of the salinity

In the more concentrated Yellowknife brine samples (> 100 g Cl/l), over 99% of the negative electrical charge is carried by chloride. Identification of the origin of the chloride is therefore essential in the study of the salt source(s) in these fluids. Despite the obvious temptation to call in seawater to account for the chloride, several ion/Cl ratios in the brines display significant excursions from their respective seawater analogues (Table 4). Moreover, the Sr isotope ratios measured therein provide strong evidence for Sr contributions from a highly radiogenic source, which could not have been supported by seawater. The main arguments and data in support of a 'rock-source' for chloride (etc.) have been provided by Frape et al. (1984), Frape and Fritz (1987), Edmunds et al. (1987), Gascoyne et al. (1987), Kamineni (1987), Nordstrom et al. (1989), Kamineni et al. (1992) and Frape et al. (1993). This approach has been challenged by Herut et al. (1990) and Bottomley et al. (1994) who showed, while differing in their reasoning, that the chloride and bromide contents of the Canadian brines could well be explained by seawater.

The following arguments support the view that the source of chloride, bromide and lithium in the Yellowknife brine is seawater. The reasoning is based on the new data (Tables 1 and 2), and in particular on the Li-isotope analyses which are presented here for the first time. The Yellowknife $\delta^{6}Li$ values are very similar to the $\delta^{6}Li$ value of modern seawater (−32.3‰), averaging −35.1‰ (Fig. 5). The four most saline brines yield an average value even closer to seawater, of −33.6‰. These values are clearly distinct from the much lighter values of the host metabasalt (−5.4‰) and unaltered MORB (−3.4 to −4.7‰, Chan et al., 1992), as well as from the intermediate $\delta^{6}Li$ value of the granodiorite (−20.8‰). The slight depletion in $\delta^{6}Li$ with respect to the marine value may reflect minor removal of this element into secondary minerals, such as chlorite and sericite, which are common alteration products of the host metabasalt adjacent to faults (Boyle, 1961). Chan et al. (1992, 1994) have shown that such uptake favors preferential removal of ^{6}Li and this may be the reason for the observed Li enrichment, but $\delta^{6}Li$ depletion, in the altered Yellowknife metabasalt samples. Therefore, the $\delta^{6}Li$ values for the Yellowknife mine waters indicate that the Li is primarily of marine origin. As shown in Fig. 5, the $\delta^{6}Li$ values are independent of the Li concentration indicating the dominance of the seawater source.

The isotopic compositions of the metabasalts studied are consistent with interaction with seawater derived brines as discussed above. It can be seen that the Li concentration increases with alteration due to incorporation into secondary phases while the isotopic composition becomes heavier (Table 3). If we assume CSR-2 is the unaltered end member, and that Li in CSR-1 and CSR-3 is a mixture of basaltic-Li and Li derived from the brine, then by mass balance, the secondary phases in CSR-1 and CSR-3 would have $\delta^{6}Li$ of −23.2 and −17.6‰, respectively. These values yield isotopic fractionation factors (α)

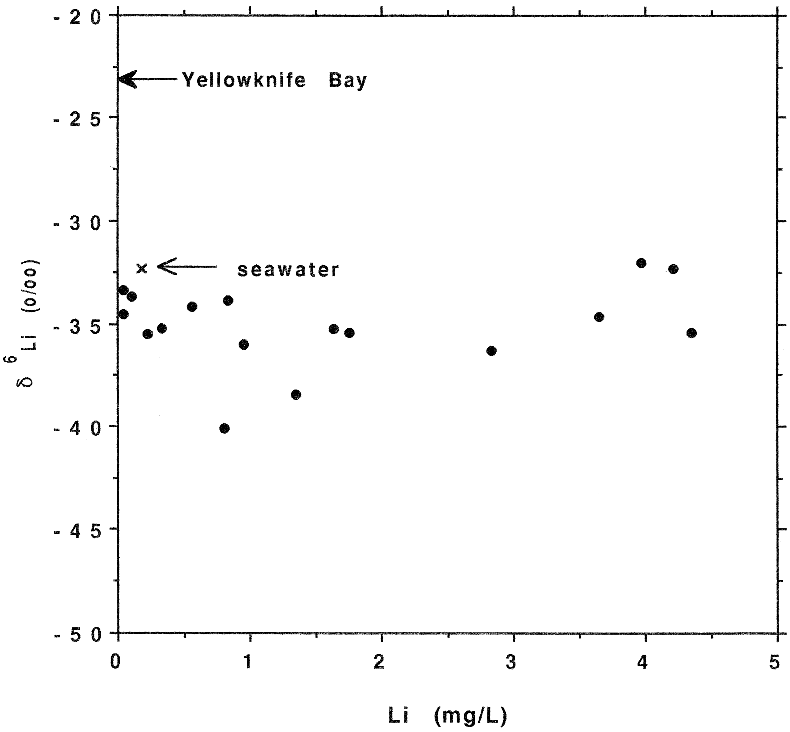

Fig. 5. Plot of the δ^6Li compositions and Li concentrations of Miramar Con mine waters. Also shown is the Li composition of present day seawater.

of 1.009 and 1.015 relative to seawater Li (−32.3‰). The temperature dependence of mineral–fluid isotopic fractionation for Li isotopes is not well known but based on the alteration of seafloor basalts, α has been empirically estimated to be 1.004 at 350°C and 1.019 at 2°C (Chan et al., 1992, 1993). Therefore, the estimated α for the Yellowknife altered metabasalts corresponds to alteration temperatures of approximately 60 to 160°C. This overlaps the temperature range estimated on the basis of the δ^{18}O of the brine sulphate (Fritz et al., 1994).

The δ^6Li of the low lithium surface water sample (1.8 μg/l) from Yellowknife Bay is −23‰. This value lies within the Li isotopic range of the world's rivers (Chan et al., 1992; Falkner et al., 1998; Huh et al., 1998) and represents the result of crustal weathering with attendant isotopic fractionation. Thus the isotopic composition of Yellowknife surface waters acquired from water/rock interaction is distinct from the marine signature of the shield brines and the low Li concentration in surface waters excludes them as a significant source of Li in the deep brines, regardless of the fraction of meteoric water in the mixture.

The linkage between Li and Cl in the Yellowknife brine is provided by bromide. Whereas the chemical properties of the two halides may result in a similar behavior during mineral–water interaction, nothing of this kind constrains the behavior of Li. The ratios between these ions vary greatly between different minerals and rocks, whereas the marine Li show a very good correlation with the chloride and bromide in the brine (Fig. 6 and Table 4). The maximum Li concentration of 4350 μg/l is about 24 × greater than seawater and is similar to the maximum observed Br enrichment. Although the Li–Br trend plots along the seawater concentration line (Fig. 6, bottom) thus establishing the conservatism of both elements, the Li–Cl trend falls above the seawater concentration line (Fig. 6, top) indicating that seawater concentration proceeded well beyond halite saturation. The conclusion from these observations is that the aforementioned ions (Cl, Br and Li) have

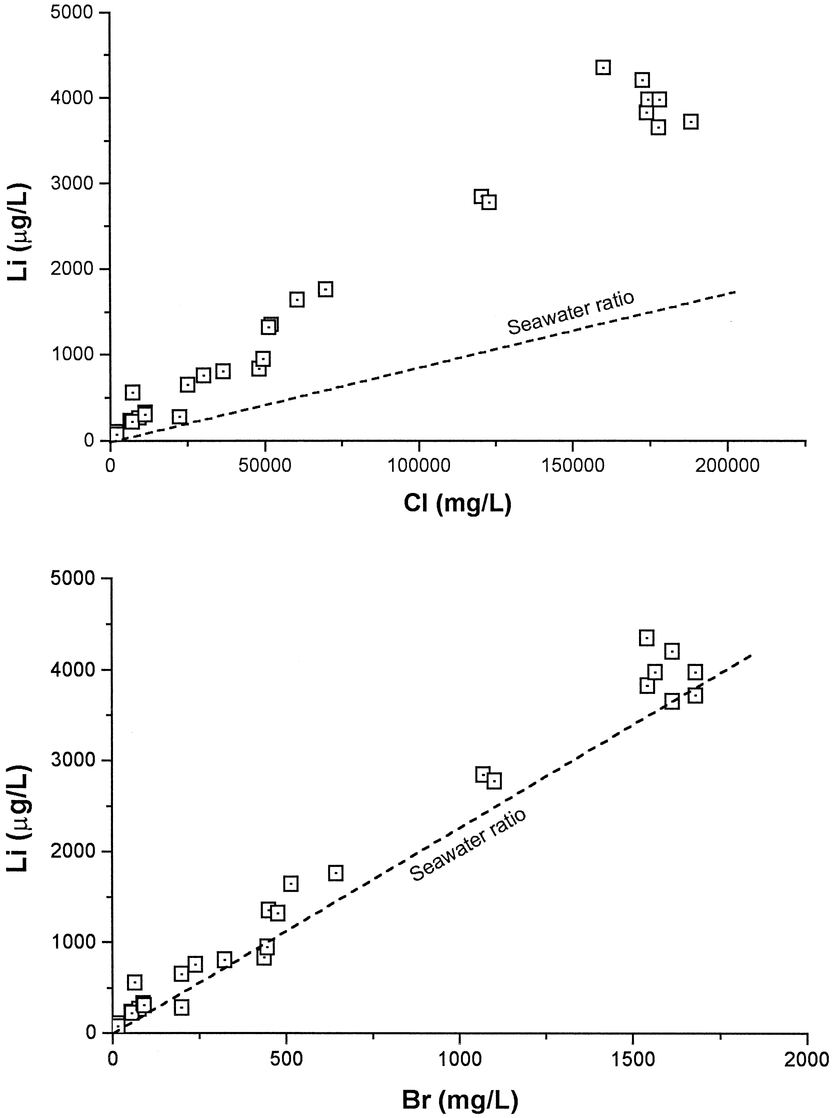

Fig. 6. Plot of Li vs. Cl concentrations (top) and Li vs. Br concentrations in Yellowknife mine waters. Also shown is the seawater concentration line.

been inherited from seawater. The enrichment of Br and Li as well as the depletion of Na, relative to chloride, are a consequence of the concentration mechanism which was responsible for the transformation of the original seawater into a hypersaline brine as discussed below.

5.2. The concentration mechanism

Two large-scale concentration mechanisms, evaporation and freezing, have been available for brine production during ocean history. Both involve the separation of (almost) pure water, as vapor and ice respectively, and both produce dense residual brines. Whereas evaporation of seawater may occur anywhere on Earth's surface, large-scale freezing of the same is obviously restricted to polar areas, the location and extent of which are dictated by plate tectonics and climate, respectively. Once created at the surface, and irrespective of their mode of formation, both brine types must obey the same hydrological laws. This includes their sinking to the bottom of the basin where they fill the interstitial space in the marine sediment. Subsequently the brines may migrate to considerable depths and distances from their original site of formation (Spencer, 1987; Bein and Arad, 1992).

Identification of the concentration mechanism is difficult for the following reasons: (a) Both evaporitic and cryogenic processes are restricted to the surface, and the sedimentary record left by them is therefore susceptible to erosion even after slight uplift; (b) The distance of migration of the fluids from their birthplace may reach hundreds of kilometers, under a completely different hydrological regime than the present one; (c) The brines formed by either concentrative process may be subsequently modified by chemical interactions with their host rocks resulting in at least partial masking of their origins.

An additional complication in the case of the Yellowknife brine, as well as for other shield brines situated near the western erosional edge of the shield, is that it could have originated from the lateral infiltration of formation brines from the adjacent Western Canada Sedimentary Basin rather than infiltrating the craton directly from above as residual brine. The significance of this latter scenario is that the residence time of the brine in the shield could be a small fraction of its total subsurface age in which case its chemical evolution may have been dominated by diagenetic processes that occurred in a basinal environment. In Section 5.2.1, we examine the validity of the seawater evaporation theory by identifying key elemental and isotopic relationships within the Yellowknife brine and comparing them to similar relationships for well characterized brines in the Alberta and Michigan Basins.

5.2.1. An evaporative seawater model

5.2.1.1. The evaporation stage. Yellowknife brine samples have high Br concentrations of up to 1682 mg/l. The mean Br/Cl ratio (mg/l) for all samples is 0.008 with a narrow range of 0.005–0.010. All ratios are significantly higher than the present day sea water ratio (0.003) and only the 3 most dilute mine waters have a Br/Cl ratio less than the mean value. In Fig. 7, we have plotted the Br and Cl concentrations of the Miramar Con mine waters and compared them to similar data for Devonian formation waters from the Alberta Basin (Hitchon et al., 1971; Connolly et al., 1990a), and highly concentrated Ca–Na/Cl brines from Devonian and Silurian-aged carbonate and evaporite formations in the Michigan Basin (Wilson and Long, 1993a,b). Also shown is seawater and its Br–Cl trajectory as it is evaporated to halite saturation (inflection point) and beyond.

The Yellowknife data follow a well defined mixing or dilution trend with a Cl–Br linear correlation coefficient (r^2) of 0.995. The good fit implies that both end members are relatively uniform in composition and that Br and Cl behave conservatively during mixing. The dilution trend intersects the seawater evaporation trend at a Br concentration of about 2000 mg/l. This value likely represents the Br concentration for the brine end member (i.e., the ‘parent’ brine) which would represent a degree of evaporation of seawater of about 30-fold. The dilute end member is present day surface water in the Yellowknife area. Yellowknife Bay, for example, has a Cl concentration of 5 mg/l and less than 50 μg/l of Br. The high and relatively uniform Br/Cl ratio of the Yellowknife brine compared to the Alberta Basin brines suggests that this brine is not formation water that infiltrated fractures and faults in the Precambrian basement rocks from the adjacent sedimentary basin. Instead, the projected Yellowknife ‘parent’ brine appears to be analogous to that of the Michigan Basin brines, although not evaporated to the same degree as the brines from Silurian age formations.

As in the case of Cl, Li displays a good linear correlation to Br ($r^2 = 0.98$) and follows closely the seawater evaporation trajectory (Fig. 8, top). This indicates that Li is largely conservative in the Yellowknife mine waters and that Li concentrations are controlled by mixing of a Li-rich brine end member and a Li-poor meteoric water end member such as Yellowknife Bay surface water which contains only 2 μg/l of Li. The Li isotopic data (Table 2) are consistent with seawater as the dominant source of Li in the mine waters. It follows, therefore, that the salinity itself is traceable to the infiltration of concentrated seawater and not to water/rock interactions as proposed by others (Frape et al., 1984).

Brines in the Alberta Basin and Michigan Basin are enriched in Li relative to the seawater evapora-

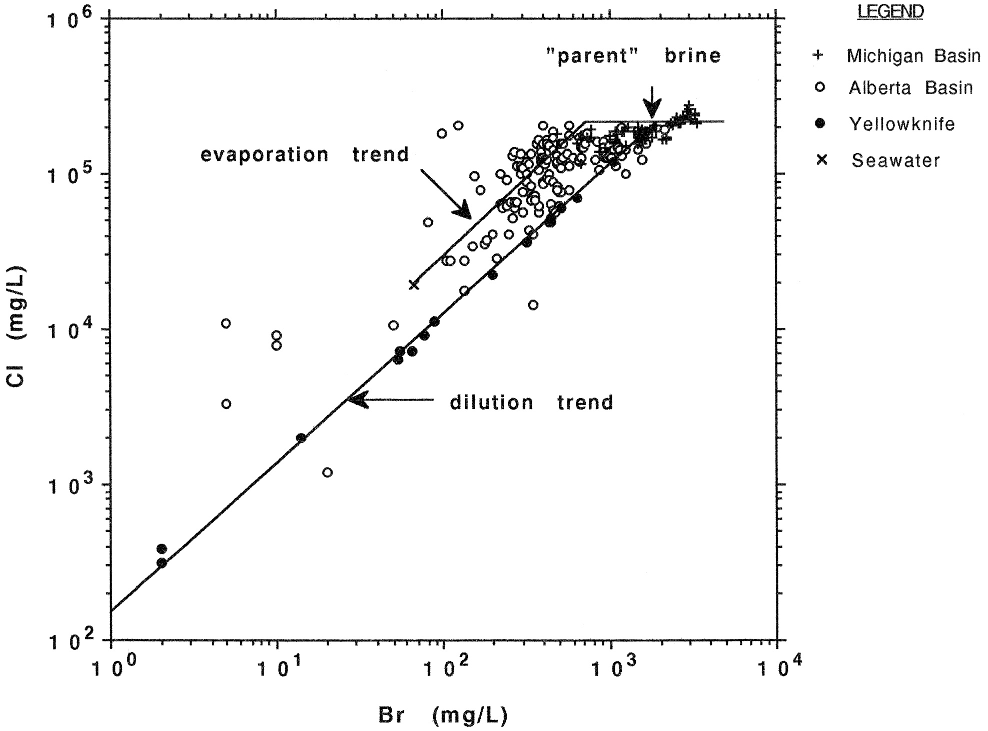

Fig. 7. Plot of the Cl and Br concentrations of Miramar Con mine waters compared to Devonian formation waters from the Alberta Basin and Devonian and Silurian formation waters from the Michigan Basin (see text). The evaporation trajectory for seawater evaporated beyond halite saturation (inflection point) and the dilution trend for Miramar Con mine waters, as the result of mixing between a deep, parent brine end member and local meteoric water, are also shown.

tion trajectory and hence are distinct from the Yellowknife brine. This enrichment is probably due to diagenetic reactions with silicate minerals, particularly clay minerals, present in clastic sedimentary strata. The fact that the Yellowknife brine does not exhibit a similar Li enrichment suggests that it did not reside within sedimentary formations for a sufficient period of time to become enriched in Li prior to infiltration into the shield. This supports the interpretation from the comparison of Br/Cl ratios that the Yellowknife brine is not infiltrated formation water from the present day Alberta Basin.

In contrast to Li, B concentrations do not show any relationship to salinity in general or Br concentrations in particular (Fig. 8, bottom). Only brines from the 1616-m level have B concentrations that are similar to that of present day seawater. Although brines in the Alberta and Michigan Basins have highly variable B concentrations, most are significantly higher than seawater and thus distinct from shield brines. Diagenetic reactions with feldspars, clay minerals, and possibly organic materials within these basins are potential boron sources for formation waters. The fact that the Yellowknife brine samples have markedly lower B concentrations than Devonian formation waters in the Alberta Basin is consistent with the interpretation of the Br and Li data that this brine is not a distal daughter of a basinal parent brine.

As shown in Fig. 4, the Yellowknife brine, and other shield brines (Frape et al., 1984) plot to the left of the global meteoric water line and are thus isotopically distinct from sedimentary formation brines which generally plot to the right of the line. This raises the question as to whether this is due to water/rock exchange of ^{18}O and/or ^{2}H or some other isotopic exchange process. Because the host rocks are a relatively minor reservoir of potentially

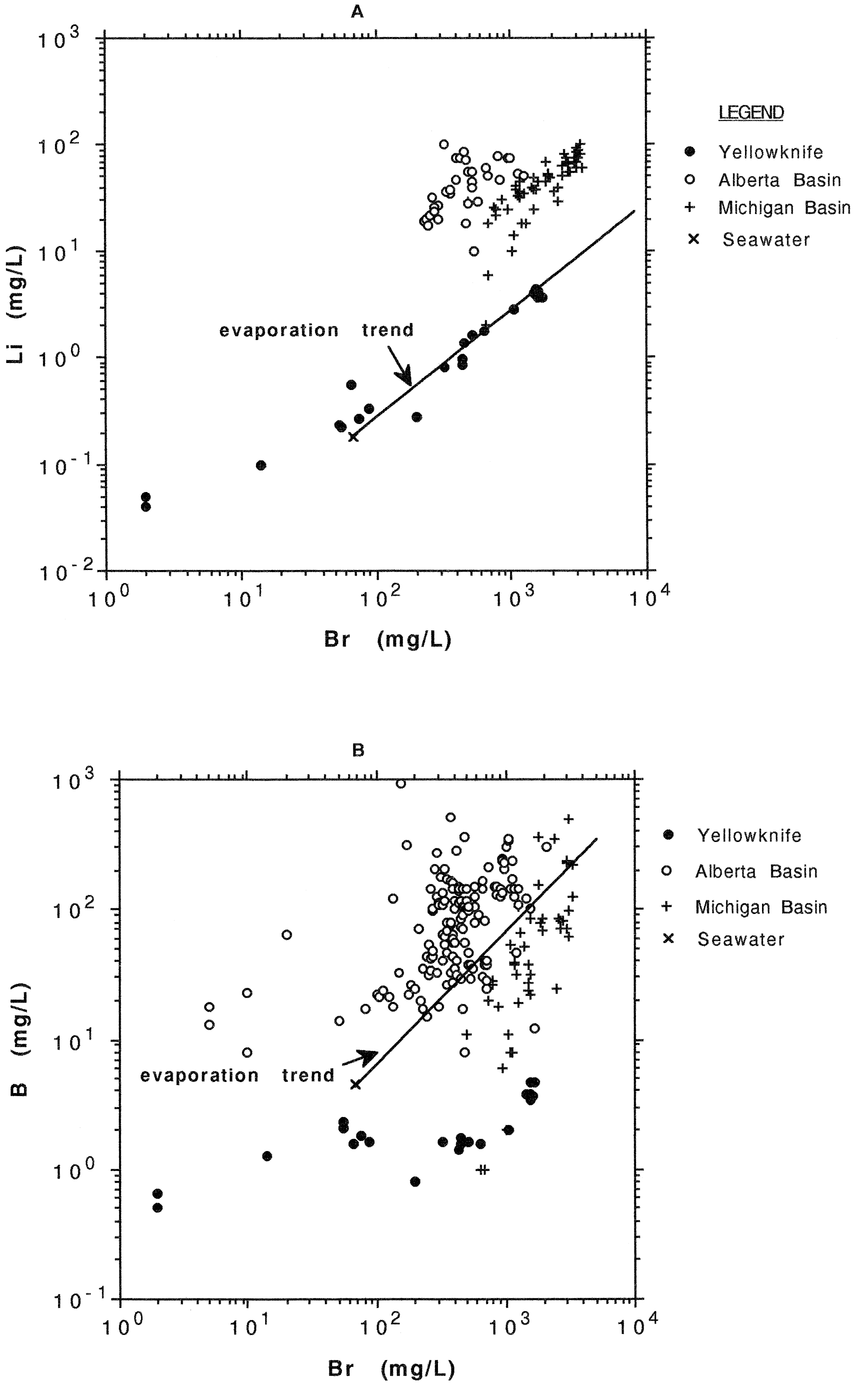

Fig. 8. Plots of the Li (top) and B (bottom) concentrations vs. the Br concentrations in Miramar Con mine waters and the various formation waters shown in Fig. 7. Also shown are the seawater evaporation trends for these elements.

exchangeable hydrogen compared to oxygen, water within these rocks should be more susceptible to oxygen isotopic exchange. At low temperatures and under conditions of low water/rock ratios, oxygen isotope exchange with silicate minerals (Kelly et al., 1986) could have resulted in the apparent shift to lighter values. If so, the oxygen isotopic composition of the brine does not provide a direct indication of the source of the brine. However, this may not be the case with respect to the hydrogen isotopic composition of the brine which may have remained essentially unaltered during its residence time within the shield.

The maximum measured δ^2H value of Yellowknife brine samples is −56‰ (Fig. 4) but the δ^2H of the brine end member inferred from Fig. 7 is unknown. However, the δ^2H of this end member can be estimated from the reasonably good linear correlation ($r^2 = 0.975$) that exists between Br and ^2H for the Yellowknife mine waters (Fig. 9). Extrapolation of the regression line to a Br concentration of 2000 mg/l, the probable approximate Br concentration of the brine end member (Fig. 7), yields an estimated δ^2H of about −40‰. This value, as well as the δ^2H values for the most concentrated Yellowknife samples, are within the δ^2H range for various Devonian connate waters in the Alberta Basin, all of which are significantly lighter than present day seawater (Fig. 4). Examples of these connate fluids include (1) some Alberta Basin Devonian formation waters (Hitchon and Friedman, 1969; Connolly et al., 1990b), (2) fluid inclusions in halite from bedded salt deposits of the Middle Devonian Muskeg Formation of the Alberta Basin (Knauth and Roberts, 1991), (3) high salinity fluid inclusions of possible Devonian age in epigenetic Cambrian dolomites of the southern Canadian Rockies (Nesbitt and Muehlenbachs, 1994), and (4) fluid inclusions in Middle Devonian dolomites which host MVT Pb–Zn deposits of probable Devonian age (Nakai et al., 1993) at Pine Point, N.W.T. (Roedder, 1984). Similarly light connate brines (δ^2H of −50 to −70‰) have

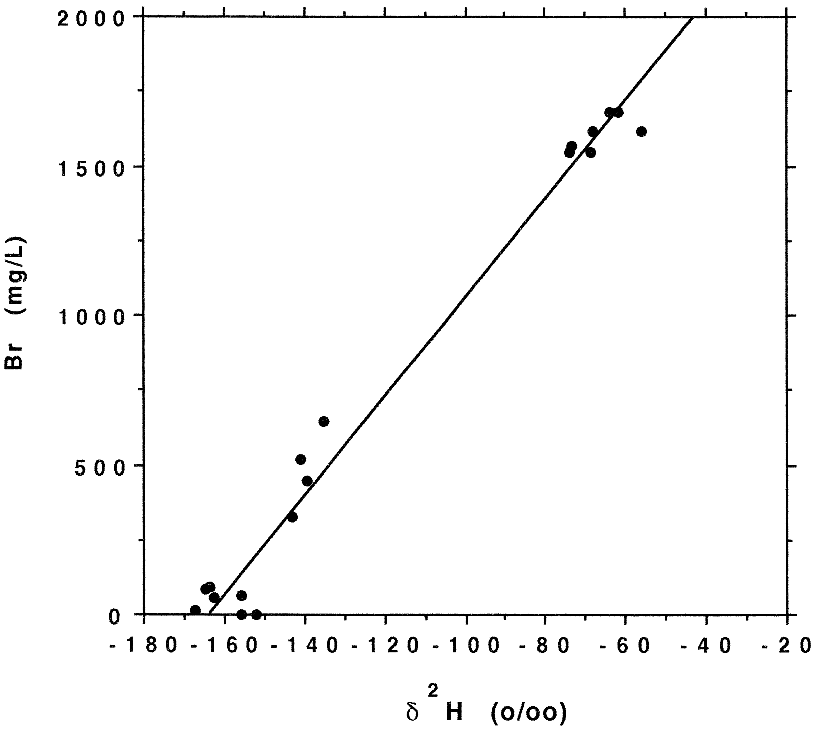

Fig. 9. Plot of the Br concentrations vs. the δ^2H compositions of Miramar Con mine waters with the linear regression line through the data.

been encountered in the Middle Devonian Dawson Bay and Prairie Evaporate Formations in the Elk Point Basin of Saskatchewan (Wittrup and Kyser, 1990).

Evaporation of present day seawater beyond about 4 × results in a reversal of the usual ^{18}O–^{2}H evaporation enrichment trajectory such that negative δ^2H values can be produced by ion hydration effects (Gonfiantini, 1986) beyond halite saturation, i.e., about 11 × seawater (Holser, 1979; Knauth and Beeunas, 1986). Therefore, the negative δ^2H of the Yellowknife brine may be a primary signature of its evaporative concentration on surface that has largely been preserved during its subsurface history. Furthermore the similarity in the δ^2H compositions of the Yellowknife brine and Alberta Basin connate fluids suggests that they may have all originated from evaporated Devonian seawater. Although similar in δ^2H, the Yellowknife brine has relatively low Cl/Br, Li/Br and B/Br ratios that clearly set it apart chemically from brines that now reside within Devonian formations of the Alberta Basin.

5.2.1.2. Post-evaporative processes. A possible Lower to Middle Devonian paleogeographic scenario of direct relevance to the origin of the Yellowknife brine is one in which the Elk Point seaway extended well to the north and east of the present day erosional edge of Lower and Middle Devonian strata (Williams, 1984). In this scenario, brines may have formed both in stable shoal areas in the now eroded portion of the Elk Point seaway as well as in the preserved Elk Point basin, visualized as a tectonic sink brine trap by Williams (1984). Such brines could have infiltrated major regional fault zones in the shield such as the McDonald fault zone (Fig. 1), which is part of the Great Slave Lake shear zone that forms the southern boundary of the Slave province with the Churchill province (Hoffman, 1987), as well as the northerly trending regional Proterozoic transcurrent faults and associated local faulting in the Yellowknife area (Fig. 2).

During evaporation of seawater in the brine trap, Br and Li appear to have behaved conservatively. The extrapolated Br concentration in the parent brine of the Yellowknife brine suggests a degree of evaporative enrichment of about 30 × seawater. If so this brine, prior to infiltration, would have been a Na–Mg/Cl brine rich in sulphate, high in potassium but very low in calcium. During subsequent infiltration through underlying sedimentary sequences, diagenetic reactions with carbonates and shales were likely important in altering the chemistry of the parent brine. Dolomitization of Middle and Upper Devonian carbonates of the Western Canada Sedimentary Basin, such as the large platform carbonates of the Elk Point Basin, is extensive (Mountjoy et al., 1992) and this could be largely responsible for the low Mg and the high Ca concentrations in the Yellowknife brine. Magnesium may also have been taken up in authigenic clay minerals such as chlorite, sepiolite and montmorillonite which are present, for example, as continuous seams in potash deposits of the Prairie Evaporate Formation (Wittrup and Kyser, 1990). Later formation of secondary alteration minerals such as chlorite and sericite within fractures in the greenstone rocks may also have been additional sinks for Mg and K, respectively.

Sulphate concentrations could have been lowered in the brine prior to penetrating the crystalline basement rocks through secondary gypsum formation from calcium released during dolomitization and/or by sulphate reduction. The sulphate source for the Pine Point sulphide ore deposits had a $\delta^{34}S$ of 19‰ (Jackson, 1971) which is within the range of values observed for sulphate in both the Miramar Con brines and in Na/Cl brines from Devonian strata of the Pine Point area (Weyer et al., 1979). However, there is no strong indication of biogenic sulphate reduction in the isotopic composition of the Yellowknife brine sulphate.

Once the brine infiltrated into the Precambrian basement rocks, albitization of calcic plagioclase may have been an additional source of Ca at the expense of Na. Albitization has been shown to be the dominant control on the Sr isotopic composition of brines at several other sites on the Canadian Shield (McNutt et al., 1990; Franklyn et al., 1991) and clearly reactions with silicates are responsible for the radiogenic Sr isotope signature for the Yellowknife brine. The observed Sr depletion with accompanying $^{87}Sr/^{86}Sr$ enrichment for altered fault zone metabasalts is consistent with the albitization process (Table 3). However, the radiogenic $^{87}Sr/^{86}Sr$ ratios of the brine samples can not be explained solely by reaction with plagioclase in the host metabasalt because the brine ratios are higher than the whole rock ratio which, in a basaltic rock, should be dominated by the ratio in the plagioclase (McNutt et al., 1990). The radiogenic brine ratios require that either some of the Sr is derived from more Rb-rich minerals in the metabasalt (such as hornblende or biotite) or that, at some point in its history, the brine interacted with felsic rock units in the Kam Group or surrounding granitic intrusive rocks (Fig. 2). Another possibility is that albitization, or other reactions with silicate minerals, occurred within the sedimentary basin during brine infiltration through underlying Cambrian–Ordovician clastic rocks that may have been present in the Yellowknife area during Devonian time (Fig. 1).

Because of the relatively high density of residual brines, infiltration into the shield to depths of several kilometers is possible until counterbalanced and partially reversed by buoyancy effects resulting from heating under the prevailing geothermal gradient (Spencer, 1987). During subsequent cooling of these brines, retrograde ^{18}O exchange with secondary silicate minerals in fractures under conditions of relatively low water/rock ratios may have resulted in the relative ^{18}O depletion of shield brines (Kelly et al., 1986).

In the absence of unusually large upward hydraulic gradients dense shield brines would be difficult to displace to surface by groundwater flow. However, lateral brine migration should occur through relatively permeable and continuous fault zones in response to regional horizontal hydraulic gradients. Flow rates would be maximized during periods of post-Devonian crustal uplift such as occurred during the uplift of the Cordillera beginning in the early Mesozoic and culminating in the Eocene (Porter et al., 1982). Topographically-driven regional groundwater flow systems were established during this time with flow occurring from southwest to northeast across the Alberta Basin (Toth, 1978; Garven, 1985). Regional flow in northern Alberta is still northeasterly at the present time (Bachu et al., 1993) and, presumably, this is also the direction of regional flow in the underlying fractured and faulted basement rocks. Given the likelihood that Devonian seas covered much of the Canadian Shield and that the direction of regional groundwater flow since then has probably been toward the craton, it is reasonable to expect that brines of Devonian age should reside in the shield well to the east and north of the present day erosional contact.

5.2.2. A seawater cryogenic model

5.2.2.1. The freezing stage. The cryogenic origin of Herut et al. (1990) is of similar status as the evaporative model in terms of its ability to explain the origin of shield brine chemistry. Bein and Arad (1992) have proposed that saline groundwaters present in coastal areas of the Baltic Sea are the result of the freezing of seawater which may occur when a glacier overrides a marine body that transgressed inland during the preceding interglacial period. The sub-Arctic setting of the Yellowknife region may have allowed the migration of brine from seawater freezing sites along the Beaufort Sea and Hudson Bay coastlines during Pleistocene glaciations. Alternatively, cryogenesis may have occurred much earlier in the Yellowknife area during late Proterozoic or Paleozoic glaciations.

Herut et al. (1990) defined the significant differences between the products of the two processes based on a comparison of data from the freezing of seawater with results from evaporation trials of similar solutions. The most important of these is the removal of SO_4 during seawater freezing in mirabilite ($Na_2SO_4 \cdot 10H_2O$), rather than in gypsum (or anhydrite) which characterizes evaporitic processes. Also, hydrohalite ($NaCl \cdot 2H_2O$), rather than its evaporitic analog halite, is the typical phase precipitated during cryogenic processes.

Fig. 10 shows the new data from Yellowknife, plotted on the Herut-type Na/Cl–Br/Cl diagram (Herut et al., 1990, Fig. 6). All of the hypersaline brine samples, ($Cl > 100$ g/l) fall along and very close to the freezing line and quasi-parallel to it, displaying a marked Na-deficit with respect to the evaporation line. Several of the less concentrated brine samples ($Cl = 30–70$ g/l) are still close to the same line and invariably above it. In view of the Na-deficit in the Yellowknife brine, the evaporitic model must contain a (post-concentrative) Na-depleting process, such as albitization. Such may be expressed by the arrows extended vertically to each data point from the overlying evaporation path ('Ab' in Fig. 10). However, if albitization is indeed respon-

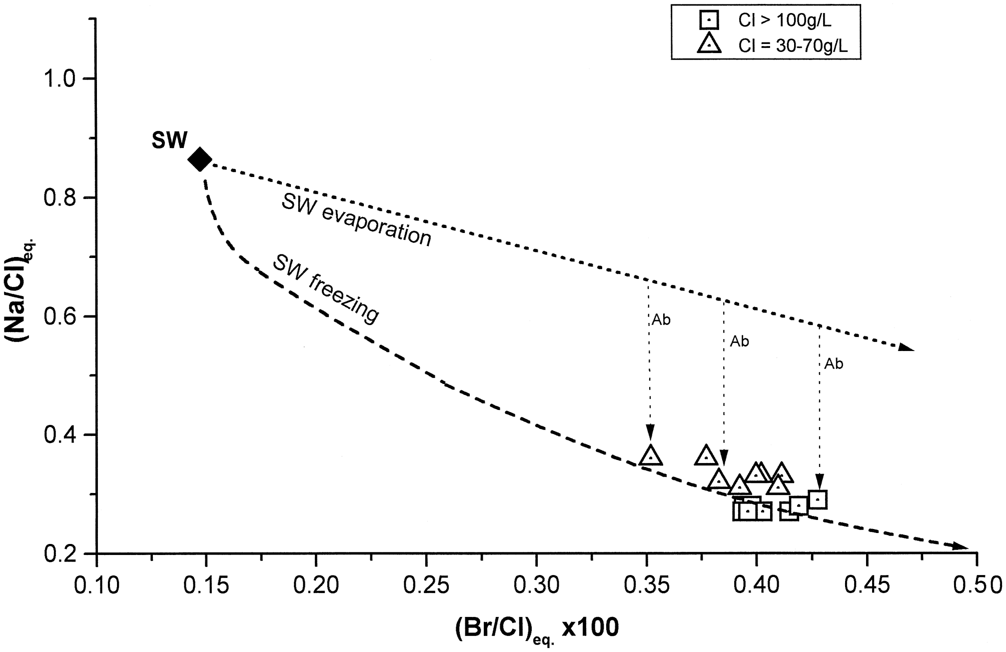

Fig. 10. The Na/Cl vs. Br/Cl relationship of Yellowknife brines as well as the seawater freezing and evaporation trends adapted from Herut et al. (1990). Note the strikingly dense grouping of the most concentrated brine samples ($Cl > 100$ g/l) along the freezing line and their absence along the evaporation line. Arrows 'Ab' represent hypothetical albitization paths.

sible for the Na depletion, it is unclear why none of the brines plot significantly above or below the freezing line, but rather scatter along it.

The degree of cryogenic concentration of seawater achieved by the Yellowknife brine before its infiltration can be estimated by comparing the Na/Cl ratio in the brine to the degree of concentration achieved by solutions with a similar Na/Cl ratio during experimental freezing of seawater. We have used for that purpose the data of Nelson and Thompson (1954) for seawater freezing experiments. The chlorinity of the seawater used in these experiments is lower than that of modern seawater, amounting to about 18 per mil. The ratios between most ions (Cl, Ca, K and Na) in the given analyses are similar to their respective values in modern seawater, but the concentration of Mg is higher relative to the other elements (for example, $Mg/Cl = 0.072$ rather 0.068 in modern seawater). Because the freezing experiments were performed with seawater of 18 per mil chlorinity, all our calculations of the cryogenic concentration factor were performed vs. Nelson and Thompson seawater, and not relative to average seawater composition. The resulting concentration factors represent average factors calculated for K and Ca. Clearly, dilution with freshwater would not affect this ratio. Table 4 shows a Na/Cl ratio of 0.27–0.28 for the brine, corresponding to a concentration factor of about 27- to 28-fold attained in laboratory freezing trials (Nelson and Thompson, 1954, Table 1). Also, the conservative behavior of Li and Br allows the use of their respective concentration ratios (Li_{brine}/Li_{sw} and Br_{brine}/Br_{sw}) to calculate the net concentration of the brine throughout its history. Both ratios display identical concentration factors for given solutions, and, in the case of the most concentrated brine samples, are about $26\times$ seawater. The same rational also reveals that the Yellowknife brine has never been in contact with halite deposits after its formation.

5.2.2.2. Post-freezing processes. The most saline (> 100 g Cl/l) Yellowknife brine samples show prominent deviations from conservative seawater behavior. These are expressed in their very low SO_4/Cl, Na/Cl and Mg/Ca concentration ratios relative to the corresponding ratios found in modern seawater (Table 4). The following is an attempt to explain these observations by the brine's surface cryogenesis, and subsequent subterranean evolution. Herut et al. (1990) have shown that the Na and SO_4 deficits observed in Canadian shield brines can be explained by precipitation of mirabilite and hydrohalite during seawater freezing. Applying their principle, and using Nelson and Thompson (1954) data, the concentration of SO_4 in brine concentrated cryogenically to 27–28 × seawater is around 40 mmol/l. This corresponds to a SO_4/Cl molar ratio of approximately 0.003. The SO_4/Cl ratio measured in the most saline Yellowknife brine samples is much lower, amounting to only 0.00042 (Table 4). The major depletion of sulphate occurred within the cryogenic site, and must have been accompanied by an equivalent depletion of Na (during mirabilite crystallization). Additional sulphate may have been lost through bacterial sulphate reduction and/or subsurface gypsum precipitation during subsequent Ca enrichment, either in sediments or in the crystalline basement rocks, as discussed below.

The very significant enrichment of Ca coupled with the almost total Mg depletion (Table 4), must have occurred via Ca–Mg exchange with a calcium mineral, such as dolomitization of $CaCO_3$. Mineral balance calculations show that both the cryogenic and evaporitic models could be responsible for the Yellowknife brine evolution (Table 5). In the cryogenic case dolomitization of the $CaCO_3$ sediment sets in after the mirabilite and hydrohalite crystallization.

The Sr/Ca ratio of the brine samples and their δ^6Li values suggest dolomitization of aragonite-rich marine sediment by the brine as the main process responsible for Ca–Mg exchange rather than interactions with silicate minerals. The following data and arguments support this conclusion. The enrichments of Sr and Ca in the brine (relative to seawater chloride) are almost identical (Table 4), and the Sr/Ca ratio in the concentrated (> 100 g Cl/l) Yellowknife samples is very similar to that of modern seawater. As only a small fraction of the Sr in the brine (some 240 ppm out of ca. 1270 ppm) can be accounted for by an initial, 28-fold cryogenic enrichment, the ratio between Sr and Ca during their release from the carbonate sediment upon dolomitization must have been similar to that of seawater. The value of the distribution coefficient of Sr between aragonite and aqueous solution, is around 1 (Kinsman and Holland, 1969), and marine aragonite, therefore, has a seawater Sr/Ca ratio. During dolomitization, however, very little of the Sr is taken up by dolomite whereas 50% of the liberated Ca is captured by this mineral. For a sediment comprised of 100% aragonite this would result in a Sr/Ca ratio in solution about twice as high as that of seawater (Sass and Starinsky, 1979). Therefore, a carbonate sediment comprised of some 50% aragonite and 50% calcite is all that is needed to yield the Sr and Ca concentrations and ratios measured in the Yellowknife brine samples. Dolomitization of aragonite and calcite is also consistent with their Li/Br ratios and δ^6Li values which are identical and similar to those of modern seawater, respectively. The concentration of Li in sedimentary carbonates is very low (Hoefs and Sywall, 1997), and dolomitization is therefore expected to affect only slightly the Li/Br ratios and δ^6Li values in the brine, if at all.

Table 5
Mineral balance during cryogenic and evaporitic brine evolution

Mineral	Freezing[a] + evolution		Evaporation[b] + evolution	
	meq/kg	% Weight	meq/kg	% Weight
Halite	–	–	7729	32.6
Hydrohalite	9962	60.1	–	–
Gysum	–	–	1232	8.5
Mirabilite	1506	15.5	–	–
Dolomite	2830	16.7	2311	17.1
Chlorite	269	1.0	219	1.0
Sericite	269	6.8	219	7.0
Albite	–	–	1436	30.2
Total		100		100

[a] Seawater degree of concentration ×27, calculated from Na/Cl ratios obtained during freezing experiments (Nelson and Thompson, 1954).

[b] Seawater concentrated ×22, calculated from Br/Cl ratios obtained during evaporation experiments (Raab, 1997).

Although dolomitization can be singled out as a major Ca–Mg mineral–brine interaction, it must have been complemented by an additional process (or processes) in view of the $^{87}Sr/^{86}Sr$ ratios measured in the brines and the extreme Mg depletion displayed by the Yellowknife brine. These observations can be explained by interaction of the Yellowknife brines with the radiogenic silicate minerals, leading to secondary Mg-silicate alteration products such as chlorite. However, it is unlikely that massive amounts of Mg were removed from the brine by chloritization since significant formation of Mg-silicate minerals would affect the Li isotopic compositions of the brines. A more precise estimate of the role of silicate alteration in the release of radiogenic Sr into the brine is, presently, impossible as $^{87}Sr/^{86}Sr$ ratio analyses of mineral separates from Yellowknife core samples are not yet available. Moreover, the migration of the brines may have allowed them to import the radiogenic Sr from rocks much richer in Rb than the local Yellowknife metabasalt. For example, Green et al. (1968) reported whole rock $^{87}Sr/^{86}Sr$ ratios of 0.7242–0.7801 for dacite units within the Kam Group and a ratio of 0.7875 for granodiorite from the Western Granodiorite batholith, which is similar to our analysis of this pluton (0.784405).

6. Conclusions

The δ^6Li data, Li/Br ratios and mineral balance strongly suggest that the salinity of the Yellowknife brine (up to 190 g Cl/l) is derived from seawater. Less clear is whether evaporative or cryogenic processes were the concentrative mechanisms responsible for their high salinity. In either case the uniformly elevated Br/Cl ratios indicate that the seawater concentration mechanism proceeded well beyond halite saturation with both the cryogenic and evaporative theories yielding similar enrichment factors for the parent brine of about 28 × and 30 × seawater, respectively.

Evidence in support of a Devonian evaporative origin include: (i) measured δ^2H values for the deepest brine samples, and a projected value (about −40‰) for the brine end member, that are similar to those for various Devonian connate brines in the Alberta Basin. However, the uniformly high Br/Cl ratio and the low Li/Br and B/Br ratios of the Yellowknife brine distinguish it from present day formation waters in Devonian strata of the Alberta Basin, strongly suggesting that it did not originate from the post-Devonian infiltration of Alberta Basin formation waters into crystalline basement rocks. (ii) the δ^{34}S compositions of Yellowknife brine sulphate (19.7 to 28.3‰) are generally significantly heavier than present day marine sulphate but are consistent with a Devonian seawater sulphate source, and (iii) the proposed Devonian seawater source is compatible with the presence of Elk Point Group evaporite deposits in the Great Slave Lake area and possible Middle Devonian paleogeographic scenarios that extend the Elk Point sea well to the east of the present day Phanerozoic erosional contact.

On the other hand, the behavior of the Na–Cl–Br system in the Yellowknife brine exactly matches that which has been observed during seawater freezing experiments in the laboratory and directly supports the cryogenic concentration mechanism. The Na/Cl ratio in the most concentrated brine (0.28) corresponds to a concentration factor of 28 × for experimental seawater freezing (Nelson and Thompson, 1954), rather consistent with the aforementioned concentration factor obtained from Li and Br.

Following seawater concentration by either of these two mechanisms, but before infiltrating into the basement rocks, the brines dolomitized aragonite-rich carbonates resulting in massive uptake of Mg and release of Ca to the brine. This process is also the reason the brine has retained a Sr/Ca ratio that is very similar to seawater. While residing within the Precambrian basement an additional component of silicate Sr and Ca was added to the brine as is evident from radiogenic $^{87}Sr/^{86}Sr$ ratios as high as 0.71475. Mineral balances calculated for the cryogenic and evaporitic models show significant quantitative differences between the products of these processes, as expressed in weight percent (wt.%). These include 36% of halite vs. 60% hydrohalite and 8% gypsum vs. 15% mirabilite. The crystallization of some 18% dolomite is required by both processes. The evaporitic model includes the formation of about 30% albite, none of which is demanded by cryogenesis.

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