SALINE WATERS AS INDICATORS

OF

ECONOMIC MINERALIZATION

Report 241-1

Submitted to

By

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and

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Introduction

It has long been known that ocean water, fresh water which has interacted with evaporites, evolved connate water in marine sedimentary rocks, and magmatic brines are all effective solvents of base metals, especially at temperatures above 300°C and at pH's below neutrality (White 1981). Because of this fact, it was thought that saline groundwater found in many wells located in the North Shore Volcanic Group and in the Duluth Gabbro Complex, NE Minnesota, might prove to be valuable in locating areas of economic mineralization. It was also hoped that saline groundwater in bedrock aquifers in contact with sulphide mineralization might have anomolously high values of base metals.

Therefore it was proposed to do the following: 1) locate saline wells within the North Shore Volcanic Group and Duluth Complex, 2) sample and analyze waters from these wells and if feasible to establish base-line values of trace metals, 3) sample and analyze saline wells associated with known areas of economic mineralization, 4) compile analyses of potable and not-potable wells from the literature, and 5) establish if there were any relationship between rock type and the incidence of saline wells.

Personnel

This project was initially conceived and undertaken by Dr. Robert B. Cook but was taken over by Dr. P. Morton in August 1984. The former is a geochemist with a chemical background, the latter a geologist with a geochemical background. Because of this, the interpretation of results comes from a geological basis rather than a chemical one.

John Ameel of the analytical Laboratory, Natural Resources Research Institute (NRRI) had prime responsibility for locating and sampling saline wells and he directed the chemical analysis for the following: T°C, conductivity, pH,

Cl⁻, F⁻, dissolved inorganic carbon (DIC) and alkalinity. Cheryl Kelley worked as his technician over the time frame of this project. All other analyses were carried out at DNR's Minerals Division Laboratory in Hibbing under the direction of Al Klaysmat.

Location of Wells

The number of saline water samples taken was limited by the difficulty in locating saline wells that were still accessible. Minnesota state law mandates that non-potable wells be plugged to prevent contamination of nearby aquifers. Also all the department of health records are confusing in that they might say well water is hard when they mean saline and visa-versa. Most of the wells sampled were located through Bill McKeever, a well-driller operating in Cook and Lake counties. He gave us names and addresses of people who had had saline wells drilled recently and that were available for sampling. John Ameel also just "knocked on doors" to locate wells. In all, 21 wells were sampled (Tables 1 and 2, Figure 1), one of them in triplicate. Of these, 5 would be considered potable.

In searching the literature, analyses of 10 bedrock wells have been located within the Duluth Complex, and 13 within the North Shore Volcanic Group (Table 4, Figure 2). Within the Duluth Complex, 3 are saline, 6 within the North Shore Volcanic Group. Nine analyses of saline water from the shaft and drill holes of the Minnamax Cu-Ni Deposit (Table 5), have also been obtained, six of which have base metal values. Of the several hundred drinking wells that are monitored by Minnesota Pollution Control Agency, only 2 are within the North Shore Volcanic Group bedrock aquifers and analyses from these have been compiled on Table 3.
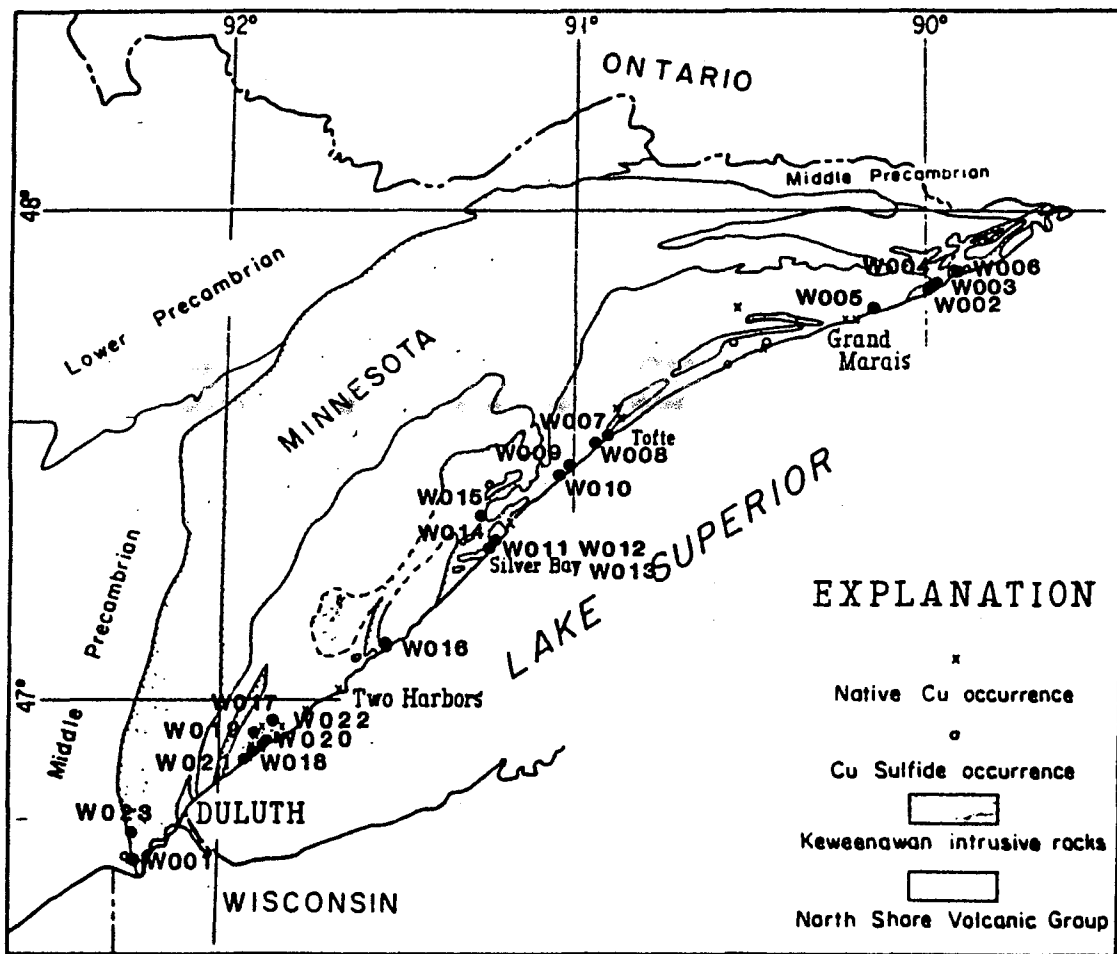
Figure 1: Geologic map of northeastern Minnesota showing well locations
sampled and copper occurrences in the North Shore Volcanic
Group (after Green, 1972)

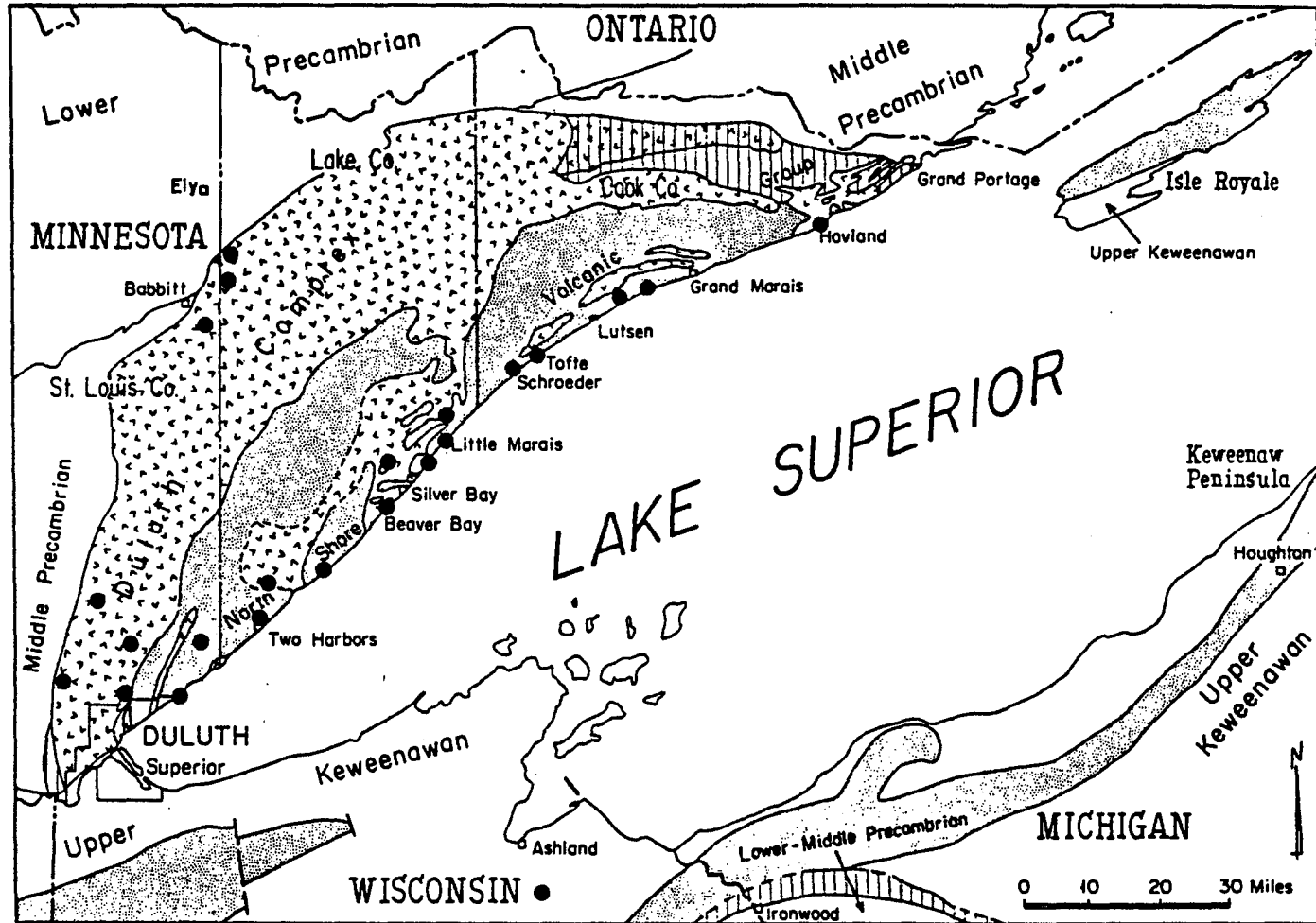Figure 2: Well locations cited in Table 4 (map after Green, 1972)

Table 1. Sampling date and mailing address of participants in the saline well study.

Sample Number	Name	Address	City	State	Zip	Sampling Date
HOO1	Nick Redulovich Jr.	11908 Becks Road	Duluth	MN	55808	-- Nov 73
HOO2	John McClure	Box 337	Grand Marais	MN	55604	12 Jun 84
HOO3	DNR Forestry Office	Box 545	Hovland	MN	55606	12 Jun 84
HOO4	Cook County Garage		Hovland	MN	55606	12 Jun 84
HOO5	Glen Leonard	Box 225, Star Route	Grand Marais	MN	55604	12 Jun 84
HOO6	LaVerne Ryden	Box 92A	Hovland	MN	55606	13 Jun 84
HOO7	Temperance River State Park	Allen Barry	Schroeder	MN	55613	13 Jun 84
HOO8	Terry MacKenzie	Box 359	Schroeder	MN	55613	13 Jun 84
HOO9	Ralph Adams	Box 155, East Star Route	Little Marais	MN	55611	13 Jun 84
HO10	Marion Calph	PO Box, East Star Route	Silver Bay	MN	55614	13 Jun 84
HO11	Pallisade Baptist Church	Box 14, Star Route	Silver Bay	MN	55614	2 Aug 84
HO12	Pallisade Baptist Church	Box 14, Star Route	Silver Bay	MN	55614	2 Aug 84
HO13	Pallisade Baptist Church	Box 14, Star Route	Silver Bay	MN	55614	2 Aug 84
HO14	Line Rauzi	Box 30, Star Route	Silver Bay	MN	55614	2 Aug 84
HO15	Finland State Forest	Eckbeck Campground	Finland	MN	55603	2 Aug 84
HO16	Marty Byrnes	Box 93, East Star Route	Two Harbors	MN	55616	2 Aug 84
HO17	Maretta Muxlow	Route 1, Box 59	Two Harbors	MN	55616	3 Aug 84
HO18	Lakeview Castle	9739 North Shore Drive	Duluth	MN	55804	3 Aug 84
HO19	John Green	10550 Old North Shore Rd	Duluth	MN	55804	17 Jan 85
HO20	Clarence B. LaSota	9799 North Shore Drive	Duluth	MN	55804	17 Jan 85
HO21	Scenic 61 Grocery	9701 North Shore Drive	Duluth	MN	55804	17 Jan 85
HO22	Bruce Berg	9829 North Shore Drive	Duluth	MN	55804	17 Jan 85
HO23	Daniel Casey	3509 Hargin Road	Duluth	MN	55810	18 Jan 85

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Table 2. Map location and well data for saline well project.

Sample Number	County	Quadrangle	Township	Range	Section	Location	Well Depth	Pipe Material	Sample Type
HOO1	St Louis	Esko MN	48 N	15 W	4	bccc	505	Iron casing	Pumped casing
HOO2	Cook	Hovland MN	62 N	4 E	30	bbcc	420	Iron casing	Capped casing
HOO3	Cook	Hovland MN	62 N	4 E	17	cdda	58	Galvanized	Nonpotable household
HOO4	Cook	Hovland MN	62 N	4 E	17	cdca	160	Galvanized	Artesian
HOO5	Cook	Grand Marais MN	61 N	2 E	7	cccd	193		Nonpotable household
HOO6	Cook	Hovland MN	62 N	4 E	11	babd	150	Plastic	Artesian
HOO7	Cook	Tofte MN	59 N	4 W	32	bbca	140+	Iron casing	Capped casing
HOO8	Cook	Schroeder MN	59 N	4 W	31	dbaa	175	Copper	Semipotable household
HOO9	Cook	Little Marais MN	58 N	5 W	30	dcda	420	Copper	Nonpotable household
HO10	Cook	Little Marais MN	58 N	5 W	31	bacc	440	Copper	Nonpotable household
HO11	Lake	Illgen City MN	56 N	7 W	21	dada	620	Galvanized	Nonpotable household
HO12	Lake	Illgen City MN	56 N	7 W	21	dada	620	Galvanized	Nonpotable household
HO13	Lake	Illgen City MN	56 N	7 W	21	dada	620	Galvanized	Nonpotable household
HO14	Lake	Illgen City MN	56 N	7 W	22	bdbb	190	Galvanized	Potable household
HO15	Lake	Illgen City MN	57 N	7 W	33	cdca	99	Galvanized	Potable
HO16	Lake	Castle Danger MN	54 N	9 W	32	acdc	600	Galvanized	Semipotable household
HO17	St Louis	Knife River MN	52 N	12 W	22	dddd	258	Galvanized	Nonpotable
HO18	St Louis	French River MN	51 N	12 W	19	ccaa	280	Copper	Potable when treated
HO19	St Louis	Knife River MN	51 N	12 W	4	dbdd	200	Copper	Potable
HO20	St Louis	French River MN	51 N	12 W	19	caac	72	Galvanized?	Nonpotable household
HO21	St Louis	French River MN	51 N	12 W	19	cccc	285	Galvanized	Semipotable
HO22	St Louis	French River MN	51 N	12 W	19	caaa	117		Nonpotable household
HO23	St Louis	Duluth Heights MN	50 N	15 W	33	baaa	750	Copper	Semipotable

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Sampling Methods

Three types of wells were sampled: 1) pumped wells used for domestic water supplies, 2) free flowing artesian wells, and 3) capped, unused non-potable wells (Table 2).

Domestic water supplies were usually sampled from an outside tap or laundry tub using a threaded hose fitting and a 1/2 inch ID tygon tube. Water was allowed to flow for 2 or more minutes before a 1 liter sample was taken for field measurements. A second liter was drawn for the dissolved inorganic carbon (DIC) sample and then 1 L and 500 mL bottles were filled for analysis.

The most critical aspect of sampling was ensuring that the sample for DIC analysis had not been mixed or equilibrated with ambient air. Gently flowing well water was collected in a 1 liter bottle through a tube held at the bottom of the bottle. The bottle was rinsed and filled from the bottom with a minimum of mixing with ambient air. The sample was drawn into a 50 mL plastic syringe through a 6 inch length of 1/8 inch ID tygon tubing. The syringe and tubing were rinsed 3 times with sample and all of the air forced from the tube before a 30 mL sample was taken. The syringe was then capped to prevent the entry of air and kept in an ice chest until it was transferred to a refrigerator at the laboratory.

In sampling artesian wells, DIC samples were taken directly from the flowing water when possible. Otherwise a 1/4 inch ID tygon tube was inserted into the outlet pipe as far as possible and water flowing through it was collected in the same way as for the domestic water supplies. Direct filling of the bottle for the DIC would have resulted in excessive air-water mixing.

Capped wells were sampled by dropping a plastic 1.5 liter Kemmerer sampler 24 meters down the 6 inch well-casing and triggering it with a brass messenger.

Care was taken to avoid air-water mixing while filling a 1 liter bottle for the DIC sample and field measurements. Additional samples were collected for the remaining analyses.

All bottles used for sample collection were pre-washed and rinsed. One liter bottles were soap washed, thoroughly rinsed with distilled water, acid rinsed with 1:1 HNO_3 followed by three rinsings with distilled-deionized water. The 500 mL bottles for metal samples were rinsed with 1:1 HCl followed by 3 rinsings with distilled-deionized water and air dried.

All samples were stored in an ice chest in the field. The 500 mL samples for metals analysis were filtered within 8 hours of collection through a 0.45 um membrane filter (Gelman GN-6) and acidified with 0.75 mL of Baker Ultrix nitric acid and stored at 4°C.

Analytical Methods

Three measurements were made in the field: pH, conductivity, and temperature. Samples were then transferred to the laboratory at NRRI where alkalinity, conductivity at 25°C, DIC, chloride, fluoride, and pH were determined. Acidified samples were submitted to the DNR Laboratory in Hibbing for metals and sulphate analysis: Ca^{+2}, Mg^{+2}, Na^+, K^+, As, Cu, Fe, Ni, Pb, U, Zn, Au, Ag, and SO_4^{-2}.

Field Measurements

A Graphics Controls Model PHM8100 meter with a Sensorex P/N S101C electrode was used to determine pH in the field. Conductivity and temperature were measured with a Yellow Springs Instrument (YSI) model 33 S-C-T meter.

Laboratory Methods (NRRI)

Alkalinity and pH: Alkalinity was determined on untreated, unfiltered water samples by the potentiometric titration to a fixed end point pH (Standard Methods, 14th edition). The pH end points of 4.5 and 4.2 were used. The laboratory pH reported was the initial pH measured for each sample using a Beckman Model 3500 pH meter equipped with a Fischer combination electrode.

Conductivity: About 100 mL of each sample were equilibrated at 25°C in a water bath. The conductivity was again measured with the YSI S-C-T meter.

Chloride: Chloride concentrations were determined by ion chromatography using a Dionex System 12 ion chromatograph with an HPIC-AG3 pre-column, HPIC-AS3 anion separation column and an AFS fiber suppressor columns. Standards from 1 to 100 ppm were analyzed and the high chloride samples were diluted with distilled-deionized water fall within that range. Chloride spikes of 50 ppm in two samples gave 99 and 100.5% recoveries.

Fluoride: Fluoride was measured with an Orion Model 94-09 fluoride specific electrode and an Orion 90-01-00 reference electrode. The standard Orion procedure was modified according to the method of Kissa (1983) for low fluoride levels. Changes made included increasing the length of time the electrode was in contact with the sample, and modified rinsing and storing procedures for the electrodes.

Dissolved inorganic carbon: DIC was determined using a method modified from Stainton (1973) and Stainton et al. (1977). A 20 mL volume of sample was acidified with 1 mL of 1 N H_2SO_4 to convert carbonates and bicarbonates to CO_2. A 29 mL volume of nitrogen carrier gas was introduced into the syringe and the pressure allowed to return to ambient before the CO_2 was partitioned into the gaseous phase by agitation. The gaseous phase of CO_2 in N_2 was injected into a

0.5 mL sample loop and introduced by a Valco 8 port valve into the carrier gas stream of an Horriba PIR-2000 CO_2 specific infra-red detector. Sample concentrations were determined from a standard curve of sodium bicarbonate standards by peak height integration with a Hewlett-Packard 3390A recording integrator.

Metals and Sulphate Analysis (DNR)

All major and trace cations were analyzed at the DNR Minerals Laboratory in Hibbing using a Perkin-Elmer (Model 603) atomic-absorption spectrophotomer (AA). Samples with concentrations greater than 0.01 mg/l were analyzed by the flame method and for concentrations less than 0.01 mg/l, samples were analyzed using the graphite furnace method. Sulphate ($SO_4^=$) concentrations were also analyzed in the Hibbing Laboratory using a standard turbidimetric method involving $BaCl_2$ (Standard Methods, 14th Ed.).

Those cations analyzed by the flame AA method were: Na^+, Ca^{+2}, Mg^{+2}, K^+, and Fe^{+2}. For analysis of Na^+ and Ca^{+2}, the water was diluted with distilled-deionized water up to 100 times original volume to bring concentrations within the range of the instrument. Mg^{+2}, K^+ and Fe^{+2} required no dilution.

Trace elements analyzed by the graphite furnace AA include As, Cu, Ni, Pb, U, Zn, Au, and Ag. Ag was always below detection (1 ug/l) and therefore is not included in Table 3. Au values were detected using the AA so three samples were sent out for neutron-activation analysis, and these analyses of the three samples revealed concentrations ranging from 0.6 ug/l to 0.7 ug/l. The AA analyses yielded <1 to 11 ug/l for the same samples so it was concluded that the concentrations determined using the AA were erroneous and are therefore not included in Table 3.

Results of Water Analyses

Introduction

According to the USGS (Heath, 1983), a classification of water quality based on total dissolved solids would be as follows:

<1,000	mg/l	fresh
1,000 - 3,000	mg/l	slightly saline
3,000 - 10,000	mg/l	moderately saline
10,000 - 35,000	mg/l	very saline
>35,000	mg/l	briny

In terms of salty taste, water with a chloride content >250 mg/l would taste salty, and according to Matthess (1982), any natural water with chloride contents in excess of 350 mg/l would be saline, and any with chloride contents >40,000 mg/l would be considered a brine. Regardless of definition, of all the waters sampled and analyzed (Table 3) 18 would be considered saline and 5 would be potable (W7, W8, W15, W19, W23). Of the 5 potable wells, 4 are used whereas W7 is not due to its high Fe content (>.3 mg/l). Analyses reported in the literature (Tables 3, 4, and 5) for groundwater in the Duluth Gabbro and North Shore Volcanic Group are, with 1 exception, either saline or fresh. The one anomaly is a true brine with a chloride ion of 46,000 mg/l.

The quality of analyses can be established by doing a cation-anion balance for each sample. Because 2 laboratories are involved, errors may be doubled. The deviation of the cation/anion ratio from 1 is plotted on Figure 3. Several samples have notable deficiencies and these are: W1, W2, W7, W8, W19, and W22. Of these W7, W8, and W19 are taken from potable wells, thus their major ion levels are low so that any minor difference in cation or anion totals may cause a great variation in the ratio. W1, W2, and W22 however are notably deficient in cation content and the analyses are suspect.

Table 3. Chemical composition of water from potable and nonpotable wells from the north shore of Lake Superior in Minnesota

Sample Number	Lab pH	Field pH	Well Temp. Deg. C	Cond. Field uS/cm	Cond. 25 deg. C uS/cm	DIC uM	Alk. as CaCO3 meq/L	Alk. as CaCO3 mg/L	Cl- mg/L	F- mg/L	SO4 mg/L	Ca++ mg/L	Mg++ mg/L	Na+ mg/L	K+ mg/L	As ug/L	Cu ug/L	Fe mg/L	Ni ug/L	Pb ug/L	U ug/L	Zn mg/L
W001	7.56	-	-	-	8800	749	0.638	31.9	3205	0.44	<1	38	40	1520	20	12	1	0.1	15	9	0.21	0.10
W002	7.47	7.51	6.0	2300	4080	885	0.796	39.8	1310	0.61	54	59	6	580	8	1	8	<0.1	7	5	0.41	0.01
W003	7.09	7.28	13.8	1920	2820	395	0.318	15.9	924	0.92	45	272	17	210	3	<1	4	<0.1	1	1	0.40	0.42
W004	7.02	7.41	7.5	2900	4500	218	0.196	9.8	1561	1.09	58	560	9	300	4	1	1	<0.1	5	3	0.37	0.03
W005	7.54	7.08	8.0	3320	4520	865	1.010	50.5	1502	1.28	31	458	15	371	4	<1	1	0.1	4	3	0.42	0.29
W006	6.82	6.94	12.0	13000	21300	243	0.185	9.3	8935	0.29	96	3460	15	1110	6	12	3	0.4	25	12	*	0.07
W007	9.00	9.20	7.5	230	177	1271	1.544	77.2	0	1.86	6	18	2	40	3	3	9	0.4	1	2	0.40	0.01
W008	9.34	9.44	11.2	400	550	756	1.170	58.5	57	2.16	10	34	2	96	3	4	3	<0.1	<1	1	0.39	0.01
W009	7.98	8.43	11.8	5000	8000	519	0.618	30.9	2978	1.00	18	1040	6	560	3	7	3	0.1	8	8	0.33	0.37
W010	9.51	10.10	7.3	1400	2370	90	0.368	18.4	760	0.78	13	164	2	275	3	6	4	<0.1	2	3	0.38	<0.01
W011	8.58	8.56	13.5	8000	9900	29	0.180	9.0	3685	1.34	35	1028	6	1014	6	8	2	0.1	12	11	0.34	0.01
W012	8.58	8.56	13.5	8000	9900	27	0.168	8.4	3732	1.34	33	1080	6	1060	4	9	2	0.1	11	11	0.38	0.01
W013	8.56	8.56	13.5	8000	9900	30	0.188	9.4	3720	1.32	35	1046	6	1030	4	9	2	0.1	13	11	0.28	0.01
W014	8.41	8.27	12.5	1600	1990	1318	1.426	71.3	620	1.12	35	66	2	346	2	5	8	<0.1	<1	3	0.36	0.02
W015	9.20	9.01	11.2	550	810	1214	1.530	76.5	203	0.66	19	12	<2	160	2	7	1	<0.1	<1	2	0.37	<0.01
W016	8.45	8.15	11.0	1520	2090	1108	1.136	56.8	534	0.68	114	96	2	346	2	4	2	<0.1	4	5	0.37	<0.01
W017	7.03	8.21	15.8	6200	8000	109	0.194	9.7	3000	0.07	109	810	16	714	2	5	1	0.1	11	11	0.31	0.16
W018	7.80	7.28	13.4	1880	2350	1573	1.552	77.6	656	<0.03	64	154	6	328	2	2	28	<0.1	<1	6	0.34	0.07
W019	7.79	-	7.4	560	910	5609	5.094	254.7	3	0.33	180	36	6	104	0	1	18	<0.1	<1	2	-	0.01
W020	7.58	7.17	7.0	2480	3660	2783	2.358	117.9	930	0.04	190	350	4	470	3	<1	<1	<0.1	<1	4	-	0.04
W021	6.96	6.90	7.2	2830	4320	236	0.194	9.7	1255	<0.03	140	300	0	630	1	1	2	<0.1	<1	3	-	0.01
W022	8.54	8.24	7.0	5600	8800	*40	0.262	13.1	2684	0.15	320	120	11	700	2	1	<1	0.2	8	10	-	.00
W023	8.39	7.98	7.6	208	324	3450	3.038	151.9	8	0.53	<1	30	9	30	2	1	<1	<0.1	<1	3	-	0.01
Mean	8.05	7.40	9.81	3387	5220	1021	1.051	52.5	1837	0.78	70	488	8	521	4	4	4	0.1	5.52	6	0.26	0.07
Log Mean	8.01	8.06	9.83	2106	3103	465	0.624	31.2	788	0.61	48	181	6	354	3	3	3	0.1		4	0.35	0.03
Other sources:																						
Gooseberry Falls St Pk (1)	9.40	9.00	8.0	456	430	-	1,680	84.0	20	0.54	87	21	<10	82	<.5	<1	7	0.1	<1	1	-	0.07
Fall Lake Campground (1)	7.60	7.00	12.0	459	460	-	4.800	240.0	12	0.14	17	160	62	15	3	<1	16	0.3	6	2	-	0.24
State Ave. all wells (1)	7.55	7.34	-	625	607	-	5.120	256.0	20	0.23	71	186	110	18	3	3	21	1.3	3	8	-	0.12
Sea water (/Kg) (2)	-	-	-	-	-	-	-	-	19350	1.30	2710	411	1290	10760	399	4	1	0.002	1	0	0.003	0.002

References
(1) Trippler, D. and Clark, T.P., 1983, Ground water quality monitoring program: A compilation of analytical data for 1982. Volume 5. Minnesota Pollution Control Agency. 136 p.
(2) Drever, J.I., 1982, The geochemistry of natural waters. Prentice-Hall, Inc., Englewood Cliffs, N.J. 07632, 388 p.

01-Jul-85   * Probable bad value - use alkalinity for calculations

Table 4: Tabulation of analyses of saline and nonsaline wells located within the North Shore Volcanic Group and the Duluth Complex (mg/l)

Sample	pH	HCO_3^-	Cl^-	$SO_4^=$	F^-	Ca^{+2}	Mg^{+2}	Na^+	K^+	Hardness as $CaCO_3$	Fe^{+2}	Mn^{+2}
Duluth Complex												
A. Saline												
13[1]	7.3	37	1390	83	2.2	170	--	760	--	430	0.5	--
H 63[2]	7.4	155	310	45	--	44	9.1	220	3.3	150	--	--
H 70[2]	8.1	94	1500	3.4	--	420	2.0	470	2.0	1100	--	--
Mean	7.6	95	1067	43.8	--	211	--	483	--	560	--	--
Log Mean	7.6	81	865	23.3	--	146	--	428	--	414	--	--
B. Nonsaline												
I[3]	6.6	97	6	8.8	0.1	29	6.9	5	2.0	100	0.06	0.11
K[3]	9.1	97	3	5.1	0.8	1.7	0.2	5	0.7	5	0.18	0.01
M[3]	6.9	185	18	19	0.3	30	10	37	0.7	120	0.09	0.00
7[1]	7.9	138	2	13	0.6	28	8.5	14	1.1	110	0.10	0.00
17[1]	--	73	2	8	<.1	8	7.8	<1	<1	52	2.10	0.80
H62[2]	8.5	167	5	3.8	--	2.7	0.1	73	0.9	7	--	--
H66[2]	7.7	115	4	9.6	--	3.1	0.3	48	0.3	9	--	--
Mean	7.8	125	5.7	9.6	0.4	14.6	4.8	26.1	0.8	58	0.61	0.04
Log Mean	7.7	119	4.3	8.5	0.3	8.3	1.6	12.4	0.8	30	0.29	0.01

Table 4: Tabulation of analyses of saline and nonsaline wells located within the North Shore Volcanic Group and the Duluth Complex (mg/l) (continued)

Sample	pH	HCO_3^-	Cl^-	$SO_4^=$	F^-	Ca^{+2}	Mg^{+2}	Na^+	K^+	Hardness as $CaCO_3$	Fe^{+2}	Mn^{+2}
North Shore Volcanic Group												
A. Saline[1]												
6	8.5	--	1400	19	--	360	--	520	--	890	1.00	--
9	9.7	12	540	170	0.1	130	0.4	320	1.5	330	0.08	0.00
11	9.1	--	370	210	1.2	70	1.0	270	1.6	178	0.08	--
15	9.7	48	420	47	0.7	100	0.0	200	0.8	250	0.06	0.03
18	--	20	46000	71	--	11200	--	17000	--	28000	1.4	--
20	--	32	700	64	2.3	136	0.0	343	----	340	0.04	<.02
23	7.5	16	1400	61	1.0	610	8.9	300	1.2	1600	0.09	0.10
Mean	8.9	26	7261	92	1.1	1801	2.1	2707	1.3	4512	0.39	0.04
Log Mean	8.9	23	1269	71	0.7	315	0.08	553	1.2	1099	0.15	0.02
B. Nonsaline[1]												
8	8.2	152	1	14	1.4	8.3	2.3	49	0.8	30	0.23	0.01
10	7.9	130	205	9.5	0.3	28	10	6.9	0.8	110	0.08	0.01
14	7.7	259	47	29	0.4	33	3.6	95	1.1	97	0.14	0.03
16	8.0	167	100	14	1.2	45	18	49	1.7	190	0.09	0.07
19	9.3	47	71	9.8	2.9	11	0	56	0.4	27	0.14	0.03
21	8.0	64	4.9	11	1.8	3.2	0	29	0.3	8	0.15	0.09
Mean	8.2	137	71.5	14.6	1.3	21	5.7	47	0.85	77	0.14	0.04
Log Mean	8.2	117	26.4	13.4	1.0	15	0.72	37	0.72	49	0.13	0.03

1 Analysis from Hydrologic Investigation Atlas HA 582
2 Analysis from USGS Water Resources Report 80-739
3 Analysis from Hydrologic Investigation Atlas, HA 586

Figure 3:

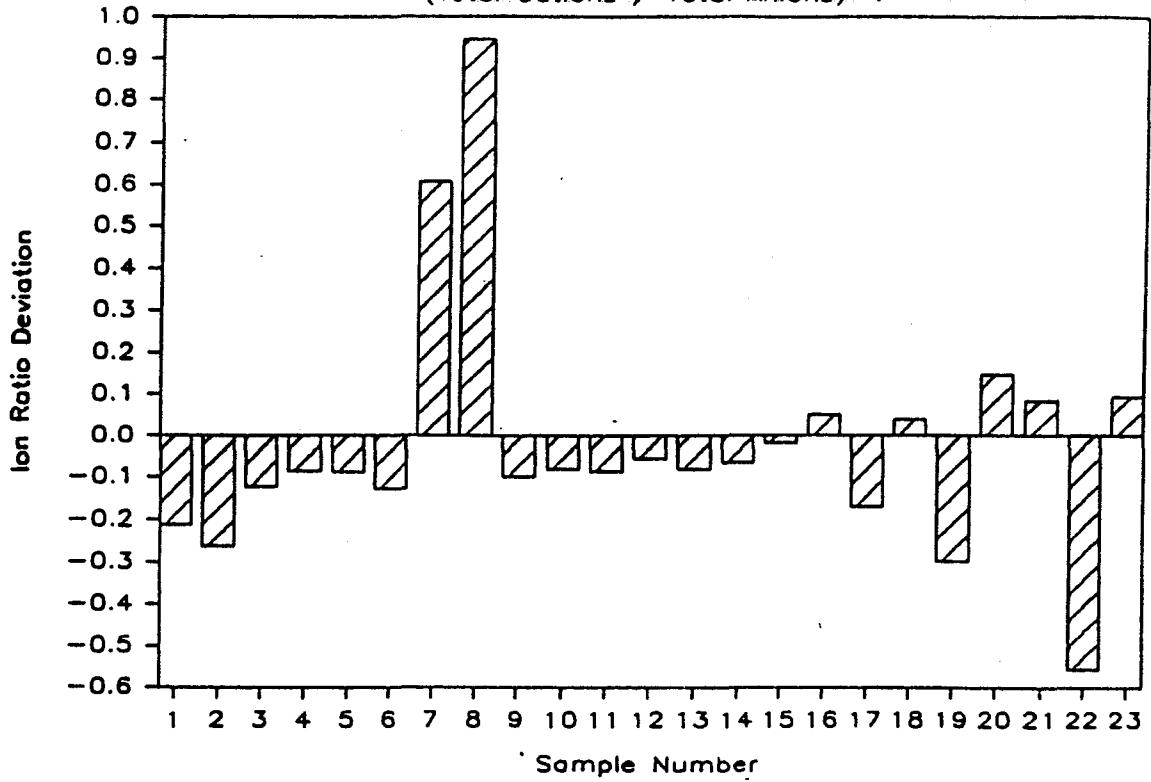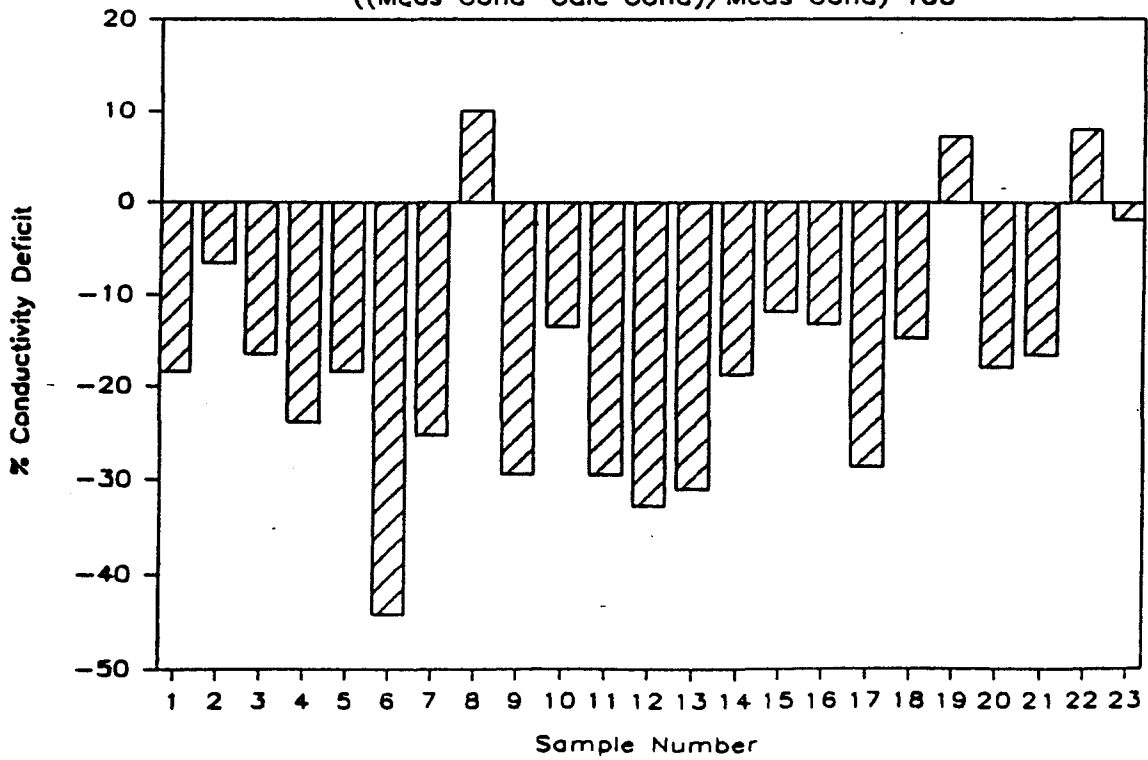## Deviation of Total Ion Ratio from One
(Total Cations / Total Anions)−1

Figure 4:

Percent Conductivity Deficit
((Meas Cond−Calc Cond)/Meas Cond)•100

Also W1 was sampled by Ralph Marsden in 1973. The water was never acidified and it was not stored in a refrigerator. Ca^{+2} is known to be unstable (Hem, 1959) under these conditions and may have precipitated out. This would not cause variation in the cation-anion ratio (as above) but it does make the analysis suspect on its own, especially because its Ca^{+2} content is only 38 mg/l. An analysis of water taken from almost the same spot in 1888 (Winchell, 1889) yielded a Ca/Na ratio (in milliequivalents [meq]) of 1.18, rather than 0.029 of W1. For this reason, and the poor cation-anion balance, W1 along with W2 and W22 are omitted from Figures 7-17.

Major Ion Content

The total anion content of the waters sampled varies from 1.77 meq/l in sample W7 to 254.6 meq/l in W6. The major anion present is always Cl^- (252 meq/l in W6) with the exception of 3 of the fresh wells (W7, W19, and W23) where HCO_3^- is the major anion (up to 5 meq/l). The sulphate content is low in all water samples. The major cations present in the waters are Ca^{+2} and Na^+. Mg^{+2} and K^+ are very low. The ratio of Na^+/Ca^{+2} (in meq) varies from a low of 0.28 in W6 to a high of 4.7 in W14 with a median value of 0.86.

Conductivities were calculated using the methods listed in Standard Methods (14th edition); calculated conductivities are typically much larger than those measured (Figure 4). There is a positive correlation of this conductivity difference with total ion content (r = +0.98) indicating that as the ionic strength increases, so does the conductivity difference. This can be explained by the decrease in activity of the ions present with the increase in concentration of the total ions present. Consequently ions are less 'mobile' than expected (Hem, 1959).

Na$^+$, Ca$^+$, K$^+$, and Mg^{+2} contents (meq) are plotted versus Cl$^-$ contents (meq) in Figures 5 through 8. Na$^+$ and Ca^{+2} exhibit a positive correlation of cation and Cl$^-$ content: linear regression for Na$^+$ vs Cl$^-$ yielded an r = 0.863. The outlier is W6, the most saline of the wells sampled. For Ca^{+2} vs Cl$^-$, there is a very strong positive correlation with r = 0.985 (Figure 6). Linear regression results in a straight line whereby:

Ca^{+2} (meq) = 0.643 Cl$^-$ (meq) -4.28

This equation has been applied to results of analyses for fresh, saline and briny waters sampled from mines in the Sudbury area (Frape and Fritz, 1982) and it was found that Ca^{+2} contents could be predicted within ±10% of the true value for Cl$^-$ contents between 1000-15,500 mg/l, however for Cl$^-$ contents greater than 50,000 mg/l (brines) the predicted values are always 10 to 15% below the real values. For waters with Cl$^-$ contents less than 1000 mg/l, the curve could not be used for accurate production. See end of report for further discussion.

K$^+$ and Mg$^+$ contents of waters are low, usually less than 0.2 ueq/l for K$^+$ and less than 1.4 ueq/l for Mg^{+2} (Figures 7 and 8). There appears to be little dependence of K$^+$ and Mg^{+2} contents with chloride content.

Analyses taken from the literature of saline and non-saline wells in bedrock aquifers in NE Minnesota are listed in Table 4. Analyses in this study are similar to those published in that in the saline waters Cl$^-$ is the dominant anion and Ca^{+2} and Na$^+$ are the dominant cations. Sulphate and bicarbonate anions are low in all waters analyzed. Mg^{+2} and K$^+$ cations are low in both saline and non-saline well-waters.

Figure 5: **Na Concentration vs. Cl Concentration**

DNR Saline Well Project
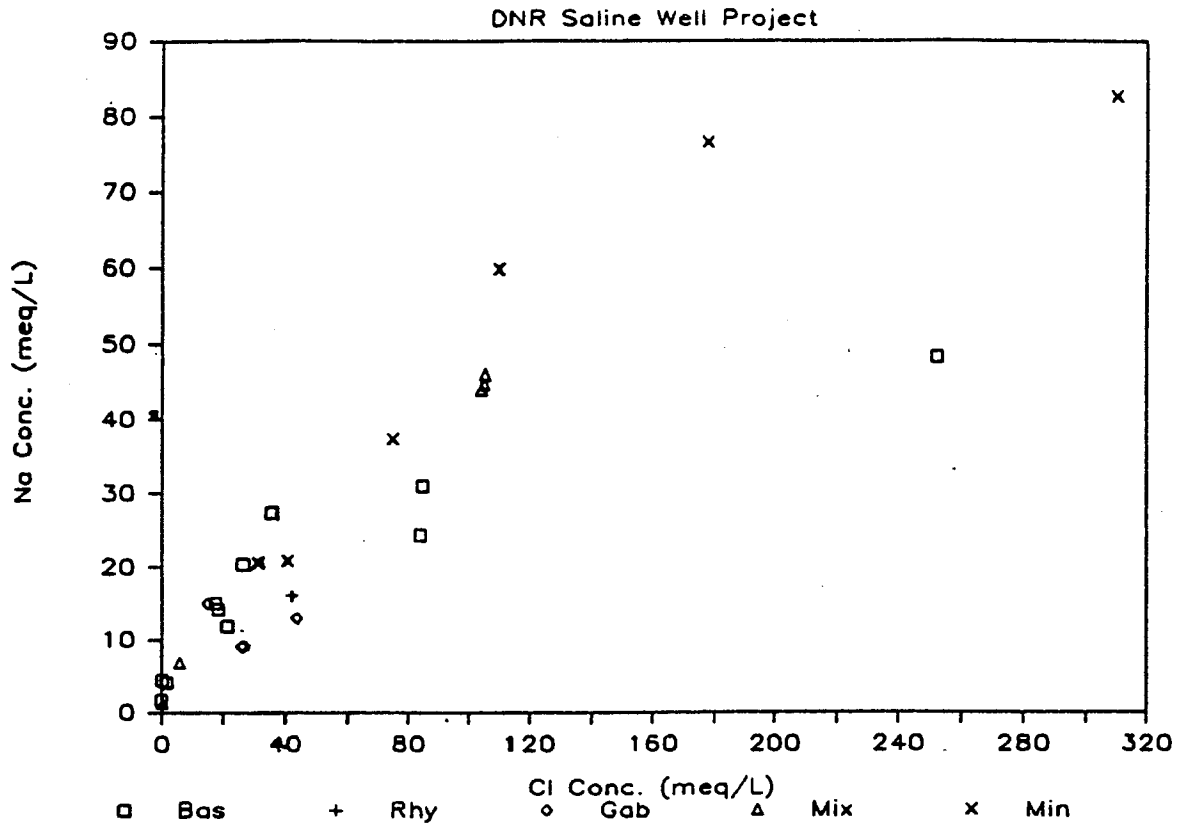
(abbreviations are Bas is basalt, Rhy is rhyolite, Gab is gabbro,
Mix is a mixture of rock types, and Min is gabbro from Minnamax)

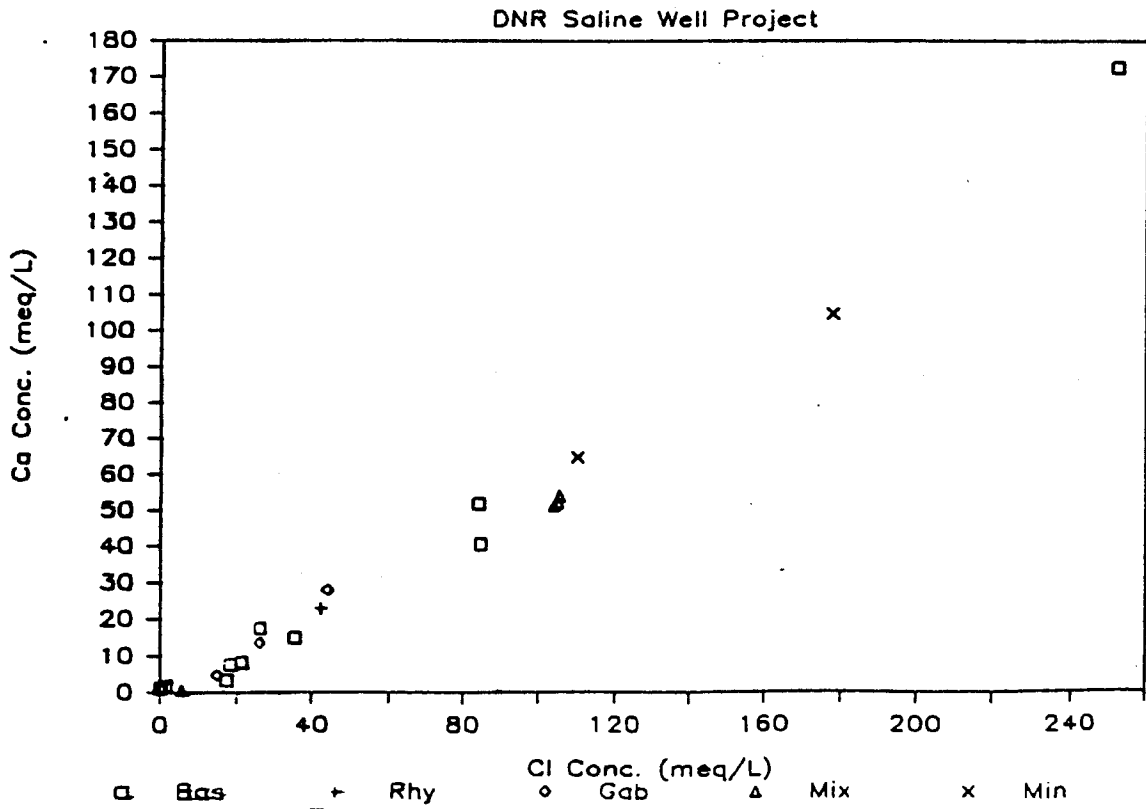Figure 6: **Ca Concentration vs. Cl Concentration**

DNR Saline Well Project

Figure 7: K Concentration vs. Cl Concentration

DNR Saline Well Project
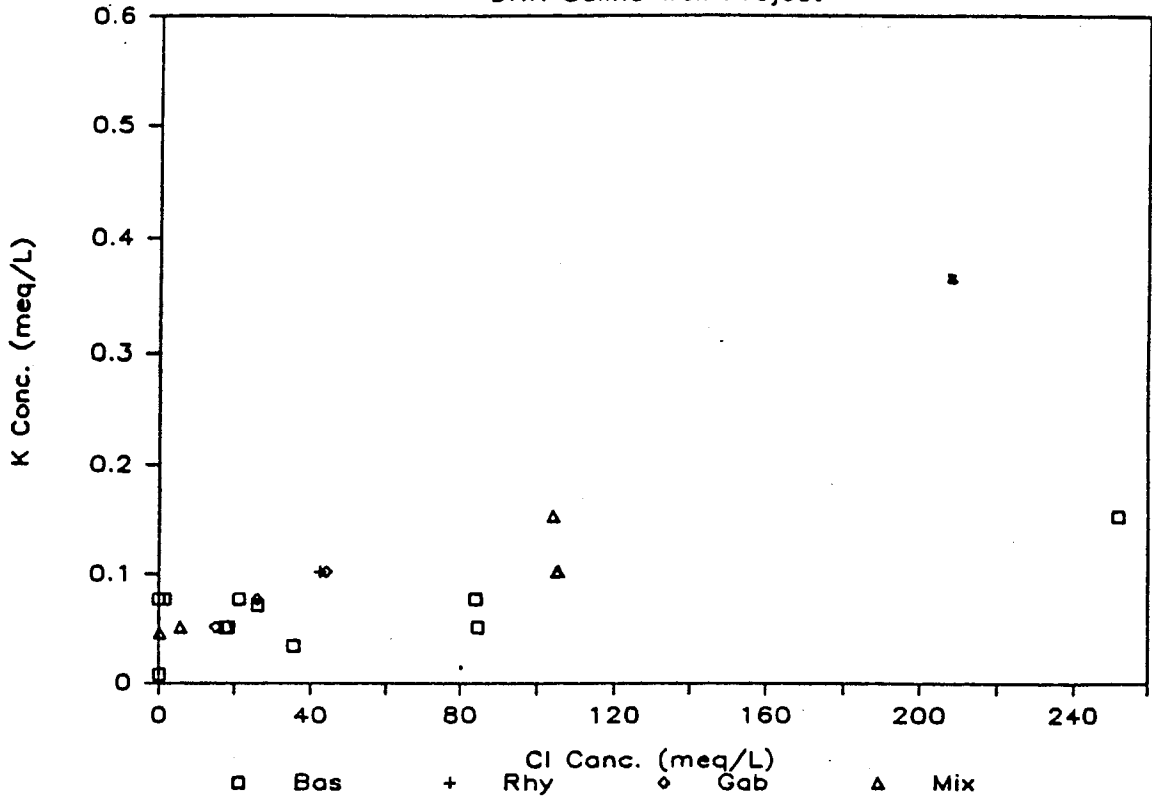
Figure 8: Mg Concentration vs. Cl Concentration

DNR Saline Well Project
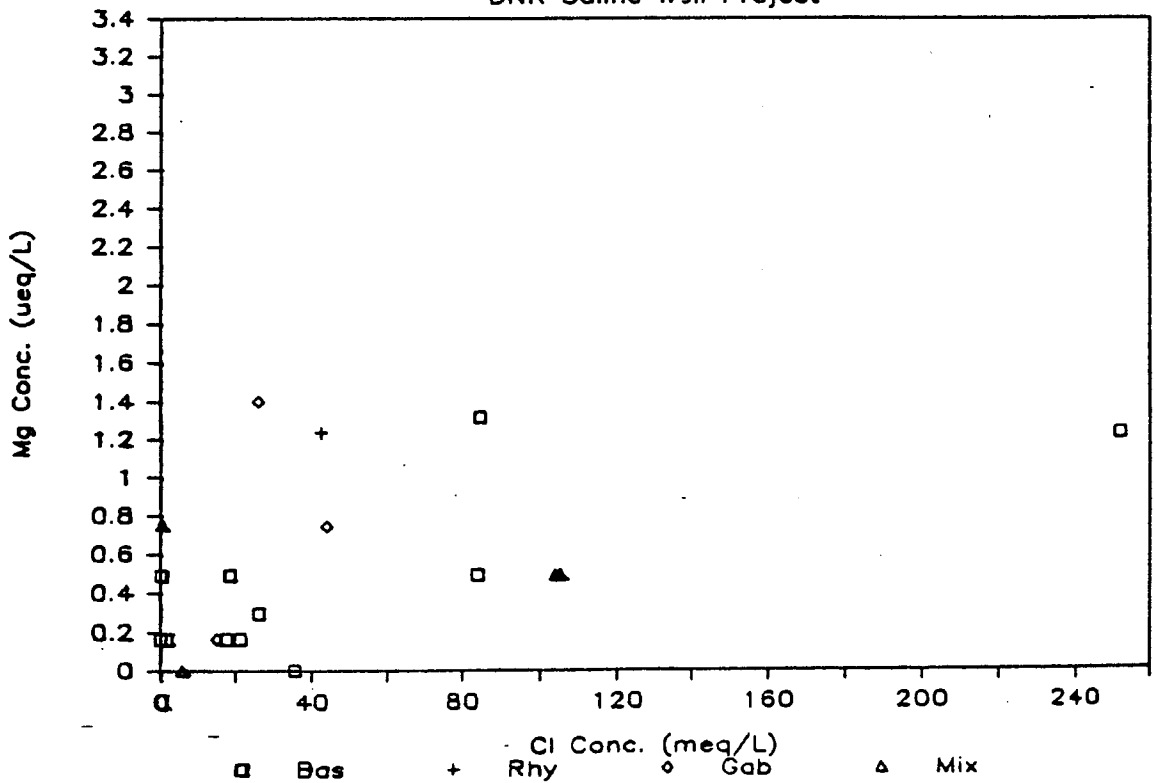
Trace Element Content

Trace element content of As, Cu, Ni, Pb, U, Fe, and Zn are generally low in all waters sampled - both saline and fresh. As varies from 0 to 12 ug/l, Cu <1 to 28 ug/l, Fe - up to 400 ug/l; Ni <1 to 25 ug/l, Pb 1-12 ug/l; U always less than 1 ug/l, and Zn up to 420 ug/l. Logarithmic means are as follows: As - 3 ug/l; Cu - 3 ug/l; Fe - 100 ug/l; Ni 5.6 ug/l; Pb 4 ug/l; U 0.35 ug/l; and Zn 30 ug/l.

Ni, Pb, Zn and Cu contents are plotted against chloride content on Figures 9 through 12. Both Ni and Pb contents show a positive correlation with chloride content whereas Cu and Zn do not. Cu vs Zn contents are plotted on Figure 13 and there appears to be no obvious relationship between the two. It is interesting to note that in the area just southwest of Two Harbors (Figure 1) in an area of known native Cu occurrences that two anomolous values for Cu were reported (W 18 and W 19). W 18 (Cu = 28 uq/l) is from a saline well, W 19 (Cu = 18 uq/l) from a potable well. Both W 18 and W 19 have Cu tubing used as pipe material (Table 2) but other samples taken from wells with Cu tubing do not have levels of Cu in excess of 4 ug/l. If this is interpreted to mean that the groundwater in W 18 and W 19 is anomolous with respect to Cu, then it means both saline and non-saline are anomalous and both could be used to predict economic mineralization.

Analyses of saline water from drill holes and the shaft of the Minnamax Cu-Ni deposit are tabulated in Table 5, and trace elements contents are plotted on Figures 9, 10, and 12 for comparison. Ni and Pb values are higher in samples with high chloride contents but contents are not higher than 18 ug/l for Pb and 22 ug/l for Ni. Copper values are always less than 3 ug/l. These values are close to the baseline values found in this study. This came as a surprise

Figure 9: Ni Concentration vs. Cl Concentration
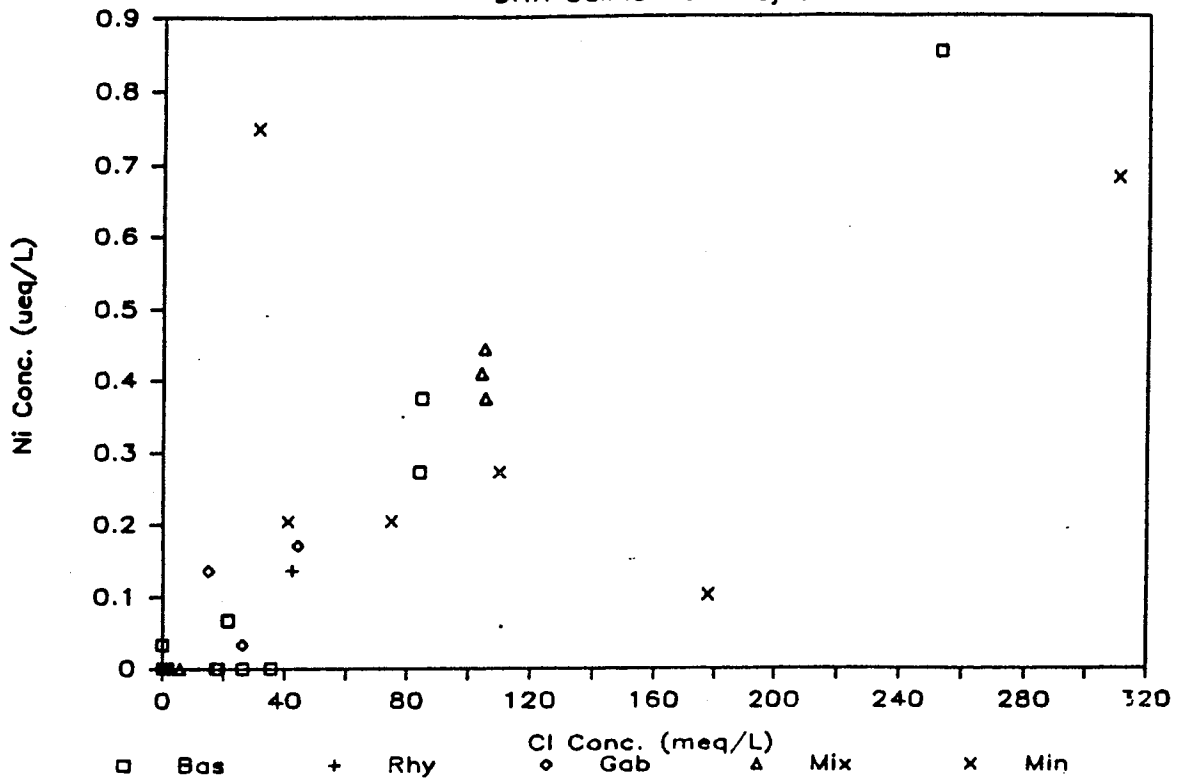
DNR Saline Well Project

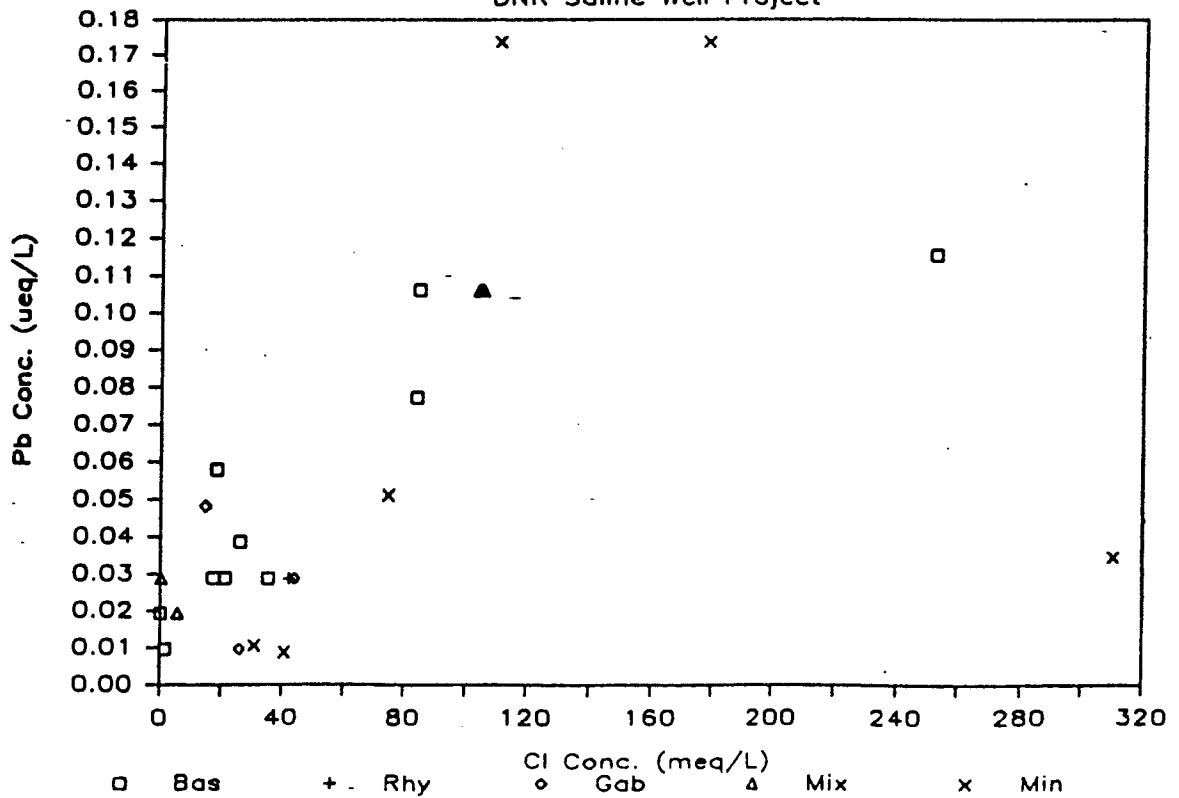**Figure 10:** Pb Concentration vs. Cl Concentration

DNR Saline Well Project

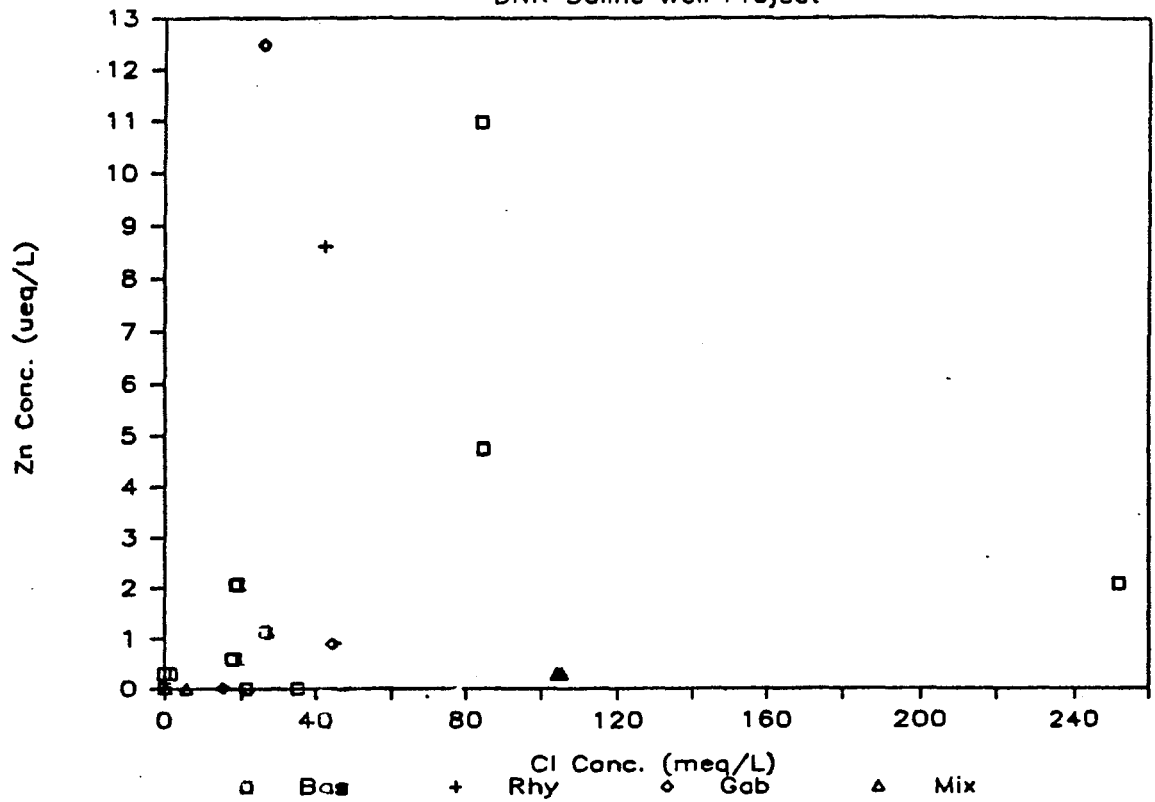Figure 11: Zn Concentration vs. Cl Concentration

DNR Saline Well Project

Cl Conc. (meq/L)

□ Bas   + Rhy   ◇ Gab   △ Mix

Figure 12: Cu Concentration vs. Cl Concentration

DNR Saline Well Project

Cl Conc. (meq/L)
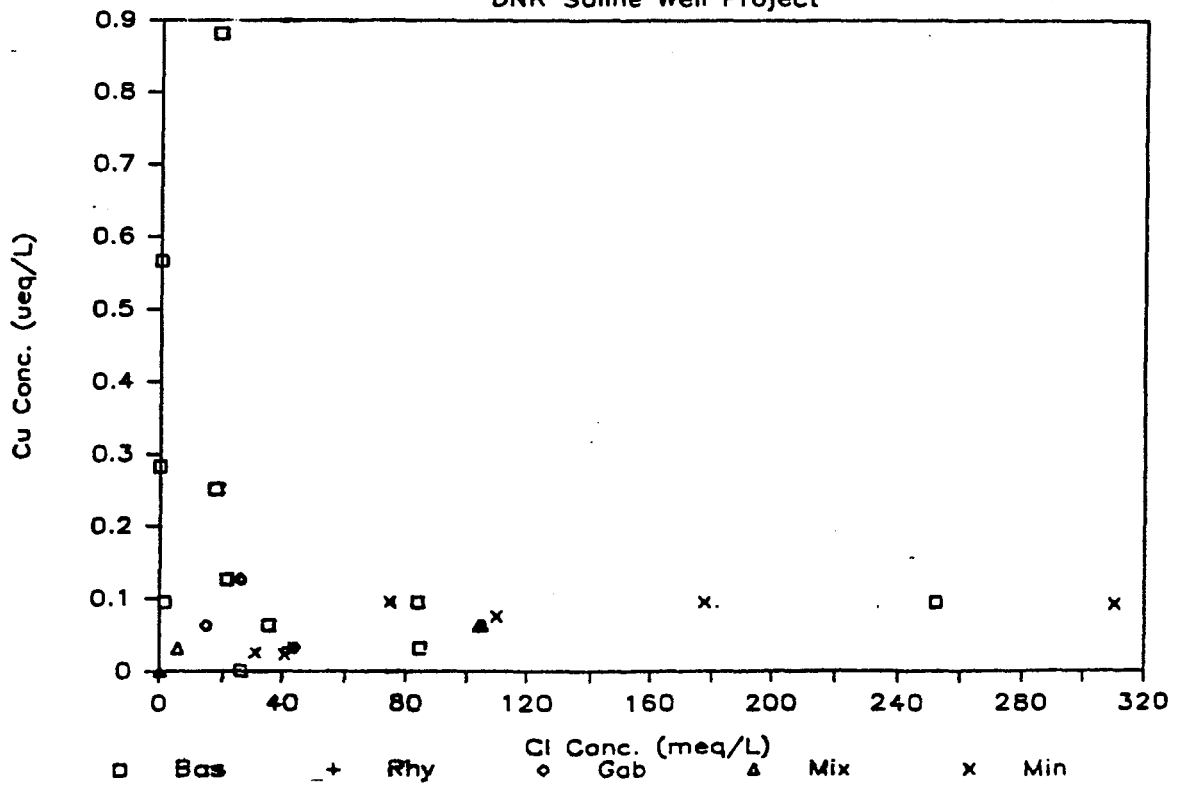
□ Bas   + Rhy   ◇ Gab   △ Mix   × Min

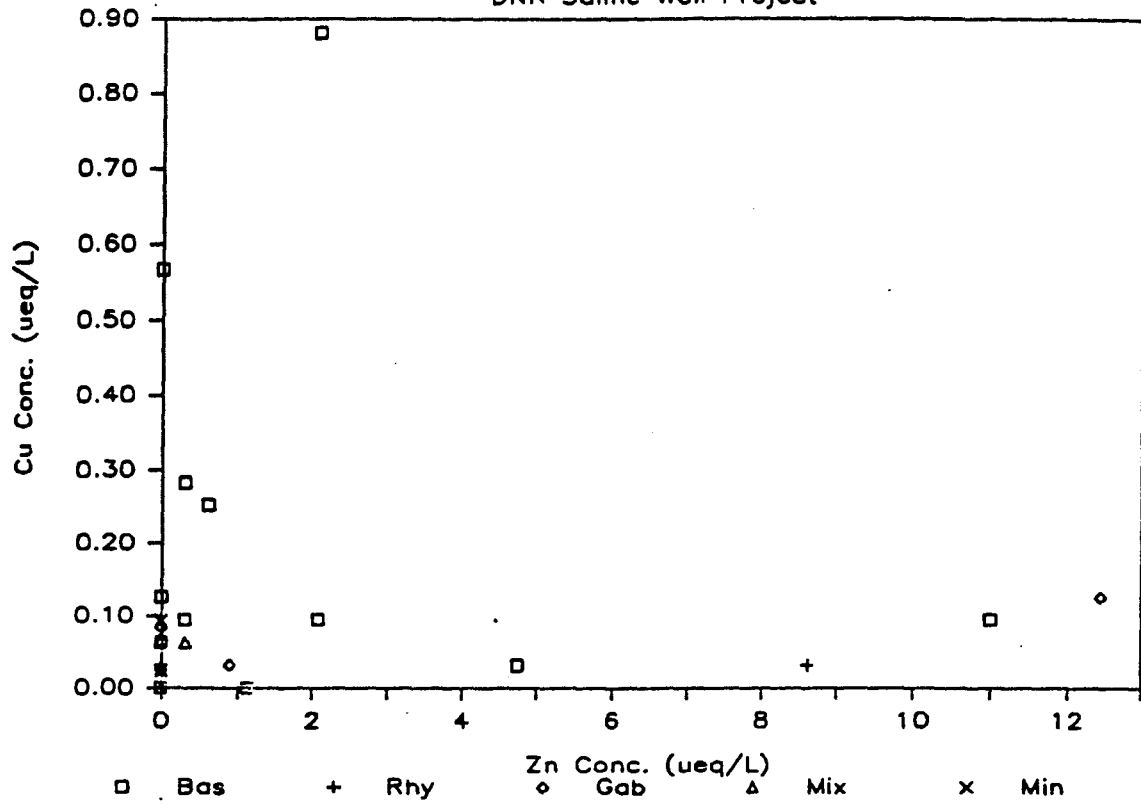**Figure 13:** Cu Concentration vs. Zn Concentration

DNR Saline Well Project

Table 5. Analyses of groundwater from shaft and drill holes at the MINNAMAX site near Babbit, MN.
(analyses from T. Hargy, Kennecott Copper)

Sample	Date	pH	Specific Conductance	Cl	SO4	Ca	Na	Hardness as CaCO3	Co	Cu	Fe	Pb	Ni	Zn
				mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Shaft														
1600 *	2/8/77	9.1	6000	1450	-	-	480	1020	-	-	N.D.	-	-	-
	2/14/77	9.0	7000	2400	-	-	710	1780	-	-	N.D.	-	-	-
1088	2/22/77	10.9	8000	2650	-	-	860	2110	3	3.0	50	5.3	6	5
1046	-	9.1	6000	1450	-	-	480	1020	N.D.	0.7	N.D.	0.9	6	N.D.
1194	3/12/77	9.3	3200	1100	-	-	450	506	-	-	-	-	-	-
	3/18/77	9.3	3500	1100	-	-	475	584	2	0.8	N.D.	1.1	22	6
Drill holes														
HAMMER 303	7/15/76	5.8	32000	11000	N.D.	-	1900	12000	2	2.9	4900	3.6	20	N.D.
1006 DDH	Jan 78	10.1	10300	6300	N.D.	2100	1760	-	2	3.0	250	18.0	3	3
1009 DDH	-	8.9	7800	3900	N.D.	1300	1380	-	2	2.4	50	18.0	8	3

N.D. = not detected
- = no information available
* = Elevation at top of shaft is 1600 ft. above sea level.

because it was hoped that the saline waters from this deposit would be anomolous with respect to Cu and Ni.

According to Siegel and Ericson (1980), concentrations of Cu, Co, and Ni in water in surficial material directly overlying mineralized zones in the Duluth Complex can exceed 100 ug/l and in the general area of the basal contact of the Duluth Gabbro, the concentration of Cu and Ni in water in surficial material is consistently higher than elsewhere. Because of this, it was hoped that saline bedrock aquifers in the Duluth Complex would be good indicators of sulphide mineralization. Results of this study indicate otherwise.

Relationship of Saline Water with Rock Type

Non-thermal saline waters and brines have been known to occur in deep mines in Michigan since the turn of the century (White et al., 1963; Fritz and Frape, 1982) and in shallow wells along the North Shore of Lake Superior in NE Minnesota (Heath, 1983). The relationship between rock type and salinity has not been well documented for NE Minnesota.

The geological control of the wells is known for nearly all of the holes sampled in this study. The cuttings from 3 of them are stored at the Minnesota Geological Survey (MGS). The type of bedrock aquifer for each hole is listed in Table 6 and the log of well W9 is given in Table 8.

Many of Bill McKeever's well-cuttings are-stored at the MGS, and at least 9 of them are from saline wells. Besides the three sampled in this study, six more are listed in Table 7 with their respective geology.

There appears to be no particular relationship between salinity and rock type of the holes sampled and/or studied (Tables 6 and 7). It appears that saline wells occur in the Duluth Complex, in thin basalt flows, in thick

Table 6: Geological control of wells sampled in this study

Saline Well	Rock Formation	Type of Control
W 1	Fond du Lac/Nopeming/ N.S. basalt?	Very little outcrop - location in contact zone between three rock formations.
W 2	Duluth Gabbro	Logged well cuttings, Penny Morton (PM)
W 3	Duluth Gabbro	John Green (JCG) geology - outcrop area.
W 4	Gabbro/basalt	JCG geology
W 5	Felsite/vesicular flow	Devils track rhyolite/contact red vesicular flow JCG - and logged drill cuttings PM.
W 6	Basalt (?)	Interpreted JCG (volcanics).
W 7	Thin basalt flows	JCG mapped geology - good ground control.
W 8	Thin basalt flows	JCG mapped geology.
W 9	Thin basalt flows	Logged well cuttings - PM (see Table 8)
W 10	Thin basalt flows	JCG geology
W 11,12,13	Basalt/felsite/diabase	(on edge of large rhyolite) JCG geology.
W 14	Basalt north of Pallisade rhyolite	JCG geology.
W 15	?? flows? sediments? diabase	No outcrop control.
W 16	Diabase	Interpolation from Two Harbors Map. JCG
W 17	Basalt	From JCG good outcrop control.
W 18	Basalt	From JCG good outcrop control.
W 19	Basalt	From JCG good outcrop control.
W 20	Basalt	From JCG good outcrop control.
W 21	Basalt	From JCG good outcrop control.
W 22	Basalt	From JCG good outcrop control.
W 23	Geology not known	

Table 7: List of saline wells with drill cuttings stored at the Minnesota Geological Survey (MGS)

MGS#	Name	T.R.S.	Water Sample	X-ray Analysis of rocks	Geological Notes	Notes from Bill Mckeever Well Driller
666	John Mclure	62-4E-30	Yes	No	0-430' of m.s. Duluth Gabbro, very fresh composition	Well was dry-blasted at 220' to produce water. Saline.
765	Thomas Savage	60-2W-16	No	Yes	0-210' red, vesicular, basalts containing epidote and white pink zeolites. 210'-400' Crumbly immature red siltstone composed of lithic clasts, quartz and feldspar. No bedding visible calcareous.	Water not sampled, salty.
861	Fred Frome	57-6W-30	No	No	Grey black basalt with minor laumontite	Salty but useable
1048	E.P. Aurelius	60-2W-16	No	No	Plagioclase rich basalt	Geology from John C. Green (JCG). Well went salty after two years.
1065	R. Fanos	61-2E-10	No	No	Kimball Creek Rhyolite	Geology from JCG. Salt water in the overburden. Bedrock water ok.
1390	Tofte Standard	59-4W-21	No	No	basalt	Initially ok turned salty afterward.
1454	Ralph Adams	58-5W-30	Yes	No	Thin basalt flows (see Table 8)	Saline
1467	Glen Leonard	61-2E-7	Yes	Yes	0-106' Devil's track rhyolite and 30' of red vesicular rhyolite Vesicles filled with white soapy mineral (saponite?)	Saline
1473	Alex Leighton	58-5W-1	No	Yes	0-390' of basalt flows. Flow in contact with water table is red muddy brown with very few vesicles.	Water not sampled but salty

Table 8: Log of Well #1454:   Water Sample W9

0 - 50'	glacial drift
50 - 60	black f.g. magnetic basalt
70 - 80	red vesicular basalt
140 - 150	gray-green basalt flow composed of red plagioclase laths and a green mineral epidote? Crumbly.
220 - 250	Red vesicular flow with white zeolite? clay? Rock is very crumbly and altered.
250 - 270	Calcareous epidote rich basalt. Plagioclase laths are red - calcite throughout.
270 - 300	red vesicular basalt
300 - 320	red vesicular basalt with calcite and white zeolite
320 - 350	Red muddy looking basalt containing up to 5% white acicular needles of zeolite. Calcite veins throughout.
350 - 360	Charcoal gray, massive basalt? or dyke
360 - 380	Vesicular gray basalt - up to 10% vesicles lined with an apple green mineral. Some calcite. _ Rock reddish-brown when wet. Plagioclase weathers red.
380 - 400	Very dirty, non-vesicular interflow sedimentary rock? Reddish brown - clay rich and calcareous.
400 - 410	Vesicular (10%) red brown basalt - no clays visible. 10% zeolites are green mineral? Some calcite.
410 - 420	Calcareous red-brown vesicular (10%) basalt. Vesicles lined with zeolite/calcite and quartz (?). 10% green sugary textured mineral?
420 - 430	Very muddy clay rich variety of above.
430 - 445	Gray-black fine-grained basalt. Some calcite, minor agate.

rhyolites, and in interflow sedimentary rocks within the North Shore Volcanic Group.

On Figures 5-13, water samples can be identified as to bedrock aquifer and there are no distinct groupings that can be related to rock type. In comparing analyses from the literature, the mean pH from saline wells of the Duluth Complex (7.6) is lower than that of the North Shore Volcanic Group (8.9) (Table 4). Mean field pH measurements from this study are 7.6 for gabbro and 8.2 for North Shore Volcanic Group.

Effect of Saline Water on Mineralogy

Well-cutting samples from three of the wells were X-rayed using a Siemens X-ray diffractometer to see if there were any changes in mineralogy as a result of interaction with saline well-water. The holes chosen were 765, 1467, and 1473 (see Table 7).

The bottom 200' of well 765 intersects a very immature "crumbly" siltstone which is composed predominantly of potassium feldspar, plagioclase, calcite, and pyroxene(?) with minor quartz. Samples at the bottom of the hole are composed of altered plagioclase with calcite, quartz and sericite. As well, all peaks on the diffractograms are less intense in samples of rock in contact with the water table. This coupled with the changes in mineralogy indicates that alteration has taken place.

In well 1467, the alteration is extreme. Rhyolite composed of sanidine and quartz (which give excellent diffraction peaks) gives way downwards to an almost amorphous sample at 190'.

Well 1473 intersects thin basalt flows composed predominantly of plagioclase and augite which give good, well-defined peaks. At the bottom of the well, the intensity of the peaks decreases but the ratio of plagioclase to augite remains

the same. There appears to be some talc(?) crystallized but there is no evidence for other phyllosilicates. In general it can be said that there has been some water-wallrock reaction in the saline wells, the extent of which cannot be truly assessed without chemical analysis of the wallrock.

Possible Origin of Saline Waters

Because of the recent interest in nuclear waste disposal, geologists (and government agencies) have been interested in groundwater location and movement within crystalline rocks (Gascoyne et al., 1985). According to Fritz and Frape (1982) in an overview of saline waters in the Precambrian Shield, more than 30 occurrences of saline waters have been recorded across the Canadian Shield (Figure 14) and they maintain that these saline waters can be expected everywhere at depths exceeding 1 km. The saline waters appear to occur in closed(?) pockets, within fractures and shear zones which are often under high pressure. Once "opened," discharges range from small seeps to flow rates which can be measured in liters/minute. Most reported saline-water occurrences are associated with operating mines.

The chemical composition of these waters are characterized as Ca-Na-Cl waters with low Mg^{+2} and K^+ contents. They are thus distinct from most sedimentary basin brines in which Na^+ dominates or higher Mg^{+2} contents exist. This is depicted in Figure 15.

The composition of the saline waters found in the North Shore Volcanic Group and the Duluth Complex are very similar to the Ca-Na-Cl waters discussed by Fritz and Frape (1982) and are very similar to the brackish waters at Sudbury Ontario (Frape and Fritz, 1982). They find that above 1 km, brackish and fresh waters exist but below 1 km, saline waters and brines exist. They also found that the total dissolved solids gradually increases with depth.
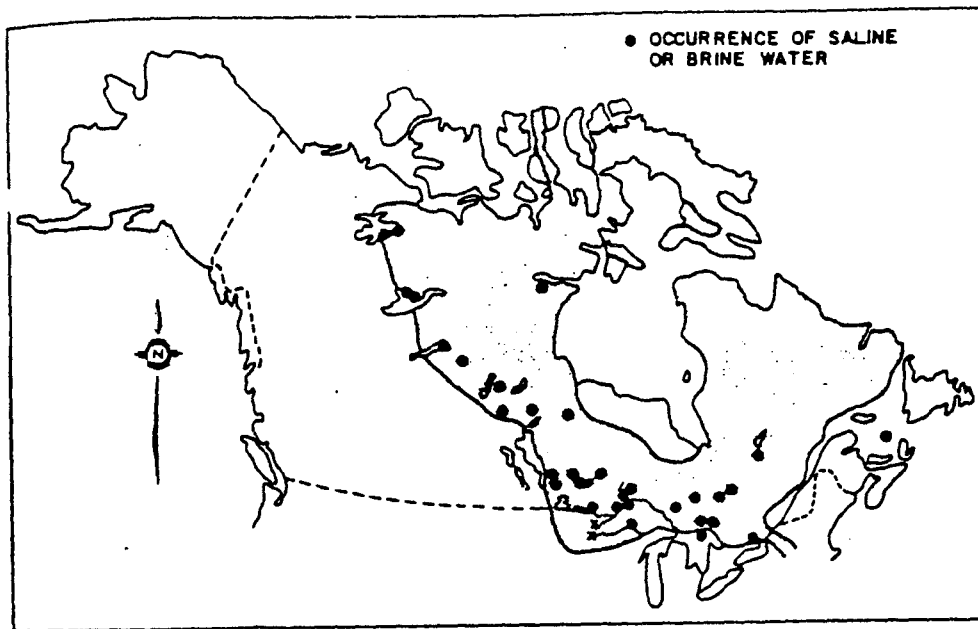
Figure 14: Location of saline or brine occurrences in the Canadian
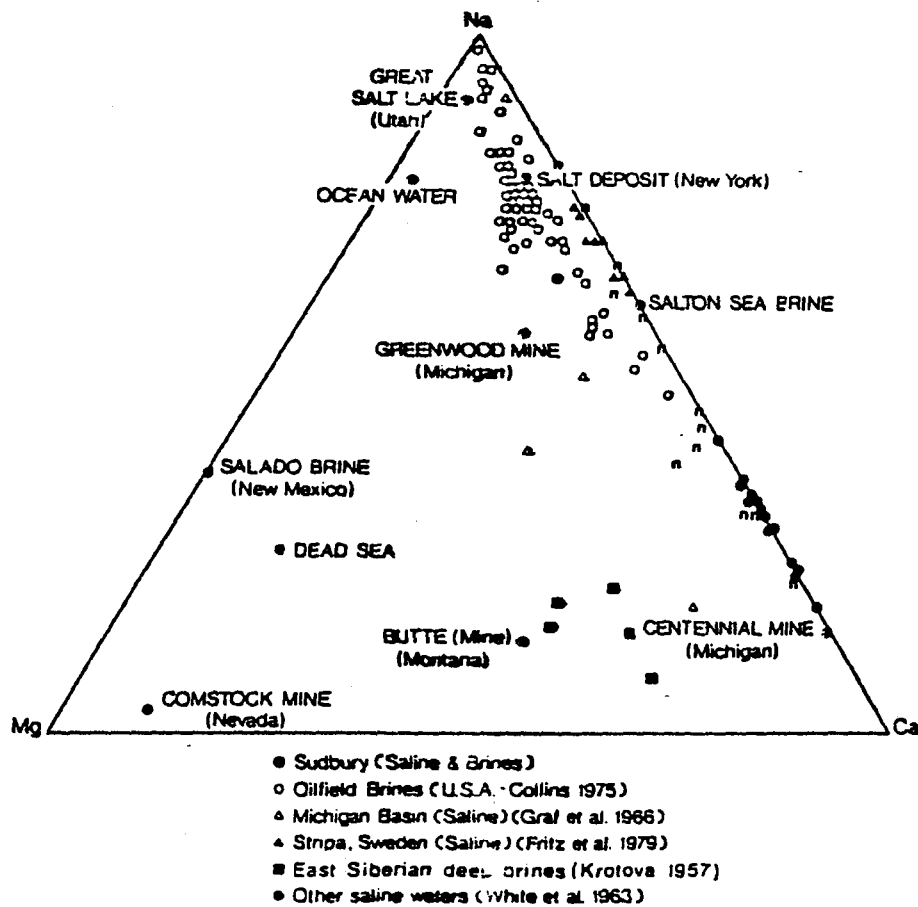Shield (from Fritz and Frape, 1982)
x is this study

Figure 15: Ternary plot of Ca–Na–Mg contents of saline and briny waters
located in various geological environments (after Frape and
Fritz, 1982) n is this study

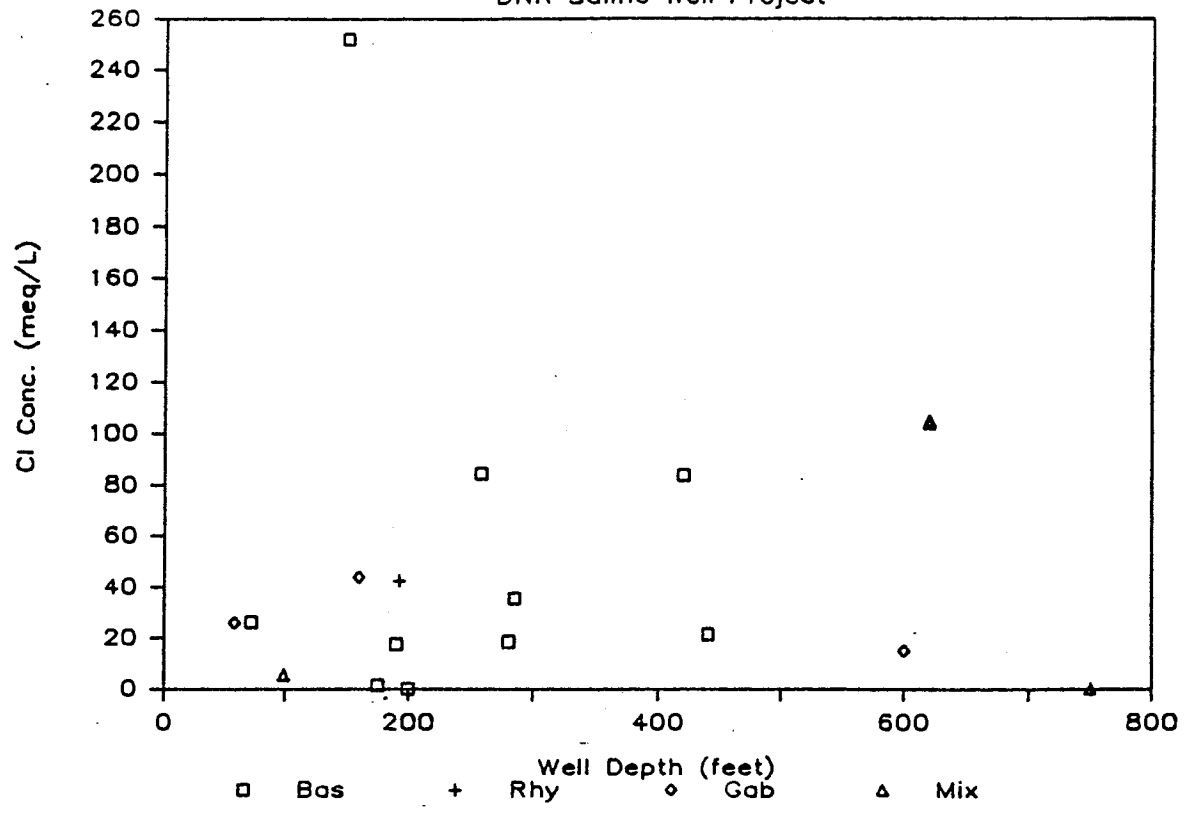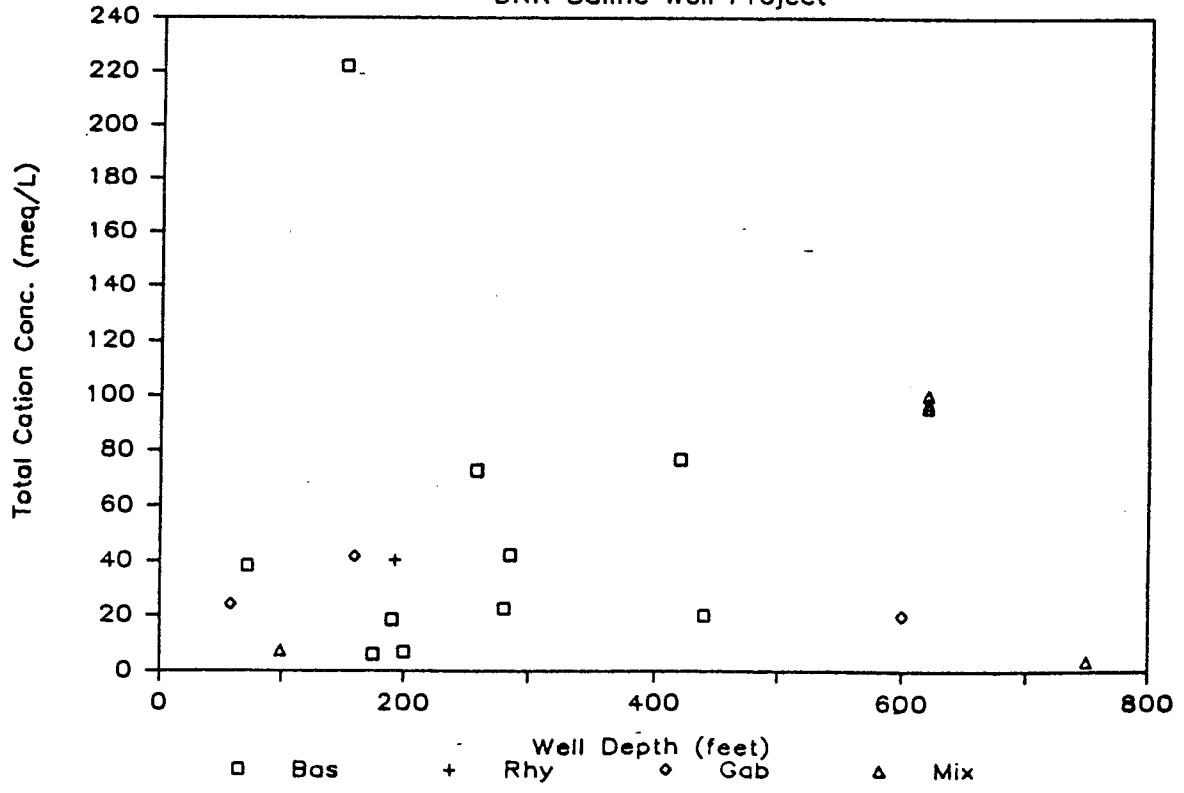Figure 16: **CI Concentration vs. Well Depth**

DNR Saline Well Project

Figure 17: **Cation Concentration vs. Well Depth**
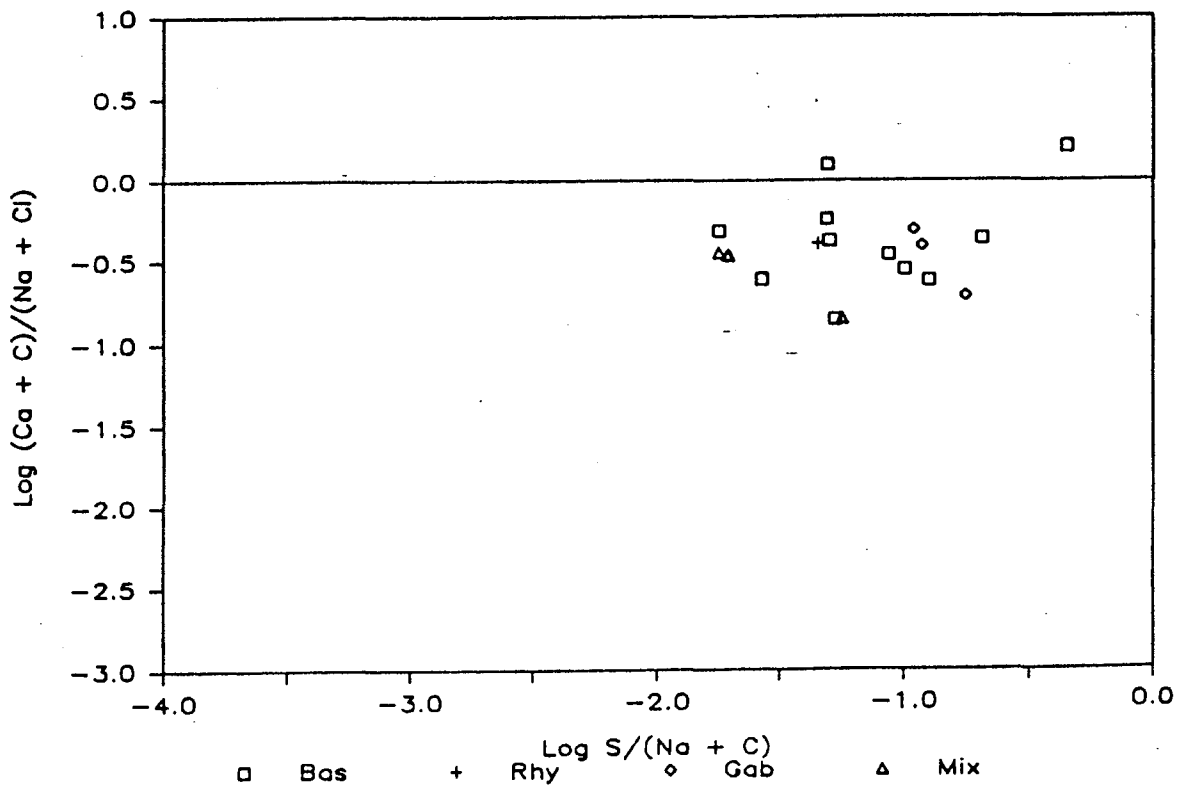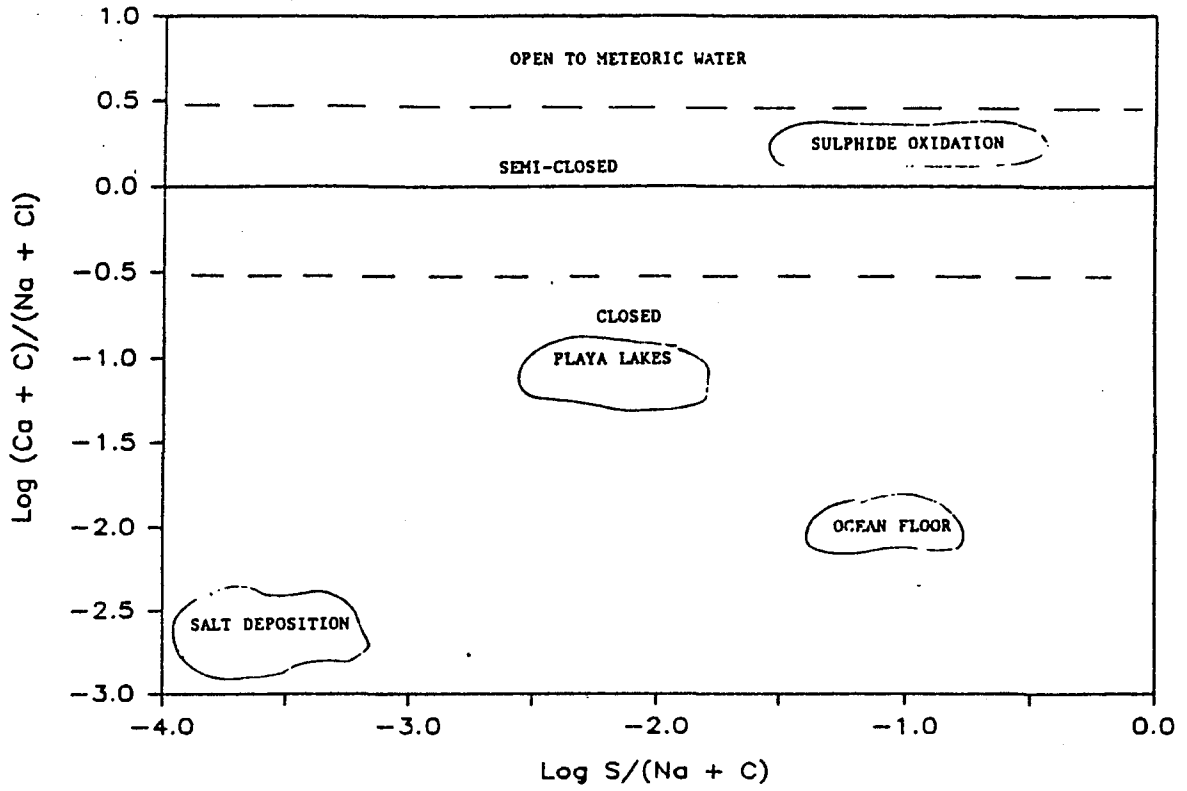

DNR Saline Well Project

Figure 18: Log ion plot showing locations of various saline and briny waters (after Paces, 1985)

Chloride content and total cation content in waters from this study are plotted against depth in Figures 16 and 17 respectively. There is a general increase in chloride and cation content with depth although the deepest well sampled was only 750 feet. The outlier W6 - was sampled at 150' but the well is artesian and the water might come from a much deeper source.

Analyses are plotted on a log-log plot used by Paces (1985) to describe the possible origin of saline waters (Figure 18). All analyses in this report plot in the semi-closed area indicating that they may be a result of mixtures of meteoric water and groundwater. Analyses of saline waters from the Sudbury mine area (Frape and Fritz, 1982) plot in the same place, whereas true brines plot further to the left, in the area of playa lakes. According to Frape and Fritz (1982), McNutt et al. (1984), and Frape et al. (1984) the isotopic composition of brackish, saline and briny waters from the Sudbury area has shown that fresh and brackish groundwaters existing at depths less than 1 km are formed probably by the interaction of meteoric water and readily leachable salts, and by the dissolution of primary silicates. Cl^- and Br^- contents seem to reflect the presence of grain boundary salts or the opening of fluid inclusions. Saline and brackish waters appear to form from the mixing of these modified meteoric waters with deep brines (see Figure 19). The origin of the deep brines themselves is not known; they are in continuous interaction with the wall rock and are therefore continuously evolving. According to Frape et al (1984) one interpretation is that "all deep brines found in the Canadian Shield should evolve toward a Ca-Cl endmember. Eventually, regardless of host rock geochemistry, only the Ca-Cl complexes would be left in solution, possibly because of the removal of other cations and anions due to exchange reactions and solubility controls of secondary mineral phases." Another interpretation may
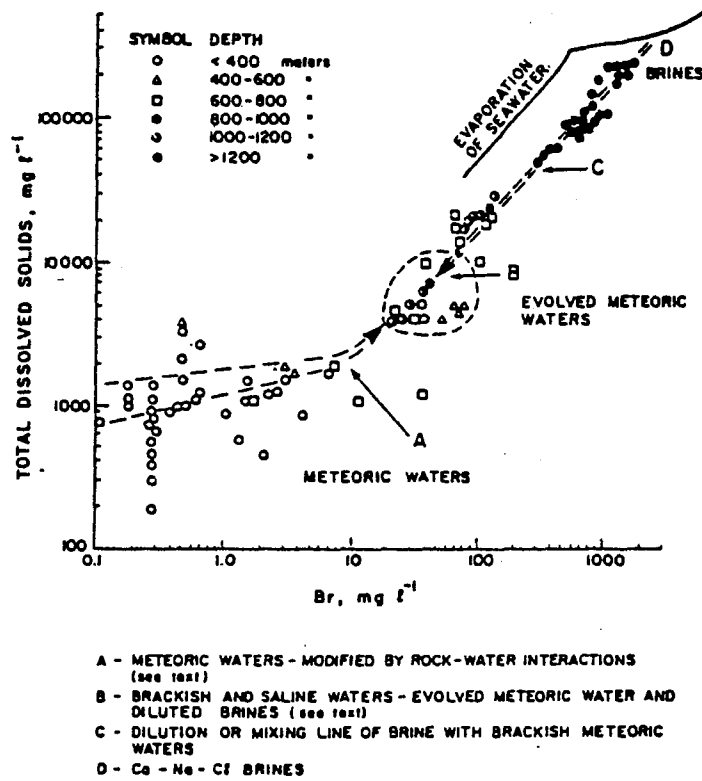
Figure 19: Possible evolutionary path and/or mixing of Canadian Shield groundwaters (after Frape et al., 1984)

well be that a distinctive Ca-Cl brine end member has invaded the rocks of the Canadian Shield at all locations and this brine has been modified by intensive rock-water interaction (Frape et al., 1984).

It is interesting to note the high dependence of Ca^{+2} or Cl^- content in the waters of this study, and also the applicability of the regression line established in this study to waters from the Sudbury area. This lends support to a Ca-Cl end member brine.

Conclusions and Recommendations

This study was initiated in hopes of using saline water as a possible indicator of sulphide mineralization. It appears from this study that sampling saline groundwater in NE Minnesota would not be the best means for indicating economic mineralization for the following reasons:

1. Saline shaft and drill hole waters on the Minnamax Cu-Ni site are not anomalous with respect to Ni, Cu, or $SO_4^=$. This was not expected.

2. Saline wells must be plugged. They are not easy to locate and sample.

3. Saline groundwater sampled in this study had pH's greater than neutrality. Metals are best leached and carried by acidic waters and this might be one reason why metal values are low.

4. Surficial groundwater is known to be anomalous in Cu and Ni contents at the Minnamax Cu-Ni site and this water is easy to sample. It may be anomalous (whereas the rock not) because of the larger surface area of the clay minerals and alteration products in the

glacial till. Also there is higher porosity and permeability in
the overburden, hence a better chance of interacting with sulphides.

Even though this study indicates that saline waters are poor indicators of
sulphide mineralization, some interesting sidelights have been noted. The
saline and brackish waters in the Duluth Complex and N.S.V.G. occur at shallower
depths than those in most occurrences in the Canadian Shield tabulated by Fritz
and Frape (1982). If they formed from the mixing of meteoric waters and deep
brines, one must assume that the incidence of fracture systems is the
determining factor in evaluating a prospective area for well-water drilling.
Locating wells should be done in conjunction with known geology, probably away
from faults and also away from possible trap rocks such as diabase dikes. To
test this thesis, it would be interesting to compile and/or map the locations of
the fracture systems, diabase dikes, and known potable and saline wells. If the
position of saline wells could be predicted, it would be a boon to well-drillers
and homeowners living in NE Minnesota.

The alteration of rocks co-existing with saline water provide another method
of possibly predicting non-potable wells. Bill McKeever quits drilling when he
encounters a red, chocolate-brown colored rock that has the texture of a 'melted
chocolate bar' when wet. The rocks in this study have indeed been altered and
the above description is rather apt. A study of the mineralogy of wall-rocks in
both saline and non-saline wells might provide insight into the above
observations.

If samples W 18 and W 19 are truly anomalous with respect to Cu, then it has
been shown in this study that bedrock acquifers can be used to predict local
areas of mineralization. What it also shows is that potable wells are just as

anomalous as saline wells, and because of their ease of sampling, they would

make better prospective geochemical sampling sites.

References

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

_____, and McNutt, R.H., 1984. Water-rock interaction and chemistry of groundwater from the Canadian Shield. Geochimica et Cosmochimica 48:1617-1627.

Fritz, P., and Frape, S.K., 1982. Saline groundwaters in the Canadian Shield - a first overview. Chem. Geol. 36:179-190.

Gascoyne, M., Davidson, C.C., Ross, J.D., and Pearson, R., 1985. Occurrence of saline waters and brines in plutons in the Canadian Shield. Abst. Joint Annual Meeting GAC-MAC, May 1985.

Green, J.C., 1972. North Shore Volcanic Group in Geology of Minnesota, a Centennial Volume. P.K. Sims and G.B. Morey, eds. 292-332.

Heath, R.C., 1983. Quality for groundwater. USGS Water-Supply Paper 2220.

Hem, J.D., 1959. Study and interpretation of the chemical characteristics of natural waters. USGS Water Supply Paper 1473, 269 pp.

Kissa, E., 1983. Determination of fluoride at low concentrations with the ion-selective electrode. Anal. Chem. 55:1445-1448.

Lindholm, G.F., Ericson, D.W., Brussard, W.L., and Hult,-M.F., 1979. Water resources of the St. Louis River Watershed, northeastern Minnesota. USGS Atlas HA-586.

Matthess, G., 1982. The properties of groundwater, translated by J.C. Harvey, John Wiley and Sons, NY. 406 pp.

McNutt, R.H., Frape, S.K., and Fritz, P., 1984. Strontium isotopic composition of some brines from the Precambrian Shield of Canada. Isotope Geoscience 2:205-215.

Olcott, P.G., Ericson, D.W., Felsheim, P.E., and Brussard, W.L., 1978. Water resources of the Lake Superior Watershed, northeastern Minnesota. USGS Atlas HA-582.

Paces, T., 1985. A unique sodium sulphate brine from metamorphic rocks of the Bohemian Massif in Central Europe. Abst. Joint Annual Meeting GAC-MAC, May 1985.

Siegel, D.I., and Ericson, D.W., 1980. Hydrology and water quality of the copper-nickel study region, northeastern Minnesota. USGS Water Resources Investigations 80-739. Open-file report.

Stainton, M.P., 1973. A syringe gas-stripping procedure for gas chromatographic determination of dissolved inorganic and organic carbon in fresh water and carbonates in sediments. J. Fish. Res. Board Can. 30:1441-1445.

_____, Capel, M.J., and Armstrong, F.A.J., 1977. The chemical analysis of fresh water, 2nd Ed. Fish. Mar. Serv. Misc. Spec. Publ. 25:21-25.

Standard Methods for the examination of water and waste water, 1975. American Public Health Association. 1193 pp.

White, D.E., 1981. Active geothermal systems and hydrothermal ore deposits. Econ. Geol. 75th Anniversary Volume: 392-423.

_____, Hem, J.D., and Waring, G.A., 1963. Chapter F. Chemical composition of subsurface waters. USGS PP 440-F. 67 pp.

Winchell, N.H., 1889. Natural Gas in Minnesota. Geological and Natural History Survey of Minnesota. Bull. 5. 39 pp.