PROVINCE OF BRITISH COLUMBIA
MINISTRY OF ENVIRONMENT
WATER MANAGEMENT BRANCH

OCCURENCE OF FLUORIDE IN GROUNDWATERS ALONG THE EASTERN COAST OF VANCOUVER ISLAND

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SYNOPSIS

Fluoride concentrations up to 13.4 mg/L have been found in groundwater from bedrock wells completed in Upper Cretaceous sedimentary rocks of the Nanaimo Group along the eastern coast of Vancouver Island. High fluoride groundwaters with concentrations greater than 1.5 mg/L are generally of the sodium-chloride, sodium-calcium-chloride or sodium-bicarbonate-chloride types. They are characterized by a moderately high pH value in the range 8.2 to 9.4 pH units, TDS in the range 250 to 1800 mg/L and negligible sulphate content (<10 mg/L). Available geologic, hydro-chemical and hydrologic data suggest that fluoride is probably derived locally from fossiliferous marine shales containing fluorapatite through dissolution and anion exchange processes under elevated pH conditions in which carbonate equilibria is a controlling factor.

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OCCURRENCE OF FLUORIDE IN GROUNDWATERS ALONG THE EASTERN COAST OF VANCOUVER ISLAND

1. INTRODUCTION

Fluoride concentrations up to 13.4 mg/L have been found in groundwater from bedrock wells at a number of localities over a distance of 160 kilometres along the eastern coat of Vancouver Island between Courtenay and Victoria (Figure 1). The distribution and source of fluoride in groundwaters in this region is of particular interest because many residents utilize groundwater as a source of drinking water and fluoride concentrations in excess of 1.5 mg/L (Ministry of Health, 1982) may produce dental fluorosis (tooth mottling) particularly among children ingesting these waters.

This report reviews the known distribution and chemical characteristics of high fluoride (>1.5 mg/L) groundwaters found in the region and discusses probable sources of fluoride. This information may be useful in anticipating where and under what conditions high fluoride groundwaters are likely to be encountered.

2. DISTRIBUTION OF HIGH FLUORIDE GROUNDWATERS

The distribution of groundwater samples showing fluoride concentrations >1.5 mg/L is shown in Figure 2. This is based on a total of 189 fluoride analyses on file with the Groundwater Section. A summary of the available data is given in Table 1. All of the samples represent groundwater from bedrock wells.

The high fluoride concentrations appear associated with wells completed in sedimentary rocks belonging to the Nanaimo Group (Figure 1). These rocks of Upper Cretaceous age are comprised principally of sandstone, conglomerate, shale and coal which occur in a belt along the eastern coast of Vancouver Island from Campbell River to the northern end of the Saanich Peninsula (Figure 1). These rocks are also found in the Port Alberni area. The Cretaceous strata were deposited some 70 to 100 million years ago in a series of sedimentary cycles ranging from fluvial to marine environments. In general the sandstones and conglomerates were deposited in fluvial-deltaic environments while the shales were deposited in marine environments.

Important physical (geologic) and hydrologic characteristics of individual wells from which high fluoride concentrations have been reported are summarized in Table 2. Well details and accurate locations are presently not available for all wells which have reported high fluoride concentrations.

Most of the high fluoride groundwaters appear associated with water-producing zones (fractures and bedding plane contacts) occurring in clay and shale layers. Based on geologic mapping by Muller and Jeletzky (1970) these zones appear to be within the Spray Formation or close to the contact with the overlying Gabriola Formation on Hornby and Gabriola Island. On Thetis and Saltspring Island the water producing zones high in fluoride appear to be within the Cedar District Formation and possibly the De Courcy and Northumberland Formations.

In the Gulf Islands high fluoride groundwaters occur in both wells drilled in coastal areas and inland areas; in wells completed above and below sea level. High fluoride groundwater do not appear associated with sea water intrusion.

The occurrence of high fluoride concentrations in groundwaters of Cretaceous rocks in North America is not particularly unusual as high fluoride levels are also found for example in the Cretaceous rocks of South Carolina (Zack, 1980) and North and South Dakota where values ranging from 2 to 9 mg/L occur (White et al, 1963). Groundwaters containing fluoride concentrations exceeding 1.0 mg/L are found for example in many regions of the United States in a wide variety of geologic terrains (Hem, 1970).

3. CHEMICAL CHARACTERISTICS OF HIGH FLUORIDE GROUNDWATERS

A summary of chemical analyses which show fluoride concentrations greater than 1.5 mg/L is listed in Table 3. A number of these represent duplicate samples from the same sites. On the basis of all fluoride analyses on file for the region and comparison of fluoride concentrations and other chemical parameters it appears that groundwaters containing fluoride occur in two general groups. The first group contains fluoride concentrations up to about 3.0 mg/L and the second group contains fluoride concentrations greater than 3.0 mg/L. This is most evident for example in a plot of fluoride concentrations versus pH (Figure 3). The majority of samples plot in a field with fluoride ranging from less than 0.1 to 3.0 mg/L and pH ranging from 6 to 9.6 pH units. Samples with fluoride concentrations above 3.0 mg/L plot within a narrow pH range from 8.2 to 9.4 pH units. As the pH values represent laboratory determinations they may not be entirely representative of in situ conditions. Some changes in pH might be expected after sampling and transport to the laboratory due to escape of CO_2 for example (Freeze and Cherry, 1979).

In general, samples having the highest fluoride concentrations exhibit the following overall chemical characteristics:

1. Groundwaters tend to be of the sodium-chloride, sodium-calcium-chloride or sodium-bicarbonate-chloride types based on concentrations of major ions in equivalents per million (epm).

2. Total dissolved solids (TDS) is moderately high in a fairly wide range from 250 to 1800 mg/L.

3. pH is relatively high in the range 8.2 to 9.4 pH units (laboratory pH values).

4. The groundwaters are moderately high in sodium (Na^+) and chloride (Cl^-) ranging from 70 to 400 mg/L and 160 to 1000 mg/L respectively.

5. Sulphates are generally negligible (<10 mg/L).

The above chemical characteristics provide some evidence for the origin of the high fluoride groundwaters. As a moderately high pH appears to be a characteristic of the high fluoride groundwaters, factors for example which would result in high pH are likely important in the chemical evolution of these high fluoride groundwaters. Before speculating on the processes and conditions that may result in these high fluoride groundwaters possible sources of naturally occurring fluoride in the region should be considered.

4. POSSIBLE SOURCES OF FLUORIDE IN GROUNDWATERS

Possible natural sources of fluoride are listed in Table 4. These include naturally occurring minerals, volcanic or fumarolic gases, phosphatic deposits and oil field brines.

Fluoride bearing minerals may be present in the rocks through which the groundwater is circulating. Naturally occurring fluoride minerals such as fluorite (CaF_2) and fluorapatite ($Ca_5(PO_4)_3F$) are common for example in igneous rocks such as granites, pegmatites and crystalline limestones.

Fluorite for example is slightly soluable in water and through dissolution can contribute fluoride ions in groundwaters. Fluorite has a solubility of 160 mg/L at pH7, 1 bar total pressure at 25°C (Freeze and Cherry, 1979). This is about one-third of the solubility of calcite for example under the same conditions.

Very high fluoride concentrations of several hundred mg/L can occur in volcanic thermal waters (Matthess, 1982) and is a common constituent in volcanic and fumurolic gases. Concentrations for example as high as 806 mgF^-/L have been reported in some hot springs in New Zealand (White et al, 1963).

Fluoride is also concentrated in the bones and teeth of marine animals in the form of a hydroxylapatite-fluorapatite. Fosil bone deposits, collectively termed collophane deposits may be a significant source of fluoride. Fluoride from these deposits can be released into groundwaters either through dissolution or ion exchange. Zack (1980) for example has attributed high fluoride concentrations in groundwaters in South Carolina to the release of fluoride from fluorapatite present in fossil shark teeth.

Oil field brines can contain fluoride concentrations up to several hundred mg/L (Todd, 1980). Upward movement and mixing of brine waters in sedimentary basins with shallow groundwaters could result in high fluoride groundwaters locally.

As the high fluoride concentrations along the eastern coast of Vancouver Island are associated with marine and non-marine sedimentary rocks of Cretaceous age it is most likely that the origin of fluoride is associated with fossil deposits containing fluorapatite or deep basin brines or both. Marine vertebrates were prolific in the Cretaceous seas and some of the shale beds in the Nanaimo Group are noted for their fossil content (Muller and Jeletzky, 1970). Although likely to be present the occurrence of fluorapatite in these fossil deposits has not been confirmed. Further examination of the bedrock deposits and chemical analyses of the materials would be required to confirm this possibility. With regards to deep basin brines there is no chemistry data available from oil exploration wells in the region and therefore this source of fluoride cannot be entirely discounted at this time.

5. CHEMICAL EVOLUTION OF FLUORIDE GROUNDWATERS

Results of laboratory studies from available literature (Zack, 1980) indicate that the solubility of fluorapatite in water is somewhat complex and apparently does not follow established principles of solubility - product equilibrium as calcite does for example. Zack (1980) reports that the solubility of fluorapatite is found to decrease with increasing pH which has been attributed to the formation of an insoluble surface complex on mineral gains that prevents further dissolution. However, at elevated pH values above 8.0, fluoride values increase again due to ion exchange processes where fluoride exchanges with hydroxyl ions (OH^-) in solution. Fluoride ions have the same charge and nearly the same ionic radius as hydroxyl ions which facilitates anion exchange reactions. The presence of sodium and chloride ions is found to inhibit the dissolution of fluorapatite.

It is likely therefore that the high levels of fluoride above 3 mg/L cannot be explained by simple dissolution of fluorapatite but could be explained by ion exchange processes at elevated pH. This is also apparent if the simple dissolution of fluorite is considered.

In Figure 4 fluoride concentrations have been plotted against calcium concentrations. The concentrations have not been reduced to activities. In this equilibrium diagram for the dissolution of fluorite based on a solubility product of $10^{-10.57}$ (Smyshlygev and Edeleva, 1962 as reported by Handa, 1975) samples above the equilibrium line are supersaturated with respect to fluorite while those below the line are undersaturated. High fluoride concentrations above 3.0 mg/L are all saturated or supersaturated with respect to fluorite. This suggests that these high concentrations cannot be explained in terms of simple dissolution of fluorite only. Lower fluoride values up to 3.0 mg/L however could be readily explained by simple dissolution of fluorite if this is the source mineral.

As a relatively high but narrow pH range appears characteristic of the high fluoride groundwaters those factors which result in elevated pH probably govern the release of fluoride from fluorapatite. The main controlling factors on pH are probably related to carbonate mineral equilibrium, partial pressure of CO_2 and possibly water-rock interactions involving clay minerals. If the equilibrium diagram for calcite dissolution (Freeze and Cherry, 1979) is considered in which pH is plotted against Ca^{2+} concentration (Figure 5) it appears that high fluoride groundwaters are all close to saturation or supersaturated with respect to calcite. A large number of groundwater samples low in fluoride are also supersaturated with respect to calcite indicating also that these Ca^{2+} concentrations cannot be accounted for by simple dissolution of calcite. This suggests that other processes besides dissolution such as ion exchange probably involving clay minerals are involved in the evolution of high fluoride groundwaters and also high calcium groundwaters.

6. SUMMARY AND CONCLUSIONS

Fluoride concentrations up to 13.4 mg/L have been found in groundwaters from bedrock wells at a number of localities over a distance of 160 kilometres along the eastern coast of Vancouver Island between Courtenay and Victoria. High fluoride groundwaters appear associated with water-producing zones in shale and clay beds within the Upper Cretaceous Nanaimo Group. Fossiliferous deposits containing fluorapatite within the shale beds may be the source of fluoride ions. Groundwaters high in fluoride tend to be of the sodium-chloride, sodium-calcium-chloride or sodium-bicarbonate-chloride types with total dissolved solids in the range 250 to 1800 mg/L. The waters are characterized also by a relatively narrow pH range from 8.2 to 9.4 pH units and negligible sulphate content (<10 mg/L). High fluoride groundwaters are generally saturated or supersaturated with respect to fluorite and also calcite. Concentrations of fluoride up to 3.0 mg/L may be readily explained by simple dissolution of fluorapatite or fluorite but concentrations as high as 13.4 mg/L are likely the result of ion exchange processes under elevated pH conditions.

Since Upper Cretaceous rocks underlie much of the settled and developed coastal areas of Vancouver Island it is likely that further development of bedrock wells in the area will result in additional reported occurrences of high fluoride groundwaters. Due to differences in well depths and variability in lithologic distribution, geologic structure and aquifer permeability, occurrences of high fluoride groundwaters will be relatively localized.

7. RECOMMENDATIONS

1. As the source of elevated fluoride concentrations in groundwater is likely from fluoride-bearing minerals in the Nanaimo Group, material sampling and chemical analyses of specific stratigraphic zones should be considered to confirm the presence and nature of fluorapatite or fluorite in these rocks. Outcrops of the Spray Formation on Gabriola Island for example could be appropriate sampling sites for these determinations.

2. As there is a possibility that deep basin brines containing high levels of fluoride may be mixing with shallow groundwaters, natural isotope sampling (O^{18}/O^{16}) of high fluoride groundwaters may indicate the presence of any brine components.

3. Water quality sampling for fluoride in areas of high groundwater use where insufficient water quality data is presently available should be considered. Analyses should include pH (field determinations where practical) and all major cations and anions.

4. Other agencies (eg. local Health Units) should be contacted to obtain available water quality information on fluoride to add to the data base.

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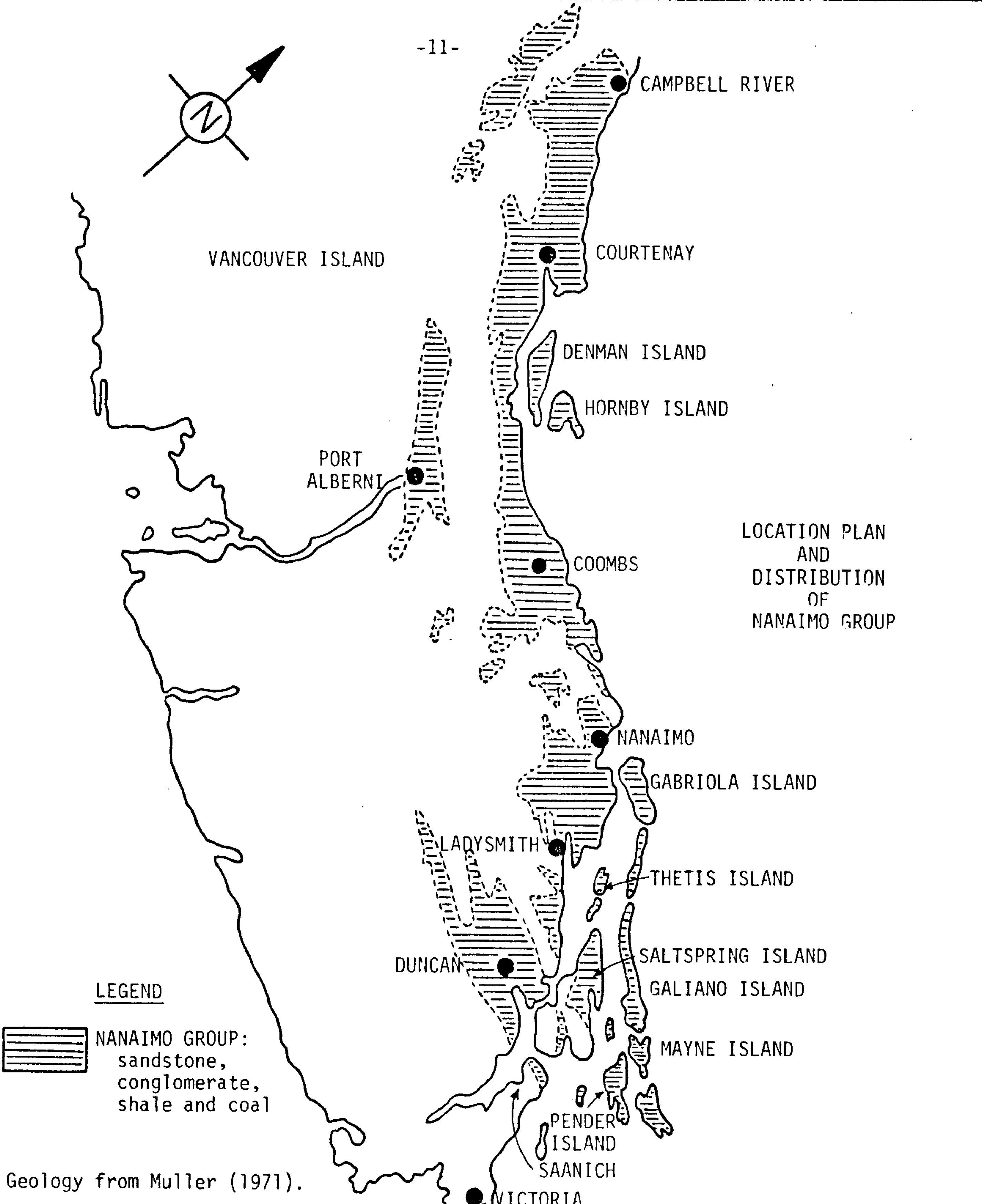

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SCALE: VERT. -- HOR. 1 cm. = 10 km. — DATE May 8, 1985	APK ENGINEER FILE No. — DWG No. Fig. 1

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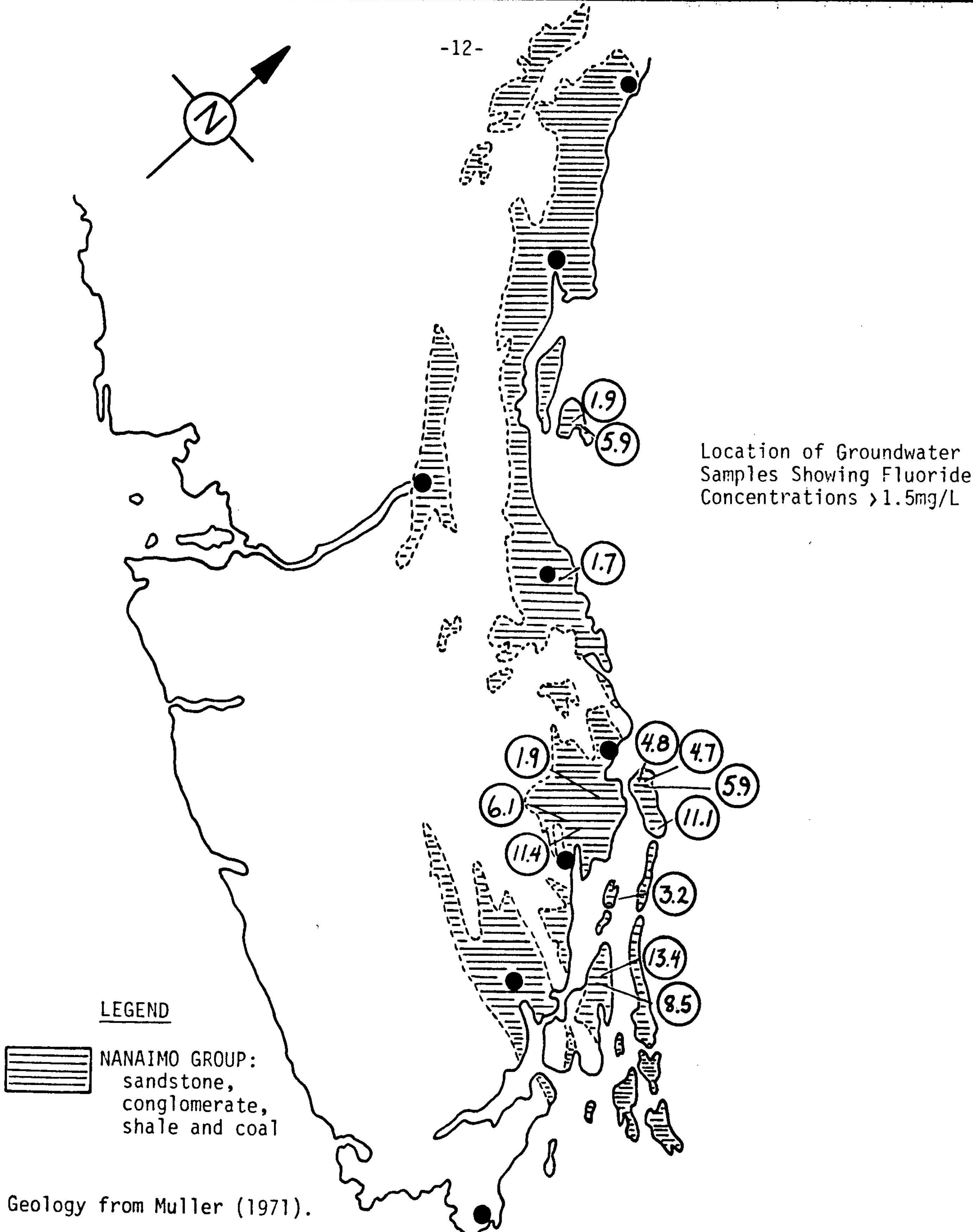

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SCALE: VERT.
HOR. 1 cm. = 10 km.

DATE May 8,1985

APK ENGINEER

FILE No. DWG. No. Fig.2

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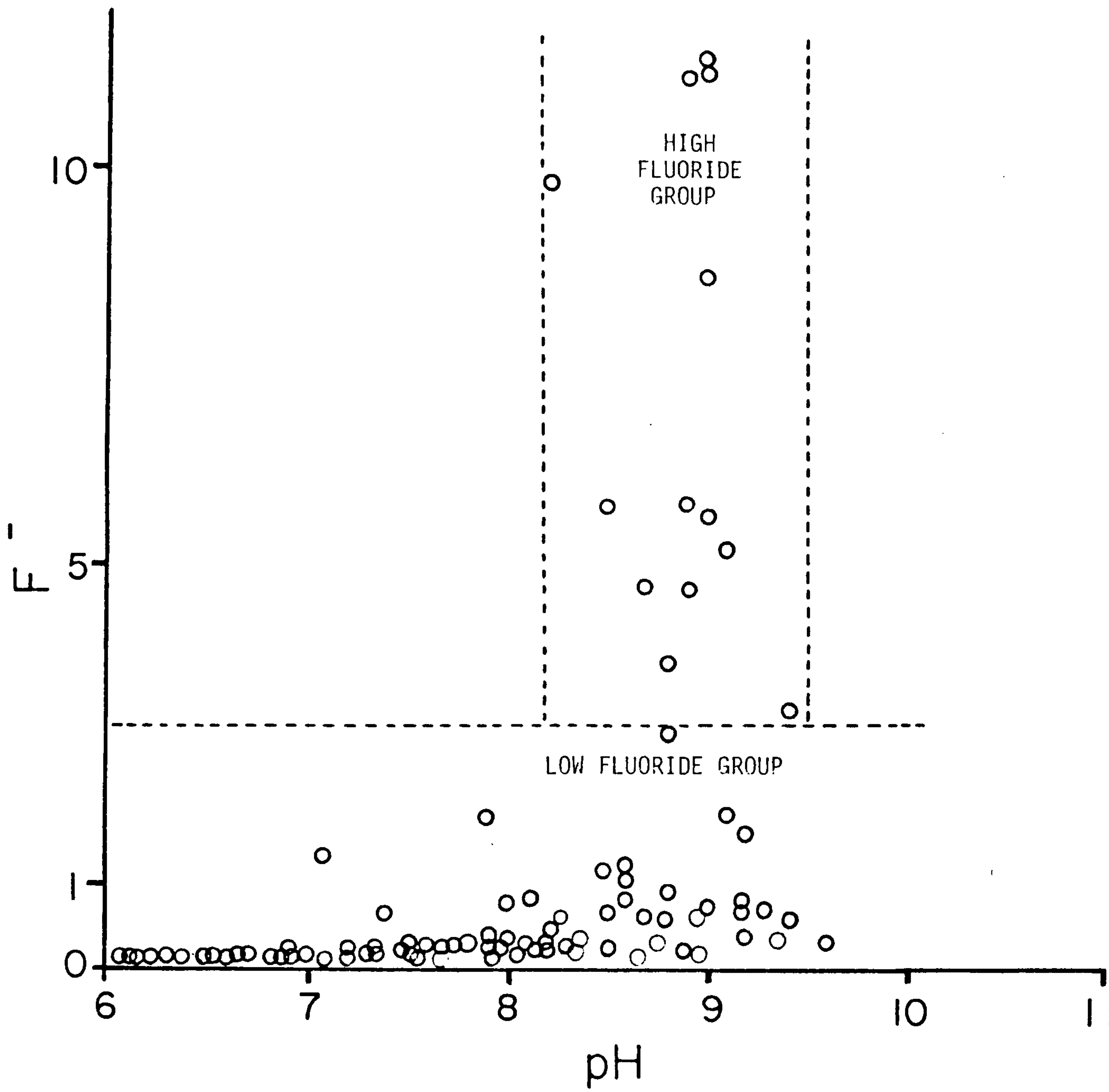

RELATION OF FLUORIDE AND pH.

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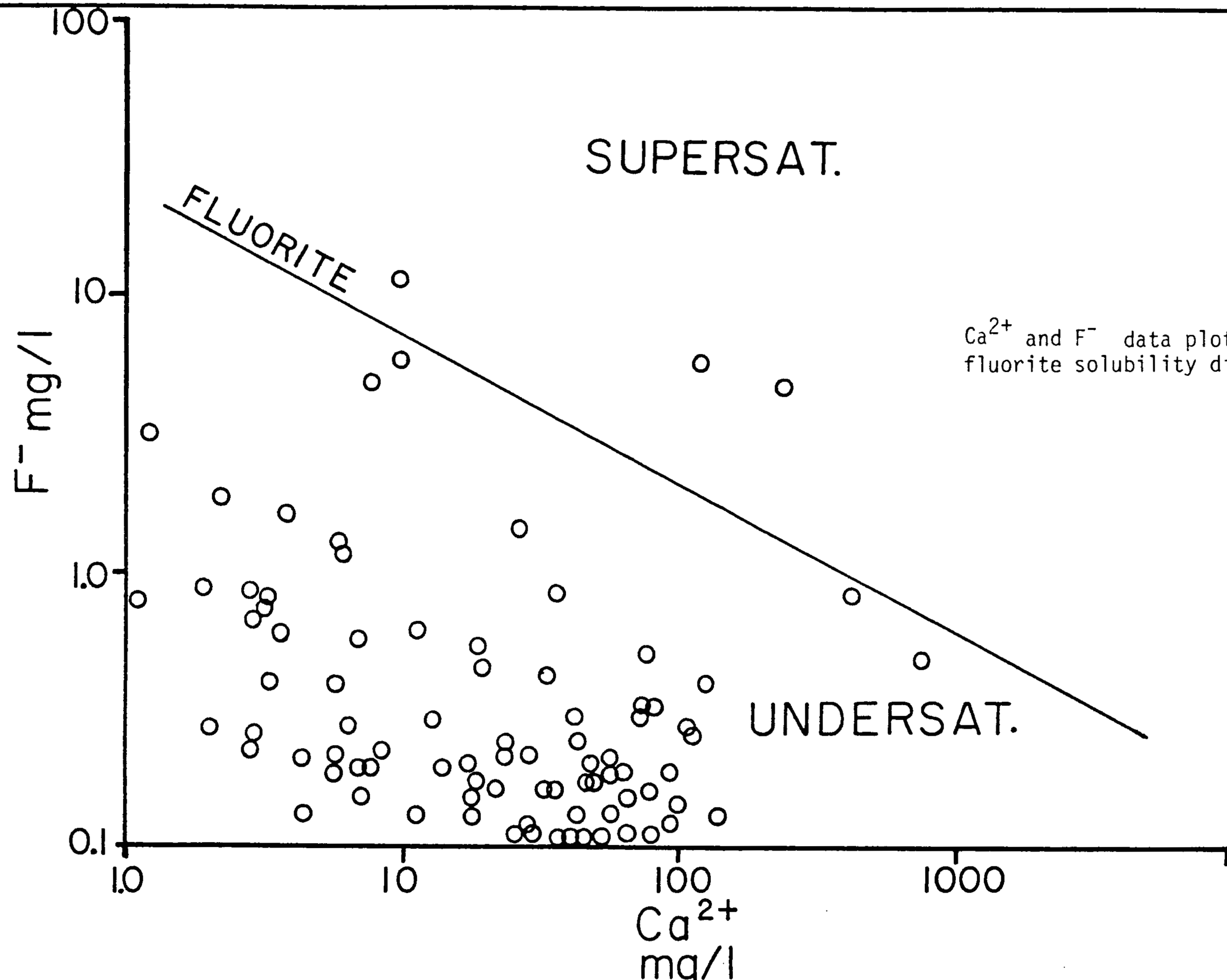
SCALE: VERT. -- HOR. -- DATE May 10, 1985	APK ENGINEER FILE No. DWG No. Figure 3



Ca^{2+} and F^- data plotted on fluorite solubility diagram.

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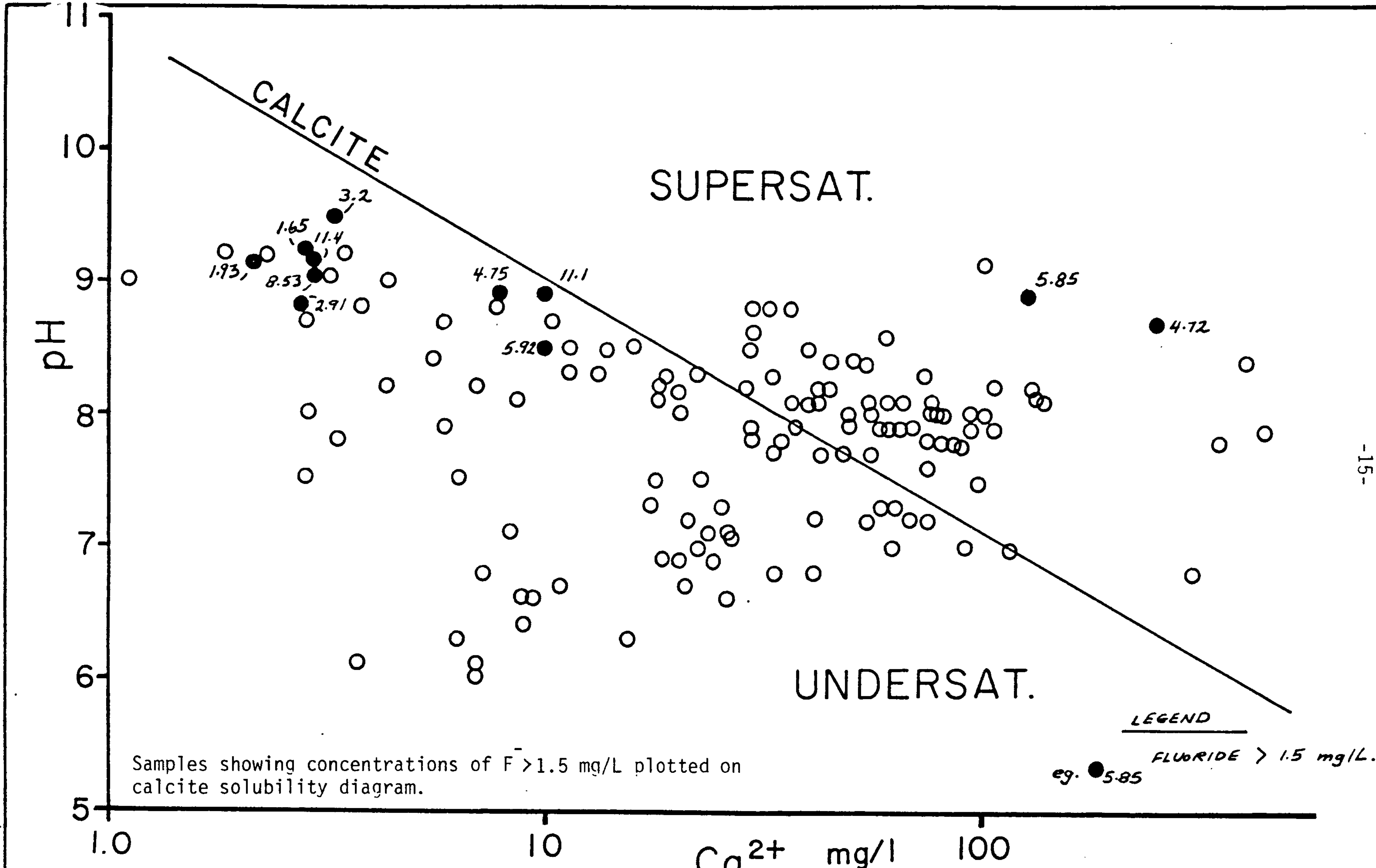

Samples showing concentrations of F^- >1.5 mg/L plotted on calcite solubility diagram.

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MAY 1985

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FILE No.
DWG. No. Fig. 5

VANCAL 8570

TABLE 1

SUMMARY OF FLUORIDE ANALYSES ON FILE

AREA	NUMBER OF SITES N	REPORTED RANGE OF VALUES mg/L F^-
Hornby Island	10	0.15 - 5.92
Denman Island	10	<0.10 - 1.27
Coombs	1	1.65
Gabriola Island	36	<0.10 -11.1
Yellow Point - Cedar	2	0.99 - 1.92
Ladysmith	6	0.26 -11.4
Thetis Island	4	0.10 - 3.20
Mill Bay	1	0.31
Saltspring Island	2	8.53 -13.4
Galiano Island	12	<0.10 - 0.82
Mayne Island	1	0.52
Pender Island	8	<0.10 - 0.58
Saanich Peninsula	96	<0.10 - 0.81
	TOTAL N = 189	

TABLE 2

SUMMARY OF WELLS WHICH SHOW HIGH FLUORIDE CONCENTRATIONS IN GROUNDWATER

LOCATION	WELL NUMBER	REPORTED FLUORIDE CONCENTRATION(s) mg/L	WELL DEPTH (feet)	STRATIGRAPHY (depth in feet)	NON-PUMPING WATER LEVEL BELOW GROUND (feet)	MAJOR WATER-PRODUCING ZONES	COMMENTS
Gabriola Island	Sec. 21 #82	11.1, 9.97	200	0-5 overburden, 5-45 sandstone, 45-80 blue shale, 80-95 sandstone, 95-120 blue clay 120-130 blue shale 130-200 blue clay	50	1/4 gpm at 124 feet 1/4 gpm at 193 feet	- major producing zones associated with blue shale and clay, probably Spray Formation
	Sec. 24 #3	5.85,5.27	220	no log available	30	10 to 13 gpm	--
	Sec. 12 #53	4.75,3.92	245	0-8 brown sandstone, 8-60 gray sandstone, 60-70 very hard, gray sandstone 70-140 gray sandstone 140-165 blue shale 165-245 blue shale - clay and shale layers	90	1 gpm at 232 feet	- major producing zone associated with shale and clay
	Sec. 21 #104	4.72,5.70	368	0-3 overburden, 3-325 sandstone, 325-368 shale	-	1 gpm, source not given	- producing zone probably in Spray Formation
	Sec. 12 #39	2.91	260	0-6 overburden, 6-30 brown sandstone, 30-165 gray sandstone, 165-175 blue clay, 175-260 brown clay, blue clay in layers	162	1/4 gpm at 205 feet 1 1/4 gpm at 260 feet	- major producing zones in clay, probably Spray Formation
Hornby Island	Sec. 9 #35	5.92	372	0-2 sandy brown soil, 2-5 clay hardpan, 5-9 gray conglomerate 9-372 conglomerate bed-rock unit with thin layers of shaley sandstone throughout	100	2gph at 160 feet 8gph at 360 feet	- Gabriola Formation possibly underlain by Spray Formation
Thetis Island	D.L. 11 #5	3.20	310	0-3 topsoil 3-130 sandstone 130-295 sandstone with shale lenses 295-310 fractured sandstone	100	1/2 gpm at 135' 2 gpm at 270' +15 gpm at 300'	- major producing zones possibly in Cedar District Formation
Saltspring Island	X2-Y15 #25	8.53	203	0-1 overburden 1-203 bedrock	5	2 1/2 gpm	- well may be in Cedar District Formation, DeCourcy Formation and/or Northum-berland Formation

TABLE 3

CHEMICAL ANALYSES OF HIGH FLUORIDE GROUNDWATER

Area	Water Type	F^-	Na^+	Ca^{2+}	Mg^{2+}	Phnl. Alk.	Tot. Alk.	Cl^-	SO_4^{2-}	pH	TDS
1. Hornby Island	Na-Cl	5.92	382	9.8	0.5	4.6	143	500	6.8	8.5	1026
2. " "	$Na-HCO_3-Cl$	1.93	268	2.2	0.4	27.3	362	164	1.6	9.1	710
3. Coombs	$Na-HCO_3$	1.65	228	2.8	0.7	39.1	460	34	1.2	9.2	584
4. Gabriola Island	-	2.91	-	2.7	0.08	-	-	-	-	8.8	234
5. " "	Na-Cl	4.75	242	7.5	0.1	6.0	44	344	<5.0	8.9	652
6. " "	-	5.7	256	-	-	-	-	-	-	9.0	1316
7. " "	Na-Cl	11.1	139	9.7	0.1	11.0	60	167	5.4	8.9	398
8. " "	-	5.27	72	-	-	-	-	-	-	9.1	245
9. " "	-	9.97	176	-	-	-	-	-	-	8.2	622
10. " "	Na-Ca-Cl	4.72	359	247	0.1	3.9	20	950	<5.0	8.7	1818
11. " "	-	3.92	280	-	-	-	-	-	-	8.8	1015
12. " "	Na-Ca-Cl	5.85	240	122	0.1	7.3	19	550	<5.0	8.9	1096
13. Yellow Point-Cedar	-	1.92	75.0	-	-	-	-	-	-	7.9	-
14. Ladysmith	-	11.4	-	3.1	0.1	-	119	-	-	9.0	526
15. "	-	11.2	198	-	-	-	-	-	-	9.0	669
16. "	-	6.13	204	-	-	-	-	-	-	-	-
17. Thetis Island	-	3.20	-	1.2	0.2	-	280	-	-	9.4	402
18. Saltspring Island	$Na-HCO_3-Cl$	8.53	322	3.0	0.6	28.7	427	166	33.2	9.0	828

All concentrations reported in mg/L except pH (reported in pH units).

TABLE 4

NATURAL SOURCES OF FLUORIDE

SOURCES	OCCURRENCE
1. Naturally occurring fluoride minerals	Igneous rocks, granites, pegmatites, volcanic rocks
Fluorite CaF_2 Fluorapatite $Ca_5(PO_4)_3F$ Hornblende Mica	Limestone and dolomite
2. Volcanic or fumarolic gases	Recent volcanic activity
3. Phosphatic deposits	Fossil bones, teeth, shells
(Collophane)	Marine phosphate deposits
4. Oil Field Brines	Sedimentary Basins